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Photo-induced deformation of microphase separation structure in liquid crystalline azobenzene block copolymers

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Introduction

The microphase separation (MPS) structure of the block copolymer films have great advantages and potentials for nanotemplating and nanopatterning materials. Recently, alignment methods for the MPS structure have been actively studied. We have demonstrated the photoalignment of MPS structure in photoresponsive liquid crystalline (LC) diblock copolymer films composed of poly(azobenzene methacrylate) (PAzMA) matrix with the non LC polymer block cylinders [1, 2]. The photoalignment method is based on the angular selected photoreaction of azobenzene side chains by the irradiation of 436 nm visible light and the co-operative molecular motions due to the liquid crystallinity. We have carried out the intensive studies of the photoalignment of the MPS cylinders by in-situ Grazing incidence small angle X-ray scattering measurement with light irradiation in the BL-15A for understanding the mechanisms of the photoalignment process. On conducting the study, we found the visible light irradiation induced the decrease of the isotropic point of the LC phase and fluctuated the MPS structure. We report herein that irradiation of visible light induces the deformation of the MPS cylinder in polystyrene-*block*- poly{10-[4-(4-pentylphenylazo) phenoxy] decyl methacrylate} (PS-*b*-P5Az10MA) thin film.

Grazing incidence small angle X-ray scattering (GI-SAXS) by utilizing the very strong and well coherent beam of synchrotron radiation source is the feasible fast measurement to determine the nanostructure in thin films. Moreover, this measurement provides in-situ studies with light irradiation.

Experimental Section

polystyrene-*block*-poly{10-[4-(4-pentylphenylazo) phenoxy] decyl methacrylate} (PS_{70}-*b*-$P5Az10MA_{94}$, M_n = 57000, M_w/M_n = 1.08) was synthesized by atom transfer radical polymerization method. The polymer employed in this study exhibited two T_g's at 100 and 62°C for the PS block and P5Az10MA polymer LC block, respectively, and smectic LC phase from T_g to 116°C. The PS_{70}-*b*-$P5Az10MA_{94}$ film was prepared onto a fused silica substrate by the spincast method. The film was annealed at 130°C for 0.5 h. Real-time GI-SAXS experiments were performed at the BL-15A beam line with a sample to detector distance of 2250 mm for the MPS structure were captured by CCD detector (Hamamatsu C7300) under 85°C of P5Az10MA LC phase. Incidence angles were chosen between 0.1 and 0.2°, and the final images are an average of 1 second exposure. For LC phase GI-SAXS images were recorded on a FR-E/RAXIS-II (rigaku) with a sample to detector distance of 300 mm. The scattering images 436 nm visible light obtained from the light source (San-ei Electronics Supercure 203S) passing through glass filters (Y43, V44) at 2.0 mW cm^{-2}.

Result and Discussion

The scattering peak in the small angle region was detected at ca. 0.21 nm^{-1} above the in-plane line in the PS-b-P5Az10MA film (Figure 1a). In the wide angle region, we observed the scattering spot at 1.98 nm^{-1} in the out-of-plane position (Figure 2a). The PS-*b*-P5Az10MA exhibits the homeotropic LC phase and perpendicular alignment cylinder phase to the substrate plane by characterization with UV absorption spectroscopy and AFM observation [2]. The scattering peaks could be assigned due to the perpendicular aligned cylinder in the small angle region and the homeotropic LC phase in the wide angle region, respectively. Under irradiation of visible light, these scattering peeks quickly disappeared (Figure 1b and 2b). When we stop the visible light irradiation, these scattering appeared again (Figure 1c and 2c). The disappearing of the azobenzene smectic LC phase indicates the photoinduced phase transition to the isotropic phase of LC. Therefore these results can be presume that visible light irradiation leads to the fluctuation of cylinder structure in the block copolymer film phase by the LC phase transition to the isotropic phase.

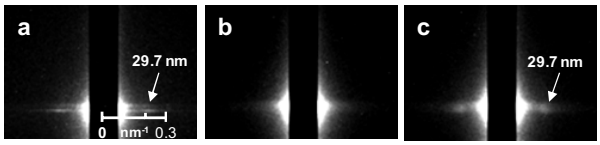

Figure 1. GI-SAXS 2D images of the initial film (a), the film under visible light irradiation at 1.0 mW cm^{-2} (b) and with light-off (c) in smaller angle region below 0.5 nm^{-1}. The scattering peaks (white allow) corresponding to the MPS cylinder domain distance.

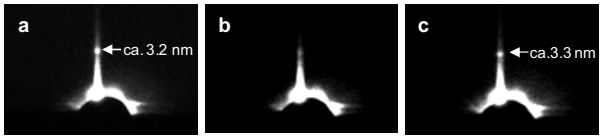

Figure 2. GI-SAXS 2D images of the initial film (a), the film under visible light irradiation at 1.0 mW cm^{-2} (b) and with light-off (c) in wider angle region below ca. 3 nm^{-1}. The scattering peaks (white allow) corresponding to the smectic LC lamella spacing.

References

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