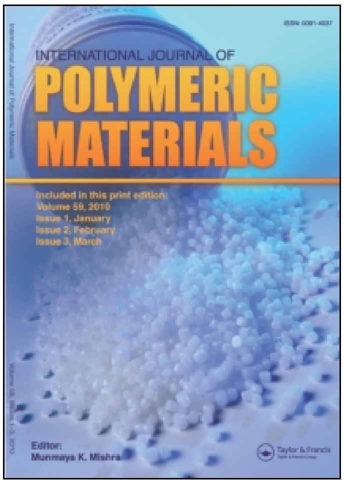

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ELECTROPOLYMERIZATION OF 2-AMINO-4-PHENYLTHIAZOLE AND CHARACTERIZATION OF THE OBTAINED POLYMER FILMS

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Electrochemical oxidative polymerization of 2-amino-4-phenylthiazole on platinum electrode in acid medium was carried out. Different reaction parameters were investigated such as current density, acid concentration, monomer concentration, and temperature with duration of time. The orders of the electropolymerization reaction were found to be 1.06, 1.10, 1.16 with respect to current density, acid concentration, and monomer concentration, respectively. The apparent activation energy (E_a) was found to be 61.04 kJ mol^{-1}. The obtained polymer films were characterized by IR, UV, ^{1}H-NMR, elemental analysis, thermogravimetric analysis, and cyclic voltammetry. The mechanism of the electrochemical polymerization reaction has been also discussed. Surface morphology of the obtained polymer film was characterized by X-ray diffraction and scanning electron microscopy.

Keywords: electropolymerization, 2-amino-4-phenylthiazole, kinetic studies, cyclic voltammetry, characterization

INTRODUCTION

The preparation of conducting polymers is an active area of both academic and industrial research because of their many potential applications in batteries [1–6], electrochromic devices [7–9], microelectronic devices [10], electrochemical chromatography [11], and as

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corrosion inhibitors to protect semiconductors and metals [12–17]. Electrochemical polymerization is a useful method for the preparation of these polymers because it is an essentially reagentless process that can be readily controlled and kept clean [18–19]. In addition, the electro-chemical method provided many advantages over the chemical methods, such as easy compositional and morphological modifications via variations and adjustments of electropolymerization conditions [i.e., methods of preparation (potentiostatic, galvanostatic, cyclic voltammetry with or without electrode rotation), nature of the electrode substrate, scan rate, and potential range]. The electropolymerization product can be made in thin film form ready for device development, and the electropolymerization method can provide the best way to study in situ the polymerization mechanism [20–24].

Conducting polymers such as polypyrrole, poly(substituted-aniline), polythiophene and poly(substituted thiophene) were readily synthesized by electro-initiation polymerization [24–31]. Recently, the number of studies on the preparation and characterization of composites, copolymers, and blends of conducting polymers has shown a significant increase.

Various techniques such as thermogravimetric analysis [32], infrared spectroscopy [33–34], scanning electron microscopy [34], UV-visible spectroscopy [21,33], cyclic voltammetry [35], and Raman Spectroscopy [36] are used for characterization of conducting polymers prepared by electropolymerization.

The electrochemical behavior of 2-amino-4-phenyl thiazole in phosphate buffer solution was previously studied by R. N. Goyal et al. [37]. They found that, the final product of the electrochemical oxidation of the 2-amino-4-phenylthiazole in the pH range between 2–11 gave an azo compound as the main product of the electrode reaction.

The kinetics of the chemical polymerization of some substituted anilines in aqueous solution and characterization of the obtained polymers by IR, UV-visible, X-ray, electron microscopy, TGA-DTA analysis and, a.c. conductivity have been investigated by Sayyah et al. [38–42]. To the best of the present authors' knowledge, no one in the literature investigate the rate of the electropolymerization reaction, reaction orders with respect to different electropolymerization parameters such as current density, monomer concentration, and acid concentration. Also, thermodynamic activation parameters such as ΔH^*, ΔS^*, and E_a for the electrochemical polymerization of 2-amino-4-phenylthiazole were not determined.

The objective of the present work is to investigate the kinetic and optimum conditions for the electrochemical polymerization of 2-amino-4-phenylthiazole as sulphur containing heterocyclic amine derivative in aqueous hydrochloric acid medium. The obtained polymer prepared at the investigated optimum condition was characterized by UV-visible, IR, thermo-gravimetric analysis, and ^{1}H-NMR spectroscopy. Cyclic voltammetry measurements were carried out at different concentrations and parameters. The surface morphology of the obtained polymer was characterized by scanning electron microscopy and X-ray diffraction.

EXPERIMENTAL

Materials

Acetophenone, bromine, glacial acetic acid, thiourea, hydrochloric acid solution, and anhydrous sodium sulphate of analytical pure grade were provided by Merk, Germany. All solutions were freshly prepared using double distilled water. 2-amino-4-phenylthiazole was synthesized in the laboratory by method reported in the literature [43]. Its high purity was obtained by recrystallization and by TLC.

Cell and Electrodes

The experimental set-up used was described previously [44–46] and consisted of rectangular Perspex cell provided with two platinum foil parallel electrodes. Each electrode has a dimension of 1 cm height and 0.5 cm width. Before each run, the platinum anode was cleaned and washed with distilled water, rinsed with ethanol, dried, and weighed. The experiments were conducted at the required temperature ±1°C with the help of circular water thermostat. At the end of the experiment, the anode was withdrawn, washed with distilled water, dried, and weighed. The polymerization current was supplied by a dc-power supply (Thurby ~ Thandar PL 330).

Electropolymerization of 2-amino, 4-phenyl thiazole

Anodic oxidative polymerization of 2-amino-4-phenylthiazole was carried out in aqueous solutions containing monomer (concentration range between 0.01 and 0.07 M) using 0.1 M Na_2SO_4 as the supporting electrolyte, and the current densities were investigated in the range between 2 and 14 mA Cm^{-2}. Electro-polymerization was carried in hydrochloric acid solution (concentration range between 0.2 and 1.6 M) at different temperatures in the range between 288 and 323°K.

Cyclic Voltammetry Measurements

A standard three-electrode cell was used in the cyclic voltammetry measurements with saturated calomel electrode (SCE) as the standard reference electrode. The auxiliary electrode was a platinum wire. The platinum-working electrode was $1 \times 0.5 \times 0.5$ cm. Before each run, the platinum electrode is cleaned as mentioned "Cell and Electrodes".

The electrochemical experiments were performed with EG&G Potentiostat/Galvanostat Model 273 supplied by EG&G Princeton Applied Research. The *I-E* curves were recorded by computer software from the same company Model 352 and 270/250.

Ultraviolet, Infrared, Thermogravimetric Analysis, and ^{1}H-NMR Spectroscopy

Ultraviolet–visible adsorption spectra of the monomer and the electropolymerized polymer sample were measured using Shimadzu UV spectrophometer (M160 PC) at room temperature in the range 200–400 nm region using dimethyl formamide as a solvent and reference.

Infrared measurements were carried out using a shimadzu FTIR-430 Jasco spectrophotometer. ^{1}H-NMR measurements were carried out using a Varian EM 360L, 60 MHz NMR spectrometer. NMR signals of the electropolymerized samples were recorded in dimethyl sulphoxide using tetramethyl silane as internal reference.

Thermogravimetric analyses of the obtained polymers were performed using a Shimadzu DT-30 thermal analyzer. The weight loss was measured from ambient temperature up to 600°C at a rate of $10°\text{C}\,\text{min}^{-1}$, to determine the degradation rate of the polymer.

Scanning Electron Microscopy and X-ray Diffraction

Scanning electron microscopic analysis was carried out using a JSM-T20 scanning electron microscope (JEOL, Japan). The X-ray diffractometer (Philips 1976 Model 1390) was used to obtain the spectrum of the polymer film adhered to the platinum electrode, under the following conditions that were kept constant for all the analysis processes:

X-ray tube: Cu; Scan speed: 8 deg.min^{-1}; Current: 30 mA; Voltage: 40 kV; Preset time: 10 s.

RESULTS AND DISCUSSION

Anodic Oxidative Electropolymerization

Effect of Time Duration

Anodic oxidative electropolymerization of 2-amino-4-phenylthiazole was studied under the influence of different plating and operating parameters. The effect of time duration on the weight of the obtained polymers was studied with different values of current densities. The data reveal that the weight of the obtained polymer increases with the increasing time duration up to 15 min and then tends to decrease as a result of degradation and the solubility of the polymer film from the platinum surface in case of all the investigated values of the current densities. The data are graphically represented in Figure 1.

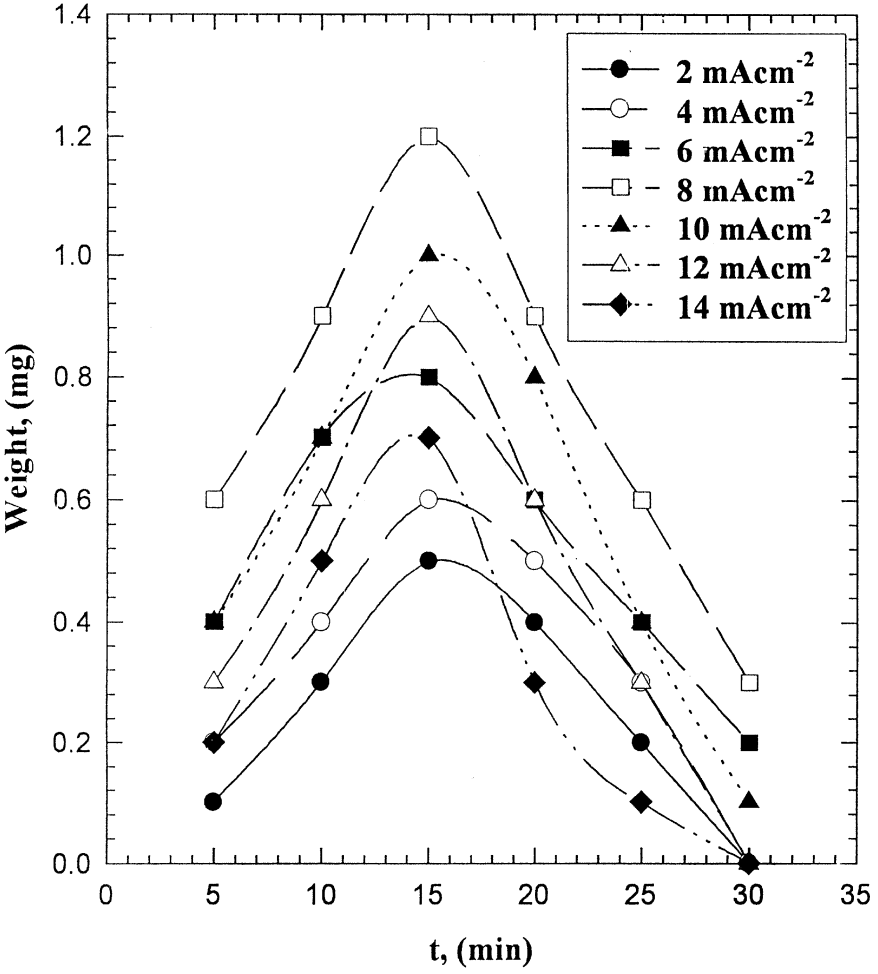


FIGURE 1 Yield-time curve for the effect of duration time on the anodic polymerization of 2-amino-4-phenylthiazole from solution containing 0.01 M monomer, 1.0 M HCl, and 0.1 M Na_2SO_4 at 303°K.

Effect of Current Density

The effect of applied current density on the anodic oxidative electropolymerization of 2-amino-4-phenylthiazole was studied at constant time intervals (15 min). The data reveal that as the applied current density increases the weight of the obtained polymer increases up to 8 mAcm^{-2} and then tends to decrease. It was observed that oxygen and chlorine evolution took place as a side reaction, especially at high current densities. Each value of the used current density was studied with different time intervals and the yield-time curve was plotted. The data are graphically represented in Figure 2A, from which the initial rate of the electropolymerization was determined. The reaction exponent with respect to the current density was determined from the slope of the straight line presented in Figure 2B. The exponent is found to be 1.06.

Effect of HCl Concentration

Anodic oxidative electropolymerization was carried out using 0.01 M monomer concentration, 0.1 M Na_2SO_4 in dimethyl formamide/water mixture (30:70), current density = 8 mAcm^{-2} at 303°K, which were kept constant, but the hydrochloric acid concentration was varied in the rang between 0.2–1.6 M. The obtained polymer film in each experiment was weighed. From the obtained data, it is clear that the maximum weight was obtained when 1.0 M HCl concentration was used. The effect of HCl concentrations in the range between 0.2 and

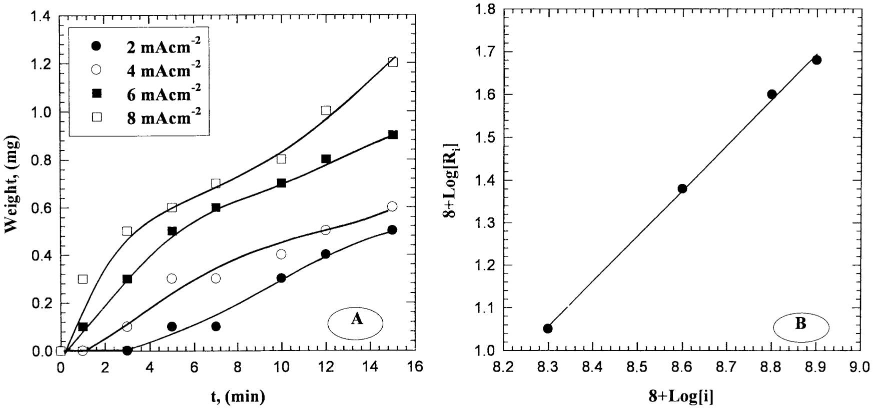


FIGURE 2 (A) Yield-time curve for the effect of current densities. (B) Double logarithmic plot of initial rate of electropolymerization versus different current densities values.

1.0 M on the polymerization rate was studied. The weight of the deposited polymer film on the platinum electrode in each experiment was plotted against the time duration as shown in Figure 3A. The initial rate of the electro-polymerization reaction was calculated and the double logarithmic plot of the initial rate vs. HCl concentration is represented in Figure 3B. A straight line is obtained that has a slope of 1.10. This means that, the order of the reaction with respect to HCl is a first-order reaction.

Effect of Monomer Concentration

The electropolymerization reaction was carried out by keeping all the afore mentioned conditions constant at 1.0 M HCl, current density = 8 mAcm^{-2}, Na_2SO_4 (0.1 M) and temperature at 303°K, but the monomer concentrations were varied in the range between 0.01 and 0.07 M. The weight of the obtained polymer film in the case of each monomer concentration was determined. The obtained data reveal that the maximum weight of the polymer film was obtained at 0.05 M. It is also noticed that the weight of the polymer film decreases at high concentrations of monomers (>0.05 M), which means that polymer degradation may occur. Each monomer concentration (in the range between 0.01 and 0.05 M) was investigated at different time intervals to show the initial rate of electropolymerization and the data are graphically represented in Figure 4A. The initial rate of electropolymerization was calculated and the double logarithmic plot of

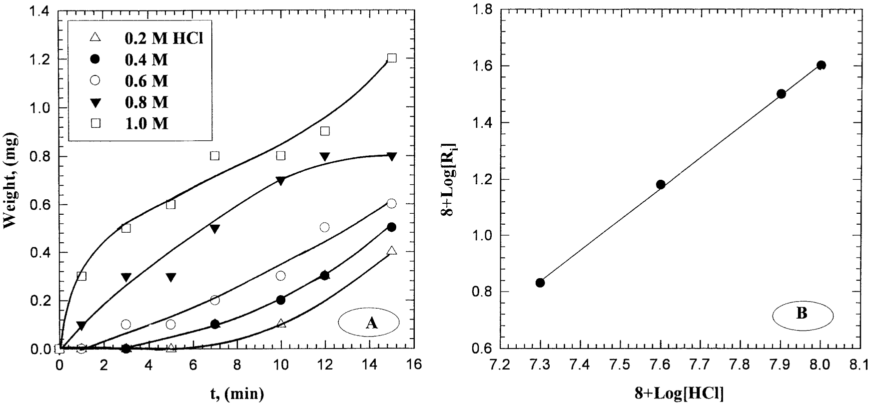


FIGURE 3 (A) Yield-time curve for the effect of HCl concentration. (B) Double logarithmic plot of initial rate of electropolymerization versus HCl concentration.

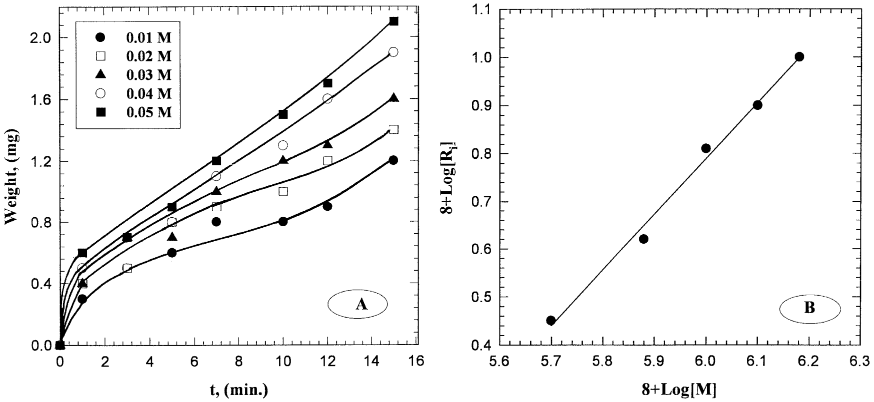


FIGURE 4 (A) Yield-time curve for the effect of monomer concentration. (B) Double logarithmic plot of initial rate of electropolymerization versus monomer concentration.

the initial rate of polymer formation vs. monomer concentration is represented in Figure 4B. This relation gives a straight line with a slope of 1.16, which means that the order of the electropolymerization reaction of 2-amino-4-phenylthiazole is a first-order reaction with respect to the monomer concentration.

Effect of Temperature

Anodic oxidative electropolymerization of 2-amino-4-phenylthiazole was carried out under the following constant conditions: 1.0 M HCl concentration, 0.05 M monomer concentration, 0.1 M Na_2SO_4, 8 mAcm^{-2}, but the reaction was carried out at different temperatures in the range between 288 and 323°K. The weight of the polymer film was calculated for each investigaged temperature. From the obtained data, it is clear that the maximum weight of the polymer is obtained at 298°K. At higher temperatures than 298°K the polymer weight decreases all over the investigated temperatures. It was also noticed during the experiments that, at higher temperatures than 298°K, some polymers are formed in the solution near the anode and do not adhere at the electrode, which means that at temperatures higher than 298° K, the adhesion of the film to the electrode is decreased. The electropolymerization rate was investigated at 288, 293, and 298°K. At each temperature the weight of the formed polymer at the anode was plotted vs. the duration time and the yield—time curve is represented in Figure 5A. The initial rate of electropolymerization was calculated at each investigated temperature and the logarithm of the initial rate was plotted vs. 1/T (Figure 5B), which gives a straight line with a slope equal to -3.188. By applying the Arrhenius equation, the apparent activation energy was calculated and was found to be 61.04 KJ mol^{-1}.

Calculation of Thermodynamic Parameters

The enthalpy and entropy of activation for the electropolymerization reaction can be calculated from the k_2 values of the following equation:

$$\text{Reaction rate} = k_2[\text{HCl}]^{1.1}[\text{current density}]^{1.0}[\text{monomer}]^{1.16}$$

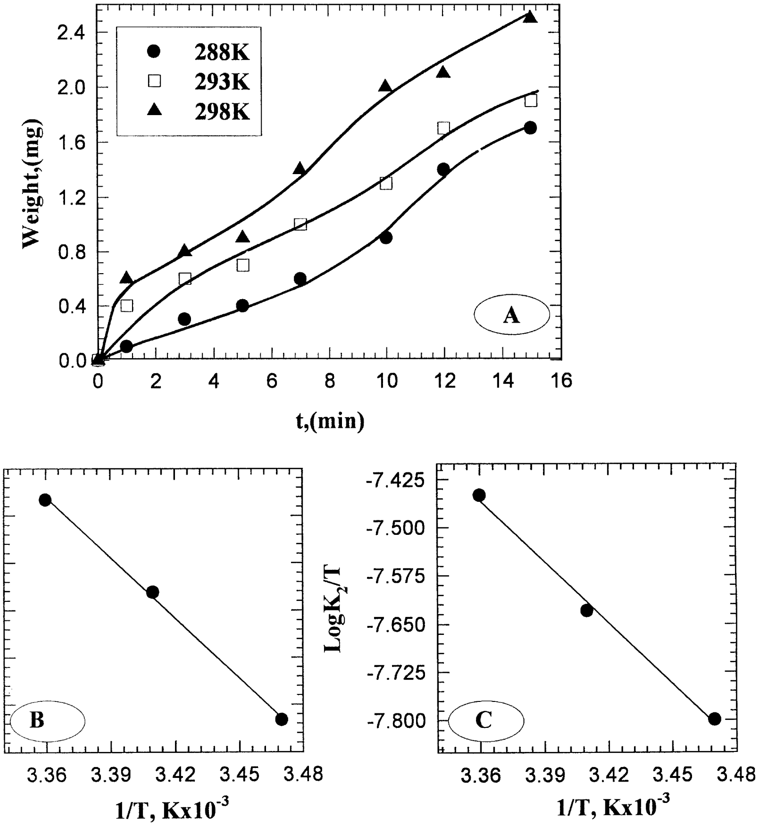


FIGURE 5 (A) Yield-time curve for the effect of temperature. (B) Arrhenius plot for the electropolymerization. (C) Eyring equation plot for the electropolymerization.

The values of k_2 at different temperatures, were calculated and the enthalpy (ΔH^*) and entropy (ΔS^*) of the activation associated with k_2 were calculated using the Eyring equation:

$$k_2 = RT/Nh\, e^{\Delta S^*/R} e^{-\Delta H^*/RT}$$

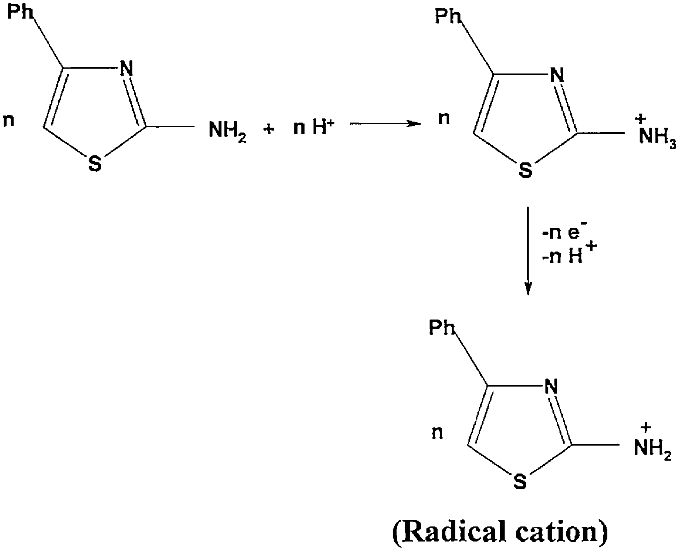
where k_2 is the rate constant, R is the universal gas constant, N is the Avogadro's number and h is Plank's constant. By plotting log k_2/T vs. $1/T$ (Figure 5C) the authors obtained a linear relationship with a slop of $-\Delta H^*/2.303R$ and an intercept of log $(R/Nh) + \Delta S^*/2.303R$. From the slope and intercept, the values of ΔH^* and ΔS^* are found to be 60.2 kJ mol^{-1} and −136.5 kg mol^{-1}, respectively.

Mechanism of the Electropolymerization

The anodic oxidative electropolymerization proceeds in several steps, as follows:

Initiation Step

In this step, the 2-amino-4-phenylthiazole monomer is oxidized by loss of electrons and formation of the radical cations as shown in Scheme 1.



SCHEME 1

Propagation Step

This step involves the interaction between the formed radical cation and a monomer to form a dimer radical cation as shown in Scheme 2.

This reaction is followed by further reaction of the formed radical cations with monomer molecules to give trimer radical cations, and so on. Quinoide structural units may occur in the polymeric chain during the polymerization reaction as mentioned in the literature [38–42,47]. The degree of electropolymerization depends on different factors such as current density, HCl concentration, monomer concentration, and temperature, as shown by the experimental data obtained from the kinetic studies. The final structure of the polymer can be illustrated as previously mentioned by Sayyah et al. [38–42].

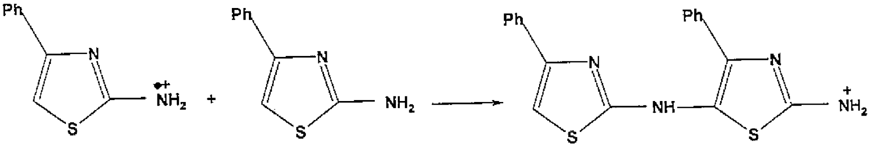
Element and Spectroscopic Analysis

Element analysis of poly(2-amono-4-phenylthiazole) was carried out in the microanalytical laboratory at Cairo University. The percentage, of C, H, N, S, and Cl are in a good agreement with those calculated for the suggested structure given in Scheme 3. The element analytical data are given in Table 1.

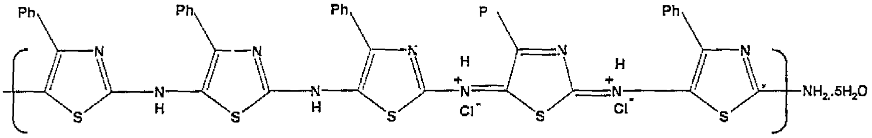
The molecular weight data obtained by GPC analysis was found to be as follows: $M_w = 238608$, $M_n = 73561$, $M_v = 190352$, and the polydispersity = 3.244.

The UV-visible spectra of the monomer and polymer show the following absorption bands:

1. In case of monomer, two absorption bands observed at $\lambda_{max} = 266$ and 292 nm may be attributed to $\pi - \pi^*$ transition (E_2 band) of the benzene ring and the B band $\pi - \pi^*$ transition (A_{1g}–B_{2u}).



SCHEME 2



SCHEME 3

TABLE 1 Element Analysis of Poly (2-amino-4-phenyl Thiazole)

Elements	C(%)	H(%)	N(%)	S(%)	Cl(%)
Calculated	51.49	3.81	13.35	15.26	8.46
Found	51.71	3.86	13.00	15.5	8.6

2. In case of polymer, two absorption bands appear at lower wavelengths (at $\lambda_{max} = 238$ and 264 nm) for $\pi - \pi^*$ transition showing a bathochromic shift. Beside these two bands an absorption band appears in the visible region at $\lambda_{max} = 360$ nm, which may be due to the high conjugation of the aromatic polymeric chains.

The infrared absorption bands and their assignments for 2-amino-4-phenylthiazole monomer and the prepared polymers are summarized in Table 2. The strong band that appears at 476 cm^{-1} for the monomer and the medium band that appears at 474 cm^{-1} for the polymer may be attributed to the out of plane deformation of skeletal C-C-S. The sharp band that appears at 619 cm^{-1} for the monomer and the corresponding medium absorption band at 618 cm^{-1} for the

TABLE 2 Infrared Absorption Bands of the IR Spectrum of 2-amino-4-phenylthiazole Monomer and the Electropolymerized Polymer Sample

Wavenumber cm^{-1}		
Monomer	Polymer	Assignment [50]
476^s	474^m	Out of plane deformation of skeletal C-C-S
619^s	613^w	NH_2 wagging in thiazole
761^m	—	Out of plane bending showing
825^m	876^m	mono-substituted benzene ring
857^m	—	Stretching vibration for S-C=N
904^m	1026^b	
1126^w	1119^w	C-S stretching in thiazole
1301^m	—	C-N skeletal in thiazole ring
1380^w	1386^m	
—	1459^m	C=N stretching vibration in quinoide structure
—	1620	C=C stretching vibration for thiazole ring
1635^s	1636	
—	3415^b	Symmetric stretching for NH_2 group
3460^b	3473^b	
—	3650^b	Stretching for free OH group in H_2O molecules present as water of crystallization in polymeric structure

s = strong; m = medium; w = weak; b = broad.

polymer could be attributed to the wagging vibration of NH_2 in the thiazole structure. The medium absorption band that appears at 1459 cm^{-1} (disappears in case of monomer) may be assigned to the stretching vibration of C = N in a quinoide structure. The strong absorption band that appears at 1635 cm^{-1} for the monomer first splits into two medium absorption bands at 1620 and 1636 cm^{-1} for the polymer, 15 ascribed to the stretching vibration for C = C in thiazole ring. The broad absorption band at 3650 cm^{-1} is attributed to the free OH group present in the polymeric structure as water of crystallization that disappears in the monomer. Other infrared absorption bands and their assignment are given in Table 2.

The ^{1}H-NMR spectrum of the prepared poly (2-amino-4-phenylthiazole) shows a multiplet signal in the region $\delta = 6.2$ to 7.7 ppm which is related to the NH proton and benzene ring protons in the polymeric structure. A singlet signal at $\delta = 10.3$ ppm is attributed to the NH_2 group protons.

As shown in Scheme 3, the presence of five water molecules for each amine chain end is confirmed by thermogravimetric analysis. The thermogravimetric data of the prepared poly(2-amino-4-phenylthiazole) is presented in Table 3. From the table, it is clear that there are four stages:

1. The first stage includes the loss of three molecules of water. In the temperature range between 25 and 235°C, the weight loss of this step was found to be 6.1%, which is in a reasonable agreement with the calculated 5.3%.
2. The second stage, in the temperature range between 235 and 287.5°C, the weight loss was found to be 4.6%, which could be

TABLE 3 Thermogravimetric Data of the Prepared Poly(2-amino, 4-phenyl thiazole)

	Weight loss (%)		
Temperature range °C	Calculated	Found	The removed molecule
25–235	5.3	6.1	$3H_2O$
235–287.5	3.6	4.6	$2H_2O$
287.5–425	7.2	8.4	2HCl
	3.35	3.8	$2NH_3$
	Remaining weight (%) above 500°C		
	—	72	—

attributed to the loss of two molecules of water. The calculated weight loss in this case equals 3.6%.

3. The third stage, in the temperature range between 287.5 and 425° C, the weight loss was found to be 12.2%, which may be due to the loss of two molecules of hydrochloric acid and two molecules of ammonia. The calculated weight loss of this stage is 10.55%.
4. In the last stage, above 500°C, a residual material (72%) remained.

Formation and Characterization by Cyclic Voltammetry

Cyclic voltammogram of electropolymerization of 2-amino-4-phenylthiazole on platinum electrode in 1.0 M HCl and 0.1 M Na_2SO_4 at 303°K was recorded and given in Figure 6 A. The cyclic voltammogram was started from -600 mV to 2000 mV (vs. SCE) with scan rate of 10 mVs^{-1} and then reversed with the same scan rate. In the absence of the monomer, the basic curve is drawn as a dashed line. In the presence of monomers, oxidation of the monomer (to give the radical cations) started at 640 mV at which the current started to rise. In this case, the voltammogram exhibits a couple of redox peaks; an anodic peak with peak potential Ep_a at 1200 mV and a cathodic peak with peak potential Ep_c at -300 mV. The Ep_a and Ep_c separation (i.e., ΔE) is high, which indicates that the electrochemical redox reaction is irreversible. The anodic peak is followed by a small capacitive current, which extends up to 2000 mV. This capacitive current could be assigned to an increase in the effective area of the electrode surface by

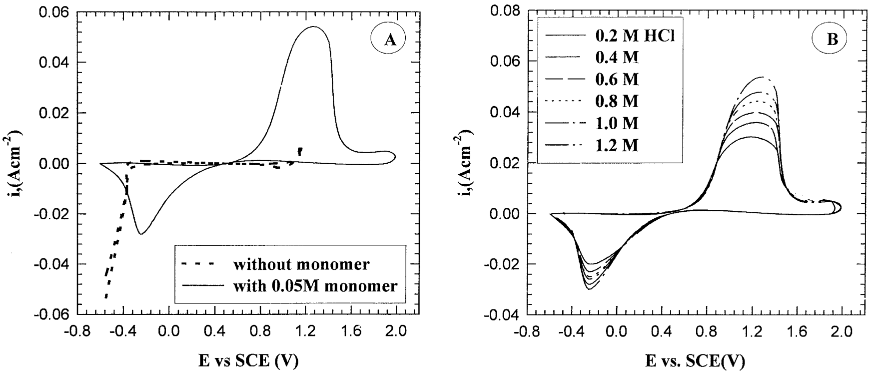


FIGURE 6 Cyclic voltammogram curves for the electropolymerization of 2-amino-4-phenylthiazole from solution contaning 0.1 M Na2SO4 at 303°K. (A) with and without 0.05 M monomer at 1.0 M HCl. (B) Effect of HCl concentration at 0.05 M monomer.

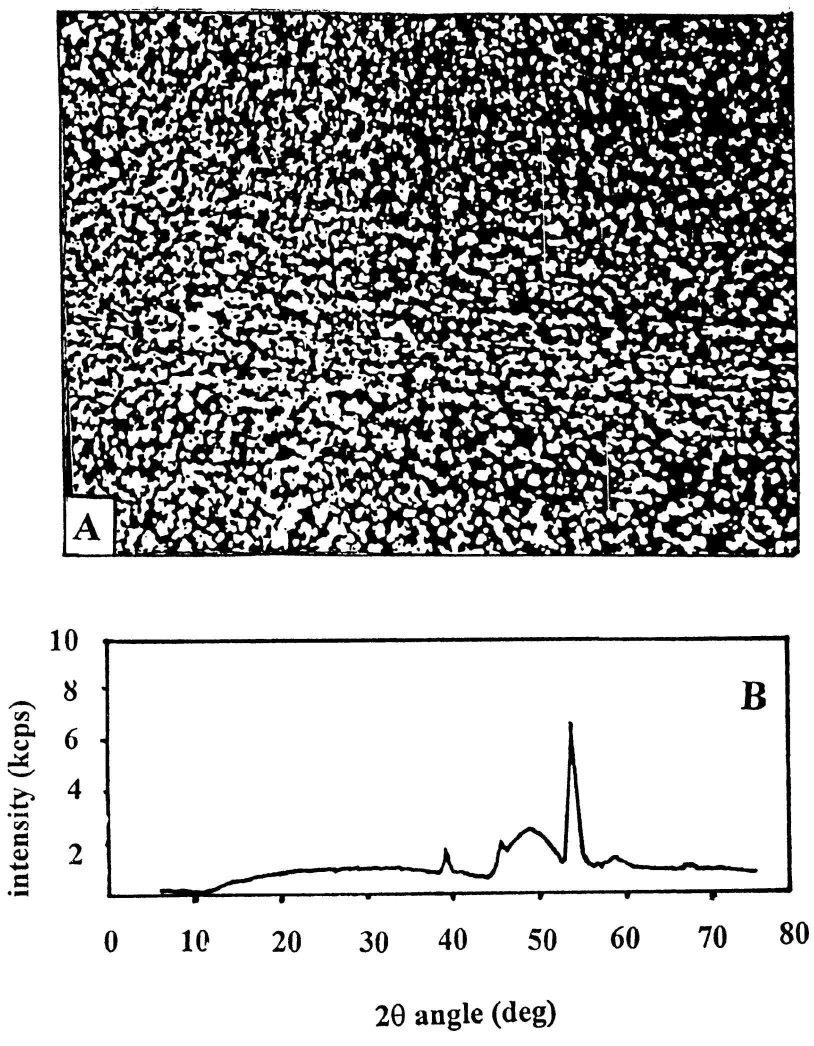


FIGURE 7 (A) Photomicrograph of the electropolymerized poly(2-amino-4-phenylthiazole). (B) X-ray diffraction patter of the electropolymerized poly (2-amino-4-phenylthiazole).

coating with the conductive polymer [48]. It is worth mentioning that the charge obtained under the anodic peak, Q_a, is always higher than that under the cathodic peak, Q_c, $(Q_a/Q_c \sim 3.5)$. This trend might be attributed to an oxidative degradation of poly(2-amino-4-phenyl thiazole) the due to very positive limit used for the electropolymerization process [49].

Cyclic voltammetric characteristics of the polymer film formation on platinum electrode as a function of the concentrations of HCl where investigated. Figure 7B represents the influence of HCl concentration (0.2 to 1.2 M) on the characteristic features of the response. As can be seen, both the anodic and cathodic peak currents are enhanced with increasing acid concentration up to 1.0 M and then start to decrease. It is observed that ΔE is eventually unaffected by variations of the acid concentration.

Surface Morphology

Homogeneous, smooth, dark brown, and well-adhering polymer films were electrodeposited on platinum surface in most conditions. The surface morphology of poly(2-amino-4-phenylthiazole) film electrodeposited from the optimum condition was examined by scanning electron microscopy. The data reveal that, the film is homogenous, compact, and consists of very fine grains of the amorphous polymer Figure (7A). X-ray diffraction pattern shows that, this polymeric film is amorphous (c.f. Figure 7B). As shown from the pattern, there is no significant peaks in the range of 2θ angle between 15 and 25°, which is characteristic for the organic polymer. The major peak at 2θ around 55° looks like a metallic peak of the platinum substrate.

CONCLUSION

In conclusion, the data reveal the following:

1. The initial rate of the electropolymerization reaction of 2-amino-4-phenylthiazole on platinum surface is relatively low. The fraction of the dissolved product may strongly depend on temperature and monomer or HCl concentration.
2. The order of the electropolymerization reaction of 2-amino-4-phenylthiazole on platinum surface is 1.06, 1.10, and 1.1 with respect to current density, acid concentration, and monomer concentration, respectively.
3. The apparent activation energy of the electro-polymerization reaction is 61.04 kJ mol^{-1}.
4. The prepared polymer film is smooth, dark brown, and well adhered to the platinum surface, and consists of very fine amorphous grains.
5. From cyclic voltammetry studies, it is clear that the voltammogram exhibits a couple of redox peaks; an anodic peak with peak potential at 1200 mV and a cathodic peak with peak potential at –300 mV.

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