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# Oxidative Chemical Polymerization of p-Sulphanilamide and Characterization of the Polymer Obtained

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The oxidative chemical polymerization of p-sulphanilamide 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 orders of the polymerization reactions with respect to hydrochloric acid, sodium dichromate, and monomer concentrations are found to be 0.73, 0.971, and 0.966, respectively. Also, the effect of temperature on the polymerization rate was studied and the apparent activation energy was calculated and its value was found to be  $24.291 \times 10^4 \text{ J/mol}$ . The characterization of the obtained polymer sample at the optimum conditions was carried out by IR, UV-visible, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, X-ray diffraction, electron microscopic, and thermogravimetric analysis. The dielectric and a.c. conductivity were investigated as a function of temperature.

**Keywords:** aqueous oxidative chemical polymerization, p-sulphanilamide characterization, order of reaction, apparent activation energy, a.c. conductivity

#### INTRODUCTION

The vigorous development of polymer science and the extensive utilization of polymeric materials in technology has led in recent years to an increased interest in various problems of chemistry and physics of conducting polymers. This is evident from the fact that, not only physicists but also synthetic chemists, technologists, and structural engineers have become more and more interested in numerous

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problems of the chemistry and physics of polyaniline (PANI) and its derivatives as a good example of conducting polymers [1].

The kinetics of aqueous oxidative chemical polymerization of 3-methylaniline, 3-chloroaniline, 3-methoxyaniline, 3-hydroxyaniline, and N-methylaniline in HCl solution using sodium dichromate as oxidant at 5°C were investigated by Sayyah and Bahgat et al. [2-7].

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]. The polymerization mechanisms and reaction kinetics of aniline in aqueous solutions have been investigated by several groups [9–18].

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 electrical conductivity of the produced polyaniline have been investigated [19–21]. Characterization of polyaniline and its derivatives by X-ray diffraction, electronic spectroscopy, IR, thermogravimetric analysis, conductivity measurements, atomic force microscopy, and scanning tunneling microscopy were conducted [22–23]. Also, the ferroelectric properties of polyaniline were observed and investigated by Bahgat et al. [6].

Generally, from an application point of view, PANI and its derivatives are considered one of the best organic conducting materials. Their synthesis is performed by chemical or electrochemical methods because of their promising properties [24–27]. In recent years, several reviews on PANI have been published [28–30].

The present study intends to investigate the kinetics of the chemical oxidative polymerization of p-sulphanilamide in aqueous hydrochloric acid medium using sodium dichromate as oxidant at 25°C. The obtained polymer is characterized by IR, <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy, elemental analysis, X-ray diffraction, electron microscopy, thermal analysis, and a.c. conductivity.

#### **EXPERIMENTAL**

#### Materials

p-sulphanilamide was provided by Merck Chemical Co. (Germany). Concentrated hydrochloric acid and ammonia solution (33%) were chemically pure grade products provided by Prolabo-Chemical Co. (UK). Twice distilled water was used as a medium for the polymerization reactions. The used sodium dichromate was a product of Merck Chemical Co. (Germany).

#### Oxidative Aqueous Polymerization of p-Sulphanilamide Monomer

The polymerization reactions were carried out in a well-stoppered conical flask 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 of the performed experiments. Kinetics of the polymerization reactions were studied according to the previously described procedures [2–7].

# Elemental Analysis, Infrared and <sup>1</sup>H- and <sup>13</sup>C-NMR Spectroscopy

The elemental analysis of the poly(p-sulphanilamide) was carried out at the micro analytical laboratory at Cairo University by oxygen flask combustion and dosimat E 415 titrator (Switzerland).

The infrared measurements were carried out using a Shimadzu FTIR-430 Jasco spectrophotometer and KBr disk technique. The <sup>1</sup>H-NMR measurements were carried out using a Varian EM 360 L, 60 MHz NMR spectrometer. The NMR signals of the prepared polymer have been recorded in dimethyl-sulphoxide (DMSO) using tetramethylsilane as internal reference. The <sup>13</sup>C-NMR measurements were carried out using a Varian EM 360 L, 100 MHz NMR spectrometer. The <sup>13</sup>C-NMR signals of the prepared polymer have been recorded in dimethyl-sulphoxide (DMSO).

## Thermal Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

The thermal gravimetric analysis and differential thermal analysis of the prepared polymer sample were performed using a Shimazu DT-30 thermal analyzer. The weight loss was measured from the ambient temperature up to 500°C, in rate of 20°C per minute to determine the degradation rate of the polymer.

### **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, a Philips 1976 Model 1390, was operated at the following conditions that 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

### **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. The samples were coated on both sides with air drying electric conducting silver in order to attain good contact. 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  $\pm 2\%$ .

# **RESULTS AND DISCUSSION**

#### **Kinetic Studies**

#### Effect of Hydrochloric Acid Concentration

The polymerization of p-sulphanilamide (0.1098 mol/L) in 25 ml of HCl with different molarities was carried out by addition of 25 ml sodium dichromate solution (0.0924 mol/L) as oxidant under nitrogen atmosphere at 25°C for different time intervals. The concentration of the monomer and oxidant were kept constant at 0.0549 and 0.0462 mol/L. respectively, during the study of HCl effect on the polymerization reaction. The experiments were carried out as described in Oxidative Aqueous Polymerization 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 are calculated and 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 HCl exponent determined from the slope of the straight line represented in Figure 2, is found to be 0.73. The order of the polymerization reaction with respect to the HCl concentration is therefore a first order.

#### Effect of Sodium Dichromate Concentration

The aqueous polymerization of p-sulphanilamide (0.1098 mol/L) was carried out in 25 ml HCl solution (1.60 mol/L) in presence of 25 ml of sodium dichromate solution, which has different molarities



**FIGURE 1** Effect of HCl concentration on the polymerization of p-sulphanilamide.

(0.0400, 0.0462, 0.0600, and 0.0800 mol/L) as oxidant under nitrogen atmosphere at 25°C for different time intervals. The total HCl and monomer molarities were fixed in the reaction medium at 0.80 and 0.0549 mol/L, respectively. The yield-time curve for each oxidant concentration was 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. From the obtained data, it is clear that the initial and overall rates of the polymerization reaction increase with increasing oxidant concentration. The oxidant exponent is calculated from the slope of the obtained

**TABLE 1** Effect of HCl Concentration on the Polymerization ofp-Sulphanilamide

Exporimont	HCl concentration	$\begin{array}{c} Rate \ of \ polymerization \\ (mol/L \cdot S \times 10^5) \end{array}$		
number	(mol/L)	Initial rate	Overall rate	
1	0.2	1.318	1.016	
2	0.4	2.098	1.065	
3	0.6	2.754	1.290	
4	0.8	3.742	1.484	



**FIGURE 2** Double logarithmic plot of initial rate of polymerization versus HCl concentration.

straight line from the relation between  $Log(R_i)$  and Log[oxid] (c.f. Figure 4). The slope is found to be equal 0.971, which means that the order of the polymerization reaction is also a first order reaction with respect to the oxidant concentration.

#### Effect of the Monomer Concentration

The effect of the monomer concentration on the aqueous polymerization of p-sulphanilamide in the presence of 25 ml of 1.60 mol/LHCl and 25 ml of 0.0924 mol/L Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution under nitrogen atmosphere at  $25^{\circ}$ C was studied. The yield-time curves data were calculated and graphically represented in Figure 5, whereas 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 increase with increasing monomer concentration. The order of the reaction with respect to monomer concentration was detected from



**FIGURE 3** The yield-time curves showing the effect of oxidant concentration on the polymerization reaction rate of p-sulphanilamide.

the slope of the linear relation between log  $R_i$  and log[M] represented in Figure 6. The slope was found to be 0.966, which means that the order of the polymerization reaction is first order with respect to the monomer concentration.

# Effect of the Reaction Temperature

The aqueous oxidative polymerization of p-sulphanilamide (0.1098 mol/L) in 25 ml of (1.60 mol/L) HCl in presence of 25 ml sodium dichromate (0.0934 mol/L) solution under nitrogen atmosphere was

Experiment	K-Cr-Q- concentration	$\begin{array}{c} Rate \ of \ polymerization \\ (mol/L \cdot S \times 10^5) \end{array}$		
number	(mol/L)	Initial rate	Overall rate	
5	0.0400	3.090	1.213	
6	0.0462	3.742	1.484	
7	0.0600	4.677	1.613	
8	0.0800	6.166	1.662	

**TABLE 2** Effect of Oxidant Concentration on the Polymerizationof p-Sulphanilamide



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

carried out at the temperatures of 5, 15, and 25°C for different periods of time. The yield-time curves are 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 rising reaction temperature.

The apparent activation energy  $(E_a)$  of the aqueous polymerization reaction of p-sulphanilamide was calculated by plotting Log(R<sub>i</sub>) against (1/T), which gave a straight line (c.f. Figure 8). From the slope and using Arrhenius equation can be calculated (E<sub>a</sub>). The apparent activation energy for this system is  $24.291 \times 10^4 \, J \cdot mol^{-1}$ .

#### Mechanism of the Aqueous Oxidative Polymerization of p-Sulphanilamide

The pattern of the aqueous oxidative polymerization of p-sulphanilamide develops in three steps.



**FIGURE 5** The yield-time curves showing the effect of monomer concentration on the polymerization reaction rate of p-sulphanilamide.

#### 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:

$$(\mathrm{HCrO}_4)^- \rightleftharpoons (\mathrm{CrO}_4)^{2-} + \mathrm{H}^+ \qquad \mathrm{K} = 10^{-5.9}$$

**TABLE 3** Effect of Monomer Concentration on the Polymerization ofp-Sulphanilamide

Franciscont	Manaman	$\begin{array}{c} Rate \ of \ polymerization \\ (mol/L \cdot S \times 10^5) \end{array}$		
number	concentration (mol/L)	Initial rate	Overall rate	
9	0.0549	3.742	1.484	
10	0.0799	5.033	2.033	
11	0.0999	6.323	2.549	
12	0.1199	7.261	3.226	



**FIGURE 6** Double logarithmic plot of initial rate of polymerization versus monomer concentration.

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

Further, the species present depend on the nature of the acid used [31]. When hydrochloric acid is used, there is an essentially quantitative conversion into the chloro chromate ion as follows:

$$CrO_3(HO)^- + H^+ + Cl^- \rightleftharpoons CrO_3Cl^- + H_2O$$

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

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



**FIGURE 7** The yield-time curve showing the effect of temperature on the polymerization reaction rate of p-sulphanilamide.



Generally, the initial step is rapid and may occur in short time,  $0-5 \min$  (autocatalitic reaction), where no polymeric product is being

TABLE 4	Effect of	f Temperature	on the	Polymeriza	ation o	of p-s	sulpl	hanil	amid	le
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		Rate of po (mol/L	$\begin{array}{c} Rate \ of \ polymerization \\ (mol/L \cdot S \times 10^5) \end{array}$		
Experiment number	Temperature (°C)	Initial rate	Overall rate		
13	5	2.655	1.194		
14	15	3.090	1.339		
15	25	3.742	1.484		



**FIGURE 8** Double logarithmic plot of initial rate of polymerization versus (1/T).

obtained. After 5 min of the polymerization reaction, the polymeric products were obtained.

### **Propagation Step**

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



This reaction is followed by further reaction of the formed dimer radical cations with monomer molecules to form trimer radical cation and so on. The degree of polymerization depends on different factors such as dichromate concentration, HCl concentration, monomer concentration, and temperature as shown from the kinetic data.

#### Termination Step

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



with solvation of the formed polymer molecules at the end  $NH_2$  group as follows:



#### 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 = 
$$K_2[HCl]^{0.73}[oxidant]^{0.97}[Monomer]^{0.96}$$

The values of  $K_2$  at different temperatures were calculated and the enthalpy ( $\Delta H^*$ ) and entropy ( $\Delta S^*$ ) of the activation associated with  $K_2$  were calculated using an Eyring equation:

$$K_2 = (RT/Nh) imes e^{(\Delta S^*/R)} imes e^{-(\Delta H^*/RT)}$$

where  $K_2$  is rate constant, R is the universal gas constant, N is Avogadro's number and h is Plank constant.

By plotting  $(K_2/T)$  versus the (1/T) (cf. Figure 9), a linear relationship is obtained with slope  $= -(\Delta H^*/2.303 \text{ R})$  and intercept  $= \log (R/Nh) + \log (R/Nh)$ 



FIGURE 9  $\mbox{Log}(k_2/T)$  versus (1/T) curve showing the thermodynamic parameters.

 $(\Delta S^*/2.303 \text{ R})$ . From the slope and intercept, the values of  $(\Delta H^*)$  and  $(\Delta S^*)$  were found to be  $23.840 \times 10^3 \text{ J/Mol}$  and  $-64.95 \text{ J/Mol} \cdot \text{K}$ , respectively. The negative value of  $(\Delta S^*)$  could be explained by the activated complex and products being more solvated by water molecules than the reactants [32]. The activated complex formation step is endothermic as indicated by the positive value of  $\Delta H^*$ . The contribution of  $\Delta H^*$  and  $\Delta S^*$  to the rate constant of the polymerization seems to compensate each other. This fact suggests that the factors controlling  $\Delta H^*$  must be closely related to those controlling  $\Delta S^*$ . Therefore, the solvation state of the activated complex could be important in determination of  $\Delta H^*$ .

#### Elemental and Spectroscopic Analysis

The elemental analysis of the poly(p-sulphanilamide) was carried out in the microanalytical laboratory at Cairo University. The percentage

The element	C%	H%	N%	S%
Calculated Found	38.3 39.00	$\begin{array}{c} 4.26\\ 3.80\end{array}$	$14.89 \\ 13.90$	$17.02 \\ 16.50$

TABLE 5 Elemental Analysis of Poly(p-sulphanilamide)

of carbon, hydrogen, nitrogen, and sulphur are in good agreement with the calculated one of the suggested structure shown in Termination Step. The elemental analysis data are given in Table 5.

The UV–Visible spectra of the monomer and polymer are represented in Figure 10. The absorption bands 204, 220, and 262 nm for the monomer and at 232 and 326 nm for the polymer could be attributed to  $\pi-\pi^*$  transitions (E<sub>2</sub>-band of benzene ring) and  $\pi-\pi^*$  transition ( $\beta$ -band (A<sub>1g</sub>–B<sub>2u</sub>)), respectively.



FIGURE 10 UV-visible spectra of the monomer and the prepared polymer.

From the IR spectra of the prepared polysulphanilamide, it is clear that the strong absorption band appearing at 544 cm<sup>-1</sup> is due to the scissoring deformation of  $(-SO_2-N-)$  group. The sharp band at  $673 \text{ cm}^{-1}$  could be attributed to the C–N bending deformation of (-Ph-N-) group. The sharp band at  $830 \text{ cm}^{-1}$  could be attributed to the out-of-plane deformation of CH group in 1,4-disubstituted benzene ring. The sharp absorption band at  $913 \text{ cm}^{-1}$  could be attributed to the deformation of  $(-SO_2-N-)$  group. The two sharp absorption bands, which appear at 1157 and  $1403 \text{ cm}^{-1}$ , could be due to the symmetric and asymmetric stretching vibrations of  $(-SO_2-N-)$  group. The sharp absorption band at  $1592 \text{ cm}^{-1}$  could be attributed to the stretching vibrations of (C=C) group in the benzene ring. The broad absorption band at  $3271 \text{ cm}^{-1}$  could be due to the hydrogen bonded NH group in amino group. The other I.R absorption bands and their assignments are tabulated in Table 6.

The <sup>1</sup>H-NMR spectrum of the prepared polymer sample shows two singlet signals at  $\delta = 2.5$  and 3.5 ppm, which are due to the solvent protons. The singlet signal appearing at  $\delta = 7.2$  ppm may be due to the NH proton in Ph-NH. The doublet-doublet signals at  $\delta 7.6-7.9$  ppm are due to the phenyl ring protons. The singlet

<b>TABLE 6</b> Assignment of	f Infrared Spectrum o	of the poly sulphanilamide
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Wave number (cm <sup>-1</sup> ) Name of ligand polysulphanilamide	Assignment [33]
544 <sup>m</sup>	Scissoring deformation of $(-SO_2N-)$ group.
673 <sup>m</sup>	Bending deformation of $C-N$ in $(Ph-N-)$ group.
830 <sup>m</sup>	Out-of-plane deformation of 1,4-disubstituted benzene ring.
853 <sup>m</sup>	Bending deformation of $(-SO_2N-)$ .
$913^{m}$ $1016^{w}$ $1095^{m}$ $1157^{s}$ $1323^{s}$ $1403^{s}$ $1592^{s}$ $1607^{s}$	$\begin{array}{l} (C-C) \mbox{ deformation in benzene ring or stretching vibration of } \\ (-SO_2N-) \mbox{ group.} \\ Symmetric vibration for (-SO_2N-) \mbox{ group.} \\ Stretching vibration for C-N \mbox{ group.} \\ Asymmetric stretching for (-SO_2N-) \mbox{ group.} \\ Stretching vibration of (C=C) \mbox{ in benzene ring.} \end{array}$
1677 <sup>m</sup>	Symmetric stretching for CH aromatic.
3110 <sup>sh</sup>	Symmetric stretching for hydrogen bonded NH group in amino
3271 <sup>b</sup>	acid.

s = strong; m = medium; w = weak; b = broad; sh = shoulder.

signal at  $\delta = 8 \text{ ppm}$  could be due to the amino group proton. The integration of amino group protons relative to the phenyl group protons to NH protons is equal to 2:3:1, which means the structure of the polymer contains free amino group as shown in Termination Step.

The <sup>13</sup>C-NMR spectrum of the prepared polymer sample is represented in Figure 11. The spectrum shows the following:

- 1. The multiplet signal at  $\delta = 40-42$  ppm is due to the carbon atom in the solvent structure.
- 2. The singlet signal at  $\delta = 125.08$  ppm could be attributed to the C5 in benzene ring.
- 3. The singlet signal at  $\delta = 128.3$  ppm may be due to the C6 in benzene ring.
- 4. The singlet signal at  $\delta = 128.9$  ppm could be attributed to the C3 in benzene ring.
- 5. The singlet signal at  $\delta = 148.3$  ppm is due to the C1 in benzene ring.
- 6. The singlet signal at  $\delta = 155.03$  ppm could be attributed to the C2 in benzene ring.
- 7. The singlet signal at  $\delta = 177.36$  ppm could be attributed to the C4 in benzene ring.

All the aforementioned spectroscopic and elemental analysis data reveal that the polymeric chain buildup occurs through the benzene ring in the meta position to  $SO_2-NH_2$  group and no migration occurs during polymerization. Furthermore, there is no presence of HCl molecules in the final structure, but solvation of the end amino group with water molecules definitely takes place. See Termination Step and the following scheme:



#### Electron Microscope and X-Ray Analysis

X-ray diffraction pattern shows that the prepared polymer sample is amorphous with partial crystallinity as shown in Figure 12. The electron microscopic picture shows the shape of the polymeric grains to be rather random with diameters ranging from  $1 \,\mu m$  to  $9 \,\mu m$ .







FIGURE 12 The X-ray diffraction pattern.

### Thermogravimetric Analysis (TGA)

The thermogram of the prepared polymer sample obtained from TGA measurement gives different stages as summarized in Table 7. The first stage is in the temperature range from 25 to 140°C. It includes the loss of one water molecule of hydration present in the suggested structure in Termination Step. The weight loss for step is found to be 2.77% but the calculated one is 2.39%. Stage 2: from the TGA curve in the temperature range between 140–290°C, a weight loss of about 8% was found, which could be attributed to three molecules of H<sub>2</sub>O, which is in good agreement with the calculated value (7.18%) for this stage. Stage 3, in the temperature range between 290–460°C, all SO<sub>2</sub> groups are lost from the polymeric chain, with an estimated weight loss of 33.71%, which is in good agreement with the calculated value (34.04%). Stage 4, in the temperature range between 460–500°C, one aniline moiety is lost, and

	Weight loss				
Temperature range (°C)	Cal.%	Found%	The removal molecule		
Ambient-140	2.39	2.77	$H_2O$		
140-290	7.18	8.00	$3H_2O$		
290-460	34.04	33.71	$4SO_2$		
460-500	12.1	10.86	Aniline moiety		
Above 500	44.29	44.3	Residue		

**TABLE 7** Thermogravimetric Analysis (TGA) of Poly(p-sulphanilamide)

the estimated weight loss for this step is found to be 10.86%, whereas the calculated value is equal to 12.1%. Above  $500^{\circ}$ C, the residue of the polymer is found to be 44.3%.

# Electrical Properties of Poly(p-sulphanilamide)

The polymer sample, which was prepared at 0.8 mol/L HCl, 0.0462 mol/L oxidant, and 0.0549 mol/L monomer at 5°C was selected for the investigation of the temperature effect on the electrical properties. The effect of temperature on both dielectric constant and a.c. conductivity of the poly(p-sulphanilamide) were investigated at different frequencies (120,  $10^3$ ,  $10^4$ , and  $10^5$  Hz). The data are graphically



FIGURE 13 The effect of temperature on the dielectric constant at different frequencies.

represented in Figure 13, from which it is clear that the dielectric constant ( $\hat{\epsilon}$ ) increases with rising temperature up to 388.6 K and then decreases to about 428 K. The phase transition is observed at 388.6 K (Figure 13) and also observed at the same temperature in the  $\sigma$ -(1/T) curve (cf. Figure 14) at 0.00257 K<sup>-1</sup>. From Figure 13 and 14, it is clear that the highest values of dielectric constant are found at 120 Hz, but the higher values of conductivity are obtained at 10<sup>5</sup> Hz.



**FIGURE 14** The effect of temperature on the a.c. conductivity at different frequencies.

## CONCLUSIONS

In conclusion, the data in this article revealed the following:

- 1. The orders of the oxidative chemical polymerization reaction are 0.73, 0.971, and 0.966 with respect to HCl concentration, oxidant concentration and monomer concentration, respectively.
- 2. The apparent activation energy  $(E_a)$  of the oxidative chemical polymerization of p-sulphanilamide is  $24.291\times10^4~J~mol^{-1}$ , the enthalpy of activation  $(\Delta H^*)$  is found to be  $23.84\times10^4~J~mol^{-1}$  and the entropy of activation  $(\Delta S^*)$  is found to be  $-64.95\,J~mol^{-1}K^{-1}$ .
- 3. From the elemental analysis, infrared, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR it can be deduced that the continuity of the polymeric chain through the benzene ring is in the meta position of  $SO_2-NH_2$  group, that no migration occurs during polymerization and there is no presence of HCl molecules in the final structure but solvation of the end amino group with water molecules does occur.
- 4. The conductivity of the prepared polymer at the optimum conditions (0.80 mol  $L^{-1}$  HCl 0.0462 mol  $L^{-1}$ , 0.0549 mol  $L^{-1}$  at 5°C), lies in the range of poor insulators.
- 5. The prepared polyp-sulphanilamide is amorphous with some crystallinity, and the polymeric grain size ranges from  $1 \,\mu\text{m}$  to  $9 \,\mu\text{m}$ .

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