Morphological and Electrochemical Properties of 3,4-Substituted Polythiophene Films Prepared by Electrochemical Polymerization

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ABSTRACT

We have synthesized 3,4-ethylenedioxythiophene (EDOT) monomer analogs such as 3,4-ethylenedioxythiophene (EOTT), 3,4-ethylenedithiathiophene (EDTT) and 3,4-methylenedithiathiophene (MEDTT), and investigated morphological and electrochemical properties of the corresponding polymer films prepared by their electrochemical polymerization. In addition, their properties were compared with those of poly(3,4-ethylenedioxythiophene) (PEDOT) film electropolymerized.

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1. Introduction

In recent years, the expectation for the next-generation electronics has grown with rapid progress of the information-oriented technology. Because of its variety and metastable position, the organic materials are hoped for application to future molecular electronics.

One of the organic materials, the conducting polymer is in lighter weights, and more flexible and furthermore it can be designed easier in low cost by wet process and roll to roll, compared with the inorganic materials. There are many examples applied for like an organic light-emitting diode (OLED),1–3 a solar battery,4–6 an organic field effect transistor (OFET),7–10 a capacitor11,12 and, so on.

High electronic conductivity is an important element for such applications. To realize high electronic conductivity, we need the superior π-conjugated system having the planar structure and mutual interactions between polymer chains. Polythiophene derivatives are most studied polymer materials for this purpose. For instance, poly(3,4-ethylenedioxythiophene) (PEDOT) indicates superior conduction properties.13,14 PEDOT, polymerized with the monomer EDOT chemically or electrically, exhibits high electric conductivities in a range of 10^3–10^4 S cm⁻¹.

In order to obtain further superior conduction properties of π-conjugated polymers, recent advanced studies focused on the modification of EDOT monomer structure by means of introducing functional groups onto its framework. On the other hand, studies on the modification of EDOT basic framework have been relatively limited so far.15

Under these backgrounds, in this work, we have synthesized 3,4-ethylenedioxythiophene (EOTT),15 3,4-ethylenedithiathiophene (EDTT)15–20 and 3,4-methylenedithiathiophene (MEDTT) monomers, and investigated morphological and electrochemical properties of the corresponding polymer films prepared by their electrochemical polymerization. As for the studied monomers such as EOTT, EDTT, and MEDTT, one or both oxygen atoms of EDOT framework were replaced by sulfur atom (see Scheme 1).

Scheme 1. Structure of thiophene derivative monomers studied in this work.

Scheme 2. Preparation of EOTT.

2. Experimental

A solution of 3,4-dimethoxythiophene (50 mmol) and 1,2-ethanediol (55 mmol) in the presence of catalytic amount of p-toluene sulfonic acid monohydrate (PTS, 5.0 mmol) was stirred for 12 h at 80°C in toluene (80 g) (see Scheme 2). After adequate reaction, the solution was extracted with 4.8% NaOH aqueous solution, then toluene was removed under reduced pressure, the mixture was purified by chromatography on silica gel with hexane. A pale yellow liquid of EOTT was obtained in 49% yield. The chemical structure of EOTT was confirmed by 1H-NMR. 1H-NMR (CDCl3); δ = 6.97 (1H, s), 6.93 (1H, s), 3.53–3.56 (1H, m), 3.14–3.16 (1H, d), 2.98–3.02 (1H, t), 1.44 (3H, d) ppm.

Following of the above-mentioned method, EOTT was provided with 2-mercaptoethanol and MEDTT was prepared with 1,2-propanedithiol. EOTT: 62% yield. 1H-NMR (CDCl3): δ = 6.75 (1H, s), 6.46 (1H, s), 4.40 (2H, m), 3.10 (2H, m) ppm. MEDTT: 75% yield. 1H-NMR (CDCl3); δ = 6.97 (1H, s), 6.93 (1H, s), 3.53–3.56 (1H, m), 3.14–3.16 (1H, d), 2.98–3.02 (1H, t), 1.44 (3H, d) ppm.
EDOT was purchased from Tokyo Chemical Industry and used as received.

Although acetonitrile is usually chosen as a solvent for electrochemical polymerization, one of the studied monomers, EDDTT is not dissolved in it. Therefore, in this demonstration, propylene carbonate was used as an electrolytic solvent since all studied monomers can be dissolved in it. Electrochemical polymerization was carried out by a galvanostatic method under the following electrolytic conditions: ITO plate anode (0.7 × 3.0 cm²), Pt plate cathode (2 × 2 cm²); electrochemical cell, undivided type; monomer concentration, 50 mM; electrolytic solution, 0.1 M Bu₄NBF₄ in propylene carbonate (25 ml); current density, 2.0 mA cm⁻²; electricity, 0.21 C.

Cyclic voltammetry of polymer films on ITO electrode was performed by a computer controlled electrochemical system. Cyclic voltammograms (CVs) were recorded with a three-electrode system using an ITO working electrode covered with the polythiophene derivative films, a Pt plate counter electrode, and SCE reference electrode in 0.1 M Bu₄NBF₄/propylene carbonate at 25°C.

The polythiophene derivative films deposited on the anode was also subjected to scanning electron microscopy (SEM).

The polythiophene derivative films obtained by the electrochemical polymerization were dedoped potentiostatically for 10 min in 0.1 M Bu₄NBF₄/propylene carbonate, and then subjected to a UV-vis measurement.

On the other hand, after the polymerization, the polymer film deposited on the working electrode was washed with propylene carbonate to remove the monomer remaining in the film, and then dried under reduced pressure. After this process, the film was removed from the working electrode and the obtained free-standing film was subjected to electrical conductivity measurement (four-probe method).

3. Results and Discussion

Colored polymer films were appeared on the anode surface by the electrochemical polymerization of all studied monomers (PEDOT: blue, PEDTT: dark green, PEOTT: slightly green-like blue, PMEDTT: dark green). However, PEOTT film was dissolved little by little into the solution during the electrochemical polymerization, and finally the slight PEOTT film was remained on the ITO anode. We did not confirm this reason. However, its asymmetric monomer unit structure might result in an increasing solubility in a polar solvent such as propylene carbonate.

The surface morphology of the polymer films prepared by the electrochemical polymerization of the studied monomers was observed by SEM (Fig. 1).

![Figure 1. SEM surface photographs of polythiophene derivatives. (a) PEDOT, (b) PEOTT, (c) PEDTT, (d) PMEDTT.](Image)

As shown in Fig. 1, all polymer film samples composed of the corresponding polymer grains. However, the PEDOT grains were well networked each others, and such a networked structure appeared on the whole film surface. The extent of the network formation decreased for the PEOTT case [see Fig. 1(b)], and the PEDTT grains were spherical structure and few networked each others, as shown in Fig. 1(c). PEOTT and PEDTT are PEDOT analogs in which one or both oxygen atoms of PEDOT are replaced by sulfur atom. Therefore, the polymer grain structure and extent of network formation seem to be related to the presence of oxygen atoms in the PEDOT framework. On the other hand, similarly to the PEDOT case, the PMEDTT grains were also well networked each others, although the monomer unit frame does not contain any oxygen atoms. PMEDTT is PEDTT analog in which a methyl group is introduced onto PEDTT framework. Hence, the introduction of a methyl group may also enable to form the networked structure in the polymer film.

In the next, the electrical conductivity of polymer films was measured by the four probe method. Unfortunately, the electrical conductivity of PEOTT film could not be measured due to its slight amounts as mentioned in the above.

The conductivity of PEDTT film was found to be ca. 6 × 10⁻² S cm⁻¹, and it was much lower than that of PEDOT film (ca. 50 S cm⁻¹). In sharp contrast, PMEDTT film showed metallic conductivity (20 S cm⁻¹), and its conductivity was comparable to that of PEDOT. As mentioned in the former section, PMEDTT is PEDTT analog in which a methyl group is introduced onto PEDTT framework. However, the morphological structure of PMEDTT film prepared by the electrochemical polymerization was highly networked, and it was not similar to that of PEDTT but to that of PEDOT. Therefore, it can be stated that the conductivity of the polymer films prepared from the studied monomers depends greatly on the morphological structure of the polymer films.

In the last, we estimated HOMO and LUMO levels of all polymer films by their cyclic voltammograms and UV-vis spectra (Table 1). When the SCE electrode is used as a reference electrode for CV measurement, HOMO level (\(E_{\text{HOMO}}\)) can be calculated using Eq. (1).²¹

\[
E_{\text{HOMO}} = E^{0\text{ red}} + 4.4 \text{ (eV)}
\]  
(1)

Where \(E^{0\text{ red}}\) represents the formal potential for doping-dedoping response in the voltammograms.

On the other hand, LUMO level (\(E_{\text{LUMO}}\)) can be calculated using Eq. (2).²¹

\[
E_{\text{LUMO}} = E_{\text{HOMO}} + E_g
\]  
(2)

Where \(E_g\) represents the band gap between HOMO and LUMO levels. The \(E_g\) can be estimated from the onset UV-vis absorption for the polymer film dedoped.

In general, the low band gap and low oxidation (doping) potential are important parameters for the construction of high conducting polymers. In this regard, PEDOT and PEOTT seem to be good candidates for this purpose. However, the conductivity of PEOTT

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Formal potential (E^{0\text{ red}}/N)</th>
<th>Onset of absorption peak (\lambda_{\text{onset}}/\text{nm})</th>
<th>HOMO level (E_{\text{HOMO}}/\text{eV})</th>
<th>LUMO level (E_{\text{LUMO}}/\text{eV})</th>
<th>Band gap (E_g/\text{eV})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT</td>
<td>-0.39</td>
<td>740</td>
<td>-4.01</td>
<td>-2.33</td>
<td>1.68</td>
</tr>
<tr>
<td>PEOTT</td>
<td>0.04</td>
<td>810</td>
<td>-4.44</td>
<td>-2.91</td>
<td>1.53</td>
</tr>
<tr>
<td>PEDTT</td>
<td>1.03</td>
<td>550</td>
<td>-5.43</td>
<td>-3.18</td>
<td>2.25</td>
</tr>
<tr>
<td>PMEDTT</td>
<td>0.80</td>
<td>535</td>
<td>-5.40</td>
<td>-3.08</td>
<td>2.32</td>
</tr>
</tbody>
</table>
was much lower compared with the other polymers tested. As mentioned in the above, this can be ascribed to few network formation on its film surface. Therefore, it can be concluded that the morphological property is most important factor for the conductivity of 3,4-substitued polythiophene films formed by electrochemical polymerization.

4. Conclusion

In this work, 3,4-ethylendioxythiophene (EDOT) monomer analogs such as 3,4-ethylenedioxythiophene (EOTT), 3,4-ethylendithiophene (EDTT) and 3,4-metylethylenedithiophene (MEDTT) were synthesized and polymerized electrochemically to form the corresponding polymer films on the ITO anode surface. In the PEDOT and PMEDTT film surfaces, polymer grains were well networked each others, and their films gave the metallic conductivities. On the other hand, PEDTT film composed of mainly non-networked grains, and hence its conductivity was much lower than that of other polymers. From these facts, it can be stated that the morphological property is most important factor for the conductivity of 3,4-substitued polythiophene films formed by electrochemical polymerization.

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