

This article was downloaded by:

On: 19 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>

### Electrochemical Polymerization of 2-Amino-4-(4-methoxyphenyl)thiazole and Characterization of the Obtained Polymer

S. M. Sayyah<sup>a</sup>; S. M. Kamal<sup>a</sup>; S. S. Abd El-Rehim<sup>b</sup>

<sup>a</sup> Polymer Research Laboratory, Chemistry Department, Faculty of Science, Cairo University, Beni-Suef Branch, Beni-Suef, Egypt <sup>b</sup> Polymer Research Laboratory, Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt

**To cite this Article** Sayyah, S. M. , Kamal, S. M. and El-Rehim, S. S. Abd(2006) 'Electrochemical Polymerization of 2-Amino-4-(4-methoxyphenyl)thiazole and Characterization of the Obtained Polymer', *International Journal of Polymeric Materials*, 55: 2, 79 – 101

**To link to this Article:** DOI: 10.1080/009140390916468

**URL:** <http://dx.doi.org/10.1080/009140390916468>

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.

## Electrochemical Polymerization of 2-Amino-4-(4-methoxyphenyl)thiazole and Characterization of the Obtained Polymer

**S. M. Sayyah**

**S. M. Kamal**

Polymer Research Laboratory, Chemistry Department, Faculty of  
Science, Cairo University, Beni-Suef Branch, Beni-Suef, Egypt

**S. S. Abd El-Rehim**

Polymer Research Laboratory, Chemistry Department, Faculty of  
Science, Ain Shams University, Cairo, Egypt

*Electrochemical oxidative polymerization of 2-amino-4-(4-methoxyphenyl)thiazole on platinum electrode in hydrochloric 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 1.10, 1.10, and 0.99 with respect to current density, HCl acid, and monomer concentrations, respectively. The apparent activation energy ( $E_a$ ) was found to be  $66.91 \text{ KJ mol}^{-1}$ . The obtained polymer films are characterized by IR, UV,  $^1\text{H-NMR}$ , elemental analysis, and cyclic voltammetry. The mechanism of the electropolymerization reaction has also been discussed.*

**Keywords:** electropolymerization, 2-amino-4-(4-methoxyphenyl)thiazole, characteriza-  
tion, cyclic voltammetry

## INTRODUCTION

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

Received 20 November 2004; in final form 7 December 2004.

Address correspondence to S. M. Sayyah, Polymer Research Laboratory, Chemistry Department, Faculty of Science, Cairo University, Beni-Suef Branch, 62514 Beni-Suef, Egypt. E-mail: smsayyah@hotmail.com

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, can be readily controlled and a clean synthesis methods [18–19]. In addition, the electrochemical method provides many advantages over the chemical methods, such as easy compositional and more morphological modifications via variations and adjustment of electropolymerization conditions (i.e., methods of preparation [potentio-static, 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 a thin film form ready for device development and the electropolymerization method can provide the best way to study the polymerization mechanism in situ [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 microscopy [36] are used for characterization of conducting polymers prepared by electropolymerization.

The electrochemical behavior of 2-amino-4-phenylthiazole 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 was the azo compound as the main product of the electrode reaction.

The kinetics of the chemical polymerization of some substituted aniline in aqueous solution and the 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 authors' knowledge, no one else in the literature investigated, the rate of the electropolymerization reaction, and the orders of the reaction with respect to different electropolymerization parameters such as current density, monomer concentration, and acid concentration for the electrochemical polymerization of 2-amino-4-(4-methoxyphenyl)thiazole, and also the calculations of thermo-dynamic activation parameters such as  $\Delta H^*$ ,  $\Delta S^*$ , and  $E_a$  for this polymerization system were not performed.

The objective of the present work is to investigate the kinetics and optimum conditions for the electrochemical polymerization of

2-amino-4-(4-methoxyphenyl)thiazole as sulphur containing heterocyclic amine derivative in aqueous hydrochloric acid medium. The obtained polymer at the investigated optimum condition was characterized by UV-visible, IR, thermogravimetric analysis, and  $^1\text{H-NMR}$  spectroscopy. Cyclic voltammetry measurements were carried out at different concentrations and parameters.

## EXPERIMENTAL

### Materials

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

### Cell and Electrodes

The experimental setup used was described previously [44–46] and consists of a 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  $\pm 1^\circ\text{C}$  using a circulating water thermostat. At the end of each experiment, the anode was withdrawn, washed with distilled water, dried, and weighed. The polymerization current was supplied by d.c.-power supply (Thurby ~ Thandar PL 330).

### Electrochemical Polymerization of 2-Amino-4-(4-methoxyphenyl)thiazole

Anodic oxidative polymerization of 2-amino-4-(4-methoxyphenyl)thiazole was carried out in aqueous solution containing monomer (concentration range between 0.01 and 0.05 M) using 0.1 M  $\text{Na}_2\text{SO}_4$  as the supporting electrolyte and the current densities were investigated in the range between 4 and 14  $\text{mAcm}^{-2}$ . Electropolymerization was carried out in hydrochloric acid solution (concentration range between 0.8 and 1.6 M) at different temperatures in the range between 278 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  $1 \times 0.5 \times 0.05$  cm. Before each run, the platinum electrode was cleaned as mentioned in Cell and Electrodes.

The electrochemical experiments were performed with an EG&G potentiostat/Gavanostat 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 $^1\text{H-NMR}$ Spectroscopy

Ultraviolet-visible absorption spectra of the monomer and the electro-polymerized polymer sample were measured using a Shimadzu UV spectrophotometer (M160 PC) at room temperature in the range 200–400 nm in dimethylformamide as a solvent and reference.

Infrared measurements were carried out using a Shimadzu FTIR-430 Jasco spectrophotometer.  $^1\text{H-NMR}$  measurements were carried out using a Varian EM 360 L, 60 MHz NMR spectrometer. NMR signals of the electropolymerized samples in dimethylsulphoxide were recorded using tetramethylsilane as internal reference.

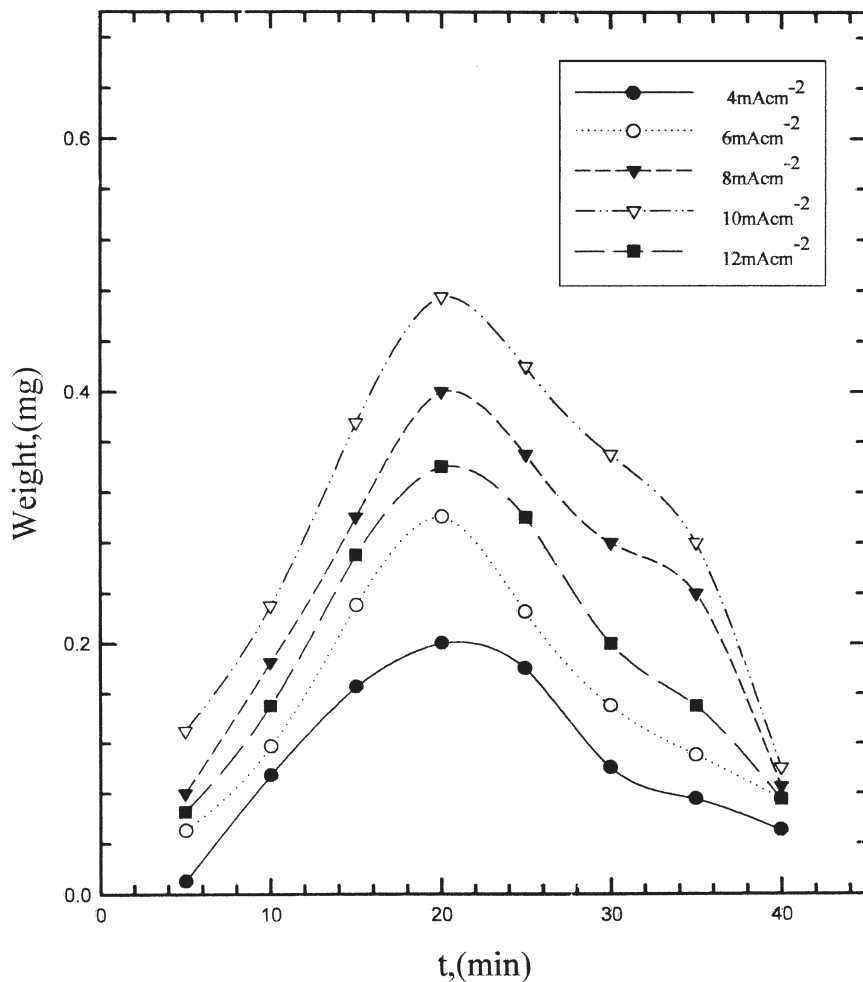
Thermogravimetric analyses of the obtained polymer at the investigated optimum conditions were performed using a Shimadzu DT-30 thermal analyzer. The weight loss in air was measured from ambient temperature up to  $600^\circ\text{C}$ , at the rate of  $10^\circ\text{C min}^{-1}$  to determine the degradation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

## RESULTS AND DISCUSSION

### Anodic Oxidative Electropolymerization

#### *Effect of Duration Time*

Anodic oxidative electropolymerization of 2-amino-4-(4-methoxyphenyl)thiazole was studied under the influence of different plating and operating parameters. The effect of time duration on the weight of the obtained polymer films was studied with different values of current densities. The data reveal that the weight of the obtained polymer film increases with increasing time duration up to 20 min. It then tends to decrease as a result of degradation and the solubility of the polymer film from the platinum surface in all investigated values of



**FIGURE 1** Yield-time curve for the effect of duration time on the anodic oxidative polymerization of 2-amino-4-(4-methoxy-phenyl)thiazole from solution containing 0.02 M monomer, 1.0 M HCl, and 0.1 M Na<sub>2</sub>SO<sub>4</sub> at 298°K.

the current densities. The data are graphically represented in Figure 1.

### **Effect of Current Density**

The effect of the applied current density on the anodic oxidative electropolymerization of 2-amino-4-(4-methoxyphenyl)thiazole was studied at constant time duration (20 min). The data reveal that, as

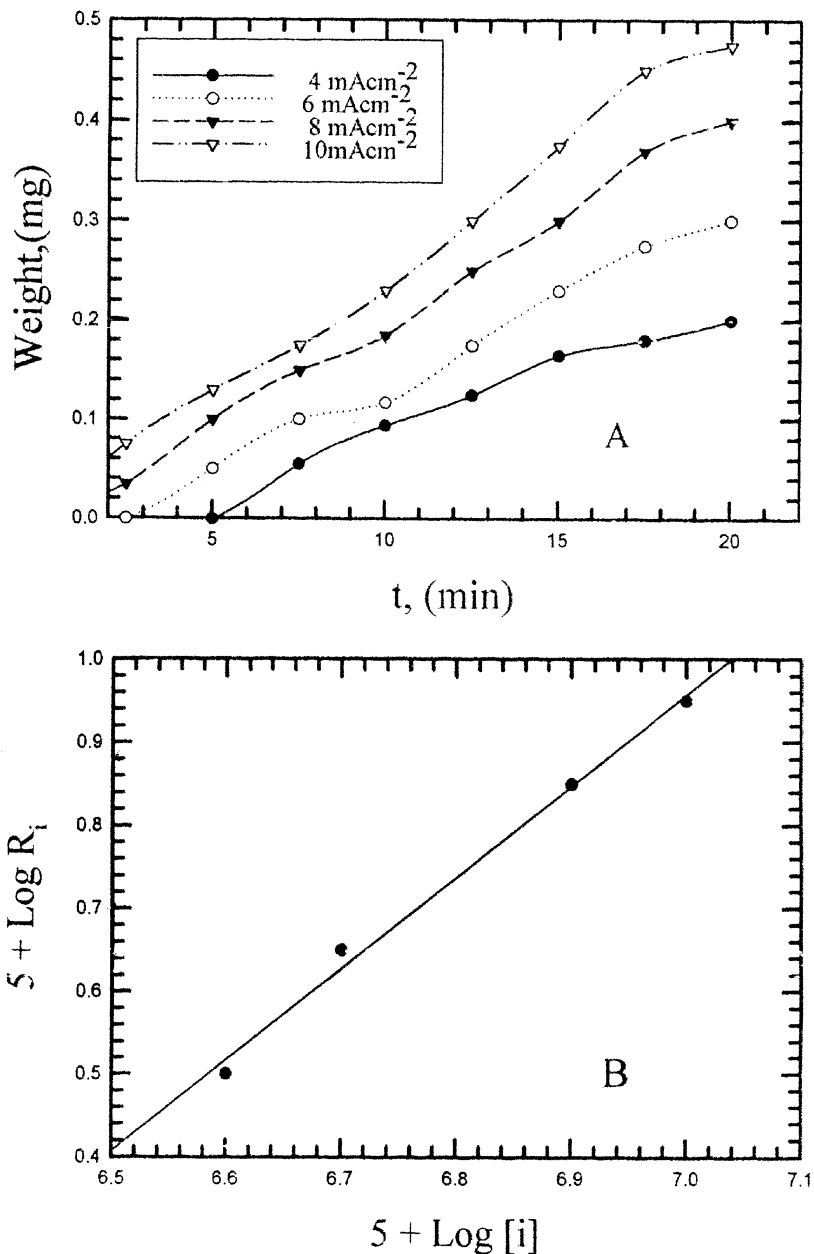
the applied current density increases, the weight of the obtained polymer increases up to  $10 \text{ mAcm}^{-2}$  and then tends to decrease. This finding implies that an oxygen and chlorine evolution takes place as a side reaction especially at high current densities. Each value of the used current density was studied with different time intervals and the yield-time curve was estimated. The data are graphically represented in Figure 2A, from which the initial rate of the electropolymerization was determined. A double logarithmic plot relating the initial rate of electropolymerization reaction to current density values is represented in Figure 2B. This relation gave a straight line. The reaction exponent with respect to the current density was determined from the slope of the obtained straight line (c.f. Figure 2B) and was found to be 1.10, which means that the order of the electropolymerization reaction with respect to the current density values is first order.

### **Effect of HCl Concentration**

Anodic oxidative polymerization was carried out using 0.02 M of monomer concentration, 0.1 M  $\text{Na}_2\text{SO}_4$  in dimethyl formamide/water mixture (30:70 v/v), current density =  $10 \text{ mAcm}^{-2}$  at 298°K, which were kept constant. But the hydrochloric acid concentration was varied in the range between 0.8 and 1.6 M. The obtained polymer film in each experiment was weighed. From the obtained data, it was noticed that the maximum weight was obtained when 1.3 M HCl concentration was used. 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 from which the initial rate of the electropolymerization reaction was calculated. The double logarithmic plot of the initial rate versus HCl concentration is represented in Figure 3B. A straight line is obtained that has a slope equal to 1.10. This means that the order of the reaction with respect to HCl concentration is first order.

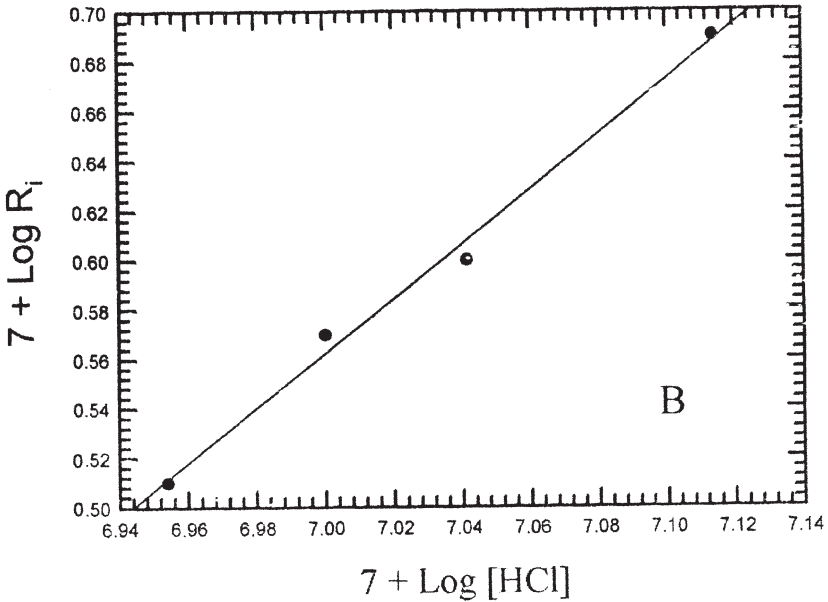
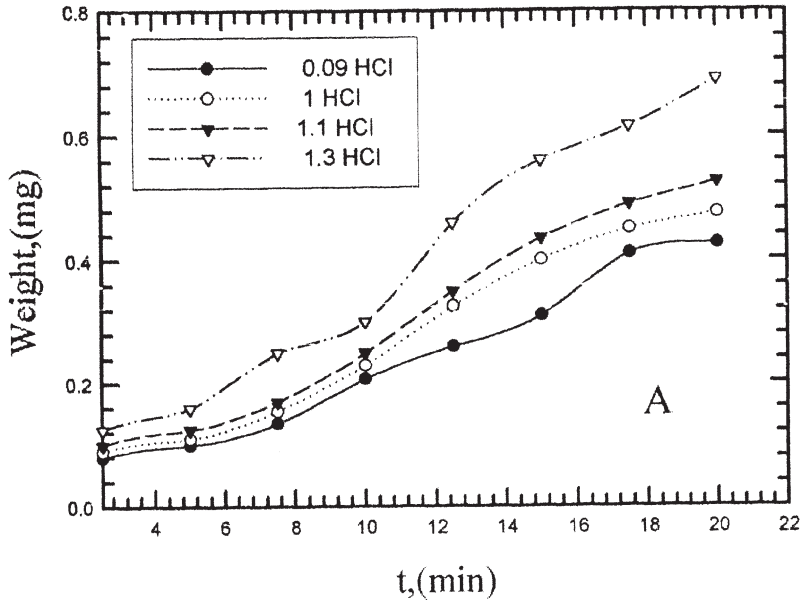
### **Effect of Monomer Concentration**

The electropolymerization reaction was carried out by keeping all the aforementioned conditions constant at 1.3 M HCl, current density =  $10 \text{ mAcm}^{-2}$ ,  $\text{Na}_2\text{SO}_4$  of 0.1 M and temperature at 298°K, but the monomer concentrations were varied in the range between 0.01 and 0.05 M. The weight of the obtained polymer film in each case was calculated. The obtained data reveal that the maximum weight of the polymer film was obtained when 0.04 M of monomer concentration was used. It was also noticed that the weight of the polymer film decreased at higher concentration of the monomer ( $>0.04 \text{ M}$ ), which means that polymer degradation may occur. Each monomer concentration

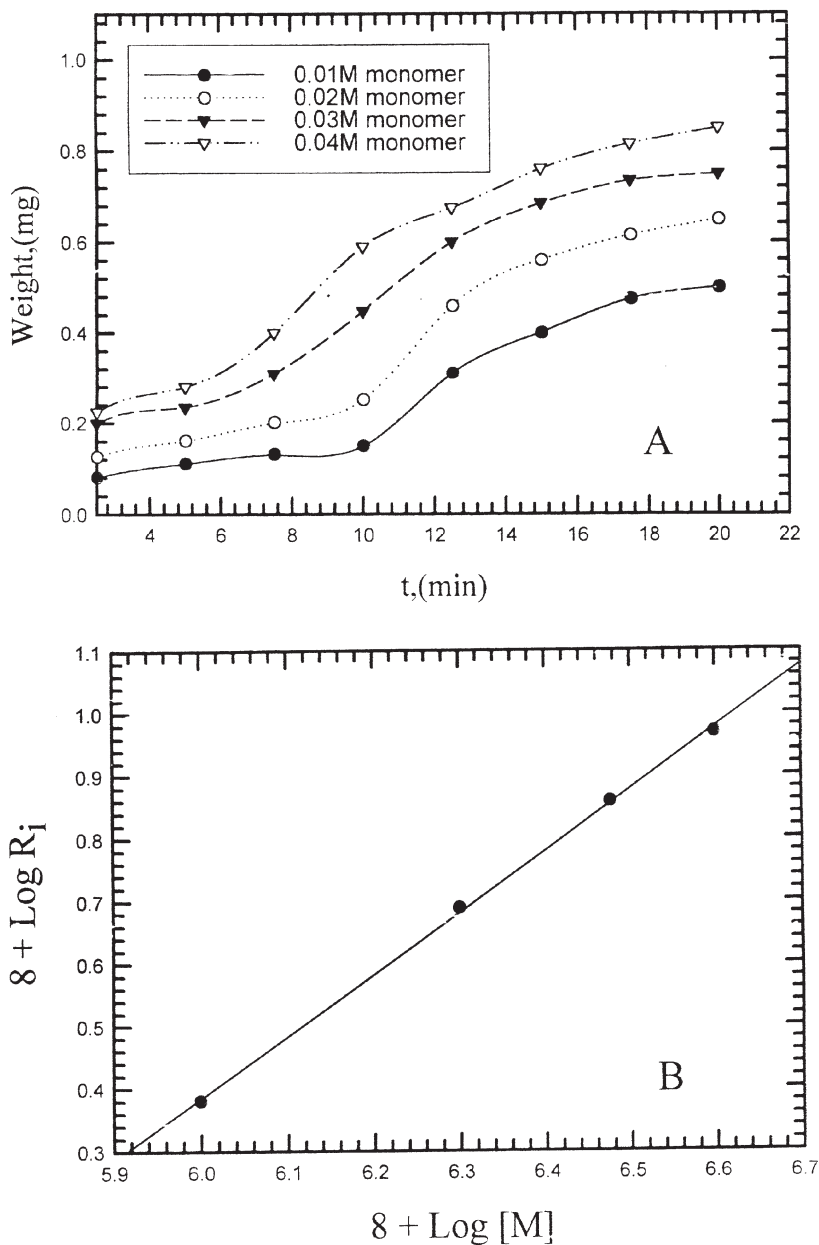


**FIGURE 2** (A) Yield-time curve for the effect of current densities; (B) Double logarithmic plot of initial rate of electropolymerization versus different current densities values. In the log-log and semi-log curves in this Figure and in the subsequent Figures 3, 4, and 5, the empty square symbols stand for the equality symbols.





**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 monomer concentration; (B) Double logarithmic plot of initial rate of electropolymerization versus monomer concentrations.

(in the range between 0.01 and 0.04 M) was investigated at different time intervals to show the effect of monomer concentration on 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 the initial rate of polymer formation versus the monomer concentration is represented in Figure 4B. This relation gave a straight line with a slope equal to 0.99, which means that the order of the electropolymerization reaction of 2-amino-4-(4-methoxyphenyl)thiazole is first order with respect to the monomer concentration.

### **Effect of Temperature**

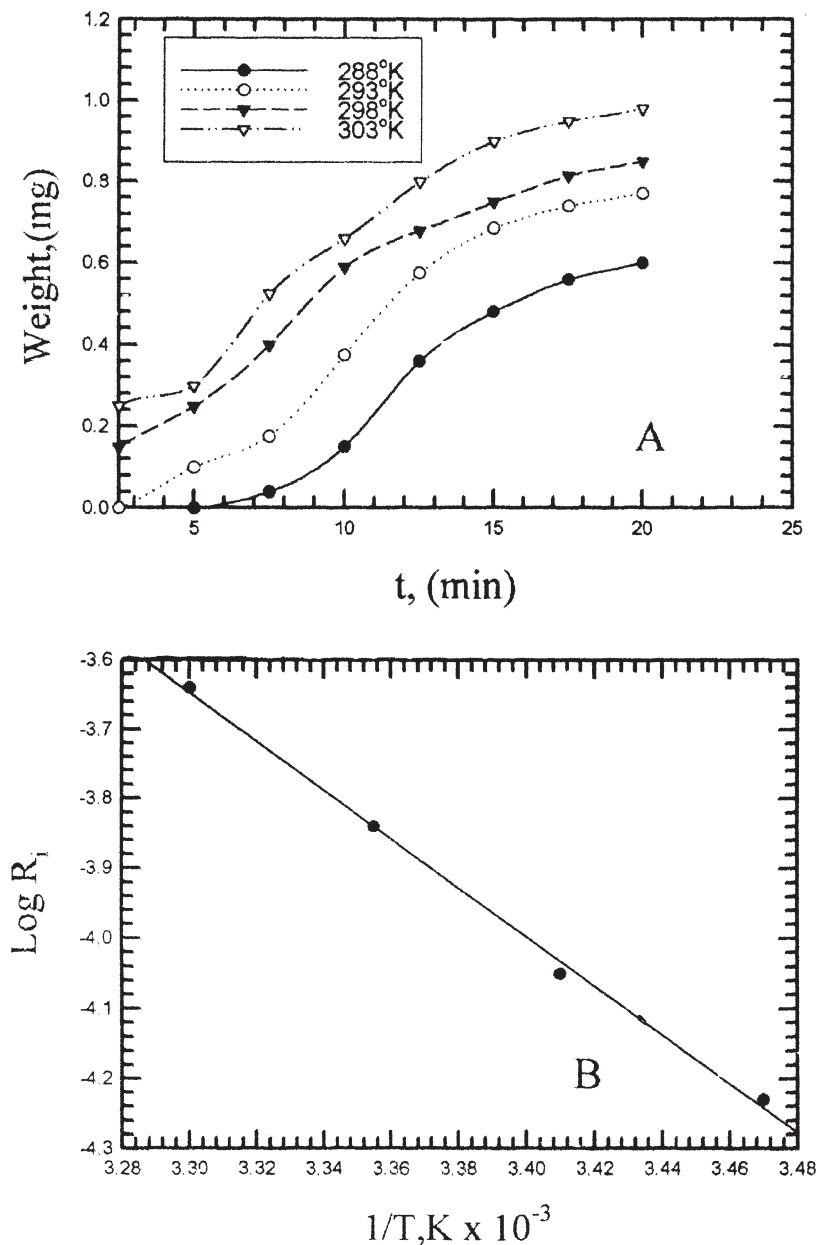
Anodic oxidative electropolymerization of 2-amino-4-(4-methoxyphenyl)thiazole was carried out under the following constant conditions: 1.3 M HCl, 0.04 M monomer, 0.1 M Na<sub>2</sub>SO<sub>4</sub> and 10 mAcm<sup>-2</sup>, but the reaction was carried out at different temperatures in the range between 278 and 323°K. The weight of polymer film was calculated at each investigated temperature. From the obtained data, it is noticed that the maximum weight of the polymer is obtained at 303°K. At higher temperature than 303°K, the polymer weight decreases with increasing temperature. It is also noticed during the experiments that, at temperatures higher than 303°K, some polymer is formed in the solution near the anode and does not adhere to the electrode. This means that, at temperature higher than 303°K, the adhesion of the polymer to the electrode decreases. The electropolymerization rate was investigated at 288, 293, 298, and 303°K. At each temperature the weight of the formed polymer at the anode was plotted versus 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 versus 1/T in Figure 5B, which gave a straight line with a slope equal to -3.501. By applying Arrhenius equation, the apparent activation energy was calculated to be 66.91 kJ/mol.

### **Calculation of Thermodynamic Parameters**

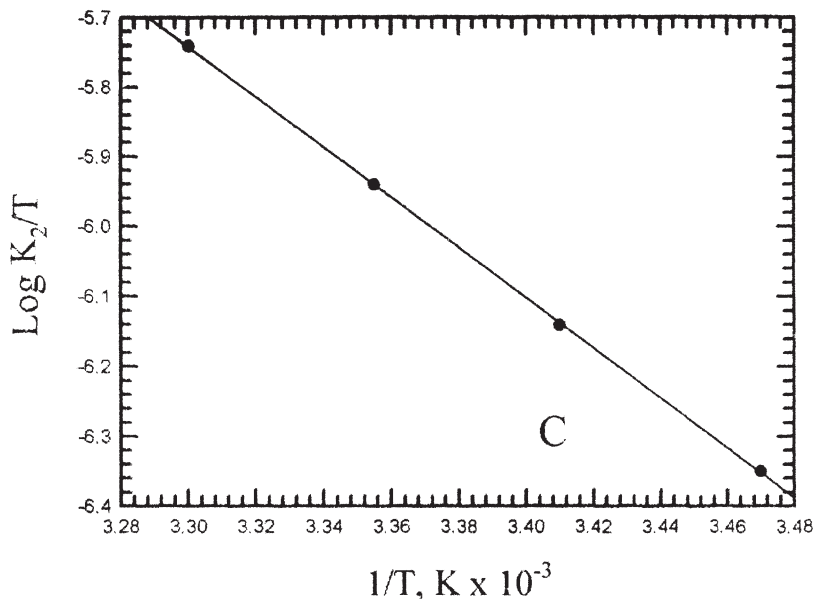
The enthalpy and entropy of activation for the electropolymerization reaction can be calculated from the K<sub>2</sub> values of the following equation:

$$\text{Reaction rate} = K_2[\text{HCl}]^{1.10}[\text{current density}]^{1.10}[\text{monomer}]^{0.99}$$

The values of K<sub>2</sub> at different temperatures were calculated and the enthalpy (ΔH\*) and entropy (ΔS\*) of the activation associated with K<sub>2</sub>



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



**FIGURE 5** Continued.

were calculated using the Eyring equation:

$$K_2 = RT/Nh e^{\Delta S^*/R} e^{-\Delta H^*/RT}$$

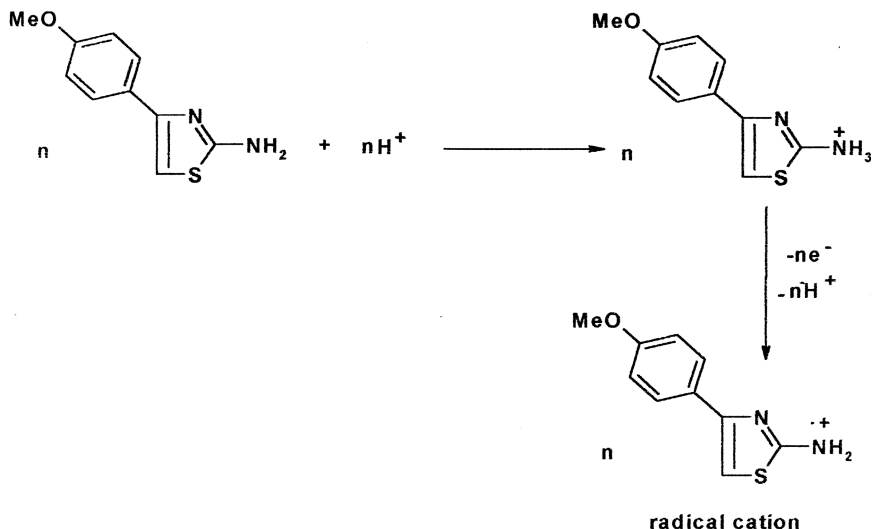
where  $K_2$  is the rate constant,  $R$  is the universal gas constant,  $N$  is the Avogadro's number and  $h$  is Plank's constant. By plotting  $\log K_2/T$  versus  $1/T$  in Figure 5C, a linear relationship was obtained with a slope of  $-\Delta H^*/2.303 R$  and an intercept of  $\log (R/Nh) + \Delta S^*/2.303 R$ . From the slope and intercept, the values of  $\Delta H^*$  and  $\Delta S^*$  are found to be  $68.66 \text{ kJ mol}^{-1}$  and  $-305.61 \text{ kJ mol}^{-1}$ , respectively.

### Mechanism of the Electropolymerization

The anodic oxidative electropolymerization proceeds in different steps as follows:

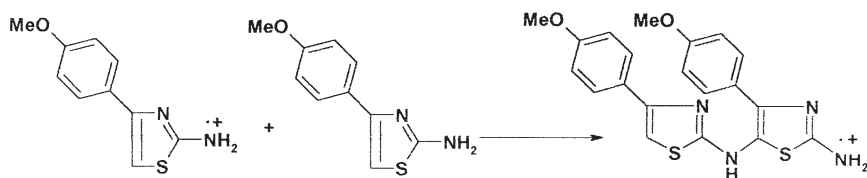
#### Initiation Step

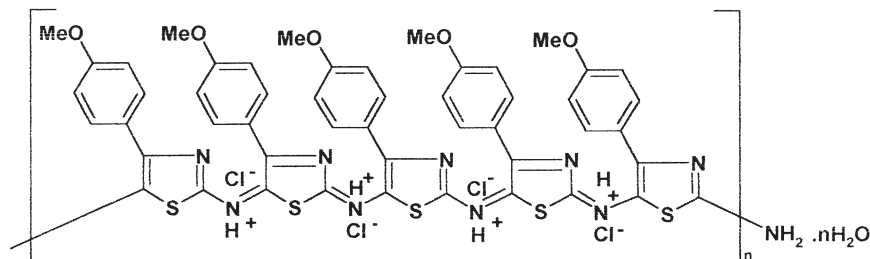
In this step, the 2-amino-4-(4-methoxyphenyl)thiazole monomer is oxidized by loss of electrons and formation of radical cations as shown in Scheme 1.

**SCHEME 1** Initiation step.**Propagation Step**

This step involves the interaction between the formed radical cation and 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. Quinoid structural units may occur in the polymeric chain during the polymerization reaction as mentioned in the literature [38–47]. 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 is illustrated in Scheme 3 as mentioned previously by Sayyah et al. [38–46].

**SCHEME 2** Propagation step.



**SCHEME 3** Structure of the synthesized polymer.

### Element and Spectroscopic Analysis

Element analysis of poly[2-amino-4-(4-methoxyphenyl)thiazole] was carried out in the microanalytical laboratory center at Cairo University. The percentages of C, H, N, S, and Cl are in good agreement with those calculated for the structure given in Scheme 3. The element analysis data are given in Table 1.

The molecular weight data obtained by GPC analysis was found to be as follows:

$M_w = 297409$ ,  $M_n = 96953$ ,  $M_v = 105473$  and the polydispersity = 3.070.

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

1. In case of monomer, three absorption bands are observed at  $\lambda_{\max} = 327.01, 330.08,$  and  $333.21$  nm, which may be attributed to  $\pi\text{-}\pi^*$  transition ( $E_2$  band) of the benzene ring and the B band  $\pi\text{-}\pi^*$  transition ( $A_{1g}\text{-}B_{2u}$ ).
2. In case of polymer one absorption band appearing at lower wavelengths (at  $\lambda_{\max} = 324.06$  nm for  $\pi\text{-}\pi^*$  transition showing bathochromic shift. Beside this band two shoulders appear at 327.5 and 330 nm. Also a broad band appears at 410 nm that could be attributed to conjugation in the polymeric chain.

**TABLE 1** Element Analysis of Poly[2-amino-4-(4-methoxy-phenyl)thiazole]

Elements	C (%)	H (%)	N (%)	S (%)	Cl (%)
Calculated	48.58	3.96	11.35	14.03	11.49
Found	48.00	4.10	11.50	13.80	12.00

The infrared absorption bands and their assignments for 2-amino-4-(4-methoxyphenyl)thiazole monomer and the prepared polymer are summarized in Table 2. The strong absorption band appearing at  $720\text{ cm}^{-1}$  for the monomer and the medium band appearing at  $726\text{ cm}^{-1}$  for the polymer may be attributed to the out of plane deformation of skeletal C–C–S.

The medium absorption band appearing at  $759\text{ cm}^{-1}$  for the polymer could be attributed to wagging vibration of  $\text{NH}_2$  in the thiazole structure. The absorption bands appearing at  $839\text{ cm}^{-1}$ , and  $825\text{ cm}^{-1}$  in case of polymer and monomer, respectively, are attributed to the 1,4-disubstituted benzene ring. The medium absorption band that appears at  $1539\text{ cm}^{-1}$  (disappears in case of monomer) may be assigned to the stretching vibration of C=N in quinoid structure. The strong

**TABLE 2** Infrared Absorption Bands of 2-Amino-4-(4-methoxyphenyl)thiazole and Its Prepared Polymer

Wave number ( $\text{cm}^{-1}$ )		Assignments [50]
Monomer	Polymer	
720 <sup>m</sup>	726 <sup>m</sup>	Out of plane deformation of C–S bond
746 <sup>m</sup>	759 <sup>m</sup>	Out of plane deformation of N–H bond
825 <sup>w</sup>	839 <sup>w</sup>	Out of plane deformation showing 1,4-disubstituted benzene ring
906 <sup>w</sup>	1031 <sup>w</sup>	In plane deformation of aromatic ring
1010 <sup>w</sup>	1132 <sup>m</sup>	
1073 <sup>m</sup>	—	
1090 <sup>m</sup>	1168 <sup>m</sup>	Stretching vibration of C–N group and C–O group
1187 <sup>s</sup>	1209 <sup>s</sup>	
—	1249 <sup>m</sup>	
1399 <sup>m</sup>	1400 <sup>m</sup>	Out of plane deformation of –O–CH <sub>3</sub> group
1494 <sup>m</sup>	1435 <sup>m</sup>	Stretching vibration of C–N in aryl NH or NH <sub>2</sub> group
—	1459 <sup>m</sup>	
—	1512 <sup>m</sup>	
1568 <sup>s</sup>	1539 <sup>s</sup>	Stretching vibration of C=C in benzene or C=N in conjugated moiety
1628 <sup>s</sup>	1602 <sup>s</sup>	
—	1673 <sup>s</sup>	
2847 <sup>m</sup>	2928 <sup>m</sup>	C–H aliphatic
2952 <sup>m</sup>	—	
3118 <sup>m</sup>	3075 <sup>m</sup>	C–H aromatic
3261 <sup>m</sup>	—	Symmetric and asymmetric stretching vibration of N–H in NH <sub>2</sub>
3387 <sup>m</sup>	—	
—	3421 <sup>m</sup>	Symmetric stretching vibration of N–H in NH <sub>2</sub> terminal group solvated by water molecules

m = medium; s = sharp; w = weak.



absorption band appearing at  $1635\text{ cm}^{-1}$  for the monomer splits into two medium absorption bands at  $1602$  and  $1673\text{ cm}^{-1}$  in case of polymer, which are ascribed to the stretching vibration for C=C in thiazole ring. The broad absorption band appearing at  $3421\text{ cm}^{-1}$  is attributed to the free OH group present in the polymeric structure as water of crystallization that disappears in case of monomer. Other infrared absorption bands and their assignment are given in Table 2.

The  $^1\text{H-NMR}$  spectrum of the prepared poly[2-amino-4-(4-methoxyphenyl)thiazole] shows a singlet signal at  $\delta = 3.82$  ppm, which is attributed to the  $\text{OCH}_3$  group protons, and a multiplet signal in the region  $\delta = 6.52$  to  $9.61$  ppm, which is related to NH proton and benzene ring protons in the polymeric structure. The singlet signal, which appears at  $\delta = 10.3$  ppm, may be attributed to the OH proton of water molecules present in the polymeric structure. When  $\text{D}_2\text{O}$  was added this signal disappeared.

As shown in Scheme 3, the presence of four-water molecule for each repeat unit is confirmed by thermogravimetric analysis. The thermogravimetric analysis data of the prepared poly[2-amino-4-(4-methoxyphenyl)thiazole] are summarized in Table 3. From the table, it is clear that there are six stages:

1. The first stage includes the loss of one molecule of water and is in the temperature range between  $25$ – $214.28^\circ\text{C}$ . The weight loss for this step is found to be  $3.49\%$  which is in a good agreement with the calculated one ( $3.16\%$ ).
2. The second stage, in the temperature range between  $214.28$  and  $358.72^\circ\text{C}$ , the weight loss was found to be  $5.08\%$ , which could be attributed to the loss of three molecules of water. The calculated weight loss of this case is equal to  $4.74\%$ .

**TABLE 3** Thermogravimetric Data of the Prepared Poly[2-amino-4-(4-methoxyphenyl)thiazole]

Temperature range $^\circ\text{C}$	Weight loss (%)		The removed molecule
	Calculated	Found	
25–214.28	3.16	3.49	$1\text{H}_2\text{O}$
214.28–358.72	4.74	5.08	$3\text{H}_2\text{O}$
358.72–442.27	14.29	14.50	$4\text{HCl}$
442.27–523.80	2.98	3.70	$2\text{NH}_3$
523.80–600	5.40	5.46	$2\text{CH}_3\text{O}$
>600	—	69.75	—

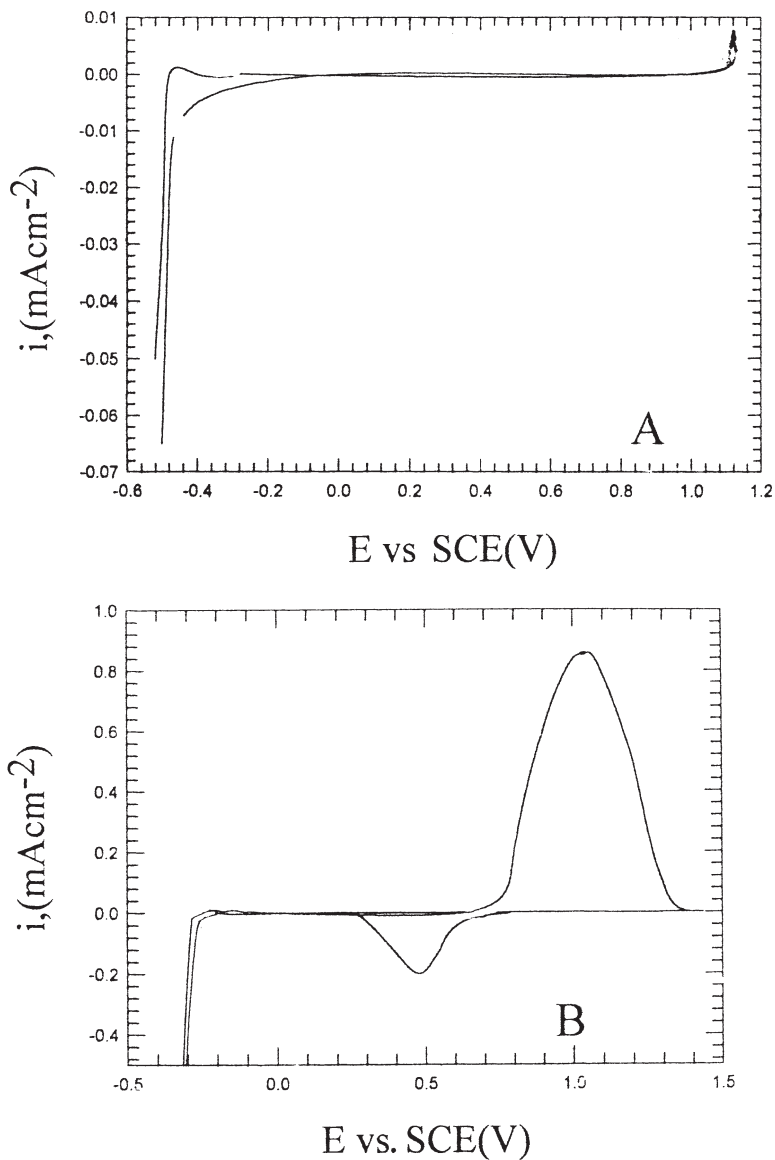
3. The third stage, in the temperature range between 358.72 and 441.27°C, the weight loss was found to be 14.5%, which may be due to the loss of four molecules of hydrochloric acid, which is in good agreement with the calculated weight loss 14.29%.
4. The fourth stage, in the temperature range between 441.27 and 523.8°C the weight loss was found to be 3.70%, which may be due to the loss of two molecules of ammonia. The calculated weight loss of this stage is equal to 2.98%.
5. The fifth stage, in the temperature range between 523.8 and 600°C, the weight loss was found to be 5.46%, which is attributed to the loss of two methoxy groups. The calculated weight loss of this stage is 5.40%.
6. The last stage, above 600°C, a residual material (69.75%) has remained as carbon and supporting electrolyte materials.

### Formation of Polymer Film and Characterization by Cyclic Voltammetry

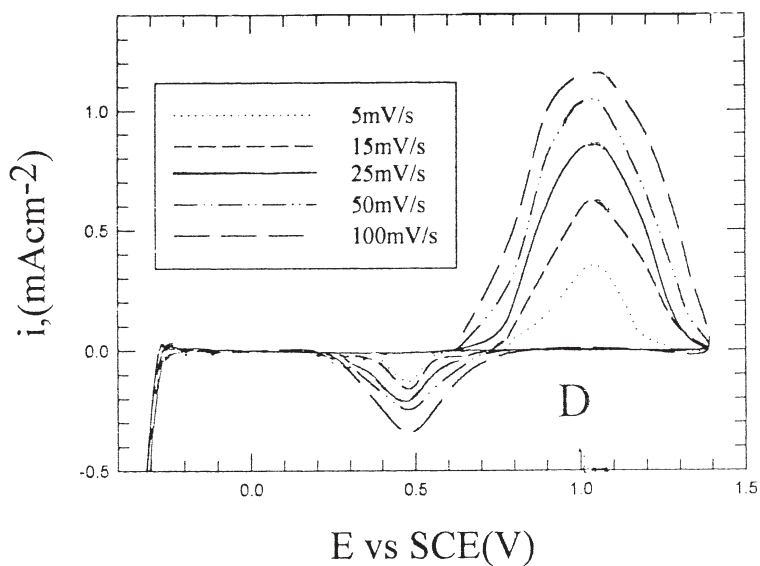
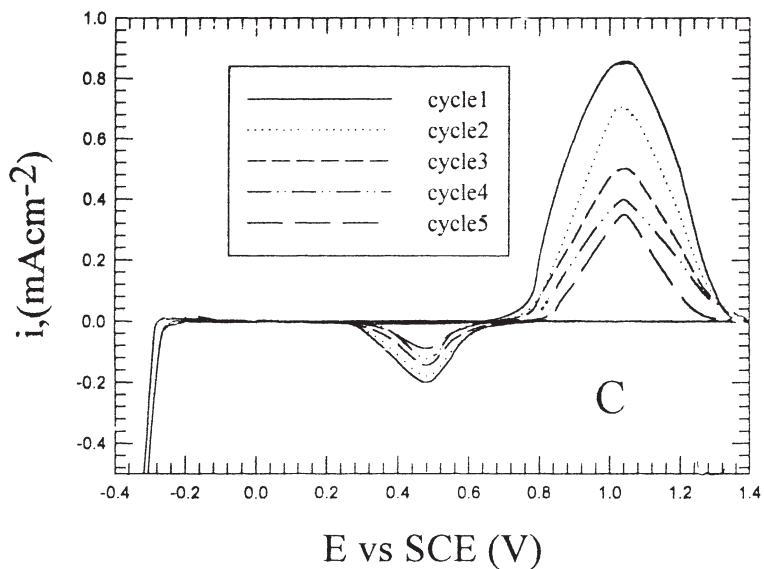
Cyclic voltammogram of polymerization of 2-amino-4-(4-methoxyphenyl)thiazole on Pt electrode, from solution containing 1 M HCl and 0.1 M Na<sub>2</sub>SO<sub>4</sub> at 298°K in the potential range from -500 to 2000 mV versus SCE at scan rate of 25 mVs<sup>-1</sup>, is represented in Figure 6B. For comparison, the cyclic voltammogram in the absence of the monomer is shown in Figure 6A. The voltammogram in the presence of monomer exhibits a couple of redox peaks; an anodic peak with peak potential  $E_{p_a}$  at 1040 mV and a cathodic peak with peak potential  $E_{p_c}$  at 480 mV. The  $E_{p_a}$  and  $E_{p_c}$  separation (i.e.,  $\Delta E$ ) is high, which indicates that the electrochemical redox reaction is irreversible. The anodic peak followed by a small capacitive current could be assigned to an increase in the effective area of the electrode surface by 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,  $Q_c$  ( $Q_a/Q_c \sim 6.929$ ).

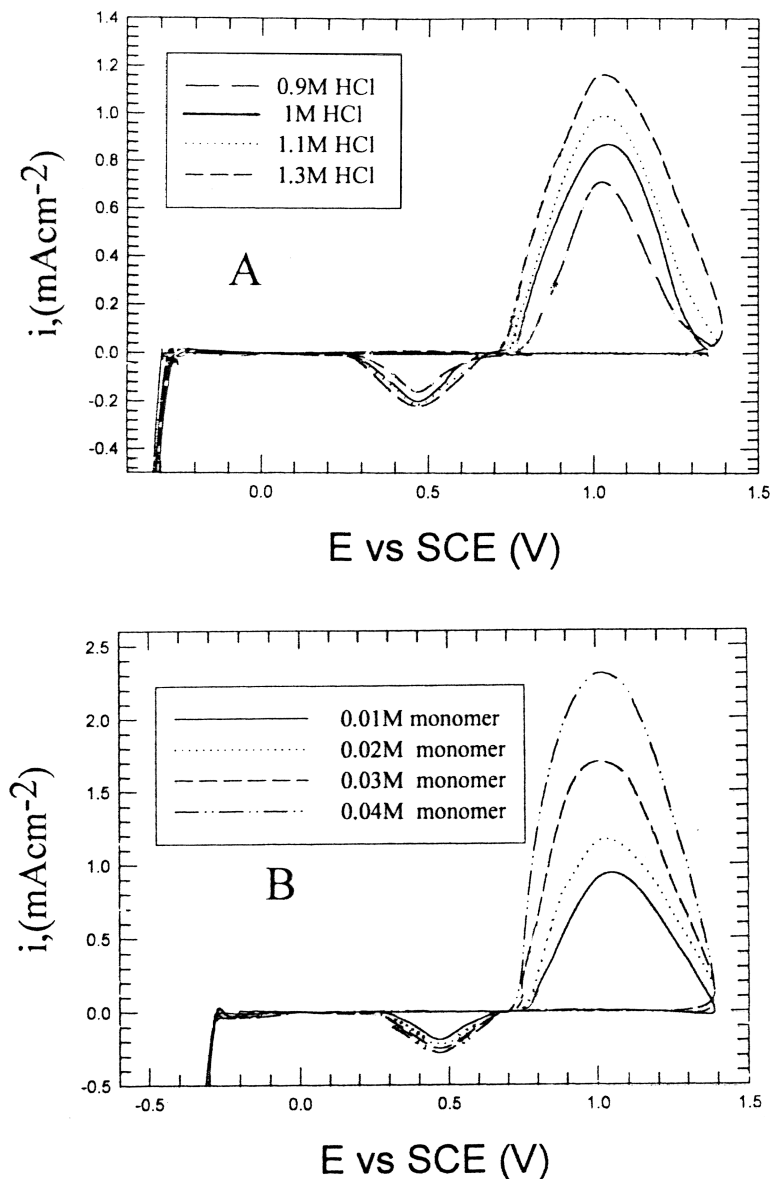
This trend might be attributed to an oxidative degradation of poly[2-amino-4-(4-methoxyphenyl)thiazole] due to the very positive limit used for electropolymerization process [49]. Moreover, it is possible that the reduction of the polymer film is not complete. Therefore the unreduced part of the film remains adhered to the electrode surface.

Figure 6C shows the effect of repetitive cycling on the electropolymerization of 2-amino-4-(4-methoxyphenyl)thiazole. The data reveal that the peak currents  $I_p$  of the anodic and cathodic peaks decrease with cycling. The decrease in the anodic current could be due to the presence of the unreduced film on the electrode surface.

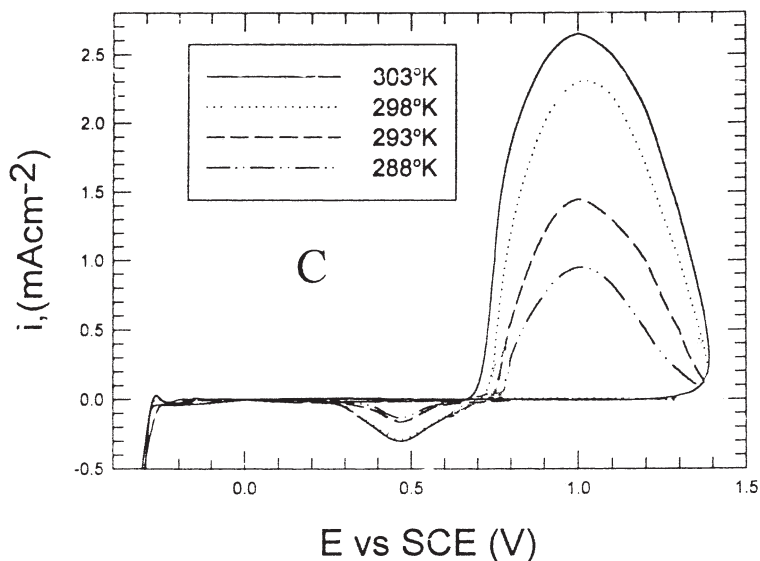


**FIGURE 6** (A) Cyclic voltammogram curve without monomer; (B) Cyclic voltammogram curve with monomer; (C) Repetitive cycling; (D) Effect of scan rate.

**FIGURE 6** Continued.



**FIGURE 7** (A) Cyclic voltammogram curves for the electropolymerization of thiazole from solution containing 0.1 M Na<sub>2</sub>SO<sub>4</sub>. (A) Effect of HCl concentrations; (B) Effect of monomer concentrations; (C) Effect of temperature.



**FIGURE 7** Continued.

Figure 6D illustrates the influence of scan rate ( $5\text{--}50\text{ mV}^{-1}$ ) on the anodic polymerization curves for 2-amino-4-(4-methoxyphenyl)thiazole on Pt electrode. The data reveal that the peak current densities  $I_p$  and  $I_c$  for the anodic and the cathodic peak, respectively, increase with increasing scan rate.

Cyclic voltammetric characteristics of the polymer film formation on platinum electrode as a function of the concentration of HCl, monomer and temperature were investigated. Figure 7A represents the influence of HCl concentration (0.9 to 1.3 M) on the characteristic features of the response. As can be seen, the anodic peak current is enhanced with increased acid concentration. As expected, the cathodic peak increases with increasing HCl concentration. Moreover, Figure 7B shows that, by increasing the monomer concentration from 0.01 to 0.04 M, the peak current as enhanced with increased monomer concentration. These results are in agreement with the kinetic data.

Figure 7C illustrates the influence of solution temperature in the range between (288 and 303°K) on the cyclic voltammetric response of the polymer formation. The data reveal that a rise of temperature up to 303°K resulted in a progressive increase of the charge included in the anodic and cathodic peaks. The data of Figure 7A–C are in agreement with those of the kinetic data.

## CONCLUSIONS

In conclusion, the data reveal the following:

1. The initial rate of the electropolymerization reaction of 2-amino-4-(4-methoxyphenyl)thiazole on platinum surface is relatively low because the calculation of the initial rate is taken on the basis of the adhered polymer film on the platinum electrode. The fraction of the dissolved product may be strongly dependent on temperature and monomer or HCl concentrations.
2. The order of the electropolymerization reaction of 2-amino-4-(4-methoxyphenyl)thiazole is 1.10, 1.10, and 0.99 with respect to current density, hydrochloric acid and monomer concentrations, respectively. The rate law is  $R_P = K_2[D]^{1.1}[HCl]^{1.1}[M]^{0.99}$ .
3. The apparent activation energy ( $E_a$ ) is 66.91 kJ/mol.
4. The prepared polymer film is a fibrillar material, smooth, yellowish brown and well adhered on platinum electrodes.
5. From cyclic voltammetry studies, it is clear that the voltammogram exhibits a couple of redox peaks, an anodic peak with peak potential at 1040 mV, and a cathodic peak with peak potential at 480 mV.
6. Further investigations on the effect of different electrolytes and presence of organic solvent on the physical properties of the prepared film and on the ability of using this material as corrosion inhibitor coating for steel should be carried out.

## REFERENCES

- [1] Kitani, A., Kaya, M., and Sasaki, K., *J. Electrochem. Soc.* **133**, 1069 (1986).
- [2] Mac Diarmid, A. G., Yang, L. S., Huang, W. S., and Humphrey, B. D., *Synth. Met.* **18**, 393 (1987).
- [3] Girard, F., Ye, S., Laperriere, G., and Belanger, D., *J. Electro-Anal. Chem.* **334**, 35 (1992).
- [4] Ye, S., Girard, F., and Belanger, D., *J. Phys. Chem.* **97**, 12373 (1993).
- [5] Ye, S. and Belanger, D., *J. Electrochem. Soc.* **141**, 149 (1994).
- [6] Morita, M., Miyazaki, S., Ishikawa, M., Matsuda, Y., Tujima, H., Adachi, K., and Anan, F., *J. Power Sources* **54**, 214 (1995).
- [7] Kobayashi, T., Yoneyama, H., and Tamoura, H., *J. Electroanal. Chem.* **161**, 419 (1984).
- [8] Genies, E. M., Lipkowski, M., Santier, C., and Viel, E., *Synth. Met.* **18**, 631 (1987).
- [9] Nguyen, M. T. and Dao, L. H., *J. Electrochem. Soc.* **136**, 2131 (1989).
- [10] Paul, E. W., Ricco, A. J., and Wrighton, M. S., *J. Phys. Chem.* **89**, 1441 (1985).
- [11] Nagaoka, T., Kakuno, K., Fujimoto, M., Nakao, H., Yano, J., and Ogura, K., *J. Electroanal. Chem.* **369**, 315 (1994).
- [12] Noufi, R., Nozik, A. J., White, J., and Warren, L. F., *J. Electro-Chem. Soc.* **129**, 2261 (1982).
- [13] Mengoli, G., Musiani, M. M., Pelli, B., and Vecchi, E., *J. Appl. Polym. Sci.* **28**, 1125 (1983).

- [14] Ohno, H., Nishihara, A., and Armoki, K., *Corros. Eng.* **36**, 361 (1987).
- [15] Lu, W., Elsenbaumer, R., and Wessling, B., *Synth. Met.* **71**, 2163 (1995).
- [16] Brusica, V., Angelopoulos, M., and Grahami, T., *J. Electro-Chem. Soc.* **144**, 436 (1997).
- [17] Bernard, M. C., Joiret, S., Hugot-Le Goff, A., and Phong, P. V., *J. Electrochem. Soc.* **148**, 12 (2001).
- [18] Yamamoto, T., Sanechika, K., and Yamamoto, A., *J. Polym. Sci.* **18**, 9 (1980).
- [19] Lim, J. W. and Dudek, L. P., *J. Polym. Sci.* **18**, 2869 (1980).
- [20] Ye, S., Do, N. T., Dao, L. H., and Vijn, A. K., *Synth. Met.* **88**, 65 (1997).
- [21] Singh, R., Narula, A. K., Tandon, R. P., Rao, S. U., Panwar, V. S., Mansingh, A., and Chandra, S., *Synth. Met.* **79**, 1 (1996).
- [22] Moteki, S. and Sykes, A. G., *J. Electroanal. Chem.* **447**, 91 (1998).
- [23] Geissler, U., Lynch, D., Rohde, N., Hallensleben, M., and Walton, D., *Synth. Met.* **84**, 171 (1997).
- [24] Viva, F., Andrade, E., Molina, F., and Florit, M., *J. Electroanal. Chem.* **471**, 180 (1999).
- [25] Miras, M., Barbero, C., and Hass, O., *Synth. Met.* **43**, 3081 (1991).
- [26] Shaolin, M. and Donghao, S., *Synth. Met.* **43**, 3085 (1991).
- [27] Middlecoff, J. and Collard, D., *Synth. Met.* **84**, 221 (1997).
- [28] Inaoka, S. and Collard, D., *Synth. Met.* **84**, 193 (1997).
- [29] Biswas, M. and Roy, A., *J. Appl. Polym. Sci.* **49**, 2189 (1993).
- [30] Ingnas, O., Liedberg, B., Chang, M., and Wynberg, H., *Synth. Met.* **11**, 293 (1985).
- [31] Geissler, U., Hallensleben, M., and Toppare, L., *Synth. Met.* **40**, 239 (1991).
- [32] Malinauskas, A. and Holze, R., *Electrochim. Acta* **43**, 2413 (1998).
- [33] Champagne, S. and Reynolds, J., *Chem. Mater* **7**, 277 (1995).
- [34] Sacak, M., Akbulut, U., and Batchelder, D., *Polym.* **39**, 4735 (1998).
- [35] Comisso, N., Daolio, S., Salmasso, R., Zecchmi, S., and Zotti, G., *J. Electroanal. Chem.* **255**, 97 (1988).
- [36] Hayat, U., Bartlett, P., and Doddi, G., *J. Electroanal. Chem.* **220**, 287 (1987).
- [37] Malik, W. U., Goyal, R. N., and Rajeshwar, J., *Bull. Chim. Soc. France* **5**, 791 (1987).
- [38] Sayyah, S. M., Abd El-Khalek, A. A., Bahgat, A. A., and Abd El-Salam, H. M., *Polym. Int.* **50**, 197 (2001).
- [39] Sayyah, S. M., Abd El-Khalek, A. A., Bahgat, A. A., and Abd El-Salam, H. M., *Int. J. Polym. Mater.* **49**, 25 (2001).
- [40] Sayyah, S. M., Bahgat, A. A., and Abd El-Salam, H. M., *Int. J. Polym. Mater.* **51**, 291 (2002).
- [41] Sayyah, S. M., Bahgat, A. A., and Abd El-Salam, H. M., *Int. J. Polym. Mater.* **51**, 915 (2002).
- [42] Sayyah, S. M., Abd El-Khalek, A. A., Bahgat, A. A., and Abd El-Salam, H. M., *Int. J. Polym. Mater.* **52**, 499 (2003).
- [43] Yun, Y. K., Leung, S., and Porco, J. A., *Biotechnology and Bioengineering (Combinatorial Chemistry)* **9**, 71 (2000).
- [44] Sayyah, S. M., Abd El-Rehim, S. S., and El-Deeb, M. M., *J. Appl. Polym. Sci.* **90**, 1783 (2003).
- [45] Sayyah, S. M., Abd El-Rehim, S. S., and El-Deeb, M. M., *Int. J. Polym. Mater.* **53**, 1 (2004).
- [46] Sayyah, S. M., Abd El-Rehim, S. S., and El-Deeb, M. M., *J. Appl. Polym. Sci.* **94**, 941 (2004).
- [47] Rong, Z. X. and Man, K. T., *Polym.* **39**, 1187 (1998).
- [48] Diaz, A. F., Castillo, J. I., Logan, J. A., and Lee, W. Y., *J. Electroanal. Chem.* **129**, 115 (1981).
- [49] Sazou, D. and Georgolios, C., *J. Electroanal. Chem.* **429**, 81 (1991).
- [50] Silverstien, R. M., Bassler, C. G., and Morill, T. C. (1974). *Spectroscopic Identification of Organic Compounds*, Wiley, New York.