Swelling of Polyelectrolyte Multilayers: The Relation Between, Surface and Bulk Characteristics

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To calculate the error propagation the formula has to be partially derivate for all measured values. For the error of the swelling water ϕ_{swell} have to be considered d_{dry} and $d_{swollen}$:

$$\phi_{swell} = \frac{d_{swollen} - d_{dry}}{d_{swollen}} \tag{S1}$$

$$\Delta\phi_{swell} = \left|\frac{\partial \phi_{swell}}{\partial d_{dry}}\right| \Delta d_{dry} + \left|\frac{\partial \phi_{swell}}{\partial d_{swollen}}\right| \Delta d_{swollen} \tag{S2}$$

$$\Delta\phi_{swell} = \left|\frac{-1}{d_{swell}}\right| \Delta d_{dry} + \left|\frac{d_{dry}}{{d_{swell}}^2}\right| \Delta d_{swell} \tag{S3}$$

For calculating the error of polymer fraction Δx the swelling water $\phi_{swollen}$, the refractive index in dried state n_{dry} and the refractive index in swollen state $n_{swollen}$ have to be considered:

$$x = \frac{n_{dry}}{n_{water} - n_{air}} - \frac{n_{swollen} - \phi_{swell} n_{water}}{(1 - \phi_{swell})(n_{water} - n_{air})} + 1 \tag{S4}$$

$$\Delta x = \left|\frac{\partial x}{\partial n_{swollen}}\right| \Delta n_{swollen} + \left|\frac{\partial x}{\partial n_{dry}}\right| \Delta n_{dry} + \left|\frac{\partial x}{\partial \phi_{swell}}\right| \Delta \phi_{swell} \tag{S5}$$

$$\begin{aligned}\Delta x = &\left|\frac{-1}{(1 - \phi_{swell})(n_{water} - n_{air})}\right| \Delta n_{swollen} + \left|\frac{1}{n_{water} - n_{air}}\right| \Delta n_{dry} \\ &+ \left|\frac{-n_{water}\phi_{swell} - n_{water}(1 - \phi_{swell}) + n_{swollen}}{(n_{water} - n_{air})(1 - \phi_{swell})^2}\right| \Delta \phi_{swell}\end{aligned} \tag{S6}$$

To find the error for the amount of void water $\Delta\phi_{void}$ the polymer fraction x and the swelling water ϕ_{swell} comes into account:

$$\phi_{void} = (1 - \phi_{swell})(1 - x) \tag{S7}$$

$$\Delta\phi_{void} = \left|\frac{\partial\phi_{void}}{\partial\phi_{swell}}\right| \Delta\phi_{swell} + \left|\frac{\partial\phi_{void}}{\partial x}\right| \Delta x \tag{S8}$$

$$\Delta\phi_{void} = |1 - x|\, \Delta\phi_{swell} + |1 - \phi_{swell}|\, \Delta x \tag{S9}$$

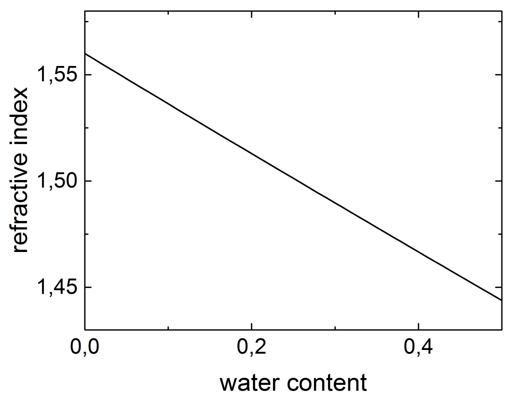

Figure S1: Change of refractive index in dependence on the water content calculated by the garnet equation

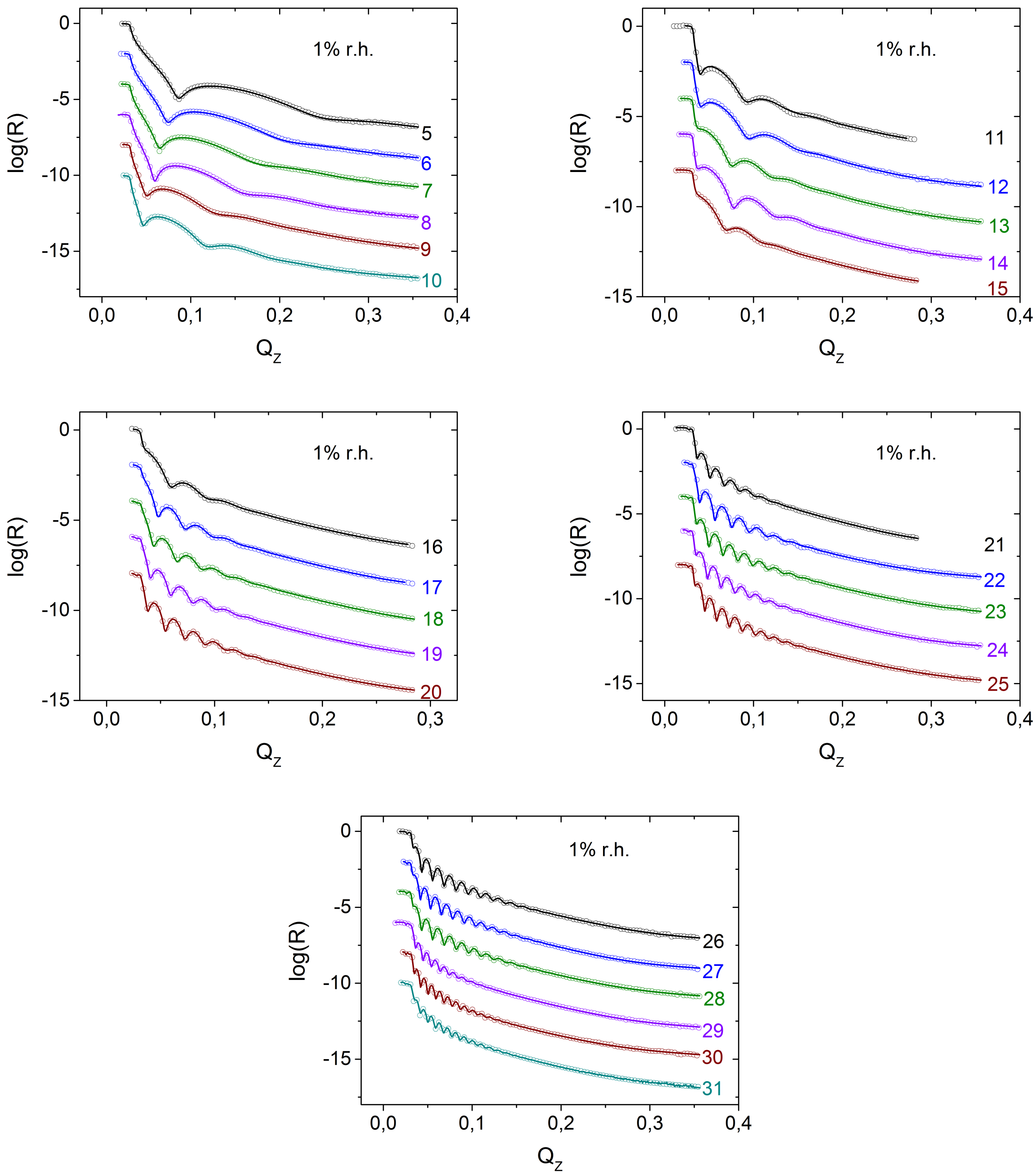

Figure S2: XRR data and fit of PEMs with 5-31 deposited layers measured at 1% r.h.. For better visualization only every 5th data point of measured data is shown in the diagram

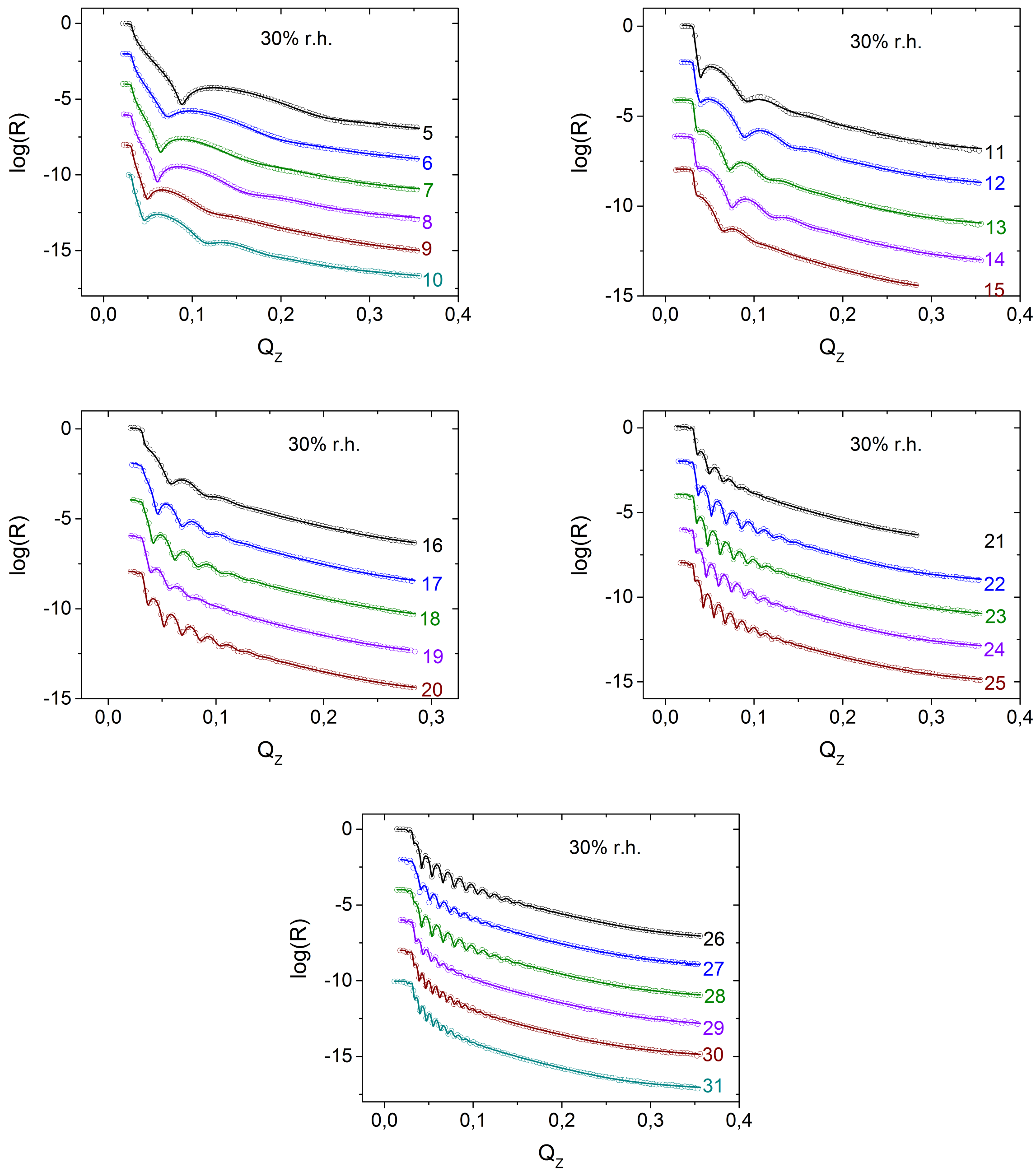

Figure S3: XRR data and fit of PEMs with 5-31 deposited layers measured at 30% r.h.. For better visualization only every 5th data point of measured data is shown in the diagram