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Microporous Films from Diblock Copolymer Micelles Based on Solvent-Induced Mechanism by Temperature Control of Casting Solution

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Introduction

Microporous (pore size ≥ 50 nm) films with highly ordered three-dimensional (3D) porous structures are technologically important for a variety of applications. They can be used, for example, as supports in catalysis,[1] as filters in separation,[2] and as building in tissue engineering.[3] Moreover, these films also exhibit interesting optical properties such as photonic bandgaps and optical stop-bands due to their spatially periodic structures.[4] A number of methods have been developed for producing such kinds of films, for example, photolithography,[5] photochemical reaction,[6] photodecomposition of self-assembled monolayers,[7] selective etching,[8] and microcontact printing.[9] François et al.[10] first reported the condensation of monodisperse water droplets on polymer solution to fabricate honeycomb films with monodisperse pores. A variety of polymers, such as star and comb polymers, block copolymers, and dendronized polymers, were used to obtain honeycomb structured films,[11−14] and the concept of such water-assisted patterning was extended. Especially, Stenzel et al. have reported the preparation of microporous films of block copolymer micelles[15] and comblike polymers,[16] using the breath figures templating technique.

More recently, we have discovered that ordered microporous surface films were constructed by casting cross-linked poly(methyl methacrylate) (PMMA) core−polystyrene (PS) shell nanospheres as slowly as possible from a hot cyclohexane solution at 20 °C.[17] The mechanism of formation of the hexagonal pore morphology can be speculated as follows. Solvent evaporation increases the superficial concentration and induced a cooling of the solution surface. Cross-linked PMMA core−PS shell nanospheres form a cubic lattice during the evaporation process. These lattice clusters lead to phase separation at less than 34 °C during the casting process because cyclohexane is a Θ solvent for PS arms. The driving force for micropore formation may be created by cyclohexane droplets around the lattice clusters composed nanospheres because cyclohexane within the leaving gaps is ejected.

On the other hand, it is well-known that as the concentration of block copolymer chains increases, they will tend to aggregate and form spherical micelles,[18] consisting of a core−corona structure. Molecular conformation of core−corona micelles is very similar to that of cross-linked core−shell nanospheres mentioned above. Our previous work[17] raises the possibility that Θ solvent-induced micropore patterning would be formed by core−corona micelles of diblock copolymers. In this Note, a well-defined PS-*block*-poly(*tert*-butyl methacrylate) (PBMA) diblock copolymer was prepared by the sequential anionic addition polymerization. It is discovered that ordered microporous films are constructed by temperature control of casting solution (cyclohexane; Θ solvent for PS chains).

Experimental Section

Materials. A well-defined PS-*block*-PBMA diblock copolymer was prepared by the sequential anionic addition polymerization using *n*-butyllithium as an initiator in tetrahydrofuran (THF) at −78 °C. The details concerning the synthesis and purification of diblock copolymer have been given elsewhere.[19] Cyclohexane and THF (Tokyo Kasei Organic Chemicals, Tokyo) were used as received.

Preparation of Microporous Films. Microporous films were constructed by casting from hot cyclohexane solution (2 wt %, 50 °C) of PS-*block*-PBMA diblock copolymer on the mica, where the solvent was evaporated as slowly as possible at 20 °C.

Measurements. The number-average molecular weight (M_n) of PS precursor and polydispersity (M_w/M_n) of PS and diblock copolymer were determined by gel permeation chromatography (GPC; Tosoh HLC-8020 high-speed liquid chromatograph, Tokyo) with THF as eluent at 40 °C, two TSK gel columns, GMH$_{XL}$ and G2000H$_{XL}$, in series, and a flow rate of 1.0 mL/min using PS standard samples as calibration.

The composition of PS-*block*-PBMA was determined by ^{1}H NMR (500 MHz, JEOL GSX-500 NMR spectrometer, Tokyo) in CDCl$_3$. The spectra exhibited the expected resonances assignable to methyl protons (δ 1.41 ppm) of *tert*-butyl groups of PBMA and aromatic protons (6.3−7.2 ppm) of PS. The M_n of diblock copolymer was evaluated from the M_n of PS precursor and composition of diblock copolymer.

The hydrodynamic radius (R_h) of micelles formed by diblock copolymers was evaluated using Stokes−Einstein equation from the diffusion coefficient (D_0) determined by dynamic light scattering (DLS; Photal TMLS-6000HL: Otsuka Electronics, Tokyo, He−Ne laser: λ_0 = 632.8 nm) data with cumulant method in cyclohexane at 40 °C (scattering angle of 90°). Sample solutions were filtered through membrane filters with a nominal pore of 0.5 μm just before measurement.

The morphology and pore size (D_n) of microporous films were investigated by the use of a JEOL JSM-T220 (Tokyo) scanning electron microscope (SEM) with a tilt angle of 30°. To observe the vertical section of microporous films, the film was broken in liquid nitrogen. The specimen was sputtered with gold. The pore size distribution (D_w/D_n) was determined by a survey of 300 samples picked up from the photographs that were obtained. D_n and D_w are defined as follows:

$$D_n = \sum n_i D_i / \sum n_i$$

$$D_w = \sum n_i D_i^2 / \sum n_i D_i$$

where D_i (i = 1, 2, ..., q) and n_i are pore size and mole fraction, respectively.

Results and Discussion

PS-*block*-PBMA diblock copolymer (SB; $M_n = 2.2 \times 10^4$, PS = 75 mol %) was prepared by anionic polymerization. The conversion was almost 100% within experimental error. The M_n of SB observed was close to the value expected from the feed ratio of monomer and initiator used. The GPC profile showed that SB had a single and narrow molecular weight distribution ($M_w/M_n = 1.18$).

Figure 1 shows the size distribution on DLS data of 2 wt % cyclohexane solution of diblock copolymer SB at 40 °C. This profile shows two kinds of particle species (particle diameter D_h: 7.2 and 214.8 nm). DLS data mean that cyclohexane

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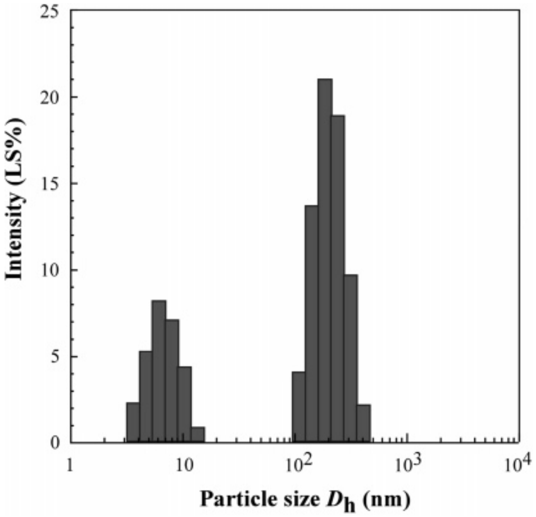

Figure 1. Size distribution on DLS data in 2 wt % cyclohexane solution of SB diblock copolymer at 45 °C.

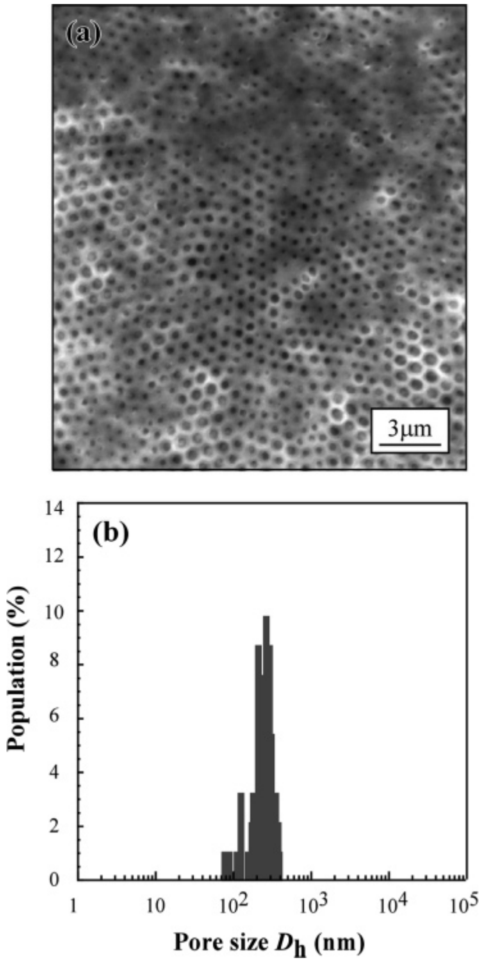

Figure 2. Top view of SEM photograph for the hexagonal micropore film (a) and pore size distribution (b).

solution of SB diblock copolymer is a mixture of diblock copolymer unimer and micelles consisting a PBMA core and a PS corona.

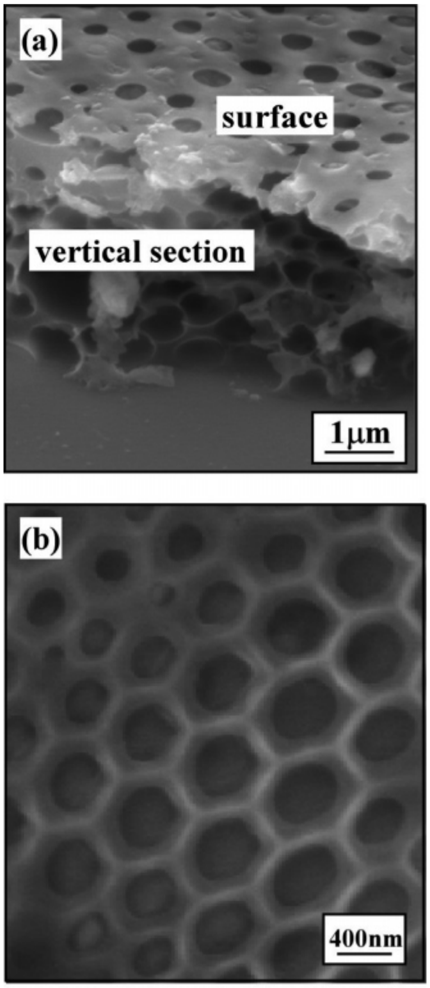

Figure 3. Vertical section of SEM photograph (a) and an enlarged SEM image of surface (b) for the ordered micropore film.

Microporous films were constructed by casting from such hot 2 wt % cyclohexane solution of SB diblock copolymer as slowly as possible at 20 °C. A typical SEM photograph (top view) of film specimen is shown in Figure 2a. It is found from this photograph that highly ordered micropores are clearly visible for the sample surface. Figure 2b shows pore size distribution of this specimen. The average pore size (D_n) is estimated to be 265 nm, and the pore size distribution ($D_w/D_n = 1.13 \pm 0.03$) is very narrow.

Figure 3a shows SEM photograph of vertical section of microporous film. This photograph indicates that such micropores locate regularly even in the bulk. On the other hand, Figure 3b shows an enlarged image of surface for microporous film. It is found that a continuous matrix (core–corona micelles) changes the shape of hexagon. These results will be discussed later.

The mechanism (see the schematic illustration in Figure 4) of formation of highly ordered pore morphology can be speculated as follows. The SB diblock copolymer takes disorder phase in dilute cyclohexane solution at more than 34 °C. As not only the solvent evaporation proceeds but also casting temperature drops, SB diblock copolymers will tend to form spherical micelles, consisting of a PBMA core and a PS corona, because cyclohexane is a Θ solvent for PS at 34 °C.[20] At some concentration, interaction between micelles will force a disorder–order transition, resulting in freezing of micelles in some superlattice. In a nonselective solvent of diblock copolymers, this corresponds to a body-centered-cubic (bcc) superstructure.[21] As mentioned in the previous works, we made clear that the core–shell nanospheres[22] and $(AB)_n$ star–block copolymers[23] having similar structure as block copolymer micelles (core–corona micelles) formed the lattice of bcc structure near the overlap threshold (C^*) by means of small-angle X-ray scattering (SAXS). On the other hand, Semenov[24] has treated theoretically

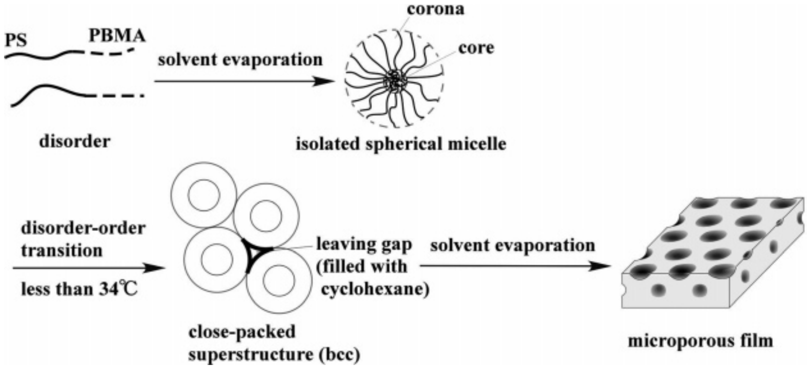

Figure 4. Schematic illustration for formation of Θ solvent-induced micropore patterning.

the superlattice formation on micelles formed by block copolymer (AB)−homopolymer mixtures. According to his results, the block copolymers form essentially spherical micelles (core−corona type) for minor B-blocks (B-blocks shorter than A-blocks). At equilibrium, copolymer domains should prefer to retain their symmetric spherical shape, thus leaving gaps filled by homopolymer chains. In our case, such leaving gaps were filled with cyclohexane solvent. Coalescence of cyclohexane droplets is inhibited by continuous nanosphere matrix. After subsequent evaporation of the solvent, polymer film having ordered micropore pattern is formed because cyclohexane within leaving gaps is vomited out. A continuous matrix consisting of core−corona micelles may change the shape of the hexagon due to the internal pressure during solvent evaporation. The pore sizes may very possibly controlled by micelle sizes, i.e., M_n of diblock copolymers. Several groups have discussed the formation of 3D microporous films[25] and submicron films[26] by means of the water-assisted method. According to their speculations, the ordered structures are formed by evaporating solutions of a simple coil-like polymer in a volatile solvent, in the presence of moisture with forced airflow across the solution surface. A hexagonally packed array of holes then forms on the surface of the polymer. When a solvent less dense than water is used, the hexagonal array propagates through the film (ordered 3D arrays). Therefore, our works provide a new route to construct the ordered microporous films based on the solvent-induced mechanism and are very different from the water-assisted method. Beattie et al.[15] have constructed honeycomb-structured porous films from amphiphilic PS-*block*-[poly(acrylic acid)−polypyrrole] [PS-*block*-(PAA−PPy)]. They expected the formation of inverse aggregates with a PPy core. During the casting process, the amphiphilic block copolymer can either rearrange around the water droplets or soluble water in the core of the inverse structure. As a result, polymers can be processed into honeycomb-structured porous films. Therefore, the mechanism of porous structure is based on the formation of block copolymer micelles similar to our method.

Not only diblock copolymers, core−shell nanospheres, and $(AB)_n$ stars but also stars with multiarms[27] and star-hyperbranched copolymers[28] formed the lattice of bcc structure near the overlap threshold (C^*). This work raises the possibility that such microporous structures would be formed by above highly branched polymers.

Conclusion

Ordered microporous films are constructed by casting PS-*block*-PBMA (SB) diblock copolymer from hot cyclohexane solution at 20 °C. The SB diblock copolymers form spherical micelles, consisting of a PBMA core and a PS corona during solvent evaporation, because cyclohexane is a Θ solvent for PS at 34 °C. At some concentration, micelles lead to a disorder−order transition, resulting in freezing of micelles in superlattice such as bcc structure. After subsequent evaporation of the solvent, polymer film having a microporous pattern is formed because cyclohexane within leaving gaps is vomited out.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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