Supporting Information

Temperature-induced transition from odd-even to even-odd effect in polyelectrolyte multilayers due to interpolyelectrolyte interactions

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**UV-Vis spectra** of the films on quartz slides are obtained with a Lambda 900 UV-Vis spectrometer by Perkin-Elmer (Wiesbaden, Germany). The absorbed intensity is calculated according to Beer-Lambert law

\[ A = \log_{10}(I_0 / I) = \gamma c_0 l \]  
(S.1)

where \( I_0 \) is the incident intensity (at a particular wavelength), \( I \) is the intensity after passage through a sample of length \( l \), \( \gamma \) is the molar extinction coefficient and \( c_0 \) is the molar concentration of the absorbing species.

From the absorption of PSS in bulk solution, one obtains from the absorbed intensity at \( \lambda = 225 \) nm

\[ \gamma_{\text{PSS}} = 8.62 \cdot 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}. \]  
(S.2)

\( \gamma_{\text{PSS}} \) refers to the molar absorption coefficient of a PSS monomer. From these equations, the adsorbed mass per unit area is determined according to .
\[
\Gamma_{\text{PSS}} = \frac{1}{\gamma_{\text{PSS}}} A(225 \text{ nm}) = 116 \text{ nmol cm}^{-2} \cdot A(225 \text{ nm})
\]  

(S.3)

Considering the molecular weight of a dissociated PSS monomer to be 183.2 Da (assuming that the PEM does not contain any counterions), one obtains

\[
\Gamma_{\text{PSS}} = 214 \text{ mg} \cdot \text{m}^{-2} \cdot A(225 \text{ nm})
\]  

(S.4)

For the films prepared in 1 M NaCl solution at room temperature, one obtains in the linear growth regime 3.5 mg/m² per deposited layer PSS (corresponding to 1.9 nmol/cm²). Assuming charge compensation, and a PAH monomer weight of 58.1 Da (again assuming a counterion free PEM), the deposited mass per layer pair and unit area is 4.6 mg/m² (3.8 nmol/cm²). These data are in good agreement with literature values (Ramos et al., Macromolecules 2010, 43, 9063).

The surface coverage of a PSS layer is tripled if the deposition temperature is risen to 55°C (cf. Fig. S1). Yet we do not know if still each PSS monomer is balanced by a PAH monomer.

Finally, we would like to estimate the maximum surface coverage per layer pair obtained with 4 M salt solution at 40°C. The ellipsometric data show that the index of refraction of the whole film of all PEMs prepared scatters less than 5 % independent of preparation conditions (1.51 ± 0.02), corresponding to a water content of 40 ± 10 % (v/v). Therefore, the layer thickness is proportional to the surface coverage. In that case the thickness per layer pair is also proportional to the surface coverage. At room temperature and grown from 1 M salt solution, the thickness per polycation/polyanion bilayer is 6.1 nm. The highest bilayer thickness (49 nm) occurs at 4 M NaCl and 40°C. These numbers suggest that the surface coverage per layer pair increases by a factor of 8, to 37 mg/m².
Fig. S1, top: Absorption spectra of PSS/PAH multilayers in the UV range. Shown are spectra of PSS-terminated multilayers consisting of 4 to 8 PSS/PAH layer pairs (the adsorption solutions contain 1 M NaCl, the temperature is 55°C). Inset: Absorption of the PSS peak (225 nm) as function of the number of layers $N$.

Bottom: Absorption of the PSS peak (at 225 nm) as function of the number of layers $N$ (1 M NaCl aqueous solution) and temperature as indicated (left). Average absorption increase per PSS layer as function of preparation temperature $T$ (right), from which the adsorbed mass per unit area for one layer is determined (right axis). Each data point corresponds to a slope of one linear fit in the left figure.
Fig. S2: Refractive indices of PSS/PAH multilayers as function of layer number/thickness prepared from solutions with 1 M NaCl concentration and temperature as indicated. The refractive index is determined according to the model depicted in Fig. 1. At 19°C, the refractive index is constant, and independent of the terminating layer. With increasing layer number \( N \) the refractive index \( n_{\text{PEM}} \) approaches the value of the core zone and the contribution of the outermost layer gets less important.

<table>
<thead>
<tr>
<th>Salt concentration</th>
<th>1 M</th>
<th>2 M</th>
<th>3 M</th>
<th>4 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{\text{x-over}} ) (cf. Fig. 6)</td>
<td>44.3 °C</td>
<td>41.1 °C</td>
<td>39.8 °C</td>
<td>36.3 °C</td>
</tr>
<tr>
<td>Onset of deviation from ( \Delta d_{\text{PAH}}=0.5\Delta d_{\text{PSS}} ) (cf. Fig. 7)</td>
<td>30-35 °C</td>
<td>30 °C</td>
<td>34 °C</td>
<td>34 °C</td>
</tr>
<tr>
<td>( T_{\text{trans}} ) on drying (ref. 1)</td>
<td>40 °C</td>
<td>30 °C</td>
<td>15 °C</td>
<td>-</td>
</tr>
<tr>
<td>( d_{\text{BL}(T_{\text{trans}})} ) by ellipsometry (cf. Fig. 4)</td>
<td>8.15 nm</td>
<td>9.22 nm</td>
<td>ca. 8.5 nm</td>
<td>-</td>
</tr>
</tbody>
</table>

Table S1: \( T_{\text{x-over}}, T_{\text{trans}} \) and \( d_{\text{BL}(T_{\text{trans}})} \) as function of the salt concentration in the preparation solution. Also given is the temperature, at which the densification of the top PSS layer starts, above this temperature deviations from \( \Delta d_{\text{PAH}}=0.5\Delta d_{\text{PSS}} \) are observed.