EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** **Effects of copolymer composition and charge on surfactant templated functionalised polyacrylamide films**	**Experiment number**: SC-2835
Beamline: ID10B	**Date of experiment**: from: 27/11/09 to: 2/12/09	**Date of report**: 30/08/2010
Shifts: 18	**Local contact(s)**: Oleg Konovalov	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

James Holdaway*
Matthew Wasbrough*
Karen Edler*

Report:

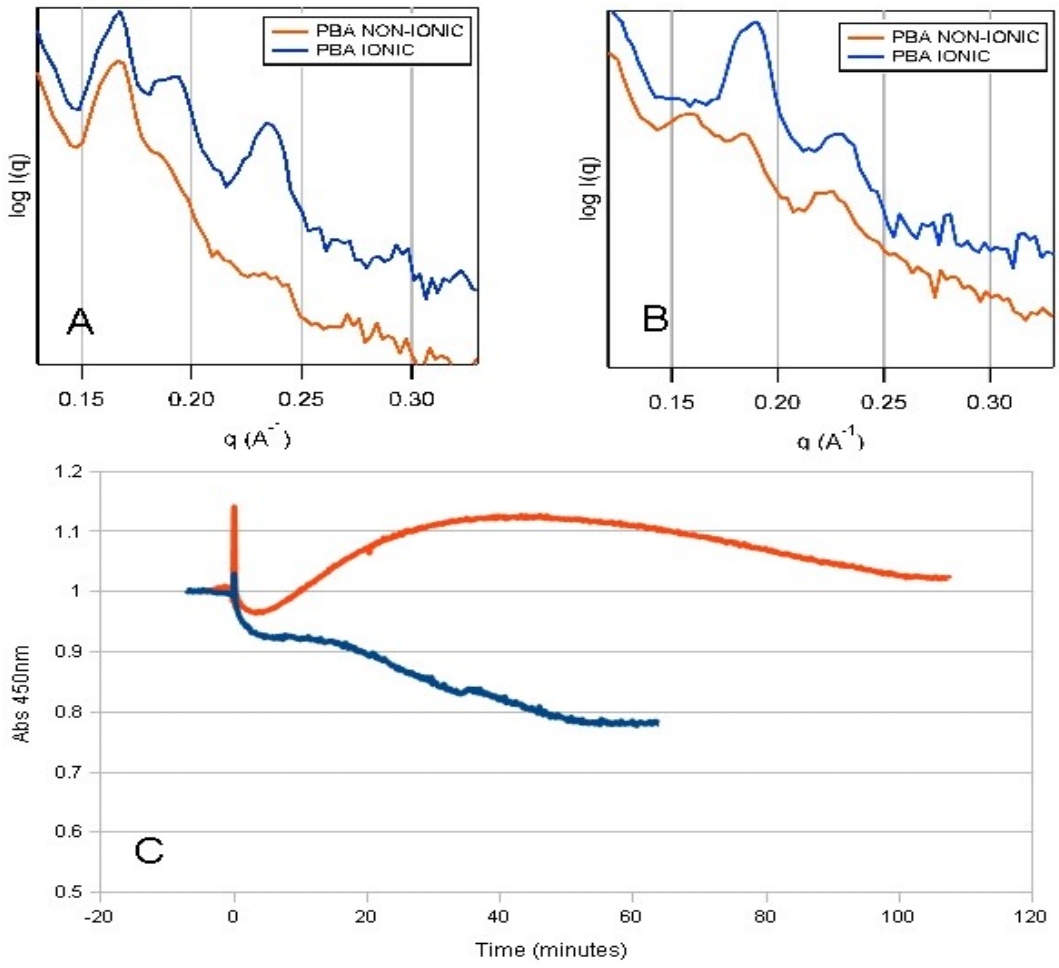
We have been investigating films formed from cat-anionic surfactant mixtures of hexadecyltrimethyl ammonium bromide (C_{16}TAB) and sodium dodecyl sulphate (SDS) since these form with a wider range of polymers including biocompatible polyacrylamide (PAAm) and polyethylene oxide (PEO)[1]. This led to the investigation of biomedical applications for these films. We have found that the mesostructure of CTAB-SDS-polymer films is highly dependent on the interactions between polymer and surfactant and we have also found that it is possible to induce phase changes in the film by varying the C_{16}TAB to SDS ratio and the structural nature of the polymer[2]. Since we have extensively studied the formation and structure of surfactant-polymer films we now have begun to investigate introducing function to the films by incorporating functional species into the polymers. Phenylboronic acids are of interest as they reversibly bind polyols such as glucose[3]. These were successfully templated in our catanionic templated C_{16}TAB/SDS films and we have compared sugar binding of these films against cast polymer films. Membranes that exhibit such selectivity could be used as saccharide recognition sensors or stimuli responsive release mechanisms if used as an encapsulation medium for therapeutic agents. This experiment aimed to determine the effects of polymer structure, polymer charge, polymer glucose binding and cat-anionic surfactant ratios on the film structures. Recovered films physical response on exposure to glucose has been been performed and related to structure.

Polyacrylamides containing phenylboronic acids (PAAM-PBA) with different phenylboronic acid monomer block lengths were used to form films to investigate the effect phenylboronic acid block length has on the formation and structure of the films. Films templated with CTAB and SDS at a total concentration of 0.05M in molar ratios of 7:3 and 9:1 to investigate the effect of the surfactant ratios on the film structure. Phenylboronic acid was incorporated in to polyacrylamide by co-polymerisation of methacrylamidophenylboronic acid and acrylamide (PAAM-PBA). Variation of the methacrylamdiophenylboronic acid block lengths within PAAM-PBA was achieved by synthesising PAAM-PBA via an aqeuous SDS micelle mediated polymerisation, performing the polymerisation at low pH to ensure partioning of methacrylamidophenylboronic acid to ensure partitioning of methacrylamidophenylboronic acid to the SDS micelles. Variation of the monomer to SDS micelle ratio in the polymerisation feed produced polymers of PBA block length of 1, 3, 6 and 9. All films were formed at pH 4, pH 7 and pH 10 to investigate the effect of the PBA charge state in PAAM-PBA on the structure of films. Films were also formed at two PAAM-PBA concentrations; 0.1% wt and 1%wt to determine the effect of polymer concentration on the structure of the films. PBA was present at 3% mole within PAAM-PBA for all

polymers and selected films were also grown in the presence of 100mM glucose to investigate the effect of glucose binding.

All film growth was monitored using an off-specular reflection technique developed in previous experiments on ID10B. When film structure had stopped changing specular reflectivity profiles were collected for each film. GISAXS patterns were also collected for each film at two incident angles; 0.045 and 0.32 degrees (Incident energy 22 keV) to probe true surface and internal mesostructure of the films. Selected GISAXS Qxy slices are presented below at Qxy=0, incident angle 0.32 degrees of films formed from CTAB and SDS in 7:3 molar ratio at 0.05M with PAAM-PBA at 0.1% are presented below.

Fig A - PAAM-PBA (PBA block length 1); when PBA is non-ionic films dominated by a single diffraction peak indicated d-spacing of 37Å whilst when PBA was charged as if in a glucose bound state a gyroid cubic phase was evident co-existent with the 37 diffraction peak. Fig B – PAAM-PBA (PBA block length 9); when PBA is non-ionic films exhibiting a primitive cubic phase were formed whilst when PBA was charged as if in a glucose bound state a gyroid cubic phase was evident. Fig C – Time dependent optical density response of the PAAM-PBA films with block length 1 (blue trace) and block length 9 (red trace) upon exposure to glucose. The large block PAAM-PBA films undergo a structural change from a primitive cubic phase to a gyroid cubic phase with a more optically dense phase during the transition where as the small block PAAM-PBA films undergo a structural change from a optically dense lamellar phase to a less optically dense gyroid cubic. These results and there relation to the structure of the films determined on the experiment will shortly be submitted for publication.



1. B.M.D. O'Driscoll, E.A. Nickels, K.J. Edler, *Chem. Commun.*, 2006, 1068.
2. K.J. Edler, M.J. Wasbrough, J.A. Holdaway and B.M.D. O'Driscoll, *Langmuir*, ASAP.
3. G. Springsteen and B. Wang, *Tetrahedron*, 2002, 58, 5291-5300.