Self-Assembly Behavior of Sugar-Based High-χ Block Copolymers in the Complex Phase Window

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Abstract

Downsizing the mask of manufacturing process has been a major issue in semiconductor industry. Nowadays, top-down lithography has been extensively studied and reached delicate lengthscale in patterning. Bottom-up molecular self-assembly has also been considered as a plausible approach to produce the mask with even smaller periodic lengthscale. Previous studies have shown that the structures with sub-10 nm domain spacing can be produced by low-molecular weight block copolymers (BCPs) exhibiting very strong segregation strength or very large χ (i.e., the Flory-Huggins interaction parameter). One effective approach of creating high-χ BCP is introducing polysaccharide (PSA) as one constituent block due to its conformational rigidity and prevalent formation of intra- and inter-molecular hydrogen bonding.

Though a number of researches have shown that PSA-based BCPs could form lamellar (LAM) and hexagonally-packed cylinder (HEX) structures with sub-10 nm size, investigation of their self-assembly behavior in the so-called "complex phase window", wherein complex structures such as bicontinuous phases and perforated layers may be formed, is very limited. Here we investigated the self-assembly behavior of a series of polyglucose-polyisoprene block copolymers bearing linear and nonlinear architecture using synchrotron X-ray scattering conducted at TLS 17A1 and TPS 25A. Double gyroid (DG) and hexagonal perforated layer (HPL) with ABC stacking sequence were discovered. In addition, non-canonical structures including HPL phase with AB stacking and Fddd bicontinuous phase were also found, showing the high diversity of structures that can be generated by sugar-based BCPs. We also identified a thermally reversible LAM-HPL transition and the effect of the configuration around the branching site on the microdomain curvature. These results demonstrated that sugar-based BCP not only forms the structures with fine domain spacing, but also displays complex structures and phase transition behavior which may expand our understanding of the self-assembly of high-χ BCP.

Keywords – high-χ block copolymers, sugar-based block copolymers, perforated layer structure, self-assembly, bicontinuous structure