Abstract Submitted
for the MAR15 Meeting of
The American Physical Society

Molecular Origins of Thermal Transitions in Polyelectrolyte Assemblies EROL YILDIRIM, Aalto University, YANPU ZHANG, Texas A&M University, HANNE S. ANTILA, Aalto University, JODIE L. LUTKENHAUS, Texas A&M University, MARIA SAMMALKORPI, Aalto University, AALTO TEAM, TEXAS A&M TEAM — Polyelectrolyte (PE) multilayers and complexes formed from oppositely charged polymers can exhibit extraordinary superhydrophobicity, mechanical strength and responsiveness resulting in applications ranging functional membranes, optics, sensors and drug delivery. Depending on the assembly conditions, PE assemblies may undergo a thermal transition from glassy to soft behavior under heating. Our earlier work using thermal analysis measurements shows a distinct thermal transition for PE layer-by-layer (LbL) systems assembled with added salt but no analogous transition in films assembled without added salt or dry systems [1]. These findings raise interesting questions on the nature of the thermal transition; here, we explore its molecular origins through characterization of the PE aggregates by temperature-controlled all-atom molecular dynamics simulations. We show via molecular simulations the thermal transition results from the existence of an LCST (lower critical solution temperature) in the PE systems: the diffusion behavior, hydrogen bond formation, and bridging capacity of water molecules plasticizing the complex changes at the transition temperature. We quantify the behavior, map its chemistry specificity through comparison of strongly and weakly charged PE complexes, and connect the findings to our interrelated QCM-D experiments.

[1] A. Vidyasagar, C. Sung, R. Gamble and J. L. Lutkenhaus, ACS Nano **6**, 6174 (2012).

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Date submitted: 14 Nov 2014 Electronic form version 1.4