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Polymer Nanostructures

Suprapolymer Structures from Nanostructured Polymer Particles

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Over the last several decades, top-down type microfabrication technologies such as photolithography have led to improvement of the arithmetic processing speed of electronic devices. In contrast, bottom-up technologies, such as molecular assembly,[1] supramolecular assembly of molecules[2] including lipid micelles,[3] and metal complexes[4,5] have received much interest because of their potential in the fabrication of nanodevices. Although bottom-up technologies have a cost advantage for the fabrication of nanometer-sized aggregates, it is difficult to form aggregates on a scale greater than tens of nanometers. In addition, aggregates such as low-molecular-weight surfactant micelles are assembled by weak interactions (e.g., hydrophobic and van der Waals interactions). Recent developments in supramolecular chemistry have enabled the formation of stable aggregates through strong interactions such as coordination bonding. Even though bulk aggregates such as crystals can be formed, it is difficult to build the molecular aggregates up to an intermediate size between nanosized and bulk, because there is no hierarchy as found in biological systems. Therefore, novel nanosized building blocks that can form mesoscale structures ranging from several tens to several hundreds of nanometers are required for bottom-up techniques.[6,7]

To overcome the size problem in molecular assembly, the assembling of polymers has been considered to be one of the best candidate methods for the formation of mesoscale structures.[8,9] By using polymers for molecular assembly, the resulting aggregates have sizes of several tens of nanometers and their stability is enhanced by the polymeric effect. Typical polymer aggregates are block copolymer micelles,[10] and the fabrication of structured polymer aggregates has been investigated by micellization of amphiphilic block copolymers.[9] In block copolymer films, various kinds of periodic phase-separation structures ranging in size from several to several tens of nanometers are formed (microphase-separation structures).[11] The morphologies of microphase-separation structures are changed depending on the type of connections between the polymer block (i.e., linear, graft, and star block), the number of polymer blocks, the ratios of polymer blocks, and the molecular weight. Wiesner and co-workers reported the preparation of mesoscale structures by isolating one unit of a microphase-separation structure from a bulk film.[12,13] A similar approach, using a hydrolysis reaction, was reported by Walther et al.[14]

We recently reported that various kinds of polymer particles can be prepared by evaporation of good solvents (e.g., tetrahydrofuran (THF)) after adding poor solvents (e.g., water) into polymer solutions (self-organized precipitation (SORP) method).[15] The particle preparation method can be applicable to versatile polymers by selection of suitable solvents. In this method, the diameter of particles can be controlled from several tens of nanometers to several micrometers by changing the concentration of the polymer solutions and the ratio of poor/good solvents. We previously prepared particles with a wide variety of phase-separation structures; for example, hydrophobic block copolymers form microphase-separation structures (lamellae and cylinders) in particles depending on their segment ratios.[16,17] Particles with macrophase-separation structures were formed in the polymer blends.[17] By using the phase separation of polymers from micro to macro scales, the inner structures of particles can be controlled.

To confirm the inner structures of the block copolymer particles, the block copolymer particles were divided along the microphase-separation structures. After the cross-linking of one polymer block in the particles, the particles were dispersed in the good solvent for the other block. Unique mesoscale structures based on phase-separation morphologies can be obtained from block copolymer nanoparticles by using such chemical and solvent treatments.

Furthermore, we demonstrate that this treatment can be applied to other types of phase-separated nanoparticles, which shows that our method is universal for the production of novel mesoscale structures derived from phase-separated polymer particles. These structures have potential for application to a versatile range of nanomaterials.

The employed homopolymers and block copolymers are summarized in Table 1. As previously described, the particles of block copolymers containing polystyrene (PSt) and polyisoprene (PI) segments (PSt-PI), a polymer blend (PSt/PI), and a polymer blend with a small amount of the PSt-PI blend (PSt/PI/PSt-PI) were prepared by the SORP method,[15] as

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Table 1: Characteristics of the block copolymers.

Polymer	M_n (PSt) [10^3 g mol^{-1}]	M_n (PI) [10^3 g mol^{-1}]	M_w/M_n	f_{PI}[a]
PSt-PI-30	17.8	12.0	1.02	0.43
PSt-PI-51	40.8	10.4	1.06	0.22
PSt-PI-76	45.0	31.0	1.05	0.44
PSt-PI-222	141.5	80.6	1.07	0.47
PSt	17.0	–	1.03	–
PI	–	12.0	1.04	–

[a] Volume fraction of PI segment in block copolymers.

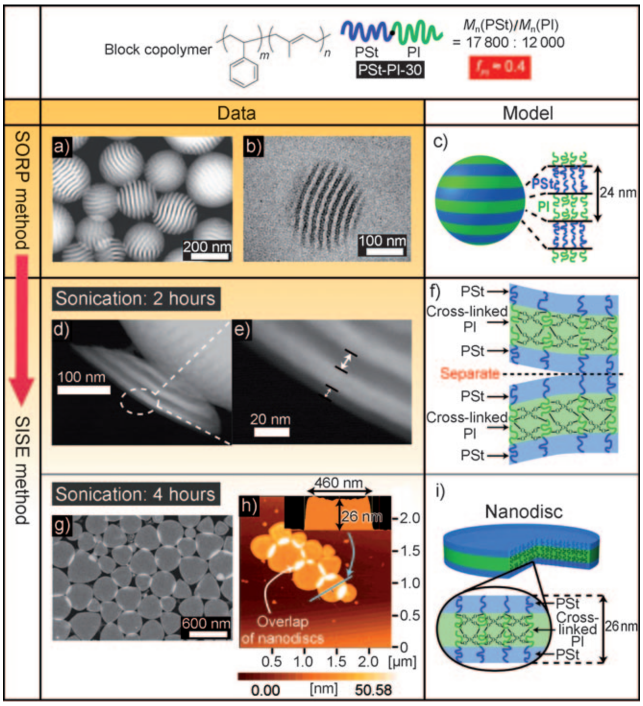

Figure 2. Nanodisks prepared from block copolymer nanoparticles with unidirectionally stacked lamellar structures. a) Dark-field STEM image; b) cross-sectional TEM image; and c) schematic model of the PSt-PI-30 nanoparticles. d,e) Dark-field STEM images at low (d) and high (e) magnification of the dispersed structures after sonication for 2 h. f) Schematic model of the cleavage by elution of the PSt segments. g) Dark-field STEM image and h) AFM image of the dispersed structures after sonication for 4 h . The inset in (h) is the cross-sectional profile at the blue line. i) Schematic model of the nanodisk consisting of two molecular layers of the block copolymers.

shown in Figure 1. Nanoparticles were stained with OsO_4 to observe the inner structures by scanning transmission electron microscopy (STEM). OsO_4 selectively reacts with the double bonds in the PI segment and consequently PI chains are cross-linked. Because cross-linked PI layers in particles are insoluble in any organic solvent, the particles can be separated from PSt layers by redispersion in organic solvents, which is referred to as the selective immobilization and selective elution (SISE) method (Figure 1).

A STEM image of the symmetrical block copolymer (PSt-PI-30) is shown in Figure 2a. The bright and dark parts are attributed to the PI moieties stained with OsO_4 and PSt moieties, respectively, exhibiting striped patterns on the nanoparticles. A cross-sectional TEM image of the particles is shown in Figure 2b, which also shows the striped patterns on the nanoparticles. This image indicates that unidirectionally stacked lamellar structures are formed in the nanoparticles, and OsO_4 reacts with the PI moieties in the center of particles. The average period of the lamellar structures was 24 nm (Figure 2c). The SISE method was applied to the lamellar particles. STEM images of the particles after sonication in THF for 2 h are shown in Figure 2d,e. Some separated parts from the particles were observed. The thickness of cross-sectional PSt layer corresponds to half of the inner PSt layer, as indicated by the white arrows in Figure 2e. This result indicates that the PSt layers in the lamellar particles were divided as illustrated in Figure 2 f. The lamellar particles were completely divided by further sonication, and disklike structures were formed (Figure 2g). The thickness of the disk structures was measured by atomic force microscopy (AFM). From AFM measurements (Figure 2h), the disk structures were determined to have uniform thickness with an average of 26 nm. Because the thickness of the nanodisks corresponds to the period of lamellar structure in the particles, the nanodisks are composed of a cross-linked PI layer sandwiched by PSt brushes, as illustrated in Figure 2i. The thickness of nanodisks can be controlled by changing the molecular weight of the block copolymers (see the Supporting Information).

A STEM image of the asymmetrical block copolymer (PSt-PI-51) is shown in Figure 3a. Hexagonally packed cylindrical structures were formed in the particles, as is also indicated by the cross-sectional TEM image of the particles (Figure 3b). The hexagonally packed dots and striped structures were observed in the same particles. This result indicates that the particles have multidomain cylindrical structures. The average center-to-center distance and diameter of the cylinders were 26 and 18 nm, respectively (Figure 3c). The SISE method was applied to the lamellar particles. A STEM image of the particles after sonication for 2 h in THF is shown in Figure 3d, and several stained wirelike structures were observed around the particles, as

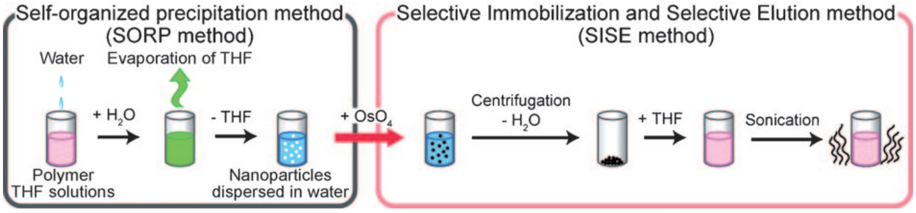

Figure 1. Preparation of suprapolymer structures: The phase-separated nanoparticles were prepared by the self-organized precipitation (SORP) method, which involves addition of a poor solvent into polymer solutions and subsequent evaporation of a good solvent. The suprapolymer structures were prepared by redispersion in a good solvent after cross-linking one polymer phase, a method referred to as the selective immobilization and selective elution (SISE) method.

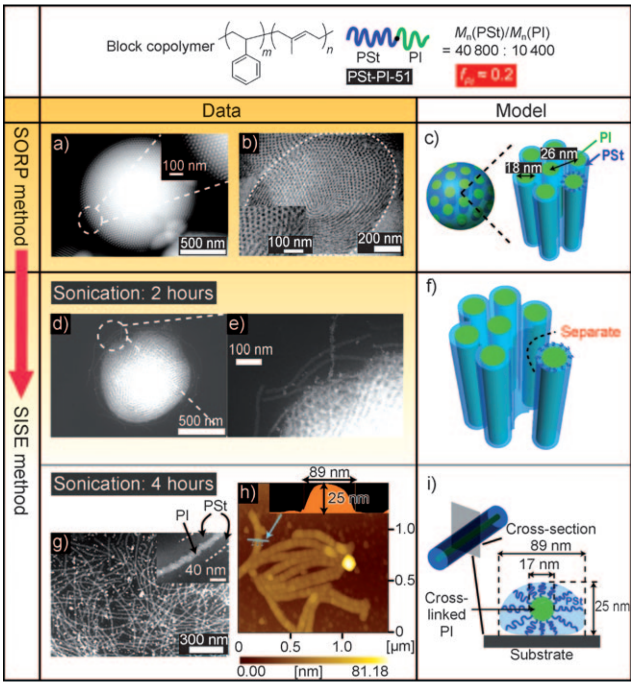

Figure 3. Nanowires prepared from block copolymer nanoparticles with cylindrical structures. a) Dark-field STEM image; b) cross-sectional TEM image; and c) schematic model of the PSt-PI-51 nanoparticles. d,e) Dark-field STEM images at low (d) and high (e) magnification of the dispersed structures after sonication for 2 h. f) Schematic model of the cleavage by elution of the PSt segments. g) Dark-field STEM image and h) AFM image of the dispersed structures after sonication for 4 h. The insets in (g) and (h) show high-magnification STEM images and the cross-sectional profiles at the blue line, respectively. i) Schematic model of the nanodisk consisting of two molecular layers of the block copolymers.

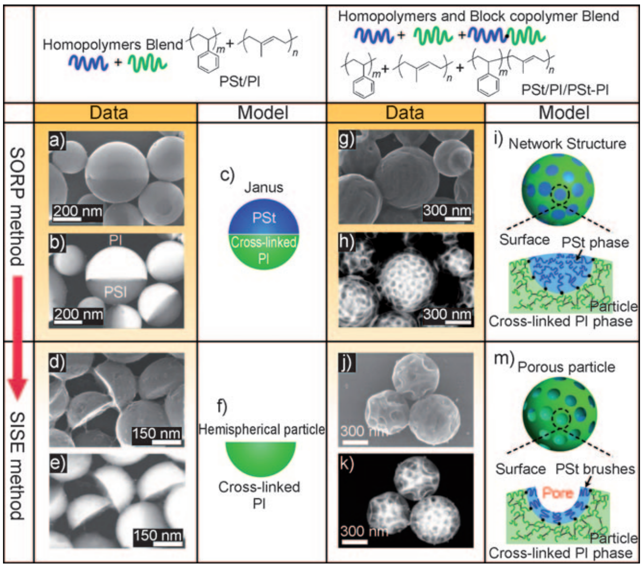

Figure 4. Hemispherical and porous nanoparticles prepared from a homopolymer blend and homopolymers with block copolymer nanoparticles. a) SEM-mode STEM image; b) dark-field STEM image; and c) schematic model of the homopolymer blend nanoparticles. d) SEM-mode STEM image and e) dark-field STEM image of the nanoparticles after applying the SISE method. f) Schematic model of the hemispherical nanoparticles. g) SEM-mode STEM image; h) dark-field STEM image; and i) schematic model of the homopolymer and block copolymer blend nanoparticles. j) SEM-mode STEM image and k) dark-field STEM image of the nanoparticles after applying the SISE method. m) Schematic model of the porous nanoparticles.

indicated by the white circle and magnified in Figure 3 e. This result indicates that the cylindrical structures partially separated from the particles (Figure 3 f). Many wire structures formed after further sonication as a result of complete elution of the cylindrical structures (Figure 3 g), and a magnified image of the wire structures showed that they have a PI core cylinder covered with PSt brushes. AFM measurements revealed that the nanowires have uniform size, and their cross-sectional height and width are 25 and 89 nm, respectively (Figure 3 h), so that the width was larger than the height. This result suggests that the PSt brushes on the surfaces of nanowires are swollen by THF, and the PSt brushes in perpendicular to the substrate shrink upon drying. In contrast, the brushes parallel to the substrate are stretched by interaction with the hydrophobic surface of the substrate (Figure 3 i)

STEM images of the stained particles prepared from a solution containing PSt/PI (PSt/PI = 1:1) are shown in Figure 4 a (SEM mode) and Figure 4 b (TEM mode). The particles are spherical and have two clear aspects—they are so-called "Janus" particles (Figure 4 c). STEM images of the particles are shown in Figure 4 d (SEM mode) and Figure 4 e (TEM mode) after applying the SISE method. The hemispherical particles composed of the stained PI phase were formed by elution of the PSt phase (Figure 4 f). It is known that block copolymers decrease interfacial tension between homopolymer blends.[18,19] Particles containing PSt, PI, and the block copolymers of PSt and PI were prepared by the SORP method. STEM images of the particles, which contain PSt, PI, and 30 % PSt-PI-76, are shown in Figure 4 g (SEM mode) and Figure 4 h (TEM mode). The particles have PI network structures in the PSt matrix (Figure 4 i) because of the decrease of the interfacial tension between PSt and PI by addition of the block copolymers. By applying the SISE method, porous particles were formed by elution of the PSt homopolymer, as shown in Figure 4 j (SEM mode) and Figure 4 k (TEM mode). The surfaces of the pores are covered with PSt brushes of the block copolymers (Figure 4 m).

Novel suprapolymer structures were prepared from phase-separated nanoparticles by using the SISE method, which involves elution of one polymer phase after cross-linking of the other. The important point of the SISE method is the use of the solubility differences between polymer segments of the block copolymers. To generate solubility difference between PSt and PI segments, the PI segments were cross-linked with OsO_4. Although OsO_4 was used as a cross-linking agent in this investigation, it is possible to cross-link polymer segments using sulfur, palladium complexes, and other metal complexes. In particular, metal complexes can be used not only for cross-linking, but also for functionalization. By using the SORP and SISE methods, novel nanomaterials can be prepared for a versatile range of applications.

Experimental Section

Preparation of nanoparticles: The polymers employed in this investigation are summarized in Table 1. All polymers were purchased from Polymer Source Inc. Ltd., Canada. PSt, PI, PSt-PI-30, PSt-PI-76, and PSt-PI-222 were each dissolved in THF to prepare 0.1 $\mathrm{g\,L^{-1}}$ solutions. PSt-PI-51 was dissolved in THF to prepare 0.1 and 0.4 $\mathrm{g\,L^{-1}}$ solutions. Mixtures of solutions containing PSt and PI (PSt/PI = 1:1) were prepared. Mixtures of solutions containing PSt, PI, and PSt-PI (PSt/PI/PSt-PI = 1:1:0.6) were also prepared. Pure water (2 mL) was added to the block copolymer and mixture solutions (1 mL) with stirring. Membrane-filtered water was then supplied to the stirred solution at a rate of 1 $\mathrm{mL\,min^{-1}}$. The mixture was stirred, and THF was evaporated at room temperature under atmospheric pressure for 2 days.

Observation of structures in the nanoparticles: The isoprene moiety in the nanoparticles was selectively stained and cross-linked with osmium tetraoxide (OsO_4). Suspensions of the particles (0.5 mL) were stained with 0.2 wt% OsO_4 (0.5 mL) for 2 h at room temperature. The stained particles were centrifuged (12000 rpm, 5 °C, 15 min) and washed with membrane-filtered water to eliminate excess OsO_4. The washed stained particles were redispersed in membrane-filtered water with ultrasonication. Water suspensions of the stained particles were dropped onto the surface of a carbon membrane placed on a Cu mesh and dried at room temperature. The phase-separation structures in the particles were observed by STEM (HD-2000, Hitachi Ltd., Japan). Cross-sectional images of particles were observed by TEM (JEM-2100F, Jeol Ltd., Japan). The stained particles were embedded in an epoxy resin (Epok-812, Wako Pure Chemical Industries, Ltd., Japan), which was cured at 60 °C for 12 h. Thin-film sections of the particle embedded cured resin (thickness: ca. 100 nm) were prepared using an ultra-microtome (Ultracut UCT, Leica Microsystems), and these were mounted on a Cu mesh covered with a carbon membrane.

Selective immobilization and selective elution method: The nanoparticles were selectively cross-linked with OsO_4. The cross-linked particles with OsO_4 were centrifuged (12000 rpm, 15 min, 5 °C) and THF was added after elimination of the supernatant water. The solutions in THF were ultrasonicated for 2 or 4 h, dropped onto the surface of a carbon membrane placed on a Cu mesh, and dried at room temperature. The mounted samples were observed by STEM and an atomic force microscope (AFM; SPA400, Seiko Instruments, Inc., Japan).

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