

Electrochemistry of 4,4-Dimethyl-2,2'-bithiophene

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ABSTRACT

Electrochemical polymerization of 4,4-dimethyl-2,2'-bithiophene (4DMBT) was conducted in a hydroxypropyl cellulose (HPC)/dimethylformamide (DMF) liquid crystalline electrolyte solution. Cyclic voltammetry and *in situ* UV-vis absorption measurements of poly(4,4-dimethyl-2,2'-bithiophene) (P-4DMBT) were carried out to investigate redox properties.

Keywords: conjugated polymer, cyclic voltammetry, *in situ* UV-vis absorption

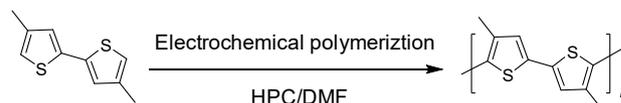
Introduction

Conjugated polymers are attractive materials because of lightness, flexibility, facile tuning of conductivity, and so on. Polythiophene derivatives are one of the most studied polymers for various applications [1]. In the previous research, 4,4-dimethyl-2,2'-bithiophene (4DMBT) was electrochemically polymerized in hydroxypropyl cellulose (HPC)/dimethylformamide (DMF) liquid crystal (LC) electrolyte solution [2]. Here, we report cyclic voltammetry and *in situ* UV-vis absorption of poly(4,4-dimethyl-2,2'-bithiophene) (P-4DMBT).

Experimental

4DMBT (monomer) was previously synthesized prior to electrochemical measurements [3]. 4DMBT and tetrabutylammonium perchlorate (TBAP) (supporting salt) were dissolved in DMF. Then, HPC was added to the solution and stirred mechanically. The electrolyte solution was stood for 1 week at room temperature to obtain a homogeneous LC solution. The LC solution was injected into a sandwiched indium tin oxide (ITO) glass electrode. Direct current of 3.0 V was applied to the cell for 10 min (Scheme 1). After electrochemical polymerization, P-4DMBT was deposited onto the ITO glass at anode side as a film. The polymer

film was washed with distilled water and acetone to remove the residual HPC, unreacted monomer, and TBAP.



Scheme 1. Electrochemical polymerization of 4,4-dimethyl-2,2'-bithiophene in hydroxypropyl cellulose (HPC)/dimethylformamide (DMF) liquid crystal solution.

Results and discussion

Cyclic voltammetry measurements of P-4DMBT film was carried out in 0.1 M TBAP acetonitrile solution between -0.1 V and 1.5 V at scan rates of 50 mV/s (Figure 1). Polymer deposited on ITO glass, Ag/Ag⁺ electrode, and platinum wire was used as working electrode, reference electrode, and counter electrode, respectively. Oxidation peak was confirmed at 1.1 V in oxidation process. Reduction signal, however, was not observed in reduction process, indicating that redox reversibility of P-4DMBT film is not good.

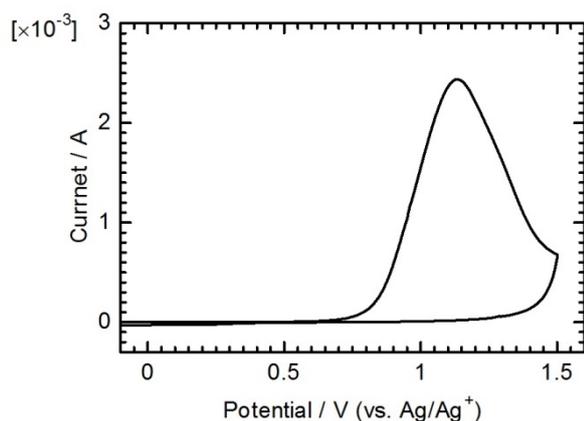


Figure 1. Cyclic voltammogram of P-4DMBT film in 0.1 M TBAP acetonitrile solution at scan rate of 50 mV/s.

In situ UV-vis absorption measurements were carried out in 0.1 M TBAP acetonitrile solution with cyclic voltammetry. UV-vis absorption spectra of P-4DMBT at oxidation process are shown in Figure 2. Absorption band at 378 nm is attributed to π - π^* transition. A new absorption band at 680 nm is attributed to polaron band (radical cation).

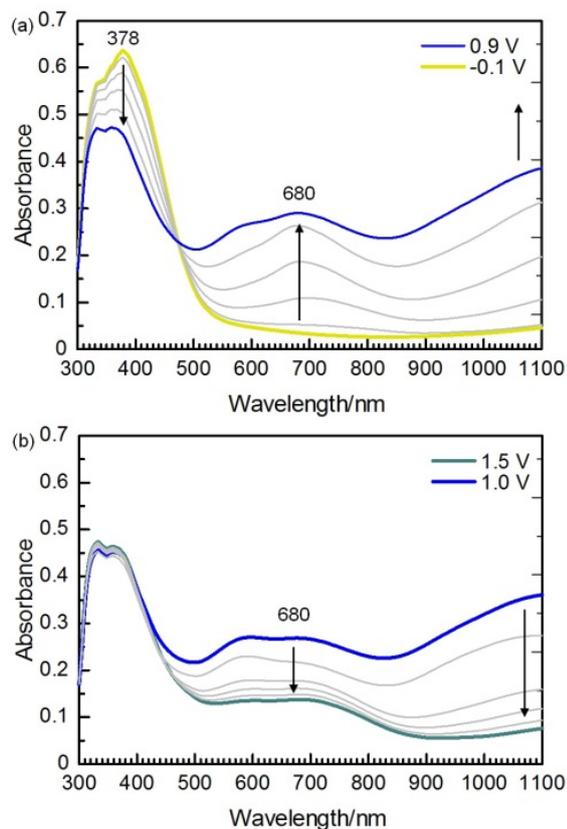


Figure 2. *In situ* UV-vis absorption spectra of P-4DMBT film in oxidation process. (a) -0.1 V-0.9 V, (b) 1.0 V-1.5 V.

The absorption intensity at 680 nm increases with application of voltages up to 0.9 V, indicating progress of electrochemical oxidation (Figure 2a). While, absorption intensity at 680 nm decreases with increase of application of voltages from 1.0 V to 1.5 V, indicating occurrence of excess oxidation at higher voltage (Figure 2b). Figure 3 shows *in situ* UV-vis absorption spectra of P-4DMBT in reduction process from 1.5 V to -0.1 V. Absorption band at 680 nm is due to polaron band. The absorption intensity decreases with application of voltages from 1.5 V to -0.1 V. Excess oxidation of the polymer in the experiment may result in degradation, or dopant (ClO_4^-) can not be removed mechanically from the polymer surface because the film thus obtained in HPC is a form of composite consisting of P-4DMBT and HPC. Excess oxidation fixes the dopant tightly in the entangled HPC with P-4DMBT.

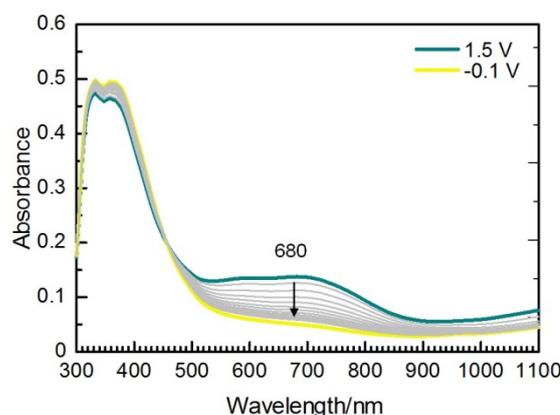


Figure 3. *In situ* UV-vis absorption spectra of P-4DMBT film at reduction process from 1.5 V to -0.1 V.

Conclusions

Redox properties of P-4DMBT film are investigated by cyclic voltammetry and *in situ* UV-vis measurements. *In situ* UV-vis absorption measurements reveal progress of oxidation during the electrochemical oxidation process from -0.1 V to 0.9 V. Excess oxidation of the polymer film is occurred during application of voltage from 1.0 V to 1.5 V.

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