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Tuning Thermal Transitions in Dry and Hydrated Polyelectrolyte Layer by Layer Assemblies with Ionic Strength and pH AJAY VIDYASAGAR, JODIE LUTKENHAUS, Texas A&M University — Layer-by-layer (LbL) assemblies are of significant interest for their potential applications in diverse fields such as energy and drug delivery. However, characterizing their thermal properties has remained a challenge. Here, we present the characterization of dry and of hydrated LbL films containing strong polyelectrolytes poly(diallyldimethylammonium chloride) (PDAC) and poly(styrene sulfonate) PSS) using modulated differential scanning calorimetry (MDSC) and temperature controlled quartz crystal microbalance with dissipation (QCM-D). Our results suggest that hydrated exponentially growing (assembled from 0.25-1.25 M NaCl solutions) PDAC/PSS LbL films have glass transition temperatures (T_g 's) between 48-51 °C, while linearly growing (assembled from 0 M NaCl) films did not. Other systems explored include poly(allylamine hydrochloride)/poly(acrylic acid)(PAH/PAA) LbL assemblies, which demonstrate linear/exponential growth depending on assembly pH conditions. These results support a standing hypothesis in that linear (or exponential) growth is observed for glassy (or rubbery) LbL films. We have also demonstrated for the first time, thermal transitions in thin PDAC/PSS LbL films using QCM-D by monitoring fluctuations in film hydration and viscoelasticity by probing the film's internal structure as a function of film depth.

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