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Volume-phase Transitions and Confined Water in Surface-tethered Poly(N-isopropylacrylamide) Networks AJAY VIDYASAGAR, RYAN TOOMEY, University of South Florida — We present a simple approach for studying volume-phase transitions in thin, mechanically anchored responsive polymer networks. The approach is based on the photo-cross-linking of copolymers synthesized from N-isopropylacrylamide (NIPAAm) and methacroyloxybenzophenone (MaBP). We monitored the swelling of poly(NIPAAm-co-MaBP) networks in contact with aqueous solution as a function of cross-link density with both neutron reflection and ATR-FTIR. Neutron reflection reveals that the volume-phase transition of tethered poly(NIPAAm) networks coincides with the miscibility gap of linear poly(NIPAAm) solutions. Whether or not the poly(NIPAAm) network undergoes a continuous or discontinuous collapse depends on its degree of cross-linking. At cross-link densities above 5 mole%, the network remains in the single-phase region of the linear solution phase diagram and shows only a continuous transition between the swollen and collapsed states. Moreover, in the collapsed state, 30-35% by volume of water remains in the network, which is independent of cross-link density. The relative position of the FTIR absorption peaks during the collapse follows very closely the amount of water in the layer and can be related to the local dielectric environment within the network.

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