Feature article

Hierarchical microstructures self-assembled from polymer systems

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ABSTRACT

Hierarchically ordered microstructures, self-assembled from copolymers, have drawn considerable attentions in the last decades. Study of hierarchical microstructure impacts many realms such as material engineering and biology science. In this article, notable recent advances in the fields of hierarchical polymeric microstructures generated in either bulk or selective solvents are highlighted, from both the experimental and theoretical/simulation aspects. The polymer systems for the hierarchical microstructures are concentrated on multiblock copolymers and polymer blends with/without non-covalent bonding interactions. Particular emphasis is placed on what governs the self-assembly of hierarchical microstructures from a diversity of designed copolymer systems, how to classify the types of non-frustrated and frustrated hierarchical structures, and where the future opportunities are.

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1. Introduction

Hierarchical assembly of materials is one of the most promising yet challenging aspects of nanoscience [1–3]. Nature has provided many elegant examples of hierarchical structural designs. For example, a tendon is a hierarchical material in which the organization is controlled over many discrete length scales, ranging from collagen fibrils to fibers [3,4]. This natural phenomenon has stimulated researchers to fabricate synthetic hierarchical materials by mimicking natural materials [3,5]. Although the feat for synthesizing hierarchical materials, in terms of complexity and precision, is still very primitive, advanced progress has already been made towards this field.

It is well-known that the structures at microscopic scales often play a unique role in determining the physical properties of the materials — transferring and amplifying molecular functions to a property at macroscopic length scales. If additional structures in the size comparable to the original microstructures are incorporated into the same materials, the physical properties should be determined by both the microstructures, probably leading to a variation of the transfer and amplification of the molecular functions to material properties. Therefore, it is able to realize an astonishing range of functions by resorting to the same constituent materials, as done by nature. In view of this, many polymer scientists have devoted their efforts to develop hierarchical

microstructures from polymer systems. The hierarchical microstructures can be defined as an ordered structure with n levels of microscopic length scales. For $n = 0$, the materials are isotropic at microscopic length scales, and $n = 1$ could represent the materials with conventional microphase-separated structures such as classical lamellar, cylindrical, and spherical phases [6]. The hierarchical microstructures are beyond these structures, exhibiting more than one length-scale structure ($n \geq 2$), such as lamellae-*in*-lamella and lamellae-*in*-cylinder.

Benefited in the latent possibility in gaining materials with various physical properties from hierarchical assembly, the field of polymer hierarchical microstructures has undergone rapid growth over the last decades. A diversity of polymer systems have emerged to create hierarchical microstructures. Recently, several reviews have been published that cover the general aspects of polymer hierarchical microstructures in either the bulk or selective solvents [7–11]. The intent of the current article is not to provide a repeat review of the hierarchical microstructures. Instead, we highlight the recent progress in understanding the physical mechanisms behind the formation of these structures, combining with our recent theory and simulation results. Since the construction of hierarchical microstructures by transferring hierarchical characteristic of molecular length scale to the next level is *neither automatic nor necessary*, establishing links for the hierarchy transfer from the molecular levels to microscopic scales requires resorting to physical means, in addition to chemical approaches [12]. Therefore, theory and simulation have been used to deepen our understanding of the polymer hierarchical microstructures, which have the advantages of (a) reducing the burdens from synthesizing complex copolymers,

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(b) gaining information that is difficult to be obtained in the experiments, and (c) predicting new hierarchical structures and unknown properties. The theory and simulation methods widely employed in studying the phase behaviors of polymers include self-consistent field theory (SCFT) [13–19], dissipative particle dynamics (DPD) simulation [20–24], Brownian dynamics (BD) simulation [25–27], and so on.

The remainder of this feature article is organized as follows. In Section 2, we review the hierarchical microstructures self-assembled from the copolymer systems in bulk. In Section 3, we present some recent advances in the hierarchical microstructures assembled in dilute solutions. In both sections, a discussion of the mechanisms behind the formation of hierarchical microstructures is presented. In the final section, we make an attempt to point some future directions for the further development of polymer hierarchical microstructures.

2. Bulk hierarchical microstructures self-assembled from copolymer systems

One principle for designing hierarchical microstructures is to utilize systems with more than two incompatible polymeric blocks. In these systems, the multiple blocks are phase-separated into multiple substructures in an integrated structure, resulting in hierarchical microstructures with multiple length scales. The formation of such kinds of structures is usually dominated by the interaction enthalpy. In these designs, macrophase separation is prohibited by introducing covalent/non-covalent bonding interactions between different blocks. In addition, the polymer systems with no more than two components are also capable of self-assembling into hierarchical microstructures, through elegantly designing the polymer architectures such as two-component multiblock copolymers with various block lengths. In these systems, the interaction enthalpy is no longer the dominant role. The conformational entropy, however, governs the formation of the hierarchical microstructures. The content in this section is organized into three subsections, including multi-component terpolymer systems, multi-component supramolecular systems, and entropy-dominated two-component systems.

2.1. Terpolymer systems

One of the well-known systems for generating hierarchical microstructures is so-called multiblock copolymer, such as ABC-terpolymer and $A(BC)_n/A(BC)_nBA$ multiblock copolymer. The ABC-terpolymers, bearing three different incompatible blocks, are the simplest yet important candidates for forming hierarchical microstructures. In terms of the relative interaction strengths between three blocks, the linear ABC-terpolymers are classified into "non-frustrated" and "frustrated" cases [28]. In non-frustrated cases, the interaction strength between two endblocks is comparable to or higher than those between the neighboring blocks. Due to the non-connectivity between the A- and C-endblocks, the A- and C-blocks are completely separated, and the formation of A/C interfaces is inhibitive. This results in core–shell or alternative hierarchical microstructures, where the substructures are arranged along the linear topology of the terpolymers [29–32].

While in the frustrated cases, the interaction strength between two endblocks is much smaller than those between other blocks, and thus the A/C contact is favored. Since the formation of A/C interfaces is not commensurate with the linear topology of ABC-terpolymers, the hierarchical microstructures formed at this case are frustrated but elegant [33–38]. For example, Li et al. have explored various frustrated microstructures from the linear ABC-terpolymer systems, using the SCFT [39,40]. These

microstructures are beyond the structures with C-core-B-shell cylinders in A-matrix, involving quadruple straight cylinders-on-cylinder, triple straight cylinders-on-cylinder, triple helices-on-cylinder, double helices-on-cylinder, single helix-on-cylinder, perforated-lamella-on-cylinder, rings-on-cylinder, and spheres-on-cylinder (Fig. 1). In these structures, the whole molecules form large-length-scale cylindrical structures, whereas the B- and C-blocks form small-length-scale structures such as rings and helices. They indicated that in the parameter space of calculations, the double and triple helical phases are the stable supercylindrical phases and the phases such as single helix-on-cylinder, rings-on-cylinder, and quadruple/triple straight cylinders-on-cylinder are metastable. The formation of the helical phases is induced by the mismatched lengths between the B- and C-cylinders, since screwing B-cylinders around C-core-cylinder with varying pitch angles is an efficient way to adjust this mismatched length ratio. In addition, the introduction of antiferromagnetic chiralities onto neighboring helical supercylinders, *i.e.*, alternative rows of left-handed and right-handed helices, is found to be preferred by the helical phases.

The topology of the ABC-terpolymers is a crucial role in determining the final hierarchical microstructures. In addition to the linear arrangement, the A-, B-, and C-blocks can also be arranged into star-like architectures. Since the three blocks are tethered at one junction point, the A/B, A/C, and B/C interfaces always exist in the microstructures (Fig. 2a). This topological requirement results in hierarchical microstructures with tiling patterns such as Archimedean tiling and quasicrystalline tiling (Fig. 2b) [41–44]. Compared with the frustrated microstructures of linear ABC-terpolymers, the A/C interfaces formed in this case are permanent, and thereby the microstructures obtained from the star ABC-terpolymers are less sensitive to the relative interaction strengths.

To fabricate hierarchical microstructures with more substructures, some researchers have incorporated more BC-blocks into the linear ABC-terpolymers. These types of copolymers are so-called $A(BC)_n/A(BC)_nBA$ multiblock copolymers. Several studies have confirmed that an increase in BC-block number (n) can increase the number of substructures in hierarchical microstructures [45,46]. As shown in Fig. 3, the $A(BC)_nBA$ multiblock copolymers, *i.e.*, P2VP-*b*-(PI-*b*-PS)$_4$-*b*-PI-*b*-P2VP, can form hierarchical lamellae with 5 alternative PI–PS–PI–PS–PI sub-layers. Compared with the three-phase structures of linear ABC-terpolymers, the hierarchical structures formed by $A(BC)_nBA$ multiblock copolymers include more small-length-scale structures with evident scale differences. The $A(BC)_n/A(BC)_nBA$ multiblock copolymer systems can also be divided into "non-frustrated" and "frustrated" cases.

In the non-frustrated cases, namely, the interaction strength between A- and C-blocks is comparable to or higher than those between other blocks, the $A(BC)_n/A(BC)_nBA$ multiblock copolymers are able to self-assemble into hierarchical microstructures with parallel packed substructures, such as parallel spheres-*in*-lamella, parallel cylinders-*in*-lamella, parallel lamellae-*in*-lamella, parallel cylinders-*in*-cylinder, and parallel spheres-*in*-sphere (Fig. 4). In these hierarchical structures, the small-length-scale structures always remain layers, whereas the large-length-scale structures change with A-block lengths. These structures were first observed in the experiments carried out by Matsushita et al. for P2VP-*b*-(PI-*b*-PS)$_4$-*b*-PI-*b*-P2VP or P2VP-*b*-(PS-*b*-PI)$_3$ multiblock copolymers, and further reproduced by the SCFT calculations (Fig. 4) [47,48].

The number of small-length-scale structures in parallel hierarchical microstructures is dependent on either the number of BC-blocks or the interaction strength between A- and BC-blocks. Wang et al. found that the number of substructures increases as the number of BC-blocks or the interaction strength between A- and BC-blocks increases [48]. The latter is consistent with the SCFT results for $A(BC)_nA$ multiblock copolymers [49]. Both the enthalpy