Distribution Functions in Photophysics of Polymers and Aromatic Molecules

K. Sienicki†

Département de physique—COPL, Université Laval, Québec, Canada G1K 7P4

Received January 31, 1990; Revised Manuscript Received April 18, 1990

ABSTRACT: A theoretical model of electronic excitation energy transport between chromophores randomly attached to the polymer has been proposed. To obtain an integrable form of the donor fluorescence decay profile, the polynomial approximation to the Gaussian distribution function was investigated and respective equations were derived in closed form. The obtained equations are valid for all experimentally accessible times. A numerical analysis of the proposed model is presented, and the influence of concentration of chromophores and polydispersity is discussed in detail. Several experimental implications of the model are presented and discussed.

I. Introduction

Recently there has been a large effort devoted to using photophysical methods to study various polymer systems in solid as well as in liquid states.[1] The use of photophysical methods to determine the polymeric structure and properties has several advantages over other experimental methods. It appears that the sensitivity of photophysical probes upon its environment can be used to probe polymer structures. The usefulness of photophysical methods to study various polymeric systems has already been established.[2-5] It is obvious that a further development of photophysical methods to study the polymer structure is closely related to our understanding of photophysical properties of molecular probes.

In recent years there has been tremendous progress in experimental and theoretical studies of electronic excitation transport in liquid and solid solutions of aromatic molecules.[5] In spite of this progress, the direct application of the methods elaborated for aromatic molecules to the polymeric systems accounts for several problems related with their specific structure. From a photophysical point of view, there are two important factors that distinguish dilute liquid or solid solutions of polymers from solutions of small aromatic molecules that contain the same concentration of chromophoric groups. First, the chromophoric groups (molecular probes) bonded to a macromolecule do not form a random set but instead have spatial correlations that are determined by the conformational statistics of the chain. The spatial correlations may be extracted from the conformational partition function expressed in the rotation isomeric-state approximation, as given by Flory.[6] Second, with the exception of infinite polymeric networks, a polymer is a spatially finite object, and a limited number of chromophores (molecular probes) can be sampled by the electronic excitation energy transport. For that reason one has to take into account a specific distribution function that reflects the structure of polymeric system. The problem of distribution functions of polymeric systems has been a subject of intense investigations for many years, and the abundance of different forms of those functions is available.[7] Before the application of distribution functions of polymeric systems and their relation to photophysical studies is discussed, it is necessary to briefly review the recent theories of excitation transport developed for small aromatic molecules.

† Present address: Département de chimie, Université de Montréal, C.P. 6128, succursale A, Montréal, PQ, Canada H3C 3J7.

Two methods of calculating the ensemble-averaged probability, $G(t)$, of finding the excitation in the donor and acceptor ensemble have been presented. In the first method the density expansion of the Green function has been advanced.[8,9] In the second method the density expansion of the self-energy in the Dyson-type expression for the Green function has been proposed by Gochanour, Andersen, and Fayer (GAF).[10] It was demonstrated[11] that Green's function can be split into three parts: $G^S(t)$, $G^D(t)$, and $G^T(t)$, where $GS(t)$ is the ensemble-averaged probability that an originally excited donor molecule is still excited at time t, $G^D(t)$ is the ensemble-averaged total probability of finding the excitation at the donor ensemble, and $G^T(t)$ is the probability of finding the excitation in the ensemble of acceptors. The GAF method originally developed for a one-component (donor–donor) system has been extended for a two-component[11] (donor-acceptor) system and many other specific systems.[12-14] The above-mentioned theoretical studies have proven to be in very close agreement with the experimental data[15,16] and the Monte Carlo simulations.[17,18]

An alternative procedure for calculation of the ensemble-averaged probability that an originally excited donor molecule is still excited at time t has been proposed by Huber et al.[19] for donor–donor migration and by Blumen and Manz[20] for donor–acceptor trapping. Those authors have considered a cumulant expansion method for two-site (pair) approximation. They obtained an exact configurational average, which lead to a power series in the acceptor concentration (for donor–acceptor transfer) and in the donor concentration (for donor–donor migration). It has been shown that when truncating this expansion to its first order, one can obtain[19-21z]

$$G^S(t) = \exp\{-t/\tau_{OD} - 2^{\Delta/n-1}\Gamma(1 - \Delta/n)c_D(t/\tau_{OD})^{\Delta/n}\} \quad (1.1)$$

for a one-component system and

$$G^S(t) = \exp\{-t/\tau_{OD} - 2^{\Delta/n-1}\Gamma(1 - \Delta/n)(c_D + c_A)(t/\tau_{OD})^{\Delta/n}\} \quad (1.2)$$

for a two-component system. In eqs 1.1 and 1.2 $\Delta = 1$–3 is the dimensionality of the medium, $n = 6, 8, 10, \ldots$ is the order of interaction, $\Gamma(x)$ is the gamma function, c_D and c_A are donor and acceptor concentrations, and τ_{OD} is the lifetime of donor fluorescence.

Although systematic theories have yielded concrete results, their application is limited due to their mathematical complexity. For this reasons, several authors have recently analyzed Huber's approach.[3,15,21,22] It has been

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shown that at moderate concentrations the cumulant expansion theory of Huber is in very good agreement with experimental data and the GAF theory.[15,21,22]

Huber's theory represents the second approximation (as a result of truncating a cumulant expression) to an exact configurational average. One can try to include higher orders of cumulant expansion while performing a configurational average.[23] However, this approach seems to be a difficult mathematical problem.

The above-mentioned theoretical approaches of GAF and Huber have been extended for polymer systems by assuming specific distribution functions.[3] Although important information has been obtained, the analysis of proposed equations is difficult due to the fact that distribution functions characteristic for polymer systems lead to nonintegrable forms of $G^S(t)$ functions. For that reason, an experimentalist may encounter a number of difficulties in the practical implementation of the equations proposed in the mentioned works. In this paper we shall show that the above difficulty can be overcome if one uses respective approximations to the distribution functions. In this way one can retain all structural information expressed by the distribution function and obtain equations that are in closed form ready for direct experimental implementation. We shall also analyze the influence of polydispersity on analysis of fluorescence data from various polymeric systems.

II. Two-Particle Model: Averaging Procedure

Their are several ways to calculate the configurational average function, $G^S(t)$. To obtain a detailed knowledge in regard to the nature of assumptions leading to the $G^S(t)$ function, we feel it to be appropriate to discuss the averaging procedure in some detail. We shall describe the statistics of energy transfer by assuming interactions between two molecules (donor and acceptor). Let us consider a set of molecules distributed in volume V containing NV sites, where N is the number of sites per unit volume. Let us defined by $p(m_1,...,m_j,n_1,...,n_k;t)$ the probability that at the moment t the sites m_1, ..., m_j are occupied by excited donor molecules and the sites n_1, ..., n_k are occupied by acceptor molecules. The rate of changes of respective probabilities is given by

$$dp(m,t)/dt = -\sum_{n(\neq m)}^{NV} k(|m-n|)\, p(m,n,t) \qquad (2.1)$$

$$dp(m,n,t)/dt = -k(|m-n|)\, p(m,n,t) - \sum_{n'(\neq m,n)}^{NV} k(|m-n'|)\, p(m,n,n',t) \qquad (2.2)$$

$$\vdots$$

where $k(x)$ represents a respective rate constant for energy transfer between sites m and n. To terminate the set of the above equations, we shall assume the Kirkwood superposition of two-particle distribution in the form

$$p(m,n,n',t) = p(m,n,t)\, p(m,n',t)\, p(n,n')/[p(m,t)\, p(n)\, p(n')] \qquad (2.3)$$

Of course, one can consider the three-particle distribution function, but this assumption leads to well-known problems with summations of respective terms in the above equations.

Assuming that the system is homogeneous and neglecting correlations between acceptor molecules ($p(n,n') \equiv p(n)\, p(n')$), one can obtain[24]

$$G^S(t) = \prod_{i=1}^{N}(1 - p + pE_i(r_i,t)) \qquad (2.4)$$

where $E_i(r_i,t)$ is the probability of finding the excitation on the originally excited donor molecule and for an isolated pair is given by

$$E_{DA}(t) = \exp\{-k(r)t\} \qquad (2.5)$$

for a donor and acceptor pair where only forward transfer is allowed and

$$E_{DD}(t) = 1/2(1 + \exp\{-2k(r)t\}) \qquad (2.6)$$

for donor and donor transfer as a result of an infinite number of energy transfers. One can notice that for number of aromatic molecules the possibility of reverse transfer from acceptor to donor is important, and in this case 2.5 takes the form given by eq 2.6.

Expanding the logarithm of eq 2.4 in powers of p, one can obtain

$$\ln G^S(t) = -\sum_{k=1}^{\infty} p^k/k \sum_{i=1}^{N}[1 - E_i(r_i,t)]^k \qquad (2.7)$$

Retaining only the first term of the series eq 2.7 and assuming a thermodynamic limit ($N/V = \rho$), one can obtain

$$\ln G^S(t) = -\rho \int_0^\infty [1 - \exp(-k(r)t)]\, u(r)\, dr \qquad (2.8)$$

for donor–acceptor transfer and

$$\ln G^S(t) = -\rho/2 \int_0^\infty [1 - \exp(-2k(r)t)]\, u(r)\, dr \qquad (2.9)$$

where ρ is the number density and $u(r)$ is the distribution function. Equations 2.8 and 2.9 have a general form

$$\ln G^S(t) = -\rho/\lambda \int_0^\infty [1 - \exp(-\lambda k(r)t)]\, u(r)\, dr \qquad (2.10)$$

where $\lambda = 1$ for donor–acceptor transfer and $\lambda = 2$ for donor–donor transfer. The rate constant $k(r)$ is given by

$$k(r) = 1/\tau(3/2)\kappa^2(\omega)\, (R_0/r)^n \qquad (2.11)$$

where τ is the lifetime of donor fluorescence, $\kappa^2(\omega)$ is a dimensionless factor describing the interaction strength of interaction between molecules as a function of their relative orientation ω, and R_0 is the Förster radius.

In the case of random and uniform distribution of molecules in one-, two-, and three-dimensional space, the respective distribution functions are $u_1(r) = 2$, $u_2(r) = 2\pi r$, and $u_3(r) = 4\pi r^2$. Substituting these distribution functions into eq 2.10, one can obtain the well-known formula in Δ-dimensional space

$$\ln G^S(t) = -c_\Delta \lambda^{\Delta/n-1}(3/2\langle\kappa^2\rangle^{\Delta/n}\Gamma(1-\Delta/n)(t/\tau_{OD})^{\Delta/n} \qquad (2.12)$$

where c_Δ is dimensionless concentration, $\Gamma(x)$ is the gamma function, and $n = 6, 8, 10, ...$ is the order of interactions. One has to notice that natural decay, $\exp(-t/\tau)$, is not included in eq 2.12.

Although eq 2.12 contains the Γ function, we are accustomed to saying that the distribution functions for one-, two-, and three-dimensional space lead to formulas that can be integrated with the result given by eq 2.14. However, this can be understood as a special case, and by introducing another distribution function that can be used in studies of polymeric systems, one will deal with formulas that are nonintegrable. For this reason, fluorescent

techniques were limited in their applications to polymeric systems. The above problem can be overcome if one notices that any distribution function can be extremely well approximated by a polynomial of which coefficients are related to the parameters characteristic for a given distribution.

Let us assume that the given distribution function $u(r)$ can be approximated by a polynomial in the form

$$u(r) = \sum_{i=0}^{\infty} a_i r^i \tag{2.13}$$

Substituting eq 2.13 into eq 2.10, we have

$$\ln GS(t) = -\rho/\lambda \int_0^{\infty} dr\, [1 - \exp(-\lambda k(r)\, t)] \sum_{i=0}^{\infty} a_i r^i \tag{2.14}$$

which after integration gives

$$\ln G^S(t) = -\rho/(n\lambda)\alpha^{1/n} \sum_{i=0}^{\infty} a_i \alpha^{i/n} n/(1 + i)\Gamma(1-(1+i)/n) \tag{2.15}$$

where rate constant $k(r)$ given by eq 2.11 has been used and

$$\alpha = \lambda(3/2)(t/\tau)(\varkappa^2)R_0^{\,n} \tag{2.16}$$

Equation 2.15 is valid for any distribution function as long as one knows its approximate form given by eq 2.13. Equation 2.15 is also valid for an arbitrary order of interactions ($n = 6, 8, 10, \ldots$); however, we will only analyze dipole–dipole interactions for which $n = 6$. One has to notice the complicated character of time dependence in eq 2.15, which is expressed by $(t/\tau)^{1/6}$ and $(t/\tau)^{i/6}$ for $i = 0$ to ∞. The particular applications of eq 2.15 we shall discuss in the next section. It is obvious that eq 2.15 is equivalent to eq 2.12 if one assumes that a distribution function is given in the form required by one-, two-, or three-dimensional medium.

III. Applications

In the previous section we have obtained the respective equation for an originally excited donor fluorescence decay profile for an arbitrary distribution function. This equation has been derived under the assumption that one is able to find a good approximation to the real distribution function in the form of a polynomial. This, as we shall show, is a very easy task when one uses standard computer programs. In this section we shall analyze several polymeric systems using specific distribution functions.

A. Distribution Functions and Their Approximations. An abundance of distribution functions for polymeric systems is available in the literature,[7] and their particular forms reflect specific applications and purpose. In its simplest form, although very general, the polymer chain can be modeled through random walks in Δ-dimensional lattices or in Δ-space ($1 \le \Delta \le 4$) in continuum approximation. Two approximations have been developed for the probability density, $P_N(r)$, for finding in a polymer consisting of N monomer units the end-to-end distance, r. In the first method, based on Gaussian random walks,[7] the probability $P_N(r)$ is given by

$$P_N(r) = [\Delta/(2\pi\langle R_N^2\rangle)]^{\Delta/2} \exp\{-\Delta r^2/(2\langle R_N^2\rangle)\} \tag{3.1}$$

where $\langle R_N^2\rangle$ is the mean-squared end-to-end distance of a walk of N steps. One has to remark that eq 3.1 is independent of solvent and thus the above function can be related to the polymer under Θ conditions.

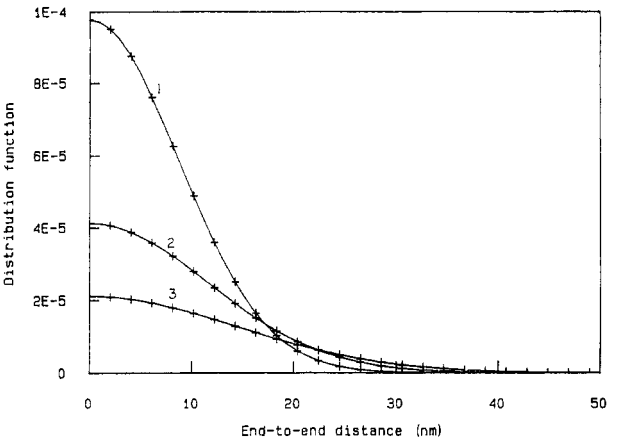

Figure 1. Gaussian distribution functions (—) as a function of end-to-end distance and their polynomial approximations (+) for several mean-squared end-to-end distances, $\langle R_N^2\rangle^{1/2}$: (1) 15 Å, (2) 20 Å, and (3) 25 Å.

A more general equation for probability density, $P_N(r)$, can be obtained by considering self-avoiding walks. One then obtains[25]

$$P_N(r) = A_1 r^{\vartheta} \exp(-A_2 r^{\delta}) \tag{3.2}$$

where

$$A_1 = \delta A_2^{(\Delta+\vartheta)/\delta}/[\Delta V_\Delta \Gamma((\Delta+\vartheta)/\delta)] \tag{3.3}$$

$$A_2 = \{\Gamma[(\Delta+\vartheta+2)/\delta]\}^{\delta/2}\{\Gamma[(\Delta+\vartheta)/\delta]\ \langle R_N^2\rangle\}^{-\delta/2} \tag{3.4}$$

where ϑ and δ are two-dimensional-dependent critical exponents and $V_\Delta = \pi^{1/2}/\Gamma(1+\Delta/2)$, $\Gamma(x)$ is the gamma function.

Equation 3.1 can also be modified by assuming the Gaussian random walks in disordered lattice, and one can obtain a respective equation in the form similar to eq 3.1 but with different coefficients reflecting disorder.[26]

One can observe that, regardless of the situation, the probability density function, $P_N(t)$, can be expressed as a Gaussian-like function. As we mentioned in the previous section, an introduction of this type of distribution function into eq 2.12 leads to a nonintegrable form of the $G^S(t)$ function. This situation can be partially relaxed by analyzing long-time properties of the $G^S(t)$ function. However, the most interesting information can be obtained for short and medium times. For that reason, we have used the polynomial approximation to respective distribution functions in the form given by eq 3.1. Figure 1 depicts a Gaussian distribution function for several mean-squared end-to-end distances. Using a standard polynomial fitting procedure, we have calculated the respective approximations to the Gaussian distribution. It turns out that the Gaussian distribution can be extremely well fitted by a polynomial. In order to check the proposed method of approximation, we have analyzed an integrable case of uniform and random distribution of luminescently active molecules and the respective distribution function in the form $u_3(r) = 4\pi r^2$. It was shown that the approximation of $U_3(r)$ by a polynomial is extremely satisfactory (see Figure 2) and fully recovers the decay profile obtained by the direct integration given by eq 2.14.

Figure 1 is just an illustration of our approach. Similar conclusions can be obtained for self-avoiding walks. The approximation of the distribution function by a polynomial appears to be a useful method in the analysis of various

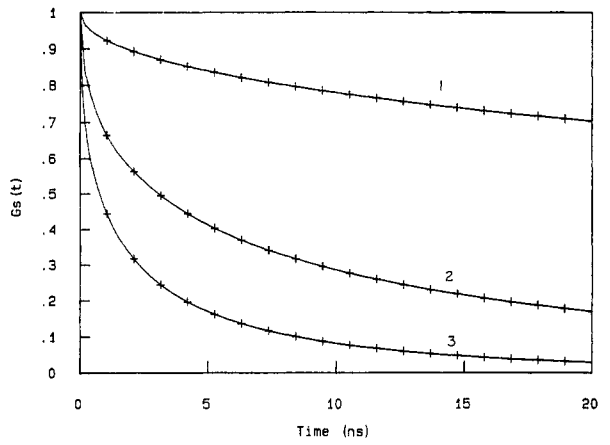

Figure 2. Donor fluorescence decay profiles for a three-dimensional system with a random distribution of chromophores for three different concentrations: (1) $c = 0.1$, (2) $c = 0.5$, and (3) $c = 1.0$. Solid lines were calculated from the exact solution (eq 2.12, and pluses denote the same decay profile calculated from eq 2.15 in which the Gaussian distribution function was approximated by a polynomial. The lifetime of donor fluorescence was assumed to be $\tau_{OD} = 20$ ns.

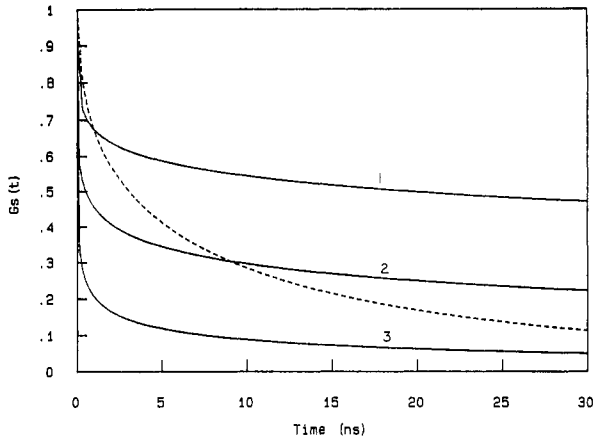

Figure 3. Donor fluorescence decay profiles for a randomly tagged monodisperse polymer with a mean-squared end-to-end distance $\langle R_N^2 \rangle^{1/2} = 37$ Å for three different concentrations of chromophores: (1) $c = 0.5$, (2) $c = 1.0$, and (3) $c = 2.0$. The broken line represents a donor fluorescence decay profile for uniformly and randomly distributed chromophores with concentration $c = 1.0$.

systems with the specific distribution of interacting molecules. In the next section we will illustrate this point.

B. Randomly Tagged Polymer. The problem of excitation transport between chromophores attached to the polymer and its relation to statistical properties of the polymer have been investigated in a number of papers.[2,3] Only in the case of oligopeptides[27] does one not have to deal with polydispersity effects since those biological macromolecules are monodisperse. However, in any other polymer system, even for so-called monodisperse polymers, one has to consider contributions from different fractions of molecular weight distribution. This remark applies especially to the energy-transfer or energy migration studies, of which observables are extremely sensitive to intermolecular distances. Before analyzing the influence of polydispersity on fluorescence decay of randomly tagged polymers, we shall analyze a monodisperse polymer.

The theoretical aspects of excitation transport between chromophores randomly attached to the polymer have been recently investigated by using a cumulant approach and a self-consistent approximation.[2] It has been shown that the cumulant approximation is correct at short times for the end-tagged polymer and for all times if the polymer contains a small number of noninteracting acceptors. In the case of the randomly tagged polymer, the ensemble-averaged probability of finding excitation on the originally excited chromophore is

$$\ln G^S(t) = -\Delta V_\Delta/2 \int_0^\infty P_N(r)\,[1 - \exp(-2k(r)\,t)]r^{\Delta-1}\,dr \quad (3.5)$$

where the distribution function, $P_N(r)$, is given by eqs 3.1 or 3.2.

Substituting eq 3.1 into eq 3.5, one can obtain

$$\ln G^S(t) = -\Delta V_\Delta/2 \sum_{i=0}^{\infty} a_i \alpha^{(i+\Delta)/n}/(i + \Delta)\,\Gamma[1 - (i+\Delta)/n] \quad (3.6)$$

At this point we underline the complex time dependence of donor fluorescence, which is expressed by the term $\alpha^{(i+\Delta)/n} \propto (t/\tau)^{(i+\Delta)/n}$. When we limit our considerations to three-dimensional space ($\Delta = 3$) and dipole–dipole interactions ($n = 6$), the time dependence of donor fluorescence is $(t/\tau)^{(i+3)/6}$, where i is the order of approximation of the polynomial. For a typical polymer, a good approximation of a distribution function can be obtained for a polynomial of third order, and, as one may notice, the time dependence of donor fluorescence is far from one expected for uniform and random distribution of molecules, which is $(t/\tau)^{1/2}$. Only one remark has to be added in regard to the Γ function in eqs 3.8 and 3.9. One can notice that if the order of the polynomial is $i \in (0,\infty)$, then the Γ function $\Gamma(1-(i+3)/6)$ has a pole for $i=3$ and at all negative integer values of its argument ($i = 9, 15, 21, \ldots$). There are two possible ways of avoiding infinite values of the Γ function at its poles. The first is by fitting a number of Gaussian distribution functions. We have observed that the contribution of coefficient a_3 is 4 orders of magnitude lower than the contribution of a_0 and 2 orders of magnitude lower than the contribution of a_1 and a_2. For that reason one can neglect terms in a polynomial approximation to a Gaussian distribution higher or equal to $i = 3$. The second way to avoid infinities is to fix the opposite sign for coefficients for which the Γ function has a pole. This procedure leads to elimination of infinities from the decay function. In the following calculations we have chosen the first method, which appears to be satisfactory for theoretical as well as experimental analysis. One can wonder about the convergence of eqs 3.6 and 2.15. The term that may lead to the problems with convergence of eq 3.6 is $\sum_{i=0}^{\infty} a_i (t/\tau)^{(i+\Delta)/n}$. If $i \to \infty$, then the term $(t/\tau)^{(i+\Delta)/n} \to \infty$ and the polynomial coefficients $a_i \to 0$. However, $a_i \to 0$ much faster than $(t/\tau)^{(i+\Delta)/n} \to \infty$. For that reason, the term $\sum_{i=0}^{\infty} (t/\tau)^{(i+\Delta)/n} \to 0$ for $i \to \infty$. The analysis of many distribution functions and the time dependence of fluorescence decay profiles has shown that eq 3.6 is converging very fast, and in the most of the cases third order of approximation is sufficient.

Figure 3 depicts fluorescence profiles of a randomly tagged polymer of which the distribution function is Gaussian with a mean-squared end-to-end distance $\langle R_N^2 \rangle^{1/2} = 37$ Å. One can notice that the fluorescence profile is very sensitive upon small variation of concentration. On the same figure, we have shown a donor fluorescence profile calculated from eq 2.14 under the assumption of uniform and random distribution of molecules in three-dimensional space. The distinct character of those profiles is evident.

C. Effect of Molecular Weight Distribution. In the above analysis we assumed that the polymer under

investigation is monodisperse. Nevertheless, in most of the cases, one has to deal with polydisperse polymers. At first glance, this basic property of polymers has an unpleasant complication. However, after a careful examination of the problem, one can observe that the polydispersity of polymers can be efficiently used in studies. Recently, we have illustrated this point of view in studies of fluorescence of poly(2-vinylnaphthalene).[28] In a similar way, one can investigate fluorescence from randomly tagged polymers or on an end-tagged polymer. However, in order to analyze the experimental data from a polydisperse sample, one has to know the respective equations describing the fluorescence phenomena.

As we mentioned in the Introduction, the number of different distribution functions has been proposed for polymers and one can choose a respective distribution function depending upon the specific situation. For the sake of simplicity, we will analyze the Schulz–Flory distribution.[29] Nevertheless, one can apply the proposed method for any kind of distribution function.

Recently, we have analyzed[30] the extent of the correlations between the squared radius of gyration and squared end-to-end distance, $\langle R_N^2 \rangle$, in random flight chains. Following Debye,[31] one can relate

$$\langle R_N^2 \rangle = Nl^2 \tag{3.7}$$

where N is the number of bonds of length l that connect $N + 1$ atoms of the same mass.

If the polymer sample can be characterized by the molecular weight distribution, $w(x_i)$, then the average probability, $\langle G^S(t) \rangle$, that the originally excited donor molecule is still excited at time t is given by

$$\langle G^S(t) \rangle = \sum_{i=1}^{\infty} w(x_i) / \sum w(x_i)\, G_i^S(t) \tag{3.8}$$

where the distribution function is assumed to be in the form proposed by Schulz–Flory[29]

$$w(x_i) = \beta^{k+1} x_i^k \exp(-\beta x_i)/\Gamma(k+1) \tag{3.9}$$

and $\beta = k/x_n$.

The numerical algorithm for calculation of eq 3.8 was organized in the following way. For given parameters as number, weight, and z average and polydispersity, the mean-squared end-to-end distance was calculated, and the obtained values have been used in the evaluation of respective coefficients in the polynomial approximation to the Gaussian distribution function. The obtained $G_i^S(t)$ functions were introduced into eq 3.8 and multiplied by the respective weights.

Figure 4 depicts fluorescence profiles of donor decay for several polydispersities and a constant number of chromophores attached to the chain. One can notice that an increase of polydispersity leads to faster decay of donor fluorescence, although the global influence of polydispersity is not very substantial, as we had anticipated. It appears that the observed faster decay of fluorescence results from an increasing contribution of fluorescence from short chains as the polydispersity of the sample is increasing.

IV. Final Remarks and Conclusions

We have described a theoretical model of excitation transport between chromophores randomly attached to the polymer. Several approximations have been proposed in order to obtain fluorescence decay profiles in their integrable form. The main assumption that we used was to approximate a Gaussian distribution function by a polynomial. It was shown that this kind of approximation is very useful and is retaining all specific parameters of the original distribution function. The numerical calculations presented in the paper serve as examples of the proposed method. Several applications of fluorescent transient measurements to study various polymeric systems with Gaussian distribution functions have been reported.[2,3,32] Presented in this paper, results can be used to simplify the analysis of experimental data. In a similar way one can investigate many other systems as end-tagged polymers, non-Gaussian random walks, the influence of the solvent, and fractal properties of polymers. The question of distribution functions at polymer interface can be addressed by using equations presented in this paper. The presented equations are in the closed form, and one can use them directly in the interpretation of experimental data.

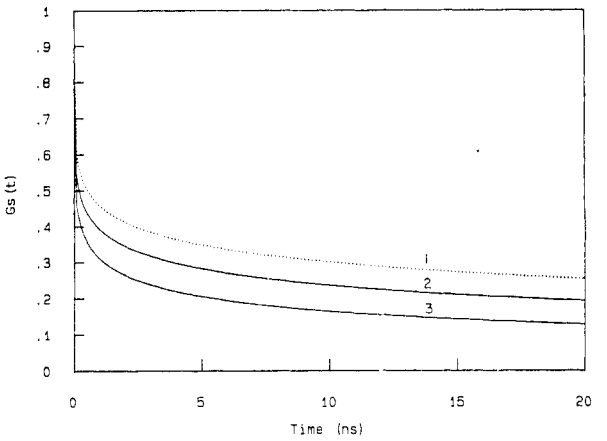

Figure 4. Donor fluorescence decay profiles for a randomly tagged monodisperse polymer (1) and a polydisperse polymer with (2) $P = M_v/M_n = 1.5$ and (3) $P = 2.0$. The concentration of chromophores was assumed to be $c = 1.0$ and the donor lifetime 20 ns. For a monodisperse polymer, $\langle R_N^2 \rangle^{1/2} = 27.14$ Å.

Acknowledgment. The author is grateful to the Departemént de physique—COPL, of the Université Laval, for financial support.

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