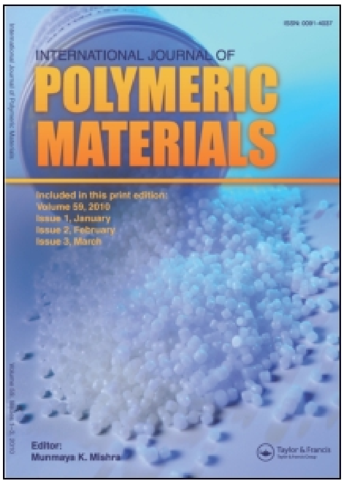

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Kinetic studies of the aqueous oxidative polymerization of 3-hydroxyaniline and characterization of the polymer obtained

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KINETIC STUDIES OF THE AQUEOUS OXIDATIVE POLYMERIZATION OF 3-HYDROXYANILINE AND CHARACTERIZATION OF THE POLYMER OBTAINED

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The aqueous polymerization of 3-hydroxyaniline (3HA) was studied using sodium dichromate as oxidant in presence of hydrochloric acid. The effect of hydrochloric acid, sodium dichromate and monomer concentration 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 increase in hydrochloric acid concentration or sodium dichromate concentration but decrease with the increase in the monomer concentration. The specific viscosity values increase with increasing of hydrochloric acid concentration or monomer concentration which means that the molecular weight of the polymer samples increases in the same direction. But the molecular weight decreases with increasing sodium dichromate concentration.

The highest a.c. conductivity value of the obtained polymer was found in case of using 0.0019 g mol/L of $Na_2Cr_2O_7$, 0.1 M HCl and 0.1 M monomer solution in the reaction medium. Some electrical properties of this 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 1.13, 1.2 and -0.909 respectively. The apparent activation energy (E_a) for this polymerization system was found to be 6.1248×10^4 J/mol. The obtained poly(3-hydroxyaniline) was characterized by UV-visible, IR spectroscopy, X-ray diffraction analysis and electron-microscopy studies. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) results were used to confirm the structure.

Keywords: Polyaniline; Poly(3-hydroxyaniline); Polymerization variables; Thermodynamic parameters; Ac conductivity; Dielectric constant; Stabilizer

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1. INTRODUCTION

Electrically conducting polymers have attracted considerable attention recently because of their many potential applications and unique electrical and optical properties. Among these conducting polymers polyaniline (PANI) has been extensively studied in the last decade because of its many promising properties *e.g.*, fast switching rates [1, 2], the ability to switch reversibly from insulating to conducting state either by electrochemical or chemical doping [3, 4]. In recent years several review papers [5 – 8] on polyaniline have been published.

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 [8]. Polymerization mechanisms and reaction kinetics of aniline in aqueous solutions have been investigated by several groups [9 – 18]. 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 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 were investigated [19 – 21].

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 [22]. The chemical polymerization conditions of polyaniline synthesized with different oxidizing agents and the physico-chemical properties were studied [23].

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 [24]. 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 [25]. It was found that the substituted 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 [26].

In the present study we intend to investigate the kinetics of the oxidative polymerization of 3-hydroxyaniline 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.

2. EXPERIMENTAL

2.1. Materials

3-hydroxyaniline provided by Merck Chemical Company (Germany). Concentrated hydrochloric acid, sulphuric 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-Hydroxyaniline Monomer

The polymerization reactions were carried out in a well-stoppered conical flasks of 250 ml capacity containing the amount of monomer (3HA) in aqueous HCl 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 at will by the addition of ammonia solution (in equivalent 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 an 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 to constant weight.

2.3. Determination of the Specific Viscosity

The specific viscosity was measured for polymer samples dissolved in concentrated sulphuric acid (0.1 g/10 ml) at 25°C using Ostwald viscometer [27].

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 – 700 nm using concentrated sulphuric acid as a solvent and reference.

The infrared measurements were carried out using Shimadzu FTIR-430 Jasco spectrophotometer and KBr disk technique.

2.5. Thermal Gravimetric and Differential Thermal Analysis

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

2.6. Electron Microscopic and X-ray Diffraction Analysis

The electron microscopy 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
Scan speed : 8 (dg/min.)
Current : 30 mA
Voltage : 40 kV
Preset time : 10 (s)

2.7. Preparation of the Thin Film Samples

The films were prepared by a solvent casting technique. A well flat glass plate provided with four leveling screws and water balance was used as a base for glass petridishes containing the material to ensure uniform thickness. The appropriate weight of poly 3-hydroxyaniline stabilized with PMMA is dissolved in 100 ml acetone as a common 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 uniformity.

2.8. 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 10^2-10^5 Hz and over a temperature range 30 – 150°C. The overall error in the a.c.conductivity did not exceed ± 2%.

3. RESULTS AND DISCUSSION

3.1. Effect of Hydrochloric Acid Concentration

The polymerization of 3-hydroxyaniline (0.545 g = 0.005 g mole) in 25 ml of HCl which had different molarities in the range (0.12 to 0.3 g mol/L) was carried out by addition of 25 ml sodium dichromate solution (0.01296 g mol/L) as oxidant under nitrogen atmosphere at 5°C for different time intervals. The concentration of both HCl and oxidant is reduced to the half of its individual values after addition of oxidant solution to the acidified monomer solution. The concentration of the monomer and oxidant are kept constant at 0.1 g mol/L and 0.006484 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, both of the initial and overall reaction rates of the polymerization reaction increase with increasing HCl concentrations from 0.06 – 0.15 M. Also, the specific viscosity and the a.c.conductivity increase in the same direction. The HCl exponent is determined from the slope of the relation represented in Figure 2, where the slope is found to be 1.13. This indicates that the order of the polymerization reaction with respect to the HCl-concentration is first order reaction.

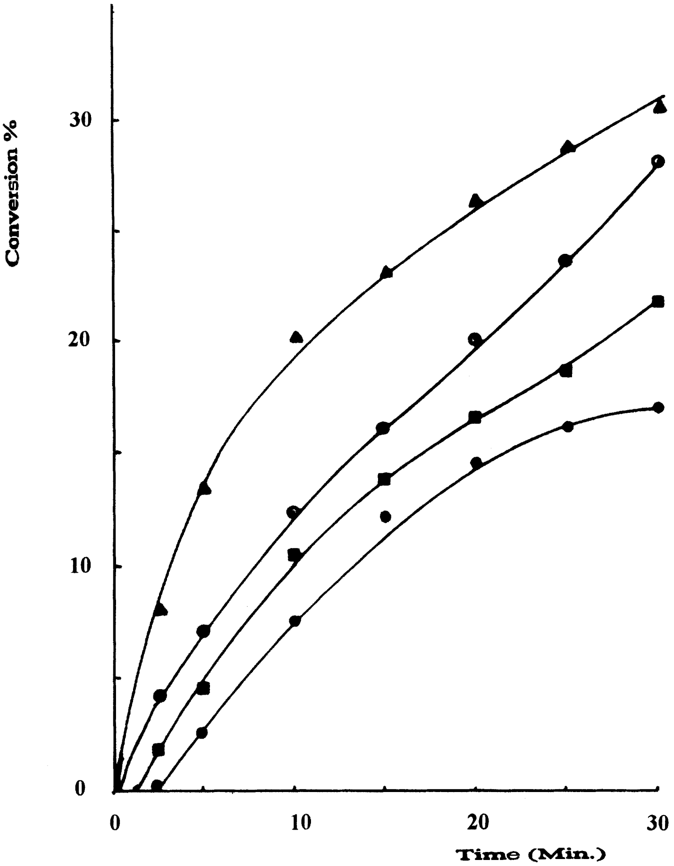


FIGURE 1 Effect of HCl concentration on the rate of polymerization of 3-hydroxyaniline.

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

Sl. no.	*Concentration of HCl (g mol/L)*	*Initial rate* $\cdot 10^6$ *(g mol/L·S)*	*Overall reaction rate* $\cdot 10^6$ *(g mol/L·S)*	η_{sp}	*Conductivity values* $\cdot 10^7$ *(S/m)*
1	0.06	12.33	4.31	0.04331	2.20
2	0.08	17.33	5.48	0.05087	2.72
3	0.10	20.66	6.39	0.05899	13.10
4	0.15	33.33	8.73	0.06756	15.10

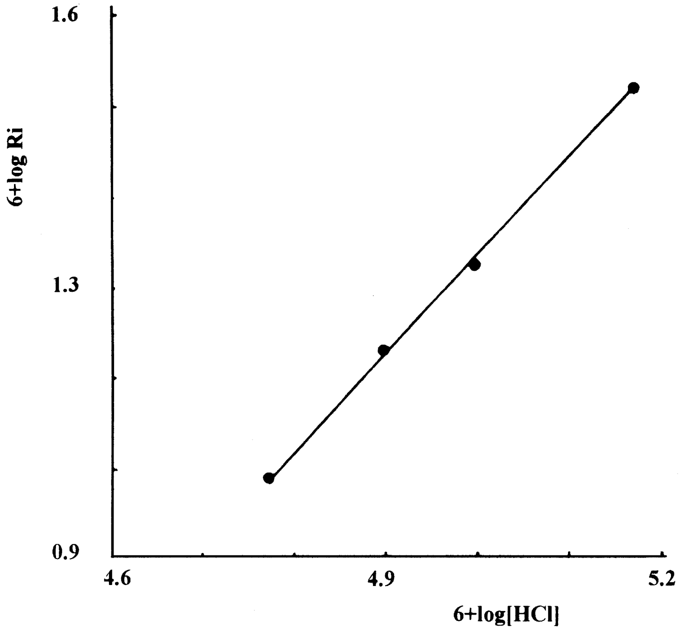


FIGURE 2 Logarithmic plot of initial rate of polymerization *versus* the logarithm of HCl concentration.

3.2. Effect of Sodium Dichromate Concentration

The aqueous polymerization of 3-hydroxyaniline (0.545 g = 0.005 g moles) in 25 ml (0.2 M) HCl solution and 25 ml of sodium dichromate solution which has different molarities (0.0038, 0.0076, 0.0095 and 0.01296 M) as oxidant under nitrogen atmosphere at 5°C for different time intervals was carried out. The total concentration of both HCl and monomer were fixed constant in the reaction medium at 0.1 M. 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 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 the increasing of the oxidant concentration, while the maximum values of a.c.conductivity is obtained for the polymer sample obtained at 0.0019 g mol/L of the oxidant concentration. The Oxidant exponent is calculated from the slope of the obtained straight line for the relation

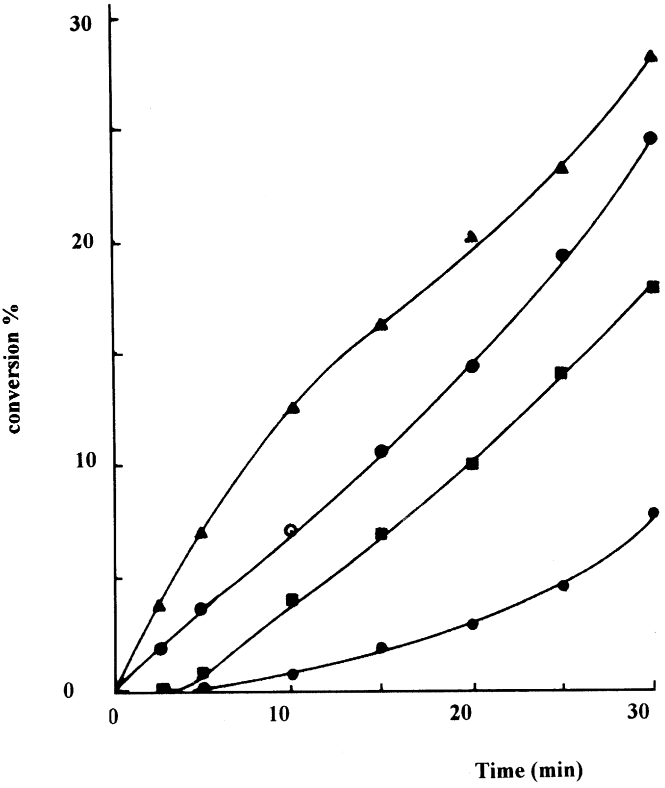


FIGURE 3 Effect of $Na_2Cr_2O_7$ concentration on the rate of polymerization of 3-hydroxyaniline.

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

Sl. no.	*Concentration* $Na_2Cr_2O_7$ *(g mol/L)*	*Initial rate* $\cdot 10^6$ *(g mol/L·S)*	*Overall reaction rate* $\cdot 10^6$ *(g. mol/L·S)*	η_{sp}	*Conductivity values* $\cdot 10^7$ *(S/m)*
1	0.00190	3.03	1.87	0.09353	19.8
2	0.00380	8.33	2.26	0.07914	14.8
3	0.00475	11.90	4.32	0.06906	15.2
4	0.00648	20.66	6.39	0.05899	13.1

represented in Figure 4. The slope is found to be equal to 1.2 which means that the order of polymerization reaction with respect to the oxidant concentration is first order reaction.

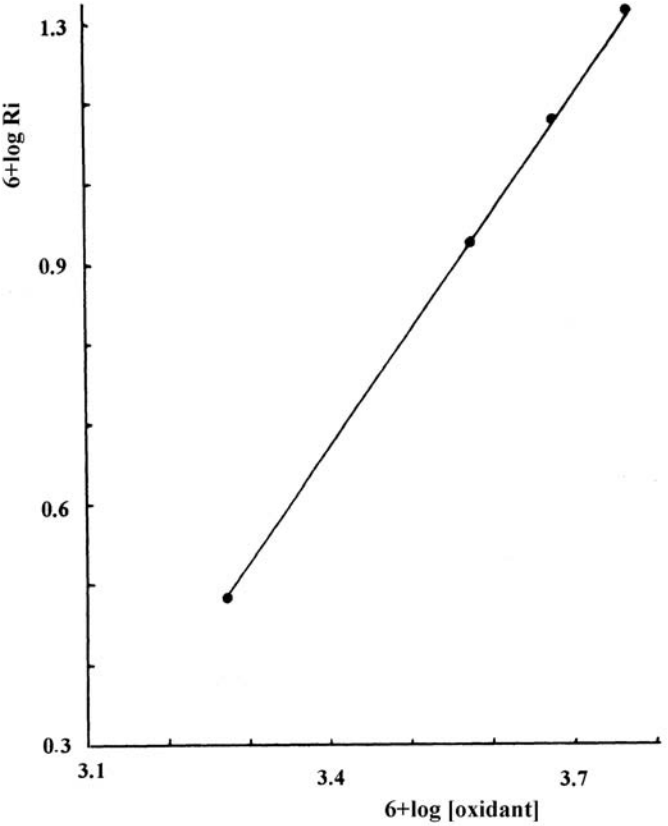


FIGURE 4 Logarithmic plot of initial rate of polymerization *versus* the logarithm of oxidant concentration.

3.3. Effect of Monomer Concentration

The effect of monomer concentration on the aqueous polymerization of 3-hydroxyaniline in the presence of 25 ml 0.2 M HCl and 25 ml of 0.01296 g mol/L $Na_2Cr_2O_7$ solution under nitrogen atmosphere at 5°C was studied. The conversion time curve data are calculated and graphically represented in Figure 5, while the calculated initial and overall reaction rates are given in Table 3, from which it is clear that both of the initial and overall reaction rates decrease with the increasing of monomer concentration. For the determination of the monomer exponent, we plot Log.R_i against the logarithm of the monomer concentration (Log.[M]). (*cf.* Fig. 6). A straight line was obtained with slope $= -0.909$. This indicates that the monomer exponent is -0.909. The specific viscosity and the a.c.conductivity of the

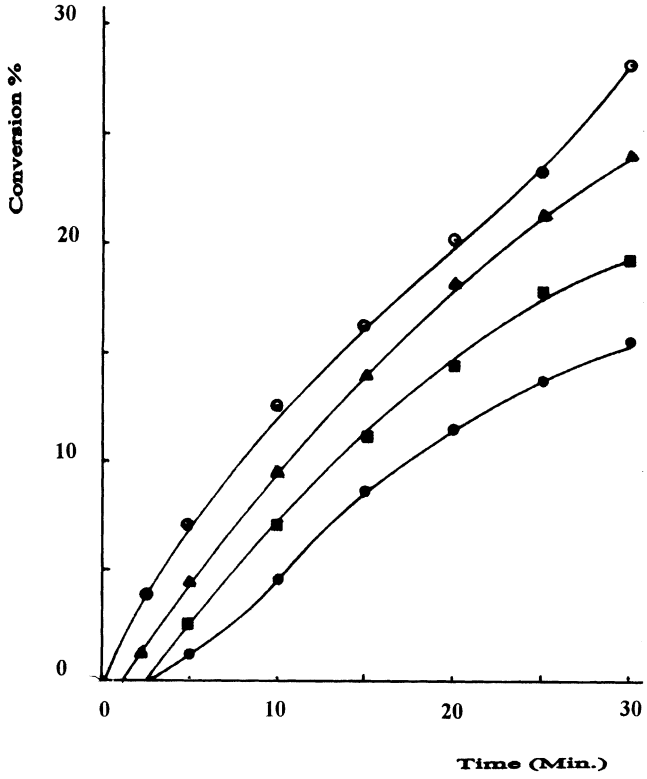


FIGURE 5 Effect of monomer concentration on the rate of polymerization of 3-hydroxyaniline.

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

Sl. no.	*Concentration monomer (g mol/L)*	*Initial rate* $\cdot 10^6$ *(g mol/L·S)*	*Overall reaction rate* $\cdot 10^6$ *(g mol/L·S)*	η_{sp}	*Conductivity values* $\cdot 10^7$ *(S/m)*
1	0.100	20.66	6.39	0.0590	13.1
2	0.115	17.82	6.10	0.0777	11.3
3	0.125	16.64	5.12	0.0921	11.6
4	0.150	14.29	4.36	0.1151	12.4

obtained polymer after 4 hours for each monomer concentration were measured and the data are given in Table 3. The specific viscosity values increase with increasing monomer concentration, while the a.c.conductivity values decrease with increasing monomer concentration up to 0.115 g mol/L,

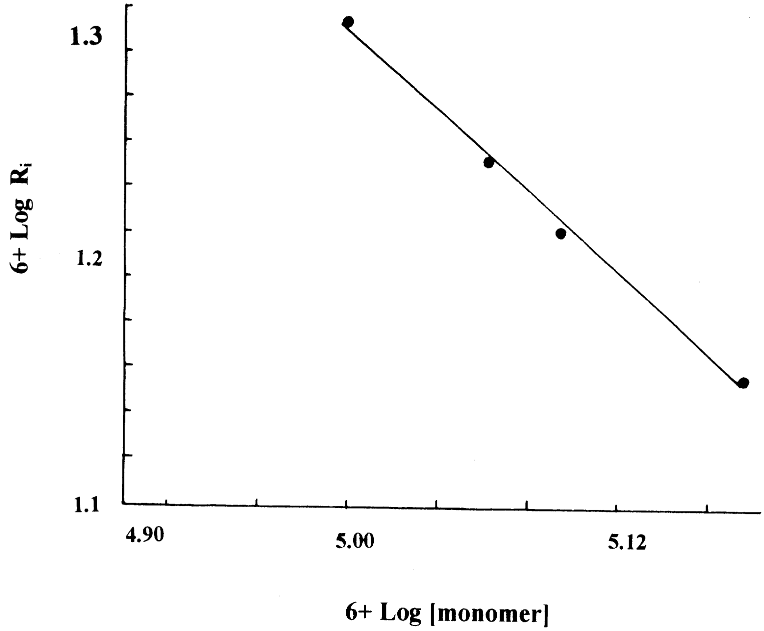


FIGURE 6 Logarithmic plot of initial rate of polymerization *versus* logarithm of monomer concentration.

then increase once again at monomer concentration equal to 0.150 g mol/L. The maximum a.c.conductivity value is found when 0.100 g mol/L monomer concentration is used.

3.4. Effect of the Reaction Temperature

The aqueous polymerization of (0.545 g = 0.005 g mole) 3-hydroxyaniline dissolved in 25 ml of 0.2 M HCl using 25 ml sodium dichromate (0.01296 M) solution under nitrogen atmosphere was carried out at 5, 10 and 15°C for different periods of time. The final concentrations of both the acid and oxidant in the polymerization reaction are 0.1 M and 0.00648 M 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 of the initial and overall reaction rates increase with raising the reaction temperature, while the specific viscosity values decrease in the same direction. The highest a.c.conductivity value was found at 5°C.

The apparent activation energy (E_a) of the aqueous polymerization reaction of 3-hydroxyaniline was calculated by plotting Log R_i against $1/T$ which gave a straight line (*cf.* Fig. 7A). From the slope and applying

TABLE 4 Effect of temperature on polymerization of (3-HA)

Sl. no.	*Temperature (°C)*	*Initial rate* $\cdot 10^6$ (*g mol/L·S*)	*Overall reaction rate* $\cdot 10^6$ (*g mol/L·S*)	η_{sp}	*Conductivity values* $\cdot 10^7$ (*S/m*)
1	5	20.66	6.390	0.0590	13.1
2	10	33.33	6.960	0.0374	0.67
3	15	52.32	8.112	0.0216	0.77

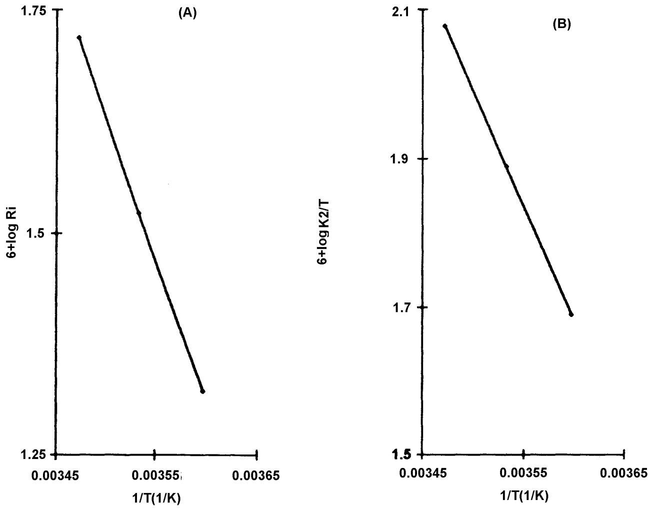


FIGURE 7 Logarithmic plot of (A) initial rate of polymerization and (B) Log.k_2/T *versus* $1/T$ (K^{-1}).

Arrhenius equation, it is found that the apparent activation energy (E_a) = 6.1248×10^4 J/mol.

3.5. Mechanism of the Aqueous Oxidative Polymerization of 3-Hydroxyaniline

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

3.5.1. The Initiation Step

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

(1) 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:

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

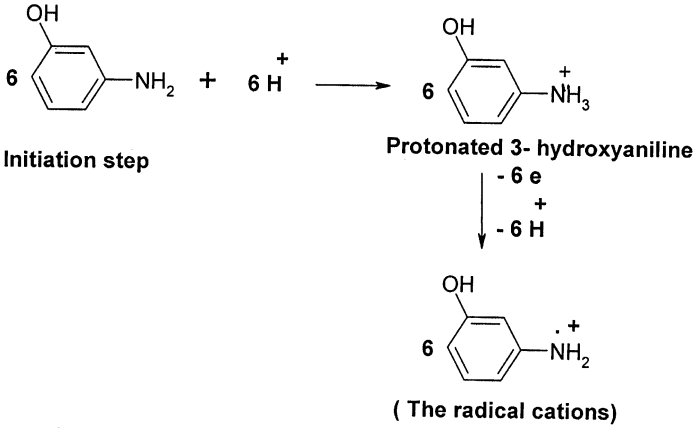
Further, the species present depend on the nature of the acid used [28]. When hydrochloric acid is used, there is essentially quantitative conversion into the chloro chromate ion as follows:

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

(2) The second step is the oxidation of 3-hydroxyaniline by loss of electrons and conversion of the chromium ion to the lower oxidation state in simultaneous steps in Scheme 1:

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

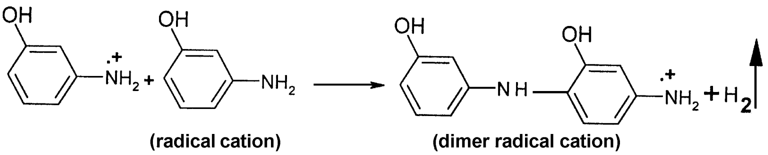
and



SCHEME 1.

3.5.2. Propagation Step

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



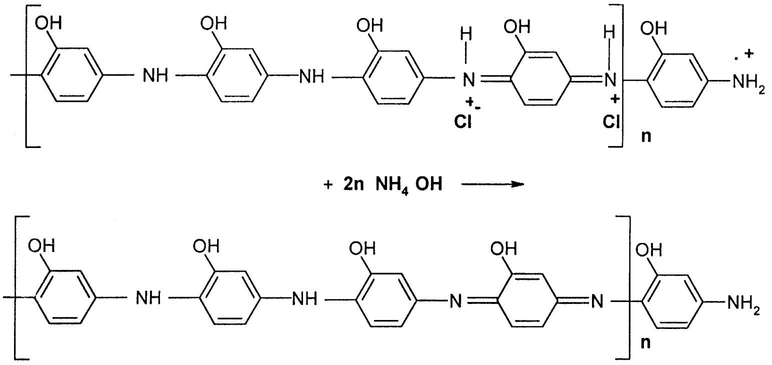
SCHEME 2.

then the reaction is followed up by further reaction of the formed dimer radical cation with monomer to form trimer radical cation and so on. Quinsoid structural units may occur in the polymeric chain during the polymerization reaction as mentioned in the literature [26]. The structure of the polymeric chain is illustrated in Scheme 5.

The degree of polymerization depend upon different factors such as dichromate concentration, HCl concentration, monomer concentration and temperature which are concluded from the obtained experimental data of the kinetic studies.

3.5.3. Termination Step

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



+

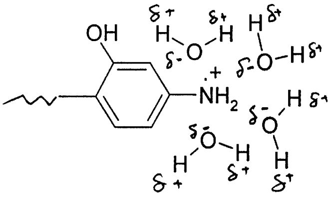
2n NH_4Cl + 2n H_2O

SCHEME 3.

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

3.6. Calculation of the Thermodynamic Parameters

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



SCHEME 4.

$$\text{Reaction Rate} = k_2[\text{HCl}]^{1.13}\ [\text{oxidant}]^{1.2}[\text{monomer}]^{-0.909}$$

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

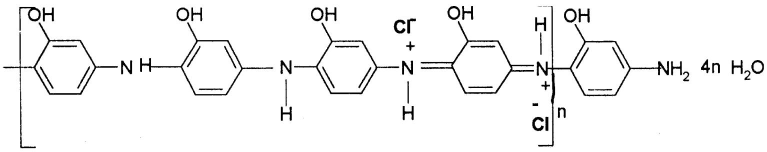
$$k_2 = \mathrm{R}T/\mathrm{Nh}e^{\Delta S/\mathrm{R}} \cdot e^{-\Delta H/\mathrm{R}T}$$

where:

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

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 $= \log(\mathrm{R/Nh}) + \Delta S^*/2.303$ R.

From the slope and intercept, the values of ΔH^* and ΔS^* were found to be 6.1248×10^4 J/mol and -236.74 J/mol K respectively. The negative value of ΔS^* could be explained by the more solvated activated complex and products by water molecules than the reactants [29]. The activated complex formation step is endothermic as indicated by the positive 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 encounter compound would be important in determination of ΔH^* [29].



SCHEME 5.

TABLE 5 Elemental analysis of poly(3-hydroxyaniline)

The element	*C%*	*H%*	*N%*	*Cl%*
Calculated %	50.44	4.55	9.80	12.43
Found %	50.35	4.60	9.76	12.50

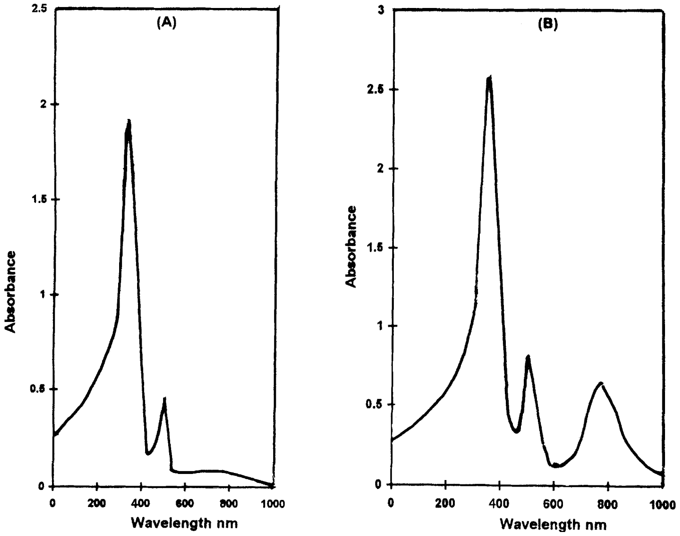


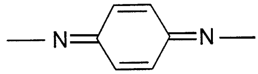
FIGURE 8 UV-visible spectra of 3-hydroxyaniline monomer (A) and the prepared poly(3-hydroxyaniline) (B).

3.7. Elemental and Spectroscopic Analysis

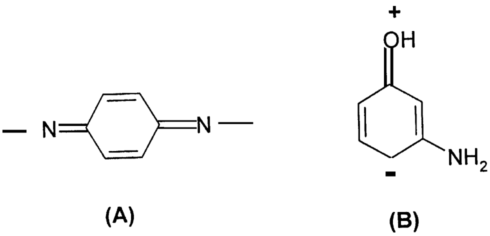
The elemental analysis of the poly(3-hydroxyaniline) was carried out in the micro analytical laboratory at Cairo University. The C%, H%, N% and Cl% are found to be in good agreement with the calculated one for the suggested structure present in Scheme 5. The elemental analytical data are given in Table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

The uv-visible spectra of the monomer and polymer are presented in Figure 8. The absorption bands at $\lambda_{max} = 360$ and 490 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 band at $\lambda_{max} = 320$ and 490 nm in case of polymer is due to the $\pi-\pi^*$ transition, B-band ($A_{1g}-B_{2u}$) while, the absorption band that appears in the visible region at $\lambda_{max} = 760$ nm may be due to the high conjugation of the aromatic polymeric chains.

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

Wave number (cm^1)		
Monomer	*Polymer*	*Assignment* [31]
540^{s}	535^{m}	→ Torsional oscillation of NH_3^+group.
–	688^{w}	Out of plane C—H deformation showing 1,3 disubstitution in benzene ring
730^{m}	–	
739^{s}	–	
774^{s}	780^{w}	
	836^{w}	Out of plane C—H deformation showing 1,4-disubstitution in benzene ring
	–	
905^{m}	–	C—O or C—N stretching vibration or in plane deformation CH aromatic or OH deformation (coupled) or NH deformation in Aryl NH or Aryl NH_2.
963^{m}	–	
999^{m}	–	
1071^{s}	1059^{w}	
1141^{s}	1124^{w}	
1178^{s}	1159^{w}	
1258^{s}	1274^{w}	
1304^{s}	–	
1389^{s}	1380^{w}	
1467^{s}	$1484^{v \cdot w}$	Stretching vibration of C=C in benzene ring or C=N in the following structure 
1507^{s}	$1515^{v \cdot w}$	
1603^{s}	1618^{m}	
2361^{m}	2355^{w}	C—N str. vibration (overtone) or combination band of the asymmetric bending and torsional oscillation of the protonated amino group.
2506^{m}	–	
2609^{m}	–	
2712^{w}	–	
2838^{w}	–	
2952^{m}	2925^{w}	
3027^{w}	–	→ CH str. aromatic
3296^{s}	–	NH str. stretching vibration of —NH group
3360^{s}	–	or the strong bonded OH group
–	3430^{b}	
–	3684^{w}	→ Str. vibration of free OH group.

The infrared absorption bands and their assignments of the monomer (3-hydroxyaniline) and the prepared polymer are summarized in Table 6. The strong band appears at 540 cm^{-1} for the monomer and the medium band appears at 535 cm^{-1} for the polymer may be attributed to the torsional oscillation of NH_3^+ group. The three absorption bands appear at 730, 739 and 774 cm^{-1} in case of monomer and the corresponding weak absorption bands in case of polymer at 688 and 780 cm^{-1} are attributed to the out of plane CH deformation showing 1,3-disubstitution in benzene ring. But, the



SCHEME 6.

absorption band appears at 836 cm^{-1} in case of polymer are attributed to the out of plane CH deformation showing 1,4-disubstitution in benzene ring. A series of absorption bands appear in the region between 905 and 1389 cm^{-1} in case of monomer and in the region between 1059 and 1380 cm^{-1} could be attributed to skeletal stretching vibration of C—O and/or C—N in aryl-NH or aryl-NH_2. The three strong absorption bands appear at 1467, 1507 and 1603 cm^{-1} in case of monomer and the very weak two bands appear at 1484 and 1515 with medium band at 1618 cm^{-1} for the polymer could be attributed to the stretching vibration of C=C in aromatic system or C=N in quinoid structure (structure (A) in Scheme 6).

A series of medium bands appear in the region 2361–2952 cm^{-1} in case of monomer and the two weak absorption bands at 2355 and 2925 cm^{-1} in case of polymer may be due to the reasonating form of the phenolic OH (Scheme 6 (B)) or combination and overtone band for C—N or the asymmetric bending and torsional oscillation of protonated amino group. The weak absorption band appearing at 3027 cm^{-1} in case of monomer is attributed to the stretching vibration of C—H in benzene ring. This band is mixed in case of polymer with the great broad band at 3430 cm^{-1} which is attributed to the stretching vibration of —NH group or the strong bonded OH group (H_2O molecules) which are present only in case of polymer [26]. The strong two bands appearing in case of monomer at 3296 and 3360 cm^{-1} are attributed to the stretching vibration of —NH group, while the weak absorption band appears at 3684 cm^{-1} in case of polymer is attributed to the free OH group.

3.8. Electron Microscope and X-ray Diffraction Analysis

X-ray diffraction pattern shows that the prepared polymer sample is crystalline material as shown in Figure 9. From which, it is clear that there are three strong peaks. The 2θ, d spacing and intensity parameters are tabulated in Table 7.

While, the electron microscope picture shows a crystalline material with elongated particles. Their size ranged from 1.309×10^{-3} mm to 11.789×10^{-3} mm as shown in Figure 10.

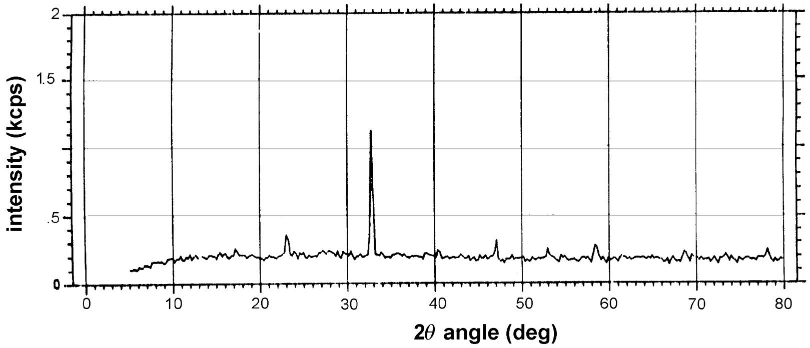


FIGURE 9 X-ray diffraction pattern of poly(3-hydroxyaniline).

TABLE 7 The strongest peaks for X-ray diffraction pattern of poly(3-hydroxyaniline)

Peak no.	2θ (*deg*)	*d*(*A*)	I/I_0	*Intensity* (*kcps*)	*Integrated int.* (*kcps·deg*)
1	32.708	2.7356	100	0.250	0.2146
2	22.942	3.8731	25	0.063	0.0263
3	58.533	1.5756	16	0.041	0.0436

FIGURE 10 The picture of scanning electron microscope of the prepared poly(3-hydroxyaniline).

3.9. Thermal Analysis

The thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) for the prepared polymer sample are investigated and the obtained curves are presented in Figure 11. The first stage includes the loss of water

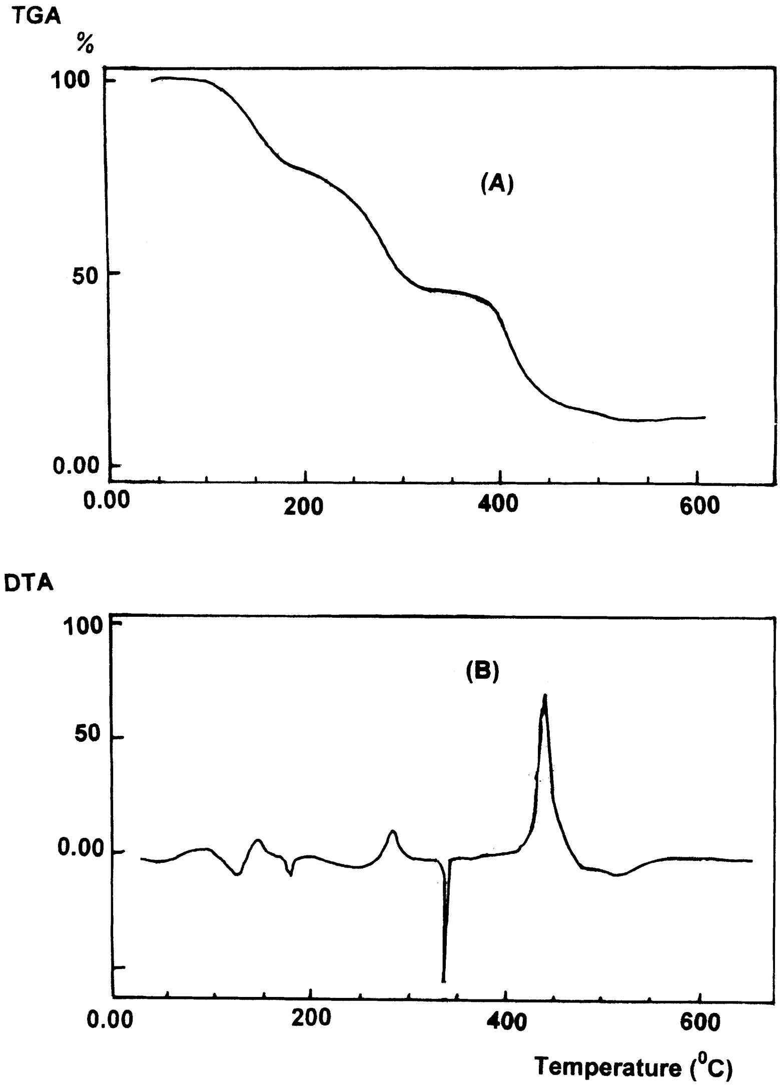


FIGURE 11 The thermal analysis of the prepared poly(3-hydroxyaniline) (A): TGA and (B): DTA.

of hydration ($4H_2O$) in the temperature range 54 – 198.8°C (mid point 144.8°C). The estimated weight loss for this step is found to be 12.82% but the calculated one is 12.61%. In DTA curve, this stage gives a broad endothermic peak at 131.15°C with change of heat equal −200.26 J/g. The endothermic peak present on DTA curve at 184.58°C with change of heat equal to 18.7 J/g may be attributed to the change of the heat capacity of the polymer. From TGA curve in the range between 200.23 and 295.22°C (mid point 266.9°C) the weight loss is found to be 24.72%, which could be attributed the loss of 2HCl molecules [35] and four phenolic OH groups which may be combined to give a water molecule and oxygen. The calculated weight loss for this stage is 24.69% which confirms the estimated one. This stage gives an exothermic peak on the DTA curve at 266.9°C with evolution of heat 255.31 J/g. On the TGA curve no weight loss is detected in the range between 297 and 360°C but on the DTA curve an endothermic peak is detected at 340°C with heat absorption equal to 2560 J/g. This peak is attributed to the melting of the polymer (Tm). The decomposition of all the polymeric phenyl rings are found in the temperature range between 384.31 and 449.05°C (mid point 418.9°C) on the TGA curve with

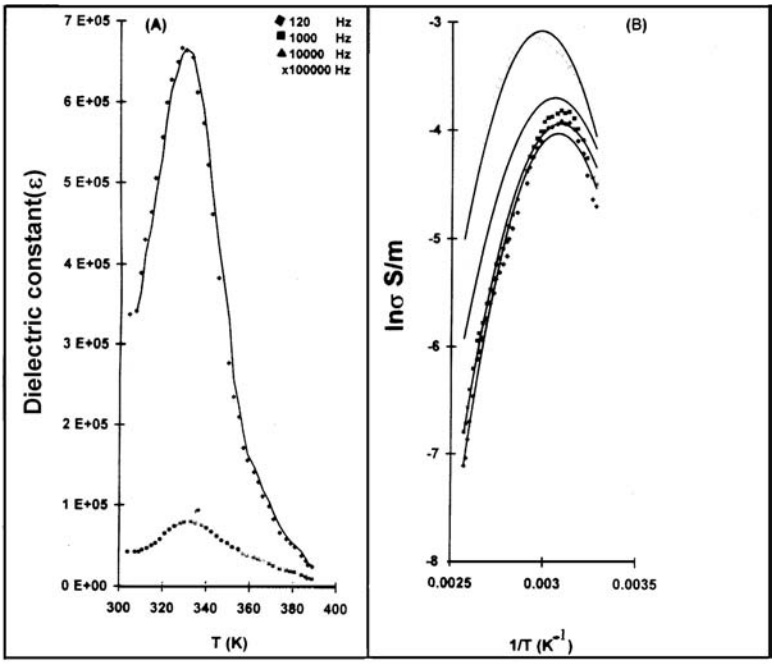


FIGURE 12 The effect of temperature on the dielectric constant (A) and ac conductivity (B) for the prepared poly(3-hydroxyaniline).

estimated weight loss 40.20% and calculated one 39.4% this step give a exothermic peak at 436.16°C on the DTA curve with heat equal to 475.37 J/g. Above a temperature of 450°C on TGA curve the polymer is completely decomposed with endothermic peak on DTA curve at about 450°C (Tox) (*cf.* Fig. 11B).

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

The polymer sample no. 1 in Table 2 which has the highest value of ac conductivity was selected for an investigation of the temperature effect on the electrical properties. The effect of temperature on both dielectric constant and ac conductivity of the poly(3-hydroxyaniline) are 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 figure, it is clear that the dielectric constant (ε\) increases with raising temperature up to 338 K then decreases again up to about 390 K. The phase transition is observed at 334 K (*cf.* Fig. 12A) and also observed at the same temperature in the σ-temperature curve (*cf.* Fig. 12B). From Figures 12A 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.

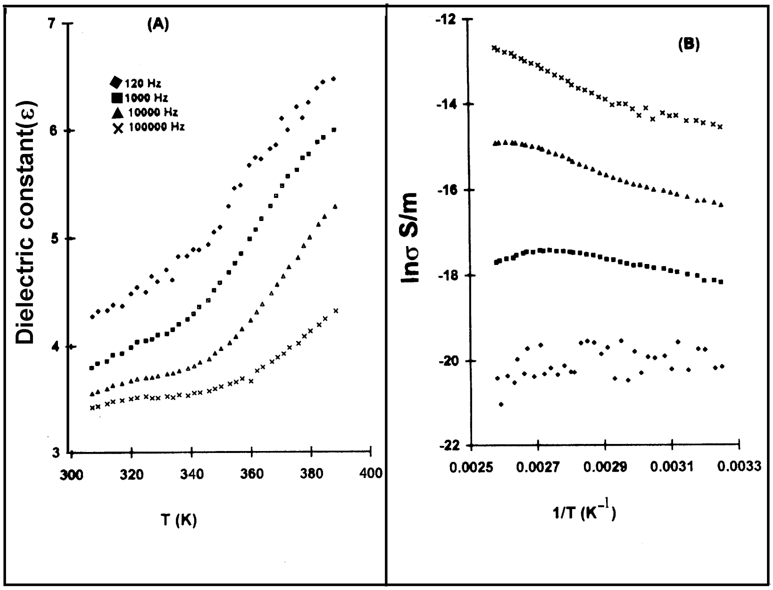


FIGURE 13 The effect of temperature on the dielectric constant (A) and ac conductivity (B) for the prepared poly(3-hydroxyaniline-PMMA film).

Further investigations on P(3-HA)-PMMA film sample were performed. All the experimental condition used for preparation of sample no. 1 in Table 2 are used in presence of PMMA (0.25, 0.50, 0.75 and 1.00 g) which has $\overline{M}_v = 4.4 \times 10^5$. The films were 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 which has higher ac conductivity value was selected to investigate the effect of temperature on both dielectric constant and ac conductivity.

The effect of temperature on both dielectric constant and ac conductivity of the PMMA-poly(3-hydroxyaniline) was investigated at different frequencies (120, 10^3, 10^4 and 10^5 Hz). The data are graphically represented in Figures 13A 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 the increase of frequency but dielectric constant decreases in the same direction. The phase transition at 338 K for P(3-HA) disappeared in the case of PMMA-P(3-HA) film as shown in Figures 13A and B, but another phase transition showing the PMMA behaviour is appeared between 350 and 360 K for the frequency range $120-10^5$ Hz. This means that the stabilization of P(3-HA) with PMMA changes the conducting property to the insulating polymer.

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