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Interplay between glass transition and thermal expansivity in absorbed and spincoated polymer films SIMONE NAPOLITANO, MICHAEL WUBBENHORST, Katholieke Universiteit Leuven — We investigated the kinetics of formation, the glass transition dynamics and the thermal expansivity of absorbed layers of polystyrene and other amorphous polymers on aluminum oxide. Extremely thin films (2 - 10 nm) were prepared following the experiment of Guiselin: polymers were either spincoated or casted on metallic surfaces and annealed at constant temperature immediately after film formation; non-absorded chains were washed away by a good solvent. Different molecular weights and solvent conditions were explored. We analyzed the shape of the observed kinetics in terms of density of active absorption sites and compared with recent experimental results. The combination of a tremendous reduction of the thermal expansion coefficients, TEC, together with non-universal changes in Tg is discussed. Finally, we add more evidence on the unusual confinement effects of poly(tert-butylstyrene). Below 50 nm, both Tg and TEC decreased. Such a mixed behavior implies an enhancement of the molecular mobility, without the presence of any free surface, but dead layers. The effect of density-conformation coupling in proximity of a non-attractive interface allows coexistence of an immobilized fraction in contact with the metal and an excess of thermal expansivity, arising from the long range effects of packing frustration penetrating inside the bulk-like core of the film.

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