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Design Rules for Thermally Responsive Polymer Brushes¹

DEBORAH LECKBAND, University of Illinois at Urbana-Champaign

Thermally responsive polymers such as poly(N-isopropylacrylamide) (PNIPAM) are extensively used to thermally tune the interfacial properties of thin polymer films. Above a lower critical solution temperature (LCST) of 32C, PNIPAM becomes insoluble in water and the chains collapse. Below the LCST the polymer chains are swollen. Yet such dramatic changes are not observed in all cases. The molecular weight and grafting density may also influence the phase behavior. This talk describes the systematic investigation of the thermally driven collapse of end-grafted PNIPAM as a function of the chain grafting density, molecular weight, and temperature. The polymer was grafted from the surface of an alkanethiol monolayer on gold containing a brominated alkanethiol initiator. The chains were synthesized by Atom Transfer Radical Polymerization (ATRP). Extensive chain collapse occurred at the highest grafting density and molecular weight, but the change in the film thickness decreased with decreasing density and molecular weight. The LCST was unchanged within 1C for all films. The force profiles measured between the PNIPAM brushes and a second surface at T below the LCST further suggest a one-dimensional phase separation within the polymer brush. These findings are compared with theoretical models of water-soluble polymers. We further discuss design criteria that impact the ability to thermally tune the interfacial properties of grafted PNIPAM films.

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