

Synthesis of new chiral inducer and preparation of semi-conducting polymer films showing fingerprint structure

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ABSTRACT

We synthesised a rod like shaped new chiral inducer to construct chiral liquid crystal electrolyte solution. Next, electrochemical polymerisation was carried out in the chiral liquid crystal electrolyte solution. The surface morphology of the polymers were observed with polarising optical microscopy. Synthesis of the new chiral inducer and preparation of semi-conducting thin film in the cholesteric liquid crystal electrolyte solution were performed.

Keywords: chirality; chiral inducer; electrochemical polymerisation; liquid crystals; semi-conducting polymers

1. INTRODUCTION

Optically active semi-conducting polymers have been prepared by electro-polymerisation of achiral monomers in a cholesteric liquid crystal electrolyte solution [1-6]. The polymer films thus synthesised show optical activities. This method can be referred to as "asymmetric electrochemical polymerization". Here, an addition of small amount of chiral compound to achiral nematic LC induces cholesteric liquid crystal as a chiral form of nematic liquid crystal. Individual molecules of cholesteric liquid crystals aggregate in helical manner. Cholesteric liquid crystals thus prepared can be used for electrolyte solution for electrochemical polymerisation. The resultant polymer films synthesised in cholesteric liquid crystals show fingerprint structure under polarising optical microscopy, which is very resemble to cholesteric liquid crystal.

In the present study, we synthesise a new type chiral inducer to prepare cholesteric liquid crystal electrolyte solution. Next, electrochemical polymerisation of bis(3,4-ethylene dioxothiophene) are carried out to obtain poly(3,4-ethylenedioxythiophene) (PEDOT), known as a semi-conducting polymer, showing vortex structure. Electrochemical polymerisation with conventional method can not obtain such an ordered structure.

2. EXPERIMENT

2. 1. Synthesis of chiral inducer

Firstly, 4-hydroxybiphenyl-4'-carboxylic acid was coupled with an optically active octanol ((R)-2-octanol) with the Mitsunobu reaction. The resultant material was dimerisation via Williamson etherification reaction to obtain compound 2S as shown Scheme 1. ¹H NMR (CDCl₃, δ from tetramethyl silane (TMS) as an internal standard) measurements evaluated the the proton attached at the stereo genic centres (sextet signal), as shown in Figure 1.

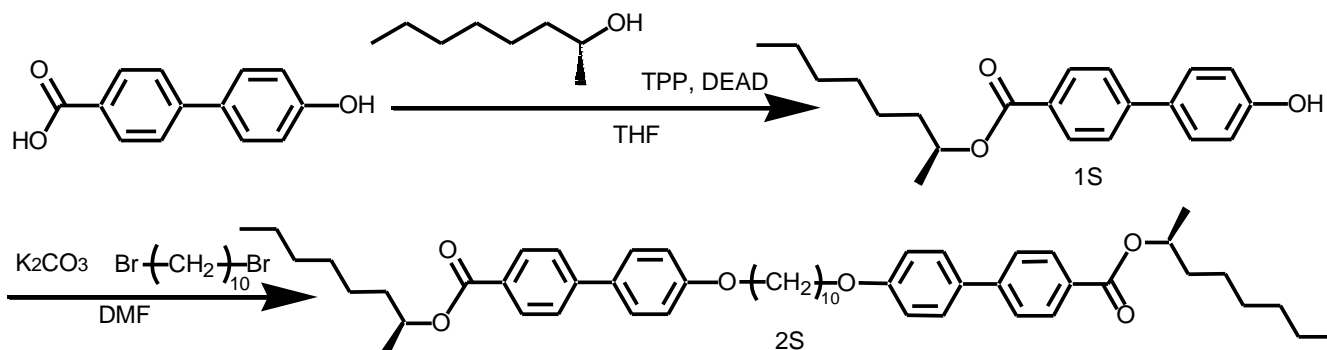
4'-Hydroxybiphenyl-4-carboxylic Acid (S)-1-Methyl-Heptyl Ester (1S).

To a solution of diethyl azodicarboxylate (0.9 mL, 2.3 mmol) and 4-hydroxybiphenyl-4'-carboxylic acid (499 mg, 2.3 mmol) in tetrahydrofuran (THF, 10 mL) were added a solution of triphenylphosphine (606 mg, 2.3 mmol) and (R)-2-octanol (387 mg, 2.9 mmol) in THF (90 mL). After stirring for 24 h at room temperature, the solvent was evaporated. The crude product was purified by silica gel chromatography (eluent: chloroform/ethyl acetate = 6/1) to afford white solid (274 mg, 36 %).

1,10-di[[*(S)*-1-Methyl-Heptyl]biphenyl-4-carboxylate-4'-oxy]decane (2S)

A solution of 4'-hydroxybiphenyl-4-carboxylic acid (*(S)*-1-methyl-heptyl ester (1S) (250 mg, 0.77 mmol), 1,10-dibromodecane (118 mg, 0.38 mmol), and K₂CO₃ (424 mg, 3.06 mmol) in *N,N*-dimethylformamide (10 mL) was stirred for 24 h at 90 °C.

The reaction mixture was extracted with ethyl acetate 3 times. The organic layer was dried over magnesium sulfate and purified by silica gel chromatography (eluent: *n*-hexane/ethyl acetate = 9/1). The solvent was removed under vacuum to afford yellow solid (8.8 mg, 1.4 %).



Scheme 1. Synthesis of chiral inducer. TPP = triphenylphosphine, DEAD = diethyl azodicarboxylate, THF = tetrahydrofuran, DMF = *N,N*-dimethylformamide.

2. 2. Synthesis of a monomer

2,2-Bis(3,4-ethylnenedioxythiophene) (bis-EDOT) was prepared by the previously reported method [7].

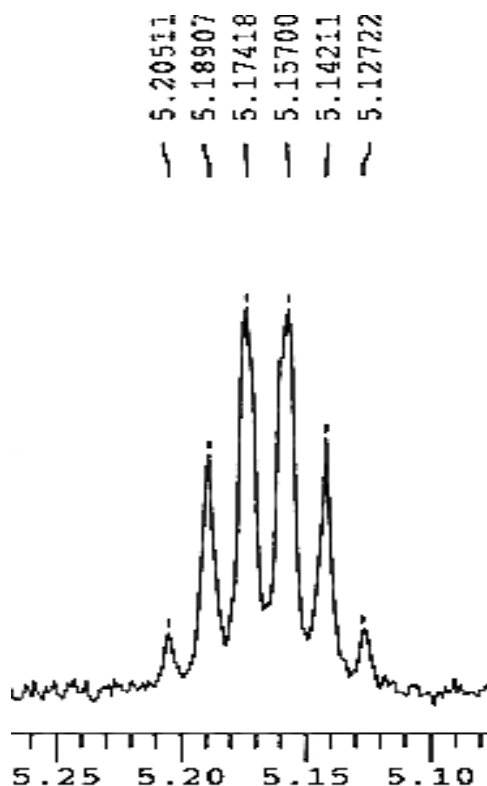
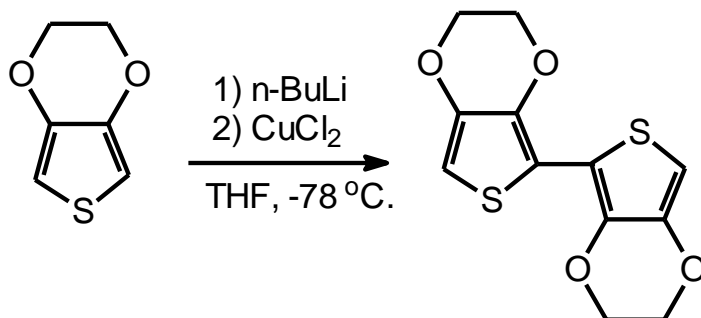


Figure 1. Sextet peak of 1,10-di[[*(S)*-1-Methyl-Heptyl]biphenyl-4-carboxylate-4'-oxy]decane (2S).

2,2-Bis(3,4-ethylenedioxythiophene) (bis-EDOT).

To a solution of 3,4-ethylenedioxythiophene (2.84 g, 20 mmol) in dried THF (70 mL) was added *n*-butyllithium (1.6 M in hexane) (12.5 mL, 20 mmol) dropwise over 5 min at $-78\text{ }^{\circ}\text{C}$. After stirring for 1 h at $-78\text{ }^{\circ}\text{C}$, CuCl_2 (2.69 g, 20 mmol) was added in one portion, and the mixture was gradually warmed up to room temperature over 2 h. Water (30 mL) and triethylamine (10 mL) was added.



Scheme 2. Synthesis of bis-EDOT.

The mixture was extracted with chloroform and the organic layer was dried over magnesium sulfate. The crude compound was passed through a short plug of silica (neutralized with triethylamine) by using chloroform as an eluent. The chloroform solution

(300 mL) was poured into hot hexane (700 mL) and cooled in 0 °C. The precipitate was collected by filtration to afford a light green yellow solid (1.53 g, 5.43 mmol, yield = 54 %). ^1H NMR (400 MHz; CDCl_3 ; TMS): δ 4.23-4.34 (m, 8H, $-\text{O}-\text{C}_2\text{H}_4-\text{O}-$), 6.27 (s, 2H, H (thiophene)). ^{13}C NMR (100 MHz; CDCl_3 ; TMS): δ 141.20, 136.99, 109.88, 97.51, 64.99, 64.59.

2. 3. Preparation of cholesteric electrolyte solution

n-Hexylcyanobiphenyl (6CB) as an achiral nematic liquid crystal shows Schlieren texture at room temperature, as shown in Figure 1.

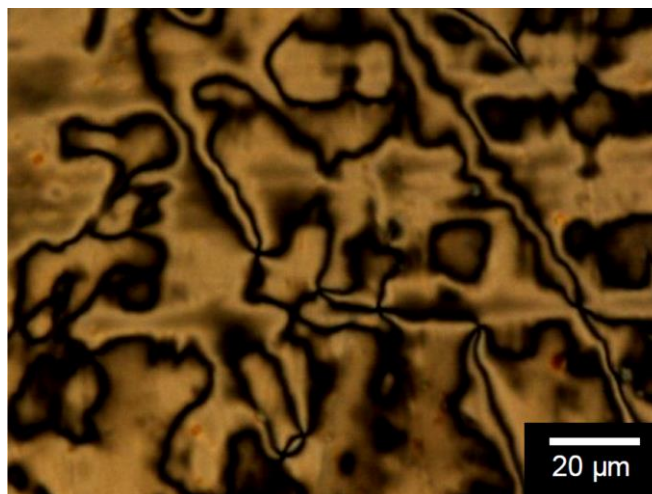


Figure 1. Polarising optical microscopy image of *n*-hexylcyanobiphenyl (6CB) at room temperature.

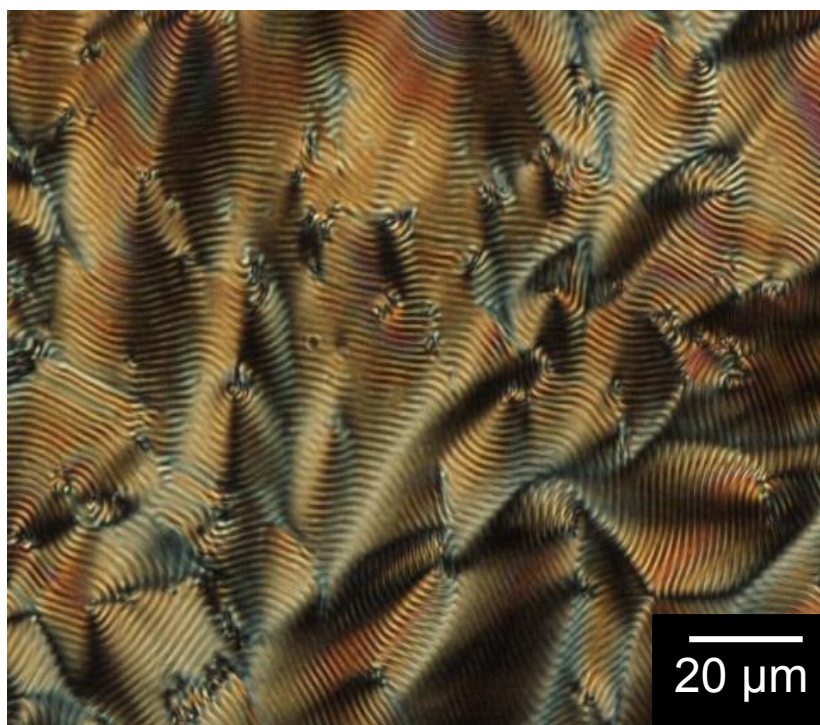


Figure 2. Polarising optical microscopy image of the cholesteric electrolyte solution containing 6CB, the monomer (bis-EDOT) and *n*-tetrabutyl ammonium perchlorate (TBAP).



Figure 3. Polarising optical microscopy image of a polymer thin film prepared in cholesteric liquid crystal electrolyte solution.

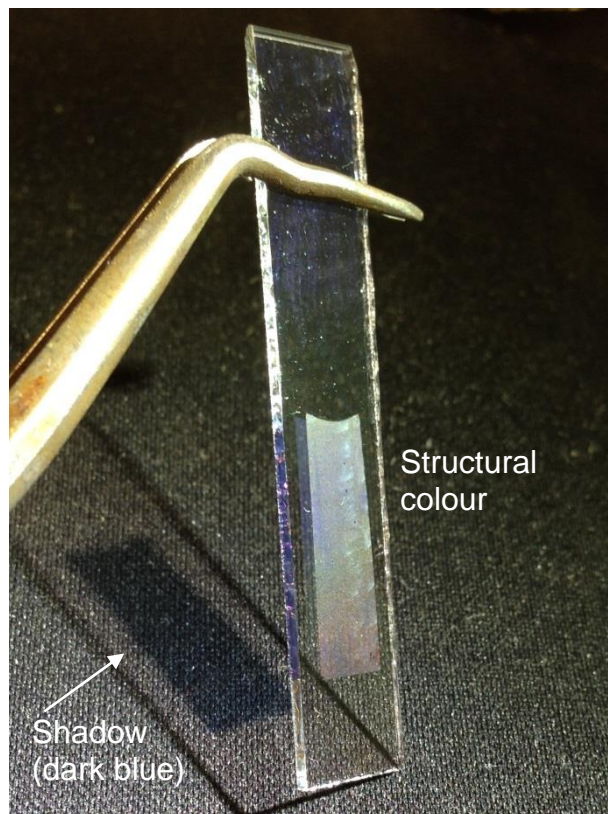
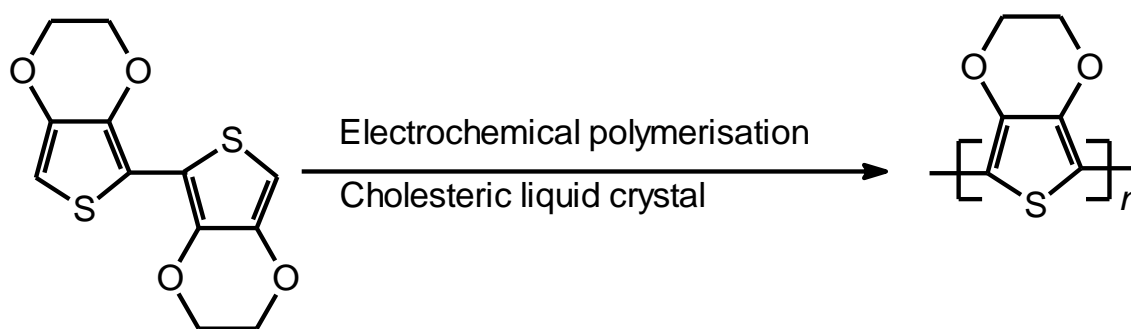


Figure 4. Polymer film exhibiting selective reflection.

An addition of small amount of chiral inducer 2S produces cholesteric liquid crystal as a chiral form of nematic phase. Figure 2 shows polarising optical microscopy image of the cholesteric electrolyte solution containing 6CB, the monomer and *n*-tetrabutyl ammonium perchlorate (TBAP). Quantity used; 2S (chiral inducer, 4.9 mg), TBAP (supporting salt, 0.543 mg), bis-EDOT (monomer, 0.575 mg), 6CB (nematic liquid crystal, 102.5 mg).

2.4. Polymerisation in cholesteric liquid crystal

Electochemical polymerisation in cholesteric liquid crystals was carried out by applying voltage of 4V to a sandwich cell charged with the cholesteric electrolyte solution containing the monomer (bis-EDOT) with 0.2 mm Tefron spacer (Scheme 3). After application of voltage for 10 min, the resultant polymer film deposited on anode side was washed and dried [8]. Figure 3 shows polarising optical microscopy image of the resultant polymer. The vortex structure can be produced by structural form imprinting from the cholesteric matrix during the polymerisation. The molecular aggergation form transcription process can be referred to as "liquid crystal asymmetric electrochemical polymerisation". Polymerisation in the nematic phase is also possible. However, the polymer prepared in the nematic liquid crystal show no vortex structure. The resultant polymer thus synthesised exhibited selective reflection, according to the periodic structure of the polymer film upon irradiation of white light, as shown in Figure 4. While, the shadow colour is dark blue (transmission colour). This is an evidence that the polymer shows butterflies like structural colour.



Scheme 3. Polymerisation.

3. CONCLUSIONS

We prepared a new chiral inducer having two stereogenic centers. This molecular form is very good affinity with nematic liquid crystals. Electrochemical polymerisation in the cholesteric liquid crystal electrolyte solution containing the monomer produced a thin polymer film showing vortex structure.

The chirality of the inducer (2S) produced helical structure of cholesteric phase from nematic phase. The resultant polymer transcribed the helical aggregation form of the cholesteric liquid crystal. This is a structural form imprinting from liquid crystals. Molecular imprinting (MIP, molecular level imprinting) may be also occurred in the polymerisation.

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