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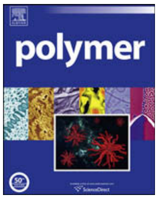

Feature Article

Hierarchical nanophase-separated structures created by precisely-designed polymers with complexity

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ABSTRACT

This review paper summarizes recent advances in self-assembly of complex polymers, focusing on three characteristic polymeric systems. The first is star-branched polymers of the ABC type, the second one consists of multiblock terpolymers with different chain lengths, while the third comprises supramacromolecular assembly systems with hydrogen and ionic bonding interactions between different polymer species. A quasicrystalline tiling structure with mesoscopic length scale has been found for the first star polymer system as well as the periodic Archimedean tiling structures, and moreover three-dimensional Zincblende network structure has been discovered. Furthermore the hierarchical structures having two length scales have been also found for the ABC star molecules whose chain length ratios, that is, A/B and/or A/C are larger than approximately five. Hierarchical structures with double periodicity have been observed for the hexablock and undecablock terpolymers and it has been revealed that their morphology changes systematically depending on composition of polymeric species. Poly(4-hydroxystyrene) (H) homopolymer was found to be dissolved into microdomain of poly(2-vinylpyridine) formed by poly(styrene-*b*-2-vinylpyridine) due to hydrogen bonding interaction, resulting in the origin of morphological transitions depending on the composition of H homopolymer added. Hierarchical structures possessing double periodicity have been found for poly(isoprene-*b*-2-vinylpyridine)/poly(styrene-*b*-4-hydroxystyrene) blends depending on both volume fractions of component polymers and blend ratio. Blends of different homopolymers with several complementary nucleotides or acid/base moieties on chain ends have been confirmed to show nanophase-separated structures as a result of successful formation of “supramacromolecules”.

1. Introduction

Nearly half a century has passed since periodic ordered structure was recognized for block copolymers [1–3]. During this period, a large number of scientific achievements have been accomplished concerning so-called “microphase-separated” structures of block copolymers. The first breakthrough in research was the visualization of phase separation with mesoscopic length scale observed by transmission electron microscopy [4], followed by the elucidation of morphological transitions occurring with composition [5–7]. In 1970s and 80s, quantitative analysis of the self-assembled structures has been carried out intensely, that is, periodic distance has been investigated both theoretically [8–11] and experimentally by use of small angle X-ray scattering technique [12,13]. Furthermore, the phase-separated structure was understood at the molecular level by observing the chain dimension and hence the conformation of individual chain in bulk by use of neutron scattering technique [14–18].

Dynamical features of phase structures were also studied extensively, i.e., phase transition among ordered structures (order–order transition) [10,19] and the order–disorder transition [10,20] behavior have been clarified by controlling the magnitudes of the interactions under variation of external fields such as shear flow and temperature.

In the middle 80s several new structures beyond the classic model were discovered turn by turn [21,22]. Therefore, phase diagram based on the composition of component polymers has been renewed. At the same time, morphologies of the molecules with a little more complex structures such as ABC linear chains [23,24], $(AB)_n$ star-branched chains [25,26], $(AB)_n$ multiblock copolymers [27], etc. have been studied extensively.

In the 21st century, morphological studies on block polymers proceeded into further higher level by designing molecules with more complex architectures. In this article, very recent advances in

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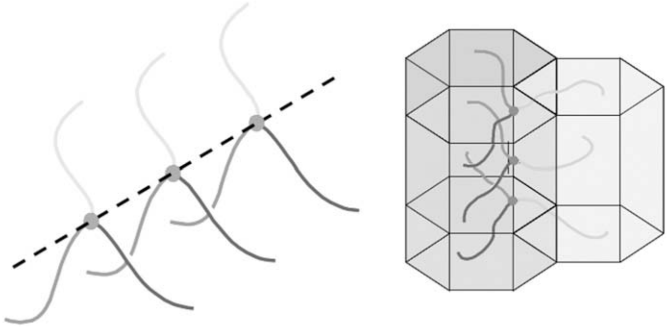


Fig. 1. Self-assembly manner of ABC star molecules.

the study of highly complex structures having characteristic chain connectivity will be presented. After late 90s, the periodic structures with mesoscopic length scale has been perceived to possess "nanoscopic" size, and therefore, the technical word, "nanophase-separated structure" will be used throughout this article instead of traditionally used "microphase-separated structure".

2. Star-branched terpolymers of the ABC type

When incompatible three component polymer chains are tethered at a junction point, the resultant star molecules of the ABC type are in a very frustrated field in bulk. That is, their junction points cannot be aligned on two-dimensional planes but on one-dimensional lines, as schematically shown in Fig. 1. Furthermore, when the chain length difference is not so large, the array of junction points tends to be straight and long one. Consequently each domain with mesoscopic sizes becomes cylinders, and their cross sections could be conformed by polygons [28,29]. This is because three interfaces, A/B, B/C and C/A are likely to be flat since there exist no junction points at interfaces and therefore chain entropy contribution to the free energy of structure formation is considerably small comparing with regular block and graft copolymer systems. As a matter of fact, Dotera predicted several tiling patterns by the diagonal bond method, a new Monte Carlo Simulation [30], while Gemma and Dotera pointed out that only three regular tilings, i.e., (6.6.6), (4.8.8) and (4.6.12) are permitted for three-branched molecules proposed as the "even polygon theorem" [31].

On the other hand, when the chain length difference is large, the junction points can also be easily aligned on curved lines and hence the self-assembled structures are allowed to be two- and three-dimensional periodic patterns. Gemma et al. also carried out the Monte Carlo simulation for a series of molecules of the $A_1B_1C_Z$ type [31]. According to their simulation, several hierarchical complex structures were predicted when Z is both large and small enough, while many tiling structures were assumed when Z is in the vicinity of 1, some of them have been known to have the feature of Archimedean tiling structures composed of regular polygons which are shown in Fig. 2 [32]. Several series of systematic experiments have been done by Matsushita and co-workers for the polymers of $I_XS_YP_Z$, where the components I, S and P denote polyisoprene, polystyrene and poly(2-vinylpyridine), respectively.

2.1. Archimedean tiling structures

Fig. 3 compares four structures for the series of $I_{1.0}S_{1.0}P_Z$ [33,34]. Fig. 3a for $I_{1.0}S_{1.0}P_{0.7}$ is a honeycomb type structure with three-fold symmetry, whose three hexagonal domains are surrounding a vertex. Therefore the structure can be represented as (6.6.6), which is one of the Archimedean tiling structures. Along the same line, Fig. 3b for $I_{1.0}S_{1.0}P_{1.2}$ is expressing (4.8.8) with four-fold symmetry, while Fig. 3d for $I_{1.0}S_{1.0}P_{1.9}$ is showing (4.6.12) with six-fold symmetry.

We can see somewhat more complex structure in Fig. 3c, which is actually binary blend of $I_{1.0}S_{1.0}P_{1.2}$ and $I_{1.0}S_{1.0}P_{1.9}$ and hence gives the average composition of $I_{1.0}S_{1.0}P_{1.3}$ [34]. There are two differently black domains of polyisoprene, therefore, the simple direct tiling is not appropriate for this structure. Then larger triangles and squares are placed on small and large black domains, the resulting structure is regular (3.3.4.3.4) assembly, which is also one of the Archimedean tiling structures as is drawn in Fig. 2. The details of this structure will be discussed in the next paragraph. This structure is complex but still possesses a crystallographic symmetry with a unit cell as given by the white dotted lines as shown at the bottom schematic image in Fig. 3c. The length of side of triangles and squares is about 80 nm, whose size is much longer than the ones ever known in any other materials as will be described in the following section.

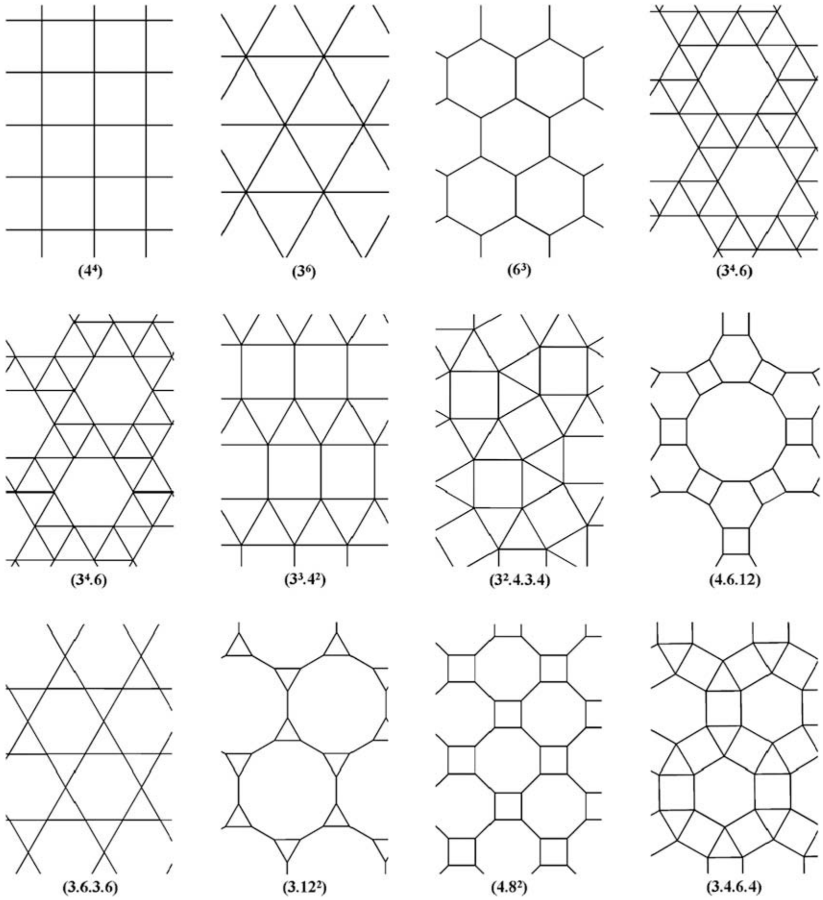
Fig. 4 shows the variation of morphology for another series, $I_{1.0}S_YP_{2.0}$ [35]. It is evident that Fig. 4a for $I_{1.0}S_{1.3}P_{2.0}$ and Fig. 4d for $I_{1.0}S_{2.7}P_{2.0}$ represent (4.6.12) and (4.8.8) tilings, respectively. Alternatively, however, the images in Fig. 4b and c exhibit the more complex tiling patterns. To make clear the tiling pattern for the sample $I_{1.0}S_{2.3}P_{2.0}$ in Fig. 4c, the enlarged image for the same sample is displayed in Fig. 5a. Here we notice that this is another (3.3.4.3.4) structure though the roles of I phase (black) and S phase (white) are different from those in Fig. 3c, namely two kinds of white polystyrene domains can be covered with polygons instead of polyisoprene for Fig. 3c as shown in Fig. 5a. Fig. 5b shows the microbeam SAXS pattern for this sample, which includes characteristic 12 spots arranged at lower q values, four of them belong to {20} group and eight of them to {21} group, their relative distance should be $\sqrt{4}/\sqrt{5}$. It should be noted that the number ratio of triangles/squares is just 2 for this periodic tiling.

2.2. Quasicrystalline tiling with dodecagonal symmetry

The extended experiments were carried out for the same series as in the previous section. Knowing that (3.3.4.3.4) periodic tiling is one of the approximants for quasicrystalline tiling with dodecagonal symmetry, the composition of the sample was varied a little by adding small amount of polystyrene homopolymer with low molecular weight. Fig. 6a shows a TEM image for the sample $I_{1.0}S_{2.7}P_{2.5}$ thus obtained [36]. The tiling manner is obviously different from that in Fig. 5a and we notice that there is six-piece assembly of triangles here and there in Fig. 6a. By careful observation of the TEM image covering a wide area, we have found that the number ratio of triangles/squares increased to approximately 2.31, which is quite close to the theoretically predicted value of $4/\sqrt{3} = 2.309$ [37]. Furthermore Fig. 6b represents a SAXS diffraction pattern for this sample, which includes 12 diffraction spots circularly-distributed at every 30°. This is an essential feature of a quasicrystal with dodecagonal symmetry, though the pattern is not perfect. The length of the sides of polygons is about 50 nm this time, whose length is longer than the values for ever observed quasicrystals in the other materials such as metal alloys (−0.5 nm) [38], chalcogenide (−2 nm) [39] and dendrimer (−10 nm) [40], pointing the hierarchical scale-up among materials.

2.3. Morphology change depending on composition which maintains a hierarchical nature

So far we presented the results on periodic tilings and an aperiodic tiling which has appeared within a relatively narrow composition range. This section deals with the major morphological change caused by large composition variation. Fig. 7



(4^4) (3^6) (6^3) $(3^4.6)$

$(3^4.6)$ $(3^3.4^2)$ $(3^2.4.3.4)$ $(4.6.12)$

$(3.6.3.6)$ (3.12^2) (4.8^2) $(3.4.6.4)$

Fig. 2. 12 Archimedean tiling patterns.

compares TEM images for $I_{1.0}S_{1.8}P_Z$ series with Z in the range $2.9 \leq Z \leq 53$ [41]. Fig. 7a for $I_{1.0}S_{1.8}P_{2.9}$ shows the (4.6.12) Archimedean tiling. Fig. 7b for $I_{1.0}S_{1.8}P_{6.4}$ is a complex lamellar structure composed of I plus S phase and P phase. As we can see at the bottom schematic figure for this morphology, the former lamellae is consisted of hexagonally-packed cylinders of I domain (black) in matrix of S phase (white), and this complex lamella and P lamella can be aligned alternatively.

With further increase of the length of P chain, structure has transferred to cylindrical (Fig. 7c) and spherical (Fig. 7d) morphology whose cylinders and spheres were phase-separated into alternating in-domain lamellae. If we pay attention to P phase in Fig. 7, its shape changes from cylinder (a) to lamella (b), and then to matrix for cylindrical assembly (c) and finally to matrix for spherical morphology (d). This transition manner is basically the same as the systematic transition for AB diblock copolymers, while the difference consists in the fact that hierarchical phase separation is always occurs for the ABC star polymer system.

2.4. *Zincblende type network structure*

We present another interesting network structure obtained for the sample $I_{1.2}S_{2.9}P_{1.0}$ [42]. The TEM images are displayed in Fig. 8, they can be assigned as four-fold [001] (a) and two-fold [011] (b) projections since they were obtained by tilting the sample specimen as much as 45°. Fig. 8c and d shows the simulated images for [100] and [110], and the agreement between a and c and also b and d is excellent. This structure includes single “diamond” network in which spherical I and P phases occupy the positions of tetrahedral centers arranged alternatively in matrix of S phase, resulting in the formation of zincblende type structure (Fig. 8e). The unit cell length of the structure is about 50 nm, which is much longer than the ones ever known for the material systems other than polymers. This structure can be probably formed due to the fact that the magnitude of the interaction between P and I is much larger than those of I–S and S–P, so that these chains are self-assembled to form spherical domains so as to make their contact area as narrow as possible.

3. Multiblock polymer systems

The repeating distance of the self-assembled periodic structures formed by block polymers can be determined by their total chain lengths, whereas the shape of their polymer/polymer interfaces, i.e., morphologies, can simply be controlled by relative chain lengths. This section considers the morphological features of multiblock copolymers and terpolymers composed of block chains with different chain lengths. Hierarchical structures with double periodicity can be anticipated for such multiblock polymers. They also have been studied in the other viewpoint such as rheological aspect [43,44] and theories [45].

3.1. *Comparison of lamellar structures – two component and three component systems*

Morphologies of triblock copolymers of the ABA type have been studied well and the domain period is known to be smaller than that of diblock copolymer with the same molecular weight and composition. If we restrict our argument to lamellar structure, roughly speaking, the domain distance for ABA triblock copolymer

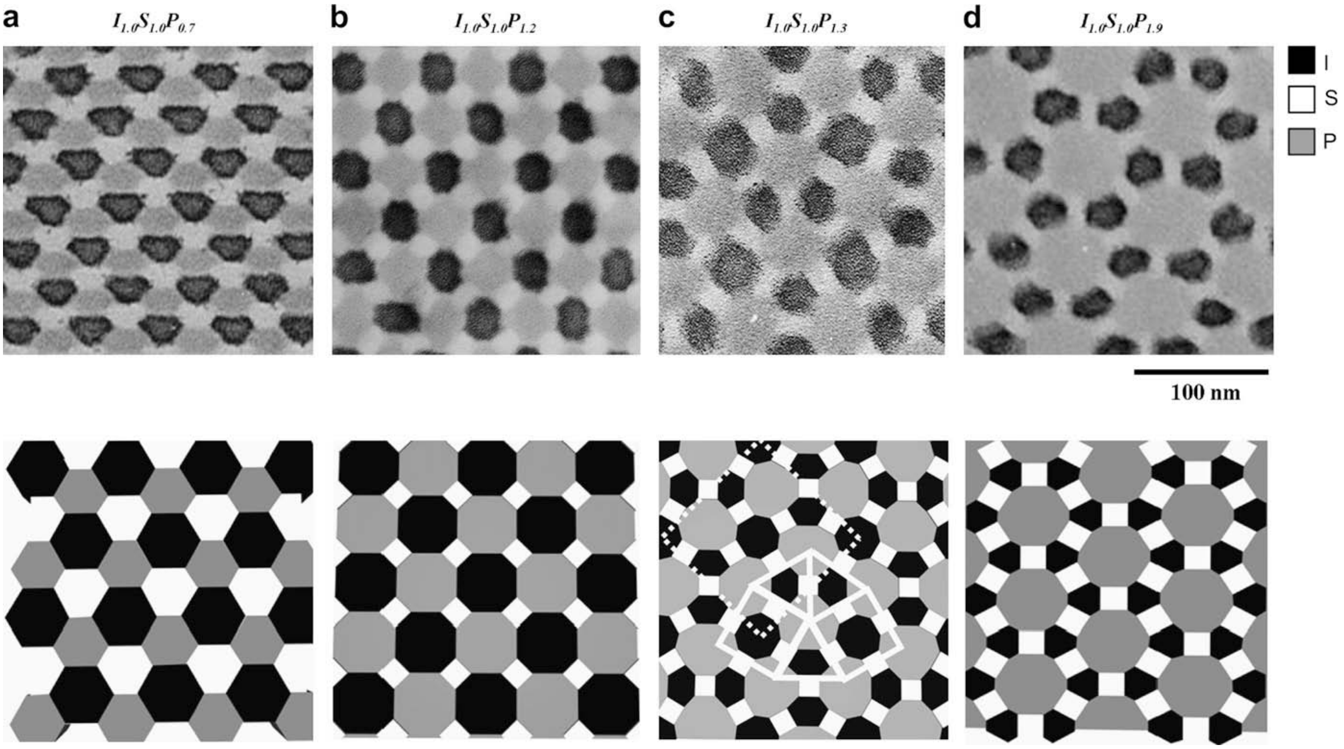


Fig. 3. Tiling patterns for $I_{1.0}S_{1.0}P_Z$. TEM images (top) and the corresponding models (bottom) (*cf*. Refs. [33,34]).

is the same as that of AB diblock copolymer with half molecular weight of ABA [46]. Furthermore, morphological transition with composition is almost the same for both copolymer systems. When the number of block increases with keeping the chain length of each block constant, the tendency of domain size contraction becomes more evident and finally reaches an asymptotic value [27]. However, the domain formation manner turns to be changed if the chain lengths of some particular chains are different from others.

One experiment was carried out by designing and preparing undecablock copolymer of the $S_{(IS)4I}S$ type, where the larger "S"

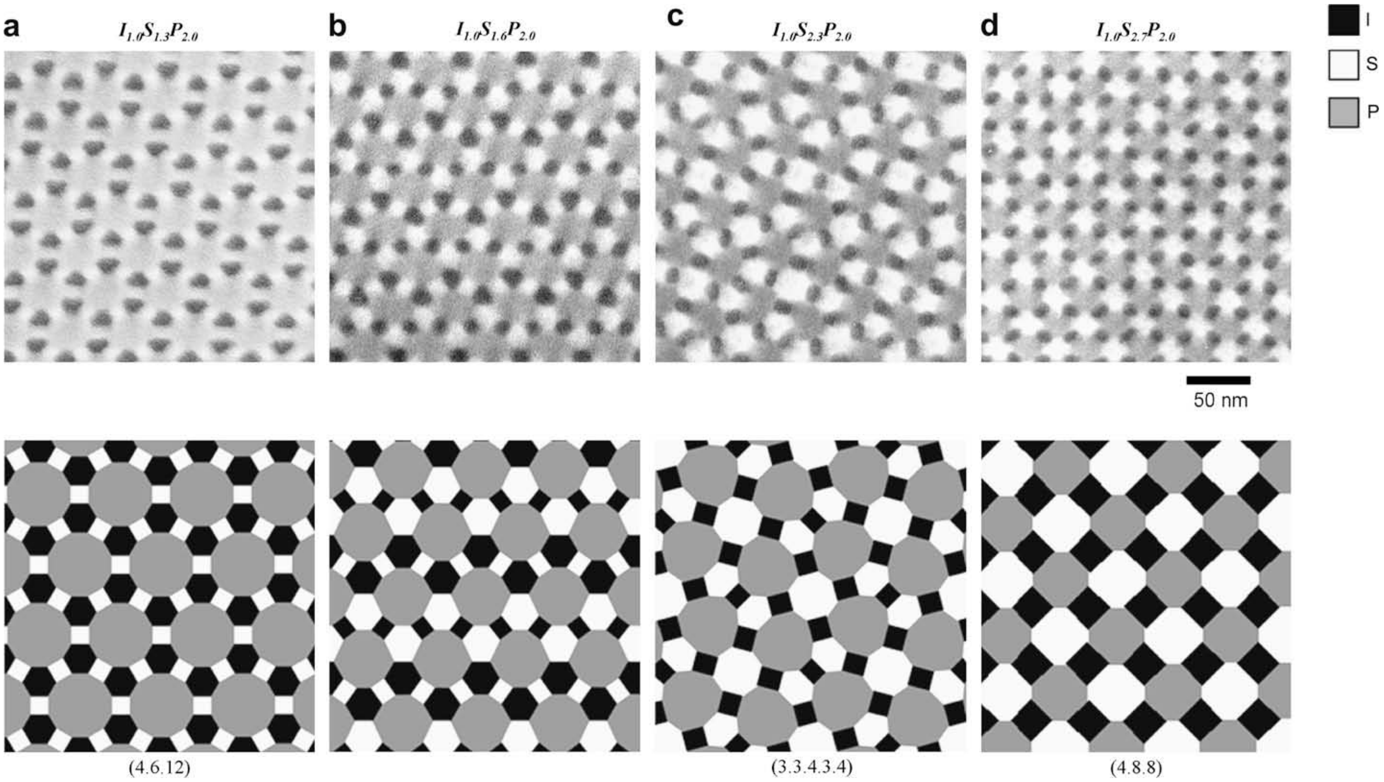


Fig. 4. Tiling patterns for $I_{1.0}S_YP_{2.0}$. TEM images (top) and the corresponding models (bottom). (*cf*. Ref. [35]).

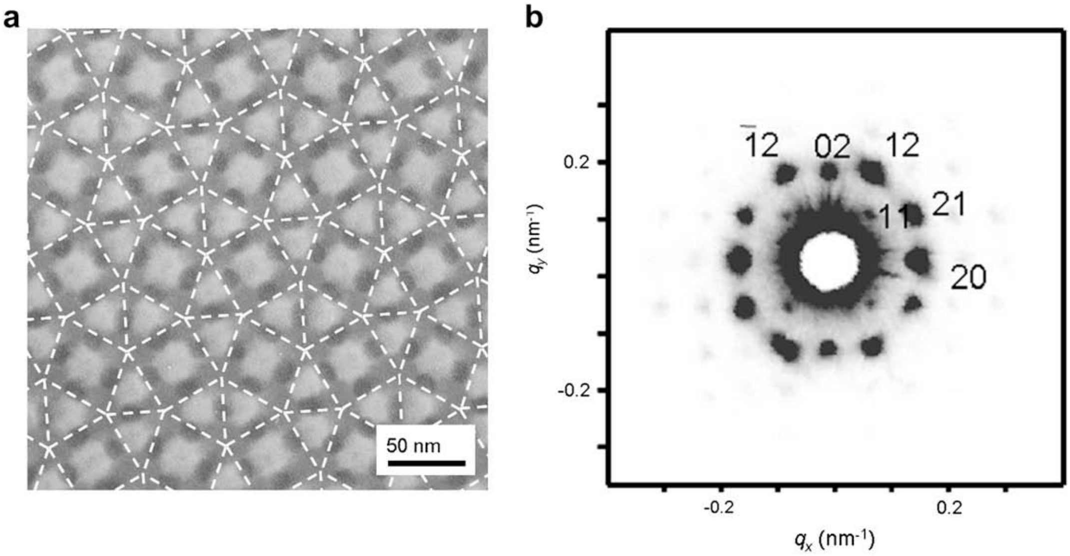


Fig. 5. The (3.3.4.3.4) Archimedean tiling from $I_{1.0}S_{2.3}P_{2.0}$. a) TEM image and b) micro-beam SAXS pattern (*cf.* Ref. [35]).

denotes longer polystyrene chains while the smaller "S" does the shorter chains and I represents polyisoprene [47]. As a result, a hierarchical lamellar structure was observed as shown in Fig. 9a, of which a repeating unit includes a thick white (S) lamella and three thin I–S–I lamellae.

When the third component is introduced, the structure changes dramatically [48]. Fig. 9b shows the periodic lamellar structure from undecablock terpolymer of the P(IS)$_4$IP type, where P denotes poly(2-vinylpyridine) [49]. It should be noted that short nonablock chains at the center is exactly the same as that in two-component S$_{(IS)4I}$S. Domain ordering for terpolymer in Fig. 9b is quite high comparing with that in Fig. 9a, and furthermore the number of thin lamellae within the large repeating distance is increased to five from three. These results are due to the stronger P–I interaction over those of S–I and S–P as discussed in the previous section, and hence it makes the thicker P lamella be a potential wall. Moreover, it was confirmed that five-layered assembly was uniquely observed, while three- and seven-layered structures have never been observed. This experimental result was well explained by the simulation work using self-consistent mean field theory assuming the much stronger interaction parameter, χ_{AB}, for the terpolymer of the type A(BC)$_n$BA over others, i.e., χ_{BC} and χ_{AC} [50].

3.2. Composition dependence

Two series of experiments were designed and carried out to investigate the composition dependent morphological change for multiblock terpolymers [51]. One is the undecablock terpolymer series mentioned partly in the previous section, while the other is the hexablock terpolymers of the P(IS)$_2$I type. One recognizes the former is just the double of the latter in terms of the number of blocks, therefore the morphological transition can be compared along the same line for both series, just as the comparison between ABA triblock and AB diblock.

Fig. 10 compares six TEM images obtained from two series, Fig. 10a–c shows for undecablock series, while Fig. 10d–f shows for hexablock series. Fig. 10a for the sample with ϕ_P of 0.08 gives gray P domain surrounded by alternating S–I lamellae as a matrix, whereas the sample with ϕ_P of 0.21 exhibits a hexagonally-packed

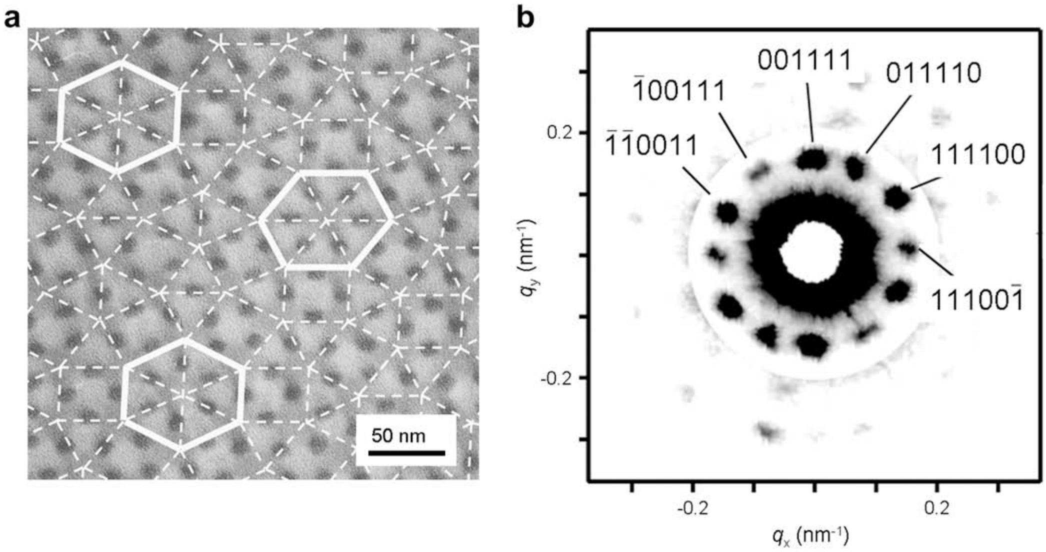


Fig. 6. Quasicrystalline tiling with dodecagonal symmetry from $I_{1.0}S_{2.7}P_{2.5}$. a) TEM image and b) micro-beam SAXS pattern (*cf.* Ref. [36]).

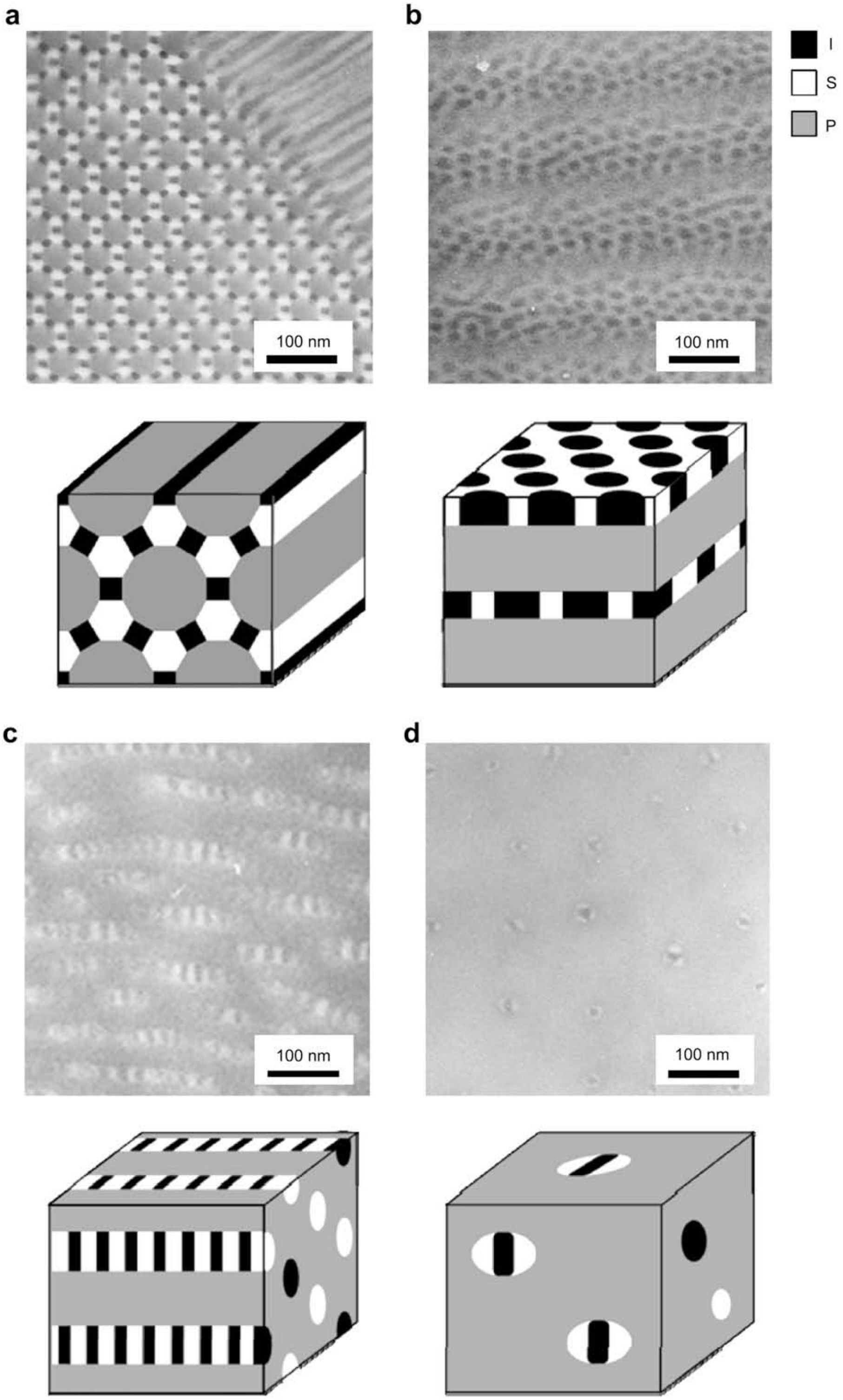


Fig. 7. Hierarchical morphologies formed by ISP star-shaped molecules. (a) $I_1 S_{1.8} P_{2.9}$, (b) $I_1 S_{1.8} P_{6.4}$, (c) $I_1 S_{1.8} P_{12}$, (d) $I_1 S_{1.8} P_{53}$. (*cf.* Ref. [41]).

cylinders of P also surrounded by alternating lamellae as shown in Fig. 10b. Fig. 10c shows essentially the same morphology as that shown in Fig. 9b. Fig. 10d for hexablock terpolymer with ϕ_P of 0.64 is another hierarchical lamellar structure though the number of thin lamellae is decreased to three from five. With further increase of ϕ_P, cylindrical and spherical structures were observed as shown in Fig. 10e and f, where concentric cylinder morphology and spherical one are displayed.

If we survey all the six TEM images, we recognize morphological transition has been taken place with volume fraction of the end block(s), P, just as the transition for simple diblock or triblock copolymers. The only and big difference between multiblock and diblock consists in the fact that the former always keep hierarchical structures due to the strategic molecular design.

Combining the results for ABC star-branched molecules stated in Section 2.4 with the present results, we can conclude the essential

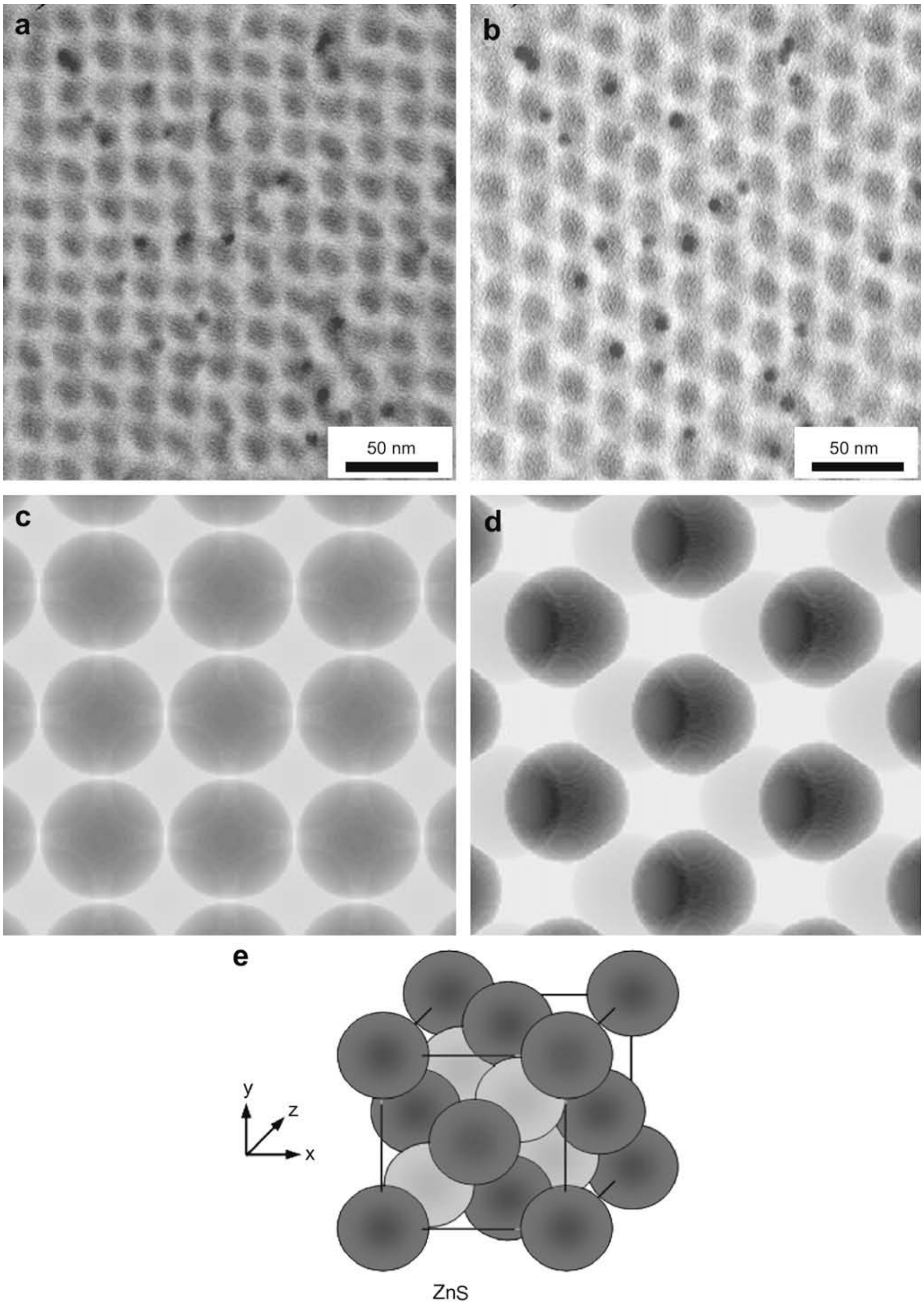


Fig. 8. Comparison of two TEM images for [001] (a) and [011] (b) views of the sample $I_{1.2}S_{2.9}P_{1.0}$. The image in b was obtained by the tilt experiment of the thin section just 45° from that in a. The simulated images for [001] (c) and [011] (d) are assuming the direct contact of spherical I and P domains in matrix of S. (e) ZnS model expressed by two spherical particles having the same volume (*cf.* Ref. [42]).

feature that block polymers tend to keep the universal rule of the morphology transition with composition of components even if the molecular architectures are complex.

4. Supramacromolecular assembly via non-covalent bonding interactions

Different polymer species in block or graft copolymers are normally connected by covalent bonds, and hence most of the bonds are quite stable under various external fields. Then, if non-covalent bonding interactions are introduced to connect chemically and physically different polymer species, a variety of highly complex structures can be created. Many papers on supramolecular assembly are known for block polymer/low molecular weight compound blends [52,53], and also for polymer/polymer with low molecular weight [54,55]. In addition to these, the complex formation from polymer/polymer mixture with relatively high molecular weights by hydrogen bonding interaction has created increasing interest in recent years [56–58]. If the manners of supramacromolecular assembly are once established, we have

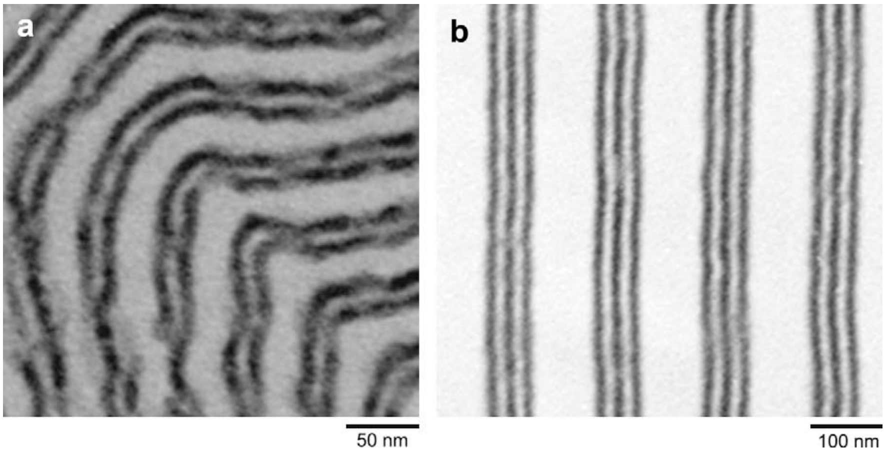


Fig. 9. Two TEM images from undecablock polymers. a) $S_{(IS)4I}S$, b) $P(IS)_4IP$ (*cf.* Refs. [47,49]).

plenty of choices. For example, homopolymer/homopolymer, block polymer/homopolymer and block polymer/block polymer complexes can be produced to give supramacromolecular self-assembled structures as will be introduced below, which can be high-performance complex soft materials. However, the works on AB block polymer/C homopolymer and AB block polymer/CD block polymer [59] are rare so far. Therefore, this section reports on three kinds of complex formation manners by utilizing hydrogen bonding and ionic bonding interactions to produce new supramacromolecular structures.

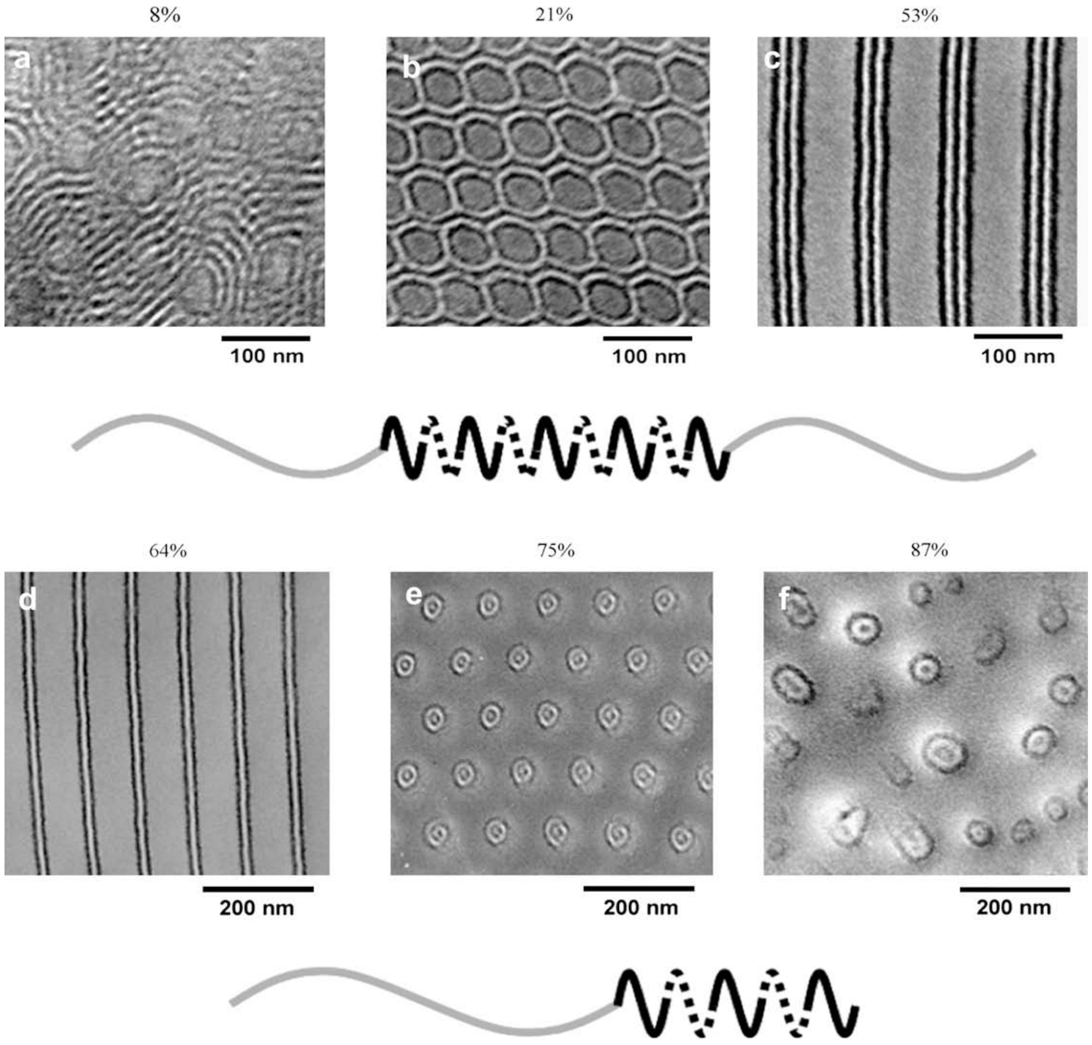


Fig. 10. Composition dependence of three-phase structures of multiblock terpolymers. a)–c) are from undecablock polymers, while d)–f) are from hexablock polymers (*cf.* Ref. [51]).

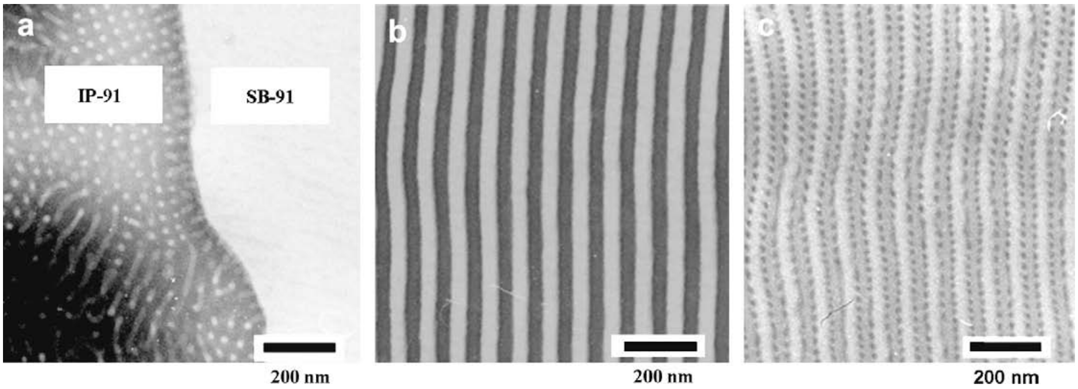


Fig. 11. Block polymer/block polymer blends. a) SB/IP stained with OsO_4, b) SH/IP stained with OsO_4 and c) SH/IP stained with I_2 (*cf.* Ref. [61]).

4.1. Block copolymer/block copolymer association

Poly(4-hydroxystyrene) (H) and poly(2-vinylpyridine) (P) are known to form aggregation in solutions of common good solvents [60]. Tetrahydrofuran (THF) is one of them; H and P mixtures in THF can be easily precipitated, even if polymer concentration is fairly low. Firstly the structure formation of block copolymer I/block copolymer II is presented, where I and II include H and P as each one of the constituents.

Poly(styrene-*b*-4-hydroxystyrene) (SH) and poly(isoprene-*b*-2-vinylpyridine) (IP) were used as two parent block polymers [61]. The former was prepared by the hydrolysis reaction of poly(styrene-*b*-4-*tert*-butoxystyrene) (SB). Fig. 11 compares bulk structures of block copolymer blends to show the distinct effect of this hydrolysis reaction. Fig. 11a shows a bright field TEM image for SB/IP (50/50 by weight) blend, whereas Fig. 11b shows that for SH/IP one, both are obtained for bulk films prepared by solvent casting from THF solutions. The volume fractions of B in SB, and hence H in SH and also P in IP are all approximately 0.1. It is evident that SB and IP are phase-separated macroscopically and form individual nanophase separation structure having spherical morphology (Fig. 11a). On the other hand, SH/IP (50/50) blend looks simple alternating lamellar structure (Fig. 11b), though S/H and I/P ratios in SH and IP are both 9/1. Furthermore, Fig. 11c shows the image for the same blend sample SH/IP stained with iodine, which selectively stains P phase. Obviously small H/P mixed domain (dark phase) is dispersed at the domain interface of S (intermediate phase) and I (dark phase), thus the nanophase-separated structure of SH/IP is a complex lamellar structure with discrete small mixed H/P phase formed by hydrogen bonding interaction in between two lamellae, namely three-phase structure from four component polymer system is created.

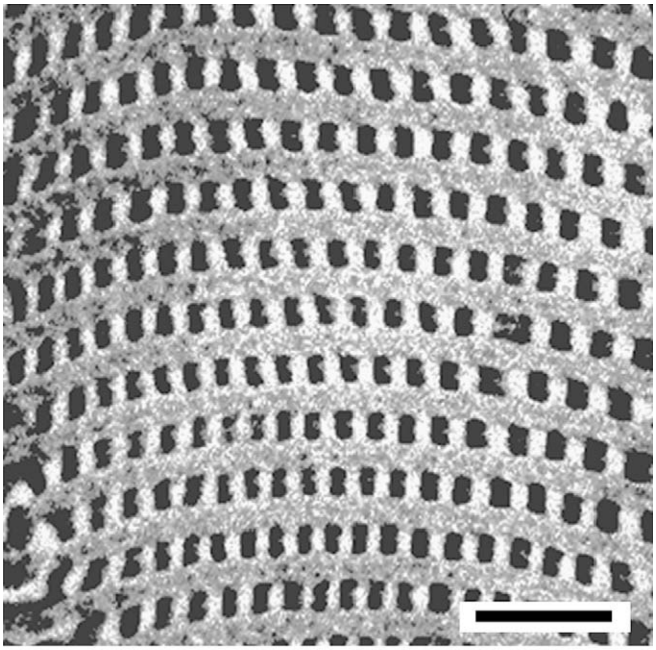


Fig. 12. Block polymer/block polymer blend. Sample: SH-55/IP-55 = 50/50. Thin section was stained with OsO_4 and I_2 (*cf.* Ref. [62]).

Alternatively, Fig. 12 expresses another binary blend of SH ($\phi_H = 0.5$)/IP ($\phi_P = 0.5$), whose volume ratio is 50/50 [62]. This is another three-phase structure composed of an H/P mixed phase appeared as simple lamellar domain and alternating rectangular prisms of S (bright) and I (dark) domains resulting in the formation of another alternating lamella. It should be noted that there are no block junction points between S and I domains, while covalent-bonded junction points are at white/gray and black/gray interfaces and multiple H–P interaction is in the mixed gray phase. Consequently this blend is forming a periodic three-phase lamellar structure having hierarchical nature.

Three-phase structures in Figs. 11 and 12 have never been observed for simple block copolymer and terpolymer systems bearing merely covalent bonds between different polymer species. Thus the utilization of non-covalent bonding interaction gives us a new way for the self-assembly of block copolymer and related systems.

4.2. Block copolymer/homopolymer association

Phase behavior of block copolymer/homopolymer blends has been studied well for last two decades. Component homopolymers are known to dissolve into microdomains of block polymers if the molecular weights of homopolymers are sufficiently low [63–65]. With increasing molecular weight of homopolymers, they tend to show in-domain segregation, namely homopolymers are segregated weakly from block copolymers but they still be within the phases of block polymers [66]. With further increase of the homopolymer molecular weight (M_H) and when M_H exceeds those of block chains (M_B), they could totally be segregated from the phases of block polymers and hence form their own macroscopic domains. The situation must be quite different if the homopolymers can be dissolved into microdomains of block chains by hydrogen bonding or the other non-covalent bonding interactions. This section deals the self-assembled structures of SP/H block copolymer/homopolymer blends in comparison with those of the regular SP/P blends [67].

Fig. 13 compares the variation of morphology for SP ($M = 167$k, $\phi_S = 0.81$)/P ($M = 8$k) blends with various blend ratios. The parent

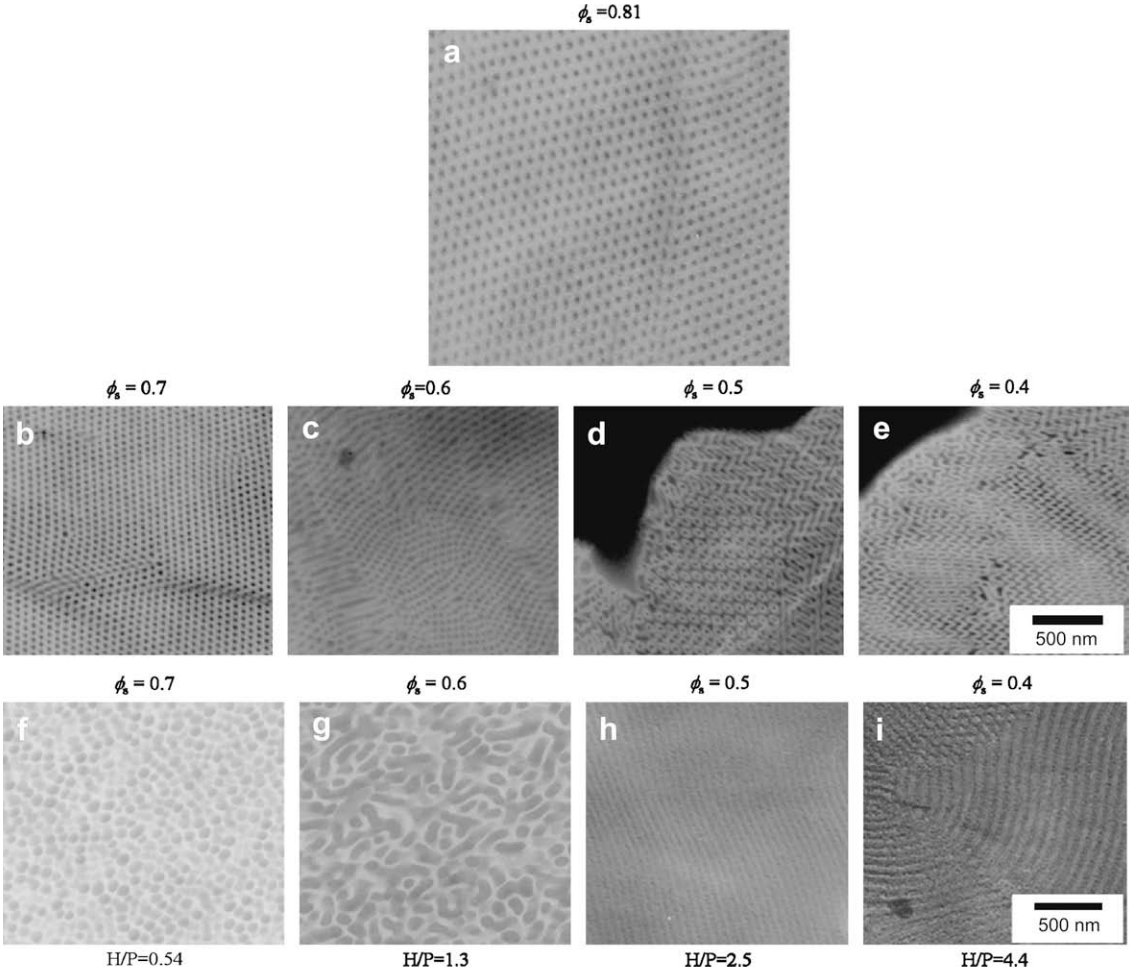


Fig. 13. Morphological variation of block copolymer/homopolymer blends. a) The parent copolymer SP-82, whose molecular weights of two blocks are 129k and 38k, b)–e) are for SP-82/P homopolymer ($M = 8$k) blends, while f)–i) are for SP-82/H homopolymer ($M = 14$k) blends. ϕ_Ss are the volume fractions of polystyrene blends (*cf.* Ref. [67]).

block polymer gives cylindrical domain structures and its morphology changes to lamellar structure with the addition of low molecular weight homopolymer. However, the blend easily reaches the miscibility limit of homopolymers (see Fig. 13d), where homopolymer H starts to segregate totally and resulted in the formation of large domains. To the contrary, however, the bottom of Fig. 13 shows the morphological change for SP/H ($M = 14$k). This blend first shows abnormal behavior upon adding a small amount of H homopolymer to the SP in THF as displayed in Fig. 13f and g, due to the formation of associated micelles which naturally collapses in solution to form spherical domains. The spherical morphology is kept during solvent evaporation and the structure is maintained with bulk. When the amount of the added homopolymer exceeds the stoichiometric ratio of phenol/pyridine, the regular morphological transition was then taken place as shown in Fig. 13h and i. This phenomenon can be understood by considering the screening effect of the added homopolymer, that is, much amount of H homopolymer can screen the P–H bare interaction in

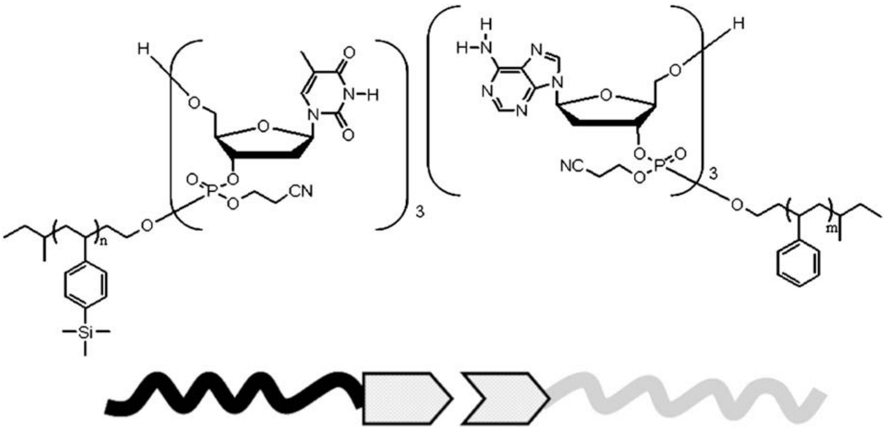


Fig. 14. Schematics of association formation between complementary oligonucleotides.

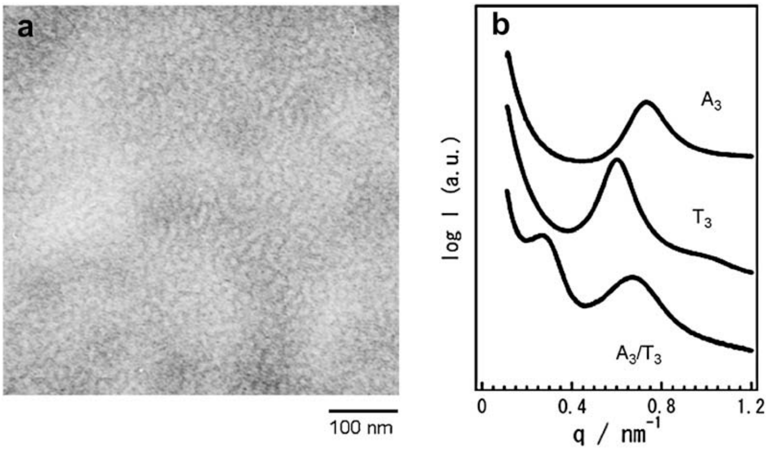


Fig. 15. Nanophase-separated structure formed by polymer blends with oligonucleotides on each polymer chain end. a) TEM image and b) SAXS diffraction pattern (*cf.* Ref. [69]).

THF and hence the added H chain can dissolve into P/H mixed phase uniformly, so as to motivate morphological transition. Thus we have found the interesting phenomena that more than ten fold amount of H relative to P can be mixed with SP block polymer, though the molecular weight of H is not extremely low.

Furthermore, it was also confirmed that the homopolymer H with molecular weight of 54k, whose value is larger than that of block P, can be easily dissolved into nanophase-separated structure as much as more than four times, i.e., H/P volume ratio exceeds four. This is the essential difference between SP/P and SP/H, because such miscibility has never been observed for the former.

The same idea but somewhat advanced one has been applied for polymers in an ionic liquid, and a thermoreversible ion gel was created by supramacromolecular assembly [68].

4.3. Homopolymer/homopolymer association

4.3.1. Hydrogen bonding interaction

Supramacromolecular assembly was investigated by introducing functional units at each end of homopolymer chains [69]. Firstly polystyrene terminated with oligonucleotides were tried to prepare by phosphoramidite method, and five units have been introduced successfully [70]. Secondly this method was extended to further fancy molecular design, and complementary oligonucleotides, i.e., 2′-deoxyadenosine and thymidine both as phosphates were attached up to three units on one end of polystyrene (S) and poly(4-trimethylsilylstyrene) (PTMSS), respectively [58]. Polystyrene capped with trimers with 2′-deoxyadenosine group and PTMSS with trimers having thymidine group, as shown in Fig. 14, are simply abbreviated as PS-A_3 and PTMSS-T_3. The generation of hydrogen bonding was confirmed by ^{1}H NMR for the blend of two polymers with different moieties in solution. Fig. 15 shows a TEM image of the blend of these two end-decorated homopolymers, i.e., PS-A_3 and PTMSS-T_3 (a) and the corresponding SAXS diffraction pattern (b). From these experimental data in both real space and reciprocal lattice space, the formation of a supramacromolecule via biocomplementary hydrogen bonding is evident. In particular, the diffraction pattern for PS-A_3/PTMSS-T_3 has two distinct peaks reflecting lamellar structure, it is quite different from the patterns for individual polymers, PS-A_3 and PTMSS-T_3.

4.3.2. Ionic interaction

The formation of supramacromolecule was also tried by introducing acid and base units at the end of homopolymer chains. A sulfonic acid group was introduced on one end of polystyrene so as to produce PS–SO_3H, while an amine group was attached on an end of polyisoprene to produce PI–NH_2 [71]. Fig. 16 expresses the variation of morphology depending on PS–SO_3H/PI–NH_2 ratio. Somewhat vague but distinct nanophase-separated structure was produced at 9/1 as is shown in Fig. 16a and the periodic structure can be recognized more clearly in Fig. 16b at 3/1. However, the mesoscopic structure tends to be unorganized with further increasing the content of PI–NH_2 as shown in Fig. 16c–e, where the phase separation in larger size is evident.

Polystyrene-*b*-poly(styrene sulfonic acid) (PS–P(SSO_3H)) with thirteen styrene sulfonic acid units were also prepared. Fig. 17 compares the variation of morphology with PS–P(SSO_3H)/PI–NH_2 ratio. Though all the TEM images are not quite clear, we can safely conclude that nanophase-separated structures were created throughout the composition range studied without causing macrophase separation. This result is quite natural considering that the SO_3H/NH_2 ratio is still larger than unity even at 1/9 since P(SSO_3H) part bears 13 functional groups. Thus the difference in the results

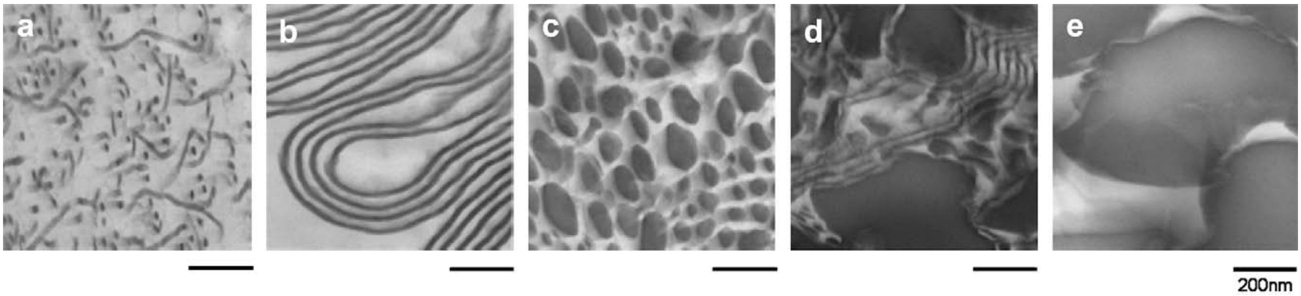


Fig. 16. Block polymer type supramacromolecular assembly by acid/base complex formation. Components are PS–SO_3H and PI–NH_2. SO_3H/NH_2 ratios are a) 9/1, b) 3/1, c) 1/1, d) 1/3 and e) 1/9 (*cf.* Ref. [71]).

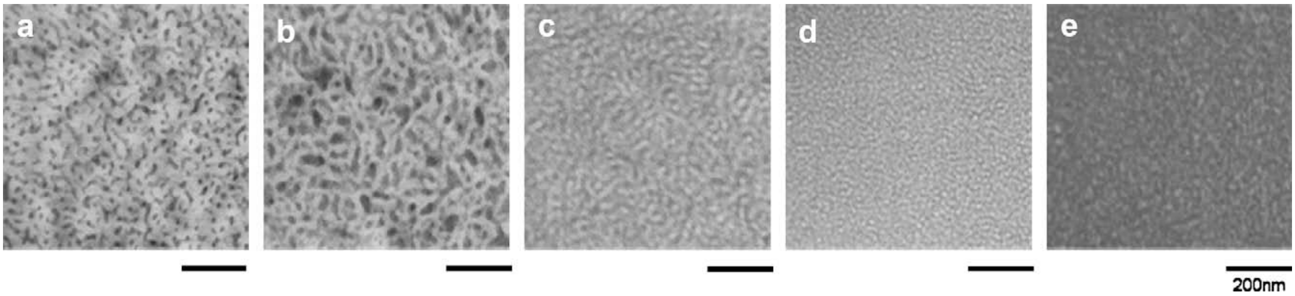


Fig. 17. Graft polymer type supramacromolecular assembly by acid/base complex formation. Components are PS–PSO$_3$H and PI–NH$_2$. SO$_3$H/NH$_2$ ratios are a) 117/1, b) 39/1, c) 13/1, d) 13/3 and e) 13/9.

between Figs. 16 and 17 can be attributed to acid/base stoichiometry of the functional group.

5. Summary

In summary, several new morphologies have been produced for newly-designed complex polymer systems. A quasicrystalline tiling structure with mesoscopic length scale has been found as well as the periodic Archimedean tiling structures for the star-branched polymers of the ABC type, and moreover three-dimensional Zincblende network structure has been discovered for the same star-branched system. Hierarchical structures with double periodicity have been observed for the hexablock and undecablock terpolymers. Very periodic hierarchical structures possessing double periodicity have been found for poly(isoprene-*b*-2-vinylpyridine)/poly(styrene-*b*-4-hydroxystyrene) blends because of hydrogen bonding interaction formed between poly(4-hydroxystyrene) (H) and poly(2-vinylpyridine) (P). Blends of homopolymers with several complementary nucleotides or acid/base moieties on chain ends have been confirmed to show nanophase-separated structures as the results of successful formation of “supramacromolecules”.

Thus the new molecular design focusing on the chain connectivity and the introduction of non-covalent bonds give new ways for the self-assembly of block copolymers and the related systems.

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