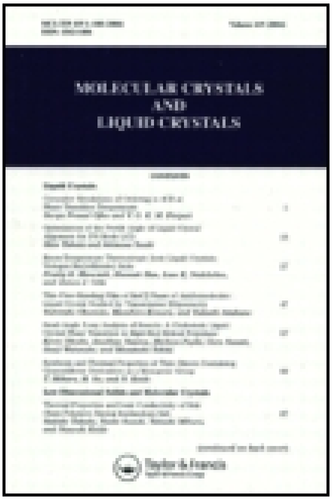

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Synthesis and Properties of Side Chain Ferroelectric Liquid Crystalline Polyacetylene Derivatives

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Novel liquid crystalline (LC) polyacetylene derivatives were synthesized to develop advanced LC conducting polymers with an ability of quick response to an electric field used as an external force. In practice, we synthesized ferroelectric LC conducting polymers by introducing fluorine-containing chiral LC groups into side chains of polyacetylenes. Phase transition behaviors of these polymers were examined by differential scanning calorimeter and polarizing optical microscope. Mesophases as well as higher order structures were evaluated with X-ray diffraction measurements. Two of the polymers synthesized showed twist grain boundary A (TGB_A*) and chiral smectic C (S_C*) phases in the heating and cooling processes. Observation of the S_C* phase allows us to expect that the polymer should exhibit the ferroelectricity.

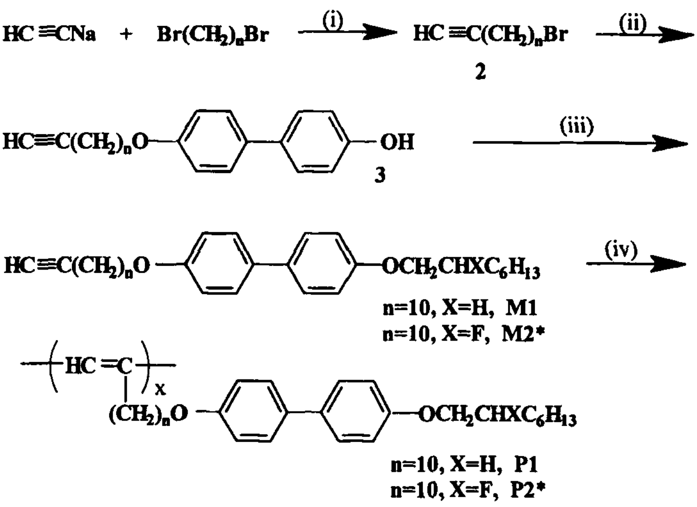
Keywords: polyacetylene derivatives; liquid crystalline phase transitions; chirality; ferroelectricity

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 [1-3]. Spontaneous orientation and externally forced alignment of the LC side chains enabled us to control electrical and optical properties as well as their anisotropies [4-6]. When an electric field is employed as an external force, ferroelectric LC (FLC) side chains should be more desirable than ordinary LC ones, because the former is expected to respond more quickly to the electric field owing to its spontaneous polarization than the latter. In other words, the spontaneous polarization formed in chiral smectic C (S_C*) phase is responsible for the ferroelectric liquid crystallinity. Recently, we synthesized polyacetylene derivatives substituted with chiroptical LC groups, and confirmed a formation of the S_C* phase attributable to the ferroelectric liquid crystallinity [7,8], although the temperature region of the liquid crystalline phase was as narrow as 5 degrees. Here, we synthesized advanced FLC polyacetylene derivatives with thermally more stable S_C* phase, by introducing fluorine-containing chiral LC groups into side chains.

EXPERIMENTAL

The chiral alcohol (*S*)-(-)-2-fluorooctanol (**1***) was prepared according to the method reported by Nohira et al [9], in which (*R*)-(+)-1,2-epoxyoctane was reacted with pyridinium poly (hydrogen fluoride) in ether. The synthetic routes of monomers and polymers are shown in Schemes 1 and 2. 12-Bromo-1-dodecyne (**2**) was prepared by reacting sodium acetylide with 1,10-dibromodecane in DMF. 4-Hydroxy-4'-(11-dodecynyloxy)biphenyl (**3**) was obtained by reacting compound **2** with 4,4'-dihydroxybiphenyl in the presence of K_2CO_3. 4-Octyloxy-4'-(11-dodecynyloxy)biphenyl (**M1**) and 4-[(*S*)-2-fluorooctyloxy]-4'-(11-dodecynyloxy)biphenyl (**M2***) were obtained by coupling compound **3** with *n*-octanol and compound **3** with compound **1***, respectively, using the Mitsunobu reaction in THF [10, 11]. In Scheme 2, ethyl 4-[(*S*)-2-fluorooctoxy]benzoate (**4***) was synthesized by coupling compound

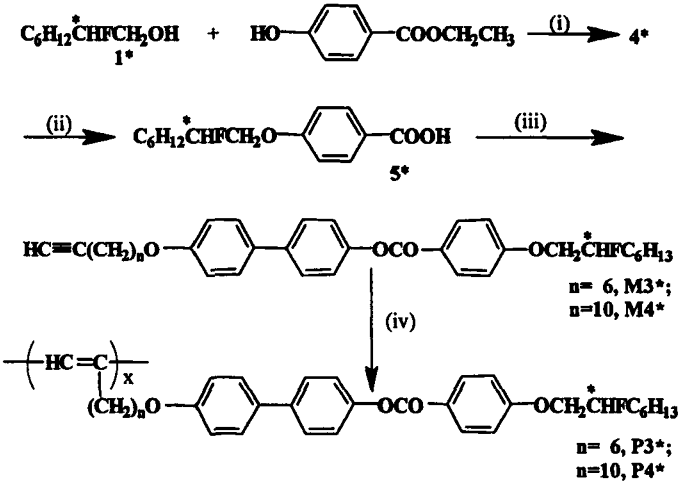


(i). DMF; (ii). K_2CO_3, 4,4'-biphenyldiol, butanone; (iii). azodicarboxylic acid diethyl ester (DEAD), triphenylphosphine (TPP), (*S*) - $C_6H_{13}CHXOH$ (X=H, F), THF; (iv). $[Rh(NBD)Cl]_2$, NEt_3, THF.

SCHEME 1

1* with ethyl *p*-hydroxybenzoate under the same condition as that of the synthesis of compound **M2***. The basic hydrolysis of compound **4*** with KOH in a solution of methanol and water, led to the formation of 4-[(*S*)-2-fluorooctoxy]benzoic acid (**5***). Besides, the esterification of compound **3** with compound **5*** in the presence of dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) gave rise to the formation of 4-[4-((*S*)-2-fluorooctyloxy)benzoyl]-4'-(9-octynyloxy)biphenyl (**M3***) and 4-[4-((*S*)-2-fluorooctyloxy)benzoyl]-4'-(11-dodecynyloxy)biphenyl (**M4***).

The LC groups of acetylene monomers, **M1** and **M2***, are composed



(i). DEAD, TPP, THF; (ii). NaOH, CH_3OH, HCl; (iii). compound 3, *N*,*N'*-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), CH_2Cl_2; (iv). $[Rh(NBD)Cl]_2$, NEt_3, THF.

SCHEME 2

of a biphenyl moiety as a mesogenic core, and a decamethylene chain as a spacer, and terminal moieties that are *n*-octyloxy and (*S*)-2-fluorooctyloxy groups, respectively. Meanwhile, the LC groups of acetylene monomer, **M3*** and **M4***, 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. Polymerizations of the acetylene monomers (**M1**, **M2***, **M3*** and **M4***) were carried out using rhodium catalyst, $[Rh(NBD)Cl]_2$-NEt_3, where NBD stands for 2,5-norbornadiene. All polymers synthesized (**P1**, **P2***, **P3*** and **P4***) were fusible and soluble in common organic solvents including tetrahydrofuran (THF).

RESULTS AND DISCUSSION

Number-average (M_n) and weight-average (M_w) molecular weights of **P1** were 9.1×10^3 and 1.4×10^4, respectively. The M_n and M_w of **P2*** were 1.5×10^4 and 4.4×10^4, respectively. The M_n and M_w of **P3*** were 1.1×10^4 and 2.7×10^4, respectively, and those of **P4*** were 1.1×10^4 and 1.8×10^4, respectively. It is found that three typical IR absorption peaks of acetylenic moiety in the monomer disappeared after the polymerization. ^{1}H-NMR measurements showed that the proton signal at 1.9 ppm of the acetylenic moiety ($\mathit{H}\mathrm{C}{\equiv}\mathrm{C}$—) in the monomer (e.g., **M4***) shifted to the lower magnetic field after the polymerization, and it was merged into the signals of the aromatic rings (6~7 ppm) of the side chain. Similarly, the ^{13}C-NMR measurements showed that the signals at 67 and 85 ppm of the acetylenic carbons ($\mathrm{H}\mathit{C}{\equiv}\mathit{C}$—) in the monomer (e.g., **M4***) shifted to the lower magnetic field after the polymerization, and they were merged into the signals of the aromatic carbons (120~140 ppm) of the side chain. These results suggest that the acetylenic moiety has changed into the olefinic moiety (—HC=C<) after the polymerization. However, the chemical shifts of the olefinic proton and

TABLE I Phase transition temperatures of LC polyacetylene derivatives

Polymer	Phase transition temperature (°C)	
	Heating	Cooling
P1	G 144 S_A 164 I	I 158 S_A—Sx 142 G
P2*	G 121 S_A 149 I	I 144 S_A —S_X 117 G
P3*	G 121 S_C* 168 TGBA* 217 I	I 214 TGBA* 158 S_C* 115 G
P4*	G 135 S_C* 182 TGBA* 217 I	I 213 TGBA* 177 S_C* 126 S_X 105 G

I: isotropic, TGBA*: twist grain boundary A, S_C*: chiral smectic C,
S_X: unidentified smectic phases, G: glassy state.

carbons in the polymer are very close to those of the aromatic phenyl and/or biphenyl moieties in the LC side chain, and therefore they were unambiguously identified. The phase transition temperatures are summarized in Table I. The acetylene monomers, **M1** and **M2***, showed no mesophase. The precursor **5*** exhibited enantiotropic N* and smectic (S) phases. This is probably due to a formation of hydrogen bonding dimer of **5***. **M3*** showed enantiotropic TGB_A* and S_C* phases. On cooling from the isotropic phase, **M4*** showed TGB_A* and S_C* phases and two unidentified higher order smectic phases. All polymers exhibited mesophases. **P1** showed smectic A (S_A) and higher order smectic phases, and **P2*** showed S_A and S_X* phases in the cooling process. XRD analysis suggested that **P2*** may exhibit a higher order smectic phase, but not S_C* one. On the other hand, **P3*** showed enantiotropic TGB_A* and S_C* phases. **P4*** showed S_C* and TGB_A* phases in the heating process, and TGB_A*, S_C* and S_X phases in the cooling one. The typical optical textures of **P4*** are shown in Fig. 1. XRD pattern of **P4*** measured in the LC phase at 190 ℃ gave two reflection peaks corresponding to the distances of 4.62 and 38.5 Å. This is typical pattern of smectic phase. At this temperature, the finger printed texture was observed in POM of **P4*** (Fig. 1, upper). The pattern of XRD and optical texture of **P4*** are characteristic of TGB_A* phase [12]. This is the first result to observe TGB_A* phase in LC conjugated polymers. When the temperature was cooled to 160 ℃, the *d*-spacing of the small angle reflection decreased from 38.5 to 33.0 Å, suggesting the formation of S_C* phase. A parabolic texture of S_C* phase for **P4*** was observed at this temperature (Fig. 1, lower). When the temperature was further cooled to 120 ℃, the *d*-spacing of the small angle reflection increased from 33.0 to 35.4 Å and the wide angle reflection became sharp.

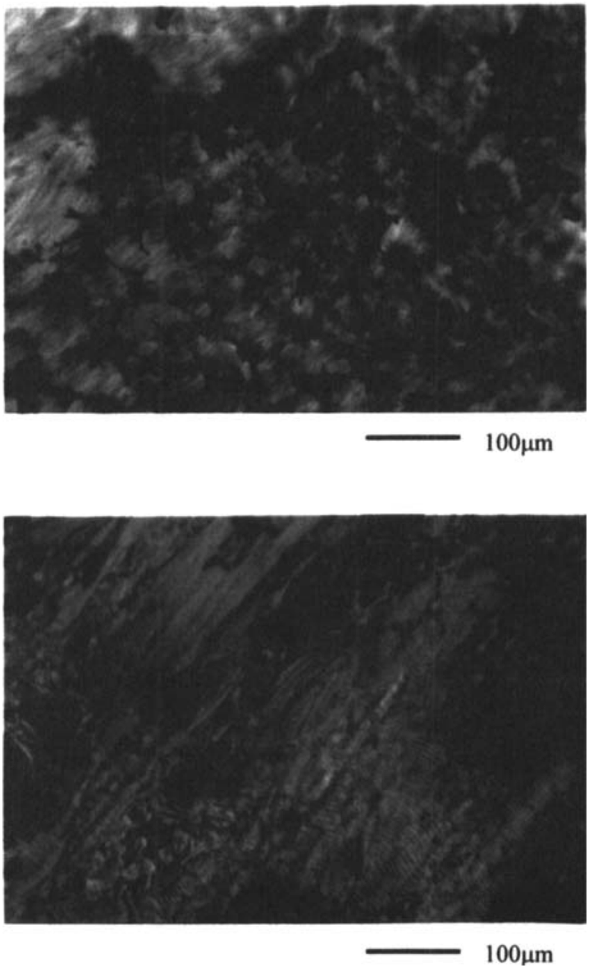


FIGURE 1. **Polarizing optical micrographs of P4*. Finger-printed texture of twist grain boundary A (TGBA*) phase at 193 ℃ (upper); Parabolic texture of chiral smectic C (S_C*) phase at 165 ℃ (lower).**

See Color Plate XXII at the back of this issue.

This suggests the formation of a tilted smectic phase. In conclusion, novel LC polyacetylene derivatives have been synthesized by introducing achiral LC group or chiral fluorine-containing LC group into side chains. Two of the polymers (**P3*** and **P4***) showed S_C* phase with an enantiotropic behavior, whose temperature region was sufficiently wide such as 50 degrees. It is therefore expected that these polymers should be available for ferroelectric LC conducting materials.

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