MAR13-2012-001015

Abstract for an Invited Paper
for the MAR13 Meeting of
the American Physical Society

Glass Transition of Polymers near Their Free Surface[1]

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Recent experiments have indicated that the relaxation dynamics near a free polymer surface may become fundamentally different from bulk α relaxation times. The dynamics lose many of the characteristics commonly associated with glasses. The dynamic properties lose their typical Vogel-Fulcher-Tammann (VFT) temperature dependence and take on an Arrhenius dependence. There is also evidence that the dynamic properties become more homogeneous near the free surface. Such direct measurements of the relaxation dynamics are rare and extremely difficult to perform on a wide range of polymeric systems. It has been shown that cooling rate-dependent glass transition temperature ($\mathrm{T_g}$) measurements can be used as an effective and simple method to estimate the relaxation dynamics of the free surface. The cooling rate is inversely proportional to the relaxation time of the film at the temperature at which the system falls out of equilibrium, $\mathrm{T_g}$. In thin polymer films, as the film thickness is decreased the dynamics of the film are affected more strongly by surface dynamics and therefore they provide a lower bound to the surface relaxation times. In thin polystyrene films measurements of $\mathrm{T_g}$ as a function of cooling rate indicate a clear onset of deviations from bulk properties at a temperature a few degrees above the bulk $\mathrm{T_g}$. We hypothesize that this could be due to either a new mode of relaxation that is exclusively available near the surface, or typical glassy dynamics that have faster time scales near the surface. In this study we investigate the effect of molecular weight and the polymer structure on the value of the onset temperature to verify whether the properties are consistent with one of these hypotheses. It is also observed that under certain conditions, where the dynamics of the free surface and the bulk relaxation dynamics are many decades apart, the system exhibits two distinct $\mathrm{T_g}$s associated with either bulk or surface relaxations. This data can be used to estimate the length scale of the surface dynamics and the length scale over which the effects penetrate into the bulk of the film.

[1] Partial support from MRSEC grant (DMR-1120901) is acknowledged.