NANO HIGHLIGHT
Dynamic Heterogeneity and the Behavior of Glass-Forming Materials at the Nanoscale

NSF NIRT Grant 0304640

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Numerous studies have shown that T_g is depressed at the nanoscale, but most of these studies are based on changes in the dynamical properties rather than changes in thermodynamical ones. The latter are important because models of the glass transition deal with thermodynamic properties. As part of our NIRT grant aimed at examining the dynamic heterogeneity and behavior of glass-forming materials at the nanoscale, the glass transition temperature and absolute heat capacity of thin polystyrene films were measured using differential scanning calorimetry as a function of film thickness. We found a depression of T_g as indicated in Figure 1, but perhaps more importantly, we observe a significant decrease in the absolute heat capacity in both the glass and liquid states, as well as a decrease in the step change in the heat capacity at T_g.[1] Future measurements are aimed at understanding these changes as well as at measuring the dynamical heterogeneity in these films.

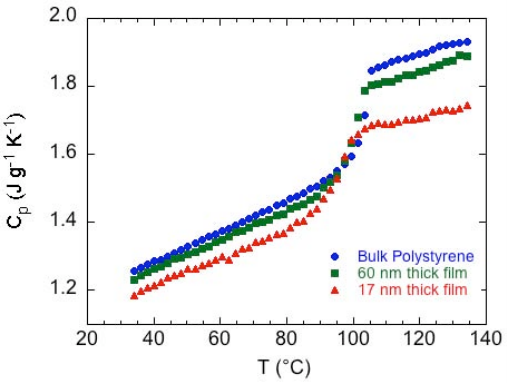

Figure 1: Absolute heat capacity for bulk polystyrene and for films of 17 and 60 nm thickness using step-scan DSC. After ref. 1.

In parallel work, the translational diffusion of rubrene in sucrose benzoate has been studied using a holographic FRAP technique which yields the translational relaxation function. We find, as shown in Figure 2, that translational diffusion of rubrene has a weaker temperature dependence than T/ηfor $T < 1.2T_g$ but, interestingly, it tracks the dielectric relaxation.[2] The enhancement of the diffusion over that predicted by the Stokes-Einstein equation is not unexpected since our probe is significantly smaller than sucrose benzoate. However, the coincidence with the dynamical behavior will be further investigated. In addition, although the observation of enhanced translational diffusion strongly suggests that the dynamics are spatially heterogeneous, further support for dynamic heterogeneity must come from rotational diffusion measurements which are currently underway.

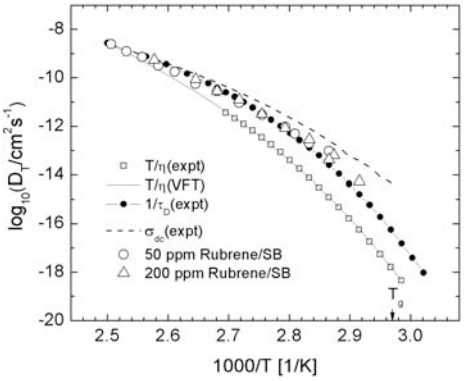

Figure 2: Translational diffusion coefficient D_T for rubrene in sucrose benzoate, T/η, dc-conductivity σ_{dc}, and $1/\tau_D$. After ref. 2.

References

1. Y. Koh, G. B. McKenna, and S. L. Simon, in preparation.
2. J. R. Rajian, W. Huang, R. Richert, and E. L. Quitevis, J. Chem. Phys., to appear, January 2006.