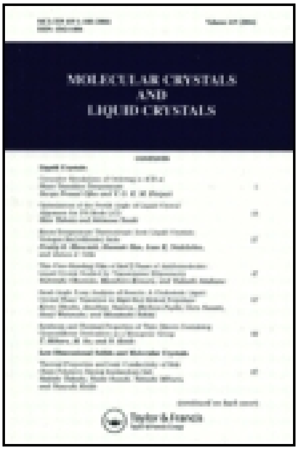

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Theory of Electronic Excitation Transfer in Polymer Micelles and Lamellae

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THEORY OF ELECTRONIC EXCITATION TRANSFER IN POLYMER MICELLES AND LAMELLAE

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Abstract We have developed a theoretical description of energy-transfer between chromophores in various geometries which correspond to actual configurations of polymers in a variety of materials. These include micelles with chromophores in the core or in the corona, such as one might obtain with a diblock copolymer in which chromophores are incorporated in one block, micelles with chromophores at the surface or at the interface between blocks, lamellae, and balls. The distribution of chromophores in this model can be random or described by a variety of functions to investigate situations such as the packing of diblocks at the interface between two homopolymeric phases and the expansion, contraction, or redistribution of micelle coronae which often accompanies changes in solvent characteristics. The calculated quantity, $G^S(t)$, is the probability of finding an initially excited chromophore still in the excited state at time t, and is directly related to fluorescence depolarization. The behavior of $G^S(t)$ in the cases of chromophores randomly distributed in an infinite plane and on a sphere is compared with analytical expressions in closed form for $G^S(t)$ in those configurations; in the case of a ball, $G^S(t)$ is compared with a previously reported expression[4] for energy-transfer in that geometry, and exact agreement is obtained. The sensitivity of this method is explored by examining $G^S(t)$ as a function of the shape and volume of the chromophore distribution.

INTRODUCTION

Electronically excited chromophores can transfer excitation among themselves through nonradiative transition dipole - transition dipole interactions, as described by Förster[1]. This electronic excitation transport (EET) among chromophores has been modeled such that a calculable quantity, $G^S(t)$, emerges, which is readily compared with experimental observables. $G^S(t)$ is a configuration-averaged probability that an excitation is on an initially excited chromophore at time t, either because the excitation has not been transferred to another chromophore, or because it has been transferred away from and returned to the initially excited chromophore. In a system containing a small number of donors and a large number of molecules which accept an excitation from a donor and do not pass it on (called a donor-trap, or DT system), $G^S(t)e^{-t/\tau}$ (where τ is the donor fluorescence lifetime in the absence of traps), is simply equal to the donor fluorescence decay. In a system without traps, EET occurs among chromophores which will continually transfer excitations (called a donor-donor, or DD system). In that case, the experimenter can excite the chromophores with a polarized excitation beam, so that chromophores with a large projection of the light's $\bar{E}$-field along their absorption dipoles are selectively excited. The time-dependent loss of fluorescence polarization anisotropy due to EET is very well approximated by $G^S(t)$.

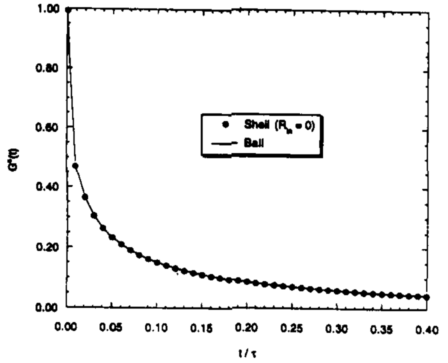
Huber[2] developed a cumulant expansion method for calculating $G^S(t)$ for EET among randomly distributed chromophores in an infinite volume. The expansion was truncated to first-order, such that only EET interactions between pairs of chromophores were considered. Baumann and Fayer[3] applied the theory to infinite one- and two-dimensional systems; Peterson and Fayer[4] extended the theory to random distributions of chromophores in restricted geometries, including a finite spherical volume and a volume with the Gaussian morphology of a polymer chain, and Marcus and Fayer[5] treated the problem of calculating $G^S(t)$ for EET between chromophores on a single sphere and on neighboring spheres. Here we present further development of this theory, enabling us to model EET among chromophores randomly and nonrandomly distributed in finite volumes having a variety of shapes. The model is shown to behave exactly as predicted in those cases for which closed-form analytical expressions describing EET are available.

RESULTS

$G^S(t)$ for Donor-Donor Transport in a Spherical Shell:

$$G^s(t) = \frac{3}{R_{out}^3 - R_{in}^3} \int_{R_{in}}^{R_{out}} e^{\frac{3(N-1)}{4(R_{out}^3 - R_{in}^3)} \int_0^{\pi} \int_{R_{in}}^{R_{out}} \left(e^{-\frac{2tR_0^6}{\tau(r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2)^3}} - 1\right) r_2^2 dr_2 \sin\theta_2 d\theta_2} r_1^2 dr_1, \qquad (1)$$

where R_{in} and R_{out} are the shell's inner and outer radii, respectively; N is the number of chromophores; t is time; R_0 is the Förster radius; τ is the fluorescence lifetime; r_1 and r_2 are the distances from the origin for the initially excited chromophore (1) and the chromophore to which the excitation is passed (2), respectively, and θ_1 and θ_2 are the angles between the sphere's *z*-axis and the radii pointing to chromophores 1 and 2, respectively.



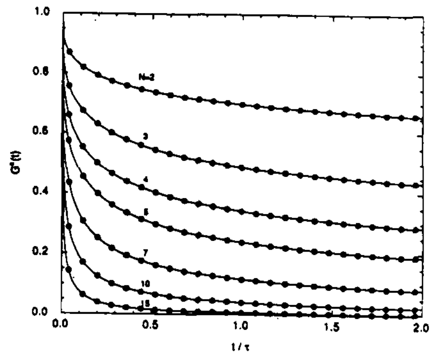
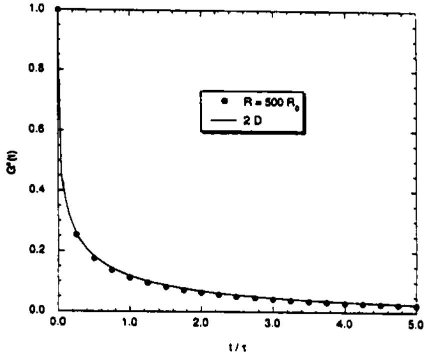


FIGURE 1 (left) Comparison of Eqn. 1 applied to chromophores randomly distributed in a ball, with Eqn. 9 from Peterson and Fayer[4].

FIGURE 2 (right) Comparison of Eqn. 1 applied to chromophores randomly distributed on a very thin spherical shell with Eqn. 4.6b from Marcus and Fayer[5].

Figure 1 compares the behavior of the expression for $G^S(t)$ in a spherical shell (Eqn. 1, filled circles) with that of Eqn. 9 in Peterson and Fayer[4] (line) for chromophores randomly distributed in a ball, where R_s is the radius of the ball. Here, $R_{in}=0$, $R_{out}=R_s=18.5$ Å, $R_0=12.3$Å, and N=30. The units of the *x*-axis are donor fluorescence lifetimes. This demonstrates that the changes made to the pre-existing expression for $G^S(t)$ do not make the expression less applicable to systems already studied. Figure 2 shows the behavior of Eqn. 1 when the inner and outer radii of the shell differ by 0.0001 Å, and R_0 is on the order of the shell radius. This approximates the situation in which chromophores are confined to a spherical surface, for which there is an analytical expression in closed form, Eqn. 4.6b in Marcus and Fayer[5]. Points calculated using that expression are represented by a line. The dots were generated using Eqn. 1. The radii of shell and sphere are 37Å; R_0 is 51.5Å. Numerical calculations of Eqn. 1 look like the exact solutions for $G^S(t)$ for chromophores randomly distributed on a sphere. Figure 3 shows how Eqn. 1 looks in the limit of an infinite plane. The plane is 0.0001Å thick, and R_1 and R_2 are 500 times R_0. This results in chromophores being extremely unlikely to transfer excitations through the core of the sphere, so that effectively, the chromophores only transfer among themselves in a plane. The dots were calculated with Eqn. 1; the line was calculated using Eqn. 4.6a in Marcus and Fayer[5], which was adapted from Baumann and Fayer[3]. Numerical calculations of Eqn. 1 very closely resemble the exact solutions for $G^S(t)$ in an infinite plane; the slight underestimate at shorter times may be due to rounding errors in the numerical calculation, or to the fact that Eqn. 1 is used in a finite geometry.



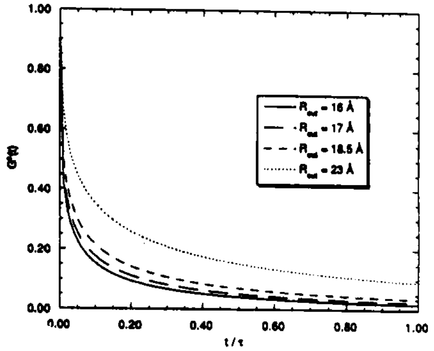


FIGURE 3 (left) Comparison of Eqn. 1 applied to chromophores randomly distributed on a very thin shell whose radius is large with respect to R_0 with an expression for EET in an infinite plane[3,5].

FIGURE 4 (right) Sensitivity of $G^S(t)$ to coronal swelling in micelles.

Figure 4 demonstrates that fluorescence anisotropy decays should change noticeably in an experimentally tractable system. Suppose we have micelles comprised of diblock copolymers in which one block is hydrophobic, and the other block is hydrophilic and bears chromophores. The micelles are formed in an aqueous solution. In this example, we look at the calculated fluorescence anisotropy decays from micelles with cores of 8 Å radius which have 30 2-vinyl naphthalene chromophores randomly packed in coronae which are 8 Å thick (solid line). If a change in solvent characteristics, such as addition of electrolytes, were to cause the coronae to swell by 1 Å in radius, the decay should look like the long-dashed line. Further swelling, to 2.5 Å, results in the dashed line, and swelling to 7 Å gives rise to the dotted line. In this case, we expect to be able to detect swelling of the coronae by about 2 Å. This method and model should allow us to study subtle changes in micellar structure.

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