

## Microphase separated structure in polystyrene-*b*-polyisoprene thin film including selective solvent for PS

Katsuhiro YAMAMOTO\*<sup>1</sup>, Naoya Umegaki<sup>1</sup>, Taito Matsitani<sup>1</sup>, Shinichi SAKURAI<sup>2</sup>

<sup>1</sup>Graduate School of Engin., Nagoya Inst. of Tech., Gokiso-cho, Nagoya 466-8555, Japan

<sup>2</sup>Graduate School of Engin., Kyoto Inst. of Tech., Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

### Introduction

Microphase separated structures of block copolymer thin films were extensively investigated recently using grazing incidence small angle X-ray scattering technique. 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 paper, effect of addition of non-volatile selective solvent on microphase separated structure in thin film will be reported. Addition of non-volatile selective solvent also induces phase transition but solvent evaporation can be suppressible. The directional phase transition can be expected by directional penetration of the solvent into the thin film. Once the structure change is induced by the solvent, the resulting morphology can remain.

### Experimental

#### Sample and thin film preparation

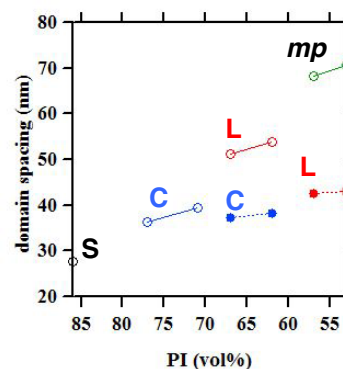
A block copolymer polystyrene-*b*-polyisoprene (PS-*b*-PI) was synthesized by sequential anionic polymerization. ( $M_w = 7.9 \times 10^4$  g/mol,  $M_n/M_w = 1.04$ ,  $\phi_{PS} = 15$  vol%). The equilibrium morphology of the synthesized PS-*b*-PI was BCC sphere structure at 413K. Thin film on silicon wafer was prepared by spin casting from mixture of toluene and diethyl phthalate (DEP) solution. DEP is selective solvent for PS. That is, polystyrene selectively solves in DEP. Thermal annealing was not conducted in this study except for spin-cast thin film from toluene solution. The film thickness of all samples was more than 100 nm which was confirmed by ellipsometry. The resulting structures in the thin film were analyzed by GISAXS at BL40B2 in SPring8 and at BL9C in Photon Factory of KEK.

### Result

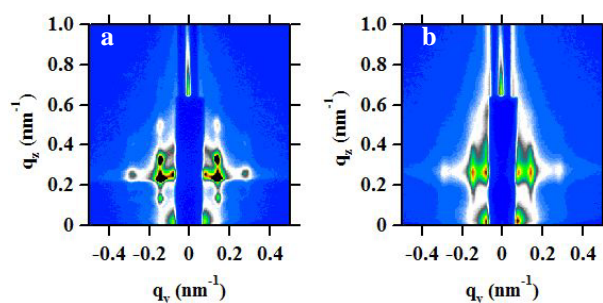
Figure 1 shows the morphology and domain spacing of thick and thin films. The morphologies and the domain spacing of the phase-separated structure against apparent initial volume fraction of PI assuming DEP selectively located in PS. As expected, the morphology in the bulk prepared by normal casting (open symbols) changed from BCC (black)  $\rightarrow$  cylinder (blue)  $\rightarrow$  lamellae (red)  $\rightarrow$  macrophase separation (green) and the domain spacing

increased with DEP content (as increase in apparent PI fraction). Figure 2 shows GISAXS patterns of the thin films obtained with different content of DEP. According to the content of DPE, different morphologies appeared as shown in Figure 2a and 2b. How much amount of DEP was included in the films? The structures of the thin films were compared with those of the thick film containing DEP. As for the thin films obtained by spin cast, considerably different morphology and the spacing appeared in comparison with the bulk at the same initial amount of DEP. Therefore, DEP amount in the thin films fell off during spin-casting from mixture. It was, however, definite that DEP solvent induced the phase transition even in the thin film. Interestingly, those morphologies in the thin films were found to be oriented. The cylinder structure (Figure 2a) was aligned parallel to the substrate surface. In contrast, the lamellar interfaces (Figure 2b) were oriented perpendicularly to the surface.

\* yamamoto.katsuhiro@nitech.ac.jp



**Figure 1.** Morphology and domain spacing of block copolymer in thick (open) and thin films vs initial apparent volume fraction of PI ( $= v_{PI} / (v_{PI} + v_{PS} + v_{DEP})$ )



**Figure 2.** GISAXS patterns of the cylindrical and lamellar structures of PS-*b*-PI including the solvent.