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Effect of Thickness on the Thermal Properties of Hydrogen Bonded Layer by Layer Assemblies CHOONGHYUN SUNG, AJAY VIDYASAGAR, KATELIN HEARN, JODIE LUTKENHAUS, Texas A&M University — Layer by layer (LbL) assemblies have attracted a lot of attention for their functional versatility and ease of fabrication. However characterizing thermal properties, especially for ultra thin LbL assemblies, has remained a challenging topic. We have investigated the role of the film thickness on the glass transition temperature  $(T_q)$  for poly(ethylene oxide)/poly(acrylic acid) (PEO/PAA) and (PEO)/poly(methacrylic acid) (PEO/PMAA) hydrogen bonded LbL assemblies in both bulk as well as in confined thin films using modulated differential scanning calorimetry (MDSC) and temperature-controlled ellipsometry. PEO/PAA LbL assemblies exhibit a well-defined  $T_g$ , both in bulk and thin films. For films less than 100 nm thick, the  $T_q$  increased slightly as film thickness decreased. On the other hand, PEO/PMAA LbL assemblies displayed clear glass transitions only after thermal treatment, which produces anhydride crosslinks. Also, the thickness dependence on  $T_g$  was less pronounced for PEO/PMAA LbL films. It was also seen that the thermal expansion coefficient ( $\alpha$ ) increased for film thickness below 200nm. We speculate that interactions between the film and substrate likely influence the thickness-dependent  $T_g$ 

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