## **Supporting Information**

## **Conformational Behavior of Grafted Weak Polyelectrolyte Chains:** Effects of Counterion Condensation and Non-electrostatic Anion Adsorption

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**Figure S-1.** Time dependence of frequency shift  $(\Delta f)$  and dissipation shift  $(\Delta D)$  for the resonator grafted with PDEM chains as a function of pH, where the shifts in  $\Delta f$  and  $\Delta D$  are obtained by subtracting the background response of the blank resonator in each corresponding PB buffer solution.

Figure S-1 shows that the increase of pH induced collapse of the grafted layer is almost reversible when the pH decreases from 10 to 4, as indicated by the fact that both  $\Delta f$  and  $\Delta D$  can almost return to the original value, that is, the grafted layer can re-swell from the collapsed state as the pH decreases. However, the kinetic processes in the collapse and swelling are some different (shown in Figure S-2).



**Figure S-2.** Frequency shift  $(\Delta f)$  dependence of dissipation shift  $(\Delta D)$  of the grafted PDEM layer in the collapse and swelling processes.

Figure S-2 shows that the collapse process does not overlap with the swelling process, indicating the weak cooperativity between the collapse/swelling and the dehydration/hydration.<sup>S1</sup> For the same  $\Delta f$ ,  $\Delta D$  in the swelling process is higher than that in the collapse process. The facts indicate that the hydration of the grafted layer produces some flexible tails on the outer layer surface, which have a pronounced effect on the dissipation. The results are similar to our previous work on the collapse and swelling of grafted poly(N-isopropylacrylamide) chains induced by temperature.<sup>S1</sup>



**Figure S-3.** SFG spectra of the PDEM homopolymer on the  $SiO_2$  surface at three different conditions, where the SFG experiments were performed with the polarization combination of SSP at room temperature.

Figure S-3 shows the SFG spectra of the PDEM homopolymer spin-coated on the SiO<sub>2</sub> surface. The films were prepared by a spin-coating of 1 mg/mL PDEM in 40 mM PB buffer, 40 mM PB buffer with 0.5 M Na<sub>2</sub>SO<sub>4</sub>, and 40 mM PB buffer with 0.5 M NaClO<sub>3</sub>, respectively. By using the established IR and Raman spectral assignments, as well as the polarization selection rules in SFG-VS, the bands in the SSP polarization combination can be attributed to the methyl symmetric vibration (2770 cm<sup>-1</sup>, N-CH<sub>3</sub>-ss), the methyl symmetric Fermi resonance (2820 cm<sup>-1</sup>, N-CH<sub>3</sub>-ss-Femi), and the symmetric mode of oxygen-linked methylene or its Fermi resonance (2970 cm<sup>-1</sup>, N-CH<sub>2</sub>-CH<sub>2</sub>-O-ss or -ss-Fermi) with some contribution from the methyl symmetric Fermi resonance (N-CH<sub>3</sub>-ss-Fermi), respectively. Figure S-3 shows that there is no obvious shift of spectral peaks after the adsorption of anions.



**Figure S-4.** The ionic strength (I) dependence of pH of PB buffer solutions for Na<sub>2</sub>SO<sub>4</sub>, NaClO<sub>3</sub>, and NaCl.

Figure S-4 shows that the pH keeps almost constant at different ionic strength for  $Na_2SO_4$ ,  $NaClO_3$ , and NaCl.



**Figure S-5.** Ionic strength (*I*) dependence of frequency shift ( $\Delta f$ ) and dissipation shift ( $\Delta D$ ) for the resonator grafted with PDEM chains immersed in NaCl solutions at pH 4, 7, and 10.

Figure S-5 demonstrates that the results at pH 4 and 7 of NaCl solutions are similar to those of the Na<sub>2</sub>SO<sub>4</sub> and NaClO<sub>3</sub> solutions. At pH 10, there is a slight increase of  $\Delta f$  and decrease of  $\Delta D$  in the lower ionic strength regime ( $I < \sim 0.05$  M), which is also similar to the result of the Na<sub>2</sub>SO<sub>4</sub> and NaClO<sub>3</sub> solutions. However, when the ionic strength is above 0.05 M, no obvious decrease of  $\Delta f$  and increase of  $\Delta D$  observed, indicating that the weak interaction between Cl<sup>-</sup> and the dimethylamino group (weak salting-in effect).



**Figure S-6.** Time dependence of frequency shift  $(\Delta f)$  and dissipation shift  $(\Delta D)$  for the resonator grafted with PDEM chains as a function of ionic strength at pH 4. (a) in NaClO<sub>3</sub> solutions; (b) in Na<sub>2</sub>SO<sub>4</sub> solutions.

Figure S-6 shows that the collapse of the grafted PDEM layer is reversible as the ionic strength decreases, as indicated by the fact that both  $\Delta f$  and  $\Delta D$  return to the original values.

## **References:**

S1. Liu, G. M.; Zhang, G. Z. J. Phys. Chem. B 2005, 109, 743-747.