Wide Neutrality Window for Block Copolymer Vertical Orientation using Incongruent Homopolymer Blended Brushes

Kaitlyn Hillery, Sharif Tasnim Mahmud, Nayanathara Hendeniya, Ava Huth, Caden Chittick, Shaghayegh Abtahi, Boyce Chang*

Department of Materials Science and Engineering, Iowa State University, Ames, Iowa, United States

Abstract

Distinctive polymer brushes play a crucial role in providing a neutral surface conducive to orientational control of block copolymers (BCPs). This bottom-up approach effectively aligns the formation of vertical lamellar and cylinder lattice structures from the BCP that is crucial to their processability in many applications. In conventional BCP self-assembly techniques, random copolymer (RCP) brushes are commonly employed to achieve substrate neutrality. However, these methods face significant drawbacks, including batch variations, lack of ability to tune surface energy during grafting, and synthetic challenges for chemically incompatible monomers. Blending homopolymer brushes to achieve mixed chemistry has been demonstrated to be effective for creating neutral substrates but requires narrow blend formulations due to macrophase segregation. To address these issues, various approaches have been proposed to mitigate inconsistencies and enhance tunability, however, surface neutrality for highly mismatched BCPs remain a challenge. Our proposition involves a system of polymer brushes composed of incongruent chain lengths. We demonstrate that tuning the composition of the incongruent blends significantly widens the neutrality window of a lamellar-forming BCP. This was attributed to the formation of an active canopy layer that is responsive to its chemical environment. This system effectively controls surface chemistry by combining the effects of chemistry and macromolecular structure, which lowers process complexity to serve as a tunable neutral brush for BCP vertical orientation.