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Monte-Carlo Simulation of Energy Migration in Uniaxially Oriented Polymer Films

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Nonradiative electronic energy migration between identical fluorophores is studied numerically in uniaxially oriented polymer films. The reorientation effect of dipole moments induced by film stretching leads to extremely different concentration- and time-courses of emission anisotropy compared to those in disordered system. In particular, the effect of a much weaker concentration depolarization of fluorescence is due to the fact that not only primarily excited molecules contribute to emission anisotropy in oriented films.

KEY WORDS: Monte-Carlo; polymer films; emission anisotropy; energy migration.

INTRODUCTION

It is well known that the concentration depolarization of fluorescence (CDF) in disordered systems can be explained by nonradiative energy migration from initially excited molecules to the other molecules of the same kind, but with a different orientation of their electronic transition dipoles. The theory of CDF in disordered systems has been developed by many authors [1–4]. The central and common point of various models is the determination of the conditional probability that the initially excited molecule at time $t = 0$ will be also excited at an arbitrary moment $t > 0$. Though no general solution has been found to this problem by now, progress already made in the theoretical description of energy migration in disordered systems allows for accurate description of most experimental data obtained for homogeneous solutions, polymer films or glasses.

However, the problem of energy migration in partly ordered systems still remains open and it is far from satisfactory solution. As an example can serve uniaxially oriented polymer film, for which the preferential distribution of dipole moments directions is obtained by mechanical stretching of the film along certain selected axis. Such oriented systems have been successfully used to determine the directions of transition dipole moments for numerous fluorophores [5–10]. They were also used to study molecular conformations and distance distributions of energy donor-acceptor pairs linked to the polymer chains [11,12]. On the other hand, stretched polymer film is a good model system for study energy transport in partly ordered systems, since the angular distribution of dipoles in space can be straightforward connected with the degree of stretching [5,6,13–15]. In this case the nonradiative energy transport can not be any longer described by models elaborated for disordered systems because of two basic reasons:

1^0 in such partly ordered systems not only primarily excited molecules contribute significantly to the emission anisotropy

2^0 in stretched polymer films the transition dipole moments of interacting molecules are not randomly oriented.

The aim of this paper is to deliver introductory information on the mechanism of energy migration in such

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uniaxially stretched films using the technique of Monte-Carlo simulation of concentration and time courses of emission anisotropy.

MONTE-CARLO SIMULATION

In a simulation, N fluorophores of a concentration C are randomly distributed in a three-dimensional cube representing a stretched film. Let us assume that the absorption transition moment of the j-th fluorophore forms an angle ϑ_j with the z-axis (which is also the film's stretching direction). By φ_j we will denote the angle between the transition moment projection $\vec{\varepsilon}_j$ onto the Oxy-plane and the x-axis. The angular configuration of simulated fluorophores is chosen from the uniform distribution on a unit sphere (i.e., the angle φ_j is taken from the uniform distribution in the interval $[0, 2\pi]$ and $\cos\vartheta_j$ is taken from the uniform distribution in the interval $[-1, 1]$) for the unstretched film. In the case of the stretched film, for a given multiplication factor R_s, the angle ϑ_j between the emission dipole and the z axis is given by the Tanizaki distribution function of the following probability density [13]:

$$f_g\left(\vartheta_j\right) = R_S^2 \sin\vartheta_j \left[1 + \left(R_S^2 - 1\right)\ \sin^2\vartheta_j\right]^{-3/2} \qquad (1)$$

The angle ϑ_j for j-th molecule is derived based on the inversion of the distribution function:

$$r_j = \int_0^{\vartheta_j} f_g(\omega)\, d\omega \qquad (2)$$

In the case of the Tanizaki distribution function, we obtain:

$$\cos\vartheta_j = \frac{R_S\, r_j}{\sqrt{1 + \left(R_S^2 - 1\right) r_j^2}}, \qquad (3)$$

where r_j denotes the pseudo random number generated based on the uniform distribution from the interval $[-1;1]$.

Next, let us denote the angle between the absorption and emission transition moments of j-th fluorophore by β. Thus, for a given vector of the absorption transition moment $\vec{\varepsilon}_j^A$ the direction of emission transition moment $\vec{\varepsilon}_j^E$ is calculated from the uniform distribution assigning the position of this vector on the cone lateral surface with the vertex angle 2β and the cone height parallel to the vector $\vec{\varepsilon}_j^A$ as it is presented in Fig. 1. The angle ψ_j on the cone basis is taken from the uniform distribution in the interval $[0, 2\pi]$. After determining the spatial and angular distribution of fluorophores, the Förster transfer rates are calculated [16]:

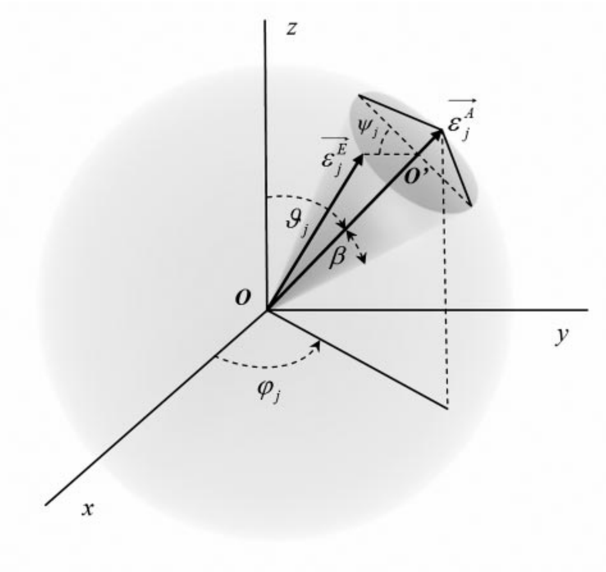

Fig. 1. Geometry of the system studied.

$$w_{x_i x_j} = \frac{\kappa_{ij}^2}{\tau_0}\left(\frac{R_0}{r_{ij}}\right)^6 \qquad (4)$$

where κ_{ij}^2 is the real orientation factor defined below:

$$\kappa_{ij}^2 = \left[\vec{\varepsilon}_i^A \cdot \vec{\varepsilon}_j^E - 3\left(\vec{\varepsilon}_i^A \cdot \vec{r}_{ij}\right)\left(\vec{\varepsilon}_j^E \cdot \vec{r}_{ij}\right)\right]^2 \qquad (5)$$

and $\vec{r}_{ij}$ denotes the distance vector between the transition moments unitary vectors $\vec{\varepsilon}_i^E$ and $\vec{\varepsilon}_j^A$, τ_0 is the mean fluorescence lifetime in the absence of energy migration.

The dynamics of the system considered is described by the master equation:

$$\begin{cases} \frac{dP_{x_i x_j}(t)}{dt} = -\frac{1}{\tau_0} P_{x_i x_j}(t) + \sum\limits_{k=1}^{N} w_{x_i x_k}(t) P_{x_k x_j}(t) \\ \qquad\qquad - \sum\limits_{k=1}^{N} w_{x_k x_i}(t) P_{x_i x_j}(t) \\ P_{x_i x_j}(0) = \delta_{ij} \end{cases} \qquad (6)$$

where $P_{x_i x_j}(t)$ is the probability density that an excitation is on the i-th fluorophore at time t, provided it was on the j-th fluorophore at time $t = 0$. δ_{ij} denotes the Kronecker delta. In the case of random systems the solution to Eqs. (6) is expressed in terms of the Green function, which has a physical meaning of the averaged conditional probability density of the excitation being found at a position $\mathbf{r}$ at time t, if it has been created at the initial time moment $t = 0$ at the origin $\mathbf{r}'$. Of special interest is the diagonal part of this function , G_{SD}, which represents the density of the initial site survival probability related directly to the concentration depolarization [17].

The effect of the finite size of the generated system is reduced by introducing periodic boundary conditions (the cube is surrounded by replicas of itself) with the minimum image convention (the molecule interacts with another molecule or its periodic image).

In the current work the "step by step" Monte Carlo simulation method is used [18–20]. Basically, this method consists in the employment of the random-number generator for the cyclic formulation of answers to two questions: when any of the preset luminescent processes takes place in the simulated system, and what kind of a process it is.

The simulation algorithm includes the following steps:

1^0 the primarily excited fluorophores are determined according to the probability $\cos^2 \vartheta_j$. These molecules can be deactivated through the following processes:

(P_1) process 1: $D^* \to D$, photon emission or nonradiative energy conversion, with the rate $1/\tau_0$, where D^* denotes excited and D unexcited molecule;

(P_2) process 2: $D^* + D \to D + D^*$, energy migration (energy transfer to the molecules of the same kind), with the transfer rate $w_{x_i x_j}$;

2^0 If j-th donor (fluorophore) molecule is excited, the values of the following total transfer rates

$$c_{1j} = 1/\tau_0 \qquad c_{2j} = \sum_{i=1, i \neq j}^{N} w_{x_i x_j}, \tag{7}$$

are calculated.

3^0 The time at which any of the investigated processes occur (cp. step 1^0) is calculated by inverting the distribution function of the probability, $p_j(t, P_k)dt$, that the process P_k appears in the time interval $(t, t + dt)$ provided that the j-th molecule was excited at time t:

$$p_j(t) = \sum_{k=1}^{2} p(t, P_k) = c_j \exp(-c_j t) \tag{8}$$

where

$$c_j = c_{1j} + c_{2j} \tag{9}$$

For this purpose a random number r_{1j} is generated and the time at which any process takes place is obtained by inverting the distribution function of the probability $p_j(t, P_k)$,

$$\int_0^{t_j} p_j(t)\,dt = r_{1j}, \text{ i.e. } t_j = -(1/c_j)\ln(1 - r_{1j}) \tag{10}$$

4^0 In this step it is determined which process took place at time t_j. By generating next random number, r_{2j}, such a value of index k can be found for which the following inequality is satisfied:

$$\sum_{i=1}^{k-1} c_{ij} < r_{2j} c_j \leq \sum_{i=1}^{k} c_{ij}, \; k = 1, 2 \tag{11}$$

If $k = 1$, then the activated molecule is quenched by a photon emission or nonradiative excitation energy conversion and it means that this pass of the simulation is finished. If $k = 2$, the energy migration takes place, and it is necessary to determine which molecule is now activated. For this reason the third random number, r_{3j} is generated and the value of the index n is found, which fulfills one of the inequalities:

$$\sum_{i=1}^{n-1} w_{x_i x_j} < r_{3j}(c_{1j} + c_{2j}) \leq \sum_{i=1}^{n} w_{x_i x_j}, \quad \text{for } n \leq N \tag{12}$$

where n is the number of next activated donor molecule. Then, after inserting the value of n for the index j, the simulation goes to step 2^0. The simulation run is finished when, after several migration acts, the process with $k = 1$ occurs in step 4^0 (photon emission or nonradiative energy conversion). After that a new simulation starts (for a new molecular spatial and angular configuration).

Having known the angular coordinates and the time moment t, at which the fluorophore emitted a photon, terminating a Monte Carlo simulation step, the components of the emission intensity along the axes, $I_x(t)$, $I_y(t)$ and $I_z(t)$ can be calculated:

$$I_z(t) = I_0 \cos^2 \vartheta_j(t), \tag{13}$$

$$I_x(t) = I_0 \sin^2 \vartheta_j(t) \cos^2 \varphi_j(t), \tag{14}$$

$$I_y(t) = I_0 \sin^2 \vartheta_j(t) \sin^2 \varphi_j(t). \tag{15}$$

where $\vartheta_j(t)$ and $\varphi_j(t)$ are the respective angles of the j-th fluorophore emission transition moment.

The emission anisotropy as a function of time was obtained in three independent ways to verify the Monte Carlo simulation accuracy, i.e., from the two equivalent equations for the random distribution of transition moments:

$$r(t) = (I_z - I_y)/(I_x + I_y + I_z), \tag{16}$$

$$r(t) = \frac{3}{2}\cos^2\vartheta_j(t) - \frac{1}{2} \tag{17}$$

as well as according to the probability $\cos^2\vartheta_j$ of detecting the photons emitted in the z-axis direction. Virtually the same emission anisotropy values were obtained independently of the method used (the differences in anisotropy did not exceed 0.1%).

Additionally, in the case of parallel emission and absorption transition moments, the Monte Carlo simulation results were compared to the theoretical formula for the emission anisotropy as a function of R_s valid in the absence of energy migration [5]:

$$r(R_s) = \frac{3}{2} \times \frac{(a^2-1)^{1/2} + 2a^2(a^2-1)^{-1/2} - 3a^2 \arcsin(1/a)}{2(a^2-1)^{-1/2} - 2\arcsin(1/a)} - \frac{1}{2}, \tag{18}$$

where $a^2 = R_s^2/(R_s^2 - 1)$

Finally, when the absorption and emission transition moments form the angle β, to verify the Monte Carlo simulation results, the comparison with the theoretical formula:

$$r(R_S, \beta) = r(R_S)\left(\frac{3}{2}\cos^2\beta - \frac{1}{2}\right) \tag{19}$$

obtained also in [5] was performed. After carrying out the above mentioned numerical tests the Monte Carlo simulations were performed for the system of fluorophores in a stretched film in the presence of energy migration. The final results are obtained by averaging the above described observables over suitably big number of spatial and angular configurations. In our simulation we performed calculations for 2000 molecules and 50000 configurations.

RESULTS AND DISCUSSION

Figure 2 shows the time course of the relative emission anisotropy and the Green function G_{SD}, for disordered ($R_{s.} = 1$) and strongly ordered film ($R_{s.} = 7$) for $\beta = 0$. Let us herein remind that the Green function $G_{SD}(t)$ is the measure of conditional probability that the molecule initially excited at $t = 0$ remains excited at a certain time $t > 0$. The results presented correspond to the case of strong energy migration ($C = 0.01$ M). It can be seen from the figure that the course of the Green function $G_{SD}(t)$ is practically indistinguishable from that of $r(t)/r_0$ for the disordered system, however, it decays much faster from $r(t)/r_0$ for the strongly ordered system ($R_{s.} = 7$).

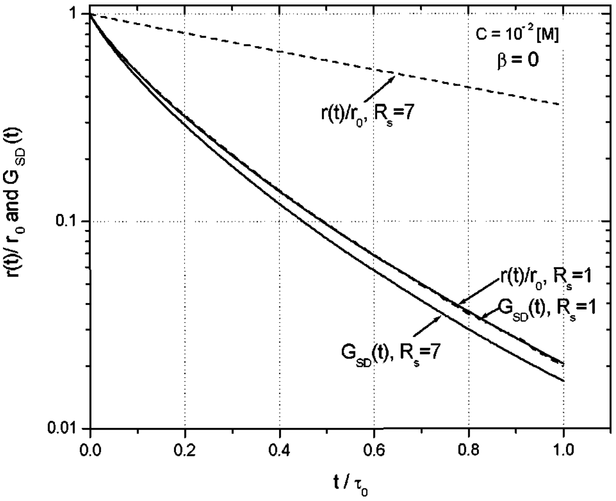

Fig. 2. Time courses of the Green function $G_{SD}(t)$ and $r(t)/r_0$ in the case of strong energy migration. The curves have been obtained using the Monte-Carlo method for $C = 0.01$ M and two critical distances $R_0 = 4.88$ nm and $R_0 = 4.87$ nm corresponding to the real system of DTCI in stretched and unstretched PVA film, respectively.

It means that in the case of strongly ordered system the assumption that only primarily excited fluorophores contribute to the emission anisotropy is not valid. This assumption is fully justified, of course, for the disordered system ($R_{s.} = 1$) as evident from Fig. 2 and it confirms the well known result [21]. In the same figure one can also compare the time courses of both Green functions. The difference between both courses is rather subtle, which means that the process of energy remigration to the initially excited site is not significantly affected by dipoles reorientation due to the polymer stretching. Nevertheless, based on the Monte Carlo results it can be concluded that the remigration of energy is somewhat weaker in strongly ordered system especially at long times after excitation.

Figure 3 shows the Monte-Carlo results of CDF for three systems differing in R_s. As expected, for disordered films ($R_s = 1$) the emission anisotropy rapidly decreases with the increase in concentration as a result of energy migration between randomly distributed fluorophores. For a moderately ordered system ($R_s = 3$) the concentration depolarization is significantly weaker and for strongly ordered system ($R_s = 7$) it is extremely weak. Such a different behavior of emission anisotropy in each system can be explained similarly as above described time-dependent regularities: with the increase in concentration more light is emitted by other than primarily excited molecules as a result of energy migration from them to initially unexcited fluorophores. Due to the preferential mutual orientation of dipoles exchanging energy in partly ordered systems the

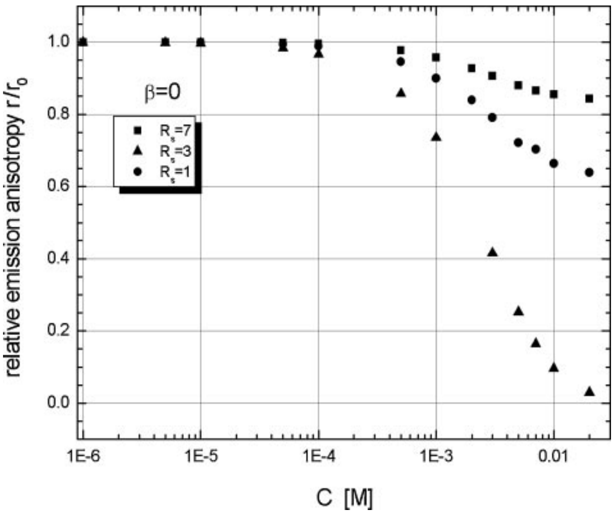

Fig. 3. Monte-Carlo results of CDF in 7 times stretched, 3 times stretched and unstretched PVA films denoted respectively as full squares, circles and triangles.

molecules receiving energy preserve partly the orientation of polarization vector of initially excited dipoles and significantly contribute to emission anisotropy. The results presented in this figure were obtained for the critical distance $R_0 = 4.87$ nm corresponding to an elongated fluorophore $3, 3'$ diethylthiacarbocyanine iodide in stretched poly(vinyl alcohol) film (for the disordered film R_0 does not practically change and it amounts to 4.88 nm [22]). It is also worth of note that the complete concentration depolarization of fluorescence takes place only for disordered systems ($R_s = 1$). For other partly ordered systems the emission anisotropy does not approach zero even in the limit of high concentrations. It tends, however, to a certain residual value characteristic for a given R_s. This interesting feature has been recently confirmed experimentally [22].

Figure 4 a-b shows the dependence of emission anisotropy on the molar concentration for several different values of the angle between the absorption and emission transition dipole moments. Fig. 4a shows the Monte-Carlo results for $R_s = 3$ (moderately ordered system) and Fig. 4b for $R_s = 7$ (strongly ordered system). It can be seen for both systems that the anisotropy courses depend very strongly on the value of β. It seems that such a strong dependence of emission anisotropy concentration course on β can be used to determine quite accurately the value of this angle for fluorophores exhibiting absorption and fluorescence spectra overlapping based on the best fit of simulated anisotropy concentration courses obtained for different R_s with the respective experimental data. Such a method would be more precise than the standard spectroscopic method due to significantly larger number of experimental points. A separate study reporting on that subject is in preparation.

An alternative presentation of the results described is given in Fig. 5. Again, Fig. 5a shows the results for $R_s = 3$ and Fig. 5b for $R_s = 7$. This time anisotropy course has been shown versus the angle for three different concentrations. Solid curve in the figure has been obtained based on the Eqs. (18)–(19) proposed by Gryczyński and Kawski [5]. Amazingly good correspondence between this expression and Monte Carlo results has been obtained for concentrations C low enough to neglect the energy migration. For concentrations C comparable or higher than the critical concentration certain discrepancy appears between the

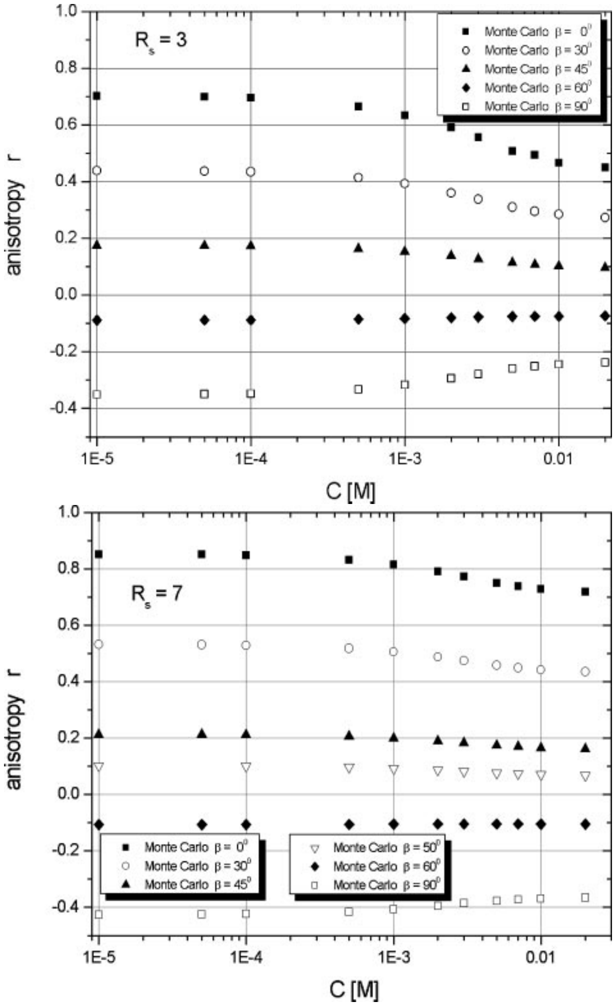

Fig. 4. The dependence of emission anisotropy on molar concentration for several values of the angle between the transition dipole moments in the absorption and fluorescence. Figure 4a shows the results of the Monte-Carlo simulation for $R_s = 3$ and Fig. 4b for $R_s = 7$.

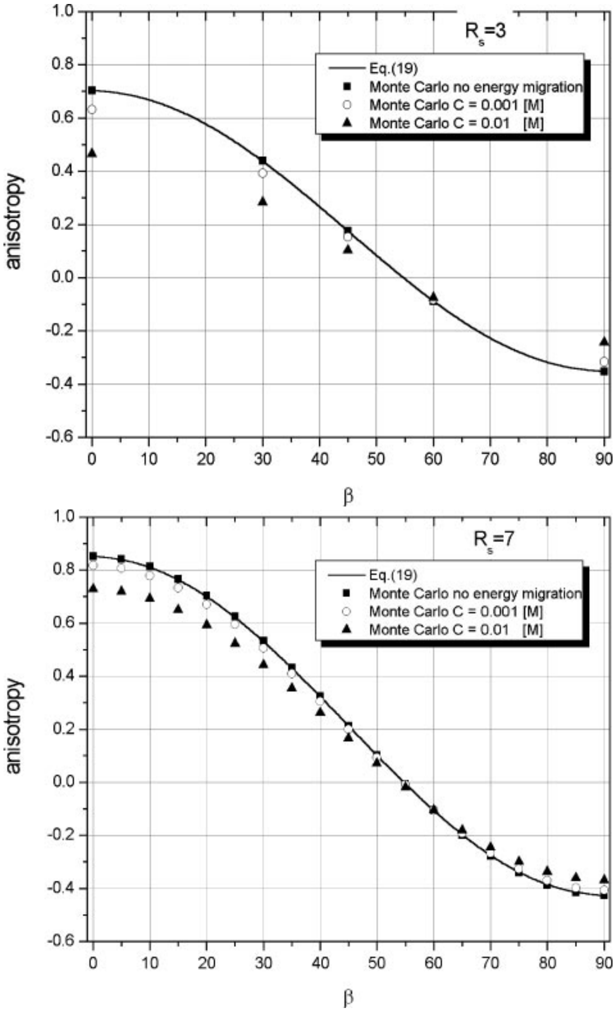

Fig. 5. Emission anisotropy versus the angle β for a couple of molar concentrations. The solid curve has been obtained based on the Gryczynski and Kawski model. Figure 5a shows the results for $R_s = 3$ and Fig. 5b for $R_s = 7$.

theory and Monte Carlo results due to the energy migration. This discrepancy is bigger for lower R_s, for which the concentration depolarization is stronger.

CONCLUSIONS AND FINAL REMARKS

It was shown in this paper that the depolarization of fluorescence in stretched polymer films due to energy migration is significantly weaker compared to disordered systems. Due to the preferential mutual orientation of interacting dipoles the molecules excited by energy transfer can also contribute significantly to the emission anisotropy. Therefore, the construction of an analytical model of multi-step energy migration in such stretched films is not easy. However, the technique of Monte-Carlo simulation allows for a very accurate prediction of the time or concentration course of emission anisotropy in a system of a given stretching factor R_s. It seems also that the comparison between the experimental emission anisotropy data and those derived from Monte-Carlo simulation for a series of concentrations can help to determine more accurately the directions of transition dipole moments of fluorophores with overlapping absorption and fluorescence spectra.

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