

Electronic excitation transport on isolated, flexible polymer chains in the amorphous solid state randomly tagged or end tagged with chromophores

Kristen A. Peterson and M. D. Fayer

Department of Chemistry, Stanford University, Stanford, California 94305

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The transport of electronic excitations among chromophores which are randomly tagged or end tagged on finite flexible polymer chains in the amorphous solid state is described. First, the previously reported first order cumulant expansion treatment of excitation transport among chromophores randomly distributed in solution is extended to treat finite volume systems with nonrandom chromophore distributions. The method is demonstrated by considering chromophores randomly distributed in a finite sphere. The results are in good agreement with a previous treatment of this problem using a density expansion. The probability of finding the initially excited chromophore, still excited at time t , $G^s(t)$, is calculated. $G^s(t)$ is directly related to fluorescence depolarization and other observables. $G^s(t)$ is then calculated for a finite flexible polymer chain in a polymer blend which is randomly tagged in low concentration with chromophores. The method permits any form of the polymer pair correlation function to be used. A specific model, a Gaussian segment distribution function, is employed, and an explicit time domain expression is obtained. This expression is compared to previous theoretical treatments which did not contain adequate descriptions of the pair correlation function. Greatly improved agreement with experiment is obtained. Excitation transfer on an end tagged coil is a limiting case of the random tagged problem. In addition, the energy transport aspect of the end tagged problem is treated exactly and the two approaches are compared.

I. INTRODUCTION

There has been considerable interest in recent years in using incoherent electronic excitation transport to study solid state polymer systems.¹⁻⁵ Excitation transport observables are sensitive to the spatial orientation and separation of chromophores. Thus, excitation transport experiments on such polymer systems can provide information on coil structure such as local segment geometry and overall chain configuration.

The morphology of a polymer coil arises from both the thermodynamic interactions of the coil with its environment and the restrictions on possible coil configurations imposed by the covalent bond geometries. Understanding the microscopic interactions of a polymer with its environment is of fundamental importance in understanding the resulting bulk properties of the system. For example, the bulk properties of a polymer blend are critically dependent on the mixing of the components on the molecular level. Excitation transport experiments can provide a direct probe of these microscopic interactions.

The two most common methods used to study the morphology of polymer chains are Rayleigh scattering and neutron scattering. Rayleigh, or light scattering has been extremely useful in studying polymers in solution.⁶ However, this technique is not easily applied to polymers in the amorphous solid state due to lack of contrast in refractive index between blend components. Neutron scattering has been successfully applied to studying isolated polymer coils in solid blends.⁷ However, the neutron scattering technique has several limitations which may be overcome by excitation transport techniques. First, in order to produce contrast, the

polymer component being investigated, or the host polymer must be deuterated. Deuteration has been shown to affect the mechanical and thermodynamic properties of a number of polymers and polymer blends.⁸ Second, a monochromatic neutron source is required, and finally, it is difficult to investigate the behavior of isolated guest polymers in a solid at very low concentrations ($< 1\%$) due to scattering from the host polymer. Many blends are already phase separated even at these low concentrations. For these types of blends in particular, excitation transport techniques will prove extremely useful. The excellent signal-to-noise ratio obtainable in excited state transport experiments allows measurements on blends with guest polymer concentrations that are orders of magnitude lower than the sensitivity limits of neutron scattering. In addition, for chains with multiple, randomly placed chromophores, the effect of the labeled monomer units on the coil conformation can be determined by performing a series of experiments on copolymers containing various mole fractions of label.

It is straightforward to understand qualitatively the relationship between excitation transport dynamics and the size of an isolated polymer coil which is randomly tagged in low concentration (or end tagged) with chromophores. An ensemble of tagged coils in a polymer blend will have some ensemble averaged root-mean-squared radius of gyration, $\langle R_g^2 \rangle^{1/2}$. If in one host $\langle R_g^2 \rangle^{1/2}$ for the guest coils is large because of favorable guest-host thermodynamic interactions, the average distance between chromophores will be large. Since the rate of excitation transport depends on $1/r^6$ where r is the chromophore separation, transport will be slow. If the same guest polymer is placed in a different host in which the guest-host thermodynamic interactions are less

favorable, the coils will contract, and the average chromophore separation will decrease. This decrease will result in more rapid excitation transport. The $1/r^6$ distance dependence makes the excitation transport observables very sensitive to small changes in $\langle R_g^2 \rangle^{1/2}$.

In addition to their use as probes of polymer structure, polymer coils tagged with chromophores are interesting in their own right. These systems are clustered excitation transport systems. The clustering of chromophores in a small finite volume can result in extremely efficient energy transport by having a very high local chromophore density. To achieve similar transport efficiency in a system of chromophores randomly distributed in a homogeneous solution requires chromophore concentrations which are difficult to achieve and suffer from problems such as excitation quenching by trapping on dimers⁹ or undesirable very high optical densities. Clustered chromophore systems may be able to mimic naturally occurring photosynthetic units in which an energy transport chromophore system is clustered around a chemical reaction center.

The accurate description of excitation transport on isolated polymer coils is an interesting and difficult problem. Chromophores attached to a polymer present an inhomogeneous medium for excitation transport. Rather than being randomly distributed, as in a solution, the positions of the chromophores are correlated through the covalent bonds of the polymer. Also, the finite size of the polymer limits the number of sites the excitation can sample. Advances in the theory of incoherent excited state transport among molecules in solution have provided accurate, quantitative predictions for experimental observables in single component (donor-donor transport) and two component (donor-donor transport with trapping) systems.¹⁰⁻¹³ Theories have also been developed for excitation transport in finite volumes¹⁴ and for disordered systems that are between two and three dimensional.¹⁵ However, due to the difficulty of including polymer structure in the problem, similar success has not been achieved for polymer systems with finite size coils.

Two theories have been developed recently which attempt to describe excitation transport on isolated polymer coils. Each includes some aspects of polymer chain structure and both provided qualitatively correct experimental predictions, but neither were quantitatively correct. Fredrickson, Andersen, and Frank (FAF)⁴ developed a theory for energy transport (with or without traps) on isolated, Gaussian polymer coils. They used an extension of the diagrammatic self-consistent method developed by Gochanour, Andersen, and Fayer^{11(a)} for excitation transport in solution. The FAF theory used the infinite chain limit (Debye form) for the segment pair-correlation function of an ideal polymer coil. Ediger and Fayer (EF)¹ modeled chromophores randomly tagged on a polymer chain of a particular radius of gyration as chromophores randomly distributed in a sphere; relating the radius of gyration of the sphere to the radius of gyration of the polymer. Polymer statistics were included by averaging over the distribution of radii of gyration using the Flory-Fisk distribution function.

$G^s(t)$, the fundamental quantity in an excitation trans-

port experiment, is the ensemble averaged probability that an initially excited chromophore is still excited at time t . $G^s(t)$ has contributions from excitations which have never left the initially excited chromophores and from excitations which have left and then returned to the initially excited chromophores. $G^s(t)$ is directly related to the time dependent fluorescence anisotropy which can be measured through time resolved fluorescence depolarization, polarized transient grating or polarized absorption techniques.^{13,16} In time-resolved fluorescence depolarization experiments, when a sample of randomly oriented chromophores is excited by a short pulse of polarized light, the time-dependent depolarization of the fluorescence can arise from two sources. In the solid state, the main source of depolarization is excited state transport. The initially excited ensemble is polarized along the direction of the excitation \bar{E} field and gives rise to polarized fluorescence. Excited state transport occurs into an ensemble of chromophores with randomly oriented dipole moments and results in unpolarized fluorescence. The second source of depolarization is chromophore motion. Although the amount of motion in solid blends at room temperature is expected to be small, it is desirable to remove any such effects. This is accomplished by obtaining data on a copolymer containing so few chromophores that no excitation transport occurs. Dividing the fluorescence anisotropy obtained from excitation transport measurements by the anisotropy obtained when no excitation transport is present removes depolarization effects from all sources other than excited state transport events.²

Figure 1(a) shows data obtained from the time-resolved fluorescence depolarization experiments on a solid blend of $\sim 20\,000$ molecular weight methylmethacrylate-2-vinylnaphthalene copolymer (mole ratio MmA: 2-VN = 10:1) in 120 000 molecular weight poly(methyl methacrylate) host taken from Ref. 2. The solid lines labeled FAF and EF are the best fits obtained from the two theories just described. It is seen that both theories are capable of reproducing the functional form of the time dependent decay. The shape of the $G^s(t)$ decays for polymer systems is distinctly different from the decay of $G^s(t)$ for a system of molecules randomly distributed in solution.² This suggests that these theories in some respects properly include the polymer statistics in the transport problem. Polymer chains in the amorphous solid state in a host environment of identical chains are expected to have the same ensemble average conformation as they would in a theta solvent.¹⁷ Theta conditions occur when excluded volume effects are exactly counteracted by chain-environment thermodynamic interactions. This system, tagged PMMA in PMMA is expected to closely approximate theta conditions, therefore we can compare these results to light scattering experiments in liquid solution, where for theta conditions, $\langle R_g^2 \rangle^{1/2} = 37 \pm 4 \text{ \AA}$.¹⁸ The FAF theory yields 50 \AA while the EF theory yields 26 \AA when fitting the data.

Figure 1(b) shows that the disparities in the excitation transport size determinations are due to inadequate descriptions of the spatial distribution of the chromophores. Figure 1(b) displays the radial pair correlation functions used in the FAF theory, the EF theory and for an idealized theta-

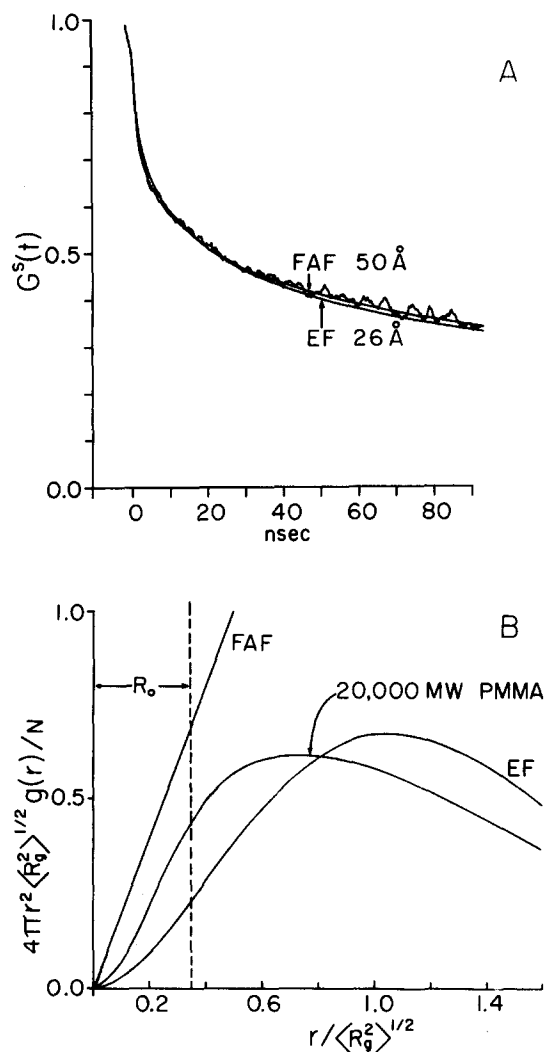


FIG. 1. (a) $G^s(t)$, the ensemble averaged probability of finding the excitation on the originally excited chromophore obtained from time-resolved fluorescence depolarization experiments (Ref. 2). The sample is a solid blend of isolated coils of an $\sim 20\,000$ molecular weight methyl methacrylate/2-vinyl naphthalene copolymer in 120 000 molecular weight poly(methyl methacrylate) (PMMA). The two theoretical curves drawn through the data [EF (Ref. 1) and FAF (Ref. 4)] are the best fits for the two theories discussed in the text. The single fitting parameter for each theory gives $\langle R_g^2 \rangle^{1/2}$ as indicated. The expected value of $\langle R_g^2 \rangle^{1/2}$ is 37 ± 4 Å. Although each theory correctly describes the shape of the data, neither is quantitatively correct. (b) Reduced radial pair correlation functions. The curves labeled EF and FAF are for the pair correlation functions contained in the EF and FAF theories used to fit the data in (a). The curve labeled "20 000 MW PMMA" was obtained by assuming Gaussian chain statistics. A statistical segment length of 16 Å with 32 statistical segments was used. This corresponds to theta-condition PMMA. The line indicating R_0 (13 Å for naphthalene) is located for an $\langle R_g^2 \rangle^{1/2}$ of 37 Å. Neither the EF nor FAF theories correctly describe the pair correlation function in the region of interest, out to one or two times R_0 . Details of the experiments and calculations contained in (a) and (b) are in Ref. 2.

condition chain. The range of distances over which the pair correlation function is important for this type of experiment is one or two times R_0 , where R_0 is the Förster critical distance for energy transfer. FAF uses an approximation that is at best applicable only to infinite chains, and when applied to a coil of finite size, overestimates the local chromophore density, causing the theory to yield an average chain configura-

tion which is too large. Conversely, the EF theory underestimates the local chromophore density, leading to a determination of the average coil size which is too small.

Although the FAF and EF theories may be useful for comparing coils of different sizes, it is desirable to have a quantitative theory capable of extracting the absolute $\langle R_g^2 \rangle^{1/2}$ from experiment. Both the FAF and EF theories involve complicated series expansions in Laplace space, making inclusion of accurate forms for the chromophore distribution function computationally exceedingly difficult.

In this paper, we present a theory for excitation transport on isolated, finite size, flexible polymer coils which contains a more reasonable model of the polymer pair correlation function, and which is amenable to the inclusion of any form of the pair correlation function. The theory is based on a method developed by Huber¹² for describing excitation transport in infinite, disordered systems. This method has the advantage of being a relatively straightforward time-domain calculation, making the inclusion of different chromophore distribution functions mathematically tractable.

We extend Huber's results to include a general chromophore pair correlation function and then apply the general equations to three specific cases. First, we will show that this method is reasonable when applied to a system of chromophores randomly distributed in a spherical finite volume. The results demonstrate that the truncated cumulant expression is useful for finite volume systems. Next we consider an isolated finite size polymer coil. A Gaussian segment distribution function (freely jointed chain) is used as the basis of a model for the necessary radial pair correlation function. Two types of transport situations are considered: (1) a small number of chromophores randomly distributed on the chain (random tagged chain) and (2) a chain where only the end monomer units contain chromophores (end tagged chain). The results of these calculations are compared to previous theoretical treatments. The results suggest that using the freely jointed chain pair correlation function in the truncated cumulant excitation transport theory provides a quantitative description of excitation transport in the tagged polymer systems.

II. THEORETICAL APPROACH

Briefly, the truncated cumulant expansion method developed by Huber¹² for describing energy transport (with or without traps) among chromophores randomly distributed in solution considers only interactions between pairs of chromophores. An exact configuration average leads to a power series in the trap concentration (for donor-trap transport) or in the donor concentration (for donor-donor transport) which is then truncated to first order. The result is identical to Förster-type equations for donor-trap transport in the limit of high trap concentration. It is an approximation for donor-donor transport since any paths involving more than two chromophores which leads to the return of the excitation to the originally excited molecule are excluded. Only the result for the excitation transport among identical chromophores (no traps) will be given here. The extension to systems with traps is straightforward.¹⁵

The quantity of interest, denoted by $G^s(t)$, is the ensemble average probability that an initially excited chromophore will be excited at time t later. Throughout this paper, $G^s(t)$ includes only the loss of excitation due to energy transport. To include the loss due to the excited state lifetime, $G^s(t)$ must be multiplied by the lifetime decay $e^{-t/\tau}$. For an infinite, disordered system, $G^s(t)$ is given by^{12(b),19}

$$\ln G^s(t) = \frac{4\pi c}{2} \int_0^\infty (e^{-2\omega_{12}t} - 1)r_{12}^2 dr_{12}, \quad (1)$$

where c is the number of chromophores per unit volume and where for incoherent, dipole-dipole (Förster type) energy transport with which we are concerned with here,

$$\omega_{12} = \frac{1}{\tau} \left(\frac{R_0}{r_{12}} \right)^6, \quad (2)$$

τ is the fluorescence lifetime and R_0 the critical transfer radius for donor-donor transport.²⁰ For experiments in high viscosity media, the chromophores are essentially static and the appropriate orientation dependent R_0 must be used.^{4(c),15} Equation (1), with Eq. (2), has an analytical solution.

$$\ln G^s(t) = -\frac{4\pi c}{3} \left(\frac{t}{\tau} \right)^{1/2} R_0^3 2^{3/5} \Gamma\left(\frac{1}{2}\right). \quad (3)$$

Figure 2 compares curves calculated by Eq. (3) with calculations from the infinite order diagrammatic theory of Gochanour, Andersen, and Fayer^{11(a)} (GAF) which has

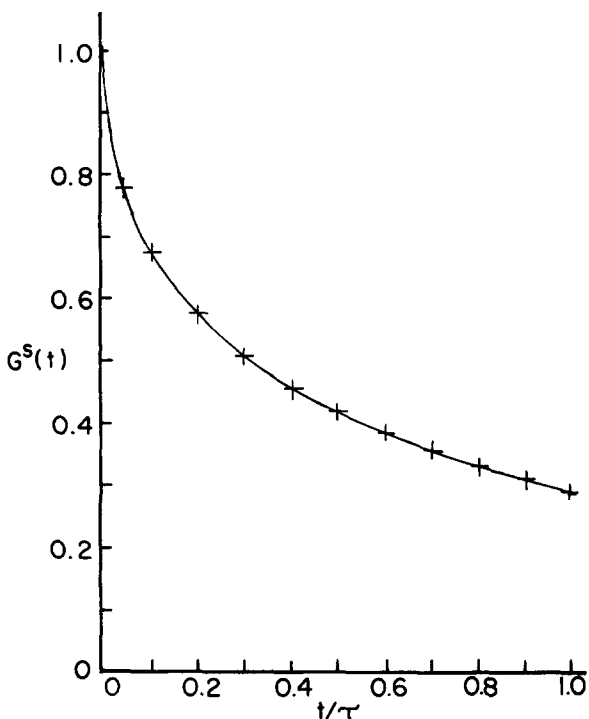


FIG. 2. A comparison of the first order cumulant expansion theory of Huber and the infinite order diagrammatic theory of Gochanour, Andersen, and Fayer (GAF) as applied to the calculation of $G^s(t)$ for donor-donor energy transport in a homogeneous, random solution. τ is the excited state lifetime. The solid line is from the GAF theory. The + locate points calculated with the cumulant expansion. The curves were calculated for the reduced concentration, $\bar{C} = 1.0$ (defined in text). However, since the curves scale with $(t/\tau)\bar{C}$, they are universal for all concentrations. These results demonstrate the accuracy of the cumulant expansion for random infinite solutions.

been shown theoretically and experimentally to be an accurate description of energy transport on the time scale of interest in a homogeneous random solution.^{13(a),13(b)} Note that the results from the two theories are indistinguishable. This is true down to $G^s(t) \cong 0.05$. The curve calculated is for a reduced concentration ($\bar{C} = \frac{4}{3}\pi R_0^3 c$) of 1.0. The curve is, however, universal for all concentrations since $G^s(t)$ scales with $(t/\tau)^{1/2}\bar{C}$. Thus the Huber theory, which is mathematically much simpler than the GAF theory is an accurate description of transport on the time scale of experimental interest for infinite solution systems.

Equation (1) can be written more generally to include cases where the chromophore distribution is other than random in an infinite volume. Two changes are necessary. First, in performing the spatial average over all configurations of molecules surrounding the initially excited molecule, the appropriate radial distribution function must be employed. This is true for nonrandom distributions in infinite or finite systems. The second change applies only to finite systems. In an infinite system, the ensemble average overall configurations is translationally invariant. Therefore the average can be performed about any starting point. In a finite system the translational invariance is lost. The ensemble averaged observable must be calculated for a particular point of initial excitation and then the observable must be averaged over all possible starting locations. The need for this is readily seen if one considers molecules randomly distributed in a finite radius sphere. The average over configurations about the center of the sphere is very different from the average about a point on the surface of the sphere.

Using the truncated cumulant treatment, first $G_1^s(t)$ is found for an initially excited chromophore (labeled 1) fixed in space, averaged over all possible positions of a second chromophore:

$$\ln G_1^s(t) = \frac{(N-1)}{2A} \int (e^{-2\omega_{12}t} - 1)P(r_{12})dr_{12}, \quad (4)$$

where N is the number of chromophores in the system. $P(r_{12})dr_{12}$ is the probability that there is a chromophore at at distance r_{12} from chromophore 1. The integral is over the physical space of the system and A is the appropriate normalization factor. Next, it is necessary to average over the possible positions of the initially excited chromophore

$$G^s(t) = \frac{1}{A} \int G_1^s(t)dr_1. \quad (5)$$

For an infinite, disordered system, $P(r_{12})dr_{12}$ is $4\pi r_{12}^2 dr_{12}$ and Eqs. (4) and (5) become Eq. (1) since all positions of chromophore 1 are equivalent.

III. MODEL CALCULATIONS

A. Chromophores randomly distributed in a sphere

In order to treat excitation transport on a finite size isolated coil randomly tagged with chromophores, it is necessary to have a formalism that can handle a finite number of particles in a finite volume. In this section we apply the cumulant treatment to the problem of molecules randomly distributed in a finite volume sphere. The results are compared to a previous treatment of this problem which uses a second

order density expansion with a Padé approximant.^{14(a)}

For a system of N chromophores randomly distributed in a sphere of radius R_s ,

$$P(r_{12})dr_{12} = 4\pi r_{12}^2 dr_{12} \quad (6)$$

and Eqs. (4) and (5) lead to

$$G^s(t) = \frac{4\pi}{A} \int_0^{R_s} \exp\left[\frac{4\pi(N-1)}{2A} \int_0^{R_s} (e^{-2\omega_{12}t} - 1)r_2^2 dr_2\right] r_1^2 dr_1, \quad (7)$$

where A is the volume of the sphere and r_1 and r_2 are the distances of chromophore 1 and chromophore 2 from the center of the sphere. The interior integral is the configuration average about a particular point of initial excitation. The exterior integral is the average over starting points. (A previous treatment of this problem using the cumulant expansion performed the average over starting points less accurately.¹⁹)

The integration in Eq. (7) is more easily handled if a change of coordinate system is made so the interior integral is over r_{12} rather than r_2 . Rather than placing the origin of the axes at the center of the sphere, the origin is placed at chromophore 1. r_1 is still the vector from the center of the sphere to chromophore one, but r_1 now defines the z axis (ϕ_1 and θ_1 are always zero). r_{12} , ϕ_{12} , and θ_{12} are the spherical coordinates describing the position of chromophore 2 from the origin (chromophore 1) and r_{12} is defined to be always in the xz plane ($\phi_{12} = 0$). Then, the upper limit of integration on r_{12} becomes

$$f(r_1, q) = [R_s^2 + r_1^2 - 2r_1^2(1 - q^2) - 2qr_1\sqrt{R_s^2 - r_1^2(1 - q^2)}]^{1/2}, \quad (8)$$

where $q = \cos \theta_{12}$ and Eq. (7) is now

$$G^s(t) = \frac{4\pi}{A} \int_0^{R_s} r_1^2 dr_1 \exp\left[\frac{2\pi(N-1)}{2A} \int_{-1}^1 dq \int_0^{f(r_1, q)} (e^{-2\omega_{12}t} - 1)r_{12}^2 dr_{12}\right]. \quad (9)$$

Figures 3 and 4 compare Eq. (9) to $G^s(t)$ curves calculated from a second order density expansion with a Padé approximant developed by Ediger and Fayer (EF) to describe excitation transport in finite volumes.^{14(a)} The curves calculated with the EF theory, which is in Laplace space, were obtained by numerical inversion. The EF theory has been demonstrated to be accurate up to relatively high concentrations.^{14(b)} In Fig. 3 several pairs of curves are shown comparing the two theories. The curves are for a number of different reduced concentrations [$C_D = N(R_0/R_s)^3$]. For concentrations up to $C_D \cong 1$, the pairs of curves are essentially indistinguishable. As discussed in the next section, the polymer experiments require relatively low concentrations for a variety of reasons. Therefore the first order cumulant treatment of the finite volume is essentially identical to the Padé approximant of the second order density expansion. Figure 4 displays calculations for three particles in a sphere. This problem was solved exactly by Ediger and Fayer in the process of obtaining the second order density expansion. The exact result is shown in addition to the Padé approximant

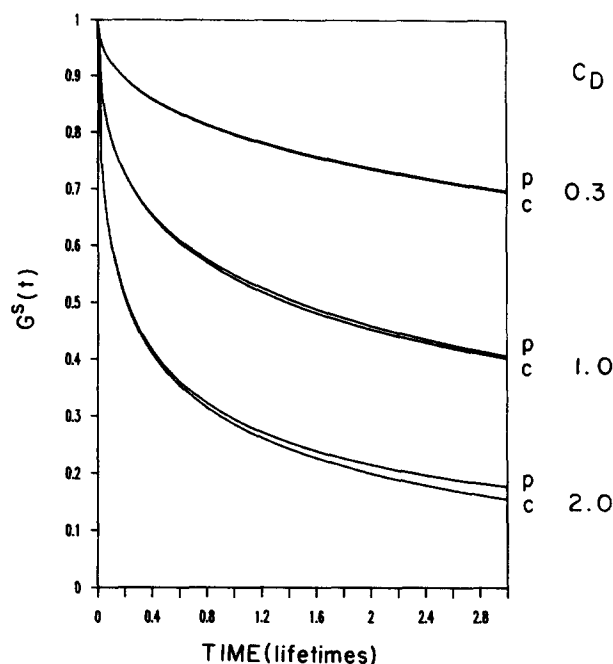


FIG. 3. $G^s(t)$ for many chromophores randomly distributed in a sphere of radius R_s for various finite volume reduced concentrations, $C_D = N(R_0/R_s)^3$. The curves labeled *c* are obtained from the first order cumulant expansion treatment. The curves labeled *p* are obtained from a second order density expansion with a Padé approximant developed by Ediger and Fayer. Up to a reduced concentration of ~ 1 , the curves are virtually identical, demonstrating the applicability of the cumulant treatment to finite volume problems.

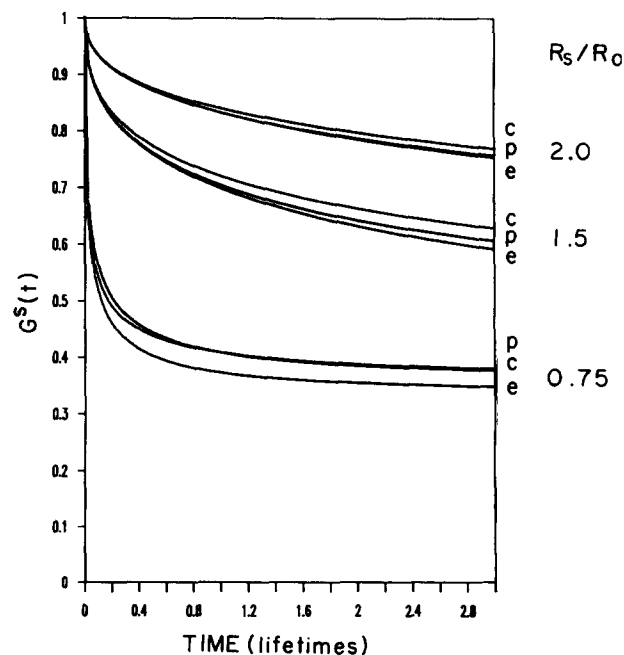


FIG. 4. $G^s(t)$ for three chromophores randomly distributed in a sphere of radius R_s . Calculations are for various values of R_s/R_0 as indicated. Curves labeled *p* and *c* are from the second order density expansion with a Padé approximant of Ediger and Fayer and the first order cumulant expansion, respectively. Curves labeled *e* are the corresponding exact solutions to this problem. Both approximate theories are in good agreement with the exact solution for low concentrations (high R_s/R_0).

and the first order cumulant expansion. At high concentration (small R_s/R_0), the cumulant treatment is a reasonable approximation. As the concentration decreases it becomes an increasingly good approximation to the exact three particle result. The errors observed at the highest concentration shown would not have a significant effect on the polymer experiments.

B. Excitation transport on isolated, flexible polymer chains randomly tagged with chromophores

In this section, we develop an expression to describe energy transport on isolated polymer chains with a small number of chromophores randomly distributed along the chain. The chromophore concentration is chosen low enough that there is a low probability of having more than one chromophore per statistical segment of the chain. This assures that there are no angular correlations among the chromophores' transition dipoles and that transport is three dimensional rather than quasi-one-dimensional (along the chain backbone). The overall concentration of tagged coils in the blend is taken to be low enough that there is no inter-chain transfer, i.e., all excitation transfer occurs among chromophores tagged on the same chain.

The forms of Eqs. (4) and (5) permit any model of the polymer pair correlation function to be used in the transport calculation. Here we are considering flexible chains and it is reasonable to use a freely jointed chain model, which obeys Gaussian statistics, in the calculations. The chain segment length is identified with the statistical polymer segment (Kuhn segment) length. In this model, the conformation averaged radial probability of finding any other polymer segment a distance r from a segment i is²¹

$$p_i(r)dr = \frac{4\pi}{(\bar{N}-1)} \sum_{\substack{j=1 \\ j \neq i}}^{\bar{N}} \left(\frac{3}{2\pi a^2 |i-j|} \right)^{3/2} \times \exp\left(\frac{-3r_{12}^2}{2a^2 |i-j|} \right) r_{12}^2 dr_{12}, \quad (10)$$

where \bar{N} is the number of statistical segments and a is the statistical segment length. Since the chromophore concentration on the chain is small we identify the probability of finding a second chromophore (labeled 2) at a distance r_{12} from an initially excited chromophore (labeled 1) placed on segment i with the probability that there is a polymer segment at that distance. Replacing r with r_{12} in Eq. (10) [this will be denoted by $p_i(r_{12})$] and multiplying by $N-1$ (N is the number of chromophores on the chain) yields the conformation averaged probability of finding another chromophore a distance r_{12} from the initially excited chromophore, excluding the small correction due to unexcited chromophores on segment i .

The correction due to unexcited chromophores on the segment containing the initially excited chromophore, i , can be included by calculating the average number (n) of unexcited chromophores on segment i and using some reasonable chromophore distribution function [$p'(r_{12})$] for this segment. Then the probability of an unexcited chromophore being a distance r_{12} away from the initially excited chromophore on the i th segment is

$$P_i(r_{12})dr_{12} = \{np'(r_{12}) + (N-1-n)p_i(r_{12})\}dr_{12}. \quad (11)$$

For low concentrations of chromophores, n is a small number and the choice of $p'(r)$ is not critical. It is only necessary to concentrate the appropriate chromophore density in the region of space of the i th segment. A simple model for $p'(r)$ is to assume that the initially excited chromophore is in the center of the segment and surrounded by a random distribution of the n chromophores, i.e.,

$$p'(r_{12})dr_{12} = 4\pi r_{12}^2 dr_{12} \quad 0 < r_{12} < a/2 \\ = 0 \quad r_{12} > a/2. \quad (12)$$

If Eq. (11) with Eq. (12) is substituted for $(N-1)P(r_{12})dr_{12}$ in Eq. (4) and the position of the initially excited chromophore is averaged over by summing the equally weighted contributions from each segment i , the expression for $G^s(t)$ is

$$G^s(t) = \frac{1}{\bar{N}} \sum_{i=1}^{\bar{N}} \left\{ \exp\left[\frac{4\pi}{2} \int_0^\infty P_i(r_{12}) \times (e^{-2\omega_{12}t} - 1) r_{12}^2 dr_{12} \right] \right\}. \quad (13)$$

The upper limit of integration in Eq. (13) can be extended to infinity since contributions to the energy transport from distances greater than several R_0 are negligible and also since $P_i(r_{12})$ becomes very small for large values of r_{12} relative to $\langle R_g^2 \rangle^{1/2}$. For small coils with large values of R_0 a limit of integration appropriate to the finite coil size may be used.

Fig. 5 displays $G^s(t)$ calculated with Eq. (13) and $G^s(t)$ calculated with the EF theory. The EF curve is the same as that in Fig. 1(a). The best fit to the data with Eq. (13) gives an a of 19.9 Å with $\bar{N} = 24$. a is the only adjustable parameter, since given a and the molecular weight, \bar{N} is determined. Using the relationship

$$\langle R_g^2 \rangle = \frac{1}{6} \langle R_{ee}^2 \rangle = \frac{1}{6} \bar{N} a^2, \quad (14)$$

(where R_{ee} denotes the end-to-end distance of the chain) to calculate the root-mean-square radius of gyration, $\langle R_g^2 \rangle^{1/2}$ is found to be 40 Å. This is in very good agreement with determinations by light scattering in liquid solution at theta condition [see discussion following Fig. 1(a)] which give a $\langle R_g^2 \rangle^{1/2}$ for 20 000 molecular weight PMMA of 37 ± 4 Å. The uppermost and lowest curves in Fig. 4 are for $\langle R_g^2 \rangle^{1/2}$ of 42° and 38 Å, respectively, demonstrating the sensitivity to changes in coil size. Thus, the method developed in this paper for calculating $G^s(t)$ for finite size isolated, flexible polymer coils is capable of providing quantitative information concerning coil dimensions when used to evaluate donor-donor excitation transport experiments. Additional detailed comparisons between the theory and a variety of recently conducted experiments, where the number of chromophores per chain and the chain length were varied, will be presented in another publication.³

Several comments need to be made at this juncture. No average over a distribution of molecular weights was performed. In principle this could be necessary if an experimental sample has a very broad dispersion of molecular weights. However, this can be avoided by using a sample with a relatively narrow molecular weight dispersion. For the random

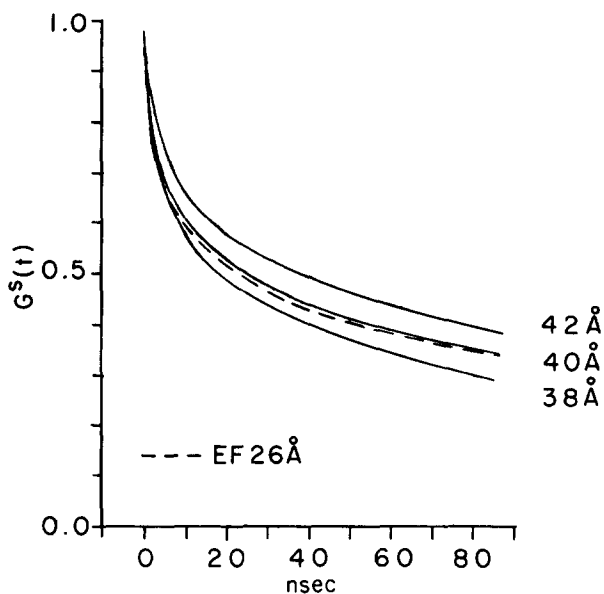


FIG. 5. $G^s(t)$ calculated using the first order cumulant expansion and Gaussian segment distribution function [Eq. (13)] for a 20 000 molecular weight PMMA chain randomly tagged with 10% of the monomer units containing a naphthalene chromophore. A value of $\langle R_g^2 \rangle^{1/2} = 40 \text{ \AA}$ gives a best fit to the data in Fig. 1(a). The expected value for theta condition is $37 \pm 4 \text{ \AA}$. The EF curve for Fig. 1(a) is included for comparison (dashed line). Also shown are $G^s(t)$ curves for $\langle R_g^2 \rangle^{1/2} = 42$ and 38 \AA , demonstrating the sensitivity of $G^s(t)$ to small changes in coil size.

distribution of chromophores along the chain considered here, the absolute number of chromophores per chain increases linearly with chain length. Therefore, the weight average molecular weight should be used. This is due to the fact that the probability of exciting a chain of length j is weighted by $n_j m_j$, where n_j is the number of chains of weight m_j . For end-tagged polymers (discussed below) the number of chromophores per chain, and thus the probability of exciting any chain, is constant regardless of molecular weight. The number average molecular weight should be used in this case.

A second potential problem, which is not as readily dealt with by sample preparation, arises from the fact that for randomly tagged polymers there is likely to be a distribution in the number of chromophores per chain length. Figure 6 compares two pairs of $G^s(t)$ curves. The curves are for different chain lengths and different percentage of chromophore containing units. The A curves have exactly N chromophores on each chain, while the B curves were calculated by averaging over a binomial distribution about N . There is no significant difference between the A and B curves. Thus, unless the distribution in the number of chromophores per chain is highly skewed, it is sufficient to use the average number of chromophores per chain in a calculation of $G^s(t)$.

For an infinite chain with a random substitution of chromophores, Eq. (13) is greatly simplified. Since all possible sites for the initially excited chromophores are equivalent, the sum over i (the location of the initially excited chromophore) is unnecessary. Also,²²

$$\lim_{N \rightarrow \infty} p_i(r_{12}) dr_{12} = \frac{3}{\pi a^2 r_{12}} r_{12}^2 dr_{12}. \quad (15)$$

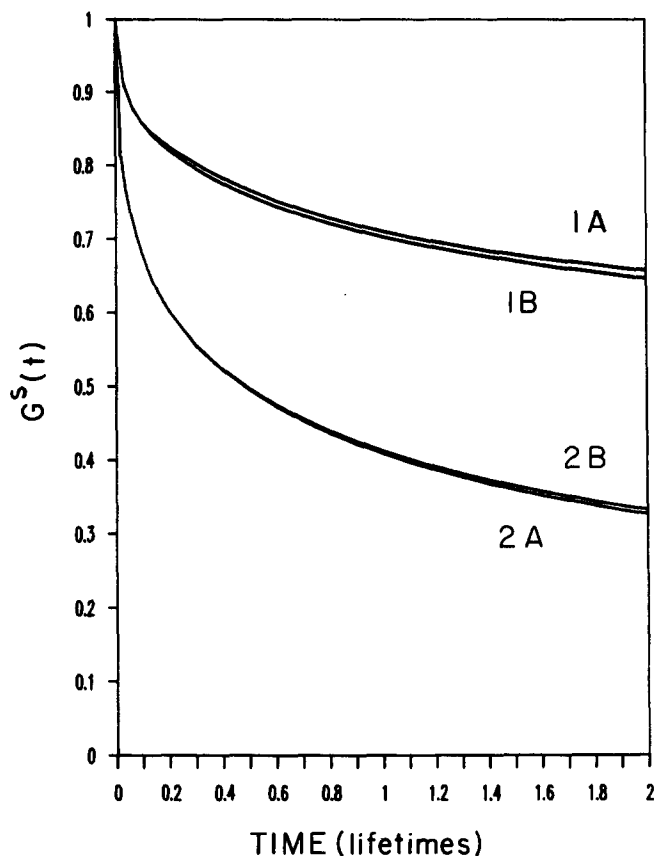


FIG. 6. $G^s(t)$ for two different length theta-condition PMMA chains containing different percentages of chromophore containing monomers. Curves labeled 1 are for 10 000 MW PMMA with 5% of the monomer units containing naphthalene. Curves labeled 2 are for 15 000 MW PMMA with ~10% of the monomer units containing naphthalene. Curves 1A and 2A have exactly 5 and 14 chromophores, respectively. Curves 1B and 2B were calculated by averaging over a binomial distribution around 5 and 14 chromophores, respectively. These curves demonstrate that a distribution in the number of chromophores on the chains has a negligible effect on the experimental observable. Therefore, an average over the distribution of the number of tags on the chains in a sample is unnecessary.

Equation (15) is the Debye function for ideal chains. $G^s(t)$ becomes

$$\ln G^s(t, N \rightarrow \infty) = \frac{6\pi c}{a^2} \int_0^\infty (e^{-2\omega_{12}t} - 1) r_{12} dr_{12}, \quad (16)$$

where c is the average number of chromophores per statistical segment. This can be evaluated to give

$$\ln G(t, N \rightarrow \infty) = -1.3794\pi c (R_0/a^2) (t/\tau)^{1/3}. \quad (17)$$

This result was previously obtained by Fredrickson *et al.*¹⁹ and it has been compared to their infinite order diagrammatic treatment of excitation transport on a randomly tagged, infinite coil and found to be in close agreement.

C. Excitation transport on isolated, flexible polymer chains end tagged with chromophores

Excitation transport experiments on a polymer with one chromophore on each end monomer unit are capable of providing direct measurement of the root-mean-square end-to-end distance ($\langle R_{ee}^2 \rangle^{1/2}$) of the chain. An end tagged chain is

a limiting case for the first order cumulant expansion treatment of a randomly tagged polymer. However, since there are only two chromophores in the system, the energy transport part of the problem can be solved exactly. For a pair of chromophores at a fixed distance r_{12} , the change with time of the probability that chromophore 1 is excited is given by

$$\frac{dp_1(t)}{dt} = \omega_{12}[p_2(t) - p_1(t)]. \quad (18)$$

This includes back transfer of excitation from chromophore 2 to chromophore 1. The additional constraints are that

$$p_1(0) = 1 \quad (19a)$$

and

$$p_1(t) + p_2(t) = 1. \quad (19b)$$

The solution to Eq. (18) is then

$$p(t) = \frac{1}{2}(1 + e^{-2\omega_{12}t}). \quad (20)$$

For a flexible, end tagged chain the chromophore distribution function is simply

$$P_{ee}(r_{12})dr_{12} = 4\pi \left(\frac{3}{2\pi \langle R_{ee}^2 \rangle} \right)^{3/2} \exp\left(\frac{-3r_{12}^2}{2\langle R_{ee}^2 \rangle} \right) r_{12}^2 dr_{12}, \quad (21)$$

where Eq. (14) has been used to replace $\bar{N}a^2$. The distribution function [Eq. (11)] used for the random tagged problem has contributions to the probability of finding a chromophore a distance r_{12} from the initial excitation at i from all other segments j on the chain. This results in a sum over all segments j and an additional contribution from segment i . For an end tagged isolated coil, one end is initially excited and transfer occurs only to the other end. Therefore, there is only a contribution from a single segment. In addition, since there is only one possible starting point, there is no average over starting points.

Using this chromophore distribution function [Eq. (21)] the ensemble average probability of finding chromophore 1 excited is

$$G^s(t) = \frac{4\pi}{2} \int_0^\infty P_{ee}(r_{12})(1 + e^{-2\omega_{12}t})r_{12}^2 dr_{12}. \quad (22)$$

As in the random tagged problem, the upper limit in the integration can be extended to infinity since contributions from distances greater than several R_0 are negligible. For small coils and large R_0 , an appropriate limit of integration can be used.

Equation (22) is exact in the description of the energy transport, any approximations occur only in the chromophore distribution function. (Whenever the term "exact" is used below, we mean just this and do not mean to imply that the total description of the energy transport on a polymer is exact.) Thus, end tagged chains can be used to investigate the applicability of various segment distribution functions to different polymer systems. Fredrickson *et al.* have also obtained an expression for the isolated, end tagged chain problem as a limiting case of an infinite order treatment in Laplace space.^{4(b)} The energy transport aspect of their treatment is also exact. Because Eq. (22) is in the time domain, it is more convenient to use. Figure 7 shows $G^s(t)$ curves for several values of $\langle R_{ee}^2 \rangle^{1/2}/R_0$ obtained from Eq.

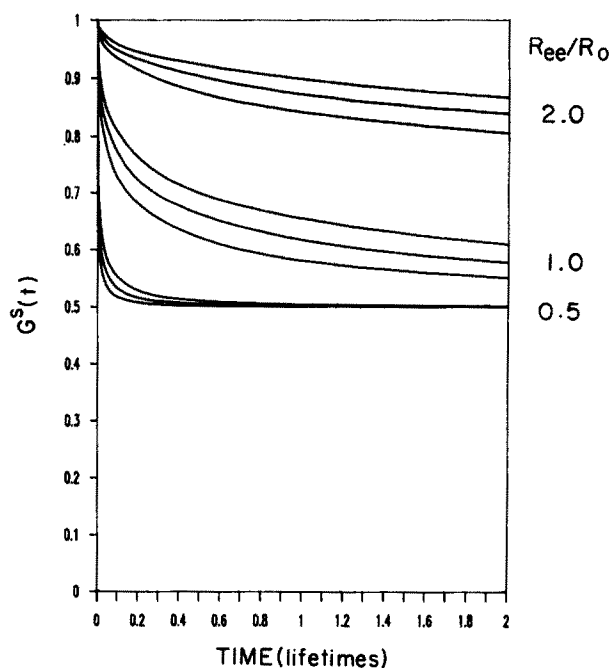


FIG. 7. $G^s(t)$ calculated for end tagged polymer chains with various ratios of $\langle R_{ee}^2 \rangle^{1/2}$ to R_0 (labeled R_{ee}/R_0 in the figure). The calculations are exact in the description of the energy transport. A Gaussian segment distribution function for the polymer was used. To show the sensitivity of $G^s(t)$ to changes in coil size, for each value of $\langle R_{ee}^2 \rangle^{1/2}/R_0$, a curve with a 10% greater ratio (upper) and a 10% smaller ratio (lower) is given.

(21) by numerical integration. In each set of curves, the upper and lower curves have $\langle R_{ee}^2 \rangle^{1/2}/R_0$ 10% larger and 10% smaller than the middle curve, respectively. This demonstrates the sensitivity of the calculation to changes in average coil dimension.

In both the random tagged and end tagged problems, $G^s(t)$ should decay asymptotically to $1/N$. Equation (22) for the end tagged chain does decay to 0.5 as it should. However, when the first order cumulant expansion is used, the value at infinite time is

$$G^s(t \rightarrow \infty) = e^{-(N-1)/2}. \quad (23)$$

When $N = 2$, this gives a value of 0.606. The worst case in the difference between the correct long time behavior and Eq. (23) occurs when there are only two chromophores present. As N increases, the error in the long time behavior becomes a smaller fraction of the total decay. This incorrect long time behavior is the source of the difference between the exact and cumulant expansion treatments for three chromophores randomly distributed in a sphere (see Fig. 4).

Even though the long time behavior of the cumulant expansion is not correct for a finite number of chromophores, the short time behavior is in excellent agreement with exact treatments. If we expand the exponential term in Eq. (22) (end tagged problem), keeping terms up to second order, and integrate, we obtain

$$G^s(t) \cong 1 - 9 \left(\frac{R_0}{R_{ee}} \right) \frac{6t}{\tau} - \frac{1458}{945} \left(\frac{R_0}{R_{ee}} \right)^2 \left(\frac{t}{\tau} \right)^2. \quad (24)$$

The expression for excitation transport on an end tagged polymer using the cumulant expansion is

$$\ln G^s(t) = \frac{4\pi}{2} \int_0^\infty P_{ee}(r_{12})(e^{-2\omega_{12}t} - 1)r_{12}^2 dr_{12}. \quad (25)$$

If the exponential in this equation is expanded, again keeping terms to second order, after integration the result is

$$G^s(t) \cong \exp \left[-9 \left(\frac{R_0}{R_{ee}} \right)^6 \frac{t}{\tau} - \frac{1458}{945} \left(\frac{R_0}{R_{ee}} \right)^{12} \left(\frac{t}{\tau} \right)^2 \right]. \quad (26)$$

For small t , this is equivalent to

$$G^s(t) \cong 1 - 9 \left(\frac{R_0}{R_{ee}} \right)^6 \frac{t}{\tau} - \frac{1458}{945} \left(\frac{R_0}{R_{ee}} \right)^{12} \left(\frac{t}{\tau} \right)^2. \quad (27)$$

Thus, the first order cumulant expansion and exact treatments are equivalent at short time. The expansions of both Eq. (22) and Eq. (23) show clearly how $G^s(t)$ scales with the various parameters. In both cases the results scale as $(R_0/R_{ee})^6 t/\tau$ at short times. This scaling has been confirmed to hold true at all time by numerical evaluation of Eqs. (22) and (25).

Since the short time behavior of the first order cumulant expansion is correct, if the asymptotic behavior for a finite number of chromophores could be improved the cumulant expansion would become an excellent approximation for a very small number of chromophores. For an end tagged chain, the exact treatment is available. For a randomly tagged chain and a reasonable number of chromophores (on the order of 10 or 20), the cumulant expansion treatment is very good at short time and reasonable at long times. At long time other factors must be considered; for example, in a fluorescence depolarization experiment, the effects of residual polarization become significant compared to the error in the asymptotic behavior.¹⁵

In principal, the end tagged approach to the determination of coil dimensions is superior to the random tagged approach because the energy transport aspect of the former can be treated exactly. However, for coils with end-to-end distances that are significantly larger than R_0 , the end tagged approach loses utility since little or no energy transport will occur.

IV. DISCUSSION

The explicit expressions used to describe excitation transport on a chain randomly tagged [Eq. (13)] or end tagged [Eq. (22)] with chromophores contain a specific model for the radial pair distribution function. The model, a Gaussian segment distribution function, is applicable to a freely jointed chain. For flexible polymers, one segment of the freely jointed chain, i.e., the statistical segment, is comprised of a number of monomer units. The statistical segment length is the distance required for correlation in direction (arising from restrictions on bond angles and rotations of the monomer units) to be lost.²³ For a theta-condition medium, the random walk description which gives rise to the Gaussian segment distribution function and the relationship between the segment length and $\langle R_g^2 \rangle^{1/2}$ [Eq. (14)], is valid. Provided the molecular weight of the chain is known, the segment length is the only adjustable parameter in the theory. Thus, theta-condition excitation transport experiments provide a measure of chain flexibility and coil dimension.

The question then arises of how to deal with a chain in a non-theta condition medium. One approach is to replace the Gaussian distribution functions used here with distributions appropriate for the particular system under consideration. Here we propose another approach which preserves the simplicity of random walk statistics.

Consider an ensemble of coils in a medium having less favorable polymer-medium interactions than a theta-condition solvent. The coils, on the average, will contract, i.e., $\langle R_g^2 \rangle^{1/2}$ will be smaller than the theta-condition value. A coil can still be considered a freely jointed chain, but it is now executing a biased walk rather than a random walk. There will be a tendency for the segments of the coil to avoid the medium. The bias will cause a more rapid turn toward the coil center than in a random walk.

Any segment of the chain is composed of a number of monomer units. If we imagine a segment being constructed by connecting the monomers one after another, a segment that starts to "head" into the unfavorable medium will have its distribution of monomer conformations skewed in a manner which will turn it around more rapidly than in a theta-condition medium. The effect is that segments which head into the unfavorable medium will have a segment length which is shorter than the average length in a theta-condition medium. In a medium which has more favorable interactions with the polymer than a theta-condition medium, segments which head into the favorable medium will have a segment length which is longer than the average length in a theta-condition medium.

We will replace a detailed description of such a biased walk by a random walk with a modified step length. The statistical segment length in a theta-condition medium a_θ , becomes an effective segment length a_{eff} . In an unfavorable medium a_{eff} is shorter than a_θ . In a favorable medium a_{eff} is longer than a_θ . In analyzing excitation transport experimental data, the equations given above are used. There is still a single adjustable parameter, a_{eff} . Equation (14) relates a_{eff} to $\langle R_g^2 \rangle^{1/2}$.

Qualitatively, the model described above can be visualized in analogy to a random walker in a shallow bowl. The walker slightly prefers to walk downhill. (The bias could involve a lower probability of taking an uphill step or the length of an uphill step could be somewhat shorter than a downhill step.) This is analogous to the unfavorable medium. An ensemble of walks in a bowl, each with step size a and number of steps N , will have a smaller root-mean-square displacement than an ensemble of walks on a plane with the same number of steps. The model describes the biased walk in the bowl as a random walk on a plane with a reduced, effective step size. A favorable medium for the polymer coil is like a walk on an inverted bowl; the effective step size in a random walk be increased over the unbiased walk step size. While the biased walk spatial distribution function is different from the random walk distribution function, the second moment ($\langle R_g^2 \rangle^{1/2}$) is not particularly sensitive to the details of the distribution function if the bias is not too great. [For semistiff or rod-like coils the Gaussian segment distribution functions in Eqs. (13) and (22), must be replaced by more applicable functions.] The net result is that the equations

developed in this paper are useful in obtaining information on coil sizes in theta and non-theta media.

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