IRG-2: Glass Transition of Irreversibly Adsorbed Nanolayers (DMR-1420541)

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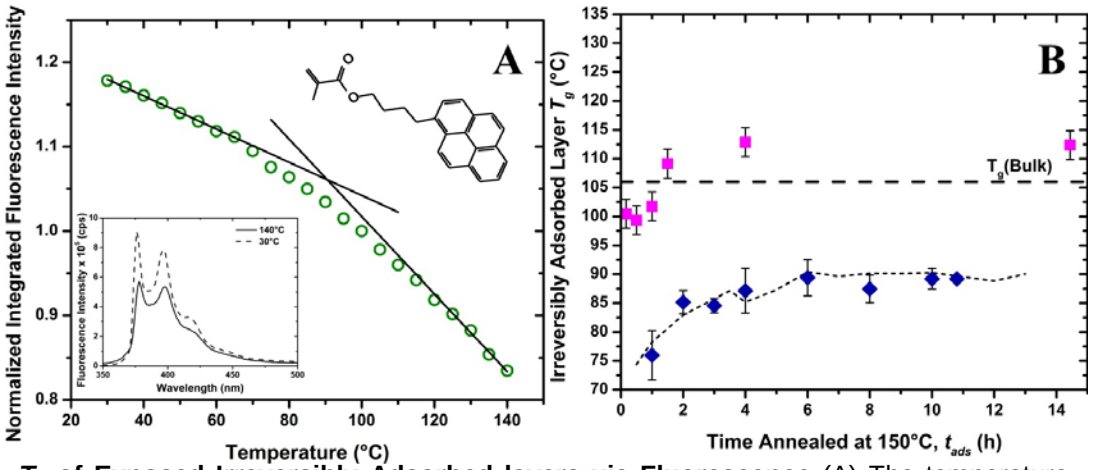
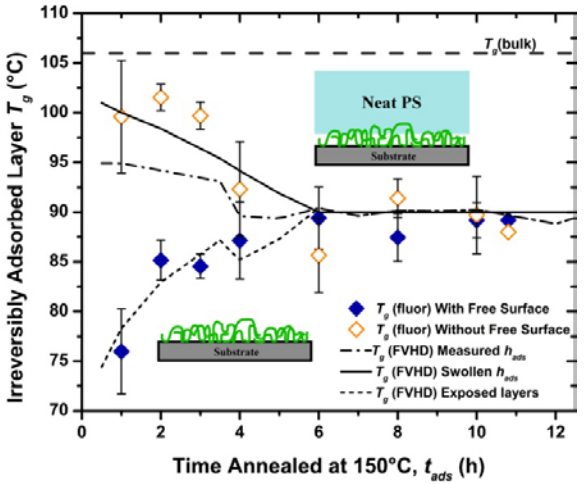
Thin polymer films in contact with a substrate serve as the enabling material for a range of emerging technologies, including nanoimprint and block copolymer lithography for microelectronics, membranes for efficient separations and drug delivery, and semiconductors for organic solar cells and electronics. A critical step in film production is thermal annealing the polymer film in the melt state to remove excess solvent, relax residual stresses and thermal history induced during formation, and—in the case of block copolymer films—induce self-assembly. During prolonged melt-state annealing, monomer-substrate interactions on the order of k_BT can lead to the formation of an irreversibly adsorbed (or physically bound) nanolayer. This adsorbed layer has been linked to changes in thin film properties and its formation has many implications in determining the glass transition temperature (Tg) of confined polymer films– which is known to depend heavily on interfacial interactions. PCCM researchers are investigating how the T_g of this adsorbed layer is influenced by the free surface and employing a fluorescence technique to directly measure the T_g of the adsorbed layer buried in a film.

Reference: Mary J. Burroughs, Simone Napolitano, Daniele Cangialosi, and Rodney D. Priestley, *Direct Measurement of Glass Transition Temperature in Exposed and Buried Adsorbed Polymer Nanolayers*, Submitted (2016).



T_g of Exposed Irreversibly Adsorbed layers via Fluorescence (A) The temperature dependence of fluorescence intensity for a 10-h irreversibly adsorbed layer, with solid lines being linear fits to the high and low temperature data. Lower inset shows temperature dependence of its spectra. Upper inset shows molecular structure of pyrenebutanol methacrylate monomer co-polymerized with styrene at low concentrations in *l*PS; (B) Exposed adsorbed layer T_g at different t_{ads} as measured by fluorescence (diamonds) and as reported for capped adsorbed layers by Napolitano[2] (squares), shifted to match respective T_g(bulk) values. Dashed line illustrates predictions by free volume holes diffusion model (FVHD).



Irreversibly adsorbed layer T_g with and without a free surface as a function of adsorption time, t_{ads}. Insets illustrate exposed and buried adsorbed layer geometries. Lines show T_g predicted by FVHD for exposed and submerged adsorbed layers.