## Formation of Low Symmetry Ordered Phases in Block Polymer Melts ${ }^{1}$

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Until recently the phase behavior of asymmetric AB diblock copolymers in the melt state was universally accepted as a solved problem: spherical domains packed on a body centered cubic (BCC) lattice. Recent experiments with low molecular weight diblocks have upended this picture, beginning with the discovery of the Frank-Kasper sigma phase in poly(isoprene)-$b$-poly(lactide) (PI-PLA) followed recently by the identification of a dodecagonal quasicrystal phase (DDQC) as a metastable state that evolves from the supercooled disordered liquid. Self-consistent mean-field theory shows that introducing conformational asymmetry ( $b_{A}>b_{B}$ where $b$ is the statistical segment length) opens a window in the phase portrait at $f_{A} \ll 1 / 2$ that supports the formation of various low symmetry ordered phases. However, contrary to the widely accepted mean-field picture, the disordered state near the order-disorder transition (ODT) is highly structured and rapid cooling of this micellar fluid several tens of degrees below the ODT temperature arrests macromolecular chain exchange transitioning the material from an ergodic to non-ergodic state. We have explored the evolution of order following such temperature quenches and during subsequent reheating using synchrotron small-angle X-ray scattering (SAXS) revealing surprising analogies with the behavior of metal alloys. This presentation will associate the formation of ordered low symmetry phases with the concept of sphericity, the tendency for the self-assembled nanoparticles to be spherical in competition with the constraints imposed by periodic and aperiodic packing without voids and subject to the condition of incompressibility. This work was conducted in collaboration with Kyungtae Kim, Morgan Schulze, Akash Arora, Ronald Lewis, Timothy Gillard, Sangwoo Lee, Kevin Dorfman and Marc Hillmyer.
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