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Exciton Migration on Polymers

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ABSTRACT: The properties of migrating excitons on chromophores substituted along a polymer chain are considered. The mean survival time of the excitons and the survival function of an exciton are studied in the presence of an exciton trap on the chain. A postulate that the mean survival time τ_n scales with the length n of the chain as n^μ is studied. It is found that for singlet (fast) diffusion $\mu = 2$ while for triplet (slow) diffusion $\mu = 1$. The methods used are a nonrigorous scaling argument and Monte Carlo calculation for singlet migration of excitons on linear polymers and stars, while a perturbative calculation proves successful for the triplet exciton diffusion case.

1. Introduction

Energy transfer within single molecules or between different molecules is of particular significance in polymer chemistry. Energy donors and acceptors (chromophores) in the molecules may be excited by incoming photons of a sufficient wavelength to form a localized excitation in a chromophore (usually called an exciton). Polymer chains may have chromophores substituted at intervals along the chains, and it is of particular interest that transfer of the exciton may occur between two of these chromophores under suitable conditions. For the sake of simplicity, it is assumed that chromophores will always be spaced at *regular* intervals along the chains.

There is experimental evidence for the transfer of excitons between chromophores in the same molecule or even between different molecules.[1] The mechanisms for these transfers have been investigated in detail (see, for example, the books by Guillet[2] and Phillips[3]). Briefly, they are (1) the induced dipole interaction (or the Förster process[4]), which is a long-ranged, nonradiative, single-step process with a range between 15 and 100 Å, and (2) the exchange mechanism (or Dexter transfer[5]), which is a short-ranged, nonradiative, single-step process with a range of about 15 Å. Furthermore, there is a distinction between excitons in the singlet or triplet state. The singlet exciton is a spin zero excited state of the chromophore with a lifetime of between 10^{-11} and 10^{-7} s and a transfer rate typically shorter than the conformational relaxation time of a polymer (say, 10^{-4}–10^{-3} s, which is typical for a crankshaft motion). The triplet exciton is a metastable spin 1 state that has a lifetime of between 10^{-6} and 10^{1} s.[2,3] Typically, the triplet state would have a transfer time longer than the conformational relaxation time of a polymer.

In a molecule where the chromophores are sufficiently close together, the transfer of excitons from one chromophore to another can be viewed as a random walk on the chromophores. Energy transfers between chromophores substituted along a polymer happen between nearest-neighbor chromophores and can also occur between any two chromophores that are close together in space in a particular conformation but are far removed from each other along the chain. This situation is illustrated in Figure 1. Experimental evidence for these processes is readily available.[1] The problem is now reduced to one of diffusion of the exciton along the polymer. This diffusion process is strongly influenced by the distribution of

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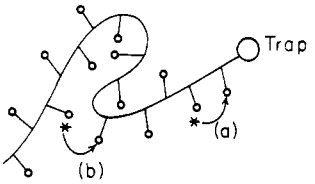

Figure 1. Transfers of excitons between chromophores on a polymer between chromophores far removed from each other along the chain but close together in space due to the configuration of the chain (b). Transfers like (a) are between nearest-neighbor chromophores.

chromophores, their orientations, and their average distances apart. In the idealized version of the situation, which we discuss here (the polymers are modeled as self-avoiding random walks), we assume (i) that the polymers live on a regular lattice, (ii) that transfers only occur between chromophores that are nearest neighbors on the lattice, and (iii) that the chromophores are uniformly spaced along the lattice polymer, each vertex of the walk representing a chromophore.

The problem outlined above is made more interesting by the addition of exciton traps on the polymer (see Figure 1). In this situation an incoming photon will be absorbed by a chromophore, forming an exciton. The exciton will then diffuse along the chromophores until it is captured by a trap where it is either radiated away or used to perform a chemical reaction. The fact that singlet excitons diffuse on a time scale much shorter than the relaxation time of a polymer defines the model for singlet diffusion to be on *frozen* polymer conformations. Measured quantities should then be averaged over all possible conformations of the polymer. In contrast to this, triplet excitons diffuse on time scales typically longer than the conformational relaxation time of polymers, and one can study the problem on an *averaged* polymer chain.

The state of affairs outlined above is of course a special case in the general study of transport and diffusion in random media (for an excellent review, see the paper by Havlin and Ben-Avraham[6]). This problem is closely related to problems encountered in the study of fluid flow through porous rocks,[7] conductivity of superionic conductors,[8] and diffusion-controlled fusion of excitons in porous membrane films, polymeric glasses, and isotropic mixed glasses.[9] The "ant-in-the-labyrinth" problem[10,11] was defined precisely to serve as a model for the diffusion problem in random media in the possible presence of traps.[12] A popular approach to this problem is by a master equation,[13,14] usually solved by developing a Green's function formalism. In the general case of random placements of chromophores in a random medium (not a polymer), Gochanour et al.[14] found that, in the long time limit, transport becomes purely diffusive. In this paper, it is assumed that the excitons migrate in a purely diffusive way (i.e., there is no correlation between two excitons diffusing on the same chain), so that their motion may be modeled by the diffusion equation.

Throughout this study each polymer chain has a single trap and has chromophores substituted along it. Once an exciton diffuses on the chain, of immediate interest is the survival probability function $S_n(t)$ of the exciton and is mean survival time τ.

This paper is organized as follows. In section 2 we study the singlet diffusion problem. A *nonrigorous* scaling argument is developed to predict the features of the problem. These predictions are then tested by treating the problem numerically. The computational approach is extended to stars, and a comparison between stars and linear polymers is made. In short, the scaling arguments predict that the

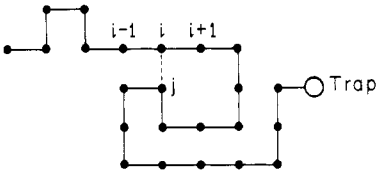

Figure 2. Exciton migration on chromophore i to either chromophores $i - 1$, $i + 1$, or j if j is near to it in space.

mean survival time τ_n of the exciton, as a function of the length of the polymer n, should behave as

$$\tau_n \sim n^2 \tag{1-1}$$

and the survival probability function $S_n(t)$ should be

$$S_n(t) \sim \frac{1}{t} e^{-A_n(t)t} \tag{1-2}$$

where

$$\lim_{n\to\infty} A_n(t) = \tau^{-1} \tag{1-3}$$

These predictions are tested by Monte Carlo calculations, which support the predictions made by the scaling arguments.

In section 3 the diffusion of triplet excitons is considered. A perturbative calculation is performed around a suitable ground state, predicting the dependence of the mean survival time τ_n of the exciton on the length n of the polymer. If we suppose that

$$\tau_n \sim n^{\mu} \tag{1-4}$$

then we find that $\mu = 1$ for triplet diffusion on polymers with self-avoiding random-walk statistics in contrast to the value $\mu = 2$ found in the case of singlet exciton diffusion. Section 4 contains some conclusions and suggestions.

2. Singlet Exciton Diffusion

This section will be devoted to an analysis of the diffusion of a singlet exciton on a polymer chain. The time scale of the diffusive process is short in comparison with the relaxation time of the polymer, so it is assumed that the process occurs on frozen polymer conformations. The specific case that is considered is that of a polymer with a trap fixed at one of its end points as illustrated in Figure 2. An exciton formed on one of the chromophores (i) can migrate to the nearest-neighbor chromophores $i - 1$ and $i + 1$, or it may migrate to a chromophore (j) in close contact to it in that chain configuration. The approach will be two-sided in this section. After some brief introductory comments, a nonrigorous scaling analysis of the exciton diffusion problem is given. The second approach is a Monte Carlo calculation designed to test the predictions of the scaling analysis.

In continuous time the diffusion of the exciton can be described by a master equation

$$\frac{\mathrm{d}}{\mathrm{d}t} p_i(t) = \sum_{j=1}^{n} (w_{ij} p_j(t) - w_{ji} p_i(t)) - u_i p_i(t) = \sum_{j=1}^{n} \mathbf{W}_{ij} p_j(t) \tag{2-1}$$

where $\mathbf{W}_{ij}$ is the transition matrix, a transfer from chromophore i to j occurs with probability w_{ij}, and u_i is the transition rate per unit time that an exciton will be absorbed into the trap from chromophore i.

$$\begin{aligned} u_i &= c \quad \text{if } i \text{ and the trap are nearest neighbors} \\ &= 0 \quad \text{otherwise} \end{aligned} \tag{2-2}$$

If $p(t) = (p_1(t), p_2(t), ..., p_n(t))$ and $p(0)$ is the initial dis-

tribution of the exciton on the polymer, then the formal solution to (2-1) is given by

$$p(t) = e^{Wt}p(0) = G(t)p(0) \tag{2-3}$$

The function $G(t)$ has matrix elements $\langle \mathbf{i}|G(t)|\mathbf{j}\rangle = G_{ij}(t)$ where $\langle \mathbf{i}|$ is the vector with all entries equal to 1 and $G_{ij}(t)$ is the conditional probability that the exciton will be at site i at time t given that it was at site j at time 0. Consequently, if all the chromophores were equally likely to be occupied at time 0, then the probability of finding the exciton at site i after time t is

$$p_i(t) = \frac{1}{n}\sum_{j=1}^{n} G_{ij}(t) \tag{2-4}$$

and the survival probability of the exciton can be expressed as

$$S(t) = \sum_{i=1}^{n} p_i(t) \tag{2-5}$$

When the eigenvalues and eigenvectors of $\mathbf{W}_{ij}$ are written as λ_i and $|\lambda_i\rangle$, the expression for $S_n(t)$ becomes

$$S_n(t) = \frac{1}{n}\sum_{i=1}^{n} |\langle \mathbf{i}|\lambda_i\rangle|^2 e^{\lambda_i t} \tag{2-6}$$

Note that since $\sum_{j=1}^{n}\mathbf{W}_{ij} = -u_i \leq 0$, and that the inequality is strict for at least one i ($= n$), λ_i is negative for all i. The long time behavior of $S_n(t)$ is dominated by the largest eigenvalue (λ_{max}) (least negative) of $\mathbf{W}_{ij}$ (see also eq 2-12 and 2-13 in the next section), the mean survival time of the exciton can thus be found from

$$\tau = \frac{-1}{\lambda_{max}} \tag{2-7}$$

since this is the slowest decaying term in eq 2-6, and it dominates the asymptotic behavior of $S_n(t)$. The quantities $S_n(t)$ and τ defined so far now only have to be averaged over all the possible polymer conformations or over a representative sample supplied by the Monte Carlo algorithm.

It is useful to consider the special case where diffusion occurs on a rigid rod with a trap at one end. Here then, only the nearest-neighbor transfers in Figure 2 are allowed. The process can be described by a discrete time diffusion equation

$$p_i(m+1) = \sum_j \Delta_{ij}p_j(m) - u_i p_i(m) \tag{2-8}$$

where $p_i(m)$ is the probability that the exciton is at chromophore i after m jumps, u_i is the probability that the exciton may be absorbed into the trap from chromophore i, and Δ_{ij} and u_i are given for the rigid rod by

$$\begin{aligned} \Delta_{ij} &= c \quad \text{if } |i-j| = 1 \\ &= 1-c \quad \text{if } i = j = 1 \text{ or } i = j = n \\ &= 1-2c \quad \text{if } 1 < i = j < n \\ &= 0 \quad \text{otherwise} \end{aligned} \tag{2-9}$$

and

$$u_i = c\delta_{in} \tag{2-10}$$

Here it is assumed that the polymer has n chromophores substituted along its length and that a trap is nearest neighbor to the nth chromophore. The number c is simply a transition probability.

The long-time behavior of an exciton diffusing on the chain is dominated by the largest eigenvalue of the transition matrix ($\Delta_{ij} - u_i\delta_{ij}$). A straightforward analysis gives the largest eigenvalue λ_{max} as approximately

$$\lambda_{max} \approx 1 - \frac{\pi^2 c}{4n^2} \tag{2-11}$$

For a large number of m of jumps, the probability that the exciton will be in the trap is approximately $1 - \lambda_{max}{}^m$. The mean survival time τ can be found from the probability that the exciton is absorbed at precisely its mth jump f_m (the first passage time), given by (the discrete analogue of $S(t)$ in eq 2-5).

$$f_m = (1 - \lambda_{max}{}^m) - (1 - \lambda_{max}{}^{m-1}) \tag{2-12}$$

The mean survival time can then be found directly from

$$\tau_n = \sum_{m=0}^{\infty} m f_m \approx \frac{4}{\pi^2 c} n^2 \tag{2-13}$$

It is thus found that the mean survival time of the exciton scales as the square of the length of the rigid rod. The function f_m is an asymptotic approximation to the survival probability function $S(t)$. A similar study for flexible polymers is performed in the next subsection.

2.1. Scaling Analysis for Singlet Diffusion. In this subsection a nonrigorous analysis of the diffusion of singlet excitons on flexible polymers is performed. In contrast to the rigid rod approximation above, it is not possible for the excitons to diffuse from any chromophore i to another j or directly into the trap due to the present conformation of the polymer. Since the polymer may have long-range contacts between chromophores, it is now necessary to evaluate the effect of these contacts. It is obviously not possible to solve eq 2-8 as above to find approximations for the mean survival time and survival probability.

On the basis of results from the study of exciton motion on deterministic fractals,[15] Byers et al.[18] postulate that the survival probability function of an exciton diffusing on a polymer in the presence of a trap (or traps) has the functional behavior

$$S_n(t) \sim e^{-At^{(d_s/2)} + Bt^{(2d_s/2)} - Ct^{(3d_s/2)} + \dots} \tag{2-14}$$

where A, B, C, ... are constants and d_s is the spectral dimension of the polymer (see Havlin et al.[6] for a review).

The renormalization group predicts that the linear DC resistance R_{res} of a polymer (modeled as an Edwards random walk or a self-avoiding random walk) should scale linearly with its length[16,17]

$$R_{res} \sim n^1 \tag{2-15}$$

This result suggests that the polymer is such an inhomogeneous object that, typically, the removal of one monomer from it would break the electric circuit. In the link and blob picture the polymer is essentially a linear object of links and blobs such that the fraction of links does not go to zero as the length of the polymer goes to infinity. The resistance of the polymer is related to its conductivity $\sigma(n)$ through $R_{res} = n(\sigma(n))^{-1}$; thus, the polymer chain has a constant conductivity. In its turn, the conductivity of the chain is related to the diffusion constant D through the Einstein relation

$$\sigma = (e^2/kT)ND \tag{2-16}$$

where e is the electron charge, T the temperature, and N is the charge carrier density. Since the polymer is linear, N is independent of the length of the polymer and hence is a constant, so that the diffusion constant is independent of the chain length and is thus a constant.

The linear nature of the polymer suggested here makes it possible to define a "chemical distance" s along the chain. Chemical distance is usually defined as the shortest path between two points on a fractal; the linear dependence of

the resistance implies that the chemical distance is just along the polymer, short-circuiting the blobs in the link and blob picture, but nevertheless proportional to the distance along the polymer chain. The spectral dimension of the polymer is then defined by[6]

$$\langle R_s(t)\rangle \sim t^{d_s/2} \tag{2-17}$$

where $R_s(t)$ is the number of distinct sites a particle has visited on the chain in a time t. This is related to the diffusion constant via the expression

$$D \approx \frac{\langle R_s(t)\rangle^2}{t} \sim t^{d_s-1} \tag{2-18}$$

and thus the spectral dimension of the polymer is 1, for t small. For large t, the chain is like a stiff rod. From (2-6) and (2-7) we expect that in (2-14)

$$d_s = 2,\ t \text{ large} \tag{2-19}$$

These arguments indicate that the polymer conformation is quite accurately represented by the link and blob picture; the excitons will diffuse from blob to blob along the links in very much the same way an exciton will diffuse from node to node on the rigid rod. Under the assumption that the mean survival time τ satisfies the relation suggested by eq 2-13

$$\tau_n \sim n^{\mu} \tag{2-20}$$

it is reasonable to expect μ to have the value 2. Furthermore, the very existence of τ is determined by the survival probability function $S(t)$ through

$$\tau = \int_0^\infty t\, S_n(t)\, dt \tag{2-21}$$

which together with the fact that the spectral dimension has value 2 (eq 2-19) and eq 2-14 indicates that $S_n(t)$ should have an asymptotic form as

$$S_n(t) \xrightarrow{t \text{ large}} \frac{1}{t} e^{-A_n(t)t} \tag{2-22}$$

where $A_n(t)$ is a funtion of t having asymptotic value

$$\lim_{t\to\infty} A_n(t) = \frac{1}{\tau_n} \tag{2-23}$$

The factor t^{-1} in eq 2-22 is for normalization. In contrast with the functional form assumed here for the survival probability function in eq 2-22, Byers et al.[18] assumed the form

$$S_n(t) \sim e^{-A_n(t)t^{\alpha(t)}} \tag{2-24}$$

and attempted to determined the exponent $\alpha(t)$ from their numerical data. Although for small values of t they found $\alpha(t)$ to be smaller than 1, as t becomes larger they find that the value of $\alpha(t)$ goes to 1. This result is not surprising in view of the scaling arguments set out in this section. Several predictions follow from these results, namely the fact that μ is expected to have the value 2 in eq 2-20, that the asymptotic behavior of $S_n(t)$ is as in eq 2-22, and that $A_n(t)$ has the limiting behavior as in eq 2-23. In this subsection a connection has been made between the diffusion of excitons on a polymer and a DC electric current flowing in a conducting polymer. This connection should not be surprising; in both cases the equation describing the physical process is the diffusion equation (for the electric current, sometimes called the Kirchhoff equation). The only difference is that the diffusion process is an initial value problem whereas the DC electric current problem is a boundary condition problem. One should therefore expect similar scaling behavior for these two problems.

Table I
$\langle R_n^2\rangle$ and τ_n of a Polymer

n	$\langle R_n^2\rangle$	τ_n	n	$\langle R_n^2\rangle$	τ_n
10	26.1 ± 0.3	196 ± 2	60	250.5 ± 3.4	5236 ± 38
20	64.6 ± 0.8	675 ± 6	70	301.6 ± 3.8	7142 ± 48
30	105.7 ± 1.3	1434 ± 12	80	348.8 ± 4.3	9214 ± 62
40	150.4 ± 1.9	2415 ± 19	90	407.0 ± 5.0	11497 ± 79
50	196.0 ± 2.6	3717 ± 28	100	406.1 ± 5.2	14204 ± 96

2.2. Numerical Results. We now report some Monte Carlo calculations carried out to test the (nonrigorous) predictions made in the previous subsection. The polymers were modeled as self-avoiding random walks on a face-centered cubic lattice, the nodes of the random walk representing the chromophores. This has the advantage that two chromophores two steps apart on the random walk can be nearest neighbors. (On a simple cubic lattice, this is not possible; at least three steps are needed between two chromophores that are nearest neighbors on the lattice but not on the chain.)

The Rosenbluth and Rosenbluth Monte Carlo method[19] similar to that of McCrackin et al.[20] was used to generate representative ensembles of polymers one at a time. The correct weight of each of the conformations w_i was calculated by considering the number of available sites for every step taken by the walk. Ensemble averages for a quantity x over an ensemble of N random walks can then be calculated from

$$\langle x\rangle = \frac{\sum_{i=1}^{N} x(i) w_i}{\sum_{i=1}^{N} w_i} \tag{2-25}$$

The random walks were stored in the computer by storing the components of the chromophores along the length of the random walks in sequence. The searching for intersecting conformations was streamlined by storing a "lattice picture" of the walk in a 100^3 bit matrix. This feature allowed the program to generate a new configuration with n chromophores by executing only $O(n)$ operations. The polymers were generated by starting with a walk with 10 steps, calculating all the necessary quantities on it, adding then 10 more chromophores, repeating the calculations for a walk now with 20 chromophores, and repeating this process until a length of 100 was reached.

The Monte Carlo algorithm was set up to generate 3000 self-avoiding random walks with a single trap attached to one end (see Figure 2). For the sample of walks we calculated the mean-square end-to-end length $\langle R_n^2\rangle$, the survival probability $\langle S_n(t)\rangle$ for t varying between 200 and 8000 jumps of the exciton from eq 2-7 and the mean survival time τ_n of the exciton from eq 2-8. The lengths of the walks were taken to increase in units of 10 steps up to a maximum length of 100. The results are in Table I.

As a test of the procedure, the scaling exponent ν was calculated for the mean-square end-to-end length of the random walk. The renormalization group suggests a scaling form

$$\langle R_n^2\rangle \sim C_0 n^{2\nu}\left(1 + \frac{a_1}{n} + \cdots + \text{nonanalytic corrections}\right) \tag{2-26}$$

where the corrections to scaling are both analytic and nonanalytic.[21] The numbers a_k are lattice dependent. To allow for these corrections to scaling, a convenient functional form approximating eq 2-26 would normally be[21,22]

$$\langle R_n^2\rangle \approx C_0(n+k)^{2\nu} \tag{2-27}$$

taking into account corrections up to order n^{-1}. The pa-

Table II
Curve Fitting To Determine 2ν for a Linear Polymer

n_{min}	C_0	k	2ν
10	1.88 ± 0.27	−0.98 ± 0.66	1.196 ± 0.032
20	1.98 ± 0.57	−0.2 ± 2.3	1.218 ± 0.070
30	1.88 ± 1.18	−1.01 ± 5.3	1.198 ± 0.124

Table III
Curve Fitting To Determine μ for a Linear Polymer

n_{min}	C_1	k	μ
10	1.58 ± 0.20	1.60 ± 0.48	1.969 ± 0.026
20	1.39 ± 0.39	2.25 ± 1.08	1.995 ± 0.048
30	1.12 ± 0.52	3.34 ± 2.46	2.031 ± 0.088

rameters (C_0, k, 2ν) should be determined by some curve-fitting procedure. A maximum-likelihood analysis using Newton's method (see references[22] for details) minimizing the least-squares error

$$\epsilon = \frac{1}{2}\sum_{m=n_{min}}^{n_{max}}\left(\frac{d_m - C_0(n+k)^{2\nu}}{\sigma_m}\right)^2 \qquad (2\text{-}28)$$

was performed where $d_m \pm \sigma_m$ is a data point with a single standard deviation as error. The fittings were done for $n_{max} = 100$ and n_{min} was increased until the parameters (C_0, k, 2ν) have converged to within 95% confidence limits.

The results are displayed in Table II. For $n_{min} = 10$ the results are already within the confidence limits of the $n_{min} = 20$ or 30 results; taking n_{min} larger than 10 brings no improvement in our estimates. Therefore, $n_{min} = 10$ is chosen as our best estimate. The results are (the errors of 95% confidence limits)

$$C_0 = 1.88 \pm 0.27$$
$$k = -0.98 \pm 0.66 \qquad (2\text{-}29)$$
$$\nu = 0.598 \pm 0.016$$

The result for ν is very close to the Flory value, and the best numerical results for the self-avoiding random walk in three dimensions,[23] giving confidence that the Monte Carlo program, is correct.

In analogy to these results, a scaling form for the mean survival time τ of the exciton was postulated from eq 2-20 and 2-27 to be

$$\langle \tau_n \rangle \approx C_1(n+k)^{\mu} \qquad (2\text{-}30)$$

An identical analysis of the mean survival time of the exciton on a polymer with one trap attached at one end gives the results in Table III. Here the best solution is found from a minimum value of n to be 20:

$$C_1 = 1.39 \pm 0.32$$
$$k = 2.25 \pm 1.08 \qquad (2\text{-}31)$$
$$\mu = 1.995 \pm 0.048$$

The value of μ is indeed very close to the predicted value of 2 from the previous subsection (eq 2-20). This result confirms the belief that the self-avoiding random walk is essentially an inhomogeneous object; there are so many "bottlenecks" in its network that, typically, the removal of a single bond would disconnect the network with a finite probability, even if n goes to infinity, making it impossible for an exciton to reach a trap or an electric current flowing along it to continue.

Apart from the predicted behavior of the mean survival time, some predictions made about the survival probability function can now be made. The behavior indicated in eq 2-22 could be tested by increasing the value of t steadily in $-(\ln S_n(t)/t) = A_n(t)$. This number should converge to the inverse value of the measured mean survival time as it is seen in eq 2-23. The results are displayed in Table IV for values of n from 10 to 100. Although the results are not good for $n = 10$ (probably because scaling does not apply for this small value of n) and worsens as n approaches 100 (since t has not been taken to large enough values), good results are found for n between 20 and 70. These results support the ideas that the spectral dimension of the polymer is indeed 2 and complements the results obtained by Byers et al.[18] for the long-time behavior of the survival functions. Finally, a plot of $A_n(t)$ against t (Figure 3) for $n = 50$ reveals that this quantity indeed converges to the inverse value of the mean survival time.

Table IV
$-[\ln S_n(t)]/t$ Compared to τ_n^{-1} for Large t

n	$-[\ln S_n(6000)]/6000 \times 10^3$	$-[\ln S_n(7000)]/7000 \times 10^3$	$-[\ln S_n(8000)]/8000 \times 10^3$	$\tau_n^{-1} \times 10^3$
10	3.292	3.226	3.174	5.100
20	1.142	1.105	1.074	1.480
30	0.640	0.619	0.601	0.697
40	0.429	0.415	0.403	0.414
50	0.306	0.296	0.289	0.269
60	0.236	0.228	0.221	0.191
70	0.187	0.180	0.174	0.140
80	0.155	0.148	0.143	0.109
90	0.134	0.128	0.123	0.087
100	0.116	0.110	0.105	0.070

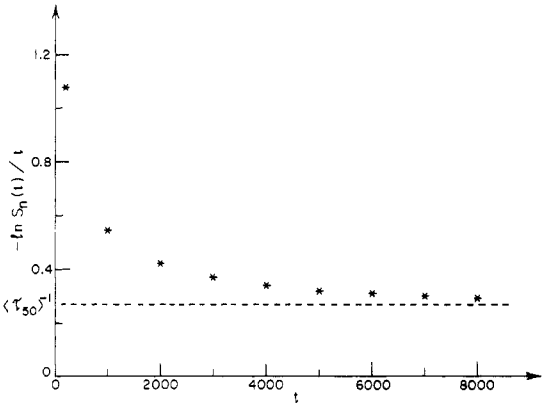

Figure 3. Function $A_n(t)$ studied by plotting $-[\ln S_n(t)]/t$ against t. The curve converges to a constant τ_n^{-1} as predicted by eq 2-23. n was taken to be 50.

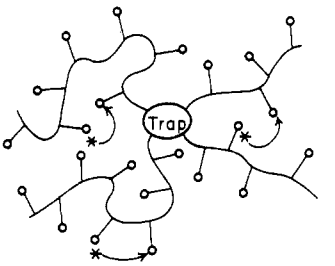

Figure 4. Star with a trap at its center. Excitons can migrate on chromophores on each arm or from arm to arm.

These numerical results given strong support for the nonrigorous arguments made about the diffusion of excitons on a polymer substituted with chromophores.

2.3. Stars. So far, the discussion of singlet exciton diffusion on a polymer substituted with chromophores has centered about a linear polymer with a trap situated at one end. It is also possible that the trap may be at the center of a polymer or at the center of a uniform star with f arms (see Figure 4).

As an example, the uniform star with 3 arms was studied numerically. The Monte Carlo algorithm was adapted to generate ensembles of correctly weighted stars, up to 54

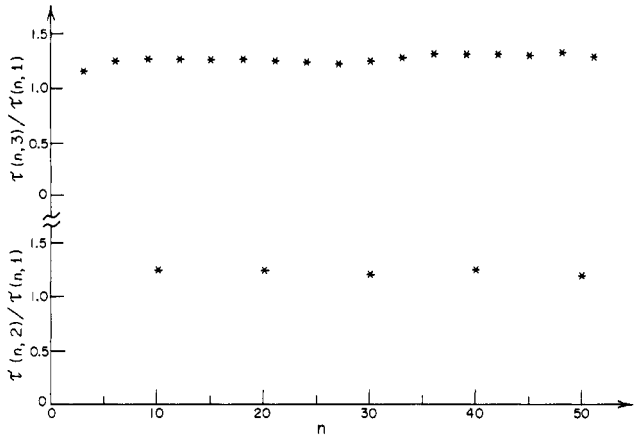

Figure 5. Steric effects on the diffusion of excitons on stars with a trap at the center studied here. The exponent μ (eq 2-34) is independent of the number of arms, since the ratio $\tau(n,f)/\tau(n,1)$ is practically constant over a wide range of n.

chromophores/arm (a total of 162 for the whole star) in steps of 3 chromophores added between measurements. Once again, the square radius of gyration $\langle R_g^2(n,3)\rangle$ of a star with n chromophores/arm was calculated, the survival probability function $S_n(3,t)$ was measured for t between 200 and 8000 jumps, and the mean survival time $\tau(n,3)$ was calculated for n in steps of 3 up to 54. The results were then analyzed in the the same manner as for linear stars. The exponent ν is expected to be the same for uniform stars and self-avoiding random walks.[24] Assuming the scaling relation (eq 2-27) for the radius of gyration, the calculation produces

$$C_0 = 0.296 \pm 0.022$$
$$k = -1.34 \pm 0.88 \qquad (2\text{-}32)$$
$$\nu = 0.57 \pm 0.01$$

for an $n_{min} = 9$ and the errors are 95% confidence limits. The value obtained for ν in this manner is reasonably close to that of the self-avoiding random walk and gives confidence in the numerical procedure generating stars.

As in the case of the linear polymer, it is expected that the exponent μ in eq 2-20 would be close to 2 for the stars. Performing a least-squares fit to the data produces a best estimate for μ, again assuming scaling as before (eq 2-30)

$$C_1 = 1.248 \pm 0.102$$
$$k = 6.38 \pm 0.84 \qquad (2\text{-}33)$$
$$\mu = 1.984 \pm 0.024$$

Here again the minimum length of the arms of the star was $n_{min} = 9$. Once again, the exponent is near the expected value of 2. The diffusion of the exciton on a star is thus qualitatively similar to that on a linear polymer.

An interesting comparison to be made between stars and linear polymers is that of the amplitude C_1 in eq 2-30. Although C_1 is expected to be independent of the number of chromophores, it is expected to depend on the number of arms f in the uniform star. Postulating thus that the mean survival time $\tau(n,f)$ of a polymer with f arms and n chromophores/arm (a total of nf chromophores in the star) scale as

$$\tau(n,f) \approx C_1(f)n^{\mu} \qquad (2\text{-}34)$$

where μ is expected to have the value 2; a plot of $\tau(n,f)/\tau(n,1)$ against n would be constant if μ is independent of the number of arms in the star. Furthermore, the ratios between $C_1(f)$ and $C_1(1)$ would give a measure of the extension of each arm in the star due to steric repulsion by the other arms, so this ratio is expected to be bigger than 1. These numbers were plotted in Figure 5. Note that the comparisons are practically constant functions and that these constants are bigger than 1, as expected, both for f taking values of 2 and 3.

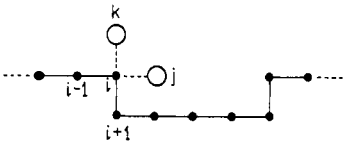

Figure 6. Triplet exciton diffusion at i to either of its nearest neighbors at $i - 1$ and $i + 1$ or to the chromophores at j and k with a probability that they occupy the sites shown.

The stars proved to have the same basic behavior as linear polymers; an exciton diffusing on one of the arms of a uniform star will only be able to tell that it is a star by the effects of steric repulsions on its mean survival time reflected in the amplitude in eq 2-34. The exponent appears to be universal.

3. Triplet Exciton Diffusion

The triplet exciton has a lifetime in a chromophore that is longer than that of the singlet exciton. In general, it is also longer than the relaxation time of a polymer. It is therefore reasonable to expect that a polymer will explore the whole of its configuration space while an exciton is confined to one of its chromophores. The physical picture is different here; at any time while the exciton resides in a chromophore, a chromophore further along the chain may approach within a distance short enough for the exciton to make a transfer to it. The probability $q(i,j)$ that an exciton will end up on a chromophore j, given that it is now on chromphore i, is thus the transition probability times the probability that j is close to i in space. This situation is explained in Figure 6. Loosely speaking, it could be argued that the exciton is diffusing on an "averaged polymer" configuration; its nearest-neighbor sites are filled with a chromophore j with the probability that this chromophore is near it in space. This averaging is of course the opposite limit from the singlet exciton diffusion problem. There the polymer was held in a fixed configuration while the diffusion process goes on; only afterward were averages taken over all the possible configurations. Here, it is necessary to average over the chain conformations before the exciton is released to diffuse along the chain.

The motion of the exciton can again be described by a continuous-time master equation

$$\frac{d}{dt}p_i(t) = \Gamma_{ij}p_j(t) - u_i p_i(t) \qquad (3\text{-}1)$$

where $p_i(t)$ is the probability that the exciton is at site i at time t and Γ_{ij} is the transition probability between sites i and j given by

$$\Gamma_{ij} = cq(i,j) \qquad \text{if } i \neq j$$
$$= -\sum_{\substack{j=1 \\ j\neq i}}^{n} cq(i,j) \qquad \text{otherwise} \qquad (3\text{-}2)$$

and u_i is the probability that the exciton will be absorbed into the trap from chromophore i, which is equal to the transition probability c times the probability that the trap will be near to it in space ($q(i, n + 1)$ if the trap is at the end of the chain, which is assumed to be the case in what follows).

The probability that two chromophores may approach each other in space if they are separated by a distance $|i$

$-j|$ along a chain, $q(i,j)$, has been studied extensively.[25-28] In general, it is given by the form

$$q(i,j) = \frac{K}{|i-j|^{\theta_s}} \tag{3-3}$$

where $|i-j|$ is the separation between two chromophores i and j along the chain, K is a constant, and θ_s is an exponent that takes the following values (from the second-order ϵ-expansion performed by des Cloizeaux[27]):

1. $\theta_0 \approx 1.92$ for end–end contacts ($i = 1$ and $j = n$).
2. $\theta_1 \approx 2.03$ for middle–end contacts (i or j is 1 or n while the other is near the middle of the polymer chain).
3. $\theta_2 \approx 2.18$ for i and j near the middle of the chain.

Equation 3-1 can thus be put into the following form (for discrete time), assuming that the trap is at the $(n+1)$th node on a chain with n chromophores

$$p_i(m+1) = \mathcal{H}_{ij}p_j(m) \tag{3-4}$$

where to a good approximation

$$\begin{aligned}\mathcal{H}_{ij} &= \frac{c}{|i-j|^{\theta_2}} \qquad \text{if } i \neq j \\ &= 1 - \sum_{\substack{j=1 \\ j\neq i}}^{n} \mathcal{H}_{ij} - \frac{c}{|n+1-i|^{\theta_1}} \qquad \text{otherwise}\end{aligned} \tag{3-5}$$

Note that $\sum_j \mathcal{H}_{ij} = 1 - c/(|n+1-i|^{\theta_1})$. As with the singlet case, the largest eigenvalue of $\mathcal{H}$ will dominate the long-time behavior of the exciton.

An immediate observation from eq 3-4 is that the properties of the diffusion process will be dominated by transfers between chromophores far removed from each other along the polymer chain. This follows from the fact that, for large n, $k^n < n^{-\alpha}$ for fixed $k < 1,\alpha$. The fact that the "contact probability" between two chromophores satisfies a law like eq 3-3 is thus responsible for this observation. The eigenvalues of $\mathcal{H}$ could be determined through a perturbative calculation about a "ground state" chosen to reflect faithfully the physics of the process. This suggests that an expansion about the eigenvalues of the "zeroth-order transition matrix"

$$\begin{aligned}\mathcal{H}_{ij}^{0} &= \gamma \qquad \text{if } |i-j| \geq 1 \\ &= 1 - n\gamma \qquad \text{if } i = j\end{aligned} \tag{3-6}$$

where γ is some, sufficiently small, positive number, is feasible. This zeroth-order transition matrix reflects the fact that single-step long-range transfers between chromophores are more likely than multiple-step transfers between the same chromophores (due to the inequality mentioned above). The stiff-rod approximation (choosing eq 2-9, the transition matrix for the stiff rod, as the zeroth order transition matrix) is found to be inadequate, a not so surprising fact, since it does not allow for the long-range transfers of excitons.

The eigenvalues of $\mathcal{H}$ are easily determined, the largest eigenvalue is $1-\gamma$ and there are $n-1$ degenerate eigenvalues $1-(n+1)\gamma$. The eigenvectors corresponding to these eigenvalues are

$$w(j) = \frac{1}{n^{1/2}} \sum_{i=1}^{n} \delta_{ij} \tag{3-7}$$

$$v_i(j) = \frac{1}{2^{1/2}}(\delta_{ij} - \delta_{i+1,j}) \qquad \text{for } i = 1, 2, \ldots, n-1 \tag{3-8}$$

Following a simple perturbative scheme[29] it is found that, up to third order, the largest eigenvalue of $\mathcal{H}$ is given by

$$\lambda_{max} = 1 - \gamma + e_1 + e_2 + e_3 \tag{3-9}$$

Table V
λ_{max} Calculated by Numerical and Perturbative Methods

n	c	λ_{max}^{num}	λ_{max}^{pert}
10	0.010	0.9991	0.9985
	0.025	0.9978	0.9964
	0.050	0.9956	0.9927
20	0.025	0.9990	0.9981
	0.050	0.9981	0.9963
50	0.025	0.9997	0.9993
	0.050	0.9994	0.9985
100	0.025	0.9998	0.9996
	0.050	0.9997	0.9993

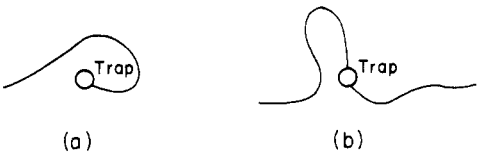

Figure 7. Important configurations in the trapping of triplet excitons. If the trap is on the end of the chain, excitons are trapped by the tadpole configurations like (a) most quickly; thus, the contact exponent θ_1 dominates the long-time behavior of the exciton. For cases where the trap is near the middle of the chain as in (b), the exponent θ_2 will dominate the long-time behavior.

where the e_i are corrections in the perturbative expansion given by

$$e_1 = \gamma - \frac{c}{n} \sum_{i=1}^{n} \frac{1}{|i|^{\theta_1}} \tag{3-10}$$

$$e_2 = \frac{c^2}{2\gamma n^2} \sum_{i=1}^{n-1} \left(\frac{1}{|i|^{\theta_1}} - \frac{1}{|i+1|^{\theta_1}} \right)^2 \tag{3-11}$$

and γ can be chosen such that $e_3 = 0$. Up to first order in perturbation theory thus

$$\lambda_{max} = 1 - \frac{c}{n} \sum_{i=1}^{n} \frac{1}{|i|^{\theta_1}} \tag{3-12}$$

To test the results of this perturbative scheme, $\mathcal{H}$ was diagonalized numerically, and the largest eigenvalues were compared to the predictions of the perturbative scheme. The results are in Table V and are good for the simple scheme carried through here, supporting the idea that the ground state (eq 3-6) reflects the physical behavior of the process well. (The values of the contact exponents were taken to be $\theta_1 = 2.03$ and $\theta_2 = 2.18$.)

It is interesting to note that there is no explicit dependence up to second-order perturbation theory of λ_{max} on the middle–middle exponent θ_2. The explicit dependence appears in third-order perturbation theory. The size of the largest eigenvalue of $\mathcal{H}$ is thus mostly determined by θ_1, the exponents governing the "tadpole configurations" (Figure 7a) of the polymer. Note that, in the scheme above, if the trap had been near the middle of the chain, the perturbative scheme would still go through in the same way as here, except that the exponents θ_1 and θ_2 would have interchanged roles. Loop configurations like in Figure 7b would then dominate the diffusion of the exciton to the trap.

For polymers with a large number of chromophores n and after a large number of transfers of the exciton m, the probability that the exciton will be in the trap is given by $1 - \lambda_{max}^{m}$ and the first passage time of the absorption is given by eq 2-12. The mean survival time of the exciton is then determined in exactly the same manner as in eq 2-13. The terms in the perturbation expansion for λ_{max} can be approximated by[30]

$$\frac{1}{n}\sum_{i=1}^{n}\frac{1}{i^{\theta_1}} = n^{-\theta_1-1}\left(\frac{n}{1-\theta_1}+\frac{1}{2}+O(n^{-1})\right) \quad \text{if } \theta_1 < 1$$
$$= \frac{1}{n}\left(\zeta(\theta_1) - \frac{n^{1-\theta_1}}{\theta_1 - 1} + O(n^{-\theta_1})\right) \quad \text{if } \theta_1 > 1 \tag{3-13}$$

where $\zeta(\theta_1)$ is the Riemann ζ function. If $\theta_1 = 1$, this sum may be approximated by $1/n \log n$. The second-order corrections can also be approximated as above, and we find

$$\frac{1}{n^2}\sum_{i=1}^{n-1}\left(\frac{1}{i^{\theta_1}} - \frac{1}{(i+1)^{\theta_1}}\right)^2 \approx \frac{{\theta_1}^2}{1+2\theta_1}(1 - n^{-1-2\theta_1})$$
$$\text{if } \theta_1 > -\frac{1}{2} \tag{3-14}$$

The mean survival time for the diffusing exciton is thus given by

$$\tau_n = \frac{1-\theta_1}{c}n^{\theta_1} + O(n^{\theta_1-1}) \quad \text{if } \theta_1 < 1$$
$$= \frac{n}{c\zeta(\theta_1)} + \frac{n^{2-\theta_1}}{(\theta_1-1)\zeta(\theta_1)} + O(n^{1-\theta_1}) \quad \text{if } \theta_1 > 1 \tag{3-15}$$

This is a very interesting result. Recall that, in the case of singlet diffusion, it was argued that the mean survival time should scale as the square of the total length of the polymer. In triplet exciton diffusion a drastically different result is found: since $\theta_1 \approx 2.03$, τ_n scales linearly with the length of the polymer chain, and the exponent μ (eq 1-4) defined in the introduction is 1. The physical picture behind this result may be explained in the following way. First-order perturbation theory models the process where an exciton would reside on a trap until it makes a direct, through-space transition to the trap. Considering this process only, we find the above results. The second-order term in perturbation theory models transitions of order c^2, as seen in eq 3.11. The contribution of these processes is small compared to the first-order processes and does not change the leading behavior found in the first-order calculation.

4. Conclusions

The main motivation of this study was the diffusion of excitons on a random structure, in this case a polymer chain. A successful application of scaling ideas, Monte Carlo calculations and perturbation theory makes predictions about the mean survival time and the exciton survival function on the polymer (network). We note the following remarks.

1. Excitons residing in chromophores may be destroyed and radiated away as photons by the processes of fluorescence (singlet excitons) or phosphorescence (triplet excitons) or internal conversion or intersystem crossing to the ground state.[2,3] This feature of the problem can be modeled by adding a diagonal term to the diffusion equations (eq 2-1 and 3-1), which is essentially the probability (say, ρ) that a chromophore may radiate an exciton away. The process is then in general described by

$$\frac{\mathrm{d}}{\mathrm{d}t}p_i(t) = \Delta_{ij}p_j(t) - \rho p_i(t) \tag{4-1}$$

where Δ_{ij} is again a transition matrix between the chromophores and the trap. It is obvious that this addition just has the effect of reducing the largest eigenvalue (eq 2-7 or 3-12) by ρ; thus, the mean survival time of the exciton in the long polymer limit, or in the case that ρ is large (approaching 1), has a dependence on n given by

$$\tau_n \sim \frac{n^{\mu}}{1 + c\rho n^{\mu}} \tag{4-2}$$

This reduces to the usual equation (eq 2-20 or 3-15) in the case that $\rho = 0$; otherwise, in the large n limit, it becomes a constant. The effect of fluorescence and phosphorescence is thus to obscure the "clean" postulate (eq 1-4) for the mean survival time of the excitons by demanding a dependence like eq 4-2 instead. This outcome should be expected in the long-chain or large ρ limits. The excitons will radiate away before they reach the traps, and τ_n will then become equal to the natural lifetime of an exciton on a single chromophore, which is a constant.

2. The study made a clear distinction between the two limiting cases of singlet (transfer time short in comparison with polymer relaxation time) and triplet diffusion (transfer time long in comparison with polymer relaxation time). Although this distinction may be slightly artificial (not based on fundamental physical differences in the diffusion process), it is nevertheless real, since the transfer times vary over many orders of magnitude between singlet and triplet excitons. The survival function $S(t)$ in general has the functional form

$$S(t) \sim \frac{1}{t}e^{-t/\tau} \tag{4-3}$$

where $\tau \sim n^{\mu}$ for a polymer with n chromophores substituted along it. The distinction between singlet (fast) and triplet (slow) diffusion is that $\mu = 2$ for singlet excitons and $\mu = 1$ for triplet excitons. The predictions made for the mean survival time of singlet and triplet excitons diffusing on a polymer with chromophores substituted at regular intervals along its length could be tested experimentally to confirm the results of this paper.

3. The expectation is that if only a small loss of excitons due to fluorescence occurs for singlet excitons, the mean survival times and survival functions will behave as predicted in eq 2-20, 2-22, and 2-23. The trick would be to observe these experimentally. In general, the polymers would have a distribution $D(n)$ of lengths around some average $\bar{n}$. In that case it is necessary to calculate the mean of the mean survival time over this distribution

$$\langle \tau_{\bar{n}} \rangle = \int D(n)\, S_n(t)\, t\, \mathrm{d}t\, \mathrm{d}n \tag{4-4}$$

and to measure it as a function of the mean length.

4. The detection of photons emitted by the trap is complicated by the fact that an excited trap may have a characteristic decay probability $r(t)$, where $r(t)$ is the probability density that the trap will emit a photon a time t after it has been excited. The probability that a trap will produce a photon at a time t after a chromophore has been excited on the chain is then the product of the probabilities that it arrives at a time t' at the trap, $S(t')$, and decays a time $(t - t')$ later, $r(t - t')$ for any $0 \le t' \le t$. The observed decay time is then

$$\int_0^t \mathrm{d}t'\, S(t')\, r(t - t') \tag{4-5}$$

In the trivial case that $r(t) = \delta(t - \tau_0)$, then the observed decay is simply $S(t - \tau_0)$. In general, however, a more complicated expression can be expected for $r(t)$, and the observed decay curves will be more complicated than the asymptotic form predicted in eq 2-22.

5. It is found that the link and blob picture of the polymer chain as a one-dimensional object[16,17] is mirrored in the characteristic behavior of the singlet exciton. As noted the conduction of a polymer and the diffusion of excitons on it are both processes described by the diffusion

equation, and the scaling properties should thus be the same.

6. It is an interesting byproduct of the study of singlet excitons on the star that it could be used to study the stretching of the arms of the star due to steric effects. A typical arm of a star has fewer loops ("short-circuits") on all length scales resulting in the observation that the amplitude of eq 2-34 is influenced but not the scaling exponent.

7. In the experimental setup, the situation may not be as clear as discussed here. In this model, we have considered a lattice version of exciton diffusion on polymer chains, and we have restricted the range of the transfers between chromophores to nearest-neighbor sites only (similar to the model studied by Byers et al.[18]). In the experimental setup, however, the range of transfers (especially Förster transfers) may be comparable to the radius of gyration of the polymer. In that case the trapping of excitons will be dominated by a single-step transfer directly into the trap.

8. The functional form assumed in this paper for the survival function $S_n(t)$ in the case of singlet exciton diffusion is summed up by eq 2-22 and 2-23. Asymptotically, the survival function is a pure exponential (since $A_n(t)$ has a constant limit as $t \to \infty$). For smaller values of t, however, this is not the case. $A_n(t)$ is dependent on t, and we calculated this dependence in Figure 3 and in Table IV to illustrate this fact. $A_n(t)$ decays to $\langle \tau_n \rangle^{-1}$ as t increases but is very different from this value for smaller values of t, leading to a nonexponential dependence of $S_n(t)$ on t for small t. This phenomenon is observed experimentally (see, for example, the paper by Byers et al.[18] and references therein).

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