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Synthesis and mesomorphic properties of chiral liquid crystals having thiolactate groups

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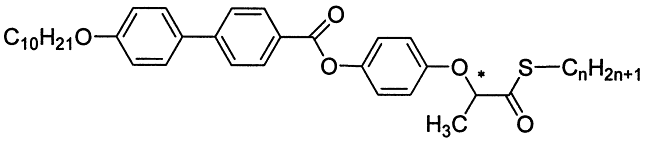
A homologous series of chiral thiolactate liquid crystals, alkyl 2-[4-(4-decyloxyphenyl)benzoyloxyphenyloxy]thiopropionates, ADBPT-*n* ($n=2$–6), was prepared from (*R*)-2-(4-hydroxyphenoxy)propionic acid. Structural effects on the mesomorphic and physical properties were investigated in terms of variation in the length of alkyl chain attached to the thiolactate group. The mesophases and their corresponding transition temperatures were identified by polarizing optical microscopy and differential scanning calorimetry. Compound ADBPT-4 exhibited SmA* and SmC* phases, whereas other compounds in the series exhibited the SmA* phase along with unidentified $\mathrm{SmX_1}^*$ and $\mathrm{SmX_2}^*$ phases. The maximum $\mathbf{P}_\mathrm{s}$ value measured for ADBPT-4 in the SmC* phase was $17.5\,\mathrm{nC\,cm^{-2}}$, suggesting the polarization of the material is rather low. The tilt angles were also measured, reaching a maximum of 48 degree.

1. Introduction

Some chiral liquid crystals containing the thiobenzoate group exhibit ferroelectric and antiferroelectric phases [1, 2]; recently, Neubert *et al.* carried out a systematic study on the effect of the thiobenzoate group in various positions in the rigid cores and linking groups on the formation of mesophases [3]. The thiobenzoate group has been reported to enhance the mesophase ranges and mesophase thermal stabilities when compared with analogous carboxylates [4–8]. Interesting mesomorphic properties have also been observed in achiral liquid crystals with thioether aliphatic chains [9].

We have previously reported studies on chiral liquid crystals with thioester groups in the chiral tail; these showed an enhancement of SmC* mesophase stability with longer achiral chain lengths [10]. The present investigation deals with the synthesis and mesomorphic properties of chiral liquid crystals containing thiolactate groups in the chiral tail. Earlier work on chiral liquid crystals derived from lactic acid showed the formation of ferroelectric and antiferroelectric phases [11–14]. The designed molecule has the general formula shown below.



ADBPT-n(n=2~6)

2. Experimental

2.1. *Characterization of materials*

The chemical structures for intermediates and target materials were analysed by ^{1}H nuclear magnetic resonance spectroscopy using a Jeol EX-400 FTNMR spectrometer. Purity was checked by thin layer chromatography and further confirmed by elemental analysis using a Perkin-Elmer 2400 elemental analyser. Transition temperatures and phase transition enthalpies were determined by differential scanning calorimetry using a Perkin-Elmer DSC7 calorimeter at a heating rate of $5^\circ\mathrm{C\,min^{-1}}$. Mesophases were principally identified from the texture of samples sandwiched between two glass plates by polarizing optical microscopy (POM) using a Nikon Microphot-FXA in conjunction with an Instec HS1 hot stage.

The physical properties of the ferroelectric phase for the materials were measured in antiparallel aligned cells purchased from E.H.C. Co. Japan. The spontaneous polarization ($\mathbf{P}_\mathrm{s}$) was measured by a triangular wave

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method [15]. The measurement of optical transmittance versus applied electric field was conducted using a He-Ne laser (5mW, 632.8nm) as a probe beam [16, 17] passing through the cell between crossed polarizers, whose axes were parallel and perpendicular to the smectic layer normal. The signals were detected with a HP54502A digital oscilloscope. The voltage applied to the cell was produced by an arbitrary wave form generator (AG1200) and amplified by a homemade power preamplifier.

2.2. *Synthesis*

The starting chiral material, (*R*)-2-(4-hydroxyphenoxy)propionic acid, was purchased from Aldrich Chemical Company with purity greater than 99%. Thin layer chromatography was performed with TLC sheets (Merck, silica gel $60F_{254}$) coated with silica; spots were detected by UV irradiation. Silica gel (MN Kieselgel 60, 70–230mesh) was used for column chromatography. The organic solvent dichloromethane was purified by treatment with CaH_2 and distilled before use. The synthetic procedures for the target compounds were carried out as outlined in the scheme.

The hydroxyl group of the starting chiral material was protected as its methylformic ester. The hydroxyl-protected compound was esterified with various thiols in the presence of *N*,*N*-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP). The protecting group was removed using ammonium hydroxide and isopropyl alcohol and the resulting hydroxy compounds were further esterified with 4-(4-decyloxyphenyl)benzoic acid using DCC and DMAP, to yield the target compounds. All the intermediates and final products were purified by column chromatography over silica gel, using dichloromethane as eluant. Detailed synthetic procedures and analytical data for the representative compound ADBPT-4 are provided below. A similar method was adopted for the preparation of other compounds in the series.

2.2.1. *(R)-2-(4-Methoxycarbonyloxyphenyloxy)propionic acid*

(*R*)-2-(4-hydroxyphenoxy)propionic acid (3.64 g, 0.02 mol) was dissolved in a solution of NaOH (0.85 g, 0.021 mol) in water (25 ml); the mixture was cooled to 0°C. Methyl chloroformate (2 g, 0.02 mol) was added dropwise, in such a way that the reaction temperature was maintained in the range 0–5°C. After complete addition, the reaction mixture was further stirred for 3 h at 0°C; it was then acidified with very dilute HCl. The resinous mass thus formed was extracted with dichloromethane and washed with water to neutral pH; the solvent was then removed under vacuum to yield 4.0 g of a pale resinous mass (85% yield). This product was used without further purification. ^1H NMR ($CDCl_3$, δ ppm): 1.5 (d, 3H, –*$CHC\mathbf{H}_3$), 4.62 (q, 1H, –*$C\mathbf{H}$–), 6.88–6.9 (d, 2H, Ar**H**), 7.1–7.26 (d, 2H, Ar**H**), 7.58 (s, 1H, –COO**H**).

2.2.2. *(R)-Butyl 2-(4-methoxycarbonyloxyphenyloxy) thiopropionate*

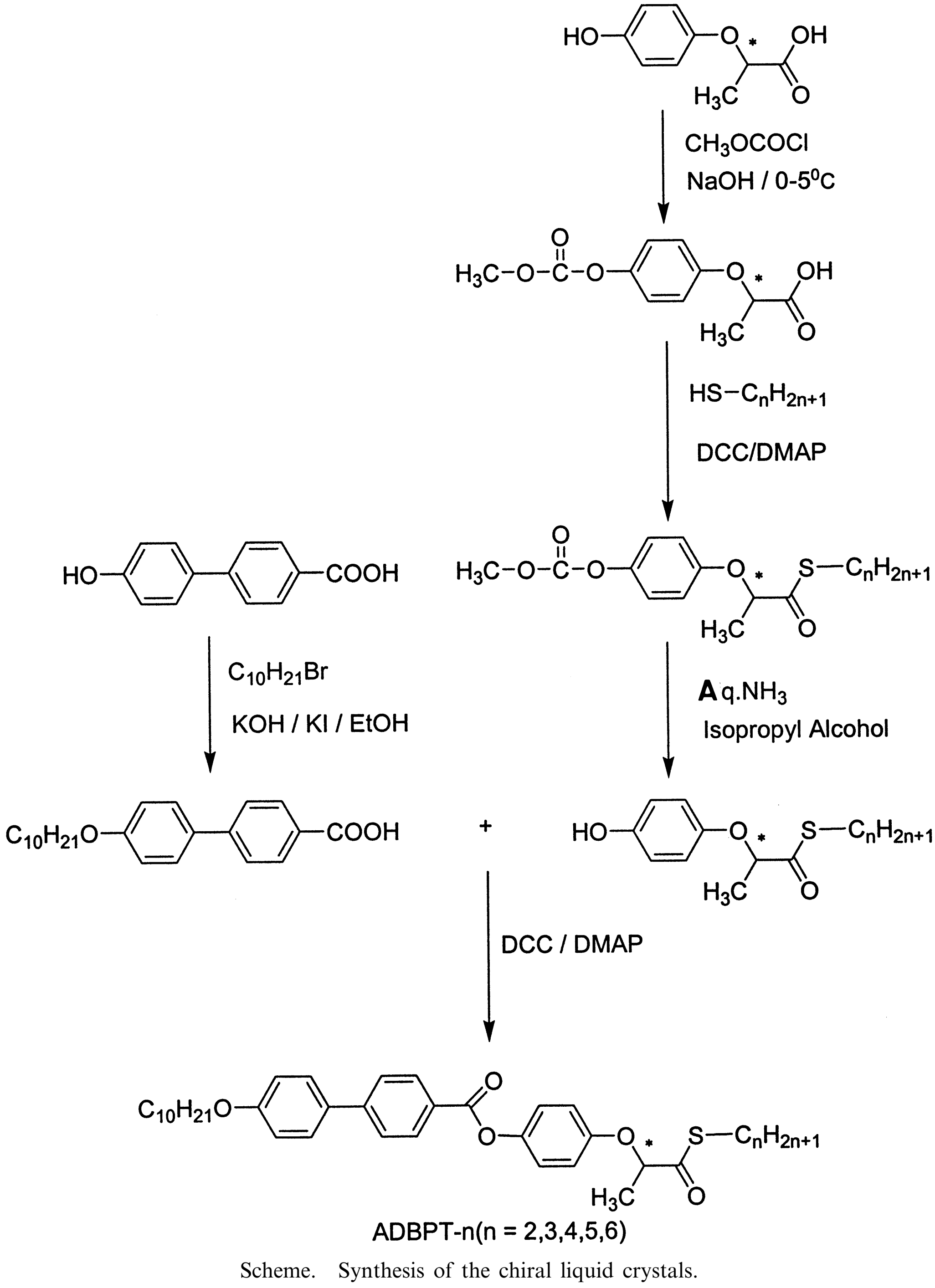
(*R*)-2-(4-methoxycarbonyloxyphenyloxy)propionic acid (1.5 g, 0.006 mol), butanethiol (0.56 g, 0.006 mol) and DMAP (0.12 g, 0.001 mol) were mixed in dry dichloromethane (25 ml). DCC (1.32 g, 0.0065 mol) was then added and the resulting mixture stirred at room temperature for 3 h; precipitated materials were removed by filtration. The solution was washed with 5% acetic acid (3 × 50 ml) and saturated aqueous NaCl (3 × 50 ml), followed by water (3 × 50 ml). The organic layer was dried over anhydrous $MgSO_4$ and filtered; the solvent was removed under reduced pressure. The product was purified by column chromatography using dichloromethane as eluant, and recrystallized from ethanol to give a white solid; yield 1.7 g (90%). ^1H NMR ($CDCl_3$, δ ppm): 0.89–0.91(t, 3H, –$CH_2C\mathbf{H}_3$)1.5(d, 3H, –*$CHC\mathbf{H}_3$), 1.45–1.46(m, 4H, –$C\mathbf{H}_2$–), 4.62(q, 1H, –*$C\mathbf{H}$–), 3.9(s, 3H, –$OC\mathbf{H}_3$) 2.89 (t, 2H, –$SC\mathbf{H}_2$–), 7.29(m, 4H, Ar**H**).

2.2.3. *(R)-Butyl 2-(4-hydroxyphenyloxy)thiopropionate*

(*R*)-Butyl 2-(4-methoxycarbonyloxyphenyloxy)thiopropionate (1.56 g, 0.005 mol) was dissolved in isopropyl alcohol (10 ml). Ammonium hydroxide (1 ml) was then added to the mixture, which was stirred at 20°C until the reaction was completed (its course being followed by TLC). The resulting mixture was diluted with water (250 ml) and extracted with diethyl ether (3 × 100 ml). After work-up, the product was purified by column chromatography over silica gel using dichloromethane/ethyl acetate (5/1) to yield 0.9 g (72%) of a pure white solid. ^1H NMR ($CDCl_3$, δ ppm): 0.89–0.91 (t, 3H, –$CH_2C\mathbf{H}_3$), 1.55 (d, 3H, –*$CHC\mathbf{H}_3$), 1.44–1.46 (m, 4H, –$C\mathbf{H}_2$–), 4.74 (q, 1H, –*$C\mathbf{H}$–), 2.91(t, 2H, –$SC\mathbf{H}_2$–), 6.25–6.8 (m, 4H, Ar**H**), 5.11 (s, 1H, –O**H**).

2.2.4. *(R)-Butyl 2-[4-(4-decyloxyphenyl)benzoyloxyphenyloxy]thiopropionate, ADBPT- 4*

(*R*)-Butyl 2-(4-hydroxyphenyloxy)thiopropionate (0.25 g, 0.001 mol), 4-(4-decyloxyphenyl)benzoic acid (0.35 g, 0.0011 mol) and DMAP (1.2 g) were mixed in dry dichloromethane (25 ml). DCC (0.31 g, 0.0015 mol) was added and the resulting mixture stirred at room temperature for one day. Precipitated materials were removed by filtration, and the solvent was removed



Scheme. Synthesis of the chiral liquid crystals.

under reduced pressure. The product was purified by column chromatography using dichloromethane as eluant, and recrystallized from ethanol to give a white solid; yield 0.55 g (95%). ^{1}H NMR ($CDCl_3$, δ ppm): 0.89–1.1 (m, 6H, –OC_9H_{18}**CH_3**, –SC_3H6**CH_3**), 1.61(d, 3H, –*CH**CH_3**), 1.28–1.8 (m, 18H, –**CH_2**–), 1.81(q, 2H, –OCH_2**CH_2**–) 4.78(q, 1H, –***CH**–), 4.01(t, 2H, –O**CH_2**–), 2.90(t, 2H, –S**CH_2**–), 6.93–6.95(d, 2H, Ar**H**), 6.99–7.0 (d, 2H, Ar**H**), 7.11–7.26 (d, 2H, Ar**H**), 7.58–7.60 (d, 2H, Ar**H**), 7.67–7.69 (d, 2H, Ar**H**), 8.20–8.22 (d, 2H, Ar**H**).

3. Results and discussion

3.1. *Mesomorphic properties*

The mesophases and their corresponding phase transition temperatures are summarized in the table.

Table. Mesophases, transition temperatures (°C) and enthalpies of transition (J/g, in square brackets) observed in the chiral liquid crystals. DSC thermograms obtained on cooling at 5°C min^{-1}.

n	M.p.	Cr		SmX_2*		SmX_1*		SmC*		SmA*		I
2	41.56 [74.4]	•	35.08 [13.92]	•	42.68[a]	•		—	98.23[a]	•	121.42 [6.99]	•
3	50.85 [17.36]	•	31.84 [19.58]	•	38.56[a]	•		—	100.05[a]	•	126.03 [7.751]	•
4	56.42 [27.82]	•	32.03 [21.04]	•		—	43.26[a]	•	103.25[a]	•	122.03 [8.39]	•
5	59.97 [83.98]	•	34.05 [16.47]	•	39.56[a]	•		—	101.23[a]	•	129.52 [7.671]	•
6	37.55 [19.4]	•	23.3 [18.83]	•	60.89[a]	•		—	108.24[a]	•	126.15 [13.06]	•

[a]Enthalpies too small for observation.

POM investigation of the compounds shows SmA*, SmC* and unidentified SmX_1* and SmX_2* mesophases. The SmA* phase was identified by its optical texture which exhibited focal-conic fans. The SmC* phase was characterized by striated focal-conic textures. The SmX_1* phase appeared as a schlieren texture with many two-brush and fewer four-tethered-brush disclinations, but failed to show the tilted phase characteristics which are discussed later in this report. It was observed that ADBPT-4 shows SmA*, SmC*, and SmX_2* mesophases on cooling. But the other compounds in the series show SmA*, SmX_1, and SmX_2* mesophases. A phase diagram is shown in figure 1; the melting temperature of the compounds increases with increasing spacer length up to $n=5$ in the chiral chain, and decreases sharply for ADBPT-6. The I–SmA* transition shows an odd–even effect depending on the length of the chiral chain.

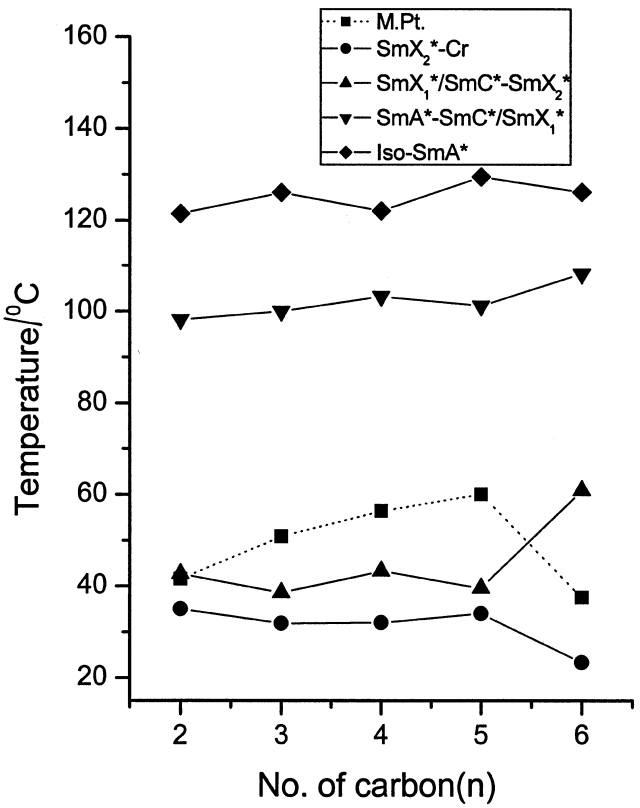


Figure 1. Plot of transition temperature as a function of spacer length on cooling.

3.2. *Switching behaviour*

The switching current behaviour of all the compounds was measured in a 5 μm homogeneous cell, under a triangular wave voltage with field frequency and amplitude 5 $V_{P\text{-}P}$. Only ADBPT-4 showed a single switching current response attributable to the formation of a ferroelectric mesophase phase; its switching profile is presented in figure 2. The switching current of all other compounds failed to show the same response, confirming that the SmX_1* phase is not a tilted mesophase.

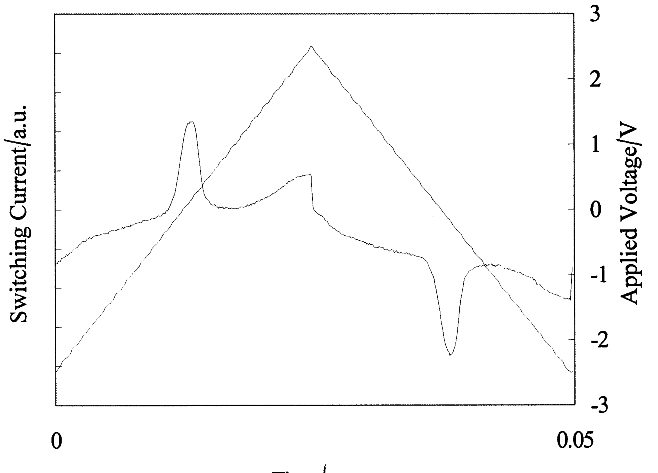


Figure 2. Switching behaviour of ADBPT-4 in the SmC* phase at 75°C in a 5 μm homogeneously aligned cell.

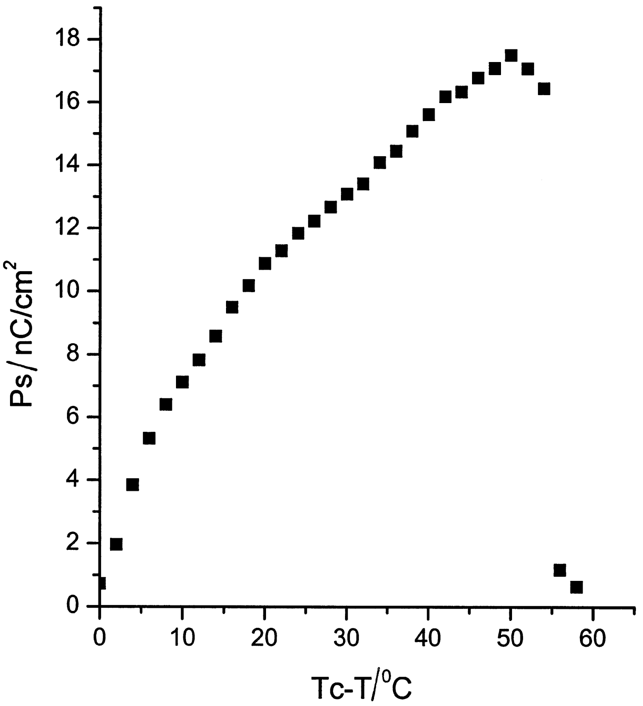


Figure 3. Spontaneous polarization as a function of temperature of ADBPT-4 in SmC* phase in a 5 µm cell.

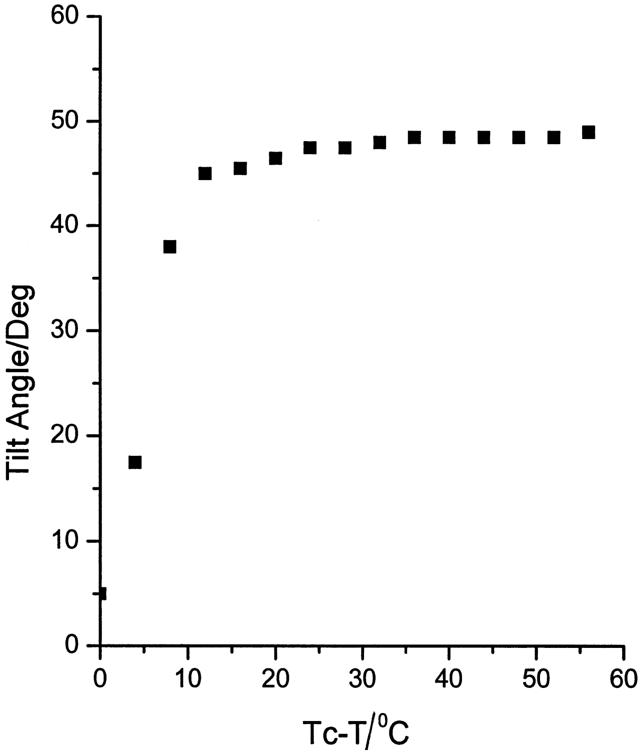


Figure 4. Plot of tilt angle versus temperature for ADBPT-4 in the SmC* phase, in a 5 µm cell.

3.3. *Spontaneous polarization*

The variation of spontaneous polarizations ($\mathbf{P}_s$) with temperature for ADBPT-4 in the SmC* phase is plotted in figure 3; its maximum of 17.5 nC cm^{-2} obtained suggests that the material has a low polarization. The $\mathbf{P}_s$ value steeply increases at the interface of the transition from SmA* to SmC* phase, and gradually decreases before crystallization.

Tilt angles were measured in a 5 µm homogeneously aligned cell. The temperature dependence of the tilt angle for ADBPT-4 in the SmC* phase is given in figure 4, showing a maximum of 48 degrees.

3.4. *Electro-optic response*

The electro-optical response for ADBPT-4 in the SmC* phase was determined with polarizer and analyser parallel or perpendicular to the smectic layer normal, in a 2 µm homogeneously aligned cell; the results are presented in figure 5. V-shaped switching was observed, similar to that reported by Inui *et al.* [18].

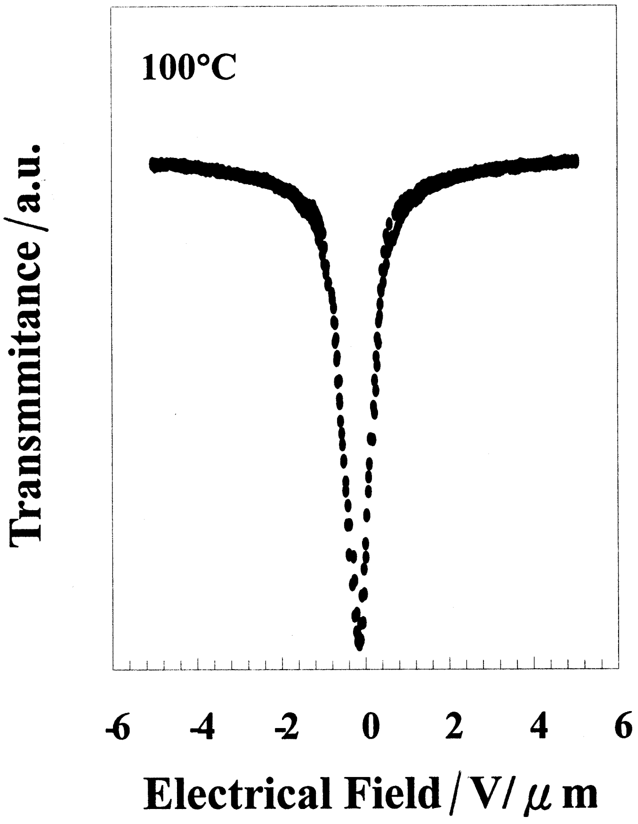


Figure 5. Electro-optical response of transmittance versus electric field obtained from ADBPT-4 in the SmC* phase, at frequency 2 Hz in a 2 µm homogeneously aligned film.

4. Conclusion

We have synthesized a series of liquid crystalline compounds having thiolactate groups in a chiral chain for the investigation of mesophases. Only ADBPT-4 displayed the ferroelectric SmC* phase. The maximum $\mathbf{P}_s$ value was observed to be $17.5\,\mathrm{nC\,cm^{-2}}$, and the maximum tilt angle reached 48° for the SmC* phase. The electro-optical response of this compound in the SmC* phase displayed thresholdless, V-shaped switching, making it a candidate for the next generation of displays [19].

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