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Spontaneous free-standing nanostructured film growth in polyelectrolyte-surfactant systems

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Substitution of a polyelectrolyte for silica during formation of surfactant-templated films produces similar nano- and macroscale structures confirming that silica acts as a polyelectrolyte during thin film self-assembly.

Surfactant-templating is the encapsulation of micelles in a matrix of amorphous inorganic material, typically silica. This technique creates ordered arrays of nanopores by self-assembly from dilute solutions of surfactant and silica precursors under mild conditions.[1] During synthesis, the micelles form surfactant-filled channels with liquid-crystalline order within a silica matrix. Removal of the surfactant leaves replica pore networks. Well-defined larger-scale structures such as thin films[2] can also form spontaneously during synthesis, occurring in materials formed from acidic solutions. We propose that the polymerising silica, acting as a network polyelectrolyte, is a crucial intermediate species in formation of both nanopores and larger scale structures.[3–6] Here we confirm our model by substituting for the silica a carbon polyelectrolyte having similar characteristics to the silica polymer. This results in formation of similar structures both macroscopically and on the nanoscale, suggesting that findings from work on polymer:surfactant interactions have relevence to sol-gel:surfactant systems and providing new insights into growth of hierarchical nanoporous materials.

We have previously investigated the spontaneous formation of unsupported nanophase silica films at the air/solution interface. Films templated with cetyltrimethylammonium bromide (CTAB), a cationic surfactant, form after a 3–8 hour induction period[2] at pH < 2, where silica polymerisation occurs through a positively charged intermediate forming extended branched polymers.[7] The silica-CTAB interaction is described as anion-mediated,[8] with the negative counteranion of the surfactant, situated between it and the positively charged silica during the templating interaction. Although templating interactions with silica could start at a monomeric level our results suggest polymeric silica species are more important.[3–6]

We find two formation mechanisms for these films, with nanostructure developing either at the surface or as particles in solution which rise to form the film, dependent on silica:surfactant ratio.[3–5] The induction time at different ratios shows a U-shaped dependency,[6] which resembles the boundary for formation of phase-separated particles in polyelectrolyte-surfactant solutions.[9] Nanostructured complexes of oppositely charged polymers and surfactants form particles in solution around the point of charge neutrality. Formation of these particles depends on the polymer:surfactant ratio, and only occurs over a threshold polymer molecular weight. Plotting the threshold molecular weight for phase separation as a function of polymer:surfactant ratio (charge on the complex) produces a U-shaped curve.[9] In the silica:surfactant system we propose that the silica polymer also undergoes a coacervation-like phase separation when film formation occurs. The induction period is the time required for the growing silica polymer to reach the required threshold molecular weight.

To test our analogy between the silica polymer and carbon polyelectrolytes we prepared a nanostructured film at the air-water interface using a polymer and surfactant having the same charge. This contrasts with the extensive range of surfactant liquid crystalline nanophase structures that assemble from *oppositely* charged polymers and surfactants,[10] forming *supported*[11] or foam films.[12]

We predicted from our silicate work that a polymer with similar characteristics would form similar hierarchical structures. In the silica case, the polymer formed is highly branched, and initially positively charged[7] (although as polymerisation continues, this charge reduces to near neutral). We therefore chose a positively charged, branched, high molecular weight polymer, polyethylenimine (PEI) which is well known to form nanostructured complexes with oppositely charged surfactants. Under the conditions used, (pH ~11), the polymer has a very low charge. Both the silicate polymer[7] and PEI[13] are polar, forming hydrogen bonds with surrounding water. In the absence of water they can also make internal hydrogen bonds (or in the silica case, covalent bonds). To prepare the films, polyethylenimine was mixed with a solution of CTAB in water.† After ~30 s in an open container an easily visible, solid film formed at the solution surface. The film was initially smooth, but developed wrinkles several millimetres across after *ca* 5 minutes. Brewster angle microscope (BAM) images indicate that the films remain relatively smooth on a micron length scale (Fig. 1(a)). This film is several hundred microns thick, and can be easily lifted from the solution surface. PEI with a lower molecular weight forms thinner films (Fig. 1(b)). In Fig. 1(b)–(d) the film was physically broken – the resulting sharp edges indicate the film is solid. Regrowth of the film is evident in (c), but regrowth is slower for low molecular weight PEI.

Solid films, easily visible to the naked eye, also grow for several other cationic surfactants but no films form for neutral or anionic surfactants. Spontaneous, rapid film growth occurs for a range of polyelectrolyte molecular weights and at all investigated CTAB concentrations. Films grow only for pH values above ~10, although the lower limit depends on the polyelectrolyte molecular weight. When grown in 0.1 M NaOH solution (pH ~12) the films are visibly thicker, and more susceptible to macroscopic wrinkling (Fig. 1(c),(d)). High humidity and added salt slow down or prevent film formation. Changing the surfactant counterion alters film formation in a

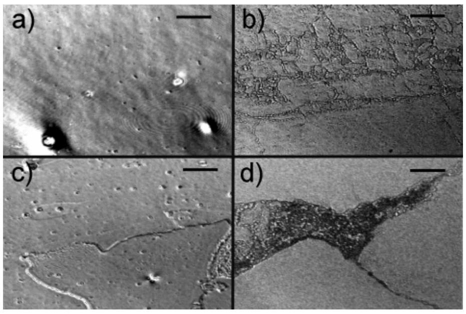

Fig. 1 BAM images of films grown at the air/water interface from 0.037 M CTAB and PEI of molecular weight (a) 750 000, (b) ~2000 (c) 750 000 with 0.1 M NaOH and (d) ~2000 with 0.1 M NaOH. The scale bar is 100 μm.

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complex way, currently under investigation. The strong dependence on humidity implies that solid film formation is linked to draining of water from the surface layer.

Ordered nanostructures within the films were observed for both high and low molecular weight PEI. The degree of ordering depends strongly on the molecular weight (Fig. 2(a), (b)) as the diffraction peak is much sharper for low molecular weight PEI. Modelling of the reflectivity data as a stack of undulating bilayers indicates a structure with alternating layers of polymer and water (22 ± 3 Å) and surfactant micelles (26 ± 5 Å). This corresponds closely with that measured for silica-surfactant films, which show alternating layers of silica (15 ± 3 Å) and surfactant (30 ± 4 Å).[14]

Addition of NaOH also promotes formation of well-ordered mesostructures, especially for low molecular weight PEI, (Fig. 2(c),(d)). At pH ~ 11 the polymer is ~ 1% protonated and at pH 12 it will have only a small residual positive charge.[15] Reducing the polyelectrolyte charge allows electrostatic interactions between CTAB micelles to determine structure to a greater degree and reduces the energy of interaction between the polyelectrolyte network and micelles. The decrease in *d*-spacing (50 Å to 46 Å for M_w ~ 2000 PEI and 51 Å to 48 Å for M_w ~ 750 000) in 0.1 M NaOH is due to decreased repulsion within the polyelectrolyte network, causing the polyelectrolyte gel between micelles to collapse. The observed *d*-spacing is similar to that found in CTAB templated films where the branched polyelectrolyte is silica rather than PEI.[5] Grazing incidence X-ray diffraction (GIXD) was carried out to investigate in-plane ordering (Fig .3). Two first order peaks (01 and 11) are clearly visible in the PEI-CTAB film (Fig. 3(a)), as is a second order 12 peak. The sharp peaks indicate formation of an ordered phase of hexagonally close-packed cylindrical micelles oriented with the long axis parallel to the plane of the interface, equivalent to that found for silica-surfactant films (Fig. 3(b)).

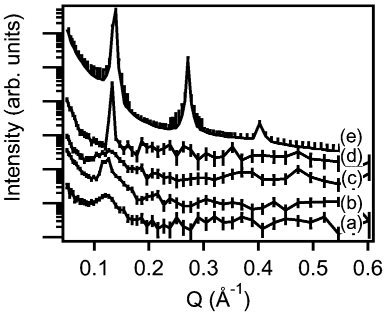

Fig. 2 Neutron reflectivity patterns† for films grown at 0.037 M d-CTAB with PEI of molecular weight (M_w) (a) 750 000, (b) ~ 2000, (c) 750 000 with 0.1 M NaOH, and (d) ~ 2000 with 0.1 M NaOH. (e) X-ray reflectivity from a silica-CTAB film grown at the air/water interface for comparison. The lines are to guides to the eye and the traces are offset for clarity.

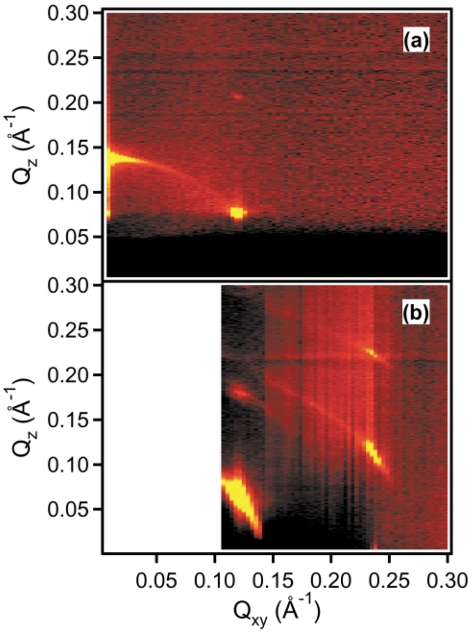

Fig. 3 GIXD from films formed at the surface of (a) PEI (M_w ~ 2000)-CTAB, 0.1 M NaOH solution (incident angle 0.94°) and (b) silica-surfactant film grown at the air/solution interface (incident angle 0.13°) for comparison.

In summary, our proposal that silica acts as a polyelectrolyte during the formation of nanostructured silica-surfactant films at the air/solution interface is supported by the similar spontaneous formation of nanostructured polyelectrolyte-surfactant films at the solution surface. This appears to be a general formation mechanism for creation of nanostructured thin films and should be applicable to form such structures from a wide range of materials.

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Notes and references

† Polyethylenimine of M_w 750 000 (Sigma), and ~ 2000 (Aldrich) was mixed with an aqueous solution of CTAB (Acros). The PEI concentration was 6 wt%. CTAB concentrations ranged from below the cmc to 0.037 M. Films were grown in shallow Teflon troughs with surface area *ca.* 63 cm². pH effects were studied for concentrations of up to 0.1 M HCl and 0.1 M NaOH. Silica-CTAB film data shown for comparison is for a film grown from a solution containing molar ratios of CTAB : tetramethoxysilane : HCl : H_2O 1.52×10^{-3} : 0.011 : 3.63×10^{-3} : 1. Preparation details are given elsewhere.[4] BAM images were taken on a NFT Nanoscope II. Neutron reflectivity on SURF (ISIS), using deuterated CTAB ($C_{16}D_{33}N(CH_3)_3Br$, QM_x Laboratories) and water:D_2O mixtures to vary neutron scattering contrasts between polymer, micelle and solvent. GIXD experiments were done on TröikaII (ID10B), at the ESRF.

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