BL-15A2/2014G169

Orientation and relaxation behaviors of lamellar micro-domains of poly(methyl methacrylate)-*b*-poly(*n*-butyl acrylate) thin film as revealed by grazing incidence small angle X-ray scattering utilizing hard and tender X-rays

Katsuhiro Yamamoto[1,2*], Itsuki Saito[1], Daiki Shimada[1] and Mayu Aikawa[1]
[1]Graduate School of Engineering, Nagoya Institute of Technology
[2]Frontier Research Institute for Materials Science, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

1 Introduction

GISAXS measurement using tender (soft) X-ray is useful tool to investigate depth-dependence structure analysis in block copolymer (BCP) morphology.[1,2]

In this report, we demonstrate the study on phase separation behavior of poly(methyl methacrylate-*b*-*n*-butyl acrylate) (PMMA-PnBA) forming a lamellar structure aligned parallel to the substrate after appropriate thermal annealing. Both components in the BCP possess polarity, and the phase-separated PMMA-PnBA is a thermoplastic elastomer. Thus, PMMA-PnBA is applicable as a pressure sensitive adhesive (PSA) material. To understand the phase-separation behavior in films (thin films) is essentially important to advance the functionality of PMMA-PnBA as a PSA material. Herein, the structure development through parameters such as the degree of lamellar orientation and the relaxation of the lamellar domain spacing using GISAXS (hard and tender X-rays) was investigated.

2 Experiment

For thin films, 5 wt% BCP (Mn = 32 000, Mw/Mn = 1.17, f_{PMMA} = 0.44 vol%) solutions were prepared with THF, followed by spin casting on a silicon substrate at 3000 r.p.m. for 30 s. The thin films were dried at room temperature. Subsequently, thermal annealing was performed at 160 °C. The thickness of the thin films was measured to be ~ 280 ± 30 nm.

To study the microphase-separated structures in thin films, GISAXS measure-ments utilizing hard X-ray and tender (soft) X-ray were performed. Hard X-ray GISAXS measurements were conducted at beamlines BL6A and BL10C of the KEK Photon Factory in Tsukuba, Japan, and BL03XU at SPring-8 in Hyogo, Japan,67,68 with wavelengths of 0.15 (BL6A), 0.1488 (BL10C) and 0.1 nm (BL03XU). At beamlines BL10C, PILATUS 2M (Dectris) detector was used, which were set at positions 2 ~ 3 m from the sample position.

3 Results and Discussion

2D GISAXS (hard X-ray) patterns with various annealing times were shown in Figure 1. The pattern of as-spun sample (Figure 1a) was shaped like an ellipse which might arise from kinetically frozen or poorly ordered structure. Partially intense scattering was observed at q_z of 0.25 – 0.28 nm-1 where was emphasized due to so-called Yoneda peak, i.e., it did not indicate specific orientation, suggesting that no orientation of phase separated structure of PMMA--PnBA appeared without thermal annealing. After the sample was thermally annealed for even 1 min, the scattering intensity around q_y = 0 (near the beam stop) grew. In addition, two clear ring-shaped scattering patterns like Debye-Scherrer rings were observed. Each scattering ring was arising from transmitted (T) and reflected (R) beams as described previous section. The scattering intensity near beam stop became strong with annealing time. This change in GISAXS pattern indicates the growth of the parallel orientation of the lamellar microdomain. The development of the normalized scattering intensity from parallel lamellar structure is shown in Figure 2. Orientation is nearly complete after annealing for 60 min. The GISAXS measurement gave structure information about domain spacing of the lamellar morphology. The domain spacing (D) of the lamellar structures aligned parallel to the surface was estimated. To determine the accurate domain spacing, the distorted wave Born approximation (DWBA) was applied for analysis of the GISAXS patterns. The experimentally estimated D values are also plotted as a function of the annealing time in Figure 2. The value of the D approached to the D_0 of the bulk sample (independently obtained to be 21.6 nm) with an increase in annealing time. The D of the parallel orientated structure was slightly smaller than D_0 even after 4h thermal annealing, i.e., the spacing collapsed vertically. Consequently, the lamellar structure was deformed along the depth direction (similar phenomena as the previous section). Thermal annealing induced the relaxation of the domain spacing and it seems taking approximately more than 2 h to complete the relaxation of D (equals to the value of the bulk) .

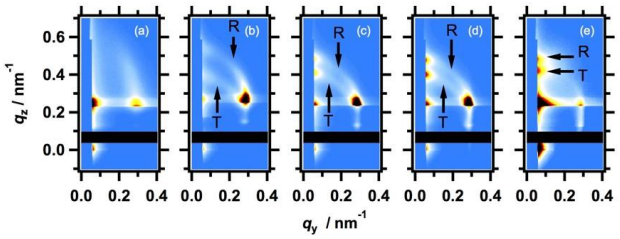

Fig. 1: GISAXS patterns (hard X-ray, 1.488 Å) of PMMA-PnBA thin film (a) as cast and (b-e) as annealed at 160 ˚C with given annealing time; (b) 1, (c) 3, (d) 5, and (e) 10 min.

As is well known, preferential wetting of surface and substrate interfaces plays an important role of orientation in thin film. According to the surface free energies, it will be predicted that PMMA (41.1 mJ/m^2) segregates to the surface of the silicon (77.4 ± 0.5 mJ/m^2) substrate, while PnBA (33.7 mJ/m^2) segregates to air surface. As a result of preferential wetting of both components, the parallel orientation of lamellar structure is induced at the surface and/or the polymer/substrate interfaces and the oriented lamellae propagates into entire film. Actually, XPS measurement indicated the PnBA component perfectly covered on the surface (within a few nanometer) after thermal annealing with only 60 sec. The segregation of each component, orientation of the lamellae, and relaxation of the domain spacing occurred in different time scale. It can be concluded that the PnBA first segregated at air surface within a minute after annealing, second the micro-phase separated structure aligned parallel to the surface, followed by relaxation of the domain spacing.

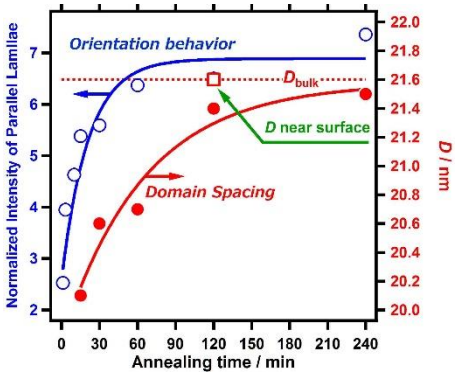

Fig. 2: Figure 10. Time evolution of the orientation of the lamellar domain (open circles) and the relaxation of the lamellar D (filled circles). The solid lines was drawn as a guide to eyes. Dotted line shows the D_0 value of the bulk. Open square indicates the D value near the surface.

The polymer thin films have reported to have different mobility dependent on the local region, i.e., near the surface, inside, or near the polymer/substrate interface. It is quite intriguing to investigate that the depth dependence of structure difference exists, in other words, whether there are difference between the structure in the vicinity of the surface and inside of the film, or not. GISAXS measurements of PMMA-PnBA thin film annealed for 2h with tender X-ray was performed with various incident angles. As shown in Figure 3a and b, in a condition of $\alpha_i < \alpha_c$, the scattering (marked arrows) of the lamellar structure oriented parallel to the substrate was considerably diffuse and broaden, while in the case of $\alpha_i > \alpha_c$, the scattering became clear and sharp. The FWHM values of scattering peak (parallel lamellar domains) in the one-dimensional GISAXS profile obtained vertically cut at various incident angles can be simulated as the same manner of the size effect of measured region as discussed in the framework of the modified Laue function. Thus, the penetration depth was controlled by the incident angles. At near the critical angle, the surface-sensitive measurement is possible as predicted. The true q_z value of the oriented lamellar structure parallel to the substrate is estimated using the experimentally observed peaks, i.e. D near the surface can be estimated. At α_i of 0.525° (penetration depth Λ of 32.4nm), D was obtained to be 21.6 nm which is equal to the D_0 value (21.6 nm) of the bulk sample. The value of D near the surface is slightly larger than the value 21.4 nm obtained from DWBA calculation (inside the whole film). This means that relaxation of the domain spacing near the film surface preceded as compared to that of the inside. According to previous reports, polymer chain near the surface indicates higher mobility (lower glass transition temperature or viscosity). Moreover, the lamellar structure started to orient from both the air/polymer and polymer/substrate interfaces which was induced by segregation of one component in the BCP. Therefore, that the faster relaxation of the D of the lamellar structure near the surface was caused by the faster orientation and higher mobility in the vicinity of the surface.

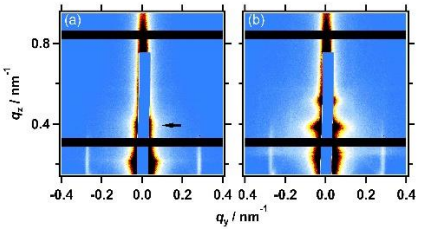

Fig.3: Tender X-ray (2.40 keV) GISAXS patterns of PMMA-PnBA thin films annealed at 160 °C for 2 hours at α_i of (a) 0.525° and (b) 0.625°.

References

[1] H. Okuda *et al*., *J. Appl. Cryst.* **44**, 380-384 (2011).

[2] I.Saito, K.Yamamoto *et al*, *Macromolecules* **48**, 8190-8196 (2015).

* yamamoto.katsuhiro@nitech.ac.jp