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Ferroelectric and antiferroelectric liquid crystals derived from (*S*)-1-methyl-2-(2'-methylsulphanylethoxy)ethanol

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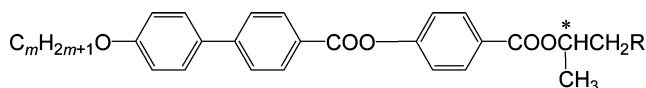
An optically active chiral material, (*S*)-1-methyl-2-(2'-methylsulphanylethoxy)ethanol was prepared by the treatment of (*S*)-propylene oxide with 2-methylsulphanylethanol under basic conditions. Its derivatives, the (*R*)-1-methyl-2-(2'-methylsulphanylethoxy)ethyl 4-(4'-alkoxybiphenyl-1-carboxyloxy)benzoates, MMSEEmCB ($m=7-12$), were then prepared for investigation of their mesomorphic properties. The results show that the materials with shorter alkyl chains ($m=7-9$) favour the formation of the antiferroelectric SmC_A^* phase, while materials with longer alkyl chains ($m=10-12$) favour the formation of the ferroelectric SmC^* phase. Switching current behaviour, electro-optical response, dielectric constant, spontaneous polarization and apparent tilt angle for the materials in the SmC^* and SmC_A^* phases were studied.

1. Introduction

Since the discovery of 'antiferroelectricity' in liquid crystals by Chandani *et al.*, many antiferroelectric materials based on the structure of MHPOBC, with optically active 2-octanol as a chiral group, have been designed and synthesized for investigation in relation to the variation of achiral and chiral alkyl groups and rigid molecular cores [1–3]. In this regard, the introduction of heteroatoms provides a useful way to modify the properties of liquid crystal materials. Sulphur in particular offers advantages such as the possibility to introduce chirality into the molecule [4–6].

Recent studies showed that some chiral materials with the chiral moiety derived from (*S*)-propylene oxide display ferroelectric and antiferroelectric phases [7, 8]. Thus, we decided to design and synthesize a new chiral moiety, (*S*)-[1-methyl-2-(2'-methylsulphanylethoxy)ethanol], by the treatment of (*S*)-propylene oxide with 2-(methylsulphanyl)-1-ethanol. This chiral moiety is structurally similar to optically active 2-octanol; an homologous series of chiral materials, (*R*)-[1-methyl-2-(2'-methylsulphanylethoxy)ethyl 4-(4'-alkoxybiphenyl-1-carboxyloxy)benzoates, MMSEEmCB ($m=7-12$), structurally similar to MHPOBC, was then prepared for the study of their mesomorphic phases and physical properties. The general structures of

MHPOBC and MMSEEmCB ($m=7-12$) are depicted below:

MHPOBC ($m=8$), R = $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ MMSEEmCB ($m=7-12$), R = $\text{OCH}_2\text{CH}_2\text{SCH}_3$

2. Experimental

2.1. Characterization of materials

The structures of the intermediates and final products were checked by thin layer chromatography and further identified by nuclear magnetic resonance spectroscopy using a Bruker Avance 500 NMR spectrometer. The purity of the final products was confirmed by elemental analysis using a Perkin-Elmer 2400 instrument. The results are listed in Table 1 where the carbon and hydrogen analytical data are in agreement with the calculated results within $\pm 1\%$.

Phase transition temperatures and enthalpy changes were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC 7 at a running rate of 5°C min^{-1} . Mesophases were identified using a Nikon Microphot-FXA polarizing optical microscope in conjunction with a Mettler FP82-HT hot stage controlled by a Mettler FP90 processor.

Commercial homogenous cells coated with polyimide as alignment film were purchased from E.H.C. Co. Ltd,

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Japan and Linkam Scientific Instruments Ltd, UK. The sample was filled into the cell by capillary action in the isotropic state. Two wires were fixed separately to the ITO-coated glass plates of the sample cell with silver paint.

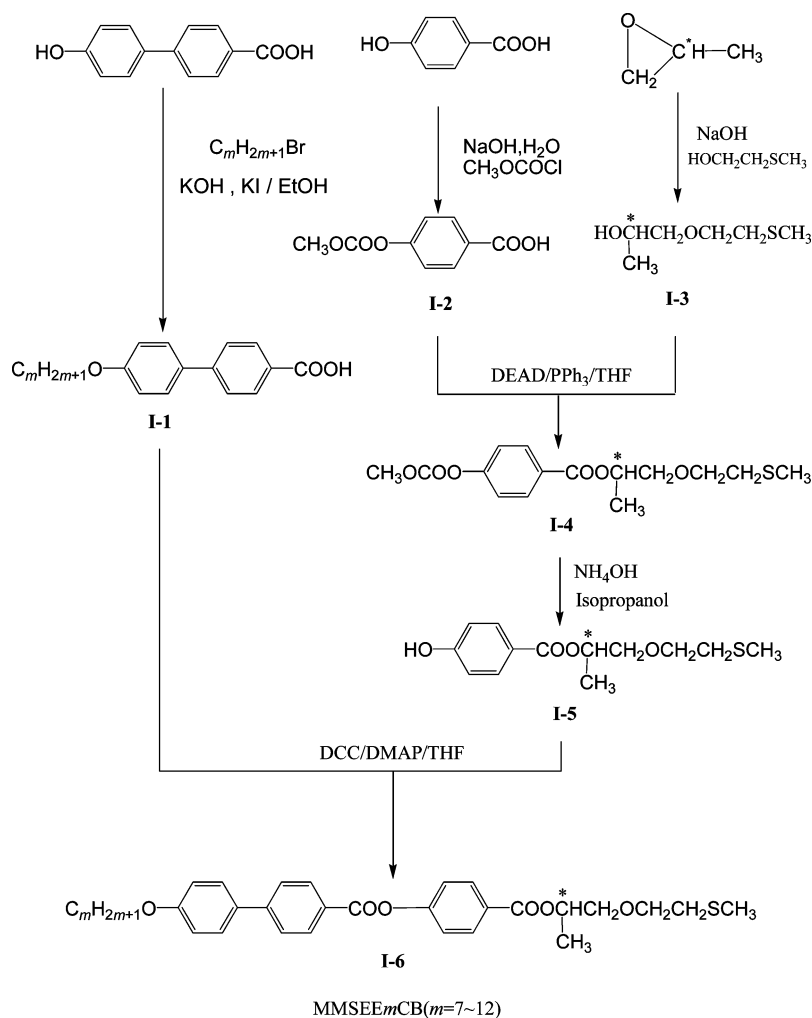
Spontaneous polarization (P_s) was measured by the triangular wave method [9]. Triangular waves were generated by a Yogawa AG1200 arbitrary waveform generator and were amplified by an NF Electronics Instrument 4005 power amplifier. The currents were measured by detecting the voltage change across a 50 kV resistor, using a HP 4284A digital oscilloscope to monitor the signals.

The measurement of optical transmittance versus applied electric field was conducted using a He-Ne laser (5 mW, 632.8 nm) as probe beam [10, 11]. The optical transmittance of the probe beam passing through the cell, between crossed polarizers with axes parallel and perpendicular to the smectic layer normal, was detected by a photodiode.

2.2. Preparation of materials

The starting chiral material, (*S*)-propylene oxide, was purchased from Sigma-Aldrich Chemie GmbH P.O., with purity greater than 99%. Thin layer chromatography was performed with TLC sheets coated with silica; spots were detected by UV irradiation. Silica gel (MN kieselgel 60, 70–230 mesh) was used for column chromatography. The organic solvents dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF), were purified by treatment with CaH_2 and LiAlH_4 , respectively, and distilled before use.

The synthetic procedures for the target compounds were carried out as outlined in scheme 1. Some intermediates in scheme 1 were prepared according to conventional synthetic methods [12]. Detailed synthetic procedures for other new intermediates and target materials are described below.



Scheme 1. Procedures for the synthesis of the chiral materials MMSEEmCB ($m=7-12$).

2.2.1. (S)-[1-Methyl-2-(2'-methylsulphanylethoxy)]ethanol, I-3. 2-(Methylsulphanyl)-1-ethanol (14.7 g, 16 mmol) and sodium hydroxide (0.1 g, 2.5 mmol) were heated together under reflux for 2 h and cooled to room temperature. (S)-propylene oxide (6.38 g, 11 mmol) was added dropwise and the reflux continued overnight. The resultant mixture was filtered, and excess 2-(methylsulphanyl)-1-ethanol removed under vacuum. The resinous mass thus obtained was distilled under high vacuum. A 50% yield (10.6 g) of pure product was obtained, b.p. 92°C/22 torr. ¹H NMR (500 MHz, CDCl₃): δ(ppm) 1.15–1.16 (d, 3H, –C*HCH₃CH₂O–, *J*=6.35 Hz), 2.16 (s, 3H, –CH₂CH₂SCH₃), 2.51 (s, 1H, –OH), 2.70–2.72 (t, 2H, –CH₂CH₂SCH₃, *J*=6.6 Hz), 3.24–3.50 (m, 2H, –CH₂OCH₂CH₂S–), 3.64–3.72 (m, 2H, –CH₂CH₂SCH₃), 3.96–4.00 (m, 1H, –C*HCH₃COO–).

2.2.2. (R)-[1-Methyl-2-(2'-methylsulphanylethoxy)]ethyl 4-(methoxycarbonyloxy)benzoate, I-4. A solution of diethyl azodicarboxylate (2.26 g, 13 mmol) and compound I-2 (1.08 g, 13 mmol) in anhydrous THF (10 ml) was added dropwise to a solution of triphenylphosphine (2.75 g, 13 mmol) and compound I-3 (1.50 g, 10 mmol) in anhydrous THF (10 ml) at room temperature with vigorous stirring; the reaction soon started. After standing overnight at room temperature, triphenylphosphine oxide was removed by filtration and the THF removed under vacuum. After work-up, the product was isolated by column chromatography over silica gel (70–230 mesh) using ethyl acetate/hexane (v/v=1/7) as eluant to give a colourless liquid; 65% yield (1.6 g) of product was obtained. ¹H NMR (500 MHz, CDCl₃): δ(ppm) 1.36–1.37 (d, 3H, –C*HCH₃CH₂O–, *J*=6.5 Hz), 2.13 (s, 3H, –CH₂CH₂SCH₃), 2.65–2.68 (t, 2H, –CH₂CH₂SCH₃, *J*=6.65 Hz), 3.58–3.68 (m, 2H, –CH₂OCH₂CH₂S–), 3.70–3.73 (m, 2H, –CH₂CH₂SCH₃), 3.92 (s, 3H, CH₃OCOO–), 5.29–5.35 (m, 1H, –C*HCH₃COO–), 7.25–7.26 (d, 2H, –ArH, *J*=8.2 Hz), 8.07–8.09 (d, 2H, –ArH, *J*=8.75 Hz)

2.2.3. (R)-1-Methyl-2-(methylsulphanyl)ethyl 4-hydroxybenzoate, I-5. Compound I-4 (0.86 g, 3 mmol) was stirred in a mixture of isopropanol (90 ml) and ammonia (28%, 30 ml) at room temperature for 50 min (TLC analysis revealed a complete reaction) and then poured into water (40 ml) with stirring. The product was extracted with dichloromethane (3 × 50 ml). The combined organic extracts were washed with brine (3 × 50 ml), dried (MgSO₄), filtered and evaporated to give a colourless oil. The oil was purified by column chromatography over silica gel (70–230 mesh) using dichloromethane as eluant. The isolated product was then dried under vacuum; 90% yield (0.77 g) of

product was obtained. ¹H NMR (500 MHz, CDCl₃): δ(ppm) 1.34–1.36 (d, 3H, –C*HCH₃CH₂O–, *J*=6.45 Hz), 2.12 (s, 3H, –CH₂CH₂SCH₃), 2.66–2.69 (t, 2H, –CH₂CH₂SCH₃, *J*=6.7 Hz), 3.58–3.69 (m, 2H, –CH₂OCH₂CH₂S–), 3.71–3.75 (m, 2H, –CH₂CH₂SCH₃), 4.69 (s, 1H, –OH), 5.27–5.32 (m, 1H, –C*HCH₃COO–), 6.84–6.86 (d, 2H, –ArH, *J*=8.7 Hz), 7.92–7.94 (d, 2H, –ArH, *J*=8.7 Hz).

2.2.4. (R)-[1-Methyl-2-(2'-methylsulphanylethoxy)]ethyl 4-(4'-alkoxybiphenyl-1-carboxyloxy)benzoates, I-6, MMSEEmCB (m=7–12). A mixture of a 4-(4'-alkoxyphenyl)benzoic acid (2.8 mmol), compound I-5 (0.8 g, 3.1 mmol), *N,N*-dicyclohexylcarbodiimide (0.35 g, 2.8 mmol), 4-dimethylaminopyridine (0.06 g, 0.28 mmol) and dry THF (15 ml) was stirred at room temperature for three days. The precipitate was filtered off and the filtrate washed with 5% acetic acid solution (3 × 50 ml), 5% saturated aqueous sodium hydrogen carbonate (3 × 50 ml) and water (3 × 50 ml); the filtrate was then dried over anhydrous magnesium sulphate (MgSO₄) and concentrated in vacuum. The residue was purified by column chromatography over silica gel (70–230 mesh) using dichloromethane as eluant. The products were crystallized from absolute ethanol and yielded 50% of pure compound. The chemical shifts of MMSEE10CB, as an example, in the ¹H NMR (500 MHz, CDCl₃) spectrum are: δ(ppm) 0.87–0.90 (t, 3H, CH₃(CH₂)₇CH₂–, *J*=6.55 Hz), 1.24–1.45 (m, 14H, CH₃(CH₂)₇CH₂–), 1.56 (s, 3H, –C*HCH₃CH₂O–, *J*=6.45 Hz), 2.14 (s, 3H, –CH₂CH₂SCH₃), 2.67–2.70 (t, 2H, –CH₂CH₂SCH₃, *J*=6.7 Hz), 3.60–3.71 (m, 2H, –CH₂OCH₂CH₂S–), 3.73–3.76 (m, 2H, –CH₂CH₂SCH₃), 4.00–4.03 (t, 2H, CH₂CH₂O–, *J*=6.55 Hz), 5.32–5.35 (m, 1H, –C*HCH₃COO–), 7.00–7.01 (d, 2H, –ArH, *J*=8.65 Hz), 7.31–7.33 (d, 2H, –ArH, *J*=8.6 Hz), 7.59–7.61 (d, 2H, –ArH, *J*=8.65 Hz), 7.69–7.71 (d, 2H, –ArH, *J*=8.3 Hz), 8.13–8.14 (d, 2H, –ArH, *J*=8.6 Hz), 8.22–8.24 (d, 2H, –ArH, *J*=8.3 Hz). Elemental analysis data are summarized in table 1.

3. Results and discussion

3.1. Mesophase properties

The phase transitions and corresponding enthalpy changes of mesophases for the MMSEEmCB series were measured by DSC. The mesophases were identified by the observation of microscopic textures under crossed polarizers; ferroelectric SmC*, antiferroelectric SmC_A* and ferroelectric SmX* (SmI* or SmF*) phases were further characterized by switching behaviour and electro-optical response. The results are summarized in table 2. A phase chart is plotted in figure 1 for

Table 1. Elemental analysis data for materials MMSEEmCB ($m=7-12$).

Compound	Theory		Experiment	
	C%	H%	C%	H%
MMSEE7CB	69.79	6.95	69.81	6.98
MMSEE8CB	70.19	7.14	70.21	7.17
MMSEE9CB	70.56	7.31	70.67	7.28
MMSEE10CB	70.92	7.48	71.08	7.45
MMSEE11CB	71.26	7.64	71.20	7.68
MMSEE12CB	71.58	7.79	71.67	7.69

Table 2. Transition temperature ($^{\circ}\text{C}$) and enthalpies ΔH (kJ mol^{-1}) (in square brackets) of chiral materials MMSEEmCB ($m=7-12$).

m	I	SmA*	SmC*	SmC _A *	SmX*	Cr	m.p. ^a					
7	•	137.48 [3.52] ^b	•	97.63 [0.13]	•	74.72 [1.67]	•	82.32 [18.71]				
8	•	134.41 [3.26]	•	103.93 [0.23]	•	90.1 [0.15]	•	67.55 [1.50]	•	39.32 [11.08]	•	83.68 [21.18]
9	•	129.17 [4.62]	•	105.23 [0.18]	•	79.1 [0.19]	•	54.6 [1.76]	•	20.5 [11.17]	•	71.57 [23.18]
10	•	125.85 [4.64]	•	104.1 [0.19]	•	45.75 [0.98]	•	31.97 [18.27]	•	48.21 [25.09]	•	64.48 [23.71]
11	•	122.59 [4.40]	•	103.86 [0.24]	•	56.45 [30.86]	•	80.15 [28.76]				
12	•	121.97 [5.23]	•	104.46 [0.19]	•	80.76 [34.12]						

^a m.p. refers to the melting point taken from a DSC theroqram recorded at a heating rate of $5^{\circ}\text{C min}^{-1}$.

^b Figures in square brackets denote enthalpies quoted in kJ mol^{-1} .

comparison of the mesophases. The SmC_A* phase appears in materials of shorter alkyl chain length ($m=7, 8, 9$). Materials with longer alkyl chain length favour the formation of SmC* phase.

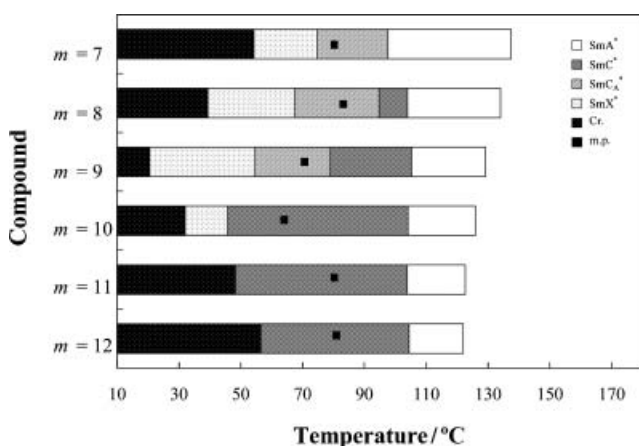


Figure 1. Phase transition temperature versus alkyl chain length m for the materials MMSEEmCB.

The mesophases of the octyl member, MMSEE8CB, may be compared with those of MHPOBC. The former shows the mesophase sequence (in $^{\circ}\text{C}$) I134.4SmA*109.9SmC*90.1SmC_A*67.6SmX*39.3Cr, the latter shows the sequence I151.5SmA*123.0SmC*121.0SmC_A*73.5Cr. It can be seen that the temperatures of the corresponding phase transitions for MMSEE8CB are relatively lower than those of MHPOBC. A higher ordered SmX* phase appeared in MMSEE8CB, lowering the thermal stability of the SmC_A* phase as compared with that of MHPOBC. An increase in achiral alkyl chain length from decyl to dodecyl suppresses the SmC_A* and SmX* phases whilst enhancing the thermal stability of the SmC* phase.

3.2. Electro-optical studies

The switching current behaviour of MMSEE8CB was measured in a $5\mu\text{m}$ thick antiparallel aligned cell under a triangular wave voltage with a field frequency of 20 Hz and amplitude of 5 V. The observed results are shown in figure 2. In the SmC* phase, the single switching peak produced by polarization reversal of the charge suggests the existence of ferroelectricity [13].

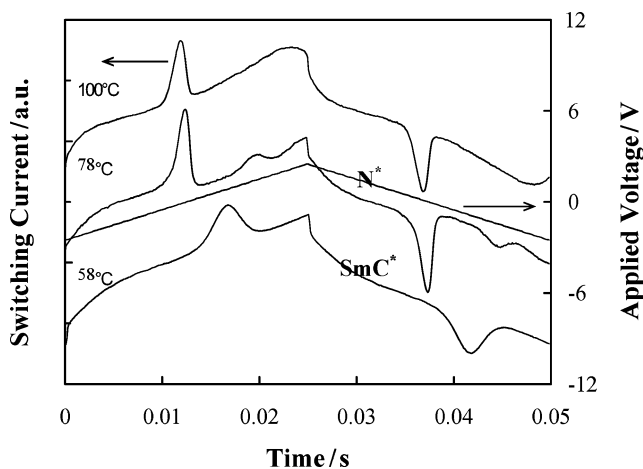


Figure 2. Switching current behaviour for MMSEE8CB in the SmC* phase at 100°C, the SmC_A* phase at 78°C and the SmX* phase at 58°C in a homogeneously aligned 5µm thick cell.

In the SmC_A* phase, two switching current peaks appeared, similar to the normal SmC* phase [14], supporting the occurrence of antiferroelectricity. When the temperature fell steadily to 67.6°C, a single peak appeared again but shifted to the right as shown in figure 2 at 58°C. This result demonstrates that the SmX* phase possesses ferroelectric properties. Whether this ferroelectric phase is SmI* or SmF*, however, has not yet been determined.

The spontaneous polarizations (P_s) for compounds MMSEEmCB ($m=8-11$), measured as a function of temperature on cooling in 5µm homogeneous cells is illustrated in figure 3. The P_s value increases steeply in

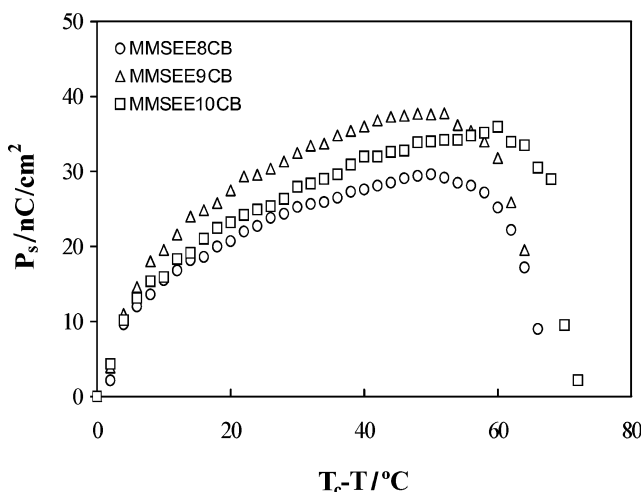


Figure 3. Spontaneous polarization plotted as a function of temperature for the materials MMSEEmCB ($m=8-11$). T_c is the temperature of the SmA*–SmC* transition.

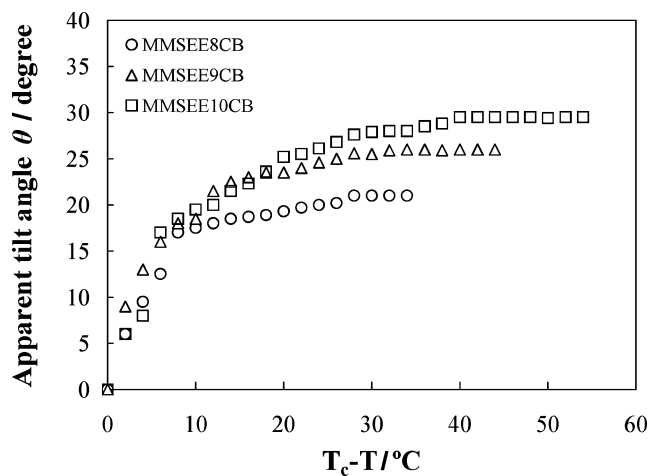


Figure 4. Optical tilt angle plotted as a function of temperature for MMSEEmCB ($m=8-10$). T_c is the temperature of the SmA*–SmC* transition.

the vicinity of the SmA*–SmC* transition and then more slowly with decreasing temperature before crystallization. The maximum P_s values measured from the three materials MMSEEmCB ($m=8-10$) are in the range 29.6–37.8 nC cm⁻². Material ($m=9$) shows the highest P_s value of all three materials.

The temperature dependence of the optical tilt angle of the materials MMSEEmCB ($m=8-10$) was also measured and the results are shown in figure 4. The optical tilt angle increases dramatically as the temperature is cooled from the SmA* region to the SmC*. The maximum optical tilt angles measured for these three materials are in the range of 21°–29.5°. The optical tilt angles tend to increase with increasing alky chain length.

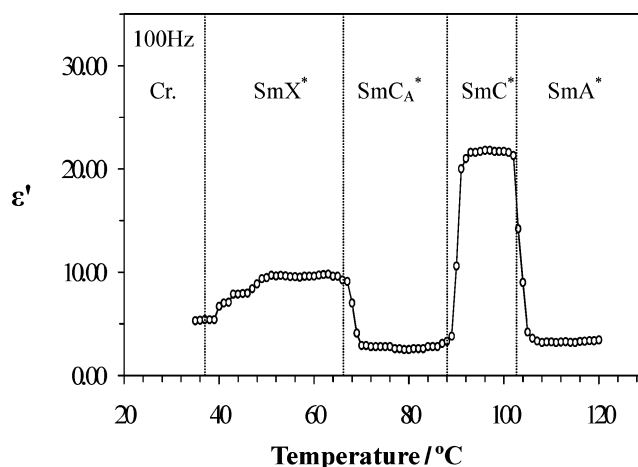


Figure 5. Temperature dependence of the dielectric constant ϵ' obtained from MMSEE8CB at 100 Hz in a 25µm thick cell.

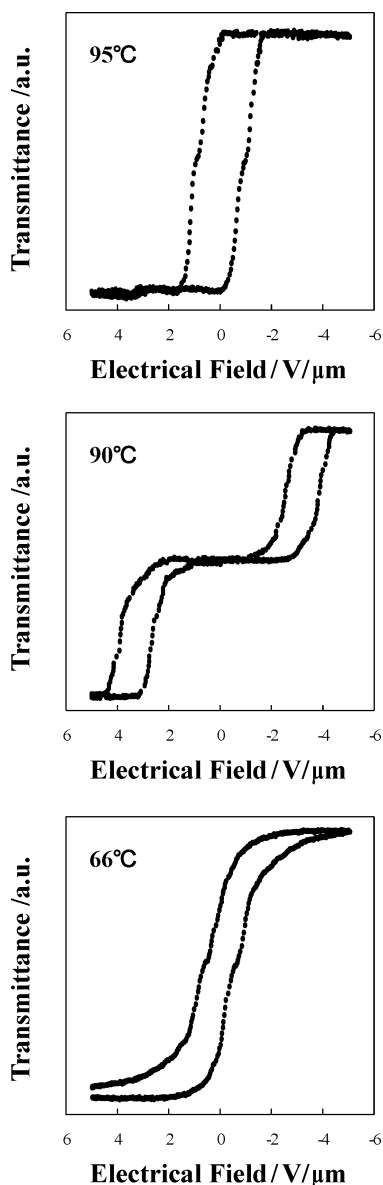


Figure 6. Curves of transmittance versus applied field for MMSEE8CB in (a) SmC^* phase, (b) SmC_A^* phase and (c) SmX^* phase at an applied frequency of 1 Hz.

The temperature dependence of the dielectric constant ϵ' was measured at 100 Hz in $25\ \mu\text{m}$ homogeneously aligned cells, with the results depicted in figure 5. On cooling, the ϵ' in the SmA^* phase is small, and increases sharply at the SmA^* to SmC^* transition. The great enhancement of dielectric constant in the SmC^* phase is due to the contribution of the Goldstone mode [14]. In the SmC^* phase, ϵ' drops to very low values indicating the formation of the SmC_A^* phase.

The electro-optical response was observed under crossed polarizers, with the axes of polarizer and

analyser parallel and perpendicular, respectively, to the smectic layer normal in $5\ \mu\text{m}$ homogeneously aligned cells. Figure 6 illustrates the variation of transmittance with electric field on application of a triangular waveform field measured in the SmC_A^* phase for compound MMSEE8CB. It can be seen that at 95°C and 1 Hz frequency, the curve of transmittance versus applied electric field displays an ideal single hysteresis loop in the SmC^* phase, corresponding to bistable switching in the ferroelectric state [15]; at 90°C and 1 Hz frequency, it displays an ideal double hysteresis loop in the SmC_A^* phase, corresponding to a tristate [15] which is the characteristic of a stable antiferroelectric phase; at 66°C and 1 Hz frequency, it displays a hysteresis loop in the SmX^* phase, demonstrating this phase exhibits ferroelectricity. This higher order ferroelectric phase requires further experimental work such as X-ray measurement to identify whether it is a SmI^* or SmF^* phase.

4. Conclusion

A new chiral component (*S*)-[1-methyl-2-(2'-methylsulphanyloxy)]ethanol was designed and synthesized as a chiral moiety for an homologous series of chiral materials, MMSEEmCB ($m=7-12$), which is structurally similar to MHPOBC, for the investigation of mesomorphic phases. The results show that shorter chain members ($m=7-9$) of the series display the antiferroelectric SmC_A^* phase. This suggests that this chiral moiety may act as a key component for generating the antiferroelectric phase. Thus, more materials based on this chiral moiety will be prepared and investigated in order to establish of the structure-property relationships.

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