Materials Science

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Real-time observation of photo-induced nanostructural change in photofunctional block copolymers

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Introduction

Many efforts have been made to induce macroscopic alignment of the microphase separated (MPS) patterns of block copolymers from viewpoints of new nanotechnologies. When block copolymers with liquid crystalline nature is employed, the regular MPS structure is formed over large areas by the cooperative effect.

Perpendicular orientation of the MPS nano-cylinders is attained by annealing at temperatures where the azobenzene polymer is in the smectic LC phase without irradiation. The in-plane aligned cylinders are obtained by gradual cooling from isotropic to room temperature while irradiation with linearly polarized light (LPL) at 436 nm is performed. These MPS orientations are interconvertible after a suitable LPL irradiation and heating/cooling processes [1].

The aim of this project is to precisely evaluate the cylinder array pattern and its orientations. Another important attempt of this research is to find conditions of real time observation of the MPS growth and reorientations by light or heating. In this work, polystyrene based azobenzene-containing polymer (PS-*b*-PAz, Fig. 1) is employed.

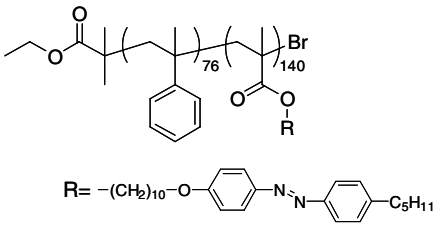

Fig. 1 chemical structure of PS-*b*-PAz

Experimental

Film preparation

Spincast films of PS-*b*-PAz were prepared from a chloroform solution. The morphology of the MPS structure was first evaluated by atomic force microscopy and then subjected to the grazing incidence small angle x-ray scattering (GI-SAXS) measurements in BL-15A of the Photon Factory.

Results and Scope

After annealing the PS-*b*-PAz film, a dot morphology was observed at the surface of the film (Fig. 2a). The GI-SAXS measurement provided peaks at 0.288° (*d*=29.7 nm) in the in-plane direction (Fig. 3), clearly indicating that the cylinder array is oriented perpendicular to the substrate surface. The spacing agreed well with the morphology observed by AFM.

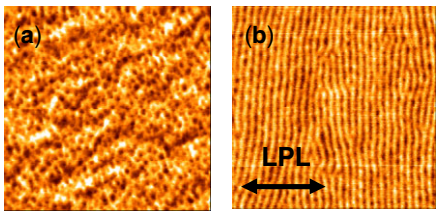

Fig. 2 AFM phase images of PS-*b*-PAz thin film before (**a**) and after (**b**) polarized Vis irradiation.

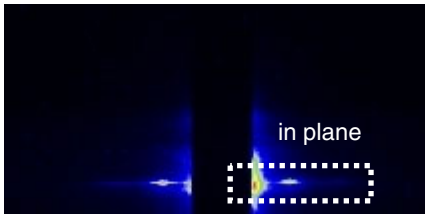

Fig. 3 GISAX image of a cylindrical microphase separated film.

After irradiation with LPL at 436 nm with appropriate heating and cooling, the nanocylinders oriented in parallel direction, the direction being orthogonal to the LPL light (Fig. 2b). The order parameter of the azobenzene orientation reached a high level as 0.7. The reorientation should involve the processes of erasure of the MPS structure followed by evolution of the MPS to the other direction.

The work is still at a stage of static structural evaluations. We are now optimizing the conditions (film thickness, temperature conditions, experimental setup etc.) to observe reorientations of the MPS nanocylinders. In the second FY, the light responsive system will be subjected to real time observation of the evolving process of MPS structure by means of GI-SAXS measurement in BL-15A.

Reference

[1] Y. Morikawa, T. Kondo, S. Nagano, T. Seki, Chem. Mater. 19, 1540 (2007).

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