Conduction in Thin Polymer Films

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Thin polymer films have been made from a variety of starting monomers and their electrical conduction has been studied.

The films are produced both by ultraviolet surface photolysis and by a cold-cathode glow-discharge technique. The samples are made in the form of a capacitor sandwich on a glass substrate with aluminium electrodes. The whole sample is made in a high-vacuum system, without breaking vacuum, using out-of-contact masking techniques.

Generally, depending on the starting monomer, the polymer films are "short"-free down to a thickness of about 100 Å, and electric fields up to 10^7 V/cm may be sustained.

The current/voltage characteristics of the films have been investigated as a function of temperature and thickness. One theory to account for the conduction in these materials is presented and compared with other approaches to the problem.

1. Introduction

In recent years, interest has increased in the uses of various thin polymer films of thickness between 100 and 5000 Å, produced by ultraviolet surface photolysis, electron bombardment, or glow discharge in a vapour. Films deposited by electron bombardment and glow discharge tend to be greatly cross-linked and relatively inert. For this reason, they have been studied for application as protective films [1]. These films have very high resistivities, of the order of 10^{18} Ω cm and are being studied for use as thin-film insulators and dielectrics. Some work on this aspect has been done on polymerised silicone pump oils [2-4]. The polymerisation effect was first observed as contamination in vacuum systems due to polymerisation of such oil vapours during electron-beam or glow-discharge operations. However, the molecular structure of these oils is rather complex and renders these materials unsuitable for the type of investigation with which this paper is concerned.

The author was interested in the conduction properties of thin polymer films, in the thickness range 100 to 1500 Å, for use as non-linear layers in future thin-film circuits. One method of increasing the conductivity of a polymer is to increase the amount of unsaturation present in

it [5]. This means increasing the concentration of double bonds between the carbon atoms. These double bonds constitute clouds of semi-localised electrons which can contribute, under certain conditions, to conductivity. If the polymer is formed, from a suitable unsaturated monomer, by either electron bombardment or glow discharge, most of the unsaturation is removed in the final film. This is because the quantum energy used in these two methods of film formation is large compared with the few electron volts of bond-dissociation energies. The result is the formation of an inert high-resistivity film. In this work, however, the films are produced by the ultraviolet irradiation of a suitable monomer gas which is absorbed on a surface. The ultraviolet photon energy used is around 4 eV, which is of the same order as the bond-dissociation energies. This is, therefore, selective in activating the monomer gas only where it is irradiated, and subsequently polymerising it without doing too much damage, such as fragmentation, to the main monomer unit in the polymer.

A typical current/voltage curve for a thin-film polymer is shown in fig. 1. It consists essentially of three regions – a linear region, a sharply changing region, and an exponential region. Other workers in this field [3, 6] have made

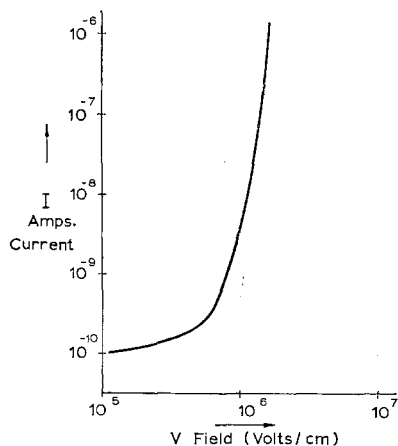*The author is now with the Plessey Automation Group, Poole, Dorset.

Figure 1 Typical current/voltage curve for a thin film polymer.

Figure 2 Potential box model for conduction process.

attempts to discover the conduction processes in polymeric films giving such characteristics, based on the use of theories and models applicable in the case of inorganic semiconductors. These approaches make use of band structure and the ideas of impurity doping. However, organic materials in general, and polymer films in particular, do not suffer impurity influence on their electrical conductivity. They are very much intrinsic conductors. The orbitals of molecules do not overlap, and an electron cannot pass in a continuous way from one molecule to another. This situation is the opposite of that which exists in inorganic semiconductors and the application of the band theory in this case is suspect.

Eley and Willis [7] proposed a conduction mechanism based on electron "hopping" or tunnelling between molecules. Fig. 2 is an energy-level description of this process and the assumption was made that the carrier density in the molecule is given by band theory. Although the application of this, in those circumstances, has already been questioned, it will serve as a first approximation. The density of states will quite probably be greater than that given by band theory, since the electron effective mass increases with the decrease in band width expected in these materials.

The expression relating current and voltage obtained by applying this approach is

$$J = A \sinh bV \exp \left(-\Delta E/2kT \right)$$

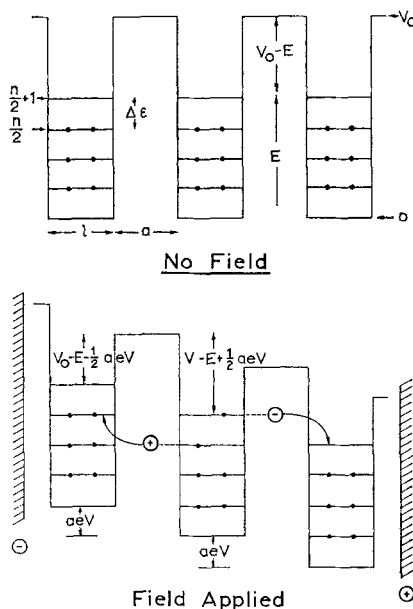where: J is the current density; V, the applied field; k, Boltzman's constant; T, the absolute

temperature; and A and b, field-independent functions whose values depend on the shape of the intermolecular barrier.

This equation predicts three regions in a current/voltage curve at a fixed temperature.

For low fields, $\sinh (bV) = bV$ with an accuracy of 1 % up to $bV = 0.3$, and

$$J = AbV \exp \left(-\Delta E/2kT \right)$$

Ohms law (linear dependence of J on V).

For intermediate fields:

$$J = (1/2A) \left(e^{bV} - e^{-bV} \right) \exp \left(-\Delta E/2kT \right)$$

For high fields: $\sinh (bV) = 1/2 \ e^{bV}$ ($V > 10^6$ V/cm) and

$$J = (A/2) \ e^{bV} \exp \left(-\Delta E/2kT \right)$$

The correctness of this approach can be judged on the values of A and b and the temperature variation obtained.

2. Experimental
2.1. The Monomers
Previous work on butadiene [8] indicated that pressures of the order of 2 torr at room temperature were required for this work. Thus unsaturated liquids with vapour pressures of this order at room temperature, or gases, were chosen for this work. The liquids used were ordinary laboratory-reagent grade, which were outgassed under a vacuum better than 10^{-3} torr at liquid-nitrogen temperature before use. The

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gases were research grade and were admitted through a previously evacuated supply line.

The liquids used were cyclo-octatetraene (COT), and acetylene dicarboxylic acid dimethyl ester (ADADE). The bases were butadiene, acetylene, and cyanogen.
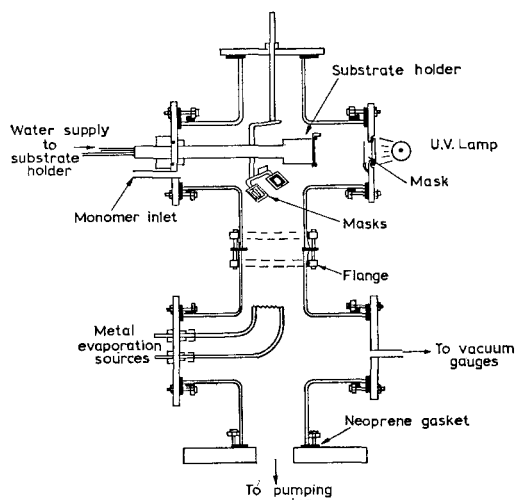

Figure 3 Vacuum chamber.

2.2. Apparatus

The samples were made in a custom-built vacuum system, fig. 3, which could be pumped out to 5×10^{-6} torr. It was pumped by a conventional, liquid-nitrogen, trapped-mercury, diffusion pump with a rotary backing pump.

The ultraviolet source was a Hanovia medium-pressure mercury lamp, of American manufacture, type 73A-10. The lamp output was rated as 120 W in the ultraviolet, between 2000 and 3500 Å.

The electrical properties of the films were evaluated using two different arrangements. Films which shorted before carrying currents up to 1 μA were evaluated by a dc method, using a Keithly electrometer to monitor currents down to 10^{-14} A. Films which had greater current-carrying capacity were evaluated on a Tetronix 575 curve-tracer at 100 c/sec. The two methods of evaluation were comparable, as no frequency variation of conductivity was found in this region.

Temperature-variation work was done in an evacuatable copper cryostat, immersed in liquid nitrogen, using ultrapure helium as the thermal transfer medium. The sample was clamped to an aluminium block together with a heater.

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2.3. Sample Preparation

The substrate was a section of a microscope slide cleaned with Teepol, distilled water, and iso-propyl alcohol, and was spun dry on a centrifuge.

The substrate was mounted on a water-cooled holder in the vacuum system, which was evacuated to 10^{-5} torr prior to each stage of the preparation which employed a single pump-down. The aluminium electrodes were evaporated from tungsten filaments through out-of-contact masks. Before irradiation, the system was flushed with the monomer vapour being used, before regulating it to the required pressure. Special precautions were taken with acetylene as it explodes spontaneously on solidifying, such as when it is in a liquid-nitrogen trap. The system was flushed with pure oxygen before being evacuated again.

Some samples were made using a dc glow-discharge technique with positive, earthed substrate for comparison with the ultraviolet-formed films. These samples were made using a flow system, with pressures of the order of 0.10 torr and voltages of the order of 1 kV.

3. Results
3.1. Current/Voltage Characteristics

Fig. 4 shows the current/voltage curves for polybutadiene films of different thicknesses, with aluminium electrodes. These curves can be seen to be similar to fig. 1. Here, however, the "knee" in the curve becomes more pronounced with an increase in thickness. This knee occurs at the same field strength for all the samples shown, namely 2.3×10^6 V/cm.

Fig. 5 is the plot of $\log_e I$ versus V for the butadiene films. These curves are clearly linear at high fields, departing from linearity at low fields because of the approximation $\sinh bV = 1/2\, e^{bV}$. The value of b is obtained from the slope of the curve and the constant A from the intercept on the field axis. Table I gives a summary of the values from the curves.

Table II is a summary of the growth conditions of various films used in this work.

The current/voltage characteristics of films, other than polybutadiene, generally have the same shape as those in fig. 4, differing, however, in the field strength and particularly in current at breakdown. The curve continues further up the current axis in some cases than in others.

Table III is a summary of the A and b values obtained for the films.
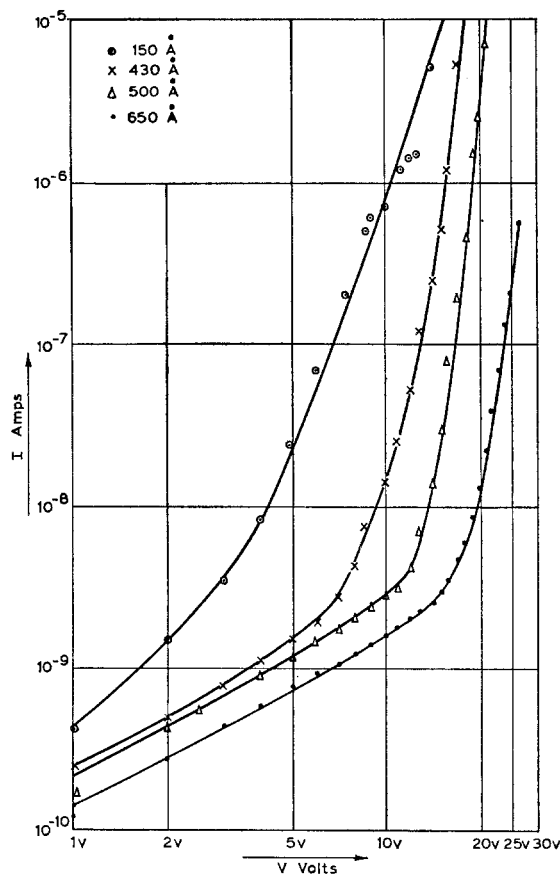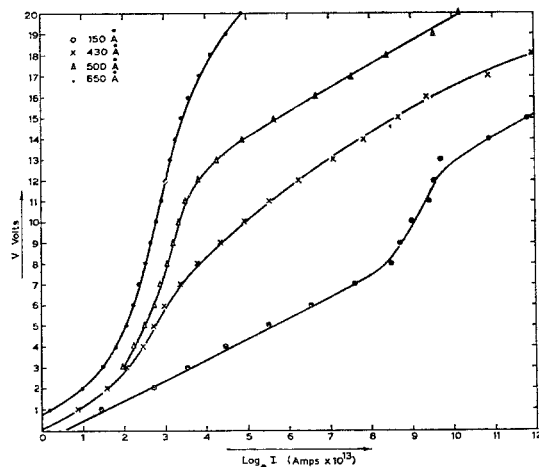
Figure 4 Current/voltage curves of polybutadiene films.

Figure 5 Plot to verify $I = A \sinh bV_0$ for butadiene.

With films made from cyanogen and acetylene, the current/voltage curves were photographed from a Tetronix curve-tracer and their temperature variation was studied. With the polycyanogen, different samples, on the same substrate, were used for the high- and low-temperature runs, referred to room temperature. Figs. 6 and 7 show the variation of the current/voltage curves with temperature between 77 and 433° K for a polycyanogen film. Fig. 8 is the curve of $\log_e I$ versus V for the high tempera-
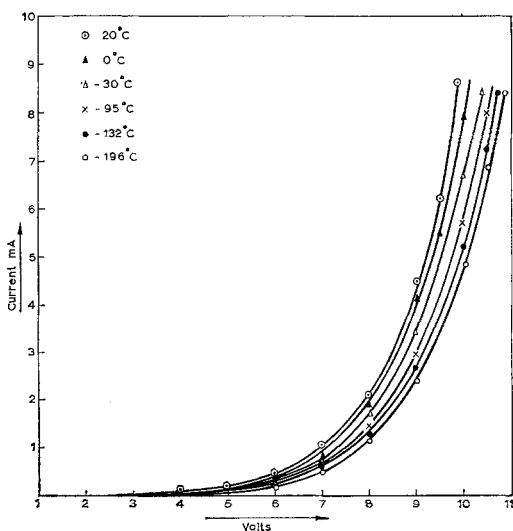
TABLE I

Sample (date)	Monomer	Method of formation	Thickness (Å)	$A(A/cm^2)$	$b(cm/V \times 10^{-6})$
24/4/64	Butadiene	Ultraviolet	430	1.6×10^{-12}	4.0
29/4/64	,,	,,	150	1.4×10^{-11}	1.5
4/5/64	,,	,,	500	2.2×10^{-13}	4.3
5/5/64	,,	,,	650	5.0×10^{-14}	3.9

TABLE II

Sample (date)	Monomer	Method of formation	Gas pressure (torr)	Time	Thickness (Å)
14/4/64	Butadiene	Ultraviolet	2	1 h	430
29/4/64	,,	,,	,,	$\frac{1}{2}$ h	150
4/5/64	,,	,,	,,	65 min	500
5/5/64	,,	,,	,,	$1\frac{1}{2}$ h	650
2/3/65	COT	,,	1	1 h	3200
4/3/65	,,	Glow discharge	0.075	$1\frac{1}{4}$ min	800
8/3/65	ADADE	,,	0.1	10 min at 1.0 mA	650
24/3/65	Acetylene	Ultraviolet	2	1 h	500
3/6/65	,,	,,	,,	40 min	350
16/2/66	Cyanogen	,,	1	1 h	130

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TABLE III

Sample (date)	Monomer	Method of formation	Thickness (Å)	A(A/cm^2)	b(cm/V × 10^{-6})
4/5/64	Butadiene	Ultraviolet	500	2.2×10^{-13}	4.3
2/3/65	COT	,,	3200	4.7×10^{-12}	1.7
4/3/65	,,	Glow discharge	800	4.0×10^{-14}	9.0
8/3/65	ADADE	,,	650	2.0×10^{-12}	2.7
24/3/65	Acetylene	Ultraviolet	500	2.0×10^{-14}	7.5
16/2/66	Cyanogen	,,	130	1.9×10^{-6}	1.13
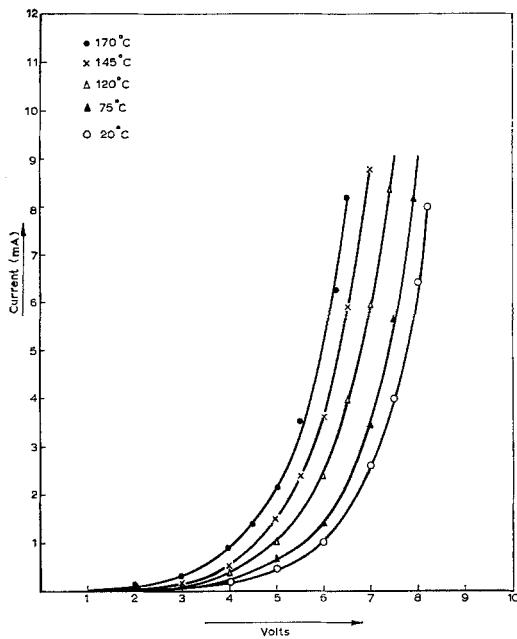
Figure 6 High-temperature I/V characteristic of polycyanogen.
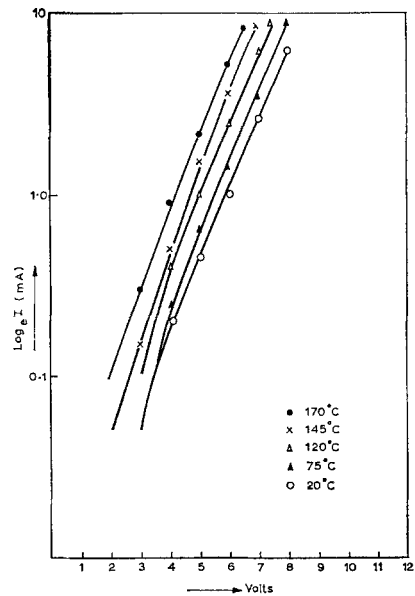
Figure 8 Plot to verify $I = A \sinh bV_0$ for polycyanogen.

Figure 7 Low-temperature I/V characteristics of polycyanogen.

ture, to obtain the A and b values. The plots for the lower temperature range are similar.

Figs. 9 and 10 are similar plots for films made from acetylene to obtain the A and b values.

Table IV is a summary of these values.

3.2. dc Activation Energies

Values of dc thermal activation energies have been obtained for those of the films which proved most interesting. Polybutadiene films have two activation energies, as shown by the plot in fig. 11. The applied voltage in this case was that of the "knee" of the current/voltage curve.

With the polyacetylene and polycyanogen samples, the temperature variation of current was measured in the three different field regions of conduction – the low-field region, on the "knee" of the I/V curve, and in the high-field region.
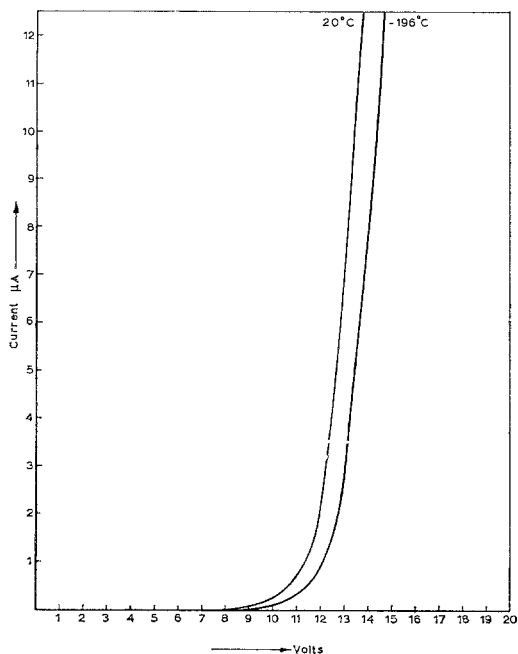
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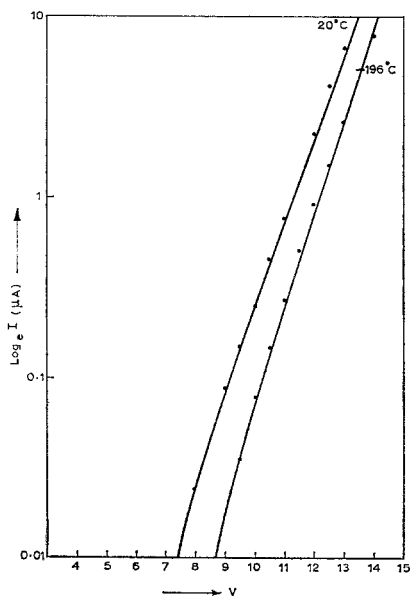Figure 9 Low-temperature I/V characteristic of poly-acetylene.

Figure 10 Plot to verify $I = A$ sinh bV_0 for polyacetylene.

Figs. 12 and 13 are the plots of $\log_e I$ versus $1/T$ for polyacetylene at "knee" and high fields. Fig. 14 is a similar plot at high fields for poly-cyanogen. Table V is a summary of the values of dc activation energies obtained at different fields for the different films.

TABLE IV Polycyanogen 130 Å.

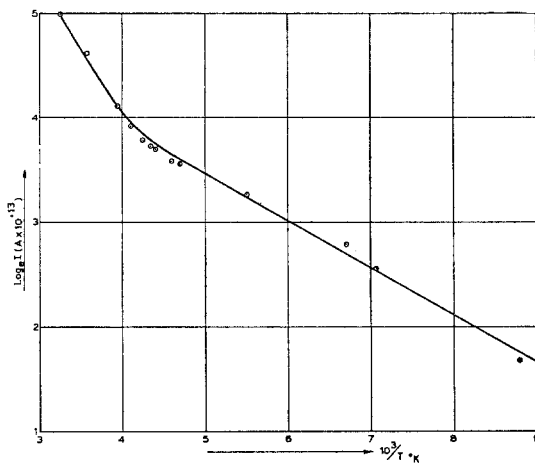| Temperature (°C)	A(A/cm^2 × 10^{-6})	b(cm/V × 10^{-6})
170	8.7	1.15
145	6.0	1.15
120	3.7	1.18
75	1.4	1.16
20	1.9	1.13
20	2.2	0.91
0	1.3	1.0
−30	1.7	0.94
−95	1.9	0.90
−132	1.6	0.91
−196	1.2	0.94
20	1.9 × 10^{-6}	3.7
−196	2.7 × 10^{-7}	4.0

Figure 11 Conductivity/temperature plot of polybutadiene.

4. Discussion

This work was started using butadiene, as this had been successfully used on previous occasions [8]. Consideration of the structure of this monomer, however, reveals that, although the monomer is unsaturated, the polymer at best can have only one double (C = C) bond per four carbon atoms (fig. 15). Any cross-linking will reduce this number. Polybutadiene was found to have a high resistivity, which is in agreement with these structure considerations and the theory of conduction by intermolecular electrons.

The shape of the current/voltage curves agreed with the theory used, so it was decided to proceed to monomers which might give more unsaturation in the polymer. For this purpose, cyclo-octatetraene (COT) and acetylene di-
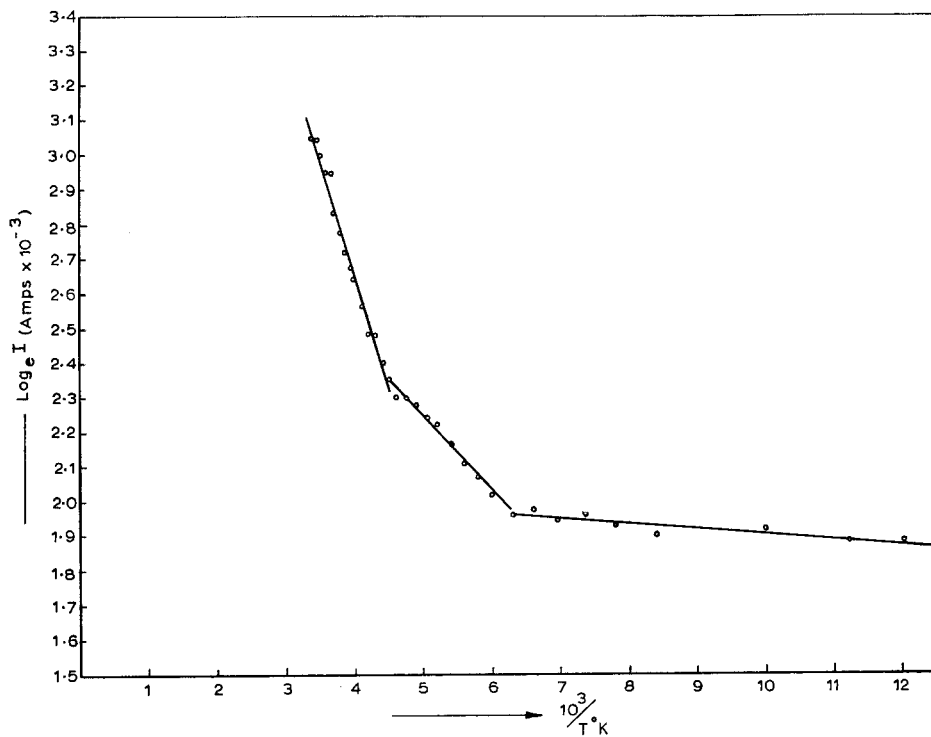
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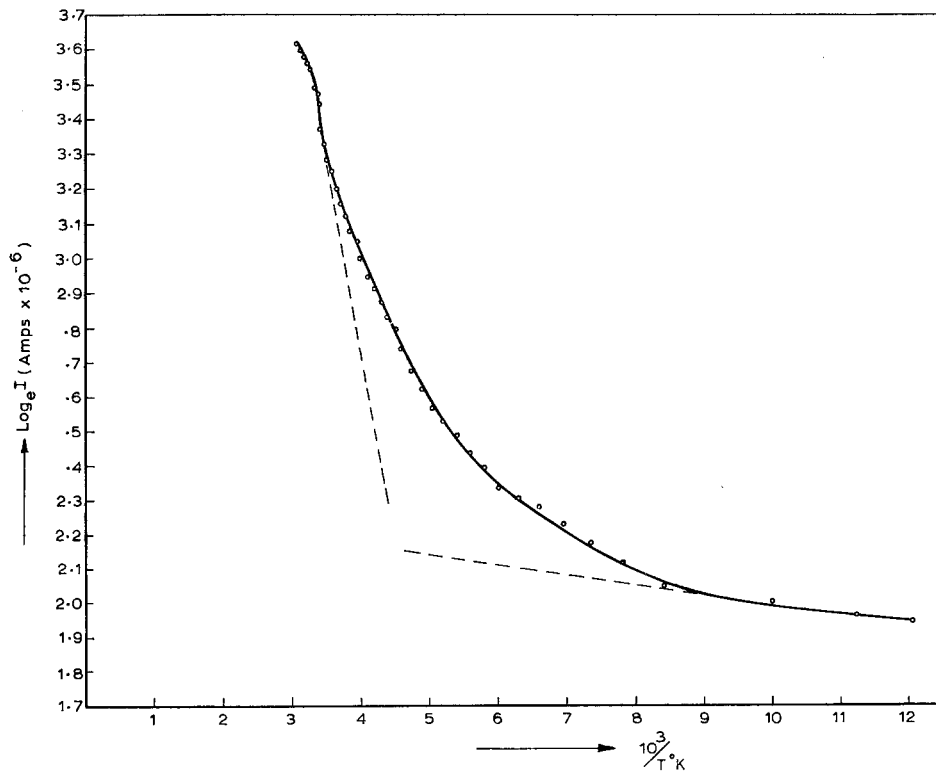*Figure 12* Conductivity/temperature plot of polyacetylene ("knee" field).

Figure 13 Conductivity/temperature plot of polyacetylene (high field).

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TABLE V

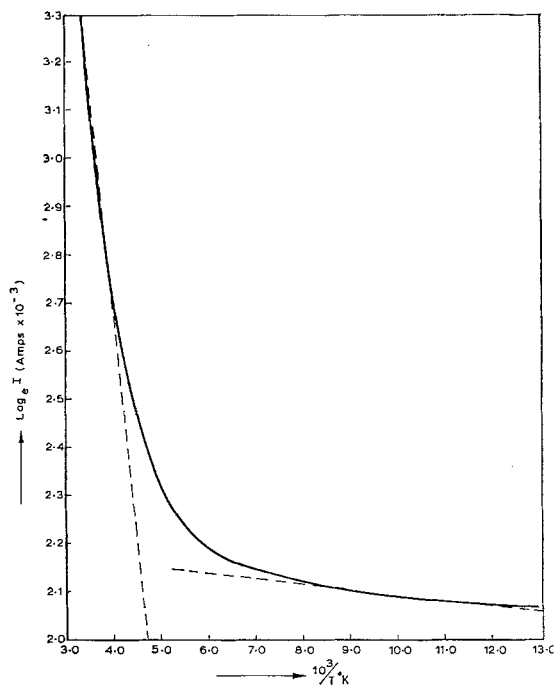| Sample (date)	Monomer	Thickness (Å)	No. of conduction regions	ΔE (eV)	Transition temperature	Field (V/cm × 10^6)
23/6/64	Butadiene	500	2	0.23/0.08	−38° C	1.5
3/6/65	Acetylene	350	1	0	—	0.57
,,	,,	,,	3	0.11/0.04/ 0.003	−51 to −115° C	1.7
,,	,,	,,	Smoothly varying	0.19/0.005	—	3.4
16/2/66	Cyanogen	130	1	0	—	1.5
,,	,,	,,	1	0	—	3.9
,,	,,	,,	2	0.16/0.002	−46 to −141° C	6.1

Figure 14 Conductivity/temperature plot of polycyanogen (high field).
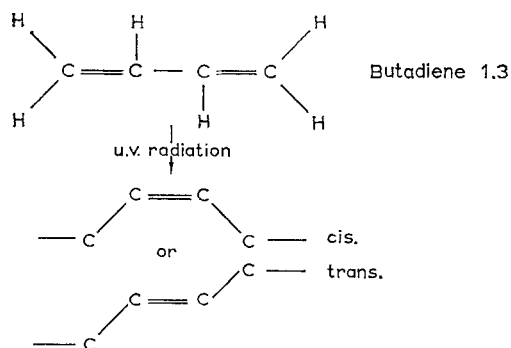
Figure 15 Possible effect of ultraviolet radiation on butadiene.

Cyclo-octatetraene   Polyvinylene

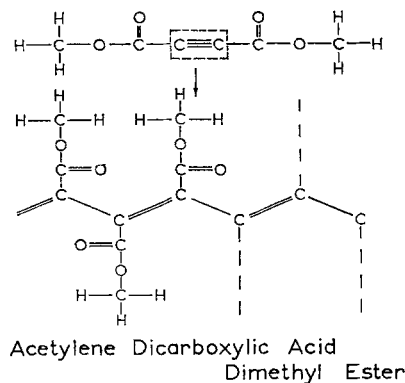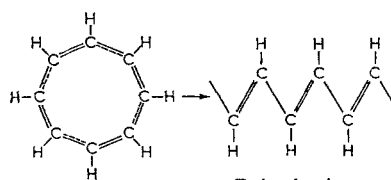Acetylene Dicarboxylic Acid Dimethyl Ester

Figure 16 Possible effect of ultraviolet radiation on other monomers.

carboxylic acid dimethyl ester (ADADE) were chosen. The structure of these two monomers and possible polymerisation products is shown in fig. 16. Here it can be seen that an un-saturated chain is possible in the polymer because, in one case, the monomer contained a triple bond. However, the COT polymer had a greater resistivity than either polybutadiene or the ADADE polymer, while still having a current/voltage curve consistent with the theory. This indicated that the conjugated, straight-chain polyvinylene is not the result of ultraviolet polymerisation of COT. The fact that the other monomer had a lower resistivity, but still not lower than that of polybutadiene, indicated that

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the unsaturated chain might exist as a backbone for conduction; but the large pendant groups would mean the number of such chains in the polymer was greatly reduced, purely on volume considerations.
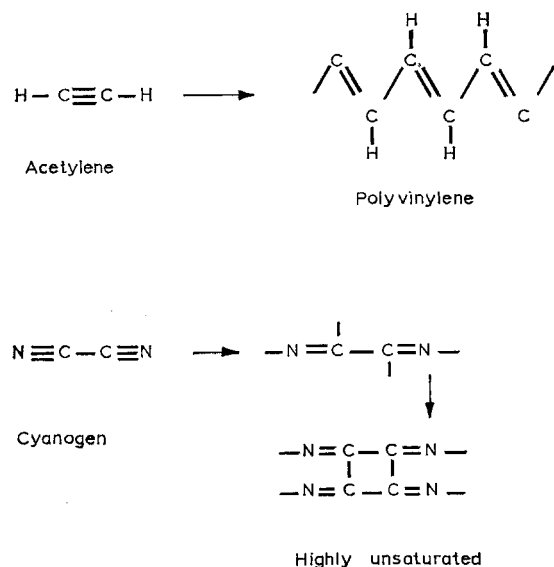

Figure 17 Possible effect of ultraviolet radiation on other monomers.

The next step was to use a monomer with a smaller molecule and with a triple bond, and acetylene seemed to be ideal. The structure is shown in fig. 17. This polymer again fitted the current/voltage curve predicted by the theory, but also had a greater current-carrying capacity. This polymer would carry 10 mA indefinitely without apparent deterioration. Such an increase in current could quite probably be accounted for by an increase in electrons in the molecule. This is more likely in the case of polyacetylene than the monomers used previously as, by starting with triple bonds, there is a greater probability of some double bonds remaining. In fact, recent work on the glow-discharge products of acetylene and nitrogen [9] has shown that it is possible, with the correct conditions, to form radicals with double and triple bonds in them, such as the cyano-radical ($-C \equiv N$). This suggests that there is a finite probability, depending on the monomer, of some double and even triple bonds remaining after irradiation.

This point was confirmed when work progressed from acetylene to cyanogen as a mono-

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mer. The structure of cyanogen is shown in fig. 17. Besides having double the number of triple bonds that acetylene has, this molecule has carbon-nitrogen bonds as well as the carbon-carbon systems used so far. It was thought interesting to see what effect, if any, the inclusion of nitrogen atoms might have on the conduction qualities of a film. The result was, in fact, a greater current capacity than even the polyacetylene films. The films of polycyanogen, although a lot thinner, carried currents of up to 50 mA at fields of 10^7 V/cm with no apparent damage. This is a power dissipation of $1\frac{1}{2}$ W/cm^2, the highest so far recorded for such films in this laboratory, and notable as the films are only 130 Å thick, as measured interferometrically. These films have current/voltage curves which fit the Eley theory. This, together with the relatively slow growth rate, indicates that all the unsaturation was not destroyed, and resonance structures may have been formed in the films.

A study of the values of A and b obtained for the various polymers reveals one major fact: while the values of b are all within an order of magnitude of each other, the A values form two groups. The cyanogen polymer alone is one group, and the other films, with carbon-carbon systems, form the other group, with A values ranging over two orders of magnitude, as shown in table III. The only really great difference in these two groups of materials is the nitrogen atom in polycyanogen, failing any information on the degree of conjugation in the polymer.

A more detailed examination of the terms A and b shows that there are two significant differences between them with regard to their component terms [7]:

$$b \propto m_e [1 - (E/V_o)]$$
$$A \propto \exp \{[-m_e (V_o - E)] [1 - (E/V_o)]\}$$

A is much more sensitive to changes in m_e, V_o, or E than is b. Now, as the band width within a molecule increases (i.e. more conjugation and π-electron cloud overlap), the electron effective mass m_e decreases toward the electron free mass m_o. If the band width were only 0.1 eV, as it might be in the more poorly conductive polymer molecules, the electron effective mass would be 43 m_o. As this effective mass approaches m_o, the above expressions show that b would be reduced by a factor over 6, and A would be increased by a factor of about 10^3. Again, a drop in b of a factor of 10

would mean an increase in A of over 10^5. Examination of table III shows that this seems to be the case for polycyanogen, in contrast to the other polymers. Also, for example, if E were 10 eV and V_0 were 20 eV, an increase of 1 eV in E would increase b by 6%, whereas it would decrease A by 250%. These figures indicate that the increased conductivity of polycyanogen over the other polymers is due to either one or a combination of two effects, increased conjugation within the polymer molecule causing a decrease in the electron effective mass, and also a decrease in size of the intermolecular potential barrier, owing to the inclusion of the nitrogen atom in the polymer backbone.

Consistent with this conclusion is the fact that table I indicates a tendency for b to increase slightly with thickness and for A to decrease more so with thickness. Consideration of the growth of these films under ultraviolet irradiation shows that the longer irradiation time required for the thicker films could result in greater damage to the underlying polymer. This would reduce the unsaturation in the molecule, giving narrower band width and higher values of m_e and b, with lower values of A. This effect is small because the high ultraviolet absorption of these films, measured after formation, indicates only slight penetration of ultraviolet into them.

A similar change in b and A can be seen in table III between COT made by ultraviolet and the glow-discharge techniques. More damage or cross-linking is expected in the glow-discharge-formed film, consistent with the increase in b and decrease in A.

The results shown in table IV do not indicate much about the correctness of this approach. There does not seem to be any significant change in the value of b between 170 and $-196°$ C. The change from 1.1×10^{-6} to 0.9×10^{-6} is not significant, because the thickness of the films measured by interferometry has an accuracy of ± 30 Å at 130 Å and, although a different sample on the same substrate was used, the film thickness varies, over the surface, by ± 30 Å; the thickness enters the calculation for b in that the slope varies inversely with thickness. The slight decrease in the values of A on decreasing temperature from 170 to $20°$ C may be significant and it is a greater variation than the $T^{\frac{3}{2}}$ relationship in the expression for A. The fact that such a decrease does not continue below $20°$ C may mean that there is a transition

temperature in this region, but no attempts were made to find it precisely.

The thermal activation energies, as shown in table V, are lower than those found in bulk polymers. For instance, Bashara and Doty [6] quoted values of 1.3 and 0.3 eV in the two regions of conduction of glow-discharge-formed polybutadiene. However, it seems significant that the higher-conductivity polymers have lower values of activation energy, in agreement with the results of Bradley and Hammes [1]. A comprehensive review of the relationships between conductivity, activation energy, and chemical structure in the case of polyacetylenes and their derivatives prepared by various bulk methods has been published by Korn-Girard and Teyssie [10].

The fact that the activation energy is not the same for all the regions of conduction and appears to be zero in some instances is not in agreement with the Eley theory. However, the physical and chemical natures of these materials are unknown quantities of sufficient importance that this point does not discredit the theory, which is basically a consideration of conducting centres separated by potential barriers. In polymer materials, the state of these centres and their relation to each other depends greatly on structure and its changes with temperature and method of formation.

5. Conclusions

The aim of this work has been to correlate the structure of a polymer film with its conduction properties. Such knowledge would facilitate the development of films with the properties required for a specific purpose. Although it has not been possible to determine the structure of these polymers, because of the small mass of material in a 1000 Å film, it has proved reasonable to propose a polymer structure based on the shape of the monomer molecule. The success of this approach can be judged from the characteristics of the polycyanogen films developed using it.

Undoubtedly, a further understanding of the mechanisms of conduction in these films will be obtained from studies on more materials and from improvements in techniques to analyse them.

Acknowledgements

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