

Preparation, Optimization, and Voltammetric Characteristics of Poly(*o*-phenylenediamine) Film as a Dopamine-Selective Polymeric Membrane

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ABSTRACT: Poly(*o*-phenylenediamine) films were electrochemically prepared on gold electrodes from the corresponding monomer in an aqueous solution at a constant potential. The polymeric films prepared in this one-step procedure were found to be thin and insoluble in the aqueous solution. Cyclic and differential pulse voltammetric techniques were used to examine the permeation properties of ascorbic acid and dopamine at the resultant polymeric film electrode. Then, the effects of the chemical and electrochemical variables (e.g., film thickness, polymerization potential, concentrations of monomer and electrolyte) on the permselectivity characteristics of the polymeric film were systematically investigated and the optimal values for each parameter were determined. Furthermore, it was found that the optimized polymer electrode was found to be stable for the successive runs. As a result, it is claimed that poly(*o*-phenylenediamine) film can be used as a dopamine-selective polymeric membrane. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 327–332, 2001

Key words: poly(*o*-phenylenediamine) film; selective polymeric membrane; dopamine sensor

INTRODUCTION

Dopamine is one of the electroactive species in central nervous systems and its function is to regulate neural interactions by reducing the permeability of gap junctions between adjacent neurons of the same type. A measure of this regulation is the concentration of dopamine released to the neurons. On the other hand, dopamine in biological liquids coexists with electroactive ascorbic acid, whose redox potential is often similar to the potential of dopamine. Therefore,

ascorbic acid reduces the sensitivity and selectivity of dopamine.¹ This problem can be circumvented by using permselective polymeric membranes.

Electrochemically generated conducting or nonconducting polymeric films have recently attracted increasing interest because of their potential applications such as in gas sensors^{2–4} and biosensors^{5–11} and as permselective membranes.^{12–14} In previous works, we demonstrated that electropolymerized films such as poly(3-methylthiophene), polyaniline, polypyrrole, poly(*o*-toluidine), and poly(1,3-phenylenediamine) could be used to distinguish between dopamine and ascorbic acid.^{15–19} On the other hand, it was reported that poly(*o*-phenylenediamine) is a ladder polymer with phenazine rings.²⁰ Poly(*o*-phenylenediamine) films can be used to immobilize en-

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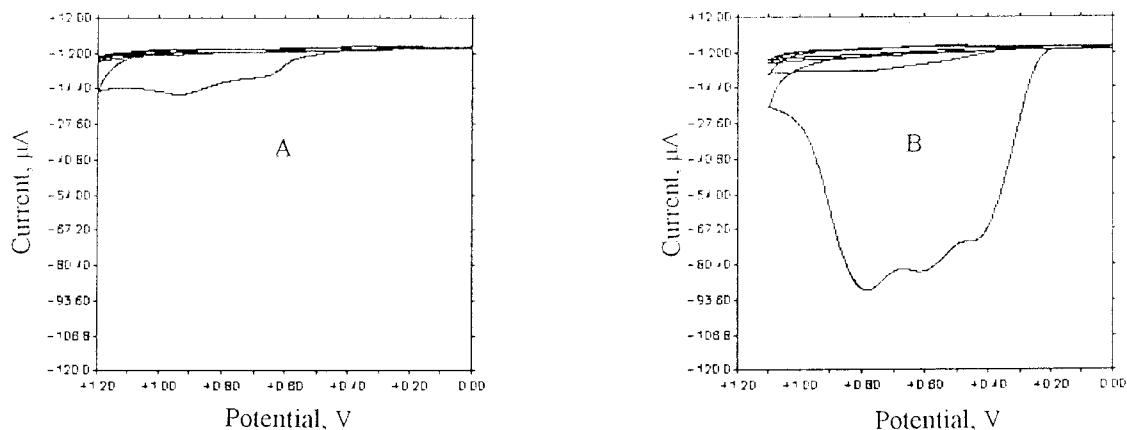


Figure 1 CVs of the bare gold electrodes in (A) 0.1M KCl and (B) 0.1M KCl + 0.05M *o*-phenylenediamine.

zymes and to prevent interference and fouling of the electrode surface.^{21,22} Also, this polymeric film has been used as a permselective membrane for halogenide ions.²³ The present article focuses on the electrochemical preparation, optimization, and voltammetric characteristics of the poly(*o*-phenylenediamine) film as a dopamine-selective polymeric membrane.

EXPERIMENTAL

Materials

o-Phenylenediamine was used as received from Merck (Darmstadt, Germany). Other chemicals used such as dopamine hydrochloride, ascorbic acid, and KCl were of analytical grade and purchased either from Sigma Chemical Co. (St. Louis, MO) or from E. Merck (Darmstadt, Germany). Doubly distilled water was used in the preparation of the solutions. Ascorbic acid and dopamine solutions were prepared freshly for each experiment. In voltammetric experiments, unless otherwise indicated, a 0.1M aqueous Na₂SO₄ solution was used as an electrolyte.

Instrumentation

Electropolymerization and voltammetric techniques such as cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed with a BAS (Bioanalytical Systems, Inc.) 100BW electrochemical analyzer. All electrochemical operations were carried out in a three-electrode cell using a bare or polymer-coated gold working electrode (geometric area: 1.98 mm²), a Ag/AgCl (BAS, MF-2063) reference electrode, and

a Pt wire coil auxiliary electrode. In the CV and DPV studies, the scan rate was 50 mV/s.

Preparation of Poly(*o*-phenylenediamine) Film

Gold working electrodes were polished with successively finer grades of diamond-polishing compounds and an aqueous alumina slurry (Johnson Matthey Catalog Co., Wand Hill, MA) down to 0.5 µm. Before starting the electropolymerization, the monomer solutions were purged by nitrogen gas for about 10 min. The nitrogen atmosphere was also maintained during the polymerization. Polymer films were prepared potentiostatically from deaerated aqueous KCl solutions of *o*-phenylenediamine. After electropolymerization, the resulting poly(*o*-phenylenediamine) coatings were rinsed with deionized water for the subsequent voltammetric studies.

Visual inspection revealed the formation of a thin and homogeneous polymeric film of brownish

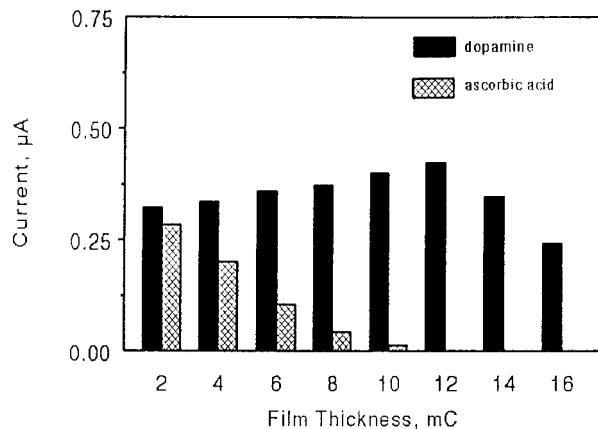


Figure 2 Effect of film thickness on the response.

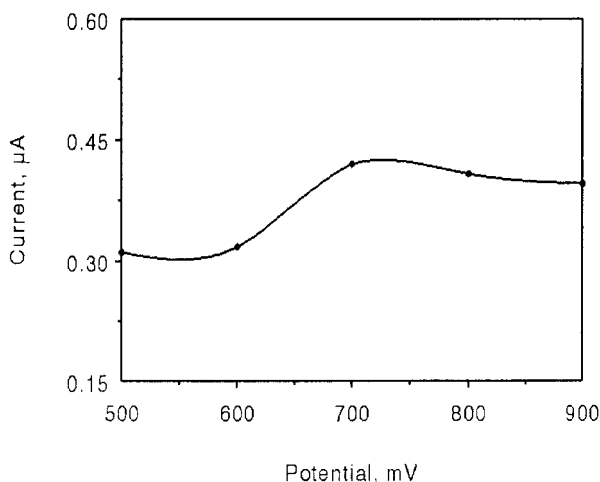


Figure 3 Effect of polymerization potential on the response.

color on the gold electrode surface. For the optimization of the electropolymerization parameters, the DPV runs were performed in 0.1M aqueous Na_2SO_4 containing 10 mM of dopamine or ascorbic acid.

RESULTS AND DISCUSSION

Typical cyclic voltammograms of the bare gold electrodes in the absence and presence of *o*-phenylenediamine are shown in Figure 1(A,B), respectively. As can be easily seen in Figure 1(B), *o*-phenylenediamine starts to oxidize at approximately 0.30 V versus Ag/AgCl. The decrease in the peak currents with subsequent cycles is indic-

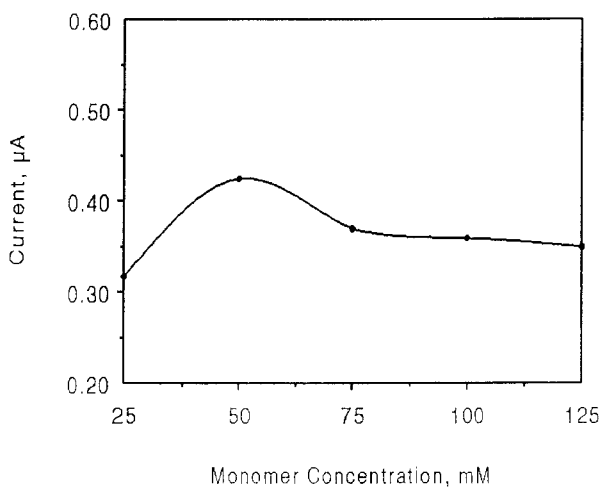


Figure 4 Effect of *o*-phenylenediamine concentration on the response.

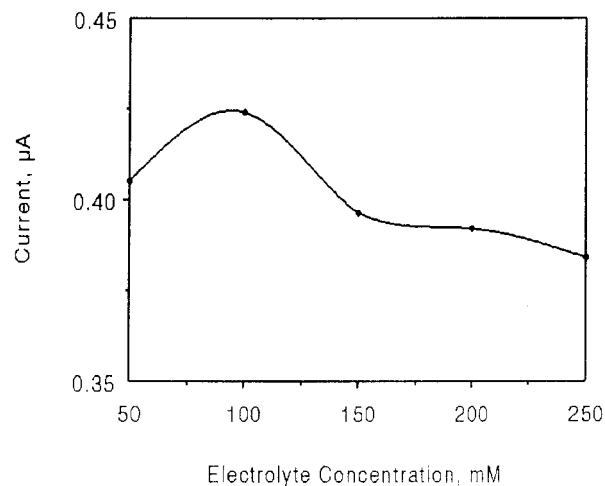


Figure 5 Effect of KCl concentration on the response.

ative of the formation of a nonelectroactive polymeric film. This behavior is typical for electrochemically grown nonelectroactive polymeric films and can be explained by blockage of the access of the monomer to the gold electrode surface on the subsequent scans.

Effect of Film Thickness

Film thickness is one of the most important parameters affecting the permselectivity characteristics of the resulting polymeric membrane. To find the optimal film thickness which allows dopamine oxidation while preventing unwanted amperometric responses from the electroactive ascorbic acid, poly(*o*-phenylenediamine) films at the desired thickness were prepared by altering the amount of charge consumed during the electrochemical polymerization.

Figure 2 shows the relation between the peak currents and film thickness. From this figure, it is easily seen that the electroactive ascorbic acid current decreases with increasing film thickness and diminishes to zero for thicknesses larger than 10 mC. This behavior means that electrode reactions do not take place on the polymeric film. On the other hand, dopamine current increases to a maximum value at a thickness of 12 mC. Thus, the optimal film thickness for the polymer electrode was chosen as 12 mC.

Effect of Polymerization Potential

The effect of the electropolymerization potential on the dopamine response of the poly(*o*-phenylenediamine) film electrode at the optimal thick-

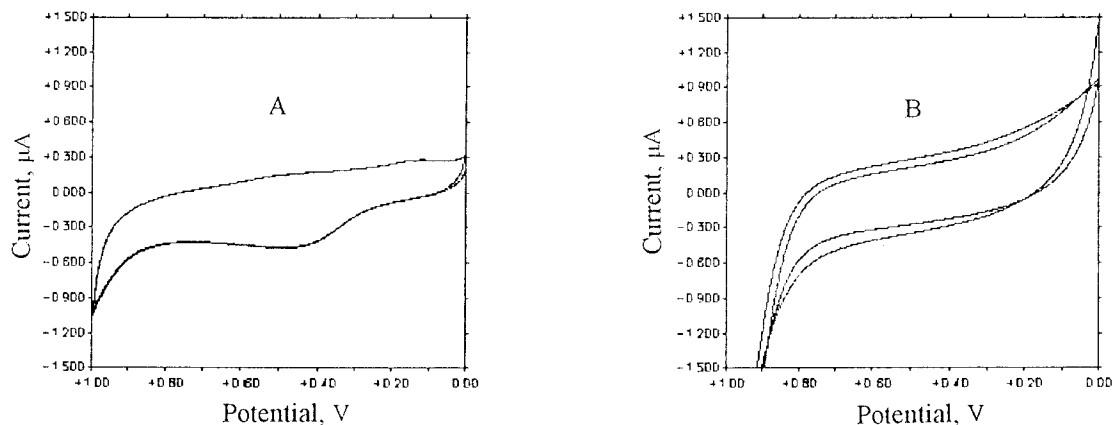


Figure 6 CVs of 10 mM ascorbic acid at the (A) bare and (B) polymer electrodes.

ness was examined in the range of 0.5–0.9 V. As depicted in Figure 3, the dopamine response increased with increasing potential and reached a maximum value at about 0.7 V, after which it decreased. Therefore, the optimum polymerization potential was chosen as 0.7 V versus Ag/AgCl. This optimal value is also suitable to ensure a controllable film growth at a slow electrolysis rate.

Effects of Monomer and Electrolyte Concentration

Figures 4 and 5 reveal the effects of concentrations of the monomer and the electrolyte used in the electropolymerization stage on the dopamine response of the poly(*o*-phenylenediamine) electrode at the optimal thickness, respectively. From

the figures, it can be easily seen that the maximum amperometric response for the electroactive dopamine was obtained with the electrode in a solution containing 50 mM *o*-phenylenediamine and 100 mM KCl. As expected, it was observed that the polymerization period decreased with increasing monomer concentration.

In brief, the optimal values of the mentioned chemical and electrochemical variables were as follows: electropolymerization potential, 0.7 V versus Ag/AgCl; polymeric film thickness, 12 mC; monomer concentration, 0.050M; and electrolyte concentration, 0.100M. Therefore, the poly(*o*-phenylenediamine)-coated electrodes prepared under the optimal conditions were used for the subsequent voltammetric measurements.

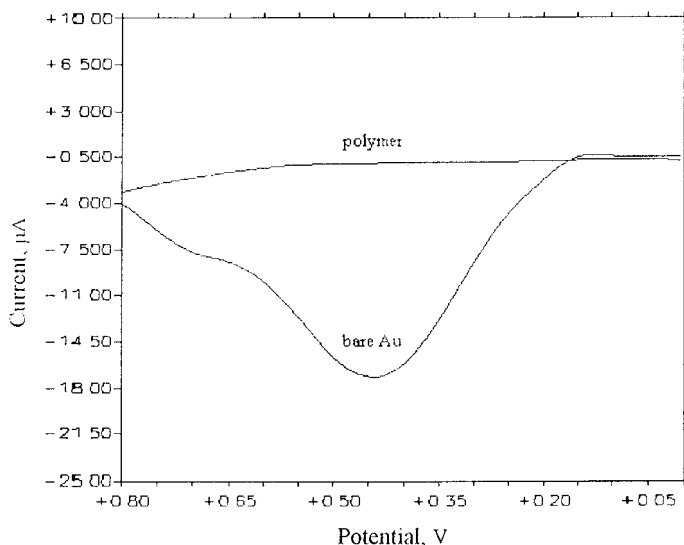


Figure 7 DPVs of 10 mM ascorbic acid at the bare Au and at the optimized polymer electrodes.

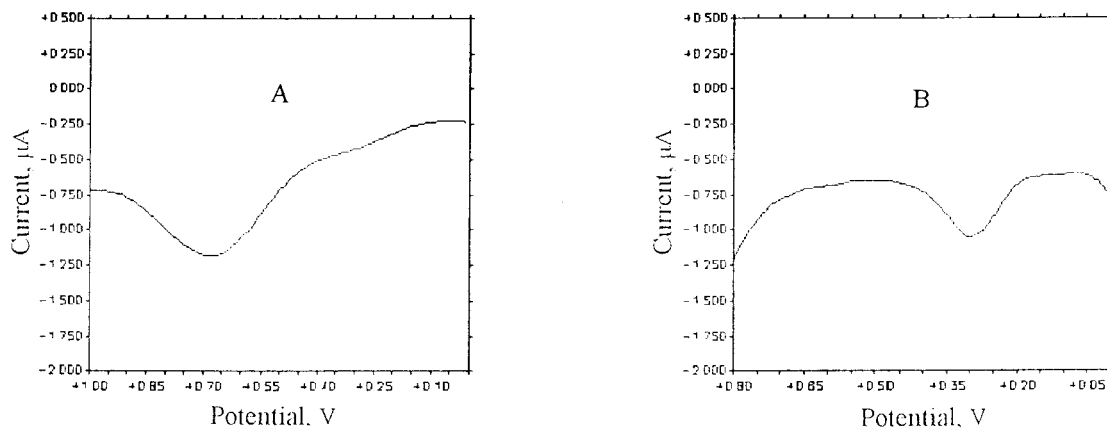


Figure 8 DPVs of 10 mM dopamine at the (A) bare and (B) polymer electrodes.

Voltammetric Characteristics of the Optimized Poly(*o*-phenylenediamine) Films

Cyclic voltammograms of ascorbic acid at the bare gold and the optimized polymer electrodes are compared in Figure 6. An oxidation peak observed at about 0.40 V for ascorbic acid [Fig. 6(A)] disappeared at the optimized polymer electrode [Fig. 6(B)].

This difference observed in the voltammograms confirms that the optimized polymeric film suppresses ascorbic acid oxidation. Moreover, this behavior of ascorbic acid observed with CV was also unquestionably supported by the DPVs as depicted in Figure 7. On the other hand, as expected and shown with DPVs in Figure 8, it is clear that the optimized polymeric film permits

penetration of dopamine when compared with the bare gold electrode.

The permselectivity characteristics of the optimized polymeric film were also examined in ascorbic acid plus dopamine mixtures as indicated in Figures 9 and 10. From these figures, it is readily seen that the dopamine peak current was unaffected with the increasing ascorbic acid concentration (Fig. 9) and that peak currents increase linearly with increasing dopamine concentration even in the presence of ascorbic acid (Fig. 10). Moreover, from the successive runs of the optimized polymeric electrode in the binary mixture, it was observed that the voltammetric responses were almost invariable (not shown). This behavior reflects

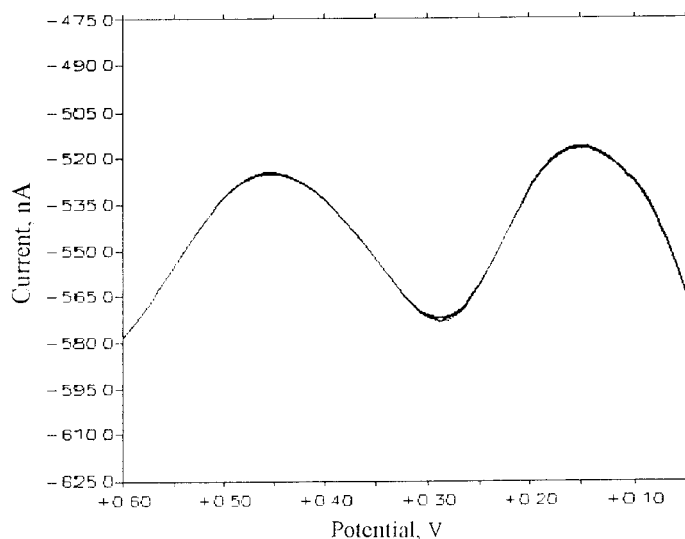


Figure 9 DPV of 10 mM dopamine at various concentrations of ascorbic acid (10–50 mM).

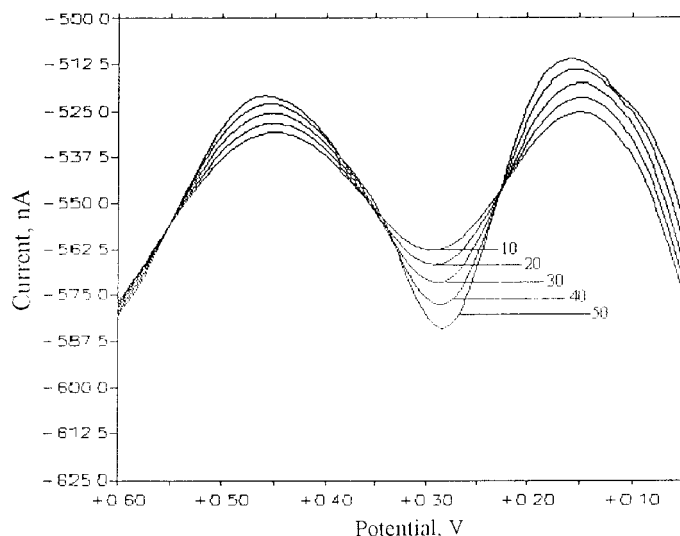


Figure 10 DPV of 10 mM ascorbic acid at various concentrations of dopamine (10–50 mM).

that the stability of the optimized polymeric film was satisfactory.

In summary, we have shown in the present article that dopamine-selective poly(*o*-phenylenediamine) film could be easily prepared electrochemically from the relevant monomer in an aqueous solution (one-step procedure). Then, the polymerization parameters affecting dopamine selectivity of the resulting polymeric film were systematically optimized. The excellent results obtained in the voltammetric studies showed that this polymeric film was selective for dopamine in the presence of an electroactive ascorbic acid. Therefore, from a technological point of view, it is claimed that this polymeric film can be used successfully as a dopamine-selective membrane.

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