Measuring the glass transition of polymer nanodroplets

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— Despite almost 2 decades of measuring the glass transition temperature ($T_g$) in thin polymer films, there is no consensus on the magnitude (or even the existence) of observed $T_g$ reductions. Recent suggestions that reduced $T_g$ values in thin polystyrene films may be nothing more than a complicated artifact of sample preparation must be taken very seriously. Reduced $T_g$ values are reported only for polymer films prepared on a non-wetting substrate where the film is unstable with respect to dewetting. In all cases only kinetic metastability allows one to measure a $T_g$ value. The fundamental problem is that an unambiguous measure of $T_g$ can only be obtained as the sample is cooled from the equilibrium liquid. No experiments involving thin polymer films have yet satisfied this condition. Our approach is to use samples prepared in the equilibrium state atop a non-wetting substrate (a collection of spherical caps). Since the droplets are already in the equilibrium state, they can be annealed for arbitrarily large times without evolution of the structure. We describe dilatometric measurements of $T_g$ for nanometer sized spherical caps of polystyrene. This technique can be used to investigate the effect of annealing history and to extend the studies of $T_g$ in high surface area to volume systems beyond polymers and into other molecular glass forming materials.

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