

# Synthesis and Physical Vapor Deposition of Low-Molecular-Weight PEDOT

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## 1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the well-known conductive polymers [1], and has been frequently used for the hole injection layer of organic devices. Since PEDOT itself is poor in processability, its films are generally fabricated by spin-coating the water dispersion of colloidal complex of PEDOT and polystyrene sulfonate (PSS) [2]. However, the water-based solution is incompatible with the fabrication processes of organic devices in many cases. Moreover, the high acidity of the PEDOT:PSS dispersion can deteriorate the device performance and lifetime. In this respect, it is significant to prepare PEDOT thin films by the physical vapor deposition method without resorting to the water dispersion of PEDOT:PSS. This paper proposes to synthesize low-molecular weight PEDOT that can be vapor-deposited to obtain thin films by the dry process. The basic optical and electrical characteristics of the deposited films were explored in terms of the degree of polymerization of the source material for vapor deposition.

## 2. Experimental

The PEDOT was synthesized according to the scheme shown in Fig. 1. 5 mmol of ethylenedioxythiophene (EDOT) was dissolved in 5 ml of chloroform, to which 0.1 mol% of both palladium acetate and copper acetate were added as catalyzer. After adding 5 mmol of trifluoroacetic acid, the mixture was stirred for 3 to 36 h at room temperature under oxygen atmosphere. PEDOT was obtained by precipitating in methanol, and then neutralize by sodium carbonate, washed with pure water, and dried in vacuum. The reaction product was dissolved in chloroform-d and identified by using  $^1\text{H-NMR}$ .

Thin films of about 20-nm thick were prepared by the conventional vapor deposition using a Knudsen-type evaporation cell at temperatures between 300 and 450°C.

The IR spectra were obtained by the reflection-absorption method for the films deposited on silver-plated glass substrates. UV-visible absorption spectra were measured for the films deposited on quartz substrates. Electrical conductivity of the film was measured in vacuum for in-plane direction by vapor-depositing gold electrodes of 30  $\mu\text{m}$  spacing and 600  $\mu\text{m}$  wide on the surface of the film deposited on a quartz substrate.

## 3. Results and Discussion

### Synthesis of PEDOT

By the oxidative reaction of EDOT, PEDOT was obtained as dark powder with the polymer yield of 20 to 60%. The  $^1\text{H-NMR}$  spectra showed chemical shift of 4.19 ppm (ethylenedioxy group) and 6.30 ppm (terminal group of PEDOT), respectively. The degree of polymerization can be calculated from the ratio of integral intensity of these peaks. Table I lists the polymer yield and the degree of polymerization for the materials synthesized with different reaction times. The product of reaction time 36 h was insoluble and the degree of polymerization was not available. The result of Table I shows that low-molecular weight PEDOT was obtained by the scheme shown in Fig. 1, and that the degree of polymerization can be controlled by adjusting the reaction time.

### Vapor Deposition of PEDOT

Uniform thin films were obtained by vapor depositing the synthesized PEDOT except for the material synthesized by reaction time of 36 h. It is considered that the molecular weight became too high to evaporate when the reaction time was longer than c. a. 30 h. With increasing the evaporation temperature from 300 to 450°C, the film growth rate increased from 2.5 to 8 nm/min systematically. Interestingly, there was no remarkable difference in the evaporation behavior for the different materials obtained with reaction times of 3 to 24 h.

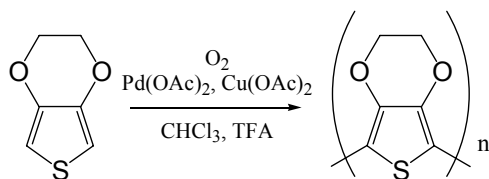


Fig. 1 Reaction scheme of PEDOT.

Table I Effect of reaction time on polymer yield and degree of polymerization.

| reaction time<br>(h) | polymer yield<br>(%) | degree of<br>polymerization |
|----------------------|----------------------|-----------------------------|
| 3                    | 23                   | 6.0                         |
| 6                    | 22                   | 9.6                         |
| 12                   | 32                   | 9.8                         |
| 24                   | 61                   | 12.3                        |
| 36                   | 56                   | insoluble                   |

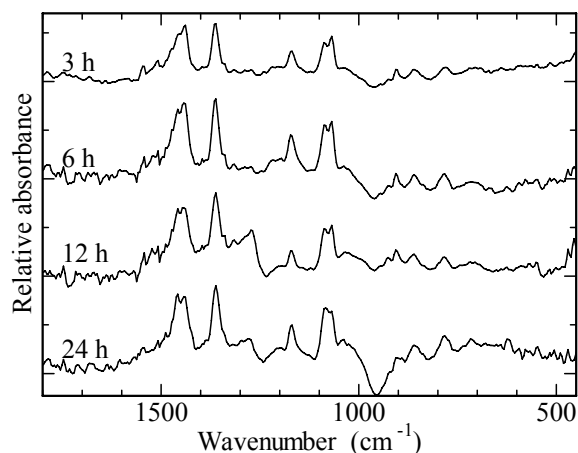


Fig. 2 IR spectra of the deposited films using the materials synthesized with different reaction times.

Figure 2 shows the IR spectra of the films deposited with the materials obtained by different reaction times. Vibration of thiophene ring was observed between  $1350\text{ cm}^{-1}$  and  $1490\text{ cm}^{-1}$ , while C-O stretching and O-C-C deformation vibrations appeared at  $1070\text{ cm}^{-1}$  and  $900\text{ cm}^{-1}$ , respectively, confirming the structure of PEDOT. For comparison, films were also prepared by spin-coating the newly synthesized materials. Significant difference was not observed between the IR spectra of the vapor-deposited and spin-coated films. Figure 3 shows the optical absorption spectra of the films deposited on quartz substrates. It was observed that the absorption edge shifts to longer wavelength as the degree of polymerization increases due to the extension of the  $\pi$  conjugation.

#### Electrical Characterization of the Deposited Films

Figure 4 shows the I-V characteristics of a film deposited from the material synthesized with the reaction time of 4 h. The measurements were made at three different positions on the film. It was found that the deposited film forms good ohmic contact with the gold electrode. As shown in Fig. 5, the conductivities of the films scattered in the range of  $10^{-4}$  to  $10^{-3}\text{ S/cm}$ . Their dependence on the reaction time is not clear at the moment.

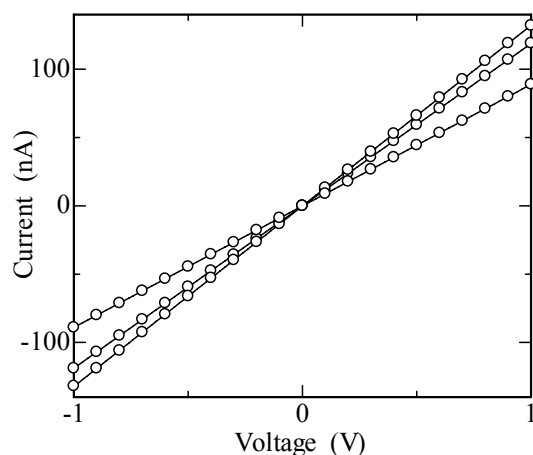


Fig. 4 I-V characteristics of a vapor-deposited PEDOT film.

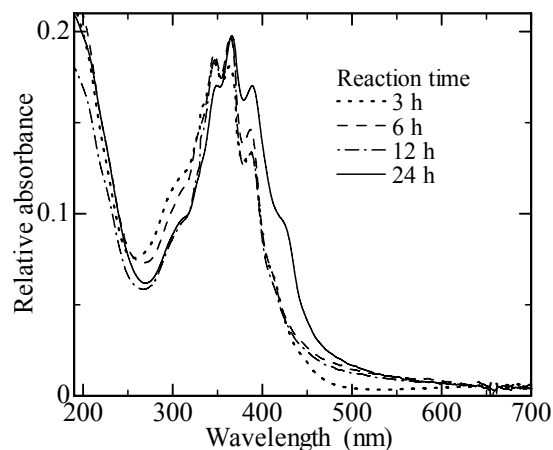


Fig. 3 Optical absorption spectra of the deposited films using the materials synthesized with different reaction times.

In this work, PEDOT was synthesized by using oxygen as the oxidizing agent with the aid of catalyzer. Unlike the common oxidizing agent as  $\text{FeCl}_3$  [2], the oxygen will not remain in the deposited films. Moreover, the films were prepared by PEDOT itself without forming a complex. Therefore, the films obtained in this work are considered to be in the undoped state, which is reflected to the relatively low value of conductivity.

#### 4. Conclusions

In conclusion, PEDOT having the degree of polymerization of about 10 was synthesized by using oxygen as the oxidizing agent. This material can be vapor-deposited to obtain uniform thin films. It is considered that the as-deposited films are in the undoped state having high resistivity. The solventless film formation of PEDOT is expected to be a convenient process for constructing organic electronic devices.

#### References

- [1] F. Jonas and L. Schrader, *Synth. Met.* **41** (1991) 831.
- [2] F. Jonas, W. Krafft, and B. Muys, *Macromol. Symp.* **100** (1995) 169.

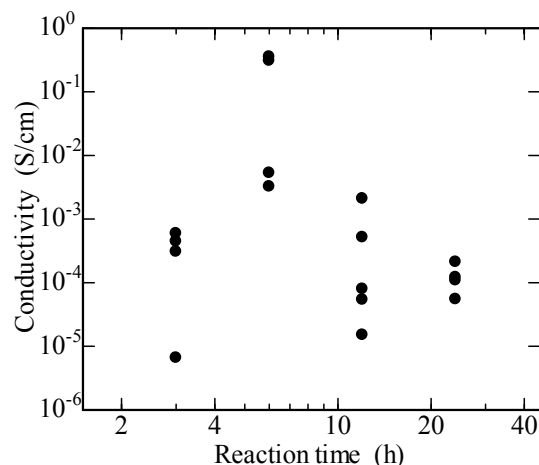


Fig. 5 Effect of reaction time on the electrical conductivity of the deposited films.