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## Liquid Crystals

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*Preliminary communication*

## Antiferroelectric phase induced by a semi-fluoroalkane positioned at the chiral tail of a molecule

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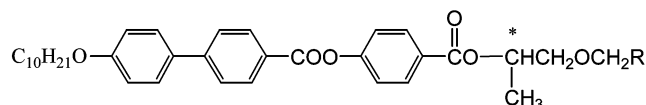
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A novel fluorinated chiral liquid crystal material derived from a newly designed optically active semi-perfluorinated alkyl chain in the chiral group, (*S*)-1-(2,2,3,3,3-pentafluoropropoxy)-2-propanol, and a non-fluorinated homologue derived from (*S*)-1-propyloxy-2-propanol, were prepared for comparison of their mesomorphic properties. The investigation of defect textures, switching behaviour and dielectric permittivity showed that the introduction of a semi-perfluorinated alkyl chain into the chiral tail of the molecule induces formation of an antiferroelectric phase.

The antiferroelectric  $\text{SmC}_A^*$  phase in chiral liquid crystals exhibits tristate switching properties and has been extensively studied both experimentally and theoretically in view of potential application in electro-optical devices [1]. Thus, many antiferroelectric materials based on the first discovered structures of (i) MHPOBC with optically active 2-octanol as a chiral group, and (ii) TFMHPOBC with optically active 1,1,1-trifluoro-2-octanol as a chiral group, have been designed and synthesized for investigation in relation to variation of achiral alkyl groups and rigid molecular cores [1, 2]. Subsequently, the origin of antiferroelectric order has been clarified and the relation between molecular structure and the occurrence of the antiferroelectric phase established and reviewed [3]. A few chiral materials with different structures and chiral groups have also been reported to possess an antiferroelectric phase [4].

Here, we report for the first time a novel fluorinated chiral liquid crystal material **I** derived from a newly designed optically active semi-perfluorinated alkyl chain in the chiral group, (*S*)-1-(2,2,3,3,3-pentafluoropropoxy)-2-propanol, that produces an antiferroelectric  $\text{SmC}_A^*$  phase. A non-fluorinated homologue **II** derived from (*S*)-1-propyloxy-2-propanol is also presented for comparison of their mesomorphic properties. The structural formulae of the materials are given below. It may be noted that semi-perfluorinated chiral materials possessing an antiferroelectric phase are only

observed in some structurally similar homologues of MHPOBC with the semi-perfluorinated alkyl chain connected to the achiral tail [5, 6].



material I: R =  $-\text{CF}_2\text{CF}_3$   
material II: R =  $-\text{CH}_2\text{CH}_3$

Detailed synthetic procedures for the preparation of the semi-perfluorinated and non-fluorinated chiral groups and their corresponding chiral materials will be described elsewhere. The purity and chemical structures of the intermediates and final products were checked by thin layer chromatography, elemental analysis using a Perkin-Elmer 2400 spectrometer, and proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectroscopy using a Bruker WP100SY FT-NMR spectrometer. The chemical shifts of material **I** (R =  $-\text{CF}_2\text{CF}_3$ ) in  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS) are:  $\delta$ (ppm) 0.90–0.87 (m, 6H,  $-\text{CH}_2\text{CH}_3$ ), 1.56–1.25 (m, 14H,  $-\text{OCH}_2\text{CH}_2(\text{CH}_2)_7-$ ), 1.83–1.80 (m, 2H,  $-\text{OCH}_2\text{CH}_2-$ ), 3.81–3.77 (m, 2H,  $-\text{CH}_2\text{OCH}_2-$ ), 3.97 (m, 2H,  $-\text{CH}_2\text{OCH}_2\text{CF}_2-$ ), 4.03–4.00 (t, 2H,  $-\text{CH}_2\text{OAr}-$ ), 5.53–5.51 (m, 1H,  $-\text{COOCHCH}_3-$ ) 6.97–6.95 (d, 2H, ArH), 7.01–6.99 (d, 2H, ArH), 7.15–7.13 (d, 2H, ArH), 7.60–7.57 (d, 2H, ArH), 7.69–7.67 (d, 2H, ArH), 8.23–8.21 (d, 2H, ArH). The chemical shifts for material **I** in  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )

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are:  $-83.85$  ( $\text{CF}_3$ ),  $-123.18$  ( $\text{CF}_2$ ). Elemental analysis for  $\text{C}_{36}\text{H}_{41}\text{F}_5\text{O}_6$  (%): calculated, C 65.05, H 6.22, found, C 65.11, H 6.27. The chemical shifts of material **I** ( $R = -\text{CH}_2\text{CH}_3$ ) in  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS) are:  $\delta$ (ppm) 0.93–0.87 (m, 6H,  $-\text{CH}_2\text{CH}_3$ ), 1.60–1.28 (m, 16H,  $\text{CH}_3\text{CH}_2\text{CH}_2-$ ), 1.82 (m, 2H,  $-\text{OCH}_2\text{CH}_2-$ ), 3.48–3.44 (m, 2H,  $-\text{CHCH}_2\text{OCH}_2-$ ), 3.63–3.57 (m, 2H,  $-\text{CH}_2\text{OCH}_2\text{CH}_2-$ ), 4.03–4.00 (t, 2H,  $-\text{CH}_2\text{OAr}-$ ), 5.53–5.51 (m, 1H,  $-\text{COOCHCH}_3-$ ), 6.99–7.01 (d, 2H, ArH), 7.30–7.32 (d, 2H, ArH), 7.61–7.58 (d, 2H, ArH), 7.71–7.69 (d, 2H, ArH), 7.15–7.12 (d, 2H, ArH), 8.24–8.22 (d, 2H, ArH). Elemental analysis for  $\text{C}_{36}\text{H}_{46}\text{O}_6$  (%): calculated, C 75.23, H 8.07; found, C 75.15, H 8.05.

Transition temperatures and enthalpy changes of the transitions for the liquid crystals were determined by differential scanning calorimetry using a Perkin-Elmer DSC7 calorimeter at heating/cooling rates of  $5^\circ\text{C min}^{-1}$ . Mesophases were identified by the observation of textures using a Nikon Microphot-FXA optical microscope under crossed polarizers, with a Mettler FP82HT hot stage in connection with a FP90 control processor. Switching behaviour and dielectric permittivity of ferroelectric and antiferroelectric smectic phases were measured in homogeneously aligned cells (E. H. C. Co. Japan) using the triangular wave method [7].

The mesophases, transition temperatures, and enthalpies of transition for the materials are listed in the table. The  $\text{SmA}^*$  phase was characterized by the formation of focal-conic texture and the  $\text{SmC}^*$  phase by the formation of striated focal-conic texture. The  $\text{SmC}_A^*$  phase also appeared as a striated focal-conic texture and was further characterized from the switching current and dielectric permittivity measurements. The switching behaviour of the  $\text{SmC}^*$  and  $\text{SmC}_A^*$  phases is presented in figure 1. In the  $\text{SmC}^*$  phase, the single switching peak produced by polarization reversal of the charge suggests the existence of ferroelectricity [7]. In the  $\text{SmC}_A^*$  phase, two switching current peaks appeared, similar to the normal  $\text{SmC}_A^*$  phase [2], supporting the occurrence of antiferroelectricity.

The temperature dependence of the dielectric constant  $\epsilon'$  measured at 100 Hz in  $25\ \mu\text{m}$  homogeneously

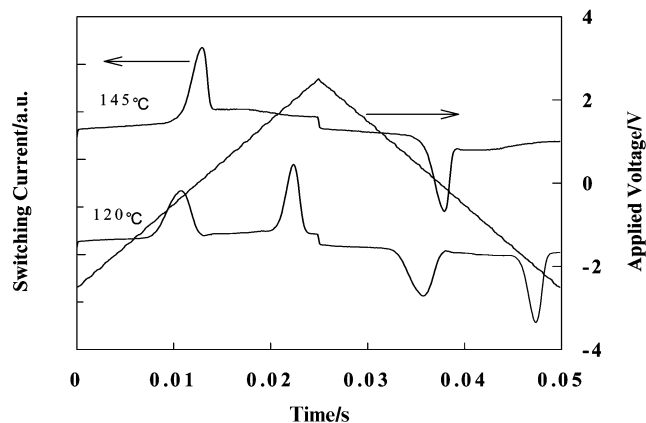


Figure 1. The switching current behaviour of material **I** in the  $\text{SmC}^*$  phase at  $145^\circ$  and the  $\text{SmC}_A^*$  phase at  $120^\circ\text{C}$ , in homogeneously aligned  $5\ \mu\text{m}$  thick cells.

aligned cells was investigated. The dielectric measurements were made using an HP4284A precision LCR meter, and data were analysed with a resistor–capacitor parallel circuit model. A plot of the dielectric constant  $\epsilon'$  as a function of temperature for material **I** is shown in figure 2(a). During cooling, the  $\epsilon'$  in the  $\text{SmA}^*$  phase is small and increases at the  $\text{SmA}^*$  to  $\text{SmC}^*$  transition. The great enhancement of dielectric constant in the  $\text{SmC}^*$  phase is due to the contribution of the Goldstone mode [8]. The temperature range of the  $\text{SmC}^*$  phase is narrow and a fall of  $\epsilon$  to very low values indicates the formation of the  $\text{SmC}_A^*$  phase. A similar plot for material **II** is shown in figure 2(b), where the characteristics of the  $\text{SmA}^*$  and  $\text{SmC}^*$  phases are seen. A continuous decrease of dielectric constant in the  $\text{SmC}^*$  phase takes place as the temperature falls. However, the cause of this decreasing trend in dielectric constant with falling temperature has, as yet, no clear explanation [9].

In summary, the fluorinated chiral material **I** exhibits enantiotropic  $\text{SmA}^*$ ,  $\text{SmC}^*$  and  $\text{SmC}_A^*$  phases, while the non-fluorinated material **II** exhibits enantiotropic  $\text{SmA}^*$ ,  $\text{SmC}^*$  and unidentified  $\text{SmX}^*$  phases. These results demonstrate that the presence of the semi-perfluorinated alkyl chain in the chiral tail suppresses the higher ordered  $\text{SmX}^*$  phase but induces an antiferroelectric  $\text{SmC}_A^*$  phase.

Table. The mesophases, transition temperatures ( $^\circ\text{C}$ ) and associated enthalpy data (in brackets,  $\text{kJ mol}^{-1}$ ) for the chiral materials **I** and **II**: from DSC data recorded at heating/cooling rates of  $5^\circ\text{C min}^{-1}$ .

Material	I	$\text{SmA}^*$	$\text{SmC}^*$	$\text{SmC}_A^*$	$\text{SmX}^*$	Cr	m.p.
<b>I</b>	•	158.8 [5.8]	• 151.4 [1.1]	• 147.4 — <sup>a</sup>	• —	• 63.1 [35.1]	• 103.0 [47.6]
<b>II</b>	•	150.7 [17.1]	• 127.7 [0.6]	—	• 48.8 [3.5]	• 25.6 [44.1]	• 62.1 [55.5]

<sup>a</sup>The enthalpy was too small to be determined by DSC.

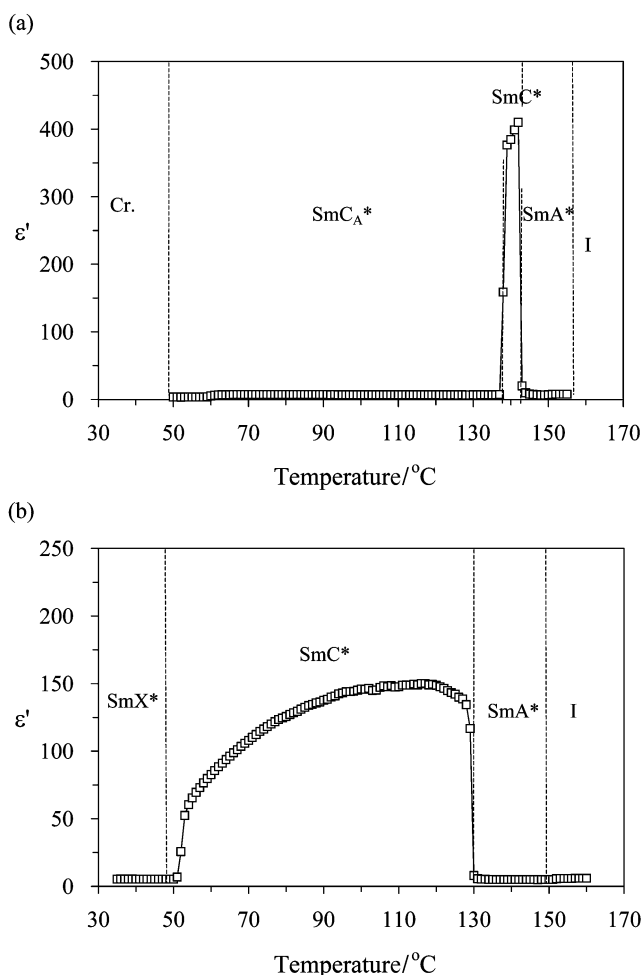


Figure 2. Temperature dependence of the dielectric constant  $\epsilon'$  for (a) material I and (b) material II, at 100 Hz in 25  $\mu\text{m}$  thick cells.

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