

# Electropolymerization of *p*-Phenylenediamine on Pt-Electrode from Aqueous Acidic Solution: Kinetics, Mechanism, Electrochemical Studies, and Characterization of the Polymer Obtained

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**ABSTRACT:** Electropolymerization of *p*-phenylenediamine (*p*PD) on Pt-electrode from a deoxygenated aqueous acid medium was carried out using cyclic voltammetry technique. The kinetic parameters were calculated by means of electrochemical data. The experimentally obtained kinetic equation was  $R_{p,E} = k_E [\text{monomer}]^{1.23} [\text{acid}]^{1.24} [\text{electrolyte}]^{0.94}$  from the value of the anodic current density. The apparent activation energy ( $E_a$ ) is found to be 65.1 kJ mol<sup>-1</sup>. The obtained polymer films have been characterized by X-ray diffraction, elemental analysis,

scanning electron microscopy, UV-vis, and IR spectroscopy. The conductivity of the polymer pellets is  $6.3 \times 10^{-7}$  S cm<sup>-1</sup>. The mechanism of the electrochemical polymerization reaction has been discussed. TGA is used to confirm the proposed structure and determination of the number of water molecules in the polymeric chain unit. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 943–952, 2010

**Key words:** electropolymerization; kinetics; cyclic voltammetry; thermal analysis; mechanism

## INTRODUCTION

The oxidative polymerizations of aromatic diamines (AD) have been carried out by electrochemical polymerization, chemically oxidative polymerization where, enzyme and photocatalyzed oxidative polymerizations are very rare.

Polymerizations of AD occur via oxidation of one amino group<sup>1–3</sup> or both amino groups<sup>4</sup> of the corresponding monomer. The obtained polymers have been extensively investigated. The polymerization mechanism is believed to be closely related to the position of amino substitution on ADs. And properties of the polymers have not been definitely reported.

AD polymers exhibit a number of advantages including; the choice of monomer, diversity, variety of macromolecular structure, variability of conductivity, multifunctionality due to one free amino group per repeat unit on the polymers and potentially wide applicability. Also AD polymers

have lower conductivity compared to the widely studied poly aniline and poly pyrrole.<sup>5</sup>

Electropolymerization of phenylenediamines (PDs)—as a type of ADs—is carried out in a single- or dual-compartment cell by employing a three-electrode cell. The used cell comprising of working, counter, and reference electrodes. The electrochemical bath consisting of monomer and supporting electrolyte both dissolved in an appropriate solvent, sometimes under inert gas as N<sub>2</sub> or Ar. Then a suitable power supply potentiogalvanostatically (cyclic voltammetry), electric current potentiostatically or galvanostatically, is applied through the solution in the cell. Finally, polymer films are deposited on the working electrode.

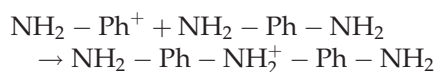
The chemical oxidative polymerization of *p*PD in acid HCl at room temperature using K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as an oxidant has been presented by Cataldo.<sup>4</sup> It is suggested that *p*PD is changed directly during oxidation to pernigraniline-like structure without passing through intermediate polymeric states involving polymeric radical cation (polarons) or carbocation.

Also Cataldo<sup>4</sup> investigated the CVs on 50 mM *p*PD aqueous solution in 0.1M HClO<sub>4</sub> at Pt-electrode. There is an initial anodic oxidation of *p*PD monomer along with the formation of bluish cation radical on the electrode, after 10 cycles no further current growth is observed because the low molecular

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weight PpPD product formed is not able to adhere to Pt-surface and dissolved in the solution. Although it has been also reported that pPD does not electropolymerized in non aqueous solvents.<sup>6</sup>

The electropolymerization of PpPD has been presented by B. Lakard et al. using CV technique on Pt wire-electrode at pH 7.0 phosphate buffer solution.<sup>7</sup> A thin insulating film was obtained. They use *ab initio* calculation to discuss the polymerization mechanism. By quantum-chemical calculation they obtain the energies of the successive intermediate involved in the mechanism. From thermochemical calculation, they confirm the mechanism is a linear not branched one with carbocation formation in the first step and have the structure;



Different types of working electrodes were used in electropolymerization of pPD including Pt, GC, IrO<sub>2</sub>, Ti, and graphite.

Sayyah et al. studied the kinetic of the electropolymerization process of different substituted aromatic amines. The kinetic equations were calculated from *ex situ* microgravimetric data<sup>8-13</sup> and from both the microgravimetric and electrochemical data.<sup>14,15</sup>

In this study, we investigate the electrodeposition of PpPD on Pt electrode from aqueous HCl solution using cyclic voltammetry technique. The kinetics, optimum conditions, and mechanism of the electrochemical polymerization will be discussed using electrochemical data. Also, the characterization of the obtained polymer film was carried out by IR, elemental analysis, TGA, SEM, and X-ray diffraction.

## EXPERIMENTAL

### Materials

*p*-Phenylenediamine (>99%) and anhydrous sodium sulfate (Merck, Darmstadt, Germany) was used as received, hydrochloric acid solution (Riedel-de Haën, Germany) and Dimethylformamide were provided by El-Naser pharmaceutical Chemical Company (Egypt). All chemicals are Analar grade. All solutions were prepared under nitrogen atmosphere in freshly double-distilled water.

### Cell and electrodes

A standard three-electrode cell was used in the cyclic voltammetry measurements with a saturated calomel electrode (SCE) as the standard reference electrode. The auxiliary electrode was a platinum wire. The dimensions of the platinum working electrode were 1 × 0.5 × 0.05 cm<sup>3</sup>. Before each run, the

working electrode was cleaned and washed with distilled water, rinsed with ethanol, and dried.

The electrochemical experiments were performed using the Potentiostat/Galvanostat Wenking PGS 95. The *i*-*E* curves were recorded by computer software from the same company (Model ECT).

### IR, elemental analysis, UV-vis and TGA

IR measurements were carried out using Shimadzu Ftir-340 Jasco spectrophotometer.

Elemental analysis was carried out in the micro-analytical center at Cairo University by oxygen flask combustion and dosimat E415 titrator (Metrohm).

The UV-vis absorption spectra of the prepared polymer samples were measured using Shimadzu UV-3101PC spectrophotometer at room temperature in the range 400–4000 nm using dimethylformamide as a solvent and reference.

TGA of the obtained polymer was performed using a Shimadzu DT-30 thermal analyzer (Shimadzu, Kyoto, Japan). The weight loss was measured from ambient temperature up to 600°C, at the rate of 10°C min<sup>-1</sup> and nitrogen 50 cc min<sup>-1</sup> to determine the degradation rate of the polymer.

### Scanning electron microscopy and X-ray diffraction

Scanning electron microscopic analysis was carried out using a JXA-840A Electron Probe Microanalyzer (JEOL, Tokyo, Japan). The X-ray diffractometer (Philips 1976 Model 1390, Netherlands) was operated under the following conditions that were kept constant for all the analysis processes:

X-raytube : Cu

Current : 30 mA

Presetttime : 10 s

Voltage : 40 kV

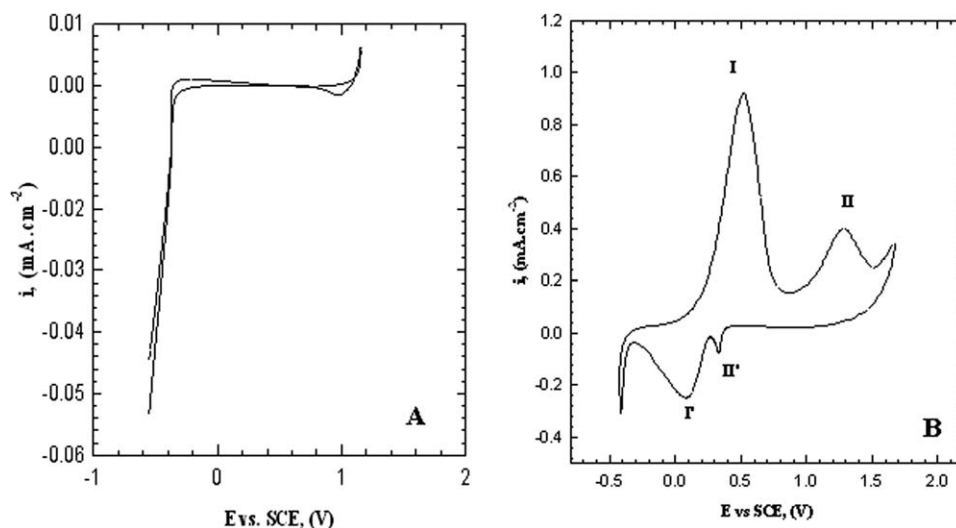
Scan speed : 8 degree min<sup>-1</sup>

## RESULTS AND DISCUSSION

### Electropolymerization of *p*-phenylenediamine

Electropolymerization of *p*-phenylenediamine on platinum electrode from the deoxygenated aqueous solution containing 0.3M HCl, 0.06M monomer and 0.1M Na<sub>2</sub>SO<sub>4</sub> as a supporting electrolyte and dopant at 298 K in the absence and presence of monomer, was studied by cyclic voltammetry at potential between -415 and +1670 mV (versus SCE) with scan rate of 25 mV s<sup>-1</sup>.

The obtained voltammogram is represented in Figure 1(A,B), respectively. The voltammogram in the absence monomer exhibit no peaks, where the



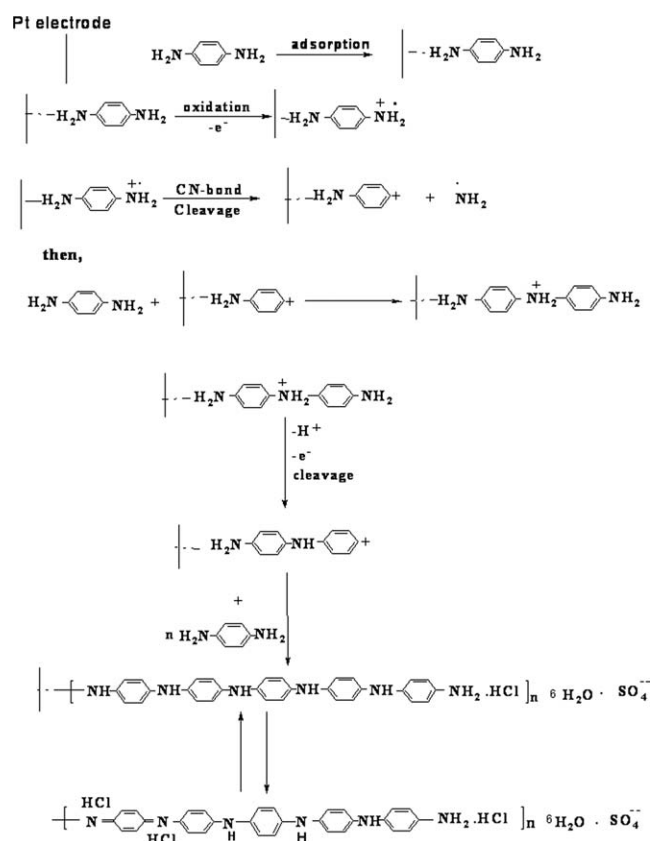
**Figure 1** Cyclic voltammogram of Pt-electrode from solution containing 0.3M HCl and 0.1M Na<sub>2</sub>SO<sub>4</sub> at 298 K with scan rate of 25 mV s<sup>-1</sup> in (A) absence of monomer, (B) 0.06M monomer.

voltammograms in the presence of monomer exhibit two oxidation peaks (I and II) that progressively developed at +520 and +1290 mV (versus SCE), repetitively. On one hand, after the adsorption of monomer to Pt electrode, the first oxidation peak (I) corresponds to removing of one electron from nitrogen atom of one of the amino groups to give radical cation. Then cleavage of CN-bond occurs this is also confirmed by quantum calculation.<sup>7</sup> The formed radical cation attacks other monomer molecule then expulsion of H<sup>+</sup> and oxidation then CN-cleavage again to form dimer radical cation,<sup>7</sup> and so on. Finally, the semiquinone radical cation (polaron state) is formed, as shown in Scheme 1.

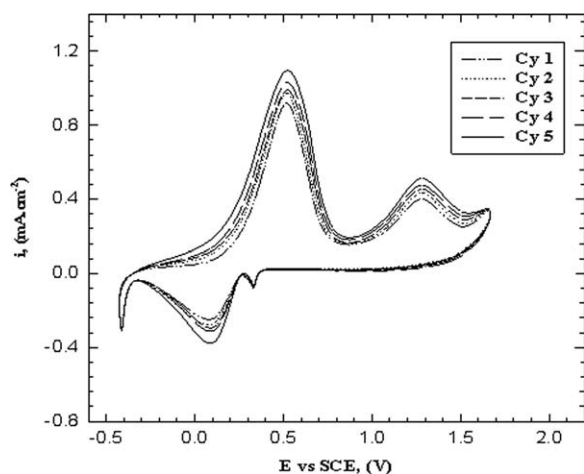
On the other hand, the second oxidation peak (II) which is assigned to the oxidation of the formed semiquinone radical cation (polaron state) to the quinone imine (bipolaron state),<sup>9,10,16</sup> occurs at +1290 mV versus SCE, and represented in Scheme 1. Therefore, the second redox process is attributed to the conversion of radical cations to the fully oxidized form (quinoidal structure). The charge included in the first peak (I) is higher than that in the second one (II), which means that not all the formed radical cations interact to give polaron and then bipolaron. The potential difference between the first and the second oxidation peak (I and II) is ≈770 mV, and no middle peaks were observed between them which confirm the nonexistence of degradation products, higher regularity, homogeneity and adherence of the deposited film to the electrode surface.<sup>16</sup>

On reversing the potential scan from +1670 to -415 mV, the reversing anodic current is very small indicating the presence of polymer layer adhered to the electrode surface. Beyond +500 mV, two cathodic peaks were formed. The first cathodic peak

(II') could be ascribed to the reduction of the bipolaron state to polaron state (conjugated to the second oxidation peak II). While the second cathodic peak (I') could be assigned to the reduction of the formed radical cation to the monomer (conjugated to the first anodic peak (I).



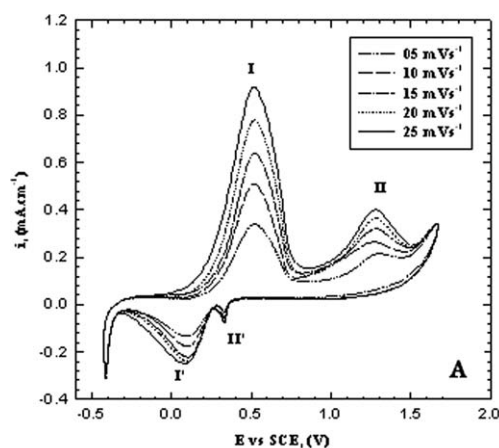
**Scheme 1** The suggested mechanism of the prepared P(*p*-PD).



**Figure 2** Repetitive cycling of electropolymerization of *p*-phenylenediamine from solution containing 0.06M monomer, 0.3M HCl and 0.1M Na<sub>2</sub>SO<sub>4</sub> at 298 K with scan rate of 25 mV s<sup>-1</sup>.

Figure 2 shows the effect of repetitive cycling on the formation of the polymer film from the deoxygenated aqueous solution containing 0.3M HCl, 0.06M monomer and 0.1M Na<sub>2</sub>SO<sub>4</sub> at 298 K. The data reveal that, the peak current densities of all anodic peaks (I and II) and cathodic peaks (I' and II') increase with repetitive cycling. The potential position of the redox peaks does not shift with increasing number of cycles, indicating that the oxidation reaction is independent on the polymer thickness.

Figure 3(A) illustrates the influence of the scan rate (5–25 mV s<sup>-1</sup>) on the potentiodynamic anodic polarization curves for *p*-phenylenediamine from the deoxygenated aqueous solution containing 0.3M HCl, 0.06M monomer and 0.1M Na<sub>2</sub>SO<sub>4</sub> at 298 K on platinum electrode. It is obvious that the anodic peak current densities ( $i_{pI}$ ,  $i_{pII}$ ) increase with the increasing of the scan rate.



**Figure 3** A: Effect of Scan rate on the of electropolymerization of *p*-phenylenediamine from solution containing 0.06M monomer, 0.3M HCl and 0.1M Na<sub>2</sub>SO<sub>4</sub> at 298 K. B: Relation between  $i_{pI}$  versus  $v^{1/2}$ .

Figure 3(B) shows the linear dependency of  $i_{pI}$  versus the square root of scan rate ( $v^{1/2}$ ). This linear relation suggests that the electropolymerization of *p*-phenylenediamine may be described by a partially diffusion-controlled process (diffusion of reacting species to the polymer film/solution interface).

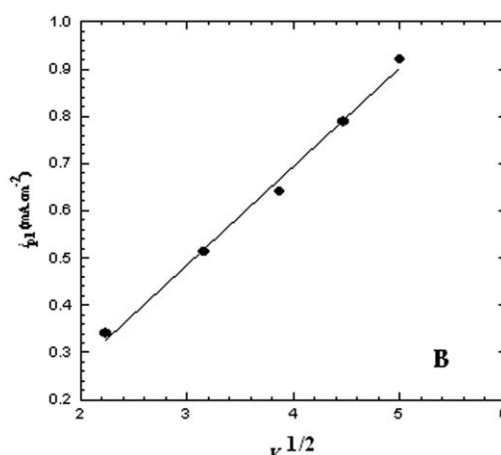
### Kinetic studies

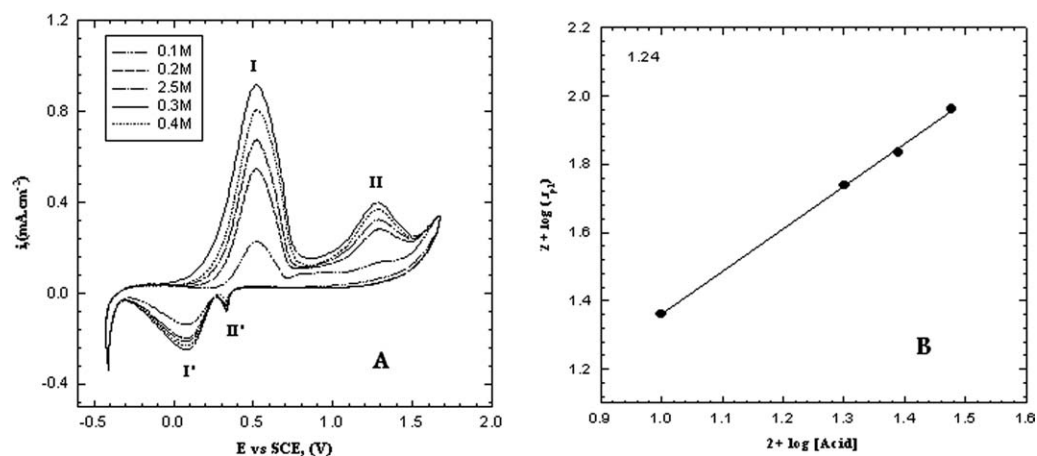
The electropolymerization kinetics were evaluated using deoxygenated aqueous solution containing monomer in the concentration range between 0.02 and 0.07M, hydrochloric acid concentration in the range between 0.1 and 0.4M, and Na<sub>2</sub>SO<sub>4</sub> in the concentration range between 0.025 and 0.125M ) at 298 K. The kinetic equation was calculated by means of electrochemical study from the values of the anodic current densities.<sup>15,16</sup>

The value of the anodic current density ( $i_p$ ) is proportional to the electropolymerization rate ( $R_{p,E}$ ) at a given concentration of the monomer, acid and electrolyte, then we can replace the electropolymerization rate by the anodic current density.<sup>14,15</sup>

### Effect of HCl concentration

Figure 4(A) represents the influence of HCl concentration in the range between (0.1 and 0.4M) on the cyclic voltammogram using scan rate of 25 mV s<sup>-1</sup>. The voltammogram shows that, the anodic peak current densities ( $i_{pI}$ ) increase with the increasing of the HCl concentration up to 0.3M, after which it began to decrease and reached maximum at a certain applied current density. A double logarithmic plot of the current density related to oxidation peak against HCl concentrations in the range between 0.1 and 0.3M is graphically represented in Figure 4(B). A straight line with slope of 1.24 was obtained.





**Figure 4** A: Potentiodynamic polarization curves for the effect of HCl concentration on the electropolymerization of *p*-phenylenediamine from solution containing 0.06M monomer and 0.1M Na<sub>2</sub>SO<sub>4</sub> at 298 K with scan rate of 25 mV s<sup>-1</sup>. B: Double logarithmic plot of the anodic current densities versus HCl concentrations.

Therefore, the reaction order with respect to HCl concentration is 1.24 order of reaction.

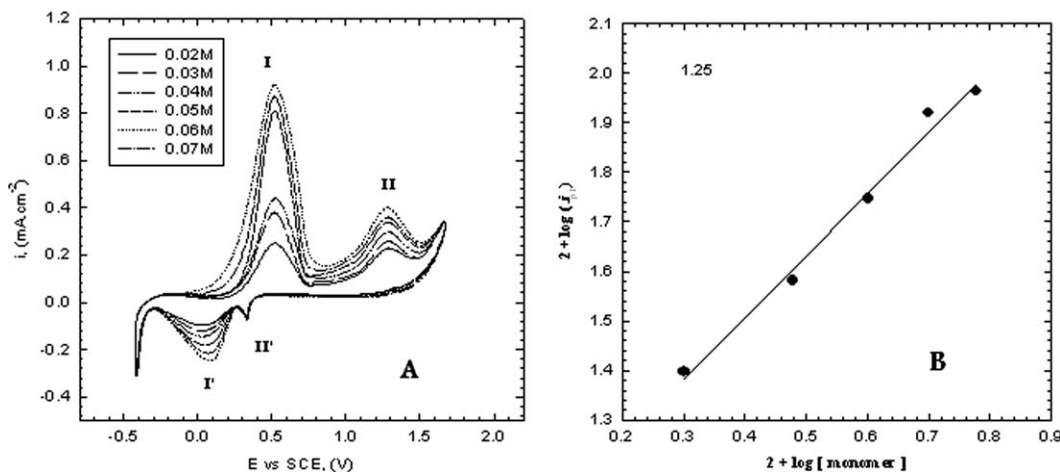
Therefore, the reaction order with respect to monomer concentration is 1.25 order of reaction.

#### Effect of monomer concentration

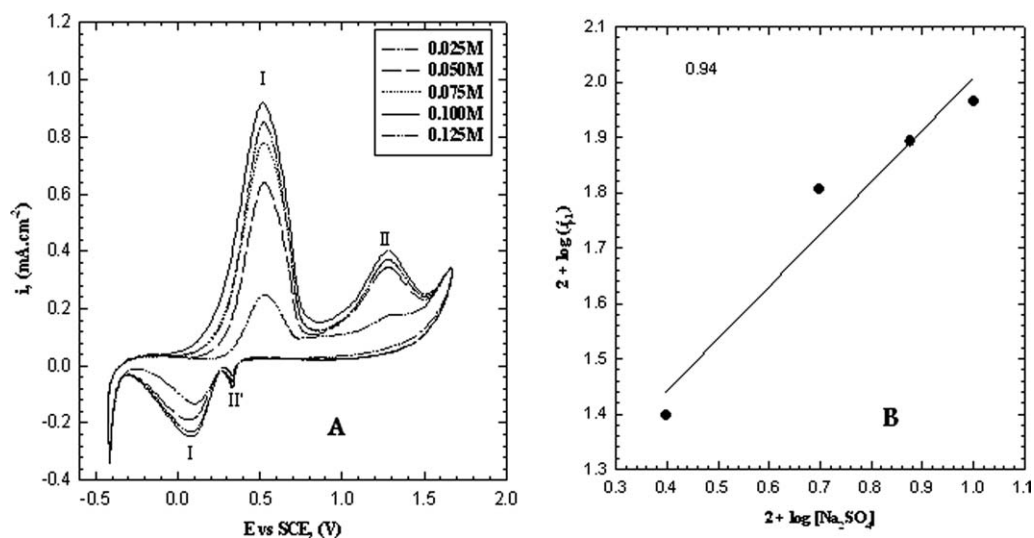
Figure 5(A) represents the influence of monomer concentration in the range between (0.02 and 0.07M) on the cyclic voltammogram using scan rate of 25 mV s<sup>-1</sup>. The voltammogram shows that, the anodic peak current densities ( $i_{p1}$ ) increase with the increasing of the monomer concentration up to 0.06M and then start to decrease with further increase of monomer concentration. A double logarithmic plot of the current density related to oxidation peak against monomer concentrations in the range between 0.01 and 0.06M is graphically represented in Figure 5(B). A straight line with slope of 1.25 was obtained.

#### Effect of electrolyte concentration

Figure 6(A) shows the effect of Na<sub>2</sub>SO<sub>4</sub> concentration in the range between (0.025 and 0.125M) on the cyclic voltammogram using scan rate of 25 mV s<sup>-1</sup> as a dopant (which is confirmed by IR-spectroscopy). The anodic peak current densities ( $i_{p1}$ ) increase with the increasing of the Na<sub>2</sub>SO<sub>4</sub> concentration up to 0.1M and then start to decrease with further increase of Na<sub>2</sub>SO<sub>4</sub> concentration. A double logarithmic plot of the current density related to oxidation peak against Na<sub>2</sub>SO<sub>4</sub> concentrations in the range between 0.025 and 0.1M is graphically represented in Figure 6(B). A straight line with slope of 0.94 was obtained. Therefore, the reaction order with



**Figure 5** A: Potentiodynamic polarization curves for the effect of monomer concentration on the electropolymerization of *p*-phenylenediamine from solution containing 0.3M HCl and 0.1M Na<sub>2</sub>SO<sub>4</sub> at 298 K with scan rate of 25 mV s<sup>-1</sup>. B: Double logarithmic plot of the anodic current densities versus monomer concentrations.



**Figure 6** A: Potentiodynamic polarization curves for the effect of electrolyte concentration on the electropolymerization of *p*-phenylenediamine from solution containing 0.3M HCl and 0.06M monomer at 298 K with scan rate of 25 mV s<sup>-1</sup>. B: Double logarithmic plot of the anodic current densities versus electrolyte concentrations.

respect to monomer concentration is a first order reaction.

Depending upon the aforementioned results, the kinetic rate law obtained from this method can be written as:

$$R_{P,E} = k_E [\text{monomer}]^{1.25} [\text{acid}]^{1.24} [\text{electrolyte}]^{0.94}$$

where,  $R_{P,E}$  is the electropolymerization rate and  $k_E$  is the kinetic rate constant.

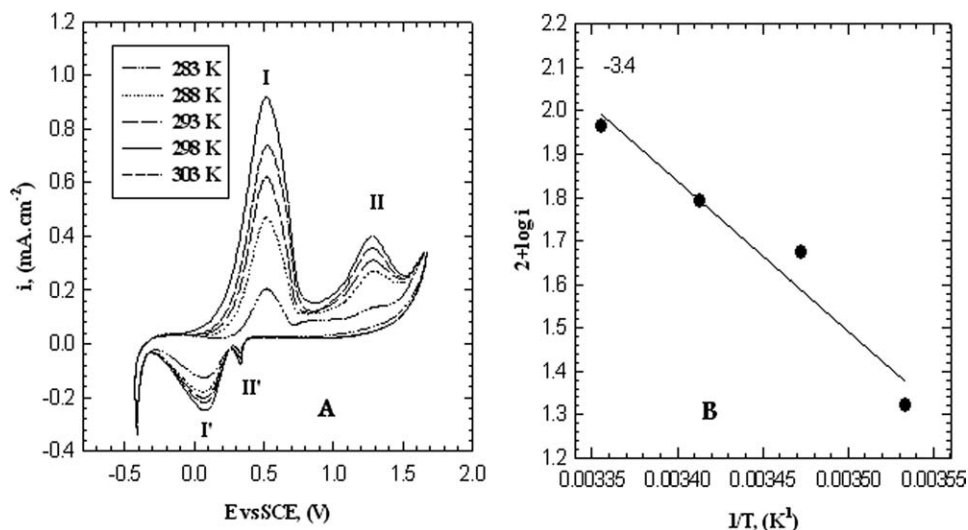
#### Effect of temperature

The potentiodynamic polarization curves as a function of the solution temperature in the range between 283 and 303 K under the optimum experimental con-

ditions as mentioned earlier were illustrated in Figure 7(A). From the figure, it is clear that, an increase of the reaction temperature up to 298 K resulted in a progressive increase of the charge included in the anodic peaks. The plot of the  $\log(i_{p1})$  versus  $1/T$  is represented in Figure 7(B), a straight line is obtained with a slope equal to  $-3.4$ . The apparent activation energy was calculated<sup>8-14</sup> using Arrhenius equation and it is found to be 65.1 kJ mol<sup>-1</sup>.

#### Elemental and spectroscopic analysis

Elemental analytical data are given in Table I, which are in a good agreement with that calculated on the basis of the suggested structure given in Scheme 1.



**Figure 7** A: Potentiodynamic polarization curves for the effect of temperature on the electropolymerization of *p*-phenylenediamine from solution containing 0.3M HCl, 0.06M monomer and 0.1M Na<sub>2</sub>SO<sub>4</sub> with scan rate of 25 mV s<sup>-1</sup>. B: Arrhenius plot of the of electropolymerization of *p*-phenylenediamine.

TABLE I  
Element Analysis of the Prepared P(*p*-PD)


Element (%)									
C		H		N		Cl		S	
Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
46.00	44.96	5.24	5.71	8.94	8.30	14.98	16.80	4.96	5.70

The presence of six water molecules for each repeat unit is confirmed by thermogravimetric analysis. The TGA steps of the prepared P*p*PD are shown in Figure 8. From the Figure, it is clear that, there are three stages during thermolysis of the polymer sample;

#### First stage

This stage includes the loss of (6H<sub>2</sub>O + SO<sub>3</sub>) molecules in the temperature rang between room and 113.9°C. The weight loss for this step was found to be (22.82%) which is in good agreement with the calculated value (24.02%).

#### Second stage

The second stage includes the loss of (3HCl + ) molecules in the temperature rang between 113.9 and 279.9°C. The weight loss for this is step was found to be (24.12%) which is in good agreement with the calculated value (23.70%).

#### Third stage

In this stage, the temperature range between 279.9 and 600°C, the weight loss was found to be (35.06%) which is attributed to the residual unit



The infrared absorption bands and their assignments for *p*-phenylenediamine and the prepared

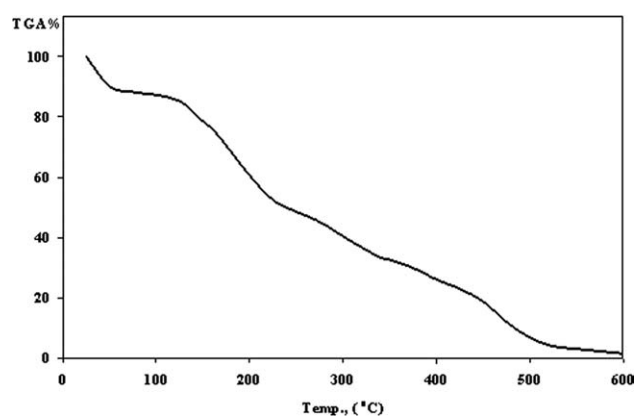


Figure 8 TGA of P*p*PD prepared at optimum conditions.

polymer are shown in Figure 9 and summarized in Table II. From which the polymer shows a weak absorption band at 760 cm<sup>-1</sup> is due to CN stretching vibration in quinonoid unit. A weak absorption band at 1142 cm<sup>-1</sup> is a result of SO<sub>4</sub><sup>2-</sup> incorporation in the polymeric chain. The very weak absorption band appearing at 1187 cm<sup>-1</sup> is attributed to Cl<sup>-</sup> incorporation. Accordingly both SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> anions are doped in the polymeric chain.<sup>17,18</sup> But no evidence for the formation of new bonds between the polymer chain and the doped anions were observed which means that the anions doped in the polymeric chains exist in the ionic form<sup>19</sup> as shown in Scheme 1. The medium band at 1563 cm<sup>-1</sup> in case of polymer could be attributed to C=N stretching vibration of quinonoid structure. A large broad absorption peak is observed from 3700 to 1800 cm<sup>-1</sup> due to electronic transitions from valence band to conduction band.<sup>20</sup> Other infrared absorption bands and their assignments are summarized in Table II.

The UV-vis spectra of *p*-phenylenediamine monomer and its homopolymer are represented in Figure 10. The spectra show the following absorption bands:

1. In case of monomer, four absorption bands appear at  $\lambda_{\max} = 207, 252, 269,$  and  $326$  nm, which may be attributed to  $\pi-\pi^*$  transition ( $E_2$  band) of the benzene ring and the  $\beta$ -band ( $A_{1g}$  to  $B_{2u}$ ).
2. In case of polymer, three absorption bands appear at  $\lambda_{\max} = 249, 266,$  and  $312$  nm, which

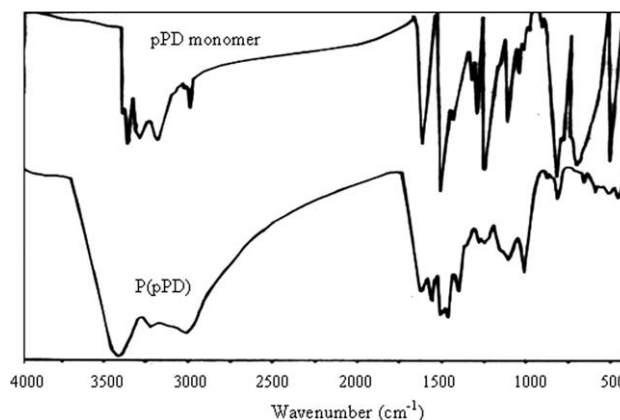
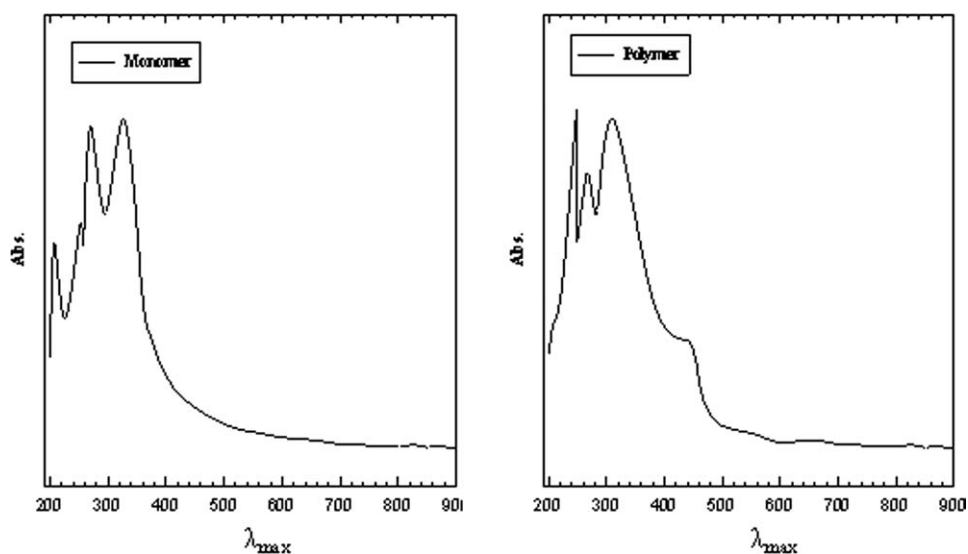


Figure 9 The IR-spectra of *p*PD monomer and its homopolymer.

**TABLE II**  
**The Infrared Absorption Bands and Their Assignments for *p*-Phenylenediamine Monomer and the Prepared Polymer**

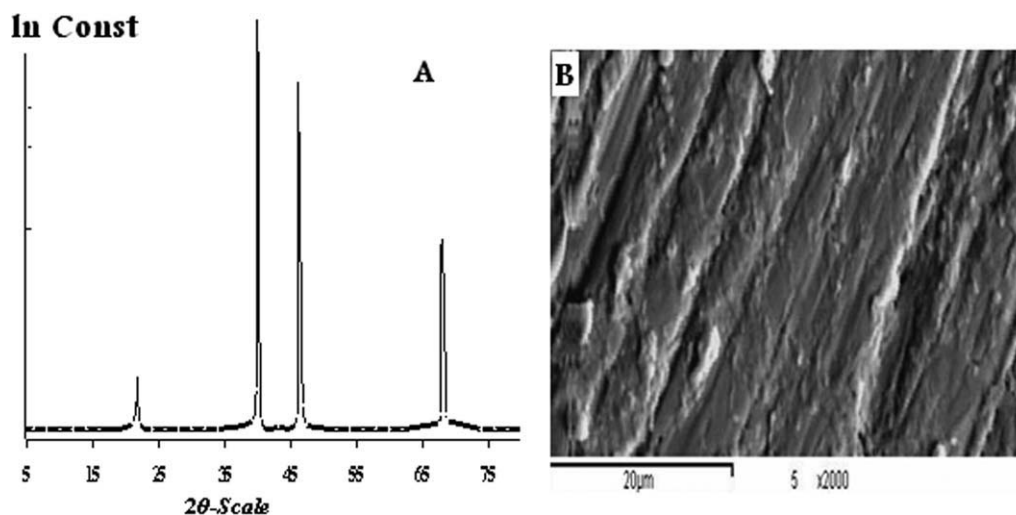
Wave number (cm <sup>-1</sup> )		Name
Monomer	Polymer	
424.5 <sup>m</sup>	424 <sup>vw</sup>	CH wagging deformation of 1,2 -disubstituted benzene ring
	464 <sup>w</sup>	
515 <sup>vs</sup>	521 <sup>w</sup>	Out-of-plane deformation of ring
	601 <sup>w</sup>	
717 <sup>s</sup>	668.7 <sup>w</sup>	CH Stretching vibration of benzene ring
-	760 <sup>w</sup>	C-N Stretching vibration in quinonoid unit
829.6 <sup>s</sup>	825.7 <sup>m</sup>	CH out-of-plane deformation
933 <sup>w</sup>	886.5 <sup>vw</sup>	
1112 <sup>w</sup>	1020 <sup>s</sup>	CH stretching vibration
1041 <sup>m</sup>	1115 <sup>b</sup>	
1065 <sup>w</sup>		
1127 <sup>s</sup>		
-	1142 <sup>w</sup>	SO <sub>4</sub> <sup>2-</sup> incorporation
	1187 <sup>vw</sup>	Cl <sup>-1</sup> incorporation
1262 <sup>s</sup>	1257 <sup>w</sup>	C-N stretching vibration
	1288.9 <sup>w</sup>	
1310 <sup>m</sup>	1406.8 <sup>m</sup>	C-C stretching vibration
1341 <sup>w</sup>	1467 <sup>s</sup>	
1445 <sup>w</sup>	1509 <sup>s</sup>	
1517 <sup>s</sup>		
-	1563 <sup>m</sup>	C=N stretching vibration of quinonoid structure
1629 <sup>s</sup>	1622 <sup>m</sup>	NH <sub>2</sub> scissoring vibration
3008.5 <sup>s</sup>	3015.7 <sup>b</sup>	CH stretching vibration of aromatic amine
3043.7 <sup>w</sup>		
3199.6 <sup>s</sup>	3150 <sup>b</sup>	NH <sub>2</sub> symmetric stretching vibration of aromatic amine
3303.5 <sup>s</sup>	3219.9 <sup>b</sup>	
3363.3 <sup>s</sup>		NH <sub>2</sub> asymmetric stretching vibration of aromatic amine
3374.4 <sup>s</sup>	3416.8 <sup>b</sup>	
3406.5 <sup>w</sup>		NH <sub>2</sub> asymmetric stretching vibration of aromatic amine or OH strong hydrogen bonded group in H <sub>2</sub> O molecules of hydration in polymer

s, strong; w, weak; b, broad; m, medium; vw, very weak.



**Figure 10** UV-vis spectra of *p*-phenylenediamine monomer and the prepared polymer.





**Figure 11** A: X-ray diffraction pattern of P(*p*-PD). B: The picture of scanning electron microscope of P(*p*-PD).

may be attributed to  $\pi$ - $\pi^*$  transition. Also an absorption band appears in the visible region at  $\lambda_{\text{max}} = 442 \text{ nm}$ , which may be due to the high conjugation of the aromatic polymeric chains and may participate in the conductivity value.

The specific conductivity of *p*(*p*-phenylenediamine) was measured on a compressed pellet made by compressing the powder polymer. The conductivity was measured with direct current from 5 to 25 V, in this range the sample showed Ohmic behavior, and found to be  $6.3 \times 10^{-7} \text{ S cm}^{-1}$ . This conductivity is in good agreements with that at literature.<sup>5</sup>

### Surface morphology

In most conditions, homogeneous, smooth, black, and well-adhering PpPD films were electrodeposited on platinum electrode surface. The X-ray diffraction pattern shows that the prepared polymer is crystalline as shown in Figure 11(A). From which it is clear that, there are one sharp peak at  $2\theta$  angle equals 21.88.

The surface morphology of the polymer obtained at the optimum conditions was examined by scanning electron microscopy. The SEM micrograph shows a smooth surface feature [c.f., Fig. 11(B)].

### CONCLUSIONS

In conclusion, the aforementioned data reveals the following:

1. The initial rate of electropolymerization reaction of PpPD on platinum electrode is relatively low. The fraction of the dissolved product may

be strongly dependent on temperature and monomer or HCl concentrations.

2. The orders of the electropolymerization reaction of PpPD on platinum electrode are 1.24, 1.25, and 0.94 with respect to HCl, monomer, and electrolyte concentration, respectively.
3. The apparent activation energy is calculated to be  $65.1 \text{ kJ mol}^{-1}$ .
4. The prepared PpPD shows a smooth surface feature with uniform thickness and has amorphous nature with small crystallinity and well adhered on platinum electrode surface.
5. From cyclic voltammetry studies, it is clear that the cyclic voltammogram consists of two anodic peaks at +520 and 1220 mV versus SCE, corresponding to the conversion of amine nitrogen to radical cation, and polaron to bipolaron and there conjugated cathodic peaks.
6. The electrodeposition of the polymer film on platinum electrode may be described partially by a diffusion-controlled process.

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