

## Notes

### Poly(3,4-ethylenedioxythiophene) Vapor-Phase Polymerization on Glass Substrate for Enhanced Surface Smoothness and Electrical Conductivity

Thuy Le Truong, Nguyen Dang Luong, and  
Jae-Do Nam\*

Department of Polymer Science and Engineering,  
SKKU Advanced Institute of Nanotechnology (SAINT),  
Suwon 440-746, Korea

Youngkwan Lee

Department of Chemical Engineering,  
Sungkyunkwan University, Suwon 440-746, Korea

Hyouk Ryeol Choi and Ja Choon Koo

School of Mechanical Engineering,  
Sungkyunkwan University, Suwon 440-746, Korea

Huu Nieu Nguyen

Department of Materials Technology,  
Hochiminh City University of Technology, Vietnam

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#### Introduction

As with other conducting polymers,<sup>1-4</sup> poly(3,4-ethylenedioxythiophene) (PEDOT) is considered as a promising material for optoelectronic devices.<sup>5-11</sup> In most of those optoelectronic applications as buffer or electrode layers, the surface and/or interface of the PEDOT coating layer substantially influences mobility, quantum efficiency and stability of charge carriers as well as assembled devices.<sup>12,13</sup> Polythiophene structure and morphology have been reported to be important for obtaining high charge-carrier transport characteristics.<sup>14,15</sup> Previous studies show that the effect of dielectric surface on charge mobility is due to surface-induced morphology of polythiophene.<sup>15,16</sup> In particular, the surface roughness of the PEDOT thin films is often required not to exceed few nanometers (<5 nm), and a uniform composition is usually required in optoelectronic device. There-

fore, the main issues of PEDOT in most electronic device applications are not only the electrical conductivity but also the film surface morphology such as film thickness, surface roughness, uniformity, etc.

In this sense, the vapor-phase polymerization (VPP) of PEDOT is a promising technology in various optoelectronic applications to provide a thin, uniform, and highly-conductive PEDOT coating.<sup>17-20</sup> The VPP PEDOT coating has been reported to give conductivities of approximately 70 S/cm and light transmittance up to 95% below 40 nm of thickness using FeCl<sub>3</sub> as the oxidizing agent.<sup>19</sup> Recently, a PEDOT film with a high conductivity, exceeding 1000 S/cm, was reported using pyridine as a base inhibitor during VPP of 3,4-ethylenedioxythiophene (EDOT).<sup>18</sup>

However, not only the conductivity enhancement but also the surface morphology of PEDOT VPP should be further explored to be adopted in optoelectronic device. In addition, the conductivity of the PEDOT coating in relation with surface smoothness and transparency should be identified to be used as thin film coating in optoelectronic devices.

In this study, VPP of PEDOT coating on the glass substrate was investigated by changing the polymerization rate using pyridine as a polymerization retardant. The polymerization rate was associated with the surface smoothness and conductivity to give a robust and transparent PEDOT coating in VPP.

#### Experimental

Fe(III) tosylate, (Fe(OTs)<sub>3</sub>, 40% solution in *n*-butanol, Baytron C) as an oxidizing agent and dopant were received from Bayer AG. The 3,4-ethylenedioxythiophene (EDOT), all solvents and reagents such as butanol, ethanol, acetone, pyridine were purchased from Sigma-Aldrich and used as supplied. The substrate materials used in this study were plain glass plates, which were at 1 mm thickness and supplied by Corning, N.Y. 14830, USA.

The glass substrate was cleaned twice in acetone by sonication prior to use and then coated with a 20 wt% oxidant Fe(OTs)<sub>3</sub> solution in butanol by spin-coating. Various amount of pyridine was added to the Fe(OTs)<sub>3</sub> solution. After drying, the samples were transferred to a gas-phase polymerization chamber using a similar experimental setup and method as reported elsewhere.<sup>17</sup> The chamber was flushed with nitrogen during polymerization, and heated to 50°C and the vapor-phase polymerization was carried out for 30 min in the atmospheric pressure, and the samples were then heated to 50-90°C for 30 min. The samples were then washed sequentially with ethanol and DI water. Finally, the PEDOT film was dried to remove the residual solvents at 80°C for 20 min.

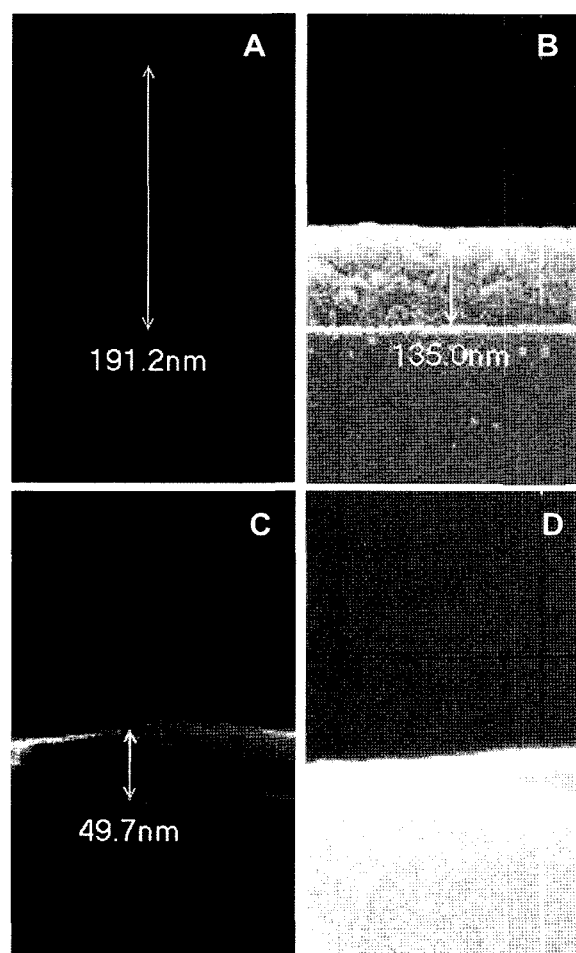
The conductivity of the samples was measured using a

\*Corresponding Author. E-mail: jdnam@skku.edu

four-point probe (Jandel Engineering Ltd.) connected to a Keithly 2400 source meter. The probe was equipped with four spring-loaded tungsten carbide needles spaced 1 mm apart. The conductivity of the PEDOT film coated on the glass plate was calculated from the surface resistivity and the film thickness, which was measured by FE-SEM (a JEOL JSM-7000F FESEM, voltage of 5.0 kV). Atomic force microscopy (Auto Probe CP Research, Thermo Microscopes, USA) was used to analyze the film surface morphology. All data manipulations and image processing were carried out using Proscan 1.7 software. All surface roughness values used in this study are the root-mean-square roughness. The absorbance of the PEDOT films was measured using UV-VIS-NIR spectrophotometer (Varian Cary 5000).

## Results and Discussion

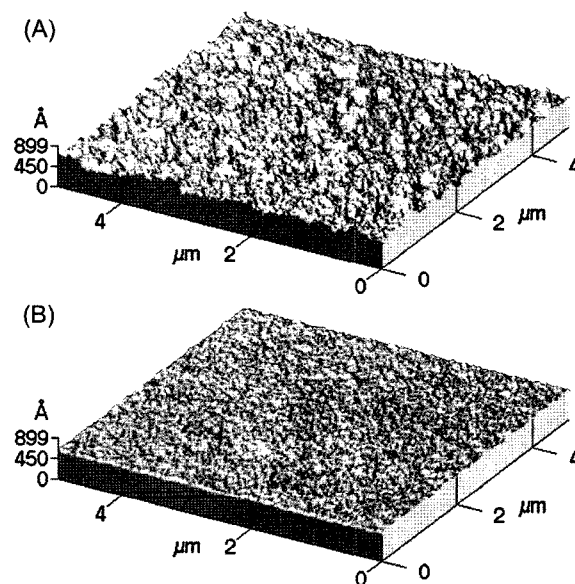
The scanning electron microscopy (SEM) images show



**Figure 1.** The cross section of PEDOT coatings on glass substrates (B) at various molar ratios of pyridine/Fe(OTs)<sub>3</sub> ratios: (A) 0, (B) 0.25, (C) 0.5, and (D) 0.75.

the cross sections of PEDOT coatings on glass substrates at various pyridine concentrations (Figure 1). The thickness of the PEDOT film decreases with increasing pyridine concentrations from 191 to 25 nm for 0 to 0.75 molar ratio of pyridine/Fe(OTs)<sub>3</sub>, respectively. In addition to the thickness, it can be seen that the structural morphology of VPP-PEDOT is also influenced by the pyridine concentration. In Figure 1(A), large PEDOT grains are formed, which could possibly provide a void spaces in the PEDOT film when pyridine was not used in the VPP process. A well-defined structure is shown in Figures 1(B) and 1(C), where the structure of PEDOT films are dense and uniform without noticeable cracks or voids when pyridine is incorporated in VPP as a polymerization retardant.

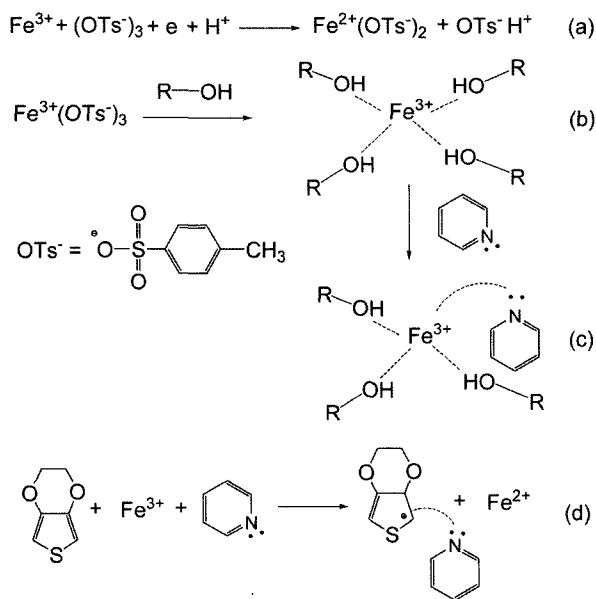
Figure 2 shows the AFM images of the PEDOT produced at different pyridine/Fe(OTs)<sub>3</sub> ratios. Figure 2(A) shows the surface of PEDOT without pyridine, where the RMS roughness is 6.9 nm. A distinct improvement of the surface roughness is observed in Figure 2(B) at a pyridine/Fe(OTs)<sub>3</sub> molar ratio of 0.5. As summarized in Table I, the surface roughness is influenced considerably by the pyridine concentration, and a minimal RMS roughness was obtained as 2.1 nm at a pyridine ratio of 0.5. This suggests that pyridine has a substantial effect on the conductivity and surface



**Figure 2.** AFM images of PEDOT-coated glass substrates at different pyridine/Fe(OTs)<sub>3</sub> ratios of (A) 0 and (B) 0.5.

**Table I. Properties of PEDOT and PEDOT/Pyridine Films**

Pyridine/Fe(OTs) <sub>3</sub> Ratio	0	0.25	0.5	0.75
Conductivity (S/cm)	30	180	$5.0 \pm 1 \times 10^2$	300
Surface Roughness-Rms (nm)	6.9	3.8	2.1	3.2
Transmittance (450 nm) (%)	18.95	60	80	86



**Scheme I.** A proposed mechanism for the effect of pyridine on PEDOT polymerization: (a) the electronic semi-equilibrium of PEDOT polymerization process, (b) and (c) pyridine coordinates with the  $\text{Fe}(\text{OTs})_3$  through the successive substitution of pyridine with the alcohol ligands via the unbonded electrons in N, (d) the stability of cation radical of EDOT.

roughness in the VPP of PEDOT.

We believe that the PEDOT structures, surface morphology and coating thickness are associated with the redox activity of  $\text{Fe}(\text{OTs})_3$ . The effect of pyridine on the oxidative polymerization of EDOT is schematically represented as shown in Scheme I. A basic inhibitor such as amine increases the pH of the reaction media, and subsequently decreases the redox activity of  $\text{Fe}(\text{OTs})_3$ .<sup>18</sup> Indeed, since the polymerization of EDOT in the presence of  $\text{Fe}^{3+}$  complies with a redox reaction, the electronic semi-equilibrium relation may be described as Scheme I. Subsequently, the electrode potential of the  $\text{Fe}^{(3+)}/\text{Fe}^{(2+)}$  redox couples can be expressed as a function of pH by the Nernst equation:

$$\begin{aligned}
 E &= E^0 + \left(\frac{2.3RT}{nF}\right) \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} + \left(\frac{2.3RT}{nF}\right) \log [\text{H}^+] \\
 &= E^* + \left(\frac{2.3RT}{nF}\right) \log [\text{H}^+] \quad (1)
 \end{aligned}$$

where  $E$  is the electrode potential of the  $\text{Fe}^{(III)}/\text{Fe}^{(II)}$  redox couple in the  $\text{Fe}(\text{OTs})_3$ -pyridine solution,  $E^0$  is the potential of the reference electrode,  $(2.3RT/nF)$  is the Nernst factor, and  $\log[\text{H}^+]$  is the pH of the  $\text{Fe}(\text{OTs})_3$  solution. The Nernst factor,  $2.3RT/nF$ , includes the gas constant ( $R$ ), Faraday's constant ( $F$ ), temperature in degrees Kelvin ( $T$ ), and the charge of the ion ( $n$ ).  $E^*$  is the standard redox potential when  $[\text{Fe}^{(3+)}]=[\text{Fe}^{(2+)}]$  and  $[\text{H}^+]=1$  M. Accordingly, the electrode

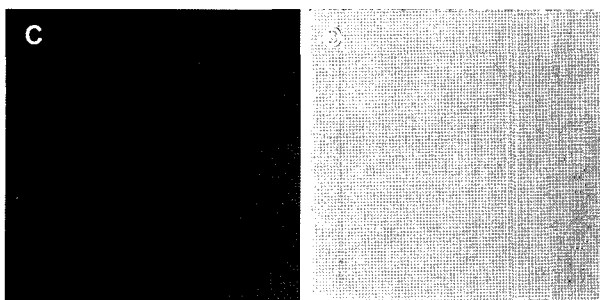
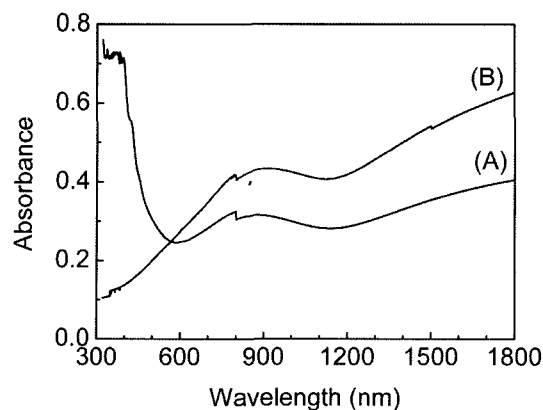
behavior is solely dependent on pH values because the other values are constants.

Therefore, the increased pyridine concentration increases the pH of the  $\text{Fe}(\text{OTs})_3$  solution, which subsequently gives reduced electrode potentials. This suggests that the increased pyridine concentration makes the reduction of  $\text{Fe}^{(3+)}$  to  $\text{Fe}^{(2+)}$  becomes more difficult and, thus, results in a decrease in the PEDOT layer thickness. According to our experiment observation, there was a color change of  $\text{Fe}^{3+}$  solution turning to darker as the molar ratio of pyridine/ $\text{Fe}^{3+}$  increases. This suggests that pyridine coordinates with the  $\text{Fe}(\text{OTs})_3$  through the successive substitution of pyridine with the alcohol ligands via the unbonded electrons in N (Schemes I(b) and I(c)). UV-vis spectroscopy (not shown here) was employed to clarify this point, where the absorption peak shifts from 505 nm for the  $\text{Fe}(\text{OTs})_3$  solution to 550 nm for the  $\text{Fe}(\text{OTs})_3$ -pyridine complex solution, which complies with the peak shift by the incorporation of imidazole.<sup>21</sup>

In addition, it is supposed that the unbonded electrons in N of pyridine may be related to the stability of cation radical of EDOT during the VPP reaction (Scheme I(d)). The enhanced stability of cation radicals of both EDOT and oligomeric chains may be attributed to resonance stabilization of hybrid electronic pairs. Therefore, the yield and quality of the product obtained by the oxidative polymerization depend on either the reactivity of the oxidants or the resonance effects of cation radicals of EDOT. Very rapid polymerization kinetics can cause the prepolymerized nanoscopic droplets to precipitate on the substrate, which subsequently increases the surface roughness.<sup>21</sup> PEDOT films produced at a high redox reactivity often provides defect sites and a low degree of intermolecular order, ultimately limiting their use in electronic devices (Figure 1(A)). For this reason, it is believed that high quality PEDOT can be obtained by controlling the polymerization rates as well as pyridine concentration to minimize the side reactions and the number of defects.

As summarized in Table I, an appropriate pyridine/ $\text{Fe}(\text{OTs})_3$  ratio provides a robust PEDOT structure with a high conductivity and smooth surface.<sup>22</sup> The appropriate polymerization rate may promote the production of a higher molecular weight PEDOT and enhance the stability of the radical cations by delocalization over a planar conjugated oligomer or polymer. At a high concentration of pyridine, the polymerization reactions are retarded to result in the formation of relatively thin PEDOT layers on the glass substrate (Figure 1(D)). However, it is believed that an excessive amount of pyridine acts as an impurity, which may well accumulate in the PEDOT coating and disturb a facile movement of charge carriers to decrease conductivity (Table I).

Figure 3 shows the UV-vis spectra of PEDOT polymerized on  $\text{Fe}^{(III)}$  tosylate and  $\text{Fe}^{(III)}$  tosylate-pyridine and its visual images, respectively. The PEDOT films with green show a significant absorbance in the 300-475 nm range and



**Figure 3.** UV-vis-NIR spectra of PEDOT coated onto a glass at different pyridine/ $\text{Fe}(\text{OTs})_3$  ratios of (A) 0 and (B) 0.5, each exhibiting the visual images of PEDOT, in (C) and (D) respectively.

low absorbance over 600 nm (Figures 3(A) and 3(C)). Meanwhile, the PEDOT film with light blue color polymerized on  $\text{Fe}(\text{OTs})_3$ -pyridine has a prominent absorption peak at around 890 nm and over 1300 nm (Figures 3(B) and 3(D)), which represents the doping process of conjugated polymer to be ascribed to the bipolaron subgap states.<sup>23</sup> The lack of absorbance above 600 nm indicates that the density of the polaronic states is low and, thus, a poorly-conductive PEDOT films are polymerized on  $\text{Fe}(\text{OTs})_3$ , which agrees with the conductivity values in Table I.

## Conclusions

Pyridine was found to give a significant effect on generating well-defined PEDOT films in vapor-phase polymerization. This additive was utilized for not only controlling polymerization rate but also stabilizing cation radicals of both EDOT and oligomeric chains during the vapor-phase reaction. At an appropriate pyridine concentration, the high-conductivity and smooth PEDOT film was synthesized as a promising thin-film coating for optoelectronic applications.

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