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Chemical Physics 274 (2001) 243–253

Chemical Physics

www.elsevier.com/locate/chemphys

Electronic energy transfer in linear polymers randomly labelled with chromophores

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Received 26 February 2001

Abstract

The fluorescence dynamics of chromophores randomly attached to an isolated flexible polymer chain was studied. For immobile chains (i.e., when the polymer chain conformation does not change during the excited state lifetime of the donor chromophore) analytical equations for the donor decay curves were obtained for both pseudo-ideal (Gaussian) and self-avoiding walk (SAW) polymer chain models. It is also concluded that the inhomogeneous broadening of chromophore spectra must be taken into account for ratios of the inhomogeneous to homogeneous spectral widths larger than 0.2. The luminescence of mobile chains was obtained in the limits of slow and fast diffusion. The donor-to-donor excited state transport was also studied for polymers randomly labeled with a single chromophore. The ensemble average probability that an originally excited chromophore is still excited at time *t* was obtained for frozen chains with both gaussian and SAW conformational distributions.

Keywords: Polymers; Fluorescence; Electronic energy transfer; Inhomogeneous broadening

1. Introduction

Polymers can exhibit intrinsic fluorescence (e.g. aromatic polymers) or extrinsic fluorescence after being labeled with fluorescence groups at specific sites. The fluorescence of polymers contains relevant structural and dynamical information on polymer systems, both in solution and in the bulk [1–3]. Particularly useful is the study of electronic energy transfer between identical and different chromophores attached to the polymer chain. In general, the energy transfer occurs by both short and long range interactions, but the long range dipole–dipole term is usually dominant [4]. The energy transfer rate by a dipole–dipole coupling mechanism has a $1/r^6$ dependence on the donor–acceptor separation r and for this reason the fluorescence decay curves strongly reflect the distribution of distances between the chromophores, providing relevant information on the conformation and dynamics of polymers. For moderate and high polymer densities, the fluorescence observables become more complex due to intermolecular energy transfer processes [1,5]. For this reason, experiments are generally performed under very

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PII: S0301-0104(01)00545-6

dilute conditions, allowing intermolecular excitation transfer to be neglected.

Some linear polymers contain donor and trap chromophores randomly distributed among the sites of the chain [2,5–11]. Usually, the occupancy of a particular site is independent of the type and number of chromophores substituted at other sites. Such polymers can be synthesized for instance by esterification of long chain dialcohols with acids containing a donor or an acceptor.

In this work, we begin by studying the direct, incoherent energy transfer from an electronically excited donor to acceptors randomly distributed along the chain backbone (Section 2.1). The fraction of sites occupied by donors is assumed to be small enough or the donor-to-donor energy transfer rate sufficiently low for the energy transport among donors to be negligible. The donor-to-donor excited state transport is also studied in Section 2.2, in the case of polymers randomly labeled with a single chromophore. We also take into account the inhomogeneous broadening of chromophore spectra in Section 2.3. The influence of polymer motion (conformation change by segmental diffusion) on energy transfer kinetics is next studied in Section 3. In all cases, we focus on a single polymer chain that is isolated from the other chains to avoid the interchain energy transfer processes. The polymers are assumed to have coil-like conformations, which implies the use of θ or good solvents to the polymer.

2. Static energy transfer

2.1. Donor-to-acceptor energy transfer

The electronic energy transfer rate by a dipole–dipole coupling mechanism between a donor and an acceptor separated by a distance r, is given by [4]

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

where τ the fluorescence lifetime of the donor in the absence of acceptors and R_0 is the Förster radius.

We will consider long polymer chains with chromophores sparsely and randomly attached to the backbone. Each segment (site) of the polymer chain can contain a chromophore with a probability $p \ll 1$, with $p = N/S$, where S is the total number of sites ($S \gg 1$) and N is the average number of acceptor chromophores in a chain. For long chains, this number (N) is subject to negligible statistical variation. However, many different donor–acceptor configurations exist, owing to the random character of the labeling procedure. The chains are supposed to be long enough so that all donor sites are equivalent, i.e., chain end contributions are negligible. Each chain contains one or more concretizations (as many as the donors) of the general configuration around a donor $K = \{x_1, x_2, \ldots, x_S\}$, where the x_j ($j = 1, 2, \ldots, S$) are two-valued independent random variables taking a zero value (empty site) with probability $1 - p$ and a 1 value (filled site) with probability p. Following the procedure developed in [12–15], the time evolution of the survival probability $P(t)$ of an electronically excited donor, in the absence of excitation transport among donors, corresponding to an acceptor configuration K and to a polymer chain conformation C, is

$$P_{C,K}(t) = \prod_{j=1}^{S} \exp\left[-tw\left(r_j^{(C)}\right)x_j^{(K)}\right], \tag{2}$$

where $w(r_j^{(C)})$ is the energy transfer rate constant between donor and the acceptor at site j, that for conformation C are at a distance $r_j^{(C)}$. For this configuration K, averaging over all chain conformations C gives, under the assumption that the distances between donor and different acceptors are uncorrelated,

$$P_K(t) = \prod_{j=1}^{S}\left\{\int_0^\infty g_j(r)\exp\left[-tw(r)x_j^{(K)}\right]\mathrm{d}r\right\}, \tag{3}$$

where $g_j(t)$ is the distribution function for the distances between donor and the acceptor at site j. The independence assumption mentioned should hold approximately for a sparse occupation of sites, i.e., when the average distance between two consecutive acceptors is large.

Finally, averaging over configurations K yields,

$$P(t)=\prod_{j=1}^{S}\left\{(1-p)+p\int_0^\infty g_j(r)\exp[-tw(r)]\,\mathrm{d}r\right\}. \tag{4}$$

Note that the previous two averages commute, i.e., their order is immaterial. Under the assumption that $p \ll 1$, Eq. (4) becomes

$$P(t)=\exp\left[-p\int_0^\infty\sum_{j=1}^{S}g_j(r)(1-\exp[-tw(r)])\,\mathrm{d}r\right] \tag{5}$$

or

$$P(t)=\exp\left[-N\int_0^\infty g(r)(1-\exp[-tw(r)])\,\mathrm{d}r\right] \tag{6}$$

with

$$g(r)=\frac{1}{S}\sum_{j=1}^{S}g_j(r) \tag{7}$$

The function $g(r)$ is thus the average distance density distribution, and is expected to approach some limiting function $g_\infty(r)$ as the polymer chain length (and therefore S) increases.

The intrinsic processes of deactivation of the donor were not considered thus far in order not to surcharge the equations. Nevertheless, as these processes are independent of the energy transfer events, they are easily considered by multiplication of the final expressions by the intrinsic donor decay, $\exp(-t/\tau)$.

The distance between any two not-so-close sites of a polymer chain obeys the same distribution as the chain end-to-end distance, $g_S(r)$ [16]. Therefore, for a sufficiently long chain, it follows from Eq. (7) that $g(r)=g_\infty(r)=g_S(r)$. For a polymer chain in a θ solvent (pseudo-ideal chain), the chain end-to-end distance is given by [16,17]

$$g_S(r)=4\pi r^2A_1\exp(-B_1r^2) \tag{8}$$

with

$$A_1=\left(\frac{3}{2\pi\langle R_S^2\rangle}\right)^{3/2},\qquad B_1=\frac{3}{2\langle R_S^2\rangle}. \tag{9}$$

In good solvents, the polymer chain conformation is described by a self-avoiding walk (SAW) in a lattice. The distribution function is no longer gaussian as in a θ solvent, being then [16,17]

$$g_S(r)=4\pi r^2A_2r^{5/18}\exp(-B_2r^{5/2}) \tag{10}$$

with

$$A_2=0.289058/\langle R_S^2\rangle^{59/36}$$

and

$$B_2=1.22271/\langle R_S^2\rangle^{5/4}, \tag{11}$$

where $\langle R_S^2\rangle$ is the average square end-to-end distance: $\langle R_S^2\rangle=Sl^2$ for a pseudo-ideal chain, and $\langle R_S^2\rangle=S^{6/5}l^2$ for a SAW chain, l being the statistical segment length (Kuhn length).

Fig. 1 shows the distribution function $g(x)$ versus the reduced distance $x=r/\sqrt{\langle R_S^2\rangle}$ for both pseudo-ideal (Eq. (8)) and SAW chains (Eq. (10)). The polymer chain in a good solvent (SAW chain) is more expanded than in a θ solvent and has a correlation hole for short distances ($g_S(0)=0$). These distribution functions mimic well (within 2%) computer simulation data and their accuracy is in general sufficient to describe the conformations of real polymer chains [16].

For a dipole–dipole interaction mechanism and a pseudo-ideal polymer chain, Eq. (6) becomes

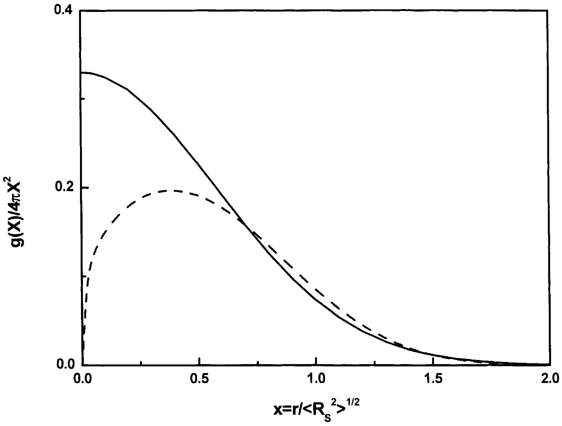

Fig. 1. Reduced distance distribution functions for a pseudo-ideal (solid line) and SAW (dashed line) polymer chains.

$$P_{\mathrm{id}}(t) = \exp\left[-6\Gamma\left(\frac{2}{3}\right)p\frac{R_0^2}{l^2}\left(\frac{t}{\tau}\right)^{1/3}\right] = \exp\left[-8.125p\frac{R_0^2}{l^2}\left(\frac{t}{\tau}\right)^{1/3}\right] \tag{12}$$

while for a SAW chain,

$$P_{\mathrm{SAW}}(t) = \exp\left[-3.872p\left(\frac{R_0}{l}\right)^{5/3}\left(\frac{t}{\tau}\right)^{23/54}\right]. \tag{13}$$

The time evolutions of the excited donor survival probability, $P(t)$, for both a pseudo-ideal chain and a SAW chain are plotted in Fig. 2 for $R_0/l = 2$ and $p = 0.01$. The pseudo-ideal chain has an initial fast decay, which is strongly attenuated in the SAW chain. This results from the shape of the distribution function $g_S(r)$ at short donor–acceptor distances. As mentioned, the distribution function $g_S(r)$ has a correlation hole at short donor–acceptor distances for the SAW chain, which does not exist in the pseudo-ideal chain case (see Fig. 1 and Eqs. (8) and (10)). Fast energy transfer processes between donor–acceptor pairs at small distances occur in the pseudo-ideal chain but not in the SAW chain.

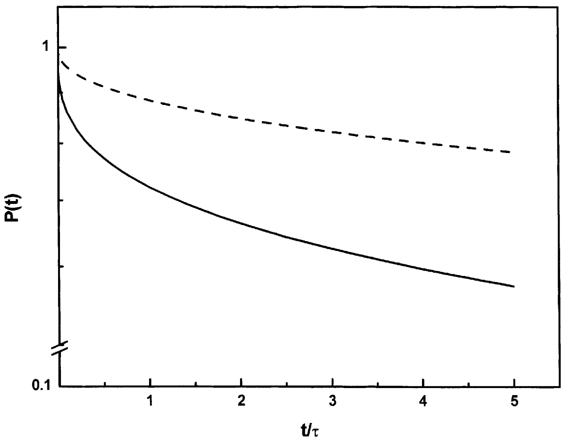

Fig. 2. Survival probability of donor excited molecules, $P(t)$, versus t/τ, for a pseudo-ideal (solid line) and SAW (dashed line) polymer chains in static regime. $R_0/l = 2$, $p = 0.01$.

2.2. Donor-to-donor transfer

The fundamental quantity for the donor-to-donor excited state transport is $G^S(t)$, the ensemble-average probability that an originally excited chromophore is still excited at time t. $G^S(t)$ contains contributions from excitations that never leave the originally excited chromophore and from excitations that return to the initially excited chromophore after one or more energy transfer events. $G^S(t)$ is related to time-resolved fluorescence depolarization measurements by $r(t) = r_0G^S(t)$, where $r(t)$ is the anisotropy of fluorescence and r_0 is the anisotropy at the initial time [5,11,18].

Considering two donors, 0 and 1, attached to the polymer chain and separated by a distance r_1, the evolution of the respective survival probabilities obeys the following coupled differential equations,

$$\frac{\mathrm{d}}{\mathrm{d}t}P_0(r_1,t) = -w(r_1)[P_0(r_1,t) - P_1(r_1,t)], \tag{14a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}P_1(r_1,t) = w(r_1)[P_0(r_1,t) - P_1(r_1,t)]. \tag{14b}$$

The solution to these equations, on the assumption that the donor 0 is excited at time zero with a probability 1, is well known,

$$P_0(r_1,t) = \frac{1}{2}(1 + \exp[-2tw(r_1)]), \tag{15}$$

where $G^S(t)$ can be obtained in the limit of the Huber approximation [19,20] as the ensemble-averaged product for all donor–donor pairs (every pair contains initially an excited donor). Then, instead of Eq. (3) one has

$$G_K^S(t) = \prod_{j=1}^{M}\left\{\frac{1}{2}\left(1 + \int_0^\infty g_j(r)\exp\left[-2tw(r)x_j^{(K)}\right]\mathrm{d}r\right)\right\}, \tag{16}$$

where M is the number of possible pairs between a given donor and all other donors (which is equal, for large M, to the number of donors attached to the polymer chain). Averaging of Eq. (16) over configurations gives

$$G^S(t) = \exp\left[-\frac{p}{2}\int_0^\infty \sum_{j=1}^{S} g_j(r)(1-\exp[-2tw(r)])\right]$$
$$= \exp\left[-\frac{M}{2}\int_0^\infty g(r)(1-\exp[-2tw(r)])\right]. \tag{17}$$

This equation can be obtained from Eq. (6) by the substitution of N by $M/2$ and $w(r)$ by $2w(r)$. For the dipole–dipole interaction mechanism, the integrals in Eq. (17) can be calculated exactly, as before. Therefore, for the pseudo-ideal polymer chain,

$$G^S_{\rm id}(t) = \exp\left[-3\cdot 2^{1/3}\Gamma\left(\frac{2}{3}\right)p\frac{R_0^2}{l^2}\left(\frac{t}{\tau}\right)^{1/3}\right]$$
$$= \exp\left[-5.118p\frac{R_0^2}{l^2}\left(\frac{t}{\tau}\right)^{1/3}\right]. \tag{18}$$

This equation was previously obtained in the framework of the Huber approximation [8,10] and using the GAF method in the two-particle approximation [11]. The three-particle approximation of the GAF method gives an exponential increase of $G^S(t)$ at long times [21]. This is a usual problem of the GAF method in systems of low dimensionality [22].

For the SAW chain, we obtain from Eqs. (10) and (17),

$$G^S_{\rm SAW}(t) = \exp\left[-2.347p\left(\frac{R_0}{l}\right)^{5/3}\left(\frac{t}{\tau}\right)^{23/54}\right]. \tag{19}$$

2.3. Inhomogeneous broadening

The decay curves of polymers bearing fluorescent groups can be influenced by the inhomogeneous broadening of both the donor and the acceptor spectra [3]. In this case the fluorescence decays, at a given temperature, are dependent on both the excitation wavelength and the pulse spectral width. We will now try to determine at which ratio between inhomogeneous, σ, and homogeneous, δ, widths of spectral broadening this influence becomes noticeable.

In the case of inhomogeneous spectral broadening, the donor survival probability, $P_{\rm inh}(t)$ (under non-selective excitation), can be written as (compare with Eq. (6)),

$$P_{\rm inh}(t) = \int {\rm d}E_1 g_{\rm D}(E_1)\exp\left[-p\int {\rm d}E_2 g_{\rm A}(E_2)\right.$$
$$\left.\times\int_0^\infty \sum_{j=1}^{S} g_j(r)\left(1-{\rm e}^{-tw(E_1-E_2,r)}\right){\rm d}r\right], \tag{20}$$

where $w(E_1-E_2,r)$ is the rate of energy transfer from a donor to an acceptor having transition energies E_1 and E_2, respectively, and $g_{\rm D}(E_1)$ and $g_{\rm A}(E_2)$ are the normalized distributions of donor and acceptor transition energies. We will consider gaussian distributions with a common width, σ, and maxima located at transition energies $E_{\rm D}$ and $E_{\rm A}$, respectively

$$g_{\rm D}(E) = \frac{1}{\sqrt{2\pi}\sigma}\exp\left[-\frac{(E_{\rm D}-E)^2}{2\sigma^2}\right], \tag{21a}$$

$$g_{\rm A}(E) = \frac{1}{\sqrt{2\pi}\sigma}\exp\left[-\frac{(E_{\rm A}-E)^2}{2\sigma^2}\right] \tag{21b}$$

and that the homogeneous spectra of emission of donors and absorption of acceptors have also a Gaussian shape of width, $\delta/\sqrt{2}$. Then the rate of energy transfer by the dipole-dipole mechanism (being proportional to the overlap integral of the spectra [4]) can be written as

$$w(E_1-E_2,r) = \frac{1}{\tau}\left[\frac{R(E_1-E_2)}{r}\right]^6 \tag{22a}$$

with

$$R^6(E_1-E_2) = R_0^6\exp\left[-\frac{(E_1-E_2)^2}{\delta^2}+\left(\frac{\Delta E}{\delta}\right)^2\right], \tag{22b}$$

where $\Delta E = E_{\rm D}-E_{\rm A}$ and R_0 is the Förster radius for the energy transfer from a donor to an acceptor having transition energies $E_2 = E_{\rm D}$ and $E_1 = E_{\rm A}$.

Introducing Eq. (22a), (22b) into Eq. (20), after evaluation of the integrals as in Section 2.1, we obtain for a pseudo-ideal polymer chain

$$P_{\mathrm{inh}}(t)=\int \mathrm{d}E_1 g_{\mathrm{D}}(E_1)\exp\left[-8.125p\frac{R_0^2}{l^2}\left(\frac{t}{\tau}\right)^{1/3}\times\int \mathrm{d}E_2 g_{\mathrm{A}}(E_2)\exp\left(-\frac{(E_1-E_2)^2}{3\delta^2}+\frac{\Delta E^2}{3\delta^2}\right)\right]. \tag{23}$$

Fig. 3 shows the results of the numerical integration of Eq. (23) for $E_{\mathrm{D}}=E_{\mathrm{A}}(\Delta E=0)$. It can be seen that the increase of inhomogeneous broadening (the ratio σ/δ) slows down the donor decay, because the broadening decreases the rate of energy transfer for all donor–acceptor pairs.

The donor decay was also calculated for $E_{\mathrm{D}}-E_{\mathrm{A}}=2\sigma$ and the results plotted in Fig. 4. The decay is faster at the beginning, slowing down for long times, because the rate of energy transfer increases for donor–acceptor pairs with $E_1-E_2<E_{\mathrm{D}}-E_{\mathrm{A}}$ and decreases for pairs with $E_1-E_2>E_{\mathrm{D}}-E_{\mathrm{A}}$. In any case, the influence of inhomogeneous broadening becomes significant only for $\sigma/\delta>0.2$.

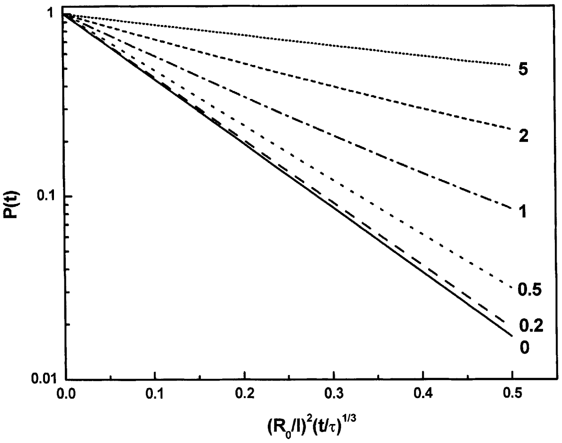

Fig. 3. Survival probability of donor excited molecules, $P(t)$, versus t/τ for a pseudo-ideal polymer chain calculated in the case of inhomogeneous spectra broadening. Maximum of the fluorescence spectrum of the donor and absorption spectrum of the acceptor chromophores are situated at the same transition energy ($E_{\mathrm{D}}=E_{\mathrm{A}}$). The values on each curve are the ratios between inhomogeneous and homogeneous widths of spectral broadening (σ/δ). $R_0/l=2,\ p=0.01$.

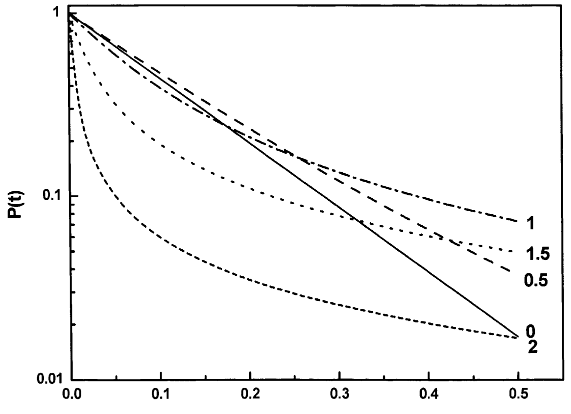

Fig. 4. Survival probability of donor excited molecules, $P(t)$, versus t/τ for a pseudo-ideal polymer chain calculated in the case of inhomogeneous spectral broadening. Maxima of the fluorescence spectrum of the donor and absorption spectrum of the acceptor chromophores are situated at the different transition energies ($E_{\mathrm{D}}=E_{\mathrm{A}}+2\sigma$). The values on each curve are the ratios between inhomogeneous and homogeneous widths of spectral broadening (σ/δ). $R_0/l=2,\ p=0.01$.

3. Polymer dynamics

The donor survival probability can be written in a general form that is suitable for considering the influence of chain motion. We begin by noting that for a given configuration K one may write

$$P_K(t)=\prod_{j=1}^{S}\left\langle \exp\left[-\int_0^t w(r_j)\,\mathrm{d}r_j x_j^{(K)}\right]\right\rangle, \tag{24}$$

where the angular brackets represent a time-dependent ensemble average, since for a single donor–acceptor pair $r_j(t)$ is a stochastic process.

Averaging over all configurations K one gets,

$$P(t)=\prod_{j=1}^{S}\left\{(1-p)+p\left\langle \exp\left[-\int_0^t w(r_j)\,\mathrm{d}r_j\right]\right\rangle\right\} \tag{25}$$

and for small p,

$$P(t) = \exp\left\{ -p\sum_{j=1}^{S}\left\langle 1 - \exp\left[-\int_0^t w(r_j)\,\mathrm{d}r_j \right]\right\rangle\right\}. \tag{26}$$

For a static system, the ensemble averages are time-independent, reducing to averages over distances, and Eq. (5) is received. In the general case, it is useful to define the random variable

$$w_j(t) = \frac{1}{t}\int_0^t w(r_j)\,\mathrm{d}r_j \tag{27}$$

allowing to rewrite Eq. (26) as

$$P(t)=\exp\left\{ -p\sum_{j=1}^{S}\left(1-\int_0^\infty f_j(w,t)\exp(-wt)\,\mathrm{d}w\right)\right\}, \tag{28}$$

where $f_j(w,t)$ is the density function for $w_j(t)$. For $t = 0$, the static case is recovered, i.e., $f_j(w,0)$ can be computed from $g_j(r)$, taking into account Eq. (1). On the other hand, for long times ergodicity is fulfilled and the time average and the ensemble average become identical,

$$\lim_{t\to\infty} w_j(t) = w_j(\infty) = \langle w_j\rangle = \int_0^\infty w(r)g_j(r)\,\mathrm{d}r \tag{29}$$

hence

$$f_j(w,\infty) = \delta[w - w_j(\infty)]. \tag{30}$$

Now, Eq. (28) can be rewritten as

$$P(t) = \exp\left\{-N\int_0^\infty f(w,t)[1-\exp(-wt)]\,\mathrm{d}w\right\} \tag{31}$$

with

$$f(w,t) = \frac{1}{S}\sum_{j=1}^{S} f_j(w,t). \tag{32}$$

For sufficiently long times, and using Eq. (30), Eq. (31) becomes,

$$P(t) = \exp\left\{ -p\sum_{j=1}^{S}[1-\exp(-w_j(\infty)t)]\right\}. \tag{33}$$

Usually, this limiting form is of little importance, because it corresponds to a very late stage of the decay, where the intensity is negligible. However, Eq. (33) is obeyed for all times of interest in case of very fast diffusion, the so-called rapid diffusion limit [23].

The treatment of cases intermediate between the static one and the rapid diffusion limit must be based on Eq. (28). In order to proceed from Eq. (28), we note that the rate distribution function $f_j(w,t)$ can be written as

$$f_j(w,t) = \int_0^\infty\int_0^\infty G_j(r,t|r_0)f_j(w,t|r,r_0)\,\mathrm{d}r\,\mathrm{d}r_0, \tag{34}$$

where $G_j(r,t|r_0)$ is the (normalized) Green function of the pair diffusion equation, giving the probability of finding a pair at distance r for time t, given that the initial distance was r_0, and $f_j(w,t|r,r_0)$ is the distribution of time-averaged rate constants at time t, given that the initial distance was r_0 and that the distance at time t is r. In this way, the integral that appears in Eq. (28), $\int_0^\infty f_j(w,t)\exp(-wt)\,\mathrm{d}w$, and whose meaning is the survival probability for a pair, can be rewritten as $\int_0^\infty g_j(r,t)\,\mathrm{d}r$, where

$$g_j(r,t) = \int_0^\infty\int_0^\infty G_j(r,t|r_0)f_j(w,t|r,r_0) \times \exp(-wt)\,\mathrm{d}w\,\mathrm{d}r_0. \tag{35}$$

According to the Feynman–Kac theorem, see e.g. [24], the function $g_j(r,t)$ obeys a modified diffusion equation. In order to consider the influence of polymer motion an appropriate model for the polymer chain should be chosen. A simple one is the Rouse–Zimm model [25,26], that consider the polymer chain as a system of n beads connected by $n-1$ harmonic springs. The mass is concentrated in the beads that move in solution with a friction coefficient, ξ. The Rouse–Zimm model includes both the hydrodynamic interactions and the excluded volume interactions that were disregarded in the primitive Rouse model. The hydrodynamic interactions result from the fact that the flow field at a given bead is perturbed by the spring forces on the other beads, transmitted through the solvent. Both models predict a spectrum of relaxation times characteristic of large scale as well as short scale diffusive motions. In our case only the large scale diffusive motions are relevant, which simplifies the problem. The very simple harmonic spring model (two beads connected by a spring) can then be used to describe the dynamics. When the distance between chromophores attached at the polymer chain ends change by small steps compared to R_0, the distribution function, $g_j(r,t)$ obeys the following diffusion equation [27–32],

$$\frac{\partial}{\partial t} g_j(r,t) = D\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} g_j(r,t) + D\frac{1}{r^2}\frac{\partial}{\partial r} \times \left(r^2 g_j(r,t) \frac{\partial V_j}{\partial r} \right) - w(r) g_j(r,t), \quad (36)$$

where D is the mutual diffusion coefficient of the chain ends, and

$$V_j(r) = U_j(r)/kT = -\ln g_j(r), \quad (37)$$

where $U_j(r)$ is a pseudo-potential of interaction between the beads, k is the Boltzmann constant and T the absolute temperature. The first two terms on the right side of Eq. (36) describe the evolution of the distribution function $g_j(r,t)$ owing to brownian motion while the third one takes into account the decrease of the number of pairs owing to the energy transfer events. The time evolution of the distribution function was obtained by integration of the differential Eq. (36) with the boundary and initial conditions,

$$\frac{\partial}{\partial r} g_j(r,t) + \frac{\partial}{\partial r} V_j(r)\Big|_{r=a} = 0, \quad (38a)$$

$$g_j(r,0) = g_j(r), \quad (38b)$$

where a is the distance of closest approach and $g_j(r)$ is the equilibrium distribution. The reflection boundary condition ensures that the chromophores cannot approach closer than the distance a.

The calculation of a general analytical expression for the donor decay in the presence of diffusion is impracticable since the general solution of the diffusion equation for $g(r,t)$ is unknown. Nevertheless, approximate solutions can be obtained in the limits of slow and fast diffusion. In the slow diffusion limit, the diffusion equation was solved using the method used by us in [33] (see Appendix A). The distribution function was obtained as an iteration row with the diffusion constant D as the small parameter. Considering only the zero-order approximation and the first-order correction term, the survival probability of excited donors for a pseudo-ideal chain is given by,

$$P^{\mathrm{id}}(t) = \exp\left[-8.125p\frac{R_0^2}{l^2}\left(\frac{t}{\tau}\right)^{1/3} - 12p\frac{Dt}{l^2} \right] \quad (39)$$

while for the SAW chain

$$P^{\mathrm{SAW}}(t) = \exp\left[-3.872p\left(\frac{R_0}{l}\right)^{5/3}\left(\frac{t}{\tau}\right)^{23/54} - 6.535p\frac{D\tau}{l^2}\left(\frac{l}{R_0}\right)^{1/3}\left(\frac{t}{\tau}\right)^{17/18} \right]. \quad (40)$$

Eqs. (39) and (40) are valid when the second term in the square brackets is smaller than the first one during the intrinsic donor lifetime, τ. This means that the inequality $D\tau < R_0^2$ must be fulfilled. The first terms of Eqs. (39) and (40) describe the static energy transfer while the second ones are the first-order corrections due to the diffusion of polymer chain ends. The decays are faster in the presence of diffusion, because the motion of polymer segments approaches excited donors and acceptors, compensating for the depletion due to the energy transfer events.

In the static case, $g_j(r,t)$ can be obtained directly from Eq. (35) with

$$G_j(r,t|r_0) = \delta(r - r_0) g_j(r_0) \quad (41)$$

and

$$f_j(w,t|r,r_0) = \delta(w - w_0), \quad (42)$$

where $w_0 = w(r_0)$, and Eq. (5) is recovered from Eq. (28). In the rapid-diffusion limit ($D \to \infty$) [30], one has

$$G_j(r,t|r_0) = g_j(r) \quad (43)$$

and

$$f_j(w,t|r,r_0) = \delta[w - w_j(\infty)] \quad (44)$$

hence

$$g_j(r,t) = g_j(r)\exp[-w_j(\infty)t] \quad (45)$$

and Eq. (33) is recovered.

For the real distribution functions the integral in Eq. (33) does not have analytical solution. In order to obtain an analytical expression, $g_j(r)$ was approximated by a rectangular function with width equal to $\sqrt{\langle R_j^2 \rangle}$ and $a \ll \sqrt{\langle R_j^2 \rangle}$. Under this approximation, for a pseudo-ideal polymer chain ($\langle R_j^2\rangle = jl^2$),

$$w_j^{\mathrm{id}}(\infty) = \frac{1}{\tau}\frac{R_0^6}{a^3\langle R_g^2\rangle^{3/2}} = \frac{1}{\tau}\frac{R_0^6}{a^3 l^3 j^{3/2}} \tag{46}$$

and

$$\begin{aligned} P^{\mathrm{id}}(t) &= \exp\left[-\frac{8\pi}{3\sqrt{3}\Gamma(5/3)}p\frac{R_0^4}{a^2l^2}\left(\frac{t}{\tau}\right)^{2/3}\right] \\ &= \exp\left[-5.358p\frac{R_0^4}{a^2l^2}\left(\frac{t}{\tau}\right)^{2/3}\right] \end{aligned} \tag{47}$$

while for the SAW chain ($\langle R_j^2\rangle = j^{6/5}l^2$)

$$\begin{aligned} w_j^{\mathrm{SAW}}(\infty) &= \frac{1}{\tau}\frac{R_0^6}{a^{3-5/18}\langle R_g^2\rangle^{(3+5/18)/2}} \\ &= \frac{1}{\tau}\frac{R_0^6}{a^{3-5/18}l^{3+5/18}j^{59/30}}, \end{aligned} \tag{48}$$

$$\begin{aligned} P^{\mathrm{SAW}}(t) &= \exp\left[-\frac{60\pi}{59\Gamma(89/59)\sin(30\pi/59)} \times p\left(\frac{R_0^6}{a^{3-5/18}l^{3+5/18}}\frac{t}{\tau}\right)^{30/59}\right] \\ &= \exp\left[-3.605p\left(\frac{R_0^6}{a^{3-5/18}l^{3+5/18}}\frac{t}{\tau}\right)^{30/59}\right]. \end{aligned} \tag{49}$$

The donor decay is not exponential even in the limit of very fast diffusion (see Eq. (33)). This is due to the fact that several acceptor configurations K exist, each with its own exponential decay in the limit of rapid diffusion. Nevertheless, diffusion, however fast, cannot interconvert configurations. Hence, the global decay is non-exponential, as it results from the averaged sum of the decays corresponding to the different configurations.

4. Conclusions

The fluorescence dynamics of chromophore-labeled polymers with energy donors and acceptors randomly distributed along the chain backbone was studied. The donor–acceptor energy transfer is irreversible and the energy migration among donors was neglected. For frozen chains (the spatial conformation of the chain does not change during the decay process), analytical expressions for the donor decay for both pseudo-ideal and SAW chains were obtained. For mobile chains analytical expressions were obtained in the limiting cases of fast and slow diffusion. It was demonstrated that the inhomogeneous broadening of chromophore spectra influences the decay curves when the width of inhomogeneous broadening, σ, is larger than 0.2δ, where δ is the width of homogeneous broadening. The donor-to-donor excited state transport was also studied for randomly labeled polymers with a single chromophore. The ensemble average probability that an originally excited chromophore is still excited at time t was obtained for frozen chains with both gaussian and SAW conformations.

Acknowledgements

This work was supported by Fundação para a Ciência e a Tecnologia, FCT (Portugal) through project POCTI 34836/FIS/2000. E.N.B. acknowledges an INVOTAN fellowship (ICCTI, Portugal).

Appendix A

To obtain approximate analytical results when diffusion is slow (small D) Eq. (36) is rewritten as follows:

$$\frac{\partial}{\partial t}g_j(r,t) = (\hat{A}+\hat{B})g_j(r,t), \tag{A.1}$$

where $\hat{A}$ and $\hat{B}$ are operators

$$\hat{B}_j = D\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + D\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial V_j}{\partial r} \tag{A.2}$$

and

$$\hat{A} = -w(r). \tag{A.3}$$

The formal solution of Eq. (A.1) is

$$g_j(r,t) = \mathrm{e}^{\hat{A}t}g_j(r) + \int_0^t \mathrm{e}^{\hat{A}(t-u)}\hat{B}_j\mathrm{e}^{\hat{A}u}g_j(r)\,\mathrm{d}u. \tag{A.4}$$

Considering that the operator $\hat{B}_j$ is small in comparison with $\hat{A}$, and using Eq. (A.4), one can obtain the solution, $g_j(r,t)$, in iterative form

$$g_j(r,t) = g_j^{(0)}(r,t) + g_j^{(1)}(r,t) + g_j^{(2)}(r,t) + \cdots \tag{A.5}$$

In the zero-order approximation we have

$$g_j^{(0)}(r,t) = \mathrm{e}^{\hat{A}t} g_j(r). \tag{A.6}$$

The correction of first order is

$$g_j^{(1)}(r,t) = \int_0^t \mathrm{e}^{\hat{A}(t-u)} \hat{B}_j g_j^{(0)}(r,u)\,\mathrm{d}u. \tag{A.7}$$

The correction of second order is

$$g_j^{(2)}(r,t) = \int_0^t \mathrm{e}^{\hat{A}(t-u)} \hat{B}_j g_j^{(1)}(r,u)\,\mathrm{d}u \tag{A.8}$$

and so on. In accordance with Eq. (28) we obtain the iteration row for luminescence kinetics

$$P(t) = \exp[-p(f^{(0)}(t) + f^{(1)}(t) + f^{(2)}(t) + \cdots)], \tag{A.9}$$

where

$$f^{(0)}(t) = \sum_{j=1}^{S} \left(1 - \int_a^\infty g_j^{(0)}(r,t)\,\mathrm{d}r\right), \tag{A.10a}$$

$$f^{(1)}(t) = -\sum_{j=1}^{S} \int_a^\infty g_j^{(1)}(r,t)\,\mathrm{d}r, \tag{A.10b}$$

$$f^{(2)}(t) = -\sum_{j=1}^{S} \int_a^\infty g_j^{(2)}(r,t)\,\mathrm{d}r. \tag{A.10c}$$

It is known [10,11] that for a pseudo-ideal polymer chain

$$\sum_{j=1}^{S} g_j(r) = \frac{12r}{l^2} \tag{A.11}$$

while for a SAW chain,

$$\sum_{j=1}^{S} g_j(r) = \frac{C}{l}\left(\frac{r}{l}\right)^{2/3} \tag{A.12}$$

with

$$C = \frac{10\Gamma\left(\frac{29}{45}\right)\Gamma\left(\frac{19}{9}\right)^{23/18}}{3\Gamma\left(\frac{59}{45}\right)^{41/18}} \cong 6.37706, \tag{A.13}$$

where $\Gamma(z)$ being the gamma function.

Introducing these results in Eqs. (A.6) and (A.7), the first two terms $f^{(0)}(t)$ and $f^{(1)}(t)$ were calculated, which after being introduced in Eq. (A.9) yielded Eqs. (39) and (40).

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