Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

A Novel Series of Chiral Fluorinated Organosiloxane Liquid Crystals

W. M. Zoghaib, C. Carboni, H. Al-Hinai, S. Al-Abri, S. Al-Kasbi, E. Al-Nasseri, M. Al-Masroori, M. Al-Yahyaee & S. Al-Busaidi

To cite this article: W. M. Zoghaib, C. Carboni, H. Al-Hinai, S. Al-Abri, S. Al-Kasbi, E. Al-Nasseri, M. Al-Masroori, M. Al-Yahyaee & S. Al-Busaidi (2015) A Novel Series of Chiral Fluorinated Organosiloxane Liquid Crystals, Molecular Crystals and Liquid Crystals, 612:1, 183-190, DOI: 10.1080/15421406.2015.1030984

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1030984

Published online: 06 Jul 2015.

Mol. Cryst. Liq. Cryst., Vol. 612: pp. 183–190, 2015

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1030984

Taylor & Francis
Taylor & Francis Group

A Novel Series of Chiral Fluorinated Organosiloxane Liquid Crystals

W. M. ZOGHAIB,[1,*] C. CARBONI,[2] H. AL-HINAI,[1]
S. AL-ABRI,[1] S. AL-KASBI,[1] E. AL-NASSERI,[1]
M. AL-MASROORI,[1] M. AL-YAHYAEE,[1] AND S. AL-BUSAIDI[1]

[1]Chemistry Department, Sultan Qaboos University, Al-Khod, Oman
[2]Physics Department, Sultan Qaboos University, Al-Khod, Oman

The synthesis and characterization of a series of chiral fluorinated low molar mass organosiloxane materials is presented. The mesogenic moiety is similar to that in the TSiKN65F mesogen reported by Naciri et al., which displays a de Vries-type S_A^* phase. The one parameter varied across the series reported herein is the length of the alkyl chain linking the mesogen moiety to the siloxane tail.

Keywords de-Vries phase; organosiloxane; chiral; smectic

1. Introduction

Ferroelectric liquid crystalline materials are of great interest due to their important industrial applications. Low molar mass organosiloxane liquid crystals are good candidates for the search of materials displaying de-Vries type phases [1–5] and have demonstrated fast switching in the S_A [6] and S_C^* phases [7–9]. Ferroelectricity is exhibited in liquid crystal molecules if the molecules are chiral (no plane of symmetry), have a dipole moment directed perpendicular to the molecular axis and if molecules are tilted with respect to the smectic layer normal. Liquid crystalline materials exhibiting chiral smectic C phase below room temperature are of great importance due to their use in flat-panel displays and light modulators [10–14].

The materials we are reporting in this communication consist of a rigid core connected to a long chain hydrocarbon head and ending with a straight trisiloxane terminus. Using three phenyl rings as the mesogenic core unit, potentially produces a wider liquid crystalline phase temperature range. The siloxane terminus reduces the phase transition temperature, broadens the liquid crystal temperature range and enhances the molecule's spontaneous polarization [15–17].

Many lateral substituents have been introduced to liquid crystal materials, the most common is a fluorine substituent. The small size of a fluorine substituent enables its incorporation into all types of liquid crystals including, calamitic, discotic and lyotropic. However, fluorine with its high electronegativity leads to significant modification of liquid

*Address correspondence to W. M. Zoghaib, Chemistry Department, Sultan Qaboos University, PO Box 36, Al-Khod 123, Oman. E-mail: zoghaibw@squ.edu.om.

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

crystalline physical properties without too much disruption to the LC phase stability. The fluoro substituent modifies melting point, mesophase morphology and transition temperature. It also decreases the melting point and $T_{N\text{-}1}$ (the upper temperature limit) of the LC phase. Increasing the number of substituents further decreases the $T_{N\text{-}1}$ but only slightly decreases the melting point [18].

Varying the hydrocarbon chain length modifies the macroscopic properties of mesogenic materials. It is well documented that rotational viscosities and tilt angles of chiral smectic C ($S_C{}^*$) molecules increase with increasing chain length [19].

2. Exprimental

2.1 Materials

Reagents were purchased from Aldrich and used as received. The catalyst dichlorodicyclopentadienyl platinum II was purchased from STREM Chemicals (Massachusetts, USA) and 1, 1, 1, 3, 3, 5, 5-heptamethyltrisiloxane was purchased from ABCR (Karlsruhe, Germany).

2.2 Methods

Proton Magnetic Resonance (^{1}H-NMR) spectra were acquired and recorded using a 400 MHz VARIAN NMR spectrometer in $CDCl_3$. Carbon Magnetic Resonance (^{13}C-NMR) spectra were recorded at 100 MHz using the same NMR spectrometer. Chemical shifts ($\delta_{\ ppm}$) were recorded in parts per million (ppm) downfield from TMS (assigned as zero ppm).

Thin layer chromatography (TLC) and preparative TLC were performed on glass plates pre-coated with silica gel, whereas flash column chromatography was performed using silica gel 60 (mesh 70-230) purchased from Aldrich.

Rotary evaporator (BUCHI) was used to evaporate solvents at low pressure. Anhydrous reaction conditions were performed under an inert atmosphere of dry Argon. THF was dried by distillation over potassium metal under Argon and used immediately.

Liquid crystal transition temperatures were identified by polarized light microscopy in conjunction with a heating/cooling stage and a temperature control unit (Linkam TMS 94). The specimens were filled by capillary action at a temperature of about 20 degrees above the transition to isotropic phase into a 5 μm thick glass cell treated for planar alignment. An indium tin oxide (ITO) transparent electrode was soldered to the inner face of the glass cell facilitating the application of an electric field to the specimen.

3. Synthesis

Preparation of compounds **1** to **6** from commercially available starting materials was described in earlier communications [4,5].

Synthesis of the homologous mesogenic series of compounds **7** to **12** was performed according to the following general method.

To a stirred solution of each of **1, 2, 3, 4, 5 and 6** in anhydrous THF (5 mL) under argon, the silylating reagent 1, 1, 1, 3, 3, 5, 5-heptamethyltrisiloxane (*l*) (1.2 molar equivalents) was added to give a yellow solution. Dichlorodicyclopentadienyl platinum II(*s*) (1 or 2 mg, 0.025 to 0.50 mmol) was added to the mixture and the solution's color turned black

after gas evolution was noticed. The reaction was monitored by TLC and quenched by adding methanol when all starting material disappeared after an average of 30 minutes. The crude was purified by flash column chromatography on silica gel (eluent: 10% ethyl acetate/hexane) followed by preparative TLC using the same solvent system to give a pure product.

(R)-4′-(heptan-2-yloxy)-3′-nitro-[1,1′-biphenyl]-4-yl-3-fluoro-4-((5-(1, 1, 3, 3, 5, 5, 5-heptamethyltrisiloxanyl)pentyl)oxy)benzoate (7). *(58.3% yield).* ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): -0.05–0.09 (m, 21H, CH_3 (32, 32′, 33, 33′, 34, 34′, 34′′), 0.67–0.87 (m, 3H, CH_3(1)), 1.14–1.30 (m, 12H, CH_2 (2, 3, 4, 29, 30, 31), 1.37 (d, 3H, CH_3(7), J 6.0 Hz), 1.55–1.61 (m, 2H, CH_2(5)), 1.77–1.84 (m, 2H, CH_2(28)), 4.07 (t, 2H, CH_2(27), J 6.6 Hz), 4.48 (sextet, 1H, CH(6), J 6.4 Hz), 6.98 (t, 1H, ArH (25), J 8.4 Hz), 7.21 (d, 2H, ArH (17,18), J 8.6 Hz), 7.51 (d, 2H, ArH (15,16), J 8.6 Hz), 7.83 (dd, 1H, ArH (22) J 2.0, 11.5 Hz), 7.62 (dd, 1H, ArH (11), J 2.4, 8.4 Hz), 7.64 (d, 1H, ArH (09), J 8.4 Hz), 7.90 (d, 1H, ArH (23), J 8.5 Hz), 7.92 (d, 1H, ArH (12), J 2.3 Hz).

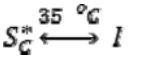
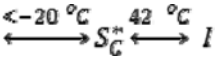
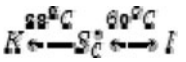
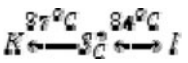
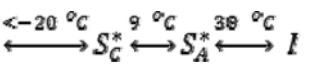
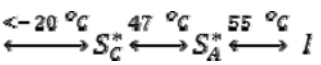
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 4.2 CH_3 (34, 34′, 34′′), 5.9 CH_3 (33, 33′), 2.8 CH_3 (32, 32′), 21.3 CH_2 (31), 33.5 CH_2 (30), 26.3 CH_2 (29), 30.6 CH_2 (28), 68.9 CH_2 (27), 151.0 C (26), 115.7 CH (25), 152.1 C (24), 126.3 CH (23), 117.7 CH (22), 123.8 C (21), 164.0 C (20), 152.0 C (19), 121.9 CH (18,17), 127.8 CH (16,15), 133.4 C (14), 129.1 C (13), 123.1 CH (12), 134.1 CH (11), 134.6 C (10), 115.6 CH (9), 152.8 C (8), 22.0 CH_3 (7), 70.1 CH (6), 32.8 CH_2 (5), 23.8 CH_2 (4), 23.2 CH_2 (3), 23.0 CH_2 (2), 20.4 CH_3 (1).

(R)-4′-(heptan-2-yloxy)-3′-nitro-[1,1′-biphenyl]-4-yl-3-fluoro-4-((6-(1, 1, 3, 3, 5, 5, 5-heptamethyltrisiloxanyl)hexyl)oxy)benzoate (8). *(21.1% yield).* ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): -0.02–0.08 (m, 21H, CH_3 (33, 33′,34,34′,35, 35′, 35′′), 0.67–0.87 (m, 3H, CH_3(1)), 1.14–1.30 (m, 14H, CH_2 (2, 3, 4, 29, 30, 31, 32), 1.32 (d, 3H, CH_3 (7), J 6.0 Hz), 1.55–1.61 (m, 2H, CH_2 (5)), 1.77–1.84 (m, 2H, CH_2(28)), 4.06 (t, 2H, CH_2(27), J 6.6 Hz), 4.47 (sextet, 1H, CH(6) J 6.3 Hz), 6.97 (t, 1H, ArH (25), J 8.4 Hz), 7.21 (d, 2H, ArH (17, 18), J 8.6 Hz), 7.51 (d, 2H, ArH (15, 16), J 8.6 Hz), 7.83 (dd, 1H, ArH (22) J 2.0, 11.5 Hz), 7.62 (dd, 1H, ArH (11), J 2.4, 8.4 Hz), 7.64 (d, 1H, ArH (09), J 8.4 Hz), 7.90 (d, 1H, ArH (23), J 8.5 Hz), 7.92 (d, 1H, ArH (12), J 2.3 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 4.2 CH_3 (35, 35′, 35′′), 5.9 CH_3 (34, 34′′), 2.0 CH_3 (33, 33′), 17.9 CH_2 (32), 21.3 CH_2 (31), 33.5 CH_2 (30), 26.3 CH_2 (29), 30.6 CH_2 (28), 72.3 CH_2 (27), 151.0 C (26), 115.7 CH (25), 147.7 C (24), 126.3 CH (23), 117.7 CH (22), 123.8 C (21), 164.0 C (20), 152.0 C (19), 121.9 CH (18,17), 127.8 CH (16,15), 133.4 C (14), 129.1 C (13), 123.1 CH (12), 134.1 CH (11), 134.6 C (10), 115.6 CH (9), 152.5 C (8), 22.4 CH_3 (7), 70.3 CH (6), 32.8 CH_2 (5), 23.8 CH_2 (4), 23.4 CH_2 (3), 23.1 CH_2 (2), 20.2 CH_3 (1).

(R)-4′-(heptan-2-yloxy)-3′-nitro-[1,1′-biphenyl]-4-yl-3-fluoro-4-((7-(1, 1, 3, 3, 5, 5, 5-heptamethyltrisiloxanyl)heptyl)oxy)benzoate (9). *(59.1% yield).* ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): -0.018–0.09 (m, 21H, CH_3 (34, 34′, 35, 35′, 36, 36′, 36′′), 0.79–0.84 (m, 3H, CH_3 (1)), 1.21–1.84 (m, 16H, CH_2 (2, 3,4, 29, 30, 31, 32, 33), 1.32 (d, 3H, CH_3(7), J 6.0 Hz), 1.55–1.61 (m, 2H, CH_2 (5)), 1.77–1.84 (m, 2H, CH_2 (28)), 4.06 (t, 2H, CH_2 (27), J 6.6 Hz), 4.48 (sextet, 1H, CH(6) J 6.4 Hz), 6.97 (t, 1H, ArH (25), J 8.4 Hz), 7.21 (d, 2H, ArH (17, 18), J 8.6 Hz), 7.51 (d, 2H, ArH (15, 16), J 8.6 Hz), 7.83 (dd, 1H, ArH (22) J 2.0, 11.5 Hz), 7.62 (dd, 1H, ArH (11), J 2.4, 8.4 Hz), 7.91 (d, 1H, ArH (09), J 8.4 Hz), 7.90 (d, 1H, ArH (23), J 8.5 Hz), 7.92 (d, 1H, ArH (12), J 2.3 Hz).

Table 1. Transition temperatures of liquid crystals **7** – **12**

LC # 7	
LC # 8	
LC # 9	
LC # 10	
LC # 11	
LC # 12	

(Sc*: Chiral smectic C, S_A*: chiral smectic A, K: crystalline, I: isotropic).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 5.0 CH_3 (36, 36′, 36″), 3.4 CH_3 (35, 35″), 2.8 CH_3 (34, 34′), 16.5 CH_2 (33), 17.9 CH_2 (32), 21.3 CH_2 (31), 33.5 CH_2 (30), 26.3 CH_2 (29), 30.6 CH_2 (28), 72.3 CH_2 (27), 151.0 C (26), 115.7 CH (25), 147.7 C (24), 126.3 CH (23), 117.7 CH (22), 123.8 C (21), 164.0 C (20), 152.0 C (19), 121.9 CH (18,17), 127.8 CH (16,15), 133.4 C (14), 129.1 C (13), 123.1 CH (12), 134.1 CH (11), 134.6 C (10), 115.6 CH (9), 152.5 C (8), 23.0 CH_3 (7), 70.1 CH (6), 32.8 CH_2 (5), 23.8 CH_2 (4), 22.5 CH_2 (3), 22.0 CH_2 (2), 15.4 CH_3 (1).

(R)-4′-(heptan-2-yloxy)-3′-nitro-[1,1′-biphenyl]-4-yl-3-fluoro-4-((8-(1, 1, 3, 3, 5, 5, 5-heptamethyltrisiloxanyl)octyl)oxy)benzoate (10). *(48.0% yield).* ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): - 0.015–0.10 (m, 21H, CH_3 (35, 35′, 36, 36′, 37, 37′, 37″), 0.80–0.88 (m, 3H, CH_3(1)), 1.10–1.61 (m, 18H, CH_2 (2, 3, 4, 29, 30, 31, 32, 33, 34), 1.32 (d, 3H, CH_3(7), J 6.0 Hz), 1.55–1.61 (m, 2H, CH_2(5)), 1.77–1.84 (m, 2H, CH_2(28)), 4.08 (t, 2H, CH_2(27), J 6.6 Hz), 4.35 (sextet, 1H, CH(6) J 6.4 Hz), 6.97 (t, 1H, ArH(25), J 8.4 Hz), 7.21(d, 2H, ArH(17,18), J 8.6 Hz), 7.51 (d, 2H, ArH(15,16), J 8.6 Hz), 7.83 (dd, 1H, ArH(22) J 2.0, 11.5 Hz), 7.60 (dd, 1H, ArH(11), J 2.4, 8.4 Hz), 7.85 (d, 1H, ArH(09), J 8.4 Hz), 7.90 (d, 1H, ArH(23), J 8.5 Hz), 7.92 (d, 1H, ArH(12), J 2.3 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 4.2 CH_3 (37, 37′, 37″), 5.5 CH_3 (36, 36′), 2.1 CH_3 (35, 35′), 16.0 CH_2 (34), 16.5 CH_2 (33), 17.9 CH_2 (32), 21.5 CH_2 (31), 33.4 CH_2 (30), 26.5 CH_2 (29), 30.4 CH_2 (28), 72.3 CH_2 (27), 151.0 C (26), 115.7 CH (25), 147.8 C (24), 126.3 CH (23), 117.6 CH (22), 123.8 C (21), 164.0 C (20), 152.0 C (19), 121.9 CH (18, 17), 127.8 CH (16, 15), 133.4 C (14), 129.1 C (13), 123.1 CH (12), 134.1 CH (11), 134.6 C (10), 115.6 CH (9), 152.2 C (8), 24.1 CH_3 (7), 70.3 CH (6), 32.8 CH_2 (5), 23.7 CH_2 (4), 21.5 CH_2 (3), 20.0 CH_2 (2), 14.4 CH_3 (1).

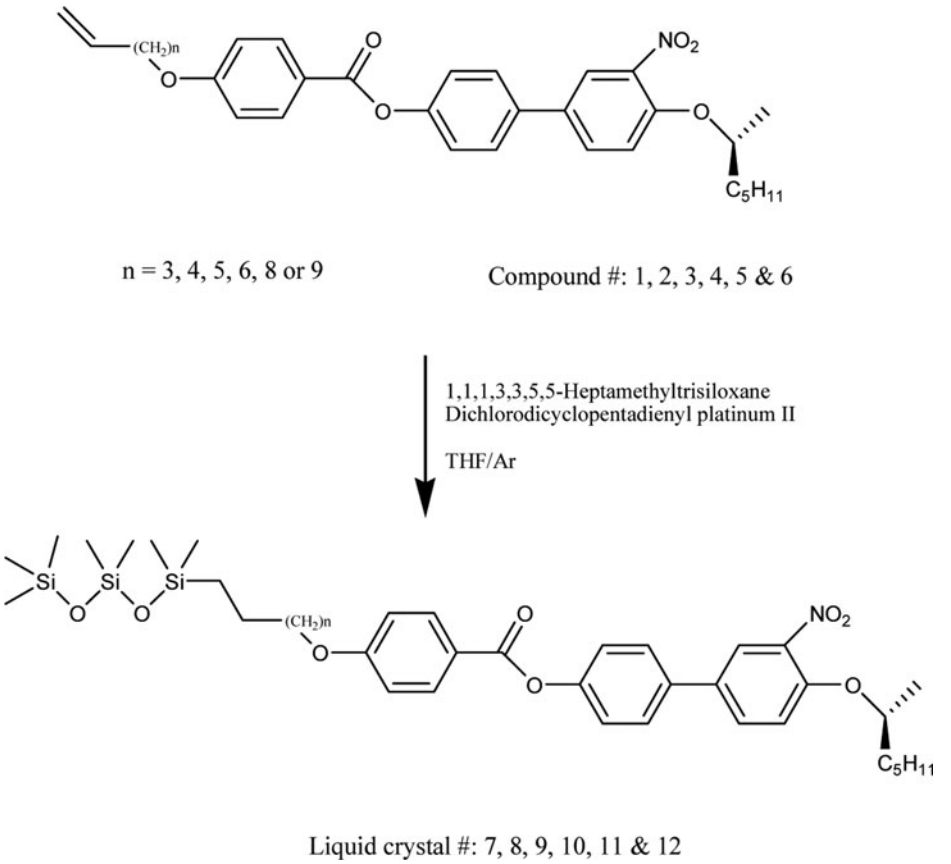


Figure 1. Preparation of liquid crystals 7 – 12 from their precursors.

(R)-4′-(heptan-2-yloxy)-3′-nitro-[1,1′-biphenyl]-4-yl-3-fluoro-4-((10-(1, 1, 3, 3, 5, 5, 5-heptamethyltrisiloxanyl)decyl)oxy)benzoate (11). *(45.2% yield).* ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): -0.007–0.16 (m, 21H, CH_3(37, 37′, 38, 38′, 39, 39′, 39′′)), 0.50 (m, 2H, CH_2 (36), 1.25–1.35 (m, 16H, CH_2 (2, 3, 4, 29, 30, 31, 32, 33), 1.35 (d, 3H, CH_3(7) J 6.0 Hz), 1.36-1.46 (m, 4H,CH_2 (34, 35), 1.58 (m, 2H, CH_2(5)), 1.87-1.95 (m, 2H, CH_2(28)), 4.04 (t, 2H, CH_2(27) J 6.6 Hz), 4.48-4.53 (sextet, 1H, CH(6) J 6.4 Hz), 6.97 (t, 1H, ArH(25) J 8.3 Hz), 7.08 (d, 1H, ArH(9) J 8.4 Hz), 7.21 (t, 2H, ArH(17,18) J 8.6 Hz), 7.55 (d, 2H, ArH(15,16) J 8.6 Hz), 7.65 (dd, 2H, ArH(22) J 2.0, 11.5 Hz), 7.86 (dd, 2H, ArH(11) J 2.4, 8.4 Hz), 7.92 (d, 1H, ArH(23) J 8.5 Hz), 7.94 (d, 1H, ArH(12) J 2.3 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 0.13 CH_3 (37, 37′), 0.49 CH_3 (39, 39′, 39′), 0.80 CH_3 (38, 38′), 13.1 CH_3(1), 18.0 CH_2(36), 19.4 CH_2(35), 22.4 CH_3(7), 23.0 CH_2(2), 24.8 CH_2(4), 25.8 CH_2(29), 26.3 CH_2(28), 28.8 CH_2(30), 29.2 CH_2(31), 29.4 CH_2(32), 31.5 CH_2(3), 33.2 CH_2(34), 39.9 CH_2(5), 69.3 CH_2(27), 70.4 CH (6), 113.2 ArCH (22), 116.5 ArCH (9), 118.2 ArCH (25), 122.1 ArCH (17,18), 123.6 ArCH (12), 127.3 C(21), 127.6 ArCH (15,16), 131.8 ArC (13), 132.3 ArC (14), 136.2 ArC (10), 136.6 ArCH (11), 140.8 ArC (19), 150.4 ArC (26), 151.82 ArC (24), 153.4 ArCH (8), 163.9 C═O (20).

(R)-4′-(heptan-2-yloxy)-3′-nitro-[1,1′-biphenyl]-4-yl-3-fluoro-4-((11-(1, 1, 3, 3, 5, 5, 5-heptamethyltrisiloxanyl)undecyl)oxy)benzoate (12). *(41% yield).* ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): -0.025–0.078 (m, 21H, CH_3(38, 38′, 39, 39′, 40, 40′, 40′′)), 0.81 (m, 2H, CH_2(36), 1.18–1.29 (m, 18H, CH_2 (2,3, 4, 29, 30, 31, 32, 33, 34)), 1.33 (d, 3H, CH_3(7) J 6.0 Hz), 1.36-1.46 (m, 4H,CH_2 (34,35), 1.53 (m, 2H, CH_2(5)), 1.78-1.83 (m, 2H, CH_2(28)), 4.06 (t, 2H, CH_2(27) J 6.6 Hz), 4.46-4.50 (m, 1H, CH(6)), 6.97 (t, 1H, ArH(25) J 8.3 Hz), 7.08 (d, 1H, ArH(9) J 8.4 Hz), 7.21 (t, 2H, ArH (17,18) J 8.6 Hz), 7.55 (d, 2H, ArH(15,16) J 8.6 Hz), 7.66 (dd, 2H, ArH(22) J 2.0, 11.5 Hz), 7.86 (dd, 2H, ArH(11) J 2.4, 8.4 Hz), 7.90 (d, 1H, ArH(23) J 8.5 Hz), 7.93 (d, 1H, ArH(12) J 2.3 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 0.13 CH_3 (38, 38′), 0.49 CH_3 (39, 39′), 0.80 CH_3 (40, 40′, 40′′), 14.1 CH_3 (1), 17.9 CH_2 (37), 18.1 CH_2 (36), 19.4 CH_2 (35), 22.4 CH_3 (7), 23.0 CH_2 (2), 24.8 CH_2 (4), 25.7 CH_2 (29), 26.3 CH_2 (28), 28.8 CH_2 (30), 29.2 CH_2 (31), 29.4 CH_2 (32), 26.5 CH_2 (3), 33.2 CH_2 (34), 39.9 CH_2 (5), 69.3 CH_2 (27), 70.4 CH (6), 113.2 ArCH (22), 116.5 ArCH (9), 118.2 ArCH (25), 122.1 ArCH (17,18), 123.6 ArCH (12), 127.3 C (21), 127.6 ArCH (15, 16), 131.8 ArC (13), 132.3 ArC (14), 136.2 ArC (10), 136.6 ArCH (11), 140.9 ArC (19), 150.4 ArC (26), 151.8 ArC (24), 153.4 ArCH (8), 165.9 C=O (20).

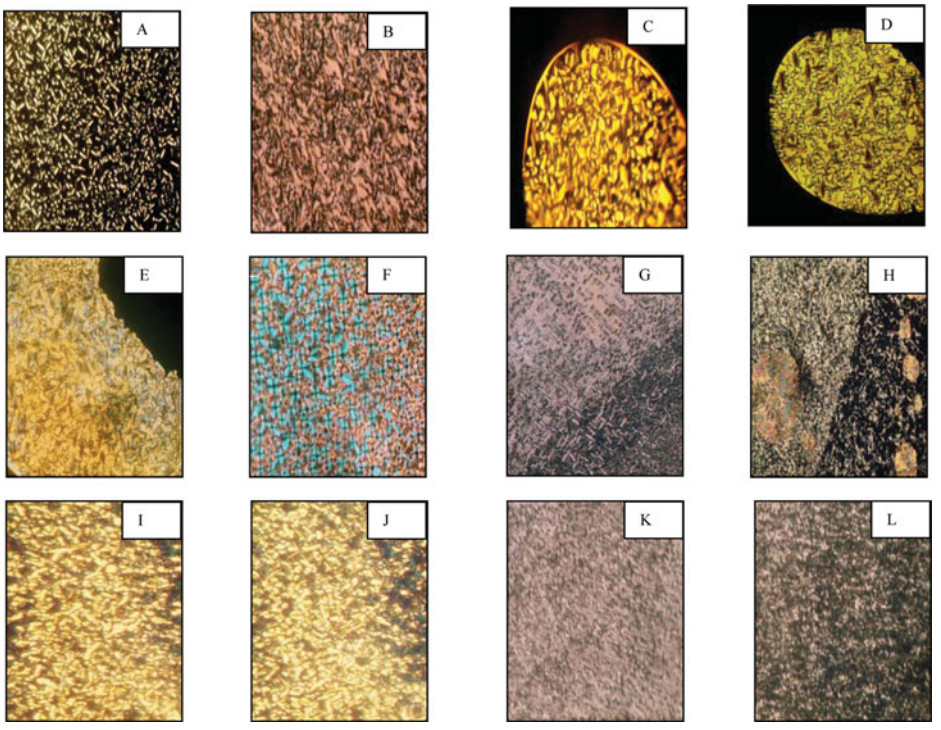


Plate 1. Some of the textures observed in the series of materials. **A**: LC 7 at 24°C, **B**: LC 7 at −20°C, most likely in a glassy phase. **C**: LC 8 at 34°C, **D**: LC 8 at −17°C. **E**: LC 9 at 40°C, **F**: LC 9 at 50°C with an applied field of +4 V/μm causing switching of the bright green focal conics. **G**: LC 10 at 78°C, **H**: LC 10 at 40°C. **I**: LC 11 at 6°C with an applied field of +4 V/μm. **J**: LC 11 at 6°C with an applied field of −4 V/μm. **K**: LC 12 at 5°C with an applied field of +8 V/μm and **L**: LC 12 at 5°C with an applied field of −8 V/μm, uniform switching is observed.

4. Polarized Light Microscopy Observations

The observations are summarized in Table 1 and texture observations are displayed in Plate 1. As it is usually the case with low molar mass organosiloxane materials there is a direct transition between the isotropic and smectic phases. The transition occurs through a 4 to 5 degree biphasic range. In almost all specimens on cooling, small bâtonnets appear in the isotropic phase, the bâtonnets do not grow in size but their number increases to give the sanded texture often observed in organosiloxane materials.

The materials **7**, **8** and **10** display a tendency to crystallize at room temperature. When heating the crystallized sample, the crystal melts directly to the isotropic phase at a temperature between 5 and 10 degrees above the isotropic to smectic transition temperature. The materials **8**, **11** and **12** display a response to an electric field down to temperatures of about -20°C. At low temperatures the response is slow, of the order of several seconds.

All the materials display an electro-optic response to an electric field that appears to be that of a $S_C{}^*$ phase. The specimens could not be aligned over sufficiently large areas to perform reliable tilt angle measurements however, the ferroelectric switching could be clearly observed inside the small domains. In the material **9**, larger domains were formed and it was observed that the tilt angle increases significantly with increasing field indicating that the phase could be a de-Vries S_A phase. In the material **12** the switching behavior changes at a temperature around 47°C and the response above this temperature is typical of a S_A phase.

5. Conclusion

A series of six chiral fluorinated organosiloxane liquid crystals was prepared with an overall moderate yield. All six LCs (differing only in the length of the hydrocarbon chain connecting the rigid core to the siloxane terminus) exhibit a smectic C phase over a wide temperature range. In at least two of the six compounds reported (LC **11** & **12**), a de-Vries Smectic A phase can also be observed. Tilt angle measurements as a function of temperature on **11** & **12** are pending.

Funding

Financial support by Sultan Qaboos University's Internal Grant number IG/SI/PHYS/12/03 is greatly appreciated.

References

[1] Kanbe, J., Inoue, H., Mizutome, A., Hanyuu, Y., Katagiri, K., & Yoshihara, S. (1991). *Ferroelectrics*, *114*, 3.

[2] Sprunt, S., Naciri, J., Ratna, B. R., & Shashidar, R. (1995). *Appl. Phys. Lett*., *66*, 1443.

[3] Handaschy, M. A., Drabik, T. J., Cotter, L. K., & Gaalema, S. D. (1990). Fast Ferroelectrics-Liquid Crystal Spatial Light Modulator with Silicon-Integrated-Circuit Active Backplane. *Optical Digital GaAs Technology, Signal processing Applications; Proc. SPIE*, *1291*, 158.

[4] Naciri, J., Ruth, J., Crawford, G., Shashindar, R., & Ratna, B. R. (1995). *Chem. Mater*, *7*, 1397.

[5] Zoghaib, W. M., Carboni, C., George, A. K., AL-Manthari, S., AL-Hussaini, A., and AL-Futaisi, F. (2011). *Mol. Cryst. Liq. Cryst.*,,Vol. *542*, 123.

[6] Newton, J., Coles, H.J., Hodge, P., & Hannington, J. (1994). Synthesis and properties of low-molar liquid-crystalline siloxane derivatives. *J. Mater. Chem.*, *4*, 869–874.

[7] Coles, H.J., Owen, H., Newton, J., & Hodge, P. (1993). New low molar mass organosiloxanes with unusual ferroelectric properties. *Liq. Cryst.*, *15*, 739–744.
[8] Coles, H.J., Owen, H.; Newton, J., & Hodge, P. (1995). Electro-optic effects in novel siloxane containing oligomeric liquid crystals II: Smectic C materials. *Proc. SPIE*, *2408*, 22–29.
[9] Kloess, P., McComb, J., Coles, H.J., & Zentel, R. (1996). Synthesis and properties of a new series of low-molar-mass organo-siloxane derivatives. *Ferroelectrics*, *180*, 233–243.
[10] Lagerwall, S.T., & Dahl, I. (1984). Ferroelectric liquid crystals. *Mol. Cryst. Liq. Cryst.*, *114*, 151–187.
[11] Lagerwall, S.T., Otterholm, B., & Skarp, K. (1987). Material properties of ferroelectric liquid crystals and their relevance for applications and devices. *Mol. Cryst. Liq. Cryst.*, *152*, 503–587.
[12] Roberts, J.C., Kapernaum, N., Giesselmann, F., Wand, M.D., & Lemieux, R.P. (2008). Fast switching organosiloxane ferroelectric liquid crystals. *J. Mater. Chem.*, *18*, 5301–5306.
[13] Grüneberg, K., Naciri, J., & Shashidhar, R. (1996). Ferroelectric properties of a fast switching cyclic siloxane oligomer. *Chem. Mater.*, *8*, 2486–2498.
[14] Keith, C., Reddy, R.A., Baumeister, U., & Tschierske, C. (2004). Banana-shaped liquid crystals with two oligosiloxane end-groups: Field-induced switching of supramolecular chirality. *J. Am. Chem. Soc.*, *126*, 14312–14313.
[15] Hsu, C.S., & Her, B.S. (1996). Synthesis of ferroelectric liquid-crystalline polymethacrylates containing 1,2-diphenylethane based mesogens. *Macromol. Chem. Phys.*, *197*, 4105–4118.
[16] Liao, C.T., Wu, Z.L., Wu, N.C., Liu, J.Y., Jiang, M.H., Zou, S.F., Lee, J.Y. (2010). Low-temperature and wide ferroelectric phase in mixtures of chiral and non-chiral tilted smectic C-type liquid crystals. *Mol. Cryst. Liq. Cryst.*, *533*, 3–15.
[17] Leadbetter, A.J., Forst, J.C., Mazid, M.A. (1979). Interlayer correlations in smectic B phases. *J. Physique Lett.*, *40*, 325–329.
[18] Collings, P. J. *et al.* (1997). In: *Introduction to Liquid Crystals*, Gray, G. W., Goodby J. W. & Fukuda, A. (Eds.), Chapter 3, Taylor & Francis: London.
[19] Chih-Hung Lin, (2013). Synthesis and Characterization of Ferroelectric Liquid Crystalline Organosiloxanes Containing 4-(4-undecanyloxy bi-phenyl-1-carboxyloxy)phenyl (2*S*,3*S*)-2-chloro-3-methylvalerate and 4-(4-undecanyloxybenzoyloxy)biphenyl (2*S*,3*S*)-2-chloro-3-methylvalerate. *International Journal of Molecular Sciences*, *14*, 21306.