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A Direct Relationship between Enhanced Surface Mobility and Tg Reduction in Thin Polymer Films ZAHRA FAKHRAAI, Department of Chemistry, University of Pennsylvania, JAMES A. FORREST, DONGPING QI, Department of Physics and Astronomy, University of Waterloo — Cooling rate dependent Tg measurements of thin polymer films show a strong correlation between the cooling rate and the confinement effects. It is observed that the Tg is more strongly dependent on the cooling rate as the film thickness is decreased. The confinement effects also become weaker at higher cooling rates and it appears that both for thick films and high cooling rates the confinement effect vanishes. The results can be plotted on an Arrhenius plot by assuming that the cooling rate is inversely related to the relaxation time as the temperature that the system falls out of equilibrium (Tg). The surface relaxation times can be independently measured using nano-hole relaxation and nanoparticle embedding techniques and the results can be plotted on the same Arrhenius plot. It is observed that the surface relaxation has much weaker temperature dependence, with an activation energy that matches the limit of zero film thickness for the rate-dependent Tg measurements. The strong correlation between surface properties obtained by direct mechanical measurements with the Tg measurements obtained by ellipsometry suggest that these two phenomena are from the same origin and one cannot be explained without the other.

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