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pH-Induced Release of Polyanions from Multilayer Films SVETLANA SUKHISHVILI, EUGENIA KHARLAMPIEVA, Stevens Institute of Technology, Hoboken, NJ 07030, JOHN ANKNER, Oak Ridge National Laboratory, Spallation Neutron Source, Oak Ridge, TN 37831, MICHAEL RUBINSTEIN, University of North Carolina, Chapel Hill, NC 27599 — Many studies deal with polymer chains irreversibly bound within electrostatically assembled layer-by-layer (LbL) films. Here we present new insights on the desorption of polymer chains assembled within layered polymer films, triggered by pH variation. Specifically, we report that in the case of a polycation assembled with poly(methacrylic acid) (PMAA) at low pH, the films selectively release the polyacid in response to an increase of external pH. By applying *in situ* Fourier transform infrared spectroscopy in attenuated total reflection mode (FTIR-ATR), we find that pH-induced film response is controlled by charge imbalance within the film. Studies of the kinetics of PMAA release reveal that the characteristic time of PMAA chain release, τ, scales with molar mass, M_w, as $M_w^{1.1\pm0.1}$. We present a theoretical model of the "sticky gel electrophoresis" of polyacids with excess charge which predicts a release time proportional to the molecular weight of released polyions and to the film thickness, in agreement with experimental results. Finally, neutron reflectivity studies show explicitly that PMAA release results in disordering of the film structure.

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