# Energy Migration along Rigid-Rod Polymer Chains

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ABSTRACT: Energy migration along rigid-rod polymer chains with an energy trap attached to one end is examined. Analytical expressions are found for the transient fluorescence intensity functions of the main-chain chromophores (donors) and the trap and for the capturing efficiency of the donor excitation energy by the trap. The validity of those expressions is verified.

## I. Introduction

Photon energy absorbed by a chromophore in $N$ closely-packed identical chromophores does not stay localized. It can be exchanged many times by energy migration among these chromophores before deactivation.[1,2] This paper focuses on singlet energy migration.

Energy migration occurs in photosynthesis.[3] In plants, the light-collecting pigment molecules, chlorophyll, are arranged in a spread-out fashion so as to expose a maximum surface area to the sun. The absorbed sunlight is then transported through energy migration to photoreaction centers and concentrated to allow processes such as two-photon oxidation of water to occur. Energy migration is also believed to occur in synthetic aromatic polymers and has been the topic of extensive studies in the past 2 decades.[1,2]

In most of the previous studies, polymers synthesized by free-radical polymerization have been used. Those polymers generally do not have well-defined structures. In cases when energy migration is detected by monitoring the efficiency of energy trapping by traps copolymerized in a small quantity with the main component, each chain of the studied samples may contain more than one randomly located energy trap. These copolymers are generally flexible, and their chains assume a random-coil conformation. Due to this random-coil conformation, distances between chromophores are uncontrolled and excimer formation is possible. Excimer-forming sites function as reversible energy traps; i.e., the energy associated with such a site is not mobile initially but is free to migrate again once the excimer dissociates. The excimer-forming sites compete with incorporated traps for the excitation energy, and excimer formation complicates data analysis.

Due to structural uncertainties, e.g., the unknown number and positions of traps or excimer-forming sites, associated with polymer chains and due to the statistical nature of the chain conformation, theories describing energy migration in such systems are generally complex[3-9] and experimental results obtained are often not completely convincing. Gelles and Frank,[8,9] for example, explained the enhancement in the ratio of excimer to monomer fluorescence emission intensity with the increase in the molar mass of styrene oligomers in terms of intramolecular energy migration. As the oligomer molar mass increases, the probability for finding at least one excimer-forming site in a chain increases. The excimer-forming site or sites may then trap an initially freely roaming exciton and thus decrease monomer but increase excimer emission. MacCallum,[10] on the other hand, argued that the phenomenon can also be accounted for without involving the concept of energy migration. According to MacCallum,[10] segments located close to the ends of a polymer chain possess a higher rotational mobility and are, therefore, less liable to form excimers. As the oligomer molar mass increases, the relative end-group concentration decreases and thus increases the fluorescence intensity ratio between excimers and monomers. Guillet has stated that "in spite of the extensive research, the quantification of the extent, and indeed the existence, of singlet energy migration remains a difficult task".[1]

Unambiguous studies require the use of polymer chains which are well-defined in structure. Preferably, the chains should be rigid and one-dimensional. The syntheses of polymer chains which meet these requirements have been reported by Sisido et al.[11] for polypeptides with pendant naphthyl,[11,12] anthryl,[13] pyryl,[14] and azobenzene[15] groups. These polypeptides assume a $\alpha$-helical main-chain conformation in trimethyl phosphate or THF. The pitch of the helical chains was determined to consist roughly of four amino acid units. The distance between two adjacent chromophores in a polypeptide can be easily adjusted by the incorporation of spacing amino acid groups. When three amino acid groups were used to space two adjacent chromophore-substituted amino acid monomers, the distance between successive chromophores was around 7 Å. Since the critical distance for the dipole–dipole energy transfer[16] between two identical chromophores can be easily as large as 20 Å such as for 9-fluoryl groups,[17] the distance of 7 Å is thus short enough to allow efficient energy exchange between two adjacent chromophores. For excimer formation, a chromophore separation distance less than 4 Å is required.[18] The fact that no excimer formation was observed in Sisido's polypeptides suggests that there was little fluctuation in the distance between two adjacent chromophores to allow them to come within a distance closer than 4 Å.

To facilitate energy migration studies using Sisido's polypeptides, one should attach an energy acceptor group to one end of a polypeptide chain. Energy migration will then increase the efficiency of energy trapping by the end group. Energy migration can then be studied using both steady-state and time-resolved fluorescence techniques. Using a steady-state fluorometer, the efficiency of energy trapping with the change in the structure of the polypeptide chain can be followed. Using time-resolved techniques, either the decay in the transient fluorescence emission intensity from the main-chain chromophores (donors) or the building up and decay in the transient intensity of the trap (acceptor) can be monitored after pulse excitation. This paper develops the theoretical

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expression for the energy trapping efficiency, and the transient fluorescence intensity functions for the main-chain chromophores and the trap. In section II, the theoretical expressions for these quantities in terms of infinite series will be established for long polymer chains. In section III, the analytic solutions derived in section II will be compared with those derived by Pearlstein by a different approach.[19] Numerical solutions of these quantities will be presented for a few sample cases. The paper finishes by drawing some conclusions in section IV.

## II. Theory

**Idealized Rigid-Rod Chain.** As a generalization to Sisido's helical polypeptide chains, I consider rigid-rod chains consisting of $N$ repeat units and each of the $N$ units bears a chromophore A. To one end of the chain is attached an energy trap T. The average distance between two adjacent A groups is assumed to be $d$, which fluctuates insignificantly when compared to the critical energy transfer distance $R_0$ between them. The length of the chain is $L = Nd$. The $d$ value is assumed to be sufficiently small to allow efficient dipole–dipole energy transfer between the chromophores but large enough to disallow processes such as excimer formation and energy transfer via the Dexter mechanism.[1]

**Fluorescence Experiments.** It is assumed that all fluorescence experiments are carried out using dilute solutions. In a dilute solution, the motions of the excitons of different polymer chains are completely independent of one another.

The discussed experimental situation consists of first exciting a single A chromophore of a polymer chain with $\delta$-pulse light. After light absorption by one of the A groups in the interior of a chain, the excitation energy is transferred from one A chromophore to another by energy migration or it may be dissipated with a rate constant $1/\tau_0$, when localized with one of the A groups, either via fluorescence emission or by a nonradiative process. The rate constant for self-deactivation is assumed to be independent of the position of A*. Finally, if excitation energy migrates to the terminal T group, it is trapped irreversibly. The trapped energy is dissipated with rate constant $1/\tau_A$.

**Energy Hopping Model.** Energy migration is depicted using a hopping model. In this model, the excitation energy is assumed to localize with a particular chromophore A for an average time period $1/k_{ex}$. After the residence time $1/k_{ex}$, the excitation energy is assumed to transfer from A* to one of its closest neighbors by the dipole–dipole interaction mechanism. The term $k_{ex}$, the rate constant for the dipole–dipole energy transfer from A* and one of its closest neighbors A, is given by[16,20]

$$k_{ex} = (1/\tau_0)(R_0/d)^6 \tag{1}$$

where $\tau_0$ is the fluorescence lifetime of chromophore A* in the absence of energy transfer to T, and $R_0$ is the critical energy transfer distance between A* and A. The $R_0$ and $d$ values are so obtained experimentally that $1/k_{ex}$ is much shorter than $\tau_0$.

The assumption of energy transfer between closest neighbors only is quite reasonable as judged by eq 1. Due to the negative sixth power dependence on the separation distance, $k_{ex}$ for energy transfer from an excited chromophore A* to a next-to-nearest A group is reduced by a factor of $(1/2)^6$ when compared to the rate constant for energy transfer from A* to its closest neighbors.

On the basis of the equal spacing assumption, the rate constant for energy transfer from A* to either the right or the left A chromophore should be equal. Thus, the energy migration in the present model is a one-dimensional random-walk process.

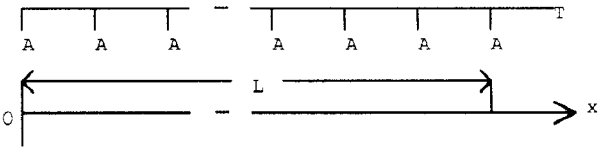


**Figure 1.** Idealized rigid-rod chain.

**Equation for $P(x,t)$.** The probability for finding the excitation energy to be with the $i$th chromophore, counting starting from the left end of a chain, at time $(t + 1/k_{ex})|_{\leftarrow}$ is denoted as $P[x_i,(t+1/k_{ex})|_{\leftarrow}]$, where $(t+1/k_{ex})|_{\leftarrow}$ represents the time after the excitation energy has just made a jump at time $t + 1/k_{ex}$ and where the symbol $\leftarrow$ denotes that time approaches $t + 1/k_{ex}$ from the right or the positive side. The excitation energy arrives at position $x_i$ only if at time $t|_{\leftarrow}$ it has jumped to either position $x_{i-1}$ or $x_{i+1}$. The excitation energy arrived at either $x_{i-1}$ or $x_{i+1}$ only has a 50% of chance to jump to position $x_i$ at time $t + 1/k_{ex}$. In the absence of self-deactivation of A*, the probability $P[x_i,(t+1/k_{ex})|_{\leftarrow}]$ is related to $P(x_{i-1},t|_{\leftarrow})$ and $P(x_{i+1},t|_{\leftarrow})$ by[21,22]

$$P[x_i,(t+1/k_{ex})|_{\leftarrow}] = (1/2)[P(x_{i-1},t|_{\leftarrow}) + P(x_{i+1},t|_{\leftarrow})] \tag{2}$$

The excitation energy of A* may get dissipated either radiatively or nonradiatively during the energy residence time $1/k_{ex}$. The rate constant for self-deactivation of A* has been assumed to be $1/\tau_0$, independent of the positions of the A* chromophores. Due to self-deactivation, the probability $P[x_{i-1},(t+1/k_{ex})|_{\rightarrow}]$ that the excitation energy is still with the $(i-1)$th chromophore just before it makes a jump at time $t + 1/k_{ex}$ is related to $P(x_{i-1},t|_{\leftarrow})$ by

$$P[x_{i-1},(t+1/k_{ex})|_{\rightarrow}] = P(x_{i-1},t|_{\leftarrow}) - (1/\tau_0)(1/k_{ex})P(x_{i-1},t|_{\leftarrow}) \tag{3}$$

Equation 3 derives directly from the rate law

$$dP(x_{i-1},t)/dt = -(1/\tau_0)P(x_{i-1},t) \tag{4}$$

by approximating $dt$ with $1/k_{ex}$. A similar expression for $P[x_{i+1},(t+1/k_{ex})|_{\rightarrow}]$ can be derived by taking the self-deactivation of the $(i+1)$th chromophore into account.

When self-deactivation processes of A* are taken into account, the energy migration equation, initially governed by eq 2 is modified to

$$P(x_i,t+1/k_{ex}) = (1/2)[1 - (1/\tau_0)(1/k_{ex})][P(x_{i-1},t) + P(x_{i+1},t)] \tag{5}$$

where the $\rightarrow$ and $\leftarrow$ signs have been dropped, because the difference between $P(x_i,t+1/k_{ex})|_{\leftarrow}$ and $P(x_i,t+1/k_{ex})|_{\rightarrow}$ is negligibly small.

**Chromophores A at the Boundaries.** Discussion so far has been focused on the interior A chromophores, i.e., A chromophores other than the first and the $N$th. The situations at the boundaries are very different from those in the interior. With the chromophore A at the left boundary (see Figure 1), it is assumed that excitation energy migrates to it and resides there for a time $1/k_{ex}$. After that, it will either bounce back to the second chromophore or stay there. The probability for either of the two events to occur is assumed to be the same. The situation is different from that for an interior chromophore where an exciton is bound to make a jump, either to the left or right, after residence time $1/k_{ex}$. The situation imposed on the first chromophore here is called a reflective boundary condition.

As soon as the excitation energy migrates to the $N$th chromophore, it is assumed that the energy is transferred

to the T group instantaneously. This approximation can be made reasonable experimentally. Let us assume that the A chromophores are 9-fluoryl groups and the T group is a 9-anthryl group. The $R_0$ value for energy transfer from one 9-fluoryl group to another is comparable to that from a 9-fluoryl to a 9-anthryl group; i.e., $R_0$ is *ca.* 20 Å for both cases. The fluoryl groups of the main chain are spaced by rigid bridging groups. The connection between the terminal T group and the $N$th A chromophore can be made flexible and shorter. This will make the rate constant for energy transfer from the $N$th 9-fluoryl group to the 9-anthryl trap much larger than that to the $(N-1)$th 9-fluoryl group.

**Solution for $P(x_i,t+1/k_{ex})$.** The term $P(x_i,t+1/k_{ex})$ of eq 5 is the probability of finding the excitation energy at the $i$th chromophore of a polymer chain at time $t + 1/k_{ex}$. Equation 5 is general, i.e., applicable to both long and short chains and can be used for solutions of $P(x_i,t+1/k_{ex})$ at any time $t$ with a computer program. To solve eq 5 for $P(x_i,t+1/k_{ex})$, one makes use of the initial condition

$$P(x_1,0) = P(x_2,0) = \ldots = P(x_N,0) = 1/N \tag{6}$$

the boundary condition

$$P(x_N,t) = 0, \quad t > 0 \tag{7}$$

and the fact that at $x_1$ one has a reflective boundary.

**Function $P(x_i,t)$ Versus a Measurable Quantity.** The term $P(x_i,t)$ is not a measurable quantity. The measurable quantity is $\sum_{i=1}^{N} p(x_i,t)$, the probability that the initially absorbed energy is still with one of the A chromophores. In fact, $\sum_{i=1}^{N} p(x_i,t)$ is proportional to the intensity of fluorescence emission from A* at time $t$ after $\delta$-pulse excitation at time zero. $\sum_{i=1}^{N} p(x_i,t)$ can be determined by making use of a time-correlated single-counting (TCSPC) instrument.

**Large $N$ Limit.** An analytical solution for $\sum_{i=1}^{N} p(x_i,t)$ is possible from this model for the long-chain limit. If $N$ value is large, the ratio $d$/L, i.e., $1/N$, approaches zero. $P(x_{i-1},t)$ and $P(x_{i+1},t)$ of eq 5 can be expanded around $x$ and be approximated by the first three terms of the Taylor series:

$$P(x_{i-1},t) = P(x,t) - [\partial P(x,t)/\partial x]d + (1/2)[\partial^2 P(x,t)/\partial^2 x]d^2 + \ldots \tag{8}$$

and

$$P(x_{i+1},t) = P(x,t) + [\partial P(x,t)/\partial x]d + (1/2)[\partial^2 P(x,t)/\partial^2 x]d^2 + \ldots \tag{9}$$

If $1/k_{ex}$ is short compared to $\tau_0$, $P(x,t+1/k_{ex})$ can be similarly expanded around $t$ and can be truncated after two terms:

$$P(x,t+1/k_{ex}) = P(x,t) + [\partial P(x,t)/\partial t](1/k_{ex}) + \ldots \tag{10}$$

Inserting eqs 8–10 into eq 5 and simplifying gives

$$\partial P(x,t)/\partial t = D\frac{\partial^2 P(x,t)}{\partial x^2} - (1/\tau_0)P(x,t) \tag{11}$$

where $D$, the phenomenological energy migration coefficient in units cm²/s, is given by[22,23]

$$D = (1/2)k_{ex}d^2 \tag{12}$$

In the large $N$ or long-chain limit, $P(x,t)$ is approximated as a continuous function. The function $P(x,t)$ can now be solved using partial differential equation 11 with the following initial (IC) and boundary (BC) conditions:

$$\text{IC:} \qquad P(x,0) = 1/L \qquad \text{if } 0 \le x \le L$$

$$P(x,0) = 0 \qquad x \text{ otherwise} \tag{11a}$$

$$\text{BC:} \qquad \partial P(x,t)/\partial x|_{x=0} = 0 \tag{11b}$$

$$P(L,t) = 0 \qquad t > 0 \tag{11c}$$

where the reflective boundary condition at $x_1$ has been translated into mathematical language in terms of eq 11b.[24] This paper focuses on the discussion of the results of the large $N$ limit.

**Serial Solution to Equation 11.** The linear homogeneous second-order partial differential equation 11 can be solved for $P(x,t)$ following procedures described in monographs on partial differential equations. The solution satisfying both the boundary and initial conditions has the serial expression:

$$P(x,t) = \sum_{n=0}^{\infty} \frac{(-1)^n \times 4}{(2n+1)\pi L} \cos\left(\frac{2n+1}{2L}\pi x\right) \times \exp\left\{-\left[\left(\frac{2n+1}{2L}\pi\right)^2 D + (1/\tau_0)\right]t\right\} \tag{13}$$

**Intensity of Fluorescence Emission from A* at Time $t$.** The fluorescence emission intensity from A* at time $t$ after $\delta$-pulse excitation, proportional to $P(x,t)$ integrated from $x = 0$ to $x = L$, can be shown to be

$$I_A(t) \propto \int_0^L P(x,t)\,dx = \sum_{n=0}^{\infty} a_n \exp(-\lambda_n t) \tag{14}$$

where $a_n$, the amplitude coefficient for the $n$th term in the summation, is

$$a_n = \frac{8}{(2n+1)^2\pi^2} \tag{14a}$$

which is, surprisingly, independent of the structural parameters of the polymer chain and the energy transfer parameter $R_0$. The sum of all $a_n$ values, as expected, normalizes to 1. $\lambda_n$ of eq 14 are given by

$$\lambda_n = 1/\tau_0 + \left(\frac{2n+1}{2L}\pi\right)^2 D \tag{14b}$$

Equation 14b indicates that the fluorescence intensity of A* decays both due to self-decay and energy migration to the trap T. The rate constant, $((2n+1)\pi/2L)^2 D$, for energy trapping is obviously not unique. Intuitively, one would expect the rate constant to be dependent on the position of the chromophore initially excited. Thus, the $n$ value can be viewed as a position index. The closer the initial excitation is to the T group, the larger the $n$ value and thus the energy trapping rate constant.

**Fluorescence Intensity Profile $I_T(t)$ of the Energy Trap T.** In formulating $I_T(t)$, I assume that T gets excited due to energy transfer from A* only. This can be made rigorously true experimentally, because there are far more donor groups than acceptor groups in the system. In the absence of direct absorption, [T*] increases due to energy transfer from A* and decays with rate constant $1/\tau_A$. The equation for the variation with time in [T*], proportional to $I_T(t)$, is

$$dI_T(t)/dt \propto -(1/\tau_A)I_T(t) + \sum_{n=0}^{\infty}(\lambda_n - 1/\tau_0)a_n \exp(-\lambda_n t) \tag{15}$$

where the $\lambda_n - 1/\tau_0$ term after the summation sign can be

viewed as the rate constant for energy transfer to the T group from those A* groups which have a position index $n$, and the $a_n \exp(-\lambda_n t)$ term is the probability that those A groups are still excited at time $t$. The summation in eq 15 takes the energy transfer from all A* groups to T into account.

The first-order ordinary differential equation 15 can be solved to yield a convolution equation:[25]

$$I_T(t) \propto \int_0^t \sum_{n=0}^{\infty} (\lambda_n - 1/\tau_0) a_n \exp(-\lambda_n s) \exp\left(-\frac{t-s}{\tau_A}\right) ds \tag{16}$$

Carrying out the above integration yields

$$I_T(t) \propto \sum_{n=0}^{\infty} a_n \frac{\lambda_n - 1/\tau_0}{\lambda_n - 1/\tau_A} [\exp(-t/\tau_A) - \exp(-\lambda_n t)] \tag{17}$$

which is very similar to the expression derived by Birks[18] for the change in excimer concentration after pulse excitation except that instead of having a single difference term between two exponential terms, [T*] here grows in and decays as the sum of a series of difference terms.

**Energy Trapping Efficiency $\chi_T$.** Steady-state fluorescence techniques are often used for studying energy migration. In carrying out a steady-state measurement, one can monitor the variation in the energy trapping efficiency $\chi_T$ as a function of $L$ and $R_0$. For those photons which are initially absorbed by the fraction $a_n$ of chromophores corresponding to position index $n$, the rate constant for energy trapping is $\lambda_n - 1/\tau_0$ and the overall rate constant for A* decay is $\lambda_n$. The efficiency of energy trapping for the chains which are initially excited at positions with index $n$ is

$$\chi_T{}^n = \frac{\lambda_n - 1/\tau_0}{\lambda_n} = 1 - 1/(\lambda_n \tau_0) \tag{18}$$

The ensemble-averaged $\chi_T$ is obtained by taking chains which are initially excited at all possible positions into account and is

$$\chi_T = \left(\sum_{n=0}^{\infty} a_n \chi_T{}^n\right) / \sum_{n=0}^{\infty} a_n \tag{19}$$

where $\sum_{n=0}^{\infty} a_n$ normalizes as mentioned before. Inserting eqs 18, 14a, and 14b into eq 19 and simplifying the resultant equation leads to

$$\chi_T = (2D\tau_0/L^2) \sum_{n=0}^{\infty} \frac{1}{1 + [(2n+1)\pi/2]^2 D\tau_0/L^2} \tag{20}$$

Thus, the overall efficiency for energy trapping only depends on the ratio between $D\tau_0/L^2$, which is intuitively reasonable.

## III. Discussion

In this section, eqs 13 and 14 will be compared to those expressions derived by Pearlstein by another approach.[19] Numberical solutions for eqs 13, 14, 17, and 20 for example cases will be shown, and the validity of these equations will be investigated.

**Equation 13 for $P(x,t)$.** The probability density for an A chromophore at position $x$ to be still in the excited state at time $t$ is given in the form of eq 13 as an infinite series. Since the contribution from the higher order terms decreases as $n$ increases, the actual calculation of $P(x,t)$ requires the summation of about the first 30 terms only. Figure 2 illustrates how $P(x,t)$, calculated using the first

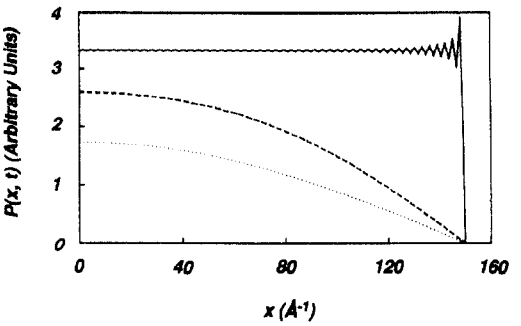


**Figure 2.** Decay of the probability density function $P(x,t)$ as a function of time: $t = 0$, (—); $t = 10$ ns, (- - -); $t = 20$ ns, (· · ·). Curves constructed using $D = 2.25 \times 10^{-5}$ cm²/s, $L = 150$ Å, and $\tau_0 = 50$ ns.

100 terms of the series, varies with time for a sample case when $D = 2.25 \times 10^{-5}$ cm²/s, $L = 150$ Å, and $\tau_0 = 50$ ns. As time increases, $P(x,t)$ decreases. The fastest decrease in $P(x,t)$ occurs at the end to which an energy acceptor is attached, as expected. The only abnormality seems to be with $P(x,t)$ at $t = 0$. At $t = 0$, $P(x,t)$, specified by eq 11a, is a step function. That the use of a Fourier series, i.e., eq 13, to approximate a step function leads to a curve oscillating around it is, however, a well-documented phenomenon in calculus.

Equation 13 compares well with a similar equation derived by Pearlstein.[19] Pearlstein considered the same problem, i.e., energy migration along rigid-rod chains with $N$ backbone chromophores and a terminal trap, from a different perspective. He started from the construction of $N$ rate equations $d\rho(i,t)/dt$ for the backbone chromophores, where $\rho(i,t)$ is the probability that the $i$th chromophore is still excited at time $t$. The solution of the $N$ simultaneous differential equations leads to a general expression for $\rho(i,t)$

$$\rho(i,t) = \exp(-t/\tau_0) \sum_{n=0}^{N-1} A_n \cos[{}^1/_2(2i+1)\alpha_n] \exp(-\Gamma_n t) \tag{21}$$

where $A_n$ is not specified in the original paper and

$$\Gamma_n = 2k_{ex} \sin^2(\alpha_n/2) \tag{22}$$

The $\alpha_n$ value of eq 21 depended on the relative magnitude of $k_{ex}$ to the rate constant for energy transfer from the $N$th A* chromophore to T. If the rate of excitation energy transfer from the $N$th A* chromophore to the terminal T group is much faster than that from the $N$th A* chromophore to the $(N-1)$th A chromophore, $\alpha_n$ was shown to be given by

$$\alpha_n = \frac{2n+1}{2N-1}\pi \tag{23}$$

In the limit of infinitely large $N$, eq 21 can be approximated by incorporating eqs 22 and 23 in it, as

$$\rho(i,t) = \sum_{n=0}^{\infty} A_n \cos\left[\frac{2n+1}{2N} i\pi\right] \times \exp\left\{-\left[(1/2)k_{ex}\left(\frac{2n+1}{2N}\pi\right)^2 + 1/\tau_0\right] t\right\} \tag{24}$$

Remembering that $x = id$ and $L = Nd$ and inserting eq 12 into eq 24, one finds that the cosine and exponential terms of eqs 13 and 24 are exactly the same.

**Donor Fluorescence Intensity Decay after $\delta$-Pulse Excitation.** Donor fluorescence intensity decay function $I_A(t)$ given by eq 14 also consists of an infinite series. It

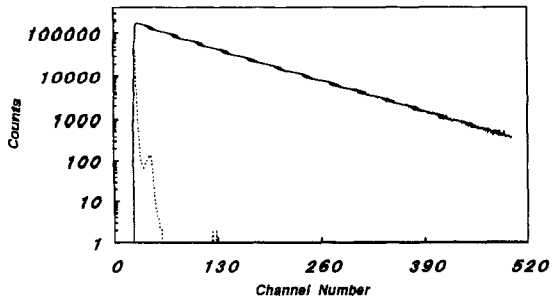


**Figure 3.** Example donor intensity decay curve constructed using $D = 1.125 \times 10^{-5}$ cm$^2$/s, $L = 150$ Å, and $\tau_0 = 50$ ns. Time per channel $\Delta t$ is equal to 0.40 ns.

**Table I. First Few $a_n$ and $\lambda_n$ Terms Calculated Using Equations 14a and 14b Assuming $D = 2.25 \times 10^{-5}$ cm$^2$/s, $L = 150$ Å, and $\tau_0 = 50$ ns**

| $n$ | $a_n$ | $\lambda_n$ ($\times 10^{-8}$ S) |
|---|---|---|
| 0 | 0.811 | 0.45 |
| 1 | 0.090 | 2.42 |
| 2 | 0.032 | 4.15 |
| 3 | 0.017 | 6.37 |

is a monotonously decaying series, since every term in the series decays as time increases. The decrease of $I_A(t)$ as a function of time for a sample case when $D = 1.125 \times 10^{-5}$ cm$^2$/s, $L = 150$ Å, and $\tau_0 = 50$ ns is illustrated in Figure 3.

Terms of the series of eq 14 decay monotonously as $n$ increases. As a matter of fact, only the first few terms are of significance to the sum. The values of the first several $a_n$ and $\lambda_n$ terms are shown in Table I for the sample case when $D = 2.25 \times 10^{-5}$ cm$^2$/s, $L = 150$ Å, and $\tau_0 = 50$ ns. It is seen that the first four terms account for 95% of the total fluorescence at short times. At sufficiently long times, all the terms with large $n$ values will have vanished and the contribution to the total fluorescence would almost exclusively come from the first few terms.

The expression for the amplitude coefficient $a_n$ of eq 14 has been derived by Pearlstein, for the limit of fast energy transfer from the $N$th A chromophore to T, as

$$a_n = \cot^2(\alpha_n/2)/[N(2N-1)] \tag{25}$$

where $\alpha_n$ is defined by eq 23. If $N$ is extremely large, $a_n$ reduces to eq 14a. This again shows the equivalence between Pearlstein's and my results.

**Transient Fluorescence Intensity Profile of the Energy Trap.** The validity of eq 17, which describes the building up and decay of the transient fluorescence intensity of the trap, can be verified by examining the forms it reduces to in the limits of infinitely large and small $1/\tau_A$ values. In the limit of infinitely large $1/\tau_A$, eq 17 reduces to

$$I_T(t) \propto \tau_A \sum_{n=0}^{m} a_n \exp(-\lambda_n t) \tag{26}$$

where the summation limit is set to a finite number $m$, because only the first few terms are of significance to the sum. Equation 26 states that, in the limit of $1/\tau_A \to \infty$, the rate of trap intensity decay is controlled by the rate of energy transfer to the trap. This is so because the rate of two sequential reactions is controlled by that of the rate-determining step.

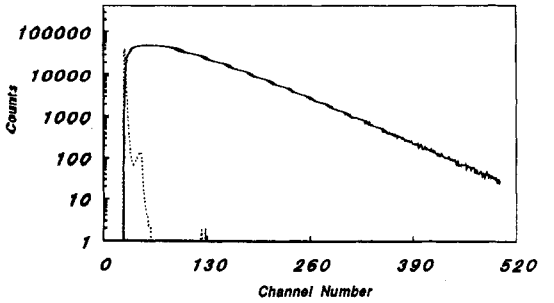


**Figure 4.** Example transient trap intensity profile constructed using $D = 2.25 \times 10^{-5}$ cm$^2$/s, $L = 150$ Å, and $\tau_0 = 22.4$ ns. Time per channel $\Delta t$ is equal to 0.5 ns.

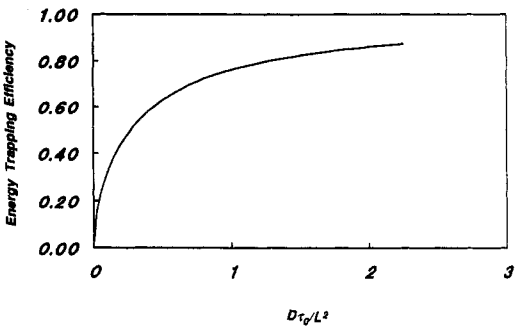


**Figure 5.** Energy trapping efficiency as a function of $D\tau_0/L^2$.

In the limit of $1/\tau_A \to 0$ and at sufficiently long times, eq 17 now reduces to

$$I_T(t) \propto \sum_{n=0}^{\infty} a_n(\lambda_n - 1/\tau_0)/\lambda_n \tag{27}$$

where all $\exp(-\lambda_n t)$ terms have been assumed to approach zero because of the sufficiently long time assumption. Equation 27 is equivalent to eq 19. That is, at sufficiently long times, the concentration of the excited traps reaches its steady-state value, which is proportional to the energy trapping efficiency. This conclusion is again intuitively reasonable.

Figure 4 illustrates the building up and decay of the transient intensity profile generated using $D = 2.25 \times 10^{-5}$ cm$^2$/s, $L = 150$ Å, $\tau_0 = 50$ ns, and $\tau_A = 22.4$ ns.

**Energy Trapping Efficiency.** The efficiency of energy trapping, $\chi_T$, is shown in eq 20 to be a function of $D\tau_0/L^2$ only. In Figure 5, the efficiency of energy trapping is plotted as a function $D\tau_0/L^2$. As $D\tau_0/L^2$ increases, $\chi_T$ increases. The disappointing feature about carrying out steady-state measurement is that there is no easy analytic relation between $\chi_T$ and parameters such as $1/L^2$. To obtain $D$, one has to fit $\chi_T$ obtained experimentally using eq 20 or a plot like Figure 5.

**Small $1/k_{ex}$ Assumption.** In deriving eq 11 and equations thereafter, I have assumed that $1/k_{ex}$ was much shorter than $\tau_0$. This can be easily achieved experimentally by using appropriate chromophores or changing the distance $d$ between adjacent A chromophores. Assuming that $d = 7$ Å, the distance found between adjacent A chromophores in Sisido et al.'s polypeptides, the use of 9-methylfluorene or $N$-methylcarbazole as the donor yields $R_0$ values ~22 Å. A simple calculation using eq 1 shows that $\tau_0/(1/k_{ex})$ for those cases are close to 1000 and thus the much shorter $1/k_{ex}$ assumption is valid.

## IV. Summary

Energy migration along rigid-rod polymer chains with an energy trap attached to one end has been theoretically examined. Analytical expressions have been found for

the description of the variation in the transient fluorescence intensities of the main-chain chromophores and the trap with time after $\delta$-pulse excitation for the limit of long chains. The fluorescence intensity decay function of the donor was then used to formulate the efficiency of energy trapping by the trapping end group. The validity of the derived equations has been investigated.

Although all discussion of this paper has been on singlet energy migration, the derived formulas are equally applicable to triplet energy migration. With triplet energy migration there are two potential problems. Large-scale chain structure fluctuation may occur during donor excitation lifetime. This is due to the long lifetime of a triplet state and is not a concern for rigid-rod chains, since structural fluctuations in such systems have been assumed to be small. The other problem with triplet excitation is that multiphoton events such as the simultaneous excitation of a chain at two sites may have a higher probability. This can, however, be eliminated by using lower-intensity light sources.

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