Supporting Information

Evaluations of Mesogen Orientation in Thin Films of Polyacrylate with Cyanobiphenyl Side Chain

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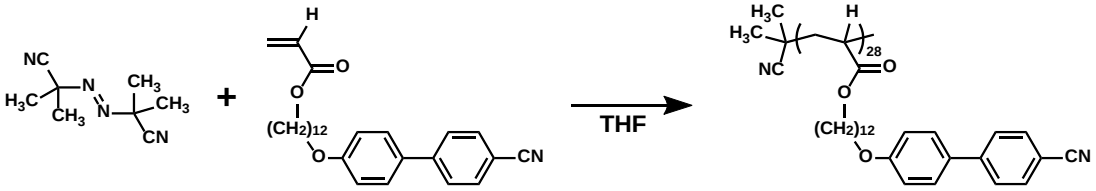
1. Materials

The cyanobiphenyl monomer was synthesized by the method in the previous paper.[S1] Tetrahydrofuran (THF) and azobisisobutyronitrile were obtained from TCI.

2. Synthesis of cyanobiphenyl monomers and polymers

2-1. Polymerization of PCBA via radical polymerization



Scheme S1

Synthetic route of PCBA is shown in Scheme S1. Azobisisobutyronitrile (AIBN) (0.82 mg, 5.0×10^{-6} mol) and 12-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)dodecyl acrylate (CBA) (433.6 mg, 1.0×10^{-3} mol) were added into a 15 mL pressure glass tube. The mixture was dissolved in tetrahydrofuran (THF) (1.0 mL) in glove box. The sealed mixture was removed from the glove box and placed for 6 h in a ChemStation at 70 ºC. The solution was poured to hexane to remove AIBN initiator and CBA monomer. The average number of repeating unit of CBA being 28 ($PCBA_{28}$); $M_n = 1.2 \times 10^4$, Mw/Mn = 1.83. Thermophysical properties evaluated by DSC: glass-13 °C–smectic A–95 °C–isotropic.

3. Characterizations

3-1. ^{1}H NMR

^{1}H NMR spectra (JNM-GSX270, JEOL) was recorded 16th steps using tetramethylsilane as the internal reference for deuterated chloroform solution (Across). A small amount of polymerized

solution was measured and conversion of polymerization was calculated based on the values of integrals of a monomer and a polymer.

3-2. Gel permeation chromatography

Gel permeation chromatography (GPC) measurement was performed with a Shodex DS-4/UV-41/RI-101 connected with two GPC columns (Shodex KF-403 and KF-405). THF was used as an eluent at a flow rate of 1.0 mL min^{-1}. The calibration of molecular weight was achieved by using polystyrene standards (TSK standard polystyrene, Tosoh).

3-3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was performed on a TA DSC Q200 MO-DSC-UV. DSC scans were performed within the temperature range from -20 to 150 °C at a heating rate of 10 °C min^{-1} under nitrogen. About 4 mg mass was used for DSC measurements for all samples. An empty aluminum pan was used as a reference.

3-4. White light interferometric microscopy

The film thickness were obtained as evaluated by a white light interferometric microscope (BW-S501, Nikon 129 Instruments).

3-5. UV-Vis absorption spectroscopy

UV-visible absorption spectra were taken on an Agilent 8453 spectrometer (Agilent Technologies). A source of illumination used a D2-W lamp.

3-6. X-ray scattering measurement (High and Low energy GI-SAXS)

X-ray scattering measurement was performed with a FR-E X-ray diffractometer equipped with R-AXIS IV two-dimensional (2D) detector (Rigaku Co.) at a voltage of 45 kV, current of 45 mA, and irradiation time of 2 h to create copper Cu Kα radiation (λ = 0.154 nm). Camera length was 300 mm for the bulk and GI-SAXS measurement. X-ray scattering patterns were recorded on an imaging plate (Fujifilm Co.). Temperature of the film sample was controlled using a ceramic heating system.

3-7. Contact angle measurements

The contact angle of a water droplet was estimated with a FACE CA-XP contact angle meter (Kyowa Interface Science). The averaged values of five measurements were obtained.

4. DSC measurement of PCBA.

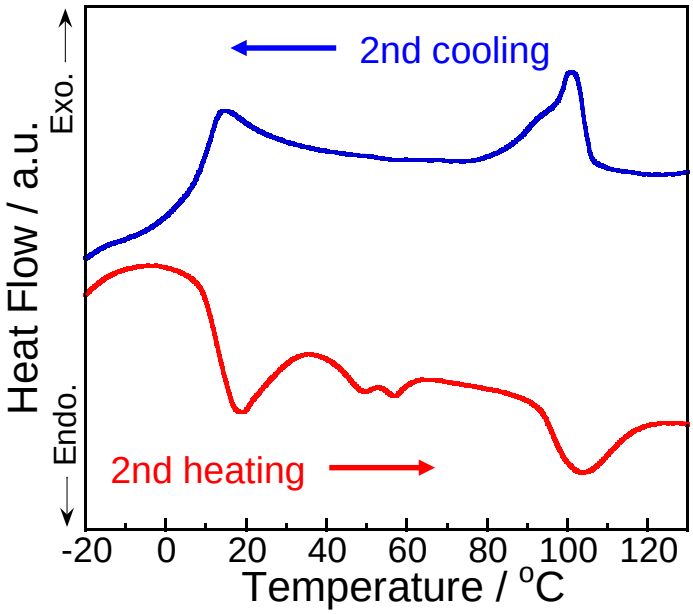


Figure S1. DSC curves of PCBA at a rate of 2 °C min^{-1}. Note that structure characterizations were performed to elucidate the origin of endothermal peaks at 50 – 60 °C in the heating process (Figure S2).

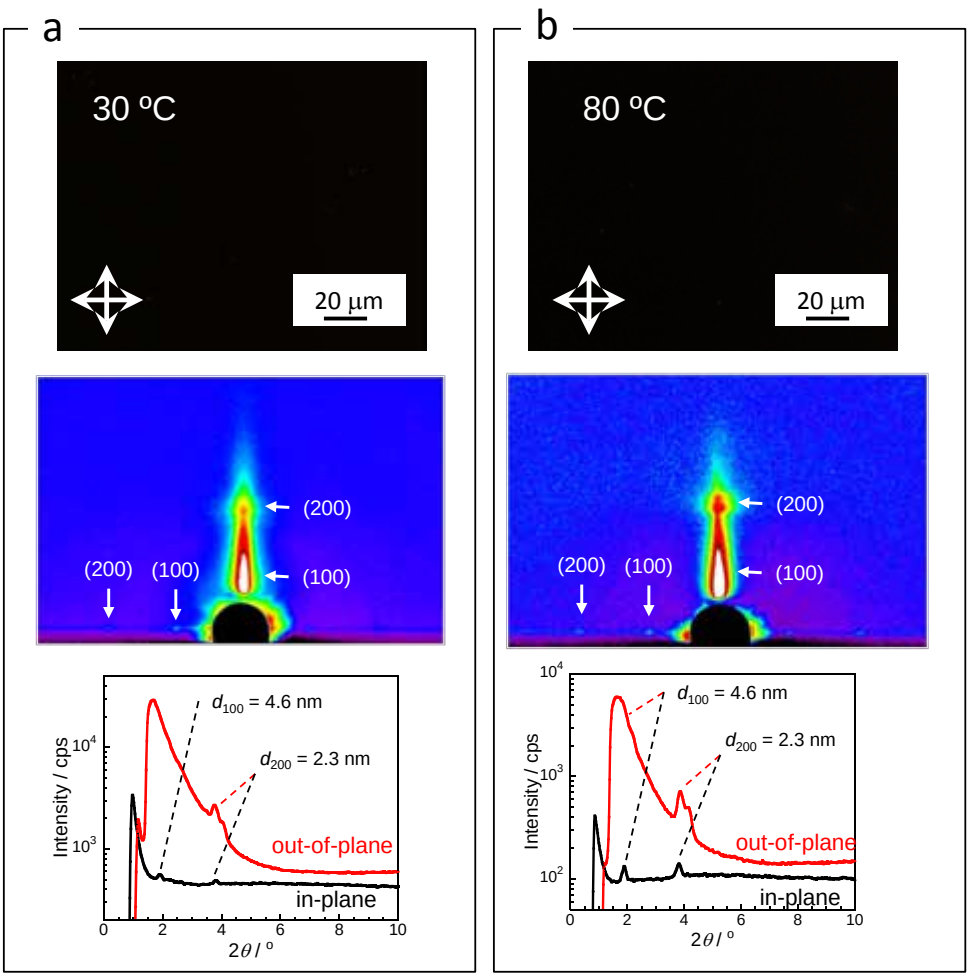
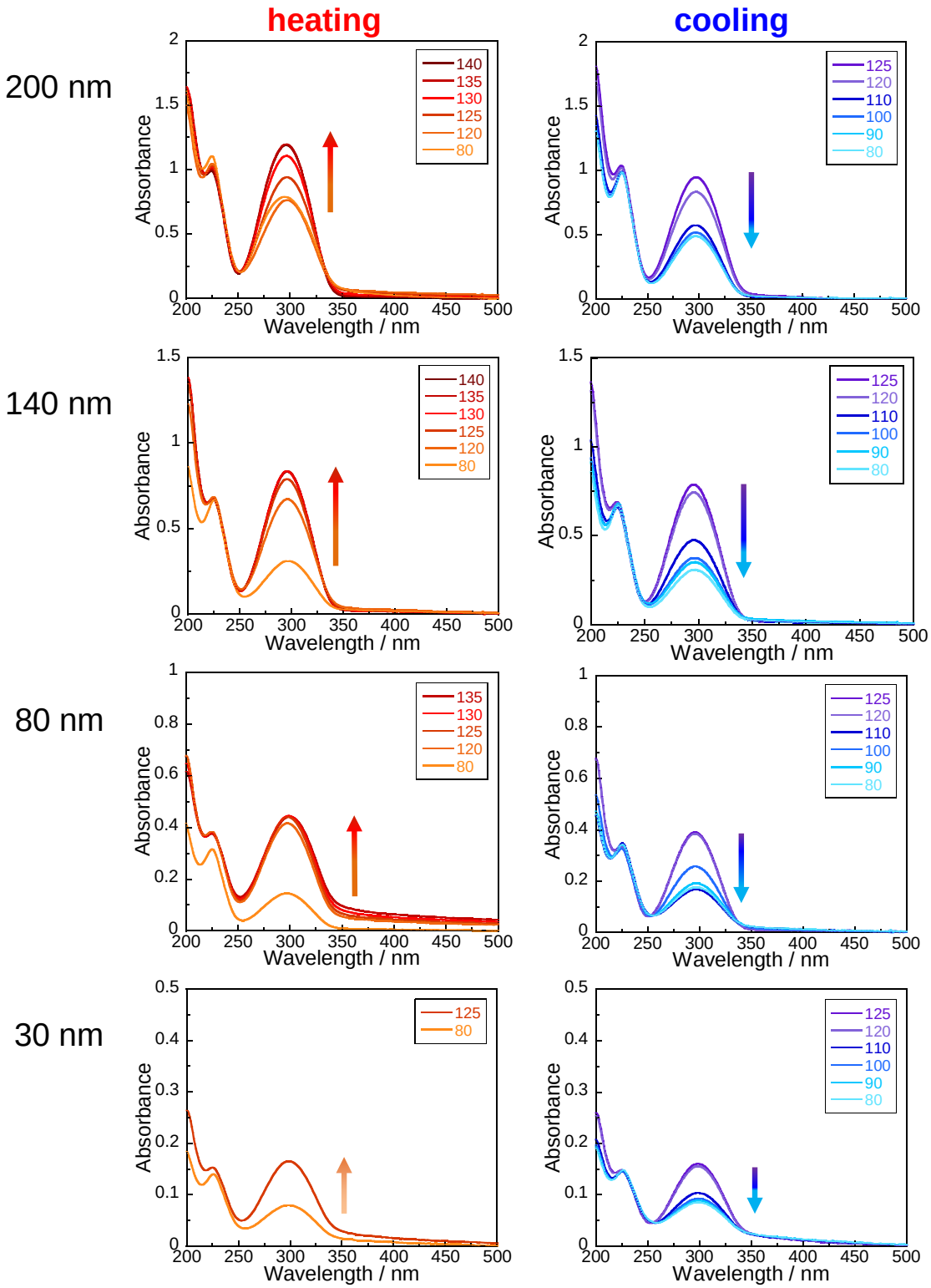


Figure S2. POM and GI-SAXS data of PCBA film (thickness 140 nm) taken at 30 °C (a) and 80 °C (b) to check the structural change around 50 – 60 °C. As shown, no appreciable difference was observed. The existence of a similar broad peak was also reported previously for a similar side chain CB polymer by Kostromin et al.[S2] Also, they also did not mentioned appreciable structural change during this minor endothermal peak.

5. UV-Vis absorption spectra of PCBA films with various film thickness.



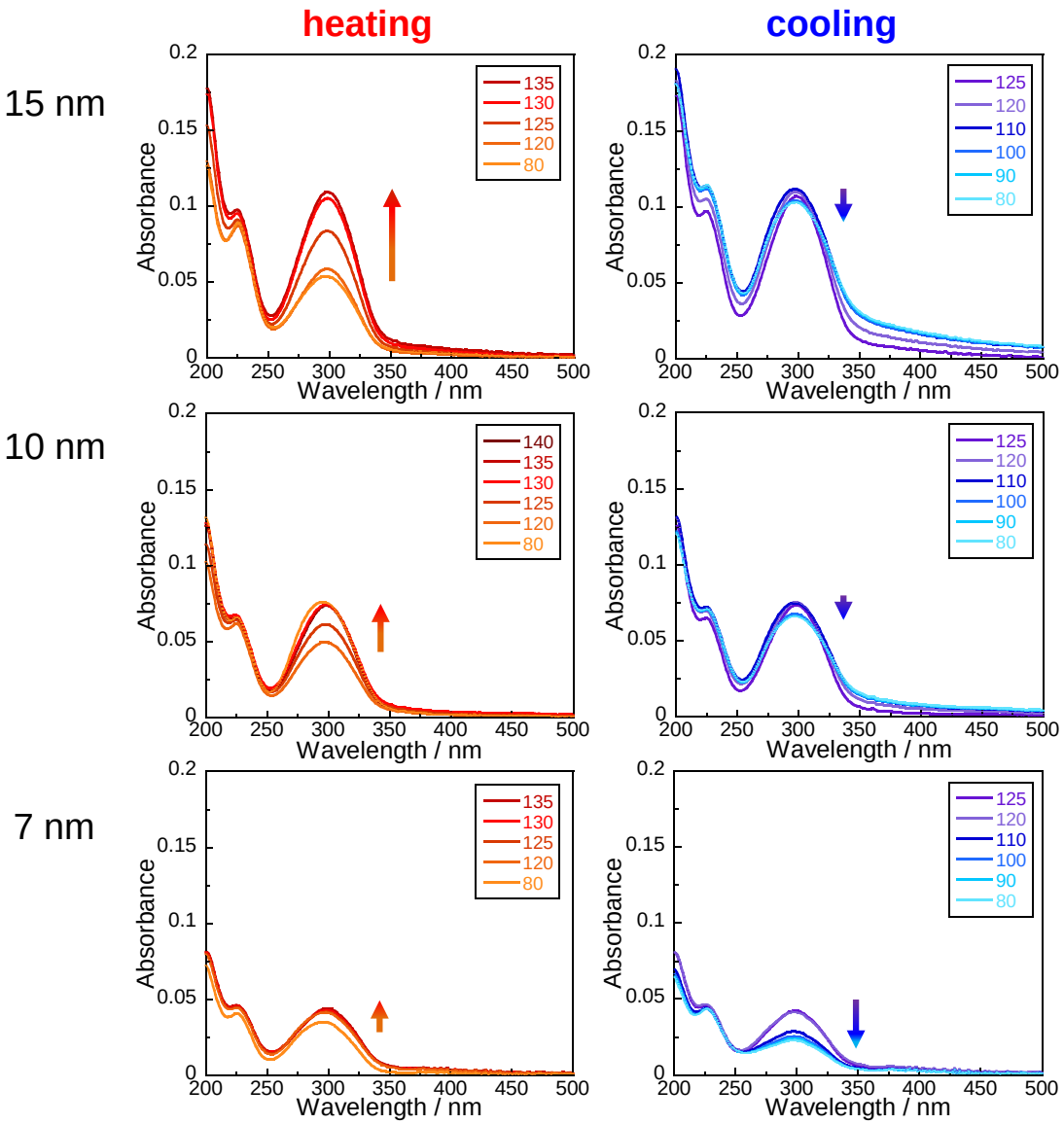


Figure S3. UV-visible absorption spectral changes accompanied by temperature changes for PCBA films with varied thicknesses.

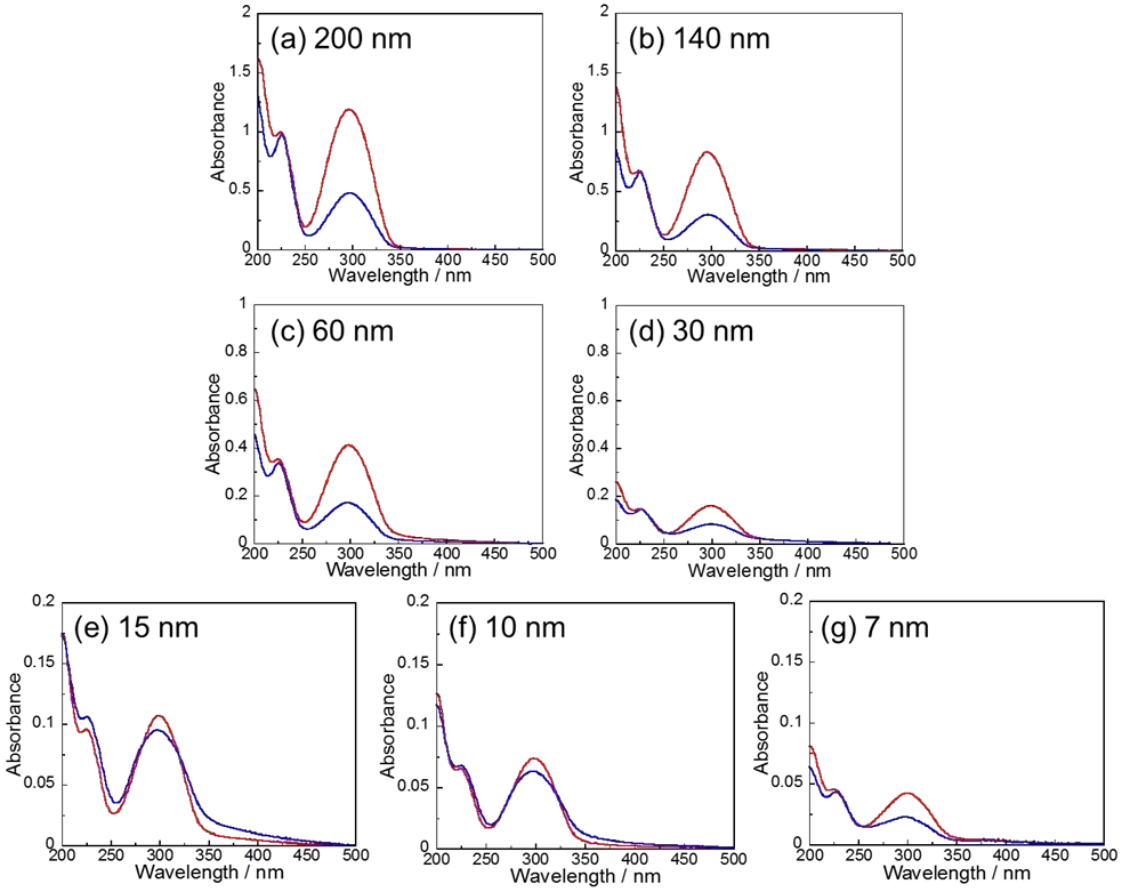


Figure S4. UV-Vis absorption spectral changes of PCBA films with 200 (a), 140 (b), 60 (c), 30 (d), 15 (e), 10 (f) and 7 (g) nm thickness at 135 (red) and 80 (blue) °C.

6. GI-SAXS measurements of PCBA films with various film thickness.

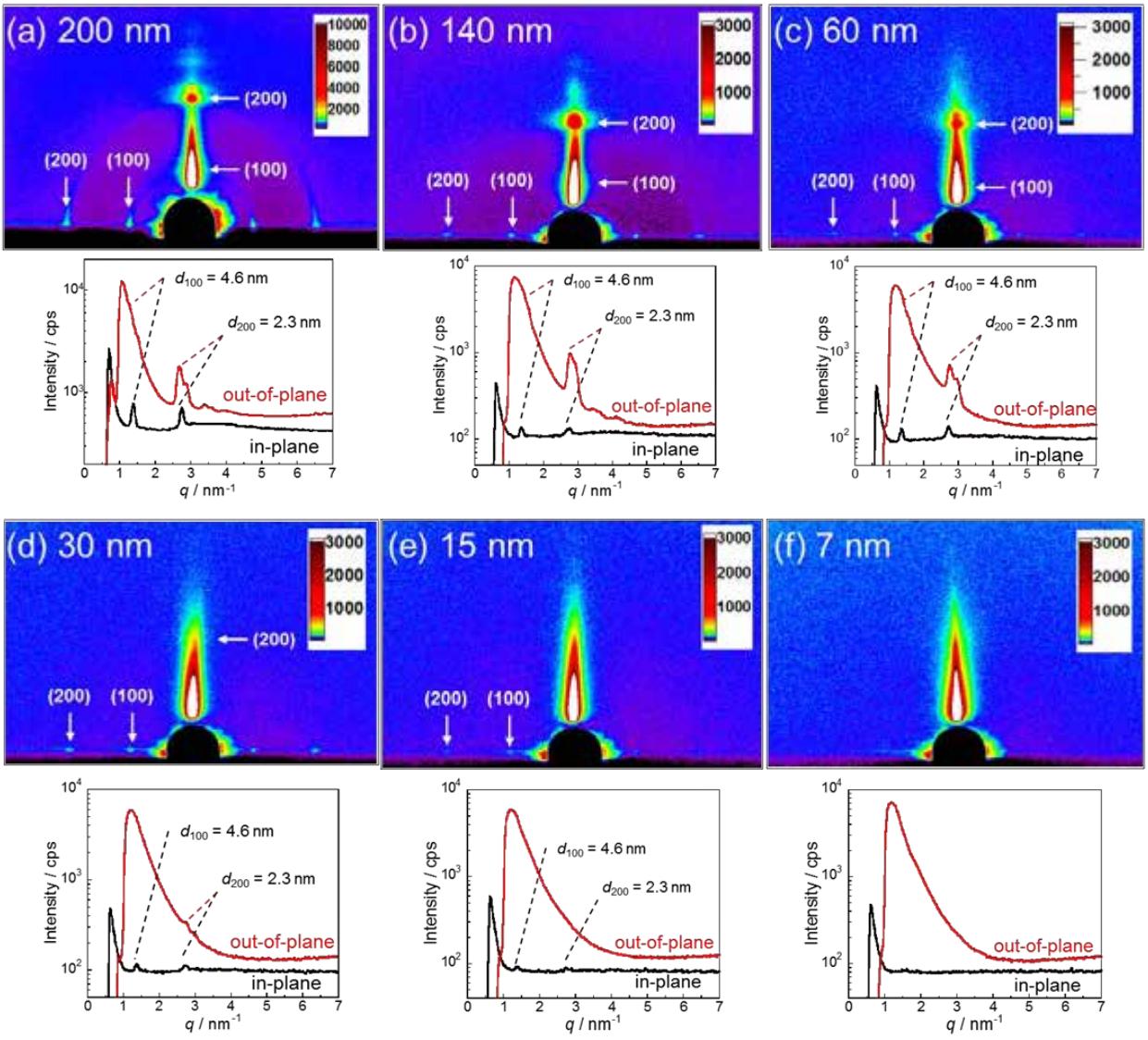


Figure S5. GI-SAXS data (Hard X-ray, 0.154 nm) of PCBA films with 200 (a), 140 (b), 60 (c), 30 (d), 15 (e) and 7 (f) nm thickness at 80 °C. In each part, upper and lower figures display 2D-XRD patterns and 1D intensity profiles (black: in-plane direction, red: out-of-plane direction), respectively.

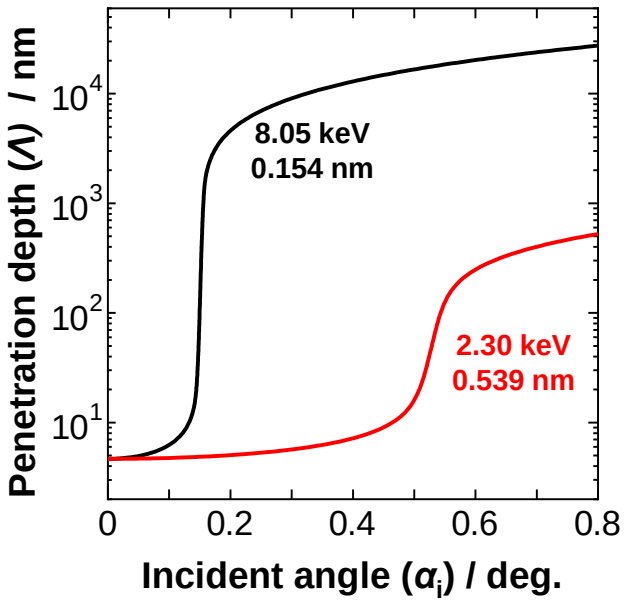


Figure S6. Estimated penetration depth in the PCBA film (density 1.1 g cm^{-3}) for X-ray of 8.05 keV (0.154 nm) and 2.30 keV (0.539 nm) (for calculation, see ref. S3).

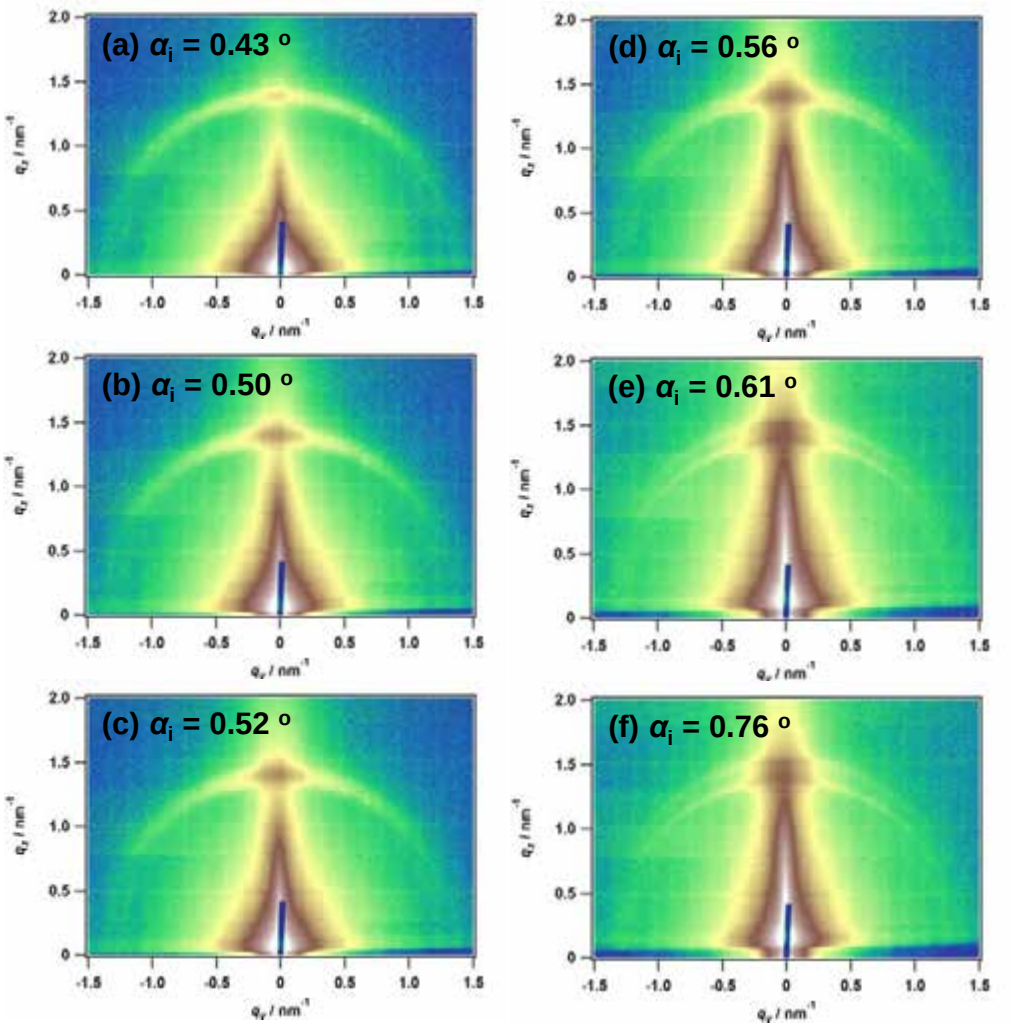


Figure S7. 2D GI-SAXS images using low energy X-ray (0.539 nm) for 140 nm thick PCBA film at α_i = 0.43 (Λ = 8 nm) (a), 0.50 (Λ = 16 nm) (b), 0.52 (Λ = 29 nm) (c), 0.56 (Λ = 167 nm) (d), 0.61 (Λ = 268 nm) (e), and 0.76 (Λ = 475 nm) (f).

References

(S1) Tanaka, D.; Nagashima, Y.; Hara, M.; Nagano, S.; Seki, T. Alternation of Side-Chain Mesogen Orientation Caused by the Backbone Structure in Liquid-Crystalline Polymer Thin Films. *Langmuir*, **2015**, *31*, 11379-11383.

(S2) Kostromin, S. G.; Sinizyn, V. V.; Tolroze, R. V., Shibaev, V. P.; Plate, N. A. Smectic “C” phase in liquid crystalline polyacrylates with CN-containing Mesogenic groups, *Makromol. Chem. Rapid Commun.* **1982**, *3*, 809-814.

(S3) Saito, I.; Miyazaki, T.; Yamamoto, K.; Depth-Resolved Structure Analysis of Cylindrical Microdomain in Block Copolymer Thin Film by Grazing-Incidence Small-Angle X-ray Scattering Utilizing Low-Energy X-rays. *Macromolecules* **2015**, *48*, 8190-8196.