Horizontally and Vertically Aligned Polymeric Nanosheets: CO_2-Induced Morphological Changes in Block Copolymer Thin Films

We have fabricated a variety of nanoporous structures using the supercritical carbon dioxide assisted block copolymer template (SCBCT) method. SCBCT uses the selective swelling of block copolymer domains followed by complete removal of carbon dioxide, creating empty voids with sizes the same as those of the block copolymer nanodomains. SCBCT also potentially induces an order-to-order transition (OOT) by changing the effective volume fraction. We have recently fabricated thin films of nanosheets composed of block copolymer bilayers templated from lamellar morphologies resulting from an OOT. The structures of these thin films on their substrates have been analyzed using grazing-incidence small-angle X-ray scattering (GISAXS).

Supercritical carbon dioxide (CO_2) is commonly used to swell polymers, and can be conveniently removed at the end of the process by depressurization. The process has been applied to block copolymers (bcps), which are composed of multiple blocky polymers self-assembled into nanodomains. The self-assembled morphologies of block copolymers are unique to the block architectures. However, CO_2 selectively swells the CO_2-philic domains of fluorinated blocks, increases the effective volume fraction of CO_2-philic domains and potentially induces an OOT. In addition, after complete removal of CO_2, the space which was occupied by the CO_2 can be converted to empty space, the fundamental effect of the SCBCT method. The first example of the application of the SCBCT technique was the introduction of spherical nanovoids (nanocells) into spherical CO_2-philic domains [1-5]. In these reports, we demonstrated that the resulting nanopores have the same shape as those of the original bcp domains. No OOT was observed during SCBCT.

We synthesized two batches of polystyrene-*b*-poly(perfluorooctylethyl methacrylate) (PS-PFMA) by sequential living anionic polymerization. The molecular weights of the PS-PFMAs were 13,000-20,000 and 7,670-10,000 g mol^{-1}. We prepared a mixture of the PS-PFMAs to adjust the volume fraction of PFMA to 33 vol%. α,α,α-trifluorotoluene (TFT) and hexafluorobenzene (HFB) were used as spin-casting solvents to prepare 500-nm-thick PS-PFMA films. TFT is a neutral solvent, and HFB a selective solvent for PFMA.

Si wafers coated with the copolymer thin films were placed in a high-pressure vessel and pressurized with CO_2 at 60°C for 1 hour with a saturation pressure of 8 MPa controlled by a backpressure regulator. The vessel was placed in an ice bath to quench the temperature to 0°C while maintaining constant pressure using continuous pumping and back-pressure control. The depressurization rate was 0.5 MPa/min for all the processes.

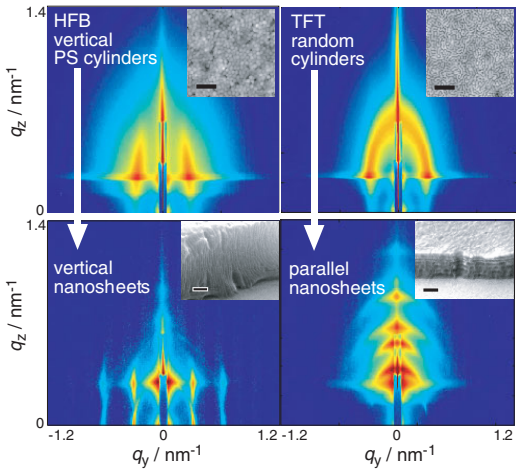

Figure 1
GISAXS patterns of the original (top) and SCBCT (bottom) films. The diffractions in the q_y direction are from in-plane structures, whereas those in the q_z direction are from structures in the depth direction. The scale bars of the AFM images (top) and the SEM images (bottom) are all 100 nm.

GISAXS experiments on the original as-cast films and the films processed by SCBCT were conducted at BL-15A of the PF, and at BL40B2 of SPring-8. In the GISAXS technique the X-ray beam impinges at a small incidence angle α onto a thin film supported on a substrate. 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 θ is the in-plane angle, α and β are the incident and scattered vertical angles to the surface plane, respectively and λ is the wavelength (1.5 Å).

The different morphologies of the PS-PFMA films spun-cast from the two different solvents (HFB and TFT) were obtained, and their GISAXS patterns and AFM in-plane views are shown in the top two panels of Fig. 1. The film from the HFB solution shows perpendicularly oriented PS cylinders, while the film from the TFT solution shows randomly oriented PFMA cylinders. The degree of orientation can be clearly distinguished from the GISAXS patterns. It should also be noted that no lamellar morphologies were found in the as-cast films.

The two films were processed with CO_2 as described above. The GISAXS patterns of the processed films are shown in the lower panels of Fig. 1, along with cross-sectional SEM images of the films. Both films show one-dimensional periodic layered structures, in which characteristic integer multiples of peak positions can be identified. For the parallel nanosheets, two sets of integer multiples of peaks are found due to the diffractions of the direct incident X-ray and of the reflected X-ray. The parallel nanosheets shown in the SEM image diffract X-rays only in the q_z direction, which is normal to the surface plane, as clearly shown in the bottom right panel of Fig. 1. On the other hand, the perpendicularly oriented nanosheets shown in the SEM image diffract X-rays only in the q_y direction, as clearly shown in the bottom left panel of Fig. 1. The GISAXS scattering patterns clearly probe the nanoporous structures, and their orientations persisting over the entire films. The porous structures, which are nanosheets in this case, were fabricated from non-lamellar initial morphologies. It can be concluded that selective swelling with CO_2 induces an OOT, and results in unique nanosheet structures that differ from the original bcp morphologies. In conclusion, horizontally and vertically stacked nanosheet structures of bcp bilayers on substrates were successfully fabricated using the SCBCT technique. The details of this study are published elsewhere [6].

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