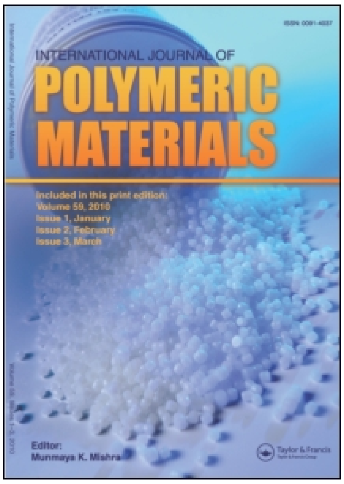

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Kinetic Studies of the Polymerization of Substituted Aniline in Aqueous Solutions and Characterization of the Polymer Obtained

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To cite this Article Sayyah, S. M. , El-Khalek, A. A. Abd , Bahgat, A. A. and El-Salam, H. M. Abd(2001) 'Kinetic Studies of the Polymerization of Substituted Aniline in Aqueous Solutions and Characterization of the Polymer Obtained', International Journal of Polymeric Materials, 49: 1, 25 — 49

To link to this Article: DOI: 10.1080/00914030108035865

URL: http://dx.doi.org/10.1080/00914030108035865

Intern. J. Polymeric Mater., 2001, Vol. 49, pp. 25–49
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Kinetic Studies of the Polymerization of Substituted Aniline in Aqueous Solutions and Characterization of the Polymer Obtained

Part 2: 3-methylaniline

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(Received 25 December 1999; In final form 28 December 1999)

The aqueous polymerization of *m*-methylaniline (*m*MA) was studied using sodium dichromate as oxidant in the 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 of hydrochloric acid concentration or sodium dichromate concentration but decrease with the increase of 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 the increase of sodium dichromate concentration. The highest a.c.conductivity value of the obtained polymer was found in case of using 0.023304 gmol/L of $Na_2Cr_2O_7$, 0.2 M HCl and 0.093225 M monomer solution in the reaction medium. The order of the polymerization reaction with respect to hydrochloric acid, $Na_2Cr_2O_7$ and monomer concentration was found to be 1.3, 1.33 and −0.83 respectively.

$$\text{Reaction Rate} = k_2[\text{HCl}]^{1.3}[\text{oxidant}]^{1.33}[\text{monomer}]^{-0.83}$$

The apparent activation energy (E_a) for this polymerization system was found to be 4.594×10^4 J/mol. The obtained poly(*m*-methylaniline) was characterized by uv-visible,

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*Corresponding author.

and IR spectroscopy. X-ray diffraction analysis and electron microscopy studies were carried out. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) results were used for the confirmation of the structure.

Keywords: Polyaniline; Poly(3-methylaniline); Polymerization; Polymerization variables; Thermodynamic parameters

1. INTRODUCTION

Recently electrically conducting polymers have attracted considerable attention 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] and the ability to switch reversibly from insulating to conducting state either by electrochemical or chemical doping [3, 4]. In recent years several review papers [5–7] 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 [7]. Polymerization mechanisms and reaction kinetics of aniline in aqueous solutions have been investigated by several authors [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 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 [18–20].

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

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 tunnelling microscopy [23]. 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 [24]. It was found that the substituted group of 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 [25].

In the present study we intend to investigate the kinetics of the oxidative polymerization of *m*-methylaniline in aqueous hydrochloric acid medium using sodium dichromate as oxidant. The obtained polymer is characterized by UV, FTIR, ^{1}H-NMR spectroscopy, X-ray diffraction, electron microscopy, thermal analysis, specific viscosity and a.c.conductivity measurements.

2. EXPERIMENTAL

2.1. Materials

3-methylaniline provided by Merck Chemical Company (Germany) was vacuum distilled and stored in absence of light before use. Concentrated hydrochloric acid, sulphuric acid and ammonia (33%) were of chemically pure grade produced 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 *m*-methylaniline Monomer

The polymerization reaction was carried out in a well-stoppered conical flask of 250 ml capacity containing the requisite amount of monomer (*m*MA) and aqueous HCl, and 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 flask were then put in an automatically controlled thermostat at the required temperature. The flasks were shaken (15 shakings/10 second/every 15 minute) 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 till constant weight.

2.3. Determination of the Specific Viscosity

The specific viscosity was measured on polymer samples dissolved in concentrated sulphuric acid (0.1 g/10 ml) at 25°C using Ostwald viscometer [26].

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.

2.5. Thermal Gravimetric Analysis

The thermal gravimetric analysis of the polymer sample was performed using a thermal analyser (SHIMAZU DT-30).The weight loss was measured from the ambient temperature up to 500°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 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 mAm
Preset time: 10(s)
Scan speed: 8 (dg/min.)
Voltage: 40 kV

2.7. Conductivity Measurements

Polymer samples in the form of compressed discs of 1.002 cm diameter and 0.2 cm in 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 $100-10^5$ 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 *m*-methylaniline (0.4988 g = 0.1864 M) in 25 ml of HCl which have different molarities (0.30, 0.40, 0.50 and 0.60 M) was carried out by addition of 25 ml sodium dichromate solution (0.046608 M) as oxidant under nitrogen atmosphere at 5°C for different time intervals. The concentration of the monomer and oxidant are kept constant at 0.093225 M and 0.023304 M respectively during the investigation of the 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 were calculated and the data are graphically represented in Figure 1, from

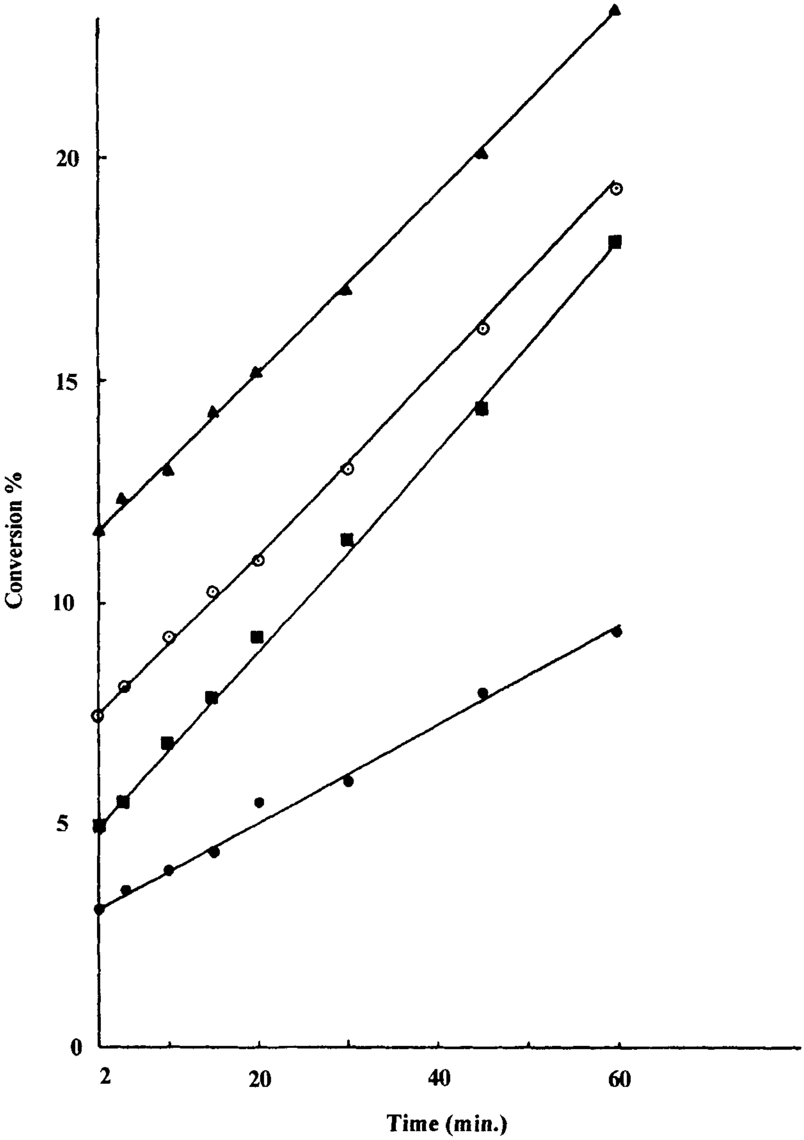


FIGURE 1 Effect of HCl concentration on the rate of polymerization of *m*-methylaniline.

which the initial rates of the polymerization reactions were calculated and tabulated in Table I. 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 I. From Figure 1 and Table I, it is clear that, both of the initial and overall reaction rates for the polymerization reaction increase with the increasing of the HCl concentrations from 0.15–0.3 M. Also, the specific viscosity values increase in the same direction. While the a.c. conductivity has its maximum value when 0.2 M HCl solution was used in the reaction medium. To determine the HCl exponent, the plot of the logarithm of the initial rate of the polymerization (Log R_i) against logarithm of the HCl concentration (Log[HCl]) was drawn and presented in Figure 2. A straight line is obtained whose slope equals 1.3, *i.e.*, the exponent of the polymerization reaction with respect to the HCl-concentration [HCl] is 1.3. This is in good agreement with what was found for aniline polymerization using $K_2Cr_2O_7$ as oxidant [27].

3.2. Effect of Sodium Dichromate Concentration

The aqueous polymerization of *m*-methylaniline (0.4988 g = 0.1864 M) in 25 ml HCl solution (0.40 M) and 25 ml of sodium dichromate solution which has different molarities (0.0310, 0.0388, 0.0466 and 0.0544 M) as oxidant under nitrogen atmosphere at 5°C for different time intervals was carried out. The total HCl and monomer molarities were kept constant in the reaction medium at 0.2 M and 0.093225 M respectively. The conversion-time curve for each oxidant concentration was calculated and the data are graphically represented in Figure 3, from which the initial rates of the polymerization reactions

TABLE I Effect of HCl concentration on the polymerization of (mMA)

Number of experiments	*Concentration of HCl g · mol/L*	*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*
1	0.15	3.885	1.39	0.07518	4.57
2	0.20	6.215	2.04	0.079136	7.33
3	0.25	8.783	2.58	0.08561	5.73
4	0.30	10.569	2.80	0.09178	2.96

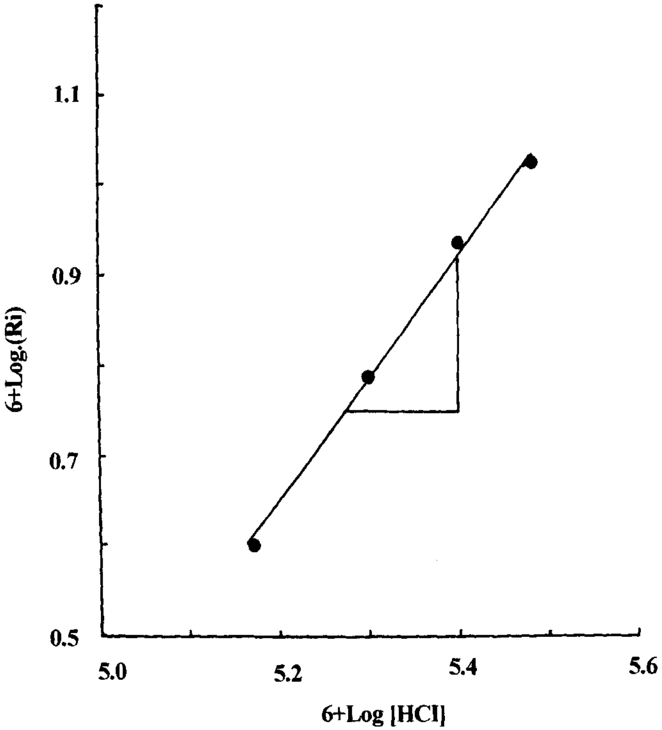


FIGURE 2 Logarithmic plot of initial rate of polymerization *versus* the logarithm of HCl concentration.

were calculated and summarized in Table II. 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 II. From the obtained data it is clear that the initial and overall reaction rates of the polymerization reaction increase with increased oxidant concentration. But the specific viscosity decreases with increased oxidant concentration, which indicates that the molecular weight of the polymer sample decreases with increased oxidant concentration. The maximum values of a.c.conductivity was found for the polymer sample obtained at 0.0233 M of the oxidant concentration. The Oxidant exponent was calculated from the slope of the obtained straight line for the relation between Log R_i *vs.* Log [oxidant] (*cf.* Fig. 4). The slope was found to be equal to 1.33 which means that

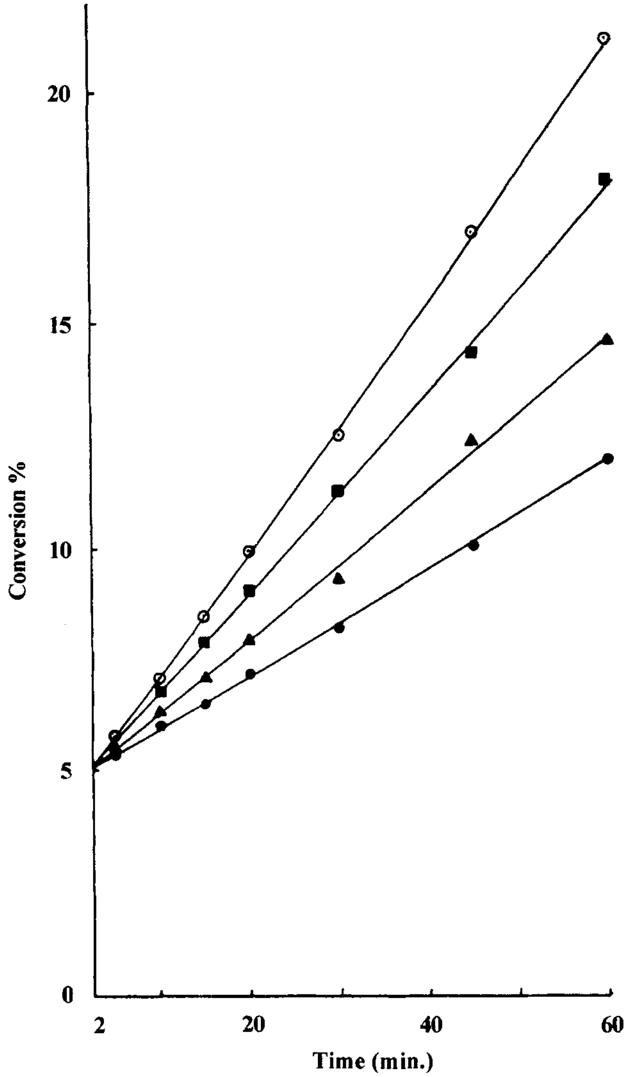


FIGURE 3 Effect of $Na_2Cr_2O_7$ concentration on the rate of polymerization of *m*-methylaniline.

the polymerization reaction with respect to the oxidant concentration is first order reaction and this result is in good agreement with what was found by different authors [28–30].

TABLE II Effect of $Na_2Cr_2O_7$ concentration on polymerization of (mMA)

Number of experiments	*Concentration* $Na_2Cr_2O_7$ *(g · mol/L)*	*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)*
1	0.0155	3.572	1.52	0.10216	4.89
2	0.0194	4.781	1.90	0.09209	4.56
3	0.0233	6.215	2.04	0.079136	7.33
4	0.0272	7.769	2.34	0.06475	6.05

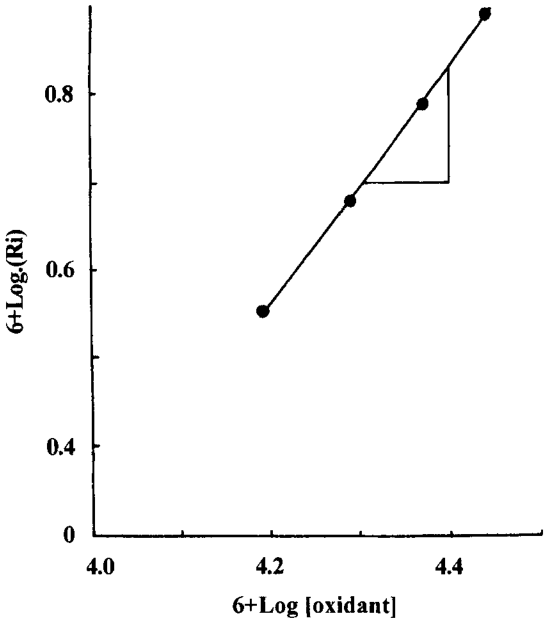


FIGURE 4 Logarithmic plot of initial rate of polymerization *versus* the logarithm of oxidant concentration.

3.3. Effect of Monomer Concentration

The effect of monomer concentration on the aqueous polymerization of *m*-methylaniline in the presence of 25 ml 0.4 M HCl and 25 ml of 0.0466 M $Na_2Cr_2O_7$ solution under nitrogen atmosphere at 5°C was studied. The conversion time curve data were calculated and are graphically presented in Figure 5, while the calculated initial and

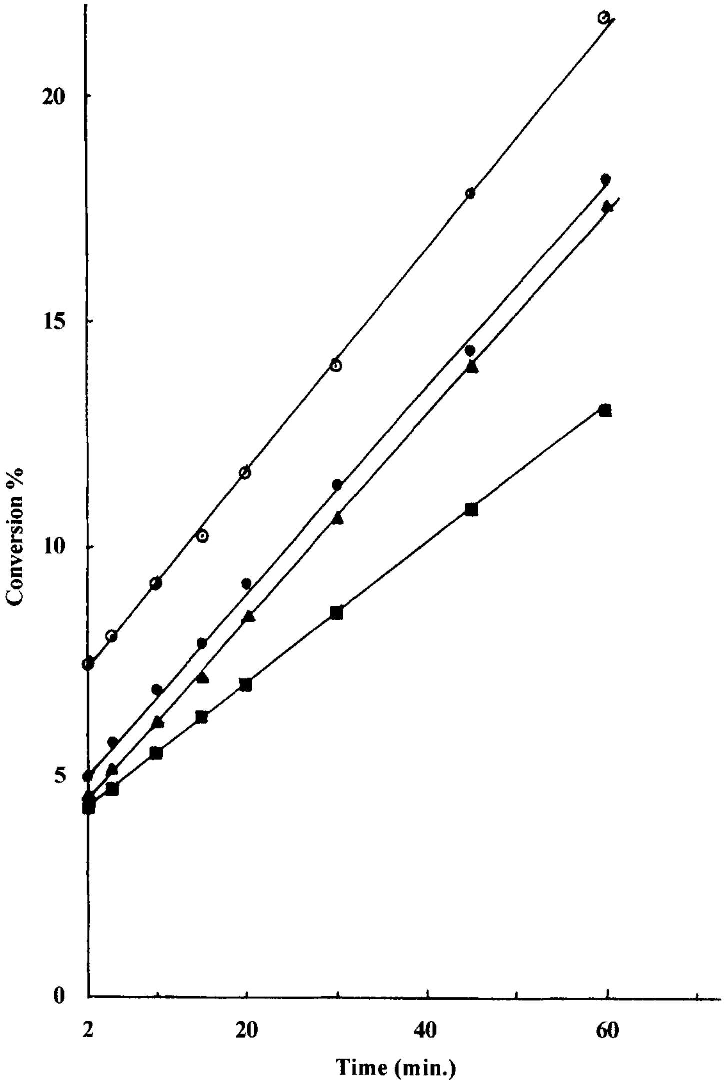


FIGURE 5 Effect of monomer concentration on the rate of polymerization of *m*-methylaniline.

overall reaction rates are given in Table III. From which it is clear that both of the initial and overall reaction rates decrease with increasing monomer concentration. For the determination of the monomer

TABLE III Effect of monomer concentration on polymerization of (mMA)

Number of experiments	*Concentration monomer* ($g \cdot mol/L$)	*Initial rate* $\cdot 10^6$ ($g \cdot mol/L \cdot S$)	*Overall reaction rate* $\cdot 10^6$ ($g \cdot mol/L \cdot S$)	η_{sp}	*Conductivity values* $\cdot 10^8$ (S/m)
1	0.0653	8.072	2.513	0.07194	3.26
2	0.0933	6.215	2.04	0.079136	7.33
3	0.1021	6.120	1.98	0.90648	4.37
4	0.1257	5.372	1.459	0.09497	4.32

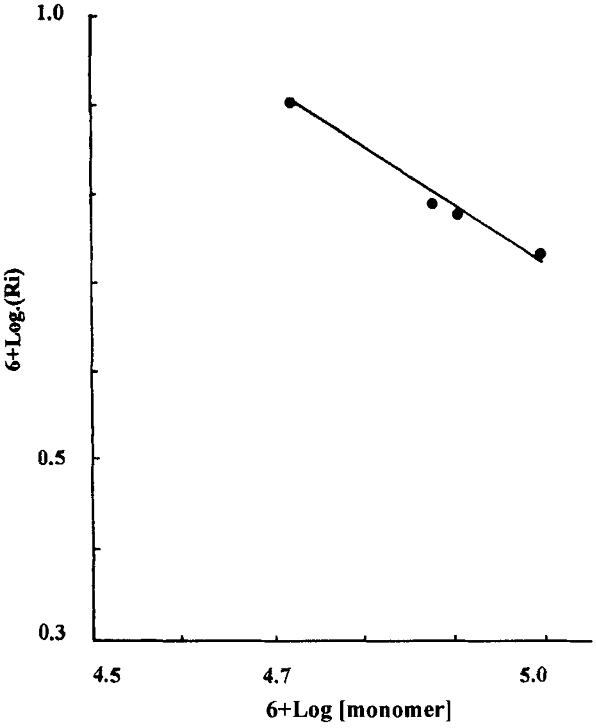


FIGURE 6 Logarithmic plot of initial rate of polymerization *versus* the logarithm of monomer concentration.

exponent, we plotted Log R_i against the logarithm of the monomer concentration (Log $[M]$). (*cf.* Fig. 6). A straight line was obtained with slope $= -0.83$. This indicates that the monomer exponent is negative order reaction. Specific viscosity and a.c.conductivity of the obtained polymer after 4 hours for each monomer concentration were measured and the data are given in Table III. The specific viscosity values increase with increased monomer concentration, while the a.c. conductivity values increase with monomer concentration up to 0.0933 g · mol/L, then decrease once again at monomer concentration equal to 0.1257 g · mol/L. The maximum a.c.conductivity was found at 0.0933 g · mol/L monomer concentration.

3.4. Effect of the Reaction Temperature

The aqueous polymerization of *m*-methylaniline (0.4988 g = 0.1864 M) in 25 ml of 0.40 M HCl after addition of 25 ml sodium dichromate (0.0466 M) solution under nitrogen atmosphere at different temperatures (5, 10 and 15°C) for different periods of time was carried out. The conversion % was calculated at different time intervals and the data are given in Table IV. 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 and a.c.conductivity values decrease with raising the reaction temperature.

The apparent activation energy (E_a) of the aqueous polymerization reaction of *m*-chloroaniline was calculated by plotting $\text{Log}\, R_i$ against $1/T$ which gave a straight line (*cf.* Fig. 7). From the slope we can get the apparent activation energy which was found to be 4.594×10^4 J/mol.

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

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

(A) The pattern of the initial 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

TABLE IV Effect of temperature (°C) on the aqueous oxidative polymerization of 0.093225 M *m*-methylaniline using 0.2 M HCl and 0.023304 M $K_2Cr_2O_7$ as oxidant

		Conversion (%) Time (min.)								*Rate of polymerization* $g\,mol \cdot L^{-1} s^{-1} \times 10^6$			*Conductivity values*
No.	*Temperature (°C)*	2	5	10	15	20	30	45	60	*Initial*	*Over all*	η_{sp}	10^6 *S/m*
1	5	4.85	5.50	6.85	7.79	9.16	11.45	14.36	18.00	6.215	2.04	0.07914	7.33
2	10	5.15	6.05	7.65	9.35	10.20	14.00	19.64	24.45	9.140	3.417	0.06906	7.08
3	15	5.65	6.55	8.70	10.15	13.00	17.18	23.50	29.60	12.491	4.591	0.05036	6.89

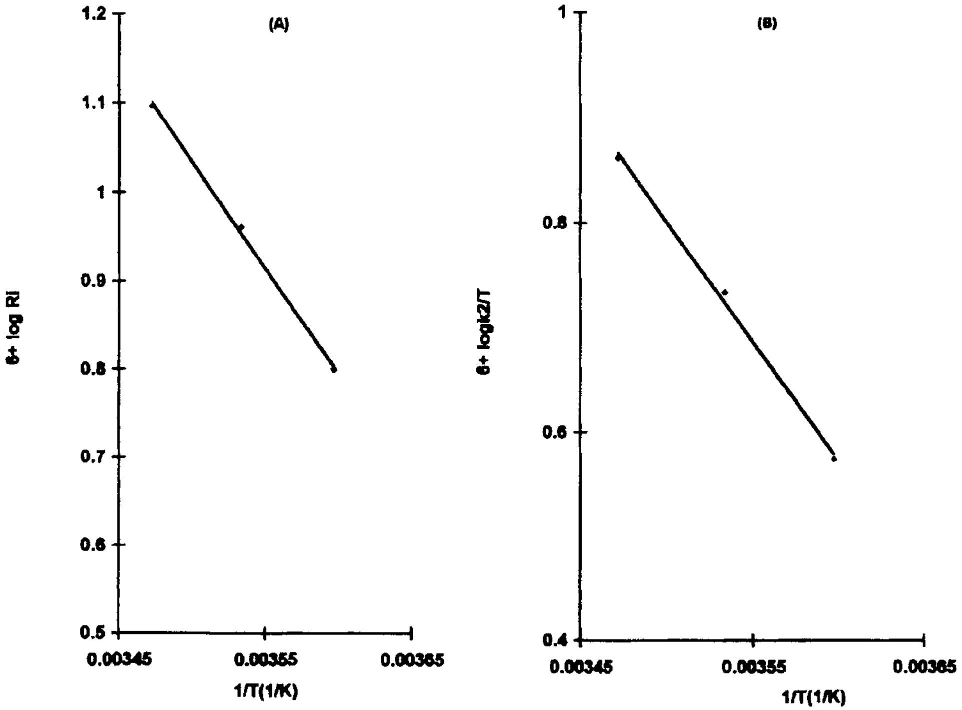


FIGURE 7 Logarithmic plot of initial rate of polymerization and Log k_2/T *versus* $1/T$ (K^{-1}).

are as follows:

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+$$

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+$$

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^-$$

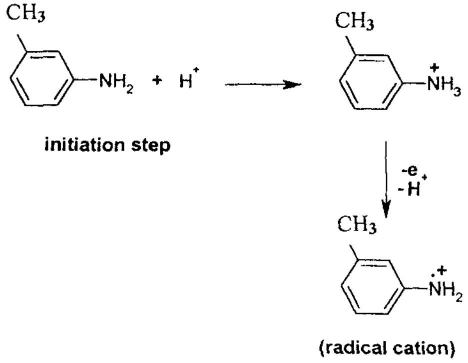
Further, the species present depend on the nature of the acid used [31]. When hydrochloric acid is used, there is essentially quantitative conversion into the chloro chromate ion as follows:

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

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

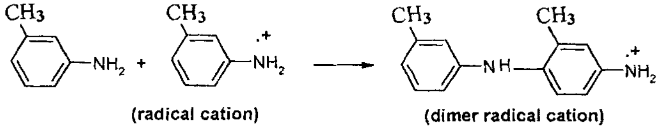
$$2CrO_3Cl^- + 6e + 14H^+ \longrightarrow 2Cr^{3+} + 2HCl + 6H_2O$$

and



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

(B) Propagation step This step involves the interaction between the formed radical cations and the monomer to form a dimer radical cation as follows:



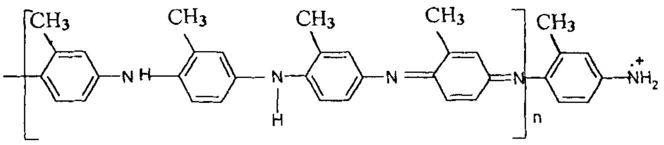
then the reaction is followed up by further reaction of the formed dimer radical cation with monomer to form timer radical cation and so on. Quininoid structural unit may occur in the polymeric chain during the polymerization reaction as mentioned in the literature [32].

From the obtained experimental data of the kinetic studies. We conclude that the degree of polymerization depends upon various factors such as dichromate concentration, HCl concentration, monomer concentration and temperature.

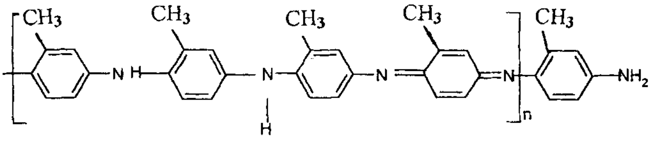
(C) Termination step The reaction is stopped by the addition of ammonium hydroxide solution in equal amounts to HCl concentration as follows:

$$A + NH_4OH \longrightarrow B + NH_4Cl + H_2O$$

where (A) is



and (B) is



3.6. Calculation of the Thermodynamic Parameters

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

$$\text{Reaction Rate} = k_2[\text{HCl}]^{1.3}[\text{oxidant}]^{1.33}[\text{monomer}]^{-0.83}.$$

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

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

where

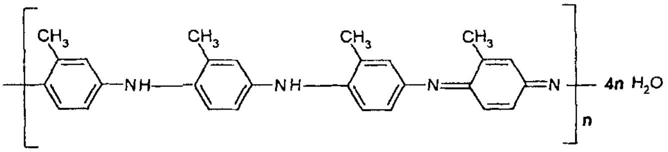
k_2 is the rate constant,
R is the universal gas constant,
N is Avogadros number and
h is plank constant.

By plotting log k_2/T *vs.* $1/T$ (*cf.* Fig. 7), we obtained a linear relationship with slope $= -\Delta H^*/2\ 303\ \mathrm{R}$ and intercept $= \log(R/\mathrm{Nh} + \Delta S^*/2.303\ \mathrm{R})$. From the slope and intercept, the values of ΔH^* and ΔS^* were found to be 4.594×10^4 J/mol and -294.700 J/mol K respectively. The negative value of ΔS^* could be explained by the higher electrostriction exerted by the activated complex on the solvated water molecules than exerted by the reactants [33]. 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 suggests 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^* [33].

3.7. Element and Spectroscopic Analysis

The element analysis of the poly(*m*-methylaniline) was carried out in the micro analytical laboratory at Cairo University. The C%, H% Cl% and N% are found to be in good agreement with the calculated one for the suggested structure present in Scheme 1. The element analytical data are given in Table V.

The UV-visible spectra of the monomer and polymer are presented in Figure 8. The absorption bands at $\lambda_{\max} = 249.5$, 307.5 and 437.5 nm



SCHEME 1

TABLE V Element analysis of poly(*m*-methylaniline)

The element	*C%*	*H%*	*N%*	*Cl%*
Calculated %	59.68	6.39	9.95	12.61
Found %	59.60	5.98	10.03	12.32

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 appearing at $\lambda_{max}=311$ nm in the case of the polymer is due to the $\pi-\pi^*$ transition, B-band ($A_{1g}-B_{2u}$) and the absorption bands appearing in the visible region at $\lambda_{max}=619$ and 805 nm may be due to the colour of polymer and high conjugation of the aromatic polymeric chains.

The infrared absorption bands of the monomer (*m*-methylaniline) and the prepared polymer and their assignments are summarized in Table VI. The three strong absorption bands appear at 677, 775, 855 and 887 cm^{-1} in case of monomer and the corresponding medium absorption bands in case of polymer at 600, 767 and 889 cm^{-1} are attributed to out of plane C—H deformation for 1,3-disubstituted benzene ring. But, the absorption band appearing at 956 cm^{-1} in the case of the polymer is attributed to 1,4-disubstituted in benzene ring. A series of absorption bands appearing in the region between 1000 and 1460 cm^{-1} could be attributed to skeletal stretching vibration of C—N in aryl-NH or aryl-NH_2 (amide I and amide II). The two sharp and splitted bands that appear in the case of monomer at 1600 and 1630 and the band at 1500 cm^{-1}, which appears also as broad splitted band in case of the polymer at 1511 and 1622 cm^{-1} could be attributed to C=C stretching vibration in aromatic system or NH deformation or the stretching vibration of the structure shown in Scheme 2 in case of polymer.

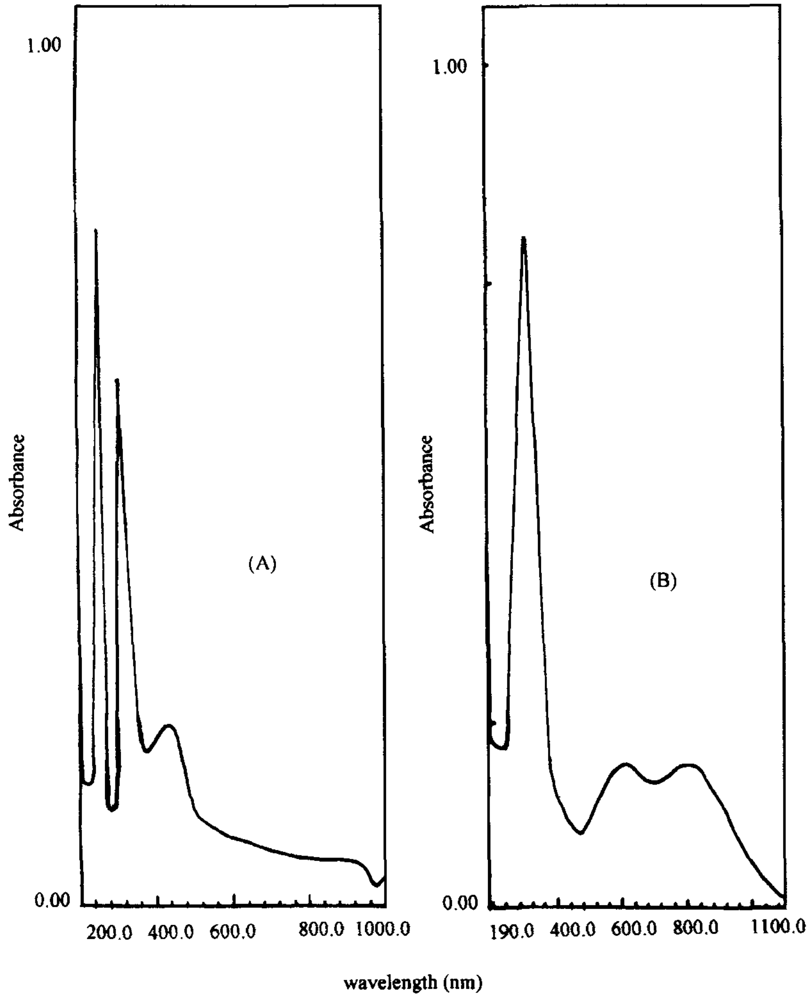
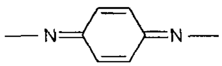


FIGURE 8 UV-visible spectra of *m*-methylaniline monomer (A) and the prepared poly(*m*-methylaniline) (B).

The two weak absorption bands at 2323 and 2371 cm^{-1} in case of the monomer are attributed to the stretching vibration of C—H in benzene ring. These bands appear in case of polymer at 2300 and 2311 cm^{-1} which could be attributed to C—N stretching vibration (overtone) or combination band for protonated primary or

TABLE VI Assignment of bands in the IR spectra of 3-methylaniline monomer and polymer

Wave number (cm^{-1})		
Monomer	*Polymer*	*Assignment* [35]
–	600^{m}	CH_3-rocking vibration
677^{s}	–	
775^{s}	767^{w}	Out of plane CH deformation showing 1,3-disubstituted benzene ring
855^{sp}	–	
887	889^{w}	
–	956^{w}	→ Out of plane CH def. for 1,4-disubstituted benzene ring
–	1022^{m}	CH str. Aliphatic or δ CH aromatic or C—N skeletal str. vibration (Aryl NH or Aryl NH_2)
1050^{w}	–	
1065^{w}	–	
–	1122^{s}	
1177^{s}	1177^{s}	
–	$1233^{s\&sp}$	
–	1278	
$1300^{s\&sp}$	–	
1320	–	
$1460^{s\&sp}$	–	
1500	1511^{b}	
$1600^{s\&sp}$	–	Str. vibration of C=C in benzene ring or NH def. of structure present in Scheme 2
1630	1622^{s}	
–	2300^{w}	C—N str. vibration (overtone) or combination band for protonated primary aromatic amine
–	2311^{w}	
2323^{w}	–	
2371^{w}	–	
2726^{w}	–	
2920^{w}	2920^{w}	→ CH str. aliphatic
3048^{w}	3040^{w}	→ CH str. aromatic
–	3200^{b}	NH str.
3290^{b}	–	
3450	3450	→ NH str. and strong bonded OH group



SCHEME 2

secondary aromatic amine. The two medium absorption bands at 2726 and 2920 cm^{-1} in case of monomer and at 2920 cm^{-1} in case of polymer could be attributed to the C—H stretching vibration of CH_3 group. The medium absorption band appearing at 3048 cm^{-1} in case of monomer and at 3040 cm^{-1} in case of polymer is attributed to the C—H stretching vibration of aromatic ring. The broad band appearing in the region 3290 to 3450 cm^{-1} in case of monomer and in the region 3200 and 3450 in case of the polymer 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 [34].

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 the shape of the grains of the polymer which ranged from spherical particles to elongated ones. Their size ranged from 4.7×10^{-3} μm to 21.2 μm as shown in Figure 9.

3.9. Thermal Analysis

The thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) for the prepared polymer sample no. 1 in Table IV for 4 hours were investigated and the obtained curves are represented in Figure 10. The first stage includes a loss of water of hydration (47.5–139.5°C). The estimated weight loss for this step was found to be 11.23% but the calculated one is 12.78%. In DTA curve, this stage give a broad endothermic peak between 30 and 97°C with evolution of heat of 921.94 J/g. In the temperature range between 141 and 278.7°C

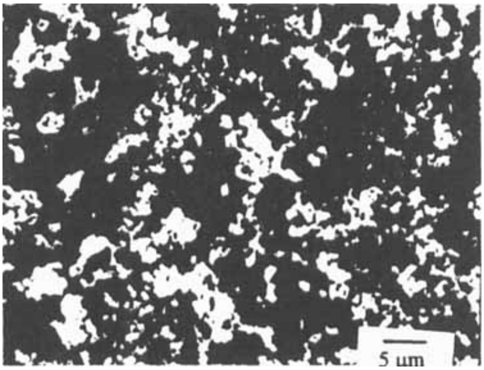


FIGURE 9 A picture of scanning electron microscopy of the prepared poly(*m*-methylaniline).

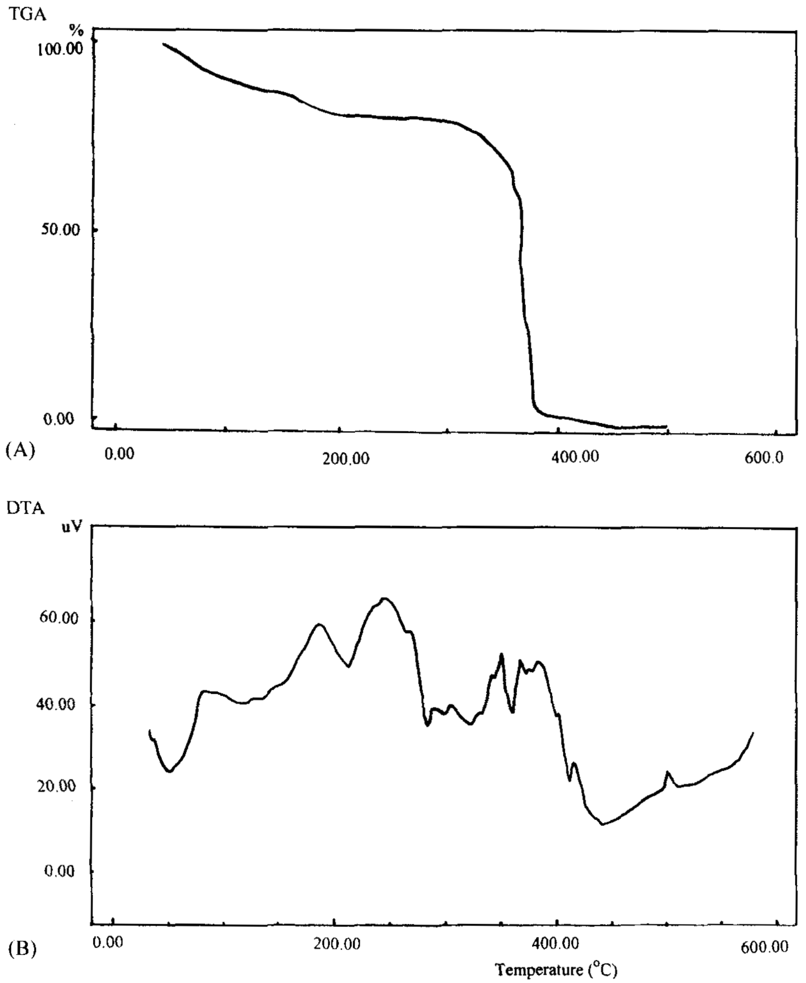


FIGURE 10 The thermal analysis of the prepared poly(*m*-methylaniline) (A): TGA and (B): DTA.

the methyl groups except of benzinoid structure are lost with weight loss % of 7.16 and the calculated one is 6.99%. The two exothermic peaks on the DTA curve in the temperature range 169–225°C and 255–280°C could be attributed to a reaction between methyl radicals. From TGA curve in the temperature range 250–350°C a weight loss of about 13.8% was found which could be attributed to the loss of

SCHEME 3

HCl molecules [35] with an endothermic peak at 288–360°C in the DTA curve. The calculated weight loss for this stage is 12.96% which confirms the estimated one. Above 350°C, all the polymeric segments of the structure (A) are destroyed, while the more stable quininoid segments, structure (B), remain (*cf.* Scheme 3).

The estimated mass loss for this step was found to be 82.0% which is in good agreement with the calculated mass loss 80.82%. From the DTA curve a broad endothermic peak is observed at 420°C. Above 450°C up to 580°C the residue of the polymer will lose small fragments on heating followed by melting as in Figures 10a and b.

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