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Photophysics of Polystyrene. 3. Trapping and Energy Migration via a Resonance Mechanism

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ABSTRACT: A theoretical model of excitation energy migration in aromatic polymers has been proposed. It has been assumed that the photophysics of polymers can be modeled as a one-dimensional system with the presence of excimers that can dissociate. In considerations, the resonance mechanism of excitation energy migration has been assumed, and respective equations for monomer and excimer fluorescence decay profiles have been obtained. A numerical analysis of monomer fluorescence decay profiles has been presented. The discussion of the numerical calculations in comparison with Monte Carlo simulations has shown that the resonance mechanism of energy migration in polystyrene is very likely to be responsible for its photophysics. A discussion of the origin of nonexponential decay profiles has been presented in connection to experimental studies of aromatic polymers.

I. Introduction

Recently, there has been a large effort devoted to the understanding of the photophysical properties of aromatic vinyl macromolecules.[1] An enormous amount of experimental work addressed the problem of energy migration and excimer formation in many polymers and copolymers. Those studies aimed at an increase of knowledge of electronic properties of polymers as well as at the study of the structural properties of polymers by use of energy transport and excimer formation. Although these experimental studies are very advanced, one can easily see the lack of sufficient theoretical studies of excitation transport in macromolecular systems.

From a photophysical point of view, there are two important topological factors that distinguish dilute solid or liquid solutions of macromolecules from solutions of small molecules that contain the same concentration of chromophoric groups. First of all, the chromophoric groups bonded to a macromolecule do not form a random set, but instead have spatial correlations that are determined by the conformation statistics of the real chain. These spatial correlations may be extracted from the conformational partition function expressed in the rotational isomeric state approximation, as reviewed by Flory.[2] Secondly, with the exception of infinite networks, a macromolecule is a spatially finite object, and a limited number of chromophores can be sampled by the excitation energy in intramolecular excitation transport.

A compilation of this structural complexity with excitation transport leads to well-known difficulties in the interpretation of transient and steady-state fluorescence data. Several phenomenological models have been proposed to explain a complex pattern of decay curves of monomer and excimer fluorescence from vinyl macromolecules.[3–7] Those models were limited to an explanation of multiexponential decay profiles. However, one has to remark that even in the simplest case of direct energy transfer, as has been shown by Förster, the decay of donor and acceptor fluorescence is nonexponential.[8] Several modifications of the mentioned models have been put forward by assuming a time-dependent rate coefficient for energy migration between chromophoric groups.[9–14]

A realistic conformation of a macromolecule has been taken into account in the Monte Carlo simulations of energy migration and trapping in polystyrene.[15,16] A polymer structure is also incorporated in the studies of Fredrickson, Andersen, and Frank (FAF)[17] and Fayer et al.[18,19] Using the theoretical methods developed for excitation transport in solutions of small molecules, FAF have analyzed excitation migration and transfer in macromolecular chains. It has been assumed that spatial correlations exist only between chromophores on the same chain; spatial correlations between chromophores on different chains are absent. In addition, it has also been assumed that the population of the trap is an irreversible process. Recently, the FAF model has been extended to the case of nonperfect traps (excimers) which can dissociate.[20] Similar theoretical methods have been applied for electronic excitation transport on isolated, flexible polymer chains with randomly tagged or end-tagged chromophores.[17–19]

There are many reports in which the authors successfully applied a one-dimensional random walk analysis to excitation transport in vinyl macromolecules.[21–23] Although this kind of analysis does not take into account the structural aspects of excitation transport, several important observations have been made. In order to develop a one-dimensional Markoffian random walk, the nearest-neighbor transfer with constant probability α has been assumed. Within the random walk theory it is very difficult to relate the probability α with electronic properties of the chromophores participating in migration of excitation. Therefore, this kind of analysis does not give an insight into the nature of the interactions responsible for energy migration. At the present moment, the problem of the nature of the interactions leading to energy migration in vinyl macromolecules has been undertaken in one paper only.[15] In the present paper, we shall develop a theoretical non-Markoffian model of a one-dimensional random walk on a polymer chain with randomly distributed chromophores, assuming nearest-neighbor jumps of excitation energy. We shall analyze the energy migration between chromophores by assuming a resonance interaction as well as an excimer dissociation.

II. Theoretical Model

It is commonly assumed that the process of energy transfer between a single donor–acceptor pair is described

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by the energy-transfer rate $k(R_i)$ in the form[24]

$$k(R_i) = 1/\tau_{0D}(R_0/R_i)^n \tag{2.1}$$

where τ_{0D} is the donor fluorescence lifetime in the absence of acceptor molecules, R_0 is the critical transfer radius for which $k = 1/\tau_{0D}$, and R_i is the position of the acceptor.

The energy-transfer rate, eq 2.1, has been derived for a single donor–acceptor pair. To calculate the decay function of donor fluorescence ($\Phi_D(t)$), one has to calculate the time- and concentration-dependent ensemble-averaged decay. This problem has been a subject of many papers of which results can be summarized as follows:[25]

$$\Phi_D(t) = \exp\{-t/\tau_{0D} - \gamma_\Delta\gamma_{DA}\Gamma(1 - \Delta/n)(t/\tau_{0D})^{\Delta/n}\} \tag{2.2}$$

where $\Delta = 1,2,3$ is the dimensionality of the space, $\Gamma(x)$ is the gamma function, γ_Δ is the orientational factor, and γ_{DA} is a dimensionless trap concentration for a number density of trap chromophores and where ρ_{DA} in Δ dimensions is defined by

$$\gamma_{DA} = V_\Delta(R_0^{DA})^\Delta\rho_{DA} \tag{2.3}$$

where V_Δ is the volume of the unit sphere in Δ dimensions.

Recently, we have shown[26-28] that in order to calculate the decay function of donor fluorescence in the presence of energy migration and transfer, one has to know the rate coefficient $k(t)$ for those processes. Defining the rate coefficient by the relation

$$k(t) = -\mathrm{d}\{\ln[\exp(-t/\tau_{0D})\Phi(t)]\}/\mathrm{d}t \tag{2.4}$$

one can obtain the following rate coefficients for energy migration ($k_{DD}(t)$) and for energy transfer ($k_{DA}(t)$):

$$k_{DD}(t) = (\Delta/n)\gamma_\Delta\gamma_{DD}\tau_{0D}^{-\Delta/n}\Gamma(1 - \Delta/n)t^{\Delta/n-1} \tag{2.5}$$

$$k_{DA}(t) = (\Delta/n)\gamma_\Delta\gamma_{DA}\tau_{0D}^{-\Delta/n}\Gamma(1 - \Delta/n)t^{\Delta/n-1} \tag{2.6}$$

Equation 2.2 describes the donor fluorescence decay for the resonance multipolar one-step energy transfer, i.e., under the assumption that $\gamma_{DD} \ll \gamma_{DA}$. It is obvious that this relation is not fulfilled in the case of vinyl macromolecules, where the concentration of excimer sites is very small ($\gamma_{DD} \gg \gamma_{DA}$). Then an efficient process of energy migration is observed. Thus eq 2.2 represents a first approximation to the proper description of energy migration between chromophores in macromolecular systems. An additional complication is introduced when, under normal experimental conditions, the process of energy trapping by intramolecular excimers is reversible.[1] It is evident that the theoretical equations describing fluorescence from macromolecules have to contain a proper description of energy migration and excimer dissociation. In the following part of the paper, we shall develop a theoretical model of those processes. In this formulation, the model is independent of the character of energy migration and energy trapping. However, by introducing explicit forms of rate coefficients as required by resonance interactions, we shall be able to analyze the obtained equations.

Because we are preliminarily interested in monomer–excimer kinetics, we shall use a notation commonly accepted in this subject, remembering that monomer (M) and excimer (E) are equivalent to donor and acceptor molecules. In the first step we will calculate monomer and excimer decay profiles, assuming that the excimer is not dissociating. In the second step we will introduce the process of excimer dissociation to the monomer and excimer decay profiles.

To obtain an equation for the monomer fluorescence decay ($M(t)$), one can follow a mathematical procedure that we recently proposed for the trapping of excitations in donor–acceptor systems[26] and obtain

$$M(t) = \mathcal{L}^{-1}\{\hat{M}^{(1)}(s)/(1 - \hat{\beta}_M)\} \tag{2.7}$$

where the circumflex and $\mathcal{L}^{-1}$ denote the Laplace and the inverse Laplace transform and where

$$M^{(1)}(t) = I_\alpha(t) \otimes f_M(t) \tag{2.8}$$

$$\beta_M = k_{MM}(t)f_M(t) \tag{2.9}$$

In eqs 2.8 and 2.9, $f_M(t)$ is the probability that excitation resides on the monomer molecule at time t (eq 2.2) after the δ-pulse excitation. The convolution ($\otimes$) of $f_M(t)$ with the excitation pulse $I_\alpha(t)$ gives the concentration of the preliminarily excited monomer molecules, eq 2.8.

Similar equations can be obtained for excimer decay ($E(t)$) after its direct excitation with rate $I_\alpha(t)$ and

$$E(t) = I_\alpha(t) \otimes f_E(t) \tag{2.10}$$

where

$$f_E(t) = \exp\{-(k_E + k_d)t\} \tag{2.11}$$

and where k_E is the rate constant for excimer fluorescence and k_d is the rate constant for excimer dissociation.

Equation 2.7 describes monomer decay that is due to monomer fluorescence energy migration and energy transfer to excimer-forming sites. Similarly, eq 2.10 describes excimer decay that is due to excimer fluorescence and excimer dissociation that leads to an excited monomer. At this point, those equations are still independent of each other. In order to calculate the total monomer and excimer fluorescence decays in the presence of energy migration, energy transfer to excimer-forming sites, and excimer dissociation, we have to link eqs 2.7 and 2.10.

After the first step of energy transfer from monomer to excimer, the total amount of excited monomers and excimers is given by

$$\mathcal{M}^{(1)}(t) = M(t) \tag{2.12}$$

$$\mathcal{E}^{(1)}(t) = k_{ME}(t)M(t) \otimes E(t) \tag{2.13}$$

where $M(t)$ and $E(t)$ are given by eqs 2.7 and 2.10, respectively.

It is clear that an excimer dissociation (with rate constant k_d) leads to an excited monomer. Thus, the total concentration of excited monomers and excimers can be expressed by the equations

$$\mathcal{M}^{(2)}(t) = \mathcal{M}^{(1)}(t) + \mathcal{M}^{(1)}(t) \otimes k_{ME}(t)M(t) \otimes k_dE(t) \tag{2.14}$$

$$\mathcal{E}^{(2)}(t) = \mathcal{E}^{(1)}(t) + \mathcal{E}^{(1)}(t) \otimes k_{ME}(t)M(t) \otimes k_dE(t) \tag{2.15}$$

Equations 2.14 and 2.15 can be rewritten in the following form:

$$\mathcal{M}^{(2)}(t) = \mathcal{M}^{(1)}(t) + \mathcal{M}^{(1)}(t) \otimes \beta \tag{2.16}$$

$$\mathcal{E}^{(2)}(t) = \mathcal{E}^{(1)}(t) + \mathcal{E}^{(1)}(t) \otimes \beta \tag{2.17}$$

where

$$\beta = k_{ME}(t)M(t) \otimes k_dE(t) \tag{2.18}$$

The term β may be also called a production term because it represents the product of the efficiency of energy transfer to the excimer and the efficiency of excimer dissociation.

After m steps of excimer formation and dissociation, the fluorescence decay of monomer and excimer has the form

$$\hat{\mathcal{M}}^{(m)}(s) = \hat{\mathcal{M}}^{(1)}(s)\{1 + \beta + \hat{\beta}^2 + ... + \hat{\beta}^m\} \tag{2.19}$$

$$\hat{\mathcal{E}}^{(m)}(s) = \hat{\mathcal{E}}^{(1)}(s)\{1 + \hat{\beta} + \hat{\beta}^2 + ... + \hat{\beta}^m\} \tag{2.20}$$

The total amount of excited monomers ($\mathcal{M}(t)$) and excimers ($\mathcal{E}(t)$) in the presence of energy migration, excimer formation, and excimer dissociation can be calculated from eqs 2.19 and 2.20 for $m \to \infty$ and

$$\mathcal{M}(t) = \mathcal{L}^{-1}\{\hat{\mathcal{M}}^{(1)}(s)/(1 - \hat{\beta})\} \tag{2.21}$$

$$\mathcal{E}(t) = \mathcal{L}^{-1}\{\hat{\mathcal{E}}^{(1)}(s)/(1 - \hat{\beta})\} \tag{2.22}$$

Using eqs 2.9 and 2.10 and eqs 2.21 and 2.22, one can obtain

$$\mathcal{M}(t) = \mathcal{L}^{-1}\{\hat{M}^{(1)}(s)/[(1 - \hat{\beta}_{\mathrm{M}})(1 - \hat{\beta})]\} \tag{2.23}$$

$$\mathcal{E}(t) = \mathcal{L}^{-1}\{\mathcal{L}[k_{\mathrm{ME}}(t)M(t)]\hat{E}(s)/(1 - \hat{\beta})\} \tag{2.24}$$

Equations 2.23 and 2.24 can be simplified substantially if one notices that the term $\hat{\beta}$ (see also eq 2.18) can be transferred to the form

$$\hat{\beta} = \mathcal{L}\{k_{\mathrm{ME}}(t)f_{\mathrm{M}}(t)\}\mathcal{L}\{k_{\mathrm{d}}E(t)\}/\{1 - \hat{\beta}_{\mathrm{M}}\} \tag{2.25}$$

Substituting eq 2.25 into eqs 2.23 and 2.24, one can obtain

$$\mathcal{M}(t) = \mathcal{L}^{-1}\{\hat{M}^{(1)}(s)(1 - \hat{\beta}_{\mathrm{M}})/[1 - \hat{\beta}_{\mathrm{M}} - \mathcal{L}\{k_{\mathrm{ME}}(t)f_{\mathrm{M}}(t)\}\mathcal{L}\{k_{\mathrm{d}}E(t)\}]\} \tag{2.26}$$

$$\mathcal{E}(t) = \mathcal{L}^{-1}\{\hat{E}(s)\mathcal{L}\{k_{\mathrm{ME}}(t)f_{\mathrm{M}}(t)\}/[1 - \hat{\beta}_{\mathrm{M}} - \mathcal{L}\{k_{\mathrm{ME}}(t)f_{\mathrm{M}}(t)\}\mathcal{L}\{k_{\mathrm{d}}E(t)\}]\} \tag{2.27}$$

Equations 2.26 and 2.27 describe monomer $\mathcal{M}(t)$ and excimer $\mathcal{E}(t)$ fluorescence decay in the presence of energy migration, excimer formation, and excimer dissociation. Those equations are in a very general form. In the next section we shall analyze the above equations for some particular forms of rate coefficients for energy migration.

III. Numerical Analysis and Discussion

In this section we shall numerically analyze the decay profiles of monomer and excimer fluorescence. The equation proposed in the previous section has been obtained for a resonance mechanism of energy migration for arbitrary (integer) dimensional space. However, there is experimental evidence that the process of energy migration in vinyl macromolecules has a one-dimensional character.[21-23] Therefore, in the following examples, we shall analyze the one-dimensional properties. The analysis of higher dimensionality can be performed in a similar way.

To calculate decay profiles of monomer and excimer fluorescence, it is necessary to obtain the explicit forms of the parameters in eqs 2.26 and 2.27, respectively. For one-dimensional dipole–dipole interactions the rate coefficients (2.5) and (2.6) have the form

$$k_{\mathrm{MM}}(t) = {}^1/_6\gamma_1\gamma_{\mathrm{MM}}\tau_{0\mathrm{M}}{}^{-1/6}\Gamma(1 - {}^1/_6)t^{-5/6} = \lambda_{\mathrm{MM}}t^{-5/6} \tag{3.1}$$

$$k_{\mathrm{ME}}(t) = {}^1/_6\gamma_1\gamma_{\mathrm{ME}}\tau_{0\mathrm{M}}{}^{-1/6}\Gamma(1 - {}^1/_6)t^{-5/6} = \lambda_{\mathrm{ME}}t^{-5/6} \tag{3.2}$$

The probability that excitation resides on the monomer molecule $f_{\mathrm{M}}(t)$ is given by

$$f_{\mathrm{M}}(t) = \exp\{-t/\tau_{0\mathrm{D}} - \int_0^t[\lambda_{\mathrm{MM}}t'^{-5/6} + \lambda_{\mathrm{ME}}t'^{-5/6}]\,\mathrm{d}t'\} \tag{3.3}$$

which after integration has the form

$$f_{\mathrm{M}}(t) = \exp\{-t/\tau_{0\mathrm{M}} - \lambda t^{1/6}\} \tag{3.4}$$

where $\lambda = \gamma_1\Gamma(5/6)(\gamma_{\mathrm{MM}} + \gamma_{\mathrm{ME}})/\tau_{0\mathrm{M}}{}^{1/6}$.

Let us analyze the Laplace transformations appearing in eqs 2.26 and 2.27. These respective Laplace transforms can be expressed by integrals in the form

$$I_1 \equiv \mathcal{L}\{f_{\mathrm{M}}(t)\} = \int_0^\infty e^{-ut}e^{-\lambda t^\nu}\,\mathrm{d}t \tag{3.5}$$

and

$$I_2 \equiv \mathcal{L}\{k_{\mathrm{MM}}(t)f_{\mathrm{M}}(t)\} = \lambda_{\mathrm{MM}}\int_0^\infty t^{\nu-1}e^{-ut}e^{-\lambda t^\nu}\,\mathrm{d}t \tag{3.6}$$

where $u = 1/\tau_{0\mathrm{M}} + s$ and $\nu = {}^1/_6$.

Unfortunately, the solutions of the above integrals seem to be impossible for the whole time domain. However, for a theoretical as well as an experimental purpose, we can analyze short- and long-time properties of eqs 3.5 and 3.6.

For large values of u, integrals I_1 and I_2 can be given in terms of their asymptotic series expansions

$$I_1 = (1/u)\sum_{m=0}^{\infty}(-1)^m/m!\Gamma(m\nu + 1)(\lambda/u^\nu)^m \tag{3.7}$$

$$I_2 = (\lambda_{\mathrm{MM}}/u^\nu)\sum_{m=0}^{\infty}(-1)^m/m!\Gamma[\nu(m + 1)](\lambda/u^\nu)^m \tag{3.8}$$

and for small values of u

$$I_1 = \lambda^{-1/\nu}\sum_{m=0}^{\infty}(-1)^m/m!\Gamma[(m + 1)/\nu](u/\lambda^{1/\nu})^m \tag{3.9}$$

$$I_2 = (\lambda_{\mathrm{MM}}/\lambda)\sum_{m=0}^{\infty}(-1)^m/m!\Gamma[(m + \nu)\nu](u/\lambda^{1/\nu})^m \tag{3.10}$$

where $\Gamma(x)$ is the gamma function.

Equations 3.7 and 3.8 represent short-time asymptotic expansions of I_1 and I_2, while eqs 3.9 and 3.10 are long-time asymptotic expansions of I_1 and I_2. The validity condition for the onset of short time is

$$t/\tau_{\mathrm{M}} < [\gamma_1\Gamma(5/6)(\gamma_{\mathrm{MM}} + \gamma_{\mathrm{ME}})]^{-6} \tag{3.11}$$

and for long-time approximation

$$t/\tau_{\mathrm{M}} > [\gamma_1\Gamma(5/6)(\gamma_{\mathrm{MM}} + \gamma_{\mathrm{ME}})]^{-6} \tag{3.12}$$

From an experimental point of view, the short-time approximation is sufficient; thus we shall only analyze this case. However, one could in a similar way analyze the long-time approximation.

Let us first analyze the case of polymer in which the process of excimer dissociation is negligible at the usual experimental conditions—as, for example, in polystyrene.[29,30] In those calculations, we had assumed that the lifetime of monomer fluorescence τ_{M} = 13 ns[29] and the Förster critical radius R_0 = 6.47 Å.[31] The dimensionless concentrations γ_{MM} and γ_{ME} were calculated from the relations

$$\gamma_{\mathrm{MM}} = R_0/\langle R\rangle \tag{3.13a}$$

$$\gamma_{\mathrm{ME}} = qR_0/\langle R\rangle \tag{3.13b}$$

where q is a fraction of the excimer sites and $\langle R\rangle$ is an average distance between chromophores. The last parameters were assumed to be $\langle R\rangle$ = 4 Å and q = 0.036.[15] Additionally, γ_1 = 0.8886 as it was assumed in correspondence to the static case of averaging.[32]

Figure 1 shows monomer decay profiles calculated for two different concentrations of excimer sites. For a given set of parameters, the influence of trapping by excimers is very small, although the influence of energy migration of decay profiles is substantial. This is a typical behavior of decay profiles for one-dimensional systems, contrary to three-dimensional systems where the concentration of traps (excimers) has a very profound influence on decay profiles. Therefore, if energy migration in the polymer can be

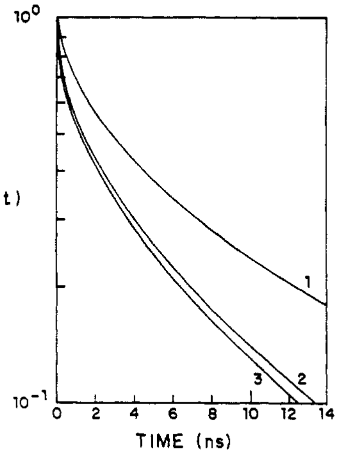

Figure 1. Monomer fluorescence decay profiles calculated for short-time approximation. Profiles 1 and 2 were calculated for $\gamma_{\rm MM} = 1.0$ and $\gamma_{\rm ME} = 0.04$, and profile 3 was calculated for $\gamma_{\rm MM} = 1.0$ and $\gamma_{\rm ME} = 0.1$. For decay profile 1 the energy migration was assumed to be zero.

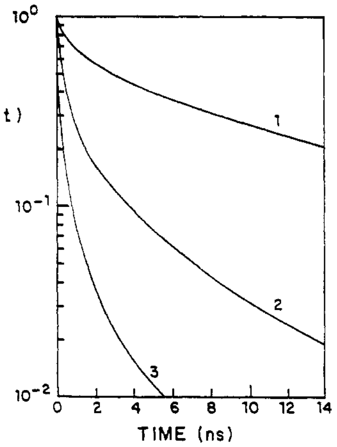

Figure 2. Monomer fluorescence decay profiles calculated for short-time approximation for different concentrations of monomers and constant concentration of excimers ($\gamma_{\rm ME} = 0.05823$): (1) $\gamma_{\rm MM} = 0.62$; (2) $\gamma_{\rm MM} = 1.62$; (3) $\gamma_{\rm MM} = 2.62$. Monomer fluorescence decay profile 1 was calculated for parameters expected for polystyrene.[15]

modeled as a Förster exchange of excitation energy between chromophores, the concentration of excimer sites does not change in a significant way the decay profile of monomer fluorescence. This observation is also illustrated in Figure 2, where monomer decay profiles have been calculated for constant concentration of excimer sites and a varying concentration of monomer. The decay profile for $\gamma_{\rm MM} = 1.62$ and $\gamma_{\rm ME} = 0.05823$ is the one that most closely corresponds to the situation expected for polystyrene in solution at a very low concentration. One can see that the influence of monomer concentration on the monomer fluorescence decay profile is very substantial. One also has to observe that the concentration of the fastest decay in Figure 2 corresponds to the critical Förster radius $R_0 = 13$ Å, which is almost 2 times larger than the one obtained from an independent spectral examination. We had made a similar observation using Monte Carlo simulations of electronic excitation energy migration in polystyrene.[15] In this work, we had observed that a concentration of excimer sites does not have a very significant influence on photophysical properties of polystyrene. The much more important influence on photophysics of polystyrene (and probably other aromatic polymers) is the nature, or more precisely the strength, of interactions between chromophores. As we know, this

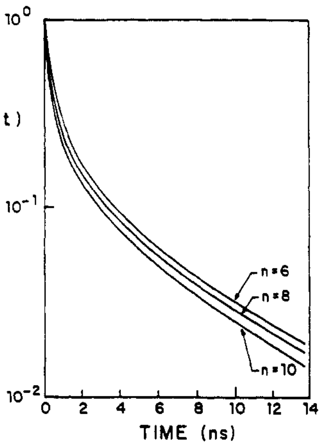

Figure 3. Monomer fluorescence decay profiles calculated for short-time approximation for different order of multipole interactions $n = 6$, 8, and 10. $\gamma_{\rm MM} = 1.62$ and $\gamma_{\rm ME} = 0.05823$.

strength can be expressed by the Förster radius if this type of interaction is responsible for energy migration in polystyrene. We have concluded[15] from the Monte Carlo simulations that, taking $R_0 = 6.47$ Å obtained from spectroscopic measurements, the fit to experimental data was poor. An improvement of agreement between the Monte Carlo simulations and the experiment was shown to be satisfactory for $R_0 \approx 13$ Å, which is twice the value of R_0 estimated from spectroscopic measurements. A similar behavior is observed from the theoretical decay profiles depicted in Figure 2. By roughly comparing the experimentally obtained decay curves,[33,34] one can conclude that the decay profile calculated within realistic parameters appears to be too slow and that the decay profile calculated for an unrealistic R_0 seems to be in closer proximity to the experimental data. One can then wonder, is this a result of a different type of interaction between chromophores or is it that energy migration in polystyrene is not one-dimensional? Although we do not know of a conclusive answer, the following comments can give an insight into the question. The Monte Carlo simulations presented in ref 15 allowed us to simulate a real three-dimensional structure of a polystyrene macromolecule. While simulating energy migration, we assumed that the excitation could jump to its five neighbors on its left as well as on its right side. In this respect, we simulated a three-dimensional energy migration in polystyrene. However, we observed that due to the small value of the critical radius ($R_0 = 6.47$ Å), the excitation energy was almost exclusively migrating between its nearest neighbors. Therefore, one can conclude that energy migration in polystyrene has principally a one-dimensional character. A sharp transition from a one- to a quasi-three-dimensional migration was observed when the critical radius R_0 was increased to the value (13 Å) which is in clear disagreement with spectroscopic estimations. This observation may suggest that a different type of interaction between chromophores is responsible for energy migration. One may suggest higher octupole interactions or exchange interactions. The last type of interaction we will analyze in a forthcoming paper. The case of higher than dipole–dipole interactions is illustrated in Figure 3. One can see that there is no significant influence of this type of interactions on decay profiles. We should remark that this behavior is characteristic only for one-dimensional energy migration and trapping.

We wish to add one comment in respect to the influence of excimer concentration on decay profiles. In the Monte Carlo simulations,[15] due to the lack of respective experi-

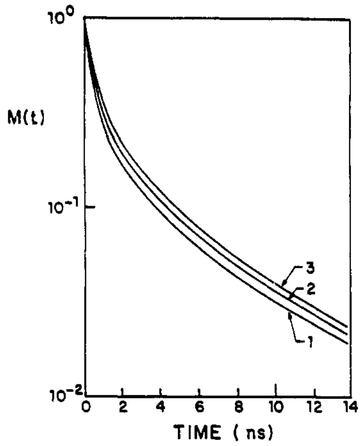

Figure 4. Monomer fluorescence decay profiles calculated for short-time approximation for different rate constants for excimer dissociation: (1) $k_d = 0$; (2) $k_d = 1.0 \times 10^7$ s^{-1}; (3) $k_d = 1.0 \times 10^8$ s^{-1}.

mental data, we had assumed that the dynamics of the chain did not influence in a significant way the photophysical properties of polystyrene. It appears that the influence of dynamics of polystyrene can bring about a continuous movement of excimer sites along the chain. For this reason, the migrating excitation energy can probe more traps than in a case where they are immobile. This possibility could also result in the decrease of the amount of chains that do not contain excimer sites.[15] However, as we have shown in Figure 1, the concentration of excimer sites has a minor influence on decay profiles.

Although it has been shown that in polystyrene at room temperature the process of excimer dissociation is negligible, we shall illustrate the general influence of excimer dissociation on monomer decay profiles. In the calculations, according to eq 2.30, we had assumed[29] that $k_E = 5.14 \times 10^7$ s. The rate constant for excimer dissociation (k_d) was taken as a variable. Figure 4 depicts the respective monomer profiles for three different k_d values. One can see that a dissociation of excimer leads to slower monomer decay.

A review of experimental data[1] and its interpretation shows that most of the authors have used multiexponential functions to analyze decay profiles of aromatic polymers. The nonadequacy of this approach in an analysis of experimental data was pointed out by several authors.[10,11] The above-discussed properties of monomer decay profiles show that by no means can one attempt to fit them to multiexponential functions. The decay profiles are *nonexponential*, regardless of the presence or absence of excimer dissociation. Only in one case can one expect a single-exponential decay. Let us assume that energy migration does not take place in the considered system and that donors and acceptors are randomly distributed in a medium. Then the probability $G^s(t)$ that excitation energy remains at the originally excited donor molecules can be given by

$$G^s(t) = \langle \exp\{-t \sum k(R_i)\} \rangle \tag{3.14}$$

where the angular brackets denote the ensemble average over the positions of molecules and where $k(R_i)$ is a rate constant for energy transfer in the form as given by eq 2.1. By taking the product of probabilities over all of the possible positions of the molecules one can obtain[35,36]

$$G^s(t) = \prod_{i=1}^{N} [1 - c_A/N + c_A/N \exp\{-k(R_i)t\}] \tag{3.15}$$

where c_A is the acceptor concentration and N is the total number of molecules in the unit volume. Equation 3.15 can be transformed into the form

$$\ln G^s(t) = -\prod_{i=1}^{N} [1 - c_A/N + c_A/N \exp\{-k(R_i)t\}] \tag{3.16}$$

If $c_A/N \approx 1$ then eq 3.16 can be approximated by

$$G^s(t) = \exp\{-t \sum k(R_i)\} \tag{3.17}$$

where the natural decay $e^{-t/\tau}$ is not included. One can see that the decay profile is exponential for all times. However, this situation can only be realized when all donor molecules have the same surroundings. Although this situation is possible, in most of the cases we can observe a deviation from exponential decay even in the simplest case of direct energy transfer.[24] This is due to the spatial disorder of the system. Therefore, even if one does assume that energy migration is absent in polystyrene (or other polymers), one has to observe monomer decay in the form already given by eq 2.2. In this section we have numerically analyzed monomer decay profiles. In a similar way one can analyze the respective excimer fluorescence decay profiles by using eq 2.27.

In these considerations we have neglected the more complicated topological aspects of energy migration in polystyrene. The system was modeled as one-dimensional. The incorporation of specific spatial distributions of chromophores is principally possible; however, it appears, at the present moment, to be difficult.

IV. Concluding Remarks

In an effort to understand the nature of interactions leading to energy migration in aromatic polymers, we have presented a theoretical model of photophysical processes for this class of macromolecules. It was assumed that excitation energy has a one-dimensional character and that excimer can dissociate. The analysis of theoretical calculations under the assumption of a resonance mechanism of energy migration reveals that this kind of interaction is very likely to be responsible for the photophysical properties of polystyrene. However, for the time being, our model could be compared to the experimental data obtained for polystyrene in solution at different temperatures in order to observe the process of excimer dissociation and its influence on decay profiles.

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