27084. We are much indebted to W. Kohn for his kind hospitality at the ITP, where this work was done.

References and Notes

(1) de Gennes, P.-G. *C. R. Hebd. Seances Acad. Sci., Ser. B* **1980**, *291*, 17.
(2) Isaacson, J.; Lubensky, T. C. *J. Phys. (Paris)* **1981**, *42*, 175; *Phys. Rev. A* **1979**, *20*, 2130.
(3) Redner, S. *J. Phys. A* **1979**, *12*, L239.
(4) Family, F. *J. Phys. A* **1980**, *13*, L325.
(5) Daoud, M.; Joanny, J. F. *J. Phys. (Paris)* **1981**, *42*, 1359.
(6) Daoud, M. *J. Phys. (Paris)* **1982**, *43*, 1781.
(7) Parisi, G.; Sourlas, N. *Phys. Rev. Lett.* **1981**, *46*, 871.
(8) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(9) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953.
(10) de Gennes, P.-G. *J. Phys. (Paris), Lett.* **1975**, *36*, 55.
(11) Daoud, M.; Jannink, G. *J. Phys. (Paris)* **1976**, *36*, 281.
(12) And the Flory exponents usually are!
(13) Domb, C. *J. Phys. A* **1976**, *9*, L141.
(14) Edwards, S. F. *Proc. Phys. Soc. London, Ser. A* **1965**, *85*, 613.
(15) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(16) Baumgärtner, A. *J. Phys. (Paris)* **1982**, *43*, 1407. Tobochnik, J.; Webman, I.; Lebowitz, J. L.; Kalos, M. H. *Macromolecules* **1982**, *15*, 549.
(17) de Gennes, P.-G. *Biopolymers* **1968**, *6*, 715.
(18) Dobson, G. R.; Gordon, G. *J. Chem. Phys.* **1964**, *41*, 2389.
(19) For the present purpose we neglect the different between the Flory Θ temperature, defined by $v(\Theta) = 0$ and the actual Θ temperature, where the second virial vanishes (when $N \rightarrow \infty$).
(20) Kawaguchi, M.; Yoshida, A.; Takabashi, A., to be published.
(21) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P.-G. *Macromolecules* **1975**, *8*, 804.
(22) Farnoux, B.; Boué, F.; Cotton, J. P.; Daoud, M.; Jannink, G.; Nierlich, M.; de Gennes, P.-G. *J. Phys. (Paris)* **1978**, *39*, 77.
(23) Wohrer, M. Thèse 3ème cycle (1976), available at CEN Saclay, S.Ph.T BP No. 2, 91191 Gif-sur-Yvette Cedex.
(24) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(25) Stephen, M. *Phys. Lett. A* **1975**, *53*, 363.
(26) Orofino, T. A.; Flory, P. J. *J. Chem. Phys.* **1957**, *26*, 1067.
(27) Stockmayer, W. H. *Makromol. Chem.* **1960**, *35*, 54.

New Approach to Probing Polymer and Polymer Blend Structure Using Electronic Excitation Transport

M. D. Ediger and M. D. Fayer*

Department of Chemistry, Stanford University, Stanford, California 94305.
Received February 8, 1983

ABSTRACT: A theoretical study of electronic excitation transport in polymer systems is presented. $G^s(t)$, the time-dependent ensemble-averaged probability that the excitation is on the originally excited chromophore, is calculated by using an approach involving a density expansion. It is shown that this quantity is a direct observable in a time-resolved fluorescence depolarization experiment. The effects of the finite volume associated with a single polymer coil or a small aggregate in a polymer blend are considered explicitly. Calculations are presented for systems having a Gaussian ensemble-average segmental distribution. The influences of density, volume, and aggregation are illustrated. $G^s(t)$ can yield reliable information about the local chromophore distribution of systems for which a lack of knowledge of the number of excimer traps prevents quantitative application of trapping experiments. The approach described here should be particularly valuable in obtaining structural information about very low concentration guest polymers in polymer blends and solutions.

I. Introduction

In recent years there has been considerable work devoted to understanding electronic excitation transport processes in polymer systems.[1] Because of their sensitivity to the spatial separation and orientation of chromophores in a polymer system, excitation transport observables contain detailed information about structural properties, e.g., coil configuration and the degree of coil extension. This information is of key importance in understanding the microscopic interaction of a polymer with its environment, and thus the macroscopic properties of polymers and polymer blends.

Recent theoretical and experimental advances have provided a detailed picture of incoherent excited-state transport among molecules distributed randomly in solutions or molecular crystals. Accurate theoretical treatments have been developed that are able to quantitatively predict experimental observables for single-component systems (donor–donor transport only) and two-component systems (donor–donor transport with donor-to-trap transfer).[2-4] Similar success in understanding energy-transport processes in polymer systems has not yet been achieved, due to the increased theoretical difficulty of including polymer structure in the problem.

Chromophores attached to an isolated polymer coil differ from independent chromophores in solution in at least two important respects. Chromophores in polymer systems are not in general randomly arranged but are correlated by the covalent bonds that join them. In addition, the finite extent of an isolated polymer coil effectively limits the number of possible sites that the excitation can sample. Therefore previous theoretical approaches that involve the thermodynamic limit,[2,3] i.e., the limit of an infinite number of sites distributed in an infinite volume, cannot be applied in many cases of interest.

Excitation transport among coil chromophores depends both on local molecular structure and on thermodynamic interactions of the coil with its environment. If an individual coil with closely spaced chromophores is dissolved in a good solvent, it will assume an extended configuration. Then, on the average, the only chromophores near the originally excited chromophore will be those most closely linked to it along the polymer backbone. The extended geometry makes the probability *small* that a chromophore from a polymer segment far removed along the backbone is in spatial proximity to the initial excitation. Thus ex-

citation transport is primarily one dimensional (along the chain) for a polymer with closely spaced chromophores in an extended configuration. In addition, the chromophore distribution will be highly nonrandom if the number of bonds between two adjacent chromophores is small. The net result will be basically one-dimensional transport among chromophores distributed neither randomly nor periodically.

If the polymer–solvent interactions are less favorable, the isolated coil will contract and excitation transport to chromophores not connected by a small number of covalent bonds will become more probable. When polymer–solvent interactions become poor, polymer molecules will aggregate and precipitate from the solution. In a two-component polymer blend, the low-concentration guest polymer can phase separate into domains of macroscopic dimensions,[5] form small aggregates of a few polymer molecules,[6] or contract far below the Θ-dimensions as an isolated coil. For these situations the local chromophore distribution is approximately random in three dimensions. This is due to the close proximity of chromophores from other coils, or for a single coil, because of the contracted molecular dimensions that bring isolated segments of the coil together. The positions and orientations of chromophores from isolated parts of a chain or from other coils will not be significantly correlated with those of the originally excited chromophore. The three-dimensional random distribution is expected to be an accurate description even for a polymer in a good solvent, if the separation between chromophores along the chain is large enough, e.g., when a chromophore containing monomer is copolymerized with a nonchromophore-containing monomer.[7]

In this paper, we present a theoretical treatment that provides a description of energy transport within a polymer coil or group of coils if the chromophore distribution is locally random in three dimensions. This model explicitly considers the coil to be *finite in extent* and is consistent with an *ensemble-averaged segmental density distribution that is Gaussian*. The observable calculated here is $G^s(t)$ (in the notation of ref 3), the ensemble-averaged probability that the excitation is still on the originally excited chromophore. $G^s(t)$ has contributions from excitations that have never left the initially excited chromophore and from those that have left and subsequently returned. Therefore an accurate theoretical treatment of $G^s(t)$ must include back-transfer. $G^s(t)$ can be calculated and measured with or without traps in the system. It is the fundamental observable for energy-transport experiments if information about the *local* environment is primarily of interest. Observables that depend on trapping (changes in the donor or trap excited-state populations) inherently contain less information about the local environment because many local environments are sampled before trapping occurs. In contrast, $G^s(t)$ is directly related to the chromophore distributions around the ensemble of originally excited chromophores.

The presence of excimers (which act as traps) in a wide variety of fluorescent polymers influences both $G^s(t)$ and trapping observables. Trapping observables are critically dependent on the precise number of traps present. Therefore, the quantitative interpretation of trapping experiments in order to obtain structural information is difficult since the number of excimer-forming sites is not readily calculated in the absence of detailed structural knowledge. As will be shown in section III, $G^s(t)$ is quite insensitive to the precise concentration of excimer traps and can provide useful information even when the number

of these traps is not precisely known.

Questions about coil dimensions and aggregation are extremely difficult to address with current techniques when the polymer concentration is very small. This is particularly true of polymer blends when a low concentration of guest polymer is mixed with another polymer. Differential scanning calorimetry, light scattering, and neutron scattering all lose their sensitivity at low concentrations. $G^s(t)$, because it can be obtained from time-resolved polarized fluorescence data, can be measured even at very low concentrations. $G^s(t)$ depends strongly on the degree of extension of a single polymer coil if a substantial probability for multidimensional transport exists. As the solvent–polymer interactions are made less favorable, the coil will contract, and $G^s(t)$ will decay faster due to the increased local concentration of chromophores attached to remote segments of the chain. $G^s(t)$ will also be sensitive to aggregation of polymer coils, either because of an increased chromophore density or, if the chromophore density does not increase, because of the larger volume of sites that the excitation can visit (increasing the finite volume). Thus questions pertaining to the physical properties of isolated coils or small aggregates in various environments can be addressed.

In the following section, we derive an expression for $G^s(t)$ that is appropriate for a three-dimensional Gaussian chromophore distribution. Illustrations are presented that demonstrate how $G^s(t)$ can yield information about coil dimensions and the presence of aggregation. In section III, we discuss the relationship of $G^s(t)$ to time-resolved fluorescence polarization data. While the connection is not always quantitatively satisfactory when excitation transport is primarily one dimensional, it will be shown that in many cases of interest the connection is simple and accurate. This is true in all cases in which the model of section II is expected to be applicable.

II. Theory

In this section, we derive an expression for $G^s(t)$ which assumes a chromophore distribution that is random in three dimensions and has an approximately Gaussian ensemble-average segmental distribution. To obtain this result, we start with an expression for the Laplace transform of $G^s(t)$ derived in a previous paper[8] (hereafter referred to as I). This expression was derived for a random chromophore distribution within a sphere of finite radius. Considering this as a model for a single coil, we average these results over the distribution of the radius of gyration to obtain the ensemble-averaged $G^s(t)$.

In I, we considered a finite spherical volume of radius R_s containing N donor chromophores and no traps. We assumed an orientation-averaged dipole–dipole interaction with the transfer rate between two chromophores given by

$$w = \frac{1}{\tau}\left(\frac{R_0}{r}\right)^6 \tag{1}$$

τ is the excited-state lifetime in the absence of energy-transport processes, r is the interchromophore separation, and R_0 is the critical transfer radius for energy transport between two donors. (In general, the orientation-dependent transfer rate needs to be considered. When chromophores in a random solution are fixed in space on the time scale of energy transfer, $G^s(t)$ for the full transfer rate can be readily obtained from $G^s(t)$ for the orientationally averaged rate.[4a,9] This simple procedure will be accurate for the model under discussion whenever there are more than two chromophores on the polymer chain.[10]) Utilizing an expansion in powers of the chromophore

density, we obtained the following approximation for the Laplace transform of $G^s(t)$:

$$\hat{G}^s(N,\beta,\epsilon) = \epsilon^{-1}\left\{1 + \frac{C_D}{(\epsilon\tau)^{1/2}}\left(1 - \frac{1}{N}\right)f_2(\beta) + \frac{C_D^2}{\epsilon\tau}\left(1 - \frac{1}{N}\right)\left[\left(1 - \frac{1}{N}\right)(f_2(\beta))^2 - \left(1 - \frac{2}{N}\right)f_3(\beta)\right]\right\}^{-1} \quad (2)$$

In this equation, ϵ is the Laplace transform variable

$$C_D = N(R_0/R_s)^3 \quad (3)$$

and

$$\beta = \left(\frac{R_s}{R_0}\right)^3\left(\frac{\epsilon\tau}{2}\right)^{1/2} \quad (4)$$

$f_2(\beta)$ and $f_3(\beta)$ are positive monotonically increasing functions of β obtained in I. Analytical approximations for them are given in the Appendix of I. In I, we demonstrated that the inverse Laplace transform of eq 2 is expected to be a very good approximation to the true solution.

We assume the model of chromophores randomly distributed in a sphere of radius R_s to be an approximate description of a single polymer coil in the subset of its possible configurations having radius of gyration R_g. Associated with this distribution of chromophores is a second moment, i.e., the radius of gyration squared ($R_g^2 = (3/5)R_s^2$). By averaging $G^s(t)$ over a distribution function for R_g, we obtain the ensemble-averaged observable. We chose the distribution function of Flory and Fisk[11] to illustrate this calculation because it has a convenient analytical form and is a reasonable approximation[12] to the exact function assuming Gaussian bond probabilities. It is given by

$$P(R_g) = \left(\frac{343}{15}\right)\left(\frac{14}{\pi\langle R_g^2\rangle}\right)^{1/2}\left(\frac{R_g^2}{\langle R_g^2\rangle}\right)^3 \exp\left(-\frac{7R_g^2}{2\langle R_g^2\rangle}\right) \quad (5)$$

where $\langle R_g^2\rangle$ denotes the expectation value of R_g^2.

Our final expression for the Laplace transform of the ensemble-averaged probability of finding the excitation on the originally excited chromophore is

$$\langle\hat{G}^s(N,\langle R_g^2\rangle,\epsilon)\rangle = \int_0^\infty dR_g\, P(R_g)\hat{G}^s(N,\beta,\epsilon) \quad (6)$$

N now refers to the number of chromophores on a single polymer chain. For the purpose of evaluating eq 6, β and C_D can be rewritten as

$$\beta = \left(\frac{5}{3}\right)^{3/2}\left(\frac{R_g}{R_0}\right)^3\left(\frac{\epsilon\tau}{2}\right)^{1/2} \quad (7)$$

$$C_D = \left(\frac{3}{5}\right)^{3/2}N(R_0/R_g)^3 \quad (8)$$

$G^s(t)$ for particular values of N and $\langle R_g^2\rangle$ is obtained by performing the inverse Laplace transform numerically.[13] $G^s(t)$ calculated in this manner does not include loss of probability due to the excited-state lifetime. This is included by multiplying by $e^{-t/\tau}$.

The energy-transport calculations presented involve an average over a chromophore distribution with a sharp cutoff. The validity of this averaging procedure can be tested qualitatively, as illustrated below.
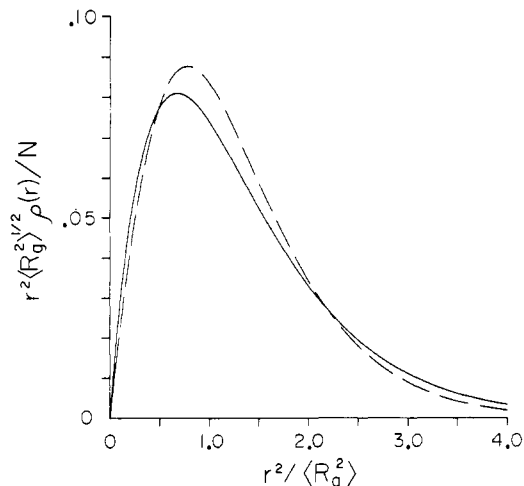

Figure 1. Comparison of the standard Gaussian ensemble-average segmental density distribution (solid line) to the density distribution implicit in this calculation (dashed line). Note that these are radial distribution functions.

Within our model, the chromophore density of a single coil in the subset of its configurations with a given R_g is

$$\rho(r,R_g) = \frac{N}{(4/3)\pi(R_g)^3}\left(\frac{3}{5}\right)^{3/2} \quad 0 < r < \left(\frac{5}{3}\right)^{1/2}R_g$$
$$= 0 \quad r > \left(\frac{5}{3}\right)^{1/2}R_g \quad (9)$$

$\rho(r,R_g)$ is normalized to N. The ensemble-averaged chromophore density is

$$\langle\rho(r,R_g)\rangle \equiv \rho(r) = \int_0^\infty dR_g\, P(R_g)\rho(r,R_g) =$$
$$\frac{N}{\langle R_g^2\rangle^{3/2}}\left(\frac{147}{50\pi}\right)\left(\frac{21}{10\pi}\right)^{1/2}\left(\frac{3r^2}{5\langle R_g^2\rangle} + \frac{2}{7}\right) \times \exp\left(\frac{-21r^2}{10\langle R_g^2\rangle}\right) \quad (10)$$

Figure 1 shows eq 10 plotted against the standard Gaussian approximation[12] (normalized to N):

$$\rho(r) = N\left(\frac{3}{2\pi\langle R_g^2\rangle}\right)^{3/2}\exp\left(\frac{-3r^2}{2\langle R_g^2\rangle}\right) \quad (11)$$

The agreement is very reasonable and demonstrates that our model is consistent with a Gaussian ensemble-average density distribution. We anticipate that the averaging process also yields a reasonable description of energy transport. It will require further theoretical investigation employing a more accurate distribution function than that implied by eq 9 to test the quantitative validity of these calculations. However, the theory as presented is certainly useful in investigating the relative effects of various environments on coil dimensions.

In Figure 2 we illustrate the general features of $G^s(t)$, the inverse Laplace transform of eq 6. These curves are intended to indicate how $G^s(t)$ is affected by changes in the various parameters. In Figure 3, we calculate $G^s(t)$ for a model based on a specific copolymer under various realistic conditions. The calculations plotted in these figures do not include decay due to the excited-state lifetime.

Figure 2A shows calculated curves of $G^s(t)$ when the density of chromophores at the center of the coil is held
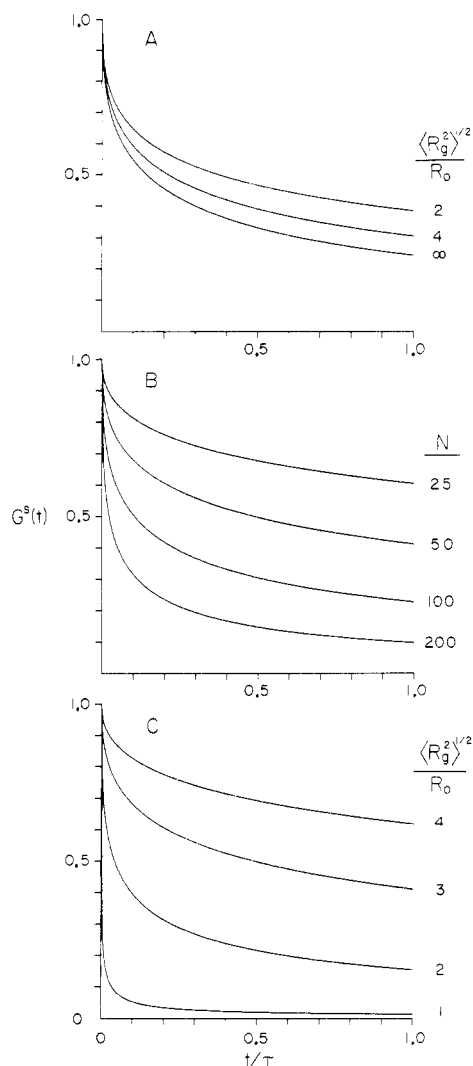
Figure 2. Effects of density and coil dimensions on $G^s(t)$, the time-dependent probability that the excitation is on the originally excited molecule. In part A, the average chromophore density is held constant while the ensemble-average radius of gyration is varied. N, the number of chromophores in the coil is 20, 160, and ∞, respectively, for $\langle R_g^2 \rangle^{1/2}/R_0$ equal to 2, 4, and ∞. For a constant chromophore density, $G^s(t)$ decays faster as the volume of accessible sites increases. In part B, the coil size is held constant while the number of chromophores is increased, thus increasing the density. $\langle R_g^2 \rangle^{1/2}/R_0$ is 3.0 for all four curves. As the chromophore density increases, $G^s(t)$ decays faster. In part C, the coil dimensions, $\langle R_g^2 \rangle^{1/2}$, are changed while the number of chromophores is fixed. There are 50 chromophores in the calculation for each curve. Since the local chromophore density increases as the coil dimensions decrease, $G^s(t)$ decays significantly faster.

Figure 3. Calculated effects of density changes and aggregation on $G^s(t)$ for a 20 000 MW copolymer of methyl methacrylate and vinylnaphthalene (mole fraction of vinylnaphthalene = 0.17). Curve A shows a calculation for a single coil ($N = 31$) under Θ-conditions ($\langle R_g^2 \rangle^{1/2} = 35$ Å). Curve B shows the same copolymer when the coil has contracted due to unfavorable interactions with the host polymer ($\langle R_g^2 \rangle^{1/2} = 28$ Å). Curve C shows an aggregate of 16 coils assuming that the average density is the same as under Θ-conditions and that the Flory–Fisk distribution of the radius of gyration can be applied to the aggregate. This is the minimum change that could be expected upon aggregation. For C, there are 496 chromophores with $\langle R_g^2 \rangle^{1/2} = 88$ Å. Curve D shows an infinite-volume calculation for a bulk sample of the pure copolymer (1 g/cm^3).

constant while the number of chromophores and $\langle R_g^2 \rangle^{1/2}$ (the ensemble-average radius of gyration) are varied together. This illustrates the influence of volume on excitation transport. As the volume increases, the number of accessible sites increases, and $G^s(t)$ decays faster as a result. In Figure 2B, $\langle R_g^2 \rangle^{1/2}$ is held constant while the number of chromophores is increased, and hence the density increases. $G^s(t)$ decays significantly faster as the local chromophore density is increased in a fixed volume. Figure 2C shows $G^s(t)$ when the number of chromophores is fixed, but $\langle R_g^2 \rangle^{1/2}$ is varied. As $\langle R_g^2 \rangle^{1/2}$ decreases, for a fixed number of chromophores, $G^s(t)$ decays much faster due to the increased local chromophore concentration.

Figure 3 shows how $G^s(t)$ is affected by changes in coil dimensions and by coil aggregation for a specific copolymer in blends with various hosts. For the purpose of illustra-
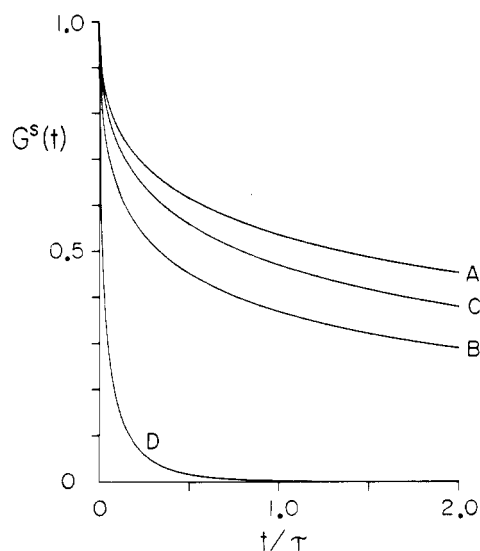
tion, parameters appropriate for a 20 000 MW copolymer of vinylnaphthalene and methyl methacrylate (mole fraction of vinylnaphthalene = 0.17) have been used. This is similar to a copolymer used by Reid and Soutar.[7] The low mole fraction of naphthalene chromophores should make the assumption of a random, three-dimensional chromophore distribution reasonable. R_0 is taken to be 11.75 Å, the same as for 2-methylnaphthalene.[14] Curve A shows $G^s(t)$ calculated for the copolymer under Θ conditions ($\langle R_g^2 \rangle^{1/2} = 35$ Å).

Curve B shows the same isolated polymer coil as it might appear at very low concentration in a polymer blend when the thermodynamic interactions between the host and guest polymers are unfavorable. The segmental density of the guest copolymer has been doubled at the center of the coil by decreasing $\langle R_g^2 \rangle^{1/2}$ to 28 Å. The Flory–Fisk distribution was again used to describe the distribution of the radius of gyration. (The absolute density for curve B corresponds roughly to that observed by Kirste et al.[6] in aggregates of poly(α-methylstyrene) dispersed within D-poly(methyl methacrylate).) Curve B could be readily distinguished from curve A by, for example, time-resolved fluorescence depolarization measurements.

Curve C shows the change in $G^s(t)$ that would be expected upon aggregation of single coils if the average chromophore density of the coils is the same as in curve A (Θ conditions). In this case only the volume accessible to the excitation (i.e., the number of sites) increases. This is clearly the minimum change that would be expected upon aggregation. If the chromophore density increased as well, the difference between curves A and C would be greater. The number of coils aggregating was taken to be 16, consistent with the observations by Kirste et al.[6] for the system described above. The calculations for curve C assume for simplicity that the Flory–Fisk distribution is still appropriate although the neutron scattering data
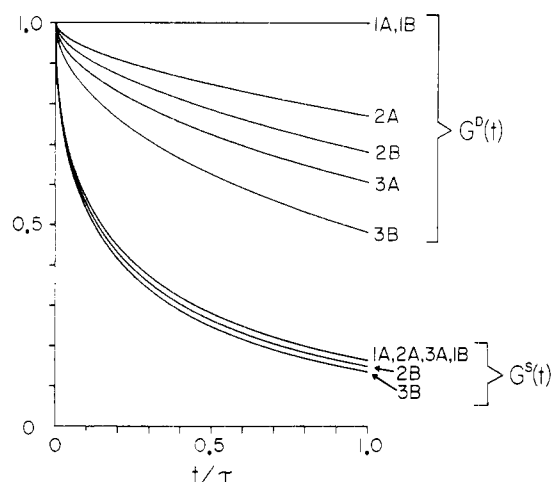
Figure 4. Comparison of the effects of excimer traps on $G^s(t)$ and $G^D(t)$, a trapping observable. $G^s(t)$ is the probability that the excitation is on the originally excited chromophore while $G^D(t)$ is the probability that an excitation has not been trapped. Curves labeled A treat the two chromophores forming the excimer as a single trap, while curves labeled B treat them as independent traps (see text). Curves 1, 2, and 3 correspond to systems in which 0, 10, and 20% of the chromophores are involved in excimer pairs, respectively. The $G^D(t)$ curves vary widely while the $G^s(t)$ curves are quite similar. This demonstrates that $G^s(t)$ contains more accessible information about the local chromophore density than trapping observables when the number of excimers is unknown.

of Kirste et al. indicate that the overall segmental distribution is not strictly Gaussian. For comparison, curve D shows an infinite-volume calculation (using ref 3) for conditions corresponding to a macroscopic volume of the pure copolymer.

III. Observables

The calculations of the previous section did not include the influence of traps on $G^s(t)$. In general, polymers can have two types of traps: chemical traps and excimers. Chemical traps have been copolymerized with the donor chromophore in order to utilize trapping as an energy-transport observable.[15] The theory presented here and in I can be easily and accurately extended to calculate $G^s(t)$ in the presence of traps.

Excimer traps have formed the basis for some excitation transport observables.[16] In polymers where excimers are formed, the number of excimer traps is difficult to measure or calculate. Since trapping observables are very sensitive to the trap concentration, this results in considerable uncertainty in the interpretation of trapping experiments. In contrast, $G^s(t)$ is relatively insensitive to the excimer trap concentration and therefore does not suffer from this uncertainty.

To demonstrate the relative insensitivity of $G^s(t)$ to excimer traps, we will use the infinite-volume theory of Loring, Andersen, and Fayer.[3b] The chromophore distribution in this treatment is random in three dimensions. The fact that the calculations are for infinite volume will not significantly affect the sensitivity to excimer traps. We will use two alternate methods of accounting for these traps. First, following the procedure of Fredrickson and Frank,[17] we consider the pair of chromophores comprising the excimer as one trap, with the donor–trap transfer rate being twice the donor–donor rate. All such calculations are labeled A in Figure 4. As a second method of accounting for excimer traps, we treat each chromophore of the excimer pair as an independent trap, with the donor–trap transfer rate equal to the donor–donor rate. This makes the excimer equivalent to two adjacent chemical

traps. All such calculations are labeled B.

Figure 4 shows the results of calculations for three different trap concentrations. Two types of observables are presented. $G^s(t)$, as discussed above, is the probability of finding the excitation on the originally excited chromophore. $G^D(t)$ is the probability that the excitation has not been trapped. ($e^{-t/\tau}G^D(t)$ is the observable when the excited-state donor decay is monitored in an excitation transport experiment.) The curves labeled "1" are for a system with no traps, curves labeled "2" are for a system in which 10% of the chromophores are involved in excimer pairs, while "3" corresponds to 20% involved in excimers. When method A is used to account for the excimers, the three different $G^s(t)$ curves are indistinguishable in the figure, while the $G^D(t)$ curves differ widely. Likewise when method B is used, the $G^D(t)$ curves vary much more than those for $G^s(t)$. Clearly, if the precise number of excimer-forming sites is unknown, $G^s(t)$ provides more accurate information about the local chromophore density than does the decay of the donor fluorescence. (Decay due to the excited-state lifetime is not included in the calculations.)

A strong connection between experimental observables, such as time-resolved fluorescence depolarization, and $G^s(t)$ has been assumed in the previous discussions. In a solution where the angular distribution of chromophores is random, the fluorescence intensity of emission parallel and perpendicular to the exciting beam ($I_\parallel$ and $I_\perp$, respectively) is related to $G^s(t)$ as follows:[4a]

$$I_\parallel \propto e^{-t/\tau}(1 + 2CG^s(t))$$

$$I_\perp \propto e^{-t/\tau}(1 - CG^s(t)) \tag{12}$$

Here, C is a time-independent constant dependent upon the degree of photoselection for the transitions involved. Two conditions need to be met for eq 12 to be applicable to polymer systems.

First, there cannot be competing depolarization processes on the same time scale as energy transport. Molecular rotation, segmental mobility, and rotation of the chromophores about single bonds must all be relatively slow. In most cases, polymer blends will satisfy this condition.

The second requirement is that emission from chromophores not originally excited must be substantially depolarized. It has been demonstrated that this is the case in a random distribution of distances and angles. Emission from chromophores not originally excited will have a fluorescence anisotropy of less than 2.5% of the anisotropy arising from the initially excited chromophores.[18] For the copolymer discussed in Figure 3, the low chromophore density along the chain ensures that there will be no substantial correlation between the transition dipole directions of any two chromophores. Thus for this copolymer, the relation between fluorescence data and $G^s(t)$ will be given by eq 12. In general, we would expect eq 12 to be accurate for all copolymers where the mole fraction of monomers that contain chromophores is low. (However, if the chromophore is part of the polymer backbone, even in low concentrations, special correlations between transition dipoles may exist in a polymer configuration that is nonspherical.)

Equation 12 will be least applicable when strong correlations exist between the dipole directions of the chromophores, such as in an aromatic vinyl homopolymer. Even for this case, however, the calculation described below suggests that eq 12 will not be seriously in error. The simplest model for two segments of a poly(2-vinylnaphthalene) (P2VN) chain is 1,3-di(2-naphthyl)propane. Ito et al.[19] have calculated the most stable configurations

for this molecule and their relative weights. While these chromophore configurations will not correspond precisely to those found in a P2VN chain, they should be a reasonable approximation.

We want to calculate the ensemble-averaged emission anisotropy of the nonoriginally excited chromophore, assuming polarized excitation. In addition, we assume that for each internal configuration there is an ensemble of molecules whose external angular orientation is random with respect to the laboratory frame. Following the general procedure of Jabloński,[18] we calculate the emission anisotropy of the acceptor chromophore for each configuration. This value is weighted by the probability of emission from that chromophore. Finally, the emission anisotropies for all the configurations are averaged, taking into account the statistical weight of each configuration.

Using this procedure, one finds the ratio of the emission anisotropy of the nonoriginally excited chromophore to that of the originally excited chromophore to be −0.23 for 1,3-di(2-naphthyl)propane. (If the two transition dipoles were always parallel, the ratio would be 1.0.) Even if transport on a P2VN chain is entirely one dimensional, this emission anisotropy should be substantially smaller in magnitude than 23%, since many more chromophores than a single nearest neighbor will be involved in transport and light emission. When transport is three dimensional, the residual anisotropy is further decreased by transport to chromophores off chain whose angular orientation will be essentially uncorrelated to the originally excited chromophore. Thus we expect eq 12 to accurately describe the relationship of $G^s(t)$ to time-resolved polarized fluorescence data or other polarization-dependent observables[20] whenever the theory presented in section II can be applied and to be a good approximation for many other situations.

IV. Concluding Remarks

In an effort to obtain structural information about polymer coils from polarization-dependent experimental observables, we have presented a theory based on a density expansion. The theory explicitly considers a distribution of coil dimensions, as well as the local disorder implicit in polymer structure when the chromophores are not connected by a small number of bonds. The theory can be readily extended to include nonrandom spatial and angular correlations, thus allowing a description of excitation transport in aromatic vinyl homopolymers in extended configurations. As presented, our theory should be useful in a wide variety of circumstances for the investigation of polymer–host interactions in solution and in polymer blends.

References and Notes

(1) For a recent review: Klöpffer, W. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 373.
(2) Haan, S. W.; Zwanzig, R. *J. Chem. Phys.* **1978**, *68*, 1879. Klafter, J.; Silbey, R. *Ibid.* **1980**, *72*, 843. Godzik, K.; Jortner, J. *Ibid.* **1980**, *72*, 4471. Huber, D. L. *Phys. Rev. B* **1979**, *20*, 2307. Movaghar, B.; Sauer, G. W.; Würtz, D. *J. Stat. Phys.* **1982**, *27*, 473.
(3) (a) Gochanour, C. R.; Andersen, H. C.; Fayer, M. D. *J. Chem. Phys.* **1979**, *70*, 4254. (b) Loring, R. F.; Andersen, H. C.; Fayer, M. D. *Ibid.* **1982**, *76*, 2015.
(4) (a) Gochanour, C. R.; Fayer, M. D. *J. Phys. Chem.* **1981**, *85*, 1989; (b) Miller, R. J. D.; Pierre, M.; Fayer, M. D. *J. Chem. Phys.* **1983**, *78*, 5138. (c) Kopelman, R. In *Top. Appl. Phys.* **1981**, *49*, 241.
(5) Manson, J. A.; Sperling, L. H. "Polymer Blends and Composites"; Plenum Press: New York, 1976, p 77ff.
(6) Kirste, R. G.; Kruse, W. A.; Ibel, K. *Polymer* **1975**, *16*, 120.
(7) Reid, R. F.; Soutar, I. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 231.
(8) Ediger, M. D.; Fayer, M. D. *J. Chem. Phys.* **1983**, *78*, 2518.
(9) Steinberg, I. Z. *J. Chem. Phys.* **1968**, *48*, 2411; Blumen, A. *Ibid.* **1981**, *74*, 6926.
(10) Ediger, M. D.; Domingue, R. P.; Fayer, M. D. *J. Chem. Phys.*, accepted.
(11) Flory, P. J.; Fisk, S. *J. Chem. Phys.* **1966**, *44*, 2243.
(12) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(13) Stehfest, H. *Commun. Assoc. Comput. Mach.* **1970**, *13*, 47, 624.
(14) Berlman, I. B. "Energy Transfer Parameters of Aromatic Compounds"; Academic Press: New York, 1973.
(15) Ng, D.; Guillet, J. E. *Macromolecules* **1982**, *15*, 728.
(16) Frank, C. W.; Gashgari, M.-A.; Chutikamontham, P.; Haverly, V. J. In *Stud. Phys. Theor. Chem.* **1980**, *10*, 187–209. Anderson, R. A.; Reed, R. F.; Soutar, I. *Eur. Polym. J.* **1980**, *16*, 945.
(17) Fredrickson, G. H.; Frank, C. W. *Macromolecules* **1983**, *16*, 1198.
(18) Jabloński, A. *Acta Phys. Pol. A* **1970**, *38*, 453.
(19) Ito, S.; Yamamoto, M.; Nishijima, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 363.
(20) Moog, R. S.; Ediger, M. D.; Boxer, S. G.; Fayer, M. D. *J. Phys. Chem.* **1982**, *86*, 4694. Waldeck, D. H.; Fleming, G. R. *Ibid.* **1981**, *85*, 2614.