Original Research Article

ELECTROPOLYMERIZATION AND CHARACTERIZATION OF NANO ORTHO METHOXY PHENOL-CO-PYRROLE FILM

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Abstract: Simple Electrochemical method has been used to prepare poly o-methoxy phenol-pyrrole P (o-MP-co-pyrrole). Effects of different reaction parameters such as temperature, monomer and acid concentrations on the growth of the copolymer are studied by using cyclic voltammetry. The kinetic studies indicate that the orders of the reaction are 2.1 and 0.75 for monomer and acid concentrations, respectively. The apparent activation energy is calculated to be 42.2 kJ/mol. In addition, the fabricated copolymer is characterized and investigated by ^{1}H-NMR, TGA, IR-UV spectroscopy, XRD, SEM and elemental analysis. Moreover, the mechanism of the reaction is proposed and discussed by using Fineman-Ross method.

Key Words: Copolymer; pyrrole; ortho methoxy-phenol; cyclic voltammetry; Kinetic studies; mechanism

INTRODUCTION

Electrochemical polymerization is a simple and attractive approach for forming a polymer film on the electrode surface (Fukuhara T, *et al.,* 2002; Matsushita M, *et al.,* 2005; and Cao H, *et al.,* 2005). The thickness of the film can be controlled and the functionality of the formed film can be selected through processing parameters (the current density, scan rate, scan number, temperature, etc.). By optimizing the fabrication parameters, the uniform coatings can be achieved (Sarac A S, *et al.,* 2004; Hua S, *et al.,* 2002; and Kumru E M, *et al.,* 2001). Polypyrrole (PPy) is one of the most popular conducting polymer due to their conductivity, good mechanical properties, and environmental stability as well as its potential use in a wide range of applications such as membranes, sensors, batteries, capacitors, and anti-corrosion films (Khalkhali R A, *et al.,* 2005; Fletcher B L, *et al.,* 2007; Liu Y C, *et al.,* 2004; and Zhou Q, *et al.,* 2007). PPy film can be synthesized from aqueous or organic media by chemical and electrochemical methods. It was synthesized electrochemically by the formation of radical-cation which then reacts with a second molecule of pyrrole leading to dipyrrole. This dimer is converted preferentially into the radical-cation which reacts with monomer leading to pyrrole trimer and finally the polypyrrole film is formed (Ramsey R P, *et al.,* 2003; and Smit M A, *et al.,* 2003). While the electrochemical process of phenols was proceed by the generation of unstable phenoxy radicals. These radicals are electrophiles capable of reacting with either the starting phenol or another radical by C–C and/or C–O coupling giving dimers (Bruno F, *et al.,* 1977; Panizza M, *et al.,* 2003; and Li XY, *et al.,* 2005). The dimer may be further oxidized to create oligomers and then polymers.

Formation of the insoluble polyphenol results in deactivation of electrode surface (Gattrell M, *et al.,* 1993; Gattrell M, *et al.,* 1992; and Ezerskis Z, *et al.,* 2002). Previously, the electro polymerization of 1-(4-methoxyphenyl)-1H-Pyrrole was studied on the carbon fiber micro electrodes (Sezgin S, *et al.,* 2012). The electropolymerization reactions were studied with a commercially new monomer at different scan rates. The cyclic voltammogram for the modified carbon fiber electrode with the resultant polymer showed enhanced cathodic and anodic peak currents that increased linearly with the different scan rate. However, there is no detailed study performed for the formation of copolymer between o-MP and pyrrole in presence of sulfuric acid medium. This attracts our interest to study the electropolymerization of o-MP-co-pyrrole on Pt electrode. Also, the kinetics and optimum conditions for the electrochemical oxidation of o-MP-co-pyrrole in aqueous H_2SO_4 medium as electrolyte are addressed. The kinetic studies for this reaction are performed to calculate the orders of reaction with respect to monomer concentration, acid concentration, and the thermodynamic activation parameters such as enthalpy (ΔH^*), entropy (ΔS^*), and activation energy (Ea) for electro-oxidation of copolymer. In addition, various techniques are used to characterize the formed polymer such as thermo gravimetric analysis (TGA), Proton nuclear magnetic resonance (^{1}HNMR), and UV-IR spectroscopy. In addition, scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to study the surface morphologies and compositions of P (o-MP-co-pyrrole) formed at different electrolytic composition, current density, and electrode configuration.

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MATERIALS AND METHODS

Materials

Pyrrole, ortho methoxy phenol (o-MP), sulfuric acid solution all were purchased for Merck, Germany. All solutions were prepared by using freshly double-distilled water.

Electrodes

The working electrode (WE) was a platinum sheet with dimensions of 1 cm length and 0.5 cm width. The auxiliary (counter) electrode (CE) was a platinum foil with the same dimensions as the WE. A saturated calomel electrode (SCE) was used as a reference electrode. Electrochemical experiments were performed using the Potentiostat / Galvanostat Wenking PGS 95.

Characterization of the electro-prepared polymers

UV-Vis absorption spectra of the prepared polymer sample were measured using Shimadzu UV spectrophotometer (M160 PC) at room temperature in the range 200-400 nm using acetone as a solvent and reference. IR measurements were carried out using shimadzu FTIR-340 Jasco spectrophotometer (Japan) by KBr pellets disk technique.

^{1}H-NMR measurements were carried out using a Varian EM 360 L, 60-MHz NMR spectrometer. NMR signals of the electro polymerized sample were recorded in dimethylsulphoxide (DMSO) using tetramethyl silane as an internal standard.

TGA of the obtained polymer was performed using a Shimadzu DT-30 thermal analyzer (Shimadzu, Kyoto, Japan). The weight loss was measured from ambient temperature up to 600℃, at the rate of 20℃ min-1 and nitrogen 50cc min^{-1} to determine the degradation rate of the polymer. Elemental analysis was carried out in the micro-analytical center at Cairo University (Cairo, Egypt) by oxygen flask combustion and dosimat E415 titrator (Metrohm).

Scanning electron microscopic (SEM) analysis was carried out on the as-prepared polymer film using a JSM-T20 Electron Probe Microanalyzer (JEOL, Tokyo, Japan). The X-ray diffraction analysis (XRD) (Philips 1976 Model 1390, Netherlands) was operated 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.

RESULT AND DISCUSSION

Electropolymerization of the binary mixture of o-MP and pyrrole

Electropolymerization of the two separate monomers (*o-MP* and *pyrrole*) and the binary mixture of the two monomers with molar ratio 1:1 in aqueous acid medium (0.3 H_2SO_4) at 313K was carried out. The obtained voltammograms are represented in Figure 1.

The data reveals that, the anodic oxidation peaks at 900 mV vs SCE in case of *pyrrole*, at 1080 mV vs. SCE in case of o-MP, and at 720 mV vs. SCE in mixture of *o-MP-co-pyrrole*. The anodic peak of comononer is attributed to the removal of electron from oxygen atom and from nitrogen atom of the hydroxyl group and amino group, respectively. This form free radical and radical cation in all cases which react with another molecule of monomer to form dimer radical and so on to form the corresponding copolymer (*o-MP*-co- *pyrrole*).
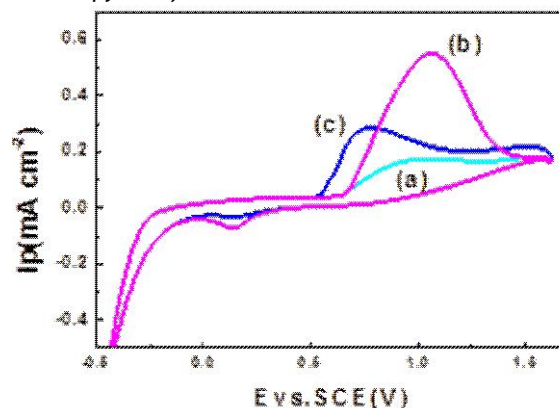

Figure 1: Cyclic voltammograms of electro-polymerization of (a) 0.07 M pyrrole (b) 0.09 M o-MP, and (c) 0.05 M of the two monomers solutions containing 0.3MH_2So_4 on Pt- electrode.

The cathodic span of the reverse scan of the binary monomer mixture has one cathodic peak at 190 Mv vs. SCE indicating that the system is reversible and indicating that the copolymer is reduced.

Effect of scan rate

Effect of scan rate on the cyclic voltammograms of co-monomer on Pt electrode is shown in Fig. (2). Figure 2 (a) shows the cyclic voltammogram of co-monomer for scan rate from 10 to 40mVs^{-1} recorded at Pt working electrode for 0.3 M H_2SO_4 and 0.05M of co-monomer at 313K. As shown in the figure, the peak current density (I_p) increases as the scan rate increased.

This behavior may be ascribed to the depletion of the species in the vicinity of the Pt surface when enough potential is applied to the Pt surface causing oxidation of species in the solution. As a result, a concentration gradient (dC/dx) appears in the solution and the peak current (I_p) is proportional to this concentration gradient (dC/dx). As the scan rate increased, the gradient increases and consequently the current (I_p) increases. The linear dependency of the anodic peak current density (I_p) on the square root of scan rate ($V^{1/2}$) is shown in Figure 2 (b) and represented by the linear regression equation:
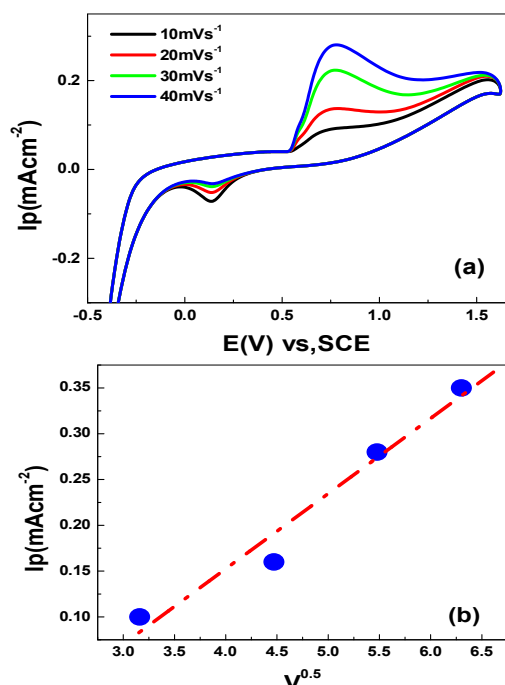
Figure 2. (a) Effect of Scan rate on electro-polymerization of co-monomer (o-MP-co-pyrrole) on Pt electrode from solution containing 0.3M H_2SO_4 at 313 K. (b) Relation between I_p and square root of scan rate.

$$Ip = 0.08V^{1/2}(mVs^{-1})^{1/2} -0.17 \qquad (1)$$

From the above equations we noted that the correlation coefficient is r = 0.98. This linear relation suggests that the electro formation of copolymer may be described by a partially diffusion - controlled process (diffusion of reacting species to the polymer film/solution interface) (Ureta-Zanatru M S, *et al.,* 2002). In addition, it suggest that, initially the electro formation of radical cation and free radical is controlled by the charge transfer process. Moreover, the negative intercept, -0.17, indicates to a decrease of the active area of the working electrode during the positive scan or the increase of the covered area of the working electrode by the adhered polymer layer. When the polymers become thick, the diffusion of reactant inside the film becomes the slowest step and the process changed to charge transfer. Using the values of I_p and scan rate, V (Vs^{-1}), the diffusion coefficient can be calculated using Randless and Sevick equation: (Randless P, 1984; and Sevick A, 1948)

$$I_P(II) = 0.4463 \, n \, F \, A \, C \, (\, n \, F \, V \, D \, / \, R \, T \,)^{1/2} \qquad (2)$$

Where n is the number of exchanged electron in the mechanism, F is Faraday's constant (96485 C mol), A is the electrode area (cm^2), C is the bulk concentration, D is the analyst diffusing coefficient ($cm^2 s^{-1}$), R is the universal gas constant (8.134 $Jmol^{-1}K^{-1}$), and T is the absolute temperature (K). The calculated values of D (at 0.6 M H_2SO_4 and

303 K with scan rate from 10 to 40 mV s^{-1}) are shown in Table 1. The values of D are seen to be slightly changed over the range of sweep rates, which again shows that the oxidation process is partially diffusion-controlled.

Effect of number of cycles

In order to examine the electrode stability, five repetitive cyclic voltammograms in a solution containing 0.05M of co-monomer in 0.3M H_2SO_4 with scan rate 30mVs^{-1} at 313K were performed. As seen in Fig. 3. The current involved in the oxidation of commoner decreases gradually as the number of cycles increased. The decrease of anodic peak with increasing the film thickness is due to the decrease in the conductivity and the rate of diffusion within the film.

Table 1: The calculated values of diffusion coefficients for different scan rates.

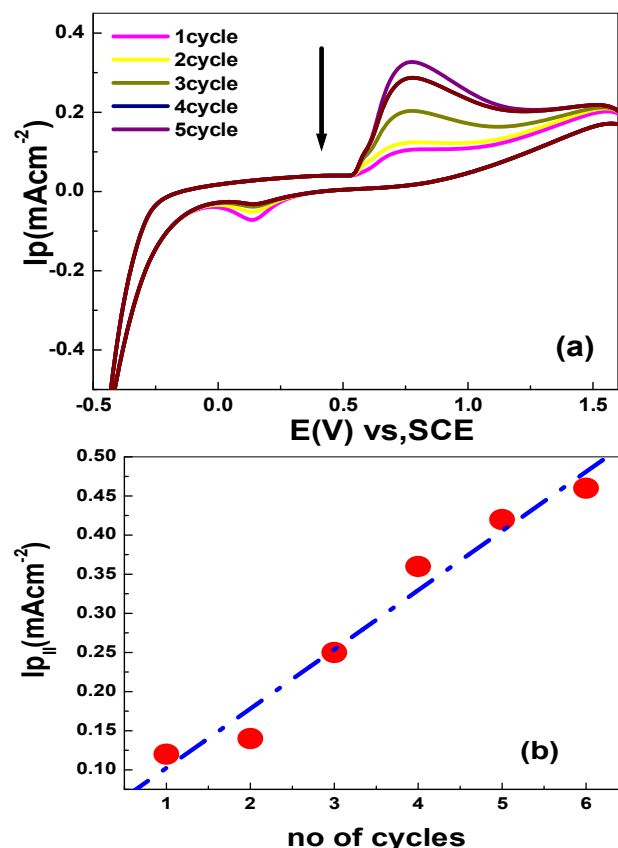| Scan rate (Vs^{-1})	Diffusing coefficient ($m^2 s^{-1}$)
0.01	1.1 x 10^{-9}
0.020	1.4 x 10^{-9}
0.030	2.8 x 10^{-9}
0.040	3.37 x 10^{-9}

Figure 3: (a) Cyclic voltammetry curves for the effect of repetitive cycles on the Electro-polymerization of 0.05M o-MP-co-pyrrole from solution containing 0.3MH_2SO_4 at 313K with scan rate 30mVs^{-1} on Pt Electrode. (b) The relation of I_p and number of cycles.

Kinetic studies

The electropolymerization kinetics were investigated by using aqueous solution containing co-monomer (o-MP-co-pyrrole) of concentration in the range between 0.02 and 0.05M where H_2SO_4 concentration in the range between 0. 1 and 0.4M at 313 K. The cyclic voltammogram for each comonomeric system and the relation between the log I_p vs. log [monomer conc.] or log I_p vs. log [H_2SO_4 Conc.] are studied to obtain the order of the reaction with respect of monomer and sulfuric acid concentrations.
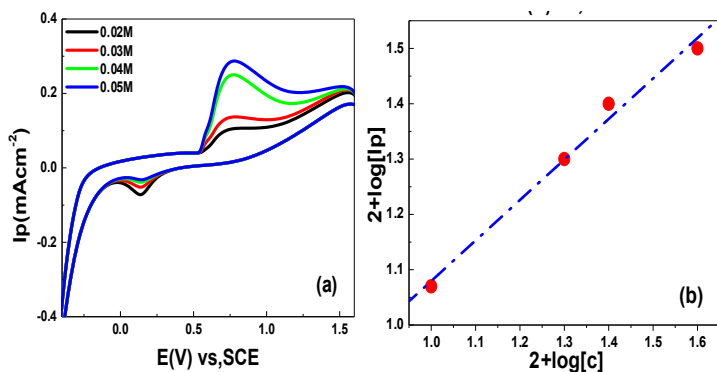

Figure 4: (a) Cyclic voltammetry curves for the effect of co-monomer concentration on the Electro polymerization process from solution containing 0.3MH_2SO_4 at 313K with scan rate 30mVs^{-1} on Pt Electrode. (b) Double logarithmic plot of I_{p1} vs. co-monomer concentrations**.**

Effect of co-monomer concentration on the electropolymerization processes

Figure 4 (a) shows the cyclic voltammograms of co-monomer at different concentrations (0.02-0.05M) in the presence of 0.3 M H_2SO_4 recorded at a scan rate 30mVs^{-1}. From the voltammogram, the oxidation peak of co-monomer appears at an electrode potential of about 0.72V. The peak current [I_p] increases as the co-monomer concentration increased to reach the maximum value and then decrease for co-monomer concentration > 0.05M .This behavior may be attributed to the decrease in the activity of the Pt electrode at higher monomer concentrations or due to competition for the active sites on the electrode surface as a result of the formation of a large number of radical cations and free radicals during the electro polymerization process. While the cathodic peak appears at 0.14V which attributed to the reduction of the copolymer film of P (o-MP-co-pyrrole). For different co-monomer concentrations, the anodic peak current density [I_p] is directly proportional to the concentration and a linear relation is obtained. The order of reaction was obtained from the slop the linear fitting to be 2.1, as shown in Fig. 4.

Effect of H_2SO_4 concentration on the polymerization process

Experiments were performed to study the effect of H_2SO_4 concentration on the electropolymerization process. This effect is shown in Fig. 5 (a) which represents cyclic voltammograms obtained for different acid concentrations (0.05- 0.4M) in 0.05M of o-MP-co-pyrrole at a scan rate of 30mVs^{-1} and temperature of 313K. The height of peak current increases with increasing the acid concentration up to 0.3 M and then decreasing at 0.4M as a result of degradation of the copolymer film. This agrees well with the well-known rule that the polymerization process is favored at low pH (Karamil H, *et al.,* 2013). The order of reaction with respect of sulfuric acid concentration was calculated from the slope of the linear relation between peak current and acid concentration, as shown in Fig. 5(b). Its value was found to be 0.75.
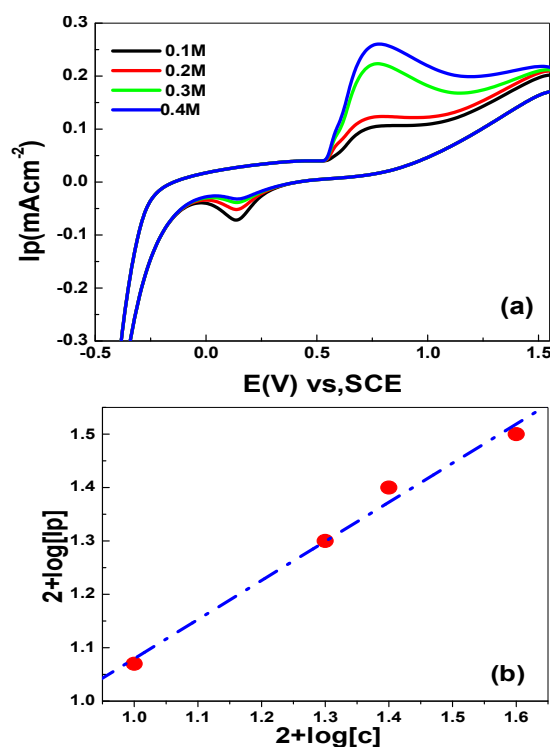

Figure 5. (a) Cyclic voltammetry curves for the effect of H_2SO_4 concentration on the Electro polymerization process from solution containing 0.05 of o-MP-co-pyrrole at 313K with scan rate 30mVs^{-1} on Pt Electrode. (b) Double logarithmic plot of I_p vs. acid concentrations.

Effect of temperature and calculation of thermodynamic parameters

The effect of temperature on the process is represented in Fig. 6. The potentiodynamic profiles of 0.05M of o-MP-co-pyrole in a solution containing 0.3M H_2SO_4 at different temperatures from 283 to 313 K is shown in Fig. 6 (a). As shown the reaction strongly depends on the temperature and I_p increases with

increasing the temperature. Reaction activation energy is calculated by plotting the relationship between the logarithm of peak current and reciprocal of absolute temperature as shown in Fig.6 (b). Straight line is obtained and the activation energy is calculated from the following equation:

$$E_a = \frac{-2.303 \times 8.314 \times \text{slope of reaction}}{1000} \quad (3)$$

Then it is found to be 42.2kJ/mol.

The enthalpy ΔH^* and entropy ΔS^* of activation for the electro polymerization reaction can be calculated from Eyring equation (Eyring H, 1935), as shown in Fig. 6(c).
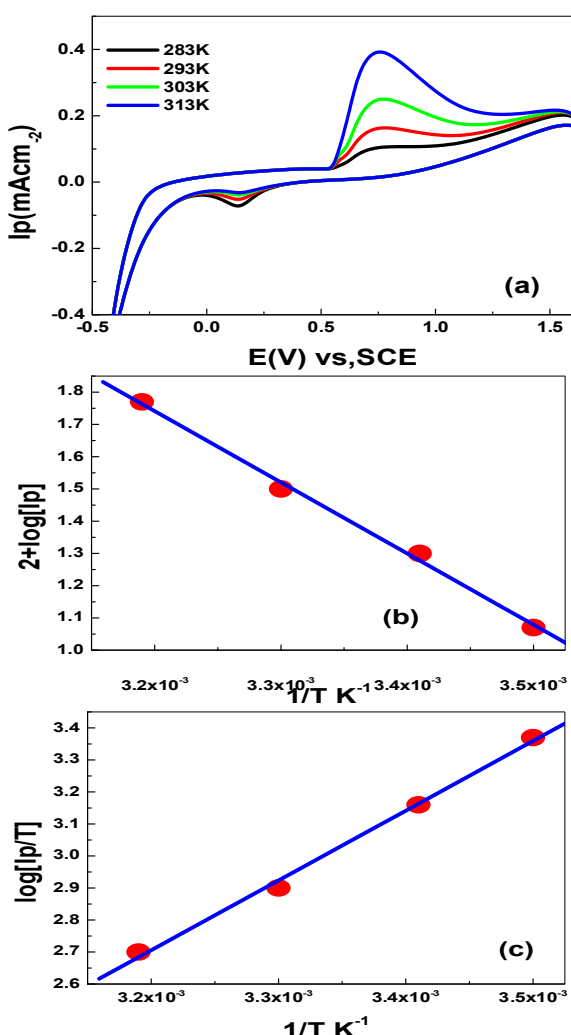

Figure 6: (a) Cyclic voltammetry curves for the effect of temperature on the electro polymerization, (b) Arrhenius plot, and (c) Eyring equation plot.

This result in linear relationships with slope equal to $\Delta H^*/2.303R$ and intercept equal to $(R/Nh) + \Delta S^*/2.303R$. From the slope and intercept values, ΔH^* and ΔS^* for pyrrole are calculated to be 41.7 kJ mol^{-1} and 186JK^{-1} mol $^{-1}$, respectively.

Copolymer structure and mechanism

The monomer reactivity ratios of the copolymerization system (r_1 and r_2) involving o Methoxy Phenol (o-MP) and Pyrrole were determined on the basis of co-monomer composition - copolymer composition relation. The copolymer composition of each sample was calculated according to the nitrogen content as follows:

$$\frac{\text{Nitrogen content of copolymer}}{\text{Nitrogen content of } M_1} = \frac{\text{Molecular weight of } M_1}{\text{Molecular weight of } M_1 + \text{Molecular weight of } M_2/b}$$

Where M_1 is the Nitrogen containing monomer (*pyrrole*) and $b = m_1/m_2$ is the molar ratios of copolymer composition.

The monomer reactivity ratios were calculated according to fineman-Ross method (Fineman M, *et al.,* 1950) using N-content as a quantitative analytical tool.

Fineman-Ross method

Two monomers are incorporated into the copolymer chain depending on their relative concentrations and reactivities. The composition of the copolymer was quantitively determined by N-content in the copolymer samples and the data are given in Table (2). The monomer reactivity ratios r_1 and r_2 of this copolymer was calculated from Fineman-Ross equation (Eq. 4) and represented in Fig .7.

$$F/f(f-1) = r_1(F^2/f) - r_2 \quad (4)$$

Where, $F = M_1/M_2$ is the molar ratio for monomer feed composition and $f = m_1/m_2$ is the molar ratio for copolymer composition.

The slope is equal to r_1 and the intercept is equal to $-r_2$. From the figure, it was found that $r_1 = 0.75$ and $r_2 = 0.4$. I.e., the values of r_1 and r_2 are less than one. In this case the propagation type 12 and 21 will be preferred than the type 11 and 22, hence M_1 can add onto M_2 at the same time. The copolymer composition data for the investigated system were calculated and the relation between the mole fraction of M_2 in the formed copolymer (n_2) and the mole fraction of M_2 in monomer feed (N_2) is represented in Fig.8.

Table 2: reactivity ratio data for o-MP (M_1) and Pyrrole (M_2) in electro polymerization reaction system.

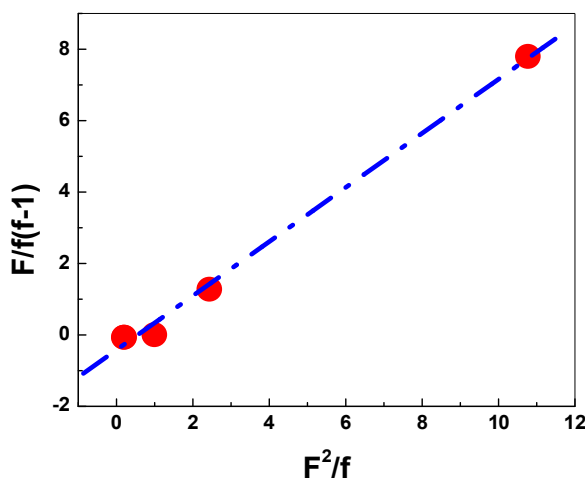| Initial monomer concentration mole reaction		N%	Copolymer composition using N-content		F^2/f	$F/f(f-1)$
M2	M1		m₁	m₂		
0.1	0.9	9.6	0.386	0.6145	0.19	-0.066
03	0.7	8.07	0.465	0.534	0.2025	-0.062
0.5	0.5	7.3	0.50165	0.4387	0.99	0.0058
0.7	0.3	4.06	0.6912	0.3088	2.43	1.28
0.9	0.1	1.4	0.88	0.117	10.77	7.8

Figure 7: Fineman–Ross plot for the determination of monomer reactivity ratio of o-MP and Pyrrole in sulfuric acid as supporting electrolyte copolymerized by electrochemical method on pt electrode.
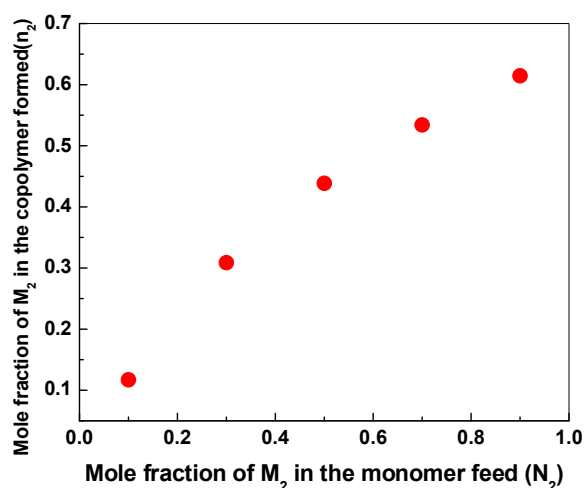

Figure 8: composition curve for the electro polymerization between (o-MP) M_1 and (pyrrole) M_2 in sulfuric acid solution on pt electrode.

The diagonal line represents the case that both monomers have identical reactivity. The values of n_2 for the copolymer are under the diagonal line indicating that the copolymers consist of a higher fraction of Pyrrole units than that of *o-MP* units and that *Pyrrole* is much more reactive than *o-MP*. From the above data, it is clear that the copolymer structure is a block copolymer structure. Therefore the copolymerization mechanism can be represented as shown in the following Scheme.

Characterization of copolymer

Elemental analysis: Elemental analysis of the prepared P (o-MP-co-pyrrole) was carried out and the experimental percentages of C, H, N and S were compared with the calculated percentages for the investigated sample. The percentage of carbon in the sample was 57% which is in a good agreement with the

calculated value (56.5%).in addition The H content in the sample was found to be 5% which is in a good agreement with the calculated value (4.4%). Also the N content in the sample was 9.5 % which is in a good agreement with the calculated value (10%), and the S content was found to be 3% which is in a good agreement with the calculated value (2.7%) in the polymer. The obtained elemental analysis is in a good agreement with the calculated data for the suggested structure in scheme 1.
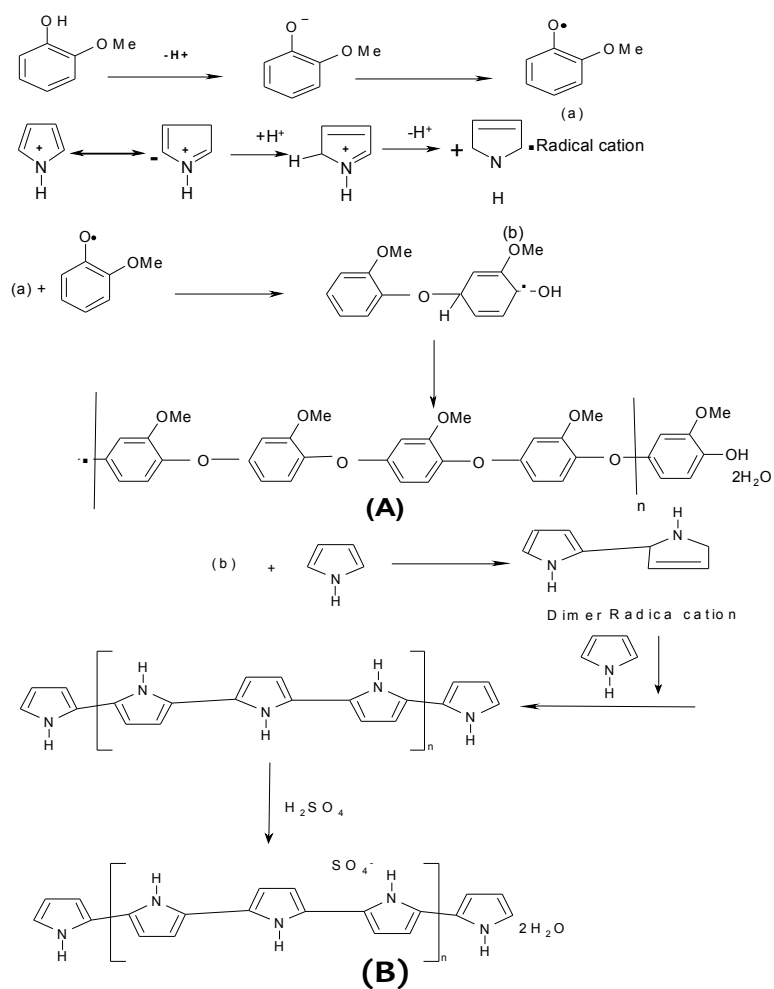
Scheme 1: *the formation of radical ion for o-Mp and pyrrole.*

The UV-Vis spectra of p (o-MP-co-pyrrole): The ultraviolet-visible spectra of P (*o-MP-co-Pyrrole*) are represented in Fig. 9. The spectra show the following absorption bands. Two absorption bands appear at λ_{max}= 230 and 270 nm which could be attributed to π-π* transition (E_2 band) of the benzene ring and the β-band (A_{1g} to B_{2u}). One absorption peak appears at λ_{max}= 320nm which could be attributed to the conjugation of the aromatic polymeric chain.
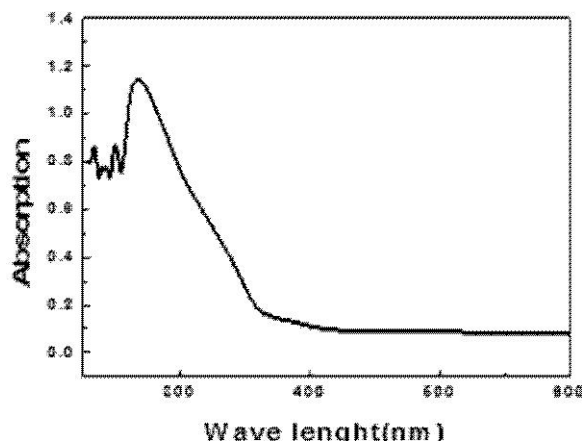
Figure 9: UV-Vis spectra of p (o-MP-co-pyrrole).

Comparative IR spectroscopic studies: The IR spectra of the prepared P (*o-MP-co-Pyrrole*), P (*o-MP*) and P (*pyrrole*) are represented in Fig.10. From the figure, it is clear that two medium absorption bands appear at 782 and 884 cm^{-1} in case of p (*pyrrole*) which could be attributed to stretching vibration of N-H in pyrrole ring. But in case of copolymer, a medium peak appears at 792 cm^{-1}. A medium absorption band at 1160 and a strong absorption band at 1042 cm^{-1} are appeared in the case of P (*pyrrole*) and P (*o-MP-co-pyrrole*), respectively. Both may be ascribed to the doping of the polymeric chains with sulphate ions. A weak absorption bands appearing at 2922, 2936 and 2918cm^{-1} in case of P (*pyrrole*), p (o-MP) and (o-MP-co-pyrrole), respectively, due to C-H stretching vibration of aromatic ring. Broad absorption band appears at 3432 cm^{-1} in case of P (*pyrrole*) *which* is attributed to NH starching vibration in pyrrole ring. In case of p (o-MP), a broad absorption peak appears at 3428cm^{-1} which could be attributed to stretching vibration of intermolecular hydrogen solvated OH group or end group OH of polymeric chain. The other IR absorption bands and their assignments are given in Table 3.
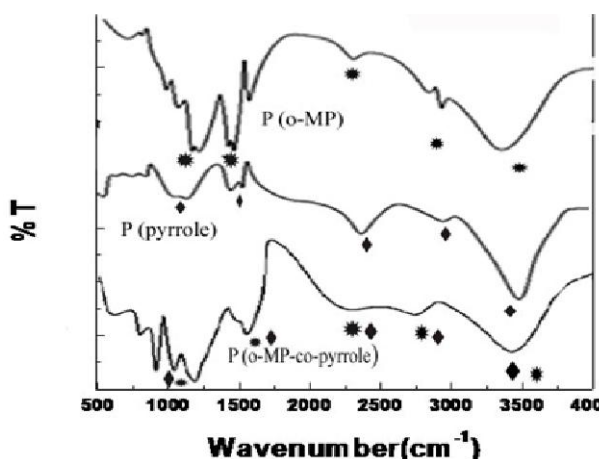

Figure 10: Comparative IR spectroscopic studies of the prepared P (o-MP-co-pyrrole) with p (o-MP) and p (Pyrrole).

^{1}H NMR of P (*o-MP-co-pyrrole*)

Figure 11 shows the ^{1}HNMR spectra of the prepared P (o-MP-co-pyrrole) in (a) DMSO and (b) DMSO+D$_2$ O. This figure shows singlet signal at δ=2.4-2.5 ppm which is attributed to solvent protons. The singlet signal appears at δ=3.8 ppm which is attributed to OH protons for water of solvation. In addition, the doublet signals appear at δ =6.7 and 6.8 ppm which ascribed to the protons of NH group. The signals at δ=7-7.2 ppm are attributed to aromatic proton of (Ar-H) and five membered ring protons. The signals of different (OH) are appeared at δ = 8.5-9 ppm which disappeared when deuterated water was added to the investigated sample as shown in Fig.11 (b).

Table 3: Infrared absorption bands of P (o-MP), p (Pyrrole), and P (o-MP-co-pyrrole) samples and their assignments.

Name			Assignment
Polypyrrole	P(OMP)	(OMP-co-pyrrole)	
782^m 884^m	--------	792^m	**Stretching vibration of N-H in pyrrole ring**
	821^w 865^w	916^m	**Tri-substituted benzene ring.**
1160^m	--------	1042^s	**SO$_4^{-2}$ incorporated in polymeric chain**
1315^w	--------	1200^b	**C-N skeletal in pyrrole ring**
	1116^m 1210^s 1258^s	1100^m	**C-O stretching vibration**
1637^m	1454^s 1502^s 1600s	1486s 1688m	**Stretching vibration of C=C**
--------	2844w	2361w	**Methoxy group**
2922w	2936w	2918.7w	**Streching vibration for CH of aromatic ring**
3432^b	--------	-----------	**Stretching for NH in pyrrole ring**
--------	3428b	-----------	**Stretching vibration intermolecular hydrogen solvated OH group or end group OH of polymeric chain**
-------	-------	3426^b	**Overlapping between OH solvated in p(o-MP) and N-H in polypyrrole .**

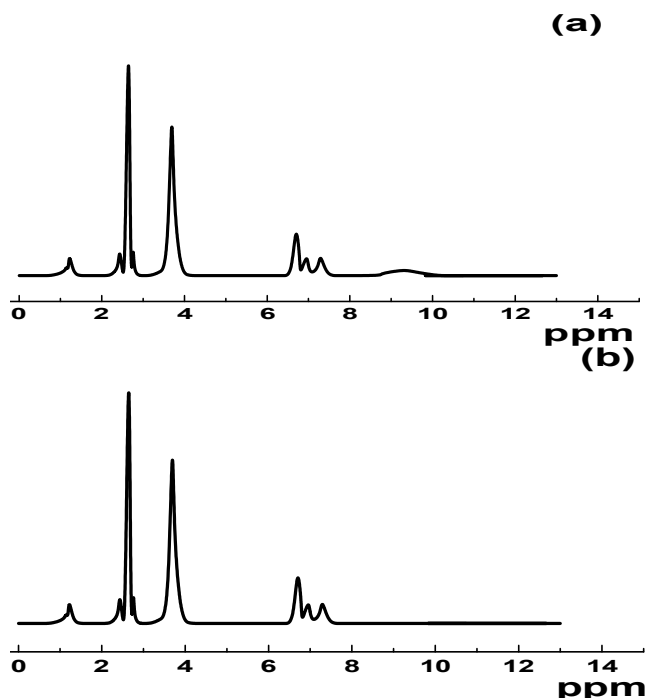Where; s: strong, w: weak, b: broad, m: medium

(a)

(b)

Figure 11: ^{1}HNMR spectra of the *P (o-MP-co pyrrole)* in (a) DMSO and (b) DMSo+D_2O.

TGA of poly (o-MP-co- pyrrole)

Thermogravimetric analysis (TGA) for the electrochemically prepared P (*o-MP-co-pyrrole*) sample has been investigated and the TGA-curve is represented in Fig. 12. The presence of five water molecules for each repeated unit is confirmed by TGA. From this figure, it is clear that there are five stages during thermolysis of the copolymer sample. These stages were summarized in Table 4. The first stage *i*ncludes the loss of 5 molecules of H_2O in the temperature range between 25° C and 220°C. The weight loss was found to be (9.2%) which is in good agreement with the calculated value (9.46%). The Second stage *i*ncludes the loss of the dopant species SO_3 and two pyrrole moieties in the temperature range between 220° C and 400°C. The weight loss for this step was found to be 24.3% which is in good agreement with the calculated value (23.8%). In the temperature range from 400° C to 500° C, The third stage *i*ncludes the loss of two units of pyrrole. The weight loss for this step was found to be (14 %) which is in good agreement with the calculated value (14 8%). The fourth stage *i*ncludes the loss of two of benzenoid ring and one pyrrole unit. The weight loss for this step was found to be (29%) which is in good agreement with the calculated value (30.3%) in the range of temperature between 500° C to 600° C. Above 600° C, The fifth stage *i*ncludes the remained carbon chain and metallic residue and the weight loss for this step was found to be(25%).
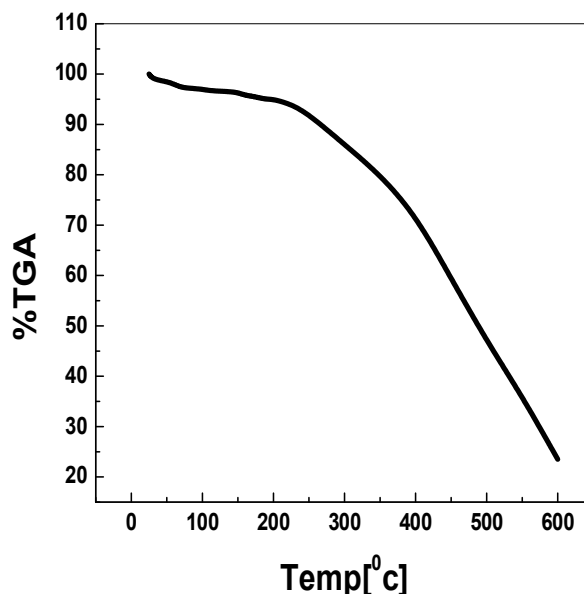

Figure 12: TGA of poly (o-MP-co-pyrrole).

Table 4: TGA data of P (o-MP-co-pyrrole).

Temperature range (^{0}C)	Weight loss (%)		The removed molecules
	Found	Calculated	
25-220	9.46	9.2	$5H_2O$
220-400	23.8	24.3	SO_3, 2 pyrrole units
400-500	14.8	14.0	2 pyrrole units
500-600	21.2	20.8	Two benzenoid rings, one pyrrole
>600	24.2	25	Remaining polymeric chain

Surface Morphology and structure of P (o-MP-co-pyrrole)

The surface morphology of the polymer obtained at the optimum conditions was examined by scanning electron microscopy. Figure 13(a) shows top- view SEM image of the electro polymerized film on Pt electrode. As shown in this figure, the morphology of the p (o- MP- co- pyrrole) surface was found to be aggregates of uniform small spherical nanoparticles. The diameters of the aggregates were found to be in the range 200 - 400nm.

In order to check the structure of the fabricated p (o-MP-co-pyrrole), the sample was analyzed by XRD as shown in Fig.13 (b). This XRD pattern confirms that the copolymer structure is amorphous. The sharp peaks after 2θ ≥ 40° are ascribed to the Pt electrode.
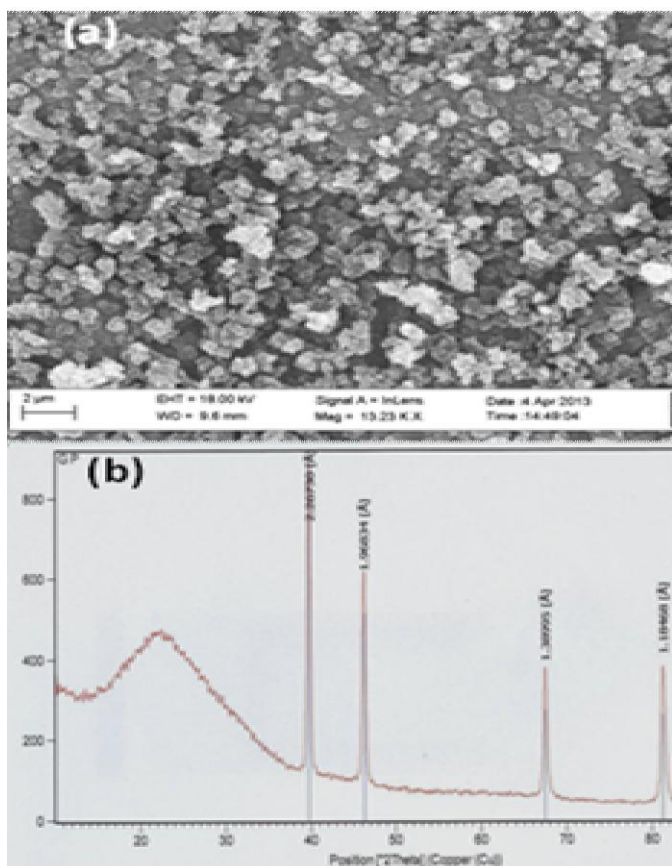
Figure 13: (a) Top-view FE-SEM image and (b) XRD of p (o-MP-co-pyrrole) on Pt electrode Prepared at the optimum conditions.

CONCLUSION

In conclusion, a novel copolymer was synthesized by the electro polymerization of o-MP-co-pyrrole on Pt electrode. The fabrication method notoriously complex process which depends on the co-monomer structure, the potential scan rate, and the temperature. The optimum concentrations of acid and monomer are 0.3 and 0.05M, respectively. From the kinetic studies of the electro polymerization, the orders of the reaction with respect to acid and monomer concentrations are 0.75 and 2.1 respectively. In addition, the apparent activation energy, enthalpy and entropy are estimated to be 42.2 kJ/mol, 41.7 kJ/mol and 186 $JK^{-1} mol^{-1}$, respectively. The electro polymerized film consists of spherical aggregates of diameters ranged from 200 to 400nm. According to the study of the mechanism, the copolymer structure was studied by fineman Ross method and the copolymer was found to be block copolymer.

REFERENCES

1. Fukuhara T, Akıyama Y, Yoneda N, Tada T, Hara S. Effective synthesis of difluorocyclohexa dienones by electrochemical oxidation of phenols oxidation of phenols. Tetrahedron Letters 2002; 43:6583.

2. Matsushita M, Kuramitz H, Tanaka S. Electrochemical oxidation for low concentration of aniline in neutral pH medium: application to the removal of aniline based on the electrochemical polymerization on a carbon fiber. Environ. Sci. Technol 2005; 39(10); 3805.

3. Cao H, Huang Y, Sun J. Uniform modification of carbon fibers surface in 3-D fabrics using intermittent electrochemical treatment. Composites Science and Technology 2005; 65: 1655.

4. Sarac AS, Bardavit Y. Electrografting of copolymer of poly [N-vinylcarbazole-co-styrene] and poly [N-vinylcarbazole-co-acrylonitrile] onto carbon fiber: cyclovoltammetric (CV), spectroscopic (UV-Vis, FT-IR-ATR), and morphological study (SEM). Progress in Organic Coating 2004; 49: 85.

5. Hua S, Brisena AL, Shi X, Mah DA and Zhou. Polyelectrolyte-Coated Nanosphere Lithographic Patterning of Surfaces: Fabrication and Characterization of Electropolymerized Thin Polyaniline Honeycomb Films. Phys. Chem.B J 2002; 106:6465.

6. Kumru EM, Springer J, Saraç AS, Bismark A. Electrografting of thiophene, carbazole, pyrrole and their copolymers onto carbon fibers: electrokinetic measurements, surface composition and morphology. Synthetic Metals 2001; 123; 391.

7. Khalkhali RA, Rus. Electrochemical Synthesis and Characterization of Electroactive Conducting Polypyrrole Polymers. Electrochem J 2005; 41 (9), 950–955.

8. Fletcher BL, McKnight TE, Fowlkes JD, Allison DP, Simpson ML, Doktycz MJ. Controlling the dimensions of carbon nanofiber structures through the electropolymerization of pyrrole. Synth. Met.J 2007; 157: 282.

9. Liu YC, Huang J M, Tsai CE, Chuang TC, Wang CC. Effect of TiO2 nanoparticles on the electropolymerization of polypyrrole. Chem. Phys. Lett. J 2004; 387:155.

10. Zhou Q, Li C M, Li J, Cui X, Gervasio D. Template-Synthesized Cobalt Porphyrin/ Polypyrrole Nanocomposite and Its Electrocatalysis for Oxygen Reduction in Neutral Medium Phys. Chem. CJ 2007; 111: 11216.

11. Ramasamy RP, Veeraraghavan B, Haran B, Popov BN.Electrochemical characterization of a

polypyrrole/Co0.2CrOx composite as a cathode material for lithium ion batteries. Power Sources 2003; 124: 197.

12. Smit MA, Ocampo AL, Espinosa-Medina MA, Sebastia´n PJ. A modified Nafion membrane with in situ polymerized polypyrrole for the direct methanol fuel cell. Power Sources 2003; 124: 59.

13. Bruno F, Pham MC, Dubois JE. Polaromicro tribometric study of polyphenylene oxide film formation on metal electrodes by electrolysis of disubstituted phenols. Electrochim Acta J 1977; 22: 451.

14. Panizza M, Cerisola G. Influence of anode material on the electrochemical oxidation of 2- naphthol: Part 1. Cyclic voltammetry and potential step experiments. Electrochim Acta J 2003. 48:3491.

15. Li XY, Cui YH, Feng YJ, Xie ZM, Gu JD. Reaction pathways and mechanisms of the electrochemical degradation of phenol on different electrodes. Wat. Res.J 2005; 39: 1972.

16. Gattrell M, Kirk DW. A study of electrode passivation during aqueous phenol electrolysis. Electrochem Soc J 1993; 140:903-911.

17. Gattrell M, Kirk DW. A Fourier Transform Infrared Spectroscopy Study of the Passive Film Produced during Aqueous Acidic Phenol Electro-oxidation. Journal of Electrochem. Soc J 1992; 139: 2736.

18. Ezerskis Z, Jusys Z. Electropolymerization of chlorinated phenols at a pt electrode in alkaline solution, part IV: A gas chromatography mass spectrometry study. Appl. Electrochem. J 2002; 32: 543.

19. Sezgin S, Ates M, Parlak EA, A Sezai Sarac AS. Scan Rate Effect of 1-(4-methoxyphenyl)-1H-Pyrrole Electro- coated on Carbon Fiber: Characterization via Cyclic Voltammetry, FTIR-ATR and Electrochemical Impedance Spectroscopy. Inter. J Electrochem. Sci. 2012; 7: 1093 - 1106.

20. Ureta-Zanatru MS, Bustos P, Berrios C, Diez MC, Mora M L, Gutierrez C. Electrooxidation of 2,4-dichlorophenol and other polychlorinated phenols at a glassy carbon electrode. Electrochim. Acta. J 2002; 47: 2399.

21. Randless P. Graphical solution of linear sweep voltammetry. Trans Faraday Soc J 1984 44:327.

22. Sevick A. Oscillographic polarography with periodical triangular voltage. Collect Czech Chem Commun J 1948; 13; 349.

23. Karamil H, Nezhad AR. Investigation of Pulse-Electropolymerization of Conductive Polypyrrole Nanostructures. International Journal of Electrochem. Sci. J 2013; 8: 8905 – 8921.

24. Eyring H. The Activated Complex in Chemical Reactions. Chem. Phys. J 1935; 3 (2): 107.

25. Finman M, Ross SD. Linear method for determining monomer reactivity ratios in copolymerization. Polymer Sci. J 1950; 52: 50.