

Supplementary Information

Synthesis and mesomorphic properties of side-chain polynorbornenes containing mono-, di- and tri-calamitic mesogenic pendant groups

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Materials

4'-Hydroxy-4-biphenylcarboxylic acid (99%), 1-Bromododecane (97%), 1-Bromohexadecane (97%), lithium aluminum hydride (95%), potassium iodide (99%), methyl 4-hydroxybenzoate (99%), 3,4-dihydroxy-benzoic acid methyl ester (99%), methyl 3,5-dihydroxybenzoate (97%), methyl 3,4,5-trihydroxybenzoate, 1-[3-(dimethyl amino) propyl]-3-ethylcarbodiimide hydrochloride (EDC·HCl, 99%), 4-(dimethylamino)pyridine (DMAP, 99%), and Grubbs catalyst (third generation) were purchased from Sigma Aldrich. Dichloromethane (CH₂Cl₂) (AR, Sinopharm) and trichloromethane (CHCl₃) (AR, Sinopharm) were distilled by refluxing over CaH₂ prior to use. Tetrahydrofuran (THF) (AR, Sinopharm) was heated under reflux over sodium for at least 8 h and distilled before use. N-(hydroxyethyl)-*cis*-5-norbornene-*exo*-2,3-dicarboximide was prepared according to literature procedure. All other reagents and solvents were obtained from commercial sources and used without further purification.

Measurements

NMR. The ¹H and ¹³C NMR spectra were recorded on an INOVA 400 MHz NMR spectrometer at ambient temperature with CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard.

GPC. The number-average molecular weight (M_n , GPC) and polydispersity (PDI) of the polymers were measured on an instrument comprised of a Waters 1515 isocratic HPLC pump, a Waters 717 plus autosampler, a Waters 2414 refractive-index

detector with three 300 mm (length) \times 7.5 mm (inner diameter) columns with a particle size of 5 μm (PL gel mixed-C, Polymer Laboratories). The measurements were performed using THF as the eluent (2.5 mg/mL) with a flow rate of 0.60 mL/min at 35 $^{\circ}\text{C}$. The calibration was carried out with a series of polystyrene standards.

DSC. Thermal behavior and phase transition temperatures of all the polymers were observed and obtained using a TA-Q100 DSC instrument. The temperature and heat flow were calibrated using standard materials (indium and zinc) at a cooling and heating rate of 10 $^{\circ}\text{C}/\text{min}$. Samples with a typical mass of about 5 mg were encapsulated in sealed aluminum pans. The DSC heating and cooling curves were recorded at a rate of 10 $^{\circ}\text{C}/\text{min}$.

POM. LC textures and birefringence of samples were examined under Leica DM-LM-P POM equipped with a Linkam THMS 600 hot stage. Samples were made by sandwiching the dried polymer powder between a glass slide and a cover glass. Generally, several heating and cooling cycles with controlled rates were carried out to measure the phase transition by detecting the birefringence and morphology change of the sample under POM. Typical LC textures could be formed when heating the sample to its isotropic temperature and then cooling to LC state at a rate of 0.5~1 $^{\circ}\text{C}/\text{min}$. If necessary, thermal annealing at certain LC temperature for several hours was also considered to make the texture more visible.

SAXS. To identify the phase structures, SAXS experiments were performed using a high-flux X-ray instrument (SAXSess mc², Anton Paar) equipped with Kratky block-collimation system and a GE ID3003 sealed-tube X-ray generator (Cu K α). The wavelength is 0.1542 nm. Samples were wrapped into aluminum foils and sandwiched in a steel sample holder. The X-ray scattering patterns were recorded in vacuum on an imaging-plate (IP) which extended to high-angle range (the q range covered from 0.06 to 29 nm^{-1} , $q = 4\pi(\sin\theta)/\lambda$, where the λ is the wavelength of 0.1542 nm and 2θ is the scattering angle). The diffraction peak positions were calibrated with silver behenate. A temperature control unit (Anton Paar TCS300) in conjunction with the SAXSess mc² was utilized to study the structure evolution as a function of temperature.

Synchrotron SAXS. 2D SAXS measurements were performed to study the phase behaviors of mechanically sheared samples at Shanghai Synchrotron Radiation Facility (SSRF, beamline BL16B1 using a three-slit system)²⁴. The energy of the X-ray radiation was 10 keV, resulting in a wavelength of 0.124 nm. The sample-to-detector distance was 1.97 m for SAXS (calibrated by beef tendon standard). Individual diffraction patterns were collected within 2-100 s with a Mar 165 area detector at a resolution of 2048 \times 2048 pixels and a pixel size of 80 μm \times 80 μm for quantitative analysis. The obtained 2D SAXS diffraction patterns were analyzed using Fit2D software. All samples were mounted on a Linkam hot stage.

2D WAXD. Structure orientation of sheared samples was investigated using a BRUKER AXS D8 Discover diffractometer with a 40 kV FL tube as the X-ray source

(Cu K α) and the VANTEC 500 detector. The oriented samples were prepared by mechanically shearing from the LC phase when applicable. The point-focused X-ray beam was aligned either perpendicular or parallel to the mechanical shearing direction. For the 2D WAXD experiments, the background scattering was recorded and subtracted from the sample patterns.

Synthesis of Precursors and Monomers. The synthetic procedures of all the monomers (NB-4-CmBA, NB-3,4-CmBA, NB-3,5-CmBA, NB-3,4,5-CmBA, m = 12, 16) are shown in Scheme 1. The experimental details are described as follows which is used NB-3,4,5-C12BA as an example.

Synthesis of ethyl 4'-hydroxy-biphenyl-4-carboxylate. To a solution of 4'-hydroxy-4-biphenylcarboxylic acid (15 g, 70.1 mmol) in 200 mL EtOH, 10 mL H₂SO₄ was added slowly dropwise at room temperature. The solution was refluxed for 8 h, and then the mixture was poured into excessive water to neutralize it to pH 8. The precipitation was filtered and washed several times with water. The residue was purified by recrystallization using EtOH to give 14 g (83%) purified product. ¹H NMR (CDCl₃, TMS), δ : 8.06–8.12 (d, 2H); 7.58–7.64 (d, 2H); 7.49–7.56 (d, 2H); 6.91–6.97 (d, 2H); 5.15–5.20 (s, 1H); 4.36–4.46 (q, 2H); 1.38–1.45 (t, 3H)

Synthesis of ethyl 4'-dodecyloxy-biphenyl-4-carboxylate. A mixture of ethyl 4'-hydroxy-biphenyl-4-carboxylate (5.00 g, 20.6 mmol), 1-bromodecane (5.64 g, 22.7 mmol) and K₂CO₃ (19.90 g, 0.14 mol) in 200 mL of acetone was refluxed for 18 h. The reaction mixture was poured into water after cooling to room temperature and the precipitation filtered which was washed several times with water. After recrystallization from EtOH, 7.29 g (86%) of purified product was obtained. ¹H NMR (CDCl₃, TMS), δ : 8.05–8.11 (d, 2H); 7.59–7.66 (d, 2H); 7.53–7.59 (d, 2H); 6.95–7.02 (d, 2H); 4.36–4.44 (q, 2H); 3.97–4.04 (t, 2H); 1.76–1.86 (m, 2H); 1.20–1.54 (m, 21H); 0.85–0.91 (t, 3H)

Synthesis of 4-chloromethyl-4'-dodecyloxy-biphenyl. Compound ethyl 4'-dodecyloxy-biphenyl-4-carboxylate (5 g, 12.2 mmol) dissolved in 100 mL of dry THF was added dropwise into a stirred suspension of LiAlH₄ (0.73 g, 19.3 mmol) in 30 mL of dry THF. The mixture was stirred at room temperature for 1.5 h. The reaction mixture was quenched with 0.7 mL of deionized water, 0.7 mL of 5% NaOH (aq), and 2.1 mL of deionized water. The as-formed solids were filtered and the filtrate was condensed to yield a white solid (4.10 g, 91%) followed by drying under vacuum at 40 °C. The crude product was then used in the next step without further purification. 2 mL of SOCl₂ was added dropwise to a solution of the product above in a mixed solvent system of CH₂Cl₂ (50 mL) and THF (50 mL), containing a catalytic amount of N,N-dimethylformamide (DMF). After stirring for 1h, the solvent was removed using a rotary evaporator and the residue was purified by column chromatography (silica gel, 2:1 hexane/CH₂Cl₂) to afford a white solid (2.77 g, 64.3%). ¹H NMR (CDCl₃, TMS), δ : 7.48–7.58 (q, 4H); 7.41–7.46 (d, 2H); 6.94–7.00 (d, 2H); 4.60–4.65 (s, 2H); 3.96–4.03 (t, 2H); 1.75–1.85 (m, 2H); 1.19–1.53 (m, 18H); 0.85–0.92 (t, 3H)

Synthesis of methyl 3,4,5-tris(4'-dodecyloxy-biphenyl-4-yl)methoxybenzoate. A

mixture of 4-chloromethyl-4'-dodecyloxy-1,1'-biphenyl (2.32 g, 6.3 mmol), methyl 3,4,5-trihydroxybenzoate (0.37 g, 2 mmol), K₂CO₃ (6.1 g, 44.1 mmol) and a catalyst amount of KI in 200 mL of DMF was heated to 80 °C under an atmosphere. The mixture was stirred under reflux for 24 h and the reaction was found to be complete by thin-layer chromatography (TLC). The reaction mixture was poured into water after cooling to room temperature and the precipitation filtered which was washed several times with water. After purification by column chromatography (silica gel, 1:1 hexane/CH₂Cl₂), 1.31 g (60.6%) product of a white solid was obtained. ¹H NMR (CDCl₃, TMS), δ: 7.40–7.58 (m, 20H), 6.89–6.99 (q, 6H), 5.15–5.21 (s, 6H), 3.95–4.03 (q, 6H), 3.88–3.92 (s, 3H), 1.76–1.86 (m, 6H), 1.21–1.52 (m, 54H), 0.85–0.92 (t, 9H)

Synthesis of N-[ethyl 3,4,5-tris(4'-dodecyloxy-biphenyl-4-yl)methoxybenzoate]-cis-5-norbornene-exo-2,3-dicarboximide (NB-3,4,5-C12BA). A mixture of methyl 3,4,5-tris((4'-dodecyloxy)-[1,1'-biphenyl]-4-yl)methoxy benzoate (1.2 g, 0.97 mmol), KOH (0.11 g, 1.94 mmol) which is dissolved by 5 mL water, and 150 mL THF was refluxed for 15 h. Thin-layer chromatography analysis indicated the reaction was completed. After the reaction mixture was concentrated to 50 mL, 500 mL water was poured into the mixture. The solution on was acidified with dilute HCl up to pH = 2 and stirred for 1 h. The precipitation was filtered and washed several times with water and cold EtOH. The crude product was dried under vacuum at 40 °C for 24 h. The crude product (1.02 g, 93%) was then used in the next step without further purification. N-hydroxyethyl-cis-5-norbornene-exo-2,3-dicarboximide (0.17 g, 0.82 mmol), the product above (1 g, 0.82 mmol), 4-dimethylaminopyridine (10 mg, 0.082 mmol) were stirred under argon atmosphere in dry dichloromethane (120 mL) at ambient temperature. At last, 1-[3-(dimethyl amino) propyl]-3-ethylcarbodiimide hydrochloride (EDC·HCl) (0.19 g, 0.98 mmol) was added to the mixture and the reaction was allowed to proceed for 24 h at room temperature. After that, the reaction solution was concentrated in vacuum. The resulting solid was purified by column chromatography (silica gel, 4:1 hexane/ EtOAc), which yielded as a white solid. (0.60 g, 52%). ¹H NMR (CDCl₃, TMS), δ: 7.37–7.59 (m, 20H); 6.88–7.00 (d, 6H); 6.18–6.25 (s, 2H); 5.14–5.23 (d, 6H); 4.38–4.44 (t, 2H); 3.89–4.04 (m, 8H); 3.19–3.24 (s, 2H); 2.66–2.70 (s, 2H); 1.76–1.86 (m, 6H); 1.19–1.53 (m, 56H); 0.83–0.94 (t, 9H). ¹³C NMR (CDCl₃, TMS), δ: 177.9, 166.0, 159.0, 158.9, 152.8, 142.7, 140.7, 140.5, 137.9, 136.0, 135.1, 133.2, 133.1, 129.2, 128.2, 126.9, 126.5, 124.8, 114.9, 109.2, 75.1, 71.1, 68.3, 62.0, 48.0, 45.4, 42.8, 37.7, 32.1, 29.9, 29.8, 29.6, 29.5, 26.2, 22.9, 14.3. MS (HR-ESI): [M+H]⁺/z calcd for C₉₃H₁₁₉NO₁₀, 1410.9; found, 1410.9

NB-4-C12BA: ¹H NMR (CDCl₃, TMS), δ: 7.90–7.96 (d, 2H); 7.55–7.60 (d, 2H); 7.44–7.55 (d, 4H); 6.94–7.03 (d, 4H); 6.25–6.29 (s, 2H); 5.11–5.16 (s, 2H); 4.39–4.45 (t, 2H); 4.97–4.03 (t, 2H); 3.88–3.93 (t, 2H); 3.23–3.28 (s, 2H); 2.68–2.74 (s, 2H); 1.76–1.85 (m, 2H); 1.20–1.53 (m, 20H); 0.85–0.92 (t, 3H). ¹³C NMR (CDCl₃, TMS), δ: 177.9, 166.0, 162.8, 159.0, 141.1, 137.9, 134.5, 133.0, 131.8, 128.2, 128.1, 127.0, 122.4, 114.9, 114.7, 70.1, 68.3, 61.4, 48.0, 45.5, 42.8, 37.7, 32.1, 29.8, 29.7, 29.5, 29.4, 26.2, 22.9, 14.3. MS (HR-ESI): [M + H]⁺/z calcd for C₄₃H₅₁NO₆, 678.3; found,

678.4.

NB-4-C16BA: ^1H NMR (CDCl_3 , TMS), δ : 7.90–8.96 (d, 2H); 7.55–7.60 (d, 2H); 7.44–7.54 (d, 4H); 6.94–7.03 (d, 4H); 6.25–6.29 (s, 2H); 5.12–5.16 (s, 2H); 4.40–4.45 (t, 2H); 3.97–4.03 (t, 2H); 3.88–3.94 (t, 2H); 3.23–3.28 (s, 2H); 2.69–2.73 (s, 2H); 1.76–1.85 (m, 2H); 1.20–1.53 (m, 28H); 0.85–0.92 (t, 3H). ^{13}C NMR (CDCl_3 , TMS), δ : 177.9, 166.0, 162.8, 159.0, 141.1, 137.9, 134.5, 133.0, 131.8, 128.2, 128.1, 127.0, 122.4, 114.9, 114.6, 70.1, 68.3, 61.4, 48.0, 45.5, 42.8, 37.7, 32.1, 29.8, 29.7, 29.5, 29.4, 26.2, 22.9, 14.3. MS (HR-ESI): $[\text{M} + \text{H}]^+ / z$ calcd for $\text{C}_{47}\text{H}_{59}\text{NO}_6$, 734.4; found, 734.4.

NB-3,4-C12BA: ^1H NMR (CDCl_3 , TMS), δ : 7.44–7.68 (m, 14H); 6.93–6.99 (d, 5H); 6.22–6.25 (s, 2H); 5.21–5.28 (s, 4H); 4.37–4.43 (t, 2H); 3.96–4.05 (t, 4H); 3.87–3.93 (t, 2H); 3.21–3.25 (s, 2H); 2.67–2.70 (s, 2H); 1.75–1.85 (m, 4H); 1.18–1.52 (m, 38H); 0.83–0.93 (t, 6H). ^{13}C NMR (CDCl_3 , TMS), δ : 177.9, 166.0, 159.0, 158.9, 153.3, 148.5, 140.7, 140.6, 137.9, 135.3, 134.9, 133.2, 133.1, 128.2, 128.1, 127.7, 127.6, 127.0, 126.9, 124.3, 122.6, 115.7, 114.9, 113.5, 71.1, 70.8, 68.2, 61.6, 48.0, 45.4, 42.8, 37.7, 32.0, 29.8, 29.7, 29.5, 29.4, 26.2, 22.8, 14.3. MS (HR-ESI): $[\text{M} + \text{Na}]^+ / z$ calcd for $\text{C}_{68}\text{H}_{85}\text{NO}_8$, 1066.6; found, 1066.6

NB-3,4-C16BA: ^1H NMR (CDCl_3 , TMS), δ : 7.44–7.68 (m, 14H); 6.93–6.99 (d, 5H); 6.22–6.25 (s, 2H); 5.22–5.27 (s, 4H); 4.37–4.43 (t, 2H); 3.96–4.05 (t, 4H); 3.87–3.93 (t, 2H); 3.21–3.25 (s, 2H); 2.67–2.70 (s, 2H); 1.75–1.85 (m, 4H); 1.18–1.52 (m, 54H); 0.83–0.91 (t, 6H). ^{13}C NMR (CDCl_3 , TMS), δ : 178.0, 166.0, 159.0, 158.9, 153.3, 148.5, 140.7, 140.6, 137.9, 135.3, 134.9, 133.2, 133.1, 128.2, 128.1, 127.7, 127.6, 127.0, 126.9, 124.3, 122.6, 115.7, 114.9, 113.5, 71.1, 70.8, 68.2, 61.6, 48.0, 45.4, 42.8, 37.7, 32.0, 29.8, 29.7, 29.5, 29.4, 26.2, 22.8, 14.3. MS (HR-ESI): $[\text{M} + \text{Na}]^+ / z$ calcd for $\text{C}_{76}\text{H}_{101}\text{NO}_8$, 1178.8; found, 1178.7

NB-3,5-C12BA: ^1H NMR (CDCl_3 , TMS), δ : 7.55–7.59 (d, 4H); 7.45–7.54 (d, 8H); 7.32–7.29 (d, 2H); 6.94–7.00 (d, 4H); 6.82–6.85 (s, 1H); 6.23–6.27 (s, 2H); 5.09–5.14 (s, 4H); 4.41–4.47 (t, 2H); 3.97–4.03 (t, 4H); 3.90–3.95 (t, 2H); 3.23–3.28 (s, 2H); 2.68–2.72 (s, 2H); 1.75–1.86 (m, 4H); 1.20–1.53 (m, 38H); 0.85–0.92 (t, 6H). ^{13}C NMR (CDCl_3 , TMS), δ : 177.9, 166.0, 160.0, 159.0, 140.9, 137.9, 134.9, 133.1, 131.6, 128.2, 127.0, 114.9, 108.5, 107.9, 100.1, 70.2, 68.2, 61.9, 47.9, 45.4, 42.8, 37.6, 32.0, 29.8, 29.7, 29.6, 29.4, 26.2, 22.8, 14.2. MS (HR-ESI): $[\text{M} + \text{Na}]^+ / z$ calcd for $\text{C}_{68}\text{H}_{85}\text{NO}_8$, 1066.6; found, 1066.6

NB-3,5-C16BA: ^1H NMR (CDCl_3 , TMS), δ : 7.55–7.59 (d, 4H); 7.45–7.54 (d, 8H); 7.32–7.29 (d, 2H); 6.94–7.00 (d, 4H); 6.82–6.85 (s, 1H); 6.23–6.27 (s, 2H); 5.09–5.14 (s, 4H); 4.41–4.47 (t, 2H); 3.97–4.03 (t, 4H); 3.90–3.96 (t, 2H); 3.23–3.27 (s, 2H); 2.68–2.72 (s, 2H); 1.75–1.86 (m, 4H); 1.20–1.53 (m, 54H); 0.85–0.92 (t, 6H). ^{13}C NMR (CDCl_3 , TMS), δ : 177.9, 166.0, 160.0, 159.0, 140.9, 137.9, 134.9, 133.1, 131.6, 128.2, 127.0, 115.0, 108.5, 107.9, 100.1, 70.2, 68.2, 61.9, 47.9, 45.4, 42.8, 37.6, 32.0, 29.8, 29.7, 29.6, 29.4, 26.2, 22.8, 14.3. MS (HR-ESI): $[\text{M} + \text{Na}]^+ / z$ calcd for $\text{C}_{76}\text{H}_{101}\text{NO}_8$, 1178.8; found, 1178.7

NB-3,4,5-C16BA: ^1H NMR (CDCl_3 , TMS), δ : 7.36–7.58 (m, 20H); 6.88–6.99 (d, 6H); 6.20–6.23 (s, 2H); 5.15–5.22 (d, 6H); 4.39–4.44 (t, 2H); 3.90–4.03 (m, 8H); 3.19–3.24 (s, 2H); 2.66–2.69 (s, 2H); 1.76–1.86 (m, 6H); 1.19–1.52 (m, 80H); 0.85–0.91 (t,

9H). ^{13}C NMR (CDCl_3 , TMS), δ : 177.9, 166.0, 159.0, 158.9, 152.8, 142.8, 140.7, 140.5, 137.9, 136.0, 135.1, 133.2, 133.1, 129.2, 128.2, 126.9, 126.6, 124.8, 114.9, 109.2, 75.1, 71.1, 68.3, 62.0, 48.0, 45.4, 42.8, 37.7, 32.1, 29.9, 29.8, 29.6, 29.5, 26.2, 22.8, 14.3. MS (HR-ESI): $[\text{M} + \text{H}]^+ / z$ calcd for $\text{C}_{105}\text{H}_{143}\text{NO}_{10}$, 1579.1; found, 1579.1

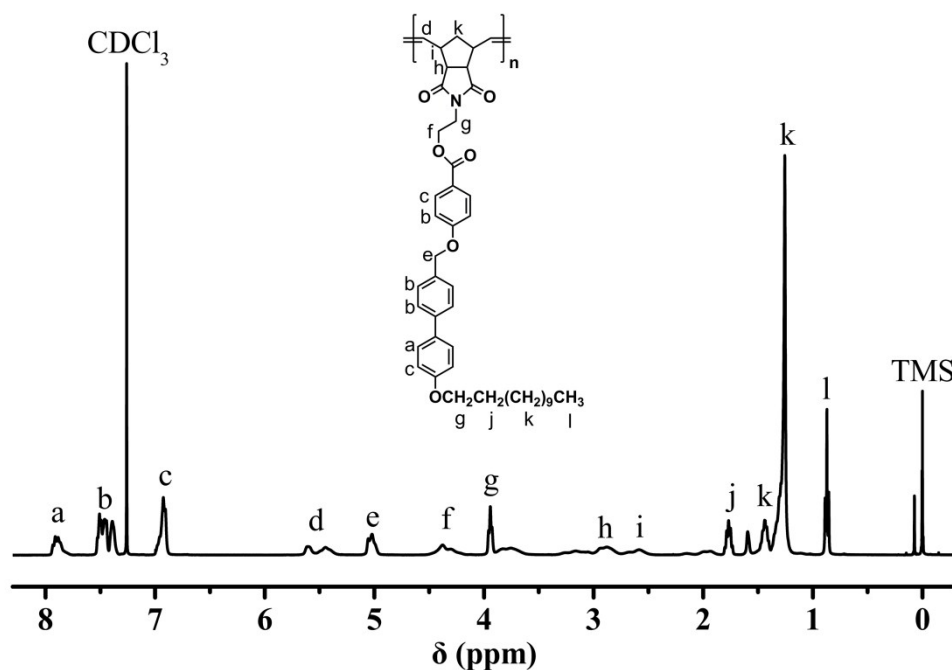
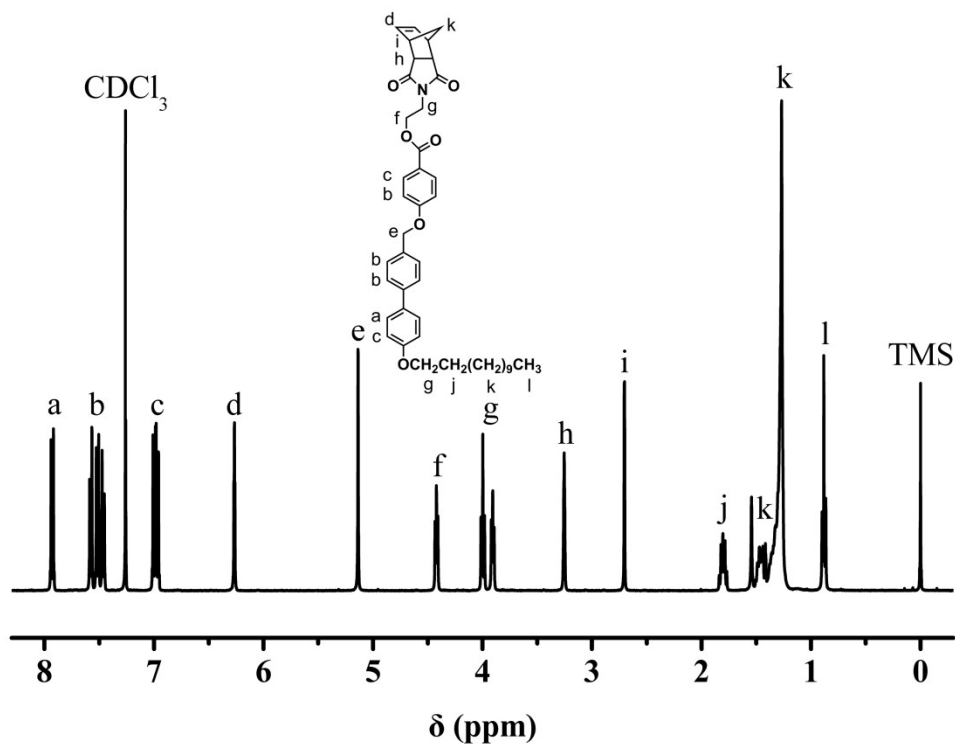
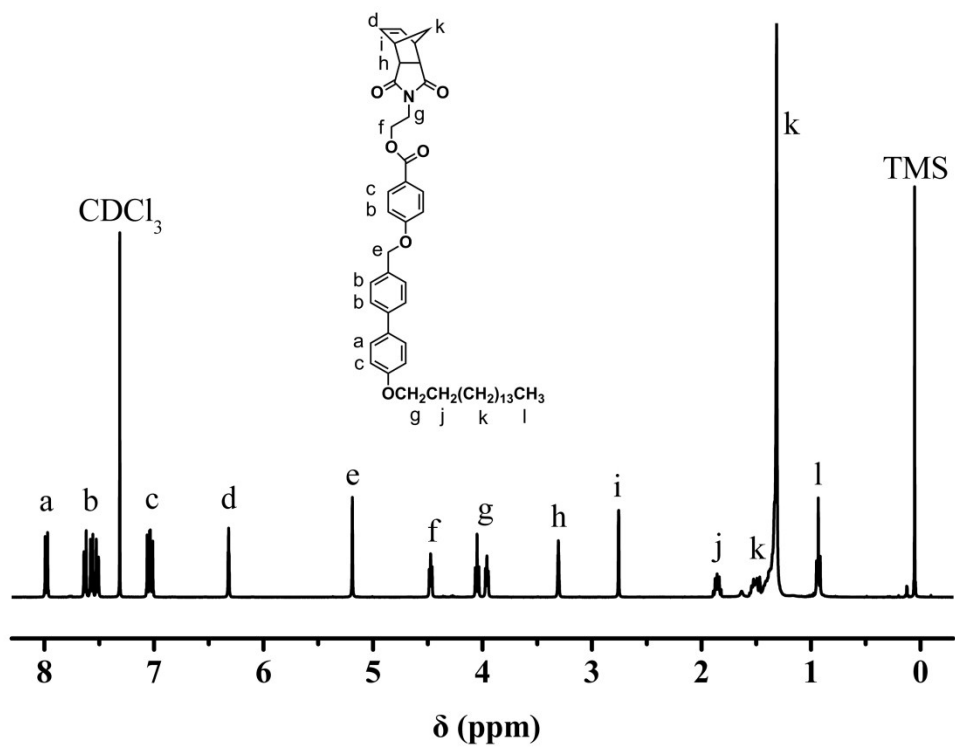
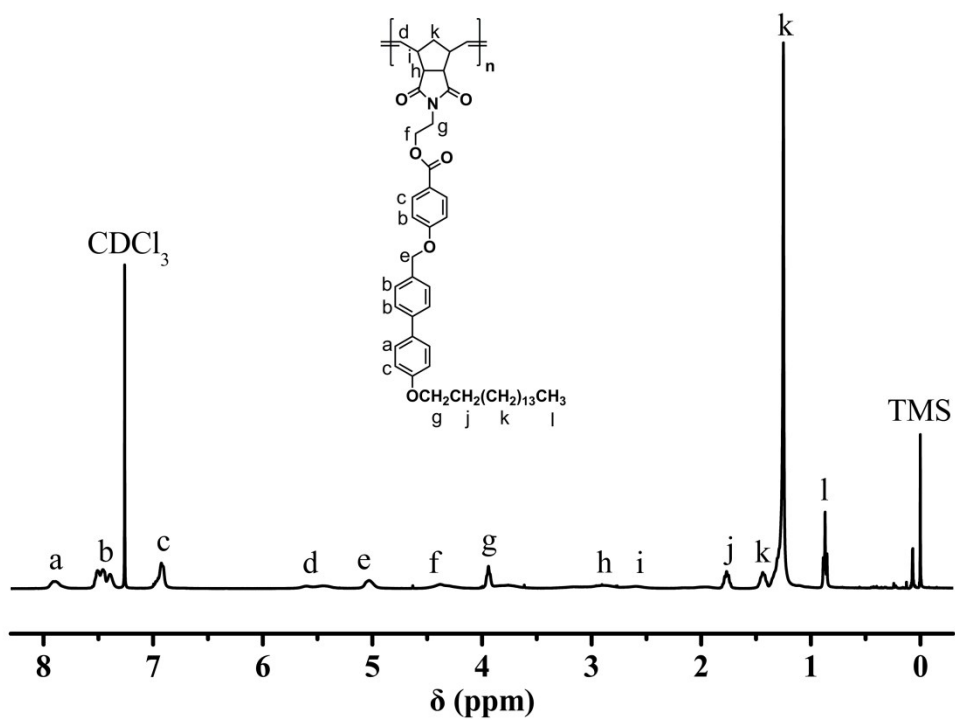


Fig. S1 ^1H NMR spectra of NB-4-C12BA (a) and PNB-4-C12BA (b) in CDCl_3



(a)



(b)

Fig. S2 ¹H NMR spectrum of NB-4-C16BA (a) and PNB-4-C16BA (b) in CDCl₃

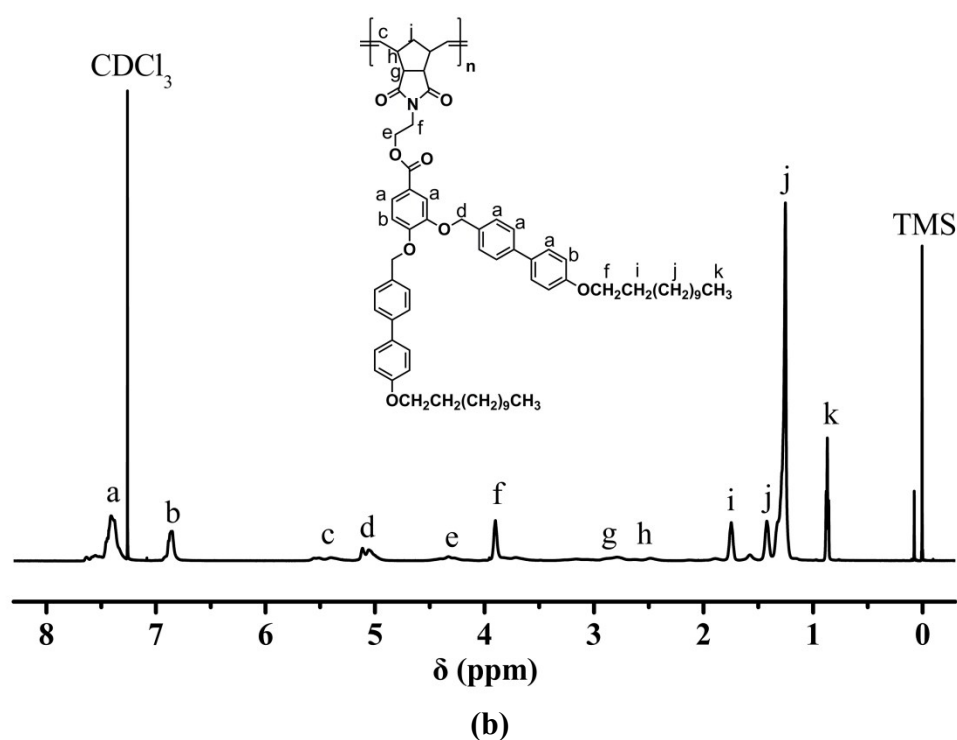
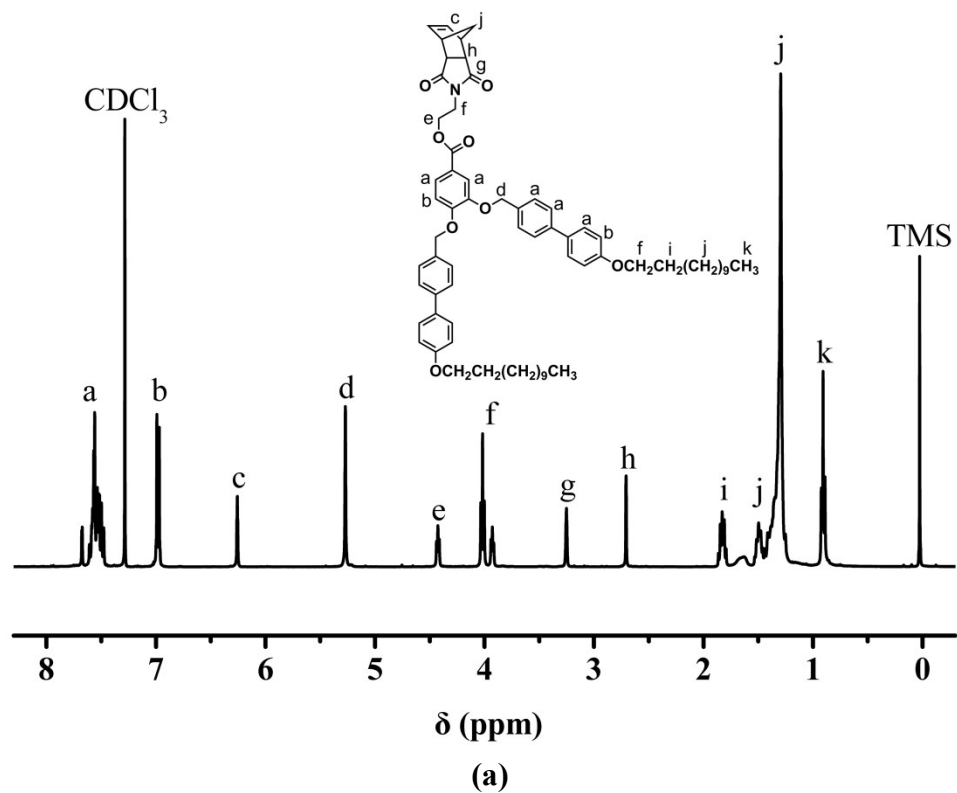


Fig. S3 ^1H NMR spectrum of NB-3,4-C12BA (a) and PNB-3,4-C12BA (b) in CDCl_3

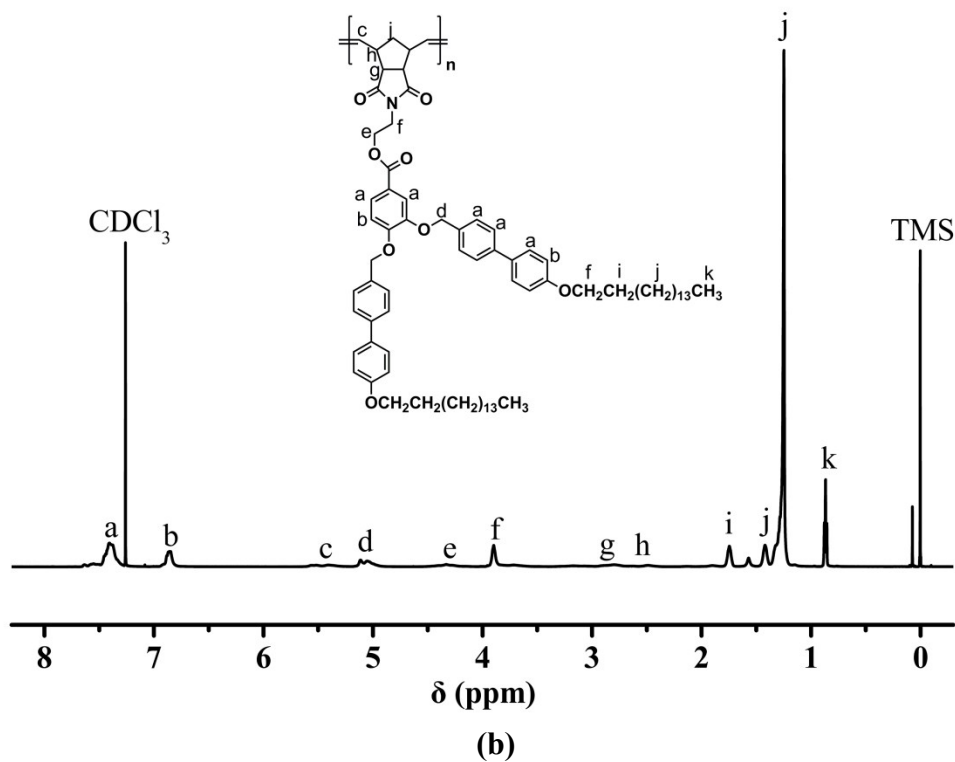
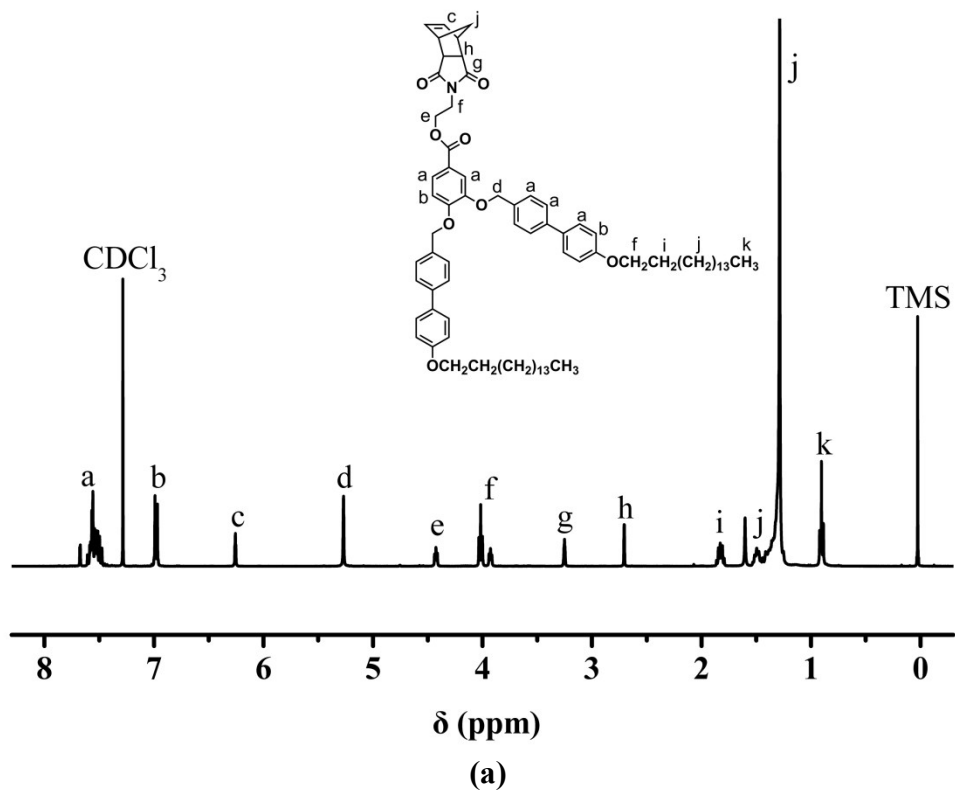


Fig. S4 ^1H NMR spectrum of NB-3,4-C16BA (a) and PNB-3,4-C16BA (b) in CDCl_3

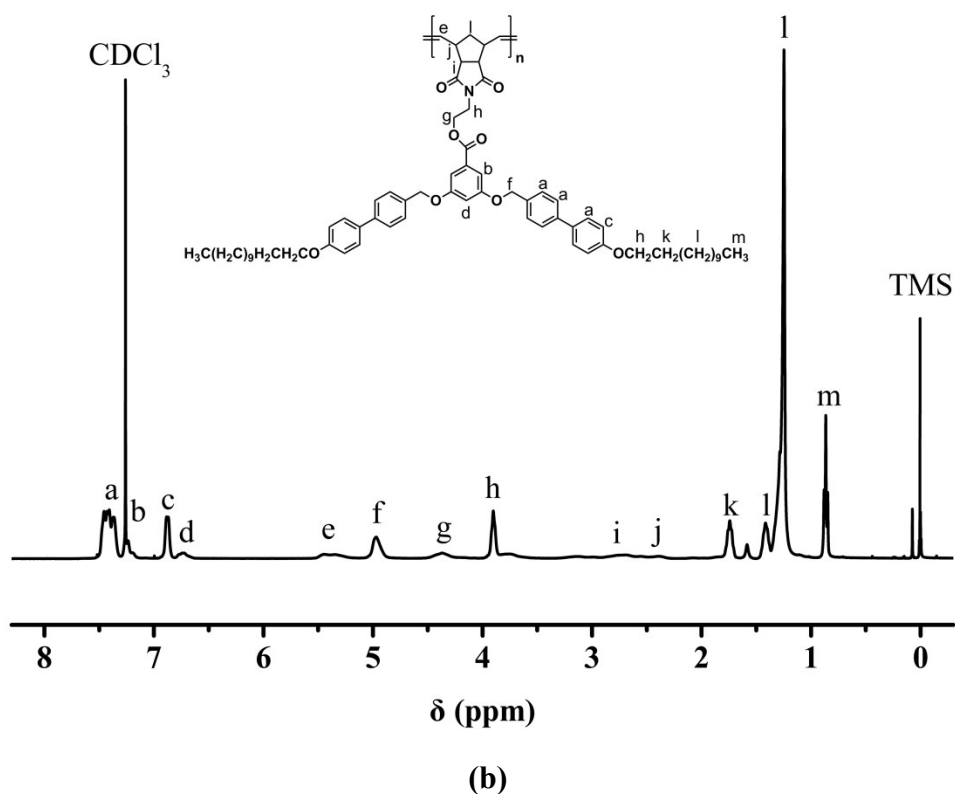
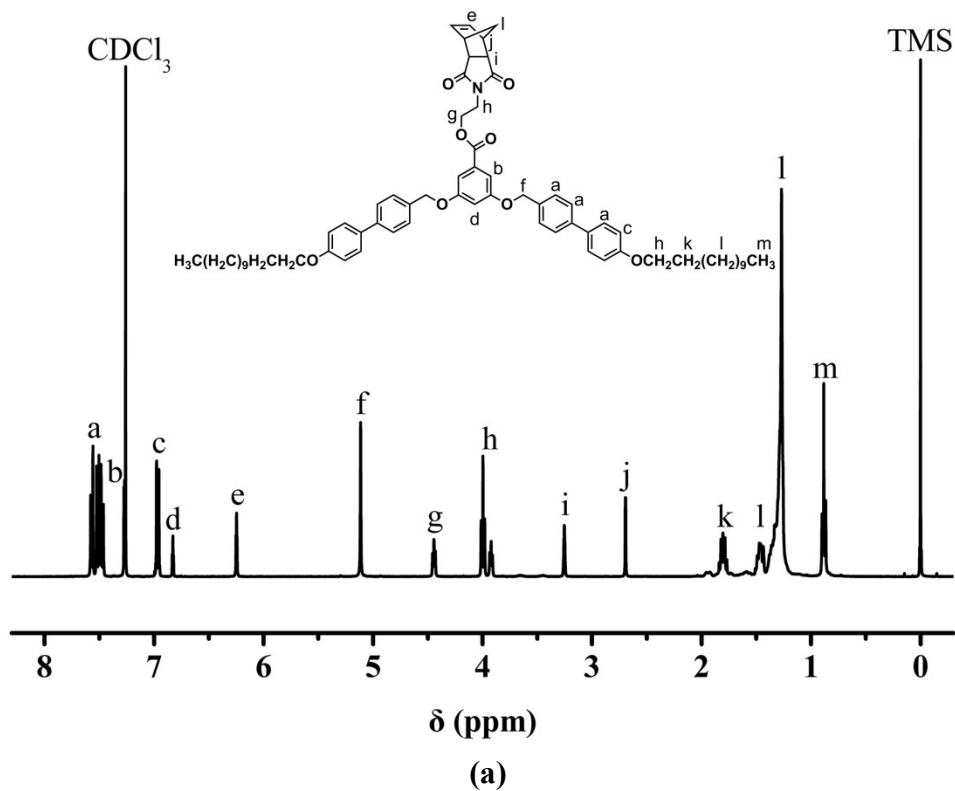
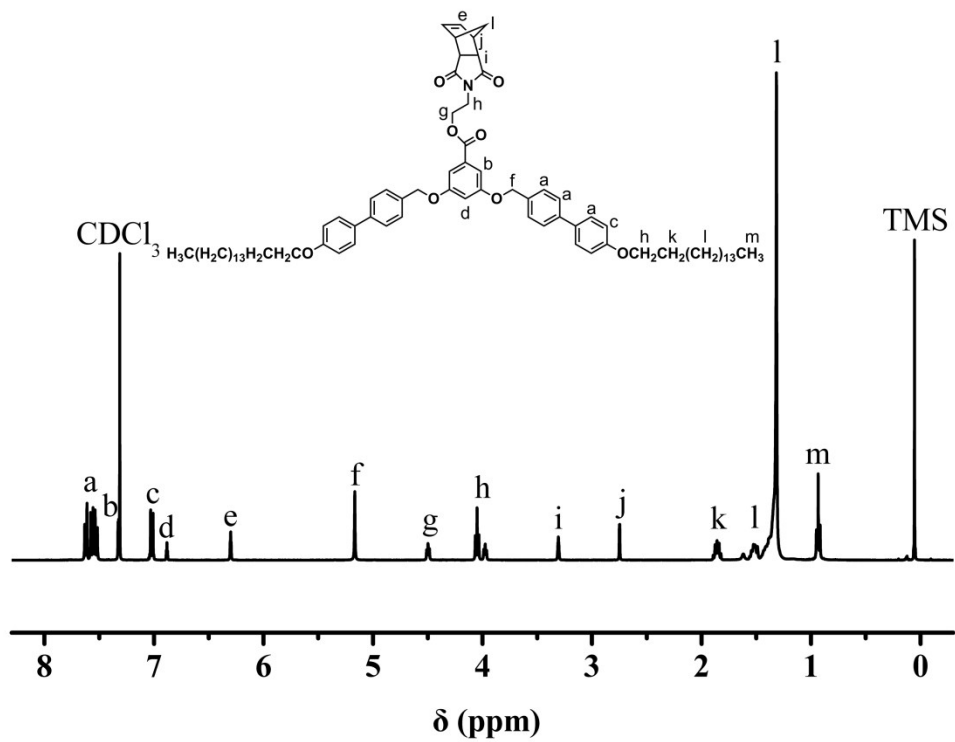
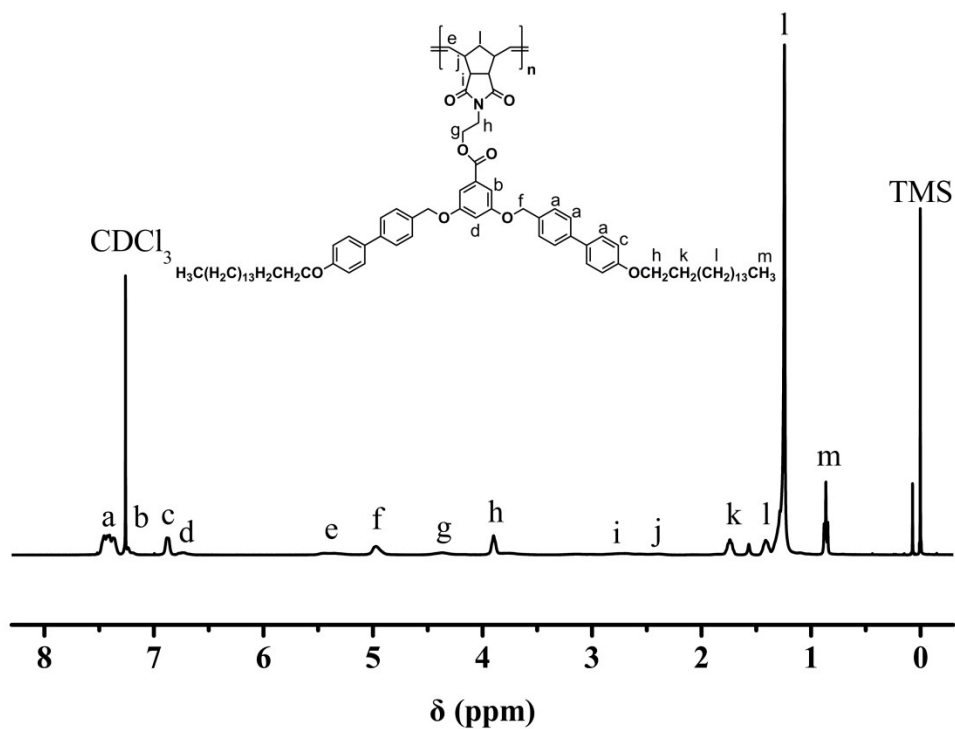


Fig. S5 ^1H NMR spectrum of NB-3,5-C12BA (a) and PNB-3,5-C12BA (b) in CDCl_3

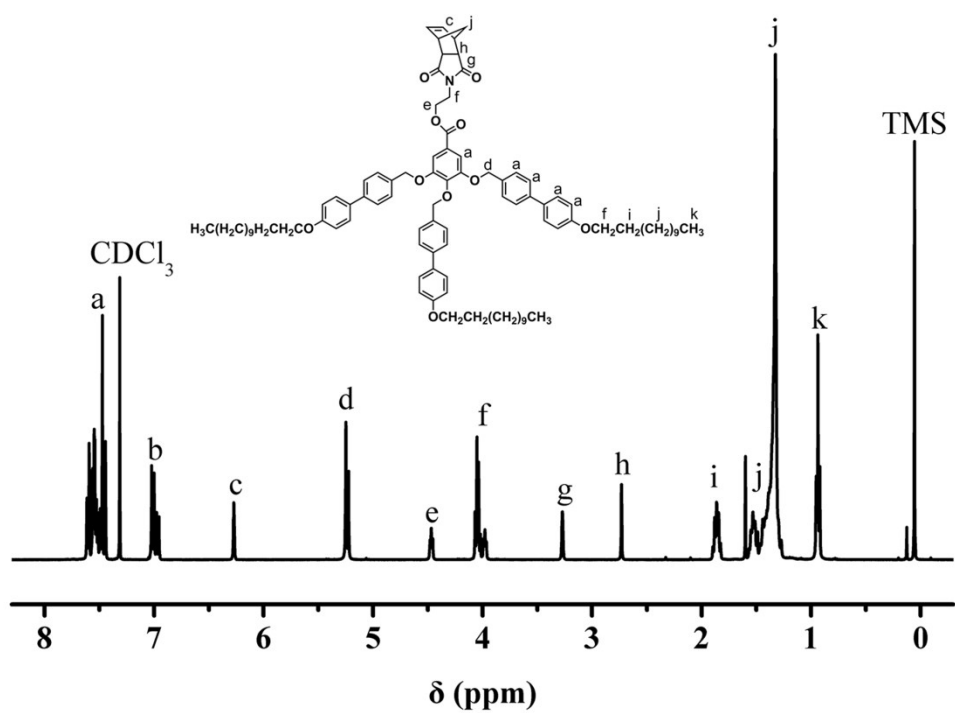


(a)

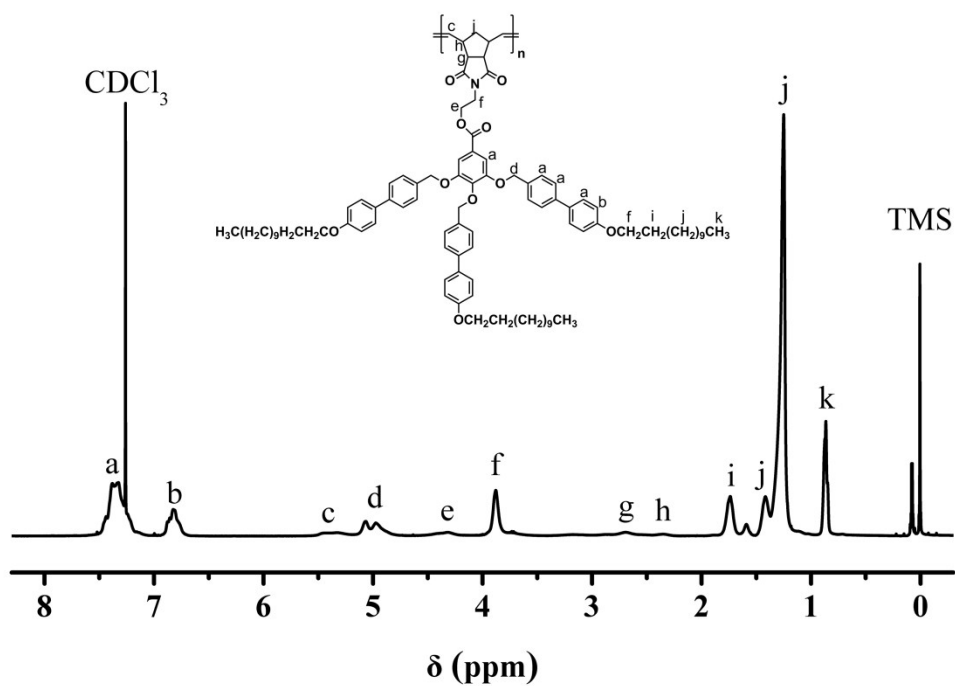


(b)

Fig. S6 ^1H NMR spectra of NB-3,5-C16BA (a) and PNB-3,5-C16BA (b) in CDCl_3

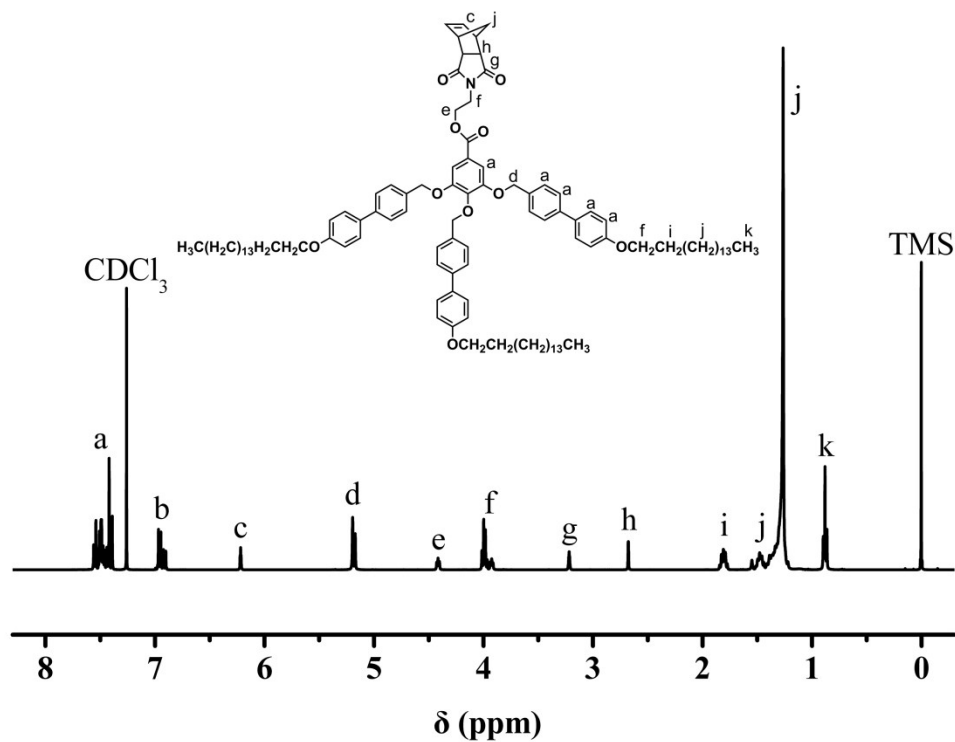


(a)

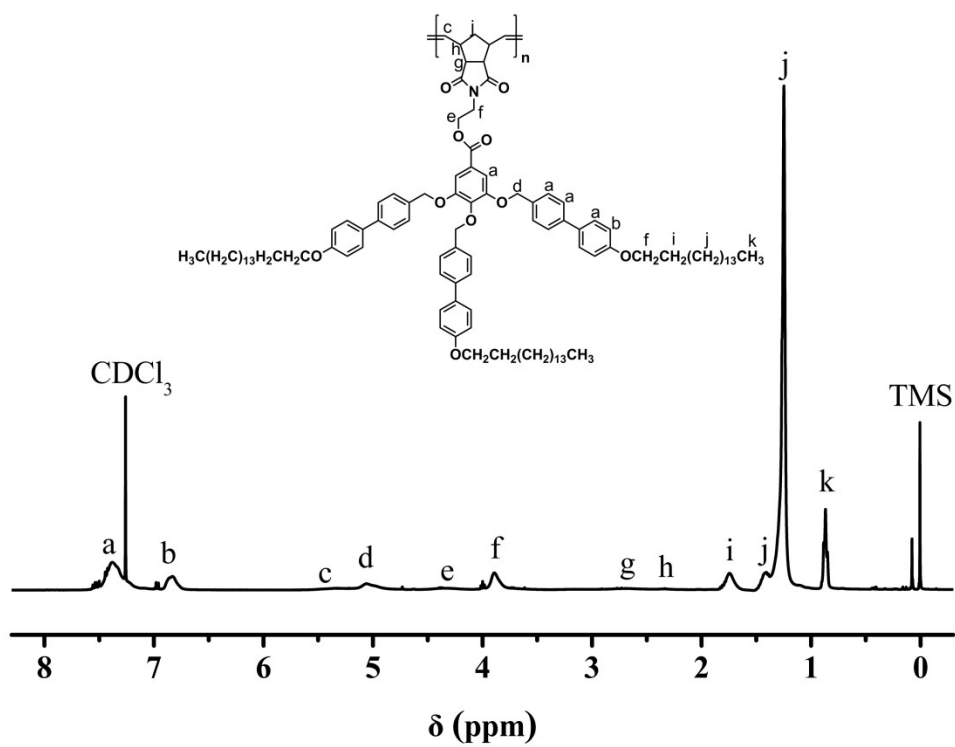


(b)

Fig. S7 ^1H NMR spectra of NB-3,4,5-C12BA (a) and PNB-3,4,5-C12BA (b) in CDCl_3



(a)



(b)

Fig. S8 ¹H NMR spectra of NB-3,4,5-C16BA (a) and PNB-3,4,5-C16BA (b) in CDCl₃

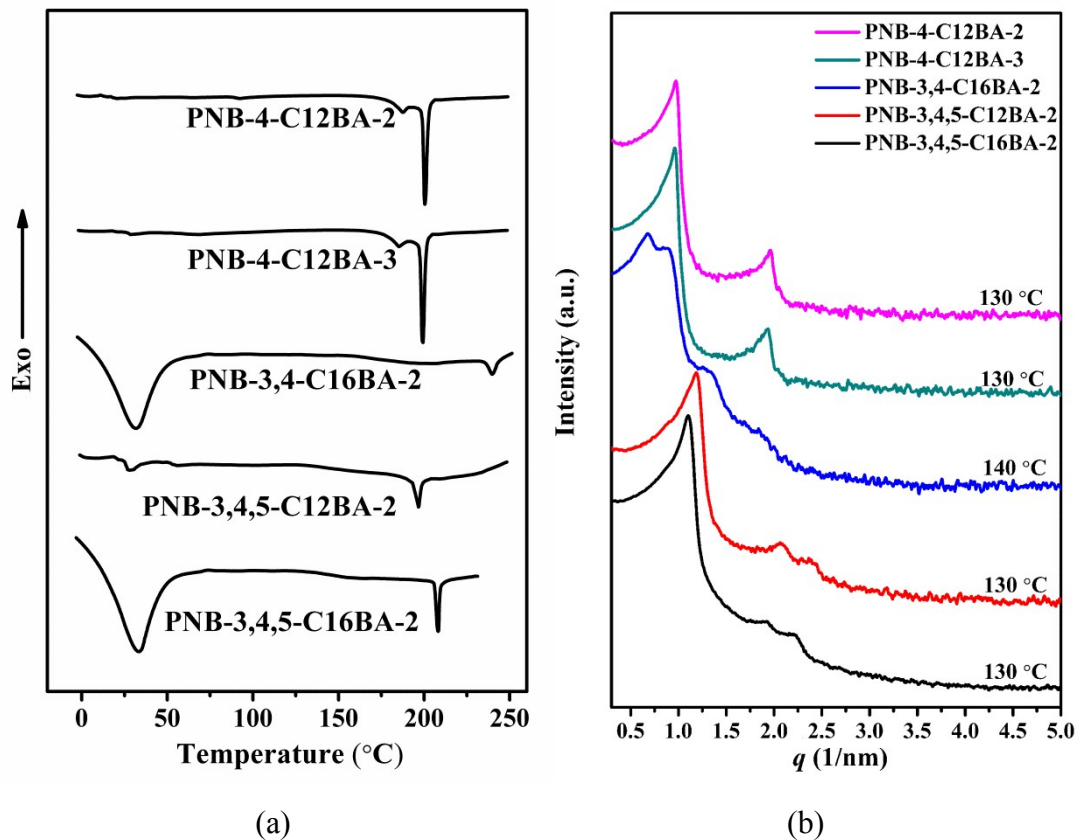


Fig. S9 DSC curves (a) and SAXS (b) profiles of PNBs with different molecular weights. The last number in each sample name refers to the No. listed in Table 1.

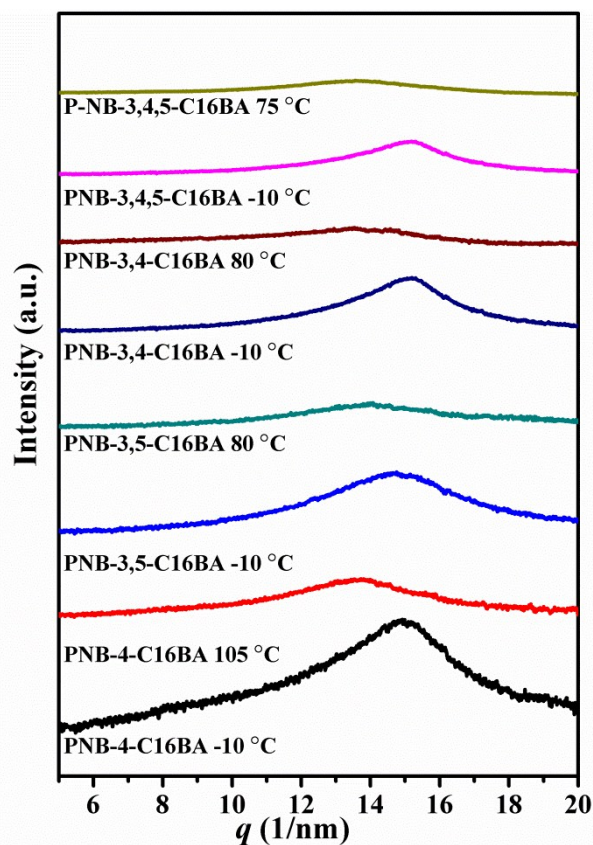


Fig. S10 WAXS profiles of PNB-4-C16BA, PNB-3,5-C16BA, PNB-3,4-C16BA and PNB-3,4,5-C16BA at different temperatures.

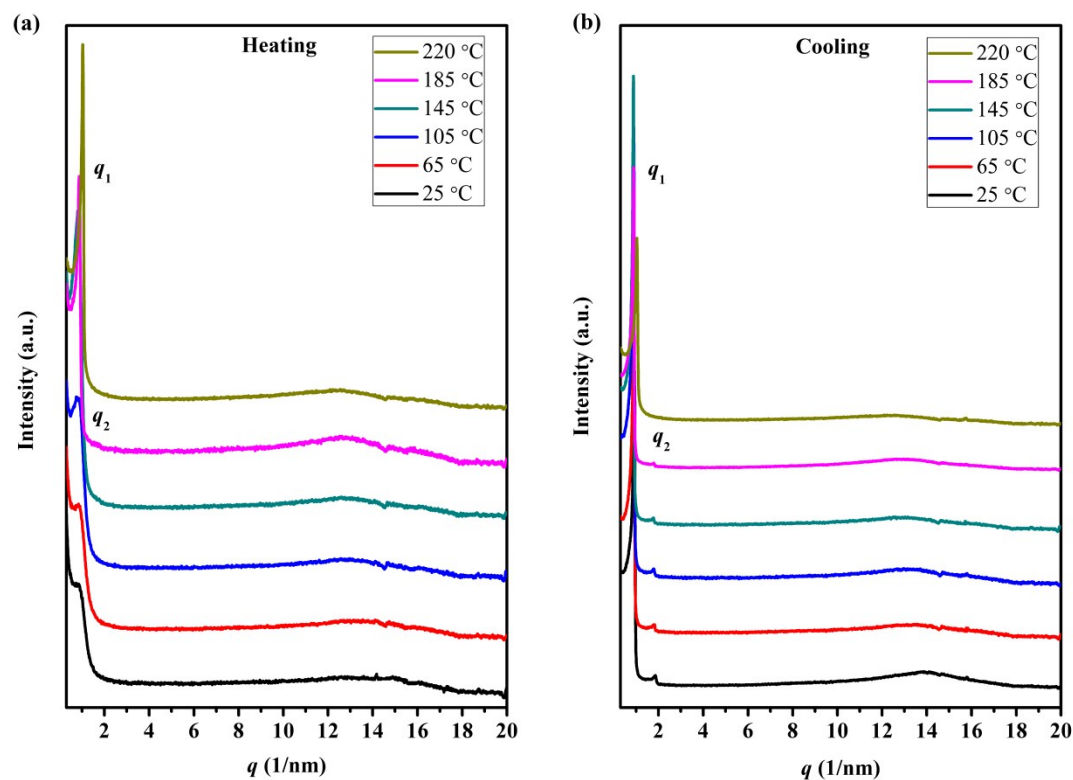


Fig. S11 Temperature dependent SAXS profiles of PNB-4-C16BA during the first heating (a) and subsequent cooling (b) processes.

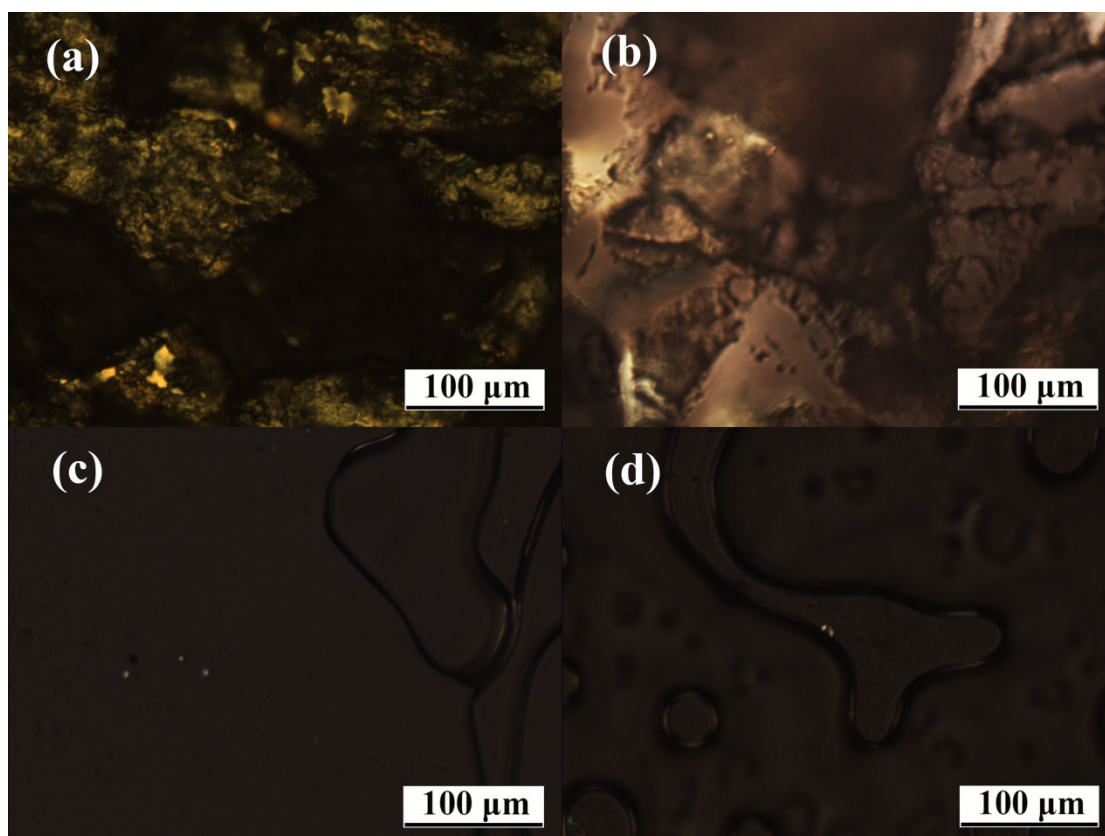


Fig. S12 POM images of PNB-3,5-C12BA at 90 °C (a) and PNB-3,5-C16BA at 100 °C (b) during heating process; PNB-3,5-C12BA at 30 °C (c) and PNB-3,5-C16BA at 30 °C when cooling from isotropic state.

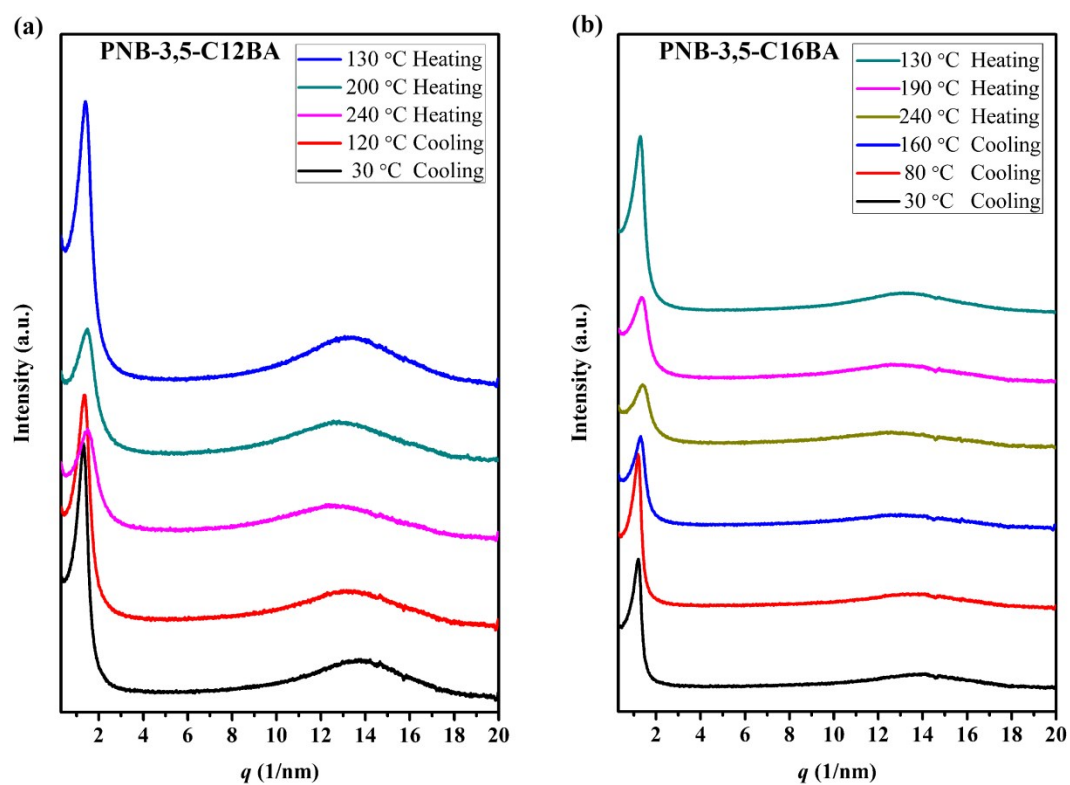


Fig. S13 Temperature dependent SAXS profiles of PNB-3,5-C12BA (a) and PNB-3,5-C16BA (b) during the first heating and subsequent cooling processes.

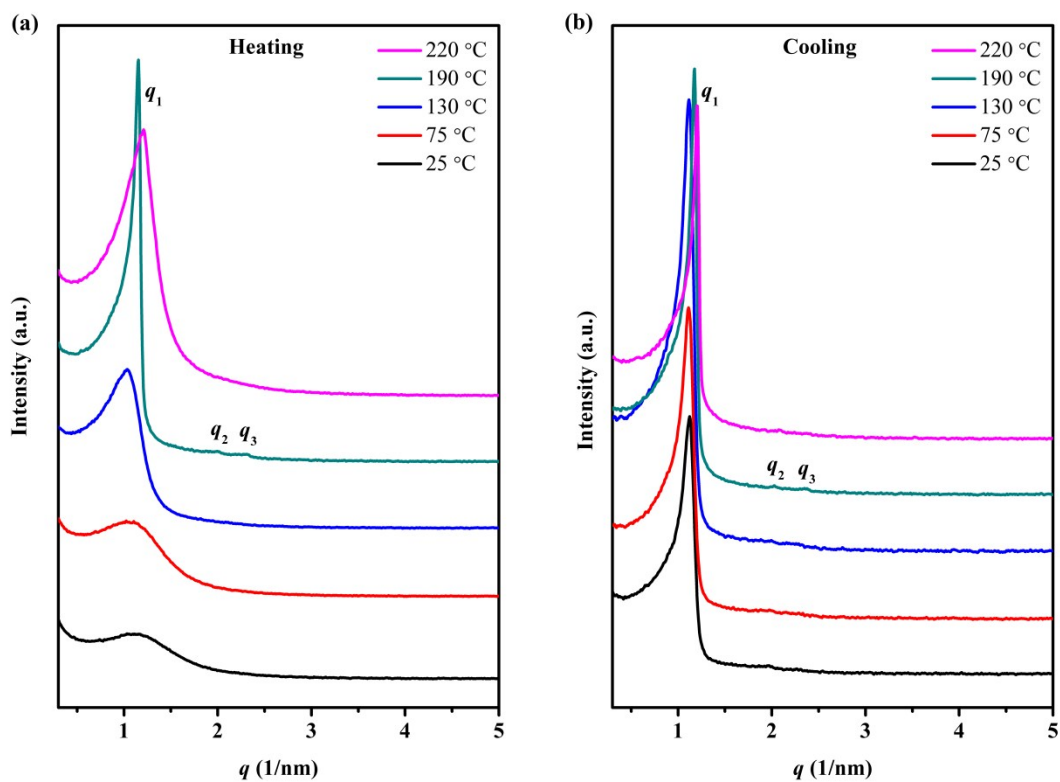


Fig. S14 Temperature dependent SAXS profiles of PNB-3,4,5-C16BA during the first heating (a) and subsequent cooling (b) processes.