SUPPORTING INFORMATION

Bent-core based main-chain polymers showing the dark conglomerate liquid crystal phase

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Experimental Section

Synthesis. A slightly different synthetic route from that reported before for monomer M was used.\(^1\) The synthetic route followed is shown in Scheme 1.

Intermediate compounds 1,\(^2\) 2,\(^2\) and 3\(^3\) were described in previous papers and the characterization data completely agree with the reported ones.
Synthesis of monomer M.

To a solution of 1.50 g (3.52 mmol) of the 3,4'-biphenyl bis-4-hydroxybenzoate (2) in 170 mL of distilled dichloromethane, 2.66 g (9.15 mmol) of 4-[4-(undec-10-enyloxy)benzoic acid and 0.043 g (0.35 mmol) of N,N-dimethylaminopyridine (DMAP) were added under argon atmosphere. The mixture was cooled in a water-ice bath and after 30 minutes, 2.03 g (1.97 mmol) of dycyclohexylcarbodiimide (DCC) were added. The reaction mixture was stirred for 24 h at room temperature. After this time, the white solid was filtered off and the solvent evaporated. The crude product was purified by crystallization from ethyl acetate. Yield: 2.30 g of white solid (67%). Rf (dichloromethane): 0.60. mp: C 104ºC Col, 146ºC I. 1H-NMR (300 MHz, CDCl3) δ: 1.33-1.48 (m, xH), 1.78-1.88 (m,4H), 2.02-2.19 (m, 4H), 4.06 (t, J=6.6Hz, 4H), 4.94 (d, J=10.2, 2H), 5.02 (d, J=17.4, 2H), 5.76-5.90 (m, 2H), 7.00 (d, J=8.7Hz, 4H), 7.20-7.25 (m, 1H), 7.32 (d, J=8.7, 2H), 7.38 (d, J=8.4Hz, 4H), 7.47 (s, 2H), 7.52 (d, J=4.8Hz, 2H),
7.68 (d, J=8.4Hz, 4H), 8.16 (d, J=8.7Hz,4H), 8.31 (dd, J₁=2.7, J₂=8.7Hz, 4H). \(^{13}\)C-NMR (300 MHz, CDCl₃) δ: 26.0, 28.9, 29.1, 29.3, 29.4, 29.5, 33.8, 68.4, 114.2, 114.4, 120.5, 120.6, 120.9, 122.0, 122.1, 124.7. 126.8, 126.9, 128.3, 129.9, 138.0, 139.2, 142.1, 150.7, 151.4, 163.8, 164.2, 164.5. FTIR (ATR-diamond): 3078 (st, ArC-H), 2924 (st, C-H), 2852 (st, OC-H), 1720 (st, ArCC=O), 1641 (st, C=C), 1602 (st as, ArC-ArC), 1510 (st sy, ArC-ArC), 1251 (st as, ArC-O-AlC), 1200 (st as, C-O), 1157 (st sy, C-O), 1055 (st sy, ArC-O-AlC) cm\(^{-1}\). EA for C₆₂H₆₆O₁₀: calc. C 76.68%, H 6.85%; found: C 76.86%, H 6.62%.

Tetramethyldisiloxane (TMDSO).

\(^1\)H NMR (400 MHz, CDCl₃): δ = 4.68 (2H, m, SiH, J = 2.8 Hz), 0.19 (12H, d, SiCH₃, J = 2.8 Hz) ppm. FTIR (ATR-diamond): 2960 (st, SiC-H), 2123 (st, Si-H), 1417 (δ as, Si-CH₃), 1254 (δ sy, Si-CH₃), 1053 (st, Si-O-Si), 874 (δ, Si-H), 829 (γ, Si-CH₃), 766 (st, Si-C) cm\(^{-1}\).

Figure SI-1. a) \(^1\)H NMR spectra for the polymers P₁ and P₂, the monomer M, and the chain extender TMDSO. b) Zoom in of the \(^1\)H NMR region from 6.0 to 4.6 ppm.
**Figure SI-2.** FTIR spectra for the polymers P1 and P2, the monomer M, and the chain extender TMDSO.

**Figure SI-3.** GPC traces for the polymers P1 and P2 in THF at 35 °C.
Figure SI-4. SAXS and WAXS radial distribution for the polymers P1 (at 70 °C and 140 °C) and P2 (at 70 °C and 160 °C) and the corresponding fitting curves.
Figure SI-5. Microphotographs of two parts of the sample of the Col texture of monomer M at 137 °C on the cooling process and X-ray diffraction pattern at 120 °C.

Figure SI-6. DSC thermogram of the second heating and cooling scans at 10 °C/min of monomer M.
Figure SI-7. Microphotographs of textures of a thin film of P2 in the mesophase at 170°C, under cross polarizers and highly illuminated, before (a) and after (b) shearing.

Figure SI-8. Polarization switching current in the SmCP phase of P1 and P2, under a triangular-wave electric field: 50 Hz, 26 Vpp μm⁻¹.

