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Synthesis and mesomorphic properties of chiral liquid crystals derived from (*S*)-2-(6-hydroxy-2-naphthyl)propionic acid with a methyleneoxy linking group

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Three homologous series of chiral materials derived from (*S*)-2-(6-hydroxy-2-naphthyl)propionic acid with a methyleneoxy linking group were synthesized for the investigation of mesomorphic properties. All the materials displayed enantiotropic SmA* and SmC* phases. The spontaneous polarization (P_s) and optical tilt angles in the SmC* phase of the chiral materials were measured. The maximum spontaneous polarizations are in the range 12.3–19.1 nC cm⁻². No significant difference could be found in the P_s values with respect to the various alkyl chiral chain lengths, n . The maximum optical tilt angles are in the range 25–30°. The optical tilt angles decrease with the increase in alkyl chain length, n .

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 (2*S*)-2-(6-methoxy-2-naphthyl)propionic acid provides an excellent platform for the design and synthesis of chiral liquid crystals due to the presence of two functional groups: the carboxylic acid group and a hydroxyl group generated by the demethylation of the methoxy group. In general, the hydroxyl group is connected as part of the core in the molecule, and the carboxylic acid is connected to a variety of alcohols to form various esters acting as chiral tails in the molecule. The designed chiral liquid crystal materials show a very rich polymorphism. For example, those having chiral tails formed by straight alkyl chains display ferroelectric and antiferroelectric phases [1, 2]; chiral materials containing two stereocentres at the chiral tails display twist ground boundary phases [3, 4] and an antiferroelectric phase [5]; chiral materials having chiral swallow-tailed esters or amides display an antiferroelectric phase [6–9].

In order to explore further, we designed and synthesized three homologous series of chiral alkyl (*S*)-2-{6-[4-(4'-alkoxyphenyl)benzyloxy]-2-naphthyl} propionates, I(m,n), II(m,n) and III(m,n), with methyleneoxy as a linking group in the core of the molecules and a straight alkyl chain in the chiral tail. The general

structural formula for these three series of chiral materials is shown in figure 1.

The mesophases and transition temperatures of these materials were identified. Their electro-optical properties, such as spontaneous polarization (P_s) and optical tilt angle, were also measured. The P_s values and optical tilt angles were compared in relation to the chiral alkyl chain lengths, n .

2. Experimental

2.1. Characterization

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

The physical properties of the ferroelectric phase of the materials were measured in homogeneously aligned cells purchased from E. H. C. Co, Japan. The spontaneous polarization was measured by a triangular

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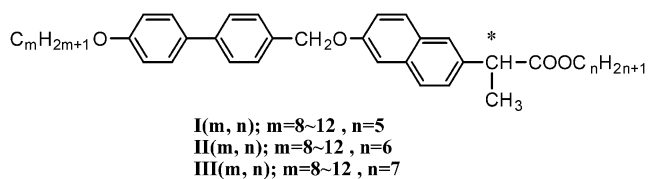


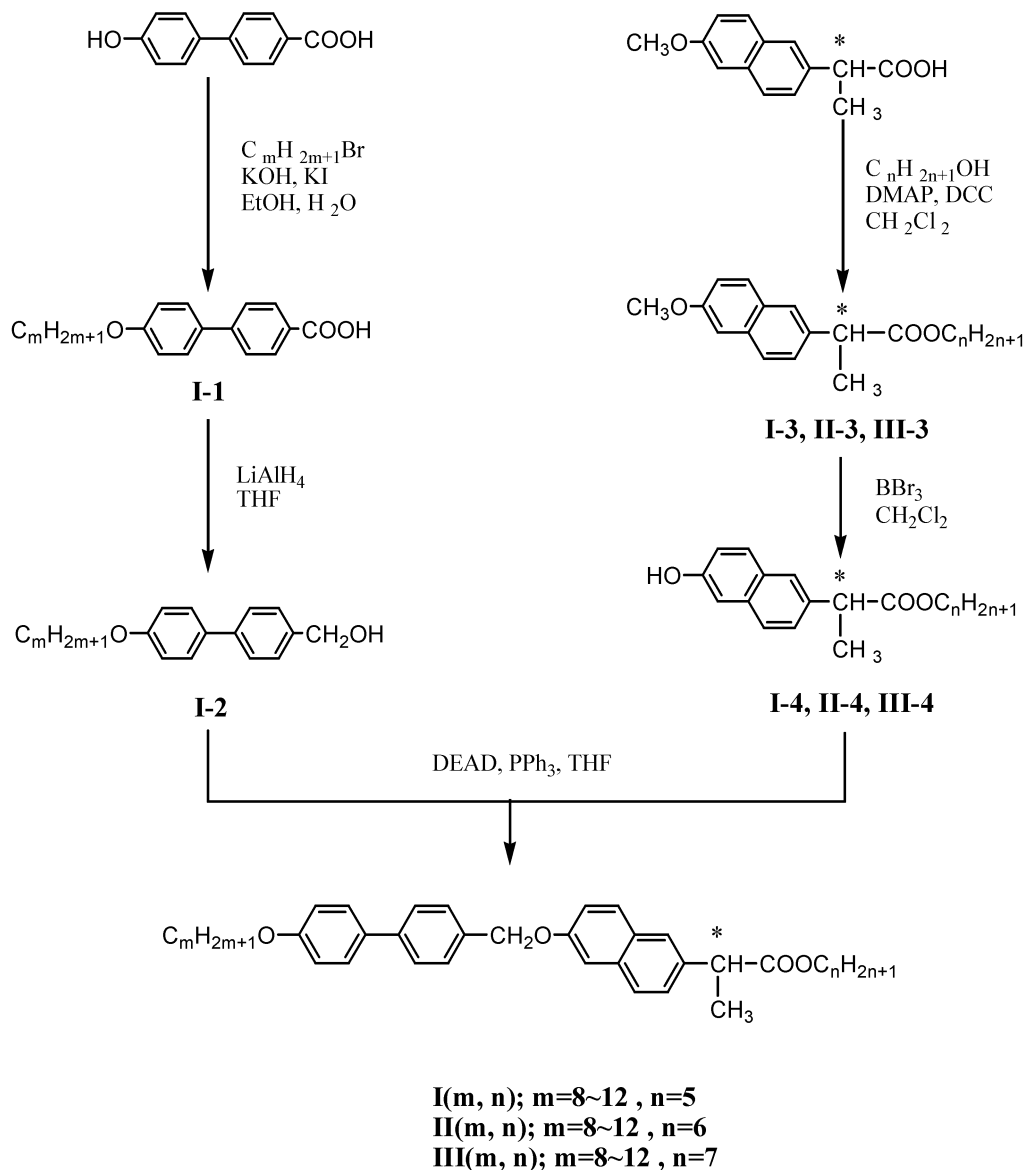
Figure 1. Structure of the chiral materials investigated.

wave method [10]. The optical tilt angle was measured using polarizing optical microscopy (POM) observations while changing the direction of an applied electric field. The optical tilt angle was measured with a cell placed in the hot stage, and the temperature dependence of the tilt angle could be determined.

2.2. Preparation of materials

The starting chiral material for the synthesis of the compounds was (*S*)-2-(6-methoxy-2-naphthyl)propionic acid, purchased from Tokyo Chemical Industry (TCI) Co. Ltd, Japan, with optical purity greater than 99%. Thin layer chromatography (TLC) 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 (CH₂Cl₂) and tetrahydrofuran (THF), were purified by treatment with CaH₂ and LiAlH₄, respectively, and distilled before use.

The synthetic processes for the target compounds were carried out as outlined in scheme 1. Detail



Scheme 1. Synthetic procedures for the target compounds I(m=8-12, n=5), II(m=8-12, n=6) and III(m=8-12, n=7).

procedures for the synthesis of the compounds are described as follows.

2.2.1. 4-(4'-Alkoxyphenyl)benzyl alcohols, I-2. 4-(4'-Alkoxyphenyl)benzoic acids (I-1, 14 mmol), LiAlH₄ (1.0 g, 28 mmol) and dry THF (250 ml) were heated together under reflux for 5 h; the mixture was then acidified by the addition of 5% HCl and filtered. The crude product was washed with cold water and recrystallized from absolute ethanol (C₂H₅OH); 72–75% yields of the materials, I-2, were obtained. A typical example of chemical shifts for I-2 (*m*=10) in ¹H NMR is: δ (CDCl₃, ppm) 0.87–0.90 (t, 3H, –CH₃), 1.26–1.83 (m, 16H, CH₃(CH₂)₈CH₂O–), 2.23 (s, 1H, OH), 3.98–4.01 (t, 2H, –CH₂OAr), 4.73–4.74 (d, 2H, –CH₂OH), 6.95–6.98 (m, 2H, ArH), 7.41–7.43 (d, 2H, ArH), 7.51–7.52 (d, 2H, ArH), 7.55–7.56 (d, 2H, ArH).

2.2.2. Alkyl (*S*)-2-(6-methoxy-2-naphthyl)propionates, I-3, II-3, III-3. The synthetic procedures for these materials were the same as those described by Taub *et al.* [11]. (*S*)-2-(6-Methoxy-2-naphthyl)propionic acid (5.0 g, 21.7 mmol), alkanols (21.7 mmol), *N,N'*-dicyclohexylcarbodiimide (DCC, 4.5 g, 21.7 mmol), 4-dimethylaminopyridine (DMAP, 0.3 g, 22 mmol) and dry dichloromethane (20 ml) were mixed and stirred at room temperature for three days. The precipitates were filtered off and the organic mixture washed with 5% acetic acid solution (3 × 50 ml), 5% saturated aqueous sodium hydrogen carbonate (3 × 50 ml) and distilled water (3 × 50 ml), then dried over MgSO₄ and concentrated in vacuum. The residue was purified by column chromatography over silica gel (70–230 mesh) using dichloromethane as eluent; 76–83% yields of the materials were obtained. A typical example of chemical shifts for I-3 in ¹H NMR is: δ (CDCl₃, ppm) 0.80–0.83 (t, 3H, –CH₂CH₃), 1.20–1.25 (m, 6H, –COOCH₂(CH₂)₃CH₃), 1.56–1.58 (d, 3H, –CHCH₃COO–), 3.93 (s, 3H, –OCH₃), 3.81–3.87 (m, 1H, –CH–), 4.04–4.08 (t, 2H, –OCH₂–), 7.07–7.09 (d, 1H, ArH), 7.12 (s, 1H, ArH), 7.38–7.40 (d, 1H, ArH), 7.63–7.64 (d, 1H, ArH), 7.66 (s, 1H, ArH), 7.70–7.72 (d, 1H, ArH).

2.2.3. Alkyl (*S*)-2-(6-hydroxy-2-naphthyl)propionates, I-4, II-4, III-4. The synthetic procedures for these materials were the same as those described by Fukuda *et al.* [12]. To the alkyl (*S*)-2-(6-methoxy-2-naphthyl)propionates (15.0 mmol) dissolved in dry CH₂Cl₂ (55 ml) was added boron tribromide (BBr₃, 2.8 ml) at –20°C. The mixture was stirred at –20°C for 5 min, and the solution slowly brought to 0°C and further stirred for about 50 min. The reaction mixture

was diluted with CH₂Cl₂ (110 ml), then poured into a mixture of saturated NH₄Cl (110 ml) and crushed ice (110 g). The organic layer was separated and washed with brine-ice, dried over MgSO₄, and the solvents were removed under vacuum. The residue was purified by column chromatography over silica gel (70–230 mesh) using CH₂Cl₂ as eluent; around 75–87% yields were obtained. A typical example of chemical shifts of I-4 in ¹H NMR is: δ (CDCl₃, ppm) 0.80–0.83 (t, 3H, –CH₂CH₃), 1.20–1.25 (m, 6H, –COOCH₂(CH₂)₃CH₃), 1.56–1.58 (d, 3H, –CHCH₃COO–), 3.81–3.86 (q, 1H, –CH–), 4.05–4.08 (t, 2H, –OCH₂–), 4.94 (s, 1H, –OH), 7.07–7.09 (d, 1H, ArH), 7.12 (s, 1H, ArH), 7.38–7.40 (d, 1H, ArH), 7.63–7.64 (d, 1H, ArH), 7.66 (s, 1H, ArH), 7.70–7.72 (d, 1H, ArH).

2.2.4. Alkyl (*S*)-2-{6-[4-(4'-alkoxyphenyl)benzyloxy]-2-naphthyl}propionates, I(*m,n*), II(*m,n*), III(*m,n*). A solution of compound I-2 (1.33 mmol) and diethyl azodicarboxylate (DEAD, 0.2 g, 1.33 mmol) in about 10 ml of anhydrous THF was added slowly to a solution of triphenylphosphine (Ph₃P, 0.3 g, 1.33 mmol) and alkyl (*S*)-2-(6-hydroxy-2-naphthyl)propionates (I-4, II-4 or III-4) (1.33 mmol) in 10 ml of anhydrous THF at room temperature while stirring. The reaction soon started, and after the mixture had been kept standing overnight at room temperature the solvent was removed under vacuum. The products were isolated by column chromatography over silica gel (70–230 mesh) using dichloromethane/hexane (V/V=7/5) as eluent and then recrystallized from absolute ethanol; 53–57% yields of the final materials were obtained. A typical example of chemical shifts for I(12, 5) in ¹H NMR is: δ (CDCl₃, ppm) 0.80–0.83 (t, 3H, CH₃(CH₂)₁₀CH₂OAr–), 0.87–0.90 (t, 2H, –COOCH₂–), 1.21–1.55 (m, 26H, CH₃(CH₂)₁₀CH₂O–, –COOCH₂(CH₂)₃CH₃), 1.56–1.57 (d, 3H, –CH(CH₃)COO–), 3.82–3.87 (q, 1H, –CH(CH₃)COO–), 3.98–4.01 (t, 2H, CH₃(CH₂)₁₀CH₂O–), 4.05–4.07 (t, 2H, –COOCH₂–), 5.20 (s, 2H, –ArCH₂OAr–), 6.96–6.97 (d, 2H, ArH), 7.22–7.25 (m, 2H, ArH), 7.39–7.41 (q, 1H, ArH), 7.51–7.52 (d, 4H, ArH), 7.57–7.59 (d, 2H, ArH), 7.67–7.74 (m, 3H, ArH).

All the target materials were analysed for purity by elemental analysis and the data are listed in table 1. Satisfactory results were obtained, within 1% of theoretical composition figures.

3. Results and discussion

3.1. Mesomorphic properties

The mesomorphic phases were first determined by texture observations. The SmA* phase was characterized

Table 1. Elemental analysis results for the compounds I($m=8-12$, $n=5$), II($m=8-12$, $n=6$) and III($m=8-12$, $n=7$).

Compound	Theoretical		Experimental	
	C/%	H/%	C/%	H/%
I(8, 5)	80.65	8.33	80.63	8.29
I(9, 5)	80.77	8.47	80.79	8.42
I(10, 5)	80.88	8.61	80.85	8.58
I(11, 5)	80.99	8.74	80.77	8.68
I(12, 5)	81.09	8.86	80.94	8.79
II(8, 6)	80.77	8.47	80.67	8.45
II(9, 6)	80.88	8.61	80.89	8.62
II(10, 6)	80.99	8.74	80.95	8.72
II(11, 6)	81.09	8.86	81.04	8.87
II(12, 6)	81.19	8.98	80.47	8.92
III(8, 7)	80.88	8.61	80.82	8.57
III(9, 7)	80.99	8.74	80.94	8.69
III(10, 7)	81.09	8.86	80.90	8.80
III(11, 7)	81.19	8.98	81.04	8.94
III(12, 7)	81.28	9.09	81.19	9.05

by the formation of a focal-conic texture and the SmC* phase by the formation of a striated focal-conic texture. The SmC* phase was further characterized by its electrical switching response in 5 μm homogeneously aligned cells under a triangular wave voltage with field frequency 20 Hz and amplitude 8 Vp-p. The switching currents exhibit one current peak in a range of temperature similar to that reported for the SmC* phase [12]. All the compounds displayed enantiotropic SmA* and SmC* phases. The enthalpies for the phase transitions were measured by DSC spectroscopy. Transition temperatures and corresponding enthalpies of transition are shown in table 2.

Plots of phase transition temperature versus elongated alkyl chain length, m , for the three series I(m,n), II(m,n), and III(m,n) are shown in figures 2–4. The results for series I(m,n) and II(m,n) show that the thermal stabilities of the SmA* phase are decreased, whereas those of the SmC* phase are increased with the increase of achiral alkyl chain length, m . In the series III(m,n), no general correlation can be found between phase stability and alkyl chain lengths, m and n .

Table 2. Transition temperatures ($^{\circ}\text{C}$) and associated enthalpy changes (kJ mol^{-1} , in square brackets) for I($m=8-12$, $n=5$), II($m=8-12$, $n=6$) and III($m=8-12$, $n=7$) (Cr=crystal; m.p.=melting point taken from DSC, heating at $5^{\circ}\text{C min}^{-1}$; SmA=smectic A; SmC=smectic C; I=isotropic).

Compound	I	SmA*	SmC*	Cr	m.p.			
I(8, 5)	•	120.83 [5.13]	•	109.97 [0.66]	•	90.07 [16.31]	•	101.88 [16.42]
I(9, 5)	•	117.84 [6.80]	•	111.77 [0.27]	•	85.81 [20.55]	•	105.90 [34.97]
I(10, 5)	•	117.87 [5.56]	•	113.13 [0.73]	•	83.94 [18.23]	•	97.93 [15.09]
I(11, 5)	•	116.52 [5.34]	•	113.37 [0.59]	•	80.64 [16.94]	•	98.83 [17.00]
I(12, 5)	•	115.30 [6.53]	•	112.28 [0.10]	•	78.02 [14.62]	•	94.75 [16.97]
II(8, 6)	•	117.88 [1.09]	•	103.35 [0.05]	•	80.05 [3.48]	•	102.22 [16.29]
II(9, 6)	•	113.46 [4.00]	•	105.48 [0.34]	•	78.72 [18.13]	•	95.10 [14.87]
II(10, 6)	•	113.5 [3.31]	•	106.90 [0.07]	•	82.59 [12.00]	•	94.69 [10.76]
II(11, 6)	•	114.71 [6.34]	•	112.38 [1.52]	•	87.50 [18.58]	•	97.52 [17.11]
II(12, 6)	•	114.05 [6.92]	•	111.97 [0.14]	•	78.86 [21.33]	•	96.85 [21.47]
III(8, 7)	•	116.09 [7.60]	•	109.83 [0.23]	•	81.60 [22.13]	•	97.08 [27.45]
III(9, 7)	•	114.61 [6.99]	•	101.80 [0.06]	•	81.61 [19.60]	•	94.14 [16.18]
III(10, 7)	•	114.29 [6.06]	•	104.52 [0.01]	•	82.26 [15.98]	•	91.87 [14.29]
III(11, 7)	•	113.50 [5.09]	•	106.90 [0.16]	•	75.45 [20.29]	•	93.02 [20.26]
III(12, 7)	•	111.12 [1.79]	•	105.60 [0.20]	•	82.89 [6.62]	•	92.96 [24.29]

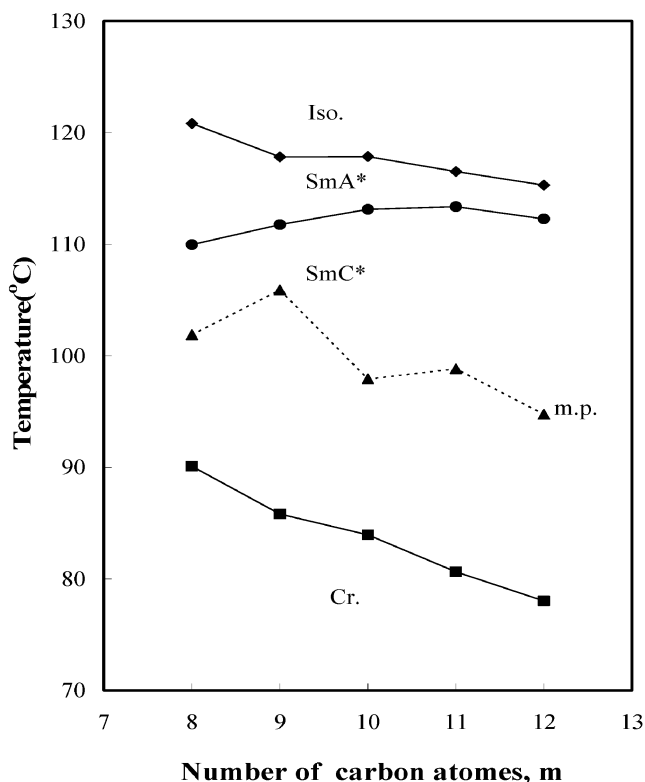


Figure 2. Phase diagram for compounds I ($m=8-12$, $n=5$) on cooling.

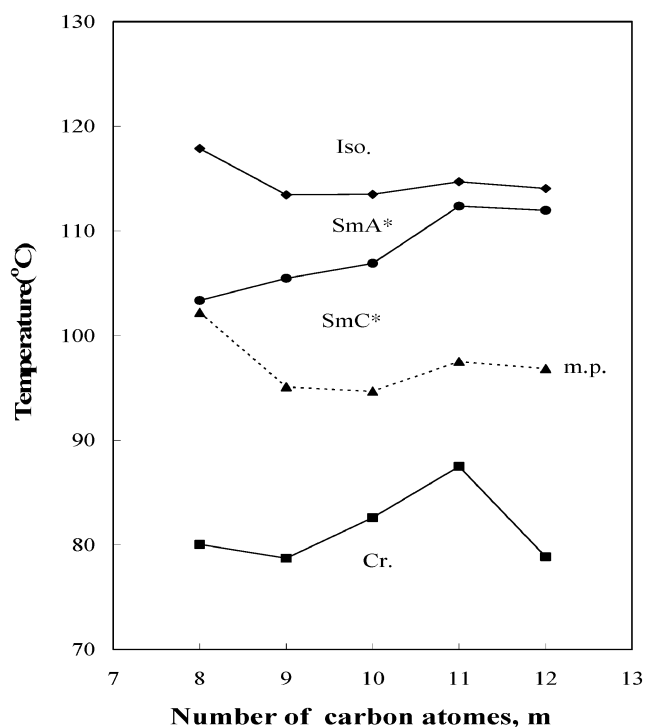


Figure 3. Phase diagram for compounds II ($m=8-12$, $n=6$) on cooling.

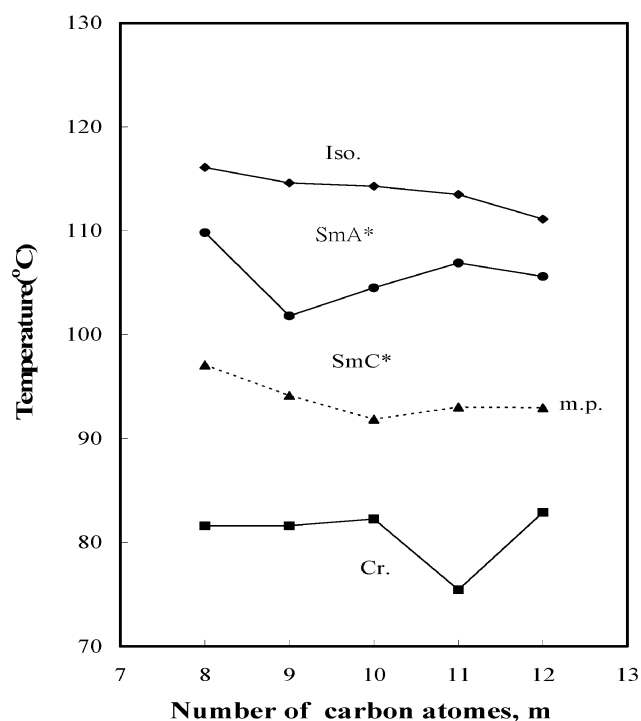


Figure 4. Phase diagram for compounds III ($m=8-12$, $n=7$) on cooling.

3.2. Spontaneous polarization

Values of spontaneous polarization (P_s) in the SmC* phase of the chiral materials in the $5\ \mu\text{m}$ parallel aligned cells were measured by a triangular wave method [10] using a frequency of 20 Hz and an amplitude of 5 V [13]. Representative results obtained for materials I(10, 5), II(10, 6) and III(10, 7) are shown in figure 5 for

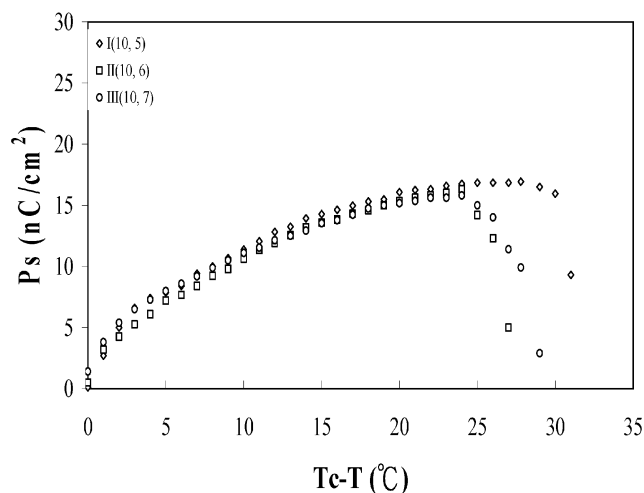


Figure 5. Spontaneous polarization plotted as a function of temperature for I(10, 5), II(10, 6) and III(10, 7). T_c is the temperature of the SmA*–SmC* transition.

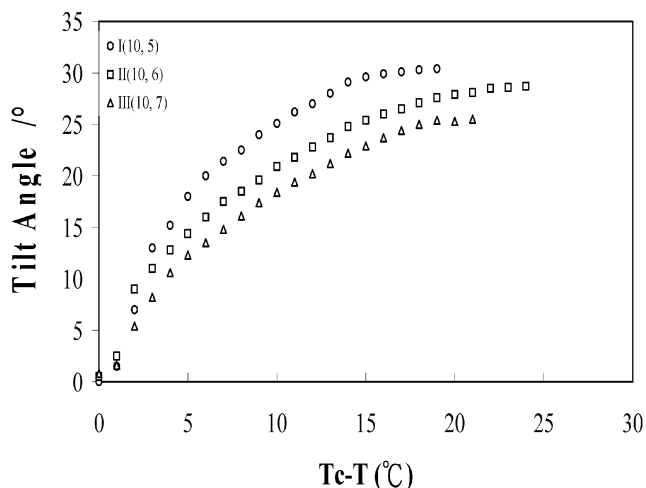


Figure 6. Temperature dependences versus optical tilt angle for compounds I(10, 5), II(10, 6) and III(10, 7).

comparison. The first increase in P_s value with lowering temperature below T_c can be attributed to decrease thermal motion. After maximum P_s is reached, further gradual decrease in temperature results in a decreasing P_s , which might be due to crystallization [14]. The maximum P_s values are in the range 15.8–16.5 nC cm⁻². There appears to be no significant difference in the P_s values with respect to the various alkyl chain lengths, n .

3.3. Optical tilt angle

The chiral liquid crystal materials were introduced into 3 μ m thick cells composed of two glass plates coated with ITO electrodes and aligning agent for the measurement of optical tilt angles in the ferroelectric SmC* phase. The sample was heated to an isotropic liquid and allowed to cool into the ferroelectric phase. Representative temperature dependences of the optical tilt angles obtained from chiral materials I(10, 5), II(10, 6) and III(10, 7) are illustrated in figure 6. The results show that the optical tilt angle increases with

decreasing temperature in the SmC* phase. The maximum tilt angle values were found to be in the range 25–30°. A decreasing tendency of the tilt angle with increasing chiral alkyl chain length, n , can be clearly seen.

4. Conclusion

Chiral liquid crystal materials derived from (*S*)-2-(6-hydroxy-2-naphthyl)propionic acid with a methyleneoxy linking group have been demonstrated to possess enantiotropic SmA* and SmC* phases. The magnitude of spontaneous polarization shows no significant difference with increase in chiral alkyl chain, n , but the apparent tilt angles decrease with increasing n . These materials have a lower spontaneous polarization than those with a carboxylate linking group [1], presumably because the methyleneoxy group has a lower transverse dipole moment than the carboxylate group.

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