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Synthesis and characterization of thiophene-containing liquid crystals

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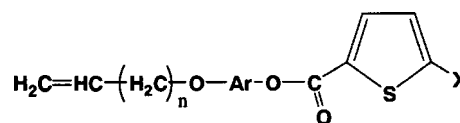
Six series of liquid crystal materials containing a 2,5-disubstituted thiophene unit were synthesized. The liquid crystal compounds obtained were characterized by NMR, differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction techniques. The properties of liquid crystalline phases were investigated as a function of spacer units, number of aromatic core rings and different terminal moieties. Cyano, methoxy and iodo groups were used as terminal groups. It is found that: (i) compounds having one thiophene ring and one phenyl ring connected by an ester group, with a length/breadth value of 2.1, exhibit no mesophase, while other compounds containing two biphenyl rings, with a length/breadth ratio of 2.7, show mesophases; (ii) the polarity of terminal groups and the flexible spacer length significantly affect the thermal behaviour of these compounds; (iii) the nematic transition range of cyano-containing compounds decreases with increasing length of the flexible spacer, and long alkenyloxy chains tend to facilitate the formation of the smectic phase and suppress the nematic phase in all the mesogenic compounds synthesized.

1. Introduction

Mesogen shape anisometry, terminal groups and flexible chain length are key variables in strategies to design new mesogens exhibiting a specific type of molecular organization in a particular temperature range [1]. There are many examples of rigid, extended chemical subunits in mesogens. The most common subunit used in synthesizing calamitic liquid crystals is the linearly *para*-substituted phenyl ring [2]. Other non-linear types subunits, such as the *meta*-substituted phenyl ring [3, 4], the furan ring [5], the pyrrolic ring [6] and the thiophene ring, have also been used in synthesizing liquid crystals. Among them, thiophene-containing compounds have attracted much attention. Over the past decade, the influence of thiophene ring systems on mesomorphic behaviour has been the subject of much investigation, and a great number of mesogenic compounds containing the thiophene ring have been synthesized and characterized [5–17]. The reason for introducing a thiophene ring into mesogens is the greater possibility with heterocyclics for the design of new mesogenic molecules. Thiophene systems are generally lower melting than their 1,4-phenylene counterparts due to reduced packing efficiency of the molecules. In addition, thiophene-based systems possess a strong lateral

dipole within their structure which promotes negative dielectric anisotropy; this eliminates the need for lateral cyano and fluoro substituents which tend to increase the molecular breadth and possibly the viscosity of the system. Moreover, the insertion of heteroatoms can strongly influence the formation of mesophases and change considerably the polarity, polarizability and sometimes the geometry of the molecules. Thereby the types of mesophase, phase transition temperatures, dielectric constants and other properties of the mesogens may be influenced [18, 19].

In this study, we synthesized six series of thiophene-based liquid crystals. Their general formula is shown below:



where n is the number of methylene units in the alkenyloxy group, Ar is a phenyl or biphenyl group and X is an iodo, methoxy or cyano group. For simplicity, these compounds are abbreviated as n PET-I, n PET-CN, n PET-OMe, n BPET-I, n BPET-CN, and n BPET-OMe. P stands for phenyl ring, BP for biphenyl group, E for ester linking group and T for thiophene ring. The mesogenic properties of the synthesized compounds were

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characterized by differential scanning calorimetry (DSC), polarizing optical microscopy and X-ray diffraction (XRD) techniques. The effect of spacer length, mesogenic core and terminal groups on the mesomorphic behaviour of the compounds is discussed.

2. Experimental

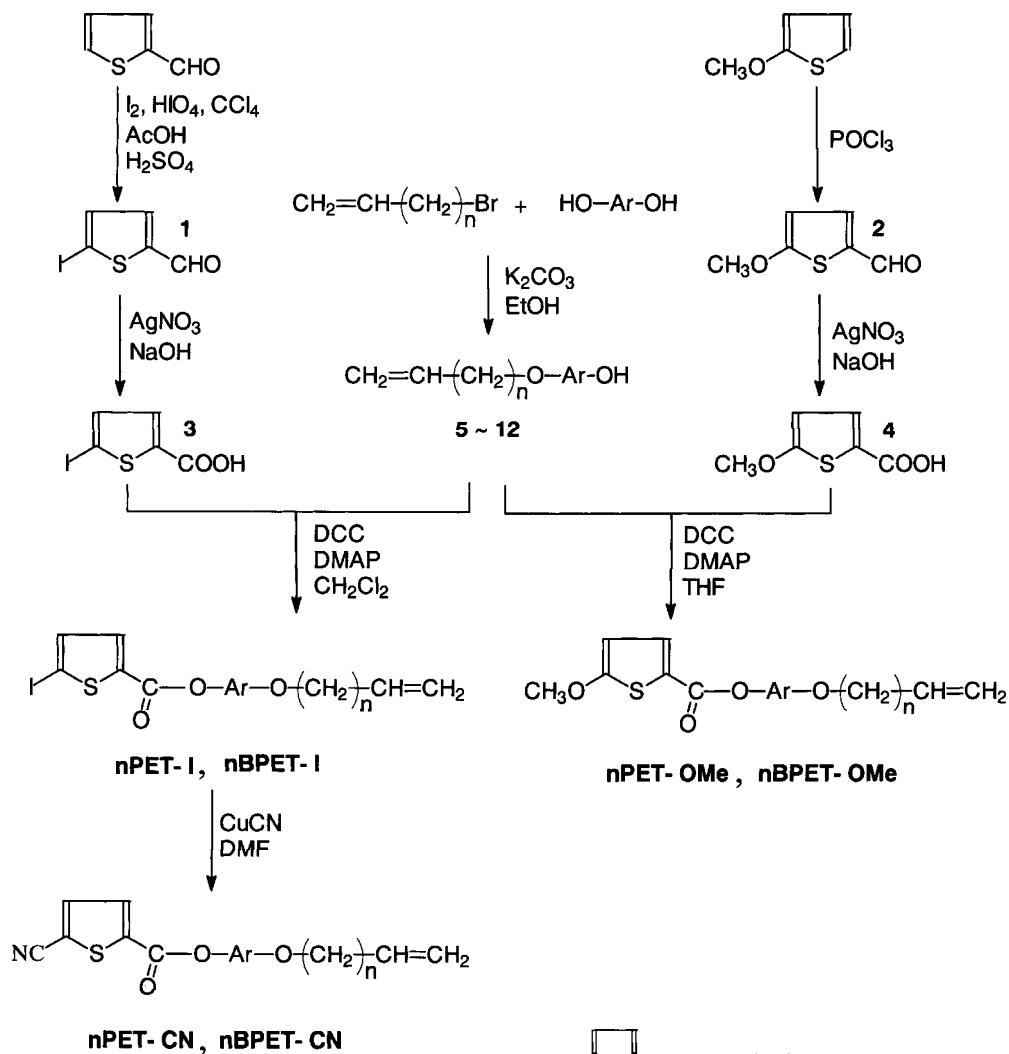
2.1. Materials

Allyl bromide, hydroquinone, 4,4'-biphenol, 2-formylthiophene, 2-methoxythiophene, dicyclohexylcarbodiimide

(DCC) and 4-dimethylaminopyridine (DMAP), all from TCI Co., Ltd, were used as received without any purification. All solvents were dried and distilled before use, and column chromatography on silica gel was performed using Merk Kieselgel 60 (70–230 mesh ASTM).

2.2. Characterization techniques

The ^1H NMR spectra of all the synthesized compounds were recorded on a Varian 300 spectrometer (300 MHz) using CDCl_3 as solvent and tetramethylsilane (TMS) as an internal standard. A Seiko/5200



| Compound | n | Ar | X |
|----------|----------------|----|----------------|
| nPET-X | n = 1, 3, 6, 9 | | X = I, CN, OMe |
| nBPET-X | n = 1, 3, 6, 9 | | X = I, CN, OMe |

Scheme.

differential scanning calorimeter was used for determining the thermal transitions and transition enthalpies. Heating and cooling rates were $10^{\circ}\text{C min}^{-1}$. The endothermic peaks pointed downward. A Carl-Zeiss Axiophot polarizing microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used to analyse thermal transitions and observe mesomorphic textures. XRD measurements were performed with a Rigaku powder diffractometer using a nickel-filtered CuK_{α} radiation.

2.3. Synthesis

The synthetic routes for the six series of thiophene-containing compounds are outlined in the scheme.

2.3.1. 5-Iodo-2-thiophenecarbaldehyde (I)

2-Formylthiophene (3.6 g, 32.4 mmol) and iodine (3.84 g, 15.1 mmol) were dissolved in 8 ml of carbon tetrachloride. Periodic acid (1.4 g, 7 mmol), distilled water (6 ml), acetic acid (16 ml) and H_2SO_4 (18N, 0.24 ml) were added to this solution. The mixture was stirred at reflux temperature (80°C) for 1 h and at room temperature (25°C) for another 12 h. After washing with 2% aqueous NaHCO_3 , the organic layer was dried over anhydrous MgSO_4 and the solvent removed in a rotary evaporator. Purification was performed using flash chromatography (silica gel, a mixture of 1:5 EtOAc/*n*-hexane as eluent) to yield 6.38 g (82.4%) of yellowish crystals. Compound 1: MS m/z 206 (M^+). $^1\text{H NMR}$

Table 1. Chemical shift δ and mass spectra data of *n*PET-I, *n*PET-CN and *n*PET-OMe.

| Compound ^a | Yield/% | MS (m/z) | $^1\text{H NMR}$ |
|-----------------------|---------|----------------------|---|
| 1PET-I | 66.4 | 386 (M^+) | 4.53 (m, 2H, $-\text{O}-\text{CH}_2-$); 5.27–5.45 (m, 2H, $-\text{CH}=\text{CH}_2$); 6.04 (m, 1H, $-\text{CH}=\text{CH}_2$); 6.92, 7.08 (2d, 4H, ArH on phenyl ring); 7.32, 7.57 (2d, 2H, ArH on thiophene ring). |
| 3PET-I | 70.5 | 414 (M^+) | 1.86 (m, 2H, $-\text{O}-\text{CH}_2-\text{CH}_2$); 2.25 (m, 2H, $-\text{CH}-\text{CH}=\text{}$); 3.96 (t, 2H, $-\text{O}-\text{CH}_2-$); 4.99–5.10 (m, 2H, $-\text{CH}=\text{CH}_2$); 5.84 (m, 1H, $-\text{CH}=\text{CH}_2$); 6.89, 7.10 (2d, 4H, ArH on phenyl ring); 7.32, 7.58 (2d, 2H, ArH on thiophene ring). |
| 6PET-I | 67.1 | 456 (M^+) | 1.35 (m, 6H, $-(\text{CH}_2)_3$); 1.74 (m, 2H, $-\text{O}-\text{CH}_2-\text{CH}_2$); 1.99 (m, 2H, $-\text{CH}_2-\text{CH}=\text{}$); 3.92 (t, 2H, $-\text{O}-\text{CH}_2-$); 4.90–5.02 (m, 2H, $-\text{CH}=\text{CH}_2$); 5.79 (m, H, $-\text{CH}=\text{CH}_2$); 6.89, 7.05 (2d, 4H, ArH on phenyl ring); 7.30, 7.55 (2d, 2H, ArH on thiophene ring). |
| 9PET-I | 71.2 | 498 (M^+) | 1.23 (m, 12H, $-(\text{CH}_2)_6$); 1.71 (m, 2H, $-\text{O}-\text{CH}_2-\text{CH}_2$); 2.01 (m, 2H, $-\text{CH}_2-\text{CH}=\text{}$); 3.92 (t, 2H, $-\text{O}-\text{CH}_2-$); 4.89–5.01 (m, 2H, $-\text{CH}=\text{CH}_2$); 5.78 (m, H, $-\text{CH}=\text{CH}_2$); 6.87, 7.05 (2d, 4H, ArH on phenyl ring); 7.30, 7.55 (2d, 2H, ArH on thiophene ring). |
| 1PET-CN | 60.8 | 285 (M^+) | 4.53 (m, 2H, $-\text{O}-\text{CH}_2-$); 2.57–5.45 (m, 2H, $-\text{CH}=\text{CH}_2$); 6.04 (m, 1H, $-\text{CH}=\text{CH}_2$); 6.92, 7.08 (2d, 4H, ArH on phenyl ring); 7.61, 7.89 (2d, 2H, ArH on thiophene ring). |
| 3PET-CN | 59.3 | 313 (M^+) | 1.86 (m, 2H, $-\text{O}-\text{CH}_2-\text{CH}_2$); 2.25 (m, 2H, $-\text{CH}_2-\text{CH}=\text{}$); 3.96 (t, 2H, $-\text{O}-\text{CH}_2-$); 4.99–5.10 (m, 2H, $-\text{CH}=\text{CH}_2$); 5.84 (m, H, $-\text{CH}=\text{CH}_2$); 6.89, 7.10 (2d, 4H, ArH on phenyl ring); 7.62, 7.88 (2d, 2H, ArH on thiophene ring). |
| 6PET-CN | 61.1 | 355 (M^+) | 1.35 (m, 6H, $-(\text{CH}_2)_3$); 1.74 (m, 2H, $-\text{O}-\text{CH}_2-\text{CH}_2$); 2.04 (m, 2H, $-\text{CH}_2-\text{CH}=\text{}$); 3.92 (t, 2H, $-\text{O}-\text{CH}_2-$); 4.90–5.02 (m, 2H, $-\text{CH}=\text{CH}_2$); 5.79 (m, H, $-\text{CH}=\text{CH}_2$); 6.89, 7.05 (2d, 4H, ArH on phenyl ring); 7.61, 7.89 (2d, 2H, ArH on thiophene ring). |
| 9PET-CN | 59.5 | 397 (M^+) | 1.23 (m, 12H, $-(\text{CH}_2)_6$); 1.71 (m, 2H, $-\text{O}-\text{CH}_2-\text{CH}_2$); 2.01 (m, 2H, $-\text{CH}_2-\text{CH}=\text{}$); 3.92 (t, 2H, $-\text{O}-\text{CH}_2-$); 4.89–5.01 (m, 2H, $-\text{CH}=\text{CH}_2$); 5.78 (m, H, $-\text{CH}=\text{CH}_2$); 6.87, 7.05 (2d, 4H, ArH phenyl ring); 7.62, 7.88 (2d, 2H, ArH thiophene ring). |
| 1PET-OMe | 65.9 | 290 (M^+) | 3.95 (s, 3H, $-\text{OCH}_3$); 4.50 (m, 2H, $-\text{O}-\text{CH}_2-$); 5.25–5.42 (m, 2H, $-\text{CH}=\text{CH}_2$); 6.02 (m, 1H, $-\text{CH}=\text{CH}_2$); 6.89, 6.26 (2d, 4H, ArH on phenyl ring); 7.68, 7.89 (2d, 2H, ArH on thiophene ring). |
| 3PET-OMe | 73.5 | 318 (M^+) | 1.91 (m, 2H, $-\text{O}-\text{CH}_2-\text{CH}_2$); 2.24 (m, 2H, $-\text{CH}_2-\text{CH}=\text{}$); 3.98 (m, 5H, $-\text{O}-\text{CH}_2-$ and $-\text{OCH}_3$); 4.99–5.10 (m, 2H, $-\text{CH}=\text{CH}_2$); 5.84 (m, H, $-\text{CH}=\text{CH}_2$); 6.88, 7.09 (2d, 4H, ArH on phenyl ring); 6.26, 7.69 (2d, 2H, ArH on thiophene ring). |
| 6PET-OMe | 64.7 | 360 (M^+) | 1.36 (m, 6H, $-(\text{CH}_2)_3$); 1.74 (m, 2H, $-\text{O}-\text{CH}_2-\text{CH}_2$); 2.04 (m, 2H, $-\text{CH}_2-\text{CH}=\text{}$); 3.98 (m, 2H, $-\text{O}-\text{CH}_2-$, $-\text{OCH}_3$); 4.90–5.02 (m, 2H, $-\text{CH}=\text{CH}_2$); 5.82 (m, H, $-\text{CH}=\text{CH}_2$); 6.89, 7.05 (2d, 4H, ArH on phenyl ring); 6.27, 7.68 (2d, 2H, ArH on thiophene ring). |
| 9PET-OMe | 70.7 | 402 (M^+) | 1.23 (m, 12H, $-(\text{CH}_2)_6$); 1.71 (m, 2H, $-\text{O}-\text{CH}_2-\text{CH}_2$); 2.01 (m, 2H, $-\text{CH}_2-\text{CH}=\text{}$); 3.98 (m, 2H, $-\text{O}-\text{CH}_2-$, OCH_3); 4.89–5.01 (m, 2H, $-\text{CH}=\text{CH}_2$); 5.78 (m, H, $-\text{CH}=\text{CH}_2$); 6.87, 7.05 (2d, 4H, ArH on phenyl ring); 6.26, 7.68 (2d, 2H, ArH on thiophene ring). |

^a According to scheme.

Table 2. Chemical shift δ and mass spectra data of *n*BPET-I, *n*BPET-CN and *n*BPET-OMe.

| Compound ^a | Yield/% | MS (<i>m/z</i>) | ¹ H NMR |
|-----------------------|---------|-----------------------|---|
| 1BPET-I | 79.8 | 462 (M ⁺) | 4.57 (m, 2H, -O-CH ₂ -); 5.29–5.47 (m, 2H, -CH=CH ₂); 6.07 (m, 1H, -CH=CH ₂); 6.97, 7.21, 7.47, 7.58 (4d, 8H, ArH on phenyl ring); 7.34, 7.61 (2d, 2H, ArH on thiophene ring). |
| 3BPET-I | 83.6 | 490 (M ⁺) | 1.91 (m, 2H, -O-CH ₂ -CH ₂ -); 2.25 (m, 2H, -CH ₂ -CH=); 4.01 (t, 2H, -O-CH ₂ -); 4.99–5.11 (m, 2H, -CH=CH ₂); 5.85 (m, 1H, -CH=CH ₂); 6.97, 7.22, 7.48, 7.55 (4d, 8H, ArH on phenyl ring); 7.34, 7.61 (2d, 2H, ArH on thiophene ring). |
| 6BPET-I | 80.4 | 532 (M ⁺) | 1.40 (m, 6H, -(CH ₂) ₃); 1.81 (m, 2H, -O-CH ₂ -CH ₂ -); 2.06 (m, 2H, -CH ₂ -CH=); 3.97 (t, 2H, -O-CH ₂ -); 4.92–5.03 (m, 2H, -CH=CH ₂); 5.82 (m, H, -CH=CH ₂); 6.97, 7.22, 7.48, 7.55 (4d, 8H, ArH on phenyl ring); 7.33, 7.61 (2d, 2H, ArH on thiophene ring). |
| 9BPET-I | 78.6 | 574 (M ⁺) | 1.31 (m, 12H, -(CH ₂) ₆); 1.80 (m, 2H, -O-CH ₂ -CH ₂ -); 2.01 (m, 2H, -CH ₂ -CH=); 3.97 (t, 2H, -O-CH ₂ -); 4.91–5.02 (m, 2H, -CH=CH ₂); 5.80 (m, H, -CH=CH ₂); 6.97, 7.22, 7.48, 7.55 (4d, 8H, ArH on phenyl ring); 7.33, 7.61 (2d, 2H, ArH on thiophene ring). |
| 1BPET-CN | 74.8 | 361 (M ⁺) | 4.57 (m, 2H, -O-CH ₂ -); 5.29–5.47 (m, 2H, -CH=CH ₂); 6.07 (m, 1H, -CH=CH ₂); 6.96, 7.24, 7.49, 7.59 (4d, 8H, ArH on phenyl ring); 7.61, 7.94 (2d, 2H, ArH on thiophene ring). |
| 3BPET-CN | 76.9 | 389 (M ⁺) | 1.91 (m, 2H, -O-CH ₂ -CH ₂ -); 2.25 (m, 2H, -CH ₂ -CH=); 4.01 (m, 5H, -O-CH ₂ - and -OCH ₃); 4.99–5.11 (dd, 2H, -CH=CH ₂); 5.85 (m, H, -CH=CH ₂); 6.93, 7.22, 7.49, 7.58 (4d, 8H, ArH on phenyl ring); 7.63, 7.91 (2d, 2H, ArH on thiophene ring). |
| 6BPET-CN | 77.5 | 431 (M ⁺) | 1.40 (m, 12H, -(CH ₂) ₆); 1.81 (m, 2H, -O-CH ₂ -CH ₂ -); 2.06 (m, 2H, -CH ₂ -CH=); 3.97–4.01 (t, 2H, -O-CH ₂ -, -OCH ₃); 4.92–5.03 (m, 2H, -CH=CH ₂); 5.82 (m, H, -CH=CH ₂); 6.96, 7.22, 7.47, 7.56 (4d, 8H, ArH on phenyl ring); 7.63, 7.91 (2d, 2H, ArH on thiophene ring). |
| 9BPET-CN | 77.1 | 473 (M ⁺) | 1.31 (m, 12H, -(CH ₂) ₆); 1.80 (m, 2H, -O-CH ₂ -CH ₂ -); 2.01 (m, 2H, -CH ₂ -CH=); 3.97 (t, 2H, -O-CH ₂ -); 4.91–5.02 (m, 2H, -CH=CH ₂); 5.80 (m, H, -CH=CH ₂); 6.93, 7.22, 7.46, 7.55 (4d, 8H, ArH phenyl ring); 7.63, 7.92 (2d, 2H, ArH thiophene ring). |
| 1BPET-OMe | 83.4 | 366 (M ⁺) | 3.97 (s, 3H, -OCH ₃); 4.56 (m, 2H, -O-CH ₂ -); 5.27–5.45 (m, 2H, -CH=CH ₂); 6.07 (m, 1H, -CH=CH ₂); 6.95, 7.23, 7.46, 7.52 (4d, 8H, ArH on phenyl ring); 6.28, 7.71 (2d, 2H, ArH on thiophene ring). |
| 3BPET-OMe | 83.6 | 394 (M ⁺) | 1.91 (m, 2H, -O-CH ₂ -CH ₂ -); 2.24 (m, 2H, -CH ₂ -CH=); 3.97–4.01 (m, 5H, -O-CH ₂ - and -OCH ₃); 4.99–5.11 (dd, 2H, -CH=CH ₂); 5.85 (m, H, -CH=CH ₂); 6.95, 7.21, 7.50, 7.54 (4d, 8H, ArH on phenyl ring); 6.30, 7.72 (2d, 2H, ArH on thiophene ring). |
| 6BPET-OMe | 85.1 | 436 (M ⁺) | 1.23 (m, 12H, -(CH ₂) ₆); 1.71 (m, 2H, -O-CH ₂ -CH ₂ -); 2.01 (m, 2H, -CH ₂ -CH=); 3.97–4.01 (t, 5H, -O-CH ₂ -, -OCH ₃); 4.92–5.03 (m, 2H, -CH=CH ₂); 5.82 (m, H, -CH=CH ₂); 6.92, 7.22, 7.46, 7.52 (4d, 8H, ArH on phenyl ring); 6.60, 7.73 (2d, 2H, ArH on thiophene ring). |
| 9BPET-OMe | 82.9 | 478 (M ⁺) | 1.23 (m, 12H, -(CH ₂) ₆); 1.71 (m, 2H, -O-CH ₂ -CH ₂ -); 2.01 (m, 2H, -CH ₂ -CH=); 3.98 (t, 5H, -O-CH ₂ -, -OCH ₃); 4.89–5.01 (dd, 2H, -CH=CH ₂); 5.78 (m, H, -CH=CH ₂); 6.94, 7.21, 7.48, 7.54 (4d, 8H, ArH on phenyl ring); 6.30, 7.73 (2d, 2H, ArH on thiophene ring). |

^a According to scheme.

(CDCl₃, 300 MHz) δ = 7.39 (m, 2H, aromatic protons), 9.77 (s, 1H, -CHO).

2.3.2. 5-Methoxy-2-thiophenecarbaldehyde (2)

A mixture of phosphorous oxychloride (4.6 g, 30 mmol) and *N,N*-dimethylformamide (4.3 g, 60 mmol) was stirred at room temperature for 30 min; 2-methoxythiophene (3.42 g, 30 mmol) was then added slowly. After stirring for 20 h at room temperature, the mixture was poured into cold water and then 5% aqueous NaOH (50 ml)

was added. The crude product was extracted three times with ethyl ether and the collected ether solution was dried over anhydrous MgSO₄. After removing the solvent, the product obtained was purified by liquid chromatography (silica gel, a mixture of 1:5 EtOAc/*n*-hexane as eluent) to yield 3.0 g (70.4%) of greenish liquid. Compound **2**: MS *m/z* 142 (M⁺). ¹H NMR (CDCl₃, 300 MHz) δ = 3.78 (s, 2H, -OCH₃), 6.39 (d, *J* = 4.2 Hz, 1H, aromatic proton), 7.45 (d, *J* = 4.5 Hz, 1H, aromatic proton).

2.3.3. 5-Iodo-2-thiophenecarboxylic acid (**3**) and 5-methoxy-2-thiophenecarboxylic acid (**4**)

Both compounds were prepared using the same method; the synthesis of compound **3** was as follows. AgNO₃ (15.0 g, 88.2 mmol) and NaOH (7.0 g, 175 mmol) were dissolved in water (30 ml) to give a dark syrup. To this ice-cooled syrup, 5-iodo-2-thiophenecarbaldehyde (5.0 g, 21 mmol) were added. The resulting solution was stirred for 24 h and then acidified with 5% aqueous HCl to yield a yellowish precipitate. This crude product was recrystallized from hot water to obtain 3.9 g (72.8%) of yellowish crystals. Compound **3**: MS *m/z* 254 (M⁺). ¹H NMR (CDCl₃, 300 MHz) δ = 7.39 (d, *J* = 3.9 Hz, 1H, aromatic proton), 7.49 (d, *J* = 3.9 Hz, 1H, aromatic proton), 9.65 (s, 1H, –COOH).

2.3.4. 4-(Alkenyloxy)phenol (**5–8**) and 4-(alkenyloxy)biphenol (**9–12**)

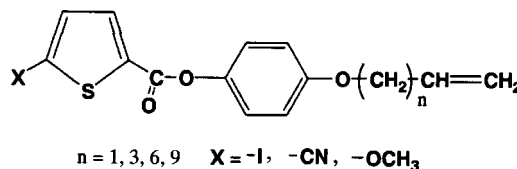
These compounds were prepared using the same method. An example for the synthesis of compound **6** follows. Hydroquinone (3.28 g, 29.8 mmol), K₂CO₃ (4.83 g, 35 mmol) and KI (0.1 g, 0.6 mmol) were dissolved in 20 ml of ethanol. The solution obtained was heated to reflux temperature and stirred for 1 h. 5-Bromo-1-pentene (3.69 g, 24.8 mmol) was slowly added and the reaction mixture heated at reflux for another 12 h. After removing the solvent under reduced pressure, the solid obtained was dissolved in 100 ml of water. This solution was acidified with 6N HCl to yield a white precipitate. Further purification was performed using liquid chromatography (silica gel, a 1:3 mixture of EtOAc/*n*-hexane as eluent) to yield 4.6 g (87.1%) of white crystals. Compound **6**: MS *m/z* 178 (M⁺). ¹H NMR (CDCl₃, 300 MHz) δ = 1.84 (m, 2H, –O–CH₂–CH₂–), 2.19 (m, 2H, =CH–CH₂–), 3.88 (t, 2H, –O–CH₂–), 4.96–5.07 (m, 2H, –CH=CH₂), 5.82 (m, 1H, –CH=CH₂), 6.75 (m, 4H, aromatic protons).

2.3.5. 4-(Alkenyloxy)phenyl 5-iodo-2-thiophenecarboxylate (*n*PET-I), 4-(alkenyloxy)phenyl 5-methoxy-2-thiophenecarboxylate (*n*PET-OMe), 4-(alkenyloxy)biphenyl 5-iodo-2-thiophenecarboxylate (*n*BPET-I) and 4-(alkenyloxy)biphenyl 5-methoxy-2-thiophenecarboxylate (*n*BPET-OMe)

Four series of compounds were synthesized by esterification of compounds **2** and **4** with the corresponding alcohols, **5–12**. The synthesis of compound 3PET-I is presented below.

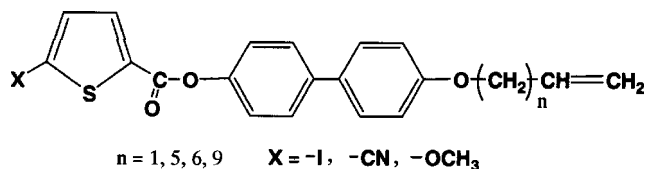
4-(4-Pentyloxy)phenol (1.03 g, 5.7 mmol), 5-methoxy-2-thiophenecarbaldehyde (1.33 g, 5.2 mmol), dicyclohexylcarbodiimide (1.08 g, 5.2 mmol) and dimethylaminopyridine (0.64 g, 0.5 mmol) were dissolved in 50 ml

Table 3. Phase transitions and transition enthalpy changes for *n*PET-I, *n*PET-CN and *n*PET-OMe. Cr: crystal, I: isotropic.



| Compound | Phase transitions/°C (corresponding enthalpy changes/kcal mol ⁻¹) | Heating Cooling |
|----------|---|--------------------|
| 1PET-I | Cr 110.0 (20.1) I I 78.9 (– 20.4) Cr | |
| 3PET-I | Cr 59.5 (16.3) I I 34.7 (– 16.3) Cr | |
| 6PET-I | Cr 51.7 (19.2) I I 20.4 (– 13.2) Cr | |
| 9PET-I | Cr 69.4 (20.8) I I 56.9 (– 21.6) Cr | |
| 1PET-CN | Cr 88.3 (24.8) I I 24.6 (– 15.0) Cr | |
| 3PET-CN | Cr 64.4 (17.4) I I 26.4 (– 17.2) Cr | |
| 6PET-CN | Cr 59.5 (16.3) I I 34.7 (– 16.3) Cr | |
| 9PET-CN | Cr 72.9 (12.6) I I 58.5 (– 12.0) Cr | |
| 1PET-OMe | Cr 63.7 (16.0) I I 15.6 (+ 14.9) Cr | |
| 3PET-OMe | Cr 60.5 (17.8) I I 11.7 (– 17.5) Cr | |
| 6PET-OMe | Cr 59.6 (18.3) I I 32.7 (– 19.6) Cr | |
| 9PET-OMe | Cr 60.9 (14.8) I I 28.2 (– 15.5) Cr | |

of dichloromethane. The resulting solution was stirred at room temperature for 48 h and then filtered. The filtrate was evaporated under reduced pressure to give the crude solid product. The obtained solid was purified by liquid chromatography (silica gel, a 1:7 mixture of EtOAc/*n*-hexane as eluent) to yield 1.5 g (70.5%) of white crystals. Compound 3PET-I: MS *m/z* 414 (M⁺). ¹H NMR (CDCl₃, 300 MHz) δ = 1.88 (m, 2H, –O–CH₂–CH₂–), 2.25 (m, 2H, =CH–CH₂–), 3.96 (t, 2H, –O–CH₂–), 4.99–5.10 (m, 2H, –CH=CH₂), 5.85 (m, 1H, –CH=CH₂), 6.90 (d, *J* = 5.7 Hz, 2H, aromatic protons), 7.09 (d, *J* = 5.6 Hz, 2H, aromatic protons), 7.32 (d, *J* = 3.9 Hz, 2H, aromatic protons), 7.58 (d, *J* = 3.9 Hz, 2H, aromatic protons)

Table 4. Phase transitions and transition enthalpy changes for *n*BPET-I, *n*BPET-CN and *n*BPET-OMe. Cr: crystal, SmA: smectic A, SmB: smectic B, SmE: smectic E, N: nematic, I: isotropic, (*): overlapped transitions.

| Compound | Transition temp./°C (corresponding enthalpy changes/kcal mol ⁻¹) | Heating Cooling |
|-----------|--|--------------------|
| 1BPET-I | Cr 167.7 (12.5) I I 163.2 (- 0.1) N 158.9 (- 11.9) Cr | |
| 3BPET-I | Cr ₁ 147.0 (*) 157.1 (12.0) N 163.5 (0.2) I I 161.1 (- 0.2) N 153.6 (- 10.3) Cr ₂ 138.0 (*) Cr ₁ | |
| 6BPET-I | Cr 145.7 (5.7) SmA 154.9 (3.8) I I 151.6 (- 2.6) SmA 141.8 (- 5.0) Cr | |
| 9BPET-I | Cr 101.8 (0.6) SmE 124.4 (9.6) SmB 137.6 (1.4) SmA 153.8 (1.8) I I 146.8 (- 1.9) SmA 133.6 (- 1.3) SmB 104.0 (- 1.2) SmE 84.2 (- 8.1) Cr | |
| 1BPET-CN | Cr 130.9 (14.4) SmA 154.4 (1.3) N 208.0 (0.3) I I 200.2 (- 0.3) N 144.6 (- 1.1) SmA 120.9 (- 14.3) Cr | |
| 3BPET-CN | Cr 113.3 (3.9) SmE 135.7 (4.1) SmA 146.4 (0.6) N 178.3 (0.6) I I 175.6 (- 0.5) N 142.7 (- 0.6) SmA 131.0 (- 4.0) SmE 99.5 (- 2.1) Cr | |
| 6BPET-CN | Cr 112.5 (17.0) SmA 137.6 (0.7) N 169.6 (0.5) I I 165.5 (- 0.5) N 134.5 (- 0.9) SmA 114.4 (- 13.1) Cr | |
| 9BPET-CN | Cr ₁ 117.1 (*) Cr ₂ 127.5 (22.1) SmA 155.3 (*) N 159.6 (1.1) I I 156.6 (- 1.1) N 152.4 (*) SmA 118.9 (- 16.5) Cr ₂ 101.8 (- 2.3) Cr ₁ | |
| 1BPET-OMe | Cr 113.8 (17.6) N 210.9 (0.9) I I 206.1 (- 0.8) N 118.6 (- 11.2) Cr | |
| 3BPET-OMe | Cr 125.0 (19.9) N 195.5 (1.0) I I 192.8 (- 0.9) N 83.4 (- 16.5) Cr | |
| 6BPET-OMe | Cr 105.7 (17.3) N 165.1 (0.8) I I 165.0 (- 0.6) N 71.4 (*) SmB 69.7 (- 14.1) 68.5 (*) Cr | |
| 9BPET-OMe | Cr 89.2 (22.1) N 153.2 (0.9) I I 151.9 (- 0.2) N 63.2 (- 0.1) SmA 56.1 (- 15.6) SmB (*) Cr | |

2.3.6. 4-(Alkenyloxy)phenyl 5-cyano-2-thiophene-carboxylate (*n*PET-CN) and 4-(alkenyloxy)-biphenyl 5-cyano-2-thiophenecarboxylate (*n*BPET-CN)

Both series of compounds were prepared using the same method. The synthesis of compound 3PET-CN is presented below.

4-(4-Pentyloxy)phenyl 5-iodo-2-thiophenecarboxylate (1.41 g, 3.4 mmol) and CuCN (0.365 g, 4.1 mmol) were dissolved in 15 ml of *N,N*-dimethylformamide. The resulting solution was heated to reflux temperature and stirred for 6 h. After cooling to room temperature, hydrated ferric chloride (1.35 g) and conc. HCl (0.34 ml) were added and the solution was stirred at 60°C for another 30 min. The reaction solution was extracted with CHCl₃, and the organic layer washed with 5N

HCl, 10% aqueous NaHCO₃ and water before drying over anhydrous MgSO₄. After the solvent was removed in a rotary evaporator, the crude product was purified by liquid chromatography (silica gel, a 1:8 mixture of EtOAc/*n*-hexane as eluent) to yield 0.63 g (59.3%) of white crystals. Compound 3 PET-CN: MS *m/z* 389 (M⁺). ¹H NMR (CDCl₃, 300 MHz) δ = 1.88 (m, 2H, -O-CH₂-CH₂-), 2.23 (m, 2H, =CH-CH₂-), 3.95 (t, 2H, -O-CH₂-), 4.98–5.08 (m, 2H, -CH=CH₂), 5.84 (m, 1H, -CH=CH₂), 6.92 (d, *J* = 6.6 Hz, 2H, aromatic protons), 7.11 (d, *J* = 6.6 Hz, 2H, aromatic protons), 7.32 (d, *J* = 3.9 Hz, 2H, aromatic protons), 7.58 (d, *J* = 3.9 Hz, 2H, aromatic protons).

Chemical shift, δ, and mass spectra data of other *n*PET-*X* and *n*BPET-*X* compounds are summarized in tables 1 and 2, respectively.

3. Results and discussion

Table 3 lists the thermal transitions of three series of compounds, *n*PET-I, *n*PET-CN and *n*PET-OMe. All these *n*PET-*X* compounds which contain only one phenyl ring in their mesogenic cores show no mesophase and present only a melting transition on the DSC scan. This could be due to the non-linearity of the thiophene ring. According to a literature report [6], the 2,5-disubstituted thiophene ring shows a 32° deviation from the hard-rod axis of the mesogenic core; this deviation causes distortion of the mesogenic core and suppresses the formation of mesophases. Molecular modelling of these *n*PET-*X* compounds is presented in figure 1. For simplicity, only one methylene group in the flexible alkenyloxy spacer was considered in the calculation. The length/breadth ratio of the mesogenic core for these *n*PET-*X* compounds is only 2.1, see figure 1(a). The length/breadth ratio may be too small for the formation of a mesophase. Gallardo and Favarin [5] reported a series of thiophene-based compounds, viz. 2-cyano-5-(4-*n*-alkoxystyryl)thiophenes which showed liquid crystalline phases. The only difference between these and *n*PET-*X* is the linking group. For the 2-cyano-5-(4-*n*-alkoxystyryl)thiophenes, the double bond linking group provides good linearity, and the length/breadth ratio of the mesogenic core is 2.8, see figure 1(b). This is why they show mesomorphism while *n*PET-*X* compounds do not.

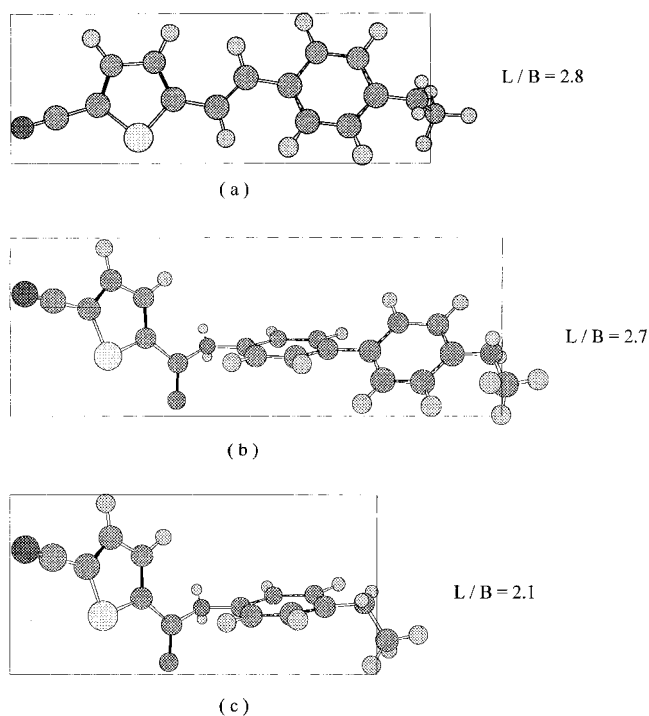


Figure 1. Optimized structures of (a) double bond linked (b) biphenyl ring-containing (c) phenyl ring containing thiophene liquid crystals, (L/B = Length/Breadth).

Table 4 reports the thermal transitions of another three series of compounds *n*BPET-I, *n*BPET-CN and *n*BPET-OMe. All these *n*BPET-*X* compounds contain a biphenyl group in their mesogenic core. The biphenyl group increases the length/breadth value of the mesogenic core. As can be seen from figure 1(c), the length/breadth value of the mesogenic core for the *n*BPET-*X* compounds is 2.7. Therefore, all these *n*BPET-*X* compounds show mesomorphic behaviour. Among the *n*BPET-I compounds, 1BPET-I presents a monotropic nematic (N) phase, 3BPET-I reveals an enantiotropic nematic phase, 6BPET-I shows an enantiotropic smectic A (SmA) phase, while 9BPET-I reveals enantiotropic SmA, SmB and SmE phases. Figure 2 presents the representative DSC thermograms of compound 9BPET-I. The heating scan shows a melting transition at 101.8°C, a SmE to SmB transition at 124.4°C, a SmB to SmA transition at 137.6°C and a SmA to isotropic transition at 153.8°C. In the cooling scan the crystallization temperature shows greater supercooling than the other three mesophase transitions. Figure 3 shows the typical SmA, SmB and SmE textures exhibited by compound 9BPET-I.

Among the *n*BPET-CN compounds, 1BPET-CN shows two enantiotropic N and SmA phases, 3BPET-CN presents enantiotropic N, SmA, and SmE phases, while both 6BPET-CN and 9BPET-CN exhibit enantiotropic N and SmA phases. Figure 4 depicts the phase transition temperatures of *n*BPET-CN as a function of *n*. This shows that the temperature range of mesophases is strongly influenced by the spacer length. The nematic temperature range decreases with increasing flexible spacer length, while the SmA range increases with increasing spacer length. Figure 5 depicts the DSC thermograms of 3BPET-CN. It exhibits a melting transition at 113.3°C, a SmE to SmA transition at 135.7°C, a SmA to N transition at 146.4°C and a N to isotropic transition at

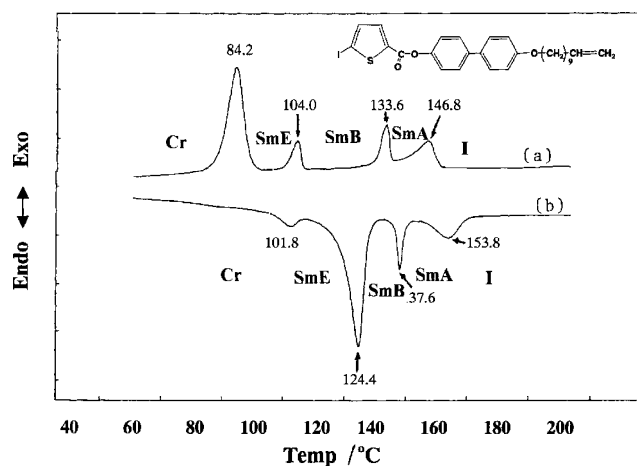
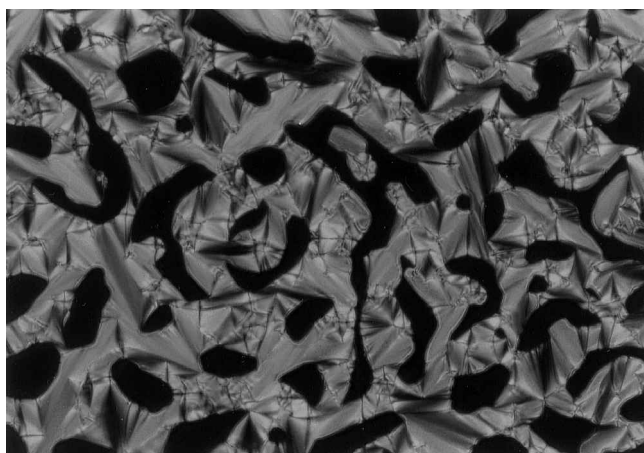
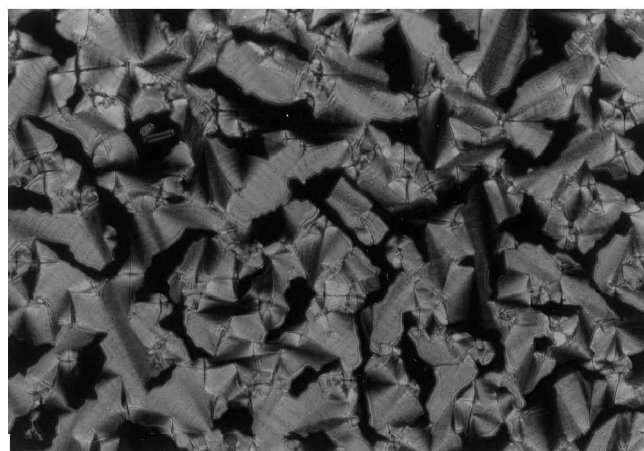


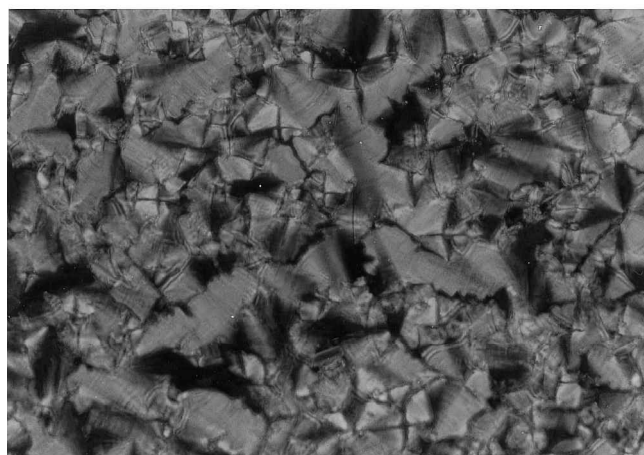
Figure 2. DSC curves of 9BPET-I: (a) first cooling (b) second heating runs.



(a)



(b)



(c)

Figure 3. Optical textures of 9BPET-I at (a) 143.0°C, (b) 120.0°C, (c) 95.0°C (crossed polarizers, magnification $\times 200$).

178.3°C. The cooling scan appears almost identical to the heating scan, except that a larger supercooling is observed for the crystallization transitions. Figures 6(a–c)

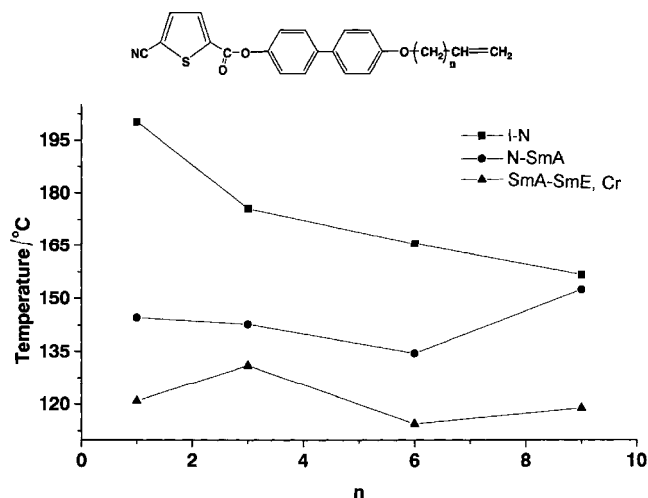


Figure 4. Plot of phase transition temperatures of n BPET-CN versus n .

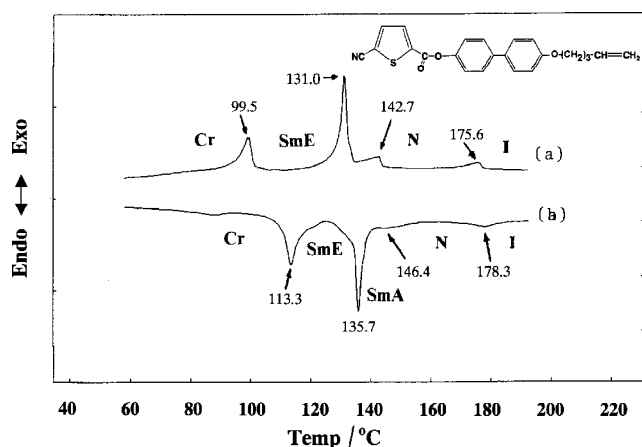
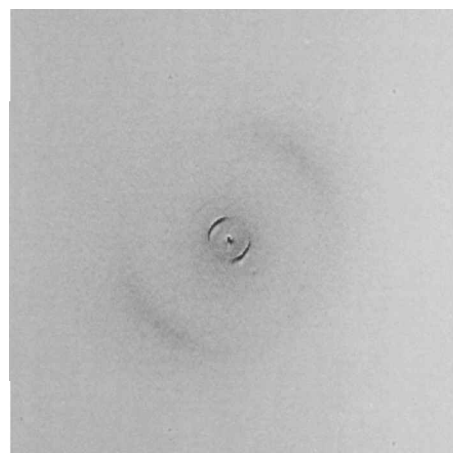


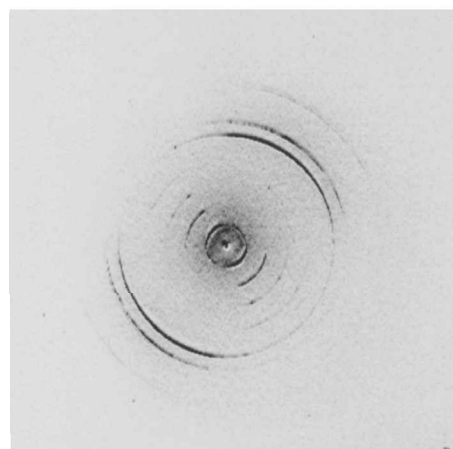
Figure 5. DSC curves of 3BPET-CN: (a) first cooling (b) second heating runs.

give the temperature-dependent XRD patterns obtained at 133.0, 110.0 and 30.0°C. Figure 6(a) shows the typical SmA XRD pattern which displays a broad diffraction in the wide angle region and a sharp diffraction in the small angle region. When the temperature was lowered to 110°C, figure 6(b), three sharp diffraction rings centered at 4.35 Å (1 1 0 and 1 1 1 planes) 4.05 Å (2 0 0 and 2 0 1 planes) and 3.10 Å (2 0 0 and 2 0 1 planes) were observed. This confirms the formation of a SmE phase [20]. When the temperature was further cooled to 30°C, figure 6(c), more diffraction rings were observed in the wide angle region. This indicates the formation of a crystalline phase.

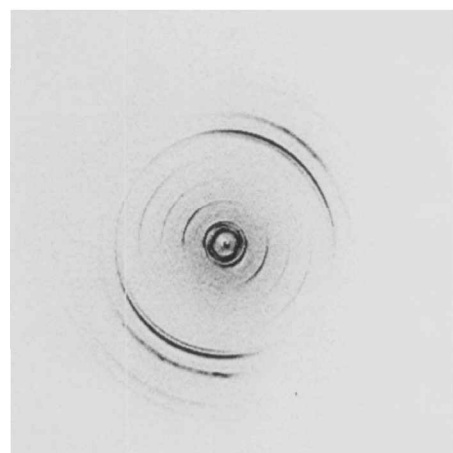
For the last series of compounds n BPET-OMe, both 1BPET-OMe and 3BPET-OMe reveal only an enantiotropic N phase while both 6BPET-OMe and 9BPET-OMe exhibit an enantiotropic N phase and monotropic SmA and SmB phases. Figure 7 illustrates the DSC thermograms exhibited by 6BPET-OMe. The heating



(a)



(b)



(c)

Figure 6. X-ray powder diffractograms of 3BPET-CN at (a) 133.0°C, (b) 110.0°C, (c) 30.0°C.

scan shows a melting transition at 105.7°C and a N to isotropic phase transition at 165.1°C. The cooling scan reveals an isotropic to N transition at 165.0°C, a N to

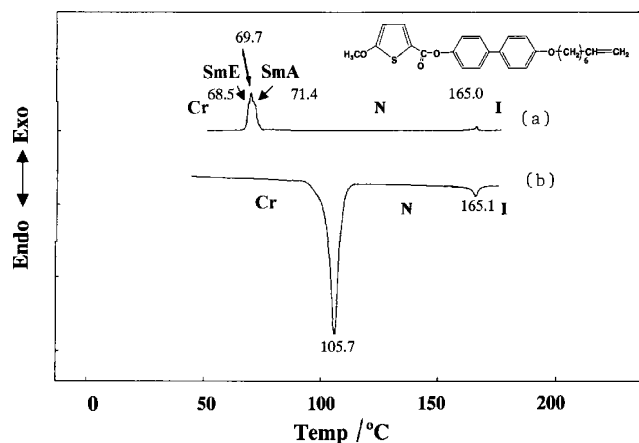


Figure 7. DSC curves of 6BPET-OMe: (a) first cooling, (b) second heating runs.

SmA transition at 71.4°C, a SmA to SmE transition at 69.7°C and a crystallization transition at 68.5°C. Figure 8 depicts textures of 6BPET-OMe. When a 6BPET-OMe sample was cooled at normal cooling rate ($10^{\circ}\text{C min}^{-1}$), N, SmA and SmE mesophases could be observed. On the other hand, by cooling this sample at a very slow rate ($0.1^{\circ}\text{C min}^{-1}$), the focal-conic texture emerged very slowly from the nematic schlieren texture as shown in figure 8 (c).

The effect of alkenyloxy spacer length on the phase transition temperatures of the *n*BPET-*X* compounds is shown in figure 9. Both melting and isotropization temperatures decrease as the spacer length increases for the three series of *n*BPET-*X* compounds. Furthermore, the nature of the mesophase depends on the spacer length. Those compounds containing a longer spacer tend to form an ordered smectic phase. This is because a longer spacer can stabilize the layer packing of the smectic phase.

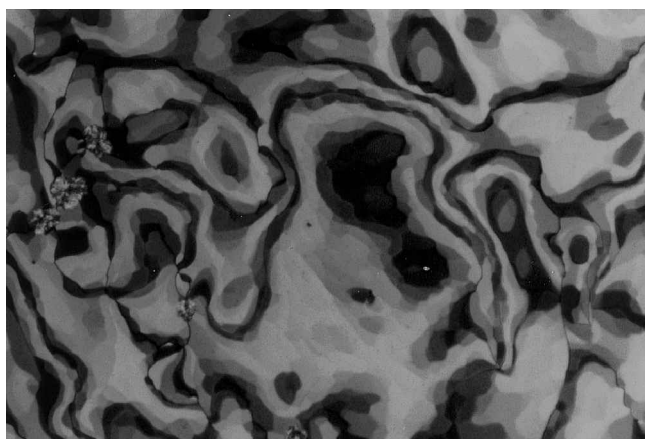
Finally, we discuss the effect of the terminal group on the mesomorphic properties of the *n*BPET-*X* compounds. As can be seen from figure 9, *n*BPET-OMe shows a higher melting transition and wider mesophase range than those of *n*BPET-CN and *n*BPET-I. The terminal group also strongly affects the nature of the mesophase. The experimental results demonstrate that a compound with a more polar terminal group tends to form a more ordered mesophase. From table 4, 1BPET-CN shows two enantiotropic nematic and SmA phases, 1BPET-OMe reveals an enantiotropic nematic phase while 1BPET-I presents only a monotropic nematic phase. This could be due to the polarity of the terminal group (the polarity of the three terminal groups increases in the following sequence: I < OMe < CN).

4. Conclusions

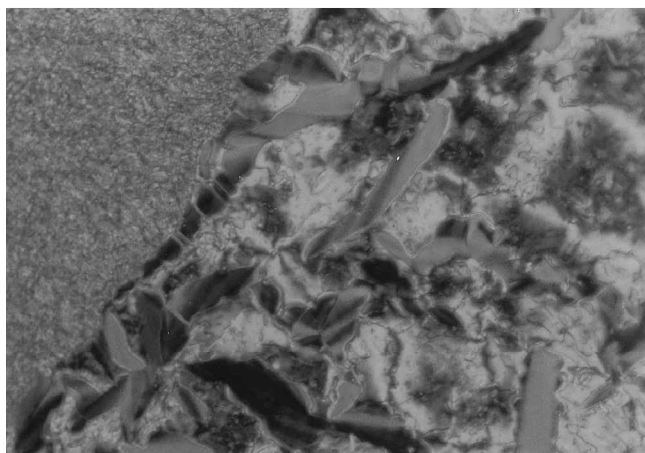
Six series of thiophene-based compound, *n*PET-*X* and *n*BPET-*X*, with *X* = I, CN and OMe, were synthesized



(a)



(b)



(c)

Figure 8. Optical textures of 6BPET-OMe at (a) 71.4°C, (b) 69.0°C, (c) 62.0°C (crossed polarizers, magnification $\times 200$).

and characterized. The first three series of compounds *n*PET-*X*, which contain a phenyl and a thiophene ring in their mesogenic core, show no mesophase. This is because

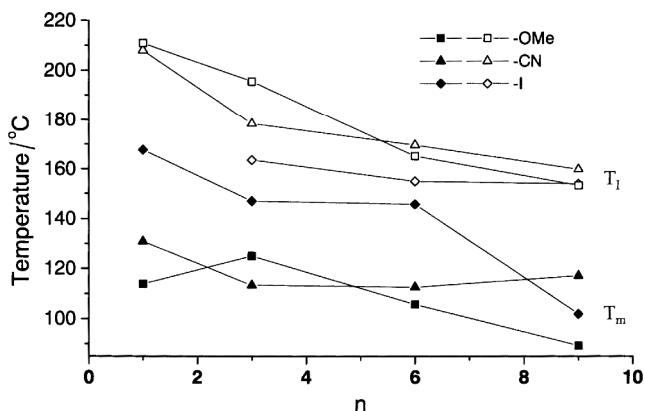
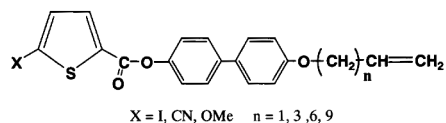


Figure 9. Clearing and melting temperatures of *n*BPET-*X* (*X* = I, CN and OMe) compounds as a function of *n*.

that the 2,5-disubstituted thiophene ring shows a 32° deviation from the axis of mesogenic core, and the length/breadth ratio of the mesogenic core is insufficiently high. The other three series of compounds *n*BPET-*X*, which contain a biphenyl ring and a thiophene ring in their mesogenic core, show mesomorphic behaviour. The nature of the mesophases formed depends on the spacer length and terminal group. Those compounds with a longer spacer tend to form ordered smectic phases. Those compounds with a more polar terminal group also have a tendency to form a more order smectic phase.

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