

Supporting Information

Polyelectrolyte brush pH-response at the silica-aqueous solution interface: A kinetic and equilibrium investigation.

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Poly(DEA) brush growth on QCM-D crystals and wafers by SI-ARGET ATRP.

The inhibitor was removed from 2-(diethylamino)ethyl methacrylate monomer (DEA, Aldrich, 99 %) using a short alumina column (activated, basic) and inhibitor-free monomer was stored at -20 °C and warmed to room temperature immediately before use. Methanol (anhydrous, 99.8 %), copper(II) bromide (99.999 %), 2,2'-bipyridine (≥99 %), and (+)-sodium L-ascorbate (≥98%) were purchased from Aldrich and used as received. Macroinitiator-modified wafers and QCM-D crystals were sealed in vials which were subsequently deoxygenated by purging with nitrogen for 15 minutes. Each vial contained 1 QCM-D crystal and 2 wafers. The QCM-D crystal was positioned on top of a PTFE support designed to support the crystal with no obstruction of the macroinitiator-modified sensor surface. The wafers were placed standing upright either side of the PTFE support with the oxidised, macroinitiator-coated surface angled downwards to prevent any deposition of insoluble reagents. DEA monomer (22.50 g) was dissolved in an equal volume of methanol (anhydrous) and was deoxygenated by purging with nitrogen for 30 minutes before copper(II) bromide (CuBr₂, 0.0109 g), 2,2'-bipyridine (bpy, 0.076 g) and sodium ascorbate (Na asc., 0.096 g) were added (DEA/CuBr₂/bpy/Na asc. molar ratios of 2500:1:10:10). The polymerisation was started by adding sufficient dark brown reaction mixture to immerse the contents of the vials. Polymerisations were carried out under a positive pressure of nitrogen at room temperature (~20 °C). Brushes of different thickness were produced by controlling the polymerisation time which ranged from 18 to 245 minutes, and a separate vial was used for each growth time. Once the target growth time was reached, the brush-modified substrates were removed from the reaction mixture, washed by multiple sequential rinses of ethanol then water, and blown dry under a stream of nitrogen before analysis.

QCM-D studies on poly(DEA) brush-modified QCM-D crystals.

The change in resonant frequency (Δf) of a QCM-D crystal can be related to the surface excess (Δm) using the Sauerbrey equation,¹ which is valid for thin films that behave elastically.²

$$\Delta m = -\frac{\rho_q l_q \Delta f}{f_0 n} \quad (\text{S1})$$

where f_0 is the fundamental frequency, n is the overtone number, and ρ_q and l_q are the specific density and thickness of the quartz crystal, respectively. The change in resonant frequency of the oscillating quartz sensor is sensitive to the amount of all material that is coupled with its motion. To analyse data from these experiments the mass calculated using the Sauerbrey equation includes a contribution due to the mass of entrained water in the film, and routinely exceeds surface excess values obtained by other methods.^{3,4} Experiments were conducted at 21 ± 0.1 °C and all reported frequency shifts are normalised by dividing by the overtone number. The third overtone is generally preferred over the fundamental overtone, as the resonator is less affected by mechanical forces associated with mounting the resonator,⁵ however, the fifth overtone was used when the third overtone was uncharacteristically noisy. The normalised overtones overlapped for the majority of the reported aqueous data, indicating that for these measurements the brush layers obeyed the Sauerbrey relationship.

Before *ex situ* adsorption of macroinitiator, the fundamental resonant frequency, f_0 , of each unmodified crystal was measured in air. After polymerisation each brush-modified crystal was re-measured in air to allow calculation of the Sauerbrey mass of each dry polymer brush. This was converted to a Sauerbrey thickness assuming a polymer density of 1.1 g/cm^3 . The resonant frequency of a crystal was seen to vary by ± 15 Hz upon reinstallation in the QCM, correlating to an error of ± 4.9 nm in the calculated Sauerbrey thickness.

QCM-D dissipation profiles of the four poly (DEA) brushes during pH cycling.

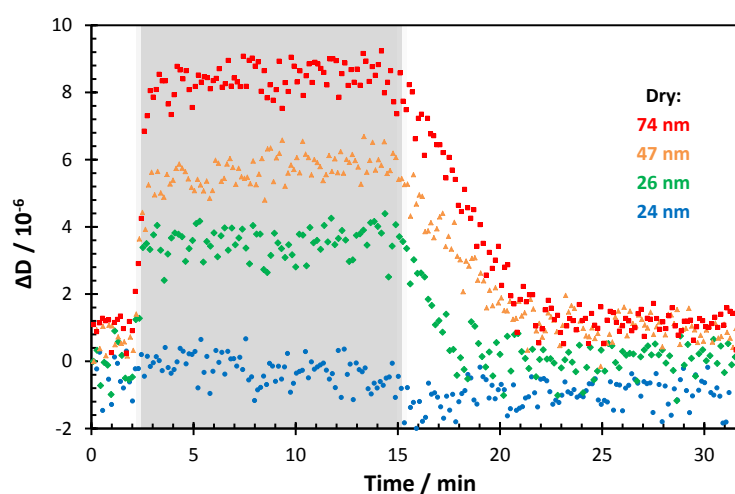


Figure S1 - QCM dissipation profiles for four poly(DEA) brushes of different thickness as the pH was cycled between pH 9 (white) and 4 (shaded), 5th overtone for all data. The frequency profile of the same transition is shown in Figure 3 of the main manuscript.

Ellipsometric volume percentage polymer for the 16 nm brush during pH cycling.

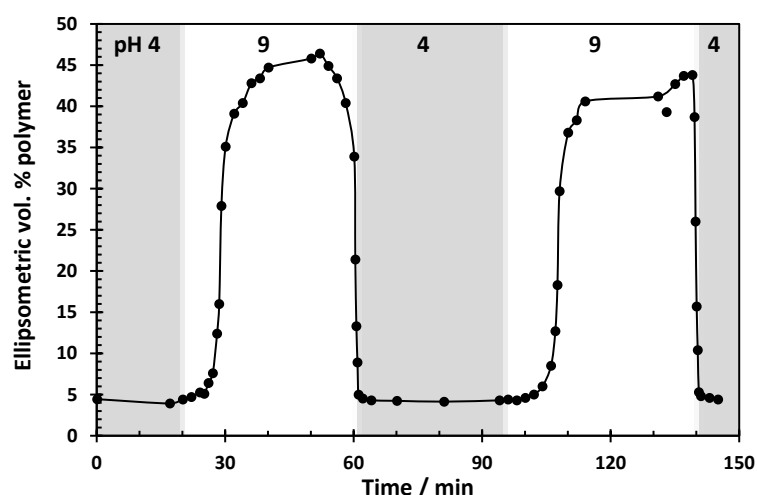


Figure S2 – Ellipsometric volume % polymer fraction as the pH was cycled between pH 9 (white) and 4 (shaded). The ellipsometric thickness and swelling ratio of the same transitions are shown in Figure 4 of the main manuscript.

For all of the ellipsometric analysis in this study we have modelled the polymer brush layer as a single slab. This yields a very good fit for the dry brush, however it becomes a less accurate as the brush becomes increasingly solvated. As a result, the absolute values of the solvated brush thickness and volume % polymer are expected to contain substantial error; indeed comparison of Figures 4 and S2 indicate that for the highly swollen brush at pH 4, the volume % polymer is underestimated and the solvent volume fraction is overestimated. However, previous studies comparing a single slab model with more accurate density profiles have demonstrated that the trends in the data are the same.⁶

References

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