Aqueous oxidative polymerization of 3-methoxyaniline and characterization of its polymer

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AQUEOUS OXIDATIVE POLYMERIZATION OF 3-METHOXYANILINE AND CHARACTERIZATION OF ITS POLYMER

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The aqueous polymerization of 3-methoxyaniline (3-OMeA) was studied using sodium dichromate as oxidant in presence of hydrochloric acid. The effect of hydrochloric acid, sodium dichromate, monomer concentration and reaction temperature on the polymerization rate, specific viscosity of the obtained polymer and a.c.conductivity was investigated. The initial and overall reaction rates increase with the increasing of hydrochloric acid concentration, reaction temperature or sodium dichromate concentration but decrease with the increasing of the monomer concentration. The specific viscosity values increase with the increasing of the hydrochloric acid concentration or the monomer concentration which means that the molecular weight of the polymer samples increases in the same direction. But the molecular weight decreases with the increase of both sodium dichromate concentration and reaction temperature. The highest a.c.conductivity value of the obtained polymers was found when 0.0205 g mol/L of $Na_2Cr_2O_7$, 0.8 g mol/L HCl and 0.0821 g mol/L of monomer were used in the reaction medium at 5° C, the electrical conductivity and dielectric constant of this polymer sample were investigated as a function of temperature. The order of the polymerization reaction with respect to hydrochloric acid, $Na_2Cr_2O_7$ and monomer concentration was found to be 0.85, 1.36 and 0.74 respectively. The apparent activation energy (E_a) for this polymerization system was found to be 7.656×10^4 J/mol. The obtained poly(3-methoxyaniline) was characterized by UV-visible and IR spectroscopy, X-ray diffraction analysis and electron microscopic studies. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) results were used for the confirmation of the suggested structure.

Keywords: poly(3-methoxyaniline), oxidative polymerization, electrical conductivity, characterization

1. INTRODUCTION

Polyaniline (PANI) as one of the electrically conducting polymers has been extensively studied in the last decade because of its many promising properties such as fast switching rates [1, 2], the ability to switch reversibly from insulating to conducting state either by electrochemical or chemical doping [3, 4], its many potential applications and unique electrical and optical properties. In recent years several review papers [5 – 7] on polyaniline have been published.

Various chemical oxidizing agents such as potassium dichromate, potassium iodate, ammonium persulfate, hydrogen peroxide, ceric nitrate and ceric sulfate have been used for the chemical oxidative polymerization of aniline [7]. Polymerization mechanisms and reaction kinetics of aniline in aqueous solutions have been investigated by several groups [8 – 17]. Generally, it is agreed that the initiation reaction involves the formation of a radical cation intermediate and the subsequent combination of two radicals cations to form the aniline dimer. After this initial step, the method by which these species proceed to form polymer is still not clearly understood, but different mechanisms have been reported for this growing step.

The morphology of synthesized PANI [18] was studied after dedoping and redoping with dodecylbenzenesulfonic acid (DBSA) and polystyrene (PS). Also, the temperature-conductivity dependence of soluble polyaniline films doped with DBSA have been studied [19]. The effect of molecular weight of PANI doped with lithium hexafluorophosphate on the temperature dc-conductivity dependence were reported [20]. Different spectroscopic methods were used for the structures provided in these works.

The effect of pH of the polymerization solutions or 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 was investigated [21 – 23].

Aniline oligomers of different degrees of oxidation have been synthesized and their structures were determined by ^{1}H- and ^{13}C-NMR and infrared spectroscopy [24]. The chemical polymerization conditions of polyaniline synthesized with different oxidizing agents and the physico-chemical properties were studied [25].

Water soluble polyanilines were prepared and characterized by X-ray diffraction, X-ray photoelectron spectroscopy, electronic spectroscopy, infrared spectroscopy, thermogravimetric analysis, conductivity measurements, atomic force microscopy and scanning tunneling microscopy [26]. Chemical polymerization of M-toluidine, O-chloroaniline and nitroaniline has been studied and characterization of the resulting polymers was performed by DSC, X-ray, IR, XPS and conductivity measurements [27]. It was found that the substituent group on aniline affects not only the polymerization reaction but also the properties of the polymers obtained.

The HCl-doped emeraldine form of polyaniline (PANI-H) was synthesized by oxidative polymerization of aniline in aqueous hydrochloric acid solution using potassium dichromate as an oxidant [28].

In the present study we intend to investigate the kinetics of the oxidative polymerization of 3-methoxyaniline in aqueous hydrochloric acid medium using sodium dichromate as oxidant. The obtained polymer is characterized by UV, FTIR spectroscopy, X-ray diffraction, electron microscopy, thermal analysis, specific viscosity and a.c.conductivity measurements. Both the ac conductivity and dielectric constant of the polymer sample (which has the highest ac conductivity) are investigated as a function of temperature.

2. EXPERIMENTAL

2.1. Materials

3-methoxyaniline provided by Merck Chemical Company (Germany) was vacuum distilled before using. Concentrated hydrochloric acid, sulfuric acid and ammonia (33%) were of chemically pure grade products provided by Prolabo-Chemical Company (England). Double distilled water was used as a medium for the polymerization reactions during the present work. Sodium dichromate used was a product of Merck Chemical Company (Germany).

2.2. Oxidative Aqueous Polymerization of 3-Methoxyaniline Monomer

The polymerization reactions were carried out in well-stopped conical flasks of 250 ml capacity containing the amount of monomer (3-OMeA), followed by the addition of the required amount of sodium dichromate solution (25 ml) to the reaction mixture under nitrogen atmosphere. The order of addition of substances was kept constant in all the performed experiments. The stoppered conical flasks were then put in an automatically controlled thermostat at the required temperature. The flasks were shaken (15 shakings/10 seconds/every 15 minutes) for definite periods of time by using automatic shaker. The reaction was stopped by the addition of ammonia solution (in equimolar amount to HCl) and cooling in ice bath. The polymer was then filtered using Buchner funnel, washed thoroughly with distilled water, methanol and finally dried in a vacuum oven at 60°C till constant weight. But, in case of the polymer samples prepared for characterization, the polymerization solutions after 4 hours were filtered without addition of ammonia solution, then washed with distilled water, air dried and finally dried under vacuum at room temperature till constant weight.

2.3. Determination of the Specific Viscosity

The specific viscosity was measured on polymer samples dissolved in concentrated sulfuric acid (0.1 g/10 ml) at 25°C using Ostwald viscometer as mentioned for PANI [29].

2.4. Ultraviolet and Infrared Spectroscopy

The ultraviolet-visible absorption spectra of the monomer and the prepared polymer samples were measured using Shimadzu UV-spectrophotometer M 1601 PC spectrophotometer at room temperature in the region 200–1000 nm using concentrated sulfuric acid as a solvent and reference.

The infrared measurements were carried out using Shimadzu FTTR-430 Jasco spectrophotometer.

2.5. Thermal Gravimetric Analysis

The thermal gravimetric analysis of the polymer sample was performed using a thermal analyzer (SHIMAZU DT-30). The weight loss was measured from ambient temperature up to 600°C in a rate of 20°C per minute. The weight loss of the sample was calculated with rising temperature to determine the degradation rate of the polymer.

2.6. Electron Microscopy and X-ray Diffraction Analysis

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

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

2.7. Preparation of Thin Film Samples

The films were prepared by a solvent casting technique. A flat glass plate provided with four leveling screws and water balance was used as a base for the glass petri dishes containing the material to ensure uniform thickness. The appropriate weight of the stabilized poly 3-methoxyaniline with PMMA is dissolved in 100 ml benzene as a solvent to give a homogeneous solution which was poured into the casting dishes (area $= 153.86\,cm^2$) to

give film samples with constant thickness (~ 0.2 cm). The rate of solvent evaporation should not be too rapid and can be controlled by placing an inverted 1000 ml beaker over the casting dish and allowing 1 cm clearance to permit air circulation. The solvent was allowed to evaporate over a period of 24 hours. The plastic film adheres at the bottom of the casting dish. A sharp bladed microspatula was used to score the film around its edges to detach it from the wall of the casting dish. The film is then covered with warm water and after a few minutes it floated to the surface from where it was gently picked up and laid flat on a nonadhering surface such as a piece of whatman No. 1 filter paper. The filter paper and the film were then placed in an oven to dry for 6 hours at 60°C. The measured thickness of the films obtained by the above manner are found to have high degree of homogeneity.

2.8. Conductivity Measurements

Polymer samples in the form of compressed discs of 1.002 cm diameter and 0.2 cm thick 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 $10^2 - 10^5$ Hz and over a temperature range $30 - 150$°C. 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 3-methoxyaniline (0.1644 g mol/L) in 25 ml of HCl which had different molarities in the range (0.4 to 1.6 g mol/L) was carried out by addition of 25 ml sodium dichromate solution (0.0411 g · mol/L) as oxidant under nitrogen atmosphere at 5°C for different time intervals. The concentration of the monomer and oxidant are kept constant at 0.0821 g · mol/L and 0.0205 g · mol/L respectively during the study of HCl effect on the polymerization reaction. The experiments were carried out as described in the experimental part and the conversion-time curve for each acid concentration is calculated and the data are graphically represented in Figure 1, from which the initial rates of the polymerization reactions are calculated and tabulated in Table 1. Specific viscosity and a.c. conductivity of the obtained polymers after 4 hours for each HCl concentration were measured and the data are given in Table 1. From Figure 1 and Table 1, it is clear that the initial, overall reaction rates and specific viscosity of the polymerization reaction increase with increasing the HCl
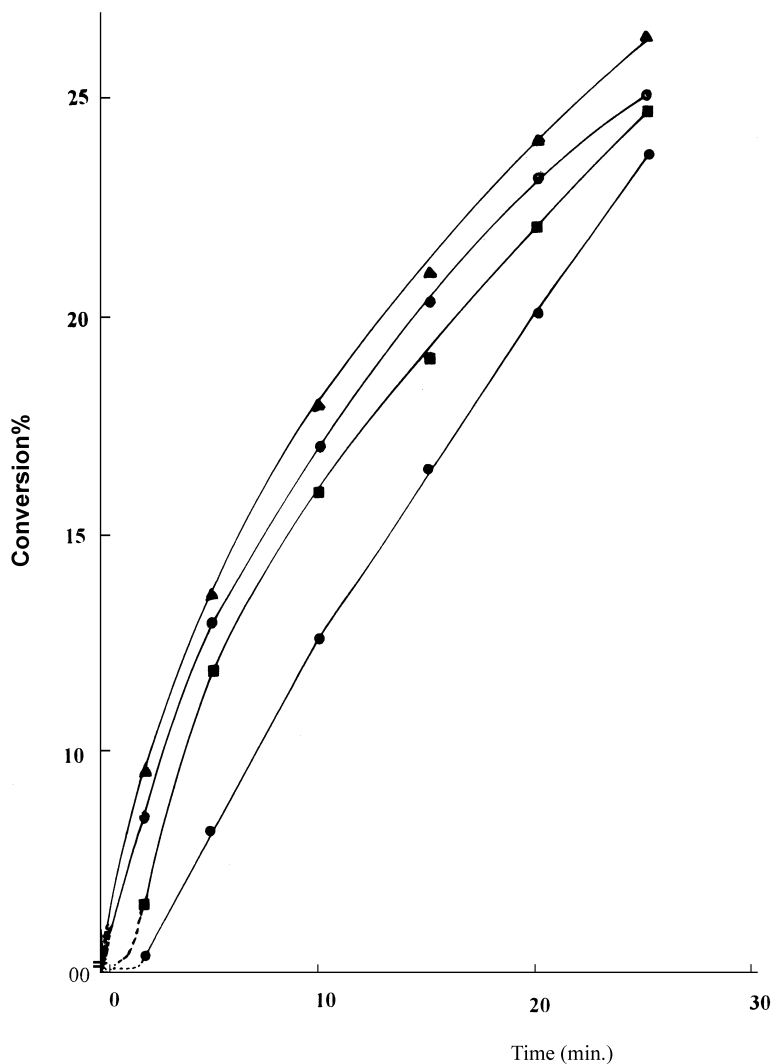
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FIGURE 1 Effect of HCl concentration on the rate of polymerization of 3-methoxyaniline. (●) 0.20, (■) 0.40, (○) 0.60, and (▲) 0.80 g mol/L.

concentrations from $0.2 - 0.8$ g mol/L. The highest a.c. conductivity value is obtained at 0.8 g mol/L HCl. The HCl exponent is determined from the relation presented in Figure 2. A straight line is obtained with a slope equals to 0.85. This indicates that the order of the polymerization reaction with respect to the HCl concentration is first order reaction.

TABLE 1 Effect of HCl concentration on the polymerization of (3-OmeA)

Sl. No.	Concentration of HCl ($g \cdot mol/L$)	Initial rate $\times 10^6$ ($g \cdot mol/L \cdot s$)	Overall reaction rate $\cdot 10^6$ ($g \cdot mol/L \cdot s$)	η_{sp}	Conductivity values $\cdot 10^8$ (S/m)
1	0.20	19.008	5.1088	0.0684	7.07
2	0.40	34.214	7.0103	0.0744	3.63
3	0.60	48.877	7.3461	0.0804	7.75
4	0.80	59.503	7.6083	0.0853	26.20
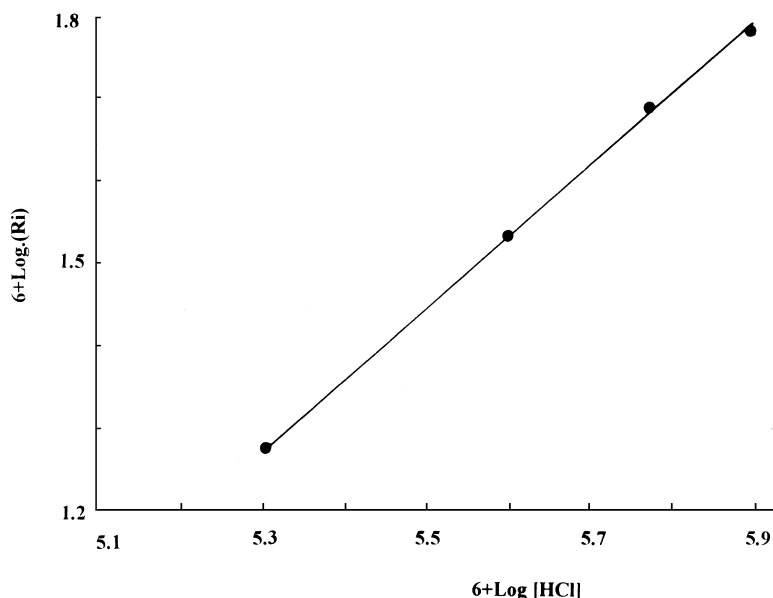
FIGURE 2 Double logarithmic plot of the initial rate of polymerization versus HCl concentration.

3.2. Effect of Sodium Dichromate Concentration

The aqueous polymerization of 3-methoxyaniline (0.1644 g mol/L) in 25 ml (1.6 g mol/L) HCl solution and 25 ml of sodium dichromate solution which has different molarities (0.0137, 0.0274, 0.0410 and 0.0548 $g \cdot mol/L$) as oxidant was carried out under nitrogen atmosphere at 5°C for different time intervals. The total concentration of both HCl and monomer were fixed in the reaction medium at 0.8 and 0.0821 $g \cdot mol/L$ respectively. The conversion-time curve for each oxidant concentration is calculated and the data are graphically represented in Figure 3, from which the initial rates of the
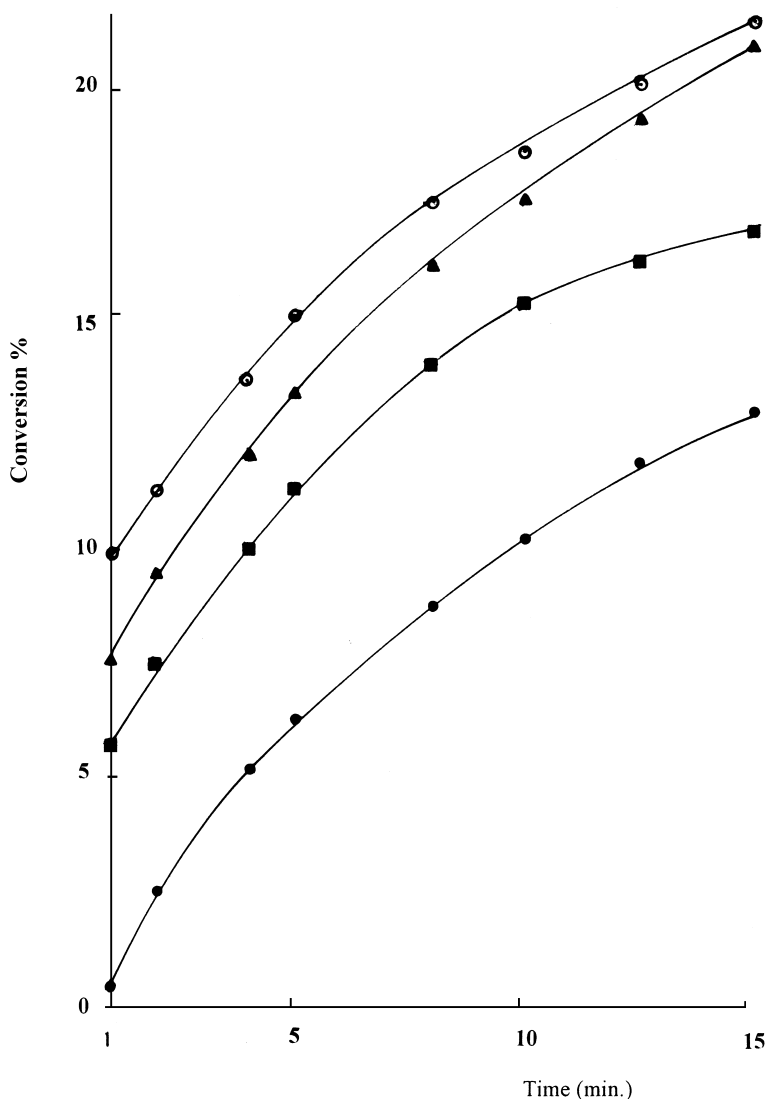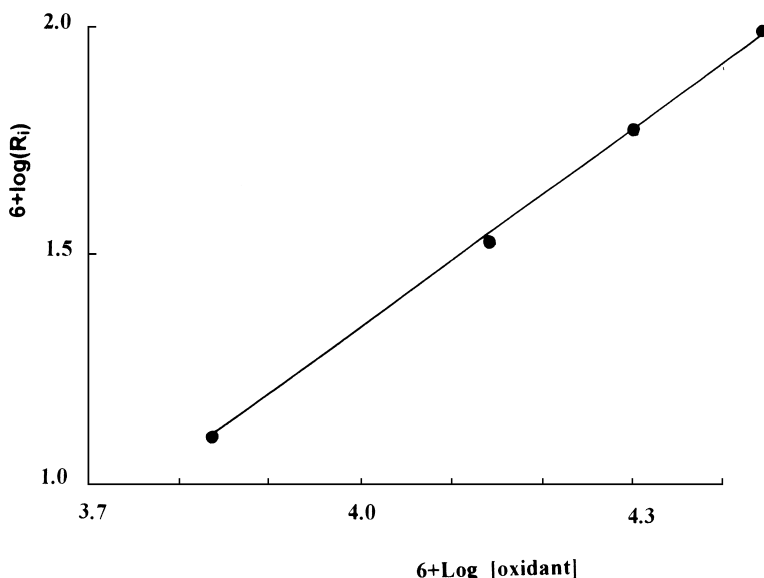
FIGURE 3 Effect of $Na_2Cr_2O_7$ concentration on the rate of polymerization of 3-methoxyaniline. (●) 0.0069, (■) 0.0137, (▲) 0.0205, and (⊙) 0.0274 g mol/L.

polymerization reactions are calculated and summarized in Table 2. Specific viscosity and a.c. conductivity of the obtained polymers after 4 hours for each oxidant concentration were measured and the data are given in Table 2. From the obtained data it is clear that the initial and overall reaction rates of the polymerization reaction increase with increasing the oxidant concentration

TABLE 2 Effect of $Na_2Cr_2O_7$ concentration on polymerization of (3-OMeA)

Sl. No.	Concentration $Na_2Cr_2O_7$ $(g \cdot mol/L)$	Initial rate $\times 10^6$ $(g \cdot mol/L \cdot s)$	Overall reaction rate $\times 10^6$ $(g \cdot mol/L \cdot s)$	η_{sp}	Conductivity values $\cdot 10^8$ (S/m)
5	0.0069	13.963	5.1009	0.1018	4.16
6	0.0137	34.214	6.2549	0.0928	7.92
7	0.0205	59.503	7.6083	0.0853	26.20
8	0.0274	97.755	7.7080	0.0703	2.75

FIGURE 4 Double logarithmic plot of the initial rate of polymerization versus oxidant concentration.

while the specific viscosity decreases in the same direction, and the maximum value of a.c.conductivity is obtained for the polymer sample obtained at 0.0205 g mol/L of the oxidant concentration. The oxidant exponent is calculated from the slope of the obtained straight line for the relation between Log R_i vs. Log[oxidant] (*cf.* Fig. 4). The slope is found to be equal to 1.36 which means that the polymerization reaction with respect to the oxidant concentration is first order reaction.

3.3. Effect of Monomer Concentration

The effect of monomer concentration on the aqueous polymerization of 3-methoxyaniline in the presence of HCl and 25 ml of 0.0410 g $\cdot$ mol/L

Na$_2$Cr$_2$O$_7$ solution under nitrogen atmosphere at 5°C was studied. The quantity of monomer is dissolved in 25 ml 1.6 M HCl. The final concentration of both HCl and Na$_2$Cr$_2$O$_7$ in the reaction medium is kept constant at 0.8 M and 0.0205 g · mol/L respectively. The conversion time curve data are calculated and graphically represented in Figure 5, while the calculated
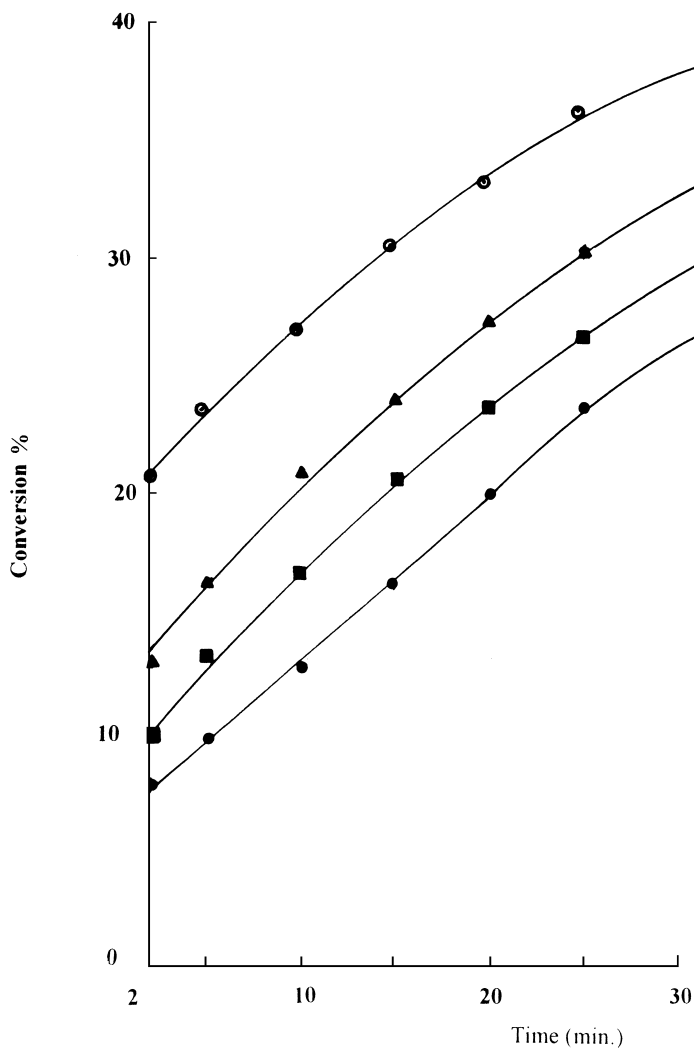

FIGURE 5 Effect of monomer concentration on the rate of polymerization of 3-methoxyaniline. (⊙) 0.0493, (▲) 0.0821, (■) 0.1150, and (●) 0.1480 g mol/L.

initial and overall reaction rates are also given in Table 3. From which it is clear that both the initial and overall reaction rates increase with the increasing of monomer concentration. The determination of the monomer

TABLE 3 Effect of monomer concentration on polymerization of (3-OMeA)

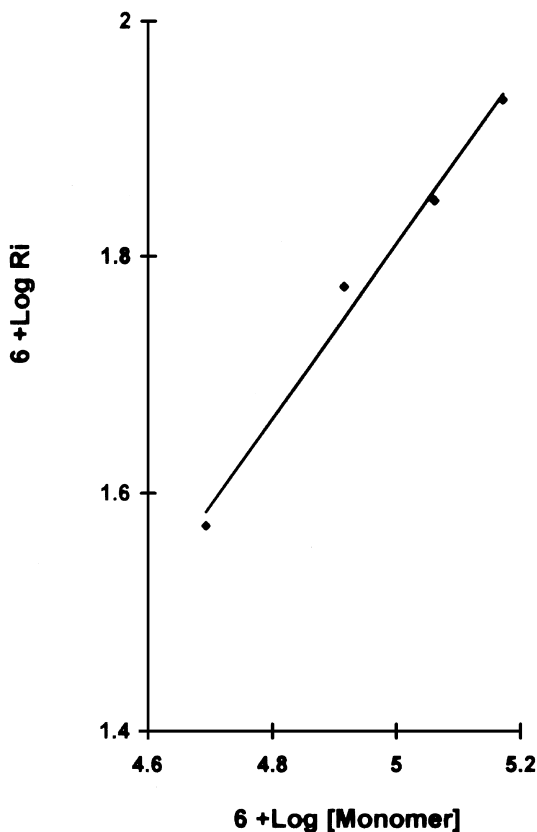| Sl. No.	Monomer concentration ($g \cdot mol/L$)	Initial rate $\times 10^6$ ($g \cdot mol/L \cdot s$)	Overall reaction rate $\cdot 10^6$ ($g \cdot mol/L \cdot s$)	η_{sp}	Conductivity values $\cdot 10^8$ (S/m)
9	0.0493	37.366	3.850	0.0778	5.23
10	0.0821	59.503	7.608	0.0853	26.20
11	0.1150	70.325	9.117	0.1063	2.43
12	0.1480	85.684	12.988	0.1153	3.36

FIGURE 6 Double logarithmic plot of initial rate of 3-methoxyaniline polymerization versus monomer concentration.

exponent is calculated from the straight line represented in Figure 6. The slope is found to be equal 0.74. This indicates that the monomer exponent is 0.74. Specific viscosity and a.c.conductivity of the obtained polymer after 4 hours for each monomer concentration were measured and the data are also given in Table 3. The specific viscosity values increase with increasing monomer concentration, while the highest a.c.conductivity values is found to be at 0.0821 g · mol/L monomer concentration.

3.4. Effect of the Reaction Temperature

The aqueous polymerization of (0.0821 g mol/L) 3-methoxyaniline dissolved in 25 ml of 1.6 M HCl using 25 ml sodium dichromate (0.041 g · mol/L) solution under nitrogen atmosphere was carried out at 5, 10 and 15°C for different periods of time. The final concentrations of the acid, oxidant and

TABLE 4 Effect of temperature (°C) on polymerization of (3-OMeA)

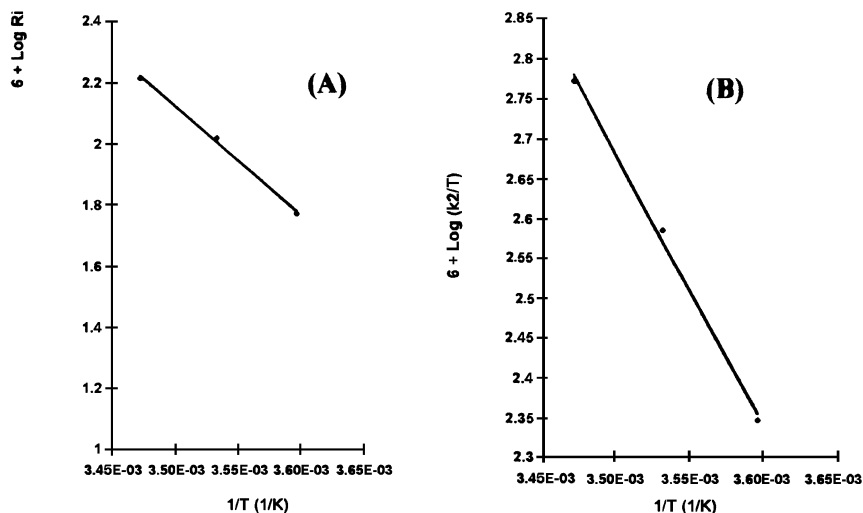| Sl. No.	Temperature (°C)	Initial rate × 10^6 (g · mol/L · s)	Overall reaction rate × 10^6 (g · mol/L · s)	η_{sp}	Conductivity values · 10^8 (S/m)
13	5	59.503	7.608	0.0853	26.20
14	10	105.274	8.033	0.0793	15.42
15	15	164.227	9.076	0.0674	5.10

FIGURE 7   Logarithmic plot of (A) initial rate of polymerization of 3-methoxyaniline and (B) Log k_2/T versus $1/T$ (K^{-1}).

the monomer in the polymerization reaction are 0.8 M, 0.0205 g · mol/L and 0.0821 g · mol/L respectively. The conversion % was calculated at different time intervals and the data are given in Table 4. From the obtained data, it is clear that both the initial and overall reaction rates increase with rising reaction temperature, while the specific viscosity values decrease with rising reaction temperature. The highest a.c. conductivity value is found at a reaction temperature of 5°C.

The apparent activation energy (E_a) of the aqueous polymerization reaction of 3-methoxyaniline was calculated by plotting Log R_i against $1/T$ which gave a straight line (*cf.* Fig. 7a). From the slope it is found that the apparent activation energy (E_a) of the aqueous polymerization reaction of 3-methoxyaniline is 7.656×10^4 J/mol.
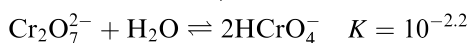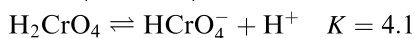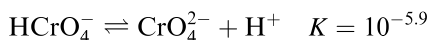
3.5. Mechanism of the Aqueous Oxidative Polymerization of 3-Methoxyaniline

The pattern of aqueous oxidative polymerization of 3-methoxyaniline develops in three steps:

3.5.1. Initiation 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:

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \quad K = 10^{-5.9}$$
$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \quad K = 4.1$$
$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^- \quad K = 10^{-2.2}$$

Further, the species present depend on the nature of the acid used [30]. When hydrochloric acid is used, there is essentially quantitative conversion into the chloro chromate ion as follows:

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

(ii) The second step is the oxidation of 3-methoxyaniline by loss of electrons and conversion of the chromium ion to the lower oxidation state in simultaneous steps as follows:

$$2CrO_3Cl^- + 6e + 14H^+ \rightarrow 2Cr^{3+} + 2HCl + 6H_2O$$
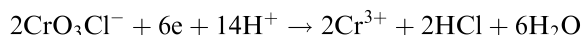
and (Scheme 1)
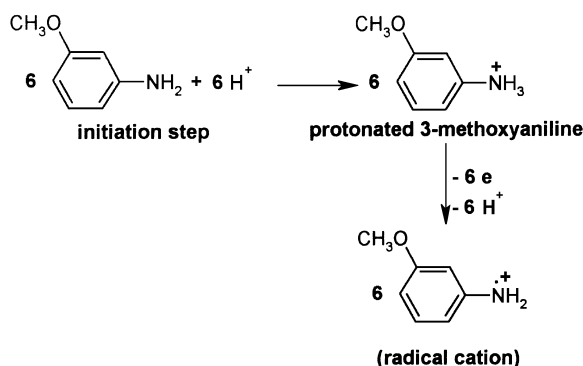
SCHEME 1

(In general, the initial step is rapid and may occur in short time (0 – 2 minutes) as shown in the conversion-time curves (*cf.* Figs. 1, 3 and 5).

3.5.2. Propagation Step

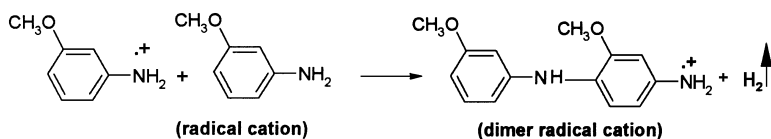This step involves the interaction between the formed radical cation and a monomer to form a dimer radical cation as in Scheme 2:

SCHEME 2

The reaction is followed by further reactions of the formed dimer radical cation with monomers to form trimer radical cation and so on. Quininoid structural unit may occur in the polymeric chain during the polymerization reaction as mentioned in the literature [28].

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

Stopping of the reaction occurs by the addition of ammonium hydroxide solution in equimolar amount to the HCl concentration present in the reaction medium (till $pH = 7$), which leads to stopping the redox reaction. The reaction could occur as in Scheme 3:

+ 2 n NH$_4$ OH $\longrightarrow$

+ 2 n NH$_4$ Cl + 2 n H$_2$O
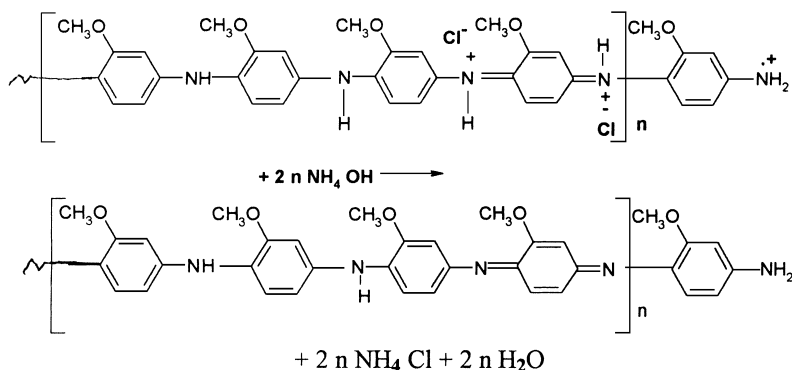
SCHEME 3

The solvation process of amino group radical cations by water molecules could occur as presented in Scheme 4. This behavior leads to the killing of +ve charge present on the amino group and stops the progress of the polymerization reaction.

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:

$$\text{Reaction Rate} = k_2[\text{HCl}]^{0.85}[\text{oxidant}]^{1.36}[\text{monomer}]^{0.74}.$$

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

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

where

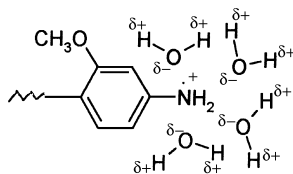k_2 is the rate constant,
R is the universal gas constant,
N is the Avogadros number and
h is Plank constant.

SCHEME 4

By plotting $\log k_2/T$ vs. $1/T$ (cf. Fig. 7b), we obtained a linear relationship with slope $= -\Delta H^*/2.303\,R$ and intercept $= \log(R/\mathrm{Nh}) + \Delta S^*/2.303\,R$. From the slope and intercept, the values of ΔH^* and ΔS^* were found to be 7.656×10^4 J/mol and -287.081 J/mol K respectively. The negative value of ΔS^* could be explained by the activated complex and produced polymer being more solvated by water molecules than the reactants [31]. The activated complex formation step is endothermic as indicated by the positive value of ΔH^*. The contributions of ΔH^* and ΔS^* to the rate constant of polymerization seem 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 encounter compound would be important in determination of ΔH^* [31].

3.7. Element and Spectroscopic Analysis

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

The UV-visible spectra of the monomer and polymer are represented in Figure 8. The absorption bands at $\lambda_{\mathrm{max}} = 282$, 393 and 510 nm for the monomer could be attributed to $\pi - \pi^*$ transition (E_2-band) of benzene ring and $\pi - \pi^*$ transition, B-band ($A_{1g} - B_{2u}$). The absorption bands at $\lambda_{\mathrm{max}} = 284.5$ and 390 nm in case of polymer are due to the $\pi - \pi^*$ transition, B-band ($A_{1g} - B_{2u}$) and the absorption band appears in the visible region at $\lambda_{\mathrm{max}} = 740$ nm may be due to the high conjugation of the aromatic polymeric chains.

The infrared absorption bands and their assignments of the monomer (3-methoxyaniline) and the prepared polymer are summarized in Table 6.
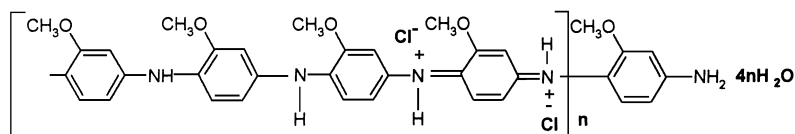
SCHEME 5

TABLE 5 Element analysis of poly(3-methoxyaniline)

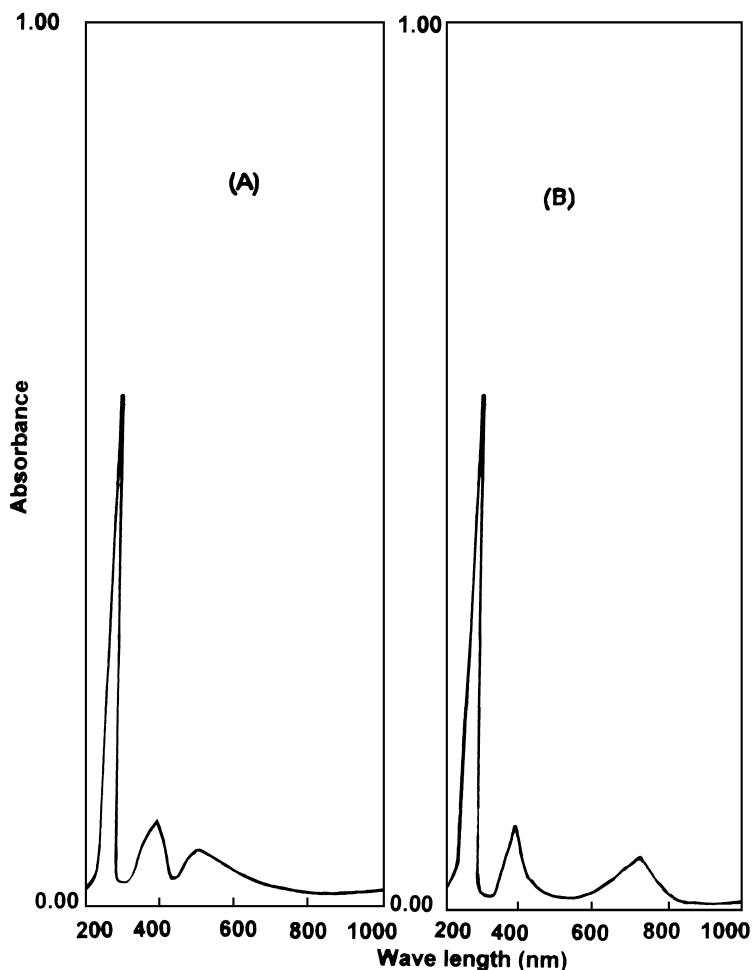| The element	C%	H%	N%	Cl%
Calculated %	53.60	4.15	8.93	11.32
Found %	53.42	4.20	8.90	11.40

FIGURE 8 UV-visible spectra of 3-methoxyaniline monomer (A) and the prepared poly(3-methoxyaniline) (B).

The medium band appearing at $505\,cm^{-1}$ for the polymer could be attributed to the torsional oscillation of NH_3^+ group. The strong absorption bands at 690, 766 and $839\,cm^{-1}$ for the monomer and the weak bands for the polymer at 683, 774 and $832\,cm^{-1}$ are attributed to the out of plane C—H deformation of 1,3-disubstituted benzene ring. The weak band at $949\,cm^{-1}$ for the polymer corresponds to the out of plane C—H deformation of 1,4-disubstituted benzene ring. The stretching vibration bands of both C—O and C—N and the out of plane bending vibration of

TABLE 6 Assignment of bands in the IR spectra of 3-methoxyaniline monomer and polymer

Wave number (cm^{-1})		
Monomer	Polymer	Assignment [33]
–	505 m	→ Torsional oscillation of NH_3^+ group
690 S	683 vw	Out of plane C—H deformation showing 1,3-
766 S	774 vw	disubstituted benzene
839 S	832 w	
–	949 w	→ CH def. showing 1,4-disubstituted benzene ring
1037 S	1030 m	C—O in OCH_3 group (1000–1300) or C—N str. vib.
1160 S	1159 w	in aryl NH or aryl NH_2 or in —N—ph—N— unit.
1210 S	1205 ⎤ m and	
1278 S	1256 ⎦ sp	or
1331 sh	1308 w	Out of plane bending vibration of CH_3 group
–	1403 ⎤ b and	
1468 sh	1455 ⎦ sp	
–	1495 ⎤ w and	
1500 S	1504 ⎦ sp	Str. vibration of C=C in benzene ring or C=N in
1601 sp	–	quinoid structure units.
1640 sp	1642 S	
2339 sp	2342 ⎤ w and	Combination and overtone band for CN or
2363 sp	2365 ⎦ sp	combination of asymmetric bending of NH_3^+ group
2839 S	2854 vw	or symmetric str. vib. of CH aliphatic
2944 sp	2929 w	
2956 sp	–	
3008 m	–	→ Str. vib of CH aromatic.
3223 m	3410 b	Sts. vib. of NH group and strong bonded OH group.
3371 S		
–	3717 w	→ Str. vib of free OH group.

CH_3 group for the monomer and the polymer appear in the range between 1030 and 1468 cm^{-1}. The weak split and strong bands which appear at 1495, 1504 and 1642 for the polymer could be attributed to C=C in quinoid structure (Scheme 6A) or in benzene ring, respectively. These bands appear for the monomer at 1500, 1601 and 1640 cm^{-1}. The two shoulder bands which appear at 2339 and 2363 cm^{-1} for the monomer could be attributed to the hyper conjugation of monomer unit (B) in Scheme 6 or combination and overtone band for CN. These bands also appear in case of polymer at 2342 and 2365 cm^{-1}. The stretching vibration of the aliphatic CH and aromatic CH for the monomer appear at 2839, 2944, 2956 and 3008 cm^{-1} respectively and for the polymer these bands appear at 2854 and 2929 cm^{-1}. The stretching vibration of NH_2 for the monomer appear at 3223 and 3371 cm^{-1}. The band which appears at 3410 cm^{-1} is due to the stretching vibration NH group or strongly bonded
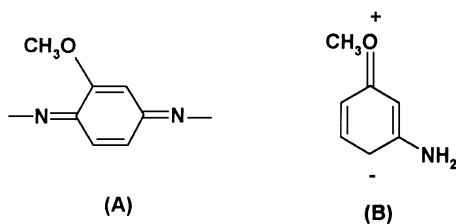
SCHEME 6

OH group, while the stretching vibration of the free OH in case of polymer appears at $3717\,cm^{-1}$.

3.8. Electron Microscopy and X-ray Diffraction Analysis

X-ray diffraction pattern shows that the prepared polymer sample is amorphous material, while the electron microscopic picture shows grains which ranged from spherical particles to elongated one. Their size ranged from 2.25×10^{-3} to $15 \times 10^{-3}\,mm$ as shown in Figure 9.
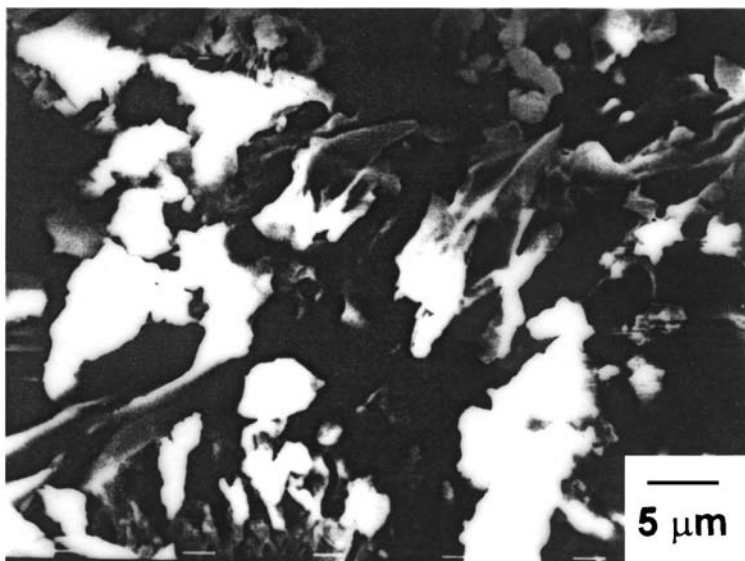
FIGURE 9 The picture of scanning electron microscope of the prepared poly(3-methoxyaniline).

3.9. Thermal Analysis

The thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) for the prepared polymer sample were investigated and the obtained curves are represented in Figure 10. From TGA curve, it is clear that the first step of the thermal decomposition is the loss of water of hydration at temperature range between 39.2 and 94.85°C (mid point 74.25°C) with weight loss equal to 12.103% and the calculated one is 11.48%. This stage is confirmed by the endothermic peak that appears at 75.86°C on DTA curve with heat absorption equal to 369.4 J/g. In the temperature range between 167.45 and 293.34°C (mid point = 228.82°C) on TGA curve, the weight loss is found to be 11.8%, which could be attributed to the loss of hydrochloric
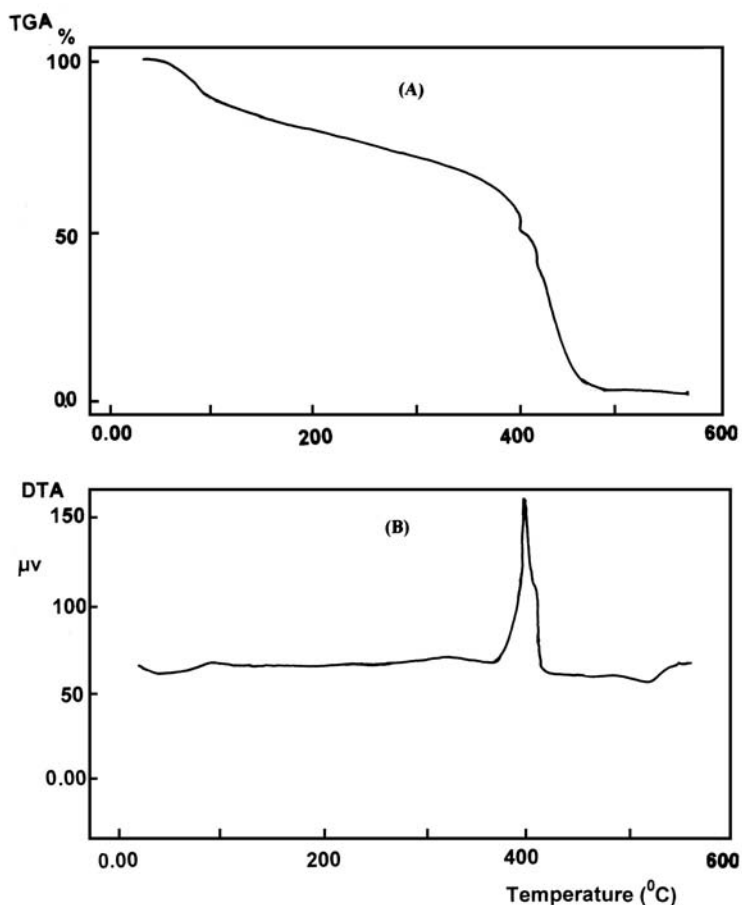

FIGURE 10   The thermal analysis of the prepared poly(3-methoxyaniline) (A) TGA and (B) DTA.

acid (2HCl molecules). The calculated weight loss for this step is equal to 11.62%. The methoxy groups (4OMe) attached to the phenyl rings in the polymeric chain are lost in the temperature range between 357.11 and 392.8 cm^{-1}. The weight loss for this step is found to be 19.75% which is a good agreement with the calculated one (20.01%). The benzenoid ring in the polymeric chain is destroyed in the temperature range between 398.34 and 439.32°C with weight loss equal to 40.74% and the calculated one equals 40.61°C, this followed by the complete decomposition of the remained quinoid units above 439.32°C. The exothermic peak present on DTA curve at 409.85°C with evolution of heat equal to 5400 J/g is attributed to the complete decomposition of the polymeric chain.

3.10. The Electrical Properties of Poly(3-Methoxyaniline)

The polymer sample number 3 in Table 2 which has the highest value of ac conductivity was selected for the investigation of the temperature effect on
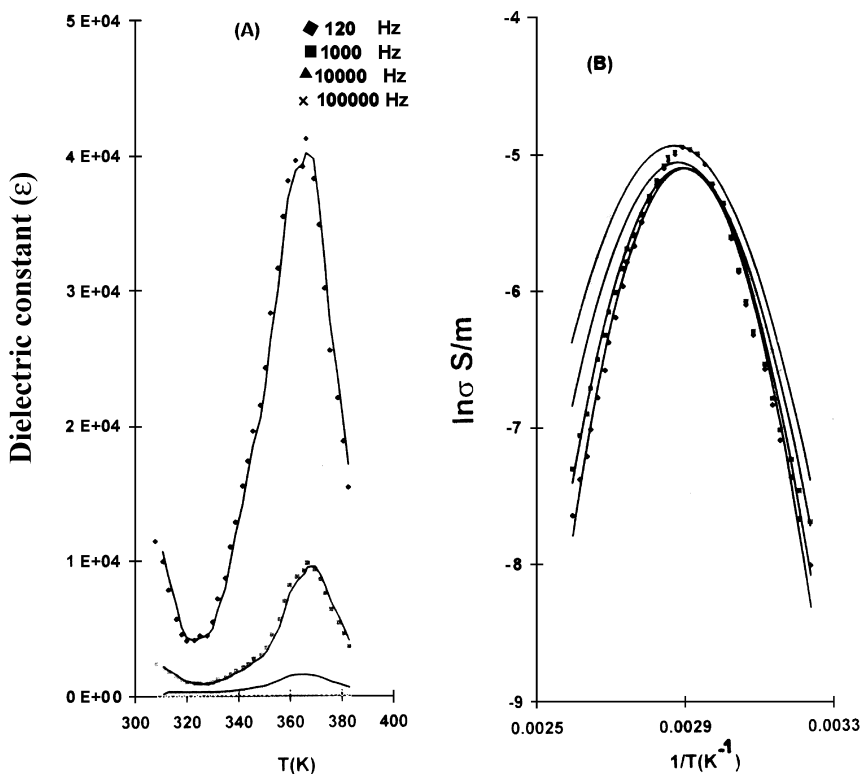

FIGURE 11 The effect of temperature on the dielectric (A) and ac conductivity (B) of the prepared poly(3-methoxyaniline).

the electrical properties. The effect of temperature on both dielectric constant and ac conductivity of the poly(3-methoxyaniline) are investigated at different frequencies (120, 10^3, 10^4 and 10^5 Hz). The data are graphically represented in Figures 11a and b. From the figure, it is clear that the dielectric constant ($\varepsilon\backslash$) increases with rising temperature up to 365 K then decreases again up to about 390 K. The phase transition is observed at 365 K (*cf.* Fig. 11a) and also observed at the same temperature in the σ-temperature curve (*cf.* Fig. 11b). From Figures 11a and b, it is clear that the highest values of dielectric constant are found at 120 Hz but, the higher values of conductivity is obtained at 10^5 Hz.

Further investigations on P(3-MA)-PMMA film sample were performed. All the experimental methods used for preparation of sample number 7 in Table 2 are used in presence of PMMA (0.25, 0.50, 0.75 and 1.00 g) which has $M_v = 4.4 \times 10^5$. The films are prepared by casting technique as explained in the experimental part. The films of 2 mm thickness were covered on both sides by Ag-electrode as in case of pure polymer. The ac conductivity of these films was investigated at room temperature and different frequencies. The sample having the highest ac conductivity value was selected to investigate the effect of temperature on both dielectric constant and ac conductivity.
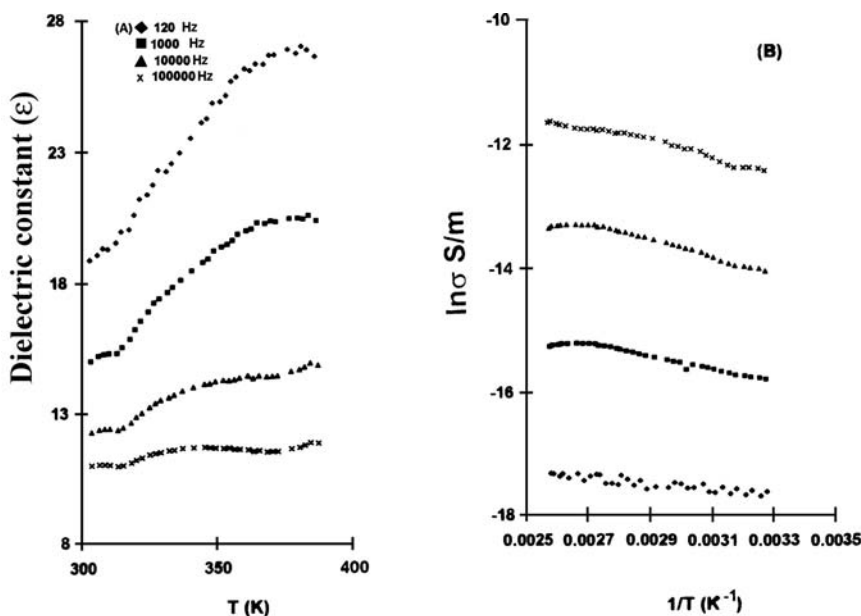

FIGURE 12 The effect of temperature on the dielectric (A) and ac conductivity (B) of the prepared PMMA-poly(3-methoxyaniline) film.

The effects of temperature on both dielectric constant and ac conductivity of the PMMA-poly(3-methoxyaniline) were investigated at different frequencies (120, 10^3, 10^4 and 10^5 Hz). The data are graphically represented in Figures 12a and b. From the figures, it is clear that both of dielectric constant and $\ln \sigma$ increase with the increase of temperature ($\sim 300 - 390$ K). Also, $\ln \sigma$ increases with increasing frequency but the dielectric constant decreases in the same direction. The phase transition at 365 K for P(3-MA) disappeared in case of PMMA-P(3-MA) film as shown in Figures 12a and b, but another phase transition showing the PMMA behavior appeared between 320 and 350 K for the frequency range $120 - 10^5$ Hz. This means that the stabilization of P(3-MA) with PMMA changes the conducting property to an insulating one.

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