Electroluminescence from polyvinylcarbazole films: 3. Electroluminescent devices

R. H. Partridge

Division of Electrical Science, National Physical Laboratory, Teddington, Middlesex, UK
(Received 22 July 1981; revised 11 October 1982)

The conditions for electroluminescence generation from organic polymer films are discussed and the development of a direct current electroluminescent device is described which is based upon a double-layer polyvinylcarbazole film. The device employed a polyvinylcarbazole/antimony pentachloride positive charge-injecting electrode and a caesium electron-injecting electrode. It emitted predominantly blue light which was visible in full artificial room lighting conditions. The electrical characteristics of the device are described and are compared with those of a single pure polyvinylcarbazole film.

INTRODUCTION

Electroluminescence has frequently been observed in inorganic materials and is now of commercial importance. It has sometimes been produced in fragile, high-purity organic crystals and also in organic solutions in the form of chemiluminescence of electrochemiluminescence. However, direct current electroluminescence, at electric fields well below breakdown values, does not appear to have been reported previously from organic polymers, although these materials have the potential advantages of cheapness, good film-forming properties and general ease of fabrication coupled with the availability of a variety of luminescent additive molecules and freedom from the need to work at high levels of chemical purity. Electroluminescence from devices based on polyvinylcarbazole films is reported here, which expands upon a brief and much earlier description[1]. These devices were capable at best of giving predominantly blue emission visible in artificial room lighting conditions while running at current densities of up to 1000 A m^{-2}. They employed a positive charge-injecting electrode formed from a PVCz film that had been reacted with SbCl$_5$ to produce a high concentration of carbazole cations, and the details of this reaction and the electrical properties of the resulting films have been described in papers 1 and 2 of this series respectively.

DESIGN

The main aim is to produce electroluminescence emission through the recombination within the material of mobile organic ions to form excited molecular states that will then revert to their ground states with photon emission. To do this in an organic polymer, in order to benefit from its good film-forming and other properties, requires finding a material that will permit a considerable degree of charge transport and whose charge carriers are the ions of molecules having a low ionization potential (for ease of initial ion formation) and appreciable fluorescence efficiency. Phosphoresence emission will not usually suffice as it suffers from collisional and oxygen quenching due to the comparatively long lifetime and paramagnetic nature of its associated triplet state, although such quenching processes are somewhat inhibited within a solid polymer matrix. Many common commercial polymers do not fit these criteria as they are good insulators and non-luminescent, although there is the possibility of treating them as purely inert matrices and doping them with suitable additives since charge transport has been observed in such systems[2]. However, the aromatic polymer polyvinylcarbazole (PVCz) does answer the criteria in most respects since its carbazole side groups are of low ionization potential and do exhibit luminescence and since, although it is an insulator, it will transport at least positive charges if these are injected into it. Such transport has in fact been extensively investigated as a result of the use of PVCz as the sensitive material in xerography[3]. Thus PVCz was used as the basic polymeric material throughout this electroluminescence study.

PVCz is an insulator because it contains no intrinsic charge carriers and thus, to be useful as an electroluminescent material, charge carriers must be injected into it. The dark injection (as opposed to photoinjection) of positive charges into PVCz has been observed by Reucroft[4] who ascribed it to Richardson–Schottky field-assisted thermionic emission favoured by electrodes of high work function. However, the current densities observed by Reucroft were much too small (less than 10^{-6} A m^{-2}) to be of use in electroluminescence production while, although much larger currents were sometimes observed in this work, as noted later, they were too unstable to be of use. Recourse was therefore made to the chemical production of potential positive charge carriers; the formation of carbazole cations by addition of

SbCl$_5$ to PVCz has been described in detail in papers 1 and 2 of this series. The important feature of this is that SbCl$_5$ has such a high electron affinity that it can directly extract electrons from carbazole molecules to form positive carbazole ions that are found to be mobile (via charge exchange with neutral carbazole groups) within the polymer.

The production of negative ions in PVCz was similarly accomplished by chemical means. Although the electron affinity of *N*-isopropylcarbazole (NIPC) in the gas phase is thought to be close to zero[5], the PVCz anion can be stabilized in the condensed phase, as shown by the work of Rembaum[6,7] on mixtures of sodium with PVCz or *N*-ethylcarbazole (NEC) in tetrahydrofuran solvent. For such electron donation from a metal to a molecule in the solid phase it is necessary that the work function ϕ of the metal shall be equal to or smaller than the solid phase electron affinity χ_S, which following Lyons[8] can be written as:

$$\phi \leqslant \chi_S = \chi_G + P \tag{1}$$

where χ_G is the gas-phase electron affinity of the molecule and where P, the polarization energy, represents the stabilization energy of the excess electron on the molecule caused by the polarization of the surrounding medium. Since χ_G is likely to be nearly zero for PVCz the maximum value of ϕ that will promote anion formation in PVCz will, from equation (1), be almost equal to the polarization energy. Sharp[9] has calculated a P value of 1.5 eV for crystalline NIPC, which is in line with values calculated for some other aromatic molecules[8,10]. However, in practice this seems rather too low for amorphous PVCz since it was found in the present work that contact between molten potassium and a PVCz film produces a dark coloration at the interface that is ascribable to absorption by PVCz anions but that vacuum evaporation of sodium onto a similar film does not (the sodium–PVCz reaction in tetrahydrofuran is promoted by a considerable ion solvation energy). Since the work functions of potassium and sodium are about 2.2 and 2.3 eV respectively, it is concluded from equation (1) that the polarization energy of solid PVCz is probably about 2.1 eV, assuming that it has a very small gas-phase electron affinity of about 0.1 eV. Likewise it is clear that only the alkali metals, and even then probably not sodium and lithium, have work functions low enough to inject electrons into PVCz films. As electrons have negligible mobility in PVCz films[11] these anions are likely to remain immobile close to the injecting alkali-metal cathode.

Once having introduced both anions and cations into a PVCz film it is necessary to check whether their recombination is likely to release enough energy to produce photon emission from, preferably, the singlet states of the excited molecules so formed. The recombination energy R will essentially be equal to the formation energy of a well separated ion pair in the solid film, which in turn is given by the solid-phase ionization potential I_S minus the solid-phase electron affinity. The former can be expressed as[8]:

$$I_S = I_G - P \tag{2}$$

where I_G is the gas-phase ionization potential, and so using equations (1) and (2) the recombination energy is given approximately by:

$$R = (I_G - \chi_G) - 2P \tag{3}$$

Experiments on chemiluminescent[12] and electrochemiluminescent[13] systems in solution have shown that the excited states that may be reached directly as a result of ion recombination are critically dependent upon the recombination energy and that states of energy higher than R will not be produced (except by later bimolecular reaction between excited molecules of lower energy). These experiments have also shown that the main primary reaction produced by recombination of a cation $^2M^+$ and anion $^2M^-$ of the same molecular species are:

$$^2M^+ + {}^2M^- \rightarrow \begin{cases} ^1M^* + M \\ ^3M^* + M \\ (M_2)^* \end{cases}$$
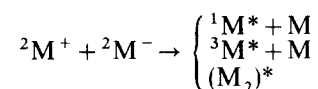
where $^1M^*$ and $^3M^*$ are singlet and triplet excited states respectively and $(M_2)^*$ is an excimer (excited dimer) in which the excitation is shared between both molecules. The excimers can also be formed in either singlet or triplet states but the latter do not seem to have been observed yet in chemiluminescent systems in solution. The most important secondary reaction is triplet–triplet annihilation:

$$^3M^* + {}^3M^* \rightarrow \begin{cases} ^1M^* + M \\ (M_2)^* \end{cases}$$
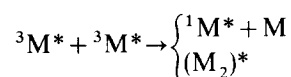
and this is usually energetically possible since, while the singlet excitation energies are always greater than the corresponding triplet ones, most organic molecules have lowest excited singlet state energies that are less than twice as large as their lowest triplet state energies.

In the case of PVCz the recombination energy calculated from equation (3) using the previous values plus a gas-phase ionization potential of 7.4 eV[14] is approximately 3.1 eV. As the lowest excited singlet state energy of PVCz is, from its absorption and fluorescence spectra, about 3.5 eV, it is doubtful whether ion recombination could give excited singlet states directly. However, PVCz also exhibits at least two different excimer states[15] (probably corresponding to two different configurations of neighbouring carbazole groups attached to a common chain[16]) and it is possible that at least one of these could be formed directly by ion recombination. The triplet state energy is about 3.0 eV from phosphorescence measurements[15] and so triplets should readily be formed. Triplet–triplet annihilation to form excited singlet states is a very pronounced reaction in dilute high molecular weight PVCz solutions at low temperature[15] but is much reduced in solid PVCz films[15,17,18] due to efficient trapping of the migrating triplets. It is not clear whether these triplet traps are effective at room temperature since, if not, then significant triplet annihilation and hence delayed fluorescence might occur (if the triplets are not too severely quenched by oxygen and collisional deactivation) but such delayed fluorescence at room temperature does not seem to have been reported.

A possible alternative electroluminescence mechanism to the ion recombination just considered is direct electron transfer from the cathode to a PVCz cation. This should occur if the Fermi surface of the metal cathode lies above the first excited state of the cation so that the electron is transferred initially into the highest unoccupied cation

energy level rather than the partially occupied level below it. The energy of the former level will be given approximately by $(I_G - P - E)$, where E is the lowest (singlet or triplet) excitation energy of the neutral molecule, and thus this type of transfer could occur for:

$$\phi \leqslant (I_G - P - E) \qquad (4)$$

Using previous values the formation of an excited singlet state of energy 3.5 eV would thus require a metal work function of about 1.8 eV which is in fact close to the approximately 1.9 eV value of the lowest work function alkali metal, caesium.

As a result of all the foregoing considerations, the general design settled upon for an electroluminescent device based on PVCz was a sandwich structure starting with a transparent conducting glass electrode upon which was cast a PVCz/SbCl$_5$ film to act as a positive charge-injecting electrode followed by a PVCz film (containing fluorescent additives) for the ion recombination to occur in and finally a caesium cathode to act as an electron injector. The pure PVCz layer was found necessary in addition to the PVCz/SbCl$_5$ layer because of the strong fluorescence quenching observed (paper 2) in the latter. Fluorescent additives such as perylene or triphenylbutadiene (TPB) were added to the pure PVCz layer to improve the fluorescence output by accepting and then emitting the excitation energy from the carbazole groups before it could be degraded by non-radiative processes. They also acted as wavelength shifters since their fluorescence lies in the visible region whereas some of the PVCz fluorescence is in the ultra-violet.

EXPERIMENTAL

Film casting, thickness measurements and thickness uniformity checks were done as described in paper 2. For the two-layer films the PVCz/SbCl$_5$ was cast onto conducting glass first and allowed to dry (the SbCl$_5$ was usually about one-fifth of the PVCz by weight). The crosslinking of the PVCz/SbCl$_5$ film (see paper 1) prevented it from redissolving when in contact with the solvent used for the casting of the second layer. Thickness measurements were made on the first layer alone and on the two layers together, thus allowing the thickness of the second layer to be obtained by subtraction. For the attempts to produce a double-layer film by brief SbCl$_5$ treatment of a single film a PVCz film containing a fluorescent additive was first cast onto conducting glass. This was then spun at about 3000 rpm and a strong solution of SbCl$_5$ in nitromethane was squirted onto it followed quickly by a similar application of pure nitromethane to remove any unreacted SbCl$_5$. The average fractional penetration depth of the SbCl$_5$ into the film was estimated by observing the fractional decrease in the additive visible light absorption spectrum since the SbCl$_5$ always reacted destructively with the additives when able to contact them.

Electrical measurements were done as described in paper 2 and all handling of caesium for the cathodes of the electroluminescent devices was done in a glovebox continually flushed with dry and oxygen-free nitrogen. As before, electrical measurements were confined to film areas whose thickness was uniform to better than one fringe of visible light.

The evaporation of sodium and lithium was done in a Metrovac Type 12 coating unit using a large liquid-nitrogen-cooled shield within the evaporation area to freeze out residual moisture and organic vapours. The sodium was evaporated from a soda-glass tube gently heated by a coil of resistance wire while the lithium was contained in a more conventional conical tungsten basket.

RESULTS

Single PVCz layer

Before studying double-layer films fitted with charge-injecting electrodes it was of interest to observe the electrical behaviour of a single layer of pure PVCz with more conventional electrodes. Previous measurements on such films by Reucroft[4] had shown that very small positive charge currents (less than 10^{-6} A m^{-2} at fields up to 10^7 V m^{-1}) could be injected into PVCz from electrodes of high work function such as platinum, gold and silver by a mechanism which was apparently diffusion-limited Richardson–Schottky field-assisted positive charge emission. Tin oxide conducting glass did not seem to contribute significantly to this injection process.

Measurements here were done by casting the PVCz films onto 'Baltracon' or 'Hyviz' conducting glass and using a mercury drop as the second electrode. The films were between 0.7 and 2.2 μm thick and so were much thinner than the 30 μm films used by Reucroft. The current through such films was generally found to be very unstable and often a complete short-circuit developed through the film, but by moving the mercury drop across the film surface it was usually possible to find some areas of comparative current stability. In such regions the current was not ohmic, as might have been expected in the case of a rather high resistance breakdown path, but markedly supralinear since it varied as approximately the square of the voltage at low electric fields while rising in some cases to as much as the fourth power of the voltage at high fields. Measurements were generally made with the conducting glass electrode positive since currents at the opposite polarity were appreciably smaller although still supralinear. Some measurements were terminated by massive electrical breakdown at high fields, occasionally giving rise to severe electrode damage.

Plots of current density J against voltage V are shown in *Figure 1* for two films cast at the same time and from the same solution but differing by a factor of 3 in thickness. A strong dependence of current on film thickness as well as voltage is evident. Also of interest is that the thinner film was supporting a current of 10 A m^{-2} at the highest voltage which is more than seven orders of magnitude greater than the currents observed by Reucroft at room temperature. Although it might be thought that this was a breakdown current, it should be noted that the PVCz films in working electroluminescence devices described later were able to sustain uniformly distributed current densities almost two orders of magnitude greater still.

The V^2 current dependence at low fields together with the strong effect of film thickness variation immediately suggest the existence of a space-charge-limited (SCL) current caused by carrier build-up near an injecting electrode due to a small rate of carrier transport across the sample. Simple SCL current theory[19] leads to a J–V relation:
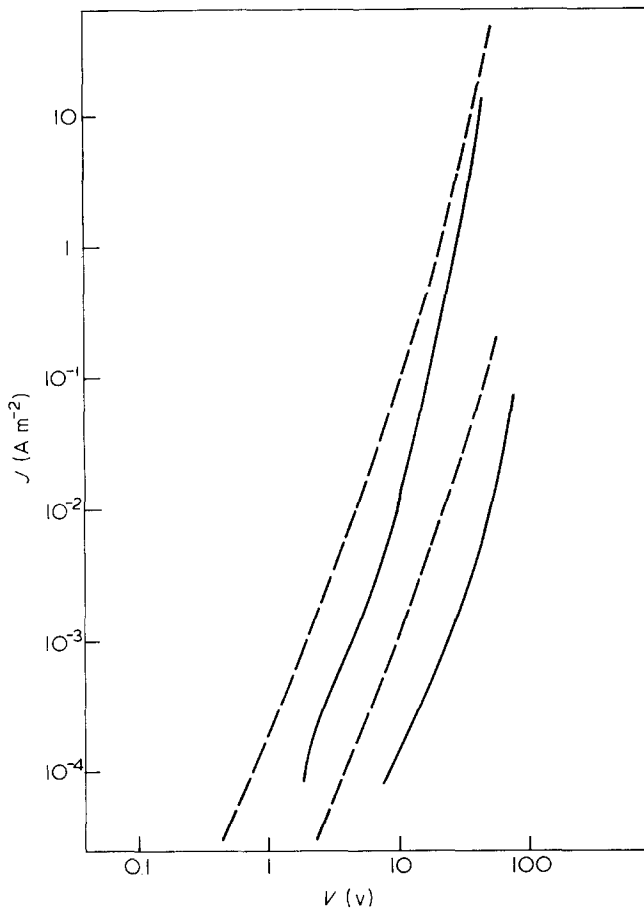
Figure 1   Current density *J versus* voltage *V* for two pure PVCz films of thicknesses 0.72 and 2.25 μm: ———— observed current densities; ——— theoretical current densities

$$J = \tfrac{9}{8}\varepsilon_r\varepsilon_0\mu\left(\frac{V^2}{L^3}\right) \qquad (5)$$

which is sometimes known as Child's law for insulating solids, where μ is the carrier mobility, ε_r and ε_0 the relative and vacuum permittivities and L is the film thickness. This however assumes a constant value for the mobility whereas Gill[11] has shown that for PVCz the mobility depends upon both temperature and field strength via the empirical relation:

$$\mu = \mu_0 \exp[-(E_0 - \beta F^{1/2})/kT_e] \qquad (6)$$

where E_0, β and μ_0 are constants, k is Boltzmann's constant, F is the electric field strength and T_e is an effective temperature. In these measurements the temperature-dependent part of equation (6) is not likely to be very important as the current was for the most part fairly low and so resistive heating of the film was fairly small, but the field dependence is likely to affect the current significantly. When the field dependence is incorporated into the simple SCL current theory (see Appendix), the effect is to make the V^2 dependence of J at low voltages shift to progressively higher powers of voltage as the voltage rises. This is shown in *Figure 1* where the theoretical $J-V$ curves for the two different thickness films are compared with the observed curves. The theoretical curves use as parameters the measured

film thicknesses, a relative permittivity for PVCz of 3.1, and values for β and $\mu_0 \exp(-E_0/kT_e)$ at 293K of 2.7×10^{-5} eV V$^{-1/2}$ m$^{1/2}$ and 1.2×10^{-12} m^2 V^{-1} s^{-1} respectively as obtained from Gill's time-of-flight measurements[11]. These curves are thus not 'fitted' to the observed $J - V$ curves in any way.

The experimental and theoretical curves in *Figure 1* are sufficiently similar to show that a real SCL current is being observed. This implies that the conducting glass electrode, which is positive in the curves shown, is able to inject a considerable density of positive charge carriers into PVCz films (since electrons are not mobile in PVCz[11]) and that likewise the mercury cathode is able to accept them. The converse is apparently also true but the somewhat smaller currents may indicate that the conducting glass is not so ready to accept positive charges as mercury. The generally erratic nature of the current may be due to the injection process being an irregular one which is promoted by high fields but also strongly affected by changes in local physical factors along the film/electrode interface.

The current in PVCz is carried via the carbazole groups[11] and so recombination of these carbazole cations with electrons at the cathode might in principle give rise to liminescence. However, from the simple energetic consideration advanced earlier, particularly equation (4), it is most unlikely that this would occur with a mercury cathode having a work function of about 4.5 eV and indeed no such luminescence could be seen either in pure PVCz films or in ones containing perylene as a fluorescent additive.

Double-layer films

Although surprisingly large positive charge currents were injected into pure PVCz films by conducting glass electrodes, these were too unstable to be useful in practice. Instead it was found that much greater current stability and considerably larger current densities could be obtained by using a PVCz/SbCl$_5$ film to inject positive charges into a pure PVCz film that had been cast on top of it. Typical $J-V$ curves for such a film and for both directions of current flow are shown in *Figure 2*. The sample in this case had an evaporated silver electrode on the pure PVCz layer but use of a mercury drop gave similar results. The $J-V$ curve in the 'forward' direction, meaning with the conducting glass positive and the PVCz/SbCl$_5$ layer thus injecting positive charges into the PVCz layer, is typical of most of the two-layer films measured in that it is distinctly 'S' shaped. The bulk of the curve is similar to that of the single PVCz film described earlier with J proportional to V^2 at intermediate fields and rising to higher powers of voltage at higher fields, but at the lowest fields J is seen to fall off sharply with voltage. This low-field behaviour suggests the presence of a potential barrier within the system similar, perhaps, to that set up by the use of aluminium electrodes on PVCz/SbCl$_5$ films (see paper 2). The barrier is unlikely to be between the conducting glass and the PVCz/SbCl$_5$ layer since this combination, when used with a mercury second electrode, gave ohmic currents at low fields (paper 2). A barrier at the interface between PVCz and PVCz/SbCl$_5$ is quite possible since, whereas the conduction in the former is via monocarbazole units, in the latter it is via dimer carbazole groups (paper 2). Since the ionization potential of the dimer carbazole is somewhat lower than that of the monocarbazoles (paper
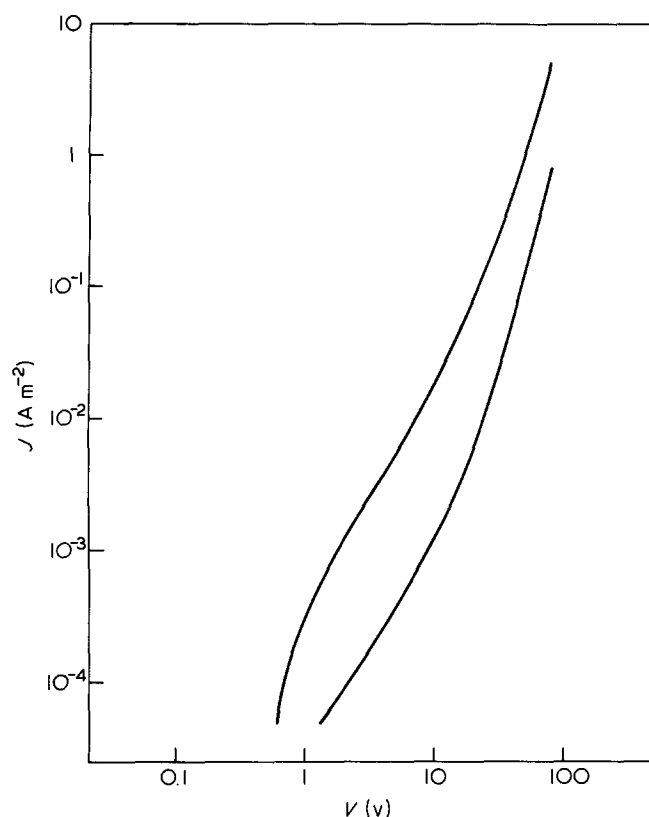
Figure 2 Current density *J versus* voltage *V* for a typical two-layer PVCz film. Upper curve has PVCz/SbCl$_5$ layer positive; lower curve, reverse polarity

1), a degree of field assistance may well be needed to transfer positive charges from the dimer to the mono groups. Also possible is a barrier due to a low degree of cation extraction at the cathode since this would tend to build up a space charge in front of it that would inhibit carrier flow. Higher applied fields would force charge extraction and hence remove the barrier. The *J–V* curve of the thinner sample in *Figure 1* does show an increased current drop as the voltage falls in the lowest voltage region which could be a similar PVCz/cathode effect.

A surprising feature of *Figure 2* is the size of the 'reverse' current, which is generally about one-tenth of the forward current. This current must be predominantly a positive charge current injected by the silver or mercury electrode since no significant electron migration has been found in PVCz, although it is possible that a negative carrier current is injected into PVCz/SbCl$_5$ and traverses that layer to recombine at the interface with the PVCz film with the positive carriers being transported across that layer.

The much greater stability of forward current flow in these two-layer films than in the single-layer PVCz films could be ascribed to smoother injection of positive charges into PVCz by PVCz/SbCl$_5$ than by conducting glass, since the glass may not always be in very good physical contact with the film and surface irregularities could give rise to enhanced field-assisted injection of a fairly unstable nature in localized areas. The increased stability in the reverse current direction (which was not generally found for the low work function electrodes, as described later) is more surprising. The PVCz/SbCl$_5$ layer may be acting as a cover for pinholes in the PVCz layer

and it may also be acting as a ballast resistance in series with the PVCz layer to limit the size of any local breakdown current (although the conducting glass and external circuit act in a similar fashion) but these alone hardly seem sufficient explanation.

J–V curves were also measured for 'two-layer' films prepared from a single PVCz cast that had been subsequently treated by a very brief contact with SbCl$_5$ solution, with the hope of obtaining only partial penetration of the film thickness by the SbCl$_5$. The currents, as measured with conducting glass on the PVCz side and a mercury electrode on the PVCz/SbCl$_5$ side, were appreciably more erratic than those of the true two-layer films. They gave ohmic conduction at low fields, probably due to some SbCl$_5$ penetration right through the film, with a change to V^2 or higher-power conduction at higher fields, and they were largely independent of the polarity of the applied field. No further use was made of them owing to their unstable currents.

As with the single-layer films, no electroluminescence was seen from double-layer films when using electrodes of medium to high work function.

Electroluminescence using low work function electrodes

According to the simple energy calculation exemplified by equations (1), (3) and (4), the generation of electroluminescence from pure PVCz films is likely to require a cathode material having a work function of around 2 eV, which in practice means an alkali metal. Caesium was chosen for this purpose since not only does it have the lowest metallic work function of all (about 1.8 eV) but it also melts at just above room temperature (301K) which aided cathode preparation.

Two-layer films were prepared on conducting glass with the upper PVCz layer containing perylene or TPB as a fluorescent additive. These were placed in a glovebox flushed with dry nitrogen, since caesium reacts violently with water and oxidizes easily. A small brass block with a funnel-shaped hole right through the centre and a connection to the external measuring circuit was carefully placed on top of the film. Caesium in a break-seal glass ampoule was melted by finger-warmth inside the glovebox and then poured into the hole in the brass block, thus contacting the upper layer of the film over an area of about 1 cm^2 and being electrically joined to the measuring circuit. The portion of the PVCz film in contact with the caesium was seen to darken slowly over a period of a few minutes due to carbazole anion formation such as has been observed spectroscopically in solutions of PVCz with sodium[6,7] or potassium[20].

The *J–V* curves of such devices in the forward direction (conducting glass positive, caesium negative) tended to exhibit the same 'S' shape as double-layer films with high work function cathodes. However, the thinnest and hence lowest resistance devices, such as the one whose characteristic is shown in *Figure 3*, often showed a very sharp increase of current with voltage at low voltages followed by a steady increase of current as about the fourth power of voltage at higher voltages. In a few cases an ohmic 'tail' was seen at low voltages instead of the sharp current rise, probably due to a rather high resistance localized leakage path. The current passed by these devices was strongly dependent upon the thickness of the pure PVCz upper layer, as can be seen from *Figure 4* where the current at 10 V (where most of the devices had a fairly constant slope on a log *J* − log *V* plot) is plotted
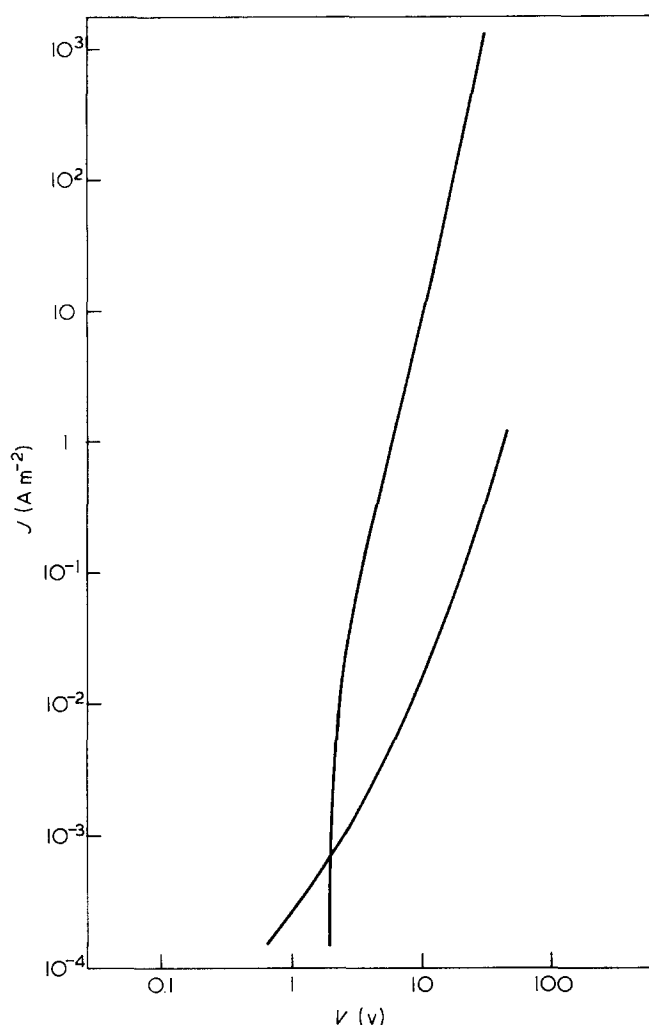
Figure 3 Current density *J versus* voltage *V* for a two-layer electroluminescent device with caesium cathode. PVCz/SbCl$_5$ layer thickness 1.51 μm and PVCz/TPB layer thickness 0.51 μm. Upper curve (at high voltages) has PVCz/SbCl$_5$ layer positive and caesium negative; lower curve, opposite polarity

the caesium cathode but are unable to migrate away from it and thus set up a permanent space charge in its vicinity. The appreciable magnitude of the reverse current at higher voltages is surprising in that positive charge injection by caesium into PVCz should be energetically very unfavourable, although it is possible that the bulk of the injection might have occurred from the brass container holding the caesium.

The prime interest in these devices lay in their considerable electroluminescence emission. This was observed through the conducting glass electrode and hence also through the PVCz/SbCl$_5$ electrode which, due to its green colour caused by absorption by the carbazole cations, absorbed about half of the emission in the 400–440 nm region. The electroluminescence was first detectable in the dark at current densities of around 0.1 A m^{-2} and increased steadily with current until at around 300 A m^{-2} it was easily visible in full artifical room lighting conditions. The emission was light blue in colour as would be expected from the fluorescence spectrum of the perylene or TPB molecules added to the PVCz layer. Its intensity was evenly distributed over the whole area of film in contact with the caesium cathode but there was no emission at all from film beneath the brass ring surrounding the caesium. This clearly demonstrates the need for a true electron-injecting cathode and it also demonstrates that electrical conduction was occurring evenly right across the film and not through a few local breakdown paths. Local breakdown was occasionally visible in a few devices in the form of a tiny spark on the film surface but this did not seem to affect the intensity of emission from the rest of the surface. The emission disappeared instantly on removing the applied voltage with no perceptible afterglow.
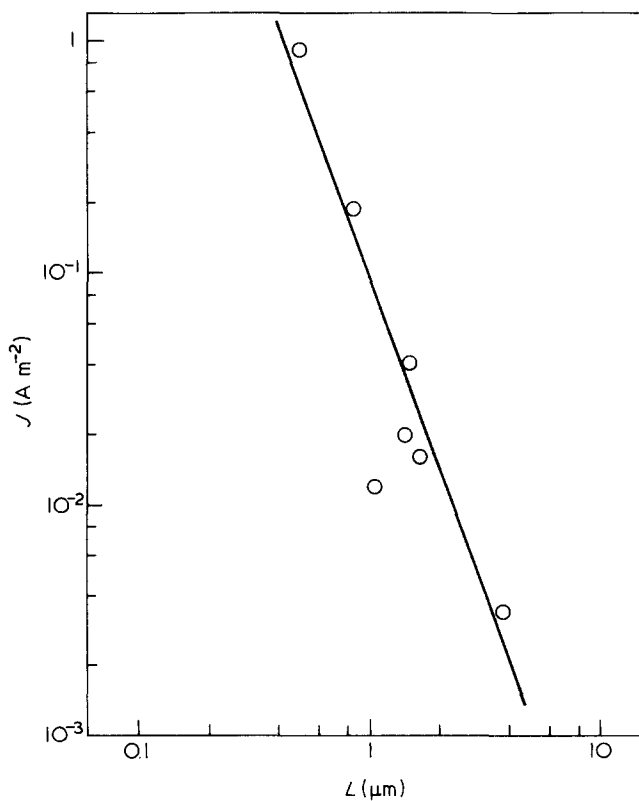
against the upper layer thickness. The slope of this plot shows the current to vary as the inverse thickness raised to approximately the power 2.8, which is sufficiently close to the Child's law value of 3 to demonstrate that the current is indeed basically space-charge-limited as expected.

The devices with the thinnest PVCz layers, such as that in *Figure 3*, gave current densities as high as 1000 A m^{-2} for voltages of about 30 V upwards. These currents were generally completely steady, apart from a slight increase with time at high currents due to an increase in carrier mobility caused by resistive heating, although sometimes erratic behaviour occurred due to temporary local electrical breakdowns while at other times a complete and permanent short-circuit would develop between the electrodes.

Currents were also observed from some devices in the reverse polarity direction but they were several orders of magnitude smaller than the forward currents at high voltages, as shown in *Figure 3*, and tended to be very erratic and often led to permanent electrical breakdown. The forward and reverse curves in *Figure 3* at low voltages suggest that an internal potential has been established which opposes the forward current. This is probably largely due to the carbazole anions which are formed by

Figure 4 Current density *J* at 10 V *versus* thickness *L* of pure PVCz layer for a number of electroluminescent devices

The colour of the electroluminescence could be altered to some extent by use of different fluorescent additives or a combination of such additives. Thus for example the use of both TPB and acridine orange (which emits in the yellow–green region) in the PVCz top layer gave an almost white emission colour.

Only caesium and lithium were tried as cathodes, where the latter was applied by vacuum evaporation and the electrical measurements were done in the vacuum, and of these two only caesium produced electroluminescence. Molten potassium dropped onto a pure PVCz film exhibited the dark coloration at the interface that is indicative of carbazole anion formation and so this would probably also have been a successful cathode material. However, neither lithium or sodium produced any colour changes when vacuum-evaporated onto PVCz films. Thus it seems probable that electroluminescence arises from the recombination of carbazole cations and anions and not from direct electron extraction by carbazole cations from a low work function cathode, although the latter process seems energetically to be rather the more favourable from the earlier discussion.

APPENDIX

SCL current for a field-dependent mobility

The simple derivation of Child's law for solids[19] uses the one-dimensional current continuity and Poisson equations:

$$J = ne\mu F \tag{7}$$

$$\frac{dF}{dx} = \frac{ne}{\varepsilon_r \varepsilon_0} \tag{8}$$

where n is the carrier concentration, but since the mobility here is field-dependent an extra relation, of the form of equation (6), is needed:

$$\mu = u \exp(wF^{1/2}) \tag{9}$$

where u and w are independent of field but dependent upon temperature.

Combining (7), (8) and (9) gives:

$$J = (u\varepsilon_r\varepsilon_0) \exp(wF^{1/2}) F\left(\frac{dF}{dx}\right) \tag{10}$$

which can be integrated as:

$$Jx = (u\varepsilon_r\varepsilon_0) \int_0^F F \exp(wF^{1/2}) \, dF \tag{11}$$

where it has been assumed that the field is zero at the injecting electrode ($x = 0$). This corresponds, from (7), to an infinite charge density at the injecting electrode but Hill[21] has shown that in fact Child's law behaviour is still obtained for finite injected charge densities as long as these are sufficient to supply the current that would be predicted by Child's law at any particular voltage.

Integrating (11) and putting $Y = wF_L^{1/2}$, where F_L is the field value at the non-injecting electrode ($x = L$) gives:

$$JL = \frac{2u\varepsilon_r\varepsilon_0}{w^4}\left(3! + e^Y \sum_{r=0}^{3} \frac{(-1)^r 3! Y^{3-r}}{(3-r)!}\right) \tag{12}$$

Using the voltage-field relationship:

$$V = \int_0^L F \, dx$$

together with (10) gives:

$$JV = (u\varepsilon_r\varepsilon_0) \int_0^{FL} F^2 \exp(wF^{1/2}) \, dF$$

which integrates to:

$$JV = \left(\frac{2u\varepsilon_r\varepsilon_0}{w^6}\right)\left(5! + e^Y \sum_{r=0}^{5} \frac{(-1)^r 5! Y^{5-r}}{(5-r)!}\right) \tag{13}$$

Thus for a given value of Y the value of J can be obtained from (12) and with this the corresponding value of V is obtained from (13). Typical such J–V curves are shown in *Figure 1* and it can be seen that the effect of the field dependence of the mobility is to make J rise increasingly faster with increasing voltage than the normal V^2 rate of Child's law. It can be shown that (12) and (13) reduce to Child's law as the field dependence factor w tends to zero.

ACKNOWLEDGEMENTS

REFERENCES

1 Partridge, R. H. U.K. Pat. 74/44704, 1974; *Chem. Abstr. 1974*, **86**, P11261
2 Pfister, G., Grammatica, S. and Mort, J. *Phys. Rev. Lett.* 1976, **37**, 1360
3 See review by Gill, W. D. in 'Photoconductivity and Related Phenomena', (Eds. J. Mort and D. M. Pai), Elsevier, Amsterdam, 1976, p. 303
4 Reucroft, P. J. and Ghosh, S. K. *J. Non-cryst. Solids* 1974, **15**, 399
5 Klopffer, W. *Z. Naturforsch. A* 1969, **24**, 1923
6 Rembaum, A., Eisenberg, A., Haack, R. and Landel, R. F. *J. Am. Chem. Soc.* 1967, **89**, 1062
7 Rembaum, A., Hermann, A. M. and Haack, R. *J. Polym. Sci. A1* 1968, **6**, 1955
8 Gutmann, F. and Lyons, L. E. 'Organic Semiconductors', John Wiley, New York, 1967, Ch. 6
9 Sharp, J. H. *Photogr. Sci. Eng.* 1967, **11**, 69
10 Batley, M., Johnston, L. J. and Lyons, L. E. *Aust. J. Chem.* 1970, **23**, 2397
11 Gill, W. D. *J. Appl. Phys.* 1972, **43**, 5033
12 Weller, A. and Zachariasse, K. *J. Chem. Phys.* 1967, **46**, 4984
13 Hercules, D. M. in 'Physical Methods of Chemistry', Part II B (Eds. A. Weissberger and B. W. Rossiter), 1971, Ch. 13
14 Okamoto, K., Ozeki, M., Itaya, A., Kusabayashi, S. and Mikawa, H. *Bull. Chem. Soc. Jpn.* 1975, **48**, 1362
15 Klopffer, W. and Fischer, D. *J. Polym. Sci. C* 1973, **40**, 43
16 Johnson, G. E. *J. Chem. Phys.* 1975, **62**, 4697
17 Yojoyama, M., Tamamura, T., Nakano, T. and Mikawa, H. *J. Chem. Phys.* 1976, **65**, 272
18 Itaya, A., Okamoto, K. and Kusabayashi, S. *Chem. Lett.* 1975, 833
19 Mott, N. F. and Gurney, R. W. 'Electronic Processes in Ionic Crystals', Oxford University Press, Oxford, 1948, Ch. 5
20 Gibson, G. K. J. and Partridge, R. H. unpublished work
21 Hill, R. M. *Thin Solid Films* 1973, **15**, 369