Crystallization Behavior of Fluorinated Crystalline Diblock Copolymers in the Confined Microphase Separated States

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Strongly segregated crystalline diblock copolymers are expected to form characteristic hierarchical structures composed of crystalline structure, long-range ordered microdomains. The crystallization behavior within the strongly segregated microdomain has not been identified yet. In this study, we investigated the crystallization behavior in poly(ethylene glycol)/highly crystalline poly(perfluoroctylethyl acrylate) (PEG/PFA-C₈) diblock copolymers. The PEG/PFA-C₈ diblock copolymers with different block composition were synthesized by atom transfer radical polymerization from PEG-macroinitiator. Small angle X-ray scattering (SAXS) measurements revealed that PEG/PFA-C₈ diblock copolymers formed lamellar and cylinder morphology microphase structures depending on the block composition. Wide angle X-ray diffraction (WAXD) measurements indicated that both PEG and PFA-C₈ components were crystallized in each phase. Differential scanning calorimetry (DSC) curves indicated that the PEG crystallization temperature depends on its volume fraction. This phenomenon is attributed to the morphology-induced confinement effect.