Triplet-State Absorption and Decay Kinetics of Poly(*N*-vinylcarbazole) and *N*-Ethylcarbazole by a Laser Excitation-Optical Probe Method

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ABSTRACT: Triplet-triplet absorption spectra and directly measured triplet decay rates have been obtained for poly(*N*-vinylcarbazole) (PVK) and *N*-ethylcarbazole (NEC) in frozen glassy solutions at 77 K. Although the PVK T-T absorption spectrum is of low resolution, it appears quite similar to that of NEC and both are similar to the known T-T absorption spectrum of carbazole itself. The directly measured triplet decay rate of NEC yields a first-order rate constant which agrees with previously determined phosphorescence decay rates, but the triplet decay of PVK shows nonexponential behavior. The kinetic data were treated by two distinctly different approaches. One assumed that conventional first- and second-order decay processes were responsible for the triplet decay. The rate constant for triplet-triplet annihilation was found to be 4.6×10^4 M^{-1} s^{-1} in this case. An alternative mode of data analysis involves labeling each polymer chain according to the number of triplet excitons it contains and assumes no intermolecular exciton migration. In this case, rate constants for the disappearance of singly and doubly excited chains were estimated. Two different techniques were also employed to extract diffusion rates from the kinetic results. A three-dimensional random-flight model yields diffusion coefficients of 10^{-11}-10^{-10} cm^2/s, but a one-dimensional model permitting only neighbor-to-neighbor hops predicts values of 10^{-13}-10^{-14} cm^2/s.

Introduction

The lowest triplet state of most organic molecules is sufficiently long-lived so that their optical absorption characteristics can be investigated with reasonable facility. Triplet-triplet absorption spectra have been recorded for a wide variety of organic compounds, and good reviews of the subject exist that summarize these data as well as molar absorptivities of the triplet species at selected wavelengths.[1,2]

It has proved to be relatively much more difficult to characterize the lowest triplet states associated with organic chromophores covalently bonded to the backbone of a polymer chain. The probable source of this difficulty is associated with the decidedly heterogeneous distribution of chromophore groups in polymers and the relatively small interchromophore separation distances within the polymer coil. In a series of papers, Mataga and co-workers were able to demonstrate that singlet-singlet annihilation plays an important role in limiting the yield of photoexcited triplets which can be obtained at high chromophore densities.[3] Singlet energy migration is very rapid in such systems and thus enhances the relative importance of the annihilative process in removing electronically excited species. Obviously, in such circumstances, intersystem crossing to the triplet state becomes less important, and reduced triplet quantum yields naturally result.

This effect has been documented in considerable detail for the case of poly(2-vinylnaphthalene) and poly(4-vinylbiphenyl) by Pratte and Webber.[4] In their work, triplet-triplet absorption spectra were obtained for these polymers, and triplet yields were compared with those for monomeric model compounds. A considerably reduced yield was observed for the polymeric species.

This turn of events is ironic since absolute measurements of triplet concentrations are required if specific rate constants for second-order reactions involving triplets are to be determined. The very important process of triplet-triplet annihilation, for example, may be determined by direct evaluation of the time dependence of the triplet decay.[5] Now it appears that the interference due to rapid singlet exciton migration might seriously limit the precision with which this annihilation rate constant may be determined and therefore limit the precision of triplet exciton diffusion rates upon which the rate constant depends.

Since the attention of this laboratory has been centered upon the triplet photophysical properties of the carbazole group, it was decided that T-T absorption experiments would be attempted on this chromophore, principally on poly(*N*-vinylcarbazole) (PVK). Earlier experiments by Masuhara and co-workers clearly indicated the magnitude of the problem.[6] In their experiments *N*-ethylcarbazole (NEC) and PVK oligomers were subjected to T-T absorption following pulsed laser excitation. The maximum T-T absorbances obtainable decreased with increasing molecular weight. From their measurements it was clear that if one intends to make quantitative measurements of triplet decay rates by optical absorption, then one must be prepared to determine absorbances on the order of 0.01 units with good precision. A description of our efforts in this direction is the subject of this paper.

Experimental Section

Chemicals. The solvent used for sample preparation was 2-methyltetrahydrofuran (MTHF) obtained from Aldrich Chemical Co. It was treated by passage through an activated alumina column followed by distillation from lithium aluminum hydride. The PVK sample used in this work was prepared by conventional free-radical polymerization of *N*-vinylcarbazole. The details of its purification and characterization have been described previously as well as those used for *N*-ethylcarbazole (NEC).[7]

Sample Preparation. Solutions of the subject compounds were prepared at known concentrations by using MTHF as solvent. For the polymer samples, concentrations were expressed in terms of the moles of chromophore units. The solutions were transferred to cylindrical absorption cells having either 0.1- or 0.5-cm optical path lengths. These cells had been previously sealed onto a 19/38 ₸ joint for attachment to the vacuum system. After evacuation by freeze-pump-thaw cycles, the samples were sealed off under vacuum and then attached to the cryotip cooling apparatus (Air Products and Chemicals Model LT-3-110). A vacuum shroud with fused silica port windows was placed over the cryotip and evacuated before the system was cooled to 77 K. All experiments reported here were carried out at 77 K.

Spectroscopic Equipment and Measurements. A diagram of the optical system is presented in Figure 1. The laser used is a Tachisto Model 401XR, the scanning monochromator is a SPEX Model 1690B, and the fixed-wavelength monochromator is a 0.25-m Jarrell-Ash instrument. The mirror shown between the probe source and the rear lens was movable. It was removed

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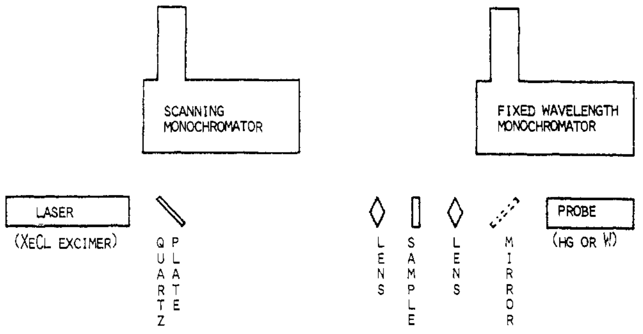

Figure 1. Schematic diagram of experimental apparatus using coaxial beams with excitation (left to right) and probe (right to left).

for triplet–triplet absorption work but was placed as shown for delayed luminescence studies.

The essential feature of the optical arrangement is that the excitation and probe beams are coaxial. By using such an arrangement it is particularly easy to direct the probe beam so that it is completely contained within the sample area which is photoexcited. This is accomplished, in the present design, by the use of a quartz beam splitter. Of course, only a small fraction of the probe beam is reflected into the monochromator slits by this plate, but the reflected intensity is easily sufficient, requiring only modest photomultiplier voltages for satisfactory signal levels. Conversely, a small percentage of the excitation beam from the laser was lost by reflection from this quartz plate, but full power from the laser was rarely used in any case, so the loss was without consequence.

Two distinct types of spectroscopic techniques were used, depending upon whether low or high sensitivity was required. In the low-sensitivity mode the monochromator was driven over the predetermined wavelength range with probe beam intensities being measured at some previously selected delay time following each excitation pulse. The laser pulse frequency and the monochromator scan rate were adjusted to yield data collection of 1 nm per channel in the 256 channels of each basic memory block used. To prepare a triplet–triplet absorption spectrum, one scan was made with the excitation beam blocked, yielding values of I_0 in each channel. Next a scan was made with the excitation beam open, yielding values of I in each channel. A computer program called Absorb was then used to calculate absorbances, that is, values of $A_{\mathrm{TT}} = \log (I_0/I)$, at each channel, and a graphics program called Dis was used to prepare the graphical representations of these spectra.

For absorption measurements requiring high sensitivity, whether for spectral or kinetic purposes, a method of opposing electrical currents was used. For digital recording this is a necessity if transmittances of 1% or less are to be measured. Thus, using an 8-bit digitizer, a full-scale vertical deflection would be represented by 256 counts but only two of these would represent the difference between I and I_0. If the photomultiplier current is partially cancelled, then a larger number of counts can be dedicated to recording the difference between I and I_0. This is particularly valuable for signal averaging with multiple scans. The recording instrument used in this work was a Nicolet LAS 12/70 signal averager. The photomultiplier output was connected directly to the inverting input of an operational amplifier used in the inverting, current-following configuration. An important characteristic of the inverting input, its current-summing property,[8] allowed the partial off-setting of the photomultiplier current. A standard current with bias opposite to the photomultiplier output was drawn from a photomultiplier power supply (Thorn-EMI-Gencom Model 3000R) through a 3.3-MΩ load resistance and applied to the amplifier input. The resulting voltage output, which is proportional to the difference in input currents, was well matched to the low input impedance of the LAS 12/70.

Spectra were observed by using the opposing current technique to record I over a relatively narrow time interval at fixed wavelengths. Typically, I was digitized in 100 channels between 1.0 and 1.10 ms after the excitation pulse. Because the triplet concentration changes negligibly in this aperture, the value of I at ca. 1.0 ms could be obtained as the average of values over all 100 channels with a concomitant attenuation of random noise. The recording of this signal is carried out by using a dual time base so that the final 155 channels are obtained at 60 ms per channel. Thus, at the end of this period the triplet concentration will have dropped to a negligible value prior to the arrival of the next excitation pulse. A very low repetition rate, usually about 15 s between laser pulses, must be used, and a minimum of 10 repetitions are averaged at each wavelength. The difference of the average probe beam intensity, $i_0 - i$, is obtained from the last channels and the first channels recorded. Let us use I_{d} to symbolize the digital count corresponding to this difference intensity. To complete the measurement the laser beam is blocked and a minimum of 10 repetitive scans are recorded to obtain the probe beam intensity in the absence of the opposing current and in the absence of a transient triplet population. This measurement also requires a decrease of vertical sensitivity by some factor s, which can vary between 1.0 and 64. Let us use I_{r} to symbolize the digital count corresponding to this reference current. The absorbance at this wavelength is then given by $A_{\mathrm{TT}}(\lambda) = \log [sI_{\mathrm{r}}(\lambda)/(sI_{\mathrm{r}}(\lambda) - I_{\mathrm{d}}(\lambda))]$. Measurements are made at 5- or 10-nm intervals throughout the range of interest.

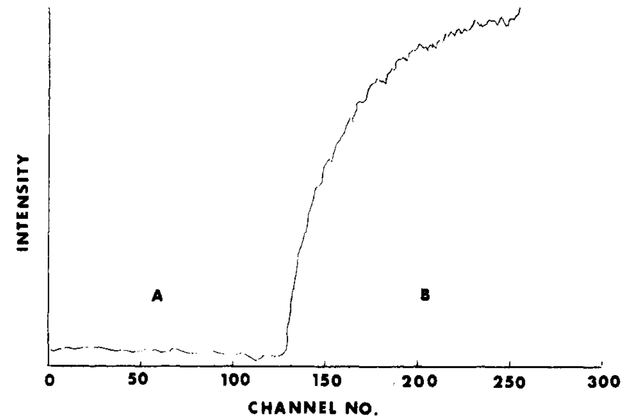

Figure 2. Intensity of probe beam at 430 nm vs. time following excitation of a solution 4.7×10^{-3} M in PVK units. A dual time base is used of 1 μs/channel to channel 127 and 60 ms/channel for the remainder. An opposing current is used to cancel most of the photomultiplier current. A 1-ms delay was inserted after excitation before sweep initiation.

Rates of triplet decay are measured by using a similar technique, but in this case the entire file of intensity vs. time is analyzed. These files are transmitted to the university's Cyber C830 computer by using a Tektronix 4025 terminal as a relay. Again, it is necessary to record the photomultiplier current in the absence of the opposing current and in the absence of transient triplets in order to provide a base for the absorbance calculations.

Experimental Results

Basic Measurement of T–T Absorptions. Since optical absorbances on the order of 0.01 or less need to be determined here, it is important at the outset to present data that demonstrate the limitations experienced when the current experimental approach is used. Information about these limitations is contained in Figure 2. Here the sample is a frozen solution of PVK in MTHF at a concentration of 4.7×10^{-3} M and at 77 K. The optical path length is 0.1 cm, and the vertical axis is the intensity of the probe beam transmitted through the solution as a function of time. The time base changes at channel 127 from 1 μs to 60 ms per channel, and a delay of 1 ms was inserted before initiation of the sweep. The result shown here is the average of 20 consecutive sweeps.

The intensity axis does not actually represent the total intensity since most of the photomultiplier current has been cancelled by using an opposing current as discussed above. There are several features of this graph that have important implications for subsequent measurements and which should be emphasized at this point. First, the intensity of the probe beam in the absence of absorbing

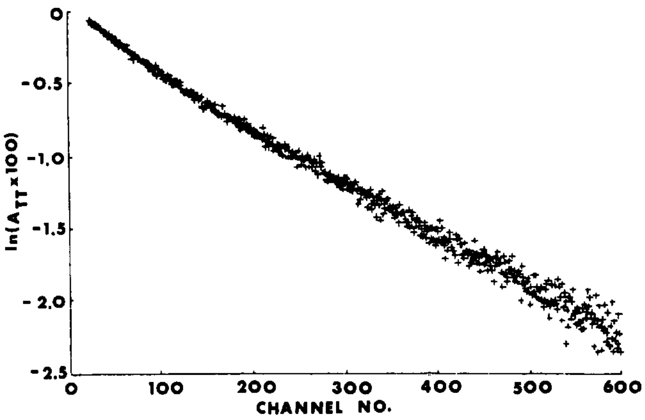

Figure 3. Logarithm of 100 × triplet absorbance at 430 nm vs. time for a solution 4.7 × 10^{-3} M in PVK chromophore units. The dwell time is 10 ms per channel.

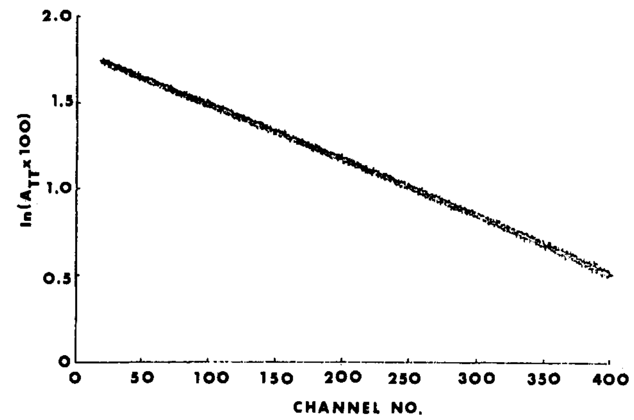

Figure 4. Logarithm of 100 × triplet absorbance at 430 nm vs. time for a solution 1.1 × 10^{-3} M in NEC. The dwell time is 20 ms.

triplets and with no opposing current was 10.520 V in this particular case. The difference voltage, $i_0 - i$, between the first and last channel of Figure 2 was 0.238 V after correction for a small amount of stray luminescence (see below). Thus, the absorbance is log (10.520/10.282) = 0.0099 at 1 ms following excitation. The major uncertainty in this experiment involves fluctuations of voltage readings corresponding to i and i_0. An estimate of ±0.008 V represents a reasonable average. This would lead, in the present example, to an uncertainty in the absorbance of ±0.0004.

The second point to notice is that the results of Figure 2 were recorded on the ±0.25-V scale, so the digital count corresponding to the voltage difference of 0.238 V was 124. If the difference had been recorded on the same scale used to measure I_0 in the absence of opposing current, that is, on the ±16-V scale, the digital count would have been a maximum of two units for this difference in voltage. Thus, the necessity of using the opposing current is clearly demonstrated.

The third point is that for some probe wavelengths there was a slight decline of intensity during the first 127-μs observation time. This was traced to a small amount of stray luminescence from the sample leaking back into the collection optics for the probe beam. The 0.238-V difference quoted above actually includes a small correction for this stray luminescence. The correction is easy to make just by recording intensity vs. time after excitation in the absence of the probe beam.

The final point is that an examination of the early stages of the second, 60-ms, time base reveals a time-dependent increase of transmitted intensity. This observation suggested that it would be possible to monitor directly the change in triplet-state concentration of PVK and hence to obtain second-order rate constants involving these species in spite of the very small absorbances encountered.

Triplet Decay Kinetics of PVK and NEC. A graph of ln ($100A_{\mathrm{TT}}$) vs. time following the excitation pulse is presented in Figure 3, where again the test sample is a solution 4.7 × 10^{-3} M in PVK chromophore units at 77 K. The graph shows a slight curvature, indicating that it is not a pure single exponential. Attempted fits to a single-exponential decay give $1/e$ values which increase as the arbitrarily chosen zero time moves to larger values. At sufficiently long times after the excitation pulse it is expected that the decay behavior would approach that of a single exponential, but triplet–triplet absorption measurements are very difficult at long times. It is much easier to monitor the long-time behavior by measuring the phosphorescence lifetime, and this has, of course, been done in earlier studies on PVK. For example, Klöpffer and Fischer reported a first-order decay time of 7.7 ± 0.9 s for PVK in MTHF at 77 K.[9]

For purposes of comparison, T–T absorption for NEC in frozen MTHF at 77 K was measured also as a function of time after excitation. A graph of ln ($100A_{\mathrm{TT}}$) vs. time is presented in Figure 4. A slight nonlinearity is observed for 200–300 ms following excitation, but the remainder of the decay shows good linearity with a lifetime of 6.9 ± 0.3 s. The phosphorescence decay of NEC in a polystyrene matrix at 77 K has also been measured, yielding a value of 6.5 ± 0.3 s.[10]

The source of the persistent nonlinearity in the data of Figure 3 is thought to be due primarily to interference from second-order T–T annihilation reactions leading to delayed fluorescence. Delayed fluorescence is, of course, a prominent emission feature of PVK both in frozen solutions and in neat films. Another explanation for these nonlinear effects could be that the first-order decay is dispersive as a result of reversible triplet-excimer formation. If this were the case, then rate constants for formation and dissociation of a triplet excimer could become involved in the overall decay process. This process is much less likely as a perturbation source because no triplet-excimer emission from frozen MTHF solutions of PVK has ever been observed.

If it is assumed that the annihilative process is primarily responsible for these nonlinear effects, then the mode of data analysis must be selected with some care. A fundamental question concerns the extent to which intermolecular triplet exciton migration occurs. If triplet excitons may freely migrate throughout the entire frozen solution both intermolecularly and intramolecularly, then the usual kinetic equations involving competing first- and second-order processes would apply as follows:

$$\mathrm{T} \rightarrow {}^1\mathrm{S}^0 + h\nu \text{ (or lattice energy)} \tag{1}$$

$$\mathrm{T} + \mathrm{T} \rightarrow {}^1\mathrm{S}^* + {}^1\mathrm{S}^0 \tag{2}$$

The integrated rate equation resulting from these two processes can be written in the form

$$\exp(k_1 t) = [k_2 T_0/(k_2 T_0 + k_1)] + (1/T)[(k_1 T_0)/(k_2 T_0 + k_1)] \tag{3}$$

where T_0 and T represent triplet concentrations at an arbitrary zero time and at time t, respectively. Clearly, the rate constant k_2 can be obtained from either the slope or the intercept of a graph of $\exp(k_1 t)$ vs. $(1/T)$. Since the method of data collection used here results in the accumulation of hundreds of thousands of data points, it was useful to design a computational method for data analysis. By use of the same data as was presented in Figure 3, a portion of the decay from channel 17 (170 ms) to channel

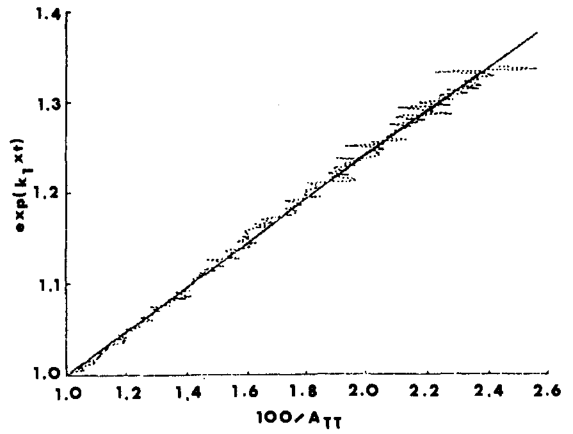

Figure 5. Graph of $\exp(k_1t)$ vs. the reciprocal of the triplet-state absorbance monitored at 430 nm. From the slope a rate constant for second-order triplet disappearance may be extracted.

217 (2.170 s) was analyzed in this way, and the result is presented in Figure 5. Actually it was more convenient to graph $\exp(k_1t)$ vs. $1/A_{\mathrm{TT}}$. This yields $k_2/\epsilon_{\mathrm{TT}}l$, where ϵ_{TT} and l are molar absorptivity and optical path length, respectively. In this experiment $l = 0.1$ cm, and the resulting value of $k_2/\epsilon_{\mathrm{TT}}$ was found to be 4.6 cm/s. Earlier work on the T–T absorption spectrum of carbazole yielded a value of 1×10^4 for ϵ_{TT} at 430 nm, thus a k_2 value of 4.6×10^4 M^{-1} s^{-1} would be obtained from these results.

The antithetical model to that of a homogeneous distribution of triplet excitons is one in which exciton migration is restricted to a single polymer chain and no intermolecular migration can take place. The essential features of such a model would be included in a system comprising three types of polymer chains that differ only in the number of triplet excitons residing on the chain. For present purposes we consider chains containing zero, one, or two excitons. Their respective concentrations may be symbolized by C_0, C_1, and C_2. Using T to symbolize the total triplet concentration, we have

$$T = C_1 + 2C_2 \tag{4}$$

and the following rate equations would also apply

$$-\mathrm{d}C_2/\mathrm{d}t = 2k_1C_2 + k_cC_2 \tag{5}$$

$$-\mathrm{d}C_1/\mathrm{d}t = -2k_1C_2 + k_1C_1 \tag{6}$$

where k_1 is again the first-order rate constant for triplet decay and k_c is the specific rate constant for C_2 disappearance by an annihilative event. Of course, C_2 would be converted into C_1 by the first-order decay of a triplet exciton, but the a priori probability of such an event would be proportional to the number of excitons on the chain. This is why the coefficient of two appears in eq 5 and 6. These equations represent a standard system of consecutive first-order processes having the solutions

$$C_2(t) = C_2(0) \exp[-(2k_1 + k_c)t] \tag{7}$$

and

$$C_1(t) = s_1 \exp(-k_1t) + s_2 \exp[-(2k_1 + k_c)t] \tag{8}$$

where $s_1 = C_1(0) + 2k_1C_1(0)/(k_1 + k_c)$ and $s_2 = -2k_1C_2(0)/(k_1 + k_c)$. Equations 4, 7, and 8 may be combined to yield an equation for the time dependence of the total triplet concentration. If, in addition, it is assumed that $k_c \gg k_1$, then one obtains

$$T(t) = 2C_2(0)[(k_c - k_1)/k_c] \exp(-k_ct) + C_1(0)[(k_c + 2k_1)/k_c] \exp(-k_1t) \tag{9}$$

Of course, eq 9 is only an approximate solution to this type of kinetic scheme since the contribution from chains containing more than two excitons has been ignored. For the experiment represented in Figure 3 at $t = 170$ ms the average number of triplet excitons per chain is 0.71, and so there will, in this case, be only minor contributions to the decay from chains containing multiple excitations. An estimate for k_c may be obtained from a fit to an exponential decay for data channels at short times after the excitation pulse. For example, using data for the time interval from 220 to 520 ms yielded a value of 1.5 s^{-1} for this rate constant, which is about 10 times larger than k_1. The relationship of rate constants such as k_c and k_2 to the diffusion rate of the triplet excitons will be discussed below.

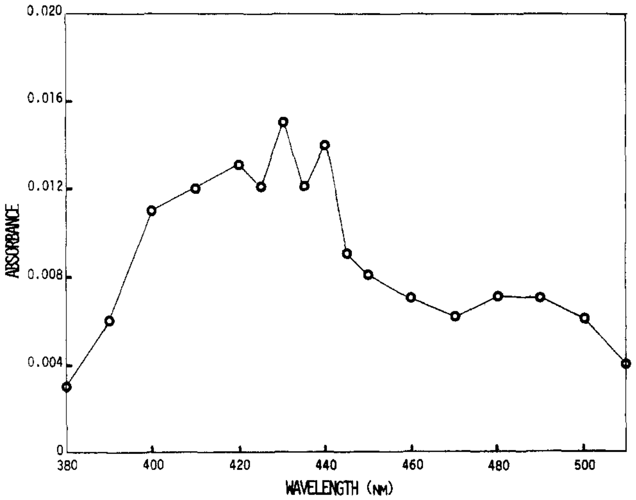

Figure 6. Triplet–triplet absorption spectrum for a solution of PVK 4.7×10^{-3} M in chromophore units at 77 K in MTHF. The absorbances are measured after a time delay of 1 ms, and each point is an average of 10 determinations.

T–T Absorption Spectra of PVK and NEC. A triplet–triplet absorption spectrum for PVK is presented in Figure 6. Although the resolution is not exceptional, it is possible to discern some prominent spectral features including an absorption maximum at 430 nm and a shoulder near 410 nm. A small peak near 490 nm is also suggested.

Much better resolution is obtained for the triplet–triplet absorption spectrum of NEC, which is presented in Figure 7. Because the probe-lamp intensity varies considerably over the relevant wavelength range, it proved more convenient to record the spectrum in two parts as shown. This spectrum for the triplet state of NEC is nearly identical with that reported by Brinen[12a] and Henry and Kasha[12b] for carbazole itself.

Discussion

The spectrum of Figure 7 is remarkable in its similarity to that of carbazole and indicates that substitution at the carbazolyl nitrogen does not strongly influence optical transitions associated with the triplet manifold. This behavior contrasts with the $^1\mathrm{S}^* \leftarrow {}^1\mathrm{S}^0$ transition of N-substituted carbazoles wherein electron-donor substituents have been shown to result in a red shift of the zero–zero band compared with carbazole, whereas electron-withdrawing substituents result in a blue shift.[13]

The T–T absorption spectrum of PVK, although not well resolved, shows a strong similarity to that of NEC and again suggests no major changes in the triplet-manifold quantum states simply by incorporation of the chromophore onto the backbone of a vinyl polymer. Such behavior should not be surprising in view of the nearly identical phosphorescence spectra of PVK and NEC in rigid glassy solvents.[14]

The resistance of triplet-state optical transitions to changes in substituents at the carbazolyl nitrogen has been

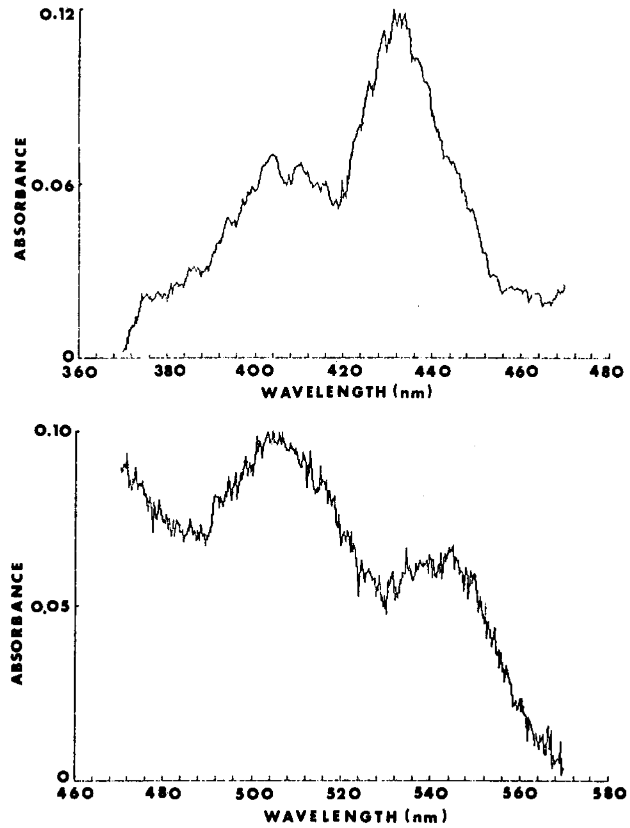

Figure 7. (Top) Triplet–triplet absorption spectrum of a solution 1.1×10^{-3} M in NEC at 77 K in MTHF, 370–470 nm. (Bottom) Same solution as above but covering wavelength range from 470 to 570 nm. The vertical scales are not comparable for the two spectra due to utilization of different laser pulse intensities.

noted previously in connection with phosphorescence spectra of poly[*N*-((vinyloxy)carbonyl)carbazole] and *N*-carbethoxycarbazole where electron-withdrawing groups are involved.[15] It was suggested that polarization of the lowest triplet state out of the molecular plane may be responsible for this effect in accord with Johnson's[16] results on N-substituted carbazoles. On the basis of the present results it appears that a similar statement may even be made for the higher triplet states of the carbazole chromophore. A definitive conclusion on this point must await results on a wider variety of N-substituted carbazoles.

The kinetic results associated with rates of triplet decay in PVK represent, to the best of our knowledge, the first attempt to make a direct evaluation of the specific rate constant for triplet–triplet annihilation in a polymeric system.[17] The detailed mechanism of this process in a rigid frozen glass is a matter of some interest since translational motion would be essentially frozen out under these conditions. Furthermore, the annihilation process has usually been characterized as encounter-controlled. In view of these two circumstances the specific rate constant k_2 will be related to the rate of triplet exciton migration. In fact, for dilute frozen glassy solutions of PVK the annihilative process has been found to be intramolecular in character,[18] so the exciton migration process to which k_2 is related is undoubtedly one involving primarily triplet energy migration among chromophore groups of the same polymer molecule. Such migratory events might include both nearest-neighbor and nonneighbor energy migration; however, no information on the relative importance of these processes is available at this time. The question has some importance, however, because it bears on the dimensionality of the process. If the exciton has three translational degrees of freedom, then a diffusion-controlled annihilative process would be calculated by

$$k_d = 4\pi r D N/1000 \qquad (10)$$

in units of M^{-1} s^{-1}. Here N is Avogradro's number, r is the encounter distance, and D is the diffusion coefficient. An estimate for D could be made from eq 4 if it were assumed that the triplet–triplet annihilation has unit efficiency and if a reasonable estimate for r can be made. Thus, identifying the experimental value for k_2 found here with k_d, one finds $rD = 6.1 \times 10^{-18}$ cm^3/s.

As an encounter distance one might choose a value of 15 Å, which has been suggested by Birks and co-workers[19] for annihilative processes in fluid solutions. On the other hand, for a polymeric system it may be more appropriate to choose a nearest-neighbor chromophore distance on the order of 3 Å. These two choices would lead to D values of 4×10^{-11} and 2×10^{-10} cm^2/s, respectively. By way of comparison, triplet exciton diffusion coefficients in polystyrene molecularly doped with 1,2-benzanthracene have been found on the order of 10^{-12} cm^2/s.[5] These values are, of course, many orders of magnitude smaller than those found for molecular diffusion in solvents having viscosities in the centipoise range (e.g., 10^{-5} cm^2/s) and imply a relatively slow migratory process for triplet excitons.

A diffusion coefficient of similar order of magnitude may be extracted from the data analysis presented above which led to a first-order rate constant, k_c, for the annihilative disappearance of doubly excited chains. Here we assume that migratory events occur only between neighboring chromophore groups separated by a distance l. The mean square displacement for n migratory events occuring in time t is $nl^2 = 2Dt$. The number of chromophore groups intervening between the two electronically excited ones can take on any value from zero to n_t where n_t is two less than the total number of chromophore groups per chain.

The diffusion coefficient, D, refers to the migration relative to a spatially fixed reference point. The diffusion coefficient of one exciton with respect to the other is $2D$. Thus, the time for an arbitrary number of n migratory hops of one exciton relative to the other is $t_n = nl^2/4D$. The average time required for an annihilation to take place would then be given by

$$t_{av} = [\sum_{j=1}^{n_t} jl^2/4D]/n_t \qquad (11)$$

The average degree of polymerization for the PVK sample used here was 333, so $t_{av} = 54945l^2/4D \times 331$. Using l = 3 Å, one finds $t_{av}D = 3.7 \times 10^{-14}$ cm^2. In terms of this model, $k_c = 1/t_{av}$, and we have obtained an estimate of 1.5 s^{-1} for k_c. It is doubtful, however, that this k_c value corresponds to the annihilative triplet disappearance only on doubly excited chains. On the other hand, k_c would be expected to be no less than k_1, the rate constant for true first-order decay of triplets to the ground state obtained from phosphorescence decay. Thus, the value for k_c is not likely to be significantly greater than 1.5 s^{-1} and no less than the 0.145 s^{-1} found for k_1. Therefore, this model leads to diffusion coefficients for triplet excitons on the order of 10^{-13}–10^{-14} cm^2/s.

Since the measured rate of triplet decay is only moderately more rapid than the pure first-order process, the effective triplet lifetimes represented by $1/k_c$ or $1/k_2T$ turn out, as would be expected, to be only slightly smaller than k_1^{-1}, at least in the time regime of this investigation. In fact, the triplet concentration represented by the data of Figure 3 at 170 ms following excitation was 1×10^{-5} M. Thus, k_2T is 0.46 s^{-1} at this time, and this may be compared with a k_c value of 1.5 s^{-1}. Thus, in effect, we are using similar lifetime values and treating them by three-dimensional vs. one-dimensional models, respectively. When similar hopping distances and diffusion coefficients are assumed, the rate of encounters are expected to be much larger in the one-dimensional model. In view of the similarity between k_2T and k_c, the natural result is a smaller predicted value of D in the one-dimensional case as is found. It is clear from these results that no completely satisfactory mode of data analysis is yet available for these polymeric systems. Additional experimental results will be needed to clarify some of the questions that the present investigation has raised. It should be noted, however, that in a system of densely populated chromophores, such as these vinyl aromatic polymers, it would be unusual to find diffusion coefficients significantly less than those obtained for small dopant molecules in polystyrene. For this reason, the one-dimensional model seems to be the less attractive alternative at this time.

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Registry No. PVK, 25067-59-8; NEC, 86-28-2.

References and Notes

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Fluorescence Quenching of Diphenylanthracene Covalently Bound to Poly(styrenesulfonate)

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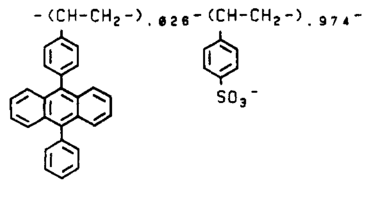
ABSTRACT: A water-soluble copolymer of styrenesulfonate and vinyldiphenylanthracene (DPA) was prepared that contained ca. 2.6 mol % DPA. The fluorescence properties of this polymer-bound chromophore were studied, with special emphasis on fluorescence quenching by the cationic quenches methylviologen (MV^{2+}) and Cu^{2+}. Both were very efficient quenchers, presumably because of electrostatic binding to the polymer coil, with an apparent quenching rate of ca. 6×10^{12} and 1.4×10^{13} M^{-1} s^{-1} for Cu^{2+} and MV^{2+}, respectively, on the basis of the initial slope of a Stern–Volmer plot. However, the quenching does not obey Stern–Volmer kinetics at higher concentrations, and the fluorescence intensity is quenched much more efficiently than the fluorescence lifetime (static quenching). For the case of MV^{2+} a weak charge-transfer (CT) complex is formed with the DPA, but in order to account for the fluorescence quenching it is necessary to postulate an additional "hydrophobic attraction" for MV^{2+} moieties to reside near a DPA without CT complexation. It is also proposed that as more MV^{2+} is attracted into the polyelectrolyte coil the DPA moieties become more protected, which is manifested by (1) a decrease in quenching efficiency and (2) a blue shift in the fluorescence excitation spectrum but with no change in the fluorescence spectrum.

Introduction

Water-soluble polymers with covalently bound hydrophobic chromophores[1–3] represent a class of microheterogeneous systems that are conceptually very similar to micelle systems in that hydrophobic materials may be solubilized in water and the chromophore may be partially protected or separated from the bulk solution. However, in the case of the polymer system the covalently bound chromophore cannot be exchanged between the elementary units and the degree of protection of the chromophore is expected to be less complete than is the case for micelles. We have proposed in an earlier paper[4] that a hydrophobic attraction can exist between an amphiphilic quencher (methylviologen) and a hydrophogic chromophore (diphenylanthracene, DPA) bound to a polyelectrolyte (deprotonated methacrylic acid). The present work explores this same phenomenon for the same quencher–chromophore pair but with a different polymer system (see Scheme I). Once again it is found that in order to un-

Scheme I



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