Electroluminescence from polyvinylcarbazole films: 1. Carbazole cations

R. H. Partridge

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

The cation-forming reactions between antimony pentachloride and various carbazole compounds were studied with a view to developing a positive charge-injecting electrode for an electroluminescent device based on films of polyvinylcarbazole. Use of polyvinylcarbazole in the reaction produced a very different cation yield from that obtained by use of a carbazole dimer and reasons for this, associated with dimerization of the monocarbazole groups, are suggested. The ionization potential and cation extinction coefficient of dimeric carbazole were measured and changes in the visible absorption spectrum of the cations were observed that are related to their microscopic environment.

Keywords Electroluminescence; polyvinylcarbazole/antimony pentachloride solutions; cations; crosslinking; extinction coefficient; ionization potential

## INTRODUCTION

Electroluminescence

Electroluminescence is a well known phenomenon amongst inorganic materials and has been intensively studied in recent years, especially during development of the now very common light-emitting diodes. Electroluminescence from organic materials is much less common, but it has been observed under certain conditions, particularly in high-purity aromatic crystals[1] and in solutions in the form of electrochemiluminescence[2]. Electroluminescence from amorphous organic plastics does not seem to have been observed previously, apart from some weak emission induced by strong alternating potentials[3,4] or near-breakdown fixed potentials[5,6] in some common polymers. Since organic polymers have the great potential advantages of cheapness, ease of fabrication and relative indifference to low levels of chemical impurities, it seemed advisable to investigate whether they could be used as the basis for an electroluminescent device of reasonable efficiency. The results of this investigation, some of which have been outlined briefly before[7], are described in the present four papers. This paper (paper 1) is concerned with the chemical production of a stable polyvinylcarbazole (PVCz) cation and with its identification, ionization potential and absorption strength, since such cations were found to act as injectors of positive charge into the solid PVCz films used for electroluminescence generation. Paper 2 concerns the optical absorption and electrical conduction of solid PVCz films containing this cation. Paper 3 describes a direct current electroluminescent device composed of a luminescent PVCz film placed between an electron-injecting caesium cathode and a positive charge-injecting anode employing the PVCz cation studied in papers 1 and 2. Finally, paper 4 considers ways of avoiding the dependence of the electroluminescent device on highly reactive alkali-metal cathodes and to this end describes experiments on exciplexes and exterplexes formed between PVCz and cyanobenzene electron-accepting molecules.

The investigations described here led to the granting of a UK Patent for the caesium cathode device, but commercial exploitation has not as yet been possible owing to the limited electroluminescence efficiency of similar devices using chemically stable cathode materials.

Cations of polyvinylcarbazole

The reaction between PVCz and antimony pentachloride, or certain other strong oxidizing agents, is known to yield a green material having appreciable conductivity[7-11]. This green reaction product is characterized by a strong absorption peak in the visible region at 430 nm, and a very broad strong absorption band in the near-infra-red having two maxima at about 1050 and 1600 nm with absorption extending out to at least 4000 nm. Under certain conditions, particularly when heat is applied to the reaction mixture, the green reaction product is replaced by a blue one which has a single strong absorption peak at about 640 nm. This blue dye was identified by Bruck[12,13] as being the dicarbazolymethyl cation:
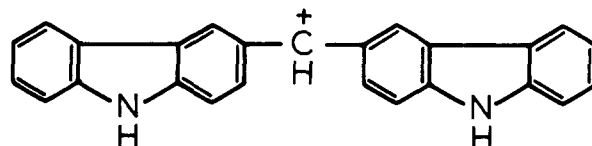
Since the green and blue species are apparently interconverted by heat, at least under some conditions, Matsumoto[9,10] has assigned the green species to a trication formed from the blue dye by removal of two more electrons:
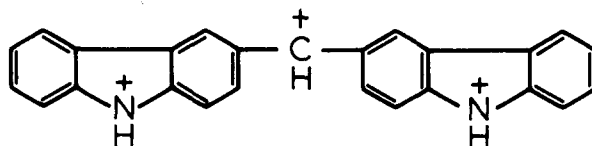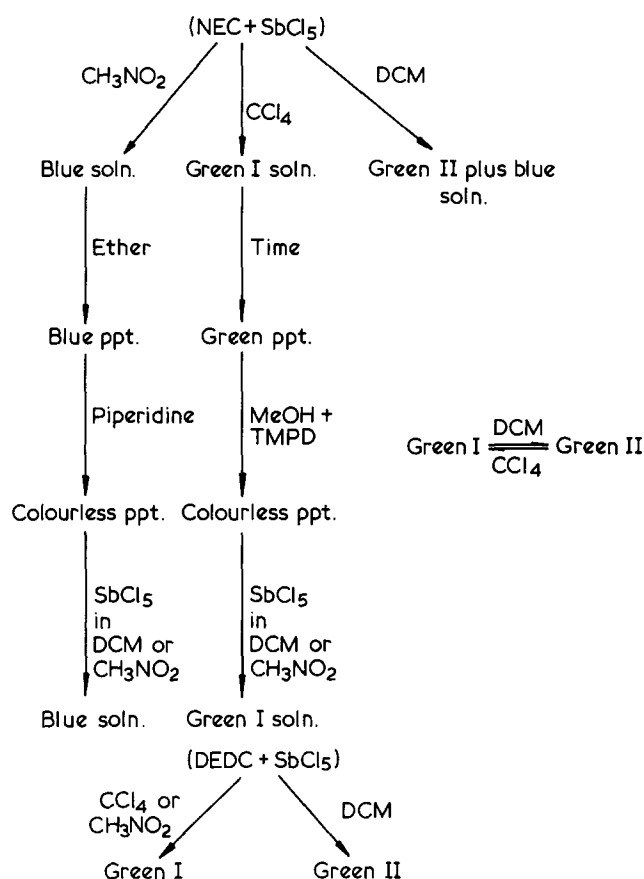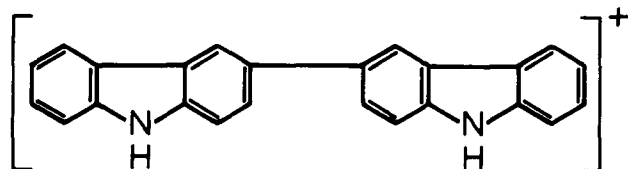
Figure 1 Reaction scheme: blue species absorbs at 640 nm; green I species absorbs at 400 nm and 850 nm; green II species absorbs at 430 nm and 1150 nm (see *Figure 2*)

On the other hand Block et al.[11] have assumed the green colour in a PVCz/tris(p-bromophenyl)ammonium hexa-chloroantimonate reaction mixture to be due to the 3,3'-dicarbazolyl cation:

However, previous studies of this cation in non-polymeric carbazoles[14-16] have found a spectrum which is somewhat similar, but by no means identical, to the spectrum in PVCz, having maxima at about 390 and 800 nm instead of 430, 1050 and 1600 nm. In view of this and of its electrical properties in the solid state, further study of the PVCz cation was warranted.

EXPERIMENTAL

The PVCz used was Luvican M170 obtained from BASF and purified by being precipitated three times from solution by methanol, followed by vacuum drying. 9,9'-diethyl-3,3'-dicarbazyl (DEDC) was prepared by the method of Maitland and Tucker[17]. All other chemicals were obtained from Koch Light Ltd and were used as received, except for $SbCl_5$ which was redistilled and N-

ethylcarbazole (NEC) which was recrystallized. All solvents were carefully dried with molecular sieve.

Ultra-violet/visible absorption measurements were made on a Perkin–Elmer 402, near-infra-red on a Perkin–Elmer 137G, and mid-infra-red on a Perkin–Elmer 457.

RESULTS AND DISCUSSION

Spectra of carbazole/$SbCl_5$

Preliminary study of the green species showed that spectra identical to those previously seen[8,9] could be obtained by reacting PVCz either with aluminium chloride in nitrobenzene or with $SbCl_5$ in dichloromethane (DCM). Thus the green species arose from the PVCz itself and not from the particular electron acceptor being used. Both of the solutions gave an intense e.s.r. signal, so the green species is an actual ion and not just a charge-transfer complex such as is formed between PVCz and weaker electron acceptors[18].

The green and blue species were studied through the reactions of NEC and DEDC (monomeric and dimeric analogues of PVCz respectively) with $SbCl_5$ in the solvents DCM, carbon tetrachloride and nitromethane. The results are summarized in the reaction scheme in *Figure 1*, with spectra shown in *Figure 2*.

It can be seen that different species are apparently produced in each of these solvents, but that the green II species is actually the same as the green I species, the 3,3'-dicarbazolyl cation, since its spectrum changes considerably as its solvent is progressively changed.

When the green precipitate in the scheme was decolorized by mixing with tetramethyl-p-phenylenediamine (TMPD), forming the well known blue TMPD cation[19], the colourless precipitate showed ultra-violet and infra-red absorption spectra very similar to DEDC. However, the precipitate had no clear melting point up to at least 280°C (DEDC melts at 190°C) and so it was probably a mixture of oligomers rather than a pure dimer.

It is clear from the scheme that the reaction of these carbazoles with $SbCl_5$ is only sensitive to solvent for the monomeric NEC and not for the dimeric DEDC or
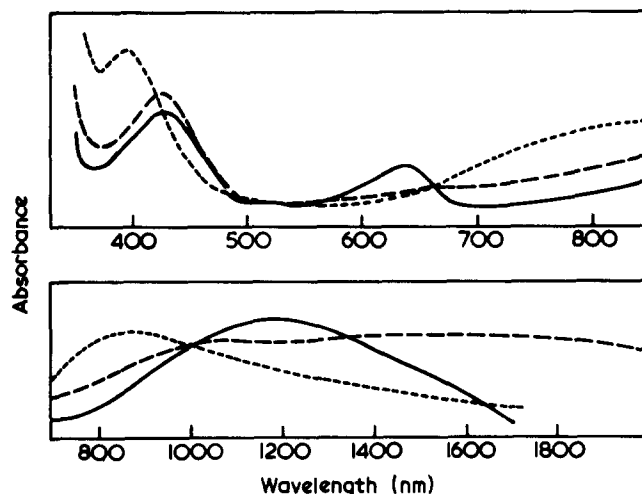

Figure 2 Absorption spectra of carbazoles with antimony pentachloride: ··· NEC in CCl_4 (green I species); ———— NEC in DCM (green II and blue species); –––– PVCz in DCM

decolorized precipitates. This NEC sensitivity must depend on whether the solvent is able to supply a methylene bridge for the dimerization reaction[20]. If it does so, then the blue dicarbazolylmethyl cation can be produced, but otherwise direct linkage of the carbazole groups yields the 3,3'-dicarbazolyl cation. The trication suggested by Matsumoto[9,10] for the green species must be discounted because there is no direct interconversion between blue and green species (production or elimination of the methylene bridge would be required) and because the green II species has been found to be the same as the green I species which had been identified before as the dicarbazolyl cation[14–16].

The change of spectrum between green I and II forms must be ascribed to a change in solvation of the cation. The I form found in CCl_4 solution (the poorer solvent, since precipitation always occurred eventually) may well be due to a fine colloidal suspension, as observed by Blomgren and Kommandeur[21] for other aromatic–$SbCl_5$ systems, which in time aggregates sufficiently to cause precipitation.
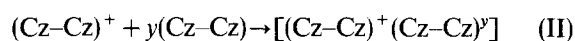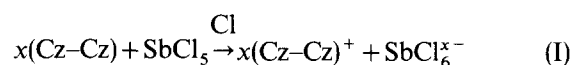
Ionization potential of carbazole dimer

The lowest ionization potential of NEC has been measured as 7.43 eV by the charge-transfer absorption band technique[18] while that of PVCz itself was found to be about 0.03 eV lower. The dimerization of two carbazole groups at the 3,3' position would be expected to cause some reduction in ionization potential due to the greater extent of π electron delocalization. Since this reduction may have an appreciable impact upon the way in which PVCz reacts with $SbCl_5$, as discussed later, and upon the migration of positive charge within solid PVCz films reacted with $SbCl_5$ (see paper 2), the dimer ionization potential was measured using DEDC as a model compound.

The measurement utilized the known linear relationship between donor ionization potential and the photon energy of the maximum of the lowest energy charge-transfer absorption band produced by complexes of several different electron donor molecules with a single electron acceptor. Tetracyanoethylene (TCNE) was used as the acceptor with NEC and DEDC successively as the donors in DCM solvent. The NEC/TCNE complex exhibits a very broad charge-transfer band extending over most of the visible region. Okamoto *et al.*[18] have shown that this band can be consistently resolved into two constituent bands for a range of monocarbazole molecules with the resolved band for NEC/TCNE occurring at 736 and 575 nm, although Landman *et al.*[22] have suggested a different way of performing this resolution. The DEDC/TCNE complex was found here to exhibit the separation of these two bands since the one at higher energy remained in about the same position (at 590 nm) as for NEC/TCNE while the lower energy band red-shifted substantially to 860 nm. Of these two bands the one at lower energy was the smallest, which favours the band resolution scheme of Okamoto *et al.* over that of Landman *et al.* From this the lowest ionization potential of DEDC is lower than that of NEC by the difference in photon energy between their respective lowest charge-transfer bands at 736 and 860 nm, namely 0.26 eV. Taking the lowest NEC ionization potential as the 7.43 eV value of Okamoto *et al.*, thus gives the DEDC ionization potential as 7.17 eV.

Dimer cation extinction coefficient

For later studies of electrical conductivity in solid PVCz films it was necessary to measure the extinction coefficient of the green dimer cation. Since the reaction of $SbCl_5$ with isolated carbazole units causes both dimerization and cation production, this was done using an already dimerized carbazole, DEDC. *Figure 3* shows the absorbance at the 430 nm peak of the dimer cation produced by reaction of DEDC with different concentrations of $SbCl_5$ in DCM. The reaction proceeded fairly slowly, taking several minutes to reach a stable absorbance value and exhibiting several isosbestic points. The sharp rise of absorbance with $SbCl_5$ concentration and abrupt change to a plateau region (with virtual disappearance of the neutral DEDC absorption) suggests an efficient irreversible reaction in which each $SbCl_5$ molecule is interacting, directly or indirectly, with a number of DEDC molecules. A reasonable reaction scheme for this is:

$$x(Cz\text{–}Cz) + SbCl_5 \xrightarrow{} x(Cz\text{–}Cz)^+ + SbCl_6^{x-} \qquad (I)$$

$$(Cz\text{–}Cz)^+ + y(Cz\text{–}Cz) \rightarrow [(Cz\text{–}Cz)^+(Cz\text{–}Cz)^y] \qquad (II)$$

where (Cz–Cz) represents DEDC and the species in square brackets represents a weak multiple charge-transfer complex formed between a DEDC cation and several neutral DEDC molecules (various dimeric complexes of aromatic molecules involving a cation and a neutral molecule have been observed[23,24]). It is assumed that DEDC molecules involved in this complex are not susceptible to further ionization by $SbCl_5$, due to their partial donation of an electron to the central cation. The extra chlorine atom required to form the stable anion $SbCl_6^{x-}$ is assumed to be taken from the solvent. Other $SbCl_5^-$ reactions are possible, such as bimolecular disproportion[25]:

$$2SbCl_5^- \rightleftarrows SbCl_4^- + SbCl_6^- \qquad (III)$$
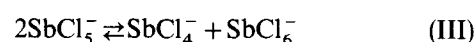
However, it is merely assumed here that each original $SbCl_5$ molecule is ultimately responsible for the production of x cations, whatever the nature of the resulting anions.

If these reactions are the only ones of importance, then:

$$\frac{\Delta}{L\varepsilon^+} = [Cz\text{–}Cz]^+ = x[SbCl_5] \qquad (1)$$

$$[Cz\text{–}Cz] = [Cz\text{–}Cz]_0 - (1+y)[Cz\text{–}Cz]^+ \qquad (2)$$

where Δ is the peak absorbance of the DEDC cation at 430 nm and a path length of L (metres), $[Cz\text{–}Cz]^+$ is the molar concentration of DEDC cations, $[Cz\text{–}Cz]$ the concentration of DEDC molecules that have been neither ionized nor incorporated in a charge-transfer complex, $[Cz\text{–}Cz]_0$ the initial DEDC concentration before addition of $SbCl_5$ and ε^+ is the extinction coefficient of the DEDC cation.

When the $SbCl_5$ concentration rises to a critical value $[SbCl_5]_c$ at which the unreacted DEDC concentration has just fallen to zero (i.e. the break point in *Figure 3*), then combination of equations (1) and (2) yields the initial DEDC concentration as:
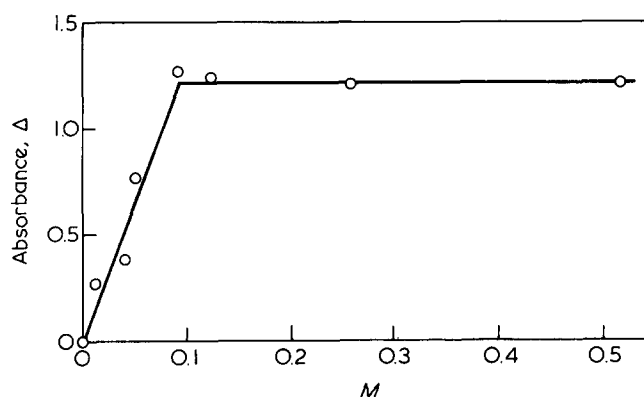
Figure 3 Absorbance, Δ, at 430 nm *versus* molar fraction M of $SbCl_5$ as compared to DEDC in DCM solution. DEDC concentration 2.6×10^{-5} mol l^{-1}

Thus
$$[Cz\text{--}Cz]_0 = x(1+y)[SbCl_5]_c$$
$$x(1+y) = 1/M_c \qquad (3)$$

where M_c is the molar ratio of the reactants at the break point of the graph.

From *Figure 3* and equations (1) and (3), values for $x\varepsilon^+$ and $x(1+y)$ are obtained at about $5.1 \times 10^7 \, l\,mol^{-1}\,m^{-1}$ and 11.1 respectively. A reasonable value for x can be obtained by first noting that the anions $SbCl_6^-$ and $SbCl_6^{3-}$ are both stable, suggesting that x could be either 1 or 3. Support for the latter figure was found by reacting $SbCl_5$ in DCM with either TMPD or perylene, whose cations have known extinction coefficients[19].* Comparison of the cation concentration produced by a known quantity of $SbCl_5$ yielded a ratio of cation to $SbCl_5$ of about 2.6 for TMPD and 2.8 for perylene. Taking x therefore as 3 in the present case gives the green cation extinction coefficient as about $1.7 \times 10^7 \, l\,mol^{-1}\,m^{-1}$, and the reaction ratio y as about 2.7. Thus it is possible to interpret *Figure 3* on the basis that eac $SbCl_5$ ionizes three DEDC molecules, and that most DEDC cations then form some type of complex with up to three neutral DEDC molecules.

An alternative method tried for obtaining ε^+ was to first redissolve in DCM some of the green precipitate from a reaction between DEDC and $SbCl_5$ in CCl_4 and to measure its absorption spectrum. A small amount of TMPD was added to this solution, causing the immediate disappearance of the green dimer cation spectrum and its replacement by the blue TMPD cation spectrum. On the assumption of a complete positive charge exchange between the two species, the observed absorption strengths plus the TMPD cation extinction coefficient then gave a green cation extinction coefficient of only $6.5 \times 10^5 \, l\,mol^{-1}\,m^{-1}$ at 430 nm. But if this value was used in the $DEDC/SbCl_5$ reaction equations given earlier, it would imply that each $SbCl_5$ molecule could produce about 80 green cations. As this is not reasonable, it was concluded that many of the TMPD cations must be reacting further soon after formation. However, it was also noted that complete removal of the green dimer

cation absorption could be achieved by addition of a much lower concentration of TMPD than the concentration of TMPD cations that was formed when excess TMPD was added. Comparison of the minimum quantity of TMPD needed to remove a dimer cation absorption peak of known size completely gave, on the assumption that each cation was removed by one TMPD molecule, an extinction coefficient of about $2.3 \times 10^7 \, l\,mol^{-1}\,m^{-1}$, which compares quite well with the value of about $1.7 \times 10^7 \, l\,mol^{-1}\,m^{-1}$ found earlier.

Polyvinylcarbazole reaction with $SbCl_5$

Figure 4 shows for PVCz the reaction plot analogous to *Figure 3* for DEDC, and provides a striking contrast to it. The much smoother rise of absorbance towards its plateau is obvious, but more significant is that the absorbance produced by low concentrations of $SbCl_5$ is almost 70 times smaller than for DEDC, while the maximum absorbance per unit concentration of carbazole groups present initially is some 8 times smaller. This profound difference is likely to be due partially to the unstable nature of the monocarbazole cation, in contrast to the considerable stability of the dicarbazyl cation. The monocarbazole cation is known to dimerize rapidly with either another similar cation or perhaps a neutral carbazole molecule[16]:

$$Cz^+ + Cz^+ \xrightarrow{-2H^+} (Cz\text{--}Cz) \qquad (IV)$$

$$Cz^+ + Cz \xrightarrow{-e-2H^+} (Cz\text{--}Cz) \qquad (V)$$
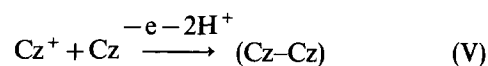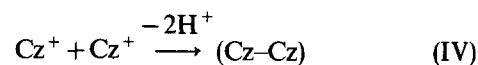
Since the carbazole material here is a polymer, these reactions represent crosslinking of the polymer, either within a particular chain or between different polymer
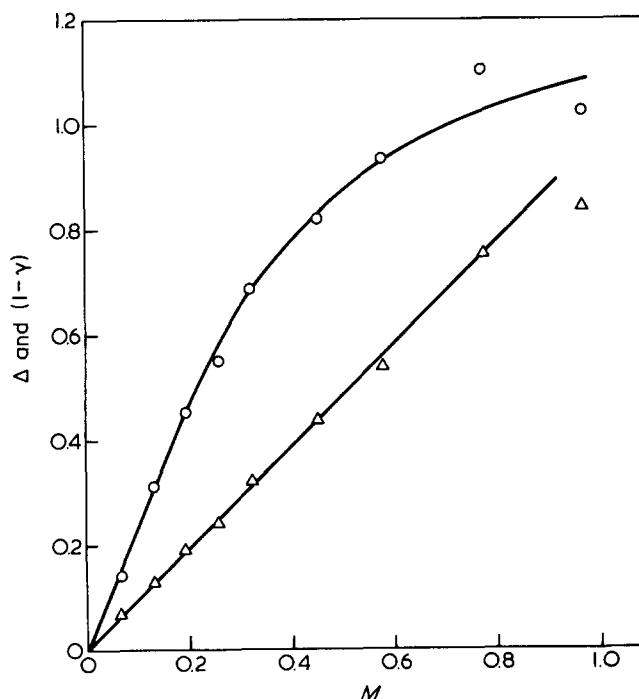
Figure 4 Absorbance, Δ, at 430 nm (circles) and crosslinked fraction of polymer $(1-y)$ (triangles) *versus* molar fraction M of $SbCl_5$ as compared to PVCz in DCM solution. Initial concentration of monocarbazole groups 3×10^{-4} mol l^{-1}

* A value of $5.98 \times 10^6 \, l\,mol^{-1}\,m^{-1}$ was obtained for the extinction coefficient of the perylene cation in DCM solution at 545 nm by observation of the decrease in neutral perylene absorption and increase in cation absorption upon addition of $SbCl_5$

chains. The bimolecular cation reaction (IV) may well be facilitated by positive charge hopping along the chains, such as is responsible for the electrical conductivity of the polymer (see paper 2).

A direct quantitive measurement of this crosslinking reaction is afforded by the fact that as the reaction proceeds the prominent absorption peaks of the isolated carbazole groups at 330 and 344 nm become progressively smaller and eventually virtually disappear. This change is not reversed if the green dimer cation absorption is removed by prolonged heating or by reaction with TMPD, but the 'bleached' polymer is then found to have become insoluble in solvents in which it had previously been soluble, owing to the crosslinking. Since DEDC shows much less prominent absorption in this region than NEC, it is clear that the loss of these peaks must be caused directly by the change of the monocarbazole groups into dimer form. The absorbance of the head of the 330 nm peak above its shoulders on either side was therefore used as a measure of the amount of monocarbazole (i.e. uncrosslinked) groups remaining in the polymer. Defining γ as the ratio of the 330 nm peak absorbance after addition of $SbCl_5$ to the absorbance of that peak before the $SbCl_5$ was added, the quantity $(1-\gamma)$ then represents the fraction of carbazole units in the polymer that have become crosslinked; this is also plotted in *Figure 3*. It can be seen that the amount of crosslinking is proportional to $SbCl_5$ concentration up to at least 70% conversion (measurements are difficult beyond this due to the increasing absorption of the green cation). It is also seen that the fractional number of carbazole units used in crosslinking is virtually equal to the molar ratio of the reactants, thus showing that each $SbCl_5$ molecule promotes the crosslinking of just one carbazole unit (i.e. two $SbCl_5$ molecules are required for each crosslink).

To explain this very different reaction behaviour of PVCz with $SbCl_5$ as compared to the previous DEDC case, a modified reaction scheme is suggested:

$$xCz + SbCl_5 \xrightarrow{+Cl} xCz^+ + SbCl_6^{x-} \qquad (VI)$$

$$Cz^+ + Cz^+ \xrightarrow{-2H^+} Cz-Cz \qquad (VII)$$

$$z(Cz-Cz) + SbCl_5 \rightarrow z(Cz-Cz)^+ + SbCl_5^{z-} \qquad (VIII)$$
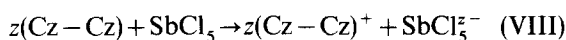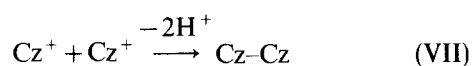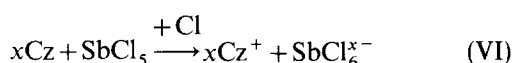
where all the Cz units are attached to a polymer backbone.

The observation that one $SbCl_5$ molecule is required for each carbazole group that is induced to crosslink can immediately be rationalized in this scheme by putting $x = 1$, but this then raises the query as to why a value of $x = 3$ should have been applicable to the parallel DEDC reaction. A possible reason for this is that, as shown earlier, the ionization potential of DEDC is about 0.26 eV lower than that of NEC (which itself is about 0.03 eV higher[18] than that of PVCz). The electron affinities of $SbCl_5$ and its anions do not seem to be known but it may be that while PVCz, NEC and DEDC can all be ionized by $SbCl_5$ only DEDC can be ionized by $SbCl_6^-$.

Reaction (V) has been omitted here because if a monocarbazole cation could react with a neutral carbazole group to form a crosslink then even with $x = 1$ each $SbCl_5$ molecule would effectively promote two carbzaole groups to crosslink and this is twice the observed rate of crosslinking. This reaction is in any case unlikely for PVCz because if it were at all common it would prevent the hopping transport of positive charges between the carbazole groups and this has been well established by experiment (see paper 2). Reaction (II) has also been omitted because any clustering of a number of carbazole groups will be severely limited in the case of a carbazole polymer, especially a crosslinked one, by steric factors imposed by the dimensions and possible conformations of the polymer chains, although weak interactions between a cation and its nearest-neighbour uncharged carbazole groups are very likely as noted later. Reaction (VIII) is the counterpart of reaction (I) for DEDC and yet the initial apparently linear portion of the absorbance curve in *Figure 4* has a much shallower gradient than that of DEDC in *Figure 3* for equivalent $SbCl_5$ concentrations. This gradient corresponds, via use of the extinction coefficient found earlier, to the production of about one dimer cation for every 20 $SbCl_5$ molecules in the PVCz case as compared to three cations for each $SbCl_5$ molecule for DEDC.

In treating reaction (VII) quantitatively, two opposite assumptions could be made. The first assumes that the rate of ionization of dimer crosslinks and of mono-carbazole groups depends mainly on their relative concentrations, in which case very few dimer cations would be formed initially when few crosslinks existed but their concentration would rise as an approximately quadratic function of added $SbCl_5$; however, this quadratic behaviour is not observed. The opposite assumption is that the probability of each dimer being ionized per encounter with an $SbCl_5$ molecule is much higher than that of a monocarbazole group, owing to the lower ionization potential of the former, such that virtually every crosslink formed is immediately ionized. This would give a linear increase of dimer cation concentration with added $SbCl_5$, as observed, but even with x and z both unity this would imply production of one dimer cation per three $SbCl_5$ molecules which is about 7 times greater than observed. It is however significant that the cation absorbance curve in *Figure 4* is approaching a saturation value corresponding to a cation concentration some 25 times smaller than the maximum possible number of crosslinks despite the fact that at M values around unity there are many unreacted $SbCl_5$ molecules in the solution. This suggests that the crosslinking process itself tends to set up a barrier to the subsequent ionization of the dimerized carbazole groups that it has formed. Such a barrier seems indeed very likely because the 3,3' dimerization of neighbouring carbazole groups attached to the same polymer chain is virtually impossible on geometrical grounds and thus dimerization must occur between groups on different chains or groups far separated along a chain that has managed to bend back upon itself. Intermolecular crosslinking between two such bulky polymer chain segments is likely to render very difficult the physical approach of the quite sizeable $SbCl_5$ molecule to the actual crosslink in order to ionize it. Therefore such ionization of crosslinks may well be difficult even at very low degrees of crosslinking and increasingly difficult at higher degrees, whereas ionization of non-crosslinked monocarbazole groups will remain quite easy up to much higher extents of crosslinking, as observed. Many of the crosslinks will thus remain un-ionized even though free $SbCl_5$ molecules remain in the solution.

Dimer cation spectrum

The spectrum of the monocarbazole cation has been difficult to obtain due to the high reactivity of the cation, but laser photolysis studies[26,27] of NEC or *N*-isopropyl-carbazole in solution at room temperature indicate that it absorbs principally at about 710 and (more strongly) at 780 nm. Irradiation of NEC in a polyethylene sheet at 77K gave similar absorptions at 720 and 795 nm, as described in paper 4. No absorption at much shorter wavelengths has been definitely established, owing to absorption by other species, but the low-temperature irradiations do show a fairly strong narrow peak at 394 nm which may belong to the monocarbazole cation.

In going from the carbazole cation to the carbazole dimer cation a reduction in energy of the highest occupied molecular orbital would be expected due to the increased extent of electron delocalization, with consequent red-shifting of the lowest absorption band. This effect can be seen, for example, by comparison of the naphthalene cation spectrum[28] with that of naphthalene dimer cations[29]. Thus it is likely that the single broad near-infra-red peak of the dimer cation at 1150 nm is the red-shifted counterpart of the NEC monocarbazole cation band containing the two peaks at about 720 and 790 nm noted above. It is also possible that the characteristic 430 nm peak of the dimer cation derives from the 394 nm band noted earlier, although assignment of the latter to the NEC monocarbazole cation is only tentative at present.

The dimer cation spectrum as normally seen is unlikely to be the spectrum of an isolated cation. The reaction between DEDC and SbCl₅ was earlier interpreted with the assumption that each DEDC cation formed a weak charge-transfer complex with up to three neutral DEDC molecules. Pairs of aromatic molecules with a single positive charge and bound together by such charge exchange forces have been found previously[23,24] and these always exhibit some absorption to the red of the isolated cation spectrum. In addition solvent shifts were noted earlier in the NEC dimer cation spectrum, probably induced by the effects of molecular aggregation when in poor solvents.

Further signs of dimer cation interaction with, presumably, neutral carbazole groups comes from the PVCz/SbCl₅ spectrum which in DCM solvents exhibits two strong broad poorly defined peaks in the near-infra-red at about 1050 and 1600 nm, as shown in *Figure 2*, instead of the single peak found at about 1150 nm for the NEC and DEDC cations. However, if SbCl₅ is reacted with an existing solid PVCz film then the 1600 nm peak is not seen, as noted in paper 2. It seems likely therefore that each PVCz dimer cation interacts as far as it is able with other neutral carbazole groups, presumably mainly its near neighbours in the polymer chain, but that the formation of at least one favourable mutual orientation for strong interaction is controlled by the permitted conformation of the polymer chains in different environments. Interactions between monocarbazole cations and neutral carbazole groups have already been postulated in laser photolysis[30] and fluorescence quenching[31] studies of PVCz solutions containing weak electron acceptors.

CONCLUSIONS

It is concluded that the green colour observed when carbazoles are reacted with strong electron acceptors in a suitable solvent is due to the formation of stable carbazole dimer cations. The absorption spectrum of these cations is considerably affected by their interactions with neighbouring neutral carbazole groups and these interactions are controlled by the relative orientations of the molecules that are permitted in particular systems by steric and solvation factors. In polyvinylcarbazole such dimer cation formation is preceded by very efficient crosslinking of the polymer chains which tends to inhibit subsequent cation formation by limiting the accessibility of the crosslinks to approach by electron acceptors.

The carbazole dimers were found to have an ionization potential of 7.17 eV and the dimer cations an extinction coefficient at 430 nm of about $1.7 \times 10^7 \, l \, mol^{-1} \, m^{-1}$.

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