

## Aging and thermal degradation of poly(*N*-methylaniline)

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### Abstract

The conductivity aging and thermal stability of poly(*N*-methylaniline) are reported. Poly(*N*-methylaniline) doped with chloride ion was electrochemically synthesized. The conductivity data obtained in the temperature range between 118 and 483 K are analysed by Arrhenius and Mott models to elucidate the conduction mechanism. The thermal degradation of both doped and dedoped samples of poly(*N*-methylaniline) in air and nitrogen atmosphere has been followed using thermogravimetric and differential thermal analysis techniques. The polymer is heat-aged at various temperatures and the aged samples are analysed by FT-IR, SEM and XRD. The thermogravimetric data are further analysed by three different methods: Horowitz and Metzger [Anal. Chem. 35 (1963) 1464], Coats and Redfern [Nature 201 (1964) 68], Chan et al. [Synth. Met. 31 (1989) 95] to evaluate the energy of activation. The applicability of the three methods for the evaluation of kinetic parameters is discussed. © 2003 Elsevier B.V. All rights reserved.

**Keywords:** Conducting polymer; Poly(*N*-methylaniline); Aging; Thermal degradation; Activation energy

### 1. Introduction

A knowledge of thermal stability of conducting polymers is important for their use in many practical applications. While the synthesis, structure and redox properties of the electroactive polymers have been reported extensively, there have been only few systematic studies on their aging and thermal degradation behaviour. There can be two strategies in the description of the aging of conducting polymers. The conduction models describe the electrical aging of conducting polymers in a quantitative manner [1]. On the other hand, the thermogravimetric data can be used to explain stability in terms of the structural changes in the polymer during thermal aging [2]. A combined use of both the approaches will be helpful not only to assess but also to devise ways to improve the stability of the conducting polymers.

A survey of literature reveals that most of the conductivity and thermal aging studies have been mainly made on polyacetylene [3,4], polyaniline doped with various counter ions [5–18], polypyrrole and polythiophene [19]. The objective of this report is to discuss the conductivity aging and thermal stability of poly(*N*-methylaniline). Poly(*N*-methylaniline)

and its sulfonated analogue have been recently characterized as cathode active materials in rechargeable batteries in this laboratory [20]. This polymer, although being a derivative of polyaniline, is different from polyaniline because of the block of the proton exchange sites by methyl substituents. As a consequence, the deprotonation of the imine group occurring during the second oxidation step of polyaniline does not occur in poly(*N*-methylaniline). In other words, poly(*N*-methylaniline) can be prevented from going to the completely oxidized pernigraniline base form thereby reducing the risk of electrochemical degradation [21,22]. Our recent study has shown that the redox stability of poly(*N*-methylaniline) is more than that of its parent polymer, polyaniline [23]. In this context, it would be worthwhile to make a systematic report on the conductivity and thermal aging of this polymer.

### 2. Experimental

*N*-Methylaniline (SRL) was purified by vacuum distillation. Poly(*N*-methylaniline) doped with chloride ion was obtained on a platinum substrate galvanostatically by applying a constant current of 2 mA cm<sup>-2</sup>. The electrolyte solution consisted of 1 M *N*-methylaniline and 1 M hydrochloric acid. Several runs of polymer preparation were

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needed to collect the polymer in bulk for the measurements of conductivity, infra-red spectroscopy, X-ray diffraction, thermogravimetry analysis (TGA) and morphological studies. The room temperature conductivity of the dry polymer sample was measured to be  $6.6 \times 10^{-4} \text{ S cm}^{-1}$ . Dedoped samples of the polymer are obtained by treatment with 0.1 M ammonium hydroxide for about 6 h.

The electrochemical preparation of the polymer was made using a scanning potentiostat/galvanostat (PAR Model 263A). The powder sample was pressed into a pellet using a Perkin Elmer hydraulic press by applying a pressure of 6 tonnes. The resistance of the pellet was measured in the temperature range between 118 and 483 K by two probe method using a digital multimeter (Model 195 A, Keithley Instruments Ltd., USA). A liquid nitrogen bath cryostat (Model DP-422, Scientific Solution, Mumbai, India) was used for low temperature resistivity measurements. The cryostat consisted of a sample chamber surrounded by vacuum isolation chamber. The sample holder was fitted with a platinum temperature sensor (Pt-100) and a  $25 \Omega$  heater. GE varnish (which has good thermal conductivity at low temperature) was used for mounting the sample. A mixture of toluene–ethanol (1:1) was used as the thinner. The electrical connections to the sample were made by conducting silver paint. The morphology was inspected by a scanning electron microscope (Hitachi S 450, 4 kV). The IR data were ob-

tained using a FT-IR spectrophotometer (JASCO-410). The thermograms were recorded at a heating rate of  $10 \text{ K min}^{-1}$  using a thermal analyser (NETZSCH-Geratebau GmbH STA 409 PC). The X-ray diffraction data were obtained (JEOL JDX-8030) at a rating of 40 kV, 20 mA. Ni-filtered Cu  $K\alpha$  radiation ( $\lambda = 0.154 \text{ nm}$ ) was used.

### 3. Results and discussion

#### 3.1. Temperature dependence of conductivity

Fig. 1 shows the variation of conductivity of poly(*N*-methylaniline) doped with chloride ion as a function of temperature. The increase in conductivity with rise in temperature from 118 to 293 K is typical of semiconductors. There is a very slow increase in the value between 293 and 351 K and thereafter the conductivity shows a gradual decrease between 351 and 483 K. This decrease in conductivity is attributed to the elimination of the dopant that leads to a decrease in the concentration of polarons. A support for the above inference is obtained from the thermogravimetry of poly(*N*-methylaniline) which will be described in detail later.

The temperature dependent conductivity data obtained in the range between 118 and 301 K can be fitted to Arrhenius

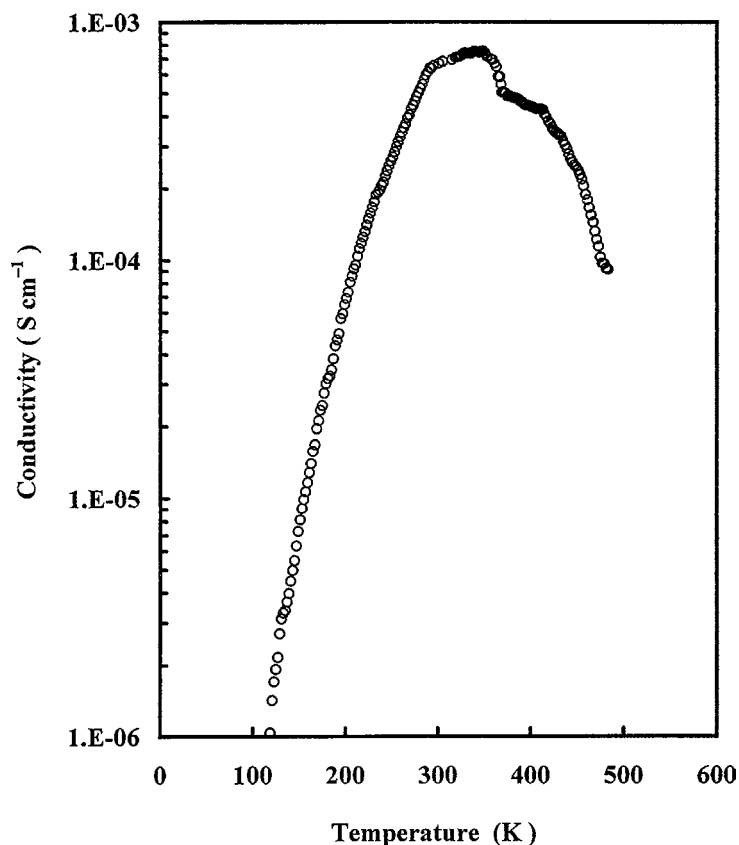


Fig. 1. Temperature dependence of electrical conductivity for poly(*N*-methylaniline) chloride.

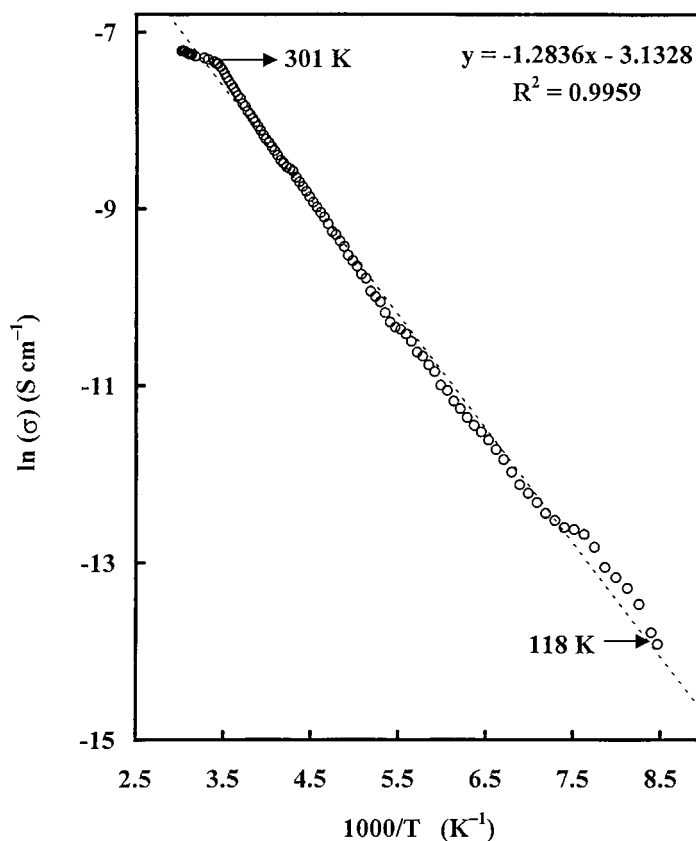


Fig. 2. Arrhenius plot of conductivity for poly(*N*-methylaniline) chloride.

equation of conductivity [24]

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad (1)$$

where  $E_a$  is the activation energy. A plot of  $\ln(\sigma)$  versus  $T^{-1}$  is a straight line (Fig. 2). The  $E_a$  value obtained from the slope is 0.11 eV.

The electrical transport mechanism can be due to Mott variable range hopping [25–27]. In this model, the conductivity is treated as temperature activated hopping from centre to centre. The lack of ordering in amorphous conducting polymers is expected to produce localized electronic states. An electron initially in a localized state can move by thermally activated hopping to another localized state and conduction occurs through variable range hopping of the electron between these localized states. The Mott model defines the relation between conductivity and temperature as below:

$$\sigma = K_0 T^{-1/2} \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right] \quad (2)$$

$$T_0 = \frac{16\alpha^3}{k_B N(E_F)} \quad (3)$$

$$K_0 = 0.39 \left[\frac{N(E_F)}{\alpha k_B}\right]^{1/2} \nu_0 e^2 \quad (4)$$

where  $\alpha^{-1}$  is the decay length of the localized state;  $\nu_0$  a hopping attempt frequency;  $N(E_F)$  the density states at the Fermi energy level;  $e$  the electronic charge;  $k_B$  the Boltzmann constant;  $T_0$  the Mott characteristic temperature and  $K_0$  the Mott characteristic conductivity parameter.

The conductivity data obtained for poly(*N*-methylaniline) in the range of temperature between 118 and 301 K are used to construct the Mott plot (Fig. 3). The Mott parameters  $T_0$  ( $1.3 \times 10^8$  K) and  $K_0$  ( $1.8 \times 10^9$  S cm $^{-1}$  K $^{1/2}$ ) are obtained, respectively, from the slope and intercept of the straight line plot. Substituting these values in equations and assuming a value of  $10^{12}$  s $^{-1}$  for  $\nu_0$  [1], the decay length  $\alpha^{-1}$  and  $N(E_F)$  are estimated to be 1.18 Å and  $8.57 \times 10^{20}$  eV $^{-1}$  cm $^{-3}$ , respectively.

There have been some reports on the temperature dependence of conductivity for polyaniline. Salaneck et al. studied the temperature dependence of conductivity in the range between 166 and 333 K for undoped and salt forms of polyanilines [28] and reported an activation energy of 0.05 eV for the dedoped form. The activation energy showed an increase from 0.037 to 0.493 eV when the doping pH was varied between 0 and 6.3 [29]. The electrical conductivity of poly(*N*-methylaniline) and its copolymer with aniline was measured by Langer over a temperature range of 200 to 400 K [30]. The activation energy of the conductance process was found to be a function of the relative concentration

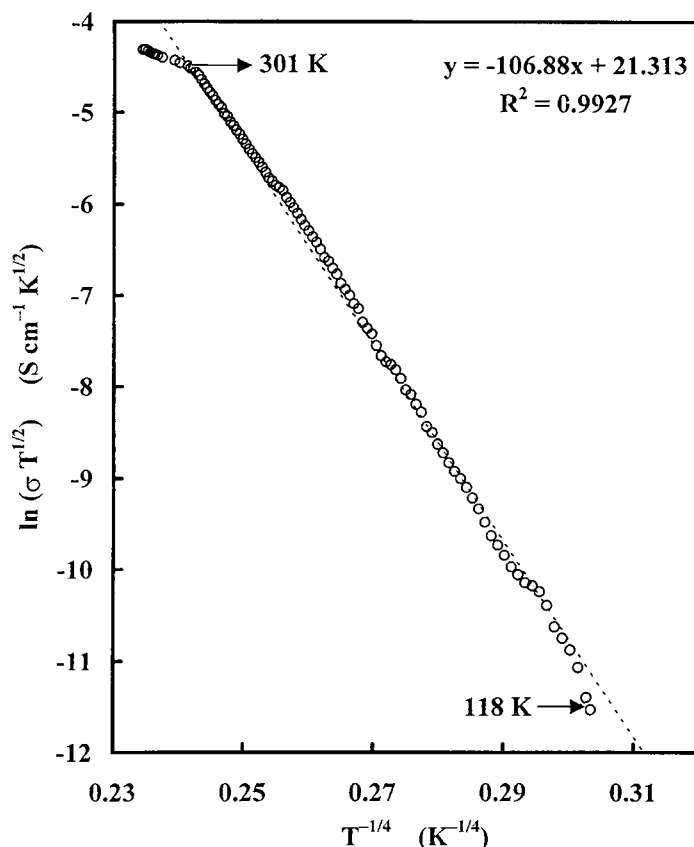


Fig. 3. Mott plot of conductivity for poly(*N*-methylaniline) chloride.

of *N*-methylaniline and aniline units in a polymer chain and it changed from 0.267 to 0.08 eV. Probst and Holze [31] suggested that the method of polymerization would be an important factor in modeling the conduction process. Borkar and Gupta [32] measured the electrical conductivity of poly(*N*-ethylaniline) in the range of temperature between 303 and 433 K and the activation energy of conductivity had been found to be 0.078 eV. The results suggested a polaron hopping conduction mechanism. The higher activation energy (0.11 eV) of poly(*N*-methylaniline) obtained in the present study is in agreement with its lower conductivity ( $6 \times 10^{-4} \text{ S cm}^{-1}$ ). It is inferred that the intrinsic charge carriers are less at room temperature in poly(*N*-methylaniline) than in polyaniline.

In spite of the availability of the large volume of literature on polyaniline, it is found that only very few reports exist on the applicability of variable range hopping model for polyaniline. In one of the earliest reports by Salaneck et al. [28], the  $T_0$  parameter for the salt form of polyaniline was given as  $7 \times 10^6 \text{ K}$ . Pingsheng et al. [29] have made a detailed study for polyaniline samples doped at different pH values. The  $K_0$  and also the  $T_0$  values increased with increasing pH. More recently Gosh et al. [17] have studied the transport properties of chloride doped polyaniline in the range between 1.8 and 300 K. The variation of conductivity was remarkably high at high temperature whereas it was very small at low temperature. From the analysis of the

results it was concluded that the high temperature conductivity obeyed the variable range hopping conduction mechanism. A cross-over from Mott ( $T^{-1/4}$ ) to Efros–Shklovskii ( $T^{-1/2}$ ) in temperature dependent conductivity was observed at 10 K.

It is difficult to make a direct comparison of the results obtained in the present study with those of literature. There are uncertainties in the value used for the phonon frequency ( $\nu_0$ ). For example Sato et al. [33] have used  $6 \times 10^{13} \text{ s}^{-1}$  for  $\nu_0$ . Gosh et al. [17] have used  $\nu_0$  values ranging from  $5 \times 10^8 \text{ s}^{-1}$  and  $8 \times 10^{12} \text{ s}^{-1}$ . A value of  $10^{12} \text{ s}^{-1}$  has been used in the present study [1]. Further the slope  $T_0$  was calculated from the plot of  $\log_{10} \sigma T^{1/2}$  versus  $T^{-1/4}$  instead of using the natural logarithmic function on the y-axis [33]. The slope obtained from  $\log_{10}$  plot can be 2 orders less than that obtained from the ln plot. The larger  $T_0$  and  $k_0$  values for poly(*N*-methylaniline) chloride compared to polyaniline chloride (Table 1) imply a short decay length and low density of states at the Fermi level.

### 3.2. Thermal stability

There are a number of reports on the thermal degradation of polyaniline [10–15,34–37]. In general, the neutral polymer showed a one-step weight loss while the doped polymer showed a two-step process. The first step was attributed to the loss of dopant counter anion and second step

Table 1  
A comparison of Mott parameters of poly(*N*-methylaniline) with those of polyaniline

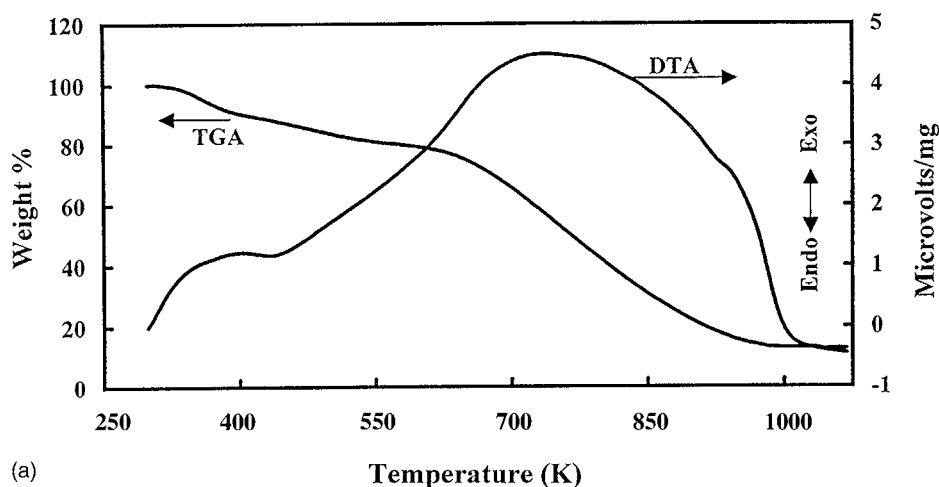
Polymer	Mott parameters		Density states at Fermi energy ( $\text{eV}^{-1} \text{cm}^{-3}$ )	Decay length, $\alpha$ ( $\text{\AA}$ )	Phonon frequency used, $\nu_0$ ( $\text{s}^{-1}$ )	Reference
	$T_0$ (K)	$K_0$ ( $\text{S cm}^{-1} \text{K}^{1/2}$ )				
Polyaniline	$7 \times 10^6$	–	–	–	–	[28]
Polyaniline chloride	$3.3 \times 10^6$ to $2.1 \times 10^{32}$	$6.9 \times 10^6$ to $2.3 \times 10^{10}$	$9.43 \times 10^{22}$	$1.15\text{--}3.14 \times 10^{-38}$	–	[29]
Polyaniline chloride (20% dopant concentration)	4529.21	–	$5.26 \times 10^{19}$	72	$5 \times 10^8$	[17]
Polyaniline chloride (40% dopant concentration)	$6.46 \times 10^5$	–	$4.88 \times 10^{17}$	65.5	$8 \times 10^{12}$	[17]
Poly( <i>N</i> methylaniline) chloride	$1.3 \times 10^8$	$1.81 \times 10^9$	$8.57 \times 10^{20}$	1.18	$1 \times 10^{12}$	Present work

to the decomposition of the backbone structure. The counter anion had significant effect on the thermal stability of the doped polymer [10]. For example, the methane sulphonate doped polyaniline was more stable (523 K) than the chloride and sulphate doped polymers (433 and 473 K, respectively). Polyaniline doped with *p*-toluenesulphonate ion [13] showed a two-step weight loss in nitrogen atmosphere but a three-step process in air. In nitrogen, the polymer had lost only 55% of its original weight at 923 K whereas it had completely decomposed in air. Also, other side reactions were evident from the second decomposition step at around 643 K in air, which was not observed in nitrogen atmosphere. Oxidation and possible structural rearrangements leading to loss in conjugation were suggested to be the primary cause for loss in conductivity on heat-aging in air.

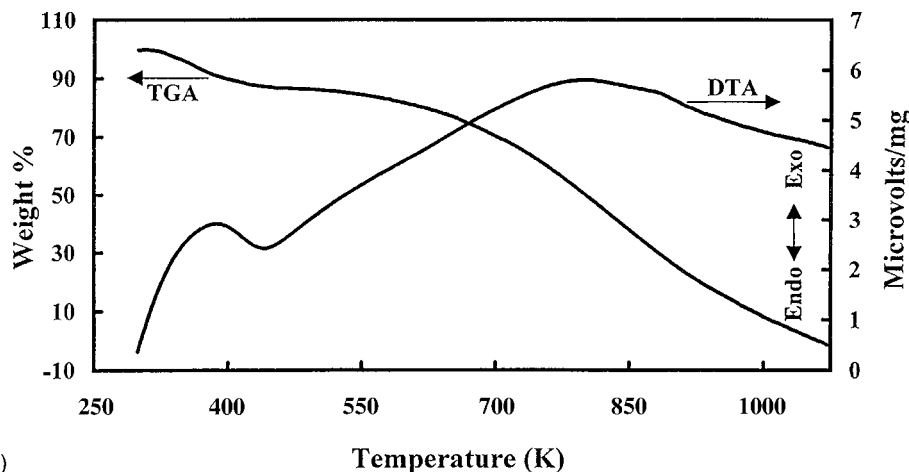
Figs. 4 and 5 show the thermograms of poly(*N*-methylaniline) obtained in air and N<sub>2</sub>, respectively. The TG in air shows a weight loss of about 10% below 393 K. Between 413 and 613 K, there is a gradual weight loss to less than

10% due to the dopant elimination. A prominent weight loss is observed between 623 and 968 K. This step is inferred to be due to the degradation of the polymer backbone structure. The thermograms in N<sub>2</sub> show a steady weight loss up to 723 K (25% weight loss) and thereafter the polymer decomposition occurs. The poly(*N*-methylaniline) can remain stable up to 743 K in air and 826 K in the presence of nitrogen. The DTA curve of poly(*N*-methylaniline) chloride shows mainly two broad exotherms. The first exotherm at 434 K indicates the elimination of dopant while the second one at 817 K corresponds to the degradation of the polymer backbone in N<sub>2</sub> atmosphere. The exotherms in air occur at lower temperatures of 293 and 743 K indicating that the degradation is rapid in the presence of air.

In order to further understand the nature of thermal decomposition of poly(*N*-methylaniline), the polymer sample was heated to various temperatures in air. Individual samples were used for heat-aging at 348 K for 140 h and at 373, 523, 623, 673 and 748 K for 1 h. The aged samples were



(a)



(b)

Fig. 4. TG and DTA curves of poly(*N*-methylaniline) in air (a) chloride doped and (b) dedoped samples.

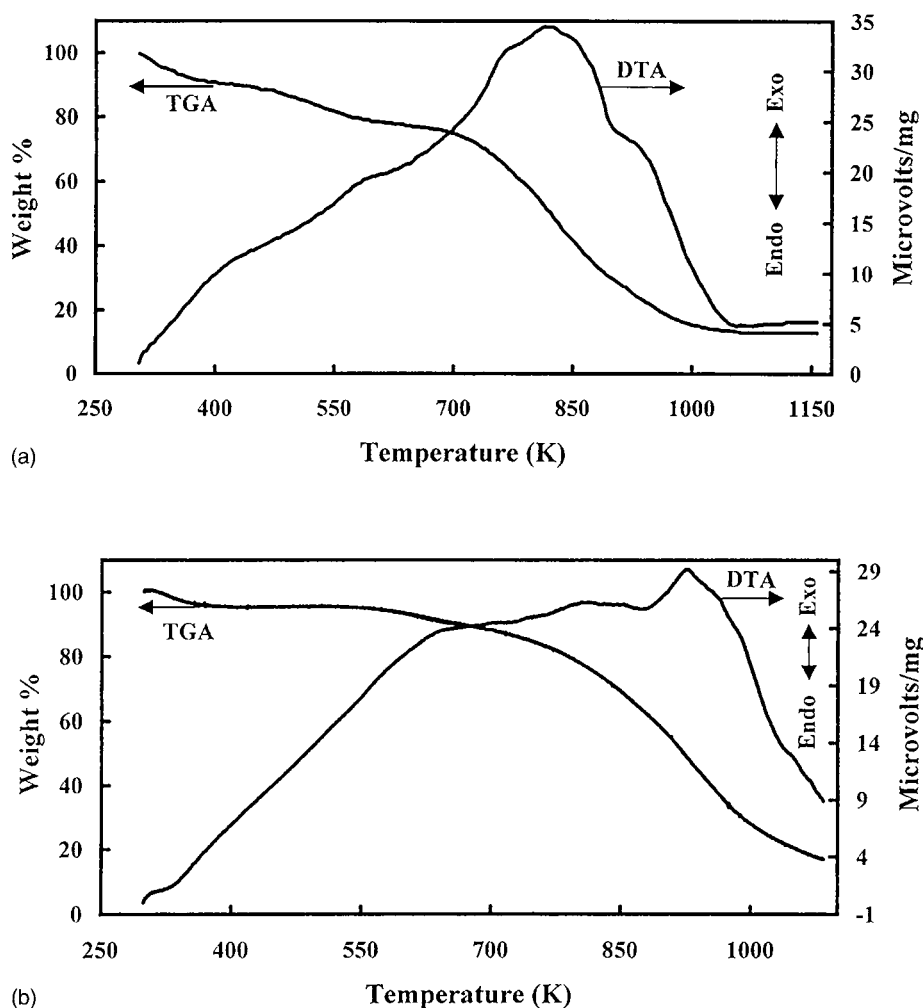


Fig. 5. TG and DTA curves of poly(*N*-methylaniline) in nitrogen (a) chloride doped and (b) dedoped samples.

analysed by FT-IR, scanning electron micrographs (SEM) and X-ray diffraction (XRD).

Fig. 6a shows the IR spectrum of the as-grown poly(*N*-methylaniline). The results are comparable with the data obtained from the literature reports on polyaniline [15] and poly(*N*-methylaniline) [38–40]. The peak at  $1084\text{ cm}^{-1}$  indicates that the polymer is doped by the chloride ion. The position of the band at  $869\text{ cm}^{-1}$  is characteristic of *para* disubstituted benzene rings that indicate the polymer formation. The presence of benzenoid ring is indicated by the band at  $1482\text{ cm}^{-1}$  and that of quinoid unit at  $1567$  and  $1383\text{ cm}^{-1}$ . The peak appearing at  $1287\text{ cm}^{-1}$  represents C–N stretching vibration. The bands at  $1228$  and  $693\text{ cm}^{-1}$  are assigned to the in-plane and out-of-plane bending motion of the aromatic ring.

The IR spectrum of the sample that is heat-aged at 373 K for 1 h (Fig. 6b) shows no major changes in the polymer structure. When the sample is heat-aged at 348 K (Fig. 6c) for about 140 h continuously, the IR spectrum shows only a very weak band for the presence of dopant ion. Also the benzenoid band at  $1482\text{ cm}^{-1}$  is less observable. Fig. 7a–e

shows the IR spectra recorded after the sample was heat-aged for 1 h at 373, 523, 623, 673 and 748 K. The results obtained after heat-aging at 523 K for 1 h show the presence of trace amount of dopant of the polymer sample with no prominent changes in the polymer structure. However, heat aging for 1 h shows the loss of benzenoid units in the polymer. Further tests at 673 and 748 K show that the polymer structure is remaining intact. The presence of the band at  $869\text{ cm}^{-1}$  in the IR spectrum of the sample heat-aged at 748 K shows that the *para* linkages are not broken. From the results, it is inferred that complete dopant elimination is possible if the sample is heated for 1 h at 623 K. Also at this temperature the polymer gets transformed from the conducting emeraldine salt form to the completely oxidized pernigraniline quinoid form. The polymer is thermally stable in the dedoped form up to 748 K which is in agreement with the results obtained from thermogravimetric studies.

The powder samples of poly(*N*-methylaniline) on heating above 600 K showed colour change from greenish black (as-grown) to dull brown indicating the possibility of a phase change as discussed below. The SEM and XRD patterns

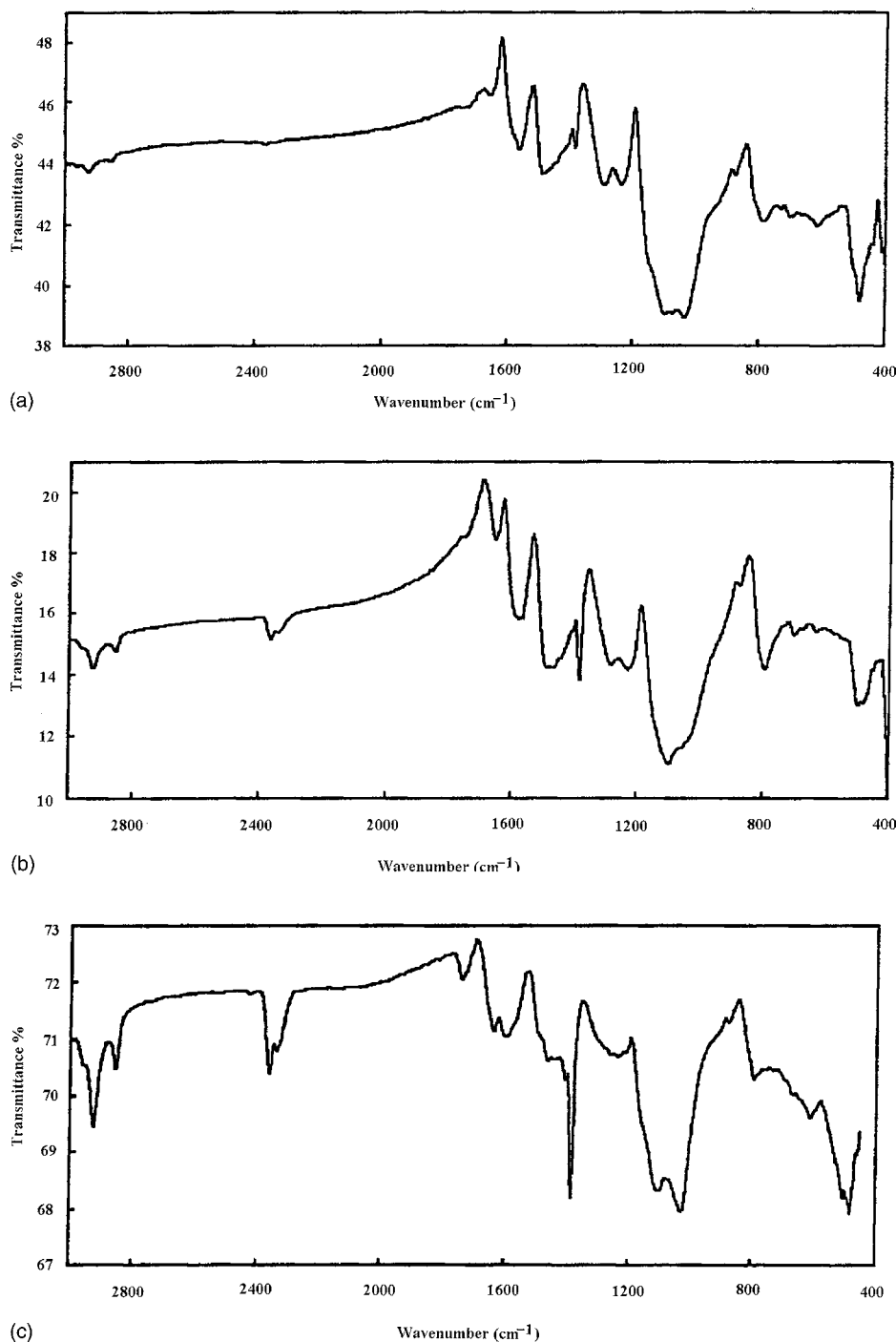


Fig. 6. (a) FT-IR spectrum of poly(*N*-methylaniline) chloride. (b) FT-IR spectrum of poly(*N*-methylaniline) chloride heat-aged at 373 K for 1 h. (c) FT-IR spectrum of poly(*N*-methylaniline) chloride heat-aged at 348 K for 140 h.

of the samples before and after heat-aging at 623 K are shown in Figs. 8 and 9. The SEM and XRD of the as-grown polymer show an amorphous structure for the polymer with no long-range order. However, the data obtained for the heat-aged sample at 623 K show the evolution of crystalline phases in the polymer. At about 623 K, the dopant anions get eliminated. The excessive dopant anions in the as-grown

polymer become disordered charge impurities making so ineffective in scattering the conduction electrons. On the other hand, the number of charged counter ion impurities are very much less in the heat-aged samples and hence resistive back scattering from them is essentially negligible. This results in a better crystalline order in the heat-aged samples.



### 3.3. Kinetic analysis of TG data

The data obtained from dynamic TG and DTA can be used to study the kinetics of a thermal decomposition reaction. Activation energy, pre-exponential factor and order of reaction can be derived. Knowledge of kinetic parameters, is one of the keys to determine the reaction mechanisms in solid phases. When changes in the mechanisms are observed, this can lead to a unique thermal behaviour and hence a better knowledge of the materials. Several math-

ematical methods are available in literature for calculating the kinetic parameters of solid state reactions [41–44]. The mathematical methods to process the TG data can be divided into model fitting and model-free methods [45]. The model fitting approach has the advantage that only one TG measurement is needed. However it suffers from an inability to determine the reaction model uniquely [46]. In spite of this unreliability, it is a quick method to become a first indication of possible values for the kinetic parameters. The alternative model-free methodology is based on isoconversional

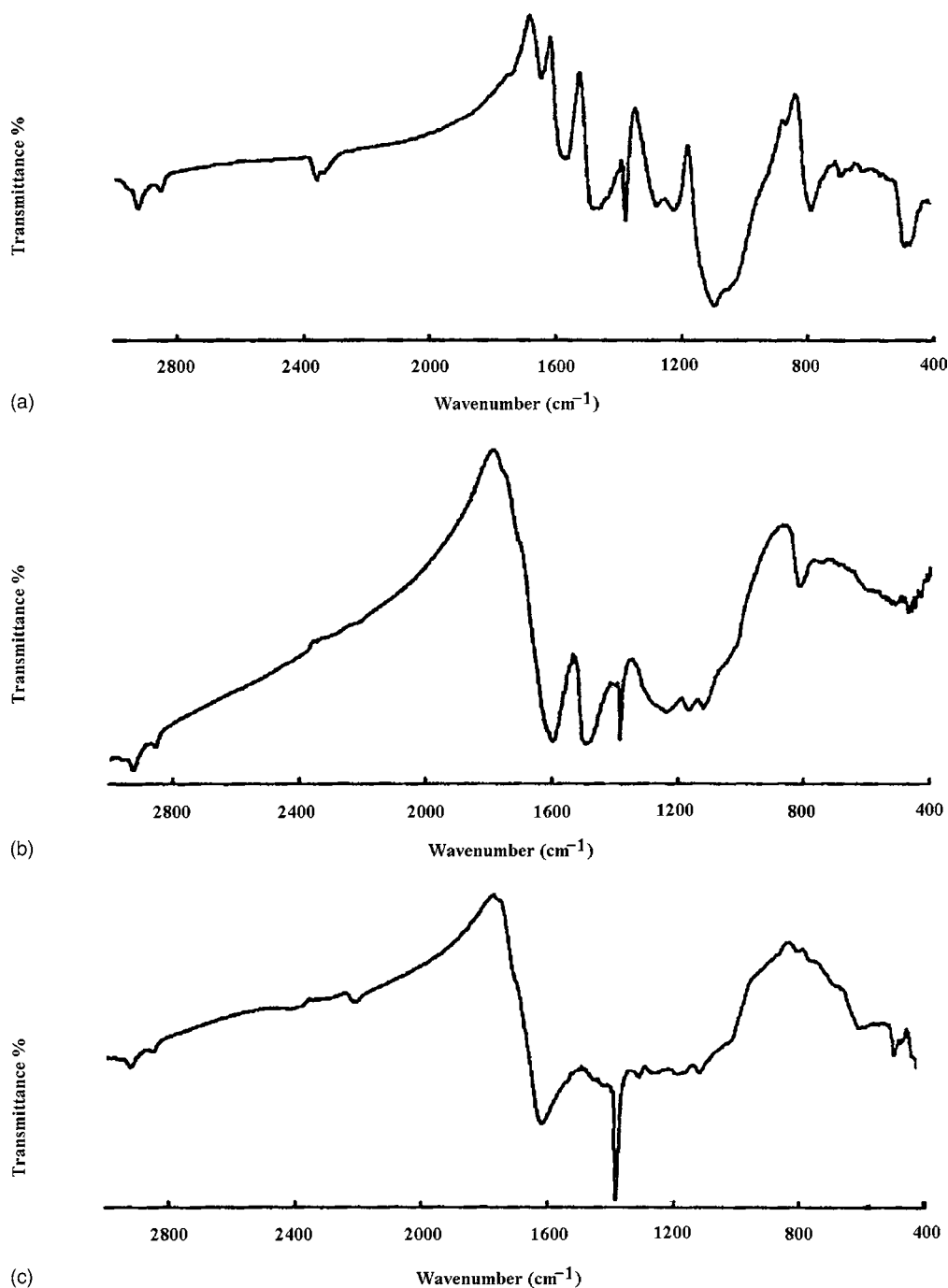


Fig. 7. FT-IR spectra of poly(*N*-methylaniline) chloride after aging at different temperature (a) 373 K, (b) 523 K, (c) 623 K, (d) 673 K and (e) 748 K.

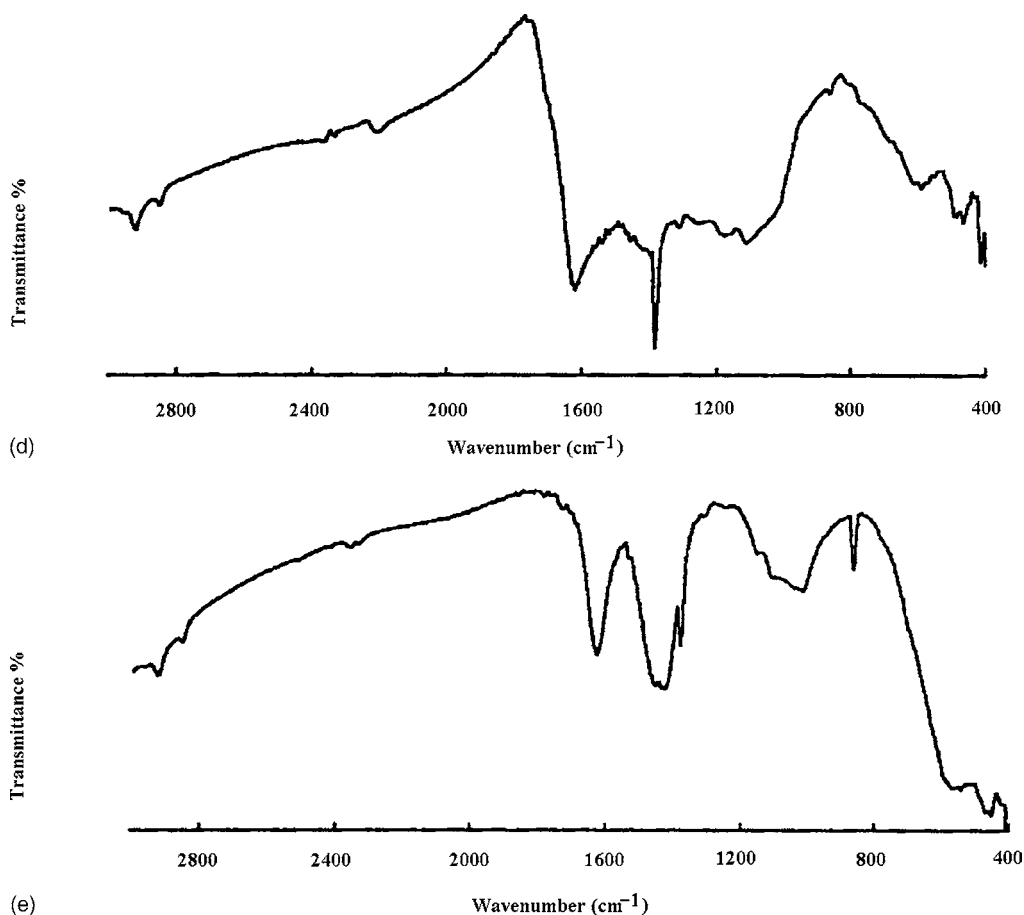


Fig. 7. (Continued).

principle. The use of these methods helps to avoid the problems that originate from the ambiguous evaluation of the reaction model. The model-free methodology allows the determination of the dependence of the activation energy on the extent of conversion and permits reliable mechanistic conclusions to be drawn. A negative aspect is the need for at least three TG experiments which makes it more time consuming.

The kinetics of heterogeneous condensed phase reactions that occur in non-isothermal conditions is usually described by the equation given below [47,48]:

$$\beta \left( \frac{d\alpha}{dT} \right) = Af(\alpha) \exp \left( -\frac{E}{RT} \right) \quad (5)$$

where  $\alpha$  is the degree of conversion,  $T$  is the temperature,  $\beta$  is the linear heating rate (constant),  $A$  is the pre-exponential factor,  $E$  is the activation energy,  $R$  is the gas constant, and  $f(\alpha)$  is the differential conversion function (reaction model). From the above equation, it turns out that the kinetic triplet ( $A$ ,  $E$ ,  $f(\alpha)$ ) gives the kinetic description of a certain reaction. In order to determine this, various procedures were developed. These can be classified into three categories: differential, integral and the so-called other special methods [49]. In this study, we have used the following three methods to

evaluate the non-isothermal kinetic parameters from the TG data.

Horowitz and Metzger [44] derived an approximate integral method to extract pyrolysis rate parameters. The method involves plotting double logarithm of the reciprocal of the weight fraction of the reactant versus temperature. A reference temperature  $T_s$  is defined such that  $T = T_s + \theta$  where  $T_s$  is experimental temperature when  $w/w_o$  is equal to 0.368 for a first-order reaction. Using this approximation the following equation is obtained:

$$\ln \left( \frac{w}{w_o} \right) = - \left( \frac{ZRT_s^2}{qE_a} \right) \exp \left[ - \left( \frac{E_a}{RT_s} \right) \left( 1 - \frac{\theta}{T_s} \right) \right] \quad (6)$$

which can be simplified further to give

$$\ln \left( \ln \left( \frac{w_o}{w} \right) \right) = \left( \frac{E_a \theta}{RT_s^2} \right) \quad (7)$$

Thus, a plot of  $\ln(\ln(w_o/w))$  against  $\theta$  shows a straight line whose slope is  $(E_a/RT_s^2)$  for any single pyrolysis reaction which gives only gaseous products. The usefulness of these equations was demonstrated by their applicability to some polymeric systems.

Coats and Redfern [50] derived an expression for determining the energy of activation which contained the order

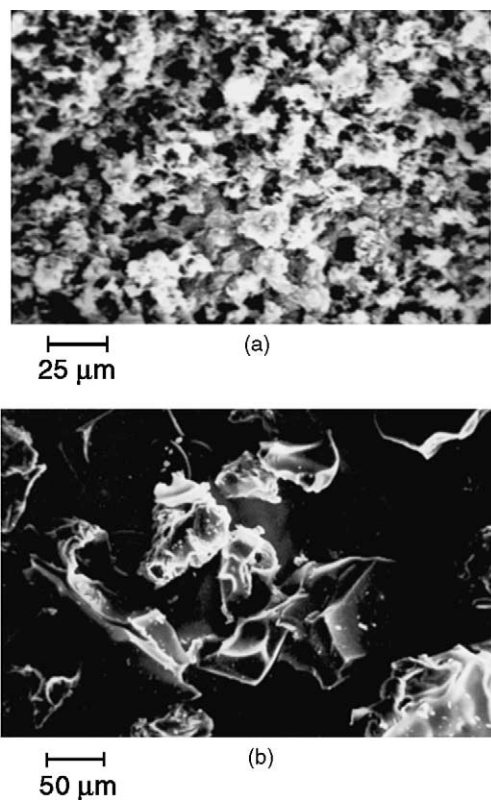


Fig. 8. Scanning electron micrographs of poly(*N*-methylaniline) chloride (a) as-grown polymer and (b) heat-aged at 623 K.

of reaction as an important parameter. The rate of disappearance of the reactant may be expressed by

$$\left(\frac{d\alpha}{dt}\right) = k(1 - \alpha)^n \quad (8)$$

where  $\alpha$  is fraction of reactant decomposed at time  $t$ ;  $n$  is order of reaction and  $k$  is rate constant given by the expression

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (9)$$

where  $A$  is frequency factor,  $R$  is universal gas constant and  $E_a$  is activation energy of the reaction. For a linear heating rate of, say,  $a$  degree per minute

$$a = \left(\frac{dT}{dt}\right) \quad (10)$$

combining Eqs. (8)–(10), rearranging and integrating:

$$\int_0^a \frac{d\alpha}{(1 - \alpha)^n} = \left(\frac{A}{a}\right) \int_0^T \exp\left(\frac{-E_a}{RT}\right) dT \quad (11)$$

$$\log_{10} \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)} \right] = \left\{ \log_{10} \left( \frac{AR}{aE_a} \right) \left[ 1 - \left( \frac{2RT}{E_a} \right) \right] \right\} - \left( \frac{E_a}{2.3RT} \right) \quad (12)$$

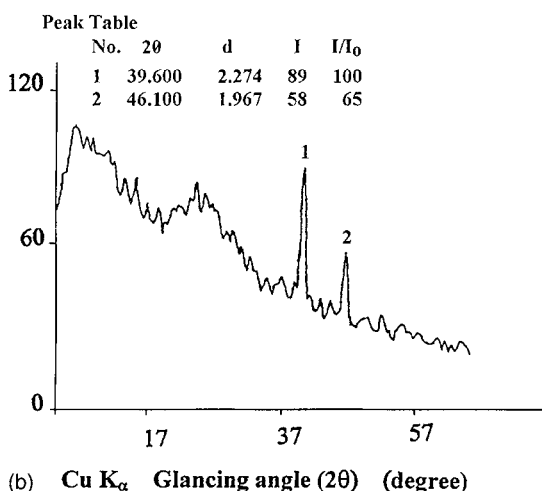
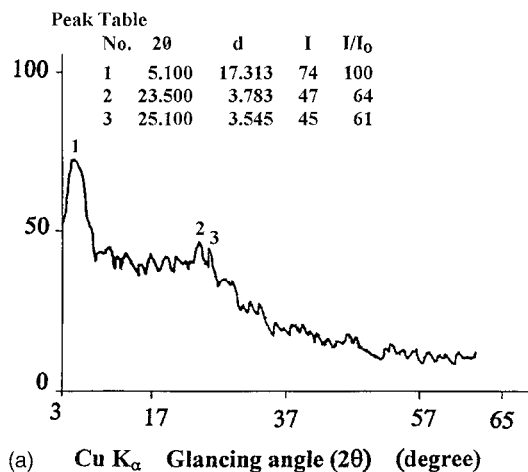


Fig. 9. XRD of poly(*N*-methylaniline) chloride powder (a) as-grown sample and (b) after aging at 623 K for 1 h.

For all values of  $n$  except  $n = 1$  in which case Eq. (11) after taking log, becomes:

$$\log_{10} \left[ -\log_{10} \frac{(1 - \alpha)}{T^2} \right] = \left\{ \log_{10} \left( \frac{AR}{aE_a} \right) \left[ 1 - \left( \frac{2RT}{E_a} \right) \right] \right\} - \left( \frac{E_a}{2.3RT} \right) \quad (13)$$

Thus, a plot of either  $\log_{10}\{1 - (1 - \alpha)^{1-n}/[T^2(1 - n)]\}$  against  $T^{-1}$  followed by the integration gives rise to the expression for  $n = 1$ . Thus, a plot of  $\log_{10}(-\log_{10}(1 - \alpha)/T^2)$  against  $T^{-1}$  should result in a straight line of slope  $-(E_a/2.3R)$ .

Chan et al. [51] followed a much simpler method for evaluating  $E_a$  of polyaniline. They used the Arrhenius plot of  $\ln(k/w)$  versus  $T^{-1}$  where  $k$  is rate of weight loss (in % (original weight) min<sup>-1</sup>) at temperature  $T$ , with 'w' as the corresponding weight (in % (original weight)) of the polymer remaining. The slope is equal to  $-(E_a/R)$ .

Figs. 10–13 show the plots obtained from kinetic analysis of the TG data of the doped and dedoped

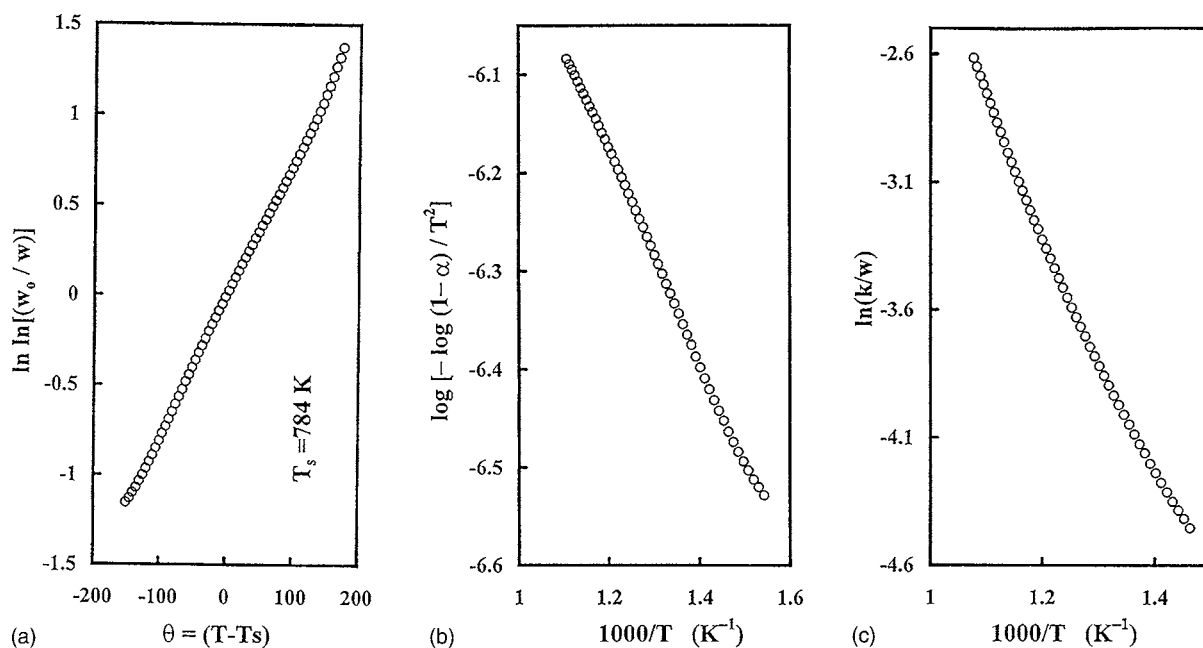


Fig. 10. Calculation of activation energy for chloride doped poly(*N*-methylaniline) in air: (a) Horowitz and Metzger method, (b) Coats and Redfern method and (c) Chan et al. method.

poly(*N*-methylaniline) samples in air and  $N_2$  atmosphere by the above three methods. The activation energy values derived from the above plots are tabulated (Table 2).

The calculation of different values for the kinetic parameters when applying different methods for processing the same experimental data is one of the controversial kinetic aspects of thermal analysis presented and discussed by Brown [52]. Recently, Budrugaec and Segal [47] made a detailed

analysis of the problems concerning the evaluation of the activation energy from non-isothermal data. They suggested that significant differences in the calculated  $E_a$  values are due to the way in which the relations that form the basis of the integral methods are derived. These relations are derived considering that the activation parameters do not depend on  $\alpha$  (degree of conversion). In the above review, the authors have shown that if  $E_a$  depends on  $\alpha$ , the use of different methods

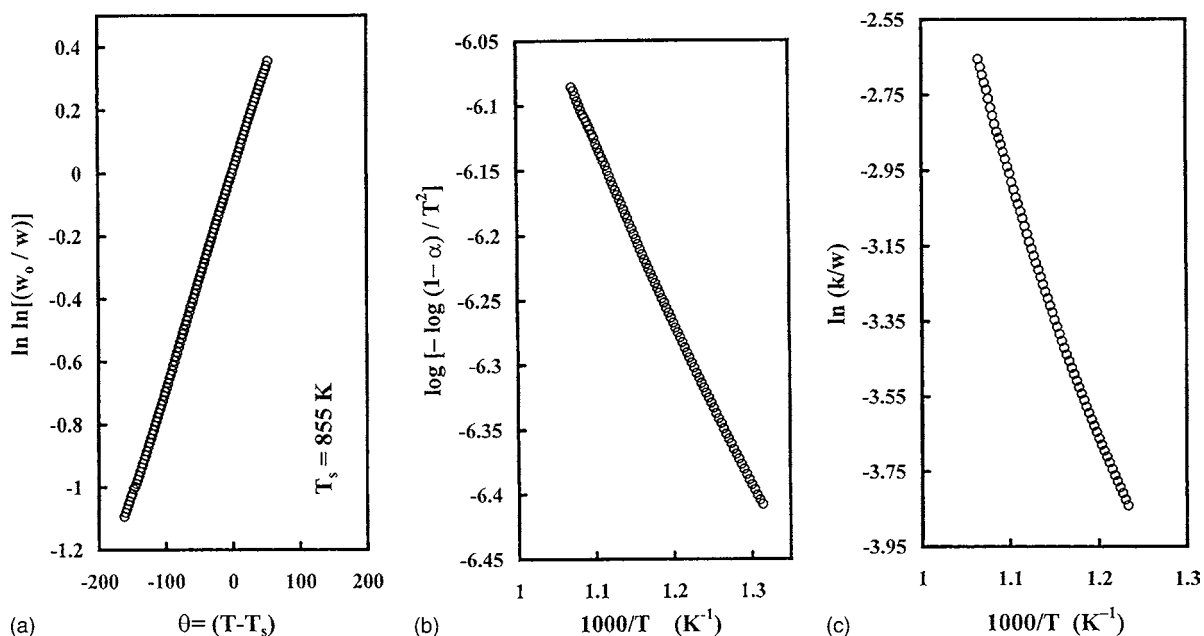


Fig. 11. Calculation of activation energy for dedoped poly(*N*-methylaniline) in air: (a) Horowitz and Metzger method, (b) Coats and Redfern method and (c) Chan et al. method.

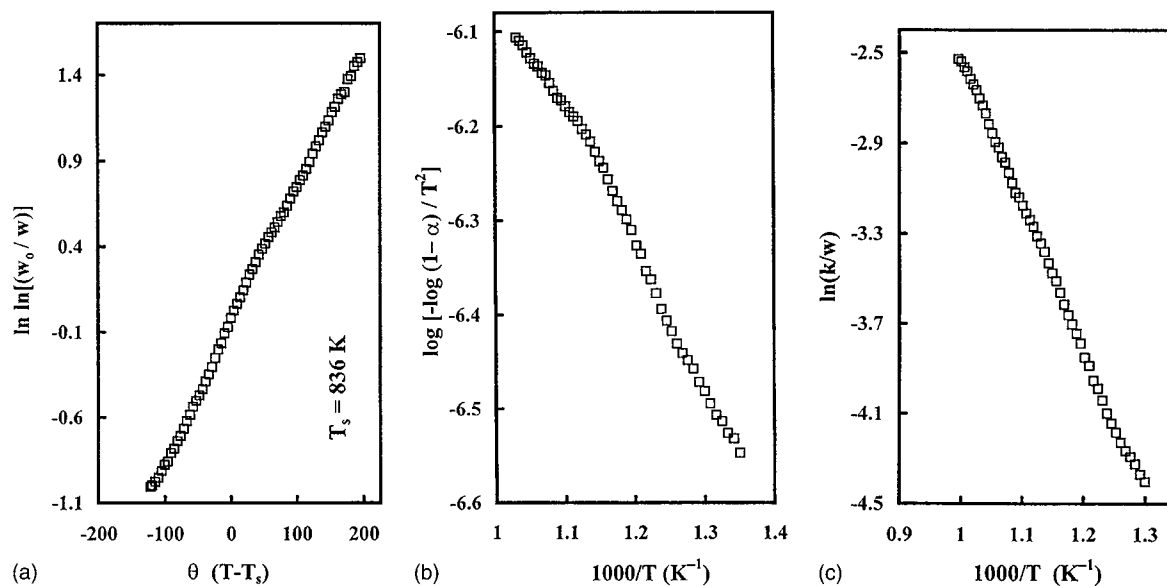


Fig. 12. Calculation of activation energy for chloride doped poly(*N*-methylaniline) in N<sub>2</sub>: (a) Horowitz and Metzger method, (b) Coats and Redfern method and (c) Chan et al. method.

leads to different values of the activation energy. Vyazovkin and Wight [46] have published a series of reports on the isothermal and non-isothermal reaction kinetics in solids. Celis et al. [45] have addressed the issue of overlapping in the thermal decomposition of a mixture of calcium and strontium oxalates. Albano et al. [53] have developed a methodology and software to evaluate the thermogravimetric data of polymers especially. The above studies have been made very recently which imply the renewed interest in this field.

In the present study, the kinetic analysis using the three methods (Horowitz and Metzger, Coats and Redfern and Chan et al.) shows that for each sample under study, a trend is found regarding the magnitude of the  $E_a$  values. The  $E_a$  values determined from the Coats and Redfern method are always lower while the values obtained by Chan et al. method are higher compared to the results obtained by Horowitz and Metzger method. The differences observed among the  $E_a$  values obtained using the three methods can be assigned

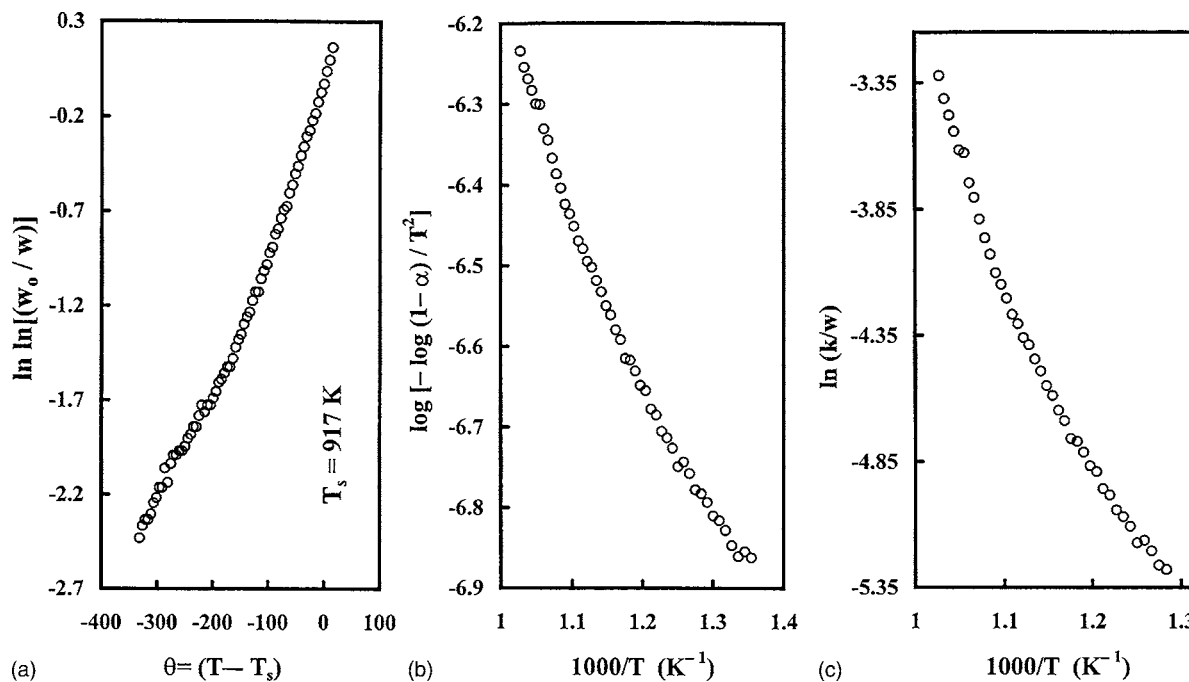


Fig. 13. Calculation of activation energy for dedoped poly(*N*-methylaniline) in N<sub>2</sub> air: (a) Horowitz and Metzger method, (b) Coats and Redfern method and (c) Chan et al. method.

Table 2

Activation energy ( $E_a$  in  $\text{kJ mol}^{-1}$ ) for doped and dedoped poly(*N*-methylaniline) in air and  $\text{N}_2$ 

Poly( <i>N</i> -methyl aniline) (experimental condition)	$E_a$ from Horowitz and Metzger method ( $\text{kJ mol}^{-1}$ )	$E_a$ from Coats and Redfern method ( $\text{kJ mol}^{-1}$ )	$E_a$ from Chan et al. method ( $\text{kJ mol}^{-1}$ )
Doped (air)	38.8	20.5	40.1
Dedoped (air)	41.3	25.8	58.7
Doped ( $\text{N}_2$ )	47.1	27.9	53.9
Dedoped ( $\text{N}_2$ )	49.6	37.3	62.6

to the different approximations of the temperature integral. These activation energies may not be the most correct, but give an idea on the range of kinetic parameters. For a serious kinetic study, the standard isothermal technique is still the recommended method. However, the present results can be treated empirically and can perhaps be used for comparative purposes. The activation energy data obtained by a particular method may still serve as a convenient means of comparing the relative thermal stabilities of the various polymers. From a complete analysis by the three methods in the present work, the Horowitz and Metzger method is recommended. The  $E_a$  values obtained by this method for the polymer decomposition step from the TG data of doped and dedoped polymers in either air or in  $\text{N}_2$  atmosphere are more consistent with each other than in the other two methods.

#### 4. Conclusions

The Arrhenius and Mott parameters obtained from the analysis of the temperature conductivity data for poly(*N*-methylaniline) suggest that the intrinsic charge carriers are less at room temperature resulting in a lower conductivity of the polymer compared to polyaniline. The conduction mechanism can be explained by 3D variable range hopping (VRH) instead of nearest neighbour hopping. Detailed thermal characterization of poly(*N*-methylaniline) shows complete dopant elimination at about 523 K and backbone rupture above 748 K. From the kinetic analysis, the dedoped sample in nitrogen atmosphere is inferred to be the most thermally stable.

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