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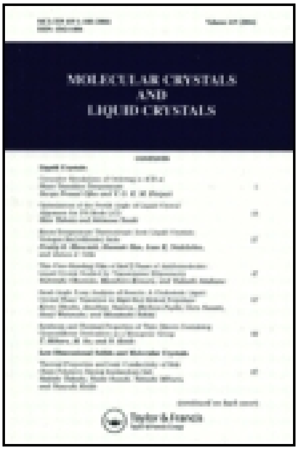

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Small Bandgap Type Liquid Crystalline Conjugated Polymers

Kazuo Akagi [a] , Hiromasa Goto [a] , Mitsuru Okuda [a] & Hideki Shirakawa [a]

[a] Institute of Materials Science, University of Tsukuba, Ibaraki, 305, Japan

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Small Bandgap Type Liquid Crystalline Conjugated Polymers

KAZUO AKAGI, HIROMASA GOTO, MITSURU OKUDA, and
HIDEKI SHIRAKAWA
Institute of Materials Science, University of Tsukuba, Ibaraki 305, Japan

Novel liquid crystalline (LC) π-conjugated polymers with small bandgaps are synthesized. The polymers consist of benzenoid and quinonoid structures of thiophene or pyrrole and a methine moiety substituted with LC group. The polymers of **1**, **2**, and **7** exhibit smectic mesophases and have bandgaps of 1.5, 2.5 and 2.3 eV, respectively, depending on resonance interaction between the main chain and the LC side chain. Feasibility of chemical doping and electrical conductivity of the polymers are confirmed. The polymer of **1** aligned by shear stress under LC phase showed a dichroism in fluorescence spectra. It is suggested that the present polymers are useful for not only self-alignable electrically conducting material, but also photoluminescent material with optical anisotropy.

Keywords: liquid crystalline conjugated polymer; small bandgap; electrical conductivity; electrical and optical anisotropies

INTRODUCTION

There are several approaches to achieve higher electrical conductivities of π-conjugated polymers. Macroscopic alignment of polymer chain, an increase of effective conjugation length, and a usage of monomer with small HOMO-LUMO gap are essential. It has been predicted from theoretical band calculations[1] and later confirmed[2,3] that poly(arylene methines) could be candidates for small bandgap conducting polymers, where benzenoid and quinonoid structures of arylene units are alternately linked with methine bridges. Meanwhile, liquid crystalline (LC) π-conjugated polymers currently developed have enabled us to control electrical conductivities and also to evoke electrical anisotropies through macroscopic alignment of main chains associated with orientation of LC side chains[4]. Here, we attempted to introduce a liquid crystalline function into the small bandgap type conjugated polymers based on the poly(arylene methines)[5] (Fig. 1), to develop advanced multi-functional materials available for electronics and photonics.

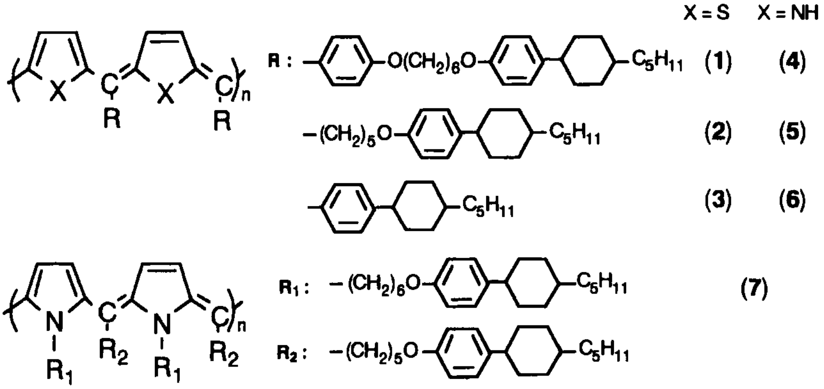

FIGURE 1 Small bandgap type LC conjugated polymers.

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EXPERIMENTAL

Synthesis

Small bandgap type LC conducting polymers were designed. The polymers consist of benzenoid and quinonoid structures of thiophene or pyrrole rings which are linked with the methine moiety substituted with LC group. In case of pyrrole, the LC group was also introduced at N-position of the pyrrole ring, to guarantee an appearance of liquid crystallinity.

LC aldehydes were prepared by oxidizing terminal hydroxy moieties of LC precursors with pyridinium chlorochromate, according to Corey reaction. Then, the polymers were synthesized through polycondensation between the thiophene or pyrrole derivative and the LC aldehyde, for which $POCl_3$ or H_2SO_4 was used as a catalyst according to Rothemund reaction (Fig. 2). Complete deprotonation on the methine moiety of the main chain was intended during the polymerization to obtain effectively conjugated methine-bridged sequences.

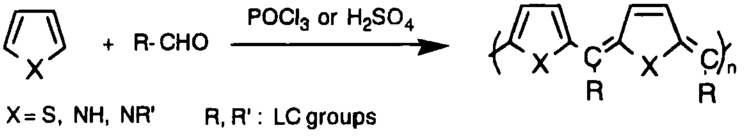

FIGURE 2 Synthetic route for small bandgap polymers with LC groups.

RESULTS AND DISCUSSION

In Table 1 are summarized polymerization results and some properties of the present polymers. The polymers of **1** ~ **4**, and **7** were fusible and soluble in common organic solvents such as THF and chloroform. Liquid crystallinities of the polymers were examined through polarizing optical microscope, DSC, and X-ray diffraction (XRD) measurements. The thiophene-based polymers, **1** and **2**, showed enantiotropic mesophases assignable to smectic E (S_E) and smectic A (S_A), respectively, and the pyrrole-based one, **7**, monotropic smectic X (S_X).

TABLE I Molecular weight[a], liquid crystallinity, and electrical conductivity.

Polymer[b]	M_n	M_w	MWD	Color	LC phase[e]	Conductivity (S/cm) Undoped	Iodine doped
1	8200	10800	1.3	emerald green	S_E	1.2×10^{-6}	9.2×10^{-4}
2	4000	4600	1.2	orange	S_A	2.2×10^{-6}	3.6×10^{-5}
3	4000	5600	1.4	dark brown	-[f]	1.5×10^{-6}	2.8×10^{-5}
4	2700[c]	3600[c]	1.3	dark brown	-[f]	1.0×10^{-6}	3.2×10^{-5}
5	-[d]	-[d]	-[d]	dark brown	-[f]	-[g]	
6	-[d]	-[d]	-[d]	dark brown	-[f]	-[g]	
7	6200	8800	1.4	red brown	S_X	1.6×10^{-7}	6.8×10^{-5}

Polymerization for 24 hrs at room temperature. [Monomer] = 1 M. [Monomer] / [Cat.] = 10. [a] Molecular weights were determined by polystyrene standard in THF. [b] Polymerization catalysts and solvents were $POCl_3$ and $CHCl_3$ for **1**, **2**, **4** ~ **6**, and H_2SO_4 and 1,4-dioxane for **3**, and $POCl_3$ and 1,4-dioxane for **7**. [c] THF soluble part. [d] Insoluble. [e] LC temperatures for **1** an **2** were 75 ~ 104, and 81 ~ 94 C°, respectively. In **7** LC phase appeared at 130 C° in the cooling process. [f] No mesophase. [g] No cast film was obtained.

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On the other hand, **1** showed absorption band with a long tail spreading over near-infrared region. Optically evaluated band-edge bandgap of **1** was 1.5 eV. In contrast, the bandgaps of **2** and **7** were 2.5 and 2.3 eV, respectively, both of which are relatively so large compared with that of **1**. The small bandgap of **1** is ascribed to π-electron resonance interaction between the conjugated main chain and the phenyl moiety of LC group that is directly linked with the main chain.

Electrical conductivities of the polymers were measured with the four-probe method by exposing the films cast from chloroform solution to an iodine vapor. Upon the doping, the conductivities increased from $10^{-7} \sim 10^{-6}$ to $10^{-5} \sim 10^{-4}$ S/cm (Table I). Unexpected lower values of the conductivities should come from shorter effective conjugation lengths that can be evaluated from number-average molecular weights. This implies that the effective conjugation length is an indispensable factor even for the small bandgap conjugated polymers.

Lastly it is worthy noting that present polymers are fluorescent. The polymer of **1** aligned by shear stress under LC phase showed a dichroism in fluorescence spectra, where the dichroic ratio defined as parallel to perpendicular intensity was about 5 (Fig. 3). Hence, the present polymers are also feasible for photoluminescent material with optical anisotropy.

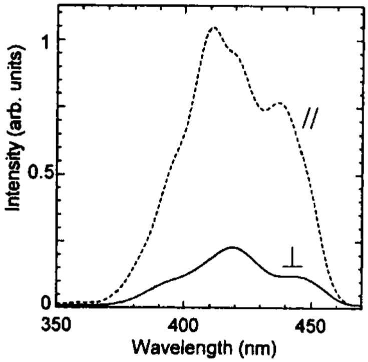

FIGURE 3 Fluorescence spectra of the polymer of **1** aligned by shear stress. Symbols of // and ⊥ indicate intensities parallel and perpendicular to main chain, respectively.

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