Horizontally and Vertically Aligned Polymeric Nanosheets: CO\textsubscript{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).

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\textsuperscript{-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\textsubscript{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.

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 \(q_x = 2\alpha/\sin\theta \cos\theta\) and \(q_z = 2\alpha/\sin\theta \sin\beta\), where \(\theta\) is the in-plane angle, and \(\alpha\) and \(\beta\) are the incident and scattered vertical angles to the surface plane, respectively.

GISAXS patterns of the original (top) and SCBCT (bottom) films. 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 \(q_x\) 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\textsubscript{2} induces an OOT, and results in unique nanosheet structures that differ from the original bcp morphologies. In conclusion, horizontally and vertically stacked nanosheets composed of block copolymer bilayers on substrates were successfully fabricated using the SCBCT technique. The details of this study are published elsewhere [6].

REFERENCES


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