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Synthesis and ferroelectric properties of new chiral liquid crystals derived from (*S*)-lactic acid with alkoxyethanols

S. -L. Wu[a]; F. -S. Lai[a]
[a] Department of Chemical Engineering, Tatung University, Taipei 104, Taiwan, ROC

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Synthesis and ferroelectric properties of new chiral liquid crystals derived from (*S*)-lactic acid with alkoxyethanols

S.-L. WU* and F.-S. LAI

Department of Chemical Engineering, Tatung University, 40 Chungshan N. Rd., 3rd Sec., Taipei 104, Taiwan, ROC

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A homologous series of chiral materials derived from (*S*)-lactic acid with alkoxyethanols has been synthesized and their mesomorphic properties investigated. The mesophases and their corresponding transition temperatures were identified by differential scanning calorimetry and polarizing optical microscopy. The spontaneous polarization and electro-optical response of ferroelectric SmC* phase are measured and reported.

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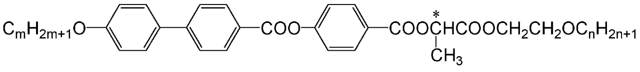
1. Introduction

Commercially available optically pure chiral moieties have been used as the building blocks for the preparation of chiral liquid crystals. Among them, chiral lactic acid provides an excellent platform for the design and synthesis of chiral liquid crystals due to the presence of two functional groups that can be used to connect to the core or the alkyl tail of a liquid crystal molecule. In general, the mesomorphic properties of the lactic acid derivatives displayed a broad ferroelectric phase [1–6], and in a few members, exhibited an antiferroeletric phase [7–10].

Our recent studies [11, 12] on some chiral swallow-tailed materials derived from (*S*)-lactic acid showed that the materials have a broad ferroelectric phase. Moreover, the electro-optical response of some materials in the ferroelectric phase showed the so-called thresholdless, V-shaped switching property. V-shaped switching was first reported by Inui *et al.* [13] in an antiferroelectric mixture. This switching mode yields attractive displays characterized by a wide viewing angle, a very large contrast ratio, high speed response and ideal analogue grey scale with no hysteresis [14]. In this paper, we report the design of a new series of chiral materials derived from (*S*)-lactic acid with alkoxyethanols for investigation. The general structural formula of the chiral materials is depicted below.



I : m = 8~12, n = 1
II : m = 8~12, n = 3
III : m = 8~12, n = 4

The physical properties of the ferroelectric SmC* liquid crystal phase, such as switching behavior, spontaneous polarization, and electro-optical properties were measured.

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 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 compounds were determined by differential scanning calorimetry using a Perkin-Elmer DSC7 calorimeter at running rates of 5°C $\min^{-1}$. Mesophases were identified principally by microscopic texture of the materials sandwiched between two glass plates under a crossed polarizing microscope using a Nikon Microphot-FXA in conjunction with a FP82HT hot stage and Mettler Toledo FP90 central processor.

The physical properties of the ferroelectric phase for the materials were measured in 5 µm homogeneously aligned cells, purchased from E. H. C. Co. Japan. The spontaneous polarization ($\mathbf{P}_s$) was measured by a triangular wave method [15]. In the measurement of optical transmittance versus applied electric field, a He-Ne laser (5 mW, 632.8 nm) was used as a 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 with an HP54502A digital

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*Corresponding author. Email: slwu@ttu.edu.tw

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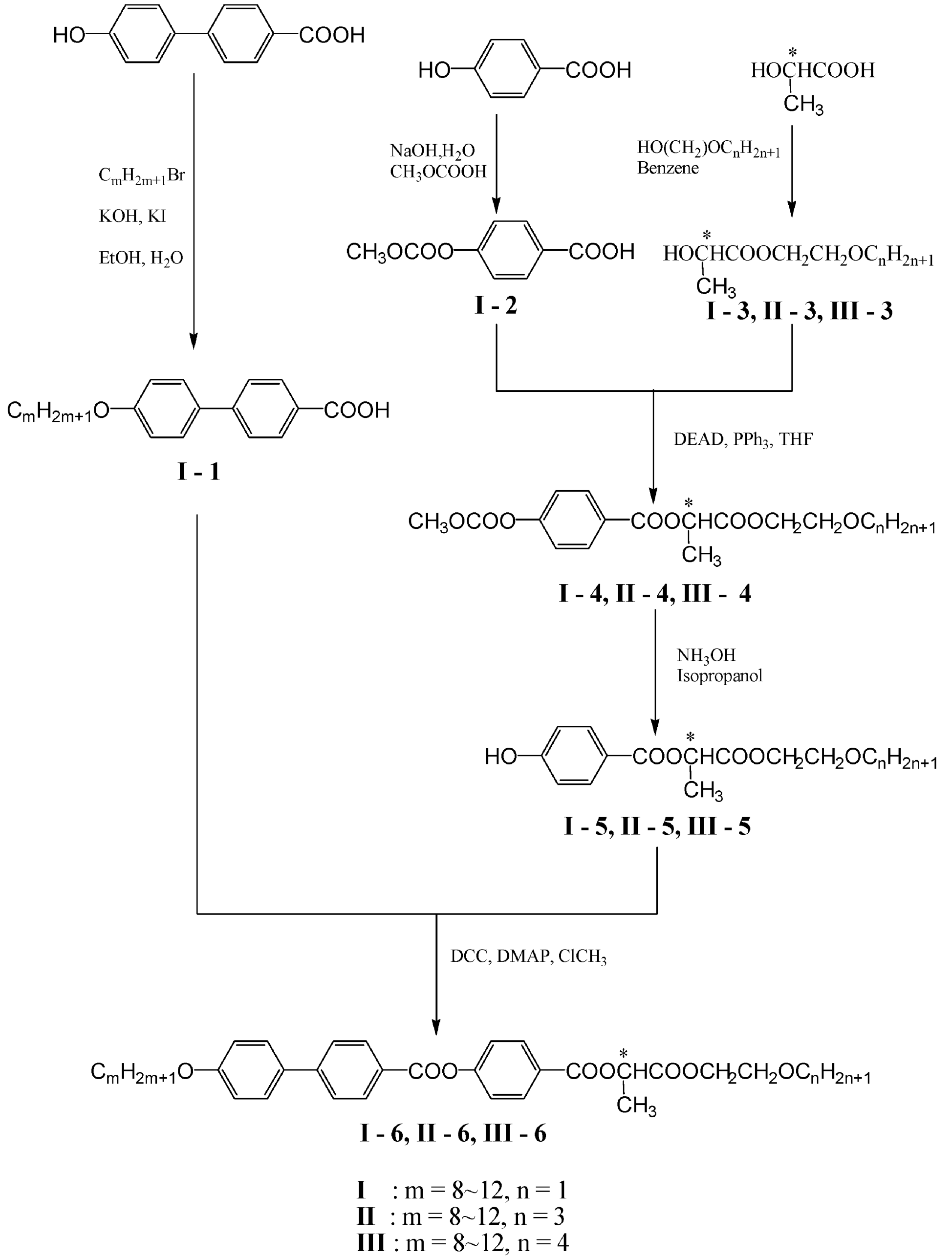
oscilloscope. The voltage applied to the cell was produced by an arbitrary wave-form generator (AG1200) and amplified by a home-made power preamplifier.

2.2. *Preparation of materials*

The starting chiral materials, (*S*)-lactic acid, 2-methoxyethanol, 2-propoxyethanol and ethylene glycol monobutyl ether were purchased from Fluka Co. Chem., Japan, 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. 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 synthetic processes for the target compounds were carried out as outlined in the scheme. Detailed procedures are described as follows.



Scheme. Synthetic procedures for the target materials, I(*m*, *n*=1), II(*m*, *n*=3) and III(*m*, *n*=4).

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2.2.1. 4-Methoxycarbonyloxybenzoic acid, I-2. To a solution of sodium hydroxide (175 mmol) in water (200 ml) maintained at 0–5°C, 4-hydroxybenzoic acid (65 mmol) was added with vigorous stirring. Methyl chloroformate (105 mmol) was then added slowly to the resulting suspension, again maintained at 0–5°C. The resulting slurry was stirred for a further 4 h and brought to pH = 3–5 by the addition of conc. hydrochloric acid and water (1/1). The voluminous precipitate was filtered and recrystallized from ethanol to give compound, **I-2** as a white solid; 75–85% yield m.p. = 175–177°C.

2.2.2. (*S*)-2-Alkoxyethyl 2-hydroxypropionates, I-3, II-3 and III-3. (*S*)-Lactic acid (55 mmol) and the appropriate alcohol (55 mmol) in 15 ml of benzene were heated reflux under with a Dean and Stark trap for 10 h. Benzene was evaporated and the residue filtered and distilled *in vacuo*. The first fraction, which was identified to be the (*S*)-lactate (**I-3**, **II-3** and **III-3**), was collected as a colourless liquid.

2.2.3. 2-Alkoxyethyl (*S*)-2-[4-(methoxycarbonyloxy)-phenylcarbonyloxy]propionates, I-4, II-4 and III-4. A solution of diethyl azodicarboxylate (DEAD, 2.26 g, 13 mmol) and compound **I-2** (2.54 g, 13 mmol) in 10 ml anhydrous THF was added dropwise to a solution of triphenylphosphine (Ph_3P, 3.4 g, 13 mmol) and compound **I-3**, **II-3** or **III-3** (10 mmol) in 10 ml anhydrous THF at room temperature with vigorous stirring. The reaction soon started. After standing the mixture overnight at room temperature, triphenylphosphine oxide was removed by filtration. THF was removed by vacuum distillation. After a work-up procedure, the products were isolated by column chromatography over silica gel (70–230 mesh) using ethyl acetate/hexane (1/4) as eluent to give compounds **I-4**, **II-4** or **III-4** as colourless liquids in 50–70% yields.

2.2.4. 2-Alkoxyethyl (*S*)-2-(4-hydroxyphenylcarbonyloxy)propionates, I-5, II-5 and III-5. Compounds **I-4**, **II-4** or **III-4** (3 mmol) were stirred in a mixture of

Table. The mesophases, transition temperatures (°C) and associated enthalpy changes (J g^{-1}, in square brackets) for materials **I**(m=8–12), **II**(m=8–12) and **III**(m=8–12).

Compound	I		SmA*		SmC*		SmX*		Cr	m.p.[a]
I(m=8)	•	144.2 [6.50]	•	103.3[b]	•	44.1 [1.86]	•	4.4 [8.12]	•	58.0 [30.89]
I(m=9)	•	150.1 [11.80]	•	115.4	•	58.6 [2.58]	•	15.4 [6.88]	•	44.9 [19.99]
I(m=10)	•	141.8 [5.76]	•	106.9	•	38.0 [1.22]	•	16.1 [14.32]	•	66.6 [46.25]
I(m=11)	•	138.2 [6.54]	•	108.1	•	—	—	34.8 [27.64]	•	68.0 [44.85]
I(m=12)	•	136.0 [8.94]	•	108.7	•	—	—	35.7 [36.39]	•	60.0 [46.03]
II(m=8)	•	138.2 [9.28]	•	94.0[b]	•	49.3 [1.67]	•	11.1 [6.24]	•	36.7 [13.65]
II(m=9)	•	134.1 [6.93]	•	95.4	•	33.2 [0.92]	•	9.9 [11.80]	•	56.6 [31.69]
II(m=10)	•	132.4 [7.36]	•	99.0	•	31.1 [1.22]	•	18.0 [19.04]	•	47.7 [28.18]
II(m=11)	•	130.4 [4.54]	•	95.0	•	43.7 [3.16]	•	29.0 [9.96]	•	43.0 [8.98]
II(m=12)	•	126.5 [6.50]	•	98.2	•	50.1 [6.50]	•	30.9 [19.38]	•	42.8 [20.32]
III(m=8)	•	133.3 [7.11]	•	92.9[b]	•	41.9 [1.17]	•	1.6 [4.48]	•	29.9 [12.51]
III(m=9)	•	123.1 [6.23]	•	92.8	•	30.2 [1.93]	•	7.7 [10.84]	•	31.8 [14.33]
III(m=10)	•	127.8 [5.66]	•	92.8	•	26.9 [1.56]	•	18.2 [16.57]	•	34.8 [20.85]
III(m=11)	•	130.0 [8.67]	•	97.5	•	38.1 [5.69]	•	25.7 [15.19]	•	39.8 [17.03]
III(m=12)	•	124.4 [6.27]	•	101.1	•	—	—	32.0 [30.39]	•	43.7 [32.37]

[a] Melting point taken from DSC thermograms recorded at heating rates of 5°C min^{-1}. [b] The SmA*–SmC* phase transition temperatures were determined by optical microscopy; the enthalpy of phase transition was too small to be determined by DSC.

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isopropanol (90 ml) and ammonia (28%, 30 ml) at room temperature for 50 min (TLC analysis revealed a complete reaction); the mixture was then poured into water (40 ml) with stirring. The products were extracted using dichloromethane (3 × 30 ml). The combined extracts were washed with brine (50 ml), dried ($MgSO_4$), filtered and evaporated to give colourless oils. The oils were purified by flash column chromatography over silica gel (70–230 mesh) using dichloromethane; then dried in vacuum to give 45–65% yields of compounds **I-5**, **II-5** or **III-5**.

2.2.5. 2-Alkoxyethyl (*S*)-2-[4-(4'-alkyloxybiphenycarbonyloxy)phenylcarbonyloxy]propionates, I-6, II-6 and III-6. 4-(4′-Alkoxyphenyl)benzoic acids (2.8 mmol), compounds **I-5**, **II-5** or **III-5** (2.8 mmol), *N*,*N*′-dicyclohexylcarbodiimide (DCC) (2.8 mmol), 4-dimethylaminopyridine (DMAP) (0.28 mmol) and dry THF (15 ml) were mixed and stirred at room temperature for 3 days. The precipitates were filtered and washed with 5% acetic acid solution (3 × 30 ml), 5% aqueous sodium hydrogen carbonate (3 × 30 ml) and water (3 × 30 ml), then dried ($MgSO_4$) and concentrated in vacuum. The residues were purified by column chromatography over silica gel (70–230 mesh) using dichloromethane as eluant. After purification by recrystallization from absolute ethanol, 50–60% yields of final products were obtained.

3. Results and discussion

3.1. *Mesomorphic properties*

The SmA* phase was characterized by the formation of focal-conic texture, and the SmC* phase by the formation of broken or striated focal-conic texture. All the materials displayed enantiotropic SmA* and SmC* phases. An unidentified SmX* phase was also observed in some materials. The mesophases and their corresponding transition temperatures measured by DSC and optical microscopy, for the target materials, are shown in the table. [For the final products, **I**(m=a) now represents compound **I-6** with m=9, etc.]

Figure 1 is a chart of mesophases obtained for the compounds **I**(m=10), **II**(m=10) and **III**(m=10), i.e. with n=1, 2 and 3, respectively. It can be seen that an increase of n results in a decrease of the thermal stability of the SmC* and SmX* phases. The material **III**(m=10) has its ferroelectric SmC* phase closer to room temperature.

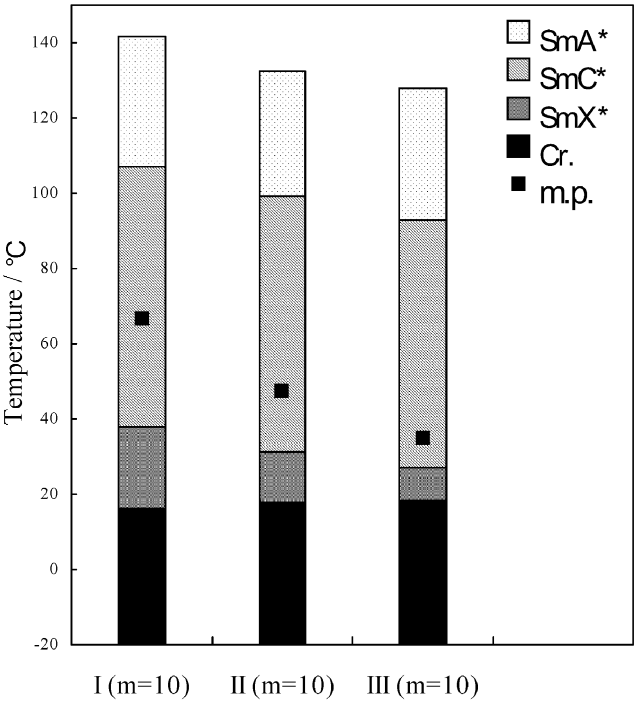

Figure 1. Phase chart of materials **I**(m=10), **II**(m=10) and **III**(m=10).

3.2. *Spontaneous polarization*

Spontaneous polarization $\mathbf{P}_s$ was determined in LC cells made of ITO coated glass whose surface had been treated with a parallel alignment of polyimide. Spontaneous polarization values were taken after slow cooling to the SmC* temperature range. The temperature dependence of P_s of materials **I**(m=9–11), **II**(m=9–11) and **III**(m=9–11) was measured at 25 Hz of applied frequency and 5 V μm^{-1} of applied voltage in 5 μm LC cells, and is illustrated in figures 2, 3 and 4, respectively. The $\mathbf{P}_s$ values depend on temperature and exhibit maxima. The first increase in $\mathbf{P}_s$ at lower temperature below T_c can be attributed to decreased thermal motion at the lower temperature. After maximum $\mathbf{P}_s$ is reached, a gradual decrease in temperature resulted in a decreasing $\mathbf{P}_s$, which might be due to crystallization [18] or the occurrence of an SmC*–SmX* phase transition. The maximum $\mathbf{P}_s$ values for the three series of materials were in the range of 28–67.9 nC cm^2.

3.3. *Electro-optical response*

The electro-optical responses were obtained under crossed polarizers, with the axes of polarizers and analyser parallel and perpendicular, respectively, to the smectic layer normal in a 5 μm homogeneously aligned cell. The responses are critically dependent on the temperature and applied frequency. Figure 5 illustrates a typical example of the electro-optical

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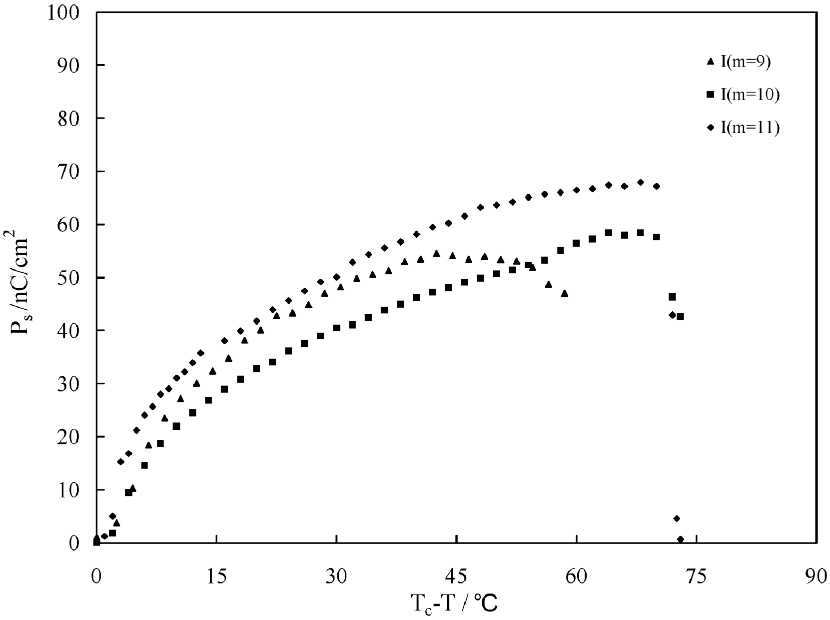

Figure 2. Spontaneous polarization plotted as a function of temperature for **I**(m=9,10,11). T_c is the temperature of the SmA*–SmC* transition.

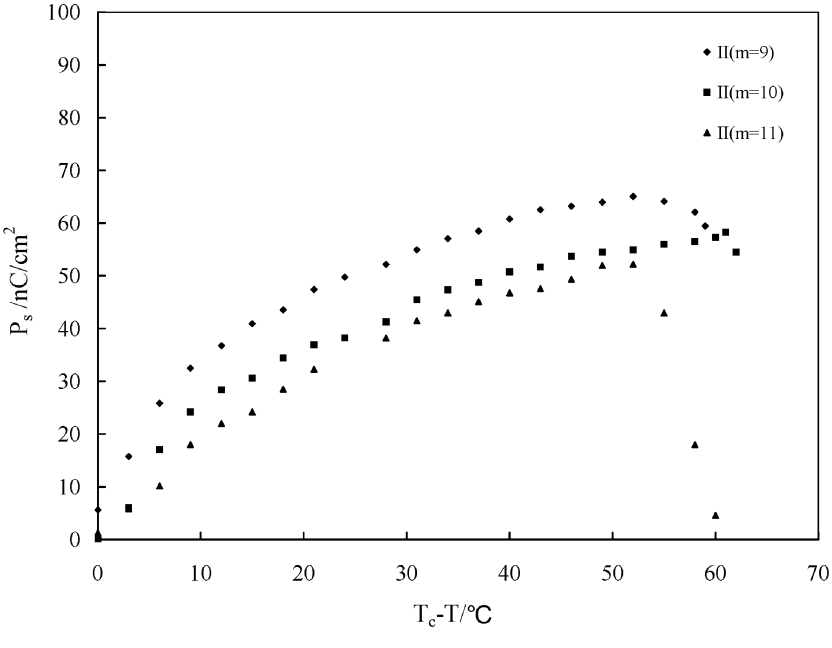

Figure 3. Spontaneous polarization plotted as a function of temperature for **II**(m=9,10,11). T_c is the temperature of the SmA*–SmC* transition.

response of transmittance vs. electric field on applying a field of triangular waveform, measured in the SmC* phase of material **III**(m=10) at 44°C and 1 Hz of applied frequency. A thresholdless, V-shaped switching curve was obtained in the ferroelectric phase of all the materials. The maximum transmittance value increases as the temperature decreases, as reported by Seomum *et al.* [19]. A slightly normal ferroelectric hysteresis was also observed; however, the hysteresis disappeared with variation of temperature and applied frequency, similar to our previous observations in other series of materials [20–22].

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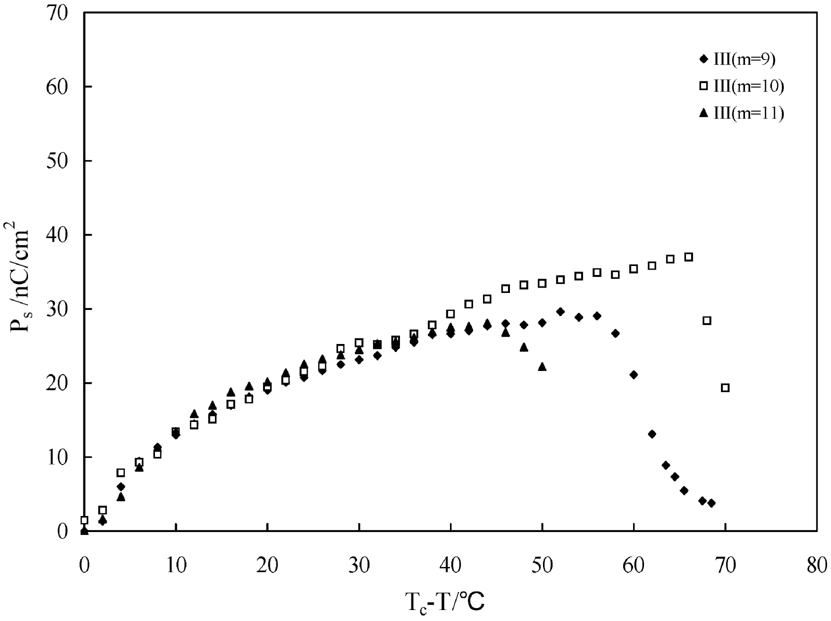

Figure 4. Spontaneous polarization plotted as a function of temperature for **III**(m=9,10,11). T_c is the temperature of the SmA*–SmC* transition.

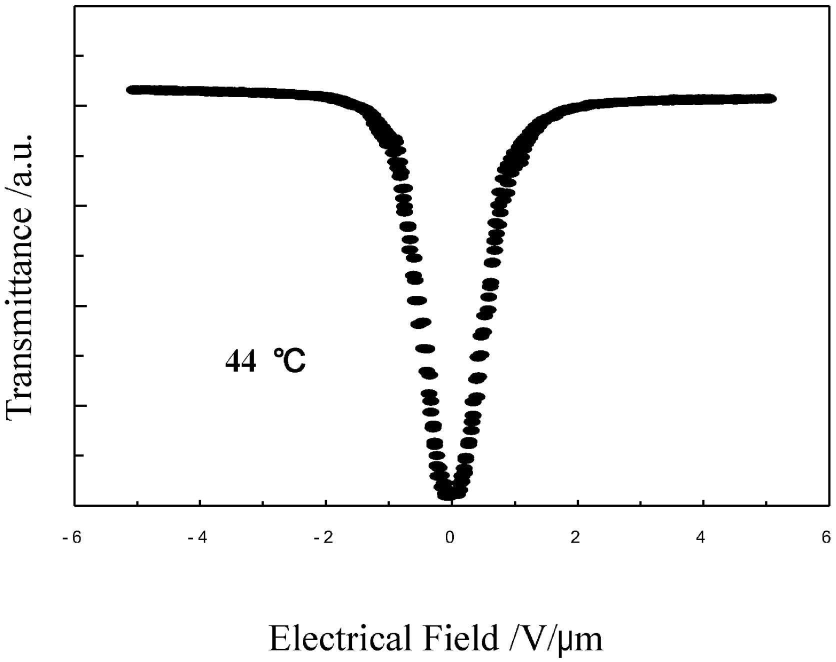

Figure 5. The electro-optical response of transmittance versus electric field obtained from the SmC* phase of material **III**(m=10) at 44°C and 1 Hz of applied frequency.

4. Conclusion

The chiral liquid crystal materials derived from (*S*)-lactic acid with alkoxyethanols displayed enantiotropic SmA* and SmC* phases with wide temperature ranges. The maximum $\mathbf{P}_s$ values, in general, decreased with increasing chain length *n*, and were in the range of 28–67.9 nC cm^{-2}. The electro-optical responses of all the chiral materials in the SmC* phase displayed characteristic V-shaped switching behaviour at appropriate temperature and frequency.

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