Supporting information

Temperature effect on build-up of exponentially growing polyelectrolyte multilayers. Exponential-to-linear transition point

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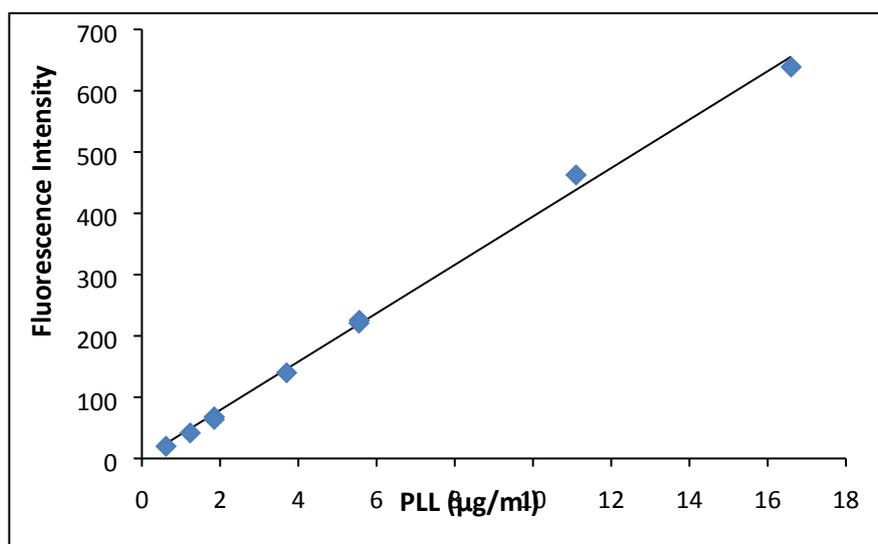
Fig. S1. FITC-PLL standard calibration curve.

Determination of the transition point

For this purpose the following process was performed using Mathematica 7.0 script (Wolfram Research, Champaign, IL): the M data points were first divided into two sub-sets: E points at low bilayer numbers and L points at high bilayer numbers ($M = E + L$). A monoexponential function f was subsequently fitted to the first E points. A straight line was then drawn through the remaining L points. It was chosen so as to intersect the graph of f at the Eth point, and its slope was chosen identical to that of f at this Eth data point, to avoid discontinuity. Next, the sum of squared residuals was calculated for all M points. This process was iterated for $5 \leq E \leq M$ (f contained three fitting parameters). The separation yielding the lowest sum of residuals indicated the optimum choice of the transition point. Similar procedure can also be performed using Excel program (Fig. S2).
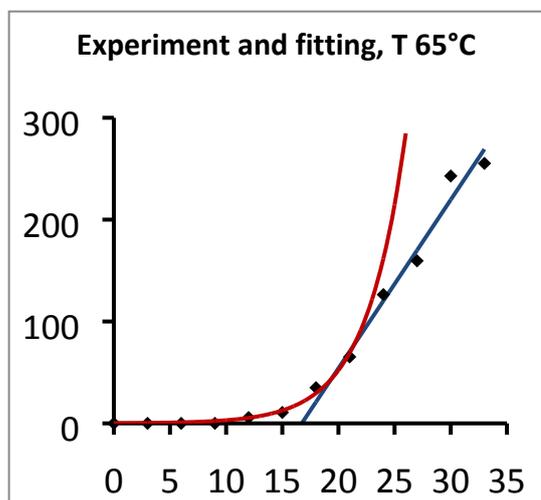
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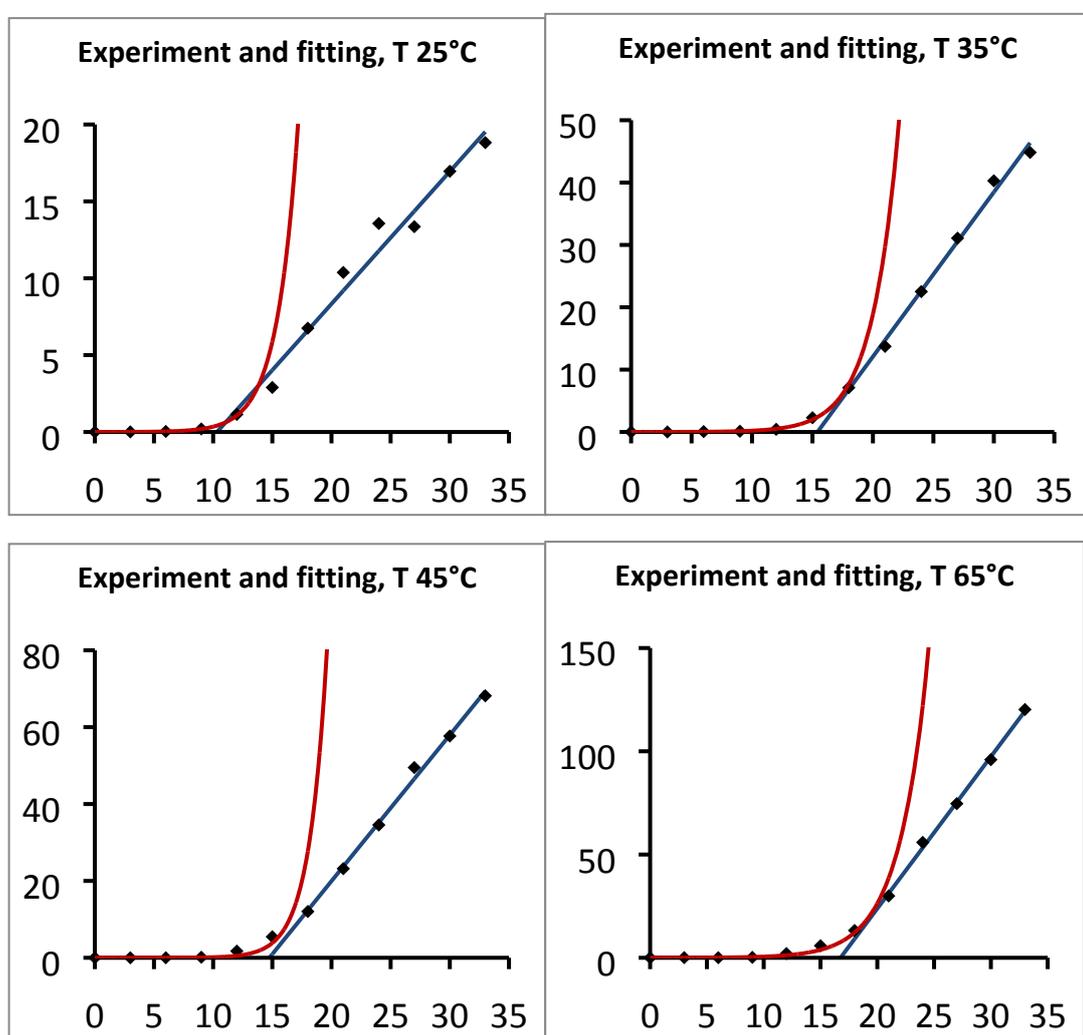
Fig. S2. Transition points for 25 °C, 45 °C, 65 °C and 85 °C. The Y-axis refer to PLL content ($\mu g^2/cm^2$) and X-axis to number of bilayers. Fitting for growth curves foe the film assembled at different temperatures was applied as described in the main text, and the exponential and linear regimes are shown for the film mass growth curves.
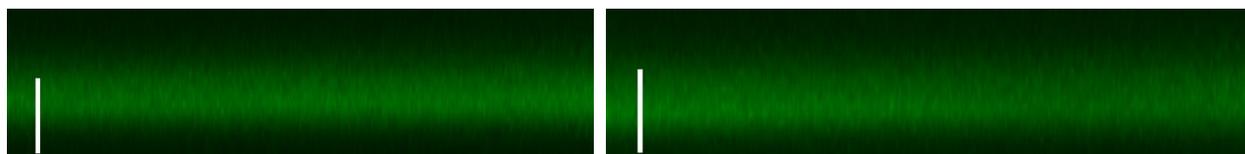

Fig. S4 CSLM z-stack for $(PLL/HA)_{30}$ prepared at 80 °C and further analyzed at 45 °C (left) followed by cooling down to 25 °C (right). The scale bar (white) is 20 μm.

Table S1. Molecular formula of polymers and activation energy calculated for multilayers formed based on the polymers.

ref	Polyanion	Polycation	Method	Ea, kJ/mol	Ea, J/mol of monomer
1	**Carboxymethyl cellulose (Na-CMC)** R = H or CH_2CO_2H Mw 550000, Mw (monomer) 346 # of monomers per molecule 1589	**Chitosan (Chi)** Mw 415000, Mw (monomer) 149 # of monomers per molecule 2785	thermogravimetric analysis Energy for film thermodegradation	≈130	82
2	**Polystyrene sulfonate (Na-PSS)** SO_3^- Mw 70000, Mw (monomer) 182 # of monomers per molecule 384	**Polyallylamine hydrochloride** · HCl NH_2 Mw 15000, Mw (monomer) 93.5 # of monomers per molecule 160	electrochemical impedance spectroscopy (EIS) Energy for polymer self-diffusion (dif coef D were evaluated)	61.4	383

One has also to note that i) the E_a should be considered for the formation of new contacts between polymers but not due to local dissociation of monomers, ii) the E_a can be considered relative to a monomer to compare a strength of interpolymer interaction.