Frustrated Phases

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Frustrated Phases of Block Copolymers in Nanoparticles

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Microphase separation structures of block copolymers have attracted much interest as novel building blocks for the creation of nanometer-scale structures. In block copolymer films, various kinds of microphase separation structures (e.g., cylindrical, lamellar, bicontinuous, and others), which are dependent on the segment ratio and molecular weight of the block copolymer, have been reported.[1] Microphase separation structures have been applied to etching masks for lithography,[2] the formation of metal arrays,[3] photonic crystals,[4,5] and laser devices,[6] because block copolymers form highly ordered nanoscale structures through simple preparation processes, such as spin coating.

Polymer nanoparticles have also received much attention in the fields of nanoscience and nanotechnology, because of their potential in optical, electronic, and biological applications.[7] In particular, nanoparticles with specific internal structures can be applied to functional materials derived from their internal structures. For example, amphiphilic block copolymer micelles, which are core–shell-type particles, are used as carriers in drug-delivery systems.[8] Block copolymer nanoparticles with microphase separation structures, such as cylindrical and lamellar structures, could possess unique chemical and physical properties. However, there are a few reports of the formation of block copolymer particles with cylindrical, lamellar, and other microphase separation structures.[9,10] The preparation of block copolymer particles is difficult with conventional methods for the preparation of polymer particles, such as an emulsion polymerization.[11,12]

We have reported that various kinds of polymer nanoparticles can be prepared by a simple solvent-evaporation process, that is, the evaporation of a good solvent from a polymer solution containing poor and good solvents; this technique is known as the SORP (self-organized precipitation) method.[13] This method can be applied to various polymers by selecting suitable solvent combinations for the polymers. For example, a hydrophobic diblock copolymer, which forms lamellar structures in its film, formed one-directionally stacked lamellar and onionlike structures in the nanoparticles.[14,15]

Herein we report the investigation of the effect of the molecular weight of block copolymer on the microphase separation structures in nanoparticles. Nanoparticles were prepared from block copolymers with a wide variety of molecular weights, ranging from 30000 to 1.5 million, by using the SORP method. Block copolymers with large molecular weight (> 0.2 million) formed nanoparticles with unique microphase separation structures (e.g., Janus-type, tennis-ball-, mushroom-, wheel-, and screwlike structures), even though their films formed only lamellar structures. Scanning transmission electron microscopy (STEM) observations revealed that the microphase separation structures in the nanoparticles are dependent on the diameters of the nanoparticle. The relationship between particle diameter and the microphase separation structures is discussed in terms of the confinement effect in nanoparticles.[16,17]

Nanoparticles were prepared from block copolymers with a wide variety of molecular weights by using the SORP method to study the effect of the molecular weight of block copolymer on the microphase separation structures in the nanoparticles. The block copolymers employed, which contained polystyrene (PSt) and polyisoprene (PI) segments, are summarized in Table 1. These block copolymers form films with lamellar structures. Each block copolymer was dissolved in tetrahydrofuran (THF), and polymer solutions were prepared at a concentration of $0.1\,\mathrm{g\,L^{-1}}$. Pure water was added into the block copolymer solution, and then THF was gradually evaporated. After evaporation of THF, the block copolymer nanoparticles were precipitated in water (Figure 1). To observe the internal structures of the block copolymer nanoparticles with STEM, the nanoparticles were stained with osmium tetraoxide (OsO_4), which selectively reacts with the double bonds in the polyisoprene segments.

As reported previously, PSt-PI-30 formed unidirectionally stacked lamellar structures in the nanoparticles[14] (Figure 2a). In the STEM image, the bright and dark parts are

Table 1: Characteristics of the block copolymers.

Polymer	M_n (PSt) [$\times 10^3$]	M_n (PI) [$\times 10^3$]	M_w/M_n	f_{PI}[a]
PSt-PI-30	17.8	12.0	1.02	0.43
PSt-PI-76	45.0	31.0	1.05	0.44
PSt-PI-266	135	131	1.10	0.52
PSt-PI-412	202	210	1.13	0.54
PSt-PI-1550	700	850	1.15	0.58

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

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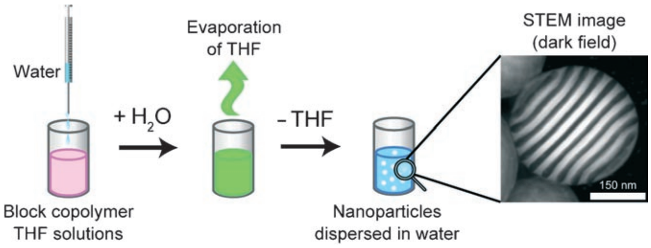

Figure 1. Method for the preparation of block copolymer nanoparticles (SORP: self-organized precipitation method).

attributed to the PI moieties stained with OsO_4 and the PSt moieties, respectively. The period of lamellar structure in the PSt-PI-30 nanoparticles was approximately 23 nm. When the molecular weight of block copolymer was increased, PSt-PI-76 also formed unidirectionally stacked lamellar structures in the nanoparticles (Figure 2b). The period of lamellar structures in the PSt-PI-76 nanoparticles was approximately 34 nm. When the molecular weight of the block copolymer was larger than 0.2 million, such as for PSt-PI-266 and PSt-PI-412, unidirectionally stacked lamellar structures were also formed in the nanoparticles (Figure 2c,g) and the periods of the lamellar structures were 63 nm and 94 nm, respectively. From these results, the period of the lamellar structures in the nanoparticles increased as the molecular weight of the block copolymers increased. However, various kinds of unique phase separation structures were also observed in addition to the lamellar structures (Figure 2d–f, h–k). In particular, for the PSt-PI-1550 nanoparticles, nonlamellar structures were formed (Figure 2m–p).

It has been reported that block copolymers form different morphologies because of the confinement of a nanoscale space relative to that of bulk films.[18,19] The morphologies are governed by the relationship between the pore size and interfacial energy between the block copolymer and the matrix. A thin film sandwiched between two flat substrates is defined as a one-dimensional (1D) confinement system, because the boundary condition is determined by the film thickness.[19–21] Nanosized cylindrical pores, such as a porous alumina membrane, are used for two-dimensional (2D) confinement systems, because cylindrical structures have two boundary conditions. In this system, the unique microphase separation structures (i.e., concentric cylindrical lamellar, stacked lamellar, and helical structures) are formed by the 2D confinement effect.[22–25] The effects of 1D and 2D confinement on the microphase separation structures have been investigated experimentally[18,21–23] and theoretically.[26–28] However, there has been no report discussing the effect of three-dimensional (3D) confinement on microphase separation structures. Recently, Yu et al. reported the morphologies in nanosized spherical pores as a 3D confinement system, as predicted by Monte-Carlo simulations.[16] It was shown that the morphologies in the 3D confinement system were dependent on the equilibrium period of the lamellar structures in the films (L_0) and the diameters of the nanopores (D). When the value of D/L_0 is larger than 2.0, the simulation results predicted that 1D stacked lamellar structures were formed. In contrast, it was suggested that various kinds of nonlamellar structures are formed when D/L_0 has values intermediate between 1 and 2.

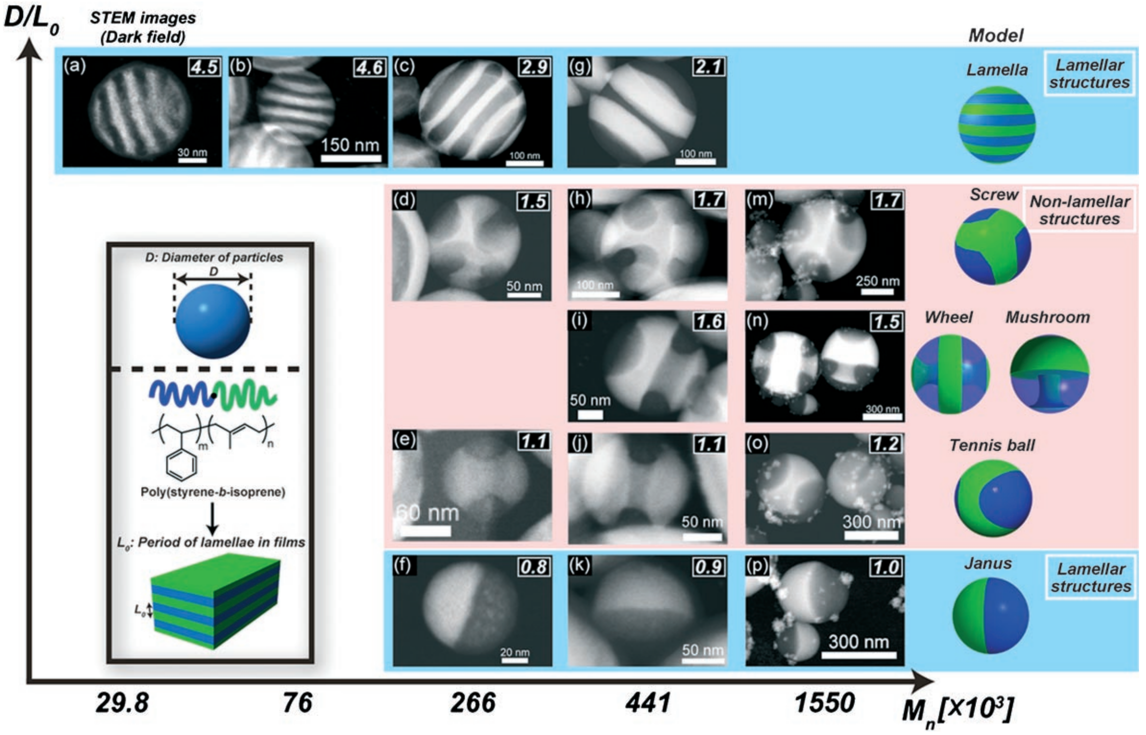

Figure 2. Microphase separation structures in nanoparticles as a function of molecular weight and the D/L_0 ratio, where D and L_0 correspond to the particle diameter and the period of lamellar structure in the films, respectively. STEM images of a) a PSt-PI-30 nanoparticle, b) PSt-PI-76 nanoparticles, c–f) PSt-PI-266 nanoparticles, g–k) PSt-PI-412 nanoparticles, and m–p) PSt-PI-1550 nanoparticles. The D/L_0 ratios are shown in the upper-right corner of each STEM image.

Taking into account the simulation results in the 3D confinement system, the morphologies of block copolymer nanoparticles are summarized by using the D/L_0 ratio (Figure 2). The values of D/L_0 are indicated in the upper right corner of each STEM image in Figure 2. When D/L_0 is larger than 2.0, unidirectionally stacked lamellar structures were formed in the nanoparticles, as predicted by the simulation results[16] (Figure 2 a–c, g). When D/L_0 has a value intermediate between 1 and 2, it is possible to form nonlamellar structures in the nanoparticles. Thus, the morphologies in the smaller nanoparticles were observed in detail. When D/L_0 is 1.7, nonlamellar structures such as screwlike structures were formed in the nanoparticles (Figure 2 d, h, m). When D/L_0 reaches around 1.5, mushroom- and wheellike structures were formed in the nanoparticles (Figure 2 i, n). These are analogous structures, which have one layer connecting with one or two pillars of the PI phases. The particle diameters of the mushroomlike structures are slightly smaller than those of the wheellike structures. When D/L_0 ranges from 1.1 to 1.2, tennis-ball-like structures were formed in the nanoparticles (Figure 2 e, j, o). These nonlamellar structures are similar to the structures predicted by the simulation. When D/L_0 is smaller than 1.0, Janus-type particles, which have two polymer phases divided at the center of the particles, were formed (Figure 2 f, k, p). The Janus structure is considered to be a single lamellar structure. From the comparison of the experimental and theoretical results, nonlamellar structures are induced by frustration from the formation of stable structures in an unsuitable space for the length of block copolymers. When the particle diameter is large, the frustration can be relaxed in the lamellar structures.

Block copolymer nanoparticles with various kinds of frustrated structures were prepared by using the effects of 3D confinement. Symmetric block copolymers, which form lamellar structures in a film, formed Janus-type, tennis-ball-, mushroom-, wheel-, and screwlike structures in nanoparticles, depending on the diameter of the nanoparticle. Nanoparticles act as a 3D confinement, so that it is possible to form various kinds of unique phase separation structures, such as helices. This report describes for the first time frustrated structures in 3D confinement systems, as a contribution to developing methods for structural control in nanostructured polymers.

Experimental Section

All block copolymers were dissolved in THF and their solutions were then prepared at a concentration of 0.1 $\mathrm{g\,L^{-1}}$. Pure water (2 mL) was added to each block copolymer solution (1 mL) with stirring. After stirring was stopped, THF was gradually evaporated at 25 °C under atmospheric pressure over 2 days, and the block copolymers were precipitated as nanoparticles. In the case of block copolymers with high molecular weight (> 0.2 million), the temperature of the mixture was kept at 10 °C during evaporation of the THF to avoid rapid precipitation of the block copolymers. To observe the phase separation structures in the block copolymer nanoparticles, staining with OsO_4 was employed, which selectively reacts with the double bonds in the polyisoprene segments. The suspensions of particles (0.5 mL) were stained with 0.2 wt % OsO_4 (0.5 mL) for 2 h at room temperature. After staining, the stained particles were centrifuged (12 000 rpm., 5 °C, 15 min) and washed with pure water to eliminate excess OsO_4. After washing, the stained particles were redispersed in pure water with ultrasonication. Suspensions of the stained particles in water were dropped onto a carbon membrane surface placed on a Cu mesh and dried at room temperature. The phase separation structures in the particles were then observed by scanning transmission electron microscopy (STEM; HD-2000, Hitachi Ltd., Japan).

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