



	<b>Experiment title:</b> <i>Mesostructure in surfactant-polymer films: investigating the incorporation of styrene</i>	<b>Experiment number:</b> SC-3042
<b>Beamline:</b> ID10B	<b>Date of experiment:</b> from: 3 November 2010 to: 8 November 2010	<b>Date of report:</b> 31 Jan 2011
<b>Shifts:</b> 18	<b>Local contact(s):</b> Dr Alexei Vorobiev	<i>Received at ESRF:</i>
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## Report:

A new method of preparing solid nanostructured polyelectrolyte films through spontaneous self-assembly at the air solution interface was recently discovered by our group.<sup>1</sup> These films are self-supporting and assemble through interactions between water-soluble neutral polymers with polarisable groups, and surfactant micelles or vesicles having a well defined range of surface charge.<sup>1-4</sup> They form spontaneously at the surface of homogeneous solutions containing both the polyelectrolyte and surfactant and can be lifted from the solution surface after cross linking onto either solid substrates or as membranes on an open mesh. Dried films retain their mesoscale structure.<sup>5</sup> We have been able to show in preliminary neutron reflectivity and small angle scattering experiments that hydrophobic molecules can be encapsulated within these films inside the hydrophobic sections of the micelles.<sup>6</sup>

The aim of this experiment was to evaluate the effect of styrene encapsulation and structures formed using different surfactant chain lengths for encapsulation in PEI/cationic surfactant films. Polymerisation of micelles swollen with monomer in lyotropic liquid crystalline solutions can be difficult to control because of rearrangement of the surfactant template due to temperature and composition changes through interdroplet diffusion and droplet exchange which occur faster than the polymerisation reaction.<sup>7</sup> In our films, the high viscosity of the hydrogel surrounding the swollen surfactant micelles prevents diffusion and micelle rearrangement on short timescales, making them potentially an ideal host for the polymerisation of hydrophobic monomers. Here we wanted to identify the structures formed when styrene was encapsulated without polymerisation, as a step towards understanding and thus predicting the behaviour of this system when polymerisation is initiated.

In this experiment we used four different surfactants with aromatic head groups and varied tail lengths as the cationic surfactants for PEI film formation to solubilise styrene; tetradecylpyridinium bromide (TDPBr), hexadecylpyridinium bromide (CPBr), tetradecyl benzyldimethylammonium bromide (BDMTDAB) and hexadecyl benzyldimethylammonium bromide (BDMHDAB). To correspond with our previous experiments on cationic surfactant/polymer films we used PEI at two molecular weights, low molecular weight ~2000Da (S-PEI) and high molecular weight ~750 000Da (L-PEI) at a concentration of 15g/L in the presence and absence of the cross-linker ethyleneglycol diglycidyl ether (EGDGE). Styrene was added at 0, 30 and 50 vol% relative to the micelle volume of the surfactants used. Each of the four surfactants (TDPBr, CPBr, BDMTDAB

and BDMHDAB) was at a concentration of 0.05M. ID10B (Troika II) was used to measure time-resolved off-specular reflectivity of films growing at the air/water interface. Once the films were formed, we carried out reflectivity and grazing incidence X-ray diffraction (GIXD) measurements on the formed films to obtain structural details of the phases within the films.

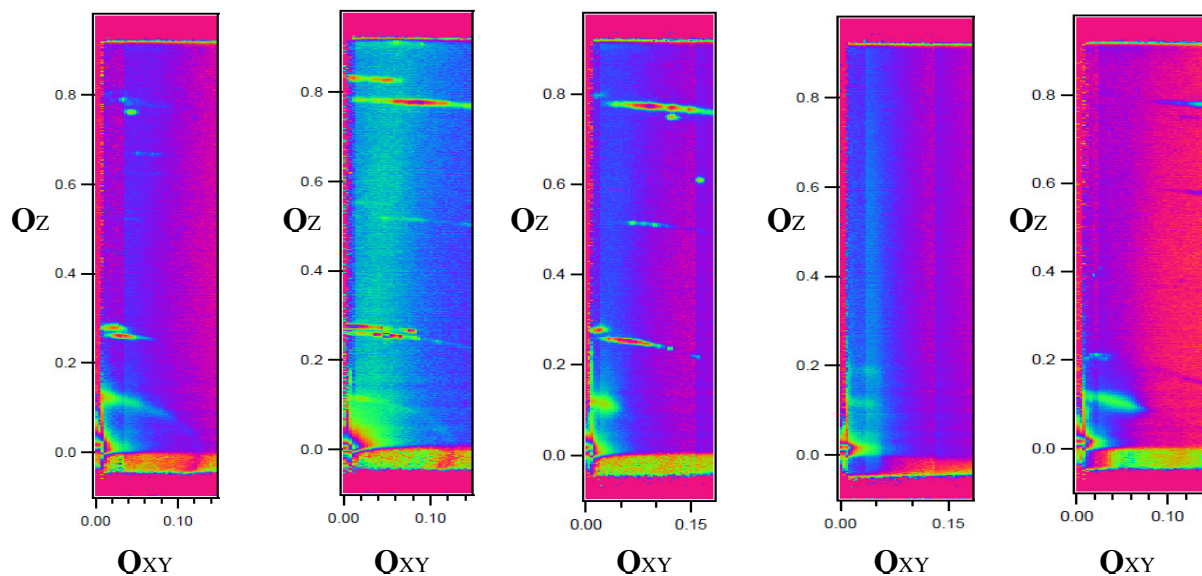


Figure 1 GIXD patterns collected on air/water interfacial films made from 0.05M surfactant/L-PEI. From left to right, BDMHDAB, BDMHDAB encapsulating 30vol% styrene, BDMHDAB encapsulating 50vol% styrene, CpBr with 0.01M EGDGE, CpBr with 0.01M EGDGE and encapsulating 50vol% styrene.

The GIXD data shows an enhancement of mesoscale structure when styrene is incorporated into films formed with BDMHDAB and CPBr. For BDMHDAB films at 50vol% of solubilised styrene the most highly ordered structure was found (figure 1). In general the surfactants with a C<sub>16</sub> tail for both headgroups (BDMHDAB and CPBr) show more ordered structures than those with a C<sub>14</sub> tail. The cross-linker ethyleneglycol diglycidyl ether improved the structure in case of CPBr while deforming the nanostructure in case of BDMHDAB. Surprisingly using a high molecular weight of PEI gives more improved structures in this system compared with low molecular weight PEI in films made using both BDMHDAB and CPBr. This is a different result from previous systems where high molecular weight PEI, although giving thicker more robust films, tended to have poorer ordering while low molecular weight PEI gave highly ordered but thinner films. In this system the most robust films are also the most ordered which is a distinct advantage for our future aim to polymerise the styrene within the membranes to make reinforced films for filtration, sensors etc or to make free-standing ordered nanostructured polystyrene structures.

## References

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