
MOLECULAR
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Luminescence Kinetics of Linear Polymer Molecules with Chromophores Regularly 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 Chemical Physics of Molecules, Technical University, Lisbon, 1049-001 Portugal

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Abstract—An analytical expression for luminescence kinetics of a polymer chain in the static regime is obtained for the case when the rotational motion of monomers, leading to the formation of excimers (traps of excitations), is frozen. The conditions are found when the inhomogeneous broadening of the chromophore spectra and the conformation motion of the polymer chain should be taken into account. © 2001 MAIK “Nauka/Interperiodica”.

INTRODUCTION

The electronic excitation energy transfer and migration in polymers are widely investigated and are commonly used to analyze the polymer structure [1, 2]. This interest has arisen because the time dependence of the donor and acceptor chromophore luminescence intensity may be related to the interchromophore distance, via the Forster’s energy transfer rate [3]. Experiments of this kind are usually made at an extremely low polymer concentration, when the energy transfer between different polymer molecules may be neglected.

There are different types of attachment of a chromophore to the polymer chain [1, 2, 4–19]. In this paper, we study the following model. Each link of the polymer chain contains a donor or acceptor chromophore. The distribution of donors along the chain is regular. The distribution of acceptors is random, their concentration being low. Such polymer molecules (unless they form globules) may be considered as one-dimensional crystals [1, 2, 12–19]. An example of such systems is provided by aromatic polymers.

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 the inhomogeneous broadening of chromophore spectra and the conformation motion of the polymer chain on the luminescence kinetics.

STATIC CONDITIONS

The polymer chain is assumed to comprise molecules of two types: acceptors (traps, e.g., excimer-forming sites), distributed randomly along the chain, and donors (monomers), distributed regularly. The concentration of traps is low, and the majority of the chain con-

sists of monomer molecules. The distribution of traps is fixed within a time interval exceeding the lifetime of the donor excited state (the rotational motion of monomers, leading to the formation of excimers, is frozen).

The excitation (exciton) is simulated by a particle performing a one-dimensional symmetric Markovian random walk along a segment of the chain comprised of monomers and bounded by the two nearest traps. The excitation is transferred only between the nearest neighbors (the polymer temperature is assumed to be higher than the θ -point of the transition). It is also assumed that an exciton has one and the same probability to find itself on any link of the polymer chain. All probabilities of jumps are the same and equal to the mean probability of the jump per unit time W . Being on any monomer, an exciton also has the probability of vanishing (in a radiative or nonradiative way) instead of jumping to the nearest monomer or trap. This probability is independent of the position of the exciton in the chain and is equal to that for the monomer compound.

Under the conditions listed above, the following equations are valid, describing the dynamics of exciton motion along the polymer chain segment, bounded by two traps and comprised of n monomers:

$$\begin{aligned} \frac{d}{dt}p_j(t) &= W[p_{j+1}(t) - 2p_j(t) + p_{j-1}(t)], \\ &2 \leq j \leq n-1, \\ \frac{d}{dt}p_1(t) &= W[p_2(t) - p_1(t)] - Vp_1(t), \end{aligned} \quad (1)$$

$$\frac{d}{dt}p_n(t) = W[p_{n-1}(t) - p_n(t)] - Vp_n(t).$$

In Eqs. (1), $p_j(t)$ is the probability of finding the exciton on the monomer j at the instant t and V is the rate con-

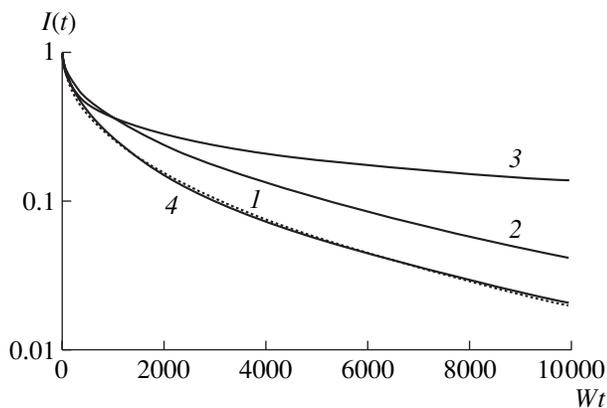


Fig. 1. Luminescence kinetics of the polymer chain in the static case. (1) The exact kinetics, calculated using formulas (3) and (4), (2) calculation by formula (7), (3) calculation by formula (8), and (4) calculation by formula (9).

stant of energy transfer from the donor (monomer) to a trap (acceptor). It is usually assumed that $V = W$. This is a reasonable assumption if the trap is an excimer-forming site of the polymer chain. Equations (1) do not include the loss of excitation related to the finiteness of the lifetime τ of the excited state, since this channel of the decay is independent of the energy transfer process, and, therefore, the total kinetics of the luminescence decay can be represented as the product of two cofactors: $\exp(-t/\tau)$ and the kinetics of the decay related to the energy transfer to the acceptor.

The kinetics of disappearance of excitation $G_n^D(t)$ localized on a polymer chain segment, comprised of n monomers, is given by the expression

$$G_n^D(t) = \sum_i^n p_i(t). \quad (2)$$

An exact formula for this function, under the initial condition $p_i(t=0) = 1/n$ ($1 \leq i \leq n$), was obtained in [12]. For the case $V = W$, it has the form [1, 12, 14]

$$G_n^D(t) = \frac{2}{n(n+1)} \sum_{k=1}^{n^*} \cot^2\left(\frac{\alpha_k}{2}\right) \times \exp\left[-4Wt \sin^2\left(\frac{\alpha_k}{2}\right)\right], \quad (3)$$

where $\alpha_k = (2k-1)\pi/(n+1)$; $n^* = n/2$ when n is even and $n^* = (n+1)/2$ when n is odd.

The luminescence kinetics $I(t)$ of the entire polymer chain is obtained by averaging expression (3) over segments with all possible n . The relevant distribution function is known and equals $c^2 n(1-c)^{n-1}$ [13, 14], where c is the acceptor concentration (the fraction of

links of the polymer chain occupied by the traps, $c \leq 1$). As a result, we have [1, 14]

$$I(t) = \sum_{n=1}^{\infty} c^2 n(1-c)^{n-1} G_n^D(t). \quad (4)$$

Evidently, $I(t=0) = 1$.

From formulas (3) and (4), we obtain the following asymptotic expression for the luminescence kinetics at short times ($Wt \ll 1$):

$$I(t) = 1 - 2cWt + c(1+c)(Wt)^2 - (Wt)^3 \left(\frac{2}{3}c + \frac{1}{3}c^2 + \frac{1}{3}c^3 \right). \quad (5)$$

In [15], for intermediate time intervals ($1 \ll Wt \ll c^2$), within the context of the diffusion approximation, assuming that $V = \infty$, another asymptotic formula was obtained:

$$I(t) = 1 - 4c\sqrt{Wt/\pi}. \quad (6)$$

Note that a linear chain consisting of N donors and two acceptors on its opposite ends, with $V = \infty$, is equivalent to a chain consisting of $N-2$ donors and two acceptors, with $V = W$ [12]. Equation (6) was also derived in [18, 19]. Bearing in mind asymptotic formula (6), the authors of [16] suggested the following approximate formula for the luminescence kinetics:

$$I(t) = \exp\left(-c\sqrt{\frac{8}{\pi}Wt}\right); \quad (7)$$

this formula is presumably valid for all times of practical importance. Finally, the authors of [14] obtained, using the t -matrix approximation, an expression for $I(t)$, presumably valid for a low concentration of traps ($c \ll 1$) and for long times ($Wt > 1$):

$$I(t) = \exp(4c^2Wt) \operatorname{erfc}[2c(Wt)^{1/2}], \quad (8)$$

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

We compared the exact kinetics [formulas (3) and (4)] with the approximate kinetics [formulas (7) and (8)] and found that expressions (7) and (8), which do not have any adequate asymptotics at short times, are not accurate in the most interesting time interval, where $I(t) > 0.001$ (see Fig. 1). We also noticed that the exact kinetics for intermediate times is very close to $(1/2)\exp(-c\sqrt{8Wt/\pi})$. For this reason, we designed an approximate kinetics, which satisfies the regularity found at intermediate times and has the exact asymp-

otic behavior (5) at short times. This kinetics is given by the expression

$$I(t) = \frac{1}{2} \exp\left(-c \sqrt{\frac{8}{\pi}} \sqrt{Wt}\right) + \frac{1 + (5 + \sqrt{8/\pi})c\sqrt{Wt}}{2[1 + 4cWt/(1 + 0.25Wt)]} \exp(-5c\sqrt{Wt}). \quad (9)$$

As follows from Fig. 1, this kinetics is sufficiently accurate over the whole, most interesting time interval, being, in practice, much more convenient than formulas (3) and (4), which require us to take into account a great number of terms (the series are slowly converging).

Formula (9) will be used below when studying the effect of the motion of a polymer molecule on luminescence kinetics, when the traps are the excimer-forming sites of the chain.

In the polymers in which only the donor–donor energy transfer is effective, a fundamental quantity, interesting both from theoretical and practical viewpoints, is $G^s(t)$ —the ensemble-averaged probability to find the initially excited chromophore still excited at the instant t . The probability $G^s(t)$ contains contributions from excitations that never abandoned the initially excited chromophore and from those that returned to this chromophore after one or several energy transfer events. As before, $G^s(t)$ does not contain a loss of excitation related to the finiteness of the chromophore excited-state lifetime. The probability $G^s(t)$ is related to the time dependence of the luminescence depolarization: $r(t) = r_0 G^s(t)$, where $r(t)$ is the luminescence anisotropy and r_0 is the initial anisotropy [4, 11, 20]. Note that for the polymers studied in this paper (without acceptors), the probability $G^s(t)$ is well known:

$$G^s(t) = \exp(-2Wt) I_0(2Wt), \quad (10)$$

where I_0 is the modified Bessel function.

INHOMOGENEOUS BROADENING

Special attention has been paid, in recent years, to polymer molecules that contain donors and acceptors with inhomogeneously broadened spectral lines [2]. In these polymers, one can observe the dependence of the luminescence kinetics on the excitation wavelength, the spectral width of the exciting pulse, and the temperature. In this paper, we make an attempt to answer the question: what is the smallest inhomogeneous broadening σ at which this effect becomes noticeable?

We will assume, for simplicity, that the normalized distribution of chromophores (donors) over the transi-

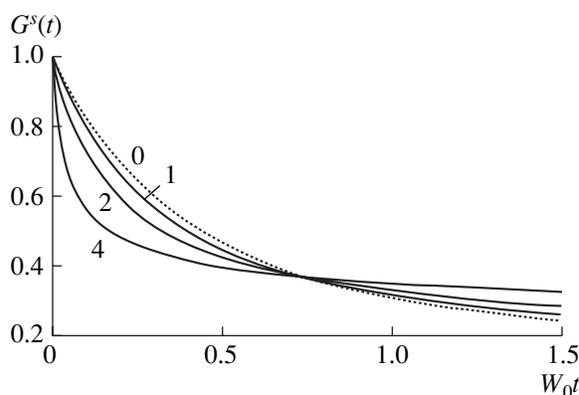


Fig. 2. Time dependence of the function $G^s(t)$ (luminescence anisotropy) for inhomogeneously broadened spectra of molecules under broad-band excitation. The numbers near the curves are the parameters σ/kT .

tion energies $g_D(E)$ is a Gaussian, with its maximum positioned at the transition energy E_D ,

$$g_D(E) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(E_D - E)^2}{2\sigma^2}\right]. \quad (11)$$

The rate of energy transfer between the nearest chromophores (from i th to j th) now depends on the energies of their transitions (E_i and E_j) and should satisfy the Boltzmann-type balance equation $W_{i \rightarrow j}/W_{j \rightarrow i} = \exp[-(E_j - E_i)/kT]$. Therefore, we can write

$$W_{i \rightarrow j} = W_0 \exp\left(-\frac{E_j - E_i}{2kT}\right) = W_0 \exp\left(-\frac{E_j - E_i}{\sigma} \frac{\sigma}{2kT}\right), \quad (12)$$

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

Under these conditions, we calculated, using the Monte Carlo method, the probability $G^s(t)$ related to the time dependence of the luminescence depolarization (the model of a linear polymer molecule, comprising 300 chromophores, with periodic boundary conditions was used). The results of the calculations are presented in Fig. 2 for the case of nonselective (broad-band) excitation of the chromophores. One can see that as inhomogeneous broadening increases (with increasing ratio σ/kT), the probability $G^s(t)$ decreases faster at shorter times, and slower at longer times, as compared to the times when inhomogeneous broadening is absent [Eq. (10)]. This result could be expected because in the presence of inhomogeneous broadening, $W_{i \rightarrow j} > W_0$ for one part of the molecules and the excitation energy leaves them faster, while for the other part, $W_{i \rightarrow j} < W_0$ and the energy transfer occurs more slowly. The latter

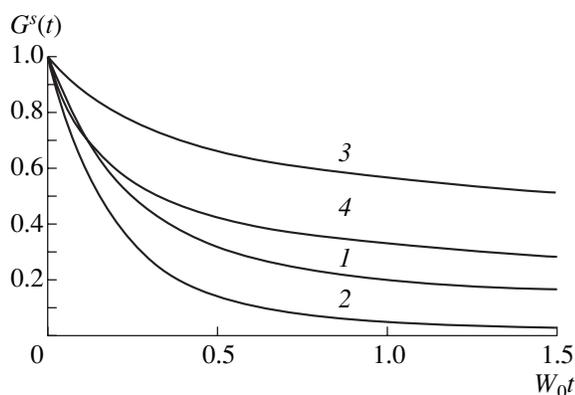


Fig. 3. Time dependence of the function $G^s(t)$ (luminescence anisotropy) for inhomogeneously broadened spectra of molecules under selective excitation ($\sigma/kT = 2$). (1) The energy of the chromophores initially excited is at the center of the inhomogeneously broadened line (11), $E = E_D$; (2) the energy of the chromophores initially excited lies on the short-wavelength side of the inhomogeneously broadened line, $E = E_D + \sigma$; (3) the energy of chromophores initially excited lies on the long-wavelength side of the inhomogeneously broadened line, $E = E_D - \sigma$; and (4) broadband excitation.

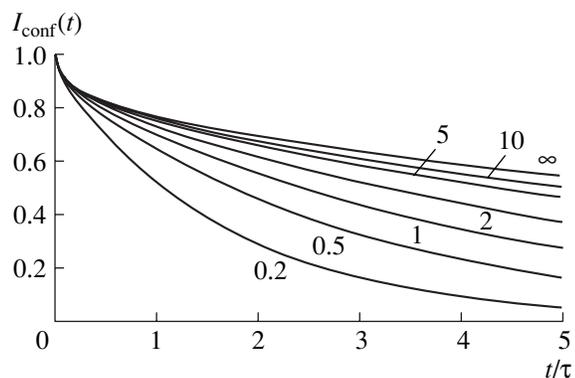


Fig. 4. Luminescence kinetics under conformation motion of the polymer chain. $W\tau = 50$ and $c = 0.02$. Figures near the curves are the values of the parameter τ_{conf}/τ .

statement is illustrated by Fig. 3, which shows the time behavior of the probability $G^s(t)$ under selective excitation of chromophores with a certain transition energy.

As follows from the data of Fig. 2, the inhomogeneous broadening should be taken into account, under nonselective excitation, when $\sigma/kT \geq 1$.

CONFORMATION MOTION OF THE POLYMER CHAIN

If the acceptor configuration (arrangement of the excimer-forming sites on the polymer chain) is fixed during the chromophore (monomer) excited-state lifetime, the luminescence kinetics is described by

Eqs. (3), (4), or (9). Now we assume that the conformation transitions may occur during the time τ , and these transitions between stable conformations are sudden and random both in time and in space. In this case, the arrangement of traps (excimer-forming sites) on the polymer chain changes abruptly, and the initial configuration of the system is forgotten after a certain time interval t . This type of conformation transition was mentioned in [13] and studied in [16, 17]. The model suggested for conformation transitions can be called "hopping." By introducing the conformation transition mean time τ_{conf} and assuming that the process of conformation changes is Poissonian, the authors of [16, 17] obtained the following equation for the luminescence kinetics $I_{\text{conf}}(t)$:

$$I_{\text{conf}}(t) = I(t)\exp(-t/\tau_{\text{conf}}) + \frac{1}{\tau_{\text{conf}}} \int_0^t I(t_1)\exp(-t_1/\tau_{\text{conf}})I_{\text{conf}}(t-t_1)dt_1, \quad (13)$$

where $I(t)$ is the luminescence kinetics in the absence of conformation transitions, described by (9). Equation (13) can be solved only numerically. Such a solution is given in [16], where function (7), strongly differing from the exact kinetics (see Fig. 1), is used as $I(t)$. For this reason, the results presented in [16] are of a qualitative nature. A correct solution of Eq. (13) is given in Fig. 4 [we used function (9) as $I(t)$ with $W\tau = 50$ and $c = 0.02$]. It follows from the data given in Fig. 4 that the conformation motion of the polymer chain can be noticed when $\tau_{\text{conf}}/\tau > 10$ (for the given trap concentration).

It is noteworthy that the luminescence kinetics becomes exponential with decreasing τ_{conf} : $I_{\text{conf}}(t) = \exp(-kt)$, where k is the rate constant. The latter constant can be found from the equation

$$k = \left(1 - \frac{1}{\tau_{\text{conf}}} \int_0^{\infty} I(t)\exp(-t/\tau_{\text{conf}})dt \right) / \int_0^{\infty} I(t)\exp(-t/\tau_{\text{conf}})dt. \quad (14)$$

Using this equation and Eq. (5), it is not difficult to calculate k in the limit of extremely short τ_{conf} :

$$k = 2cW. \quad (15)$$

This result can be easily explained. The polymer chain is separated by traps into segments of finite length. In the limit of short τ_{conf} , the exciton has an equal probability to be at any monomer of the segment, and this probability is independent of time. Each segment has two traps on its ends, with the rate constant of the energy transfer from the monomer to the trap being W . For this reason, the luminescence kinetics becomes exponential, with the rate constant determined by Eq. (15).

The time τ_{conf} is the model parameter, which is equal to the inverse rate constant of conformational transi-

tions and which can be obtained by comparing the experimental and calculated luminescence kinetics of aromatic polymers.

CONCLUSION

In this paper, we studied the kinetics of luminescence of chromophores attached to each link of a long polymer chain. In a static case, when the polymer chain does not change its conformation during the lifetime of the monomer excited state, we obtained analytical expression (9) for the luminescence kinetics.

The calculations using the Monte Carlo method showed that the inhomogeneous broadening of the chromophore spectra should be taken into account when the inhomogeneous broadening σ is greater than or equal to kT .

The hopping model of conformation motion of the polymer chain, leading to changes in positions of the excimer-forming sites along the chain, is studied. This type of motion is important when $\tau_{\text{conf}} \leq 10\tau$, where τ_{conf} is the time of conformation transformations. It is shown that the luminescence kinetics becomes exponential with decreasing τ_{conf} . The relevant rate constant is calculated.

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

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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. M. N. Berberan-Santos and B. J. Valeur, *Chem. Phys.* **95**, 8048 (1991).

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