Electrochemical synthesis and characterization of poly[3′-(4-formyl-3-hydroxyphenyl)-5,2′:5′,2″-terthiophene] film

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Abstract

A conducting polymer was electrochemically prepared on a Pt electrode with newly synthesized 3′-(4-formyl-3-hydroxyphenyl)-5,2′:5′,2″-terthiophene (FHPT) in a 0.1 M TBAP/CH2Cl2 solution. The poly[FHPT] film was characterized with cyclic voltammetry, in situ UV–vis spectroscopy, in situ conductivity measurements, and EQCM. From in situ UV–vis spectroscopy results, it was confirmed that generation of polaron and bipolaron was directly related to the conductivity of the poly[FHPT] film. The conductivity was 4.5 S/cm at +1.5 V. The poly[FHPT] film showed a specific catalytic response for the proton at the current media below pH 4. It also exhibited a specific catalytic response by metal ions.

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1. Introduction

Widespread interest in the tailor-made conducting polymers has arisen because of their large fields of specific application, such as electroluminescent devices, batteries, sensors and electromagnetic interference shielding materials [1−3]. More specifically, during the past few years, efforts aimed at synthesizing conducting polymers in which inorganic ligands are incorporated into the polythiophene backbone have increased, since such systems could have broad potential applicabilities, such as molecular recognition, electrochromic display and electrocatalysis with coordinating a specific transition metal [4−7].

Tetradentate Schiff-bases (salen) are one of the most extensively studied ligands in coordination chemistry. They can only coordinate with a large number of transition and lanthanide ions, with possess numerous interesting properties related to the catalysis and electrochemistry [8,9]. Considering the large variety of merits concerned with both the conducting polythiophenes and the salen ligands, the combination of the two systems, i.e. polythiophenes incorporated by salen into their π-backbone may create materials having unique properties originated from the electronic communication of the metal center with the π-backbone. For example, a variety of thiophenes incorporated by salen based metal complexes have been electrochemically polymerized to form films on electrodes, which have exhibited characteristic electrochromisms [10,11] and sensor capabilities [12]. We have currently studied for the synthesis of a conducting polythiophenes incorporating morganic and organometallic complexes, and in the study of their physical properties [13−15].

Herein we report the electrochemical synthesis and physical properties of a polythiophene ladder system π-conjugated by tetradentate Schiff-base ligands as a novel type of conducting polymer. The polymers have a unique structure which the 3′-positions of two terthiophene strands are cross-linked by one salen bridge in every repeating unit. The incorporated salen moiety will shield the β-positions of the thiophene rings and enhance the selectivity of α-coupling between thiophene units during polymerization reaction, which ensure the high conjugation of the resulting polymer. In addition, the effective communication between the chelating units and the conjugated-system...
will be ensured, since the salen ligand is π-conjugated duplica-

tively to both the polymer π-strands.

The data in the present study reflect a simple prepara-

tion method of poly[3-(4-formyl-3-hydroxyphenyl)-5,2′-5′,2′-

terthiophene, FHPT] as a monomeric building block and its elec-

tropolymerization. The preliminary characterization of these

polymer films was done in respect of cyclic voltammetry (CV),

in situ UV–vis spectroscopy, in situ conductivity and EQCM.

2. Experimental

2.1. Materials

Tetra-o-butyl ammonium perchlorate (TBAP) from Fluka Co.

was recrystallized twice from absolute ethanol and dried under

vacuum conditions of 10⁻³ Torr. Dichloromethane (Aldrich,

99.8%, anhydrous, sealed under N₂ gas) was used as received.

All other reagents used in this study were extra pure grade

reagents (Aldrich, USA). All solutions were prepared with dou-

ble distilled water (18.2 MΩ). 3-(4-formyl-3-hydroxyphenyl)-

5,2′-5′,2′-terthiophene was prepared according to the known

procedure [16].

2.2. Apparatus

A single-compartment cell housing three electrodes was used

for voltammetric and in situ UV–vis spectrophotocatalytic

measurements. Electrochemical experiments were carried out

employing a Model 273 Potentiostat/Galvanostat from EG&G

Princeton Applied Research and Model KST-CV 104A, 4 Chan-

nel Potentiostat/Galvanostat, Kosentech (Korea).

In situ UV–vis spectra were taken using an Ocean Optics

S2000 spectrometer with a charge-coupled device (CCD) array

detector, which was configured to a near normal incidence

reflectance mode using a bifurcated quartz optical fiber. Details

of the spectrophotocatalytic system have been described else-

where [17]. In situ conductivity measurements were carried out

using the method similar to that first described by Wrighton and

coworkers [18]. An insulating gap was introduced onto the gold

film electrode, which had been prepared by vacuum evaporation,

by cutting it with a razor blade. The gap, which was determined

to be about 10 μm using the optical microscope, was bridged by

growing poly[FHPT] film between the two split gold electrodes.

Currents were then read with applied voltages across the poly-

mer bridge between split Pt electrode and Ohm’s law was used to

calculate the resistances. The electrochemical quartz crys-

tal microbalance (EQCM) measurements were performed using a

Seiko EG&G Model QCA 917 quartz crystal analyzer con-

trolled by M270 software. An AT-cut 9 MHz Pt-plate quartz

crystal (model QA-AM9-Pt) was used as a resonator. A Pt-

coated quartz crystal working electrode was mounted on a model

QA-CL3 electrode holder. The sensitivity of the quartz crystal

electrode was calibrated by potentiostatic deposition of silver

from a silver nitrate solution using the equation: \( \Delta f = -M_{eq} \cdot C_j \cdot Q(\Omega) \) from the Sauerbrey relationship [19]. The sensitivity fac-

tor was 6.07 ± 0.5 ng cm⁻² Hz⁻¹ for the crystal electrodes used

in this experiment. This is in agreement with the theoretically

calculated sensitivity based on the Sauerbrey equation using

appropriate constants (5.61 ng cm⁻² Hz⁻¹).

A platinum disk (area 7.5 mm²) served as a working elec-

trode, while a platinum spiral wire was used as a counter elec-

trode. An Ag/AgCl (in saturated KCl) electrode, separated from

the measuring solution by bridging it with a 0.1 M TBAP solu-

tion in dichloromethane, was used as a reference electrode for

a non-aqueous experiment. The platinum disk electrode was

polished to a mirror finish with 0.1 μm alumina powder. The

potential between the limits for hydrogen and oxygen evolution

was cycled in a 1 M H₂SO₄ solution until well-defined cyclic

voltammograms (CVs) were obtained for a Pt electrode sur-

face. After this, the electrodes were rinsed with doubly distilled

water and dichloromethane, and then dried before being used

for subsequent experiments. Nitrogen gas was purged through

the solution for 15 min before every measurement and above

the solution during measurement.

3. Results and discussion


Fig. 1(b) shows the structure of poly[FHPT] composed of

nanoparticles (~200 nm). Fig. 1(a) shows cyclic voltammo-

grams recorded during polymerization in a 1 mM FHPT/0.1 M

TBAP containing dichloromethane solution, where the poten-

tial was cycled at 100 mV/s between +0.4 and +1.5 V versus

Ag/AgCl (saturated KCl) 30 times. As can be seen, the monomer

was oxidized at +1.3 V during the first anodic scan, followed

by the deposition of the polymer film on the electrode surface

immediately. The first reverse scan after the oxidation of the

monomer produced subsequent cathodic peaks of the oxidation

products at about +0.9 V. The second anodic scan shows the cor-

responding oxidation peak to the poly[FHPT] that was formed

during the first potential cycle. As the potential cycling con-

tinued between +0.4 and +1.5 V, CV peaks appeared at +0.9/+1.3 V,

which corresponds to the redox peaks of polymer formed on

the electrode surface. The peaks became gradually larger and

the anodic peak potentials shifted to a more positive direction

as the number of potential cycles increased. The color of the

resulting polymer that formed on the Pt disk electrode was yel-

low.
lowish brown. CVs also were recorded for the poly[FHPT] film deposited electrode in a blank 0.1 M TBAP/CH₂Cl₂ solution without the monomer. Broad redox peaks of the polymer film were observed around +1.2/+0.8 V versus Ag/AgCl electrode in the blank electrolyte solution. As the number of potential cycles increased, the current of the redox peak slowly decreased. This means that the electrochemical activity slowly decreased as the potential cycling continued. However, the decrease in the electrochemical activity of this polymer film was less than that of other polymer films. The stability factor, defined as the number of cycles required for the area under the redox peak to decrease by one half, was 200 cycles for the polymer film [16]. This indicates that the stability of the polymer film is more comparable to other organic conductive polymers [20] formed on the electrode.

3.2. Characterization of poly[FHPT] film deposited on the electrode

To determine the amount of the polymer deposited on the electrode, EQCM experiments were done during polymerization in a 1 mM monomer containing electrolyte solution. The EQCM experiments, in which one face of the quartz resonator was used as a working electrode, were carried out simultaneously with CV. Steady polymer growth was confirmed with a decrease in frequency as the number of cycles increased. In the present study, weight change during 30 cycles was estimated to be \( -6.3 \times 10^{-6} \text{g cm}^{-2} \) (frequency shifts: \(-1037 \text{Hz}\)).

To investigate the morphology and the thickness of the polymer film deposited on the electrode, SEM pictures were taken. Fig. 2 displays the morphology of the polymer film, which were grown during 30 potential cycles in a 0.1 M TBAP/CH₂Cl₂ solution containing 1 mM FHPT. The polymer film exhibits aggregated round-shape particles and high porosity. The thickness of the film used for this study was determined to be \( \sim 2 \mu m \). SEM picture shows that the polymer film was composed of particles size of \( \sim 200 \text{nm} \).

Fig. 2. SEM images: a plane view of the poly[FHPT] film (thickness \( \sim 2 \mu m \)).

In situ conductivity and UV–vis spectra of the poly[FHPT] film. Conductivity measurements for the poly[FHPT] film were done using an in situ technique, applying various potentials in both aqueous and non-aqueous solutions. The resistances were measured across a \( \sim 10 \mu m \) gap between polymer-bridged gold electrodes in a CH₂Cl₂ solution containing 0.1 M TBAP, while the potential varied from 0.0 to +1.6 V.

Fig. 3. In situ resistance (●) and conductivity (○) of poly[FHPT] film measured as a function of the applied potential in a 0.1 M TBAP/CH₂Cl₂ solution.

Fig. 4 shows a series of the absorption spectra recorded (a) during a potential cycle in a 0.1 M TBAP/CH₂Cl₂ solution containing 1 mM FHPT, and (b) for the polymer film in a blank solution without the monomer, from 0.0 to +1.5 V and back to 0.0 V, with a reflective platinum electrode. The scan rate was 5 mV/s. Altogether 88 spectra were recorded over a 3.0 V potential span. Each spectrum was printed out at a 25 mV interval (Fig. 4 shows the data for 30 of these spectra). The spectrum recorded in the 44th wavelength scan (store number) between 300 and 1000 nm corresponds to that when the potential was reversed, i.e. +1.5 V. An absorption band responsible to the monomer was observed at 380 nm. At the first scan, from 0.0 to +1.2 V, no changes were observed in the spectra. However, a new absorption band immediately began to appear at 850 nm, when the potential went to +1.2 V. This was due to the deposition of the polymer by the oxidation of the monomer. When the electrode potential reached 1.4 V, other absorption bands began to appear at about 680, 850 and 940 nm. During the reverse (cathodic) scan, from +1.5 to 0.0 V, the bands at 850 nm decreased. The intensity of the absorption band at 480 nm increased as the potential moved towards +0.5 V. Therefore, the absorption band that appeared at 480 nm should correspond to the absorption of photons by the polymer at a neutral state, which arises from \( \pi-\pi^* \)
transition of electrons on the thiophene backbone. The increasing intensity of the band at 850 nm, observed during the reverse scan to +0.8 V, may be due to the oxidation of the polymer film, which indicates the formation of polaron on the thiophene backbone. The later increase in the intensity of the band at 940 nm, in the same forward scan at over +1.2 V, is mainly related to the formation of bipolarons. On the reverse scan, the intensity of the polaron band decreased. However, the one due to bipolarons at 940 nm remained until the potential reverse scan reached +1.0 V.

Table 1

<table>
<thead>
<tr>
<th>Various ion</th>
<th>Response current of a poly[FHPT] modified electrode at pH 3.50 blank buffer solutions and 1.0 × 10^{-3} M various metal ions in a 0.1 M KNO₃ solution (scan rate:100 mV/s, pH 4–6)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>i_{pa} (µA)</td>
</tr>
<tr>
<td>Cu^{2+}</td>
<td>–107.1</td>
</tr>
<tr>
<td>Zn^{2+}</td>
<td>–72.2</td>
</tr>
<tr>
<td>Al^{3+}</td>
<td>–159.6</td>
</tr>
<tr>
<td>Fe^{2+}</td>
<td>–69.9</td>
</tr>
<tr>
<td>H^{+}</td>
<td>–32.6</td>
</tr>
</tbody>
</table>

From this, it was confirmed that generation of polaron and bipolaron was directly related to the conductivity of the polymer film.

3.3. The response of poly[FHPT] film

Poly[FHPT] film showed a specific response for the proton at the current media below pH 4. It also exhibited a specific response for certain metal ions, especially for Al(III) ions at pH 7.4, even in trace levels. Well-defined and very sensitive anodic current flowed in the presence of Al(III) ions in a test solution. The results lead to the assumption that the property originated from the specific oxidation of the polymer by Al(III) ions in trace levels. This property of poly[FHPT] film was successfully applied for the selective determination of Al(III) ions in trace levels. This method was evaluated using a real standard urine sample. The result shows the best sensitivity for Al(III) ion determination when compared with other analytical methods [16]. Table 1 shows response current of a poly[FHPT] modified electrode for the proton and certain metal ions.

4. Conclusions

A newly synthesized thiophene analogue (FHPT) was polymerized on a Pt electrode, in a 0.1 M TBAP/CH₂Cl₂ solution. It was characterized with cyclic voltammetry, in situ UV–vis, in situ conductivity measurements, SEM and EQCM. The polymer film on the electrode was characterized to be typical of a conducting polymer revealing the conductivity of 4.5 S/cm at +1.5 V. The polymer film on the electrode was characterized to be typical of a conducting polymer revealing the conductivity of 4.5 S/cm at +1.5 V. The poly[FHPT] film showed a specific catalytic response for the proton at the current media below pH 4. It also exhibited a specific catalytic response for certain metal ions, especially for Al(III) ions at pH 7.4, even in trace levels. The results lead to the assumption that the catalytic property originated from the specific oxidation of the polymer by Al(III) ions in trace levels. This property of the polymer was successfully applied for the selective determination of Al(III) ions in trace levels.

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References