Thermotropic Liquid Crystalline Polyimides with Siloxane Linkages: Synthesis, Characterization, and Liquid Crystalline Behavior

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Running Head: Synthesis of Polyimides

Synthesis and characterization of 1b-1c, 2b-2e, 3b-3e, and 6a-6j.

Synthesis of 4-(5-Hexenyloxy)nitrobenzene (1b). The title compound, **1b**, was synthesized by the same procedure as **1a** performed with 2.79 g (20.0 mmol) of 4-nitrophenol, 4.15 g (30.1 mmol) of K₂CO₃, 4.01 g (24.6 mmol) of 6-bromo-1-hexene, and 40 mL of CH₃CN. The compound, **1b**, (4.11 g, 93% yield) was then isolated as a yellow oil after the vacuum. IR (NaCl), ν (cm⁻¹): 2942.8 (Alkyl C-H), 1639.2 (C=C), 1592.9 (Ar C-C), 1511.9, 1342.2 (-NO₂). ¹H NMR (300 MHz, CDCl₃, δ , ppm, 25 °C): 8.19 (d, J=9.3, ArH, 2H), 6.94 (d, J=9.3, ArH, 2H), 5.89-5.76 (m, vinyl proton, 1H), 5.08-4.97 (m, vinyl proton, 2H), 4.06 (t, J=6.5, -CH₂-, 2H), 2.14 (q, J=7.1, -CH₂-, 2H), 1.89-1.80 (m, -CH₂-, 2H), 1.63-1.49

(m, -CH₂-, 2H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm, 25 °C): 164.3, 141.4, 138.3, 126.0, 115.1, 114.5, 68.8, 33.4, 28.5, 25.3.

Synthesis of 4-(3-Butenyloxy)-2-methylnitrobenzene (1c). The title compound, **1c**, was synthesized by the same procedure as **1a** performed with 3.05 g (19.9 mmol) of 3-methyl-4-nitrophenol, 4.27 g (30.9 mmol) of K₂CO₃, 4.02 g (29.8 mmol) of 4-bromo-1-butene, and 50 mL of CH₃CN. The compound, **1c**, (2.61 g, 63% yield) was then isolated as a yellow oil after the vacuum. IR (NaCl), ν (cm⁻¹): 2935 (Alkyl C-H), 1643 (C=C), 1581 (Ar C-C), 1512, 1338 (-NO₂). ¹H NMR (300 MHz, CDCl₃, δ, ppm, 25 °C): 8.08 (d, J=9.9, ArH, 1H), 6.81-6.78 (m, ArH, 2H), 5.95-5.82 (m, vinyl proton, 1H), 5.22-5.11 (m, vinyl proton, 2H), 4.08 (t, J=6.9, -CH₂-, 2H), 2.62 (s, -CH₃, 3H), 2.61-2.53 (m, -CH₂-, 2H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm, 25 °C): 162.5, 142.2, 137.2, 133.8, 127.7, 118.1, 117.7, 112.3, 67.9, 33.5, 21.8.

Synthesis of 1,5-Bis[4-(4-nitrophenoxy)butyl]-1,1,3,3,5,5-hexamethyltrisiloxane (2b). The title compound, **2b**, was synthesized by the same procedure as **2a** performed with 5.11 g (26.4 mmol) of **1a**, 2.10 g (10.1 mmol) of 1,1,3,3,5,5-hexamethyltrisiloxane, 30 drops of Karstedt's catalyst, and 20 mL of toluene. The compound, **2b**, (5.68 g, 95% yield) was then isolated as a pale yellow oil after the vacuum. IR (NaCl), ν (cm⁻¹): 2954.4 (Alkyl C-H), 1592.9 (Ar C-C), 1515.8, 1338.4 (-NO₂), 1261.2 (Si-C). ¹H NMR (300 MHz, CDCl₃, δ, ppm, 25 °C): 8.19 (d, J=9.3, ArH, 4H), 6.93 (d, J=9.0, ArH, 4H), 4.04 (t, J=6.3, -CH₂-, 4H), 1.89-1.80 (m, -CH₂-, 4H), 1.57-1.46 (m, -CH₂-, 4H), 0.62-0.57 (m, -CH₂-, 4H), 0.08 (s, Si-CH₃, 12H), 0.03 (s, Si-CH₃, 6H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm, 25 °C): 164.4, 141.4, 126.0, 114.5, 68.6, 32.5, 19.8, 18.0, 1.42, 0.315. Anal. Calcd. For C₂₆H₄₂N₂: C, 52.49; H, 7.12; N, 4.71. Found: C, 52.88; H, 6.95; N, 4.71.

Synthesis of 1,7-Bis[4-(4-nitrophenoxy)butyl]-1,1,3,3,5,5,7,7-octamethyltetrasiloxane (2c). The title compound, **2c**, was synthesized by the same procedure as **2a** performed with 4.27 g (22.1 mmol) of **1a**, 2.82 g (9.98 mmol) of 1,1,3,3,5,5,7,7-octamethyltetrasiloxane, 30 drops of Karstedt's catalyst, and 20 mL of toluene. The compound, **2c**, (5.00 g, 75% yield) was then isolated as a pale yellow oil after the

vacuum. IR (NaCl), ν (cm^{-1}): 2958.3 (Alkyl C-H), 1592.9 (Ar C-C), 1515.8, 1342.2 ($-\text{NO}_2$), 1261.2 (Si-C). ^1H NMR (300 MHz, CDCl_3 , δ , ppm, 25 $^\circ\text{C}$): 8.19 (d, $J=9.3$, ArH, 4H), 6.93 (d, $J=9.3$, ArH, 4H), 4.05 (t, $J=6.3$, $-\text{CH}_2-$, 4H), 1.89-1.80 (m, $-\text{CH}_2-$, 4H), 1.57-1.47 (m, $-\text{CH}_2-$, 4H), 0.63-0.57 (m, $-\text{CH}_2-$, 4H), 0.09 (s, Si- CH_3 , 12H), 0.04 (s, Si- CH_3 , 12H). ^{13}C NMR (75 MHz, CDCl_3 , δ , ppm, 25 $^\circ\text{C}$): 164.4, 141.4, 126.0, 114.5, 68.6, 32.5, 19.8, 18.0, 1.34, 0.314. Anal. Calcd. For $\text{C}_{28}\text{H}_{48}\text{N}_2$: C, 50.27; H, 7.23; N, 4.19. Found: C, 50.37; H, 7.03; N, 4.21.

Synthesis of 1,7-Bis[6-(4-nitrophenoxy)hexyl]-1,1,3,3,5,5,7,7-octamethyltetrasiloxane (2d). The title compound, **2d**, was synthesized by the same procedure as **2a** performed with 3.32 g (15.0 mmol) of **1b**, 1.53 g (5.42 mmol) of 1,1,3,3,5,5,7,7-octamethyltetrasiloxane, 30 drops of Karstedt's catalyst, and 15 mL of toluene. The compound, **2d**, (3.79 g, 97% yield) was then isolated as a pale yellow oil after the vacuum. IR (NaCl), ν (cm^{-1}): 2923.6 (Alkyl C-H), 1592.9 (Ar C-C), 1515.8, 1342.2 ($-\text{NO}_2$), 1261.2 (Si-C). ^1H NMR (300 MHz, CDCl_3 , δ , ppm, 25 $^\circ\text{C}$): 8.19 (d, $J=9.3$, ArH, 4H), 6.93 (d, $J=9.3$, ArH, 4H), 4.04 (t, $J=6.5$, $-\text{CH}_2-$, 4H), 1.89-1.77 (m, $-\text{CH}_2-$, 4H), 1.53-1.33 (m, $-\text{CH}_2-$, 12H), 0.57-0.50 (m, $-\text{CH}_2-$, 4H), 0.07 (s, Si- CH_3 , 12H), 0.04 (s, Si- CH_3 , 12H). ^{13}C NMR (75 MHz, CDCl_3 , δ , ppm, 25 $^\circ\text{C}$): 164.6, 141.9, 126.2, 114.8, 69.3, 33.4, 29.3, 26.0, 23.5, 18.6, 1.56, 0.57. Anal. Calcd. For $\text{C}_{32}\text{H}_{56}\text{N}_2$: C, 53.00; H, 7.78; N, 3.86. Found: C, 52.94; H, 7.58; N, 3.72.

Synthesis of 1,7-Bis[4-(3-methyl-4-nitrophenoxy)butyl]-1,1,3,3,5,5,7,7-octamethyltetrasiloxane (2e). The title compound, **2e**, was synthesized by the same procedure as **2a** performed with 2.37 g (11.4 mmol) of **1c**, 1.44 g (5.09 mmol) of 1,1,3,3,5,5,7,7-octamethyltetrasiloxane, 20 drops of Karstedt's catalyst, and 12 mL of toluene. The compound, **2e**, (3.05 g, 86% yield) was then isolated as a pale yellow oil after the vacuum. IR (NaCl), ν (cm^{-1}): 2958.3 (Alkyl C-H), 1581.3 (Ar C-C), 1511.9, 1338.4 ($-\text{NO}_2$), 1257.36 (Si-C). ^1H NMR (300 MHz, CDCl_3 , δ , ppm, 25 $^\circ\text{C}$): 8.07 (d, $J=9.3$, ArH, 2H), 6.79-6.76 (m, ArH, 4H), 4.02 (t, $J=6.5$, $-\text{CH}_2-$, 4H), 2.62 (s, $-\text{CH}_3$, 6H), 1.87-1.78 (m, $-\text{CH}_2-$, 4H), 1.57-1.46 (m, $-\text{CH}_2-$, 4H), 0.63-0.57 (m, $-\text{CH}_2-$, 4H), 0.09 (s, Si- CH_3 , 12H), 0.05 (s, Si- CH_3 , 12H). ^{13}C NMR (75

MHz, CDCl₃, δ , ppm, 25 °C): 162.9, 142.1, 137.2, 127.7, 118.0, 112.3, 68.4, 32.6, 21.9, 19.8, 18.0, 1.36, 0.329. Anal. Calcd. For C₃₀H₅₂N₂: C, 51.69; H, 7.52; N, 4.02. Found: C, 51.52; H, 7.28; N, 3.83.

Synthesis of 1,5-Bis[4-(4-aminophenoxy)butyl]-1,1,3,3,5,5-hexamethyltrisiloxane (3b). The title compound, **3b**, was synthesized by the same procedure as **3a** performed with 2.79 g (4.69 mmol) of **2b**, 0.0262 g of Pd/C (10 wt%), and 15 mL of EtOAc. The compound, **3a**, (2.48 g, 99% yield) was then isolated as a light brown oil after the vacuum. IR (NaCl), ν (cm⁻¹): 3359.4 (N-H), 2954.4 (Alkyl C-H), 1623.8 (N-H), 1511.9 (Ar C-C), 1238.1 (Si-C). ¹H NMR (300 MHz, CDCl₃, δ , ppm, 25 °C): 6.74 (d, J=8.7, ArH, 4H), 6.63 (d, J=9.0, ArH, 4H), 3.87 (t, J=6.3, -CH₂-, 4H), 3.39 (s, NH₂, 4H), 1.81-1.71 (m, -CH₂-, 4H), 1.54-1.43 (m, -CH₂-, 4H), 0.61-0.55 (m, -CH₂-, 4H), 0.07 (s, Si-CH₃, 12H), 0.02 (s, Si-CH₃, 6H). ¹³C NMR (75 MHz, CDCl₃, δ , ppm, 25 °C): 152.5, 139.9, 116.5, 115.7, 68.4, 33.1, 19.9, 18.1, 1.45, 0.344.

Synthesis of 1,7-Bis[4-(4-aminophenoxy)butyl]-1,1,3,3,5,5,7,7-octamethyltetrasiloxane (3c). The title compound, **3c**, was synthesized by the same procedure as **3a** performed with 2.26 g (3.38 mmol) of **2c**, 0.0209 g of Pd/C (10 wt%), and 15 mL of EtOAc. The compound, **3c**, (2.05 g, 99% yield) was then isolated as a light brown oil after the vacuum. IR (NaCl), ν (cm⁻¹): 3359.4 (N-H), 2958.3 (Alkyl C-H), 1623.8 (N-H), 1511.9 (Ar C-C), 1238.1 (Si-C). ¹H NMR (300 MHz, CDCl₃, δ , ppm, 25 °C): 6.74 (d, J=9.0, ArH, 4H), 6.63 (d, J=9.0, ArH, 4H), 3.88 (t, J=6.3, -CH₂-, 4H), 3.39 (s, NH₂, 4H), 1.81-1.72 (m, -CH₂-, 4H), 1.54-1.43 (m, -CH₂-, 4H), 0.62-0.56 (m, -CH₂-, 4H), 0.08 (s, Si-CH₃, 12H), 0.04 (s, Si-CH₃, 12H). ¹³C NMR (75 MHz, CDCl₃, δ , ppm, 25 °C): 152.5, 139.9, 116.5, 115.8, 68.4, 33.1, 19.9, 18.1, 1.35, 0.334.

Synthesis of 1,7-Bis[6-(4-aminophenoxy)hexyl]-1,1,3,3,5,5,7,7-octamethyltetrasiloxane (3d). The title compound, **3d**, was synthesized by the same procedure as **3a** performed with 2.71 g (3.73 mmol) of **2d**, 0.0150 g of Pd/C (10 wt%), and 15 mL of EtOAc. The compound, **3d**, (2.47 g, 99% yield) was then

isolated as a light brown oil after the vacuum. IR (NaCl), ν (cm^{-1}): 3359.4 (N-H), 2923.6 (Alkyl C-H), 1623.8 (N-H), 1511.9 (Ar C-C), 1238.1 (Si-C). ^1H NMR (300 MHz, CDCl_3 , δ , ppm, 25 $^\circ\text{C}$): 6.74 (d, $J=9.3$, ArH, 4H), 6.63 (d, $J=8.7$, ArH, 4H), 3.87 (t, $J=6.6$, $-\text{CH}_2-$, 4H), 3.40 (s, NH_2 , 4H), 1.78-1.68 (m, $-\text{CH}_2-$, 4H), 1.47-1.32 (m, $-\text{CH}_2-$, 12H), 0.57-0.51 (m, $-\text{CH}_2-$, 4H), 0.06 (s, Si- CH_3 , 12H), 0.04 (s, Si- CH_3 , 12H). ^{13}C NMR (75 MHz, CDCl_3 , δ , ppm, 25 $^\circ\text{C}$): 152.5, 139.9, 116.5, 115.8, 68.8, 33.3, 29.5, 25.9, 23.3, 18.4, 1.36, 0.347.

Synthesis of 1,7-Bis[4-(4-amino-3-methylphenoxy)butyl]-1,1,3,3,5,5,7,7-octamethyltetrasiloxane (3e).

The title compound, **3e**, was synthesized by the same procedure as **3a** performed with 2.62 g (3.76 mmol) of **2e**, 0.0230 g of Pd/C (10 wt%), and 10 mL of EtOAc. The compound, **3e**, (2.38 g, 99% yield) was then isolated as a light brown oil after the vacuum. IR (NaCl), ν (cm^{-1}): 3363.3 (N-H), 2935.1 (Alkyl C-H), 1608.3 (N-H), 1504.2 (Ar C-C), 1238.1 (Si-C). ^1H NMR (300 MHz, CDCl_3 , δ , ppm, 25 $^\circ\text{C}$): 6.67-6.60 (m, ArH, 6H), 3.87 (t, $J=6.5$, $-\text{CH}_2-$, 4H), 3.33 (s, NH_2 , 4H), 2.15 (s, $-\text{CH}_3$, 6H), 1.81-1.71 (m, $-\text{CH}_2-$, 4H), 1.53-1.43 (m, $-\text{CH}_2-$, 4H), 0.62-0.56 (m, $-\text{CH}_2-$, 4H), 0.08 (s, Si- CH_3 , 12H), 0.04 (s, Si- CH_3 , 12H). ^{13}C NMR (75 MHz, CDCl_3 , δ , ppm, 25 $^\circ\text{C}$): 152.4, 138.1, 124.1, 117.4, 116.1, 113.1, 68.4, 33.2, 20.0, 18.1, 17.8, 1.36, 0.334.

Synthesis of Polyimide 6a. The above general procedure was applied using 0.258 g (0.560 mmol) of **3a**, 0.122 g (0.559 mmol) of **4a**, and 2.15 g of NMP. IR (Si wafer), ν (cm^{-1}): 2954 (Alkyl C-H), 1782 (C=O), 1724 (C=O), 1400 (C-N), 1254 (Si-C). Anal. Calcd. For $\text{C}_{34}\text{H}_{38}\text{N}_2$: C, 63.52; H, 5.96; N, 4.36. Found: C, 63.13; H, 6.00; N, 4.16.

Synthesis of Polyimide 6b. The above general procedure was applied using 0.899 g (1.68 mmol) of **3b**, 0.366 g (1.68 mmol) of **4a**, and 7.15 g of NMP. IR (Si wafer), ν (cm^{-1}): 2958 (Alkyl C-H), 1782 (C=O), 1724 (C=O), 1400 (C-N), 1254 (Si-C). Anal. Calcd. For $\text{C}_{36}\text{H}_{44}\text{N}_2$: C, 60.30; H, 6.19; N, 3.91. Found: C, 60.11; H, 6.14; N, 3.75.

Synthesis of Polyimide 6c. The above general procedure was applied using 0.589 g (0.967 mmol) of **3c**, 0.211 g (0.967 mmol) of **4a**, and 4.54 g of NMP. IR (Si wafer), ν (cm^{-1}): 2958 (Alkyl C-H), 1782 (C=O), 1724 (C=O), 1396 (C-N), 1254 (Si-C). Anal. Calcd. For $\text{C}_{38}\text{H}_{50}\text{N}_2$: C, 57.69; H, 6.37; N, 3.54. Found: C, 57.58; H, 6.27; N, 3.43.

Synthesis of Polyimide 6d. The above general procedure was applied using 1.09 g (1.64 mmol) of **3d**, 0.357 g (1.64 mmol) of **4a**, and 8.20 g of NMP. IR (Si wafer), ν (cm^{-1}): 2958 (Alkyl C-H), 1782 (C=O), 1724 (C=O), 1400 (C-N), 1254 (Si-C). Anal. Calcd. For $\text{C}_{42}\text{H}_{58}\text{N}_2$: C, 59.54; H, 6.90; N, 3.31. Found: C, 59.37; H, 6.80; N, 3.05.

Synthesis of Polyimide 6e. The above general procedure was applied using 1.23 g (1.93 mmol) of **3e**, 0.420 g (1.93 mmol) of **4a**, and 9.34 g of NMP. IR (Si wafer), ν (cm^{-1}): 2958 (Alkyl C-H), 1774 (C=O), 1720 (C=O), 1381 (C-N), 1254 (Si-C). Anal. Calcd. For $\text{C}_{40}\text{H}_{54}\text{N}_2$: C, 58.65; H, 6.64; N, 3.42. Found: C, 58.38; H, 6.65; N, 3.06.

Synthesis of Polyimide 6f. The above general procedure was applied using 0.467 g (1.01 mmol) of **3a**, 0.298 g (1.01 mmol) of **4b**, and 3.01 g of NMP. IR (Si wafer), ν (cm^{-1}): 2954 (Alkyl C-H), 1770 (C=O), 1716 (C=O), 1389 (C-N), 1254 (Si-C). Anal. Calcd. For $\text{C}_{40}\text{H}_{42}\text{N}_2$: C, 66.82; H, 5.89; N, 3.90. Found: C, 66.58; H, 5.96; N, 3.74.

Synthesis of Polyimide 6g. The above general procedure was applied using 1.09 g (2.04 mmol) of **3b**, 0.599 g (2.04 mmol) of **4b**, and 9.54 g of NMP. IR (Si wafer), ν (cm^{-1}): 2958 (Alkyl C-H), 1770 (C=O), 1712 (C=O), 1389 (C-N), 1257 (Si-C). Anal. Calcd. For $\text{C}_{42}\text{H}_{48}\text{N}_2$: C, 63.61; H, 6.10; N, 3.53. Found: C, 63.71; H, 6.09; N, 3.48.

Synthesis of Polyimide 6h. The above general procedure was applied using 0.306 g (0.502 mmol) of **3c**, 0.148 g (5.02 mmol) of **4b**, and 2.57 g of NMP. IR (Si wafer), ν (cm^{-1}): 2958 (Alkyl C-H), 1770 (C=O), 1712 (C=O), 1389 (C-N), 1257 (Si-C). Anal. Calcd. For $\text{C}_{44}\text{H}_{54}\text{N}_2$: C, 60.94 ; H, 6.28 ; N, 3.23. Found: C, 60.81 ; H, 6.13 ; N, 3.04.

Synthesis of Polyimide 6i. The above general procedure was applied using 0.994 g (1.49 mmol) of **3d**, 0.439 g (1.49 mmol) of **4b**, and 8.12 g of NMP. IR (Si wafer), ν (cm^{-1}): 2958 (Alkyl C-H), 1770 (C=O), 1712 (C=O), 1389 (C-N), 1254 (Si-C). Anal. Calcd. For $\text{C}_{48}\text{H}_{62}\text{N}_2$: C, 62.44 ; H, 6.77 ; N, 3.03. Found: C, 62.01 ; H, 6.65 ; N, 2.77.

Synthesis of Polyimide 6j. The above general procedure was applied using 0.896 g (1.41 mmol) of **3e**, 0.414 g (1.41 mmol) of **4b**, and 7.41 g of NMP. IR (Si wafer), ν (cm^{-1}): 2958 (Alkyl C-H), 1774 (C=O), 1720 (C=O), 1381 (C-N), 1254 (Si-C). Anal. Calcd. For $\text{C}_{46}\text{H}_{58}\text{N}_2$: C, 61.71 ; H, 6.53 ; N, 3.13. Found: C, 61.56 ; H, 6.49 ; N, 2.83.