Supporting Information

Homogeneity, Modulus and Viscoelasticity of Polyelectrolyte Multilayers by Nano-Indentation: Refining the Buildup Mechanism

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Wet vs. dry thickness: Buildup of PDADMA/PSS multilayer

The concentration of the polyelectrolyte solutions of PDADMAC and PSS was 10 mM and their ionic strength was adjusted to 1 M by NaCl. 14 layers were first assembled to enable reliable indentation measurements, then AFM was used to obtain the wet thickness of the film (in 10mM NaCl) by scanning over a scratch. The dry thickness was measured with an ellipsometer. Buildup continued to 15, 18, 19, 22, 23, 26, 27, 30, 31, 40, 41, 50 and 51 layers. Wet and dry thicknesses were obtained for each of these layers. The jump in thickness was higher when PDADMA was added as the final layer indicating a higher swelling and degree of hydration then PSS ending film, as seen in Figure S1.

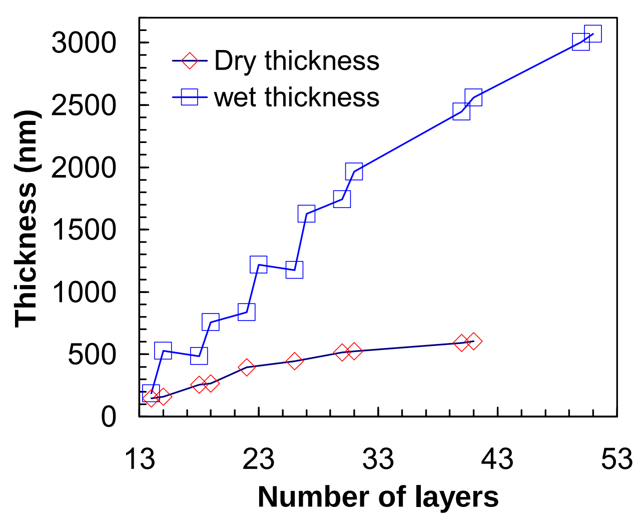


Figure S1. Dry and wet thickness of PDADMA/PSS multilayer starting from 14 layers. Wet thickness was obtained in 10 mM NaCl using AFM by scanning over a scratch, while dry thickness was measured by ellipsometry. Films with odd number of layers were PDADMA-ending while even number of layers corresponded to PSS-ending films.

Table 1. Wet thickness and modulus measurements at different number of layers. This data is plotted in Figure S1

Number of layers	Wet thickness (nm)	Modulus (MPa)
14	184	375
15	527	1.23
18	483	119.6
19	756	1.35
22	836	98.6
23	1220	9.8
26	1170	87.4
27	1630	8.3
30	1740	74.6
31	1970	9.1
40	2448	52.6
41	2560	12
50	3000	76
51	3070	9.7

Fitting profile

Figure S3 shows the force *vs*. indentation profile for $(PDADMA/PSS)_{15}$ prepared in 1 M NaCl and dipped in 0.1 M NaCl during measurement. A punch fit was used to obtain the apparent modulus; the radius of the tip was 10 nm. The curve was fitted up to 50 nm indentation. The apparent modulus of this film was 70 MPa.

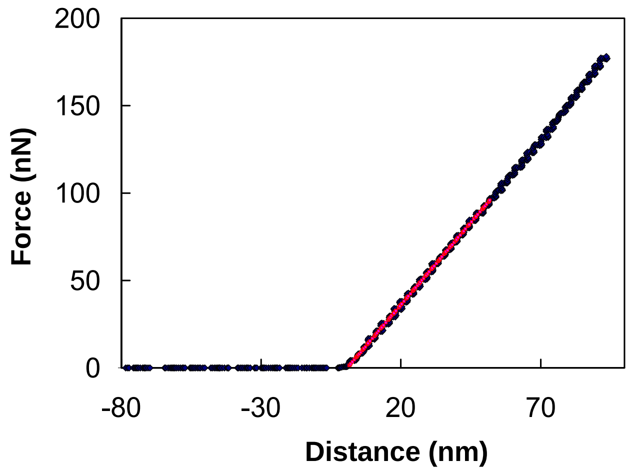


Figure S2. Punch fitting example for a force *vs*. indentation graph of $(PDADMA/PSS)_{15}$ prepared in 1 M NaCl and dipped in 0.1 M during measurement. The graph was fitted up to 50 nm of indentation; the radius of the tip was 10 nm. The apparent modulus was 70 MPa.

Surface morphology of dry and wet PSS and PDADMA ending films

Figure S4 depicts line scans taken across the image shown in Figure 5. The multilayers were terminated with either PSS or PDADMA and imaged dry or in situ in 10 mM NaCl (wet). When the PEMU is terminated with PSS the surface roughness is about the same, although the wet film appears to be slightly more swollen laterally. However, there is a significant increase in the surface roughness for the water-swollen PDADMA-topped PEMU.

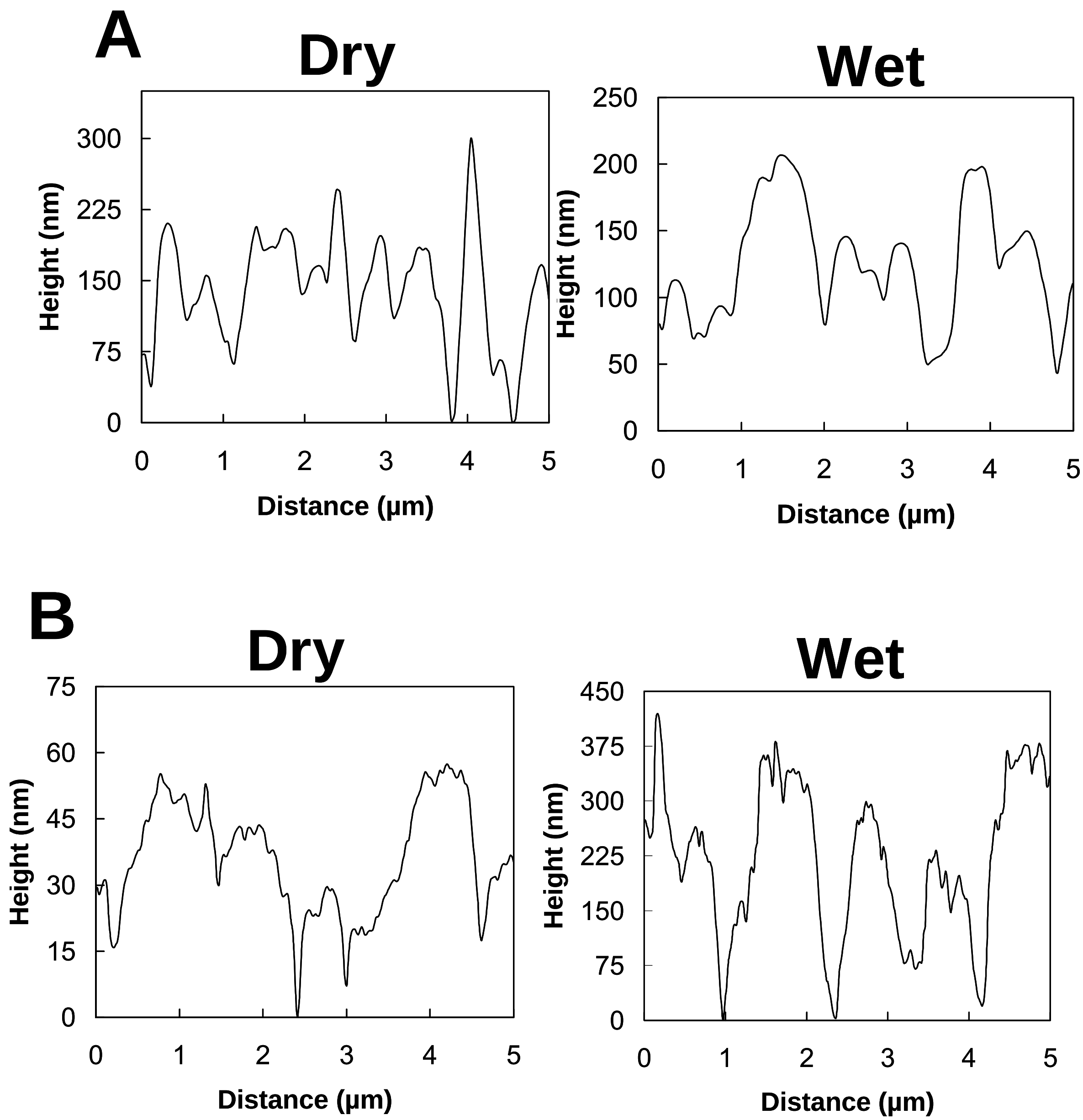
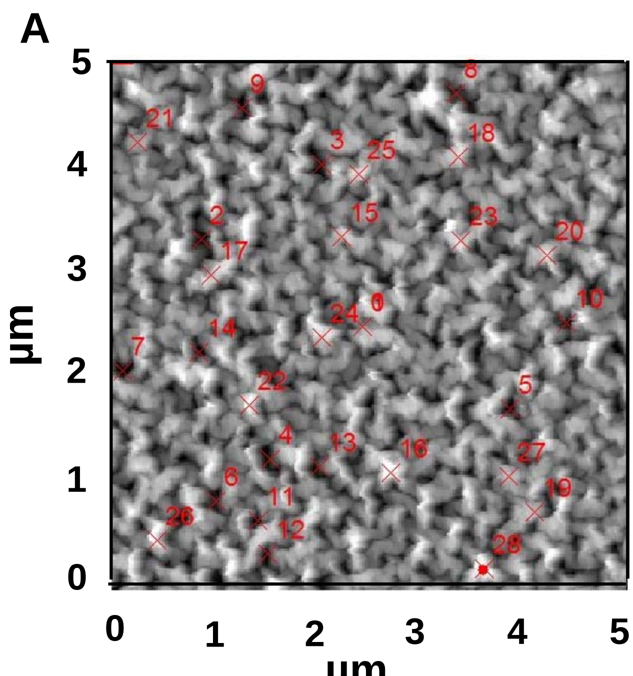


Figure S3. (A) Surface contour of PSS ending films, $(PDADMA/PSS)_{15}$, under wet (10 mM NaCl) and dry conditions. (B) Surface contour of PDADMA, $(PDADMA/PSS)_{15}PDADMA$, ending film under wet and dry conditions.

Mechanical homogeneity of dry PSS and PDADMA ending films

(PDADMA/PSS)$_{15}$ and the same multilayer after adding a PDADMA layer were imaged in AC mode under dry conditions. Force curves were performed on various spots along the images corresponding to peaks and valleys (see Figure S4). The film was quite stiff so AC160-TS tips with a spring constant of 40 N/m were used. For PSS ending film (Figure S4-A), the modulus of the peaks was 1.8 ±0.2 GPa and that of the valleys was 1.9 ±0.3 GPa. For PDADMA ending films (Figure S4-B, the modulus of the Peaks was 2.6 ±0.1 GPa, and that of the valleys was 2.4 ±0.1 GPa. This also showed that despite the roughness the composition is homogeneous even for the dry films, and hence there was no evidence of phase separation.



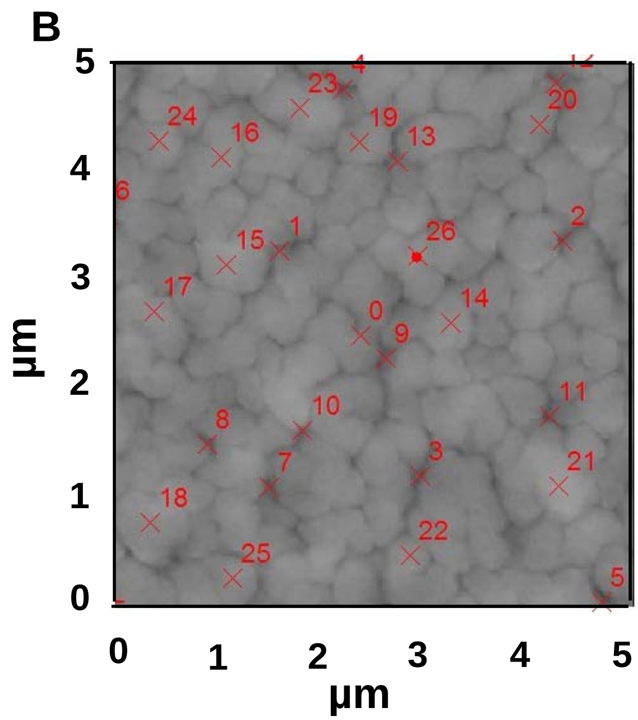


Figure S4. A and B are AFM images of (PDADMA/PSS)$_{15}$ and (PDADMA/PSS)$_{15}$PDADMA respectively. The images were recorded under dry conditions. Force curves were taken on various spots on the images that corresponded to peaks and valleys.

Effect of substrate stiffness on the apparent modulus of (PDADMA/PSS)$_{15}$ during layer by layer build up

As shown in Figure 1 in the main paper, indentation measurements started at the 14th layer because a minimum film thickness is required to avoid contributions of the substrate of the tip deflection, which would make the PEMU appear stiffer. To estimate this minimum thickness, films with 14, 18, 30, and 50 layers were compared. All films ended in PSS. Force curve measurements were performed in 10 mM NaCl. The resulting force vs. indentation profile was fitted from 0 to 2 nm, then 2 to 4 nm and up to 30 nm.

E_{app}/E_{PEMU} was plotted as a function of indentation, where E_{app} is the apparent modulus at each indentation and E_{PEMU} is the modulus of the PSS-terminated film at "infinite" (i.e. where the tip no longer "feels" the substrate) thickness, taken here as 70 MPa. Figure S5 shows the deviation of the apparent modulus from E_{PEMU} as the indentation increases. For thinner films E_{app} starts to deviate at shorter indentation than for thicker films. For sufficiently thick films the apparent modulus remained independent of indentation depth.

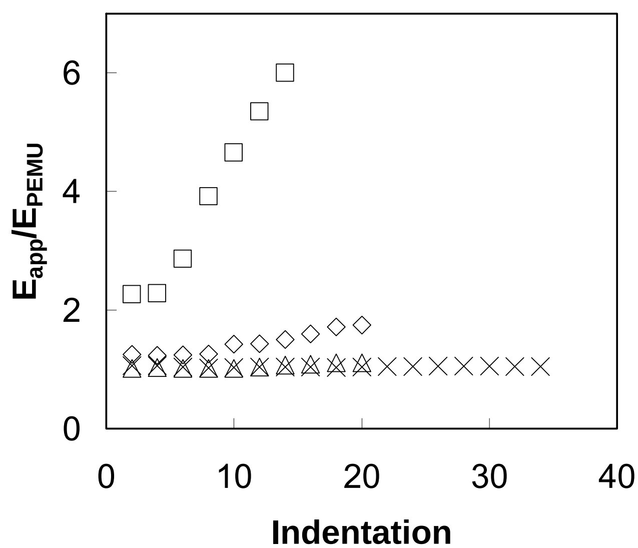


Figure S5. Films with 14 layers (□), 18 layers (◊), 30 layers (Δ), and 50 layers (x) (all ending in PSS). Force curves were performed for each film in 10 mM NaCl. Force vs. indentation curves were fitted from 0 to 2 nm, 2 to 4 nm, and so on, up to 30 nm indentation. For thinners films, E_{app} deviated from E_{PEMU} at shorter indentation as compared to thick films.