

Preparation of Polythiophene Films Showing Optical Activity by Electrochemical Polymerisation in Cholesteric Liquid Crystal Containing Coumarine

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ABSTRACT

We carried out electrochemical polymerisation in a cholesteric liquid crystal electrolyte solution. The polymer film prepared in the cholesteric liquid crystal showed chiropticality even though its monomer is an achiral. The surface morphology of the polymer was observed with polarising optical microscopy. Optical and electric properties were examined by UV-vis optical absorption, circular dichroism spectroscopy, and cyclic voltammetry.

Keywords: chiral inducer; coumarine; electrochemical polymerisation; liquid crystals

1. INTRODUCTION

Electrochemical polymerisation is one of the effective methods for preparation of conjugated polymer films. Mechanism of the polymerisation is considered to be oxidative reaction.

In general, common solvents such as acetonitrile, sulfuric acid aqueous solution, and propylene carbonate have been employed for electrochemical polymerisation [1-3]. Although these isotropic liquids are suitable for electrochemical polymerisation, control of the conformation and morphology of the polymer chains cannot be performed.

Recently, electrochemical polymerisation in liquid crystal has been developed, and the resultant polymer films have the similar form to that of the matrix liquid crystal [4-5].

In this study, we carried out electrochemical polymerisation of an achiral monomer in cholesteric liquid crystal medium containing coumarine. The polymer film shows optical activity, although the monomer is achiral. This indicates cholesteric liquid crystal as chiral solvent for electro-polymerisation can induce chirality of the polymer film.

2. EXPERIMENT

2. 1. Synthesis of chiral inducer

1,10-di[[(*S*)-1-methyl-heptyl]biphenyl-4-carboxylate-4'-oxy]decane (2*S*) was prepared by the previously reported method [6].

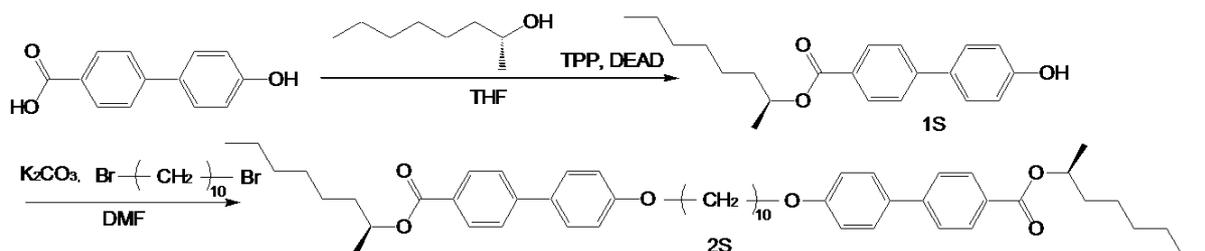
Firstly, 4-hydroxybiphenyl-4'-carboxylic acid was coupled with an optically active octanol ((*R*)-2-octanol) with the Mitsunobu reaction. The resultant material was dimerisation via Williamson etherification reaction to obtain compound 2*S*, as shown in Scheme 1.

4'-Hydroxybiphenyl-4-carboxylic Acid (*S*)-1-methyl-heptyl ester (1*S*)

To a solution of diethylazodicarboxylate (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 (2*S*)

A solution of 4'-hydroxybiphenyl-4-carboxylic acid (*S*)-1-methyl-heptyl ester (1*S*) (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%).



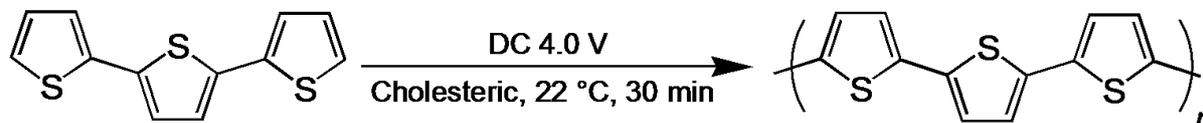
Scheme 1. Synthesis of chiral inducer. TPP = triphenylphosphine, DEAD = diethyl azodicarboxylate, THF = tetrahydrofuran, DMF = *N,N*-dimethylformamide.

2. 2. Preparation of cholesteric electrolyte solution and polymerisation in cholesteric liquid crystal

Cholesteric liquid crystal materials can be obtained by adding chiral inducer to nematic liquid crystal. *n*-Hexylecyanobiphenyl (6CB, nematic liquid crystal) and an addition of small amount of chiral inducer 2*S* induces cholesteric liquid crystal. Figure 1 (left) shows polarising optical microscopy image of the cholesteric electrolyte solution containing 6CB, the monomers, and *n*-tetrabutyl ammonium perchlorate (TBAP). Quantity used; 2*S* (chiral inducer, 2.96 mg), TBAP (supporting salt, 0.511 mg), terthiophene (monomer, 1.67 mg), coumarine (additive, 1.43 mg) 6CB (nematic liquid crystal, 89.04 mg). This is so called fingerprint texture, which is a typical of cholesteric liquid crystal.

Electochemical polymerisation in cholesteric liquid crystals was carried out by applying voltage of 4 V across indium-tin-oxide (ITO) coated glass cell charged with the cholesteric electrolyte solution containing the monomers (terthiophene) with 0.2 mm Teflon spacer (Scheme 2). After application of voltage for 30 min, the resultant polymer film was washed with hexane and tetrahydrofuran to remove the liquid crystal electrolyte solution. Figure 1

(right) shows polarising optical microscopy image of the polymer film. The texture is not similar to that of cholesteric liquid crystal but some morphology may be transcribed from the liquid crystalline medium.



Scheme 2. Electrochemical polymerisation. DC = direct current.

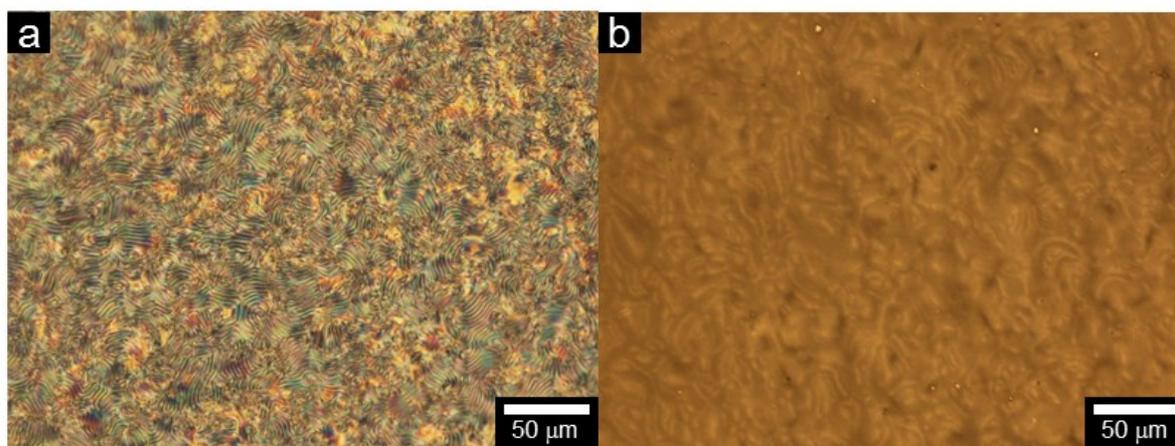


Figure 1. Polarising optical microscopy image of the cholesteric electrolyte solution (left, a) and the resultant polymer (right, b).

2. 3. Infrared absorption spectroscopy

The polymer, coumarine and chiral inducer (2S) were characterized by infrared absorption spectroscopy (Figure 2). The polymer does not show the signal at around 1710 cm^{-1} , which is characteristic of C=O vibration.

This suggests that the coumarine molecules and chiral inducer (2S) are not captured into the polymer.

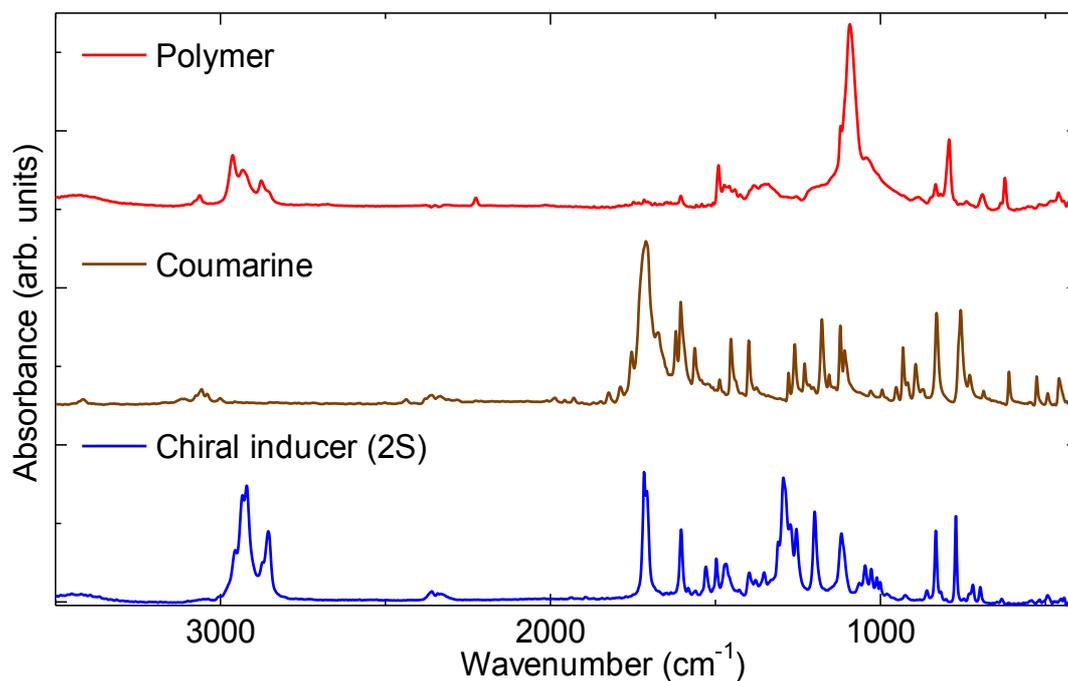


Figure 2. Infrared absorption spectra of the polymer film, coumarine, and the chiral inducer.

2. 4. UV-vis absorption spectroscopy

Figure 3 shows absorption spectrum of the polymer film in the reduced state. The maximum absorption wavelength is at around 450 nm due to π - π^* transition of the main chain.

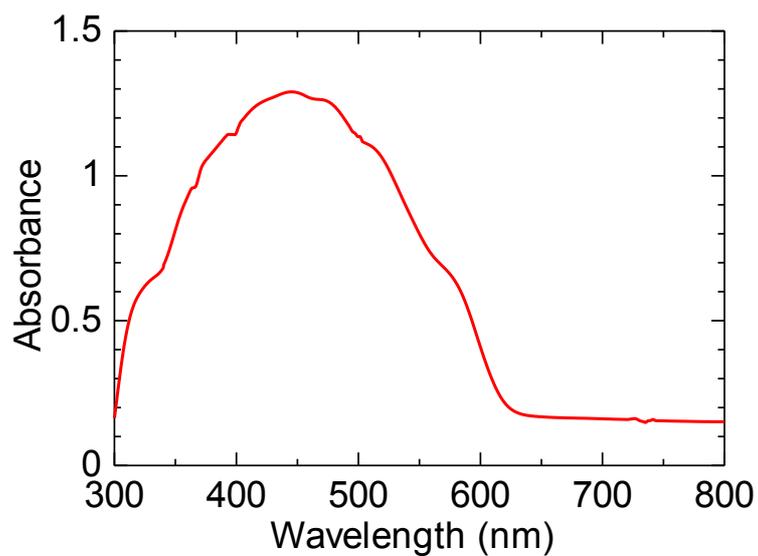


Figure 3. UV-vis absorption spectrum of the polymer film.

2. 5. Circular dichroism spectroscopy

Figure 4 displays circular dichroism (CD) spectrum of the polymer film in the reduced state, showing first-negative and second-positive Cotton effect from 600 nm to 300 nm. In addition, the transition point from negative to positive corresponds to the maximum absorption wavelength (450 nm). This type of Cotton effect is referred to as Davydov splitting, indicating the polymer forms left handed helical aggregation. [7]

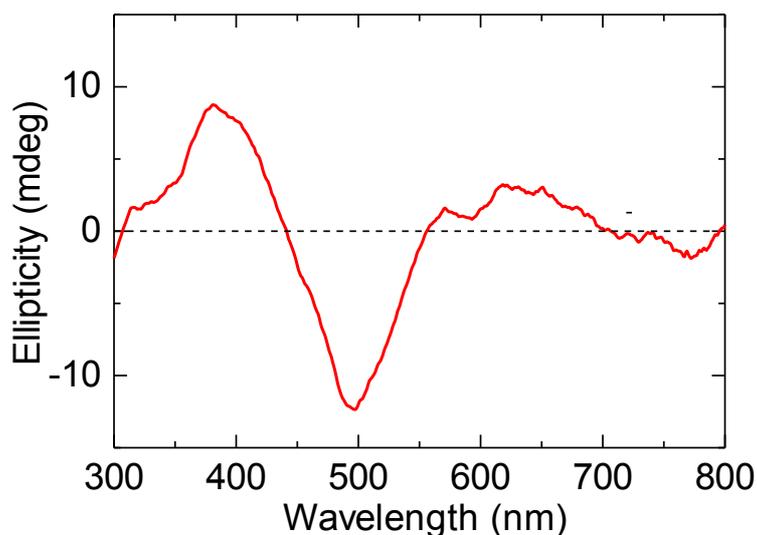


Figure 4. Circular dichroism spectrum of the polymer film.

2. 6. Cyclic voltammetry

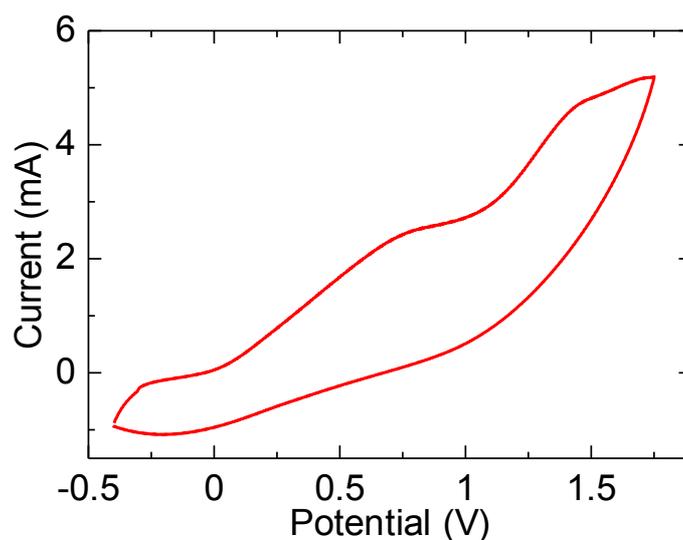


Figure 5. Cyclic voltammogram of the polymer film.

Figure 5 shows the cyclic voltammetry of the polymer film on an ITO working electrode versus Ag/Ag⁺ reference electrode with a Pt wire counter electrode immersed in 0.1 M TBAP in acetonitrile at a rate of 100 mVs⁻¹. This redox behavior is a typical of conducting polymers. On the oxidation process, the peaks around 0.75 and 1.4 V are attributed to the generation of polarons and bipolarons, respectively.

3. CONCLUSIONS

Electrochemical polymerisation in cholesteric liquid crystal produced the polymer film. The polymer film shows optical activity even though the surface morphology shows no fingerprint texture. This indicates that cholesteric liquid crystal medium induces chirality to the polymer, and cholesteric liquid crystal like fingerprint texture is not essentially required for optical activities. Moreover, if coumarine molecules are captured into polymers, this composite would exhibit fluorescence with electro- chiroptical activity.

Acknowledgments

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