

Supramolecular Ordered Structures of Main-chain/Side-chain Liquid Crystalline Polymer based on “Jacketing” Effect with Different Length of Spacer: From Hierarchical Structure to Smectic Structure

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The synthetic route of the monomers Mn (n = 2, 4, 6, 8, 10)

Synthesis of 1-4'-butoxy-4-biphenol

4,4'-biphenol(16.7g, 0.089mol), K₂CO₃(12.4g, 0.089mol), and 90 ml N, N - dimethylformamide (DMF) were added to a three-necked bottom flask with continuous magnetic stirring and then add alpha bromobutane (12.3g, 0.089 mol) of DMF (200 ml) solution into the bottom flask, heating reflux for 5h. After the complete reaction, the reaction solution was poured into cool water for the white solid product, dried by vacuum. After drying, the crude product was purified by recrystallization and column chromatography, the solvent removed by rotary evaporation apparatus, get the white flake crystal. Yield, 46%. mp:160-162°C. ¹H NMR (DMSO-d₆) δ (ppm): 9.47 (s, 1 H, -OH), 7.45 (d, 2 H, Ar-H), 7.41 (d, 2 H, Ar-

H), 6.92 (d, 2 H, Ar-H), 6.84 (d, 2 H, Ar-H), 3.93 (t, 2 H, CH₂O), 1.68 (m, 2 H, CH₂), 1.42 (m, 2 H, CH₂), 0.92 (t, 3 H, CH₃).

Synthesis of ω -(4'-butoxy biphenyl-4-yloxy)-1-bromo-ethane

The mixture of 1,2-dibromoethane (22.8 g, 123 mmol), K₂CO₃(8.5 g, 62 mmol), 1-4'-butoxy-4- biphenol(10 g, 4.1×10^{-2} mol) and acetone (50 mL) was added into a 100 mL round bottom flask with continuous magnetic stirring, and heating reflux for 24 h under the protection of Nitrogen, Cool to room temperature, then pour reaction solution into the amount of water slowly, solid precipitation, filtration, The crude product was purified by column chromatography, get a white flake crystal. Yield, 72%. ¹ H NMR(CDCl₃) δ (ppm): 7.45 (q, 4 H, Ar-H), 6.94 (q, 4 H, Ar-H), 4.32 (t, 2 H, -OCH₂-), 4.00 (t, 2 H, -OCH₂-), 3.65 (t, 2 H, -CH₂Br), 1.82 (m, 2 H, -CH₂-), 1.53 (m, 2 H, -CH₂-), 0.99 (t, 3 H, -CH₃). Yield: 70%.

Synthesis of 2-vinyl p-biphtalic acid

Vinyl p-biphtalic acid was prepared using the procedure described by zhang et al.

¹H NMR (DMSO-*d*₆) δ (ppm): 8.24 (s, 1H, Ar-*H*), 7.92 (d, 2H, Ar-*H*), 6.67 (d, 2H, =CH-), 5.75 (d, 1H, =CH₂), 5.42(d, 1H, =CH₂)

Synthesis of 2,5-bis{[6-(4-butoxy-4'-oxybiphenyl) ethyl]oxycarbonyl}styrene

2-vinyl p-biphtalic acid(3.84 g, 2.5×10^{-2} mol), KHCO₃(5.0 g, 5.0×10^{-2} mol), ω -(4'-butoxy biphenyl-4-yloxy)-1-bromo-ethane(10.5 g 5.0×10^{-2}), 20 mL N, N - dimethylformamide (DMF) and a drop of nitrobenzene was added into a 100 mL bottom flask. Heating to 100 °C for 24 h. Filter and the filtrate was poured slowly into some cold water, solid precipitation, filtration, vacuum drying, the crude product was purified by column chromatography, get white solid product, the yield is estimated to

be about 51%. ¹ H NMR(CDCl₃) δ (ppm): 8.38 (s, 1 H, Ar-H), 8.05 (q, 2 H, Ar-H), 7.56 (q, 4 H, Ar-H), 7.38 (d, 2 H, =CH-), 7.06 (m, 4 H, Ar-H), 5.89 (d, 1 H, =CH₂), 5.51 (d, 1 H, =CH₂), 4.81 (m, 4 H, -OCH₂-), 4.47 (m, 4 H, -OCH₂-), 5.11 (t, 4 H, -OCH₂-), 1.92 (m, 4 H, -CH₂-), 1.62 (m, 4 H, -CH₂-), 1.11 (t, 6 H, -CH₃) . ¹³ C NMR(CDCl₃) δ (ppm): 166.80(C=O), 165.80(C=O), 157.65-157.72(biphenyl C-O), 139.84 (aromatic C-CH=CH₂), 134.86 (aromatic C-C=O), 133.44-133.60 (aromatic and =CH-), 132.39 (aromatic C-C=O), 130.67 (aromatic meta C-CH=CH₂), 128.36-128.58 (biphenyl C ortho to C-O), 127.83-127.93 (biphenyl C-O), 127.84 (=CH₂), 114.93-115.14(biphenyl C ortho to C-O), 67.92 (-OCH₂-), 63.98(-OCH₂-), 63.89 (-OCH₂-), 31.50 (-CH₂-), 19.40 (-CH₂-), 13.99 (-CH₃).

Other monomers with different length of flexible alkyl spacer were synthesized by the same method.

Synthesis of 2,5-bis{[4-(4-butoxy-4'-oxybiphenyl) butyl]oxycarbonyl}styrene

¹ H NMR(CDCl₃) δ (ppm): 8.24 (s, 1 H, Ar-H), 7.92 (q, 2 H, Ar-H), 7.45 (d, 4 H, Ar-H), 7.38 (s, 2 H, =CH-), 6.94 (m, 4 H, Ar-H), 5.75 (d, 1 H, =CH₂), 5.42 (d, 1 H, =CH₂), 4.43 (m, 4 H, -OCH₂-), 4.01 (m, 8 H, -OCH₂-), 1.99 (m, 8 H, -CH₂-), 1.77 (m, 4 H, -CH₂-), 1.52 (m, 4 H, -CH₂-), 0.98 (t, 6 H, -CH₃).

¹³ C NMR(CDCl₃) δ (ppm): 166.90 (C=O), 165.85 (C=O), 158.43-158.10 (biphenyl C-O), 138.84 (aromatic C-CH=CH₂), 133.86 (aromatic C-C=O), 132.44-132.60 (aromatic and =CH-), 131.39 (aromatic C-C=O), 129.67 (aromatic meta C-CH=CH₂), 128.31-128.40 (biphenyl C ortho to C-O), 127.83-127.79 (biphenyl C-O), 118.84 (=CH₂), 114.86-114.89 (biphenyl C ortho to C-O), 67.91 (-OCH₂-), 67.43 (-OCH₂-), 63.55 (-OCH₂-), 31.50 (-CH₂-), 25.66-26.19 (-CH₂-), 19.40 (-CH₂-), 13.99 (-CH₃).
Yield: 78%.

Synthesis of 2,5-bis{[6-(4-butoxy-4'-oxybiphenyl) hexyl]oxycarbonyl}styrene

^1H NMR(CDCl_3) δ (ppm): 8.24 (s, 1 H, Ar-H), 7.92 (d, 2 H, Ar-H), 7.45 (d, 4 H, Ar-H), 6.94 (d, 4 H, Ar-H), 6.67 (d, 1 H, =CH-), 5.75 (d, 1 H, =CH₂), 5.42 (d, 1 H, =CH₂), 4.35 (t, 4 H, -CH₂-), 4.00 (t, 8 H, -CH₂-), 1.80 (m, 12 H, -CH₂-), 1.54 (m, 12 H, -CH₂-), 0.98 (t, 3 H, -CH₃).

^{13}C NMR: 166.02(C=O), 165.92(C=O), 158.28-158.42 (biphenyl C-O), 139.56 (aromatic C-CH=CH₂), 135.08 (aromatic C-C=O), 133.44-133.60 (aromatic and =CH-), 132.83 (aromatic C-C=O), 130.35 (aromatic meta C-CH=CH₂), 128.16-128.40 (biphenyl C ortho to C-O), 127.76-127.86 (biphenyl C), 127.66 (=CH₂), 114.89-114.92 (biphenyl C ortho to C-O), 67.93-67.98 (-OCH₂-), 65.53 (-OCH₂-), 64.02 (-OCH₂-), 29.33 (-CH₂-), 28.60-28.76 (-CH₂-), 25.76-25.98 (-CH₂-), 19.38 (-CH₂-), 13.94 (-CH₃).

Synthesis of 2,5-bis{[8-(4-butoxy-4'-oxybiphenyl) butyl]oxycarbonyl}styrene

^1H NMR(CDCl_3) δ (ppm): 8.23 (s, 1 H, Ar-H), 7.91 (q, 2 H, Ar-H), 7.43 (q, 4 H, Ar-H), 7.38 (d, 2 H, =CH-), 6.92 (m, 4 H, Ar-H), 5.73 (d, 1 H, =CH₂), 5.41 (d, 1 H, =CH₂), 4.32 (t, 4 H, -OCH₂-), 3.97 (m, 8 H, -OCH₂-), 1.81 (m, 12 H, -CH₂-), 1.50 (m, 20 H, -CH₂-), 0.98 (t, 6 H, -CH₃).

^{13}C NMR(CDCl_3) δ (ppm): 167.10 (C=O), 166.80 (C=O), 158.35-158.37 (biphenyl C-O), 140.14 (aromatic C-CH=CH₂), 135.16 (aromatic C-C=O), 133.44-133.60 (aromatic and =CH-), 132.86 (aromatic C-C=O), 131.17 (aromatic meta C-CH=CH₂), 129.36-129.58 (biphenyl C ortho to C-O), 127.76-127.93 (biphenyl C-O), 128.84 (=CH₂), 114.88-115.01 (biphenyl C ortho to C-O), 68.18 (-OCH₂-), 67.89 (-OCH₂-), 63.98(-OCH₂-), 31.51 (-CH₂-), 29.35-29.60 (-CH₂-), 28.76-28.79 (-CH₂-), 26.12-26.18 (-CH₂-), 19.40 (-CH₂-), 13.99 (-CH₃).

Synthesis of 2,5-bis{[10-(4-butoxy-4'-oxybiphenyl) decyl]oxycarbonyl}styrene

^1H NMR(CDCl_3) δ (ppm): 8.23 (s, 1 H, Ar-H), 7.91 (q, 2 H, Ar-H), 7.43 (q, 4 H, Ar-H), 7.38 (d, 2 H, =CH-), 6.92 (m, 4 H, Ar-H), 5.73 (d, 1 H, =CH₂), 5.41 (d, 1 H, =CH₂), 4.32 (t, 4 H, -OCH₂-), 3.97 (m, 8 H, -OCH₂-), 1.81 (m, 12 H, -CH₂-), 1.50 (m, 28 H, -CH₂-), 0.98 (t, 6 H, -CH₃) .

^{13}C NMR(CDCl_3) δ (ppm): 167.10 (C=O), 166.80 (C=O), 158.35-158.37 (biphenyl C-O), 140.14 (aromatic C-CH=CH₂), 135.16 (aromatic C-C=O), 133.44-133.60 (aromatic and =CH-), 132.86 (aromatic C-C=O), 131.17 (aromatic meta C-CH=CH₂), 129.36-129.58 (biphenyl C ortho to C-O), 127.76-127.93 (biphenyl C-O), 128.84 (=CH₂), 114.88-115.01 (biphenyl C ortho to C-O), 68.18 (-OCH₂-), 67.89 (-OCH₂-), 63.98(-OCH₂-), 31.51 (-CH₂-), 29.35-29.60 (-CH₂-), 28.76-28.79 (-CH₂-), 26.12-16.18 (-CH₂-), 19.40 (-CH₂-), 13.99 (-CH₃).

Figure S1-S6.

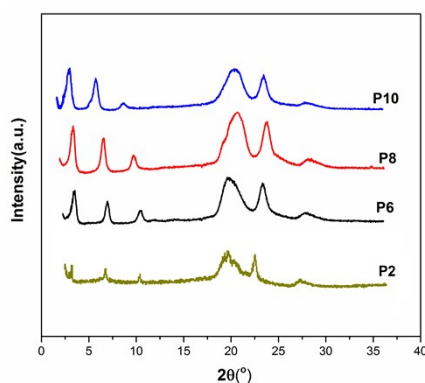


Figure S1. Set of 1D WAXD powder patterns of Mn($n=2, 6, 8, 10$)

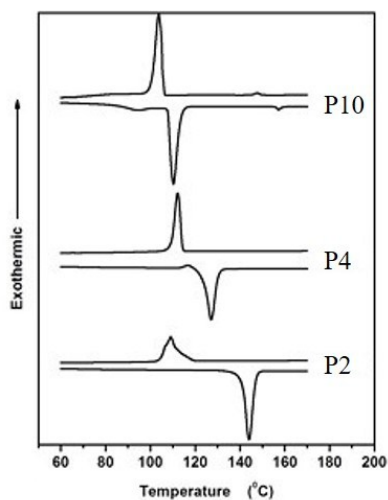


Figure S2. DSC thermograms of P2, P4 and P10 at a rate 10 °C /min during the

process of heating and the process of cooling.

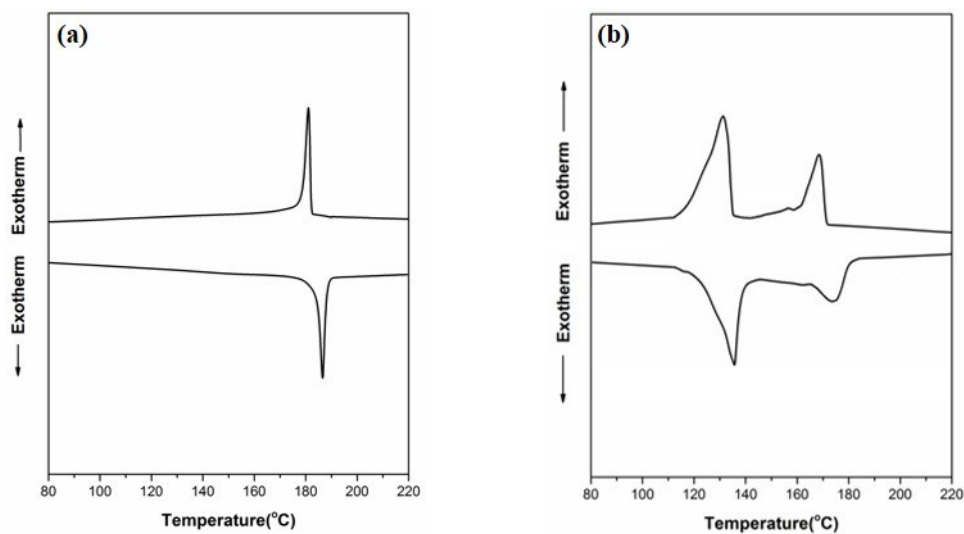


Figure S3. DSC thermograms of P4 (a) and P8 (b) at a rate 10 °C /min during the process of heating and the process of cooling.

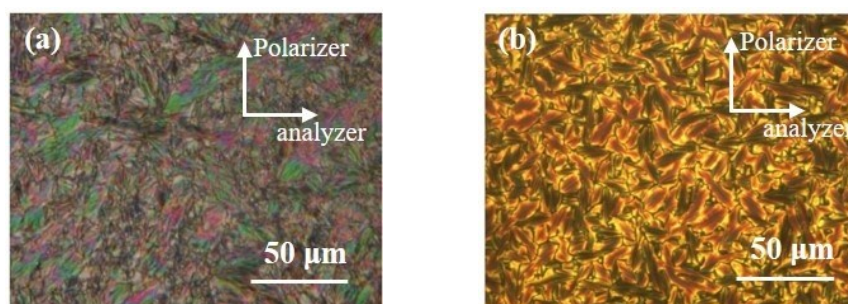


Figure S4. Representative textures of P4 (a) and P8 (b) at 170 °C (200 × magnification).

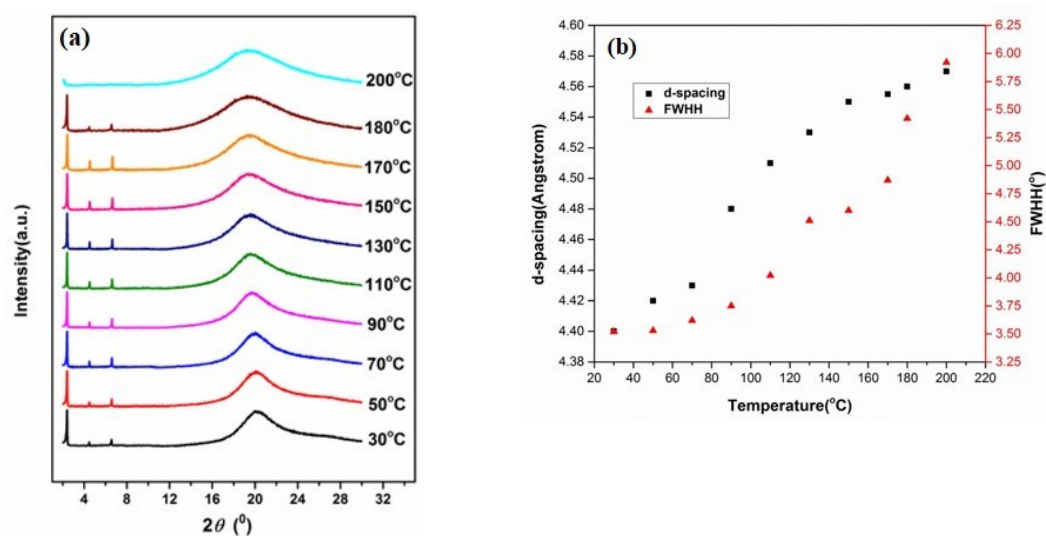


Figure S5. Set of 1D WAXD powder patterns of P4 at different temperatures recorded upon cooling (a), and d-spacing at the peak position and full width of half-

height (fwhh) of the high-angle diffraction/scattering as functions of temperature (b).

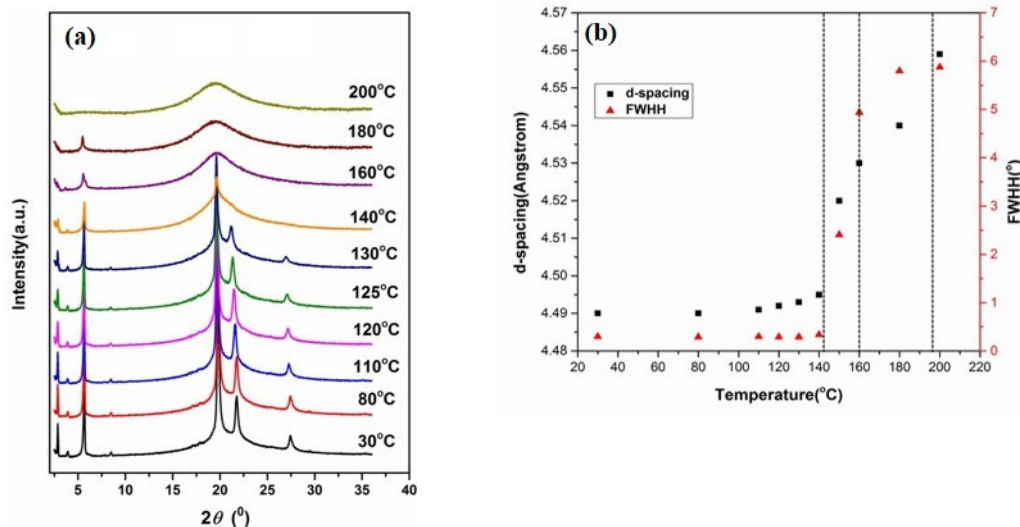


Figure S6. Set of 1D WAXD powder patterns of P8 at different temperatures recorded upon cooling (a), and d-spacing at the peak position and full width of half-height (fwhh) of the high-angle diffraction/scattering as functions of temperature (b).

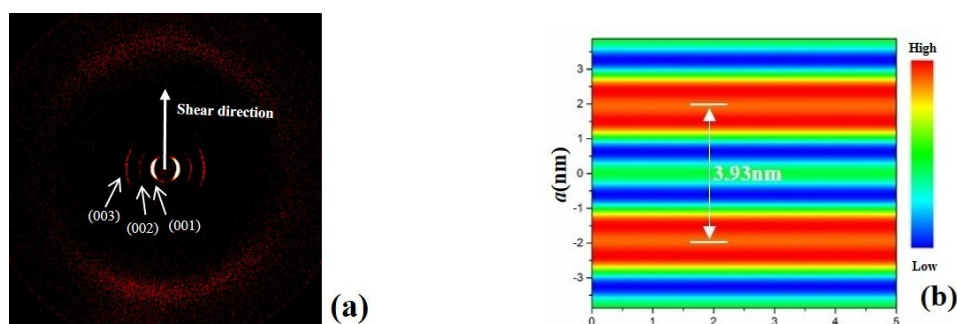


Figure S7. 2D WAXD patterns of P4 recorded with X-ray beam perpendicular to the shear direction(x-direction) at room temperature. (b) Relative electron density map of smectic structure of P4.

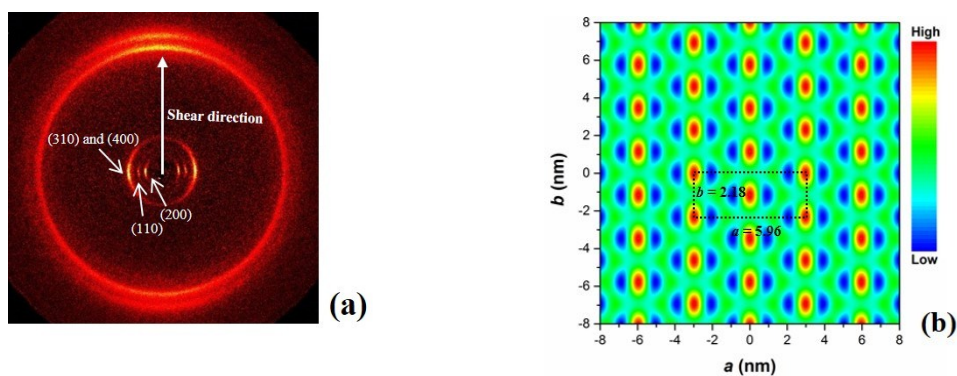


Figure S8. 2D WAXD patterns of P4 recorded with X-ray beam parallel to the

shear direction(x-direction) at room temperature. (b) Relative electron density map of P8.

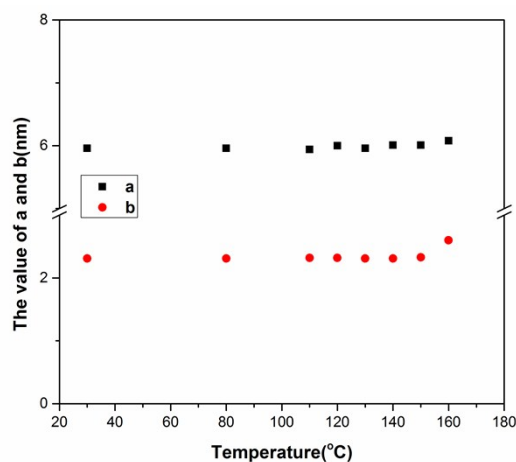


Figure S9. Temperature dependence of the calculated a and b of the rectangular lattice of P8.

The values of intensity and the phase used for Fourier reconstruction was given in S-Table 1 and the possibility maps was outlined in figure S10,(the structure of P6 and P8 was similar to P10, so, we just outlined the possibility maps of P10.)

S-Table 1. The values of intensity and the lattice of the P_n ($n = 6, 8, 10$)

Sample	The values of intensity				Lattice
	I_{200}	I_{110}	I_{310}	I_{400}	
P6	2228	931	2904	4843	Rectangular
P8	2225	274	3452	3445	
P10	1333	1296	4127	3634	

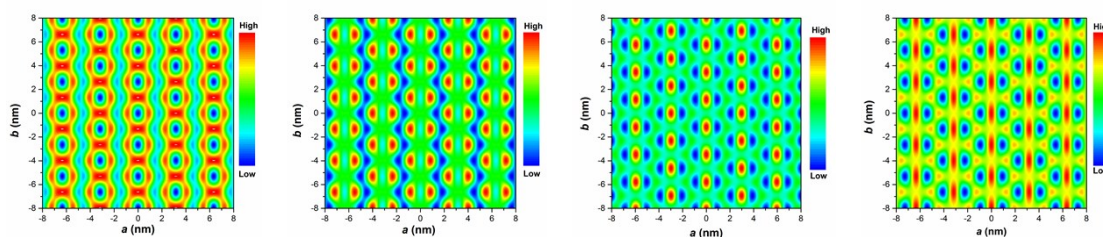


Figure S10. Others Relative electron density map of structure of P10.