Optical Materials 59 (2016) 34–38

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Excitation energy transfer in partly ordered polymer films differing in donor and acceptor transition moments orientation

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ARTICLE INFO

Article history:
Received 27 October 2015
Received in revised form 19 January 2016
Accepted 1 March 2016
Available online 5 March 2016

Keywords:
Energy transfer
Emission anisotropy
PVA films
Partly ordered systems
Monte Carlo simulations

ABSTRACT

Based on spectroscopic measurements selected properties of nonradiative Förster energy transport are studied in uniaxially stretched polyvinyl alcohol thin films for three systems differing in donor and acceptor transition moments orientation relative to the axis of stretching. In particular, donor – acceptor emission anisotropy spectra yield completely different regularities for these systems in uniaxially stretched films, whereas they are similar in unstretched films. In particular it is shown that acceptor fluorescence can be either strongly polarized after nonradiative energy transfer in stretched films or depolarized depending on the angular distribution of acceptor transition moments in the matrix. Donor and acceptor emission anisotropy decays exhibit similar regularities to those of steady-state measurements. The obtained results are analyzed with the help of Monte Carlo simulations.

1. Introduction

Polymer films have numerous applications in various industrial and biomedical sectors such as functional and protective coatings, biocompatible medical implants, advanced membranes, sensors [1,2]. Ordered polymer films doped with fluorophores are well known materials used in polarization spectroscopy, to determine transition moments directions of molecules, their conformations or to study properties of nonradiative energy transport process [3–5].

Excitation energy transport has been widely studied for donor and acceptor transition moments randomly distributed in space [6,7]. It is well known that for such disordered systems sensibilized fluorescence emitted by acceptors excited exclusively through energy transfer from donors is almost totally depolarized [8]. This is because only primarily excited molecules (by linearly polarized light) contribute to emission anisotropy. However, as shown recently, quite different observations have been reported for uniaxially oriented polymer films, where emission anisotropy of molecules excited via energy migration or transfer remain high [9–11].

As a result of mechanical uniaxial stretching of the polymer film along fixed axis, the directions of transition dipole moments of elongated fluorophores loose their random orientation and exhibit certain nonrandom distribution relative to the axis of stretching. This means, in turn, that energy transfer takes place from an initially excited donor to an acceptor, transition moment direction of which is correlated with that of donor. On a macroscale, we can consider the value of the averaged orientation factor as a certain measure of these correlations. The averaging over all molecular configurations can lead to a much more pronounced change of the orientation factor in such a macroscopically nonrandom system compared to the random systems or systems which are locally nonrandom. The angular correlations between the directions of transition dipole moments are mostly responsible for the effect of emission anisotropy preservation in uniaxially stretched one component polymer films, where the excitation energy visits many chemically identical sites an arbitrary number of times [9–11].

Unlike one – component systems, one can imagine different physical situations in uniaxially oriented polymer matrices doped with donors and acceptors of excitation energy. Chemically non-identical donors and acceptors can be selected in such a way that their transition moments are located differently towards respective long molecular axes. For example, if transition moments of both donor and acceptor are parallel to their long molecular axes, then they orientate quite efficiently upon matrix stretching towards this axis of stretching. On the other hand, if transition moment of the donor is perpendicular to long molecular axis, but

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http://dx.doi.org/10.1016/j.optmat.2016.03.005
0925-3467/

acceptor transition moment is parallel to its long molecular axis, then upon matrix stretching both orientations of donor and acceptor transition moments are totally different. As a result, quite different emission anisotropy courses and the values of orientation factors should be obtained in both discussed cases. Such manipulations on donor – acceptor orientations may be interesting as they can deliver valuable lacking information on the mechanism of energy transfer processes in partly ordered systems.

The aim of this work is to partly fill this gap and investigate energy transfer mechanism in two-component donor – acceptor systems in uniaxially oriented polymer films. To perform this both steady state and time resolved emission anisotropy measurements were carried out for disordered and uniaxially stretched polymer matrices. The analysis of the experimental results is supported by Monte Carlo simulations of emission anisotropy upon energy transfer and the orientation factor between the interacting species. The Monte Carlo method applied for the analysis of energy transfer mechanism has been in detail described previously [12,13].

For investigations three differently orientating donor – acceptor systems were selected: system I: Diethyloxycyanine Iodide (donor, DOCI) – Diethylthiacyanine Iodide (acceptor, DTCI) with parallel orientation of both donor and acceptor transition moments towards respective long molecular axis; system II: Diethyloxycyanine Iodide (donor, DOCI) – Rhodamine 101 (acceptor, R101) with parallel orientation of donor transition moments and no specific orientation of acceptor transition moments (plane, not elongated R101 molecule); and system III: Acridone (donor) – DOCI (acceptor) with the donor transition moment perpendicular towards the long molecular axis and acceptor transition moment parallel to long molecular axis.

Molecular objects used in this study as donors and acceptors of excitation energy are highly fluorescent, stable and important probes in many applications. They are for example known as membrane potential probes, play a role of sensitizers in photodynamic therapy and are used in optical materials and laser technology to name just a few [14,15].

2. Experimental

Analytically pure acridone, DOCI, DTCI, R101 and poly (vinyl alcohol) (PVA) were obtained from Fluka. The dyes were dissolved in 5% water – ethanol solution of PVA at temperature $T = 323$ K to obtain homogeneous solution. Then samples were left in a clean place to allow water evaporation and seasoned for about a week before stretching and measurements. Uniaxial stretching of the films was performed at a temperature $T = 313$ K using a simple device designed in our laboratory. The fluorescence signal was always recorded from the central small area of the sample. The optical density of the film was low enough to neglect the inner filter effects [16].

Absorption spectra were measured using Shimadzu 1650 spectrophotometer. Fluorescence spectra were measured upon so called front face excitation and observation of sample fluorescence using spectrofluorometer constructed in our laboratory and described previously [17]. Steady-state emission anisotropy was measured with two-channel single photon counting apparatus [18]. Time resolved emission anisotropy measurements were performed in the usual way with our pulsed spectrofluorometer especially dedicated to measurements from thin layers. Similarly to other measurements, the emission anisotropy decays were performed in the front face mode upon the excitation $\lambda_{exc} = 375$ nm and at $\lambda_{exc} = 445$ nm with the use of laser head LDH-D-C-375 with controller PDL 800-D, PCI-board for TCSPC TimeHarp 200 (PicoQuant, Germany). Fluorescence light was recorded by the H10721P-01 photomultiplier (Hamamatsu Photonics K.K., Japan) combined with the slit of Czerny-Tuner spectrograph Shamrock 303i-B (Andor Technology, UK). Analysis was obtained with FluoFit Pro version (PicoQuant, Germany). The measurements were also independently performed with Fluotime 200 spectrofluorometer (PicoQuant).

3. Results and discussion

Fig. 1abc shows absorption, fluorescence spectra recorded for (1a) DOCI and DTCI, (1b) DOCI and R101, (1c) acridone and DOCI. The fluorescence spectra were obtained for the following excitation wavelengths: DOCI ($\lambda_{exc} = 460$ nm), DTCI ($\lambda_{exc} = 520$ nm), R101 ($\lambda_{exc} = 520$ nm), acridone ($\lambda_{exc} = 380$ nm). The spectra presented in Fig. 1abc 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.

Fig. 1abc presents also emission anisotropy spectra recorded for disordered ($R_S = 1$–wheels) and uniaxially stretched PVA films ($R_S = 3$ – triangles and $R_S = 5$ – squares,) for (1a) DOCI – DTCI (1b) DOCI – R101 and (1c) acridone – DOCI systems. R_S is the stretching factor of the film along the selected direction of stretching. The emission anisotropy spectra were obtained for the following excitation wavelengths: DOCI–DTCI ($\lambda_{exc} = 450$ nm), DOCI–R101 ($\lambda_{exc} = 450$ nm), acridone – DOCI ($\lambda_{exc} = 380$ nm). Mention should be made that the overlaps between the fluorescence spectrum of acceptor and absorption spectrum of the donor for DOCI–R101 and acridone –DOCI systems are negligible in each case considered, therefore the effect of reverse energy transfer from acceptor to donor does not occur [7,18].

Moreover, in the case of DOCI (donor) –DTCI (acceptor) system the overlap between the emission spectrum of DTCI and absorption spectrum of DOCI is also insignificant. The critical concentration (i.e. the concentration at which the probability of transfer is 1/2) for reverse energy transfer resulting from this overlap exceeds 0.1 M which means that at donor dye concentration in this work ($C_D = 0.001$ M) the reverse energy transfer is unlikely to occur effectively.

It can be seen from Fig. 1abc that for all disordered films emission anisotropy decreases rapidly when passing from the donor to the acceptor fluorescence band and at long wavelengths, where mostly acceptors emit fluorescence, it attains very low values ($r \cong 0.05$). This fact results from random distribution of fluorophores to which energy transfer from initially excited donors takes place in unstretched polymer matrix. This observation is in satisfactory agreement with former theoretical predictions [8,19]. It has been calculated that acceptors excited via single step energy transfer emit practically depolarized light $r_1 \approx 0.01$. Our results obtained by high precision Monte Carlo technique are similar. For acceptors excited after single step energy transfer we obtained $r_1 = 0.0104$ and after two steps further depolarization takes place $r_2 = 0.0011$. Somewhat higher ($r \approx 0.05$) experimental emission anisotropies recorded in the acceptor fluorescence band result from residual contribution of highly polarized donor fluorescence.

However, emission anisotropy spectra differ completely for each uniaxially stretched system. Instead of fluorescence depolarization one can see in Fig. 1a that the emission anisotropy is preserved in the acceptor fluorescence band both for $R_S = 3$ (moderately ordered system) and $R_S = 5$ (strongly ordered system). The effect of emission anisotropy preservation after energy transfer results from the preferential orientation of transition dipole moments of elongated donors and acceptors taking part in energy transfer. It is well known that the transition moments of most of the elongated molecules are parallel to the long molecular axis and tend to orientate towards the direction of matrix stretching [20,21]. Slight repolarization effect observed in the acceptor