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Luminescence Kinetics of Chromophores Attached to the Ends of a Flexible Polymer Chain

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Abstract—We studied the effect of the size of a polymer molecule, of the type of its motion in solution, and of the homogeneous and inhomogeneous broadening of its spectra on the luminescence kinetics of chromophores attached to the ends of a polymer chain. *© 2000 MAIK "Nauka/Interperiodica".*

INTRODUCTION

The electronic excitation energy transfer between donor and acceptor chromophores attached to a polymer chain is widely used as a tool for studying the polymer structure [1, 2]. The time dependence of the fluorescence intensity of donors and acceptors after pulsed excitation can be related to the distance between donors and acceptors via the rate of Förster energy transfer [3]. Such experiments are usually performed in very diluted solutions when energy transfer between different polymer molecules can be neglected. Of course, the energy transfer at moderate polymer concentrations cannot be neglected. The interpretation of experiments in such systems is a much more complicated problem because the observed quantities should be obtained from a solution of the many-particle problem of energy transfer [1, 4]

There are several types of the attachment of chromophores to polymer molecules. First, each polymer molecule can contain exactly one donor and one acceptor chromophore [5, 6]. Some biomolecules belong to this category, as do some polymers synthesized from macromolecules containing functional groups with different reaction ability with respect to donors and acceptors (excitation traps). Second, donors and acceptors can be randomly distributed along the polymer chain [1, 4, 6–11]. In this case, the probability of finding a chromophore in a certain unit of the polymer chain is independent of the number and type of chromophores located in other polymer-chain units. Third, each unit of the polymer chain is occupied, with a probability equal to unity, by a donor or acceptor chromophore. The distribution of chromophores along the polymer chain is random. The concentration of acceptors is low. Such polymer molecules can be simulated with a one-dimensional linear array [1, 2, 12–16]. One of the examples of such systems are aromatic polymers.

The aim of this paper is to study a direct incoherent energy transfer from the excited donor to another donor or acceptor, both of which that are attached to a polymer chain, and to examine the influence of the inhomogeneous broadening of the spectra of chromophores and the motion of a polymer molecule (the diffusion and hopping mechanisms of a change in the polymer chain configuration) on the energy transfer kinetics. Here, we will focus our attention on an isolated polymer chain (the polymer concentration is assumed to be low enough for the interaction between the chromophores attached to adjacent polymer chains to be neglected). We will assume that the solvent is suitable and that a polymer is found above the θ transition point. It is known that a polymer chain collapses above the temperature θ and the probability density of finding the ends of the polymer chain at a specified distance will differ from that used in this paper. We will study the case of the isotropic dipole–dipole interaction between chromophores, when the rate of energy transfer is described by the expression

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

Here, τ is the lifetime of the excited state of a donor, R_0 is the Förster radius, and r is the distance between chromophores.

STATISTICAL REGIME

As was mentioned above, there exist several models of the chromophore attachment to a polymer molecule. Here, we will consider the case of one donor and one acceptor localized at different ends of the polymer chain and will neglect reverse energy transfer to a donor. Then, we have the following differential equation for the decay of the excited state of the donor $p(t)$

$$\frac{d}{dt}p(r, t) = -w(r)p(r, t). \tag{2}$$

Equation (2) does not contain the excitation decay caused by a finite lifetime of the fluorescent state because this decay channel does not depend on energy transfer. Therefore, the total decay kinetics can be represented as a product of the term $\exp(-t/\tau)$ and the decay function caused by energy transfer to acceptors. Note that r in Eq. (2) does not depend on time because we neglect (in this part of the paper) the polymer motion during energy transfer. The distance r depends, of course, on the polymer chain configuration. Assuming that at the zero moment a donor is excited with the unit probability, we obtain from (2) the following time evolution of $p(r, t)$

$$p(r, t) = \exp[-tw(r)]. \tag{3}$$

The kinetics $I(t)$ of donor luminescence caused by irreversible energy transfer from donors to acceptors can be obtained by averaging expression (3) over all configurations with the distribution function $g_N(r)$. In the space of the dimensionality d, we have

$$I(t) = dV_d\int_0^\infty r^{d-1}g_N(r)e^{-tw(r)}dr, \tag{4}$$

where $V_d = \pi^{d/2}/\Gamma(1 + d/2)$, $\Gamma(x)$ is the gamma function, and $g_N(r)$ is the probability density of finding a polymer consisting of N units in which the distance between the chain length is equal to r.

For an ideal polymer chain (a Gaussian chain), we have [2, 17]

$$g_N(r) = A_1\exp(-B_1r^2),$$
$$A_1 = \left(\frac{d}{2\pi\langle R_g^2\rangle}\right)^{d/2}, \quad B_1 = \frac{d}{2\langle R_g^2\rangle}, \tag{5}$$

$$g_N(r) = A_1\exp(-B_1r^2),$$
$$A_2 = \frac{\delta B_2^{(d+\vartheta)/\delta}}{dV_d\Gamma[(d+\vartheta)/\delta]}, \tag{6}$$
$$B_2 = \left\{\frac{\Gamma[(d+\vartheta+2)/\delta]}{\Gamma[(d+\vartheta)/\delta]\langle R_g^2\rangle}\right\}^{\delta/2},$$

where R_g is the radius of the polymer knot, $\langle R_g^2\rangle = a^2N$ for an ideal chain, $\langle R_g^2\rangle = a^2N^{2\nu}$ for a nonideal chain, a is the length of a statistical segment (unit), and ϑ and δ are critical factors that depend on the dimensionality. The critical factors ϑ and δ can be written as $\vartheta = (\gamma - 1)/\nu$ and $\delta = (1 - \nu)^{-1}$, where γ and ν are two universal critical factors depending on d. The self-consistent Flori theory in the space of an arbitrary dimensionality d yields [17]

$$\nu = 3/(d+2), \quad d \le 4;$$
$$\gamma = 1, d = 1; \quad \gamma \approx 4/3, d = 2; \quad \gamma \approx 7/6, d = 3. \tag{7}$$

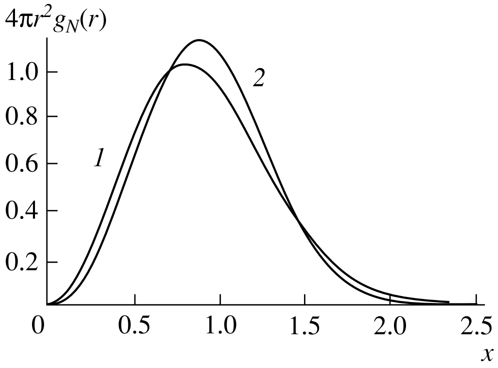

Fig. 1. Dependences of the distribution function $4\pi r^2g_N(r)$ for (*1*) ideal and (*2*) nonideal polymer chains on the dimensionless distance $r/\sqrt{\langle R_g^2\rangle}$.

Therefore, we obtain from Eqs. (7) and (6) in the three-dimensional space (we will consider below only this case)

$$\nu = 3/5, \quad \vartheta = 5/18, \quad \delta = 5/2,$$
$$A_2 = 0.289058, \quad B_2 = 1.22271. \tag{8}$$

Figure 1 shows the distributions functions (5) and (6) multiplied by $4\pi r^2$. For the polymer chain with the bulk interaction, the distribution function is narrower and its maximum is shifted to larger distances, while, in the region of small values, its values are smaller than those of the distribution function for a Gaussian chain.

Note that the results of the Flori theory [see Eqs. (8)] are very close (within 2%) to the results of computer simulations ($\nu = 0.59$ [17]) and their accuracy is sufficient for any real polymer chain.

Equations (4)–(6), and (8) allow one to calculate the averaged decay of the excitation when the donor and acceptor molecules are located at the ends of the polymer chain. By substituting (5) or (6) into (4), we obtain the decay law for ideal and nonideal polymer chains, respectively. For an ideal chain, we have

$$I_{\text{id}}(t) = \frac{2}{\pi^{1/2}}\int_0^\infty y^{1/2}\exp\left(-y - \frac{9T}{8y^3}\right)dy,$$
$$T = \frac{R_0^6}{\langle R_g^2\rangle^3}\frac{t}{\tau}, \tag{9}$$
$$\langle R_g^2\rangle = a^2N.$$

Note that kinetics (9) depends only on the parameter T. The integral (9), however, written in a less convenient form, was numerically analyzed in paper [6] for specific values of parameters R_0, R_g, and τ. Its long-time asymptotic ($t/\tau \gg 1$) was obtained in [5] by the method of steepest descent; however, the time beginning from which this asymptotic could be applied was not indi-

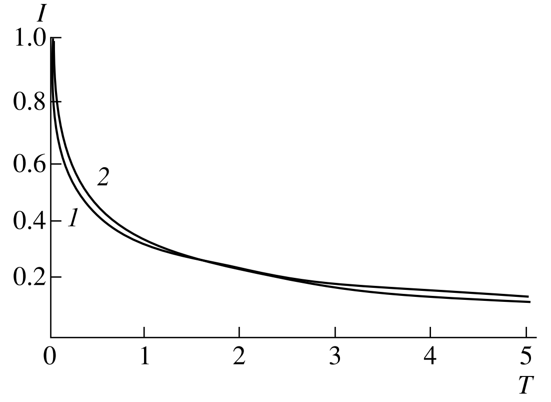

Fig. 2. Luminescence kinetics for (*1*) ideal and (*2*) nonideal polymer chains. Within the time interval shown in the figure, the difference between the curves amounts to 10%.

cated. Our numerical calculation of the integral in (9) showed that kinetics (9) can be approximated by the function

$$I_{\mathrm{id}}(t) = (1 + 2.45T^{1/4})\exp(-2^{5/4}T^{1/4}) \tag{10}$$

with the accuracy better than 1% for all times. Only one parameter (its final values is 2.45) was used upon variation. Thus, kinetics (10) (after multiplication by the factor $\exp(-t/\tau)$ that takes into account the final lifetime of the excited state of the donor) can be used for the interpretation of experimental results.

For a nonideal chain (with bulk interaction), we obtain

$$\begin{gathered} I_{\mathrm{nid}}(t) = \frac{1}{\Gamma(1 + 14/45)} \\ \times \int_0^\infty y^{14/45} \exp\left[-y - \left(\frac{\Gamma(19/9)}{\Gamma(59/45)}\right)^3 \frac{T}{y^{12/15}}\right] dy, \\ T = \frac{R_0^6}{\langle R_g^2 \rangle^3} \frac{t}{\tau}, \\ \langle R_g^2 \rangle = a^2 N^{2\nu}. \end{gathered} \tag{11}$$

This integral depends only on one parameter, T. The asymptotic form of expression (11) at long times was calculated in paper [5]. Our numerical analysis showed that kinetics (11) can be represented by the function

$$I_{\mathrm{nid}}(t) = (1 + 1.75T^{73/306})\exp(-2.1122T^{5/17}), \tag{12}$$

with an accuracy of better than 3% for all times. The deviation from the exact kinetics (11) is observed only in the time interval $0 < T < 0.4$.

By comparing expressions (10) and (12) with experimental data, we can try to determine the type of the polymer chain under study and the radius of the polymer knot (Fig. 2).

In polymers, where the donor–donor energy transfer takes place, a fundamental quantity from the theoretical and experimental point of view is the function $G^s(t)$, which represents the ensemble-averaged probability of the initial excitation of a chromophore at the moment t. The function $G^s(t)$ contains the contributions from excitations that never left the initially excited chromophores and from the excitations that returned to the initially excited chromophores after one or more hops. This function does not contain the excitation decay related to the lifetime of the excited state. The function $G^s(t)$ is related to the time-resolved measurements of the fluorescence depolarization [$r(t) = r_0G^s(t)$, where $r(t)$ is the fluorescence anisotropy and r_0 is the anisotropy at the initial moment [4, 11, 18]].

By considering two donors (the first and second) localized at the opposite ends of the polymer chain, we can write the following differential equations for the decay of excited states of donors $p_1(t)$ and $p_2(t)$:

$$\begin{aligned} \frac{d}{dt}p_1(r, t) &= -w(r)[p_1(r, t) - p_2(r, t)], \\ \frac{d}{dt}p_2(r, t) &= w(r)[p_1(r, t) - p_2(r, t)]. \end{aligned} \tag{13}$$

The solution of these equations, assuming that the first donor was excited with the unit probability at the initial moment, has the form

$$p_1(r, t) = \frac{1}{2} + \frac{1}{2}\exp[-2tw(r)]. \tag{14}$$

The function $G^s(t)$ is obtained by averaging expression (14) over all configurations with the distribution function $g_N(r)$ [see expressions (5) and (6)]. Note that the integrals obtained are similar to integrals (9) and (11) if we make the substitution $T \longrightarrow T_1$ in them, where

$$T_1 = \frac{2R_0^6}{\langle R_g^2 \rangle^3} \frac{t}{\tau} \tag{15}$$

[one can see this from expressions (3) and (14)]. They were numerically integrated for specific values of the parameters R_0, R_g, and τ in [6]. By approximating the numerical calculations, we obtained the equation

$$G^s_{\mathrm{id}}(t) = \frac{1}{2} + \frac{1}{2}(1 + 2.45T_1^{1/4})\exp(-2^{5/4}T_1^{1/4}) \tag{16}$$

for an ideal polymer chain (with an accuracy of better than 1%) and the equation

$$\begin{gathered} G^s_{\mathrm{nid}}(t) = \frac{1}{2} + \frac{1}{2}(1 + 1.75T_1^{73/306}) \\ \times \exp(-2.1122T_1^{5/17}) \end{gathered} \tag{17}$$

for a nonideal polymer chain (with an accuracy of better than 3%).

It is natural that $G^s(t) \longrightarrow 1/2$ for $t \longrightarrow \infty$ (Fig. 3), because each chain contains exactly two donors, and excitation can reside on each of them with equal probability.

INHOMOGENEOUS BROADENING

Considerable recent attention has been focused on polymer molecules containing chromophores under conditions of the inhomogeneous broadening of their spectra [2]. In such polymers, one can observe the dependence of the luminescence kinetics on the excitation wavelength (upon selective excitation), temperature, and the exciting pulse width. Here, we will try to determine for which ratio of the inhomogeneous σ and homogeneous δ spectral widths this dependence can be observed.

In the case of inhomogeneous broadening of the spectra, the luminescence kinetics $I_{\text{inh}}(t)$ observed upon nonselective excitation can be written in the form

$$I_{\text{inh}}(t) = \int g_{\text{D}}(E_1)dE_1 \int g_{\text{A}}(E_2)dE_2 \times \int dr 4\pi g_N(r) e^{-tw(E_1-E_2,\,r)}, \tag{18}$$

where $w(E_1 - E_2, r)$ is the rate of energy transfer from a donor to an acceptor, which have the electronic transition energies E_1 and E_2, respectively, and $g_{\text{D}}(E_1)$ and $g_{\text{A}}(E_2)$ are the normalized distributions of donor and acceptor chromophores over the electronic transition energies. We will assume for simplicity that, first, these distributions are described by Gaussians with equal widths and maxima located at the electronic transition energies E_{D} and E_{A},

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

$$g_{\text{A}}(E) = \frac{1}{\sqrt{2\pi}\sigma}\exp\left[-\frac{(E_{\text{A}}-E)^2}{2\sigma^2}\right], \tag{19}$$

$$E_{\text{D}} - E_{\text{A}} = \Delta E,$$

and, second, the homogeneous luminescence spectra of donors and acceptors are also described by Gaussians with the width δ. Then, the rate of dipole–dipole energy transfer, which is proportional to the overlap integral of the spectra [3], can be written as

$$w(E_1 - E_2, r) = \frac{1}{\tau}\left[\frac{R_0(E_1-E_2)}{r}\right]^6,$$

$$R_0^6(E_1 - E_2) = R_0^6 \exp\left[-\frac{(E_1-E_2)^2}{\delta^2} + \left(\frac{\Delta E}{\delta}\right)^2\right], \tag{20}$$

where R_0 is the Förster radius of energy transfer from a donor to an acceptor and E_{A} and E_{D} are the electronic transition energies of a donor and an acceptor, respectively.

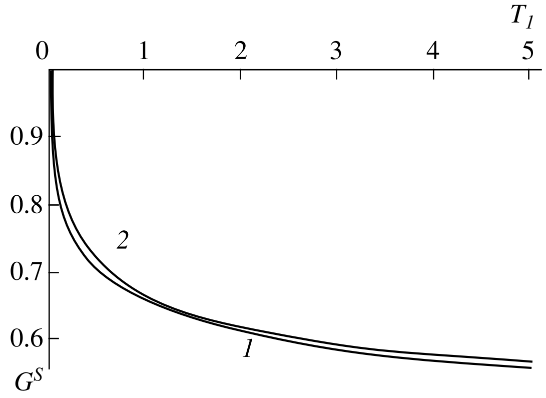

Fig. 3. Fluorescence depolarization kinetics for (*1*) ideal and (*2*) nonideal polymer chains. The difference between the curves amounts to 10%.

Note that the third integral in Eq. (18) was already calculated [see, for example, Eq. (10) for an ideal polymer chain]. By using this result and substituting (20) into (18), we obtain

$$I_{\text{inh}}(t) = \int g_{\text{D}}(E_1)dE_1 \int g_{\text{A}}(E_2)dE_2$$

$$\times [1 + 2.45T^{1/4}(E_1 - E_2)]\exp[-2^{5/4}T^{1/4}(E_1 - E_2)],$$

$$T(E_1 - E_2) = \frac{t}{\tau}\frac{R_0^6}{\langle R_g^2\rangle^3} \times \exp\left[-\frac{(E_1-E_2)^2}{\delta^2} + \left(\frac{\Delta E}{\delta}\right)^2\right]. \tag{21}$$

The kinetics (21) was calculated numerically. The results are presented in Fig. 4 for the case of $E_{\text{D}} = E_{\text{A}}$ (or $\Delta E = 0$). One can see that the increase in the inhomogeneous broadening (in the ratio σ/δ) results in the slowing down of the luminescence kinetics (21) because the inhomogeneous broadening reduces the rate of energy transfer for all donor–acceptor pairs [see Eq. (20)]. The luminescence kinetics for the case $\Delta E = 2\sigma$ is shown in Fig. 5. The kinetics becomes faster at short times and slows down at long times because the rate of energy transfer is far greater for the donor–acceptor pairs with $E_1 - E_2 < \Delta E$ [see (20)] than for the pairs with $E_1 - E_2 > \Delta E$. In any case, the influence of the inhomogeneous broadening is noticeable if $\sigma/\delta > 0.2$.

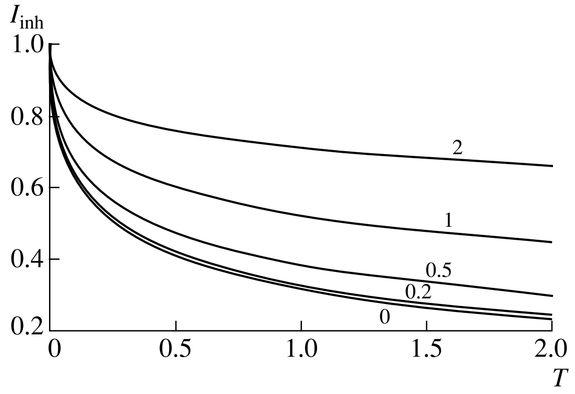

Fig. 4. Luminescence kinetics for an ideal polymer chain taking into account the inhomogeneous broadening of the spectra. A maximum of the luminescence spectrum of donors coincides with that of the absorption spectrum of acceptors ($E_A = E_D$). The values of σ/δ are shown at the curves.

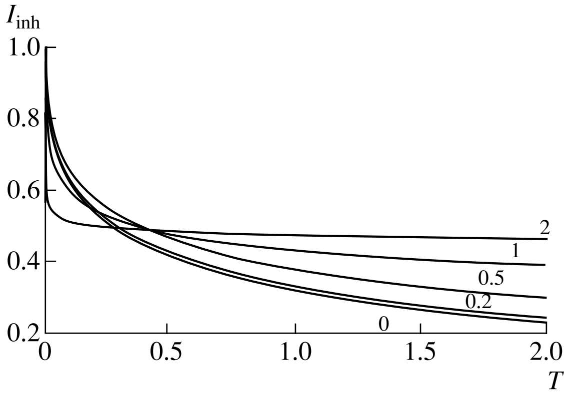

Fig. 5. Luminescence kinetics for an ideal polymer chain taking into account the inhomogeneous broadening of the spectra. A maximum of the luminescence spectrum of donors is shifted by 2σ ($E_D - E_A = 2\sigma$) relative to that of the absorption spectrum of acceptors. The values of σ/δ are shown at the curves.

EFFECT OF THE MOTION OF A POLYMER MOLECULE

The effect of the motion of a polymer chain in diluted solutions on the rate of intramolecular reactions between reaction groups attached to a flexible polymer chain has been studied in papers [19–21]. The influence of this motion on the luminescence kinetics has been studied in papers [22–26]. The chain motion was described in [19–21] by a generalized diffusion equation. It was assumed that the reaction occurs if reaction groups come within some short distance of each other (the contact reaction). The asymptotics of the reaction rate at short and long times were found. However, the authors of [19–21] failed to obtain the total reaction kinetics. Energy transfer (quenching of luminescence) is a similar process. The only difference (from the theoretical point of view) is the dependence of the reaction rate on the distance between chromophores [see (1)]. It is natural that this process was also described by the diffusion equation [22–26].

In this case, the luminescence kinetics is described by the expression

$$I_{\text{dif}}(t) = 4\pi\int_0^\infty r^2 g_N^*(r,t), \tag{22}$$

where $g_N^*(r,t)$ is the distribution function of the excited donors and unexcited acceptors over their separation, which are attached to the ends of the polymer chain having N units. At the initial moment, $g_N^*(r, t = 0) = g_N(r)$. In the static case, $g_N^*(r,t) = g_N(r)\exp[-tw(r)]$ [see (4)]. It is known [17, 22, 23] that loose units are involved in the Brownian motion in a dense solvent with a diffusion constant D, and the distribution $g_N(r)$ can be treated as the energy term if the interaction energy of the units is introduced as

$$V(r) = U(r)/kT = -\ln g_N(r). \tag{23}$$

Then, we can write the equation

$$\begin{gathered}\frac{\partial}{\partial t}g_N^*(r,t) = D\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}g_N^*(r,t)\\ + D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 g_N^*\frac{\partial V}{\partial r}\right) - w(r)g_N^*(r,t),\\ \frac{\partial}{\partial r}g_N^*(r,t) + \frac{\partial}{\partial r}V(r)|_{r=r_0} = 0,\\ g_N^*(r,0) = g_N(r).\end{gathered} \tag{24}$$

This approximation is known in the theory of diffusion-controlled reactions of polymers as the harmonic spring model [19]. The first two terms on the right-hand side of Eq. (24) describe a change in the distribution function $g_N^*(r, t)$ caused by the Brownian motion of the units (containing chromophores) in the spherical field $U(r)$, while the third term describes a decrease in the distribution function caused by the energy transfer from the excited donor to the acceptor; r_0 is the distance of the closest approach. The boundary condition (24) means that chromophores cannot come within a distance of each other less than r_0.

In papers [22, 25, 26], Eqs. (24) were solved numerically for the case of short polymer chains ($N = 4$–22) and special distribution functions $g_N(r)$. In papers [23, 24], these equations were solved for an ideal polymer chain. Comparison with experimental data showed that the diffusion coefficient can achieve the value 10^{-5} cm^2/s [24–26]. However, the values of parameters

D, R_0, R_g, and τ at which the diffusion motion of the ends of the polymer chain can be experimentally observed were not found.

By introducing new variables (the dimensionless distance x, time T [see (11)], and diffusion constant d)

$$x = \frac{r}{\sqrt{\langle R_g^2\rangle}},\qquad d = \frac{D\tau\langle R_g^2\rangle^2}{R_0^6}, \tag{25}$$

as well as the new function $f(x, T)$ defined by the expression

$$g_N^*(x, T) = f(x, T)g_N(x), \tag{26}$$

we can rewrite equations (22)–(24) for an ideal polymer chain in the form

$$I_{\text{dif}}(T) = 4\pi\int_0^\infty x^2 f(x, T)g_N(x)dx,$$

$$g_N(x) = \left(\frac{3}{2\pi}\right)^{3/2}\exp\left(-\frac{3}{2}x^2\right),$$

$$\frac{\partial}{\partial T}f(x, T) = d\frac{\partial^2}{\partial x^2}f + d\frac{\partial}{\partial x}f\left(\frac{2}{x} - \frac{\partial V}{\partial x}\right) - \frac{1}{x^6}f, \tag{27}$$

$$\left.\frac{\partial}{\partial x}f(x, T)\right|_{x = x_0} = 0,$$

$$f(x, 0) = 1,$$

$$\frac{\partial V}{\partial x} = 3x.$$

Equations (27) were solved numerically for $x_0 = r_0/\sqrt{\langle R_g^2\rangle} = 0.01$. The results are presented in Fig. 6. One can see that diffusion is important if $d = D\tau\langle R_g^2\rangle^2/R_0^6 > 10^{-5}$. Note that the kinetics becomes exponential ($I_{\text{dif}}(t) \sim \exp(-k_{\text{dif}}t)$, where k_{dif} is the rate constant) when d increases. In the limit of very fast diffusion,

$$k_{\text{dif}} = \frac{1}{\tau}4\pi\int_{r_0}^\infty\left(\frac{R_0}{r}\right)^6 g_N(r)r^2dr. \tag{28}$$

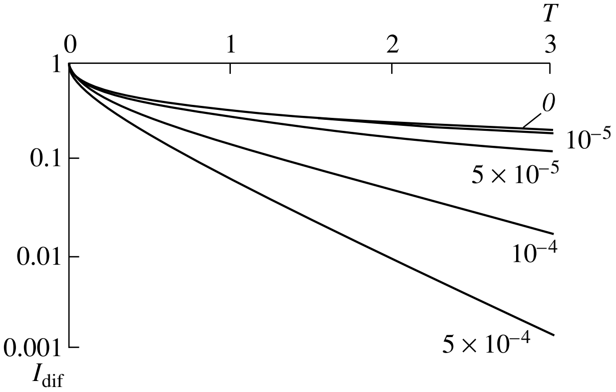

Fig. 6. Luminescence kinetics for an ideal polymer chain in the diffuse approximation. The values of the dimensionless diffusion coefficient d [formula (25)] are shown at the curves.

We can obtain from this equation for an ideal polymer chain [see (5)] the following expression for the rate constant $k_{\text{dif}}^{\text{id}}$ (with an accuracy up to a numerical coefficient of about 1):

$$k_{\text{dif}}^{\text{id}} \cong \frac{1}{\tau}\frac{R_0^6}{\langle R_g^2\rangle^{3/2}r_0^3}. \tag{29}$$

For a nonideal chain [see (6)], the rate constant is (with the same accuracy)

$$k_{\text{dif}}^{\text{nid}} \cong \frac{1}{\tau}\frac{R_0^6}{\langle R_g^2\rangle^{(3+5/18)/2}r_0^{3-5/18}}. \tag{30}$$

One can see that the difference between $k_{\text{dif}}^{\text{id}}$ and $k_{\text{dif}}^{\text{nid}}$ is quite small. By deriving expressions (29) and (30) from (28), we replaced the probability density $g_N(r)$ by a rectangular function with the width $\sqrt{\langle R_g^2\rangle}$ and assumed that $r_0 \ll \sqrt{\langle R_g^2\rangle}$. For this reason, expressions (29) and (30) are correct with an accuracy to a numerical coefficient of ~1.

Note that the diffuse approximation is valid if the distance between chromophores attached to the ends of the polymer chain changes (during the motion of polymer units) by small steps compared to the Förster radius R_0. The diffusion equation can be used for the description of the luminescence kinetics only in this case.

In general, one can suggest another type of motion of a polymer molecule, which is an alternative to the diffusion motion. One can assume that configuration transitions take place (the distance between donor and acceptor chromophores changes simultaneously) and that these transitions between stable configurations occur suddenly and randomly in time and space [13, 16, 27]. Therefore, the distance between chromophores changes in such a way that the initial configuration of the system is forgotten after some time t. This is the so-called hopping model of the polymer motion. The dis-

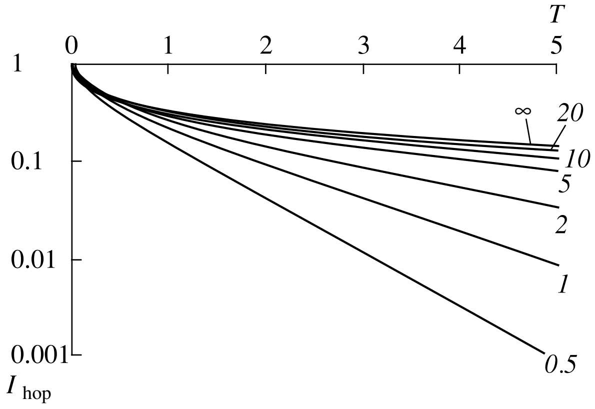

Fig. 7. Luminescence kinetics for an ideal polymer chain in the hopping approximation. The values of the dimensionless changing time of the chain configuration $T_{\mathrm{conf}} = R_0^6\tau_{\mathrm{conf}}/\langle R_g^2\rangle^3\tau$ are shown at the curves.

tance between chromophores changes compared to the Förster radius after each hop. By introducing the average time τ_{conf} of the configuration change and assuming that this change can be described by the Poisson process, we can obtain the following integral equation for the luminescence kinetics:

$$I_{\mathrm{hop}}(t) = I(t)\exp(-t/\tau_{\mathrm{conf}}) + \frac{1}{\tau_{\mathrm{conf}}}\int_0^t I(t_1)\exp(-t_1/\tau_{\mathrm{conf}})I_{\mathrm{hop}}(t-t_1)dt_1, \quad (31)$$

where $I(t)$ is the luminescence kinetics in the absence of the configuration change, which is described by Eqs. (9) or (10) for an ideal chain and by Eqs. (11) or (12) for a nonideal chain. (Note that Eq. (31) was obtained in [16, 27] for another polymer model in which each unit of a polymer molecule contains a chromophore, while quenchers are dimers whose position in the chain changes upon a change in the chain configuration. However, the derivation of the equation is also valid in the case considered here.)

After the introduction of the dimensionless time (11), Eq. (31) was solved numerically for an ideal polymer chain [$I(t) = I_{\mathrm{id}}(t)$ in Eq. (31)]. One can see from Fig. 7 that the polymer motion should be taken into account if the dimensionless time of the configuration variation $T_{\mathrm{conf}} = R_0^6\tau_{\mathrm{conf}}/\langle R_g^2\rangle^3\tau < 20$.

Note that when T_{conf} decreases, the luminescence kinetics becomes exponential: $I_{\mathrm{hop}}(t) \sim \exp(-k_{\mathrm{hop}}t)$, where k_{hop} is the rate constant. The latter can be obtained from the expression

$$k_{\mathrm{hop}} = \left(1 - \frac{1}{\tau_{\mathrm{conf}}}\int_0^\infty I(t)\exp(-t/\tau_{\mathrm{conf}})dt\right)\Big/\int_0^\infty I(t) \times \exp(-t/\tau_{\mathrm{conf}})dt. \quad (32)$$

By using this equation, we obtain the rate constant $k_{\mathrm{hop}}^{\mathrm{id}}$ for an ideal polymer chain [$I(t) = I_{\mathrm{id}}(t)$, see Eqs. (5) and (9)]

$$k_{\mathrm{hop}}^{\mathrm{id}} = \frac{1}{\tau_{\mathrm{conf}}}\alpha_{\mathrm{id}}T_{\mathrm{conf}}^{1/2} = \frac{1}{\tau_{\mathrm{conf}}}\alpha_{\mathrm{id}}\frac{R_0^3}{\langle R_g^2\rangle^{3/2}}\left(\frac{\tau_{\mathrm{conf}}}{\tau}\right)^{1/2}. \quad (33)$$

This yields $k_{\mathrm{hop}}^{\mathrm{id}} \propto (\tau_{\mathrm{conf}})^{-1/2}$.

The rate constant for a nonideal polymer chain [$I(t) = I_{\mathrm{nid}}(t)$, see Eqs. (6) and (11)] is

$$k_{\mathrm{hop}}^{\mathrm{nid}} = \frac{1}{\tau_{\mathrm{conf}}}\alpha_{\mathrm{nid}}T_{\mathrm{conf}}^{59/108}, \quad (34)$$

where α_{id} and α_{nid} are numerical coefficients ~1 ($\alpha_{\mathrm{id}} \approx \alpha_{\mathrm{nid}} \approx 1$). One can see that the difference between $k_{\mathrm{hop}}^{\mathrm{id}}$ and $k_{\mathrm{hop}}^{\mathrm{nid}}$ is small.

Comparison of the expressions for k_{dif} and k_{hop} shows that the diffusion and hopping mechanisms of motion yield different dependences on R_0 and $\langle R_g^2\rangle$. This allows one to determine in principle the type of motion of a polymer molecule.

CONCLUSIONS

We studied the luminescence kinetics for chromophores attached to the ends of an isolated flexible polymer chain. In the static case (when a polymer chain does not change its configuration during the lifetime of the excited state of the chromophore), we obtained Eqs. (10) and (12) for the luminescence kinetics (for ideal and nonideal polymer chains, respectively), which are valid for all times. We showed that the inhomogeneous broadening σ of the spectra of chromophores should be taken into account if it is large enough: $\sigma > 0.2\delta$, where δ is the homogeneous width of the spectrum.

In the dynamic case (when a flexible polymer chain changes its configuration during the excited-state lifetime of the donor chromophore), we studied the diffusion and hopping limits of the motion of a polymer molecule. We showed that these motions should be taken into account if the dimensionless diffusion constant d [see Eq. (25)] is large enough, i.e., $d > 10^{-5}$ (in the diffusion limit), or the dimensionless time of the configuration change is short, i.e., $T_{\mathrm{conf}} < 20$ (in the hopping limit). The luminescence kinetics becomes exponential with increasing diffusion constant or with decreasing average time of the configuration change.

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