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Transient absorption studies on 3,6-dibromo polyvinylcarbazole and its model compounds

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Abstract

3,6-Dibromo-*N*-ethylcarbazole (DBNEC) and its polymeric analogue poly-3,6-dibromovinylcarbazole (PDBVCz) were studied by transient absorption spectroscopy. The transient absorption spectrum of the 3,6-dibromo-*N*-ethylcarbazole radical cation and decay rate constants of radical cations of 3,6-dibromo-*N*-ethylcarbazole and its polymeric analogue are presented. In the case of unsubstituted carbazole, the ratio of the yield of radical cation of monomer to polymer is 2.0, whereas in the case of PDBVCz, under the same experimental conditions, the yield of the radical cation is an order of magnitude less in comparison with the monomer model compound DBNEC. This drastic difference in yield has been correlated to the difference in the conformational structure of the polymer as evidenced by nuclear magnetic resonance spectroscopy. © 1997 Elsevier Science S.A.

Keywords: Transient absorption; Polyvinylcarbazole

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1. Introduction

An approach to studying the structure–function relationships of photoconducting polyvinylcarbazoles has involved research on the effect of substitution in the carbazole rings of the polymer, in addition to study of the photoinduced transients [1–7,11]. In particular, 3,6-dibromo substituted carbazoles have been studied [4–7], since the 3 and 6 positions in the carbazole chromophore are the most reactive sites. Dimerization of the carbazole units in the polymer chain has been postulated on photoexcitation, leading to carbazole dimer radical cations and dications, which act as trap sites for the charge carrier. Thus a direct comparison of the 3 and 6 substituted carbazole polymer with respect to the unsubstituted analogue polyvinylcarbazole, is expected to provide vital clues regarding the structure–photoconductivity relationships.

Polyvinylcarbazole (PVCz) has been widely studied on account of its photoconducting properties [2,3,8]. It has been shown that the photoconductivity of PVCz is due to the formation of the radical cation (the charge carrier) by photoexcitation [9,10]. The magnitude of photocurrent in these polymers depends on the efficiency of the formation of the charge carrier and also on the mobility of the charge carrier. Transient absorption studies on PVCz have indicated the formation of monomeric and dimeric radical cations by ionic photodissociation [11]. Hence, our interest was to investigate the photoconducting properties of poly-3,6-dibromo-*N*-vinylcarbazole (PDBVCz) where bonded dimer is not possible owing to the non-availability of 3 and 6 positions for dimerization. Moreover, the bulkiness of the bromine groups may lead to different geometries for the non-bonded dimer, leading to a profound effect on the photoconducting property of this polymer in relation to that of PVCz. In the case of PVCz, Masuhara et al. [12] have shown that the relative efficiency of charge carrier (cation radicals) formation, after ionic photodissociation, is lesser than that of the monomer model compound *N*-ethylcarbazole (NEC). It has also been observed that the efficiency of charge carrier formation depends critically on the structure of the polymer [13,14]. Therefore, it would be of interest to understand the efficiency of charge carrier formation in PDBVCz and its monomer model compound 3,6-dibromo-*N*-ethylcarbazole (DBNEC) relative to PVCz and NEC. We note that although the mechanism of formation of the charge carrier, cation radicals, is different (vide infra), it is not unreasonable to compare the relative yields, since the reference for both polymers is the corresponding monomer (the mechanism is not expected to be different for the monomer and the corresponding polymer). Ito et al. [4] have studied in detail the time resolved

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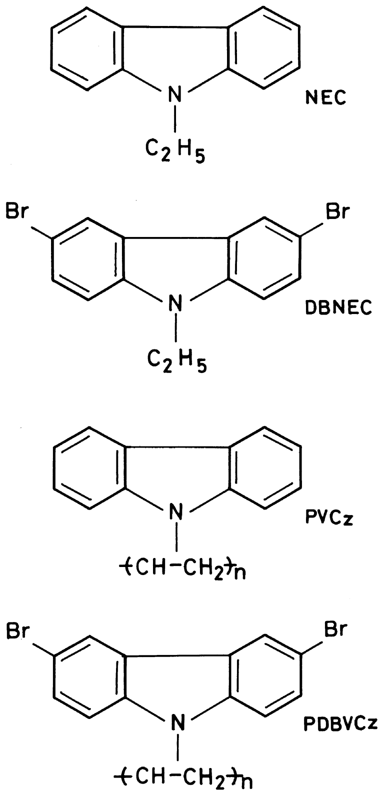
emission and absorption spectra of a polymer containing this group and concluded that the bulkiness of the bromine atom may force the chromophore into a preferential configuration where interaction can be exerted in the triplet state. However, no transient absorption data are available for the polymer PDBVCz, but transient absorption of the triplet state has been reported for a similar polymer 2-(3,6-dibromo-9-carbazolyl)ethyl methacrylate and its copolymer with methyl methacrylate [4]. In this paper we report the transient absorption spectra of DBNEC radical cation, relative yield measurements for radical cations of PDBVCz, PVCz, NEC and DBNEC.

2. Experimental methods

The structures of the compounds studied are shown in Scheme 1. NEC was obtained from Aldrich and was purified extensively by column chromatography followed by recrystallization from methanol. PVCz was also obtained from Aldrich and purified by several reprecipitations from tetrahydrofuran (THF) solution by methanol. For both samples the purity was confirmed by recording the nuclear magnetic resonance (NMR) spectra and fluorescence spectra (which indicate the impurity fluorescence). NEC was brominated to obtain DBNEC [15], which was also purified using a similar procedure as in the case of NEC. Phthalic anhydride was used as received. Bromination of the polyvinylcarbazole was carried out by the procedure reported in Ref. [16], where complete bromination was achieved. We used the same procedure and obtained a similar yield of product. Hence, it is expected that bromination is complete. Moreover, the absorption spectrum of PDBVCz prepared by the polymerization of the prebrominated monomer is similar to that of PDBVCz prepared by bromination of PVCz. These observations confirm that the structures of the polymer prepared by both methods are similar, indicating complete bromination. The PDBVCz was purified by reprecipitation from THF solution from methanol. Sample solutions contained typically 10^{-3} M carbazole and 10^{-1} M phthalic anhyride in DMF. After each laser flash, samples were replaced to avoid accumulation of photoproducts or other intermediates. A third harmonic output (355 nm) of an Nd-YAG laser was used for photoexcitation and a xenon lamp was used for probing the transient absorption with PMT detector. The time resolution of the instrument was around 100 ns. The NMR spectra were recorded in d_6-dimethylsulphoxide at room temperature.



Scheme 1. Structure of the compounds.

3. Results and discussion

The photoprocess under investigation is shown in Scheme 1, where Cz is a carbazole group, ^{1}Cz is carbazole in the singlet excited state and ^{3}Cz is in the triplet state. It is well known that on excitation of the carbazole chromophore in the presence of an acceptor, charge transfer from either the singlet or triplet excited state of the carbazole leads to the formation of carbazole cation radicals and acceptor anion radicals. We used phthalic anhydride (PA), a well known electron acceptor, to quench the excited states of the carbazoles investigated:

$$\mathrm{Cz} + h\nu \rightarrow {}^1\mathrm{Cz} \rightarrow {}^3\mathrm{Cz}$$

$${}^1\mathrm{Cz} + \mathrm{Pa} \rightarrow \mathrm{Cz}^{+\cdot} + \mathrm{PA}^{-\cdot}$$

$${}^3\mathrm{Cz} + \mathrm{PA} \rightarrow \mathrm{Cz}^{+\cdot} + \mathrm{PA}^{-\cdot}$$

The concentration of carbazole chromophore was adjusted to have an absorbance of 0.3 at the excitation wavelength (355 nm). The concentration of PA was approximately 10^{-1} M, in order to quench effectively most of the excited states. In the case of DBNEC, quenching is expected to be mainly from the triplet excited state, since the singlet to triplet intersystem crossing efficiency is very high owing to intramolecular heavy atom effect [4–7].

The transient absorption spectra of the DBNEC/PA system are shown in Fig. 1. The spectra contain two bands centred around 420 nm and 800 nm. The band at 420 nm is assigned to the PA radical anion by comparison with the spectrum reported previously [17,18] and the band at 800 nm is assigned to the DBNEC radical cation. The transient decays were measured at 420 nm and 780 nm and are shown in Fig. 2. The rate constants for the second-order fitting of the observed decay are given in Table 1. The extinction coefficient of the NEC radical cation at 780 nm has been reported to be 3×10^3 M^{-1} cm^{-1} [19]. The concentration of the radical cation of

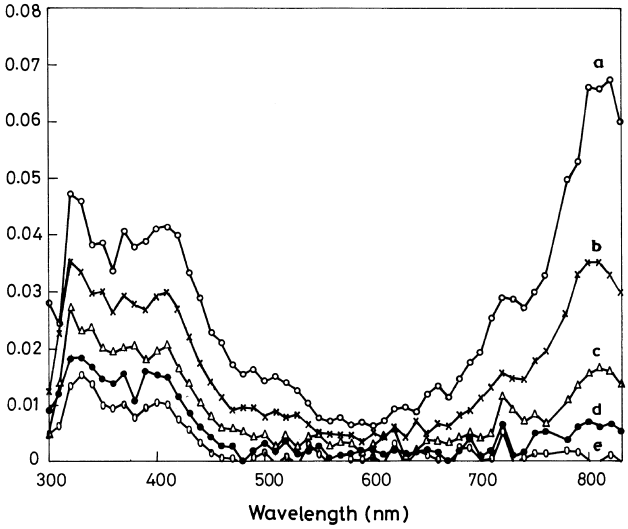


Fig. 1. Transient absorption spectra of dibromo-*N*-ethylcarbazole and phthalic anhydride at various delays: (a) 6 μs, (b) 14 μs, (c) 30 μs, (d) 58 μs, (e) 138 μs.

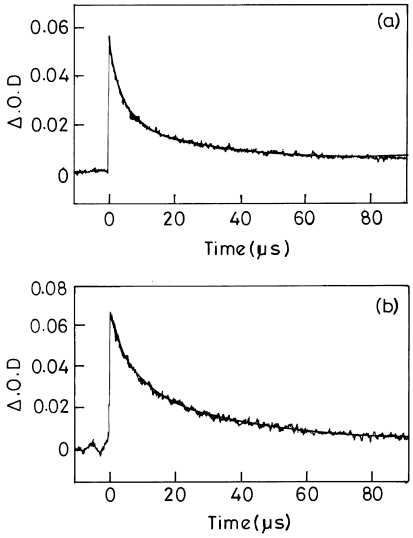


Fig. 2. Decay of the transients of DBNEC (a) at 420 nm, (b) at 780 nm.

NEC formed by photoexcitation has been determined using this extinction coefficient. The extinction coefficient of the PA radical anion at 420 nm has been calculated on the assumption that the concentration of the radical cation and that of the radical anion are equal immediately after photoexcitation. The calculated extinction coefficient of the PA radical anion has been used for calculating the extinction coefficient of radical cations of PVCz, DBNEC and PDBVCz, assuming one to one mole concentration for the formation of radical cations and anions. Thus, from the initial carbazole concentration and the concentration of cations known from the extinction coefficient, we have calculated the relative yield of the formation of radical cations in this system.

A similar experiment was carried out for the DBNEC polymer PDBVCz. The transient decay curves are shown in Fig. 3, for the same wavelengths. Using the procedures presented earlier, the rate of decay, extinction coefficient and the radical yield have been calculated and are presented in Table 1. Under the same experimental conditions the transient absorption spectra were also recorded along with the decays for both NEC and PVCz. Since these spectra and decays have already been reported [18], they are not shown here. However, the data are summarized in Table 1. For a reasonable comparison of the yield and rate of decay of brominated carbazoles with that of the unsubstituted carbazoles, we have repeated the transient studies on NEC and PVCz.

From Table 1 it can be seen that the ratio of the relative yield of the radical cation formation for monomer to polymer is about 2.0 for PVCz. Masuhara et al. [12] have observed a relative yield of the radical cation for monomer to polymer ranging from 2.3 to 7.2 depending on the initial concentration of the substrate and excitation source. Hence the relative yields in the present study were measured by retaining a constant laser intensity for all the measurements. The concentration of the substrates was adjusted to obtain the OD of 0.3 at 355 nm. Since the extinction coefficients of the respective monomer and polymer were nearly the same, the corresponding concentrations were nearly equal. It has to be noted that, although the mechanism of formation of radical cations for NEC and PVCz could be different from that of their brominated analogues, a comparison of the relative yield of cations in the polymer with respect to the monomer is valid. This is not unreasonable since the mechanism of formation is unlikely to be much different for the monomer and polymer, as the photophysics has been found to be similar for both [20].

It can be seen from Table 1 that the rate constant for the decay of the radical anion is always higher than that of the radical cation except for PVCz (in PVCz, the additional route for decay of the radical cation is dimerization, which would explain the faster decay). This reflects the fact that the solution state ion recombination is not the only source for decay

Table 1
Rate of decay, extinction coefficient and yield

Compound	Rate constant at 420 nm ($M^{-1} s^{-1}$)	Rate constant at 780 nm ($M^{-1} s^{-1}$)	Extinction coefficient at 780 nm ($M^{-1} cm^{-1}$)	Yield of the radical cation (%)
NEC	3.4×10^{10}	2.1×10^{9}	3000	2.18
PVCz	8.9×10^{9}	6.7×10^{10}	2566	1.1
DBNEC	6.9×10^{9}	6.0×10^{9}	4482	14.9
PDBVCz	3.3×10^{10}	5.9×10^{9}	4375	0.84

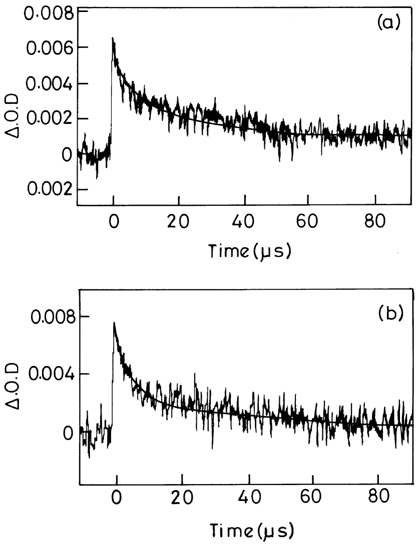


Fig. 3. Decay of the transients of PDBVCz (a) at 420 nm, (b) at 780 nm.

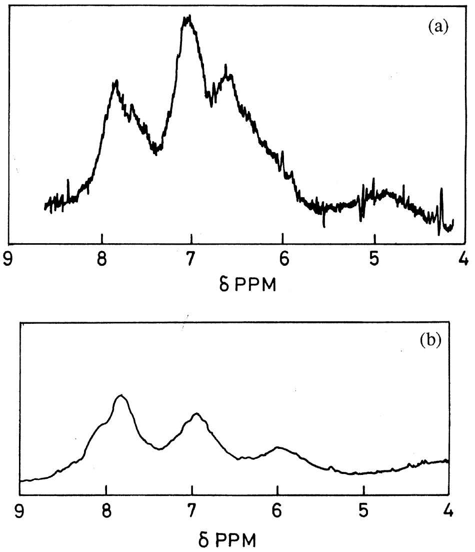


Fig. 4. NMR spectra of (a) PVCz and (b) PDBVCz.

of the radicals, and oxidation of the anion by oxidants such as trace amounts of oxygen can also contribute to the decay of the anion. In oxygen saturated solution we have found that the rate constant for the decay of the radical cation decreases, whereas for the radical anion it increases owing to electron transfer quenching from the anion to the oxygen.

In our experiment we have observed that in the case of unsubstituted carbazole, the ratio of the yield of radical cation of monomer to polymer is 2.0, whereas in the case of PDBVCz, under the same experimental conditions, the yield of the radical cation is an order of magnitude less in comparison with the monomer model compound DBNEC. As a drastic change in the yield is not expected, the reasons for the lesser yield in the polymer compared with monomer [14] can be (a) interaction of the excited states in the polymer chain leading to a faster decay of the excited states compared with the monomeric analogue, (b) preferential solvation of the ions of the end groups compared with middle groups thus inducing faster decay of less stable radical cations of the middle groups, and (c) the presence of different kinds of predissociative states (prior to the formation of radical cations) in the polymer, like the monomeric excited state, triplet excimers with different configurations such as partial overlapping and sandwich dimers. These different predissociative states may have different non-radiative routes which may lead to a lesser yield for the polymer. In fact, Ito et al. [20] have shown that the triplet state of the dibromocarbazole group has a weaker stabilization energy compared with the unsubstituted carbazole group. This difference in the stability may lead to faster decay of the less stable triplet state of PDBVCz. Hence the reduction in the ratio of the relative yield of the radical cation for monomer to polymer in the case of PDBVCz may be related to the conformation of the excited state from which the radical cations are formed.

It is known that pendant chromophoric conformations in a polymeric network can be studied qualitatively by NMR [2]. In particular, overlap of carbazole units has been identified in a number of polymeric systems [2]. Similarly, we have recorded the NMR spectra of the polymers to understand the conformations of these polymers. The NMR spectra of PVCz and PDBVCz are shown in Fig. 4. It is expected that the shielded aromatic protons appearing at lower δ than the normal aromatic protons indicate interaction between the neighbouring carbazole groups [1]. It can be seen from Fig. 4 that aromatic protons of PDBVCz appear at higher δ than those of PVCz. This indicates that the overlap of the carbazole group is less in the dibrominated analogue than in PVCz. This is quite likely as the size of the bromine substituent may force the carbazole groups into a particular geometry, which may cause the reduction in the overlap between carbazole groups. This reduction in overlap between the carbazole groups may affect the conformation of the excimers in the case of dibromocarbazole chromophores. Thus, the formation of triplet excimers or any other predissociative dimeric intermediates may be unlikely.

Another possibility for the reduction in the yield of the PDBVCz with respect to the monomer can be related to the lack of access to the carbazole chromophores by the quencher due to steric factors. Thus the acceptor, PA, perhaps is only able to interact with pendant carbazoles which are exposed, i.e. the end groups and also the units in the periphery of the polymer structure.

4. Conclusion

Transient absorption spectroscopy has been applied to find the relative yield of the radical cations for PVCz and PDBVCz. It has been found that the ratio of the relative yield of the radical cation for monomer to polymer depends on the structure of the polymer. NMR spectroscopy has been used to study the structure of these polymers qualitatively. This reduction in the yield of the radical cation may have an impact on the photoconducting properties of these polymers.

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