



	Experiment title: Mesostucture in titania-surfactant films grown in the presence of salts and soluble polymers	Experiment number: CH-2611
Beamline: ID 10B	Date of experiment: from: 11 FEB 08 to: 19 FEB 08	Date of report: 27 FEB 08
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Report:

This experiment represents part of our ongoing research studying the spontaneous formation of titanium dioxide-based films at the air-liquid interface from ethanolic solutions containing minimal water. Our previous in-house SAXS experiments have shown ordering in the calcined films varied dependant upon reagent conditions used. In this experiment the ID10B, Trokia II, beamline was used to measure time resolved off-specular reflectivity, reflectivity profiles and grazing incidence X-ray diffraction (GID) patterns from titania-surfactant films. The aim of this experiment was to observe the structural effects of adding salt to the rection systems and adding polyethylene-oxide to the polymeric surfactant templated films. Series of both partially fluorinated surfactant and block copolymer templated films formed from ethanolic solutions were studied. In both cases films are observed to form in benchtop preparation and in silica systems addition of salt has previously been noted to influence silicate film structure, while addition of soluble polymers produces films with enhanced mechanical strength so we wished to also investigate their effect on structure in titania films.

Experiments used the partially fluorinated surfactant Zonyl FSO-100 and a polyethylene-poly-(ethylene glycol) (PEPEG) block copolymer as templates for film formation. Surfactant, acid and titania concentrations were varied in both the presence and absence of salt and additional polymer. FSO-100 based films utilised reagent ratios of 1 FSO-100 : 135 C₂H₅OH : 4.6 HCl : 0.62 Ti(Obuⁿ)₄ with variations covering 0.5 – 1.5 FSO-100, 0.28 – 1.0 Ti(Obuⁿ)₄ and 0 – 5.9 HCl. The PEPEG preparations used reagent ratios of 1 PEPEG : 1250 C₂H₅OH : 13.5 HCl : 265 H₂O : 15.5 TiCl₄ with variation of 0.5 – 2.0 PEPEG; 5.2 – 15.8 TiCl₄ and 0 – 6.2 HCl. The effect of salt addition was studied using saturated solutions of NaCl in ethanol and other reagents in the listed ranges while polymer addition was studied using a mole ratio of PEPEG to PEO of 1 : 0.05. Time resolved off-specular reflectivity experiments were conducted to observe film formation and reflectometry profiles and GID measurements were performed on developed films to observe any variation in

ordering. However, GID measurements were often limited by the rapid evaporation of the ethanol solvent.

Film formation was often observed by the loss of the specular reflectivity peak in the time resolved experiments, although in some cases a new peak developed. As shown in *Figure 1*, in the case of PEPEG films the loss of the specular peak was observed to occur within 20 seconds while a gradual decline was observed for FSO-100 based films. The data suggests that the the PEPEG films form rough films quickly while FSO-100 based films both take longer to form and are smoother at the interface.

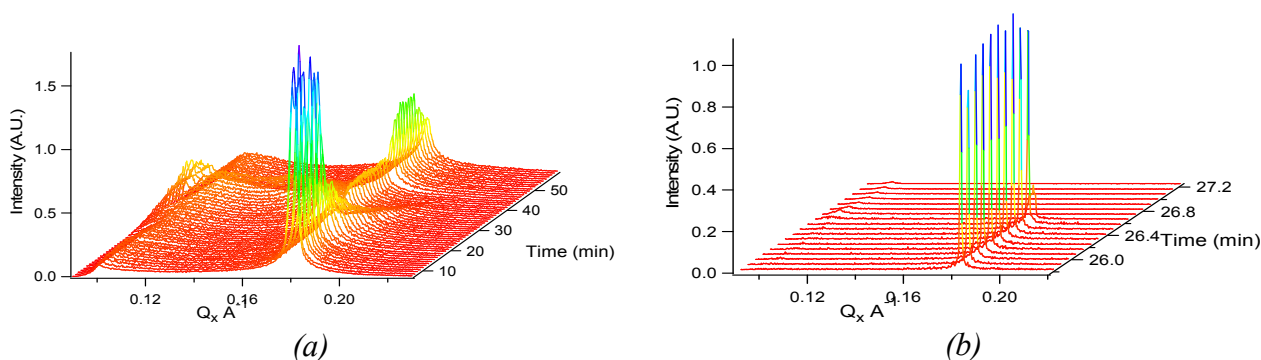


Figure 1: Time resolved reflectivity of, (a), FSO-100 templated and, (b), PEPEG templated titania films developing at the air-solution interface.

These observations suggest that there are two different mechanistic pathways for film formation with different surfactants, and experiments with added salt or polymer did not change these trends. The addition of salt to FSO-100 film preparations appears to delay the loss of the specular peak, suggesting slower film formation, and appears to reduce, rather than improve, the structuring present in the film. In PEPEG film neither the addition of PEO polymer or of salt greatly alter the film formation or structure, as shown in *Figure 2*. It is expected that ongoing modelling of these results will clarify any subtle changes occurring in these systems.

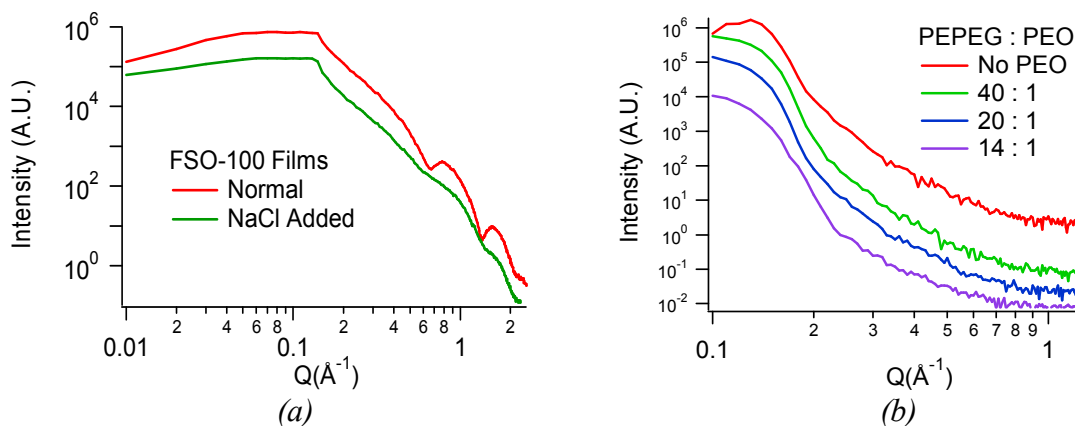


Figure 2: Reflectivity profiles showing the effect of, (a), added salt and, (b), added polymer.

These results for salt addition are at odds with the expected behaviour of non-ionic surfactants in the presence of salt, where enhanced phase separation resulting in mesostructures with a higher degree of ordering is observed.. It is possible that the limitingly low concentrations of salt possible in an ethanol solution are insufficient to have a significant impact upon the film structure.