

Thermal studies on polyindole and polycarbazole

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Abstract

The time and temperature dependences of conductivity of electrochemically prepared polyindole and polycarbazole perchlorates are analysed to understand the aging process and mechanism of conduction. Arrhenius and Mott plots suggest a variable range hopping (VRH) mechanism for polyindole and nearest-neighbour hopping for polycarbazole. The degradation behaviour has been studied by thermogravimetry (TG) and differential thermal analysis (DTA) techniques. The thermal reactions involve loss of dopant, followed by degradation of the polymer backbone. The decomposition temperatures of polyindole and polycarbazole are higher than the values reported in the literature for polyaniline, polypyrrole and polythiophene. The energy of activation for the polymer degradation process has been calculated using three methods and the results are compared. © 1998 Elsevier Science S.A.

Keywords: Polyindole; Polycarbazole; Thermal degradation; Arrhenius models; Mott models; Energy of activation

1. Introduction

The use of conducting polymers in many practical applications depends on their environmental, electrochemical and thermal stabilities. While their synthesis, structure and electrochemical properties have been studied extensively, the thermal characterization has received little attention. A survey of the literature indicates that most of the thermal degradation studies have been made with polyaniline doped with various counter ions [1–12]. A few papers report the thermal stability of polypyrrole and polythiophene [13–16].

The electrochemical synthesis of polyindole from acetonitrile [17] and polycarbazole from acetonitrile [18], dimethyl formamide [19] and aqueous-methanolic solution [20] have been reported in the literature. While few studies have been made on the electrochemical behaviour of polyindole [21–23], polycarbazole has been widely applied in electrocatalysis [18] and battery research [24,25].

In this study, the time and temperature dependences of conductivity have been made to understand the aging process and the mechanism of conduction. We report the results obtained on the thermogravimetry (TG) and differential thermal analysis (DTA) of electrochemically prepared polyindole and polycarbazole.

2. Experimental

Indole (SRL), carbazole (Merck), acetonitrile (Qualigens) and methanol (Qualigens) were purified and used. Anhydrous lithium perchlorate (Aldrich) dried for 24 h in vacuum was used as the supporting electrolyte in acetonitrile.

Polyindole and polycarbazole were synthesized as reported in the literature [17,20]. The synthesis was carried out at room temperature in N₂ atmosphere using a scanning potentiostat (PAR model 362) on a platinum electrode by electrolysis of a solution of acetonitrile containing 0.1 M indole and 0.1 M LiClO₄ at 0.8 V versus Ag reference. Potentiostatic oxidation of 5 × 10⁻³ M carbazole at 0.7 V versus Ag in a medium containing 75 vol.% methanol and 25 vol.% 1 M perchloric acid in water gave green polycarbazole film on a platinum electrode.

The resistance of bulk samples was measured by the four-probe method using a Keithley meter (195 A digital multimeter). No free-standing films could be obtained, but sufficient material was collected from three or four identical experimental runs of preparative electrolysis and the powder samples were pressed into pellets by applying pressure of about 7 Torr using a hydraulic press. Two contact copper leads were made using silver conducting paste and the resistance was measured at room temperature. The conductivity of polyindole perchlorate was found to be 1.5 × 10⁻² S cm⁻¹ and that of polycarbazole perchlorate to be 5 × 10⁻⁴ S cm⁻¹.

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The thermograms were recorded using a thermogravimetric analyser (Simultaneous Thermal Analysis System 1500, UK) in the presence of air/nitrogen atmosphere.

3. Results and discussion

3.1. Time dependence of conductivity

Very few studies have been found in the literature on the aging of conducting polymers. In particular, Mohammad et al. [26] have made some interesting observations on the decay of conductivity in ambient and dry conditions for polyacetylene, polypyrrole and polythiophene at 353 and 448 K. Their plots of conductivity versus time showed two distinct steps. Step one was attributed to the loss of counter ions by some complex reaction such as moisture compensation in ambient conditions, proton abstraction, electron transfer, decomposition and volatilization of products. Step two was attributed to the oxidative degradation reactions of the polymer backbone involving substitution, addition and chain scission.

The measurement of time dependence of conductivity is significant for two reasons:

- (i) the temperature dependence of conductivity can be measured in a reliable way only when time-dependent changes are slow on the time scale employed during temperature changes;
- (ii) the structural changes that may occur on annealing the sample at constant temperatures may be understood.

The annealing of polyindole perchlorate at 373 K did not lead to a drastic change in conductivity even after 50 h of standing. Hence further aging tests were carried out at 423 K. Fig. 1(a) and (b) shows the variation of resistance with time at an annealing temperature of 423 K for perchlorate-doped polyindole and polycarbazole, respectively. Both

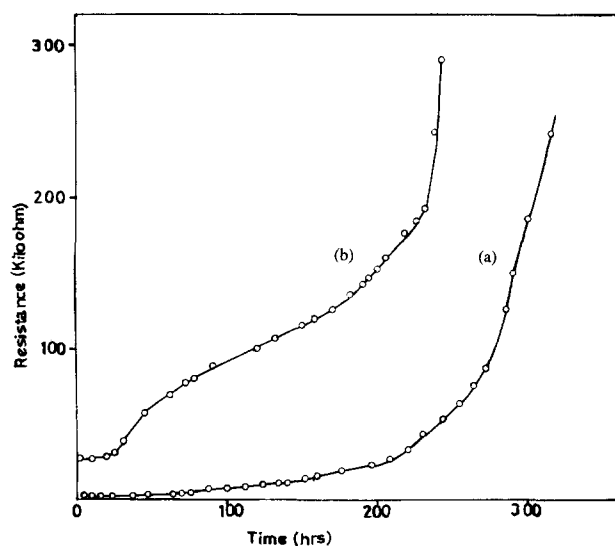


Fig. 1. Change in resistance at 423 K with aging time for (a) polyindole perchlorate and (b) polycarbazole perchlorate.

curves show two distinct steps of loss in conductance. A slow and gradual change in resistance occurs up to about 185 h and thereafter a rapid increase in resistance is observed. After about 300 h, a microscopic examination of the pellet showed thin cracks being developed, indicating the loss of mechanical strength as a result of aging at this temperature. The initial loss in resistance corresponding to the first step is due to the elimination of the dopant as judged from the IR spectra of the aged sample not showing the characteristic bands for the perchlorate ion at 1140, 1090 and 630 cm^{-1} . The second step is inferred to be due to the structural reorganization that may occur as a result of the loss of dopant and loss in conjugation of the polymer backbone.

3.2. Temperature dependence of conductivity

In general, conducting polymers behave like semiconductors in the temperature dependence of conductivity [27]. A few exceptions, however, have been reported. Park et al. [28] have reported that polyacetylene doped with ferric chloride showed anomalous behaviour. The conductivity gently increased as the temperature decreased in the range of 220–300 K. Reghu and Subramanyam [29] reported that lightly and moderately doped polypyrrole films showed abrupt increase in conductivity with decreasing temperature in a very low temperature region below 5 K. They explained the phenomenon by a tunnelling transport. Sato et al. [14] reported that the conductivity of a polypyrrole film doped with PF_6^- ions showed a metallic-like temperature dependence below 20 K.

In this study, the conductance measurements have been made in the range of temperature between 308 and 458 K and it should be mentioned here that this temperature interval is generally not enough to determine in detail the transport mechanism. Fig. 2(a) and (b) shows the variation of conductance of polyindole perchlorate and polycarbazole perchlorate, respectively. The increase in conductance with rise in temperature is typical of semiconductors. The decrease in conductivity at temperatures above 423 K is attributed to the elimination of the dopant that led to a decrease in the concentration of polarons.

In semiconductors, the conductivity around room temperature follows the well-known Arrhenius law [30]:

$$\sigma(T) = \sigma_0 \exp(-E_g/2kT) \quad (1)$$

where E_g is the activation energy of conductivity.

A plot of $\ln(R_0/R)$ versus T^{-1} is a straight line (Fig. 3). The E_g values obtained from the slopes are 0.24 and 0.99 eV for polyindole and polycarbazole, respectively. These values are higher compared to those of some of the well-known conducting polymers reported in the literature [11,13,31,32] (Table 1). In general, films with high conductivity exhibit thermal activation behaviour with a very low activation energy [33]. Choi et al. [32] have recently analysed the temperature dependence of electrical conductivity for the pressed pellet of polyindole (BF_4^-) in the range of temper-

Table 1
Reported E_g values of some conducting polymers

Polymer-dopant	Conductivity (σ) ($S\text{ cm}^{-1}$)	Temperature range (K)	E_g from Arrhenius plot (eV)	Ref.
Polyaniline-sulfate	0.3	166–333	0.100	[11]
Polythiophene-tetrafluoroborate	60	125–500	0.014	[13]
Polypyrrole-perchlorate	10	200–500	0.053	[31]
Polyindole-tetrafluoroborate	3.7×10^{-3}	182–400	0.400	[32]
Polyindole-perchlorate	1.5×10^{-2}	308–450	0.240	this work
Polycarbazole-perchlorate	5.0×10^{-4}	308–450	0.993	this work

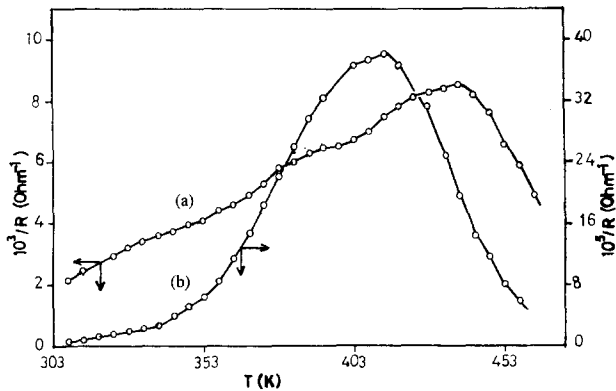


Fig. 2. Temperature dependence of electrical conductance of (a) polyindole perchlorate and (b) polycarbazole perchlorate.

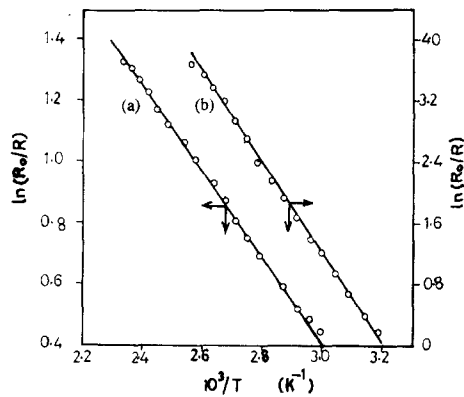


Fig. 3. Arrhenius plot of conductivity for (a) polyindole perchlorate and (b) polycarbazole perchlorate.

ature between 170 and 400 K. The E_g value obtained from the slope of the plot was 0.4 eV which is slightly higher than the value obtained in the present study. This difference may be attributed to the presence of two different dopants. The higher E_g values obtained for polyindole and polycarbazole in this study indicate that the intrinsic charge carriers are less at room temperature in the two polymers. This has led to a decrease in their conductivity values.

The midgap states could act as hopping centres and the electrical transport mechanism could be due to variable range hopping (VRH), as it is in an amorphous semiconductor. To obtain experimental evidence for validating this view the results are analysed to fit the Mott model [34,35] which

defines the relation between conductivity and temperature as below:

$$\sigma = K_o T^{-1/2} \exp[-(T_o/T)^{1/4}] \quad (2)$$

$$T_o = 16\alpha^3/k_B N(E_F) \quad (3)$$

$$K_o = 0.39[N(E_F)/\alpha k_B]^{1/2} \nu_o e^2 \quad (4)$$

where α^{-1} is the decay length of the localized state; ν_o is the hopping attempt frequency; $N(E_F)$ is the density of the Fermi energy level; e is the electronic charge; k_B is the Boltzmann constant, and T_o and K_o are the Mott characteristic parameters.

Fig. 4(a) shows the Mott plot for polyindole. The Mott parameters T_o (7.6×10^5 K) and K_o (3.5×10^5 $S\text{ cm}^{-1} K^{1/2}$) are obtained, respectively, from the slope and intercept of the straight line plot in the range of temperature between 308 and 438 K. Substituting these values in Eqs. (3) and (4) and assuming a value of $6 \times 10^{15} \text{ s}^{-1}$ for ν_o [36], the decay length α^{-1} and $N(E_F)$ are estimated to be 5.68 \AA and $1.33 \times 10^{21} \text{ eV}^{-1} \text{ cm}^{-3}$ states, respectively, and these are comparable with the values reported for polypyrrole containing various counter ions ($\alpha^{-1} = 5\text{--}15 \text{ \AA}$ and $N(E_F) = 3.7 \times 10^{21}\text{--}1.4 \times 10^{24} \text{ eV}^{-1} \text{ cm}^{-3}$) [14]. Maddison et al. [37] measured the electrical conductivity of lightly (8 S cm^{-1}) and normally (26 S cm^{-1}) doped polypyrrole *p*-toluenesulfonate films in the range of temperature between 4 and 350 K. They reported that the Mott VRH model was obeyed at higher temperatures for both types. The reported values of T_o , α^{-1} and $N(E_F)$ were, respectively, 4.6×10^4 K, 3 \AA and $1.67 \times 10^{23} \text{ eV}^{-1} \text{ cm}^{-3}$. A positive thermoelectric power and a negative Hall coefficient of the polypyrrole sample supported the hopping mechanism of conductivity.

In the case of polycarbazole, the Mott plot does show a straight line fit in the range of temperature between 308 and 383 K (Fig. 4(b)), but the slope and intercept give very high values of T_o and K_o , resulting in unrealistic values of α^{-1} and $N(E_F)$. The decay length (α^{-1}) is generally assumed to be about the length of the monomer [37]. In that case, the order of decay length must be polycarbazole > polyindole > polypyrrole, but this is not observed. Furthermore, the lower conductivity of polycarbazole is expected to give rise to a lower value of $N(E_F)$. The present results give rise to an $N(E_F)$ value higher by seven orders of magnitude.

The present results show that the electrical conduction of polyindole can be explained by variable range hopping

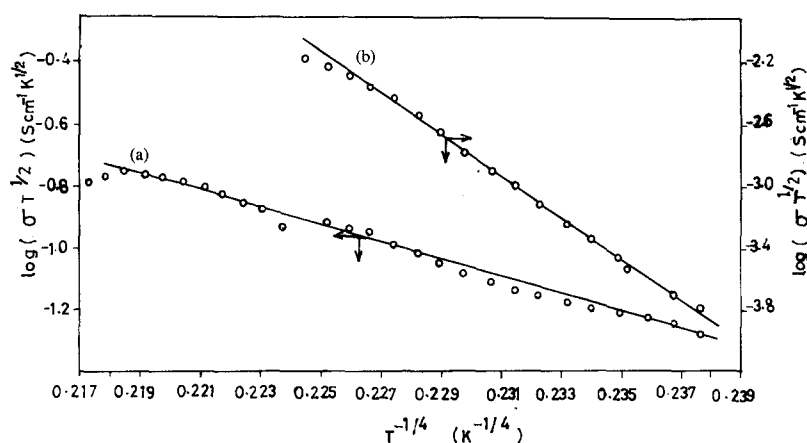


Fig. 4. Mott plot of conductivity for (a) polyindole perchlorate and (b) polycarbazole perchlorate.

(VRH) and in the case of polycarbazole the conductivity fitted the Arrhenius equation better than the Mott equation in the range of temperature studied, suggesting nearest-neighbour hopping.

3.3. Thermal degradation

3.3.1. Polyindole

Fig. 5 shows the TG and DTA curves of polyindole. Since simple heating of polyindole (ClO_4^-) in air resulted in bumping and mild explosion, only dedoped polyindole was subjected to the thermal analysis. The dedoping process involved repeated treatment with 5% sodium hydroxide solution and thorough washing in distilled water. The TG of polyindole in air shows an initial weight loss of less than 3% at temperatures below 343 K (step 1) and a prominent weight loss in the range of temperature between 673 and 923 K (step 2). On the other hand the DTA indicates three decomposition processes at 623, 797 and 885 K, respectively.

The small weight loss of 3% observed in the TG (step 1) could be due to a loss of moisture trapped in the polymer. The prominent weight loss (step 2) is inferred to be due to the degradation of the skeletal polyindole backbone chain structure which also corresponds to the step 2 and step 3 of the DTA (797 to 885 K). The small peak at 623 K in the DTA (step 1) could not be due to the presence of any residual dopant in the polymer as the perchlorate dopant elimination is generally observed at a temperature less than 573 K [4,10,38].

The TG of polyindole in nitrogen (Fig. 6(a)) is qualitatively similar to that of the curve obtained in air. Although the thermal degradation is slowed down, a composite wave is obtained in the range of temperature between 673 and 973 K. This result indicates that the products have not been formed due to the decomposition of the polymer involving oxidation processes.

The anodic oxidation of indole in acetonitrile gave *N,N*-diethyl-3-oxamylindole as the major product [39]. Surface-enhanced Raman scattering spectra of roughened silver electrodes immersed in indole solution at a stationary poten-

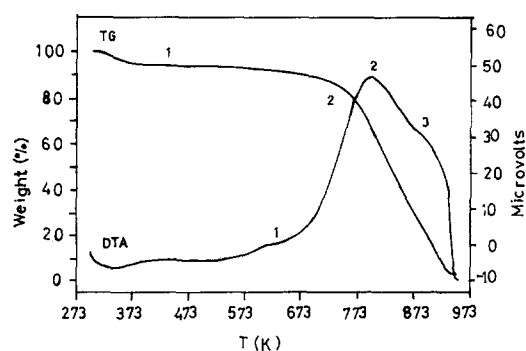


Fig. 5. TG and DTA curves of dedoped polyindole in air.

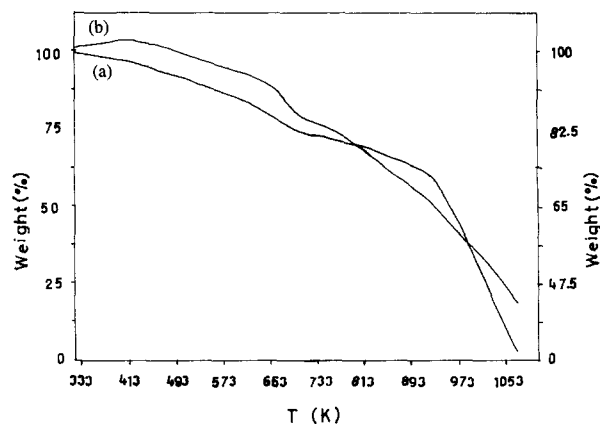


Fig. 6. TG curves of dedoped (a) polyindole and (b) polycarbazole in nitrogen.

tial electrode indicated that the electrode surface was covered partially by adsorbed indole molecules and partially by very thin layer of oligomers [40]. Recent literature reports indicate that the electropolymerization of indole in acetonitrile containing LiClO_4 does not always lead to a single product of doped polyindole. Jackowska et al. [41] have reported that three coloured compounds could be separated chromatographically from the electropolymerized product but they have not attempted to identify them. The cyclic voltammogram of polyindole film in the background electrolyte showed that the electron transfer process involved two electroactive

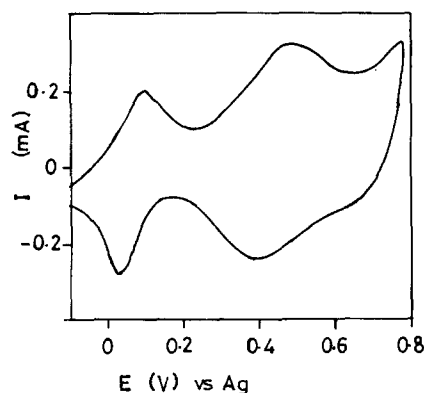


Fig. 7. Cyclic voltammogram of polyindole perchlorate deposited on a platinum substrate (300 mC) in acetonitrile containing 0.1 M LiClO₄ at a sweep rate of 50 mV s⁻¹.

species. The UV measurements of the solutions extracted using a microsyringe during polyindole deposition showed two absorption maxima at 375 and 425 nm [32]. Mackintosh and Mount [42] have recently found evidence for the formation of a trimer in addition to the polymer during the electropolymerization of indole 5-carboxylic acid in acetonitrile and both the products showed good electroactivity.

Our electrochemical studies with polyindole films obtained on a platinum substrate in acetonitrile containing 0.1 M LiClO₄ as supporting electrolyte show the presence of two electroactive species in the film (Fig. 7). However, the distribution of the two species depend on the synthesis conditions like indole concentration, polymerization potential and electrolyte concentration [43]. On the basis of the above data, the three peaks observed in the DTA of undoped polyindole in the present study have been attributed to the different products formed during electropolymerization of indole. Attempts to separate the three products for further identification are in progress.

3.3.2. Polycarbazole

The TG and DTA of polycarbazole perchlorate in air show two distinct steps (Fig. 8). The first step, involves a weight loss of about 25% in the temperature range 343 to 623 K. This step is inferred to be due to the elimination of the perchlorate dopant. The decomposition of polycarbazole backbone occurs in the range between 723 and 873 K. The TG of polycarbazole in nitrogen (Fig. 6(b)) shows a partial degradation (less than 50% weight loss at 1053 K) while in air the degradation is complete at a lower temperature of 873 K.

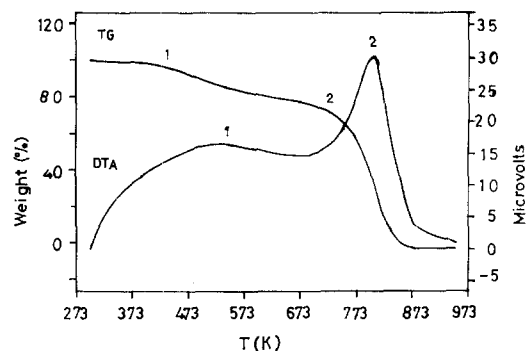


Fig. 8. TG and DTA curves of polycarbazole perchlorate in air.

It may be of interest to note that the decomposition temperature of pristine polycarbazole is higher than that of polyindole and also compared to the values reported in the literature for polyaniline, polypyrrole and polythiophene.

3.4. Kinetic analysis of TG data

The data obtained from dynamic TG can be used to study the kinetics of thermal decomposition reaction as a way to circumvent the need to perform multiple isothermal runs; activation energies, pre-exponential factor and order of reaction can be derived. However, these results may have to be treated empirically and can perhaps be used for comparative purposes rather than for calculation of absolute parameters. The activation energy data may serve as a convenient means of comparing the relative thermal stabilities of a series of substances. Several methods have been developed for the kinetic analysis of TG data but few attempts have been made to compare them critically [38].

Table 2 summarizes the results obtained from the kinetic analysis of TG data for the polymer degradation (step 2) in an oxygen atmosphere. Three methods have been employed for the calculation of energy of activation (Figs. 9 and 10). The parameters involved in the graphical plots are: θ = temperature (T) – reference temperature (T_s); w_0 is the initial weight of the sample; w_f is the final weight of the sample; w_t is the remaining weight loss percent of the sample; α is the fraction of the sample decomposed at time t (wt. loss/100); k is the weight loss percent of the sample; R is the gas constant and E_a is the energy of activation.

It is inferred that:

- (i) the values of energy of activation calculated using methods (a) and (b) (see Table 2) agree reasonably with

Table 2
Kinetic analysis of TG data of polyindole and polycarbazole

Method	X-axis	Y-axis	Slope	E_a (kJ mol ⁻¹)	
				Polyindole	Polycarbazole
(a) Horowitz and Metzger [44]	θ	$\ln \ln [(w_0 - w_t)/(w_i - w_t)]$	E/RT^2	85.5	114
(b) Coats and Redfern [45]	T^{-1}	$\log [-\log(1 - \alpha)/T^2]$	$-E/2.303R$	74.0	108
(c) Chan et al. [46]	T^{-1}	$\ln(k/w_t)$	$-E/R$	105.0	150

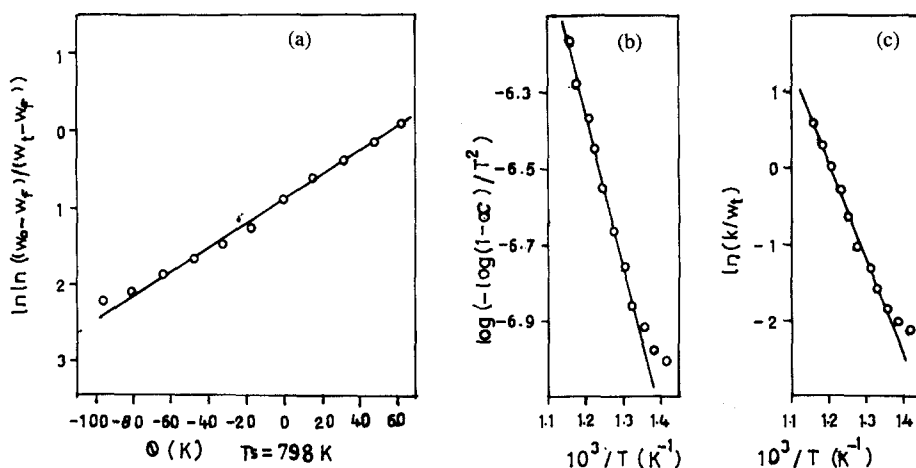


Fig. 9. Calculation of activation energy for polyindole degradation in air by (a) Horowitz and Metzger, (b) Coats and Redfern and (c) Chan et al. (see Table 2).

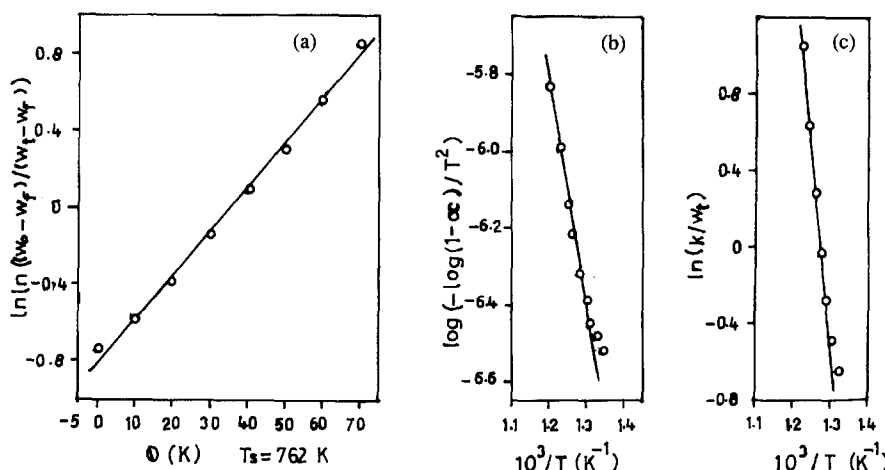


Fig. 10. Calculation of activation energy for polycarbazole degradation in air by (a) Horowitz and Metzger, (b) Coats and Redfern and (c) Chan et al. (see Table 2).

each other, although the value obtained by method (a) is slightly higher (about 13%);

(ii) the calculated values using method (c) are higher by 40% for both polymers;

(iii) polycarbazole is apparently more stable than polyindole;

(iv) a comparison of these values with those reported in the literature for polyaniline shows that polyindole and polycarbazole are thermally more stable than polyaniline ($E_a = 22\text{--}77 \text{ kJ mol}^{-1}$) [38].

4. Conclusions

Annealing of perchlorate-doped polyindole and polycarbazole samples at 429 K resulted in rapid increase in resistance after about 185 h, indicating the loss of dopant and loss in conjugation of the polymer backbone. Arrhenius and Mott plots in the temperature range between 308 and 458 K suggest variable range hopping for polyindole and nearest-neighbour hopping for polycarbazole. The kinetic analysis of thermo-

gravimetry data showed that polyindole and polycarbazole are thermally more stable than polyaniline.

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