## SUPPORTING INFORMATION

Influence of Side Chain Hydrolysis on the Evolution of Nanoscale Roughness and Porosity in Amine-Reactive Polymer Multilayers

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Figure S1. ${ }^{1} \mathrm{H}$ NMR spectra for unhydrolyzed $\mathbf{P 1}$ (bottom) and a representative partiallyhydrolyzed $\mathbf{P} \mathbf{1}_{\mathbf{x}}$ polymer (top). Spectra were obtained in $\mathrm{CDCl}_{3}$ rather than in acetone- $\mathrm{d}_{6}$ to minimize H -exchange in an attempt to identify signals from the amide and carboxylic acid hydrogen in partially-hydrolyzed $\mathbf{P} \mathbf{1}_{\mathbf{X}}$. Inspection of the spectrum for $\mathbf{P} \mathbf{1}_{\mathbf{X}}$ shows that these peaks are not readily discernible; the only difference between the spectrum of $\mathbf{P 1}$ and that of $\mathbf{P} \mathbf{1}_{\mathbf{X}}$ is a slight broadening of the azlactone methine $(\mathrm{CH})$ backbone proton at $\sim 2.70 \mathrm{ppm}$.


Figure S2. Quantitative ${ }^{13} \mathrm{C}$ NMR spectra used to analyze the degree of azlactone group hydrolysis in partially-hydrolyzed $\mathbf{P} \mathbf{1}_{\text {A-d }}$ derivatives, as shown on the figure. The inset shows a selected area of the spectrum for $\mathbf{P} \mathbf{1}_{\mathbf{B}}$, over the approximate range $\sim 52$ to 72 ppm . The degree of hydrolysis was computed by the equation Percent Hydrolysis $=\left[I_{\text {ring-opened }} /\left(I_{\text {ring-opened }}+I_{\text {ring- }}\right.\right.$ closed $)]$. For example, for $\mathrm{P}_{\mathrm{B}}$, Percent Hydrolysis $=[0.20 /(0.20+1.00)]=0.167$ or $16.7 \%$. The associated error in degree of hydrolysis was obtained by assuming an error of $\pm 5 \%$ in the value of each integral, and by propagating through the percent hydrolysis calculation. All values and associated errors are given in Table 1 of the main text.


Figure S3. Gel permeation chromatography (GPC) traces for $\mathbf{P 1}$ (black) and $\mathbf{P 1}_{\mathbf{x}}$ (blue). The near overlap in the chromatograms indicates that the molecular weights and dispersities of the polymers are similar.


Figure S4. Representative advancing water contact angle photos for 35 bilayer $\mathrm{PEI} / \mathbf{P} \mathbf{1}_{\mathbf{X}}$ films assembled using $\mathbf{P} \mathbf{1}_{\mathbf{A}}$ to $\mathbf{P} \mathbf{1}_{\mathbf{D}}$, as indicated on the figure. This data is collected and presented with standard deviations in Figure 4B.


Figure S5. A) Receding water contact angles and B) contact angle hysteresis (defined as the difference in advancing and receding contact angles) for 35 bilayer films assembled using PEI and the model polymer $\mathbf{P} \mathbf{1}_{\mathbf{x}}$, and $\mathrm{PEI} / \mathbf{P} \mathbf{1}_{\mathbf{A}}$ to $\mathbf{P} \mathbf{1}_{\mathbf{D}}$, as indicated on the figure, before (black bars) and after (grey bars) treatment with decylamine. Error bars in A) represent the average of at least three measurements made on different locations of each film, and error bars in B) were computed by propagating the error in advancing and receding contact angles through the hysteresis calculation. The corresponding advancing water contact angle data is shown in Figure 4B and Figure S4.

