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Solvent Annealing Induced Highly Perpendicular Orientation of Cylindrical Microdomains in Block Copolymer Thin Film and Fabrication of Hexagonally Arrayed Nano-channels

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1 Introduction

Microphase separated structures of block copolymer (BCP) thin films were extensively investigated by grazing incidence small angle X-ray scattering technique (GISAXS). Controlling the morphology and particularly the orientation behaviour of phase-separated structures in both thin and thick films has received considerable attention because of their potential nanofabrication application. In the thin film, surface-polymer interaction, confinement effect, and the film thickness are really important factor to give a morphology that is different from those in the bulk. In this report, solvent annealing method was applied to the thin film of ~ 500 nm in thickness (relatively thicker than usual film) and effect of initial morphology after spin-casting from common and selective solvents on equilibrium structure in the film will be reported.

2 Experiment

BCP Polystyrene (PS)-*b*-poly(4-hydroxy styrene) (PHS) was synthesized by anionic polymerization. Toluene and trahydrofuran (THF) were used for solvent of PS-*b*-PHS and annealing, respectively. Poly(ethyleneglycol) monometyl ether (PEG, M_n = 550) was blended in the solution. The mixture PS-*b*-PHS, PEG in toluene solution was spin-cast on a silicon wafer. After fully drying the thin film, the film was put in a chamber filled with THF vapor for solvent annealing. The structure in the thin film was analysed by GISAXS.

3 Results and Discussion

The microphase separated structure of PS-*b*-PHS / PEG blend thin film with thickness of 500 ~ 600 nm and solvent annealing effect on orientation behaviour of the structure in the thin film were investigated by grazing incidence small angle X-ray scattering (GISAXS). The toluene was selective solvent for PS and poor-solvent for PHS and PEG. In the toluene solution, the spherical microdomain was formed because of shrinking of the PHS/PEG domains. The equilibrium morphology of the block copolymer itself and the blend sample was confirmed to be a hexagonally packed cylinder in the bulk and thin film. After THF vapour annealing of the film for several minutes, the highly ordered and perpendicular oriented cylindrical structure was attained. Atomic force microscopic measurement revealed a hexagonal array in top of the surface. The perpendicular nano-channels were fabricated after removing PEG oligomer from the PHS/PEG cylindrical domains by washing with water. These were revealed by GISAXS (as shown in Figure 1) and AFM measurements. After removing PEG, the scattering intensity became considerably high. The increase in the GISAXS intensity was ascribed to removing PEG from cylinders and nano-holes were created in the film. One-dimensional profiles in the GISAXS patterns indicated *in-plane* scatterings at q_z ~ 0.35. These profiles are slightly different except for peak positions. The paracrysltalline distortion theory (hexagonally packed cylinder) revealed the detailed structure of cylinders. The structural parameters are summarized in Table 1. Before removing PEG, the contrast between PS matrix and PHS/PEG domain was seen. After removing PEG, the contrast between hole and the others was enhanced.

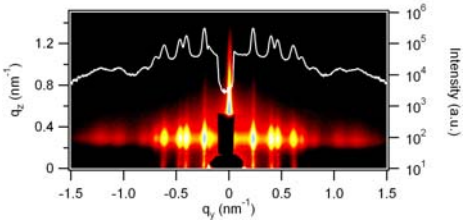

Fig. 1. GISAXS pattern of PS-*b*-PHS thin film having the hexagonally arrayed nano holes.

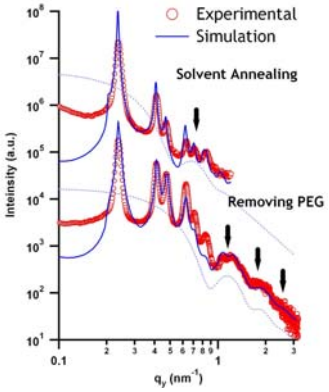

Fig. 2. *In-plane* GISAXS profiles before and after removing blended PEG components from the cylinders. Thick arrows indicate the form factor of cylinders (thin lines). The blue lines were simulated profiles.

Table 1: Structural Parameters of Cylinders

	d-spacing	Radius	$\phi_{cylinder}$
Solvent Ann.	26.7 nm	7.5 nm	21.5 %
Remv. PEG	26.7 nm	4.5 nm	7.5%

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