Triplet Photophysical Properties of Poly(*N*-vinylcarbazole) in Fluid Solutions and in Solid Films in the Submicrosecond Time Regime

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ABSTRACT: Triplet photophysical properties of poly(*N*-vinylcarbazole) (PVCA) have been examined in fluid solutions and in solid films using time resolution of a few hundred nanoseconds to several microseconds. In fluid solutions the intensity of delayed excimer fluorescence (def) increases with time following excitation and goes through a maximum at a delay time near 300 ns. A kinetic model describing the formation and decay of the various triplet species is proposed, which reproduces the experimental observations using the rate constant for trapping of mobile triplet excitons as a fitting parameter. The best fit yields a minimum value for the trapping rate constant of 2.0×10^9 M^{-1} s^{-1}, assuming every chromophore is a potential trap site. When transient triplet–triplet absorption methods are used, the second-order rate constant for the triplet–triplet annihilation (TTA) in fluid solution is found to be 2.5×10^8 M^{-1} s^{-1}. Solid films at 10 K also show a maximum in the intensity of def recorded as a function of time. For solid films a best fit to the experimental results is achieved with a trapping rate constant of 8×10^5 M^{-1} s^{-1}. This rate constant is similar to that recently determined for triplet quenching in copolymers containing the carbazolyl group and is probably controlled by the rate of energy migration.

Introduction

The triplet-state properties of poly(*N*-vinylcarbazole) (PVCA) have been a favorite subject of investigation for many years.[1-3] The polymer not only is photoconducting[1] but also exhibits a rich array of triplet photophysical activity including phosphorescence, delayed fluorescence (df), and delayed excimer fluorescence (def). Rates of triplet exciton migration of PVCA in solid films and in rigid frozen matrices have also been reported.[4-6]

In most of the earlier investigations, time resolution on the order of a millisecond or so was commonly used and was certainly sufficient to include most of the relevant photophysical events occurring in frozen glasses or solid films at 77 K. There are, however, certain triplet photophysical processes that demand that a faster time scale be used for their observation. An example is the process of the trapping of triplet excitons at excimer-forming sites along the polymer chain. To the best of our knowledge, no experimental results have been acquired that could be used to extract information of this type for triplets although excited singlet state properties have been extensively investigated in the picosecond to nanosecond time range.[7] Furthermore, very little time-resolved work has been done on triplet-state properties of polymers in fluid solutions at ambient temperature.

For these reasons it seemed worthwhile to examine the kinetic aspects of triplet-state processes in PVCA in the time regime from a few nanoseconds to several microseconds in fluid solutions at ambient temperature. Initial experiments indicated that the delayed fluorescence spectra obtained under these conditions were excimeric in character. This observation was of interest since the delayed fluorescence emission from frozen solutions of PVCA has mixed excimeric and monomeric character. Since excimeric delayed fluorescence is usually thought to occur by a heteroannihilation process between a mobile exciton and an exciton trapped at an excimer-forming site (efs),[2] it was of interest to investigate the mechanism of the triplet trapping reaction in these fluid solutions. Thus, the major thrust of this work was to attempt an evaluation of the rate of triplet exciton trapping in fluid solutions of PVCA.

It is also the case that excimeric delayed fluorescence is observed from solid films of PVCA.[8] Thus, to complement the fluid state work, an attempt was also made to evaluate the rate of triplet exciton trapping in solid films.

In order to carry out the kinetic analyses required to evaluate these trapping rate constants, it was necessary to obtain values for the specific rate constants for triplet–triplet annihilation (TTA) in each of the media. Fortunately, recent experiments by Ito and co-workers[3] on solid films of carbazole-containing copolymers provided a reasonable estimate for the TTA rate constant in the solid film state. For fluid solutions of PVCA it proved necessary to carry out a subsidiary determination of the specific rate constant for TTA. These latter experiments had to be performed using transient triplet–triplet absorption.

Apart from the necessity of having the TTA rate constants available in order to evaluate the trapping rate constants, it was beneficial to have them available for comparative purposes. Before this work was undertaken, it was anticipated that the trapping rate constants would turn out to be essentially the same as those for TTA. This expectation was based upon the belief that a combination of exciton migration and translational diffusion would control the rate of both processes. It was recently found, however, that the rate constant for triplet trapping at an excimer-forming site in fluid solutions of poly(2-vinylnaphthalene) (P2VN) was significantly larger than that for the corresponding TTA in this polymer.[9] It was therefore of interest to determine if a similar situation would hold for PVCA as an indication of the possible generality of this effect. In the following pages the results of these efforts are described.

Experimental Section

PVCA was prepared in the laboratory by free-radical polymerization.[10] Also, the method of purification of all chemicals used in this work has been described elsewhere.[10] Solutions of PVCA were prepared in purified benzene and transferred to the freeze-down bulb of the cell apparatus. The solutions were then thoroughly degassed by several freeze–pump–thaw cycles and sealed off under vacuum. The cell apparatus consists of a 10-mm path length rectangular quartz cell, which has

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been joined to a 50-mL freeze-down bulb through a T. After degassing, the solution is simply tipped into the rectangular cell.

Films of PVCA were prepared by dissolving about 3–4 mg of the polymer in about 0.5 mL of benzene and then depositing the solution dropwise on a quartz plate. The solvent was allowed to evaporate in a solvent-saturated atmosphere for about 3 h. It was then placed in a vacuum oven at 100 °C for 24–48 h to remove the last traces of solvent.

The source of excitation was a Tachisto Model 401XR XeCl excimer laser, which could also be operated as a nitrogen laser. The emission signal from the sample was passed through a Spex Model 1680B monochromator using a 0.36–1.8-nm band-pass. It was then detected by a 4-ns rise time photomultiplier, which was either connected directly to a Nicolet 12/70 Signal Averager or through a fast amplifier (Stanford Research Systems, Inc., Model SR 440, dc 300-MHz amplifier) to the Nicolet. A terminating resistor of 50 Ω was used in the cable connection to the Nicolet in order to avoid distortion of the arrival time of the signal.

The optical absorption of transient triplets was observed following a laser excitation pulse. A probe beam directed toward the monochromator slit was made to traverse the cuvette at right angles to the direction of the excitation beam. The decay of the optical absorption was monitored at a number of different probe wavelengths from 360 to 500 nm. The dc probe source was a battery-operated tungsten lamp, the exceptional stability of which is found to be extremely valuable in these experiments. After each excitation pulse the probe intensity is measured as a function of time using some preset delay time to initiate the measurement. The data files consisting of absorbance versus time are converted to files of concentration versus time using the known value of the molar absorptivity of the triplet at the probe wavelength. Typically, absorbances of a few tenths of a unit are found for pulse intensities on the order of 10^{-3} einstein/L·pulse. This translates into triplet concentrations on the order of 10^{-5} M.

In the experiments involving solid films, cooling and temperature control were maintained by a Joule–Thomson closed-cycle liquid-helium cooling system (R. G. Hansen and Associates) combined with a tip heater. Typical uncertainties in the temperature measurements were ±1 K.

Experimental Results

A. Solutions. It was mentioned above that the delayed fluorescence spectra from fluid solutions of PVCA appeared excimeric in character. The results displayed in Figure 1 of the time-resolved df spectra indicate that this is only partially true. The spectra seen here are definitely broad and red-shifted, but, at the shortest delay times after excitation, a small amount of structured emission will be noted near 355 nm. The emission in the central region from 370 to 490 nm is broad and structureless as is typical of excimeric delayed fluorescence. At the longest delay time there may be two components in the structureless region. One is centered near 390 nm and the other near 425 nm. This may be compared with the prompt fluorescence emission where one component is found near 370–375 nm (this is often called the "second excimer").[7,11–13] The only difference between the ordinary prompt fluorescence spectra and the df spectra is a small alteration in the positions of the components. In the case of df, the position of each component is red-shifted compared to that of prompt fluorescence. The delayed fluorescence that is excimeric in character is called the delayed excimer fluorescence (def).

Note that in Figure 1 the def exhibits a maximum at a delay time of 250 ns. This effect is more clearly demonstrated in Figure 2 where the def intensity at 420 nm is graphed as a function of time. These data clearly show that a maximum intensity occurs near 300 ns. It should be mentioned that the minimum time resolution in these experiments is ±50 ns. The solid line in Figure 2 represents the experimental results whereas the dashed line is a calculated curve obtained using methods that will be described below. The three spectra of Figure 1 indicate that, if a wavelength very close to the band origin were selected, there would be a monotonic decrease in the corresponding df intensity over the time range being monitored rather than a buildup and decay as is observed at wavelengths corresponding to def emission.

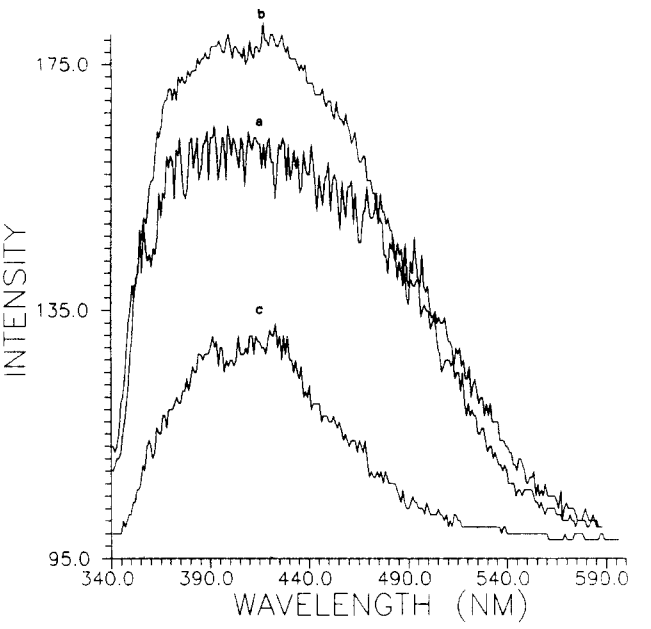

Figure 1. Delayed luminescence spectra of PVCA of 1.192×10^{-3} M in monomer in benzene at ambient temperature. Delay times after excitation are (a) 180, (b) 250, and (c) 550 ns.

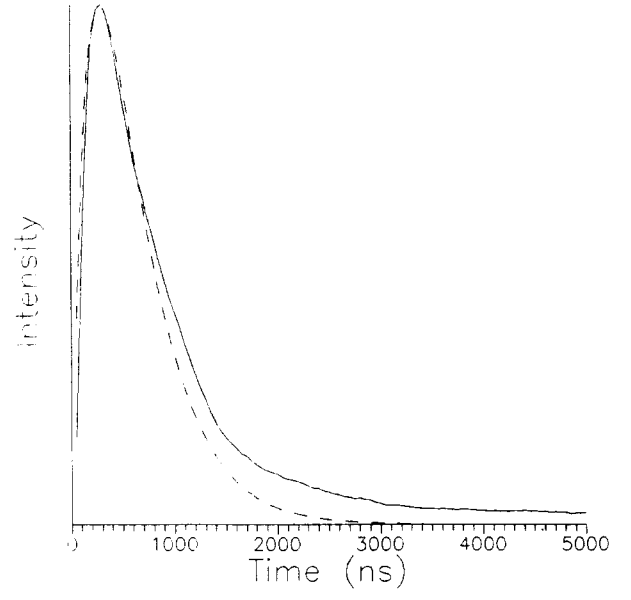

Figure 2. Decay of delayed fluorescence intensity of PVCA in fluid solution at 420 nm: exptl, solid curve; calcd, dashed curve.

Triplet–triplet absorption spectra in fluid solutions of PVCA were gathered in a time-resolved fashion, and Figure 3 summarizes the results. The decays of the triplet–triplet absorption signals were also analyzed to extract the rate constant for TTA as will be discussed below.

B. Films. Figure 4 shows the time-resolved characteristics of PVCA-delayed luminescence spectra from solid films at 10 K. In these spectra the source of excitation was the XeCl laser. Here also the structured emission is strongly overlapped with the broad emission. The broad emission from 370 to 490 nm is again characteristic of

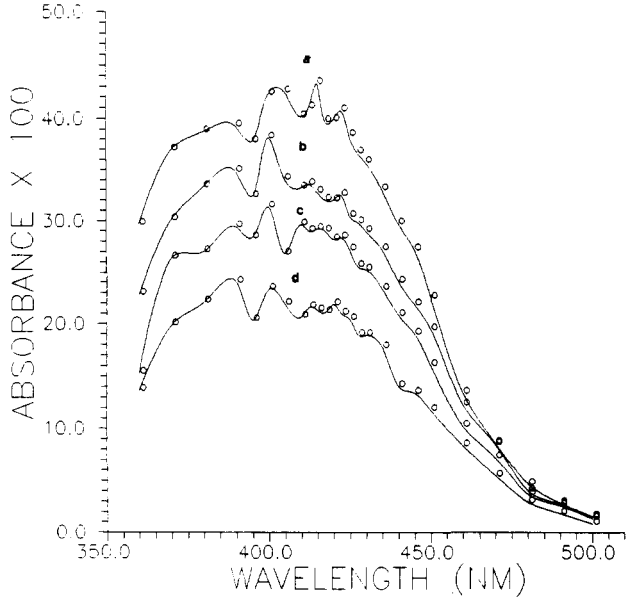

Figure 3. Time-resolved triplet–triplet absorption spectra of PVCA in benzene solution. Delay times after excitation are (a) 7, (b) 15, (c) 25, and (d) 50 μs.

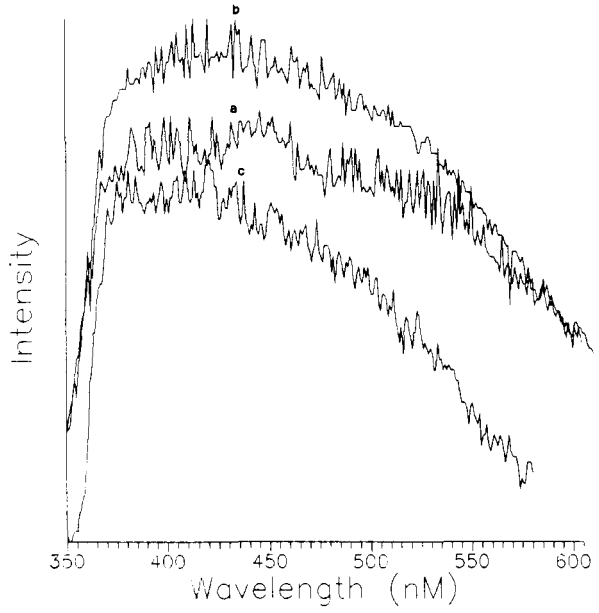

Figure 4. Delayed luminescence spectra from a solid film of PVCA at 10 K. Delay times after excitation are (a) 150, (b) 200, and (c) 500 ns.

excimeric fluorescence and may be identified as def. It is evident from these spectra that the def intensity also exhibits a maximum near 200 ns. This is more clearly demonstrated in Figure 5 where the def, monitored at 420 nm, is graphed as a function of time. A maximum at 200 ns is clearly observed.

Discussion

A. Solutions. The shortest delay time used in recording these spectra was 180 ns, and so a matter of some concern is whether any contribution from the prompt fluorescence may be contaminating the emission signals that have been ascribed to delayed fluorescence. A survey of the literature shows that the reported values of the lifetime for the prompt monomeric fluorescence varies between 3 and 6 ns whereas that for excimeric fluorescence varies between 13 and 36 ns for PVCA in fluid solutions.[11,12] Hence, there is no possibility of contamination of df or def by prompt fluorescence with the delay times used here.

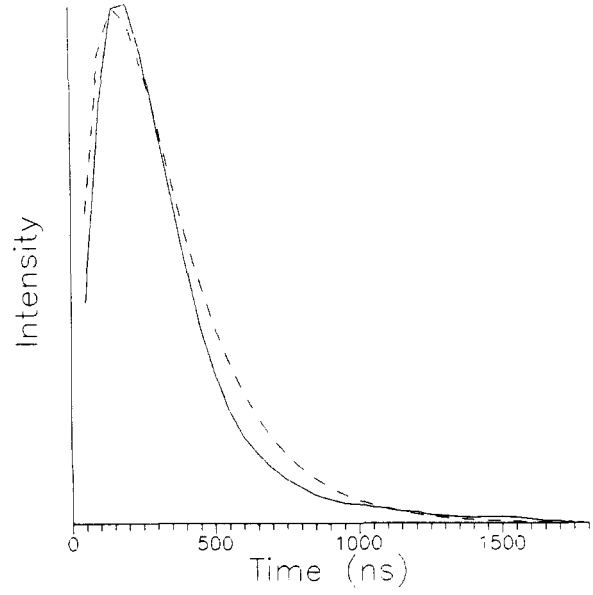

Figure 5. Time dependence of delayed fluorescence intensity from a PVCA solid film at 10 K monitored at 425 nm: exptl, solid curve; calcd, dashed curve.

The build-up period in the intensity of def implies that the species responsible for this emission is also increasing with time. There are actually two possible modes of def production that might be considered. One of these would be TTA involving two mobile triplet excitons (see step 3 below) followed by trapping of the excited singlet state produced at an efs in the molecule. If this were the correct mechanism, then the build-up period observed would be due to a corresponding rise in the concentration of mobile triplet excitons. The specific rate constant for intersystem crossing of the carbazole chromophore in *N*-methylcarbazole is 3.8×10^7 s^{-1}.[14] Assuming a similar value is appropriate for PVCA, then mobile triplet formation would be 90% complete in about 60 ns. The current time limitations of the equipment would make it impossible to observe a rise time of this magnitude. Thus, it is apparent that the rise time that is observed for the def emission is due to a slower process.

The other mode of def formation is via triplet–triplet heteroannnihilation as indicated in step 5. The rate of this process will be controlled to some extent by the concentration of trapped triplet excitons (T_{tr}) produced in step 4. If this mechanism were the correct one, then the rise time would be associated with the formation of these trapped species. Our subsequent analysis of the rate data assumes that this is, in fact, the case and the remaining discussion is based on this assumption. The relative rates of homoannihilation, step 3, and heteroannihilation, step 5, may be judged by the relative contributions of df and def in the time-resolved luminescence spectra. The df signal is only a minor contributor even at the shortest delay times and gives way to a totally excimer delayed fluorescence at longer times on the order of 500 ns. Thus, one may conclude that the concentration of T_{tr} species must be rather large compared to T_1 at these longer times.

The following kinetic scheme is intended to summarize the relevant processes:

$$^1S^* \xrightarrow{k_1} {}^1S_0 + h\nu \text{ (or heat)} \quad (1)$$

$$^1S^* \xrightarrow{k_{isc}} T_1 \quad (2)$$

$$T_1 + T_1 \xrightarrow{k_2} {}^1S^* + {}^1S_0 \quad (3)$$

$$T_1 + {}^1E_0 \xrightarrow{k_{tr}} T_{tr} \quad (4)$$

$$T_1 + T_{tr} \xrightarrow{k_2} {}^1E^* + {}^1S_0 \quad (5)$$

$$^1E^* \rightarrow {}^1E_0 + h\nu \text{ (or heat)} \quad (6)$$

In these equations $^1S^*$ is the excited singlet state, $^1E^*$ is the singlet excimer, T_1 is the mobile triplet, T_{tr} is the trapped triplet, and $^1S_0$ is the ground state of an isolated chromophore. We provisionally define $^1E_0$ as an efs and note that this assignment does seem appropriate for solid films. For fluid solutions, on the other hand, there is less certainty about the exact identity of the trapping partner as discussed below. Equations 1 and 2 describe the first-order processes taking place from the excited singlet state whereas eq 3 and 5 describe the second-order processes of triplet–triplet annihilation. Equation 4 describes the trapping of triplet excitons by the efs, and eq 6 describes the decay of singlet excimers.

In order to fit this model to the experimental results, one needs to determine the concentration of mobile triplets, T_1, and trapped triplets, T_{tr}, as a function of time. The intensity of monomeric df is proportional to the square of the concentration of T_1 whereas the intensity of def is proportional to the product of the concentrations of T_1 and T_{tr}, the necessary differential equation for the formation and decay of T_1 is

$$d[T_1]/dt = k_{isc}[^1S^*] - k_{tr}[^1E_0][T_1] - 2k_2[T_1]^2 - k_2[T_1][T_{tr}] \quad (7)$$

where $[^1S^*] = [^1S(0)] \exp[-k_M t]$, $k_M = k_1 + k_{isc}$, and $[^1S(0)]$ is the concentration of excited singlet states at $t = 0$. The differential equation describing the time dependence of T_{tr} is

$$d[T_{tr}]/dt = k_{tr}[^1E_0][T_1] - k_2[T_1][T_{tr}] \quad (8)$$

Equations 7 and 8 can be solved numerically by using the fourth-order Runge–Kutta method[15] with initial conditions $[T_1](0) = [T_{tr}](0) = 0$. Since these equations are coupled they have to be solved simultaneously. This can be readily done in the Runge–Kutta method by defining two functions, $F_1(t,T_1,T_{tr}) = d[T_1]/dt$ and $F_2(t,T_1,T_{tr}) = d[T_{tr}]/dt$.[16]

In order to calculate the concentration of T_1 and T_{tr} from eq 7 and 8 values of the different constants involved in these equations need to be known. The value of k_2 has been determined by the transient triplet–triplet absorption method as mentioned above and described in more detail below. The value for k_1 of 1.66×10^8 s^{-1} was obtained from the lifetime of the monomeric prompt fluorescence.[7,11-13] The rate constant for intersystem crossing for PVCA has not been determined, but a value of 3.8×10^7 s^{-1} has been found for *N*-methylcarbazole.[14] To achieve a best fit to the experimental data, $k_{tr}[^1E_0]$ and $k_{isc}[^1S(0)]$ are taken as variable parameters. It was found, however, that the quality of the fit is very insensitive to the assumed value of $k_{isc}[^1S(0)]$ but very sensitive to $k_{tr}[^1E_0]$. For the results quoted below, a fixed value of $k_{isc}[^1S(0)]$ equal to 10^3 M s^{-1} was used. The solution of eq 7 gives the concentration of T_1 as a function of time whereas the solution of eq 8 gives the concentration of T_{tr} as a function of time. These concentrations are then used to calculate the intensity of def as a function of time. The calculated intensity is multiplied by a constant selected in order to match the experimental intensity at some predetermined delay time. Then the rest of the calculated curve is multiplied by this same constant in order to provide a good comparison with the experimental data. Typical results of such calculations are presented in Figure 2 by the dashed curve. A step size of 50 ns has been used here and found to give sufficient accuracy for present purposes. A few tests were made using a 10-fold smaller step size, but the numerical results were not significantly altered. The calculations show that a value of $k_{tr}[^1E_0] = 2.4 \times 10^6$ s^{-1} reproduces the experimental curve very well.

The actual value of the trap site concentration is unknown, but it cannot be larger than the total concentration of chromophores (2.38×10^{-3} M). Using this value of $[^1E_0]$, a lower limit for the trapping rate constant is found to be 2.0×10^9 M^{-1} s^{-1}. It may be mentioned here that this value is nearly the same as the one found recently for poly(2-vinylnaphthalene) in solution[9] and is 1 order of magnitude smaller than the trapping rate constant recently obtained for singlet excitons in PVCA.[7]

B. Determination of k_2 in Fluid Solution. It will be noted that the same rate constant has been used for both steps 3 and 5 in the mechanism above. Both of these processes are assumed to depend upon the migration rate of T_1 either by translational motion or by energy transfer. Since T_{tr} is assumed to be an immobile trap site, one might expect the rate of step 5 to be smaller than that of step 3 by a factor of 2. This is not the case, however, since the a priori probability of encounters between identical species is one-half that between different species.

A method using transient absorption has been employed in the evaluation of k_2. The triplet-state concentrations determined in this part of the work were all obtained using delay times of 1 μs or greater. Since there is no spectroscopic evidence for the occurrence of the homoannihilation process at such long delays, it was assumed that the kinetics may be interpreted in terms of a competition between the first-order decay and the second-order heteroannihilative process. One difficult aspect of the transient absorption approach is that distinct triplet absorption spectra for the mobile triplet and the trapped triplet are not found as may be seen from Figure 3. The sum of the time-dependent concentrations of the triplets may be determined from $[T_1] + [T_{tr}] = A(1/e_1 + 1/e_{tr})$ where A is the optical absorbance and the e's are molar absorptivities of the two types of triplets. We have used a value of 10^4 M^{-1} cm^{-1} for both e_1 and e_{tr}[17] and have, therefore, abandoned any distinction between the two triplet species so that the resulting values of k_2 are uncertain to this extent. With this assumption a simplified approach for the decay of the triplet states may be taken

$$T \xrightarrow{k_T} {}^1S_0 + h\nu \text{ (or heat)} \quad (9)$$

$$T + T \xrightarrow{k_2} {}^1S^* + {}^1S_0 \quad (10)$$

where k_T is the first-order triplet decay rate constant, k_2 is the second-order triplet–triplet annihilation rate constant, and T represents either T_1 or T_{tr}. The differential equation used to describe the time dependence of the triplet concentration is

$$-d[T]/dt = k_T[T] + 2k_2[T]^2 \quad (11)$$

The solution to this equation is

$$\exp(k_T t) = A + B(1/[T]) \quad (12)$$

where $A = 1 - B = 2k_2[T_0]/(2k_2[T_0] + k_T)$ and $[T_0]$ is the triplet concentration at an arbitrary zero time. Using long times after the excitation where second-order processes no longer contribute to the decay, the slope of a plot of the log of absorbance against time yielded $k_T = 3.05 \times 10^3\ s^{-1}$.

A plot of $\exp(k_T t)$ vs $(1/[T])$ gives a straight line, and k_2 can be determined either from the slope or from the intercept of the straight line. A least-squares fit to the data yields a value for k_2 of $2.5 \times 10^8\ M^{-1}\ s^{-1}$. As expected for these fluid solutions, this rate constant is several orders of magnitude larger than that obtained for rigid solutions at 77 K.[6]

As mentioned in the Introduction, one might expect the processes of triplet–triplet annihilation and of triplet trapping to be the same order of magnitude if they are both viewed as being diffusion controlled. In rigid solutions at 77 K or in solid films of polymers it has been shown that energy migration among pendant carbazolyl chromophores occurs at frequencies on the order of 10^3–$10^4\ s^{-1}$.[3] Assuming that these migrations may be approximated by three-dimensional random flights, the mean-square displacement in time t, $\langle d^2 \rangle$, may be expressed as $6Dt$, where D is the diffusion coefficient, or by nl^2, where n is the number of migratory events in time t and l is the average length per migration step. Assuming an average migration step of 0.3 nm and a migration frequency of $10^4\ s^{-1}$, then the mean-square displacement per second is expected to be $9 \times 10^{-16}\ m^2$ and D is therefore predicted to be $1.3 \times 10^{-16}\ m^2/s$.

In fluid solutions the net diffusion coefficient of a triplet exciton may be determined from the relation $k_2 = 4\pi rDN/1000$ where r is the encounter radius (assumed to be 1.5 nm) and N is Avogadro's number. The calculated value from the experimentally determined rate constant for TTA is $2.2 \times 10^{-11}\ m^2/s$. Of course, this diffusion coefficient consists of events occurring by energy migration plus those occurring by translational diffusion, but the fractional contribution of each is currently unknown. If the rate of energy migration is not greatly influenced by temperature between 77 K and ambient temperature, then one may conclude that translational processes are most important in controlling the rate of triplet–triplet annihilation in these fluid solutions and energy migration probably makes a negligible contribution. In fact, the calculations suggest that there may be as much as 5 orders of magnitude difference between translational diffusion and energy migration. On the other hand, the temperature dependence of the of triplet exciton migration rate has, to the best our knowledge, never been evaluated in this temperature range. There is evidence, however, that this rate is temperature dependent from 10 to 40 K[8] and it is probable that this dependence persists to higher temperatures. It seems clear that independent experiments will be required to provide a quantitative resolution of this question.

The experimental results show that the trapping rate constant is about 1 order of magnitude larger than that of TTA. This indicates that some other more rapid process than diffusion is controlling the trapping rate. There are not many possibilities for such a process that come to mind since the implication is that trap formation occurs during a time interval that is short compared with the residence time of the localized exciton. One process that could account for these rate characteristics is internal rotation around backbone carbon bonds. That is, during the lifetime of a triplet exciton at a given chromophore, a neighboring chromophore may rotate into a position suitable for excimer formation. If this is the case, then the rate process depicted by step 4 in the mechanism above is somewhat misleading since the existence of an efs would not be necessary for trapping to occur. Additionally, the partner involved in trap formation need not necessarily be a neighbor since cooperative backbone rotations could occur producing contacts between nonneighbors. Thus, although the trapping reaction is necessarily a bimolecular process, the partner with which the mobile triplet interacts is not well-defined. Until the identity of the reacting partners can be identified with more precision, we will continue to use step 4 as written but redefine $^1E_0$ as a trapping partner rather than as an efs.

C. Solid Films. In solid films of PVCA at 10 K the delayed luminescence spectra also show a build-up period in the submicrosecond time range. However, the maximum occurs at a shorter time in the solid film state than in fluid solution. Delayed fluorescence spectra from solid films of PVCA are very broad and structureless, indicating the presence of strong interactions between chromophores. It may be noted that in solid films both intra- and intermolecular excimer formation is possible.

The study of Ito and co-workers[3] on the triplet energy migration in poly[(carbazolylethyl methacrylate)-*co*-(methyl methacrylate)] film suggests a rise of sensitized phosphorescence from a triplet energy acceptor, 1,4-dibromonaphthalene. According to their work, the specific rate constant for trapping of a mobile triplet exciton at a quencher depends upon the concentration of carbazolyl chromophores contained in the copolymer. At the largest chromophore concentration used in their study a rate constant of $2.5 \times 10^6\ M^{-1}\ s^{-1}$ was found.

If we now apply to the build-up and decay portions of the def signal in solid films of PVCA the same analytical approach employed for solutions, all of the same parameters may be used with the exception of k_2, which we take to be the same as the trapping rate constant reported by Ito and co-workers[3] for their copolymer having the largest carbazole content. The best fit to the experimental data in this case yields a value of $4.5 \times 10^6\ s^{-1}$ for $k_{tr}[^1E_0]$. When the value of Itaya and co-workers is used for the concentration of chromophores in a solid film of PVCA (5.8 M)[4] and when the upper limit for the concentration of the excimer forming sites is again taken to be equal to the chromophore concentration, then a lower limit for the trapping rate constant of the triplet excitons by the excimer-forming sites in solid films at 10 K becomes $k_{tr}^F = 8 \times 10^5\ M^{-1}\ s^{-1}$. This value is, in fact, nearly the same as the quenching rate constant obtained by Ito and co-workers at 77 K for the copolymers that they studied.[3] On the other hand, Klöpffer and Fischer[18] have estimated the triplet trap concentration in solid films of PVCA at 77 K to be less than 5×10^{-3} mol/mol. When this estimate and the chromophore concentration quoted above are used, the trapping rate constant would be $1.6 \times 10^8\ M^{-1}\ s^{-1}$. This trap concentration may not be valid for the films studied here, however, since a temperature of 10 K was used. At this lower temperature a larger class of configurations between chromophore pairs would qualify as traps; therefore, an estimate that approximately one-half of the chromophores are involved in trap formation, suggesting pairwise interactions between all chromophores, may be more reasonable. In any event, the assumption that all chro-

mophores are traps produces a lower limit to the trapping rate constant. Hopefully an independent method for evaluating the concentration of trap sites can be developed to yield quantitative values for these important rate constants.

Conclusions

When time resolution in the submicrosecond regime is used, it has been possible to determine some important rate constants related to the triplet-state processes of PVCA in fluid solutions. These include the rate of triplet–triplet annihilation and the rate of trapping of triplet excitons by the excimer-forming sites. The lifetime for first-order relaxation of triplets is 300 μs and the trapping of triplet excitons, which apparently controls the shape and the position of the maximum in the def–time profile, takes place on the time scale of several hundred nanoseconds. Solid films of PVCA at 10 K also produce a buildup in the intensity of delayed excimer fluorescence as a function of time in the nanosecond time regime. It is proposed that this buildup in def results from a corresponding buildup in the concentration of trapped triplet excitons. Also, from the knowledge of the position of the maximum in the intensity of def as a function of time it has been possible to evaluate the trapping rate constant of the triplet excitons by excimer-forming sites.

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Monomeric Surfactants for Surface Modification of Polymers

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ABSTRACT: The surfaces of poly(methyl methacrylate) and a UV-curable acrylic lacquer have been modified by the addition of small amounts of polymerizable, monomeric surfactants and a surface-active polymer. In the system used, the surfactants concentrate at interfaces toward less polar phases. Addition of 1% w/w of a monomeric surfactant to an acrylic lacquer gives a surface concentration of 50% at the interface toward air. The rate of surface enrichment is primarily dependent on the size of the surfactant molecules and on the viscosity of the bulk material to which it is added. Comparison shows that the surfactant-modified surface layers are thicker than monolayers made by the Langmuir–Blodgett technique. The behavior of monomeric surfactants in the outmost surface layer of a modified film is, however, similar to that of a monolayer formed in a Langmuir–Blodgett balance. Contact angle hysteresis measurements show that the surface-active monomers concentrating in the surface of a modified lacquer film become more and more closely packed when the total surfactant concentration is increased.

Introduction

Many properties of a material are dependent primarily on the surface structure and on the chemical composition of the outmost surface layer. Wetting and coating characteristics, frictional behavior, and physiological compatibility are examples of such properties. In several applications is difficult to find a material with both appropriate bulk properties and required surface properties. It is therefore often desirable to combine the surface properties of one material with the bulk properties of another. With polymers, this can be done through surface modification, i.e. by altering the chemical structure of a thin surface layer without affecting the bulk properties of the material. Several methods for modification of polymer surfaces have been developed,[1] including chemical methods,[2] plasma treatment,[3] and grafting reactions involving UV irradiation.[4] The latter technique is made even more effective if the bulk samples is doped with a small amount of a photoinitiator which, on

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