

## Supporting Information

### Alignment Control of Smectic Layer Structures in Liquid-Crystalline Polymers by Photopolymerization with Scanned Slit Light

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Figure S1. DSC thermograms (third scan) of the monomers and polymers.

Figure S2. A schematic of the optical setup used for photopolymerization.

Figure S3. Polarized UV-vis absorption spectra of the resultant polymers.

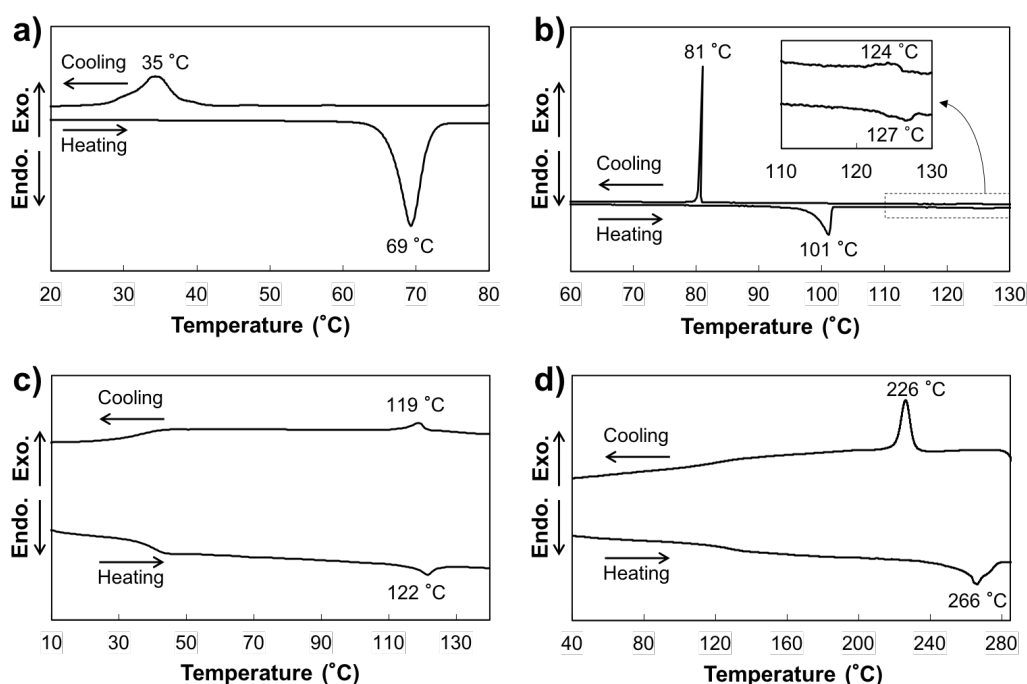
Figure S4. POM images and polarized IR absorption spectra of the films polymerized with flood illumination.

### Text S1. Preparation procedure of a glass cell

To conduct photopolymerization, glass cells (20 x 20 mm; cell gap 2-5  $\mu\text{m}$ ) were prepared by adhering two glass substrates with glue containing silica spacers (Thermo scientific, 9000 Series). Before assembling the cells, glass substrates were washed ultrasonically consecutively with 1 wt% neutral detergent in water, distilled water, and then 2-propanol. The cell gap of all glass cells was measured with a UV-vis spectrophotometer (V-650ST, JASCO) and the Fabry-Perot measurement method.<sup>S1</sup>

### Text S2. DSC thermograms of monomers and polymers

To determine photopolymerization temperature, thermal transitions of monomers and polymers were measured by differential scanning calorimetry (DSC) as shown in figure S1. For the preparation of polymer samples for DSC, photopolymerizable mixtures were injected into glass cells with the cell gap of 10  $\mu\text{m}$  and photopolymerized by irradiation throughout the cell.

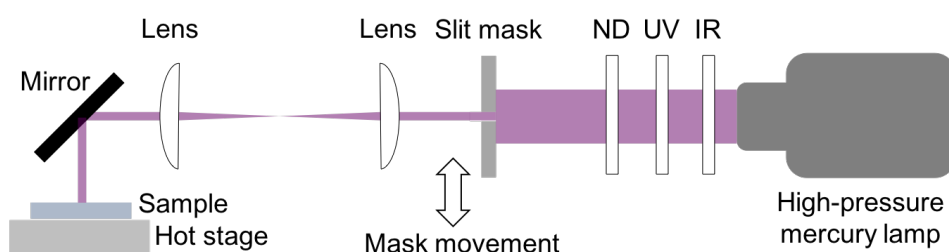


**Figure S1.** DSC thermograms (third scan) of the monomers and polymers. (a) **A6CB** and (b) **A0CB** monomers and polymerized samples from prepared mixtures of (c) **A6CB** and (d) **A0CB**. Scanning rate was 10  $^{\circ}\text{C}/\text{min}$  for (a, c and d) and 1  $^{\circ}\text{C}$  for (b).

A polymer obtained from **A6CB** shows reentrant nematic-ematic-nematic-isotropic phase transitions, but the polymers with high molecular weight ( $M_n$  higher than 20,000) exhibit a phase transition only around 120 °C corresponding to nematic-isotropic phase transition without any other LC phase transitions.<sup>S2</sup> As observed in figure S1c, the DSC thermogram of the polymer obtained from **A6CB** exhibited a phase transition peak. Considering that the polymer was synthesized in bulk and crosslinked, it is reasonable that the polymer film here exhibited only the nematic LC phase.

### Text S3. Optical setup for the photopolymerization experiments

For photopolymerization, 365-nm UV light from a high-pressure mercury lamp (USH-500SC, USHIO) was used (figure S2). For the photopolymerization of **A6CB** mixture, glass filters IRA-25S and UV-36A (AGC Techno Glass, Co.) were equipped, and light intensity was controlled to 1.2 mW/cm<sup>2</sup> with a neutral density filter (ND-50, AGC Techno Glass, Co.). In the case of the photopolymerization of **A0CB**, the intensity was set at 4.2 mW/cm<sup>2</sup> with the other combination of glass filters (IRA-25S, UV-33S, AGC Techno Glass, Co.)



**Figure S2.** A schematic of the optical setup used for photopolymerization. IR: IR filter, UV: UV-bandpass filter, and ND: neutral-density filter.

### Text S4. Characterization methods

Observation of optical anisotropy:

The optical anisotropy of the polymerized film (Figure 2a and b) was observed with a polarized optical microscope (BX-53, Olympus).

Evaluation of cyanobiphenyl alignment by UV-vis measurement:

The evaluation of the anisotropy of cyanobiphenyl moieties was performed with a UV-

vis spectrophotometer (V-650ST, JASCO) equipped with a rotatable stage and a polarizer. Order parameter was calculated by averaging the absorbance in a range of 333-337 nm, which corresponds to the absorption band of cyanobiphenyl moieties. Polar plots (Figure 2c and d) were generated from the averaged absorbance in a range of 333-337 nm measured by rotating the film by every 10°.

Orientation evaluation of functional moieties by FTIR measurement:

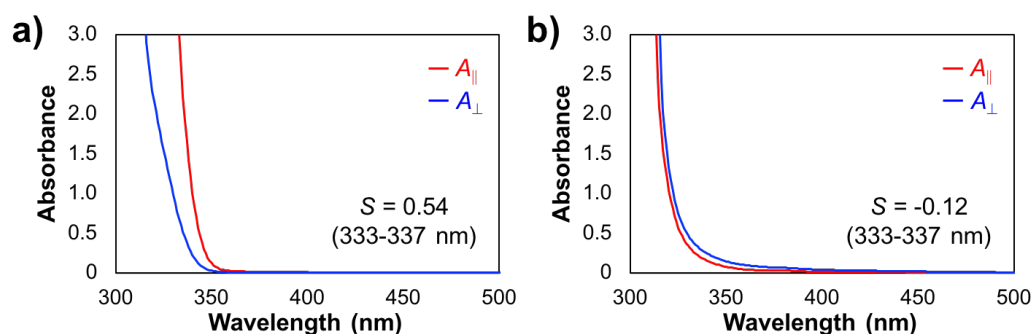
The orientation evaluation from the dichroism of the C≡N and C=O stretching vibration was performed with an FTIR spectrometer (FT/IR-6100, JASCO) with a rotatable film holder and a polarizer. To circumvent the issue that glass substrates used absorbs the incident IR light and thus disturb FTIR measurement, we opened the glass cells to take out the polymerized film and made them freestanding with a thickness of 2-5 μm.

Nanostructure evaluation by GI-SAXS measurement:

GI-SAXS data for the evaluation of anisotropic nanostructure of the films were acquired with a Nano-Viewer with a PILATUS detector (Rigaku Co.). CuKα radiation ( $\lambda = 1.541 \text{ \AA}$ ) was used as an X-ray radiation source, and the incident angle was set at 0.196°. The film of which one side was exposed to air was prepared for X-ray measurement by removing a glass plate from a glass cell. The  $d$  values, representing the spacing of periodic structures, were calculated by the equation [ $d = 2\pi/q$ ], where  $q$  is the scattering vector obtained from the diffractograms inserted in Figure 3c and d.

### **Text S5. Polarized UV-vis absorption spectra of the polymerized films**

To evaluate the alignment of mesogenic cyanobiphenyl moieties in the resultant **A6CB** and **A0CB** polymer films by polymerized with 1D scanned slit light, polarized UV-vis absorption spectra were measured (figure S3). We assumed that the lower order parameter  $S$  of the **A0CB** film (-0.12) than that of **A6CB** film (0.54) is due to the rotational structure of the smectic layers (Figure 3e) in which some of the **A0CB** mesogens have tilted angle from 0 to 90°.



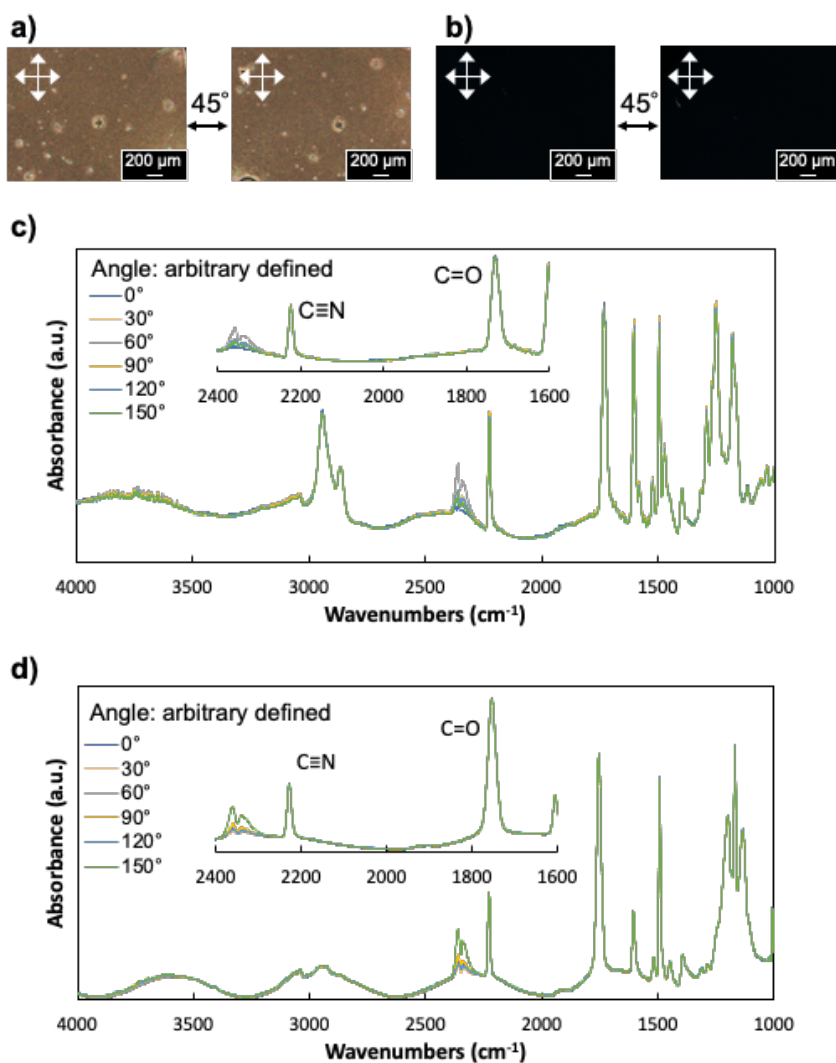
**Figure S3.** Polarized UV-vis absorption spectra of the resultant polymers. (a) **A6CB** and (b) **A0CB** polymer film.  $A_{\parallel}$  and  $A_{\perp}$  represent the absorbances parallel and perpendicular to the scanning direction, respectively.

#### **Text S6. POM images and polarized IR absorption spectra of the films polymerized with flood illumination**

As a control experiment, we conducted photopolymerization of **A6CB** and **A0CB** mixtures with flood illumination, and evaluated molecular alignment of these resultant polymer films by POM and FTIR measurements (figure S4). On the contrary to the films fabricated with 1D scanned slit light depicted in Figure 2, the films polymerized with flood illumination have never exhibited uniform optical anisotropy (figure S4a and b). Polarized IR absorption spectra of these films revealed that the  $C\equiv N$  and  $C=O$  groups had no dichroism (figure S4c and d), suggesting that mesogens and polymer main chains were not aligned in both **A6CB** and **A0CB** films fabricated by flood illumination.

#### **Reference for Supporting Information:**

- S1. Jiang, P.; Bertone, J. F.; Hwang, K. S.; Colvin, V. L. Single-Crystal Colloidal Multilayers of Controlled Thickness. *Chem. Mater.* **1999**, *11*, 2132–2140.
- S2. Tomikawa, N.; Itoh, T.; Okazaki, Y.; Adachi, M. A.; Tokita, M.; Watanabe, J. Molecular Weight Dependence of Phase Behavior in Side-Chain Liquid Crystalline Polymer Which Exhibits Reentrant Nematic Phase. *Jpn. J. Appl. Phys.* **2005**, *44*, L381–L384.



**Figure S4.** POM images and polarized IR absorption spectra of the films polymerized with flood illumination. POM images of films photopolymerized with **A6CB** (a) and **A0CB** (b). Polarized IR absorption spectra of the resultant films photopolymerized with **A6CB** (c) and **A0CB** (d). Flood illumination was conducted for 10 min. For the photopolymerization of **A0CB**, ratio of **A0CB:HDDMA** was 99.8:0.2 (mol%), and light intensity was 5.0 mW/cm<sup>2</sup>. Other experimental conditions were the same as photopolymerization with 1D scanned slit light.