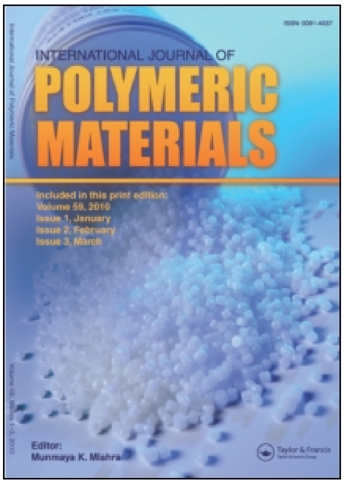

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# Electrochemical Synthesis and Characterization of Poly(o-anisidine) Film with Various Dopants: A Comparative Study

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# Electrochemical Synthesis and Characterization of Poly(o-anisidine) Film with Various Dopants: A Comparative Study

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*In the present work, the doped (composite) films of póly(o-anisidine)–polyvinylsulphonic acid (POA-PVS), poly(o-anisidine)–toluenesulphonic acid (POA-pTS), and poly(o-anisidine)–dodecylbenzenesulphonic acid (POA-DBS) were synthesized on a platinum electrode, using electrochemical polymerization. These synthesized films were characterized by electrochemical techniques, 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 dodecylbenzenesulphonic acid (DBS). The POA-DBS composite film exhibits good electrochemical properties, conductivity with a uniformly porous surface morphology which can be used for the immobilization of biocomponent.*

**Keywords:** composite film, dopants, galvanostatic, o-anisidine

## INTRODUCTION

Conducting polymer technology has made rapid progress during the past 20 years. The main objective has been to produce simple, easy to handle, useful, faster, more sensitive and smaller sensor devices for daily routine purposes [1–11]. The main feature of a conducting polymer has been a conjugated backbone that can be subjected to

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oxidation or reduction by electron acceptors or donors, resulting in what are frequently termed dopant materials. The formation of a complex between the polymer and the dopant results in a 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. In recent years, issues related to the electrochemical polymerization and characterization of substituted polyanilines as alternatives of polyaniline has been the focus of research activity [12,13].

Among the polyaniline derivatives, o-anisidine has been extensively used because of its easy polymerization, high electrical conductivity, chemical stability and ability to form freestanding films. It is cheap and easily processible, well-characterized, and is probably one of the most suitable polymers, 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. However, the structural and mechanical behavior of poly(o-anisidine) as a biosensor is yet to be explored. The o-anisidine can easily be synthesized by electrochemical oxidation of the monomer with the formation of doped conducting films. The electrochemically deposited POA films are dependent on many parameters: type of dopant, nature of solvent, temperature, pH of the solution and applied potential/current during the electropolymerization [14–17].

The stability of the polymer matrix depends on the anion size. The anions play an important role during the electrosynthesis. They are divided into three groups, small (inorganic) anions, e.g., ($Cl^-$, $NO_3^-$, $HSO_4^-$), medium (mainly organic) anions, e.g., p-toluenesulphonate (pTS), and large polymeric anions, e.g., dodecylbenzenesulphonic acid (DBS) and polyvinylsulphonate (PVS) [18].

The POA film can be doped with small anions ($Cl^-$, $NO_3^-$, $HSO_4^-$), which can be incorporated into the film upon oxidation. However, the polymer matrix formed with small anions has poor stability. To overcome this problem, the POA film needs to be synthesized with a large anion like dodecylbenzenesulphonic acid (DBS). Since the large anions are not able to leave the polymer matrix it can result in a stable polymer matrix. The polymer synthesized with DBS causes the ions inserted into the films to maintain the charge neutrality during reduction, which is very useful for the immobilization of the biocomponent. The presence of polyelectrolyte in the polymerization solution results in increased growth rate, higher compactness and improved environmental stability of the synthesized film [19–21].

Conducting polymers have been extensively used in biosensors [22], EMI shielding [23], lightweight batteries [24], electrochromic display devices [25], electronic devices [26], actuators [27] and electrochromic materials [28].

The aim of the present investigation is to improve the stability of synthesized POA film by using large and medium-sized anions such as PVS, pTS, DBS, and to synthesize the porous POA matrix so that it can be used for biosensing applications. The synthesized POA films were characterized by using electrochemical technique, conductivity measurement, UV-visible, FTIR and SEM.

## EXPERIMENTAL

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

The o-anisidine monomer was distilled twice before use. The dopants polyvinylsulfonic acid (PVS) (Aldrich) (25 wt% solution in water), p-toluenesulfonic acid (pTS) and dodecylbenzenesulfonic acid (DBS) (Loba Chemie) were used. All of the above dopants were obtained from Rankhem Ranbaxy New Delhi (India). An aqueous solution of o-anisidine (99%) and dopants was 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 ($HNO_3$) or sodium hydroxide (NaOH).

The electropolymerization of o-anisidine was carried out by galvanostatic technique, in one compartment electrochemical cell at temperature 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 fixed the monomer concentration at 0.2 M, dopant concentration at 0.5 M, pH of the solution at 1, and current density of 1 $mA/cm^2$ during the synthesis of POA films. The deposited POA film was 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 a Shimadzu 1601 UV-visible spectrophotometer. The FTIR spectra were recorded using a Shimadzu FTIR-8400 series, in the region 400–4000 cm$^{-1}$. The scanning electron micrographs were recorded using a JEOL JSM-6360A analytical system. The conductivity was measured by using a four-probe technique (Model DRF-02 Owen 1038-Optochem International, New Delhi).

## RESULTS AND DISCUSSION

### Galvanostatic Studies of POA-PVS, POA-pTS, and POA-DBS Doped Films

The potentiograms recorded during the synthesis of POA films with the dopants PVS, pTS and 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. The POA film was galvanostatically synthesized with 0.2 M monomer, 0.5 M dopants, pH-1 and current density of 1 mA/cm$^2$ at temperature 27°C. In order to have high conductivity, the polymerization potential should be minimum [29]. The lowest polymerization potential was recorded for DBS as compared with PVS and pTS. This indicates that the synthesized POA film with DBS dopant will have higher conductivity than the other two dopants.

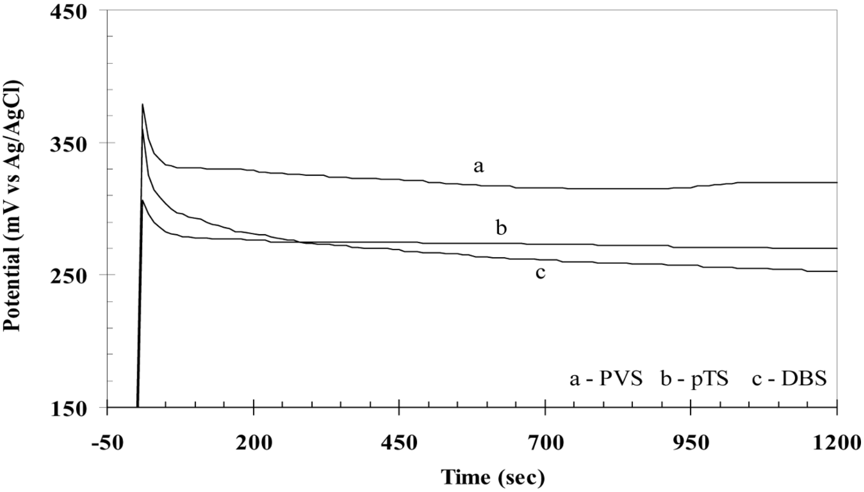

**FIGURE 1** Potential-time curves of POA films with dopants PVS, pTS and DBS for pH-1.0, 1 mA/cm$^2$ current density and temperature 27°C.

**TABLE 1** Relation between the Conductivity and the Plateau Potential in the Presence of Various Dopants

| Sr. No. | POA: Dopants | Plateau potential (mV) | Conductivity (S/cm) |
|---|---|---|---|
| 1. | POA-PVS film | 320 | $1.04 \times 10^{-2}$ |
| 2. | POA-pTS film | 270 | $4.44 \times 10^{-2}$ |
| 3. | POA-DBS film | 253 | $7.61 \times 10^{-2}$ |

The conductivity follows the order DBS > pTS > PVS, which may depend upon the size of the anion. The electrical conductivity of the composite films is illustrated in Table 1. It shows a very good resemblance to the polymerization potential recorded during the polymerization. This reveals that the synthesized POA film with DBS has higher conductivity and provides a more stable polymer matrix which is advantageous for immobilization of biocomponents.

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

The UV-visible spectra of synthesized POA film with PVS, pTS and DBS are shown in Figure 2. A green colored film shows 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, plus a

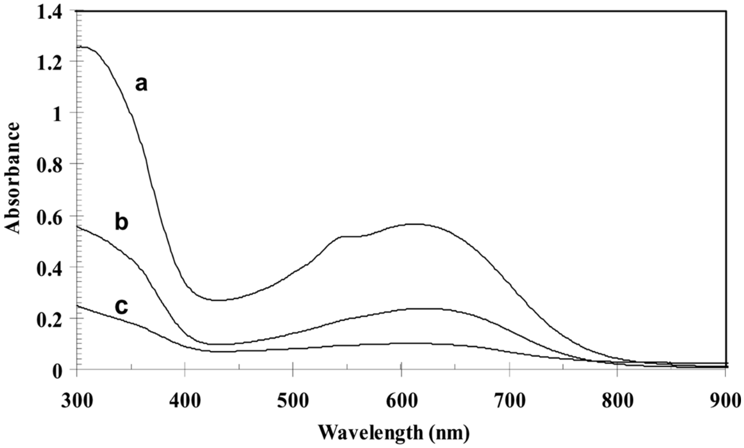

**FIGURE 2** UV-visible spectra of POA film with dopants a, DBS, b, pTS and c, PVS.

strong peak appearing at 600 nm, attributed to an intermolecular charge transfer excitation associated with a quinidine ring, whereas a tail at 800 nm indicates the formation of emeraldine salt (ES) with higher conductivity. It shows a very strong resemblance to earlier reported work [30,31].

## FTIR Studies of POA-PVS, POA-pTS, and POA-DBS Doped Films

The FTIR assignments of POA film with PVS, pTS and DBS are listed in Table 2. The characteristic band at 3435.0 cm$^{-1}$ arises mainly from N-H stretching. The band at 1656.7 cm$^{-1}$ arises from C=N group while the band at 952.8 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. It shows a very good resemblance with earlier reported work [30].

## SEM Studies of POA-PVS, POA-pTS, and POA-DBS Doped Films

The surface morphology of the POA film synthesized with various dopants at pH-1 and current density of 1 mA/cm$^2$ was studied using scanning electron microscope (SEM). The SEM pictures are shown in Figures 3–5 for DBS, pTS, and PVS, respectively. It is observed that POA doped with DBS shows a sponge-like structure with excellent porosity, suitable for biosensor application. A globular structure consisting of small granules is observed in the POA doped with pTS. We observed large granules with less porosity for the POA-PVS film.

**TABLE 2** Comparison of FTIR Bands of POA Films with the Dopants PVS, pTS, and DBS

| | Observed peaks (cm$^{-1}$) in | | |
|---|---|---|---|
| Functional group | PVS | pTS | DBS |
| N−H | 3436.9 | 3431.1 | 3435.0 |
| C=N group | 1656.7 | 1656.7 | 1656.7 |
| C−O group | 1425.3 | 1423.4 | 1423.4 |
| O−C=O | 952.8 | 952.8 | 952.8 |
| C−H | 1313.4 | 1315.4 | 1315.4 |

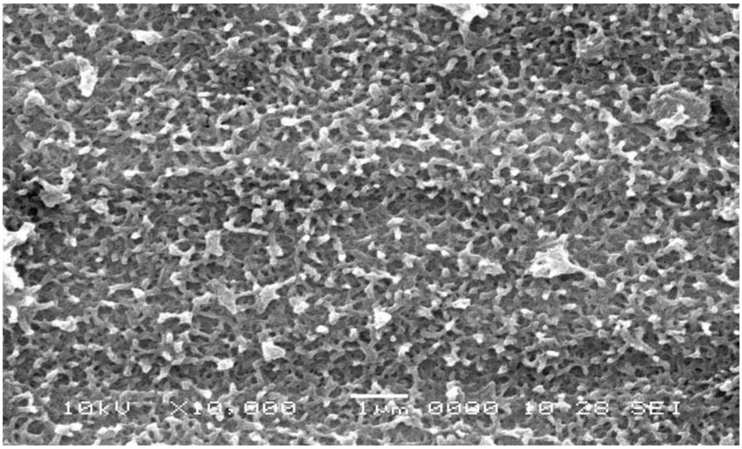

**FIGURE 3** SEM picture of synthesized POA with DBS dopant.

## CONCLUSION

POA films with the dopants PVS, pTS and DBS have been successfully synthesized. The conductivity of the POA film synthesized with DBS was found to be $7.61 \times 10^{-2}$ S/cm. The UV-visible spectra show systematic changes with the conductivity. The FTIR spectra confirm the formation of POA in the presence of all three dopants. The

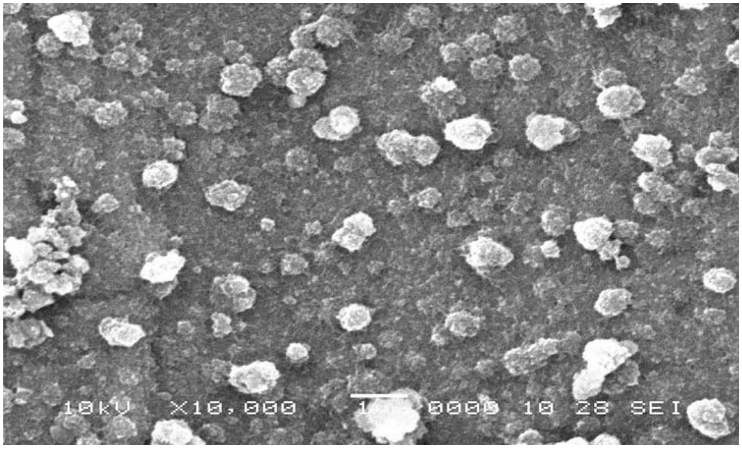

**FIGURE 4** SEM picture of synthesized POA with pTS dopant.

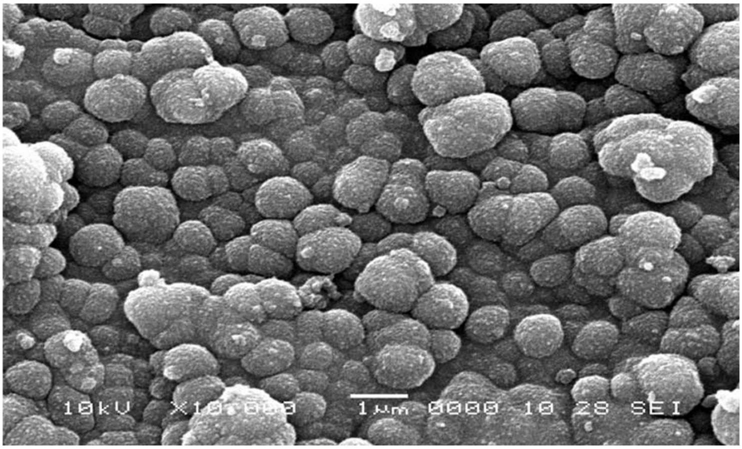

**FIGURE 5** SEM picture of synthesized POA with PVS dopant.

POA-DBS composite films show good electrochemical properties and conductivity, as well as polymer matrix with uniform and porous surface morphology which can be used for the immobilization of biocomponents.

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