

Supporting Information for:

“Mesogen-Jacketed Liquid Crystalline Polymers and Elastomers Bearing Polynorbornene Backbone”

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Synthesis of intermediate 10. Typical procedure: to prepare 4-dodecyloxy-benzoic acid methyl ester: 4-Hydroxybenzoic acid methyl ester (15.00 g, 98.6 mmol), KOH (6.36 g, 113.3 mmol), benzene (20 mL) and DMF (20 mL) were added into a 250mL round-bottom flask. The reaction mixture was heated to 50 °C, 1-bromo-dodecane (25.98 mL, 108.4 mmol) was then slowly added into the above flask *via* a syringe. The reaction solution was refluxed for 6 hours and then cooled to r.t. After filtering off inorganic salts, the resulting solution was concentrated by rotary evaporation to give a pale yellow crude solide, which was redissolved in 150 mL diethylether and washed by 10% sodium bicarbonate aqueous solution (75 mL, twice), water (75 mL, twice), then dried over sodium sulfate. The organic solution was concentrated by rotary evaporation to give the desired product (28.38 g, Yield: 90%) as a white solid. ¹H NMR (500 MHz, CDCl₃) □ □ 7.99 (d, J = 8.1 Hz, 2H), 6.92 (d, J = 8.5 Hz, 2H), 4.02 (s, 2H), 3.90 (s, 3H), 1.81 (s, 2H), 1.37 (m, 18H), 0.90 (s, 3H).

Synthesis of intermediate 11. Typical procedure: to prepare 4-dodecyloxy-benzoic acid: 4-dodecyloxy-benzoic acid methyl ester (22.11 g, 72.2 mmol), KOH (4.46 g, 79.4 mmol), water (40 mL) and ethanol (40 mL) were added into a 250mL round-bottom flask. The reaction solution was refluxed at 100 °C for 6 hours and then cooled to r.t. The resulting solution was neutralized by adding 3M HCl until pH ~ 1. The appearing solid was filtered and washed by ethanol and water. The crude solid was recrystallized in methanol to give the desired product (18.78 g, Yield: 85%) as a white solid. ¹H NMR (500 MHz, CDCl₃) □ □ 8.06 (d, J = 8.0 Hz, 2H), 6.94 (m, 2H), 4.04 (m, 2H), 1.82 (s, 2H), 1.38 (m, 18H), 0.90 (s, 3H).

Synthesis of intermediate 13. Hydroquinone (5.00 g, 45.4 mmol) and *tert*-butyl methyl ether (30 mL) were added into a 100mL round-bottom flask. Under a nitrogen atmosphere, bromine (2.85 mL, 55.6 mmol) was slowly added into the above flask *via* a pressure-equalizing dropping

funnel in 20 minutes at $-15\text{ }^{\circ}\text{C}$. The reaction mixture was stirred at $-15\text{ }^{\circ}\text{C}$ for 2 hours. The reaction solution was then concentrated by rotary evaporation and the resulting crude solid was recrystallized in chloroform to give the desired product (5.92 g, Yield: 69%) as a yellow solid. ^1H NMR (500 MHz, CDCl_3) δ 8.10 (s, 2H), 6.99 (s, 1H), 6.84 (d, $J = 8.4\text{ Hz}$, 1H), 6.69 (m, 2H), 3.01 (s, 1H).

Synthesis of intermediate 15. Typical procedure: to prepare **M-I-12**: 4-dodecyloxy-benzoic acid (26.23 g, 85.7 mmol), intermediate **13** (8.10 g, 42.9 mmol), DMAP (1.05 g, 8.57 mmol) and dry CH_2Cl_2 (200 mL) were added into a 500mL round-bottom flask. Under a nitrogen atmosphere, DCC (21.22 g, 102.9 mmol) was added into the above flask in one portion at r.t. The reaction mixture was stirred at r.t. for 12 hours. After filtering off the solids, the reaction solution was then concentrated by rotary evaporation and the resulting crude solid was recrystallized in methanol to give the desired product (15.37 g, Yield: 81%) as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 8.17 (dd, $J = 19.7, 7.8\text{ Hz}$, 4H), 7.56 (s, 1H), 7.29 (m, 2H), 7.00 (m, 4H), 4.07 (s, 4H), 1.84 (s, 4H), 1.42 (m, 16H), 0.92 (s, 6H).



































