Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supplementary Information

Equations used for calculating reflectance of brush layers

Following Henrie et al.,[1] the reflectance R(λ) of brush layers on silicon wafers was calculated assuming normal incidence at a wavelength λ using

$$R(\lambda) = \left| \frac{n_f(n_c - n_s)\cos\phi + i(n_c n_s - n_f{}^2)\sin\phi}{n_f(n_c + n_s)\cos\phi + i(n_c n_s + n_f{}^2)\sin\phi} \right|^2$$

Where n_c, n_f and n_m are the refractive indices of the cover (air), film and substrate (silicon) respectively. Refractive indices are assumed to be real (i.e. absorption loss of silicon is neglected). ϕ is the phase delay due to propagation through the film, given by

$$\phi = k_0 n_f h$$

Where $k_0 = 2\pi/\lambda$ and h is the thickness of the film.

Detailed analysis of pH-induced brush swelling kinetics

The swelling kinetics presented in Figure 3c for PDPA brushes immersed in borate and citrate buffer solutions after switching from pH 7.3 (deswollen) to pH 6.5 (swollen) were analyzed in further detail.

Only ellipsometric Δ was recorded in this kinetic scan, precluding proper ellipsometric fitting to convert these measurements into thicknesses. However, by assuming an initial thickness of 55 nm (best fit to dry thickness), expected Δ values could be calculated for a range of swollen thicknesses by (i) using a single slab EMA model and (ii) assuming that the polymer volume fraction scales consistently with the swelling ratio (conserving the total polymer content). The thickness-Δ curve derived in this way was used to convert the Δ values into swollen thicknesses. For the model used here, the thickness-Δ relationship is almost linear, producing a thickness-time plot (Figure S1) that is almost identical to the Δ-time plot shown in Figure 3c.

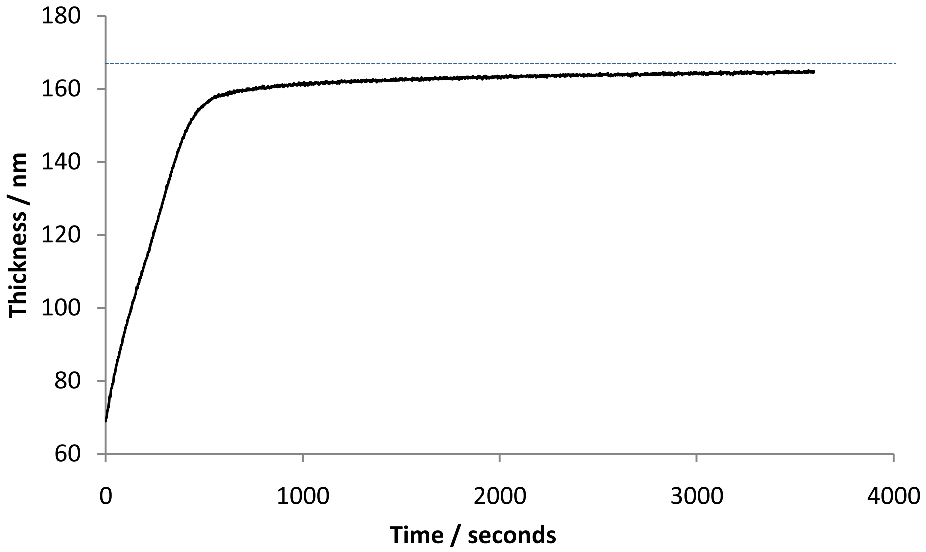

Figure S1. Variation of swollen thickness with time for PDPA brushes after a pH change from 7.3 to 6.5, fitted as detailed in the supplementary text. Time is from the re-acquisition of the signal after the pH change. The horizontal dotted line represents the assumed ultimate swollen thickness used in subsequent calculations.

To analyse the swelling kinetics, the thickness data was replotted as the natural logarithm of the difference between the actual thickness at any given time and an assumed final thickness, *S* of 167 nm (Figure S2). Thus an exponential decay approach to the final thickness should appear as a straight line with negative gradient.

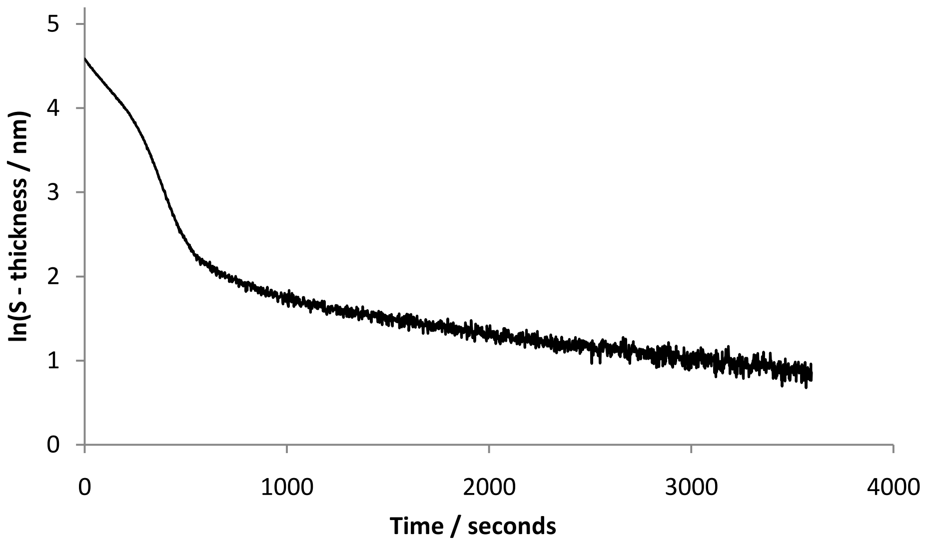

Figure S2. Change in thickness with time for the swelling brush replotted as the natural logarithm of the difference between the actual thickness at any given time and a calculated final thickness, *S* of 167 nm.

It is clear from this plot that there are at least two distinct regimes: a regime of rapid change at short times (< 500 s) and rather slower change at longer times (> 1000 s). In fact, two clear stages of fast change can be discerned: less rapid from 0 – 200 s, and more rapid from 200 – 500 s. The three stages can be well fitted by single exponential decays, as shown in Figure S3 (plotted using the logarithm as in Fig S2) and Figure S4 (linear scales). The fitted half-life periods are 220 s, 110 s and 2300 s (to 2 s.f.) for the early, intermediate and late regimes respectively.

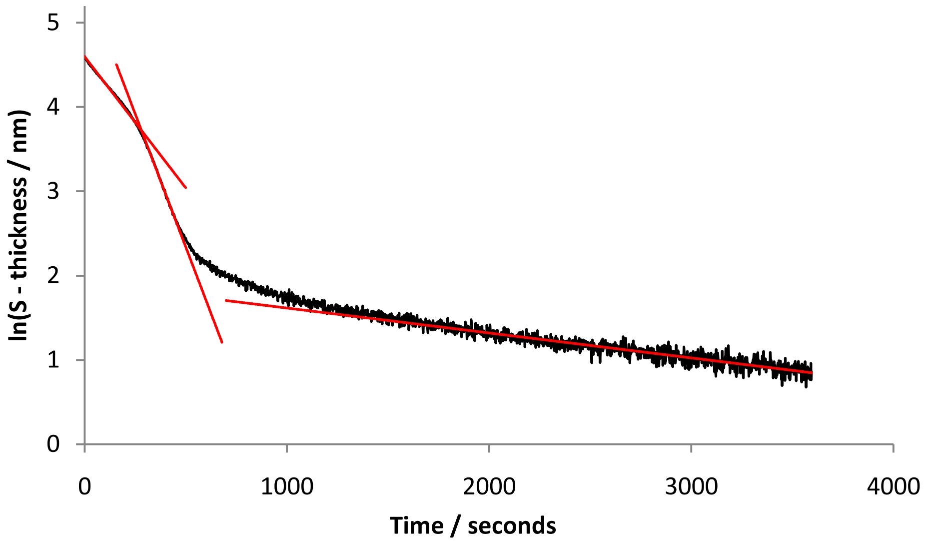

Figure S3. ln(*S* – thickness) against time for the swelling brush (see Fig S2), fitted with three single exponential decays (red lines).

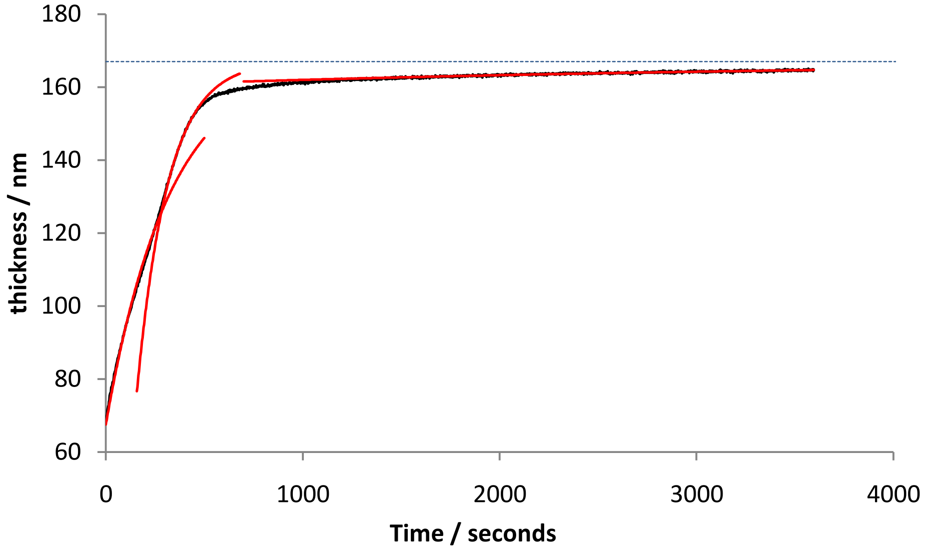

Figure S4. Increase in brush thickness with time for the swelling brush, fitted with three single exponential decays (red lines).

Note that choosing a different value for the assumed final thickness *S* alters the shape of the curve, but does not affect the observation of three distinct regimes. Three distinct regimes are also visible in the raw Δ data (Figure S5).

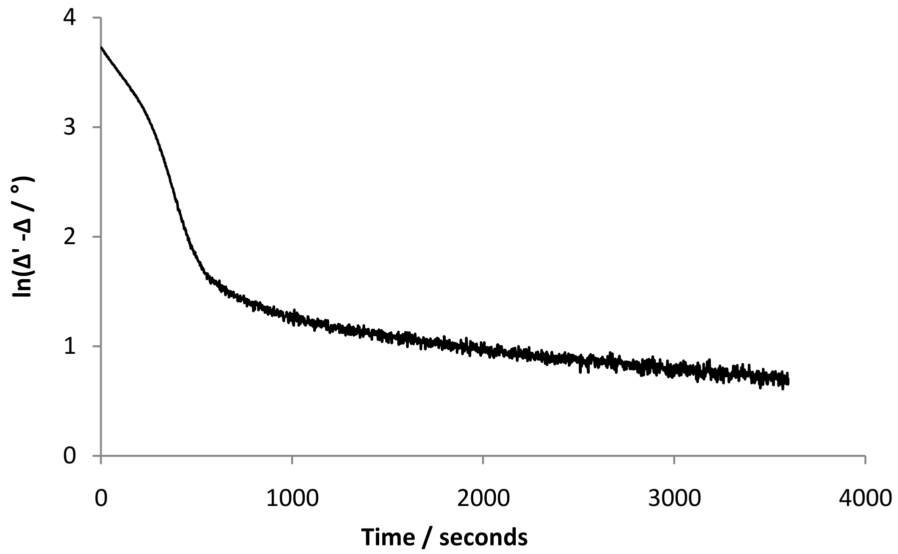

Figure S5. Change in Δ with time for the swelling brush, plotted as the natural logarithm of the difference between Δ and an assumed final value Δ*'* = 155 °

It seems unlikely that the brush would in fact swell at three distinct rates, especially with the intermediate regime being the fastest. It is more likely that there is a change in the density profile of the brush during swelling, from a box/slab-like profile when deswollen to a Gaussian, exponential or more complex[2] density profile when swollen. The simple single-slab model used in this work cannot account for such density profile changes, producing the apparently complex swelling kinetics. Unfortunately, since the ellipsometric parameters during swelling could only be recorded at a single wavelength (unlike the thickness measurements presented in the main paper, which are the result of a spectroscopic scan) there is insufficient data to fit a more complex density profile. Clearly, more work is needed to investigate the observed swelling phenomenon.

References

1. J. Henrie, S. Kellis, S. Schultz and A. Hawkins, *Opt. Express*, 2004, **12**, 1464-1469.
2. M. Geoghegan, L. Ruiz-Perez, C. C. Dang, A. J. Parnell, S. J. Martin, J. R. Howse, R. A. L. Jones, R. Golestanian, P. D. Topham, C. J. Crook, A. J. Ryan, D. S. Sivia, J. R. P. Webster and A. Menelle, *Soft Matter*, 2006, **2**, 1076-1080.