# Electronic Excitation Energy Migration in Partly Ordered Polymeric Films

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Multistep intermolecular energy migration between elongated fluorophores (carbocyanines) in uniaxially oriented polymer films is studied based on fluorescence depolarization and Monte-Carlo simulations. Contrary to disordered systems it is found experimentally that the concentration depolarization of fluorescence in uniaxially oriented films is extremely weak despite effective energy migration. Based on the concentration depolarization experiment in the ordered matrix it is possible to estimate the angle between absorption and fluorescence transition moments of carbocyanines. The values of that angle are very close to those obtained from other methods.

**KEY WORDS:** Fluorescence depolarization; carbocyanines; Monte-Carlo simulation; energy migration and transfer; uniaxially oriented polymer films; fluorescent aggregates.

## INTRODUCTION

Nonradiative electronic energy transport has been a subject of extensive investigations and interest over past years, since it delivers crucial information on complex molecular systems [1–4]. All theories of energy transport in disordered systems rely on a common assumption that only primarily excited molecules can preserve information on the orientation of the exciting light electric vector and contribute to the observed emission anisotropy [5–8]. Though this assumption has been well justified theoretically and checked experimentally in numerous disordered systems, its application to describe partly ordered systems (at macroscopic or microscopic level) seems doubtful [9, 10]. This issue can be very important to establish an appropriate model for energy transport in numerous partly ordered systems. Even more important, it can also affect the number and quality of information on molecular conformations of biomolecules, molecular logic gates or the mechanism of photosynthesis in artificial or natural partly ordered systems. Specific distribution of molecular transition moments in ordered systems depends on many factors and in most cases is not fully known. However, is it relatively well defined for elongated fluorophores in a uniaxially oriented polymer film, which is one of the reasons for using it as a good model partly ordered medium [11–17]. It is well known that due to polymer stretching in a certain arbitrarily defined axis, elongated fluorophores (and therefore their transition moments) assume preferential orientation along that direction and the degree of their orientation can be connected with the stretching multiplication factor $R_S$ and/or linear dichroism data. In such an ordered system, the mutual orientation of fluorophores exchanging excitation energy is highly correlated. As a result emission anisotropy is "transferred" together with excitation energy and it is strongly preserved during the migration process (contrary to disordered systems). In other words information on the orientation of exciting light electric vector can be kept in such a system until fluorescence occurs. The degree to which this information is preserved should depend strongly on the angle formed by the molecular transition moments in absorption and fluorescence. It seems that this fact can be useful in some topic

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applications (for example constructing molecular opto-electronic devices). Monte-Carlo simulations of energy migration in uniaxially stretched polymer films performed in [9], suggested that based on the concentration depolarization experiment in a uniaxially oriented film it should be possible to determine the angle between the transition moments in absorption and fluorescence. In this work, we would like to estimate the values of that angle for several carbocyanines based on the comparison between experimental and simulated values of concentration-dependent emission anisotropy in uniaxially oriented polymer films. We would like also to deliver further information on the mechanism of energy migration in such partly ordered media.

## EXPERIMENTAL DETAILS

As fluorophores we selected 3,3′ diethylthiacarbocyanine iodide (DTCI), 3,3′-diethyl-9-methylthiacarbocyanine iodide (MDTCI), and 3,3′-diethylthiacyanine iodide (DTTHCI). All dyes produced by Fluka were of analytical grade. They represent a class of elongated molecules, which orientate well in the stretched polymeric matrix. The dyes were dissolved in 5% water–ethanol mixture of poly(vinyl alcohol) (PVA) at temperature $T = 350$ K to obtain homogeneous solutions. The samples were left for evaporation in dust-free environment for about a week.

The degree of orientation of transition dipole moments was controlled by mechanical stretching of the film according to the standard procedure used in dichroic measurements [17]. The thickness $d$ of oriented samples used in emission anisotropy measurements was small enough to fulfil the relation: $2.3\varepsilon^{\max}Cd \leq 0.1$, where $\varepsilon^{\max}$ is the maximum value of the extinction coefficient. Upon this condition the re-absorption and re-emission effects are negligible [18]. The disordered thin films used as a reference were prepared similarly as in [19]. The absorption spectra were measured using Zeiss M-40 spectrophotometer. The fluorescence spectra and fluorescence quantum yields of donor and acceptor were measured upon front face excitation and observation of sample fluorescence using sensitive home-made spectrophotometer described elsewhere [20]. Fluorescence anisotropy was measured using two-channel single photon counting apparatus constructed in our laboratory [21, 22]. Mean fluorescence lifetimes were determined from exponential fluorescence decays using commercially available Edinburgh FLA 900 pulsed fluorometer equipped with appropriate LEDs (Nanoleds, IBH) as the excitation source.

## MONTE-CARLO SIMULATION

For the quantitative analysis of experimental data we performed Monte-Carlo simulations of emission anisotropy. Since the detailed procedure has been described previously [9] we will here draw attention only to selected details. In a simulation, $N$ fluorophores of a concentration $C$ are randomly distributed in a three-dimensional cube representing a stretched film. For a given stretching multiplication factor $R_S$, the angle $\vartheta_j$ between the transition dipole moment in absorption and the $z$-axis is given by the Tanizaki distribution function of the following probability density [11, 12]:

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

The angle $\vartheta_j$ for $j$th molecule is derived based on the inversion of the distribution function:

$$r_j = \int_0^{\vartheta_j} f_g(\omega)\mathrm{d}\omega \quad (2)$$

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

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

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

After determining the spatial and angular distribution of fluorophores, the Förster transfer rates are calculated [23]:

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

where $\kappa_{ij}^2$ is the real orientation factor defined below:

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

and $\vec{r}_{ij}$ denotes the distance vector between the transition moments unitary vectors $\overrightarrow{\varepsilon_i^E}$ (emission) and $\overrightarrow{\varepsilon_j^A}$ (absorption), $\tau_0$ is the mean fluorescence lifetime in the absence of energy migration.

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

$$\begin{cases} \dfrac{\mathrm{d}P_{x_i x_j}(t)}{\mathrm{d}t} = -\dfrac{1}{\tau_0}P_{x_i x_j}(t) + \sum_{k=1}^{N} w_{x_i x_k}(t)P_{x_k x_j}(t) - \sum_{k=1}^{N} w_{x_k x_i}(t)P_{x_i x_j}(t) \\ P_{x_i x_j}(0) = \delta_{ij} \end{cases} \quad (6)$$

where $P_{x_i x_j}(t)$ is the probability density that an excitation is localized on the $i$th fluorophore at time moment $t$, provided it was on the $j$th fluorophore at the initial moment of time $t = 0$. $\delta_{ij}$ is the Kronecker delta. For random systems, the solution to Eq. (6) can be 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 **r** at time $t$, if it has been created at the initial time moment $t = 0$ at the origin **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 [24, 25]. For the uniaxially stretched films, the problem of multistep energy migration has not been solved analytically until now, therefore the use of Monte-Carlo simulation technique is even more important.

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:

$$I_z(t) = I_0 \cos^2 \vartheta_j(t), \tag{7}$$

$$I_x(t) = I_0 \sin^2 \vartheta_j(t) \cos^2 \varphi_j(t), \tag{8}$$

$$I_y(t) = I_0 \sin^2 \vartheta_j(t) \sin^2 \varphi_j(t) \tag{9}$$

where $\varphi_j(t)$ is the angle formed by the projection of emission transition moment onto OXY plane and $x$-axis (it has a uniform distribution over $[0; 2\pi]$).

It is easy then to determine the emission anisotropy:

$$r(t) = (I_z - I_y)/(I_x + I_y + I_z), \tag{10}$$

In the excited state the absorption and emission transition moments can generally form certain angle $\beta$. This case in the absence of energy migration is well described by classical formula proposed by Gryczyński and Kawski [13–16]:

$$r(R_S, \beta) = r(R_S) \left( \frac{3}{2} \cos^2 \beta - \frac{1}{2} \right), \tag{11}$$

$$r(R_S) = \frac{3}{2} \frac{(a^2 - 1)^{1/2} + 2a^2(a^2 - 1)^{-1/2} - 3a^2 \arcsin(1/a)}{2(a^2 - 1)^{-1/2} - 2 \arcsin(1/a)} - \frac{1}{2}, \tag{12}$$

where $a^2 = R_S^2/(R_S^2 - 1)$. We obtained excellent agreement of Monte-Carlo results with that formula at low dye concentrations. After carrying out several numerical tests, Monte-Carlo simulations were performed for the stretched film in the presence of energy migration. Final results were obtained by averaging over a big number of spatial and angular molecular configurations. In our simulation, we performed calculations for 2000 molecules and 250000 configurations. Under such conditions, the results of simulation remained practically independent of further
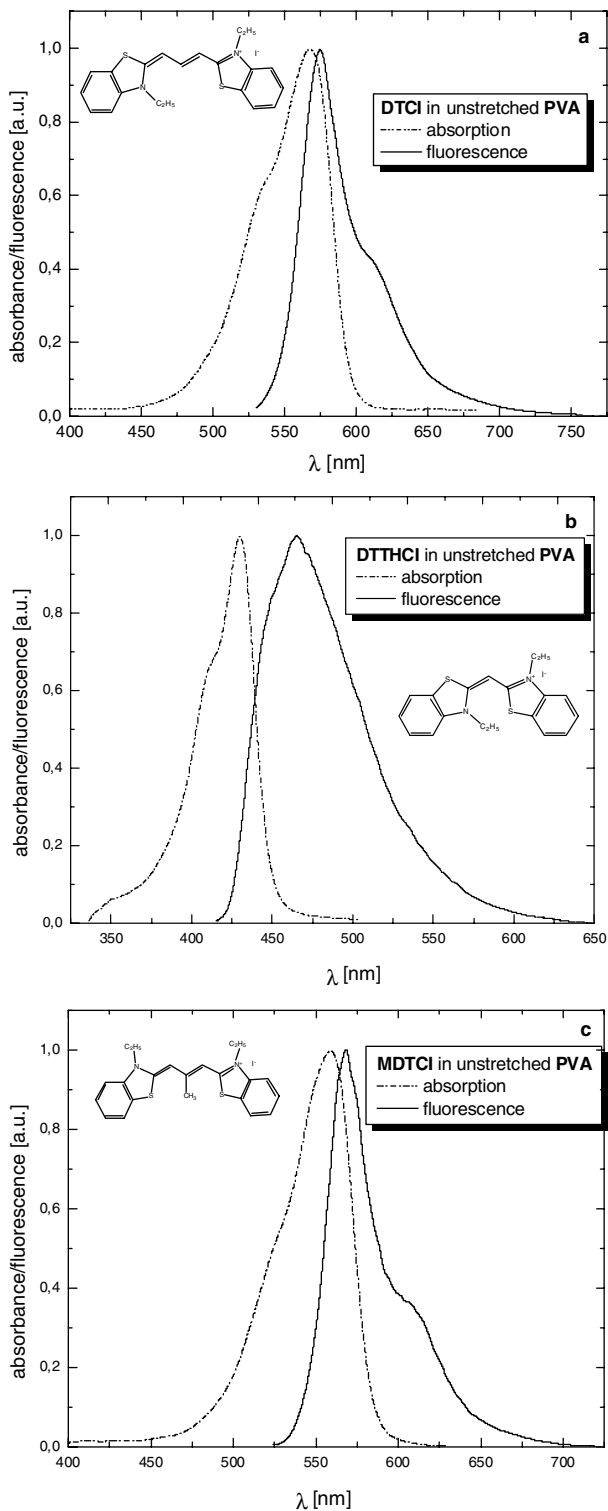


**Fig. 1.** Absorption (*dashed line*) and fluorescence (*solid line*) spectra of DTCI (a), DTTHCI (b), and MDTCI (c) in unstretched PVA film at $c = 0.0001$ M. Chemical formulas of the compounds studied are also shown in respective figures.

**Table I.** Selected Energy Transfer and Spectroscopic Parameters of Carbocyanines Studied in Stretched and Unstretched PVA Films at $T = 293$ K.

|  | $n \pm 0.001$ | $\eta_{OM} \pm 10\%$ | $r_{OM} \pm 0.003$ | $\tau_{OM} \pm 0.1$ (ns) | $R_0^{MM} \pm 0.5$ (Å) | $\langle \kappa^2 \rangle$ |
|---|---|---|---|---|---|---|
| DTCI in PVA |  |  |  |  |  |  |
| $R_S = 7$ | 1,655 | 0,33 | 0,83 | 3,9 | 48,7 from [26] | 0,457 |
| $R_S = 1$ | 1,660 | 0,33 | 0,31 | 3,8 | 48,8 from [26] | 0,476 |
| DTTHCI in PVA |  |  |  |  |  |  |
| $R_S = 7$ | 1,655 | 0,23 | 0,84 | 2,2 | 26,4 from [27] | 0,457 |
| $R_S = 1$ | 1,660 | 0,23 | 0,36 | 2,3 | 26,3 from [27] | 0,476 |
| MDTCI in PVA |  |  |  |  |  |  |
| $R_S = 7$ | 1,655 | 0,18 | 0,83 | 2,5 | 40.2 | 0,457 |
| $R_S = 1$ | 1,660 | 0,18 | 0,32 | 2,6 | 38.6 | 0,476 |

increase of configurations number even at the highest fluorophore concentration (relative change did not exceed 0.1%). Steady-state emission anisotropy results were obtained by time averaging of Eq. (10).

Using the definition of the orientation factor (5) we have also performed the Monte-Carlo simulation of its real average values in the ordered systems studied. This is necessary, since the angular distribution of transition moments in uniaxially stretched films is generally different than in the disordered medium.

## RESULTS AND DISCUSSION

Figure 1(a)–(c) shows absorption and fluorescence spectra of three carbocyanines in poly(vinyl alcohol) matrix at $T = 293$ K. Strong overlap between absorption and fluorescence spectra can be seen indicating the possibility of effective energy migration. The spectra presented in the figure were taken in disordered polymer matrix. The process of stretching did not induce significant change in the steady-state absorption and fluorescence spectra at low concentration. Table I shows the values of the most important spectroscopic and energy transfer parameters of the molecules studied in ordered and disordered films. It can be seen from the table that whereas the critical distances in both the systems remain practically the same, the difference in limiting emission anisotropy values $r_0$ between disordered and ordered films is enormous. This fact results, of course, from the distinct redistribution of fluorophores (and their transition moments) from random distribution in the unstretched film to highly correlated angular distribution in the uniaxially stretched polymer matrix. Table I also shows the values of the average orientation factor determined from the Monte-Carlo simulation. Surprisingly, despite distinct change in angular distribution of transition moments, the value of $\langle \kappa_{ij}^2 \rangle = 0.457$ simulated in ordered one-component systems ($R_S = 7$)

occurred quite close to that derived in disordered rigid systems $\langle \kappa_{ij}^2 \rangle = 0.476$ [28]. Figure 2 shows more detailed information on the extremely weak dependence of $\langle \kappa_{ij}^2 \rangle$ on $R_S$. Mention should herein be made that this result cannot be arbitrarily extended to ordered two or multicomponent energy donor–acceptor systems.

Since in the perfectly ordered systems the theoretical range of obtainable emission anisotropy is distinctly broadened (from $-0.5$ to $1.0$) compared to disordered systems (from $-0.2$ to $0.4$) depending on the angle $\beta$ between transition moments in absorption and fluorescence, we wondered if it was possible to estimate relatively small angles $\beta$ expected for elongated carbocyanines based on the comparison between absolute measured and simulated emission anisotropy concentration courses in uniaxially stretched polymer films ($R_S = 7$).

Figure 3 shows the simulation results and experimental data of emission anisotropy in strongly ordered
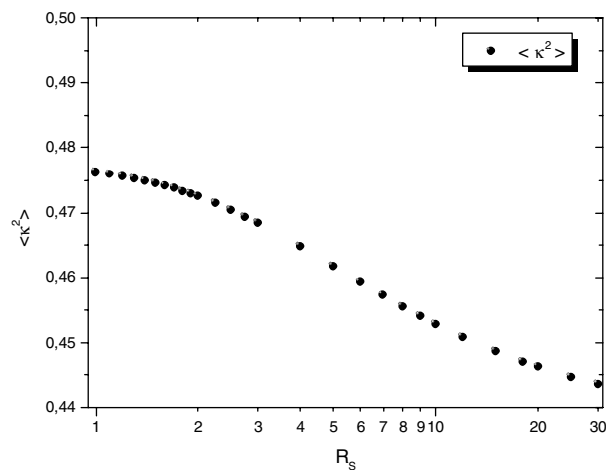
**Fig. 2.** The effect of order parameter $R_S$ on the mean value of the orientation factor obtained from Monte-Carlo simulation.
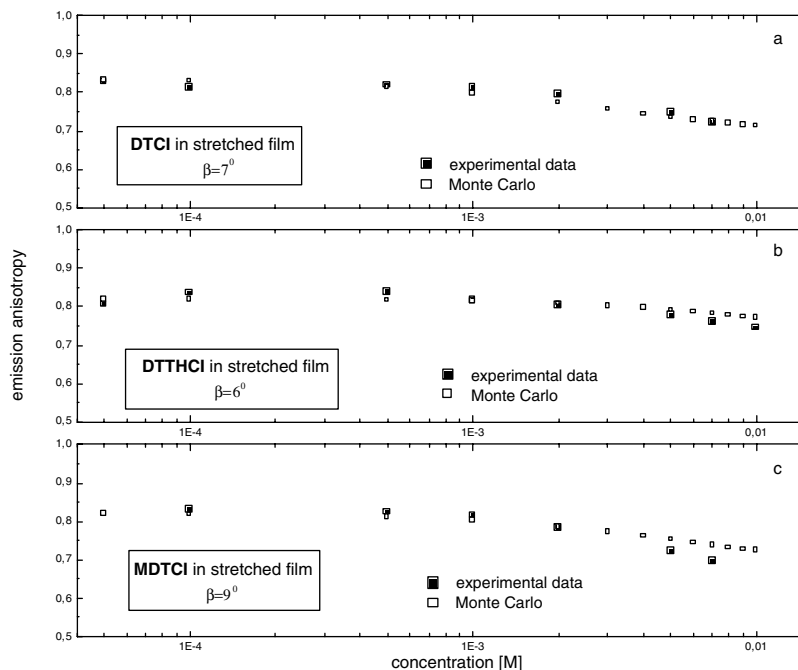
**Fig. 3.** Emission anisotropy concentration courses in uniaxially stretched PVA films ($R_S = 7$) for DTCI (a), DTTHCI (b), and MDTCI (c). *Full squares* correspond to experimental data, whereas *empty squares* to Monte-Carlo results.

systems ($R_S = 7$) for the best-fitting angle between the absorption and fluorescence transition moments and for the spectroscopic parameters listed in Table I. As seen from the figure, the best agreement between the simulation courses and experimental data takes place for the following values of angle $\beta$ between the absorption and emission transition moments of fluorophores studied: 7° for DTCI, 6° for DTTHCI, and 9° for MDTCI. These results stay in a quite good agreement with those estimated from emission anisotropy measurements at low dye concentrations in anhydrous glycerol at $T = 283$ K using the general Perrin equation:

$$r(\beta) = \frac{2}{5}\left(\frac{3}{2}\cos^2\beta - \frac{1}{2}\right), \qquad (13)$$

from which the following values of $\beta$ were obtained: 10° for DTCI ($r_0 = 0.381$), 8° for DTTHCI ($r_0 = 0.389$), and 10° for MDTCI ($r_0 = 0.381$). Emission anisotropy was measured with an accuracy of 0.003. Additionally, a comparison of Gryczyński–Kawski expressions (11) and (12) with a set of emission anisotropy data obtained for 12 different $R_S$ at low concentration was made for each molecule studied [29]. The best agreement was obtained for the following values of $\beta$: 7° for DTCI, 7° for DTTHCI, and 3° for MDTCI. From the data provided it follows that the values of $\beta$ are small and comparable independently of

the method used. Slight tendency towards higher $\beta$ values estimated from the Perrin formula may result from residual rotational depolarization in glycerol. Simultaneously, it was found from linear dichroism data that the transition dipole moment in absorption should be located parallel to the long molecular axis for carbocyanines as indicated by linear dependence between stretching multiplication factor $R_S$ and linear dichroism $R_D$ [29]. This fact holds true also for many other elongated molecules. It seems therefore that the analysis of energy migration in uniaxially oriented films can provide reliable information on the angle $\beta$ between transition moments in absorption and fluorescence, even if these angles are relatively small. We are going to study separately the case of high angles $\beta$ by this method (for example in acridone derivatives and some flavins).

Figure 4(a)–(c) shows the comparison between the results of Monte-Carlo simulation, GAF model of energy transport, and experimental data of relative emission anisotropy versus concentration for disordered systems. The concentration depolarization of fluorescence is remarkable in each subfigure of Fig. 4 due to strong energy migration between randomly distributed fluorophores (full symbols). Mention should be made that in the case of disordered films the analytical expressions describing concentration depolarization of fluorescence
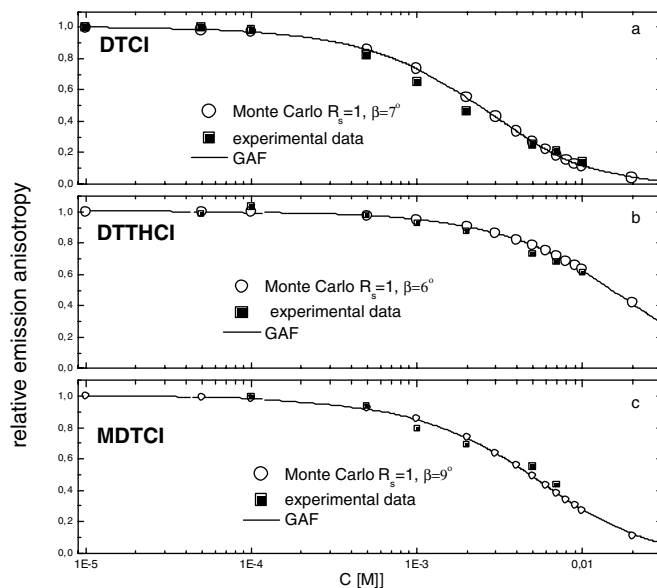
**Fig. 4.** Emission anisotropy concentration courses in unstretched PVA films ($R_S = 1$) for DTCI (a), DTTHCI (b), and MDTCI (c). *Full squares* correspond to experimental data, *empty circles* to Monte-Carlo results, and *solid line* to GAF model.

are known, which are valid for $\beta = 0$ [1,4,24,25,30,31]. These expressions were obtained within the framework of the hopping and self-consistent diagrammatic models. Though distinctly different in their analytical form they yield practically the same results for the systems studied. Since the dynamics of the system is described by the master equation in the Monte-Carlo method, we will use the expression obtained within the self-consistent diagrammatic model of energy transport [24]. Gochanour, Andersen, and Fayer (hereafter GAF) managed to solve the equation set (6) using diagrammatic Green's function expansions of the Laplace transform $G^S$ ($\epsilon$) in powers of $\epsilon$ within the three-body approximation. For emission anisotropy the following expression has been obtained:

$$\frac{r}{r_0} = \frac{\eta_i}{\eta} = 1 - \left(\frac{\pi Q}{2}\right)^{1/2} \gamma_M + \left(\frac{4}{\pi}\right) \cdot 0.1887 Q \gamma_M^2 \tag{14}$$

where $\eta_i$ is the quantum yield of initially excited monomers, $\eta$ is their total quantum yield, $r_0$ denotes the limiting emission anisotropy,

$$Q = \left[\frac{-x + (x^2 + y)^{1/2}}{y}\right]^2 \tag{15}$$

$$x = \sqrt{\frac{\pi}{2}} \frac{\gamma_M}{2}, \qquad y = 0.1887 \gamma_M^2 \tag{16}$$

$$\gamma_M = \frac{\sqrt{\pi}}{2} \frac{C}{C_0} \tag{17}$$

$C$ is the monomer concentration and $C_0$ denotes critical concentration for monomer–monomer energy migration corresponding to the respective critical distance $R_0$. Solid lines in Fig. 4(a)–(c) have been obtained based on Eq. (14). Very good agreement obtained between experimental data and theory can be seen for all disordered systems, though $\beta = 0$ is assumed in the theoretical model. Mention should be made that equally good agreement has been obtained between experimental data and Monte-Carlo simulation results for the same values of $\beta$ as in ordered systems. This is understandable having in mind that energy transport in disordered systems is much less sensitive to $\beta$.

Finally, we would like to stress that the results of concentration depolarization experiments presented here concern concentrations not exceeding $C = 0.01$ M. The reason for this is that at higher concentrations we observed strongly fluorescent aggregates. The formation of such aggregates leads to the change from one-component to multicomponent system. Moreover, fluorescent aggregates can act as imperfect traps for excitation energy and change significantly the properties of energy transport [4]. Figure 5 shows an example of MDTCI fluorescence spectra measured at low and high dye concentration in disordered polymeric film. The formation of an additional
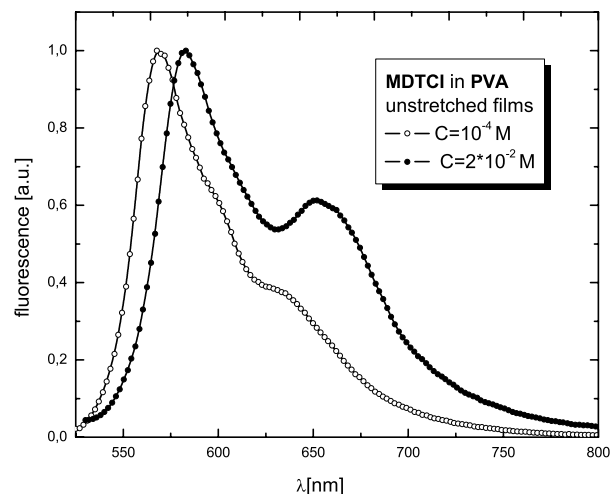
**Fig. 5.** Fluorescence spectra of MDTCI at low ($c = 0.0001$ M) and high ($c = 0.02$ M) concentration. The latter spectrum is shifted to the red and additional band at that side of the spectrum appears due to the formation of aggregates.

fluorescence band at the "red" side of fluorescence spectrum was observed at high dye concentration, which is attributed to aggregates. Similar behavior of other carbocyanines in frozen solutions and polymers was reported in [32–34] and it was attributed to fluorescent J-aggregates formed in the ground state. The detailed properties of concentrated solutions of carbocyanines will be reported separately.

## CONCLUSIONS

Contrary to disordered systems, it was found that energy migration in ordered polymer films does not lead to significant concentration depolarization of fluorescence for elongated molecules, the transition moments of which well orientate in the polymeric matrix along the direction of stretching. Using Monte-Carlo method the average value of the orientation factor in stretched polymer films was determined, which occurred surprisingly similar to that of rigid disordered systems. Based on the comparison between the Monte-Carlo simulation results and the measurements of emission anisotropy versus concentration, it is possible to estimate the angle between transition moments in absorption and fluorescence of molecules, which participate in the process of energy migration. The angles determined from concentration depolarization of fluorescence and general Perrin formula as well as Gryczyński–Kawski model are in good agreement, which supports our analysis. At extremely high carbocyanine concentrations,

the formation of fluorescent J-aggregates was discovered, which can affect the mechanism of energy transport.

## ACKNOWLEDGMENT

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