The Effect of Chain Rigidity on the Self-Assembly of Functional Block Copolymers

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Nanostructuring of functional macromolecules, such as proteins or semiconducting polymers, promises to enable the development of a wide range of exciting new materials. Block copolymers provide an elegant route to self-assemble such nanostructured phases through segregation of the different blocks on the 10-100 nm molecular length scale. The rodlike nature of many common functional polymers, such as helical proteins or main-chain conjugated semiconducting polymers, complicates self-assembly of rod-coil block copolymers by changing the chain topology as compared to traditional block copolymers and creating an interplay between liquid crystalline interactions and microphase separation. Understanding both the equilibrium nanostructured phases accessible in these rod-coil block copolymers and the molecular alignment within these phases is critical to controlling the properties of these materials.

To develop a fundamental understanding of self-assembly in rod-coil systems, we have prepared a model rod-coil diblock copolymer with accessible phase transitions and used it to chart the phase diagram for this class of materials. Side chain functionalizing the rod block to make it chemically similar to the coil reduces the rod-rod and rod-coil interactions, allowing both order-disorder and liquid crystalline phase transitions to be investigated. Liquid crystalline aligning interactions between the blocks promote the formation of lamellar phases across most of the ordered region of the phase diagram, with heating above the order-disorder transition resulting in both nematic and isotropic phases. At high coil fraction and high asymmetry in size between the rod and coil, hexagonal arrangements of rectangular rod nanodomains are also observed. Aligning the samples in a magnetic field allows the rod orientation within the nanostructured phase to be determined.

Independent measurements of the temperature dependence of the rod-rod and rod-coil interaction parameters allow this system-specific phase diagram to be converted to a universal phase diagram for all block copolymers with a rod-coil molecular structure. Measurements of the nematic-isotropic transition in rod homopolymers as a function of molecular weight are used to estimate the Maier-Saupe rod-rod interaction parameter for nematic liquid crystals. The Flory-Huggins rod-coil interaction parameter is quantified through measurements of the interfacial segregation of a rod-coil block copolymer to the interface between rod and coil homopolymers. Self-consistent field theory is used to model the interfacial excess of block copolymer as a
function of the rod-coil interaction strength, allowing the rod-coil interaction parameter to be estimated by comparison with experimental results.