Abstract Submitted for the MAR17 Meeting of The American Physical Society

Effects of ion size and charge asymmetry on the salt distribution in polyelectrolyte blends and block copolymers¹ HA-KYUNG KWON, KEN-NETH R. SHULL, Northwestern University, JOS W. ZWANIKKEN, University of Massachusetts Lowell, MONICA OLVERA DE LA CRUZ, Northwestern University — Polyelectrolytes have received much attention as potential candidates for rechargeable batteries, membrane fuel cells, and drug delivery carriers, as they can combine the electrochemical properties of the charged components with the mechanical stability and biocompatibility of the polymer backbone. The role of salt in determining the bulk and interfacial behaviors of polyelectrolytes has been of particular interest, as the miscibility has shown to depend significantly on salt identity and concentration. Recent studies employing the SCFT-LS method have shown that ionic correlations can enhance phase separation in polyelectrolytes and can induce selectivity in neutral solvents. Here, we extend the theory to investigate the role of salt in strongly correlated polyelectrolytes. We find that in lamellae-forming block copolymers, the addition of monovalent, symmetric salt can lead to a decreased lamellar spacing due to increased selectivity of the salt. When multiple electrostatic interactions are introduced via size and valency asymmetry in the salt pair, the bulk phase behavior and salt distribution across interfaces are significantly altered, as size and charge mismatch can transform the charge ordering seen in monovalent, symmetric salts.

¹This work was performed under the following financial assistance award 70NANB14H012 from U.S. Department of Commerce, National Institute of Standards and Technology as part of the Center for Hierarchical Materials Design (CHiMaD).

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Date submitted: 09 Nov 2016

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