A study on the temperature dependence of the electrical conductivity of a pyrolysed cyano-substituted polyamide derived from 1,4-bis(2-cyano-2-carboxyvinyl)benzene

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An unsaturated polyamide with pendant cyano groups was prepared from 1,4-bis(2-cyano-2-carboxyvinyl)benzene, and its electrical conductivity was studied, as a function of temperature, following pyrolysis at 550, 650 and 700°C. The results show that the unpyrolysed polymer has insulating properties at room temperature, whereas a dramatic increase of the electrical conductivity is observed with increasing pyrolysis temperature, ranging from 6.451×10^{-6} S cm^{-1} at 550°C to 8.130×10^{-1} S cm^{-1} at 700°C. The temperature dependence of the electrical conductivity of the pyrolysed polymer suggests that the resulting material has semiconducting properties. The observed electrical conductivity is thermally activated, and may be associated with both intermolecular and intramolecular conduction processes, with activation energies ranging from 0.13 to 0.02 eV for the intermolecular conduction process and from 0.26 to 0.05 eV for the intramolecular process, depending on the pyrolysis temperature that is used.

(Keywords: cyano-substituted polyamide; electrical conductivity; pyrolysis)

INTRODUCTION

The increasing number of scientists that are currently working in the field of electrically conducting polymers, is a result of the interest shown in these materials, both for potential technological applications and also in basic research. The broad nature of the subject makes it impossible to describe in detail any general references dealing with the subject, but a number of special reports[1-3] provide the interested reader with a general picture of the complexity of the subject, and the range of conductivities which may be achieved by chemical and physical treatment of the base polymers.

Aromatic polyamides are well known for their superior thermal stability properties. Some of them can be used as flame resistant fibres, and as high strength and high modulus fibres, as well as high performance plastics[4]. It is also known, that in order to achieve high electrical conductivities in organic polymers, the presence of extended π-electron orbitals is necessary[5]. In addition it is known that pyrolysis produces an extended conjugation of the π-electron orbitals, which in turn increases the number of charge carriers, and thus the electrical conductivity. The purpose of this present work is to investigate the temperature dependence of the electrical conductivity of a cyano-substituted polyamide over a range of different pyrolysis temperatures.

EXPERIMENTAL

1,4-Bis(2-cyano-2-carboxyvinyl)benzene (**1**) was used as the starting material for preparing a new class of unsaturated polyamides which contained pendant cyano groups[6]. *Scheme 1* outlines the preparation of compound **1**, the corresponding acid chloride (**2**) and a typical polyamide (**3**). Specifically, 1,4-benzenedicarboxyaldehyde reacted with cyanoacetic acid in the presence of glacial acetic acid to afford the dicarboxylic acid **1**. The latter reacted with thionyl chloride to yield the acid chloride **2**, while the polyamide **3** was prepared from the reaction of **2** with an equimolar amount of 4,4'-diaminodiphenylether, in the presence of triethylamine[6]. The monomers were characterized by both i.r. and ^{1}H n.m.r. spectroscopy, as well as by elemental analysis. Characterization of the polyamide was accomplished by i.r., d.t.a., t.g.a. and intrinsic viscosity measurements[6].

Upon curing at ~300°C, polyamide **3** afforded a crosslinked resin. This resin was stable up to ~400°C in N_2, and gave a char yield of 64% at 800°C[6].

The polyamide **3** was pressed to form pellets of 10 mm in diameter. The thickness of the pellets varied, but the average value was less than 1 mm. Each pellet was put into an alumina boat, which was then heated in a quartz tube, contained in a Leeds and Northrup furnace. Nitrogen of extremely high purity (99.999%) was passed through the quartz tube during the entire pyrolysis process. The samples were then left in the oven for 20 h after the preset pyrolysis temperature had been reached.

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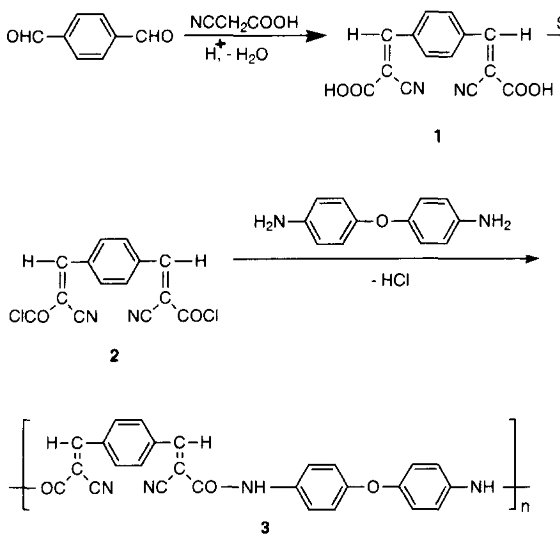

Scheme 1

Following pyrolysis, the pellet was mounted on the sample holder of a cryostat. The bulk electrical resistivity was measured using the Van der Pauw method[7]. The four contacts required were made on the circumference of the pellet using conductive silver paste. The temperature was varied over the range from 100 to 600 K. A constant current, obtained from a Hewlett–Packard Constant Current Supply (Model HP6181 DC), was allowed to flow through the sample and the voltage drop was measured with either a Fluke voltmeter or a Keithley electrometer (Model 610 CR), depending on the resistance of the sample. Specifically, the Keithley electrometer was used when the resistance of the samples, that had been pyrolysed at 550 and 650°C, showed a large increase (i.e. at low temperatures), and an input impedance for the measuring instrument of $10^{14}\,\Omega$ was necessary. The resistivity was calculated from the following relationship:

$$\rho=\frac{\pi t}{2\ln 2}\frac{(V_{3,4}+V_{4,1})}{I}f \qquad (1)$$

where t is the thickness of the pellet, $V_{3,4}$ and $V_{4,1}$ are the voltage drops between contacts 3 and 4 on one hand and between contacts 4 and 1 on the other hand, when a constant current is flowing through contacts 1 and 2, and 2 and 3, respectively. The correction factor f depends on the symmetry of the contacts on the pellet and is a function of the ratio $R_{3,4}/R_{4,1}$, where $R_{3,4}$ and $R_{4,1}$ are the resistances across contacts 3 and 4, and 4 and 1, respectively. This factor satisfies a rather complicated relationship[7]. If the ratio is approximately equal to unity, f is determined by a simplified relationship which was developed by Van der Pauw in his original work[7]. For the purpose of this present work, f has been calculated by letting the ratio $R_{3,4}/R_{4,1}$ vary in the fourth decimal digit. Furthermore, the ratio was kept below 1.2 by adjusting the position of the contacts on the circumference of the samples. Consequently, equation (1) is the rigorous relationship developed by Van der Pauw and is independent of sample shape. In this present study the average thickness t was taken as 1.5 mm, since pyrolysis increased the apparent volume of the pellet. The temperature was preset using an Oxford temperature controller, and when thermal equilibrium was established the resistivity of the sample was measured.

RESULTS AND DISCUSSION

An attempt was made to elucidate the structure of the residue obtained from the pyrolysis of polyamide **3** by using Fourier transform infra-red (*FT*i.r.) spectroscopy, as well as t.g.a. and d.t.a. measurements. *Figure 1* shows the *FT*i.r. spectra of both polyamide **3** and the residue resulting from its pyrolysis at 700°C for 20 h in a N_2 atmosphere. The polyamide displayed characteristic absorptions at 3445–3340 cm^{-1} (N–H stretching), 3070 and 1502 cm^{-1} (aromatic), 2209 cm^{-1} (C–N), 1670 cm^{-1} (C=O), 1628 cm^{-1} (C=C), 1532 cm^{-1} (N–H deformation and C–N stretching) and 1230 cm^{-1} (C–N stretching and N–H bending). In contrast, the pyrolysed sample did not display any absorption bands, thus confirming complete carbonization of the residue.

When polyamide **3** was subjected to pyrolysis in a N_2 atmosphere, it lost weight, but still yielded a residue that retained the dimensional integrity of the sample. Most of the weight loss occurred between 400 and 600°C, which was attributed to thermal degradation. As the pyrolysis was continued at higher temperatures, a reduced weight loss took place, which was confirmed by t.g.a. studies. It is believed that a progressive carbonization process occurs upon pyrolysing the polymer at relatively high temperatures in a N_2 atmosphere. *Figure 2* gives the t.g.a. traces of the samples that were obtained by pyrolysing polyamide **3** for 20 h in N_2, at temperatures of 550 and

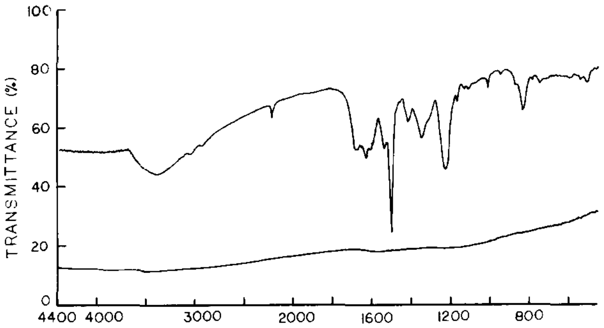

Figure 1 *FT*i.r. spectra of polyamide **3** before pyrolysis (top) and following pyrolysis at 700°C (bottom)

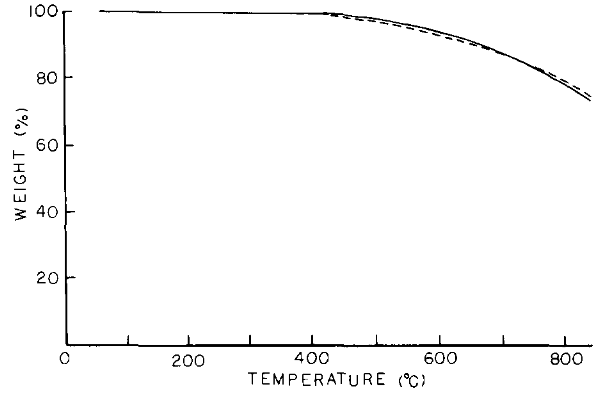

Figure 2 T.g.a. traces of polyamide **3** pyrolysed at 550°C (——) and 700°C (– – –)

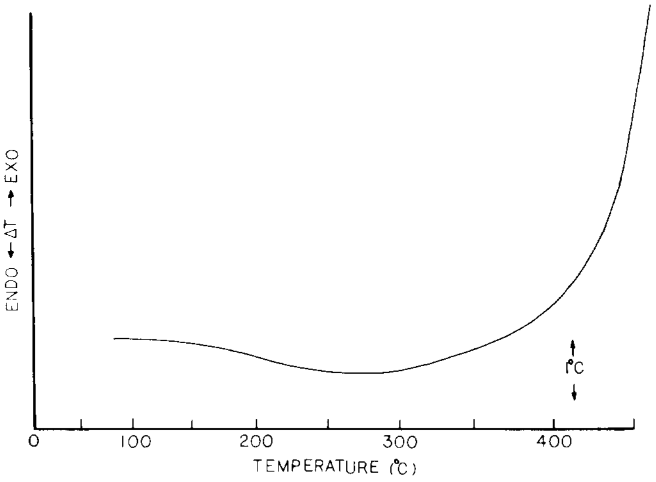

Figure 3 D.t.a. trace of polyamide **3** pyrolysed at 700°C

700°C. They started to lose weight at ~430°C, and afforded char yield of 76–78% at 800°C. The d.t.a. trace of the latter sample in N_2 (see *Figure 3*) showed a large exotherm above 400°C, which is attributed to its thermal degradation.

The room-temperature resistance of polyamide **3** was measured before pyrolysis, and a value $>10^{13}\,\Omega$ was found, which is the upper limit of the measuring capability of the apparatus used. Similar insulating behaviour for other polymers of this class have been reported by Keller[8] and Walton and Gratz[9]. This value suggests that the unpyrolysed polyamide **3** behaves as an insulator. This behaviour is typical of unprocessed or undoped polymers. Following pyrolysis at different temperatures the electrical conductivity increases. *Figure 4* shows the conductivity as a function of the measuring temperature, as deduced from resistivity measurements, for three different pyrolysis temperatures, namely 550, 650 and 700°C. It can be clearly seen that, for a given pyrolysis temperature, the conductivity increases with increasing temperature. This behaviour is typical of semiconductors. For the lowest pyrolysis temperature, the conductivity changes from $5\times10^{-8}\,\mathrm{S\,cm^{-1}}$ at 150 K to $8\times10^{-4}\,\mathrm{S\,cm^{-1}}$ at 570 K, i.e. a change of four orders of magnitude. The temperature dependence of the conductivity of the polymer that was pyrolysed at 700°C is not as strong as that found for the corresponding 550°C sample, although the conductivity has increased enormously, ranging from $1\times10^{-1}\,\mathrm{S\,cm^{-1}}$ at 100 K to almost $3\times10^{1}\,\mathrm{S\,cm^{-1}}$ at 570 K. The room temperature conductivities, measured on samples with pyrolysis temperatures of 550, 650 and 700°C, are 6.451×10^{-6}, 1.498×10^{-1} and $8.130\times10^{-1}\,\mathrm{S\,cm^{-1}}$, respectively.

In order to better understand the observed behaviour of the pyrolysed polymer, the results were analysed by three different methods. According to the first of these, namely the variable-range hopping model, developed by Mott and Davis[10], the conductivity follows the relationship

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^n\right] \qquad (2)$$

with σ_0 and T_0 as parameters. The exponent n takes the values of 1/2 or 1/4, with the former value corresponding to one-dimensional and the latter to three-dimensional hopping conductivity, respectively. By applying a non-linear, least-squares curve fitting computer program, it was possible to fit the experimental results to equation (2) for $n=1/2$ and 1/4. The results of this treatment for

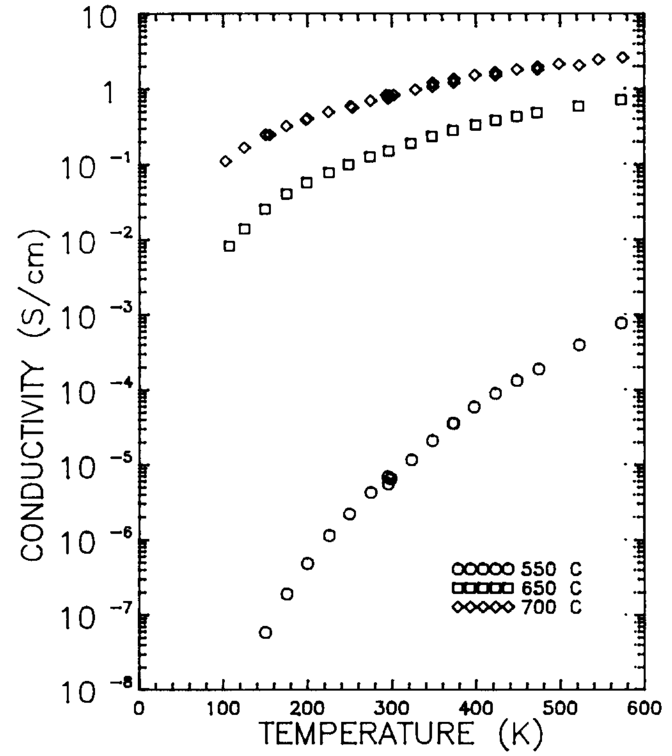

Figure 4 Temperature dependence of the electrical conductivity of polyamide **3** pyrolysed at different temperatures: (○) 550; (□) 650; and (◇) 700°C

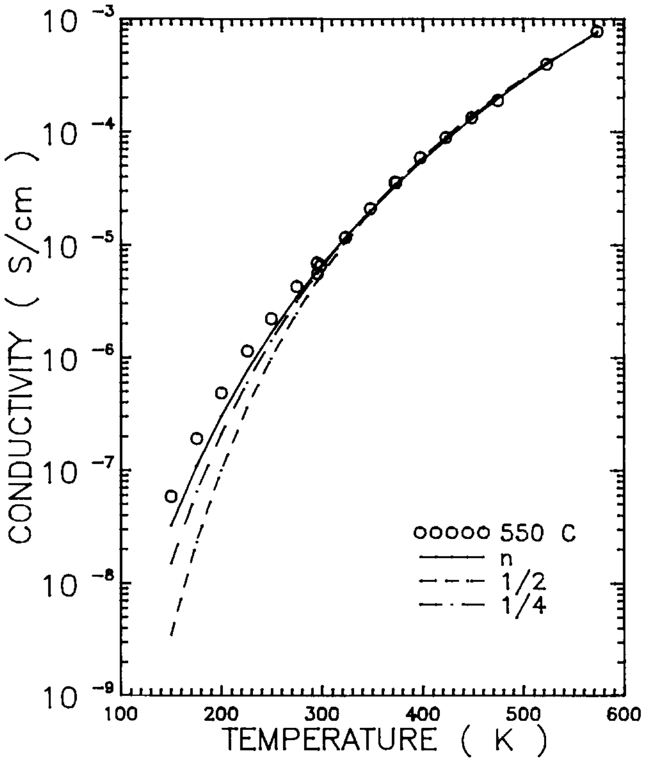

Figure 5 Non-linear least-squares fitting of the electrical conductivity of polyamide **3**, pyrolysed at 550°C, to equation (2): (○) experimental data; (——) n determined by the program; (- - -) $n=1/2$; and (— · —) $n=1/4$

pyrolysis temperatures of 550, 650 and 700°C are shown in *Figures 5*, *6* and *7*, respectively, where the dashed lines represent the fitting of the results to equation (2). It is obvious that this fitting fails to describe the results over the entire temperature region, being good only in the high-temperature region. The values of the parameters σ_0 and T_0 for $n=1/2$ and 1/4 are given in *Table 1*.

According to the second approach, a distribution of barrier heights between the allowed carrier states is assumed, and n in equation (2) may take any value between 0 and 1 (ref. 11). The results obtained by this treatment of the experimental data are shown by the continuous lines in *Figures 5–7* for the various pyrolysis temperatures. *Table 2* gives the values of the parameters σ_0, T_0 and n in equation (2) for these different temperatures. However, the values of these parameters are such that no rational relationship to the pyrolysis

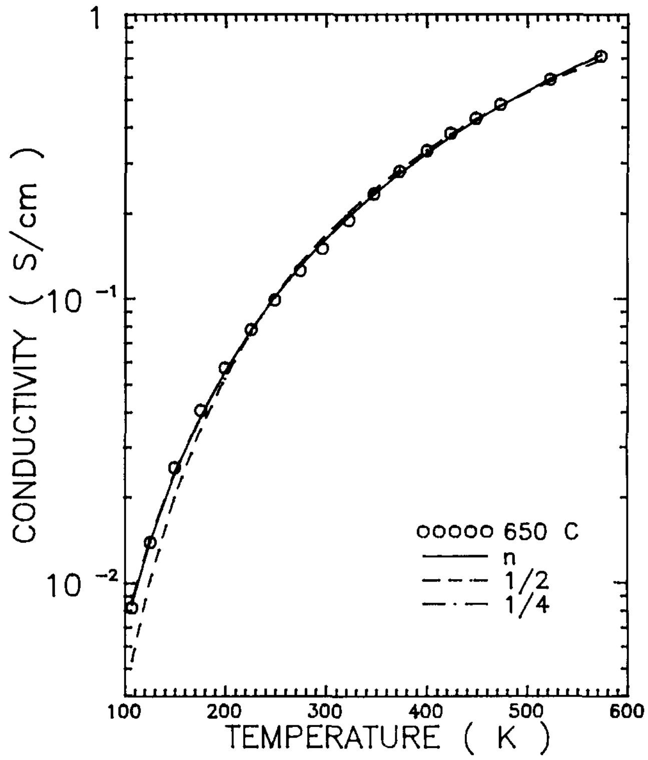

Figure 6 Non-linear least-squares fitting of the electrical conductivity of polyamide 3, pyrolysed at 650°C, to equation (2): (○) experimental data; (——) n determined by the program; (---) $n=1/2$; and (—·—) $n=1/4$

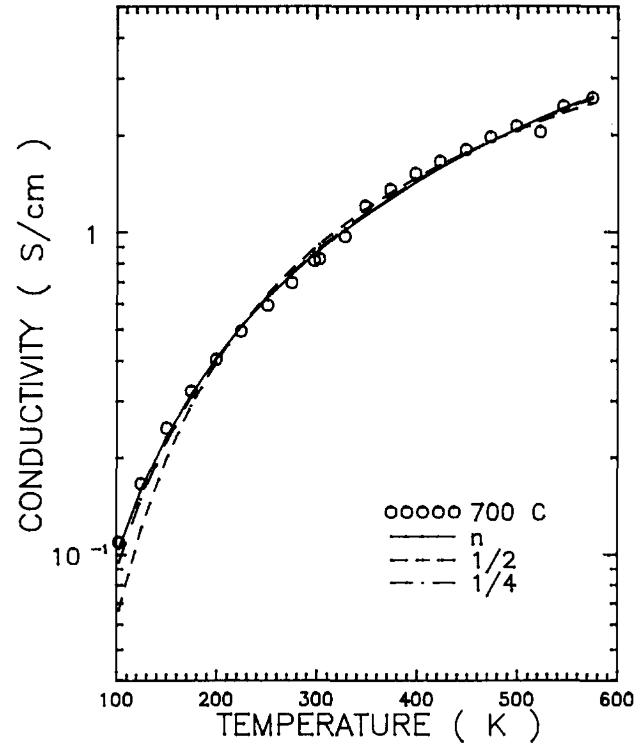

Figure 7 Non-linear least-squares fitting of the electrical conductivity of polyamide 3, pyrolysed at 700°C, to equation (2): (○) experimental data; (——) n determined by the program; (---) $n=1/2$; and (—·—) $n=1/4$

Table 1 Values of the parameters σ_0 and T_0 in equation (2) for $n=1/2$ and 1/4

Pyrolysis temperature (°C)	$n=1/2$ σ_0 (S cm^{-1})	$n=1/2$ T_0 (K)	$n=1/4$ σ_0 (S cm^{-1})	$n=1/4$ T_0 (K)
550	2.80×10^{2}	94 618	4.85×10^{8}	3.14×10^{8}
650	2.82×10^{1}	7878	3.54×10^{3}	2.99×10^{6}
700	3.57×10^{1}	4051	1.22×10^{3}	8.24×10^{5}

Table 2 Values of the parameters σ_0, T_0 and n for different pyrolysis temperatures

Pyrolysis temperature (°C)	σ_0 (S cm^{-1})	T_0 (K)	n
550	2.426×10^{44}	5.818×10^{33}	6.576×10^{-2}
650	2.008×10^{3}	1.402×10^{6}	2.655×10^{-1}
700	4.525×10^{4}	5.304×10^{8}	1.658×10^{-1}

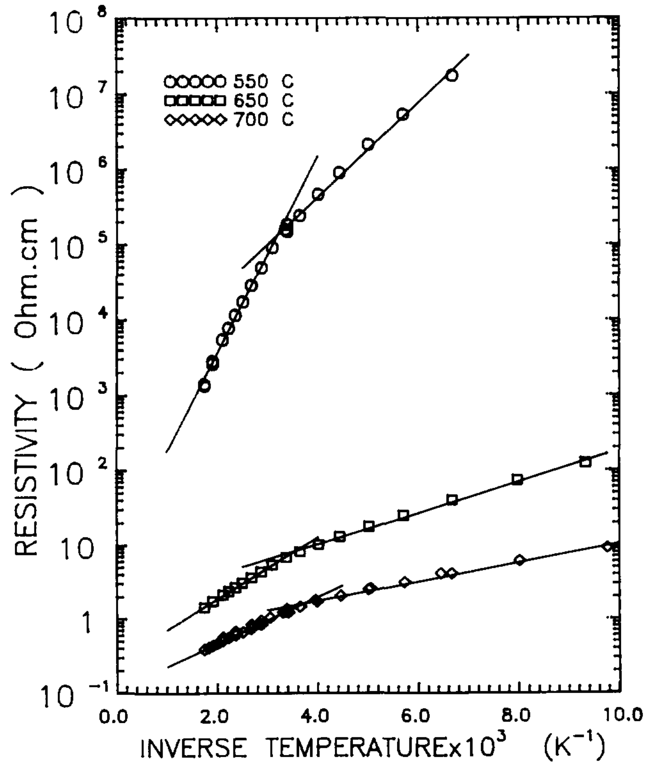

Figure 8 Temperature dependence of the resistivity of polyamide 3 pyrolysed at different temperatures: (○) 550; (□) 650; and (◇) 700°C

Table 3 Values of ρ_0 and ΔE for the low- and high-temperature regions

Pyrolysis temperature (°C)	Low temperatures ρ_0 (Ω cm)	Low temperatures ΔE (eV)	High temperatures ρ_0 (Ω cm)	High temperatures ΔE (eV)
550	1.18×10^3	0.13	8.191	0.26
650	1.444	0.04	2.63×10^{-1}	0.08
700	2.57×10^{-1}	0.02	8.67×10^{-2}	0.05

temperature seems to exist, nor may any physical significance be attributed to them.

By using the third approach, the resistivity was plotted *versus* the inverse of the temperature for the three pyrolysis temperatures (see *Figure 8*). This presentation of the resistivity data suggests that there are two distinct temperature regions, and within each of these the resistivity may be described by an equation of the following form:

$$\rho = \rho_0 \exp\left(\frac{\Delta E}{kT}\right) \qquad (3)$$

This indicates that electrical conductivity in the samples can be attributed to two different mechanisms, both of which are thermally activated. *Table 3* gives the values of ρ_0 and the activation energies ΔE for the two different temperature regions. These values were determined by applying the same non-linear least-squares curve fitting program to equation (3). It should be noted that the activation energies for the high-temperature region are greater than the corresponding energies for the low-temperature region. These different activation energies may be attributed to intramolecular and intermolecular charge transport, respectively. Specifically, the activation energy which corresponds to the low-temperature region, is associated with the intermolecular conducting process, whereas the intramolecular conductivity is characterized by the activation energy corresponding to the high-temperature region. *Table 3* gives the values of ρ_0 and ΔE for the low- and high-temperature regions at different pyrolysis temperatures. However, a definite conclusion can be drawn only if a molecular structure analysis is carried out, which is not possible in this case, owing to the lack of the necessary apparatus.

CONCLUSIONS

From the above mentioned analysis of the experimental results it is obvious that both the variable-range hopping model of Mott and Davis[10] and the stretched exponential model of Cowan *et al.*[11] fail to satisfactorily describe the experimental results. On the other hand, the thermally activated model for the conductivity seems to describe the experimental results rather well, leading to the conclusion that the observed conductivity is due to both intermolecular and intramolecular hopping processes.

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