Journal of Materials Science and Chemical Engineering, 2017, 5, 64-70
http://www.scirp.org/journal/msce
ISSN Online: 2327-6053
ISSN Print: 2327-6045

# Electrochemical Polymerization of 4,4-Dimethyl-2,2'-Bithiophene in Concentrated Polymer Liquid Crystal Solution

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**How to cite this paper:** Eguchi, N., Kawabata, K. and Goto, H. (2017) Electrochemical Polymerization of 4,4-Dimethyl-2,2'-Bithiophene in Concentrated Polymer Liquid Crystal Solution. *Journal of Materials Science and Chemical Engineering*, **5**, 64-70.
https://doi.org/10.4236/msce.2017.52007

**Received:** January 20, 2017
**Accepted:** February 17, 2017
**Published:** February 20, 2017

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## Abstract

Electrochemical polymerization of 4,4'-dimethyl-2,2'-bithiophene (4DMBT) was carried out in a concentrated solution of hydroxypropyl cellulose (HPC) liquid crystal in *N*,*N*-dimethylformamide. Infrared absorption spectra suggested that the resultant polymer film contains HPC. This study demonstrates an electrochemical preparation of a polymer composite having liquid crystal order. We proposed a helical stacking composite model.

## Keywords

Conjugated Polymer, Electrochemical Polymerization, Polymer Liquid Crystal, Hydroxypropyl Cellulose

## 1. Introduction

Polythiophene is one of the most studied conductive polymers and referred to as synthetic metals. 4,4'-Dimethyl-2,2'-bithiophene (4DMBT) is a thiophene derivative having alkyl group [1]-[14]. Electrochemical polymerization of conductive polymers gives high crystalline polymer film, but the control of the morphology is still a developmental issue. To solve this, an employment of template in molecular level is studied. Hydroxypropyl cellulose (HPC) is a cellulose derivative having solubility in water and organic solvents. Previous study indicates that HPC can be used as a template for production of polymers [15]. In this research, we synthesized a poly(4DMBT) (abbreviated as P-4DMBT) by electrochemical polymerization in concentrated HPC liquid crystal electrolyte solution. HPC liquid crystal solution is prepared by dissolving HPC in *N*,*N*-dimethylformamide (DMF). The HPC/DMF having small amount of supporting salt shows lyotropic liquid crystallinity at an appropriate concentration. Furthermore, HPC shows cholesteric lyotropic liquid crystalline phase with helical aggregation structure in

DMF solution. Therefore, liquid crystal HPC can be used as a helical template during electrochemical polymerization. This research performs electrochemical polymerization of 4DMBT in liquid crystalline HPC solution. Surface observation of the polymer film thus obtained is carried out by polarizing optical microscopy. Measurements of Fourier transforming infrared absorption and UV-VIS absorption confirm the chemical structure of the polymer composite film.

## 2. Experimental

### 2.1. Materials

A monomer 4DMBT was previously synthesized [16]. HPC was obtained from Wako Pure Chemical Industries, Ltd. (Japan) and used without further purification. Tetrabutylammonium perchlorate (TBAP) was obtained from Tokyo Chemical Industry (TCI, Japan) and used without further purification. DMF was obtained from Nacalai Tesque, (Japan) and used as received.

### 2.2. Synthesis

Electrochemical polymerization of 4DMBT in HPC was carried out (**Figure 1**). Constituents of electrolyte solution are shown in **Table 1**. First, 4DMBT and TBAP (supporting salt) were dissolved in DMF. Next, HPC was added to the solution and stirred mechanically by glass rod at room temperature. After mixing very well, the electrolyte solution was injected into sandwich cell with two ITO glass electrode (ITO = indium tin oxide). The method of sandwich cell polymerization was developed by our group previously. The cell was left for ca. 24 h at room temperature. Direct current (dc) of 4.0 V was applied across the cell for 60 min. A thin polymer film (P-4DMBT) was prepared on an anode side electrode. After electrochemical polymerization, the sandwich cell was soaked into the distilled water to remove the residual HPC from the polymer surface. After over 30 min, the cell was disassembled. The polymer film was washed with a sufficient amount of distilled water, and acetone to remove the residual HPC, TBAP and unreacted monomer. The polymer film was dried under atmospheric pressure.

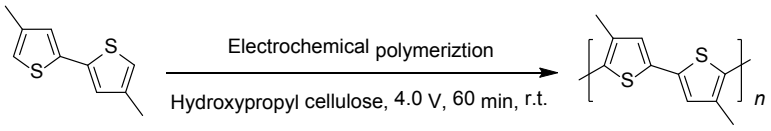


**Figure 1.** Scheme of electrochemical polymerization of 4,4'-dimethil-2,2'bithiophene (P-4DMBT) in hydroxypropyl cellulose.

**Table 1.** Constituents of electrolyte solution.

| Monomer | Matrix | Solvent | Supporting salt |
|---|---|---|---|
| | HPC[b] | *N*,*N*-dimethylformamide (DMF) | $(C_4H_9)_4N^+ClO_4^-$ (TBAP[c]) |
| 4DMBT[a] 4.5 mg | 700.6 mg | 369.5 mg | 1.1 mg |

a: 4,4'-dimethyl-2,2'bithiophene; b: *N*,*N*-dimethylformamide; c: Tetrabutylammonium perchlorate.

### 2.3. Measurements

Polarizing optical microscopy measurements were carried out by using ECLIPS LV 100 high-resolution polarizing microscope (Nikon). Fourier Transform Infrared absorption spectrum was obtained with a FT-IR 4600 (Jasco) by using the KBr method. UV-VIS absorption spectroscopy was carried out by using V-630 (Jasco).

## 3. Results

### 3.1. Polarizing Optical Microscopy

The polymer film thus obtained in liquid crystal HPC was examined by polarizing optical microscopy (POM). A POM image of the P-4DMBT is shown in Figure 2. From POM observation, fingerprint like texture derived from cholesteric liquid crystal was confirmed. In this system, HPC/DMF electrolyte solution forms lyotropic cholesteric liquid crystallinity having helical structure at a certain concentration. HPC plays a role of helical template, and transcription of helical structure to the polymer from HPC can be occurred.

### 3.2. Fourier Transform Infrared Absorption

Fourier transform infrared (FT-IR) absorption spectra for HPC, the monomer, and resultant film are shown in Figure 3. Absorption band at 3431 $cm^{-1}$ is due to hydroxyl group in the pyranose unit of HPC. Absorptions band at 2967 $cm^{-1}$ and 2932 $cm^{-1}$ is due to $CH_2$ and CH stretching vibration. Absorption band at 1533 $cm^{-1}$ is due to C=C stretching vibration. Absorption band at 1079 $cm^{-1}$ is due to C-O-C stretching vibration. This result revealed that the resultant polymer contains HPC in the film. This is because that the main chain was entangled with HPC during electrochemical polymerization to form helical composite (Figure 4).

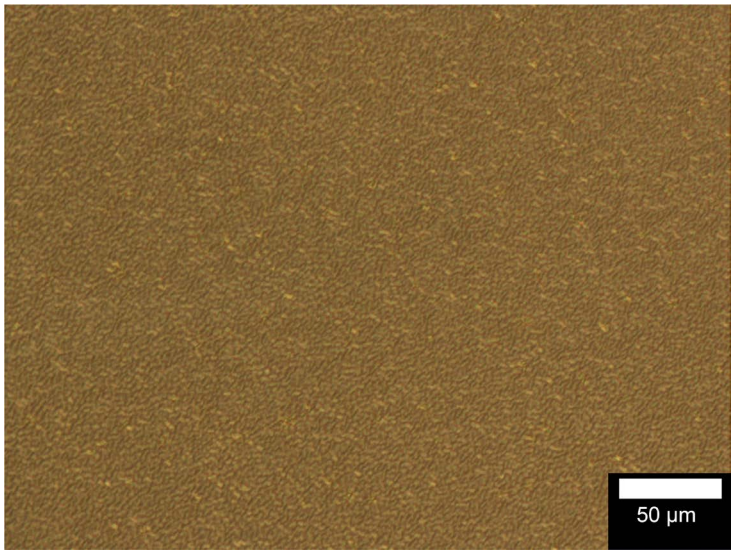


Figure 2. Polarizing optical microscopy image of poly(4,4'-dimethil-2,2'-bithiophene) (P-4DMBT) film.

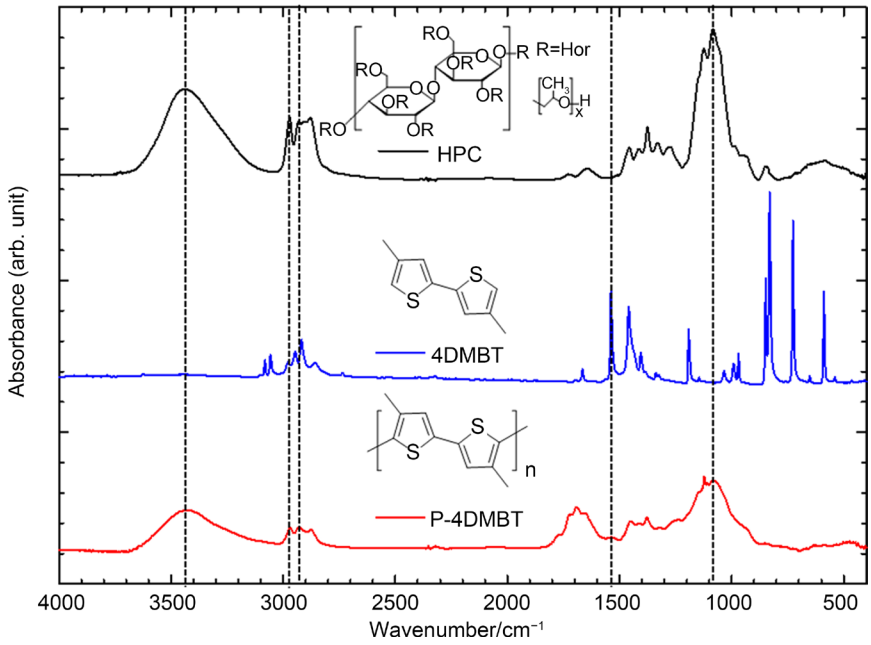


**Figure 3.** FT-IR spectra of hydroxypropyl cellulose (HPC, black line), 4,4'-dimethyl-2,2'-bithiophene (4DMBT, blue line) and poly(4,4'-dimethyl-2,2'-bithiophene) (P-4DMBT, red line).

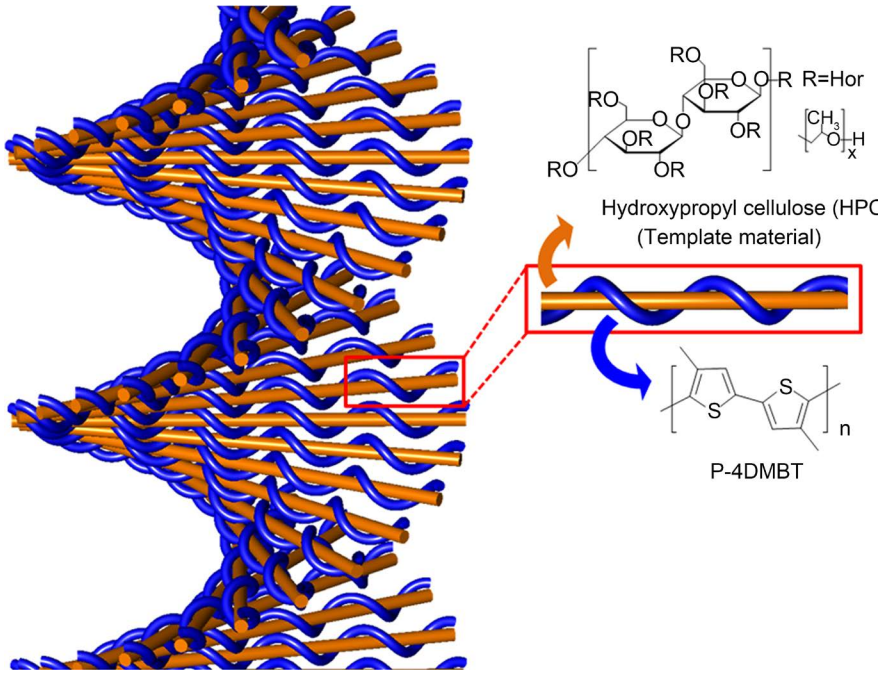


**Figure 4.** Possible structure of P-4DMBT/HPC composite. HPC (orange rod) and P-4DMBT (blue helical).

### 3.3. UV-Vis Absorption

UV-Vis absorption spectra of P-4DMBT (as prepared film) are shown in Figure 5. An absorption band at 700 nm is due to polarons, and > 850 nm is due to bipolarons. A neutral form (reduced form), polarons (radical cations), and bipolarons (dications) are illustrated in Figure 6. As prepared film is a doped form

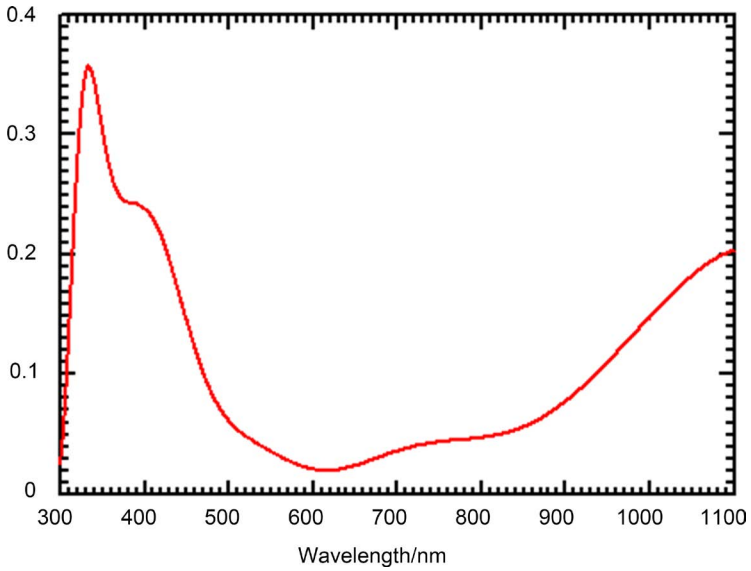


**Figure 5.** UV-VIS absorption spectra of as prepared P-4DMBT.

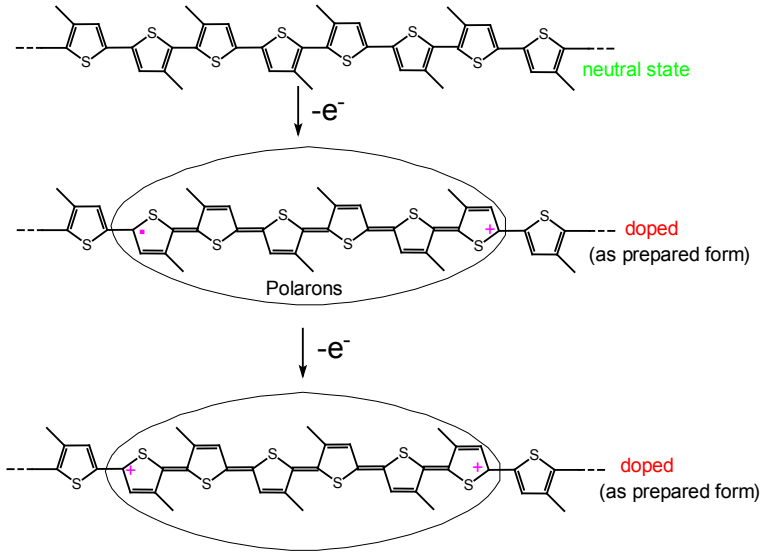


**Figure 6.** Polarons (radical cations) and bipolarons (dications).

having polarons and bipolarons in the main chain.

The main chain of P-4DMBT is twisted and the charge carriers can be gradually twisted in one handed direction to form helical structure on the cellulose. In this case, the helical charge carriers in the main chain can be referred to as "chiralions" [17]. The chiralions have been found after original development of asymmetric electrochemical polymerization, and liquid crystal solvent asymmetric polymerization [18]. The resultant polymer can be referred to as "helical synthetic metals".

## 4. Conclusion

In this research, electrochemical polymerization of 4DMBT was carried out in liquid crystal hydroxypropyl cellulose (HPC). The FT-IR absorption spectros-

copy revealed that the polymer film was to be a composite of P-4DMBT and HPC. The polymer can be entangled in helical manner with HPC in the propagation process in the electrochemical polymerization reaction.

## Acknowledgements

We would like to thank Tsukuba Research Centre for Interdisciplinary Materials Science (TIMS).

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