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Influence of the Free Interface on the Glass Transition Temperature of Irreversibly Adsorbed Polystyrene Thin Films MARY BURROUGHS, RODNEY PRIESTLEY, Department of Chemical and Biological Engineering, Princeton University — Polymers confined to the nanometer length scale have been shown to exhibit deviations in the glass transition temperature (T_g) from that of the bulk. Confinement effects on T_g have largely been attributed to the combined influences of the free surface and substrate interface. Recent work with polymer thin films has investigated a phenomenon at the substrate interface in which polymer chains physically adsorb to the substrate when annealed at sufficient temperature. This process, dubbed "irreversible adsorption" has been connected with changes in T_g under confinement. We seek to investigate how the competition between enhanced mobility at the free surface and arrested mobility due to irreversible adsorption at the substrate influences the glass transition temperature in polymer thin films. Here we use fluorescence, a technique capable of probing local dynamics, to study the T_g of a model system consisting of polystyrene (PS) irreversibly adsorbed on silica. Incorporating fluorescently-labeled PS in a series of single and multi-layer films, we selectively measure the T_g of adsorbed layers, with and without a free surface, as a function of annealing time. We then further anneal the bilayer films and measure changes in the T_g of the irreversibly adsorbed layers to investigate chain interpenetration and its implications for the influence of irreversible adsorption on the T_g distribution throughout the film.

Mary Burroughs
Department of Chemical and Biological Engineering, Princeton University

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