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ORIGINAL RESEARCH ARTICLE

Oxidative chemical polymerization kinetics of o-chloroaniline and characterization of the obtained polymer in aqueous hydrochloric acid solution using $K_2CR_2O_7$ as oxidizing agent

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Abstract: The oxidative chemical polymerization of o-chloroaniline (OClA) was studied in hydrochloric acid solution using potassium dichromate as oxidant at 5 ± 0.2ºC. 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 1.035, 1.116 and 0.966 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 18.49 kJ/mol. The obtained polymer was characterized using elemental analysis, XPS, IR and UV-visible. 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.

Key Words: Oxidative Chemical Polymerization, O-Chloroaniline, Characterization, Kinetics.

INTRODUCTION

Polyaniline (PANI) is one of the most studied conducting polymers due to its simple synthesis method, excellent environmental stability in the electro-conducting form, electrical, optical properties and various potential applications; in many high-performance devices [1, 2]. Various chemical oxidizing agents, such as potassium dichromate [3] potassium iodate [4] hydrogen peroxide [5] ferric chloride or ammonium persulphate were used [6]. The applications of polyaniline are limited due to its poor processability [8], 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 [9], poly (styrene) sulphonic acid [10] and phosphoric acid esters [11]. An alternative method to obtain soluble conductive polymers is the polymerization of aniline derivatives. The studied aniline derivatives are alkyloxy, hydroxy, chloroaniline or substitution at the nitrogen atom was reported by Sayyah *et al.*, [12-15] to improve the solubility of polyaniline. The substituted group of anilines affects not only the polymerization reaction but also the properties of the polymer obtained. The chemical oxidation of aniline to poly aniline has been monitored by the colour and acidity changes during dispersion polymerization of aniline [16]. A small amount of various P-phenylenediamine or benzidine was found to accelerate the formation of poly aniline. The ability of such compounds to form cation radicals upon oxidation allows them to act as mediators in electron transfer process.

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

MATERIAL AND METHODS

o-Chloroaniline provided by Prolabo Chemical Co., (England). 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.

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Oxidative Aqueous Polymerization of o-chloroaniline (OClA) Monomer

The polymerization reaction was carried out in a well-stoppered conical flask of 250ml capacity; addition of OClA amount in 25ml HCl of known molarity followed by the addition of the required amount of potassium dichromate as oxidant in water (25ml) to the reaction mixture. The orders of substances addition were kept constant in all the performed experiments. The stoppered conical flasks were then placed in an automatically controlled thermostat at the required temperature. The flasks were shaken (15 shakings/10 s/15min) by using an automatic shaker. The flasks were 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°C.

Elemental Analysis, Infrared and Ultraviolet Spectroscopy

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

X-Ray Photoelectron Spectroscopy (XPS)

An XPS spectrum was obtained on 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.

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 °C at rate of 20 °C /min to determine the rate of degradation of the polymer.

X-Ray diffractometer (philip1976. Model 1390) 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 Π (Japan).

Calculations

Determination of Conversion Yield: The conversion yield of the polymer to the monomer was determined by the weighing of the dry obtained polymer (P) divided by the weight of the monomer (w) as calculated in the following equation:

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

Determination of the Polymerization Rate: The rate of polymerization was determined in the following:

$$\text{Rate}\,(R_i) = \frac{P}{\text{V x M. wt xt}}\ (\text{gm ol / L. sec}) \qquad (2)$$

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.

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:

$$\text{Log(K)} = \frac{-Ea}{2.303RT} + C \qquad (3)$$

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

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

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

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 we obtain the following equation:

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

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

RESULTS AND DISCUSSION

Determination of the optimum polymerization conditions

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

Effect of Potassium Dichromate Concentration

Both of the monomer and HCl concentrations are fixed at 0.2 M while the oxidant concentrations were varied from 0.02 to 0.5M at 5 ± 0.2°C to study the effect of oxidant concentration ($K_2Cr_2O_7$). The yield –time - curve is represented in Fig.1, from which it is clear that, the obtained yield increase with the increase of $K_2Cr_2O_7$ concentration reaching maximum value at 0.2M. From the left part of the curve it is clear that, the polymer yield increase from 0.02M up to 0.2M then decreases from 0.2M 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-chloroaniline ion radical, which takes place immediately and therefore, yield increases with the increase of potassium dichromate concentration up to 0.2M. But in the second part of the curve, the polymer yield decreases with increasing $K_2Cr_2O_7$ concentration, may be due to a high concentration of oxidant which promote the formation of low molecular weight oxidation product and also degrade the produced polymer which becomes easily soluble in reaction medium [3].

Effect of HCl Concentration

The effect of HCl concentration on the aqueous oxidative polymerization of (OClA) was investigated using constant concentration of $K_2Cr_2O_7$ at 0.2M, monomer concentration at 0.1M and using different concentrations of HCl at 5 ± 0.2°C. The yield –time curve was represented in Figure 2). From which it is clear that, obtained yield increases in the acid concentrations range from 0.02 to 0.5 then decreases gradually up to 0.8M. This behavior may be due to, at higher concentration of HCl, the degradation of the polymer in the early stages of the reaction, which may be due to the hydrolysis of polyemeraldine chain [3, 17].

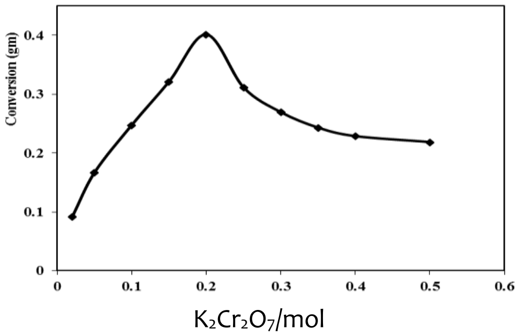


Figure 1: Effect of $K_2Cr_2O_7$ concentration on the aqueous oxidative chemical polymerization of (OClA).

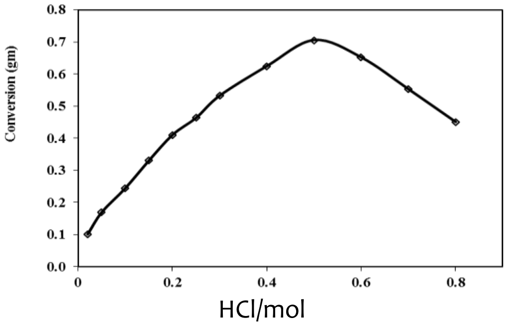


Figure 2: Effect of HCl concentrations on the aqueous oxidative chemical polymerization of (OClA).

Effect of o-Chloroaniline (OClA) Concentration

The effect of monomer concentration on the polymerization yield was investigated in the range of monomer concentrations from 0.02 to 0.8M and the data was represented in Figure 3. From which it is clear that, the optimum yield formation condition is obtained at 0.2M of the monomer concentration.

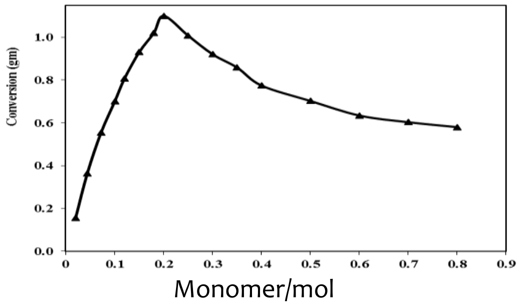


Figure 3: Effect of monomer concentration on the aqueous oxidative chemical polymerization of (OClA).

The Kinetic Studies of the Polymerization

Effect of Potassium Dichromate Concentration: The aqueous oxidative polymerization reaction of o-chloroaniline (0.2M) in 25 ml of HCl (0.5M) solution after addition of 25ml of potassium dichromate solution which have different concentrations (0.05, 0.1, 0.15 and 0.2M) as oxidant at 5 ± 0.2°C for different time intervals were carried out. The total HCl and monomer concentration were kept constant in the reaction medium at 0.5M and 0.2M respectively. The conversion-time curve for each oxidant concentration is calculated and graphically represented in Fig.4. From the obtained data it is clear that, both of the initial and overall reaction rates of the polymerization reaction increase with increasing of the oxidant concentration. The oxidant exponent is calculated from the slope of the obtained straight line from the relation between (log R_i) and (log oxidant), which is represented in Fig.5. The slope is found to be 1.035 which means that the polymerization reaction of o-chloroaniline with respect to the oxidant is first order reaction.

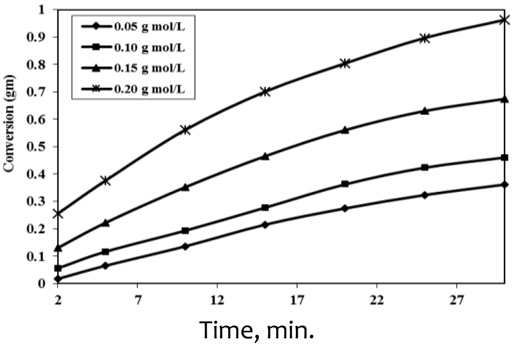


Figure 4: Conversion - time curve of the effect of potassium dichromate concentration on the polymerization of OClA.

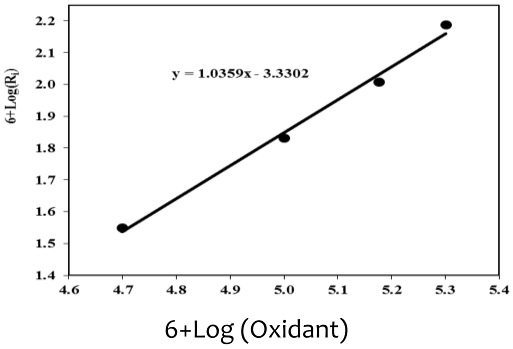


Figure 5: Double logarithmic plot of the initial rate and oxidant concentration for polymerization of (OClA).

Effect of Hydrochloric Acid Concentration

The aqueous oxidative polymerization reaction of o-chloroaniline (0.2M) in 25 ml of HCl solution which had different concentrations were carried out by addition 25 ml of potassium dichromate solution (0.2M) as oxidant at 5±0.2°C for different time intervals. The concentration of monomer and oxidant were kept constant in the reaction medium at 0.2M. The experiments were carried out as described in the experimental part, the conversion-time curve for each HCl concentration is calculated and graphically represented in Fig.6. From the data obtained it is clear that, both of the initial and overall rates of the polymerization reaction increase with the increasing of HCl concentration. The HCl exponent is calculated from the slope of the obtained straight line from the relation between (log R_i) and (log HCl), which is represented in Fig.7. The slope is found to be 1.116 which means that the polymerization reaction of o-chloroaniline is first order reaction with respect to the HCl concentration.

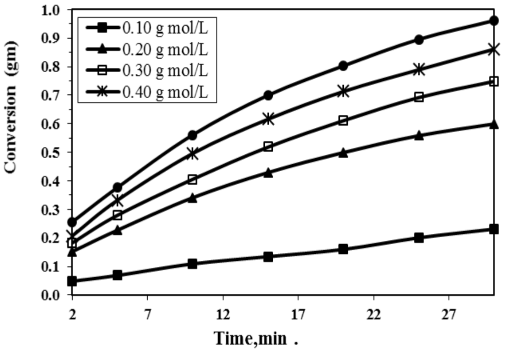


Figure (6): Conversion -time curves showing the effect of HCl concentration on the aqueous oxidative polymerization of (OClA)

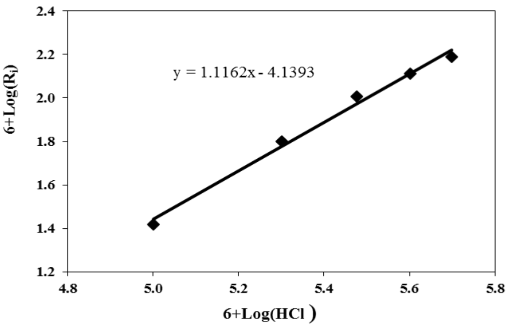


Figure (7): Double logarithmic plot of the initial rate and HCl concentration on the oxidative chemical polymerization of (OClA).

Effect of Monomer (OClA) Concentration

The effect of monomer concentration on the aqueous oxidative polymerization reaction of o-chloroaniline in the presence of 25ml of HCl solution (0.5M) and 25 ml of potassium dichromate solution (0.2M) as oxidant at 5±0.2°C for different time intervals. The concentration of HCl and oxidant are kept constant in the reaction medium at 0.2M. The experiments were carried out as described in the experimental part 2.2. The conversion-time data are calculated for different intervals and graphically represented in Fig.8. On taking the polymer yield into consideration, the weight of the obtained polymer increase, therefore both of the initial and overall rates of the polymerization reaction increase with the increasing of monomer concentration. The monomer exponent is calculated from the slope of the obtained straight line from the relation between (log R_i) and (log monomer), which represented in Fig. 9. The slope is found to be 0.966 which means that the polymerization reaction of o-chloroaniline with respect to the monomer is first order reaction.

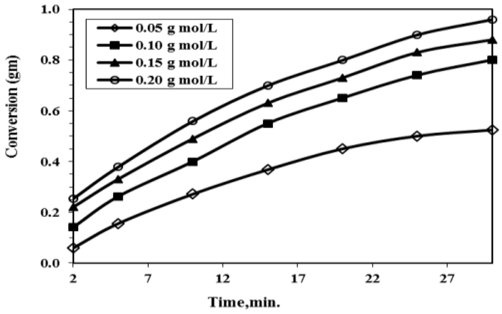


Figure (8): Conversion -time curves for the aqueous oxidative chemical polymerization of (OClA).

Calculation of the Thermodynamic Activation Parameters

The aqueous polymerization of o-chloroaniline (0.2M) in 25 ml of HCl (0.5M) in the presence of potassium dichromate (0.2M) was carried out at 5, 10 and 15°C for different time periods. The conversion- time curves are graphically represented in Fig.10, from which it is clear that both of the initial and overall reaction rates increase with raising of reaction temperature. The apparent activation energy (E_a) of the aqueous polymerization reaction of (OClA) was calculated using Arrhenius equation (3).

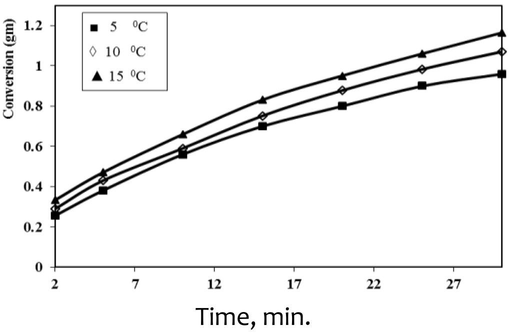
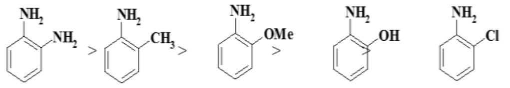


Figure 10: Conversion -time curves for the effect of temperature on the aqueous oxidative chemical polymerization of (OClA).

By plotting log R_i against 1/T, which gave a straight line as shown in Fig.11 and from the slope we can calculate the activation energy. The apparent activation energy for this system is 18.49 kJ/mol.

From our pervious publications, it is clear that the apparent activation energy of poly o-phenylenediamine [17], poly o-tolidine [18], poly o-methoxyaniline [19] and poly o-hydroxyaniline [20] have the following order:



Which means that, the reactivity of the investigated amine toward polymerization have the reverse of the above order. The Enthalpy and entropy of activation for the polymerization reaction can be calculated by the calculation of K_2 from the following equation:

$$\textbf{Reaction Rate} = K_2\,[\text{oxidant}]^{1.036}\,[\text{HCl}]^{1.116}\,[\text{monomer}]^{0.966} \qquad (5)$$

The calculated values of K_2 at 5, 10 and 15 °C were 0.941×10^{-6}, 1.107×10^{-5} and 1.222×10^{-5} respectively. The enthalpy (ΔH^*) and entropy (ΔS^*) of activation associated with k_2, were calculated using Eyring equation (5).

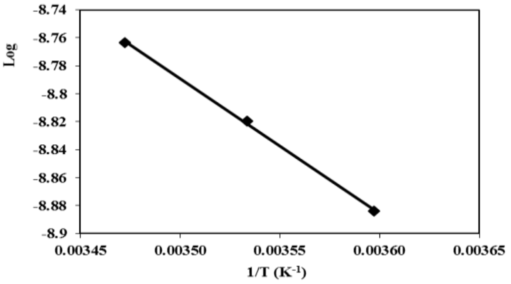


Figure (11):The relation between the logarithem of initial rate and (1/T) for aqueous oxidative polymerization of (OClA)

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 obtained, the values of ΔH^* and ΔS^* were calculated and it is found to be 15.137 $kJmol^{-1}$ and -295.30 $Jmol^{-1}K^{-1}$ 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.

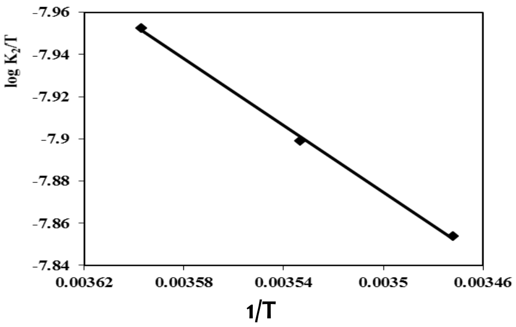


Figure 12: The relation between log K_2/T and $1/T$ for oxidative chemical polymerization of (OClA)

Polymerization mechanism

The aqueous oxidative polymerization of (OClA) is described in the experimental section, and follows three steps [3].

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

$$K_2Cr_2O_7 + H_2O + 2H^+ = 2K^+ + 2H_2CO_4 \qquad (7)$$

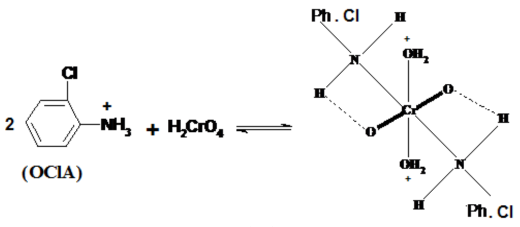
This reaction is controlled by the change in pH, the orange red dichromate ions $(Cr_2O_7)^{2-}$ are in equilibrium with the $(HCrO_4)^-$ in the range of pH-values between 2 and 6, but at pH below 1 the main species is (H_2CrO_4) and the equilibria can occur as follows:

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

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

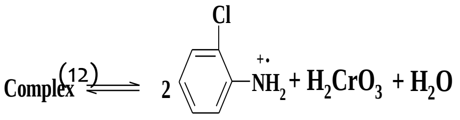
$$2(HCrO_4)^- \rightleftharpoons (Cr_2O_7)^{2-} + H_2O \quad K = 10^{-2.2} \qquad (10)$$

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



(11)

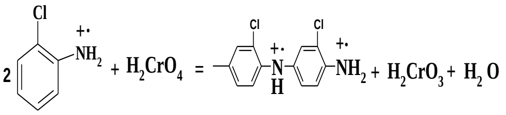
The complex undergoes dissociation to form monomer cation radical as shown in equation (12):



(12)

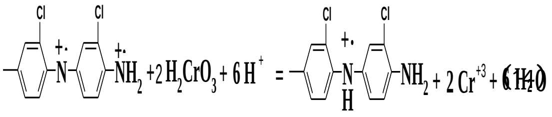
Generally, the initial step is rapid and may occur in short time, 0–5 min (autocatalitic reaction).

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) [17]. 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.



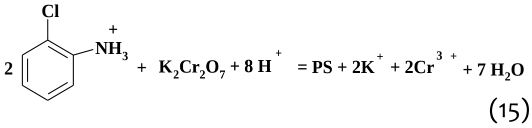
(13)

parasemidine (PS)



Pemigraniline salt

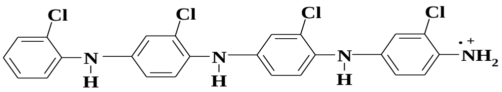
This reaction is followed by further reaction of the formed dimmer radical cations with monomer molecules to form trimer radical cations and so on. The degree of polymerization depends on different factors such as dichromate concentration, HCl concentration, monomer concentration, and temperature. By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



(15)

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



Characterization of poly o-chloroaniline

The Solubility: The solubility of o-chloroaniline 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-chloroaniline is completely soluble in N-methyl pyrrolidone and dimethylformamide (DMF), while completely insoluble in benzene and hexane.

Table 1: The solubility of poly o-chloroaniline in different solvents at 20 °C.

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

●, soluble; ○ slightly soluble; ■ insoluble.

The Elemental Analysis: The data obtained from the elemental analysis using oxygen flask combustion and a dosimat E415 titirator shows that, the found carbon contents in all of the prepared o-chloroaniline polymer is lower than the calculated values. 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 poly o-substituted aniline samples which were 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-chloroaniline, the XPS study was conducted as mentioned under point 2.4.

X-Ray Photoelectron Spectroscopy (XPS) Characterization

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-chloroaniline 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 $(C_6H_6)_2Cr^{3+}$ [17].

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).

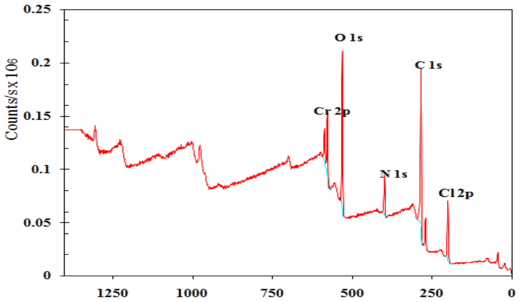
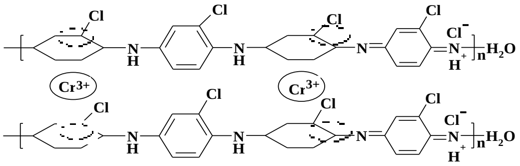


Figure 13: X-Ray Photoelectron Spectroscopy (XPS) survey elemental composition of (POClA).



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

Table 2: The XPS elemental analysis of poly o-chloroaniline derivatives

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

XPS Spectra of (POClA)

Four main peaks were obtained for C1s spectra of poly (OClA) as shown in Figure 14-a). The sharp peak appearing at 283.96 eV is attributed to C-H (C_1) bond, while the peak appearing at 284.17 eV is attributed to C-C (C_2) bond. The peak appearing at 285.98 eV is assigned to C-N (C_3) bond while, the peak appearing at 287.44 eV is attributed to C-O or C-N^+ (C_4) bond [17-26].

N1s Figure 14-b) shows the XPS N1s spectrum of (POClA) which has three distinct curves. The first two peaks are assigned to imine (-N=) at 398.66 eV and amine (-NH-) at 399.28 eV. Moreover, the peak appears at 400.58eV is due to positively charged nitrogen atom (N^+).

Two distinct oxygen species contributes to the oxygen 1s signals in the conducting polymers (Fig.14-C). The distinct energy peaks at 531.38 and 532.88 eV could be attributed to Cr_2O_3 and C-OH respectively.

The Cl 2p spectrum of (POClA) 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 199.63, 199.84, and 201.68 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 199.84 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 (POClA) 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 576.28 eV ±0.2 eV was assigned to Cr_2O_3 which is in agreement with what was found by P. Chowdhury *et al.*, [3] and P. Stefanov *et al.*, [25]. There is also a component visible correspond to $Cr_2p_{1/2}$ at 586.16 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).

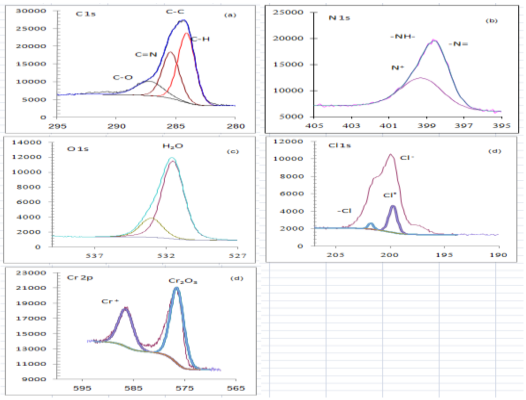


Figure 14: X-Ray photoelectron spectroscopy (XPS) spectra of (POClA).

The Infrared Spectroscopic Analysis of o-Chloroaniline (OClA) Monomer and its Analogs Polymer (POClA)

The IR spectra of the o-chloroaniline (OClA) Monomer and its polymer (POClA) is represented in Figure 15), while the absorption band values and their assignments are summarized in table 3. The medium absorption band appearing at 531 cm^{-1} for monomer and the broad absorption band appearing at 545 cm^{-1} in case of polymer may be attributed to the stretching vibration of C-Cl. The three sharp absorption bands which appear at 600, 745 and 866 cm^{-1} in case of the monomer and the corresponding medium absorption bands for the polymer at 673, 751 and 828 cm^{-1} are attributed to out of plane C-H deformation foe 1,3 –di-substitution in benzene ring. A series of absorption bands appearing in the region from 928…. 1082 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 sharp absorption band appearing at 1239 cm^{-1} which could be attributed to stretching vibration C-N in case of monomer, appears at 1175 cm^{-1} with slightly shift in case of polymer. The sharp absorption band appearing at 1308 cm^{-1} ion case of monomer, which could be attributed to in plane stretching deformation of C-H bonds in aromatic ring, appears at 1326cm^{-1} in case of polymer. The sharp absorption bands appearing at 1488 and 1584 cm^{-1} in case of the monomer and the corresponding abroad absorption bands appearing at 1500 and 1590 cm^{-1} in case of the polymer are attributed to stretching vibration for C=C in benzene ring of quinoid unit. The medium absorption band appearing at 3030 cm^{-1} in case of monomer and the broad absorption band appearing at 3039cm^{-1} in case of polymer may be attributed to symmetric stretching vibration of N-H. The medium absorption band appearing at 3400 cm^{-1} which could be attributed to asymmetric stretching vibration for NH group in case of monomer, appears as abroad absorption band at 3409 cm^{-1} in case of polymer.

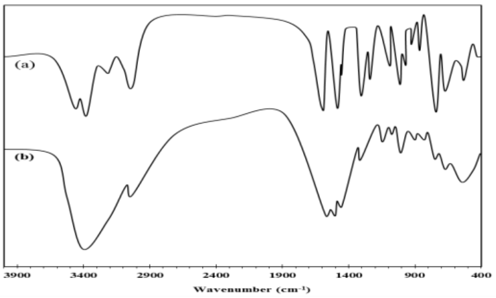


Figure 15: The infrared spectrum of (OClA) (a) and it analogous polymer (POClA) (b).

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

Wave number(cm^{-1})		Assignments
(OClA)	(POClA)	
435^s	—	
531^m	545^m	Stretching vibration of C- NH or torsio
600^s	—	
—	673^b	
745^s	—	
—	751^w	Out-of-plane bending deformation of CH in 1,2 disubstituted in benzene ring
866^s	—	
—	820^w	
	879^w	
928^s	—	
971^s	—	
1025^w	—	Out-of-plane bending of C-H bonds of aromatic ring
—	1049^b	
1082^m	—	
—	1117^w	
—	1175^w	Symmetric stretching vibrations of C-N group
1239^{sh}	—	
1308^s	—	Plane stretching deformation of C-H bonds in aromatic ring
—	1326^b	
1488^{sh}	—	
	1500^b	Stretching vibrations for C=C in benzene ring or C=N in quinoid unit
1584^s	—	
—	1590^b	
3030^m	—	Symmetric stretching vibrations of N-H
—	3039^b	
3400^m	—	Asymmetric stretching vibrations for NH group
—	3409^b	

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

The UV-visible Spectra of o-Chloroaniline (OClA) and its Polymer (POHA)

The UV-visible spectra of (OClA) and its polymer (POClA) are represented in Figure 16); the spectra show the following absorption bands:

(1) In case of monomer, two absorption bands appear at λ_{max} = 206 and 227 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, two absorption bands appear at λ_{max} = 223 and 249 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} = 428 nm which may be due to the high conjugation of the aromatic polymeric chains.

(3)

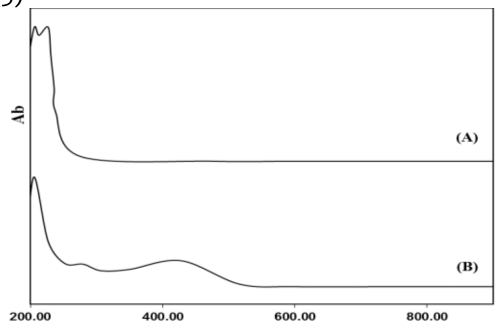


Figure 16: UV-visible spectra of (OClA) (A) and its analogous polymer (POClA) (B).

Thermal Gravimetric analysis (TGA) of (POClA)

Thermo-gravimetric analysis (TGA) of (POClA) 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 29.5-122.6°C, the weight loss of this step was found to be 3.21 % which is in a good agreement with the calculated one (3.41%).

2. The second stage, in the temperature range between 122.6-203.8 °C the weight loss was found to be 6.65 %, which could be attributed to the loss of one HCl molecule. The calculated weight loss is in good agreement with the found one (c.f. table 3-23).

3. The third stage, in the temperature range between 203.8-320.3°C, the weight loss

was found to be 11.79 %, which is attributed to the lost of four (NH_2) groups. The found weight loss is in good agreement with the calculated one 12.11 %.

4. The fourth stage, in the temperature range between 320.3-400.0°C, the weight loss was found to be 16.95 %, which could be attributed to the lost of one molecule of C_6H_3-NH. The found weight loss is in good agreement with the calculated one 17.22 %.

5. The fifth stage, in the temperature range between 400.0-523.4°C, the weight loss was found to be 13.78 %, which is attributed to the lost of one molecule of phenyl ring. The found weight loss is in good agreement with the calculated one 14.19 %.

6. The latest stage, above 523.38°C. The remained polymer molecule was found to be 47.62% including the metallic residue, but the calculated one was found to be 46.46 %.

From our pervious publications, it is clear that the thermal stability of poly o-phenylenediamine [17], poly o-tolidine [18], poly o-methoxyaniline [19] and poly o-hydroxyaniline [20] have the following order:

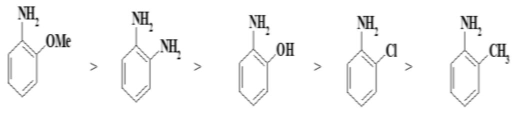


Figure 17: The thermal Gravimetric analysis (TGA) for (POClA).

Table 4: The Thermogravimetric analysis of prepared poly o-chloroaniline.

Name	Temperature range °C	Weight loss (%)		The removed molecule
		Calc.	Found	
(POClA)	33.01-105.6	2.97	2.99	H_2O
	105.6-255.6	6.02	5.93	HCl
	255.6-449.8	23.42	23.23	4Cl
	449.8-525	27.21	26.90	$(2C_6H_3)NH$
	525-650	14.84	14.98	C_6H_3-NH
	Remaining weight (%) above 600	25.54	25.97	………

The X-Ray Diffraction Analysis and Transmission Electron Microscope of Poly o- Chloroaniline

The X-Ray Diffraction Patterns of the prepared polymers is represented in Fig.18. The degree of crystallinity [24] is calculated by separating intensities due to amorphous and crystalline phase on diffraction phase. Computer aided curve resolving technique is used to separate crystalline and amorphous phases of diffracted graph. After separation, hump or crystalline (A_c) area of the diffracted pattern is divided crystalline (A_c) and amorphous components (A_a). Percentage of crystallinity X_c % is measured as ratio of crystalline area to Total area.

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

Where A_c = Area of crystalline phase, Aa = Area of amorphous phase and X_c = Degree of crystallinity.

The degree of crystallinity for poly o-chloroaniline (POClA) was found to be 35.67%.

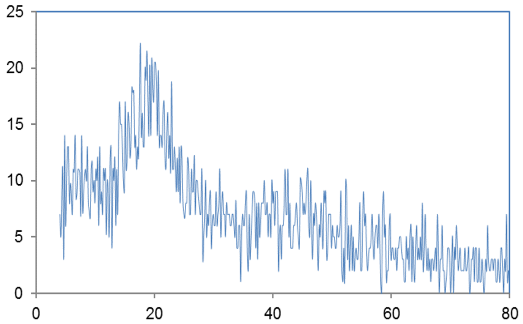


Figure 18: X-ray poly o-chloroaniline.

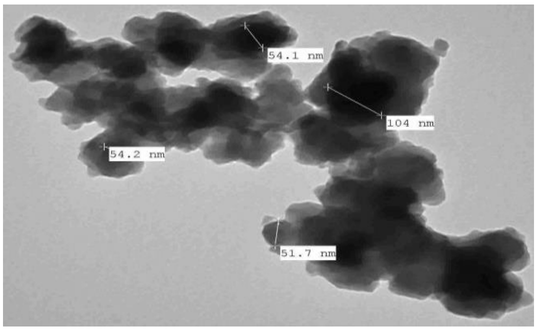


Figure 18: The transmission electron microscope of poly o-chloroaniline (POClA)

Figure 18 shows TEM image of POClA polymer which seems to be spherical or ellipsoidal particles with approximate diameter of 51-104 nm either separated or linked with each other

CONCLUSIONS

In the present work POClA incorporated with potassium dichromate and HCl has been successfully achieved. The optimum yield formation of POClA is obtained at 0.2M potassium dichromate 0.2M of the monomer and 0.5M hydrochloric acid concentrations. The initial and overall rate of polymerization reaction increases with increasing the oxidant, monomer and HCl concentrations. The exponent of oxidant, monomer and HCl was found to be 1.035, 0.966 and 1.116 respectively. The chrome is present between polymer chains as a sandwich-bonded C_6H_6-C_6H_6 groups and the usual formation procedure is hydrolyzing the reaction mixture with dilute acid which gives the cation $(C_6H_6)_2Cr^{3+}$. The reactivity of POClA relative to the investigated amine toward the polymerization process has the highest order. The TGA analysis of POClA shows its high thermal stability.

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