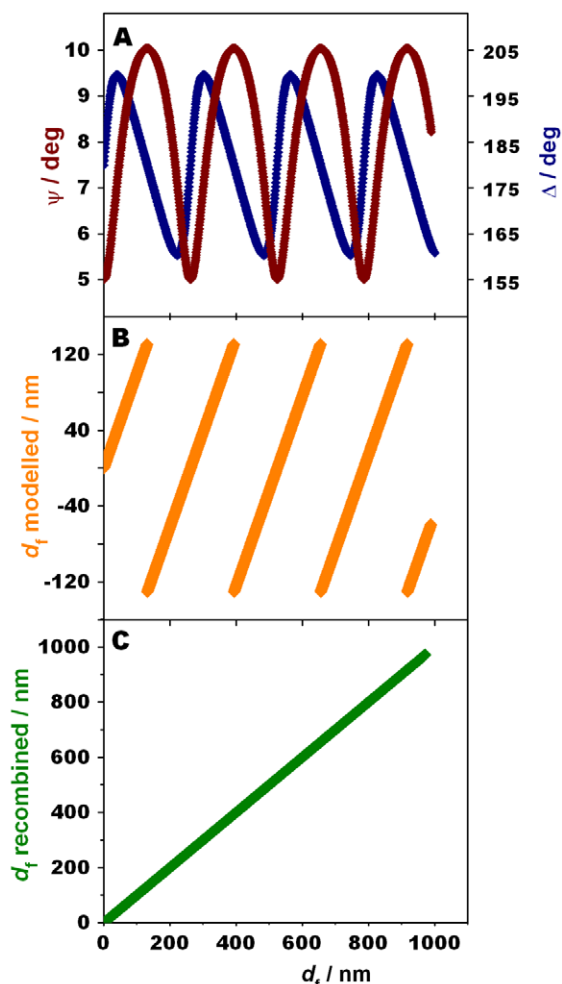


Growth-collapse mechanism of PEI-CTAB films at the air-water interface

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Electronic Supplementary Information

Validation of numerical iteration and data recombination steps for ellipsometry

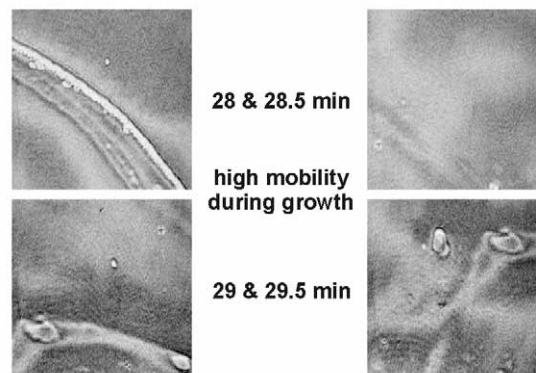


10 **Fig. ESI1** (A) Simulation of ψ and Δ for a LPEI-CTAB film with a refractive index of $n_f=1.430$ at the air-water interface recorded at an incident angle of $\theta = 50^\circ$ with respect to the film thickness, d_f , (B) the numerical derivation of the film thickness from these simulated data, and
15 (C) the recombined actual film thickness after eliminating steps resulting from discontinuities in the film thickness.

Here we present a validation the numerical iteration and recombination processes of summing the film thickness over discontinuities resulting from the cyclic nature of the ellipsometric parameters. First, we carried out a simulation using Film Wizard software^{ESI1} to generate ψ and Δ for a film of refractive index $n_f = 1.430$ at the air-water interface at an incident

angle of 50° (fig. ESI1A). The data were then evaluated using the numerical iteration process of the Ellipsometry program^{ESI2} to calculate the film thicknesses (fig. ESI1B). Discontinuities in the film thicknesses resulting from the cyclic nature of the response of the ellipsometric parameters were then resolved in a recombination process (fig. ESI1C). The maximum error in any data point as a result of the numerical iteration and recombination
25 processes in this validation exercise is just 0.03%. The same processes as in panels ESI1B (calculation of film thickness) and ESI1C (resolving of discontinuities) were applied to the experimental data present in fig. 3 of the main article.

Image sequence indicative of high mobility during film growth from Brewster angle microscopy



35 **Fig. ESI2** Brewster angle microscopy images of a film comprising 0.2 wt% LPEI and 1 mM CTAB (cf. fig. 6A). The images were taken at surface ages of 28.0, 28.5, 29.0 and 29.5 min. Each image has a width of
40 340 μm . The different regions of the film shown in reasonably quick succession indicate its high mobility during the growth period.

LPEI-CTAB films are visibly most mobile during their rapid growth stage, as revealed by the comparison of Brewster angle microscopy images with ellipsometry data. To make this point,
45 fig. ESI2 shows four distinct regions of the film imaged in sequential 30-s acquisitions. The damping of the ψ wave with time in ellipsometry is consistent with the incoherent averaging of ψ values over a finite distribution of film thicknesses which pass through the field of view of the microscope within the 0.6-s
50 stabilisation time of each measurement. The films become mobile once again during their collapse to the thin film limit.

References

- ESI1. Film Wizard; Scientific Computing International: Carlsbad, CA, 1999.
55 ESI2. P. Petrov, Ellipsometry program, Lund, 1994-2001, v. 1.3.1.