Surface Morphology Development in Multilayered Films Prepared by Layer-by-Layer Deposition

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We report the fabrication of free-standing multilayered thin films based on the layer-by-layer (LbL) deposition method. The isolation of multilayer thin film allows us to characterize the materials properties of such films in great detail. Poly(acrylic acid) (PAA) and hydrophobically modified poly(ethylene oxide) (HM-PEO) multilayer films have been prepared using the LbL method based upon hydrogen bonding interactions. The LbL film composition and thermal properties were obtained as a function of the number of layer pairs using thermal gravimetric analysis (TGA) as well as differential scanning calorimetry (DSC). Above the critical number of layer pairs, the HM-PEO/PAA multilayer films exhibit complex surface structure owing to the hydrophobic nature of HM-PEO (i.e., micelle formation). The unique surface morphology was studied using optical microscopy and fluorescence microscopy, where pyrene dyes incorporated into the hydrophobic cores of HM-PEO micelles, allowed us to monitor the sites of HM-PEO micelles. We demonstrate that the film morphology can be controlled by varying the solvent polarity, temperature, molecular weight of HM-PEO and assembly technique.