

Synthesis and characterization of Ppy-PVS, P(NMP)-PVS and their co-polymer Ppy-P(NMP)-PVS films by galvanostatic method

V.K. Gade¹, D.J. Shirale¹, P.D. Gaikwad¹, K.P. Kakde¹, P.A. Savale¹, H.J. Kharat¹, B.H. Pawar² and M.D. Shirsat^{1*}

¹Optoelectronics and Sensor Research Laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad-431004 Maharashtra, India

²Department of Physics, S. G. B. Amravati University, Amravati-444 601 Maharashtra, India

*E-mail: mds_bamu@yahoo.co.in

Received: 14 December 2006 / Accepted: 13 February 2007 / Published: 1 March 2007

The electrochemically synthesized Polypyrrole-Polyvinyl Sulphonate (Ppy-PVS), Poly(N-methylpyrrole) - Polyvinyl Sulphonate (P(NMP)-PVS) and their co-polymer Polypyrrole-Poly(N-methylpyrrole)-Polyvinyl Sulphonate (Ppy-P(NMP)-PVS) films on indium tin oxide (ITO) coated glass electrode have been investigated by galvanostatic method. This study reveals that as compared to (P(NMP)-PVS) and (Ppy-P(NMP)-PVS), the Ppy-PVS film provide a polymer matrix with very good porosity, mechanical and environmental stability, uniform surface morphology and higher conductivity, which is suitable for the immobilization of biocomponent. The synthesized films were characterized using electrochemical technique, electrical conductivity, Fourier-transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM).

Keywords: Polypyrrole; co-polymer; electrochemical polymerization; galvanostatic

1. INTRODUCTION

Electrically conductive polymers have been considered as interesting materials since its electrical conductivity could be increased by doping it with a suitable electron-withdrawing group or an electron-donating group [1, 2]. In a π -conjugated polymer such as polyacetylene, polyaniline [3], poly(p-phenylene vinylene), or polythiophene, polypyrrole (Ppy) and poly(N-methylpyrrole) (P(NMP)), the interchange of single and double bonds in the polymer backbone leads to various energy states and transfer of electrons through the backbone. Among the conductive polymers, Ppy is one of the most extensively studied because it possesses highly conductive, oxygen resistant, and in noxious

characteristics, which are favorable for various applications [4, 5]. Ppy offers tremendous technological applications such as fabrication of molecular electronic devices [6], an electrodes for solid-state batteries [7], an solid electrolytes for capacitors [8], electromagnetic interference shielding materials [9], ion-sensors [10,11], and static charge dissipating coating. Ppy can be conventionally prepared by a stoichiometric oxidative polymerization [12, 13] of pyrrole using an oxidant or by an electrochemical polymerization [14, 15].

Polypyrrole and its family e.g. Poly (*N*-methylpyrrole) is an important member of intrinsically conducting polymers which can be synthesized by electrochemical or chemical methods. It is reported to be a stable polymer that has excellent retention of its electrical, chemical, thermal, and mechanical properties [16, 17]. The Ppy and P(NMP) has a nodular, cauliflower-like surface morphology, the roughness of which depends on the electrochemical synthesis conditions [18]. Smoother films with improved surface can be synthesized by careful choice of synthesis parameters, such as pH [19], synthesis temperature, time, type of dopant and concentrations [18]. The Ppy can be synthesized with an electrical conductivity ranging from 10^{-4} to 10^2 S/cm.

The remarkable switching capability of these electroactive materials (conducting polymers) between the conducting oxidized (doped) and the insulating-reduced (undoped) state is the basis of many applications. Among others, the poly-conjugated 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 viz polyacetylene, polythiophene, polypyrrole, polyindole and polyaniline have been extensively used for immobilization of enzymes. Among the conducting polymers, polypyrrole has been widely studied because it can be easily polymerized, with ease of membrane formation, high conductivity and chemical stability [20-22]. However, P(NMP) film has been studied by very few researchers [23,24]. Aqueous electropolymerization may be an alternative which can eliminate the use of toxic chemicals. Advantages of aqueous electropolymerization include: (1) the aqueous solutions used are environmentally favorable. The use of aqueous solutions also greatly lowers the costs for materials and waste disposal. (2) This technique combines the formation of the polymer and deposition of the coating in one process. The process is energy-effective and can be easily automated. (3) Mild reaction conditions such as room temperature, low current or potential are used. The production cost is relatively low. (4) The Ppy and P(NMP) can be easily synthesized by electrochemical oxidation of the monomer with formation of doped conducting films. The electrochemically deposited Ppy and P(NMP) films are dependent on many parameters viz. current density, monomer type, monomer concentration, electrolyte type, electrolyte concentration, pH of the reaction medium and the reaction time used during the electrodeposition etc. [25-27].

Doping materials can increase the stability, mechanical strength and conductivity of Ppy and P(NMP) matrix. The materials, which can be doped with Ppy and P(NMP), are Nafion, polyvinyl alcohol, polystyrene sulphonate, poly (methylmethacrylate), dodecylbenzene sulphonate, p-toluene

sulphonate and polyvinyl sulphonate [28, 29]. It has been reported that use of polyelectrolyte in polymerization solution with pyrrole and *N*-methylpyrrole causes to increase growth rate, higher compactness of the synthesized film and improved environmental stability [30, 31]. The stability of polymer matrix depends on anions. The anions play an important role during the electrosynthesis. The anions are divided into three groups, (a) small inorganic anions; such as NO_3^- , (b) medium sized anions (mainly organics); such as dodecylsulphonate, *p*-toulenesulphonate and (c) large polymeric anions; such as polyvinylsulphonate [32].

In general, the mobility of anions in Ppy and P(NMP) films depends on the size of the anions; small anions have good mobility, medium anions have average or bad mobility and large polyanions are not able to leave the Ppy film at all. The ion exchange properties and stability of polypyrrole (Ppy)-polyvinylpyrrolidone (PVP) and polypyrrole (Ppy)-polyvinyl alcohol (PVA) and polypyrrole (Ppy)-polystyrene sulphonate (PSS) composites have been studied by some authors [33, 34]. However, it is still important to find high quality polymers and effective dopants showing their desirable properties for specific application.

We have synthesized and characterized the Ppy-PVS in our earlier reported work [35]. In present investigation, we have synthesized P(NMP)-PVS films as well as the co-polymer Ppy-P(NMP)-PVS films on ITO coated glass electrode by galvanostatic method. The synthesized films were characterized using electrochemical technique, electrical conductivity, FTIR spectra and scanning electron microscopy (SEM).

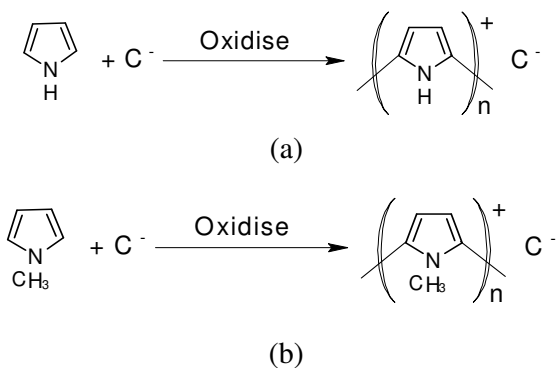
2. EXPERIMENTAL

Ppy films were prepared by galvanostatic electrochemical synthesis, which provides a constant oxidative current at the anode. The electrochemical deposition of Ppy-PVS, P(NMP)-PVS and their co-polymer Ppy-P(NMP)-PVS films were carried out by using a galvanostatic technique at temperature 27 °C in a one-compartment, three-electrode glass cell. The ITO coated glass plate was used as a working electrode, platinum foil as a counter electrode and Ag/AgCl as a reference electrode. The electrolyte solution was prepared in deionized water with 0.1 M pyrrole (98 %) (Spectrochem) and 0.1 M *N*-methylpyrrole (Rankem) which was double distilled and kept refrigerated until use. The dopant 0.025 M PVS (Aldrich) was used. The applied current density 1 mA/cm² and the 3.0 pH were kept constant during synthesis of polymer films. After synthesis the polymer coated electrodes were rinsed thoroughly in deionized water dried in cold air and then used for subsequent characterization.

The synthesized composite films were subjected to various characterization viz. galvanostatic electrochemical technique, electrical conductivity measured by Keithley 6514 electrometer, the FTIR spectrum of synthesized composite films were carried out using Shimadzu FTIR-8400 series, using KBr pellets in the region 350-4000 cm⁻¹, the scanning electron micrographs were recorded, using JEOL JSM-6360A SEM machine.

3. RESULTS AND DISCUSSION

The conducting Ppy and/ P(NMP) film can be electrochemically synthesized according to the following (scheme 1) reaction:



Scheme 1: Polymerization reaction of (a) pyrrole and/ (b) *N*-methylpyrrole in the presence of C^- (where, C^- is counterion, which may be PVS)

The oxidation of pyrrole and/ *N*-methylpyrrole yields a charged polymer film with incorporated anions (**scheme 1**). The pyrrole and/ *N*-methylpyrrole units have positive charges, which are balance by anions that are incorporated into the polymer matrix during polymerization. The Ppy and/P(NMP) is electroactive as it can be switched from the oxidized to reduced state by applying a potential between the working and reference electrode.

The potential time curves of the galvanostatically synthesized Ppy-PVS, P(NMP)-PVS and Ppy-P(NMP)-PVS composite films are shown in **Fig. 1**. In fact, the behaviour of the galvanostatic synthesis overshoot during the first few seconds probably indicates difficult formation of dimmers and oligomers. After this, potential remains constant suggesting that building up of the film proceeds according to the same reaction along the full thickness of the polymer. We have recorded the lowest polymerization potential for Ppy-PVS film with higher conductivity and uniform morphology. Slightly higher polymerization potential recorded for co-polymer Ppy-P(NMP)-PVS film than that of Ppy-PVS film. However, the surface morphology of the synthesized Ppy-P(NMP)-PVS film was non uniform. The highest polymerization potential was recorded for P(NMP)-PVS film which results in poor conductivity as well as non uniformity.

The scanning electron micrographs of synthesized Ppy-PVS, P(NMP)-PVS and Ppy-P(NMP)-PVS composite films are shown in **Fig. 2, 3 and 4** respectively. It can be seen that, the surface morphology of the Ppy-PVS film has good uniformity, porosity. However, it was non uniform for Ppy-P(NMP)-PVS as well as P(NMP)-PVS films. The SEM result shows good resemblance with earlier reported work [36, 37].

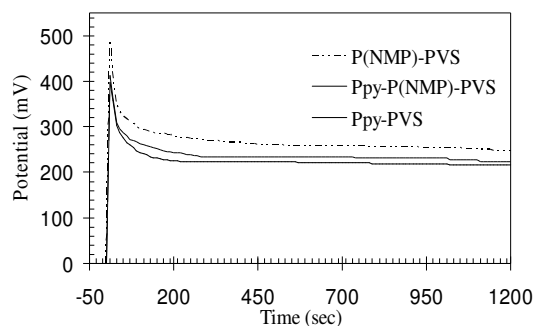


Fig. 1. Potential-time curve of Ppy-PVS, P(NMP)-PVS and their co-polymer Ppy-P(NMP)-PVS films at pH 3.0, 1 mA/cm² current density and T=27°C

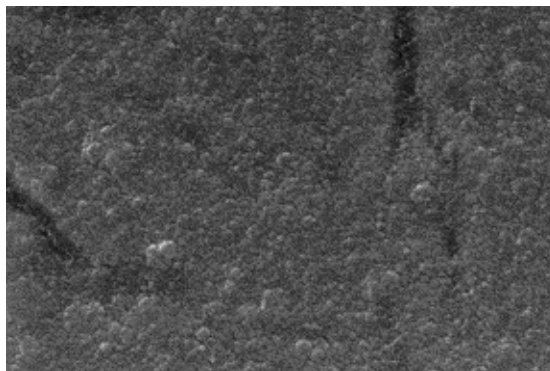


Fig. 2. SEM of Ppy-PVS film at pH 3.0, 1 mA/cm² current density and T=27°C

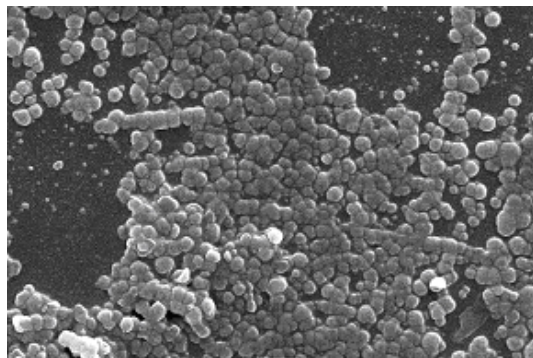


Fig. 3. SEM of P(NMP)-PVS film at pH 3.0, 1 mA/cm² current density and T=27°C

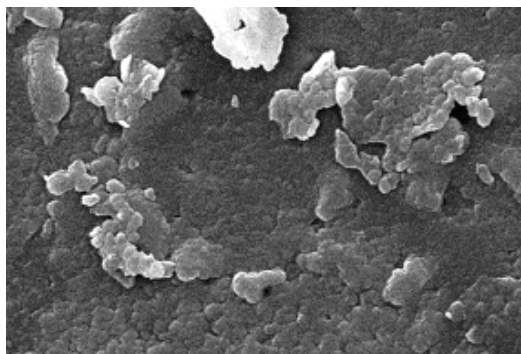


Fig. 4. SEM of co-polymer film Ppy-P(NMP)-PVS at pH 3.0, 1 mA/cm² current density and T=27°C

Table 1. Relation between the electrical conductivity and the plateau potential of Ppy-PVS, P(NMP)-PVS and their co-polymer Ppy-P(NMP)-PVS films

Sr No	Various Polymer Films	Plateau Potential (mV)	Electrical Conductivity (S/cm)
1	Ppy-PVS	217	2.412×10^{-3}
2	Ppy-P(NMP)-PVS	224	1.210×10^{-3}
3	P(NMP)-PVS	248	0.988×10^{-3}

The Ppy and P(NMP) film can have any electrical conductivity spanning a range of about several orders of magnitude, depending on the concentration of the dopant anion added into the

electrolyte prior to the electrochemical synthesis. A common feature of intrinsically conducting polymers is the presence of conjugation that provides a significant degree of delocalization of π -electrons along the polymer chains. The overlapping molecular orbitals allow carrier mobility along the polymer chain. Undoped conjugated polymers do not contain intrinsic charge carriers. They introduced by a process called ‘doping’ which, in polymers, is a redox process involving charge transfer leading to creation of charged species. The prerequisites for electronic conductivity are both the presence of charge carriers and an orbital system to provide mobility to carriers [18]. The sulphonate ions of the PVS provide a charged surface for electrostatic interactions between the enzyme and the surface [38, 39]. The electrical conductivity of synthesized composite films Ppy-PVS, P(NMP)-PVS and Ppy-P(NMP)-PVS is 2.412×10^{-3} S/cm, 1.210×10^{-3} S/cm and 0.988×10^{-3} S/cm respectively as illustrated in **Table 1**. It shows very good resemblance with polymerization potential recorded during polymerization.

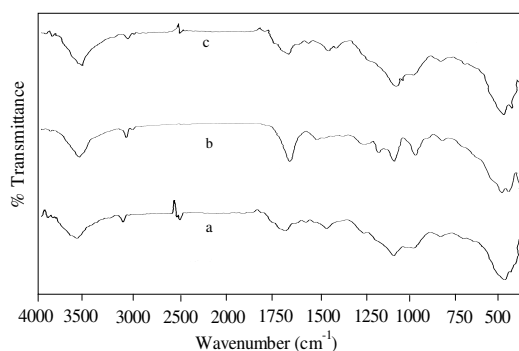


Fig. 5. FTIR spectra of a) Ppy-PVS, and b) P(NMP)-PVS c) Ppy-P(NMP)-PVS at pH 3.0, 1 mA/cm^2 current density and $T=27^\circ\text{C}$

The FTIR spectrum of synthesized composite Ppy-PVS, P(NMP)-PVS and Ppy-P(NMP)-PVS are shown in **Fig. 5**. All three spectrums showed the broad peak at $3400\text{-}3500 \text{ cm}^{-1}$ corresponds to N-H stretching. The incorporation of the counter anion in the polymer is evidenced by the peaks at $2924\text{-}3000$ and 2850 cm^{-1} assigned to aliphatic $-\text{CH}_3$ and $-\text{CH}_2$, related to the sulphonate anion. Further evidence of the presence of this anion in the polymer film is revealed by peaks at 1380 and $1600\text{-}1640 \text{ cm}^{-1}$ which may be assigned to SO_2 stretch in sulphonates. The vibration bands are observed at $1728\text{-}1784 \text{ cm}^{-1}$ ($\text{C}=\text{O}$), $1527\text{-}1548 \text{ cm}^{-1}$ (N-H bending). These bands correspond to the characteristic bands for Ppy and P(NMP); it shows very good agreement with earlier reported work [40, 41]. Thus, the FTIR spectral results confirm the formation of polypyrrole Ppy and P(NMP).

4. CONCLUSIONS

The electrochemical, electrical, optical and morphological properties of composite Ppy-PVS, P(NMP)-PVS and Ppy-P(NMP)-PVS (at 1 mA/cm^2 current density and pH 3.0) have been successfully studied. The characterization study reveals that the composite Ppy-PVS film provide uniform, porous and stable polymer matrix as compared with P(NMP)-PVS and Ppy-P(NMP)-PVS which is suitable for immobilization of biocomponent. The composite Ppy-PVS film shows highest conductivity $2.412 \times$

10^{-3} S/cm with lower polymerization potential. The FTIR spectra of composite Ppy-PVS confirm the presence of organic groups as well as occurrence N-H stretching.

References

1. C.K. Chiang, M.A. Dury, S.C. Gau, A.J. Heeger, E.J. Louis, A.G. MacDiarmid, Y.W. Park, H. Shirakawa, *J. Am. Chem. Soc.* 100 (1978) 1013.
2. J.Y. Kim, D.W. Ihm, Y. Furukawa, M. Tasumi, *Korea Polym. J.* 6 (1998) 302.
3. F. Wang, X. Jing, *Korea Polym. J.* 4 (1996) 89.
4. G. Tourillon, F. Ganiem, *J. Electroanal. Chem.* 135 (1982) 172.
5. Y.H. Lee, W.S. Shim, D.S. Lee, *Polymer Korea* 23 (1999) 587.
6. S. Chao, M.S. Wrighton, *J. Am. Chem. Soc.* 109 (1987) 2197.
7. L.W. Shacklette, R.R. Chance, D.M. Ivory, G.G. Miller, R.H. Baughman, *Synth. Met.* 1 (1979) 101.
8. L.H.M. Krings, E.E. Havinga, J.J.T.M. Donkers, *Synth. Met.* 54 (1993) 453.
9. H. Kuhn, R. Gregory, W. Kimbrell, *Int. SAMPE Electron. Conf.* 3 (1989) 570.
10. M.D. Imisides, R. John, P.J. Reiley, G.G. Wallace, *Electroanalysis* 3 (1991) 879.
11. T. Lindfors, J. Bobacka, A. Lewenstam, A. Ivaska, *Electrochim. Acta* 43 (1998) 3503.
12. I.W. Kim, J.Y. Lee, H.S. Lee, *Synth. Met.* 78 (1996) 177.
13. A.D. Child, H.H. Kuhn, *Synth. Met.* 84 (1997) 141.
14. Y. Shen, M. Wan, *J. Polym. Sci., Polym. Chem. Ed.* 20 (1982) 1089.
15. W.S. Shim, Y.H. Lee, I.Y. Yeo, J.Y. Lee, D.S. Lee, *Synth. Met.* 104 (1999) 119.
16. J. Rodriguez, H.J. Grande, T.F. Otero, *Conductive Polymers: Synthesis and Electrical Properties*, in: H.S. Nalwa (Ed.), *Handbook of Organic Conductive Molecules and Polymers*, Vol. 2., *John Wiley and Sons Ltd, Chichester*, 1997, pp. 413–468.
17. V.T. Truong, *Synth Met* 52 (1992) 33.
18. A. Kaynak, *Mater Res Bull* 32 (1997) 271.
19. J. Unsworth, P.C. Innis, B.A. Lunn, Z. Jin, G.P. Norton, *Synth Met* 53 (1992) 59.
20. V.K. Gade, D.J. Shirale, P.D. Gaikwad, H.J. Kharat, K.P. Kakde, P.A. Savale, M.D. Shirsat, in: M.D. Shirsat (Ed), *Microwaves and Optoelectronics*, Anshan Tunbridge Wells, UK, 2005, p. 459.
21. A. Chaubey, M. Gerard, R. Singhal, V.S. Singh, B.D. Malhotra, *Electrochim. Acta* 46 (2000) 723.
22. U. Johanson, M. Marandi, T. Tamm and J. Tamm, *Electrochim. Acta* 50 (2005) 1523.
23. D.J. Shirale, V.K. Gade, P.D. Gaikwad, H.J. Kharat, K.P. Kakde, P.A. Savale, S.S. Hussaini, N.R. Dhumane, M.D. Shirsat, *Mat. Lett.* 60 (2006) 1407.
24. W. Su, Jude O. Iroh, *Synth Met.* 114 (2000) 225.
25. Y.H. Lee, J.Y. Lee, D.S. Lee, *Synth. Met.*, 114 (2000) 347.
26. P.C. Wang, A.G. MacDiarmid, *Synth. Met.* 119 (2001) 367.
27. P.D. Gaikwad, D.J. Shirale, V.K. Gade, P.A. Savale, K.P. Kakde, H.J. Kharat, M.D. Shirsat, *Bull. Mater. Sci.* 29, 4, (2006) 417
28. F.R. Fan, A.J. Bard, *J. Electrochem. Soc.* 133 (1986) 213.
29. S.E. Lindsey, G.B. Street, *Synth. Met.* 10 (1984) 67.
30. J.R. Reynolds, M. Pyo, Y.J. Qiu, *Synth. Met.* 55 (1993) 1388
31. T.F. Otero, V. Olazabal, *Electrochem. Soc.* 133 (1996) 213.
32. N. Balci, E. Bayramli, L. Toppare, *J. Appl. Polym. Sci.* 64 (1997) 667.
33. Z. Chen, A. Okimoto, T. Kiyonaga, *Anal. Chem.* 71 (1999) 1834.
34. K. Hyodo, M. Omae, *Electrochim. Acta* 35 (1990) 1245.
35. V.K. Gade, D.J. Shirale, P.D. Gaikwad, K.P. Kakde, P.A. Savale, H.J. Kharat, M.D. Shirsat, *Int. J. Polymeric Materials* 56 (2007) 107

36. R. Singh, A.K. Narula, R.P. Tandon, S.U.M. Rao, V.S. Panwar, A. Mansingh, S. Chandra, *Synth. Met.* 79 (1996) 1.
37. J. Reut, N. Reut, A. Opik, *Synth. Met.* 119 (2001) 81.
38. I. Fernandez, M. Trueba, C. A. Nunez, J. Rieumont, *Surface Coatings and Tech.* 191 (2005) 134.
39. K.S. Jang, H. Lee, B. Moon, *Synth. Met.* 143 (2004) 289.
40. M.D. Migahed, T. Fahmy, M. Ishra, A. Barakat, *Polymer Testing* 23 (2004) 361.
41. S. Lamprakopoulos, D. Yfantis, A. Yfantis, D. Schmeisser, J. Anastassopoulou, T. Theophanides, *Synth. Met.* 114 (2004) 229.