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Effect of Water on the Thermal Transition Observed in Polyelectrolyte Complexes YANPU ZHANG, Artie McFerrin Department of Chemical Engineering Texas AM University, PIOTR BATYS, Department of Chemistry Aalto University, FEI LI, JODIE LUTKENHAUS, Artie McFerrin Department of Chemical Engineering Texas AM University, MARIA SAMMALKORPI, Department of Chemistry Aalto University, DR. JODIE LUTKENHAUS COLLABORATION, DR. MARIA SAMMALKORPI COLLABORATION — Polyelectrolyte complexes (PECs), formed by the association of oppositely charged polyelectrolytes in solution, undergo a glass transition-like event of an unclear nature. This transition event has been detected using calorimetry or mechanical techniques. The observed thermal transition temperature (T_{tr}) is influenced by both the complexation condition and subsequent addition of water. Recent simulation work suggests that water with the polyelectrolyte plays dual roles: weakening polyelectrolyte ion pairs and also undergoing a subtle dehydration process with increasing temperature. Here, we present the influence of water on two pairs of PECs, poly(diallyldimethylammonium chloride) −poly(sodium 4-styrenesulfonate) (PDAC−PSS), and poly(allylamine hydrochloride)−poly(acrylic acid) (PAH−PAA), in which the PEC structure and composition are affected by complexation conditions, NaCl concentration or pH values. Modulated differential scanning calorimetry (MDSC) reveals a T_{tr} that decreases in value with increasing hydration and decreasing polyelectrolyte-polyelectrolyte ion pairing. We show the collapse of all T_{tr} values into a single master curve when plotted against the ratio of water molecules per polyelectrolyte-polyelectrolyte ion pair.

Yanpu Zhang
Artie McFerrin Department of Chemical Engineering Texas A
M University

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