Molecular mechanisms associated with non-linear growth regimes of polyelectrolyte multilayers

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Nonlinear growth regimes of electrostatically assembled polyelectrolyte multilayer films are studied ellipsometrically under in situ conditions. Poly(styrenesulfonate) (PSS) and poly(diallyldimethylammonium) (PDADMA) with different molecular weights in 0.1 mol/L NaCl and 30 min adsorption time are used. Always, the linear growth is preceded by a parabolic growth regime. Neutron reflectivity shows that the center of mass of PSS molecules is vertically immobile, in both the parabolic and linear growth regimes. For films made from binary PDADMA mixtures, the compositions in the film and the adsorption solution are nearly identical. The parabolic growth regime is attributed to the different linear charge density of PDADMA and PSS and described by a molecular model.

If the molecular weight of PSS is reduced below a threshold, 25 kDa, the multilayer build-up starts with an exponential growth regime, and pronounced PSS interdiffusion is found with neutron reflectivity. The exponential build-up regime is extended on decrease of PSS molecular weight. For films made from binary PSS mixtures, addition of less than 1 mol % PSS with molecular weight above the threshold prevents the formation of an exponential growth regime.