ELECTROCHEMICAL CHARACTERIZATION OF THE NANO Py/DDS/SiO₂ FILM ON A COPPER ELECTRODE

ELEKTROKEMIJSKA KARAKTERIZACIJA NANOPLASTI Py/DDS/SiO₂ NA BAKRENI ELEKTRODI

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Keywords: 4,4'-diaminodiphenyl sulfone, cyclic voltammetry, SEM, nanosize, copper electrode

1 INTRODUCTION

Progressive research in the field of conducting polymers has led to the development of the materials with a great potential for commercial applications, including lightweight batteries, light-emitting diodes, capacitors, electrochromic devices, optical and electronic devices. Conducting-polymer films have shown promising applications in the field of biosensors and bioelectrochemistry by providing an active matrix with controlled morphology for immobilization of biological materials as well as transduction of electrical signals. If an electrode surface is modified with a conducting-polymer film, then the modified electrode can be used as a sensor. Polyaniline is among the most important organic conducting polymers having a high conductivity but poor processability. In order to increase its processability and utility, researchers studied the derivatives of polyaniline prepared with different methods. Homopolymerization of aniline derivatives has been effective in the preparation of substituted polyanilines. Increased torsional angles and the presence of a substituent result in a decreased orbital overlap of electrons and nitrogen lone pairs; however, substituted polyanilines exhibit conjugations and conductivities that are significantly lower than those of polyaniline. Several researchers have employed different post treatments after the synthesis of polymer films; however, there are no systematic studies on this aspect. On the other hand, when a polyaniline layer was deposited first and the electropolymerization was continued in a solution of 4,4'-diaminodiphenyl sulfone (DDS), a progressive transformation of the electrochemical behavior of the original polyaniline film was observed. The polyaniline promotes the polymerization by providing electrocatalytic sites and nucleation centers. Thus, the conducting polyaniline surface is protected well and leads to a better modification. Chemical polymerization of DDS also leads to new polymers. Interestingly, both newly formed polymers are found to have a nanostructure. The preparation...
of nanostructured conducting materials has become an important branch of materials research.13 Many research groups have reported various kinds of polymer nanocomposites, like polyaniline, PEDOT, and polypyrrole.14–16 Hence, it seemed interesting to study the formation and properties of the new nanostructured polymeric material produced with a reaction of polyaniline and DDS during redox cycling. DDS, an important pharmaceutical compound, is used as an antileprotic drug.17–19 Utilization of the materials of biointerest for the preparation of newer nanopolymeric materials assumes their importance in the present environment. They are also used in the sorption and transport of carbon dioxide20–22 and cured in epoxy networks.23 Here we present the results obtained from a formation of a nanosized electroactive polymer through an electrochemical and chemical polymerization of 4.4’-diaminodiphenyl sulfone (DDS) and the characterizations of the new polymer. The electrical conductivity of the copolymers increased greatly, from 6.00 × 10⁻⁴ S cm⁻¹ to 2.55 × 10⁻¹ S cm⁻¹, with the increasing aniline content. The electrochemical studies performed on these copolymer films revealed their electrochromic sites corresponding to individual units. In another study an electroactive conducting polymer, poly(pyrrole-co-4.4’-diaminodiphenyl sulfone), was prepared from pyrrole and 4.4’-diaminodiphenyl sulfone (DDS) using cyclic voltammetry on a copper electrode surface.24,25 The present study reports an electrochemical synthesis of a new nanosized poly(Py-co-DDS) and its characterization with the SEM, XRD, and FTIR techniques. Furthermore, the solubility in different solvents, conductivity and electrochromic behavior of the copolymer were evaluated and reported.

2 EXPERIMENTAL WORK

Pyrrole (Merck; 99 %) was distilled before use and all the test solutions were freshly prepared. DDS and methanol were purchased from Merck. Nano SiO₂ (Allderich, Germany, 40 nm diameter particles) and a phosphate buffer solution (PBS) with a pH of 7.0 as the electrolyte were prepared with 0.1 M NaH₄PO₄–Na₂HPO₄, while the pH was adjusted with 0.1 M HCl and 0.1 M NaOH. Cyclic voltammetry (CV) was carried out using a Potentiostat/Galvanostat EG&G Model 263 A, USA, with a PC and an electrochemical set up controlled with the M 270 software. A Pt counter electrode, an Ag/Ag⁺ reference electrode and a computer-controlled JASCO V-530, UV-Vis spectrophotometer. Scanning electron microscopy (SEM) images were taken using a VEGA HV (high potential) 1 500 V at various magnifications. A conducting poly(aniline-co-diaminodiphenyl sulfone) was synthesized and characterized and it was shown that the reactivity of 4.4’-diaminodiphenyl sulfone was greater than that of aniline.26 Our electrochemically synthesized copolymer of aniline and 4.4’-diaminodiphenyl sulfone exhibited novel electrochromic properties.26 In this paper, the electrochemical copolymerization of pyrrole (Py) with 4.4’-diaminodiphenyl sulfone (DDS) and nanoparticles of SiO₂ is presented. The solubility of copolymers was studied with various organic solvents.

3 RESULTS AND DISCUSSION

3.1 Electrochemical copolymerization of pyrrole, 4.4’-diaminodiphenyl sulfone and nanoparticle SiO₂

Figure 1 shows the cyclic voltammogram of 0.01 M DDS in 4 M H₂SO₄, 0.1 M SiO₂ and the ethanol mixture obtained between −1 V and 1.5 V at a scan rate of 100 mV s⁻¹ on a copper electrode. The voltammogram exhibits one broad oxidation peak at 0.2 V in the first cycle. The anodic peak is caused by an oxidation of the amino group in the phenyl ring of DDS in 4 M H₂SO₄, 0.1 M SiO₂ and ethanol medium. After the completion of the polypyrrole coating was recorded in the horizontally attenuated total reflectance mode in the spectral range of 400–500 cm⁻¹ using a Bruker spectrometer, Vector Series 22, Germany. Spectroelectrochemical studies were performed in a quartz cuvette with a path length of 1 cm utilizing an optically transparent working electrode, an indium tin oxide (ITO) plate (10 Ω cm⁻²), a Pt counter electrode, an Ag/Ag⁺ reference electrode and a computer-controlled JASCO V-530, UV-Vis spectrophotometer. Scanning electron microscopy (SEM) images were taken using a VEGA HV (high potential) 1 500 V at various magnifications. A conducting poly(aniline-co-diaminodiphenyl sulfone) was synthesized and characterized and it was shown that the reactivity of 4.4’-diaminodiphenyl sulfone was greater than that of aniline.26 Our electrochemically synthesized copolymer of aniline and 4.4’-diaminodiphenyl sulfone exhibited novel electrochromic properties.26 In this paper, the electrochemical copolymerization of pyrrole (Py) with 4.4’-diaminodiphenyl sulfone (DDS) and nanoparticles of SiO₂ is presented. The solubility of copolymers was studied with various organic solvents.

![Figure 1: Cyclic voltammetric behavior of 0.01 M DDS and SiO₂ in 4 M H₂SO₄ and ethanol at a scan rate of 100 mV s⁻¹ using a copper working electrode](image-url)
tenth cycle, the working electrode was washed with ultrapure water and a light brown film was seen on the surface of the copper electrode. The film was thin and further growth was inhibited due to its low conductivity.

Figure 2 represents the cyclic voltammograms of the growth of PPy on a stationary copper electrode in 4 M H2SO4, 0.1 M SiO2 and ethanol medium with a potential range of –1 V to 1.5 V and a scan rate of 100 mV s\(^{-1}\). In the first anodic scan, a peak corresponds to the oxidation of PPy to produce a Py cation radical (PyR) that was observed at 0.2 V. Another peak observed in this first cycle at 1.03 V was due to the oxidation of ethanol.27

The CVs of the second and subsequent cycles during the electrochemical polymerization of Py show two anodic peaks at 0.3 and 0.8 V. The progressive increases in the current of the peak at 0.3 V suggest a continuous formation of PPy films on the surface of the copper electrode.

The cyclic voltammogram of 0.01M DDS, 0.1 M SiO2 and 0.01 M Py in the 4 M sulfuric acid and ethanol is presented in Figure 3. The potential range applied and the scan rate selected here are the same as in the previous cases. The CVs show two oxidation peaks at –0.5 V and 1 V in the first cycle representing the formation of a pyrrole cation radical (PyR) and a 4,4’-diaminodiphenylsulfone cation radical (DDSCR), respectively. These peaks were assigned to the reduction of polymer products formed with a reaction between the intermediate species PyCR and DDSCR, respectively. According to the CVs recorded during the further cycles, i.e., the second to the tenth cycles, one oxidation and one reduction peak at 0.8 V and 0.3 V, respectively, appeared and they were both intensifying during these cycles. Thus, the CVs recorded during the copolymerization of 0.01 M DDS, 0.1 M SiO2 and 0.01 M Py in the 4 M sulfuric acid and ethanol clearly differ from the CVs recorded during the homopolymerization of either Py or DDS alone. The twin redox characteristics28 noticed for the polymerization of Py were virtually merged into a single redox process in the cases of the copolymerization of Py and DDS. The above mentioned oxidation and reduction waves disappeared and one anodic and one cathodic peak appeared at 0.8 V and 0.3 V, respectively. These redox peaks show an effective increase of the current from the second cycle onwards. At the end of the tenth cycle, a dark-green copolymer film was observed on the surface of the copper electrode.

Copolymers were prepared from different molar feed ratios of Py and the copolymer formation was influenced by the Py concentration. The concentration of a Py monomer was plotted against the total charge of the formation of electroactive, oxidative, conducting copolymer
films (Figure 4). Figure 4 shows that the total charge is on a rapid increase due to the increase in the Py concentration until Py reaches 0.01 M, when the increase in the charge slows down depending on the Py concentration. These observations indicate an increasing number of Py units in the copolymer formation.

3.2 Effect of the scan rate

The copolymer film of poly(pyrrrole-co-4,4'-diaminodiphenyl sulfone-SiO$_2$) was washed with ultrapure water and a monomer-free background solution and then the film was scanned in the solution in the range of 0 mV to 1.5 mV. The cyclic voltammogram presented in Figure 5 resembles that of the electroactive polymer obtained during the copolymerization of Py and DDS. The main oxidation-peak current increased linearly (Figures 5 and 6) as the scan rate increased from 50 mV s$^{-1}$ to 300 mV s$^{-1}$ indicating the presence of the electroactive copolymer film.

3.3 Effect of pH

The copolymer film formed on the surface of the copper electrode was washed with ultrapure water and a monomer-free solution. Then the film was scanned in the monomer-free solution and the pH range between 4 and 9 was considered. The voltammetry range between 0 V and 1.5 V was considered. The CV (Figure 7) resembles that of the electroactive polymer obtained earlier. The maximum current was observed for pH 7 and the minimum for pH 4.

The peak voltammetric current decreased with the increasing pH (Figure 7), indicating an involvement of H$^+$ ions. The film was also first cycled at a high pH of 7.0 (Figure 7). Thus, when the copolymer film was scanned at pH 4 the increase in the current was due to the change in the dopant. The effect of pH was studied on the copolymer films of Py, SiO$_2$ and DDS at various monomer concentrations and similar results were observed.

3.4 UV-Vis spectra and conductivity of copolymers

In-situ UV-Vis spectrolelectrochemistry provides a useful tool for studying the electropolymerization and intermediate products analysis. To study the spectroelectrochemical properties of the copolymer, the copolymer film was electrochemically deposited on an ITO glass plate at a constant potential of 1.2 V vs Ag/Ag$.^+$ To ensure a consistent content of the electroactive polymer on the electrode surface between poly-

![Figure 5: Effect of the scan-rate variation on the cyclic voltammetry of the poly(Py-co-DDS/SiO$_2$)-film-coated copper electrode from 50 mV s$^{-1}$ to 300 mV s$^{-1}$ in the 4 M H$_2$SO$_4$ medium](image1)

![Figure 6: Effect of the scan-rate variation on the poly(Py-co-DDS/SiO$_2$)-film-coated copper electrode from 50 mV s$^{-1}$ to 300 mV s$^{-1}$ in the 4 M H$_2$SO$_4$ medium](image2)

![Figure 7: Effect of the pH variation from 4 to 9 on the poly(Py-co-DDS/SiO$_2$)-film-coated copper electrode in the acidic, neutral and basic media](image3)
merizations, the same amount of charge was passed during copolymerization. After deposition, the blue, oxidized ITO-adhered films were washed with the monomer-free electrolyte solution before recording the spectra at various applied potentials in the 0.1 M H₂SO₄ medium. Since all of the copolymer films are blue in their oxidized state, each film was subsequently reduced to determine whether there was a direct correlation between the monomer compositions and electrochromic response. As an illustration, the spectra of the copolymer films obtained from 0.3 M pyrrole, 0.1 M SiO₂ and 0.1 M DDS at various applied potentials are presented in Figure 8. When the applied potentials changed from 0 V to 1.5 V, the spectra exhibited absorption bands at 320 nm and 390 nm; the former one may be due to a π-π* transition and the latter one may be a benzenoid band. As the applied potential expanded to the oxidation side, the film color changed from yellow to blue. Apart from these bands, an additional broad band was observed in the visible region. The wavelength maxima of this band depended on the applied potentials. When an applied potential changed from 0.0 V to 0.8 V, an absorption band was obtained between 320 nm and 390 nm, exhibiting neutral yellow due to the formation of cation radicals (polaronic forms). As the potential varied from 0.0 V to 0.8 V, the absorption band shifted to the lower-energy side, i.e., a bath chromic shift was observed. The non-conducting blue film may be formed because of the fully oxidized copolymer. The feed ratio of the DDS monomer increased to 0.5 M and the film was coated as previously. After the deposition, the oxidation film was dark blue, indicating a higher amount of DDS in the copolymer. Here the π-π* transition and benzenoid bands were also observed.

The conductivity of this copolymer film was measured with a four-probe conductivity meter. At room temperature the conductivity of the copolymer, poly(Py-co-DDS/SiO₂), was determined to be 5.98 × 10⁻² S cm⁻¹. Thus, the conductivity of the copolymer is lower than that of Py/SiO₂ (6.68 × 10⁻² S cm⁻¹) and higher than that of polyDDS/SiO₂ (6.01 × 10⁻³ S cm⁻¹).

3.5 FTIR spectral behavior of copolymers

The IR spectrum, Figure 9, reveals the presence of different species involved in the fabrication of the composite polymer. The bands at (3470, 3350, and 3215) cm⁻¹ correspond to the N-H stretching vibration, whereas the bands at (3050, 2970, and 2850) cm⁻¹ result from the aromatic C-H stretching vibration. The peak at 1600 cm⁻¹ is due to the stretching deformation of the quinone ring. The 1280 cm⁻¹ band is assigned to the C-N stretching in the secondary aromatic amine, whereas the peaks at 1080 cm⁻¹ and 1150 cm⁻¹ represent the aromatic C-H in-plane bending modes. The out-of-plane deformation of C-H in the 1.4-disubstituted benzene ring is located at 835 cm⁻¹. The bands at 1302 cm⁻¹ and 555 cm⁻¹ correspond to the S=O stretching and S=O bending mode, respectively, of the sulfone group of the PDDS shift of their frequency and intensity in poly(Py-co-DDS/SiO₂) to 1308 cm⁻¹ and 576 cm⁻¹, respectively.

3.6 SEM and XRD

Chemically copolymerized materials were characterized with a SEM analysis. A SEM photograph (Figure 10a) of the copolymer formed from 0.3 M Py/SiO₂ and 0.02 M DDS showed a leave-like structure. This irregular structure confirmed the formation of the copolymer. The grain size of the material is 60 nm. When the concentration of DDS increased to 0.03 M, the formed copolymer exhibited only small changes in the structure (Figure 10b). When the incorporation of DDS increased
to 0.1 M, the SEM photograph (Figure 10c) exhibited different, irregular, broken nanostructures.

The crystalline regions in the copolymers are characterized by the presence of relatively sharp peaks. The amorphous regions are visible due to broad, low intensity peaks. The X-ray diffraction profile (Figure 11) of the copolymer indicates a substantial degree of crystallinity in the doped forms. The base form of the copolymer with low DDS/SiO2 exhibited less crystallinity than the highly doped form. The use of the Scherrer equation is the primary technique for determining the size or thickness of the polymer crystallites. The crystallite size of the copolymer was determined by employing the XRD results and the Scherrer equation (1):

\[ L = \frac{K\lambda}{\beta(2\theta) \cos \theta} \]  

Here \( K \) is the shape factor of the average crystallite (the expected shape factor is 0.9), \( \lambda \) is the wavelength (usually 0.154056 nm), \( \beta \) is the peak position and FW is the full width at half maximum. By employing the above method, the crystallite size of the copolymer was determined as 50 nm confirming the presence of nanostructured copolymers. This is the first report on the crystallite size of a copolymer of pyrrole/SiO2 and 4.4'-diaminodiphenyl sulfone. However, earlier findings showed a similar result for poly 4.4'-diaminodiphenyl sulfone.24

4 CONCLUSION

The copolymer of pyrrole and 4.4'-diaminodiphenyl sulfone was prepared electrochemically using the continuous-cycling method in a solution of 4 M H2SO4, SiO2 and ethanol, with different concentrations of both pyrrole and 4.4'-DDS. The copolymer formation was more significant with the feed concentrations of 0.01 M Py and 0.01 M 4.4'-DDS and exhibited a varying, cyclic voltammetric behavior. The synthesized poly(Py-co-DDS/SiO2) films demonstrated a good adherence in acidic and neutral solvents and were found to be electroactive. The copolymer films were responsive up to pH 7.0 in the acid and neutral media. The formation of the copolymer, poly(Py-co-DDS/SiO2), was further ascertained from the FTIR and SEM data. The XRD results revealed the formation of a nanosized copolymer. These results indicate that the copolymers herein can be used in the development of dynamic electrochromic devices and their conducting films can be used to modify the electrodes that are used as sensors.

5 REFERENCES
