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, Kenichi Mochizuki & Kazuo Akagi (2001): Polaron-Type Magnetic Conjugated Polymer with Liquid Crystallinity, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 481-489

To link to this article: http://dx.doi.org/10.1080/10587250108025327

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 481-489
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Polaron-Type Magnetic Conjugated Polymer with Liquid Crystallinity

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We synthesized *poly*(*para*- and *meta*-phenylenevinylene) derivative with liquid crystalline group. The polymer is composed of *p*-phenylenevinylene as a spin generating unit and *m*-phenylene as a ferromagnetic spin coupling unit. The polymer showed nematic LC phase. The polymer was doped by iodine to generate the polaron, after the polymer was cooled down through the LC phase. ESR measurements showed that the spin concentration increased by means of external magnetic force alignment of the polymer.

Keywords: conjugated polymer; polaron; nematic LC; external magnetic force alignment

INTRODUCTION

High-spin organic molecules based on intermolecular through-bond magnetic ordering have been extensively studied to realize organic magnetism. Theoretical work suggested that a polaron, radical cation obtained by doping of conjugated polymeric segments, when linked by appropriate π topologies, could serve a good spin alignment for ferromagnetism. Up to now, the intrachain spin alignment has been achieved in the conjugated polymer with stable radical groups[1]. However, no interchain spin alignment has been succeeded, giving no ferromagnetic conjugated polymer. Here, we introduced

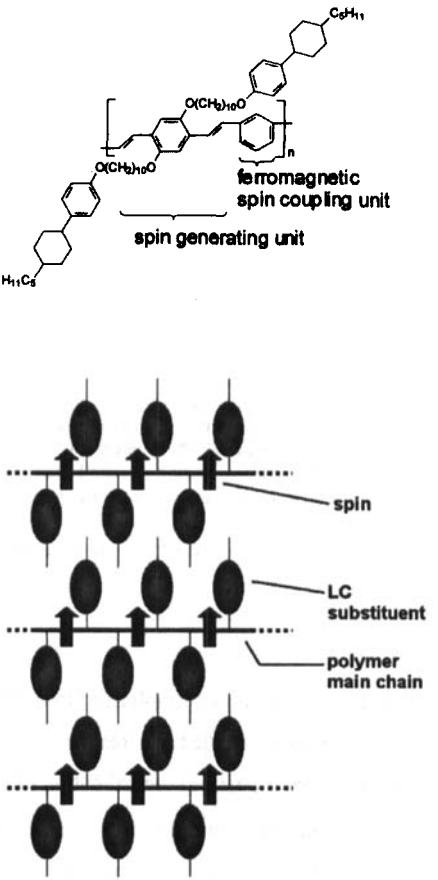


FIGURE 1 Molecular structure of the polaron type LC conjugated polymer (upper), and illustration of molecular orientation of the polymer (below).

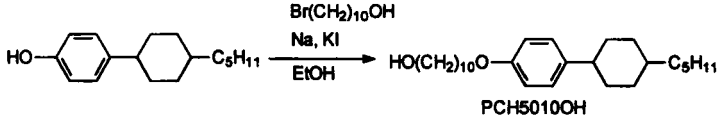
liquid crystalline (LC) substituents into the side chains of conjugated polymer, to reduce interchain diamagnetic interaction and also to construct macroscopic spin alignment using orientation ability of LC groups [2].

We adopted a polaron on the polymer main chain, instead of stable radical group such as phenoxy radical. In the polaronic model, a magnetic material consists of spin generating unit and the ferromagnetic coupling unit, which insures high spin pair wise interactions between spin coupling units. Furthermore the spins could be aligned accompany with molecular orientation with the aid of liquid crystallinity.

EXPERIMENTAL

Synthesis

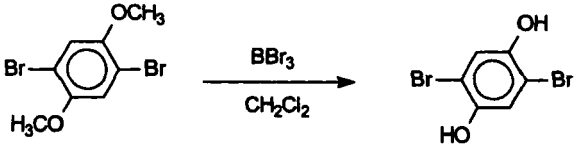
10-(*p-trans*-4-Pentylcyclohexyl)phenoxy)-1-decanol (PCH5010OH): Sodium (0.48 g, 21 mmol) was dissolved into ethanol (20 ml), and *p-trans*-4'-pentylcyclohexylphenol (5.19g, 21 mmol) was added to this solution at room temperature. Bromodecanol was added to the reaction mixture and refluxed for 24h. The solvent was evaporated, and the product was recrystallized from ethanol to yield PCH5010OH (where, PCH, 5, 0, 10, and OH stand for *p-trans*-4'-pentylcyclohexylphenyl, the terminal alkyl group, ether oxygen, a number of flexible methylene spacer, and hydroxy moiety, respectively) (y = 80.9 %). IR (KBr, cm^{-1}): 3364 (ν_{OH}); 2918, 2850 (ν_{CH2}); 1513 ($\nu_{C=C}$); 1248 (ν_{C-O-C}).



SCHEME 1

2,5-Dibromohydroquinone:

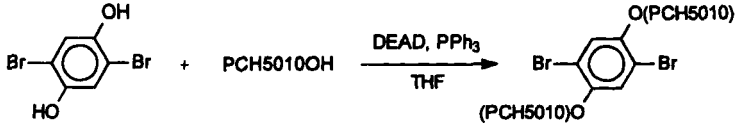
1,4-Dibromo-3,6-dimethoxybenzene (13 g, 45 mmol) was dissolved in dichloromethane (20 ml). Tribromoborane was very slowly added to the solution. After 24h, the solution was poured into large amount iced water, and filtered off. The filtrate was dried under reduce pressure to yield 10.9 g of 2,5-dibromohydroquinone (y = 90%). IR (KBr, cm^{-1}): 3280 (ν_{OH}); 1510 ($\nu_{C=C}$).



SCHEME 2

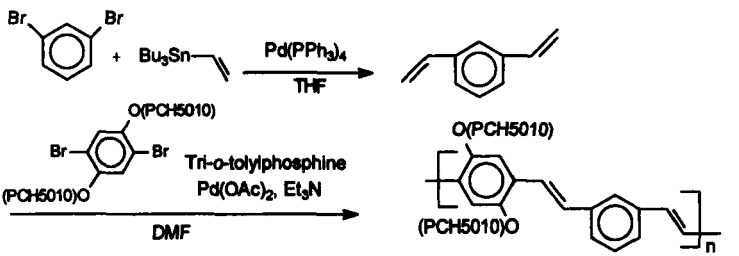
Bis(3-(4-(4-pentylcyclohexyl)phenoxy)decyloxy)1,4-dibromobenzene:

A solution of azodicarboxylic acid diethyl ester (DEAD) (8.70g, 20 mmol), triphenylphosphine (TPP) (5.24 g, 20mmol), 2,5-dibromohydroquinone (2.68 g, 10 mmol), and PCH5010OH (8.06 g, 20.0 mmol) in 20 ml of THF was stirred for 24 h at room temperature. Then the solvent was evaporated and purified by recrystallization from ethanol to yield 3.80 g of desired material (y = 37 %). IR (KBr, cm^{-1}): 2927, 2848 (ν_{CH2}); 1501 ($\nu_{C=C}$), 1251 (ν_{C-O-C}).



SCHEME 3

The polymer was prepared by one pot synthesis; a mixture of bis(3-(4-(4-pentylcyclohexyl)phenoxy)decyloxy)1,4-dibromobenzene (3.52 g, 3.39 mmol), tetrakis(triphenylphosphine)palladium (0) [$Pd(PPh_3)_4$] (0.48 g, 0.4 mmol) and tributyl(vinyl)tin (2.16 g, 6.78 mmol) was stirred for 24h at 60 °C, according to Stille reaction. Then 1,3-diiodobenzene (1.12 g, 3.39 mmol), palladium(II)acetate (105 mg, 0.49 mmol), tri-*o*-tolylphosphine (718 mg, 2.35 ml), 10 ml of DMF and 5ml of triethyl amine were added to the reaction mixture. The solution was refluxed at 100 °C for 1 week. The reaction was terminated by pouring the mixture into a large amount of methanol, and dilute HCl/methanol solution. The polymer was filtered off and washed with methanol. The polymer was dried under reduced pressure to yield 1.12 g of polyphenylenevinylene derivative with LC substituent (yield = 32.8 %).



SCHEME 4

RESULTS AND DISCUSSION

GPC measurement

Number-averaged (M_n) and weight-averaged (M_w) molecular weights of the polymer was evaluated with GPC measurement using polystyrene standard; $Mn = 7100$, $Mw = 11000$, $Mw/Mn = 1.5$.

Chemical structure and phase transition

In IR spectrum of the polymer, the aromatic C-H stretching vibration was observed at 2921 cm^{-1}. The absorption at 1511cm^{-1} is attributed to C=C stretching vibration of phenylene ring. The characteristic C-O-C stretching vibration at 1248 cm^{-1} is observed. The absorption at 827 cm^{-1} is characteristic of the C-H out-of-plane bending vibration. The chemical structure of the polymer was also confirmed by means of ^{1}H- and ^{13}C-NMR measurements. Overall, the IR and NMR spectra were in good agreement with the proposed structure.

The UV-Vis absorption bands at 277 and 302 nm were assigned to $\pi \rightarrow \pi^*$ transition of phenylene ring in the side chain and that of conjugated main chain, respectively.

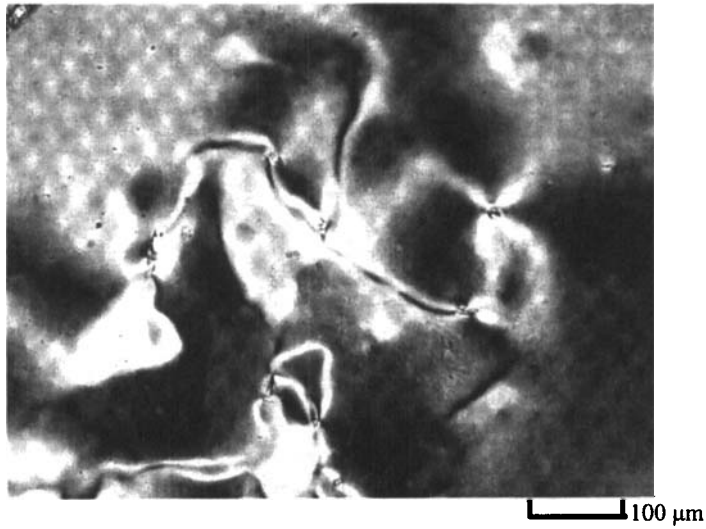


FIGURE 2 Polarizing optical micrograph of the polymer at 74 °C in the cooling process.

Phase transition temperatures (°C) determined by DSC are as follows.

$$G \underset{35}{\overset{76}{\rightleftharpoons}} N \underset{81}{\overset{87}{\rightleftharpoons}} I$$

where G, N, and I stand for glassy, nematic, and isotropic, respectively. The polymer exhibited nematic liquid crystallinity with typical schlieren texture in both cooling and heating processes, as shown in Figure 2.

ESR measurement

Two kinds of polymer sample were prepared for ESR measurements; One is an as-prepared (non-oriented) sample. Another is a spontaneously oriented sample. The latter was prepared by heating the polymer up to the isotropic state and the cooling it to room temperature through LC state. These sample were iodine-doped to generate polaron type unpaired electrons. Also, we examined the change of spin concentration of the doped sample as a function of doping time. The oriented sample has a large amount of spin concentration by ca. 10 times than the non-oriented one. This suggests that the spontaneous orientation might serve as a favorable environment for both stabilization of polaron type unpaired electrons and substantial spin alignments, even though this sort of orientation is not a mono domain structure but a multi domain one.

Furthermore, we carried out ESR measurement for the polymer which was macroscopically aligned by external magnetic force. The polymer was melted by heating in the ESR tube, and it was gradually cooled to the LC temperature by applying an external magnetic field. After the alignment of the polymer was completed in LC state, the polymer was further cooled down to room temperature to give a solid sample available for ESR measurement. Figure 3 shows ESR spectra for the polymer at room temperature. The

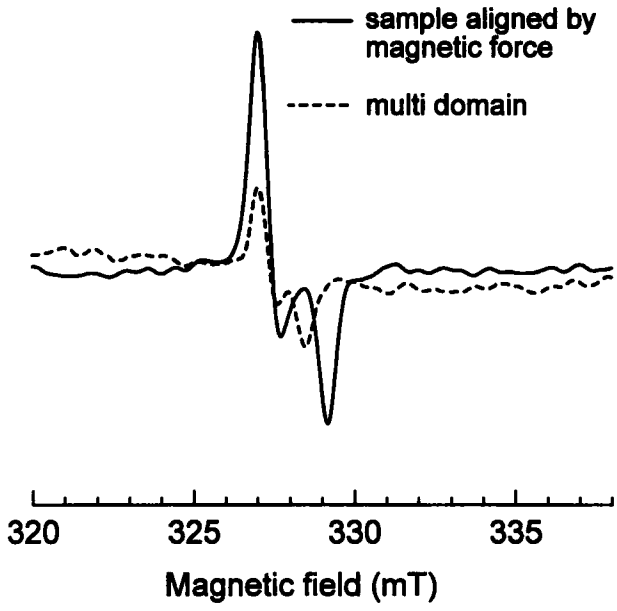


FIGURE 3 ESR spectra of the iodine doped polymers.

samples were doped for 600 min by *in-situ* gas phase of iodine at room temperature. The spin concentration of the aligned sample is higher than that of the non-aligned sample. This can be due to a macroscopic alignment of LC using an external magnetic force, leading to enhancement in ESR intensity. Further investigation of magnetic property using SQUID is currently under way.

CONCLUSION

We synthesized a polaron type LC conjugated polymer through one-pot polymerization with Stille reaction followed by Heck reaction. The polymer showed nematic LC. The ESR results suggested that the spontaneous orientation might serve as a favorable environment for both stabilization of polaron type unpaired electrons and substantial spin alignments. Molecular alignment of LC by external magnetic force can be lead to enhancement of macroscopic spin alignment for 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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