

AWARD ACCOUNTS

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Precise Molecular Design of Complex Polymers and Morphology Control of Their Hierarchical Multiphase Structures

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This report reviews the recent advances in morphological studies on block copolymer and related multiple component polymer systems that possess characteristic chain connectivity and non-covalent bonding interactions, which were mostly done in our research group. Among many topics, three types of multi-phase systems are picked up and examined in this article. The first system consists of multiblock terpolymers. Hierarchical structures having double periodicity have been formulated for sample polymers including block chains with different lengths. The second one is represented by star-shaped terpolymers of the ABC type, which easily form three-phase cylinder-like structure whose cross sections exhibit periodic tiling structures. They show several Archimedean tilings and one of them forms quasicrystalline tiling with dodecagonal symmetry. The third one is composed of block copolymer/block copolymer blends or a block copolymer/homopolymer blend with hydrogen bonding interactions. It has been found these blends represent very striking phase structures including new mesoscopic tiling structures. These structures with new self-assembly manners due to strategic molecular design open the door to production of many highly functional materials.

KEY WORDS: Block Polymer / Morphology / Hierarchical Structure / Archimedean Tiling / Quasicrystalline Tiling /

Studies on self-assembling structures of block copolymers have started in the 1960s, when the first reports on the discovery of highly periodic structures for block copolymers in bulk and in concentrated solutions were published.^{1,2} Successively, these structures were verified by measurements of viscoelastic and thermal properties^{3,4} and finally observed by morphological studies with electron microscopy.^{5,6} The basic concept of morphological transition with composition was proposed during this period,⁷ since then the concept has been the basis of any morphological studies in block copolymer-based complex systems. Subsequently, started from the 1970s through the early 1990s, morphological features were extensively studied both by theoretical⁸⁻¹⁰ and experimental works.¹¹⁻¹³ During this period, physical aspects of several properties such as phase transition and phase stability were fully focused, where the order-order phase transition^{9,14} or order-disorder transition^{9,15} was investigated by varying the magnitudes of the external field such as shear flow and/or temperature. Moreover, nanophase-separated structures were explored at the molecular level using neutron scattering methods by introducing deuterium labeling technique in this period.^{16,17} The next generation occurred during the late 1980s and 1990s when complex morphologies with periodic surfaces were identified, some of which included bicontinuous structures for two-component linear¹⁸ and star-branched¹⁹ copolymers, as well as tricontinuous structures for three-component linear terpolymers.²⁰ The peculiar morphology for an amphiphilic diblock copolymer-aluminosilicate nanocomposite was

also reported.²¹ Among these, ABC linear terpolymers have been fully investigated and several superlattice structures were found including triply-periodic tricontinuous gyroid.²²⁻²⁴ In addition to these studies a series of experiments designed to cover a triangle phase diagram are still ongoing.²⁵ However, it is evident that the production of new polymer morphologies is limited if the molecular architectures are restricted to conventional chain connectivity parameters.

Multiblock polymers composed of blocks with different chain lengths are conceived to give hierarchical structures with double periodicity. Preliminary, bulk structure of an undecablock copolymer of the S(IS)₄IS type, whose two end S chains are long, and whose remaining nine blocks are short, was examined and a hierarchical lamellae-in-lamella structure was observed, whose repeating unit includes one thick S lamella and three thin lamellae.²⁶ Accordingly, a simulation was carried out for the copolymer of the A(BA)_n type, whose one end A block is long, in bulk and the n-dependence of the self-assembled structure was discussed.²⁷

Star-shaped terpolymers bearing incompatible components inevitably tend to exhibit characteristic three-phase structures due to their restricted constraint in space. Both experimental and theoretical works have been known and mostly cylinder-like structures have been reported, whose results will be described later.

Furthermore, a new molecular design strategy for forming hierarchical domain structures was proposed for a block copolymer/low molecular weight chemical substances, where

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supramolecular interactions generate between a copolymer component and a low molecular weight compound which produces new complex structures.^{28,29}

Under this background, three-phase nanophase-separated structures from three- and four-component polymer systems are the principle attention of this article. Among many architectures adopted, the three systems listed below are the focus of this report and the very recent advances for each system are exhibited.

- 1) Hierarchical structures with double periodicity for multi-block terpolymers with different block lengths.
- 2) Two-dimensional tiling patterns for star-shaped terpolymers of the ABC type -the Archimedean tilings and a dodecagonal quasicrystalline tiling.
- 3) Hierarchical self-assembled patterns for block copolymer blends and block copolymer/homopolymer blends, as a result of hydrogen bonding.

EXPERIMENTAL PROCEDURES

All the polymer samples were synthesized by well-controlled anionic polymerizations carried out under vacuum in sealed glass apparatuses, and hence they were confirmed to be monodisperse in both molecular weight and composition after careful purification. The sample films for morphological observation were obtained by casting solvent from dilute solutions of tetrahydrofuran, which is a common good solvent for all polymer species adopted in this work, followed by drying and annealing at higher temperature than glass transition temperatures of all polymer components. Nanophase-separated structures were observed combining transmission electron microscopy with small angle X-ray scattering. Osmium tetroxide, which stains polyisoprene phase heavily and poly-(2-vinylpyridine) phase moderately, and iodine, which stains P phase selectively, were used as staining agents for the TEM experiments. Two Japanese synchrotron radiation sources, the photon factory at Tsukuba and the SPring-8 facility at Hyogo, were used to pursue X-ray diffraction experiments. Particularly, a micro-beam SAXS apparatus installed at beam line 40XU of SPring-8 was exclusively used to determine tiling characteristics of the sample films with relatively small grains.

Creation of New Self-assembled Structures Due to Innovative Molecular Design

Hierarchical Structures with Double Periodicity for Multi-block Terpolymers with Different Block Lengths. Three phase bulk structures of three undecablock terpolymers of the P(IS)₄IP type and three hexablock terpolymers of the PI(SI)₂I type were observed. It should be noted that the latter are just half size of the formers so that two polymer sets are comparable each other. TEM observation results are compared in Figure 1,³⁰ where the volume fraction of the end block chain(s) is increasing from (a) 0.08 through (f) 0.88. A spherical structure whose spheres(gray) are distributed in lamellar phase-separated S-I matrix as shown in Figure 1(a) ($\phi_P = 0.08$), cylinders are hexagonally embedded in S-I matrix

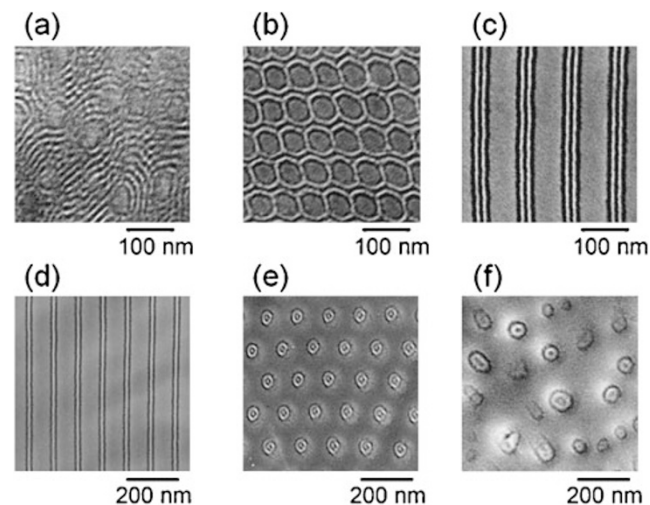


Figure 1. Various morphologies of undecablock terpolymers of the P(IS)₄IP type ((a), (b), (c)) and hexablock terpolymers of the PI(SI)₂I type ((d), (e), (f)). Volume percentages of P component are (a) 8%, (b) 21%, (c) 53%, (d) 64%, (e) 75% and (f) 88%, respectively.

in Figure 1(b) ($\phi_P = 0.21$), while three-phase lamellar structure composed of one thick P lamella and five thin S-I lamellae is shown in Figure 1(c) ($\phi_P = 0.53$). Another lamellar structure with one thick lamella and three thin lamellae is shown in Figure 1(d) for the hexablock terpolymer with ϕ_P of 0.64. Co-axial S-I cylinders in P matrix is shown in Figure 1(e) with ϕ_P of 0.75, while concentric spheres are distributed in P matrix at ϕ_P of 0.88 as shown in Figure 1(f). Thus it was found that all the terpolymers form hierarchical three-phase structures. Overlooking all these structures, one notices that short polyisoprene and polystyrene chains from alternating lamellae, whereas P domain transformed from sphere to cylinder, to lamellae, then eventually turned to be matrix with increasing volume fraction of P domain. In summary, conventional morphology transition is taken place with keeping hierarchical nature.

Among these structures, the highly oriented lamellar structure for the sample with ϕ_P of 0.53 was displayed in Figure 2 to show long range ordering.³¹ The repeating distances are 16 nm for IS and 88 nm for PISISI. It was confirmed that the number of thin lamellae is always kept five, the reason was explained by simply counting the number of possible ways for polymer chains to fill multi-layered structures. In short, the number of possible ways is the largest for five-layered structure over three-, seven- and nine-layered structures. This type of molecular design provides a variety of new domain formation mechanisms.

Two-dimensional Tiling Patterns for Star-shaped Terpolymers of the ABC Type -the Archimedean Tilings and a Dodecagonal Quasicrystalline Tiling. A striking feature of the phase-separated structures of star-shaped terpolymers in bulk consists in the restricted alignment of their junction points in space. If three component polymers are immiscible with one another and are long enough to give stable nanophase-separated structures, the junction points must be aligned on lines in contrast to the

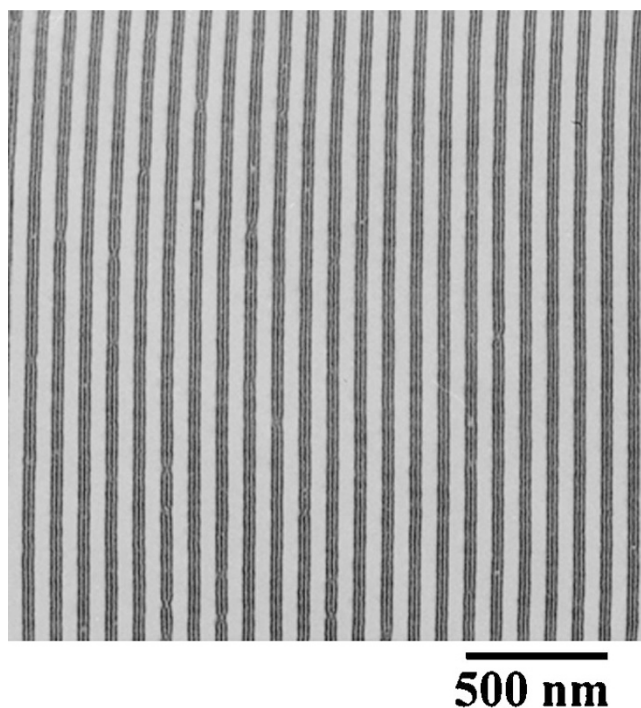


Figure 2. Hierarchical lamellar structure with double periodicity for undeca-block terpolymer of the P(IS)₄IP type, whose volume fraction of two P end blocks is 0.53. An ultrathin section of the samples was stained with osmium tetroxide.

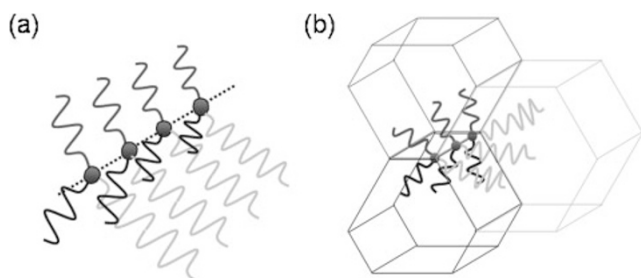


Figure 3. Schematics of a) one-dimensional array of ABC star-shaped terpolymer molecules and b) their self-assembly manner to form a cylinder-like structure.

regular linear block co- and terpolymers whose junction points are always on two- and three-dimensional planes. This limiting condition encourages the formation of anisotropic cylinder-like structures as shown in Figure 3.

The cross-section of the anisotropic structure exhibits two-dimensional tiling patterns with several polygons. Regarding to meeting manners of regular polygons without room, only twelve patterns are known, which have been summarized as the Archimedean tiling patterns³² (Figure 4).

Dotera applied the lattice Monte Carlo simulation to this type of star-shaped molecules and predicted many possible tiling patterns,³³ while Gemma *et al.* further extended this method and predicted the structures for a series of molecules of the type A_{1.0}B_{1.0}C_X, covering a wide X range and found several simpler Archimedean tiling patterns, *i.e.*, (6.6.6),

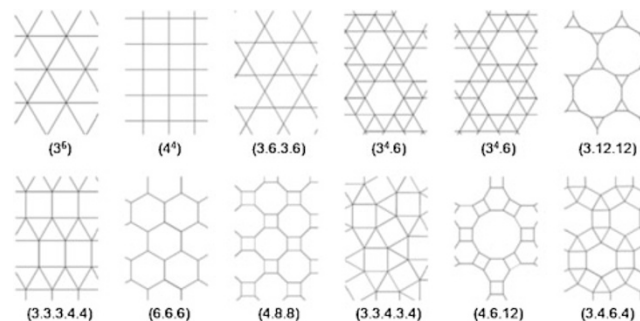


Figure 4. The uniform assembly classes of regular polygons known as the Archimedean tiling patterns (The original figures are seen in p63 in reference 32).

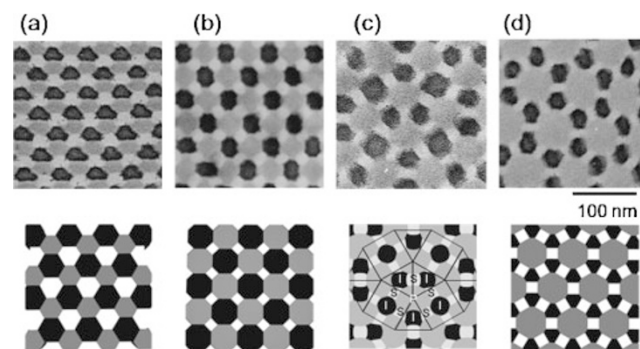


Figure 5. Four Archimedean tiling patterns from terpolymers of the type I_{1,0}S_{1,0}P_X. The structures are assigned as (a) (6³)(X = 0.7), (b) (4.8²)(X = 1.2), (c) (3².4.3.4)(X = 1.3) and (d) (4.6.12)(X = 1.9), respectively.

(4.8.8) and (4.6.12), derived under an even polygon theorem.³⁴ Archimedean tiling patterns were experimentally observed for this type of molecules composed of several polymer components. Hucktadt *et al.* reported (4.6.12) and (4.8.8) structures for a polystyrene-polybutadiene-poly-2-vinylpyridine (PS-PB-P2VP) terpolymer,³⁵ while Sioula *et al.* reported a (4.6.12) structure for polystyrene-polyisoprene-polymethylmethacrylate,³⁶ though systematic study has not been known until recently.

As a typical example of systematic experiments,^{37,38} Figure 5 compares four kinds of electron micrographs from a star-shaped terpolymer of the type I_{1,0}S_{1,0}P_X. I and S arms are common and their molecular weights are 49 k and 45 k, respectively, so that the total molecular weight of terpolymers are all larger than 100 k. From careful comparison of the schematic images at the bottom in Figure 5 and the patterns in Figure 4, one notifies that the observed structure includes (6.6.6) (Figure 5(a), X = 0.7), (4.8.8) (Figure 5(b), X = 1.2), (3.3.4.3.4) (Figure 5(c), X = 1.3) and (4.6.12) (Figure 5(d), X = 1.9) Archimedean tiling patterns, whose unit cell size is in the order of 100 nm. Among these, the features of the (3.3.4.3.4) structure will be described in detail below.^{38,39}

Another example of systematic experiments, Figure 6 compares four kinds of electron micrographs from a terpolymer-based polymer blends of the type, I_{1,0}S_YP_{2,0}, a series of

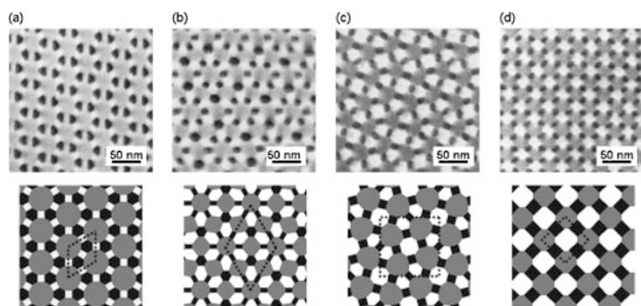


Figure 6. Four Archimedean tiling patterns from terpolymers of the type $I_{1,0}S_Y P_{2,0}$. The structures are assigned as a) (4.6.12)($Y = 1.3$), b) (3.4.6.4)($Y = 1.8$), c) $(3^2.4.3.4)$ ($Y = 2.3$) and d) (4.8^2) ($Y = 2.7$), respectively.

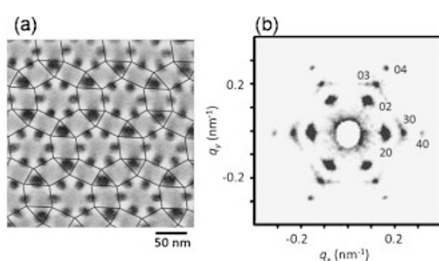


Figure 7. (a) Superimposed (3.4.6.4) tiling pattern on a TEM image for $I_{1,0}S_{1,8}P_{2,0}$ and b) the corresponding SAXS diffraction pattern.

polymers prepared by blending low molecular weight polystyrene(3 k) and polyisoprene(3 k) homopolymers with a star-shaped terpolymer, whose molecular weight is 73.1 k.⁴⁰

Figure 6(a) ($Y = 1.3$) shows a (4.6.12) pattern, while Figure 5(d) ($Y = 2.7$) indicates a (4.8.8) tiling pattern, whose unit cell size is in the order of 50 nm, since the molecular weight of the parent polymer is apparently lower than those of the previous series. The simple and direct tilings are apparently not hold for Figure 6(b) and 6(c), therefore, these structures were analyzed in more detail below.

Figure 6(b) 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. In Figure 7(a) an imaginary tiling was superimposed on the TEM image in Figure 6(b), by putting a point on every S domain and connecting them. 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 which is one of the Archimedean tilings. X-Ray diffraction map is in Figure 7(b), where surprisingly periodic hexagonal pattern is conceived. According to careful analysis, it was found that the repeating distance for a characteristic array of P domains, *ca.* 40 nm, is quantitatively in good agreement with the TEM result in Figure 7(a).

Figure 6(c) 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, whereas P domain is unimodal. In Figure 8(a), an

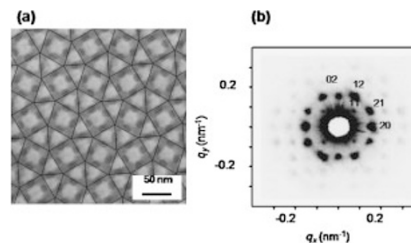


Figure 8. (a) Superimposed $(3^2.4.3.4)$ tiling pattern on a TEM image for $I_{1,0}S_{2,3}P_{2,0}$ and (b) the corresponding SAXS diffraction pattern.

imaginary tiling was superimposed on the TEM image in Figure 6(c). By putting a point at every center of P domain this time and connecting them, we have a very interesting assembly of triangles and squares. That is, every vertex is uniquely surrounded by tri.-tri.-squ.-tri.-squ., so that the structure is designated $(3.3.4.3.4)$ which represents one of the Archimedean tiling patterns.^{38–40} 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 8(b) expresses an X-ray diffraction intensity map for this polymer sample. In this rarely-seen pattern, among the characteristic twelve diffraction spots, four are assigned to be {02} and remaining eight to be {12}. The magnitudes of scattering vectors for {12} and {02} are $\sqrt{5}$ and $\sqrt{4}$, respectively, so that three diffractions (12), (02) and (12) 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 metal alloy system known as the Frank-Kasper phase⁴¹ which has a characteristic length scale of around 0.5 nm,⁴² and a dendrimer system with a length scale of about 10 nm.⁴³ 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.

If we have another viewpoint for this somewhat complex periodic structure, it is known that (3.3.4.3.4) is one of the approximants to a two-dimensional quasicrystalline tiling with doedecagonal symmetry.⁴⁴ Then we explored more detailed region by changing chemical composition of the system. In reality, low molecular weight S and P homopolymers were added some more and had a blend sample with the composition of $I_{1,0}S_{2,7}P_{2,5}$. Figure 9(a) shows a new structure obtained from this sample, where the assembling manner is apparently different from that for (3.3.4.3.4). Imaginary tiling was also added on the TEM image and one recognizes the characteristic six-piece-assembly of triangles distributed randomly, which is one of the important features for quasicrystalline pattern.⁴⁵ Accordingly Figure 9(b) shows SAXS diffracted pattern, which clearly represents twelve equivalent diffracted spots appeared at every 30 deg showing the indispensable feature of doedecagonal quasicrystal. The pattern is not perfect but it also shows higher order peaks and they ensure the quasicrystalline tiling. Figure 10 expresses much wider view of the structure. As we can notice from the superimposed auxiliary lines on the TEM

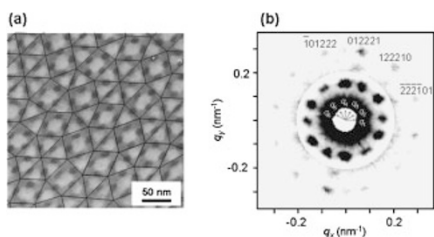


Figure 9. (a) Superimposed quasicrystalline tiling on a TEM image for $I_{1.0}S_{2.7}P_{2.5}$ and (b) the corresponding SAXS pattern with dodecagonal symmetry.

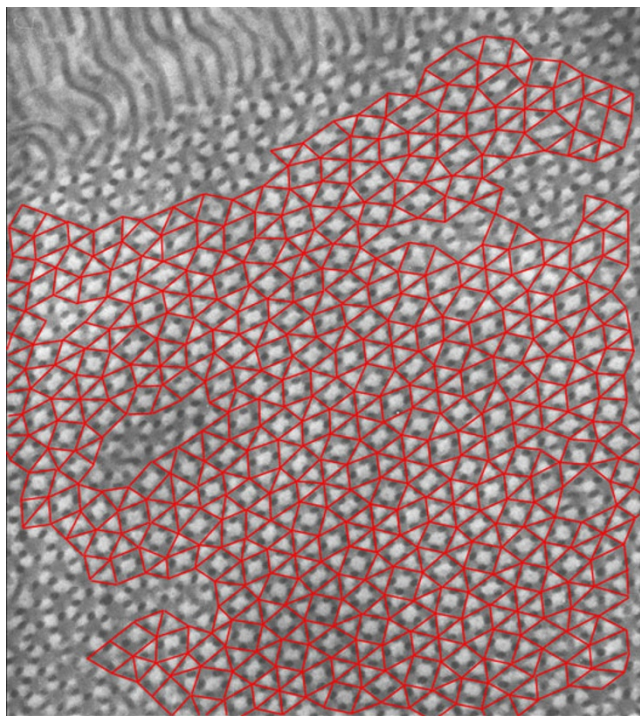


Figure 10. A wide view TEM image and superimposed the triangle-square tiling. The triangle/square number ratio is $461/200 = 2.305$.

image, we can count the number of triangles(461) and squares(200), and their ratio is $461/200 = 2.305$. This value is pretty close to that for the theoretical value of $4/\sqrt{3} = 2.309$, and this agreement is another strong evidence of the quasicrystalline nature of the pattern.

Since the observed triangles and squares are distorted to some extent, the observed pattern in Figure 10 was transcript into a pattern with regular triangles and squares, which is exhibited in Figure 11. Six colored tilings are used for this pattern, they are basically composed of two kinds of approximants. The first one is (3.3.4.3.4) tiling(pink, blown and violet) and the other is 8/3 crystal(yellow and green). The red ones are consecutive squares, which is a possible manner for random tiling, while transition region is in white.

On the whole we can conclude that a quasicrystalline structure has been created from an ABC star-branched terpolymer/homopolymer blend, though it is not a perfect

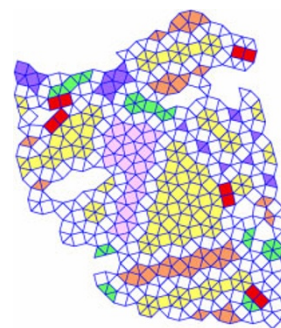


Figure 11. Transcribed schematic tilings from the image in Figure 10. Five crystallographic approximants are identified, three of them(pink, blown and violet) are (3.3.4.3.4) tilings and two of them(yellow and green) are 8/3 crystal.

quasicrystal. The size of the basic unit is approximately 50 nm, whose size is much larger than those of the other materials ever known. Thus the present result indicates the universality of the dodecagonal symmetry, covering a variety of materials such as metal alloys,⁴⁶ chalcogenides⁴⁷ and a liquid crystalline molecule.⁴⁸

Furthermore, hierarchical structures have been found for the same type of star-shaped molecules when the chain length of one component becomes much longer than those of the remaining two components.^{49,50}

Hierarchical Self-assembled Patterns for Block Copolymer Blends and Block Copolymer/Homopolymer Blends. New classes of self-assembly mechanisms can arise if intermolecular interactions besides covalent bonds are introduced into block copolymer systems. Hierarchical structure formation with multiple periodicity was first attempted by ten Brinke *et al.*²⁸ They investigated a block copolymer/low molecular weight compound blend system and observed 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. Hogen-Esch *et al.* investigated the structure of a diblock copolymer/diblock copolymer blend that included a hydrogen bonding interaction and observed a three phase structure,⁵¹ while Jiang *et al.* observed hierarchical structures from a triblock terpolymer/diblock copolymer system, styrene-*block*-butadiene-*block*-*tert*-butylmethacrylate(SBT)/styrene-*block*-2-vinylpyridine,⁵² where poly(*tert*-butylmethacrylate) was partially saponificated.

Asari *et al.* investigated the phase structures of diblock/diblock and triblock/diblock polymer blend systems by utilizing hydrogen bonding interaction between poly(hydroxystyrene) and poly(2-vinylpyridine). Figure 12 compares nanophase-separated structures with/without hydrogen bonding.⁵³ Figure 12(a) expresses the structure of simple blend from poly(isoprene-*block*-2-vinylpyridine)(IP, $\phi_P = 0.1$), and poly(styrene-*block*-4-*tert*-butoxystyrene)(SB, $\phi_B = 0.1$), while Figure 12(b) shows the blend from IP and poly(styrene-

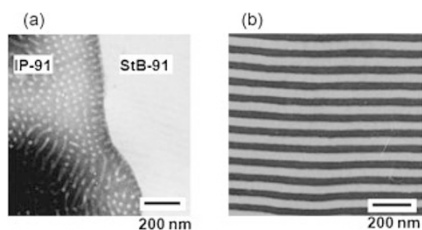


Figure 12. Direct comparison of two copolymer sets with and without hydrogen bonding interaction. (a) The blend of poly(isoprene-*block*-2-vinylpyridine)(IP) and poly(styrene-*block*-4-*tert*-butoxystyrene)(SB) and (b) the blend of IP and poly(styrene-*block*-4-hydroxystyrene)(SH), both cast from dilute solutions.

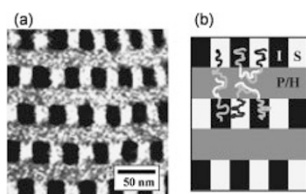


Figure 13. Hierarchical three phase structure formed by IP($\phi_P = 0.5$)/SH($\phi_H = 0.5$) = 1/1 diblock/diblock copolymer blend. (a) Enlarged TEM image of the blend sample. (b) The domain assembly and possible molecular arrangement in this structure.

block-4-hydroxystyrene)(SH, $\phi_H = 0.1$). It is evident from these two figures that Figure 12(a) includes two microphase-separated structures which were naturally produced as the result of macrophase separation between component block polymer chains in solution and successively in bulk, whereas Figure 12(b) shows simple microphase-separated structure. It was confirmed that P/H mixed phase was distributed periodically at lamellar interface as thin cylinders for the latter though TEM images were not shown here. This means P and H components can be mixed into single phase and actually three-phase structure can form from the present four-component polymer system.

On the basis of polymer complex formation ability between P and H treated above, bulk structures of block copolymer/block copolymer blends and block copolymer/homopolymer blends were examined. Figure 13(a) shows a TEM image for a IP($\phi_P = 0.5$)/SH($\phi_H = 0.5$) = 1/1 diblock copolymer blend.⁵⁴ It can be seen in Figure 13(a) 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 cylinders-in-lamella hierarchical morphology was produced. The domain assembly manner was schematically shown in Figure 13(b), where rectangular cylinders from I and S are alternatively aligned in every two lamellae, and furthermore the locations of dark and white regions, that is, I and S domains, are alternative.

Figure 14(a) shows the structure of the PIP($\phi_P = 0.1$)/SH($\phi_H = 0.1$) = 2/1 blend, which reveals doubly periodic cylindrical structures as a result of the bridge conformation of the PIP triblock copolymer in the blend.⁵⁵ That is, P/H mixed

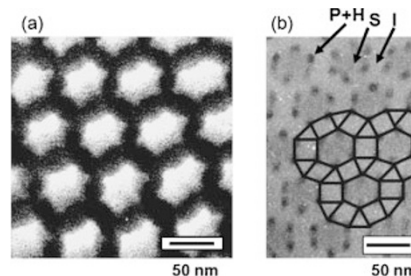


Figure 14. Three phase structure formed by PIP($\phi_P = 0.1$)/SH($\phi_H = 0.1$) = 2/1 triblock/diblock copolymer blend. The sample specimens were stained with (a)OsO₄ and (b)I₂. Comparing two images, it is evident that P and H forms mixed one phase and created thin cylinders(black region in (b)), they are aligned at six vertices of hexagonal S domain(bright region in (a)) surrounded by I domain(dark region in (a)).

phase forms cylinders distributed at six corners of hexagonal S domain in I matrix as clearly shown in Figure 14(b), where sample film was stained with I₂ and hence the contrast of P phase was selectively enhanced. By using auxiliary lines as shown in Figure 14(b), this sample has been found to possess the (3.4.6.4) Archimedean tiling structure.

Furthermore, phase structures of poly(styrene-*block*-2-vinylpyridine)s and H homopolymers are now undergoing, where very interesting phase transition and mixing behavior have been clarifying. This system can be applied to the creation of periodic nano-porous or related hybrid materials for many applications, *via* removal of homopolymers by chemical or physical treatment followed by filling of nano-particles.

In summary the introduction of ionic- and hydrogen bonding interactions into the structural formation of block polymers provides many new classes of self-assembling mechanisms of those molecules, which may lead to production of highly functional soft materials for a variety of use such as optical uses taking advantage of longer periodicity, 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(YM) with many co-workers. YM would like to express his deep thanks to Prof. A. Takano at Nagoya University for daily minute discussion in the course of pursuing researches. YM is grateful to Prof. T. Dotera at Kyoto University for fruitful discussion on structure formation mechanism in ABC star-branched terpolymer systems. He also thanks Prof. G. ten Brinke at University of Groningen for discussion about the hierarchical structure formation. Furthermore he greatly thanks to Drs. T. Asari, A. Noro, K. Hayashida and Mrs. W. Kawashima, Y. Nagata, J. Masuda who were responsible for the researches as graduate students at Nagoya University for their hard and good jobs.

Received: September 11, 2007

Accepted: November 26, 2007

Published: January 17, 2008

REFERENCES

1. A. A. Rembaum, F. R. Eills, R. C. Morrow, and A. V. Tobolsky, *J. Polym. Sci.*, **61**, 155 (1962).
2. A. Skoulios, G. Tsouladze, and E. Franta, *J. Polym. Sci. C.*, **4**, 507 (1963).
3. H. Hendus, K. H. Illers, and E. Ropte, *Kolloid Z. Z. Polym.*, **110**, 216 (1967).
4. M. Matsuo, T. Ueno, H. Horino, S. Chujiyo, and H. Asai, *Polymer*, **9**, 425 (1968).
5. K. Kato, *J. Polym. Sci., Part B: Polym. Lett.*, **4**, 35 (1966).
6. T. Inoue, T. Soen, H. Kawai, M. Fukatsu, and M. Kurata, *J. Polym. Sci., Part B: Polym. Lett.*, **6**, 75 (1968).
7. M. Matsuo, S. Sagae, and H. Asai, *Polymer*, **10**, 79 (1969).
8. H. Helfand, *Macromolecules*, **8**, 552 (1975).
9. L. Leibler, *Macromolecules*, **13**, 1602 (1980).
10. T. Ohta and K. Kawasaki, *Macromolecules*, **19**, 2621 (1986).
11. T. Hashimoto, M. Shibayama, and H. Kauai, *Macromolecules*, **13**, 1237 (1980).
12. R. W. Richard and J. L. Thomason, *Polymer*, **22**, 58 (1981).
13. Y. Matsushita, H. Choshi, T. Fujimoto, and M. Nagasawa, *Macromolecules*, **13**, 1053 (1980).
14. G. H. Fredrickson, *J. Rheol.*, **38**, 1045 (1994).
15. F. S. Bates, J. H. Rosedale, and G. H. Fredrickson, *J. Chem. Phys.*, **92**, 6255 (1990).
16. G. Hadziioannou, C. Picot, A. Skoulios, M.-L. Ionescu, A. Mathis, R. Duplessix, Y. Gallot, and J.-P. Lingelser, *Macromolecules*, **15**, 263 (1982).
17. Y. Matsushita, K. Mori, Y. Mogi, R. Saguchi, I. Noda, M. Nagasawa, T. Chang, C. J. Glinka, and C. C. Han, *Macromolecules*, **23**, 4317 (1990).
18. H. Hasegawa, H. Tanaka, K. Yamasaki, and T. Hashimoto, *Macromolecules*, **20**, 1651 (1987).
19. D. B. Alward, D. J. Kinning, E. L. Thomas, and L. J. Fetters, *Macromolecules*, **19**, 215 (1986).
20. Y. Mogi, K. Mori, Y. Matsushita, and I. Noda, *Macromolecules*, **25**, 5412 (1992).
21. A. C. Finnefrock, R. Ulrich, G. E. S. Toombes, S. M. Gruner, and U. Wiesner, *J. Am. Chem. Soc.*, **125**, 13084 (2003).
22. M. W. Matsen, *J. Chem. Phys.*, **108**, 785 (1998).
23. J. Suzuki, M. Seki, and Y. Matsushita, *J. Chem. Phys.*, **112**, 4862 (2000).
24. V. Abetz and T. Goldacker, *Macromol. Rapid. Commun.*, **21**, 16 (2000).
25. T. H. Epps, E. W. Cochran, T. S. Bailey, R. S. Waletzko, C. M. Hardy, and F. S. Bates, *Macromolecules*, **37**, 8325 (2004).
26. Y. Nagata, J. Masuda, A. Noro, D. Cho, A. Takano, and Y. Matsushita, *Macromolecules*, **38**, 10220 (2005).
27. R. Nap, N. Sushko, I. Erukhimovich, and G. ten Brinke, *Macromolecules*, in press.
28. J. Ruokolainen, R. Mäkinen, M. Torkkeli, T. Makela, R. Serimaa, G. ten Brinke, and O. Ikkala, *Science*, **280**, 557 (1998).
29. R. Nap and G. ten Brinke, *Macromolecules*, **35**, 952 (2002).
30. J. Masuda, A. Takano, Y. Nagata, A. Noro, and Y. Matsushita, *Phys. Rev. Lett.*, **97**, 098301 (2006).
31. J. Masuda, A. Takano, J. Suzuki, Y. Nagata, A. Noro, K. Hayashida, and Y. Matsushita, *Macromolecules*, **40**, 4023 (2007).
32. B. Grünbaum and G. C. Shephard, "Tilings and Patterns" Freeman New York 1986.
33. T. Dotera, *Phys. Rev. Lett.*, **82**, 105 (1999).
34. T. Gemma, A. Hatano, and T. Dotera, *Macromolecules*, **35**, 3225 (2002).
35. H. Hückstädt, A. Göpfert, and V. Abetz, *Macromol. Chem. Phys.*, **201**, 296 (2000).
36. S. Sioula, Y. Tselikas, and N. Hadjichristidis, *Macromolecules*, **30**, 1518 (1997).
37. A. Takano, S. Wada, S. Sato, T. Araki, K. Hirahara, T. Kazama, S. Kawahara, Y. Isono, A. Ohno, N. Tanaka, and Y. Matsushita, *Macromolecules*, **37**, 9941 (2004).
38. A. Takano, W. Kawashima, A. Noro, Y. Isono, N. Tanaka, T. Dotera, and Y. Matsushita, *J. Polym. Sci., Part B: Polym. Phys.*, **43**, 2427 (2005).
39. K. Hayashida, W. Kawashima, A. Takano, Y. Shinohara, Y. Amemiya, Y. Nozue, and Y. Matsushita, *Macromolecules*, **39**, 4869 (2006).
40. K. Hayashida, A. Takano, S. Arai, Y. Shinohara, Y. Amemiya, and Y. Matsushita, *Macromolecules*, **39**, 9402 (2006).
41. F. C. Frank and J. S. Kasper, *Acta Crystallogr.*, **11**, 184 (1958).
42. G. Bergman and D. P. Shoemaker, *Acta Crystallogr.*, **7**, 857 (1954).
43. B. Chen, X. Zeng, U. Baumeister, G. Ungar, and C. Tschierske, *Science*, **307**, 96 (2005).
44. P. Stampfli, *Helv. Phys. Acta.*, **59**, 1260 (1986).
45. K. Hayashida, T. Dotera, A. Takano, and Y. Matsushita, *Phys. Rev. Lett.*, **98**, 195502 (2007).
46. H. Chen, D. X. Li, and K. H. Kuo, *Phys. Rev. Lett.*, **60**, 1645 (1988).
47. M. Conrad, H. Krumeich, and B. Harbrecht, *Angew. Chem., Int. Ed.*, **37**, 1384 (1998).
48. X. Zeng, G. Unger, Y. Liu, V. Percec, A. E. Dulcey, and J. K. Hobbs, *Nature*, **428**, 157 (2004).
49. A. Takano, W. Kawashima, S. Wada, K. Hayashida, S. Sato, K. Hirahara, S. Kawahara, Y. Isono, N. Tanaka, D. Kawaguchi, and Y. Matsushita, *J. Polym. Sci., Part B: Polym. Phys.*, **45**, 2277 (2007).
50. K. Hayashida, A. Takano, N. Tanaka, and Y. Matsushita, *Macromolecules*, **40**, 3695 (2007).
51. J. Pan, M. Chen, W. Warner, M. He, L. Dalton, and T. E. Hogen-Esch, *Macromolecules*, **33**, 7835 (2000).
52. S. M. Jiang, A. Göpfert, and V. Abetz, *Macromolecules*, **36**, 6171 (2003).
53. T. Asari, S. Matsuo, A. Takano, and Y. Matsushita, *Polym. J.*, **38**, 258 (2006).
54. T. Asari, S. Matsuo, A. Takano, and Y. Matsushita, *Macromolecules*, **38**, 8811 (2005).
55. T. Asari, S. Arai, A. Takano, and Y. Matsushita, *Macromolecules*, **39**, 2232 (2006).



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