

Emulsion-Induced Ordered Microporous Films Using Amphiphilic Poly(ethylene oxide)-*block*-Poly(*n*-butyl isocyanate) Block Copolymers

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ABSTRACT: Well-defined poly(ethylene oxide)-*block*-poly(*n*-butyl isocyanate) (PEO-*block*-PBIC; AB) diblock copolymers were prepared with trichloropentadienyl titanium (IV) (CpTiCl₃) catalyst. Ordered microporous films (hexagonal pattern) were constructed by emulsion micelles of A₁₁₀B₂₃₀ diblock copolymer (the subscript indicates the degree of polymerization of each block component) formed from CHCl₃/H₂O/tetrahydrofuran (THF) = 100/5/10 (v/v) solution. The addition of THF promoted uniform micelles in immiscible CHCl₃/H₂O mixed solvent as well as the effect of phase transfer catalyst. Diblock copolymers formed spherical micelles, consisting of a PEO core and a PBIC corona. At some con-

centration, interaction between micelles forced a disorder–order transition, resulting in freezing of micelles in some superlattice. Subsequently, the leaving gaps among micelles were filled by PBIC block chains on a corona through the evaporation of organic solvents. At last, water within hydrophilic PEO core was vomited through the film matrix. We also constructed the microporous films using A₁₁₀B₂₃₀ diblock copolymer by the current water-assisted method. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3753–3759, 2008

Key words: rod-coil diblock copolymer; microporous film; emulsion-induced method; water-assisted method

INTRODUCTION

Microporous materials, those with pore diameters greater than 50 nm, have a wide range of application in chemistry. Since François and coworkers¹ first utilized the condensation of monodisperse water droplets on polymer solution to fabricate honeycomb films with monodispersed pores, in which pores exhibited as hexagonal arrays, their method aroused great interest. A variety of polymers, such as star and comb polymers, and block copolymers were used to obtain honeycomb-structured films,^{2–4} and the concept of such water-assisted patterning was extended. Especially, Stenzel and coworkers have reported the preparation of microporous films of block copolymer micelles⁵ and comb-like polymers,⁶ using the breath figures templating technique. On the other hand, dendronized polymers are rod-like in shape due to the steric hindrance imposed by the bulky dendritic side groups attached to each repeating unit. Cheng et al.⁷ have reported the fabrication of honeycomb-patterned films from the amphiphilic dendronized block copolymers by on-solid surface

spreading method and on-water spreading method based on self-organization of water droplets. Moreover, Imhof and Pine⁸ reported the microporous structure to use sol-gel processing to deposit an inorganic material at the exterior of the droplets in a monodisperse emulsion.

More recently, we have provided a new route to construct the ordered microporous films based on Θ solvent-induced mechanism using core-shell nanospheres⁹ and diblock copolymers.¹⁰ According to our results, core-shell nanospheres or core-corona micelles (formed by diblock copolymers) formed the lattice of body-centered cubic (bcc) structure near the overlap threshold (C^*) by temperature control of casting solvent. The shell or corona parts were composed of polystyrene (PS) segments. Therefore, leaving gaps among spherical lattices were filled with cyclohexane solvent (Θ solvent for PS). After evaporation of the solvent, polymer films having ordered micropore pattern were formed.

On the other hand, polyisocyanates (PIC) are unusual class of polymeric materials that adopt helical conformations both in solution and in bulk.^{11–14} Numerous characterization techniques have shown that PIC is stiff-chain polymers whose properties depend on several parameters, such as the nature of the isocyanate side group, temperature, solvent, and molecular weight.^{15,16} Consequently, they may behave

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either as rigid rods or as semiflexible, wormlike chains. A combination of PIC with flexible chains in diblock copolymers or more complex macromolecular architectures provides new challenges in nanotechnology regarding the microphase separation, the ordering kinetics, and the self-assembly behavior in solution.^{17–19}

In this article, well-defined poly(ethylene oxide)-*block*-poly(*n*-butyl isocyanate) (PEO-*block*-PBIC) diblock copolymers were prepared with trichlorocyclopentadienyl-titanium (IV) (CpTiCl₃) catalyst. It is discovered that ordered microporous films are constructed by emulsion micelles of such amphiphilic diblock copolymers formed from chloroform (CHCl₃)/water (H₂O)/tetrahydrofuran (THF) solution or by the current water-assisted method. The formation mechanisms of both microporous films are discussed in detail.

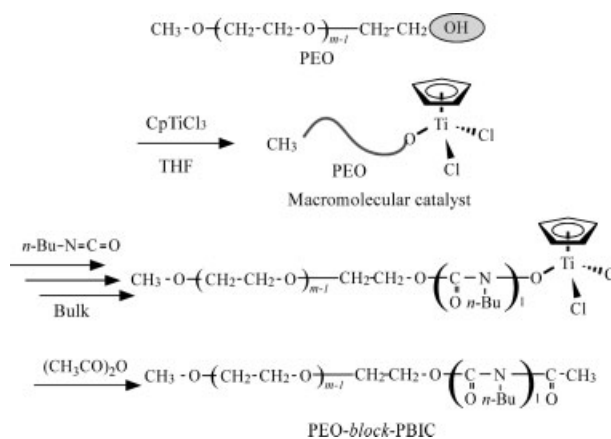
EXPERIMENTAL

Materials

n-Butyl isocyanate (BIC; Tokyo Kasei Organic Chemicals, Tokyo) was dried over calcium hydride (CaH₂) and distilled *in vacuo*. Poly(ethylene glycol) methyl ether (PEO; $M_n = 2000$ and 5000), CpTiCl₃ (Aldrich, Milwaukee), CHCl₃, THF, diethyl ether, acetic anhydride (Tokyo Kasei Organic Chemicals, Tokyo), and CaH₂ (Kanto Kagaku Reagent Division, Tokyo) were used as received.

Synthesis of PEO-*block*-PBIC diblock copolymers

The living coordination polymerization of isocyanates was reported by Patten and Novak^{20,21} using organotitanium (IV) complexes of the type TiCl₃(OCH₂CF₃) and CpTiCl₂L [Cp = cyclopentadiene and L = -OCH₂CF₃, -N(CH₃)₂, or -CH₃]. The replacement of one of the chlorine atoms with the bulkier and more electron-donating Cp group reduces the Lewis acidity of the titanium center, and the polymerization of isocyanate proceeds in a slower but more controlled manner. With this methodology, several isocyanates were polymerized. Furthermore, a diblock copolymer of PEO and poly(*n*-hexyl isocyanate) was synthesized.²² Then, PEO-*block*-PBIC diblock copolymers were prepared in accordance with above reference. The synthesis route is shown in Scheme 1. All procedures were carried out with standard high-vacuum techniques using break-sealed method. CpTiCl₂(OPEO) macromolecular catalyst was prepared from a mixture of CpTiCl₃ and PEO (1 : 1 molar ratio) in THF (dried over CaH₂) at 40°C and the solvent was removed *in vacuo*. This macromolecular catalyst was dissolved in BIC. The polymerization was allowed to take place at room temperature for 24 h under rigorous stirring.



The viscosity built up rapidly, and the solution solidified. Termination was achieved by the addition of acetic anhydride. THF was added to dissolve the polymer. The polymer was precipitated into diethyl ether and dried in a vacuum oven.

Preparation of microporous films

Microporous films were constructed by following two methods. (a) Emulsion-induced method: A typical procedure was as follows. The emulsion solution of amphiphilic diblock copolymers [0.1 wt % solution of CHCl₃/H₂O/THF = 100/5/10 (v/v)] was prepared under ultrasonic irradiation and this solution was cast on the mica substrate, where the solvent was evaporated as slowly as possible at 20°C. (b) Water-assisted method: a 0.1 wt % CHCl₃ solution of diblock copolymers was cast on the mica substrate. The vapor of water (produced by bubbling of N₂) was applied to the solution surface for a few minutes. Subsequently, the solvent was evaporated as slowly as possible at 20°C.

Measurements

The polydispersity (M_w/M_n) of diblock copolymers was determined by gel permeation chromatography (GPC; Tosoh HLC-8020 high-speed liquid chromatograph, Tokyo) with CHCl₃ as eluent at 30°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 PEO-*block*-PBIC was determined by ¹H-NMR (500 MHz, JEOL GSX-500 NMR spectrometer, Tokyo) in CDCl₃. The spectra exhibited the expected resonances assignable to methyl protons (δ 0.94 ppm) of *n*-butyl groups of PBIC and methylene protons (3.65 ppm) of PEO. The number-average molecular weight (M_n) of diblock copolymer

TABLE I
Polymerization Conditions and Results of Diblock Copolymers^a

Code	Polymerization conditions			Diblock copolymers		
	102[I] ^b (mmol)	[M] ^c (mmol)	Temp. (°C)	10 ⁻⁴ M _n ^d	M _w /M _n ^e	PBIC block ^f (mol %)
A45B145	15.3	8.88	25	1.64	1.51	76.3
A110B230	23.0	44.4	40	2.78	1.77	67.6

^a Polymerized in bulk for 24 h.

^b Macromolecular catalyst CpTiCl₂(OPEO).

^c Monomer *n*-butyl isocyanate.

^d Determined from M_n of PEO precursor and composition of diblock copolymer.

^e Determined by GPC profiles in CHCl₃ as eluent using PS standard samples.

^f Determined ¹H NMR spectrum in CDCl₃.

was evaluated from the M_n of PEO precursor and composition of diblock copolymer.

The hydrodynamic radius (R_n) of emulsion micelles formed by diblock copolymers was evaluated using Stokes-Einstein equation from the diffusion coefficient (D₀) determined by dynamic light scattering (DLS; Photal TMLS-6000HL; Otsuka Electronics, Tokyo, He-Ne laser: λ₀ = 632.8 nm) data with cumulant method in the prescribed solution at 25°C (scattering angle of 90°). Mixed solvent was filtered through membrane filters with a nominal pore of 0.2 μm just before measurement. Emulsion micelles of diblock copolymers were prepared by using this solvent under ultrasonic irradiation.

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:

$$D_n = \frac{\sum n_i D_i}{\sum n_i}$$

$$D_w = \frac{\sum n_i D_i^2}{\sum n_i D_i}$$

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

RESULTS AND DISCUSSION

Synthesis and characterization of diblock copolymers

Well-defined PEO-*block*-PBIC diblock copolymers (AB: A and B indicate PEO and PBIC blocks, respectively) were prepared by living coordination polymerization. The polymerization conditions and results of diblock copolymers are listed in Table I.

Typical GPC profiles of diblock copolymer A₁₁₀B₂₃₀ and PEO precursor are shown in Figure 1 using refractive index (RI) detector, where the subscripts indicate the degree of polymerization (DP_n) of each block component. The GPC distribution of A₁₁₀B₂₃₀ has a single and relatively broad polydispersity (M_w/M_n = 1.77) and shifts to the high-molecular-weight side compared with that of the PEO precursor. To elucidate the M_n of diblock copolymer, we determined the composition of diblock copolymers by ¹H-NMR spectra in CDCl₃. Figure 2 shows a typical ¹H-NMR spectrum of A₁₁₀B₂₃₀ diblock copolymer. The single peak observed at δ 3.65 ppm (a) is attributed to the methylene protons of PEO block. A strong peak at 0.94 ppm (e) is assignable to the methyl protons of *n*-butyl group of PBIC block. The composition of PBIC block (67.6 mol %) was determined from the signal intensity ratio of methyl protons (e) to the methylene protons (a). Subsequently, the M_n of diblock copolymer was evaluated from the M_n of PEO precursor and composition of diblock copolymer. These characteristics are also listed in Table I.

Water-assisted microporous films

We first employed the current water-assisted method for the fabrication of microporous films. Prelimi-

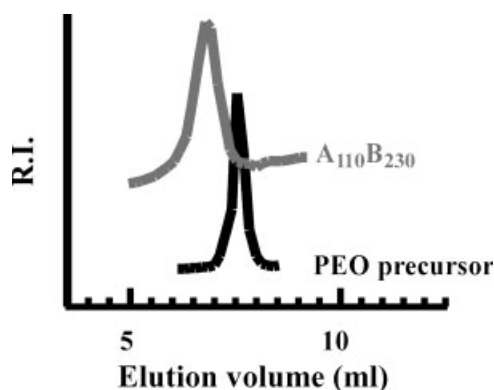


Figure 1 GPC profiles of A₁₁₀B₂₃₀ diblock copolymer and PEO precursor.

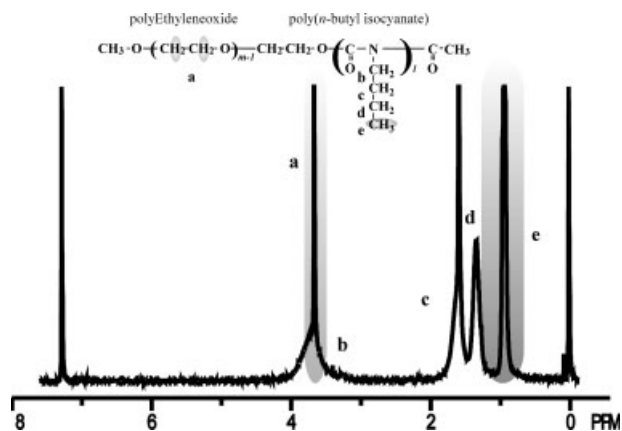


Figure 2 $^1\text{H-NMR}$ spectrum of $A_{110}B_{230}$ diblock copolymer in CDCl_3 .

nary experiments were carried out using $A_{45}B_{145}$ diblock copolymer, varying the concentration of casting solution (0.05–1.0 wt % CHCl_3 solution). As a result, 0.1 wt % casting solution indicated moderate micropore patterning as shown in Figure 3 (top view of SEM photograph; $D_n = \sim 60\text{--}400$ nm). Then, the film fabrication was performed using $A_{110}B_{230}$ diblock copolymer composed of long block segments under the same condition. Typical SEM photographs of film specimens are shown in Figure 4, where Figures 4(a–c) indicate the top view, the vertical section, and pore size distribution, respectively. It is found from Figures 4(a,c) that highly ordered micropores (average-pore size $D_n = 1300$ nm) are clearly visible for the sample surface but the pore size distribution ($D_w/D_n = 1.21$) is relatively broad. The vertical section as shown in Figure 4(b) also indicates that such microporous film is constructed with single layer. The pore sizes decreased with increment of M_n of each block sequence as the template.

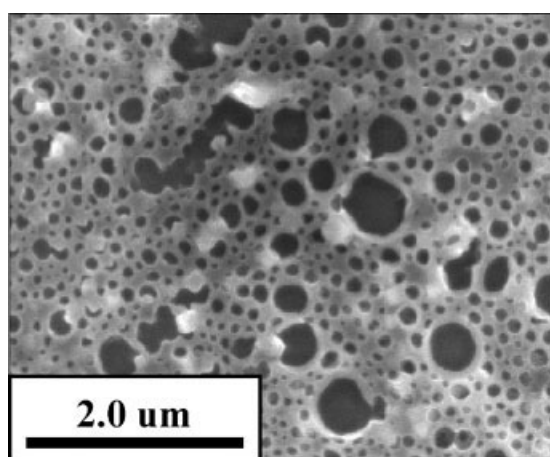


Figure 3 Top view of SEM photograph of microporous film $A_{45}B_{145}$ prepared by water-assisted method.

The mechanism of formation of the pore morphology can be speculated as follows (see the illustration in Fig. 5). Solvent evaporation increases the superficial concentration and induces a cooling of the solution surface. Hydrophilic PEO chains stop the water droplets by throwing their arms and stabilize sterically water droplets on the surface of casting solution. After CHCl_3 solvent evaporation, hydrophobic PBIC block chains form a continuous matrix. At last, water droplets are evaporated and a polymer film that has the ordered micropore pattern at the film surface is formed.

Emulsion-induced microporous films

PEO-*block*-PBIC diblock copolymers can be speculated to form emulsion micelles due to amphiphilic nature. First, the emulsion solution of $A_{110}B_{230}$ diblock copolymer [$\text{CHCl}_3/\text{H}_2\text{O} = 100/5$ (v/v)] was prepared under ultrasonic irradiation and this solution was cast on the mica substrate, where the solvent evaporated as slowly as possible. Figure 6(a) shows the top view of SEM photograph of the film specimen. The micropores ($D_n = 640$ nm) are clearly visible for the sample surface but the pore size distribution seems not so narrow. This means that

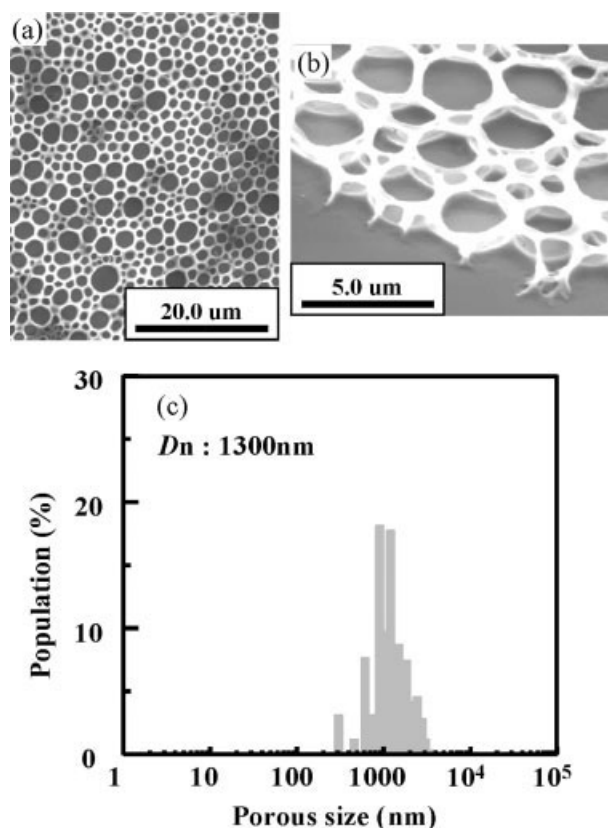


Figure 4 Top view (a) and vertical section (b) of SEM photographs, and pore size distribution of microporous film $A_{110}B_{230}$ prepared by water-assisted method.

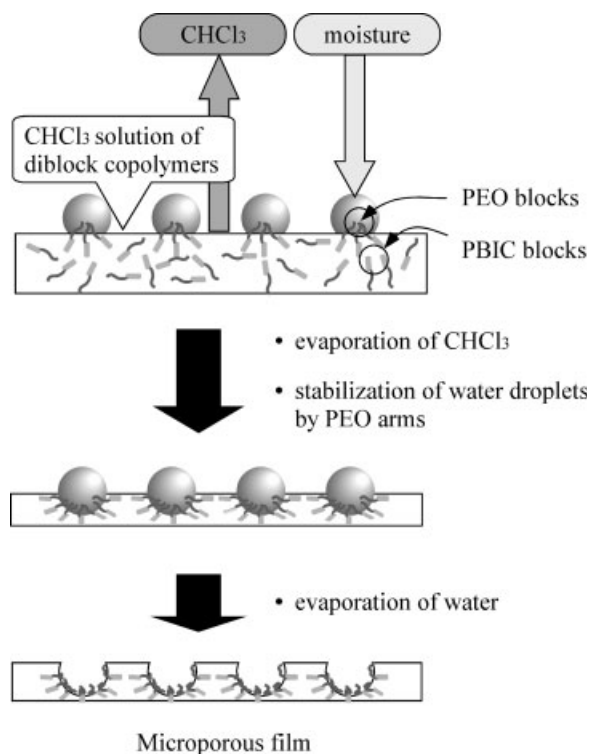


Figure 5 Schematic illustration of a microporous film of diblock copolymer prepared by water-assisted method.

emulsion micelles formed are not so uniform. Figure 6(b) shows the micelle size distribution on DLS data of corresponding emulsion solution of $A_{110}B_{230}$ at 25°C . This profile has unimodal distribution (particle diameter $D_h = 780$ nm). The pore size of the film obtained is in well agreement with such micelle size.

Next, we examined the effect of organic/aqueous solvent phases on the formation of emulsion micelles. The emulsion solution of $A_{110}B_{230}$ diblock copolymer was prepared in $\text{CHCl}_3/\text{H}_2\text{O}/\text{THF}$ [100/5/10 (v/v)] ternary system. Figure 7(a) shows the top view of SEM photograph for the film specimen. It is found from this photograph that highly ordered hexagonal microspheres are clearly visible for the sample surface. Figure 7(b) shows pore size distribution of this specimen. The average pore size (D_n) is estimated to be 850 nm and the pore size distribution ($D_w/D_n = 1.10$) is very narrow. THF is miscible with both CHCl_3 and water. Therefore, the addition of THF was speculated to promote uniform micelles in immiscible $\text{CHCl}_3/\text{H}_2\text{O}$ mixed solvent as well as the effect of phase transfer catalyst. Figure 7(c) shows the micelle size distribution on DLS data of corresponding solution of $A_{110}B_{230}$ at 25°C . This profile has unimodal distribution ($D_h = 2200$ nm). However, the micelle size is extremely larger than the pore size obtained ($D_n = 850$ nm). As mentioned earlier, the average micelle size was 780 nm, when $\text{CHCl}_3/\text{H}_2\text{O}$ was used [see Fig. 6(b)]. It seems that

the rearrangement of emulsion micelles occurs during solvent evaporation, because ternary solvent composition changes in the process of solvent evaporation. A problem concerning the kinetics of how the micelles developed when the solvents evaporated has been left unsolved.

The emulsion-induced mechanism (see the schematic illustration in Fig. 8) of formation of highly ordered pore morphology can be speculated as follows. The PEO-*block*-PBIC diblock copolymers form spherical micelles, consisting of a PEO core and a PBIC corona, because CHCl_3 fraction is too high. 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.²³ Subsequently, the leaving gaps among micelles are filled by PBIC block chains on a corona through the evaporation of organic solvents such as CHCl_3 and THF. At last, water within hydrophilic PEO core is vomited through the film matrix. PEO phase also deforms to hexagonal shape. Thus deformation behaviors were also observed in latex film²⁴

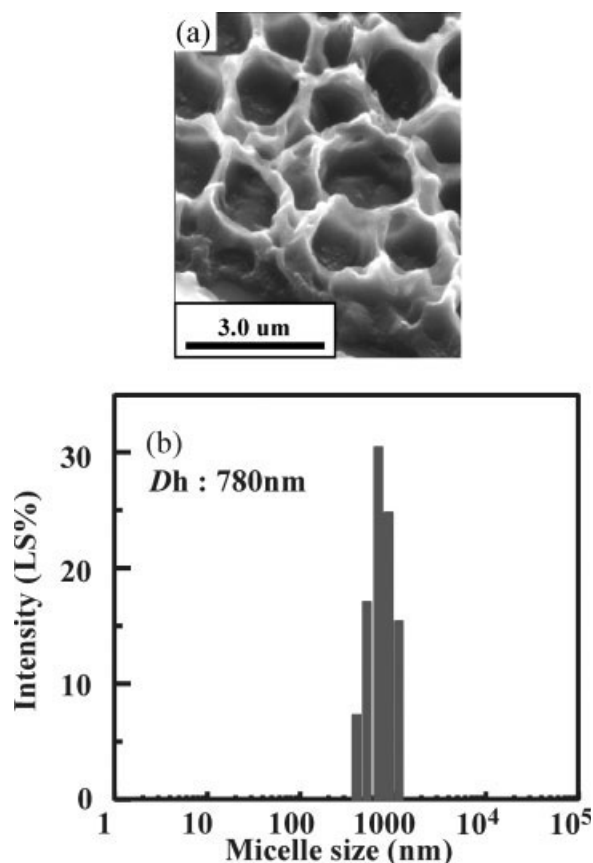


Figure 6 Top view of SEM photograph of microporous film $A_{110}B_{230}$ prepared by emulsion micelles [$\text{CHCl}_3/\text{H}_2\text{O} = 100/5$ (v/v)] (a) and size distribution on DLS data in 0.1 wt % $\text{CHCl}_3/\text{H}_2\text{O}$ [100/5 (v/v)] solution at 25°C .

and crosslinked core-shell nanospheres.²⁵ An important question of why the leaving gaps are filled with rod PBIC blocks has been left. In general, rod-coil diblock copolymers such as poly(*n*-hexyl isocyanate)-*block*-PS showed a zig-zag lamellar morphology.¹⁸ In fact, the cast film (CHCl₃ solvent) of A₁₁₀B₂₃₀ diblock copolymers used in this work also

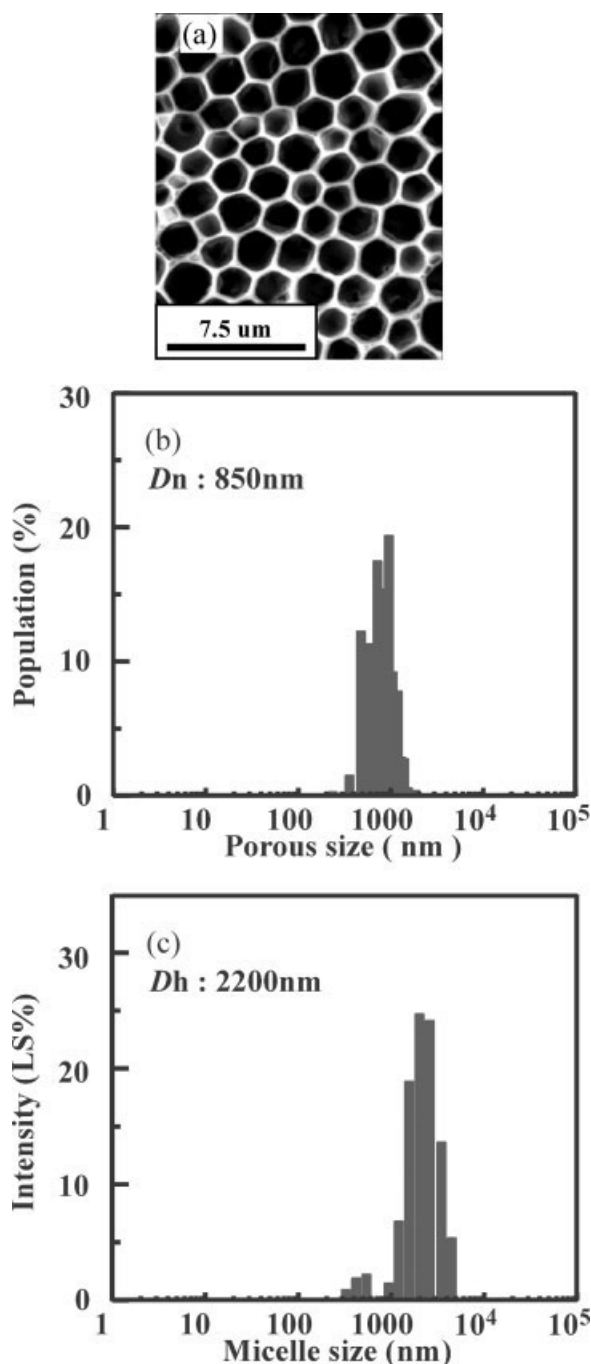


Figure 7 Top view of SEM photograph (a), pore size distribution (b) of microporous film A₁₁₀B₂₃₀ prepared by emulsion micelles [CHCl₃/H₂O/THF = 100/5/10 (v/v)], and size distribution on DLS data in 0.1 wt % CHCl₃/H₂O/THF [100/5/10 (v/v)] solution at 25°C.

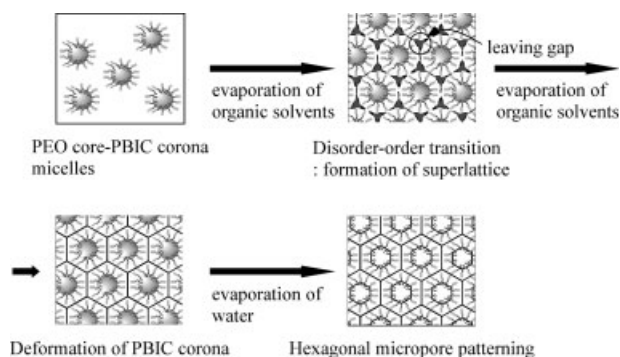


Figure 8 Schematic illustration of a microporous film of diblock copolymer by emulsion-induced method.

showed a zig-zag-like lamellar morphology. PBIC may not behave as the rigid polymer, because this polyisocyanate takes dynamic helical conformation in solution. Then, the generation of microporous films by emulsion-induced method seems universal phenomena for amphiphilic coil-coil diblock copolymers.

CONCLUSIONS

Ordered microporous films are constructed using PEO-*block*-PBIC amphiphilic diblock copolymers by emulsion-induced and water-assisted methods. Especially, emulsion-induced method is a new route to construct the ordered microporous films based on the superlattice formation of emulsion micelles. The pore sizes may be possibly controlled by micelle sizes, i.e., M_n of diblock copolymers. This work raises the possibility that such microporous structures would be formed by general coil type of amphiphilic diblock copolymers.

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