

Conducting complexes of vacuum-cyclized polyacrylonitrile and iodine

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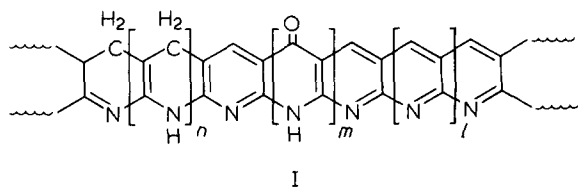
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Polyacrylonitrile, thermally cyclized in a vacuum, was found to form conducting complexes with iodine. These complexes would not form until the thermal treatment of polyacrylonitrile resulted in a certain minimum cyclicity, or number of cyclized rings per fused segment in the polymer chain, as measured by infra-red spectroscopy. Cyclized polyacrylonitrile-iodine complexes approaching two iodine atoms per cyclized six-member ring had a room-temperature conductivity of $10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ with an activation energy of 0.60 eV.

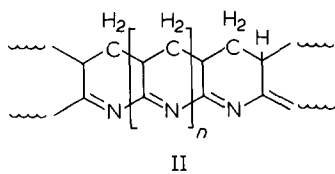
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INTRODUCTION

Several studies have been made on conducting complexes based on oxidized cyclized polyacrylonitrile (PAN)^{1,2} and it has been proposed that oxidatively stabilized PAN has the following structure³:



Structure I is highly conjugated and may thus be expected to have a high electrical conductivity when doped. Structure II depicts the proposed structure for PAN when thermally cyclized in a vacuum³. The latter structure is also highly conjugated by virtue of its system



of alternating single and double bonds and should become electrically conducting when doped with a suitable donor or acceptor. Assignments of many of the bands in its infra-red spectrum have been made⁴⁻⁶, making it possible to characterize the starting material and also the resulting complex. Consequently, vacuum-cyclized PAN is an attractive system for studying the dependence of conductivity on cyclicity (the number of cyclized rings per fused segment) and doping.

In this work, PAN subjected to temperatures in excess of 200°C was exposed to iodine vapour at ambient

temperatures. It was found that when the cyclicity, as determined by infra-red spectroscopy, is below a certain critical value, no measurable uptake of iodine occurs. However, when the cyclicity exceeds this value, iodine is absorbed by the polymer to the extent of two iodine atoms per cyclized six-membered ring, reaching an ultimate conductivity of $10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$.

EXPERIMENTAL

Two types of PAN samples were prepared. In type one, tows of PAN homopolymer fibres (Celanese Corporation, Celanese Research Co., Summit, NJ, USA), were mounted on quartz spindles. In type two, fibres from the same source were used to make a 3% dimethylsulphoxide solution, from which thin films were made by deposition of the solution on glass plates. After the solvent was evaporated off, the films were soaked for several days in water to remove the remaining solvent. The films were then air-dried.

Each sample, whether a fibre-carrying spindle or a film, was placed in a Pyrex tube. The tube had a thermocouple mounted on its exterior adjacent to the film or the spindle. The tube was evacuated to a pressure of $< 10^{-3}$ Torr and maintained under vacuum overnight. The tube was then lowered into a furnace set at 200°C. After the tube reached 200°C, as indicated by the thermocouple, the set point of the furnace was raised by about 20°C and the sample was maintained at the new temperature for 1 h. This process was repeated until the desired final temperature was reached. Each sample was maintained at the final temperature T_f for times exceeding 0.5 h or longer. The tube was cooled to room temperature, and the sample was removed from the tube and weighed. For each fibre tow, the resistance was measured; for each film the infra-red spectrum was obtained.

The sample was then transferred to a vial, which was placed in a tube containing iodine crystals. This tube was evacuated, thereby exposing the sample to an atmosphere

consisting only of iodine at its room-temperature vapour pressure. After an interval sufficient for the sample to absorb a measurable amount of iodine, the tube was opened, the sample weighed, and the resistance of the fibre tow or the infra-red spectrum of the film measured. The sample was again exposed to iodine vapour, and the resistance or infra-red spectrum and the weight recorded until no measurable change occurred over a period of days. Initially, the various measurements were done in nitrogen. Since short periods of exposure to air were found to have no significant effect on the measured values, the bulk of the measurements reported here were made under ambient conditions.

The resistance measurements were made using a Keithley 610°C electrometer, using copper, Electrodog, and platinum contacts. The contacts were always checked to verify that they were ohmic. Measured sample resistance was independent of the type of contact used. Measurements were made on tows and single fibres. Tows were always employed for measurements when the conductivity of a sample was below $10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$.

The infra-red spectra were measured on a Nicolet MX-1 FTi.r. spectrometer.

RESULTS

Weight gain

Samples heat-treated at temperatures T_F in the range of 260°–400°C achieved a final specific weight gain corresponding to $I/M = 1.63 \pm 0.12$, where I is the number of iodine atoms absorbed by the sample and M is the number of monomer units in the sample. This value obtained for I/M is very high in comparison with that obtained for polyacetylene (≈ 0.25) (ref. 7). However, it is close to the value of 2.0 observed for poly(4-vinylpyridine) iodine complexes⁸. In this heat-treatment temperature range, the final value attained for I/M did not depend on the heat-treatment temperature or on the length of time that the sample was exposed to elevated temperatures. However, the final value of I/M attained for samples heat-treated in the limited range of 220°–240°C was extremely sensitive to both the temperature of heat-treatment and the length of time that the sample remained at elevated temperatures. For samples heat-treated in the latter range the final I/M values varied from 0 to 1.75. Samples heat-treated at 220°C had to be held at this temperature for over 8 h in order for a measurable absorption of iodine to be observed on subsequent exposures of the samples of iodine vapour.

Infra-red spectra

Spectra before exposure to iodine vapour. Shown in Figure 1 are the infra-red spectra of four films of PAN heated at $T_F \sim 240^\circ\text{C}$ and below, and prior to iodine vapour exposure. The spectra are labelled A to D according to the decreasing amount of iodine that they absorbed when subsequently exposed to iodine vapour and no further weight gain was observed.

All the samples show absorptions at 1615, 1580 and 3220 cm^{-1} which are attributable to cyclized PAN⁴⁻⁶. The ultimate I/M values attained by the samples upon exposure to iodine vapour increase with the relative intensities of these absorptions. The samples also show absorption at 2240 cm^{-1} due to uncyclized nitrile groups, the relative intensity of which decreases from A to D.

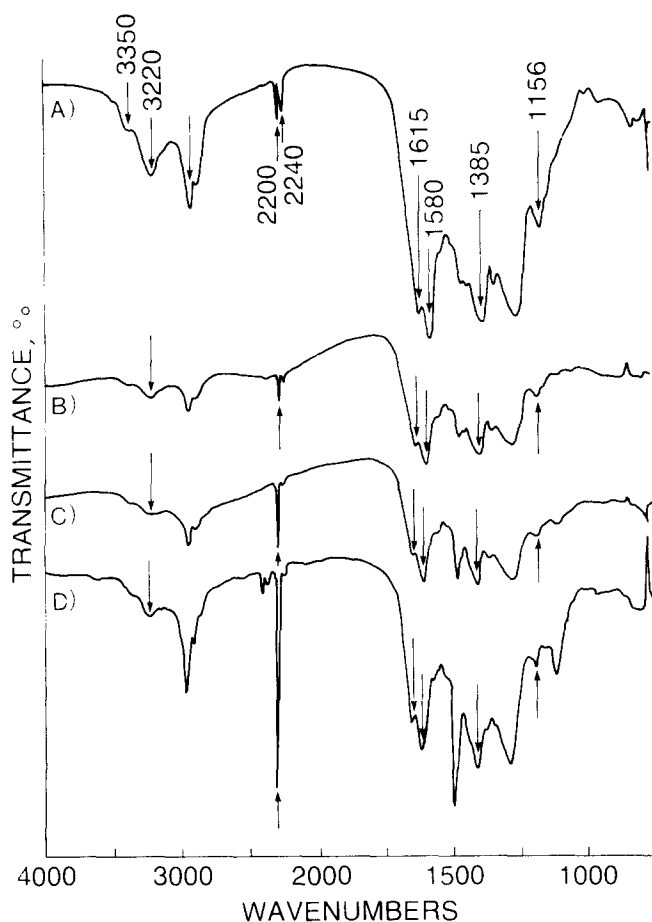
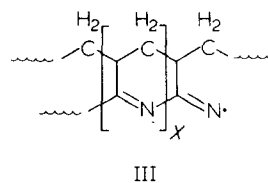


Figure 1 Infra-red spectra of vacuum-cyclized PAN before exposure to iodine vapour. A: a sample which attained a final $I/M = 1.53$ (the sample was heated for 1.5 h at 241°C); B: a sample which attained a final $I/M = 1.40$ (the sample was heated for 1 h at 238°C); C: a sample which attained a final $I/M = 0.68$ (the sample was heated for 0.7 h at 238°C); and D: a sample which attained a final $I/M = 0.0$ (the sample was pyrolysed for 3 h at 222°C)

Shown in Figure 2 is a plot of the final I/M attained by the samples upon exposure to iodine vapour versus the absorbance ratio A_{1615}/A_{2240} . The points in this plot are in good agreement with the curve shown, which was derived on the basis of the argument advanced below.

Iodine molecules form a complex with the double bonds in the system of alternating single and double bonds which is formed when PAN cyclizes. In order for a stable iodine complex to form, that system must be highly conjugated, as in the case of a highly fused system (III)



where the cyclicity x exceeds a certain minimum value, n . Each double bond in a fused segment of minimum cyclicity n can complex one iodine molecule. The maximum number of iodine atoms which can thus be complexed will be given by equation (1), where L_x is the number of fused segments of cyclicity x in the sample.

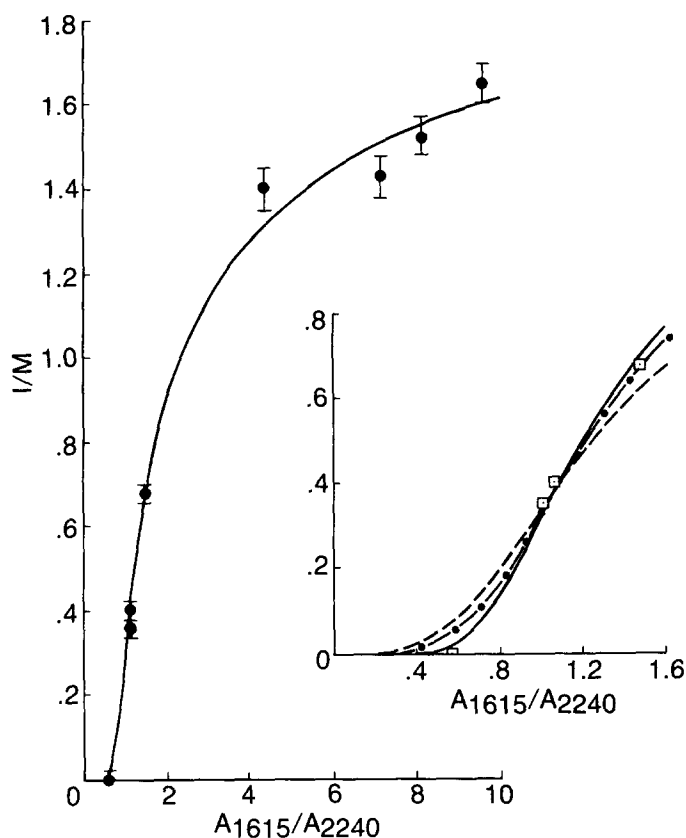
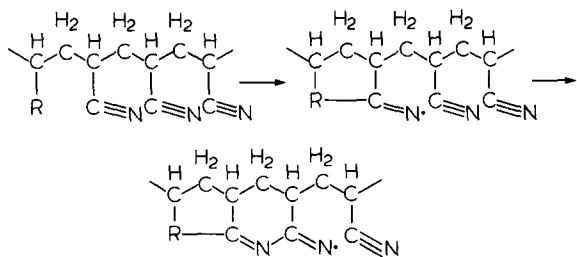


Figure 2 Plot of the final value I/M versus absorbance ratio, A_{1615}/A_{2240} . The solid curve is a plot of equation (13) with $n=18$. Inset: plot of I/M versus A_{1615}/A_{2240} with an expanded abscissa. The rectangles are experimental points; the curves are plots of equation (13) with (—) denoting $n=6$, (---) denoting $n=12$, and (- - -) denoting $n=18$

$$I = 2 \left(\sum_{x=n}^{\infty} xL_x \right) \quad (1)$$

In order to evaluate L_x , a cyclization scheme must be proposed. It is reasonable to argue that there are R initiators on the unreacted polymer chain which can react as follows:



It follows that a nitrile radical is always present to carry the reaction along the polymer chain.

Let L_x be the number of fused segments of cyclicity x having a nitrile radical on the end. If termination of the chain reaction is unlikely, as will indeed be the case if the molecular weight of the sample is reasonably high, the concentration of L_x will be controlled by the kinetic equation (2) where k_{x-1} is the rate constant for formation of a fused segment of cyclicity x from a fused segment of cyclicity $x-1$, and k_x is the rate constant of reaction of a

fused segment of cyclicity x to form a longer segment of cyclicity $x+1$.

$$dL_x/dt = k_{x-1}L_{x-1} - k_xL_x \quad (2)$$

It is not unreasonable to assume that $k = k_{x-1} = k_x = k_{x+1} \dots$, and so the subscript can be deleted and equation (2) rewritten as:

$$dL_x/dt = k(L_{x-1} - L_x) \quad (3)$$

Such a kinetic scheme leads to a Poisson distribution⁹. In this case the number of fused segments of cyclicity x is given by:

$$L_x = R_0(kt)^x e^{-kt}/x! \quad (4)$$

where R_0 is the number of initiators initially present in the sample, L_x is given by equation (4) since $dL_1/dt = kR_0 - kL_1$, and $R_t = R_0 e^{-kt}$ instead of the value $dL_1/dt = -kL_1$ as given in ref. 9. The value of I can now be found by substituting equation (4) into equation (1), thus obtaining:

$$I = 2 \left[\sum_{x=n}^{\infty} xR_0(kt)^x e^{-kt}/x! \right] \quad (5)$$

For convenience, equation (5) is rearranged to:

$$I = 2 \left[\sum_{x=1}^{\infty} xR_0(kt)^x e^{-kt}/x! - \sum_{x=1}^{n-1} xR_0(kt)^x e^{-kt}/x! \right] \quad (6)$$

from which it follows that:

$$I = 2 \left\{ ktR_0 - ktR_0 e^{-kt} \left[\sum_{x=1}^{n-1} (kt)^{x-1}/(x-1)! \right] \right\} \quad (7)$$

Now $krR_0 = N_c$, the total number of cyclized nitrile groups in the polymer. If the initiators are uniformly distributed throughout the polymer, R_0 is proportional to M , the number of monomer units initially present in the polymer. But M is equal to the number of cyclized monomer units, N_c , plus the number of uncyclized monomer units, N_u , plus the number of groups at the ends of fused segments (which is equal to R_0). Hence,

$$R_0 = pM = p(N_c + N_u + R_0) \quad (8)$$

where p is the ratio of initiators to monomer units. Solving equation (8) yields:

$$R_0 = \frac{p}{(1-p)} (N_c + N_u) = N_c/kt \quad (9)$$

and

$$kt = \frac{(1-p)}{p} \cdot \frac{N_c/N_u}{(1 + N_c/N_u)} \quad (10)$$

Letting $z = N_c/N_u$ gives

$$kt = f(z) = \frac{(1-p)}{p} \cdot \frac{z}{(1+z)} \quad (11)$$

Substitution of equation (11) into equation (7) yields

$$I = 2f(z)R_0 \left\{ 1 - e^{-f(z)} \left[\sum_{x=1}^{n-1} f(z)^{x-1} / (x-1)! \right] \right\} \quad (12)$$

Equation (11) gives the number of iodine atoms absorbed by the sample. The term measured is I/M , the number of iodine atoms absorbed per monomer unit. Dividing by M and taking into account $R_0 = pM$, one obtains

$$I/M = 2pf(z) \left\{ 1 - e^{-f(z)} \left[\sum_{x=1}^{n-1} f(z)^{x-1} / (x-1)! \right] \right\} \quad (13)$$

In order to evaluate z , we note that $N_c = \epsilon_{1615} A_{1615} / l$ and $N_u = \epsilon_{2240} A_{2240} / l$, where the ϵ values are extinction coefficients, the A values are the absorbances, and l is the sample thickness. Thus $z = N_c / N_u = EA_{1615} / A_{2240}$, where $E = \epsilon_{1615} / \epsilon_{2240}$ is a constant. It follows that equation (13) can be fit to the spectroscopic data in terms of three parameters: p , the ratio of the initiators to monomer units; n , the minimum cyclicality needed to form a stable iodine complex, and E .

The solid curve in Figure 2 was constructed using equation (13) with $p = 0.0165$, $n = 18$ and $E = 0.46$. The values of the parameters used to construct this curve were obtained from a least squares fit of equation (13) to the data. Evidently, a fused segment of cyclicality ≥ 18 is needed before sufficient conjugation is attained such that iodine will form a stable complex with the six-membered rings. A value of cyclicality ≥ 18 seemed to be quite large. Therefore, the best least squares fits of equation (13) to the data were obtained holding n constant at 3, 6, 9 and 12 and only varying p and E . The sum of the squares of the deviations of the calculated values from the measured values of I/M were only 20% larger than the best least squares fit values in the case of cyclicality ≥ 12 , 50% larger in the case of cyclicality ≥ 9 , 150% larger for cyclicality ≥ 6 , and 500% larger for cyclicality ≥ 3 . Shown in the insert for Figure 2 are three plots of the calculated values of I/M obtained from equation (13) with $n = 6$, $p = 0.0525$ and $E = 0.565$; $n = 12$, $p = 0.0252$ and $E = 0.485$; and with $n = 18$, $p = 0.0165$ and $E = 0.46$. An expanded abscissa is used so that the differences between the three plots can be clearly seen. A substantial value of the cyclicality is necessary before enough conjugation occurs so that a stable complex with iodine will form.

Infra-red spectra after exposure to iodine vapour. Shown in Figure 3 are the infra-red spectra measured after the samples had been exposed to iodine vapour for a long enough time that no further weight gain of the sample was measured upon further exposure to iodine vapour. The samples used to obtain the spectra in Figure 3 were the same samples used in Figure 1 before the samples were exposed to iodine vapour.

Comparison of the corresponding spectra in Figures 1 and 3 gave the following observations.

(1) The bands at 3350 , 1385 and 2200 cm^{-1} in the exposed samples had decreased in intensity compared with the unexposed samples. The bands at 3350 and 1385 cm^{-1} are usually attributed to N-H vibrations, and the band at 2200 cm^{-1} are usually attributed to N-H vibrations, and the band at 2200 cm^{-1} to a highly conjugated nitrile⁴⁻⁶. Both groups might be expected to form at the end of a fused segment. Apparently, one of the effects of the absorption of iodine is to decrease the

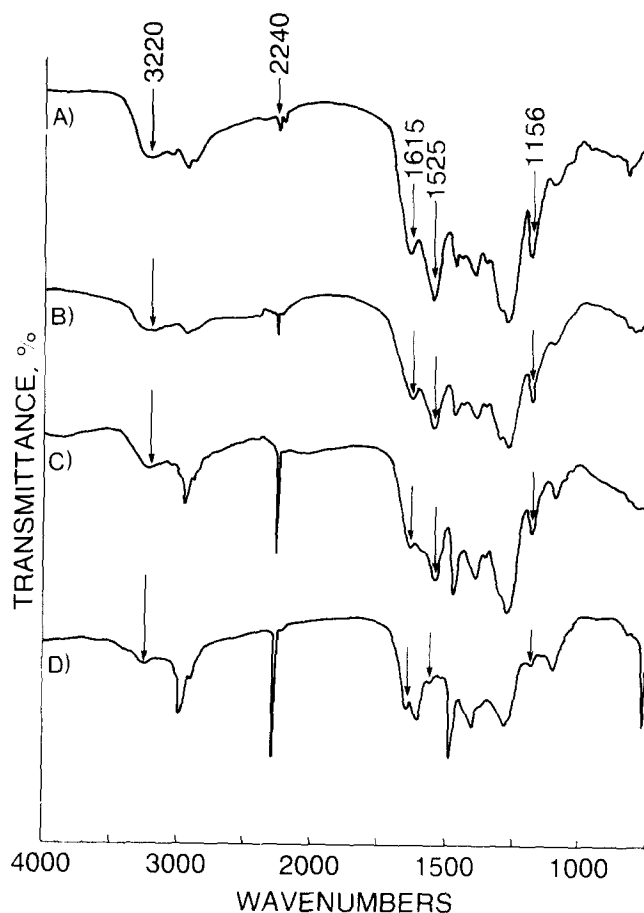


Figure 3 Infra-red spectra of vacuum-cyclized PAN after exposure to iodine vapour. The labels A-D correspond to those in Figure 1

intensity of the absorption of end groups to the fused segments.

(2) The absorption at 1580 cm^{-1} had shifted to the lower wavenumber 1525 cm^{-1} , and its intensity was somewhat greater in the iodine-complexed sample. This band is usually attributed to a C=N stretching mode. It is common for vibrational modes in molecules complexed with heavy atoms to be shifted to lower frequencies. The intensity of the absorption at 1156 cm^{-1} was also enhanced by the addition of iodine. This band is attributed to a C-N stretching mode.

It is clear from the above observations that the absorption of iodine affects those vibrational frequencies in the infra-red spectrum of pyrolysed PAN attributed to the fused segments obtained upon heating, and it has no observable effect on the vibrational frequencies of the uncyclized monomer units. In addition, the most pronounced changes are seen in those bands involving the vibration of a nitrogen atom. This suggests that the iodine atoms absorbed by the cyclized PAN are closely associated with the sequence of alternating single and double bonds about the nitrogen atoms in the fused segments.

The infra-red spectra obtained after iodine exposures from samples which absorbed different quantities of iodine may now be compared. Referring again to Figure 3, we note that the vibrational bands attributable to the fused segments undergo the greatest change upon exposure to iodine vapour in the case of sample A. This

sample absorbed 1.53 atoms of iodine per monomer unit. Alternatively, the vibrational bands attributable to the fused segments in sample D have hardly changed upon exposure to iodine. The latter sample was exposed to iodine vapour for a period twice as long as that of A, yet no measurable absorption of iodine was observed. Since the infra-red spectrum indicates that there are fused segments in the polymer with which the iodine could react, the absence of a change in weight combined with the infra-red spectral details indicates that iodine is not reacting with the fused segments in sample D. Evidently, formation of a fused segment is not sufficient for complex formation. The bands at 3350 and 1580 cm^{-1} , characteristic of the uncomplexed fused segments, are still prominent in the spectra of samples B and C. The latter samples absorbed 1.4 and 0.68 iodine atoms per monomer unit, respectively. This spectral information is additional evidence that some fused segments do not react with iodine. These observations are consistent with the postulate that a fused segment must possess a minimum cyclicicity before iodine will form a stable complex with it.

Electrical conductivity

Shown in Figure 4 is a typical plot of the logarithm of the conductivity, σ , versus I/M . The conductivity that develops upon iodine doping was found to be independent of the heat-treatment temperature T_F to which the samples had been subjected. Samples heat-treated within the temperature range of 245° to 400°C attained an ultimate I/M between 1.5 and 1.8. Upon exposure to iodine vapour the conductivity increased very rapidly for a small increase in I/M . As the quantity of iodine absorbed increased, the conductivity increased more slowly with the amount of iodine absorbed, approaching an asymptotic value of $5 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$. The σ versus I/M curve could be reversed by removing iodine from the polymer. Approximately 30% of the iodine could be removed by vacuum pumping on the sample, and 90% by soaking the sample in methanol.

The variation of σ with temperature was measured in the temperature range of -296° to $+25^\circ\text{C}$. The samples

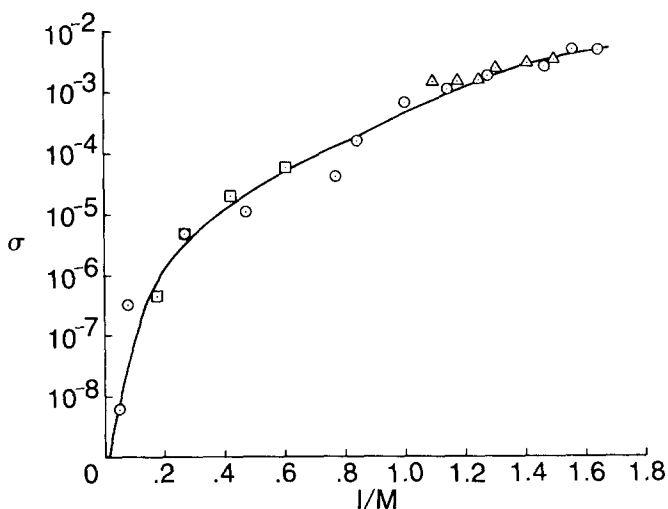


Figure 4 Plot of σ at room temperature versus I/M : O, sample increasing in weight on exposure to iodine vapour; Δ , sample decreasing in weight due to removal of iodine vapour by vacuum pumping; \square , sample decreasing in weight due to removal of iodine by soaking in methanol

studied had values of I/M varying from 0.7 to 1.5. For all samples studied, plots of $\log \sigma$ versus $1/T$ with T in degrees kelvin produced a straight line. The slope of the lines obtained from the $\log \sigma$ versus $1/T$ plots was the same for all samples, yielding a value for the conduction activation energy $E_a = 0.59 \pm 0.03 \text{ eV}$.

The conductivity follows the relationship,

$$\sigma = \sigma_0 e^{-E_a/kt} \quad (14)$$

Since $\sigma = ne\mu$, where n is the concentration of charge carriers, e the charge on the electron, and μ the mobility of the charge carriers, it should be possible to deduce from the value of σ_0 whether it is the carrier concentration or the mobility that is thermally activated. If the mobility is thermally activated the conduction process is a hopping mechanism characteristic of amorphous solids. In the case of the most conductive samples, with $\sigma = 5 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature, the above-measured value of E_a leads to $\sigma_0 = 4.8 \times 10^7 \text{ ohm}^{-1} \text{ cm}^{-1}$. Since $\sigma_0 = n_0 e \mu_0$, we have $\sigma_0/e = n_0 \mu_0 = 3 \times 10^{26} \text{ cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$. The maximum value that may be expected for n_0 is $9 \times 10^{21} \text{ cm}^{-3}$, based on the assumption that every two iodine atoms absorbed donate one charge carrier to the polymer. Using this maximum possible value of n_0 , a minimum possible value of $3 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is obtained for μ_0 . If the mobility is not thermally activated, μ would have this value at room temperature. But such large values of the room temperature mobility are implausible. It is more likely that the mobility is thermally activated, indicating that the conduction arises from a hopping mechanism. If the measured activation energy is the activation energy for hopping, then the room-temperature mobility would be of the order of $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This value is of the same order of magnitude as the mobilities measured in polymeric conductors^{7,10}.

CONCLUSION

Infra-red absorption and weight measurements confirm the inference that vacuum-pyrolysed PAN will not absorb iodine until the length of the fused segments formed by heat treatment exceeds a certain number of cyclized units. Fused segments of cyclicicity ≥ 18 absorb up to two iodine atoms per six-membered ring. The resulting complex exhibits a thermally activated electrical conductivity. The most probable conduction mechanism is a hopping mechanism.

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