

Supporting Information for:

“Poly(Vinyl Benzoate)-Backbone Mesogen-Jacketed Liquid Crystalline Polymers”

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General considerations.

Palladium chloride (PdCl₂), lithium acetate, cupric bromide, diethylazodicarboxylate (DEAD), dicumyl peroxide (DCP), 2,2-dimethoxy-2-phenylacetophenone, and tetrabutylammonium fluoride solution (TBAF, 1M in THF) were purchased from Aldrich Inc. Dichloromethane, toluene and DMF were distilled from CaH₂ under argon. THF was distilled from sodium-benzophenone ketyl under argon. Other chemical reagents were used without further purification. All non-aqueous reactions were conducted in oven-dried glassware, under a dry nitrogen atmosphere. All flash chromatography was performed using Macherey-Nagel MN Kieselgel 60 (0.063-1.2 mm).

¹H NMR spectra were obtained using a Bruker HW500 MHz spectrometer (AVANCE AV-500) and recorded in CDCl₃ (internal reference 7.26 ppm). Fourier transform infrared (FT-IR) spectra were obtained with a Nicolet 5700 FT-IR spectrometer (Thermo Electron Scientific Instruments Corp). Gel permeation chromatography (GPC) was performed on an HP 1100 high pressure liquid chromatography (HPLC), equipped with an HP 1047A refractive index detector and a Plgel MIXED-C 300-7.5 mm column (packed with 5 μm particles). The column packing

allowed the separation of polymers over a wide molecular weight range of 200-3000000 g/mol. THF was used as the eluent at a low flow rate of 1 mL/min at 35 °C. Polystyrene standards were used as the references. A UV lamp (20 mW/cm², λ = 365 nm; LP-40A; LUYOR Corporation) was used to irradiate the samples to perform the photo-polymerization and crosslinking reactions.

Differential scanning calorimetry (DSC) spectra were recorded on a TA Instruments Q20 instrument (New Castle, DE) under nitrogen purge at a heating rate of 10 °C/min from -10 to 250 °C. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA7.

POM observations of LC textures of the monomers, polymers and elastomers were performed on an Olympus BX53P microscope with a Mettler PF82HT hot stage. The images were captured using a Microvision MV-DC200 digital camera with Phenix Phmias2008 Cs Ver2.2 software.

One-dimensional (1D) WAXD experiments were carried out on a Philips X'Pert Pro diffractometer with an X'celerator detector and a 3 kW ceramic tube as the X-ray source (Cu K α) in the reflection mode. A temperature control unit (Paar Physica TCU 100) in conjunction with the X'Pert Pro was utilized to study the structure evolutions as function of temperature. Two-dimensional (2D) WAXD experiments were performed using a Bruker D8Discover diffractometer with VANTEC 500 as a 2D detector. The diffraction patterns were recorded in the transmission mode at ambient temperature using uniaxially oriented fiber or film samples. For both the 1D and 2D WAXD experiments, the reflection peak positions were calibrated with silicon powder ($2\theta > 15^\circ$) and silver behenate ($2\theta < 10^\circ$). Background scattering was recorded and subtracted from the sample patterns.

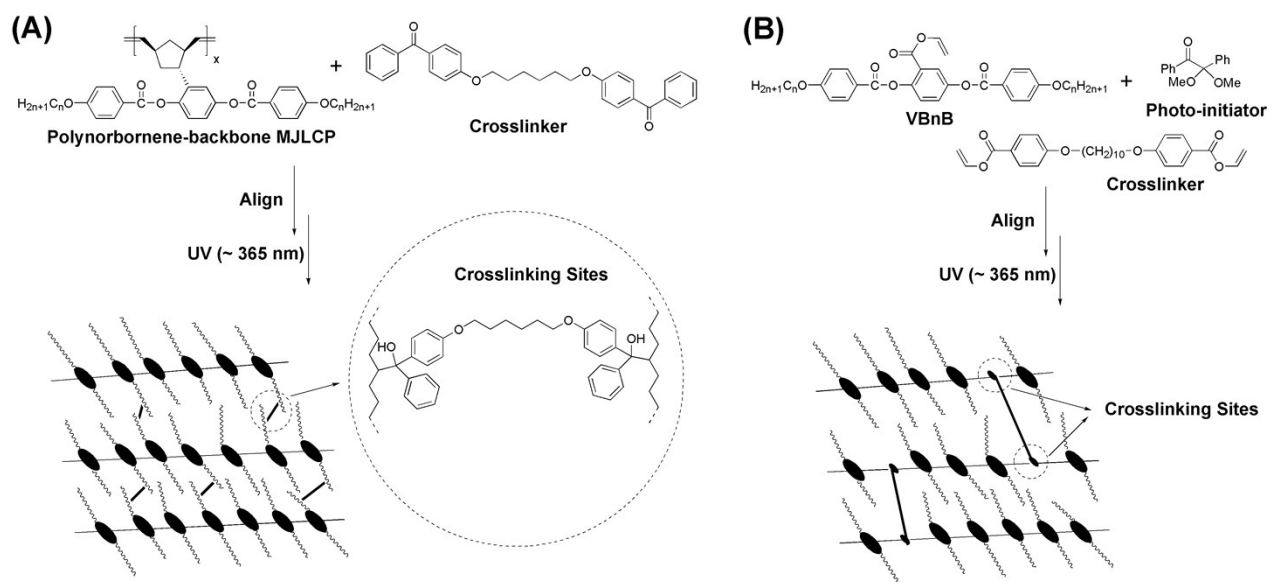
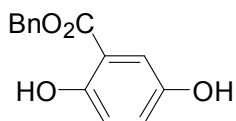


Fig. S1 Schematic illustrations of (A) previously reported polynorbornene-backbone MJLCE which is cross-linked on the mesogen alkyl chains, and (B) this novel poly(vinyl benzoate)-backbone xMJLCP which is cross-linked on the polymer main chains.



9

Benzyl 2,5-Dihydroxybenzoate (9). 2,5-Dihydroxybenzoic acid **8** (6.16 g, 40.0 mmol) was dissolved in dry DMF (60 mL). NaHCO₃ (9.9 g, 117.8 mmol) was added and the reaction mixture was stirred at 70 °C for 1 h. Benzyl bromide (6.84 g, 40.0 mmol) were then added slowly and the mixture was stirred at 70 °C for additional 7 h. After cooling to room temperature, the reaction mixture was diluted with 200 mL water and extracted twice with n-hexane/ethyl acetate (1/1, 100 mL). The organic layer was washed twice with water, followed by drying over anhydrous magnesium sulfate. Then, the filtrate was concentrated under reduced pressure to give crude products. The final purification was carried out by column chromatography to give the product **9** (7.6 g, Yield: 77.7 %) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 7.47 - 7.34 (m, 5H), 7.31 (d, 1H, J = 3.05 Hz), 7.04 - 6.81 (m, 2H), 5.36 (s, 2H), 4.52 (s, 2H).

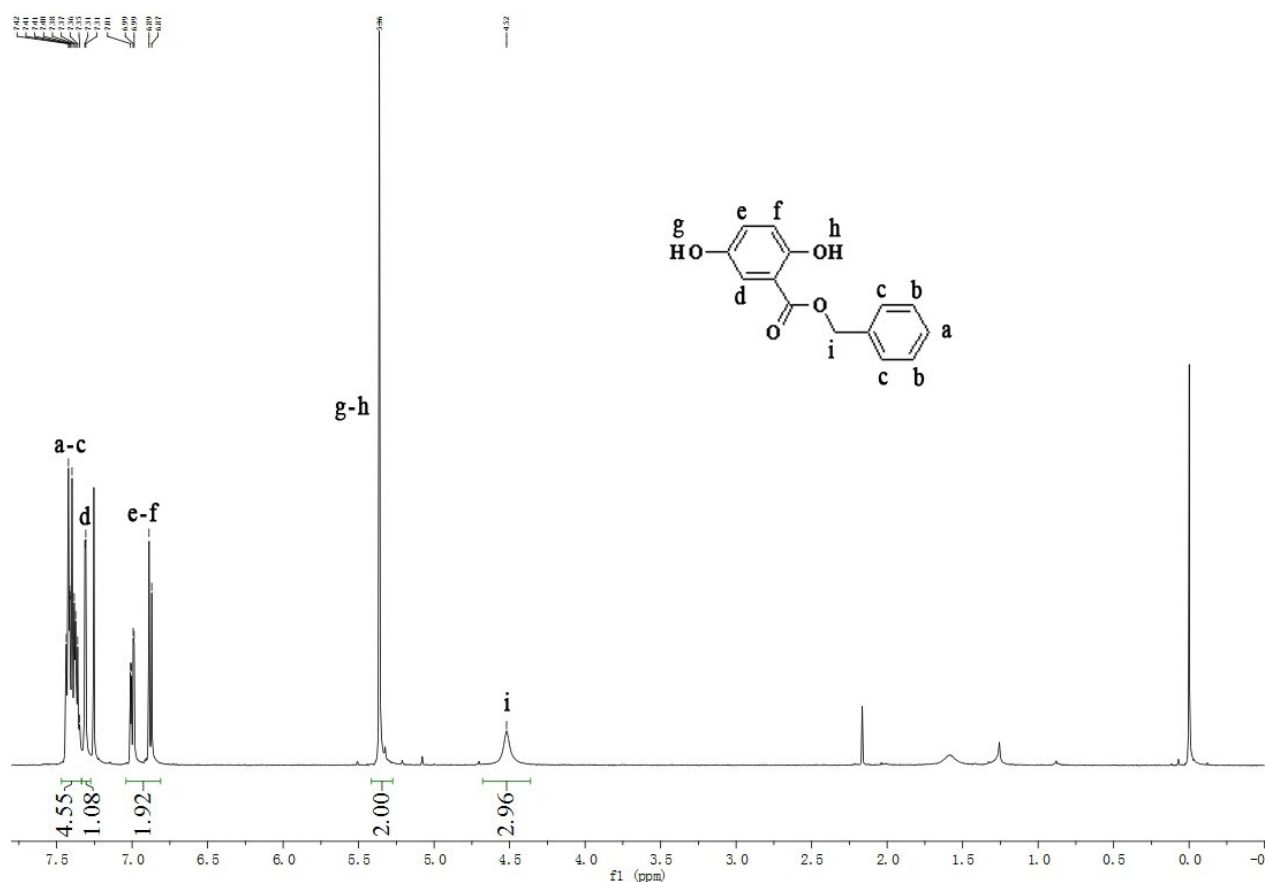
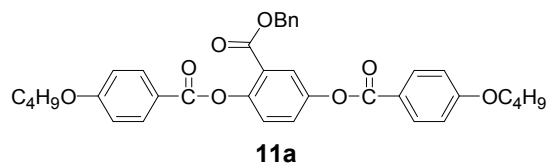


Fig. S2 ¹H NMR spectrum of Compound **9**.



Benzyl 2,5-Di(4'-butyloxybenzoyloxy)benzoate (11a). 4-Butyloxybenzoic acid (**10a**) (10.5 g, 54.0 mmol), compound **9** (6.0 g, 24.6 mmol), DMAP (0.8 g, 5.4 mmol) and dry CH₂Cl₂ (150 mL) were added into a 250 mL round-bottom flask. Under a nitrogen atmosphere, DCC (11.1 g, 54.0 mmol) was added into the above flask in one portion at r.t. The reaction mixture was stirred at r.t. for 12 h. After filtering off the solids, the reaction solution was then concentrated by rotary evaporation and the resulting crude solid was recrystallized in methanol to give the desired product (12.3 g, Yield: 84%) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 8.25 - 8.01 (m, 4H), 7.9 (d, 1H, J = 2.85 Hz), 7.26 - 7.24 (m, 7H), 7.04 - 6.86 (m, 4H), 5.19 (s, 2H), 4.06 (t, 4H, J = 6.45 Hz), 1.8 (m, 4H), 1.5 (m, 4H), 1.0 (t, 6H, J = 7.25 Hz).

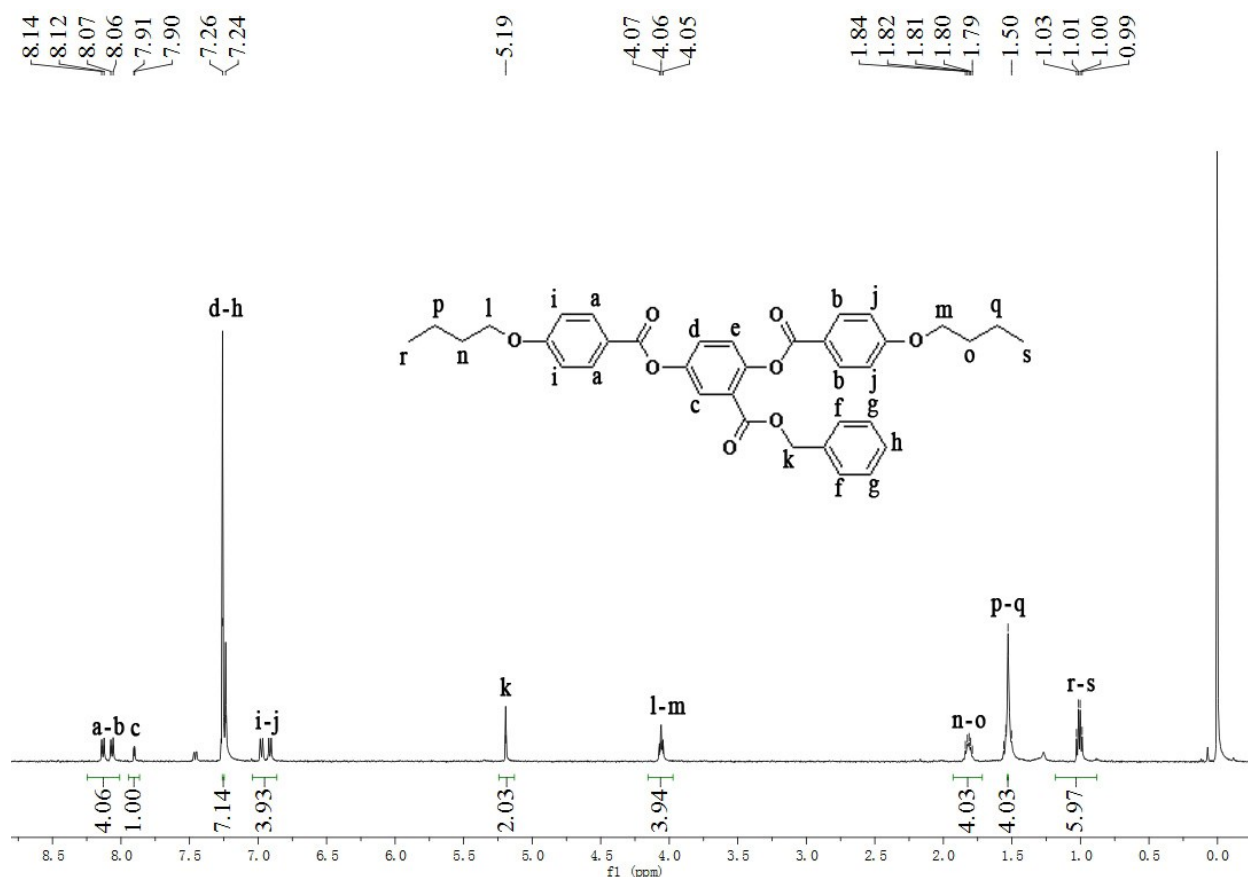
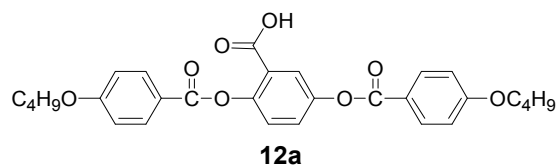


Fig. S3 ¹H NMR spectrum of Compound **11a**.



2,5-Di(4'-butyloxybenzoyloxy)benzoic Acid (12a). Hydrogen was allowed to bubble through a stirred suspension of 10 % Pd/C (3.0 g) in 200 mL of dichloromethane for 15 minutes. Benzyl ether **11a** (12.3 g, 20.6 mmol) was added, and the reaction mixture was stirred at r.t. for 10 h. After filtering through a celite pad, the filtrate was concentrated, and the product (9.6 g, 92 %) was further dried under vacuum. ^1H NMR (500 MHz, CDCl_3): δ 8.23-8.07 (m, 4H), 7.9 (d, 1H, J = 2.85 Hz), 7.69-7.38 (dd, 2H, J = 8.7, 2.9 Hz), 7.04 - 6.92 (m, 4H), 4.06 (t, 4H, J = 3.5 Hz), 1.83 (m, 4H), 1.52 (m, 4H), 1.00 (m, 6H).

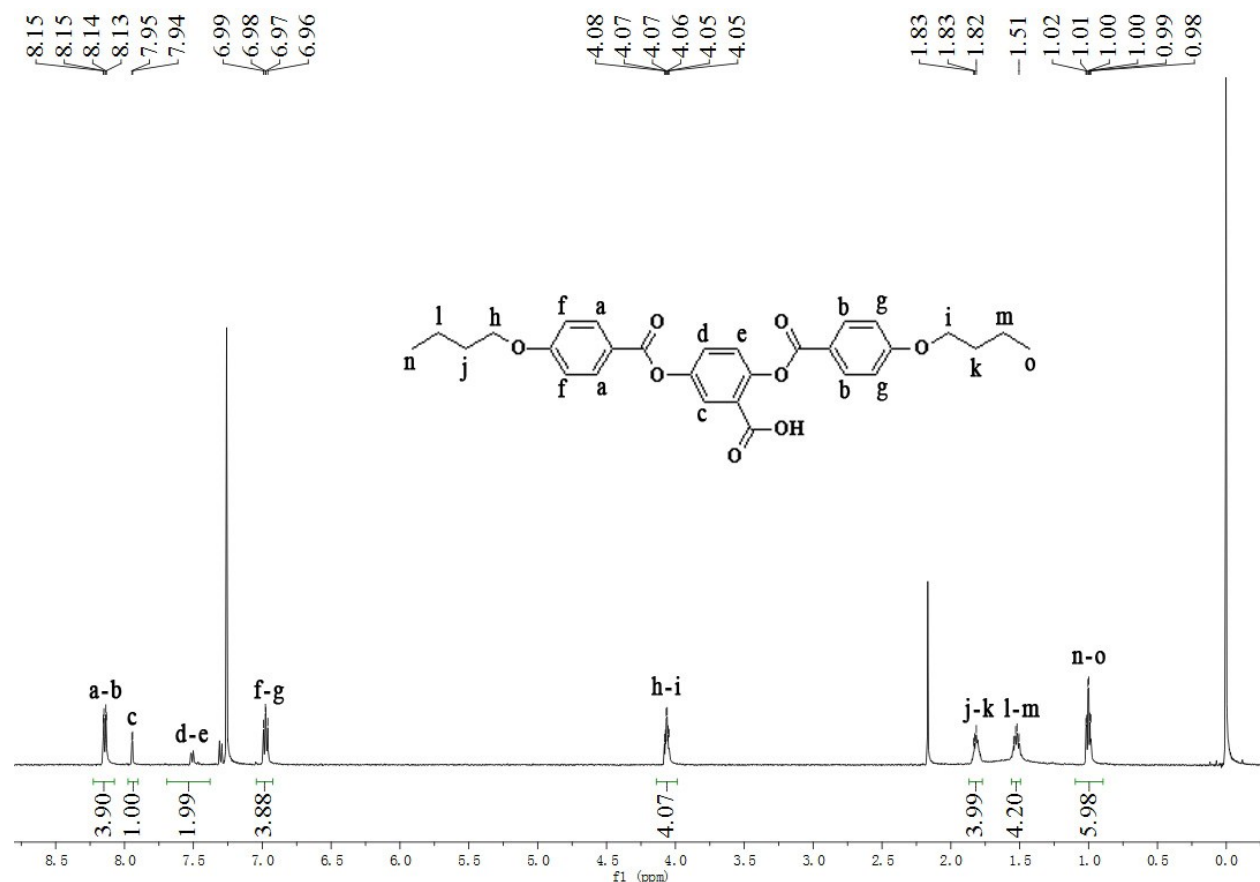
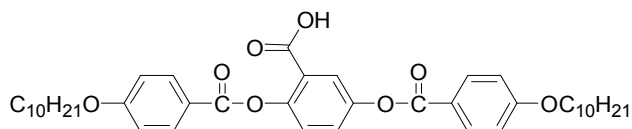


Fig. S4 ^1H NMR spectrum of Compound **12a**.



12b

2,5-Di(4'-decyloxybenzoyloxy)benzoic Acid (12b). **12b** was prepared following the above described procedure. ^1H NMR (500 MHz, CDCl_3) : δ 8.13 (t, $J = 7.8$ Hz, 4H), 7.94 (d, $J = 2.3$ Hz, 1H), 7.50 (dd, $J = 8.6, 2.4$ Hz, 1H), 7.29 (d, $J = 8.8$ Hz, 1H), 6.96 (dd, $J = 12.9, 8.7$ Hz, 4H), 4.12 – 3.99 (m, 4H), 1.93 – 1.71 (m, 4H), 1.59 – 1.16 (m, 30H), 0.89 (t, $J = 6.3$ Hz, 6H).

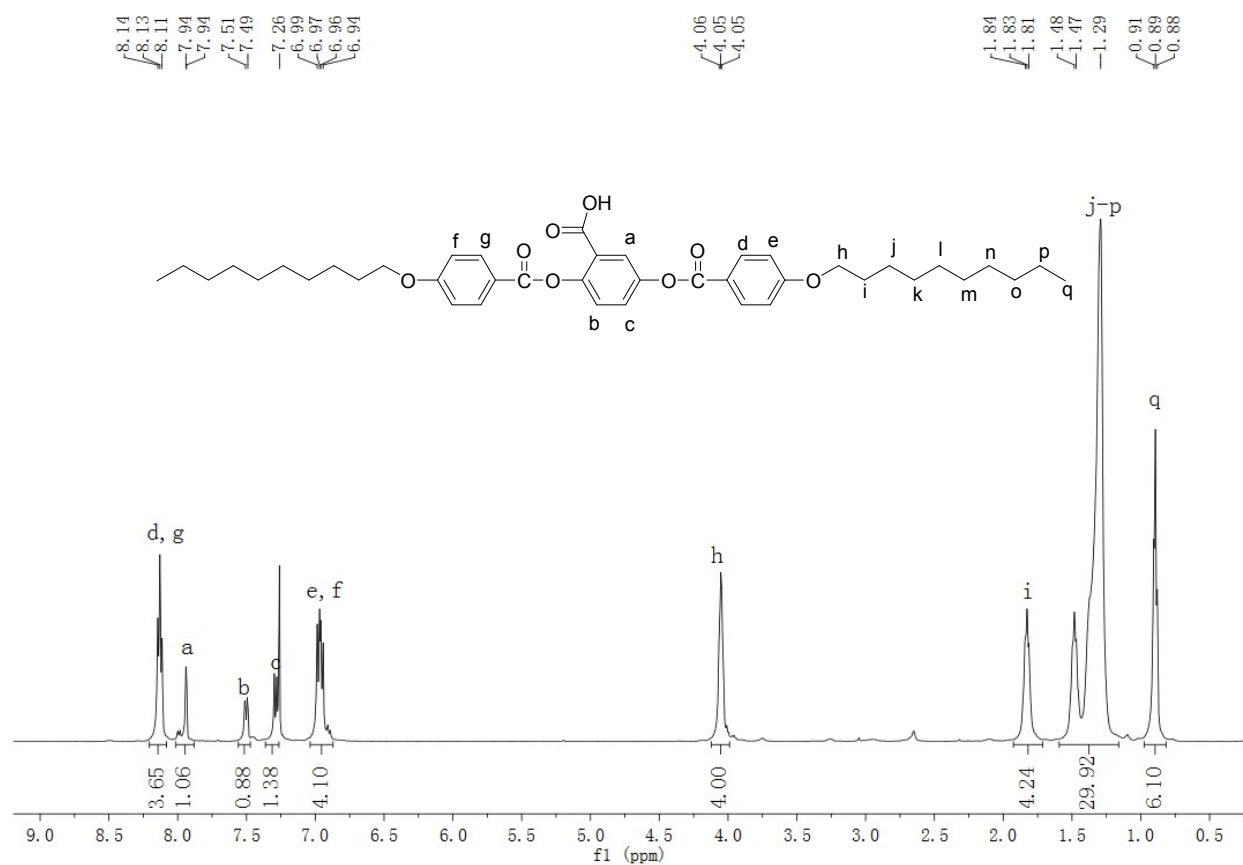
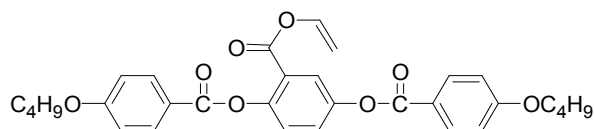


Fig. S5 ^1H NMR spectrum of Compound **12b**.



13a

Monomer **VB4B (13a)**. In a 100 mL round-bottom flask, palladium chloride (1.2 mg, 0.01 mmol), lithium acetate (65.2 mg, 0.99 mmol) and cupric bromide (5.5 mg, 0.025 mmol) were added under nitrogen atmosphere, to a solution of vinyl acetate (1.70 g, 19.75 mmol) in dry THF (50 mL) at room temperature. The reaction mixture was heated to 70 °C and then a solution of intermediate **12a** (1.00 g, 1.98 mmol) in dry THF (20 mL) was slowly added *via* syringe. After stirring at 70 °C for 24 h, the mixture was filtered and washed with ethyl acetate, and then concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (n-hexane : EtOAc = 10 : 1) to give the desired product (0.56 g, Yield: 53.3%) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ 8.17 (t, *J* = 8.2 Hz, 4H), 7.97 (d, *J* = 2.8 Hz, 1H), 7.55 – 7.47 (m, 1H), 7.41 – 7.28 (m, 2H), 6.99 (d, *J* = 8.2 Hz, 4H), 4.69 (d, *J* = 15.6 Hz, 1H), 4.54 (d, *J* = 6.2 Hz, 1H), 4.07 (t, *J* = 5.6 Hz, 4H), 1.90 – 1.75 (m, 4H), 1.60 – 1.45 (m, 6H), 1.00 (t, *J* = 7.3 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 164.38, 164.04, 163.33, 163.19, 148.16, 147.90, 140.50, 132.03, 131.91, 127.43, 124.76, 120.74, 113.93, 113.87, 98.15, 67.57, 67.52, 30.63, 29.19, 18.69, 13.30. MS ES+(*m/e*): 555 (M+Na⁺, 100%). Phase sequence and transition temperatures: Cr – 117 °C – N – 150 °C – Iso (on heating, determined by POM), Iso – 148 °C – N – 94 °C – Cr (on cooling).

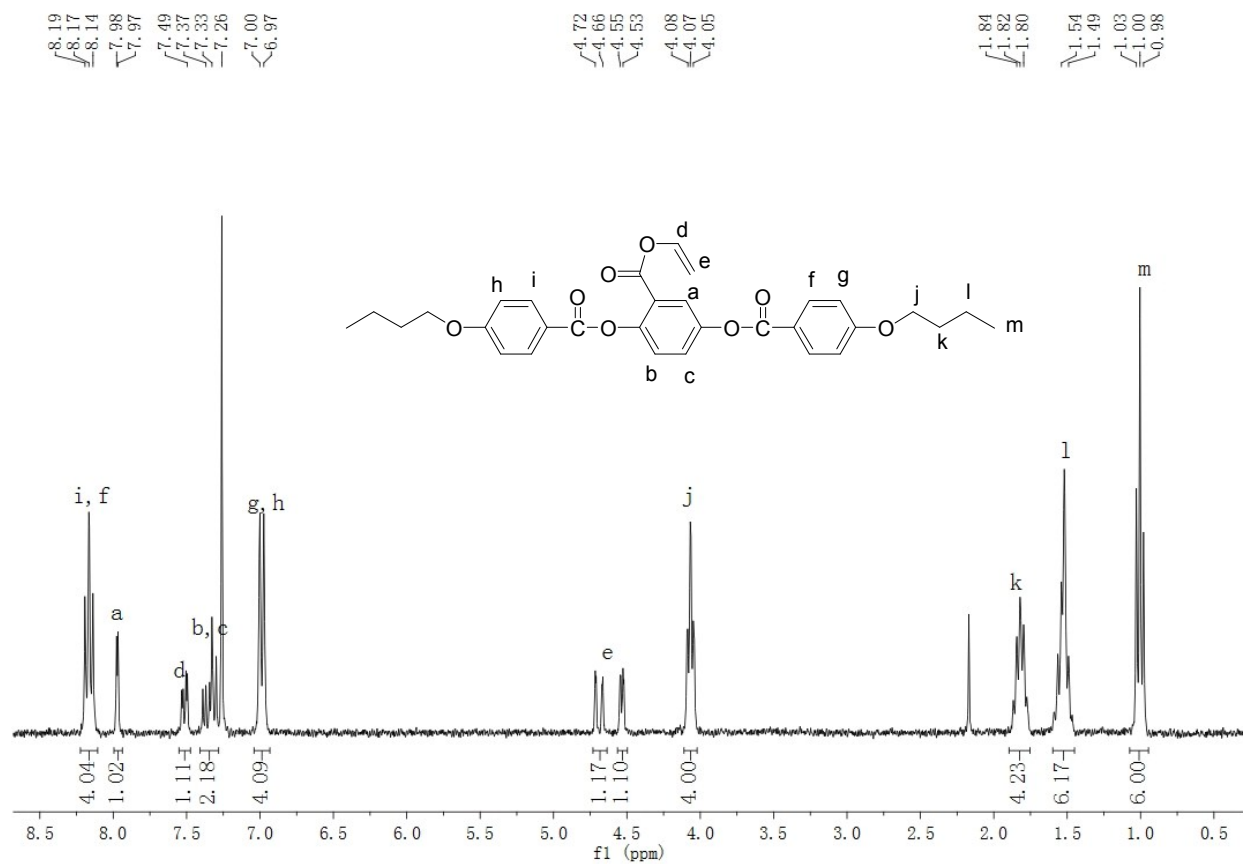


Fig. S6 ^1H NMR spectrum of Compound 13a.

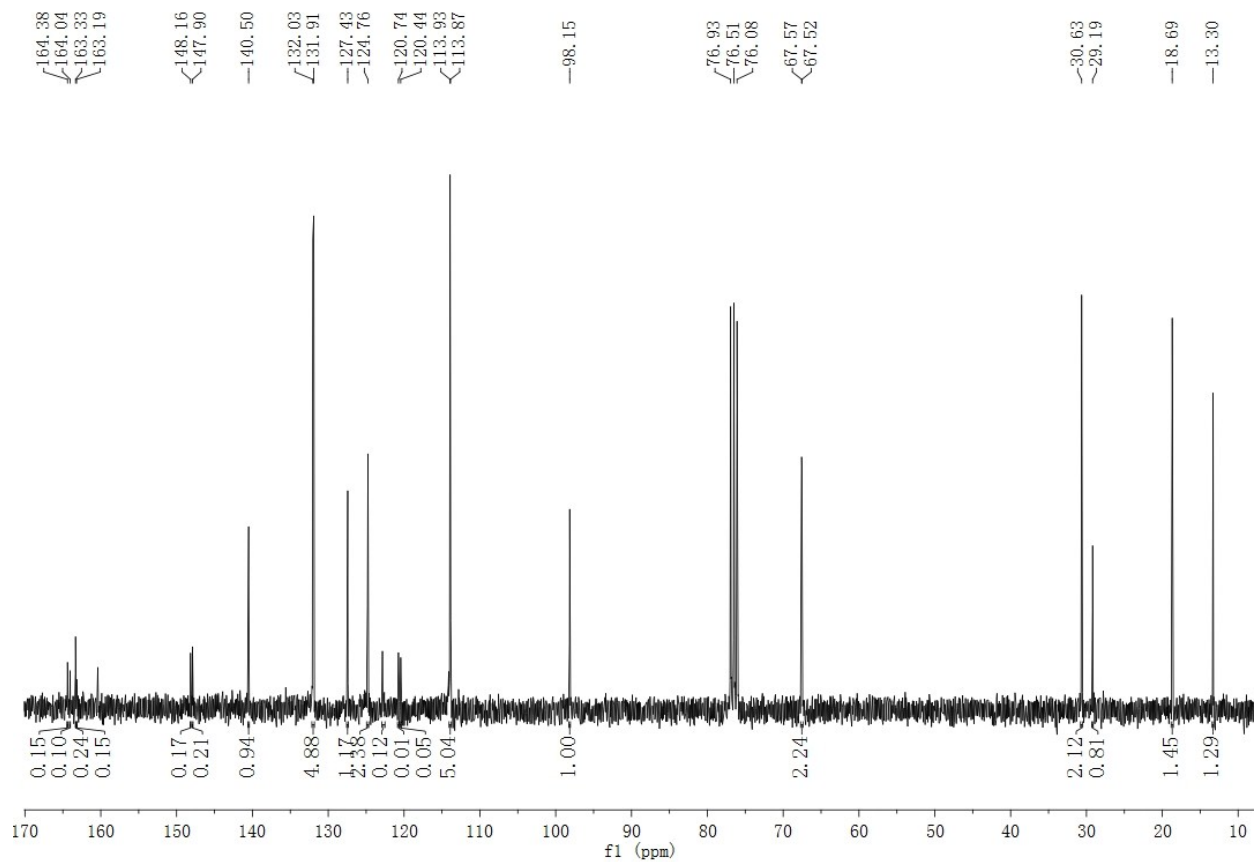


Fig. S7 ^{13}C NMR spectrum of Compound **13a**.

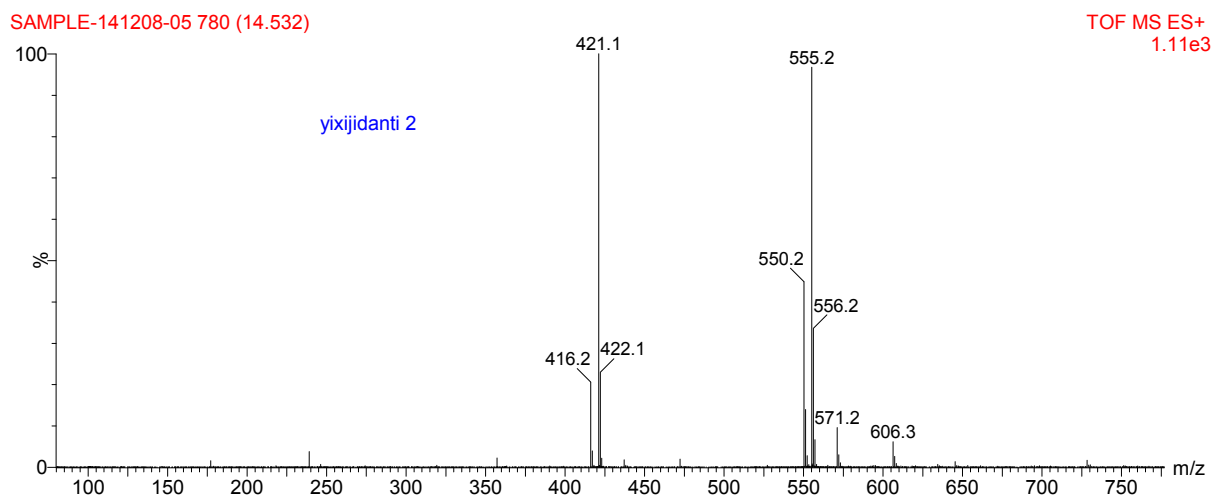
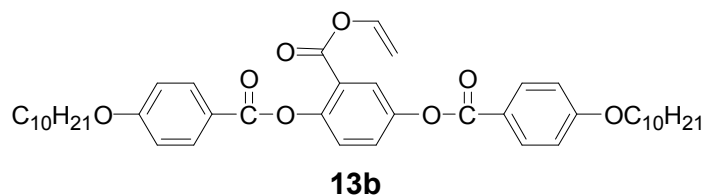


Fig. S8 Mass spectrum of Compound **13a**.



Monomer VB10B (13b). **13b** was prepared following the above described procedure. ^1H NMR (500 MHz, CDCl_3): δ 8.16 (dd, $J = 12.6, 8.9$ Hz, 4H), 7.97 (d, $J = 2.8$ Hz, 1H), 7.51 (d, $J = 8.6$ Hz, 1H), 7.40 – 7.28 (m, 2H), 6.98 (d, $J = 7.3$ Hz, 4H), 4.68 (d, $J = 15.0$ Hz, 1H), 4.53 (d, $J = 4.8$ Hz, 1H), 4.04 (d, $J = 3.4$ Hz, 4H), 1.82 (s, 4H), 1.53 – 1.19 (m, 32H), 0.88 (t, $J = 6.7$ Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3): δ 163.82, 163.69, 160.89, 148.66, 148.40, 140.99, 132.53, 132.40, 127.93, 125.30, 125.27, 114.43, 114.37, 98.66, 68.40, 68.35, 31.89, 29.69, 29.54, 29.35, 29.30, 29.09, 25.98, 22.67, 14.09. Phase sequence and transition temperatures: Cr – 90 °C – N – 115 °C – Iso (on heating, determined by POM), Iso – 113 °C – N – 39 °C – Cr (on cooling).

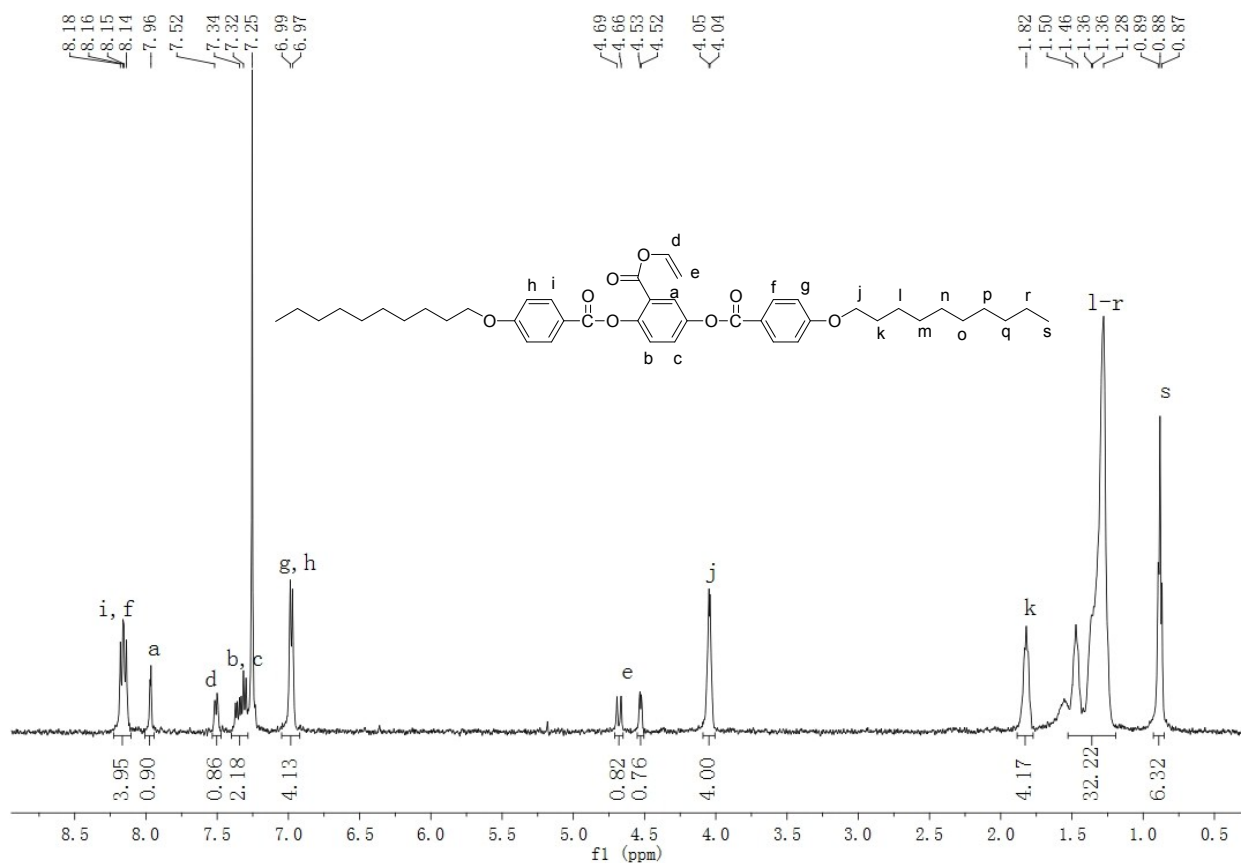


Fig. S9 ^1H NMR spectrum of Compound **13b**

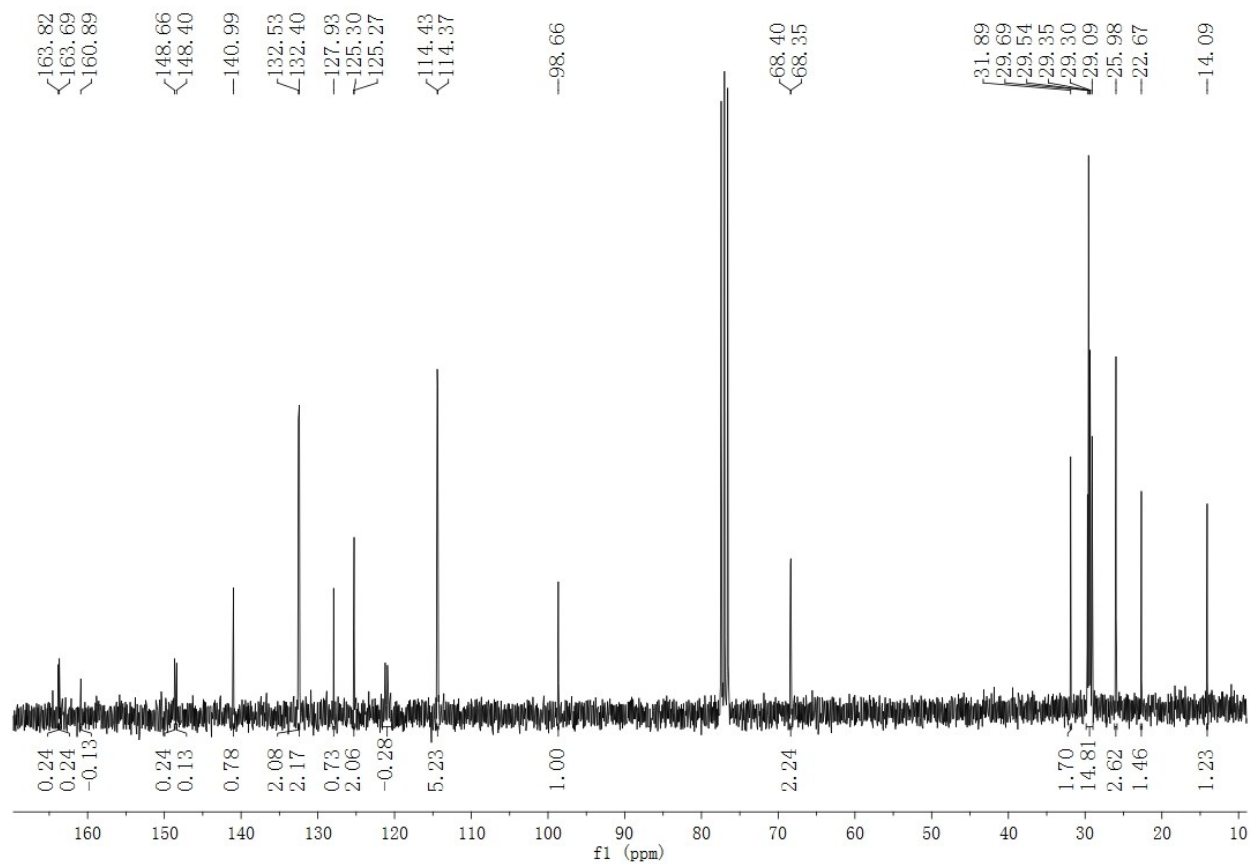
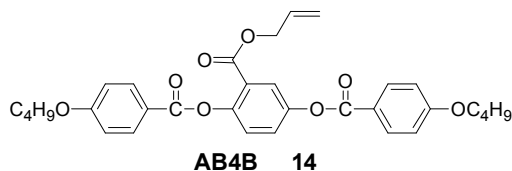


Fig. S10 ^{13}C NMR spectrum of Compound **13b**



Monomer **AB4B** (**14**). In a 100 mL round-bottom flask, TBAF (1M in THF, 1.2 equiv) and allyl bromide (0.28 g, 2.33 mmol) were added into a solution of intermediate **12a** (1.00 g, 1.98 mmol) in dry THF (50ml). The reaction was stirred at room temperature for 2 h. The mixture was filtered and washed with ethyl acetate, and then concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (n-hexane : EtOAc = 10 : 1) to give the desired product (0.87 g, Yield: 80.6%) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 8.25 (d, J = 7.1 Hz, 4H), 8.01 (s, 1H), 7.56 (d, J = 8.6 Hz, 2H), 7.08 (d, J = 7.7 Hz, 4H), 5.87 (s, 1H), 5.33 (d, J = 17.5 Hz, 1H), 5.22 (d, J = 10.4 Hz, 1H), 4.75 (d, J = 5.2 Hz, 2H), 4.17 (d, J = 6.2 Hz, 4H), 1.91 (d, J = 6.9 Hz, 4H), 1.61 (s, 4H), 1.10 (t, J = 7.1 Hz, 6H). Anal. Calcd for C₃₂H₃₄O₈: C, 70.31; H, 6.27. Found: C, 70.02; H, 6.18. Phase sequence and transition temperatures: Cr – 102 °C – N – 109 °C – Iso (on heating, determined by POM), Iso – 105 °C – N – 78 °C – Cr (on cooling).

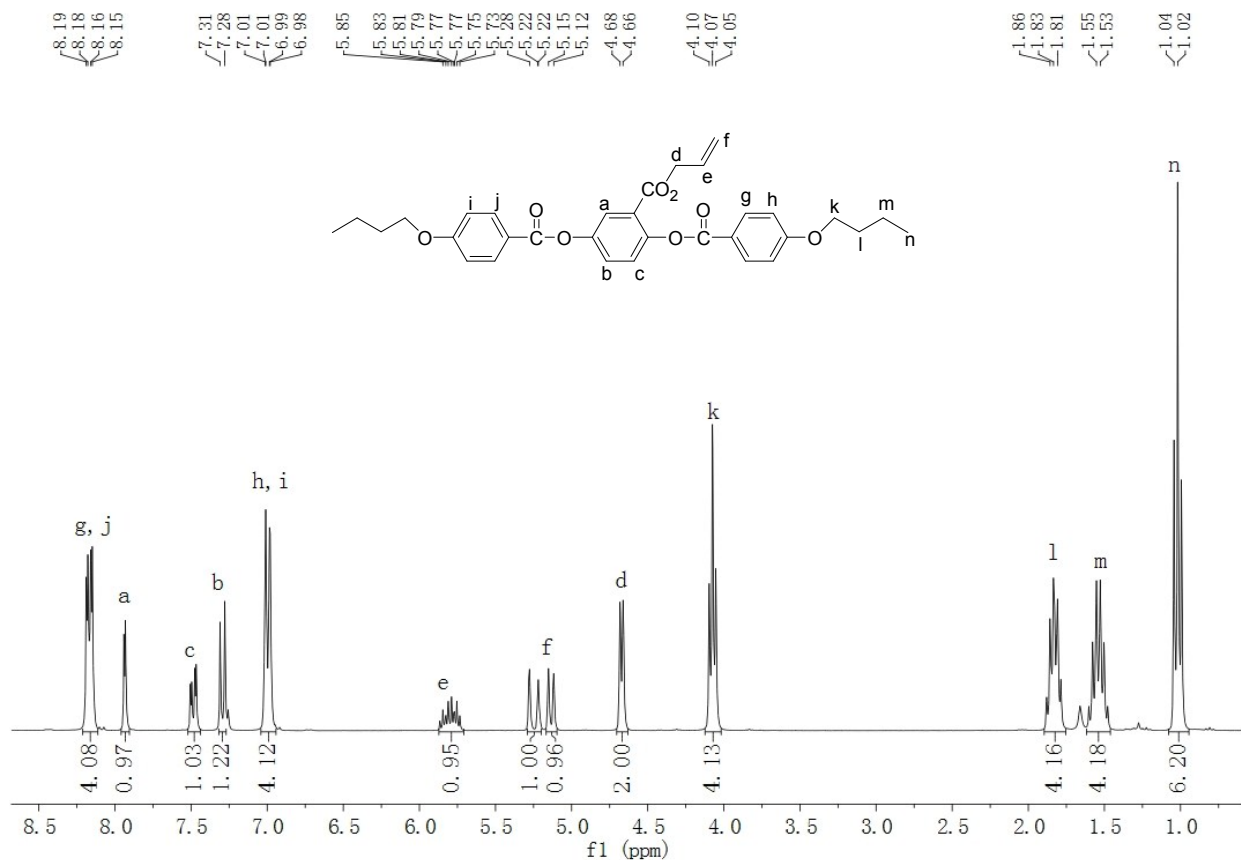


Fig. S11 ¹H NMR spectrum of Compound **14**.

PVB4B: ^1H NMR (500 MHz, CDCl_3): δ 7.89 (m), 6.90 (m), 4.98 (m), 4.03 (m), 1.64 (m), 0.95 (m).

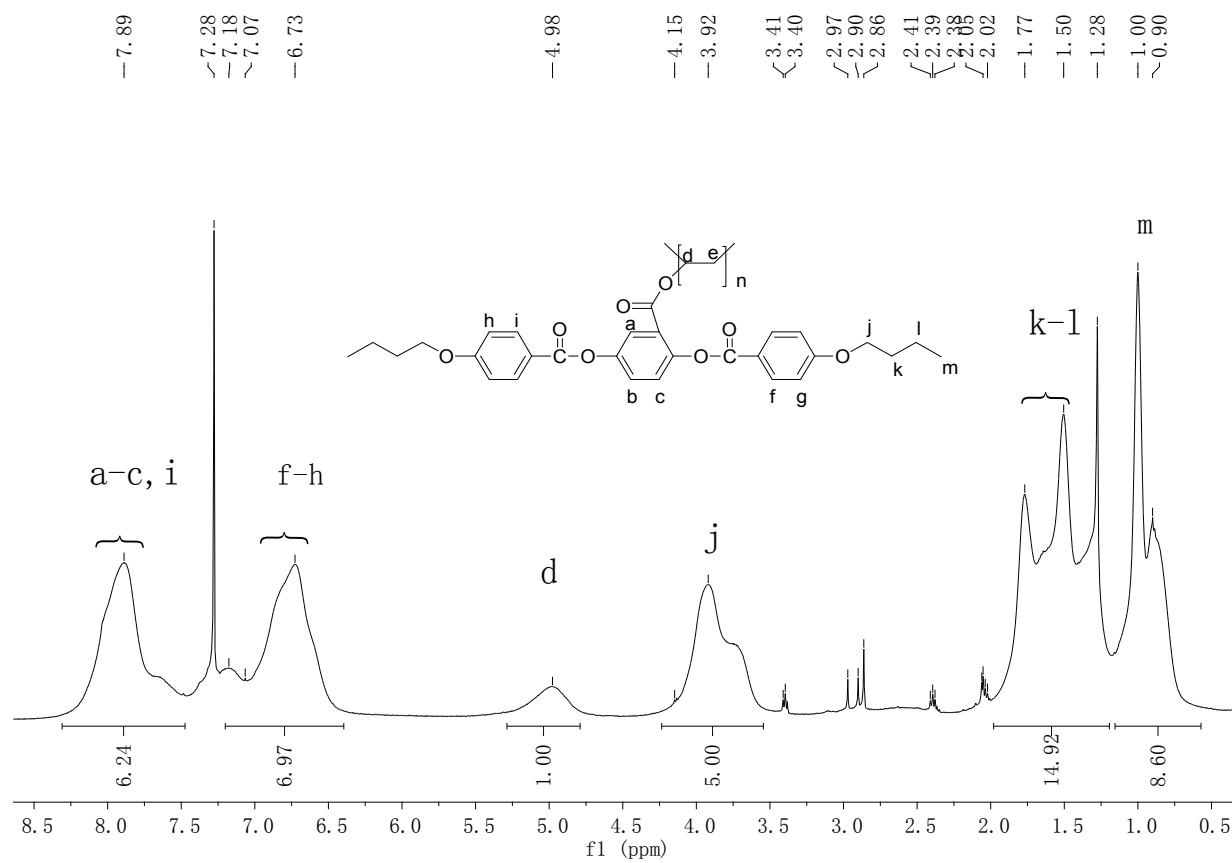


Fig. S12 ^1H NMR spectrum of **PVB4B**.

PVB10B: ^1H NMR (300 MHz, CDCl_3): δ 8.08 (m), 6.91 (m), 5.11 (m), 3.99 (m), 1.90 – 1.13 (m), 0.89 (m).

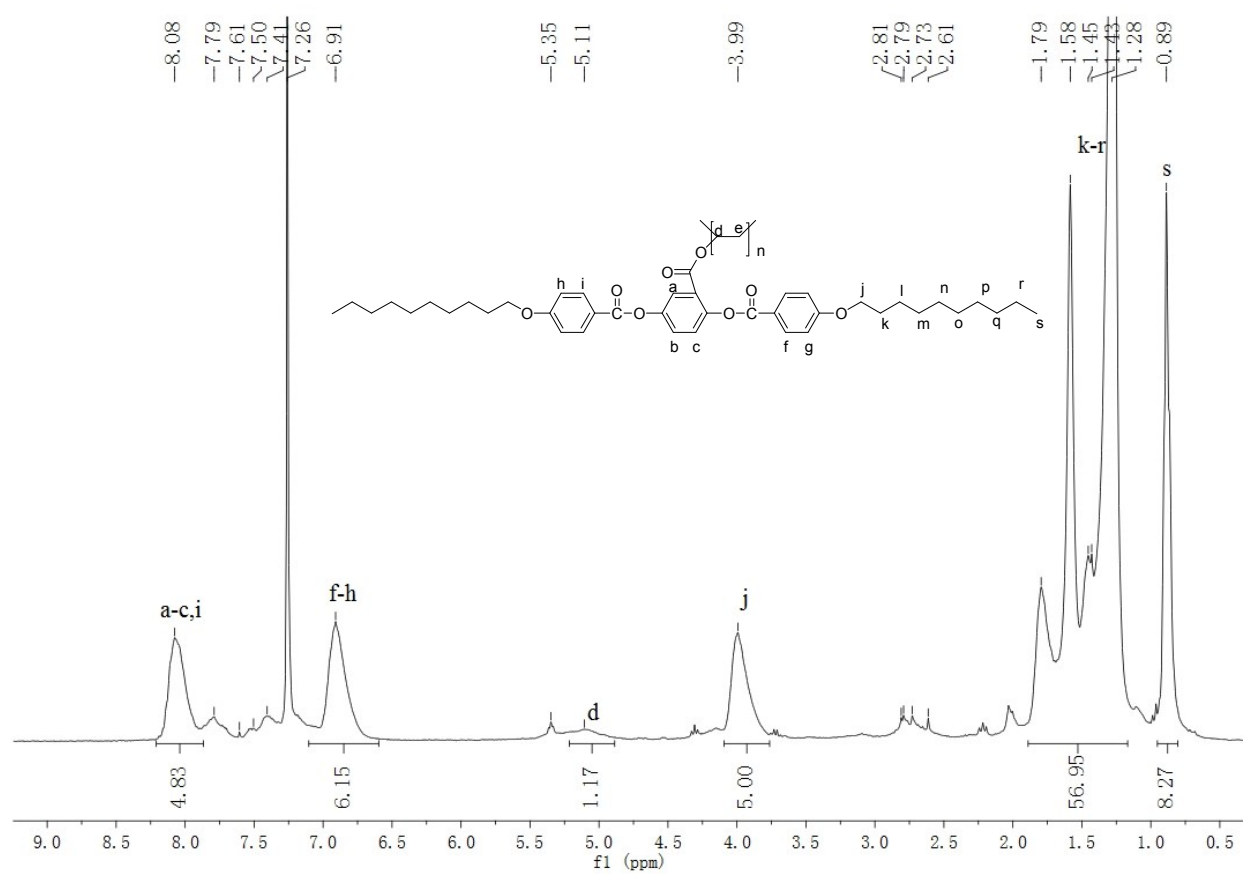
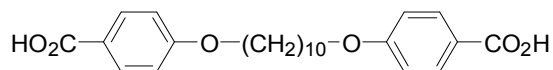


Fig. S13 ^1H NMR spectrum of PVB10B.

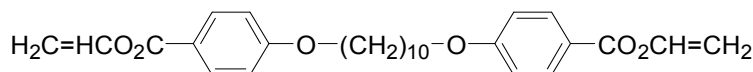


17

DEAD (2.44 mL, 15.1 mmol) was added *via* syringe with stirring and under nitrogen to a solution of a mixture of 4-hydroxy-benzoic acid methyl ester (2.00 g, 13.1 mmol), decane-1,10-diol (1.15 g, 6.57 mmol) and triphenylphosphine (3.61 g, 13.8 mmol) in 100 mL dry THF. The reaction mixture was allowed to stir for 12 h at 25 °C, and was then concentrated by rotary evaporation to give an orange oil which was directly subjected to purification by flash chromatography (n-hexane : EtOAc = 30 : 1) to give a white solid (2.21 g). This solid intermediate was dissolved in 60 mL methanol/H₂O (10/1), lithium hydroxide monohydrate (2.37 g, 50.0 mmol) was then added to the solution. The reaction mixture was refluxed overnight, then was acidified with conc. HCl to pH=2. Water (200 mL) was added, and the solution was cooled. The resulting precipitate was filtered out, washed with water, air-dried. Flash chromatography (n-hexane : EtOAc = 3 : 1) to provided **17** (1.65 g, Yield: 61% in 2 steps) as a white solid. ¹H NMR (500 MHz, DMSO): δ 7.87 (d, *J* = 8.8 Hz, 4H), 6.99 (d, *J* = 8.8 Hz, 4H), 4.02 (t, *J* = 6.4 Hz, 4H), 1.70 (dd, *J* = 13.8, 6.6 Hz, 4H), 1.51 – 1.17 (m, 3H).



Fig. S14 ¹H NMR spectrum of Compound **17**.



18

In a 100 mL round-bottom flask, palladium chloride (3.1 mg, 0.026 mmol), lithium acetate (172.6 mg, 2.62 mmol) and cupric bromide (14.6 mg, 0.065 mmol) were added under nitrogen atmosphere, to a solution of vinyl acetate (4.50 g, 52.27 mmol) in dry THF (50 mL) at room temperature. The reaction mixture was heated to 70 °C and then a solution of intermediate **17** (1.00 g, 2.64 mmol) in dry THF (20 mL) was slowly added *via* syringe. After stirring at 70 °C for 24 h, the mixture was filtered and washed with ethyl acetate, and then concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (n-hexane : EtOAc = 10 : 1) to give the desired product (0.85 g, Yield: 75.5%) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 8.03 (t, *J* = 11.0 Hz, 2H), 7.50 (dd, *J* = 13.9, 6.2 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 2H), 5.03 (d, *J* = 14.0 Hz, 1H), 4.66 (d, *J* = 6.2 Hz, 1H), 4.02 (t, *J* = 6.4 Hz, 2H), 1.85 – 1.75 (m, 2H), 1.46 (d, *J* = 7.1 Hz, 2H), 1.34 (s, 4H). ¹³C NMR (75 MHz, CDCl₃): δ 163.04, 162.91, 141.04, 131.60, 120.46, 113.77, 97.09, 67.77, 29.19, 28.93, 28.80, 28.57, 25.46 MS ES+(*m/e*): 489 (M+Na⁺, 100%).

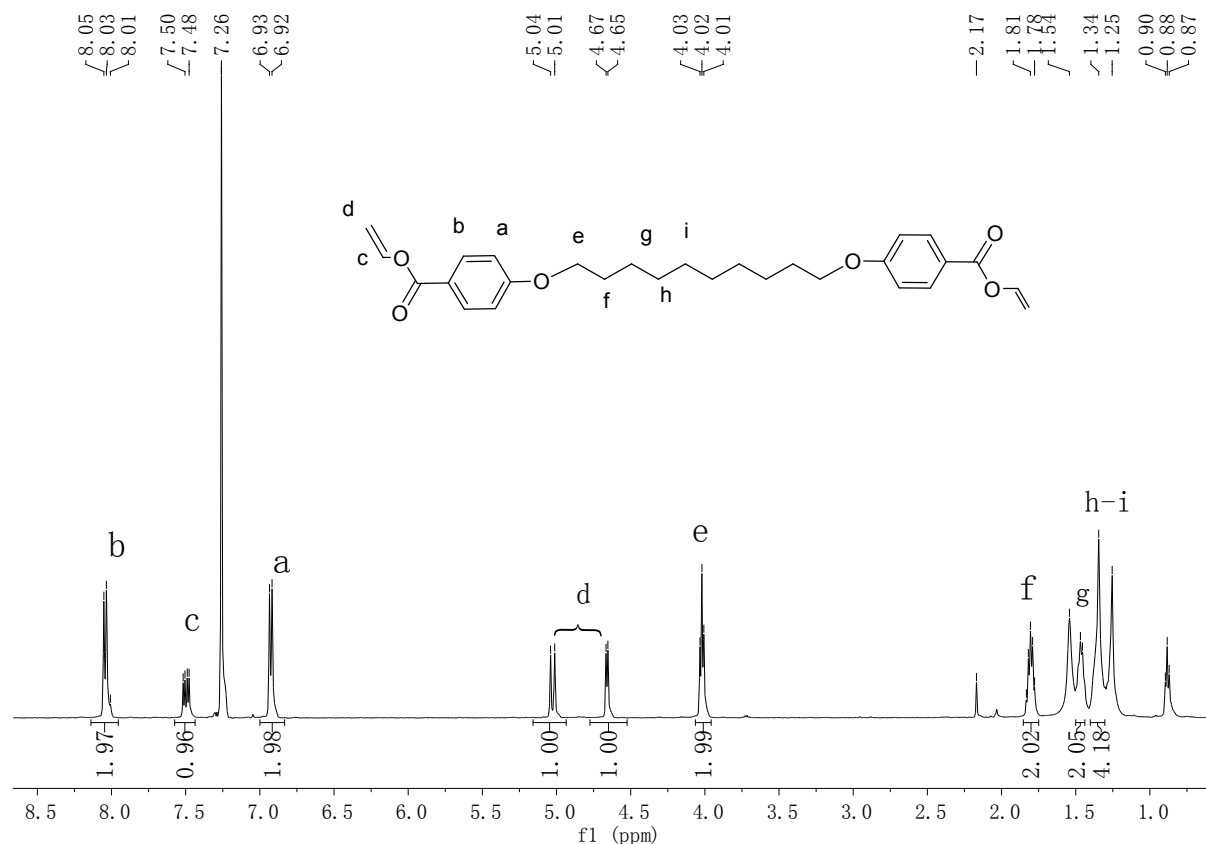


Fig. S15 ¹H NMR spectrum of Compound **18**.

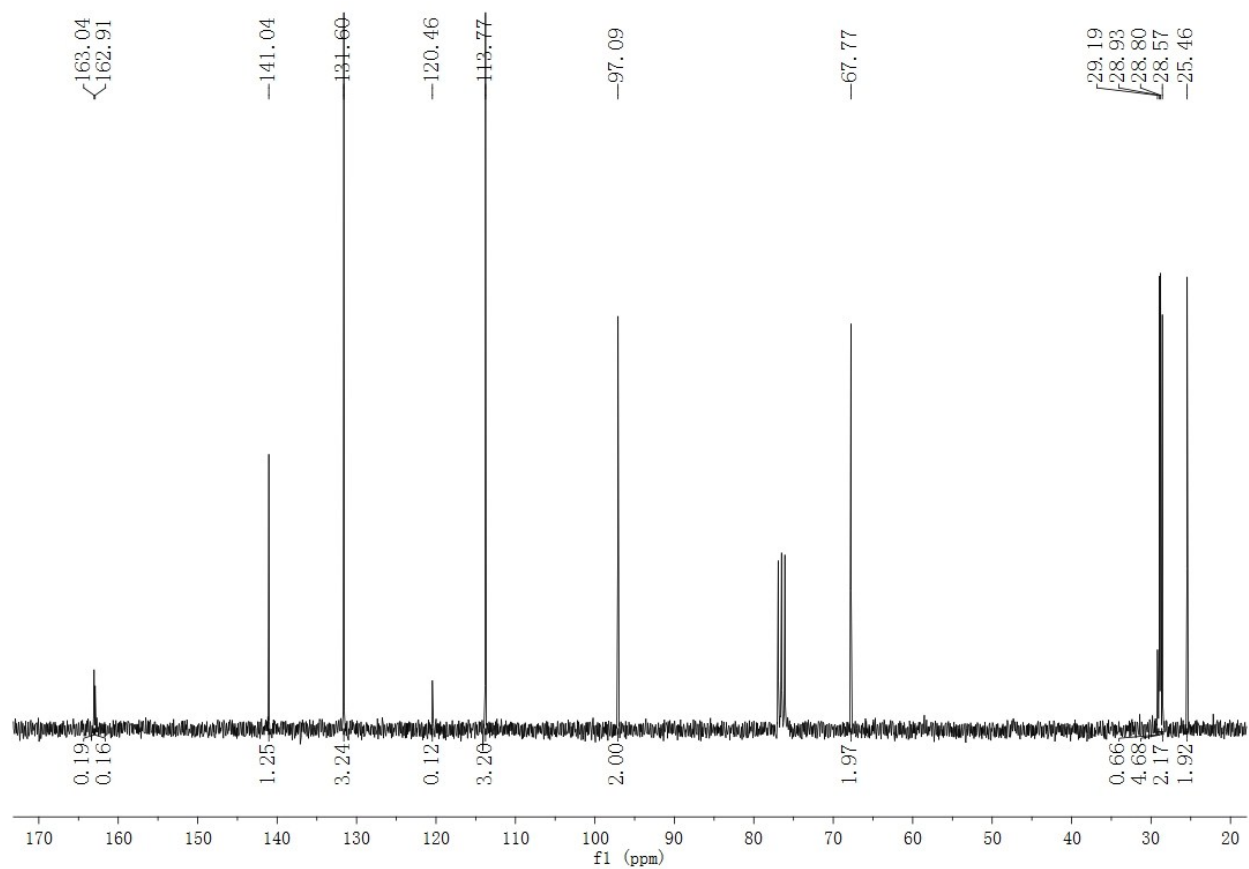


Fig. S16 ^{13}C NMR spectrum of Compound **18**.

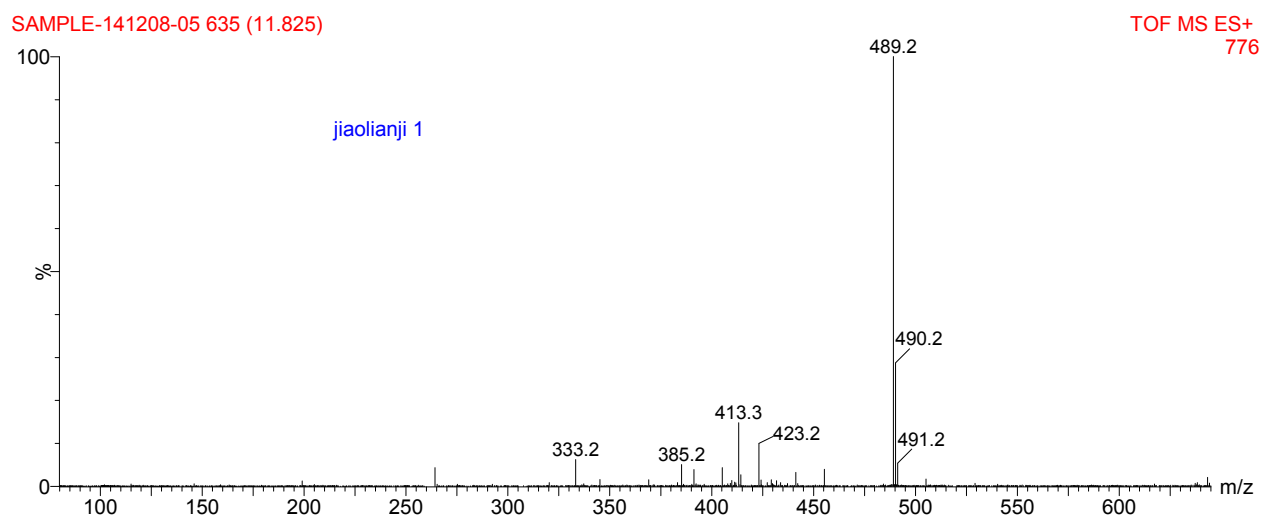


Fig. S17 Mass spectrum of Compound **18**.

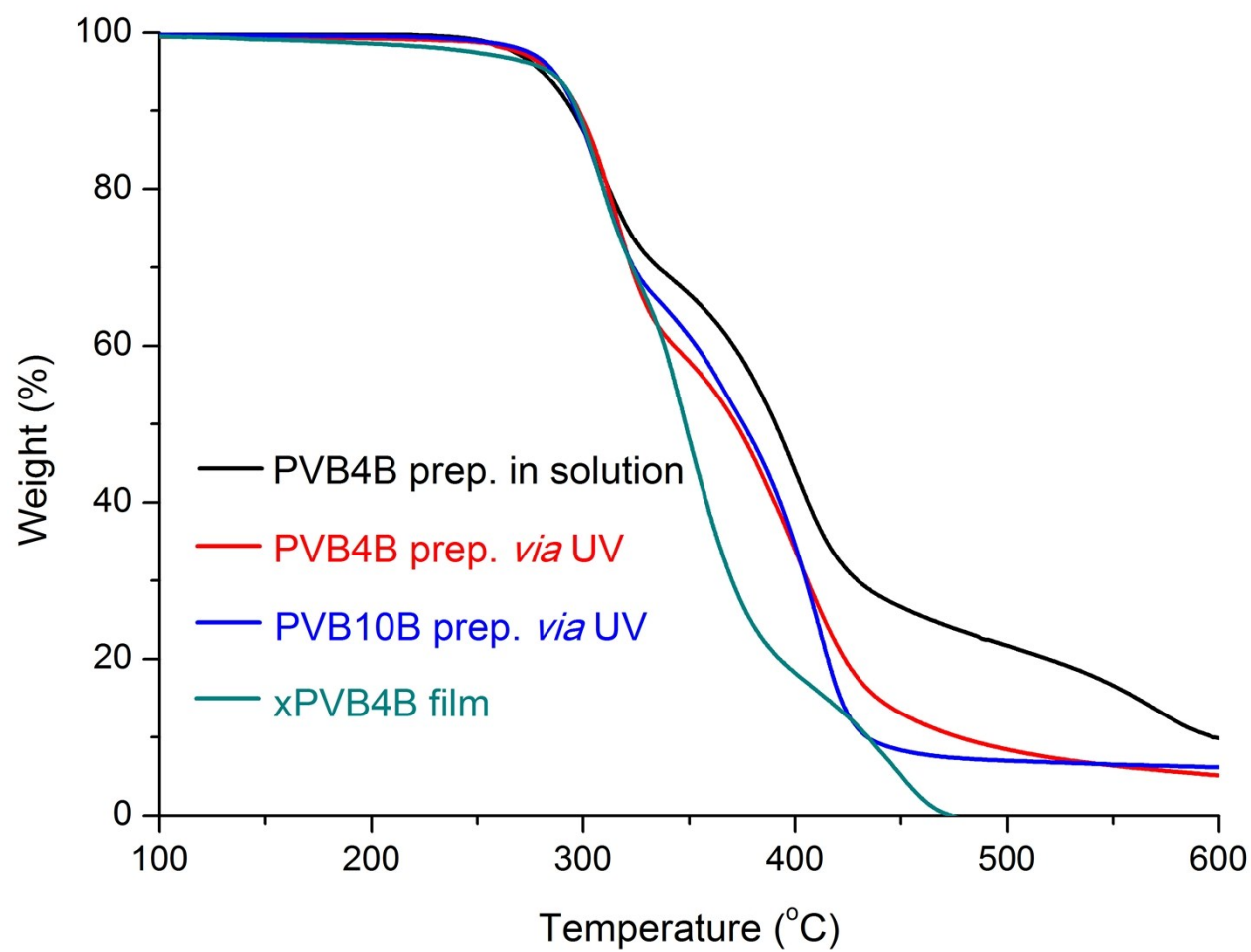


Fig. S18 Thermogravimetric analysis of **PVB4B** and **PVB10B** polymer samples.

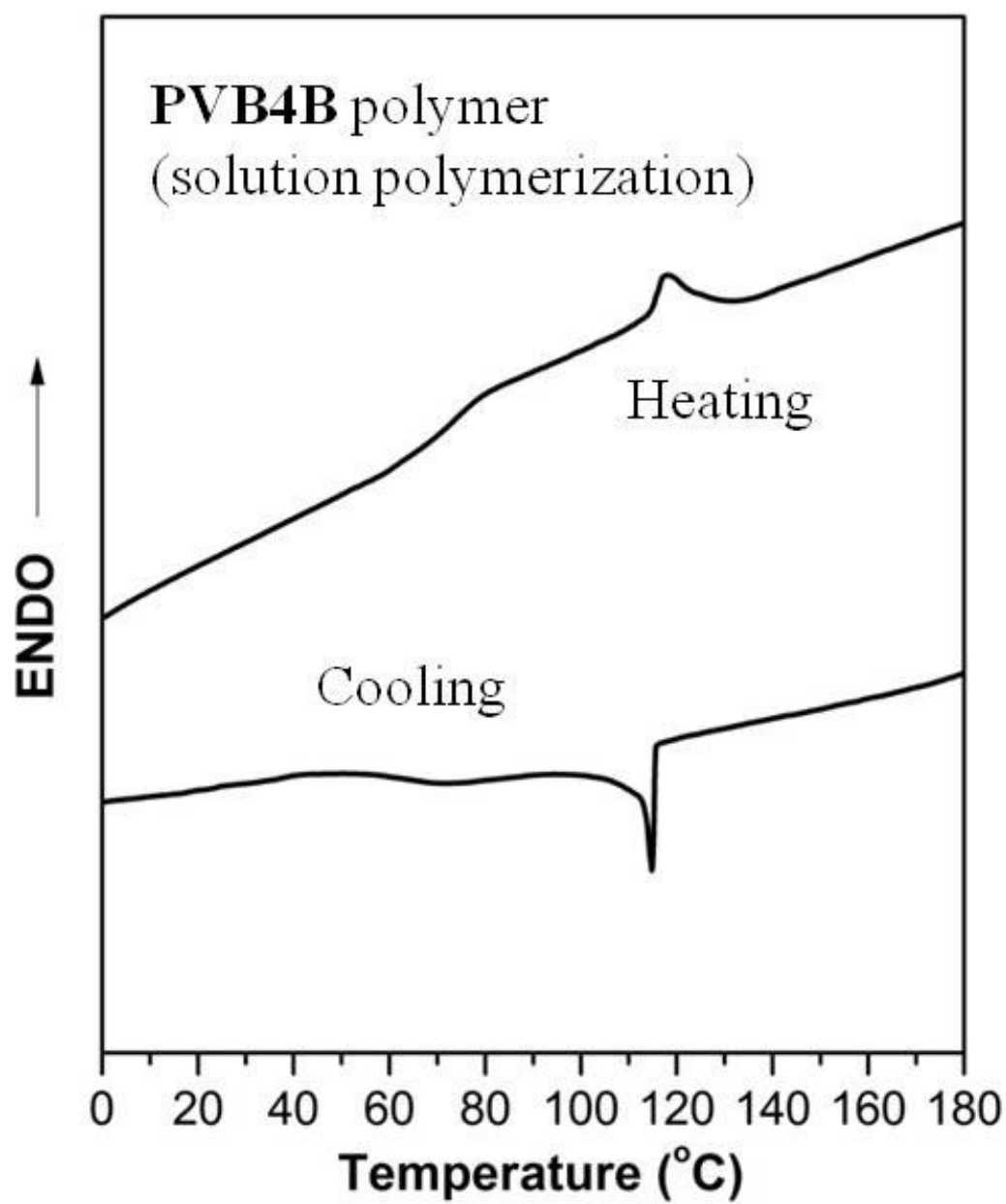


Fig. S19 DSC curves of polymer **PVB4B** prepared by solution polymerization.

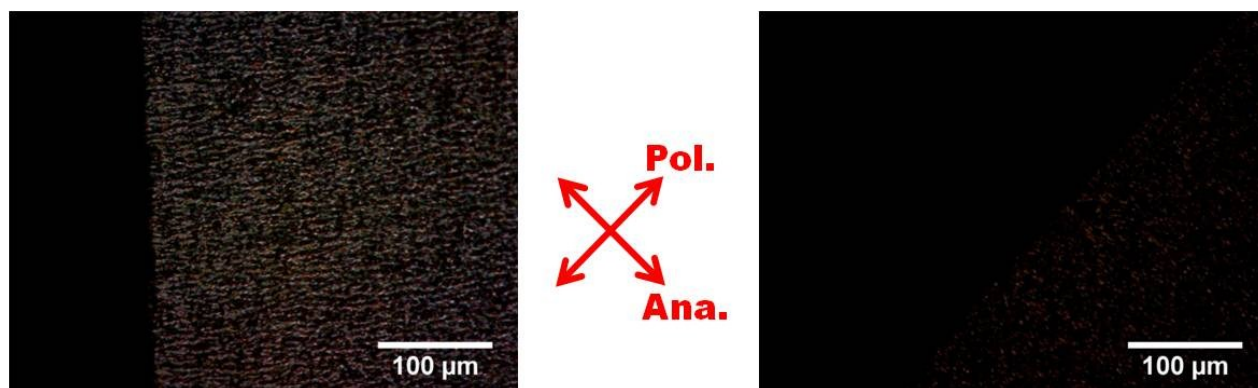


Fig. S20 Polarized optical microscope images of a homogeneous-aligned **xPVB10B** film.

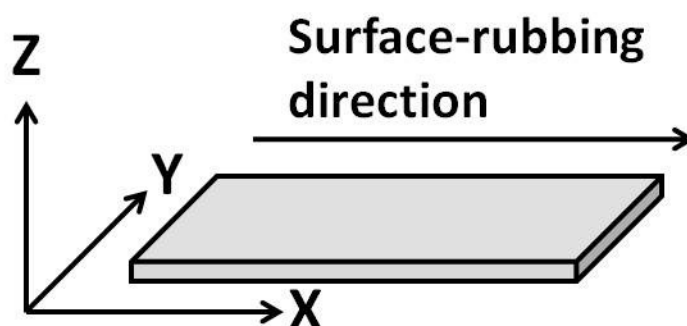
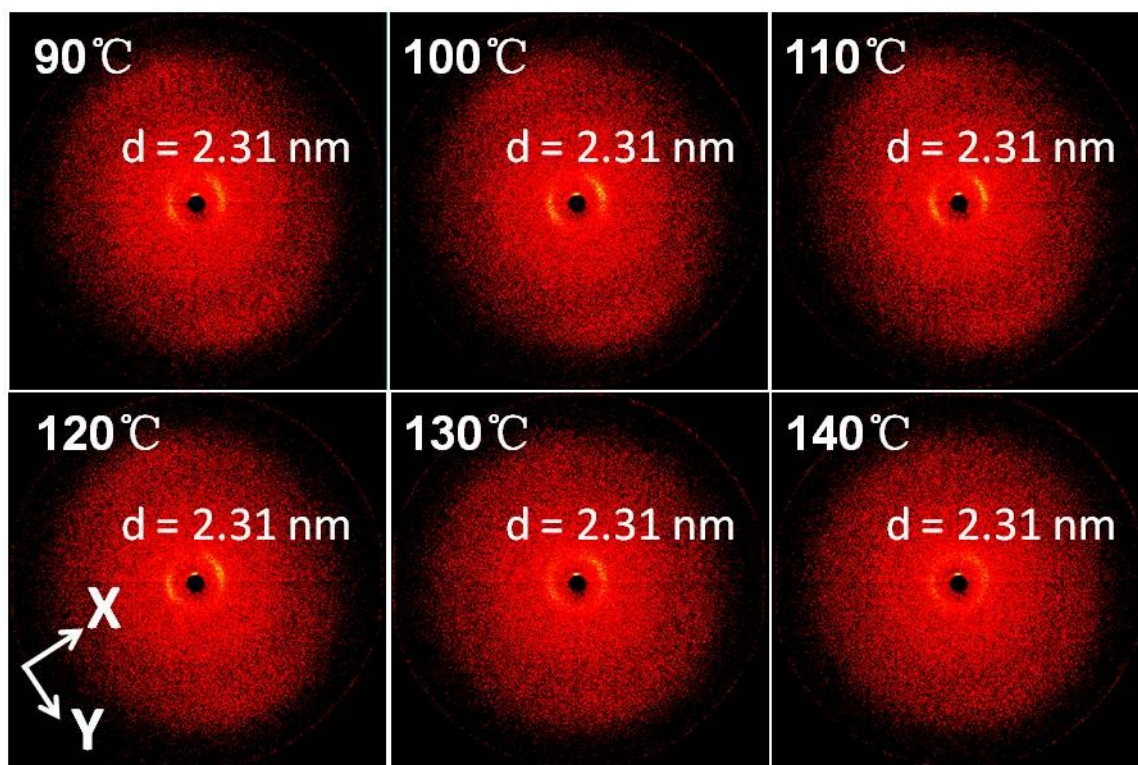


Fig. S21 2D WAXD pattern of a homogeneous-aligned **xPVB4B** film recorded at 90, 100, 110, 120, 130, and 140 °C during heating process, with the X-ray incident beam parallel to the film normal direction.

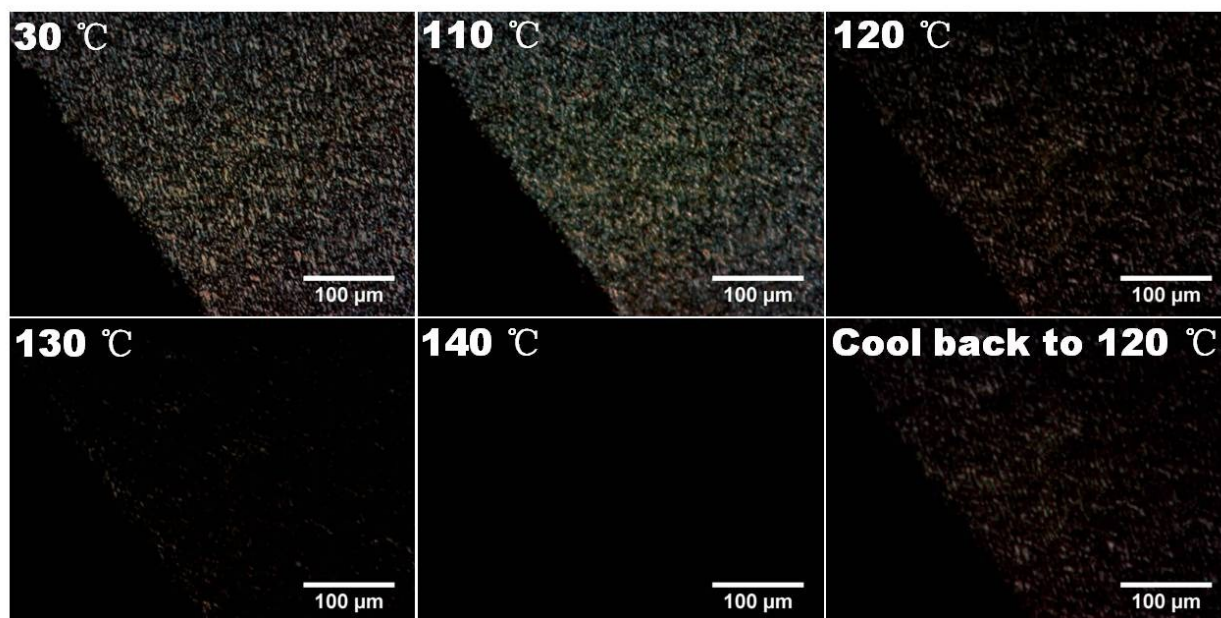


Fig. S22 Polarized optical microscope images of a homogeneous-aligned **xPVB10B** film stripe recorded at 30, 110, 120, 130,140 °C during heating process, and 120 °C during cooling process.

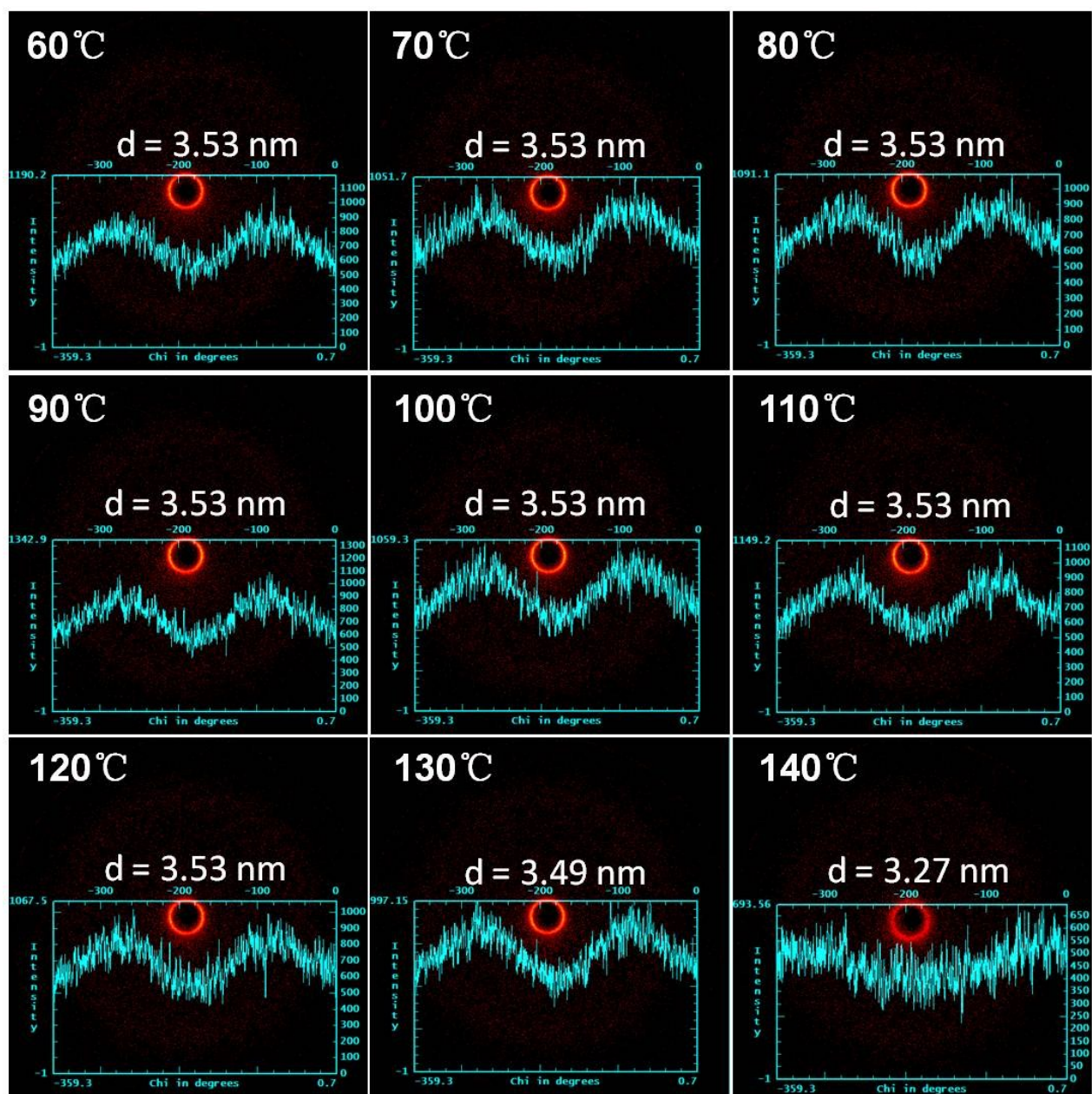


Fig. S23 2D WAXD pattern (azimuthal scan in the low-angle region) of a homogeneous-aligned xPVB10B film recorded at 60, 70, 80, 90, 100, 110, 120, 130, and 140 °C during heating process, with the X-ray incident beam parallel to the film normal direction.