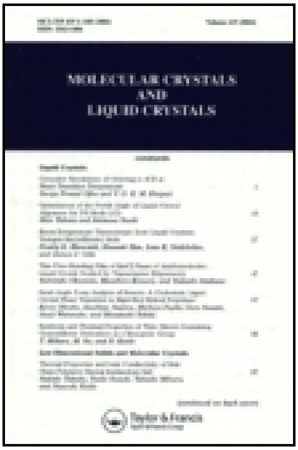

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Xiaoman Dai, Harunori Narihiro, Hiromasa Goto, Kazuo Akagi & Hiroshi Yokoyama (2001): Synthesis and Properties of Polythienylene Derivatives with Fluorine-Containing Chiral Liquid Crystalline Substituents (II), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 355-361

To link to this article: http://dx.doi.org/10.1080/10587250108025314

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 355-361
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Synthesis and Properties of Polythienylene Derivatives with Fluorine-Containing Chiral Liquid Crystalline Substituents (II)

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Novel side-chain type liquid crystalline (LC) polythienylene derivatives were synthesized by introducing fluorine-containing chiral LC substituents into the 3-position of thiophene rings, to achieve a quick response to electric field by virtue of ferroelectric liquid crystallinity (FLC). The polymers synthesized were fusible and soluble in ordinary organic solvents. UV-Vis absorption bands were observed in the region from 350 to 400 nm. Measurements of differential scanning calorimetry (DSC), polarizing optical microscope (POM), and X-ray diffraction (XRD) indicated that the polymers have various LC phases. Particularly, one of the polymer showed chiral smectic C (Sc*) phase, that is characteristic of the FLC mesophase. It was found that the effective conjugation length of main chain increased after the spontaneous orientation of the LC side chains. The polymer showed a drastic increase of dielectric constant in the temperature region of S_C* phase, which can be regarded as typical FLC behavior.

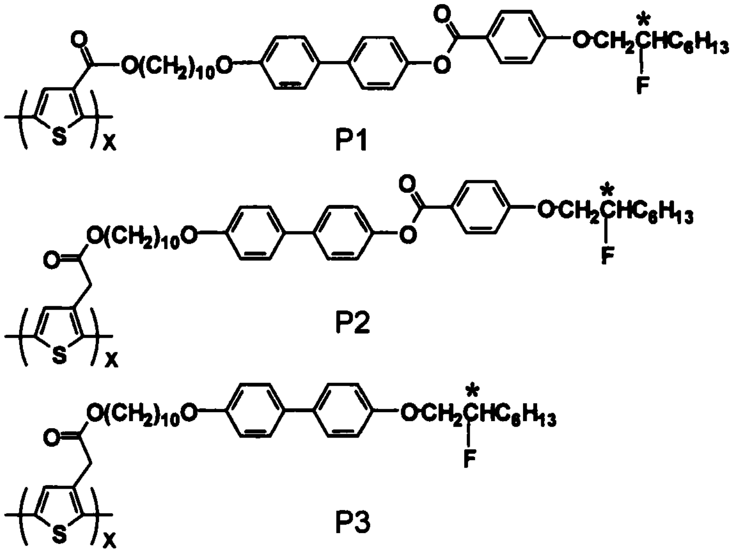
Keywords: conjugated polymers; polythienylene derivatives; ferroelectricity; chiral smectic C phase; dierectric constant

INTRODUCTION

Conjugated polymers with liquid crystalline (LC) groups in side chains have been drawing current interests from view points of multifunctional electrical and optical materials [1-8]. Spontaneous orientation and externally forced alignment of the LC side chains enabled us to control electrical and optical properties as well as their anisotropies. Polythienylene derivatives with LC side chains are one of the most interesting polymers [5,6], because of its profound electrical and optical properties. Meanwhile, it is well known that ferroelectric LC (FLC) molecules respond more quickly to the electric field used as an external force than ordinary LC ones, and the spontaneous polarization formed in chiral smectic C (S_C*) phase is responsible for the ferroelectric liquid crystallinity [7,8]. In this study we synthesized novel FLC polythienylene derivatives, and examined the temperature dependence of dielectric constant of the polymers.

EXPERIMENTAL SECTION

We prepared three type of polythienylene derivatives with fluorine-containing chiral liquid crystalline substituents (see, Scheme 1). All ^{1}H-NMR and ^{13}C-NMR spectra were measured with a BRUKER 500 MHz FT-NMR spectrometer. $CDCl_3$ 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) apparatus at a constant heating and cooling rates of 10 °C/min. Optical textures were obserbed using a Nikon polarizing microscope equipped with a Linkam THMS 600 hot stage. Molecular weights of the polymers were



Scheme 1

determined by gel permeation chromatography (GPC) equipped with a Shodex A-80M 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 diffractmeter, in which X-ray power and scanning rate were set at 200 mW and 5 deg/min, respectively.

RESULT AND DISCUSSION

All polymers synthesized (**P1**, **P2** and **P3**) were fusible and soluble in common organic solvents such as THF. Weight-average (M_w) molecular weights and Number-average (M_n) molecular weights of **P1**, **P2** and **P3** were 12800 ~ 54800 and 4800 ~ 12000, respectively.

All polymers showed various mesophases. Phase transition temperatures are summarized in Table I. **P1** showed enantiotropic S_A phases. **P2** showed enantiotropic S_A, S_C^* and S_B phases (Fig. 1). **P3** showed S_A phase in the heating process, and S_A and S_X^* phases in the cooling process. XRD analysis suggested that the S_X^* phase of **P3** might be a higher order smectic phase.

TABLE II Phase transition temperatures of polymers

Polymers	Phase transition temperature (°C) Heating Cooling
P1	G 197 S_A 203 I
	G 147 S_A 174 I
P2	G 133 S_B 160 S_C^* 176 S_A 201 I
	G 130 S_B 142 S_C^* 162 S_A 198 I
P3	G 95 S_A 100 I
	G 92 S_X^* 96 S_A 98 I

I: isotropic, S_A: smectic A, S_B: smectic B, S_C^*: chiral smectic C, G: glassy state, S_X: unidentified (chiral) smectic phases.

Fig. 1 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** were assigned to the π - π^* 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 was assigned to the π - π^* transition of mesogenic substituent. The absorption band of the conjugated main of **P1** was slightly red-shifted to 422 nm in the cast film. This may be due to the in-plane alignment occurring in the cast film.

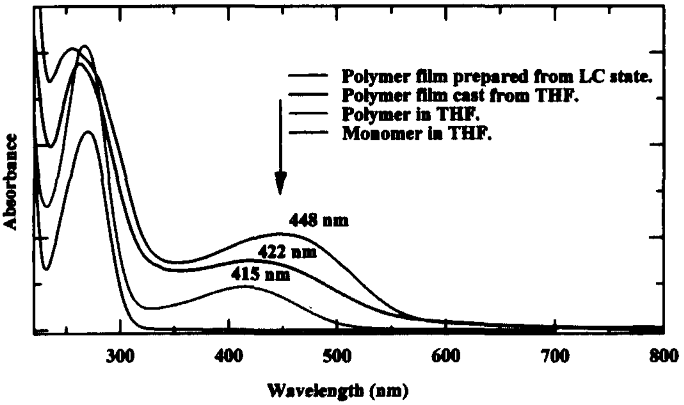


FIGURE 1 UV-Vis absorption spectra of **P1** and **M1**
See Color Plate XXIII at the back of this issue.

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 π-conjugation of the main chain. Namely, the alignment of the main chain, that is associated with spontaneous orientation of the LC side chain in the LC phase, should give rise to an increase of coplanarity of the main chain. The same effects were also observed in **P2**.

Temperature dependence of dielectric constant of **P2** is shown in Figs. 2 and 3. The dielectric constant suddenly increased in the temperature region of S_C* phase. This is a typical ferroelectric behavior of FLC, because the dielectric constant (ε) of ferroelectric material is inversely proportional to the absolute temperature according to Curie-Weiss' law, i.e., $\varepsilon = C\ (T - T_C)^{-1}$, where C is a Curie constant and T_C is a Curie temperature. At the same time, the dielectric constant increased with an increase of frequency. This tendency is due

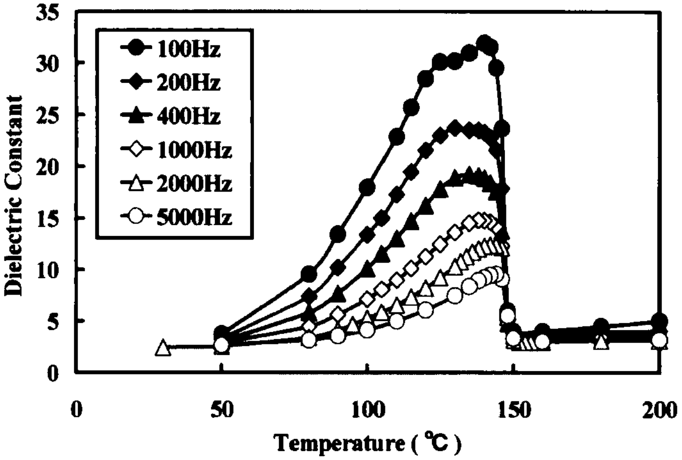


FIGURE 2 Temperature dependence of dielectric constant of **P2** (100 Hz ~5000 Hz)
See Color Plate XXIV at the back of this issue.

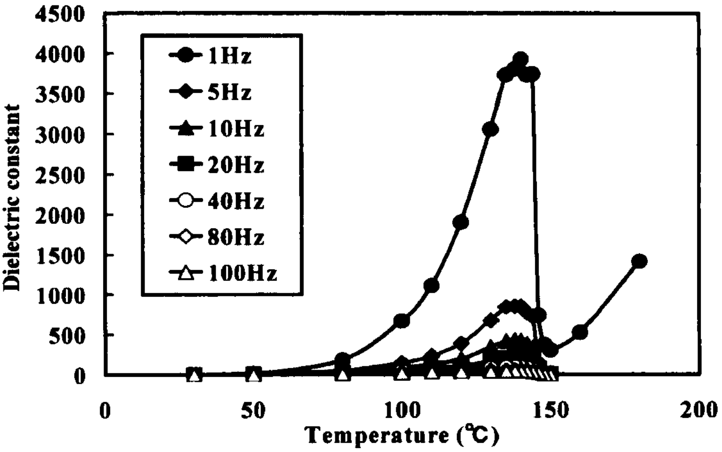


FIGURE 3 Temperature dependence of dielectric constant of **P2** (1 Hz ~100 Hz)
See Color Plate XXV at the back of this issue.

to a high viscosity of LC conjugated polymer.

CONCLUSION

Polythienylene derivatives with fluorine-containing chiral LC substituents were synthesized. One of the polymers exhibited a S_C^* phase, which is indispensable for ferroelectricity. It was found that the effective 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.

Acknowledgments

This work was supported by the Akagi project of Tsukuba Advanced Research Alliance (TARA) of University of Tsukuba.

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