Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information (ESI†)

Specific Ion Modulated Thermoresponse of Poly(*N*-isopropylacrylamide) Brushes

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Wafer and QCM Sensor Preparation

2.5 × 1.5 cm oxidised silicon wafers were exposed to UV/ozone for 15 min, sonicated in water for 15 min, replacing water every 5 min, then immersed in 10 wt% NaOH for 30 s. QCM sensors were exposed to UV/ozone for 15 min, rinsed with copious water then the silica surface of the sensors was covered with 10 wt% NaOH for 30 s. Rinsed wafers and QCM sensors were dried under a stream of N_2.

pNIPAM Brush Synthesis Details

Functionalised wafers and sensors were placed in 30 mL glass vials and deoxygenated for 15 min under vented N_2 flow with the QCM sensors positioned on Teflon stands to ensure the functionalised surfaces were not obstructed. $CuBr_2$, HMTETA, NIPAM and solvent were deoxygenated in a round bottomed flask while stirring for 15 min. The ascorbic acid was then added and the solution deoxygenated for a further 15 min over which time the solution changed colour from transparent blue to opaque pale yellow. 9 mL of the polymerisation solution (enough to submerge the functionalised wafers and QCM sensors) was then syringed into the reaction vials to initiate the brush polymerisation. This was carried out under slight positive N_2 pressure at ambient temperature (22±0.5 °C). When the target polymerisation time was reached the wafers and QCM sensors were removed from the reaction vials and rinsed with ethanol followed by copious water and dried under a stream of N_2. Sister wafers were grown in the reaction vial with QCM sensors to allow dry brush thickness values to be estimated for the brushes on the QCM sensors. Previous brush syntheses on ellipsometry-specific QCM sensors (Q-Sense, QSX335) suggest that brushes grown on the QCM sensors have similar dry brush thickness values to brushes grown on wafers under identical polymerization conditions (the ‘sister’ wafer).[1] Therefore, the dry thickness value reported here for the brush-modified QCM sensor was determined from the sister wafer.

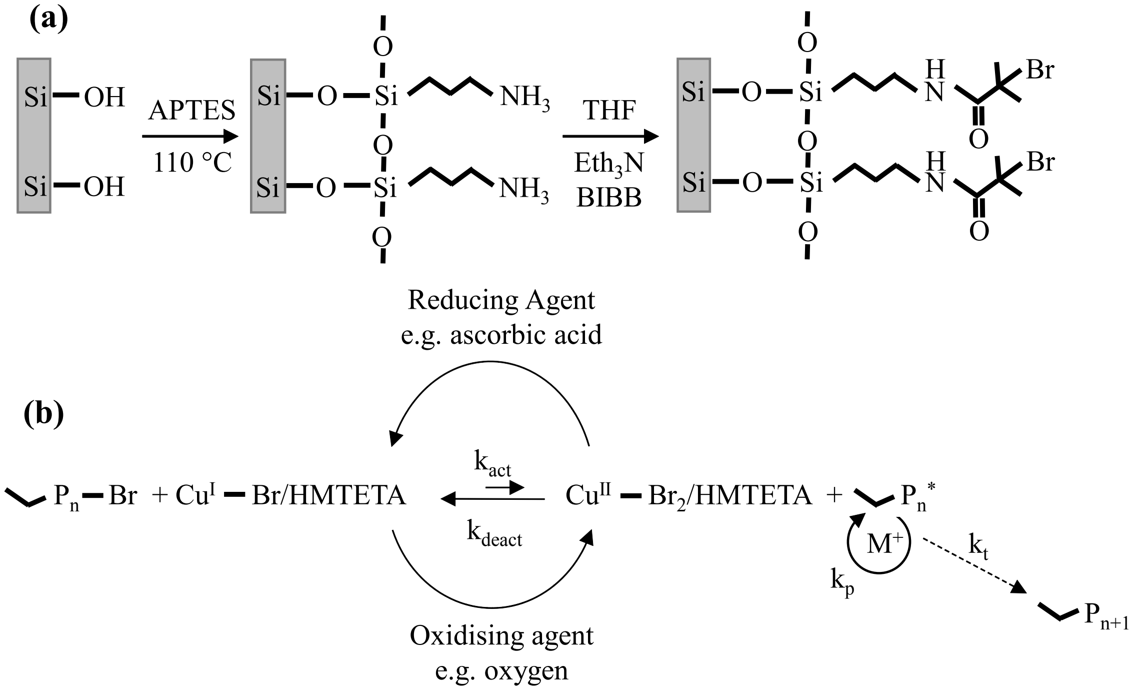


Figure S1: (a) Bromination of silica substrate, (b) Surface initiated ARGET ATRP of pNIPAM

Ellipsometric Data Fitting Protocol and Optical Model

For dry ellipsometry modelling, the real (n) and imaginary (k) components of the refractive indices of each material utilised were: silicon, $n = 4.15$, $k = 0.0439$;[2] silica, $n = 1.461$, $k = 0$;[3] and pNIPAM, $n = 1.52$, $k = 0$.[4] Three angles of incidence (60°, 50°, and 42°) were used for dry thickness measurements and the reported dry thickness is the average of three distinct positions on the wafer surface. For solvated (wet) experiments, an additional parameter for water was included with $n = 1.335$ and $k = 0$.[5] The n and k values for water were employed for all electrolyte solutions; at the highest electrolyte concentration (250 mM) there was minimal difference in the refractive index of the solution or the fitted brush thickness.

For solvated experiments, the equilibrium brush thickness was determined by averaging a minimum of 4 min of Δ and Ψ measurements from the plateaued constant region and fitting these data using a multilayer slab model. The multilayer slab model used here consisted 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] As this study was conducted using a single wavelength fixed angle ellipsometer, more detailed modelling of the solvated brush thickness such as multi-slab or gradient-slab models would be unreliable due to the increased number of unknowns that need to be fitted. Edmondson et al. have previously shown that although using a slab model isn't as accurate as more complex gradient layer models, the trend in the data are expected to be equivalent.[7] The maximum error of the solvated brush thickness measurement was approximately ±3 nm established from the noise in the Δ and Ψ data.

Polymerisation Growth Kinetics

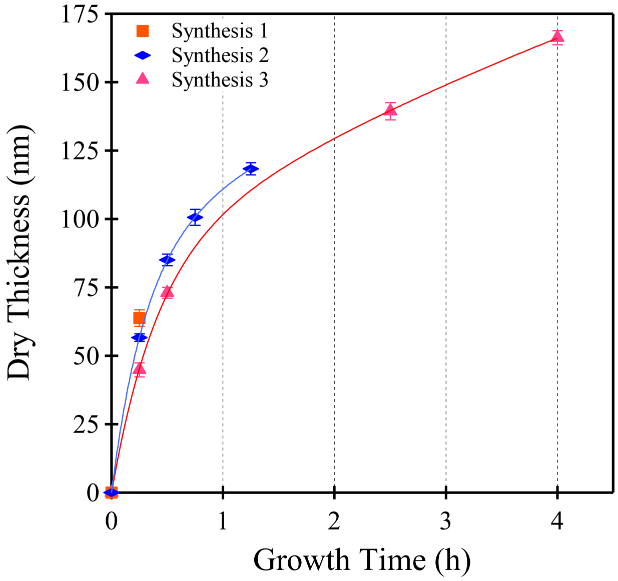
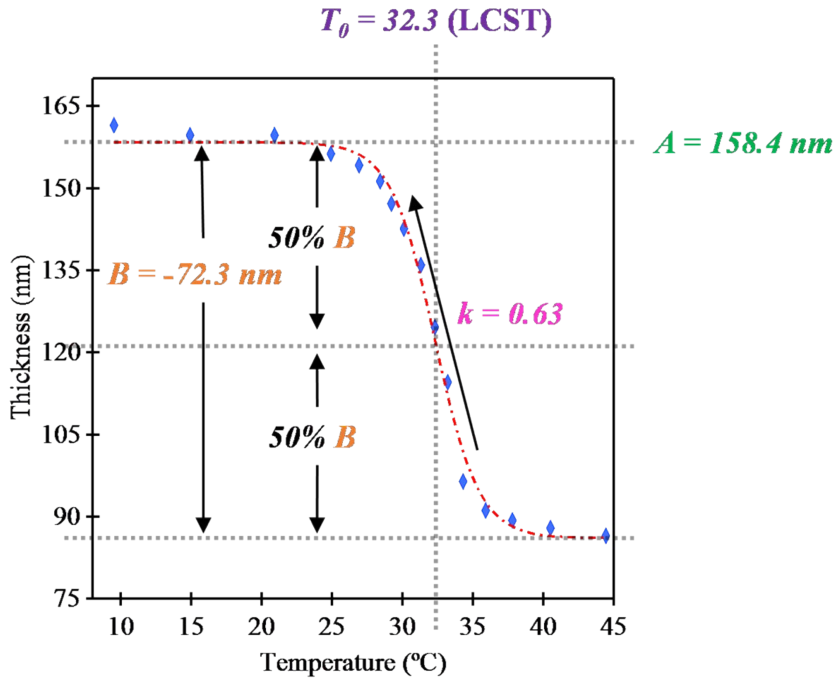


Figure S2. Dry brush thickness (ellipsometry) as a function of polymerisation time for three successive syntheses. Error bars display 1 standard deviation in repeat measurements for three positions across wafer.

Sigmoidal Fit Example Showing All Parameters



Sigmoidal curve equation: $$y = A + \frac{B}{1+exp\left(k(T_0-T)\right)}$$

Figure S3: Ellipsometric thickness of a pNIPAM brush in MilliQ water as a function of temperature showing the parameters used for the sigmoidal fit where y is the measured thickness as a function of temperature, T. The constant A represents the plateau value of the given parameter at low T, and B is the change in this parameter to the plateau value at high T. The value T_0 represents the temperature at which the parameter has changed by 50%, and is used here as a measure of the LCST. The constant k (in °C^{-1}) is the steepness of the curve, or transition rate.

Table S1: Full list of sigmoidal fit parameters.

		Pure Water			
		LCST (°C)	**Rate (°C^{-1})**	**A (*y* units)**	**B (*y* units)**
Ellipsometry (nm)	pure water	32.3 ± 0.2	0.63 ± 0.08	158.4 ± 1.3	-72.3 ± 2.2
QCM Δ*D*		31.9 ± 0.1	1.0 ± 0.1	104.9 ± 1.8	-98.4 ± 2.6
Contact Angle (°)		31.9 ± 0.5	3.3 ± 1.1	13.8 ± 0.1	10.6 ± 0.2
	Ionic Strength (mM)	**Acetate**			
		LCST (°C)	**Rate (°C^{-1})**	**A (*y* units)**	**B (*y* units)**
Ellipsometry (nm)	10	32.3 ± 0.2	0.71 ± 0.10	158.0 ± 1.3	-71.2 ± 2.3
	100	29.5 ± 0.1	0.83 ± 0.07	157.3 ± 1.3	-69.7 ± 2.0
	250	26.4 ± 0.2	1.0 ± 0.1	158.0 ± 2.1	-66.8 ± 2.5
QCM Δ*D*	10	31.5 ± 0.1	1.0 ± 0.1	112.4 ± 1.5	-110.4 ± 2.6
	100	29.5 ± 0.1	1.0 ± 0.1	97.9 ± 1.7	-94.4 ± 2.5
	250	26.4 ± 0.1	1.1 ± 0.12	106.9 ± 2.5	-101.3 ± 2.8
Contact Angle (°)	10	31.9 ± 0.5	3.3 ± 1.1	14.2 ± 0.2	9.8 ± 0.3
	100	29.2 ± 0.5	2.5 ± 0.63	13.7 ± 0.2	10.4 ± 0.3
	250	26.5 ± 0.5	2.5 ± 0.63	14.0 ± 0.1	10.0 ± 0.3
	Ionic Strength (mM)	**Thiocyanate**			
		LCST (°C)	**Rate (°C^{-1})**	**A (*y* units)**	**B (*y* units)**
Ellipsometry (nm)	10	32.6 ± 0.1	0.83 ± 0.07	159.8 ± 1.3	-69.4 ± 2.1
	100	33.9 ± 0.2	0.67 ± 0.09	161.8 ± 1.3	-71.0 ± 2.2
	250	35.1 ± 0.1	0.71 ± 0.05	164.5 ± 0.8	-69.0 ± 1.2
QCM Δ*D*	10	32.1 ± 0.1	1.1 ± 0.12	106.2 ± 1.6	-105.1 ± 2.6
	100	32.7 ± 0.1	1.0 ± 0.10	110.4 ± 1.4	-104.5 ± 2.4
	250	32.5 ± 0.2	0.67 ± 0.04	115.2 ± 2.5	-116.1 ± 3.6
Contact Angle (°)	10	32.4 ± 0.5	3.3 ± 1.1	13.9 ± 0.1	10.1 ± 0.1
	100	33.4 ± 0.5	3.3 ± 1.1	13.8 ± 0.1	10.4 ± 0.1
	250	33.9 ± 0.5	3.3 ± 1.1	13.6 ± 0.2	10.2 ± 0.3

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