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TGB phases in chiral swallow-tailed liquid crystals with a methyleneoxy linking group

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A homologous series of chiral swallow-tailed materials with a methyleneoxy linking group, 1-ethylpropyl (*S*)-2-[6-[4-(4-alkoxyphenyl)benzyloxy]-2-naphthyl]propionates, *Em*PNP ($m=8-12$), has been synthesized for investigation. Polarizing optical microscopy observations demonstrated that the materials exhibit a N^* phase and two frustrated phases: the twist grain boundary smectic A^* (TGB_A^*) and smectic C^* (TGB_C^*) phases. All of the materials exhibit a wide TGB phase temperature range. The spontaneous polarization and apparent tilt angle of the TGB_C^* phase for compounds in surface stabilized geometry in $5\ \mu\text{m}$ homogeneously aligned cells were also measured and reported.

1. Introduction

In 1972, de Gennes [1] predicted the existence of a twisted smectic phase. A possible structure for this new phase was proposed by Renn and Lubensky [2] in 1988 and called the twist grain boundary (TGB) phase. Experimental detection of a TGB phase composed of smectic A layers (TGB_A^*) was reported by Goodby *et al.* in 1989 [3, 4]; a TGB_C phase was reported by Nguyen *et al.* in 1992 [5] and a TGB_C^* phase by Shao *et al.* in 1993 [6]. Recently, many new phases, such as the melted grain boundary (MGB) phase [7, 8], undulated twist grain boundary ($UTGB_C^*$) phase [9] and antiferroelectric TGB phase [10], have been observed.

The TGB phase is a frustrated structure exhibiting a cholesteric director field and a smectic layer structure. It is not easy to acquire stable equilibrium. Many experimental systems have been studied in order to establish the influence of molecular structure on the thermal stability of the TGB phases. Results indicate that the thermal stability is influenced by the linking group between the two phenyl rings near the chiral centre, such as $-N=N-$, $-CH=CH-$, $-C\equiv C-$ or a single bond [11]. Moreover our earlier investigations on naphthalene-containing chiral liquid crystals with two chiral centres [12] and swallow-tail groups [13–15] established that these compounds exhibited TGB phases, indicating the influence of the chiral component on the formation of TGB phases.

For a better understanding, we changed the linking group on the main core structure of the molecule from the carboxylate group [14, 15] to a methyleneoxy group and investigated the resulting mesomorphic and physical properties.

2. Experimental

2.1. Characterization of materials

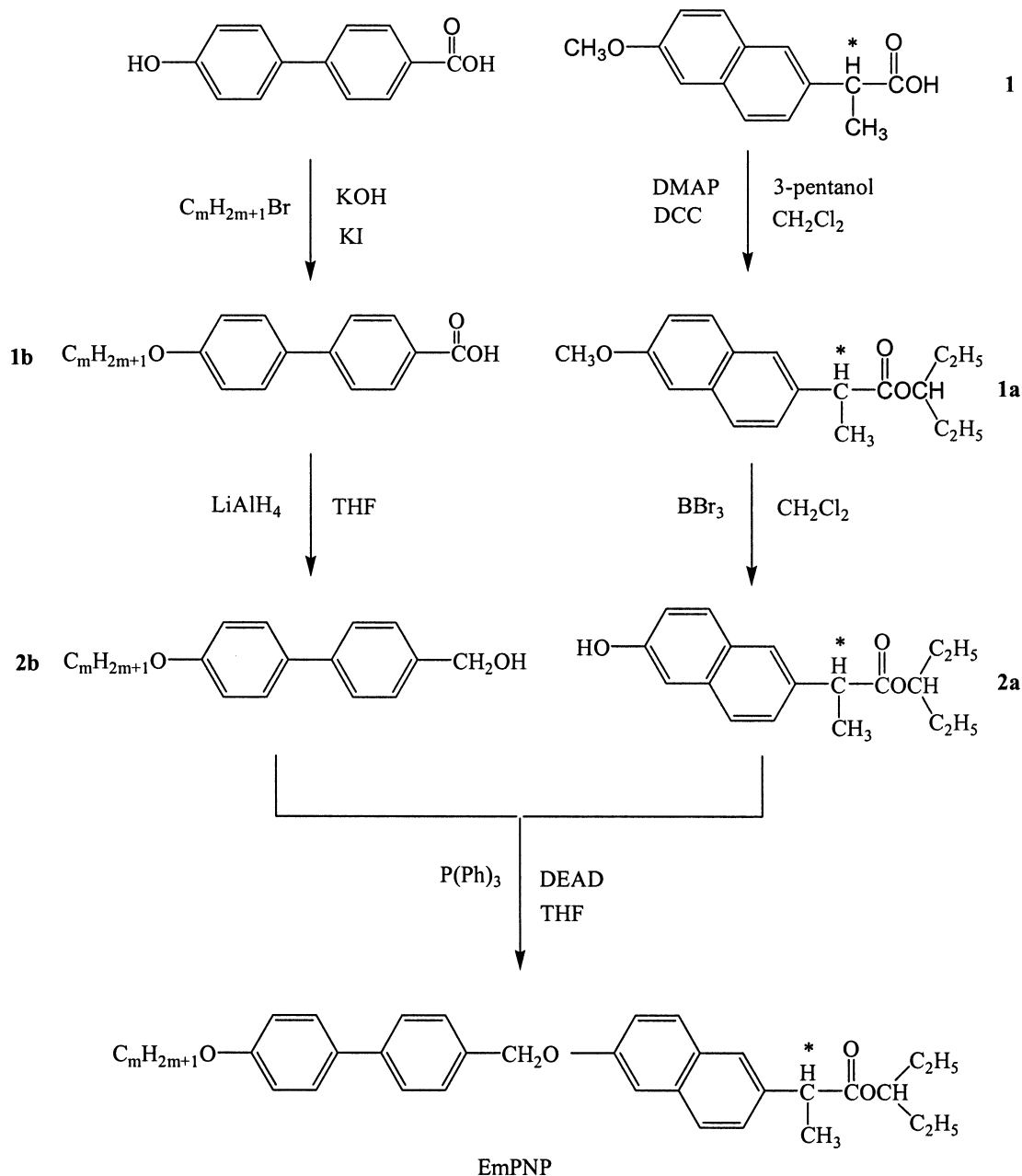
The chemical structures of the target materials were identified by proton nuclear magnetic resonance (^1H NMR) spectroscopy using a Bruker Avance 500 NMR spectrometer. Purity was established by elemental analysis using a Perkin-Elmer 2400 instrument. Transition temperatures and associated enthalpies were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC 7; heating and cooling rates were $5^\circ\text{C}\ \text{min}^{-1}$. Since the $TGB_A^*-TGB_C^*$ transition peaks were too small to observe by calorimetry, the transition temperature was detected by the switching current behaviour. Mesophases were identified by the observation of textures using a Nikon Microphot-FXA optical microscope with a Mettler FP82-HT hot stage. The switching current behaviour and spontaneous polarization were studied using a surface-stabilized ferroelectric liquid crystal (SSFLC) configuration and the triangular wave method [16]. Homogeneously aligned cells with rubbed polyimide were purchased from E.H.C. Co., Japan. The optical tilt angle was measured by polarizing optical microscopy (POM) while varying the direction of an applied electric field.

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2.2. Preparation of materials

The starting chiral material for the synthesis of compounds *Em*PNP was (*S*)-2-(6-methoxy-2'-naphthyl)propionic acid, purchased from Tokyo Chemical Industry (TCI) Co. Ltd, Japan, with optical purity greater than 99% enantiomeric excess. The synthetic procedures were similar for all the target compounds, and are outlined in the scheme. The acid **1** was esterified with 1-ethylpropanol in the presence of DCC and

DMAP to produce the esters 1-ethylpropyl (*S*)-2-(6-methoxy-2'-naphthyl)propionate **1a**. The methoxy group of this ester was demethylated by treatment with BBr_3 . The resulting hydroxy group of the alkyl (*S*)-2-(6-hydroxy-2'-naphthyl) propionate **2a** was subsequently reacted with a variety of 4-(4-alkoxyphenyl)benzyl alcohols ($m=8-12$) **2b**, using diethyl azodicarboxylate (DEAD) and triphenyl phosphine (Ph_3P), to produce the target materials *Em*PNP. Detailed procedures for these syntheses of these compounds are described below.



Scheme. Synthetic procedures for the target compounds *Em*PNP ($m=8-12$).

2.2.1. 4-(4-Alkoxyphenyl)benzoic acids, 1b. A mixture of 4'-hydroxybiphenyl-4-carboxylic acid (50 mmol) and ethanol (200 ml) was heated under reflux until clear, then added to a solution of potassium hydroxide (100 mmol) and potassium iodide (KI, 8 mmol) in water (50 ml). This mixture was heated under reflux, 1-bromodecane (150 mmol) added, and the reflux continued for a further 18 h. Aqueous potassium hydroxide (100 ml, 10%) was added, and after a further 2 h reflux the mixture was acidified with aqueous HCl and filtered. The crude product was washed with cold water and recrystallized from glacial acetic acid and absolute ethanol; a 60–70% yield of compound **1b** was obtained.

2.2.2. 4-(4-Alkoxyphenyl)benzyl alcohols, 2b. Lithium aluminum hydride (LiAlH_4 , 28 mmol) was slowly added to a mixture of compound **1a** and dry tetrahydrofuran (THF, 100 ml) at room temperature. The mixture was heated under reflux for 8 h, then cooled to 0°C , and water (100 ml) added. The mixture was acidified with aqueous HCl, filtered, and the crude product washed with cold water and recrystallized from ethanol; approximately 80% yields of compounds **2b** were obtained. Typical analytical data for: 4-(4-decyloxyphenyl)benzyl alcohol: ^1H NMR (CDCl_3); δ (ppm): 0.9 (t, 3H, CH_2CH_3), 1.6–1.7 (t, 1H, OH), 1.8 (m, 2H, CH_2CH_3), 4.0 (t, 2H, RCH_2O), 4.7–4.8 (d, 2H, ArCH_2OH), 6.9–7.7 (m, 8H, ArH).

2.2.3. 1-Ethylpropyl (S)-2-(6-methoxy-2'-naphthyl) propionate, 1a. The acid **1** (25 mmol) and 3-pentanol (27.5 mmol) were dissolved in dry dichloromethane (100 ml). After the addition of DCC (27.5 mmol) and DMAP (2.5 mmol) the solution was stirred at room temperature for 5 days. The precipitate was filtered off and washed with dichloromethane. The filtrate was successively washed with 5% acetic acid, 5% aqueous sodium hydroxide and water, and then dried over anhydrous magnesium sulphate and concentrated under vacuum. The residue was purified by column chromatography on silica gel (70–230 mesh) using dichloromethane as eluent. The ester isolated, in 80% yield, was identified by its ^1H NMR spectrum and used directly for the ensuing reaction without further purification. ^1H NMR (CDCl_3); δ (ppm): 0.6–1.6 (m, 10H, RCH_2CH_3), 1.6 (d, 3H, CHCH_3), 3.8–3.9 (q, 1H, ArCHCOO), 3.9 (s, 3H, CH_3O), 4.8–4.9 (m, 1H, COOCH), 7.1–7.7 (m, 6H, ArH).

2.2.4. 1-Ethylpropyl (S)-2-(6-hydroxy-2'-naphthyl) propionate, 2a. The ester **1a** (22.5 mmol) dissolved in dry dichloromethane (82.4 ml) was mixed with

tribromoborane (4.12 ml) at -20°C ; the mixture was stirred at -20°C for 5 min, and at 0°C for 50 min. After diluting with dichloromethane (164.8 ml), the solution was poured into a mixture of saturated aqueous ammonium chloride (82.4 ml) and ice chips. The organic layer was separated and washed with brine ice, dried over anhydrous sodium sulphate, and concentrated under vacuum. The residue was purified by silica gel (70–230 mesh) column chromatography; the alcohol **1a** was collected in 40% yield. ^1H NMR (CDCl_3); δ (ppm): 0.6–1.7 (m, 10H, RCH_2CH_3), 1.6 (d, 3H, CHCH_3), 3.8–3.9 (q, 1H, ArCHCOO), 4.8–4.9 (m, 1H, COOCH), 5.7 (s, 1H, OH), 7.0–7.7 (m, 6H, ArH).

2.2.5. 1-Ethylpropyl (S)-2-{6-[4-(4-alkoxyphenyl)benzyloxy]-2'-naphthyl}propionates, EmPNP. A solution of diethyl azodicarboxylate (DEAD, 1.5 mmol) and the compound **2b** (1.5 mmol) in anhydrous THF (6 ml) was added dropwise to a solution of triphenyl phosphine (Ph_3P , 2.5 mmol) and the compound **2a** (1.5 mmol) in 8 ml anhydrous THF at room temperature with vigorous stirring. The mixture was stirred at room temperature for 24 h, and the THF removed under vacuum. After work-up, the products were isolated by column chromatography; yields of 20–30% of the final compounds were obtained. A typical example of analytical results obtained for E10PNP is given as follows. Elemental analysis for $\text{C}_{41}\text{H}_{52}\text{O}_4$: calculated, C 80.88, H 8.61; found, C 80.71, H 8.64%. ^1H NMR (CDCl_3); δ (ppm): 0.7 (t, 3H, CH_2CH_3), 0.8–1.0 (m, 6H, $\text{CH}(\text{CH}_2\text{CH}_3)_2$), 1.8–1.9 (m, 2H, $\text{RCH}_2\text{CH}_2\text{O}$), 3.8–3.9 (q, 1H, ArCHCOO), 4.0 (t, 2H, $\text{CH}_2\text{CH}_2\text{O}$), 4.7–4.9 (m, 1H, COOCH), 5.2–5.3 (s, 2H, ArCH_2O), 6.9–7.8 (m, 14H, ArH). ^1H NMR data and elemental analysis for the target materials are in accord with expected results.

3. Results and discussion

Transition temperatures and enthalpies for the materials under study were determined principally by DSC at a scanning rate of 5°C min^{-1} . Mesophases were identified by microscopic texture observation using POM. The observation of a characteristic fan-like texture indicated the existence of the chiral nematic (N^*) phase. The TGB_A^* phase was identified by the typical spiral filament texture [3, 17–19], as shown in figure 1 obtained from compound E12PNP at 97.6°C . Because in some areas in figure 1, the optic axis is oriented along the direction of light propagation, these areas appear black. The TGB_A^* phase can also be identified by the Grandjean-like steps texture [20] in a homogeneously aligned cell. As the temperature was

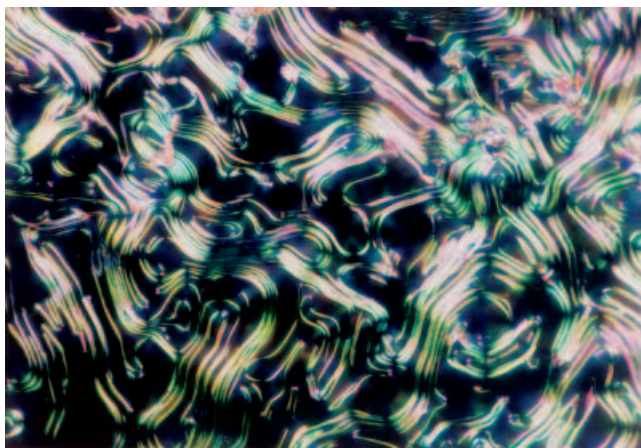


Figure 1. Coloured spiral filament texture of the TGB_A^* phase obtained from compound E12PNP under POM at 97.6°C (magnification $\times 500$).

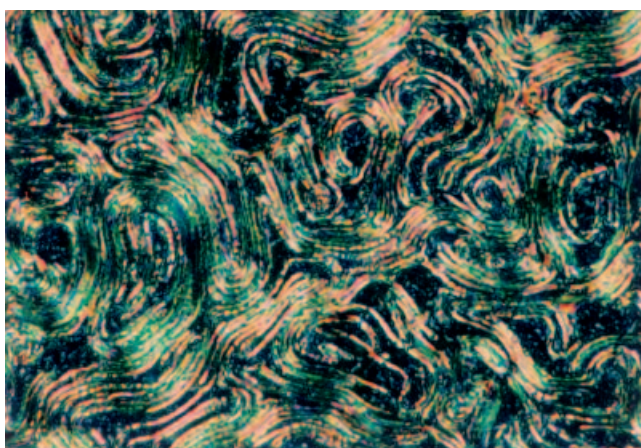


Figure 2. Coloured spiral filament texture with striated lines of the TGB_C^* phase obtained from compound E12PNP at 79.9°C (magnification $\times 400$).

decreased, the sample underwent a transition from the TGB_A^* to TGB_C^* phase, and the filament texture gradually displayed declination lines. This spiral filament texture with striated disclination lines indicated the existence of the TGB_C^* phase [6, 12, 19, 21, 22] as shown in figure 2 obtained from compound E12PNP at 79.9°C .

Mesophases and phase transition temperatures for the compounds $EmPNP$ are listed in table 1. The enthalpies of the $TGB_A^*-TGB_C^*$ transitions were too small to be detected by DSC, the temperatures of these transitions were therefore measured by the switching current technique [16]. A phase diagram plot is presented in figure 3. In this series, all of the compounds show the TGB phases with broad temperature ranges. With increasing chain length m , the temperature range of the TGB_C^* phase became wider, whereas those of the N^* and TGB_A^* phases exhibited no significant change.

Our previous results on the structurally similar compounds with a carboxylate linking group showed a phase sequence $I-BP_{II}-N^*-TGB_A^*-SmA^*-SmC_A^*-Cr$ [14, 15] where the TGB_A^* phase existed in a narrow temperature range. The present results show that the methyleneoxy linking group dramatically changes the phase sequence to $I-N^*-TGB_A^*-TGB_C^*-Cr$ with a broad temperature range of the TGB phases. This clearly suggests that reducing the polarity of the linking group from carboxylate to methyleneoxy is beneficial to the formation of the TGB phases.

The switching current behaviour of compound E12PNP in the TGB_C^* phase was investigated in a $5\mu\text{m}$ thick homogeneous cell and measured at a frequency of 5 Hz. The result of the switching current behaviour for compound E12PNP is presented in figure 4. All the compounds displayed single and sharp peaks, a typical characteristic of ferroelectric switching.

Table 1. Transition temperature T ($^\circ\text{C}$) and associated enthalpy ΔH (J g^{-1}) (in italics) data for the compounds $EmPNP$ ($m=8-12$) at 5°C min^{-1} scanning rate.

m	I	N^*	TGB_A^*	TGB_C^*	Cr	m.p.
8	• 121.4 <i>4.3</i>	• 116.5 <i>a</i>	• 101.2 ^c <i>b</i>	• 95.2 <i>51.4</i>	• 121.9 <i>50.4</i>	
9	• 118.3 <i>7.3</i>	• 114.5 <i>a</i>	• 100.1 ^c <i>b</i>	• 94.1 <i>58</i>	• 125.8 <i>78.7</i>	
10	• 114.2 <i>4.94</i>	• 110.3 <i>a</i>	• 100.8 ^c <i>b</i>	• 81.3 <i>38.7</i>	• 113.5 <i>48.9</i>	
11	• 110.9 <i>6.2</i>	• 107.4 <i>a</i>	• 93.8 ^c <i>b</i>	• 72.7 <i>40.5</i>	• 105.7 <i>40.3</i>	
12	• 111.2 <i>3.79</i>	• 109.1 <i>a</i>	• 96.2 ^c <i>b</i>	• 69.2 <i>18.7</i>	• 85.7 <i>15.2</i>	

^aThe enthalpy of the $N^*-TGB_A^*$ transition was added to that of the $I-N^*$ transition. ^bThe enthalpy was too small to be measured. ^cTransition temperature determined by switching current behaviour at cooling rate 5°C min^{-1} .

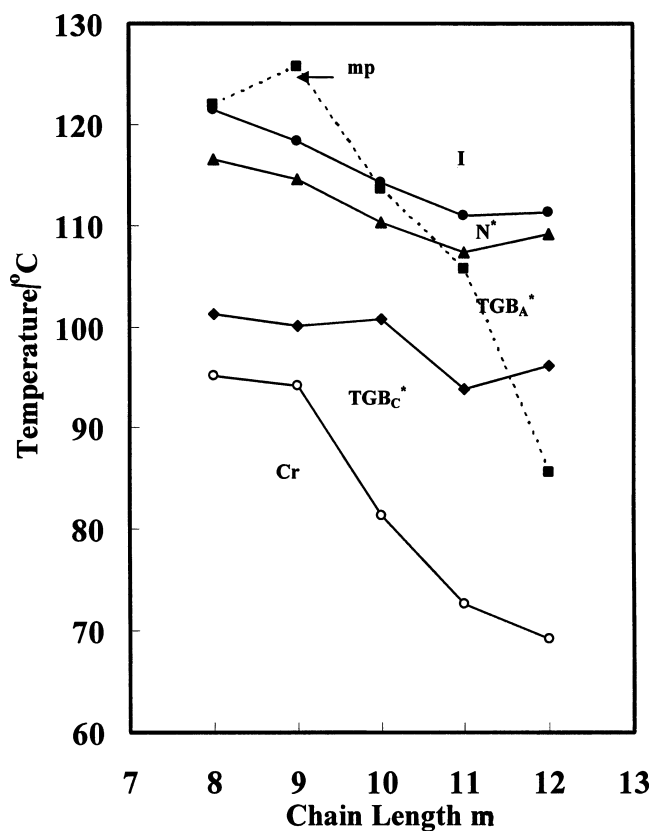


Figure 3. Plot of transition temperature as a function of chain length m for compounds $EmPNP$ ($m=8-12$).

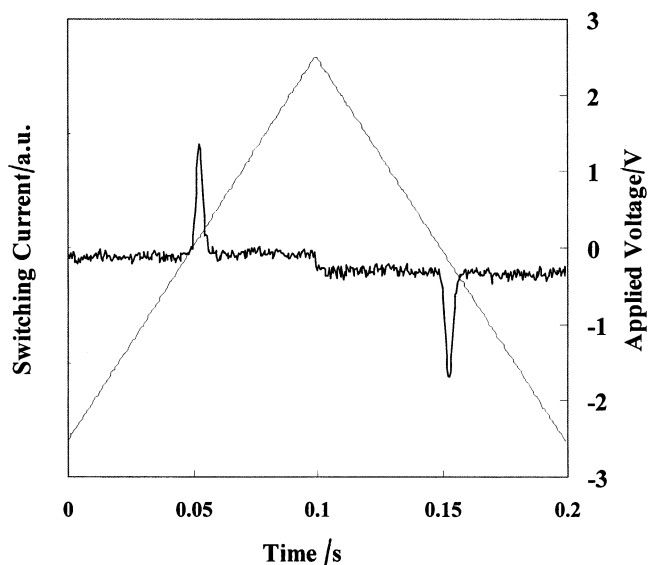


Figure 4. Switching behaviour of compound E12PNP in the TGB_C^* phase in a $5\mu\text{m}$ thick homogeneously aligned cell measured at 80°C and a frequency of 5 Hz.

The spontaneous polarization of compounds $EmPNP$ was measured as a function of temperature on cooling in $5\mu\text{m}$ thick homogeneous cells and measured at a frequency of 20 Hz. The results for compounds $EmPNP$ ($m=10-12$) are shown in figure 5. It can be seen that the spontaneous polarization increases with decreasing temperature. The maximum P_s value for compound $EmPNP$ is approximately 21 nC cm^{-2} .

The tilt angle was measured by POM. The compounds were filled into $5\mu\text{m}$ thick homogeneous cells and an electric field applied to obtain a single domain. Figure 6 shows the optical tilt angle as a function of temperature in the SSFLC geometry of the TGB_C^* phase for compounds $EmPNP$ ($m=10, 11$). The optical tilt angle of the TGB_C^* phase increased with decreasing temperature, reaching a value of about 30° .

4. Conclusion

Our results demonstrate that the chiral swallow-tailed compounds derived from (*S*)-2-(6-hydroxy-2'-naphthyl)propionic acid with a methyleneoxy linking group favour the formation of TGB phases. As compared with the structurally similar compounds containing a carboxylate linking group, it is clearly shown that by reducing the polarity of the linking group on changing to a methyleneoxy group, the TGB phase is stabilized over a wide temperature range. This suggests that the enhanced stability of the TGB phases results

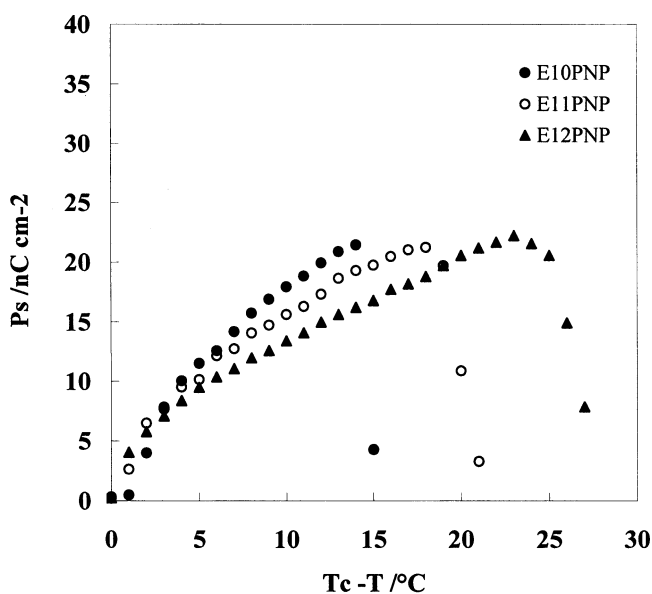


Figure 5. Temperature dependence of the spontaneous polarization for $EmPNP$ ($m=10-12$) in $5\mu\text{m}$ thick homogeneously aligned cells measured at a cooling rate of 1°C min^{-1} and a frequency of 20 Hz. T_c is the temperature of the $TGB_A^*-TGB_C^*$ transition.

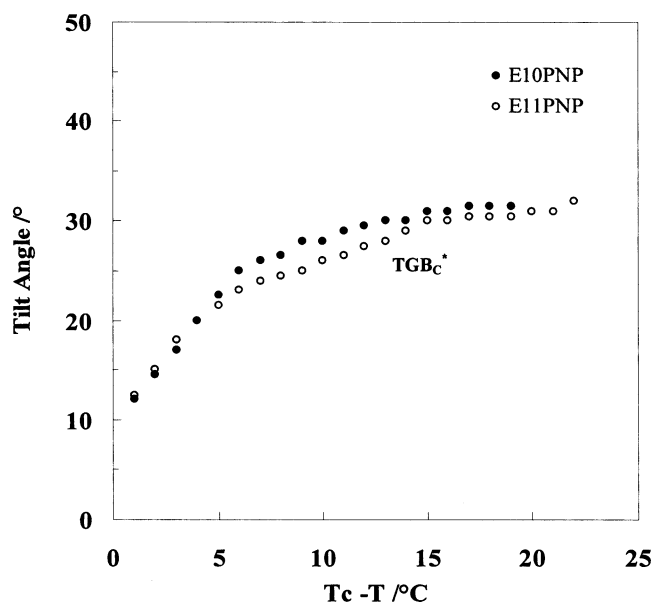


Figure 6. Temperature dependence of optical tilt angle measured for compounds E_m PNP ($m=10, 11$) in $3\mu\text{m}$ thick homogeneously aligned cells.

from the methyleneoxy group weakening the interactions between molecules that induce the formation of smectic layers.

References

- [1] P.G. De Gennes. *Solid State Commun.*, **10**, 753 (1972).
 [2] S.R. Renn, T. Lubensky. *Phys. Rev. A*, **38**, 2132 (1988).

- [3] J.W. Goodby, M.A. Waugh, S.M. Stein, E. Chin, R. Pindak, J.S. Patel. *Nature*, **337**, 449 (1989).
 [4] J.W. Goodby, M.A. Waugh, S.M. Stein, E. Chin, R. Pindak, J.S. Patel. *J. Am. chem. Soc.*, **111**, 8119 (1989).
 [5] H.T. Nguyen, A. Bouchta, L. Navailles, P. Barois, N. Isaert, R.J. Twieg, A. Maaroufi, C. Destrade. *J. Phys. II Fr.*, **2**, 1889 (1992).
 [6] R. Shao, J. Pang, N.A. Clark, J.A. Rego, D.M. Walba. *Ferroelectrics*, **147**, 255 (1993).
 [7] I. Dozov, G. Durand. *Europhys. Lett.*, **28**, 25 (1994).
 [8] I. Dozov. *Phys. Rev. Lett.*, **74**, 4245 (1995).
 [9] P.A. Pramod, R. Pratibha, N.V. Madhusudana. *Curr. Sci.*, **73**, 761 (1997).
 [10] J.G. Meier, P. Pudquist, A.S. Petrenko, J.W. Goodby, S.T. Lagerwall. *Liq. Cryst.*, **29**, 179 (2002).
 [11] C. Da Cruz, J.C. Rouillon, J.P. Marcerou, N. Isaer, H.T. Nguyen. *Liq. Cryst.*, **28**, 125 (2001).
 [12] S.-L. Wu, W.-J. Hsieh. *Liq. Cryst.*, **21**, 783 (1996).
 [13] S.-L. Wu, P.-C. Yen, W.-J. Hsieh. *Liq. Cryst.*, **34**, 741 (1998).
 [14] S.-L. Wu, W.-J. Hsieh. *Chem. Mater.*, **11**, 852 (1999).
 [15] S.-L. Wu, P.-L. Chang. *Liq. Cryst.*, **29**, 1355 (2002).
 [16] K. Miyasato, S. Abe, H. Takezoe, A. Fukuda, E. Kuze. *Jpn. J. appl. Phys.*, **22**, L661 (1983).
 [17] A.S. Slaney, J.W. Goodby. *J. mater. Chem.*, **1**, 5 (1991).
 [18] I. Dierking, F. Giebelmann, J. Kuberow, P. Zugenmaier. *Liq. Cryst.*, **17**, 234 (1994).
 [19] S.-L. Wu, J.-H. You, B.-J. Uang. *Liq. Cryst.*, **28**, 69 (2001).
 [20] I. Dierking, S.T. Lagerwall. *Liq. Cryst.*, **26**, 83 (1999).
 [21] W. Kuczynski, H. Stegemeyer. *Ber. Bunsenges phys. Chem.*, **98**, 1322 (1994).
 [22] W. Kuczynski, H. Stegemeyer. *Mol. Cryst. liq. Cryst.*, **260**, 377 (1995).