sults of David et al.[19] When mol % VBP decreases to 24.1% as PMMA-VBP-2, both Λ and ω drop by at least a full order of magnitude. What little energy migration may be present in this copolymer probably occurs via nonnearest-neighbor interactions.

Conclusions

Intramolecular energy migration in polymers does not lead to an enhancement of their efficiencies as photosensitizers when the rate-determining sensitization step occurs at several orders of magnitude below the diffusion-controlled limit. Any apparent polymer effect in this case is in all probability due to preferential solvation. For sensitization reactions approaching the diffusion-controlled limit, a polymer effect is seen when the mole fraction of sensitizer monomer in the polymer becomes sufficiently high to permit facile intramolecular energy migration.

Acknowledgment. This work was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2448 from the Notre Dame Radiation Laboratory.

Registry No. Benzophenone, 119-61-9; poly(4′-vinylbenzophenone) (homopolymer), 25668-24-0; 1-methylnaphthalene, 90-12-0; cumene, 98-82-8; tetrahydrofuran, 109-99-9; methyl methacrylate–4′-vinylbenzophenone copolymer, 30421-95-5.

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Electronic Excited-State Transport and Trapping on Polymer Chains

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ABSTRACT: A theoretical analysis of incoherent transport and trapping of electronic excitations among chromophores on polymer chains is presented. The theory is applicable to macromolecules in viscous solution, to polymers dispersed in amorphous solid materials, and to bulk polymers. The chains are assumed to contain a small concentration of randomly placed donor and trap chromophores. A density expansion for the transport Green function is the basis of the theory. The approach is general, but calculations are performed for the special case of Förster transfer and ideal chains. Padé approximants for the Green function that include two- and three-particle correlations are constructed for this case. Various limits of these approximate solutions are discussed. Connections are made between the Green function and the observables in time-dependent and photostationary fluorescence depolarization experiments and also to the observables in transient and steady-state trap fluorescence experiments.

I. Introduction

The application of fluorescence techniques to the study of polymer structure and dynamics is an important branch of polymer physics.[1,2] Techniques that utilize electronic excitation transfer (EET), such as concentration fluorescence depolarization[3] and trapping by excimers,[4] are extremely sensitive probes of local segment density and motion. Until recently, however, the theoretical foundation for the many-body aspects of EET problems in noncrystalline materials had not been established.

The problem of incoherent excitation transfer in a homogeneous material containing stationary randomly distributed donor chromophores was formulated in the language of statistical mechanics by Haan and Zwanzig[5,6] and solved approximately by various methods,[5-9] including the graphical analysis of Gochanour, Andersen, and Fayer (GAF).[7] The GAF method was extended to the case of a two-component homogeneous mixture of randomly distributed donor and trap chromophores by Loring, Andersen, and Fayer (LAF).[10] In a recent paper[11] (hereafter referred to as paper I), we applied the GAF analysis to the case of transport among chromophores randomly distributed on a polymer chain. In this problem, unlike the problems mentioned above, there are correlations among the positions of the chromophores because they are attached to the backbone of the same polymer chain. Ediger and Fayer[12] have also addressed the EET problem in polymeric systems, using a different model for the chromophore statistics.

In paper I, we performed calculations for the special case of Förster transfer among chromophores distributed randomly on an isolated ideal Gaussian chain. We investigated three types of approximations to the Green function for excitation transfer: the self-consistent approximations used by GAF, cumulant approximants based on an expansion in powers of the density of chromophores, and Padê approximants based on the same density expansion. We found that for this problem, in which all excitation transfer is intramolecular, a certain Padê approximant, the three-particle Padê, provides an accurate and computationally feasible solution.

The analysis and results in paper I are applicable to an extremely dilute polymer solution. In this paper we extend the theory to the case of higher polymer concentrations and also to the case in which both donors and traps are present. We consider polymer chains that contain small concentrations of a single type of donor and a single type of trap chromophore randomly distributed along the contour of the chains. There are correlations among the positions of chromophores on the same chain, but for simplicity we assume there are no correlations between the positions of chromophores on different chains. In addition, it is assumed that excitations can be transferred from donor to donor and donor to trap, but the trapping step is taken to be irreversible.

For such a system and Förster transfer, the three-particle Padê should be an accurate approximation to the Green function for the following reasons. In the limit where excitation transfer is predominantly intramolecular (which corresponds to the limit of low polymer concentration and/or flexible chains), the problem is equivalent to that of the isolated chains considered in paper I. We have demonstrated that the three-particle Padê is accurate in this regime.[11] In the limit where the excitation transfer is predominantly intermolecular, the intramolecular correlations are irrelevant and the problem becomes physically equivalent to that of a homogeneous solution of randomly placed chromophores. The three-particle Padê is also accurate in this limit.[13] Since it works well in both limits, we expect that the three-particle Padê will be adequate for the intermediate case in which intramolecular and intermolecular transfer are competitive.

II. Transport Dynamics and the Green Function

The theory presented in this section is limited to the transport of incoherent excitations, and chromophore diffusion is assumed to be negligible. No assumptions are made about the density of the material, however, so the theory should be equally applicable to homogeneous melts, amorphous solids, and viscous macromolecular solutions. The theory makes use of an expansion of the Green function in powers of the density, and thus it might appear that the theory is not valid for concentrated solutions and melts. However, the relevant expansion parameter is actually the density of chromophores, not the density of matter, and we assume that the chromophores constitute only a small fraction of the total material present.

To derive an expression for the transport Green function, we adopt the approach of LAF. The polymeric system being considered contains stationary donor and trap chromophores. Initially, it is assumed that the excitation transfer rates between two donor chromophores, w_{jk}, and between a donor chromophore and a trap chromophore, v_{jl}, depend only on interchromophore separation

$$w_{jk} = w(|\mathbf{r}_j - \mathbf{r}_k|)$$
$$v_{jl} = v(|\mathbf{r}_j - \mathbf{r}_l|) \tag{2.1}$$

The donor–donor transfer rate is taken to be symmetric, and w_{jj} is defined to be zero. Furthermore, transfer of excitations from trap to donor or trap to trap is forbidden in this transport model.

As in the theory of GAF and LAF, we can omit consideration of fluorescence deexcitation in the solution of the energy-transfer problem. Section IV discusses the generalization of the result to incorporate finite lifetimes for both excited species. We assume that only the donors can absorb radiation and that the subsequent migration of the excitation is governed by a Pauli master equation. The solution of this equation, averaged over all configurations of the chromophores, is described by a Green function $G(\mathbf{r},t)$ that can be expressed as a sum of three parts[10]

$$G(\mathbf{r},t) = G^{\mathrm{S}}(t)\delta(\mathbf{r}) + G^{\mathrm{M}}(\mathbf{r},t) + G^{\mathrm{T}}(\mathbf{r},t) \tag{2.2}$$

$G^{\mathrm{S}}(t)$ is the probability that an excitation created at time 0 is at time t on the donor chromophore where it originated. $G^{\mathrm{M}}(\mathbf{r},t)$ is related to the probability that it is at time t on another donor chromophore a distance $\mathbf{r}$ away. $G^{\mathrm{T}}(\mathbf{r},t)$ is related to the probability that at time t the excitation is on a trap a distance $\mathbf{r}$ away. In the present paper we restrict our attention to calculating the time dependence of donor and trap fluorescence and are not concerned with the distance dependence of the transport. Thus, we define

$$G^{\mathrm{M}}(t) = \int \mathrm{d}\mathbf{r}\; G^{\mathrm{M}}(\mathbf{r},t)$$
$$G^{\mathrm{T}}(t) = \int \mathrm{d}\mathbf{r}\; G^{\mathrm{T}}(\mathbf{r},t)$$
$$G^{\mathrm{D}}(t) = G^{\mathrm{S}}(t) + G^{\mathrm{M}}(t) \tag{2.3}$$

$G^{\mathrm{D}}(t)$ is the total probability that an excitation is on a donor at a time t after absorption of the photon and is related to the time dependence of the intensity of donor fluorescence. Similarly, $G^{\mathrm{T}}(t)$ is the total probability that an excitation is on a trap at a time t after absorption of the photon and is related to the time dependence of trap fluorescence. $G^{\mathrm{S}}(t)$ is related to the time dependence of the polarization of donor fluorescence. Since the total amount of excitation is conserved in the absence of fluorescence and other decay processes, these various parts of the Green function satisfy

$$G^{\mathrm{D}}(t) + G^{\mathrm{T}}(t) = 1 \tag{2.4}$$

at all times. The Laplace transforms of these functions will be denoted $\hat{G}^{\mathrm{S}}(\epsilon)$, $\hat{G}^{\mathrm{M}}(\epsilon)$, $\hat{G}^{\mathrm{D}}(\epsilon)$, and $\hat{G}^{\mathrm{T}}(\epsilon)$, where ϵ is the Laplace transform variable.

The approach taken by GAF, by LAF, and in paper I was to expand the Green function in a perturbation series in powers of the transfer rate. The terms in this perturbation expansion were represented as diagrams. Haan and Zwanzig[5,6] derived a density expansion for the Green function, and GAF and LAF identified the nth term in the density expansion with the sum of all perturbation series diagrams involving $n + 1$ sites. In paper I we used the fact that the diagrams for the polymeric problem had the same topological structure as the diagrams of GAF. This allowed us to use the density expansion for the homogeneous problem with only slight modifications to account for polymer statistics. For the present problem our diagrams are structurally identical with those of LAF, so we can immediately write down the corresponding polymeric density expansion from their results.

For the polymeric system described in section I, all the time-dependent and photostationary fluorescence observables can be obtained from the two functions $\hat{G}^{\mathrm{S}}(\epsilon)$ and $\hat{G}^{\mathrm{D}}(\epsilon)$. Equations 2.3 and 2.4, however, allow us to obtain approximations for $\hat{G}^{\mathrm{S}}(\epsilon)$ and $\hat{G}^{\mathrm{D}}(\epsilon)$ from corresponding approximations for $\hat{G}^{\mathrm{M}}(\epsilon)$ and $\hat{G}^{\mathrm{T}}(\epsilon)$. By modifying the expressions of LAF to incorporate the present polymer statistics, we obtain the sum of all perturbation series diagrams in the expansions of $\hat{G}^{\mathrm{M}}(\epsilon)$ and $\hat{G}^{\mathrm{T}}(\epsilon)$ that include all possible excitation transfers within clusters of two and three chromophores.

$$\begin{aligned}\epsilon\hat{G}^{\mathrm{M}}(\epsilon) = {} & \int \mathrm{d}\mathbf{r}_{12}\ [q_{\mathrm{D}}g_2(\mathbf{r}_{12}) + \rho_{\mathrm{D}}]\left[\frac{w_{12}}{\epsilon + 2w_{12}}\right] + \\ & \int \mathrm{d}\mathbf{r}_{12}\int \mathrm{d}\mathbf{r}_{13}\ \{q_{\mathrm{D}}{}^2g_3(\mathbf{r}_{12},\mathbf{r}_{13}) + \\ & \rho_{\mathrm{D}}{}^2 + q_{\mathrm{D}}\rho_{\mathrm{D}}[g_2(\mathbf{r}_{12}) + g_2(\mathbf{r}_{13}) + g_2(\mathbf{r}_{23})]\} \times \\ & \left\{\frac{-w_{12}}{\epsilon + 2w_{12}} + (\epsilon w_{12} + w_{12}w_{13} + w_{12}w_{23} + w_{13}w_{23})/[\epsilon^2 + \right. \\ & \left. 2\epsilon(w_{12} + w_{13} + w_{23}) + 3(w_{12}w_{13} + w_{12}w_{23} + w_{13}w_{23})]\right\} \\ & + \int \mathrm{d}\mathbf{r}_{12}\int \mathrm{d}\mathbf{r}_{13}\ \{q_{\mathrm{D}}q_{\mathrm{T}}g_3(\mathbf{r}_{12},\mathbf{r}_{13}) + \\ & \rho_{\mathrm{D}}\rho_{\mathrm{T}} + \rho_{\mathrm{D}}q_{\mathrm{T}}[g_2(\mathbf{r}_{12}) + g_2(\mathbf{r}_{13}) + g_2(\mathbf{r}_{23})]\} \times \\ & \left\{\frac{\epsilon w_{12}}{(\epsilon + w_{12} + v_{31})(\epsilon + w_{12} + v_{32}) - w_{12}{}^2} - \frac{w_{12}}{\epsilon + 2w_{12}}\right\} + \ldots\end{aligned} \tag{2.5}$$

$$\begin{aligned}\epsilon\hat{G}^{\mathrm{T}}(\epsilon) = {} & \int \mathrm{d}\mathbf{r}_{12}\ [q_{\mathrm{T}}g_2(\mathbf{r}_{12}) + \rho_{\mathrm{T}}]\left[\frac{v_{12}}{\epsilon + v_{12}}\right] + \\ & \int \mathrm{d}\mathbf{r}_{12}\int \mathrm{d}\mathbf{r}_{13}\ \{q_{\mathrm{D}}q_{\mathrm{T}}g_3(\mathbf{r}_{12},\mathbf{r}_{13}) + \\ & \rho_{\mathrm{D}}\rho_{\mathrm{T}} + \rho_{\mathrm{D}}q_{\mathrm{T}}[g_2(\mathbf{r}_{12}) + g_2(\mathbf{r}_{13}) + g_2(\mathbf{r}_{23})]\} \times \\ & \left\{\frac{v_{32}w_{12} + v_{31}(\epsilon + w_{12} + v_{32})}{(\epsilon + w_{12} + v_{31})(\epsilon + w_{12} + v_{32}) - w_{12}{}^2} - \frac{v_{31}}{\epsilon + v_{31}}\right\} - \\ & \int \mathrm{d}\mathbf{r}_{12}\int \mathrm{d}\mathbf{r}_{13}\ \{q_{\mathrm{T}}{}^2g_3(\mathbf{r}_{12},\mathbf{r}_{13}) + \rho_{\mathrm{T}}{}^2 + \rho_{\mathrm{T}}q_{\mathrm{T}}[g_2(\mathbf{r}_{12}) + \\ & g_2(\mathbf{r}_{13}) + g_2(\mathbf{r}_{23})]\}\left\{\frac{v_{21}v_{31}}{(\epsilon + v_{21})(\epsilon + v_{21} + v_{31})}\right\} + \ldots\end{aligned} \tag{2.6}$$

In eq 2.5 and 2.6, q_{D} and q_{T} are defined as the average number of donor and trap chromophores, respectively, per statistical segment[14,15] of the polymer. The quantities ρ_{D} and ρ_{T} are the bulk number densities of donors and traps, and $g_2(\mathbf{r}_{12})$ and $g_3(\mathbf{r}_{12},\mathbf{r}_{13})$ are two- and three-particle intrachain correlation functions defined by[11]

$$g_2(\mathbf{r}_{12}) = \frac{1}{N}\sum\sum\Phi_{ij}^{[1]}(\mathbf{r}_{12}), \qquad i \neq j \tag{2.7}$$

$$g_3(\mathbf{r}_{12},\mathbf{r}_{13}) = \frac{1}{N}\sum\sum\sum\Phi_{ijik}^{[2]}(\mathbf{r}_{12},\mathbf{r}_{13}), \qquad i \neq j \neq k \tag{2.8}$$

The total number of segments per chain is given by N, and $\Phi_{ijkl}^{[t]}\ldots(\mathbf{r}_{ij},\mathbf{r}_{kl},\ldots)$ is a reduced distribution function for t intramolecular relative distances between segments.

III. Calculations for Infinite Chains with Ideal Statistics and the Förster Rate

In paper I we presented arguments that the polymeric systems of primary experimental interest are dilute in chromophores and satisfy

$$q_{\mathrm{D}},\ q_{\mathrm{T}} \ll 1 \tag{3.1}$$

It was also discussed that for such a system the lattice sums in eq 2.7 and 2.8 can be replaced by integrals over a continuous chain contour. For ideal, Gaussian statistics[14,15] and infinite chains we obtained the following expressions for the correlation functions[11]

$$g_2(\mathbf{r}_{12}) = 3/\pi a^2 r_{12} \tag{3.2}$$

$$g_3(\mathbf{r}_{12},\mathbf{r}_{13}) = \left[\frac{3}{2^{1/2}\pi a^2}\right]^2\left(\frac{1}{r_{12}r_{13}} + \frac{1}{r_{12}r_{23}} + \frac{1}{r_{13}r_{23}}\right) \tag{3.3}$$

Equation 3.2 is the well-known Debye pair correlation function.[15] In eq 3.2 and 3.3, a represents the effective statistical segment length.[14]

The integrals required in eq 2.5 and 2.6 have been evaluated by using eq 3.2, eq 3.3, and the isotropic Förster rate[10,16]

$$w(r) = \tau^{-1}(R_0{}^{\mathrm{DD}}/r)^6 \tag{3.4}$$

$$v(r) = \tau^{-1}(R_0{}^{\mathrm{DT}}/r)^6 \tag{3.5}$$

$R_0{}^{\mathrm{DD}}$ is the interchromophore separation where the donor–donor transfer rate is τ^{-1}, and $R_0{}^{\mathrm{DT}}$ is defined as the separation at which the donor–trap rate is τ^{-1}. The measured lifetime of the excitation on an isolated donor chromophore is $\tau = \tau_{\mathrm{D}}$. Evaluation of eq 2.5 and 2.6 involved both numerical and analytical quadrature. Portions of the integrals had been previously obtained by Haan,[6] GAF, LAF and in paper I. Our results can be written in the form of density expansions for $\hat{G}^{\mathrm{M}}(\epsilon)$ and $\hat{G}^{\mathrm{T}}(\epsilon)$

$$\begin{aligned}\epsilon\hat{G}^{\mathrm{M}}(\epsilon) = {} & 1.4548\bar{c}_{\mathrm{D}}(\epsilon\tau)^{-1/3} + 1.1107c_{\mathrm{D}}(\epsilon\tau)^{-1/2} - \\ & 1.6988\bar{c}_{\mathrm{D}}{}^2(\epsilon\tau)^{-2/3} - \alpha_1(\varkappa)\bar{c}_{\mathrm{D}}\bar{c}_{\mathrm{T}}(\epsilon\tau)^{-2/3} - \\ & 2.7513c_{\mathrm{D}}\bar{c}_{\mathrm{D}}(\epsilon\tau)^{-5/6} - \alpha_3(\varkappa)c_{\mathrm{D}}\bar{c}_{\mathrm{T}}(\epsilon\tau)^{-5/6} - \\ & 0.80555c_{\mathrm{D}}{}^2(\epsilon\tau)^{-1} - \alpha_2(\varkappa)c_{\mathrm{D}}c_{\mathrm{T}}(\epsilon\tau)^{-1} + \mathcal{O}(c^3)\end{aligned} \tag{3.6}$$

$$\begin{aligned}\epsilon\hat{G}^{\mathrm{T}}(\epsilon) = {} & 2.3094\bar{c}_{\mathrm{T}}(\epsilon\tau)^{-1/3} + 1.5708c_{\mathrm{T}}(\epsilon\tau)^{-1/2} - \\ & 3.9364\bar{c}_{\mathrm{T}}{}^2(\epsilon\tau)^{-2/3} + \alpha_4(\varkappa)\bar{c}_{\mathrm{D}}\bar{c}_{\mathrm{T}}(\epsilon\tau)^{-2/3} - \\ & 5.8803c_{\mathrm{T}}\bar{c}_{\mathrm{T}}(\epsilon\tau)^{-5/6} + \alpha_6(\varkappa)c_{\mathrm{D}}\bar{c}_{\mathrm{T}}(\epsilon\tau)^{-5/6} - \\ & 1.5708c_{\mathrm{T}}{}^2(\epsilon\tau)^{-1} + \alpha_5(\varkappa)c_{\mathrm{D}}c_{\mathrm{T}}(\epsilon\tau)^{-1} + \mathcal{O}(c^3)\end{aligned} \tag{3.7}$$

where the dimensionless intramolecular chromophore concentrations are defined by

$$\bar{c}_{\mathrm{D}} = \pi q_{\mathrm{D}}(R_0{}^{\mathrm{DD}}/a)^2 \tag{3.8}$$

$$\bar{c}_{\mathrm{T}} = \pi q_{\mathrm{T}}(R_0{}^{\mathrm{DT}}/a)^2 \tag{3.9}$$

and the dimensionless bulk chromophore concentrations are defined as in LAF

$$c_{\mathrm{D}} = (4\pi/3)(R_0{}^{\mathrm{DD}})^3\rho_{\mathrm{D}} \tag{3.10}$$

$$c_{\mathrm{T}} = (4\pi/3)(R_0{}^{\mathrm{DT}})^3\rho_{\mathrm{T}} \tag{3.11}$$

The four dimensionless concentrations are not independent and are related by

$$\bar{c}_{\mathrm{D}}c_{\mathrm{T}} = \varkappa\bar{c}_{\mathrm{T}}c_{\mathrm{D}} \tag{3.12}$$

with

$$\varkappa = R_0{}^{\mathrm{DT}}/R_0{}^{\mathrm{DD}} \tag{3.13}$$

The quantities $\alpha_1(\varkappa), \alpha_2(\varkappa), \ldots, \alpha_6(\varkappa)$ are numerical integrals that depend on the ratio of the Förster radii and are tabulated in Table I. $\alpha_2(\varkappa)$ and $\alpha_5(\varkappa)$ are related to the numerical integrals α and β of LAF by

$$\alpha_2(\varkappa) = 3.0002 - \alpha(\varkappa) \tag{3.14}$$

$$\alpha_5(\varkappa) = 1.1184 - \beta(\varkappa) \tag{3.15}$$

We have used eq 3.12 to eliminate the $\bar{c}_{\mathrm{D}}c_{\mathrm{T}}$ terms in eq 3.6 and 3.7. The $\mathcal{O}(c^3)$ corrections in these equations arise from excitation transfer within all possible clusters of four chromophores (donors and traps).

Density expansions for $\hat{G}^{\mathrm{S}}(\epsilon)$ and $\hat{G}^{\mathrm{D}}(\epsilon)$ are obtained by substituting eq 3.6 and 3.7 into the Laplace transform of eq 2.3 and 2.4. The class of Padé approximants that was formulated by Haan[6] and utilized in paper I can be obtained by reexpressing the density expansions of these two functions as expansions of $[\epsilon\hat{G}^{\mathrm{S}}(\epsilon)]^{-1}$ and $[\epsilon\hat{G}^{\mathrm{D}}(\epsilon)]^{-1}$ in powers of the four dimensionless concentrations. This particular Padé is suggested by the formal structure of the Green function.[6,11] The n-particle Padé approximant is

Table I
Numerically Evaluated Integrals Required in Eq 3.6, 3.7, 3.16, and 3.17

$\varkappa$	$\alpha_1(\varkappa)$	$\alpha_2(\varkappa)$	$\alpha_3(\varkappa)$	$\alpha_4(\varkappa)$	$\alpha_5(\varkappa)$	$\alpha_6(\varkappa)$
0.10	6.1293	2.9994	5.3676	3.3723	1.1168	2.5751
0.50	6.4982	2.9208	7.8480	2.7701	0.9614	3.1075
1.0	5.9619	2.7611	9.5781	1.3854	0.5885	2.2699
5.0	4.3858	2.6365	19.908	0.0688	0.0518	0.3651
10.0	4.1038	2.6342	33.365	0.0167	0.0067	0.1579

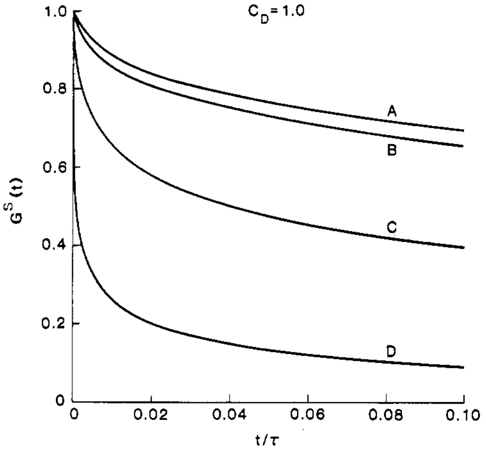

Figure 1. Inverse Laplace transform of $\hat{G}^S(\epsilon)$ as a function of chain stiffness. In all curves, $c_D = 1.0$. Curves A, B, C, and D correspond to $\bar{c}_D = 0.01$, 0.10, 1.0, and 5.0, respectively.

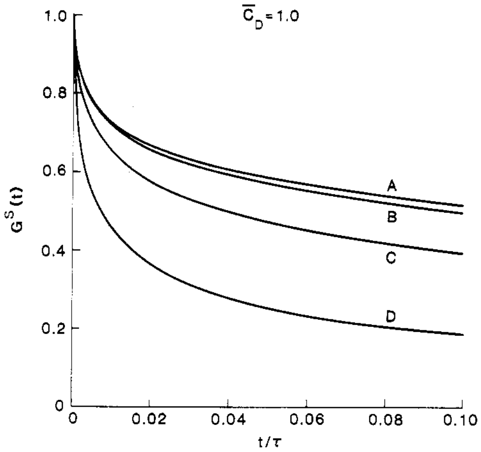

Figure 2. Inverse Laplace transform of $\hat{G}^S(\epsilon)$ as a function of the density of chains. In all curves, $\bar{c}_D = 1.0$. Curves A, B, C, and D correspond to $c_D = 0.01$, 0.10, 1.0, and 5.0, respectively.

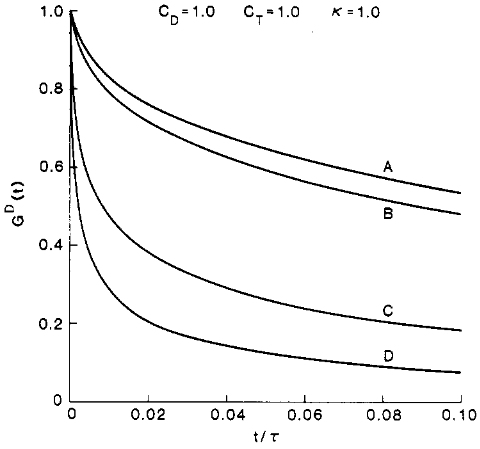

Figure 3. Inverse Laplace transform of $\hat{G}^D(\epsilon)$ as a function of chain stiffness. In all curves, $c_D = c_T = \varkappa = 1.0$. Curves A, B, C, and D correspond to $\bar{c}_D = \bar{c}_T = 0.01$, 0.1, 1.0, and 2.0, respectively.

defined as containing all terms in the expansions of $[\epsilon\hat{G}^S(\epsilon)]^{-1}$ and $[\epsilon\hat{G}^D(\epsilon)]^{-1}$ that have powers of c_D, $\bar{c}_D$, c_T, and $\bar{c}_T$ of total order $n - 1$. The highest order approximant that can be constructed from eq 3.6 and 3.7 with eq 2.3 and 2.4 is the desired three-particle Padé, which was discussed in section I. The three-particle approximants for $\hat{G}^S(\epsilon)$ and $\hat{G}^D(\epsilon)$ are given by

$$\begin{aligned}\hat{G}^S(\epsilon) = \epsilon^{-1}\{1 + [2.309\bar{c}_T + 1.455\bar{c}_D](\epsilon\tau)^{-1/3} + \\ [1.571c_T + 1.111c_D](\epsilon\tau)^{-1/2} + [1.397\bar{c}_T^2 + 0.4176\bar{c}_D^2 + \\ (6.719 + \alpha_4(\varkappa) - \alpha_1(\varkappa))\bar{c}_D\bar{c}_T](\epsilon\tau)^{-2/3} + \\ [1.375\bar{c}_Tc_T + (5.130 + \alpha_6(\varkappa) - \alpha_3(\varkappa))\bar{c}_Tc_D + \\ 4.570\bar{c}_Dc_T + 0.4804\bar{c}_Dc_D](\epsilon\tau)^{-5/6} + [0.8966c_T^2 + \\ 0.4281c_D^2 + (3.489 + \alpha_5(\kappa) - \alpha_2(\kappa))c_Tc_D](\epsilon\tau)^{-1}\}^{-1}\end{aligned} \quad (3.16)$$

$$\begin{aligned}\hat{G}^D(\epsilon) = \epsilon^{-1}\{1 + 2.309\bar{c}_T(\epsilon\tau)^{-1/3} + 1.571c_T(\epsilon\tau)^{-1/2} + \\ [1.397\bar{c}_T^2 + \alpha_4(\varkappa)\bar{c}_T\bar{c}_D](\epsilon\tau)^{-2/3} + [1.375\bar{c}_Tc_T + \\ \alpha_6(\varkappa)\bar{c}_Tc_D](\epsilon\tau)^{-5/6} + [0.8966c_T^2 + \alpha_5(\varkappa)c_Tc_D](\epsilon\tau)^{-1}\}^{-1}\end{aligned} \quad (3.17)$$

Figures 1 and 2 show the time dependence of $G^S(t)$ for a polymeric system containing a single type of chromophore (i.e., all donors). These results were obtained by using eq 3.16 with $\bar{c}_T = c_T = 0$ and the Stehfest algorithm[17] for numerical inversion of the Laplace transform. Figure 1 illustrates the effect of chain stiffness on the decay of $G^S(t)$. As the statistical segment length increases relative to R_0^{DD}, the chain becomes stiff and expanded, $\bar{c}_D$ decreases, and the decay of the initial site excitation probability, $G^S(t)$, is slower. Figure 2 demonstrates the importance of intermolecular transport. Increasing c_D at fixed $\bar{c}_D$ corresponds to increasing the density of chains. Comparison of the two figures indicates that the effects of intermolecular and intramolecular transport on the decay of $G^S(t)$ are comparable when $c_D^2 \sim \bar{c}_D^3$.

In the absence of traps, two limits of eq 3.16 are of particular interest. First we consider the dilute case, $c_D << \bar{c}_D$. In this limit we retrieve the three-particle Padé approximant for $\hat{G}^S(\epsilon)$ that was derived in paper I for an isolated chain. $G^S(t)$ is a universal function of the *single* variable $\bar{c}_D^3t/\tau$ in this regime. The opposite limit, $\bar{c}_D << c_D$, is achieved by maintaining a high density of chains, or by increasing the statistical segment length, a. Equation 3.16 (with $\bar{c}_T = c_T = 0$) is identical with the three-particle Padé of Haan[6] in this limit, and $G^S(t)$ is a universal function of c_D^2t/τ. Ediger and Fayer[13] have shown that this Padé is an excellent approximation to the GAF three-body self-consistent result.

Figures 3 and 4 illustrate the time dependence of $G^D(t)$, the inverse Laplace transform[17] of eq 3.17, for a polymeric system containing both donor and trap chromophores. As before, increasing chain stiffness leads to a slower decay of the donor excitation probability, $G^D(t)$, while increasing the bulk density of chromophores enhances its decay.

A special case of the general transport and trapping result, eq 3.17, is obtained when $q_D << q_T << 1$. This problem can be treated as direct excitation transfer from an isolated donor to an ensemble of surrounding traps and is often referred to as the direct-trapping problem. Two limiting cases are again of interest. In the isolated-chain

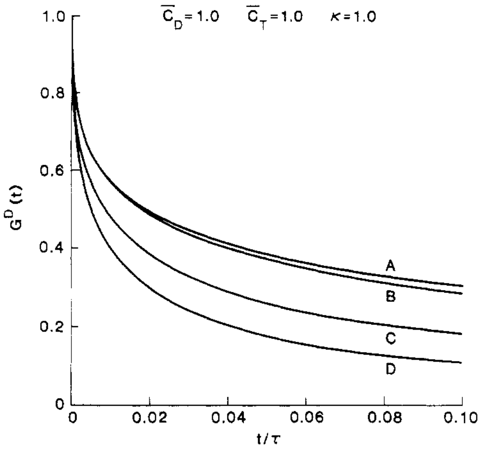

Figure 4. Inverse Laplace transform of $\hat{G}^D(\epsilon)$ as a function of the density of chains. In all curves, $\bar{c}_D = \bar{c}_T = \varkappa = 1.0$. Curves A, B, C, and D correspond to $c_D = c_T = 0.01$, 0.1, 1.0, and 2.0, respectively.

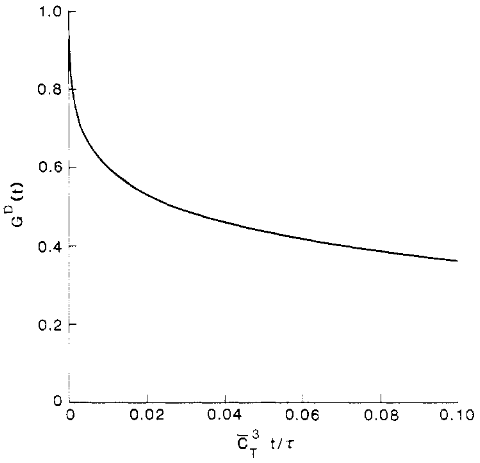

Figure 5. Inverse Laplace transform of $\hat{G}^D(\epsilon)$ in the intramolecular, direct-trapping limit, $q_D << q_T << 1$, $c_T << \bar{c}_T$.

limit, $c_T << \bar{c}_T$, excitations initially on the small donor population are transferred directly to traps residing on the same chain. For this case $G^D(t)$ is a function of the single variable $\bar{c}_T{}^3t/\tau$. A universal curve for $G^D(\bar{c}_T{}^3t/\tau)$ is shown in Figure 5. In the high-density regime, $\bar{c}_T << c_T$, excitations are transferred directly to traps residing on different chains. This limit corresponds to the classical Förster result for direct transfer to randomly distributed traps and has an analytical solution[18]

$$G^D(t) = \exp(-[\pi c_T{}^2t/\tau]^{1/2}) \qquad (3.18)$$

In Figure 6 we have plotted the exact result, eq 3.18, and the $q_D << q_T << 1$, $\bar{c}_T << c_T$ limit of eq 3.17 as universal functions of $c_T{}^2t/\tau$, the appropriate dimensionless time for this problem. The three-particle Padé is seen to be very accurate in this concentration regime.

In this section approximate expressions for the Green function have been developed that are both accurate and computationally practical. At this point we turn to consider the relationship between the Green function and experimental transient and photostationary fluorescence observables.

IV. Connections with Experimental Observables

For rigid polymeric systems, such as blends or glasses, the chromophores are not free to rotate on the time scale of a fluorescence experiment. As a result, the orientation-dependent Förster rate, rather than the orientation-averaged rates of eq 2.1, 3.4, and 3.5, should be used. As discussed previously,[11,19,20] the correct results for this case can be obtained from the expressions in eq 3.16 and 3.17 by the replacement

$$\begin{aligned} \bar{c}_D &\to \gamma_2\bar{c}_D \\ \bar{c}_T &\to \gamma_2\bar{c}_T \\ c_D &\to \gamma_3c_D \\ c_T &\to \gamma_3c_T \end{aligned} \qquad (4.1)$$

where γ_2 and γ_3 are given by[19]

$$\begin{aligned} \gamma_2 &= 0.8468 \\ \gamma_3 &= 0.8452 \end{aligned} \qquad (4.2)$$

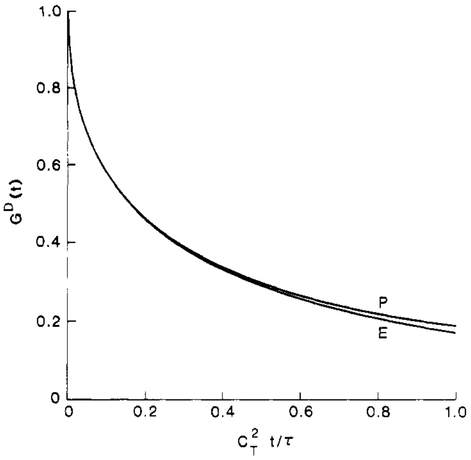

Figure 6. Inverse Laplace transform of $\hat{G}^D(\epsilon)$ in the intermolecular, direct-trapping limit, $q_D << q_T << 1$, $\bar{c}_T << c_T$. The universal curves in the figure are the exact analytical solution derived by Förster (eq 3.18), labeled E, and the three-particle Padé approximant in this limit, labeled P.

For fluorescence depolarization experiments on systems with no traps, the relationship between $G^S(t)$ and the observables is the same as that discussed in paper I, provided the substitutions mentioned above are made. See eq 59–63 of paper I.

In a time-resolved trapping experiment, the observer has the option to monitor the decay of the donor fluorescence intensity, the rise and decay of the trap fluorescence intensity, or both. LAF have shown that the donor and trap fluorescence observables can be easily calculated from $\hat{G}^D(\epsilon)$. If $N^T(t)$ represents the probability that an excitation is on a trap when the donor lifetime is $\tau_D = \tau$ and the trap lifetime is τ_T, then the Laplace transform of $N^T(t)$ is given by[10]

$$\hat{N}^T(\epsilon) = [1 - (\epsilon + \tau_D{}^{-1})\hat{G}^D(\epsilon + \tau_D{}^{-1})]/[\epsilon + \tau_T{}^{-1}] \qquad (4.3)$$

The time-dependent donor and trap fluorescence intensities[19,21] are directly related to $G^D(t)$ and $N^T(t)$

$$i_D(t) = q_{FD}\tau_D{}^{-1}\exp(-t/\tau_D)G^D(t) \qquad (4.4)$$

$$i_T(t) = q_{FT}\tau_T{}^{-1}N^T(t) \qquad (4.5)$$

where q_{FD} and q_{FT} are the respective fluorescence quantum efficiencies of the donor and trap chromophores. The donor fluorescence intensity can be obtained through Laplace inversion[17] of eq 3.17, and the trap intensity results from inversion of eq 4.3 in conjunction with eq 3.17.

Photostationary fluorescence data are often expressed in terms of the ratio of integrated trap to donor fluorescence intensities. The ratio is given by[4,19,21]

$$\frac{I_T}{I_D} = \frac{q_{FT}}{q_{FD}}\left[\frac{\chi}{1-\chi}\right] \qquad (4.6)$$

where χ is the trapping efficiency and is related to $\hat{G}^{D}(\epsilon)$ by

$$\chi = 1 - \tau^{-1}\hat{G}^{D}(\tau^{-1}) \tag{4.7}$$

Equation 3.17 provides an explicit expression for the trapping efficiency. We emphasize that the changes described in eq 4.1 must be made before eq 3.17 is used for rigid polymeric systems. In nonviscous macromolecular solutions containing donors and traps, the results of section III for the orientation-averaged Förster rate may be more appropriate.

V. Discussion and Conclusions

The fluorescence observables for a polymeric material with donor and trap chromophores can provide information about the structure of the material. The observables depend on two types of properties. The first, which includes the concentration of polymer molecules and the number of chromophores per monomeric unit, are quantities that are, in principle, under the control of the experimenter. The second are microscopic properties that are not under experimental control, such as the Förster radii, the fluorescence lifetimes, quantum efficiencies of fluorescence, and the Gaussian segment length. Fluorescence experiments will be most powerful if this second class of properties is insensitive to the first class, which is likely to be the case at sufficiently small chromophore concentrations. This would permit a set of experiments on a series of prepared samples to be used to extract the values of many or all of the second class of microscopic properties.

The theory presented here can be useful even if such a set of experiments cannot be performed. If some of the microscopic properties are known from other experiments or can be estimated, then fluorescence experiments can give a way of measuring the others. For example, if the fluorescence and excitation transfer properties of the chromophores are known, the experiments can provide a value of Flory's characteristic ratio, C_{∞}, which is a measure of the chain stiffness.

The results derived here were obtained by assuming that the polymeric material is homogeneous, that the chains are ideal, and that the transfer rate is of the Förster r^{-6} form. Thus, the theory can provide a starting point for detecting deviations from homogeneity, ideal chain behavior, and Förster transfer. The theory can also be extended to include such deviations. It may be possible to apply the analysis to the study of polymeric materials undergoing phase separation.

Acknowledgment. We thank R. F. Loring for several informative discussions. This work was supported by the National Science Foundation (Grant CHE 81-07165) (H.C.A.) and by the NSF–MRL program, administered by the Center for Materials Research at Stanford University (G.H.F. and C.W.F.). In addition, G.H.F. thanks Exxon for a teaching fellowship.

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