SUPPORTING INFORMATION

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

Nélida Gimeno[a]‡, *Antoni Sánchez-Ferrer*[b]‡, *Nerea Sebastián*[c], *Raffaele Mezzenga*[b], *M. Blanca Ros*[a]*

[a] Departamento de Química Orgánica, Facultad de Ciencias, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, CSIC, 50009 Zaragoza, Spain.

[b] ETH Zurich, Institute of Food, Nutrition & Health, Food & Soft Materials Science Group Schmelzbergstrasse 9, LFO, E23-29, CH-8092 Zürich, Switzerland.

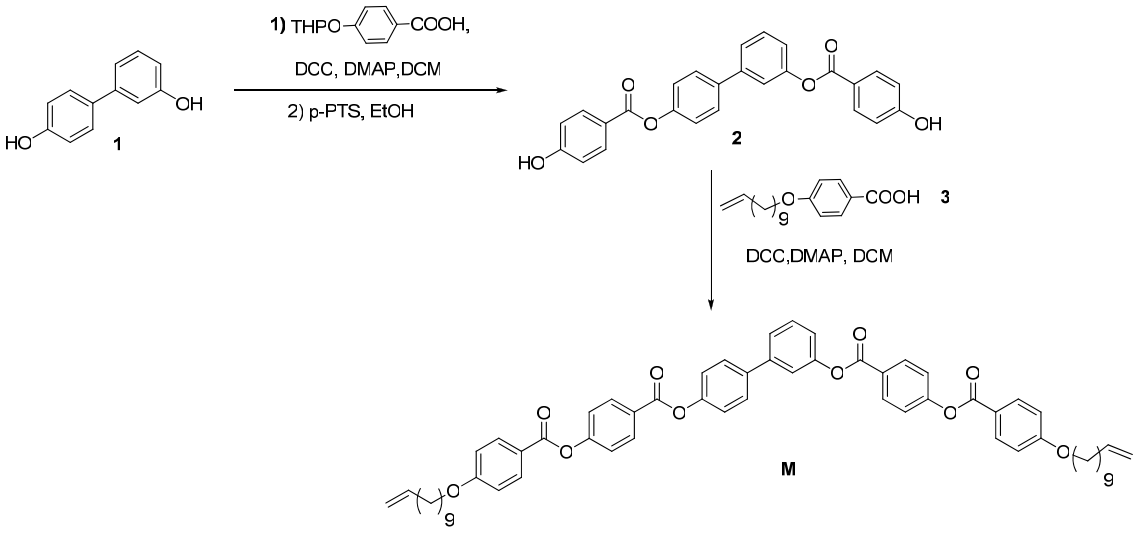
[c] Departamento de Física Aplicada II. Facultad de Ciencia y Tecnología. Universidad del País Vasco. Apdo. 644. 48080-Bilbao, Spain.

‡ The first two authors contributed equally to this study.

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.



Scheme 1. Synthetic route of monomer **M.**

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%). R_f (dichloromethane)**:** 0.60. mp: C 104ºC Col_r 146ºC I. ^{1}H-NMR (300 MHz, $CDCl_3$) 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, J_1=2.7, J_2=8.7Hz, 4H). ^{13}C-NMR (300 MHz, $CDCl_3$) 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, $CDCl_3$): δ = 4.68 (2H, m, SiH, *J* = 2.8 Hz), 0.19 (12H, d, $SiCH_3$, *J* = 2.8 Hz) ppm. FTIR (ATR-diamond): 2960 (st, SiC-H), 2123 (st, Si-H), 1417 (δ as, Si-CH_3), 1254 (δ sy, Si-CH_3), 1053 (st, Si-O-Si), 874 (δ, Si-H), 829 (γ, Si-CH_3), 766 (st, Si-C) cm^{-1}.

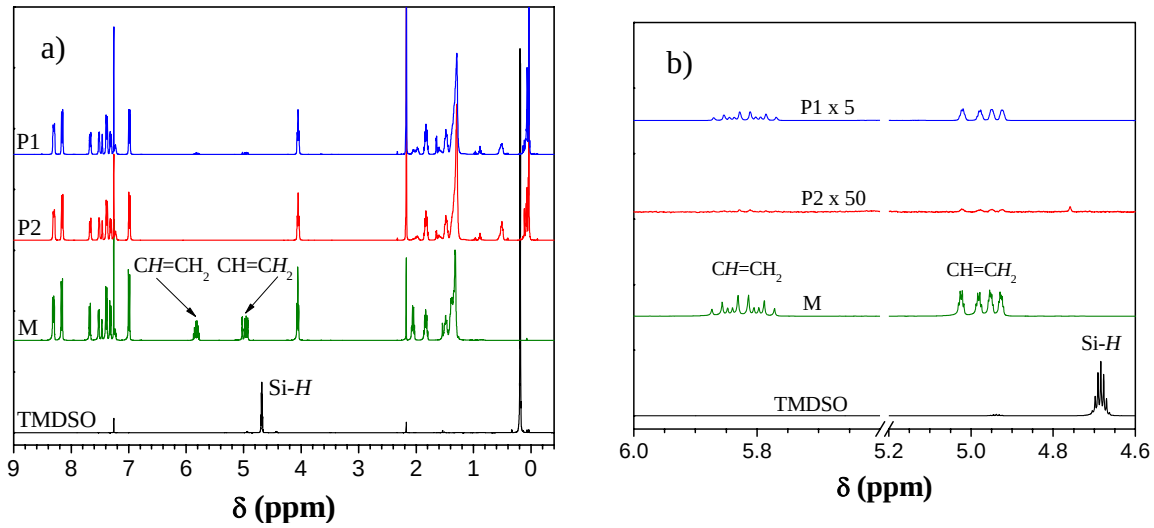


Figure SI-1. a) ^{1}H NMR spectra for the polymers **P1** and **P2,** the monomer **M**, and the chain extender **TMDSO**. b) Zoom in of the ^{1}H NMR region from 6.0 to 4.6 ppm.

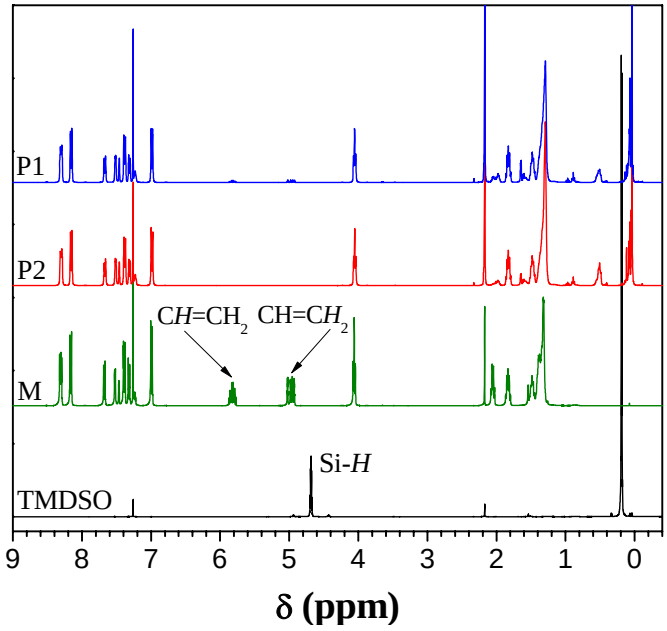


Figure SI-2. FTIR spectra for the polymers **P1** and **P2,** the monomer **M**, and the chain extender **TMDSO**.

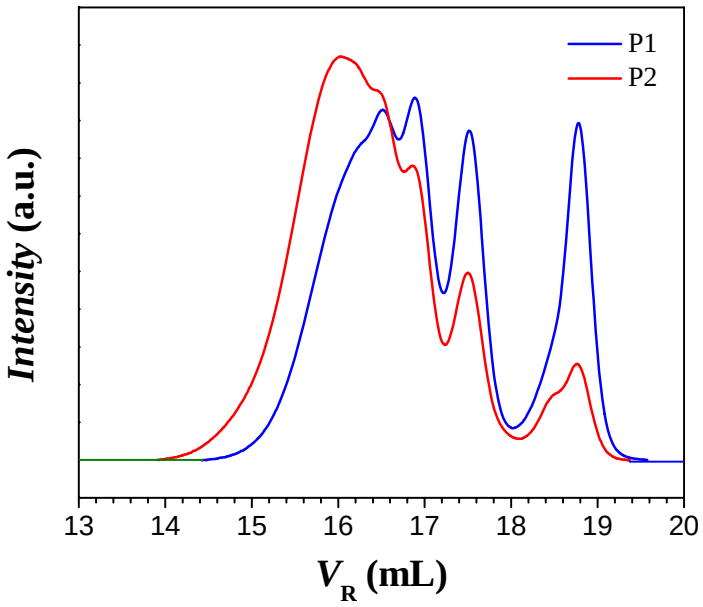


Figure SI-3. GPC traces for the polymers **P1** and **P2** in THF at 35 °C.

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.

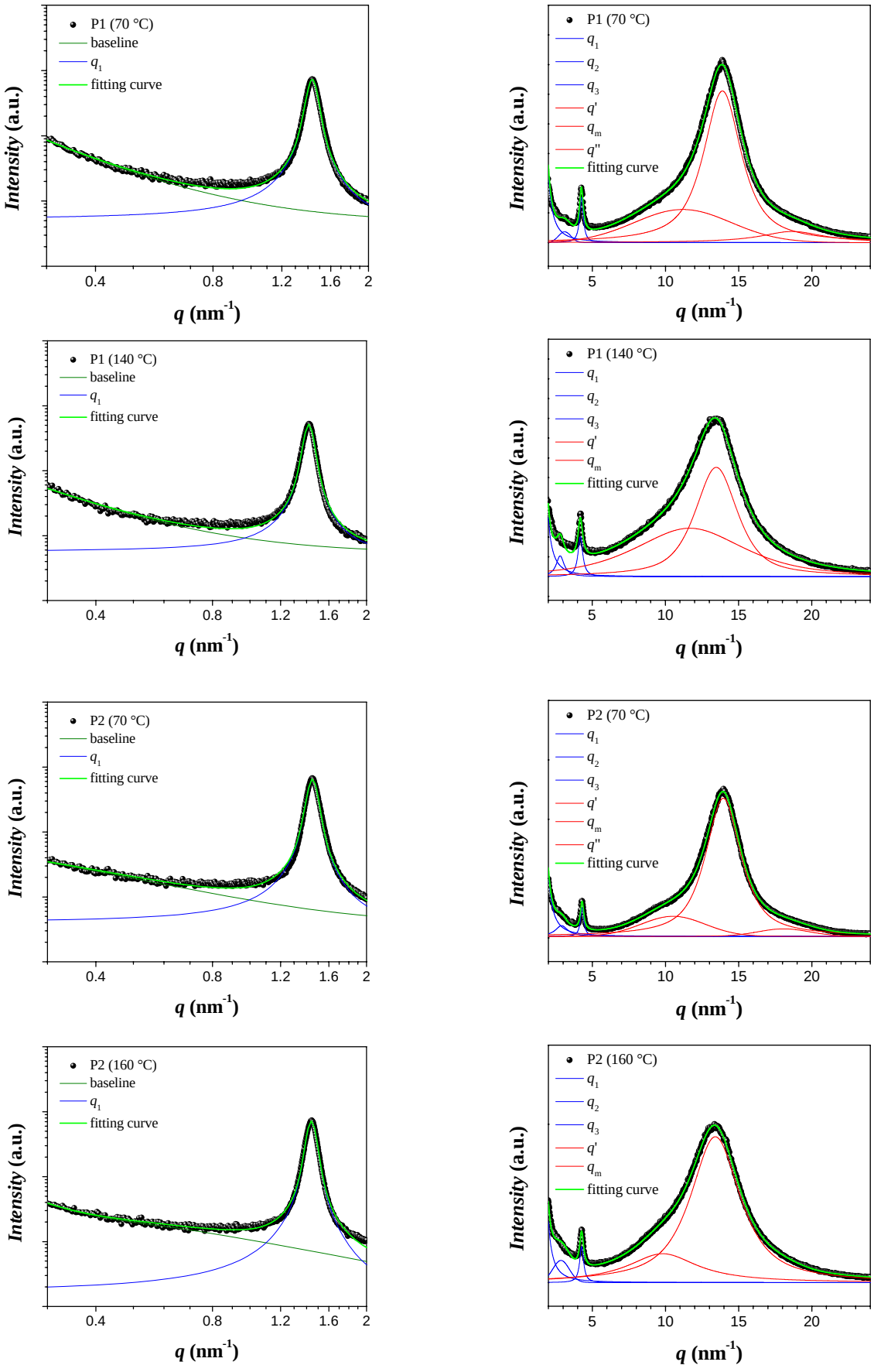


Figure SI-5. Microphotographs of two parts of the sample of the Col_r texture of monomer M at 137 ºC on the cooling process and X-ray diffraction pattern at 120 ºC.

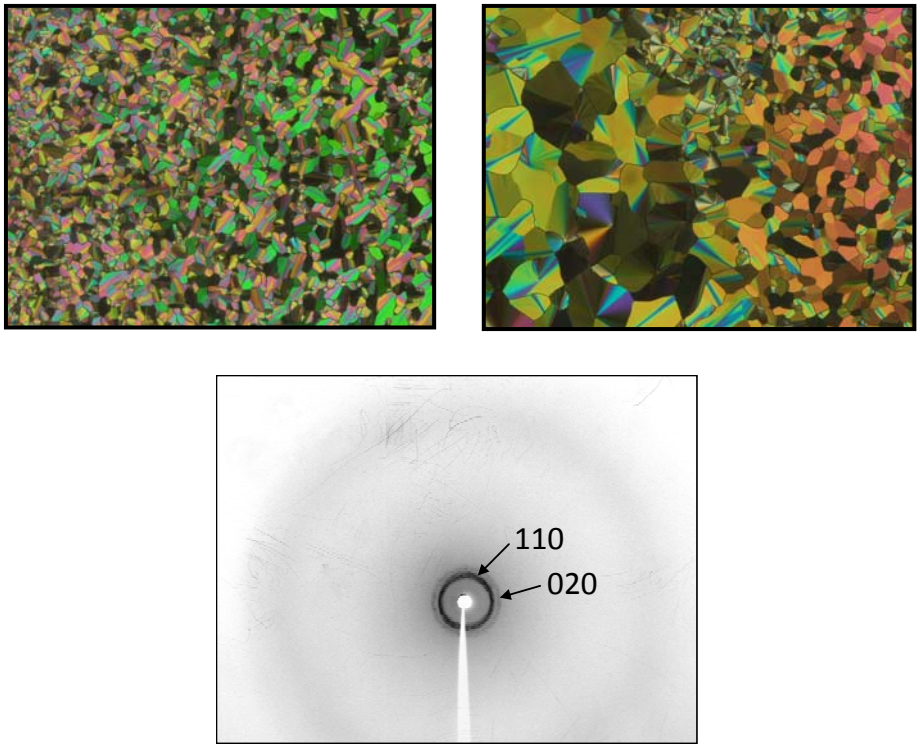


Figure SI-6. DSC thermogram of the second heating and cooling scans at 10ºC/min of monomer **M**.

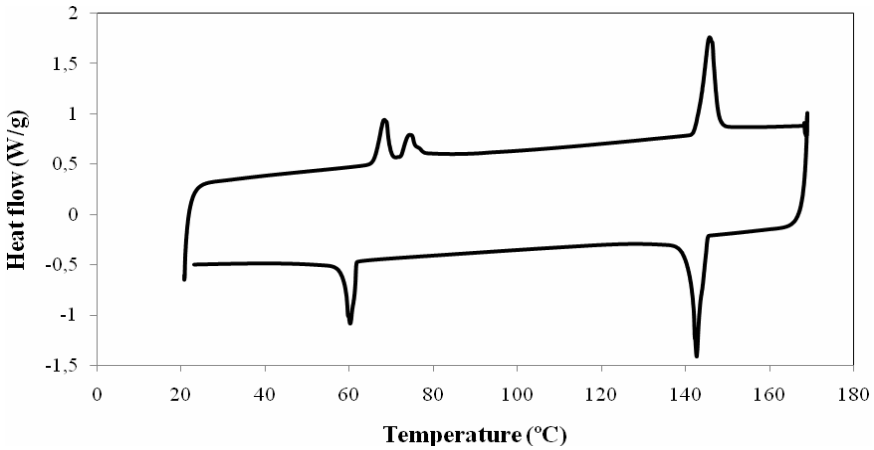


Figure SI-7. Microphotographs of textures of a thin film of **P2** in the mesosphase at 170ºC, under cross polarizers and highly illuminated, before (a) and after (b) shearing.

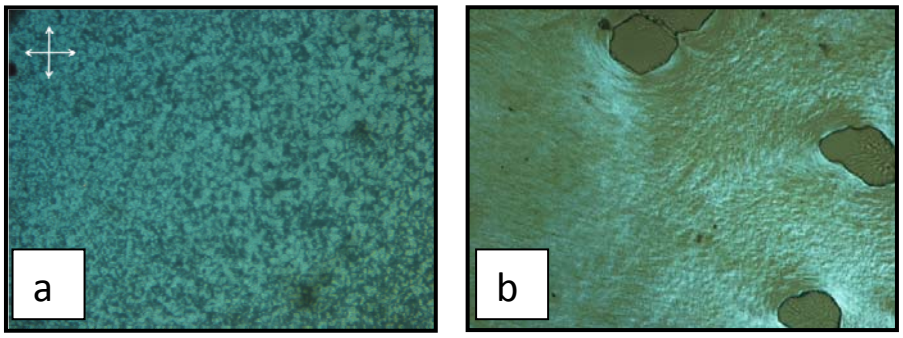
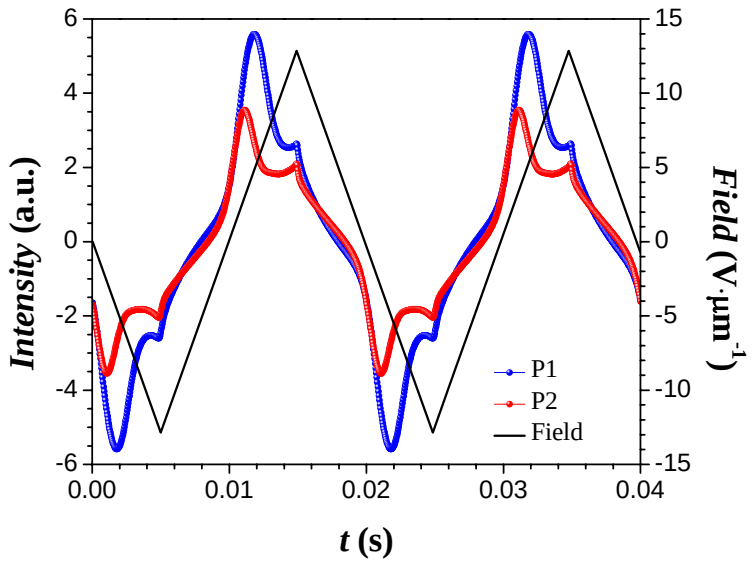


Figure SI-8. Polarization switching current in the SmCP phase of **P1** and **P2**, under a triangular-wave electric field: 50 Hz, 26 Vpp μm^{-1}.



[1] Keith, C.; Reddy, R. A.; Prehm, M.; Baumeister, U.; Kresse, H.; Chao, J. L.; Hahn, H, Lang, H.; Tschierske, C. Chem. *Eur. J.*, **2007**, *13*, 2556.

[2] J. Barberá, N. Gimeno, L. Monreal, R. Piñol, M.B. Ros, J.L. Serrano. *J. Amer. Chem. Soc.* **2004**, *126*, 7190.

[3] R. Achten, A. Koudijs, M. Giesbers, A. T. M. Marcelis, E. J. R.Sudholter, *Liq. Cryst.* **2005**, *32*, 277 – 285.