Supporting information

Pathways toward photoinduced alignment switching in liquid crystalline block copolymer films

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1. GI-SAXS measurements: On the rapid cooling process

PBMA-*b*-PAz used in this study exhibited the thermal properties as glass-55-smectic C-90-smectic A-115-isotoropic. GI-SAXS measurements of a photoaligned PBMA-*b*-PAz film were carried out at various temperatures. Figure S1 shows the 2D GI-SAXS profiles from the smectic layer at 50 °C (a, smectic C), 95 °C (b, smectic A), and room temperature after rapid (c) and slow (d) cooling from 95 °C.

At 50 °C, the diffraction spots were observed at an angle of 30° form the horizontal direction, indicating that the layer structure was tilted at this angle from the film plane. This result evidently reflects the smectic C state. At 95 °C, the spots were observed along the horizontal line, showing the formation of vertically oriented smectic layer in the smectic A.

Measurements at room temperature after rapid cooling from 95 °C gave the similar 2D profiles as obtained at 95 °C (c). This fact indicates that the layer structure of smectic A phase was frozen by the rapid cooling process, and therefore, data of GI-SAXS measurements after rapid cooling to room temperature reflects the structure in the smectic A phase. On the other hand, when the sample was slowly cooled down to room temperature, two types of scattering spots reflecting the smectic A and smectic C phases appeared. Data in Figure 3 were obtained after the rapid cooling process.

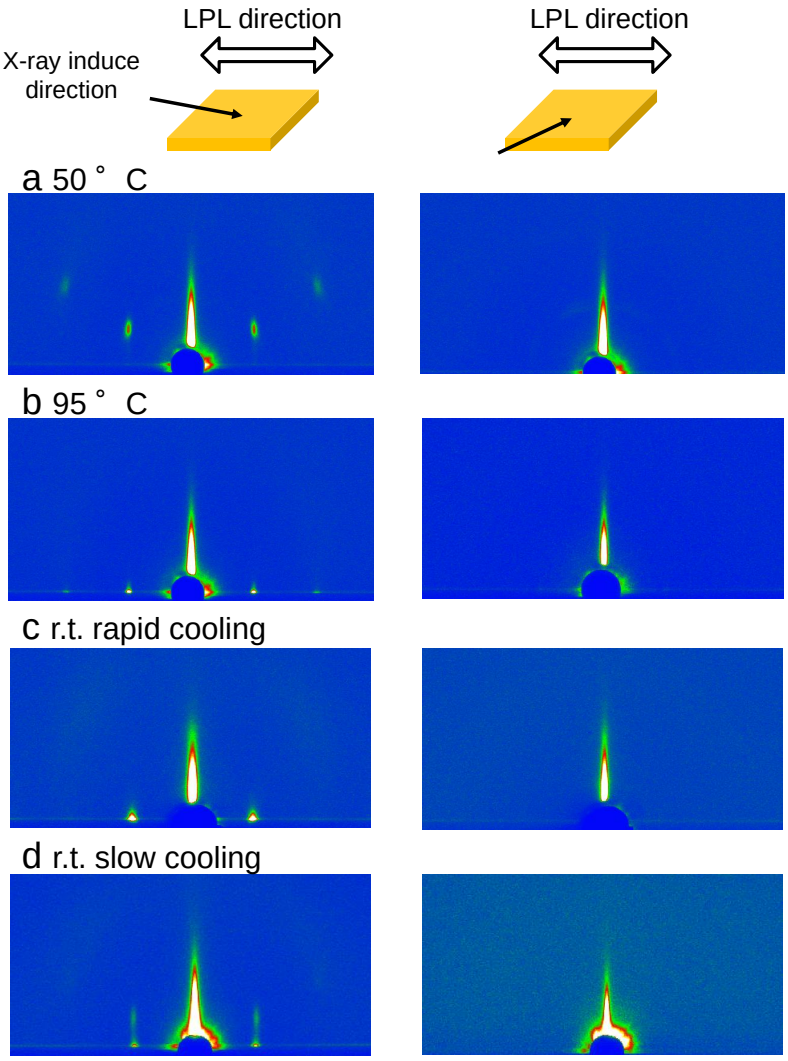

Figure S1. GI-SAXS data obtained at 50 °C (a), 95 °C (b), and at room temperature via rapid (c) and slow (d) cooling.

2. Structural fluctuations at an early stage of 2nd LPL irradiation.

We detected small but significant distance changes at an early stage of 2nd LPL irradiation by GI-SAXS measurements using the synchrotron X-ray (λ = 0.150 nm) at BL-6A, KEK Photon Factory in Tsukuba. With this apparatus, both the layer spacing of smectic layer and the cylinder-to-cylinder distance were evaluated simultaneously using PILATUS 100K and 300K detectors (DECTRIS AG), respectively.

The scattering peaks from LC layer in the in-plane direction shifted by 0.04 nm^{-1}

from q = 1.87 (3.4 nm) to 1.82 nm^{-1} (3.5 nm) at 15 mJ cm^{-2} light dose (Figure S2). On the other hand, the peaks derived from MPS cylinder arrays shifted a 0.02 nm^{-1} wider position, from q = 0.20 (31 nm) to 0.22 nm^{-1} (28 nm), respectively (Figure S3). The slightly higher values of the cylinder to cylinder distance from those described in the text stem from the difference in the temperature measured. The higher temperature resulted in the larger distance.

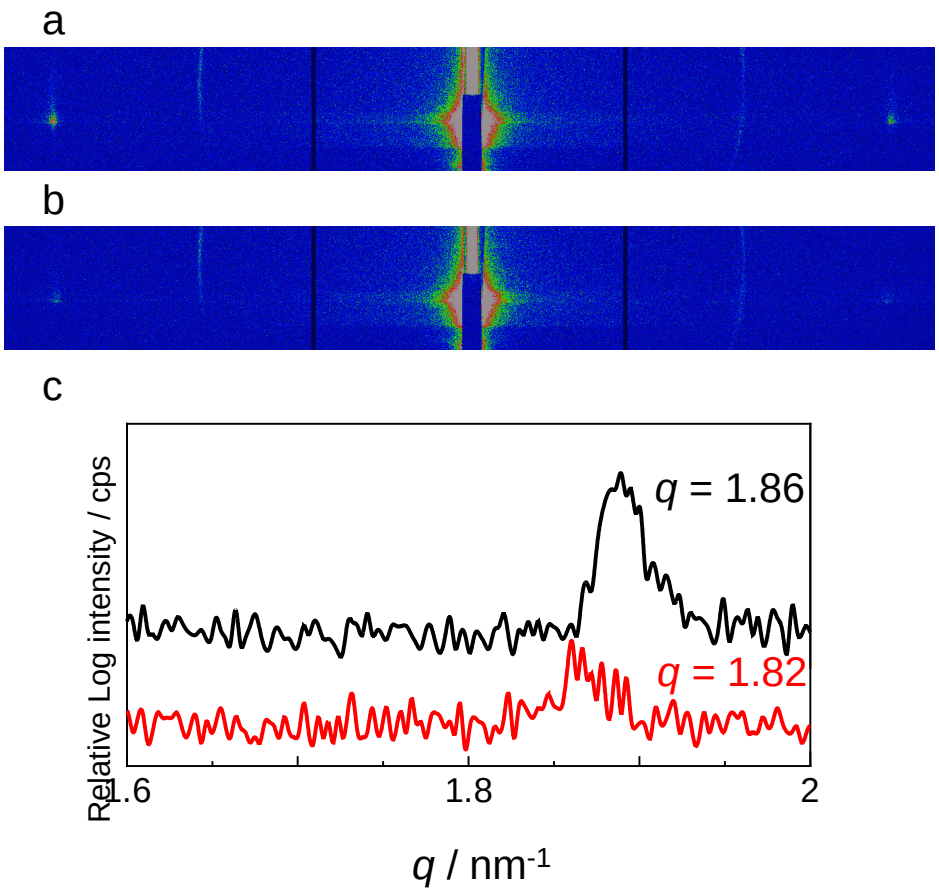

Figure S2. 2D images of GI-SAXS measurements of after 2nd LPL irradiation. The light exposure doses were 0 (just irradiated) (a) and 15 (b) mJ cm^{-2}. The in-plane 1D profiles are shown in c.

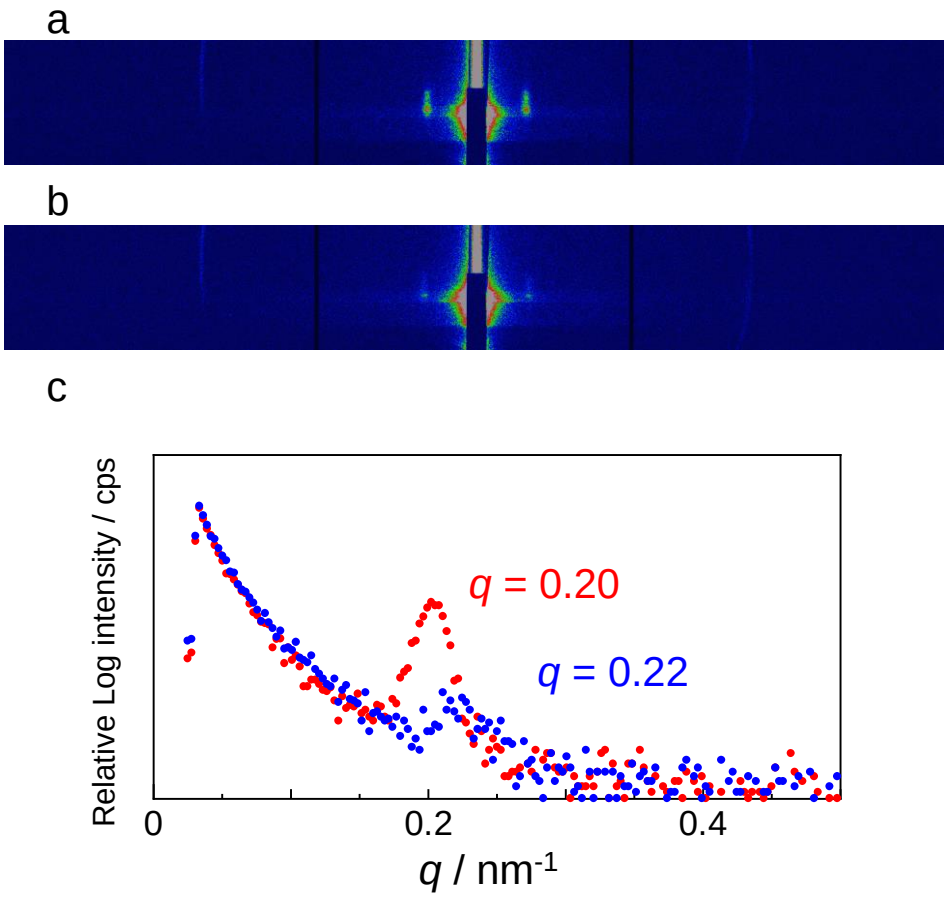

Figure S3. 2D images of GI-SAXS measurement of active photoalignment under LPL irradiation. The light exposure doses were zero (just irradiated) (a) and 15 (b) mJ cm^{-2}. The in-plane 1D profiles are shown in c.

3. POM observations

The POM observation of LC film is a facile method to evaluate the grain structure above micrometer levels. Figure S4 shows series of POM photos for an annealed film before irradiation (a), irradiated film after 1st LPL at 600 mJ cm^{-2} (initially photoalined film) (b), after 2nd LPL irradiation at 80 mJ cm^{-2} (transient state) (c) and at 600 mJ cm^{-2} (orthogonally realigned film) (d). In each set, crossed polarizers were rotated by 45 °.

The film before LPL irradiation (a), most of the field was dark, indicative of existence of smaller domains below the optical resolution. For other images (b – d), divided domains exhibited dark/bright inversions upon 45° rotation of the crossed polarizers.

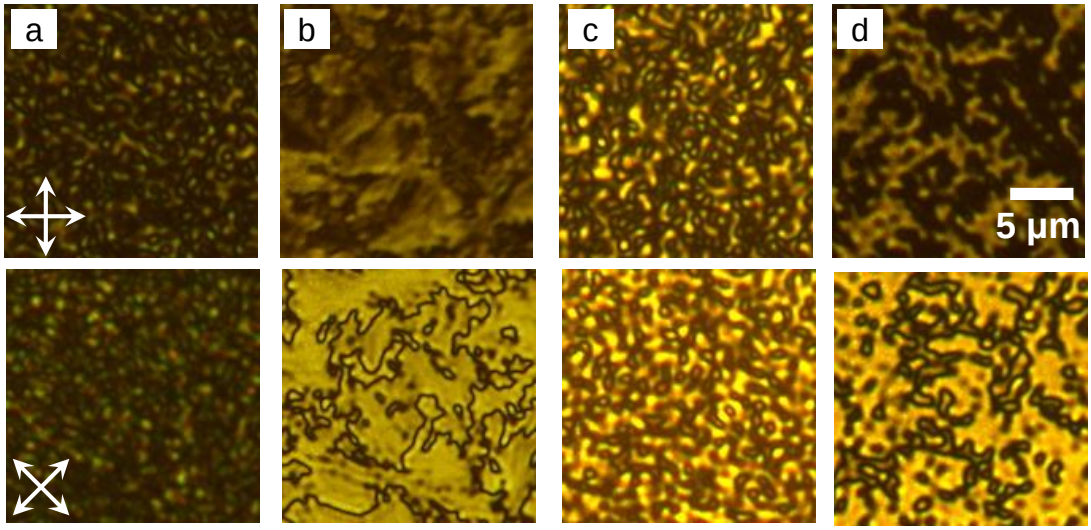

Figure S4. POM images for an annealed film before irradiation (a), irradiated film after 1st LPL at 600 mJ cm^{-2} (initially photoalined film) (b), after 2nd LPL irradiation at 80 mJ cm^{-2} (transient state) (c) and at 600 mJ cm^{-2} (orthogonally realigned film) (d).