



Review

Crystallization assisted self-assembly of semicrystalline block copolymers

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ABSTRACT

The self-assembly of block copolymers (BCPs) in the presence of crystallization as the second driving force is reviewed, for BCPs in the bulk, thin films, single crystals and micelles. The crystallization of semicrystalline BCPs in the bulk is introduced briefly and the unique morphologies of semicrystalline BCPs at various levels due to crystallization are discussed. The thin film morphologies shown by crystalline BCPs are summarized in terms of the factors affecting the relative strengths of various driving forces. Special attention is paid to the thin film morphologies of functional BCPs containing crystalline poly(3-alkylthiophene) and perylene bisimide units. The single crystal morphologies of semicrystalline BCPs are also presented. Finally, the micellar morphologies of BCPs with a semicrystalline core are reviewed. The controlled and living growth of crystalline micelles, which is the unique characteristic of such micelle, is then discussed.

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1. Introduction

Block copolymers (BCPs), consisting of immiscible segments, can undergo microphase separation in the bulk and in thin films under certain conditions. Microphase separation will drive BCPs to self-assemble into a variety of ordered nano-structures, including spheres, cylinders, gyroids and lamellae, depending on the composition of the BCP [1,2]. These ordered nano-structures are useful for the fabrication of thermoplastic elastomers and can also be applied in lithography, nanomaterials and optoelectronic devices [3,4]. By contrast, when BCPs are dissolved in a selective solvent, micelles with a soluble corona and insoluble core can be formed at a concentration higher than the critical micellization concentration (cmc). The driving force for the formation of micelles is the solvophilic/solvophobic force. Block copolymer micelles can be used as nano-carriers for drugs and catalysts and have wide applications in the fields of biomedical material and catalysis.

Semicrystalline BCPs contain at least one crystallizable block. The polymer crystals usually have a thickness dimension of tens of nanometers. Such a size is comparable with the dimension of the microdomains formed by microphase separation. As a result, semicrystalline BCPs are usually used to construct a nano-confined environment to investigate the confined crystallization of polymers [5–10]. The crystallization behavior and morphology of semicrystalline

BCPs, including crystalline/rubbery, crystalline/glassy and double crystalline BCPs, have been extensively reviewed by other authors [11–13]. Moreover, in selective solvents, semicrystalline micelles of BCPs may be obtained when the core of the micelles is formed by the insoluble crystalline block.

Crystals can be defined as materials having a three-dimensional ordered structure. Thus crystallization can also be viewed as one of the driving forces for the self-assembly into an ordered structure [14], along with the microphase and solvophilic/solvophobic driving forces. When crystallization is introduced into a BCP, it may compete with the driving force of microphase separation in the bulk and thin film or with the solvophilic/solvophobic driving force in the selective solvent. On the other hand, crystallizability of a polymer is strongly dependent on temperature and therefore we can regulate the relative strength of crystallization and other driving forces. Crystallization is usually a kinetically controlled process. Various structures may be trapped by controlling the crystallization pathway. These characteristics of crystallization lead to abundant morphologies for semicrystalline BCPs and a range of morphologies. In this paper, we intend to review the self-assembly morphologies of BCPs in the bulk, thin films, single crystals and micelles formed with the assistance of crystallization, focusing on the unique characteristics and regulation of BCP morphology due to the presence of crystallization as the second driving force.

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