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Real-time observation of photo-induced nanostructural change in photofunctional block copolymers

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Introduction

The microphase separation (MPS) structure of the block copolymer films can form the highly ordered nanostructures self-assembly which have great advantages and potentials for nanotechnology applications. Recently, it has been demonstrated the photoalignment of MPS structure in liquid crystalline (LC) diblock copolymer films composed of poly(azobenzene methacrylate) (PAzMA) matrix with the non LC polymer block cylinder [1]. The photoalignment method is based on the angular selected photoreaction of azobenzene side chains and the collective molecular motions due to the liquid crystallinity. The nanocylinders are aligned orthogonal to the direction of the electric field vector of irradiated polarized light. The key mechanism of the successful photoalignment control is presumed that the photoaligned LC structure of PAzMA block induces the preferential orientation of the cylindrical MPS structure in the thin film. To achieve a fundamental understanding of the photoalignment process, there is a great need to observe the photoalignment motion of both LC structure and MPS structure in real-time and in-situ.

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. In the present report, the real time observations of the MPS photoaligment behaviours in the PAzMA LC block copolymer film were attained by the GI-SAXS measurement focussing on reorientation of both LC phase and MPS structure.

Experimental Section

poly(butylmethacrylate)-*block*-poly{10-[4-(4-pentylphenylazo) phenoxy] decyl methacrylate} (PBM$_{70}$-*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 20 and 62 ^{o}C for the PBM block and P5Az10MA polymer LC block, respectively, and smectic LC phase from T_g to 116 ^{o}C. The PBM$_{70}$-*b*-P5Az10MA$_{94}$ film was prepared onto a fused silica substrate by the spincast method. Real-time GI-SAXS experiments were performed at the 15A beam line with a sample to detector distance of 2250 mm for the MPS structure and 1340 mm for the LC phase. The scattering images were captured by CCD detector (Hamamatsu C7300). Incidence angles were chosen between 0.1 and 0.2 °, and the final images are an average of 1 second exposure. 436 nm liner polarized light (LPL) obtained from the light source (San-ei Electronics Supercure 203S) passing through glass filters (Y43, V44) and a polarizer. The sample film was pre-oriented by irradiation with LPL at 110 ^{o}C.

Result and Discussion

Initially, the scattering peak due to nanocylinders was detected at ca. 0.23 nm^{-1} in the in-plane direction when the incident of the X-ray beam was perpendicular to the electric field vector of the irradiated LPL in the GI-SAXS measurement. The scattering peak corresponding to LC phase was observed at 1.9 nm^{-1} in the in-plane direction with the crossing angle to the LPL vector, reasonably. The in-situ real-time observation was performed in photoorientational change of the cylindrical structure under LPL irradiation. Figure 1 shows the time resolved scattering profiles of the appearance and disappearance peaks due to the P5Az10MA LC phase (a) and the cylindrical structure (b), respectively. Judging from the data, the orientational changes of LC phase and MPS structure are performed in almost the same time scale.

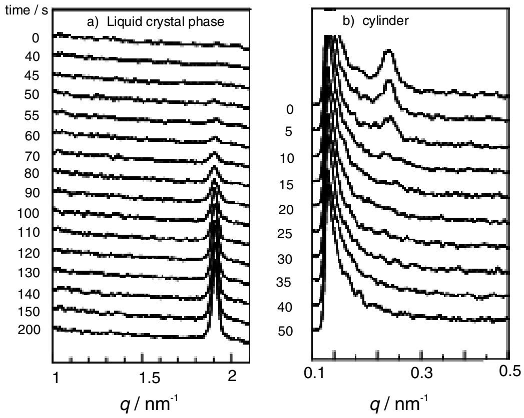

Figure 1. Real time GI-SAXS peaks in the photoreorientation MPS structure system: the appearance and disappearance peaks due to the P5Az10MA LC phase (a) and the cylindrical structure (b), respectively.

References

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