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Glass transition of star-shaped thin polymer films EMMANOUIL GLYNOS, BRADLEY FRIEBERG, University of Michigan, GEORGIOS SAKELLARIOU, University of Athens, PETER GREEN, University of Michigan — We show that the glass transition temperatures, T_g, of thin polystyrene (PS) films, supported by oxidized silicon substrates (SiOx), depends on functionality, f, and the degree of polymerization of the arm, N_arm, of the macromolecule. The T_gs of star-shaped PS films with thickness H=30nm, T_g(30nm) with f as high as 64 were investigated. The T_g(30nm) of linear PS thin films, is less than the average bulk T_g, T_g(bulk). For molecules of N_arm about100, the T_g(30nm) of a macromolecule with f =3 was equal to that of a linear PS. However, the T_g(30nm) increased with increasing f, reaching a maximum of at f =8 where T_g(30nm) was higher than T_g(bulk). For larger values of f, T_g (30nm) decreased monotonically with increasing f and for f =64theT_g(30nm) became comparable to T_g(bulk). The magnitude of this effect is weaker for much larger values of N_arm. We rationalized these observations in term of two competing entropic: the increasing entropic attraction of the macromolecules to interfaces, with increasing f, and an increasing intermolecular entropic repulsion of these macromolecules with increasing f, and/or decreasing N_arm.

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