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Highly Perpendicular Orientation of Cylindrical Microdomains in Polystyrene-*b*-poly(4-hydroxyl styrene)/PEG Oligomer Blend Thin Film

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Introduction

Microphase separated structures of block copolymer thin films were extensively investigated by grazing incidence small angle X-ray scattering technique (GISAXS). Controlling the morphology and particularly the orientation behavior 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. Some researchers have achieved perpendicular orientation of cylindrical morphology of block copolymer in thin film by controlling above factors. The study on orientation of microphase separated structure has been reported extensively. Solvent annealing, ion doping, surface modification of substrate (controlling interfacial energy) and thickness controlling related to the commensurability of domain spacing with film thickness are effective ways to orient the microphase separated structures. In a thicker film, we reported spontaneous perpendicular orientation of cylindrical microdomains in a block copolymer normal cast film. Selective solvent casting gave nonequilibrium morphology because one block fully shrank. Since vitrification of the shrunk chains occurred during evaporation of the solvent, the nonequilibrium morphology was finally arrested after completely dry. Appropriate annealing induced phase transition from nonequilibrium (sphere) to equilibrium structure (cylinder) and spontaneous orientation has been done. In this paper, the 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.

Experimental

A block copolymer polystyrene-*b*-poly(4-hydroxy styrene (PS-*b*-PHS) was synthesized by sequential anionic polymerization. (M_w = 3.35 × 10^4 g/mol, M_n/M_w = 1.10, ϕ_{PS} = 20 vol%). The poly(ethylene glycol) (PEG, M_n = 550) was blended in the solutions of PS-b-PHS until total volume fraction of PS in polymers equaled to 30 vol%. The equilibrium morphology of the synthesized PS-*b*-PHS was a hexagonally packed cylindrical structure. Thin film on silicon wafer was prepared by spin casting from toluene and tetrahydrofuran (THF) solutions (9.1wt%). Toluene is selective solvent for PS and THF is common solvent for all components. The film thickness of all samples was about 500 nm. The thin film was exposed to THF vapor in an annealing chamber. The structures in the film were analyzed by GISAXS at BL9C and BL15A in Photon Factory of KEK.

Result

No microphase separated structure in the THF solution was observed. In contrast, in toluene solution, the spherical microdomain was formed because of shrinking of the PHS/PEG domains. The spherical structure (disorder) in the spin-coated thin film from toluene solution was first observed as shown in Figure 1(a). After THF vapour annealing of the film for several minutes, the highly ordered and perpendicular oriented cylindrical structure was attained as shown in Figure 1 (b). Atomic force microscopic measurement revealed a hexagonal array in top of the surface. On the other hand, perpendicular orientation was fully failure when the thin film made by spin cast from THF solution and subsequent THF vapour annealing (resulted in parallel cylinders).

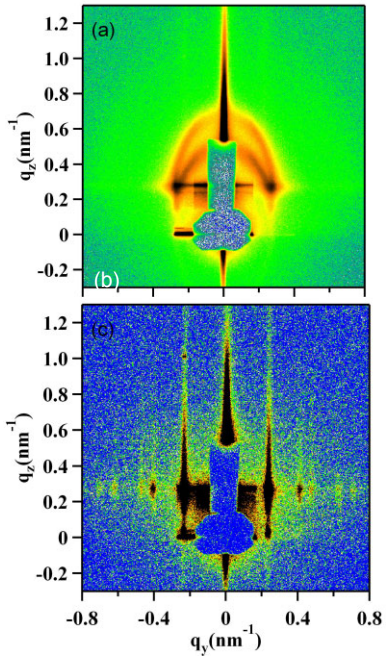

Figure. 1. GISAXS patterns of PS-*b*-PHS/PEG thin film (~500nm) obtained by (a) spin casting from toluene solution without annealing (as cast) and (b) after annealing with THF vapour.

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