Supporting Information

for

Synthesis and Self-Organization of Azobenzene Containing Hemiphasmidic Side-Chain Liquid-Crystalline Polymers with Different Spacer Lengths

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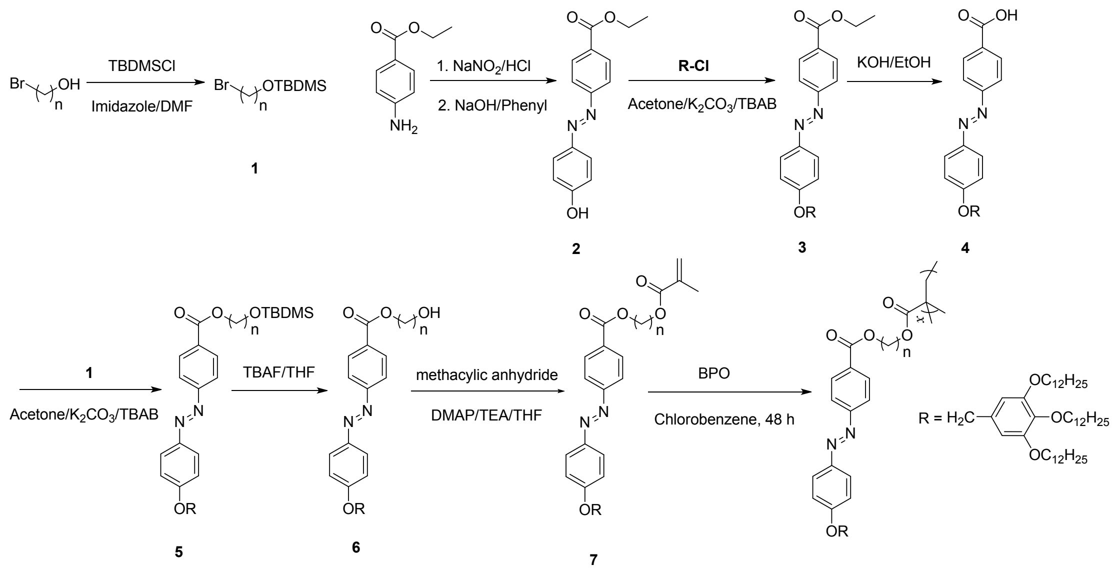
1. Molecular characterization data



Compound 1

n = 2: ^{1}H NMR (400 MHz, CD_3Cl): δ (ppm) = 3.89 (t, *J* = 6.4 Hz, 2H), 3.39 (t, *J* = 6.4 Hz, 2H), 0.91 (s, 9H), 0.09 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 63.52, 33.25, 25.83, 18.33, -5.26. FTMS (ESI): calcd. for $C_8H_{20}B_rOSi[M+H]^+$: m/z = 239.048; found: 240.987. Elemental analysis (%) calcd. for $C_8H_{19}B_rOSi$: C, 40.17; H, 8.01; found: C, 40.30; H, 8.02.

n = 6: ^{1}H NMR (400 MHz, CD_3Cl): δ (ppm) = 3.61 (t, *J* = 6.4 Hz, 2H), 3.41 (t, *J* = 6.4 Hz, 2H), 1.90-1.83 (m, 2H), 1.56-1.49 (m, 2H), 1.47-1.41 (m, 2H), 1.39-1.34 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 63.02, 33.86, 32.83, 32.64, 27.99, 25.98, 25.04, 18.36, -5.27. FTMS (ESI): calcd. for $C_{12}H_{28}B_rOSi[M+H]^+$: m/z = 295.109; found: 295.109. Elemental analysis (%) calcd. for $C_{12}H_{27}B_rOSi$: C, 48.80; H, 9.22; found: C, 48.82; H, 9.36.

n = 10: ^{1}H NMR (400 MHz, CD_3Cl): δ (ppm) = 3.60 (t, *J* = 6.4 Hz, 2H), 3.40 (t, *J* = 6.4 Hz, 2H), 1.89-1.82 (m, 2H), 1.52-1.47 (m, 2H), 1.44-1.38 (m, 2H), 1.33-1.27 (m, 10H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 63.30, 33.98, 32.88, 32.86, 29.51, 29.39, 28.76, 28.19, 26.00, 25.80, 18.38, -5.27. FTMS (ESI): calcd. for $C_{16}H_{36}B_rOSi[M+H]^+$: m/z = 351.171; found:

351.172. Elemental analysis (%) calcd. for $C_{16}H_{35}B_rOSi$: C, 54.68; H, 10.04; found: C, 54.73; H, 10.11.

n = 14: ^{1}H NMR (400 MHz, CD_3Cl): δ (ppm) = 3.60 (t, *J* = 6.4 Hz, 2H), 3.40 (t, *J* = 6.4 Hz, 2H), 1.89-1.82 (m, 2H), 1.52-1.47 (m, 2H), 1.44-1.38 (m, 2H), 1.33-1.27 (m, 10H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 63.30, 33.98, 32.88, 32.86, 29.51, 29.39, 28.76, 28.19, 26.00, 25.80, 18.38, -5.27. FTMS (ESI): calcd. for $C_{16}H_{36}B_rOSi[M+H]^+$: m/z = 351.171; found: 351.172. Elemental analysis (%) calcd. for $C_{16}H_{35}B_rOSi$: C, 54.68; H, 10.04; found: C, 54.73; H, 10.11.

Compound 2

^{1}H NMR (400 MHz, CD_3Cl): δ (ppm) = 8.18 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 5.89 (s, 1H), 4.43 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 166.24, 162.28, 156.21, 147.24, 132.55, 131.30, 126.26, 123.10, 116.86, 61.74, 14.58. Elemental analysis (%) calcd. for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22, N, 10.36; found: C, 66.84; H, 5.37; N, 10.43.

Compound 3

^{1}H NMR (400 MHz, CD3Cl): δ (ppm) = 8.18 (d, J = 8.4 Hz, 2H), 7.95 (d, *J* = 9.2 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.64 (s, 2H), 5.04 (s, 2H), 4.41 (q, *J* = 7.2 Hz, 2H), 4.00-3.94 (m, 6H), 1.83-1.70 (m, 6H), 1.48-1.41 (m, 9H), 1.38-1.18 (m, 48H), 0.88 (t, *J* = 6.4 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 166.16, 161.83, 155.30, 153.41, 147.17, 138.22, 131.62, 131.14, 130.55, 125.17, 115.21, 106.23, 73.47, 70.75, 69.21, 61.20, 31.94, 30.36, 29.77, 29.72, 29.66, 29.38, 26.15, 26.12, 22.70, 14.35, 14.12. FTMS (ESI): calcd. for $C_{58}H_{93}N_2O_6$ $[M+H]^+$: m/z = 913.703; found: 913.700. Elemental analysis (%) calcd. for $C_{58}H_{93}N_2O_6$: C, 76.27; H, 10.15; N, 3.07; found: C, 76.47; H, 10.30; N, 3.02.

Compound 4

^{1}H NMR (400 MHz, CD_3Cl): δ (ppm) = 8.26 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 9.2 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 6.64 (s, 2H), 5.05 (s, 2H), 4.00-3.94 (m, 6H), 1.84-1.72 (m, 6H), 1.48-1.41 (m, 6H), 1.38-1.18 (m, 48H), 0.88 (t, *J* = 6.4 Hz, 9H).^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 170.70, 161.98, 155.94, 153,42, 147.17, 138.22, 131.29, 131.12, 130.18, 125.29, 122.49, 115.25, 106.23, 73.40, 70.77, 69.22, 31.94, 30.36, 29.77, 29.72, 29.66, 29.42, 29.38, 26.15, 26.12, 22.70, 14.12. FTMS (ESI): calcd. for $C_{56}H_{89}N_2O_6$ $[M+H]^+$: m/z = 885.671; found: 885.670. Elemental analysis (%) calcd. for $C_{56}H_{88}N_2O_6$: C, 75.97; H, 10.02; N, 3.16; found: C, 76.04; H, 10.01; N, 3.02.

Compound 5

n = 2: ^{1}H NMR (400 MHz, CD_3Cl)： δ (ppm) = 8.19 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 9.2 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.64 (s, 2H), 5.05 (s, 2H), 4.43 (t, *J* = 5.0 Hz, 2H), 4.00-3.94 (m, 8H), 1.83-1.71 (m, 6H), 1.48-1.43 (m, 6H), 1.38-1.18 (m, 48H), 0.91-0.86 (m, 18H), 0.09 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 166.12, 161.12, 155.35, 153.40, 147.15, 138.17, 131.36, 131.13, 130.65, 125.18, 122.36, 115.20, 106.19, 73.47, 70.75, 69.19, 66.41, 61.33, 31.94, 30.35, 29.77, 29.71, 29.66, 29.43, 29.41, 29.38, 26.15, 26.11, 25.84, 22.70, 18.33, 14.13, -5.27. FTMS (ESI): calcd. for $C_{64}H_{107}N_2O_7Si$ $[M+H]^+$: m/z = 1043.784; found: 1043.782. Elemental analysis (%) calcd. for $C_{64}H_{106}N_2O_7Si$: C, 73.85; H, 10.40; N, 2.65; found: C, 73.66; H, 10.24; N, 2.68.

n = 6: δ (ppm) = 8.18 (d, *J* = 8.5 Hz, 2H), 7.95 (d, *J* = 9.0 Hz, 2H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.63 (s, 2H), 5.04 (s, 2H), 4.35 (t, *J* = 6.5 Hz, 2H), 4.00-3.94 (m, 6H), 3.62 (t, *J* =

6.5 Hz, 2H), 1.83-1.71 (m, 8H), 1.59-1.53 (m, 2H), 1.50-1.41 (m, 6H), 1.34-1.18 (m, 52H), 0.90-0.86 (m, 18H), 0.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 166.19, 161.86, 155.35, 153.44, 147.21, 138.31, 131.66, 131.18, 130.55, 125.18, 122.37, 115.24, 106.30, 73.48, 70.77, 69.27, 65.31, 63.09, 32.75, 31.95, 30.38, 29.78, 29.72, 29.67, 29.45, 29.41, 29.38, 28.80, 26.17, 26.13, 25.58, 22.71, 18.38, 14.11, -5.25. FTMS (ESI): calcd. for $C_{68}H_{115}N_2O_7Si$ $[M+H]^+$: m/z = 1099.847; found: 1099.848. Elemental analysis (%) calcd. for $C_{68}H_{114}N_2O_7Si$: C, 74.40; H, 10.53; N, 2.52; found: C, 74.27; H, 10.45; N, 2.55.

n = 10: δ (ppm) = 8.17 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 9.2 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 9.2 Hz, 2H), 6.64 (s, 2H), 5.05 (s, 2H), 4.34 (t, *J* = 6.4 Hz, 2H), 4.00-3.94 (m, 6H), 3.60 (t, *J* = 6.4 Hz, 2H), 1.83-1.71 (m, 8H), 1.59-1.43 (m, 8H), 1.34-1.18 (m, 60H), 0.89-0.86 (m, 18H), 0.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 166.22, 161.83, 155.30, 153.41, 147.16, 138.21, 131.66, 131.14, 130.55, 125.18, 122.36, 115.20, 106.22, 73.47, 70.75, 69.21, 65.40, 63.33, 32.89, 31.94, 30.36, 29.77, 29.72, 29.66, 29.56, 29.49, 29.43, 29.42, 29.38, 29.30, 28.74, 26.15, 26.12, 26.06, 26.00, 25.80, 22.70, 18.39, 14.12, -5.25. FTMS (ESI): calcd. for $C_{72}H_{123}N_2O_7Si$ $[M+H]^+$: m/z = 1155.909; found: 1155.911. Elemental analysis (%) calcd. for $C_{72}H_{123}N_2O_7Si$: C, 74.82; H, 10.64; N, 2.42; found: C, 74.03; H, 10.60; N, 2.37.

n = 14: ^{1}H NMR (400 MHz, CD_3Cl): δ (ppm) = 3.60 (t, *J* = 6.4 Hz, 2H), 3.40 (t, *J* = 6.4 Hz, 2H), 1.89-1.82 (m, 2H), 1.52-1.47 (m, 2H), 1.44-1.38 (m, 2H), 1.33-1.27 (m, 10H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 63.30, 33.98, 32.88, 32.86, 29.51, 29.39, 28.76, 28.19, 26.00, 25.80, 18.38, -5.27. FTMS (ESI): calcd. for $C_{16}H_{36}B_rOSi[M+H]^+$: m/z = 351.171; found: 351.172. Elemental analysis (%) calcd. for $C_{16}H_{35}B_rOSi$: C, 54.68; H, 10.04; found: C, 54.73; H, 10.11.

Compound 6

n = 2: ^{1}H NMR (400 MHz, CD_3Cl): δ (ppm) = 8.20 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.64 (s, 2H), 5.05 (s, 2H), 4.51 (t, *J* = 4.8 Hz, 2H), 4.01-3.94 (m, 8H), 1.83-1.71 (m, 6H), 1.48-1.43 (m, 6H), 1.38-1.18 (m, 48H), 0.89-0.86 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 166.40, 161.88, 155.44, 153.35, 147.08, 138.16, 131.05, 130.85, 130.68, 125.19, 122.38, 115.17, 107.05, 106.17, 73.41, 70.70, 69.16, 66.83, 61.42, 31.88, 30.30, 29.71, 29.65, 29.60, 29.35, 29.32, 26.05, 22.64, 14.06. FTMS (ESI): calcd. for $C_{58}H_{93}N_2O_7$ $[M+H]^+$: m/z = 929.698; found: 929.698. Elemental analysis (%) calcd. for $C_{58}H_{92}N_2O_7$: C, 74.96; H, 9.98; N, 3.01; found: C, 74.75; H, 9.94; N, 3.00.

n = 6: δ (ppm) = 8.18 (d, *J* = 6.8 Hz, 2H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.92 (d, *J* = 6.8 Hz, 2H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.65 (s, 2H), 5.06 (s, 2H), 4.37 (t, *J* = 5.6 Hz, 2H), 4.01-3.96 (m, 6H), 3.68 (t, *J* = 5.2 Hz, 2H), 1.86-1.73 (m, 8H), 1.66-1.60 (m, 2H), 1.52-1.45 (m, 6H), 1.34-1.18 (m, 52H), 0.91-0.88 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 166.19, 161. 85, 155.33, 153.41, 147.16, 138.21, 131.56, 131.14, 130.55, 125.19, 122.38, 115.21, 106.22, 73.47, 70.75, 69.21, 65.19, 62.84, 32.65, 31.94, 30.37, 29.78, 29.72, 29.67, 29.44, 29.38, 28.74, 26.16, 26.12, 25.88, 25.46, 22.71, 14.12. FTMS (ESI): calcd. for $C_{62}H_{101}N_2O_7$ $[M+H]^+$: m/z = 985.758; found: 985.761. Elemental analysis (%) calcd. for $C_{62}H_{100}N_2O_7$: C, 75.56; H, 10.23; N, 2.84; found: C, 75.60; H, 10.34; N, 2.86.

n = 10: δ (ppm) = 8.17 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 9.2 Hz, 2H), 6.64 (s, 2H), 5.05 (s, 2H), 4.35 (t, *J* = 6.8 Hz, 2H), 4.00-3.94 (m, 6H), 3.64 (t, *J* = 6.8 Hz, 2H), 1.83-1.71 (m, 8H), 1.58-1.43 (m, 8H), 1.34-1.18 (m, 60H), 0.89-0.86 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 166.22, 161.84, 155.31, 153.41, 147.16, 138.22, 131.64, 131.14, 130.55, 125.18, 122.36, 115.21, 106.23, 73.47, 70.76, 69.21, 65.38, 63.09, 32.81, 31.94, 30.36, 29.77, 29.71, 29.66, 29.51, 29.44, 29.38, 29.25, 28.72, 26.15, 26.12, 26.04, 25.73, 22.70, 14.12. FTMS (ESI): calcd. for $C_{66}H_{109}N_2O_7$ $[M+H]^+$: m/z = 1041.823; found: 1041.821. Elemental analysis (%) calcd. for $C_{72}H_{123}N_2O_7Si$: C, 76.11; H, 10.45; N, 2.69; found: C, 75.54; H, 10.50; N, 2.68.

n = 14: ^{1}H NMR (400 MHz, CD_3Cl): δ (ppm) = 8.17 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.64 (s, 2H), 5.05 (s, 2H), 4.35 (t, *J* = 6.8 Hz, 2H), 3.97 (m, *J* = 6.4 Hz, 6H), 3.63 (t, *J* = 6.8 Hz, 2H), 1.83-1.71 (m, 8H), 1.58-1.43 (m, 8H), 1.38-1.22 (m, 68H), 0.89-0.86 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 166.22, 161.87, 155.34, 153.44, 147.21, 138.31, 131.69, 131.17, 130.55, 125.18, 122.36, 115.25, 106.31, 73.49, 70.77, 69.27, 65.40, 63.11, 32.85, 31.94, 30.38, 29.77, 29.72, 29.66, 29.64, 29.62, 29.59, 29.53, 29.45, 29.41, 29.38, 29.29, 28.75, 26.16, 26.13, 26.07, 25.76, 22.70, 14.11. FTMS (ESI): calcd. for $C_{70}H_{117}N_2O_7$ [M-H+Na]+: m/z = 1119.69; found: 1119.86. Elemental analysis (%) calcd. for $C_{70}H_{116}N_2O_7$: C, 76.69; H, 10.65; N, 2.55; found: C, 75.46; H, 10.54; N, 2.36.

Compound 7

n = 2: ^{1}H NMR (400 MHz, CD_3Cl): δ (ppm) = 8.18 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 9.2 Hz, 2H), 6.64 (s, 2H), 5.60 (m, 1H), 5.05 (s, 2H), 4.62-4.50 (m, 2H), 4.53-4.51 (m, 2H), 4.00-3.94 (m, 6H), 1.96 (broad, 3H), 1.83-1.71 (m, 6H), 1.48-1.43 (m, 6H), 1.38-1.18 (m, 48H), 0.89-0.86 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 167.18, 165.84, 161.92, 155.51, 153.42, 147.15, 138.24, 135.96, 131.13, 130.90, 130.72, 126.14, 125.24, 106.24, 73.48, 70.77, 69.22, 62.87, 62.39, 31.94, 30.37, 29.77, 29.72, 29.44, 26.16, 26.12, 22.70, 14.12. FTMS (ESI): calcd. for $C_{62}H_{97}N_2O_8$ $[M+H]^+$: m/z = 997.724; found: 997.725. Elemental analysis (%) calcd. for $C_{62}H_{96}N_2O_8$: C, 74.66; H, 9.70; N, 2.81; found: C, 74.72; H, 9.82; N, 2.80.

n = 6: δ (ppm) = 8.17 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 9.2 Hz, 2H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 9.2 Hz, 2H), 6.64 (s, 2H), 6.10 (m, 1H), 5.55 (m, 1H), 5.05 (s, 2H), 4.36 (t, *J* = 6.4 Hz, 2H), 4.17 (t, *J* = 6.8 Hz, 2H), 4.00-3.94 (m, 6H), 1.94 (broad s, 3H), 1.82-1.73 (m, 8H), 1.55-1.45 (m, 8H), 1.34-1.18 (m, 52H), 0.89-0.86 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 167.52, 166.18, 161. 86, 155.35, 153.42, 147.18, 138.25, 136.51, 131.55, 131.15, 130.55, 125.23, 122.38, 115.22, 106.25, 73.47, 70.76, 69.23, 65.14, 64.61, 31.94, 30.37, 29.77, 29.72, 29.66, 29.44, 29.38, 28.68, 26.16, 26.12, 25.78, 22.70, 18.33, 14.12. FTMS (ESI): calcd. for $C_{66}H_{105}N_2O_8$ $[M+H]^+$: m/z = 1053.787; found: 1053.786. Elemental analysis (%) calcd. for $C_{66}H_{104}N_2O_8$: C, 75.24; H, 9.95; N, 2.66; found: C, 75.45; H, 9.95; N, 2.57.

n = 10: δ (ppm) = 8.17 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 9.2 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 9.2 Hz, 2H), 6.64 (s, 2H), 6.09 (m, 1H), 5.54 (m, 1H), 5.05 (s, 2H), 4.35 (t, *J* = 6.8 Hz, 2H), 4.14 (t, *J* = 6.8 Hz, 2H), 4.00-3.94 (m, 6H), 1.94 (broad s, 3H), 1.82-1.73 (m, 8H), 1.58-1.43 (m, 8H), 1.34-1.18 (m, 60H), 0.89-0.86 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 167.55, 166.20, 161. 84, 155.31, 153.41, 147.16, 138.21, 136.57, 131.64, 131.16, 130.54, 125.18, 125.12, 122.36, 115.21, 106.22, 73.47, 70.74, 69.21, 65.36, 64.81, 31.94, 30.36, 29.77, 29.72, 29.66, 29.44, 29.27, 29.23, 28.74, 28.62, 26.15, 26.12, 26.05, 25.98, 22.70, 18.33, 14.12. FTMS (ESI): calcd. for $C_{66}H_{105}N_2O_8$ $[M+H]^+$: m/z = 1053.787; found: 1053.786. Elemental analysis (%) calcd. for $C_{66}H_{104}N_2O_8$: C, 75.24; H, 9.95; N, 2.66; found: C, 75.45; H, 9.95; N, 2.57. FTMS (ESI): calcd. for $C_{70}H_{113}N_2O_8$ $[M+H]^+$: m/z = 1109.849; found: 1109.846. Elemental analysis (%) calcd. for $C_{70}H_{112}N_2O_8$: C, 75.77; H, 10.17; N, 2.52; found: C, 75.41; H, 10.08; N, 2.36.

n = 14: ^{1}H NMR (400 MHz, CD_3Cl): δ (ppm) = 3.60 (t, *J* = 6.4 Hz, 2H), 3.40 (t, *J* = 6.4 Hz, 2H), 1.89-1.82 (m, 2H), 1.52-1.47 (m, 2H), 1.44-1.38 (m, 2H), 1.33-1.27 (m, 10H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 63.30, 33.98, 32.88, 32.86, 29.51, 29.39, 28.76, 28.19, 26.00, 25.80, 18.38, -5.27. FTMS (ESI): calcd. for $C_{16}H_{36}B_rOSi$ $[M+H]^+$: m/z = 351.171; found: 351.172. Elemental analysis (%) calcd. for $C_{16}H_{35}B_rOSi$: C, 54.68; H, 10.04; found: C, 54.73; H, 10.11.

2. Reconstruction of electron density maps of P-*n*s

The reconstruction of relative electron density distribution in real space is carried out based on the experimental XRD data using the formula for 2-dimensional Fourier transformation:

$$\rho(x,y)-\rho_0=\sum_{hk}F(hk)\exp\left[-2\pi(hx+ky)\right].$$

Where ρ is the average electron density and *x, y* are the fractional coordinates of a point in the unit cell. *F*(*hk*) is the complex structure factor and its modulus is related to the diffraction intensities *I*(*hk*) by $\left|F(hk)\right|=\sqrt{I(hk)}$. The diffraction intensities need to be multiplicity corrected. The summation is executed over all possible integer combination of (*hk*) except for (00). The lattice is chosen as centrosymmetric, and then the structure factors are real and is given by $F(hk)=\pm\left|F(hk)\right|$, with corresponding possible phase of 0 (+) or π (-). Then the relative electron density can be expressed as

$$\rho(x,y)-\rho_0=\sum_{hk}\pm\sqrt{F(hk)}\cos\left[-2\pi(hx+ky)\right].$$

For the hexagonal columnar phase, three clear peaks can be assigned to reflection (10), (11), (20). The electron density maps have been calculated using the suitable phase combinations for the corresponding reflections. We found that the right phases of "+--" for all hexagonal phases. For the rectangular columnar phase, we considered five peaks which are related to reflection (20), (11), (31),

(02) and (22), and the corresponding right phase combinations are "++-++".

3. Estimation of core radius (R_C) for P-*n*s in hexagonal columnar phase

The radius (R_C) of the core domain occupied by the polymethacrylate main-chain and the flexible spacer within the column of Φ_H was estimated according to the equation below:

$$\frac{\frac{85}{1.2}+\frac{14n}{0.9}}{\frac{M_{\mathrm{rep}}}{\rho}} \times 2\sqrt{3}R_H^{\ 2} = \pi R_C^{\ 2} \qquad \text{(S1)}$$

In this equation, n is the number of methylene units of spacer, M_{rep} the molecular weight of repeating unit, ρ the experimental density measured at 25 °C, R_H the column radius which is a half of the a parameter of the hexagonal lattice. The numbers of 85 and 14 in Eq. S1 are the molar mass of $CH_2C(CH_3)(COO)$ and CH_2 group, respectively. We assume that the densities of polymethacrylate main-chain and alkyl spacer are 1.2 and 0.9 g/cm^3, respectively.

4. Supporting figures

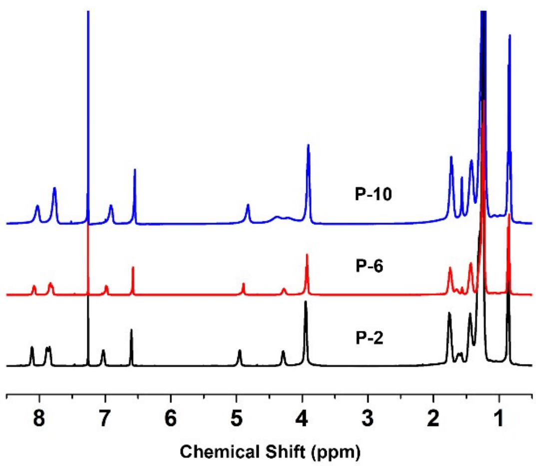


Fig. S1 ^{1}H NMR spectra of the polymers P-2, P-6 and P-10 in $CDCl_3$.

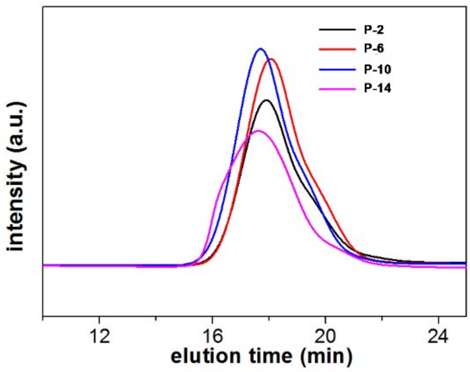


Fig. S2 GPC traces of P-*n* (*n* = 2, 6, 10, and 14) calibrated with polystyrene standard.

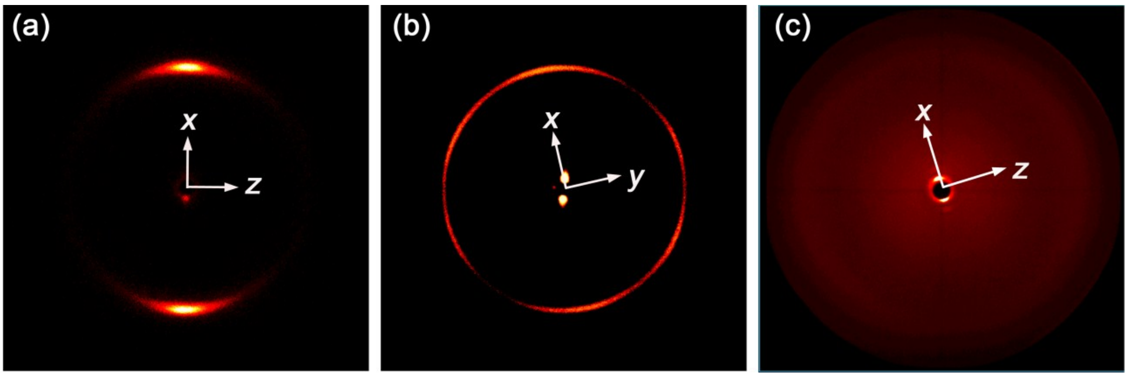


Fig. S3 (a) and (b), 2D XRD patterns of P-2 with X-ray perpendicular and parallel to the shear direction, respectively. The patterns were recorded using Nanostar U small-angle X-ray scattering instrument (Bruker AKS). (c) 2D XRD pattern of P-2 with X-ray perpendicular to the shear direction recorded using Bruker D8 Discover diffractometer with GADDS as 2D detector.

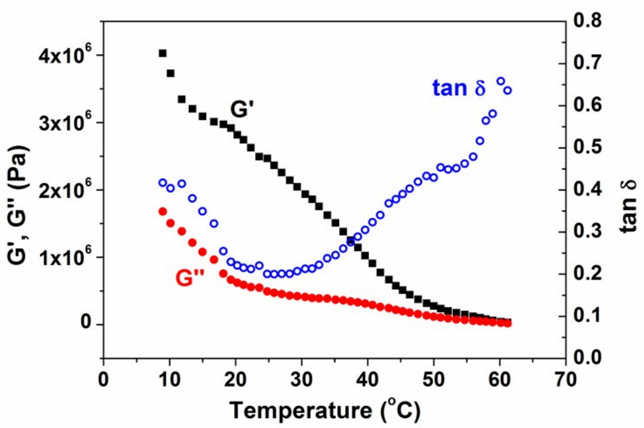


Fig. S4 DMA result of P-14. As shown in Fig. 6 of DSC result, the low temperature endothermic process related to the melting of ordered packing of alkyl tails peaks at ~10 °C. Therefore, the maximum of tanδ at around 12 °C may still correspond to the alkyl tail melting. After alkyl tail melting, *G*' tends to reach a plateau. The further decline of *G*' starts at ~20 °C, which may be more related to the glass transition of P-14. In this case, we suggest that the T_g of P-14 is around 20 °C.

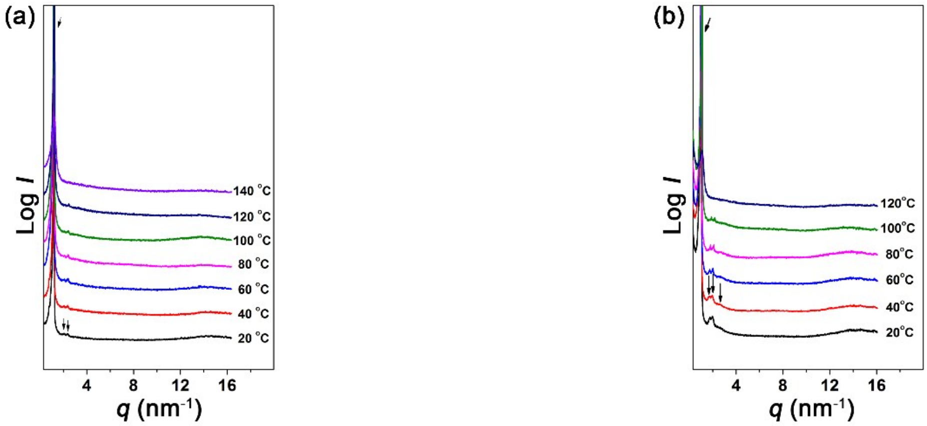


Fig. S5 Thermal 1D XRD results (a) P-2 and (b) P-6 upon heating.

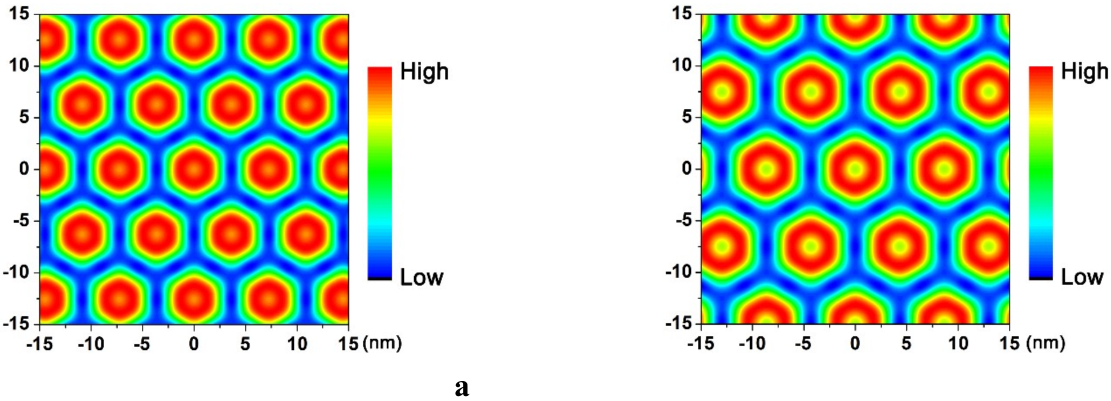


Fig. S6 Relative electron density map of the Φ_H phase for (a) P-6 and (b) P-14 calculated based on XRD results.