Supporting Information

Instability of surface-grafted weak polyacid brushes on flat substrates

Casey J. Galvin[1,2], Erich D. Bain[1,3], Adam Henke[4], Jan Genzer[1,*]

1 Department of Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, NC
2 Okinawa Institute of Science Technology Graduate University, Onna-son, Okinawa 904-0497 Japan
3 U.S. Army Research Laboratory, Aberdeen Proving Ground, MD 21005
4 California Institute for Biomedical Research, La Jolla, CA 92037

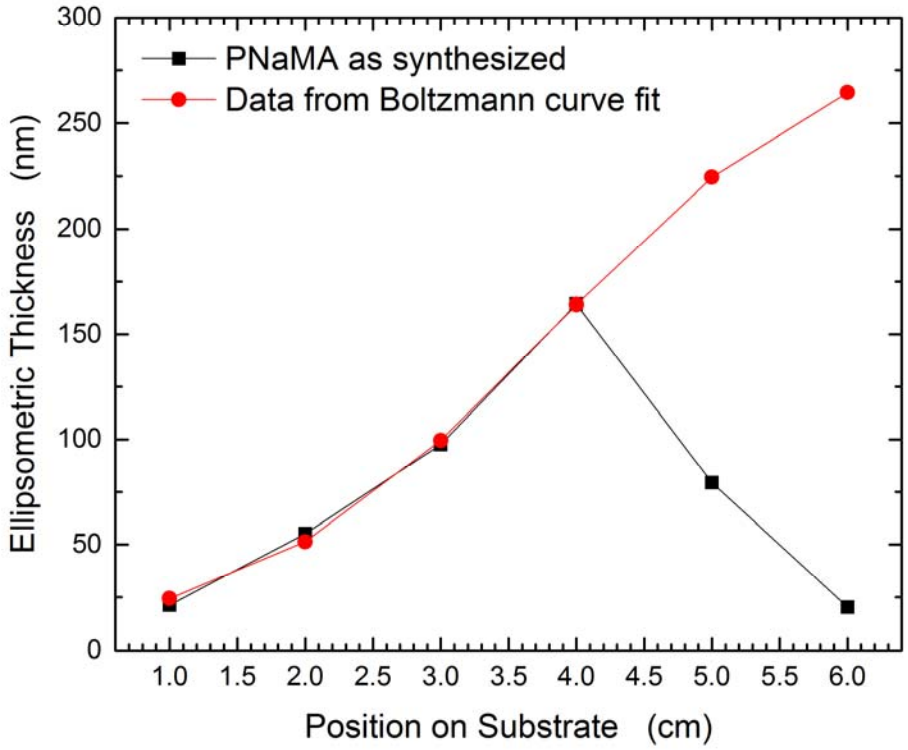

Figure S1. In order to estimate the grafting density (σ) of the densest regions of the polymer brush (> 4.0 cm), a Boltzmann curve (red) was fit to the first four data points (1.0 ~ 4.0 cm). From this curve, the expected thickness of the brush at high σ was estimated. By assuming σ = 0.5 chains/nm^2 at 6.0 cm, a value based on recent experiments[1], the σ value for other points on the brush was estimated as $\sigma_{6.0cm}*(h_x/h_{6.0cm})$ where $\sigma_{6.0cm}$ is the assumed value at 6.0 cm, $h_{6.0cm}$ is the thickness at 6.0 cm, and h_x is the thickness at the position of interest. This scaling is based on a mass balance which assumes that the molecular weight of the polymer chains is constant with σ.

* Corresponding author: jgenzer@ncsu.edu

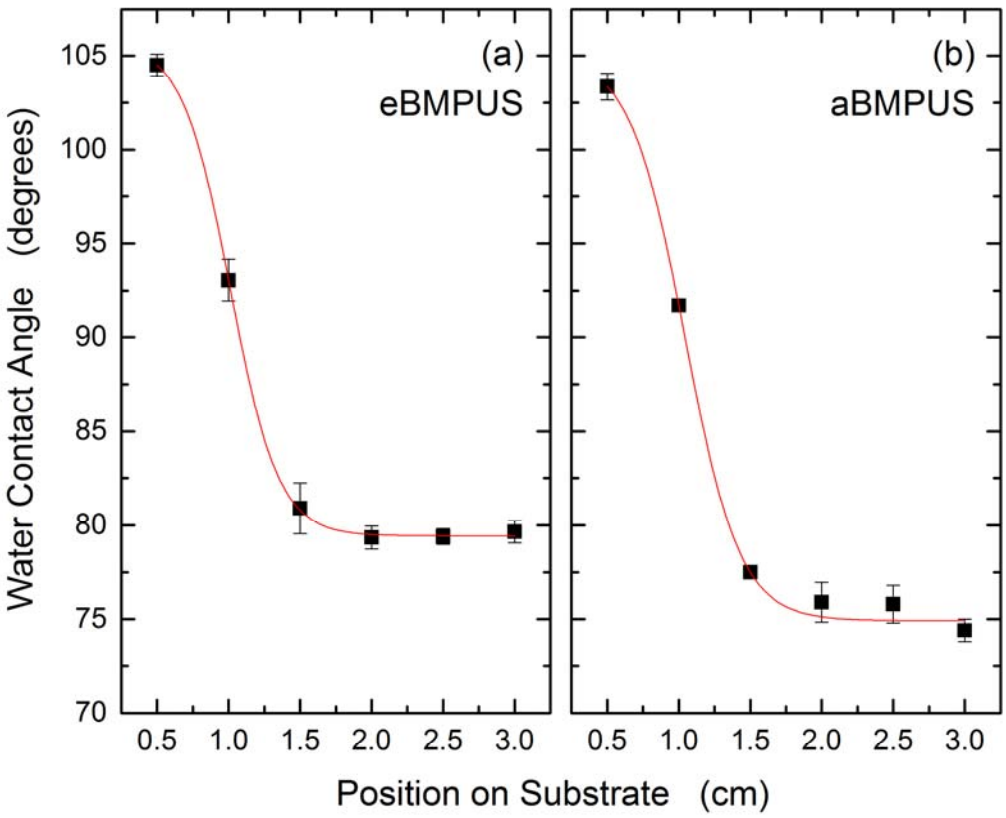

Figure S2. (a) eBMPUS gradient profile measured by water contact angle showing a smooth variation from octyltrichlorosilane (OTS; WCA = 105°) to eBMPUS (WCA = 79°). Red line is fit of data by tanh equation to demonstrate the smooth, sigmoidal shape of the gradient. (b) aBMPUS gradient profile measured by water contact angle showing a smooth variation from octyltrichlorosilane (OTS; WCA = 105°) to aBMPUS (WCA = 76°). Note that aBMPUS exhibits a lower water contact angle than eBMPUS. The red line is fit of data by tanh equation to demonstrate the smooth, sigmoidal shape of the gradient.

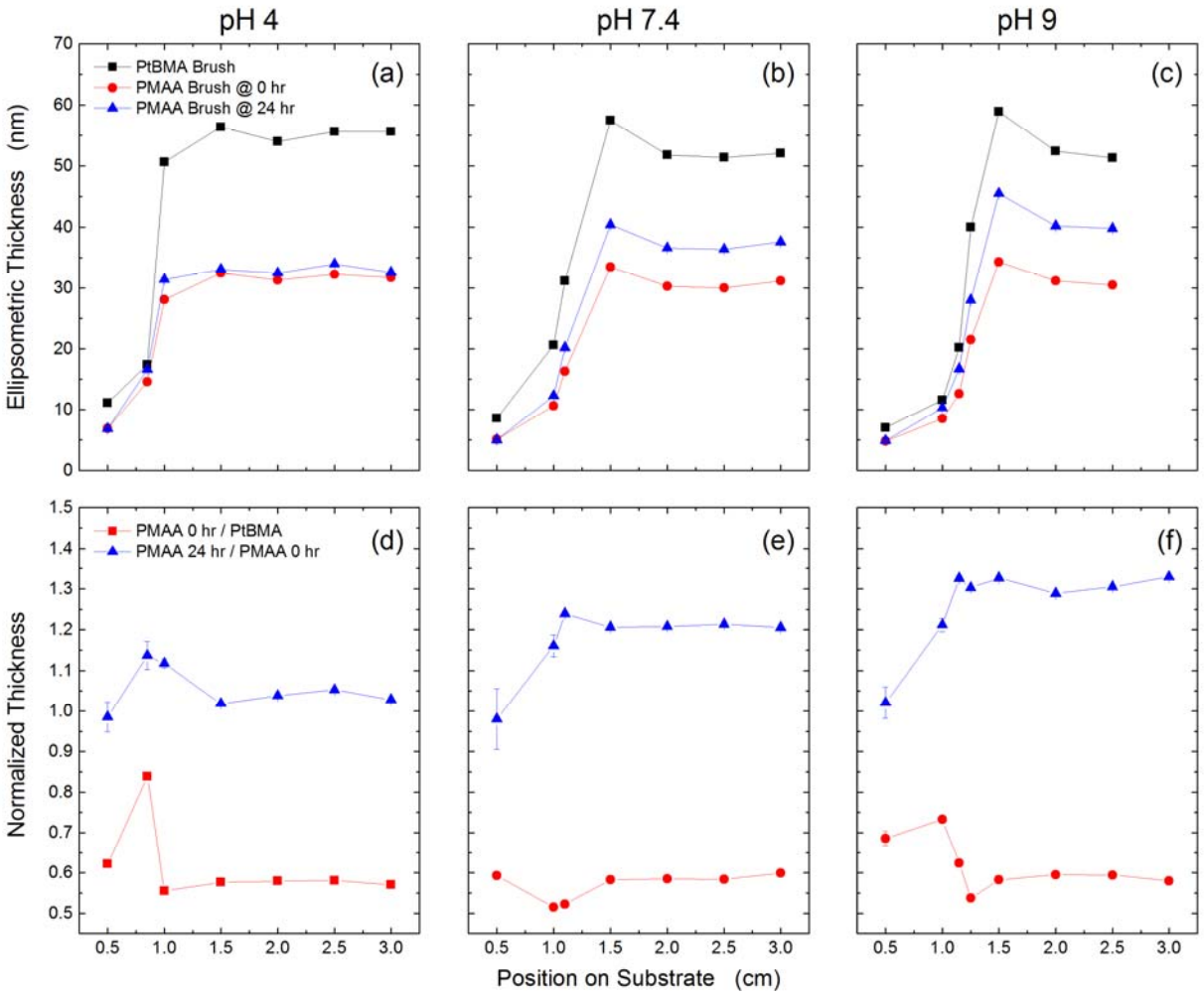

Figure S3. Data for eBMPUS brushes through 24 hours of incubation for all pH levels. Panels (a) – (c) plot the thicknesses measured using ellipsometry as a function of position on the substrate for the initial PtBMA brush (black), PMAA brush prior to incubation (red) and the PMAA brush following incubation for 24 hours (blue). Panels (d) – (f) plot the thickness of the PMAA brushes prior to incubation normalized by the PtBMA thickness (red) and thickness after 24 hours incubation normalized by the thickness of the PMAA brush prior to incubation (blue).

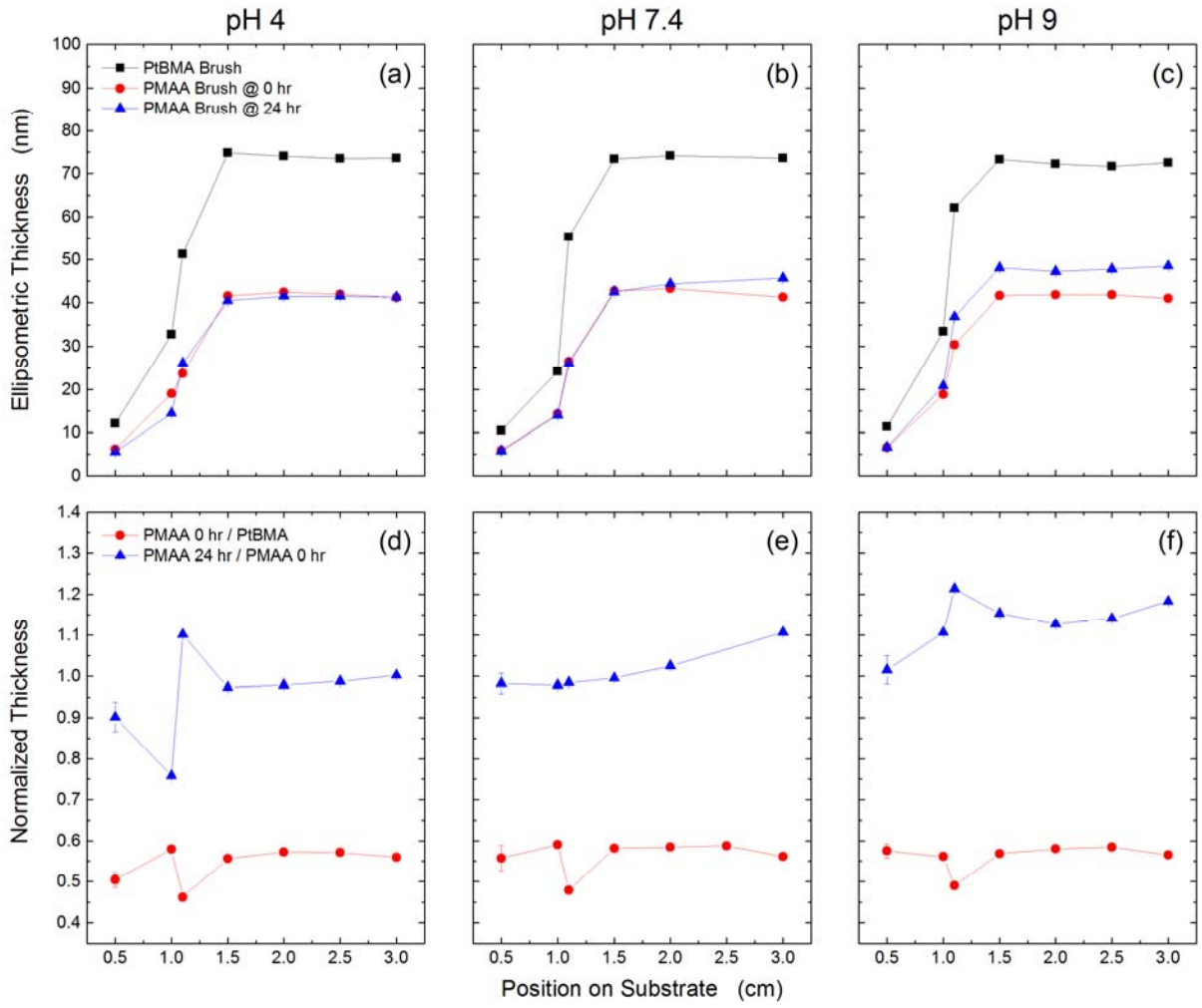

Figure S4. Data for aBMPUS brushes through 24 hours of incubation for all pH levels. Panels (a) – (c) plot the thicknesses measured using ellipsometry as a function of position on the substrate for the initial PtBMA brush (black), PMAA brush prior to incubation (red) and the PMAA brush following incubation for 24 hours (blue). Panels (d) – (f) plot the thickness of the PMAA brushes prior to incubation normalized by the PtBMA thickness (red) and thickness after 24 hours incubation normalized by the thickness of the PMAA brush prior to incubation (blue).

Table S1. Estimation of thickness reduction for complete hydrolysis of PtBMA to PMAA

Property	tBMA	MAA
Molecular Weight (M_0) (g/mol)	142.2	86.09
Density[a] (ρ) (g/cm^3)	0.875	1.015
Monomer volume (v_0) (cm^3)	2.70×10^{-22}	1.41×10^{-22}

a) Data taken from supplier website (www.sigmaaldrich.com)

The reduction in thickness for complete hydrolysis of PtBMA to PMAA can be estimated as:

$$\frac{\Delta h}{h_{PtBMA}} = 1 - \frac{\mathrm{v}_{0,\mathrm{MAA}}}{\mathrm{v}_{0,\mathrm{tBMA}}} = 0.48$$

where h_{PtBMA} is the thickness of the PtBMA brush, Δh is the difference between the PtBMA and PMAA brush thicknesses, and v_0 is the monomer volume for MAA or tBMA monomer, respectively (see **Table S1**). This result is consistent with that observed in Figures S4 and S5 for both the eBMPUS and aBMPUS initiator samples. This value represents an estimate based on monomer physical properties, and does not fully capture the effect of polymerization and confinement of the chains to the surface. Nonetheless, the result suggests substantially all of the PtBMA units are hydrolyzed to PMAA, and insignificant levels of chain degrafting have occurred during hydrolysis.

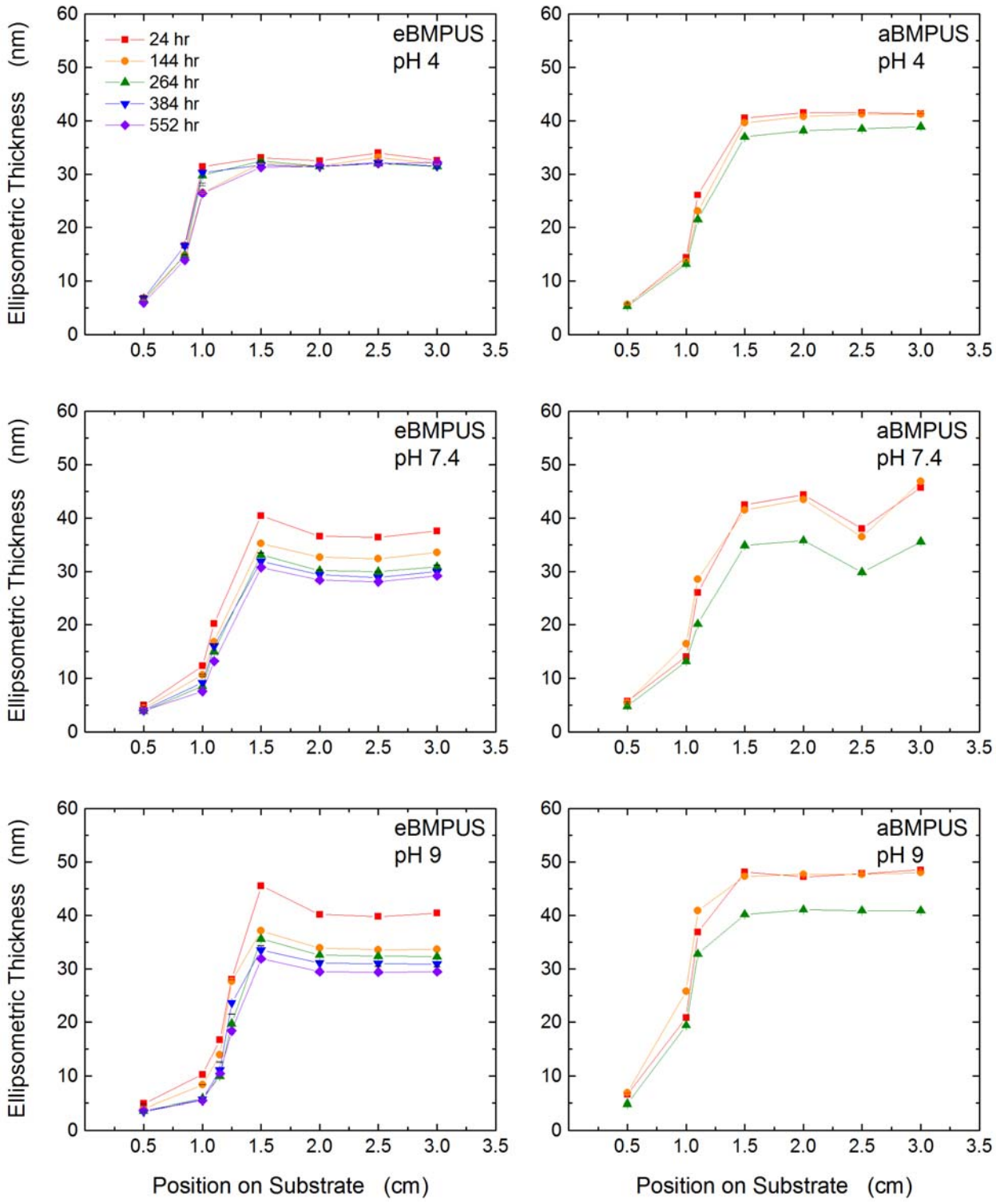

Figure S5. Raw data for σ gradient samples used to construct **Figure 6** in the main text. The panels plot the ellipsometric thickness as a function of distance from the OTS reservoir (*i.e.,* position on the substrate) for each incubation time period.

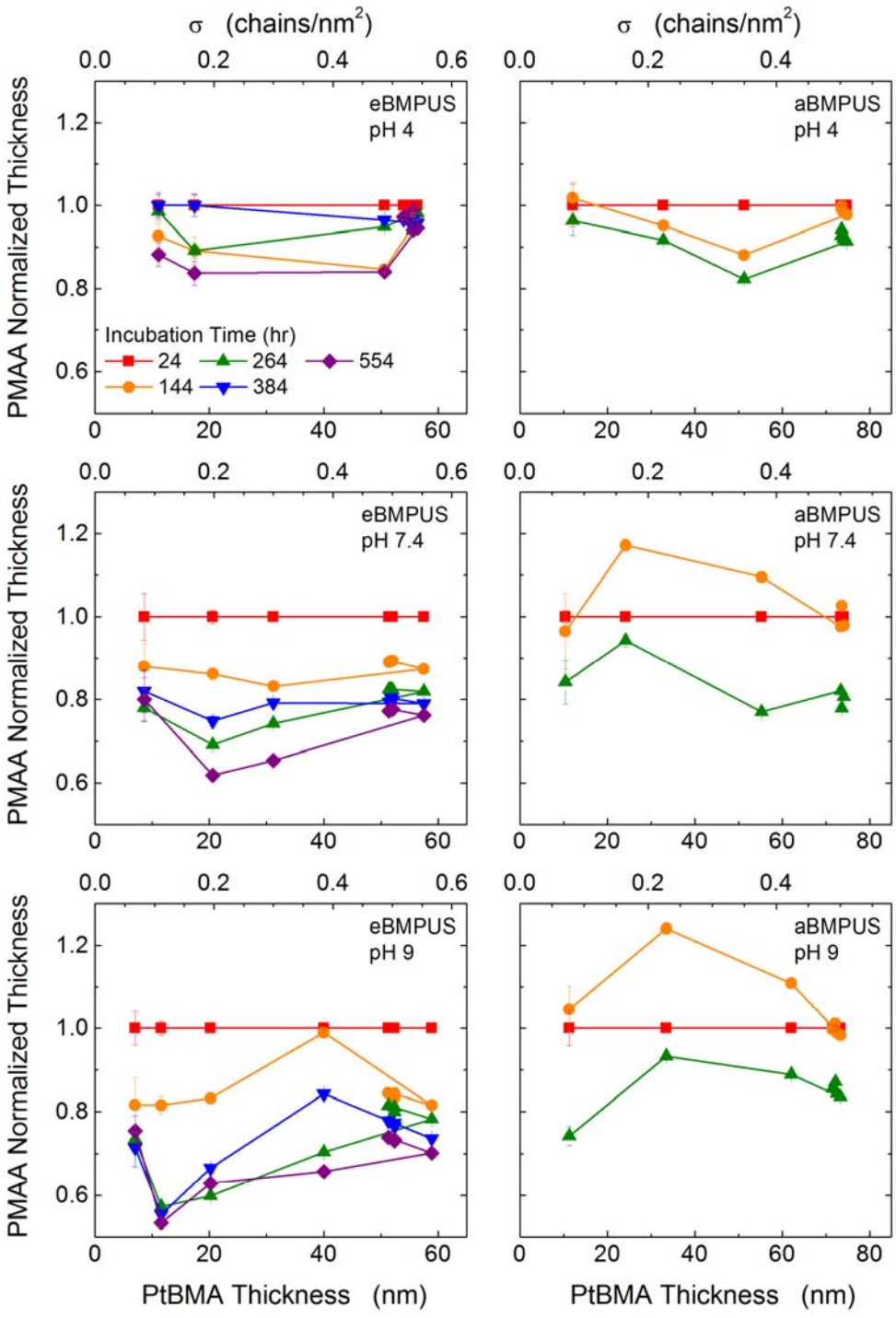

Figure S6. Full figure of Figure 6 in main text, showing thickness normalized to 24 hours for samples incubated at pH 4, 7.4 and 9 up to 554 hours. The data are plotted against the initial PtBMA thickness at each measurement point on the lower abscissa, which is used to estimate grafting density (σ) on the upper abscissa.

References

(1) Patil, R. R.; Turgman-Cohen, S.; Šrogl, J.; Kiserow, D.; Genzer, J. Direct Measurement of Molecular Weight and Grafting Density by Controlled and Quantitative Degrafting of Surface-Anchored Poly(methyl Methacrylate). *ACS Macro Lett.* **2015**, *4*, 251–254.