Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Materials of

"Swelling Enhancement of Polyelectrolyte Brushes Induced by External Ions"

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1. *Proof of the adjustment of grafting density by mixing inert PS with reactive PS*

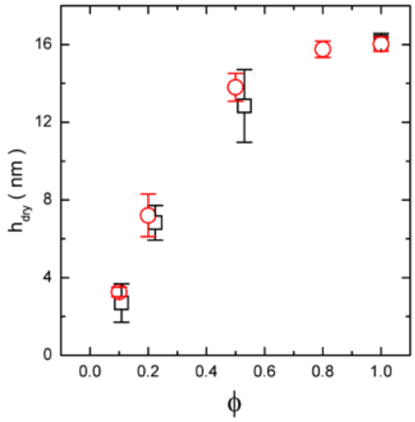

Figure S1 Values of thickness of the PS brushes at its dry state as a function of the fraction of the reactive PS (PS-NH_2, blank square: 32 × 10^3 g·mol^{-1}, M_w/M_n = 1.04; red circle: M_n = 120 × 10^3 g·mol^{-1}, M_w/M_n = 1.04) in its mixture with non-reactive PS (PS, blank square: 33 × 10^3 g·mol^{-1}, M_w/M_n = 1.04; red circle: M_n = 120 × 10^3 g·mol^{-1}, M_w/M_n = 1.13).

2. *Determination of degree of sulfonation of PSSNa brushes by XPS spectroscopy*

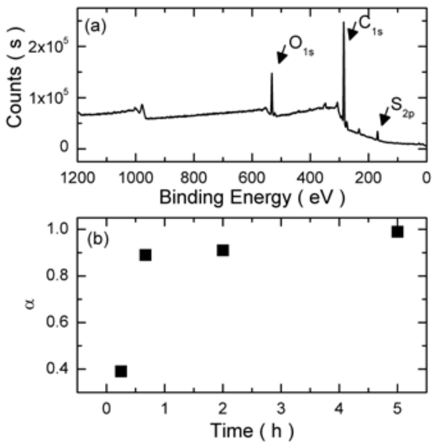

Figure S2 (a): XPS spectra of PSSNa-235k brushes (σ = 0.06 chain·nm^{-2}). (b): The degree of sulfonation α as a function of time for PSSNa-235k brushes. α was calculated by $\alpha = y/(x+y)$, in which x and y denotes the amount of S or C element, respectively. Under same experimental condition, the degree of sulfonation is independent on the brushes' thickness. The experiments were performed on an ESCALAB 220I-XL photoelectron spectrometer system (VG Scientific) with an Al Kα X-ray source (1486.6 eV). Constant analyzer energy mode was used and survey scans were collected from 0 to 1100 eV.

3. Least mean-squared-error fitting of ellipsometry measurements

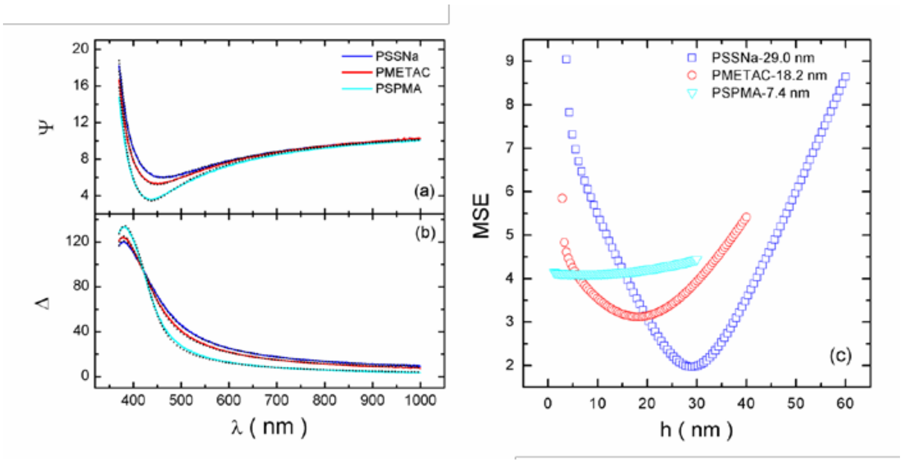

Figure S3 (a) and (b): The plot of Ψ and Δ against λ for the brushes in salt-free solutions: PSSNa-60k brushes (σ = 0.07 chain·nm^{-2}), PMETAC-58k brushes (σ = 0.09 chain·nm^{-2}) and PSPMA-12k brushes (σ = 0.25 chain·nm^{-2}). The data are fitted by the dash lines. (c) The plot of mean-square-error against h for the corresponding brushes in (a) and (b). It can be found that the higher the brush height, the more obvious the minimum of mean-squared-error. That is, the higher the optic contrast between the swollen brush layer and the salt solution, the more accurate the fitted thickness. And it is why the bars for PSPMA brushes are wider than the other brushes in Figure 1.

As described in CompleteEASE Data Analysis Manual:

$$MSE = \sqrt{\frac{1}{3n-m}\sum_{i=1}^{n}\left[\left(N_{E_i}-N_{G_i}\right)^2+\left(C_{E_i}-C_{G_i}\right)^2+\left(S_{E_i}-S_{G_i}\right)^2\right]}\times 1000 \quad \text{(S1)}$$

where E and G represent the measured value and the model generated value respectively, n is the number of wavelengths for measurement, m is the number of fit parameters, and $N=\cos(2\Psi)$, $C=\sin(2\Psi)\cos(\Delta)$, $S=\sin(2\Psi)\sin(\Delta)$.

4. *QCM-D data of PSSNa-60k brushes at all overtones*

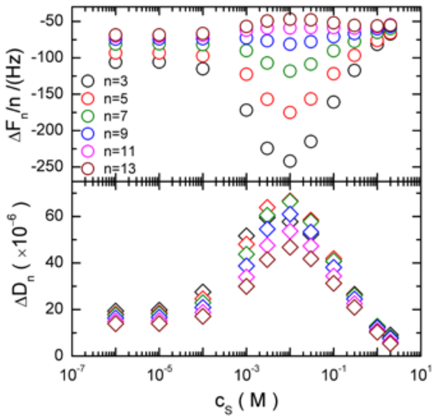

Figure S4 Data of frequency and dissipation of PSSNa-60k brushes (σ = 0.07 china·nm^{-2}) as a function of salt concentration (NaCl) at different overtones (n = 3, 5, 7, 9, 11, 13). The data demonstrate that, due to the relatively large contribution from dissipation to frequency change at higher overtone, the variation of frequency (n = 11 and 13) exhibits opposite trend compared with lower overtone (n = 3, 5, 7, 9).

5. *QCM-D data of PNIPAM-7k brushes*

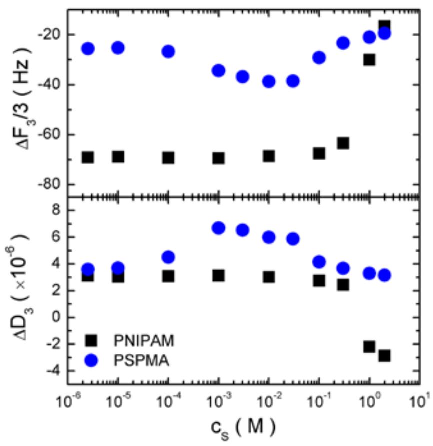

Figure S5 Typical data of frequency and dissipation change (at 3rd overtone) of PNIPAM-7k brushes (σ = 0.30 china·nm^{-2}) and PSPMA-12k brushes (σ = 0.25 china·nm^{-2}) as a function of salt concentration.

6. *Invalidity of QCM-D data analysis for thick PSSNa brushes (PSSNa-235k)*

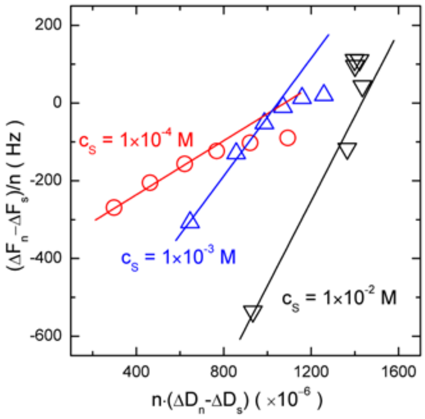

Figure S6 The plot of $\left(\Delta F_n - \Delta F_s\right)/n$ against $n \cdot \left(\Delta D_n - \Delta D_s\right)$ for the thick PSSNa-235k brushes (σ = 0.06 chain·nm^{-2}). The fittings by Eq. 5 are demonstrated by the solid lines. The deviation of the fitting to the experimental data is obvious, indicating that such an approach of data analysis by Eq. 5 is not valid for thick brushes. The reason is that the layer thickness is bigger than the penetration depth of the acoustic wave generated by the chip.