Macromolecules 1991, *24*, 1969–1974

Energy Transfer on Ring Polymers

E. J. Janse van Rensburg* and S. G. Whittington

Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada

Received June 14, 1990; Revised Manuscript Received October 26, 1990

ABSTRACT: The properties of migrating excitations on ring polymers are investigated numerically. We show that, in the presence of traps, an excitation has a mean survival time τ which behaves as n^{μ}, where n is the number of chromophores in the ring polymer, and that $\mu \approx 2$ in a good solvent. We consider the effects on μ of a deteriorating solvent and of multiple traps.

1. Introduction

The excitation of a molecule by a photon of appropriate wavelength is a subject that has attracted much attention in physics and chemistry. If the excitation is delocalized in the molecule (or *chromophore*), then it is called an exciton.[1,2] It is interesting that a nonradiative transfer of excitations may occur between two chromophores that are "near" to each other.[3] The mechanisms for this process have been investigated in detail.[1,2] They are mainly the induced dipole interaction (or the Förster process[4]), which is a long-ranged interaction, and the exchange mechanism (or Dexter transfer[5]), which is a short-ranged process.

Chromophores may be substituted along a polymer. It is therefore possible that a transfer of an excitation between two chromophores may occur in the same polymer, or even between different polymers, providing that the chromophores are near to each other in space. This situation is often modeled by representing the polymer as a self-avoiding walk, with the vertices representing the chromophores.[6-8] This model assumes a uniform spacing of chromophores and that transfers of excitations only occur between chromophores which are nearest neighbors on the lattice.

This situation is usually studied by assuming that the dynamics of the excitation is that of a particle which hops in an uncorrelated fashion from chromophore to chromophore (i.e., there are no excitation–excitation interactions or coherence between migrating excitations). We say that the motion of the excitation is diffusive on the polymer backbone. There are two limiting cases in this problem.[2,3,8] *Slow diffusion*, usually that of a triplet excitation,[2,3] occurs on a time scale that is long when compared to the configurational relaxation time of a polymer. We considered this case for linear polymers in a previous study.[8] In this paper we consider *fast diffusion*, usually that of a singlet excitation,[2,3] which occurs on a time scale shorter than the configurational relaxation time of the polymer. We also choose to work with *ring polymers* and to compare the results to our earlier work[8] on fast diffusion on linear polymers and stars. There are several advantages in considering ring polymers. The first is that there are no end effects due to endpoints in the ring polymer. There are qualitative differences between sites near the ends of a linear polymer and sites near the middle which may affect the results in a numerical simulation. Second, the different topology of a ring polymer may also affect the migrating excitations. In fact, we expect that the ring polymer will occupy a smaller region in space than a linear polymer of the same length, so transfer from chromophores into excitation traps will be more effective. This suggests that the topology of the molecule may influence the lifetime of an excitation. It is expected that the mean survival time, $\langle \tau \rangle$, of an excitation on a polymer will scale as[8]

$$\langle \tau_n \rangle \sim n^{\mu} \tag{1.1}$$

where μ is an exponent which has value near 2 for linear polymers and stars. In this paper we calculate the exponent μ for ring polymers. If μ is again near 2, then it seems likely that the topology of molecules will have little effect on the "waiting time" of captured excitations migrating into a trap in an experimental situation, if the transfers occur on a time scale that is short in comparison with the relaxation time of the molecule.

In general, the transfer of excitations will occur until spontaneous emission occurs, or until a trap is encountered, or until excimer formation and fluorescence destroy the excitation. We shall only consider the effect of traps on the lifetime of the excitation. We therefore assume in our model that spontaneous emission does not occur, that the density of excitations is so low that collisions can be neglected, and that excimer formation is suppressed.

Diffusion in random media is an important problem that has received wide attention in the literature.[9,10] It is used to model fluid flow in porous rocks,[11] conductivity of superionic conductors,[12] and transfer of excitons in porous membranes, polymeric glasses, and isotropically mixed glasses.[13]

We organize this paper as follows. Section 2 is concerned with our numerical techniques. We discuss the calculation of survival times and define the exponential, integrated, and normalized survival times. We consider some general features of the problem, particularly the stretched exponential behavior expected for short times. We also consider the simulation of lattice polygons, which model ring polymers, and briefly discuss the pivot algorithm for polygons and its application to this problem. In section 3 we present and discuss our results. The case of a single trap on a ring polymer in a good solvent is first considered in section 3.1. In section 3.2 we study the effects on the survival times of multiple traps and, in section 3.3, the effects of the solvent. The stretched exponential regime of the survival probability is examined in section 3.4. We conclude the paper in section 4 with a discussion of our results and with some suggestions for further study.

2. Numerical Techniques

2.1. Definitions and Notation. A *polygon* ω is a sequence of lattice sites $\omega_0, \omega_1, ..., \omega_n$ and associated edges such that $\omega_0 = \omega_n$, ω_i and ω_{i+1} are neighbors in the lattice and $\omega_1, \omega_2, ..., \omega_n$ are all distinct. We model the conformational properties of a ring polymer by those of a polygon where the vertices of the polygon are regarded as chromophores. Suppose that a vertex of ω is an excitation trap with probability p. Let an excitation be transferred from vertex to vertex, and let z_t be the number of distinct vertices that the excitation visits in t jumps. Then the probability that the excitation is not in a trap after t jumps is

$$f_t = (1-p)^{z_t} \tag{2.1}$$

The survival probability function $S_n(t)$ of the excitation on ω is the average of f_t over all possible paths of the excitation on ω and over all the configurations of ω (including an average over the initial position of the excitation). Symbolically

$$S_n(t) = \langle (1-p)^{z_t} \rangle \tag{2.2}$$

It is now known[14-17] that in the d-dimensional cubic lattice Z^d, $S(t) \sim e^{-\lambda t^{d/(d+2)}}$, where λ is a constant which depends on p and d. Diffusion on fractals has also received attention.[9,18-21] A cumulant expansion[18] of eq 2.2 naturally leads to a series of approximations to $S_n(t)$. In particular, to second order we have

$$S_n(t) \approx e^{-\lambda \hat{z}_t + \lambda^2 \sigma_t^2/2} \tag{2.3}$$

where $\hat{z}_t = \langle z_t \rangle$ and $\sigma_t^2 = \langle z_t^2 \rangle - \langle z_t \rangle^2$. λ is a constant depending on p. It was pointed out that this expansion is only slowly convergent for 1-dimensional systems,[22] so that eq 2.3 is not a good approximation to the survival probability function in low dimensions. Equation 2.3 does, however, show an important property of the survival probability function. It is known that[10]

$$\hat{z}_t \sim t^{d_s/2} \tag{2.4}$$

where d_s is the spectral dimension of the fractal under consideration. Since $d_s < 2$, we expect that $S_n(t)$ will be a "stretched exponential". In the case of diffusion on a polymer, it is believed that $d_s = 1$.

So far we have ignored the fact that ω is a finite object. To consider this, we describe the process by a master equation

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t} p_i(t) &= \sum_{j=1}^{n} W_{ij} p_j(t) \\ &= \sum_{j=1}^{n} (w_{ij} p_j(t) - w_{ji} p_i(t)) - u_i p_i(t) \end{aligned} \tag{2.5}$$

where $p_i(t)$ is the probability that the excitation is at the ith vertex at time t. A transfer per unit time from chromophore j to i occurs with probability w_{ij}, and u_i is the transition rate per unit time from chromophore i into the excitation traps. Let **O** be the right eigenvectors of **W** ($=[W_{ij}]$) and let Λ be the eigenvalues (i.e., $\sum_{k=1}^{n} W_{ik} O_{kj} = O_{ij} \Lambda_j$). Suppose that $p_j(0) = \sum_{k=1}^{n} O_{jk} A_k$. Then the formal solution to eq 2.5 is

$$p_i(t) = \sum_{j=1}^{n} O_{ij} e^{\Lambda_j t} A_j \tag{2.6}$$

and the survival probability function $S_n(t)$ is given by

$$S_n(t) = \sum_{i,j=1}^{n} O_{ij} e^{\Lambda_j t} A_j \tag{2.7}$$

The largest eigenvalue ($\lambda_{\max}$) of W_{ij} (the least negative) will dominate $S_n(t)$ for large t, so that we can write that

$$S_n(t) \sim e^{-t/\tau_e} \tag{2.8}$$

for large t, where $\tau_e = -\lambda_{\max}^{-1}$. We call τ_e the *exponential survival time* of the excitation. On a finite object, the stretched exponential behavior predicted by eq 2.2–2.4 will give way to eq 2.8. We therefore expect to be able to observe the stretched exponential behavior only for small t.

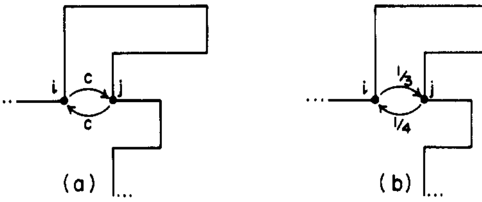

Figure 1. (a) Symmetric transfer of excitations: an excitation jumps from chromophore i to j and from j to i with the same probability c. (b) Nonsymmetric transfer of excitations: an excitation jumps from a chromophore i to a nearest neighbor (j) with a probability $1/l$, where l is the number of nearest neighbors to i.

If $p_i(t)$ and **O** are normalized, then $S_n(0) = 1$. We define the mth moment of the *integrated survival time* of the excitation by

$$\tau_{\text{int}}^{m} = \sum_{t=0}^{\infty} S_n(t) t^{m-1} \tag{2.9}$$

The moments of the *normalized survival time* are

$$\tau_{\text{nor}}^{m} = \tau_{\text{int}}^{m+1} / \tau_{\text{int}} \tag{2.10}$$

The exponential, integrated, and normalized survival times are all measures of the lifetime of an excitation on a network.

There are two possible choices for **W** in eq 2.5. The first choice is a symmetric one: We choose some number $c = W_{ij} = W_{ji}$; i.e., the probability per unit time (c) of a jump from i to j is equal to the probability for a jump from j to i. We illustrate this in Figure 1a. The probability that no jump occurs is $(1 - lc)$, where l is the number of neighbors of the vertex on the polygon. The nonsymmetric case is defined by conserving probability at each vertex on ω. Therefore, the probability of a jump from i to j depends on the number of neighbors to i on the polygon. If i has l neighbors, then the probability for a jump to j is $1/l$. We illustrate this case in Figure 1b. The nonsymmetric case requires much more numerical work than the symmetric case, since solving eq 2.5 requires the diagonalization of a nonsymmetric matrix. We shall therefore concentrate on the symmetric case in this paper and only consider the nonsymmetric case briefly in section 3.1.

2.2. Numerical Simulation. In this section we briefly consider the simulation of polygons using the pivot algorithm. The pivot algorithm is a Monte Carlo algorithm which was invented by Lal[24] for the simulation of self-avoiding walks in the canonical ensemble. The algorithm was studied in detail by Madras and Sokal[25] and was later extended to polygons[26,27] and subsequently studied on the fcc lattice.[28] We shall perform our simulation on the fcc lattice. The basic elementary move of the algorithm is as follows: Consider two different vertices ω_i and ω_j on ω, the current polygon, chosen uniformly and at random. With these pivots, apply an elementary transformation from a list of possible transformations to the shorter piece of the polygon. If the result is a (self-avoiding) polygon, then it is accepted, becoming the current polygon. Otherwise, it is rejected, and the current polygon does not change. The list of possible elementary transformations is given by the octahedral group, the symmetry group of the cubic lattices. Among others, the elements of this group are point reflections (inversions), reflections through lattice planes containing two of the three Cartesian axes of the fcc, reflections through planes inclined at 45° to two axes and containing the third axes (45° planes), and 90° rotations about the axes. In each case the "origin" of the transformation is taken to be the midpoint of the line segment joining the two pivots. The following is known:[28]

Theorem. The pivot algorithm applied to polygons on the fcc lattice is ergodic, provided that inversions, lattice plane reflections, and either 45° plane reflections or 90° rotations have positive probability to occur as elementary transformations in the Monte Carlo algorithm.

Let R_n be the set of all polygons. The pivot algorithm may be considered as a realization of a Markov chain on R_n. Let us now consider reversibility and the simulation of a bad solvent. Let $R_n(m) \subset R_n$ be the set of all polygons with n vertices and m contacts between vertices which are not joined by an edge in the polygon. Let the cardinality of $R_n(m)$ be $p_n(m)$. We assign equal weight to the polygons in $R_n(m)$. The effect of the solvent is taken into account by introducing an attractive monomer–monomer interaction (or "contact potential") between the vertices. For each $\omega \in R_n(m)$ we assign a weight $e^{m\phi}$, where ϕ is a reduced energy associated with the monomer–monomer interaction. The algorithm realizes a Markov chain on R_n with an invariant probability measure[28,29]

$$\pi_\omega(m) = \frac{e^{m\phi}}{\sum_{m=0}^{\infty} p_n(m)e^{m\phi}} \quad \text{for each } \omega \in R_n \qquad (2.11)$$

where ω has m contacts. If $\omega,\nu \in R_n$, then eq 2.11 implies that

$$\lambda(\omega \rightarrow \nu) = e^{(m'-m)\phi}\lambda(\nu \rightarrow \omega) \qquad (2.12)$$

where $\lambda(\omega \rightarrow \nu)$ is the probability of obtaining ν from ω via pivots and where ω has m contacts and ν has m' contacts.

This algorithm was programmed in FORTRAN77 on an Apollo 10000. Pivots were selected with uniform probability. Inversions, lattice plane reflections, 45° plane reflections, and 90° rotations were used as possible transformations. For each choice of pivots, we picked an elementary transformation with uniform probability from a list of possible transformations. To compensate for bias in our simulation due to the initial configuration, we discarded the first 150 000 iterations before we took observations. Hash coding[30,31] was used to check for self-intersections and to count the number of contacts. Autocorrelations were calculated by using time–series analysis.[25] The transition matrix **W** (eq 2.5) can be constructed easily from the hash table and was diagonalized by using the standard EISPACK routines for symmetric and nonsymmetric matrices.

3. Numerical Results

3.1. Single Trap in a Good Solvent. In this section we consider the validity of eq 1.1 for ring polymers in a good solvent, where there is one excitation trap substituted on the polymer. We also compare the symmetric and nonsymmetric cases discussed in section 2.1.

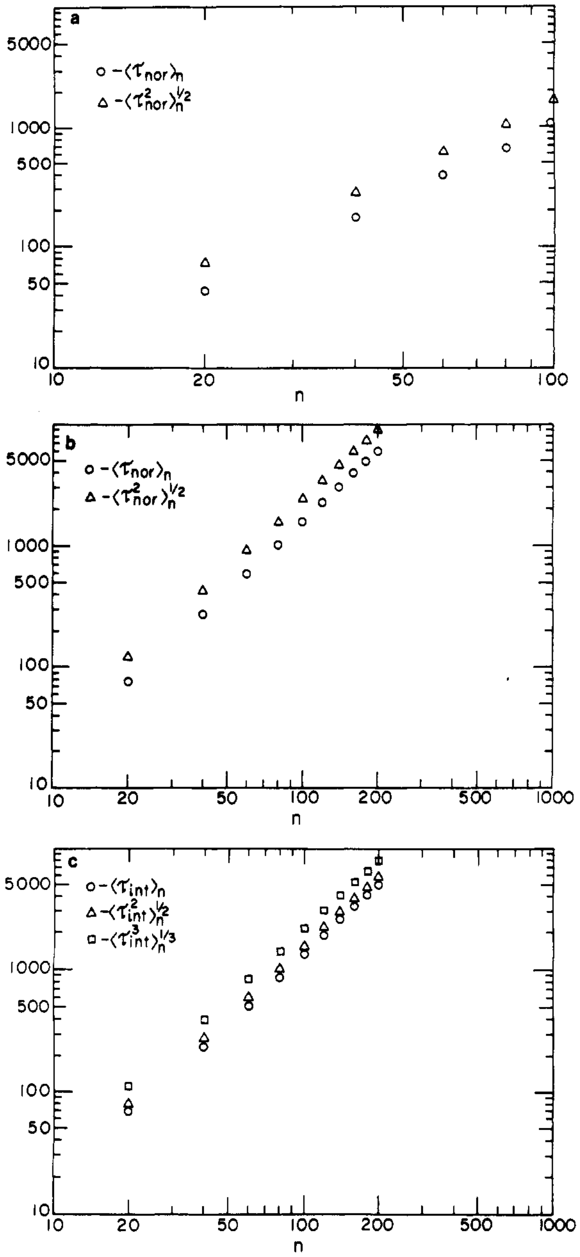

Figure 2. (a) $\langle \tau_{\mathrm{nor}} \rangle_n$ and $\langle \tau^2_{\mathrm{nor}} \rangle_n^{1/2}$ vs n for the nonsymmetric problem. (b) $\langle \tau_{\mathrm{nor}} \rangle_n$ and $\langle \tau^2_{\mathrm{nor}} \rangle_n^{1/2}$ vs n for the symmetric case. (c) $\langle \tau_{\mathrm{int}} \rangle_n$, $\langle \tau^2_{\mathrm{int}} \rangle_n^{1/2}$, and $\langle \tau^3_{\mathrm{int}} \rangle_n^{1/3}$ vs n for the symmetric case. In all these cases there was one trap on the ring polymer.

The diagonalization of a nonsymmetric matrix is an expensive procedure, so we limited our investigation into this case to the situation described here. We generated polygons with length n between 20 and 100 vertices. We minimized correlations between polygons by calculating the survival times after every m iterations, where we increased m from 10 for small n to 40 for n near 100. A time–series analysis showed that the autocorrelations are short in these cases. We calculated the mean exponential and mean normalized survival times (eqs 2.8 and 2.10) over 1000 iterations, and the normalized survival times are shown in Figure 2a. These plots are linear, strongly supporting postulate (1.1). A least-squares analysis of our data, assuming that $\langle \tau \rangle_n = C_0(n + k)^{\mu}$, where k is a constant which partially takes account of the effects of corrections to scaling for small n and C_0 is the amplitude and μ the exponent in eq 1.1, gives

$$\langle \tau_e \rangle_n = 0.13(n + 1.2)^{(1.97\pm0.06)} \qquad (3.1)$$

$$\langle \tau_{\mathrm{nor}} \rangle_n = 0.20(n - 2.3)^{(1.87\pm0.08)} \qquad (3.2)$$

$$\langle \tau^2_{\mathrm{nor}} \rangle_n^{1/2} = 0.27(n - 0.6)^{(1.90\pm0.06)} \qquad (3.3)$$

where the errors are each one standard deviation. The expected value of μ is 2, which is within the 95% confidence limits of the above results.

The symmetric case is computationally a much easier calculation. We can therefore perform more iterations and explore the behavior of the mean survival times at larger values of n. As before, we measured the survival times after every m iterations, where we increased m from 10 if $n = 20$ to $m = 100$ for $n = 200$. For $n \leq 140$ we performed 5000 measurements, but for $n \geq 160$, only 2500 measure-

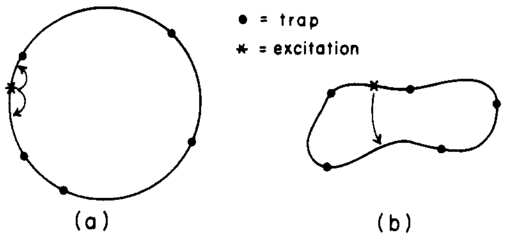

Figure 3. (a) Typical transfer in a ring polymer with p traps if we assume that the traps divide the polymer into p linear pieces. (b) Since our calculations indicate that $\mu \neq 2$, we conclude that processes like these must contribute significantly to the transfer of excitations.

ments were performed. We calculated $\langle\tau_e\rangle_n$, and the moments $\langle\tau_{\rm int}\rangle_n$ and $\langle\tau_{\rm nor}\rangle_n$. In Figure 2b we plot $\langle\tau_{\rm nor}\rangle_n$ and $\langle\tau^2{}_{\rm nor}\rangle_n{}^{1/2}$ against n, and in Figure 2c we plot $\langle\tau_{\rm int}\rangle_n$, $\langle\tau^2{}_{\rm int}\rangle_n{}^{1/2}$, and $\langle\tau^3{}_{\rm int}\rangle_n{}^{1/3}$ against n on a log-log scale. As expected, the plots are linear, confirming a relation like eq 1.1. Assuming a dependence as in eq 3.1-3.3 a least-squares analysis gives

$$\langle\tau_e\rangle_n = 0.18(n + 2.1)^{(1.97\pm0.02)} \tag{3.4}$$

$$\langle\tau_{\rm nor}\rangle_n = 0.17(n + 2.0)^{(1.97\pm0.02)} \tag{3.5}$$

$$\langle\tau^2{}_{\rm nor}\rangle_n{}^{1/2} = 0.30(n + 2.0)^{(1.95\pm0.02)} \tag{3.6}$$

$$\langle\tau_{\rm int}\rangle_n = 0.14(n + 3.0)^{(1.97\pm0.02)} \tag{3.7}$$

$$\langle\tau^2{}_{\rm int}\rangle_n{}^{1/2} = 0.19(n + 2.4)^{(1.95\pm0.02)} \tag{3.8}$$

$$\langle\tau^3{}_{\rm int}\rangle_n{}^{1/3} = 0.28(n + 2.3)^{(1.93\pm0.02)} \tag{3.9}$$

Again, we find that $\mu \approx 2$. These results are numerically indistinguishable from the results for the nonsymmetric case, and the two cases seem to share the same properties. For the rest of the paper we consider only the symmetric case. These results are also similar to those obtained for linear polymers and uniform stars.[8] The survival time of an excitation which is migrating in the presence of a trap seems to be quite insensitive to the topology of the molecule. In fact, the n^2 rule seems to be universal. The longer the polymer (or star or ring polymer), the more effective it is at capturing photons, but the less effective it is in trapping the energy of the photon in an excitation trap where it might be of use in an experimental situation.

3.2. Multiple Traps. In this section we explore the effects of multiple traps on the mean survival times of an excitation. Suppose that we fix the number of vertices n in the polygon and that we turn q of them into excitation traps, as illustrated in Figure 3a. A first approximation to this situation would be to postulate that the traps separate the polygon into p linear pieces, which do not interact and which have an average length n/p. Assuming that eq 1.1 holds for each of the p segments separately, the mean survival time is

$$\langle\tau\rangle_n \approx C_0(n/p)^{\mu} \tag{3.10}$$

where we expect $\mu = 2$. Equation 3.10 assumes that processes such as those in Figure 3b are rare events. That is, every excitation on a segment will be absorbed by a trap at one of its endpoints. Should this assumption not be true, then the value of the exponent μ might differ significantly from 2. To test this assumption, we calculated the mean survival times over 2500 iterations, for $n = 100$. The number of traps was gradually increased from 1 to 20.

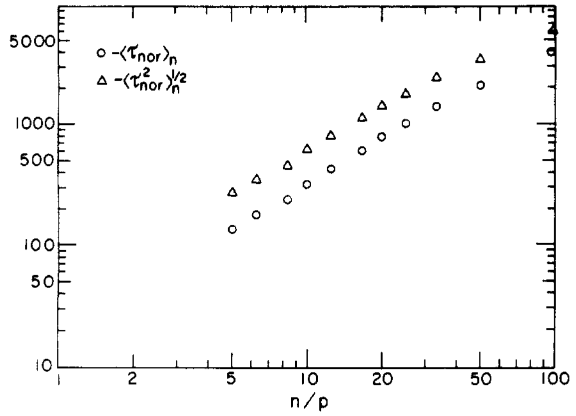

Figure 4. $\langle\tau_{\rm nor}\rangle_n$ and $\langle\tau^2{}_{\rm nor}\rangle_n{}^{1/2}$ vs n/p, where p is the number of traps on the ring polymer on a log-log scale. We chose $n = 100$.

Our results are shown in Figure 4, which is a graph of $\langle\tau_{\rm nor}\rangle_n$ and $\langle\tau^2{}_{\rm nor}\rangle_n$ against n/p on a log-log scale. The curves are essentially linear, except for the smaller values of p. If we ignore the points at $n/p = 100$ and 50, then a least-squares analysis gives

$$\langle\tau_{\rm nor}\rangle_n = 12.5(n/p + 0.71)^{(1.26\pm0.06)} \tag{3.11}$$

$$\langle\tau^2{}_{\rm nor}\rangle_n{}^{1/2} = 29.5(n/p + 0.63)^{(1.28\pm0.07)} \tag{3.12}$$

The measured values of μ are very different from 2. There are two possible explanations for this. Either transfers of excitations from chromophores to traps such as in Figure 3b play a significant role or we are observing an effective value of μ, which is a result of the small values of n used in this calculation. We found similar values for the exponential and integrated survival times. A more careful analysis than above is necessary to explain these results. A calculation taking into account the effect of processes such as those in Figure 3b would be very helpful, as would simulations at much larger values of n.

3.3. Effect of the Solvent. The quality of the solvent has significant effects on the radius of gyration and on other properties of a polymer. If the quality of the solvent deteriorates (ϕ increases in eq 2.11), then there is a point at which the polymer undergoes a collapse transition,[32,33] precipitating from the solution. This transition is associated with an increase in the number of nearest-neighbor contacts between the monomers in the polymer. This strongly suggests that the transfer of excitations on the polymer will be influenced by the solvent. Since the number of contacts increases, it is likely that the mean survival time will decrease as ϕ increases. To investigate this effect, we calculated the mean survival time on ring polymers of length $n = 40$ and 100, while we increased ϕ from 0 (good solvent) to 0.175 (bad solvent). The results are shown in Figure 5. The mean survival time decreases as we increase ϕ.

As discussed above, at $\phi = 0$ we expect that the asymptotic behavior will be $\langle\tau\rangle \sim Cn^{\mu}$ with $\mu = 2$. Watson[34,35] has given convincing arguments that the mean-square radius of gyration exponent will be independent of ϕ until ϕ reaches a critical value at which collapse occurs. Similarly, we expect that μ will be equal to 2 for all ϕ less than this critical value. However, there will be strong crossover effects resulting in a ϕ-dependent effective exponent.

Above the critical value of ϕ, the polygon is precipitated from the solution and is collapsed into a region of volume proportional to n and linear dimension proportional to

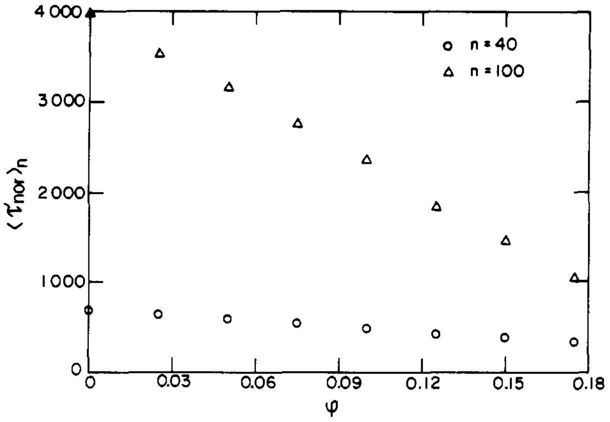

Figure 5. $\langle \tau_{\text{nor}} \rangle_n$ vs ϕ. The top curve is for $n = 100$ and the bottom curve for $n = 40$.

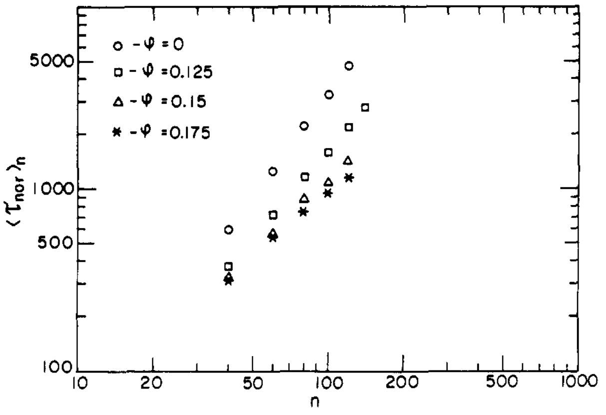

Figure 6. $\langle \tau_{\text{nor}} \rangle_n$ vs n for various values of ϕ.

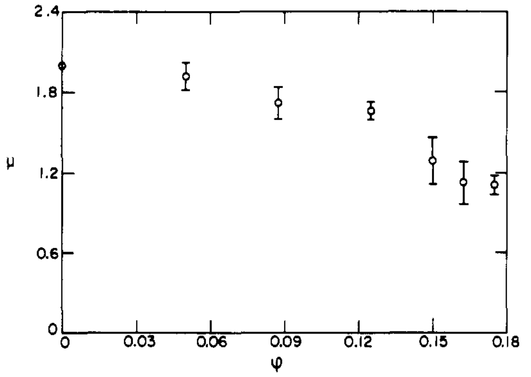

Figure 7. Effective exponent μ as a function of ϕ.

$n^{1/3}$. If we assume that every monomer in the polygon has contacts in all directions, then the shortest path between any excitation and a trap is at most $n^{1/3}$. This is to be compared to the belief[8] that in a good solvent this distance is linear in n. Although transfers between chromophores that are not nearest neighbors on the polygon are thought to be relatively unimportant in the good solvent regime, they will be much more important in the collapsed polygon.

We measured the effective value of μ as a function of ϕ. In Figure 6 we plot $\langle \tau_{\text{nor}} \rangle_n$ against n on a log–log scale, for values of ϕ between 0 and 0.175. The linearity of the relationship is maintained for a large range of ϕ values. A least-squares analysis of the data produces an effective value of μ in each case. In Figure 7 we show the dependence of μ and ϕ, and it is clear that μ decreases as ϕ approaches its critical value. We observe at first a slow drop in μ for $\phi \leq 0.125$, followed by a faster drop for larger values of ϕ. In the collapsed polygon we expect from the above remarks that μ is at most $^2/_3$. In our simulation it drops from 2.00 to approximately 1, suggesting that it may be difficult to explore the fully collapsed state by our methods.

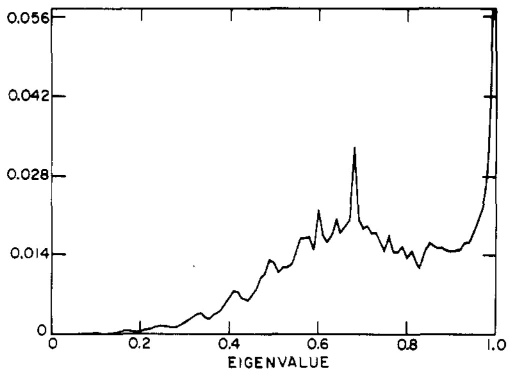

Figure 8. Eigenvalue distribution for $n = 100$ in a good solvent.

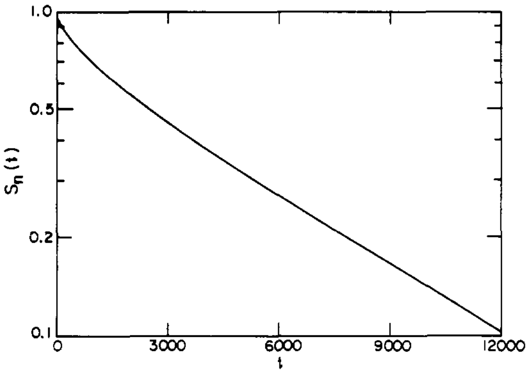

Figure 9. Survival probability function against t on a log–linear scale.

3.4. Survival Probability Function. In this section we consider the properties of the survival probability function. It is now well established[7] that the survival probability function $S_n(t)$ (eq 2.7) should behave as a "stretched exponential" for appropriate values of t. $S_n(t)$ is a sum of exponential terms, so for large t we expect it to be dominated by the slowest decaying term in this sum (given by the largest eigenvalue, λ_m). An inspection of the typical eigenvalue distribution (Figure 8 is the distribution for a ring polymer of length 100 and one trap) suggests that the eigenvalues are closely packed toward the larger values and taper off rapidly as they get smaller. The eigenvalues close to λ_m contribute to $S_n(t)$ for intermediate values of t. For large t, however, λ_m dominates $S_n(t)$. This behavior is vividly illustrated in Figure 9, which is a plot of log $S_n(t)$ against t. The curve straightens out as t is increased but deviates significantly from a straight line in the intermediate and short time range. The decay is nonexponential for small t, which illustrates the stretched exponential behavior.

Byers et al.[7] developed a method for exposing the stretched exponential nature of $S_n(t)$, assuming that

$$S_n(t) \approx C_0 e^{-A(t)t^{\alpha(t)}} \tag{3.13}$$

where $A(t)$ and $\alpha(t)$ are functions to be determined and where we expect that

$$\lim_{t \to \infty} \alpha(t) = 1 \tag{3.14}$$

In the stretched exponential regime we expect that $\alpha(t) < 1$. Approximations to $A(t)$ and $\alpha(t)$ can be calculated from our data by using the "time window" idea of Byers et al.[7] We select a window $(t - \lambda, t + \lambda)$, λ some fixed number, to approximate $\alpha(t)$ by a least-squares fit of log $|\log S_n(t)|$ against log t. In our calculations, it proved sufficient to choose $\lambda = 50$.

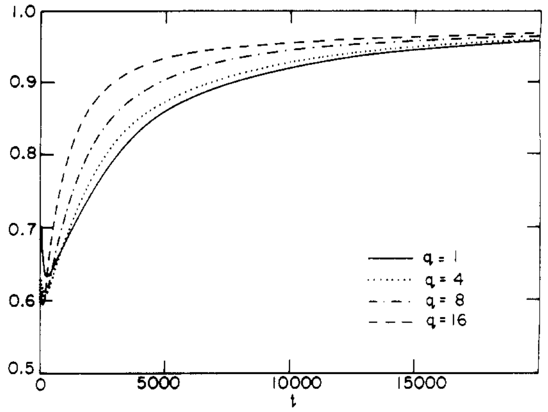

Figure 10. $\alpha(t)$ against t for a ring polymer of length 100 in a good solvent. The number q indicates the number of excitation traps present.

In Figure 10 we plot $\alpha(t)$ against t for a ring polymer of length 100 in a good solvent and for 1, 4, 8, and 16 excitation traps substituted along it. We see that $\alpha(t) \to 1$ as t increases, but for small t we see that $\alpha(t)$ is significantly smaller than 1, exposing a stretched exponential regime in $S_n(t)$. We expect the minimum value of $\alpha(t)$ to be $^1/_2$, as suggested by eqs 2.3 and 2.4 and from the fact that the polymer has spectral dimension 1.

These results compare well with the known behavior in linear polymers.[7] We therefore conclude that ring polymers show essentially the same excitation-transfer properties as linear polymers.

4. Conclusions

1. In this paper we considered the behavior of an excitation on a ring polymer in the presence of traps. It is known that the mean survival time of an excitation on a linear polymer or on a uniform star with n vertices[8] is proportional to n^2. We extended this result to ring polymers in this paper. It seems likely that we can expect this behavior to extend to all uniform polymer networks (where every branch has the same length). The survival of excitations on networks that are not uniform remains to be considered. These networks include among others lattice trees, lattice animals, etc.

2. We considered briefly the case where the transfer matrix **W** is nonsymmetric. This case is computationally much more expensive, but its results cannot be distinguished from the symmetric case. Since all the elements of **W** are real, the complex eigenvalues and eigenvectors of **W** will occur in complex conjugate pairs. An examination of eq 2.7 indicates that this will set up oscillations in the survival probability function (which is still dominated by the largest eigenvalue in the large time limit) and which is necessarily real. We did not observe such oscillations, but they could be hidden by noise in the data. Over a large sample the oscillations will also be "averaged out", so that they will be hard to observe. It is not clear which of the two models (symmetric and nonsymmetric) discussed in this paper is the more realistic one.

3. We limited our discussions and investigation to short-ranged transfers (only between nearest-neighbor lattice sites). If we consider longer range transfers, such as Förster transfers, (where the probability of transfer between two chromophores a distance r apart is proportional to r^{-6}), then we find that $\mu = 1.76 \pm 0.04$. The longer range transfer seems to reduce the value of the scaling exponent for ring polymers of the lengths that we considered. In the large n limit we expect that $\mu = 2$ and that the value of μ that we observe is only an effective value: If longer range transfers dominate the process, we expect that the process of trapping will be dominated by a single transfer right into the trap from any chromophore on the polymer backbone. Therefore, we should not see any n dependence at all. We therefore conclude that even for Förster transfers the migration of excitations is mainly from neighboring chromophores to each other, which produces the n^2 behavior.

4. It seems from our data in section 3.2 that processes such as in Figure 3b contribute significantly to the final picture. This is interesting, since it implies that there are significant long-range interactions between sections of the polygon which are linearly far removed from one another.

5. We ignored the effects of fluorescence and phosphorescence. Similarly, we did not consider excimer formation or excited-state annihilation. These processes will influence the form of eq 1.1 by putting an upper limit on the mean survival time (in the $n \to \infty$ limit). Therefore, if we have only one trap on the polymer, then (if n is large enough) the excitation will be destroyed before it gets absorbed by the trap, at an average time that is independent of n.

Acknowledgment. This research was financially supported by NSERC of Canada.

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