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Structures and Properties of Side-Chain Liquid Crystalline Polynorbornenes Containing Amide Group: Hydrogen Bonding Interaction and Spacer Length Effect

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Materials and Characterization Techniques

Materials

The Grubbs third generation catalyst and *exo*-5-norbornenecarboxylic acid were obtained from Sigma-Aldrich. Anhydrous dichloromethane (DCM) and tetrahydrofuran (THF) were obtained by passing HPLC-grade solvents through columns packed with activated 4 Å molecular sieves. Other reagents were obtained from Heowns, TCI or J&K Chemicals without further purification.

Instruments and Measurements

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on a Bruker APX400 spectrometer at room temperature using deuterated chloroform or DMSO as the solvent and tetramethylsilane (TMS) as the internal standard. Elemental analysis data was obtained by the Elementar Vario EL instrument. Electron Spray Mass Spectrometry (ESI-MS) were recorded on a Bruker APEX IV mass spectrometer.

Gel permeation chromatography (GPC) was carried out on a Waters 515 GPC instrument using THF as an eluent at a flow rate of 1.0 mL/min at 35 °C. The GPC calibration curve was obtained with linear polystyrene standards.

Differential scanning calorimetry (DSC, TA Q100 with a mechanical refrigerator) calibrated with benzoic acid and indium was used to study the phase transitions of the samples. The powder sample was encapsulated in a hermetically sealed aluminum pan with a weight of 1 – 2 mg. During the DSC experiments, the heat history was erased by the first heating to above the isotropic temperature. Afterward, the first cooling and second heating curves were recorded at a rate of 10 °C/min.

One-dimensional (1D) and two-dimensional (2D) X-ray diffraction (XRD) experiments were carried out with Ganesha system (SAXSLAB) equipped with a multilayer focused Cu Kα radiation as the X-ray source (Genix 3D Cu ULD) and a 2D semiconductor detector (Pilatus 300 K, DECTRIS, Swiss). The thermal XRD experiment was performed using a Linkam HFSX350-GI stage. To record the structure evolution of the sample during stretching, the XRD experiment was performed using a Linkam TST350 tension stage.

The 2D XRD images in the Supporting Information were obtained using a Bruker D8

Discover diffractometer with a Vantec 500 detector.

Tensile test of the film samples was carried out using Q800 DMA (TA, American). The Young Modulus was calculated by the slope of stress-strain curves below the strain of 1% (0.5% for **P8-8** and **P8-10**). The films were prepared by hot compression at 150 °C for 5 minutes using a tablet compressing machine (FY-15, SCJS, China)

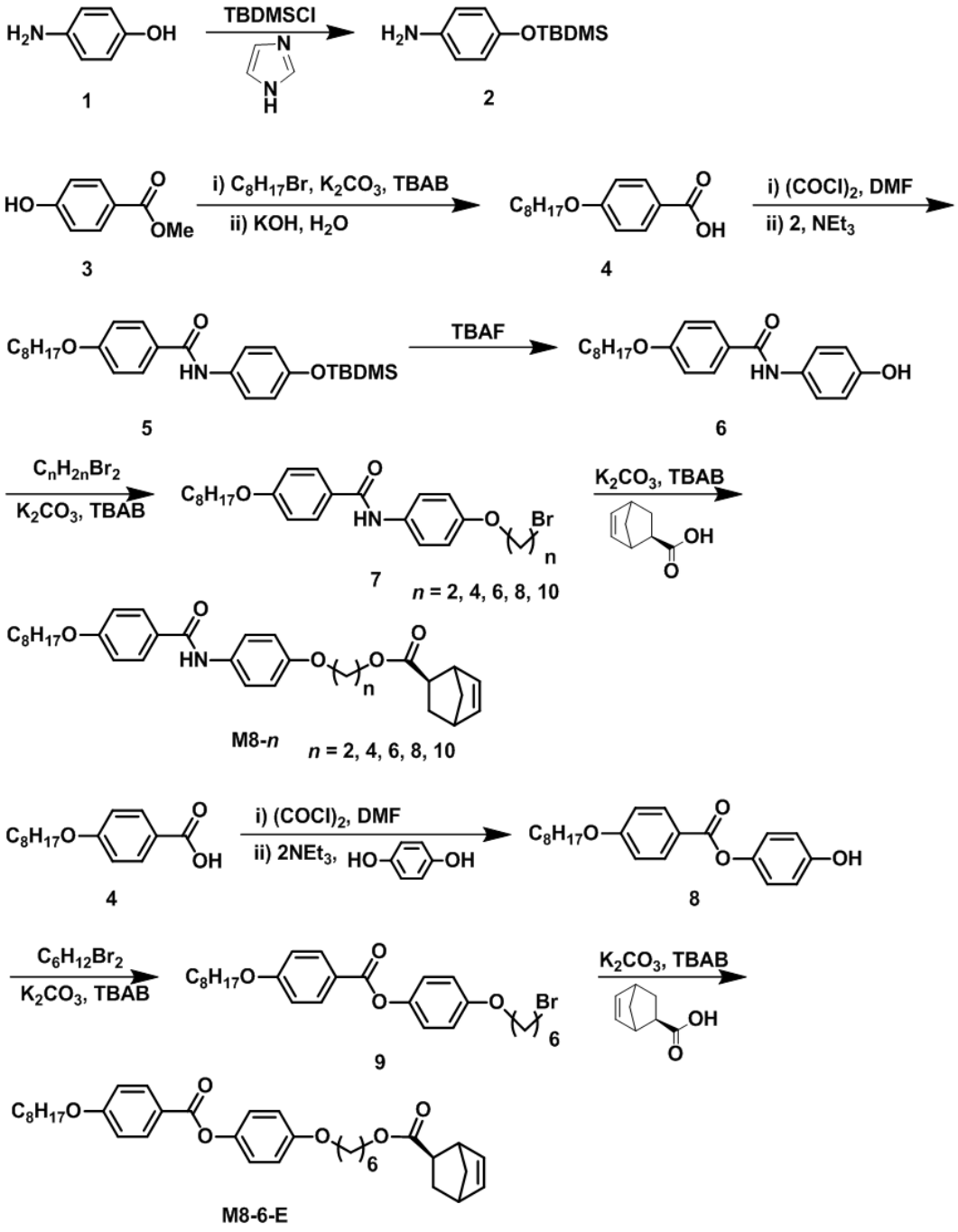
FT-IR spectra were gained on a Thermo Fisher Nicolet 6700 spectrometer with 2 cm^{-1} resolution, 8 scans were accumulated. The sample was prepared by dropping the THF solution of sample with a concentration of 1 wt% the KBr plate. After solvent evaporation, the sample was heated to above the isotropic temperature followed by slow cooling to room temperature. The oriented film for FTIR were obtained by stretching the viscous melt at a rate of ~1 cm/s at a temperature slightly higher than the isotropic temperature (T_i). To measure the FT-IR spectra at various temperatures, a Linkman FT-IR 600 hot stage was used.

Synthesis and Molecular Characterization

Synthetic Route

The chemical structures and synthetic routes of monomers **M8-*n*s** and **M8-6-E** are shown in Scheme S1. The experimental details and characterization data are shown as follows.

Scheme S1. The synthesis routes of **M8-*n*s** and **M8-6-E**



4-((*tert*-butyldimethylsilyl)oxy)aniline (2)

4-aminophenol (5.00 g, 45.9 mmol), imidazole (5.00 g, 73.4 mmol) and 100 mL tetrahydrofuran (THF) were added to a 250 mL round-bottom flask. Butylchlorodimethylsilane (TBDMSCl, 9.00 g, 60 mmol) was solved by 20 mL THF, then added to the former solution in ice bath. The mixture was refluxed 30 minutes at room temperature. The solution was cloudy when the reaction was complete. 150 mL H_2O was added into the solution. The product was extracted by trichloromethane (TCM, 50 mL × 2). A small amount of anhydrous Na_2SO_4 was then added to this organic solution. 30 minutes later, the granular salts were filtered and rinsed with TCM. After evaporation of the solvent, the crude product was purified by column chromatography using PE/EA (5:1, v/v) as the eluent. **2** was obtained as light brown liquid in yield of 87.6%. **^{1}H-NMR** (400 MHz, $CDCl_3$, δ, ppm): 6.66 (m, 2H), 6.57 (m, 2H), 3.41 (s, 2H), 0.96 (s, 9H), 0.19 (s, 6H).

4-(octyloxy)benzoic acid (4)

Methyl 4-hydroxybenzoate (10.00 g, 66 mmol), 1-bromooctane (15.20 g, 79 mmol), K_2CO_3 (18.2 g, 132 mmol), catalytic amounts of tetrabutylammonium bromide (TBAB), and 150 mL acetone were added to a 250 mL round-bottom flask. The mixture was refluxed overnight under stirring. Then the mixture was filtered to remove the insoluble salt. The filtrate was evaporated to dryness under reduced pressure. 150 mL ethanol was added into the flask of crude product. 2 mL of an aqueous solution of KOH (5.52g, 99 mmol) was added dropwise to the ethanol solution. The mixture was refluxed overnight under stirring. The reaction mixture was then evaporated to remove ethanol under reduced pressure, and dissolved in THF. The mixture was adjusted to pH = 1 by addition of an aqueous 1 M HCl solution, extracted with ether (50 mL × 3). A small amount of anhydrous Na_2SO_4 was then added to this organic solution. 30 minutes later, the granular salts were filtered and rinsed with ether. The pure product was get by recrystallization using ether. **4** was obtained as white needle-like crystals in yield of 66%. **^{1}H-NMR** (400 MHz, $CDCl_3$, δ, ppm): 8.05 (m, 2H), 6.93 (m, 2H), 4.02 (t, 2H), 1.81 (m, 2H), 1.46 (m, 2H), 1.40 – 1.29 (m, 8H), 0.89 (t, 3H).

***N*-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-4-(octyloxy)benzamide (5)**

4 (5.0 g, 20 mmol) and 100 mL anhydrous dichloromethane (DCM) was added to 250 mL round-bottom flask. Oxalyl chloride (3.4 mL, 40 mmol) and three drops of dimethyl formamide

(DMF) was added in ice bath. After 2 hours under stirring at room temperature, the solvent and excess oxalyl chloride were removed by a rotary evaporator. 50 mL new anhydrous DCM was added to the flask. 50 mL anhydrous DCM dissolving **2** (5.36 g, 24 mmol) and triethylamine (3.04 g, 30 mmol) was added dropwise to the former solution. After 4 hours at room temperature, the reaction was quenched by 50 mL H_2O. The organic phase was then washed by 50 mL saturated $NaHCO_3$ solution and 50 mL saturated NaCl solution in turn. After 30 minutes drying by anhydrous Na_2SO_4, the granular salts were filtered. After evaporation, the crude product was purified by recrystallization using DCM/methanol. **5** was obtained as white solid in yield of 73.5%. **^{1}H-NMR** (400 MHz, $CDCl_3$, δ, ppm): 7.81 (m, 2H), 7.64 (s, 1H), 7.46 (m, 2H), 6.95 (m, 2H), 6.83 (m, 2H), 4.01 (t, 2H), 1.81 (m, 2H), 1.47 (m, 2H), 1.40 – 1.29 (m, 8H), 0.98 (s, 9H), 0.89 (t, 3H), 0.19 (s,6H).

***N*-(4-hydroxyphenyl)-4-(octyloxy)benzamide (6)**

5 (3.40 g, 14.7 mmol) was dissolved by 80 mL THF in a 250 mL round-bottom flask. 14.9 mL THF solution of 1 M TBAF was added dropwise in ice bath. After 1 hour reaction at room temperature, the solution was concentrated to about 5 mL by evaporation. Then the mixture was dropped into 80 mL H_2O slowly under stirring in beaker. After stirring overnight, the product was gotten by suction filtration and infrared drying. **6** was obtained as white solid in yield 100%. **^{1}H-NMR** (400 MHz, DMSO-D6, δ, ppm): 9.87 (s, 1H), 9.20 (s, 1H), 7.91 (m, 2H), 7.50 (m, 2H), 7.02 (m, 2H), 6.72 (m, 2H), 4.03 (t, 2H), 1.73 (m, 2H), 1.42 (m, 2H), 1.34 – 1.27 (m, 8H), 0.87 (t, 3H).

***N*-(4-(4-bromobutoxy)phenyl)-4-(octyloxy)benzamide (7, *n* = 4)**

6 (3.00 g, 8.79 mmol), 1,4-dibromobutane (19.0 g, 88.0 mmol), K_2CO_3 (6.06 g, 44.0 mmol), catalytic amounts of TBAB and 100 mL acetone were added to 250 mL round-bottom flask. The mixture was refluxed overnight. The reaction mixture was filtered to remove the insoluble salt. By evaporation, the acetone was removed. The mixture was washed by petroleum ether three times to remove 1,4-dibromobutane. The crude product was dissolved by DCM, then washed by 50 mL H_2O, 50 mL saturated $NaHCO_3$ solution and 50 mL saturated NaCl solution in turn. After 30 minutes drying by anhydrous Na_2SO_4, the granular salts were filtered. After evaporation, white solid product **7** was obtained in yield 90.0%. The product reacted in the next process directly without further purification.

(1*R*,2*S*,4*R*)-4-(4-(4-(octyloxy)benzamido)phenoxy)butyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (M8-*n*, *n* = 4)

7 (1.76 g, 3.69 mmol), *exo*-5-norbornenecarboxylic acid (0.60 g, 4.35 mmol), K_2CO_3 (2.55 g, 18.5 mmol), catalytic amounts of TBAB and 150 mL THF were added to 250 mL round-bottom flask. The mixture was refluxed overnight. The reaction mixture was filtered to remove the insoluble salt. By evaporation, the acetone was removed. The crude product was dissolved by TCM, then washed by 50 mL H_2O, 50 mL saturated $NaHCO_3$ solution and 50 mL saturated NaCl solution in turn. After 30 minutes drying by anhydrous Na_2SO_4, the granular salts were filtered. The pure product **M8-4** can be obtained by recrystallization using DCM/methanol as white solid in yield 81.1%.

n = 2: **^{1}H-NMR** (400 MHz, $CDCl_3$, δ, ppm): 7.81 (d, 2H), 7.68 (m, 1H), 7.53 (d, 2H), 6.95 (d, 2H), 6.92 (d, 2H), 6.15 – 6.09 (m, 2H), 4.45 (m, 2H), 4.18 (t, 2H), 4.01 (t, 2H), 3.06 (s, 1H), 2.93 (s, 1H), 2.28 (m, 1H), 1.94 (m, 1H), 1.81 (m, 2H), 1.54 (m, 1H), 1.47 (m, 2H), 1.41 – 1.30 (m, 10H), 0.89 (t, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$, δ, ppm): 176.27, 165.15, 162.06, 155.39, 138.12, 135.74, 131.71, 128.79, 126.83, 121.98, 115.12, 114.45, 68.28, 66.44, 62.77, 46.74, 46.34, 43.08, 41.68, 31.82, 30.40, 29.35, 29.24, 29.15, 26.01, 22.67, 14.12. **HRMS (ESI positive)**: $[M+H]^+$ cacd for $C_{31}H_{39}NO_5$ m/z 506.290100; found 506.289763. **Elemental analysis (EA, %)**: calcd for $C_{31}H_{39}NO_5$ C, 73.63; H, 7.77; N, 2.77; found C, 73.68; H, 7.83; N, 2.74.

n = 4: **^{1}H-NMR** (400 MHz, $CDCl_3$, δ, ppm): 7.81 (d, 2H), 7.67 (m, 1H), 7.51 (d, 2H), 6.95 (d, 2H), 6.89 (d, 2H), 6.15 – 6.09 (m, 2H), 4.16 (m, 2H), 4.00 (m, 4H), 3.04 (s, 1H), 2.92 (s, 1H), 2.22 (m, 1H), 1.92 (m, 1H), 1.81 (m, 6H), 1.52 (m, 1H), 1.47 (m, 2H), 1.41 – 1.30 (m, 10H), 0.89 (t, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$, δ, ppm): 176.33, 165.13, 162.02, 155.80, 138.07, 135.78, 131.25, 128.78, 126.90, 122.00, 114.85, 114.43, 68.27, 67.63, 64.12, 46.64, 46.40, 43.21, 41.65, 31.82, 30.36, 29.35, 29.24, 29.15, 26.01, 25.98, 25.52, 22.68, 14.12. **HRMS (ESI positive)**: $[M+H]^+$ cacd for $C_{33}H_{43}NO_5$ m/z 534.321400; found 534.321012. **Elemental analysis (EA, %)**: calcd for $C_{33}H_{43}NO_5$ C, 74.27; H, 8.12; N, 2.62; found C, 74.38; H, 8.03; N, 2.68.

n = 6: **^{1}H-NMR** (400 MHz, $CDCl_3$, δ, ppm): 7.81 (d, 2H), 7.67 (m, 1H), 7.51 (d, 2H), 6.94 (m, 2H), 6.88 (d, 2H), 6.15 – 6.09 (m, 2H), 4.10 (m, 2H), 4.01 (t, 2H), 3.95 (t, 2H), 3.04 (s, 1H), 2.92 (s, 1H), 2.22 (m, 1H), 1.92 (m, 1H), 1.81 (m, 4H), 1.68 (m, 2H), 1.53 - 1.42 (m, 7H), 1.39 – 1.25 (m,

10H), 0.89 (t, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$, δ, ppm): 176.37, 165.14, 162.00, 155.96, 138.05, 135.79, 131.13, 128.79, 126.93, 122.01, 114.85, 114.42, 68.27, 68.09, 64.44, 46.64, 46.38, 43.22, 41.65, 31.82, 30.34, 29.35, 29.24, 29.20, 29.15, 28.66, 26.01, 25.81, 25.78, 22.67, 14.12. **HRMS (ESI positive)**: $[M+H]^+$ cacd for $C_{35}H_{47}NO_5$ m/z 562.352700; found 562.352319. **Elemental analysis (EA, %)**: calcd for $C_{35}H_{47}NO_5$ C, 74.83; H, 8.43; N, 2.49; found C, 74.94; H, 8.34; N, 2.55.

n = 8: **^{1}H-NMR** (400 MHz, $CDCl_3$, δ, ppm): 7.81 (d, 2H), 7.69 (m, 1H), 7.50 (d, 2H), 6.94 (m, 2H), 6.88 (m, 2H), 6.15 – 6.09 (m, 2H), 4.08 (m, 2H), 4.01 (t, 2H), 3.95 (t, 2H), 3.04 (s, 1H), 2.92 (s, 1H), 2.22 (m, 1H), 1.92 (m, 1H), 1.79 (m, 4H), 1.64 (m, 2H), 1.53 – 1.43 (m, 5H), 1.39 – 1.25 (m, 16H), 0.89 (t, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$, δ, ppm): 176.37, 165.20, 161.93, 156.02, 138.04, 135.80, 131.13, 128.82, 126.94, 122.08, 114.84, 114.37, 68.25, 68.23, 64.56, 46.63, 46.38, 43.24, 41.65, 31.82, 30.33, 29.35, 29.27, 29.25, 29.24, 29.19, 29.15, 28.69, 26.01, 25.97, 25.90, 22.67, 14.12. **HRMS (ESI positive)**: $[M+H]^+$ cacd for $C_{37}H_{51}NO_5$ m/z 590.384000; found 590.384205. **Elemental analysis (EA, %)**: calcd for $C_{31}H_{39}NO_5$ C, 75.35; H, 8.72; N, 2.37; found C, 75.39; H, 8.61; N, 2.42.

n = 10: **^{1}H-NMR** (400 MHz, $CDCl_3$, δ, ppm): 7.81 (m, 2H), 7.63 (s, 1H), 7.50 (m, 2H), 6.95 (m, 2H), 6.89 (m, 2H), 6.15 – 6.09 (m, 2H), 4.08 (m, 2H), 4.01 (t, 2H), 3.95 (t, 2H), 3.04 (s, 1H), 2.92 (s, 1H), 2.22 (m, 1H), 1.92 (m, 1H), 1.79 (m, 4H), 1.63 (m, 2H), 1.53 – 1.42 (m, 5H), 1.38 – 1.26 (m, 20H), 0.89 (t, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$, δ, ppm): 176.37, 165.13, 162.00, 156.04, 138.04, 135.80, 131.07, 128.78, 126.96, 122.01, 114.88, 114.42, 68.30, 68.27, 64.60, 46.63, 46.38, 43.24, 41.65, 31.81, 30.32, 29.47, 29.44, 29.35, 29.28, 29.24, 29.15, 28.71, 26.01, 25.95, 25.90, 22.66, 14.11. **HRMS (ESI positive)**: $[M+H]^+$ cacd for $C_{39}H_{55}NO_5$ m/z 618.415300; found 618.414873. **Elemental analysis (EA, %)**: calcd for $C_{39}H_{55}NO_5$ C, 75.81; H, 8.97; N, 2.27; found C, 75.74; H, 9.13; N, 2.28.

4-hydroxyphenyl-4-(octyloxy)benzoate (8)

4 (5.0 g, 20 mmol) and 100 mL anhydrous DCM was added to 250 mL round-bottom flask. Oxalyl chloride (3.4 mL, 40 mmol) and three drops of DMF was added in ice bath. After 2 hours under stirring at room temperature, the solvent and excess oxalyl chloride were removed by a rotary evaporator. 50 mL new anhydrous DCM was added to the flask. 50 mL anhydrous DCM dissolving hydroquinone (4.40 g, 40 mmol) and trimethylamine (3.04 g, 30 mmol) was added

dropwise to the former solution. After 4 hours at room temperature, the reaction was quenched by 50 mL H_2O. The organic phase was then washed by 50 mL saturated $NaHCO_3$ solution and 50 mL saturated NaCl solution in turn. After 30 minutes drying by anhydrous Na_2SO_4, the granular salts were filtered. After evaporation, the crude product was purified by column chromatography using DCM as the eluent. **8** was obtained as white solid in yield of 34.6%. **^{1}H-NMR** (400 MHz, $CDCl_3$, δ, ppm): 8.13 (d, 2H), 7.04 (d, 2H), 6.96 (d, 2H), 6.83 (d, 2H), 4.91 (m, 1H), 4.04 (t, 2H), 1.82 (m, 2H), 1.48 (m, 2H), 1.40 – 1.29 (m, 8H), 0.89 (t, 3H).

4-((6-bromohexyl)oxy)phenyl-4-(octyloxy)benzoate (9)

8 (2.00g, 5.40 mmol), 1,6-dibromohexane (13.2g, 54.0 mmol), K_2CO_3 (3.72 g, 27.0 mmol), catalytic amounts of TBAB and 100 mL acetone were added to 250 mL round-bottom flask. The mixture was refluxed overnight. The reaction mixture was filtered to remove the insoluble salt. By evaporation, the acetone was removed. The crude product was dissolved by DCM, then washed by 50 mL H_2O, 50 mL saturated $NaHCO_3$ solution and 50 mL saturated NaCl solution in turn. After 30 minutes drying by anhydrous Na_2SO_4, the granular salts were filtered. After evaporation, the crude product was purified by column chromatography using DCM as the eluent (500 mL PE first to remove the 1,6-dibromohexane). **9** was obtained as white solid in yield of 94%. **^{1}H-NMR** (400 MHz, $CDCl_3$, δ, ppm): 8.13 (d, 2H), 7.10 (d, 2H), 6.96 (d, 2H), 6.91 (d, 2H), 4.03 (t, 2H), 3.96 (t, 2H), 3.43 (t, 2H), 1.94 – 1.87 (m, 2H), 1.84 – 1.77 (m, 4H), 1.54 – 1.43 (m, 6H), 1.40 – 1.29 (m, 8H), 0.89 (t, 3H).

(1*R*,2*S*,4*R*)-6-(4-((4-(octyloxy)benzoyl)oxy)phenoxy)hexyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (M8-6-E)

9 (2.00 g, 3.96 mmol), *exo*-5-norbornenecarboxylic acid (0.65 g, 4.75 mmol), K_2CO_3 (2.73 g, 19.8 mmol), catalytic amounts of TBAB and 150 mL THF were added to 250 mL round-bottom flask. The mixture was refluxed overnight. The reaction mixture was filtered to remove the insoluble salt. By evaporation, the acetone was removed. The crude product was dissolved by DCM, then washed by 50 mL H_2O, 50 mL saturated $NaHCO_3$ solution and 50 mL saturated NaCl solution in turn. After 30 minutes drying by anhydrous Na_2SO_4, the granular salts were filtered. The pure product **M8-6-E** was obtained by column chromatography using PE/DCM (1:1, v/v) as the eluent as white solid in yield 29.8%. **^{1}H-NMR** (400 MHz, $CDCl_3$, δ, ppm): 8.13 (d, 2H), 7.10 (d,

2H), 6.96 (d, 2H), 6.91 (d, 2H), 6.15 – 6.10 (m, 2H), 4.10 (m, 2H), 4.04 (t, 2H), 3.96 (t, 2H), 3.04 (s, 1H), 2.92 (s, 1H), 2.22 (m, 1H), 1.92 (m, 1H), 1.81 (m, 4H), 1.69 (m, 2H), 1.54 – 1.42 (m, 7H), 1.40 – 1.26 (m, 10H), 0.89 (t, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$, δ, ppm): 176.36, 165.35, 163.47, 156.70, 144.46, 138.04, 135.80, 132.22, 122.51, 121.69, 115.07, 114.26, 68.33, 68.21, 64.43, 46.64, 46.39, 43.23, 41.65, 31.81, 30.35, 29.34, 29.23, 29.19, 29.11, 28.67, 26.00, 25.80, 25.78, 22.67, 14.11. **HRMS (ESI positive)**: $[M+H]^+$ cacd for $C_{35}H_{46}O_6$ m/z 563.336716; found 563.335442. **Elemental analysis (EA, %)**: calcd for $C_{35}H_{46}O_6$ C, 74.70; H, 8.24; found C, 74.00; H, 8.18.

The monomer of **M12-6** was synthesized using 1-bromododecane instead of 1-bromooctane at the initial step. Shown below are the characterization data of **M12-6**.

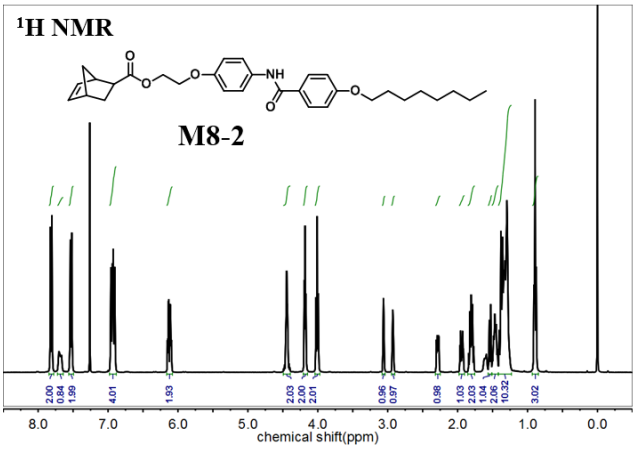
4-(dodecyloxy)benzoic acid: **^{1}H-NMR** (400 MHz, $CDCl_3$, δ, ppm): 8.05 (m, 2H), 6.93 (m, 2H), 4.02 (t, 2H), 1.81 (m, 2H), 1.46 (m, 2H), 1.40 – 1.29 (m, 16H), 0.88 (t, 3H).

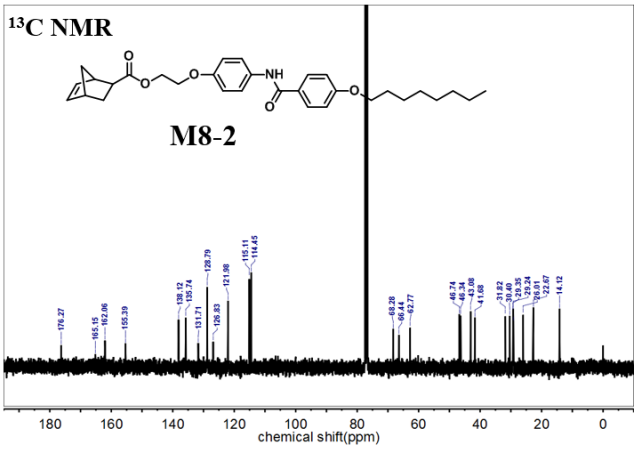
***N*-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-4-(dodecyloxy)benzamide**: **^{1}H-NMR** (400 MHz, $CDCl_3$, δ, ppm): 7.80 (m, 2H), 7.60 (s, 1H), 7.46 (m, 2H), 6.95 (m, 2H), 6.83 (m, 2H), 4.01 (t, 2H), 1.81 (m, 2H), 1.47 (m, 2H), 1.40 – 1.29 (m, 16H), 0.98 (s, 9H), 0.88 (t, 3H), 0.19 (s,6H).

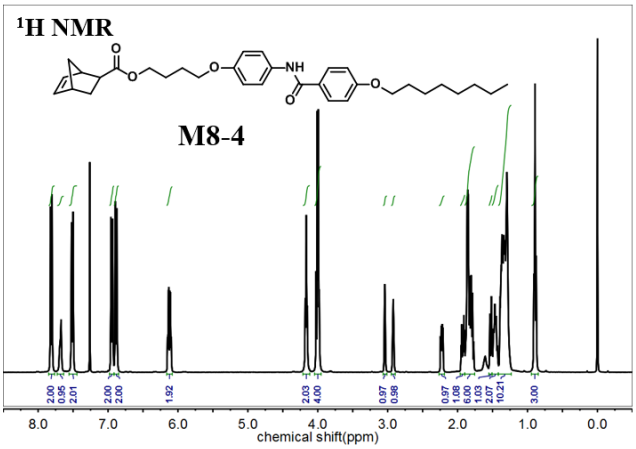
4-(dodecyloxy)-*N*-(4-hydroxyphenyl)benzamide: **^{1}H-NMR** (400 MHz, DMSO-D6, δ, ppm): 9.84 (s, 1H), 9.20 (s, 1H), 7.90 (m, 2H), 7.50 (m, 2H), 7.01 (m, 2H), 6.72 (m, 2H), 4.03 (t, 2H), 1.73 (m, 2H), 1.42 (m, 2H), 1.34 – 1.27 (m, 16H), 0.85 (t, 3H).

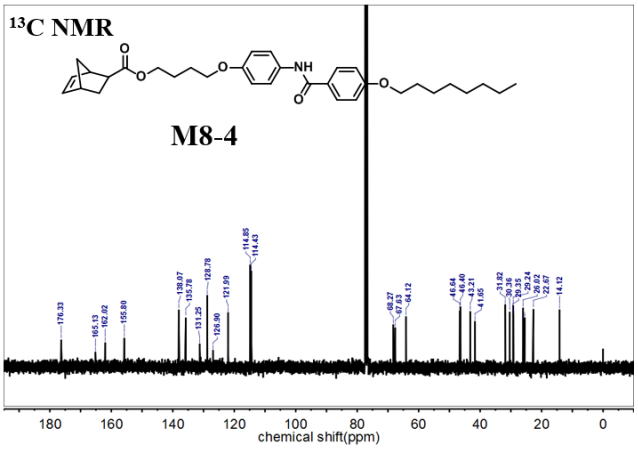
(1*R*,2*S*,4*R*)-6-(4-(4-(dodecyloxy)benzamido)phenoxy)hexyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (M12-6): **^{1}H-NMR** (400 MHz, $CDCl_3$, δ, ppm): 7.81 (d, 2H), 7.65 (m, 1H), 7.51 (d, 2H), 6.95 (m, 2H), 6.89 (d, 2H), 6.15 – 6.09 (m, 2H), 4.10 (m, 2H), 4.01 (t, 2H), 3.96 (t, 2H), 3.04 (s, 1H), 2.92 (s, 1H), 2.23 (m, 1H), 1.95 – 1.90 (m, 1H), 1.84 – 1.76 (m, 4H), 1.72 – 1.63 (m, 2H), 1.55 - 1.42 (m, 7H), 1.39 – 1.26 (m, 18H), 0.89 (t, 3H). **^{13}C-NMR** (100 MHz, $CDCl_3$, δ, ppm): 176.37, 162.02, 155.98, 138.05, 135.79, 131.06, 128.80, 126.93, 122.03, 114.86, 114.43, 100.02, 68.28, 68.10, 64.44, 46.64, 46.38, 43.23, 41.65, 31.94, 30.34, 29.68, 29.65, 29.61, 29.58, 29.40, 29.37, 29.20, 29.15, 28.67, 26.01, 25.81, 25.78, 22.71, 14.15. **HRMS (ESI positive)**: $[M+H]^+$ cacd for $C_{39}H_{55}NO_5$ m/z 618.415300; found 618.415522. **Elemental analysis (EA, %)**: calcd for $C_{39}H_{55}NO_5$ C, 75.81; H, 8.97; N, 2.27; found C, 75.61; H, 8.86; N, 2.28.

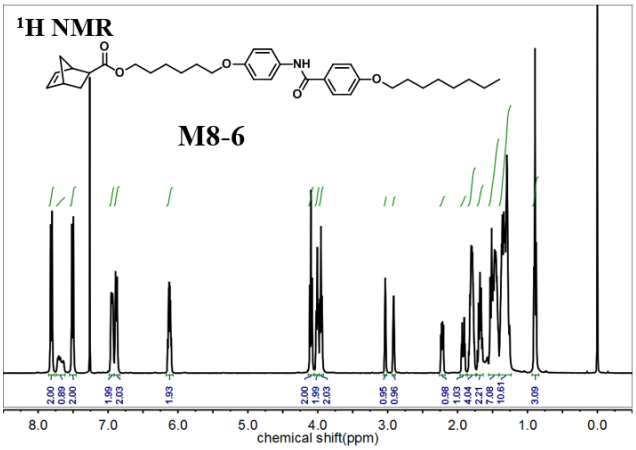
NMR Spectra of the Monomers and Polymers

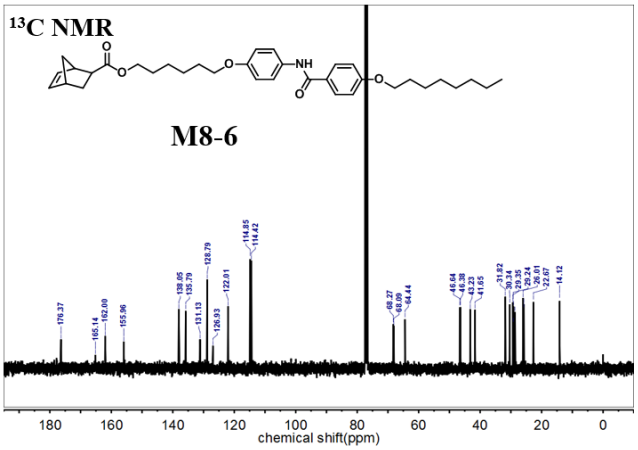


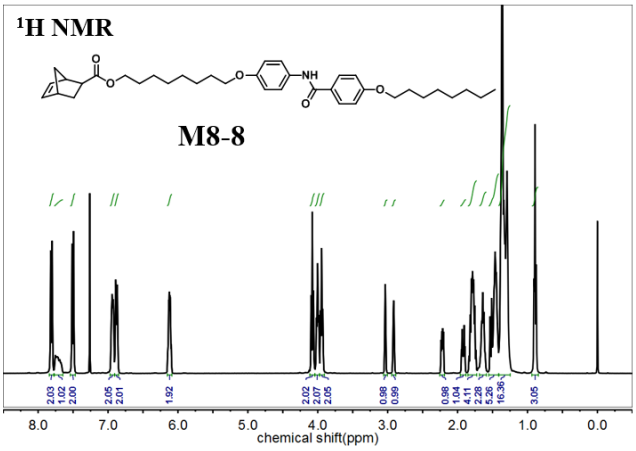


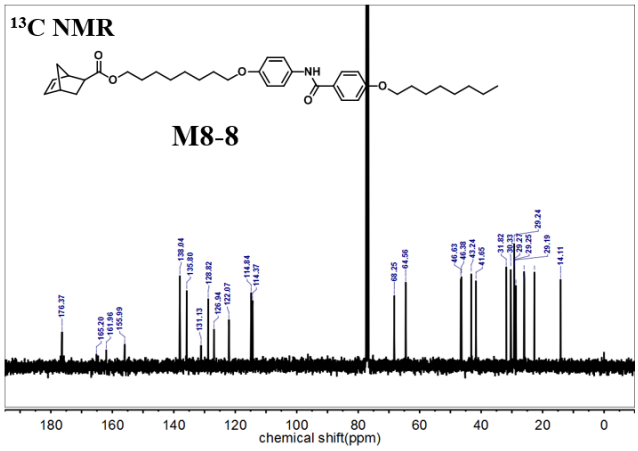


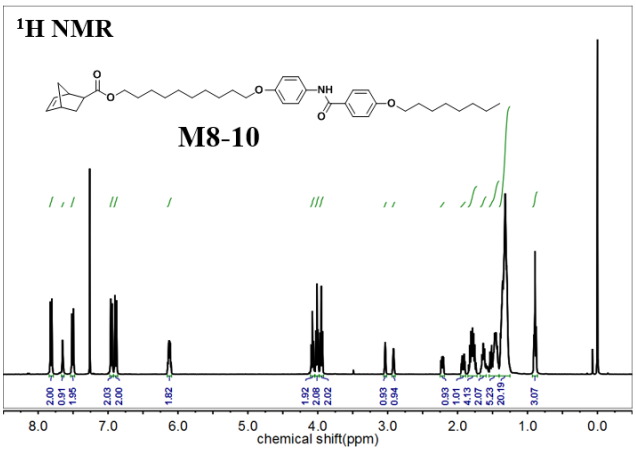


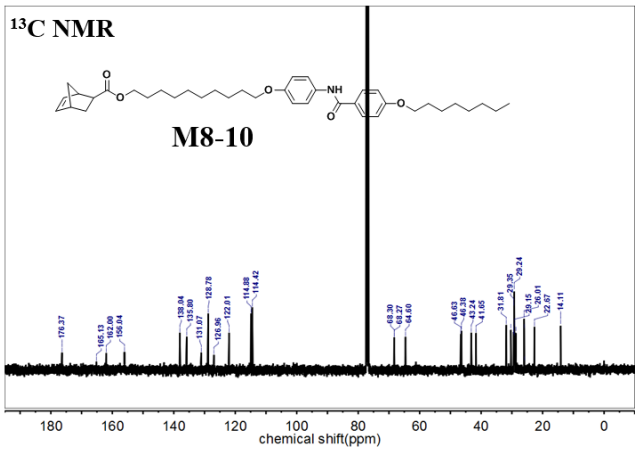


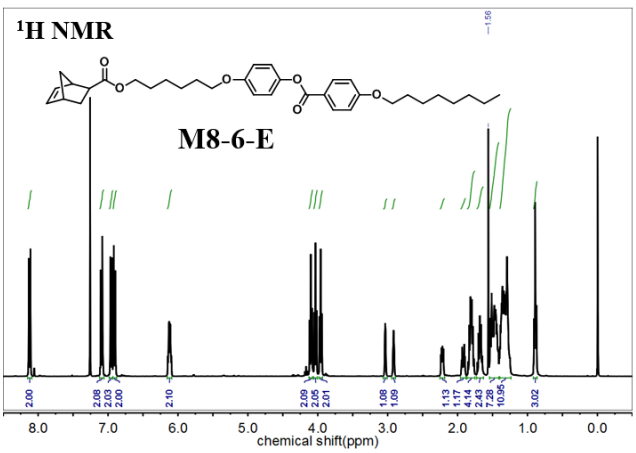


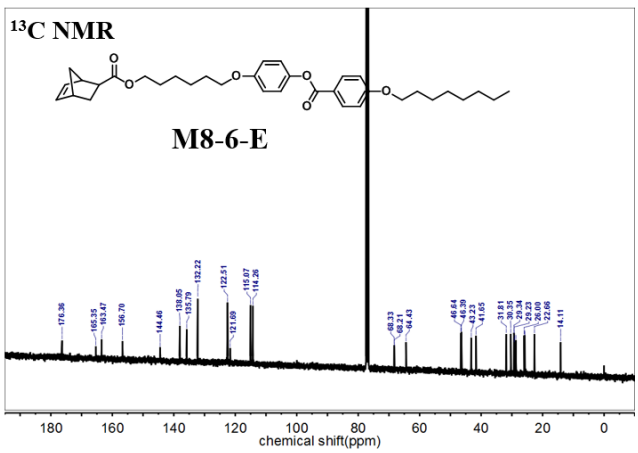

^{1}H NMR
M8-8
chemical shift(ppm)

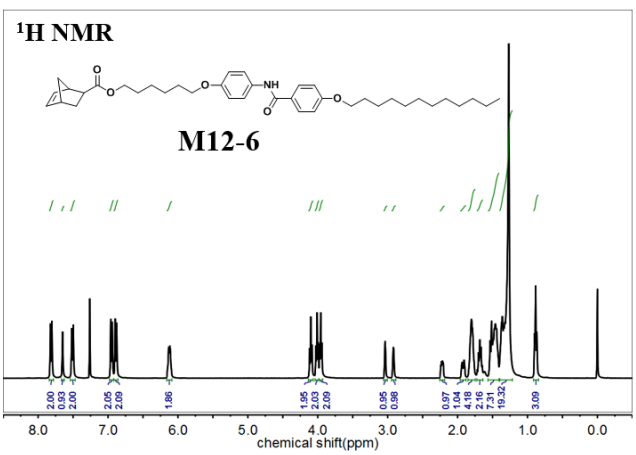

^{13}C NMR
M8-8
chemical shift(ppm)

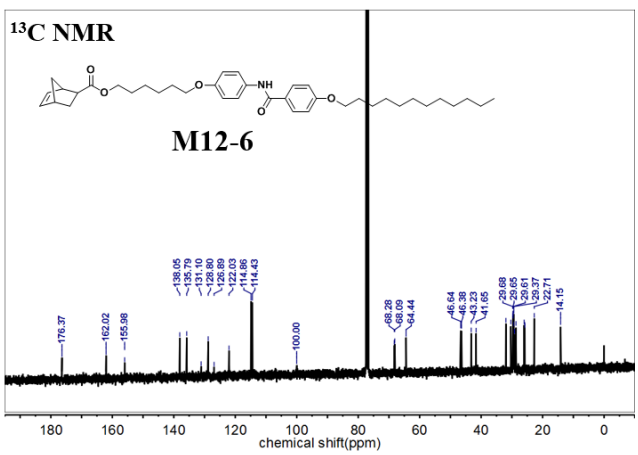

^{1}H NMR
M8-10
chemical shift(ppm)

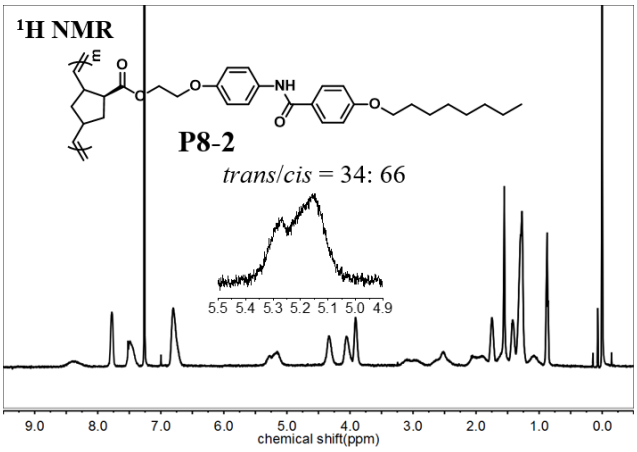

^{13}C NMR
M8-10
chemical shift(ppm)

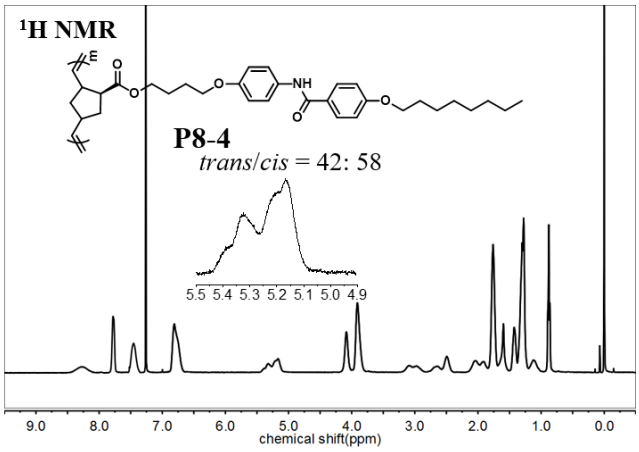

^{1}H NMR
M8-6-E
chemical shift(ppm)

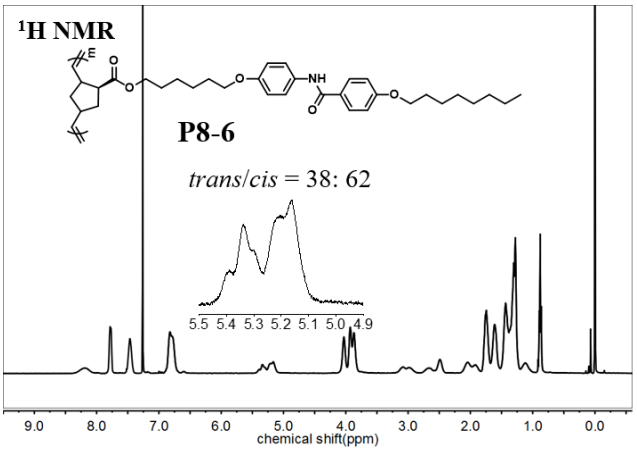

^{13}C NMR
M8-6-E
chemical shift(ppm)

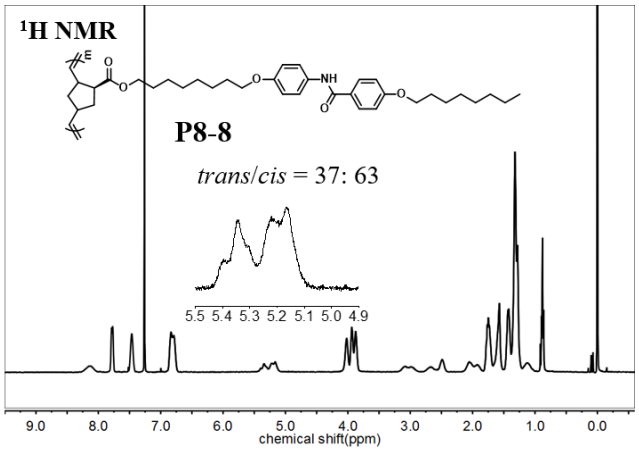

^{1}H NMR
M12-6
chemical shift(ppm)

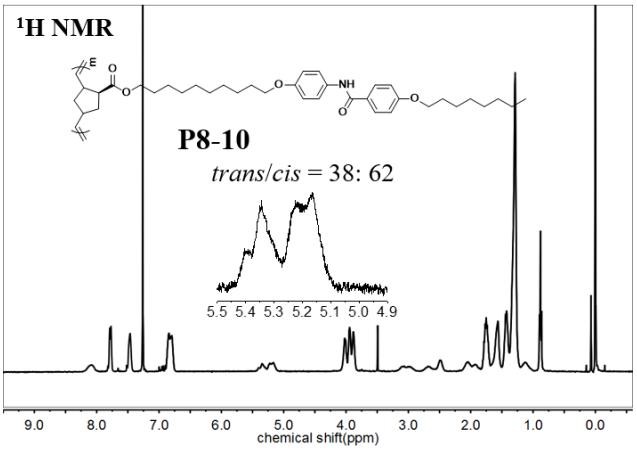

^{13}C NMR
M12-6
chemical shift(ppm)

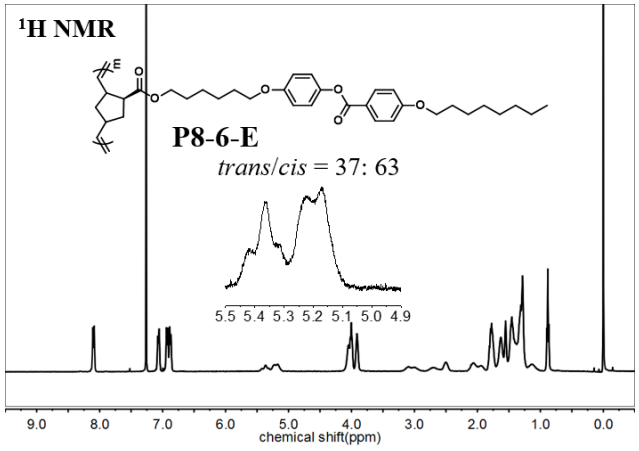

¹H NMR
P8-2
trans/cis = 34: 66
chemical shift(ppm)

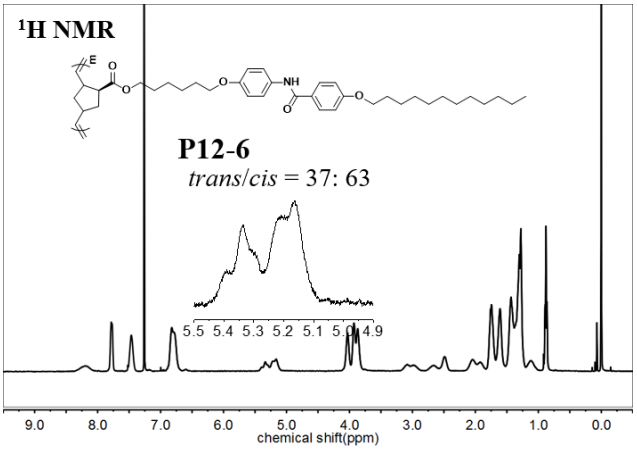

¹H NMR
P8-4
trans/cis = 42: 58
chemical shift(ppm)


¹H NMR
P8-6
trans/cis = 38: 62
chemical shift(ppm)


¹H NMR
P8-8
trans/cis = 37: 63
chemical shift(ppm)


¹H NMR
P8-10
trans/cis = 38: 62
chemical shift(ppm)


¹H NMR
P8-6-E
trans/cis = 37: 63
chemical shift(ppm)


¹H NMR
P12-6
trans/cis = 37: 63
chemical shift(ppm)

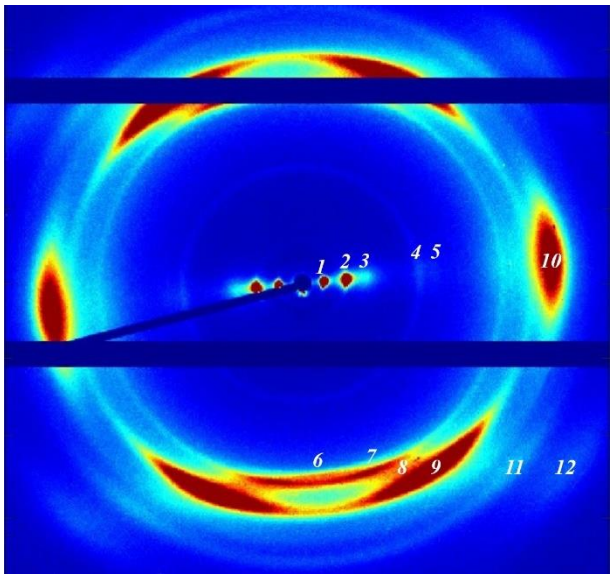
Additional Experimental Data

Table S1 ~ Table S5

Table S1. Molecular characteristics of **P8-*n***s and **P8-6-E**

Sample	M_n (10^5 g/mol)	PDI	character
P8-2	2.99	1.31	clumpy
P8-4	2.48	1.37	clumpy
P8-6	3.41	1.35	flocculent
P8-8	2.92	1.29	flocculent
P8-10	2.25	1.44	flocculent
P8-6-E	1.59	1.53	clumpy

Table S2. Experimental and calculated *q*-values and *d*-spacings of **P8-10**

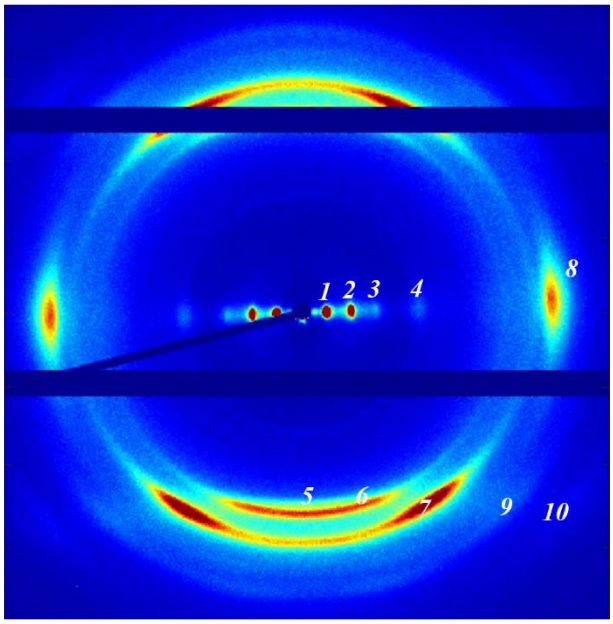


Number	(*hkl*)	*d* (nm)		*q* (nm^{-1})	
		Exp[a]	Cal[b]	Exp[a]	Cal[b]
1	002	4.27	4.27	1.47	1.47
2	004	2.14	2.14	2.93	2.94
3	006	1.43	1.42	4.40	4.42
4	100	0.790	0.786	7.95	7.99
5	105	0.701	0.714	8.96	8.80
6	010	0.503	0.509	12.5	12.3
7	015	0.480	0.488	13.1	12.9
8	017	0.455	0.470	13.8	13.4
9	110	0.427	0.427	14.7	14.7
10	200	0.393	0.393	16.0	16.0
11	1 1 12	0.357	0.366	17.6	17.2
12	210	0.314	0.311	20.0	20.2

[a] Experimental values observed.

[b] Calculated values based on the orthorhombic unit cell of a = 0.786 nm, b = 0.509 nm, c = 8.54 nm.

Table S3. Experimental and calculated *q*-values and *d*-spacings of **P8-6**

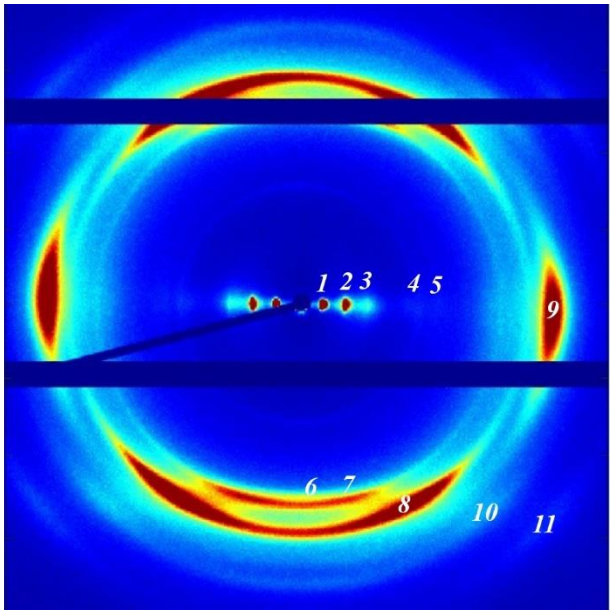


Number	(*hkl*)	*d* (nm)		*q*/ (nm^{-1})	
		Exp[a]	Cal[b]	Exp[a]	Cal[b]
1	002	3.83	3.83	1.64	1.64
2	004	1.92	1.92	3.28	3.27
3	006	1.28	1.28	4.92	4.91
4	100	0.800	0.786	7.85	7.99
5	010	0.503	0.509	12.5	12.3
6	015	0.480	0.483	13.1	13.0
7	110	0.427	0.427	14.7	14.7
8	200	0.393	0.393	16.0	16.0
9	1 1 12	0.357	0.355	17.6	17.7
10	210	0.311	0.311	20.2	20.2

[a] Experimental values observed.

[b] Calculated values based on the orthorhombic unit cell of a = 0.786 nm, b = 0.509 nm, c = 7.66 nm.

Table S4. Experimental and calculated *q*-values and *d*-spacings of **P8-8**

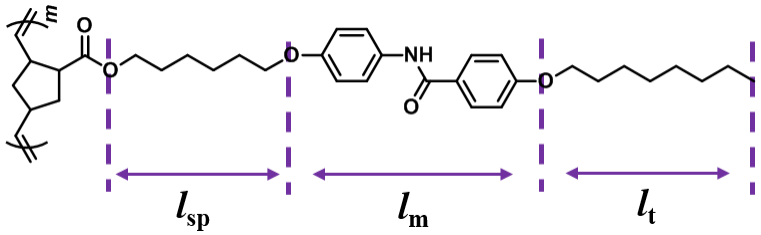


Number	(*hkl*)	*d* (nm)		*q* (nm^{-1})	
		Exp[a]	Cal[b]	Exp[a]	Cal[b]
1	002	4.03	4.03	1.56	1.56
2	004	2.01	2.02	3.13	3.11
3	006	1.35	1.34	4.65	4.69
4	100	0.793	0.780	7.92	8.06
5	105	0.691	0.702	9.09	8.95
6	010	0.503	0.510	12.5	12.3
7	015	0.480	0.486	13.1	12.9
8	110	0.427	0.427	14.7	14.7
9	200	0.390	0.390	16.1	16.1
10	1 1 12	0.357	0.360	17.6	17.5
11	210	0.311	0.310	20.2	20.3

[a] Experimental values observed.

[b] Calculated values based on the orthorhombic unit cell of a = 0.780 nm, b = 0.510 nm, c = 8.06 nm.

Table S5. Calculated length of spacer, mesogen and tail of **P8-*n*s** and **P8-6-E**



	P8-2	**P8-4**	**P8-6**	**P8-8**	**P8-10**	**P8-6-E**
l_{sp} (nm)	0.38	0.63	0.88	1.12	1.37	0.88
l_m (nm)	1.30	1.30	1.30	1.30	1.30	1.28
l_t (nm)	0.99	0.99	0.99	0.99	0.99	0.99

Fig. S1 ~ Fig. S14

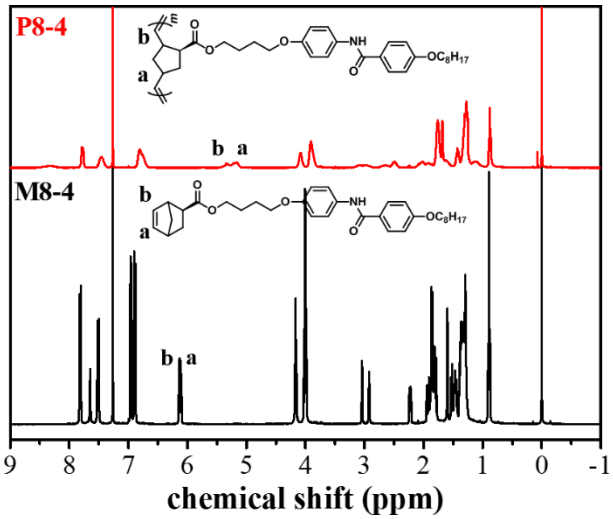


Fig. S1 The ^{1}H NMR spectrograms of **M8-4** and **P8-4**.

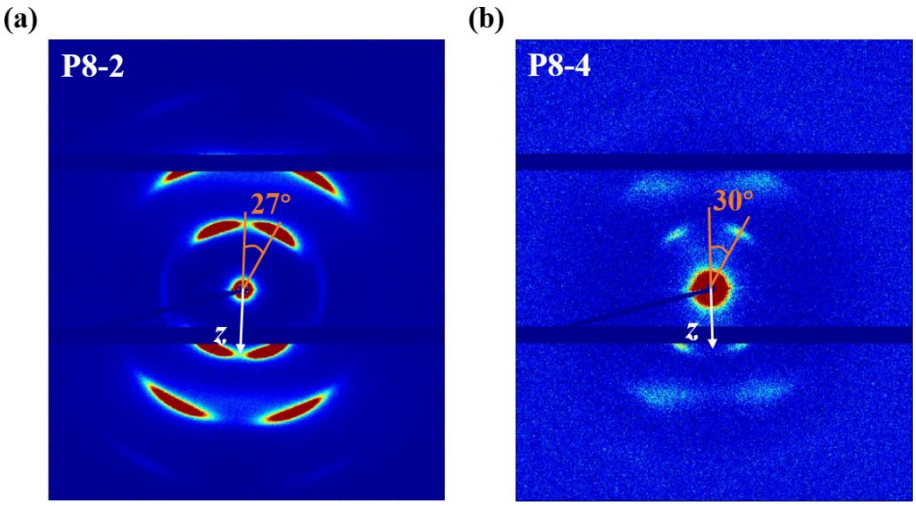


Fig. S2 2D XRD patterns of the low angle region of stretched film samples of (a) **P8-2** and (b) **P8-4** recorded at room temperature. The *z*-axis is stretching direction.

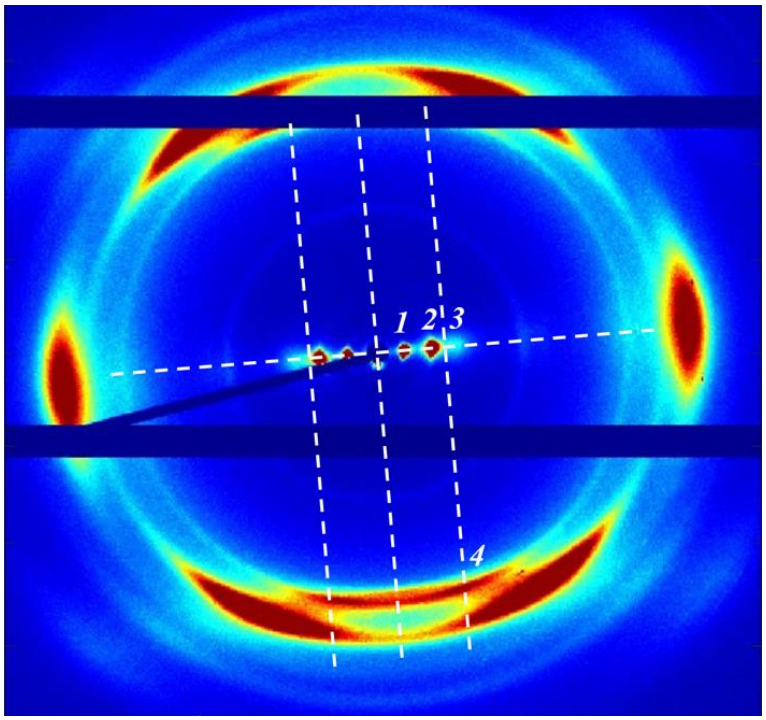


Fig. S3 2D XRD pattern of stretched film sample of **P8-10**. The dotted white lines are parallel or perpendicular to the stretching direction for indexation.

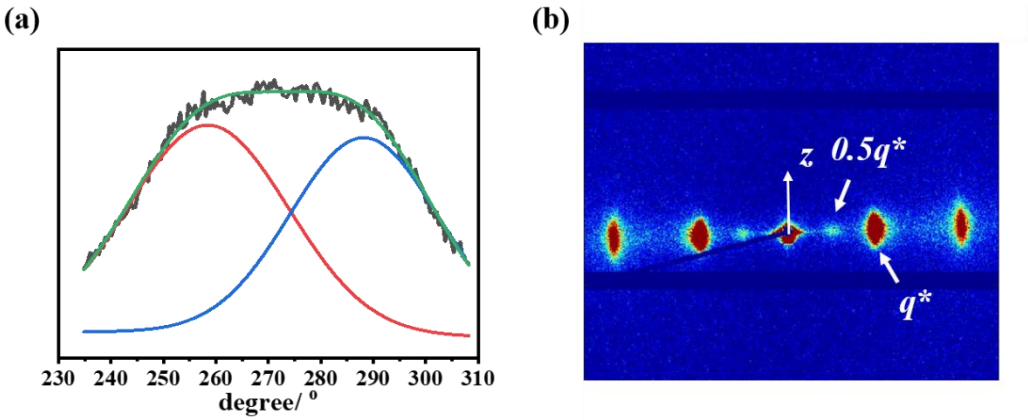


Fig. S4 (a) Azimuthal integration (black line) of spot *4* of P8-6 and peak separation of this peak (red and blue line); (b) 2D XRD pattern of the low angle region of the stretched film sample of **P8-6**. The *z*-axis is stretching direction.

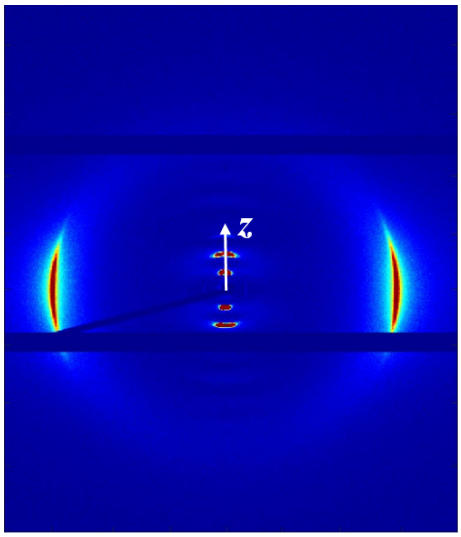


Fig. S5 2D XRD pattern of the stretched film sample of **P8-6-E**. The *z*-axis is stretching direction.

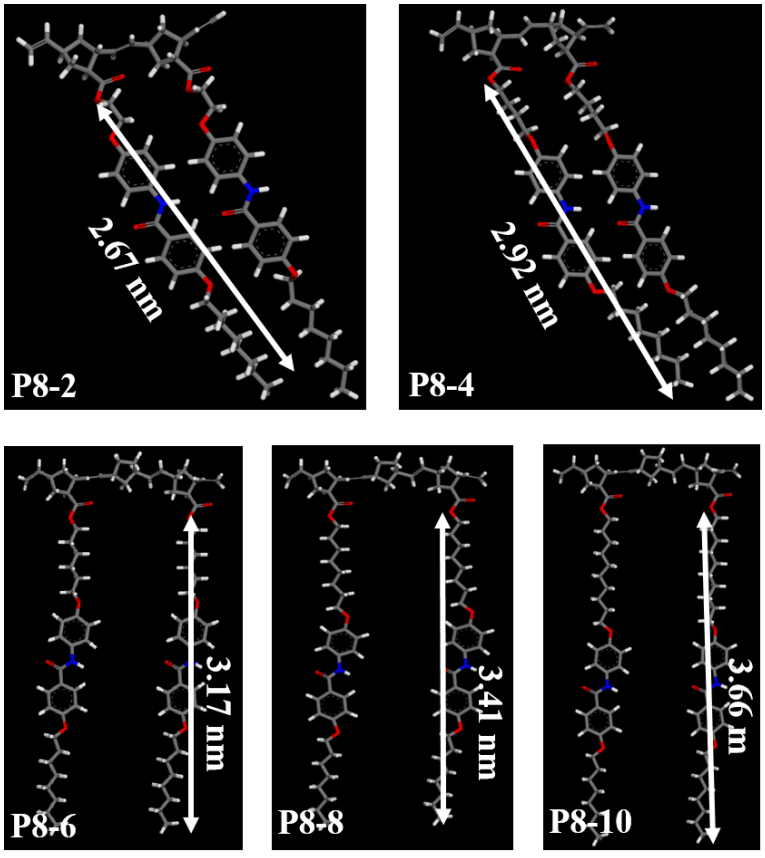


Fig. S6 The calculated length of side chains of **P8-*n*s** from Materials Studio.

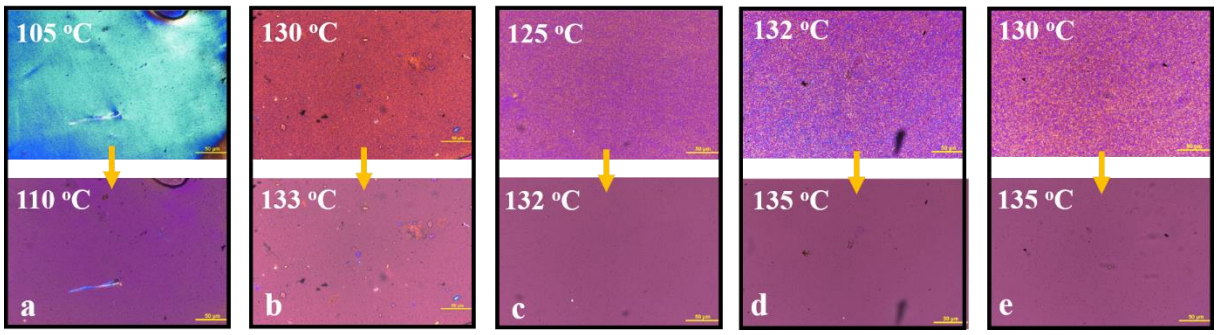


Fig. S7 Isotropic transition of **P8-*n*s** observed under POM upon heating. (a) **P8-2**; (b) **P8-4**; (c) **P8-6**; (d) **P8-8**; (e) **P8-10**.

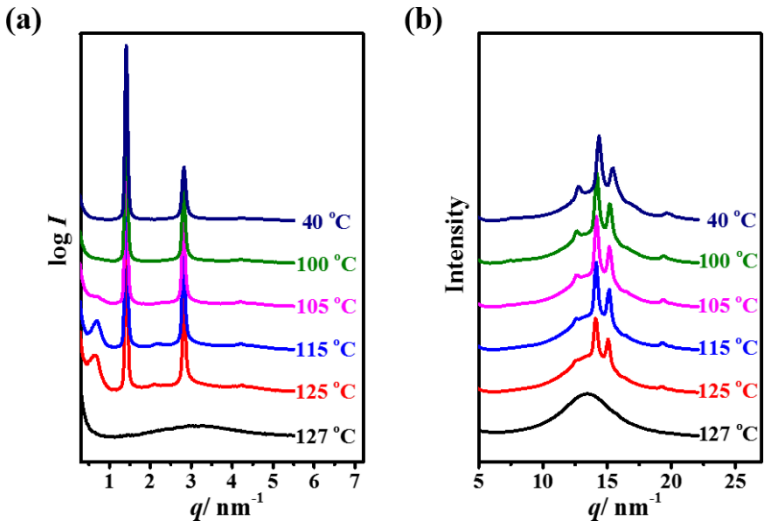


Fig. S8 1D XRD profiles of **P8-10** recorded at various temperatures during cooling. (a) and (b), low angle and high angle region, respectively.

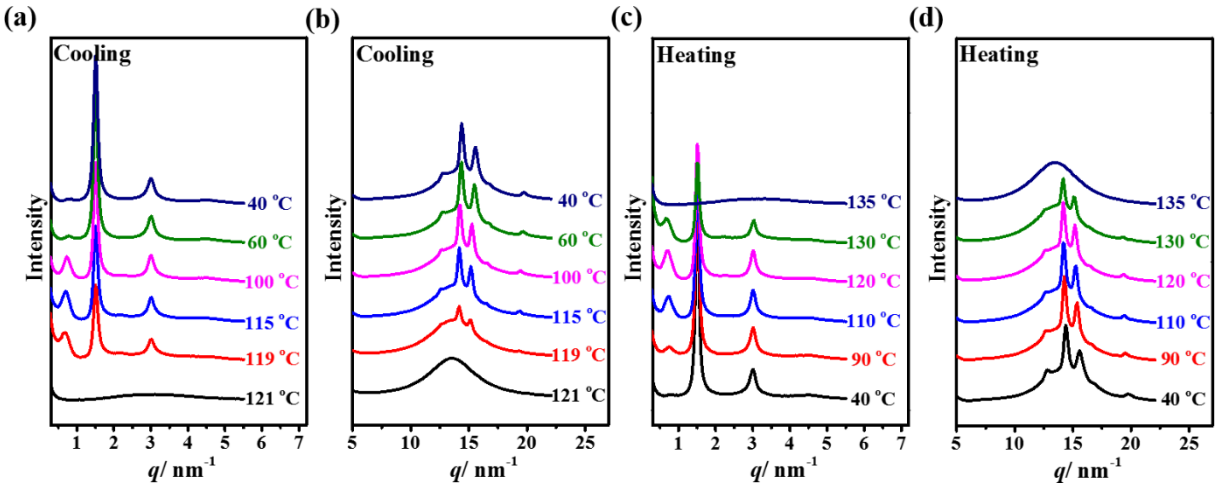


Fig. S9 1D XRD profiles of **P8-8** recorded at various temperatures upon (a, b) cooling and (c, d) subsequent heating. (a) and (c), low angle region; (b) and (d), high angle region. It is noted that upon relatively fast cooling some residual diffraction at 0.5q* could be seen at low temperatures. However, it would disappear after thermal annealing.

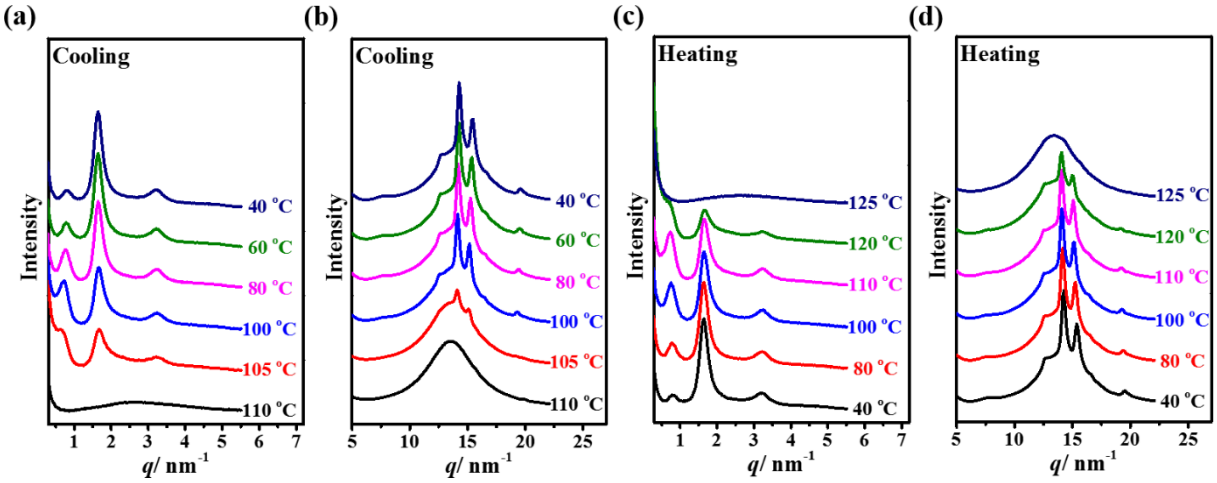


Fig. S10 1D XRD profiles of **P8-6** recorded at various temperatures upon (a, b) cooling and (c, d) subsequent heating. (a) and (c), low angle region; (b) and (d), high angle region.

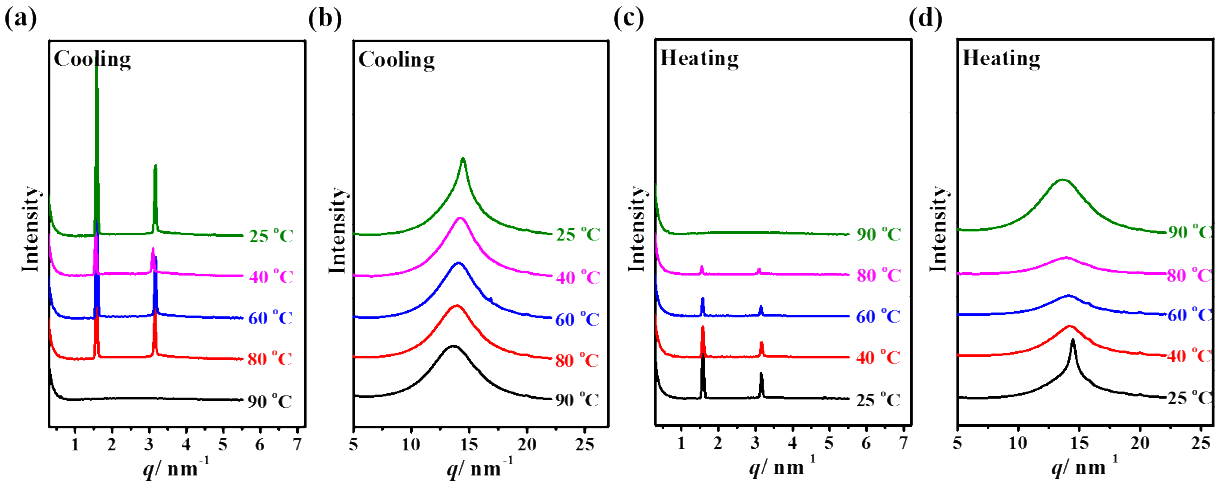


Fig. S11 1D XRD profiles of **P8-6-E** recorded at various temperatures upon (a, b) cooling and (c, d) subsequent heating. (a) and (c), low angle region; (b) and (d), high angle region.

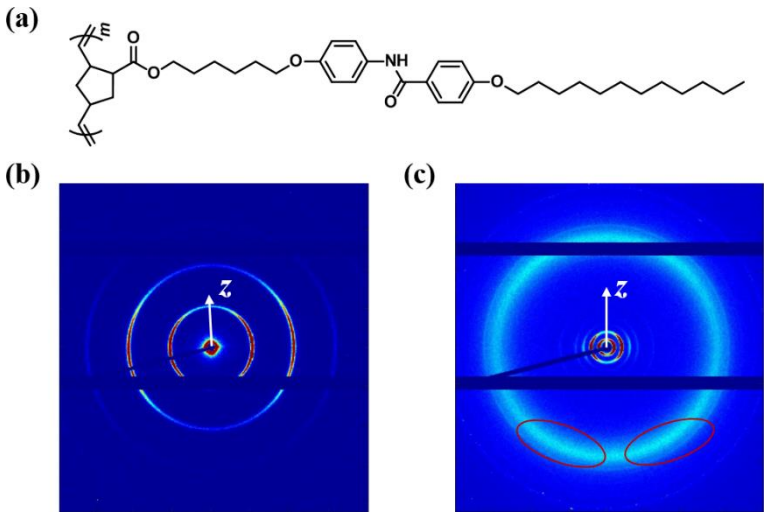


Fig. S12 (a) Chemical structure of **P12-6**; (b) and (c), 2D XRD patterns of the stretched film sample of **P12-6** recorded at room temperature. (b) shows the low angle diffractions. The oriented film was obtained by melt drawing. *z* direction is the stretching direction.

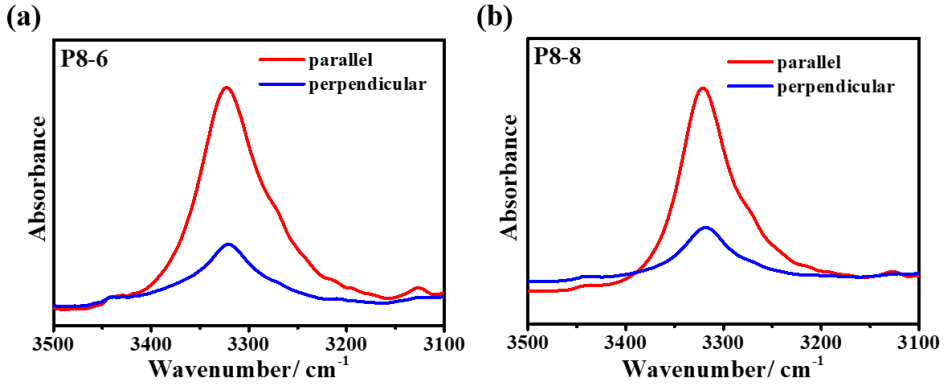


Fig. S13 Polarized FT-IR spectra of the oriented films of (a) **P8-6**; (b) **P8-8**. The red and blue curves represent the data measured with polarizer parallel and perpendicular to the stretching direction, respectively.

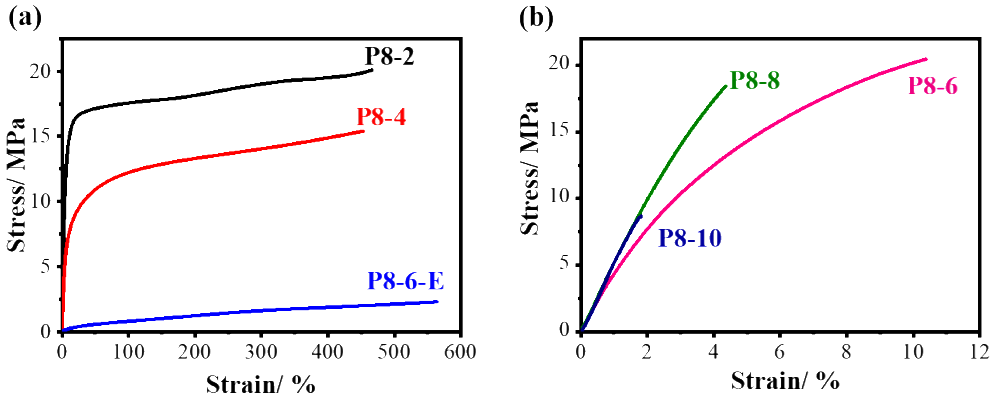


Fig. S14 Stress-Strain curves of **P8-*n*s** measured at 30 °C. (a) **P8-2**, **P8-4** and **P8-6-E**; (b) **P8-6**, **P8-8** and **P8-10**.