



	Experiment title: Surfactant control of mesostructure in polyelectrolyte-surfactant films	Experiment number: SC-2452
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Report:

This experiment continues our work on the formation of mesostructured polymer-surfactant films that grow spontaneously at the air-water interface¹. Here we investigated the role of the role of the surfactant in producing specific nanostructures within the films. Previous results obtained from films of alkyltrimethylammonium bromides (C_n TAB) and polyethylenimine (PEI) have shown mainly 2D hexagonal structures². We have also studied films made from C_{16} TAB mixed with sodium dodecyl sulfate (SDS) and PEI, in these films we have mainly observed lamellar structures³. For both cylindrical micelles and lamellar phases, diffusion of molecules out of the membranes in release applications must occur through a lengthy and confined path, meaning single file diffusion through cylinders or slow diffusion in 2D through a lamellar layer. Diffusion through a bicontinuous cubic phase or a perforated micellar cubic phase occurs in 3D thus providing more efficient and controllable release profiles. We therefore aimed to control the nanostructures in the film by altering the surfactant to select micelle structures with particular curvatures, to tailor the film structures.

The curvature of mesoscale structures is controlled by changing the ratio of surfactant headgroup area to tail length and volume. We replaced the trimethylammonium headgroup of the C_{16} TAB with triethylammonium, thus increasing the headgroup size for this template. Hexadecyltriethylammonium bromide (C_{16} TEABr) has been shown in silica-surfactant systems to consistently produce perforated $Pm3n$ micellar cubic phases in the composite silica-surfactant phase^{4, 5}. Similarly we increased the tail volume of the surfactant by using didodecyldimethylammonium bromide (DDAB) which, previous SANS results have shown, form lamellar structures in solution. To bridge the gap between these two extremes in curvature we mixed C_{16} TAB with DDAB in ratios of 2:1 and 20:1 C_{16} TAB to DDAB. These ratios were used as they represent a 1:1 and a 10:1 C_{16} : C_{12} tail. In our catanionic systems we need to alter the packing between cationic and anionic surfactants to change the curvature. Experiments in silica systems have shown that mixtures of C_{16} TAB with sodium laurate (SL), $C_{11}H_{23}COONa$, are especially efficient in templating the $Ia3d$ bicontinuous cubic phase⁶. Since our polymer-surfactant films show many similarities with film structures prepared using silica/surfactant syntheses we expect to find similar structural effects in our films.

These five surfactant solutions were used to form films with two molecular weights of PEI, 2000 and 750,000, and at two total surfactant concentrations. The films were prepared in situ

and analysed using reflectivity and grazing incidence diffraction. Film formation occurred very rapidly in these solutions so we were unable to monitor the appearance of diffraction peaks by the time-resolved off-specular measurements. The structure can be clearly seen in the reflectivity patterns: the most ordered films were made with 2000 Mw PEI with DDAB, DDAB:CTAB and CTEABr surfactants and are shown below. The CTAB:SL film only showed good structure with 750,000Mw PEI and that reflectivity pattern is also shown below.

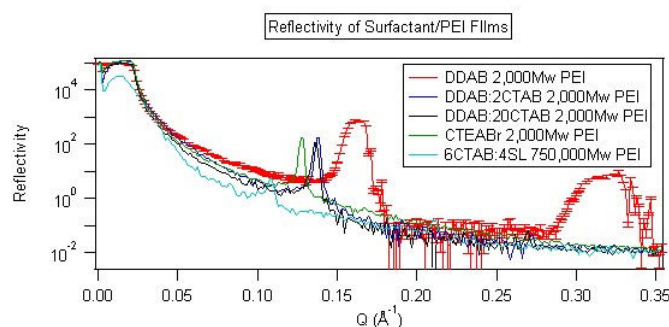


Figure 1 Some reflectivity patterns collected of films made with PEI and various surfactants. Error bars are included for the DDAB trace only for ease of viewing.

The reflectivity patterns from the DDAB, DDAB:CTAB and CTEABr solutions agree with the patterns previously recorded with neutron reflectivity, showing that these films are highly reproducible. The CTAB:SL pattern is similar to those of the other surfactants except the much lower intensity peaks suggest less ordering. However the reflectivity patterns show only those peaks present along the $Q_{xy}=0$ axis, so for oriented hexagonal and cubic phases many peaks are not seen. We clarified the structure by using GID measured at two angles, the true grazing incidence showing us the proper surface structure, and a higher angle corresponding to the angle of the first order peak, which probes the structure deeper into the films. Representative higher angle GID patterns are below.

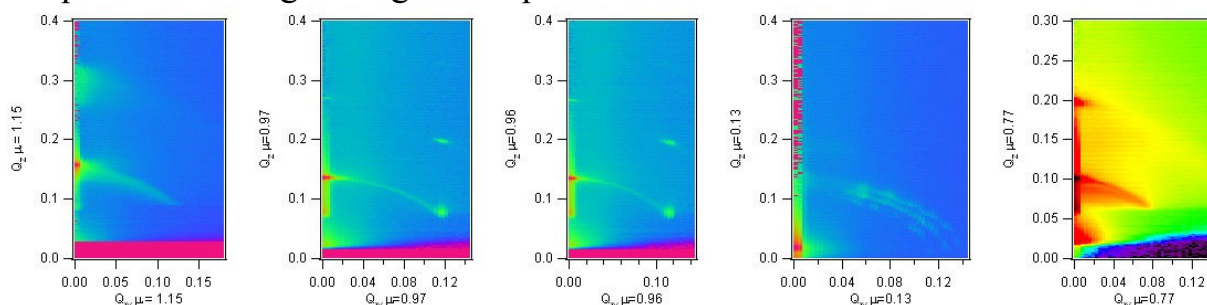


Figure 2 GID patterns from left to right of PEI films with DDAB, DDAB:2CTAB, DDAB:20CTAB, CTEABr, CTAB:SL

These results show that, as predicted, the DDAB film is lamellar and the DDAB:CTAB mixtures appear to have 2D hexagonal structures. The CTEABr appears cubic as predicted, and is probably a $Pm3n$ phase. The CTAB:SL pattern shows mainly a lamellar structure, however the film is not as well structured as the others and on a close inspection a weak peak is visible which could point to a cubic structure. Further analyses of these patterns and their trends with polymer molecular weight and concentrations are ongoing.

References:

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