

Supporting Information: Hydration in Weak Polyelectrolyte Brushes

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Polymer Synthesis

All reagents were used as received from the suppliers without further purification unless otherwise noted. Proton and carbon Nuclear Magnetic Resonance (NMR) spectra were obtained in CDCl₃ on a Varian VNMRS 500 NMR spectrometer. Chemical shifts were referenced to TMS at 0 ppm for both proton and ²⁹Si, and to CDCl₃ at 77.23 ppm for carbon.

Homopolymer and copolymer brushes were grown from silicon surfaces that were piranha cleaned and decorated with initiators made of 2-bromo-N-(11-(dichloro(methyl)silyl)undecyl)-2-methylpropanamide, synthesis of which is described below. The initiator-modified surface, monomers [*tert*-butylmethacrylate (tBMA) and 2-hydroxyethylmethacrylate (HEMA)], solvent benzene (1:1, v/v) and ethylbromoacetate (8 mM), the sacrificial initiator, were added to a Schlenk flask. The 4,4'-dinonyl-2-2'-dipyridyl ligand, CuBr and CuBr₂ [Monomer/Cu(I)/ Cu(II) = 215/2.70/9.96] were weighed separately, mixed into a paste and then also added to the flask.

The reaction mixture was immediately subjected to three freeze-pump-thaw cycles, sonicated for 2 minutes and then placed in an oil bath preheated to 60°C for 18 hours to grow the PtBMA or P(tBMA-*co*-HEMA) brushes. After polymerization the silicon substrates were rinsed with methanol and dried in a nitrogen stream. The reaction mixture was dissolved in tetrahydrofuran (THF) and passed through a silica gel plug to remove copper species prior to size exclusion chromatography (SEC) analysis of the polymer grown in solution. Recovered and purified polymers were analyzed by ¹H NMR and compositions were found to be consistent with feed compositions (< 3% different). Deprotection of the PtBMA and P(tBMA-*co*-HEMA) brushes was performed by immersing the brush-modified substrates in a solution of trifluoroacetic acid (TFA) in dichloromethane (30% v/v).

Synthesis of 2-bromo-2-methyl-N-(undec-10-enyl)propanamide

Under nitrogen, an oven-dried 500-mL recovery flask was charged with 1-amino-10-undecene (16.93 g, 0.10 mol), triethylamine (1.13 g, 0.11 mol), 250 mL of dichloromethane, and a stir bar. A 125-mL pressure-equalizing addition funnel with a nitrogen inlet was attached to the flask, and the stirred solution cooled in an ice-water bath under nitrogen flow. A solution consisting of α -bromo-isobutyryl bromide (25.8 g, 0.11 mol) in 50 mL dichloromethane was transferred under nitrogen to the addition funnel, and added drop-wise over the course of 15 min to the stirred reaction mixture at 0°C. Toward the end of the addition, the solution became turbid. The water-ice bath was removed and stirring continued at ambient temperature overnight. The turbid solution was transferred to a separatory funnel and washed with 0.2 M HCl (2 \times 300 mL), deionized water (1 \times 300 mL), 5% NaHCO₃ (1 \times 300 mL), and finally saturated NaHCO₃ (1 \times 300 mL). The volatiles were removed from the straw-colored solution to afford the crude product

(amber-colored oil) in quantitative yield. The amide (31.7 g) was transferred to a custom glass rig and dried under vacuum for 2 days at ambient temperature; thence small fractions were distilled into all-glass ampules fitted with break-seals. This compound distilled at an external bath temperature of approximately 130-150°C; a small fraction was sampled for confirmation by ^1H and ^{13}C NMR, and an early fraction of 5.2 g was reserved for the next synthetic step.

In preparation for the hydrosilylation reaction, $\text{HSi}(\text{CH}_3)\text{Cl}_2$ (99%, Aldrich), and $(\text{CH}_3)_3\text{SiCl}$ (99%, Aldrich) were dried by stirring over CaH_2 overnight and then were distilled into ampules. Hexanes were dried over $n\text{-BuLi}$, benzene and toluene was purified over poly(styryl) lithium, THF was purified over K/Na alloy; these solvents were docked at the vacuum line and out-distilled as needed. Pt catalyst [Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, solution in xylene, Aldrich] was transferred to a vacuum apparatus, diluted with benzene and distributed into ampules.

Synthesis of 2-bromo-N-(11-(dichloro(methyl)silyl)undecyl)-2-methylpropanamide

The hydrosilylation was accomplished, *in vacuo*, in a specially prepared all-glass apparatus equipped with break-seals for the addition of reagents and constrictions for the closure and transfer of products. The apparatus, built with an integral condenser, was designed to have exactly one low point for effective and unambiguous turnover by reflux, and it was affixed to the high-vacuum line by means of an all-glass bridge equipped with a Teflon stopcock. The apparatus was evacuated under high-vacuum, after which 100 mL THF was in-distilled. The stopcock was closed. The break-seal of $(\text{CH}_3)_3\text{SiCl}$ was ruptured, so that 0.25 g of TMSCl in 1 mL benzene was added. The solution was left to stir and modestly reflux/silanize overnight from a 40°C bath to the 20°C apparatus and 10°C condenser. The following morning, ampules

of Pt catalyst (0.1% in benzene, 1 mL) and 2-bromo-2-methyl-N-(undec-10-enyl)propanamide (5.2 g, 16.3 mmol) were opened and these contents were allowed to reflux under the same conditions for 15 additional minutes. $\text{HSi}(\text{CH}_3)\text{Cl}_2$ (5.18 g, 45.0 mmol) was then added to the solution to initiate the hydrosilylation reaction. The reaction was allowed to progress for 18 hours at 37-40°C (external T). All volatile contents were then out-distilled from the apparatus and collected to a waste reservoir docked elsewhere on the vacuum line. The product was vacuumed overnight and then 30 mL hexanes were in-distilled. The apparatus was detached by sealing a constriction above the condenser and all of the product solution was then poured and distributed to attached ampules. One of these small ampules was fitted further with an NMR tube; and this aliquot was re-evacuated, constituted with dry CDCl_3 , and sealed under vacuum into the NMR tube. A larger ampule was diluted in toluene to a concentration suitable for future use and distributed into break-open ampules.

Polymer Brush Characterizations

The weak PE brushes were characterized by optical ellipsometry and atomic force microscopy (AFM). Topographical images acquired by AFM in tapping mode show the films to be uniform and homogeneous. Ellipsometric measurements were made using a Beaglehole Instruments Picometer ellipsometer, with ellipsometric parameters measured at angles of incidence between 60° and 80°, using steps of 1°. Thicknesses were determined by fitting the entire data set using a refractive index nominally constrained to 1.48. The properties of homopolymer and copolymer brushes are listed in **Table S1**. Ellipsometric grafting density is calculated using the formula $\Gamma_{\text{ellipsometry}} = d_{\text{ellipsometry}} \rho N_A / M_n$, where ρ is the bulk density of the polymer from the literature (1.02 g/cm³ for PtBMA, 1.015 g/cm³ for PMAA, and 1.15 g/cm³ for

PHEMA), N_A is Avogadro's number, M_n is the number average molecular weight of the recovered, free polymer chains, and $d_{\text{ellipsometry}}$ is the ellipsometric layer thickness. This standard treatment does not account for adsorbed water in the polymer layer, which can produce anomalously large values of film thickness $d_{\text{ellipsometry}}$ or variations in film mass density from bulk literature values. The grafting density values listed above are in fact significantly larger than those derived self-consistently from neutron reflectivity measurements.

Table S1: Properties of PMAA and P(MAA_{1-r}-co-HEMA_r) brushes. Here r is the mole fraction of HEMA in the copolymer, $d_{\text{ellipsometry}}$ is the ellipsometric thickness of the polymer layer in humid air, M_n is the number average molecular weight and PDI is the polydispersity index of the polymer chains grown in solution measured by SEC. Grafting density $\Gamma_{\text{ellipsometry}}$ is calculated using the ellipsometric thickness measured in air.

r	$d_{\text{ellipsometry}}$ (Å)	M_n (g/mol)	PDI	$\Gamma_{\text{ellipsometry}}$ (10^{-2} Å ⁻²)
0	195	53,500	2.3	0.22
0.2	219	39,000	2.1	0.36
0.3	83	23,400	1.4	0.23

Buffer Recipes and Preparation Procedure

Table S2. Amounts of buffer species and sodium chloride required to make 100 ml buffer solution of 10 mM ionic strength at pH values given.

pH	Buffer species	Mass of buffer	
		species (g)	Mass of NaCl (g)
3	Phosphoric acid	0.098	0.007
6	MES free acid ^a	0.195	0.03
8	MOPS ^b	0.209	0.006

^a2-(*N*-morpholino)ethanesulfonic acid

^b3-(*N*-morpholino)propanesulfonic acid

Buffer Preparation Procedure

1. Dissolve the given amount of buffer species in approximately 90 ml of deionized water.
(For neutron reflectivity measurements, D₂O was used.)
2. Add the given amount of NaCl. Dissolve it completely.
3. Adjust to desired pH with small amounts of 1M sodium hydroxide (NaOH) or 1M hydrochloric acid (HCl) previously made using deionized water.
4. Add deionized water (D₂O) to set the volume to exactly 100 ml.

Hydration Calculation

Recall the four equations defining polymer-film hydration in humid air and in contact with a pH-controlled D₂O buffer solution.

$$\Sigma_{\text{hum}} = f_{\text{hum}} \Sigma_{\text{H}} + (1 - f_{\text{hum}}) \rho S \quad (\text{S1})$$

$$\mu / \rho = (1 - f_{\text{hum}}) d_{\text{hum}} \quad (\text{S2})$$

$$\Sigma_{\text{pH}} = f_{\text{pH}}\Sigma_{\text{D}} + (1 - f_{\text{pH}})\rho S, \quad (\text{S3})$$

$$\mu / \rho = (1 - f_{\text{pH}})d'_{\text{pH}}, \quad (\text{S4})$$

Four unknown quantities, ρ (mass density of dry polymer film), μ/ρ (the dry thickness of the polymer film), f_{hum} (volume fraction of water in the film in humid air), and f_{pH} (volume fraction of water in the film exposed to pH-controlled D₂O buffer solution) are expressed in terms of four quantities derived from two fitted reflectivity data sets, d_{hum} , Σ_{hum} (fitted thickness and SLD, respectively, of polymer film in humid air), d'_{pH} , and Σ_{pH} (fitted thickness and SLD, respectively, of polymer film against buffer solution) and three known quantities, S (stoichiometry of monomers comprising the polymer), Σ_{H} (SLD of water adsorbed from air), and Σ_{D} (SLD of pH-controlled D₂O buffer solution). Apply straightforward, if somewhat tedious algebra to express the four unknown quantities in terms of the others,

$$\rho = \frac{1}{S} \frac{\Sigma_{\text{D}}(\Sigma_{\text{H}} - \Sigma_{\text{hum}})d_{\text{hum}} - \Sigma_{\text{H}}(\Sigma_{\text{D}} - \Sigma_{\text{pH}})d'_{\text{pH}}}{(\Sigma_{\text{H}} - \Sigma_{\text{hum}})d_{\text{hum}} - (\Sigma_{\text{D}} - \Sigma_{\text{pH}})d'_{\text{pH}}}, \quad (\text{S5})$$

$$\mu / \rho = \frac{d_{\text{hum}}(\Sigma_{\text{H}} - \Sigma_{\text{hum}})^2 + d'_{\text{pH}}(\Sigma_{\text{hum}}\Sigma_{\text{D}} - \Sigma_{\text{hum}}\Sigma_{\text{pH}} - \Sigma_{\text{H}}\Sigma_{\text{D}} + \Sigma_{\text{pH}}\Sigma_{\text{H}})}{\Sigma_{\text{H}}^2 - \Sigma_{\text{hum}}\Sigma_{\text{H}} - \Sigma_{\text{H}}\Sigma_{\text{D}} + \Sigma_{\text{hum}}\Sigma_{\text{D}}}, \quad (\text{S6})$$

$$f_{\text{hum}} = \frac{\Sigma_{\text{hum}}\Sigma_{\text{H}} - \Sigma_{\text{hum}}^2 - \Sigma_{\text{H}}\Sigma_{\text{D}} + \Sigma_{\text{hum}}\Sigma_{\text{D}}}{\Sigma_{\text{H}}^2 - \Sigma_{\text{hum}}\Sigma_{\text{H}} - \Sigma_{\text{H}}\Sigma_{\text{D}} + \Sigma_{\text{hum}}\Sigma_{\text{D}}} - \left(\frac{d'_{\text{pH}}}{d_{\text{hum}}} \right) \frac{\Sigma_{\text{hum}}\Sigma_{\text{D}} - \Sigma_{\text{hum}}\Sigma_{\text{pH}} - \Sigma_{\text{H}}\Sigma_{\text{D}} + \Sigma_{\text{H}}\Sigma_{\text{pH}}}{\Sigma_{\text{H}}^2 - \Sigma_{\text{hum}}\Sigma_{\text{H}} - \Sigma_{\text{H}}\Sigma_{\text{D}} + \Sigma_{\text{hum}}\Sigma_{\text{D}}}, \quad (\text{S7})$$

$$f_{\text{pH}} = \frac{\Sigma_{\text{pH}}\Sigma_{\text{D}} - \Sigma_{\text{pH}}^2 - \Sigma_{\text{H}}\Sigma_{\text{D}} + \Sigma_{\text{pH}}\Sigma_{\text{H}}}{\Sigma_{\text{D}}^2 - \Sigma_{\text{pH}}\Sigma_{\text{D}} - \Sigma_{\text{H}}\Sigma_{\text{D}} + \Sigma_{\text{pH}}\Sigma_{\text{H}}} - \left(\frac{d_{\text{hum}}}{d'_{\text{pH}}} \right) \frac{\Sigma_{\text{pH}}\Sigma_{\text{H}} - \Sigma_{\text{hum}}\Sigma_{\text{pH}} - \Sigma_{\text{H}}\Sigma_{\text{D}} + \Sigma_{\text{hum}}\Sigma_{\text{D}}}{\Sigma_{\text{D}}^2 - \Sigma_{\text{pH}}\Sigma_{\text{D}} - \Sigma_{\text{H}}\Sigma_{\text{D}} + \Sigma_{\text{pH}}\Sigma_{\text{H}}}. \quad (\text{S8})$$