

This article was downloaded by:

On: 30 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

Synthesis and Characterization of POA-PVS-DBS, POA-PVS-pTS, POA-pTS-DBS Co-Dopants Composite Films: A Comparative Study

P. A. Savale^a; Kunal Datta^a; Prasanta Ghosh^a; Mahendra D. Shirsat^a

^a Optoelectronics and Sensor Research Laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, India

Online publication date: 04 December 2009

To cite this Article Savale, P. A. , Datta, Kunal , Ghosh, Prasanta and Shirsat, Mahendra D.(2010) 'Synthesis and Characterization of POA-PVS-DBS, POA-PVS-pTS, POA-pTS-DBS Co-Dopants Composite Films: A Comparative Study', *International Journal of Polymeric Materials*, 59: 2, 87 – 97

To link to this Article: DOI: 10.1080/00914030903192393

URL: <http://dx.doi.org/10.1080/00914030903192393>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Synthesis and Characterization of POA-PVS-DBS, POA-PVS-pTS, POA-pTS-DBS Co-Dopants Composite Films: A Comparative Study

P. A. Savale, Kunal Datta, Prasanta Ghosh,
and Mahendra D. Shirsat

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

In the present study, the composite films of poly(*o*-anisidine)–polyvinyl sulphonic acid–dodecyl benzene sulphonic acid (POA-PVS-DBS), poly(*o*-anisidine)–polyvinyl sulphonic acid–toluene sulphonic acid (POA-PVS-pTS), and poly(*o*-anisidine)–toluene sulphonic acid–dodecyl benzene sulphonic acid (POA-pTS-DBS) were synthesized on platinum electrode, using electrochemical polymerization. The POA-PVS-DBS, POA-PVS-pTS, and POA-pTS-DBS composite films were synthesized with 0.2 M *o*-anisidine, 0.4:0.1 M (PVS-DBS), 0.4:0.1 M (PVS-pTS), and 0.4:0.1 M (pTS-DBS) co-dopants, 1.0 pH and 1 mA/Cm² applied current density at 27°C temperature, respectively. These synthesized films were characterized by using an electrochemical technique, conductivity measurement, UV-visible spectroscopy, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The optimal film growth was achieved for synthesis of the POA film in the presence of polyvinyl sulphonic acid–dodecyl benzene sulphonic acid (PVS-DBS). The POA-PVS-DBS composite film exhibits good

Received 3 July 2009; in final form 14 July 2009.

The authors are thankful to the Department of Chemistry and the Department of Physics, University of Pune, India.

Address correspondence to Mahendra D. Shirsat, Optoelectronics and Sensor Research Laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad – 431 004, Maharashtra, India. E-mail: mdshirsat_bamu@yahoo.co.in

electrochemical properties, and high conductivity with uniform and porous surface morphology which can be used for the immobilization of bio-component.

Keywords co-dopants, composite film, electrochemical technique, o-anisidine

INTRODUCTION

One of the outstanding achievements in the field of science and technology in the recent years, after a succession of marvels like lasers and computers, is the conducting polymers. The wide spectrum of conducting polymers used in day-to-day life have desired properties like good flexibility, high strength, special electrical properties, quick and mass production, resistance to chemicals and moisture, and ease of fabrication in a variety of shapes [1–11]. The materials with potential properties have always been the driving power for the development and progress in the field of technology-oriented applications [12–16]. Thin films of conducting polymers of desired physical and chemical properties can be synthesized by using chemical and electrochemical polymerization. Electrochemical synthesis of conducting polymers is highly advantageous among the various reported methods of synthesis of conducting polymers, since it is simple, cost-effective, can be carried out in a single compartment glass cell, reproducible, and the synthesized films have desired thickness and uniformity [17–24].

The conducting properties and surface morphology of the polymer film depend on the method of synthesis and various electrochemical process parameters, such as monomer and dopant concentration, type of co-dopant, synthesis temperature, pH of the solution and applied potential/current during the electrochemical polymerization [25–34]. In recent years, the basic issue related to electrochemical polymerization and characterization of substituted polyaniline to explore the possibilities of utilizing o-anisidine, p-anisidine, m-anisidine, o-toluidine, p-toluidine and m-toluidine as alternatives to polyaniline in the technological applications has been the focal point of research activities [35,36]. Among the polyaniline derivatives, poly(o-anisidine) is well-characterized and probably one of the most suitable polymers, because it is cheap, easily processible and has chemical stability. It has the ability to form freestanding films with high electrical conductivity, 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 bio-components.

Conducting polymers have extensive use in biosensors [37], EMI shielding [38], lightweight batteries [39], electrochromic display devices [40], electronic devices [41], actuators [42] and electrochromic materials [43]. The main feature of a conducting polymer has been the conjugated backbone that can be subjected to oxidation or reduction by electron acceptors or donors, resulting in what is frequently termed as doping. The formation of a complex between

the polymer and the dopant results in considerable increase in electron mobility resulting in enhanced electrical conductivity. 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. The conjugated conducting polymers have been recently proposed for biosensing applications because of a number of favorable characteristics, like direct and easy deposition on sensor electrode by electrochemical oxidation of monomer, control of thickness and redox conductivity.

The stability of polymer film depends on anion size. The anions play an important role during the electrosynthesis. There are small-sized (inorganic) anions, e.g., (Cl^- , NO_3^- , HSO_4^-), medium-sized (mainly organic) anions, e.g., p-toluenesulphonate (pTS), and large-sized polymeric anions e.g., dodecyl benzene sulphonic acid (DBS) and polyvinylsulphonate (PVS) [44]. The POA film can be doped with small-sized anions which can be incorporated into the film on oxidation. But, the polymer film formed with small anions has poor stability. To overcome this problem, the POA film needs to be synthesized with large-sized anions like p-toluenesulphonate (pTS), polyvinylsulphonate (PVS) and dodecyl benzene sulphonic acid (DBS) and their various combinations.

It is reported that the large-sized anions are not able to leave the polymer matrix, thus resulting in a stable polymer film. The polymer synthesized with large-sized anions causes the ions inserted into the films to maintain the charge neutrality during reduction, which is very useful for the immobilization of bio-components. The presence of polyelectrolyte in the polymerization solution results in increased growth rate, higher compactness and improved environmental stability of the synthesized film [45–47]. Few researchers have studied the influence of large-sized ions like PVS, pTS, and DBS on the physical, chemical and electrical properties of various conducting polymers during their electrochemical synthesis [48–52].

The aim of the present research work is to study the influence of various combinations of the co-dopants PVS-DBS, PVS-pTS, and pTS-DBS on the physical, chemical and electrical properties of electrochemical synthesized POA films so that it can be used for biosensing applications. These synthesized POA films were characterized by using an electrochemical technique, conductivity measurement, UV-visible spectroscopy, FTIR and SEM.

EXPERIMENTAL

Preparation of POA-PVS-DBS, POA-PVS-pTS, and POA-pTS-DBS Composite Films

The o-anisidine monomer was distilled twice before use. The dopants polyvinyl sulfonic acid (PVS) (Aldrich) (25 wt% solution in water), p-toluene sulfonic acid (pTS) and dodecyl benzene sulfonic acid (DBS) (Loba Chemie)

were used. Aqueous solutions of *o*-anisidine (99%) and dopants were prepared in distilled water. The reference electrode was kept in close proximity to the working electrode to minimize the electrolytic ohmic drop. The pH was adjusted by adding nitric acid (HNO₃) or sodium hydroxide (NaOH).

The electropolymerization of *o*-anisidine was carried out by galvanostatic technique in one compartment electrochemical cell at a temperature of 27°C. A platinum rectangular sheet (20 mm × 10 mm × 0.25 mm) was used as a counter-electrode and another rectangular platinum sheet (20 mm × 5 mm × 0.25 mm) was used as a working electrode. The reference electrode was Ag/AgCl. All three electrodes were placed vertically in the cell. An 80 ml solution was used for each reaction. The pH of the electrolyte was measured by a calibrated Elico LI120 pH meter.

We have used 0.2 M *o*-anisidine, 0.4:0.1 M (PVS-DBS), 0.4:0.1 M (PVS-pTS), and 0.4:0.1 M (pTS-DBS) co-dopants, 1.0 pH and 1 mA/Cm² applied current density at 27°C temperatures during the synthesis of POA films. The deposited POA films were tested for conductivity, uniformity and porous surface morphology. The electrochemical characterization was carried out by galvanostatic technique, which maintains a constant current throughout the reaction. The optical absorption studies of these films were carried out in the wavelength range 300–900 nm using the UV-visible spectrophotometer Shimadzu 1601. The FTIR spectra were recorded using the Shimadzu FTIR-8400 series, in the region 400–4000 cm⁻¹. The scanning electron micrographs were recorded using JEOL JSM-6360A analytical system. The conductivity was measured by using the four-probe technique (Model DRF-02 Owen 1038-Optochem International, New Delhi).

RESULTS AND DISCUSSION

Galvanostatic Studies of POA-PVS-DBS, POA-PVS-pTS, and POA-pTS-DBS Composite Films

The potentiograms recorded during the synthesis of POA films with co-dopants PVS-DBS, PVS-pTS and pTS-DBS are shown in Figure 1. In fact, the behavior of the galvanostatic synthesis overshoot during the first few seconds probably indicates the formation of dimers and oligomers. After this, the potential remains constant, suggesting that building up of the film proceeds towards the full thickness of the polymer. In order to have high conductivity, the polymerization potential should be minimum [30]. The lowest polymerization potential was recorded for PVS-DBS as compared to PVS-pTS and pTS-DBS co-dopants. This indicates that the synthesized POA film with PVS-DBS co-dopant will have higher conductivity than the other two co-dopants.

It follows from the comparison of conductivities (pTS-DBS > PVS-pTS > PVS-DBS) in each case that the same may be dependant upon the size of

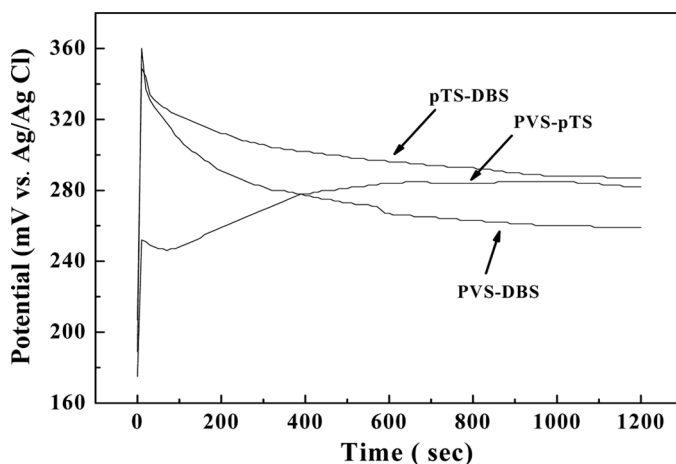


Figure 1: Potential-time curve of POA films with co-dopants PVS-DBS, PVS-pTS and pTS-DBS for 1.0 pH, 1 mA/Cm² current density and temperature 27°C.

the anion. The electrical conductivity of synthesized composite films is illustrated in Table 1. It shows very good correlation with polymerization potential recorded during the polymerization. This reveals that the synthesized POA film with PVS-DBS co-dopant will have higher conductivity and provides more stable polymer film, which is more advantageous for immobilization of bio-components.

UV-Visible Studies of POA-PVS-DBS, POA-PVS-pTS, and POA-pTS-DBS Composite Films

The UV-visible spectra of synthesized POA films with PVS-DBS, PVS-pTS and pTS-DBS co-dopants are shown in Figure 2. Green-colored films of PVS-DBS, PVS-pTS and pTS-DBS show a peak appearing at 300 nm which is assigned to a $\Pi \rightarrow \Pi^*$ electronic transition between the valence and conduction bands of the polymer. The film of PVS-DBS shows a strong peak appearing at 600 nm, attributed to an intramolecular charge transfer excitation associated with quinidine ring, whereas a tail at 800 nm indicates the formation of emeraldine salt (ES) with higher conductivity. It shows a good

Table 1: Relation between the conductivity and the plateau potential of various co-dopants.

Sr. No.	POA: Co-dopants	Plateau potential (mV)	Conductivity (S/cm)
1.	POA -pTS-DBS film	287	2.42×10^{-2}
2.	POA -PVS-pTS film	282	2.72×10^{-2}
3.	POA -PVS-DBS film	259	3.21×10^{-2}

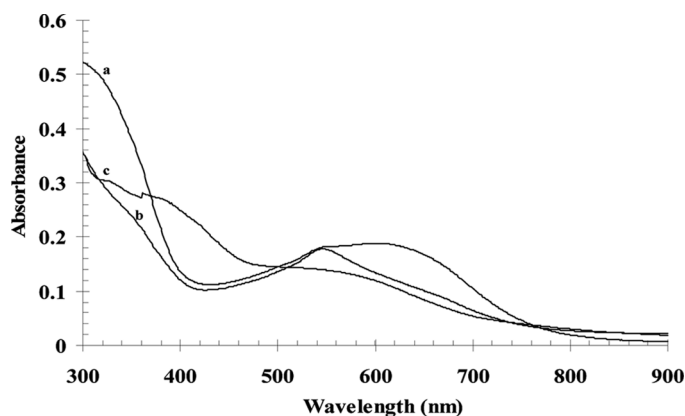


Figure 2: UV-visible spectra of POA films with co-dopants (a) PVS-DBS, (b) PVS-pTS and (c) pTS-DBS.

similarity with earlier reported work [32,52]. The films of PVS-pTS and pTS-DBS show strong peaks appearing at 546 nm and 560 nm respectively, indicating the formation of emeraldine base (EB), whereas the tail at 800 nm indicates the formation of a mixed semiconducting phase.

FTIR Studies of POA-PVS-DBS, POA-PVS-pTS, and POA-pTS-DBS Composite Films

The FTIR spectra of POA films with co-dopants (a) PVS-DBS, (b) PVS-pTS and (c) pTS-DBS are shown in Figure 3. The FTIR assignments are listed in

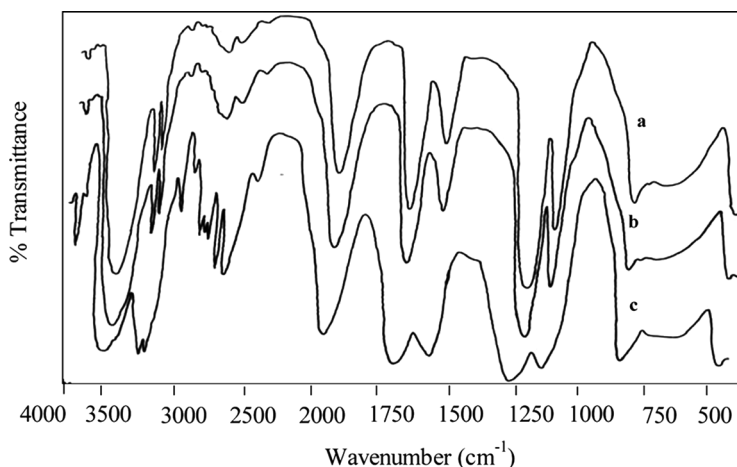


Figure 3: FTIR spectra of POA films with co-dopants (a) PVS-DBS, (b) PVS-pTS and (c) pTS-DBS.

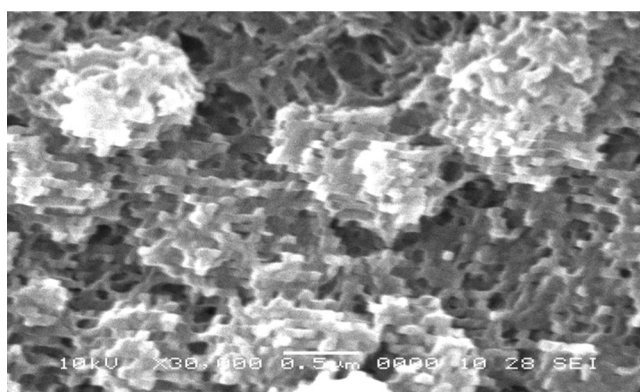
Table 2: Comparison of FTIR bands of POA films with co-dopants PVS-DBS, PVS-pTS and pTS-DBS.

Functional group	PVS-DBS	Observed peaks (cm ⁻¹) in PVS-pTS	pTS-DBS
N-H	3435.0	3433.1	3446.6
C=N group	1656.7	1656.7	1658.7
C-O group	1423.4	1423.4	1425.3
O-C=O	952.8	952.8	950.8
C-H	1315.4	1315.4	1311.5

Table 2. The characteristic band at 3435 cm⁻¹ arises mainly from N-H stretching, the band at 1656.7 cm⁻¹ arises from C=N group while the band at 952 cm⁻¹ arises from O-C=O. The characteristic band at 1423.4 cm⁻¹ arises mainly from C-O group whereas the band at 1315.4 cm⁻¹ arises from C-H stretching. Thus, FTIR spectral results confirm the structure of POA film. They show very good resemblance to earlier reported work [52].

SEM Studies of POA-PVS-DBS, POA-PVS-pTS, and POA-pTS-DBS Composite Films

The surface morphology of the POA films synthesized with various dopants at pH 1 and current density 1 mA/Cm² was studied using scanning electron microscope (SEM). The SEM pictures are shown in Figures 4–6 for co-dopants PVS-DBS, PVS-pTS, and pTS-DBS, respectively. From the SEM it is observed that the sponges with whitish and blackish colors clearly indicate the effect and presence of co-dopants PVS-DBS. It is observed that POA doped with co-dopants PVS-DBS shows a sponge-like structure with excellent porosity, which is highly favorable for biosensor applications. A globular

**Figure 4:** SEM picture of synthesized POA film with PVS-DBS co-dopant.

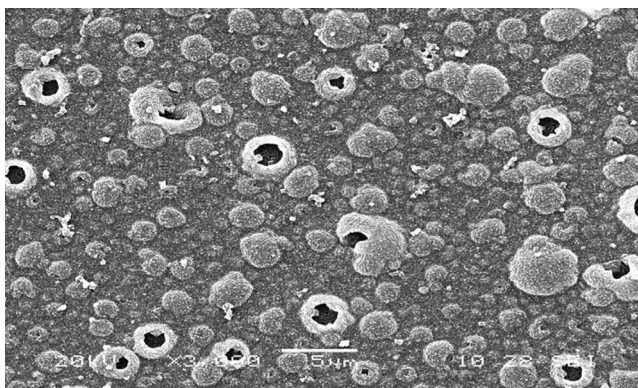


Figure 5: SEM picture of synthesized POA film with PVS-pTS co-dopant.

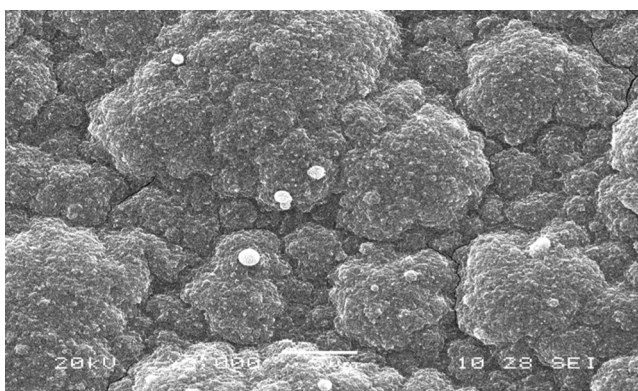


Figure 6: SEM picture of synthesized POA film with pTS-DBS co-dopant.

structure consisting of small and large spread granules with some black holes of varying diameters, is observed on the surface of film. This may be due to the effect and presence of co-dopants PVS-pTS, whereas we observed small white granules on the globular structure showing less porosity for the co-dopants pTS-DBS film.

CONCLUSION

The POA films with co-dopants PVS-DBS, PVS-pTS and pTS-DBS have been successfully synthesized. The conductivity of the POA film synthesized with PVS-DBS was found to be 3.21×10^{-2} S/cm. The UV-visible spectra show the systematic changes with the conductivity. The FTIR spectra confirm the formation of POA in the presence of PVS-DBS. The POA-PVS-DBS composite films

show good electrochemical properties, conductivity as well as polymer film with uniform and porous surface morphology, which is more advantageous for immobilization of bio-components.

REFERENCES

- [1] Gerard, M., Chaubey, A., and Malhotra, B. D. *Biosens. Bioelectron.* **17**, 345 (2002).
- [2] Shirale, D. J., Gade, V. K., Gaikwad, P. D., Kharat, H. J., Kakde, K. P., Savale, P. A., Hussaini, S. S., Dhumane, N. R., and Shirsat, M. D. *Trans. SAEEST* **40**, 128 (2005).
- [3] Zang, S., Wright, G., and Yang, Y. *Biosens. Bioelectron.* **15**, 273 (2000).
- [4] Vidal, J. C., Garcia, E., and Castillo, J. R. *Anal. Sci.* **18**, 537 (2002).
- [5] Zeravik, J., Ruzgas, T., and Franek, M. *Biosens. Bioelectron.* **18**, 1321 (2003).
- [6] Savale, P. A., Shirale, D. J., Gaikwad, P. D., Kharat, H. J., Kakde, K. P., Gade, V. K., and Shirsat, M. D. (2005). In *Microwaves and Optoelectronics*. M. D. Shirsat, Eds., Anshan, Tunbridge Wells, UK, pp. 409.
- [7] Junior, L. R., Neto, G. O., Fernandes, J. R., and Kubota, L. T. *Talanta.* **51**, 547 (2000).
- [8] Gade, V. K., Shirale, D. J., Gaikwad, P. D., Savale, P. A., Kakde, K. P., Kharat, H. J., and Shirsat, M. D. *React. Funct. Polym.* **66**, 1420 (2006).
- [9] Palmisano, F., Rizzi, R., Centonze, D., and Zambonin, P. G., *Biosens. Bioelectron.* **15**, 531 (2000).
- [10] Shirale, D. J., Gade, V. K., Gaikwad, P. D., Savale, P. A., Kakde, K. P., Kharat, H. J., and Shirsat, M. D. *Int. J. Polym. Anal. Charact.* **11**, 369 (2006).
- [11] Gazman-Vazquez de Prada, Pena, N., Mena, M. L., Reviejo, A. J., and Pingarron, J. M. *Biosens. Bioelectron.* **18**, 1279 (2003).
- [12] Cooper, J. C., and Halt, E. A. H. *Electroanalysis.* **5**, 385 (1993).
- [13] Zhou, T. A., Nie, L. H., and Yao, S. Z. *J. Electroanal. Chem.* **1**, 293 (1993).
- [14] Kitani, A., Kaya, M., and Sasaki, K. *J. Electrochem. Soc.* **133**, 1609 (1986).
- [15] Contractor, A. Q., Suresh Kumar, T. N., Narayanan, R., Sukeerathi, S., Lal, R., and Srinivasan, R. *Electrochim. Acta.* **39**, 1321 (1994).
- [16] MacDiarmid, A. G. *Synth. Met.* **84**, 27 (1997).
- [17] Schultze, J. W., and Karabulut, H. *Electrochimica. Acta.* **50**, 1739 (2005).
- [18] Garnier, F., Tourillon, G., Gazard, M., and Dubois, J. C. *J. Electroanal. Chem.* **148**, 299 (1983).
- [19] Savale, P. A., Shirale, D. J., Gaikwad, P. D., Gade, V. K., Kharat, H. J., Kakde, K. P., and Shirsat, M. D. (2004). *Proc. of National Workshop on Thin Film Preparation and Characterization Techniques for Energy Conversion TFPCT*, pp. 7.
- [20] Desben-Monvernay, A., Lacaze, P. C., Dubois, J. E., and Desben, P. L. *J. Electroanal. Chem.* **152**, 87 (1983).
- [21] Harsanyi, G. *Sens. Rev.* **20**, 98 (2000).
- [22] Pal, P. S., and Sarkar, P. *Indian Chem. Soc.* **79**, 211 (2002).

- [23] Skotheim, T. A. (Ed). (1986). In *Handbook of Conducting Polymers*. Vol. II, Marcel Dekker Inc., New York.
- [24] Salaneck, W. R., Clark, D. T., and Samuelsen, E. J. (Eds.) (1991). In *Science and Application of Conducting Polymers*. Adam Hilger, Bristol.
- [25] Lei, J., Cai, Z., and Martin, R. C. *Synth. Met.* **46**, 53 (1992).
- [26] Patil, S., Mahajan, J. R., More, M. A., Patil, P. P., Gosavi, S. W., and Gangal, S. A. *Polym. Int.* **46**, 99 (1998).
- [27] Crupila, E. L., and Kankhare, J. *Synth. Met.* **1402**, 55 (1993).
- [28] Stankovic, R., Palvic, O., Vojnovic, M., and Jovanovic, S. *Eur. Polym. J.* **30** (3), 385 (1994).
- [29] Patil, S., Mahajan, J. R., More, M. A., and Patil, P. P. *Mater. Lett.* **35**, 108 (1998).
- [30] Shirale, D. J., Gade, V. K., Gaikwad, P. D., Kharat, H. J., Kakde, K. P., Savale, P. A., Hussaini, S. S., Dhumane, N. R., and Shirsat, M. D. *Mater. Lett.* **60**, 1407 (2006).
- [31] Borole, D. D., Kapadi, U. R., Kumbhar, P. P., and Hundiwal, D. G. *Polym. Plast. Technol. Eng.* **42**, 415 (2003).
- [32] Pawar, P., Wankhede, M. G., Patil, P. P., and Sainkar, S. R. *Mater. Sci. Eng. A* **347**, 365 (2003).
- [33] Koinkar, P. M., Wankhede, M. G., More, M. A., Patil, P. P., and Gangal, S. A. *Synth. Met.* **130**, 193 (2002).
- [34] Gaikwad, P. D., Shirale, D. J., Gade, V. K., Savale, P. A., Kharat, H. J., Kakde, K. P., Hussaini, S. S., Dhumane, N. R., and Shirsat, M. D. *Bull. Mater. Sci.* **29**, 169 (2006).
- [35] Mattoso, L. H. C., and Bulhoes, L. O. S. *Synth. Met.* **52**, 171 (1993).
- [36] Mattoso, L. H. C., Manoher, S. K., MacDiarmid, A. G., and Epstein, A. J. *J. Polymer Sci. A: Polymer Chem.* **33**, 1227 (1995).
- [37] Roth, S., and Graupher, W. *Synth. Met.* **57**, 3623 (1993).
- [38] Bartlett, P. N., and Birkin, P. R. *Anal. Chem.* **65**, 1118 (1993).
- [39] Depaoli, M. A. G., Giroto, E. M., Gazotti, W. A., and Macdiarmid, A. G. *Electrochim. Acta.* **44**, 2983 (1999).
- [40] Delccuw, O. M. M., Simenan, M., Brown, A. R., and Einerchand, R. E. F. *Synth. Met.* **87**, 53 (1997).
- [41] Kaneto, K., Kaneko, M., Min, Y., and Macdiarmid, A. G. *Synth. Met.* **71**, 2211 (1998).
- [42] Chen, S. A., and Cho, C. J. *Synth. Met.* **79**, 93 (1996).
- [43] Skotheim, T. A., Elsenbsumsr, R. L., and Reynolds, J. R. (1998). *Handbook of Conducting Polymers*. Second Edition, Marcel Dekker, New York, pp. 59.
- [44] Chen, Z., Okimoto, A., and Kiyonaga, T. *Anal. Chem.* **71**, 1834 (1999).
- [45] Otero, T. F., and Olazabal, V. *Electrochim. Acta.* **41**, 213 (1996).
- [46] Yue, J. W., Jhao, H., Cromack, K. R., Epstein, A. J., and MacDiarmid, A. G. *J. Am. Chem. Soc.* **113**, 2265 (1991).
- [47] Hallik, A., Alumaa, A., Sammelselg, V., and Tamm, J. *J. Solid State Electrochem.* **5**, 65 (2001).

- [48] Gaikwad, P. D., Shirale, D. J., Gade, V. K., Savale, P. A., Kakde, K. P., Kharat, H. J., and Shirsat, M. D. *Bull. Mater. Sci.* **29**, 1 (2006).
- [49] Shirale, D. J., Gade, V. K., Gaikwad, P. D., Savale, P. A., and Shirsat, M. D. *Mater. Lett.* **61**, 1372 (2007).
- [50] Gade, V. K., Shirale, D. J., Gaikwad, P. D., Kakde, K. P., Savale, P. A., Kharat, H. J., and Shirsat, M. D. *Int. J. Polym. Mater.* **56**, 1 (2007).
- [51] Shirale, D. J., Gade, V. K., Gaikwad, P. D., Savale, P. A., Kakde, K. P., Kharat, H. J., and Shirsat, M. D. *Int. J. Electrochem. Sci.* **1**, 62 (2006).
- [52] Savale, P. A., and Shirsat, M. D. *Int. J. Polym. Mater.* **57**, 506 (2008).