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Measuring graft stability in a tethered polyelectrolyte film by X-ray and neutron reflectivity MICHAEL D. DIMITRIOU, NIST Center for Neutron Research, CASEY J. GALVIN, NC State Chemical and Biomolecular Engineering Department, SUSHIL K. SATIJA, NIST Center for Neutron Research, JAN GENZER, NC State Chemical and Biomolecular Engineering Department — The instability of tethered polymer films in mild conditions has recently brought into question the limits of use of such layers in certain technologies, such as anti-fouling coatings. In order to better understand the process of chain degrafting in a polymer brush, we have used X-ray reflectivity (XR) and neutron reflectivity (NR) to examine tethered layers of poly(2-dimethylaminoethyl methacrylate) (PDMAEMA). Exposing an $\approx$ 30 nm thick film of PDMAEMA brushes grafted on flat silica-coated substrates to a range of relative humidities (RH) resulted in reproducible thickness changes as measured by XR, illustrating the need of ambient solvent to induce degrafting. The thickness change showed non-linear behavior, increasing rapidly above $\approx$ 70% RH and swelling to $\approx$ 230% of its original thickness at $\approx$ 99% RH. In order to better understand the apparent diffusive process of vapor into the brush, we have exposed brushes to isotopically labeled vapors. Using XR and NR, we examined the extent of modification in scattering length density within the brush using box and gradient models, and discuss the apparent entropic and enthalpic forces at play. We also conducted *in situ* aqueous measurements of similar samples to comprehend the degrafting process of a polymer brush. Through an appropriate choice of model, we detect variations in grafting density as a function of incubation time.

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