Archimedean Tiling Structures from ABA/CD Block Copolymer Blends Having Intermolecular Association with Hydrogen Bonding

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ABSTRACT: Self-assembled phase structures of ABA/CD block copolymer blends were investigated. A pair of poly(2-vinylpyridine-*block*-isoprene-*block*-2-vinylpyridine) (PIP-91) whose molar ratio of polyisoprene and poly(2-vinylpyridine) is 0.93:0.07 and poly(styrene-*block*-4-hydroxystyrene) (SH-91) whose molar ratios is 0.86:0.14 were used as samples. Two component polymers, i.e., poly(2-vinylpyridine) and poly(4-hydroxystyrene), are confirmed to form complex via hydrogen-bonding interaction by ^{1}H nuclear magnetic resonance (NMR) analysis. Structural observation using transmission electron microscopy (TEM) reveals that PIP-91/SH-91 blends form new regular three-phase cylindrical structures having I, S, and P/H phases, the third one being conformed of intermolecular complex from P and H chains. The cross sections of the structures show periodic two-dimensional tiling patterns from regular polygons, which must be due to "bridged" PIP chains. Consequently, new mesoscopic Archimedean tiling patterns, that is, ($3^3.4^2$) and (3.4.6.4), have been formed from this blend system.

Introduction

Block polymers composed of incompatible components are known to be self-assembled to form various microphase-separated structures with repeating period of 10−100 nm in bulk,[1−4] so that they have been paid higher attention as candidates of highly functional materials[5] having ordered structures in mesoscopic scale. Morphological features of several types of block copolymers, such as AB,[6−9] ABA,[10−12] AB_2,[13,14] ABC linear,[15−21] and ABC star-shaped[21−24] molecules, have been investigated extensively so far. Most of the structures observed in those studies consist of thermodynamically stable structures, and they vary their morphological features depending on molecular parameters such as molecular weight, compositions, molecular architecture, and so on. Their mesoscopically periodic structural features were utilized for creation of structure-based materials, such as nanoobjects,[25,26] mesoporous,[27−30] and stimuli-responsive materials.[31,32] From this viewpoint, formation of highly ordered hierarchical structures[33,34] is one of the important aspects to produce the high functional materials. Furthermore, recently several hierarchical structures have been obtained from complex block copolymer systems, i.e., block copolymer blends,[35−38] multiblock polymers,[39] block polymer/surfactant system,[27] and so on. For example, Abets et al. utilized block copolymer blend with miscible block components and observed multiphase superlattice structures.[37]

On the other hand, biological systems were generally built up higher-ordered structures by making use of the several kinds of interactions, that is, ionic, hydrogen-bonding, and hydrophobic interactions. In short, biological supramolecular architectures, such as viruses, proteins, RNAs, and DNAs, were formed by noncovalent interactions. Harmonic acts of several interactions leads to form definite self-assembled structures with various functions in biological systems.[40−45] If we can introduce several interactions into usual block polymer systems, higher-ordered structures will be obtained as the result of new self-assembling manner at different hierarchical level from regular ones.[33] We have already reported on three-phase complex hierarchical structures from AB/CD block copolymer blends[38] having interactive components B and D by selective hydrogen bonding. The idea adopted in that work is useful to give a new morphology control method by introducing peculiar chain assembly manner in addition to conventional one due to intramolecular repulsive interactions between component polymer chains.

Furthermore, intermolecular association via hydrogen bonding between components A and D in an ABA triblock and CD diblock polymer blend system gives various kinds of supramolecular structures since some fractions of ABA molecules adopt bridge conformation. Figure 1 shows the two types of assembling manners, i.e., triangle and square patterns. The closed loop obtained for ABA/CD block copolymer blend system, whose side length is just one molecular length of ABA molecules owing to the bridged conformation of B chains, could lead to the new assembly of regular polygons, as is shown at the right in Figure 1. Therefore, these polygonal linking units could be the basic frameworks of self-assembled structures when the polymer blends form the nanophase-separated structures. Thus, the ABA/CD system is interesting in the sense that new various self-assembled structures must be formulated from intermoleculer association through the A/D complex due to bridged ABA chains. Consequently, the anisotoropic cylindrical structures will be easily produced, whose cross sections give two-dimensional polygonal tiling patterns; therefore, the investigation of structural analysis is a very attractive theme from the viewpoint of 2D crystallography. In this paper, we report on nanophase-separated structures for ABA/CD polymer blends with A/D complex formation by hydrogen-bonding interaction. Poly(2-vinylpyridine) (P) and poly(4-hydroxystyrene) (H) are known to be good partners for association via hydrogen bonding; therefore, poly(2-vinylpyridine-*block*-isoprene-*block*-2-vinylpyridine) (PIP-91) and poly(styrene-*block*-4-hydroxystyrene) (SH-91) were used as component block copolymers in this work.

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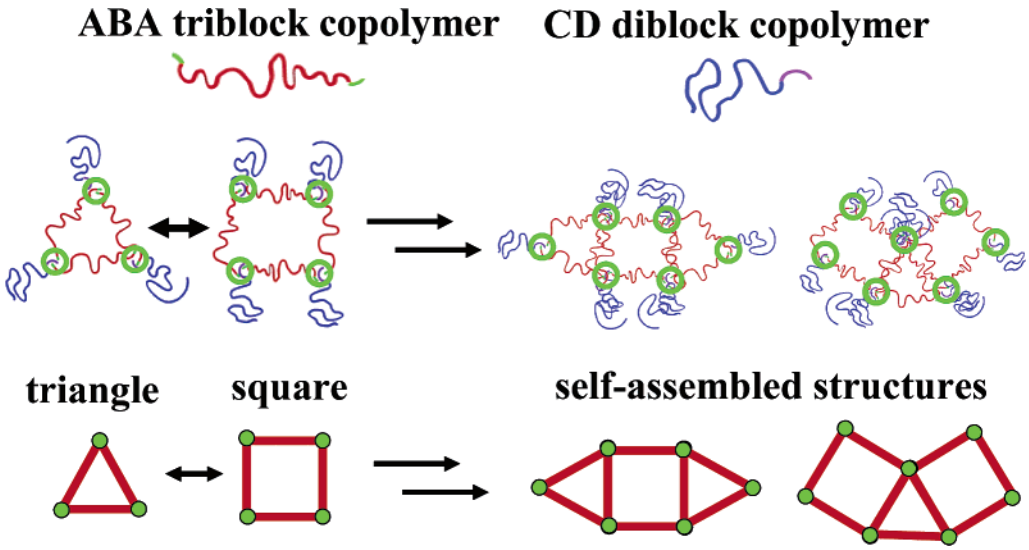

Figure 1. Schematic drawing of two types of self-assembled "closed-loop" structures, i.e., triangle and square, and their assembly.

Table 1. Molecular Characteristics of PIP and SH Block Copolymers

	$M_w \times 10^{-4}$			mole fractions			
polymers	precusors[a]	copolymers[b]	M_w/M_n[c]	I	P	S	H
PIP-91	8.3	9.2	1.04	0.93	0.07		
SH-91	7.7	8.6	1.03			0.86	0.14

[a] Determined by MALLS. [b] Estimated form M_ws of precursors by MALLS and mole fractions by ^{1}H NMR. [c] Estimated by GPC. [d] Calculated from ^{1}H NMR spectra.

Experimental Part

Preparation and Characterization of Block Specimens. Monodisperse poly(2-vinylpyridine-*block*-isoprene-*block*-2-vinylpyridine) (PIP-91) was prepared by a two-step living anionic polymerization in THF using potassium naphthalenide as a bifunctional initiator at −78 °C, whose experimental conditions are exactly the same as reported earlier.[12] Preparation and characterization methods for poly(styrene-*block*-4-*tert*-hydroxystyrene) (SH-91) diblock copolymer were described in a previous paper.[38]

Molecular weights of polyisoprene and polystyrene precursors were measured by a multiangle laser light scattering apparatus, model DOWN-EOS, of Wyatt Technology, in THF at 35 °C. The d*n*/d*c* values measured by an interferometric reflectmeter, OPTILAB DSP, of Wyatt Technology, are 0.126 for polyisoprene and 0.185 for polystyrene in THF at 35 °C. Molecular weight distribution was estimated by gel permeation chromatography using HLC-8020 of TOSOH Corp. with THF as an eluent at 38 °C equipped with three G4000H$_{HR}$ columns of TOSOH Corp. About 2 wt % tetramethylethylenediamine was added to THF to avoid adsorption of poly(2-vinylpyridine) block on polystyrene gel. ^{1}H NMR analysis was carried out to determine the composition of the block copolymers using a Varian INOVA 500 MHz. Solvents used are tetrahydrofuran-d_8 (THF-d_8) for PIP-91 and mixed solvent of $CDCl_3$ and dimethyl-d_6 sulfoxide for SH-91. Total molecular weights of block copolymers were estimated by using M_w's for precursors and mole fractions thus determined. Table 1 summarizes the evaluated molecular characteristics of PIP-91 and SH-91 block copolymers.

Preparations of Blend Films and Morphological Observations. For the film preparation, 5 wt % THF stock solutions of PIP triblock copolymer and SH-91 block copolymer were separately prepared. Blend thin films were made by solvent casting from the mixture of these solutions. Appropriate amount of these solutions were added to the Teflon Petri dishes and evaporated for 1 day, followed by drying for another day in a vacuum oven. All the dried sample films were transparent. To estimate the hydrogen-bonding association in the solvent casting process of blend samples, ^{1}H NMR experiments were carried out at 20 °C, where tetrahydrofuran-d_8 (THF-d_8) was used as a solvent. The chemical shifts were referred to the solvent peak of CH_2Cl_2 at 5.5 ppm.

Blend sample films obtained by solvent casting and annealing were cut into ultrathin sections with thickness of ca. 50 nm by an ultramicrotome, Ultracut UCT of LEICA. The sections were stained with OsO_4 for 1 h and I_2 for 10 min. Nanophase-separated structures were observed by a transmission electron microscope (TEM), H-800, of Hitachi under an acceleration voltage of 100 kV. It is known from our experience for several simple cases that I, P, H, and S show deep, intermediate, light, and very light contrasts, respectively, by OsO_4 staining, while the P domain is selectively stained with I_2.

Results

First, the association behavior of the PIP-91/SH-91 blend system in THF solution was examined. It is known that associative two polymer blends such as P and H spontaneously produce stoichiometric complexation between two chemical speices in solutions.[46] According to this chemical feature, the present polymer blends form associated structures in solution, and the structures could be kept even in bulk state.

Figure 2 compares the ^{1}H NMR spectra from a triblock copolymer, PIP-91, a diblock copolymer SH-91, and their blends at several compositions. In their blends the hydroxyl peak at 7.85 ppm shows a downfield shift and line broadning with decreasing the fraction of SH chains, which is attributed to the hydrogen bonding between a nitrogen atom on a pyridine ring for P and a hydrogen atom on a hydroxyl unit for H. Additionally, a proton resonance on a pyridine unit shifts slightly to upfield with increasing the fraction of SH chains, indicating the difference in chemical environment in THF-d_8. Thus, association behavior between P and H components was detected clearly for this blend in solution.

Figure 3 compares the bright field TEM images of PIP-91/SH-91 = 1/1 diblock copolymer blend. A typical image for the sample film stained with OsO_4 is shown in Figure 3a, where two contrasts can be conceived and the structure looks like a simple alternating lamellar one. On the contrary, Figure 3b

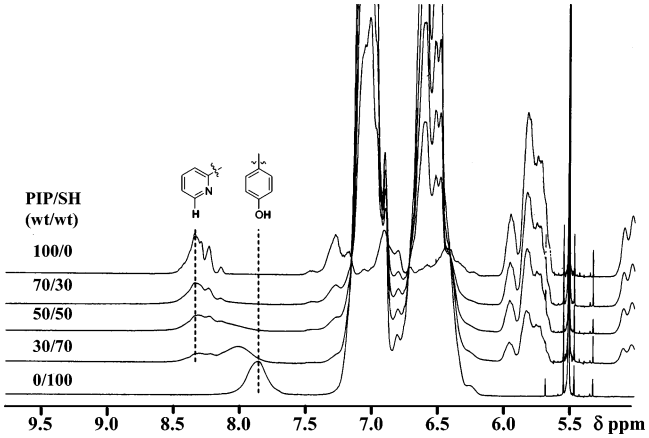

Figure 2. ^{1}H NMR spectra of PIP-91, SH-91, and their blends at several compositions in THF-d_8. The native positions of the pyridyl proton for PIP-91 triblock polymer and hydroxyl proton peak for SH-91 were designated as dotted lines to make clear the peak shifts and the peak broadening by hydrogen bonding.

shows a TEM image from the same sample but stained with I_2. It is clearly shown that the isolated cylinders are emerged in between lamellar layers, indicating that P blocks are included in the intermediate minor phase, in contrast to the simple lamellar-like structure in Figure 3a. However, it should be noted that the periodic lamellar length of ca. 55 nm is apparently shorter than that for IP/SH diblock copolymer blend with almost the same molecular weight.[38] Therefore, it can be assumed that the block copolymer chains for the present blend system have different conformation in the lamellar domains from those of the IP/SH system. That is, I chains in the PIP-91/SH-91 blend should possess bridge-type or loop-type conformations in three-phase structure, while I and S chains are elongated from P/H associated microdomain with tail-type conformation. Moreover, as is shown in a square drawn at the center of Figure 3b, a pair of P/H mixed domains, which sandwich I and S lamellar domains, are located at the same height, while two adjacent pairs are positioned at the different height so as to repel each other.

Another interesting cylindrical structure was obtained for the blend with different mixing ratio. Figure 4a shows the TEM image from the blend of PIP-91/SH-91 = 2/1 stained with OsO_4. It is apparent that hexagonal domains, which must be cross sections of cylinders, are packed hexagonally, whose domain shape is quite unusual. The area ratio of dark region for I chains to the bright region for the other three components in Figure 4a is 1.7, and this ratio is quite consistent with the volume fraction ratio of I/(S + P +H) = 1.6 for the present blend. Figure 4b shows the TEM image from the same sample but stained with I_2. In this image, all the vertices of the hexagonal cylinders are occupied by the minor third phase, which must be P/H mixed domain. We are convinced that the hexagonally packed hexagonal cylinders resulted from the new self-assembled manner generated for the present blend system. The other packing pattern based on rhombuses was also observed for the same blend; however, it only fills a small fraction.

Discussion

As was mentioned in the Introduction, the ABA/CD block copolymer blends might form polygonal closed-loop structures via intermolecular association having bridged ABA chains. The resulting self-assembled structures in the condensed system could be cylinder-based ones. Therefore, several tiling patterns such as the cross sections of packed cylinders can be easily observed by TEM experiments. The most regular two-dimensional tiling manner must be 11 Archimedean tiling patterns with equilateral regular polygons, as is shown in Figure 5.[24] We will discuss the observed structures in relation with these regular polygonal tilings in this paper.

A part of the TEM image for PIP-91/SH-91 = 1/1 in Figure 3b is enlarged and displayed in Figure 6a. By connecting P/H mixed phases, red auxiliary lines are partly drawn to make clear the domain packing manner, resulting in the combination of squares and triangles. Here, it should be noted that a side of square is about 30 nm, which is a little larger than the unperturbed end-to-end distance of the bridged polyisoprene middle block chain in the PIP-91 triblock copolymer. The unperturbed end-to-end distance of polyisoprene chain of the present copolymer whose molecular weight is 82K was estimated to be 21 nm using the experimentally observed segment length, 0.60 nm, for polyisoprene with vinyl side chains predominantly.[47] Thus, it was confirmed that intermolecular association as was anticipated previously has taken place for the present blend, resulting in forming closed loops. The

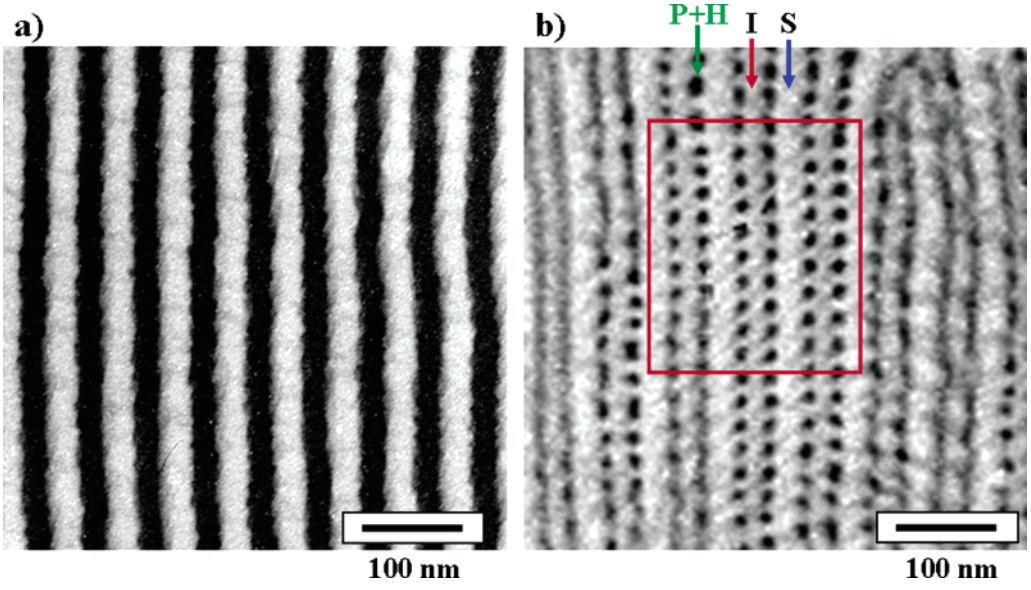

Figure 3. TEM images of PIP-91/SH-91 = 1/1 blend. Sample specimens were stained with (a) OsO_4 and with (b) I_2.

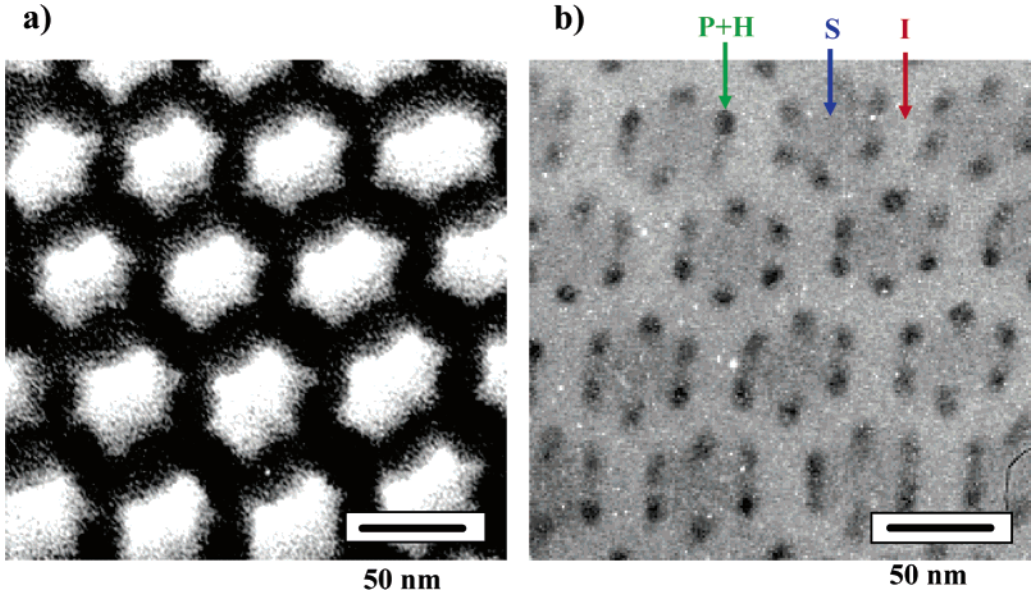

Figure 4. TEM images of PIP-91/SH-91 = 2/1 blend. Sample specimens were stained with (a) OsO_4 and with (b) I_2.

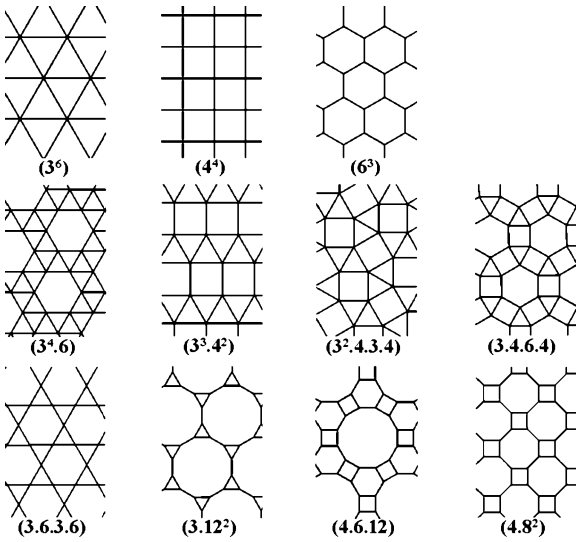

Figure 5. (a) The known 11 Archimedean tiling patterns. The common feature of there tilings is the tessellation of regular polygons provided that all the vertices are under the same environment.

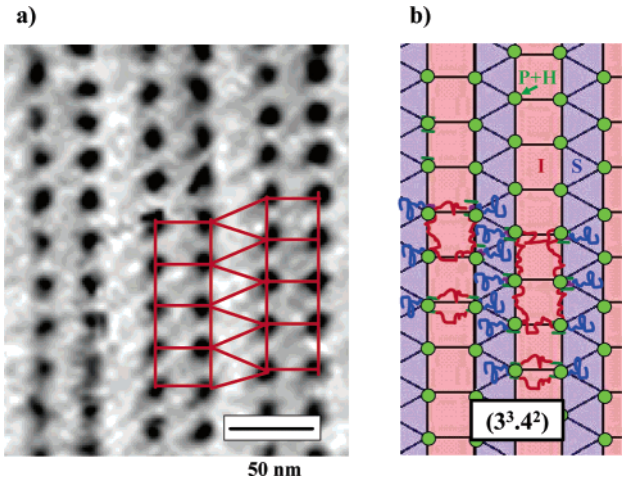

Figure 6. (a) An enlarged TEM image of PIP-91/SH-91 = 1/1 blend. Auxiliary red lines are partly drawn to make clear the domain packing manner. (b) Schematic drawing of a microdomain assembly for the corresponding blend observed in (a); it represents the $(3^3.4^2)$ Archimedean tiling pattern.

microdomain arrangement of this blend is schematically drawn in Figure 6b, and partitions of two component polymer chains are also displayed. In the structure P and H chains can be mixed into one minor phase designated as green circles, whereas I and S chains are both self-assembled individually to form two lamellar domains. By carefully comparing this tiling manner and those of the Archimedean tilings in Figure 5, we notice that the tiling in Figure 6b corresponds to the $(3^3.4^2)$ tiling structure, where every green domains are surrounded by three triangles and two squares. Thus, it is concluded that PIP-91/SH-91 = 1/1 blend show unique cylindrical structure whose cross section has the feature of the $(3^3.4^2)$ Archimedean tiling, though nanosize domains are deformed and triangles and squares are not quite regular.

A part of the TEM image for PIP-91/SH-91 = 2/1 in Figure 4b is enlarged and displayed in Figure 7a. Similarly to the case of Figure 6a, by connecting P/H mixed phases, which stayed on the vertices of hexagons, auxiliary red lines are again partly drawn in Figure 7a. The typical length of red lines in I phase is about 30 nm, which is the same length as that of a square observed in the lamellar structure for PIP-91/SH-91 = 1/1. Therefore, this length can be conceived as a common characteristic length of closed loops, whose side length is associated with the end-to-end distance of the bridged I chain of PIP triblock copolymer in these blends. Thus, it was confirmed that the common intermolecular association manner of two block copolymers essentially defines the peculiar cylinder-based nanophase-separated structures irrespective of the blend ratio.

The microdomain arrangement for this structure is schematically drawn in Figure 7b, and partitions of two block copolymers are also displayed. P and H chains can be mixed into one minor phase designated as green circles as was the case for PIP-91/SH-91 = 1/1. Here, I and S chains are both self-assembled individually to form two phases with no chemical junction points between them. Namely, S chains form the hexagonal cylinder-like domains surrounded by continuous cylinder-shell-like I domains from excessive PIP chains. This packing manner is quite reasonable considering double excess amount of triblock copolymer chains. Comparing this tiling manner and Archimedean tiling patterns again, we notice the tiling in Figure 7b corresponds to the (3.4.6.4) tiling structure, where every green domain is surrounded by one triangle, two squares from I phase, and

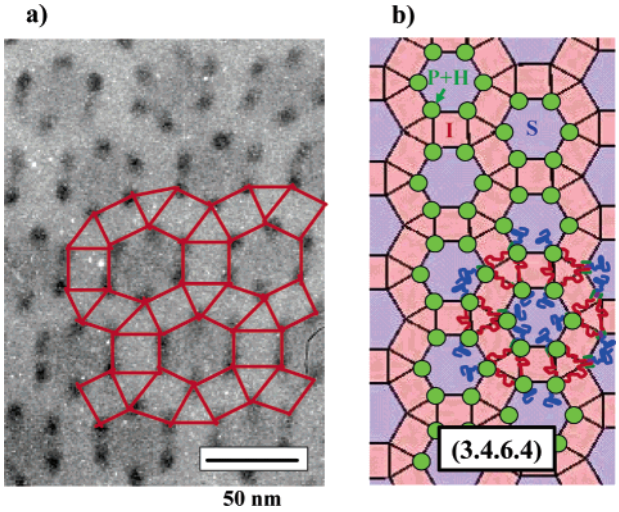

Figure 7. (a) An enlarged TEM image of PIP-91/SH-91 = 2/1 blend. Auxiliary lines are partly drawn to make clear the domain packing manner, where I phase is constructed with the combination of squares and triangles and S phase gives the hexagons. (b) Schematic drawing of a microdomain assembly for the corresponding blend observed in (a); it represents the (3.4.6.4) Archimedean tiling.

one hexagon from S phase. Therefore, it is concluded that PIP-91/SH-91 = 2/1 blend shows another cylindrical structure whose cross section has the feature of the (3.4.6.4) Archimedean tiling pattern with mesoscopic length scale. The same kind of tiling pattern was observed for a triblock terpolymer of the ABC type[48] and a star-shaped terpolymer of the ABC type;[49] however, the structure observed in the present study is new in the sense that the minor domain locates at all the vertices of hexagons.

Recently, ABC-star terpolymers composed of I, S, and P have been confirmed to show various Archimedean tiling structures.[22−24] In the case of ABC-star terpolymer, since there is a topological restriction that linking points have to be aligned on a line, it strongly leads to the cylinder-based three-phase structures. In contrast, the present blend system observed includes two different interactions: one is a repulsive interaction between block chains in molecules, and the other one is an attractive one between polymer chains in different molecules. Consequently, the associative polymers tend to give a mixed single phase, and this phase behaves as "giant" junction points for the native copolymers, resulting in the formation of cylinder-like structures. This must be the reason for observation of new mesoscopic Archimedean tiling structures, and the molecular design adopted in this work will present a new category of morphology design.

Conclusion

Bulk morphologies of symmetric and asymmetric ABA/CD block polymer blends were studied and compared. From the morphological observation for these blends, P chains and H chains can be mixed into one phase in bulk. The blending of block polymers being capable of intermolecular hydrogen bonding interaction is a novel method to give highly ordered cylinder-based structures. It has been found that the hierarchical structural formation is strongly regulated with the bridged conformation of a B block chain in an ABA triblock copolymer. Namely, the symmetric PIP-91/SH-91 = 1/1 blend exhibits cylinder-in-lamellar three-phase structure whose cross section has the feature of the ($3^3.4^2$) two-dimensional Archimedean tiling pattern, while the asymmetric PIP-91/SH-91 = 2/1 blend shows another peculiar cylindrical three-phase structure with the (3.4.6.4) two-dimensional symmetry. It should be stressed on the fact that the distance between the minor complex domains is about the same for two cases, so that we were able to propose a novel method to create highly ordered hierarchical 2D nanostructures from block polymer blends.

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References and Notes

(1) Matsuo, M.; Ueno, T.; Horino, H.; Chujyo, S.; Asai, H. *Polymer* **1968**, *9*, 425.
(2) Helfand, E.; Tagami, Y. *J. Chem. Phys.* **1972**, *56*, 3592.
(3) Lodge, T. P. *Macromol. Chem. Phys.* **2003**, *204*, 265.
(4) Ruzette, A. V.; Leibler, L. *Nat. Mater.* **2005**, *4*, 19.
(5) Forster, S.; Plantenberg, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 689.
(6) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(7) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.
(8) Inoue, T.; Soen, T.; Hashimoto, T.; Kawai, H. *J. Polym. Sci., Part A-2* **1969**, *7*, 1283.
(9) Matsushita, Y.; Mori, K.; Mogi, Y.; Saguchi, R.; Noda, I.; Nagasawa, M.; Chang, T.; Glinka, C. J.; Han C. C. *Macromolecules* **1990**, *23*, 4387.
(10) Richards, R. W.; Thomason, J. L. *Macromolecules* **1983**, *16*, 982.
(11) Matsushita, Y.; Nomura, M.; Watanabe, J.; Mogi, Y.; Noda, I.; Imai, M. *Macromolecules* **1995**, *28*, 6007.
(12) Noro, A.; Iinuma, M.; Suzuki, J.; Takano, A.; Matsushita, Y. *Macromolecules* **2004**, *37*, 3804.
(13) Matsushita, Y.; Momose, H.; Yoshida, Y.; Noda, I. *Polmyer* **1997**, *38*, 149.
(14) Matsushita, Y. *J. Phys. Soc. Jpn.* **1996**, *65* (Suppl. A), 119.
(15) Mogi, Y.; Kotsuji, H.; Kaneko, Y.; Mori, K.; Matsushita, Y.; Noda, I. *Macromolecules* **1992**, *25*, 5408.
(16) Nakazawa, H.; Ohta, T. *Macromolecules* **1993**, *26*, 5503.
(17) Suzuki, J.; Seki, M.; Matsushita, Y. *J. Chem. Phys.* **2000**, *112*, 4862.
(18) Stadler, R.; Auschra, C.; Beckmann, J.; Krappe, U.; Voigt-Martin, I.; Leibler, L. *Macromolecules* **1995**, *28*, 3080.
(19) Matsen, M. W. *J. Chem. Phys.* **1998**, *108*, 785.
(20) Jiang, S. M.; Gopfert, A.; Abetz, V. *Macromolecules* **2003**, *36*, 6171.
(21) Hadjichristidis, N.; Itatrou, H.; Pitsikalis, M.; Pispas, S.; Avgeropoulos. A. *Prog. Polym. Sci.* **2005**, 30, 725.
(22) Yamauchi, K.; Takahashi, K.; Hasegawa, H.; Iatrou, H.; Hadjichristidis, N.; Kaneko, T.; Nishikawa, Y.; Jinnai, H.; Matsui, T.; Nishioka, H.; Shimizu; M.; Furukawa, H. *Macromolecules* **2003**, *36*, 6962.
(23) Takano, A.; Wada, S.; Sato, S.; Araki, T.; Kazama, T.; Kawahara, S.; Isono, Y.; Ohno, A.; Tanaka, N.; Matsushita, Y. *Macromolecules* **2004**, *37*, 9941.
(24) Takano, A.; Kawashima, W.; Noro, A.; Isono, Y.; Tanaka, N.; Dotera, T.; Matsushita, Y. *J. Polym. Sci., Polym. Phys. Ed.* **2005**, *43*, 2427.
(25) Saito, R. *Macromolecules* **2001**, *34*, 4299.
(26) Ulrich, R.; DuChesne, A.; Templin, M.; Wiesner, U. *Adv. Mater.* **1999**, *11*, 141.
(27) Ikkala, O.; ten Brinke, G. *Chem. Commun.* **2004**, 2131.
(28) Ikkala, O.; ten Brinke, G. *Science* **2002**, *295*, 2407.
(29) Valkama, S.; Ruotsalainen, T.; Kosonen, H.; Ruokolainen, J.; Torkkeli, M.; Serimaa, R.; ten Brinke, G.; Ikkala, O. *Macromolecules* **2003**, *36*, 3986.
(30) Rzayev, J.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2005,** *127*, 13373.
(31) Ruokolainen, J.; Makinen, R.; Torkkeli, M.; Makela, T.; Serimaa, R.; ten Brinke, G.; Ikkala, O. *Science* **1998**, *280*, 557.
(32) Li, M. H.; Keller, P.; Yang, J.; Albouy, P. A. *Adv. Mater.* **2004**, *16*, 1922.
(33) Hecht, S. *Mater. Today* **2005**, *8* (3), 48.
(34) Marsh, G. *Mater. Today* **2005**, *5* (9), 20.
(35) Goldacker, T.; Abetz, V.; Stadler, R.; Erukhimovich, I.; Leibler, L. *Nature (London)* **1999**, *398*, 137.
(36) Goldacker, T.; Abetz, V. *Macromol. Rapid Commun.* **1999**, *20*, 415.
(37) Abetz, V.; Goldacker, T. *Macromol. Rapid Commun.* **2000**, *21*, 16.
(38) Asari, T.; Matsuo, S.; Takano, A.; Matsushita, Y. *Macromolecules*, **2005**, *38*, 8811.
(39) Nagata, Y.; Masuda, J.; Noro, A.; Cho, D.; Takano, A.; Matsushita, Y. *Macromolecules* **2005**, *38*, 10220.
(40) Saenger, W. *Principles of Nucleic Acid Structure;* Springer-Verlag: New York, 1984; Chapter 18.

(41) Bloomfield, V.; Carpenter, I. L. *Polyelectrolytes; Science and Technology;* Hara, M., Ed.; M. Dekker: New York, 1993; pp 77−125.
(42) Chow, C. C.; Bogdan, F. M. *Chem. Rev.* **1997**, *97*, 1489.
(43) Hermann, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 1891.
(44) Houk, K. N.; Leach, A. G.; Kim, S. P.; Zhang, X. *Angew. Chem., Int. Ed.* **2003**, *42*, 4872.
(45) Horne, R. W. In *Molecular Plant Virology*; Davies, J. W., Ed.; CRC: Boca Raton, FL, 1985; Vol. 1, pp 1−41.
(46) Jiang, M.; Li, M.; Xiang, M.; Zhou, H. *Adv. Polym. Sci.* **1999**, *146*, 121.
(47) Takano, A.; et al., manuscript in preparation.
(48) Matsushita, Y.; Yamada, K.; Hattori, T.; Fujimoto, T.; Sawada, Y.; Nagasawa, M.; Matsui, C. *Macromolecules* **1983**, *16*, 10.
(49) Sioula, S.; Hadjichristidis, N.; Thomas, E. L. *Macromolecules* **1998**, *31*, 8429.

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