Formation of polyelectrolyte multilayers: ionic strengths and growth regimes

Kan Tang, Nicolaas A. M. Besseling

Upon increasing ionic strength layer-by-layer (LbL) growth patterns for the poly-anion/poly-cation combination, polydiallyl-dimethylammonium chloride/polystyrene sulfonate (PDADMAC/PSS), studied by in-situ by optical reflectometry, vary from linear for the lowest salt concentrations to exponential for higher ionic strengths. The slope of linear growth at the lowest ionic strengths increases with increasing [NaCl]. During the LbL process at 0.5 M NaCl we observe a crossover from exponential to linear growth for which the slope is orders of magnitude larger than those observed at low salt concentrations. These growth behaviors, which are reported for many other LbL-PEM systems as well, can be explained from the generic features of the phase diagram of aqueous solutions of mixtures of oppositely charged poly-electrolytes. For the lowest ionic strength film growth upon exposure to a poly-electrolyte solution can be understood as adsorption of a monolayer at an essentially solid substrate formed by previously added poly-electrolyte. At higher ionic strength a poly-electrolyte film is fluid owing to weaker screened electrostatic interactions among poly-electrolytes. Then, newly arriving poly-electrolyte can be absorbed by the entire film that is already present, leading to exponential growth.