Supporting Online Material for

Large-Area Three-Dimensional Molecular Ordering of a Polymer Brush by One-Step Processing

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Materials and Methods

1. Materials. Unless otherwise noted, reagents were used as received from Aldrich Chemical [2-hexyl-1-decanol (97%) and methacrylic anhydride (94%)], Tokyo Chemical Industry (TCI) [phenol (99%), 10-bromo-1-decanol (85%), tert-butylidimethylchlorosilane (TBDMSCl, 98%), and tetrabutylammonium fluoride (TBAF, 1 M in tetrahydrofuran (THF))], and Wako Pure Chemical Industries [ethyl p-aminobenzoate (98%), imidazole (98%), N,N'-diisopropylcarbodiimide (DIPC, 99%), p-toluene sulfonic acid monohydrate (99%), 4-dimethylaminopyridine (DMAP, 99%), triethylamine (99%), 2,2'-azobisisobutyronitrile (AIBN, 98%), NaNO₂ (98.5%), NaHCO₃ (> 99%), Cs₂CO₃ (> 95%), and KOH (85%)]. 4-(Dimethylamino)pyridinium 4-toluenesulfonate (DPTS) was prepared according to a reported procedure (S1). CH₂Cl₂ was dried over CaH₂ and freshly distilled prior to use. THF was refluxed over a mixture of Na and benzophenone and freshly distilled before use. Other dehydrated solvents were used as received from Wako Pure Chemical Industries or Kanto Chemicals. Uniaxially stretched polytetrafluoroethylene (PTFE, Teflon™) sheets (300 mm x 10 m x 0.1 mm) were purchased from Flon Industry and cut into a proper size before use.

2. General. Column chromatography was carried out with Wakogel silica C-200 (particle size: 75–150 µm). Preparative size-exclusion chromatography (SEC) was performed using a 50 mm-ϕ x 1.5 m-long column (Bio-Beads™ S-X1 Beads, Bio-Rad) with toluene as an eluent. Analytical SEC was performed at 40 °C on a TOSOH model HLC-8220 GPC system equipped with a refractive index (RI) detector, using THF as an eluent at a flow rate of 0.35 mL/min on linearly connected three polystyrene gel columns (TSKgel SuperMultiporeHZ-M, TOSOH). The molecular weight calibration curve was obtained by using standard polystyrenes (Shodex STANDARD SM–105, Showa Denko). ¹H and ¹³C NMR spectra were recorded at 25 °C on a JEOL model JNM-ECA500 spectrometer, operating at 500 and 125 MHz, respectively, where chemical shifts (δ in ppm) were determined with respect to tetramethylsilane as an internal reference. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on an Applied Biosystems model MDS SCIEX 4800 Plus MALDI-TOF/TOF™ Analyzer using dithranol as a matrix. Electronic absorption spectra were recorded on a JASCO model V-670 UV/VIS/NIR spectrophotometer. Infrared (IR) spectra were recorded at 25 °C on a JASCO model FT/IR-4100 Fourier transform infrared spectrometer with an attenuated total reflection (ATR) equipment (ATR PRO450-S). Polarized IR spectra were recorded at 25 °C on a JASCO model FT/IR-4100 Fourier transform infrared spectrometer connected to an Irtcon IRT-5000 microscope unit. Differential scanning calorimetry (DSC) was performed on a Mettler–Toledo model DSC 1 differential scanning calorimeter, where temperature and enthalpy were calibrated with In (430 K, 3.3 J/mol) and Zn (692.7 K, 12 J/mol)
standard samples using sealed Al sample pans. Cooling and heating profiles were recorded and analyzed using the Mettler–Toledo STAR® software system. Polarized optical microscopy (POM) was performed on a Nikon model Eclipse LV100POL optical polarizing microscope equipped with a Mettler–Toledo model FP90 controller attached to a FP82HT hot stage. Hot press was performed on an Imoto Machinery model IMC-180C compact press. Film thicknesses were measured using a Mitutoyo model MDQ-30M micrometer. Photoirradiation was conducted at 25 °C using an Asahi Spectra model MAX-302 xenon light source (300 W) with band pass filters (Asahi Spectra) of $\lambda = 360 \pm 2$ nm for UV irradiation and $\lambda = 480 \pm 2$ nm for visible light irradiation. The light intensity was measured using an Ophir model 3A-P thermopile sensor and a NOVA power meter.

Reagents and conditions: (a) TBDMSCl, imidazole, DMF, 25 °C; (b) NaNO₂, phenol, hydrochloric acid, 5 °C; (c) 3, Cs₂CO₃, DMF, 50 °C; (d) KOH, THF, 25 °C; (e) 2-hexyl-1-decanol, DPTS, DIPC, CH₂Cl₂, 25 °C; (f) TBAF, THF, 25 °C; (g) 6, DPTS, DIPC, CH₂Cl₂, 25 °C; (h) 6, DPTS, DIPC, CH₂Cl₂, 40 °C; (i) methacrylic anhydride, DMAP, triethylamine, THF, 50 °C.
**Compound 3.** To a DMF solution (20 mL) of a mixture of 10-bromo-1-decanol (15.0 g, 63.2 mmol) and imidazole (8.61 g, 126 mmol) was added TBDMSCl (14.3 g, 94.9 mmol), and the mixture was stirred at 25 °C for 3 hours under Ar. The reaction mixture was poured into a saturated aqueous solution of NH₄Cl and extracted with AcOEt. The combined organic extract was washed successively with water and brine, and an organic phase separated was dried over anhydrous MgSO₄ and then evaporated to dryness under a reduced pressure. The residue was subjected to column chromatography (SiO₂, hexane/AcOEt 10/1 v/v) to allow isolation of 3 as colorless oil (22.0 g, 62.6 mmol) in 99% yield. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 3.60 (t, J = 6.9 Hz, 2H), 3.40 (t, J = 6.9 Hz, 2H), 1.85 (m, 2H), 1.60–1.47 (m, 2H), 1.35–1.24 (m, 10H), 0.89 (s, 9H), 0.05 (s, 6H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 63.30, 33.97, 32.88, 32.85, 29.51, 29.39, 28.76, 28.19, 25.99, 25.79, 18.38, –5.25. FT-IR (ATR): ν (cm⁻¹) 2926, 2854, 1462, 1253, 1097.

**Compound 4.** This compound was synthesized according to a literature (S2). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.18 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 5.35 (s, 1H), 4.42 (q, J = 6.9 Hz, 2H), 1.43 (t, J = 6.9 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 166.30, 158.87, 155.28, 147.23, 131.58, 130.57, 125.43, 122.37, 115.92, 61.28, 14.35. FT-IR (ATR): ν (cm⁻¹) 3384, 1689, 1590, 1280, 1223. HRMS (MALDI-TOF mass): calcd. for C₁₅H₁₅N₂O₃ [M + H]⁺: m/z = 271.1083; found: 271.1080.

**Compound 5.** To a DMF solution (40 mL) of 3 (20.0 g, 56.9 mmol) was successively added 4 (15.4 g, 56.9 mmol) and Cs₂CO₃ (22.3 g, 68.3 mmol), and the mixture was stirred at 50 °C for 12 hours under Ar. The reaction mixture was allowed to cool to 25 °C, filtrated off from an insoluble fraction, and washed with CH₂Cl₂. The filtrate was diluted with AcOEt, washed successively with a saturated aqueous solution of NH₄Cl, water, and brine, and an organic phase separated was dried over anhydrous MgSO₄ and then evaporated to dryness under a reduced pressure. The residue was recrystallized from a mixture of EtOH/AcOEt (10/1 v/v), affording 5 as orange solid (20.3 g, 37.5 mmol) in 66% yield. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.17 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 4.41 (q, J = 6.9 Hz, 2H), 4.05 (t, J = 6.9 Hz, 2H), 1.82 (m, 2H), 1.55–1.45 (m, 4H), 1.42 (t, J = 6.9 Hz, 3H), 1.40–1.25 (m, 10H), 0.87 (s, 9H), 0.05 (s, 6H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 166.19, 162.33, 155.37, 146.88, 131.51, 130.54, 125.19, 122.31, 114.80, 68.45, 63.33, 61.17, 32.90, 29.57, 29.51, 29.44, 29.37, 29.18, 26.00, 25.81, 18.39, 14.36, –5.24. FT-IR (ATR): ν (cm⁻¹) 2929, 2853, 1714, 1602, 1581, 1500, 1273, 1255, 1105. HRMS (MALDI-TOF mass): calcd. for C₃₁H₉₉N₂O₄Si [M + H]⁺: m/z = 541.3462; found: 541.3444.
**Compound 6.** To a THF (200 mL) solution of 5 (5.41 g, 10.0 mmol) was successively added EtOH (40 mL) and an aqueous solution of KOH (1 M, 20 mL), and the mixture was stirred at 25 °C for 6 hours. The reaction mixture was poured into a saturated aqueous solution of NH₄Cl and extracted with AcOEt. The combined organic extract was washed successively with water and brine, dried over anhydrous MgSO₄, and then evaporated to dryness under a reduced pressure. The residue was recrystallized from EtOH, affording 6 as orange solid (3.96 g, 7.73 mmol) in 77% yield. ¹H NMR (500 MHz, DMSO-d₆, 60 °C): δ (ppm) 8.15 (d, J = 8.0 Hz, 2H), 7.93 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H), 7.15 (d, J = 8.6 Hz, 2H), 4.12 (t, J = 6.3 Hz, 2H), 3.59 (t, J = 6.3 Hz, 2H), 1.78 (m, 2H), 1.53–1.42 (m, 4H), 1.40–1.24 (m, 10H), 0.89 (s, 9H), 0.05 (s, 6H). ¹³C NMR (125 MHz, DMSO-d₆, 60 °C): δ (ppm) 167.26, 161.76, 154.08, 146.05, 134.44, 133.44, 130.18, 124.59, 121.71, 114.92, 67.92, 62.21, 31.98, 28.62, 28.55, 28.40, 28.38, 28.29, 25.54, 25.14, 24.96, 17.62, −5.93. FT-IR (ATR): ν (cm⁻¹) 3300–2200, 2926, 2852, 1676, 1600, 1581, 1501, 1248, 1139, 1099. HRMS (MALDI-TOF mass): calcd. for C₂₉H₄₅N₂O₄Si [M + H]⁺: m/z = 513.3149; found: 513.3152.

**Compound 7.** To a CH₂Cl₂ solution (10 mL) of 6 (1.00 g, 1.98 mmol) was successively added DPTS (0.114 g, 0.390 mmol) and DIPC (0.320 g, 2.54 mmol), and the mixture was stirred at 25 °C under Ar until all the reagents were dissolved. 2-Hexyl-1-decanol (0.473 g, 1.98 mmol) was added to the resulting solution, and the mixture was stirred at 25 °C for 12 hours under Ar. The reaction mixture was poured into water and extracted with CH₂Cl₂. The combined organic extract was washed successively with water and brine, and an organic phase separated was dried over anhydrous MgSO₄ and then evaporated to dryness under a reduced pressure. The residue was subjected to column chromatography (SiO₂, CHCl₃) to allow isolation of 7 as red oil (1.44 g, 1.96 mmol) in 97% yield. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.16 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H), 7.15 (d, J = 8.6 Hz, 2H), 4.26 (d, J = 5.7 Hz, 2H), 4.05 (t, J = 6.3 Hz, 2H), 3.60 (t, J = 6.3 Hz, 2H), 1.87–1.75 (m, 3H), 1.55–1.22 (m, 38H), 0.92–0.85 (m, 15H), 0.05 (s, 6H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 166.31, 162.33, 155.38, 146.88, 131.58, 130.51, 125.19, 122.34, 114.80, 68.45, 68.01, 63.33, 37.49, 32.90, 31.92, 31.83, 31.49, 29.97, 29.64, 29.57, 29.51, 29.44, 29.37, 29.32, 29.18, 26.79, 26.77, 26.00, 25.81, 22.69, 22.66, 18.39, 14.11, −5.24. FT-IR (ATR): ν (cm⁻¹) 3000–2200, 2924, 2854, 1719, 1599, 1582, 1501, 1489, 1317, 1094. HRMS (MALDI-TOF mass): calcd. for C₄₅H₇₇N₂O₄Si [M + H]⁺: m/z = 737.5653; found: 737.5626.

**Compound 8.** TBAF (1.0 M in THF, 3.85 mL, 3.85 mmol) was added to a THF solution (5 mL) of 7 (1.42 g, 1.93 mmol), and the mixture was stirred at 25 °C for 2 hours under Ar. The reaction mixture was evaporated to dryness under a reduced pressure, and a CH₂Cl₂ solution of the residue was washed with a saturated aqueous solution of NH₄Cl. An organic phase separated was dried...
over anhydrous MgSO₄ and evaporated to dryness under a reduced pressure. The residue was subjected to column chromatography (SiO₂, CHCl₃) to allow isolation of 8 as red solid (1.18 g, 1.89 mmol) in 98% yield. ¹H NMR (500 MHz, CDCl₃):  δ (ppm) 8.16 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 4.26 (d, J = 5.7 Hz, 2H), 4.05 (t, J = 6.3 Hz, 2H), 3.60 (broad t, 2H), 1.87–1.75 (m, 3H), 1.61–1.53 (m, 2H), 1.51–1.18 (m, 37H), 0.92–0.84 (m, 6H). ¹³C NMR (125 MHz, CDCl₃):  δ (ppm) 166.31, 162.33, 155.38, 146.89, 131.59, 130.52, 125.19, 122.34, 114.80, 68.43, 68.02, 63.09, 37.48, 32.81, 31.92, 31.83, 31.49, 29.97, 29.64, 29.57, 29.53, 29.48, 29.42, 29.35, 29.32, 29.17, 26.79, 26.77, 26.00, 25.74, 22.68, 22.66, 14.11. FT-IR (ATR): ν (cm⁻¹) 3416, 2924, 2852, 1714, 1600, 1578, 1499, 1269, 1252, 1135. HRMS (MALDI-TOF mass): calcd. for C₃₉H₆₃N₂O₄ [M + H]⁺: m/z = 623.4788; found: 623.4801.

**Compound 9.** To a CH₂Cl₂ solution (10 mL) of 6 (0.80 g, 1.56 mmol) was successively added DPTS (0.0915 g, 0.312 mmol) and DIPC (0.256 g, 2.03 mmol), and the mixture was stirred at 25 °C under Ar until all the reagents were dissolved. Compound 8 (0.972 g, 1.56 mmol) was added to the resulting solution, and the mixture was stirred at 25 °C for 12 hours under Ar. The reaction mixture was poured into water and extracted with CH₂Cl₂. The combined organic extract was washed successively with water and brine, and an organic phase separated was dried over anhydrous MgSO₄, and then evaporated to dryness under a reduced pressure. The residue was subjected to column chromatography (SiO₂, CHCl₃) to allow isolation of 9 as orange solid (1.58 g, 1.41 mmol) in 91% yield. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.17 (d, J = 8.0 Hz, 2H), 8.16 (d, J = 8.0 Hz, 2H), 7.93 (d x 2, J = 8.0 Hz, 4H, overlapped), 7.90 (d x 2, J = 8.6 Hz, 4H, overlapped), 7.01 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H), 4.34 (t, J = 6.9 Hz, 2H), 4.25 (d, J = 5.7 Hz, 2H), 4.05 (t, J = 6.9 Hz, 2H), 3.60 (t, J = 6.9 Hz, 4H, overlapped), 1.88–1.75 (m, 7H), 1.57–1.20 (m, 50H), 0.95–0.82 (m, 15H), 0.05 (s, 6H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 166.30, 166.23, 162.32, 155.38, 146.87, 131.58, 131.51, 130.54, 130.51, 125.20, 122.34, 122.32, 114.80, 68.45, 68.43, 68.02, 65.34, 63.33, 37.48, 32.90, 31.92, 31.83, 31.49, 29.97, 29.64, 29.57, 29.51, 29.46, 29.44, 29.38, 29.35, 29.32, 29.25, 29.18, 28.72, 26.79, 26.77, 26.00, 25.81, 22.68, 22.66, 18.39, 14.11, –5.24. FT-IR (ATR): ν (cm⁻¹) 2922, 2854, 1705, 1600, 1578, 1498, 1281, 1251, 1136. HRMS (MALDI-TOF mass): calcd. for C₆₈H₁₀₅N₄O₇Si [M + H]⁺: m/z = 1117.7753; found: 1117.7778.

**Compound 10.** By a procedure similar to that for 8, compound 10 was obtained in 93% yield (3.12 g, 3.11 mmol) from 9 (3.73 g, 3.34 mmol) and TBAF (1.0 M in THF, 6.7 mL, 6.7 mmol). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.17 (d, J = 8.0 Hz, 2H), 8.16 (d, J = 8.0 Hz, 2H), 7.93 (d x 2, J = 8.0 Hz, 4H, overlapped), 7.90 (d x 2, J = 8.6 Hz, 4H, overlapped), 7.00 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H), 4.35 (t, J = 6.9 Hz, 2H), 4.25 (d, J = 5.7 Hz, 2H), 4.04 (t x 2, J = 6.9 Hz,
4H, overlapped), 3.64 (t, J = 6.9 Hz, 2H), 1.88–1.75 (m, 7H), 1.62–1.53 (m, 2H), 1.52–1.20 (m, 49H), 0.92–0.84 (m, 6H). 13C NMR (125 MHz, CDCl3): δ (ppm) 166.31, 166.23, 162.33, 155.38, 146.88, 131.58, 131.52, 130.54, 130.51, 125.20, 122.34, 114.80, 68.43, 68.02, 65.34, 63.08, 37.48, 32.81, 31.92, 31.83, 31.49, 29.97, 29.64, 29.57, 29.53, 29.48, 29.46, 29.44, 29.42, 29.35, 29.32, 29.25, 29.17, 28.72, 26.79, 26.77, 26.00, 25.74, 22.69, 22.66, 14.13.  

FT-IR (ATR): ν (cm⁻¹) 3574, 2920, 2851, 1709, 1602, 1582, 1500, 1279, 1252, 1139. HRMS (MALDI-TOF mass): calcd. for C₆₂H₉₁N₄O₇ [M + H]⁺: m/z = 1003.6888; found: 1003.6895.

**Compound 11.** By a procedure similar to that for 9, except that the reaction temperature was 40 °C, compound 11 was obtained in 96% yield (3.44 g, 2.30 mmol) from 6 (1.23 g, 2.39 mmol), DPTS (0.140 g, 0.478 mmol), DIPC (0.392 g, 3.11 mmol), and 10 (2.40 g, 2.39 mmol). 1H NMR (500 MHz, CDCl₃): δ (ppm) 8.17 (d x 2, J = 8.0 Hz, 4H, overlapped), 8.16 (d, J = 8.0 Hz, 2H), 7.93 (d x 3, J = 8.0 Hz, 6H, overlapped), 7.90 (d x 3, J = 8.6 Hz, 6H, overlapped), 7.00 (d x 3, J = 8.6 Hz, 6H, overlapped), 4.35 (t x 2, J = 6.9 Hz, 4H, overlapped), 4.25 (d, J = 5.7 Hz, 2H), 4.08–4.01 (m, 6H), 3.60 (t, J = 6.9 Hz, 2H), 1.86–1.74 (m, 11H), 1.61–1.53 (m, 2H), 1.52–1.20 (m, 61H), 0.92–0.84 (m, 6H). 13C NMR (125 MHz, CDCl₃): δ (ppm) 166.30, 166.22, 162.32, 155.38, 146.87, 131.58, 131.51, 130.54, 125.20, 122.32, 114.80, 68.45, 68.01, 65.33, 63.08, 37.48, 32.81, 31.92, 31.83, 31.49, 29.97, 29.64, 29.57, 29.53, 29.48, 29.46, 29.44, 29.42, 29.35, 29.32, 29.25, 29.18, 28.72, 26.79, 26.77, 26.04, 26.01, 25.82, 22.69, 22.66, 18.40, 14.11, –5.24. FT-IR (ATR): ν (cm⁻¹) 2923, 2853, 1712, 1600, 1580, 1501, 1282, 1252, 1139. HRMS (MALDI-TOF mass): calcd. for C₉₁H₁₃₃N₆O₁₀Si [M + H]⁺: m/z = 1497.9852; found: 1497.9862.

**Compound 12.** By a procedure similar to that for 8, compound 12 was obtained in 96% yield (2.20 g, 1.59 mmol) from 11 (2.47 g, 1.65 mmol) and TBAF (1.0 M in THF, 3.3 mL, 3.3 mmol). 1H NMR (500 MHz, CDCl₃): δ (ppm) 8.17 (d x 2, J = 8.0 Hz, 4H, overlapped), 8.16 (d, J = 8.0 Hz, 2H), 7.93 (d x 3, J = 8.0 Hz, 6H, overlapped), 7.90 (d x 3, J = 8.6 Hz, 6H, overlapped), 7.00 (d x 3, J = 8.6 Hz, 6H, overlapped), 4.35 (t x 2, J = 6.9 Hz, 4H, overlapped), 4.25 (d, J = 5.7 Hz, 2H), 4.08–4.01 (m, 6H), 3.60 (broad q, J = 5.7 Hz, 2H), 1.86–1.74 (m, 11H), 1.61–1.53 (m, 2H), 1.52–1.20 (m, 61H), 0.92–0.84 (m, 6H). 13C NMR (125 MHz, CDCl₃): δ (ppm) 166.29, 166.22, 162.32, 155.36, 146.86, 131.57, 131.50, 130.52, 130.50, 125.19, 122.32, 114.79, 68.41, 68.01, 65.33, 63.06, 37.47, 32.80, 31.91, 31.82, 31.48, 29.96, 29.63, 29.56, 29.52, 29.47, 29.45, 29.43, 29.41, 29.34, 29.31, 29.24, 29.17, 28.71, 26.78, 26.77, 26.02, 26.00, 25.74, 22.69, 22.65, 14.12. FT-IR (ATR): ν (cm⁻¹) 3565, 2921, 2851, 1712, 1602, 1581, 1501, 1280, 1255, 1138, 1107. HRMS (MALDI-TOF mass): calcd. for C₈₅H₁₁₉N₆O₁₀ [M + H]⁺: m/z = 1383.8988; found: 1383.8909.
**Compound 1.** To a THF solution (5.0 mL) of a mixture of 12 (0.50 g, 0.361 mmol) and DMAP (0.022 g, 0.18 mmol) were successively added methacrylic anhydride (0.123 g, 0.795 mmol) and triethylamine (0.080 g, 0.80 mmol), and the mixture was stirred at 50 °C for 6 hours under Ar. The reaction mixture was allowed to cool to 25 °C, concentrated under a reduced pressure, and diluted with CH₂Cl₂. The residue was washed successively with a saturated aqueous solution of NH₄Cl, water, and brine, and an organic phase separated was dried over anhydrous MgSO₄ and then evaporated to dryness at 25 °C under a reduced pressure. The residue was subjected to column chromatography (SiO₂, CHCl₃) to allow isolation of 1 as orange solid (0.455 g, 0.313 mmol) in 87% yield. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.17 (d x 2, J = 8.0 Hz, 4H, overlapped), 8.16 (d, J = 8.0 Hz, 2H), 7.93 (d x 3, J = 8.0 Hz, 6H, overlapped), 7.90 (d x 3, J = 8.6 Hz, 6H, overlapped), 7.00 (d x 3, J = 8.6 Hz, 6H, overlapped), 6.10 (m, 1H), 5.54 (m, 1H), 4.35 (t x 2, J = 6.9 Hz, 4H, overlapped), 4.25 (d, J = 5.7 Hz, 2H), 4.14 (t, J = 6.9 Hz, 2H), 4.08–4.01 (m, 6H), 1.94 (broad s, 3H), 1.86–1.75 (m, 11H), 1.67 (tt, J = 6.9 Hz, 6.9 Hz, 2H), 1.53–1.20 (m, 60H), 0.92–0.84 (m, 6H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 166.30, 166.22, 162.31, 155.37, 146.89, 136.58, 131.59, 130.51, 125.19, 125.12, 122.34, 114.80, 68.42, 68.02, 64.81, 37.49, 31.92, 31.83, 31.49, 29.97, 29.64, 29.57, 29.46, 29.45, 29.35, 29.32, 29.25, 29.18, 28.72, 26.73, 26.77, 26.02, 25.98, 22.69, 22.66, 14.13, 14.11. FT-IR (ATR): ν (cm⁻¹) 2921, 2853, 1704, 1602, 1581, 1500, 1268, 1256, 1102, 838. HRMS (MALDI-TOF mass): calcd. for C₈₉H₁₂₅N₆O₁₁ [M + H]⁺: m/z = 1451.9250; found: 1451.9298.

**Compound 2.** To a THF solution (5.0 mL) of a mixture of 8 (1.08 g, 1.73 mmol) and DMAP (0.106 g, 0.864 mmol) was successively added methacrylic anhydride (0.586 g, 3.80 mmol) and triethylamine (0.385 g, 3.80 mmol), and the mixture was stirred at 50 °C for 6 hours under Ar. The reaction mixture was allowed to cool to 25 °C, concentrated under a reduced pressure, and diluted with CH₂Cl₂. The solution was washed successively with a saturated aqueous solution of NH₄Cl, water, and brine, dried over anhydrous MgSO₄, and then evaporated to dryness at 25 °C under a reduced pressure. The residue was subjected to column chromatography (SiO₂, CHCl₃/hexane 1/1 v/v) to allow isolation of 2 as red oil (1.12 g, 1.63 mmol) in 94% yield. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.16 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 6.10 (m, 1H), 5.54 (m, 1H), 4.26 (d, J = 5.7 Hz, 2H), 4.14 (t, J = 6.9 Hz, 2H), 4.05 (t, J = 6.9 Hz, 2H), 1.95 (broad s, 3H), 1.86–1.76 (m, 3H), 1.71–1.62 (m, 2H), 1.53–1.20 (m, 36H), 0.92–0.84 (m, 6H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 167.56, 166.30, 162.31, 155.37, 146.89, 136.58, 131.59, 130.51, 125.19, 125.12, 122.34, 114.80, 68.42, 68.02, 64.81, 37.49, 31.92, 31.83, 31.49, 29.97, 29.64, 29.57, 29.46, 29.44, 29.34, 29.32, 29.24, 29.17, 28.62, 26.79, 26.77, 26.00, 25.97, 22.68, 22.66, 18.34, 14.12. FT-IR (ATR): ν (cm⁻¹) 2921, 2853, 1704, 1602, 1581, 1500, 1268, 1256, 1102, 838. HRMS (MALDI-TOF mass): calcd. for C₄₃H₆₇N₂O₅ [M + H]⁺: m/z = 691.5050; found: 691.5065.
Polymerization of 1 (poly-1). Monomer 1 (0.50 g, 0.344 mmol) was placed in a Schlenk flask (25 mL), and the inner atmosphere was strictly purged with Ar. A stock solution of AIBN (4.59 mM) in anhydrous benzene was degassed by freeze-pump-thaw cycles (three times). This stock solution (0.75 mL) was introduced using a syringe into the above flask containing 1, and the mixture was stirred at 60 °C. After 48 hours, the reaction mixture was poured into MeOH (150 mL), and a red precipitate formed was corrected by filtration and subjected to preparative SEC with toluene as an eluent, to allow separation of a polymeric fraction from 1. The polymeric fraction was concentrated (~10 mL) under a reduced pressure to a small volume, which was then added dropwise to hexane (150 mL). A precipitate thus formed was collected by filtration and dried at 25 °C under a reduced pressure to give poly-1 (366 mg) as red solid in 73% yield. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.17–8.05 (m), 7.95–7.77 (m), 7.02–6.84 (m), 4.36–4.18 (m), 4.05–3.82 (m), 1.84–1.67 (m), 1.65–1.52 (broad), 1.50–1.18 (m), 0.90–0.82 (m). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 166.24, 166.13, 166.02, 162.30, 162.20, 155.33, 155.29, 155.16, 146.84, 146.81, 131.56, 131.50, 130.49, 125.18, 122.33, 122.31, 114.76, 114.73, 114.64, 68.38, 67.99, 65.31, 37.46, 31.91, 31.81, 31.47, 29.96, 29.63, 29.56, 29.50, 29.46, 29.45, 29.41, 29.35, 29.31, 29.28, 29.25, 29.17, 28.70, 26.77, 26.75, 26.14, 26.00, 25.97, 22.67, 22.65, 14.11. FT-IR (ATR): ν (cm⁻¹) 2924, 2853, 1714, 1599, 1599, 1581, 1500, 1250, 1137. SEC analysis (THF, polystyrene standards): number-avaraged molecular weight (Mn) = 1.5 x 10⁵ g/mol (degree of polymerization DP = 103), polydispersity index (Mw/Mn) = 2.0 (fig. S1).

Polymerization of 2 (poly-2). Monomer 2 (0.30 g, 0.434 mmol) was placed in a Schlenk flask (25 mL), and the inner atmosphere was strictly purged with Ar. A stock solution of AIBN (9.65 mM) in anhydrous benzene was degassed by freeze-pump-thaw cycles (three times). This stock solution (0.45 mL) was introduced using a syringe into the flask containing 2, and the mixture was stirred at 60 °C. After 48 hours, the reaction mixture was poured into MeOH (150 mL), and a red precipitate formed was corrected by filtration and reprecipitated twice from MeOH (150 mL) and then hexane (150 mL). A precipitate thus formed was collected by filtration and dried at 25 °C under a reduced pressure to give poly-2 (273 mg) as red solid in 91% yield. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.16–8.06 (m), 7.93–7.79 (m), 6.98–6.86 (m), 4.26–4.15 (m), 4.04–3.79 (broad), 1.82–1.68 (broad), 1.67–1.53 (broad), 1.47–1.16 (m), 1.09–0.99 (broad), 0.95–0.78 (m). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 177.40, 166.14, 162.19, 155.23, 146.83, 131.62, 130.47, 125.16, 122.33, 114.67, 68.33, 68.01, 65.02, 45.24, 44.91, 37.43, 31.90, 31.81, 31.43, 29.96, 29.71, 29.63, 29.55, 29.37, 29.31, 28.28, 28.21, 26.75, 26.72, 26.13, 22.67, 22.64, 18.56, 16.90, 14.12, 14.10. FT-IR (ATR): ν (cm⁻¹) 2923, 2853, 1717, 1600, 1582, 1500, 1250, 1138. SEC analysis (THF, polystyrene standards): Mn = 1.1 x 10⁵ g/mol (DP = 159), Mw/Mn = 2.9 (fig. S1).
4. Synchrotron X-Ray Diffraction Analysis. Small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) experiments were carried out at BL45XU in SPring-8 (Hyogo, Japan) with a imaging plate area detector, a R-AXIS IV++ (Rigaku). The scattering vector, \( q = \frac{4\pi \sin \theta}{\lambda} \), and the position of incident X-ray on the detector were calibrated using several orders of layer reflections from silver behenate (\( d = 58.380 \, \text{Å} \)), where \( 2\theta \) and \( \lambda \) are scattering angle and wavelength of X-ray (0.90 Å), respectively. The sample-to-detector distances for SAXS and WAXD measurements were 2.5 and 0.5 m, respectively. The scattering/diffraction images recorded were integrated along the Debye-Scherrer ring, affording one-dimensional intensity data using the FIT2D software (S3). The cell parameters were refined using the CellCalc ver. 2.10 software (S4).

**Poly-1.** A powdery sample was placed into a 1.0 mm-ϕ glass capillary in a temperature-controlled heating block and once heated to 130 °C for melting. The resultant sample was then exposed to an X-ray beam for 10 (WAXD) or 100 (SAXS) seconds at given temperatures (fig. S3). The reflections obtained at the mesophase (115 °C) were successfully indexed by a rectangular lattice with lattice parameters \( a \) and \( b \) of 218(5) Å and 147(1) Å, respectively. Observed and model-calculated \( d \)-spacings are shown below. The reflections are satisfied with the crystallographic selection rules for the \( P2_1/a \) symmetry; (a) \( h00: h = 2n \); (b) \( 0k0: k = 2n \), where \( n \) is an integer. Film samples were clipped with tweezers or sandwiched by sapphire glasses and exposed at 25 °C to an X-ray beam for 100 seconds. The resulting SAXS profiles (Figs. 2D and 2E) indicate that the lattice structure of poly-1 in the film is essentially identical to that in the bulk sample.

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**Monomer 1.** A powdery sample was placed into a 1.0 mm-ϕ glass capillary in a temperature-controlled heating block and once heated to 130 °C for melting, followed by being cooled to 25 °C. The resultant sample was then exposed to an X-ray beam for 10 (WAXD) or 100 (SAXS) seconds at given temperatures (fig. S3). The reflections obtained at the mesophase (115 °C) were successfully indexed by a rectangular lattice with lattice parameters \( a \) and \( b \) of 218(5) Å and 147(1) Å, respectively. Observed and model-calculated \( d \)-spacings are shown below. The reflections are satisfied with the crystallographic selection rules for the \( P2_1/a \) symmetry; (a) \( h00: h = 2n \); (b) \( 0k0: k = 2n \), where \( n \) is an integer. Film samples were clipped with tweezers or sandwiched by sapphire glasses and exposed at 25 °C to an X-ray beam for 100 seconds. The resulting SAXS profiles (Figs. 2D and 2E) indicate that the lattice structure of poly-1 in the film is essentially identical to that in the bulk sample.
seconds. The reflections obtained at 25 °C were successfully indexed by a lamellar structure with an interlayer distance of 87 Å (fig. S10A), comparable to the molecular length of 1. Hot pressing of 1 with Teflon sheets did not give a free-standing film. Therefore, this compound was sandwiched with a Teflon sheet and a sapphire glass plate and then hot-pressed. After the Teflon sheet was peeled off, the film, remained on the sapphire glass plate, was exposed at 25 °C to an X-ray beam for 100 seconds. The reflection profile in its 2D SAXS image (fig. S10B) was characteristic of a lamellar structure identical to that observed for the bulk sample (fig. S10A). Note that the molecules of 1 in the film are unidirectionally oriented along the drawing direction of the Teflon sheet.
Supporting Figures

**Fig. S1.** Analytical SEC profiles of poly-1 (red) and poly-2 (black) monitored by a refractive index detector.

**Fig. S2.** DSC traces on second heating/cooling cycles of poly-1 (red) and poly-2 (black) (scan rate 5 °C/min).
Fig. S3. (A) Small- and (B) wide-angle regions of X-ray diffraction patterns of poly-1 in a glass capillary on first cooling from 130 (isotropic melt) to 25 °C.
Fig. S4. Quantification of SAXS data for evaluating the degrees of lattice orientation ($\gamma$) of poly-
1 in (A) 5 µm- and (B) 10 µm-thick hot-pressed films prepared with parallel-arranged Teflon
sheets and (C) 5 µm- and (D) 10 µm-thick hot-pressed films prepared with orthogonally arranged
Teflon sheets. Illustrations of the hot-pressed films show analytical data, provided that the degrees of lattice orientation on both sides of the films are identical to one another. The estimation of the degrees of lattice orientation was carried out by a method similar to that reported by Daxer and Fratzl (S5). Thus, the 2D SAXS images were integrated along the Debye–Scherrer ring to obtain scattering intensity profiles as a function of scattering vector \( q \) ranging from 0 to 0.2 Å (left), where \( \alpha = \frac{I_1}{I_1 + I_2} \); \( I_1 \) and \( I_2 \) denote integrals of the blue and yellow parts, respectively. \( \alpha \) represents contribution of both oriented and non-oriented poly-1 to the total scattering at \( q = 0.079–0.090 \) Å\(^{-1} \) corresponding to the scattering from the (020) plane. Then, the scattering intensities at \( q = 0.079–0.090 \) Å\(^{-1} \) were plotted against azimuthal angle \( \theta \) (right), where \( \beta = \frac{I_3}{I_3 + I_4} \); \( I_3 \) and \( I_4 \) denote integrals of the blue and yellow parts, respectively. \( \beta \) represents contribution of oriented poly-1 alone to the total scattering. The degree of lattice orientation is defined as \( \gamma = \beta/\alpha \). If all poly-1 molecules are randomly oriented in the film, \( \gamma \) should be zero. On the other hand, if all of them align unidirectionally, \( \gamma \) should be unity. Analysis of the scattering data of the 5 µm- and 10 µm-thick hot-pressed films of poly-1 showed that (1) \( \gamma \) (= the degree of lattice orientation) is not affected by whether the Teflon sheets used for hot pressing is arranged orthogonally or in parallel and (2) \( \gamma \) of the 10 µm-thick film is a nearly half of that of the 5 µm-thick one. Since the lattice orientation most likely develops, equally on both side of the film, toward the inner side from the contact interface with the Teflon sheets, the hot-pressed films adopt a bimorph configuration consisting of a randomly oriented interior layer sandwiched by unidirectionally oriented exterior layers. Based on this configurational feature, thicknesses of the unidirectionally oriented layers, estimated from the \( \gamma \) values of the hot-pressed films, are almost comparable to one another (2.1–2.6 µm).
**Fig. S5.** POM micrographs at 25 °C under crossed polarizers. Hot-pressed films of poly-1 (5 µm in thickness) prepared with (A) parallel and (B) orthogonally arranged Teflon sheets. The films were tilted at 0 ° (left), 45 ° (center), and 90 ° (right) relative to the transmission axis of the analyzer. Sky blue arrows represent the transmission axes of the polarizer (P) and analyzer (A), while green and blue arrows denote the drawing directions of the upper and lower Teflon sheets, respectively.
Fig. S6. Polarized IR spectra of a hot-pressed film prepared with parallel-arranged Teflon sheets at azimuthal angles $\theta = 0$ (upper) and $90^\circ$ (lower). The azimuthal angle is defined as zero when the polarizing direction of the incident light is parallel to the drawing direction of the Teflon sheets. Stretching vibrations at 1716 (red), 1600 (blue), 1275 (green), 1254 cm$^{-1}$ (yellow) are due to C=O (ester), C$_{Ar}$–C$_{Ar}$ (azobenzene), C–O (ester), C$_{Ar}$–O (ether) groups, respectively.
Fig. S7. (A) Photomechanical bending motion of a hot-pressed film (5 mm x 6 mm x 10 µm) of poly-1 upon exposure to UV light (\(\lambda = 360 \pm 2\) nm, 17.2 mW/cm\(^2\)) and subsequent exposure to visible light (\(\lambda = 480 \pm 2\) nm, 30.8 mW/cm\(^2\)). The hot pressing was conducted with parallel-arranged Teflon sheets. The displacement of the free edge of the film from the initial position was measured directly using a grid sheet. (B) Changes in displacement of the film upon alternating irradiation with UV and visible lights.

Fig. S8. Electronic absorption spectral changes at 25 °C of a spin-coated film of poly-1 upon exposure to (A) UV light (\(\lambda = 360 \pm 2\) nm, 2.7 mW/cm\(^2\)) and (B) subsequent exposure to visible light (\(\lambda = 480 \pm 2\) nm, 4.8 mW/cm\(^2\)). The optically transparent sample film was prepared by spin coating of a toluene solution (1 wt%) of poly-1 on a quartz plate (0.9 cm x 0.9 cm) at 2000 rpm, heated at 130 °C, and then annealed at 115 °C for 1 hour.
Fig. S9. Schematic representation of tensile and contractile strains in hot-pressed films prepared with (A) parallel and (B) orthogonally arranged Teflon sheets. On cooling poly-1 from its hot-pressed state to room temperature, each polymer lattice expands (with respect to the $b$ axis) and contracts (with respect to the $a$ axis) along and across the drawing direction of the Teflon sheet, respectively. These dimensional changes result in generation of tensile and contractile strains, respectively, on both sides of the film. (A) When the drawing directions of the Teflon sheets for hot pressing are parallel to each other, the tensile and contractile strains generated on one side of the film are parallel to those, respectively, on the other. Irrespective of the cutting direction, the competing balance between the upper- and lower-side strains in the film is not broken upon cutting the film into two rectangular pieces. Hence, the cut pieces remain flat (see photographs). (B) When the drawing directions of the Teflon sheets for hot pressing are orthogonal to each other, the tensile and contractile strains generated on one side of the film are orthogonal to those, respectively, on the other. Upon cutting the film into two rectangular pieces, the competing balance between the upper- and lower-side strains in the film is broken. Consequently, the cut pieces bend spontaneously (see photographs).
Fig. S10. (A) 1D SAXS pattern of a powdery sample of monomer 1 in a capillary at 25 °C on cooling from its isotropic melt. Inset shows a scattering profile in a wide-angle region. The \(d\)-spacings of the reflection peaks from (100), (200), (300), and (400) planes are 87.0, 43.4, 30.3, 23.1 Å, respectively. (B) 2D SAXS image of a film prepared by hot pressing 1 sandwiched with a Teflon sheet and a sapphire glass plate. Blue arrow denotes the drawing direction of the Teflon sheet. (C) Schematic structures of 1 and its lamellar assembly.
Supporting References