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Growth-collapse mechanism of polyethyleneimine with cetyltrimethylammonium bromide (PEI-CTAB) films at the air-water interface

Initial work on the self-assembly of thick nanostructured polymer-surfactant films focussed on the system polyethyleneimine (PEI) with cetyltrimethylammonium bromide (CTAB). Membranes involving the high molecular weight, [long] polymer (LPEI) were shown to be sufficiently robust to be recovered onto a mesh [4]. The structure of the LPEI-CTAB films at the air-solution interface involves a 2D hexagonal phase of close-packed cylindrical micelles surrounded by a polymer-water matrix. Previous work has indicated that thick film formation is driven by an evaporative steady state [5]. It was also noted that films do not form under acidic conditions, yet questions remained about the nature of the film growth process.

In the present work we have used three complementary reflectometry techniques to gain an elevated understanding of the PEI-CTAB system for which we have revealed a remarkable growth-collapse mechanism [6]. First we employed a novel approach to track quantitatively the film thickness on the micron scale using an optical technique in the Partnership for Soft Condensed Matter (PSCM) laboratory called ellipsometry. This work represented – to our knowledge – the first quantification of the thickness of films on the micron scale at the air-water interface.

Figure 1A-D shows the changing film thickness for four solutions with a range of polymer concentrations, each with 1 mM CTAB

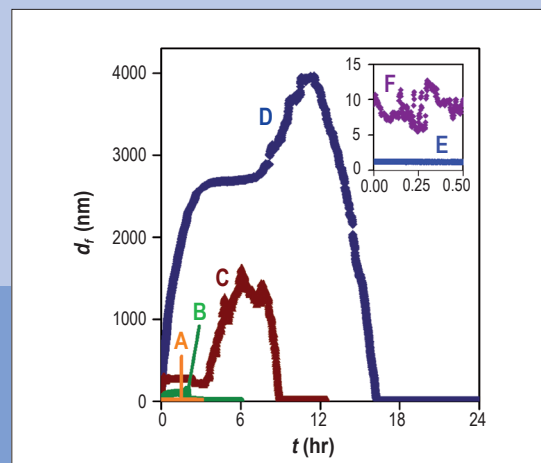


Figure 1: Time-resolved layer thickness, d_f , with respect to the surface age, t , from ellipsometry measurements of LPEI-CTAB films where c_{PEI} is (A) 0.025 wt%, (B) 0.05 wt%, (C) 0.1 wt% and (D) 0.2 wt% and $c_{CTAB} = 1$ mM; (E) an SPEI-CTAB film where $c_{PEI} = 1$ wt% and $c_{CTAB} = 1$ mM; (F) an LPEI-CTAB film where $c_{PEI} = 0.2$ wt% and $c_{CTAB} = 0.1$ mM.

above its critical micelle concentration (cmc). A growth-collapse mechanism is observed in each case: after initial growth, the thickness reaches a plateau (up to 4 μ m) before undergoing a period of instability, followed by total collapse. Figure 1E-F shows measurements with CTAB below its cmc and with LPEI swapped for a low molecular weight, [short] polymer (SPEI); both films are 2–3 orders of magnitude thinner. The growth of the thick PEI-CTAB films is clearly enhanced by the interaction of long hyperbranched polymer chains with surfactant micelles.

With such an insightful pre-characterisation of the system we then carried out structural measurements using neutron reflectometry on FIGARO. Data were recorded of the film state shown in figure 1B to track a Bragg diffraction peak at about 0.1 \AA^{-1} during the growth-collapse mechanism (figure 2). The Bragg peak changes sharpness with its highest intensity coming just after the thick film is fully formed. The subsequent broadening of the peak suggests that the micellar ordering in the films becomes less well-defined during the period of instability after the film growth is complete. During this time the spacing between micelles in the film also varies, with the smallest d-spacing (57.1 \AA) observed at the same surface age as the narrowest diffraction peak (about 1 h), suggesting that large domains of tightly packed micelles are present at this time. As the film ages, the peak position moves

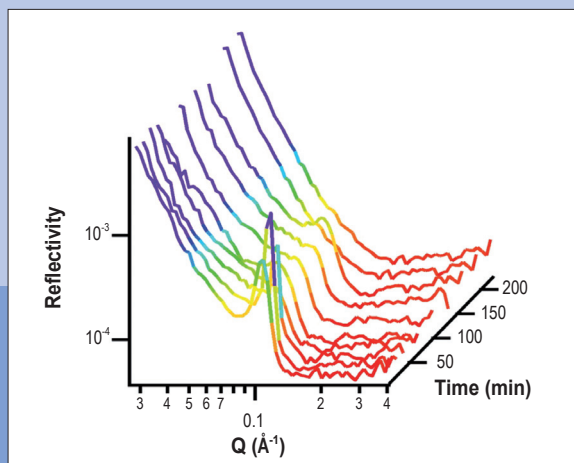


Figure 2: Specular neutron reflectivity profiles of an LPEI-CTAB film at the air-water interface where $c_{PEI} = 0.05$ % and $c_{CTAB} = 1$ mM.

Polymer-surfactant mixtures are used in countless formulations encountered in our everyday lives such as detergents, conditioners, cosmetics, paints and foods [1]. There has been sustained interest in understanding molecular interactions in such systems, and also in developing new methods to prepare ordered materials at surfaces for applications in responsive coatings, encapsulation/release and sensors [2]. Over the last decade there has also been a drive to prepare self-assembled nanostructured films at the air-solution interface [3]. The present work provides new insight into the interfacial mechanism of an intriguing system which has high potential for use in a range of applications.

to smaller momentum transfer, indicating an expansion of the mesostructure due to increasing distance between micelles in the domains of the ordered phase. The Bragg peak disappears completely after 3h which coincides well with the total collapse of the film from ellipsometry.

We also recorded optical images of films to track changes in lateral film morphology on the micron scale using another technique in the ILL laboratories, Brewster angle microscopy (figure 3). In the thin film regime at the start (2min) and end (160min) of the process the film is evenly textured and mobile. The lateral morphology of the films is similar when it is thickest (60min) except that it is now solid and stationary. In contrast, during growth (15min) there are linear ripples indicating the presence of long range correlations of $> 300\mu\text{m}$, and during collapse (140min) circular defects are evident. These observations suggest that film collapse may occur by the opening up of point defects or perhaps by spinodal decomposition.

In conclusion, as a result of the use of three complementary reflectometry techniques on the PEI-CTAB system, we are now in a position to propose an interfacial mechanism. The generation of macroscopic films is due to the interaction between trimethylammonium groups on the surface of surfactant micelles with lone pairs of electrons on the primary amine groups of long polymer chains, which adsorb to the surface under an evaporative steady state. The arrest in the growth is consistent with the adsorption of CO_2 into the solution which increases the cationic polyelectrolyte charge density. Collapse is caused by the film breaking up as it dries combined with thinning as the solution acidifies. This insight can be useful for potential applications, e.g., the harvesting of solid polymer-surfactant membranes at the optimal time for defined film thickness and nanoscale structure.

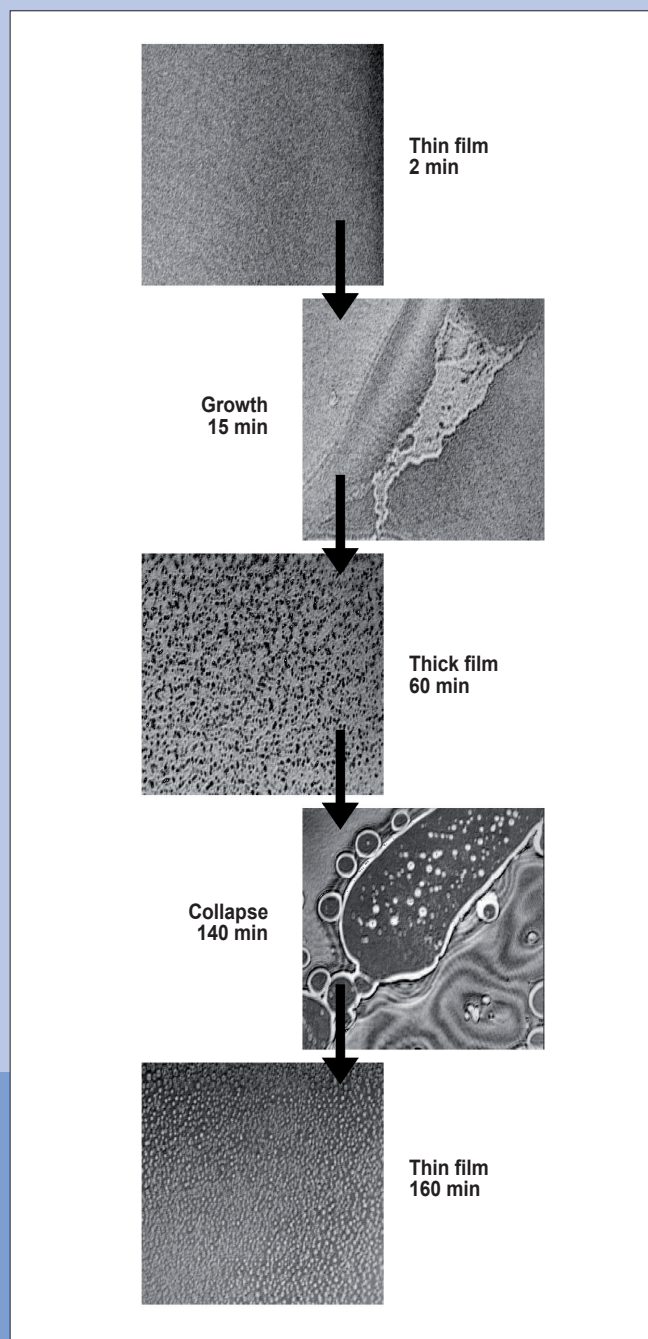


Figure 3:
Brewster angle microscopy images showing the lateral morphology on the micron scale of an LPEI-CTAB film at the air-water interface where $c_{\text{PEI}} = 0.05\%$ and $c_{\text{CTAB}} = 1 \text{ mM}$. Each image has a width of $340 \mu\text{m}$.