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Dynamics of electronic energy transfer in linear chain polymers

E.N. Bodunov, M.N. Berberan-Santos *, J.M.G. Martinho

Centro de Química-Física Molecular, Instituto Superior Técnico, 1049-001 Lisboa, Portugal

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Abstract

The influence of chain conformational motion and of inhomogeneous broadening on the kinetics of incoherent energy transport in linear polymer chains is considered. The main results obtained are: (i) A simple expression for the donor decay law in the static case. (ii) Also in the static case, it is concluded that inhomogeneous broadening affects the dynamics of incoherent energy transport if the width of inhomogeneous broadening is larger than kT. (iii) Chain conformational motion becomes important if the average time for conformational change is much shorter than the intrinsic lifetime. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Electronic excitation transport and transfer between chromophores attached to polymer chains has been widely studied and used as a structural probe [1,2]. The time dependence of the donor and trap fluorescence intensities following pulse excitation can be related to the interchromophore separation through the Förster transfer rate [3]. Such experiments are generally performed under very dilute conditions, allowing interchain transfer to be neglected.

There are several different types of chromophore attachment to a linear polymer chain [1,2,4–18]. In the situation to be discussed, the following is considered. The polymer chains contain donor and acceptor chromophores, the distribution of donor chromophores along the chain is regular, while the trap (acceptor) distribution is random and its concentration is small. For polymer solutions in good solvents, the chain adopts an extended conformation and the energy transport can be considered as occurring in a one-dimensional lattice [1,2,12–18]. The chromophore can be part of the backbone, as in aromatic polymers (e.g. polystyrene) or can be covalently attached to it.

The aim of this Letter is to study the direct, incoherent energy transfer from an electronically excited donor to other donor or acceptor molecules in the above conditions. Both the influence of inhomogeneous broadening of chromophore spectra and of polymer conformational motion on energy transfer kinetics is investigated.

2. Static regime

The polymer molecule is assumed to consist of two types of sites: traps (acceptors, for example excimer-forming sites), distributed randomly along the linear chain, and nontraps (donors or monomer sites), distributed regularly along the chain.

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* Corresponding author.

E-mail address: berberan@ist.utl.pt (M.N. Berberan-Santos).

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The traps are in small concentration; the bulk of the chain consists of nontrap sequences of donor sites. The trap distribution over the polymer chain is fixed in the time scale of interest (rotational motion of monomers which leads to excimer formation is frozen).

The exciton is modeled as a particle executing a symmetric one-dimensional Markovian random walk on a region which has the same number of sites as the polymer molecule has donor units. Only nearest-neighbour transfers are considered (the polymer is supposed to be well above its θ-temperature, a temperature at which the chain end-to-end distribution is Gaussian). The exciton is assumed to have an equal probability of beginning at any site on the chain. All hop probabilities are assumed to be identical, and equal to the average jump probability per unit time, W. For any hop, the exciton has also a probability of decay (radiatively or nonradiatively) instead of hopping to a neighbouring site. This probability is assumed to be site independent and equal to that of the monomeric model compound. It is usually assumed that the rate constant for energy transfer from a donor to an acceptor, V, is equal to W. This is a reasonable approximation if the trap is an excimer-forming site.

The exact solution for the normalized donor decay law is known [1,12,14]

$$I(t) = \sum_{n=1}^{\infty} c^2 n (1-c)^{n-1} G_n^{\mathrm{D}}(t), \tag{1}$$

$$G_n^{\mathrm{D}}(t) = \frac{2}{n(n+1)} \sum_{k=1}^{n^*} \cot^2\left(\frac{\alpha_k}{2}\right) \times \exp\left[-4Wt\sin^2\left(\frac{\alpha_k}{2}\right)\right], \tag{2}$$

where c is the fraction of sites containing acceptors, $c \leqslant 1$, and $\alpha_k = (2k-1)\pi/(n+1)$, $n^* = n/2$ if n is even and $n^* = (n+1)/2$ if n is odd (n is the number of sites in a segment containing only donors, i.e., enclosed between two traps).

Eq. (1) does not include the loss of excitation due to intrinsic decay because this channel is independent of the energy transfer and thus the overall decay factorizes into the product of the intrinsic decay $\exp(-t/\tau)$ by the decay function given above. Here τ is the intrinsic lifetime of the donor excited state.

From Eqs. (1) and (2), one can obtain the short-time asymptotic behaviour for $I(t)$ ($Wt \ll 1$)

$$I(t) = 1 - 2cWt + c(1+c)(Wt)^2 - (Wt)^3\left(\frac{2}{3}c + \frac{1}{3}c^2 + \frac{1}{3}c^3\right). \tag{3}$$

For the intermediate time domain ($1 \ll Wt \ll c^{-2}$) and in the framework of the diffusion approximation and $V = \infty$, a distinct asymptotic function was obtained by several authors [15,18,19]

$$I(t) = 1 - 4c\sqrt{Wt/\pi}. \tag{4}$$

Note that a linear chain with N donors and containing one acceptor at each end, and for which $V = \infty$, is equivalent to a chain with $N-2$ donors and containing one acceptor at each end, but for which $V = W$ [12]. An approximate formula valid for all times of interest was suggested by Palszegi et al. [16]:

$$I(t) = \exp\left(-c\sqrt{\frac{8}{\pi}Wt}\right). \tag{5}$$

This relation was used in [16] to describe the influence of polymer motion on luminescence kinetics when the traps were excimer-forming sites.

On the other hand, by application of the t-matrix approach, Fredrickson and Frank [14] obtained an expression for $I(t)$ supposedly valid for small trap concentration, $c \ll 1$, and long times, $Wt > 1$

$$I(t) = \exp(4c^2 Wt)\operatorname{erfc}\left[2c(Wt)^{1/2}\right], \tag{6}$$

where $\operatorname{erfc}(x)$ is the complementary error function.

We compared the exact decay law (Eqs. (1) and (2)) with the approximate ones (Eqs. (5) and (6)) and noted that Eqs. (5) and (6) have no correct asymptotics at short times and are not accurate in the most important time domain (see Fig. 1). We also noted that at intermediate times $I(t)$ is very close to $(1/2)\exp(-c\sqrt{8Wt/\pi})$. Based on these observations, we constructed an approximate expression which is accurate at intermediate times and has the correct asymptotic Eq. (3) at short times:

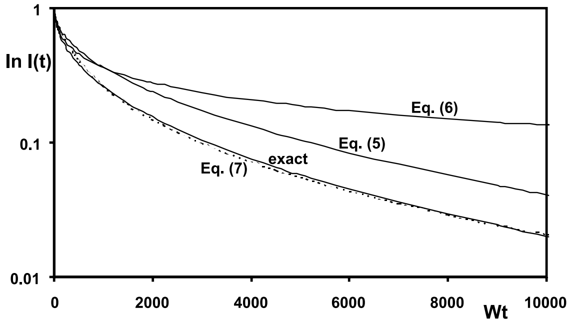

Fig. 1. Comparison of the exact expression for the donor decay kinetics in the static regime, Eq. (1), with the approximate ones (Eqs. (5) and (6)), and with the ad hoc one, Eq. (7). It is seen that Eqs. (5) and (6) have no correct asymptotics at short times and are not accurate within the most interesting time domain.

$$I(t) = \frac{1}{2}\left[\exp\left(-c\sqrt{\frac{8}{\pi}Wt}\right) + \frac{1 + (5 + \sqrt{8/\pi})c\sqrt{Wt}}{1 + 4cWt/(1 + Wt/4)}\exp\left(-5c\sqrt{Wt}\right)\right]. \tag{7}$$

The first term of this expression is just one-half of Eq. (5), a good approximation for relatively long times, where the second term is negligible. The second term corrects the short-time inaccuracy of the first term. The exponential of the second term and the respective pre-exponential factor are chosen so that for the short-time domain ($Wt \ll 1$) the correct asymptotic form, Eq. (3), is recovered (up to the second power in time), the numerical value of the parameter in the exponential being chosen in order to give a good fit to the exact curve. As one can see from Fig. 1 this relation is satisfactory for all times of interest (for $I(t) > 0.001$). Eq. (7) will be used in Section 4 in the study of the effect of polymer chain motion when traps are excimer-forming sites.

For donor–donor excited-state transport, the fundamental quantity of theoretical and experimental interest is $G^s(t)$, the ensemble-average probability that an originally excited chromophore is 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 transfer events. As before, $G^s(t)$ does not contain the loss of excitation due to the intrinsic decay. $G^s(t)$ is connected with time-resolved fluorescence depolarization data ($r(t) = r_0 G^s(t)$ where $r(t)$ is the anisotropy of fluorescence and r_0 is the anisotropy at the initial time [4,11,20]). In the absence of traps, $G^s(t)$ is well known,

$$G^s(t) = \exp(-2Wt)I_0(2Wt), \tag{8}$$

where I_0 is the zero-order modified Bessel function.

3. Inhomogeneous broadening

In the last years a special attention was paid to polymers containing donor and acceptor chromophores having inhomogeneous spectral broadening [2]. In such polymers one has to observe the influence of the excitation wavelength on luminescence kinetics under selective excitation, the role of temperature and of excitation pulse width. In this Letter, we try to answer the question: at which value of inhomogeneous spectral broadening width, σ, one can start to notice its influence?

For simplicity, we will consider that the normalized distribution of chromophores (donors) over transition energies, $g_D(E)$, has Gaussian shape and its maximum is situated at the transition energies E_D,

$$g_D(E) = \frac{1}{\sqrt{2\pi}\sigma}\exp\left[-\frac{(E_D - E)^2}{2\sigma^2}\right]. \tag{9}$$

The rate of energy transfer, $W_{i\to j}$, between two nearest-neighbour chromophores (from i to j) depends now on their transition energy, E_i and E_j, has to obey Boltzmann-type balance equation ($W_{i\to j}/W_{j\to i} = \exp[-(E_j - E_i)/kT]$), and can be written as

$$W_{i\to j} = W_0\exp\left(-\frac{E_j - E_i}{2kT}\right) = W_0\exp\left(-\frac{E_j - E_i}{\sigma}\frac{\sigma}{2kT}\right), \tag{10}$$

where W_0 is the rate of energy transfer between chromophores having the same transition energies, k is the Boltzmann constant, and T is the temperature.

Under these conditions, the survival probability $G^s(t)$ connected with time-resolved fluorescence depolarization data was calculated numerically using the Monte-Carlo method. For this purpose, a linear chain with 300 chromophores was used, and periodical boundary conditions applied. The results of calculations are shown in Fig. 2 for the case of nonselective (broadband) excitation of chromophores. One can see that when the importance of inhomogeneous broadening increases (i.e., when the ratio σ/kT increases) the probability $G^s(t)$ decreases faster at short times and slower at long times (see Eq. (8)). These results were expected because one fraction of the molecules has $W_{i\to j} > W_0$ and thus decays faster, while another fraction has $W_{i\to j} < W_0$ and decays slower. Inhomogeneous broadening is significant whenever $\sigma/kT \geqslant 1$.

4. Influence of chain conformational motion

If a configuration of acceptors (excimer-forming sites) is stable during the lifetime of the chromophore then the kinetics of luminescence is described by Eq. (1) or Eq. (7). It is now supposed that conformational transitions occur during the lifetime of the chromophore, and that these transitions are sudden and random both in time and in space along the chain. The overall structure of traps (excimer-forming sites) is thus dynamically changing, so that the initial configuration of the system is forgotten after some time t. Introducing the mean time for conformational change, τ_{conf}, and assuming a Poissonian process, the following integral equation for the donor decay, $I_{\text{hop}}(t)$, was obtained [16,17]:

$$I_{\text{hop}}(t) = I(t)\exp(-t/\tau_{\text{conf}}) + \frac{1}{\tau_{\text{conf}}}\int_0^t I(t_1) \times \exp(-t_1/\tau_{\text{conf}}) I_{\text{hop}}(t-t_1)\,\mathrm{d}t_1, \tag{11}$$

where $I(t)$ is the luminescence intensity in the absence of conformational change described by Eq. (1) or (7). This equation was solved numerically [16] using the approximate equation (5) for $I(t)$ instead of the exact result, Eqs. (1) and (2). Correct solutions of Eq. (11) are shown in Fig. 3 (we used Eq. (7) for $I(t)$ with $W\tau = 50,\ c = 0.02$). From our results it is concluded that polymer conformational change is important for $\tau_{\text{conf}}/\tau < 10$ (for a given concentration of traps).

Note that when τ_{conf} decreases, the kinetics becomes exponential, $I_{\text{hop}}(t) \sim \exp(-kt)$, where k is the rate constant, which can be obtained from the equation

$$k = \left(1 - \frac{1}{\tau_{\text{conf}}}\int_0^\infty I(t)\exp(-t/\tau_{\text{conf}})\,\mathrm{d}t\right) \Bigg/ \int_0^\infty I(t)\exp(-t/\tau_{\text{conf}})\,\mathrm{d}t \tag{12}$$

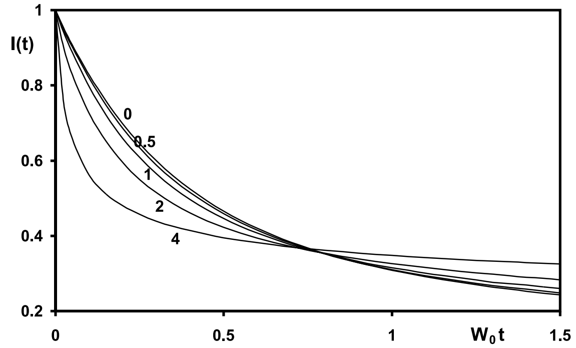

Fig. 2. Effect of inhomogeneous broadening on the donor survival probability. The dimensionless parameter σ/kT is shown next to each curve.

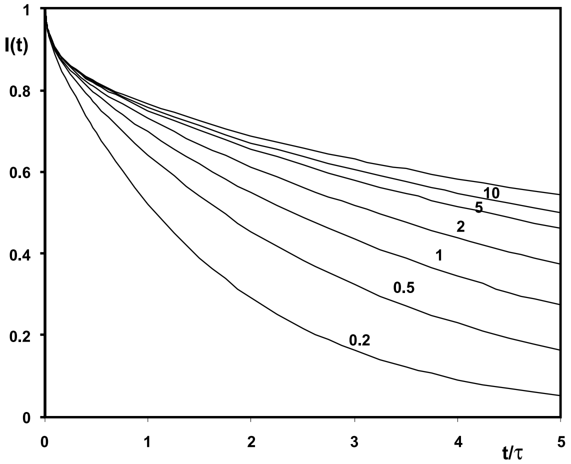

Fig. 3. Effect of chain conformational motion on the donor survival probability, numerically computed using Eqs. (7) and (11), with $W\tau = 50$ and $c = 0.02$. The dimensionless parameter τ_{conf}/τ is shown next to each curve.

Using this equation and Eq. (7), one can obtain the rate constant k in the limit of very small τ_{conf} as

$$k = 2cW. \tag{13}$$

This result is expected since, owing to the presence of traps, the polymer chain is sectioned in finite-length segments. In the limit of very small τ_{conf}, an exciton has an equal probability to be found at any monomer site on the chain and this probability is independent of time. Each segment has two traps at its ends, the rate constant for nearest-neighbour energy transfer (from a donor to an acceptor) is W, and therefore the rate constant is given by Eq. (13) and the donor decay is exponential.

It should be possible to extract τ_{conf} from experimental decays, by applying the appropriate model to fluorescence trapping.

5. Summary and conclusions

In this Letter, the kinetics of luminescence of chromophores attached to each segment of a linear polymer chain was studied. In the static case, when the polymer chain does not change its conformation during the chromophore lifetime, the analytical expression Eq. (7) is obtained.

It was shown that inhomogeneous broadening of chromophore spectra is important if the width of inhomogeneous broadening, σ, is larger than kT.

The hopping model of polymer conformational change was also considered. This kind of polymer motion becomes important if the time for conformational change is short enough, $\tau_{\mathrm{conf}}/\tau < 10$. In the limit of very fast conformational change compared to the intrinsic donor lifetime, an exponential donor decay is predicted.

Acknowledgements

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