Electronic Supplementary Informations:

Influence of the Side-Chain Structure and Molecular Weight on the Re-entrant Behaviors of Mesogen-Jacketed Liquid Crystalline Polymers

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S1 Synthesis of monomers

The chemical structures and synthetic procedures of monomers are illustrated in Scheme 2 and 3. For convenience the monomers, 2,5-bis[(benzyloxy-alkyl)oxycarbonyl]-styrenes, 2,5-bis [(diphenylmethoxy-alkyl)oxycarbonyl]-styrenes, and 2,5-bis [(triphenylmethoxy-alkyl)oxycarbonyl]-styrenes, were abbreviated named Mv-m-Bn, Mv-m-DPM, Mv-m-Tr respectively, where m is the number of the methylene units between the terephthalate core and terminal groups in the side chains and m=2, 4, 6, 8, 10, 12, and the corresponding polymers were named Pv-m-Bn, Pv-m-DPM, Pv-m-Tr. 2-vinylterephthalic acid (VTA) were facilely synthesized according to the reported procedures. The experimental details were described as follows using Mv-6-Bn and Mv-6-DPM as examples.

Synthesis of 6-benzyloxy-1-hexanol

According to literature, 6-benzyloxy-1-hexanol was easy to synthesis and obtain. To a solution of 1,6-hexane diol (3.00 g, 17.5 mmol) in anhydrous THF was slowly added 60% NaH in oil suspension (2.04 g, 17.5 mmol) followed by the addition of benzyl bromide (0.77 g, 19.3 mmol). The reaction mixture was stirred at 25 ^{o}C for 6h, quenched with cold water, extracted with CH_2Cl_2 (3×100 mL) and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and concentrated to give the crude material which was then purified by column chromatography on silica gel using petroleum ether/EtOAc (3:1) to give product (3.33 g, 91%) as a colourless oil. ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.40-1.64 (m, 8H, -CH_2- and 1H, -O*H*), 3.46-3.49 (m, 2H, -OCH_2-), 3.63-3.66 (m, 2H, -OCH_2-), 4.51 (s, 2H, -OCH_2-), 7.34 (s, 5H, Ar-*H*).

Synthesis of 2,5-bis[(benzyloxy-hexyl)oxycarbonyl]-styrene (Mv-6-Bn)

6-benzyloxy-1-hexanol (3.33 g, 16.0 mmol), VTA (1.52 g, 8.0 mmol), N,N′-dicyclohexylcarbodiimide (DCC, 4.90 g, 24.0 mmol), 4-(dimethylamino)pyridine (DMAP, 0.10 g, 0.8 mmol), and dried CH_2Cl_2 (100 mL) were mixed in a 250 mL round-bottomed flask and stirred at ambient temperature for 24 h. The floating solid was filtrated, and the solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography with with ethyl acetate and petroleum ether (v:v=1:5) as eluent, and then condensed eluent to yield a colorless liquid, yield: 42%. IR(KBr):=*C*H_2 (2971, 908), -*C*H_2- (2928, 2852, 1457), -*COO*- (1719, 1290, 1238), -*C*-*O*-*C*- (1106, 1066, 1023), Ar (1621, 1561, 740-700). ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.28-1.79 (m 16H, -CH_2-),3.46-3.49 (t, 4H, -OCH_2-), 4.30-4.36 (m, 4H, -OCH_2-), 4.50 (s, 4H, -OCH_2-), 5.40-5.43 (d, 1H, =CH_2), 5.72-5.77 (d, 1H, =CH_2), 7.29-7.45(m, 10H, Ar-*H* and 1H, -C*H*=), 7.87-7.95 (m, 2H, Ar-*H*), 8.23 (s, 1H, Ar-*H*). Mass Spectrometry (MS) (m/z) $[M + Na]^+$ Calcd for $C_{36}H_{44}O_6Na$, 595.721.; found, 595.529.

Synthesis of 2,5-bis[(benzyloxy-alkyl)oxycarbonyl]-styrenes (Mv-m-Bn, m =2, 4, 8, 10, 12)

All the other monomers were synthesized and characterized in a similar way. The characterization data of Mv-m-Bn (m =2, 4, 8, 10, 12) were listed in the below.

The characterization data of Mv -m-Bn (m =2, 4, 8, 10, 12)

2-benzyloxy-1-ethanol: ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.73 (s, 1H, -O*H*), 3.60-3.62 (m, 2H, -OCH_2-), 3.74-3.78 (m, 2H, -OCH_2-), 4.57 (s, 2H, -OCH_2-), 7.30-7.35 (m, 5H, Ar-*H*).

2,5-bis[(benzyloxy-2-ylmethyl)oxycarbonyl]styrene (Mv-2-Bn): ^{1}H NMR (δ, ppm, $CDC1_3$): δ=3.82-3.83 (d, 4H, -OCH_2-), 4.51-4.55 (t, 4H, -OCH_2-), 4.61-4.62 (d, 4H, -OCH_2-), 5.39-5.42 (d, 1H, =CH_2), 5.74-5.78 (d, 1H, =CH_2), 7.30-7.47(m, 10H, Ar-*H* and 1H, -C*H*=), 7.92-7.99 (m, 2H, Ar-*H*), 8.27 (s, 1H, Ar-*H*). Mass Spectrometry (MS) (m/z) $[M + Na]^+$ Calcd for $C_{28}H_{28}O_6Na$, 483.508.; found, 483.474.

4-benzyloxy-1-butanol: ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.40-1.86 (m, 4H, -CH_2-), 2.08 (s, 1H, -O*H*), 3.51-3.54 (m, 2H, -OCH_2-), 3.66-3.70 (m, 2H, -OCH_2-), 4.53 (s, 2H, -OCH_2-), 7.31-7.34 (m, 5H, Ar-*H*).

2,5-bis[(benzyloxy-4-ylmethyl)oxycarbonyl]styrene (Mv-4-Bn): ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.85-1.94 (m, 8H, -CH_2-), 3.52-3.57 (m, 4H, -OCH_2-), 4.34-4.39 (m, 4H, -OCH_2-), 4.52 (s, 4H, -OCH_2-), 5.40-5.43 (d, 1H, =CH_2), 5.72-5.76 (d, 1H, =CH_2), 7.30-7.45(m, 10H, Ar-*H* and 1H, -C*H*=), 7.87-7.94 (m, 2H, Ar-*H*), 8.22 (s, 1H, Ar-*H*). Mass Spectrometry (MS) (m/z) $[M + Na]^+$ Calcd for $C_{32}H_{36}O_6Na$, 539.614.; found, 539.441.

8-benzyloxy-1-octanol: ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.33-1.63 (m, 12H, -CH_2- and 1H, -O*H*), 3.45-3.48 (m, 2H, -OCH_2-), 3.62-3.65 (m, 2H, -OCH_2-), 4.50 (s, 2H, -OCH_2-), 7.34 (s, 5H, Ar-*H*).

2,5-bis[(benzyloxy-8-ylmethyl)oxycarbonyl]styrene (Mv-8-Bn): ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.35-1.79 (m 24H, -CH_2-),3.45-3.48 (t, 4H, -OCH_2-), 4.30-4.35 (m, 4H, -OCH_2-), 4.50 (s, 4H, -OCH_2-), 5.40-5.43 (d, 1H, =CH_2), 5.73-5.77 (d, 1H, =CH_2), 7.29-7.45(m, 10H, Ar-*H* and 1H, -C*H*=), 7.88-7.96 (m, 2H, Ar-*H*), 8.23 (s, 1H, Ar-*H*). Mass Spectrometry (MS) (m/z) $[M + Na]^+$ Calcd for $C_{40}H_{52}O_6Na$, 651.827.; found, 651.583.

10-benzyloxy-1-decanol: ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.29-1.61 (m, 16H, -CH_2- and 1H, -O*H*), 3.45-3.48 (m, 2H, -OCH_2-), 3.62-3.65 (m, 2H, -OCH_2-), 4.50 (s, 2H, -OCH_2-), 7.34 (s, 5H, Ar-*H*).

2,5-bis[(benzyloxy-10-ylmethyl)oxycarbonyl]styrene (Mv-10-Bn): ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.30-1.78 (m 32H, -CH_2-),3.45-3.48 (t, 4H, -OCH_2-), 4.32-4.34 (m, 4H, -OCH_2-), 4.50 (s, 4H, -OCH_2-), 5.41-5.43 (d, 1H, =CH_2), 5.73-5.77 (d, 1H, =CH_2), 7.29-7.46(m, 10H, Ar-*H* and 1H, -C*H*=), 7.89-7.96 (m, 2H, Ar-*H*), 8.23 (s, 1H, Ar-*H*). Mass Spectrometry (MS) (m/z) $[M + Na]^+$ Calcd for $C_{44}H_{60}O_6Na$, 707.933.; found, 707.577.

12-benzyloxy-1-dodecanol: ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.27-1.61 (m, 20H, -CH_2- and 1H, -O*H*), 3.45-3.48 (m, 2H, -OCH_2-), 3.62-3.66 (m, 2H, -OCH_2-), 4.50 (s, 2H, -OCH_2-), 7.35 (s, 5H, Ar-*H*).

2,5-bis[(benzyloxy-12-ylmethyl)oxycarbonyl]styrene (Mv-12-Bn): ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.27-1.78 (m 40H, -CH_2-),3.45-3.48 (t, 4H, -OCH_2-), 4.32-4.34 (m, 4H, -OCH_2-), 4.50 (s, 4H, -OCH_2-), 5.41-5.43 (d, 1H, =CH_2), 5.73-5.78 (d, 1H, =CH_2), 7.33-7.46(m, 10H, Ar-*H* and 1H, -C*H*=), 7.89-7.96 (m, 2H, Ar-*H*), 8.23 (s, 1H, Ar-*H*). Mass Spectrometry (MS) (m/z) $[M + Na]^+$ Calcd for $C_{48}H_{68}O_6Na$, 764.040.; found, 763.661.

Synthesis of 6-diphenylmethoxy-1-hexanol

According to literature, 1,6-hexane diol (3.78 g, 32.6 mmol), and diphenylmethanol (3.00 g, 16.3 mmol) was added into 120 mL dichloroethane in a 250 mL three-necked flask, And then, the reaction mixture was heated at 85 °C. After the reaction was refluxed for only one hour, much of solvent was removed by rotating evaporation. Then the reaction mixture was extracted with CH_2Cl_2 and water for three times, dried over anhydrous $MgSO_4$ and concentrated to give the crude material which was then purified by column chromatography. The final product of 6-benzyloxy-1-hexanol was a colorless liquid, yield: 67%. ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.36-1.70 (m, 8H, -CH_2- and 1H, -O*H*), 3.44-3.47 (t, 2H, -OCH_2-), 3.61-3.65 (t, 2H, -OCH_2-), 5.33 (s, 2H, -OCH_2-), 7.22-7.35 (m, 10H, Ar-*H*).

Synthesis of 2,5-bis[(diphenylmethoxy-hexyl)oxycarbonyl]-styrene (Mv-6-DPM)

The synthetic method of monomer 2,5-bis[(diphenylmethoxy-hexyl)oxycarbonyl]-styrene were similar with the 2,5-bis[(benzyloxy-hexyl)oxycarbonyl]-styrene and the synthetic process were not described here. Yield: 47%. IR(KBr):=*CH*$_2$ (916), -*CH*$_2$- (2922, 2852, 1450), -*COO*- (1716, 1285, 1239), -*C*-*O*-*C*- (1104, 1070, 1025), Ar (3087, 3061, 3028, 1599, 1561, 1491, 756-700). ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.46-1.81 (m, 16H, -CH_2-), 3.44-3.48 (t, 4H, -OCH_2-), 4.30-4.35 (m, 4H, -OCH_2-), 5.33 (s, 2H, -OC*H*-), 5.39-5.42 (d, 1H, =CH_2), 5.72-5.76 (d, 1H, =CH_2), 7.21-7.44 (m, 20H, Ar-*H* and 1H, -C*H*=), 7.87-7.94 (m, 2H, Ar-*H*), 8.23 (s, 1H, Ar-*H*). Mass Spectrometry (MS) (m/z) $[M + Na]^+$ Calcd for $C_{48}H_{52}O_6Na$, 747.913.; found, 747.549.

Synthesis of 2,5-bis[(diphenylmethoxy-alkyl)oxycarbonyl]-styrenes (Mv-m-DPM, m =2, 4, 8, 10, 12)

All the other monomers were synthesized and characterized in a similar way. The characterization data of Mv -m-DPM (m =2, 4, 8, 10, 12) were showed in the below.

The characterization data of Mv -m-DPM (m =2, 4, 8, 10, 12)

2-diphenylmethoxy-1-ethanol: ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.635 (s, 1H, -O*H*), 3.59-3.61 (t, 2H, -OCH_2-), 3.78-3.80 (t, 2H, -OCH_2-), 5.41 (s, 1H, -OC*H*-), 7.31-7.35 (m, 10H, Ar-*H*).

2,5-bis[(diphenylmethoxy-2-ylmethyl)oxycarbonyl]styrene (Mv-2-DPM): ^{1}H NMR (δ, ppm, $CDC1_3$): δ=3.81-3.85 (m, 4H, -OCH_2-), 4.54-4.58 (m, 4H, -OCH_2-), 5.35-5.37 (d, 1H, =CH_2), 5.45-5.46 (d, 2H, -OC*H*-), 5.72-5.77 (d, 1H, =CH_2), 7.22-7.45 (m, 20H, Ar-*H* and 1H, -C*H*=), 7.92-7.96 (m, 2H, Ar-*H*), 8.28 (s, 1H, Ar-*H*). Mass Spectrometry (MS) (m/z) $[M + Na]^+$ Calcd for $C_{40}H_{36}O_6Na$, 635.700.; found, 635.411.

4-diphenylmethoxy-1-butanol: ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.69-1.76 (m, 4H, -CH_2- and 1H, -O*H*), 3.47-3.52 (m, 2H, -OCH_2-), 3.65-3.70 (m, 2H, -OCH_2-), 5.35 (s, 2H, -OCH_2-), 7.30-7.33 (m, 10H, Ar-*H*).

2,5-bis[(diphenylmethoxy-4-ylmethyl)oxycarbonyl]styrene (Mv-4-DPM): ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.80-1.95 (m, 8H, -CH_2-), 3.52-3.54 (m, 4H, -OCH_2-), 4.34-4.39 (m, 4H, -OCH_2-), 5.34 (s, 2H, -OC*H*-), 5.39-5.42 (d, 1H, =CH_2), 5.72-5.86 (d, 1H, =CH_2), 7.23-7.44 (m, 20H, Ar-*H* and 1H, -C*H*=), 7.86-7.93 (m, 2H, Ar-*H*), 8.22 (s, 1H, Ar-*H*). Mass Spectrometry (MS) (m/z) $[M + Na]^+$ Calcd for $C_{44}H_{44}O_6Na$, 691.806.; found, 691.494.

8-diphenylmethoxy-1-octanol: ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.32-1.64 (m, 12H, -CH_2- and 1H, -O*H*), 3.43-3.46 (t, 2H, -OCH_2-), 3.62-3.63 (t, 2H, -OCH_2-), 5.33 (s, 2H, -OCH_2-), 7.24-7.33 (m, 10H, Ar-*H*).

2,5-bis[(diphenylmethoxy-8-ylmethyl)oxycarbonyl]styrene (Mv-8-DPM): ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.34-1.77 (m, 24H, -CH_2-), 3.43-3.46 (t, 4H, -OCH_2-), 4.30-4.35 (m, 4H, -OCH_2-), 5.33 (s, 2H, -OC*H*-), 5.39-5.42 (d, 1H, =CH_2), 5.72-5.77 (d, 1H, =CH_2), 7.23-7.45 (m, 20H, Ar-*H* and 1H, -C*H*=), 7.88-7.96 (m, 2H, Ar-*H*), 8.23 (s, 1H, Ar-*H*). Mass Spectrometry (MS) (m/z) $[M + Na]^+$ Calcd for $C_{52}H_{60}O_6Na$, 804.019.; found, 803.675.

10-diphenylmethoxy-1-decanol: ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.28-1.66 (m, 16H, -CH_2- and 1H, -O*H*), 3.43-3.46 (t, 2H, -OCH_2-), 3.62-3.65 (t, 2H, -OCH_2-), 5.33 (s, 2H, -OCH_2-), 7.23-7.35 (m, 10H, Ar-*H*).

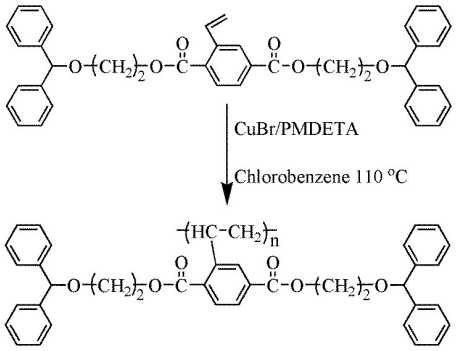
2,5-bis[(diphenylmethoxy-10-ylmethyl)oxycarbonyl]styrene (Mv-10-DPM): ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.29-1.78 (m, 32H, -CH_2-), 3.43-3.46 (t, 4H, -OCH_2-), 4.30-4.35 (m, 4H, -OCH_2-), 5.33 (s, 2H, -OC*H*-), 5.40-5.43 (d, 1H, =CH_2), 5.73-5.77 (d, 1H, =CH_2), 7.23-7.45 (m, 20H, Ar-*H* and 1H, -C*H*=), 7.88-7.96 (m, 2H, Ar-*H*), 8.23 (s, 1H, Ar-*H*). Mass Spectrometry (MS) (m/z) $[M + Na]^+$ Calcd for $C_{56}H_{68}O_6Na$, 860.126.; found, 859.732.

12-diphenylmethoxy-1-dodecanol: ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.22-1.66 (m, 20H, -CH_2- and 1H, -O*H*), 3.43-3.46 (t, 2H, -OCH_2-), 3.62-3.65 (t, 2H, -OCH_2-), 5.33 (s, 2H, -OCH_2-), 7.22-7.34 (m, 10H, Ar-*H*).

2,5-bis[(diphenylmethoxy-12-ylmethyl)oxycarbonyl]styrene (Mv-12-DPM): ^{1}H NMR (δ, ppm, $CDC1_3$): δ=1.27-1.80 (m, 40H, -CH_2-), 3.42-3.46 (t, 4H, -OCH_2-), 4.30-4.35 (m, 4H, -OCH_2-), 5.33 (s, 2H, -OC*H*-), 5.40-5.43 (d, 1H, =CH_2), 5.73-5.77 (d, 1H, =CH_2), 7.23-7.45 (m, 20H, Ar-*H* and 1H, -C*H*=), 7.88-7.96 (m, 2H, Ar-*H*), 8.23 (s, 1H, Ar-*H*). Mass Spectrometry (MS) (m/z) $[M + Na]^+$ Calcd for $C_{60}H_{76}O_6Na$, 916.232.; found, 915.859.

S2 Synthetic procedures of Pv-2-DPM via ATRP

A dry glass tube was charged with CuBr, PMDETA, Mv-2-DPM, 2-Bromoisobutyryl bromide initiator, and chlorobenzene. The mixture was degassed by four freeze-pump-thaw cycles and sealed under vacuum. The tube was place into an oil bath preset at 110 °C. After an expected period of time, the polymerization was terminated by putting the tube into ice/water mixture, the tube was broken. The product was diluted with THF and passed through a basic alumina column to remove copper complex. The polymer was precipitated into petroleum ether, followed by drying at 50 °C under vacuum for 24 h, the Pv-2-DPMs were obtained.



Scheme S1 Chemical structure and synthesis of Pv-2-DPMs

S3 IR spectrum results of monomers and corresponding polymers

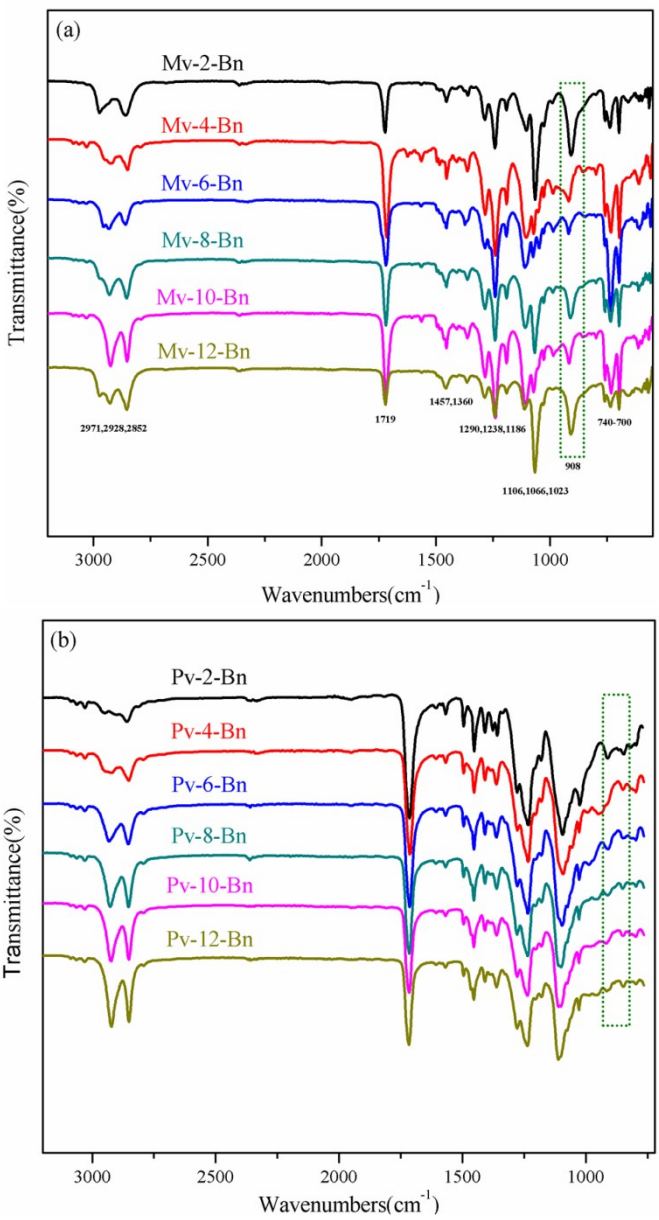


Figure S1: IR spectra results of monomers Mv-n-Bn (a) and polymers Pv-n-Bn (b).

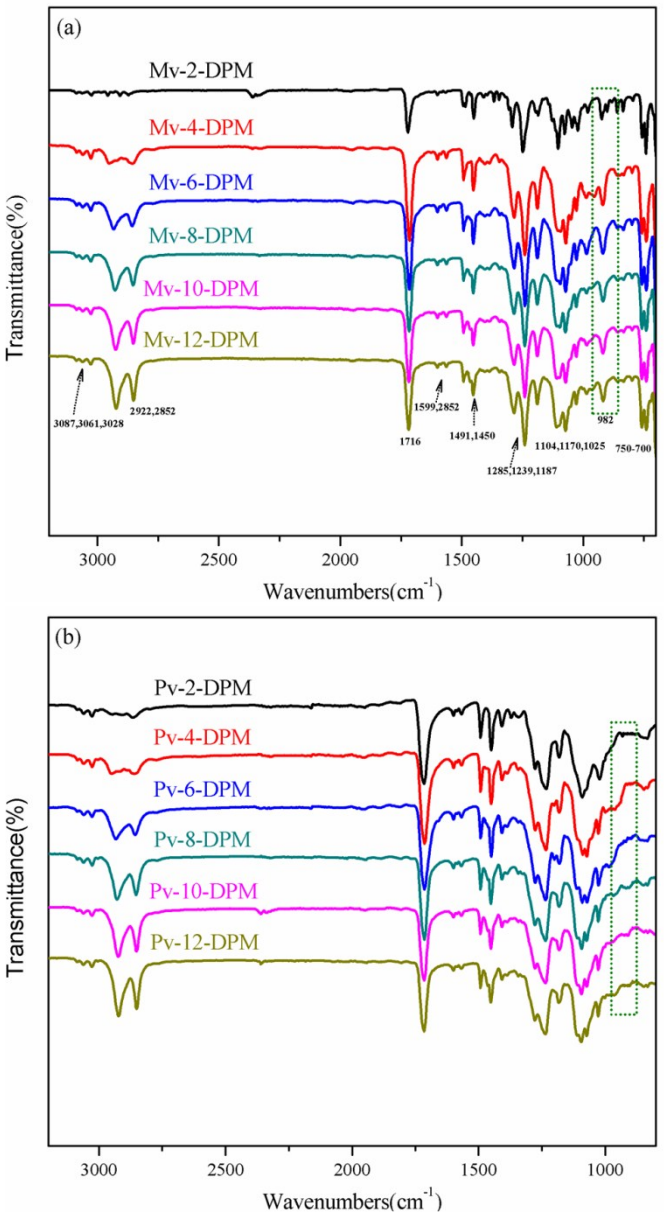


Figure S2: IR spectra results of monomers Mv-n-DPM (a) and polymers Pv-n-DPM (b).

S4 GPC curves of Pv-2DPMs

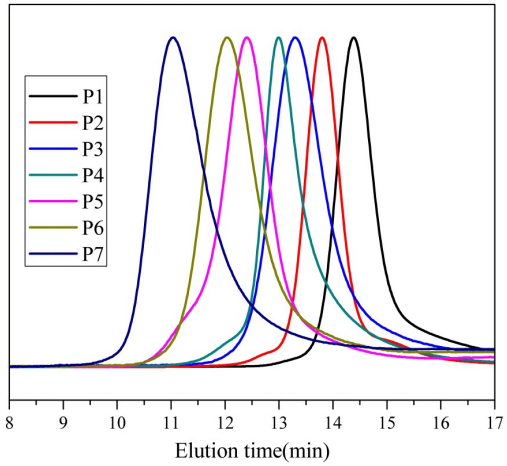


Figure S3: GPC traces of the polymers Pv-2-DPMs

S5 Molecular characteristics and properties of the series of Pv-2-DPMs

Table S1 Molecular characteristics and properties of the series of Pv-2-DPMs

Sample	M_n ($\times 10^{-4}$)[a]	PDI[a]	T_g (^oC)[c]	T_1 (^oC)[d]	Liquid crystallinity[d]
P1	1.73	1.12	44.4		No
P2	3.40	1.18	44.8	224	Yes
P3	4.97	1.16	45.7	162	Yes
P4	5.73	1.19	45.8	143	Yes
P5	8.48	1.15	45.5	137	Yes
P6	9.71	1.21	45.6		Yes
P7	13.73	1.24	45.5		Yes

S6 The change of reflection light intensity curves upon heating and cooling process

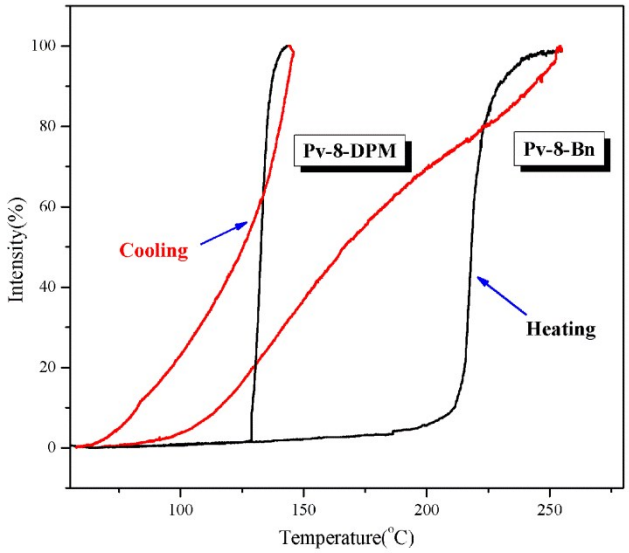


Figure S4: Reflection light intensity curves of heating and subsequent cooling of Pv-8-Bn and Pv-8-DPM at a rate of 10 °C /min.

S7 DSC curves of polymers Pv-2-DPMs

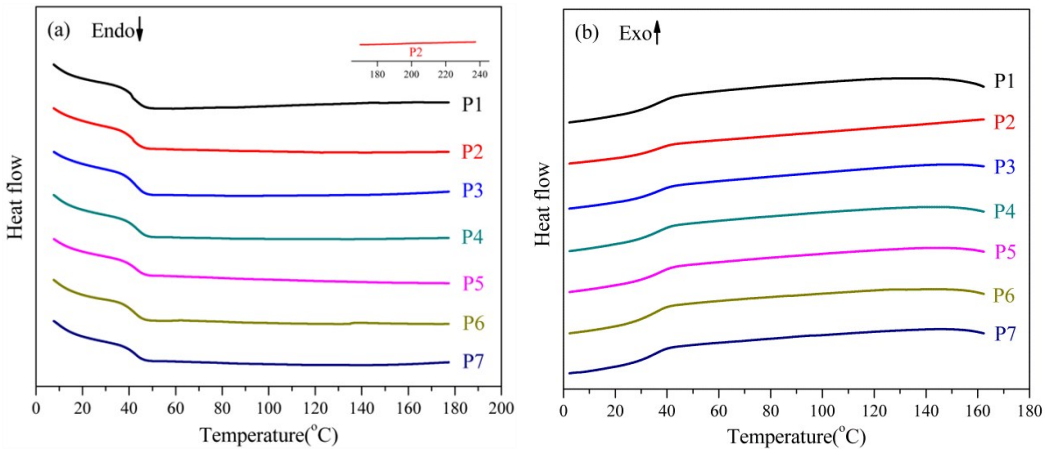


Figure S5: DSC curves of polymers Pv-2-DPMs during the second heating scan (a) and the first cooling scan (b) at a rate of 10 °C /min under nitrogen atmosphere.

S8 1D WAXD patterns of P1

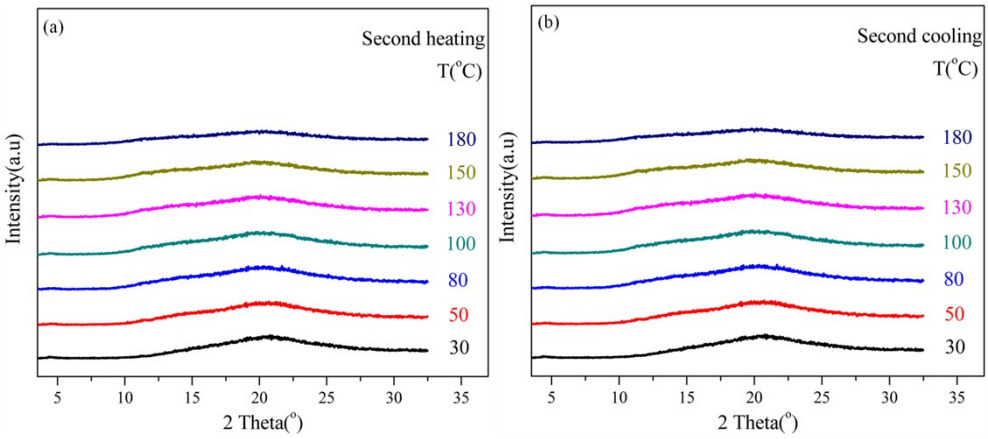


Figure S6: 1D WAXD patterns of P1 during the second heating (a) and subsequent cooling (b)