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Investigating the effect of chain architecture on the dynamics of thin entangled polymer films ETHAN GLOR, ZAHRA FAKHRAAI, Univ of Pennsylvania — Recent work in polymer physics shows that the structural relaxation time near a free surface of a thin polystyrene film is significantly different from that of the bulk polymer. This can have a large influence on their properties. For instance, studies have shown that polystyrene thin films exhibit a decreased glass transition temperature as the thickness decreases below 60 nm. A wide range of experimental techniques show that the dynamics at the free surface of polystyrene have a weaker temperature dependence than that of the bulk. Here we use cooling rate dependent T_g measurements (CR-Tg) to show that the dynamics in thin, entangled polystyrene films are directly influenced by the free surface. These studies also show that the deviations from bulk dynamics begin at a particular temperature (T*), providing an explanation for why some studies observe no interfacial effects in ultra-thin polymer films. A puzzling aspect of this work is that computational studies and studies on molecular glasses, which also exhibit enhanced surface dynamics, do not observe T*. We use CR-Tg to study thin films of various polymers to determine 1. If T* is a phenomenon common to all polymer glasses, and 2. If the value of T* is dependent on the chemistry or T_g of the polymer.

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