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Synthesis and ferroelectric properties of chiral swallow-tailed liquid crystals derived from (*S*)-2-[1-(2-ethylbutoxy)]propanol

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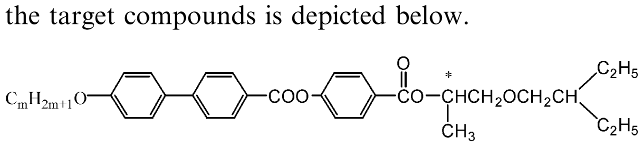
(*S*)-2-[1-(2-Ethylbutoxy)]propanol was designed and synthesized as a chiral building block for the preparation of chiral liquid crystals. Its derivatives, the (*S*)-2-[1-(2-ethylbutoxy)]propyl 4-[4-(4-alkoxyphenyl)phenoyloxy]benzoates, EP*m*PPB (*m*=8–12), were prepared and their mesomorphic phases investigated. The results showed that the chiral materials displayed enantiotropic SmA* and SmC* phases, while those with shorter alkyl chains (*m*=8–10) displayed an additional unidentified SmX* phase. The switching current, spontaneous polarization, tilt angle, dielectric constant and electro-optical response for the materials in the ferroelectric SmC* phase were measured. The electro-optic responses of the materials in polyimide film-coated, homogeneously aligned cell exhibit thresholdless, V-shaped switching in the ferroelectric phase.

1. Introduction

Chiral liquid crystals derived from highly optically pure chiral precursors have shown wide varieties of liquid crystal phases, such as frustrated phases (BP and TGB), ferroelectric and antiferroelectric phases [1, 2]. The chiral precursors used as building blocks for the chiral molecules were generally commercially available optically active compounds such as 2-alkanols, lactic acid and 2-(6-methoxy-2-naphthyl)propinic acid. Some of the chiral precursors, such as 2-trifluoroalkanol, 2-fluoralkanol and α-halohydrin, derived from L-amino acids, were also specially designed and synthesized for the preparation of chiral molecules for the purpose of investigating the new mesophases and physical properties.

In this work, we have designed and synthesized a new chiral precursor (*S*)-2-[1-(2-ethylbutoxy)]propanol by the reaction of (*S*)-propylene oxide with 2-ethylbutanol, and have prepared a series of chiral swallow-tailed compounds, the (*S*)-2-[1-(2-ethylbutoxy)]propyl 4-[4-(4-alkoxyphenyl)phenoyloxy]benzoates, EP*m*PPB (*m*=8–12), for the study of their mesomorphic phases and physical properties. The general structural formula for the target compounds is depicted below.



EP*m*PPB (m=8~12)

Achiral materials with swallow-tailed terminal moieties have been demonstrated to possess the $\mathrm{SmC_{alt}}$ phase with antiferroelectric-like structure [3, 4]. Our previous studies involved chiral swallow-tailed materials possessing ferroelectric and antiferroelectric behaviour with thresholdless, V-shaped switching [5–7]. V-shaped switching was first found and reported by Inui *et al.* [8] in a mixture of antiferroelectric liquid crystals. This type of antiferroelectric mixture has been studied extensively due to its promising potential for use in display devices [9–14].

2. Experimental

2.1. *Characterization of the materials*

The chemical structures for intermediates and target materials were analysed by nuclear magnetic resonance spectroscopy using a Jeol EX-400 FT-NMR spectrometer. The purity was checked by thin layer chromatography and further confirmed by elemental analysis using a Perkin-Elmer 2400 spectrometer. Transition temperatures and phase transition enthalpies of the materials were determined by differential scanning calorimetry using a Perkin-Elmer DSC7 calorimeter at running rates of 1–20°C $\mathrm{min^{-1}}$. Mesophases were identified principally by microscopic texture of the materials sandwiched between two glass plates, under crossed polarizers using a Nikon Microphot-FXA microscope in conjunction with a Mettler FP82 hot stage.

The physical properties of the ferroelectric phase for the materials were measured in homogeneously aligned

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cells purchased from E. H. C. Co. Japan. The magnitude of spontaneous polarization (**P**$_s$) was measured by a triangular wave method [15]. The measurement of optical transmittance versus applied electric field was conducted using a He-Ne laser (5 mW, 632.8 nm) as probe beam [16, 17]. The optical transmittance of the probe beam passing though the cell between crossed polarizers, whose axes were parallel and perpendicular to the smectic layer normal, was detected by a photodiode. The signals were detected using a HP54502A digital oscilloscope. The voltage applied to the cell was produced by the arbitrary wave-form generator (AG1200) and amplified by a homemade power preamplifier.

2.2. *Preparation of materials*

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

The synthesis of the target compounds was carried out as outlined in the scheme. Detailed procedures for the syntheses of compounds EP*m*PPB (*m*=8–12) are described below.

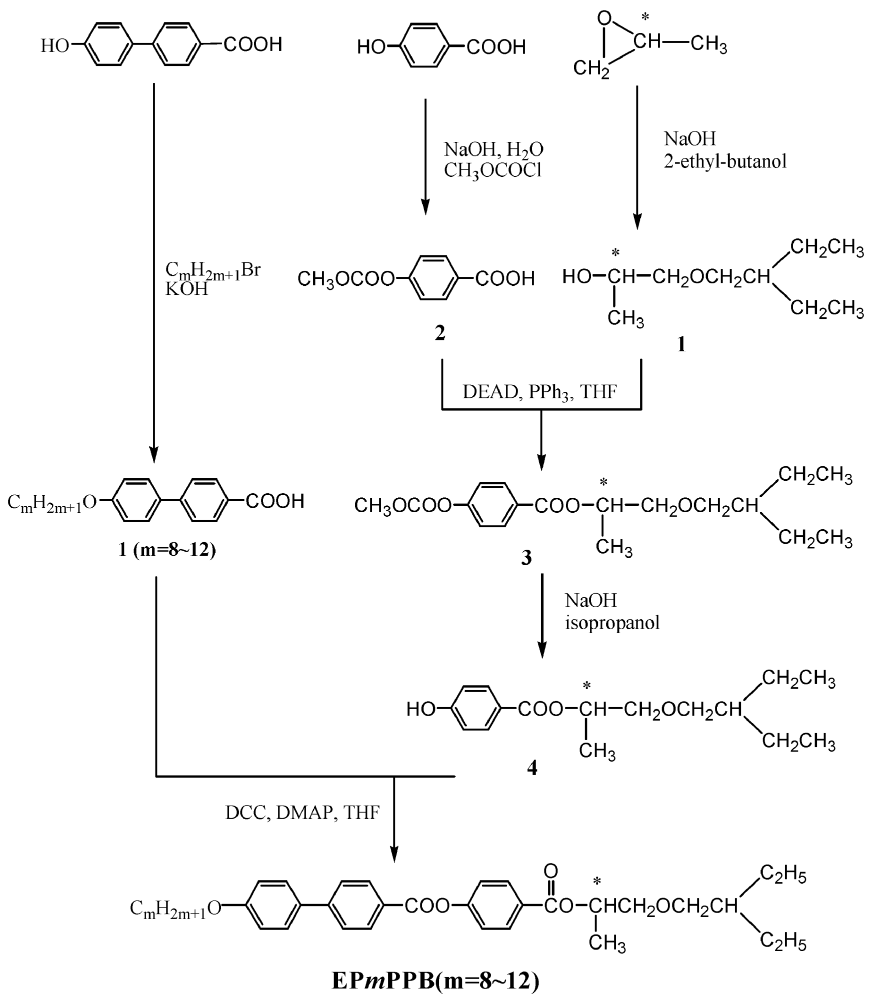
2.2.1. 4-(4-Alkyloxyphenyl)benzoic acids, 1**(m=8–12).** 4′-Hydroxybiphenyl-4-carboxylic acid (5.3 g, 25 mmol) and ethanol (200 ml) were mixed, and a solution of potassium hydroxide (2.8 g, 50 mmol) and potassium iodide (KI) (0.6 g, 3.6 mmol) in distilled water (50 ml) added. The mixture was heated under reflux for 1 h. 1-Bromoalkane (75 mmol) was then added dropwise and the reflux continued for a further 12 h. Aqueous potassium hydroxide (100 ml, 10%) was added, the mixture heated under refluxed for 2 h, then acidified with 5% HCl and filtered. The crude product was washed with cold water and recrystallized from glacial acetic acid and absolute ethanol. Yields of 60–70% of the materials **1**(*m*=8–12) were obtained.

2.2.2. 4-Methoxycarbonyloxybenzoic acid, 2 **[18].** To a solution of sodium hydroxide (7.5 g, 175 mmol) in water (200 ml) at 0°C, 4-hydroxybenzoic acid (9 g, 65 mmol) was added with vigorous stirring. Methyl chloroformate (10 g, 105 mmol) was then added slowly to the resulting suspension which was maintained at 0–5°C. The resulting slurry was stirred for 4 h and brought to Ph 5 by the addition of conc. hydrochloric acid/water (1/1). The voluminous precipitate was filtered off and recrystallized from ethanol to give a white solid. An 85% yield of compound **2** was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) are: δ (ppm) 3.92 (s, 3H, $OC\mathbf{H}_3$), 8.10–7.23 (d,d, 4H, Ar**H**), 8.15 (s, 1H, COO**H**).

2.2.3. (*S*)-2-[1-(2-Ethylbutoxy)]propanol, 3 **[19].** 2-Ethylbutanol (48.8 g, 55 mmol) and sodium hydroxide (0.1 g, 2.5 mmol) were mixed and heated under reflux for 2 h. After cooling to room temperature, (*S*)-propylene oxide (6.38 g, 11 mmole) was added dropwise and the reflux resumed overnight. The resultant mixture was filtered, and excess 2-ethylbutanol removed under vacuum. The resulting resinous mass was distilled under vacuum to yield 20% of pure product, b.p. 80°C/32 torr. ^{1}H NMR (400 MHz, $CDCl_3$) are: δ (ppm) 0.89–0.86 (m, 6H, $(CH_2C\mathbf{H}_3)_2$), 1.14–1.13 (d, 3H, $CH^*C\mathbf{H}_3$), 1.34–1.35 (m, 4H, $CH(C\mathbf{H}_2CH_3)_2$), 1.36–1.35(m, 1H, $CH_2C\mathbf{H}(CH_2)_2$), 3.21–3.19 (s, 1H, O**H**), 3.40–3.32 (m, 4H, $C\mathbf{H}_2OC\mathbf{H}_2$), 3.95 (m, 1H, $HOC\mathbf{H}^*CH_3$).

2.2.4. (*S*)-2-[1-(2-Ethylbutoxy)]propyl 4-(methoxycarbonyloxy)benzoate, 4 **[19].** A solution of diethyl azodicarboxylate (DEAD, 2.2 g, 13 mmol) and compound **2** (2.5 g, 13 mmol) in anhydrous THF (12 ml) was added dropwise to a solution of triphenylphosphine (Ph_3P, 3.4 g, 13 mmol) and compound **3** (1.42 g, 10 mmol) in anhydrous THF (12 ml) at room temperature with vigorous stirring; the reaction soon started. After holding the mixture overnight at room temperature, the triphenylphosphine oxide was removed by filtration, and THF was removed under vacuum. After the work-up procedure, the products were isolated by column chromatography over silica gel (70–230 mesh) using ethyl acetate/hexane (V/V=2/8) as eluent to give a colourless liquid. A 65% yield of compound **4** was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 0.86–0.82 (m, 6H, $(CH_2C\mathbf{H}_3)_2$), 1.29 (d, 3H, $CHC\mathbf{H}_3$), 1.36–1.31(m, 4H, $CH(C\mathbf{H}_2CH_3)_2$), 1.43–1.36(m, 1H, $CH_2C\mathbf{H}$), 3.61–3.41 (m, 4H, $C\mathbf{H}_2OC\mathbf{H}_2$), 3.91 (s, 3H, $COOC\mathbf{H}_3$), 5.32–5.28 (m, 1H, $OC\mathbf{H}^*CH_3$), Ar**H**, 8.10–7.24 (d,d, 4H).

2.2.5. (*S*)-2-[1-(2-Ethylbutoxy)]propyl 4-hydroxybenzoate, 5 **[19].** Compound **4** (1.0 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 using dichloromethane (3 × 50 ml). The combined organic extracts were washed with brine (3 × 50 ml),



Scheme. Procedures for the synthesis of chiral materials EP*m*PPB (*m*=8–12).

dried (MgSO$_4$), filtered and evaporated to give a colourless oil. The oil was purified by flash column chromatography over silica gel (70–230 mesh) using dichloromethane, then dried *in vacuo*. Compound **5** was obtained in 85% yield and identified for the ^{1}H NMR spectr. ^{1}H NMR (400 MHz, CDCl$_3$): δ(ppm) 0.86–0.82 (m, 6H, $(CH_2\mathbf{CH_3})_2$), 1.22–1.21 (d, 3H, $CH\mathbf{CH_3}$), 1.34–1.33(m, 4H, $CH(\mathbf{CH_2}CH_3)_2$), 1.69(m, 1H, $CH_2\mathbf{CH}$), 3.69–3.35 (m, 4H, $\mathbf{CH_2OCH_2}$), 5.30–5.26 (m, 1H, $O\mathbf{CH}^*CH_3$), 6.84–6.62 (s, 1H, **OH**), Ar**H**, 7.94–7.26 (d,d, 4H).

2.2.6. Synthesis of (*S*)-2-[1-(2-ethybutoxy)]propyl 4-[4-(4-akyloxyphenyl)phenoyloxy]benzoates, EPmPPB(m=8–12) [19]. A mixture of the required 4-(4-alkyloxyphenyl)benzoic acid (2.8 mmol), compound **5** (0.8 g, 3.1 mmol) N,N′-dicyclohexylcarbodiimide (0.3 g, 2.8 mmol), 4-dimethylaminopyridine (0.05 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), then dried over MgSO$_4$ and concentrated under vacuum. The residue was purified by column chromatography over silica gel (70–230 mesh) using dichloromethane as eluent. After purification by recrystallization from absolute ethanol, 62–70% yields of final product were obtained. ^{1}H NMR, typical for EP10PPB, (400 MHz, CDCl$_3$): δ(ppm) 0.88–0.85 (m, H, $CH_2\mathbf{CH_3}$), 1.55–1.25 (m, 19H, $\mathbf{CH}(\mathbf{CH_2}CH_3)_2$, $OCH_2CH_2(\mathbf{CH_2})_7$), 1.82 (m, 2H, $OCH_2\mathbf{CH_2}$), 3.61–3.36 (m, 4H, $\mathbf{CH_2OCH_2}$) 4.03–4.00 (t, 2H, $ArO\mathbf{CH_2}$) 5.31–5.28 (m, 1H, $O\mathbf{CH}^*CH_3$) 8.24–6.99 (d,d, 12H, Ar**H**).

All the target materials were analysed by elemental analysis for the purity, with satisfactory results.

3. Results and discussion

3.1. *Mesomorphic properties*

The transition temperatures of mesophases of EP*m*PPB (*m*=8–12) were determined by DSC in conjunction with optical microscopy. Mesophase identification was carried out principally by the texture observation with the optical microscope. The SmA* phase was characterized by the formation of focal-conic textures and the SmC* phase by the formation of broken focal-conic textures. The materials EP*m*PPB (*m*=11 and 12) displayed enantitropic SmA* and SmC* phases, while materials EP*m*PPB (*m*=8–10) possessed an additional unidentified SmX* phase. The mesophases and their corresponding transition temperatures measured by DSC calorimetry at heating/cooling rates of 5°C min^{-1} are listed in the table. A plot of phase transition temperatures versus determined alkyl chain length *m* for EP*m*PPB (*m*=8–12) is shown in figure 1. It can be seen that the materials exhibit ferroelectric SmC* phases of wide temperature range. Clearing points decrease as *m* increases but the SmC*–Cr transition temperature increases; that is, the thermal stabilities of the SmA* and SmC* phases are suppressed as *m* increases.

3.2. *Switching behaviour*

The physical properties for the materials were measured in 5 μm homogeneous cells. Figure 2 shows the electrical switching response of EP10PPB in a 5 μm thick homogeneous cell under a triangular wave voltage with field frequency of 1 Hz and amplitude of 5 V_{p-p}. The switching currents display one peak in the rangs 45–115°C, similar to the behaviour reported for ferroelectric SmC* phases [20]. It is interesting to find that at 40°C, where the SmX* phase exists, a typical ferroelectric single switching peak also occurs, but the relative position of the peak is significantly shifted. This anomaly is further observed in the tilt angle measurement.

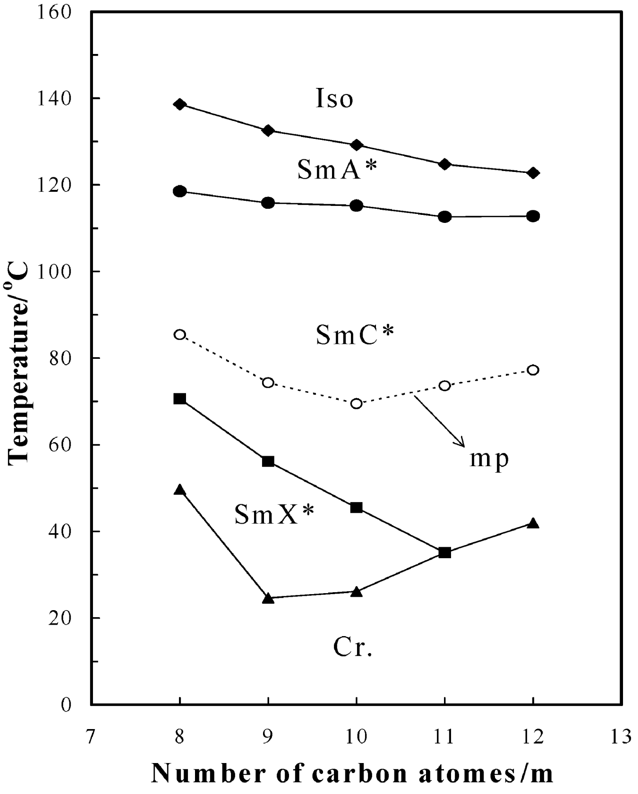


Figure 1. Plot of transition temperature as a function of terminal alkyl chain length for EP*m*PPB (*m*=8–12) on cooling.

3.3. *Spontaneous polarization*

The temperature dependence of spontaneous polarization ($\mathbf{P}_s$) of the materials is illustrated in figure 3. The $\mathbf{P}_s$ value increased rapidly from the Curie point with decrease in temperature. This phenomenon resulted from an increase in molecular rotation freedom at the higher temperature causing a dispersive dipole orientation. No significant correlation of $\mathbf{P}_s$ value with variation in alkyl chain length was found. Figure 3 indicates that the maximum $\mathbf{P}_s$ values of compounds EP*m*PPB (*m*=9–11) are in the range 45.3–40.6 nC cm^{-2}.

Table. Transition temperatures (°C) and associated enthalpy changes (??, in square brackets) for the chiral materials.

Material	I		SmA*		SmC*		SmX*		Cr	m.p.
EP8PPB	•	138.6 [10.9]	•	118.5 [1.4]	•	70.6 [4.3]	•	49.7 [5.3]	•	85.4 [48.0]
EP9PPB	•	132.5 [8.5]	•	115.8 [0.2]	•	56.1 [2.6]	•	24.6 [14.2]	•	74.3 [34.9]
EP10PPB	•	129.2 [5.2]	•	115.2 [0.5]	•	45.4 [1.5]	•	26.1 [17.2]	•	69.5 [29.3]
EP11PPB	•	124.6 [8.8]	•	112.6 [1.7]	•			35.0 [35.0]	•	73.6 [54.1]
EP12PPB	•	122.8 [4.5]	•	112.8 [2.4]	•			41.9 [40.9]	•	77.2 [52.8]

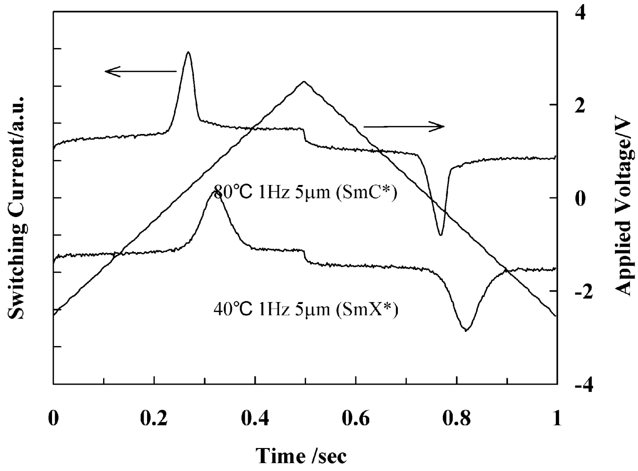


Figure 2. Switching behaviour of EP10PPB in the SmC* and SmX* phases at 80°C and 40°C, respectively.

3.4. *Tilt angle*

Samples were sandwich-packed in 2 μm thick homogeneously aligned cells for the apparent tilt angle measurement. Figure 4 shows that tilt angles (θ) are small at the SmA*–SmC* phase transition and then increase rapidly as the temperature falle below the Curie point. As the temperature drops to the SmX* phase, a gradual decrease of θ occurs for the materials EP9PPB and EP10PPB. This result seems to imply that the SmX* phase is a ferroelectric SmI* or SmF* phase, however, X-ray measurement is needed to identify the phase. The maximum apparent tilt angle is about 31–35°. The results also show that the apparent tilt angle increases with increase of the non-chiral chain length.

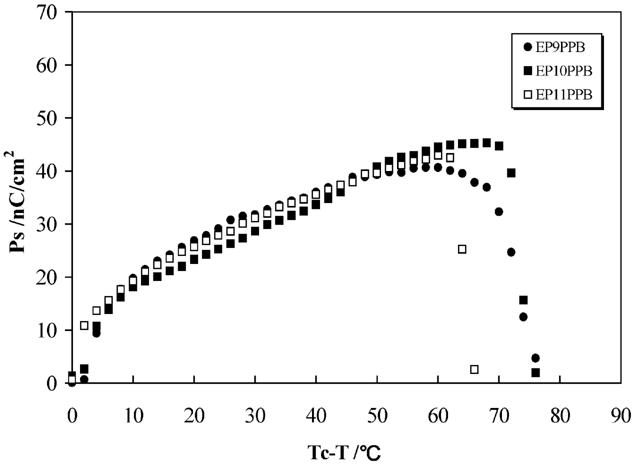


Figure 3. Spontaneous polarization plotted as a function of temperature for EP*m*PPB (m=9–11). T_c is the temperature of the SmA*–SmC* transition.

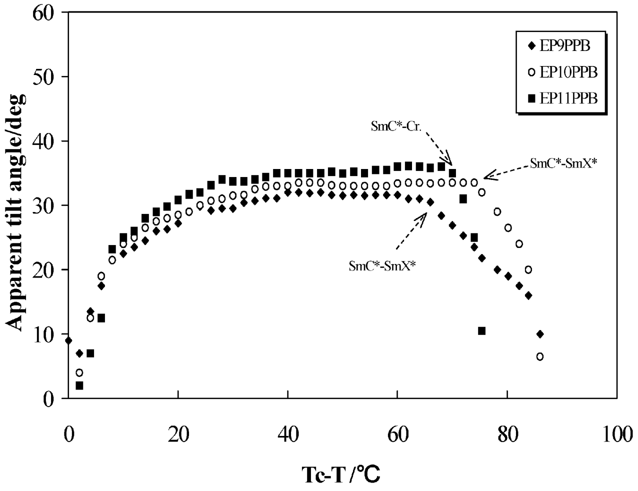


Figure 4. Temperature dependence of apparent tilt angle for the materials EP*m*PPB (m=9–11).

3.5. *Dielectric constant*

Figure 5 shows the temperature dependence of the dielectric constants ε' for the material EP10PPB measured at 100 Hz in 25 μm homogeneous cells. The ε' values in the SmA* phase are small, and the characteristic point corresponding to the SmA* to SmC* transition is clear. The great increase of dielectric constant on cooling to the SmC* phase is due to the contribution of the Goldstone mode [21]. The characteristic of the ferroelectric SmC* phase was thus be well confirmed.

3.6. *Electro-optical responses*

The electro-optical responses were obtained under crossed polarizers, where the axes of polarizer and

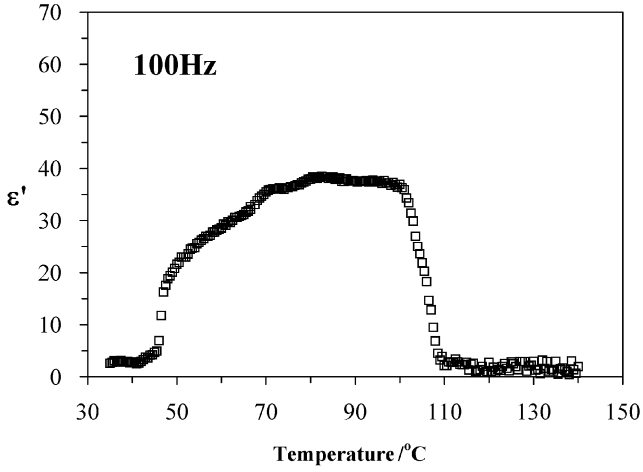


Figure 5. Temperature dependence of dielectric constant for EP10BPP. The measurement was carried out at cooling rate of 1°C min^{-1} and a frequency of 100 Hz.

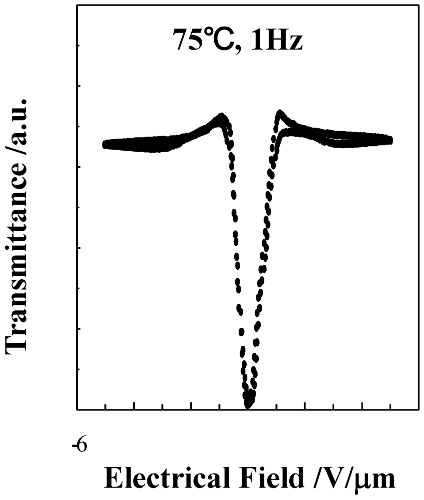


Figure 6. Electro-optical response of transmittance versus electric field obtained from EP10PPB in the SmC* phase at 75°C and 1 Hz frequency of applied triangular wave.

analyser were parallel and perpendicular, respectively, to the smectic layer normal in a homogeneously aligned cell. Figure 6 illustrates the V-shaped switching of transmittance versus electric field on application of a field of triangular waveform in the SmC* phase, for EP10PPB in a 5 µm homogeneous cell. The responses are critically dependent on temperature and frequency.

4. Conclusion

Chiral swallow-tailed materials EP*m*PPB (*m*=8–12) derived from (*S*)-2-[1-(2-ethylbutoxy)]propanol have been demonstrated to possess ferroelectric SmC* phases. In this phase these materials displayed V-shaped switching in their electro-optical response. In our previous studies, ferroelectric and antiferroelctric liquid crystals containing chiral swallow-tailed groups also displayed V-shaped switching in their electro-optical response. This implies that the molecular structures of the materials may affect the appearance of this type of switching mode in the liquid crystal cell. However, the role of the molecular structure on switching behaviour has not yet been fully explored, and requires more work to establish the relationship.

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