Macromolecules

Volume 40, Number 4 February 20, 2007

Review

Creation of Hierarchically Ordered Nanophase Structures in Block Polymers Having Various Competing Interactions

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Received September 30, 2006; Revised Manuscript Received December 6, 2006

ABSTRACT: Since the beginning of this century, new polymer morphologies beyond the conventional ones have been found in several complex polymer systems. This article summarizes the very recent advances in morphological studies on block copolymer-based multiple component polymer systems that possess characteristic chain connectivity and noncovalent bonding interactions. Among those, three types of multiphase systems are examined here. The first system consists of star-shaped terpolymers of the ABC type, which exhibit several Archimedean tiling structures. The second one is represented by a block copolymer/homopolymer blend or a block copolymer/block copolymer blend with hydrogen-bonding interactions. It has been found these blends also exhibit new mesoscopic tiling structures. The third one is composed of multiblock copolymers and terpolymers. Hierarchical structures having double periodicity have been formulated for sample polymers including block chains with different lengths. These new morphologies arising from intricate molecular design open the door to creation of many new and innovative functional materials.

Introduction

The current era in this new century can be regarded as the fourth generation of advancement of morphological investigations of block copolymers. The first generation occurred in the 1960s and early 1970s, when the first reports of the existence of highly periodic structures for block copolymers in concentrated solution and bulk were published.[1,2] Subsequently, these structures were verified by determination of viscoelastic and thermal properties[3,4] and conclusively confirmed by morphological studies with electron microscopy.[5,6] The concept of morphological transition according to composition was proposed during this period,[7,8] and modern morphological studies continue to be based upon this concept. The second generation occurred during the mid-1970s through the early 1990s, when morphological features were fully investigated both by theoretical[9−11] and experimental studies.[12−14] During this period, physical properties such as phase transition and phase stability were vigorously studied. The order−order phase transition[10,15] or order−disorder transition[10,16] was explored by varying the magnitudes of the interactions under controlled alteration of external conditions such as temperature and/or shear flow. Furthermore, nanophase-separated structures were studied at the molecular level using neutron scattering techniques.[17,18] The third generation occurred during the late 1980s and 1990s when complex new morphologies were identified, some of which included bicontinuous structures for two-component linear[19,20] and star-branched[21] copolymers, an amphiphilic diblock copolymer−aluminosilicate nanocomposite,[22] and tricontinuous structures for three-component linear terpolymers,[23] together with theoretical works using self-consistent-field theory.[24,25] Among these morphologies, linear triblock terpolymers of the

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10.1021/ma062266h CCC: $37.00

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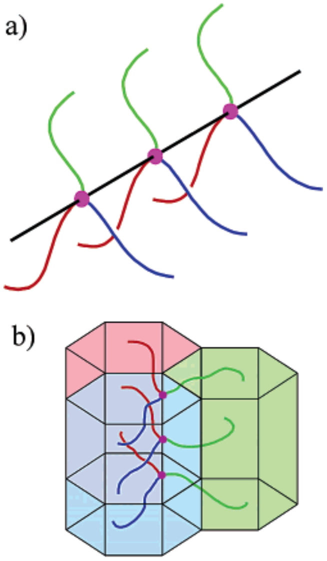

Figure 1. Schematics of (a) one-dimensional alignment of junction points and (b) cylinder-based self-assembly of an ABC star-shaped terpolymer.

ABC type have been extensively studied, and several superlattice structures including tricontinuous gyriod structures were reported.[26−30] In addition to these studies, a series of investigations designed to cover a triangle phase diagram are ongoing.[31] However, it conceived that the creation of more complex and/or hierarchical polymer morphologies is limited if the molecules are restricted to simple and conventional chain connectivity parameters.

Additionally, from a different aspect of polymer morphology, a new molecular design strategy for forming hierarchical domain structures was proposed for a block copolymer/low molecular weight compound, where ionic- and hydrogen-bonding interactions generate between a copolymer component and a low molecular weight compound which serves as the basis for new structures with double periodicity.[32,33]

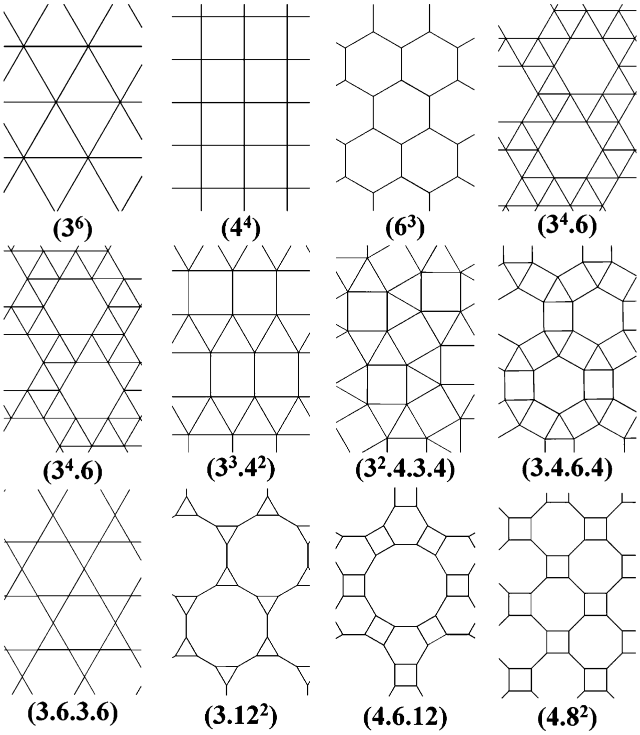

Figure 2. Uniform assembly classes of regular polygons known as the Archimedean tiling patterns. These figures were drawn referring to the original figures shown on p 63 in ref 36.

On this basis, a three-phase polymer system is the principal focus of this report. At least three different chemical/physical interactions compete with one another, making possible the formation of several different hierarchical domain structures. Among several possible architectures, the three systems listed below are the focus of this article, and the recent advances for each system are introduced and insights are provided when appropriate: (1) tiling patterns for star-shaped terpolymers of the ABC type; (2) hierarchical self-assembled patterns for block copolymer blends and block copolymer/low molecular weight compound blends; (3) complex structures with double periodicity for multiblock copolymers and terpolymers with different block lengths.

Tiling Patterns for Star-Shaped Terpolymers of the ABC Type

The molecules of this type are in very constrained states both in solution and particularly in bulk. The multicomponent micelles formed in selective solvents were studied by Lodge et al. recently for many poly(ethylethylene)−poly(ethylene oxide)−poly(perfluoropropylene oxide) terpolymers with different compositions, and several fascinating self-assembled structures were observed by cryomicrotoming/electron microscopy.[34,35]

A striking feature of the phase-separated structures of star-shaped terpolymers in bulk consists in the restricted alignment of their junction points. If three-component polymers are immiscible with one another and are long enough to give stable three-phase structures, the junction points cannot be aligned on two-dimensional planes but must be aligned on lines instead. This limiting condition encourages the formation of two- and three-dimensional structures. In short, if the lengths of three chains of star-shaped molecules are not comparable, they tend to adopt three-dimensional structures. On the contrary, if the lengths of three-component polymers are not apart one another,

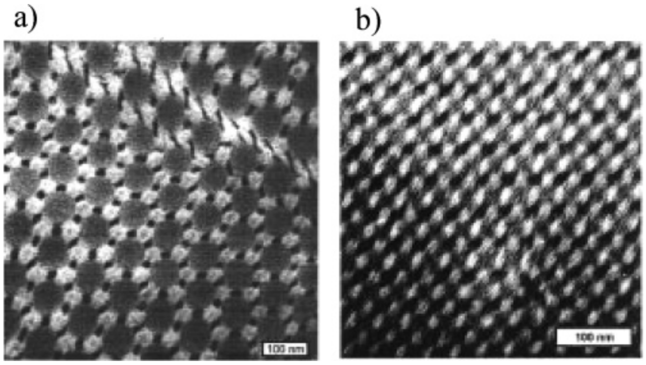

Figure 3. Complex structures for PS−PB−P2VP star terpolymers showing (a) (4.6.12) and (b) (4.8^2) tiling patterns. (The original figures are in ref 39.)

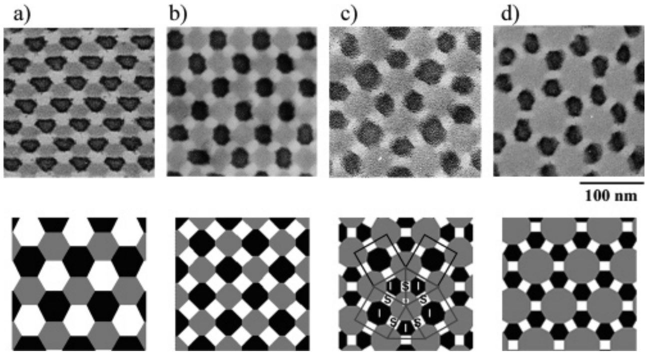

Figure 4. Four Archimedean tiling patterns for $I_{1.0}S_{1.0}P_X$. The structures are assigned as (a) (6^3) (X = 0.7), (b) (4.8^2) (X = 1.2), (c) (3^2.4.3.4) (X = 1.3), and (d) (4.6.12) (X = 1.9).

the molecules choose anisotropic cylinder-based structures, as shown in Figure 1. The cross section of the anisotropic structure adopts two-dimensional tiling patterns with polygonal domains. With regard to assembly of regular polygons, only 12 patterns, which have been designated as Archimedean tiling patterns[36] (Figure 2), are known if only one type of vertex is allowed in each tiling.

Dotera first applied the lattice Monte Carlo simulation to this type of molecule and predicted possible tiling patterns,[37] while Gemma et al. further extended this method and concentrated on a series of molecules of the type $A_{1.0}B_{1.0}C_X$, covering a wide X range and simulated a structural transition with X that included several Archimedean tiling patterns, i.e., (6.6.6), (4.8.8), and (4.6.12), derived under an even polygon theorem.[38]

Archimedean tiling patterns were observed for this class of molecules composed of various components. Hückstädt et al. reported (4.6.12) and (4.8.8) structures for a polystyrene−polybutadiene−poly(2-vinylpyridine) (PS−PB−P2VP) terpolymer as shown in Figure 3,[39] while Sioula et al. observed a (4.6.12) structure for polystyrene−polyisoprene−poly(methyl methacrylate).[40] As typical examples of these systematic experiments,[41,42] Figure 4 compares four kinds of electron micrographs from a star-shaped terpolymer of the type $I_{1.0}S_{1.0}P_x$, where I, S, and P denote polyisoprene, polystyrene, and poly(2-vinylpyridine), respectively. From careful comparison of the images at the bottom in Figure 4 and the patterns in Figure 2, one clearly recognizes that the observed structure includes (6.6.6) (Figure 4a, X = 0.7), (4.8.8) (Figure 4b, X = 1.2), (3.3.4.3.4) (Figure 4c, X = 1.3), and (4.6.12) (Figure 4d, X = 1.9) Archimedean tiling patterns, whose unit cell size is around 100 nm. Among these, the details for the (3.3.4.3.4) structure are described below.[43]

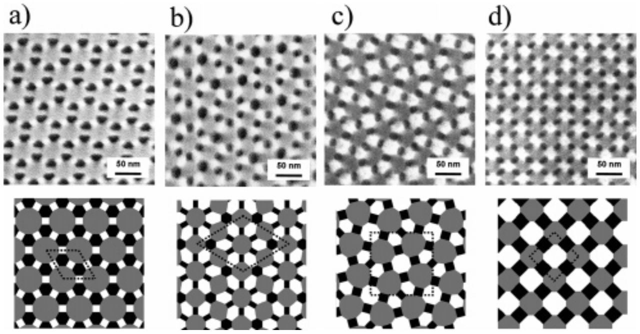

Figure 5. Four Archimedean tiling patterns for $I_{1.0}S_YP_{2.0}$. The structures are assigned as (a) (4.6.12) (Y = 1.3), (b) (3.4.6.4) (Y = 1.8), (c) (3^2.4.3.4) (Y = 2.3), and (d) (4.8^2) (Y = 2.7). The dark, light, and gray regions correspond to I, S, and P phases.

Another series of the type $I_{1.0}S_YP_{2.0}$ was investigated by blending polystyrene and polyisoprene homopolymers with star-shaped terpolymers.[44] The results are summarized in Figure 5 for samples with Y of (a) 1.3, (b) 1.8, (c) 2.3, and (d) 2.7. Figure 5a shows a (4.6.12) pattern, while Figure 5d indicates a (4.8.8) tiling pattern. The tile assembly manner for Figure 5d is the same as that of Figure 4b, though the roles for the I and S domains are reverse.

Figure 5b for $I_{1.0}S_{1.8}P_{2.0}$ shows a new tiling pattern, where the I chains are distributed into squares and hexagons and the P chains are split into octagons and dodecagons, while the S chains remain in unimodal hexagons. Obviously, direct tiling does not fit to any Archimedean tilings; therefore, skeletal tiling was attempted. By putting a point at every S domain and connecting the points, we have a very interesting assembly composed of triangles, squares, and hexagons as superimposed on the TEM image in Figure 6a. We notice this more complex tiling pattern than those with even polygons, such as (6.6.6) and (4.8.8), can be assigned as (3.4.6.4) assembly pattern, since every vertex is surrounded with triangle−square−hexagon−square, which is one of the Archimedean tilings. Figure 6b shows a very periodic hexagonal X-ray diffraction pattern for this sample, and the repeating distance for a characteristic array of P domains is quantitatively in good agreement with the TEM result in Figure 6a.

Figure 5c for $I_{1.0}S_{2.3}P_{2.0}$ shows another periodic pattern, which has hexagonal and octagonal S domains with squared I domains and decagonal P domains. Figure 7a represents another superimposed tiling on the TEM image displayed in Figure 5c. By putting a point at every center of P domains this time and connecting the points, we have a very interesting assembly of triangles and squares. That is, every vertex is uniquely surrounded by triangle−triangle−square−triangle−square, so that the structure is designated (3.3.4.3.4) or (3^2.4.3.4), which represents one of the Archimedean tiling patterns.[42,44] It should be noted that the triangle/square ratio is exactly 2 for this complex but very periodic structure with its tile size being in the range of ca. 50 nm. Figure 7b expresses an X-ray diffraction intensity map for this polymer sample; among the characteristic 12 diffraction spots, four are {02} and eight are {12}. The magnitudes of scattering vectors for {12} and {02} are $\sqrt{5}$ and $\sqrt{4}$, respectively, and hence three diffractions (12), (02), and $(\bar{1}2)$ are aligned on a straight line.

This tiling pattern has been known to exist in various materials other than polymers such as, for example, the Crom iron alloy system known as the Frank−Kasper phase, which has a characteristic length scale of around 1 nm,[45] and a dendrimer system with a length scale of about 10 nm.[46] Thus, the newly identified mesoscopic (3.3.4.3.4) structure represents an extension for a further scaled-up hierarchical level of the known series. Furthermore, mesoscopic quasicrystals will appear

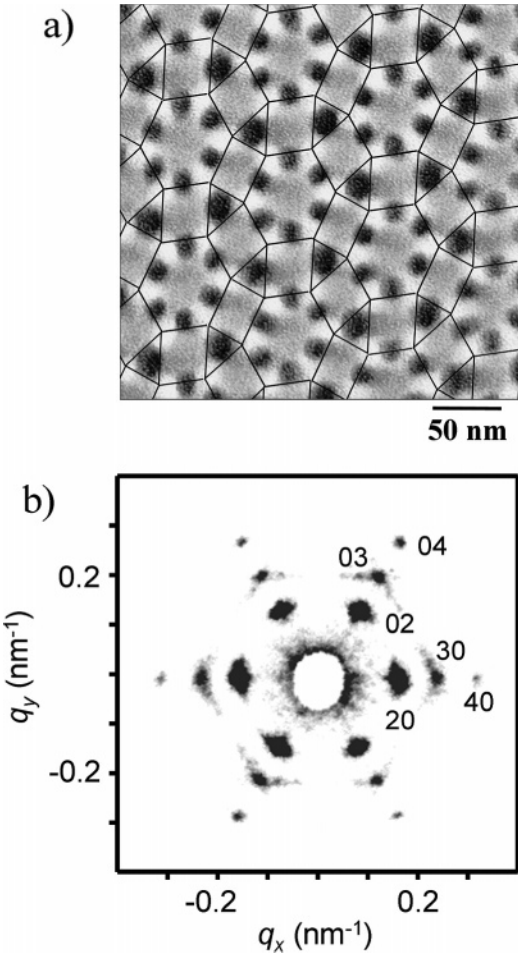

Figure 6. (a) Superimposed (3.4.6.4) tiling pattern on a TEM image for $I_{1.0}S_{1.8}P_{2.0}$ shown in Figure 5b and (b) the corresponding SAXS diffraction pattern.

if the ratio of the triangles to the squares can be increased to $4/\sqrt{3}$ by slight alteration of the composition ratio.[47]

Hierarchical Self-Assembled Patterns for Block Copolymer-Based Blend Systems with Hydrogen-Bonding Interactions

If noncovalent bonded intermolecular interactions are introduced into block copolymer systems, several new classes of self-assembly mechanisms can arise. Hierarchical structure formation with double periodicity was first attempted by ten Brinke et al., who investigated a block copolymer/low molecular weight compound blend system.[32] Figure 8 shows the TEM image which indicates two mesoscopic orders from a pentadecylphenol blend with polystyrene−poly(4-vinylpyridine) block copolymer, whose poly(4-vinylpyridine) block was protonated. This includes a regular lamellar structure for the block copolymer and another in-lamella periodicity, whose stacking direction is perpendicular to the regular lamellar array formed by the suspended compound.

Hogen-Esch et al. investigated the structure of a AB/CD diblock copolymer blend that included a hydrogen-bonding interaction and observed a three-phase structure,[48] while Jiang et al. observed hierarchical structures from a styrene-*block*-butadiene-*block*-*tert*-butyl methacrylate (SBT)/styrene-*block*-2-vinylpyridine,[49] where poly(*tert*-butyl methacrylate) was partially saponificated.

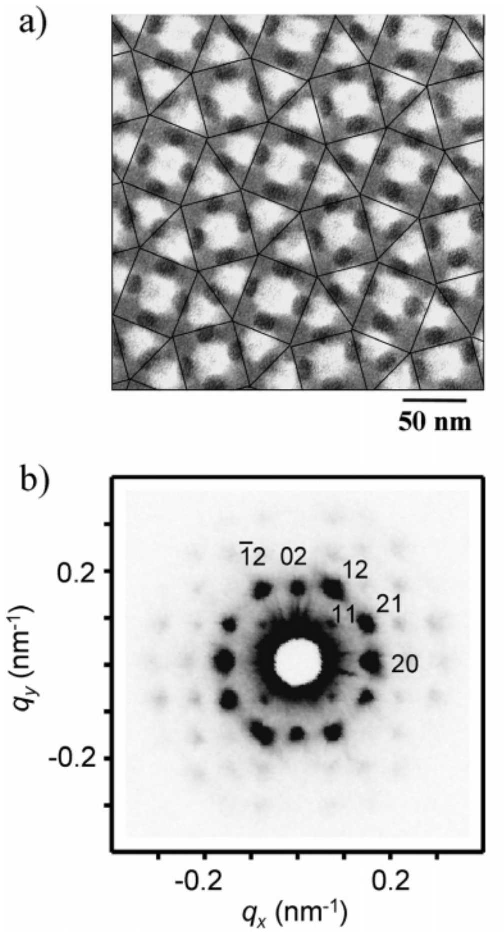

Figure 7. (a) Superimposed (3^2.4.3.4) tiling pattern on a TEM image for $I_{1.0}S_{2.3}P_{2.0}$ shown in Figure 5c and (b) the corresponding SAXS diffraction pattern.

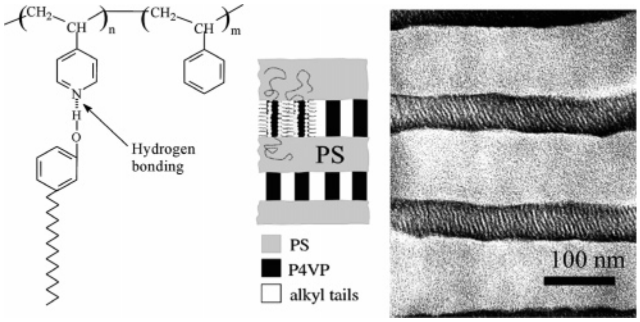

Figure 8. Hierarchical self-assembly of PS−P4VP block copolymer with 3-pentadecylphenol (courtesy of Gerrit ten Brinke, Olli Ikkala, and Janne Ruokolainen).

On the other hand, Asari et al. found that the hydrogen-bonded block copolymer blends exhibit several Archimedean tiling patterns in bulk.[50] Figure 9a shows a TEM image for a IP(ϕ_P = 0.5)/SH(ϕ_H = 0.5) = 1/1 diblock copolymer blend, where H denotes poly(4-hydroxylstyrene), and this polymer and poly(2-vinylpyridine) (P) are known to form a complex by hydrogen bonding. It can be seen in Figure 9a that component P in IP and component H in SH can be mixed into one lamella, while polyisoprene (I) and polystyrene (S) form alternative cylindrical domains. Consequently, a three-phase hierarchical morphology was produced, its two-dimensional space group is assigned to be *c*2*mm*, and this pattern is different from that shown in Figure 8. Figure 9b shows the structure of the

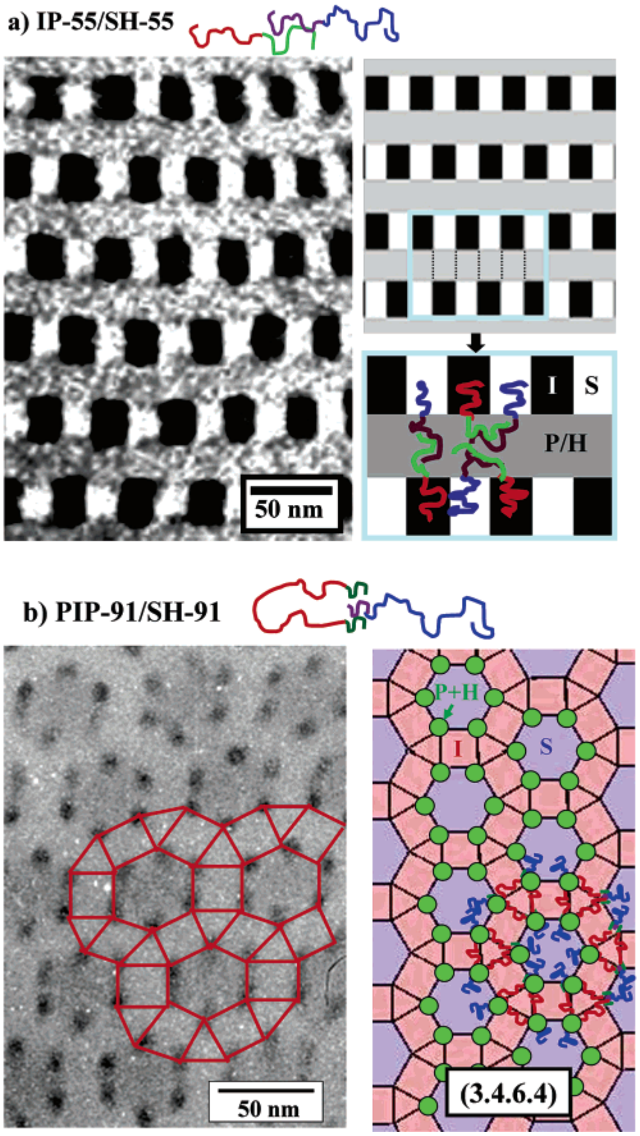

Figure 9. (a) Hierarchical three-phase structure formed by IP(ϕ_P = 0.5)/SH(ϕ_H = 0.5) diblock/diblock copolymer blend at weight ratio of 1/1. The alternating rectangular black and white domains are cylindrical I and S phases, and the third gray domain represents the P/H mixed phase created by hydrogen-bonding interaction. (b) Another three-phase structure formed by PIP(ϕ_P = 0.1)/SH(ϕ_H = 0.1) triblock/diblock copolymer blend at weight ratio of 2/1. The minor component P and H forms one mixed phase, and they are aligned at six vertices of hexagonal S domain surrounded by I domain.

PIP(ϕ_P = 0.1)/SH(ϕ_H = 0.1) = 2/1 blend, which reveals another very interesting tiling pattern as a result of the bridge conformation of the PIP triblock copolymer in the blend. By drawing auxiliary lines as shown in Figure 9b, the skeletal pattern of this sample has been found to have he feature of the (3.4.6.4) Archimedean tiling structure.[51]

Thus, the introduction of ionic- and hydrogen-bonding interactions into the structural formation of block polymers provides a variety of new classes of self-assembling mechanisms of those molecules, which may lead to production of highly functional polymeric materials. For example, this idea can be applied to formation of block polymer/homopolymer blends for production of periodic nanoporous or related hybrid materials for many applications via removal of homopolymers by chemical or physical treatment followed by filling of nanoparticles.

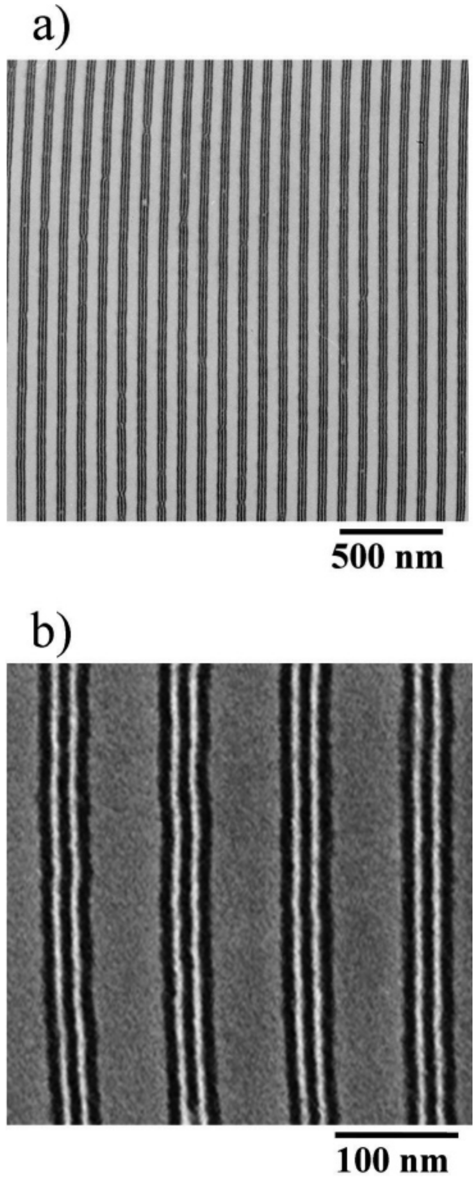

Figure 10. Hierarchical lamellar structure with double periodicity for undecablock terpolymer of the P(IS)$_4$IP type, whose volume fraction of two P end blocks is 0.53. (a) Low-magnification TEM image obtained from an ultrathin section stained with osmium tetroxide and (b) high-magnification TEM image for a section stained with OsO$_4$ and I$_2$ to make clear the intermediate contrast for P phase.

Complex Structures with Double Periodicity for Multiblock Copolymers and Terpolymers with Different Chain Lengths

Studies on two-component multiblock copolymers have been carried out for several purposes. Matsushita et al. observed the n dependence of lamellar domain spacing for the multiblock copolymer of the (IS)$_n$ ($1 < n < 4$) type,[52] while Spontak et al. reported on the n dependence of morphological and elastic properties for (SI)$_n$ copolymers.[53] Furthermore, Wu et al. studied the loop−bridge transition of lamellae forming heptablock copolymers of ISISISI,[54] while the effect of block numbers on the order−disorder transition and viscoelastic properties of linear two-component copolymers of the type S(IS)$_n$ with n up to five was reported.[55] However, all of these studies are merely investigations of the extension of the simple di- and triblock copolymers in terms of chain connectivity.

Alternatively, multiblock polymers composed of blocks with different chain lengths are conceived to give hierarchical structures having multiple periodicity. Bulk structures of an undecablock copolymer of the S(IS)$_4$IS type, whose two end S chains are long and whose remaining nine blocks are short, were investigated, and a hierarchical lamellae-in-lamella structure was observed.[56] Recently, a simulation was carried out for the copolymer of the A(BA)$_n$ type in bulk, whose chain length of each block in multiblock sequence in parentheses is considerably shorter than that of an end A block, and the *n* dependence of the self-assembled structure was argued.[57]

Additionally, three-phase bulk structures of an undecablock terpolymer of the P(IS)$_4$IP type were also examined, as shown in Figure 10.[58] A complex and regular lamellar structure with double periodicity is clearly seen. The long-range order is extremely high, and the repeating unit includes one thick P lamella (gray) and five thin lamellae, three of which are I domains (black) and the remaining two are S domains (white), as clearly shown in Figure 10b. The repeating distances are 16 nm for IS and 88 nm for PISISI. This type of molecular design provides a variety of new domain formation mechanisms, and additional new hierarchical structures will appear in the near future.

In summary, fascinating hierarchical domain structures for three-phase complex polymer systems with competing physical/chemical interactions have been introduced. The proposed molecular systems and future innovations thereof are expected to produce crucially fundamental and practical achievements, examples of which will include the formation of periodic tiling patterns, production of high-performance soft materials such as optical materials, and development of separative applications.

Acknowledgment. The research achievements on the molecular design of complex polymer systems and their hierarchical structures have been attained under the collaboration of the present author (Y.M.) with many co-workers. Y.M. expresses his deep thanks to Prof. A. Takano at Nagoya University for his skilful experiments on sample preparation and morphological observation and also for minute discussions in the course of pursuing researches. Y.M. is grateful to Prof. T. Dotera at Kyoto University for fruitful discussions on structure formation mechanism and the resulting tiling patterns in ABC star-branched terpolymers. He also thanks Prof. G. ten Brinke at University of Groningen for discussions about the structure formation with double periodicity from a mainly theoretical viewpoint. Furthermore, he greatly thanks Drs. T. Asari, A. Noro, and K. Hayashida and Mrs. W. Kawashima, Y. Nagata, and J. Masuda, who were responsible for researches as graduate students at Nagoya University for their hard work.

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MA062266H