

Electrocopolymerization of a Binary Mixture of Pyrrole and 2-amino-4-phenylthiazole: Kinetic Studies, Copolymer Structure, and Applications as Corrosion Protection for Mild Steel in Acid Medium

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Received 27 February 2006; accepted 16 June 2006

DOI 10.1002/app.25143

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Electrochemical copolymerization of a binary mixture of pyrrole and 2-amino-4-phenylthiazole on platinum electrode in acid medium was carried out. The kinetic parameters were calculated using *ex situ* microgravimetric and electrochemical data. The experimentally obtained kinetic equations were $R_{p,W} = k_W [\text{acid}]^{1.16} [\text{monomer}]^{1.85}$ from microgravimetric data and $R_{p,E} = k_E [\text{acid}]^{1.1} [\text{monomer}]^{1.9}$ from the values of the anodic current density using cyclic voltammetry technique. The apparent activation energy was calculated by the two techniques and is found to be 32.55 and 29.6 kJ/mol from microgravimetric

and electrochemical data respectively. The monomer reactivity ratios (r_1 and r_2) were calculated according to Fineman–Ross method and the copolymer structure was determined from the obtained data, which is found to be a block copolymer structure. The applications of the prepared copolymer as corrosion protection of mild steel in acid medium are studied. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 4047–4058, 2007

Key words: electrocopolymerization; kinetics; copolymer structure; pyrrole; 2-amino-4-phenylthiazole

INTRODUCTION

Electropolymerization of conducting polymers form a relatively new class in polymer science and have the potential of being used in a large number of different applications in batteries,^{1–6} electrochromic devices,^{7–9} microelectronic devices,¹⁰ sensors,^{11–18} and as corrosion inhibitors to protect semiconductors and metals.^{19–24}

Conducting polymers containing two compounds can be prepared as copolymers, composites, bilayers, or blends. This is done for the improvement of the physical, chemical, mechanical, and electrical properties of the homopolymers.

Sayyah et al.²⁵ studied the electrocopolymerization and characterization of a binary mixture of 3-chloroaniline and 2-amino-4-phenylthiazole on platinum electrode in acid medium under different reaction conditions such as temperature, current density, hydrochloric acid, and monomer concentrations with varying time duration. They found that the copolymer structure is a block structure and the initial rate of the electrocopolymerization is low. The order of the electrocopolymerization reaction is 1.29, 0.97, and 1.94 with respect to current density, hydrochloric

acid, and monomer concentration, respectively. The apparent activation energy was 38.87 kJ/mol.

The effect of monomer and electrolyte concentration on the kinetics of the electropolymerization of pyrrole on platinum electrode from acetonitrile solution was investigated using microgravimetric studies, polymerization charge, anodic charge of the control voltammograms, anodic and cathodic charge of the control chronoamperograms.²⁶ From the obtained data, they found that the kinetic rate equations from microgravimetric determination is $R_p = k [\text{pyrrole}]^{0.5} [\text{ClO}_4^-]^{0.5}$, from polymerization charge is $R_p = k [\text{pyrrole}]^{0.4} [\text{ClO}_4^-]^{0.5}$, from anodic charge is $R_p = k [\text{pyrrole}]^{0.4} [\text{ClO}_4^-]^{0.5}$, and from anodic and cathodic charge is $R_p = k [\text{pyrrole}]^{0.4} [\text{ClO}_4^-]^{0.4}$.

Genies et al.²⁷ studied the kinetic of the electrochemical charge transfer in polypyrrole by the determination of the apparent diffusion coefficient (D_{app}) of the transferred species by a chronoabsorptometric method. The data show that the D_{app} is a function of the electrolyte concentration in the solution in contact with the polymer film.

The kinetics of the chemical and electrochemical polymerization of some meta, ortho, and N-substituted aniline, thiazole derivatives, and pyrrole in hydrochloric acid solution were investigated by Sayyah et al.^{28–36} The orders of the electropolymerization reaction with respect to some reaction parameters such as current density, monomer, and acid concentrations were calculated. The rate laws and the appa-

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rent activation energies (E_a) of the chemical and electrochemical polymerization process were determined. The characterization of the obtained polymers was carried out using spectroscopic analysis.

The objective of the present work is to investigate the kinetics of the electrochemical copolymerization of a binary mixture of pyrrole and 2-amino-4-phenylthiazole in aqueous (DMF/H₂O, 30 : 70, v/v) hydrochloric acid medium by *ex situ* microgravimetric and electrochemical techniques, using different acid and monomer concentrations. Also, the monomer reactivity ratios (r_1 and r_2) were calculated using Fineman–Ross method. Applications of the prepared copolymer as corrosion protection of mild steel in acid medium are studied by Tafel method.

EXPERIMENTAL

Materials

Pyrrole, hydrochloric acid solution, anhydrous sodium sulfate, and dimethyl formamide are of analytical pure grade provided from Merck (Germany). 2-Amino-4-phenyl thiazole was synthesized in our laboratory by the method reported in the literature.³⁷ All solutions are freshly prepared using double distilled water.

Cell and electrodes

Three electrode cell for cyclic voltammetry technique

A standard three-electrode cell was used with saturated calomel electrode (SCE) as the standard reference electrode. The auxiliary electrode was a platinum wire. The dimensions of the platinum foil-working electrode were 1 cm × 0.5 cm × 0.05 cm. Before each run, the platinum electrode was cleaned and washed with distilled water, rinsed with ethanol, and dried. The experiments were conducted at the required temperature (with an allowance of ±1°C), maintained using a circular water thermostat.

The electrochemical experiments were performed using the Potentiostat/Galvanostat Wenking PGS 95, connected to the computer. The *I*-*E* curves were recorded using computer software (Model ECT).

Two electrode cell for *ex situ* microgravimetric technique

The experimental set up used was described elsewhere^{25,33–36} and consisted 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 (with an allowance of ±1°C), maintained using a 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 using a constant potential DC-power supply (Thurby Thandar PL 330).

Molecular weight determination

Molecular weights of the obtained copolymer samples were determined using GPC instrument model HP-6890(FID), HP-Hawelt (USA), column type HP-5 5% phenylmethylsiloxane (30 m length and 250 μm diameter). The flow rates of O₂, H₂, N₂, and the carrier gas were 300, 30, 25, and 0.6 mL/min, respectively, at 45°C.

Corrosion measurements

Working electrode

The working electrode used in the present work was made from mild steel specimen (98.5% Fe, 0.33% C, 0.24% Si, 0.52% Mn, 0.04% Cr, and 0.02% S) axially embedded in an Araldite holder to offer an active flat disc-shaped surface of 2 cm² area. Prior to each experiment, the working electrode was polished successively with fine grade emery papers. The polished metal surface was rinsed with acetone and distilled water before electrodeposition of polymer film on its surface.

Preparation of the copolymer film on mild steel working electrode

The electrical circuit used for the electrodeposition of the copolymer consisted the electropolymerization cell in which the steel working electrode (acted as anode) and a platinum foil electrode (acted as cathode) were immersed and fixed in their appropriate positions in the test solution (H₂O/DMF (30 : 70, v/v)) containing 0.1M Na₂SO₄, as supporting electrolyte, and the monomer. At the end of each experiment, the working electrode was removed, washed with distilled water, and dried before use in the corrosion experiments. The obtained copolymer films adhered well to the mild steel electrode surface.

Corrosion measurements

The working electrode (steel coated by copolymer film), platinum auxiliary electrode, and SCE (as reference) were introduced into the electrolytic cell containing 1M HCl solution. Potentiodynamic polarization measurements were performed using the Potentiostat/Galvanostat Wenking PGS 95, connected to the computer. The experiments were carried out by changing the electrode potential automatically at a scan rate of 25 mVs⁻¹ from -580 to -520 mV and the *I*/*E* curves were recorded using computer software

(Model ECT). For each run, a freshly prepared solution and new set of electrodes were used. Each run was conducted at constant temperature $\pm 1^\circ\text{C}$, maintained using circular water thermostat.

RESULTS AND DISCUSSION

Electrochemical copolymerization

Cyclic voltammograms of 0.05M pyrrole (Py), 0.05M 2-amino-4-phenylthiazole (APTh), and 0.05M comonomers (molar ratio 1 : 1) from aqueous solution (30 : 70 DMF/H₂O) containing 1.0M HCl and 0.1M Na₂SO₄ at 303 K with scan rate of 25 mV s⁻¹ are shown in Figure 1. The data show that the onset potentials for the oxidation of pyrrole and 2-amino-4-phenylthiazole

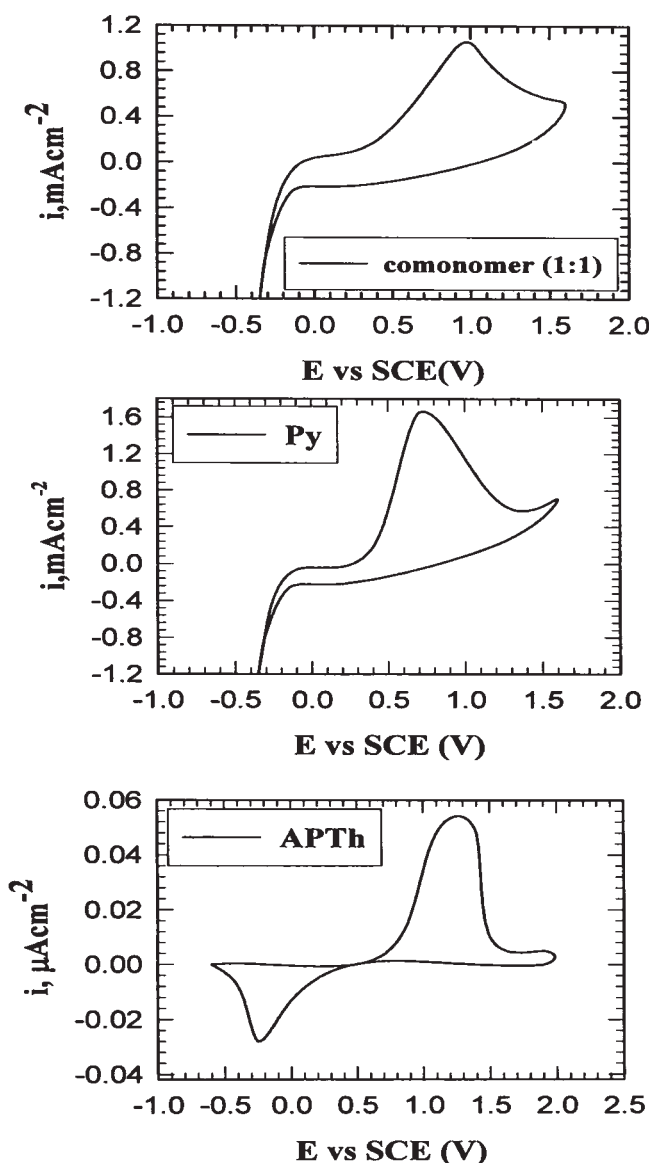


Figure 1 Cyclic voltammogram curves of Pt electrode in 1M HCl aqueous solution containing 0.1M Na₂SO₄ in the presence of 0.05M Py, 0.05M APTh, and 0.05M comonomer with scan rate of 25 mV s⁻¹ at 303 K.

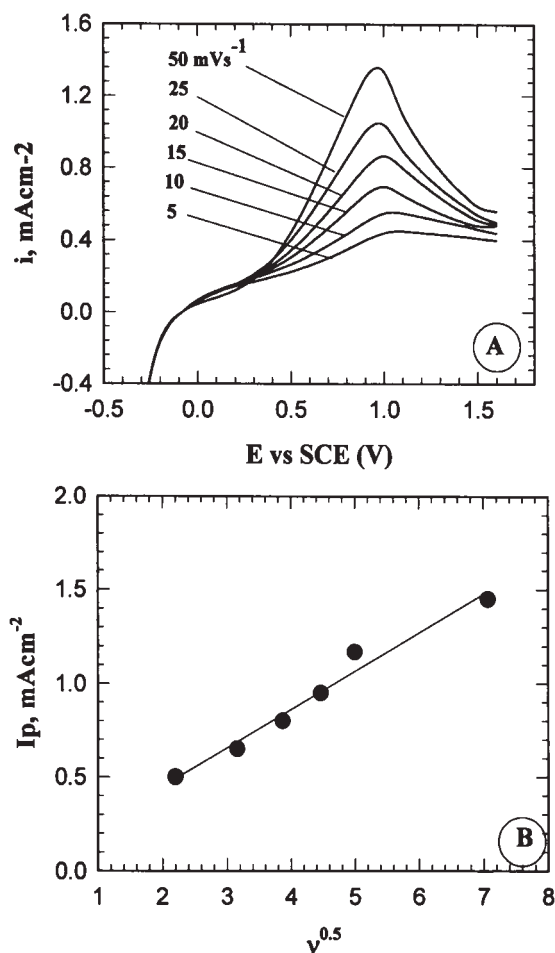


Figure 2 A: Effect of scan rate on the electrocopolymerization of a binary mixture of Py and APTh from solution containing 0.05M comonomers (1 : 1), 1.0M HCl and 0.1M Na₂SO₄ at 303 K. B: Relation between I_p vs $v^{0.5}$.

are 700 and 1200 mV, respectively. This potential is related to the oxidation of monomers to radical cation, which is considered to be the first step in the polymerization of the conducting polymer.^{33–36,38} The lower onset potential for the oxidation of pyrrole by comparison with 2-amino-4-phenylthiazole indicates that the oxidation of pyrrole is faster than that of 2-amino-4-phenylthiazole.

The cyclic voltammogram of the comonomers with molar ratio 1 : 1 gives one oxidation peak at 900 mV that may correspond to the oxidation of the two monomers. The onset potential for the oxidation of the comonomer shifts to lower potential than that of 2-amino-4-phenylthiazole, indicating that a mixture of the comonomer is oxidized more easily than did 2-amino-4-phenylthiazole alone. It is indicative of the predominance of pyrrole on the initiation of the copolymerization reaction, which indicates that the number of pyrrole segments in the copolymer chain is higher than in 2-amino-4-phenylthiazole.

The influence of scan rate (5–50 mV s⁻¹) on the electrocopolymerization of the binary mixture under

investigation on platinum electrode was studied and the data are graphically represented in Figure 2(A). The data reveal that the current densities of the anodic peaks (I_{pa}) increase with the increase in the scan rate.

Figure 2(B) shows the linear dependence of anodic current densities versus the square root of the scan rate (I_{pa} vs. $v^{0.5}$). This linear relation suggests that the electrogeneration of the copolymer film on the electrode surface may be described partially by diffusion-controlled process (diffusion of reacting species to the polymer film/solution interface).

Figure 3 shows the repetitive cycling of the electrocopolymerization of a binary mixture of pyrrole (Py) and 2-amino-4-phenylthiazole (APTh) (molar ratio 1 : 1). The data show that the current densities of the anodic peaks (I_{pa}) decrease as the number of cycle increase due to the film become thicker. An increase in the thickness of the deposited film decreases its conductivity and also decreases the rate of the diffusion within the film.

Kinetic studies

The electrocopolymerization kinetics were analyzed from aqueous (DMF/H₂O 30 : 70, v/v) solution containing 0.1M Na₂SO₄ at 303 K with different concentrations of HCl and monomer. The kinetic equation was calculated from two different sets of data:¹ by means of *ex situ* microgravimetric study (two electrode cell),² by means of electrochemical study from

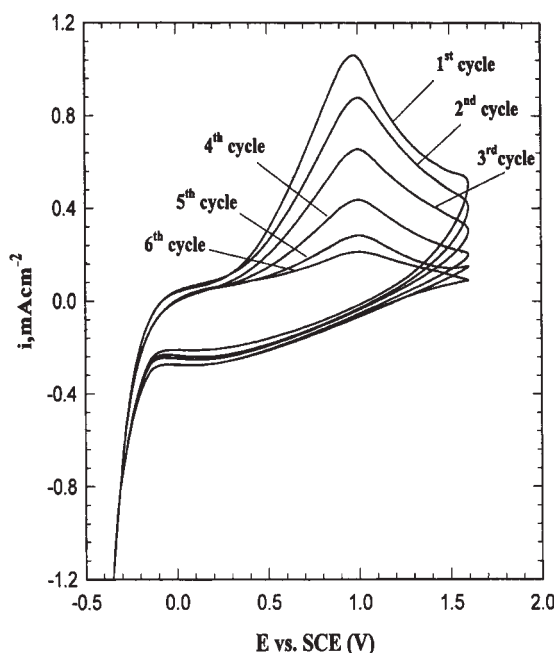


Figure 3 Repetitive cycling of the electrocopolymerization of a binary mixture of Py and APTh from solution containing 1.0M HCl, 0.05M comonomer (1 : 1), and 0.1M Na₂SO₄ at 303 K with scan rate of 25 mV s⁻¹.

the values of the anodic current densities (three electrode cell).

Ex situ microgravimetric study

The copolymerization rate at constant voltage ($R_{P,W}$) is defined as the polymer mass (M) obtained per unit time according to the following equation:³⁹

$$R_{P,W} = dM/dt = k_W[\text{Acid}]^a[\text{Monomer}]^b \quad (1)$$

where a and b are the reaction orders and k_W is the kinetic rate constant calculated from *ex situ* microgravimetric study. The value of the reaction order associated with the acid concentrations $[\text{Acid}]^a$ is obtained by keeping the monomer concentration $[\text{Monomer}]$ constant and varying the acid concentration. Equation (1) can then be rewritten as

$$R_{P,W} = k_W[\text{Acid}]^a \quad (2)$$

or expressed logarithmic as

$$\log R_{P,W} = \log k_W + a \log[\text{Acid}] \quad (3)$$

By plotting the logarithmic of the copolymerization rate against the logarithmic of the acid concentration, a straight line was obtained, its slope corresponds to the value of the reaction order.

Figure 4(A) shows the evaluation of the electrogenerated copolymer weight as a function of the polymerization time from different HCl concentrations (0.2, 0.4, 0.6, and 0.8) with monomer concentration fixed at 0.05M (molar ratio 1 : 1), Na₂SO₄ at 0.1M, and temperature at 303 K. The upper limit of acid concentration (0.8M) is limited by the maximum weight of the adhered copolymer on the platinum electrode. The copolymerization rate was calculated at each concentration and the double logarithmic plot of the copolymerization rate versus HCl concentrations yields a straight line [cf. Fig. 4(B)]. Least square analysis yields the following equation:

$$\log R_{P,W} = 0.3 + 1.16 \log[\text{Acid}]$$

where the value of the slope (1.16) corresponds to the reaction order with respect to the acid concentrations.

The effect of monomer concentrations were carried out by keeping the acid concentration fixed at 0.8M, Na₂SO₄ at 0.1M, and temperature at 303 K. The monomer concentrations were varied in the range between 0.02 and 0.08M (molar ratio 1 : 1) and the weight of the obtained copolymer film in each case was determined. From the obtained data, we notice that the maximum weight of the copolymer film was obtained when a monomer concentration of 0.06M was used. The electrocopolymerization was performed with different monomer concentrations in the range between 0.02

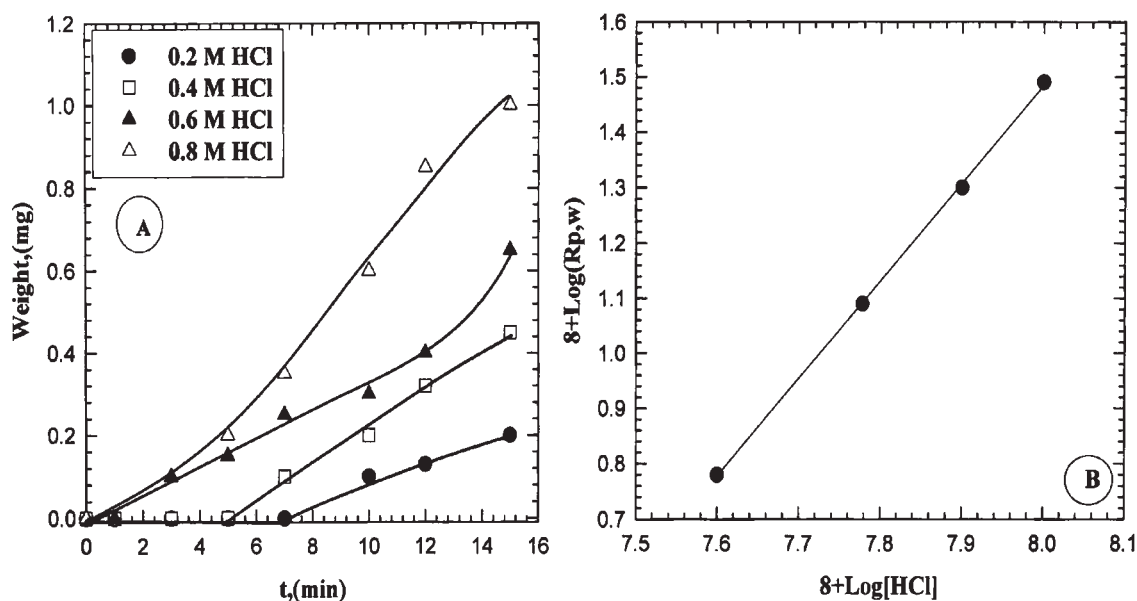


Figure 4 A: Yield-time curves for the effect of HCl concentrations. B: Double logarithmic plot of the initial rates of the electrocopolymerization vs HCl concentrations.

and 0.06M (molar ratio 1 : 1) at different polymerization time interval and the data are represented in Figure 5(A). The copolymerization rate was calculated and the double logarithmic plot of the copolymerization rate versus the monomer concentration is represented in Figure 5(B). This relation gave a straight line whose equation is

$$\log R_{p,w} = 0.1 + 1.85 \log[\text{Monomer}]$$

where the value of the slope corresponds to the order of the reaction with respect to the monomer concentrations.

The kinetic rate law obtained from an *ex situ* microgravimetric study for the electrocopolymerization reaction can be expressed as follows:

$$R_{p,w} = k_w[\text{Acid}]^{1.16}[\text{Monomer}]^{1.85}$$

Electrochemical study

The kinetic equation was calculated from the values of the anodic current densities produced at each concentration during the electrogeneration of the copolymer. The values of the anodic current density (I_{pa}) is proportional to the electrocopolymerization rate ($R_{p,E}$) at

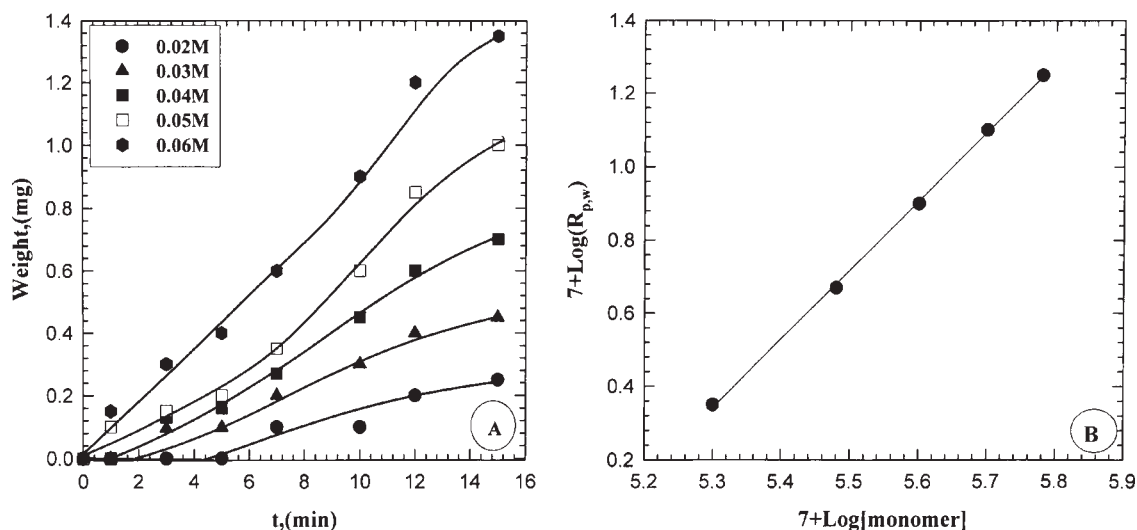


Figure 5 A: Yield-time curves for the effect of monomer concentrations. B: Double logarithmic plot of the initial rates of the electrocopolymerization vs monomer concentrations.

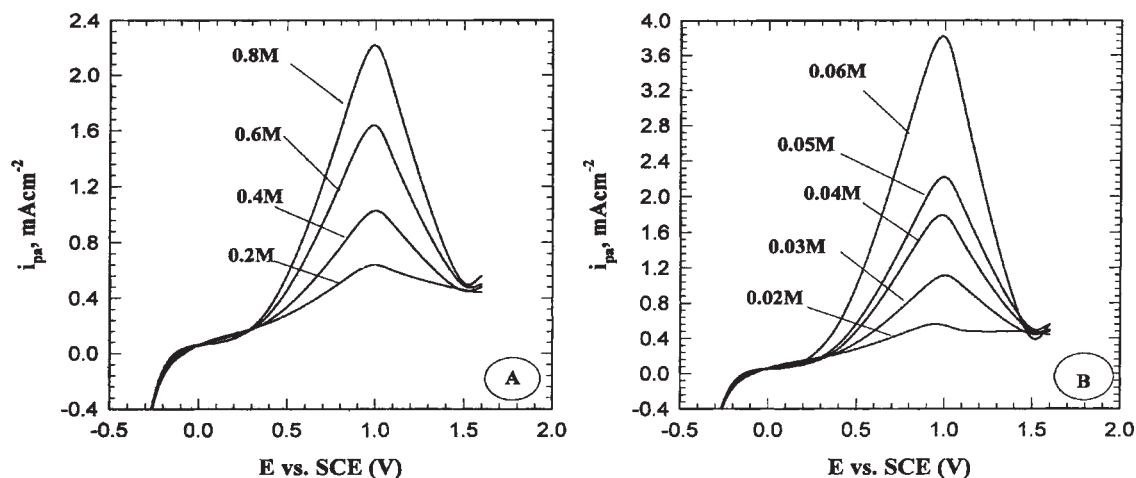


Figure 6 A: Potentiodynamic polarization curves for the effect of HCl concentrations on the electrocopolymerization of a binary mixture of Py and APTh from solution containing 0.05M monomer (1 : 1), 0.1M Na₂SO₄ at 303 K with scan rate of 25 mV s⁻¹. B: Potentiodynamic polarization curves for the effect of monomer concentrations on the electrocopolymerization of a binary mixture of Py and APTh from solution containing 0.08M HCl (1 : 1), 0.1M Na₂SO₄ at 303 K with scan rate of 25 mV s⁻¹.

a given concentration of the comonomer and acid concentration, then we can replace the electrocopolymerization rate with the anodic current density.⁴⁰ Therefore, the kinetic rate law can be expressed as follows:

$$R_{P,E} = I_{pa} = k_E[\text{Acid}]^a[\text{Monomer}]^b$$

where a and b are the reaction orders with respect to acid and monomer concentrations respectively, and k_E is the kinetic rate constant calculated from the electrochemical study.

Potentiodynamic polarization curves as a function of acid concentrations (0.2, 0.4, 0.6, and 0.8M) and monomer concentrations (0.02, 0.03, 0.04, 0.05, and 0.06M) using molar ratio (1 : 1) in the potential range between -400 and 1600 mV with scan rate of 25 mV s⁻¹ are graphically represented in Figure 6(A,B). The data show that the anodic current densities increase with

the increase in the acid and monomer concentrations up to the optimum concentrations, determined by the weight technique as previously mentioned by Sayyah et al.^{33,34}

The double logarithmic plot of the anodic current densities versus acid or monomer concentrations are represented in Figure 7(A,B). Both graphs show a good linearity and the slopes give the reaction order values with respect to the acid and the monomer concentrations. Therefore, the kinetic rate law would them be as

$$R_{P,E} = k_E[\text{Acid}]^{1.1}[\text{Monomer}]^{1.9}$$

By comparing both kinetic equations calculated from *ex situ* microgravimetric study and from electrochemical study, it can be concluded that there is a good agreement between the reaction order with respect to

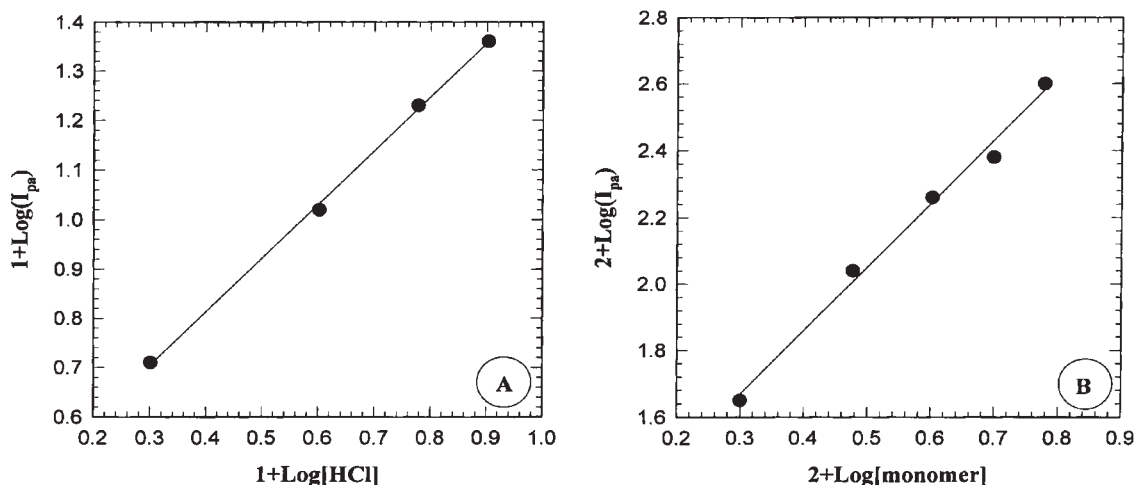


Figure 7 A: Double logarithmic plot of the initial rates of the electrocopolymerization vs HCl concentrations. B: Double logarithmic plot of the initial rates of the electrocopolymerization vs monomer concentrations.

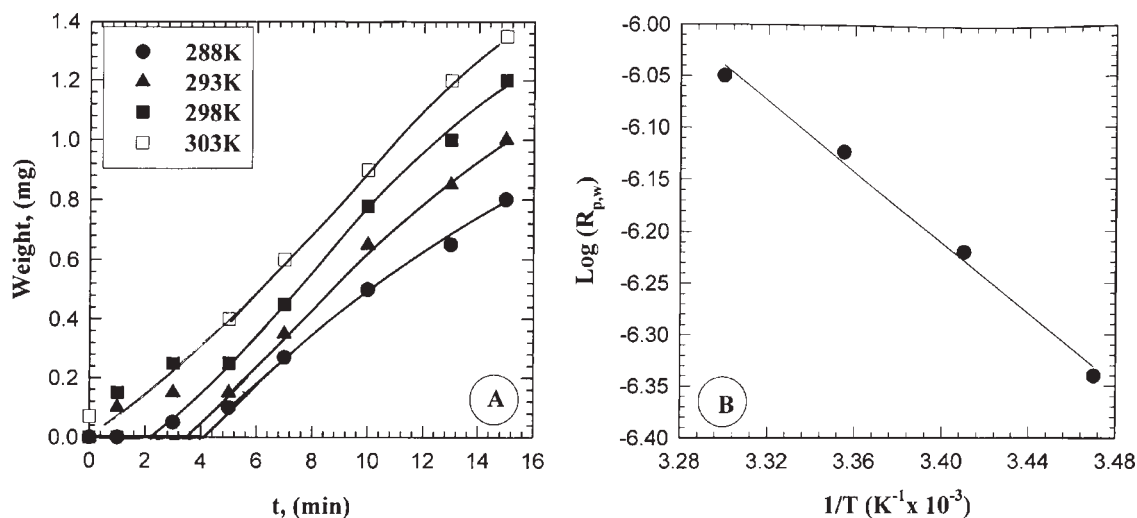


Figure 8 A: Yield–time curves for the effect of temperature. B: Arrhenius plot of the anodic oxidative electrocopolymerization of a binary mixture of Py and APTh from solution containing 0.06 monomer (1 : 1 molar ratio), 0.8M HCl and 0.1M Na_2SO_4 .

the acid and the monomer concentrations (determined by different techniques), indicating that there is no significant parallel reactions occur on the electrode and the current efficiency remains constant during the copolymerization reaction.²⁶

Temperature effect

Effect of temperature on the electrocopolymerization of a binary mixture of pyrrole (Py) and 2-amino-4-phenyl thiazole (APTh) was carried out by *ex situ* microgravimetric study under the following constant conditions: 0.8M HCl, 0.06M monomer (molar ratio 1 : 1), and 0.1M Na_2SO_4 but the reaction was carried out at different temperatures in the range between 288 and 323 K. The maximum weight of the copolymer

film was recorded at 303 K. It is noticed during the experiments that, at temperatures higher than 303 K, some copolymers are formed in the solution near the anode and not adhered at the electrode, which means that, at temperatures higher than 303 K, the adhesion of the film to the electrode is decreased. The electrocopolymerization of a binary mixture was carried out at different temperatures 288, 293, 298, and 303 K for different time intervals as shown in Figure 8(A). The rate of the electrocopolymerization was calculated at each investigated temperature and the logarithm of the electrocopolymerization rate was plotted versus $1/T$ [cf. Fig. 8(B)], which gives a straight line with a slope equal to -1.7 . By applying Arrhenius equation, the apparent activation energy was calculated and it is found to be 32.5 kJ/mol.

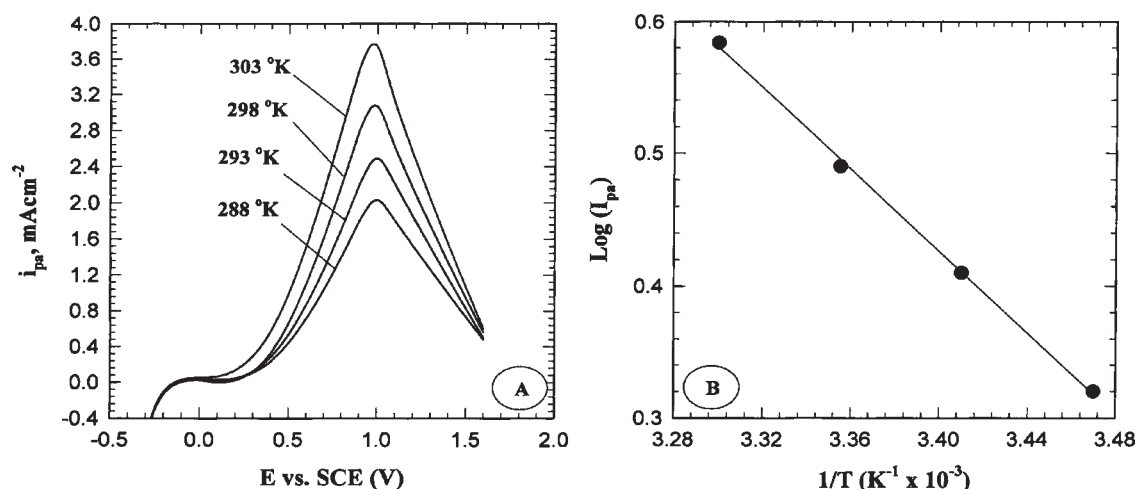


Figure 9 A: Potentiodynamic polarization curves for the effect of temperature on the electrocopolymerization of a binary mixture of Py and APTh from solution containing 0.06M monomer (1 : 1), 0.8M HCl, and 0.1M Na_2SO_4 with scan rate of 25 mV s^{-1} . B: Arrhenius plot of the electrocopolymerization of a binary mixture of Py and APTh.

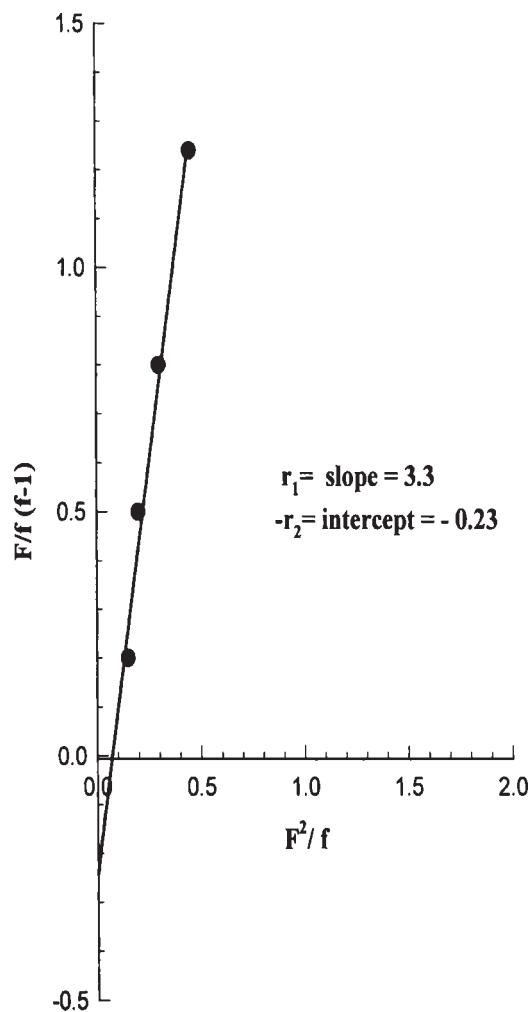


Figure 10 Fineman–Ross plot for the determination of the monomer reactivity ratios of P(Py-co-APTh) in aqueous HCl solution copolymerized by electrochemical method on Pt electrode.

Figure 9(A) illustrates the potentiodynamic polarization curves as a function of the solution temperature in the range between 288 and 303 K. It is clear that the anodic current densities increase with the increase in the solution temperature. The logarithmic plot of the electrocopolymerization rate versus $1/T$ [cf. Fig. 9(B)] gives a straight line with a slope equal to -1.55 and then the apparent activation energy was calculated using Arrhenius equation and is equal to 29.6 kJ/mol.

Copolymer structure and the mechanism

The monomer reactivity ratios of the copolymerization system (r_1 and r_2) involving pyrrole and sulfur containing monomer (2-amino-4-phenylthiazole) were determined based on comonomer composition–copolymer composition relationship. The monomer reactivity ratios were calculated according to Fineman–Ross method.⁴¹

Fineman–Ross method

The two monomers are incorporated into the copolymer chain depending on their relative concentrations and reactivities. The composition of the copolymer was quantitatively determined by sulfur analysis of the copolymer samples. The monomer reactivity ratios r_1 and r_2 of this copolymer was calculated from Fineman–Ross relationship between $F/f(f-1)$ and F^2/f (cf. Fig. 10), where $F = M_1/M_2$ (molar ratio for monomer composition); $f = m_1/m_2$ (molar ratio for copolymer composition).

The slope and the intercept are $r_1 = 3.3$ and $r_2 = 0.23$, respectively. From the data, the value of r_1 is greater than 1 and r_2 is less than 1. In this case the propagation reaction type 11 and 21 will be preferred than the type 12 and 22; hence, the probability of M_1 (pyrrole) entering into the copolymer chain is higher as compared to M_2 (2-amino-4-phenylthiazole). Therefore, the formed copolymer will be richer in M_1 as suggested from the values of the onset oxidation potentials of the two monomers and the comonomers.

The copolymer composition data for the investigated system is calculated and the relation between the mole fraction of M_1 in the formed copolymer (n_1) and the mole fraction of M_1 in the monomer feed (N_1) is represented in Figure 11. The diagonal line represents the case that both monomers have identical reactivity. All of the values of n_1 for the copolymers are above the diagonal line, indicating that the copolymers consist of a higher fraction of pyrrole units than that of 2-amino-4-phenylthiazole units and that the

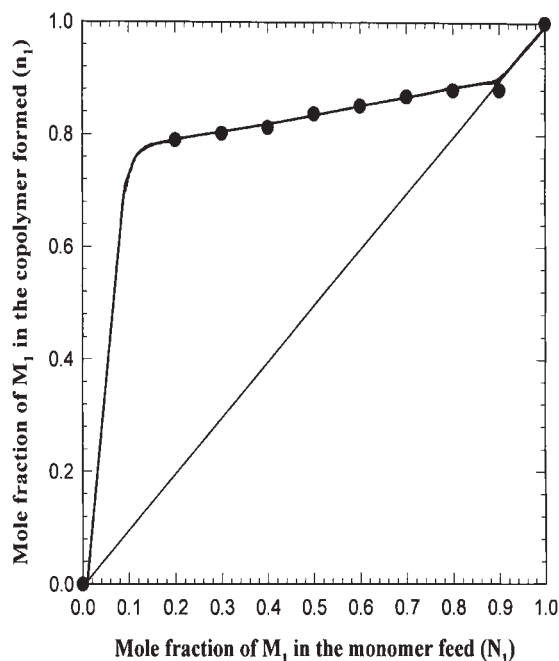
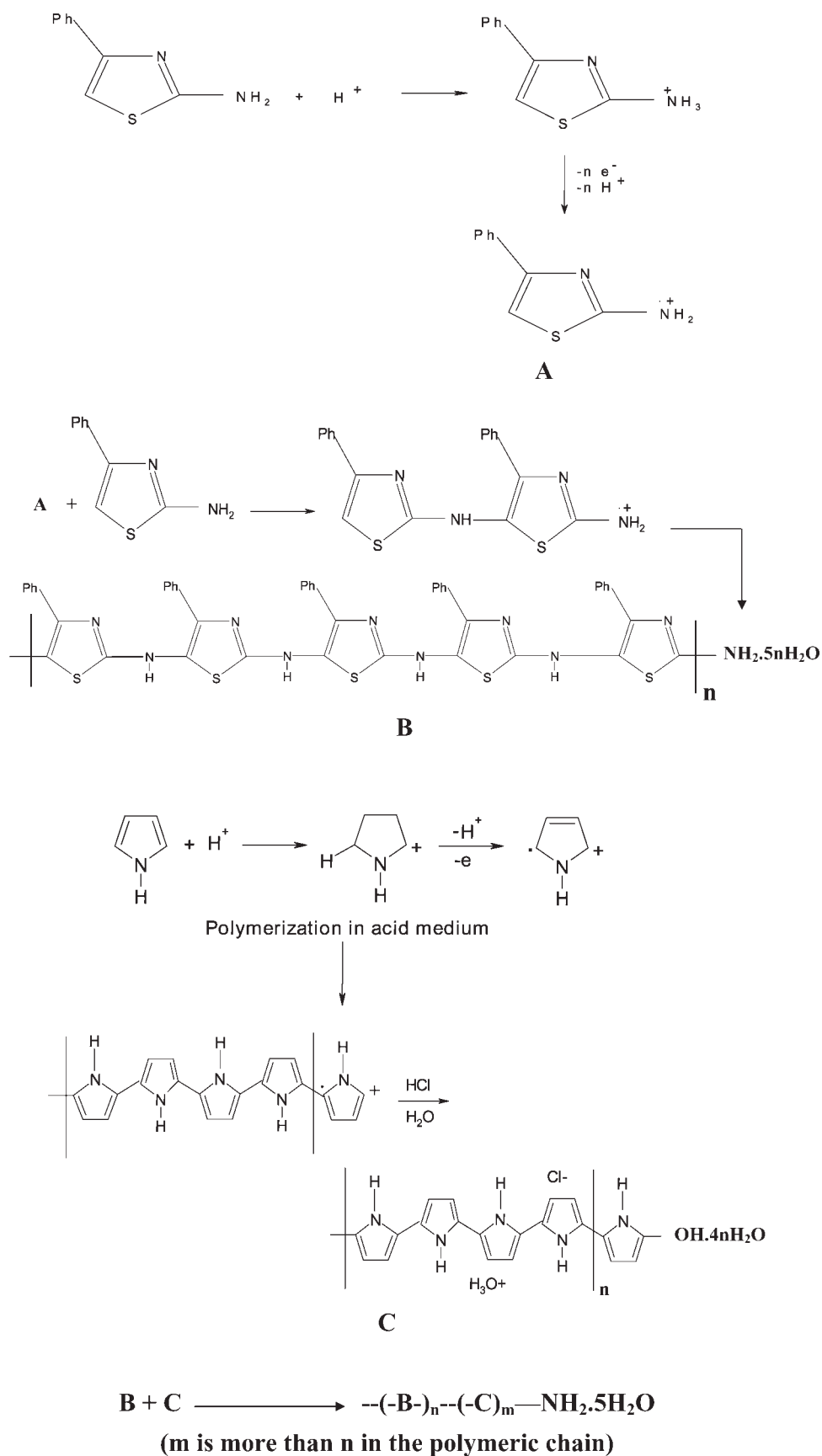


Figure 11 Composition curve for the electrocopolymerization between Pyrrole (M_1) and 2-amino-4-phenyl thiazole (M_2) in aqueous HCl solution on Pt-electrode.



Scheme 1.

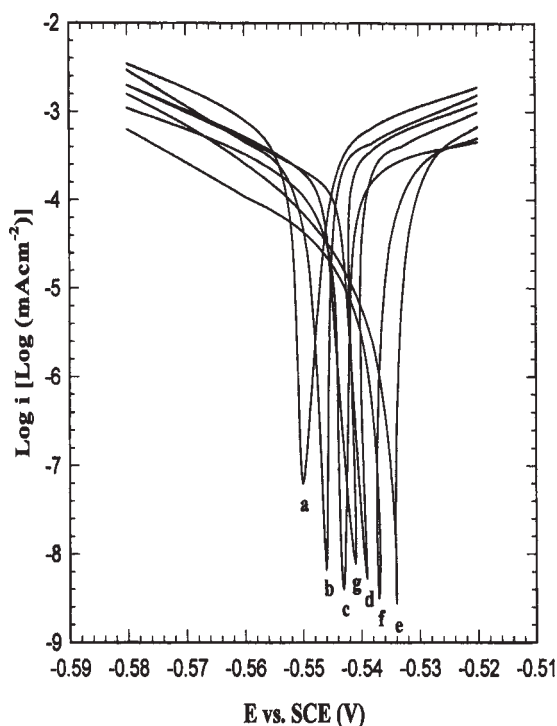


Figure 12 Potentiodynamic polarization curves of mild steel in 1M HCl coated with the prepared copolymer. The coat was deposited on the steel electrode from aqueous solution (30 : 70 DMF/H₂O (v/v)) containing 0.05M monomer (1 : 1) and 0.1M Na₂SO₄ under the influence of different duration time (a) uncoated, (b) 3, (c) 5, (d) 7, (e) 10, (f) 12, and (g) 15 min at 298 K.

pyrrole is much more reactive than 2-amino-4-phenylthiazol. From the above data, the structure of the obtained copolymer is a block structure and therefore the copolymerization mechanism can be represented as shown in Scheme 1.

The structural units of polypyrrole and poly(2-amino-4-phenylthiazole) was suggested previously by Sayyah et al.^{33,34}

The molecular weight data of the obtained copolymer sample prepared at 0.8M HCl, 0.06M monomer (1 : 1), and 0.1M Na₂SO₄ at 303 K obtained by GPC analysis was found to be as follows: $M_w = 1,282,567$, $M_n = 621,341$, $M_v = 1,172,930$, and the polydispersity = 2.064.

Applications of the prepared copolymer as corrosion protection of mild steel in acid medium

The corrosion behavior of mild steel without coat and coated with poly(pyrrole-co-2-amino-4-phenylthiazole) in 1M HCl at 25°C was investigated potentiodynamically from -580 to -520 mV at scan rate of 25 mV s⁻¹. The coated polymer films were electrodeposited on the steel surface under different conditions such as polymerization time and monomer concentration. The corrosion current (I_{corr}) was obtained by Tafel

extrapolation method, where large cathodic and anodic polarizations provide the cathodic and anodic polarization curves for the respective corrosion process.⁴²

Effect of polymerization time

Figure 12 shows the potentiodynamic anodic and cathodic polarization curves of steel electrode coated with the prepared copolymer at different polymerization time. The electrochemical parameters such as corrosion current (I_{corr}) and corrosion potential (E_{corr}) from these measurements are summarized in Table I. The data reveal that the presence of copolymer coat inhibit the corrosion of steel in 1M HCl, since the value of I_{corr} decreases by coating the steel electrode with the copolymer film. In the same time, the presence of the copolymer film on the electrode surface slightly shifts the corrosion potential (E_{corr}) to more positive values. It is clear that the presence of the polymer film on the electrode surface increases the cathodic and anodic polarization compared with the free sample without coating and the increase in the anodic polarization is more pronounced than that in case of cathodic polarization. The inhibition of steel corrosion seems to be due to the presence of the barrier copolymer film on the electrode surface, which increase the resistance of the charge transfer across the interface.

The protection efficiency ($P\%$) for the copolymer coat was calculated from the following equation:⁴³

$$P\% = (I_{corr}^0 - I_{corr})/I_{corr}^0 \times 100$$

where I_{corr}^0 and I_{corr} are the corrosion current for uncoated and coated steel electrode respectively, and the calculated values of $P\%$ are also listed in Table I. The data reveal that the protection efficiency increases with increase in the time of the electrocopolymerization up to 10 min. Further increase in the time duration (more than 10 min) leads to a decrease of the protection efficiency.

The increase in the protection efficiency with the electrocopolymerization time could be attributed to

TABLE I
Electrochemical Parameters for Mild Steel Electrode in 1M HCl Coated with the Copolymer Films Prepared at Different Polymerization Time

Time (min)	I_{corr} ($\times 10^5 \mu\text{A cm}^{-2}$)	E_{corr} (mV, vs. SCE)	P (%)
Blank	10	-550	—
3	4.3	-546	57
5	3.1	-541	69
7	2.5	-539	75
10	1.2	-533	88
12	2.3	-537	77
15	2.7	-543	73

TABLE II
Electrochemical Parameters for Mild Steel Electrode
in 1M HCl Coated with the Copolymer Films
Prepared at Different Monomer Concentrations

[Monomer] (mol/L)	I_{corr} ($\times 10^5 \mu\text{A cm}^{-2}$)	E_{corr} (mV vs. SCE)	P (%)
Blank	10	-550	—
0.01	5.6	-548	44
0.02	4.7	-545	53
0.03	3.5	-542	65
0.04	2.1	-537	79
0.05	1.2	-533	88
0.06	1.9	-539	81
0.07	2.5	-541	75

the increase in the polymer weight and consequently the film thickness. The decrease in the protection efficiency observed at a long time resulted from the decrease of the thickness of the coated film due to the solubility of the coated film.

Effect of monomer concentration

Potentiodynamic cathodic and anodic polarization curves of steel electrode coated with the prepared copolymer films at different monomer concentrations were studied and the electrochemical parameters (I_{corr} , E_{corr} , and $P\%$) are calculated and summarized in Table II. It is obvious that the protection efficiency of the coated films increases with the increasing of the monomer concentration up to 0.05M then starts to decrease with further increase of the monomer concentration.

This increase in the protection efficiency with increasing the monomer concentration may be attributed to the increase of the copolymer weight and consequently the film thickness, while the decrease in the protection efficiency observed at higher monomer concentration ($>0.05M$) resulted from the faster rate of the electrocopolymerization at higher monomer concentrations ($>0.05M$) has no sufficient time for copolymer chains to stick smoothly on the electrode surface.⁴⁴

CONCLUSIONS

1. The onset potentials for the oxidation of pyrrole and 2-amino-4-phenylthiazole monomers are 700 and 1200 mV, respectively, while the onset potential for the oxidation of the comonomer is 900 mV. The onset potential for the oxidation of the comonomer shifts to lower potential than that of 2-amino-4-phenyl thiazole indicating that a mixture of the comonomer is oxidized more easily than 2-amino-4-phenylthiazole alone.
2. The kinetic rate law obtained from an *ex situ* microgravimetric study for the electrocopolymerization reaction is $R_{P,E} = k_E [\text{Acid}]^{1.1} [\text{Monomer}]^{1.9}$.

While the kinetic rate law obtained from the potentiodynamic study for the electrocopolymerization reaction is $R_{P,E} = k_E [\text{Acid}]^{1.1} [\text{Monomer}]^{1.9}$. The agreement between the order of the reaction with respect to the acid and the monomer concentrations, which determined by different techniques, indicates that there is no significant parallel reactions occur on the electrode.

3. The apparent activation energies were calculated by the two techniques and are found to be 32.55 and 29.6 kJ/mol from microgravimetric and potentiodynamic measurements, respectively.
4. From the monomer reactivity ratios ($r_1 = 3.3$ and $r_2 = 0.23$), it is clear that the copolymer structure is a block one. The relation between N_1 and n_1 indicate that the formed copolymer is richer in pyrrole, which confirmed by cyclic voltammetry studies.
5. The maximum protection efficiency for mild steel (88%) was found when the prepared copolymer film was deposited at 10 min and using 0.05M monomer concentration.

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