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Fluorescence Quenching and Singlet Energy Migration in Poly(2-vinylnaphthalene) and Poly(*N*-vinylcarbazole)[†]

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ABSTRACT: The CCl_4 quenching of the monomeric (M) and excimer (D) fluorescence of poly(2-vinylnaphthalene) (P2VN) and poly(*N*-vinylcarbazole) (PVCz) in room-temperature CH_2Cl_2 solutions is compared with monomeric and dimeric model compounds in order to estimate Λ_s, the singlet migration rate. Values in excess of 10^{-5} cm^2 s^{-1} were found for the M excited state of PVCz but $\Lambda_s \approx 0$ is estimated for the P2VN M and D states and the PVCz D state. In addition it was found that the concentration dependence for D quenching deviates from that expected from a model in which the M state is the only precursor to D. A kinetic model is proposed to account for these and other observations concerning the singlet excited state of polymers.

Introduction

Excited states of aromatic chromophores that are pendent to a polymer backbone are perturbed by the polymer environment in at least two ways: (1) excimer formation with neighboring chromophores is often facile and the fluorescence spectrum may be dominated by excimer fluorescence; (2) energy migration among the chromophores may occur, such that extrinsic quenching of the excited state may be more efficient than would be calculated assuming only the very slow diffusion of the polymer-bound chromophore. The objective of the present experiment is to estimate Λ_s, the singlet exciton migration rate, for poly(2-vinylnaphthalene) (P2VN) and poly(*N*-vinylcarbazole) (PVCz) by comparing the fluorescence quenching rate (with respect to CCl_4, in CH_2Cl_2 solutions) of the monomer fluorescence with the monomeric model compounds 2-ethylnaphthalene and *N*-ethylcarbazole. In addition the quenching of the excimer band of 1,3-dicarbazolylpropane (DCP) and 1,3-dinaphthylpropane (DNP) will be compared to the longer wavelength fluorescence band of PVCz and P2VN. The analysis will show that Λ_s is quite significant for the monomeric excited singlet state of PVCz but is essentially zero for both excimer singlet states and the monomer state of P2VN.

We have also found that the corrected Stern–Volmer plots of the excimer quenching (see eq 5 and Figure 4; vide infra) show a deviation from linearity that cannot be accounted for by the assumption that the excimer is quenched by two routes: (1) direct quenching and (2) quenching of a precursor state, the excited monomer singlet. Similar observations have been made by Ishii et al.[1] for polystyrene. We will speculate that these nonlinearities imply direct excitation of the excimer state or, equivalently, not all monomer states are precursors for the excimer state.

Experimental Section

All solvents were spectroquality grade and did not show any spurious absorption or fluorescence under the conditions of the quenching experiment. Solutions were made up to have an optical density of approximately 1.0 at the excitation wavelength ($\sim 10^{-3}$ M for naphthalene, $\sim 10^{-4}$ M for carbazole, both expressed in terms of the chromophore units). This relatively high optical density allowed a good range of quencher concentration to be explored while retaining a favorable S/N ratio. No significant concentration dependence of the Stern–Volmer quenching constant was found. For steady-state measurements the solutions were air saturated, which eliminates a possible source of error due to accidental admission of air to a deoxygenated solution. The fluorescence intensity was very stable with time. The fluorescence spectra and relative intensities were measured on a SPEX Fluorolog instrument, which has very good sensitivity because of its photon counting detection system. Aliquots of the CCl_4 quencher (typically 5 μL) were added directly to a known volume (typically 3.00 mL) of the fluorescence solution. All experiments were carried out in duplicate for a given run, with excellent agreement between the duplicate runs. The values reported later were obtained from a number of independent experiments with good agreement. As we will see, the quenching constant for a polymer depends strongly on the wavelength of observation because of the overlap of the monomeric and excimeric emissions. This has been discussed previously by Pfister et al.[2] for PVCz.

A series of determinations of the quenching constant were made by direct measurement of the fluorescence decay rate upon addition of CCl_4. A quadrupled (265 nm) Nd:YAG picosecond laser system was used, with a detector response time of approximately 1.5 ns. Interference filters (340, 365, or 430 nm) in addition to glass cutoff filters were used to isolate the part of the fluorescence spectrum of interest. Decay curves were digitized with a Tektronix transient recorder (Model 7912) and signal-averaged with a PDP-11 and associated software. For the polymers and 1,3-dicarbazolyl propane the decay was nonexponential, as expected from earlier work.[3-6] The method used to obtain a "best fit" (in the least-squares sense) was as follows: (1) the long-time portion of the excimer fluorescence decay was fit to a single exponential; (2) the monomer fluorescence was fit to a biexponential function ($Ae^{-at} + Be^{-bt}$) in which one of the rate constants was constrained to be equal to the rate obtained from the excimer. This method corresponds to the results anticipated if the excimer dissociation to re-form the monomeric excited state is possible or if spectral overlap of the monomer and excimer fluorescence occurs.[7] An example of the monomer and excimer decay curves and the biexponential fit for PVCz is presented in Figure 1. For these experiments the solutions were continuously bubbled with argon, using a fluorescence cell designed for this purpose, with aliquots of CCl_4 added without exposing the solution to the atmosphere. The quenching constants quoted later were based on the change of a and b in the previous expression with CCl_4 addition. All solutions were prepared to have an OD of approximately 0.8 at 265 nm. Fluorescence lifetimes were also determined for aerated solutions, to allow a determination of the quenching constant from the steady-state Stern–Volmer constant. While the agreement between these two methods is not exact, it is satisfactory within the overall experimental error. In principle, one would expect the fluorescence decay method to be more precise because it is more direct. Unfortunately the time response of the detection system is inadequate for [CCl_4] in excess of $\sim$0.05 M (depending on the fluorophore) and the imprecision of the kinetic fit is such that the two types of experiments are of comparable precision. In some cases (the monomer of P2VN or the excimer of 1,3-dicarbazolylpropane) the fluorescence intensity was relatively low,

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[†] Dedicated to Professor W. A. Noyes, Jr., in memorium, deceased Nov 25, 1980.

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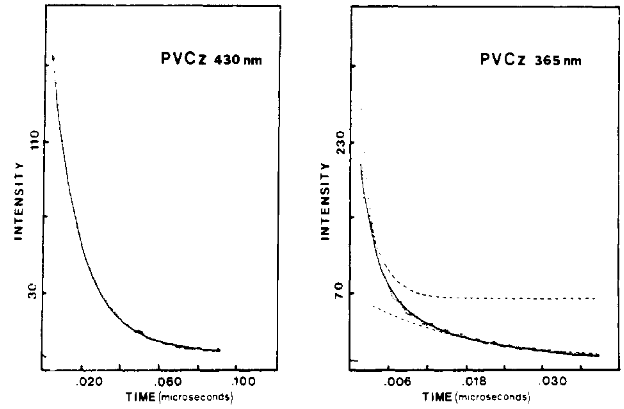


Figure 1. Typical fluorescence decay curves for PVCz, illustrating multiexponential decay characteristics. The instrument response function to the laser pulse is also illustrated (··· in the 365-nm curve). See text for method of fitting decay curves. These decay curves are averages of several equivalent laser flashes.

which decreases the accuracy of any fit.

The sample of P2VN was synthesized in our laboratory by using a free-radical polymerization (AIBN initiator) in benzene at 65 °C. According to a GPC elution, the molecular weight is approximately 85 000 (based on other known samples of P2VN) with a polydispersity on the order of 1.5. The sample of PVCz was obtained from Aldrich Chemical Co. The GPC estimate of the molecular weight is 500 000. Both polymer samples were extensively purified by reprecipitation of a benzene solution into methanol. The DCP was a gift from W. Klöpffer (Battelle Institute, Frankfurt am Main, West Germany) and was used without further purification. *N*-Ethylcarbazole and 2-ethylnaphthalene were obtained from Aldrich Chemical Co. The former required purification by vacuum sublimation and multiple recrystallizations from ethanol. The DNP was synthesized by following the procedure of Chandross and Dempster[8] for 1,3-bis(β-naphthyl)propane, with a few modifications. The β,β-chalcone was reduced by high-pressure hydrogenation, using a Pd catalyst. The ketone was reduced by the Wolff–Kishner reaction, similar to the procedure of Chandross and Dempster[8] for their 1-α-naphthoyl-2-α-naphthylethane reduction. Purification was effected by a combination of recrystallizations from 1:9 benzene–petroleum ether and column chromatography on silica gel, using hexane as eluant (the nonpolar DNP is very well separated from the ketone precursors by this procedure). The final product showed a single component by TLC and gas chromatography–mass spectroscopy (parent ion m/e 296 as expected) and good crystal formation (colorless plates) but the melting point (97.5 °C) was slightly lower than quoted in ref 8.

Results

If an excited state E is quenched by a collision with a quencher Q, the simplest form of the rate equation for E is

$$\mathrm{d}[\mathrm{E}]/\mathrm{d}t = I_{\mathrm{ex}} - (k_{\mathrm{E}} + k_{\mathrm{qE}}[\mathrm{Q}])[\mathrm{E}] \qquad (1)$$

which under steady-state conditions leads to the well-known Stern–Volmer equation

$$[\mathrm{E}]_0/[\mathrm{E}]_{\mathrm{Q}} = 1 + (k_{\mathrm{qE}}/k_{\mathrm{E}})[\mathrm{Q}] \qquad (2)$$

in which the Stern–Volmer quenching constant $K_{\mathrm{SV}} = k_{\mathrm{qE}}/k_{\mathrm{E}}$ $(=\tau_{\mathrm{E}}k_{\mathrm{qE}})$ provides a measure of the efficiency of the quenching. In our experiment the quantity $F_0/F_{\mathrm{Q}} - 1$ (in which F_0, F_{Q} are the intensities of fluorescence in the absence and presence of quencher, respectively) is determined and can be fit by a least-squares method to the best straight line. The slope of this fit yields $(K_{\mathrm{SV}})_{\mathrm{obsd}}$. (As we will see below, if E is an excimer state formed by a precursor monomeric excited state, the equation equivalent to eq 2 shows a quadratic dependence on [Q].) One of the most striking observations is the very strong dependence of the K_{SV} value on the observation wavelength for systems that are capable of excimer formation. This is illustrated in Figure 2 for poly(2-vinylnaphthalene) (P2VN) and poly(*N*-vinylcarbazole) (PVCz). A similar wavelength dependence exists for DCP and DNP. As is implied by the results displayed in Figure 2, the appearance of the fluorescence spectrum changes drastically as quencher is added. This is illustrated in Figure 3. This observation shows that the excimer is quenched much more efficiently than the monomeric singlet (largely as a result of their different lifetimes) but also demonstrates that if one makes an unfortunate choice of wavelength to characterize the polymer quenching, misleading K_{SV} values can result.

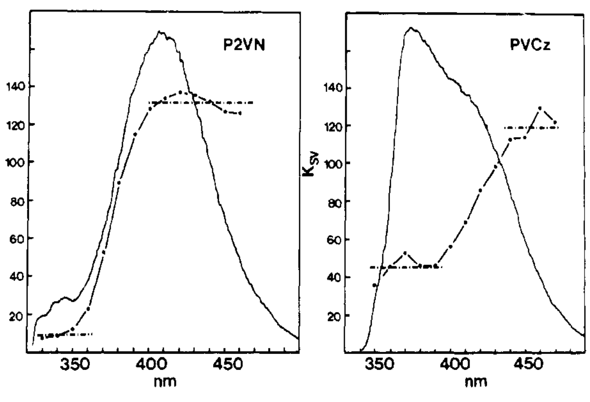


Figure 2. Dependence of $(K_{\mathrm{SV}})_{\mathrm{obsd}}$ on the wavelength for P2VN and PVCz. The unquenched fluorescence spectrum of each of these molecules is also illustrated.

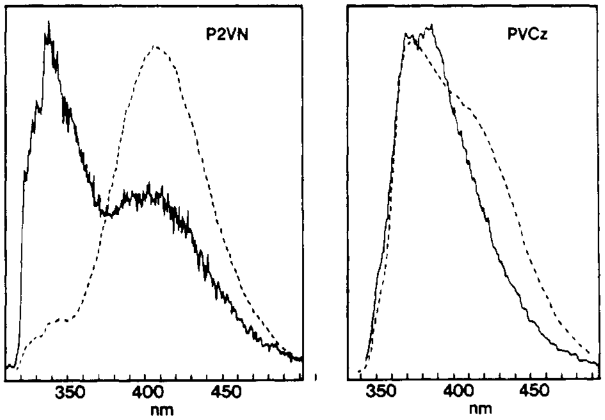


Figure 3. Fluorescence spectrum of P2VN and PVCz in the presence (full line) and absence (dashed line) of quencher. The quencher concentrations and sensitivity factors for each of the full-line spectra are as follows: (a) P2VN, [$\mathrm{CCl_4}$] = 0.277 M, sensitivity approximately 20×; (b) PVCz, [$\mathrm{CCl_4}$] = 0.277 M, sensitivity approximately 10×.

The kinetics of the monomeric and excimeric excited singlet states are considerably more complicated than expressed by eq 1 and 2 because of the association/dissociation processes that interrelate M (monomeric excited singlet) and D (excimeric excited singlet). For the M state[4] the rate equation is

$$\mathrm{d}[\mathrm{M}]/\mathrm{d}t = I_{\mathrm{ex}}{}^{\mathrm{M}} - (k_{\mathrm{M}} + k_{\mathrm{qM}}[\mathrm{Q}])[\mathrm{M}] + k_{\mathrm{d}}[\mathrm{D}] \qquad (3)$$

where $I_{\mathrm{ex}}{}^{\mathrm{M}}$, k_{M}, and k_{qM} have the same meaning as in eq 1 but the last term describes the finite rate of dissociation of an excimer to form M and a ground-state chromophore, i.e., D → M + G. The steady-state solution to eq 3 does not yield a straight-line Stern–Volmer plot except in the limit that $k_{\mathrm{d}}[\mathrm{D}]$ can be ignored. For our particular cases the Stern–Volmer plot for the monomeric fluorescence is fit reasonably well by a straight line. This implies that the last term in (3) can be ignored, especially at higher

Table I
Stern–Volmer Quenching Constants for P2VN, DNP, PVCz, and DCP

	K_{SV}^{M}, M^{-1}	$(K_{SV}^{D})_{obsd}$, M^{-1}	$(K_{SV}^{D})_1$,[c] M^{-1}	$(K_{SV}^{D})_2$,[d] M^{-1}
P2VN	9	75[a]	44	66
DNP	15	113[b]	~42	98
PVCz	49	126[b]	19	77
DCP	59	220[b]	49	161

[a] Obtained from fit of quenching data to general quadratic, where $(K_{SV}^{D})_{obsd}$ is the first-order coefficient. [b] Based on first-order term in plot of $(F_0/F_Q)_D$. [c] Based on initial slope of $(F_0/F_Q)_D(F_Q/F_0)_M$ (see Figure 4). [d] $(K_{SV}^{D})_{obsd} - K_{SV}^{M}$, which, according to eq 7, should equal $(K_{SV}^{D})_1$.

quencher concentrations, where [D] has been diminished much more than [M] (see Figure 3).

For the excimeric state we can write

$$d[D]/dt = k_a[M] - (k_D + k_{qD}[Q])[D] + I_{ex}^{D} \quad (4)$$

where k_a is the pseudo-first-order association rate of M + G → D, k_D is the intrinsic decay rate of D (including k_d, dissociation of D to re-form M), and k_{qD} is the quenching rate of the D state. The last term in eq 4 represents the direct excitation of D, which requires that a pair of chromophores have the necessary mutual configuration that very fast formation of a D state results (this is not the same as a ground-state dimer in the sense that no new $S_0 \rightarrow S_1$ absorption band need result). This term is normally omitted from discussions of polymeric excimers because previous work has implied that the fraction of "preformed" excimer sites is small[9] (although see the paper by Irie et al.[10] dealing with this possibility for poly(1-vinylnaphthalene)). As we will see later, our results can be taken to show that I_{ex}^{D} is significant. If I_{ex}^{D} is ignored, then the steady-state solution of eq 4 leads to the following expressions:[11]

$$(F_0/F_Q)_D(F_Q/F_0)_M = 1 + (k_{qD}[Q])/k_D = 1 + K_{SV}^{D}[Q] \quad (5)$$

and from eq 3 (if k_d can be ignored)

$$(F_0/F_Q)_M = 1 + (k_{qM}/k_M)[Q] = 1 + K_{SV}^{M}[Q] \quad (6)$$

$$\begin{aligned}(F_0/F_Q)_D &= (1 + K_{SV}^{D}[Q])(1 + K_{SV}^{M}[Q]) \\ &= 1 + (K_{SV}^{D} + K_{SV}^{M})[Q] + K_{SV}^{D}K_{SV}^{M}[Q]^2 \end{aligned} \quad (7)$$

Thus there should be a simple relationship between the observed Stern–Volmer constants in these various types of plots. Our data do not conform to these expectations (a similar observation was made by Ishii et al.[1] with respect to polystyrene of different tacticities). For example, all plots of the quantity in eq 5 show a negative deviation from a straight line at higher CCl_4 concentrations, with particularly strong deviations being observed for PVCz and DCP (see Figure 4).[12] For PVCz and DCP there is no statistically significant dependence on $[CCl_4]^2$ when $(F_0/F_Q)_D$ is fit to a general quadratic equation (see Figure 5).[13-15] For P2VN the quenching of the dimer fluorescence is nonlinear, but the coefficient of the first-order term is not equal to K_{SV}^{M} plus the initial slope of the data in Figure 4. In Table I we have summarized the Stern–Volmer constants for P2VN, DNP, PVCz, and DCP. K_{SV}^{D} was calculated in two ways: (1) from the initial slope of the quantity in eq 5 and 2 by subtracting K_{SV}^{M} from the coefficient of the first-order term in eq 7. These values agree very poorly, showing that the assumptions made in deriving these equations are evidently not valid for the present system. These results imply that a simple excimer–monomer equilibration scheme, such as that suggested by Birks for small molecules,[16] is not appropriate for polymer systems. As we will see in the Discussion, this seems to be a slowly developing concensus from other polymer photophysical experiments.

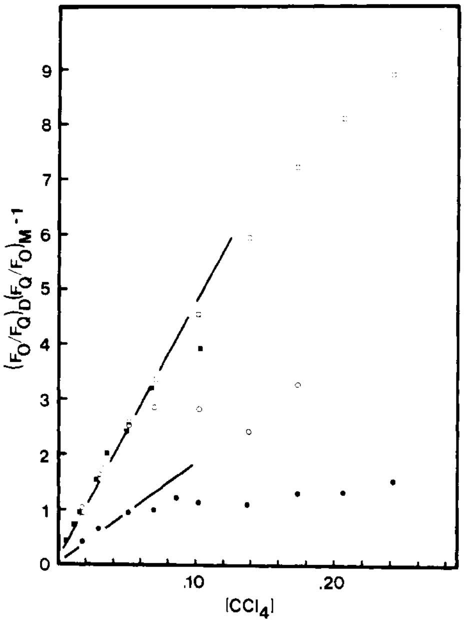


Figure 4. Plot of $(F_0/F_Q)_D(F_Q/F_0)_M - 1$ vs. $[CCl_4]$ (mol/L) for P2VN (□), DNP (■), PVCz (●), and DCP (○) for a typical experiment.

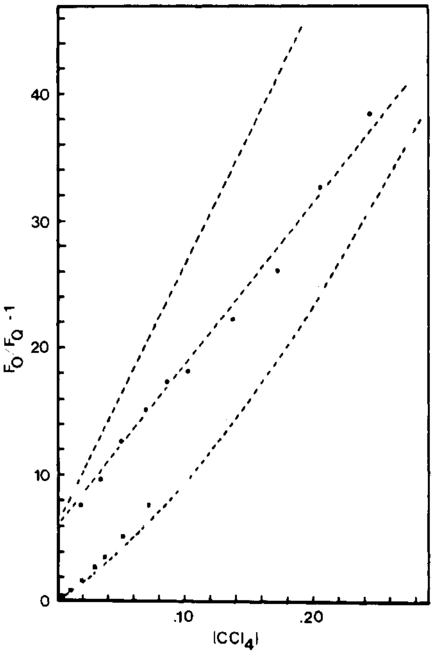


Figure 5. Plot of $(F_0/F_Q)_D - 1$ vs. $[CCl_4]$ (mol/L) for P2VN (□), DNP (■), PVCz (●), and DCP (○) for data from typical experiment. Dashed line represents the best least-squares fit to the data (quadratic for P2VN, linear for PVCz and DCP). The data for PVCz and DCP have been displaced by +6 units to prevent extensive overlap of the individual curves.

Table II
K_{SV}, k_{qE}, and $\Lambda_s/\bar{D}$ Data

species	K_{SV},[a] M^{-1}	τ,[b] ns	$k_{qE}^{SV} \times 10^{-9}$,[c] $M^{-1}\ s^{-1}$	$(\Lambda_s/\bar{D})_{SV}$[d]	$k_{qE}^{\tau} \times 10^{-9}$,[e] $M^{-1}\ s^{-1}$	$(\Lambda_s/\bar{D})_{\tau}$[d]
P2VN-M	9.2 ± 2.4	7.4 (7.4)	1.24 ± 0.33 (1.24)			~0
P2VN-D	66.0 ± 4.0	25.2 (34.5)	2.61 ± 0.16 (1.91)	~0	2.38 ± 0.04	~0
EtN	52.7 ± 0.3	9.5 (9.5)	5.55 ± 0.03 (5.55)		5.76 ± 0.20	
DNP-M	15.3 ± 0.5	3.3	4.68			
DNP-D	113 ± 1	19.0 (45.3)	5.92		3.40	
PVCz-M	49.5 ± 1.3	2.45 (2.76)	20.2 ± 0.53 (18.0)	1.4-1.7	20.4 ± 4.3	1.7-2.9
PVCz-D	77	12.0 (16.5)	6.4 (4.66)	~0	6.04 ± 0.28	~0
EtCz	96.0 ± 3.0	6.3 (7.2)	15.1 ± 0.5 (13.3)		10.4 ± 0.6	
DCP-M	59.3 ± 1.3	3.6 (4.9)	16.6 ± 0.2 (12.3)		14.9 ± 0.9	
DCP-D	218.0 ± 9.0	13.3 (15.2)	16.3 ± 0.8 (14.3)		11.3 ± 0.7	

[a] Average over several wavelengths and experiments, obtained from least-squares analysis. [b] Lifetime in ns. Results in parentheses are for argon-bubbled solution. [c] $k_{qE}^{SV} = K_{SV}/\tau$, where the τ value for aerated solution is used. [d] $(\Lambda_s/\bar{D})_{SV}$ and $(\Lambda_s/\bar{D})_{\tau}$ use k_{qE}^{SV} and k_{qE}^{τ}, respectively. The upper and lower values of $\Lambda_s/\bar{D}$ for PVCz-M are calculated with DCP and EtCz as the monomeric model compound, respectively. [e] Obtained from $k_E^Q = k_E + k_{qE}^{\tau}[Q]$.

Certainly the effect of solvent on the polymer fluorescence spectrum is known, but not with such small additions of a second solvent.

An important observation in our work is the curvature of the "corrected" excimer fluorescence quenching curve (eq 5, Figure 4) in conjunction with good linearity of the monomeric fluorescence quenching curve. From eq 4 we may write the following for the steady-state fluorescence of D:

$$(F_Q)_D \propto k_a[M]_Q/(k_D + k_{qD}[Q]) + I_{ex}^D/(k_D + k_{qD}[Q]) = k_a[M]_0/[k_D(1 + K_{SV}^M[Q])(1 + K_{SV}^D[Q])] + I_{ex}^D/[k_D(1 + K_{SV}^D[Q])] \quad (8)$$

If the direct excitation term is finite, then the quenching of $(F_Q)_D$ will be similar to that of a simple fluorescence species when $k_a[M]_Q \ll I_{ex}^D$. On the basis of our results for PVCz, this condition is satisfied when the monomeric fluorescence is quenched to approximately 15–20% of the initial value. We note a recent report by Tagawa et al.[17] of the very early time development (0–3 ns, 10-ps resolution) of M and D fluorescence for PVCz excited by pulse radiolysis. Both the M and D fluorescence (at 380 and 420 nm, respectively) are observed to grow in during this time period, with a substantial intensity of both emissions present at zero time. The 380-nm emission shows almost no growth during the 0-3-ns period, showing that this emission is from a directly excited state. The 420-nm emission shows a significant growth during this same period, implying a combination of direct excitation and population via a state with a lifetime on the order of 2.6 ns.[6] Thus we believe that our results demonstrate that a significant number of "preformed D sites" are present in our polymers (especially PVCz) and DCP. We will return to this point in the Discussion.

It is puzzling that the quenching results of Pfister et al.[2] (using electron-withdrawing species) could be fit by the simple Birks scheme (eq 5–7) while ours cannot. We note that the K_{SV} values obtained by Pfister et al.[2] were considerably smaller than those obtained herein for CCl_4. Thus they observe curvature in $(F_0/F_Q)D^{PVCz}$ for quencher concentrations higher than our maximum CCl_4 concentration. One may speculate that quencher-specific solvation of the polymer could occur which distorts either the "concentration" of the quencher or the coil configuration.

One of the objectives of the present study is to determine the significance of singlet energy migration in these polymers. The simplest interpretation of k_{qE} is by the application of the modified Smoluchowski–Einstein equation[18]

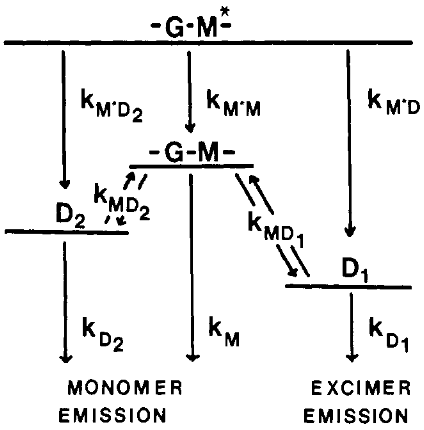
$$k_{qE} = 4\pi N_0(D_E + D_Q + \Lambda_s)PR \times 10^{-3} \quad (9)$$

in which D_E and D_Q are the diffusion constants of the excited chromophore and quencher, respectively, and Λ_s is the singlet exciton migration rate. P and R are the quenching probability per collision and sum of radii for E and Q. N_0 is Avogadro's number. We will assume that $D_E \approx 0$ for a chromophore on the polymer chain and $\Lambda_s \approx 0$ for the monomeric model compound. If one then assumes that the product PR is roughly the same for the polymer-bound chromophore and the model compound,[19] then

$$(k_{qE}^{\text{polymer}} - \tfrac{1}{2}k_{qE}^{\text{monomer}})/\tfrac{1}{2}k_{qE}^{\text{monomer}} = \Lambda_s + \tfrac{1}{2}(D_Q - D_E)/\tfrac{1}{2}(D_Q + D_E) \quad (10)$$

Since Q and E (the monomeric model compound) are both small molecules, their diffusion constants will be similar and $D_Q - D_E \approx 0$. We may also define $\bar{D} = {}^1/_2(D_Q + D_E)$, in which case the expression on the left-hand side of eq 10 yields an estimate of $\Lambda_s/\bar{D}$. These are given in Table II, along with other photophysical parameters and the comparison of k_{qE} values from the Stern–Volmer quenching and the lifetime quenching experiments. The assumption that the product PR is the same for a given type of chromophore is strengthened by the reasonable agreement between the EtCz and DCP-M, or EtN and DNP-M.[20] We also note that the quenching rate is always higher for a carbazole compound than the corresponding naphthalene compound, which must reflect the difference in the properties of the S_1 state. The expression used to evaluate $\Lambda_s/\bar{D}$ (eq 10) is rather sensitive to the net experimental error in both k_{qE} values, such that for $\Lambda_s/\bar{D} < 1$, Λ_s may be taken as essentially zero within experimental error. By this criterion only PVCz-M shows an experi-

Scheme I



mentally significant $\Lambda_s/\bar{D}$. Both excimer states are shown to have essentially zero migration rate (which is not surprising) and the P2VN-M state is also shown to have zero mobility. This state appears to form the excimer state rapidly (as evidenced by its short fluorescence lifetime and its relatively low fluorescence intensity) so it is not surprising that $\Lambda_s/\bar{D} \approx 0$ is found. Accordingly, $\Lambda_s/\bar{D}$ would be expected to be larger for naphthyl polymers that show less excimer fluorescence (such as the naphthyl acrylates). Certainly Holden and Guillet[21] have shown that polymers of this latter class transfer energy efficiently to an acceptor molecule (anthracene) situated at the polymer ends.

Discussion

Our observations may be summarized as follows: (1) the quenching of the monomer (M) and excimer (D) fluorescence of P2VN and PVCz (and DCP and DNP) leads to the conclusion that the D state is not formed exclusively via the M state, especially for the carbazole-containing species, and (2) the singlet migration constant (Λ_s) is nonzero (within experimenal error) only for PVCz-M. Our Λ_s value for PVCz is similar to that found for polystyrene by Ishii et al.[19b] and the energy migration length, defined by $l = (2\tau\Lambda_s)^{1/2}$ (taking[1] $\bar{D} = D_{CCl_4} = 1.5 \times 10^{-5}$ cm^2/s), is ~40 Å, again of the order found for polystyrenes.[22] The accepted interpretation of the PVCz-M state is due to Johnson,[4] in which M is a partially formed excimer (also see Itaya et al.[15]). Since we have found $\Lambda_s \neq 0$ for this "M" state one of the following two possibilities must be true: (1) the required geometry for this state is found at frequent intervals along the chain such that energy migration is possible (presumably by a Förster-type process) or (2) the M state is in equilibrium with an excitonic state (vide infra). In the case of P2VN-M the M → D formation rate must be very fast compared to energy migration, which is consistent with the smaller value of the transition dipole moment of the naphthalene chromophore. In this case P2VN-M is different from the polystyrene M state. In all cases the D state appears to be an energy trap, as one would expect.

There have been a number of recent studies of the temporal dependence of fluorescence of polymers of the type discussed herein.[17,22] Sophisticated techniques have allowed very short times to be explored[17] or the long-time decay curves to be very carefully analyzed.[6,22] Some of the results have been mentioned in the preceding section, but we will briefly review them here. For PVCz both the high-energy dimer (emitting at 380 nm) and the low-energy dimer (emitting at 420 nm) are populated at times short compared to the fastest decay rate observed in fluorescence.[17] Thus there must be a nonradiative precursor state to both these states. Since we have found $\Lambda_s \neq 0$ at 380 nm, we can speculate that this state is excitonic or is in equilibrium with an excitonic state. Roberts et al.[6] have observed that the PVCz fluorescence at 360 nm required a three-exponential function for a satisfactory fit, which was taken to imply the existence of two high-energy excimers, one of which cannot interconvert to a low-energy excimer. A similar suggestion was made by Holden et al.[22] to explain the disagreement between the long-time decay rate of the monomeric and excimeric fluorescence in naphthyl methacrylates. Detailed studies have not been carried out of P2VN, but for poly(1-vinylnaphthalene)[3b] monomeric fluorescence is observed at long times that seems to arise from "excimer" to "monomer" conversion. In Scheme I we have presented a representation that contains all the elements previously observed in polymer singlet state studies as well as the present one (in this representation the reverse rates k_{D_1M} and k_{D_2M} have not been drawn in explicitly for clarity). In this representation M* and M are monomeric excited states, M* being the Franck-Condon state formed initially by the excitation. Both M* and M may be excitonic. G is the ground state of the pendent groups on the polymer. D_2 and D_1 are the high- and low-energy excimer states, respectively. In the case of naphthyl methylacrylates D_2 may be essentially coenergetic with M but cannot form state D_1, presumably for steric reasons. This is equivalent to setting k_{D_2M} equal to zero. The direct formation of D_1 from G-M* is equivalent to the $I_{ex}{}^{D}$ term in eq 4. Since the curvature in the corrected excimer fluorescence quenching curve is smaller for P2VN and DNP than the carbazoles (see Figure 4), one may speculate that $k_{M^*D_1}$ and $k_{M^*D_2}$ are less important in this case. We see that if the dissociation process is finite (i.e., $k_{D_1M} \neq 0$), the monomeric emission can be triexponential. If D_1 and D_2 dissociation can be neglected (i.e., $k_{D_1M} \approx 0$, $k_{D_2M} \approx 0$), the monomeric emission is biexponential but neither decay rate will equal k_{D_1}. The quenching of the D_2 state can be enhanced by singlet migration if $k_{D_2M} \neq 0$ (this situation seems to hold for PVCz) but will not be enhanced if $k_{D_2M} \approx 0$ (the P2VN case?). The main reasons for presenting the kinetic scheme of Scheme I are (1) to point out the relation of the present results to previous work and (2) to demonstrate the greatly enhanced complexity of excimer equilibria in polymer systems relative to the scheme of Birks[16] for small, independently diffusing molecules.

The possibility of using intrapolymer energy transfer to provide for an "antenna effect" in photochemical sensitizations is an attractive application of polymer photophysics. The results of the present study and studies by Guillet and co-workers[3a,21] seem to point to the general result that polymers with low excimer formation rates would be most desirable in this regard. The present method is a fairly simple way to estimate Λ_s but suffers from a lack of precision such that $\Lambda_s/\bar{D}$ must be in excess of unity before one can safely assume that $\Lambda_s > 0$. Hopefully more precise and more direct methods will be forthcoming.

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(6) Roberts et al. (Roberts, A. J.; Cureton, C. G.; Phillips, D. *Chem. Phys. Lett.* **1980**, *55*, 554) have argued that the decay at 360 nm required a three-exponential fit. Our signal-to-noise ratio would not allow a meaningful fit of this type to be undertaken.

(7) This follows the kinetic scheme of Johnson as applied to PVCz.[4] More recent work[6,23] has suggested that the fluorescence decay in the monomer region is more complex than a simple monomer–excimer dissociation. Our experimental precision is not adequate to detect these small differences and the biexponential form is able to provide a reasonably good fit to the experimental data.

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(9) Frank and Hurrah (Frank, C. W.; Hurrah, L. A. *J. Chem. Phys.* **1974**, *61*, 1526) have estimated that the fraction of preformed excimer pairs in P2VN at 20 °C is approximately 10^{-2}. (b) Similarly Klöpffer (Klöpffer, W. *J. Chem. Phys.* **1969**, *50*, 2337) has estimated this fraction to be 10^{-3} for PVCz, based on his fluorescence quenching data.

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(11) These results have been presented eariler in ref 1 and 2. Reference 1 has the full quenching expressions for the case in which k_d cannot be ignored.

(12) The data plotted in Figures 4 and 5 is an average of several wavelengths in the monomer and excimer region (e.g., for P2VN, use 330–350 nm for M and 400–460 nm for D). The Stern–Volmer constants for this averaged data are essentially the same as the average of the Stern–Volmer constants for the data at each wavelength treated independently.

(13) All least-squares fits were done by using the MINITAB statistical package installed on The University of Texas computer system.

(14) This is in contradiction to ref 2, where relations 6 and 7 were used to obtain $K_{SV}{}^{M}$ and $K_{SV}{}^{D}$ for PVCz quenching by trichloro- and tribromoacetic acid. In ref 2 quencher concentrations up to 10× the present work were used. An analysis like ref 2 was used in ref 15 for quenching by dimethyl terephthalate.

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(20) Because of the larger physical size of DCP, it is reasonable to assume that $D_{DCP} < D_{EtCz}$. However, singlet energy transfer can occur between the two chromophores, such that $R_{DCP} > R_{EtCz}$. Thus if $P_{DCP} \approx P_{EtCz}$, the net quenching rates would be expected to be comparable. A similar argument can be made for DNP.

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(22) Klöpffer[9b] estimated Λ_s to be on the order of 200 Å for films of PVCz. Presumably this larger Λ_s value reflects the absence of chromophore mobility in solution, which can produce a singlet exciton trap during the lifetime of PVCz-M.

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Kinetics of Doping and Degradation of Polyacetylene by Oxygen

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ABSTRACT: The kinetics of oxidative degradation of various cis/trans compositions of polyacetylene have been studied. It has been shown that the degradation process follows an initial doping that is normally observed for polyacetylene with other electron acceptors. The kinetics of degradation are first order and have been modeled with consecutive reaction theory. Two first-order rate constants are observed with higher trans content materials (>50% trans). For a given trans content, the rate constants provide identical activation energies. The activation energies range from ~9 (30 and 60% trans) to 13.8 kcal/mol (~98% trans). Simultaneous conductivity–oxygen uptake experiments indicate maximum conductivity at 0.14 O_2 molecules per -CH=CH- unit. These results indicate the absolute necessity for an oxygen-free environment to obtain the intrinsic electrical properties of this interesting polymer.

The doping of polyacetylene [$(-CH{=}CH-)_n$] to highly conductive metallike behavior has recently been the subject of intense study.[1-5] Such dopants as the halogen gases,[5] AsF_5, BF_3, BCl_3, SO_2, NO, and HCN[1] have been studied. With the exception of one paper,[1] the effect of oxygen, which is a pervasive electron acceptor, has not been studied. In that paper, $(-CH{=}CH-)_n$ was prepared with an oxygen content as low as 0.7 wt %. It was noted that exposure to oxygen for long time periods caused irreversible chemical changes in the material. Unfortunately, those studies were conducted on compressed powder pellets of $(-CH{=}CH-)_n$ and results are difficult to extrapolate to continuous films. Since the oxidative degradation process can have profound effects on the ultimate properties of $(-CH{=}CH-)_n$, we have undertaken a study on the effect of oxygen on the conductivity and the kinetics of degradation of continuous polyacetylene films. Preliminary accounts of this work have appeared.[6-8]

Experimental Section

Polyacetylene was prepared by the method of Shirakawa[9] and was approximately 160-μm thick. Samples were stored in an O_2-free environment (<0.8 ppm). Initially, the sample was 90% cis as determined by infrared measurements. Various cis/trans ratios were obtained via thermal treatment. A 98% trans sample was made by heating a cis sample at 200 °C for 3 h in an argon atmosphere. Cis–trans ratios cited are prior to oxidation.

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