Swelling of polyelectrolyte and polyzwitterion brushes by humid vapors

JAN GENZER, CASEY GALVIN, North Carolina State Univ, MICHAEL DIMITRIOU, SUSHIL SATIJA, NIST — Swelling behavior of polyelectrolyte and polyzwitterion brushes derived from poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) in water vapor is investigated using a combination of neutron and X-ray reflectivity and spectroscopic ellipsometry over a wide range of relative humidity (RH) levels. The extent of swelling depends strongly on the nature of the side-chain chemistry. For parent PDMAEMA, there is an apparent enrichment of vapor at the polymer/air interface. Despite extensive swelling at high humidity level, no evidence of charge repulsion is found in weak or strong polyelectrolyte brushes. Polyzwitterionic brushes swell to a greater extent than the quaternized brushes studied. However, for RH levels beyond 70%, the polyzwitterionic brushes start to exclude water molecules, leading to a decline in water volume fraction from the maximum of 0.30 down to 0.10. Using a gradient in polymer chain grafting density, we provide evidence that this behavior stems from the formation of inter- and intramolecular zwitterionic complexes.