

## Supporting Information

*Exploring the heteroatom effect on polyelectrolyte multilayer assembly: the neglected polyoniums.*

Lara A. Al-Hariri, Andreas Reisch and Joseph B. Schlenoff

Department of Chemistry and Biochemistry, Tallahassee, Florida 32306

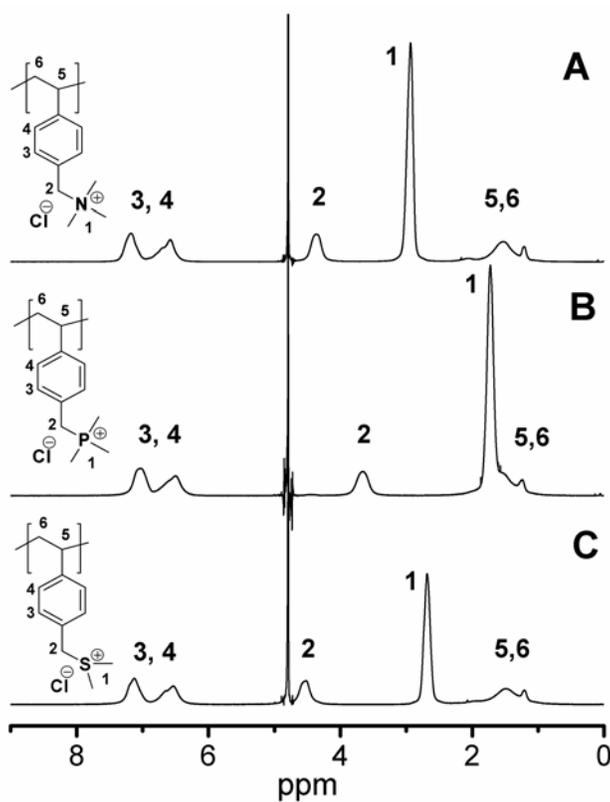


Figure S1:  $^1\text{H}$  NMR spectra of (A) PVBTMA, (B) PVBTMP and (C) PVBDMS in  $\text{D}_2\text{O}$ .

The stability of PVBTMA and PVBTMP was monitored by recording  $^1\text{H}$  NMR spectra of 50 mM of the polycation in 1.5 M NaCl in  $\text{D}_2\text{O}$  after different times of storage.  $^1\text{H}$  NMR spectra of PVBTMA and PVBTMP do not show any changes in the peaks after 20 weeks of storage (Fig S2/S3, respectively) indicating that these polymers are stable over extended periods of time. It is noteworthy that the stability test described above is done in harsh condition (1.5 M NaCl) that resembles the conditions in the PEMU.

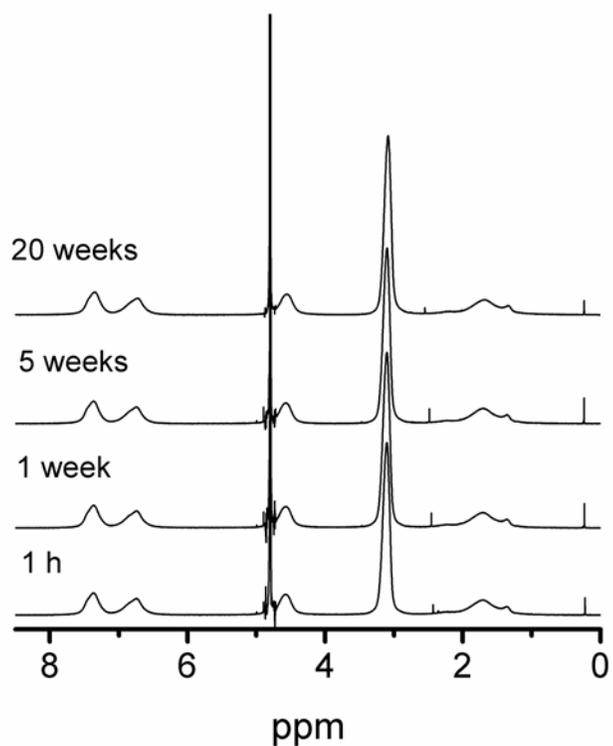


Figure S2:  $^1\text{H}$  NMR of PVBTMA in 1.5 M NaCl in  $\text{D}_2\text{O}$  after different times of storage (from bottom to top: 1 h, 1 week, 5 weeks, 20 weeks).

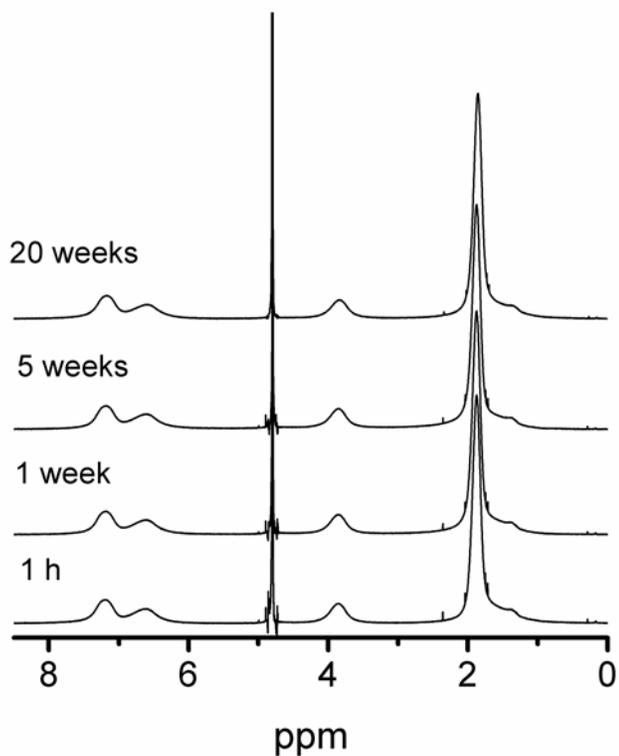


Figure S3: <sup>1</sup>H NMR of PVBTMP in 1.5 M NaCl in D<sub>2</sub>O after different times of storage (from bottom to top: 1 h, 1 week, 5 weeks, 20 weeks).

The following figure shows the adsorbed mass of PEI(PSS/Polyoniums) from 0.25 M NaCl on a gold coated quartz crystals versus number of layers measured by QCM. Figure S4 shows that the three polyoniums have a linear growth of hydrated mass versus number of layers. PSS/PVBTMP has a slightly higher adsorbed mass compared to PSS/PVBTMA and PSS/PVBDMS which have the same adsorbed mass versus number of layers deposited.

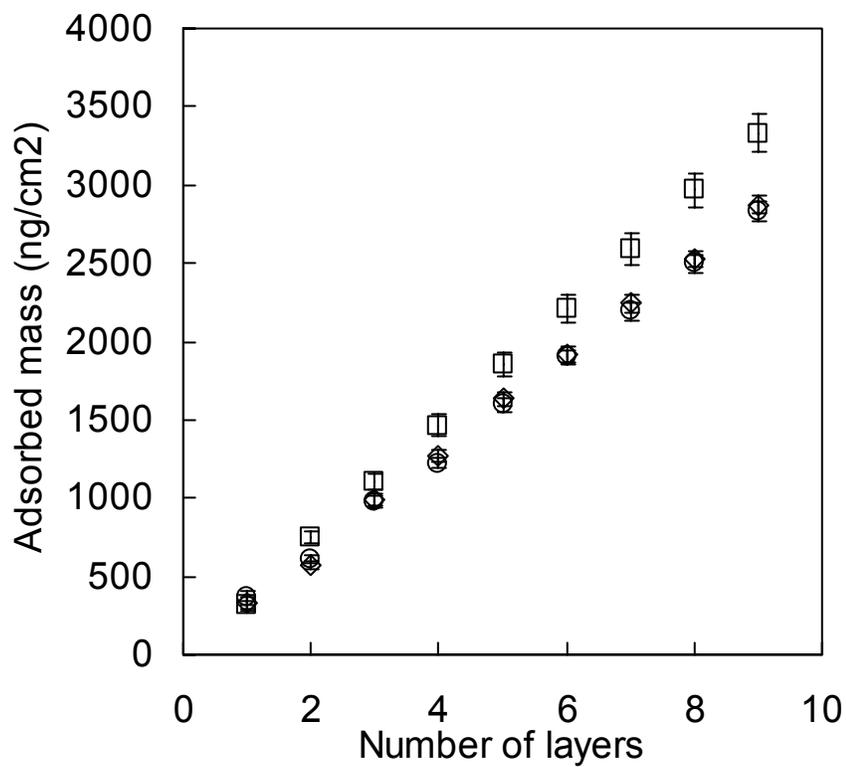
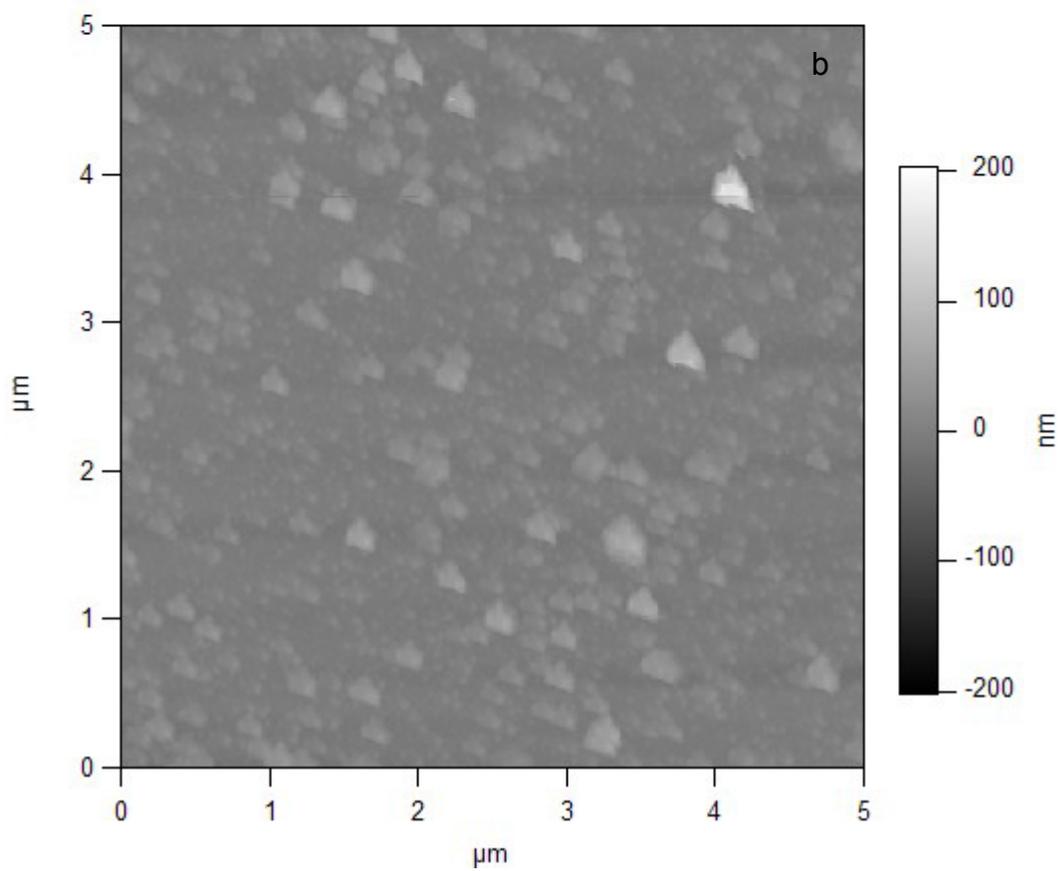
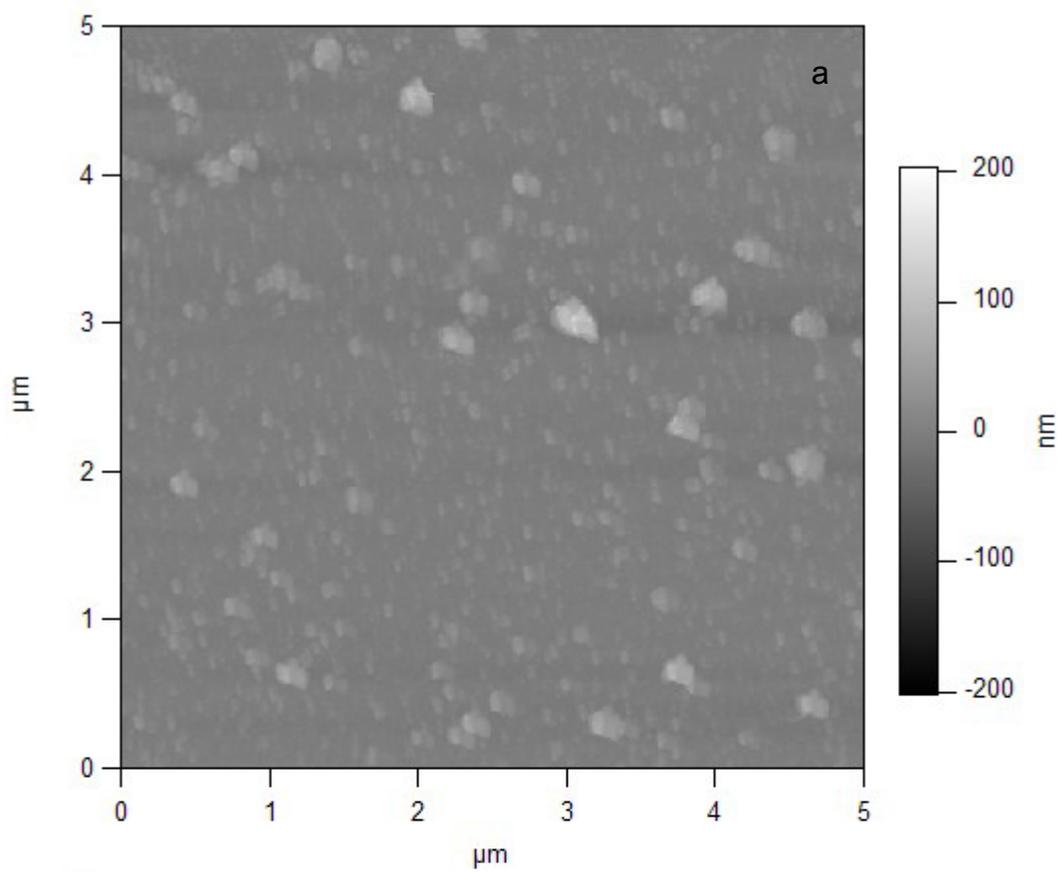


Figure S4: Adsorbed mass of (◇) PEI(PSS/PVBTMA)<sub>n</sub>, (□) PEI(PSS/PBVTMP)<sub>n</sub> and (○) PEI(PSS/PVBDMS)<sub>n</sub> 0.25 M NaCl versus number of layers as determined by quartz crystal microbalance using the Sauerbrey equation. (The experimental conditions are the same as described in the main text.)



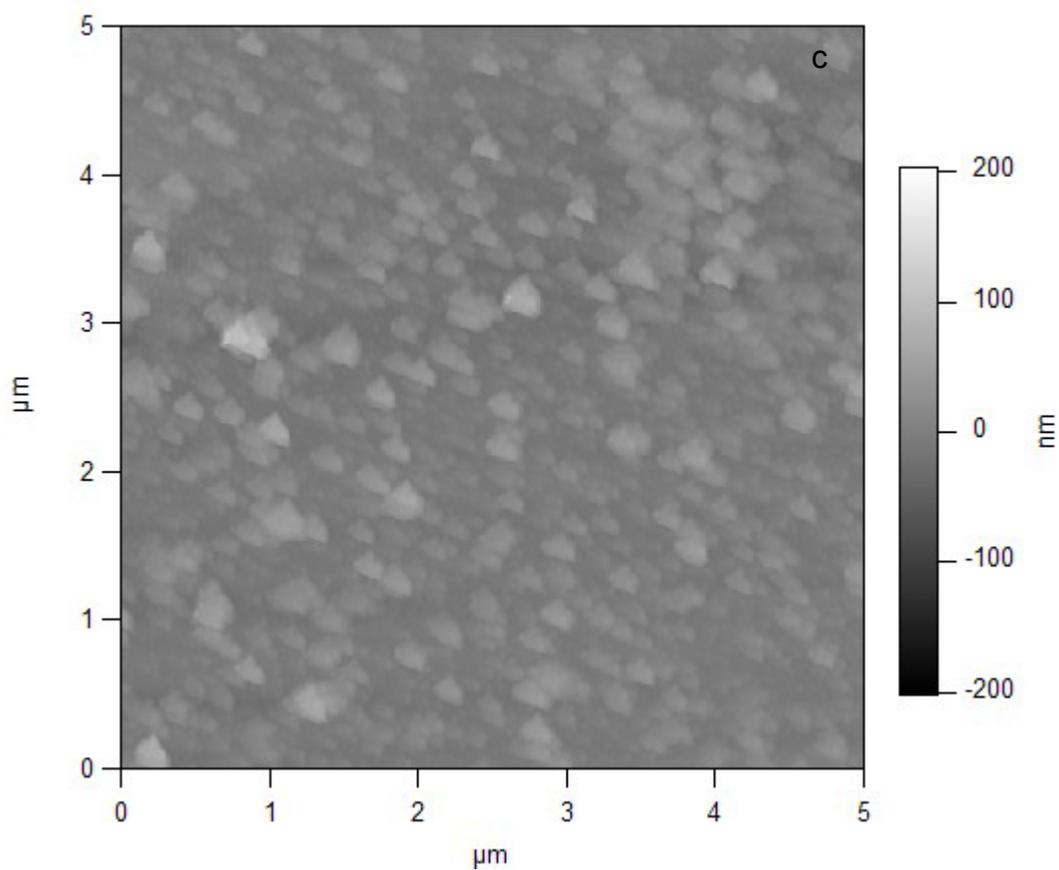


Figure S5: AFM images showing surface morphology of (a) PEI(PSS/PVBTMA)<sub>4</sub>, (b) PEI(PSS/PVBTMP)<sub>4</sub>, and (c) PEI(PSS/PVBDMS)<sub>4</sub> built from 0.25 M NaCl. The RMS roughness of the multilayers is provided in the main text.