In-Situ Reflectometry Observation on Structural Changes of Thin Self-Assembled Block Copolymer Films

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Abstract. The structural changes induced by solvent contact or heating were observed for thin spin-coated polystyrene-block-poly(2-vinylpyridine) diblock copolymer (PS-P2VP) films using in-situ neutron reflectivity and grazing-incidence small-angle X-ray scattering (GISAXS) techniques. The lamellarly-ordered PS-P2VP film showed some structural changes in contact with water though it is a poor solvent for both the component polymers, while the original structure was recovered after drying the film. When toluene was used as a selectively good solvent for PS, the thin film was dissolved into the solvent. On the other hand, the thin as-prepared PS-P2VP film with spherical microdomains exhibited laterally a pair of scattering spots symmetrical relative to the specular reflection ridge in the GISAXS pattern, indicating the existence of some lateral structural correlation in the film. On a temperature jump up to 200°C, these two scattering spots started to disappear around the glass transition temperature, and then almost completely vanished at 200°C unexpectedly though the PS-P2VP used here should be kept in the strong-segregation state. The spherical structure could be completely disordered or kept ordered but with lateral distortion in its orientation. Being cooled down to a room temperature again, the two scattering spots were recovered, and became more intense with their position shifting slightly to lower QY-region than before heating due to the improvement in ordering.

1. Introduction

Block and graft copolymers with incompatible components self-assemble into highly ordered microphase-separated structures with a molecular scale in bulk or in concentrated solution. So far there have been many studies on the microphase-separated structures, and it has been clarified that
their morphology and size depend on the primary structure, i.e., composition, molecular weight, and molecular architecture, of block and graft copolymers.\textsuperscript{2,3}

We have intensively investigated the interfacial structure of two-component block copolymers with different molecular architectures for the understanding of microphase-separated structure at the molecular level, by using a high depth resolution of neutron reflectivity (NR) measurement.\textsuperscript{4,5} The simplest geometry of an alternating lamellar structure among the other morphologies was utilized for adopting reflectivity measurement, and most of the NR measurements were performed at room temperature, which is far below the glass transition temperature ($T_g$) for the component polymers. The lamellar structures were preferentially oriented along the direction parallel to the surface of the thin spin-coated films. The interfacial thicknesses evaluated were almost constant irrespective of the difference in molecular architecture of the block copolymers, and had much larger values than the prediction of a mean-field theory. This discrepancy between the experimental result and theoretical prediction in the interfacial thickness was quantitatively explained by considering the thermal fluctuations produced on polymer interfaces during annealing procedure at high temperature above $T_g$. However, it is important for further understanding of microphase-separated structure to observe the process of self-assembling or structural change as well as the static equilibrium structure.

In this study, the structural changes induced by solvent contact or heating were observed for thin block copolymer films by using in-situ NR and grazing-incidence small-angle X-ray scattering (GISAXS) measurements.

2. Experimental

The samples used here were two polystyrene-\textit{block}-poly(2-vinylpyridine) (PS-P2VP) diblock copolymers with different volume fractions, $\phi_{PS}$, of the PS block chain in a molecule, 0.53 and 0.90. They were synthesized by an anionic polymerization method. Both of them have molecular weights more than 120x$10^5$, and also the apparent indices of polydispersity less than 1.05. The PS block chain of the copolymer with $\phi_{PS}$ of 0.53 was deuterated for neutron experiment. It was confirmed by morphological observation that the PS-P2VPs with $\phi_{PS}$ of 0.53 and 0.90 exhibit an alternating lamellar and spherical structure in bulk, respectively. The thin film specimens were prepared by spin-coating the dilute PS-P2VP solution in p-dioxane on polished surfaces of quartz or silicon wafers. The thin spin-coated films of the PS-P2VP with $\phi_{PS}$ of 0.53 were sufficiently annealed at 180°C in a vacuum to have the well-ordered phase-separated structure prior to solvent contact.

NR measurement was performed on the SPEAR reflectometer\textsuperscript{6} at a pulsed-neutron source of Manuel Lujan Jr. Neutron Scattering Center, Los Alamos National Laboratory, USA. The white neutrons with the wavelengths, $\lambda$, ranging from 0.15 to 1.6 nm were used with a Time-of-Flight (TOF) analysis method. The geometrical configuration of a conventional solid/liquid cell was utilized to make the thin block copolymer film on the quartz contact with solvent. In NR measurement specular reflection was observed for exploring the sample structure along the direction perpendicular to the solid/liquid interface. GISAXS measurement was carried out on a beam line for small-angle scattering (BL-15A)\textsuperscript{7} at Photon Factory (PF), High Energy Accelerator Research Organization, Tsukuba, with an evacuated high-temperature cell. The wavelength of X-ray was 0.154 nm, and an image intensifier with a cooled CCD was used as a two-dimensional detector. The camera length was set at about 2 m.

3. Preliminary results

3.1. Structural changes of a thin lamellarly-ordered block copolymer film with solvent contact

The structural changes by the contact with solvent were examined for a thin self-assembled PS-P2VP diblock copolymer film using in-situ time-resolved NR measurement with a data acquisition time of 30 minutes using a conventional solid/liquid cell. Figure 1 shows specular NR profiles for the thin lamellarly-ordered PS-P2VP film before and after the contact with water (D$_2$O) as a function of neutron momentum transfer, $Q_z (=4\pi/\lambda)\sin\theta$, where $\theta$ is the incident angle of the neutron) along the direction perpendicular to the film surface. The profile before the water contact was measured in a
normal manner, in which the neutron beam was incident from air phase onto the film surface, and exhibited a few distinct Bragg peaks corresponding to the lamellar structure preferentially oriented along the film surface. It should be noted that the critical $Q_z$ value for total reflection was apparently shifted to the lower-$Q_z$ side in the profile after the water contact, since the neutron beam was incident onto the film interface with solvent through the quartz (scattering length density, $\rho\Sigma b_i$, of $4.18\times10^{-4}$ nm$^{-2}$). Just after the film was made contact with D$_2$O ($\rho\Sigma b_i=6.35\times10^{-4}$ nm$^{-2}$), the Bragg peaks became ambiguous. The preliminary data analysis with a model fitting implied that water penetrated into the thin block copolymer film and caused some structural changes in the film, that is, the expansion of lamellar thickness and the broadening of lamellar interface, although water is a poor solvent for both of PS and P2VP. Again, the original lamellar structure was almost perfectly recovered after drying the film. On the other hand, Figure 2 shows the NR profiles for the thin lamellarly-ordered PS-P2VP film in contact with deuterated toluene ($\rho\Sigma b_i=5.66\times10^{-4}$ nm$^{-2}$), which is a selective solvent, that is, a good solvent for PS but a poor solvent for P2VP. The reflectivity profile was drastically changed after the contact with toluene. The Bragg peaks corresponding to the lamellar structure completely disappeared in the profile, suggesting that the block copolymer film was dissolved into the selective solvent.

Figure 1 NR profiles for the thin lamellarly-ordered PS-P2VP diblock copolymer film before and after the contact with D$_2$O.

Figure 2 NR profiles for the thin lamellarly-ordered PS-P2VP block copolymer film before and after the contact with deuterated toluene.
3.2. Thermally-induced ordering of spherical microdomains in a thin block copolymer film
The ordering process of a spherical structure induced by heating was explored for the thin PS-P2VP film using in-situ time-resolved GISAXS measurement with the exposure time of just 1 second. Figure 3 shows the two-dimensional GISAXS patterns for the as-prepared thin PS-P2VP film before and after a temperature jump up to 200˚C. The as-prepared thin film exhibited laterally two scattering spots symmetrical relative to the specular reflection ridge, i.e., the Z-axis, at \(Q_y \approx \pm 0.19 \text{ nm}^{-1}\) in the GISAXS pattern, implying that the phase-separation already took place with weak lateral structural correlation. After the temperature jump, these two scattering spots started to disappear at \(T_g \approx 110˚C\), of the component polymers, and then almost completely vanished when the temperature reached at 200˚C. The block copolymer itself keeps the very high \(\chi N\) value, i.e., the index of segregation power, more than 100 as at 200˚C, where \(\chi\) is the Flory-Huggins interaction parameter and \(N\) is the degree of polymerization, and should be in the strong-segregation state with the \(\chi N\) sufficiently higher than 10.5. It suggests that spherical microdomains could be completely disordered or kept ordered but laterally distorted in their orientation. Being cooled down to room temperature again after 30 minutes at 200˚C, the two scattering spots were recovered, and slightly shifted to lower \(Q_y\) (~\(\pm 0.17 \text{ nm}^{-1}\)) and became more intense than before the temperature jump due to the improvement in the ordering.

Figure 3 GISAXS patterns for the as-prepared thin PS-P2VP film before and after the temperature jump up to 200˚C (from left to right).

The neutron reflectivity experiments shown here were performed under the Inter-University Research Program on Pulsed-Neutron Scattering at Oversea Facilities. N. T. is indebted to the supports by a Grant-in-Aid for Creative Scientific Research (16GS0417) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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