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Steric effects on the phase behavior of end-tethered temperature-responsive polymers CHARLES HOGSHEAD, EVANGELOS MANIAS, Materials Sci & Eng; Penn State University — End-tethering polymers from a planar surface at high grafting density results in an apparent spatial confinement originating from interchain steric repulsion. This effective confinement can alter the phase behavior of temperature-responsive polymers in solution, relative to their bulk solution behavior. Here we report on experiments where we synthesized tethered polymer layers with a gradient in grafting density. The systems studied were temperature-responsive alternating copolymers in aqueous solutions. Under-water AFM was used to directly observe the tethered chain collapse upon heating through the bulk LCST, and the resulting reversible adhesion switch. The transition of the tethered layers occurs at temperatures that are similar to the binodal points of the respective solution, but over a much broader temperature range. This behavior is consistent with the collapse being a cooperative conformational transition, reflecting the effects of chain confinement, rather than a first-order thermodynamic LCST transition (as these same polymers exhibit in bulk aqueous solutions). The onset-temperature of the transition, of both the tethered layers and the LCST, was tailored by varying the copolymer composition, i.e., by tuning the hydrophilic/hydrophobic balance within the chain.

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