Patterned Surfaces in Self-Organized Block Copolymer Films with Hexagonally Ordered Microporous Structures

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Abstract: A novel fabrication of the patterned surfaces in the polymer films was demonstrated by using the self-organizing character of the block copolymers of polystyrene-*b*-oligothiophenes and polystyrene-*b*-aromatic amide dendron. Hexagonally arranged open pores with a micrometer-size were spontaneously formed by casting the polymer solutions under a moist air flow. The amphiphilic character of the block copolymers played the crucial role as a surfactant to stabilize the inverse emulsion of water in the organic solvent, and subsequently the aggregated structure of the hydrophilic oligothiophene or aromatic amide dendron segments remained on the interiors of the micropores. The chemical composition on the top of the surface of the microporous films was characterized by energy-filtering transmission electron microscopy (EFTEM) or a time-of-flight secondary ion mass spectrometer (ToF-SIMS). The characterizations clearly indicated that the patterned surfaces in the self-organized block copolymer films with the hexagonally ordered microporous structures were fabricated in a single step.

Keywords: block copolymer, patterned surface, microporous structure, oligothiophene, dendron.

Introduction

As feature sizes in advanced technology devices such as microelectronic and optic devices or biosensors are scaled down, suitable new organic and polymeric materials must be developed for the requirements. In particular, nano- or micro-patterning of self-assembled monolayers or polymer films is an essential part of these applications.[1-11] Simultaneously, fabrication of the surfaces tailored and nano- (micro-) patterned with complex organic functional groups has also become increasingly important in these applications especially for the signal transduction or the molecular recognition.[10,12] In most cases, however, it requires tedious combining techniques with multi-steps to achieve this kind of fabrications except for the micro contact printing of self-assembled monolayers.[11,13] Thus, it is important to develop the further facile new approaches for creating such a patterned surface in a variety of organic and polymeric films.

A possible strategy is the use of self-organizing character of polymeric materials especially block copolymers to

produce the patterned surfaces.[14,15] We recently reported the abilities in polystyrene-*b*-oligothiophene block copolymers (PS-*b*-OT) to form the micrometer-sized hexagonally ordered porous structure and the patterned heterogeneous surface with complexes of polystyrene and oligothiophene simultaneously via the self-organization. The films were prepared by casting a polymer solution under a moist air flow on a variety of substrates such as glass slides, silicon wafers, and polyimide films. In this case, the moist air flow provides the micro-droplets of water that work as a template for the micropores in the condensing and self-assembling block copolymer solution.[14-20] After evaporation of the solvent and water, we characterized by using a time-of-flight secondary ion mass spectrometer (ToF-SIMS) that the oligothiophene segment still remained at the interiors of the micropores, which had been the interface with the water droplets until the evaporation completed.[15] The amphiphilic character of PS-*b*-OT would play the crucial role as a surfactant to stabilize the inverse emulsion of water in the organic solvent during the formation of the micrometer-sized hexagonally ordered porous structure. This simple self-organizing approach could be one of the efficient methods to create the

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chemically and topologically patterns on the surfaces of the films.

In our continuing investigation of the versatility of this study, herein, we report a successful fabrication of more elaborate the patterned surfaces over areas in the square centimeter range by self-organization of PS-*b*-OT and polystyrene-*b*-aromatic amide dendron block copolymer with carboxyl end groups (PS-*b*-AAD). The characterization of the patterned surfaces was carried out by using ToF-SIMS and energy-filtering transmission electron microscopy (EFTEM).

Experimental

Materials. Unless otherwise noted, all reagents were purchased from Aldrich, Tokyo Kasei Kogyo Co. (TCI), and Wako Pure Chemical Industries (WAKO), and used without further purification. Styrene was purified by washing with NaOH aq (1 M) to remove inhibitor before stirring with CaH$_2$ for 24 h, then vacuum-distilled. Tetrahydrofuran (THF) was distilled over sodium/benzophenone. Toluene was distilled over CaH$_2$. CuCl was used after washing with 2 M HCl aq. and water, then dried in *vacuo* at 150 °C for 24 h. Silicon wafers or glass slides were used as received.

Polystyrene-*b*-Oligothiophene Block Copolymers (PS-*b*-OT)s. A series of polystyrene-*b*-oligothiophene block copolymers (PS-*b*-OT)s, polystyrene-*b*-quaterthiophene (PS-4T), polystyrene-*b*-sexithiophene-*b*-polystyrene (PS-6T-PS), and quaterthiophene-*b*-polystyrene-*b*-quaterthiophene (4T-PS-4T), was used. PS-4T (GPC: M_w=3,330 and M_w/M_n= 1.08, MALDI-ToF-MS: M_w=2,710 and M_w/M_n=1.05), PS-6T-PS (GPC: M_w=7,760 and M_w/M_n=1.12, MALDI-ToF-MS: M_n=5,140 and M_w/M_n=1.08), 4T-PS-4T (GPC: M_n= 4,070 and M_w/M_n=1.08, MALDI-ToF-MS: M_n=4,820 and M_w/M_n=1.10). A description of synthesis is given in ref. 15. The corresponding chemical structures are shown in Scheme I.[15]
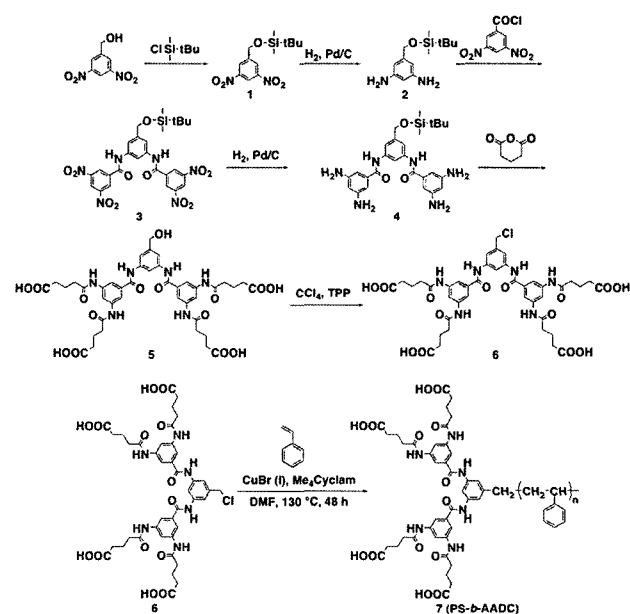
Polystyrene-*b*-Aromatic Amide Dendron with Carboxyl End Groups (PS-*b*-AAD). The PS-*b*-AADs were
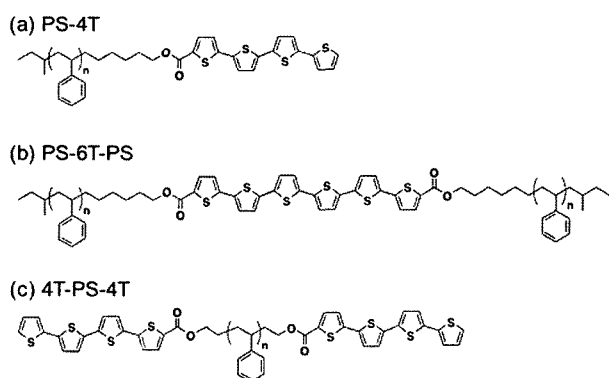
prepared by atom transfer radical polymerization (ATRP) of styrene in the presence of the aromatic amide dendron (ADD) as a dendritic initiator. The procedure is as follows.

The dendritic initiator of ADD **6** was synthesized according to Scheme II. A solution of *t*-butyldimethylchlorosilane (12.66 g, 84 mmol) in DMF (30 mL) was added dropwise to a solution of 3,5-dinitrobenzylalcohol (13.87 g, 70 mmol) at room temperature, and stirring was continued at this temperature for 3 h. The reaction mixture was poured into a large amount of water, and then the precipitation was filtered, washed with water several times. The product was dried in *vacuo* at 50 °C for 24 h to give **1** (Yield: 99%). The compound **1** (9.37 g, 30.0 mmol) was stirred in the presence of 10% Pd/C (3.19 g, 5 mol%) in ethanol under hydrogen atmosphere at room temperature for 48 h. The solution was filtered through celite, and then evaporated to dryness. The product was collected and dried in *vacuo* at 50 °C for 24 h to give **2** (Yield: 91%). To a solution of compound **2** and triethylamine (8.33 mL, 60 mmol) in THF (200 mL) was added dinitrobenzoyl chloride (16.6 g, 72 mmol), and stirring was continued at room temperature for 6 h. The solution was poured into a large amount of water, and the precipitation was filtered. The product was washed by refluxing a mixture solvent of ethanol/*n*-hexane (v/v=1/2) to give **3** (Yield: 88%). The reduction of **3** was carried out the same procedure that used for the synthesis of **2** to give **4** (Yield: 79%). To a solution of **4** (1.04 g, 2 mmol) in DMAc (15 mL) was added glutaric anhydride (1.36 g, 12 mmol) and the mixture was stirred under nitrogen atmosphere at room temperature for 5 h. The solution was poured into 1 M HCl aq. solution to give product **5** (Yield: 80%, MALDI TOF MS: *m/z* calcd

(a) PS-4T

(b) PS-6T-PS

(c) 4T-PS-4T

Scheme I. Chemical structures of polystyrene-*b*-oligothiophene block copolymers (PS-*b*-OT).

Scheme II. Synthesis of polystyrene-*b*-aromatic amide dendron with carboxyl end groups (PS-*b*-ADD).

for $C_{41}H_{46}N_6O_{15}$ 885.84 (M+Na$^+$), found 884.14 (M+Na$^+$)). A solution of **5** (0.129 g, 0.15 mmol) in DMF (3 mL) was added to a solution of carbon tetrachloride (0.231 g, 1.5 mmol) and triphenylphosphine (0.393 g, 1.5 mmol) in DMF (2 mL) and the mixture was stirred at room temperature for 48 h. The solution was poured into a large amount of chloroform, and the precipitation was filtered and washed with chloroform. The precipitation was dissolved in dilute NaOH aq. and filtered off, then 1 M HCl aq. was added to precipitate again. This was repeated three times to give product **6** (Yield: 86%, MALDI TOF MS: *m/z* calcd for $C_{41}H_{45}Cl_1N_6O_{14}$ 904.28 (M+Na$^+$), found 904.20 (M+Na$^+$)).

A dry round bottomed flask was charged with CuCl, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me$_4$Cyclam), styrene (1 mL, 8.73 mmol), DMF, and a magnetic stir bar (initiator/Copper halogen/ligand = 1/1/8). The flask was sealed with a rubber septum and degassed by three freeze-pump-thaw cycles. The flask was immersed in an oil bath and stated at 130 °C, and the dendritic initiator **6** was added. After the polymerization, the solution was poured into a mixture of methanol and 1 M HCl aq. (v/v=9/1). The resulting polymer was collected, washed with methanol, and dried in *vacuo* at 40 °C for 24 h. A number-average of molecular weight and the polydispersity index (PD) of the polymer **7** were estimated by gel permeation chromatography (GPC) in THF. The M_n and PD values were 30,500 and 1.35, respectively.

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). ToF-SIMS analysis was performed using a TRIFT III (ULVAC-PHI) spectrometer. Negative ion spectra and images were recorded using a 15 keV primary beam of ^{69}Ga$^+$ liquid metal ion at a current of 2 nA with a pulse width of 18.0 ns. The spectra and images were acquired for 10 min from a 100 m^2 surface area with a primary ion dose of about 1×10^{12} ions/cm^2. A low-energy pulsed electron gun (28.0 eV) was used for surface charge compensation.

Scanning Electron Microscopy (SEM). An environmental scanning electron microscope (ESEM) (Philips XL20 ESEM-FEG) equipped with a field emission gun was used. In order to observe the structure without conductive coating, ca. 0.8 Pa of water vapor was introduced in the sample chamber of the ESEM to prevent charge build-up. 5 to 6 keV of electron beam was used for the observation to obtain secondary electron images.

Energy-Filtering Transmission Electron Microscopy (EFTEM). A leo922 Energy-filtering transmission electron microscope (EFTEM), with which an omega-type electron spectrometer is equipped, was operated at an acceleration voltage of 200 kV to observe the cross-sections of the films. For specimen preparation, the polymer solution was cast on a cured epoxy plate (Queto812), and then it was embedded in the same epoxy resin to be cured at 60 °C overnight. Sections of 50 nm thickness were cut by ultramicrotomy. Energy-filtered images were acquired by 2 K × 2 K slow scan

CCD camera.

Results and Discussion

Micropatterned Oligothiophene Surfaces. To clarify the effect of the primary block copolymer structures for formation of the micrometer-sized hexagonally ordered porous structure in the films, three different types of (PS-*b*-OT)s were used, namely PS-4T, PS-6T-PS, and 4T-PS-4T.[15]

Based on our previous reports, the microporous films were prepared by casting a 0.25 wt% polymer solution (0.2 mL) in carbon disulfide at room temperature (23 °C) under a moist air flow on a variety of substrates such as glass slides, silicon wafers and polyimide films. The humidity and flow rate were kept at 85% and 3.0 L min^{-1}, respectively. The solvent and water completely evaporated within 30 sec, and the films formed over an area of 2~3 cm^2. Interference color appeared on the solution surface immediately after a moist air flow started, indicating the formation of ordered structure of water droplets of an order of micron with a narrow size distribution. The formation of hexagonally packed micropores was clearly observed in the SEM images of the films of PS-4T and 4T-PS-4T in Figure 1(a) and 1(c), respectively. The open porès on the surfaces showed of the extremely narrow size distributions, and the diameters of PS-4T and 4T-PS-4T were approximately 1.7 and 2.1 μm, respectively. When the concentration of the polymer solution increases from 0.25 to 0.50 wt%, the diameters of open pores of these polymer films became smaller to approximately 1.0 and 1.2(micro)m, respectively. On the other hand, a 0.10 wt% polymer solution led to form the micropores with larger pore sizes approximately 3.5 and 3.7 μm, respectively. Furthermore, the diameters can be also controlled by changing the humidity of the moist air flow. When the humidity only changed from 85% to 70%, the pore sizes of PS-4T and 4T-PS-4T decreased to approximately 0.8 and 1.0 μm, respectively. In contrast, 90% humidity provided approximately 2.8 and 3.4 μm, respectively. In contrast, PS-6T-PS failed to show a periodic micro-porous structure in the film as seen in Figure 1(b) regardless of our exploring the optimum film preparation condition such as humidity, solution concentration and solvents. The interference color did not appear clearly on the way of this film formation. These findings indicate that the block copolymers with oligothiophene segment termini, which are more hydro-philic than PS, effectively stabilize the water droplets with the narrow size distribution while the mid oligothiophene segment does not work as emulsifier. This could be due to the aggregation of oligothiophene termini at the interface between the solutions and water droplets. It seems to be difficult for PS-6T-PS to form the stable interface layer compared with PS-4T and 4T-PS-4T because of the center position of the oligothiophene segment in the polymer structure and the rigidity of 6T. We also consider that the molecular weights and fractions of the oligoth-
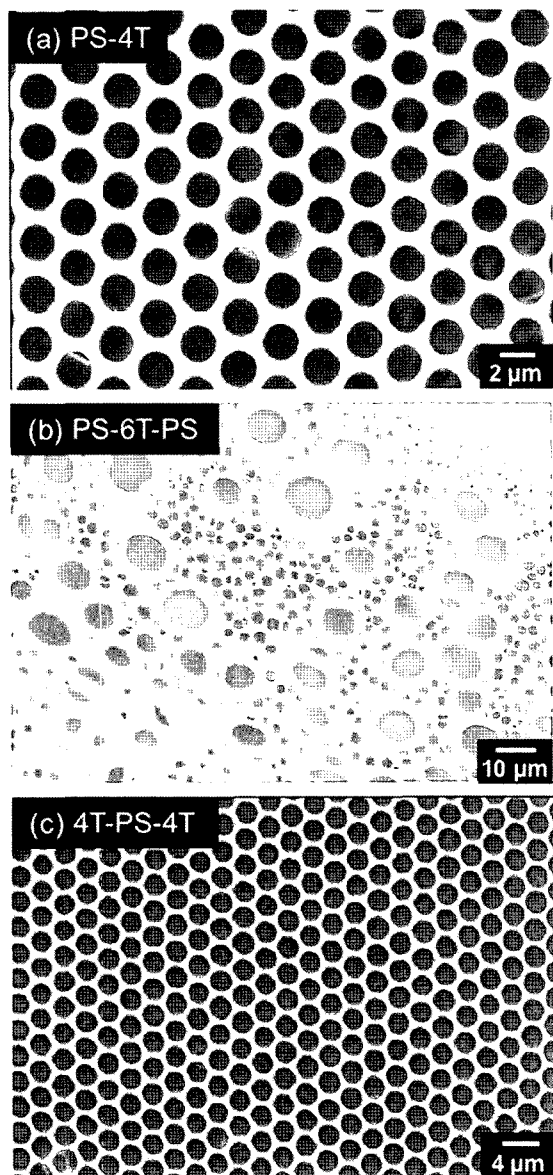
Figure 1. SEM images of microporous structures for (a) PS-4T, (b) PS-6T-PS, and (c) 4T-PS-4T.
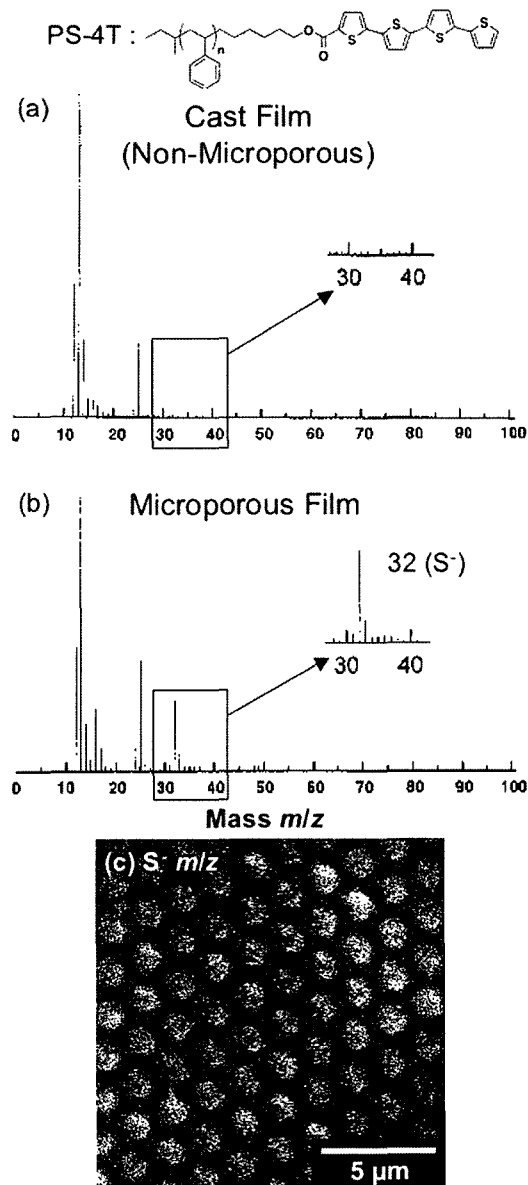

Figure 2. TOF-SIMS spectrum and image of PS-4T film with microporous structure. (a) Negative ion spectrum for non-microporous film, (b) Negative ion spectrum for hexagonally ordered microporous film, (c) Mapping image of m/z 32 (S⁻). The bright color section shows stronger secondary ion intensity of 32.

iophene segment may also be the important factors for forming the stable interface layer, this experiment is now under investigation.

To characterize the surface structures, we use a scanning electron microscope (SEM) to confirm the topological porous structure in micrometer scale and a ToF-SIMS to map the chemical composition of the top surface (within 1 nm) to prove the chemical heterogeneity. ToF-SIMS was employed to measure the chemical composition on the top of the surface of the microporous PS-4T film. ToF-SIMS has a high surface sensitivity of 10-20 Å for organic molecules with a submicrometer lateral resolution, which enables us to map the surface chemical composition of our microporous struc-

ture.[21] The surface sensitivity is essential for this study because the surface 4T layer is expected to be only approximately 15 Å of the quarterthiophene termini, even if 4T molecules align perpendicular to the surface. A film with the non-microporous structure casted from the same polymer solution of PS-4T without a moist air flow was used for the reference sample. As shown in Figure 2(a), the secondary ions from the surface were identical to those of homo polystyrene. The oligothiophenes are not present in the top 10-20 Å of the surface of the non-microporous film. Hence,

this surface is covered with PS segment. However, from the microporous films, the remarkable characteristic peak in negative ion in Figure 2(b) was found at $m/z = 32$, which is assigned to S⁻. Obviously the source for S⁻ must be oligothiophenes. Since the intensity of S⁻ is strong enough to be mapped spatially within the static SIMS limit, we are able to resolve the in-plane distribution of the oligothiophenes.

The characteristic secondary ions of m/z 32 (S⁻) are mapped in Figure 2(c), where brighter areas have stronger secondary ion intensity of 32. The image clearly indicates hexagonally packed brighter circles, which correspond to oligothiophenes of 4T. The size and shape of the all circles are almost uniform and the diameter is approximately 2 μm, which is a good agreement with that of the SEM image. This image clearly indicates that the oligothiophene of PS-4T forms the aggregated structure on the interiors of the micropores while the real surface is covered with polystyrene as expected. It should be emphasized that such a patterned surface in the hexagonally ordered microporous film is fabricated in a single step via self-organization of the block copolymers under a moist air flow. No other high-tech pieces of apparatus are required. The ToF-SIMS results also indicated the block copolymer partitions itself at the interface between the polymer solution and water droplets during the microporous film formation.

Micropatterned Polar Polymer Surfaces with Carboxyl Groups. Based on the above results of PS-4T, we next attempt to create a stable hydrophilic surface which composed of a large number of polar functional groups at the interiors of micropores. Because polar polymer surfaces possessing polar functional groups such as hydroxyl, carboxyl or amino groups are widely utilized for biocompatible materials for the introduction of biologically active surfaces, surfaces that resist protein absorption and sensor molecules for molecular recognition and signal transduction. Many of these applications also often require submicron- or micron-level two-dimensional arrays, which the surfaces covered with complex organic functional groups such as polar and non-polar functional groups for developing the biological integrated devices. However, in general, it is difficult to create a polar surface which is composed of a large number of polar groups in polymeric materials because any non-polar groups in the polymer must be masked at the air-solid (film) interface to produce a low energy thermodynamically stable surface. Furthermore, one critical problem, surface reconstruction, limits the creation of stable polar polymer surfaces with polar functional groups.

To remedy these problems, we designed and prepared a novel aromatic dendronized block copolymer, polystyrene-*b*-aromatic amide dendron with carboxyl end groups, named as PS-*b*-ADD (a number-average of molecular weight M_n 30,500, polydispersity index PD 1.35). The same film preparation technique of self-assembly templating process with water droplets can be produced the formation of periodic
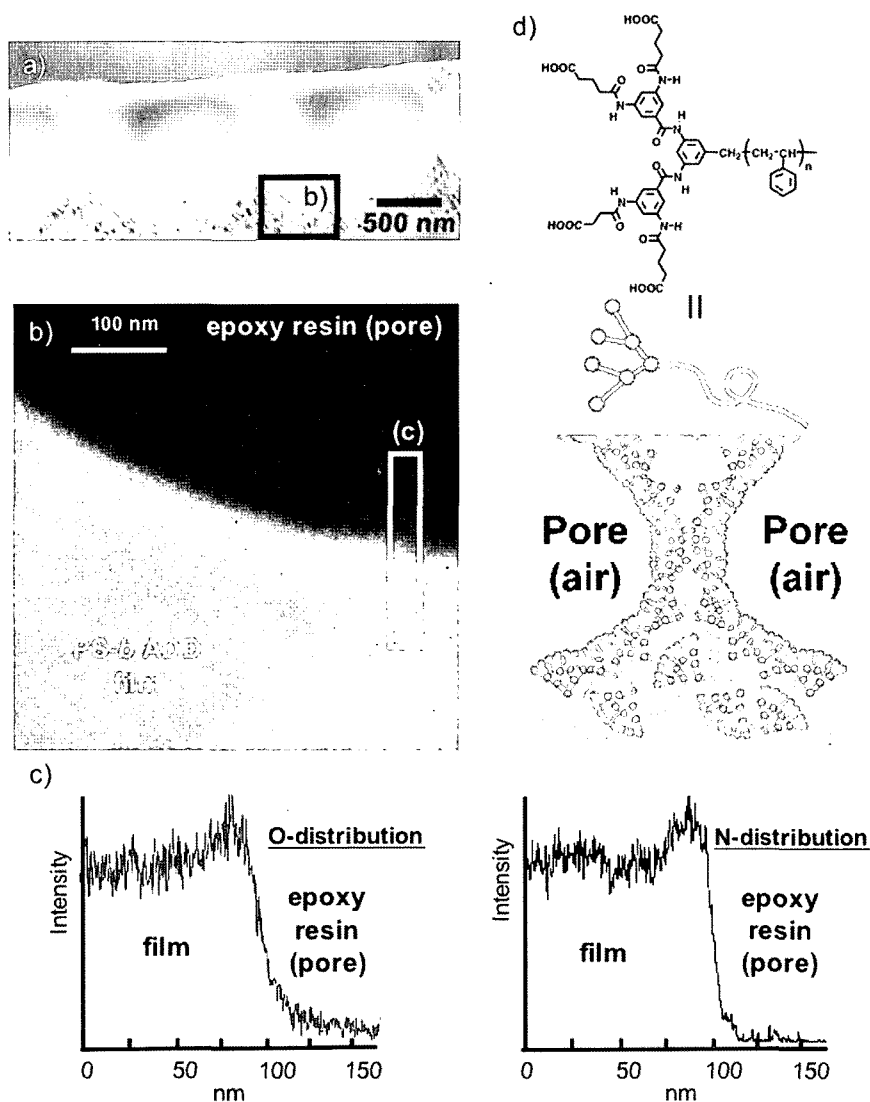
microporous structure of PS-*b*-ADD, in which the interiors of the micropores are covered with the carboxyl groups of the aromatic amide dendron termini. Branching structure of the aromatic amide dendron would play a role to avoid the reconstruction of the carboxyl groups on the top of the surface of micropores because of the intra- or intermolecular interactions of the aromatic amide groups.

Films were prepared from 0.1 mL of a 0.5 wt% polymer solution in toluene on glass slides or silicon wafers by casting at room temperature under a moist air flow. The solvent completely evaporated within 60 sec, and a periodic microporous structure was obtained in the entire film (Figure 3). Observations under a SEM confirmed the formation of hexagonally packed micropores with a narrow size distribution. The diameter of the open pores on the surface is approximately 0.5 μm.

This microporous film was sectioned perpendicular and horizontal to the substrate to give thin specimens which, after embedding in epoxy resin, were observed under an EFTEM. Elemental distribution maps were created using the three-window exponential law, using the energy windows at 364, 384 and 406 eV for the nitrogen map, and 476, 512 and 542 eV for the oxygen map. The intensity profiles shown at the interface between the micropores of PS-*b*-ADD and the epoxy resin were obtained from the nitrogen and the oxygen distribution maps along the line shown in the corresponding image in Figure 4. It was revealed that the intensities of both of the nitrogen and the oxygen distributions around the surface of the micropores are higher than the other region in the film. It should be emphasized that the aromatic amide dendron with carboxyl end groups
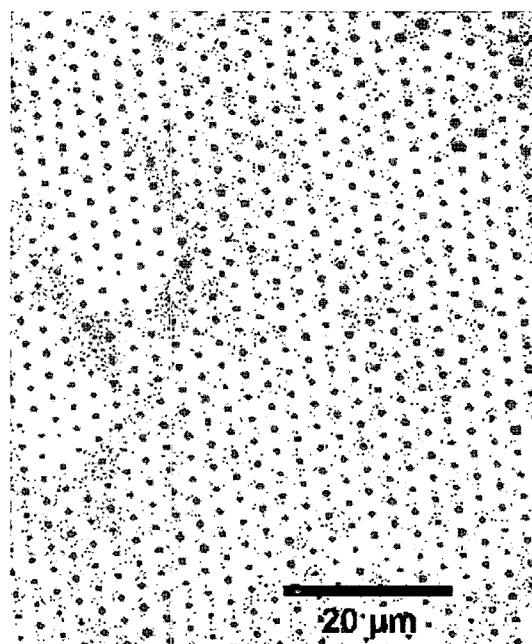
Figure 3. SEM image of microporous structure of PS-*b*-ADD.

Figure 4. Microporous structure of PS-*b*-ADD. a) SEM image of perpendicularly cross-sectioned film to the substrate, b) EFTEM image of cross section of the microporous film, c) Oxygen and nitrogen distribution profiles of the line of (c) in b) of TEM image, d) Schematic representation of patterned surface in PS-*b*-ADD film.

forms the aggregated structure on the interiors of the micropores.

Conclusions

In a summary, a novel method to make a patterned surface in polymer films has been developed using the self-organizing block copolymers. The polystyrene based block copolymers having oligothiophene and aromatic amide dendron termini formed hexagonally packed micropores in the films via a self-assembly templating process with water droplets. We observed using the ToF-SIMS imaging the periodic oligothiophene chemical pattern, in which only the interiors of the micropores are covered with oligothiophenes, in the top 10-

20 Å layer of the surface. The segregated structure of the aromatic amide dendron with carboxyl end groups at the top surface of the micropores was found by the intensity profiles of the nitrogen and the oxygen distribution maps of EFTEM images. The patterned surfaces can be further designed and tuned by the choice of blocks to offer very promising applications such as microelectronics, light-emitting diodes, photonic crystals, and biosensors.

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