In Situ Analysis of the Glass Transition Temperature of Irreversibly Adsorbed Polymer Nanolayers

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— When a polymer thin film is annealed in the melt state, individual chains can strongly adsorb to the supporting substrate in a manner that appears to be irreversible. This irreversible adsorption of polymer chains results from the large number of individual contacts made between monomer units and the substrate that stabilize the polymer from desorption. The formation and development of irreversibly adsorbed layers with increased annealing time has been shown to correlate with changes in their structure and dynamic properties and may impact the properties of thin polymer films. Here we investigate the link between deviations in the glass transition temperature ($T_g$) of polymer thin films from the bulk value and the growth of irreversibly adsorbed nanolayers. Through the use of fluorescence spectroscopy, we are able to directly measure $T_g$ of polystyrene adsorbed nanolayers in an exposed geometry and in situ. The results allow us to examine the influences of interfaces and molecular weight on the $T_g$ of adsorbed nanolayers throughout their development. By undertaking these studies, critical information is obtained that assists in the design and processing of technologies in which thin polymer films are placed in contact with solid interfaces.

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