

# Electropolymerization of PoPD From Aqueous Solutions of Sodium Dodecyl Benzene Sulfonate at Conducting Glass Electrode

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**ABSTRACT:** Electropolymerization of poly(*o*-phenylenediamine) (PoPD) film was performed in a micellar aqueous solution containing sodium dodecyl benzene sulfate (SDBS) by cyclic voltammetry at conducting glass electrode. The experimental results showed that the anionic micelle, i.e., SDBS, can greatly catalyze the electropolymerization reaction of *o*PD and reduce its oxidation potential from 0.97 to 0.74 V (vs. saturated calomel electrode). In the anionic micellar media, the local concentration of *o*-phenylenediamine (*o*PD) on the surface of electrode may be increased, and the *o*PD cation radicals are more stabilized in the hydrophobic microcircumstance of micelle,

which is available to avoid hydrolysis degradation of PoPD and enhance the stability of the PoPD film. The spectroscopy and morphology of the films were characterized by FTIR spectroscopy and atomic force microscopy, respectively. The results suggested the possible presence of columnar structures when the electropolymerization is performed in the micellar medium. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1928–1932, 2007

**Key words:** surfactant; *o*-phenylenediamine; electropolymerization; conducting glass electrode

## INTRODUCTION

Conducting polymer has attracted great attention because of their interesting electrical, electrochemical, and optical (linear and nonlinear) properties since its discovery two decades ago.<sup>1–7</sup> Conducting polymers can be used in many fields.<sup>8</sup> The different applications need conducting polymers having different properties, thus, the synthesis of new types of conducting polymers is very important in the field of material science. Electrochemical polymerization is proved to be one of the most useful approaches for conducting polymers synthesis, whose advantage is that the process of polymerization and the coating formation take place simultaneously at the working electrode.<sup>9,10</sup>

Polymers with fused ring systems and ladder type polymers have been studied by many groups.<sup>11</sup> One reason for this extensive research is the expected suppression of the band gap and improved electronic

properties in these materials because of the rigid planar polymer backbone in the form of a double-stranded molecule. Poly-*o*-phenylenediamine (PoPD) is one of a relatively new conducting polymer with specific features of the charge transfer mechanism. Its conductive form can easily be obtained by the electrochemical method.<sup>12</sup> There have been a number of reports on the synthesis and structural properties of PoPD.<sup>13,14</sup> The potential applications of PoPD have also been reported by several authors in the field of rechargeable cells,<sup>15</sup> electrochromic devices,<sup>16</sup> sensors,<sup>17</sup> catalysis of some important electrochemical reactions,<sup>18</sup> and corrosion inhibition.<sup>19</sup> Formally, PoPD may be classified into conductive polymers of the aniline series. However, unlike chain polymers of polyaniline and derivatives which are similar to it, PoPD has a ladder structure containing phenazine-type fragments, which affect the kinetic scheme of electrode processes.

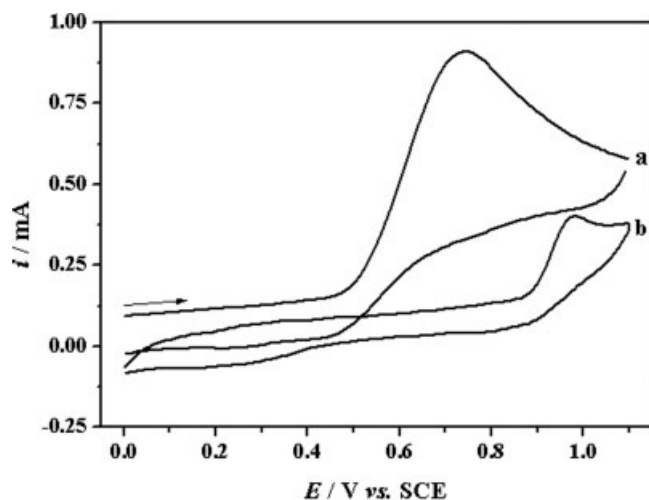
Despite a multitude of works studying properties of PoPD films by miscellaneous physicochemical and electrochemical methods, the properties and mechanism of its electrochemical synthesis are not clear yet. In this article, we described the effect of the surfactant on the electropolymerization of *o*-phenylenediamine (*o*PD) in acid solution at conducting glass electrode. The physicochemical and structural properties of PoPD obtained in these conditions can be related to the electrocatalytic effect of sodium dodecyl benzene sulfate (SDBS).

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**Figure 1** Cyclic voltammograms of 0.05 mol/L oPD in 1 mol/L  $\text{H}_2\text{SO}_4$  aqueous solutions with (a) and without (b) 2 mM SDBS at ITO electrode.

## EXPERIMENTAL

### Reagents and materials

Indium tin oxide (ITO, sheet resistance:  $8 \Omega/\text{square}$ ) conducting glass was obtained from Libbey-Owens Ford. oPD  $\sim 99\%$  (Aldrich Chemical) was sublimated under vacuum at  $80^\circ\text{C}$  before use. All other chemicals were of analytical-reagent grade. Water ( $18 \text{ M}\Omega \text{ cm}$ ) purified in a Milli-Q purification system (Millipore) was used for all dilutions and sample preparations.

### Methods and instrumentation

Electrochemical measurements were carried out with a model CHI660A electrochemical analyzer (CH Instrumental) controlled by a personal computer. A three-electrode system was used in the measurements, with an ITO or PoPD/ITO electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the auxiliary electrode. The PoPD was synthesized from a 0.05M solution of oPD at an ITO electrode (the area of the electrode surface equal to  $0.5 \text{ cm}^2$ ) in an aqueous micellar media (2 mM SDBS + 1 mol/L  $\text{H}_2\text{SO}_4$ ) by potential scanning for 50 cycles.

Branson 2000 ultrasonic cleaner was used for cleaning the electrodes and the PoPD film. FTIR spectrophotometer (Perkin-Elmer) was used to achieve the FTIR spectra of PoPD film. Atomic force microscopy images reported in this study were obtained using a Nanoscope<sup>TM</sup> IIIa Scanning Probe Microscope (Veeco Metrology Group).

## RESULTS AND DISCUSSION

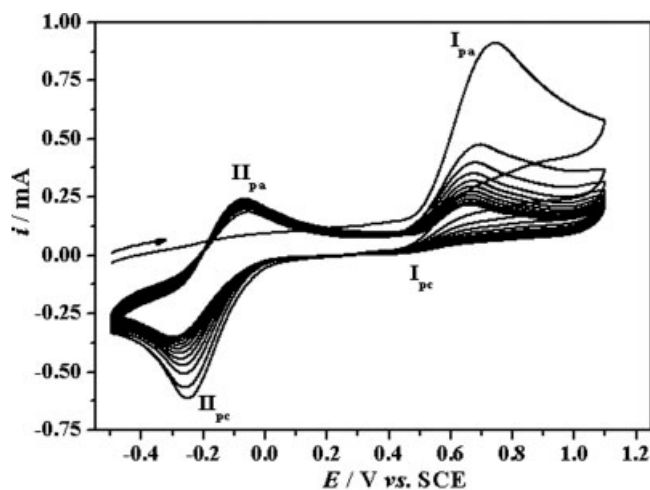
### Electropolymerization of oPD in the micellar media at ITO electrode

One major drawback of the electropolymerization of electroactive species in aqueous media is their oxida-

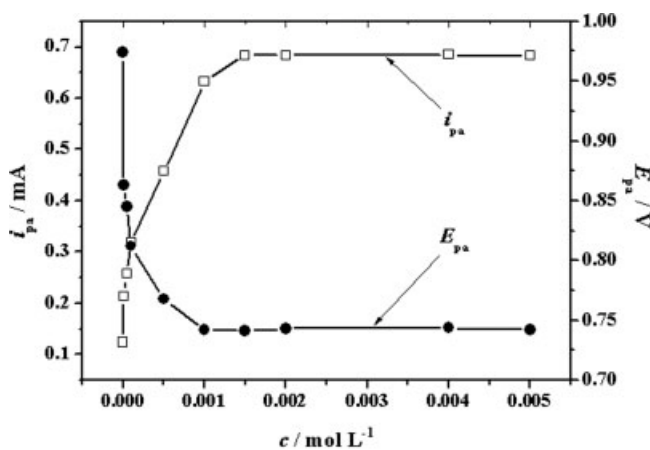
tion potential, which is generally higher than that of water.<sup>20,21</sup> To solve this problem, one can use aqueous micellar media, containing suitable surfactants, in which the oxidation potential can be lowered, thus allowing the electroactive species oxidation and film electrodeposition on metallic surfaces. Figure 1 shows the cyclic voltammograms of 0.05 mol/L oPD in aqueous solutions with [Fig. 1(a)] or without [Fig. 1(b)] the addition of 2 mM SDBS at ITO electrode. Obviously, the presence of SDBS in the solution reduces the overvoltage of oPD oxidation, shifting the  $E_{\text{pa}}$  value negatively by 226 mV. The peak current was enhanced about six times, compared with the response of oPD in aqueous solutions without SDBS.

The successive cyclic voltammograms of 0.05 mol/L oPD at an ITO electrode in an aqueous micellar media (2 mM SDBS + 1 mol/L  $\text{H}_2\text{SO}_4$ ) by potential scanning between  $-0.5$  and  $1.1$  V versus SCE are shown in Figure 2. With the cyclic voltammetry scan continues, the color of the electrolyte close to the surface of ITO electrode changes gradually from pale red to dark red, implying the formation of oligomers dissolved or dispersed in the solution. Simultaneously, a brown polymer film was deposited on the ITO surface. After 50 cycles, the working electrode was entirely covered by the polymer film.

It can be seen from the Figure 2, in the first cycle, the anodic current increases quickly beginning at 0.5 V, and a peak with a large current occurs at 0.74 V, which corresponds to the oxidation of the oPD monomer. In subsequent scanning, the cathodic peaks found at  $-0.27$  V corresponding to the reduction of the PoPD already formed, and the anodic peaks found at  $-0.06$  V are due to the oxidation of the PoPD. The peaks current of  $I_{\text{pa}}$  and  $I_{\text{pc}}$  decreased proportionally with the number of scans. In contrast, the peaks



**Figure 2** Successive cyclic voltammograms of 0.05 mol/L oPD in an aqueous solution of 2 mM SDBS and 1 mol/L  $\text{H}_2\text{SO}_4$  at ITO electrode (the area of electrode surface equals to  $0.5 \text{ cm}^2$ ). Scan rate: 100 mV/s.



**Figure 3** Plots of SDBS concentrations versus the oxidation peak current (□) and potential (●) of oPD at ITO electrode.

current of  $I_{pa}$  and  $I_{pc}$  tends to increase, which indicated the accretion of the deposits on the electrode surface. We presumed that the  $I_{pa}$  and  $I_{pc}$  were the redox peaks of the polymer, and  $I_{pa}$  and  $I_{pc}$  were redox peaks of the oPD monomer itself. This discrimination was based on two observations. First, peak  $I_{pa}$  appeared only from the second scan while  $I_{pa}$  and  $I_{pc}$  presented in all scans. In other words, the oxidation of peak  $I_{pa}$  was associated with the existence of a polymer. The second observation related to the different change of the peaks current. In other words, peak  $I_{pa}$  represented a different process compared with peak  $I_{pa}$ .

The experimental results showed that the PoPD film can be formed easily on the ITO surface in an aqueous medium, that is, the anionic micelle (SDBS) can greatly catalyze the electropolymerization reaction of oPD and reduce its oxidation potential. The results may be explained as follows: First, the SDBS molecule is an alkylarylsulfonate, which contains an electron-rich aromatic nucleus and can be adsorbed on the electrode surface by polarization of  $\pi$  electrons.<sup>22</sup> Second, by the solubilization of the anionic micelle media, the local concentration of oPD on the electrode surface may be increased, which caused that the oPD is easily to access the electrode surface and might result in much faster kinetics of its redox. Third, the oPD cation radicals are more stabilized in the hydrophobic micro-circumstance of micelle, which is available to avoid hydrolysis degradation of PoPD and enhance the stability of the PoPD film.

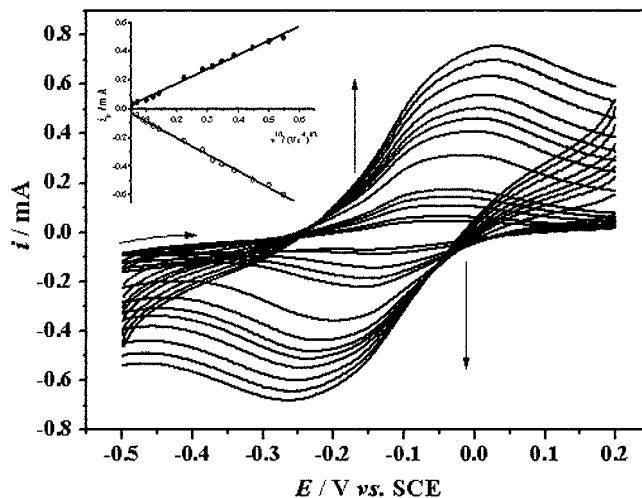
### The effect of SDBS concentration on electropolymerization

To evaluate the role of surfactants more precisely in the electropolymerization rate, we investigated the effect of varying SDBS concentrations on the electro-

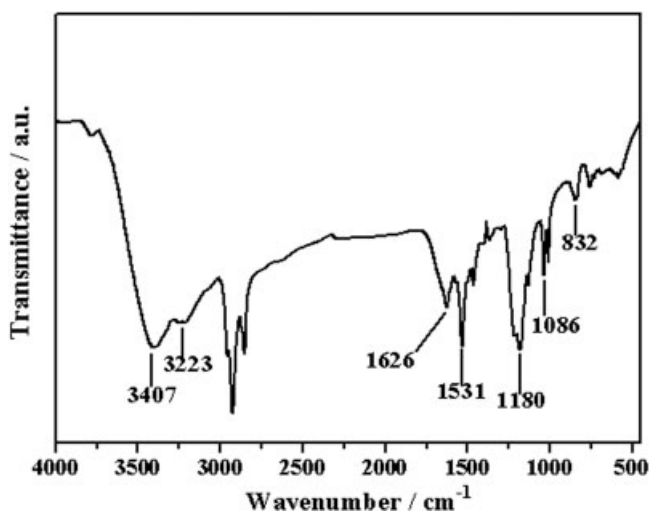
chemical oxidation of oPD (Fig. 3). From this Figure, it was clear that the oxidation peak current of oPD increased with the augment of SDBS concentration, whereas the oxidation peak potential decreased. After the SDBS concentration reaching higher than the critical micelle concentration (CMC; 1.2 mM), both the peak current and the peak potential reached a plateau value. It can be explained as follows: below CMC, the extent of surfactant aggregation was small, the solution including essentially monomeric species; in these conditions, there was a strong interaction occurred between dodecyl benzene sulfate (DBS<sup>-</sup>) anion and the radical-cations of oPD<sup>+•</sup> formed during the first step of the electropolymerization mechanism,<sup>23</sup> which resulted in the increase of oxidation current and the decrease of oxidation potential. When the SDBS concentration went beyond the CMC value, the free SDBS monomer concentration remain practically constant and all possibly SDBS species were complexed. As a result, the oPD molecules become incorporated into the micellar phase, which implied the invariance of the oPD oxidation potential and current.<sup>24</sup>

### Electrochemical behavior of PoPD

The scan rate dependence of the CV curves of PoPD/ITO electrode was shown in Figure 4. On the basis of the relationship between the scan rate and redox peak currents, both the anodic and cathodic peak currents were proportional to the square root of the potential scan rate (Fig. 4, Inset). The result indicated that the electrode reaction of PoPD was controlled by mass transfer.<sup>4</sup> The anodic peak potentials appeared at about 0.0 V and shift slightly toward the positive



**Figure 4** Cyclic voltammograms of the PoPD/ITO electrode in 1 mol/L H<sub>2</sub>SO<sub>4</sub> at scan rates of 3, 5, 10, 15, 20, 50, 80, 100, 120, 150, 200, 250, 300 mV/s. Inset: Plots of the anodic (●) and cathodic (○) peak current versus the square root of the scan rates.



**Figure 5** FTIR spectra of PoPD prepared in  $\text{H}_2\text{SO}_4$  solutions with 2 mM SDBS.

potentials upon varying the scan rate from 3 to 300 mV/s, while the cathodic peak potentials shift straightly to the more negative direction with the scan rate increase. This identified that the kinetic effects may mainly exist in the reduction process of the film.<sup>12</sup>

This result was at some variance with that reported in Ref. <sup>25</sup> where the peak currents were neither proportional to  $v$  nor to  $v^{1/2}$  for the similar films. The main reasons accounting for this phenomenon are usually as follows: slow heterogeneous electron transfer, effects of local rearrangements of polymer chains, the low conductivity, and the thickness of the film in our experiments.<sup>4,26</sup>

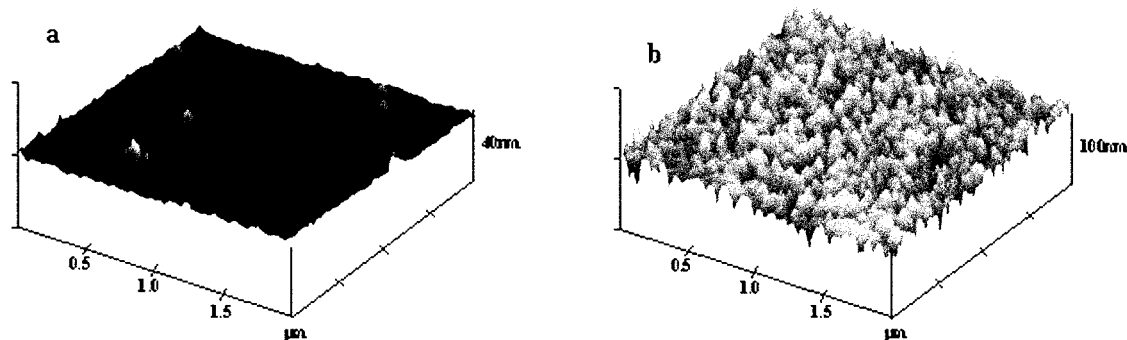
### FTIR Spectra of the PoPD Film

Figure 5 shows the FTIR spectrum of the PoPD film. The possible structure can be deduced from the infrared spectra of PoPD. Among other investigators, Harada et al.<sup>27</sup> have studied in detail the infrared spectra of polyaniline at different states of oxidations and pro-

tonation. On the basis of their assignment, we can interpret the absorption bands at 3407 and 3223  $\text{cm}^{-1}$  in terms of N—H stretching. Distinct peaks observed at 1620 and 1530  $\text{cm}^{-1}$  are attributed to quinoid (1620  $\text{cm}^{-1}$ ) and benzenoid (1530  $\text{cm}^{-1}$ ) ring stretching vibrations of the emeraldine form of PoPD.<sup>28</sup> On the basis of the relative intensity of these two bands, it is possible to estimate roughly the ratio between the quinonediimine and the benzene units in PoPD.<sup>27</sup> If we apply this to our ladder polymer, we can see that in this case the ratio is about 1 : 1. A further indication is the out of plane bending of benzene ring at 832  $\text{cm}^{-1}$ , which is consistent with the tetrasubstituted benzene ring.<sup>29</sup> The chemical structure of PoPD was given in the Refs. 13, 27, 28, 30, 31. It is worthwhile to note that the strong bands located around 1180 and 1086  $\text{cm}^{-1}$ , attributable to the stretching vibrations of the sulfate group,<sup>32</sup> can be clearly seen, which should be from the  $\text{DBS}^-$  anions incorporated into the polymer matrix. These bands change little when switching the film from the oxidized to reduced state, suggesting that the  $\text{DBS}^-$  anions remain trapped in the film.

### The morphology of PoPD

Sakmeche et al.<sup>24</sup> have studied the influence of surfactant on the morphology of PEDOT and found that the films present a columnar perpendicular oriented structure when the surfactant concentration is greater than the CMC. They have explained these results as the interaction between the monomer and the hydrophobic chain of the surfactant, leading to a micellar encapsulation of the monomer. We also investigated the structure of PoPD film by AFM and the result is similar to the Ref. 24. Figure 6 shows three-dimensional AFM images of ITO electrode and PoPD film synthesized at ITO in micellar aqueous media. The rms roughness of ITO electrode is about 0.744 nm, while that of PoPD film is about 16.4 nm. From Figure 6(b), the polymeric nodules or islands can be observed over the whole scanned area, which indicate



**Figure 6** Three-dimensional AFM images of ITO electrode (a) and PoPD film (b) electrodeposited from SDBS aqueous micellar solution.



the islands structure result from a three-dimensional nucleation growth of polymer.

### CONCLUSIONS

In this study, we have used an anionic surfactant to electropolymerize oPD in aqueous solution at ITO electrode. Addition of this surfactant has the advantage of lowering the oxidation potential of oPD and improving the property of electrode/solution interface. In the anionic micellar media, the local concentration of oPD on the surface of electrode may be increased, and the oPD cation radicals are more stabilized in the hydrophobic microcircumstance of micelle, which is available to avoid hydrolysis degradation of PoPD and enhance the stability of the PoPD film. The spectroscopy and morphology of the films were characterized by FTIR spectroscopy and atomic force microscopy, respectively. As suggested by the AFM analysis, PoPD chains probably constitute a columnar structure when the electropolymerization is performed in the micellar medium.

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