John H. Dillon Medal Lecture: Self-assembly of rod-coil block polymers
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While the self-assembly of coil-like block copolymers into morphologies with well-defined nanometer-sized periodicities is now classic, the translation of this strategy to functional polymers with non-Gaussian chain shapes is significantly more complicated. Control and predictive understanding of nanoscale structure in rod-coil block copolymer systems are of particular importance in both conjugated polymers (for optoelectronic devices) and biomimetic polymers. Our work is targeted at gaining a fundamental understanding of the thermodynamics and kinetics of self-assembling functional rod-coil block copolymer systems, and then applying this to conjugated polymers to understand structure-property relationships in plastic electronics. We demonstrate that phase space for weakly segregated model systems is described by the Flory-Huggins block interaction parameter ($\chi N$), the Maier-Saupe parameter ($\mu N$) (which parameterizes rod-rod interactions and also scales with temperature), the coil volume fraction ($\varphi_{\text{coil}}$), and a geometrical asymmetry term ($\nu$) to account for aspect ratio differences in the rod and coil. Further, we also find that careful molecular design to moderate molecular interactions is essential in creating controllable systems. In particular, both sidechain substitution and sequence control can be used to control melting temperatures and liquid crystalline interactions in order to create a processing window in which self-assembly can occur.