Architecture-enabled control of polymer properties and self-assembly in Janus and ternary graft block copolymers

An N. Le, Zi-Hao Guo, Xiaowei Fu, Mingjiang Zhong

Block copolymers (BCPs) have been widely investigated as nanostructured materials for a range of applications due to their ability to self-assemble into a variety of phase-separated nanostructures. However, a remaining challenge that limits the widespread application of block copolymers (BCPs) is a lack of independent control of the self-assembled nanostructure and bulk properties in a single polymer material, as both are dependent on the molecular structure of the BCP. We have demonstrated that Janus graft BCPs synthesized via ring-opening metathesis polymerization of poly(lactic acid) and polydimethylsiloxane containing branched macromonomers offer such tunability: the length of the side chains controls the domain spacings, and the length of the backbone independently controls the thermomechanical properties of the graft BCP. Covalent preorganization of the block interface allows for rapid formation of stable self-assembled nanostructures with ultra-small domain sizes (down to 5.68 nm). We also propose adding a third side chain into our graft BCP design, which may allow for diversification of the self-assembled morphologies, while still maintaining desirable self-assembly kinetics.