Phase Behavior and Dynamics of Model Tapered Diblock Polymers

Abstract: Increased understanding and precise control over the nanoscale structure and dynamics of microphase separated block copolymers would advance development of mechanically robust but conductive materials for battery electrolytes, among other applications. Using a combination of numerical statistical mechanical theory and molecular simulations, we study the phase behavior and dynamics of tapered block polymers, which are AB diblock polymers with a gradient region inserted between the pure A and B blocks such that the composition smoothly transitions from A to B (or B to A in the case of inverse tapers). Using self consistent field theory, we predicted a widening of the bicontinuous double gyroid region of the phase diagram for moderate length normal tapers versus diblocks, suggesting taper length can be used as a control parameter to obtain network phases even at high molecular weight, as may be desirable in transport applications. We further used coarse-grained molecular dynamics (MD) simulations and fluids (classical) density functional theory (fDFT) in concert to study the same system from two compatible points of view. Both methodologies can capture the microphase separation of block copolymers, using similar monomer-based chain models and including local packing effects. Free energies of various microphases are readily accessible from fDFT, which allows us to efficiently determine the equilibrium nanostructure over a large parameter space. Meanwhile, MD allows us to visualize specific polymer conformations in 3D over time (e.g. MD simulations show how the chains fold back and forth across the interface in inverse tapered polymer systems) and to calculate dynamic properties (e.g. diffusion of penetrants in normal tapers is significantly faster than that in inverse tapers).

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Lisa Hall is the H. C. “Slip” Slider Assistant Professor at the Ohio State University. She joined OSU in 2012, having completed her Ph.D. with Prof. Ken Schweizer at the University of Illinois and a subsequent postdoctoral appointment with Amalie Frischknecht and Mark Stevens at Sandia National Laboratories. Her research group uses statistical mechanical theory and molecular dynamics simulations to understand the structure and dynamics of nanostructured polymers. Systems of interest include ion containing block copolymers, ionomers, and nanocomposites. She received a CAREER award from the National Science Foundation in 2015, centered on efficiently modeling ion conduction in block copolymer electrolytes.