Electroluminescence from polyvinylcarbazole films: 2. Polyvinylcarbazole films containing antimony pentachloride

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A study was made of the optical absorption and electrical conduction of polyvinylcarbazole films that had been reacted with antimony pentachloride to produce a stable population of carbazole dimer cations. The films were semiconductors with low-field conductivities ranging up to about 10^{-3} ohm^{-1} m^{-1} and depending strongly on their $SbCl_5$ content, while the conduction at high fields was found to be field-dependent. After consideration of various alternatives, a qualitative model is suggested for this conduction which involves positive charge hopping between carbazole dimer crosslinks at a rate depending upon the crosslink concentration and upon temperature-dependent factors such as the relative orientation of neighbouring dimer groups and shifts in molecular energy levels due to small changes in molecular environment throughout the polymer.

Keywords Electroluminescence; polyvinylcarbazole/antimony pentachloride films; electrical conductivity; charge hopping; carrier mobility; cations

INTRODUCTION

During investigations into the possibility of producing d.c. electroluminescence from polyvinylcarbazole (PVCz) films it was established that a positive charge-injecting electrode for such a device could be made by reacting PVCz with $SbCl_5$ to produce a substantial concentration of stable cations within the film. The cations so produced, which give the polymer a distinctive green colour, and the qualitative aspects of the reaction were considered in paper 1 of this series. One conclusion of this was that the cations were carbazole dimer cations, as had been suggested by some authors previously, which were formed from carbazole dimer polymer crosslinks created in a previous stage of the overall reaction.

Here the optical and electrical properties of PVCz/$SbCl_5$ thin films are described, which extends earlier measurements performed only upon powders[1–4]. From these measurements and from the cation studies in paper 1, a qualitative model for the observed semiconductivity of PCVz/$SbCl_5$ films is suggested.

EXPERIMENTAL

The PVCz used was Luvican M170 obtained from BASF and purified by three precipitations with methanol followed by vacuum drying. Films were prepared either by the slow evaporation of PVCz/$SbCl_5$ solutions on a suitable substrate or by the application of a solution followed by rapid spinning of the substrate.

For the slow evaporation method PVCz and $SbCl_5$ were first reacted together in dichloromethane (DCM) solvent, taking care to keep the $SbCl_5$ concentration well below about 1 g l^{-1} and the PVCz concentration always greater than the $SbCl_5$ concentration in order to avoid massive precipitation. The solution was poured into an 8 cm diameter glass ring with flat ground edges standing on a horizontal glass substrate. The solvent evaporation rate was controlled by a glass cover placed over the ring and having a hole in its centre. An excessive rate of evaporation of the very volatile DCM would cause the formation of dark green 'waves' in the solution, probably due to local precipitation promoted by a temperature fall caused by evaporative cooling. The film thickness was controlled by the concentration and volume of the casting solution.

For the spinning method, which was used only for pure PVCz films as it required a high solution concentration, the PVCz was usually dissolved up in a 5:1 mixture of toluene/cyclohexanone (DCM was much too volatile) to a concentration of about 50 g l^{-1}. This solution was then applied to the substrate before or during its spinning at about 3000 rpm. The films produced by this method tended to be more uniform but also thinner than those of the other method.

Film preparation was always done in a dry air glovebox to minimize any interference by moisture. However, although $SbCl_5$ itself fumes strongly in moist air the PVCz/$SbCl_5$ solution was very stable and indeed could be kept in direct contact with liquid water for many weeks before appreciable fading of the characteristic green colour occurred.

Most films were cast directly onto transparent electrically conducting glass, usually Balzers 'Baltracon' but sometimes Pilkington's 'Hyviz', since this immediately provided one electrode.

Film thicknesses and uniformities were measured by thin-film interference methods using interference fringes observed either in transmission or reflection by a Perkin–Elmer 402 spectrophotometer. Thicknesses were calculated on the assumption that the refractive index of a

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PVCz/SbCl$_5$ film was the same as that of a pure PVCz film, namely 1.642 at 630 nm and 1.654 at 546 nm. Film areas used for electrical measurements were checked to be uniform to be better than one interference fringe, which was typically around 10% of the film thickness.

Electrical measurements were made in air on portions of film of known thickness and uniformity using the conducting glass as one electrode. The other electrode was generally a mercury drop confined within a small open-ended plastic cylinder, giving an electrode area of about 1 cm^2. This electrode could thus be quickly applied to any portion of a cast film (these were about 30 cm^2 in area) and subsequently moved on to a different portion. The applied potential and resulting current were each fed into an Analog Devices 755 logarithmic amplifier so that a log current–log voltage curve could be plotted directly. For the more highly conducting films a correction had to be made for the voltage drop across the conducting glass substrate.

RESULTS

Physical properties of PVCz/SbCl$_5$ films

Films cast from a solution of PVCz/SbCl$_5$ in DCM were green, shiny and fairly brittle. Despite the brittleness, films thicker than a few micrometres could sometimes be stripped off the glass substrate in water and then mounted in metal frames to give a self-supporting film of several square centimetres area. The green colour of such films tended to fade appreciably over a period of some months and this fading was accelerated by heating in air or vacuum.

Once cast from DCM solution the films were found to be insoluble in DCM, suggesting that the crosslinking reaction described previously (paper 1) leads to the formation of a microprecipitate held in suspension; indeed if the PVCz and SbCl$_5$ concentration were too high, massive precipitation occurred. Furthermore, whereas a typical casting solution (4 g l^{-1} of PVCz and 1 g l^{-1} of SbCl$_5$) could usually be pushed through a filter of 5 μm pore size it would generally not go through a filter with somewhat smaller pores unless it had first been through the 5 μm filter. However, by such prefiltering it was often possible ultimately to pass it through a 0.2 μm pore size filter, and the visible absorption spectrum of the filtrate was identical to that of the original unfiltered solution. Such formation of colloidal particles has previously been suggested by Matsumoto^2 on the basis of electron spin resonance studies of similar solutions.

A film of pure PVCz cast from DCM solution could be reacted afterwards with SbCl$_5$ to produce the familiar green colour if the SbCl$_5$ was diluted in a liquid such as nitromethane, which is polar and a non-solvent for PVCz but which does penetrate into the film. However, SbCl$_5$ diluted in a non-polar liquid such as carbon tetrachloride had no effect at all upon a pure PVCz film unless a few drops of DCM or nitromethane were added to it. An overlong contact with the SbCl$_5$ solution produced a very dark green film which wrinkled and flaked. The wrinkling was caused by expansion of the film due to penetration of the SbCl$_5$ into it and, very possibly, structural changes caused by the crosslinking reaction. Soaking of the pure PVCz film in nitromethane alone caused very little film expansion.

For the films cast from PVCz/SbCl$_5$ solution it was found that on average

$$\left(\frac{\Delta}{tM}\right)\simeq 2 \qquad (1)$$

where Δ is the absorbance of the film at the 430 nm peak, t is the film thickness (in μm) and M is the ratio of SbCl$_5$ to PVCz molar concentrations in the original casting solution (the PVCz molar concentration being measured in terms of individual carbazole units). For a solution of PVCz/SbCl$_5$ in DCM it was found previously (paper 1) that at low values of M

$$\Delta=\varepsilon^+LK[\mathrm{SbCl_5}]=\varepsilon^+LKM[\mathrm{PVCz}] \qquad (2)$$

where ε^+ is the extinction coefficient of the cation (measured to be 1.7×10^7 l mol^{-1} m^{-1} at 430 nm), K is the average number of cations produced by each SbCl$_5$ molecule at low values of M (about 0.043), L is the path length (in metres) and [SbCl$_5$] and [PVCz] are molar concentrations. If (2) is applied to the solid film, assuming the PVCz density to be the same (1.2 kg l^{-1}) as in pure solid PVCz, then the (Δ/tM) value obtained is 4.8 as compared with the observed value of about 2. The reason for this discrepancy is not clear but seems largely linked to undetected variations in casting technique. The observed (Δ/tM) values varied between about 1.2 and 3.6 although casts were done in nominally similar conditions.

Film spectra

The visible and near-infra-red absorption spectrum of the green films was very similar to that of the original solution (see paper 1), with peaks at 430, 1100 and 1600 nm, and absorption extending out to around 4000 nm. However, the 1600 nm peak of the film was barely resolved from the 1100 nm peak whereas in the solution it was quite clearly separate. Indeed if the green film was formed by reaction of SbCl$_5$ with an existing pure PVCz film, then the 1600 nm peak was not seen at all. It may well be, as suggested in paper 1, that the 1100 and 1600 nm peaks represent two very different conformations of neutral carbazole groups around the basic dimer cation and interacting with it, and that the conformation giving rise to the latter peak is difficult to attain in an existing solid film.

The characteristic blue fluorescence of pure PVCz films (caused by emission from at least two different carbazole excimer conformations^5) was found to be very efficiently quenched in PVCz/SbCl$_5$ films. This is likely to be due to excitation energy transfer from the neutral carbazole groups to the upper excited states of the cations followed by loss of this energy through the very low lying electronic states (giving rise to the 1100 and 1600 nm peaks) of these species.

The infra-red spectrum of the PVCz/SbCl$_5$ film was conveniently observed by starting measurements with a pure PVCz film that had been stripped and mounted, self-supporting, in a metal frame. After measurement of its infra-red spectrum, the film was then immersed in a weak solution of SbCl$_5$ in nitromethane to promote cation formation and was then removed, washed in pure nitromethane, dried and measured again. It was then immersed in a solution of tetramethylphenylenediamine (TMPD) in nitromethane as this was found previously (paper 1) to 'bleach' the green colour by positive charge transfer from the polymer cations to the TMPD. Finally, the film was soaked in pure methyl alcohol to remove the TMPD, dried and measured once more. The initial SbCl$_5$

treatment was found to give increased absorption over virtually the whole spectrum from the ultra-violet to at least 250 cm^{-1}, but in particular it broadened many of the pure PVCz peaks in the 1000–1600 cm^{-1} range while producing new broad absorptions at about 1550, 1080, 850, 580 and 330 cm^{-1} together with narrower peaks at 1270, 870 and 795 cm^{-1}. The TMPD treatment largely removed the broad absorptions at 1550, 1080 and 850 cm^{-1}, which can thus be ascribed to the polymer cation itself, and also the 330 cm^{-1} peak which has been assigned by Matsumoto[2,3] to the $SbCl_6^-$ and/or $SbCl_6^{3-}$ anions. The peaks at 1270, 870 and 795 cm^{-1} that were produced by $SbCl_5$ but not removed by TMPD are the counterparts of the peaks that were found at 1255, 880 and 803 cm^{-1} in an authentic sample of 9,9′-diethyl-3,3′-dicarbazyl but not in *N*-ethylcarbazole (NEC), and are thus associated with the dimerization (crosslinking) reaction produced in PVCz by $SbCl_5$. The 880 cm^{-1} and 803 cm^{-1} peaks have been ascribed[6] to the 1,2,4 trisubstitution of the benzene rings in dimerized carbazole.

Electrical measurements

The current flowing through a PVCz/$SbCl_5$ film was found to be ohmic (i.e. proportional to applied voltage and inversely proportional to film thickness) at fields less than about 10^6 V m^{-1}. This contrasts with the current through a pure PVCz film which is very non-linear (see paper 3). The current was also independent of the relative polarity of the Baltracon and mercury electrodes. However, when the mercury electrode was replaced by a vacuum-evaporated aluminium electrode the current was found to be asymmetric with respect to electrode polarity and extremely non-linear. With the aluminium electrode negative and the conducting glass positive, the current was very small at low voltages compared with the mercury electrode values but then rose abruptly as approximately the fifteenth power of voltage over three decades of current (for an applied voltage of 1.5–2 V), followed by a further rise as about the square of voltage to bring it eventually to about the value that it would have had if a mercury electrode had been used. Under reverse polarity the current was again small at low voltage, increasing initially as the square of voltage, but became unstable and breakdown occurred at a comparatively low field ($\sim 10^6$ V m^{-1}). This behaviour indicates that a potential barrier has been established at the aluminium/film interface. This might be associated with the somewhat lower work function of aluminium (4.1 eV) as compared to mercury (4.5 eV) but is more probably due to an actual chemical reaction between the aluminium and the $SbCl_6^-$ anions (or other $SbCl_5$ reaction products) in the film since slow degradation of the aluminium electrodes was observed.

Subsequent measurements were made only on the 'ohmic' system of Baltracon/mercury electrodes. It was found here that at high fields ($>10^6$ V m^{-1}) the current increased more rapidly than the voltage. This non-linearity was partly due to resistive heating of the sample which caused an increase in carrier mobility. It is known from earlier work on PVCz/$SbCl_5$ powders[1,4] that the conductivity is strongly thermally activated, with activation energies in the 0.15–1 eV range depending on the type of PVCz used and its $SbCl_5$ content, but this temperature dependence was not studied here.

By increasing the voltage across the sample rapidly the current–voltage curve could be plotted with negligible contribution from resistance heating. It was then apparent that at higher fields the current was still supra-ohmic, a fact not noticed in the earlier powder studies which used fields below 7×10^5 V m^{-1}. This was not unexpected since the time-of-flight measurements of Gill[7] have shown that the carrier mobility in both pure PVCz films and in PVCz films doped with the strong electron acceptor trinitrofluorenone (TNF) is a function of both temperature and field strength, where the dependence on field strength, F, is of the form:

$$\exp\left(\frac{pF^{1/2}}{kT_c}\right)$$

where p is a constant not affected by the presence of TNF while T_c is an effective temperature and k is Boltzmann's constant.

If the conduction mechanism in PVCz/$SbCl_5$ is basically similar to that in pure PVCz, differing only in the presence of intrinsic carriers rather than relying on photoinjected carriers, then the current density would be expected to be given by

$$J = Ne\mu F = (Ne\mu_0)F\exp\left(\frac{pF^{1/2}}{kT_c}\right) \tag{3}$$

where N is the carrier density, e the electronic charge and μ_0 the (temperature-dependent) mobility at zero field. However, this expression could not in general be fitted to the observed J–F curves, although an approximate fit could be obtained in some cases by use of the generalized form

$$J = aF\exp(bF^n) \tag{4}$$

where a and b are constants while n varied from sample to sample between about 0.5 and 2. A much better fit was obtained by use of the function

$$J = \alpha\sinh\beta F \tag{5}$$

where α and β are constants, as this could be fitted to all the J–F curves with β varying by only about 20% from an average value of 2.0×10^{-7} m V^{-1} and having no obvious correlation with the $SbCl_5$ content of the film when the latter was varied by more than a decade to give a conductivity variation approaching four decades (see below). Typical plots of this type are shown in *Figure 1*.

The only case studied in which equation (3) could be fitted to a reasonable length of the observed J–F curve was that of the film with lowest $SbCl_5$ content (2 wt% of $SbCl_5$ as compared to PVCz in the casting solution). Here, over the low-field portion of the curve, the measured value of the constant (p/kT_c) was 5.8×10^{-4} m$^{1/2}$ V$^{-1/2}$ which does happen to be close to the value of 5.95×10^{-4} m$^{1/2}$ V$^{-1/2}$ calculable from the data of Gill[7] for a pure PVCz film at 293K. However, this set of data does also fit equation (5) reasonably well, as shown in *Figure 1*.

The conductivity of the PVCz/$SbCl_5$ films was found to be very sensitive to their $SbCl_5$ content. The low-field conductivities are shown in *Figure 2* as plotted against Δ/t. *Figure 2* includes results for films both cast from PVCz/$SbCl_5$ solution and cast from pure PVCz solution

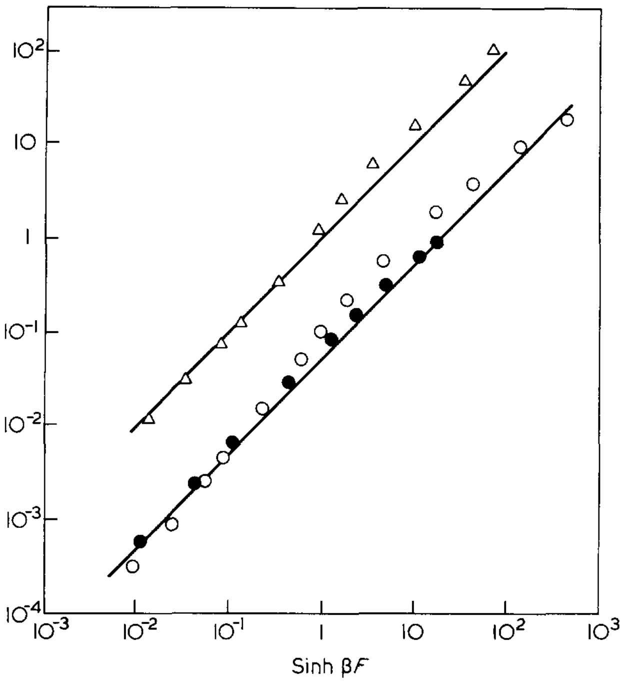

Figure 1 Current density J *versus* sinh βF for three different PVCz/SbCl$_5$ films where F is field strength: ○, film 2.1 μm thick, (Δ/t) of 0.024, β taken as 1.9×10^{-7} m V^{-1}; △, film 1.58 μm thick, (Δ/t) of 0.184, β taken as 2.2×10^{-7} m V^{-1}, current densities have been divided by 10; ●, film 1.83 μm thick, (Δ/t) of 0.322, β taken as 2.4×10^{-7} m V^{-1}, current densities have been divided by 1000

with subsequent treatment of the solid film with SbCl$_5$ in nitromethane, but these are not distinguished from one another as there was little difference between results from the two types. The addition of 40 wt% NEC to PVCz in solution followed by casting and then subsequent SbCl$_5$ treatment also had little effect on the conductivity, so apparently monomeric carbazole is linked into the conduction process by SbCl$_5$ just as easily as carbazole groups attached to the polymer. Likewise mixing of substantial amounts of pure PVCz with an existing PVCz/SbCl$_5$ solution prior to casting still gave a conductivity much as would have been expected on the basis of the total SbCl$_5$ content of the mixture, as shown in *Figure 2.*

Figure 2 indicates an empirical relationship between conductivity and carbazole cation concentration of roughly

$$\sigma \propto \left(\frac{\Delta}{t}\right)^{4.2} \qquad (6)$$

although as can be seen the scatter of individual values is appreciable due, presumably, to variations in casting technique. A similar variation of conductivity was found by Block *et al.*[4] using a powder of PVCz that had been oxidatively dimerized by tris(*p*-bromophenyl)ammonium hexachloroantimonate to produce a material probably very similar to the one produced here by direct SbCl$_5$ oxidation. For their material the exponent in equation (6) was approximately 3.6 for the most highly oxidized material, although falling to rather lower values as the ion concentration decreased.

The conductivity of one PVCz/SbCl$_5$ film was measured six months after its initial casting, during which time it was kept in a dry air atmosphere. In this period the green colour of the film faded appreciably, with the absorbance, and hence the cation concentration, declining by a factor of 4 and its conductivity likewise declining by about the degree indicated by equation (6).

DISCUSSION

Analysis of experimental data

Of prime interest here are the electrical properties of PVCz/SbCl$_5$ films. The extensive studies undertaken on PVCz/TNF films[8], largely in relation to their use in xerography, have demonstrated the basic features of the conduction process. Conduction can occur through both positive and negative charge carriers. The positive charges are based on the carbazole groups of the polymer, as these have relatively low ionization potentials, and the charges move from one such group to the next through the material. However, the polymeric nature of the material is not of primary importance since similar conductivity has been observed[9,10] in an inert polycarbonate polymer

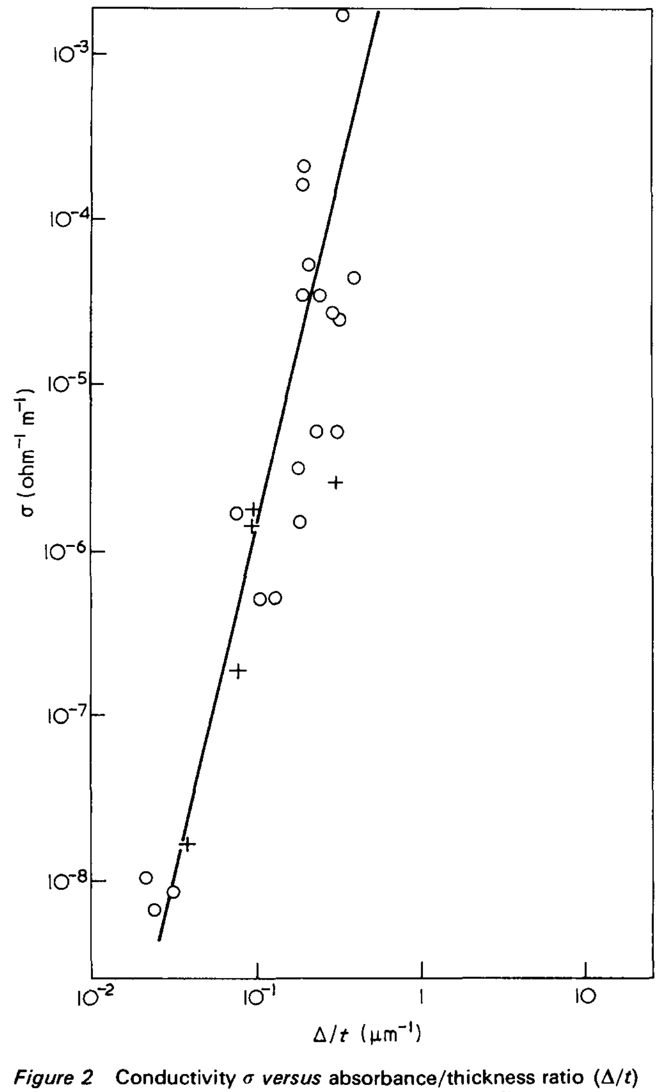

Figure 2 Conductivity σ *versus* absorbance/thickness ratio (Δ/t) for PVCz/SbCl$_5$ films: ○, films of PVCz/SbCl$_5$; +, films made from PVCz/SbCl$_5$ solution to which 40 wt% of pure PVCz or NEC was added just prior to casting

doped with *N*-isopropylcarbazole (NIPC). The basic conduction mechanism appears to be thermally and field-assisted electron transfer from a neutral carbazole group to a carbazole cation situated nearby. The probability of such transfer increases as the distance between the neighbouring molecules decreases, and hence in the case of an inert matrix doped with carbazole (or other organic molecules of low ionization potential) the conductivity rises strongly with increasing dopant concentration. The negative carriers are based on the TNF molecules (other strong electron acceptors would probably act in a similar way) and move via electron transfer from a TNF anion to a neutral TNF molecule; such conduction is indeed observed, with greater efficiency, in pure TNF. The carbazole and TNF molecules tend to bind together as a charge-transfer complex, since one is a good electron donor and the other a good electron acceptor, and this produces a prominent charge-transfer absorption band which gives a strong brownish coloration to the material. This complexing has apparently little effect on the electron transfer process via the TNF molecules but it does appear to prevent positive charge conduction via carbazole groups directly complexed with TNF molecules. Despite the appreciable interaction between carbazole and TNF, the PVCz/TNF is an insulator in the dark since it contains a negligible number of free ions. Conduction occurs only when charges are injected into the material from outside or when light absorption within it produces ion pairs that can be separated under the influence of an external field.

The PVCz/$SbCl_5$ system is different from the PVCz/TNF system in that $SbCl_5$ is so much stronger an electron acceptor than TNF that it actually causes ionization of the carbazole groups and this produces a standing population of carbazole cations and $SbCl_6$ anions, as described in paper 1. Thus PVCz/$SbCl_5$ contains a large concentration of 'intrinsic' carriers and so exhibits appreciable dark conductivity while PVCz/TNF remains an insulator in the dark.

Any positive charge conduction in PVCz/$SbCl_5$ must be carried via carbazole molecules but it is not clear whether there is any corresponding electron conduction via the $SbCl_6$ anions and, if so, how its magnitude compares with the positive charge contribution. Proof of a very substantial positive charge conduction in the overall PVCz/$SbCl_5$ conductivity comes from the experiments on double-layer films made up of one pure PVCz and one PVCz/$SbCl_5$ layer described in paper 3. Here the PVCz/$SbCl_5$ was used as a positive charge-injecting layer for the pure PVCz film, and since the latter does not significantly transport electrons[7] the substantial observed current must have been a positive charge current passing through the PVCz/$SbCl_5$ layer. Furthermore, since on occasion the current passing through the two-layer film approached that which would have been obtained from a single PVCz/$SbCl_5$ film of equivalent thickness, it must be concluded that positive carriers contribute a very appreciable part, if not the whole, of the total conduction current in these films.

If positive charges are the majority carriers then it might be expected that their mobility would be that of the positive charges already studied in pure PVCz by time-of-flight measurements and that the current through PVCz/$SbCl_5$ would have been given by a direct application of equation (3). The carrier density N could then, assuming a negligible contribution from negative carriers, be identified with the cation concentration where, using previous definitions:

$$N = \left(\frac{N_A \Delta \times 10^6}{t\varepsilon^+}\right) \text{ cations m}^{-3} \tag{7}$$

where N_A is Avogadro's number and film thickness t is still measured in micrometres.

Combining (3) and (7) and neglecting the field dependence of the mobility thus gives the low-field ohmic conductivity as

$$\sigma_0 = \frac{J}{F} = \left(\frac{10^3 e\mu_0 N_A}{\varepsilon^+}\right)\left(\frac{\Delta}{t}\right) \tag{8}$$

Clearly equation (8) does not yield the observed conductivity behaviour of equation (6), but it does predict conductivities of the right magnitude at the middle of the range of (Δ/t) values used. Putting into it ε^+ as $1.7 \times 10^7\,\text{l mol}^{-1}\,\text{m}^{-1}$ (from paper 1) and μ_0 as $1.2 \times 10^{-12}\,\text{m}^2\,\text{V}^{-1}\,\text{s}^{-1}$ (from time-of-flight measurements in pure PVCz[7]) gives:

$$\sigma_0 = 6.8 \times 10^{-6}\left(\frac{\Delta}{t}\right) \text{ ohm}^{-1}\,\text{m}^{-1} \tag{9}$$

Comparison of equation (9) with the line on *Figure 2* shows that the two intersect at a (Δ/t) value of 0.15, indicating that for (Δ/t) less than 0.15 the PVCz/$SbCl_5$ mobility is *less* than that for pure PVCz, while the converse is true at values greater than 0.15.

Two important characteristics of PVCz/$SbCl_5$ conductivity that thus need explanation are the steep increase of conductivity with (Δ/t) and the fall of mobility below the pure PVCz value at low $SbCl_5$ concentrations. They are probably linked with the fact that in pure PVCz the conduction takes place by charge exchange between monocarbazole groups whereas in PVCz/$SbCl_5$ the charge exchange is probably predominantly between dimer carbazole groups (at least for the higher (Δ/t) values). The carbazole dimer was found to have an ionization potential about 0.26 eV lower than that of a monocarbazole group (paper 1) and thus positive charges could transfer with relative ease from monocarbazole to dimer carbazole groups but the reverse transfer would be much more difficult as considerable thermal or field activation would be needed. In fact, a low concentration of carbazole dimers amongst a much higher concentration of monocarbazole groups would constitute a set of carrier 'traps' relative to conduction through the monocarbazoles, while in the reverse case conduction amongst the dimers should be little affected by the presence of a lesser number of monocarbazoles. The mobility of positive charges in just such a binary system of organic donor molecules has been studied in time-of-flight measurements by Pfister *et al.*[10], who used polycarbonate as an inert matrix and loaded it with NIPC and triphenylamine (TPA) molecules, which differ in ionization potential by 0.47 eV. It was indeed found that addition of a small amount of the lower ionization potential molecule, TPA, could reduce the transit time of the positive charges in a predominantly NIPC system by up to two orders of magnitude whereas the transit times in a predominantly TPA system were unaffected by substantial amounts of NIPC. It was also noted that the

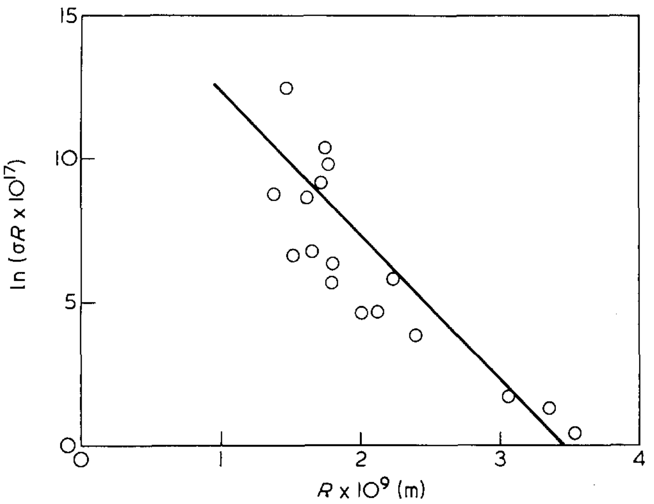

Figure 3 Plot of ln(σRx10^{17}) *versus* average dimer separation distance R for films from *Figure 2*

transit time was more than an order of magnitude faster for the low ionization potential TPA than for NIPC when each were alone at similar concentrations.

Applying these observations to the PVCz/$SbCl_5$ system the fall in mobility below the pure PVCz value for low $SbCl_5$ concentrations can thus be ascribed to the positive charge trapping effects of dimer carbazole groups in a basically monocarbazole conduction system while the steep increase in conductivity with $SbCl_5$ concentration is ascribed to increasingly efficient conduction between the dimer carbazoles as their concentration increases and hence their mutual separation decreases.

In treating the conduction of low-mobility amorphous organic solids it is generally assumed that the conduction process is basically one of charge hopping from one molecule to another where each charge is strongly localized upon a particular molecule between hops rather than being delocalized over a large number of molecules as would be the case for a band model of conduction. If such hopping is essentially a tunnelling process, then its rate will be controlled by the degree of overlap between the wavefunctions of each cation and its neighbouring uncharged molecule, which will be strongly dependent upon their mutual separation. An expression for the mobility of one such system, the thermally assisted hopping of small polarons in the non-adiabatic case, can be written as[7,11]:

$$\mu=\left(\frac{ve}{6kT}\right)R^2\exp\left[-\left(\frac{2R}{R_0}+\frac{E}{kT}\right)\right] \qquad (10)$$

where R is the average distance between adjacent conducting molecules, R_0 is the 'localization radius' of the positive charge while on a particular molecule, E is the activation energy for the thermal assistance, k is Boltzmann's constant and v is a vibration frequency.

In combining equation (10) with (3) to obtain an expression for the conductivity, values are needed for the carrier density N and the average intersite hopping distance R. The carrier density can be equated with the cation concentration given in equation (7) if, as before, any negative carrier current is neglected. The average intersite hopping distance is taken as the inverse cube root of the concentration of hopping sites available. If such hopping is indeed predominantly between the dimer carbazole rather than monocarbazole groups, then the hopping site concentration will be equal to half the concentration of the monocarbazole groups that have dimerized. As shown in paper 1 approximately one carbazole group is dimerized for every $SbCl_5$ molecule added to PVCz (up to at least 70% conversion). Assuming a PVCz film density of 1.2 kg l^{-1} and taking a molecular weight of 193 for each carbazole-containing chemical repeat group in the polymer thus gives the concentration of dimerized carbazole groups as about $1.9\times10^{24}M\text{l}^{-1}$, where as before M is the molar ratio of $SbCl_5$ molecules to monocarbazole groups in the reaction mixture. Thus R is given by:

$$R\simeq(1.9M)^{-1/3}\times10^{-9}\ \text{m} \qquad (11)$$

M can be replaced by (Δ/t) through use of equation (1) to give:

$$R\simeq\left(\frac{0.95\Delta}{t}\right)^{-1/3}\times10^{-9}\ \text{m} \qquad (12)$$

Combining equations (3), (7), (10) and (12) and neglecting the temperature and field dependence of the mobility then yields:

$$(\sigma R)\propto\exp\left(\frac{-2R}{R_0}\right) \qquad (13)$$

where R is given by equation (12).

A plot of ln(σR) against R according to equation (13) is shown in *Figure 3*. Although the experimental scatter is appreciable, a plausible straight line can be drawn and from the slope of this an R_0 value of about 4 Å is obtained, which seems quite reasonable for the localization radius of a positive charge on a dicarbazole unit.

In deriving equation (13) via equation (10) it was assumed that the temperature-dependent part of the latter was not of importance. However, a plot in *Figure 4* of the activation energy measurements of Yamamoto *et al.*[1] and Block *et al.*[4] shows that, as the conductivity rises from about $10^{-8}\,\text{ohm}^{-1}\text{m}^{-1}$ to $10^{-3}\,\text{ohm}^{-1}\text{m}^{-1}$ with increasing cation concentration, the activation energy falls from about 0.52 eV to about 0.18 eV. Such a change might be allowed for in equation (10) by introducing an empirical relation between E and σ (and hence (Δ/t) via equation (6)) based on *Figure 4*, but if this is done the modified form of equation (13) which is produced yields a negative value for R_0. This is probably because the observed activation energy change is accompanied by a substantial change in the pre-exponential factor of equation (10).

The form of mobility suggested by equation (10) is by no means the only one that can be envisaged. The model of Bagley[12], which considers the carriers to be purely thermally activated over a set of regular barriers set a distance λ apart and being of height E, gives a mobility of:

$$\mu=\left(\frac{2\lambda v}{F}\right)\exp\left(-\frac{E}{kT}\right)\sinh\left(\frac{\lambda eF}{2kT}\right) \qquad (14)$$

where v is now the attempt frequency for barrier hopping. This form, in which the mobility is field-dependent at high

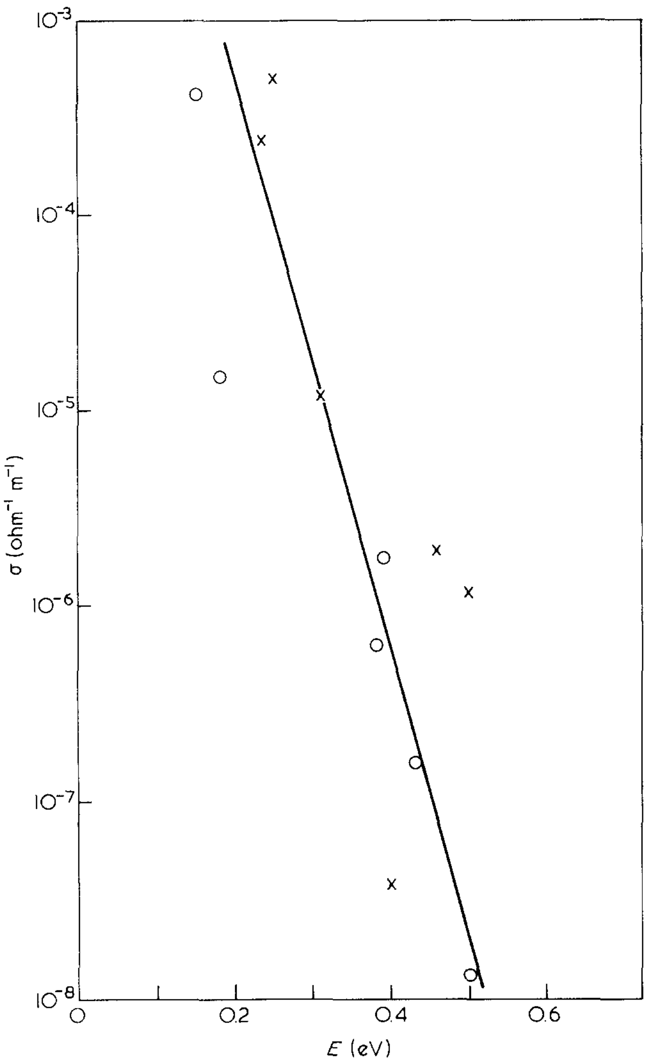

Figure 4 Conductivity *σ versus* activation energy *E* for PVCz containing carbazole dimer cations: ○, data of Block *et al.*[4]; x, data of Yamamoto *et al.*[1]

fields but independent of field at low fields, leads to a conductivity of:

$$\sigma=(2\nu e)N\lambda\exp\left(-\frac{E}{kT}\right)\frac{1}{F}\sinh\left(\frac{\lambda eF}{2kT}\right) \qquad (15)$$

This has the advantage of apparently explaining the observed field dependence of the PVCz/SbCl$_5$ film conductivity, which as shown earlier seems to have just this sinh form. The constant β from equation (5), found to have a value of about $2\times10^{-7}\,\mathrm{m\,V^{-1}}$, can then be identified with $(\lambda e/2kT)$ which leads at room temperature to a barrier separation λ of about 100 Å. However, not only does this λ value seem unrealistically large but it is also independent of the SbCl$_5$ concentration since β was approximately constant for a variety of SbCl$_5$ contents. Thus the conductivity predicted by equation (15) depends only on the SbCl$_5$ concentration via the carrier density term N and hence indicates a purely linear relation between conductivity and cation concentration which is not found in practice.

Seki[13] has proposed a model that combines features of the small polaron and Bagley models to produce a mobility expression:

$$\mu=\left(\frac{2\lambda_0}{\tau_0}\right)\frac{1}{F}\exp\left(-\frac{2R}{R_0}-\frac{U}{kT}\right)\sinh\left(\frac{e\lambda_0F}{2kT}\right) \qquad (16)$$

where the energy levels of the molecular hopping sites are assumed to fluctuate in an approximately regular fashion throughout the material with an average amplitude of U and over an average distance of λ_0 (which is expected to be a number of molecular spacings in size) and where τ_0 is a constant with the dimension of time.

If the spatial fluctuations of the molecular energy levels are assumed to be largely independent of the extent of the polymer crosslinking, then the field-dependent term in equation (16) will be independent of SbCl$_5$ concentration, as found in practice. The λ_0 value will be the same as the 100 Å derived for λ on the Bagley model but will here be of a rather more reasonable size since it is deemed to represent a number of molecular spacings.

The low-field conductivity on the Seki model can be written as

$$(\sigma R^3)\propto\exp\left(\frac{-2R}{R_0}\right)$$

if we again neglect the temperature dependence and assume that λ_0 is indeed independent of SbCl$_5$ content. The resulting plot of $\ln(\sigma R^3)$ against R is similar to *Figure 3* but produces a rather larger R_0 value of about 5.8 Å. Thus the Seki model does provide a plausible mathematical fit to the observed variation of PVCz/SbCl$_5$ conductivity with both field and SbCl$_5$ concentration. However, it is not clear how in practice the supposed characteristic distance for energy level fluctuations of about 100 Å should be interpreted or whether the energy amplitude of this fluctuation is really likely to be as great as the 0.5 eV indicated from activation energy measurements on samples of low cation concentration (see *Figure 4*).

A different model again is that of Hirsch[14,15] who has suggested that the carrier transport is by small polaron hopping, as considered earlier, but is controlled by the presence of charged traps. This interpretation arose from the observations in time-of-flight measurements that the mobility of carriers in PVCz and in PVCz/TNF has an activation energy component which varies as the square root of the applied field (see equation (3)). Such behaviour in inorganic semiconductors is generally explained by the Poole–Frenkel effect in which the barrier height of charged or Coulomb centres is reduced by the applied field and thus the activation energy for carrier escape from the trap is lowered. The model is mathematically similar (with re-definition of parameters) to the small polaron model (see equation (10)), although Hirsch derives a wavefunction overlap correction for the p-type orbitals of aromatic molecules, and it has the great merits of being internally consistent in respect of available experimental data and of breaking down the large observed mobility activation energy into a sum of several smaller constituents. However, doubts have been expressed about a Poole–Frenkel interpretation[7] and in particular as to whether an appreciable concentration of charged traps is likely to exist in 'pure' PVCz without detection. A further difficulty in this regard is associated with the fact that in PVCz, which conducts via positive carriers only, the Coulomb traps would be organic anions and would thus probably trap the carriers by recombining with them (as in the case of the electroluminescence described in paper 3) to form a neutral impurity molecule adjacent to a carbazole group. However, to release the carrier again, which is necessary if the 'trap' is not to become a 'sink', the impurity molecule must re-ionize the carbazole group with only a little help (~ 0.1 eV[15]) from thermal energy. Such carbazole ionization is what $SbCl_5$ molecules accomplish when added to PVCz in a suitable solvent, but this is only possible because $SbCl_5$ is a very strong inorganic electron acceptor. Such ionization does not seem possible for any organic acceptors since only charge-transfer complexes and not separated ion pairs are produced[16] when PVCz is reacted with the strongest organic acceptors such as tetracyanoethylene, tetracyanoquinodimethane and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone which have electron affinities[17] of about 2.8, 2.8 and 3.1 eV, respectively. The presence of any even stronger acceptors as fortuitous impurities in all types of PVCz seems unlikely. Of course in PVCz/$SbCl_5$ such acceptors are deliberately added, but here the field dependence of the conductivity was shown earlier not to be of the Poole–Frenkel type.

Qualitative model of PVCz/$SbCl_5$ conductivity

The subject of charge transport in low-mobility amorphous materials has been much studied and debated over the last few years, particularly in relation to the chalcogenide glasses but also in relation to polymers and predominantly here to PVCz in view of its importance in xerography. Two main classes of models have emerged from this work. One is based on transport through definite energy bands, as for crystalline materials although with the bands rather less well defined, but with multiple carrier trapping occurring to slow down the overall rate of charge transport. The other assumes carriers to be strongly localized upon individual sites and to progress from site to site by hopping due, generally, to thermally assisted tunnelling. For low-mobility organic systems like PVCz there seems little doubt that a basically hopping type model is the most appropriate[18] since as already noted the hopping sites can be directly identified as carbazole molecular groups and transport can be viewed as a redox process in which electrons are exchanged between cations and neutral molecules. Such transport in PVCz and similar materials has been found to show very distinctive behaviour in time-of-flight measurements in that, instead of a well defined carrier transit time, a broad dispersion of transit times is generally observed such that the mean carrier velocity apparently falls off with traverse distance, so making it impossible to define a normal carrier mobility. This type of transport was treated in a key paper by Scher and Montroll[19] who used a stochastic model which envisaged the carriers executing a time-dependent random walk through a lattice of hopping sites and governed by a hopping time distribution function. This distribution of hopping times was assumed to arise from fluctuations in the separation distances of the hopping sites, owing to the disordered nature of the amorphous material, and from fluctuations in the potential barriers between the sites. The model predicted that, if charge was injected into one side of a slab sample and induced to drift through it by an electric field, then instead of the charges moving with a uniform mean velocity and Gaussian charge density distribution, as would occur if the hopping time distribution function represented a single transition rate, they would move at a mean velocity that steadily decreased with time and with a very asymmetric charge density distribution. This behaviour is due to the wide distribution of carrier hopping times which means that while some carriers initially move rapidly through the sample many others wait for long periods before making significant progress.

Much discussion has followed the original Scher and Montroll analysis but it has still not been fully established whether fluctuations in site separation distances alone can give rise to the observed dispersion in carrier transit times or whether substantial variations in site energy levels (i.e. carrier trapping) must also be present[20]. Pfister and Scher[18] are of the opinion that in practice disorder in both hopping distances and activation energies is probably present and cannot be separated from one another; they further emphasize that the presence of disorder alone does not necessarily yield observable dispersive transport but that this depends upon the microscopic transport parameters. A good example of this latter point is PVCz itself which changes from dispersive to non-dispersive transport[21] as its temperature is raised above about 420K whereas bromine-substituted PVCz, which is apparently more disordered than PVCz due to the substitution, exhibits dispersive transport at all temperatures.

One important cause of hopping rate variations in amorphous organic materials is likely to be changes in the mutual orientations of the hopping site molecules, as Slowik and Chen[22] have calculated that the overlap integral between the highest occupied orbitals of neighbouring carbazole molecules, to which the hopping rate is very sensitive, can vary by up to seven orders of magnitude for different mutual orientations at a fixed centre-of-mass distance. Slowik and Chen[23] also noted that molecular rotation (or libration) thus provides a most important mechanism for time variation of the overlap integral. Following on from this, Pfister and Scher[18] emphasized that the observed activation energy for carrier transport may contain at least four separate terms, the polaron binding energy E_p due to each carrier polarizing the matrix material in its immediate vicinity, the site-to-site fluctuation of the hopping site energy levels due to the molecular disorder E_d, the rotational or librational activation energy controlling fluctuations in molecular site orientation E_r and, where applicable, the energy separation E_t between the energy levels of any chemical traps present and the levels of the dominant carrier hopping sites.

In seeking an at least qualitative model of conduction in PVCz/$SbCl_5$ it has already been shown that hopping transport by tunnelling between carbazole molecules (rather than by pure thermal activation as in the Bagley model) is the most likely general transport mechanism for PVCz/$SbCl_5$ as well as for pure PVCz. Likewise it has been shown that the production of carbazole dimer crosslinks having lower ionization potentials than the monocarbazole groups is likely to constitute a set of carrier traps (for very low $SbCl_5$ contents) and from the above discussion this would be expected to cause an initial increase in the carrier transport activation energy over the PVCz transport activation energy[7] of about 0.65 eV. In fact, activation energies as high as 1.0 eV were observed by Block *et al.*[4] in their lowest-conductivity samples, although it would be of interest to see confirmation of this from time-of-flight studies on lightly crosslinked samples. As the crosslink concentration rises with $SbCl_5$ content so the hopping conduction may be assumed to take place increasingly between dimer rather than monocarbazole groups, giving a sharp rise in mobility after the initial fall. But the effect of the crosslinking may well also be to reduce the fluctuations in distance between adjacent polymer chains by literally tying them together and in addition to reduce considerably the degree to which the individual carbazole groups can rotate or librate and thus to reduce the thermally induced fluctuations in the overlap integrals between molecular sites. Hence the term E_t in the overall charge transport activation energy will be steadily eliminated as the dimer groups become the major hopping sites, E_r will be reduced as rotation is inhibited by crosslinking and E_d may fall somewhat as thermal fluctuations in interchain distances are likewise reduced by crosslinking. The net effect should be a substantial fall in the conductivity activation energy (following its rise at very low crosslinking levels) and this is clearly shown by *Figure 4*.

The highest room-temperature mobility for PVCz/$SbCl_5$ deduced in this work of $3.6 \times 10^{-10}\,m^2\,V^{-1}\,s^{-1}$ corresponds, using an activation energy of 0.18 eV, to a mobility of $5 \times 10^{-7}\,m^2\,V^{-1}\,s^{-1}$ as $(1/T) \rightarrow 0$. This is still several orders of magnitude smaller than similar mobilities measured in organic crystals, including those of NIPC[24]. This is probably due to the relatively slow transport rate of hopping conduction in most physically realizable amorphous systems as compared with the much more rapid coherent narrow band conduction possible in crystalline materials. This is shown dramatically by Gill's[25] time-of-flight measurements on TNF where the mobility of crystalline TNF was shown to be more than four orders of magnitude greater than that of solid amorphous TNF and its activation energy only 0.1 eV as compared to 0.63 eV.

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