

## Characterization of Ferroelectric Liquid Crystalline Polythiophene Derivatives

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**Abstract:** Chiral liquid crystalline (LC) substituent with fluorine-containing asymmetric moiety was introduced into the 3-position of thiophene ring. Polymerizations of 2,5-dibrominated thiophene derivatives were carried out through dehalogenative polycondensations. Polythiophene derivatives thus prepared were fusible and soluble in ordinary organic solvents. Absorption band was observed in the range from 400 to 415 nm. Phase transition behaviors of the polymers and monomers were examined by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction analysis. The polymers showed several types of smectic phases in the heating and cooling processes. Besides, one of the polymers exhibited a striated fan-shaped texture in polarizing optical microscope. This is attributed to a formation of chiral smectic C (Sc\*) phase, which is indispensable for ferroelectricity. The ferroelectric behavior was also confirmed by examining the temperature dependence of dielectric constant of the polymer.

**Key word:** Polythiophene, Conjugating polymer, Ferroelectricity, Liquid crystal, Dielectric constant.

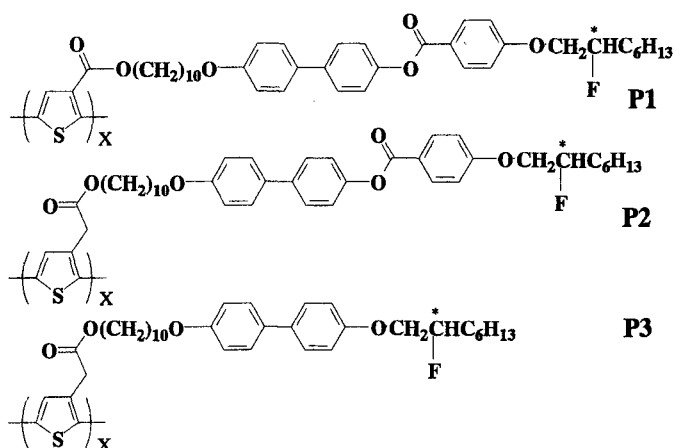
### 1. INTRODUCTION

Various types of liquid crystalline (LC) conjugated polymers have been successfully synthesized to cultivate fruitful molecular electronics [1-8]. Polythiophene derivative with LC side chain is one of the most intriguing polymer [6], because its profound electrical and optical properties are expected to be controlled using molecular orientation of LC side chain. It is well known that ferroelectric LC (FLC) molecules have abilities to respond more quickly to the electric field used as an external force than ordinary LC ones, and that the ferroelectric liquid crystallinity owes to spontaneous polarization generated in chiral smectic C phase [7]. In this study we synthesized novel FLC polythiophene derivatives through introduction of fluorine-containing chiroptical LC group into the 3-position of the thiophene ring.

### 2. EXPERIMENTAL SECTION

Three types of polythiophene derivatives containing fluorinated asymmetric moiety in the LC side chains were synthesized (Scheme 1). Characterizations of the polymers and corresponding monomers were carried out by means of different scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD).

All <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured with a BRUKER 500 MHz FT-NMR spectrometer. CDCl<sub>3</sub> was used as non-proton solvent and TMS was used as internal standard. Infrared spectra were measured with a Jasco FT-IR 550 spectrometer using KBr method. Phase transition temperatures were determined using a Perkin-Elmer differential scanning calorimeter (DSC 7) with a constant heating/cooling rate of 10 °C/min, and texture observations were made using a Nikon polarizing microscope equipped with a Linkam THMS 600 hot stage. The molecular weights of polymers were determined by gel permeation chromatography (GPC) equipped with a Shodex A-80M



Scheme 1 Structures of polythiophene derivatives.

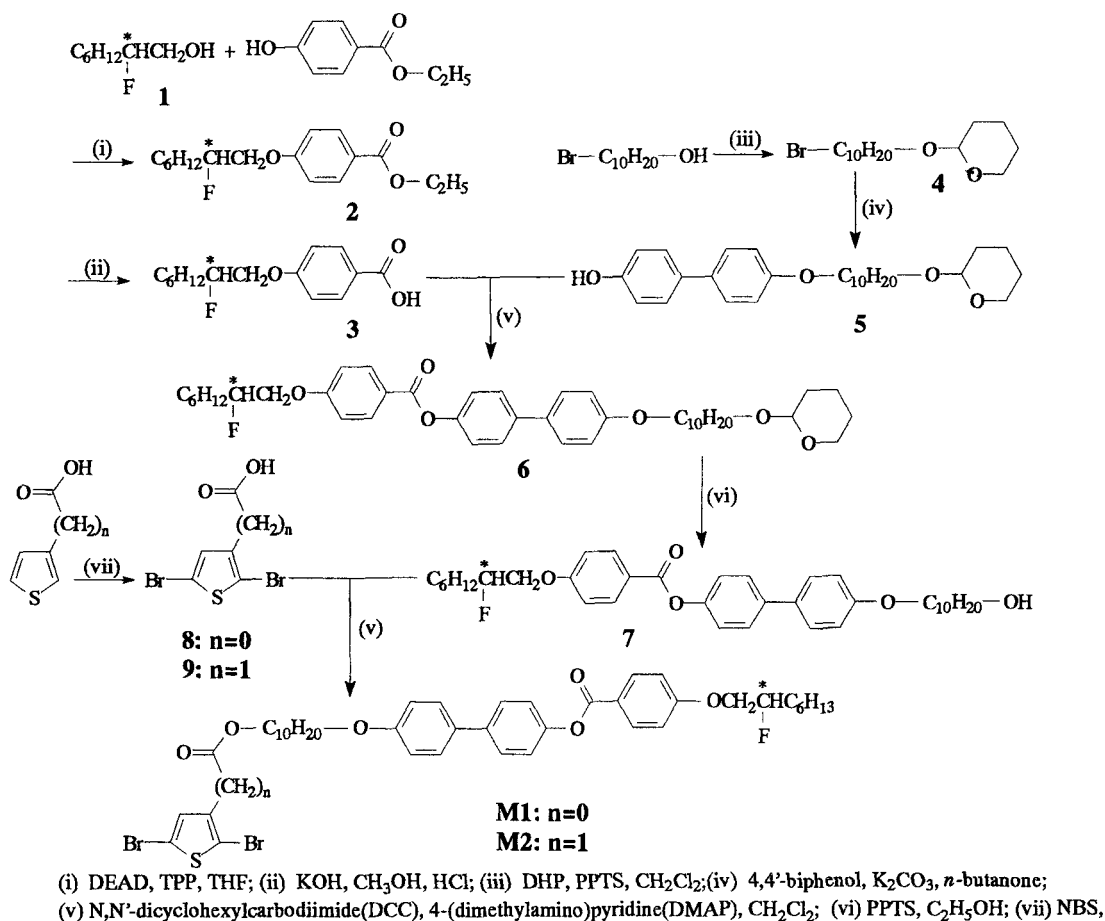
column and a Jasco HPLC 870-UV detector, and THF was used as solvent during measurements. XRD measurements were performed with a Rigaku D-3F diffractometer, in which X-ray power and scanning rate were set at 200 mW and 5 deg/min, respectively.

### 3. RESULTS AND DISCUSSION

The synthetic routes of monomers and polymers are shown in Schemes 2. The chiral alcohol (*S*)-(-)-2-fluorooctanol (**1**) was prepared according to the method suggested by Nohira et al [9], in which (*R*)-(+)-1,2-epoxyoctane was reacted with pyridinium poly (hydrogen fluoride) in ether.

Table 1 Polymerization of liquid crystalline polythiophene derivatives

Polym	Mn	Mw	Mw / Mn	D.P.
P1	12000	47400	3.9	17
P2	11600	54800	4.7	16
P3	4800	12800	2.6	8



Scheme 2 Synthesis of monomer M1 and M2

Table 2 Phase transition temperatures of LC precursor, monomers, and polymers

Compound	Phase transition temperature (°C)	
	Heating	Cooling
3	C 105 S <sub>x</sub> 121 N* 138 I	I 135 N* 118 S <sub>x</sub> 96 C
6	C 89 S <sub>x</sub> 98 S <sub>c</sub> * 141 N* 151 I	I 149 N* 139 S <sub>c</sub> * 96 S <sub>1</sub> * 85 S <sub>J</sub> * 77 C
7	C 152 S <sub>c</sub> * 159 N* 180 I	I 176 N* 150 S <sub>c</sub> * 136 C
M1	C 79 S <sub>B</sub> 86 S <sub>c</sub> * 102 S <sub>A</sub> 131 N* 139 I	I 138 N* 131 TGB <sub>A</sub> 130 S <sub>A</sub> 94 S <sub>c</sub> * 85 S <sub>B</sub> 52
M2	C 59 C <sub>1</sub> 71 S <sub>x</sub> 92 S <sub>c</sub> * 104 S <sub>A</sub> 128 N* 132 I	I 131 N* 127 S <sub>A</sub> 104 S <sub>c</sub> * 90 S <sub>x</sub> 50 C
P1	G 197 S <sub>A</sub> 203 I	I 174 S <sub>A</sub> 147 G
P2	G 133 S <sub>B</sub> 160 S <sub>c</sub> * 176 S <sub>A</sub> 201 I	I 198 S <sub>A</sub> 162 S <sub>c</sub> * 142 S <sub>B</sub> 130 G
P3	G 95 S <sub>A</sub> 100 I	I 98 S <sub>A</sub> 96 S <sub>x</sub> * 92 G

I: isotropic, N\*: chiral nematic, S<sub>A</sub>: smectic A, S<sub>B</sub>: smectic B, S<sub>c</sub>\*: chiral smectic C, S<sub>1</sub>\*: chiral smectic I, S<sub>J</sub>\*: chiral smectic J, TGB<sub>A</sub>:twist grain boundary A, G: glassy state, C, C<sub>1</sub>: crystal, S<sub>x</sub>: unidentified (chiral) smectic phases.

In Scheme 2, ethyl 4-[(*S*)-2-fluorooctoxy] benzoate (2) was synthesized by coupling 1 with ethyl *p*-hydroxybenzoate, according to the Mitsunobu reaction in THF [10,11]. The basic hydrolysis of 2 with KOH in a solution of methanol and water gave rise to 4-[(*S*)-2-fluorooctoxy] benzoic acid (3).

The hydroxyl group of 10-bromodecanol was protected as a tetrahydropyranyl ether (4). Compound 5 was prepared by reacting 4 with 4,4'-dihydroxybiphenyl in the presence of K<sub>2</sub>CO<sub>3</sub>. Besides, the esterification between 5 and 3 in the presence of dicyclohexylcarbodiimide (DCC) and

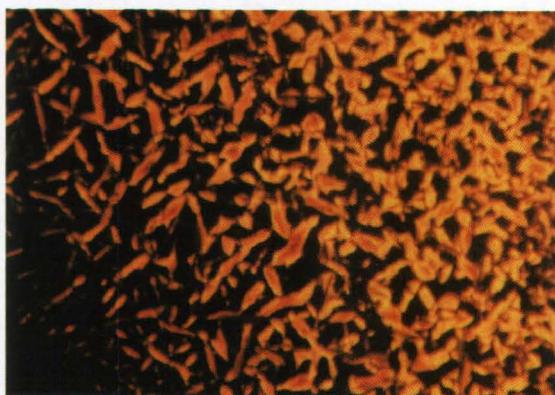


Figure 1 Polarizing optical micrograph of **P1**.  
Batonnets texture  $S_A$  phase at 200 °C

4-dimethylaminopyridine (DMAP) gave rise to compound **6**. Deprotection of **6** was carried out in presence of pyridinium *p*-toluenesulfonate (PPTS), giving compound **7**.

Bromination of thiophene-3-carboxylic acid and 2-(3-thienyl)acetic acid with *N*-bromosuccinimide (NBS) in DMF resulted in the formation of 2,5-dibromothiophene-3-carboxylic acid (**8**) and 2-(2,5-dibromo-3-thienyl)acetic acid (**9**). The 2,5-dibrominated thiophene monomers, **M1** and **M2**, were synthesized by esterification between **7** and **8**, and **7** and **9**, respectively, under the same condition as that of the synthesis of **6**.

The other type of thiophene monomer, **M3** was synthesized as similar to Scheme 2, but two aromatic rings were employed in the mesogenic core.

The LC groups of **M1** and **M2** are composed of a biphenyl moiety linked with a phenyl moiety via an ester linkage as a mesogenic core, a decamethylene chain as a spacer, and (*S*)-2-fluorooctyloxy group as a terminal moiety. Meanwhile, the LC group of **M3** is composed of a biphenyl moiety as a mesogenic core, and a decamethylene chain as a spacer, and (*S*)-2-fluorooctyloxy group as a terminal moiety. The polymerizations of 2,5-dibrominated thiophene monomers were carried out through dehalogenative

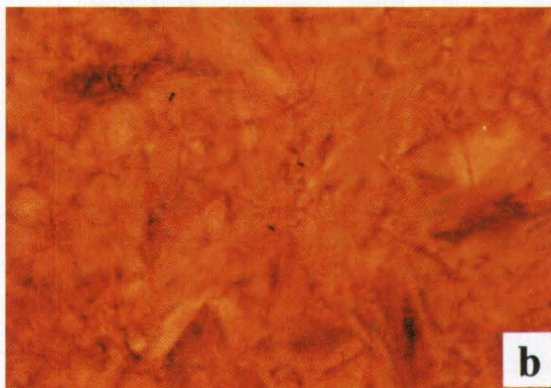
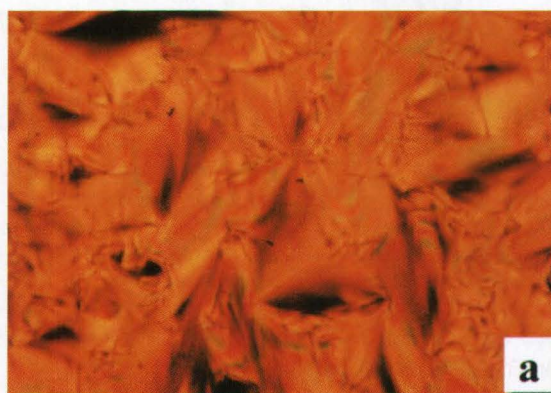


Figure 2 Polarizing optical micrographs of **P2**.  
Fan-shaped texture of  $S_A$  phase at 194 °C (a);  
Striated fan-shaped texture of  $S_C^*$  phase at 144 °C (b).

polycondensation, giving poly (3-FLC substituted thiophene) derivatives, **P1**, **P2** and **P3**.

All polymers synthesized (**P1**, **P2** and **P3**) were fusible and soluble in common organic solvents including tetrahydrofuran (THF). Number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights of **P1**, **P2** and **P3** are summarized in Table 1.  $M_n$  are from 4800 to 12000, and  $M_w$  are from 12800 to 54800.

All polymers exhibited mesophases. Phase transition temperatures are summarized in Table 2. **P1** showed enantiotropic  $S_A$  phases (Fig. 1). **P2** showed enantiotropic  $S_A$ ,  $S_C^*$  and  $S_B$  phases (Fig. 2). XRD pattern of **P2** measured in the LC phase at 180 °C showed two reflection peaks corresponding to the distances of 4.60 and 37.6 Å. The optical textures of  $S_A$  phases of **P2** are shown in Fig. 2 (a). When the temperature was lowered to 160 °C, the *d*-spacing of the small angle reflection decreased from 37.6 to 35.4 Å, suggesting the formation of  $S_C^*$  phase. A striated fan-shaped texture of  $S_C^*$  phase of **P2** was observed at this temperature (Fig. 2, b). When the temperature was further lowered to 135 °C, the

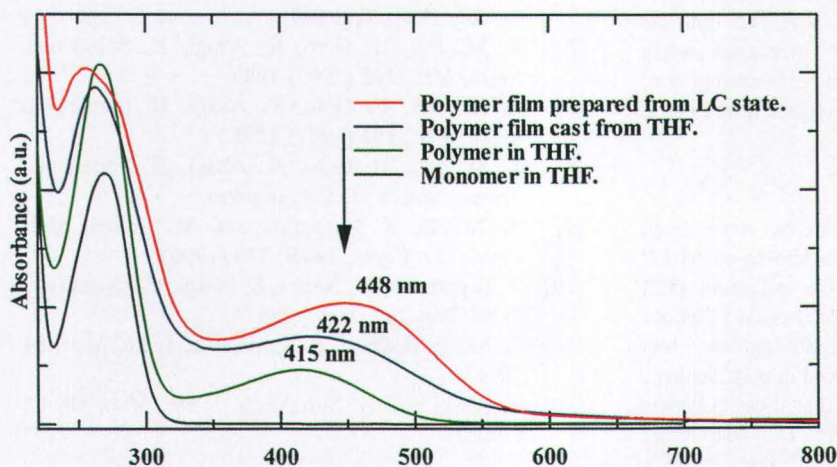


Figure 3 UV-Vis Spectra of film and in solvent for **P1** and **M1**

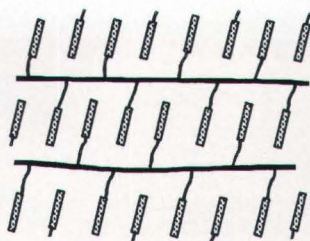


Figure 4 Molecularly assembled structure of LC-polythiophene derivatives in the smectic phase

$d$ -spacing of the small angle reflection increased from 35.4 to 39.1 Å and the wide angle reflection became sharp. This result suggests the formation of  $S_B$  phase. This structure remained unchanged in its glass state. This is the first observation of  $S_C^*$  phase in LC polythiophene derivatives, which allows us to expect an evolution of ferroelectricity in this polymer. On the other hand, **P3** showed  $S_A$  and  $S_X^*$  phases on the cooling process. XRD analysis suggested that **P3** may have a higher order smectic phase.

Fig. 3 shows UV-Vis absorption spectra of **P1** as well as the corresponding monomer (**M1**). Two absorption bands at 267 and 415 nm observed in THF solution of **P1** are assigned to the  $\pi-\pi^*$  transition of the mesogenic core of the side chain and that of the conjugated main chain, respectively. In fact, **M1** only showed an absorption band at 265 nm, which is assigned to the  $\pi-\pi^*$  transition of mesogenic substituent. The absorption band of the conjugated main of **P1** was slightly red-shifted to 422 nm in case of cast film. This may be due to the in-plane alignment [12] occurred in the cast film.

It is of interest to note that the remarkable red-shift to 448 nm was observed, when the cast film was heated up to the isotropic phase and then cooled down through LC state to the solid state. This shift can be rationalized with the enhancement of  $\pi$ -conjugation of the main chain. Namely, the alignment of the main chain, that is associated with spontaneous orientation of the LC side chain occurring in the LC phase, should give rise to an increase of coplanarity of the main chain (Fig. 4). The same red-shift were also observed in **P2**.

The temperature dependence of dielectric constant of **P2** is showed in Fig. 5. It was observed that the dielectric constant was suddenly increased when temperature was lowered from the temperature region of  $S_A$  to that of  $S_C^*$  phase. This is a typical ferroelectric behavior of FLC.

#### 4. CONCLUSION

Novel LC polythiophene derivatives have been synthesized by introducing fluorine-containing chiral LC group into side chains. One of the polymers (**P2**) showed  $S_C^*$  phase with an enantiotropic behavior, whose LC temperature region was as wide as 20 degrees. It is the first case that  $S_C^*$  phase was observed in polythiophene derivatives. It is therefore expected that these polymers should be feasible for ferroelectric LC conducting materials. It was also found that the effective

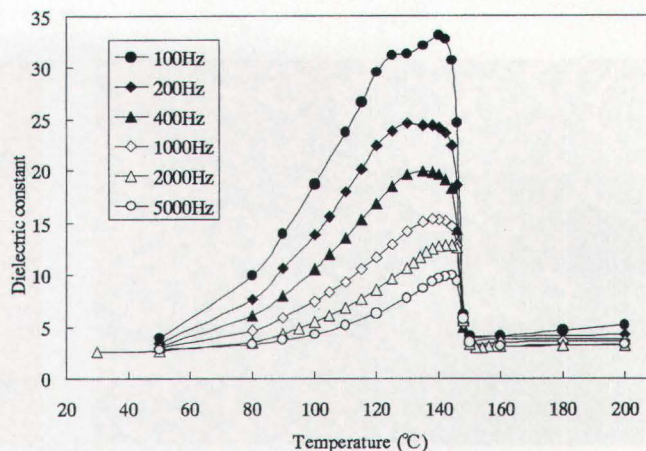


Figure 5 The temperature dependence of dielectric constant of **P2**

conjugation length of the main chain increased after the spontaneous orientation of the LC side chains. The ferroelectric behavior was confirmed by examining the temperature dependence of dielectric constant of the polymer.

#### 5. ACKNOWLEDGMENTS

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