Preparation kinetics and characterization of poly o-hydroxyaniline in aqueous hydrochloric acid solution using $K_2Cr_2O_7$ as oxidizing agent

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Abstract: *The oxidative chemical polymerization of o-hydroxyaniline (OHA) was studied in hydrochloric acid solution using potassium dichromate as oxidant at $5\pm0.2\ ^0C$. The effects of potassium dichromate, hydrochloric acid and monomer concentrations on the polymerization reaction were investigated. The order of reaction with respect to potassium dichromate, hydrochloric acid and monomer concentrations were found to be 0.939, 0.961 and 1.123 respectively. Also, the effect of temperature on the polymerization rate was studied and the apparent activation energy of the polymerization reaction was found to be 23.05 kJ/mol. The obtained polymer was characterized using XPS, IR, UV-visible and elemental analysis. The surface morphology of the obtained polymer was characterized by X-ray diffraction and transmission electron microscopy (TEM). The TGA analysis was used to confirm the proposed structure and number of water molecules in each polymeric chain unit.*
Keywords: *oxidative chemical polymerization, o-hydroxyaniline, characterization, kinetics.*

I. Introduction

The polymer material is first found as an insulator material and the idea that polymers or plastics could conduct electricity is considered absurd [1]. The wide application of polymer as an insulating material is the reason to studied and developed in the first place. In fact, these materials are commonly used for surrounding copper wires and manufacturing the outer structures of electrical appliances that prevent humans from coming in direct contact with electricity. In the recent years, scientists discovered a type of conjugated polymer called 'polyacetylene' could become highly electrically conductive after undergoing a structural modification process called doping [2, 3]. The polymer is called a 'conjugated polymer' because of the alternating single and double bonds in the polymer chain with presence a delocalized μ-electron system with an "intrinsic" wide band gap that defines their affinity for electrons [4]. The de-localized electrons may move around the whole system which produces the charge carriers to make them conductive.

The doping process is an effective method to produce conducting polymers which allows electrons to flow due to the formation of conduction bands. As doping occurs, the electrons in the conjugated system, which are loosely bound, are able to jump around the polymer chain. Electric current will be produced when the electrons are moving along the polymer chains. Several examples of conjugated conducting polymers are polyacetylene [5], polypyrrole [6], polyaniline [7, 8] and polythiopene [9]. Polyaniline has an important member in the intrinsically conducting polymer (ICP) family, owing to its ease of preparation, excellent environmental stability, various forms, interchangeable oxidation states, electrical, optical properties and economic cost [10, 11]. The applications of polyaniline are limited due to its poor processability [12], which is true for most conducting polymers. Several studies have been done in order to improve the solubility of polyaniline, among them, using functionalized protonic acids as dopant, like p-toluene-sulphonic acid, octyl-benzene-sulphonic acid, dodecyl benzene-sulphonic acid [13], poly (styrene) sulphonic acid [14] and phosphoric acid esters [15]. An alternative method to obtain soluble conductive polymers is the polymerization of aniline derivatives. The investigated aniline derivatives are alkyloxy, hydroxy, chloroaniline and substitution at the nitrogen atom was reported by S.M.Sayyah et.al [16-19] to improve the solubility of polyaniline. The substituted group of aniline affects not only the polymerization reaction but also the properties of the polymer obtained. The kinetics of chemical polymerization of 3-methylaniline, 3-chloroaniline, 3-hydroxyaniline , 3-methoxyaniline and N-methyl aniline in hydrochloric acid solution using sodium dichromate as oxidant and characterization of the polymer obtained by IR, UV-visible and elemental analysis, X-ray diffraction , scanning electron microscopy, TGA-DTA analysis and ac conductivity have been reported by reported by S.M.Sayyah et.al [16-19].

The present work intends to study the solubility and kinetics of the oxidative chemical polymerization of o-hydroxyaniline in aqueous HCl medium and potassium dichromate as oxidant. The obtained polymer is characterized by XPS, IR, UV-visible, TGA, elemental analysis, X-ray, and transmission electron microscopy (TEM).

II. Experimental:

2.1. Materials:

o-Hydroxyaniline provided by Winlab Co., (UK). Concentrated hydrochloric acid, pure grade product, provided by El-Nasr pharmaceutical chemical Co., Egypt. Potassium dichromate provided by Sigma-Aldrich chemical Co., (Germany). Doubly distilled water was used to prepare all the solutions needed in the kinetic studies.

2. 2. Oxidative Aqueous Polymerization of o-Hydroxyaniline (OHA) Monomer:

The polymerization reaction was carried out in a well-stoppered conical flask of 250 ml capacity; addition of (OHA) amount in 25 ml HCl of known molarity followed by the addition of the required amount of potassium dichromate as oxidant in water (25 ml) to the reaction mixture. The orders of addition of substances were kept constant in all the performed experiments. The stoppered conical flask was then placed in an automatically controlled thermostat at the required temperature. The flask was shaken (15 shakings/10 s/15 min) by using an automatic shaker. The flask was filtrated using a Buchner funnel, and then the obtained polymer was washed with distilled water, and finally dried till constant weight in vacuum oven at 60 ^{o}C.

2.3. Elemental Analysis and X-Ray Photoelectron Spectroscopy (XPS):

The carbon, hydrogen and nitrogen contents of the prepared polymer was carried out in the micro analytical laboratory at Cairo University by using oxygen flask combustion and a dosimat E415 titirator (Switzerland).

An XPS spectrum was carried out using XPS-thermo scientific spectrometer, Model: K-ALDH in Central Metallurgical Research and Development Institute (CMRDI). Polymer was mounted on a standard sample holder using double-sided adhesive tape. Survey and XPS spectra were obtained with Al Kα monochromatic X-ray with the resolution of 0.7eV.

2.4. Infrared and Ultraviolet Spectroscopy:

The infrared spectroscopic analysis of the prepared polymer was carried out in the micro analytical laboratory at Cairo University using a Shimadzu FTIR-430 Jasco spectrophotometer and KBr disc technique.

The ultraviolet-visible absorption spectra of the monomer and the prepared polymer sample was measured using Shimadzu UV spectrophotometer (M 160 PC) at room temperature in the range 200-900 nm using dimethylformamide as a solvent and reference.

2.5. Thermal Gravimetric Analysis (TGA), Transmission Electron Microscopy (TEM) and X-Ray Analysis:

Thermal gravimetric analysis (TGA) of the polymer sample was performed using a SHIMADZU DT-30 thermal analyzer. The weight loss was measured from ambient temperature up to 600 ^{0}C at rate of 20 ^{0}C /min to determine the rate of degradation of the polymer.

X-Ray diffractometer (philip1976.model1390) was used to investigate the phase structure of the polymer powder under the following condition which kept constant during the analysis processes Cu: X-ray tube, scan speed =8/min, current=30mA, voltage =40kv and preset time=10s.

The inner cavity and wall thickness of the prepared polymer was investigated using transmission electron microscopy (TEM) JEOL JEM-1200 EX П (Japan).

2.6. Calculations:
2.6.1. Determination of Conversion Yield:

The conversion yield of the monomer to the polymer was determined by the weighing of the dry obtained polymer (P) divided by the weight of the monomer (w) and was calculated in the following way:

$$\text{Conversion yield} = \frac{\text{Polymer Yield(P)}}{\text{Weight of Momoner (w)}} \qquad (1)$$

2.6.2. Determination of the Polymerization Rate:

The rate of polymerization was determined in the following:

$$\text{Rate}(R_i) = \frac{P}{V \times M.wt \times t} \ (\text{gmol} / L.\text{sec}) \qquad (2)$$

Where (P) is the weight of polymer formed at time (t) in seconds, (V) is the volume of the reaction solution in liters and (M. wt) is the molecular weight of the monomer.

2.6.3. Calculation of the Apparent Energy of Activation.

The apparent activation energy (E_a) of the aqueous polymerization reaction was calculated using the following Arrhenius equation:

Where (K) is the rate, (R) is the universal gas constant, (T) is the reaction temperature and (C) is constant.

2.6.4. Determination of Enthalpy (ΔH^*) and Entropy (ΔS^*) of Activation:

Enthalpy of activation (ΔH^*) and entropy (ΔS^*) were calculated using transition state theory equations (Eyring equation):

$$K = \frac{RT}{Nh} e^{\Delta S^*/R} . e^{-\Delta H^*/RT} \qquad (4)$$

Where (K) is the rate constant, (N) is the Avogadro's number, (R) is the universal gas constant and (h) is planks constant.

By dividing the above equation by (T) and taking its natural logarithm, the following equation obtained:

$$Ln\left(\frac{K}{T}\right) = Ln\frac{R}{Nh} + \frac{(\Delta S^*)}{R} + \frac{(-\Delta H^*)}{RT} \qquad (5)$$

A plot of Ln (k/T) against (1/T) is linear, with a slope equals to (-ΔH^*/R) and intercept equals to (Ln. k/h + ΔS^*/R). Therefore ΔH^* and ΔS^* can be calculated from the slope and intercept respectively.

III.   Results And Discussion:

3.1. Determination of the Optimum Polymerization Conditions:

To optimize the conditions for polymerization of o-hydroxyaniline (OHA), the concentrations of potassium dichromate, hydrochloric acid and monomer were investigated with keeping the total volume of the reaction mixture constant at 50 ml.

3.1.1. Effect of Potassium Dichromate Concentration on the Polymerization Reaction:

Both of the monomer and HCl concentrations are fixed at 0.1 M while the oxidant concentrations were varied from 0.02 to 0.5M at 5 ± 0.2°C to investigate the optimum polymerization condition of OHA. The conversion curve was represented in figure (1), from which it is clear that, the obtained polymer increased with the increase of $K_2Cr_2O_7$ concentration reaching maximum value at 0.3M. From the left part of the curve it is clear that, the polymer yield increases from 0.02M to 0.3M then decreases from 0.3M to 0.5M. This could be due to the fact that, in the first part of the curve, the produced initiator ion radical moieties activate the backbone and simultaneously produced the o-hydroxyaniline ion radical, which takes place immediately and therefore, yield increases with the increase of potassium dichromate concentration up to 0.3M. But in the second part of the curve, the polymer yield decreases with the increasing of $K_2Cr_2O_7$ concentration, which may be due to the formation of low molecular weight oxidation product at high concentration of oxidant (> 0.3) which promote the formation of low molecular weight oxidation produced and make it easily soluble in the reaction medium [20].

3.1. 2. Effect of HCl Concentration on the Polymerization Reaction:

The effect of HCl concentration on the aqueous oxidative chemical polymerization of OHA was investigated using constant concentration of $K_2Cr_2O_7$ at 0.3M and monomer concentration at 0.1M but using different concentrations of HCl at 5 ± 0.2°C. The conversion curve was represented in figure (2). From which it is clear that, the obtained yield increases in the acid concentrations range from 0.02 to 0.2 then decreases gradually up to 0.3M. This behavior may be due to, at higher concentration of HCl, the degradation of the polymer could be occur in the early stages of the reaction [20, 21].
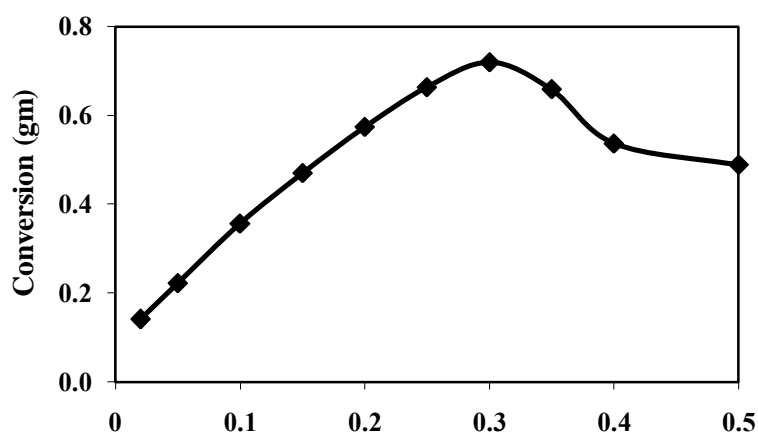
Figure (1): Effect of $K_2Cr_2O_7$ concentration on the aqueous oxidative chemical polymerization of o-hydroxyaniline (OHA).
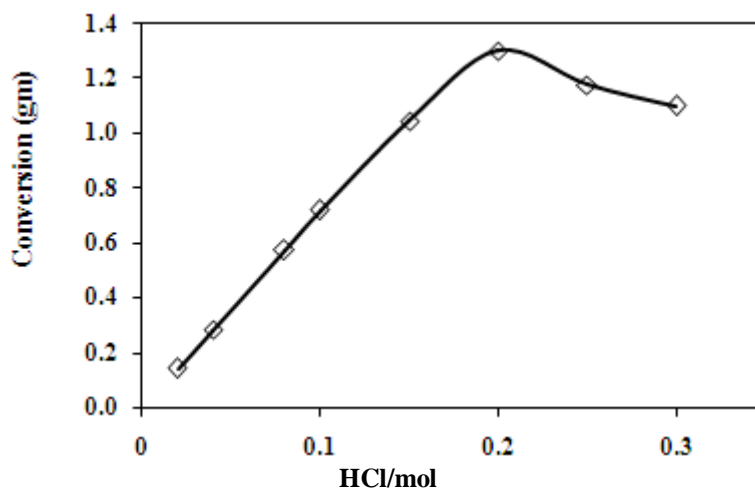

Figure (2): Effect of HCl concentrations on the aqueous oxidative chemical polymerization of o-hydroxyaniline (OHA).

3.1. 3. Effect of o-Hydroxyaniline (OHA) Concentration on the Polymerization Reaction:

The effect of monomer concentration on the polymerization yield was investigated in the range of monomer concentrations from 0.02 to 0.5M and the data are represented in figure (3). From which it is clear that, the optimum yield is obtained by using 0.1M of monomer concentration.
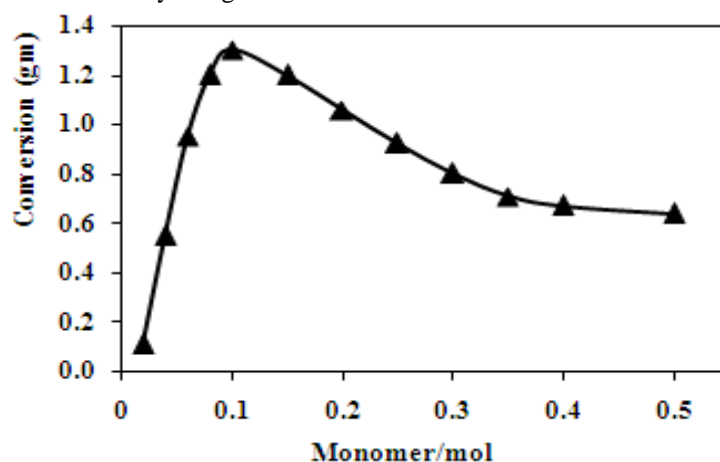
Figure (3): Effect of monomer concentration on the aqueous oxidative polymerization of o-hydroxyaniline (OHA).

3.2. The Kinetic Studies of the Polymerization Reaction of (OHA):
3.2.1. Effect of Potassium Dichromate Concentration:
          The aqueous polymerization of OHA (0.1 mol) was carried out in 25 ml of HCl solution (0.2 mol) in the presence of 25 ml potassium dichromate as oxidant of different molarities (0.06 – 0.30) at 5 ± 0.2 ^{0}C for different time intervals. The yield-time curves for each oxidant concentration are graphically represented in figure (4). The initial and overall reaction rates were determined using equation (2). The initial and overall reaction rate of the polymerization reaction increases with the increase of oxidant concentration in the range between 0.06 - 0.30 mol/l. The oxidant exponent was determined from the relation between logarithms of the initial rate of polymerization log (R_i) against logarithm of the oxidant concentration. A straight line was obtained which has a slope of 0.939 as represented in figure (5). This means that the polymerization reaction of (OHA) is a first order reaction with respect to the oxidant.
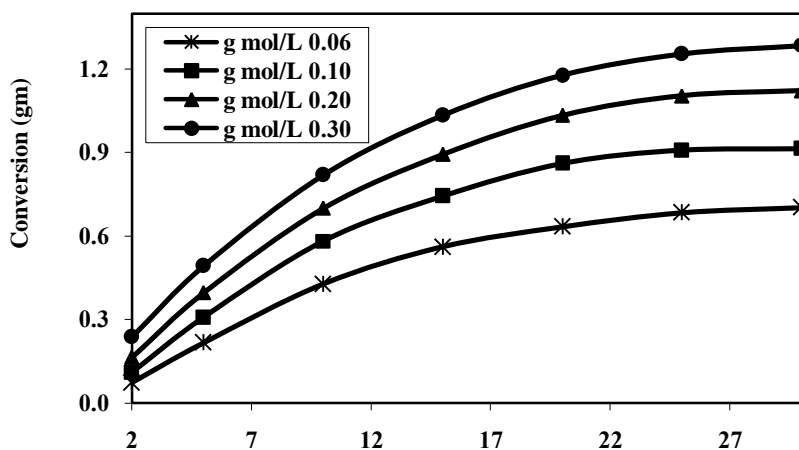

Figure (4): Conversion - time curve for the effect of potassium dichromate concentration on the polymerization of (OHA).
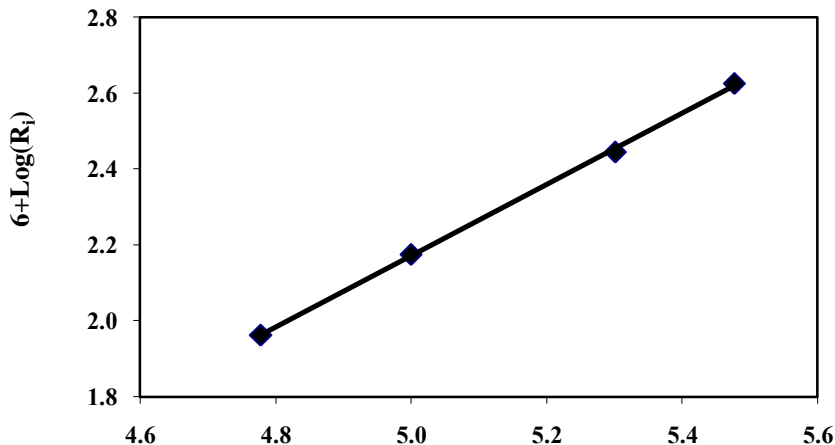

Figure (5): Double logarithmic plot of the initial rate and oxidant concentration for polymerization of o-hydroxyaniline (OHA).

3.2.2. Effect of Hydrochloric Acid Concentration:
          The polymerization of o-hydroxyaniline (OHA) (0.1 mol) in 25 ml of HCl with different molarities was carried out by addition of 25 ml potassium dichromate (0.3mol/L) as oxidant at 5 ± 0.2 ^{0}C for different time intervals. The concentrations of the monomer and oxidant were kept constant during the study of HCl concentration effect on the polymerization reaction. The experiments were carried out as described in section 2.2, and the yield-time curves were plotted (c.f. figure (6)). From which it is clear that both the initial and overall reaction rates of the polymerization reaction increase with the increasing of HCl concentrations in the range between 0.05 - 0.2 mol/L. The HCl exponent is determined from the slope of the straight line represented in figure (7) and was found to be 0.961, which means that the polymerization reaction order with respect to the HCl concentration is a first order reaction.
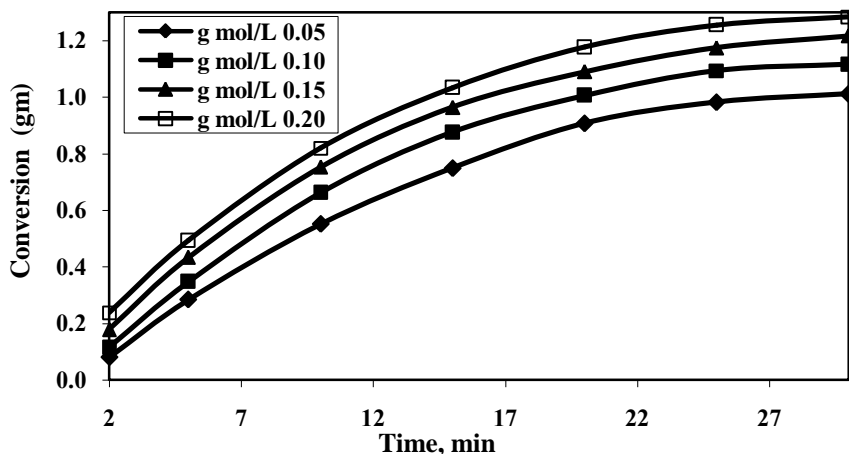
Figure (6): Conversion – time curves showing the effect of HCl concentration on the aqueous oxidative polymerization of (OHA)
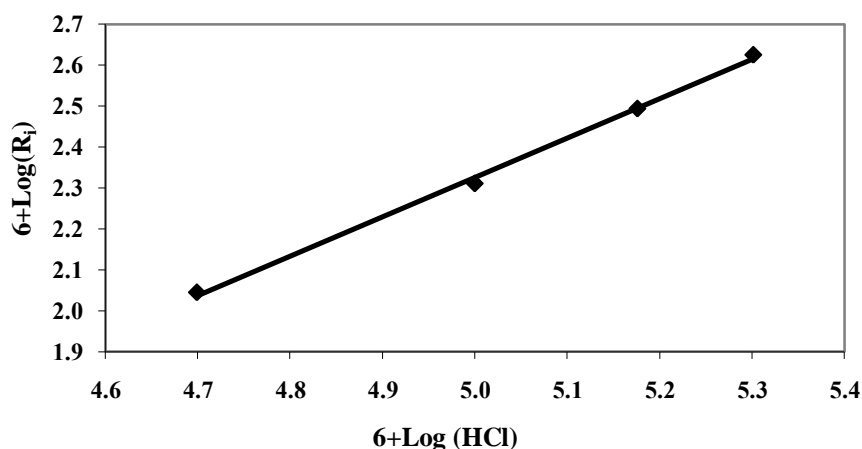

Figure (7): Double logarithmic plot of the initial rate of aqueous oxidative chemical polymerization in case of and HCl concentration of (POHA).

3.2.3. Effect of Monomer (OHA) Concentration:

The aqueous oxidative chemical polymerization of (OHA) was carried out in 25 ml of HCl solution (0.2mol/L) in the presence of 25 ml potassium dichromate (0.3mol/L) as oxidant at $5\pm 0.2\ ^0$C for different time intervals. The yield-time curve was plotted for each monomer concentration used. The yield-time curve for each monomer concentration is graphically represented in figure (8). The monomer exponent was determined from the slope of the straight line represented in figure (9) for the relation between log R_i and log of the monomer concentration. The slope of this linear relationship was found to be 1.123. This means that the polymerization reaction with respect to the monomer concentration is a first order reaction.
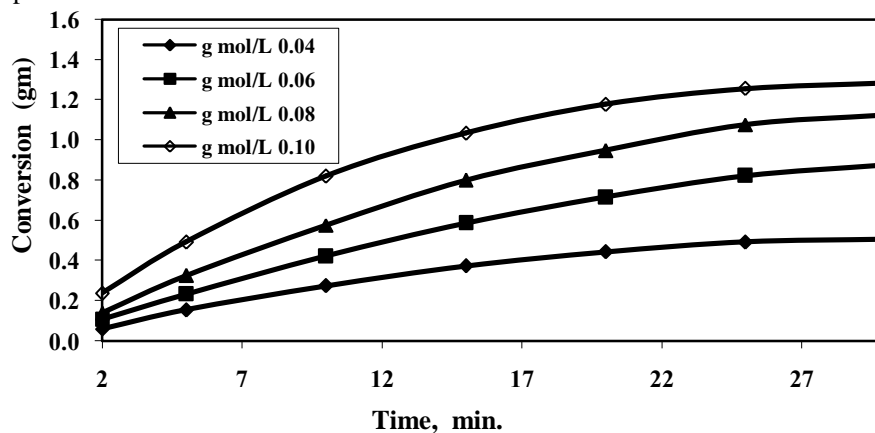

Figure (8): Conversion - time curves for the effect of monomer concentration on the aqueous chemical oxidative polymerization of (OHA).
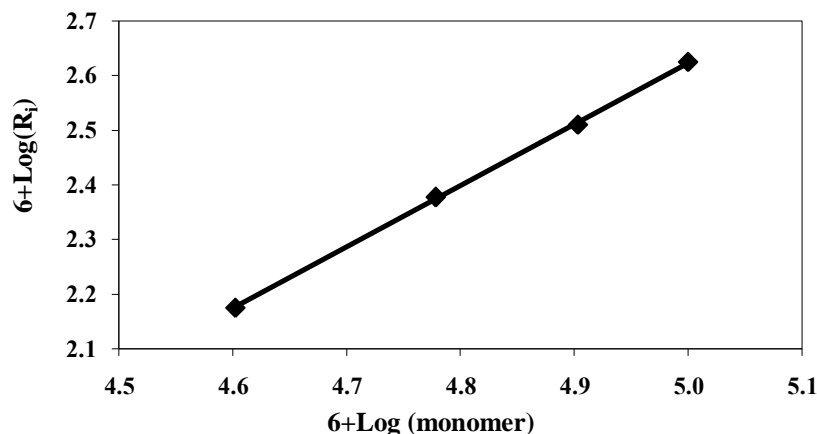
Figure (9): Double logarithmic plot of the initial rate and monomer concentration of o-hydroxyaniline (OHA).

3.2.4. Calculation of the Thermodynamic Activation Parameters:

The polymerization of OHA (0.1 mol/L) in 25 ml of 0.2 mol/L HCl in presence of 25 ml potassium dichromate (0.3 mol/L) as oxidant was carried out at 5, 10 and 15 ^{0}C for different time intervals. The yield- time curves were graphically represented in figure (10), from which it is clear that both of the initial and overall reaction rates increase with raising the reaction temperature. The apparent activation energy (E_a) of the aqueous polymerization reaction of (OHA) was calculated using the Arrhenius equation (3).
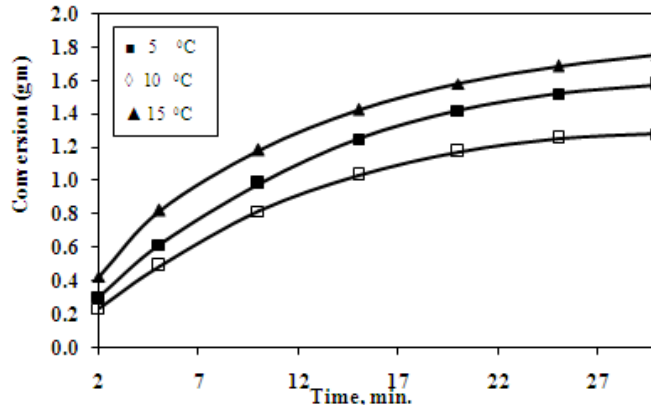

Figure (10): Conversion - time curve for the effect of temperature on the aqueous oxidative chemical polymerization of (OHA).

By plotting log R_i against 1/T, a straight line was produce as shown in figure (11). The apparent activation energy for this system is found to be 23.05 kJ/mol. The Enthalpy and entropy of activation for the polymerization reaction can be calculated by the calculation of K_2 from the following equation:

$$\text{Reaction Rate} = K_2 \,[\text{oxidant}]^{0.939}\,[\text{HCl}]^{0.961}\,[\text{monomer}]^{1.123} \qquad (6)$$

The calculated values of K_2 at 5, 10 and 15 ^{0}C were found to be 1.086×10^{-5}, 1.274×10^{-5} and 1.537×10^{-5} respectively. The enthalpy (ΔH^*) and entropy (ΔS^*) of activation associated with k_2, were calculated using Eyring equation (5).
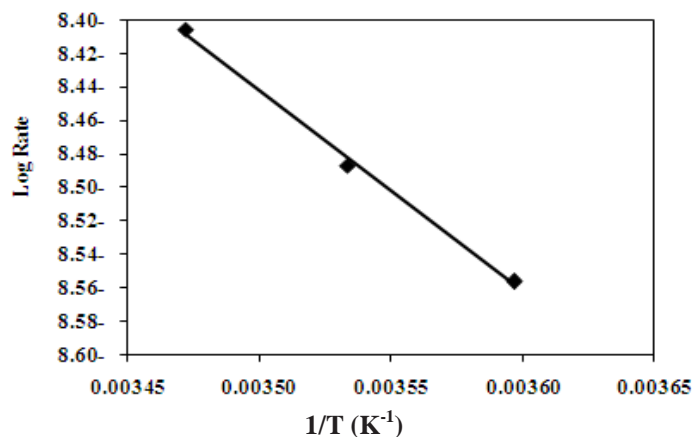

Figure (11): The relation between the logarithm of initial rate and (1/T) for POHA.

Figure (12) shows the relation between K_2/T vs $1/T$, which gives a linear relationship with slope equal to $(-\Delta H^*)/R$ and intercept equal to (log R/Nh $+\Delta S^*/R$). From the slops and intercept, the values of ΔH^* and ΔS^* were calculated and it is found to be 20.70 $kJmol^{-1}$ and -264.95 $Jmol^{-1}K^{-1}$ respectively.

The intramolecular electron transfer steps for the oxidation reaction are endothermic as indicated by ΔH^* value. The contributions of ΔH^* and ΔS^* to the rate constant seem to compensate each other. This fact suggests that the factors controlling ΔH^* must be closely related to those controlling ΔS^*. Therefore, the solvation state of the encounter compound could be important in determination of ΔH^*. Consequently, the relatively small enthalpy of activation can be explained in terms of the formation of more solvated complex.
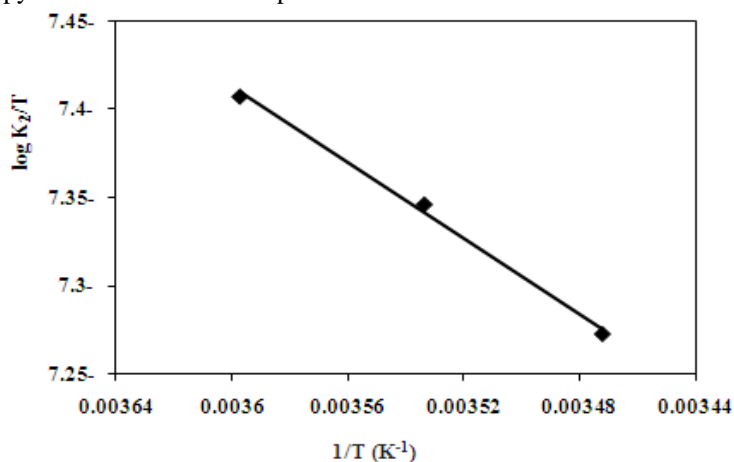

Figure (12): The relation between log K_2/T with $1/T$ for the chemical oxidative polymerization of o-hydroxyaniline (OHA).
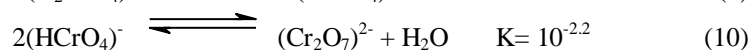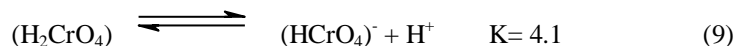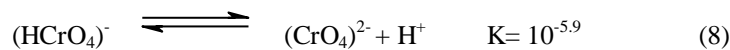
3.3. Polymerization Mechanism:

The aqueous oxidative polymerization of o-hydroxyaniline (OHA) is described in the experimental section, and follows three steps [22].
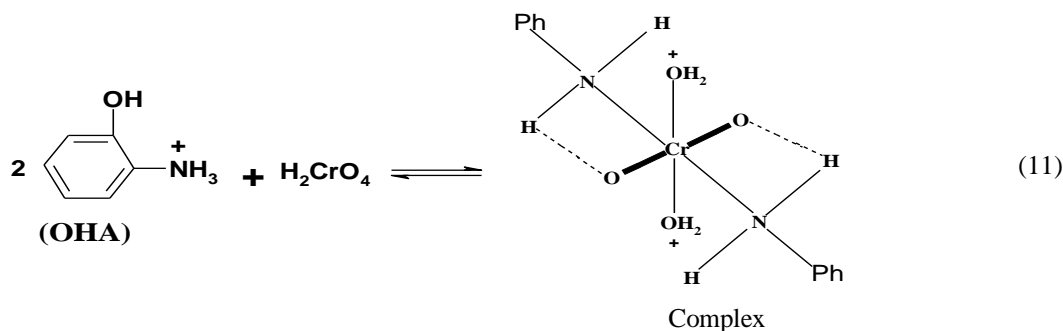
The Initiation Step

Potassium dichromate in acidified aqueous solution produces chromic acid as shown in equation (7):

$$K_2Cr_2O_7 + H_2O + 2H^+ = 2K^+ + 2H_2CO_4 \qquad (7)$$
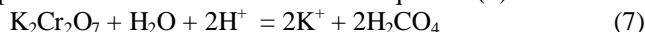
This reaction is controlled by the change in pH, the orange red dichromate ions$(Cr_2O_7)^{2-}$ are in equilibrium with the $(HCrO_4)^-$ in the range of pH-values between 2 and 6, but at pH below 1 the main species is (H_2CrO_4) and the equilibria can occur as follows:

$$(HCrO_4)^- \rightleftharpoons (CrO_4)^{2-} + H^+ \qquad K= 10^{-5.9} \qquad (8)$$

$$(H_2CrO_4) \rightleftharpoons (HCrO_4)^- + H^+ \qquad K= 4.1 \qquad (9)$$

$$2(HCrO_4)^- \rightleftharpoons (Cr_2O_7)^{2-} + H_2O \qquad K= 10^{-2.2} \qquad (10)$$

The chromic acid withdraws one electron from each protonated o-hydroxyaniline and probably forms a metastable complex as shown in equation (11):
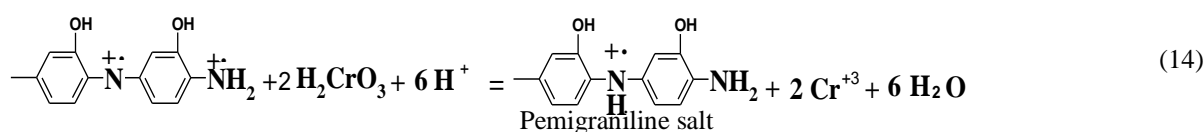

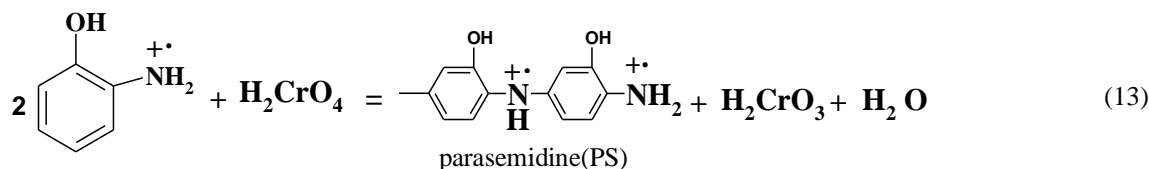$$(11)$$

Complex

The complex undergoes dissociation to form monomer cation radical as shown in equation (12):
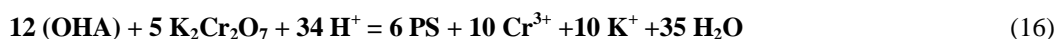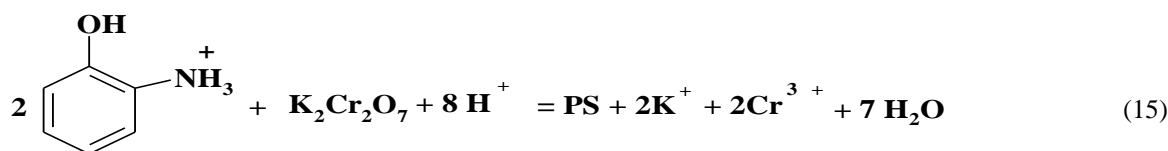

$$(12)$$
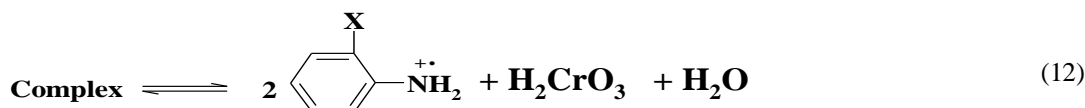
Generally, the initial step is rapid and may occur in short time, 0–5 min (autocatalitic reaction).

Propagation Step

This step involves the interaction between the formed radical cation and the monomer to form a dimer radical cation**.** In the case of Cr (VI) oxidation of the organic compounds, Cr (VI) is reduced to Cr (IV) first and then to Cr (III) [20]. Transfer of two electrons from two monomer ion radical by H_2CrO_4 produces para semidine salt along with chromous acid $H_2Cr_2O_3$ (Cr (IV)). The intermediately produced Cr (IV) oxidizes para semidine to pemigraniline salt (PS) at suitable low pH and the PS acts as a catalyst for conversion of radical cation to polymer.

$$2 \ [OHA\text{-radical cation}] + H_2CrO_4 = [PS] + H_2CrO_3 + H_2O \tag{13}$$

parasemidine(PS)

$$[\text{dimer}] + 2 H_2CrO_3 + 6 H^+ = [\text{Pemigraniline salt}] + 2 Cr^{+3} + 6 H_2O \tag{14}$$

Pemigraniline salt

This reaction is followed by further reaction of the formed dimmer radical cations with monomer molecules to form trimer radical cations and so on. The degree of polymerization depends on different factors such as dichromate concentration, HCl concentration, monomer concentration, and temperature. By adding equations (7), (11), (12), (13) and (14).

$$2 \ [OHA\text{-}NH_3^+] + K_2Cr_2O_7 + 8 H^+ = PS + 2K^+ + 2Cr^{3+} + 7 H_2O \tag{15}$$

$$12 \ (OHA) + 5 \ K_2Cr_2O_7 + 34 \ H^+ = 6 \ PS + 10 \ Cr^{3+} + 10 \ K^+ + 35 \ H_2O \tag{16}$$

Termination Step

Termination of the reaction occurs by the addition of ammonium hydroxide solution in an equimolar amount to HCl present in the reaction medium (till pH = 7), which leads to cessation of the redox reaction. The reaction could occur as follows:
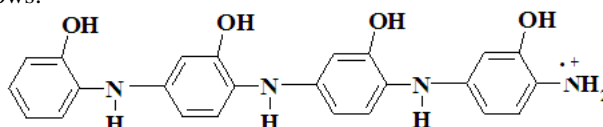
3.4. Characterization of Poly o-hydroxyaniline:
3.4.1. The Solubility:

The solubility of o-hydroxy aniline was investigated in N-methyl pyrrolidone (NMP), dimethylformamide (DMF), acetone, methanol, iso propanol, benzene, hexane and chloroform. The solubility data are listed in table (1). The poly o-hydroxyaniline is completely soluble in N-methyl pyrrolidone and completely insoluble in chloroform, benzene and hexane.

Table (3-23): The solubility of poly o-hydroxyaniline in different solvents at 20 ^{0}C.

Solvent	NMP	DMF	Acetone	Methanol	Iso propanol	Chloroform	Benzene	Hexane
POHA	●	●	○	●	○	■	■	■

●, soluble; ○ slightly soluble; ■ insoluble.

3.4.2. The Elemental Analysis:

The data obtained from the elemental analysis using oxygen flask combustion and a dosimat E415 titirator shows that, the found carbon content in the prepared poly o-hydroxyaniline is lower than the calculated value. This is due to the formation of chromium carbide during the heating step and measuring process while the found values of nitrogen and hydrogen are in good agreement with the calculated data for the suggested structure present in scheme (1). By measuring another sample of poly o-hydroxyaniline which is prepared by using ammonium persulfate as oxidant, the found value of carbon is higher than sample which is prepared by using potassium dichromate as oxidant. For more information about the chemical composition of poly o-hydroxyaniline, the XPS study was conducted as mentioned under point 2.3.

3.4.3. X-Ray Photoelectron Spectroscopy (XPS) Characterization:
3.4.3.1. XPS Survey Elemental Composition:

X-Ray Photoelectron Spectroscopy (XPS) is used to study the composition of materials, which detect elements starting from Li (Z=3) and higher elements. Hydrogen (Z = 1) and helium (Z = 2) cannot be detected due to the low probability of electron emission. XPS survey begins from 0 to 1400 (eV) as shown in figures (13). The XPS survey scan spectrum of poly o-hydroxyaniline show the presence of C, N, O, Cl and Cr. The Cl was present as doping anion in the polymer sample. Chrome was found in the prepared polymer sample due to the preparation condition using potassium dichromate as oxidant. It is possible for chromium ion (Cr^{3+}) to present between polymer chains as a sandwich-bonded between these phenyl groups as shown in scheme (1) and the usual formation procedure is occur by the hydrolyses of the reaction mixture with dilute acid which gives the cation $(C_6H_6)_2Cr^{3+}$ [22].

The XPS elemental analysis of the prepared polymers are given in table (2). The data shows that there is a good agreement with the calculated one for the suggested structures present in scheme (1).
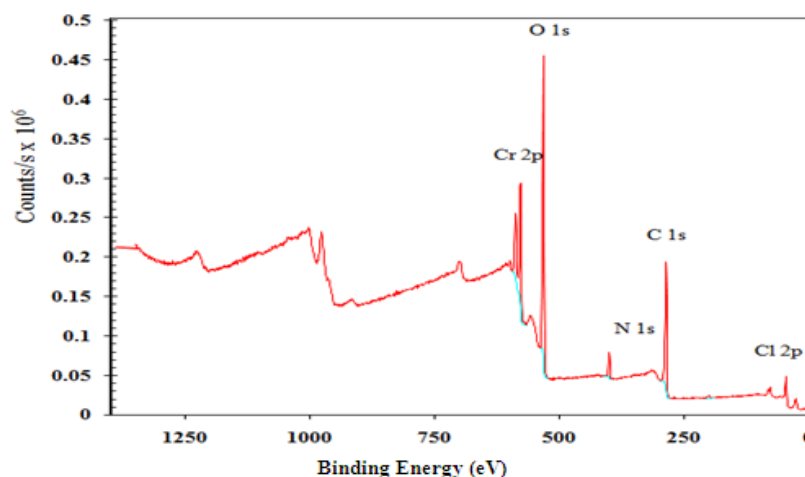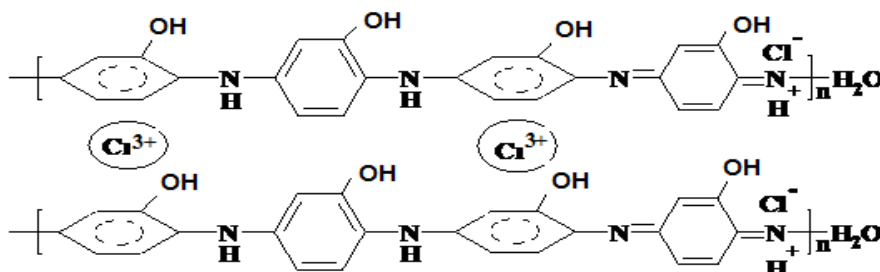

Figure (13): X-Ray Photoelectron Spectroscopy (XPS) survey elemental composition of (POHA).

Scheme (1).Structure of the prepared poly o- substituted aniline.

Table (2): The XPS elemental analysis of poly o-hydroxy aniline derivatives

Name	C%		N%		Cl%		O %		Cr %	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
POHA	56.32	57.05	10.95	10.26	6.94	6.99	15.64	16.01	10.15	9.69

3.4.3.2. XPS Spectra of Poly o-hydroxyaniline (POHA):

Four main peaks were obtained for C1s spectra of (POHA) as shown in Figure (14-a). The sharp peak appearing at 284.58 eV is attributed to C-H (C_1) bond, while the peak appearing at 284.21 eV is attributed to C-C (C_2) bond. The peak appearing at 285.37 eV is assigned to C-N (C_3) bond while, the peak appearing at 288.48 eV is attributed to C-O or C-N$^+$ (C_4) bond [23-25].

N1s Figure (14-b) shows the XPS N1s spectrum of (POHA) which has distinct peak at about 399.18 eV, characteristic of the –NH- structure of sponges and insures presence of steric strain associated with the amine group. The steric strain may be relieved by sequestration of proton from –CH$_3$ which lead to the formation of very stable ionic complex containing hydrogen bond N-H-N$^+$ bride [25, 26].

Two distinct oxygen species contributes to the oxygen 1s signals in the conducting polymers (Figure (14-C)). The distinct energy peaks at 530.68 and 532.79 eV could be attributed to Cr$_2$O$_3$ and C-OH respectively.

The Cl 2p spectrum of (POHA) is shown in figure (14-d). In order to estimate the anion Cl at the surface, Cl 2p peaks are fitted with a number of spin-orbit doublets (Cl 2p$_{1/2}$ and Cl 2p$_{3/2}$) doublets with the B.E.

for the $C12p_{3/2}$ peaks at about 197.26, 197.42, and 199.28 eV. The lowest and the highest B.E. components are attributable to the ionic and covalent chlorine species (Cl⁻ and -Cl), respectively. The chlorine species (Cl[*]) with the intermediate appear at B.E. of 197.42 eV. The lower B.E. value of the Cl[*] species compared to the Cl species suggests the presence of chloride anion in a more positive environment, probably arising from an increase in the number of positively charged nitrogen in the polymer chain associated with the formation of polarons and bipolarons.

The Cr spectrum of (POHA) is shown in Figure (14-e). The main components corresponding to different chemical chromium species were observed in the high-resolution $Cr_2p_{3/2}$ spectrums. The first peak at 576.78 eV ±0.2 eV was assigned to Cr_2O_3 which is in agreement with what was found by P.Chowdhury et.al [20] and P. Stefanov et.al [26], also indicated by a distinct O1s peak at 579.88 eV typical for Cr_2O_3 which may be adsorbed on polymer surface during chromous acid $H_2Cr_2O_3$ oxidation process. There is also a component visible correspond to $Cr_2p_{1/2}$ at 586.73 eV, which was attributed to Cr^{3+}. This data reveal that, chromium ion present between benzene rings of polymeric chain as shown in scheme (1).
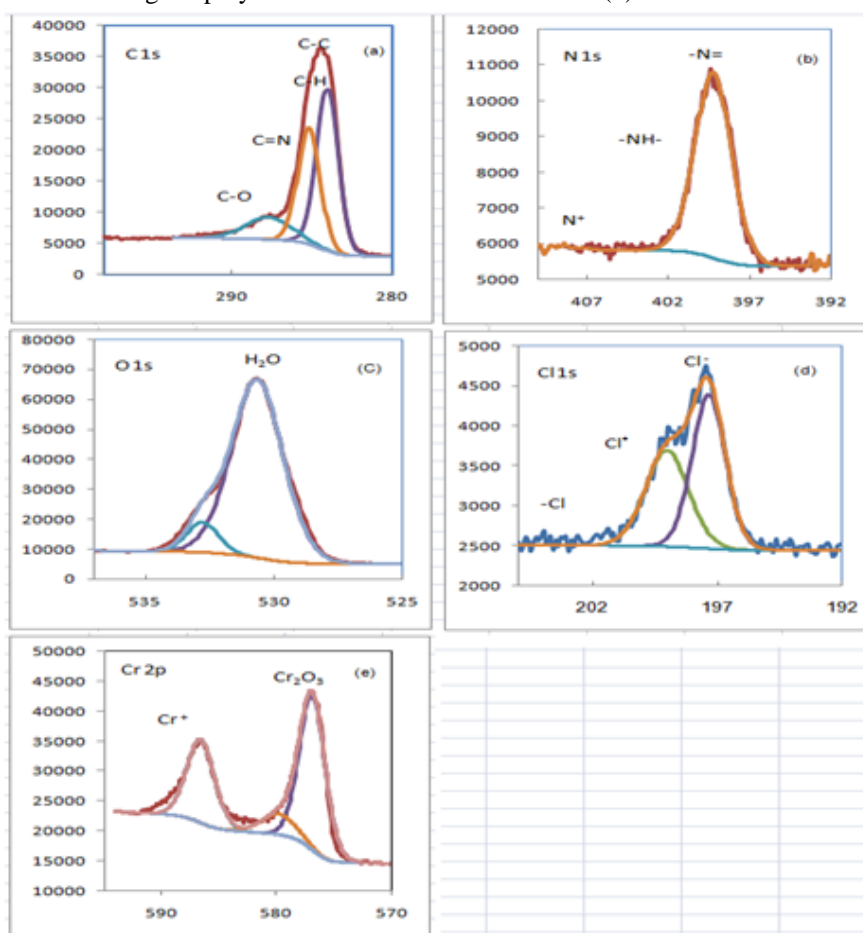
Binding energy (eV)
Figure (14): X-Ray photoelectron spectroscopy (XPS) spectra of (POHA).

3.4.4. The Infrared Spectroscopic Analysis of o-Hydroxyaniline (OHA) Monomer and its Analogs Polymer (POHA):

The IR spectrum of the o-hydroxyaniline (OHA) monomer and its polymer (POHA) is represented in Figure (15), while the absorption band values and their assignments are summarized in table (3). The medium absorption band appearing at 491 cm⁻¹ for monomer and the medium absorption band appearing at 525 cm⁻¹ in case of polymer may be attributed to the torsional oscillation of NH_3^+ group. The strong absorption band appearing at 740 cm⁻¹ may be due to the out of plane CH deformation of 1,3-disubstitiation in benzene ring in case of monomer, appears at 750 cm⁻¹ with slightly shift in case of polymer. A series of absorption bands appearing in the region from 800 …. 1132 cm⁻¹ which could be attributed to out-of-plane bending of C-H bonds of aromatic ring in both cases (monomer and polymer). The medium absorption band appearing at 1220 cm⁻¹ which could be attributed to bonding vibration C-OH in case of monomer, appears at 1275 cm⁻¹ with slightly shift in case of polymer. The medium absorption band appearing at 1403 cm⁻¹ which may be attributed to bending deformation of C-H group attached to benzene ring in case of monomer, appears at 1420 cm⁻¹ with

slightly shift in case of polymer. The sharp absorption band appearing at 1509 cm^{-1} which could be attributed to N-H bending deformation in case of monomer, appears at 1556 cm^{-1} with slightly shift in case of polymer.

The sharp absorption band appearing at 1600 cm^{-1} in case of monomer and the shoulder band appearing at 1639cm^{-1} in case of polymer could be attributed to symmetric stretching vibration of C=C in aromatic system or C=N in quinoid structure. The shoulder band, appearing at 3015 cm^{-1} which may be due to an overtone of the N–H bending vibration in case of monomer, disappear in case of polymer. The sharp absorption bands appears at 3202 and 3373 cm^{-1} which could be attributed to symmetric stretching vibration for –OH and -NH groups in case of monomer, while appearing as a broad band at 3481 cm^{-1} due to the merging of two individual absorption peaks from the stretching vibrations of –OH group and –NH$_2$ group in case of polymer.

Table (3): Infrared absorption bands and their assignments of (OHA) monomer and its analogs polymer (POHA).

Wave number(cm^{-1})		Assignments
(OHA)	(POHA)	
417^{sh}	—	Torsional oscillation of NH$_3$ group
445^{b}	—	
491^{m}	—	
—	525^{b}	
544^{m}	—	
574^{sh}	—	
740^{s}	—	Out of plane deformation of CH for 1,2- disubstituted benzene ring
—	750^{b}	
—	800^{sh}	Out of plane C-H deformation of 1,2-disubistuition of benzene ring
806^{sh}	—	
826^{s}	—	
899^{s}	—	
—	915^{w}	
1024^{w}	—	
—	1132^{b}	
1220^{m}	—	Bonding vibration C-O-H
1273^{s}	—	
—	1275^{b}	
1403^{m}	—	Bending deformation of C-H group attached to benzene ring
—	1420^{sh}	
1467^{s}	—	
1509^{s}	—	N-H bending deformation
—	1556^{b}	
1600^{s}	—	Symmetric stretching vibration of C=C in aromatic system or C=N in quinoid structure
—	1639^{sh}	
2587^{b}	—	Stretching vibration of C–N or combination bands of the asymmetric bending and torsional oscillation of the protonated amino group
2713^{b}	—	
—	2787^{sh}	
2956^{m}	—	
3015^{sh}	—	
3202^{s}	—	Symmetric stretching vibration for –OH and -NH. groups
3373^{s}	—	
—	3481^{b}	

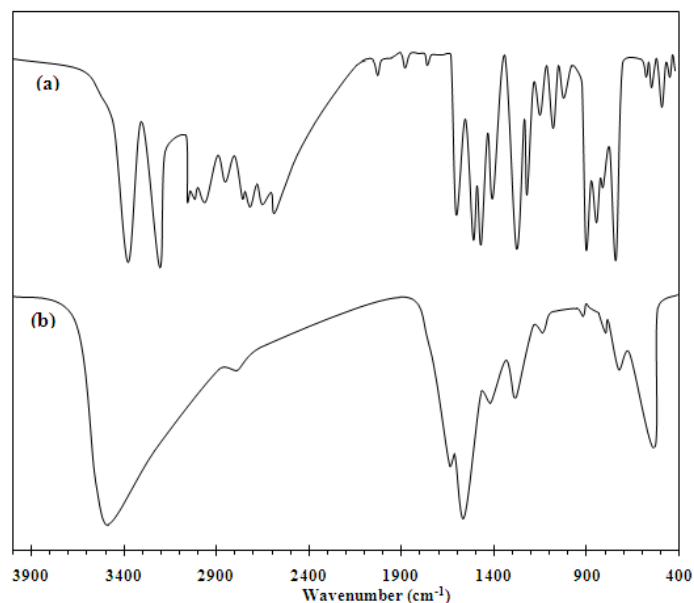s= sharp   m= medium   w=weak   b=broad   sh=shoulder

Figure (15): The infrared spectrum of (OHA) monomer (a) and it analogous polymer (POHA) (b).

3.4.5. The UV-visible Spectra of o-Hydroxyaniline (OHA) and its Polymer (POHA):

The UV-visible spectra of (OHA) and its polymer (POHA) are represented in figure (16); the spectra show the following absorption bands:

(1) In case of monomer, two absorption bands appear at λ_{max} = 215 and 244 nm which may be attributed to π-π^* transition (E$_2$-band) of the benzene ring and the β-band ($A_{1g} - B_{2u}$).

(2) In case of polymer, the absorption band appear at λ_{max} = 224 and 258 nm which may be attributed to π-π^* transition showing a bathochromic shift. Beside these two bands, broad absorption band appears in the visible region at λ_{max} = 448 nm which may be due to the high conjugation of the aromatic polymeric chain.
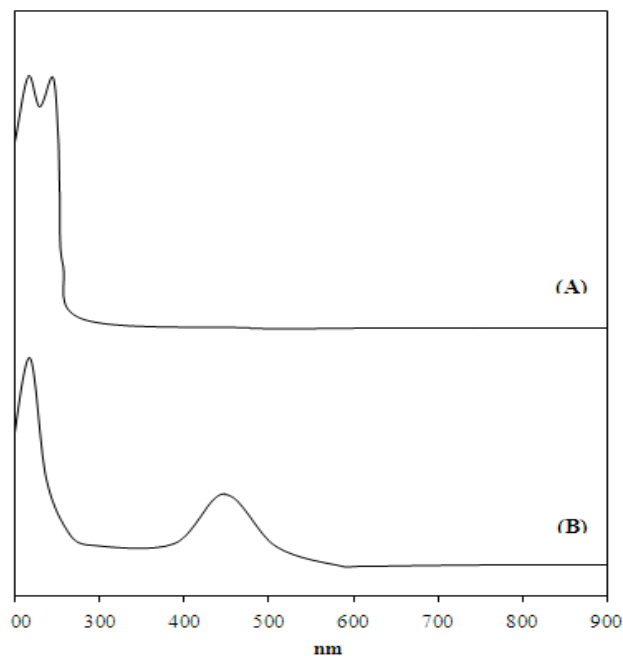

Figure (16): UV-visible spectra of (OHA) (A) and its analogous polymer (POHA) (B).

3.4.6. Thermal Gravimetric analysis (TGA) of (POHA):
Thermogravimetric analysis (TGA) of (POHA) has been investigated and the TGA-curve is represented in figure (17). The calculated and found data are summarized in table (4). The thermal degradation steps are summarized as follows:

(1)The first stage includes the loss of one water molecule in the temperature range between 34.87-125.6 °C the weight of loss this step was found to be 3.38 % which is in a good agreement with the calculated one (3.38 %).

(2)The second stage, in the temperature range between 125.6-219.3 °C the weight loss was found to be 6.89 %, which could be attributed to the loss of one HCl molecule. The found weight loss is in good agreement with the calculated one (6.86 %).

(3)The third stage, in the temperature range between 219.3-370.2 °C, the weight loss was found to be 12.72 %, which is attributed to the loss of four molecules of OH groups. The found weight loss is in good agreement with the calculated one 12.77 %.

(4)The fourth stage, in the temperature range between 370.2-468.7 °C, the weight loss was found to be 16.86 %, which is attributed to the loss of one molecule of (C_6H_3) NH. The found weight loss is in good agreement with the calculated one 16.90 %.

(5)The fifth stage, in the temperature range between 468.7-600°C, the weight loss was found to be 13.92 %, which is attributed to the loss of phenyl ring C_6H_3. The found weight loss is in good agreement with the calculated one 14.09 %.

(6)The last stage, above 600.00 °C, the remained polymer molecule was found to be 46.20 % including the metallic residue but the calculated one is equal to 46.30 %.
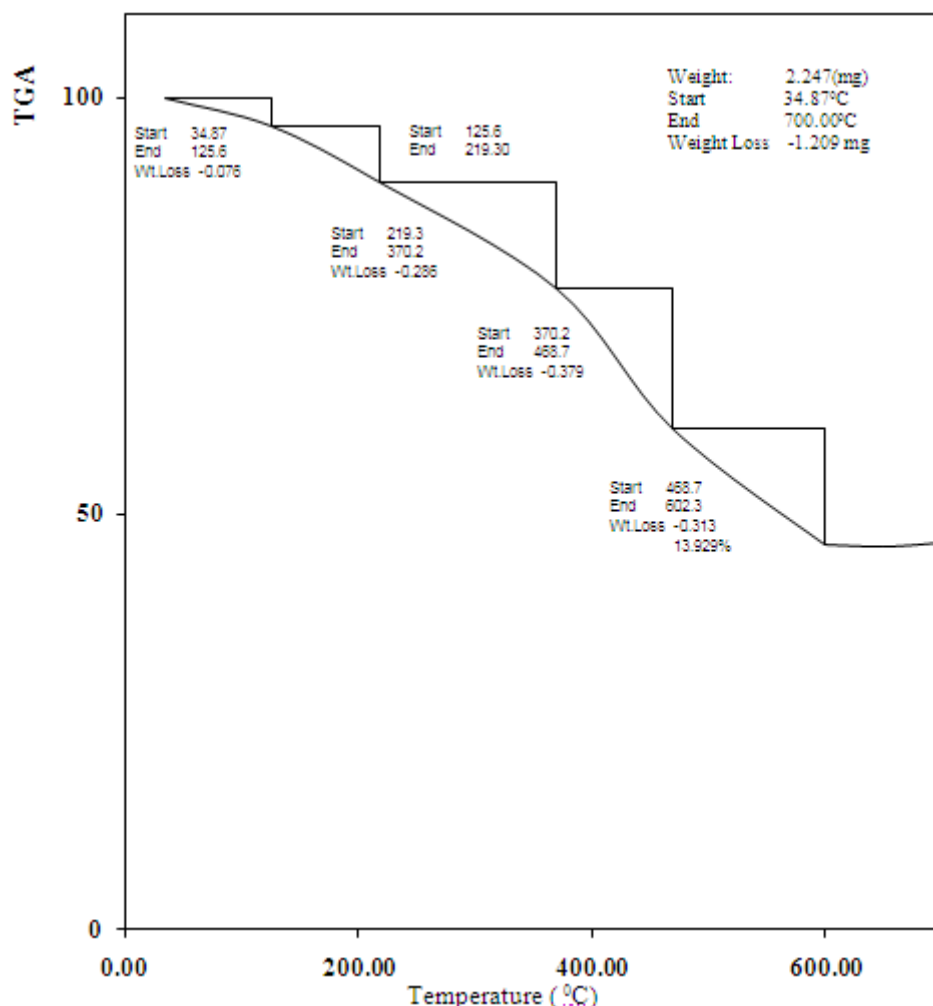

Figure (17): The thermal Gravimetric analysis (TGA) for (POHA).

Table (4): Thermogravimetric data of the prepared poly o-hydroxy aniline samples

Name	Temperature range ^0C	Weight loss (%)		The removed molecule
		Calc.	Found	
(POHA)	34.87-125.6	3.38	3.38	H_2O
	125.6-219.3	6.86	6.89	HCL
	219.3-370.2	12.77	12.72	4OH
	370.2-468.7	16.90	16.86	$(C_6H_3).NH$
	468.7-600	14.09	13.92	(C_6H_3)
	Remaining weight (%) above 600	46.00	46.20	…….

3.4.7. The X-Ray Diffraction Analysis and Transmission Electron Microscope of Poly o- Hydroxyaniline:
The X-Ray diffraction Patterns of the prepared polymers is represented in figure (18). The degrees of crystallinity for all polymers have been estimated using following equation:

$$\text{Degree of crystallinity (Xc) \%} = \frac{Ac}{Ac+Aa} \qquad (17)$$

where A_c is area of hump or crystalline phase, A_a area of amorphous phase and X_c is degree of crystallinity. Computer aided curve resolving technique is used to separate crystalline and amorphous phases of diffracted graph. The degree of crystallinity for poly o-hydroxyaniline (POHA) was found to be 43.7%.
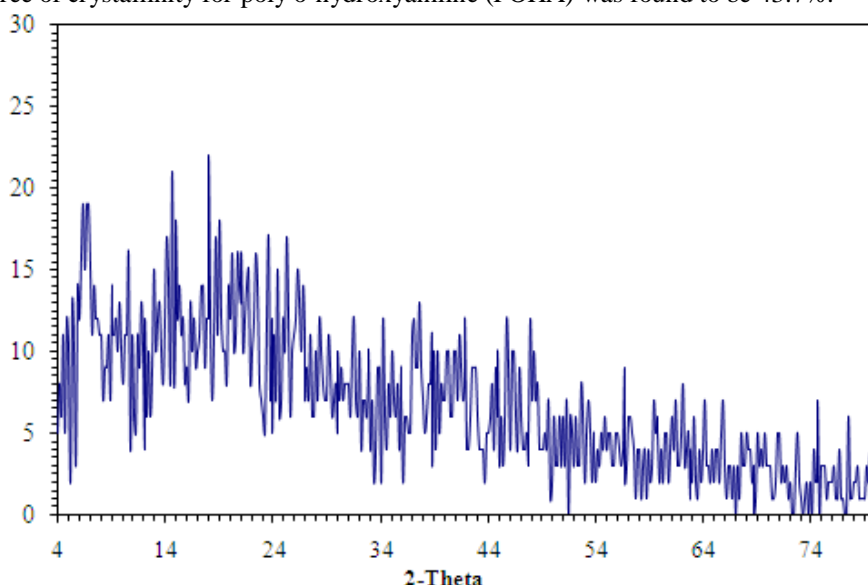

Figure (18):X-ray poly o-hydroxyaniline (POHA).

Figure (19) shows TEM image of POHA polymer which seems to be spherical or ellipsoidal particles with approximate diameter of 59-81 nm either separated or linked with each other
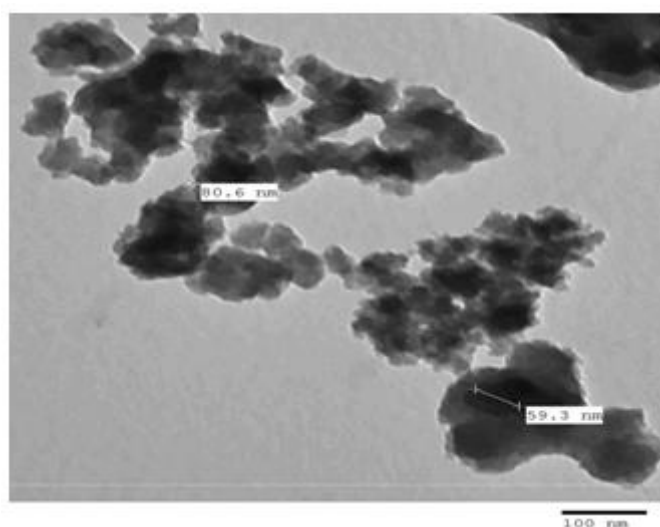

Figure (19): The transmission electron microscope of poly o-hydroxyaniline (POHA).

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