Stony Brook University

Department of Materials Science and Chemical Engineering

In-Person Departmental Colloquium

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1:00 – 2:00 p.m.
Old Engineering Room 301

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Glass Transition and Dynamics of Nanoscopically Confined Polymer

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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. In this presentation, I want to highlight two recent examples from my group that aimed to advance the field of understanding polymers in confinement and at interfaces. In the first part of the talk, 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. In the second part of the talk, we present an experimental methodology to allow for the first direct measurement of the local glass transition temperature (T_g) in block copolymers. This is achieved by incorporating fluorescence-bearing monomers at specific locations along the polymer chain, allowing the labeled monomers local environment to be interrogated via fluorescence. As an example, in lamellar forming poly(butyl methacrylate-b -methyl methacrylate) diblock copolymers, a strong gradient in glass transition temperature, T_g , of the higher-T_g block, 42 K over 4 nm, was mapped with nanometer resolution. These measurements also revealed a strongly asymmetric influence of the domain interface on T_g , with a much smaller dynamic gradient being observed for the lower-T_g block. We also find that chain connectivity plays an important role in setting the glassy dynamics in diblock copolymers.

Biosketch

Rodney D Priestley is the Dean of the Graduate School at Princeton University. He is the Pomeroy Betty Perry Smith Professor in the Department of Chemical and Biological Engineering and the Associate Director of the Princeton Center for Complex Materials. He obtained his Ph.D. in Chemical Engineering from Northwestern University in 2008. His research involves describing and developing complex materials, especially nanoparticles, thin polymer films, and nanocomposites, focusing on material properties at small length scales. From designing next-generation biocompatible surfactants to creating ultra-stable polymer films resistant to properties changes upon heating, his work impacts industries ranging from personal care to aerospace. His recent interests include the use of polymers in sustainability and their implications on the environment. Recent recognitions include the 2020 American Physical Society Dillon Medal and 2020 American Chemical Society Macro Letters-Biomacromolecules-Macromolecules Young Investigator Award.