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Molecular Simulations of Confined Crystallization in the Microdomains of Diblock Copolymers

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Abstract
Crystallization confined in the microdomains of diblock copolymers represents the strategy of “structure-in-structure” self-assembly in the hierarchical fabrication of polymeric nano-materials. This review is a survey on the molecular-level understanding of crystallization confined in lamellar, cylindrical and spherical microdomains of diblock copolymers. Separate situations such as hard confinement, soft confinement and double crystallization are discussed and compared the simulation results with the relative experiments. The confinement effects on guiding the preference of crystal orientations were interpreted. Molecular simulations were proved to be a useful tool in understanding such a delicate fabrication of nano-materials.

Keywords
Diblock copolymers, self-assembly, crystallization, nano-confinement, crystal orientations, molecular simulations

1. Introduction

Diblock copolymers are two polymer chains chemically different and covalently bonding from one end to the other. When two blocks are thermodynamically incompatible to each other, diblock copolymers assemble themselves into an ordered structure with the domain sizes of different chemical species restricted at the nano-scale molecular level. The balance between component repulsion and chain connectivity of two amorphous blocks results in rich geometries of microphase domains (below abbreviated as microdomains). For instance, with the compositions deviating from symmetric blocks, the equilibrium microdomains of diblock copolymers under the conditions of strong segregation vary from the alternating lamellae (lam), the hexagonal cylinders (hex), to the body-centered-cubic spheres (bcc) [1-6]. Their nano-scale self-assembly shows numerous potential applications that have attracted a broad attention [7-16].

The crystallization behaviors of semi-crystalline diblock copolymers have been extensively investigated [17-23]. If one or both blocks of diblock copolymers are crystalline, denoted separately as *crystalline-amorphous* or *crystalline-crystalline* diblock copolymers, phase behaviors of these semi-crystalline diblock copolymers become complicated. Under the same compositions, competition between microphase separation (at the temperature T_{ODT} with its reverse process called as order-disorder