

Spatial Distribution of Solvent Penetrated into a Block Copolymer Thin Film

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A block copolymer with incompatible components exhibits a complicated phase-separation behavior in a thin film due to a geometrical confinement effect as well as interaction with a supporting substrate and air. In this study, structural changes of a phase-separated block copolymer thin film with poly(styrene) (PS) and poly(2-vinylpyridine) (P2VP) induced by solvent contact were observed by *in-situ* neutron reflectometry using a conventional solid/liquid cell.

The samples used are a PS-P2VP diblock copolymer showing an alternating lamellar structure in bulk, and its counterpart with a deuterated PS (*d*PS) block chain. The thin film specimens of the block copolymers were prepared by spun-coating on thick quartz blocks, and then were well annealed at the temperature above T_g before the reflectivity measurement. The different solvents were used: methanol and toluene as a selective solvent for P2VP and PS, respectively, and water as a common non-solvent. All the solvents used are fully deuterated for a neutron experiment. The neutron reflectivity measurements were performed on two pulsed-neutron reflectometers: SPEAR at LANSCE, USA and ARISA-II at J-PARC, Japan.

When the *d*PS-P2VP diblock copolymer thin film was contacted with methanol, the differences in a reflectivity profile implied that the structural changes were induced by the penetration of the methanol into the film during the solvent contact, and the original structure was almost recovered after drying it. On the other hand, in the case of toluene, the diblock copolymer thin film was easily dissolved into the solvent, and the original structure was never recovered. Further, the contact with water also induced the changes in a reflectivity profile, even though water is a common non-solvent. To examine clearly a depth distribution of deuterated solvent, the neutron reflectivity measurements were conducted on the thin films of the non-deuterated PS-P2VP.