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Probing the mechanism of non-linear growth of polyelectrolyte multilayers VICTOR SELIN, Department of Materials Science Engineering, Texas AM University, College Station, Texas 77843, USA, JOHN ANKNER, Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA, SVETLANA A. SUKHISHVILI, Department of Materials Science Engineering, Texas AM University, College Station, Texas 77843, USA — We report a study of the non-linear growth of electrostatically assembled polyelectrolyte multilayer films (PEM). PEM films were assembled by the layer-by-layer (LbL) technique using poly(methacrylic acid) as a polyanion and quaternized poly-2-(dimethylamino)ethyl methacrylate as a polycation. During film build-up, the thickness evolution as well as water uptake of PEM films were measured by in situ ellipsometry, whereas neutron reflectometry was used to probe the evolution of film internal structure as a function of deposition time. First, we found that during non-linear growth, films remain in a highly swollen hydrogel-like state, but the swelling ratio demonstrated an odd/even effect, with much larger hydration of the PEM when the terminal layer was the polycation. Second, while polycation chains were able to diffuse into the bulk of the film with a diffusion constant several orders of magnitude lower than in their free, unbound state, polyanion invasion was limited to the film surface. The amounts of the polycation and the polyanion adsorbed per deposition cycle were also drastically different. We quantify chemical composition and water content in the film, and correlate these data with the depth polyelectrolyte chains penetrate within the film during PEM construction.

Viktor Selin
Texas A
M Univ