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## Liquid Crystals

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### Synthesis and ferroelectric properties of chiral liquid crystals derived from (S)-1-propyloxy-2-propanol

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# Synthesis and ferroelectric properties of chiral liquid crystals derived from (*S*)-1-propyloxy-2-propanol

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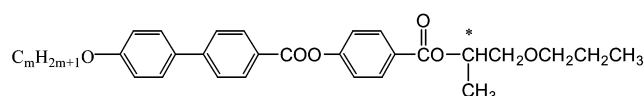
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A new optically active chiral moiety, (*S*)-1-propyloxy-2-propanol, was designed and synthesized by the treatment of 1-propanol with (*S*)-propylene oxide under basic conditions. Its derivatives, the (*R*)-1-propyloxy-2-propyl 4-[4-(4-alkoxyphenyl)phenoxy]benzoates, PPmPPB ( $m=8-12$ ), were prepared for the investigation of mesomorphic properties. All of the chiral materials displayed enantiotropic SmA\* and SmC\* phases, and the shorter alkyl chain members ( $m=8-11$ ) 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 in polyimide film-coated homogeneously aligned cells exhibit thresholdless, V-shaped switching in the ferroelectric phase.

## 1. Introduction

The mesogenic behaviour of chiral liquid crystals is strongly dependent on the chiral moieties in their molecules. Thus, commercially available optically active chiral moieties such as 2-alkanols, lactic acid and  $\alpha$ -halohydrin derived from L-amino acids [1] are generally used for the preparation of chiral liquid crystals. Some chiral moieties, however, have been designed and synthesized by using chiral auxiliaries [2, 3]. From the results of mesogenic behaviour, a correlation between molecular structure and mesogenic properties can be made [4].

A wealth of optically active pure epoxides is commercially available; while there are possibilities of preparing chiral epoxides directly from alk-1-enes [5]. Epoxides have also been reacted with C-nucleophiles to give chiral alcohols with concomitant linkages [6]. In this work, we have designed and synthesized, by the reaction of (*S*)-propylene oxide with an O-nucleophile, propanol, a new optically active chiral moiety, (*S*)-1-propyloxy-2-propanol. Its derivatives, the (*R*)-1-propyloxy-2-propyl 4-[4-(4-alkoxyphenyl)phenoxy]benzoates, PPmPPB ( $m=8-12$ ), were prepared for the study of the mesomorphic phases and their physical properties. The general structural formula for the target compounds is depicted below.

PPmPPB( $m=8-12$ )

It may be noted that the structure of the designed materials is closely similar to that of the well known antiferroelectric liquid crystal material 4-[(1-methylheptyloxy)carbonyl 4'-octyloxy-4-biphenyl]carboxylate, MHPOBC. The reported mesophase sequence for MHPOBC is I(151.5°C)SmA\*(123.0°C)SmC\*(121.0°C)SmC<sub>A</sub>\*(73.5°C)Cr. More detailed mesophases have been well studied and reported as I(156.0°C)SmA\*(122.0°C)SmC<sub>α</sub>\*(120.7°C)SmC<sub>β</sub>\*(119.0°C)SmC<sub>γ</sub>\*(118.3°C)SmC<sub>A</sub>\*(66.0°C)SmI\*(30°C)Cr [7–12].

## 2. Experimental

### 2.1. Characterization of the materials

The chemical structures of intermediates and target materials were analysed by nuclear magnetic resonance spectroscopy using a JEOL EX-400 FTNMR 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

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materials were determined by differential scanning calorimetry using a Perkin-Elmer DSC7 calorimeter at running rates from 1°C to 20°C min<sup>-1</sup>. Mesophases were principally identified by microscopic textures 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 cells purchased from E. H. C. Co., Japan. The spontaneous polarization ( $P_s$ ) was measured by a triangular wave method [13]. The measurement of optical transmittance versus applied electric field was conducted using a He-Ne laser (5 mW, 632.8 nm) as a probe beam [14, 15]. The optical transmittance of the probe beam passing through 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 an HP54502A digital oscilloscope. The voltage applied to the cell was produced by an arbitrary wave-form generator (AG1200) and amplified by a home-made power preamplifier.

## 2.2. Preparation of materials

The starting chiral material, (*S*)-propylene oxide, was purchased from Aldrich Chemical Co. USA, with optical 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. Anhydrous organic solvents, dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and tetrahydrofuran (THF), were purified by treatment with CaH<sub>2</sub> and LiAlH<sub>4</sub>, respectively, and distilled before use.

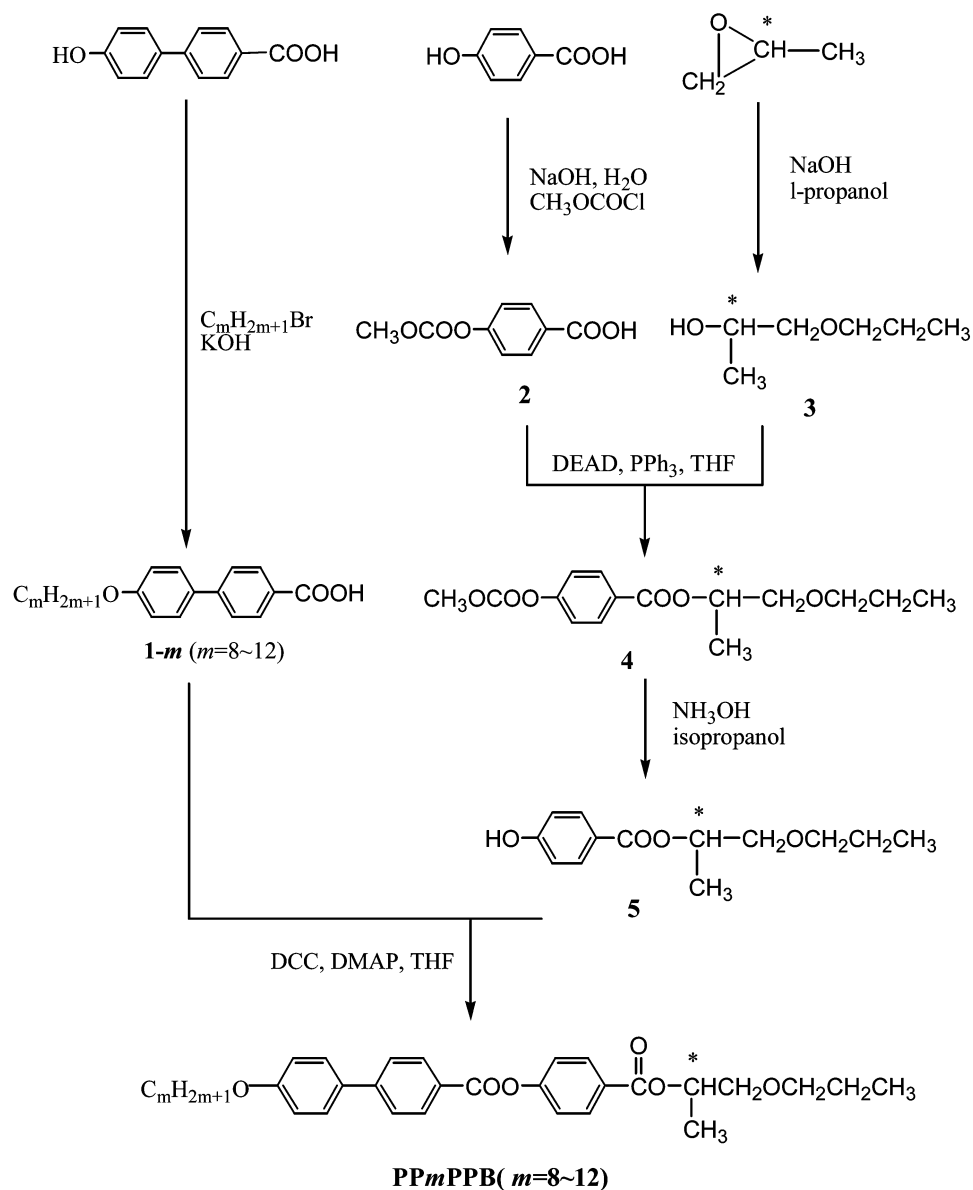
The synthetic procedures for the target compounds were carried out as outlined in Scheme 1. Detailed procedures for the syntheses of compounds PP*m*PPB (*m*=8–12) are described in the following sections.

**2.2.1. (*R*)-1-Propyloxy-2-propyl 4-(methoxycarbonyloxy) benzoate, 4.** 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<sub>3</sub>P, 3.4 g, 13 mmol) and compound 3 (1.18 g, 10 mmol) in anhydrous THF (12 ml) at room temperature with vigorous stirring. The reaction soon started. After the mixture had been held overnight at room temperature, triphenylphosphine oxide was removed by filtration; THF was then removed under vacuum. The product was finally isolated by column chromatography over

silica gel (70–230 mesh) using ethyl acetate/hexane (*v/v*=2/8) as eluant to give a colourless liquid; 65% yield of compound 4 was obtained. The chemical shifts of compound 4 in <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) are:  $\delta$  (ppm) 0.87–0.91 (t, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.34–1.36 (d, 2H, CH\*CH<sub>3</sub>), 1.55–1.58 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.42–3.61 (m, 4H, CH<sub>2</sub>OCH<sub>2</sub>), 3.92 (s, 3H, COOCH<sub>3</sub>), 5.28–5.32 (m, 1H, OCH\*CH<sub>3</sub>), 7.26–7.29 (d, ArH), 8.07–8.10 (d, 4H, ArH).

**2.2.2. (*R*)-1-Propyloxy-2-propyl 4-hydroxybenzoate, 5.** Compound 4 (0.88 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 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), dried (MgSO<sub>4</sub>), filtered and evaporated to give a colourless oil. The oil was purified by flash column chromatography over silica gel (70–230 mesh) using dichloromethane; the resulting oil was then dried in vacuum. An 80% yield of compound 5 was obtained and identified by its <sup>1</sup>H NMR spectrum. The chemical shifts of compound 5 in <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) are:  $\delta$  (ppm) 0.87–0.91 (t, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.34–1.36 (d, 2H, CH\*CH<sub>3</sub>), 1.55–1.58 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.42–3.60 (m, 4H, CH<sub>2</sub>OCH<sub>2</sub>), 5.27–5.31 (m, 1H, OCH\*CH<sub>3</sub>), 6.32 (s, 1H, OH), 7.26–7.28 (d, ArH), 8.09–8.12 (d, 4H, ArH).

**2.2.3. (*R*)-1-Propyloxy-2-propyl 4-[4-(4-alkoxyphenyl) phenoxy]benzoates, PP*m*PPB (*m*=8–12).** A mixture of 4-(4'-alkoxyphenyl)benzoic acids (2.8 mmol), compound 5 (0.73 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 precipitates were filtered off and the filtrates washed with 5% acetate acid solution (3 × 50 ml), 5% saturated aqueous sodium hydrogen carbonate (3 × 50 ml) and water (3 × 50 ml), dried over anhydrous magnesium sulphate and concentrated in vacuum. The residue was purified by column chromatography over silica gel (70–230 mesh) using dichloromethane as eluant. After purification by recrystallization from absolute ethanol, 70–80% yields of final products were obtained. The chemical shifts for material PP10PPB, as an example, in <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) are:  $\delta$  (ppm) 0.87–0.93 (m, 6H, CH<sub>2</sub>CH<sub>3</sub>), 1.28–1.60 (m, 16H, CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>), 1.82 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 3.44–3.63 (m, 4H, CH<sub>2</sub>OCH<sub>2</sub>), 4.00–4.03 (t, 2H, ArOCH<sub>2</sub>), 5.29–5.33 (m, 1H, OCH\*CH<sub>3</sub>), 6.99–7.01 (d, 2H, ArH),



Scheme 1. Procedures for the synthesis of chiral materials PP<sub>m</sub>PPB (*m*=8–12).

Table 1. Elemental analysis data for the materials PP<sub>m</sub>PPB (*m*=8–12).

Material	Theory		Experiment	
	% C	% H	% C	% H
PP8PPB	74.70	7.74	74.63	7.75
PP9PPB	74.99	7.91	74.71	7.83
PP10PPB	75.23	8.07	75.15	8.05
PP11PPB	75.48	8.22	75.39	8.23
PP12PPB	75.72	8.36	75.71	8.34

7.27–7.30 (d, 2H, ArH), 7.58–7.61 (d, 2H, ArH), 7.69–7.71 (d, 2H, ArH), 8.12–8.15 (d, 2H, ArH), 8.22–8.24 (d, 2H, ArH).

All the target materials were analysed by elemental analysis for purity, with results shown in table 1.

### 3. Results and discussion

#### 3.1. Mesomorphic properties

The transition temperatures of mesophases of PP<sub>m</sub>PPB (*m*=8–12) were determined by DSC in conjunction with optical microscopy. Mesophase identification was carried out principally by the texture observation of

Table 2. Transition temperatures ( $^{\circ}\text{C}$ ) and associated enthalpy data (in brackets,  $\text{J g}^{-1}$ ) for the chiral materials  $\text{PP}m\text{PPB}$  ( $m=8-12$ ), taken from DSC thermograms at cooling rates of  $5^{\circ}\text{C min}^{-1}$ .

Material	I	SmA*	SmC*	SmX*	Cr.	m.p. <sup>a</sup>
PP8PPB	• 159.4 (13.8) <sup>d</sup>	• 126.2 (0.3)	• 87.9 (3.7)	• 39.5 (4.6)	• 82.2 (80.8)	
PP9PPB	• 153.8 (11.8)	• 128.5 (0.5)	• 56.2 (2.8)	• 20.1 (21.5)	• 73.1 (41.2)	
PP10PPB	• 150.7 (24.7)	• 127.7 (0.6)	• 48.8 (3.5)	• 25.6 (44.1)	• 62.1 (55.5)	
PP11PPB	• 147.8 (9.8)	• 127.8 (0.4)	• 48.7 (0.7)	• 48.2 (39.4)	• 39.4 (28.2)	
PP12PPB	• 144.6 (13.6)	• 125.6 (0.8)	• —	• 44.6 (53.5)	• 71.5 (56.3)	

<sup>a</sup>Melting point taken from DSC thermograms recorded at heating rates of  $5^{\circ}\text{C min}^{-1}$ .

the optical microscope. The SmA\* phase was characterized by the formation of focal-conic textures, the SmC\* phase by the formation of striated focal-conic textures. An unidentified SmX\* phase was observed in the shorter alkyl chain materials  $\text{PP}m\text{PPB}$  ( $m=8-11$ ). The mesophases and their corresponding transition temperatures measured by DSC calorimetry for the materials are listed in table 2. It can be seen that they exhibit a wide temperature range for the ferroelectric SmC\* phase. The clearing point decreases as  $m$  increases, but the temperatures of the SmC\*–SmX\* or SmC\*–Cr transitions are increased. That is, the thermal stabilities of the SmC\* phases are suppressed as  $m$  is increased.

### 3.2. Physical properties

The physical properties of the materials were measured in  $5\mu\text{m}$  homogeneous cells. Figure 1 shows the

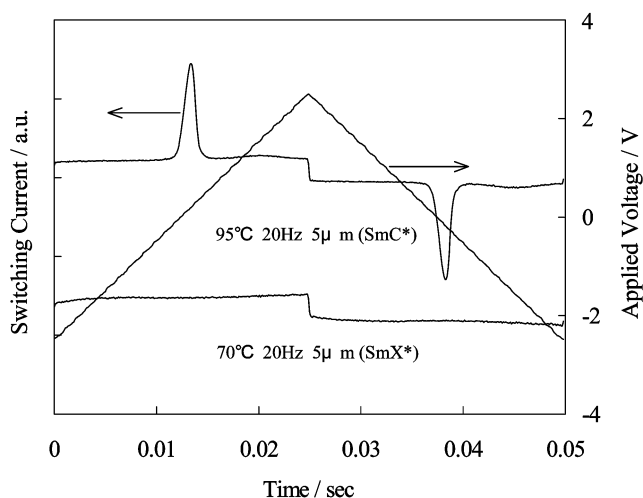


Figure 1. Switching behaviour of PP8PPB in the SmC\* and SmX\* phases at  $95^{\circ}\text{C}$  and  $70^{\circ}\text{C}$ , respectively.

electrical switching response of a  $5\mu\text{m}$  thick PP8PPB homogeneous cell under a triangular wave voltage with a field frequency of 20 Hz and amplitude of 5 V. The switching currents display one current peak from  $126^{\circ}\text{C}$  to  $87^{\circ}\text{C}$  similar to the behaviour reported for the ferroelectric SmC\* phase [11]. However, the switching current peak disappears when the SmC\* phase transforms to the SmX\* phase at  $86^{\circ}\text{C}$ . The switching current of the SmX\* phase failed to show a response in switching, confirming that the SmX\* phase is not a tilted mesophase but is a higher ordered smectic phase. The antiferroelectric SmC<sub>A</sub>\* phase found in MHPOBC is not detected in this series of materials. It seems that one methylene group at the chiral tail of the molecule replaced by an oxygen atom suppresses the formation of the SmC<sub>A</sub>\* phase leading to a higher ordered smectic phase.

The temperature dependence of spontaneous polarization ( $P_s$ ) in the SmC\* phase of the materials was

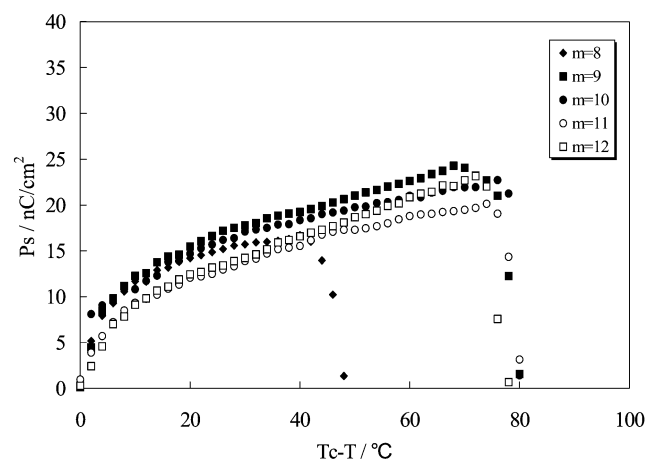


Figure 2. Spontaneous polarization plotted as a function of temperature for  $\text{PP}m\text{PPB}$  ( $m=8-12$ ).  $T_c$  is the temperature of the SmA\*–SmC\* transition.

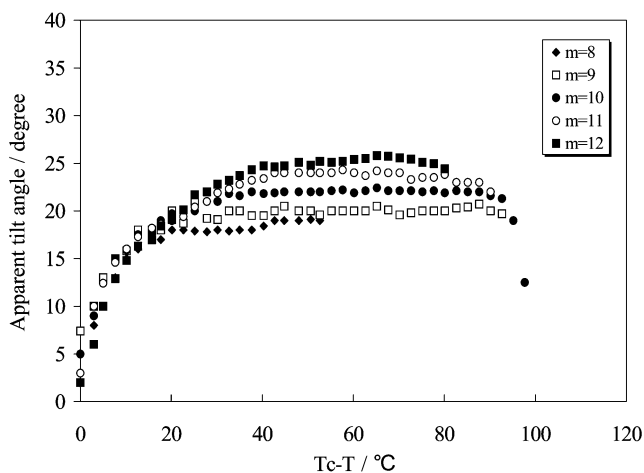


Figure 3. Temperature dependence of apparent tilt angle for the materials PPmPPB ( $m=8-12$ ).

measured and is illustrated in figure 2. The  $P_s$  increased rapidly from the Curie point with decrease in temperature. No significant correlation of  $P_s$  with variation of alkyl chain length was found. Figure 2 shows that the maximum  $P_s$  values of compounds PPmPPB ( $m=8-12$ ) are in the range  $16.7-24.2 \text{ nC cm}^{-2}$ .

The materials were sandwich-packed in  $2 \mu\text{m}$  thick homogeneously aligned cells for the measurement of apparent tilt angle. Figure 3 shows that the tilt angles are small at the  $\text{SmA}^*-\text{SmC}^*$  phase transition and then increase strongly as the temperature falls below the Curie point. The maximum apparent tilt angle is about  $19^\circ-25^\circ$ . The results also show that the apparent tilt angle increases with increasing non-chiral chain length.

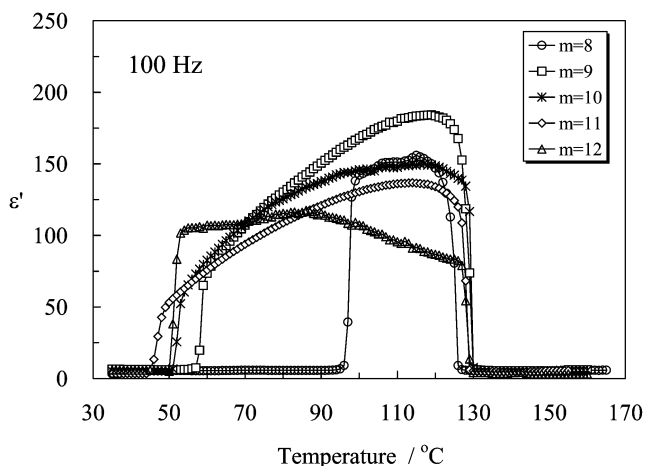


Figure 4. Temperature dependence of dielectric constant ( $\epsilon'$ ) for the materials PPmPPB ( $m=8-12$ ). Measurements were carried out at cooling rate of  $1^\circ\text{C min}^{-1}$  and a frequency of 100 Hz.

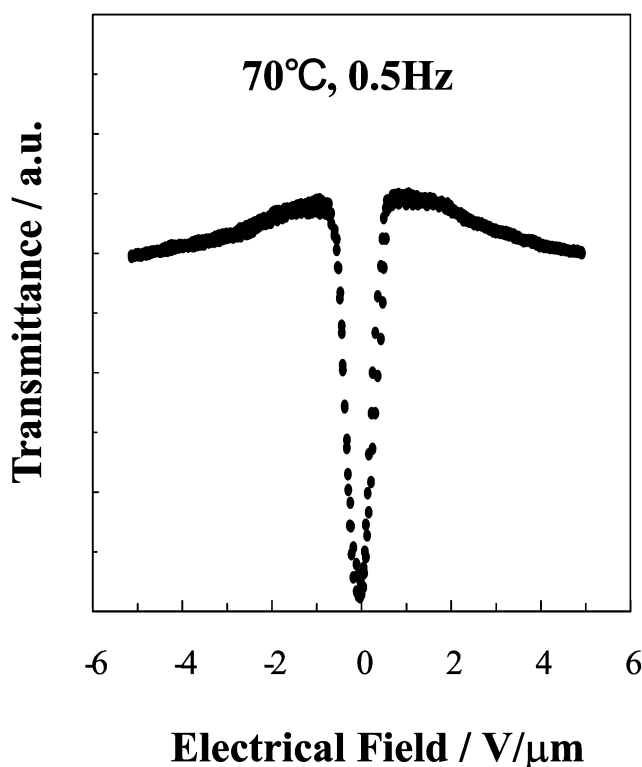


Figure 5. Electro-optical response of transmittance versus electrical field obtained from PP10PPB in the  $\text{SmC}^*$  phase at  $70^\circ\text{C}$  and 0.5 Hz frequency of applied triangular wave.

Figure 4 shows the temperature dependence of the dielectric constants  $\epsilon'$  for the materials PPmPPB ( $m=8-12$ ) measured at 100 Hz in  $25 \mu\text{m}$  homogeneous cells. The  $\epsilon'$  values in the  $\text{SmA}^*$  phase are small and the characteristic point corresponding to the  $\text{SmA}^*$  to  $\text{SmC}^*$  transition is clear in the figure. The large increase in dielectric constant on cooling to the  $\text{SmC}^*$  phase is due to the contribution of the Goldstone mode [16]. This characteristic of the ferroelectric  $\text{SmC}^*$  phase is thus well confirmed.

The electro-optical responses were obtained under crossed polarizers where the axes of polarizer and analyser were parallel and perpendicular, respectively, to the smectic layer normal in a homogeneously aligned cell. Figure 5 shows the response of transmittance versus electric field on applying a field of triangular waveform in the  $\text{SmC}^*$  phase, measured for a representative material PP10PPB in a  $5 \mu\text{m}$  homogeneous cell. A V-shaped switching property was observed similar to that reported by Inui *et al.* in an antiferroelectric mixture [17]. A display device using this V-shaped switching antiferroelectric mixture was reported to show high performance, such as wide viewing angle, high contrast, full colour and high speed,

and is considered as a candidate for the next generation display [17, 18].

#### 4. Conclusion

Chiral materials PP $m$ PPB ( $m=8-12$ ) derived from (*S*)-1-propyloxy-2-propanol have been demonstrated to possess the ferroelectric SmC\* phase. In this phase the materials displayed V-shaped switching in their electro-optical response. These materials that contain a new chiral group derived from (*S*)-propylene oxide, providing a new molecular design for ferroelectric liquid crystals for future study.

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