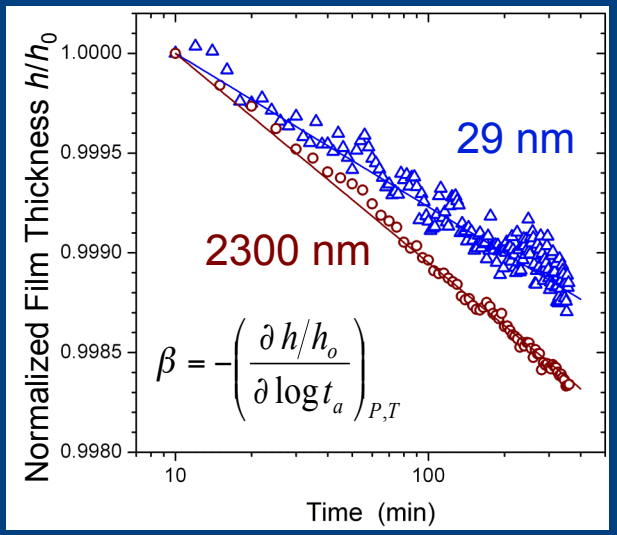
Structural Relaxation of Polymers in Nanoconfined Geometries

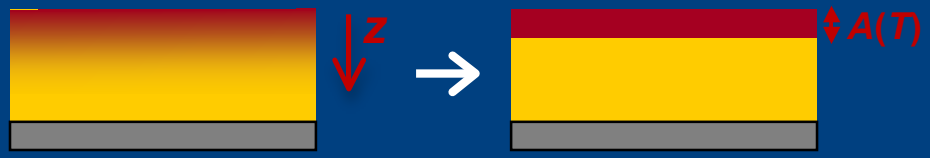
Connie B. Roth, Department of Physics, Emory University, Atlanta, GA

Physical aging in thin polymer films is important for the long-term stability of various applications, e.g., gas separation membranes. Various studies have observed changes in the aging rate with decreasing film thickness, the exact cause of which is still unknown in most cases.

We have developed a streamlined ellipsometry method of measuring the physical aging rate of thin polymer films with varying chemical structure. A comparison of the temperature dependence of the aging rate for thick (2400 nm) and thin (30 nm) polystyrene films supported on silicon indicate that the aging rate for the thinner films is reduced at all temperatures.



We attribute this decrease in physical aging rate for ultrathin supported films to enhanced dynamics near the free surface, and demonstrate using a gradient and two layer model that the effects are related to the glass transition temperature T_g reductions in <100 nm thick films.



$$\beta(h,T) = \beta_{\text{bulk}}(T)\frac{1}{h}\int_0^h \left[1-\exp\left(-\frac{z}{\lambda(T)}\right)\right]dz = \beta_{\text{bulk}}(T)\left[1-\frac{\lambda(T)}{h}\left\{1-\exp\left(-\frac{h}{\lambda(T)}\right)\right\}\right]$$