Nonexponential Transient Behavior in Fluorescent Polymeric Systems

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ABSTRACT: A simple one-dimensional electronic energy transport model is used to compute the integrated, average density of monomer excitations, $G^D(t)$, for a dilute solution of an aromatic vinyl polymer. The time behavior of $G^D(t)$ is nonexponential for a simple kinetic scheme that includes electronic energy migration, rotational sampling, and the usual decay processes for a single monomer and excimer species. The fluorescence response functions for the monomer and excimer ($i_M(t)$ and $i_E(t)$) are related to $G^D(t)$ and, *in general, are not given in terms of multiple exponentials.* A time-independent trapping rate constant is not able to describe the trapping of singlet excitations at excimer-forming sites in the presence of electronic energy migration. The ratio of excimer-to-monomer quantum yields (ϕ_E/ϕ_M) is obtained directly from the Laplace transform of $G^D(t)$. A simple expression is obtained for the quantum yield ratio, which may be useful for the interpretation of photostationary-state fluorescence experiments in solutions and solid blends of aromatic vinyl polymers. The most significant result of this work is the demonstration that numerically resolved exponentials cannot uniquely determine an excited-state kinetics scheme.

I. Introduction

Recent time-resolved fluorescence studies on various aromatic homopolymers and copolymers have led to a great deal of discussion regarding the excited-state kinetics in such systems.[1–11] Most of the polymers studied are capable of forming intramolecular excimers, so the important experimental observables in these systems are the radiative decay of the excited monomer and the buildup and decay of the excimer. In poly(*N*-vinylcarbazole),[1] poly(1-vinylnaphthalene),[8] poly(2-vinylnaphthalene),[8] poly(1-naphthyl methacrylate),[8] and copolymers of 1-vinylnaphthalene and methyl methacrylate,[11] it has been found that the monomer emission intensity can be empirically fit to a triple exponential

$$i_M(t) = A_1e^{-\lambda_1 t} + A_2e^{-\lambda_2 t} + A_3e^{-\lambda_3 t} \qquad (1)$$

All of these studies point to the fact that the Birks kinetic scheme,[12] which treats excimer formation between small molecules in solution as a collisional process, is not applicable to intramolecular excimer formation in macromolecules.

Except for a few claims to the contrary,[13] it is generally accepted that trapping of the singlet exciton in the aromatic polymers proceeds via radiationless energy migration to an excimer-forming site (EFS). In solution, the trapping process is enhanced by rotational sampling of an EFS during the lifetime of the monomeric species. Macroscopic diffusion of chromophores into excimer configurations is also present, but this phenomenon is expected to be much less important for polymers than for small molecules. In the most general situation, excimer formation in solutions of macromolecules proceeds through a complex pathway involving energy transport, segmental rotation, and chromophore diffusion. It should *not* be expected that the kinetics in such a system can be described in terms of a simple trapping rate constant, k_{EM}, as has been commonly assumed.[3,6,11]

Recent theoretical studies of electronic energy transport (EET) and trapping in random systems of donor and trap species have shown that fluorescence decays are, in general, *nonexponential.*[14–20] Specifically, Wieting[14] has shown that the trapping dynamics in one-dimensional and quasi-one-dimensional molecular crystals cannot be described by a trapping rate *constant*; rather, a trapping rate *function* $k(t)$ must be used. The form of $k(t)$ proposed by Wieting leads to nonexponential transient fluorescence decays for the donor and acceptor species. Klafter[21] has developed expressions for the asymptotic behavior of $k(t)$, applicable to systems with primarily one-dimensional character, and various transport mechanisms. Using a diagramatic technique developed by Gochanour,[16] Loring[17,18] has shown the fluorescence decays for randomly distributed donors and traps in one, two, and three dimensions to be nonexponential, and Huber[19,20] has demonstrated the same result with a t matrix and coherent potential approach. In a recent study,[22] we have illustrated that ideal chains containing randomly distributed donor and trap chromophores can also exhibit nonexponential transient fluorescence behavior.

In spite of these results, there have been numerous attempts to identify numerically resolved exponentials with physical entities in complicated excited-state kinetic schemes. Some of the schemes proposed for the aromatic polymers hypothesize the existence of additional monomeric excited states,[4–6,11] while others suggest additional excimeric species.[1,10] While it is likely that the kinetics may indeed be more complicated than originally believed, the proposed kinetic schemes do not provide unique explanations for the observed decays. In the presence of electronic energy migration, practically any kinetic scheme can lead to nonexponential behavior that can be resolved into a finite series of exponentials.

We will demonstrate in this paper that the morphological characteristics of a polymer will determine a distribution of topologically distinct energy transport pathways from monomer to EFS. With each pathway is associated a characteristic transport time; the observed fluorescence decay is the ensemble average over all possible migrative paths. We intend to show that multiexponential decays can be explained in terms of a few dominant energy transport pathways, with characteristic times that do not correspond to the lifetimes of additional physical entities. It will become apparent that valid conclusions regarding excited-state kinetics in the aromatic polymers cannot be based on the number of numerically resolved exponentials.

II. Model

The photostationary-state excimer/monomer quantum yield ratios in solid blends of the aromatic vinyl polymers have been adequately described in terms of one-dimensional[23,24] and three-dimensional[25] energy transport models. In a previous treatment of aromatic polymers in solution,[26] however, the EET process was greatly oversimplified in order to emphasize rotational sampling of excimeric sites. Here, we will attempt to describe more accurately the

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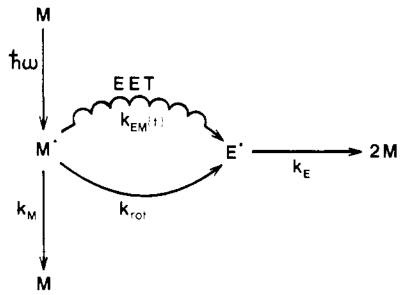

Figure 1. Simple excited-state kinetic scheme for a single monomer and excimer species. On absorption of a quantum of radiation, an unexcited monomeric chromophore (M) is promoted to the first singlet excited state (M*). The excited monomer can undergo radiative or nonradiative decay (rate constant k_M), participate in excimer formation through electronic excited-state migration (trapping rate function $k_{EM}(t)$), or form an excimer (E*) directly through rotational sampling (rate constant k_{rot}). The excimer trap may decay radiatively or nonradiatively with rate constant k_E.

general situation in polymer solutions, where both singlet energy migration and segmental rotation contribute to the excimer formation process.

To illustrate how nonexponential behavior can arise in fluorescent polymers, we have chosen to model dilute chains of an aromatic vinyl homopolymer (such as polystyrene or poly(vinylnaphthalene)) in a "good" solvent. In such a system the random coils will be extended and isolated, causing energy migration to proceed in a primarily one-dimensional fashion along the chain backbone.[22-25] The dominant EFS trap species in this morphological situation will be the adjacent intramolecular excimer;[27] for simplicity we will neglect excimer formation between different parts of the same chain. Furthermore, a very simple kinetic scheme with a single monomer and excimer species will be assumed.

Figure 1 depicts the excited-state kinetics of our hypothetical polymer. The excited monomer can proceed to the excimer via two pathways: segmental rotation with a rate constant k_{rot}, or one-dimensional energy migration described by a characteristic trapping rate *function* $k_{EM}(t)$. The presence of a higher dimensional energy transport pathway or the inclusion of excimer dissociation and other kinetic complications will not affect the conclusions of the foregoing analysis. The general transient fluorescence behavior in any case will be seen to be nonexponential.

The dominant configurational parameter governing the rate of EET is the interchromophore separation, regardless of whether multipole or exchange interactions are considered. Since the lattice spacing in crystalline naphthalene (c = 6 Å) is comparable with the average distance between adjacent chromophores on a poly(vinylnaphthalene) chain, the observed singlet exciton hopping time in the crystalline system ($t_H \sim O(10^{-12}$ s)[28]) can be used as an order-of-magnitude estimate of the upper limit to the EET rate in the polymer. Segmental reorientation times for polystyrene in solution, however, have been estimated by electron spin resonance[29] to be considerably slower, $t_{rot} \sim O(10^{-10}$ s) at 300 K. As a result, it is reasonable to assume that there exists a range of moderate experimental conditions where segmental rotation is at least an order of magnitude slower than energy migration. The formalism to be presented in this section will be based on a model polymeric system that satisfies this criterion.

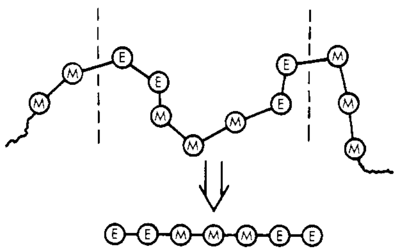

Figure 2. Segmental decomposition. A high molecular weight polymer chain with an equilibrium excimer-forming site population can be thought of as a sequence of segments, each segment consisting of an unbroken string of monomeric chromophores bounded at both ends by an excimer trap. If only adjacent chromophore resonance interactions are considered, the traps are disruptive and all electronic energy migration is restricted to within a segment.

If only nearest-neighbor resonance interactions are considered and segmental rotation takes place on a slower time scale than energy migration, the excited-state dynamics of a polymer chain can be treated in the following manner. First, the equilibrium EFS population of a high molecular weight polymer is allowed to divide the chains into finite-length segments of monomeric chromophores (see Figure 2). The excimer traps on the ends of such a segment are considered to be disruptive,[30,31] in that they terminate any down-chain energy migration. Next, since rotation is assumed slower than migration, the primary effect of segmental rotation will not be to disturb the equilibrium trap population but to directly trap the excitation during its residence on a particular monomeric chromophore. Under these conditions, the dynamics of isolated, incoherent electronic excitations for a finite segment of n monomeric chromophores can be described by a Pauli master equation[30]

$$\frac{d}{dt}p_j'(t) = W[p_{j+1}'(t) - 2p_j'(t) + p_{j-1}'(t)] - (k_M + k_{rot})p_j'(t), \qquad 2 \le j \le n-1 \tag{2a}$$

$$\frac{d}{dt}p_1'(t) = W[p_2'(t) - p_1'(t)] - Vp_1'(t) - (k_M + k_{rot})p_1'(t) \tag{2b}$$

$$\frac{d}{dt}p_n'(t) = W[p_{n-1}'(t) - p_n'(t)] - Vp_n'(t) - (k_M + k_{rot})p_n'(t) \tag{2c}$$

In eq 2, $p_j'(t)$ represents the probability that an excitation exists on monomeric chromophore "j" at time t. The quantity W represents the rate constant for nearest-neighbor EET between two donor (monomer) chromophores, averaged over the transition moment orientation and interchromophore separation associated with each rotational dyad. Similarly, V represents the conformational average of the rate constant for EET from a donor chromophore to an adjacent chromophore in an EFS (i.e., a trap site). The rate constant k_M reflects the total rate of monomer decay by radiative and nonradiative processes in the absence of EET and rotational sampling. Finally, the rate constant k_{rot} is used to represent the rate at which a singlet excitation on a monomeric chromophore is transformed into an excimer by segmental rotation.

Since an excimer in the dissociated state consists of two monomeric chromophores, a reasonable approximation for the donor-trap rate constant is

$$V \cong W \tag{3}$$

If an effective lifetime is defined by

$$\tau^{-1} \equiv k_M + k_{rot} \tag{4}$$

eq 3 with the substitution

$$p_j(t) = p_j'(t)\exp(t/\tau) \tag{5}$$

leads to a simplified master equation

$$\frac{d}{dt}p_j(t) = W[p_{j+1}(t) - 2p_j(t) + p_{j-1}(t)], \qquad 2 \le j \le n-1 \tag{6a}$$

$$\frac{d}{dt}p_1(t) = W[p_2(t) - 2p_1(t)] \tag{6b}$$

$$\frac{d}{dt}p_n(t) = W[p_{n-1}(t) - 2p_n(t)] \tag{6c}$$

The donor response function for a segment of length n can be defined by

$$G_n{}^{D}(t) = \sum_{i=1}^{n} p_i(t) \tag{7}$$

Pearlstein[30] gives expressions for $G_n{}^{D}(t)$ with the uniform initial condition

$$p_j(t = 0) = 1/n, \qquad 1 \le j \le n \tag{8}$$

and no-flux boundary conditions

$$p_0(t) - p_1(t) = 0 = p_n(t) - p_{n+1}(t) \tag{9}$$

In the case of $V/W = 1$, the expression takes the form

$$G_n{}^{D}(t) = \frac{2}{n(n+1)}\sum_{k=1}^{n^*}\cot^2\left(\frac{\alpha_k}{2}\right)\exp\left[-4Wt\sin^2\left(\frac{\alpha_k}{2}\right)\right] \tag{10a}$$

with

$$\alpha_k \equiv \frac{(2k-1)\pi}{n+1} \tag{10b}$$

and

$$n^* \equiv n/2, \qquad n \text{ even}$$
$$n^* \equiv (n+1)/2, \qquad n \text{ odd} \tag{10c}$$

The corresponding response function for an entire chain is obtained by averaging the finite-segment result over all segment lengths. This average must allow for the initial excitation of excimeric sites. Fitzgibbon[23] has shown that for spatially uniform excitation, the probability that a photon is absorbed by a monomeric chromphore in a segment of length n is

$$P(n,L) = (L - n - 3)q^2(1-q)^{n+1}(n/L), \qquad n \le L - 4$$

where L is the total chain length expressed in monomer units and q is the equilibrium fraction of conformational *dyads* in adjacent intramolecular EFS. Thus, for infinite molecular weight chains the appropriate ensemble-averaged response function is given by

$$G^{D}(t) = \sum_{n=1}^{\infty} q^2 n(1-q)^{n+1} G_n{}^{D}(t) \tag{11}$$

It is clear that

$$G^{D}(t = 0) = (1-q)^2 = 1 - f_R \tag{12}$$

where f_R is the equilibrium fraction of *chromophores* in adjacent intramolecular EFS.[27] Equation 12 is the relation between the chromophore and dyad trap fractions for infinite molecular weight chains. The dyad trap fraction, q, can be obtained rigorously from equilibrium statistical methods[32] if it is known which dyads are capable of forming excimers. For polystyrene and poly(2-vinylnaphthalene) the principal excimer-forming dyad is believed to be the trans–trans meso dyad.[23,24]

The average donor (monomer) response function, $G^{D}(t)$, represents the probability that a single excitation produced at $t = 0$ is still residing on a monomeric chromophore at time t, if the excitation has an infinite lifetime (cf. eq 5). Equations 10 and 11 indicate that $G^{D}(t)$ has the form of an infinite series of exponentials, in general, a *nonexponential* result. We will show in section III that $G^{D}(t)$ can be directly related to the monomer and excimer fluorescence response functions,[12] $i_M(t)$ and $i_E(t)$. In addition, $G^{D}(t)$ completely determines the photostationary-state quantum yield ratio ϕ_E/ϕ_M. Thus, to study the presence of nonexponential behavior, it will be sufficient to consider $G^{D}(t)$.

At large excimer trap fractions, q, there will be a finite number of exponentials that contribute to the sum in eq 11. The conformationally averaged EET rate constant, W, and the magnitude of q will determine a set of dominant modes for the decay of $G^{D}(t)$. With each mode will be associated a characteristic time given by $[4W\sin^2(\alpha_k/2)]^{-1}$, which *does not correspond to the lifetime of any excited species in the system. Instead, each characteristic decay time is associated with a dominant energy transport pathway from donors to traps.* Thus, even with the simplest of kinetic schemes, the presence of energy migration can lead to the observation of multiexponential decays. Furthermore, there is no reason to expect that only two or three exponentials will contribute to $G^{D}(t)$ at large trap fractions. The number of exponentials observed will depend not only on the dynamics of the system but also on the finite resolution of the transient apparatus and fitting routines.

By an application of the t-matrix approach of Huber,[19] we obtain an expression for $G^{D}(t)$ valid for small trap concentrations, $q \ll 1$, and long times, $tW > 1$

$$G^{D}(t) = (1-q)^2\exp(4q^2Wt)\,\text{erfc}\,[2q(Wt)^{1/2}] \tag{13}$$

where erfc (x) is the complementary error function. Equation 13 is clearly a nonexponential result; indeed, it exhibits diffusive asymptotic behavior

$$G^{D}(t) \sim [4\pi q^2Wt]^{-1/2}(1-q)^2, \qquad t \to \infty \tag{14}$$

In recent work that appeared after this study was completed, Movaghar[33] has presented an exact solution to the trapping problem in one dimension and has shown that it differs in analytic form with the t-matrix result, eq 13, for small trap fractions. However, significant quantitative differences in the time behavior of the two solutions only appear at long times when $G^{D}(t)$ has decayed to a small fraction of its initial value. Thus, the transient and photostationary results presented here should adequately describe the fluorescence response of our model chains.

III. Analysis of Response

The next task is to relate $G^{D}(t)$ to the observables in a transient or photostationary fluorescence experiment.[17,18,22] First, two normalized excited-state probabilities are defined: $H^{M}(t) \equiv$ probability of an excitation being on a monomer at time t if the monomer has a finite lifetime given by $\tau = [k_M + k_{rot}]^{-1}$; $H^{E}(t) \equiv$ probability of an excitation being on an excimer trap at time t if the monomer lifetime is τ and the excimer lifetime is infinite. From the definition of $G^{D}(t)$ and the substitution made in eq 5, it is evident that $H^{M}(t)$ is given by

$$H^{M}(t) = \exp(-t/\tau)G^{D}(t) \tag{15}$$

In addition, the kinetic scheme of Figure 1 requires that $H^{M}(t)$ and $H^{E}(t)$ satisfy the population equations

$$\frac{d}{dt}H^{M}(t) = -\frac{1}{\tau}H^{M}(t) - k_{EM}(t)H^{M}(t) \tag{16a}$$

$$\frac{d}{dt}H^{E}(t) = k_{rot}H^{M}(t) + k_{EM}(t)H^{M}(t) \tag{16b}$$

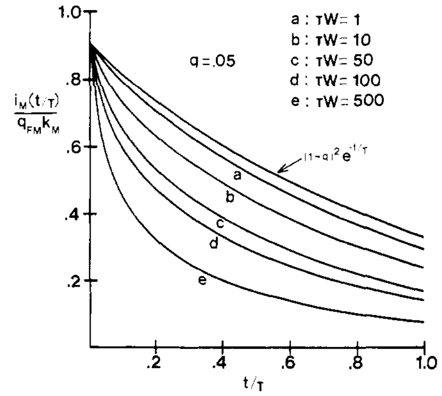

Figure 3. Transient behavior of the monomer fluorescence response function, $i_M(t)$. At a fixed dyad trap fraction, q, the decay of $i_M(t/\tau)$ becomes highly nonexponential as the energy transport rate, or $\alpha \equiv W\tau$, is increased. For very small values of α, rotation and monomer decay dominate energy migration and the response function is close to a single exponential, $i_M(t/\tau)/q_{FM}k_M \cong (1 - q)^2 \exp(-t/\tau)$.

Equations 15 and 16a require that the trapping rate function be given by

$$k_{EM}(t) = -\frac{d}{dt}[\ln G^D(t)] \tag{17}$$

Insertion of eq 15 and 17 into eq 16b leads to the result

$$\frac{d}{dt}H^E(t) = k_{rot}e^{-t/\tau}G^D(t) - e^{-t/\tau}\frac{d}{dt}G^D(t) \tag{18}$$

Since

$$G^D(t = 0) = 1 - f_R \tag{19a}$$

and

$$H^E(t = 0) = f_R \tag{19b}$$

the Laplace transform of eq 18 is given by

$$\tilde{H}^E(s) = [1 - (s + k_M)\tilde{G}^D(s + 1/\tau)]/s \tag{20}$$

The monomer decay function is defined as $P_M(t) \equiv$ cumulative probability of monomer decay (radiative and nonradiative) by time t. It is easily seen that $P_M(t)$ is given by

$$P_M(t) = 1 - H^M(t) - H^E(t) \tag{21}$$

Equation 20 and the Laplace transform of eq 15 lead to an expression for the transform of $P_M(t)$

$$\tilde{P}_M(s) = \frac{k_M}{s}\tilde{G}^D(s + 1/\tau) \tag{22}$$

A primary experimental observable in transient fluorescence experiments is the monomer fluorescence response function,[12] defined as

$$i_M(t) = q_{FM}\frac{d}{dt}P_M(t) \tag{23}$$

with $q_{FM} \equiv$ quantum efficiency for monomer fluorescence. Noting that $P_M(t = 0) = 0$ and making use of eq 22 allow calculation of the Laplace transform of $i_M(t)$

$$\tilde{i}_M(s) = q_{FM}k_M\tilde{G}^D(s + 1/\tau) \tag{24}$$

A similar analysis of the trap fluorescence leads to

$$\tilde{i}_E(s) = \frac{q_{FE}k_E[1 - (s + k_M)\tilde{G}^D(s + 1/\tau)]}{s + k_E} \tag{25}$$

where $\tilde{i}_E(s)$ is the Laplace transform of the excimer fluorescence response function, $q_{FE} \equiv$ quantum efficiency of excimer fluorescence, and $k_E \equiv$ rate of excimer decay by radiative and nonradiative processes.

Previous Monte Carlo results[23,24] indicate that the equilibrium adjacent intramolecular trap concentration is very small for polystyrene and poly(2-vinylnaphthalene). Thus, eq 13 should provide a good approximation to the donor response function of our model polymer. With this choice for $G^D(t)$, the Laplace transform inversions required in eq 24 and 25 can be performed analytically. We obtain

$$i_M(t) = q_{FM}k_M(1 - q)^2 \exp[(4q^2W - k_M - k_{rot})t] \operatorname{erfc}[2q(Wt)^{1/2}] \tag{26}$$

and

$$i_E(t) = q_{FE}k_E\{A \exp(-k_Et) - B \exp[(4q^2W - k_M - k_{rot})t] \times \operatorname{erfc}[2q(Wt)^{1/2}] - C \exp(-k_Et) \times \operatorname{erf}[(k_M + k_{rot} - k_E)^{1/2}t^{1/2}]\} \tag{27}$$

with

$$A \equiv 1 + (1 - q)^2\lambda \tag{28a}$$

$$B \equiv (1 - q)^2(\lambda + 1) \tag{28b}$$

$$C \equiv (1 - q)^2\lambda\left[\frac{4q^2W}{k_M + k_{rot} - k_E}\right]^{1/2} \tag{28c}$$

$$\lambda \equiv \frac{k_M - k_E}{4q^2W + k_E - k_M - k_{rot}} \tag{28d}$$

Figure 3 illustrates the time behavior of eq 26 for several values of a dimensionless rate parameter, $\alpha \equiv W\tau = W/(k_{rot} + k_M)$. At very small values of α, the behavior of $i_M(t)$ is dominated by rotational and decay processes, making the response function nearly a single exponential. At larger values of α, EET is rapid, and Figure 3 demonstrates that the monomer fluorescence response function exhibits highly nonexponential behavior. It is interesting to note that single-exponential monomer decay has been observed for polystyrene (PS) in solution,[34] while the poly(2-vinylnaphthalene) (P2VN) monomer exhibits complex, multiexponential behavior.[8] Although the PS study was performed with less sophisticated techniques, this result may indicate that EET is considerably slower in PS than in P2VN.

Figures 4 and 5 show the time dependence of $i_E(t)$, computed with eq 27. Figure 4 demonstrates that as the energy transport rate is increased, the peak of the excimer emission intensity is shifted toward shorter times, and the overall intensity is larger. Thus, rapid EET moves excitations to traps quickly and also decreases the probability that an excitation will be lost into monomer emission. Figure 5 illustrates that the excimer fluorescence intensity at a fixed energy transport rate is greatly enhanced by rotational sampling. Segmental rotation acts uniformly throughout the lifetime of the monomeric species, however, shifting the maximum excimer intensity peak to longer times with increasing rotation rate. Both rotational sampling and electronic energy migration strengthen excimer emission at the expense of the monomer.

To complete the transient analysis, we note that for sufficiently small trap concentrations, eq 13 and 17 lead to an expression for the trapping rate function

$$k_{EM}(t) \cong (4q^2W/\pi t)^{1/2}, \qquad q^2 \ll \pi/16tW \tag{29}$$

Wieting[14] and Klafter[21] have found similar $\sim t^{-1/2}$ ex-

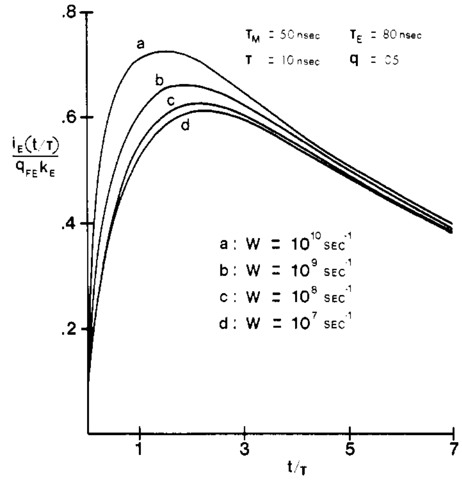

Figure 4. Transient behavior of the excimer fluorescence response function as a function of the conformationally averaged energy transport rate. For fixed monomer and excimer lifetimes ($\tau_M \equiv 1/k_M$, $\tau_E \equiv 1/k_E$) and fixed effective monomer lifetime in the presence of segmental rotation ($\tau \equiv 1/(k_{rot} + k_M)$), the effect of increasing the EET rate is to move excitations to traps more rapidly. As a result, the intensity of excimer emission is increased, and the maximum intensity is shifted to shorter times.

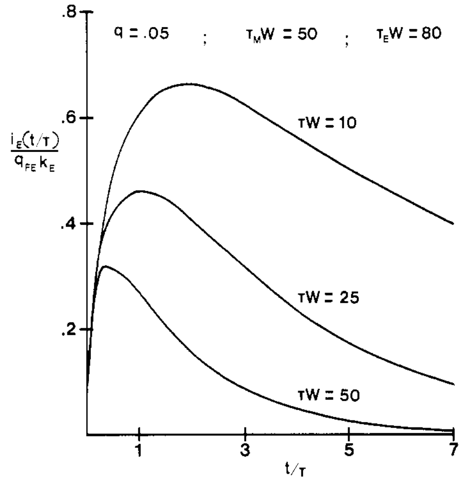

Figure 5. Effect of rotational sampling on the excimer fluorescence response function. With $\tau_M W$ and $\tau_E W$ fixed, the effect of decreasing $\alpha \equiv \tau W = W/(k_{rot} + k_M)$ is to increase the rate of rotational sampling. The lower curve corresponds to $\tau = \tau_M$, or $k_{rot} = 0$. As the rotational rate is increased, excimer emission is favored over monomer decay throughout the lifetime of the monomer. Thus, the overall excimer intensity is increased, and the peak is shifted to longer times.

pressions for the trapping rate function via random walk formalism in one dimension. In addition, attempts to fit experimental data to expressions derived from trapping rate functions of the form

$$k(t) = C_1 + C_2t^{-1/2} \tag{30}$$

have met with considerable success in molecular crystals.[15,28] Physically, C_1 characterizes the asymptotic trapping rate due to energy migration in three dimensions, while C_2 determines the extent of the short-time, nonexponential behavior resulting from both one- and three-dimensional transport. Equation 30 leads to a monomer response function of the form

$$i_M(t) = q_{FM}k_M \exp[-(C_1 + 1/\tau)t - 2C_2t^{1/2}] \tag{31}$$

We suggest that eq 31 may be applicable to fluorescent polymeric systems with a quasi-one-dimensional migrative pathway.[14,21]

In a photostationary-state fluorescence experiment with one excited monomer and excimer species, the quantum yield ratio is given by

$$R \equiv \frac{\phi_E}{\phi_M} = \frac{q_{FE}}{q_{FM}}\left[\frac{1 - M}{M}\right] \tag{32}$$

with ϕ_E (ϕ_M) ≡ fluorescence quantum yield of excimer (monomer) and M ≡ probability that an absorbed quantum will end up in radiative or nonradiative *monomer* decay. In general, M contains all the morphological and dynamical information to specify the path of an excitation in the polymeric system. It is important to realize that eq 32 is a general result *that does not assume Birks kinetics.* It should also be noted that the definition of M presented here differs from previous analysis.[23] An expression for M when no excimer dissociation is present is given by the long-time limit of $P_M(t)$. From eq 22 and the final value theorem for Laplace transforms, it follows that

$$M = \lim_{t\to\infty} P_M(t) = k_M\tilde{G}^D(s = 1/\tau) \tag{33}$$

Using eq 13 for $\tilde{G}^D(s)$, we obtain results for a small fraction of EFS

$$M = k_M\tau(1 - q)^2/(1 + 2q(\tau W)^{1/2}) \tag{34}$$

and

$$R = \frac{q_{FE}}{q_{FM}} \times \left[\frac{k_{rot}/k_M + 2q[1 + (W/k_M)^{1/2}(1 + k_{rot}/k_M)^{1/2}] - q^2}{(1 - q)^2}\right] \tag{35}$$

Equation 35 has very interesting limiting behavior. If rotation is slow compared to migration, so that $W/k_M \gg k_{rot}/k_M > 1$, and $W > \tau k_{rot}^2/(4q^2)$, eq 35 becomes

$$R \cong \frac{q_{FE}}{q_{FM}}\left[\frac{2q}{(1 - q)^2}\right]\left[\frac{Wk_{rot}}{k_M^2}\right]^{1/2} \tag{36}$$

Equation 36 may be applicable to high molecular weight naphthalene polymers in solution at room temperature. Support for this claim comes from the fact that if a Stokes law expression is assumed for k_{rot}, the ratio has the viscosity dependence

$$R \sim \eta^{-1/2} \tag{37}$$

This result agrees quite well with the experimental results of Fitzgibbon,[26] who found that photostationary fluorescence data for 300 000 molecular weight poly(2-vinylnaphthalene) in toluene could be fit to an empirical expression of the form

$$R = A\eta^{-\beta} \tag{38}$$

with a best-fit value of the exponent $\beta = 0.511$.

In a situation where segmental rotation is extremely fast and energy migration is negligible, the $(W,q) \to 0$ limit of eq 35 is

$$R \cong \frac{q_{FE}}{q_{FM}}\left(\frac{k_{rot}}{k_M}\right) \tag{39}$$

Equation 39 is identical with the β-regime result, obtained from the Birks scheme when the excimer dissociation rate is assumed much smaller than k_E.[26]

As a final special case, we consider a miscible solid blend below the glass transition temperature. In this situation it is reasonable to take $k_{\mathrm{rot}} = 0$, so that eq 35 becomes

$$R = \frac{q_{\mathrm{FE}}}{q_{\mathrm{FM}}}\left[\frac{2q(1 + (W/k_{\mathrm{M}})^{1/2}) - q^2}{(1 - q)^2}\right] \tag{40}$$

Equation 40 shows that R is proportional to f_{R} for small trap concentrations. Furthermore, it has been demonstrated that q shows Arrhenius temperature behavior.[24] Thus, we propose that a series of experiments to obtain the temperature dependence of the quantum efficiency ratio in a miscible solid blend could be used as a means of verifying eq 40, since the temperature behavior of R has been previously reported.[27]

IV. Discussion and Conclusions

We have demonstrated with a simple, one-dimensional model that electronic energy migration can lead to nonexponential or multiexponential fluorescence decays, even with only one monomer and excimer species. The rate of trapping in a macromolecular system is dictated by the energy transport mechanism, the rate of rotational sampling, and any other processes that can lead to excimer formation, such as inter- and intrachain diffusion. If EET plays a dominant role in the photophysics of the polymeric system, it should be clear that use of a trapping rate constant is not appropriate for the kinetic analysis of exciton trapping. At very high temperatures in nonviscous solvents, however, rotational sampling and excimer dissociation could become the rate-determining steps to excimer formation, allowing a rate constant formalism. Nevertheless, our preliminary calculations indicate that EET in the aromatic vinyl polymers is very rapid. In support of this is the fact that similar transient fluorescence behavior has been observed both in glassy films and in solution.[4] Thus, it is likely that energy migration must be included in the kinetic analysis for the majority of morphological situations and experimental conditions.

In reality, the random coil of an aromatic polymer provides a quasi-one-dimensional pathway for the transport of electronic excitations. Although we have treated the problem in terms of a single-step, one-dimensional random walk, there will certainly be some three-dimensional EET across loops in the chain and between chromophores on separate chains. Nevertheless, the conclusions drawn from the simple one-dimensional model will still apply to a higher dimensional transport pathway. Quasi-one-dimensional migration will simply alter the distribution of migrative paths, producing a different set of characteristic decay modes.

Overall, we must acknowledge that excimer formation in the aromatic polymers may proceed through a very complex series of energy transport steps, intermediate excited-state entities, and dynamical processes. Fundamental experiments must be performed that will elucidate the underlying photophysical processes before the exceedingly complex problem of a polymer in solution can be addressed. We emphasize that a particular set of numerically fit exponentials cannot uniquely determine the excited-state kinetics in such a system. Thus, rate parameters obtained from multiexponential fits of fluorescence data must be viewed with some skepticism.

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