Relationship between Polyelectrolyte Bulk Complexation and Kinetics of their Layer-by-Layer Assembly

Supporting Information

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Film growth using ellipsometry for PAA/PDMAEMA pair at pH 5 and pH 6

Ellipsometry was carried out to monitor the growth of salt-free PAA/PDMAEMA system at pH 5 and 6. Ellipsometric responses, Ψ and Δ, were acquired over a wavelength range from 600 to 1100 nm, simultaneously at a 75^{o} angle of incidence over dry films using a Woolam (M2000V, NE, USA) ellipsometer. The films were grown on a silica wafer by submerging into alternate PAA and PDMAEMA solutions. The concentration and duration of deposition is identical to QCM experiments in the text. Ψ and Δ were recorded as a function of wavelength λ and were fitted to a two-layer model consisting of silica/PEM in order to extract the PEM properties which was taken to be a homogenous medium (Cauchy material) with a given height, d, and a wavelength dependent refractive index, $n_{PEM} = A_{PEM} + B_{PEM} / (\lambda / nm)^2$. d, A_{PEM}, B_{PEM} were simultaneously fitted by the software provided by the manufacturer. The results of ellipsometry are presented in Figure S1.

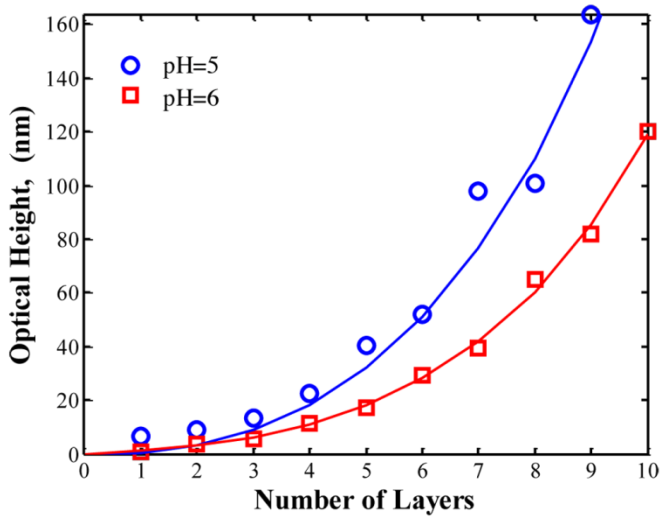

Figure S1. Ellipsometry measurements of film height for PAA/PDMAEMA LbL layers at room temperature in the absence of salt.

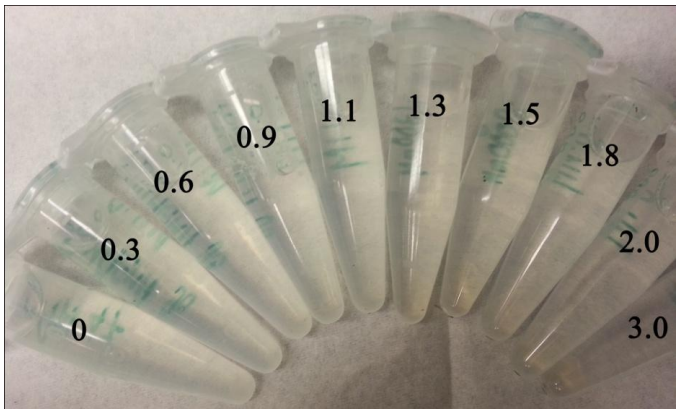

Figure S2. Phase behavior of PAA/PDMAEMA mixtures with equi-molar concentrations of monomers at pH 3 and room temperature. Numbers indicate the KCl concentration in moles, M.

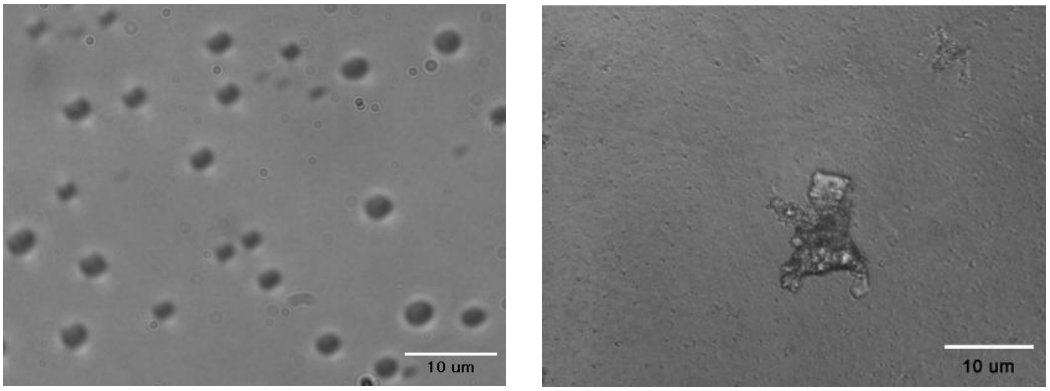

Figure S3. Typical optical micrographs used in distinguishing a coacervate phase from a precipitate phase for PAA/PDMAEMA at pH 7 at 900 mM KCl salt (left), and PAA/PDMAEMA at pH 5 at 300 mM KCl salt (right).

Effect of ionic strength at pH 7 for PAA/PAH pair

Interestingly, a similar non-monotonic response of the growth rate to salt concentration is observed for PAA/PAH as was observed for the other two PE pairs at pH 7. In fact, for PAA/PAH, precipitation occurs at salt concentrations of up to 200 mM KCl while the corresponding LbL growth is slow, but exponential; see Fig. S4. For KCl concentrations above 200 mM, growth is faster and initially has an exponential character while the corresponding complex phases are coacervates with increasing fluidity and transparency with increased salt. At the highest salt concentrations, above 400 mM, growth begins to slow down, and loses its exponential character after multiple layers have deposited. Complexation is visible even in the presence of 2 M KCl, which indicates the strength of the electrostatic interactions between PAA and PAH due to PAH being a primary amine, as discussed earlier.

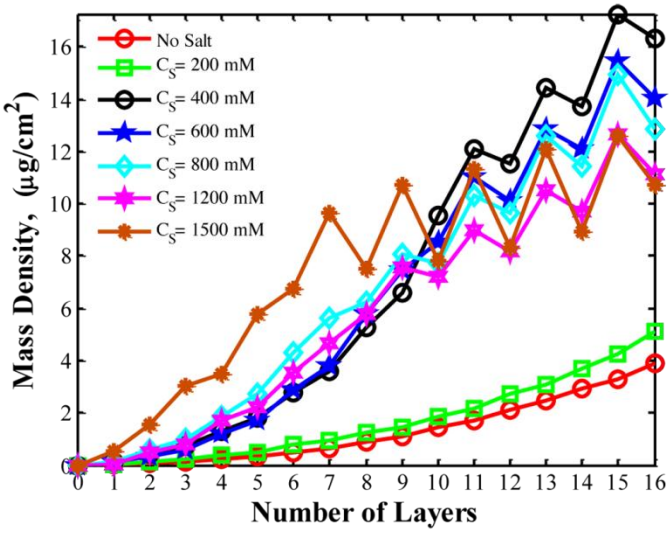

Figure S4. Effect of KCl concentration on PEM growth kinetics