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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Version of record first published: 27 Oct 2006

To cite this article: Hiromasa Goto & Kazuo Akagi (2001): Ferroelectric Liquid Crystalline Conjugated Polymer with Small-Bandgap - Synthesis and Properties of Poly(pyrrylenemethine) Derivative, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 491-497

To link to this article: http://dx.doi.org/10.1080/10587250108025328

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 491-497
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Ferroelectric Liquid Crystalline Conjugated Polymer with Small-Bandgap – Synthesis and Properties of Poly(pyrrylenemethine) Derivative

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Novel ferroelectric liquid crystalline (FLC) π-conjugated polymer with small-bandgap was synthesized. The polymer consists of benzenoid and quinonoid structures of pyrrole and methine moiety substituted with FLC group. The polymer exhibits Sc* phase and has a band-gap of 2.1 eV. The spontaneous polarization of the polymer is evaluated to be 118 nC/cm^2.

Keywords: benzenoid and quinonoid structures; small-bandgap; ferroelectricity; conjugated polymer

INTRODUCTION

According to a theoretical prediction based on band calculations, polyarylenemethines could be small-bandgap conducting polymers[1]. Methine-bridged polymers with alternate benzenoid and quinonoid units might be promising candidates for the small-bandgap polymer. In practice, Jenekhe and Chen synthesized a periodic block polymer consisting of aromatic and quinonoid segments and proposed a superlattice for this system[2]. Here we report synthesis and properties of novel small-bandgap polymer with ferroelectric liquid crystalline (FLC) group as a substituent to

develop a quickly switching LC conducting polymer.

EXPERIMENTAL

Synthesis

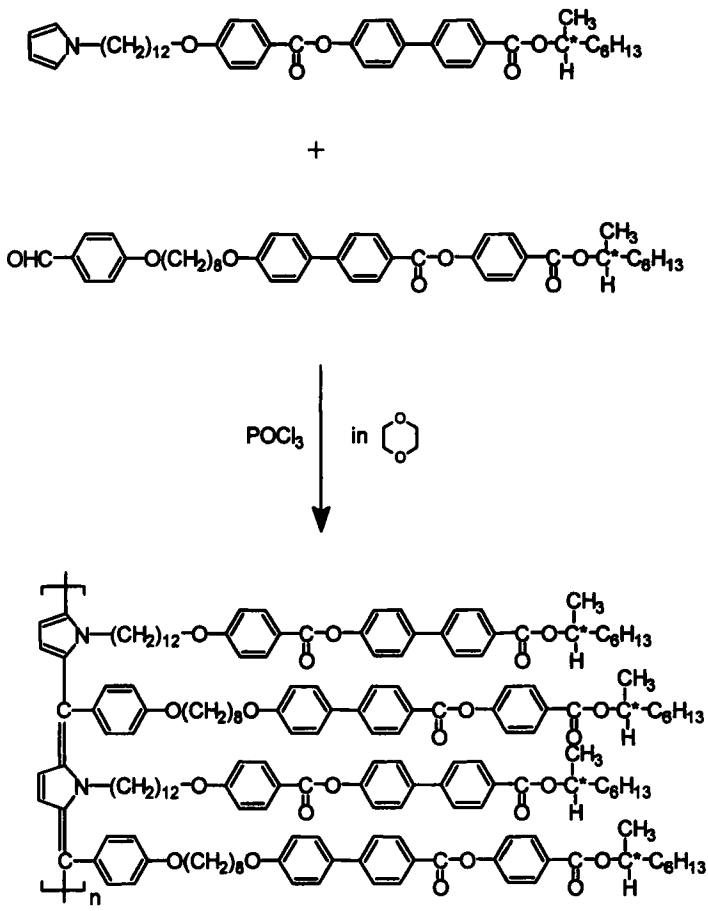
According to Rothemund reaction, polymerization was carried out through a coupling reaction between a N-substituted FLC pyrrole and a FLC group having aldehyde moiety in its terminal site, using $POCl_3$ as a catalyst under argon atmosphere. Completely deprotonated polymer was obtained, which was confirmed through absence of methine proton in ^{1}H-NMR spectrum.

RESULTS AND DISCUSSION

The polymer was fusible and soluble in organic solvent such as tetrahydrofuran (THF) and chloroform. Number-average molecular weight (M_n), weight-average molecular weight (M_w), and molecular weight distribution (MWD) of the polymer was 37500, 59100, and 1.6, respectively, according to polystyrene standard. Degree of polymerization was 14. Liquid crystallinity of the polymer was examined through polarizing optical microscopy, DSC, and XRD measurements. The polymer showed enantiotropic mesophases of smectic A and smectic C* (S_C*) phases. Transition temperatures (°C) of the polymer are as follows.

G 105 S_C* 138 S_A 152 I

It is found from polarizing optical microscopy observation that the S_C* structure is kept unchanged even in glassy state. The optical textures of the polymer are shown in Figure 1. These are typical patterns of smectic phases.



SCHEME 1 Synthesis of pyrrole-based methine bridged polymer with FLC.

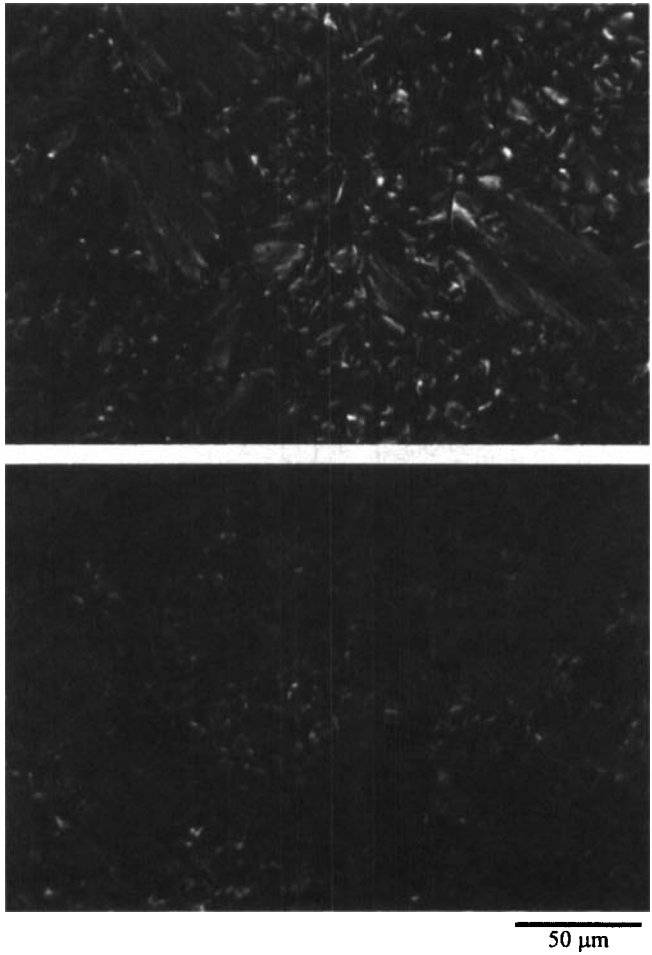


FIGURE 1 Polarizing optical micrographs of the polymer. Fan-shaped texture of S_A phase at 145 °C (upper); striated fan-shaped texture of S_C* phase at 100 °C (lower). See Color Plate XXXIX at the back of this issue.

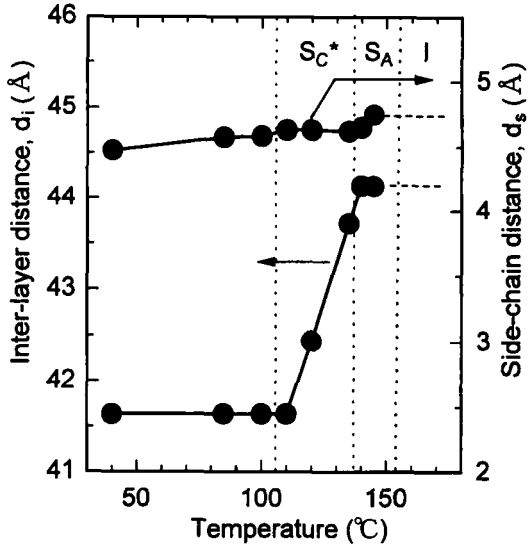


FIGURE 2 Temperature dependence of inter-layer distance (d_i) and side-chain distance (d_s) of the polymer.

In both heating and cooling processes, the striated fan-shaped texture was observed. Next, XRD of the polymer were measured at various temperatures. Figure 2 shows temperature dependences of inter-layer distance (d_i) and side-chain distance (d_s) of the polymer, where d_i and d_s were evaluated from halos at small and wide angles in XRD pattern, respectively. The inter-layer distance in S_A phase is 44 Å, which agrees with the calculated length of inter chain distance between polymers. The inter-layer distance slightly decreased with decreasing temperature. This suggests that the side chains begin to incline. The side-chain distance also decreased with decreasing temperature. This is accompanied with the change of tilt angle of LC side chains upon the

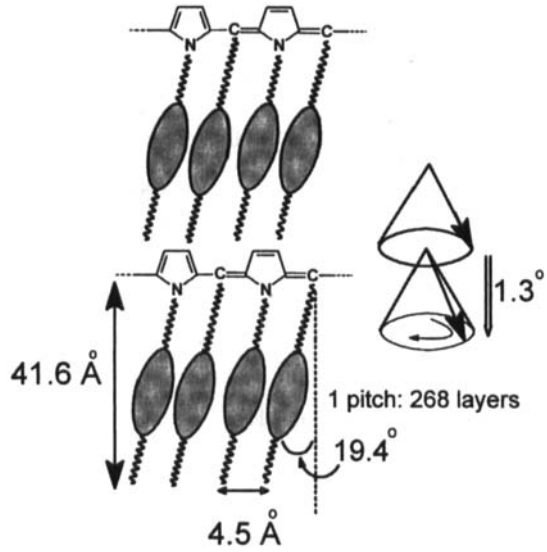


FIGURE 3 Schematic stacking structure of the polymer in S_C^* phase.

phase transition from S_A to S_C^* phase. Figure 3 shows schematic stacking structure of the polymer in S_C^* phase. The tilt angle was estimated to be ca. 20 degree from vertical line against the smectic layer. It was elucidated that the side chain of LC group gradually rotates by 1.3 degree layer by layer. Thus, it was calculated that one helical pitch is composed of 268 layers.

A hysterisis curve of polarization against electric field was observed in the S_C^* phase by using Sawyer-Tower method. Spontaneous polarization (Ps) value was estimated from the hysterisis loop. The maximum value of Ps was 118 nC/cm^2 for the polymer.

The UV-Vis spectrum of the polymer has absorption bands at 278, 357, and 413 nm, where the bands at 413 nm shows a long tail spreading over

near-infrared region. Optically evaluated band-edge band gap was 2.1 eV. This value is relatively small due to a co-existence of benzenoid and quinonoid structures in the repeating unit of the polymer.

Acknowledgments

This work was supported by Grant-in-Aids for scientific Research from the Ministry of Education, Culture and Science, and in part by the Akagi project of Tsukuba Advanced Research Alliance (TARA) of University of Tsukuba.

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