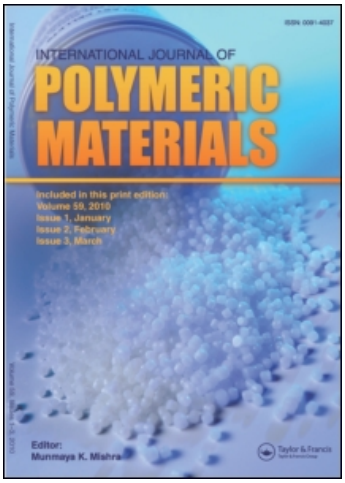

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Influence of Process Parameters on the Conductivity and Surface Morphology of Polypyrrole Films

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To cite this Article Gade, V. K. , Shirale, D. J. , Gaikwad, P. D. , Savale, P. A. , Kakde, K. P. , Kharat, H. J. and Shirsat, M. D.(2007) 'Influence of Process Parameters on the Conductivity and Surface Morphology of Polypyrrole Films', International Journal of Polymeric Materials, 56: 2, 167 — 176
To link to this Article: DOI: 10.1080/00914030600758272
URL: http://dx.doi.org/10.1080/00914030600758272

International Journal of Polymeric Materials, 56:167–176, 2007

ISSN: 0091-4037 print/1563-5333 online
DOI: 10.1080/00914030600758272

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Influence of electrochemical process parameters such as monomer and electrolyte concentrations, current density, pH of the electrolyte, and type of electrolyte have been studied during polymerization of polypyrrole (Ppy). The changes in the conductivity of synthesized Ppy film for different electrolytes were observed by chronopotentiograms recorded during the electrochemical polymerization and it was confirmed by measuring it using four probe techniques. It was found that the electrochemical process parameters have a considerable influence on the conductivity of the film. The Ppy film was synthesized on a platinum substrate by electrochemical polymerization with different electrolytes such as potassium nitrate, sodium nitrate, sulphuric acid, hydrochloric acid, potassium chloride, sodium chloride, oxalic acid, and sodium salicylate, under galvanostatic condition over a wide range of pH of the reaction medium and applied current density. The different concentration ratios of pyrrole and sodium nitrate were considered during synthesis of Ppy films. It has been observed that the polymerization potential increases with the pH and applied current density. One could synthesize Ppy film with very good surface morphology and conductivity with optimized process parameters. The characterization of synthesized Ppy film was done by electrochemical technique, electrical

Received 10 April 2006; in final form 21 April 2006.

The authors are thankful to the University Grants Commission, New Delhi, India for the financial assistance and one of the authors (VKG) expresses gratitude for an awarding fellowship under the FIP scheme of UGC. The authors are also thankful to Department of Chemistry and Department of Physics, University of Pune, India.

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conductivity, Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM).

Keywords: electrochemical polymerization, galvanostatic, platinum, polypyrrole

INTRODUCTION

Polypyrrole is a promising material for commercial applications because of its good environmental stability, electrochemical preparation, and biocompatibility. Aqueous electrochemical process is an environment friendly and efficient technique being used for synthesis of conducting polymers [1–3]. Ppy can often be used for biosensors, gas sensors, microactuators, antielectrostatic coatings, solid electrolytic capacitor, electrochromic windows, displays, packaging, polymeric batteries, electronic devices and functional membranes [4–6]. However, conductive Ppy is insoluble and infusible, which restricts its processing and applications, This problem has been extensively investigated and new application fields have been explored in the past several years; for example, Ppy-based polymers can be used to load and release drugs and biomolecules [7–11]. It is preferably being used for biosensor applications.

Organic conducting polymers have recently emerged as a new class of electroactive materials and are interesting subjects for research and development [11–14]. The remarkable switching capability of these electroactive materials between the conducting oxidized (doped) and the insulating-reduced (undoped) state is the basis of many applications. Among others, the polyconjugated conducting polymers have been recently proposed for biosensing applications because of a number of favorable characteristics, such as (1) direct and easy deposition on sensor electrode by electrochemical oxidation of monomer, (2) control of thickness, and (3) redox conductivity. Various conducting polymers have been extensively considered as the material for immobilization of enzymes, such as polyacetylene, polythiophene, polypyrrole (Ppy), polyindole, and polyaniline. Among these conducting polymers, Ppy is well characterized and is probably one of the most suitable polymers for biosensor applications because it has good environmental stability and biocompatibility. Its low oxidation potential enables a conducting polymer film to be grown from aqueous solutions that is compatible with most of the biological elements. Moreover, its easy polymerization, high electrical conductivity, chemical stability, and ability to form freestanding films are added advantages for its application to biosensors [15–16].

The galvanostatic (constant current) method of synthesis of conducting polymer on platinum electrode offers an effective and efficient control of properties of Ppy film. By selecting appropriate electrolyte, and/or varying polymerization parameters, for example, concentration of monomer, concentration of electrolyte, pH, and current density one can synthesize a good quality of polymer film. However, these variations will be associated with changes in the conductivity and morphology of the film [12,17]. In fact, the conducting polymers are being used for biosensing application because they provide an excellent matrix for entrapment of biocomponent and also facilitate electron transfer process. Therefore, the synthesized conducting polymer film should have porous surface morphology and high conductivity. The present investigation has taken the monomer pyrrole and synthesized the conducting polymer Ppy by electrochemical polymerization using the galvanostatic method. The authors studied the influence of various parameters such as (1) type of electrolytes, (2) concentration of monomer and electrolyte, (3) current density, (4) pH of the aqueous solution, and so on, on conductivity and surface morphology of synthesized Ppy film so that it can be used for biosensing applications.

EXPERIMENTAL

The Pyrrole monomer was distilled twice before use. Sodium nitrate ($NaNO_3$), potassium nitrate (KNO_3), hydrochloric acid (HCl), sodium chloride (NaCl), potassium chloride (KCl), sulphuric acid (H_2SO_4), oxalic acid ($C_2H_2O_4 \cdot 2H_2O$), and sodium salicylate ($C_7H_5NaO_3$) were used as supporting electrolytes. All reagents were provided by Rankhem, Ranbaxy, New Delhi, India.

Aqueous solutions of pyrrole (98%) and various electrolytes were prepared in deionized water. Different concentration ratios of pyrrole and supporting electrolytes were considered for the synthesis of Ppy film. The pH was adjusted by nitric acid or sodium hydroxide and measured by a calibrated pH meter. The electropolymerization of pyrrole was carried out by a galvanostatic technique, in one compartment electrochemical cell. A platinum foil ($20\,mm \times 40\,mm \times 0.25\,mm$) was used as a counter electrode (cathode) and another platinum foil ($20\,mm \times 10\,mm\ \ 0.25\,mm$) was used as a working electrode (anode). The reference electrode was a saturated calomel electrode (SCE). All three electrodes were placed vertically in the cell. An 80 ml solution was used for each experiment. After each experiment, the polymer-coated platinum foil was rinsed with distilled water and dried at 50°C.

The characterization of Ppy film was carried out by electrochemical techniques. The electrical conductivity was measured by Keithley 6514 Electrometer, the FTIR spectra was recorded, using Testscan Shimadzu FTIR-8000 series, using KBr pellets in the region between 500 and 4000 cm^{-1}. The scanning electron micrograph was recorded using JEOL JSM-6360 A Analytical SEM.

RESULTS AND DISCUSSION

A typical galvanostatic electropolymerization chronopotentiogram [17] is shown in Figure 1. It shows the anodic peak at which the polymerization process starts and the plateau at which the polymerization process reaches a stable state with time, indicating the completion of the process. All these stages are affected by the following process parameters: pyrrole concentration, electrolyte concentration, time of deposition, applied current density, surface pretreatment, and the pH of the electrolyte. In fact, the recorded polymerization potential should be as small as possible so that there is high conductivity of the film.

The chronopotentiograms recorded during synthesis of Ppy with various electrolytes at pH 3.0 and temperature 27°C are shown in Figures 2, 3, and 4. An aqueous solution (80 ml) containing 0.1 M pyrrole and 0.1 M sodium nitrate and deionized water with pH 3.0 was prepared. It was subjected to electrochemical polymerization by galvanostatic method at temperature 27°C with 1 mA/cm^2 applied current density. A similar experiment was repeated for the other electrolytes potassium nitrate, sulphuric acid, hydrochloric acid, sodium chloride, potassium chloride, sodium salicylate, and oxalic acid. The

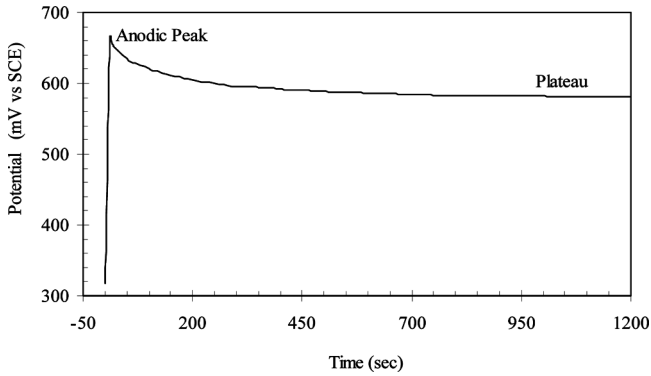

FIGURE 1 A typical galvanostatic electropolymerized chronopotentiogram (E-t curve).

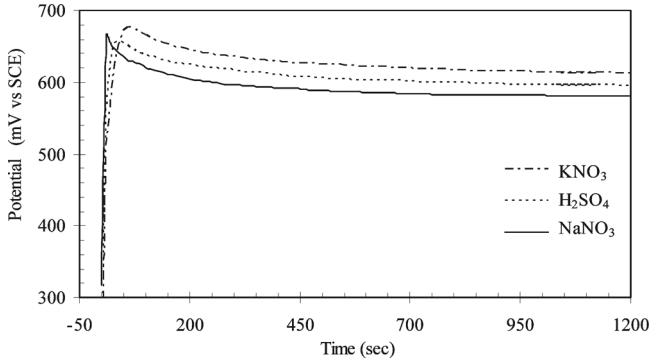

FIGURE 2 Chronopotentiogram recorded during electrochemical polymerization of Ppy at pH 3.0, current density 1 mA/cm^2 and T = 27°C for potassium nitrate, sulphuric acid, and sodium nitrate with 0.1:0.1 molar concentration ratio of pyrrole and electrolytes.

lowest polymerization potential was recorded for the electrolytes sodium nitrate, potassium chloride, and oxalic acid, and we could also synthesize Ppy film with very good surface morphology and conductivity. Comparing the chronopotentiogram recorded during synthesis of Ppy with the three electrolytes sodium nitrate, potassium chloride, and oxalic acid and synthesized Ppy it was found that the lowest polymerization potential was recorded for sodium nitrate and the synthesized Ppy film with sodium nitrate had a very good surface morphology and conductivity. The conductivity of Ppy film with these

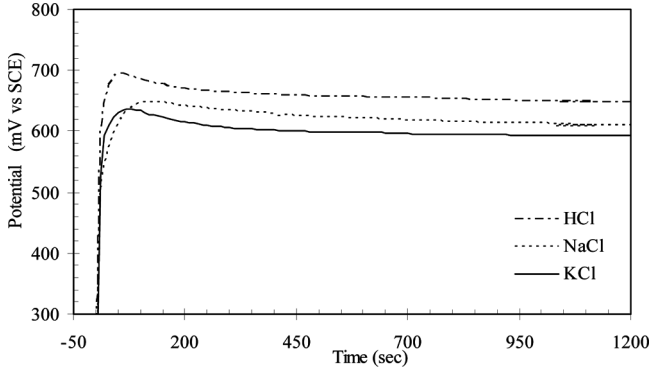

FIGURE 3 Chronopotentiogram recorded during electrochemical polymerization of Ppy at pH 3.0, current density 1 mA/cm^2 and T = 27°C for hydrochloric acid, sodium chloride, and potassium chloride with 0.1:0.1 molar concentration ratio of pyrrole and electrolytes.

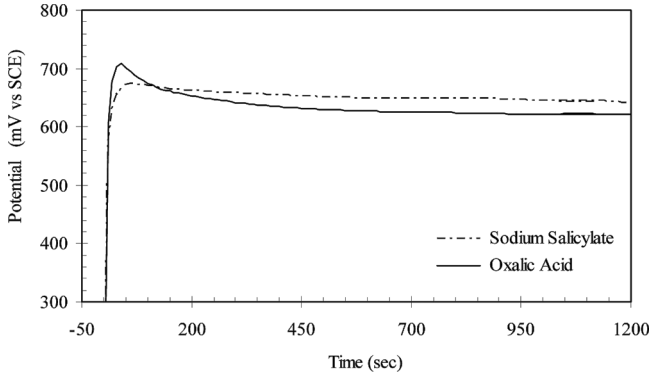

FIGURE 4 Chronopotentiogram recorded during electrochemical polymerization of Ppy at pH 3.0, current density 1 mA/cm^2 and T = 27°C for sodium salicylate and oxalic acid with 0.1:0.1 molar concentration ratio of pyrrole and electrolytes.

three electrolytes was measured using four-probe method with Keithley 6514 Electrometer. The electrical conductivity and plateau potential of these three synthesized Ppy films are presented in Table 1. The data in Table 1 clearly indicate that the conductivity depends on the anion present in the electrolytes and follows the order $NO_3^- > Cl^- > COO^-$. This dependence may be related to the plateau potentials. The plateau (polymerization) potential for sodium nitrate is less than the other two electrolytes because of the mobility and size of the ions. It can also be seen that as the plateau potential increases there is a decrease in the conductivity. The conductivity depends on the mobility of the ions in solution [17–18]. The authors experimentally found large conductivity of synthesized Ppy film with sodium nitrate as compared to the other two electrolytes. This clearly indicates that the mobility of nitrate ions in aqueous solution (0.1 M sodium nitrate, 0.1 M of pyrrole in 80 ml deionized water) is certainly more than that of the other two electrolytes.

TABLE 1 Relation between the Conductivity and the Plateau Potential of Different Electrolytes

Sr No.	Ppy film with electrolytes	Plateau potential (mV)	Electrical conductivity (S/cm)
1	Sodium nitrate	581	1.412×10^{-4}
2	Potassium chloride	593	1.010×10^{-4}
3	Oxalic acid	621	0.774×10^{-4}

The concentration of monomer and electrolyte significantly affects the surface morphology and conductivity of Ppy film. Therefore, in order to optimize the molar concentration ratio of Ppy and sodium nitrate, different concentration ratios as 0.1:0.2, 0.2:0.1, and 0.1:0.1 have been considered. It was subjected to electrochemical polymerization at pH 3.0 and temperature 27°C with applied current density of 1 mA/cm^2. The chronopotentiograms recorded are shown in Figure 5. It was observed that 0.1:0.1 ratio recorded the lowest polymerization potential and the synthesized Ppy film was having very good surface morphology and conductivity. Similarly, the applied current density and pH are also important parameters and need to be optimized. The authors have synthesized Ppy films for various current densities (0.5, 1, 2, and 4 mA/cm^2) at different pH (2.0, 3.0, and 4.0). The chronopotentiograms for various current densities and pH are shown in Figures 6, 7, and 8. In fact, the authors have recorded the lowest polymerization potential for 0.5 mA/cm^2 applied current density but could not synthesize the Ppy film with a good surface morphology. However, at current density 1 mA/cm^2 and pH 3.0 a Ppy film could be synthesized with very good surface morphology and relatively high conductivity.

The FTIR spectrum of a synthesized Ppy film with optimized process parameters is shown in Figure 9. It was recorded using Testscan Shimadzu FTIR-8000 series, using KBr pellets in the region between 500 and 4000 cm^{-1}. The broad peak at 3419 cm^{-1} corresponds to N−H stretch. The two peaks at 2956 and 2923 cm^{-1} are due to C−H

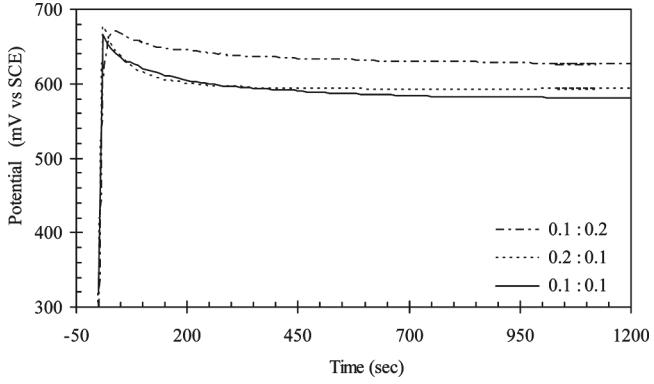

FIGURE 5 Chronopotentiogram recorded during electrochemical polymerization of Ppy at pH 3.0, current density 1 mA/cm^2 and T = 27°C for different molar ratios of pyrrole and sodium nitrate.

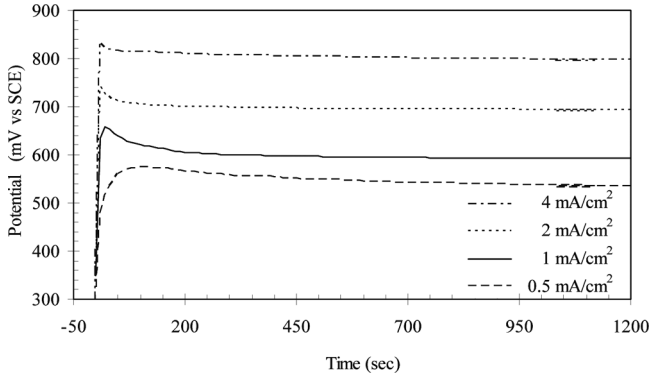

FIGURE 6 Chronopotentiogram recorded during electrochemical polymerization of Ppy at pH 2.0 and T = 27°C for different current densities with 0.1:0.1 molar concentration ratio of pyrrole and sodium nitrate.

vibrations. The strong band at 1541 cm^{-1} is due to C=C stretching. Thus, the FTIR spectral results confirm the formation of polypyrrole. It shows very good agreement with earlier reported work [19–20].

A scanning electron micrograph of Ppy film synthesized with optimized process parameters was recorded. The micrograph was submitted to the editor, but because of poor contrast it is not reproduced here. Nevertheless, from it is clear that the morphology of the synthesized Ppy film is highly porous with micro-globular structure. This is in very good agreement with earlier reported work [21–22].

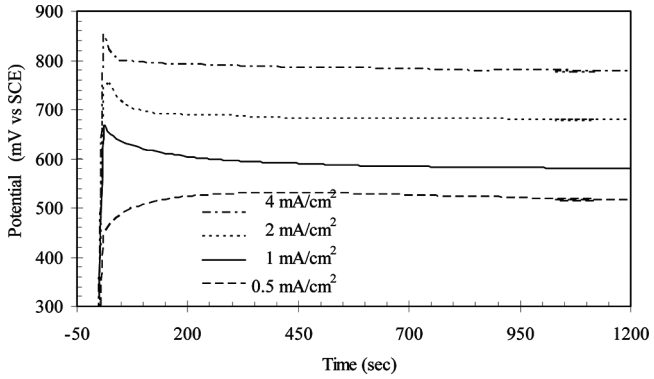

FIGURE 7 Chronopotentiogram recorded during electrochemical polymerization of Ppy at pH 3.0 and T = 27°C for different current densities with 0.1:0.1 molar concentration ratio of pyrrole and sodium nitrate.

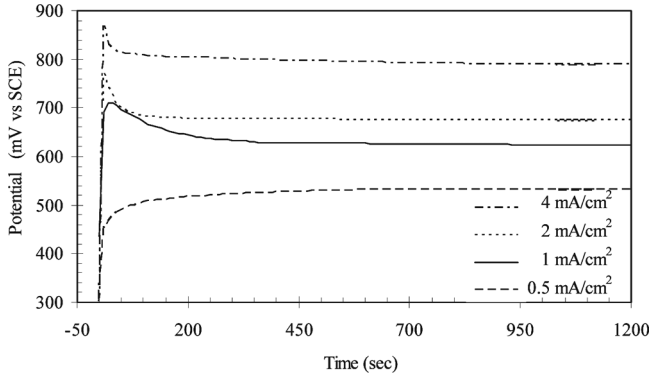

FIGURE 8 Chronopotentiogram recorded during electrochemical polymerization of Ppy at pH 4.0 and T = 27°C for different current densities with 0.1:0.1 molar concentration ratio of pyrrole and sodium nitrate.

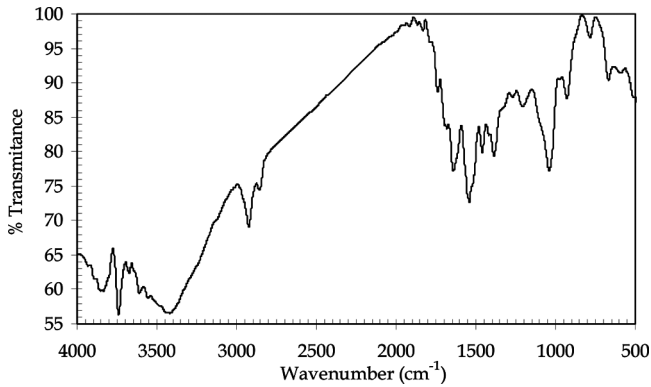

FIGURE 9 The FTIR spectra of Ppy film synthesized with optimized process parameters.

CONCLUSION

The influence of electrochemical process parameters on the surface morphology and the conductivity of Ppy film were studied. The 0.1:0.1 concentration ratio of pyrrole and sodium nitrate at pH 3.0 with applied current density of 1 mA/cm^2 are an excellent combination for the synthesis of Ppy film. The Ppy film synthesized with optimized process parameters has resulted in a uniform, porous, and microglobular surface morphology with enhanced electrical conductivity. These features of Ppy film make it suitable for biosensor applications.

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