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Electronic Supporting Information (ESI†)

Hydrophobic effects within the dynamic pH response of polybasic tertiary amine methacrylate brushes

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Wafer and QCM sensor preparation

Silicon wafers with a natural oxide layer and silica-modified QCM sensors were cleaned and rendered hydrophilic by first irradiation with UV/O_3 before being sonicated in Milli-Q water for 15 mins, with the water replaced every 5 min. The surfaces were then immersed in a 10 wt% sodium hydroxide solution for exactly 30 s before being rinsed with copious amounts of Milli-Q water and dried under a stream of nitrogen.

Brush synthesis details

Initiator-functionalised wafers and QCM sensors were placed in sealed 30 mL glass vials which were deoxygenated for 15 min under vented nitrogen flow. The QCM sensors were placed on Teflon (PTFE) stands to ensure that the initiator-functionalised surfaces were unimpeded. Copper(II) bromide, 2,2’-bipyridine, monomer and solvent were accurately (to 4 decimal places) weighed into a 100 mL round bottom flask. The flask was sealed, sonicated for 30 s to aid dissolution of the catalyst and ligand and deoxygenated for 15 min. The reducing agent (either sodium ascorbate or ascorbic acid) was added to the flask which was subsequently sonicated for 3 min and stirred for an additional 3 min, thereby creating the reaction mixture. The brush polymerisation was started by syringing ~10 mL (enough to fully immerse the surfaces) of the reaction mixture into the vials containing the wafers and QCM sensors. Polymerisations were carried out under a slight positive pressure of nitrogen at ambient temperature (22 ± 0.5 °C). Once the target polymerisation time was reached the reaction mixture was pipetted out of the vials and replaced with ethanol (performed twice). This step ensures that the polymerisation was quenched, *i.e.* brush growth stopped. The brush-modified surfaces were then rinsed with ethanol followed by Milli-Q water and gently dried

under nitrogen flow. During the synthesis of each brush-modified QCM sensor, brushes were grown, in tandem, on oxidised silicon wafers in the same polymerisation solution, allowing dry brush thickness values to be estimated for the brushes on the QCM sensors (since direct thickness measurements on the QCM sensors was not possible, see below).

Ellipsometry of dry brushes

In the modelling the real (*n*) and imaginary (*k*) components of the refractive indices of each material employed were: silicon, n = 4.15, k = 0.0439;[1] silica, n = 1.461, k = 0;[2] the three polymers, n = 1.52, k = 0;[3] and aqueous 10 mM potassium nitrate electrolyte, n = 1.335, k = 0. Dry brush thickness measurements were performed at three angles of incidence (60°, 50°, and 42°) and at three distinct locations on the wafer to improve the accuracy of the measurement and to check for consistency of brush growth across the surface. Green laser diffraction fringes were observed at the edge of the brush-modified QCM sensors when dry ellipsometric measurements were attempted at the centre. This suggests that no optically infinite layer exists to form the base of a well-defined optical profile.[4] Therefore the dry thicknesses of the brushes grown on the QCM sensors could not be reliably measured. However previous brush syntheses on ellipsometry-specific QCM sensors (QSX335, Q-Sense, Sweden) suggest that brushes grown on the QCM sensors have similar dry brush thickness values to brushes grown on wafers under identical polymerisation conditions *i.e.* brushes synthesised at the same time and in the same polymerisation solution (the 'sister' wafer).[5] As such dry brush thickness values reported here for the brush-modified QCM sensors are that of the brush grown on the sister wafer.

Ellipsometry multilayer-slab model for solvated polymer brushes

The solvated (wet) brush thickness values were determined from the recorded ψ and Δ data using a multi-slab model consisting of sequentially; a 1 mm silicon layer, a 2.5 nm silica layer (measured), a linear effective medium approximation (EMA, a method of interpolating the dielectric properties, such as refractive index, for a layer of mixed composition) layer of water and polymer of unknown thickness and composition, and a final ambient water layer to give an ensemble solvated brush thickness average over the size of the measurement spot.[6] Each layer in the model is assumed to have a constant density throughout the thickness, *i.e.* as a slab. This study was conducted using a single wavelength, fixed angle ellipsometer which makes more detailed modelling of the solvated brush layer, such as multi-slab or gradient-slab models, unreliable due to the increased number of unknowns that need to be fitted. Earlier work on solvated brushes by Edmondson *et al.* has shown that although using a slab model can lead to inaccuracies in the absolute fitted thickness relative to

more complex gradient layer models (which more accurately describe the polymer density profile), the trends in the data are expected to be equivalent.[7] In this work, brush thickness values obtained using a graded layer with an exponential density decay, and those calculated using a slab model were closely correlated. Fitted brush thickness values from the graded model (using a root-mean-square measure of layer thickness) varied between 72% and 89% of the single slab thickness, with the brush thickness values from both models having a very good linear correlation with an R^2 = 0.995. Since the brushes studied in this prior work had very similar thickness values and swelling ratios to the current work we have good confidence that the single slab model closely mimics the true changes in brush thickness.

Calculation of maximum swelling and collapse rates

The maximum rates of brush swelling and collapse were obtained from the gradient of the trendline fitted through the points at which the change in swelling ratio (ellipsometry) and frequency (QCM) as function of time was the highest in magnitude as shown in Figure S1 for the brush swelling kinetics monitored via ellipsometry and QCM-D.

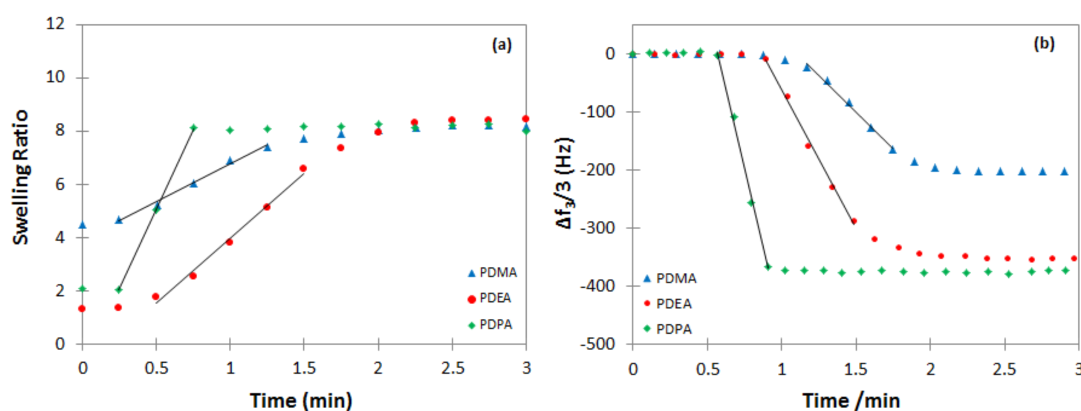

Figure S1. Brush swelling kinetics for (a) *in situ* ellipsometry and (b) QCM-D measurements. The solid lines indicate where the brushes exhibit their peak swelling rates.

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