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# **Synthesis and Properties of Polythienylene Derivatives with Fluorine-Containing Chiral Liquid Crystalline Substituents (I)**

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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. Polythienylene derivatives thus prepared were fusible and soluble in ordinary organic solvents. Phase transition behaviors of the polymers and monomers were examined by differential scanning calorimetry, polarizing optical microscope, and X-ray diffraction. The polymers and precursors showed several types of mesophases 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 ( $S_C^*$ ) phase, which is indispensable for ferroelectricity.

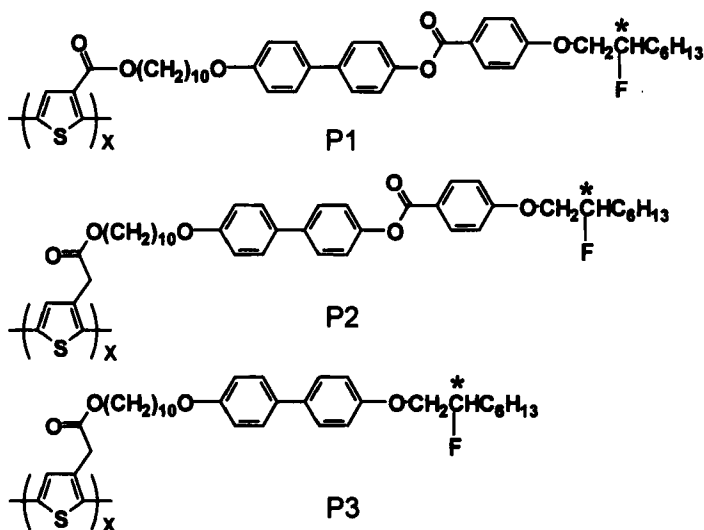
**Keywords:** conjugated polymers; polythienylene derivatives; ferroelectricity; chiral smectic C phase

## **INTRODUCTION**

Various types of liquid crystalline (LC) conjugated polymers have been successfully synthesized to cultivate fruitful molecular electronics [1-8]. Polythienylene (so-called Polythiophene) derivatives with LC side

chain is one of the most intriguing polymer [5,6], 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 [7,8]. In this study we synthesized novel FLC polythienylene derivatives through introduction of fluorine-containing chiroptical LC group into the 3-position of the thiophene ring.

## EXPERIMENTAL SECTION



Scheme 1

Three types of polythienylene derivatives containing fluorinated asymmetric moiety in the LC side chains were synthesized, as shown in 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).

## RESULTS AND DISCUSSION

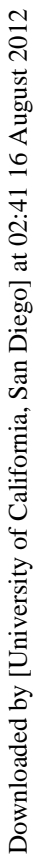
Chiral LC monomers, **M1** and **M2**, were synthesized using the synthetic routes shown in Schemes 2. **M1** and **M2** are composed of a biphenyl moiety linked with a phenyl moiety via an ester linkage as a mesogenic core, a decamethylene or a hexamethylene chain as a spacer, and (*S*)-2-fluorooctyloxy group as a terminal moiety.

The other type of thiophene monomer, **M3** was synthesized with a similar manner to Scheme 2, although the mesogenic core was just biphenyl moiety, but not three rings moiety adopted in **M1** and **M2**.

The polymerizations of 2,5-dibrominated thiophene monomers were carried out through dehalogenative polycondensations. Thus polythienylene derivatives with chiral LC substituents at the 3-position

TABLE I Polymerization results of chiral LC polythienylene derivatives

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



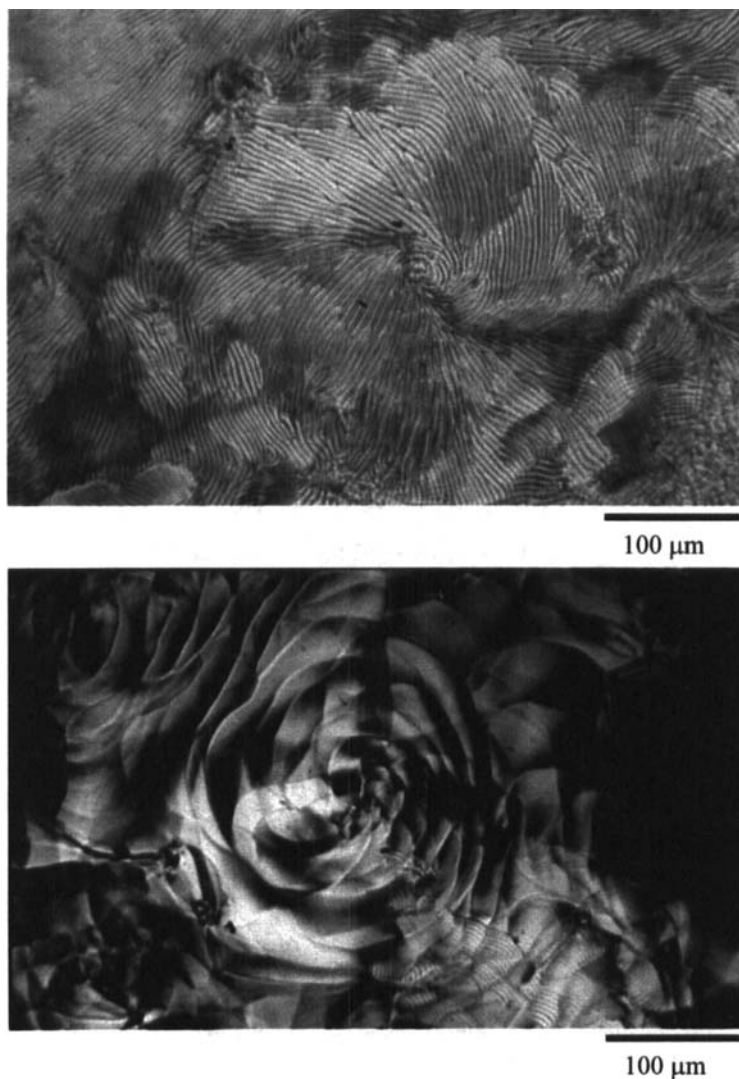
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TABLE II Phase transition temperatures of LC precursors, monomers, and polymers

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

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>I</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.



**FIGURE 1** Polarizing optical micrographs of compound **6**.  
Shell-printed texture of chiral smectic C ( $S_C^*$ ) phase at 104 °C (upper);  
Rose - like texture of chiral smectic I ( $S_I^*$ ) phase at 91 °C (lower)  
See Color Plate XXVI at the back of this issue.



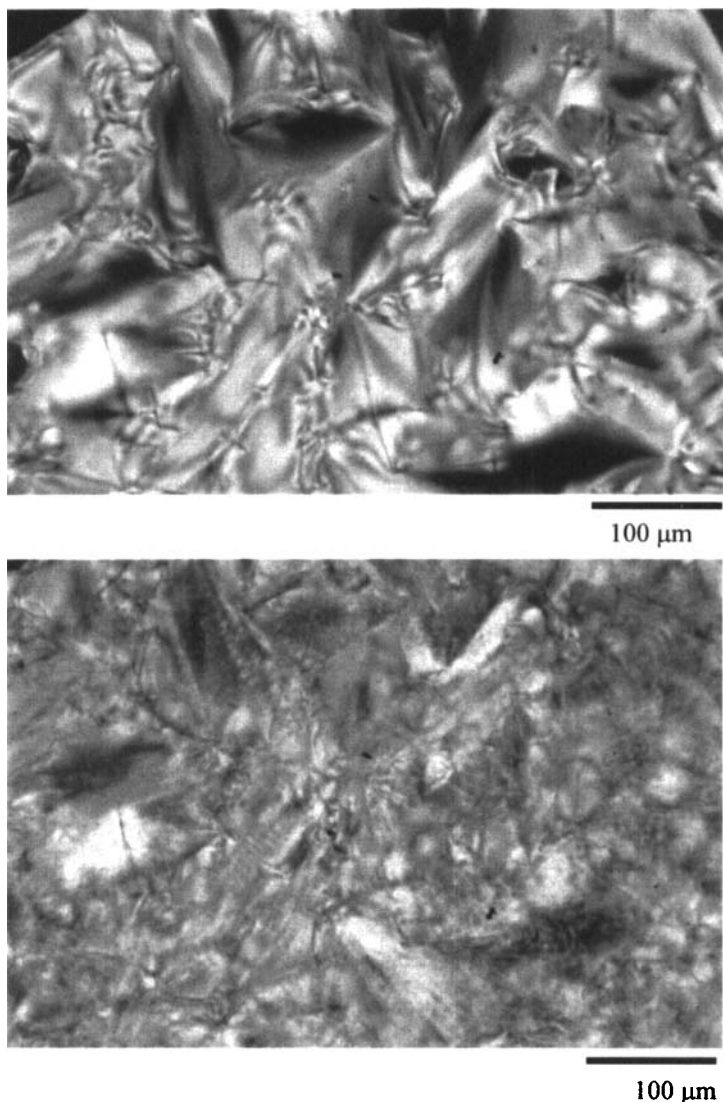


FIGURE 2 Polarizing optical micrographs of **P2**.

Fan-shaped texture of smectic A ( $S_A$ ) phase at 194 °C (upper);  
 Striated fan-shaped texture of chiral smectic C ( $S_C^*$ ) phase at  
 144 °C (lower). See Color Plate XXVII at the back of this issue.

of the thiophene rings, **P1**, **P2** and **P3**, were synthesized.

All polymers were fusible and soluble in common organic solvents including tetrahydrofuran (THF). Number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights of polymers are summarized in Table 1.  $M_n$  and  $M_w$  were 4800 to 12000 and 12800 to 54800, respectively. All polymers and precursors exhibited mesophases. Phase transition temperatures are summarized in Table II. The precursor **6** exhibited an enantiotropic nature of chiral nematic ( $N^*$ ), smectic  $C^*$  ( $S_C^*$ ), and chiral smectic I ( $S_I^*$ ) phase, a shell-printed texture of  $S_C^*$  phase and a rose-like texture of  $S_I^*$  phase are clearly seen in Fig. 1. The thiophene monomers, **M2** and **M3**, showed enantiotropic  $N^*$ ,  $S_A$  and  $S_C^*$  phases. **P1** showed an enantiotropic  $S_A$  phase. **P2** showed enantiotropic  $S_A$ ,  $S_C^*$  and  $S_B$  phases. A fan-shaped texture of  $S_A$  phase and a striated fan-shaped texture of  $S_C^*$  phase are shown in Fig. 2.

## CONCLUSION

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

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