

#### **Research Article**

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# Chemical synthesis of polypyrrole doped with dodecyl benzene sulfonic acid

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#### Abstract

Among the conducting polymers, polypyrrole (PPY) is one of the most attractive polymer due to its wide range of applications related to its good stability and conductivity. How-ever its insolubility in some common organic solvents limits its wide range of applications. In the present work an attempt has been made to synthesize soluble and stable PPY by inverse emulsion polymerization using dodecyl benzene sulfonic acid (DBSA) as a dopant as well as surfactant. A mixture of chloroform and 2-butanol was used as a novel dispersion medium and benzoyl peroxide as an oxidant. Optimizing the concentration of monomer and oxidant, the percent yield of PPY salts was calculated. Intrinsic viscosity of the PPY salts was calculated using capillary viscometer and was found to be dependent upon monomer concentration. Synthesized PPY salts were characterized by FTIR, XRD, SEM and CV. The thermal stability of the PPY-DBSA was determined by TGA in which a thermogram showing three step decomposition patterns was obtained. The synthesized PPY-DBSA was found to be stable upto 520 °C, which is so far the highest thermal stability reported for PPY.

# Keywords: Polypyrrole, FTIR, TGA, XRD, SEM, CV.

# Introduction

Intrinsically conducting polymers are organic materials that conduct electricity and have extended  $\pi$  bonding systems. They show good electrical as well as optical properties which were previously shown only by inorganic systems.<sup>1</sup> Today's all conducting polymers are the derivatives of polypyrrole, polyaniline and polythiophene. Among all the conducting polymers polypyrrole is the most widely studied conducting polymer because of its easily oxidizable nature, water solubility, commercial availability, high conductivity, best environmental stability and redox properties.<sup>2</sup> Almost all of these properties depend upon the method of preparation of polypyrrole as well as upon the nature of dopant used.<sup>3</sup> Polypyrrole was the first polymer showing high conductivity among all the conducting polymers. It was first synthesized in 1916 and has a vast variety of applications as in biosensors<sup>4</sup>, gas sensors<sup>5</sup>, coatings<sup>6</sup>, wires<sup>7</sup>, electrolytic capacitors<sup>10</sup>, microactuators<sup>8</sup> and battery electrodes<sup>9</sup>. Their coatings are very stable and thus used in carbon composites.<sup>10</sup> Similarly corrosion of metals can also be prevented by the use of polypyrrole blends.<sup>11</sup> Investigation of the structure, applications in technology, chemical and physical properties requires the synthesis of soluble conducting PPY. Several methods such as substitution on nitrogen or  $\beta$ -carbon of pyrrole rings, copolymerization and doping etc. have done for the improvement of solubility of PPY. Many studies have been made on increasing the solubility of PPY by modifying the pyrrole monomer in such a way that the intermolecular attractions are weakened. Attaching an alkyl group to pyrrole monomer is the best example of increased solubility of PPY. Emulsion/Inverse emulsion polymerization is one of the most promising method in improving the processability of PPY. In this process, pyrrole a protonic acid, and an oxidant are mixed with water and a non-polar solvent. But due to entrapment of PPY in the emulsion along with some by-products of the reaction makes difficult to obtain the product in pure form.

In most cases the products were isolated by adding some solvent to break the emulsion and collect the products.<sup>12-14</sup>

Recently we have reported a new pathway for the synthesis of soluble polypyrrole salt by inverse emulsion polymerization using a mixture of chloroform and 2-butanol as a novel dispersion medium.<sup>15</sup> This method was found to be unique in the sense that after the completion of reaction two phases were separated from each other. An aqueous phase consisting of unreacted dodecylbenzenesulfonic acid (DBSA), benzoyl peroxide, 2-butanol and other by-products of the reaction while the organic phase consisting of PPY-DBSA. A highly pure PPY-DBSA in powder form was separated from the organic phase by washing several times with acetone. The resulting PPY-DBSA was found to have im-proved solubility in some organic solvents. Although the results were encouraging but some unusual behavior was also observed for different properties of polypyrrole, which was assumed to be caused by the the use of a relatively higher amount of the oxidant in the polymerization bath. The high amount of oxidant was supposed to result in overoxi-dation of the monomer, which ultimately effected the properties of the resulting PPY. To check the hypothesis further, a systematic study for the synthesis of PPY was carried out following the above mentioned pathway in which the amount of oxidant was kept lower and other parameters such as amount of monomer and surfactants were also varied simi-larly. As expected, this time the synthesized polypyrrole showed good properties (similar to those reported in literature). The purity and electroactivity of the polymer was con-firmed by Cyclic voltammetry. Effects of various reaction parameters on yield, intrinsic viscosity, morphology, structure, crystallinity of polymers were also investigated. TGA data showed that the resulting PPY was thermally stable upto a temperature of about 520 oC which is so far the highest thermal stability for PPY.

### **Experimental**

Reagent grade pyrrole (Fluka Chemie) was distilled prior to use as a monomer, DBSA (Sigma Aldrich), benzoyl peroxide (Scharlau), chloroform (Scharlau), 2-butanol (Aldrich), acetone (Scharlau), THF (Scharlau), DMSO (Scharlau), m-cresol (BDH Chemicals), 1-propanol (Across) and Toluene (Scharlau) were used as received. In a typical experiment 0.29 mol of chloroform was taken in a round bottom flask. Then 0.00125 mol of benzoyl peroxide was added to it under mechanical stirring. After that 0.13 mol of 2-butanol, 0.00373 mol of DBSA and 0.43x10<sup>-3</sup> mol of pyrrole was added to this reaction mixture. At the end 0.28 mol water was added due to which milky white emulsion was formed. This mixture turned black in 5 hours and was proceeded for 24 hours upon stirring. The solution was then put into separating funnel and the bottom black organic layer (polypyrrole) was separated. This layer was taken in a petri dish, 50 mL of acetone was added to it and dried for 24 hours at room temperature. A film of black powder (polypyrrole) was formed. By the addition of small amount of acetone to the petri dish, the film broke into flakes. It was then washed with acetone and then dried in a dessicator. The experimental conditions were optimized by stepwise changing concentration of monomer, oxidants and surfactants. The polymers obtained with varying amounts of pyrrole were labeled as PPY 1, PPY 2, PPY 3, PPY 4, PPY 5, PPY 6 where the concentrations of pyrrole were  $0.43 \times 10^{-3}$  mol,  $0.72 \times 10^{-3}$  mol,  $1.02 \times 10^{-3}$  mol,  $1.3 \times 10^{-3}$  mol,  $1.6 \times 10^{-3}$  mol and  $1.9 \times 10^{-3}$  mol, respectively. Similarly the samples with different amounts of benzoyl peroxide were labeled as PPY 7, PPY 8, PPY 9, PPY 10 where the concentrations of benzoyl peroxide were  $1.25 \times 10^{-3}$  mol,  $1.67 \times 10^{-3}$  mol,  $2.08 \times 10^{-3}$  mol and  $2.50 \times 10^{-3}$  mol, respectively. PPY 11, PPY 12, PPY 13 represents the samples where the concentrations of surfactants were  $3.73 \times 10^{-3}$  mol,  $4.35 \times 10^{-3}$  mol and  $4.97 \times 10^{-3}$  mol

The % yield of the PPY-DBSA salts was calculated by using the formula

Viscosities of PPY-DBSA were determined using Ostwald's capillary viscometer. The time of flow of the different concentrations (0.02, 0.04, 0.06, 0.08 g/mL) of PPY-DBSA was measured and from this the  $\eta_{sp}$  and  $\eta_{rel}$  of the solutions were calculated. Chloroform was used as solvent. Relative viscosity  $[\eta_{rel}]$  and specific viscosity  $[\eta_{sp}]$  were calculated using formula

$$\eta_{rel} = \frac{d_{1}t_{1}}{d_{2}t_{2}}$$
(2)  
$$\eta_{sp} = \eta_{rel} - 1$$
(3)

where d is density and t time. Subscript 1 represents solution and 2 solvent.  $[\eta]$  was obtained by linear extrapolation of the line of  $(\eta_{sp}/c)$  vs concentration and the line of  $(\ln \eta_{rel}/c)$  vs concentration to the same intercept at zero concentration.<sup>16</sup> Cyclic voltammograms (CVs) were recorded using bipotentiostat model 2323 (ALS Japan) using three electrode cell having gold disc electrode as working electrode, gold coil as counter and saturated calomel as reference electrode. 0.5 M H<sub>2</sub>SO<sub>4</sub> was used as electrolyte. The samples dissolved in THF were dip coated on the gold disc electrode, dried in air and then CVs were recorded by cycling the potential between  $E_{SCE}$  = -0.2 to 0.6 V and keeping the scan rate constant i.e., 50 mV/s. Similarly in another experiment the CVs of the samples were recorded keeping the potential window constant i.e., E<sub>SCE</sub>= -0.2 to 0.6 V but changing the scan rate from 10 mV/s to 100 mV/s. The surface morphology of the PPY-DBSA salts was studied by using JEOL Scanning Electron Microscope Model JSM-5910 (Japan) where the samples were mounted on aluminium stubs to which conductive tap was attached for surface analysis. XRD of PPY-DBSA salt was carried out by using JDX-3532 (JEOL JAPAN) X-ray diffractometer with the wavelength of 1.54 °A. Thermal stability of the samples was estimated using Diamond TG/DTA (Perkin Elmer USA) analyzer by heating them at the rate of 10  $^{\circ}$ C/min in N<sub>2</sub> atmosphere.

# **Results and Discussion**

#### Effect of reaction parameters on percent yield of PPY-DBSA

Percent yield is the most important factor in any synthesis process and is effected by different reaction parameters such as amount of monomer and oxidant. A polymerization process can results in a good yield of the polymer if different reaction parameters are optimized. In this work PPY-DBSA salt was prepared by inverse emulsion polymerization by optimizing the concentration of monomer (pyrrole) and oxidant (Benzoyl peroxide) and the % yield was checked. The effects of these parameters on yield were tested and are discussed as follows:

#### Effect of amount of Pyrrole

Fig. 1a shows the effect of amount of pyrrole on percent yield of PPY-DBSA. It was found that the % yield of the product was

highest in case of PPY 6 which means that the incorporation of the surfactant into the polymer chain increases with the increase in the amount of monomer and this results in the increase in the yield of polymer. A steady increase in the yield of PPY 6 was observed which may be attributed due to the increase in molecular collision with the increase in monomer molecules in the polymerization medium due to which polymerization is enhanced and thus yield of polymer increases.

#### Effect of amount of oxidant

The effect of the amount of oxidant, benzoyl peroxide on percent yield of PPY-DBSA is shown in Fig. 1b. It was found that increase in the amount of BPO, in the presently studied range, increases the yield of PPY. Formation of pyrrole cations become beneficial with increasing oxidant amount due to which chain propagation reaction is promoted resulting in the increase in polymer chain length and yield of polymer. Few polymerizable active centres are created when concentration of oxidant is less and as a result chain propagation reaction is favoured but the yield of polymer decreases.



Figure 1: (a) Effect of amount of pyrrole on the yield of PPY-DBSA (b) Effect of the amount of benzoyl peroxide on the yield of PPY-DBSA

## Solubility

A small amount of PPY-DBSA salt was added to various solvents like m-cresol, THF, DMF, DMSO, toluene and chloroform to observe the solubility. It was found that the PPY samples having higher concentrations of DBSA were highly soluble in these organic solvents. This increased solubility is attributed to:

- greater weakening of the intermolecular interaction
- micelle effect in which the monomer is confined inside the micelle in a localized environment surrounded by dopant
- obstruction of the cross linking between PPY chains

Cross linking reaction of pyrrole during polymerization and the interactions among PPY chains decreases as a result of high concentration of sulfonic acid from DBSA increasing the solvating effect due to long alkyl chain of DBSA which in turn increases the interactions between the solvent and PPY chains. So the synthesis of soluble PPY by chemical method not only needs large molecular size dopant but the strong solvating effect is also needed in order to increase the interaction between PPY chains and solvent.<sup>17</sup>

#### Intrinsic Viscosity

Measurement of the solute's contribution to the viscosity ( $\eta$ ) of a solution is called intrinsic viscosity [ $\eta$ ]. It can also be defined as the ratio of specific viscosity ( $\eta_{sp}$ ) to the concentration at infinite dilution, where specific viscosity ( $\eta_{sp}$ ) is one minus relative viscosity ( $\eta_{rel}$ ).

Fig. 2 (a-d) shows the  $[\eta]$  of the PPY-DBSA samples. It can be seen that the  $[\eta]$  of PPY increases with the increase in monomer amount in the polymerization bath i.e., PPY 3< PPY 4< PPY 5< PPY 6 (Fig. 2a-d). As intrinsic viscosity is directly related with the molecular weight of a polymer so it can be concluded that the molecular weight of PPY-DBSA increases with increase in monomer amount in the polymerization process.<sup>18</sup> This increase may be attributed to the greater number of radical cations

formation resulting in the increase in the growth of polymer and intrinsic viscosity of the polymer.



Figure 2: Intrinsic viscosity of PPY-DBSA salts

## **Cyclic Voltammetry**

Cyclic voltammetric technique is the most widely used technique giving us information about the electrochemical reactions. Like most of the conjugated polymers, polypyrrole can also be oxidized and reduced. Anionic sites are formed during reduction which requires cations for charge compensation or anion expulsion. Similarly polarons (PPY<sup>+</sup>) and bipolarons (PPY<sup>2+</sup>) are formed upon oxidation on the PPY chains.

Fig. 3a shows the CV of the PPY-DBSA sample labelled as PPY 4. Two sets of redox peaks were observed in this sample. The anodic peak being at  $E_{SCE}$ = 0.14 V while the cathodic peak was observed at  $E_{SCE}$ = 0.18 V. Similarly Fig. 3b shows the CV of the

PPY 5 sample in which the anodic peak is observed at 0.58 V <sup>19</sup> while the cathodic peak at  $E_{SCE}$ = 0.23 V exactly matching with the results reported elsewhere<sup>20</sup> showing the existence of cathodic and anodic peaks assigned to the reversible formation of PPY doped with DBSA.

For a truly reversible process involving one electron transfer, the anodic cathodic separation should be  $E_{SCE}$ = 0.59 V. Table 1 shows the anodic cathodic separation being less than  $E_{SCE}$ = 0.59 V which is therefore assigned to the formation of weak cathodic peaks due to removal of cations of DBSA.

Comparison of the two samples shows a shift of both oxidation and reduction peaks shown in Table 1.

Table 1: Observed anodic and cathiodic peaks in PPY-DBSA samples

Sample	Anodic peak (V)	Cathodic peak (V)	Anodic and cathodic peak separation (V)
PPY 4	0.14	0.18	0.04
PPY 5	0.58	0.23	0.35



**Figure 3:** CVs of (a) PPY 4 and (b) PPY 5 on gold electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub>; (c) CV of PPY 4 on gold electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> at different scan rates; (d) Plot of square root of scan rate versus current for PPY 4 in 0.5 M H<sub>2</sub>SO<sub>4</sub>

Fig. 3c shows the CV of PPY 4 recorded at different scan rates from 10 mV/s to 100 mV/s by cycling the potential at  $E_{SCE}$ = -0.2 to 0.6 V. A linear relationship was found between scan rates and peak currents when the anodic peak current was plotted versus the square root of scan rates as shown in Fig. 3d. This shows that the electrochemical process of PPY is kinetically controlled.

# **XRD of PPY-DBSA**

XRD analysis of PPY-DBSA salts showed that the synthesized salts were semicrystalline in nature. A broad peak can be observed each in PPY 3 (Fig. 4a) and PPY 4 (Fig. 4b) in region between  $2\theta=10^{\circ}$  to  $30^{\circ}$  showing small shoulders at  $2\theta=14^{\circ}$ ,  $17^{\circ}$ ,  $18^{\circ}$  and  $21^{\circ}$  in these samples. Similarly PPY 5 (Fig. 4c) and PPY 6 (Fig. 4d) also shows broad peaks having shoulders at  $2\theta=19^{\circ}$ ,  $21^{\circ}$  and  $22^{\circ}$ .

The small shoulder at  $2\theta=14^{\circ}$  in Fig. 4a is assumed to be due to the closed packing of benzene rings and indicates crystalline domains in the amorphous PPY powder.<sup>21</sup> Similarly the shoulder at  $2\theta=17^{\circ}$  (Fig. 4a) and  $2\theta=19^{\circ}$  (Fig. 4c, 4d) in the various samples of PPY represents the spacing between the ring planes of benzene ring in the adjacent PPY chains. Generally the XRD patterns of the conducting polymers show broad peaks in the form of hump, that is supposed to indicate semicrystalline nature. So the broad peaks observed for all samples of polypyrrole can be assigned to the semicrystallinity. Appearance of clear broad peaks in PPY 5 and PPY 6 as compared to PPY 3 and PPY 4 implies that the former have more ordered arrangement of PPY chains than the latter which have smooth uniform surface and that crystallinity increases with increase in monomer concentration.<sup>22</sup>

## SEM of PPY-DBSA

Fig. 5a shows the SEM at lower magnification while 5b shows the SEM at higher magnification of the PPY samples synthesized at different PPY amounts in the polymerization bath. Uniform, porous and granular surface morphology is shown in each case of the PPY-DBSA samples preffered for applications like gas sensing promoting the adsorption of gas molecules through the surface, though the size of particles effected by pores varies due to the different mole ratios of PPY in each sample. Low magnification SEM of all the samples shows the aggregation of particles which may be due to the increased interchain interaction showing the crystallinity in coincide with the result of conductivity. Thus the morphology of the conducting polymers is very much related to the electrical conductivity.<sup>23</sup>

At lower magnification SEM of PPY-DBSA shows cauliflower like surface morphology. This is also called broken egg shell like morphology that may have resulted from phase segregation There is distribution of small particles randomly across the surface which may be due to the excess DBSA that was not removed during the process of rinsing. Comparison of the SEM images of all the samples shows no significant change in the shapes of PPY but the porosity decreases with the increase in monomer amount. Porosity is directly related to the solubility decreasing with the decrease in the number of pores. Thus the polymer with less number of pores shows less solubility. So PPY 3 having greater porosity shows greater solubility as compared to PPY 6 having less porosity with decreased solubility.



Figure 4: XRD patterns of PPY-DBSA salts



Figure 5: SEM of PPY-DBSA samples

# **TGA of PPY-DBSA**

The thermal stability of PPY-DBSA samples was studied by thermogravimetric analysis. Three distinct weight losses were observed in all of the samples as shown in Fig. 6. The first weight loss corresponds to the elimination and evaporation of moisture as reported by many authors.<sup>24</sup> The second weight loss show the removal of DBSA component of the polymer as reported by Truong *et al.*<sup>25</sup> and the third weight loss i.e., at high temperature represents the breaking of the PPY chain resulting in the formation of volatile gases. It was observed for PPY samples that the degradation temperature increased with an increase in monomer amount. Fig. 6. shows the TGA curves of the different PPY samples.

Fig. 6a shows a thermogram for PPY 3 representing three step degradation process. The first step showing a weight loss of 3% starting from room temperature ( $30^{\circ}$ C) to  $70^{\circ}$ C and ascribes to the removal of moisture and elimination of water molecules in the PPY matrix. This weight loss is 4% for PPY 4 (Fig. 6b) from 30 °C to 100 °C, 4.5% for PPY 5 (Fig. 6c) from 30 °C to 104 °C and 5% for PPY 6 (Fig. 6d) from 30 °C to 111 °C.

The second step shows a weight loss of 55% for PPY 3 from 283-512°C demonstrate the removal of DBSA component of the PPY. This weight loss is 56% for PPY 4 from 286-514°C, 57% for PPY 5 from 292-517°C and 58% for PPY 6 from 297-520°C as shown in Fig 6.

The third step is degradation step represent the breaking of the PPY chain leading to the formation of volatile gases and is an exothermic process. Degradation of PPY 3 starts at  $512^{\circ}$ C (Fig. 6a), PPY 4 at 514 °C (Fig. 6b), PPY 5 at 517 °C (Fig. 6c) and PPY 6 at 520 °C (Fig. 6d). An increase in the degradation temperature of the PPY samples shows that thermal stability increases with increase in monomer concentration.

The synthesized PPY doped with DBSA in the present work is found to be thermally stable upto a temperature of about 520°C which is so far the highest thermal stability reported for PPY. So it can be used in various technologies where high temperature is required.



Figure 6: TGA curves of PPY-DBSA samples

# FTIR of PPY-DBSA

Fig 7a-d shows the FTIR spectrum of the various samples of PPY (PPY 3, PPY 4, PPY 5, PPY 6). A little or almost no influence on the IR frequency of absorption is observed for all PPY samples presented in Fig.7. The PPY-DBSA characteristic

vibration peaks are in the range of 700-1800 cm<sup>-1</sup>. FTIR spectrum of PPY 3 (Fig. 7a) shows a peak in the range of 2320-2354 cm<sup>-1</sup> which corresponds to the aromatic and aliphatic C-H stretching vibrations showing that below 2000 cm<sup>-1</sup> IR absorption peaks are effected by the pyrrole units of PPY-DBSA while above 2000 cm<sup>-1</sup> IR peaks corresponds to the DBSA units

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of the PPY-DBSA salt. The intensity of these peaks decreases with the increase in monomer amount because the pyrrole unit contains less aromatic C-H bonds and do not contains aliphatic C-H bonds at all.<sup>26</sup>

Out of plane wagging of the carbonyl group is represented by the peak at 1703 cm<sup>-1</sup>. Peak at 1551 cm<sup>-1</sup> shows the stretching vibration of C=C. Similarly stretching vibrations of C-N ring is represented by the small peak at 1468-1475 cm<sup>-1</sup>. Another peak at 1316 cm<sup>-1</sup> is associated with the bending vibrations of N-H.

The peak at 1205 cm<sup>-1</sup> relates to the S=O stretching vibrations of  $SO_3^-$  of the DBSA units in PPY-DBSA broadening with doping concentration and is also called crystalline band. Skeletal vibrations of PPY involving delocalization of  $\pi$  electrons is found to be influenced by PPY doping. It has been observed that with an increase in the amount of monomer, the intensity of this peak decreases showing the decrease in the dopant effect with an increase in monomer concentration. The small shift in crystalline band with increase in monomer amount may also be effected by molecular mass of PPY samples.



Figure 7: FTIR spectrums of PPY-DBSA salts

In plane wagging of the C-H is shown by the peak at  $1039 \text{ cm}^{-1}$  while out of plane wagging of C-H corresponds to the peaks in the range of 914-921 cm<sup>-1</sup>. The characteristic vibrations of DBSA are shown by the peak at 679 cm<sup>-1</sup>. The presence of sulphonate groups of DBSA is confirmed by the peaks at 609 cm<sup>-1</sup>. Similarly the band at 575 cm<sup>-1</sup> is due to stretching vibrations of C-S and S-O showing that in the PPY backbone

sulphonic acid groups are introduced. Amount of polymer has some effect on the increase in the intensity of this peak showing the increase in the amount of PPY with higher proportion of Pyrrole.

All the FTIR peaks of the synthesized PPY are found to match well with the peaks in the literature confirming the formation of PPY-DBSA salt in present work.



Scheme 1: Reaction mechanism for the synthesis of polypyrrole

# Conclusions

PPY-DBSA salts were successfully prepared by inverse emulsion polymerization using dodecyl benzene sulfonic acid as a dopant as well as surfactant, benzoyl peroxide as an oxidant while a mixture of chloroform and 2-butanol as a novel dispersion medium. The resulting PPY-DBSA was collected in powdered form with high purity and good yield. The solubility of the synthesized PPY-DBSA salts was checked in different organic solvents like m-cresol, THF, DMSO, DMF etc. and was found to be soluble. It was found that the concentration of monomer and oxidant effected the yield of PPY-DBSA salts. Intrinsic viscosity of the PPY-DBSA salts was calculated by using capillary viscometer and was found to be dependent upon monomer amount in the polymerization bath. FTIR confirmed the presence of various functional groups in the PPY-DBSA salts and changes in intensity of the functional groups was observed. Semicrystalline nature of the PPY-DBSA salts was confirmed by XRD. Increase in the amount of monomer caused the appearance of sharp peaks in the XRD patterns showing increase in the ordered arrangement of the PPY chains. SEM micrographs showed the granular morphology of the PPY-DBSA salts and porosity decrease was observed with increase in monomer concentration. TGA results showed so far the highest thermal stability of the PPY-DBSA salts i.e., 520°C. The electrochemical behaviour of the PPY-DBSA salts was studied by CV confirming good electroactivity of the polymer.

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