How irreversible adsorption affects segmental dynamics and glass transition temperature

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Growing experimental evidence shows that the behavior of thin polymer layers strongly depends on the degree of adsorption, the number density of monomers pinned onto the supporting substrate. Several groups have independently observed that properties as wettability, viscosity and thermal expansion are affected by prolonged annealing in the liquid state, even at timescales exceeding the equilibration time of a bulk melt. In this talk, after introducing the physics behind the mechanisms of irreversible adsorption, I shall review some of these observations, focusing on those related to the thermal glass transition and to the segmental dynamics. Based on the information collected on several polymers, I will discuss on different models that could explain the origin of the striking correlation between the value of the glass transition temperature of 1D confined polymers and the degree of adsorption. After presenting new results on the interplay between segmental dynamics and formation of adsorbed layers, I will demonstrate that, differently than what currently speculated, the transformations materials undergo during adsorption do not mimic physical aging. A new molecular mechanism is proposed.