Synthesis and Characterization of Ferroelectric Side Chain Liquid Crystal Polymers bearing Banana-Shaped Chiral Mesogens

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Abstract: A series of ferroelectric liquid crystal polymers having banana-shaped side chain mesogens were synthesized through photo-polymerization of epoxide moiety. 2,5-disubstituted-thiophene sub-unit was used in synthesizing the banana-shaped monomers. These liquid crystal compounds were characterized by NMR, differential scanning calorimetry (DSC) and optical polarized microscopy (POM). Mesomorphism was investigated as a function of spacer units. All the synthesized low molar mass banana-shaped compounds exhibit smectic blue phase, but chiral smectic C phase could be observed only on compounds having longer spacer. The clearing temperature of low molar mass compounds fluctuated a little when spacer length varies. All polymers exhibit cholesteric mesophase and an observable glass transition. These liquid crystalline compounds reveal strong photoluminescence at visible region (λ_{max} = 475 nm for M9EPX) and have potential use in polarized organic light emitting diode materials.

Keywords: Banana-shape, Ferroelectricity, Smectic blue phase.

Introduction

Ferroelectric liquid crystal (FLC) was discovered in 1975 by Meyer et al. [1] and since the physics as well as technology of FLC have been extensively developed [2-5]. Recently, there has been considerable interest in the synthesis of liquid crystalline compounds, which may exhibit ferroelectric mesophases in an attempt to promote the development of novel fast-switching electro-optic display devices.

FLCs generally consists of a linear mesogenic core attached with a chiral moiety, which is responsible for the formation of ferroelectric mesophases. However, molecular theory of ferroelectricity in liquid crystals developed by Osipov et al. [6] points out that overall molecular shape also plays an important role in ferroelectricity. Nori et al. [7] have reported that banana-shape compounds without chiral moiety also exhibit ferroelectric mesophases. Since then, 'banana-shaped' mesogens have turned into a major liquid crystal sub-field and several groups are currently working on these materials [8-13]. In spite of the indepth studies on these 'banana-shaped' mesogens, the influence on the mesomorphism of introducing a chiral moiety into banana-shaped mesogens is not yet clearly understood.

2,5-Disubstituted thiophene systems are well known to show 32 degrees deviation from the hard rod axis of the analogous compound with phenyl ring. This makes 2,5-disubstituted thiophene ring is an ideal sub-unit in constructing banana-shape mesogens. Over the past decade, the influence of thiophene ring systems on mesomorphic behavior has been the subject of some investigations, and consequently a great number of mesogenic compounds containing thiophene ring have been synthesized and characterized [14-26]. Investigations have shown that thiophene systems have generally lower melting point than their analogous 1,4-phe-

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nylene counterparts due to a reduced packing efficiency of the molecules. In addition, thiophene-based systems possess a strong lateral dipole within their structure which promotes negative dielectric anisotropy, thus eliminating the need for lateral cyano- and fluoro-substituents which tend to increase the molecular breadth and possibly the viscosity of the system.

In this paper, for the purpose of exploring the mesomorphism of banana-shape LC baring a chiral moiety, we have synthesized and characterized a series of ferroelectric liquid crystal polymers containing banana-shape side chain mesogenic units. The mesogenic core used in this study consists of one thiophene ring in the middle linked with two other phenyl rings *via* a triple bond and carboxylic group and (S)-(-)-2-methyl-1-butanol was used as a chiral agent. The influence of different flexible alkyl spacer length on mesomorphism was investigated.

Experimental

1. Materials

α,ω-Dibromoalkanes, 10-undecen-1-ol, 4-iodophenol, 3-methyl-1-butyn-3-ol, 2-thiophenaldehyde, (S)-(-)-2-methyl-1-butanol, 4-hydroxybenzoic acid, 4-iodophenol, dicyclohexylcarbodiimide (DCC), hexamethylphosporous triamide (HMPT) and 4-dimethylamino pyridine (DMAP) were purchased from TCI Co., Ltd. and used as received. *Trans*-dichlorobis(triphenylphosphine)palladium(II) was purchased from Stren Chemicals and used as received. All solvents were dried and distilled prior to use and column chromatography on silica gel were performed using Merk Kieselgel 60 (70-230 mesh ASTM).

2. Techniques

The ^{1}H 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 differential scanning calorimeter (DSC) instrument was used for determining the thermal transitions and transition enthalpies. A Carl-Zeiss Axiophot polarizing microscope equipped with a Mellter FP 82 hot stage and a Mellter FP 80 central processor was used to observe the mesomorphic textures. RF-5301PC spectrofluorophotometer was used to record the photoluminescence intensity.

3. Monomer synthesis

Monomers were synthesized, following the same experimental procedure as shown in scheme 1. Alkenyl halides with lower carbon number (**1-3**) were synthesized from their corresponding dibromides using HMPT and their homologues with higher carbon number (**4**) were synthesized from their corresponding alcohol.

3.1 4-Iodo(phenyloxy)-1-alkene (**5-8**)

4-Iodo(phenyloxy)-1-alkenes were synthesized by etherification of 4-iodophenol with ω-bromo-1-alkene.

3.2 Typical procedure for the synthesis of 1-iodo-4-(4-pentenyloxy)benzene (**6**)

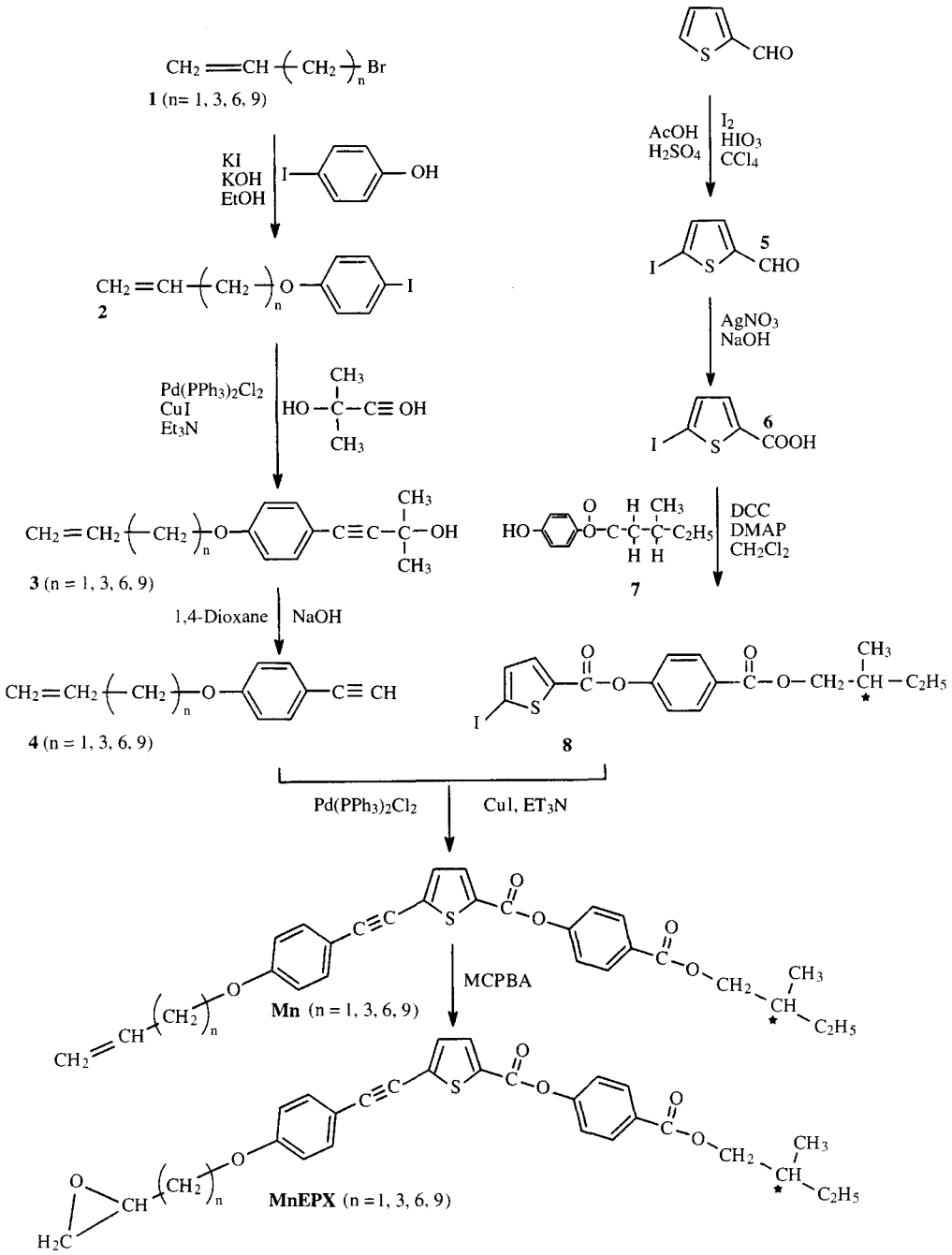
A mixture of 4-iodophenol (10 g, 45 mmol), KOH (3.3 g, 50 mmol), KI (0.2 g) and 100 mL of ethanol were mixed and stirred for 1 h under reflux conditions. 5-Bromo-1-pentene (**2**) (7.84 g, 50 mmol) was slowly added to this mixture and refluxed for another 8 h. After removing the solvent under reduced pressure, the solid was dissolved in 100 mL water, and HCl (6 N) was added slowly to adjust the pH to 6, to provide the crude product. Further purification was performed using column chromatography on silica gel eluting with EtOAc/*n*-hexane (1/8) to yield white crystals of **6**. Yield: 1.1 g (85.5%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 1.92 (m, 2H, $-CH_2-(C\underline{H}_2)-CH_2$), 2.15 (m, 2H, $-CH_2-(C\underline{H}_2)-CH_2$), 3.89 (t, 2H, $O-C\underline{H}_2-$), 4.97 (m, 2H, $C\underline{H}_2=CH-$), 5.86 (m, ^{1}H, $CH_2=C\underline{H}-$), 6.62 (d, 2H, aromatic protons), and 7.47 (d, 2H, aromatic protons). Anal. Calcd for $C_{11}H_{13}OI$: C, 45.67; H, 4.50. Found: C, 45.76; H, 4.35.

3.3 2-Methyl-4-[4-(alkenyloxy)phenyl]-3-butyn-2-ol (**9-12**)

These compounds were synthesized by the coupling reaction of 2-methyl-3-butyn-2-ol with the corresponding aryl bromides.

3.4 Synthesis of 2-methyl-4-[4-(4-pentenyloxy) phenyl]-3-butyn-2-ol (**10**)

1-Iodo-4-(4-pentenyloxy)benzene (**6**) (10.0 g, 34.6 mmol), 2-methyl-3-butyl-2-ol (120 mmol), and dry triethylamine (80 mL) in THF (100 mL), the catalysts bis(triphenylphosphine)palladium(II) chloride (0.15 g), copper(I) iodine (0.15 g) and triphenylphosphine (0.3 g) were mixed together [27] and stirred well. The mixture was refluxed for 24 h, cooled to room temperature and filtered to remove the precipitate. The filtrate was evaporated under reduced pressure to give the crude product. Purification was carried out using flash column chromatography on silica gel eluting with ethyl acetate/*n*-hexane (1/8) to yield 6.9 g (81.5%) of white crystal of **10**. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 1.67 (s, 6H, $-C((C\underline{H}_3)_2OH)$, 1.84 (m, 2H, $-CH_2-(C\underline{H}_2)-CH_2$), 2.16 (m, 2H, $-CH_2-(C\underline{H}_2)-CH_2$), 3.92



Scheme 1. Synthetic route for **Mns** and **MnEPXs**.

(t, 2H, O–C<u>H</u>$_2$–), 5.01 (m, 2H, C<u>H</u>$_2$=CH–), 5.81 (m, 1H, CH$_2$=CH–), 6.80 (d, 2H, aromatic protons), and 7.30 (d, 2H, aromatic protons). Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.69; H, 8.20. Found: C, 78.80; H, 8.11.

3.5 1-(1-Ethynyl)-4-(alkenyloxy)benzene (**13-16**)

Typical procedure for the synthesis of 1-(1-ethynyl)-4-(4-pentenyloxy)benzene **14** Sodium hydroxide (2.04 g, 51.0 mmol) was added to a solution of 2-methyl-4-[4-(4-pentenyloxy)phenyl]-3-butyn-2-ol (**10**) (5.0 g, 21.0 mmol). The mixture was refluxed for 12 h, cooled to room temperature and filtered. The filtrate was evaporated under reduced pressure and then purified using flash chromatography on silica gel to yield compound **14**. Eluent: ethyl acetate/*n*-hexane (1/8). Yield 3.3 g (85.5%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 1.83 (m, 2H, –CH$_2$–(C<u>H</u>$_2$)–CH$_2$), 2.15 (m, 2H, –CH$_2$–(C<u>H</u>$_2$)–CH$_2$), 2.97 (s, 1H, –C=C<u>H</u>), 3.90 (t, 2H, O–C<u>H</u>$_2$–),

5.01 (m, 2H, $C\underline{H}_2$=CH–), 5.80 (m, 1H, CH_2=C$\underline{H}$–), 6.81 (d, 2H, protons), and 7.35 (d, 2H, aromatic protons). Anal. Calcd for $C_{13}H_{14}O$: C, 83.87; H, 7.53. Found: C, 83.68; H, 7.66.

3.6 5-Iodo-2-thiophenecarbaldehyde (**17**)

A mixture of 2-formylthiophene (3.6 g, 32.4 mmol), iodine (3.84 g, 15.1 mmol) in carbon tetrachloride (8 mL), periodic acid (1.4 g, 7 mmol), distilled water (6 mL), acetic acid (16 mL) and H_2SO_4 (18 N, 0.24 mL) were mixed well, stirred under reflux temperature (80 °C) for 1 h and at room temperature (25 °C) for another 12 h. After washing with 2% $NaHCO_3$ the organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography eluting with mixed solvent of ethyl acetate and *n*-hexane (1/5) to yield 6.38 g (82.4%) of yellowish crystals of **17**: MS m/z 206 (M^+), and ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 7.39 (m, 2H, aromatic protons) and 9.77 (s, 1H, –C$\underline{H}$O).

3.7 5-Iodo-2-thiophenecarboxylic acid (**18**)

$AgNO_3$ (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 cooled syrup, 5-iodo-2-thiophenecarbaldehyde (5.0 g, 21 mmol) (**17**) was added and stirred for 24 h. Hot water was added to this mixture to give a solution and the solution was then filtered. To this yellowish solution, 5% HCl was added slowly to give the crude product. The crude product was recrystallized in hot water to obtain yellowish crystals of **18**: Yield: 3.9 g (72.8%). MS m/z 254 (M^+), and ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 7.39 (d, J = 3.9 Hz, 1H, aromatic proton), 7.49 (d, J = 3.9 Hz, 1H, aromatic proton), and 9.65 (s, 1H, –COO$\underline{H}$).

3.8 (S)-(-)-2-Methylbutyl-4-hydroxybenzoate (**19**)

In a round-bottomed flask, 4-hydroxybenzoic acid (5.0 g, 36 mmol), (S)-(-)-2-methyl-1-butanol (4.76 g, 54 mmol), DCC (8.2 g, 40 mmol), DMAP (0.37 g, 3 mmol) and dried THF (50 mL) were added at lower temperature and stirred overnight under N_2 at 4 °C. The solution was filtered and the filtrate was washed with 10% HCl solution and 5% $NaHCO_3$ solution and then the solvent was removed under reduced pressure to yield a crude product. The product was purified by flash chromatography on silica gel eluting with diethyl ether/dichloromethane (1.25/1) to yield 6.4 g (85.2%) of **19**. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 0.92-1.02 (m, 6H, –CH($C\underline{H}_3$)$_2$), 1.23 (m, 2H, –($C\underline{H}_2$)–), 1.85 (m, 1H, –C$\underline{H}$(CH_3)–), 4.12 (m, 2H, O–$C\underline{H}_2$–), 6.89 (d, 2H, aromatic protons), and 7.91 (d, 2H, aromatic protons). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.23; H, 7.69. Found: C, 69.35; H, 7.89.

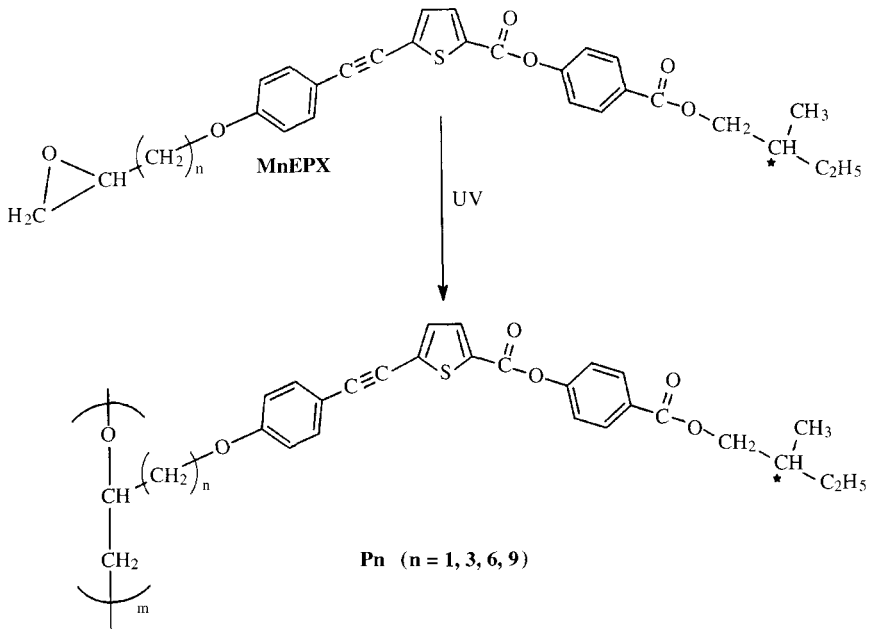
3.9 4-[((S)-(-)-2-Methylbutoxy)carbonyl]phenyl 5-iodo-2-thiophenecarboxylate (**20**)

In a round-bottomed flask, (S)-(-)-2-methylbutyl 4-hydroxybenzoate (**19**) (3.3 g, 16.0 mmol), 5-iodo-2-thiophenecarboxylic acid (3.8 g, 15.0 mmol), DCC (4.1g, 20.0 mmol), DMAP (0.24 g, 2.0 mmol) and dried THF (50 mL) were mixed at low temperature and stirred overnight under N_2 at 4 °C. The reaction mixture was filtered, and the filtrate was washed with 5% HCl solution, 5% $NaHCO_3$ solution. Further purification was effected by flash column chromatography on silica gel. A mixture of ethyl acetate/*n*-hexane (1:20) was used as eluent. Yield 4.9 g (73.4%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 0.93-1.03 (m, 6H, –C$\underline{H}_3$), 1.42 (m, 2H, –($C\underline{H}_2$)–), 1.85 (m, 1H, –C$\underline{H}$(CH_3)–), 4.20 (m, 2H, O–$C\underline{H}_2$–), 7.26 and 8.24 (dd, 4H, aromatic protons on benzene ring), and 7.30 and 7.63 (d, 2H, aromatic protons on thiophene ring). Anal. Calcd for $C_{17}H_{17}0_4SI$: C, 45.84; H, 3.82. Found: C, 45.70; H, 3.77.

3.10 4-[((S)-(-)-2-Methyl-1-butoxy)]carbonyl]phenyl-5-{2-[4-(alkyloxy)phenyl]-1-ethynyl}-2-thiophenecarboxylate (**M1**, **M3**, **M6** and **M9**)

These compounds were synthesized by the coupling reaction of 4-[((S)-(-)-2-methyl-1-butoxy)-carbonyl]phenyl 5-iodo-2-thiophenecarboxylate with [4-(1-ethynyl)phenoxy]-1-alkylene. An example for the synthesis of **M3** is outlined below:

To a solution of 4-[((S)-(-)-2-methyl-1-butoxy)-carbonyl]phenyl-5-iodo-2-thiophene-carboxylate (3.1 g, 7.1 mmol), 1-(1-ethynyl)-4-(4-pentenyloxy)-benzene (1.4 g, 7.4 mmol), and dry triethylamine (80 mL) in THF (100 mL), they catalysts bis (triphenylphosphine)palladium(II) chloride (0.045 g), copper(I) iodide (0.45 g) and triphenylphosphine (0. 1 g) were mixed and heated under reflux (80 °C) for 24 h, cooled to room temperature and the precipitated material was removed. The filtrate was evaporated under reduced pressure to give the crude product. Purification was done using flash chromatography on silica gel eluting with ethyl acetate/*n*-hexane (1/8) to yield 2.4 g (67.8%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 1.01 (m, 6H, –CH–$C\underline{H}_3$–$CH_2C\underline{H}_3$), 1.30 and 1.50 (m, 2H, –$C\underline{H}_2$–CH_3); 1.85 (m, 1H, –C$\underline{H}$(CH_3)–), 1.85 (m, 4H, –O–CH_2–CH_2–$C\underline{H}_2$–CH=), 2.24 (m, 4H, –O–CH_2–$C\underline{H}_2$–CH_2–CH=), 3.98 (t, 2H, –O–$C\underline{H}_2$–CH_2–), 4.16 and 4.21 (m, 2H, –O–$C\underline{H}_2$–CH(CH_3)$_2$–), 5.00 (m, 2H, –CH=C$\underline{H}_2$), 5.81 (m, 1H, –C$\underline{H}$=CH_2), and 6.80-8.20 (6d, 10H, aromatic protons). Anal. Calcd for



Scheme 2. Photo-polymerization of **Pns**.

$C_{30}H_{30}O_5S$: C, 71.71; H, 5.98. Found: C, 71.92; H, 6.10.

3.11 4-[((S)-(1)-2-Methyl-l-butoxy)]carbonyl]phenyl-5-(2-{4-[3-(2-oxiranyl)alkyloxy]-phenyl}-l-ethynyl)-2-thiophenecarboxylate (**MlEPX**, **M3EPX**, **M6EPX** and **M9EPX**)

Oxidation of the terminal double bond of 4-[((S)-(-)-2-methyl-1-butoxy)carbonyl]phenyl-5-{2-[4-(alkenyloxy)phenyl]-1-ethynyl}-2-thiophenecarboxylate result these compounds. An example for this procedure is given below for **M3EPX**:

To a solution of 4-[(2-methylbutoxy)carbonyl] phenyl-5-{2-[4-(4-pentenyloxy)-phenyl]-l-ethynyl}-2-thiophenecarboxylate (1.5 g, 2.9 mmol) in dried CH_2CI_2, 3-chloroperoxybenzoic acid (1.0 g, 5.8 mmol) was added. The mixture was stirred under nitrogen for 24 h and washed with KOH (10%) three times and then with water. The organic layer was dried over $MgSO_4$ and the solvent was removed under vacuum. The crude product was further purified by flash chromatography on silica gel eluting with ethyl acetate/*n*-hexane (1/9) to yield 0.98 g (65.3%) of **M3EPX**. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 1.02 (m, 6H, $-CH-C\underline{H}_3-CH_2C\underline{H}_3$), 1.32 and 1.51 (m, 2H, $-C\underline{H}_2-CH_3$), 1.84 (m, 1H, $-C\underline{H}(CH_3)-$), 1.84 (m, 4H, $-O-CH_2-CH_2-C\underline{H}_2-CH=$), 2.22 (m, 4H, $-O-CH_2-C\underline{H}_2-CH_2-CH=$), 2.44 and 2.74 (2t, 2H, $-C\underline{H}_2-$ in oxirane ring), 2.94 (m, 1H, $-C\underline{H}-$), 3.99 (t, 2H, $-O-C\underline{H}_2-CH_2-$), 4.14 and 4.20 (m, 2H, $-O-C\underline{H}_2-CH(CH_3)_2-$), 5.01 (m, 2H, $-CH=C\underline{H}_2$), 5.80 (m, 1H, $-CH=CH_2$), and 6.79-8.19 (6d, 10H, aromatic protons). Anal. Calcd for $C_{30}H_{30}O_6S$: C, 69.50; H, 5.79. Found: C, 69.71; H, 5.90.

4. Cationic photo-polymerization of MnEPXs

Polymers were synthesized by cationic photo-polymerization of the obtained monomers as shown in scheme 2. An example for the synthesis of polymer **P3** is given below:

4-[((S)-(-)2-Methyl-1-butoxy)]carbonyl]phenyl-5-2-[4-(4-pentenyl-oxy)-phenyl]-1-ethynyl-2-thiophenecarboxylate (0.5 g, 1.0 mmol), 0.01g photo-initiator (diphenyliodonium-hexafluoroarsenate) were dissolved in 5 mL of CH_2C1_2. The mixture was stirred for 10 min to make sure the monomer and photo-initiator were well mixed. After removing the solvent under vacuum, the monomers were placed on a heated glass slide (the temperature was controlled within the mesomorphic temperature range of monomers) and then radiated with high power UV radiation for 10 min. The obtained polymers were purified by reprecipitation from methanol for three times. The completion of the polymerization of epoxide moieties was confirmed by the disappearance of peaks on ^{1}H NMR spectrum of **M9EPX** over the range 2-3 ppm.

Results and Discussion

1. Phase behavior of low molar mass compounds

The phase sequences were determined by microscopic observation, and the transition temperatures were measured by differential scanning calo-

Table I. Phase transitions and transition enthalpy[a] changes for **Mns** and **MnEPXs**.

Compound	Phase transitions/°C (Corresponding enthalpy changes/Kacl·mol)[b] Heating / Cooling
M1	$\frac{Cr_1\ 73.5\ (13.0)\ Cr_2\ 108.3\ (10.9)\ I}{I\ 74.5\ (-0.2)\ Ch\ 51.6\ (-0.1)\ S_A\ 37.2\ S_m\ blue}$
M3	$\frac{Cr\ 81.4\ (13.4)\ Ch\ 91.2\ (-)\ I}{I\ 88.3\ (-0.2)\ Ch\ 76.1\ (-0.5)\ S_A\ 37.1\ (-9.7)\ S_m\ blue}$
M6	$\frac{Cr\ 98.4\ (16.8)\ I}{I\ 81.3\ (-0.3)\ Ch\ 75.6\ (-1.2)\ S_A\ 22.0\ (-)\ S_C^*\ 10.8\ (-2.8)\ S_m\ blue}$
M9	$\frac{Cr\ 59.1\ (15.6)\ S_A\ 93.5\ (1.8)\ I}{I\ 86.5\ (-1.7)\ S_A\ 58.8\ (-0.1)\ S_C^*\ 11.9\ (-0.4)\ S_X - 2.4\ (-5.8)\ S_m\ blue}$
M1EPX	$\frac{Cr\ 109.7\ (16.7)\ I}{I\ 84.7\ (-0.3)\ Ch\ 42.7\ (-0.2)\ S_A\ 22.9\ (-6.4)\ S_m\ blue}$
M3EPX	$\frac{Cr\ 76.6\ (12.9)\ Ch\ 88.3\ (1.0\ I}{I\ 84.7\ (-0.3)\ Ch\ 67.7\ (-0.5)\ S_A\ 27.9\ (-7.4)\ S_m\ blue}$
M6EPX	$\frac{Cr\ 96.8\ (21.1)\ I}{I\ 90.5\ (-0.3)\ Ch\ 76.6\ (-0.6)\ S_A\ 24.5\ (\bullet)\ S_x\ 12.5\ (-0.4)\ S_m\ blue}$
M9EPX	$\frac{Cr\ 59.4\ (12.1)\ S_A\ 78.5\ (0.5)\ Ch\ 86.7\ (1.1)\ I}{I\ 82.7\ (-0.3)\ Ch\ 74.5\ (-0.5)\ S_A\ 34.8\ (\bullet)\ S_C^*\ 21.8\ (-0.1)\ S_X\ 10.7\ (-0.1)\ S_m\ blue}$

(a) Transition determined by POM observation.
(b) Cr: Crystal, Ch: Cholestorie; S_A: Smectic A; S_C^*: Chiral smectic C; I: Isotropic.

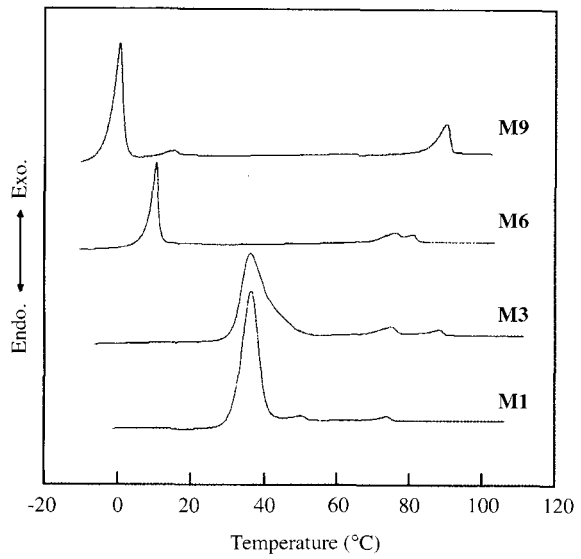


Figure 1. DSC thermograms of **Mns**.

rimetry on heating and cooling with a scanning rate of 10 °C/min. The phase transition temperatures and transition enthalpies of **Mns** and **MnEPXs** were summarized in Table I, where the following observations were noticed. (i) All the cooling scans exhibit more mesophases than heating scans; (ii) **Mns** and **MnEPXs** compounds all show cholesteric, S_A and S_m blue phases except for **M9**; (iii) **M1**, **M6**, **M1EPX** and **M6EPX** exhibit monotropic mesophases while **M3**, **M9**, **M3EPX** and **M9EPX** show enantiotropic mesophases; (iv) S_C^* phase was observed only on **M6**, **M9** and **M9EPX** which contained lengthier spacer.

Figure 1 depicts the DSC cooling curves of **Mns** series. **M1** and **M3** show very similar thermal behavior. When these samples were cooled down from isotropic state, a small exothermic peak was observed on the DSC traces of **M1** and **M3**. The peaks were assigned as isotropic to Ch transition because the small enthalpy represents a minor order change between the two phases. When the temperature was further lowered, another small peak which was attributed to the Ch–S_A transition, was found on the DSC traces of **M1** and **M3**. This S_A phase changes directly to a more ordered Sm blue phase at even lower temperature. Taking **M1** as an example, it shows an isotropic to cholesteric transition at 74.5 °C, a cholesteric to S_A transition at 51.6 °C and a S_A to smectic blue phase transition at 37.2 °C. Figure 2 depicts cholesteric oily streaks, smectic focal conical fan and blue phase textures exhibited by **M1**. The DSC trace of **M6** shows an isotropic to cholesteric transition at 81.3 °C, a cholesteric to S_A transition at 75.6 °C, an undetectable S_A to chiral smectic C (S_C^*) at 22.0 °C and a S_C^* to smectic

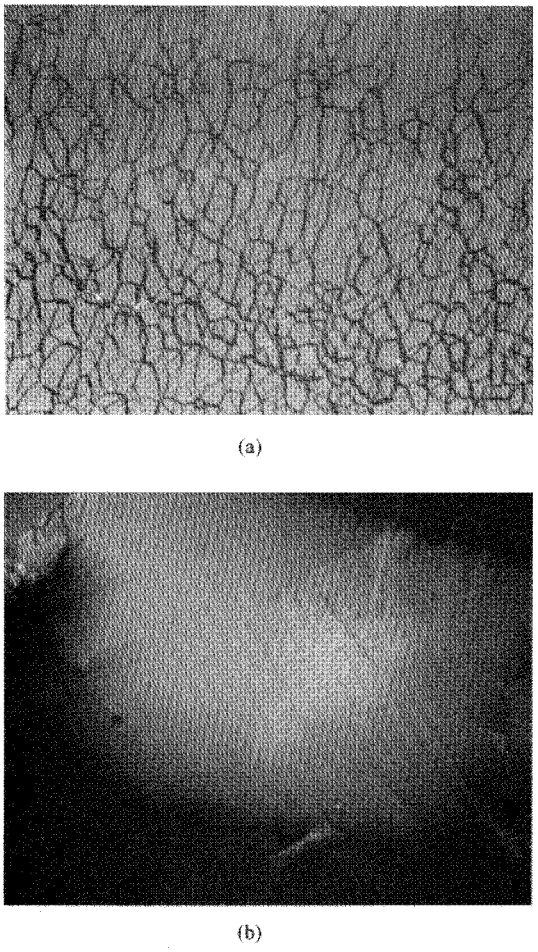


Figure 2. Optical polarizing micrographs displayed by M1: (a) cholesteric phse at 70 °C (200×) and (b) smectic blue phase at 30 °C (200×).

blue phase at 10.8 °C. For **Mns** series, **M9** is the only compound which shows no cholesteric phase. It shows an isotropic to S_A transition at 86.5 °C, a S_A to chiral smectic C transition (S_C*) at 58.8 °C, a S_C* to an unidentified S_X at 11.9 °C and a S_X to smectic blue phase at -2.4 °C. Figure 3 depicts the smectic spiral fan, S_C* and unidentified S_X textures exhibited by **M9**.

It is well known that the thermal transitions of the liquid crystals are strongly influenced by their flexible spacers. Figure 4 shows the mesophase transition temperatures of **Mns** observed on cooling scans. It shows that the clearing temperatures fluctuate a little when flexible spacer length varies and this is in consistent with the results published earlier [28,29]. Furthermore, the S_A temperature range increases with increasing spacer length while the cholesteric temperature range decreases.

For **MnEPX** series, the oxidation of terminal double bond into epoxide moiety slightly changes the mesomorphism. Figure 5 shows the DSC curves

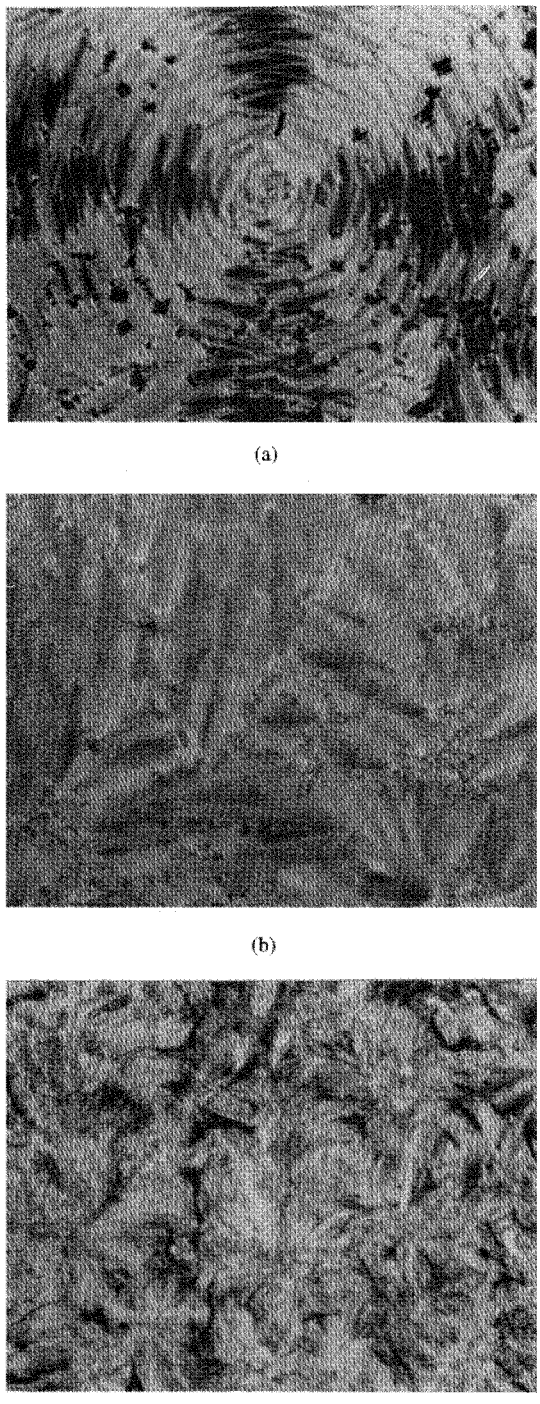


Figure 3. Optical polarizing micrographs displayed by M9: (a) S_A phase at 70 °C (200×), (b) S_C* phase at 45 °C (200×), and (c) S_X phase at 20 °C (200×).

of **MnEPXs**. In comparison with their double bond counterparts, there are some minor changes in their DSC scans. These includes the appearance of Ch phase in **M9EPX** and the disappearance of S_C* in **M6EPX**. For the DSC trace of **M9EPX**, it shows an isotropic to Ch transition at 82.7 °C, a Ch to S_A

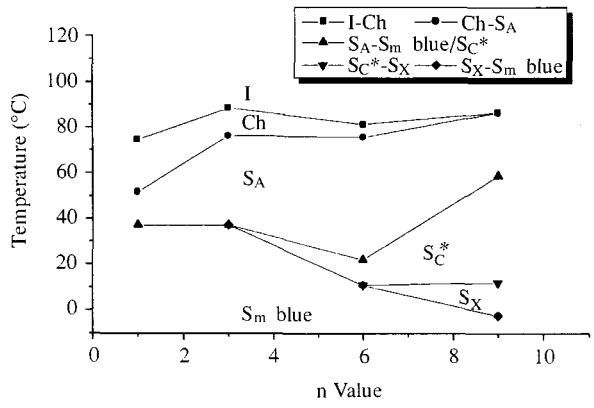


Figure 4. Plot of transition temperatures versus n for **Mns**.

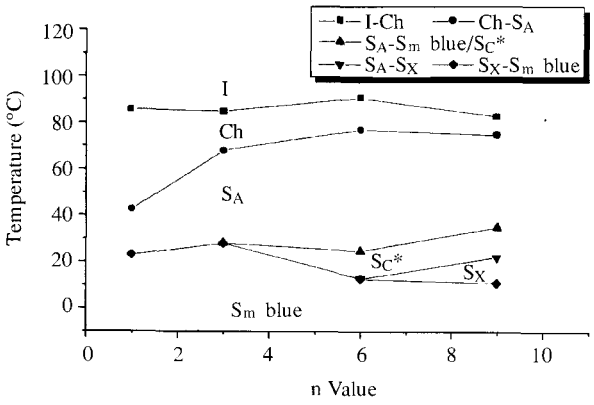


Figure 6. Plot of transition temperatures versus n for **MnEPXs**.

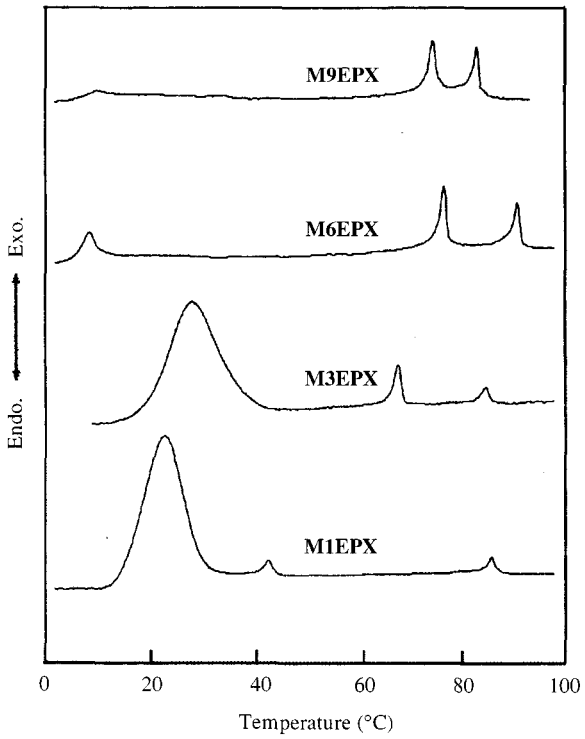


Figure 5. DSC thermograms of **MnEPXs**.

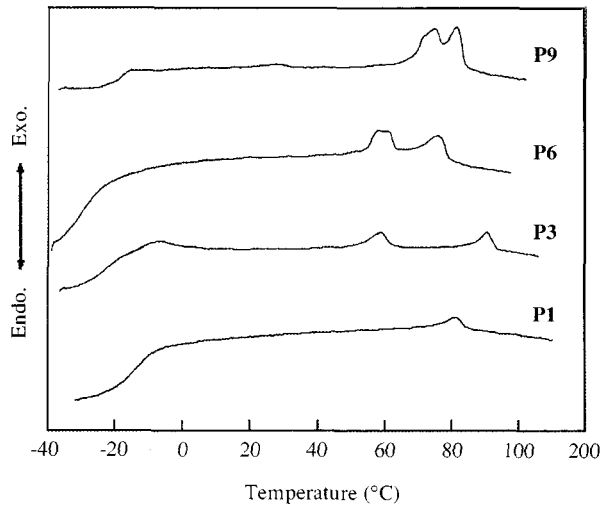


Figure 7. DSC thermograms of **Pns**.

transition at 74.5 °C, a S_A to S_C* transition at 34.8 °C, a S_C* to S_X transition at 21.8 °C, and a S_X to S_m blue transition at 10.7 °C. Figure 6 shows the transition temperatures observed on DSC cooling scans of compound **MnEPXs**. The cholesteric temperature range decreases with increasing the spacer length while the S_A temperature range goes toward the opposite trend. It is observed that the introduction of polar epoxide moiety tends to facilitate the formation of the cholesteric phase.

2. Phase behavior of polymers

The transition temperatures and transition enthalpies of **Pns** were summarized in Table II and their DSC curves were shown in Figure 7. All polymers show enantiotropic cholesteric mesophases and observable glass transition temperatures. When **P9** was cooled down from isotropic state, oily streaks were found as shown in Figure 8(a), indicating the formation of cholesteric phase. These oily streaks changed to homeotropic S_A texture as illustrated in Figure 8(b) and then entered to S_C* at lower temperature (see Figure 8(c)). This S_C* texture was frozen at temperature under T_g.

3. Photoluminescence measurement

The photoluminescence property of these compounds is measured in their solution state using $CHCl_3$ as solvent. Compounds were dissolved into $CHCl_3$ solution to prepare 10^{-4} M solution. The exciting wavelength was set to be 375 nm. Figure 9 shows the photoluminescence spectrum of **M9EPX** and λ_{max} was located at 475 nm. The photolumines-

Table II. Phase transitions(a) and transition enthalpy changes for **Pns**.

Compound	Phase transitions/°C (Corresponding enthalpy changes/Kacl·mol)[b] Heating / Cooling
P1	$\frac{T_g - 14.8\ S_A\ 56.6\ (5.1)\ Ch\ 84.0\ (0.1)\ I}{I\ 81.7\ (-0.2)\ Ch - 11.9\ T_g}$
P3	$\frac{T_g - 18.6\ S_A\ 75.2\ (8.3)\ Ch\ 94.7\ (0.2)\ I}{I\ 91.7\ (-0.2)\ Ch\ 59.2\ (-0.2)\ S_A - 19.8\ T_g}$
P6	$\frac{T_g - 25.4\ S_X\ 63.4\ (\bullet)\ S_A\ 66.0\ (4.5)\ Ch\ 79.2\ (0.2)\ I}{I\ 70.5\ (-0.2)\ Ch\ 54.1\ (-0.2)\ S_A - 28.1\ T_g}$
M9	$\frac{T_g\ 6.4\ S_{X1}\ 44.6\ (\bullet)\ S_{X2}\ 54.3\ (5.0)\ S_C{}^*\ 79.9\ (\bullet)\ S_A\ 82.3\ (\bullet)\ 86.8\ (0.8)\ I}{I\ 82.7\ (\bullet)\ Ch\ 79.3\ (\bullet)\ S_A\ 75.2\ (-0.9)\ S_C{}^*\ 4.5\ T_g}$

(a) Overlapped transitions.
(b) T_g: Glassy; Cr: Crystal, Ch: Cholestoric; S_A: Smectic A; $S_C{}^*$: Chiral smectic C; I: Isotropic.

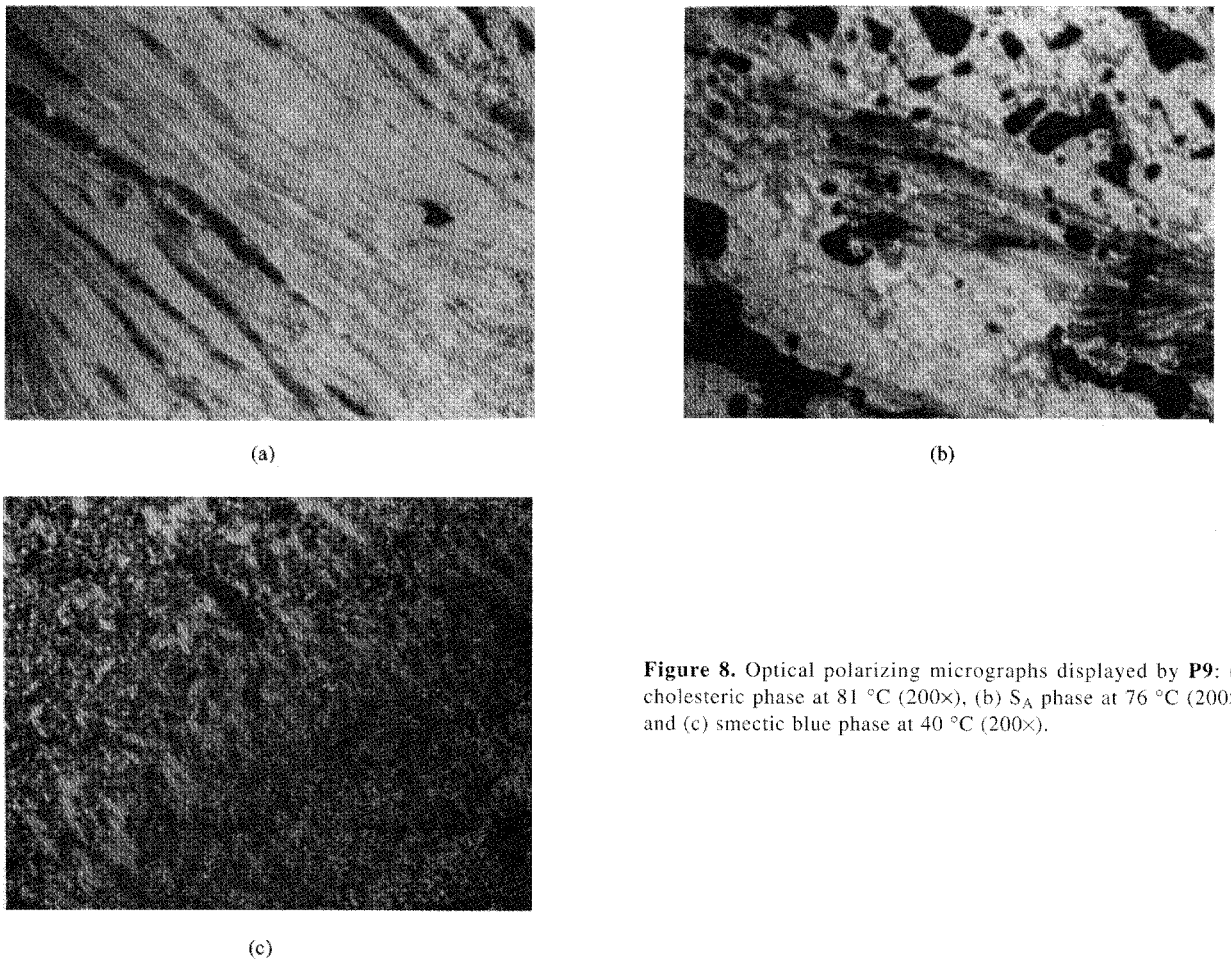


Figure 8. Optical polarizing micrographs displayed by **P9**: (a) cholesteric phase at 81 °C (200×), (b) S_A phase at 76 °C (200×), and (c) smectic blue phase at 40 °C (200×).

cence property of these compounds is attributed to their highly conjugated core structure.

Conclusion

A series of ferroelectric liquid crystal polymers having banana-shaped mesogens which includes 2, 5-disubstituted-thiophene were synthesized and characterized. These low molar mass banana-shape compounds showed cholesteric and smectic blue phase. Compounds having longer spacer revealed a $S_C{}^*$ phase besides the cholesteric and smectic blue phases. The clearing temperatures of these low mo-

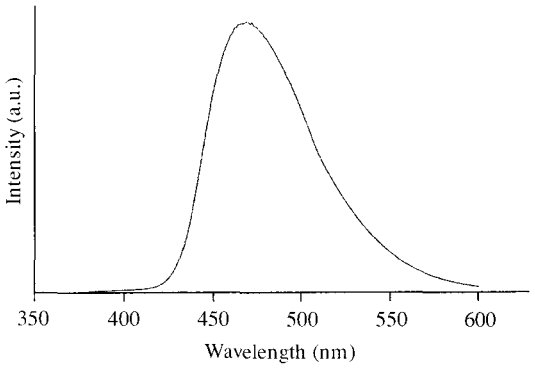


Figure 9. photoluminescent spectrum of **M9EPX**.

lar mass compounds remained nearly unchanged (fluctuates within 10 °C) when the flexible spacer was extended. All the polymers show cholesteric mesophases and observable glass transitions. Like low molar mass compounds S_C^* was also observed for polymer having longer spacer.

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