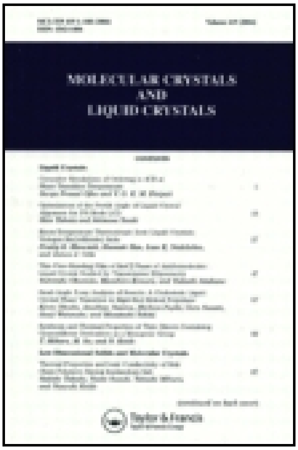

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Geminate Pair Recombination in Polyvinylcarbazole

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Dedicated to Professor Martin Pope on the occasion of his 70th birthday

(*Received 15 Nov 1989*)

Temporal decay of delayed luminescence (DL) of PVK excited by 4.02 eV photons of an excimer laser has been studied in the time domain 10 μs to 20 s at 297 K and 80 K, respectively, and at selected emission wavelengths (388 nm, 418 nm, 500 nm). At 297 K, DL is controlled by the recombination of geminately bound electron-hole pairs because under the high excitation doses employed, triplet-triplet annihilation occurs on a faster time scale. At 80 K fusion among localized triplet states contributes to DL as well. In combination with literature data for different systems studied in the time domain 10 s to 10^4 s the present results confirm that geminate pair recombination in disordered organic solids obeys a hyperbolic decay law in accord with the predictions of both Monte Carlo simulation and localization theory for systems with built-in energetic disorder.

1. INTRODUCTION

To interpret delayed luminescence (DL) in condensed organic phases different approaches have been developed depending on the system under study. Experts in molecular crystals consider DL to be the consequence of the annihilation of two triplet excitons.[1–3] This is an unambiguous assignment if triplet excitons are generated by direct $T_1 \leftarrow S_0$ absorption, yet need not in general be true if primary excitation occurs into the singlet manifold. If the photon energy if sufficiently above the $S_2 \leftarrow S_0$ absorption gap, electron-hole (eh) pairs may be generated intrinsically in addition to $S_1 \rightsquigarrow T_1$-induced triplets. They can recombine to form singlet states which subsequently can decay radiatively. The reason why this process is commonly neglected as a contributor to DL is the short eh recombination time, identified with the time a carrier needs to diffuse across a distance of a few lattice distances and usually assumed to be much shorter than the fluorescence decay time. In fact, Braun and Scott[4] have demonstrated that geminate pair (GP) recombination of an electron with its sibling anthracene radical counterion in liquid hexane is in accord with this notion. It occurs on a 10 . . . 100 ps time scale and is diffusion controlled as Hong and Noolandi[5] predicted.

Nevertheless, in 1965 Pope and coworkers[6,7] provoked the molecular crystal world when discovering the existence of a charge pair state in crystalline tetracence living for as long as 100 ns. Evidence was based on the double quantum photoelectric effect.[1] Although it became clear later on that it cannot be the free CT state that lives so long but a trapped one[8] this result turned out to be a challenge for future molecular crystal spectroscopy. It initiated much subsequent work on photoelectronic properties of molecular crystals, such as the experiments of Hanson[9] as well as those of Sebastian et al.[10,11] establishing the existence of direct CT transitions in molecular crystals. On the other hand, photochemists never hesitated in attributing DL to the delayed recombination of photo-generated charge carriers.[12] Notably the work of Albrecht and coworkers[13,14] demonstrated conclusively that two quantum excitations of an aromatic molecule incorporated in an inert, frozen solution can ionize the molecule by ejecting an electron subsequently trapped in the vicinity of the counterion. In a rigid matrix recombination requires either detrapping of the electron or long distance tunnelling which both may take a long time to occur. Recombination induced DL is therefore diffusion controlled. It usually decays in a non-exponential fashion[15,16] and may last for hours which clearly rules out any involvement of triplet states.

By recognizing that it is charge localization which causes the delay in the eh recombination kinetics it is straightforward to conjecture that the velocity of eh recombination in a solid is controlled by the degree of disorder of the sample. Stimulated by the vast amount of work—both experimental and theoretical—on photoluminescence in systems like amorphous silicon and by the work of Mort *et al.*[17] on extraordinarily long eh pair lifetimes in polyvinylcarbazole (PVK), Ries and Bässler[18] have conducted a Monte Carlo computer simulation study aimed at rationalizing the kinetics of geminate pair recombination in systems with built-in energetic disorder. In view of the enormous mathematical difficulties this case had not been treated analytically so far. Their analysis predicts a power law decay of the type t^{-s} with s close to unity for the luminescence decay. It has been verified in course of DL experiments with pure[19] and doped PVK,[20] a material which, however, has previously be shown to be a candidate for triplet-fusion controlled DL.[21-23] In this paper the previous experiments on PVK have been extended. They demonstrate that at least at photon doses sufficiently high to ensure that triplet-triplet fusion processes are fast, DL is controlled by geminate pair recombination, the signature being a hyperbolic decay with time.

2. EXPERIMENTAL

Cationically polymerized PVK (molecular weight (3 . . . 5) × 10^6) was kindly placed at our disposal by Professor W. Klöpffer. Low molecular weight impurities, such as anthracene, were removed by threefold precipitation with methanol from benzene solution and by subsequent gel permeation chromatography using Merckogel OR 6000. The benzene used for film deposition from solution was dried and saturated with argon to reduce the oxygen content. Oxygen-free films, typically 10 μm thick, were deposited on copper supports by letting the solvent slowly evaporate under an argon atmosphere.

The sample was attached to the cold finger of a home built cryostat, operated at either 80 K or 297 K, and excited by 4.02 eV photons of an excimer laser. The energy per laser pulse could be varied between 10 μJ cm^{-2} and 5 mJ cm^{-2}. To select the delayed luminescence of the sample a home built phosphoroscope was used providing an observation time window extending from 10 μs to 10 s. By dividing the time frame into 10 segments and by appropriate adjustment of the load resistor of the photomultiplier, the dynamic range of the detection system could be extended to cover a range of 5 decades. The repetition rate of the laser, triggered by the phosphoroscope, varied between 0.25 Hz (for detection times <100 ms) and <0.1 Hz (for longer detection times), respectively. The multiplier output was recorded by a transient digitizer (Tektronix 2430). After accumulating 64 to 256 decay curves the signal was fed into a computer for data processing and re-assemblage of the entire decay pattern. Spectrally selected decay curves were generated by the use of interference filters. The temporal evolution of the luminescence spectra was monitored by a gated optical multichannel analyser (OMA).

3. RESULTS

Delayed luminescence decay patterns of PVK recovered at 80 K and 297 K under high intensity excitation energy (5 mJ cm^{-2} per pulse) within spectral windows centered around 388 nm, 418 nm and 500 nm are presented in Figure 1 while Figure 2 shows the spectrally integrated decay pattern at both high and low (20 μJ cm^{-2} per pulse) excitation energies. Although generally obeying power law dependences, spectrally sensitive variations are noted that will be referred to in the discussion. The dependence of the emission intensity, integrated over the observation time window, on the incident photon dose I_{ex} is shown in Figure 3a,b for 80 K and 297 K, respectively. It is linear to superlinear at low I_{ex} and tends to saturate at $I_{ex} > 1$ mJ $(cm^2 \cdot pulse)^{-1}$. The emission spectrum changes with time (Figure 4). At short delay times fluorescence is emitted from a strongly overlapping excimer with emission maximum near 420 nm and a trap emitting near 380 nm and associated with a weakly overlapping pair of adjacent carbazole groups.[21,24] Trap phosphorescence, attributed to a triplet excimer,[21,25] prevails at long times.

4. DISCUSSION

Upon exciting PVK with 4.02 eV photons about 14% of all absorption events end up with the generation of coulombically bound electron hole pairs (GPs) with intrapair distance ≈22 Å[26]; about 15% create carbazole triplet states (based on a S_1 lifetime of 4 ns and an intersystem crossing rate constant of $3.8 \times 10^7 s^{-1}$).[22] The rest populate the carbazole S_1 manifold and may become subject to more efficient intersystem crossing after trapping at a singlet excimer forming site. The contributors to delayed emission can be GPs via delayed geminate pair recombination (GPR) as well as triplet states via phosphorescence (P) and bimolecular annihilation (TT processes), respectively. An essential goal of the following analysis is to identify these contributions.

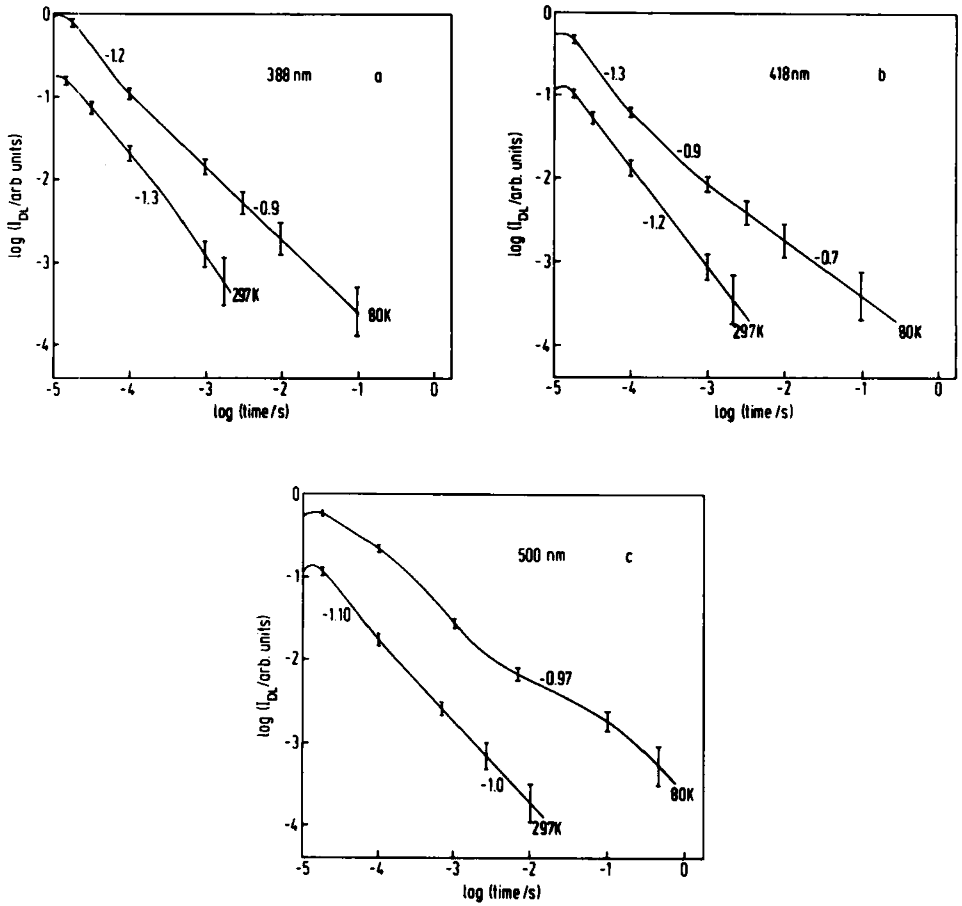

FIGURE 1 Decay of the delayed luminescence emitted from a PVK sample at 297 K and 80 K, respectively, after excitation with 4.02 eV photons of an excimer laser (pulse duration 20 ns). The excitation energy I_{ex} per pulse was 5 mJ cm^{-2} equivalent to 7.5×10^{15} photons cm^{-2}. Decay patterns in a), b) and c) were recorded with interference filters centered about 388 nm, 418 nm and 500 nm, respectively.

Consider triplet excitation kinetics first. After cessation of the excitation pulse, the decay of the triplet density $[T]$ is governed by the rate equation

$$[\dot{T}] = -(k_p + \upsilon c_t)\,[T] - \gamma[T]^2 - \gamma_t[T][T_t] \qquad (1)$$

where k_p^{-1} is the intrinsic triplet lifetime, υc_t, is the rate at which an excitation migrating at an exchange rate υ will be captured by a trap present at mole fraction c_t, γT^2 and $\gamma_t T T_t$ denote homofusion of free triplets and heterofusion of a free and a trapped triplet excitation respectively.[1] To estimate γ we make the plausible assumption that motion of a free triplet excitation in PVK is incoherent and controlled by the energetic disorder of the triplet energies of the carbazole moiety.

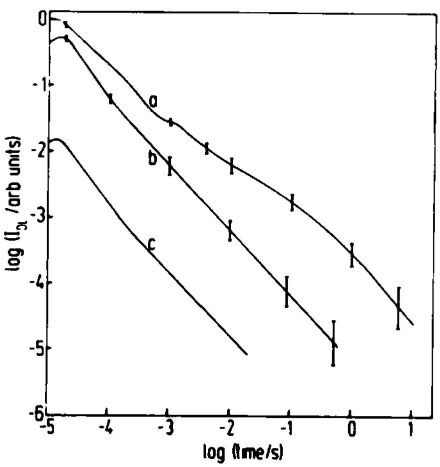

FIGURE 2 Spectrally integrated delayed fluorescence recorded at: (a) I_{ex} = 5 mJ (cm^2 pulse)$^{-1}$; T = 80 K. (b) I_{ex} = 5 mJ (cm^2 pulse)$^{-1}$; T = 297 K. (c) I_{ex} = 20 μJ (cm^2 pulse)$^{-1}$; T = 297 K.

This concept has gained credence by the work on exciton transport studies in organic glasses[27,28] and orientationally disordered cyrstals.[29] From the former,[27,28] we estimate the Gaussian width σ of the density of triplet states in a non-crystalline organic solid to be about 300 cm^{-1}. This concept predicts $D(T) = D_o \exp[-(0.64\ \sigma/kT)^2]$ for the temperature dependence of the steady state diffusivity of triplet excitations. Since $\gamma = 8\pi RD$, $\gamma(T)$ can be estimated provided γ_o characterizing bimolecular triplet-triplet annihilation in a hypothetical crystalline counterpart structure is known. Taking $\gamma_o = 3.5 \times 10^{-12}$ cm^3 s^{-1} as measured for crystalline naphthalene,[30] the steady state diffusivity and, hence, γ can be estimated from γ ($\gamma = \gamma_o \exp[-(T_o/T)^2]$ where D_o is the diffusivity in the hypothetical crystalline

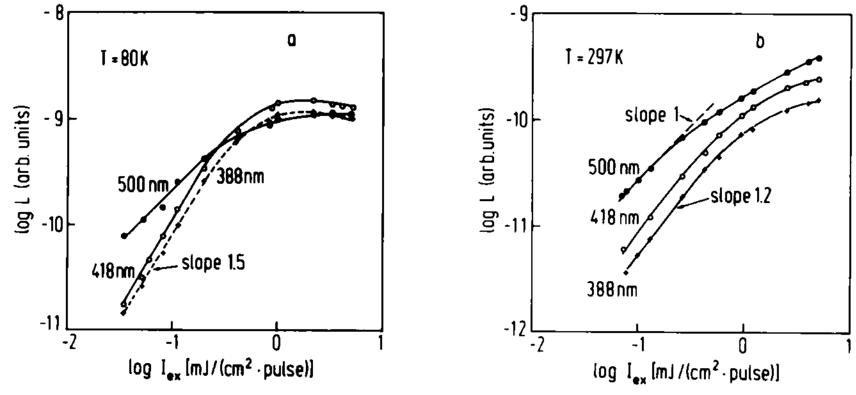

FIGURE 3 Integrated intensity L of the delayed luminescence as a function of exciton intensity recorded with 388 nm, 418 nm and 500 nm interference filters. Data in a) and b) were taken at 80 K and 297 K, respectively.

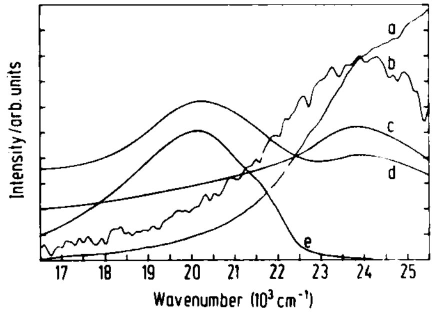

FIGURE 4 Temporal evolution of the spectrum of the delayed luminescence recorded at 80 K with a gated optical multichannel analyser (I_{ex} = 3.2 mJ (cm^2 pulse)$^{-1}$).

curve	delay time	width of the detection window
a	0	240 ns
b	500 ns	5 μs
c	5.5 μs	50 μs
d	55 μs	200 μs
e	1 s	500 ms (measured with OMA III system)

counterpart system and $kT_o = 0.64\sigma$,[31] i.e. T_o = 280 K. This yields γ(297 K) $\simeq 10^{-12}$cm^{3}s^{-1} and γ(80 K) $\simeq 1.2 \times 10^{-17}$cm^{-3}. At the highest photon dose employed, I_{ex} = 5 mJ cm^{-2} per pulse, the initial triplet excitation density is $[T_o] \cong 10^{19}$ cm^{-3} assuming an absorption coefficient[26] $\alpha = 3.6 \times 10^4$ cm^{-1}. Consequently, $\gamma[T_o]_{max} \cong 10^7$s^{-1} and 2×10^2s^{-1} at 297 K and 80 K, respectively. The above γ implies a triplet excitation hopping frequency υ of order 10^{10} s^{-1} at room temperature. Adopting the results of Burkhart and Aviles[23] that at 297 K triplets are essentially free in PVK, we ignore trapping and arrive at the following predictions regarding both the dependence of the ingegrated DL intensity L = $\int_{\tau_d}^{\infty} I_{DF}\,dt$, τ_d being the dead time of the phosphoroscope (10μs), on the incident photon dose I_{ex} and the DL decay pattern of PVK at room temperature contingent on the assumption that it be dominated by triplet processes. The delayed fluorescence (DF) intensity is then:

$$I_{(DF)} \propto [\dot{S}] = \eta\gamma[T]^2 \qquad (2)$$

where η is the fraction of *TT* fusion events leading to singlet formation. At high triplet densities,

$$L = \int_{\tau_d}^{\infty} I_{DF}dt \propto [T(t)] = [T_o]/(1 + \gamma[T_o]t)\eta[T_o] \text{ and } (1 + \gamma[T_o]\tau_d)^{-1} \qquad (3a)$$

which becomes $L \propto \eta(\gamma\tau_d)^{-1}$. At low I_{ex} where first order triplet decay prevails,

$$L \propto (n\gamma\tau_p[T_o]^2 e^{-2\tau_d/\tau_p}) \propto I_{ex} \qquad (3b)$$

τ_p being the triplet lifetime. The temporal decay of I_{DF} should obey a t^{-2} law at $t \geq \tau_d$ merging into an exponential decay at long times, the decay time being around 2.5 ms. (In Reference 23 free triplet lifetimes of 4.0 and 7.2 ms have been reported.) The present experimental results collected at 297 K are at variance with these predictions: (i) the $I_{DF}(t)$ decay closely follows a t^{-1} law (Figure 1), (ii) the decay of the spectrally integrated DL intensity extends to 1s and (iii) I_{DF} vs I_{ex} curves deviate little from linearity at moderate I_{ex} before approaching saturation at high I_{ex} (Figure 3b). Other compelling evidence against the dominance of *TT* fusion at 297 K is provided by the earlier observation[20] that the introduction of triplet traps, 0.5 eV deep, does not affect the DL intensity. We therefore reinforce our earlier claim that under the present experimental conditions the essential contribution to DL in PVK at 297 K is due to slow, i.e. disorder-mediated recombination of eh pairs.

Before addressing the question why GPR-dominated DL overrides the *TT* contribution, we shall consider the time dependence of GPR first. The framework for analysing the GPR dynamics in random organic solids has been laid out by the Monte Carlo simulation work of Ries and Bässler[18] whose main results shall be briefly recalled. The essential feature of the carrier transport bands in a random organic solid is the splitting of these bands into a Gaussian density of states (DOS), typically 0.1 eV wide. A carrier initially created at random at a given distance r_o from a stationary countercharge executes a time-dependent random walk within the coulombic potential. Approximately 90% of all carriers recombine with the sibling carrier within, say 6 orders of normalized time, the time unit (t_o) being the jump time of a charge carrier in a crystalline counterpart hopping system. (From mobility data in crystalline *N*-isopropylcarbizole,[32] $t_o \simeq 10^{-13}$s can be estimated.) The survivors can either dissociate or recombine, the branching ratio depending on temperature. Because of the continuing energetic relaxation of the carriers within the DOS, the diffusivity and hence the rate at which a hopping carrier reaches the countercharge keeps decreasing, approximately following a t^{-1} law. In the long time domain the number of GPs changes only very little and the time dependence of the number of recombination events per unit time, $R(t) = k_r(t)n(t)$, is determined by that of $k_r(t)$, i.e., $R \simeq t^{-1}$. (More rigorously, $R(t) \propto (t_o/t_o)$ ln $t/t_o)^{-1}$ which can be approximated by $R \sim t^{-1.04}$ for $t/t_o > 10^4$.) At shorter times, $R(t)$ decays faster ($R(t) \sim t^{-1.3}$) reflecting both the depletion of the GP reservoir and the decrease of $k_r(t)$. The long time decay behavior is consistent with the prediction of Dunstan's distant pair model[33] for eh recombination in systems like amorphous silicon, despite the differences in the concept; Dunstan's model ignores, e.g., the presence of the coulombic potential. The MC simulations justify the following approximation: surviving GPs, initially created at an intrapair distance of 3 lattice constants, completely lose their site memory after, say, 6 orders in normalized time and acquire a mean intrapair distance of about 10 lattice distances where the coulombic potential is negligible compared to the intrinsic potential fluctuations of the hopping sites. On the time scale of the present experiment it is therefore the built-in intrinsic disorder that controls R. For a disorder parameter $\sigma/kT \geq 10$ the diffusivity is temperature independent and governed by tunnelling transitions among non-nearest sites whereas for decreasing σ/kT, temperature activated jumps become progressively important. In the presence of shallow traps the initial GPR decreases according to the branching ratio between GPR and trapping. Subsequent thermally-assisted detrapping manifests itself in the appearance of a shoulder in the $R(t)$ curve and in the stretching the time scale of the long time decay pattern by a Boltzmann factor.

If at high excitation densities, inter-pair distances become comparable to intrapair separations, annihilation of the heterocharges of different eh pairs, equivalent to non-geminate (bimolecular) eh pair recombination has to be considered in addition to first-order GPR, thus

$$\frac{d[\mathrm{eh}]}{dt} = -k_r[\mathrm{eh}] - f\gamma_{\mathrm{eh}}[\mathrm{eh}]^2 \qquad (4)$$

where both k_r and γ_{eh} are functions of time and f is either ½ or 1 depending on whether one or both pairs of heterocharges annihilate. Since the quadratic term in Equation (4) causes a reduction of the fraction of eh pairs still present when the phosphoroscopic detection of DF begins, the integrated DL intensity is expected to rise linearly with I_{ex} at moderate I_{ex} and—for reasons discussed in conjunction with TT fusion—approach saturation at high I_{ex}. Since charge carrier motion is more dispersive than is triplet transport because the DOS for charge carriers is about 3 times as broad as that for triplets, saturation should be approached more gradually than in the case of triplet fusion. The deviation of $L(I_{\mathrm{ex}})$ curves of Figure 3b near $I_{\mathrm{ex}} = 1$ mJ per cm^2 and pulse is in accord with the gist of this argument. At this concentration the average interpair separation is 50 Å while intrapair distances are 20–25 Å. The correlation among the constituents of an individual GP is therefore abandoned and mutual annihilation processes become more operative. It is worth noting that the turn-over from mono- to bimolecular kinetics should occur independent of temperature since both $k_r(t)$ and $\gamma_{\mathrm{eh}}(t)$ should carry the same T-dependence.

Decay of GPR luminescence only reflects the pair recombination kinetics if the recombination rate exceeds the reciprocal lifetime of the molecular state that is populated. This condition is fulfilled for singlet but not for triplet states, except at very long times.

DL decay in PVk at 297 K appears to be a perfect verification of the GPR concept. The spectrally integrated emission exhibits an initial decay slightly faster than t^{-1} ($t^{-1.2...1.3}$) that merges into a t^{-1} decay for $t > 100$ μs extending to ≈1 s at high I_{ex} (Figure 2). The decay pattern is independent of I_{ex} as it should be since non-geminate instead of bimolecular eh annihilation prior to the opening of the phosphoroscopic detection causes randomization of intra-pair distances.

Spectrally selected decay patterns indicate little spectral selectivity except that the 388 nm band decays somewhat faster for $t \gtrsim 500$ μs (Figure 1a). This band is due to weakly trapped singlet states (trap II emission) produced only if the recombination event does not occur at an excimer site. Hence the precursor GP can only be weakly trapped and is therefore preferentially subject also to early time dissociation that depletes the reservoir.

The above results seem to contradict the experiments of Klöpffer *et al.*[21] as well

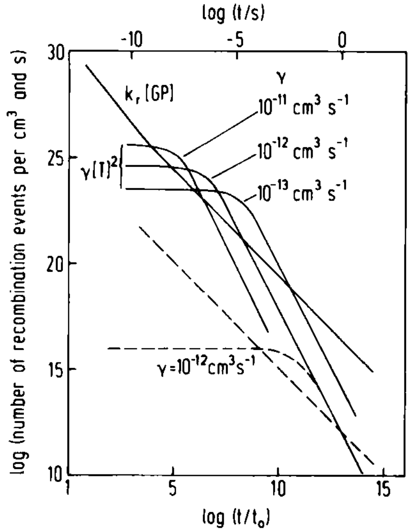

FIGURE 5 Comparison of the contribution to delayed fluorescence resulting from geminate pair recombination occurring at a rate k_r[GP] and bimolecular triplet annihilation occurring at a rate $\gamma[T]^2$, respectively. Full curves are calculated for equal initial geminate pair and triplet concentrations 2×10^{18} cm^{-3} (full curves, γ as indicated) and 2×10^{14} cm^{-3} (dashed curves), respectively. The k_r[GP] is calculated from the Monte Carlo simulation results of Reference 18, setting $k_r = 10^{12}$ s^{-1} at $t = t_0 = 10^{-13}$ s.

as those of Burkhart and Aviles[23] indicating that triplet annihilation does occur in PVK. This problem is solved by taking into account that GPR is a dispersive kinetic process. The condition for GPR to control DF is

$$k_r[\mathrm{GP}] > \eta\gamma[\mathrm{T}]^2 \qquad (5)$$

The crucial point is that the GP recombination rate, i.e. k_r[GP], decreases with time. On the other hand, triplet relaxation studies in organic glasses[28,35] indicate that near room temperature, relaxation has been completed on the time scale of the present experiment, i.e. γ can safely be assumed time-independent. Fulfillment of inequality (5) therefore depends on both the excitation density and the time frame in which DL is monitored. In Figure 5 the calculated GPR and the T^2 contribution to delayed fluorescence have been plotted assuming that the initial concentration of GPs and triplet excitations are approximately equal, amounting to 2×10^{18} cm^{-3} (attained at $I_{ex} \cong 1$ mJ per cm^2 and pulse) and 2×10^{14} cm^{-3} (moderate intensity case), respectively. In the former case $\gamma[T]^2$-curves are drawn for $\gamma = 10^{-11}$, 10^{-12} and 10^{-13} cm^3 s^{-1}, respectively. The k_r[GP]-curve is taken from Monte Carlo simulation [30] after setting the maximum recombination coefficient at $t = t_0 = 10^{-13}$ s equal to 10^{12} s^{-1}. The message of Figure 5 is that at short times GPR always controls delayed singlet production. There is, however, a regime where $\gamma[T]^2 > k_r$[GP]. It increases in magnitude with decreasing γ and shift towards longer times when either γ or [T] decrease. In the long time limit the linear GPR contribution dominates again. At the high photon doses employed in the current study the *TT* dominated DF regime is terminated before the phosphoroscopic detection begins to respond (10 μs). (This analysis would suggest that the slightly superlinear decay of $I_{DF}(t)$ at short times reflects some contribution from *TT* processes rather than the depletion of the GP reservoir.) Reducing I_{ex} to values used by Klöpffer *et al.*[21] shifts the TT regime into the time domain of their phosphoroscopic detection.

The situation changes upon lowering the temperature to 80 K. Experimentally, $L(I_{ex})$ relations for DL emission at 388 nm and 418 nm, (but not 500 nm) acquire a superlinear section at low I_{ex}, and pass through a shallow maximum before approaching saturation (Figure 3a) and $I_{DL}(t)$ curves exhibit a shoulder when plotted on a log-log scale (Figures 1 and 2). Both effects are a signature of the involvement of a superimposed non-linear process contributing to DL in the spectral range of fluorescence emission which can only be triplet fusion. The scenario is rather complex: At 80 K, triplet motion within the distribution of hopping states (DOS) is likely to still carry some dispersion on a time scale of, say 1 ms[3]. Recombination of triplets migrating within the tail states of the DOS would therefore be dispersive following a t^{-s} law with $1 < s < 2$. Additional triplet localization in moderately deep structural traps, not efficient at 297 K, is also likely to occur implying the involvement of fusion between free and trapped triplets.[21,23] The recent work of Efremov *et al.*[35] suggests that direct long range annihilation of localized triplet excitations leading to an $I_{DF} \propto t^{-0.8}$ decay has also to be considered. Although the $I_{DF}(t)$ decay recorded at 80 K and 388 nm ($I_{DF}(t \sim t^{-0.9}$, Figure 1a) follows the latter prediction law quite closely, we are reluctant to pursue this analysis further until additional experimental data concerning dispersive triplet annihilation in organic glasses becomes available.

We wish to point out that, even at 80 K, GPR dominated DF becomes progressively important at high photon doses where, by virtue of the above argument, *TT* processes are shifted towards shorter times. Since at low *T*, depletion of the GP reservoir by dissociation is absent, GPR-controlled DL must increase upon sample cooling in accord with the experimental observation.

At low temperatures and long times after excitation DL emitted at ~500 nm is attributed to phosphorescence from triplet-excimer forming traps,[25] while at short times the tail emission from singlet excimers prevails. The short time decay of I_{DL} monitored at 500 nm and 80 K must therefore reflect delayed production of trapped S_1 excitations via delayed GPR and triplet fusion. The shoulder that appears near 100 ms is due to radiative decay of triplets that escaped annihilation and triplets formed in course of GPR. In the long time limit phosphorescence approaches a t^{-1} law extending to 10 s without any indication of monomolecular decay. We consider this as evidence that the long time decay monitors the rate at which GPs collapse to produce a triplet state. (Recall that spin statistics predict a 3:1 ratio for triplet to singlet production via eh recombination.)

Previously[21] the 80 K phosphorescence decay of PVK has been analysed in terms of a superposition of two exponentials with 2.1 and 9.6 s decay time. Bearing in mind that a hyperbolic decay extending over one decade can with reasonable accuracy be deconvoluted into two exponentials, we consider it more likely that the triplet lifetime is shorter (the bending of the $I_{DL}^{500}(t)$-curve would suggest a lifetime of about 0.5 s) and the long time behavior reflects GPR controlled production of trapped triplets. The phosphorescence contribution to I_{DL}^{500} is only detectable at low temperatures because at room temperatures triplets are quenched by impurities such as residual O_2.

At this point a clarifying remark concerning our earlier work[19] appears in order. We found that upon sample cooling the temporal decay of the spectrally integrated intensity becomes weaker, approaching $t^{-0.6}$ at 20 K. The spectrally selected studies described herein indicate that this is a superposition effect: At long times excimer phosphorescence, which varies only weakly at intermediate times, contributes to the DL thereby accidentally reducing the slope of lg I_{DL} vs lg t plots.

5. CONCLUDING REMARKS

This study confirms that in PVK delayed fluorescence can arise from both geminate pair recombination and triplet-triplet annihilation. Which process dominates depends on the incident photon dose and the time domain for monitoring luminescence. The experiments also show that the rate of geminate pair recombination follows a $t^{-1.0 \ldots 1.1}$ law over 5 decades in time (100 μs to 10 s). On the basis of literature results, the range of validity of this hyperbolic decay law can even be extended to 10^4 s: By surveying a large number of commercial polymers, Mendenhall and Agarwal[16] detected afterglow attributed to recombination of photogenerated charges.It followed a t^{-s} law with s ranging from 0.67 to 1.17 within a time domain (10...20 s) to 600 s. Moan and Steen[15] studied the recombination luminescence of photo-detached electrons with the sibling cations in a 77 K ethylene glycol/H_2O glass doped with tryptophan and found a $t^{-1.09}$ decay on a time scale 10^2 to 10^4 s following prompt triplet decay. Combining this information we come up with the conclusion that the energetic disorder model, predicting an $I(t) \propto t^{-1}$ law or, more accurately, an $I(t) \propto t \ln t \simeq t^{-1.04}$ law, is the appropriate model to treat geminate pair recombination in disordered organic solids. This appears to be another success of the Movaghar-Ries-Grünewald-localization theory[36] which has laid out an analytical framework for rationalizing the empirical Monte Carlo simulation results[30] and is superior to the extension of the original Hong-Noolandi[5] concept to amorphous inorganic solids.[37]

Acknowledgments

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References

1. For a review see M. Pope and C. E. Swenberg, Electronic Processes in Organic Crystals (Clarendon Press, Oxford, 1982).

2. R. G. Kepler, J. C. Caris, P. Avakian and E. Abramson, *Phys. Rev. Letts.*, **10**, 400 (1963).
3. S. Singh, W. L. Jones, W. Siebrand, B. P. Stoicheff and W. G. Schneider, *J. Chem. Phys.*, **42**, 330 (1965).
4. T. W. Scott and C. L. Braun, *Chem. Phys. Letts.*, **127**, 501 (1986).
5. K. M. Hong and J. Noolandi, *J. Chem. Phys.*, **68**, 5163 (1978); *J. Chem. Phys.*, **69**, 5026 (1978).
6. M. Pope, H. Kallmann and J. Giachino, *J. Chem. Phys.*, **42**, 2540 (1965).
7. M. Pope, J. Burgos and J. Giachino, *J. Chem. Phys.*, **43**, 3367 (1965).
8. S. Arnold, M. Pope and T. K. T. Hsieh, *Phys. Stat. Sol. (b)*, **94**, 263 (1979).
9. S. C. Abbi and D. M. Hanson, *J. Chem. Phys.*, **60**, 319 (1974).
10. L. Sebastian, G. Weiser and H. Bässler, *Chem. Phys.*, **61**, 125 (1981).
11. L. Sebastian, G. Peter, G. Weiser and H. Bässler, *Chem. Phys.*, **75**, 103 (1983).
12. For a review of the work before 1972 see R. Lesclaux and J. Joussov-Dubien, Organic Molecular Photophysics (J. B. Birks, ed., J. Wiley, London, 1973).
13. G. E. Johnson and A. C. Albrecht, *J. Chem. Phys.*, **44**, 3162, 3179 (1966).
14. H. S. Pilloff and A. C. Albrecht, *J. Chem. Phys.*, **49**, 4891 (1968).
15. J. Moan and H. B. Steen, *J. Phys. Chem.*, **75**, 2887 (1971).
16. G. D. Mendenhall and H. K. Agarwal, *J. Appl. Polym. Sci.*, **33**, 1259 (1987).
17. J. Mort, M. Morgan, S. Grammatica, J. Noolandi and K. M. Hong, *Phys. Rev. Letts.*, **48**, 1411 (1982).
18. B. Ries and H. Bässler, *J. Molec. Electron*, **3**, 15 (1987).
19. F. Stolzenburg, B. Ries and H. Bässler, *Ber. Bunsenges. Phys. Chem.*, **91**, 853 (1987).
20. F. Stolzenburg, B. Ries and H. Bässler, *J. Molec. Electron*, **3**, 149 (1987).
21. G. Rippen, G. Kaufmann and W. Klöpffer, *Chem. Phys.*, **52**, 165 (1980).
22. W. Klöpffer, *Chem. Phys.*, **57**, 75 (1981).
23. R. D. Burkhart and R. G. Aviles, *Macromolecules*, **12**, 1073, 1078 (1979).
24. G. E. Johnson, *J. Chem. Phys.*, **62**, 4697 (1975).
25. R. D. Burkhart and J. Dawood, *Macromolecules*, **19**, 447 (1986).
26. G. Pfister and D. J. Williams, *J. Chem. Phys.*, **61**, 2416 (1974).
27. R. Richert and H. Bässler, *J. Chem. Phys.*, **84**, 3567 (1986).
28. J. Lange, B. Ries and H. Bässler, *Chem. Phys.*, **128**, 47 (1988).
29. W. Schrof, E. Betz, H. Port and H. C. Wolf, *Chem. Phys. Letts.*, **123**, 300 (1988).
30. T. Nakayama, M. Higuchi, S. Fujiwara and N. Itoh, *J. Lum.*, **12/13**, 153 (1976).
31. B. Movaghar, M. Grünewald, B. Ries, H. Bässler and D. Würtz, *Phys. Rev. B*, **33**, 5545 (1986).
32. J. H. Sharp, *Photogr. Sci. Engng.*, **11**, 69 (1967).
33. J. Dunstan, *Phil. Mag. B*, **46**, 572 (1982); *Phil. Mag. B*, **49**, 191 (1984).
34. R. Richert, H. Bässler, B. Ries, B. Movaghar and M. Grünewald, *Phil. Mag. Lett.*, **59**, 95 (1989).
35. N. A. Efremov, S. G. Kulikov, R. I. Pasorov and Yn. V. Romanowski, *Chem. Phys.*, **128**, 9 (1988).
36. B. Movaghar, B. Ries and M. Grünewald, *Phys. Rev. B*, **34**, 5574 (1986).
37. J. Noolandi, K. M. Hong and R. A. Street, *Solid. State Comm.*, **34**, 45 (1986).