### Supplementary Materials

## Adsorption Properties of Soft Hydrophobically Functionalized PSS/MA Polyelectrolytes

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#### 1. Synthesis of hydrophobically functionalized poly(4-styrenosulfonic-co-maleic acid)



Figure S1. Synthetic routes for hydrophobically functionalized poly(4-styrenosulfonic-co-maleic acid)

For the synthesis of the hydrophobically functionalized poly(4-styrenosulfonic-co-maleic acid) a 4.8 % solution of PSS/MA in distilled water was prepared. For each 1 g of polyelectrolyte (5.46 mmol of -COOH groups), appropriate amounts (0.98 mmol or 2.62 mmol for the degree of grafting equal to 15% or 40 %, respectively) of *N*-Ethyl-*N'*-(3-dimethylaminopropyl)carbodiimide hydrochloride and N-hydroxysuccinimide were added and mixed to dissolve all ingredients. Next, dissolved in hydrochloric acid dodecylamine or hexadecylamine (0.82 mmol or 2.18 mmol for the degree of grafting equal to 15% or 40 %, respectively) and catalytic amounts of 4-N,N'-dimethylaminopyridine (DMAP) were added. The ratio of water to concentrated HCl solution was 2:1 (v/v). The mixture was stirred at 40 °C (for dodecylamine derivatives) or 60 °C (for hexadecylamine derivatives) for 48 h. After reaction completion the precipitated *N*-Ethyl-*N'*-(3-dimethylaminopropyl)urea was removed by filtration followed by solution dialysis in distilled water (4x4L, 4 days, MWCO 3500). The obtained solution was finally filtered and freeze-dried.

#### PSS/MA-g-C12NH2(15%): Yield: 55%

IR/cm<sup>-1</sup>: 3407 (O-H, stretching), 2988 (C-H, stretching), 1716 (C=O, stretching – carboxylic acid), 1656 (C=O, stretching – amide), 1240 (C-O, stretching)

<sup>1</sup>H NMR/ppm D<sub>2</sub>O: -CH<sub>3</sub> (0.93-0.96, t), -CH(CO)- (1.29-3.31, broad m), -(CH<sub>2</sub>)<sub>8</sub>-CH<sub>3</sub> (1.71-1.74, m), -NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>- (1.99-2.01, m), -NCH<sub>2</sub>CH<sub>2</sub>- (2.66-2.68, m), -NCH<sub>2</sub>- (2.95-2.06, m), CH (Ar, 5.71-7.92, broad m)

#### PSS/MA-g-C12NH2(40%): Yield: 43%

IR/cm<sup>-1</sup>: 3405 (O-H, stretching), 2985 (C-H, stretching), 1715 (C=O, stretching – carboxylic acid), 1651 (C=O, stretching – amide), 1244 (C-O, stretching)
<sup>1</sup>H NMR/ppm D<sub>2</sub>O: -CH<sub>3</sub> (0.96-0.99, t), -CH(CO)- (1.36-3.50, broad m), -(CH<sub>2</sub>)<sub>9</sub>-CH<sub>3</sub> (1.76-1.79, m), -NCH<sub>2</sub>CH<sub>2</sub>- (2.74-2.76, m), -NCH<sub>2</sub>- (2.99-3.11, m), CH (Ar, 6.00-7.99, broad m)

#### **PSS/MA-g-C**<sub>16</sub>**NH**<sub>2</sub>(15%): Yield: 51%

IR/cm<sup>-1</sup>: 3412 (O-H, stretching), 2965 (C-H, stretching), 1719 (C=O, stretching – carboxylic acid), 1648 (C=O, stretching – amide), 1234 (C-O, stretching)
<sup>1</sup>H NMR/ppm D<sub>2</sub>O: -CH<sub>3</sub> (0.93-0.95, t), -CH(CO)- (1.25-3.30, broad m), -(CH<sub>2</sub>)<sub>12</sub>-CH<sub>3</sub> (1.71-1.74, m), - NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>- (1.98-2.01, m), -NCH<sub>2</sub>CH<sub>2</sub>- (2.66-2.68, m), -NCH<sub>2</sub>- (2.95-2.06, m), CH (Ar, 5.86-7.92, broad m)

#### PSS/MA-g-C16NH2(40%): Yield: 46%

**IR/**cm<sup>-1</sup>: 3407 (O-H, stretching), 2990 (C-H, stretching), 1716 (C=O, stretching – carboxylic acid), 1645 (C=O, stretching – amide), 1250 (C-O, stretching)

<sup>1</sup>H NMR/ppm D<sub>2</sub>O: CH<sub>3</sub> (0.95-0.98, t), -CH(CO)- (1.50-3.34, broad m), -(CH<sub>2</sub>)<sub>13</sub>-CH<sub>3</sub> (1.74-1.77, m), -NCH<sub>2</sub>CH<sub>2</sub>-(2.71-2.73, m), -NCH<sub>2</sub>- (2.99-2.09, m), CH (Ar, 5.90-7.99, broad m)

2. <sup>1</sup>H NMR spectra



Figure S2. <sup>1</sup>H NMR spectra of the non-functionalized PSS/MA (0 – 8 ppm range)



Figure S3. <sup>1</sup>H NMR spectra of the synthesized hydrophobically functionalized poly(4-styrenosulfonic-co-maleic acid) with amide linking group (0 - 8 ppm range)



Figure S4. <sup>1</sup>H NMR spectra of the synthesized hydrophobically functionalized poly(4-styrenosulfonic-co-maleic acid) with amide linking group (0.5 - 3.5 ppm and 5.5 - 8.0 ppm ranges)



Fig. S5. The example of the QCM-D data obtained by monitoring the deposition of the copolymer (PSSMA-g-C<sub>12</sub>NH<sub>2</sub> (40%)) on top of the multilayer film. A - changes in the frequency during copolymer deposition on top of the (PDADMAC/PSS)<sub>4</sub>PDADMAC films and rinsing solution of 0.15M NaCl in pH=7 and pH=11. B - changes in the frequency during copolymer deposition on top of the (PDADMAC/PSS)<sub>4,5</sub> films and rinsing solution of 0.15M NaCl in pH=7 and pH=3. Spikes observed at c.a. 850 s are artifacts, disregarded in the analysis.



Fig. S6. The example of the QCM-D data obtained by monitoring the formation of the (PDADMAC/PSS)<sub>4</sub>PDADMAC multilayer film.



Fig. S7. The FTiR spectra in the PSS fingerprint region for (PDADMAC/PSS)<sub>4</sub>PDADMAC film without (dashed line) and with adsorbed copolymer layer (solid line): A. PSS/MA; B. PSS/MA-g-C<sub>12</sub>NH<sub>2</sub> (15%); C. PSS/MA-g-C<sub>12</sub>NH<sub>2</sub> (40%).





Figure S8. The FTIR spectra of (PDADMAC/PSS)<sub>4</sub>PDADMAC multilayer film with adsorbed copolymer as the last layer during the exposure to the alkaline environment pH=11. The dashed line illustrates the spectrum obtained after exposure for 30 minutes at pH=11 and flushing with 0.15M NaCl solution pH=7. Top – PSS/MA, bottom - PSS/MA-g-C<sub>12</sub>NH<sub>2</sub> (40%).