**Supporting information**

**Mesomorphic and structural properties of liquid-crystalline side chain polymethacrylates: from smectic C\* to columnar phases**

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**1. Synthesis of the methacrylate** **reactive monomers**

The initial materials and reagents were purchased from Sigma-Aldrich, Acros Organics or Lach:Ner. All solvents used for the synthesis were “p.a.” grade. 1H NMR spectra were recorded on Varian VNMRS 300 instrument; deuteriochloroform (CDCl3) and hexadeuteriodimethyl sulfoxide (DMSO-*d*6) were used as solvents and the signals from the solvents served as internal standard. Chemical shifts (δ) are given in ppm and *J* values are given in Hz. Signals were identified by APT, gCOSY and gHMBC experiments. For all azo compounds, only spectra of *E* isomer are given. Elemental analyses were carried out on Elementar vario EL III instrument. The purity of all final compounds was checked by HPLC analysis (high-pressure pump ECOM Alpha; column WATREX Biospher Si 100, 250 × 4 mm, 5 μm; detector WATREX UVD 250) and was found to be > 99.8 %. Column chromatography was carried out using Merck Kieselgel 60 (60 - 100 μm).

Methacrylate reactive monomers for this study were designed as analogues of similar low molecular weight mesogens with photosensitive azobenzene units showing smectic phases [S1]. General synthetic route leading to all mesogenic monomers is given on Scheme S1. Starting ester **1** was obtained by the synthetic procedure described in ref. [S2]. **1** was alkylated by m-chloroalkyl tosylate (m = 6 or 10) and subsequently subjected to basic hydrolysis giving carboxylic acids **2a**-**b**. The last aromatic ring of the molecular core of mesogen was connected by the means of DCC coupling of acids **2a**-**b** with the chiral phenols **3a**-**b** with appropriate length of alkyl chain, which were synthesized following the known procedure [S3]. Then the esters **4a-d** were subjected to Finkelstein reaction and finally the reaction of formed iodo-derivatives with potassium methacrylate yielded target monomers MHA-m/n.



Scheme S1: Synthesis of MHA m/n rmonomers.

*4-{[4´-(6-Chlorhexyloxy)phenyl]diazenyl}benzoic acid (****2a****)*

Mixture of 6-chlorohexyl 4-methylbenzenesulfonate (24.0 g, 82.53 mmol), **1** (20.0 g, 74.97 mmol) and anhydrous potassium carbonate (34.20 g, 0.25 mol) in acetone (500 mL) was refluxed for 12 h. After cooling the resulting mixture was poured into water. The precipitate was filtered off, washed with water and pressed thoroughly. Obtained red solid was dissolved in ethanol (700 mL) at 60 °C and with stirring treated with solution potassium hydroxide (8.25 g 0.21 mol) in ethanol (80 mL). After stirring for 1 h, most of the solvent was distilled off under reduced pressure and the residue poured into diluted hydrochloric acid (350 mL, 1 : 9). The red precipitate was filtered off and crystallized from isopropyl alcohol. Yield 26.20 g (88 %) of acid **2a**.

1H NMR (DMSO-*d*6)  8.10 (2 H, d, *J =*8.3, H-2, H-6), 7.81 - 7.92 (4 H, m, H-3, H-5, H-2´, H-6´), 7.12 (2 H, d, *J =*8.9 H3´, H-5´), 4.11 (3 H, t, *J =*6.4, CH2O), 3.60 (2 H, t, *J =*6.8, CH2Cl), 1.62 – 1.87 (4 H, m, C**H**2CH2O, C**H**2CH2Cl), 1.20 – 1.52 (4 H, m, 2 × CH2).

13C NMR (DMSO-*d6*): 166.84 (COO), 161.76 (C-4´), 153.92 (C-4), 146.13 (C-1´), 132.70 (C-1), 130.14 (C-2´, C-6´), 124.62 (C-2, C-6), 121.66 (C-3, C-5), 115.00 (C-3´, C-5´), 68.00 (CH2O), 45.11 (CH2Cl), 31.85 (**C**H2CH2Cl), 28.57 (**C**H2CH2O), 26.03 (**C**H2(CH2)2Cl), 25.18 (**C**H2(CH2)2O).

*4-{[4´-(10-Chlordecyloxy)phenyl]diazenyl}benzoic acid (****2b****)*

Following the procedure described for **2a**: **1** (23.0 g, 85.06 mmol) was alkylated with 10‑chlordecyl 4-methylbenzenesulfonate (32.50 g, 93.68 mmol) and subsequent hydrolysis yielded 29.40 g (83 %) of acid **2b**.

1H NMR (DMSO-*d*6): 8.10 (2 H, d, *J* = 8.3, H-2, H-6), 7.81 – 7.92 (4 H, m, H-3, H-5, H-2´, H-6´), 7.12 (2 H, d, *J* = 8.9 H3´, H-5´), 4.11 (3 H, t, *J* = 6.4, CH2O), 3.60 (2 H, t, *J* = 6.8, CH2Cl), 1.61 – 1.88 (4 H, m, C**H**2CH2O, C**H**2CH2Cl), 1.21 – 1.66 (12 H, m, 6 × CH2).

13C NMR (DMSO-*d6*): 166.81 (COO), 161.77 (C-4´), 153.91 (C-4), 146.12 (C-1´), 132.72 (C-1), 130.15 (C-2´, C-6´), 124.63 (C-2, C-6), 121.63 (C-3, C-5), 115.05 (C-3´, C-5´), 68.02 (CH2O), 45.12 (CH2Cl), 31.84 (**C**H2CH2Cl), 28.55 (**C**H2CH2O), 28.51 (**C**H2(CH2)4O), 28.40 (**C**H2(CH2)4Cl), 28.34 (**C**H2(CH2)3O), 27.93 (**C**H2(CH2)3Cl), 26.01 (**C**H2(CH2)2Cl), 25.15 (**C**H2(CH2)2O).

*(S)-1-(Hexyloxy)-1-oxopropan-2-yl-4´´-[(4-{[4´-(6-chlorhexyloxy)phenyl]diazenyl}benzoyl)oxy]benzoate (****4a****)*

Acid **2a** (3.0 g, 8.31 mmol) and chiral phenol **3a** (2.44 g, 8.29 mmol) were dissolved in dry dichloromethane (150 mL), the mixture was cooled to ca. 0 °C and *N*,*N*´‑dicyclohexylcarbodiimide (DCC) (1.80 g, 8.72 mmol) and 4‑(*N,N‑*dimethylamino)pyridine (DMAP) (0.21 g, 1.72 mmol) were added. Reaction mixture was stirred and let warm to room temperature. After ca. 4 h, the TLC indicated completion of the reaction. The resulting mixture was filtered and the filtrate was evaporated. The residue was purified by column chromatography on silica, using dichloromethane – acetone, 99 : 1 as eluent. Yield 4.49 g (85 %) of **4a**.

1H NMR (CDCl3): 8.35 (2 H, d, *J*= 8.5, H-2, H-6), 8.20 (2 H, d, *J*= 8.8, H-2´´, H-6´´), 7.97 – 8.10 (4 H, m, H-3, H-5, H-2´, H-6´), 7.36 (2 H, d, *J*= 8.8, H-3´´, H-5´´), 7.04 (2 H, d, *J*= 9.1, H-3´, H-5´), 5.35 (1 H, q, *J*= 6.7, CH\*), 4.12 – 4.25 (2 H, m, CH\*COOC**H**2), 4.07 (2 H, t, *J*= 6.5, CH2OAr), 3.55 (2 H, t, *J*= 6.7, CH2Cl), 1.70 – 1.92 (6 H, m, 2 × C**H**2CH2O, C**H**2CH2Cl), 1.65 – 1.70 (5 H, m, C**H**2CH2OOC, CH\*C**H**3), 1.19-1.45 (8 H, m, 4 × CH2), 0.89 (3 H, t, *J*= 6.5, CH2C**H**3).

13C NMR (CDCl3): 170.80 (CH\***C**OO), 165.15 (COOAr), 164.14 (**C**OOCH\*), 162.50 (C-4´), 155.94 (C-4), 154.84 (C-4´´), 146.83 (C-1´), 131.57 (C-2, C-6), 131.30 (C-2´´, C-6´´), 129.88 (C-1), 127.20 (C-1´´), 125.35 (C-2´, C-6´), 122.61 (C-3, C-5), 121.73 (C-3´´, C-5´´), 114.85 (C-3´, C-5´), 69.28 (CH\*), 68.41 (CH2O), 65.57 (**C**H2OOC), 45.19 (CH2Cl), 32.62 (**C**H2CH2Cl), 31.33 (**C**H2CH2CH3), 29.43 (**C**H2CH2O), 28.44 (**C**H2CH2OOC), 26.86 (**C**H2(CH2)2Cl), 25.26 (**C**H2(CH2)2O), 25.41 (**C**H2(CH2)2OOC), 22.49 (**C**H2CH3), 17.14 (**C**H3CH\*), 13.97 (CH2**C**H3).

*(S)-1-(Decyloxy)-1-oxopropan-2-yl-4´´-[(4-{[4´-(6-chlorhexyloxy)phenyl]diazenyl}benzoyl)oxy]benzoate (****4b****)*

Analogously to the procedure for ester **4a**, acid **2a** (3.0 g, 8.31 mmol) and chiral phenol **3b** (2.90 g, 8.27 mmol) were dissolved in dry dichloromethane (150 mL), the mixture was cooled to ca. 0 °C and *N*,*N*´‑dicyclohexylcarbodiimide (DCC) (1.80 g, 8.72 mmol) and 4‑(*N,N‑*dimethylamino)pyridine (DMAP) (0.20 g, 1.64 mmol). The mixture was stirred at room temperature for 24 h and then filtered. The filtrate was evaporated and the residue purified by column chromatography (silica gel, dichloromethane – acetone, 99 : 1). Yield 5.04 g (88 %) of **4b**.

1H NMR (CDCl3): 8.35 (2 H, d, *J*= 8.5, H-2, H-6), 8.20 (2 H, d, *J*= 8.8, H-2´´, H-6´´), 7.97 – 8.10 (4 H, m, H-3, H-5, H-2´, H-6´), 7.36 (2 H, d, *J*= 8.8, H-3´´, H-5´´), 7.04 (2 H, d, *J*= 9.1, H-3´, H-5´), 5.35 (1 H, q, *J*= 6.7, CH\*), 4.12 – 4.25 (2 H, m, CH\*COOC**H**2), 4.07 (2 H, t, *J*= 6.5, CH2OAr), 3.55 (2 H, t, *J*= 6.7, CH2Cl), 1.70 – 1.92 (6 H, m, 2 × C**H**2CH2O, C**H**2CH2Cl), 1.65 – 1.70 (5 H, m, C**H**2CH2OOC, CH\*C**H**3), 1.16 – 1.58 (16 H, m, 8 × CH2), 0.89 (3 H, t, *J*= 6.5, CH2C**H**3).

13C NMR (CDCl3): 170.80 (CH\***C**OO), 165.15 (COOAr), 164.14 (**C**OOCH\*), 162.50 (C-4´), 155.94 (C-4), 154.84 (C-4´´), 146.83 (C-1´), 131.57 (C-2, C-6), 131.30 (C-2´´, C-6´´), 129.88 (C-1), 127.20 (C-1´´), 125.35 (C-2´, C-6´), 122.61 (C-3, C-5), 121.73 (C-3´´, C-5´´), 114.85 (C-3´, C-5´), 69.28 (CH\*), 68.41 (CH2O), 65.57 (**C**H2OOC), 45.19 (CH2Cl), 32.62 (**C**H2CH2Cl), 31.33 (**C**H2CH2CH3), 29.43 (**C**H2CH2O), 29.14 – 29.43 (4**×**CH2), 28.44 (**C**H2CH2OOC), 26.86 (**C**H2(CH2)2Cl), 25.98 (**C**H2(CH2)2O), 25.42 (**C**H2(CH2)2OOC), 22.50 (**C**H2CH3), 17.12 (**C**H3CH\*), 13.97 (CH2**C**H3).

*(S)-1-(Hexyloxy)-1-oxopropan-2-yl-4´´-[(4-{[4´-(10-chlordecyloxy)phenyl]diazenyl}benzoyl)oxy]benzoate (****4c****)*

Preparation of compound **4c** was analogous to the preparation of compound **4a**. Reaction of acid **2b** (2.10 g, 5.04 mmol) with chiral phenol **3a** (1.48 g, 5.03 mmol) in dry dichloromethane (50 mL) in the presence of dicyclohexylcarbodiimide (1.10 g, 5.22 mmol) and DMAP (0.13 g, 1.06 mmol) yielded 3.10 g (89 %) of **4c**.

1H NMR (CDCl3): 8.35 (2 H, d, *J*= 8.5, H-2, H-6), 8.20 (2 H, d, *J*= 8.8, H-2´´, H-6´´), 7.97 – 8.10 (4 H, m, H-3, H-5, H-2´, H-6´), 7.36 (2 H, d, *J*= 8.8, H-3´´, H-5´´), 7.04 (2 H, d, *J*= 9.1, H-3´, H-5´), 5.35 (1 H, q, *J*= 6.7, CH\*), 4.12 – 4.25 (2 H, m, CH\*COOC**H**2), 4.07 (2 H, t, *J*= 6.5, CH2OAr), 3.55 (2 H, t, *J*= 6.7, CH2Cl), 1.70 – 1.92 (6 H, m, 2 × C**H**2CH2O, C**H**2CH2Cl), 1.65 – 1.70 (5 H, m, C**H**2CH2OOC, CH\*C**H**3), 1.16 – 1.58 (16 H, m, 8 × CH2), 0.89 (3 H, t, *J*= 6.5, CH2C**H**3).

13C NMR (CDCl3): 170.80 (CH\***C**OO), 165.15 (COOAr), 164.14 (**C**OOCH\*), 162.50 (C-4´), 155.94 (C-4), 154.84 (C-4´´), 146.83 (C-1´), 131.57 (C-2, C-6), 131.30 (C-2´´, C-6´´), 129.88 (C-1), 127.20 (C-1´´), 125.35 (C-2´, C-6´), 122.61 (C-3, C-5), 121.73 (C-3´´, C-5´´), 114.85 (C-3´, C-5´), 69.28 (CH\*), 68.41 (CH2O), 65.57 (**C**H2OOC), 45.19 (CH2Cl), 32.62 (**C**H2CH2Cl), 31.33 (**C**H2CH2CH3), 29.43 (**C**H2CH2O), 29.12 – 29.41 (4**×**CH2), 28.44 (**C**H2CH2OOC), 26.86 (**C**H2(CH2)2Cl), 25.98 (**C**H2(CH2)2O), 25.42 (**C**H2(CH2)2OOC), 22.51 (**C**H2CH3), 17.12 (**C**H3CH\*), 13.98 (CH2**C**H3).

*(S)-1-(Decyloxy)-1-oxopropan-2-yl-4´´-[(4-{[4´-(10-chlordecyloxy)phenyl]diazenyl}benzoyl)oxy]benzoate (****4d****)*

Preparation of compound **4d** was analogous to the preparation of compound **4a**. Reaction of acid **2b** (2.10 g, 5.04 mmol) with chiral phenol **3b** (1.76 g, 5.02 mmol) in dry dichloromethane (50 mL) in the presence of dicyclohexylcarbodiimide (1.10 g, 5.22 mmol) and DMAP (0.13 g, 1.06 mmol) yielded 3.42 g (91 %) of **4d**.

1H NMR (CDCl3): 8.35 (2 H, d, *J*= 8.5, H-2, H-6), 8.20 (2 H, d, *J*= 8.8, H-2´´, H-6´´), 7.97 – 8.10 (4 H, m, H-3, H-5, H-2´, H-6´), 7.36 (2 H, d, *J*= 8.8, H-3´´, H-5´´), 7.04 (2 H, d, *J*= 9.1, H-3´, H-5´), 5.35 (1 H, q, *J*= 6.7, CH\*), 4.12 – 4.25 (2 H, m, CH\*COOC**H**2), 4.07 (2 H, t, *J*= 6.5, CH2OAr), 3.55 (2 H, t, *J*= 6.7, CH2Cl), 1.70 – 1.92 (6 H, m, 2 × C**H**2CH2O, C**H**2CH2Cl), 1.65 – 1.70 (5 H, m, C**H**2CH2OOC, CH\*C**H**3), 1.11 – 1.63 (24 H, m, 12 × CH2), 0.91 (3 H, t, *J*= 6.5, CH2C**H**3).

13C NMR (CDCl3): 170.80 (CH\***C**OO), 165.15 (COOAr), 164.14 (**C**OOCH\*), 162.50 (C-4´), 155.94 (C-4), 154.84 (C-4´´), 146.83 (C-1´), 131.57 (C-2, C-6), 131.30 (C-2´´, C-6´´), 129.88 (C-1), 127.20 (C-1´´), 125.35 (C-2´, C-6´), 122.61 (C-3, C-5), 121.73 (C-3´´, C-5´´), 114.85 (C-3´, C-5´), 69.29 (CH\*), 68.42 (CH2O), 65.57 (**C**H2OOC), 45.18 (CH2Cl), 32.62 (**C**H2CH2Cl), 31.33 (**C**H2CH2CH3), 29.43 (**C**H2CH2O), 29.17 – 29.58 (8**×**CH2), 28.44 (**C**H2CH2OOC), 26.85 (**C**H2(CH2)2Cl), 25.98 (**C**H2(CH2)2O), 25.41 (**C**H2(CH2)2OOC), 22.51 (**C**H2CH3), 17.12 (**C**H3CH\*), 13.97 (CH2**C**H3).

*(S)-1-(pentyloxy)-1-oxopropan-2-yl-4-{[4-({4´-[6-(methacryloyloxy)hexyloxy]phenyl}diazenyl)benzoyl]oxy}benzoate (*MHA-6/5*)*

Intermediate **4a** (1.90 g, 3.05 mmol) was dissolved in isobutyl(methyl)ketone (MIBK) (120 ml), potassium iodide (10.0 g, 60.24 mmol) was added and the suspension was refluxed with vigorous stirring for 10 h. The resulting mixture was filtered and the solvent distilled off under reduced pressure. Solid residue was dissolved in dry THF (20 ml) and added to the stirred mixture of anhydrous potassium methacrylate (1.20 g, 9.66 mmol) and a trace of hydroquinone in dry DMSO (120 ml) at room temperature. The reaction mixture was stirred overnight under dry conditions. Resulting mixture was poured into water (300 ml) and decanted. The residue was dissolved in diethylether (200 ml), washed with water (3 × 50 ml) and brine (50 ml). Organic layer was dried with anhydrous sodium sulphate and the solvent removed under reduced pressure. Crude MHA-6/5was purified by column chromatography on silica using dichloromethane - acetone (99 : 1) as eluent. Yield 1.49 g (73 %). 1H NMR (CDCl3)  8.34 (2 H, d, *J =*8.2, H-2, H-6), 8.20 (2 H, d, *J =*8.8, H-2´´, H-6´´), 7.96 – 8.0 (4 H, m, H-3, H-5, H-2´, H-6´), 7.36 (2 H, d, *J*= 8.8, H-3´´, H-5´´), 7.03 (2 H, d, *J =*8.8, H-3´, H-5´), 6.11 (1 H, m, *trans-*C**H**2=), 5.51 – 5.58 (1 H, m, *cis-*C**H**2=), 5.35 (1 H, q, *J =*7.0, CH\*), 4.12 – 4.26 (4 H, m, 2 × COOCH2), 4.07 (2 H, t, *J =*6.2, CH2OAr), 1.95 (3 H, m, =CCH3), 1.81 – 1.92 (2 H, m, C**H**2CH2OAr), 1.68 – 1.80 (2 H, m, C**H**2CH2O), 1.65 (5 H, m, C**H**2CH2OOCCH\*, CH\*C**H**3), 1.41 – 1.59 (2 H, m, C**H**2(CH2)3O), 1.21 – 1.40 (4 H, m, 2 × CH2), 0.89 (3 H, t, *J*= 6.7 Hz, CH2C**H**3).

13C NMR (CDCl3) 170.80 (CH\***C**OO), 167.54 (C**C**OO), 165.15 (COOAr), 164.14 (**C**OOCH\*), 162.50 (C-4´), 155.94 (C-4), 154.84 (C-4´´), 146.83 (C-1´), 131.57 (C-2, C-6), 131.30 (C-2´´, C-6´´), 129.88 (C-1), 127.20 (C-1´´), 125.35 (C-2´, C-6´), 125.27 (**C**H2=C), 122.61 (C-3, C-5), 121.73 (C-3´´, C-5´´), 114.85 (C-3´, C-5´), 69.28 (CH\*), 68.41 (CH2O), 65.57 (**C**H2OOC), 64.63 (**C**H2OOC=), 29.43 (**C**H2CH2O), 28.55 (**C**H2CH2OOC=), 28.04 (**C**H2CH2OOC), 25.47 (**C**H2(CH2)2OOC), 25.41 (**C**H2(CH2)2OOC), 25.26 (**C**H2(CH2)2O), 22.14 (**C**H2CH3), 17.14 (**C**H3CH\*), 13.95 (CH2**C**H3). Elemental analysis for C38H44N2O9 (672.78): calculated C 67.84 %, H 6.59 %, N 4.16 %; found C 67.60 %, H 6.64 %, N 4.13 %.

*(S)-1-(decyloxy)-1-oxopropan-2-yl-4-{[4-({4´-[6-(methacryloyloxy)hexyloxy]phenyl}diazenyl)benzoyl]oxy}benzoate (*MHA-6/10*)*

Using the procedure described for MHA-6/5, **4a** (2.50 g, 3.37 mmol) was dissolved in isobutyl(methyl)ketone (MIBK) (150 ml), potassium iodide (10.0 g, 60.24 mmol) was added and the suspension was refluxed with vigorous stirring for 12 h. Obtained iodo-derivative was reacted with anhydrous potassium methacrylate (1.26 g, 10.15 mmol) in dry DMSO (150 ml). Crude MHA 6/10was purified by column chromatography on silica using dichloromethane - acetone (99.8 : 0.2) as eluent. Yield 1.92 g (77 %).

1H NMR (CDCl3): 8.33 (2 H, d, *J =*8.8, H-2, H-6), 8.19 (2 H, d, *J =*8.8, H-2´´, H-6´´), 7.94 – 8.00 (4 H, m, H-3, H-5, H-2´, H-6´), 7.35 (2 H, d, *J*= 8.8, H-3´´, H-5´´), 7.03 (2 H, d, *J =*8.8, H-3´, H-5´), 6.10 (1 H, m, *trans-*C**H**2=), 5.51 – 5.58 (1 H, m, *cis-*C**H**2=), 5.34 (1 H, q, *J =*7.0, CH\*), 4.10 – 4.26 (4 H, m, 2 × COOCH2), 4.06 (2 H, t, *J =*6.2, CH2OAr), 1.94 (3 H, m, =CCH3), 1.75 – 1.89 (2 H, m, C**H**2CH2OAr), 1.56 – 1.74 (7 H, m, 2 Ч C**H**2CH2O, CH\*C**H**3), 1.42 – 1.55 (2 H, m, C**H**2(CH2)3O), 1.17 – 1.41 (14 H, m, 3 × CH2), 0.87 (3 H, t, *J*= 6.7 Hz, CH2C**H**3).

13C NMR (CDCl3): 170.80 (CH\***C**OO), 167.54 (C**C**OO), 165.15 (COOAr), 164.14 (**C**OOCH\*), 162.50 (C-4´), 155.94 (C-4), 154.84 (C-4´´), 146.83 (C-1´), 131.57 (C-2, C-6), 131.30 (C-2´´, C-6´´), 129.88 (C-1), 127.20 (C-1´´), 125.35 (C-2´, C-6´), 125.27 (**C**H2=C), 122.61 (C-3, C-5), 121.73 (C-3´´, C-5´´), 114.85 (C-3´, C-5´), 69.32 (CH\*), 67.83 (CH2O), 65.58 (**C**H2OOC), 64.63 (**C**H2OOC=), 31.88 (**C**H2CH2CH3), 29.49 (**C**H2CH2O), 28.95 – 29.30 (4**×**CH2), 28.55 (**C**H2CH2OOC=), 28.48 (**C**H2CH2OOC), 25.77 (**C**H2(CH2)2O, **C**H2(CH2)2OOC), 25.73 (**C**H2(CH2)2OOC), 22.68 (**C**H2CH3), 18.35 (CCH3), 17.14 (**C**H3CH\*), 14.13 (CH2**C**H3). Elemental analysis for C43H54N2O9 (742.91): calculated C 69.52 %, H 7.33 %, N 3.77 %; found C 69.29 %, H 7.65 %, N 3.74 %.

*(S)-1-(hexyloxy)-1-oxopropan-2-yl-4-{[4-({4´-[10-(methacryloyloxy)decyloxy] phenyl}diazenyl)benzoyl]oxy}benzoate (*MHA-10/6*)*

Analogously as for MHA 10/6, **4c** (1.5 g, 2.02 mmol) was converted to iodo-derivative and then reacted with potassium methacrylate (0.75 g, 6.04 mmol) under the same conditions. Yield 1.18 g (79 %) of monomer MHA-10/6.

1H NMR (CDCl3): 8.33 (2 H, d, *J =*8.8, H-2, H-6), 8.19 (2 H, d, *J =*8.8, H-2´´, H-6´´), 7.92 – 8.01 (4 H, m, H-3, H-5, H-2´, H-6´), 7.35 (2 H, d, *J*= 8.8, H-3´´, H-5´´), 7.02 (2 H, d, *J =*8.8, H-3´, H-5´), 6.10 (1 H, m, *trans-*C**H**2=), 5.52 – 5.58 (1 H, m, *cis-*C**H**2=), 5.34 (1 H, q, *J =*7.0, CH\*), 4.10 – 4.26 (4 H, m, 2 × COOCH2), 4.05 (2 H, t, *J =*6.2, CH2OAr), 1.94 (3 H, m, =CCH3), 1.76 – 1.89 (2 H, m, C**H**2CH2OAr), 1.57 – 1.75 (7 H, m, 2 Ч C**H**2CH2O, CH\*C**H**3), 1.43 – 1.56 (2 H, m, C**H**2(CH2)3O), 1.20 – 1.42 (14 H, m, 3 × CH2), 0.88 (3 H, t, *J*= 6.7 Hz, CH2C**H**3).

13C NMR (CDCl3): 170.80 (CH\***C**OO), 167.54 (C**C**OO), 165.15 (COOAr), 164.14 (**C**OOCH\*), 162.50 (C-4´), 155.94 (C-4), 154.84 (C-4´´), 146.83 (C-1´), 131.57 (C-2, C-6), 131.30 (C-2´´, C-6´´), 129.88 (C-1), 127.20 (C-1´´), 125.35 (C-2´, C-6´), 125.27 (**C**H2=C), 122.61 (C-3, C-5), 121.73 (C-3´´, C-5´´), 114.85 (C-3´, C-5´), 69.32 (CH\*), 67.83 (CH2O), 65.58 (**C**H2OOC), 64.63 (**C**H2OOC=), 31.88 (**C**H2CH2CH3), 29.49 (**C**H2CH2O), 28.95 – 29.30 (4**×**CH2), 28.55 (**C**H2CH2OOC=), 28.44 (**C**H2CH2OOC), 25.98 (**C**H2(CH2)2O), 25.75 (**C**H2(CH2)2OOC), 25.41 (**C**H2(CH2)2OOC), 22.68 (**C**H2CH3), 18.35 (CCH3), 17.13 (**C**H3CH\*), 14.10 (CH2**C**H3). Elemental analysis for C43H54N2O9 (742.91): calculated C 69.52 %, H 7.33 %, N 3.77 %; found C 69.33 %, H 7.63 %, N 3.73%.

*(S)-1-(decyloxy)-1-oxopropan-2-yl-4-{[4-({4´-[6-(methacryloyloxy)decyloxy]phenyl}diazenyl)benzoyl]oxy}benzoate (*MHA-10/10*)*

Using the procedure described for MHA-6/6, 4d(1.70 g, 2.27 mmol) was dissolved in isobutyl(methyl)ketone (MIBK) (100 ml), potassium iodide (7.0 g, 42.17 mmol) was added and the suspension was refluxed with vigorous stirring for 12 h. Obtained iodo-derivative was reacted with anhydrous potassium methacrylate (0.85 g, 6.84 mmol) in dry DMSO (100 ml). Crude MHA-10/10was purified by column chromatography on silica using dichloromethane - acetone (99.9 : 0.1) as eluent. Yield 1.51 g (83 %).

1H NMR (CDCl3): 8.33 (2 H, d, *J =*8.8, H-2, H-6), 8.19 (2 H, d, *J =*8.8, H-2´´, H-6´´), 7.91 – 8.05 (4 H, m, H-3, H-5, H-2´, H-6´), 7.35 (2 H, d, *J*= 8.8, H-3´´, H-5´´), 7.02 (2 H, d, *J =*8.8, H-3´, H-5´), 6.09 (1 H, m, *trans-*C**H**2=), 5.51 – 5.57 (1 H, m, *cis-*C**H**2=), 5.34 (1 H, q, *J =*7.0, CH\*), 4.10 – 4.26 (4 H, m, 2 × COOCH2), 4.05 (2 H, t, *J =*6.5, CH2OAr), 1.94 (3 H, m, =CCH3), 1.75 – 1.88 (2 H, m, C**H**2CH2OAr), 1.54 – 1.73 (7 H, m, 2 Ч C**H**2CH2O, CH\*C**H**3), 1.12 - 1.53 (24 H, m, 12 × CH2), 0.88 (3 H, t, *J*= 6.7 Hz, CH2C**H**3).

13C NMR (CDCl3): 170.80 (CH\***C**OO), 167.54 (C**C**OO), 165.17 (COOAr), 164.15 (**C**OOCH\*), 162.51 (C-4´), 155.94 (C-4), 154.84 (C-4´´), 146.83 (C-1´), 131.55 (C-2, C-6), 131.31 (C-2´´, C-6´´), 129.87 (C-1), 127.20 (C-1´´), 125.35 (C-2´, C-6´), 125.27 (**C**H2=C), 122.62 (C-3, C-5), 121.75 (C-3´´, C-5´´), 114.84 (C-3´, C-5´), 69.31 (CH\*), 67.83 (CH2O), 65.57 (**C**H2OOC), 64.63 (**C**H2OOC=), 31.88 (**C**H2CH2CH3), 29.14 – 29.58 (8**×**CH2, **C**H2CH2O), 28.55 (**C**H2CH2OOC=), 28.44 (**C**H2CH2OOC), 25.98 (**C**H2(CH2)2O), 25.75 (**C**H2(CH2)2OOC), 25.41 (**C**H2(CH2)2OOC), 22.68 (**C**H2CH3), 18.35 (CCH3), 17.13 (**C**H3CH\*), 14.10 (CH2**C**H3). Elemental analysis for C47H62N2O9 (799.02): calculated C 70.65 %, H 7.82 %, N 3.51 %; found C 70.31 %, H 7.75 %, N 3.47 %.

**2. Mesomorphic properties of the MHA-m/n monomers**

Mesomorphic properties of the MHA-m/n mpnomers are summarized in Table S1. The DSC heating/cooling runs for two compounds, selected as examples, are presented in Fig. S1. Representative characteristic textures observed with the help of optical polarization microscopy for MHA-10/6 mesogen are presented in Fig. S2. All compounds exhibit a broad temperature range of the orthogonal SmA\* and tilted SmC\* phases. Depending on molecular structure, the polar tilted SmC\* phase can be overcooled to room temperature before the onset of the crystal (Cr) phase; a distance between characteristic equidistant dechiralisation lines observed in the Sm-C\* phase corresponds to the helical pitch about 1.5µm. The temperature of the Iso – SmA\* phase transition slightly decreases with the length of both chains attached to chiral and non-chiral molecular terminal elements. An increase of the length of these chains results in broadening of the range of existence of the ferroelectric SmC\* phase, similarly to Ref. [S4, S5]. The melting point as well as the temperature of the SmA\* - SmC\* phase transition decrease upon increase of the length of alkyl chain at chiral carbon atom (at the same length of non-chiral terminal chain). For all compounds under study the SmC\* phase remains stable in the supercooled state, i.e. below the melting point; the crystallization does not occur even under applied electric field. Moreover, the uniform alignment of the SmC\* phase texture in planar (bookshelf) orientation can be easily obtained by applying of a low frequency a.c. electric field.

Table S1.Characteristics of various phases for MHA-m/n series: melting point, m.p., clearing point, c.p. and phase transition temperatures (in °C); corresponding enthalpy changes, ΔH (kJ mol−1), determined from DSC for the second temperature run are shown in brackets.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | m.p. | c.p. | phase |  | | phase |  | phase |  | phase |
| **MHA**-**6/5** | 90.6  [+54.1] | 106.6  [+1.6] | **Cr** | 61.3  [-50.1] | **SmC\*** | | 103.3  [-0.2] | **SmA\*** | 106.0  [-1.2] | **Iso** |
| **MHA**-**6/10** | 54.7  [+30.4] | 98.6  [+3.6] | **Cr** | 21.3  [-14.5] | | **SmC\*** | 74.7  [-0.1] | **SmA\*** | 97.6  [-3.8] | **Iso** |
| **MHA-10/6** | 56.1  [+45.0] | 116.2  [+3.1] | **Cr** | 14.9  [-20.7] | | **SmC\*** | 95.0  [-0.4] | **SmA\*** | 115.0  [-3.6] | **Iso** |
| **MHA-10/10** | 56.3  [+40.2] | 111.3  [+4.0] | **Cr** | 17.8  [-19.9] | | **SmC\*** | 84.3  [-0.3] | **SmA\*** | 109.3  [-3.9] | **Iso** |



Fig. S1.DSC heating and cooling runs (indicated by horizontal arrows) for the selected methacrylate mesogens: MHA-6/5(a) and MHA-10/10(b). Vertical arrows indicate the phase transition temperatures; the corresponding mesophases are specified along the heating/cooling runs .

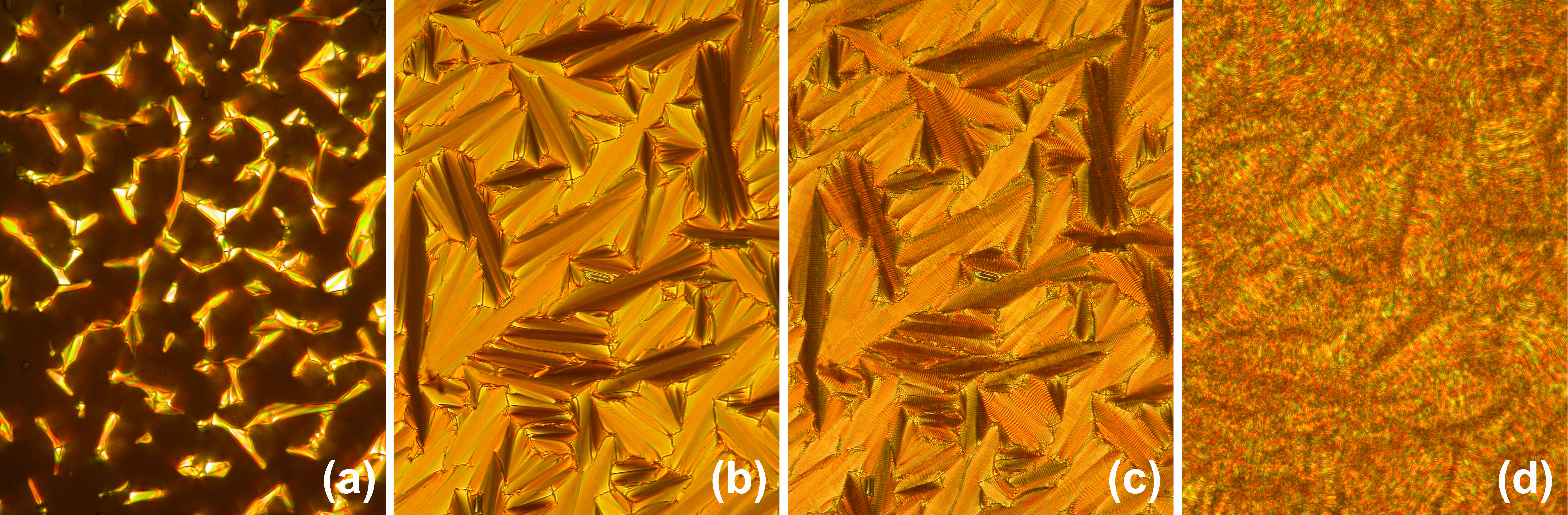


Fig. S2.Microphotographs of the characteristic textures observed using optical polarisation microscopy on cooling of the MHA-10/6 monomer placed in a 12 μm thick planar electrooptic cell: (a) appearance of the smectic bâtonnets at the Iso-Sm-A\* phase transition at about 115oC; (b) fan-shaped texture of the Sm-A\* phase at about 109oC; (c) fan-shaped texture with equidistant dechiralization lines of the SmC\* phase at about 90oC; the crystal phase at about 10oC. The width of each microphotograph is about 180 µm.

**References.**

## **[S1] Novotná V, Hamplová V, Bubnov A, Kašpar M, Glogarová M, Kapernaum N, Bezner S, Giesselmann F.** First photoresponsive liquid-crystalline materials with small layer shrinkage at the transition to the ferroelectric phase. **J Mater Chem.** 2009; **19**: 3992-3997.

[S2] **Kašpar M, Bubnov A, Hamplová V, Pirkl S, Glogarová M. New ferroelectric liquid crystalline materials with an azo group in the molecular core. Liq Cryst. 2004; 31: 821-830.**

[S3] Kašpar M, Hamplová V, Pakhomov SA, Bubnov A, Guitard F, Sverenyák H, Stibor I, Vaněk P, Glogarová M. [New series of ferroelectric liquid crystals with four ester groups](javascript:void(0)). Liq. Cryst. 1998; 24: 599-605.

[S4] Hamplová V, Bubnov A, Kašpar M, Novotná V, Lhotáková Y, Glogarová M. New antiferroelectric liquid crystalline materials containing a keto group and two lactate groups. Liq Cryst. 2003; 30: 1463-1470.

[S5] Bubnov A, Vacek C, Czerwinski M, Vojtylová T, Piecek W, Hamplová V. Design of polar self-assembling lactic acid derivatives with the keto group possessing sub-micrometre helical pitch. Beilstein J Nanotechnology. 2018; 9: 333-341.