

# Organization for Cultural Diversity in Science Seminar



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### “Molecular Dynamics and Glass Formation of Nanoscopically Confined Polymer”

**Abstract:** Many technological advances are driven by the ongoing emergence of nanostructured polymers as the critical component to enable innovation. Yet, from a materials design perspective, we cannot presume that the bulk properties of polymers define their behavior when physically confined to nanoscale dimensions. This is, in fact, not true, as there is now convincing evidence that the nanoscale properties of polymers, including the glass transition temperature, can be profoundly different from the bulk. Here, I discuss two overarching questions in the field: 1) What are the molecular dynamics at the free surface of polymer glasses? and 2) How can we overcome the effect of confinement on the reduction in the glass transition temperature? Regarding the first question, we introduce a time-resolved nano-creep experiment to probe the dynamics at the surface of polymer glasses. We reveal a new mode of molecular dynamic at the surface: pseudoentanglements. This phenomenon causes unentangled chains to exhibit surface mechanical response and dynamics that are characteristic of entangled polymers. For entangled chains, the phenomenon prolongs and stiffens the entangled response. In both cases, the breadth of the entangled response grows on cooling, leading to a breakdown of time-temperature-superposition at the surface. Counterintuitively, this new mode of slow surface dynamics emerges precisely because surface dynamics are accelerated relative to the bulk. Concerning the latter question, we demonstrate that ultrathin polymer films with an ultradense brush morphology – defined with respect to approaching the maximum theoretical value of crystalline chain packing – exhibits a significant enhancement in thermal stability, as manifested by an exceptionally high  $T_g$  and low expansivity. For instance, a 5 nm thick polystyrene brush film exhibits a  $\sim 75$  K increment in  $T_g$  and  $\sim 90$  % reduction in expansivity compared to a spin-cast film of comparable thickness. Our results establish how the film morphology can overcome confinement and interfacial effects in controlling material properties, and how this can be achieved by the dense packing and molecular ordering in the amorphous state of the ultradense brushes prepared by surface-initiated atom transfer radical polymerization in combination with a self-assembled monolayer of initiators.

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