Abstract Submitted
for the MAR12 Meeting of
The American Physical Society

Diffusion of Polyelectrolyte Chains within Multilayer Films SVETLANA SUKHISHVILI, LI XU, ALIAKSANDR ZHUK, Stevens Institute of Technology, NJ 07030, JOHN ANKNER, Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA — Using a series of polycations synthesized by atom transfer radical polymerization, we investigate the relative importance of the effects of hydrophobicity, polymer charge density, and steric hindrance to charge pairing on chain dynamics within polyelectrolyte complexes (PECs) and within polyelectrolyte multilayer (PEM) films. First, by applying fluorescence correlation spectroscopy (FCS), ellipsometry and fluorescence recovery after photobleaching (FRAP), we found that the dynamics of chain exchange within PECs is directly correlated with the mode (linear *vs.* exponential) of PEM film growth. Second, through a combination of neutron reflectometry (NR) and FRAP techniques to the same PEM types, we found that diffusion of polyelectrolyte chains within multilayer films is highly anisotropic, with diffusion coefficients being 10^4-10^5 higher in a direction parallel to the substrate compared to that perpendicular. Chain mobility was also controlled by ionic strength of annealing solutions and steric hindrance to ionic pairing of interacting polyelectrolytes.

This work was supported by the National Science Foundation under Award DMR-0906474 (S.S.). Neutron measurements were performed at the Spallation Neutron Source at the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the DOE under contract No. DE-AC05-00OR22725.

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Date submitted: 22 Nov 2011

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