Optics and Spectroscopy, Vol. 91, No. 5, 2001, pp. 694–703. Translated from Optika i Spektroskopiya, Vol. 91, No. 5, 2001, pp. 740–749.

Luminescence Kinetics of Linear Polymer Molecules with Chromophores Randomly Distributed along the Chain

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

**Russian State Hydrometeorological University, St. Petersburg, 195196 Russia*
e-mail: bodunov@mail.admiral.ru
***Center of Physical Chemistry of Molecules, Technical University, Lisbon, 1049-001 Portugal*

Received March 23, 2001

Abstract—Luminescence kinetics of chromophores randomly attached to an isolated flexible polymer chain is studied. In the static case, when the polymer chain does not change its conformation during the donor excited-state lifetime, analytical equations are derived for the luminescence kinetics of both ideal and nonideal polymer chains. The conditions are formulated when the inhomogeneous broadening should be taken into account. For the dynamic case, the diffusion and hopping mechanisms of the polymer motion are studied. © *2001 MAIK "Nauka/Interperiodica".*

INTRODUCTION

The energy transfer and migration of electronic excitations in polymers is widely studied and commonly used to analyze their structure [1, 2]. The reason is that the time dependence of the luminescence intensity of donor and acceptor chromophores can be connected with the interchromophore distance by means of Forster's energy transfer rate [3]. Such experiments are usually performed at very low polymer concentrations, which makes it possible to neglect the energy transfer between different polymer molecules.

There are several ways of attaching chromophores to a polymer chain [1, 2, 4–19]. In this paper, we study the following model. Each link of the polymer chain may contain, with a certain probability, a donor or acceptor chromophore so that all the chromophores are distributed along the chain in a random way [1, 4, 6–11]. Such polymer molecules can be synthesized by esterification of a long chain of dialcohols by acids containing donors or acceptors and showing the same reactivity with respect to the alcohol.

The goal of this paper is to study the direct incoherent energy transfer from an excited donor to another donor or acceptor under the above conditions. We also study the effect of inhomogeneous broadening of the chromophore spectrum and the motion of the polymer chain (for the diffusion and hopping mechanisms of conformation changes) on luminescence kinetics. We will focus our attention on a single polymer molecule isolated from other molecules (the polymer concentration is assumed to be sufficiently low). This assumption is made in order to simplify the problem and neglect the interaction between neighboring polymer chains, which may give rise to the energy transfer between chromophores localized on different chains. We will also assume that the solvent is strong and the temperature of the polymer is above the θ-point of the transition, so that we can use known distribution functions for the distance between the ends of the polymer chain. Finally, we will consider the case of the isotropic dipole–dipole interaction between the chromophores, when the energy transfer rate $w(r)$ can be written in the form

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

where τ is the lifetime of the donor chromophore excited state, R_0 is the Forster radius, and r is the distance between the chromophores.

STATIC MODE

As was mentioned above, there are several models of chromophore attachment to a polymer molecule. In this paper, we assume that there is a certain probability that a chromophore can attach to any link of the polymer chain. To neglect the energy migration over the donors, we assume that the concentration of the chromophore-donors is low. Then, we have the following differential equation for the decay of the excited donor state $p(t)$ due to the energy transfer to the acceptors:

$$\frac{d}{dt}p(t) = -\sum_{i=1}^{M} w(r_i)p(t), \tag{2}$$

where r_i is the distance between the donor and the ith acceptor and M is the number of acceptors attached to the polymer chain. Equations (2) do not contain any loss of excitation related to a finite lifetime of the excited donor state, since this channel of the decay has nothing to do with the energy transfer process. Thus, the total kinetics of the luminescence decay can be represented as a product of two factors: $\exp(-t/\tau)$ and the decay kinetics related to the energy transfer to the acceptor. Note that r_i in Eq. (2) is independent of time because, in this part of the paper, we neglect the motion of the polymer chain during the lifetime of the excited donor state. The distances r_i evidently depend on the chain conformation.

Assuming that the donor is initially excited with the probability equal to unity, we obtain from Eq. (2)

$$p(t) = \exp\left[-t\sum_{i=1}^{M} w(r_i)\right] = \prod_{i=1}^{M} \exp[-tw(r_i)]. \quad (3)$$

The donor luminescence kinetics $I(t)$, related to the energy transfer to acceptors, is obtained by averaging (3) over all conformations with the distribution function $g_N(K, r)$ [($g_N(K, r)$ is the probability density used to find the distance between the donor and the acceptor in the polymer, consisting of K links, equal to r, and N is the number of links in the polymer chain between the donor and the acceptor]. In the d-dimensional space we have

$$\begin{aligned} I(t) &= \left[\frac{1}{K}\sum_{N=1}^{K} dV_d \int_0^\infty r^{d-1} g_N(K, r) e^{-tw(r)} dr\right]^M \\ &= \left[1 - \frac{1}{K}\sum_{N=1}^{K} dV_d \int_0^\infty r^{d-1} g_N(K, r)(1 - e^{-tw(r)}) dr\right]^M, \end{aligned} \quad (4)$$

where $V_d = \pi^{d/2}/\Gamma(1 + d/2)$ and $\Gamma(x)$ is the gamma function. Note that the distance between two points of the polymer chain (which are not too close to each other), separated by N links, and the distance between the ends of the polymer chain consisting of N links satisfy one and the same distribution function [20]. Therefore, by denoting $g_N(r) \equiv g_N(N, r)$, we can simplify Eq. (4) and use the following equality:

$$g_N(K, r) = g_N(r). \quad (5)$$

This equality imposes restrictions upon the results obtained below: they are valid at a low chromophore concentration when the average number of links of the polymer chain between the donor and the nearest acceptor is sufficiently large.

For the ideal (Gaussian) polymer chain, $g_N(r)$ has the form [5, 20]

$$g_N(r) = A_1 \exp(-B_1 r^2), \quad (6)$$

where

$$A_1 = \left(\frac{d}{2\pi\langle R_g^2\rangle}\right)^{d/2}, \quad B_1 = \frac{d}{2\langle R_g^2\rangle}.$$

For a nonideal chain (a chain with the volume interaction), we have [5, 20]

$$g_N(r) = A_2 r^{\vartheta} \exp(-B_2 r^{\delta}), \quad (7)$$

where

$$A_2 = \frac{\delta B_2^{(d+\vartheta)/\delta}}{dV_d \Gamma[(d+\vartheta)/\delta]},$$

$$B_2 = \left\{\frac{\Gamma[(d+\vartheta+2)/\delta]}{\Gamma[(d+\vartheta)/\delta]\langle R_g^2\rangle}\right\}^{\delta/2}.$$

Here R_g is the radius of gyration of a polymer ball ($\langle R_g^2\rangle = a^2 N$ for an ideal chain and $\langle R_g^2\rangle = a^2 N^{2\nu}$ for a nonideal chain, where a is the statistical length of a link) and ϑ and δ are the dimension-dependent critical indices. These critical indices can be written as $\vartheta = (\gamma - 1)/\nu$ and $\delta = (1 - \nu)^{-1}$, where γ and ν are two universal critical indices depending on d. The self-consistent field method (Flory theory) in a space with the dimension d yields [20]

$$\begin{gathered} \nu = 3/(d+2), \quad d \le 4, \\ \gamma = 1\ (d = 1), \quad \gamma \approx 4/3\ (d = 2), \quad \gamma \approx 7/6\ (d = 3). \end{gathered} \quad (8)$$

Therefore, for the three-dimensional space (which is the case under consideration), we have from Eqs. (7) and (8)

$$\begin{gathered} \nu = 3/5, \quad \vartheta = 5/18, \quad \delta = 5/2, \\ A_2 = 0.289058/\langle R_g^2\rangle^{59/36}, \quad B_2 = 1.22271/\langle R_g^2\rangle^{5/4}. \end{gathered} \quad (9)$$

The functions $4\pi x^2 g_N(x)$ (where $x = r/\sqrt{\langle R_g^2\rangle}$) for the ideal and nonideal polymer chains are shown in Fig. 1.

Note that the results of the Flory theory (9) are very close (within two percent) to those obtained by computer simulation ($\nu = 0.59$ [20]), with the accuracy being sufficient for any real polymer chain.

When studying the excitation transfer in a system of finite size (the polymer chain has K links), one has to make two spatial averages. The first is the average over all possible positions of acceptors with respect to the position of the initially excited donor (localized, e.g., on the ith link of the polymer chain). This will give us kinetics of the luminescence decay $I_i(t)$ for the given initial conditions. The second is the average over all possible positions of the initially excited donor (in the system of finite dimensions, these positions are not

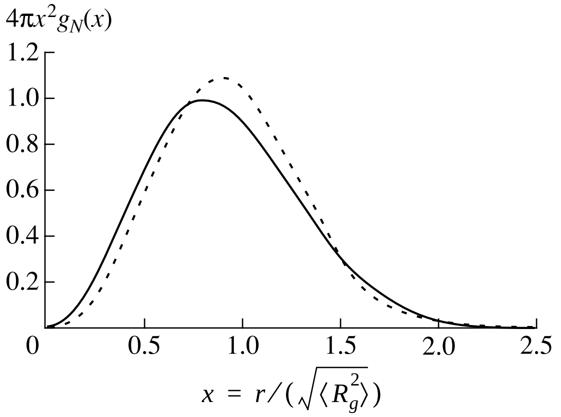

Fig. 1. The distribution function for the (solid line) ideal and (dashed line) nonideal chains.

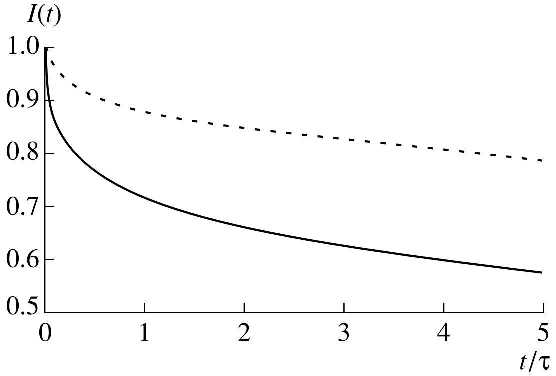

Fig. 2. Luminescence kinetics for the (solid line) ideal and (dashed line) nonideal polymer chains. $R_0/a = 2$, $c = 0.01$.

equivalent). This problem was solved numerically for an ideal polymer chain in [6, 7] using the GAF method [21] and in [4, 8–10] using the Huber approximation [22, 23].

The problem of excitation transfer in a polymer chain becomes much easier for an infinite chain (K, $M \longrightarrow \infty$ under the condition that $M/K = \text{const}$). In this case, there is no necessity to calculate the second average, since all positions of the initially excited donor are equivalent. Thus, with allowance for formula (5), we have

$$I(t) = \exp\left[-c\int_{-\infty}^{\infty} dN \int_{0}^{\infty} dr 4\pi r^2 g_N(r)(1 - e^{-tw(r)})\right], \quad (10)$$

where c is the mean number of acceptor chromophores falling into one link of the polymer chain ($c \ll 1$). For the case of dipole–dipole interaction, both integrals in Eq. (10) can be calculated exactly. As a result, for the luminescence kinetics $I_{\text{id}}(t)$ of the ideal polymer chain, we have

$$\begin{aligned} I_{\text{id}}(t) &= \exp\left[-6\Gamma\left(\frac{2}{3}\right)c\frac{R_0^2}{a^2}\left(\frac{t}{\tau}\right)^{1/3}\right] \\ &= \exp\left[-8.125c\frac{R_0^2}{a^2}\left(\frac{t}{\tau}\right)^{1/3}\right], \end{aligned} \quad (11)$$

and for the luminescence kinetics $I_{\text{nid}}(t)$ of the nonideal chain, we have

$$I_{\text{nid}}(t) = \exp\left[-3.872c\left(\frac{R_0}{a}\right)^{5/3}\left(\frac{t}{\tau}\right)^{23/54}\right]. \quad (12)$$

The luminescence given by Eq. (12) decays slower than Eq. (11) (see Fig. 2, $R_0/a = 2$, $c = 0.01$), since, for the nonideal polymer chain, $g_N(r) \longrightarrow 0$ when $r \longrightarrow 0$ [see Eq. (7)], while for the ideal chain $g_N(r) \longrightarrow \text{const}$ when $r \longrightarrow 0$ [see Eq. (6)].

In polymers where only the donor–donor energy transport occurs, a fundamental quantity, interesting in both a theoretical and a practical sense, is $G^s(t)$—the ensemble-averaged probability that the initially excited chromophore still remains excited at the instant t. This probability contains contributions from excitations that never abandoned the initially excited chromophore and from excitations that returned to that chromophore after one or several energy transfer events. As before, $G^s(t)$ does not contain any loss of excitation related to a finite lifetime of the excited chromophore state. The probability $G^s(t)$ is related to the time dependence of luminescence depolarization: $r(t) = r_0 G^s(t)$, where $r(t)$ is the anisotropy of luminescence and r_0 is its initial anisotropy [4, 11, 24].

Consider two chromophores (the zeroth and first) attached to different links of the polymer chain. The dynamics of their excited states $p_0(t)$ and $p_1(t)$ is described by the equations

$$\begin{aligned} \frac{d}{dt}p_0(r_1, t) &= -w(r_1)[p_0(r_1, t) - p_1(r_1, t)], \\ \frac{d}{dt}p_1(r_1, t) &= w(r_1)[p_0(r_1, t) - p_1(r_1, t)], \end{aligned} \quad (13)$$

where r_1 is the distance between the chromophores. Solutions of these equations, under the assumption that at the initial instant only the zeroth chromophore is excited with the unit probability, has the form

$$p_0(r, t) = \frac{1}{2} + \frac{1}{2}\exp[-2tw(r_1)]. \quad (14)$$

In the Huber approximation [22, 23], $G^s(t)$ is obtained by averaging the product of functions (14) for all pairs of chromophores (with each pair containing one excited chromophore):

$$G^s(t) = \left\langle \prod_{i=1}^{M} \left\{ \frac{1}{2} + \frac{1}{2}\exp[-2tw(r_i)] \right\} \right\rangle$$
$$= \left\langle 1 - \frac{1}{2}[1 - e^{-2tw(r)}] \right\rangle^{M}. \qquad (15)$$

Here, M is the number of pairs, equal to the number of chromophores (donors) attached to the polymer chain. The broken brackets denote averaging over all conformations. Assuming, as when deriving Eq. (10), that the polymer chain is infinitely long, we obtain

$$G^s(t) = \exp\left[-\frac{c}{2}\int_{-\infty}^{\infty} dN \int_0^{\infty} dr 4\pi r^2 g_N(r)(1 - e^{-2tw(r)})\right], \qquad (16)$$

where c is the mean number of donor chromophores falling into one link of the polymer chain. In the case of dipole–dipole interaction, the integrals entering Eq. (16), can be calculated exactly. Note that Eq. (10) differs from (16) by the substitutions $c \longrightarrow c/2$ and $R_0^6 \longrightarrow 2R_0^6$. Therefore, from Eq. (11), using the above substitutions, for the ideal polymer chain we have

$$G^s_{\text{id}}(t) = \exp\left[-2^{1/3} \times 3\Gamma\left(\frac{2}{3}\right)c\frac{R_0^2}{a^2}\left(\frac{t}{\tau}\right)^{1/3}\right]$$
$$= \exp\left[-5.118c\frac{R_0^2}{a^2}\left(\frac{t}{\tau}\right)^{1/3}\right]. \qquad (17)$$

Expression (17) was obtained in [8, 10] within the framework of the Huber approximation and in [11] using the GAF method in a two-particle approximation. A three-particle approximation of the GAF method leads to the function $G^s(t)$ exponentially growing in time. This is a common problem of the GAF method in a low-dimensional system [25].

For the nonideal polymer chain, using formulas (7) and (16), we have

$$G^s_{\text{nid}}(t) = \exp\left[-2.347c\left(\frac{R_0}{a}\right)^{5/3}\left(\frac{t}{\tau}\right)^{23/54}\right]. \qquad (18)$$

Formula (18), again, can be obtained from formula (12) by the substitutions $c \longrightarrow c/2$ and $R_0^6 \longrightarrow 2R_0^6$, in the same way as formula (17) was obtained from (11).

INHOMOGENEOUS BROADENING

In recent years special attention has been paid to polymer molecules containing donors and acceptors which exhibit inhomogeneous broadening of their spectral lines [2]. In such polymers, one can observe the dependence of the luminescence kinetics on the excitation wavelength, on the exciting pulse width, and on the temperature. In this paper, we try to answer the following question: what is the smallest inhomogeneous width σ where we can notice this effect?

In the case of inhomogeneous broadening of the spectra, the luminescence kinetics of donors $I_{\text{inh}}(t)$ (under nonselective excitation of the chromophores attached to a long polymer chain) can be written as

$$I_{\text{inh}}(t) = \int dE_1 g_D(E_1)\exp\left[-c\int dE_2 g_A(E_2)\right.$$
$$\left.\times \int_{-\infty}^{\infty} dN \int_0^{\infty} dr 4\pi r^2 g_N(r)(1 - e^{-tw(E_1 - E_2, r)})\right], \qquad (19)$$

where $w(E_1 - E_2, r)$ is the rate of energy transfer from the donor (with the transition energy E_1) to the acceptor (with the transition energy E_2), and $g_D(E_1)$ and $g_A(E_2)$ are the normalized distributions of donors and acceptors over the transition energies. For simplicity, we will make the following assumptions. First, let these distributions be Gaussians with equal widths and let their peaks be located at the transition energies E_D and E_A:

$$g_D(E) = \frac{1}{\sqrt{2\pi}\sigma}\exp\left[-\frac{(E_D - E)^2}{2\sigma^2}\right],$$
$$g_A(E) = \frac{1}{\sqrt{2\pi}\sigma}\exp\left[-\frac{(E_A - E)^2}{2\sigma^2}\right], \qquad (20)$$
$$E_D - E_A = \Delta E.$$

Second, let the homogeneously broadened luminescence spectra of donors and the absorption spectra of acceptors also be of Gaussian shape, with their widths being the same and equal to $\delta/\sqrt{2}$. Then, the energy transfer rate controlled by the dipole–dipole interaction, proportional to the spectral overlap integral [3], can be written as

$$w(E_1 - E_2, r) = \frac{1}{\tau}\left[\frac{R(E_1 - E_2)}{r}\right]^6,$$
$$R^6(E_1 - E_2) = R_0^6\exp\left[-\frac{(E_1 - E_2)^2}{\delta^2} + \left(\frac{\Delta E}{\delta}\right)^2\right], \qquad (21)$$

where R_0 is the Forster radius of the donor–acceptor energy transfer, with the donor and acceptor energies being $E_1 = E_A$ and $E_2 = E_D$.

Note that the third and fourth integrals in Eq. (19) were already calculated [see, e.g., formula (11) for the

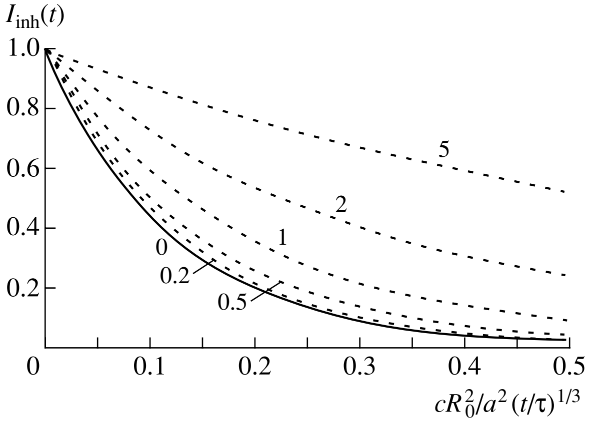

Fig. 3. Luminescence kinetics of the ideal polymer chain for inhomogeneously broadened spectra. The maximum of the donor emission spectrum coincides with that of the acceptor absorption spectrum ($E_D = E_A$). The numbers near the curves are the inhomogeneous/homogeneous linewidth ratios σ/δ.

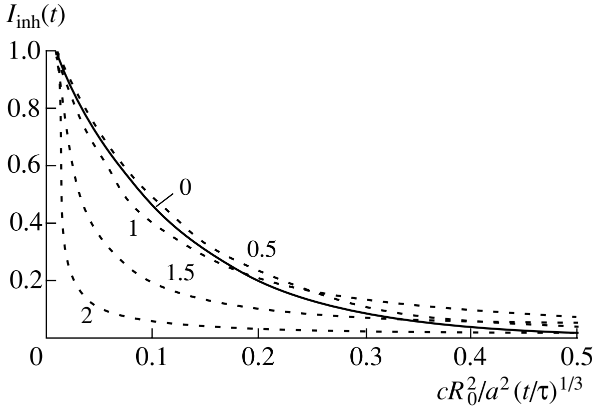

Fig. 4. Luminescence kinetics of the ideal polymer chain for inhomogeneously broadened spectra. The maxima of the donor emission spectrum and acceptor absorption spectrum are located at different transition energies ($E_D = E_A + 2\sigma$). The numbers near the curves are the inhomogeneous/homogeneous linewidth ratios σ/δ.

ideal polymer chain]. Using this result and substituting (21) unto (19), we obtain

$$I_{\text{inh}}(t) = \int dE_1 g_D(E_1)\exp\left[-8.125c\frac{R_0^2}{a^2}\left(\frac{t}{\tau}\right)^{1/3} \times \int dE_2 g_A(E_2)\exp\left(-\frac{(E_1-E_2)^2}{3\delta^2}+\frac{\Delta E^2}{3\delta^2}\right)\right] \qquad (22)$$

for the ideal polymer chain.

The luminescence kinetics (22) was calculated numerically. The results of the calculations are shown in Fig. 3 for the case $E_D = E_A$ (or $\Delta E = 0$). As is seen from Fig. 3, the increase of the inhomogeneous broadening of the spectra (i.e., the ratio σ/δ) slows down luminescence decay, because inhomogeneous broadening reduces the energy transfer rate for all donor–acceptor pairs [this is evident from Eq. (21)]. The luminescence kinetics for the case $\Delta E = 2\sigma$ is shown in Fig. 4. The luminescence decay becomes faster at shorter times and slower at longer times. This results from the fact that when $\Delta E = 2\sigma$, the energy transfer rate in the donor–acceptor pairs, for which $E_1 - E_2 < \Delta E$, increases, while in the pairs with $E_1 - E_2 > \Delta E$, it decreases as compared to the case where inhomogeneous broadening is absent. It follows from Figs. 3 and 4 that the inhomogeneous broadening of the spectra should be taken into account when $\sigma/\delta > 0.2$.

CONFORMATION MOTION OF A POLYMER CHAIN

The effect of the motion of a polymer molecule in diluted solutions on the rate of intramolecular reaction between reactive groups attached to the ends of a flexible polymer chain was studied in [26–33]. In [26–28], it was assumed that the reaction occurs when the reactive groups approach close enough to one another (contact reaction), and that the resulting polymer motion was described using the generalized diffusion equation. The asymptotic behavior of the reaction at short and long times was calculated. The energy transfer (luminescence quenching) is a similar process. The only distinction (from the theoretical point of view) is in the dependence of the reaction rate on the distance between the chromophores. This is why the studies of the effect of polymer motion upon luminescence kinetics [29, 30] also employed the diffusion equation.

For polymer molecules with a random arrangement of chromophores along the polymer chain, the following equation for luminescence kinetics is valid:

$$I_{\text{dif}}(t) = \exp\left[-c\int_{-\infty}^{\infty} dN \int_{r_0}^{\infty} dr\, 4\pi r^2 (g_N(r) - g_N^*(r, t))\right], \qquad (23)$$

where $g_N^*(r, t)$ is the distribution function for distances between an excited donor and a nonexcited acceptor and N is the number of links in the polymer chain between the donor and the acceptor. Initially, $g_N^*(r, t = 0) = g_N(r)$. In the static situation, $g_N^*(r, t) = g_N(r)\exp[-tw(r)]$ [see Eq. (10)]. It is known [20, 29, 30] that free links perform Brownian motion in a solvent with a certain diffusion coefficient D, and that the distribution function may be treated as an energy term by introducing the interaction energy $U(r)$:

$$V(r) = U(r)/kT = -\ln g_N(r), \qquad (24)$$

where k is the Boltzmann constant and T is the absolute temperature. Thus, we can write the equation [29–33]

$$\begin{aligned}\frac{\partial}{\partial t}g_N^*(r,t) &= D\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}g_N^*(r,t)\\ &+ D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 g_N^*\frac{\partial V}{\partial r}\right) - w(r)g_N^*(r,t)\end{aligned} \tag{25}$$

with the boundary and initial conditions

$$\left.\frac{\partial}{\partial r}g_N^*(r,t) + \frac{\partial}{\partial r}V(r)\right|_{r = r_0} = 0,$$

$$g_N^*(r,0) = g_N(r),$$

where r_0 is the distance of closest approach.

The first two terms on the right-hand side of Eq. (25) describe changes in the distribution function $g_N^*(r, t)$ due to the Brownian motion of the links in the spherical field $U(r)$, while the third term describes changes in the same function due to the energy transfer from the excited donor to the acceptor. The initial condition signifies that the chromophores cannot approach each other at a distance closer than r_0.

Equation (25) was solved numerically in [29, 31, 33] for the case of short polymer chains and a special form of the distribution function $g_N(t)$, and in [30, 31] for the case of the ideal chain. A comparison with experimental data has shown that the diffusion coefficient can be as high as 10^{-5} cm^2 s [31–33]. In all the papers cited above, another model of attachment of a chromophore to a polymer molecule was studied; namely, the donor and the acceptor were attached to the ends of the polymer chain.

For the polymer with a random distribution of chromophores along the chain one has, first, to numerically solve Eq. (25) separately for each value of N, and then perform averaging over N [see Eq. (23)]. This is a very tedious procedure. For this reason, we obtained the analytic solution to Eq. (25) in the limit of slow diffusion. To do that, we used a method tested in [34], where the solution of the diffusion equation was sought in the form of an iteration series in terms of the small parameter D, and only the two first terms were retained (the zeroth approximation and the first-order correction proportional to the diffusion coefficient). In this case, for the dipole–dipole mechanism of the energy transfer, we have

$$g_N^*(r,t) = g_N(r)\exp\left(-\frac{R_0^6 t}{r^6\tau}\right) + g_N^{(1)}(r,t), \tag{26}$$

where the first-order correction $g_N^{(1)}(r, t)$ can be found from the equation

$$\begin{aligned}&g_N^{(1)}(r,t)\\ &= \int_0^t \exp\left[-\frac{R_0^6(t-t')}{r^6\tau}\right] H g_N(r)\exp\left(-\frac{R_0^6 t'}{r^6\tau}\right)dt'.\end{aligned} \tag{27}$$

The action of the operator H in Eq. (27) upon the function $f(r, t) = g_N(r)\exp(-R_0^6 t/r^6\tau)$ is defined as

$$\begin{aligned}Hf(r) &= D\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}f(r,t)\\ &+ D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 f(r,t)\frac{\partial}{\partial r}V(r)\right).\end{aligned} \tag{28}$$

Taking into account that $g_N(r) = \exp[-V(r)]$ [see Eq. (24)], expression (28) can be rewritten in the form

$$Hf(r) = D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 g_N(r)\frac{\partial}{\partial r}\exp\left(-\frac{R_0^6 t}{r^6\tau}\right)\right). \tag{29}$$

When computing the integrals entering into Eq. (23), we also used the following formulas. It is known [10, 11] that for the ideal polymer chain

$$\int_{-\infty}^{\infty} g_N(r)dN = \frac{3}{\pi a^2 r}. \tag{30}$$

For the case of the nonideal chain, our calculation yielded

$$\int_{-\infty}^{\infty} g_N(r)dN = \frac{C}{a^d}\left(\frac{a}{r}\right)^{d-1/\nu}, \tag{31}$$

where

$$C = \frac{2\Gamma\left(\frac{\nu(d+\vartheta)-1}{\nu\delta}\right)}{\nu d V_d\Gamma\left(\frac{d+\vartheta}{\delta}\right)}\left[\frac{\Gamma\left(\frac{d+\vartheta+2}{\delta}\right)}{\Gamma\left(\frac{d+\vartheta}{\delta}\right)}\right]^{\frac{1-\nu(d+\vartheta-\delta)}{2\nu}}.$$

Omitting intermediate manipulations, fulfilled for the three-dimensional space ($d = 3$, $C \cong 0.50747$), we present the final result. For the luminescence kinetics $I_{\mathrm{dif}}^{\mathrm{id}}(t)$ of the ideal polymer chain, we obtain

$$I_{\mathrm{dif}}^{\mathrm{id}}(t) = \exp\left[-8.125c\frac{R_0^2}{a^2}\left(\frac{t}{\tau}\right)^{1/3} - 12c\frac{Dt}{a^2}\right], \tag{32}$$

and for the nonideal chain

$$I^{\mathrm{nid}}_{\mathrm{dif}}(t) = \exp\left[-3.872c\left(\frac{R_0}{a}\right)^{5/3}\left(\frac{t}{\tau}\right)^{23/54} - 6.535c\frac{D\tau}{a^2}\left(\frac{a}{R_0}\right)^{1/3}\left(\frac{t}{\tau}\right)^{17/18}\right]. \qquad (33)$$

Equations (32) and (33) are correct when the second term in square brackets is smaller than the first one (within the time span of the order of the excited-state lifetime τ). This means that the inequality $D\tau < R_0^2$ should be satisfied. The first terms in Eqs. (32) and (33) describe static quenching, and the second terms are the first-order corrections related to the diffusion motion of the polymer chain links. As one can see, the polymer motion enhances the luminescence quenching.

Equation (25) can also be solved in the approximation of extremely fast diffusion (the case of total mixing [35]). In this case, the diffusion is so strong that a decrease of the function $g_N^*(r, t)$ at small r is immediately counterbalanced by diffusion from larger distances. For this reason, the distribution function $g_N^*(r, t)$ retains its shape [coincident with that of $g_N(r)$], while its magnitude exponentially decays in time [34, 35]. Thus, taking into account the normalization condition $4\pi\int g_N(r)r^2dr = 1$ and omitting intermediate calculations, similar to those presented in [34], we have

$$g_N^*(r, t) = g_N(r)\exp(-k_{\mathrm{dif}}(N)t),$$

$$k_{\mathrm{dif}}(N) = \frac{4\pi}{\tau}\int_{r_0}^{\infty}\left(\frac{R_0}{r}\right)^6 g_N(r)r^2dr, \qquad (34)$$

$$I_{\mathrm{dif}}(t) = \exp\left(-c\int_{-\infty}^{\infty}dN(1-e^{-k_{\mathrm{dif}}(N)t})\right).$$

To obtain the rate constants from these equations for the ideal ($k^{\mathrm{id}}_{\mathrm{dif}}(N)$) and nonideal ($k^{\mathrm{nid}}_{\mathrm{dif}}(N)$) polymer chains, we replace the distribution function $g_N(r)$ with a rectangular function with the width $\sqrt{\langle R_g^2\rangle}$ and assume that $r_0 \ll \sqrt{\langle R_g^2\rangle}$. Therefore, the equations obtained below for $k_{\mathrm{dif}}(N)$ will be correct to within a numerical factor of the order of unity. Thus, for the ideal chain [see Eq. (6), $\langle R_g^2\rangle = a^2N$], we obtain

$$k^{\mathrm{id}}_{\mathrm{dif}}(N) = \frac{1}{\tau}\frac{R_0^6}{r_0^3\langle R_g^2\rangle^{3/2}} = \frac{1}{\tau}\frac{R_0^6}{r_0^3a^3N^{3/2}},$$

$$I^{\mathrm{id}}_{\mathrm{dif}}(t) = \exp\left[-\frac{8\pi}{3\sqrt{3}\Gamma(5/3)}c\frac{R_0^4}{r_0^2a^2}\left(\frac{t}{\tau}\right)^{2/3}\right] = \exp\left[-5.358c\frac{R_0^4}{r_0^2a^2}\left(\frac{t}{\tau}\right)^{2/3}\right], \qquad (35)$$

and for the nonideal chain [see Eq. (7), $\langle R_g^2\rangle = a^2N^{2\nu}$, $\nu = 3/5$], we have

$$k^{\mathrm{nid}}_{\mathrm{dif}}(N) = \frac{1}{\tau}\frac{R_0^6}{r_0^{3-5/18}\langle R_g^2\rangle^{(3+5/18)/2}} = \frac{1}{\tau}\frac{R_0^6}{r_0^{3-5/18}a^{3+5/18}N^{59/30}},$$

$$I^{\mathrm{nid}}_{\mathrm{dif}}(t) = \exp\left[-\frac{60\pi}{59\Gamma(89/59)\sin(30\pi/59)} \times c\left(\frac{R_0^6}{r_0^{3-5/18}a^{3+5/18}}\frac{t}{\tau}\right)^{30/59}\right] = \exp\left[-3.605c\left(\frac{R_0^6}{r_0^{3-5/18}a^{3+5/18}}\frac{t}{\tau}\right)^{30/59}\right]. \qquad (36)$$

As is seen, the luminescence kinetics is not exponential even in the limit of extremely fast diffusion [see Eqs. (35) and (36)]. The reason for this is that the links containing chromophores perform Brownian motion inside a confined space of different volume. The size of the latter is determined by N, i.e., the number of links between the donor and acceptor.

Note that this (diffusion) approximation is valid when the distance between the chromophores attached to the polymer chain changes (upon motion of the links) by small steps compared with R_0, i.e., the Forster energy transfer radius. It is only in this case that the diffusion equation can be used to describe the luminescence kinetics.

In principle, it is possible to suggest another model of polymer motion, alternative to that of diffusion. One can assume that conformation transitions may occur (with corresponding changes of the distances between the donor and the acceptor), and that these transitions between stable conformations are sudden and random both in time and in space [13, 16, 36, 37]. The distance between the chromophores changes, in this case, in such a way that the initial conformation of the system appears to be completely forgotten after a certain time. This model of polymer motion may be called the hopping model. The distance between the chromophores, after each jump, appears to be considerably changed as compared to the Forster radius.

Note that Eq. (23) is valid for any type of polymer motion (rather than only for diffusion). In the case of the hopping mechanism, this equation for the luminescence kinetics $I_{\text{hop}}(t)$ can be rewritten as

$$I_{\text{hop}}(t) = \exp\left[-c\int_{-\infty}^{\infty} dN(1 - I_{\text{hop}}(N, t))\right]. \tag{37}$$

Here, we used the normalization condition $4\pi\int g_N(r) r^2 dr = 1$ and introduced the function

$$I_{\text{hop}}(N, t) = 4\pi\int_0^{\infty} g_N^*(r, t) r^2 dt. \tag{38}$$

This function has the meaning of luminescence kinetics of a polymer chain comprised of N links and possessing one donor and one acceptor on opposite ends of the chain [29–33, 37].

By introducing the mean time of the conformation change (τ_{conf}) and assuming that the process of conformation changes is Poissonian, we obtained the following equation for the luminescence kinetics $I_{\text{hop}}(N, t)$ [37]:

$$\begin{aligned} I_{\text{hop}}(N, t) &= I(N, t)\exp(-t/\tau_{\text{conf}}) \\ &+ \frac{1}{\tau_{\text{conf}}}\int_0^t I(N, t_1)\exp(-t_1/\tau_{\text{conf}}) I_{\text{hop}}(N, t - t_1) dt_1. \end{aligned} \tag{39}$$

Here, $I(N, t)$ is the luminescence kinetics in the absence of conformation transitions. For the ideal polymer chain, this kinetics is described by the equation [37]

$$I(N, t) = \frac{2}{\pi^{1/2}}\int_0^{\infty} y^{1/2}\exp\left(-y - \frac{27T}{8y^3}\right)dy,$$

where $T = \frac{R_0^6}{\langle R_g^2\rangle^3}\frac{t}{\tau}$ ($\langle R_g^2\rangle = a^2N$). The function $I(N, T)$ is approximated, to within one percent, by the function [37]

$$I(N, t) = (1 + 2.45T^{1/4})\exp(-2^{5/4}T^{1/4}), \tag{40}$$

while for the nonideal chain ($\langle R_g^2\rangle = a^2N^{2\nu}$, $\nu = 3/5$), it is approximated by Eq. [37]

$$\begin{aligned} I(N, t) &= \frac{1}{\Gamma(1 + 14/45)} \\ &\times\int_0^{\infty} y^{14/45}\exp\left[-y - \left(\frac{\Gamma(19/9)}{\Gamma(59/45)}\right)^3\frac{T}{y^{12/5}}\right]dy, \end{aligned}$$

which, in turn, to within three percent, is reproduced by the function [37]

$$I(N, t) = (1 + 1.75T^{73/306})\exp(-2.1122T^{5/17}). \tag{41}$$

(Note that Eq. (39) was obtained in [16, 36] for another model of attachment of chromophores to the polymer chain and for another type of conformation transition but that derivation appears to be valid in the case under consideration as well).

Equation (39) is to be solved separately for each value of N. After that, one should calculate the luminescence kinetics (37). This is a very time consuming task. Analytical results can be obtained only in the limit of very small τ_{conf}.

It was shown in our paper [37] that when τ_{conf} reduces, kinetics (39) becomes exponential: $I_{\text{hop}}(N, t) \sim \exp(-k_{\text{hop}}(N)t)$, where $k_{\text{hop}}(N)$ is the rate constant obtained from the equation

$$\begin{aligned} k_{\text{hop}}(N) &= \left(1 - \frac{1}{\tau_{\text{conf}}}\int_0^{\infty} I(N, t)\right. \\ &\left.\times\exp(-t/\tau_{\text{conf}})dt\right)\Big/\int_0^{\infty} I(N, t)\exp(-t/\tau_{\text{conf}})dt. \end{aligned} \tag{42}$$

For this reason, in the limit of small τ_{conf}, Eq. (37) can be rewritten in the form

$$I_{\text{hop}}(t) = \exp\left[-c\int_{-\infty}^{\infty} dN(1 - e^{-k_{\text{hop}}(N)t})\right]. \tag{43}$$

Using Eq. (42), we obtained [37] the rate constant $k_{\text{hop}}^{\text{id}}(N)$ for the ideal polymer chain

$$k_{\text{hop}}^{\text{id}}(N) = \frac{1}{\tau_{\text{conf}}N^{3/2}}\left(\frac{R_0}{a}\right)^3\left(\frac{\tau_{\text{conf}}}{\tau}\right)^{1/2} \tag{44}$$

and the rate constant $k_{\text{hop}}^{\text{nid}}(N)$ for the nonideal chain

$$k_{\text{hop}}^{\text{nid}}(N) = \frac{1}{\tau_{\text{conf}}N^{59/30}}\left(\frac{R_0}{a}\right)^{59/18}\left(\frac{\tau_{\text{conf}}}{\tau}\right)^{59/108}. \tag{45}$$

Substituting these results in Eq. (43) and integrating, we obtain the luminescence kinetics $I_{\text{hop}}^{\text{id}}(t)$ for the ideal polymer chain

$$I_{\text{conf}}^{\text{id}}(t) = \exp\left[-5.358c\frac{R_0^2}{a^2}\left(\frac{\tau_{\text{conf}}}{\tau}\right)^{1/3}\left(\frac{t}{\tau_{\text{conf}}}\right)^{2/3}\right] \tag{46}$$

and the luminescence kinetics $I_{\text{hop}}^{\text{nid}}(t)$ for the nonideal chain

$$I_{\text{hop}}^{\text{nid}}(t) = \exp\left[-3.605c\frac{R_0^{5/3}}{a^{5/3}}\left(\frac{\tau_{\text{conf}}}{\tau}\right)^{5/18}\left(\frac{t}{\tau_{\text{conf}}}\right)^{30/59}\right]. \tag{47}$$

Note again that Eqs. (46) and (47) are valid in the limit of small τ_{conf}.

The time τ_{conf} is the model parameter: it equals the inverse rate constant of conformation transitions and can be obtained by the comparison of theoretical and experimental data.

By comparing the luminescence kinetics (46) and (47) obtained in the hopping limit of the polymer motion, with kinetics (35) and (36) obtained in the diffusion limit, we see that they similarly depend on time but differently on R_0. This fact can be used to make clear (by replacing chromophores attached to the polymer chain) the kinds of motion of a polymer in a solvent.

CONCLUSION

In this paper, we studied the kinetics of luminescence of chromophores randomly distributed over an isolated flexible polymer chain (a chromophore can be attached with a certain probability to each link of the polymer chain). The energy transfer between the chromophores was assumed to be of the dipole–dipole type. In the static case, when the polymer chain does not change its conformation during the excited-state lifetime, we obtained, for the ideal and nonideal chains, formulas (11) and (12) for the luminescence kinetics and formulas (17) and (18) for the emission anisotropy.

It was shown that the inhomogeneous broadening of the luminescence spectra of donors and absorption spectra of acceptors should be taken into account when an inhomogeneous broadening σ is large enough ($\sigma > 0.2\delta$, where δ is the homogeneous broadening).

In the dynamic case, when a flexible polymer chain changes its conformation during the excited state lifetime, we considered the diffusion and hopping limits of the polymer chain motion. In the diffusion limit, we derived formulas (32) and (33) for the luminescence kinetics of the ideal and nonideal chains, respectively. This type of motion obviously is not of great importance when the diffusion coefficient is sufficiently small ($D\tau \ll R_0^2$). We have shown that even in the limit of very fast diffusion ($D \longrightarrow \infty$) the luminescence kinetics remains nonexponential [see Eqs. (35) and (36)]. This results from the fact that acceptors attached to different links of the polymer chain perform Brownian motion in a confined space of different size.

We also studied the hopping limit of changes in the polymer chain conformation (an alternative to the diffusion limit). This type of polymer motion is important when the time of existence of a stable conformation is sufficiently short. We obtained analytical expressions for the luminescence kinetics in the limit of extremely short τ_{conf}. The kinetics remains nonexponential. The reason for this is the same as in the case of diffusion.

Note once again that the luminescence kinetics differs from that given in this paper by the factor $\exp(-t/\tau)$, which takes into account a finite lifetime of the excited chromophore states.

ACKNOWLEDGMENTS

E. N. Bodunov is grateful to INVOTAN (ICCTI, Portugal) for financial support.

REFERENCES

1. S. E. Webber, Chem. Rev. **90**, 1469 (1990).
2. B. Mollay and H. F. Kauffmann, in *Disordered Effects on Relaxation Processes*, Ed. by R. Richert and A. Blumen (Springer-Verlag, Berlin, 1994), pp. 509–541.
3. Th. Forster, Ann. Phys. (Leipzig) **2**, 55 (1948).
4. A. H. Marcus, D. M. Hussey, N. A. Diachun, and M. D. Fayer, J. Chem. Phys. **103**, 8189 (1995).
5. A. K. Roy and A. Blumen, J. Chem. Phys. **91**, 4353 (1989).
6. G. H. Fredrickson, H. C. Andersen, and C. W. Frank, J. Chem. Phys. **79**, 3572 (1983).
7. M. D. Edinger and M. D. Fayer, Macromolecules **16**, 1839 (1983).
8. K. A. Petersen and M. D. Fayer, J. Chem. Phys. **85**, 4702 (1986).
9. K. A. Petersen, A. D. Stein, and M. D. Fayer, Macromolecules **23**, 111 (1990).
10. G. H. Fredrickson, H. C. Andersen, and C. W. Frank, J. Polym. Sci., Polym. Phys. Ed. **23**, 591 (1985).
11. G. H. Fredrickson, H. C. Andersen, and C. W. Frank, Macromolecules **16**, 1456 (1983).
12. R. M. Pearlstein, J. Chem. Phys. **56**, 2431 (1972).
13. P. D. Fitzgibbon and C. W. Frank, Macromolecules **15**, 733 (1982).
14. G. H. Fredrickson and C. W. Frank, Macromolecules **16**, 572 (1983).
15. B. Ya. Balagurov and V. G. Vaks, Zh. Éksp. Teor. Fiz. **65**, 1939 (1973) [Sov. Phys. JETP **38**, 968 (1974)].
16. T. Palszegi, I. M. Sokolov, and H. F. Kauffmann, Macromolecules **31**, 2521 (1998).
17. I. M. Sokolov, J. Mai, and A. Blumen, J. Lumin. **76–77**, 377 (1998).
18. B. Movaghar, G. W. Sauer, and D. Wurtz, J. Stat. Phys. **27**, 473 (1982).
19. A. I. Onipko, L. I. Malysheva, and I. V. Zozulenko, Chem. Phys. **121**, 99 (1988).
20. A. Yu. Grosberg and A. R. Khokhlov, *Statistical Physics of Macromolecules* (American Inst. of Physics Press, New York, 1994).
21. C. R. Gochanour, H. D. Andersen, and M. D. Fayer, J. Chem. Phys. **70**, 4254 (1979).
22. D. L. Huber, Phys. Rev. B **20**, 2307 (1979).
23. D. L. Huber, Phys. Rev. B **20**, 5333 (1979).
24. M. N. Berberan-Santos and B. Valeur, J. Chem. Phys. **95**, 8048 (1991).
25. I. Rips and J. Jortner, Chem. Phys. **128**, 23 (1988).
26. G. Wilemski and M. Fixman, J. Chem. Phys. **60**, 866 (1974).
27. M. Doi, Chem. Phys. **9**, 455 (1975).
28. B. Fridman and B. O'Schaughnessy, Macromolecules **26**, 4888 (1993).

29. E. Haas, E. Katchalski-Katzir, and I. Z. Steinberg, Biopolymers **17**, 11 (1978).
30. G. Liu and J. E. Guillet, Macromolecules **23**, 2969 (1990).
31. G. Liu and J. E. Guillet, Macromolecules **23**, 2973 (1990).
32. J. R. Lakowicz, J. Kusba, W. Wiczk, *et al.*, Chem. Phys. Lett. **173**, 319 (1990).
33. J. R. Lakowicz, J. Kusba, I. Kryczynski, *et al.*, J. Phys. Chem. **95**, 9654 (1991).
34. E. N. Bodunov, M. N. Berberan-Santos, and J. M. G. Martinho, Chem. Phys. Lett. **297**, 419 (1998).
35. V. L. Ermolaev, E. N. Bodunov, E. B. Sveshnikova, and T. A. Shakhverdov, *Nonradiative Transfer of Electron Excitation Energy* (Nauka, Leningrad, 1977).
36. I. M. Sokolov, J. Mai, and A. Blumen, J. Lumin. **76–77**, 377 (1998).
37. M. N. Berberan-Santos, E. N. Bodunov, and J. M. G. Martinho, Opt. Spektrosk. **89**, 953 (2000) [Opt. Spectrosc. **89**, 876 (2000)].

Translated by V. Zapasskiĭ