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Liquid Crystals

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To cite this Article Wu, S. -L. and Lin, T. -C.(2005) 'Ferroelectric liquid crystals derived from (*S*)-2-(6-methoxy-2-naphthyl)propionic acid with non-fluorinated or semi-fluorinated alkanes at a chiral terminal chain', *Liquid Crystals*, 32: 6, 797 – 804

To link to this Article: DOI: 10.1080/02678290500158500

URL: <http://dx.doi.org/10.1080/02678290500158500>

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Ferroelectric liquid crystals derived from (*S*)-2-(6-methoxy-2-naphthyl)propionic acid with non-fluorinated or semi-fluorinated alkanes at a chiral terminal chain

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(Received 29 September 2004; accepted 29 November 2004)

Two series of ferroelectric liquid crystals derived from (*S*)-2-(6-methoxy-2-naphthyl)propionic acid, with non-fluorinated or semi-perfluorinated alkanes positioned at a chiral terminal chain, have been synthesized and characterized by differential scanning calorimetry, polarizing optical microscopy and electro-optical measurements. The non-fluorinated compounds, 1-hexyl (*S*)-2-[6-[4-(4-alkanoyloxyphenyl)benzoyloxy]-2-naphthyl]propionates exhibit rich mesomorphism—the BP_{II}, N*, TGB_A*, SmA* and SmC* phases. The fluorinated compounds display only the SmA* and SmC* phases, suggesting that the fluorination promotes the formation of smectic phases. In addition, the SmA* and SmC* phases of the fluorinated compounds have enhanced thermal stability as compared with the corresponding phases of the non-fluorinated compounds. The spontaneous polarization (P_s values) for the non-fluorinated compounds are higher than those of the fluorinated compounds at any reduced temperature below the SmA*–SmC* transition. The electro-optical responses measured for these compounds in the ferroelectric phase displayed thresholdless, V-shaped switching.

1. Introduction

Ferroelectric liquid crystals (FLCs) have been extensively investigated since the discovery of DOBAMBC (*p*-decyloxybenzylidene-*p'*-amino-2-methylbutylcinnamate) by Meyer *et al.* [1]. Conventional rod-like molecules of ferroelectric liquid crystals are composed of a rigid core with two flexible hydrocarbon tails, at least one of which is chiral. In order to determine correlations between molecular structure and physical properties, many types of material have been prepared utilizing various molecular designs to target desired properties [2]. It is generally acknowledged that a simple change in the length of achiral aliphatic terminal chains can significantly affect the mesomorphic properties of liquid crystals [3]. Chiral chains with different chemical structures also have an important effect on helical twist sense and the magnitude and direction of spontaneous polarization [4].

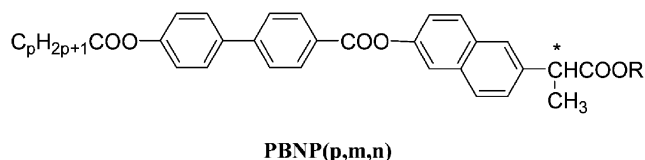
Liquid crystals incorporating fluorine atoms frequently exhibit unusual characteristics, of use in LCD devices, and their development attracts much interest

[5–7]. Recently, many studies have focused on the modification of achiral chains by the introduction of a semi-fluorinated alkyl chain, the results indicating that the smectic phase is strongly promoted thereby [8–23]. These, include examples of single-benzene-ring compounds with a semi-fluorinated chain unexpectedly exhibiting stable smectic phase [8–14]. It may be possible to use one- or two-benzene-ring rigid cores with a semi-fluorinated alkyl chain as a means for molecular design that will introduce a ferroelectric SmC* phase. So far as we are aware, the effect of fluorination of the terminal chiral chain on mesomorphic properties has not yet been explored.

In this study, therefore, we prepared for investigation five homologous series of chiral materials derived from a chiral moiety, (*S*)-2-(6-methoxy-2-naphthyl)propionic acid—(*S*)-MNP—in conjunction with non-fluorinated and fluorinated straight alkyl chains attached to the external side of the chiral centre. The general structural formula of the materials, PBNP(*p,m,n*) are depicted below.

The advantages of the molecular structure of (*S*)-MNP in the synthesis of liquid crystals and the study of mesomorphic properties are as follows: (1) mesogens with a naphthalene core can give a quasi-bookshelf

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R = (CH₂)_m(CF₂)_nH: series I. PBNP(p,6,0), R = (CH₂)₆H

R = (CH₂)_m(CF₂)_nF: series II. PBNP(p,2,4), R = (CH₂)₂(CF₂)₄F

structure free from zig-zag defects in a homogenous cell [24]; (2) the chiral centre of (*S*)-MNP is directly attached to the naphthalene ring of the rigid core, and demethylation readily gives the hydroxy analogue; (3) (*S*)-MNP possessing high optical purity is commercially available. A large number of liquid crystal materials derived from (*S*)-MNP have been synthesized and shown to exhibit ferroelectric or antiferroelectric phases [25–29].

2. Experimental

2.1. Characterization of Materials

The structures of the intermediates and final products were checked by thin layer chromatography and further identified by nuclear magnetic resonance spectroscopy using a Bruker Avance 500 NMR spectrometer. The purity of the final products was confirmed by elemental analysis using a Perkin-Elmer 2400 instrument. The carbon and hydrogen analytical data agreed with calculated results within $\pm 1\%$.

Phase transition temperatures and enthalpy changes were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC 7 at a running rate of 5°C min^{-1} . Mesophases were identified using a Nikon Microphot-FXA polarizing optical microscope (POM) in conjunction with a Mettler FP82-HT hot stage controlled by a Mettler FP90 processor.

Commercial homogenous cells coated with polyimide as alignment film were purchased from E.H.C. Co. Ltd, Japan and Linkam Scientific Instruments Ltd, UK. The sample was filled into the cell by capillary action in the isotropic state. Two wires were fixed separately to the ITO-coated glass plates of the sample cell with silver paint.

Spontaneous polarization (P_s) was measured by the triangular wave method [30]. Triangular waves were generated by a Yagawa AG1200 arbitrary waveform generator and were amplified by an NF Electronics Instrument 4005 power amplifier. The currents were measured by detecting the voltage change across a

resistor of 50 k Ω , using a HP 54502A digital oscilloscope to monitor the signals.

The measurement of optical transmittance versus applied electric field was conducted using a He-Ne laser (5 mW, 632.8 nm) as probe beam [31, 32]. The optical transmittance of the probe beam passing through the cell, between crossed polarizers with axes parallel and perpendicular to the smectic layer normal, was detected by a photodiode.

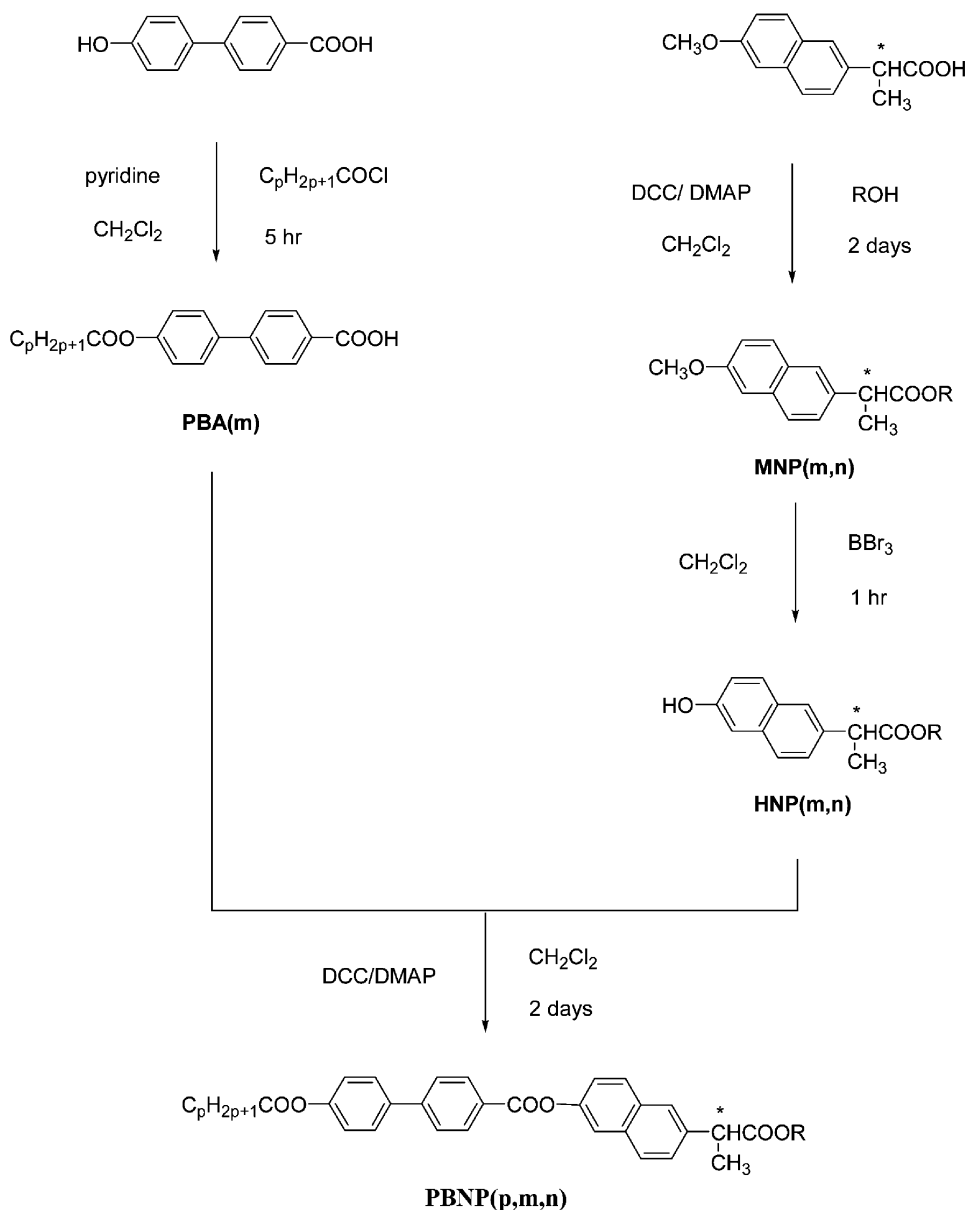
2.2. Synthesis of materials

3,3,4,4,5,5,6,6,6-Nonafluoro-1-hexanol (97%), octanoyl chloride (99%), nonanoyl chloride (96%), decanoyl chloride (98%), lauryl chloride (98%) and 1-hexanol (98%,) were purchased from Aldrich. (*S*)-2-(6-Methoxy-2-naphthyl)propionic acid (>99% enantiomeric excess) and 4-(4-hydroxyphenyl)benzoic acid (98%,) were purchased from TCI. *N,N'*-dicyclohexyl carbodiimide (DCC) (99%,) and 4-dimethylaminopyridine (DMAP) (98%,) were purchased from Fluka. All compounds were used as received.

The synthetic procedures for 4-(4-alkanoyloxyphenyl)benzoic acid PBA(*m*) [33] and PBNP(*p,m,n*) [34] were carried out in the same manner as described in previous papers, and are shown in the scheme. Detailed procedures are described as follows.

2.2.1. 4-(4-Alkanoyloxyphenyl)benzoic acids, PBA(*m*; *m*=7–11). The alkanoyl chloride (14 mmol) was slowly added to a solution of 4'-hydroxybiphenyl-4-carboxylic acid (17 mmol) in dried pyridine/dichloromethane (1/6). The reaction mixture was stirred under reflux for 5 h, then added to a solution of hydrochloric acid in water cooled in an ice-water bath. The precipitate was filtered off and recrystallized from absolute ethanol; yields 60–70%. Typical NMR data for PBA(*m*=11) are given. ¹H NMR (CDCl₃) δ (ppm) 0.87–0.90 (t, 3H, RCH₃), 1.28–1.43 (m, 16H, (CH₂)₈CH₃), 1.76–1.79 (m, 2H, CH₂CH₂COO), 2.58–2.61 (t, 2H, CH₂COO), 7.19–7.20 (d, 2H, ArH), 7.63–7.68 (dd, 4H, ArH), 8.16–8.18 (d, 2H, ArH), (carboxylic acid H not detected).

2.2.2. 1-Hexyl (*S*)-2-(6-methoxy-2-naphthyl)propionate, MNP(6,0). (*S*)-2-(6-Methoxy-2-naphthyl)propionic acid (6.22 g, 27 mmol) and 1-hexanol (2.5 g, 24 mmol) were dissolved in dry dichloromethane (100 ml). After addition of DCC (5.5 g, 27 mmol) and DMAP (0.3 g, 2.4 mmol), the solution was stirred at room temperature for two days. The precipitate was filtered off and washed with dichloromethane. The filtrate was successively washed with 5% aqueous acetic acid, 5% aqueous sodium hydroxide and water, then dried over anhydrous magnesium sulphate and concentrated under



Scheme 1. Synthesis procedures for the target compounds PBNP(*p,m,n*).

vacuum. The residue was purified by column chromatography on silica gel (Merck, 70–230 mesh) using dichloromethane as eluent. The isolated ester was an oily liquid obtained in 86% yield. 1H NMR ($CDCl_3$): δ (ppm) 0.81–0.84 (t, 3H, *RCH*₃), 1.21–1.27 (m, 8H, $(CH_2)_4CH_3$), 1.53–1.59 (m, 3H, ArCH(CH_3)COO), 3.83–3.87 (q, 1H, ArCH(CH_3)COO), 3.92 (s, 3H, CH_3O), 4.06–4.08 (t, 2H, $COOCH_2$), 7.12–7.15 (m, 2H, ArH), 7.41–7.43 (dd, 1H, ArH), 7.67 (s, 1H, ArH), 7.71–7.72 (d, 2H, ArH).

2.2.3. 3,3,4,4,5,5,6,6,6-Nonafluoro-1-hexyl (*S*)-2-(6-methoxy-2-naphthyl)propionate, MNP(2,4).

Prepared in

an analogous manner to MNP(6,0), the yield was 83%. 1H NMR ($CDCl_3$): δ (ppm) 1.56–1.59 (t, 3H, ArCH(CH_3)COO), 2.38–2.45 (m, 2H, $COOCH_2CH_2$), 3.84–3.89 (q, 1H, ArCH(CH_3)COO), 3.92 (s, 3H, CH_3O), 4.31–4.43 (doublet of quintet, 2H, $COOCH_2$), 7.11 (d, 1H, ArH), 7.13–7.16 (dd, 1H, ArH), 7.37–7.40 (dd, 1H, ArH), 7.66 (s, 1H, ArH), 7.69–7.71 (d, 2H, ArH).

2.2.4. 1-Hexyl (*S*)-2-(6-hydroxy-2-naphthyl)propionate, HNP(6,0).

The ester MNP(6,0) (6.6 g, 21 mmol) dissolved in dry dichloromethane (77 ml) was mixed with boron tribromide (10.2 g, 41 mmol) at $-20^\circ C$ for

5 min, then at 0°C for 1 h. After diluting with dichloromethane (154 ml), the solution was poured into a mixture of saturated aqueous ammonium chloride (77 ml) and ice chips (77 g). 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 (Merck, 70–230 mesh) column chromatography using dichloromethane as eluent. The product in 64% yield was collected after recrystallization from hexane. ¹H NMR (CDCl₃): δ (ppm) 0.80–0.88 (t, 3H, RCH₃), 1.21–1.25 (m, 8H, (CH₂)₄CH₃), 1.54–1.57 (m, 3H, ArCH(CH₃)COO), 3.83–3.84 (q, 1H, ArCH(CH₃)COO), 4.05–4.07 (t, 2H, COOCH₂), 5.06 (s, 1H, OH), 7.08–7.10 (dd, 1H, ArH), 7.12 (d, 1H, ArH), 7.38–7.40 (dd, 1H, ArH), 7.63–7.68 (m, 2H, ArH), 7.70–7.72 (d, 1H, ArH).

2.2.5. 3,3,4,4,5,5,6,6,-Nonafluoro-1-hexyl (S)-2-(6-hydroxy-2-naphthyl)propionate, HNP(2,4). Prepared in an analogous manner to HNP(6,0), the yield was 56%. ¹H NMR (CDCl₃): δ (ppm), 1.58–1.60 (t, 3H, ArCH(CH₃)COO), 2.38–2.45 (m, 2H, COOCH₂CH₂), 3.85–3.87 (q, 1H, ArCH(CH₃)COO), 4.32–4.42 (doublet of quintet, 2H, COOCH₂), 5.03 (s, 1H, OH), 7.09–7.11 (dd, 1H, ArH), 7.12–7.13 (d, 1H, ArH), 7.36–7.38 (dd, 1H, ArH), 7.64–7.66 (d, 2H, ArH), 7.70–7.72 (d, 1H, ArH).

2.2.6. 1-Hexyl (S)-2-{6-[4-(4-alkanoyloxyphenyl)benzoyloxy]-2-naphthyl}propionates, PBNB(p,6,0). The esters PBNP(p,6,0) were synthesized in the same manner as described for esters MNP(6,0). A mixture of PBA(m) (2.2 mmol), alcohol HNP(6,0) (2.0 mmol), DCC (2.2 mmol), DMAP (0.2 mmol) and dry dichloromethane (20 ml) was stirred at room temperature for two days. After purification, 20–30% yields of products were obtained. All materials were analysed and identified satisfactorily. A typical example of analytical data for PBNP(11,6,0) is given. Elemental analysis: calculated, C 77.84, H 8.02; found, C 77.87, H 8.08. ¹H NMR (CDCl₃): δ (ppm) 0.83–0.87 (t, 3H, RCH₃), 0.88–0.90 (m, 3H, RCH₃), 1.22–1.61 (m, 27H, RCH₂), 1.77–1.80 (m, 2H, CH₂CH₂COO), 2.58–2.61 (t, 2H, CH₂CH₂COO), 3.87–3.92 (q, H, ArCH(CH₃)COO), 4.07–4.09 (t, 2H, COOCH₂), 7.21–8.32 (m, 14H, ArH).

2.2.7. 3,3,4,4,5,5,6,6,-Nonafluoro-1-hexyl (S)-2-{6-[4-(4-alkanoyloxyphenyl)benzoyloxy]-2-naphthyl}propionates, PBNP(p,2,4). Prepared in an analogous manner to PBNB(p,6,0), the yields were 20–30%. All materials were analysed and identified satisfactorily. A typical example of analytical data for PBNP(11,2,4) is given. Elemental analysis: calculated, C 62.85, H 5.39; found,

C 62.89, H 5.37. ¹H NMR (CDCl₃): δ (ppm) 0.87–0.90 (t, 3H, RCH₃), 1.28–1.63 (m, 19H, RCH₂), 1.77–1.80 (m, 2H, CH₂CH₂COO), 2.38–2.48 (m, 2H, COOCH₂CH₂), 2.58–2.61 (t, 2H, CH₂CH₂COO), 3.91–3.93 (q, H, ArCH(CH₃)COO), 4.34–4.42 (doublet of quintet, 2H, COOCH₂), 7.21–8.32 (m, 14H, ArH). ¹⁹F NMR (CDCl₃): δ (ppm) –81.36 (3F, CF₂CF₃), –114.08 (2F, CF₂CF₃), –124.85 (2F, CH₂CF₂CF₂), –126.34 (2F, CH₂CF₂CF₂).

3. Results and discussion

3.1. Mesomorphic properties

The mesophases and their phase transition temperatures for compounds PBNP(p,m,n) were determined by a combination of DSC and POM. The BP_{II} phase was characterized by the formation of blue-grey platelets [35], and the N* phase was characterized by its scale-like texture; the TGB_A* phase was identified by a spiral filaments texture [36–38]. The SmA* displayed the pseudo-homeotropic or focal-conic texture and the SmC* phase showed the petal or broken focal-conic texture.

The mesophases, transition temperatures and the corresponding phase transition enthalpies for PBNP(p,6,0) and PBNP(p,2,4) with the same alkyl chain length (m+n=6) at the chiral tail are listed in the table. The non-fluorinated material PBNP(7,6,0) exhibits the frustrated phases (BP_{II} and TGB_A*), N*, SmA* and unknown CrX* phases. On increasing the achiral alkyl chain length, an additional SmC* phase is formed. This result is dramatically changed in the fluorinated series of materials, in which only the SmA* and SmC* phases appear, suggesting that chiral tails containing a semi-perfluorinated alkyl chain have a tendency to form the smectic phase. It has been reported that the introduction of a semi-perfluorinated alkyl chain into the achiral chain of a liquid crystal molecule can also favour the smectic phase and dominate the mesomorphic behaviour [20, 21, 39]. These observations are mainly attributed to two reasons [40–43]. Firstly, the fluorinated alkyl groups are considerably more extended and rigid than non-fluorinated groups due to a greater energy difference (9.7 kJ mol⁻¹) between *trans* and *gauche* conformations. The linear conformation of the fluorinated alkyl groups can increase the molecular length/breadth ratio in comparison with the non-fluorinated analogue and therefore enhance the thermal stability of a smectic phase [40, 41]. Secondly, the perfluorinated segments are incompatible with both alkyl chains and aromatic cores; they prefer to form their own aggregation, resulting in a tendency to smectic phases formation [42, 43].

Table. Transition temperature T (°C) and enthalpies ΔH (kJ mol⁻¹, in italics) of the transition for compounds PBNP(*p*,6,0) and PBNP(*p*,2,4) at 5°C min⁻¹ scanning rate.

Compound	I	BP _{II}	N*	TGB _A *	SmA*	SmC*	CrX** ^c	Cr	m.p.
PBNP(7,6,0)	• 147.3	• 146.7	• 142.6	• 142.1	• 63.3	—	• 56.1	• 88.5	
	<i>0.58</i>	<i>a</i>	<i>1.03</i>	<i>b</i>	<i>2.72</i>		<i>10.9</i>	<i>19.2</i>	
PBNP(8,6,0)	• 143.8	• 143.1	• 140.3	• 139.2	• 112.3	• 56.8	• 45.7	• 89.5	
	<i>0.14</i>	<i>a</i>	<i>0.74</i>	<i>b</i>	<i>c</i>	<i>3.77</i>	<i>8.41</i>	<i>22.8</i>	
PBNP(9,6,0)	• 143.2	• 142.1	• 139.7	• 139.2	• 114.6	• 57.2	• 44.8	• 87.7	
	<i>0.36</i>	<i>a</i>	<i>0.80</i>	<i>b</i>	<i>0.05</i>	<i>21.1</i>	<i>9.50</i>	<i>18.2</i>	
PBN-P(10,6,0)	• 139.8	• 139.4	• 138.0	• 137.4	• 122.2	• 58.7	• 44.2	• 89.0	
	<i>0.05</i>	<i>a</i>	<i>1.02</i>	<i>b</i>	<i>0.32</i>	<i>10.1</i>	<i>10.1</i>	<i>20.5</i>	
PBN-P(11,6,0)	• 138.7	• 138.1	• 137.3	• 136.5	• 124.9	• 57.9	—	• 88.5	
	<i>4.4</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>0.44</i>	<i>15.7</i>		<i>21.2</i>	
PBNP(7,2,4)	• 205.2	—	—	—	• 161.8	• 98.7	• 85.1	• 118.0	
	<i>7.22</i>				<i>c</i>	<i>2.12</i>	<i>8.24</i>	<i>23.1</i>	
PBNP(8,2,4)	• 197.5	—	—	—	• 173.3	• 97.8	• 59.1	• 118.1	
	<i>7.03</i>				<i>0.12</i>	<i>9.10</i>	<i>2.00</i>	<i>26.3</i>	
PBNP(9,2,4)	• 191.9	—	—	—	• 175.1	• 98.6	• 61.9	• 108.8	
	<i>5.53</i>				<i>0.25</i>	<i>3.30</i>	<i>16.9</i>	<i>18.4</i>	
PBN-P(10,2,4)	• 185.7	—	—	—	• 174.1	• 88.6	—	• 108.6	
	<i>7.19</i>				<i>0.65</i>	<i>23.6</i>		<i>25.0</i>	
PBN-P(11,2,4)	• 181.1	—	—	—	• 173.1	• 89.9	—	• 97.3	
	<i>3.95</i>				<i>0.29</i>	<i>11.7</i>		<i>11.6</i>	

^aThe enthalpies of the BP_{II}-N* and I-BP_{II} transitions were added together. ^bThe enthalpies of the TGB_A*-SmA* and N*-TGB_A* transitions were added together. ^cThe enthalpy was too small to be measured. ^dThe enthalpies of the TGB_A*-SmA*, N*-TGB_A* and BP_{II}-N* transitions were added together with that of the I-BP_{II} transition. ^eThe unknown smectic crystal phase.

The phase diagrams of the two series of materials are plotted in figures 1 and 2, respectively, for comparison. For both series, the temperature range of the SmA* phase becomes narrower while that of the SmC* phase becomes wider as the length of terminal achiral chain increases. The differences in thermal stability of the SmC* phase, for corresponding achiral alkyl chain length of these two series of compounds, decrease with increasing length of the achiral alkyl chain. For example, the difference of thermal stability in the SmC* phase between PBNP(8,6,0) and PBNP(8,2,4) is 61.0°C, but that between PBNP(11,6,0) and PBNP(11,2,4) is 48.2°C.

3.2. Switching behaviour and spontaneous polarization

The switching current behaviour was measured in a 5 μm homogenous cell under a triangular wave voltage, with a field frequency of 20 Hz and amplitude of 5 V. The switching current measurements for PBNP(10,6,0) and PBNP(11,2,4) in the SmC* phase are shown in figure 3. The characteristic switching peak results from the charge produced by polarization reversal [30], suggesting the existence of ferroelectricity. The switching behaviour of other fluorinated series of compounds is similar to these observations.

The spontaneous polarizations (**P_s**) for compounds PBNP(*p*,6,0) and PBNP(*p*,2,4), measured as a function of temperature on cooling in 5 μm homogeneous cells is illustrated in figures 4 and 5, respectively. The **P_s** value increases steeply in the vicinity of the SmA*-SmC* transition and then increases with decreasing temperature before crystallization. The maximum **P_s** values of compounds PBNP(*p*,6,0) are in the range 20–40 nC cm⁻², while that of compounds PBNP(*p*,2,4) are in the range 15–30 nC cm⁻². The **P_s** value is clearly reduced by the introduction of a semi-perfluorinated segment into the chiral alkyl chain. These results are similar to previous reports in which an achiral semi-fluorinated chain was introduced into liquid crystal compounds [20].

3.3. Electro-optical response

Optical transmittance versus electric field was measured for PBNP(*p*,*m*,*n*) in 2 μm thick homogenous cells using applied triangular waveforms of varying frequency. The electro-optical responses of PBNP(11,6,0) and PBNP(11,2,4) show hysteresis and W-shaped switching at the SmA*-SmC* transition. At suitable temperatures of the SmC* phase for both materials, hysteresis-free and V-shaped switching occur, as shown in figure 6.

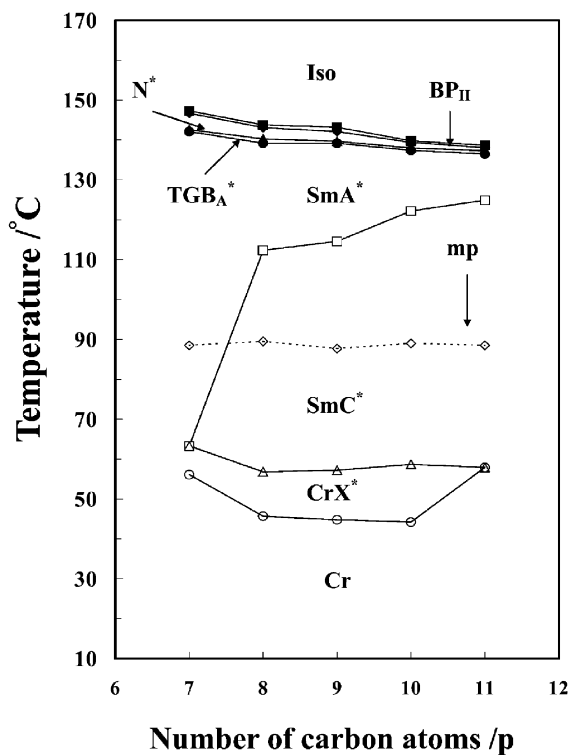


Figure 1. Phase diagram of PBNP($p,6,0$), plotted as temperature versus the number of carbon atoms in the achiral chain.

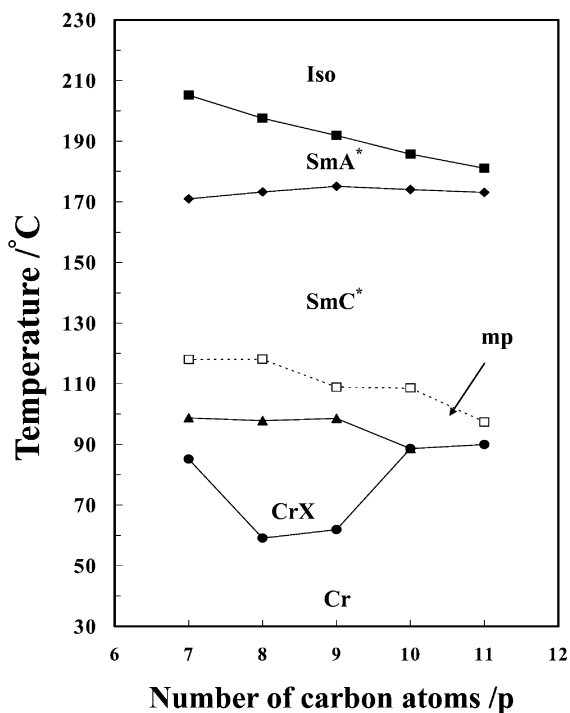


Figure 2. Phase diagram of PBNP($p,2,4$) plotted as temperature versus the number of carbon atoms in the achiral chain.

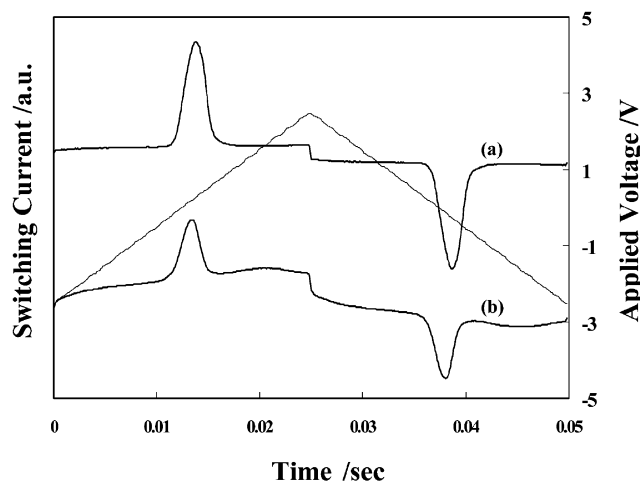


Figure 3. Switching current behaviour measured in the SmC* phase of (a) PBNP(10,6,0) and (b) PBNP(10,2,4) in homogeneously aligned 5 μm cells.

The electro-optical responses indicate that all the materials show V-shaped switching, although a slight hysteresis is probably seen. However, detailed investigations (texture observation and switching behaviour) have revealed that these compounds are indeed ferroelectric and not antiferroelectric liquid crystals; the origin of the V-switching is still uncertain and under discussion [44–48]. These results also show that the fluorinated and non-fluorinated ferroelectric liquid crystals with low P_s values can form V-shaped switching behavior at low frequencies of the applied electric fields, similarly to the previous reports [49, 50].

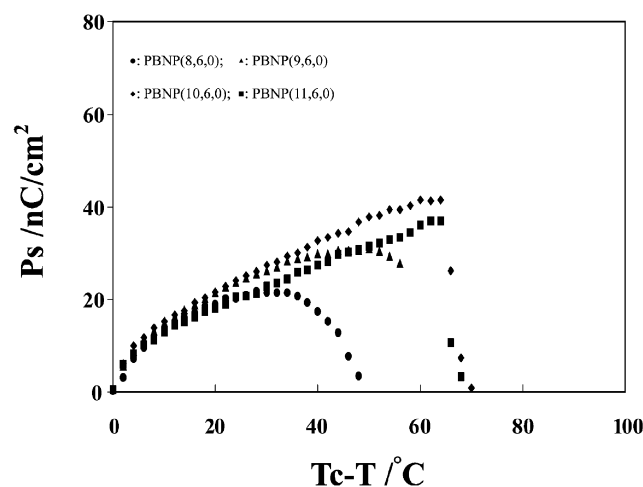


Figure 4. Spontaneous polarization plotted as a function of temperature for compounds PBNP($p,6,0$). T_c is the temperature of the SmA*–SmC* phase transition.

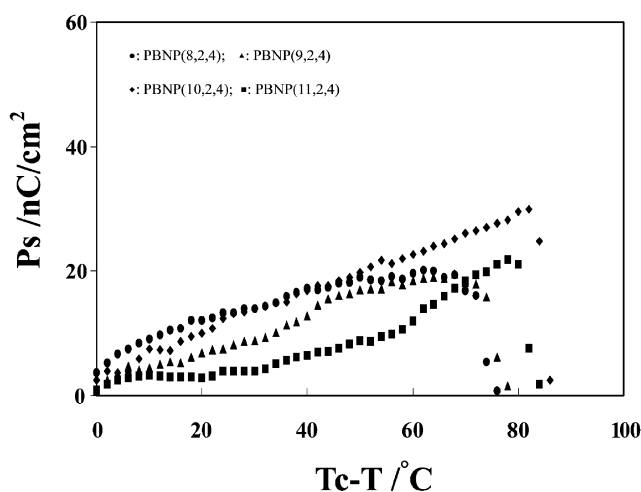


Figure 5. Spontaneous polarization plotted as a function of temperature for compounds PBNP(*p*,2,4). T_c is the temperature of the SmA*–SmC* phase transition.

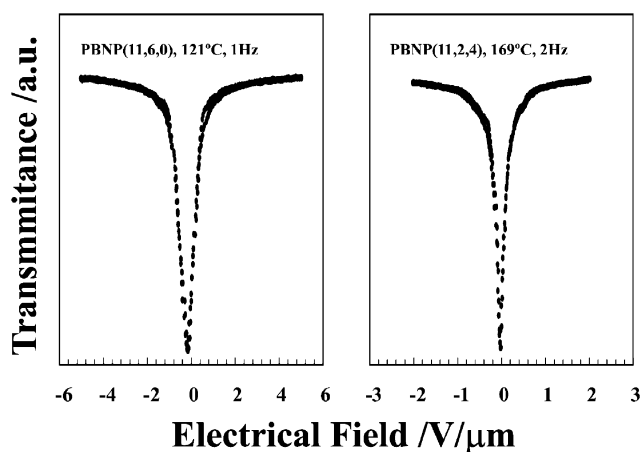


Figure 6. V-shaped switching obtained from PBNP(11,6,0) and PBNP(11,2,4) at appropriate temperatures and frequencies.

4. Conclusion

Non-fluorinated and fluorinated compounds derived from (*S*)-2-(6-methoxy-2-naphthyl)propionic acid have been demonstrated to exhibit ferroelectric SmC* phases. The non-fluorinated homologues exhibits polymorphism, whereas the four fluorinated homologues display only the SmA* and SmC* phases, suggesting that fluorination favours the formation of smectic phases. The non-fluorinated compounds possess a larger spontaneous polarization than the corresponding fluorinated compounds. Furthermore, these non-fluorinated and fluorinated compounds with low spontaneous polarization can exhibit thresholdless, V-shaped switching in the SmC* phase.

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