Nanoporous structures templated from block copolymer morphologies

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Abstract. We studied nanoporous structures templated from block copolymer morphologies using carbon dioxide swelling and de-swelling. The volume where carbon dioxide occupied turns into empty space after de-swelling. As a pressure of carbon dioxide increases, the effective volume fraction of block copolymer changes due to the selectivity of carbon dioxide. The swollen morphology of block copolymer changes from its original neat morphology and a variety of nanoporous structures appear after de-swelling. Consequently, unique nanoporous structures depending on the process pressure were obtained.

1. Introduction
Block copolymers have been studied primarily due to their unique self-assembled morphologies with a size scale of tens of nanometers. For diblock copolymers, which have the simplest architecture among various kinds of block copolymers, spheres with body centered cubic symmetry, cylinders with hexagonal symmetry and one dimensionally periodic lamellae have been known as thermodynamically allowed morphologies for decades. In the late 1990’s, a bicontinuous cubic phase known as double gyroid was added to the equilibrium morphologies.

Fabrication of nanostructures has been receiving strong attention in fundamental science as well as in industrial applications.[1,2] However, large-area structured surfaces and thin films on the nanometer scale still remains a challenge for conventional fabrication methods. In order to overcome the difficulties of large-area production, molecular self-assembly has been considered to be a serious candidate. One of such self-assembled materials is block copolymer, which has been considered for nano-technological applications not only due to the scale of the nanodomains, but also the convenient tunability of size, shape, and periodicity by changing their molecular structures.[3-6] However, available size, shape and symmetry in block copolymer templating are restricted by the molecular structures; therefore, fine-tuning requires precisely controlled polymerization.

Supercritical carbon dioxide is an inexpensive, non-toxic and non-flammable fluid, which was widely applied for materials synthesis and process.[7] Gas-like diffusivities, the continuously tunable solvent power and selectivity, and the complete elimination at the end of the process make carbon dioxide very attractive.[8] Particularly, carbon dioxide has been used to make microcells, cells with a
diameter of the order of micrometer.[9-11] However, reducing the size and obtaining non-spherical shapes have been a big challenge. Our group has, nevertheless, demonstrated that carbon dioxide can be used to fabricate nanometer scale cells using fluorinated block copolymers as templates for CO₂ foams. CO₂ was used as a porogen to introduce nanometer cells and pores in the nanodomains of bulk and thin film of block copolymers having fluorinated blocks.[12-15] The key to the successful introduction of nanometer cells and pores is selective swelling of the CO₂-philic fluorinated block domains with CO₂. After complete removal of CO₂, the volume occupied with CO₂ turns into empty voids. The size of cells can be tuned by changing process conditions with the same template. Moreover, this methodology can be applied to thin films [13,14] as well as monoliths and also to another sphere forming non-fluorine bcp, a block copolymer of polystyrene and CO₂-philic polydimethylsiloxane.[16] Here we report that selective swelling with CO₂ of bcp thin films induces morphological changes and results in unique non-spherical nanostructures that differ from the original bcp morphology.

2. Experimental

2.1. Polymer Synthesis and Sample Preparation.
We synthesized polystyrene-\(b\)-poly(perfluorooctylethyl methacrylate) (PS-PFMA) with two different block fractions by sequential living anionic polymerization. The molecular weights of blocks in two PS-PFMAs are 20,000-13,000 and 10,000-7,670 g mol\(^{-1}\).[15] The molecular weights of the PS blocks were determined by gel permeation chromatography, and the molecular weights of the PFMA blocks were determined by \(^1\)H-nuclear magnetic resonance. Two PS-PFMAs were mixed in order to adjust the average volume fraction of PFMA to 33 vol% and named as PSPFMA33.

\(\alpha,\alpha,\alpha\)-trifluorotoluene (Aldrich) was used as spin-casting solvents, and were named as TFT. 500-nm-thick PS-PFMA films were prepared by spin-casting of those solutions onto silicon wafers. The silicon wafers (Shinetsu Co.) were used as received.

2.2. \(sc\)CO₂ Process.
A stainless steel high-pressure vessel for CO₂ processes was connected to a high-pressure liquid chromatography pump (JASCO PU-2086 plus) with a cooling head and to a back-pressure regulator (JASCO SCF-Bpg). Films of PS-PFMA were placed in the high-pressure vessel at 60 °C for 30 min with a constant pressure. The vessel was placed in an ice bath to quench the films to 0 °C while maintaining the pressure using the pump and regulator. After the temperature and pressure were stabilized, pressure was released. The depressurization rate was controlled at 0.5 MPa/min.

2.3. Spectroscopic Ellipsometry.
Film thickness and refractive index were measured with a JASCO M-220 ellipsometer with incident light in a wavelength range of 400-800 nm at an incident angle of 60° with respect to the surface normal. The refractive indices of the nanocellular thin films were computed assuming constant refractive indices throughout the films.

2.4. Reactive Ion Etching.
The etching process to expose embedded nanostructures to the surface was performed with a reactive ion etcher (SAMCO compact etcher FA-1) with a CF₄ flow rate of 2 mL/min, a pressure of 10 Pa, and a power density of 10 W/cm². Under this condition, the etching rate for PS-PFMA copolymer thin films is \(\sim\)1 nm/s.

2.5. Scanning Electron Microscopy.
Films were fractured in the liquid nitrogen in order to expose the internal structures to the surface. The cyro-fractured surface was obtained using an environmental scanning electron microscope (ESEM) (Philips XL20 ESEM-FEG) equipped with a field-emission gun under high-vacuum conditions. A 10
keV electron beam was used for the observation. No conductive coatings were applied onto the specimen surfaces.

2.6. Grazing incident small angle X-ray scattering (GISAXS).
GISAXS experiments were conducted at 15A beamline of Photon Factory in KEK. A sample was placed in a vacuum chamber with Kapton windows on a computer controlled goni stage. The X-ray beam impinges at a small incident angle $\alpha$ onto a thin film supported on a substrate. The scattered X-ray was detected with an image intensifier accompanied with a two dimensional charge coupled device camera. Experimental detail of GISAXS at SPring-8 can be found elsewhere\textsuperscript{13}. The wave vectors are defined as $q_y= (2\pi/\lambda)\sin \theta \cos \beta$ and $q_z= (2\pi/\lambda)(\sin \alpha + \sin \beta)$, where $\theta$ is the inplane angle, $\alpha$ and $\beta$ are incident and scattered vertical angles to the surface plane, respectively, and $\lambda$ is a wavelength (1.5Å).

3. Results and Discussion
The mixture of PS-PFMAs described in the Experimental section was dissolved in TFT and then spin-casted onto silicon wafers. A typical thickness of those films was 500 nm, which was measured by ellipsometry. The thin films were then placed in a high-pressure vessel and pressurized with carbon dioxide as described in the experimental section for 30 minutes at a various pressure and at 60 °C. Then the whole vessel was placed in an ice bath to reduce temperature down to 0 °C and to freeze the swollen morphology by the glass transition of PS in carbon dioxide. Carbon dioxide pressure was then slowly reduced to remove carbon dioxide without destroying the structures of the block copolymer.

Previously, we reported that this mixture of block copolymers presents the nanosheet structure parallel to the substrate when processed with 8 MPa of carbon dioxide.[15] We further increased the carbon dioxide pressure to swell the block copolymer film and then removed carbon dioxide. An example of the SEM images of the films processed at 10 MPa of carbon dioxide is shown in Figure 1. The thin film on substrate was scratched at liquid nitrogen temperature and processed with RIE to provide a cross-sectional view of the films. Similar to previously obtained nanosheet structure, we again find nanosheets stacking on silicon substrate. However, the morphology is not as homogeneous as that at 8 MPa [15] and many defects are observed. It should be noted that SEM does not observe the domains of block copolymers due to lack of electron density contrast between the domains but observe the topographical structures on the surface. Therefore, the structures here are planar pores or nanosheets stacking on a substrate. Such structure is confirmed with the GISAXS pattern shown in Figure 1b. All the Bragg peaks appear on the $q_z$ axis, which indicate the periodic structure perpendicular to the surface. The peaks are assigned to two sets of integer multiples of the first order peaks of direct and reflected components. The GISAXS pattern of this film is essentially the same as in that in our previous publication [15], where detailed peak assignment can be described.

We further increased the carbon dioxide pressure and found a significantly different structure at 22 MPa. An example of SEM image of the top surface of such structure and its GISAXS pattern are shown in Figure 2a and b. A top layer of nanosheets stacking on a substrate is observed and the orientation of nanosheets is similar to the cross-sectional image of the same copolymer processed at 10 MPa in Figure 1. However, we clearly find that a lot of cylindrical rods are connected to the nanosheets. GISAXS pattern in Figure 2b also shows the disappearing Bragg peaks on the $q_z$ axis, which clearly indicates layered sheets are broken down. The nanosheets are apparently transformed into cylindrical rods similar to the order-to-order transition (OOT) of block copolymer morphology from lamellae to hexagonal cylinders. Although we don’t find any order in the cylindrical rods, the shape of the nano-sized objects obeys the trend of OOT in block copolymers. It is interesting to find that a plane of nanosheets is broken down into cylindrical rods. The structure apparently is in the course of transition and is not in equilibrium. This could be due to the fairly high molecular weight of block copolymers, which reduces the mobility and slows down the OOT process. There is another
possibility of such a mixed structure caused by the mixed block copolymers to adjust the volume fraction. We further increased pressure and checked if this is in the course of OOT or phase separation of two different molecular weight block copolymers showing two different morphologies, i.e. lamellae and cylinders.

As a pressure of saturation increases to 30 MPa, we found that the structure completely changed to cylindrical rods and the nanosheets completely disappeared as shown in Figure 3a. GISAXS pattern in Figure 3b shows no Bragg peaks of the layered sheet structure. Only the strong form factor near the rectangular beam stopper is found. These results suggest that the morphology changed from lamellae to cylinders during the carbon dioxide process and, after carbon dioxide removed, cylindrical rods appeared. It is interesting to note that those cylinders are not ordered at all. They even show branches and form a network. We don’t understand the reason at this point since the structural observation is limited after carbon dioxide is removed. Further in-situ study is necessary to fully understand those phenomena.

Figure 2. Top view of PSPFMA33 thin films casting from TFT after the scCO₂ process at a saturation pressure of 22 MPa. The bar indicates 200 nm. (b) GISAXS pattern of PSPFMA33 thin films casting from TFT after the scCO₂ process at a saturation pressure of 22 MPa. An incident angle was set to 0.2 degree.
Figure 3. Top view of PSPFMA33 thin films casting from TFT after the scCO₂ process at a saturation pressure of 30 MPa. The bar indicates 100 nm. (b) GISAXS pattern of PSPFMA33 thin films casting from TFT after the scCO₂ process at a saturation pressure of 30 MPa. An incident angle was set to 0.2 degree.

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