

# Interfacial Segment Distribution of a Diblock Copolymer in a Polymer Thin Film

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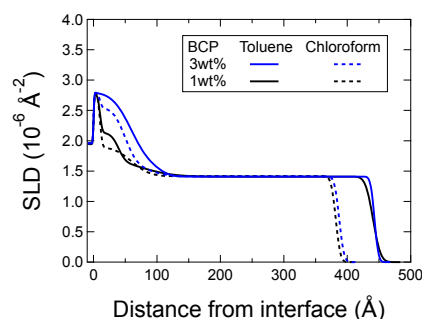
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The composite polymer material forms various morphologies of phase-separated structure with interface between the different phases. The interfacial width between the phases is one of important factors for enhancing mechanical strength of the composite material or adhesion strength. Neutron reflectometry is an indispensable technique for structural analysis on a surface, an interface, and a thin film with a high spatial resolution of sub-nm scale in a non-destructive manner. So far, the interfacial segregation of the component has been clarified for the polymer blend thin films with the different molecular weights or the different tacticity by using neutron reflectometry [1, 2]. In this study, the interfacial segment distribution of a diblock copolymer in a polymer thin film was investigated by neutron reflectometry with a deuterium labeling method.

A diblock copolymer of deuterated styrene and 2-vinylpyridine with the molecular weight of  $44 \times 10^3$  and  $17 \times 10^3$ , respectively, was used. The poly(2-vinylpyridine) (P2VP) has strong affinity to the hydrophilic surface of a silicon substrate. The blend thin films of hydrogenous polystyrene (hPS) with the molecular weight of  $10 \times 10^3$  or  $51 \times 10^3$  and the diblock copolymer were prepared by spin-coating from the dilute solution of chloroform or toluene, which is a common good solvent or selective solvent for polystyrene, respectively. Neutron reflectivity (NR) measurement was conducted on the SOFIA neutron reflectometer [3] at the BzL16, Materials and Life Science Experimental Facility (MLF), Japan Proton Accelerator Research Complex (J-PARC), Tokai, Ibaraki, Japan. The depth scattering length density (SLD) profile was obtained by a conventional model analysis on the specular reflectivity data.

The as-prepared blend thin films exhibited the interfacial segregation of the diblock copolymer, and its segregation was more enhanced by thermal annealing. The interfacial segregation of the block copolymer was more pronounced in the hPS with the higher molecular weight. Figure 1 compares the depth SLD profile for the hPS thin films with the diblock copolymer, spin-coated from the solution in toluene or chloroform. It was found that the diblock copolymer having the higher SLD segregates at the interface with the silicon substrate, because the SLD profile exhibited the higher value near the interface. Moreover, the block copolymer more segregated at the interface in the hPS thin film prepared from toluene than from chloroform due to the difference in solvency for the component.



**Figure 1** The SLD profile as a function of distance from the interface for the PS thin films with the diblock copolymer spin-coated from the solution in toluene or chloroform.

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[3] K. Mitamura, N. L. Yamada, H. Sagehashi, N. Torikai, H. Arita, M. Terada, M. Kobayashi, S. Sato, H. Seto, S. Goko, M. Furusaka, T. Oda, M. Hino, H. Jinnai, A. Takahara, *Polym. J.*, **45**, 100 (2013).