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Structural Relaxations in Bulk and Thin Film Polymers: Role of Macromolecular Architecture

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Structural relaxations that occur in polymers quenched below the glass transition temperature, T_g , are responsible for time-dependent changes in physical properties that include optical, specific volume and the enthalpy. This phenomenon, physical aging, has been of interest in bulk polymers for decades and much is understood. The aging rate, R , is known to increase as the temperature at which the glass ages, T' , decreases below T_g , due to the increasing departure from structural equilibrium; it then decreases with further decreases in T . We show that the aging rates of star-shaped polymers are slower than their linear analogs of the same degree of polymerization, N . Whereas the temperature dependence of R is independent of N for linear chains, it depends on the functionality, f , and on the degree of polymerization per arm, N' , of the star-shaped macromolecules. R decreases with increasing f , for N' less than a threshold degree of polymerization, which increases with increasing f . The aging of very thin films ($h \sim 100$ nm) is dependent on the distance, z , from an external interface. With the use positron annihilation spectroscopy (PALS) we determined the z -dependence of the T_g in thin films and showed that the aging rate is largely determined by the difference between the local glass transition temperature of the films and T' . Finally we show that the aging rates of linear and star-shaped macromolecules are consistent with experimental findings of glassy dynamics in both systems.