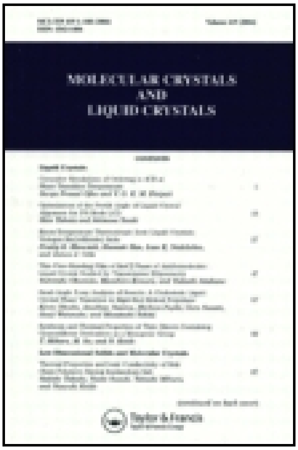


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Synthesis and Properties of Ferroelectric Liquid Crystalline Poly (p-Phenylenevinylene) Derivatives

Jun Oguma [a], Xiaoman Dai [a] & Kazuo Akagi [a]

[a] Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki, 305-8573, JAPAN

Version of record first published: 27 Oct 2006

To cite this article: Jun Oguma, Xiaoman Dai & Kazuo Akagi (2001): Synthesis and Properties of Ferroelectric Liquid Crystalline Poly (p-Phenylenevinylene) Derivatives, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 331-338

To link to this article: http://dx.doi.org/10.1080/10587250108025311

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 331-338
Reprints available directly from the publisher
Photocopying permitted by license only

Synthesis and Properties of Ferroelectric Liquid Crystalline Poly (*p*-Phenylenevinylene) Derivatives

JUN OGUMA, XIAOMAN DAI and KAZUO AKAGI

Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305–8573, JAPAN

Poly(*p*-phenylenevinylene) (PPV) derivatives with ferroelectric liquid crystallinity were synthesized by substituting fluorine-containing chiral liquid crystalline (LC) groups into the side chains. The *di*-substituted monomer showed various LC phases such as chiral nematic (N*), twist grain boundary A (TGBA), and chiral smectic C (S_C*) phases. The PPV polymers showed a stable enantiotropic S_C* phase characteristic of ferroelectricity, as well as a fluorescence.

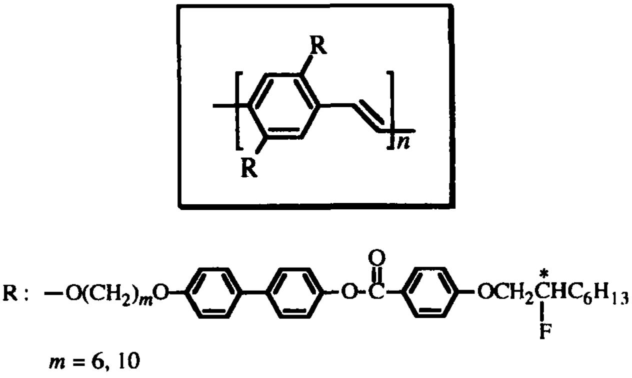
Keywords: ferroelectirc liquid crystal; poly(*p*-phenylenevinylene); chiral smectic C phase; fluorescence

INTRODUCTION

It is well known that π-conjugated aromatic polymers such as poly(*p*-phenylene) (PPP) and poly(*p*-phenylenevinylene) (PPV) are promising candidates for not only electrical conductors but also optically luminescent materials[1,2]. Meanwhile, the side chain type liquid crystalline (LC) conjugated polymers recently put forward have shed light on control of electrical conductivities through externally forced macroscopic alignment in LC mesophases[3]. In the previous works, we synthesized novel LC-PPPs and LC-PPVs[4–6], and macroscopically aligned them under magnetic field of 10 Tesla in LC phase to construct mono-domain structure. The polymers thus aligned showed electrical and optical anisotropies[7].

However, it took a substantial time, e.g., at least a couple of minutes, for the LC aromatic conjugated polymers to be aligned under magnetic field, because of their high viscosity. One of the promising way to achieve the quick alignment is to adopt the polymers with ferroelectric liquid crystallinity (FLC) under an external electric field. In fact, we synthesized FLC polyacetylenes[8] and polythiophenes [9], and confirmed that they showed chiral smectic C ($S_C{}^*$) phase ascribed to FLC phase.

Here, we present the first FLC-PPV derivatives which allow us to control quickly the orientation and their electrical and optical properties using an electric field. The synthesis of the FLC-PPV was carried out by introducing fluorine-containing chiral LC substituents into both side chains of PPV, as shown in Scheme 1.

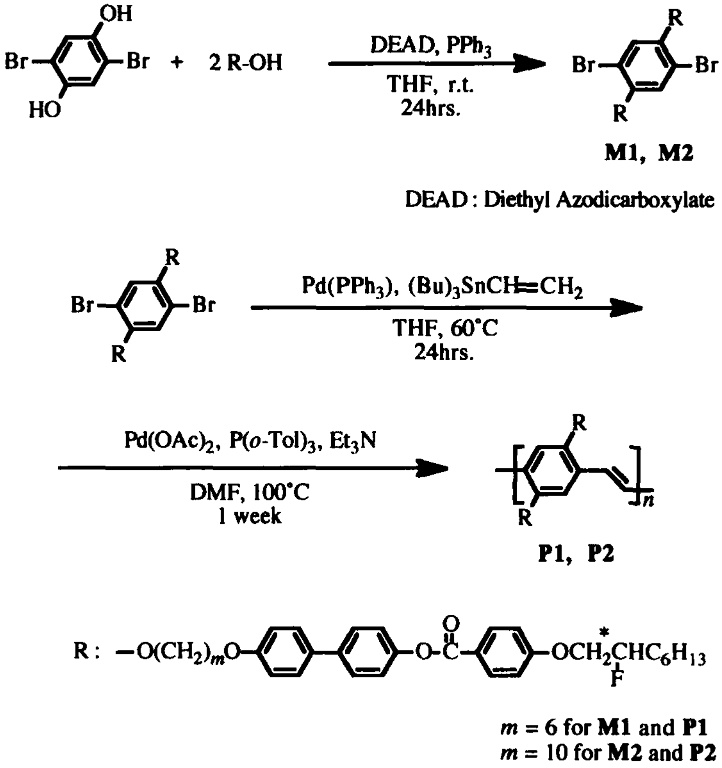


SCHEME 1 Molecular structures of FLC-PPVs

EXPERIMENTAL

Synthetic routes of FLC substituents are shown in literature[8,9]. 2,5-Dibrominated monomers (**M1** and **M2**) were synthesized by Mitsunobu coupling reaction[10]. Polymerizations were carried out through Stille coupling reaction[11] followed by

Heck coupling reaction[12] (Scheme 2). Molecular structures of monomers and polymers were confirmed by ^{1}H-,^{13}C-NMR, IR spectra, and elemental analysis. Molecular weights of polymers were measured by GPC with polystyrene standard. Phase transition temperatures were determined with differential scanning calorimeter (DSC). Optical textures was observed through polarizing optical microscopy. Spectroscopic properties were examined by UV-Vis and fluorescence spectra.



SCHEME 2 Synthetic routes of FLC-PPVs

RESULTS AND DISCUSSION

Liquid crystallinities of monomers (**M1**, **M2**) are summerized in Table I. **M1** and **M2** exhibited various LC phases; twist grain boundary A (TGBA), chiral nematic (N*), and chiral smectic C (S_C*) phases. Optical textures of TGBA and S_C* phases are shown in Fig. 1(a) and (b), respectively. Note that the striated texture of Fig 1(b) was observed only after electric field was applied to the sample that was placed between ITO substrates.

The polymers (**P1**, **P2**) were fusible and soluble in ordinary organic solvents. Polymerization results are cited in Table II. Number-average molecular weight (Mn) of **P1** and **P2** were 6400 and 6100, respectively.

TABLE I Liquid crystallinities and phase transition temperature of monomers

monomer	phase transition temperatures (°C) heating process cooling process
M1	K --- Sx_1 130 S_C* --- TGBA 160 N* 180 I
	K --- Sx_2 101 Sx_1 130 S_C* --- TGBA 160 N* 180 I
M2	K --- Sx_1 96 S_C* --- TGBA 146 N* 160 I
	K 75 Sx_2 94 Sx_1 96 S_C* --- TGBA 146 N* 160 I

TABLE II Molecular weights and optical properties of polymers

polymer	Mn[a]	Mw[b]	d[c]	D.P.[d]	λ_{max}[e, f] (nm)[g]	Em[h] (nm)[g]	Ex[i] (nm)[g]
P1	6400	13000	2.0	5	268	425	356
P2	6100	11000	1.8	5	267	420	356

a: number-avarage. b: weight-avarage. c: Mw/Mn. d: degree of polymerization.
e: absorption. f: absorption corresponding to LC side chains. g: measured in $CHCl_3$.
h: emission. i: excitation.

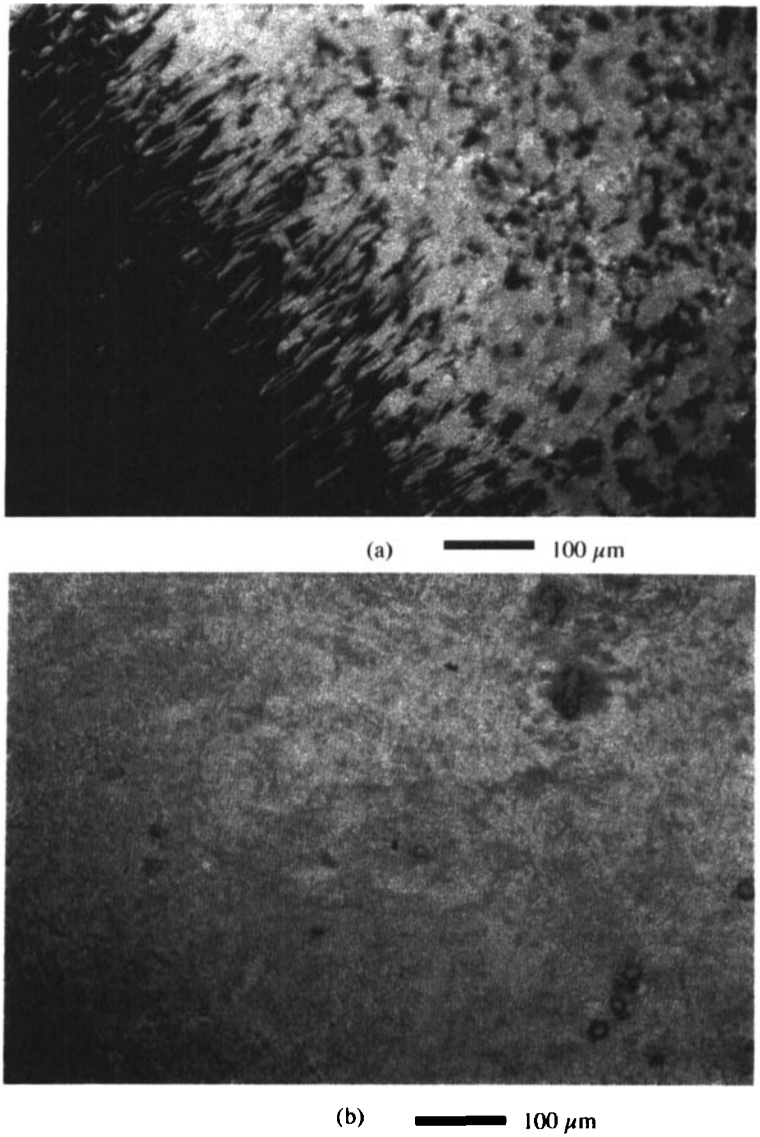


FIGURE 1 Polarizing optical micrographs of monomer (**M2**) TGBA phase at 150 °C (a) and S_C* phase at 111°C (b) in cooling process.
See Color Plate XVIII at the back of this issue.

Absorption bands of **P1** and **P2** in $CHCl_3$ were observed at 268 and 267 nm, respectively. These bands were assigned to the $\pi - \pi^*$ transition of mesogenic cores of the side chains. Although absorption bands of polymer main chain was not observed clearly, the long tail was observed up to 500 nm, as shown in Fig. 2 (left). The present polymers are fluorescent; **P2** showed a fluorescence band at 425 nm and a shoulder at 471 nm, both of which were assigned to the emissions from non-aggregated and aggregated structures, respectively. It is of interest that the fluorescence bands exhibited a dependence of polymer concentration, where relative intensities of the band and shoulder were reversed in such a high concentration as 0.1 mmol/l, as shown in Fig. 2 (right). Meanwhile, **P1** showed a fluorescence band at 420 nm where no notable change was observed even in high concentration, in contrast to the case of **P2**. This implies that **P1** tends to exist in non-aggregated structure, but not in aggregated one. It can be therefore understood that the favorableness of the polymer aggregation in the excited state should be sensitively affected by the difference in the methylene spacer length (m) of LC substituents between **P1** ($m = 6$) and **P2** ($m = 10$).

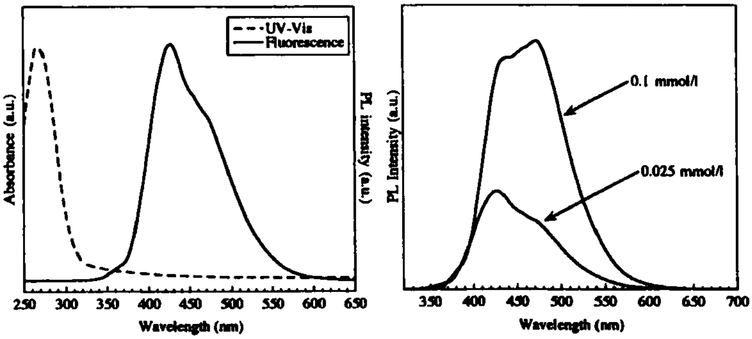


FIGURE 2 UV-Vis absorption and fluorescence spectra (left) and the concentration dependence of fluorescence spectra of polymer (**P2**).

Liquid crystallinities of the polymers are summarized in Table III. The polymers showed striated optical textures characteristic of $S_C{}^*$ phase in enantiotropic manner

(Fig. 3). Temperature region ranges of S_C*phase in **P1** and **P2** were 20° and 30°, respectively. The helical pitch evaluated from the striae of **P2** was 4.5 μm. Polarizing optical microscope scope suggested that the polymers have higher-order smectic phase (S_X) besides the S_C* phase.

TABLE III Liquid crystallinities and phase transition temperature of FLC-PPVs

polymer	phase transition temperatures (°C)
	heating process
	cooling process
P1	G 100 Sx 145 S_C* 160 I
	G --- Sx 139 S_C* 158 I
P2	G 65 Sx 87 S_C* 116 I
	G 65 Sx 87 S_C* 116 I

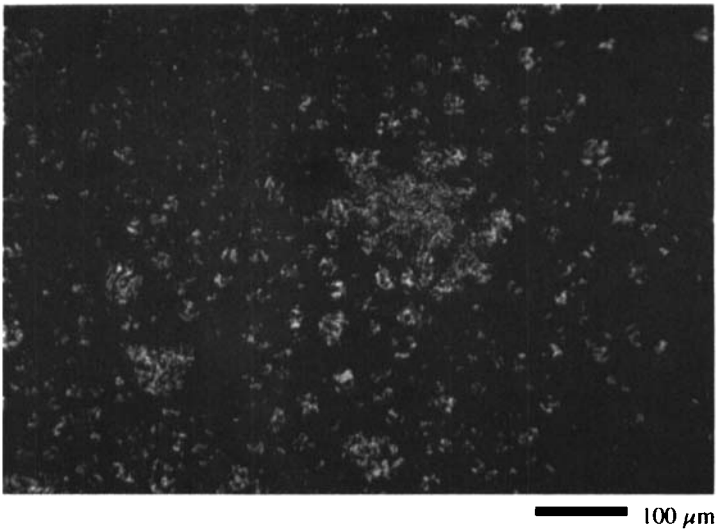


FIGURE 3 Polarizing optical micrograph of polymer (**P2**) at 107°C in cooling process.
See Color Plate XIX at the back of this issue.

CONCLUSION

Novel FLC-PPV derivatives have been synthesized by introducing fluorine-containing chiral LC groups into side chain. The polymers showed stable S_C* phase with enantiotropic behavior, whose temperature region were as wide as 20 ~ 30 °. They were also found to be fluorescent. The present polymers are expected to be available for ferroelectric LC conducting and luminescent materials.

References

[1] H.S. Nalwa (ed.), *Handbook of Organnic Cunductive Molecules and Polymers*, Wiley, New York, 1997.

[2] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackey, R.H. Friend, P.L. Burn, A.B. Holmes, *Nature*, **347**, 539 (1990).

[3] (a) S.-Y. Oh, K. Akagi, H. Shirakawa, K. Araya, *Macromolecures*, **26**, 6203 (1993). (b) K. Akagi, H. Goto, Y. Kadokura, H. Shirakawa, S.-Y. Oh, K. Araya, *Synth. Met.*, **69**, 13 (1995). (c) K. Akagi, H. Shirakawa, *Macromol Symp.*, **104**, 137 (1996). (d) K. Akagi, H. Shirakawa, in D.L. Wise, et al (eds.), *Electrical and Optical Polymer Synthesis: Fundamentals, Methods, and Application*, Marcel Dekker, 28, p. 983, 1998.

[4] K. Akagi, J. Oguma, H. Shirakawa, *J. Photopolym. Sci. Tech.*, **11**, No. 2, 249 (1998).

[5] J. Oguma, K. Akagi, H. Shirakawa, *Synth. Met.*, **101**, 86 (1999).

[6] K. Akagi, J. Oguma, S. Shibata, R. Toyoshima, I. Osaka, H. Shirakawa, *Synth. Met.*, **102**, 1287 (1999).

[7] J. Oguma, R. Kawamoto, H. Goto, K. Akagi, H. Shirakawa, K. Itoh, *proceeding of ICSM2000*.

[8] K. Akagi, H. Goto, H. Shirakawa, *Synth. Met.*, **84**, 313 (1997) X.M. Dai, H. Goto, K. Akagi, H. Shirakawa, *Synth. Met.*, **102**, 1289 (1999).

[9] X.M. Dai, H. Goto, K. Akagi, H. Shirakawa, *Synth. Met.*, **102**, 1291 (1999).

[10] O. Mitsunobu, M. Yamada, *Bull. Chem. Soc. Jpn.*, **40**, 2380 (1967).

[11] J.K. Stille, *Angew. Chem. Int. Ed. Engl.*, **25**, 508 (1986).

[12] R.F. Heck, *Org. React.*, **27**, 345 (1982).