Pseudo-Rodlike Molecules with Hockey-Stick-Shaped Mesogen

E-Joon Choi, a* Kyung-Min Park, a Dae-Yoon Kim, b Kwang-Un Jeong, b* and Ji-Hoon Lee c

a*Department of Polymer Science and Engineering, Kumoh National Institute of Technology, Gumi 730-701, Korea. E-mail: ejchoi@kumoh.ac.kr.
bDepartment of Polymer-Nano Science and Technology, Chonbuk National University, Jeonju 561-756, Korea. E-mail: kujeong@jbnu.ac.kr.
cAdvanced Electronics and Information Research Center, Division of Electronics Engineering, Chonbuk National University, Jeonju 561-756, Korea.
Supplementary Information

2. Experimental

2.1. Synthesis of compound 3a
A mixture of compound 1 (0.6 g, 0.93 mmol), 2,3,4-trifluorobenzoic acid (0.16 g, 0.90 mmol), DCC (0.18 g, 0.87 mmol), and DMAP (0.01 g, 0.08 mmol) in DCM (60 ml) was stirred at room temperature for 24 h. The urea formed was removed by filtration, the filtrate was washed with 5% aqueous acetic acid and water, and the solvent was evaporated in vacuo. The solid residue was purified by flash column chromatography on silica gel using chloroform as eluent. Yield: 40%; IR (KBr pellet, cm⁻¹): 3075 (aromatic C–H stretch), 2917, 2850 (aliphatic C–H stretch), 1739 (conj. C=O stretch), 1603, 1511 (aromatic C=C stretch), 1273, 1193, 1166 (C–O, C–F stretch); ¹H NMR (400 MHz, CDCl₃, δ in ppm): 8.35–8.25 (t, 4H, Ar–H), 8.11–8.08 (s, 1H, Ar–H), 8.05–8.08 (s, 1H, Ar–H), 7.78–7.73 (d, 1H, Ar–H), 7.44–7.34 (m, 4H, Ar–H), 7.07–7.03 (d, 2H, Ar–H), 3.99–3.91 (t, 2H, Ar–O–C₂H₅), 1.81–1.72 (m, 2H, Ar–O–CH₂–CH₂–), 1.48–1.39 (m, 2H, Ar–O–CH₂–CH₂–), 0.90–0.83 (t, 3H, –CH₃); Anal. Calcd for C₄₆H₄₃F₃O₉: C 69.34, H 5.44; Found: C 69.93, H 5.75.

2.2. Synthesis of compound 3b
Quantities: compound 1 (0.5 g, 0.78 mmol), 3,4,5-trifluorobenzoic acid (0.13 g, 0.73 mmol), DCC (0.15 g, 0.72 mmol), and DMAP (0.01 g, 0.08 mmol). The experimental procedure was as described for the preparation of compound 3a. Yield: 35%; IR (KBr pellet, cm⁻¹): 3075 (aromatic C–H stretch), 2920, 2850 (aliphatic C–H stretch), 1736 (conj. C=O stretch), 1603, 1511 (aromatic C=C stretch), 1273, 1197, 1163 (C–O, C–F stretch); ¹H NMR (400 MHz, CDCl₃, δ in ppm): 8.34–8.24 (t, 4H, Ar–H), 8.18–8.13 (d, 1H, Ar–H), 8.05–8.03 (s, 1H, Ar–H), 7.91–7.82 (t, 1H, Ar–H), 7.65–7.58 (t, 1H, Ar–H), 7.54–7.48 (d, 1H, Ar–H), 7.42–7.33 (m, 4H, Ar–H), 7.13–7.07 (d, 2H, Ar–H), 6.94–6.88 (d, 2H, Ar–H), 3.97–3.91 (t, 2H, Ar–O–CH₂–), 1.81–1.72 (m, 2H, Ar–O–CH₂–CH₂–), 0.90–0.83 (t, 3H, –CH₃); Anal. Calcd for C₄₆H₄₃F₃O₉: C 69.34, H 5.44; Found: C 69.93, H 5.75.

2.3. Synthesis of compound 3c
Quantities: compound 1 (0.5 g, 0.78 mmol), 2,4,6-trifluorobenzoic acid (0.13 g, 0.73 mmol), DCC (0.15 g, 0.72 mmol), and DMAP (0.01 g, 0.08 mmol). The experimental procedure was as described for the preparation of compound 3a. Yield: 42%; IR (KBr pellet, cm⁻¹): 3075 (aromatic C–H stretch), 2920, 2850
(aliphatic C–H stretch), 1745 (conj. C=O stretch), 1603, 1511 (aromatic C=C stretch), 1263, 1197, 1166 (C–O, C–F stretch); $^1$H NMR (400 MHz, CDCl$_3$, δ in ppm): 8.32–8.24 (t, 4H, Ar–H), 8.17–8.12 (d, 1H, Ar–H), 8.09–8.07 (s, 1H, Ar–H), 7.64–7.57 (t, 1H, Ar–H), 7.57–7.52 (d, 1H, Ar–H), 7.44–7.33 (m, 4H, Ar–H), 7.14–7.07 (d, 2H, Ar–H), 6.95–6.88 (d, 2H, Ar–H), 6.85–6.77 (t, 2H, Ar–H), 3.97–3.91 (t, 2H, Ar–O–CH$_2$–), 1.81–1.72 (m, 2H, Ar–O–CH$_2$–CH$_2$–), 1.49–1.39 (m, 2H, Ar–O–CH$_2$–CH$_2$–CH$_2$–), 1.38–1.16 (m, 18H, –CH$_2$–), 0.9–0.83 (t, 3H, –CH$_3$); Anal. Calcd for C$_{46}$H$_{43}$F$_3$O$_9$: C 69.34, H 5.44; Found: C 69.68, H 5.79.

**Figure 1.** DSC thermograms of compounds (rate = 10 °C/min): lower curve: second heating; middle curve: first heating; upper curve: first cooling.
Figure 2. Cross-polarizing optical micrographs (magnification 200×). Compound 3a: (a) on cooling, $T = 168^\circ$C; (b) on heating, $T = 166^\circ$C; (c) after shearing, $T = 166^\circ$C. Compound 3b: on cooling, (d) $T = 167^\circ$C; (e) $T = 163^\circ$C; (f) on heating, $T = 166^\circ$C.
Figure 3. Sets of 1D WAXD powder patterns of 3b obtained at various temperatures during heating (a) and cooling (b) at a rate of 2.5 °C/min.