Depth distribution of different solvents in a phase-separated block copolymer thin film

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Abstract. The structural change induced by the contact with different solvents was investigated for a diblock copolymer thin film, of polystyrene (PS) and poly(2-vinylpyridine) (P2VP), forming a lamellar structure by in-situ neutron reflectometry with a conventional cell for the measurement on solid/liquid interfaces. In the case of methanol, which is a selective solvent for P2VP, the structural change was induced by the penetration of methanol into the film, and the original lamellar structure was almost recovered by drying the film even after the solvent contact. On the other hand, when toluene was used as a selective solvent for PS, the block copolymer thin film was easily dissolved into toluene, and its original state was never recovered after the solvent contact. Further, water induced the structural change in the block copolymer thin film similarly to methanol, though it is a poor solvent common for PS and P2VP.

1. Introduction
A block copolymer exhibits rather complicated phase-separation behavior in a thin film, compared with in bulk, due to the interplay of the geometrical confinement effect, the interfacial interaction with a supporting substrate and air, and so on. So far there have been many studies on a block copolymer thin film, and it has been reported on a block copolymer thin film that the orientation of microdomains is dependent on the film thickness, the surface roughness as well as the surface energy of a substrate, etc., and islands or holes are formed on the film surface according to the film thickness relative to the domain size [1]. Also, many attempts have been made to control the self-assembled structure of a block copolymer in a thin film for various practical applications. Neutron reflectometry is a powerful tool for the structural analysis on material interfaces and thin films because of its high spatial resolution of a few Å in a non-destructive manner. As for the block
copolymers thin film forming a lamellar structure, the interfacial thickness between different component lamellae and the segment distribution in a lamellar microdomain were clarified by neutron reflectometry combined with a deuterium-labeling method [2, 3].

In this study, the structural change induced by the contact with different solvents was investigated for the diblock copolymer thin film forming a lamellar structure by in-situ neutron reflectometry with a conventional cell for the measurement on solid/liquid interfaces, to understand the interfacial behavior of a block copolymer thin film in contact with a solvent sub-phase.

2. Experimental
The samples used in this study are a hydrogenous polystyrene-\textit{b}-poly(2-vinylpyridine) (\textit{h}-PS-\textit{b}-P2VP) diblock copolymer with the total molecular weight and the volume fraction of a PS block chain in the molecule of about $1.2 \times 10^7$ and 0.50, respectively, and its counterpart (\textit{d}-PS-\textit{b}-P2VP) with almost the same molecular characteristics as \textit{h}-PS-\textit{b}-P2VP except that the PS block chain is deuterated. Both of them exhibit an alternating lamellar structure in bulk. The low molecular weight solvents with different solvency for the block copolymer were used: methanol and toluene as a selective solvent for P2VP and PS, respectively, and water as a common poor solvent for both components of the block copolymer.

The thin film specimens for the reflectivity measurement were prepared by spin-coating 2wt% \textit{p}-dioxane solution of the block copolymer on the polished surface of 10mm-thick quartz blocks with the dimension of 60mm×60mm, and then were annealed at 180°C in a vacuum for 3-5 days before use.

Neutron reflectivity (NR) measurements were performed on two pulsed-neutron reflectometers: SPEAR at Los Alamos National Laboratory, Los Alamos, USA and ARISA-II [4] at the BL16 beamline, Materials and Life Science Experimental Facility (MLF), Japan Proton Accelerator Research Complex (J-PARC), Tokai, Japan. A conventional cell for the measurement on solid/liquid interfaces was used to keep the block copolymer thin film, prepared on the thick quartz block, contact with the solvent sub-phase during NR measurement. The neutron beam is incident from the side face of the quartz block onto the interface between the quartz block and the solvent phase, and the reflected intensity of neutron is detected through the quartz block with a path length of 60 mm. The transmissivity of neutron is estimated to be around 0.2 from a total cross-section for the used quartz. The specular reflection was observed, and the data were analyzed by a model fitting method with the variation in scattering length density along the direction perpendicular to the film surface.

3. Results and Discussion
To observe the effects of solvent contact on the phase-separated structure clearly, most of the following NR measurements were conducted on the block copolymer with a deuterated PS block chain

![Figure 1](image-url) 

\textbf{Figure 1.} The specular NR profile as a function of $Q_z$ for the \textit{d}-PS-\textit{b}-P2VP thin film in contact with \textit{d}-methanol, along with those before and after the solvent contact.
unless it is mentioned. Figure 1 compares the specular NR profile for the \textit{d}-PS-\textit{b}-P2VP thin film in contact with deuterated methanol (CD$_3$OD), which is a selective solvent for P2VP, with those taken in a dried state before and after the solvent contact, as a function of neutron momentum transfer, $Q_z$ ($=(4\pi/\lambda)\sin \theta$, where $\lambda$ and $\theta$ are the wavelength and the incident angle of neutron, respectively), along the direction perpendicular to the film surface. It should be noted that the reflectivity profiles for the thin film in the dry state were measured by a normal manner, in which the neutron is incident from air onto the film surface prepared on the quartz block. The reflectivity profile (red closed circles) for the film before the solvent contact presented a few distinct Bragg peaks implying that the formed lamellar microdomains are preferentially oriented along the direction parallel to the film surface. The solid black line superimposed on the experimental data is the preliminary fitting result calculated from the variation in scattering length density, $\rho(\Sigma b_i)$, as shown by the red line in the inset, along the perpendicular direction to the film surface. This indicates that \textit{d}-PS and P2VP lamellae are alternatively stacked with the domain spacing of about 530 Å in the 800Å-thick film. It was also found that \textit{d}-PS lamella appears at the air surface of the film due to its lower surface energy, while P2VP lamella does at the interface of the film with the quartz block because of its preferential affinity to the quartz.

When this \textit{d}-PS-\textit{b}-P2VP thin film was made contact with \textit{d}-methanol, which is a good solvent for P2VP but a poor solvent for PS, the Bragg peaks in the reflectivity profile (blue closed circles) became weaker than those before the solvent contact. It should be noted that the critical $Q_z$ position for total reflection was shifted to the lower-$Q_z$ region, since the neutron reflection was observed through the quartz block with relatively high $\rho(\Sigma b_i)$ against the deuterated solvent, though the transmissivity of the quartz block is not exactly considered into normalizing the reflectivity data. The black solid line on the measured profile was calculated from $\rho(\Sigma b_i)$ variation, indicated by the blue solid line in the inset, assuming that \textit{d}-methanol does not penetrate inside the film at all so that no structural changes are induced. It is apparent that the reflectivity profile thus calculated does not agree with the experimental data. This implies that some amount of methanol penetrates into the film, and induces the structural change of the lamellar microdomains during the contact with solvent. Levicky et al. [5] previously reported similar results by a NR measurement that methanol induced the selective swelling of P2VP lamellae for a PS-\textit{b}-P2VP diblock copolymer thin film. Then, by drying the film after the solvent contact, the Bragg peaks in the profile (orange closed circles) were almost recovered but their position was shifted to the higher-$Q_z$ region, reflecting that the size of lamellar microdomains became smaller. This may be attributed to a kind of solvent-annealing effect by the penetration of methanol into the film during the contact.

\begin{figure}[h]
\includegraphics[width=\textwidth]{figure2.png}
\caption{The specular NR profile for the \textit{h}-PS-\textit{b}-P2VP thin film in contact with D$_2$O, along with those in the dried state before and after the solvent contact.}
\end{figure}
In the case of d-toluene, which is recognized as a good solvent for PS but a poor solvent for P2VP, the distinct Bragg peaks observed in the dried state almost completely disappeared by the contact with toluene, though the reflectivity profiles are not shown here [6]. Those Bragg peaks were never recovered even by drying the film after the solvent contact. This suggests that the block copolymer thin film was easily dissolved into toluene, compared with methanol described above. This difference between toluene and methanol may be caused by their subtle difference in the solvency for the component polymers, though both are a selective solvent.

When the d-PS-b-P2VP thin film was made contact with deuterated water, D₂O, which is known as a common poor solvent for PS and P2VP, the induced change in the reflectivity profile of the block copolymer thin film was similar to the case of methanol, though the reflectivity profiles are not shown here [6]. However, the sample labeling adopted was not suitable for examining whether water penetrates into the film, since both the block copolymer and the solvent are deuterated. Thus, to facilitate observing the distribution of solvent in the block copolymer thin film, non-deuterated h-PS-b-P2VP thin film was prepared and made contact with deuterated solvent, D₂O. As presented in Figure 2, the reflectivity profile (red closed circles) for the non-deuterated block copolymer film before the solvent contact exhibits the weak peaks originated from the phase-separated structure, since the difference in \( \rho(\Sigma b_i) \) is not so large between a non-deuterated PS and a P2VP. The black solid line on that profile is the reflectivity calculated from \( \rho(\Sigma b_i) \) distribution, shown by the red solid line in the inset, along the direction perpendicular to the film surface suggesting a phase-separated state in the film with the thickness of about 1,500 Å although the calculated reflectivity is very similar to but not perfectly fitted with the experimental one yet. As this film was made contact with D₂O, the reflectivity profile presents slightly more discernible peaks in a low-\( Q_z \) region than that before D₂O contact. Actually, the calculated reflectivity profile does not agree with the experimental data (blue closed circles), assuming no penetration of D₂O into the film so that simply replacing an air phase with a D₂O sub-phase without any structural changes of the thin film, as shown by the blue solid line in the inset. This implies that some D₂O may penetrate into the film somehow though it is a common poor solvent for both the components, that is, PS and P2VP, of the block copolymer. At present, the exact mechanism for the water penetration is not clear yet. Further experiments as well as data analysis are required to clarify the mechanism of water penetration into the block copolymer thin film.

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