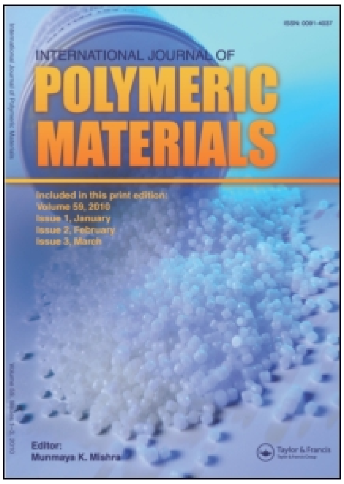

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AQUEOUS OXIDATIVE CHEMICAL POLYMERIZATION OF N-METHYLANILINE IN ACID MEDIUM AND CHARACTERIZATION OF THE OBTAINED POLYMER

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The oxidative chemical polymerization of N-methylaniline was studied in hydrochloric acid solution using sodium dichromate as oxidant at 5° C under nitrogen atmosphere. The effect of hydrochloric acid, sodium dichromate and monomer concentration on the polymerization reaction was investigated. The order of reaction with respect to hydrochloric acid, sodium dichromate and monomer concentration was 0.816, 0.735 and -0.83 *respectively. Also, the effect of temperature on the polymerization rate was studied and the apparent activation energy of this polymerization reaction was found to be* 1.999×10^4 *J/mol. The characterization of the obtained polymer sample at the optimum conditions was carried out by IR, UV-visible,* ^{1}*H-NMR, X-ray diffraction, electron microscope and thermogravimetric analysis. The ac conductivity of the obtained polymer samples was measured and the highest values were found for the samples prepared at hydrochloric acid, sodium dichromate and monomer concentrations of 0.200, 0.0094 and 0.1869 mol/L respectively at 5° C.*

Keywords: aqueous oxidative chemical polymerization, N-Methylaniline characterization, order of reaction, apparent activation energy, ac conductivity

INTRODUCTION

Polyaniline, PANI, has been extensively studied in the last decade as an electrically conducting polymer, that shows many promising properties. Fast switching rates [1, 2], the ability to switch reversibly from insulation to conducting state either by electrochemical or chemical doping [3, 4], and their unique properties are some of PANI potential applications. Several review papers on polyaniline have been published recently [5–7]. Moreover, PANI has been extensively

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studied because it is the only known conjugated polymer with a chain in which nitrogen instead carbon atoms bridges the benzenoid and quinoid rings and plays an important role in π-bond formation and the electrical interaction conduction consequently.

Polymerization of aniline takes place in aqueous medium using sodium dichromate as oxidant in presence of hydrochloric acid. The obtained polyaniline was characterized by X-ray diffraction, electron microscopic studies and thermal analysis. The unusually high dielectric constant of the produced polyaniline gives an indication of its important dielectric properties. The ferroelectric phenomenon of this polymer was observed and confirmed by studying pyroelectricity, hysteresis loop and polarization as a function of temperature. This observation is unique for this polymer, which has the advantage of being prepared at room temperature [8].

Various chemical oxidizing agents such as potassium dichromate, potassium iodate, ammonium persulphate, hydrogen peroxide, ceric nitrate and ceric sulphate have been used for the chemical oxidative polymerization of aniline [7]. Several research groups have been engaged in investigation of the polymerization mechanisms and reaction kinetics of aniline in aqueous solutions [9–18]. Generally, it is agreed that the initiation reaction involves the formation of a radical cation intermediate and subsequent combination of two radical cations to form aniline dimer. After this initial step, the method by which these species proceed to form the polymer is still not clearly understood, but different mechanisms have been reported for this growing step. The morphology of synthesized PANI [19] was studied after dedoping and redoping with dodecylbenzenesulphonic acid (DBSA) and polystyrene (PS). The effect of pH of the polymerization solutions or the effect of acid concentration, reaction time, relative and absolute reactant concentrations on the polymer yield, chemical composition and the electrical conductivity of the produced polyaniline were investigated [20–22].

Water soluble PANI was prepared and extensively studied by X-ray diffraction, X-ray spectroscopy (XPS), electronic spectroscopy, infrared spectroscopy IR, thermogravimetric analysis (TGA), conductivity measurements, atomic force microscopy and scanning tunneling microscopy [23]. Further studies of the chemical polymerization of m-toluidine, o-chloroaniline and nitroaniline by DSC, X-ray, IR and conductivity measurements were performed [24]; it was found that the substituted group of aniline affects not only the polymerization reaction but also the properties of the polymer obtained. HCl-doped emerldine form of polyaniline (PANI-H) was synthesized by oxidative polymerization of aniline in aqueous hydrochloric acid solution using potassium dichromate as an oxidant [20].

The kinetics of the chemical polymerization of 3-methylaniline, 3-chloroaniline, 3-hydroxyaniline and 3-methoxyaniline in aqueous HCl solution using sodium dichromate as oxidant and characterization of the obtained polymers by IR, UV-visible, X-ray, electron microscope, TGA-DTA analysis and ac conductivity have been investigated by Sayyah et al. [25–28].

In the present study, we investigate the kinetics of the oxidative chemical polymerization of N-methylaniline in aqueous hydrochloric acid medium using sodium dichromate as oxidant. The obtained polymer is characterized by UV, IR, ^{1}H-NMR, X-ray diffraction, electron microscope, thermogravimetric analysis and ac conductivity measurements.

2 EXPERIMENTAL

2.1 Materials

N-methylaniline provided by Merck Chemical Co. (Germany) was vacuum distilled and stored in absence of light before use. Concentrated hydrochloric acid and ammonia solution (33%) were of chemically pure grade products provided by Prolabo-Chemical Co. (UK). Twice distilled water was used as a medium for the polymerization reactions. The sodium dichromate used was a product of Merck Chemical Co. (Germany).

2.2 Oxidative Aqueous Polymerization of N-Methylaniline monomer

The polymerization reactions were carried out in a well-stoppered conical flasks of 250 ml capacity; addition of the monomer amount followed by the addition of the required amount of sodium dichromate solution (25 ml) to the reaction mixture was carried out under nitrogen atmosphere. The order of addition of substances was 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 seconds/every 15 minutes) by using an automatic shaker during the kinetic study. The reaction was stopped at will by the addition of ammonia solution (in equivalent amount to the used HCl in the polymerization reaction). The polymer was then filtered using a Buchner funnel, washed thoroughly with distilled water and finally dried to constant weight in a vacuum oven at 60°C. However, in the case of the polymer samples prepared for characterization after 3 hours, the polymerization solutions were filtered after addition of methanol only (30 ml) as nonsolvent, then washed with distilled water, and finally dried under vacuum at room temperature to constant weight.

2.3 Ultraviolet, Infrared and ^{1}H-NMR Spectroscopy

Ultraviolet-visible absorption spectra of the monomer and the prepared polymer sample were measured using a Shimadzu UV-spectrophotometer M 1601 PC spectrophotometer at room temperature in the region 200–600 nm, using chloroform as a solvent and reference.

The infrared measurements were carried out using a Shimadzu FTIR-430 Jasco spectrophotometer and KBr disk technique. The ^{1}H-NMR measurements were carried out using Varian EM 360 L, 60 MHz NMR spectrometer. The NMR signals of the prepared polymer have been recorded in deutrated chloroform using tetramethyl silane as internal reference.

2.4 Thermal Gravimetric Analysis (TGA)

The thermal gravimetric analysis of the polymer sample was performed using a SHIMAZU DT-30 thermal analyzer. The weight loss was measured from ambient temperature up to 800°C, at a rate of 20°C per minute to determine the degradation rate of the polymer.

2.5 Electron Microscopy and X-Ray Diffraction Analysis

The electron microscopic analysis was carried out using a JSM-T20 Scanning electron microscope, JEOL, Japan. The X-ray diffractometer type Philips 1976 Model 1390 was operated at the following conditions, which were kept constant overall during the analysis processes:

[X-ray tube: Cu; Scan speed: 8 (dg/min.); Current: 30 mA Voltage: 40 kV; Preset time: 10(s)]

2.6 Conductivity Measurements

Polymer samples in the form of compressed discs of 1.002 cm diameter and 0.2 cm thickness were used in the present investigation. Good contact was attained by covering the samples on both sides with air–drying electric-conducting silver paste. The a.c. conductivity was measured using a Philips RCL bridge (digital and computerized) at a frequency range of 10^2–10^5 Hz. The overall error in the a.c. conductivity did not exceed $\pm 2\%$.

3 RESULTS AND DISCUSSION

3.1 Effect of Hydrochloric Acid Concentration

The polymerization of N-methyaniline (0.1870 mol./L) in 25 ml of HCl with different molarities was carried out by addition of 25 ml sodium dichromate solution (0.0188 mol/L) as oxidant under nitrogen atmosphere at 5° C for different time intervals. The concentration of the monomer and oxidant were kept constant at 0.0935 and 0.0094 mol/L respectively, during the study of HCl effect on the polymerization reaction. The experiments were carried out as described in section 2.2, and the yield-time curve was plotted for each acid concentration used. The data are graphically represented in Figure 1, from which the initial and overall rates of the polymerization reactions were evaluated and tabulated in Table 1. Ac conductivity of the obtained polymers after 3 hours was measured for each HCl concentration and the data are also given in Table 1. From Figure 1 and Table 1, it is clear that both the initial and overall reaction rates of the polymerization reaction increase with increasing HCl concentrations in the range 0.2−0.8 mol/L. The ac conductivity has its maximum value when 0.60 mol/L HCl solution was used in the reaction medium. The HCl exponent determined from the slope of the straight line represented in Figure 2 is found to be 0.816. The polymerization with respect to the HCl concentration is therefore a first order reaction.

3.2 Effect of Sodium Dichromate Concentration

The aqueous polymerization of N-mehtylaniline (0.1870 mol./L) was carried out in 25 ml HCl solution (0.40 mol/L) in the presence of 25 ml of sodium dichromate solution of different molarities (0.0048, 0.0096, 0.0141 and 0.0188 mol/L) as oxidant under nitrogen atmosphere at 5° C for different time intervals. The total HCl and monomer molarities were fixed in the reaction medium at 0.20 and 0.0935 mol/L, respectively. The yield-time curve for each oxidant concentration is calculated and the data are graphically represented in Figure 3, from which the initial and overall rates of the polymerization reactions are calculated and summarized in Table 2. The ac conductivity of the obtained polymers after 3 hours was measured for each oxidant concentration and the data are also given in Table 2. From the obtained data, it is clear that the initial and overall rates of the polymerization reaction increase with increasing oxidant concentration, while the maximum value of ac conductivity is found for the polymer sample obtained at 0.00705 mol/L of the oxidant concentration. The oxidant exponent is calculated from the slope of the obtained straight line

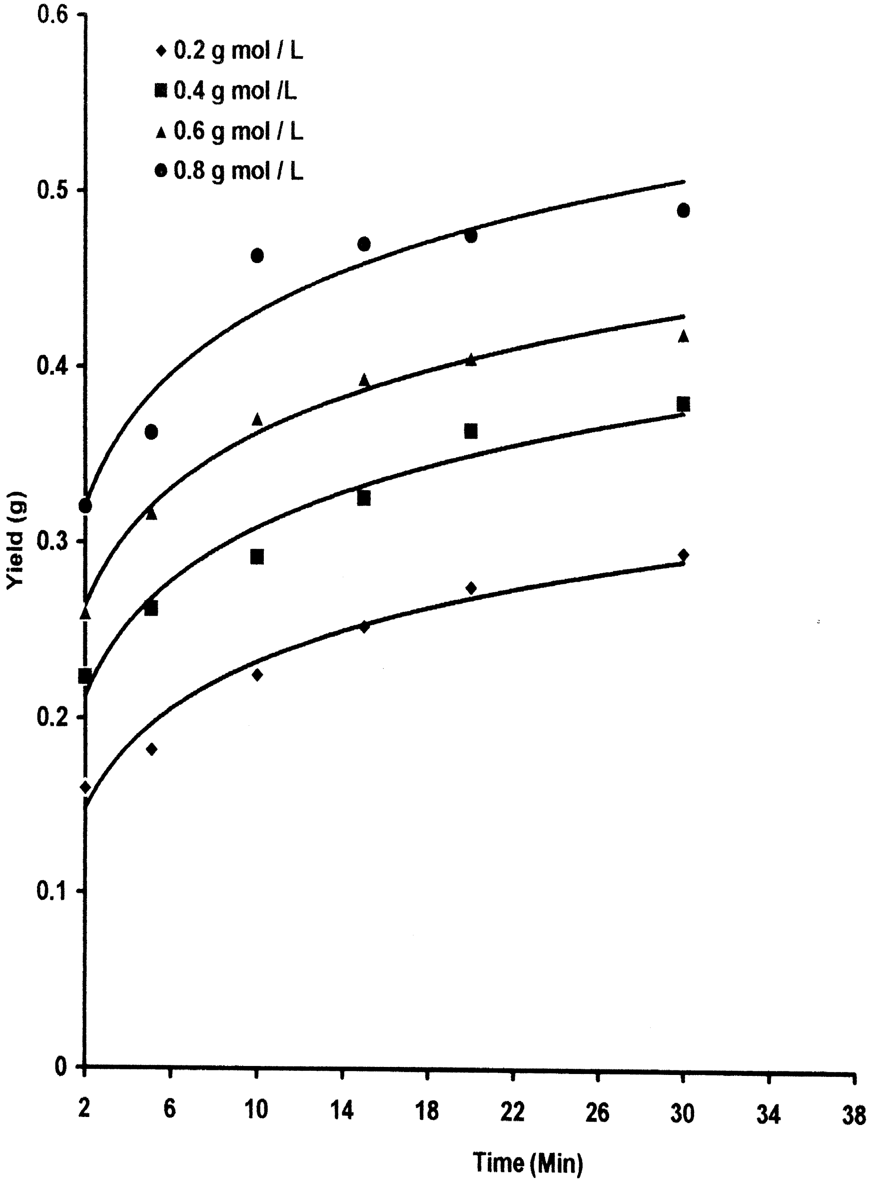


FIGURE 1 Yield-time curves for the effect of hydrochloric acid concentration on the aqueoues oxidative polymerization of N-methylaniline.

TABLE 1 Effect of HCl Concentration on the Polymerization of N-methylaniline

Exp. No.	Concentration of HCl (mol L^{-1})	Initial rate $\times 10^5$ (mol $L^{-1}.s^{-1}$)	Overall reaction rate $\times 10^5$ (mol $L^{-1}.s^{-1}$)	Conductivity values.10^7 (S m^{-1})
1	0.20	6.916	0.4515	0.27
2	0.40	9.441	0.4575	2.92
3	0.60	11.885	0.4648	4.18
4	0.80	14.450	0.4888	1.53

given in Figure 4. The slope is found to be equal to 0.735, which means that the polymerization is also a first order reaction with respect to the oxidant concentration.

3.3 Effect of the Monomer Concentration

The effect of monomer concentration on the aqueous polymerization of N-methylaniline in the presence of 25 ml of 0.40 mol/L HCl and 25 ml of 0.0188 mol/L $Na_2Cr_2O_7$ solution under nitrogen atmosphere at 5° C was studied. The yield-time curves data were calculated and graphically represented in Figure 5, while the calculated initial and overall reaction rates are given in Table 3. The polymerization process depends mainly on the number of the formed radical cations from the monomer molecules, which also depends on the oxidant concentration. The ratios of the oxidant concentration to the monomer are 0.1005, 0.0670, 0.0503 and 0.0402. From this it is clear that the oxidant concentration relative to the monomer concentration decrease, i.e. the number of the formed radical cations decrease with increasing monomer concentration and consequently the yield decreases in the same direction. Also, at higher monomer concentration, the viscosity of the reaction solution is relatively high, which makes the mobility of the radical cations lower than in the case of lower monomer concentration. Therefore, both the initial and overall reaction rates decrease with increasing monomer concentration. The monomer exponent is obtained from the slope of the straight line represented in Figure 6. The exponent is -0.83, which means that the order of the reaction with respect to the monomer concentration is pseudo-first order reaction. The ac conductivity of the obtained polymer sample after 3 hours for each monomer concentration was measured and the data are given in Table 3. The maximum ac conductivity value is found when using 0.1869 mol/L monomer concentration.

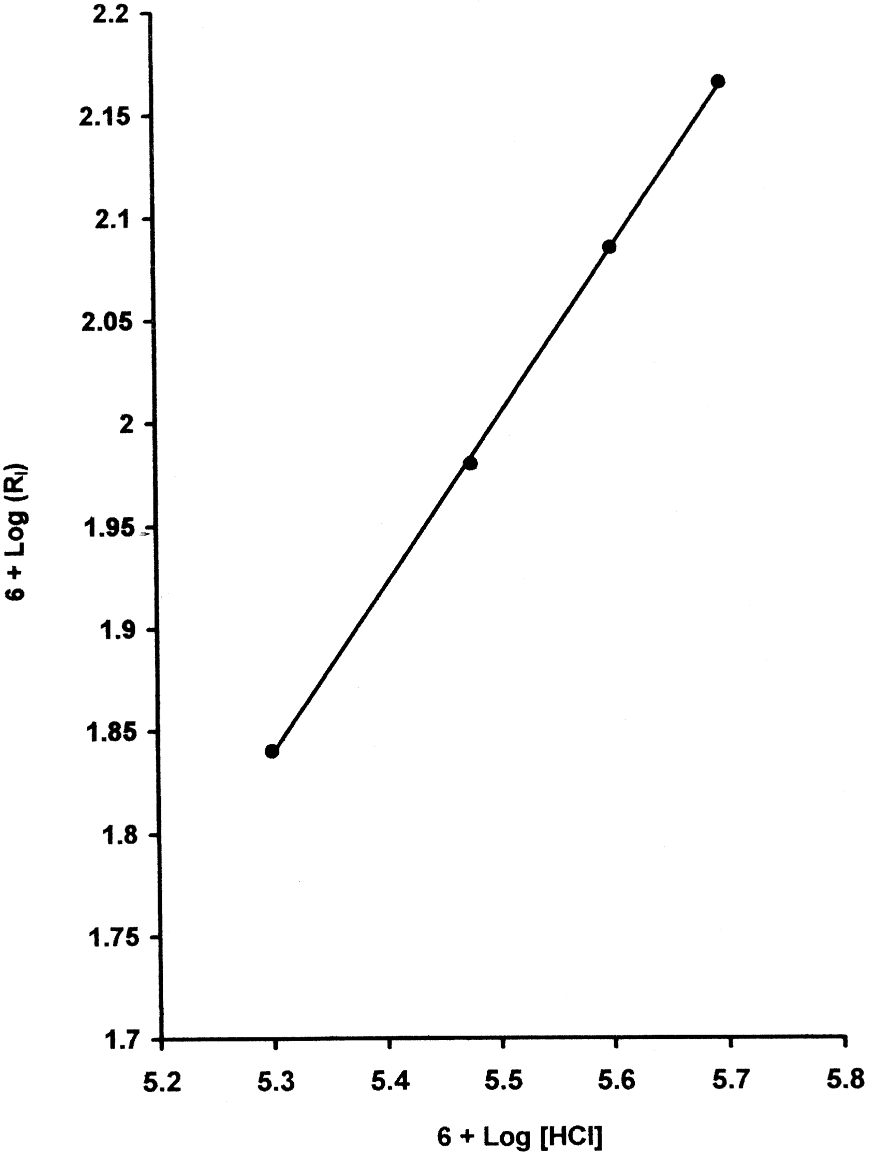


FIGURE 2 Double logarithmic plot of the initial rate and hydrochloric acid concentration.

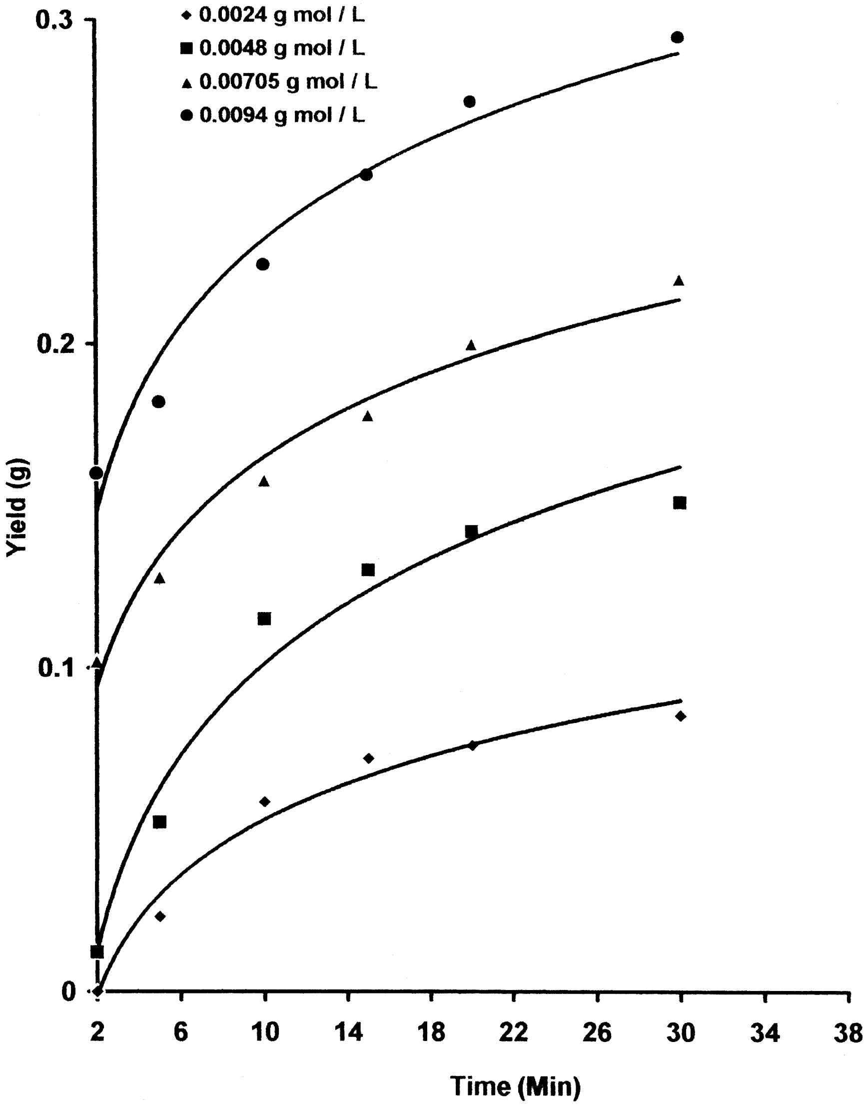


FIGURE 3 Yield-time curves for the effect of sodium dichromate concentration on the aqueoues oxidative polymerization of N-methylaniline.

3.4 Effect of Reaction Temperature

The aqueous polymerization of N-methylaniline (0.1869 mol L^{-1}) in 25 ml of 0.40 mol L^{-1} HCl in presence of 25 ml sodium dichromate (0.0188 mol L^{-1}) solution under nitrogen atmosphere was carried out

TABLE 2 Effect of $Na_2Cr_2O_7$ Concentration on the Polymerization of N-mehtylaniline

Exp. No.	$Na_2Cr_2O_7$ Concentration (mol L^{-1})	Initial rate $\times 10^5$ (mol L^{-1}.s^{-1})	Overall reaction rate $\times 10^5$ (mol L^{-1}.s^{-1})	Conductivity values $\times 10^7$ (S m^{-1})
5	0.00240	2.530	0.1345	1.96
6	0.00480	2.614	0.2578	2.50
7	0.00705	4.984	0.3548	3.91
8	0.00940	6.916	0.4515	0.27

at 5, 10 and 15 °C for different periods of time. The yield-time curve was graphically represented in Figure 7, and the polymerization rate data were calculated and given in Table 4. From which, it is clear that both the initial and overall reaction rates increase with increasing reaction temperature while, ac conductivity has its maximum value at 10°C.

The apparent activation energy (E_a) of the aqueous polymerization reaction of N-methylaniline was calculated by plotting Log R_i against 1/T, which gave a straight line (c.f. Figure 8A). From the slope and using the Arrhenius equation we can calculate E_a. The apparent activation energy for this system is 1.999×10^4 J mol^{-1}.

3.5 Mechanism of the Aqueous Oxidative Polymerization of N-Methylaniline

The pattern of the aqueous oxidative polymerization of N-methylaniline develops in three steps:

3.5.1 The Initial Step

This step is the reaction between dichromate ion and hydrochloric acid, which can be discussed as follows:

(i) 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. The equilibria are as follows:

$$\begin{array}{lll} HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ & & K = 10^{-5.9} \\ H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ & & K = 4.1 \\ Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^- & & K = 10^{-2.2} \end{array}$$

Further, the species present depend on the nature of the acid used [29]. When hydrochloric acid is used, there is an essentially quantitative conversion into the chloro chromate ion as follows:

$$CrO_3(OH)^- + H^+ + Cl^- \rightarrow CrO_3Cl^- + H_2O$$

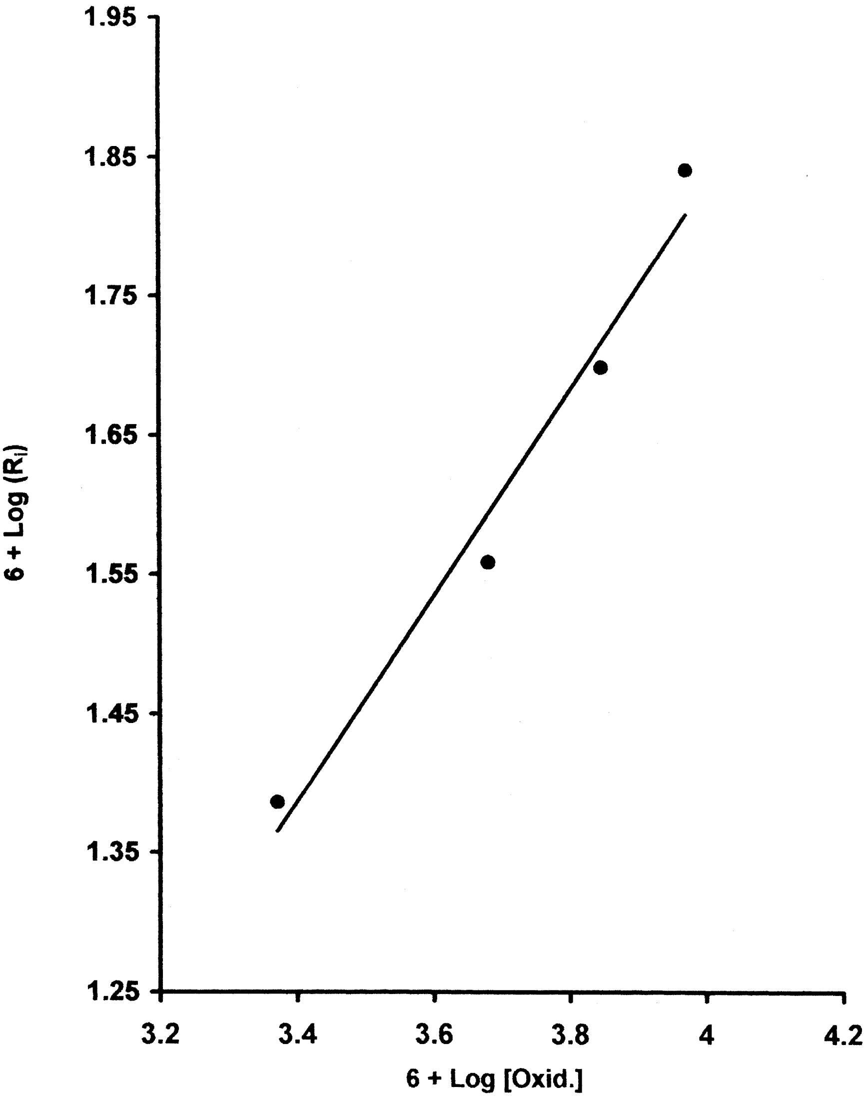


FIGURE 4 Double logarithmic plot of the initial rate and sodium dichromate concentration.

(ii) The second step is the oxidation of N-methylaniline by loss of electrons and conversion of the chromium ion to the lower oxidation state in simultaneous steps as follows:

$$2CrO_3Cl^- + 6e + 14H^+ \rightarrow 2Cr^{3+} + 2HCl - 6H_2O$$

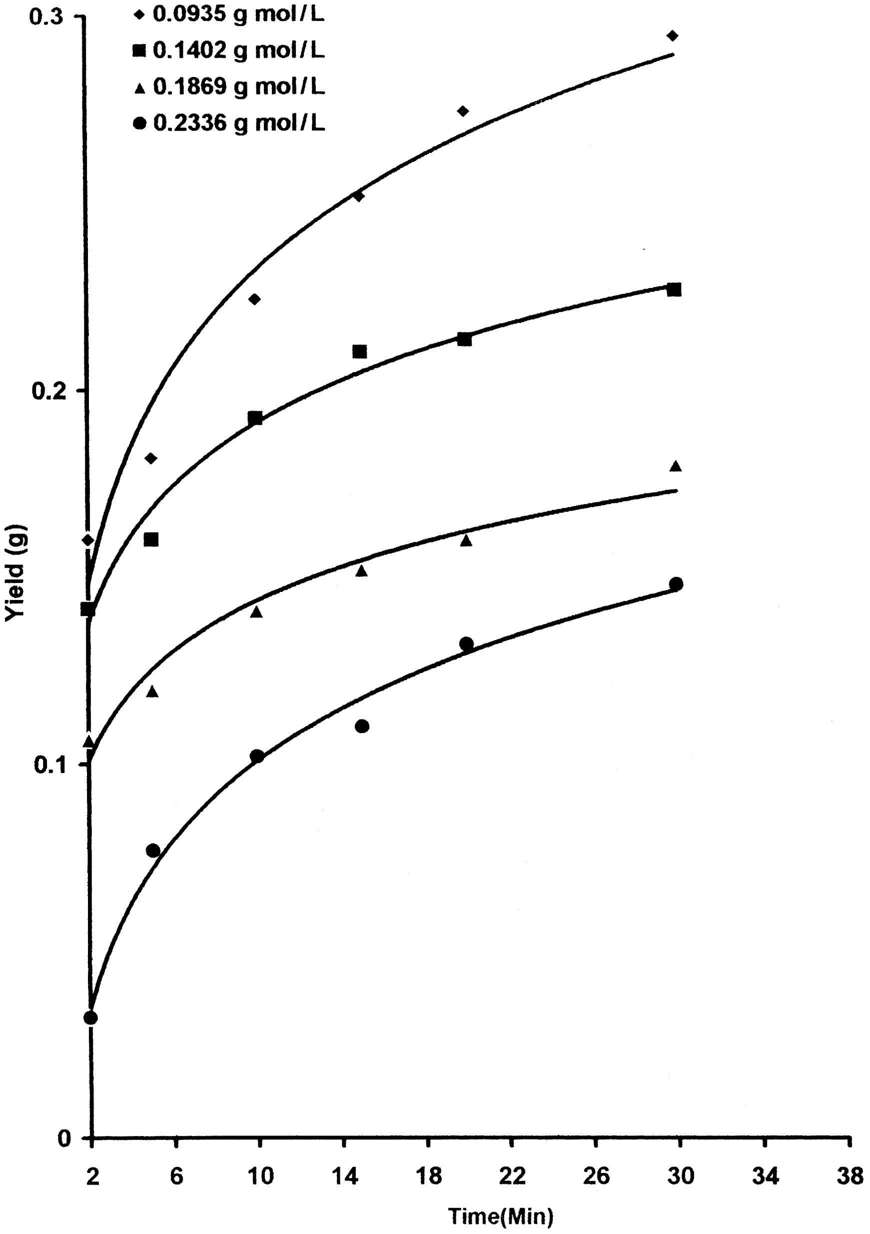
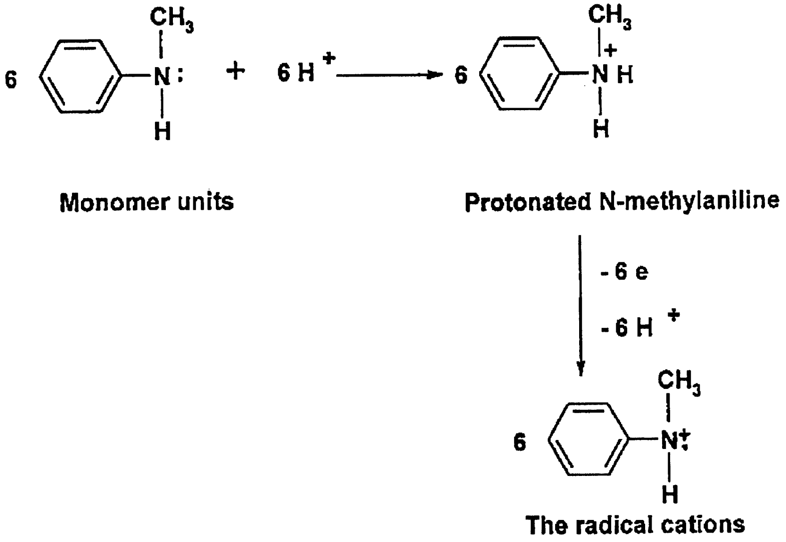


FIGURE 5 Yield-time curves for the effect of monomer concentration on the aqueoues oxidative polymerization of N-methylaniline.

TABLE 3 Effect of Monomer Concentration on the Polymerization of N-Methylaniline

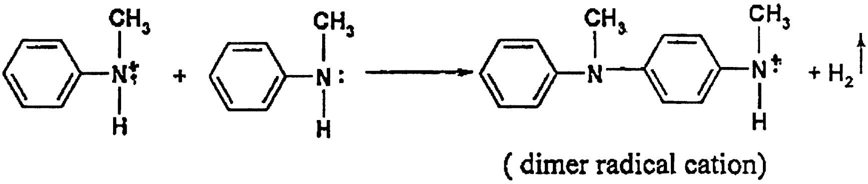
Exp. No.	Concentration of monometer (mol L^{-1})	Initial rate $\times 10^5$ (mol $L^{-1}.s^{-1}$)	Overall reaction rate $\times 10^5$ (mol $L^{-1}.s^{-1}$)	Conductivity values $\times 10^7$ (S m^{-1})
9	0.0935	6.915	0.455	0.27
10	0.1402	5.794	0.4074	2.00
11	0.1869	4.424	0.2369	23.40
12	0.2336	3.162	0.1281	14.80



Generally, the initial step is rapid and may occur in a short time, 0–2 minutes, (autocatalytic reaction), where no polymeric product is being obtained. After two minutes of the polymerization reaction, the polymeric products were obtained in a yield between 23 and 495 mg (c.f. Figs. 1, 3 and 5).

3.5.2 Propagation Step

This step involves the interaction between the formed radical cation and the monomer to form a dimer radical cation as follows:



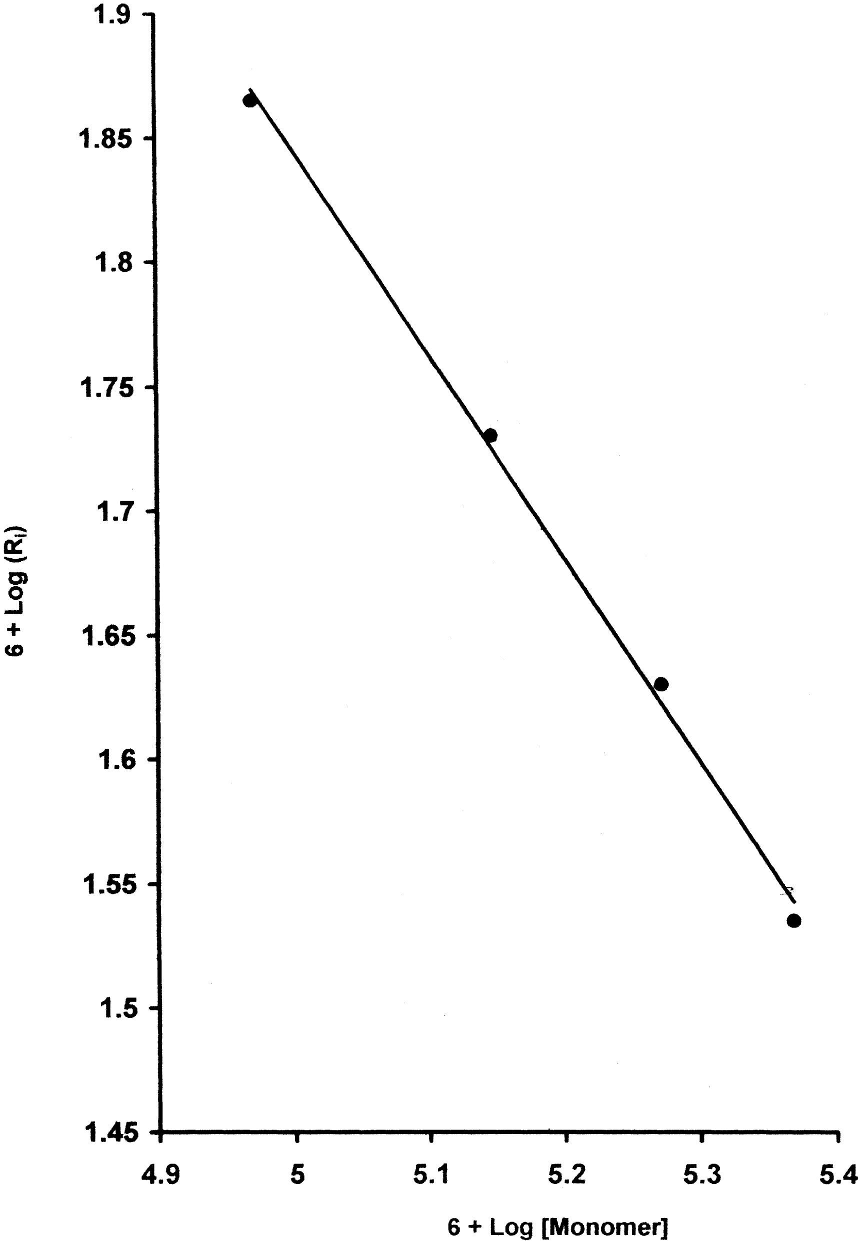


FIGURE 6 Double logarithmic plot of the initial rate and monomer concentration.

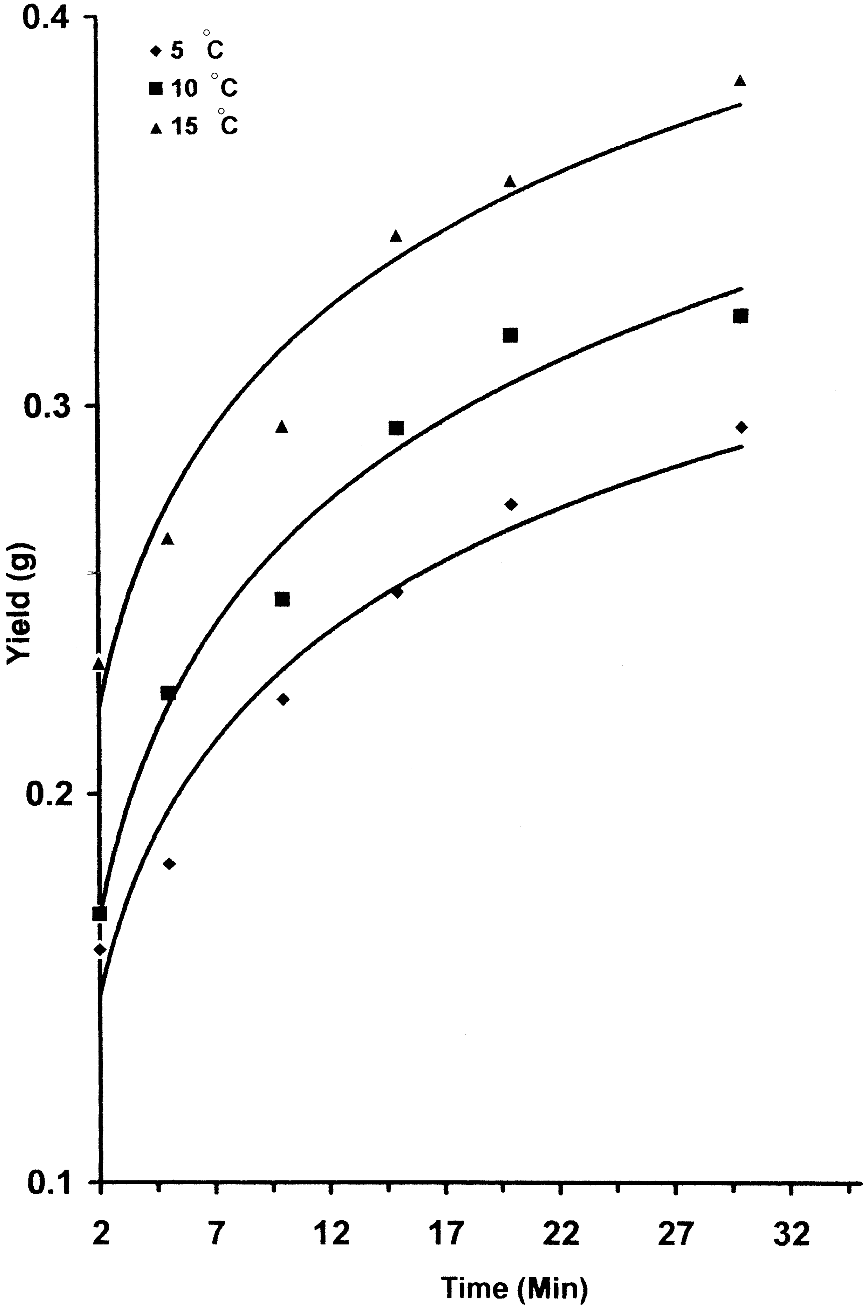


FIGURE 7 Yield-time curves for the effect of temperature (°C) on the aqueoues oxidative polymerization of N-methylaniline.

TABLE 4 Effect of the Reaction Temperature on the Polymerization of N-Methylaniline

Exp. No.	Temperature (°C)	Initial rate $\times 10^5$ (mol $L^{-1}.s^{-1}$)	Overall reaction rate $\times 10^5$ (mol $L^{-1}.s^{-1}$)	Conductivity values $\times 10^7$ (S m^{-1})
13	05	6.916	0.4515	0.27
14	10	8.100	0.4615	2.34
15	15	9.460	0.4725	1.07

This reaction is followed by further reaction of the formed dimer radical cations with monomer molecules to form trimer radical cations and so on. Quinoid structural units may occur in the polymeric chains during the polymerization reaction as mentioned in the literature [30].

The degree of polymerization depends upon different factors such as dichromate concentration, HCl concentration, monomer concentration and temperature as shown by the obtained experimental data of the kinetic studies.

3.5.3 Termination Step

Termination of the reaction occurs by the addition of ammonium hydroxide solution in equimolar amounts to HCl present in the reaction medium (till pH = 7), which leads to cessation of the redox reaction. The reaction could occur as follows (Scheme 1):

3.6 Calculation of the Thermodynamic Parameters

The enthalpy and the entropy of activation for the polymerization reaction can be calculated by the calculation of k_2 from the following equation:

$$Reaction\ Rate = k_2[HCl]^{0.816}[oxidant]^{0.735}/[monomer]^{0.83}$$

The values of k_2 at different temperatures were calculated and the enthalpy (ΔH^*) and entropy (ΔS^*) of the activation associated with k_2 were calculated using an Eyring equation:

$$k_2 = RT/Nh\ e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT}$$

where k_2 is the rate constant, R is the universal gas constant, N is Avogadro's number and h is Plank constant.

By plotting log k_2/T vs 1/T (c.f. Fig. 8 B), we obtained a linear relationship with slope $= -\Delta H^*/2.303$ R and intercept = log (R/Nh) + $\Delta S^*/2.303$ R.

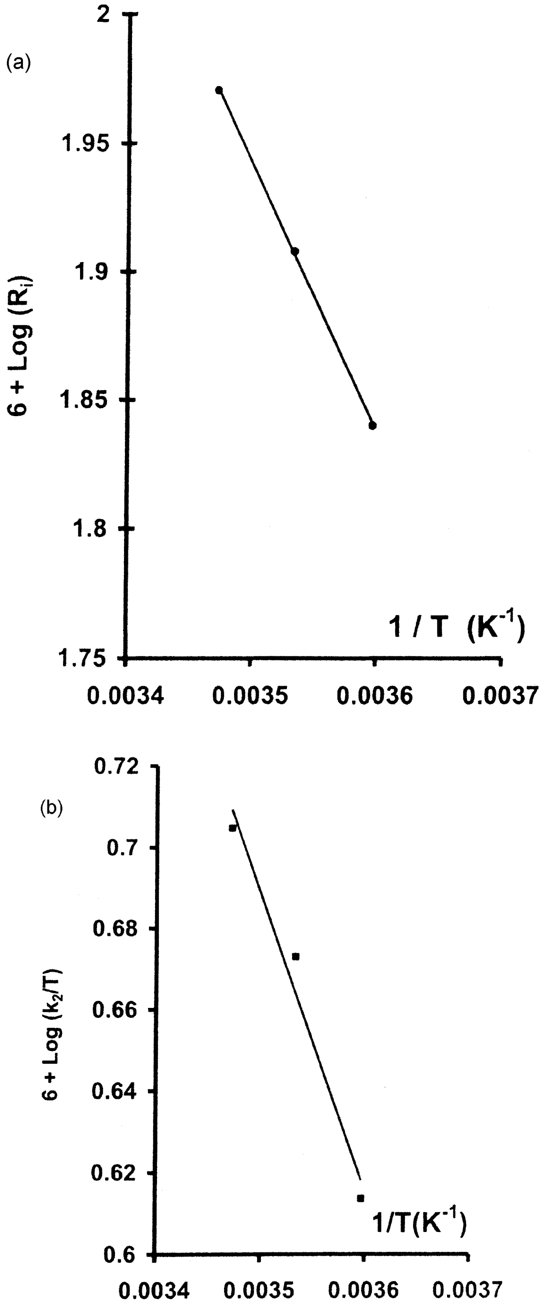
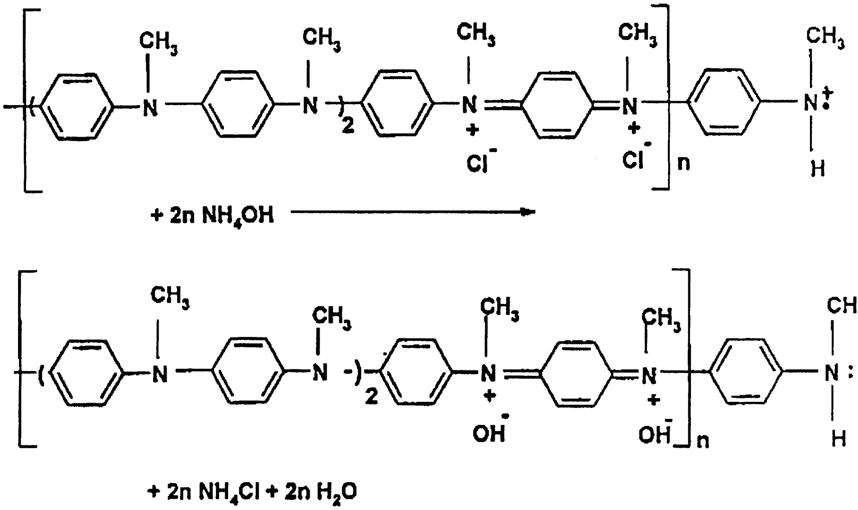


FIGURE 8 (a) The relation between logarithm of the initial rate and (1/T). (b) The relation between Log (k_2/T) and 1/T.



SCHEME 1 The proposed termination mechanism.

From the slope and intercept, the values of ΔH* and ΔS* were found to be 1.761×10^{4} J mol^{-1} and -237.18 J mol^{-1} K^{-1}, respectively. The negative value of ΔS* could be explained by the activated complex and products being more solvated by water molecules than the reactants [31]. The activated complex formation step is endothermic as indicated by the +ve value of ΔH*. The contribution of ΔH* and ΔS* to the rate constant of polymerization seems to compensate each other. This fact suggest that the factors controlling ΔH* must be closely related to those controlling ΔS*. Therefore, the solvation state of the activated complex could be important in determination of ΔH*.

3.7 Elemental and Spectroscopic Analysis

The elemental analysis of the poly(N-methylaniline) was carried out in the micro analytical laboratory at Cairo University. The Percentages of C, H, N and Cl are in good agreement with the calculated one for the suggested structure present in Scheme 3. The elemental analytical data are given in Table 5.

The UV-visible spectra of the monomer and polymer are represented in Figure 9. The absorption bands at 217 and 308 nm for the monomer and 225,247 and 307 nm in case of the polymer could be attributed to π-π^* transition (E_2-band) of benzene ring π-π^* transition and B-band (A_{1g}-B_{2u}), respectively. The absorption band, which

TABLE 5 Elemental Analysis of Poly(N-mehtylaniline)

The element	C%	H%	N%	Cl%
Calculated %	65.20	6.40	10.86	9.12
Found %	65.40	5.90	11.10	8.70

appears at 492 nm in case of polymer, may be due to the high conjugation of the aromatic polymeric chains.

The infrared absorption bands and their assignments for the prepared polymer sample are summarized in Table 6. The medium absorption band appears at 475 cm^{-1} and the strong one appears at 619 cm^{-1}, they may be attributed to the out of plane stretching vibration of C–H in methyl group. The medium absorption band appearing at 850 cm^{-1} is attributed to an out of plane C–H deformation showing 1,4-disubstituted benzene ring. The absorption bands that appear in the region 116—1350 cm^{-1} are attributed to C–N stretching vibration or overtone of CH deformation. The absorption bands that appear at 1385 and 1465 cm^{-1} are attributed to the stretching vibration of CH in methyl group. The strong and split band at 1618 and 1623 cm^{-1} is due to the stretching vibration of C=C in benzene ring or C=N in quinoid unit. The great broadening of the band in the region 3237—3547 cm^{-1} may be attributed to superimposed NH group and strong bonded OH group bands.

The ^{1}H-NMR spectrum of the prepared polymer sample shows a singlet signal at $\delta = 1.25$ ppm for the methyl group protons. The solvent protons appear as singlet, douplet and singlet signals in the range 2.95—3.6 ppm, respectively. The multiplet signals that appears at $\delta = 6.8$—7.36 ppm are attributed to the benzene ring protons and NH group proton.

3.8 Electron Microscope and X-Ray Diffraction Analysis

X-ray diffraction pattern shows that the prepared polymer sample is a microcrystalline material as shown in Figure 10. The 2θ, d spacing and intensity parameters for the three strongest peaks are tabulated in Table 7.

The electron microscopic picture shows the shape of the grains of the polymer, which ranged from spherical particles to an elongated one. Their size ranged from 25.13×10^{-3} mm to 157×10^{-3} mm as shown in Figure 11.

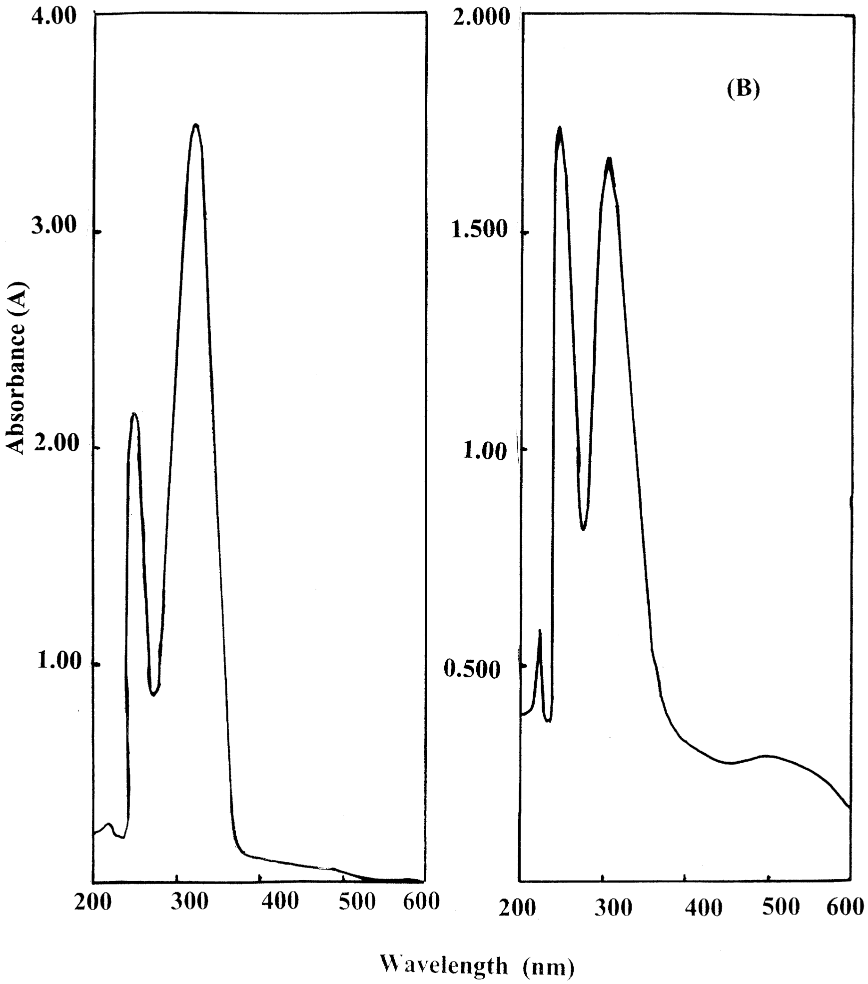


FIGURE 9 UV-visible spectra of (a) N-methylaniline monomer and (b) the prepared poly(N-methylaniline).

3.9 Thermogravimetric Analysis (TGA)

The thermogram of the prepared polymer sample obtained from TGA measurement is presented in Figure 12. The first stage on the TGA curve in the temperature range (21.3–137°C) includes the loss of one water moleclule of hydration present in the suggested structure in Scheme 2. The weight loss for this step is estimated to be 2.319% and calculated 2.32%. From the TGA curve in the temperature range

TABLE 6 Assignment of Bands in the IR Spectra of N-methylaniline

Wave number (cm^{-1})	Assignment [31]
475^{m}	Out of plane CH deformation (CH_3)
619^{s}	
850^{m}	Out of plane CH deformation showing 1,4-disubstituted benezene ring
1116^{w}	C–N stretching vibration or in plane
1181^{w}	δ CH deformation in aromatic ring
1250^{w}	
1352^{w}	
1385^{m}	CH stretching vibration of CH_3
1464^{w}	
$1618^{s\&sp}$	stretching vibration of C=C in benezene of C=N in quinoid ring
1623	
2122^{w}	C–N stretching vibration (overtone)
3237^{w}	
$3414^{b\&sp}$	NH stretching vibration
3476	
3547	strong bonded OH group

between 142 and 354°C, a weight loss of about 19.63% was found, which could be attributed to the loss of 3 H_2O, 2Cl and 2CH_3, which is in good agreement with the calculated value (20.05%) for this stage. In the temperature range between 355.2 and 442°C all methyl groups

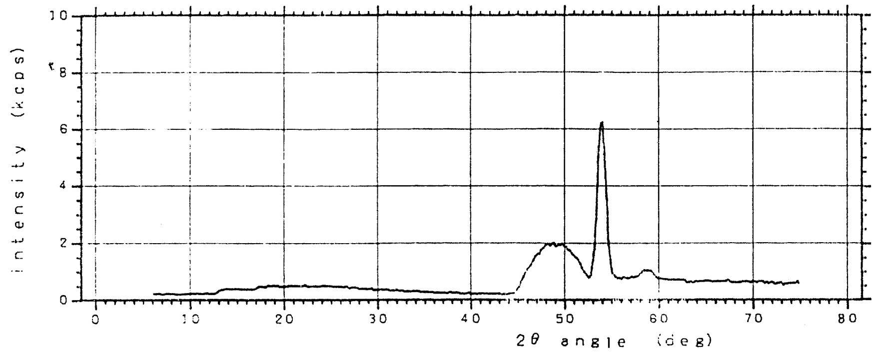


FIGURE 10 The X-ray diffraction pattern of the prepared poly(N-methylaniline).

TABLE 7 The 2θ,d Spacing Intensity Parameters for the Three Strongest Peaks of the Prepared Polymer Sample

peak no.	2θ deg	d (A)	I/I_0	Intensity (kcps)	Integrated int. (kcps. deg)
1	53.966	1.6976	100	2.824	3.8356
2	48.324	1.8818	30	0.848	2.5129
3	49.409	1.8430	29	0.817	2.0500

($4CH_3$), which are bonded to the N-atom are lost from the polymeric chain, with an estimated mass loss of 7.85%, which is in good agreement with the calculated value 7.76%. In the temperature range 442.5–697° C all the polymeric segments are destroyed. The estimated weight loss for this step is found to be 67.46%, while the calculated value is equal to 69.86%. Above 613° C the residue of the polymer is found to be 2.818%.

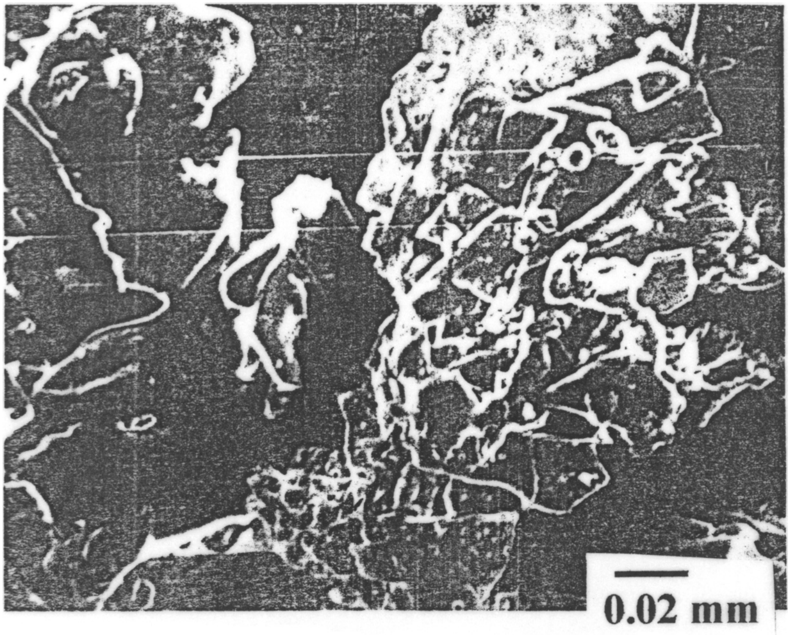


FIGURE 11 The electron scanning micrograph of the prepared poly(N-methylaniline).

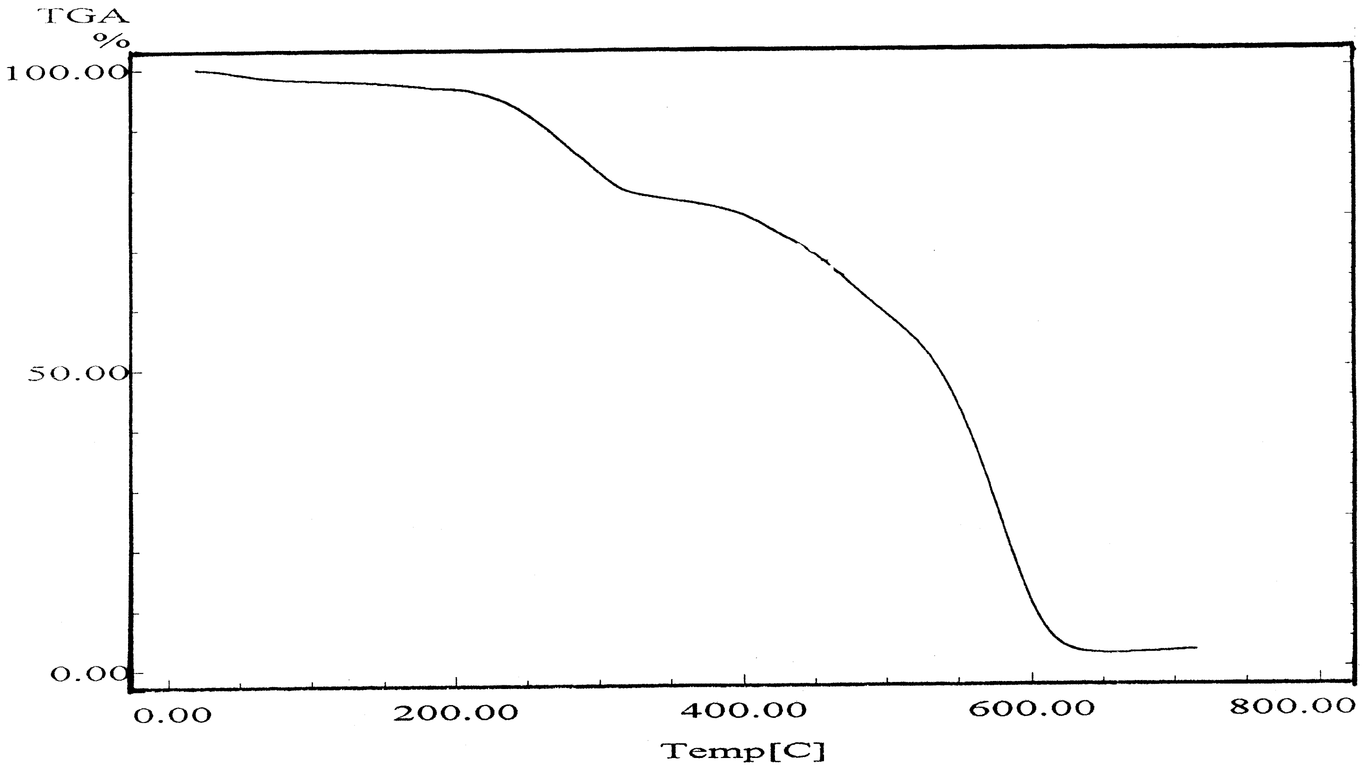
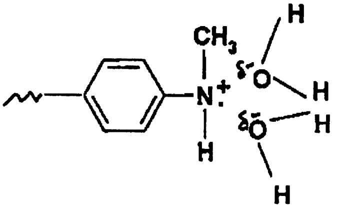
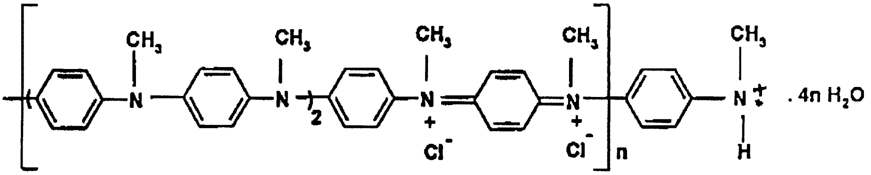


FIGURE 12 The thermogravimetric analysis (TGA) of the prepared poly(N-methylaniline).

The + ve charge present on the terminal amino group may be killed by solvation process [26] as follows:



SCHEME 2 Possible neutralization process.



SCHEME 3 The suggested structure of poly(N-methylaniline).

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