

On the triplet state of poly(*N*-vinylcarbazole)

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Received 4 October 2004; in final form 3 November 2004

Available online 18 November 2004

Abstract

Triplet state properties including transient triplet absorption spectrum, intersystem crossing yields in solution at room temperature and phosphorescence spectra, quantum yields and lifetimes at low temperature as well as singlet oxygen yields were obtained for poly(*N*-vinylcarbazole) (PVK) in 2-methyl-tetrahydrofuran (2-MeTHF), cyclohexane or benzene. The results allow the determination of the energy value for the lowest lying triplet state and also show that triplet formation and deactivation is a minor route for relaxation of the lowest excited singlet state of PVK. In addition, they show the triplet state is at higher energy than reported heavy metal dopants used for electrophosphorescent devices, such that if this is used as a host it will not quench their luminescence.

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1. Introduction

Poly(*N*-vinylcarbazole) (PVK) is an important non-conjugated organic polymer, whose initial studies (reviewed in [1]) concentrated on its application in photocopiers. Although its use in this has now been superseded by other materials, it is still an important and well-studied organic polymer, whose use has been suggested for areas ranging from electroluminescence [2] to photorefractive systems [3]. For many of these applications, a knowledge of the photophysics is important, and fluorescence properties, particularly excimer formation kinetics and dynamics were extensively studied and discussed during the 1970s and 1980s of the past century [4–8]. In addition, a number of studies were reported on phosphorescence, delayed fluorescence and triplet energy transfer at low temperatures in films and solid solutions of PVK [9–11]. Although PVK was the first reported electroluminescent polymer [2], the devel-

opment of efficient light emitting conjugated polymers [12] led to a loss in interest in the use of this system in devices. In these polymer light emitting diodes (PLEDs), emission comes from the singlet states of the conjugated polymers and electron correlation effects on electron-hole recombination limit efficiency to a maximum of 25–50% [13], with the rest being lost as nonemitting triplet states. However, it was shown that by the use of phosphorescent heavy metal complexes, initially in organic LEDs [14] and subsequently in polymeric ones [15] that it is possible to capture this triplet energy and produce light emitting devices with very high efficiencies. This has led to a renewed interest in the application of PVK and related carbazole polymers in this area, since both theoretical calculations [16] and experimental measurements [17] show that these make excellent hosts for the triplet emitters. Knowledge of the triplet properties of these polymers is a prerequisite for optimising their efficiency.

Although the earlier reports on the photophysics of PVK did contain much valuable information, a number of important questions remain unanswered. This Letter

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addresses these and presents a complete characterization of PVK triplet state, including quantitative determination of the intersystem crossing, phosphorescence and singlet oxygen yields. It is to our best knowledge the first time that the triplet state of PVK can be considered to be completely characterized.

2. Experimental

Poly(*N*-vinylcarbazole) (Acros organics) and other solutes were of the purest grades available, and were used without further treatment. The solvents were of spectroscopic or equivalent grade and were used without further purification.

Luminescence spectra were recorded on Jobin-Ivon SPEX Fluorolog 3–22 spectrometers using the 1934 D phosphorimeter accessory. The phosphorescence quantum yield was determined using benzophenone ($\phi_{\text{Ph}} = 0.84$) as a standard [18]. All spectra were corrected for the instrumental response of the equipment.

Triplet–singlet difference absorption spectra and yield were obtained using an Applied Photophysics laser flash photolysis equipment pumped by the third harmonic of a Nd:YAG laser (Spectra Physics) with excitation wavelength of 355 nm. First-order kinetics was observed for the decay of the lowest triplet state. The transient spectra (300–650 nm) were obtained by monitoring the optical density change at 5–10 nm intervals, averaging at least 10 decays at each wavelength.

The triplet formation quantum yields of PVK in 2-MeTHF were determined by energy transfer to β -carotene. All measurements were carried out at 20 ± 2 °C and the solutions were degassed with argon.

The triplet quantum yield, ϕ_{T} , determination was made according to the equation [19,20]:

$$\phi_{\text{T}} = \phi_{\text{T}}^{\text{ref}} \frac{\Delta\text{OD}_{\text{S}}}{\Delta\text{OD}_{\text{Ref}}} \cdot \frac{k_{\text{Obs}}^{\text{S}}}{k_{\text{Obs}}^{\text{S}} - k_{\text{O}}^{\text{S}}} \cdot \frac{k_{\text{Obs}}^{\text{ref}} - k_{\text{O}}^{\text{ref}}}{k_{\text{Obs}}^{\text{ref}}}, \quad (1)$$

where $k_{\text{Obs}}^{\text{S}}$ is the observed rate constant ($k_{\text{T}} = 1/\tau_{\text{T}}$) for decay of β -carotene triplet state in a solution with PVK, $k_{\text{Obs}}^{\text{ref}}$ is the observed rate constant ($k_{\text{T}} = 1/\tau_{\text{T}}$) for β -carotene triplet state in a solution of benzophenone plus β -carotene, k_{O}^{S} and $k_{\text{O}}^{\text{ref}}$ are the rate constants of the triplet state of PVK and benzophenone in the absence of β -carotene, $\Delta\text{OD}_{\text{S}}$ is the absorbance of β -carotene triplet at 540–550 nm in the solution of PVK plus β -carotene, $\Delta\text{OD}_{\text{Ref}}$ is the absorbance of β -carotene triplet at 540–550 nm in the solution of benzophenone plus β -carotene.

In all cases the signal was assigned to a triplet state because:

- (i) it was sensitized by the triplet donor benzophenone (triplet energy 3.0 ± 0.1 eV),
- (ii) it sensitized β -carotene triplet,

- (iii) it decayed by first-order kinetics with microsecond lifetimes.

Triplet state absorption spectra were also characterised by pulse radiolysis using the Free Radical Research Facility, Daresbury, UK. Here, 200 ns to 2 μ s high energy electron pulses from a 12 MeV linear accelerator were passed through solutions in a 2.5 cm optical path-length quartz cuvette attached to a flow system. This has been described in detail elsewhere [21]. All solutions were bubbled with argon for about 30 min before experiments.

Singlet oxygen yields, measured at the FRRF (Daresbury laboratories), were obtained by direct measurement of the phosphorescence at 1270 nm followed the irradiation of an aerated solution of the polymer in cyclohexane with excitation at 266 nm from a Nd:YAG laser with a setup elsewhere described [22]. Biphenyl in cyclohexane ($\phi_{\Delta} = 0.73$) was used as standard [18].

3. Results and discussion

Fig. 1 shows the delayed fluorescence and phosphorescence spectra of PVK in 2-methyltetrahydrofuran (2-MeTHF) at 77 K. The two spectra shown were obtained with two different delays after the exciting flash. Notice that the intensity of the delayed fluorescence decreases with the increase in this delay. The spectra is vibrationally resolved showing an onset of phosphorescence at 400 nm (3.1 eV), a maximum at 448 nm and additional peaks at 420 and 472 nm, with shoulders at ≈ 510 and 550 nm, corresponding to a vibronic progression with separation ≈ 175 meV. An identical spectrum was previously reported for PVK under similar experimental conditions [9]. For carbazole itself the phosphorescence maximum (434 nm) is blue-shifted. The quantum yield for PVK phosphorescence (ϕ_{ph}) resulting from the integration of the phosphorescence band and using benzophenone as standard under the same experimental conditions gives a value of $\phi_{\text{ph}} = 0.085$.

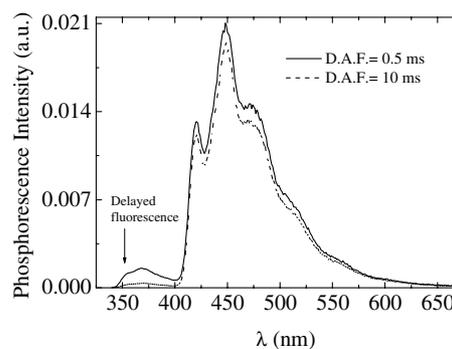


Fig. 1. Phosphorescence emission spectra of PVK in 2-MeTHF at 77 K. Delay after flash 0.5 ms (full line) and 10 ms (dash line).

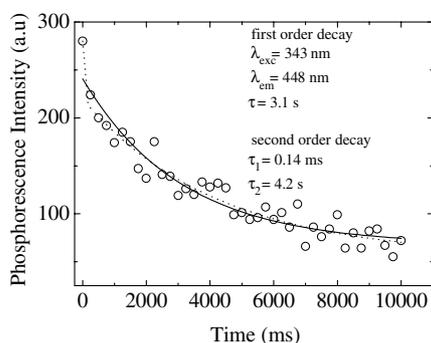


Fig. 2. Phosphorescence decay of PVK in 2-MeTHF. Shown as inset are values corresponding to the fits to a first (full line) and second (dot line) order decay law.

The phosphorescence decay obtained under the above conditions is found to be inconsistent with first order decay kinetics (Fig. 2). A second order fit leads to a decay with 4.2 s as the major component (Fig. 2). As previously reported for PVK in films [23], the additional fast component may result from triplet–triplet (T–T) annihilation leading to some residual delayed fluorescence. This is not likely to influence the phosphorescence lifetime. However, the quantum yield for triplet formation (ϕ_T) will be equal to or greater than the phosphorescence yield, and the presence of T–T annihilation suggests this is a lower limit for ϕ_T . Notice that others have found in the same experimental conditions a phosphorescence lifetime of 7.7 s, but this resulted from the averaged value of several PVK samples with different molecular weights and polydispersity [9]. Although some discrepancy exists between the two absolute values, the long-lived nature of the phosphorescence is totally compatible with the lowest lying triplet state being of π, π^* origin [24]. Since it is known that the lowest singlet excited state is also of π, π^* origin, it is likely that the $S_1 \sim \rightarrow T_1$ intersystem crossing process should be highly forbidden. This could explain in part the limited amount of quantitative data available on the triplet state of PVK.

The transient triplet–singlet difference absorption spectrum of PVK in 2-MeTHF solution at room temperature was generated by laser excitation at 355 nm, and shows a maximum at 389 nm, with further vibronic structure (Fig. 3) and lifetime $\tau_T = 1.56 \mu\text{s}$. This was identified as a triplet because it was quenched by oxygen and was sensitized by the triplet donor benzophenone and it sensitized β -carotene triplet.

Attempts were also made to obtain the T–T absorption spectrum in benzene solution using the pulse radiolysis energy transfer technique [25]. Here, the triplet states of conjugated organic polymers (S) can be selectively produced by energy transfer from appropriate sensitizers (A) following pulse radiolysis of benzene solutions in the reaction sequence

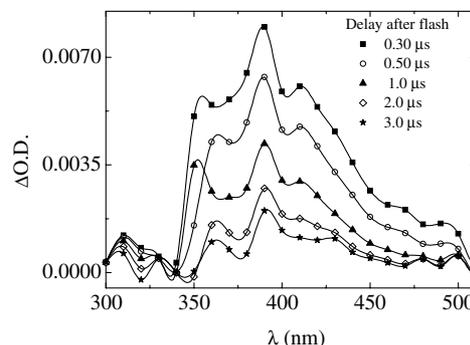
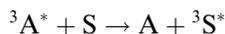
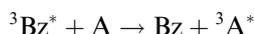
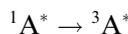
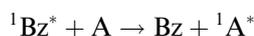
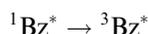


Fig. 3. Transient T–T spectra of PVK in 2-MeTHF at room temperature.



subject to the kinetically demanded concentration ratio $[\text{Bz}] \gg [\text{A}] \gg [\text{S}]$. In this case, in the presence of the sensitizers methoxyacetophenone (triplet energy 3.1 eV, [18]) or 1,2-dichlorobenzene (triplet energy 3.5 eV [18]) very similar transient absorptions around 390 nm were seen to those on laser excitation, confirming assignment to the triplet absorption. No transients were observed with sensitizers of lower energy, giving a limit to the triplet energy of PVK in solution at room temperature of $3.0 \pm 0.1 \text{ eV}$, in very good agreement with the phosphorescence data. This is somewhat higher but more reliable than the previously reported value of 2.5 eV [26].

From the laser flash photolysis experiments, a value for the triplet yield was obtained by the energy transfer method as described in Section 2, giving a value $\phi_T = 0.047$. Even though the experimental errors associated with this value are normally fairly high (typically $\pm 50\%$), the reason that this is markedly lower than the phosphorescence yield is not completely clear. However, it is possible that, because of the short triplet lifetime of PVK in solution, scavenging by the β -carotene is incomplete.

A study was made of the sensitized yield of singlet oxygen formation following laser excitation at 355 nm of a solution of PVK in cyclohexane. From the singlet oxygen phosphorescence at 1270 nm, and comparison with biphenyl, a singlet oxygen yield (ϕ_Δ) of 0.15 was obtained at room temperature. The overall data for the triplet state formation (ϕ_T) and deactivation (ϕ_{Ph} and ϕ_Δ) suggests that formation of the triplet state of

PVK is an inefficient channel for relaxation of the lowest excited singlet state.

The S_1 and T_1 states are both of π, π^* origin and, according to El-Sayed rules [27], this is consistent with the low intersystem crossing yield observed for PVK. The highly resolved phosphorescence and transient T–T spectra are compatible with the rigid structure of the carbazole ring. However, the photophysical behaviour contrasts with that of the parent carbazole, where from the fluorescence yield ($\phi_F = 0.41$), lifetime ($\tau_F = 12.4$ ns) [28] and intersystem crossing triplet yield ($\phi_T = 0.36$) [29] it can be seen that the rate constants for the different deactivation processes (k_F , k_{IC} and k_{ISC}) are of similar orders of magnitude. Also for carbazole the ϕ_{Ph} value is higher (0.24) [30] than in PVK although the phosphorescence decay is similar (6.8 s) [31]. All of the above points to the existence of either a degree of delocalization between carbazole units on PVK, or another pathway of deactivation of the triplet state compared with carbazole itself. The markedly lower values for the triplet and phosphorescence yields suggest some level of interaction between neighboring carbazole units, and since there is no evidence for excimer formation in the triplet state, it is likely, as has previously been suggested for PVK in solid solutions [9–11], that efficient triplet energy transfer takes place both in the solid state and solution between the carbazole moieties. With triplet states, this is likely to involve Dexter transfer [32] through electron exchange. The feasibility of such a mechanism is supported by the observation of very rapid electron transfer between carbazole units on PVK chains [33].

4. Conclusions

In conclusion, we have demonstrated that PVK has a triplet energy of 3.0 eV, which is higher than that of commonly used heavy metal phosphorescent dopants, such as Irppy₃ (2.4 eV) [34], which means that it cannot quench the triplet state of the dopant. Further, we have shown that singlet–triplet intersystem crossing is relatively inefficient in this polymer. This means that if the polymer is used in devices, any singlet states formed on charge recombination can efficiently transfer energy to dopants by processes such as Forster energy transfer [35].

Acknowledgements

We are grateful to POCTI, FCT, FEDER and the Royal Society for funding. Pulse radiolysis and singlet oxygen experiments were carried out at the Free Radical

Research Facility in the Synchrotron Radiation Department of the CLRC Daresbury Laboratory, Warrington, UK, with the support of the European Commission through the ‘Improving Human Potential’ Transnational Access to Major Research Infrastructures Contract HPRI-CT-2002-00183.

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