

# Spectroscopic investigation of organic co-doped PMMA for optical fiber technology

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The spectroscopic investigation of poly(methyl methacrylate) (PMMA) co-doped with organic dyes (Fluorescein and Rhodamine B) is presented. The pair of dyes have been chosen for energy transfer mechanism investigation in PMMA host. The theoretical calculations of energy transfer based on obtained spectra measurements showed that non-radiative process occurs during excitation of specimens. The results of measurements and calculations of Fluorescence Resonant Energy Transfer (FRET) efficiency for excitations at 405 nm and 460 nm wavelength are determined. Investigated influence of excitation showed possibility of luminescence spectra modification. The tunable emission was obtained for different excitation wavelength and dyes concentration in PMMA.

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**Keywords:** poly(methyl methacrylate) (PMMA), Organic luminescent dyes, Fluorescein, Rhodamine B, Fluorescence Resonant Energy Transfer (FRET)

## 1. Introduction

The luminescence phenomenon in optical materials allows to construct sensors of many physical values, such as: ultraviolet (UV) or infrared (IR) radiation, temperature, acidity (pH), concentration of gases, genetic code (DNA) detection, microscopic observation and water tracers [1-7]. Some of last applications for detection of bacteria use such phenomena as two photon bioluminescence and resonant energy transfer mechanism in co-doped materials [8-12]. Usually the main problem is concerned with the material which can be used to observe efficient luminescence properties. A lot of applications use glass as an active host matrix for luminescent sensors [13-15]. The main advantages of glass are long term stability of its optical properties and high damage power threshold. Unfortunately, maximum concentration of luminescent dyes is lower compared to polymeric materials. The other case concerns well known idea which is using optical fibers as a sensing element. However, fabrication of active polymeric optical fibres is difficult because its low thermal conductivity and bubbling effect caused by evaporation of polymerization residues during drawing process. The proper polymerization procedure is a key to obtain high quality optical fibre structures used for short distance telecommunication and sensors [16-18]. There are also reported numerous applications of polymeric optical fibers doped by fluorescent organic dyes as new sources of light and lasers [19-21]. The well known polymers like polycarbonate (PC), polystyrene (PS) and poly(methyl methacrylate) (PMMA) are good candidates for optical applications. Nowadays, the material science engineering of polymers allows to obtain novel groups of polymeric materials for light guide applications e.g. cyclic olefin copolymer (COP) and epoxy-based polymers (e.g. SU-8) [22-24]. The new luminescent polymers doped with rare earth nanocrystals and organic luminescent dyes causes

growing interest of luminescent sensing applications [25-27]. These novel materials have high impact for optical fibre sensors [28-30]. The co-doped materials allows to obtain desired luminescent properties in specific spectrum e.g. the luminescence in VIS range can be useful in many fields of applications in medicine and chemistry [31-34]. The well known group of luminescent organic dyes are xanthenes. They are widely used because of high quantum yield (typically above 0.7), limited photobleaching effect and good solubility in many solvents. PMMA because of its high optical transmission in VIS range, high flexibility, good solubility in organic solvents and low cost is suitable for most optical applications. It is worth to note that PMMA also doesn't interact with the dyes molecules and not significantly affect to molecules luminescent characteristics such as: quantum yield, absorption, emission and decay time. The proposed in the paper composition of PMMA doped with two organic dyes Fluorescein and Rhodamine B is attractive for Fluorescence Resonant Energy Transfer (FRET) investigations.

## 2. Theoretical Background

The energy levels of organic molecules compared to lanthanides can be described as a broad bands rather than discrete states. It is caused by vibrational relaxation of dye molecules. The fluorescence resonance energy transfer between molecules in organic solvents is well known and it was described in the literature [35-36]. The phenomenon is usually described, using Förster theory, as a energy exchange between molecules of donor D and acceptor A. The relaxation of an optically excited donor is obtained by transfer of its energy to an acceptor. One of the main condition the occurrence of energy transfer mechanism is overlapping spectra of donor emission and acceptor

absorption. The efficiency of FRET depends on the inverse sixth power of the distance between the donor and acceptor. The presented energy transfer system shows high overlapping region of Fluorescein emission and Rhodamine B absorption spectra. The energy transfer in co-doped material can occur using radiative and non-radiative transitions. The radiative transfer is based on emission of photon from donor molecule and excitation the acceptor. It occurs for average distance between energy exchanging molecules bigger than the photon wavelength. The non-radiative energy transfer mechanism is dominant for smaller distances. The efficiency of FRET gives an opportunity to investigate distances between the two molecules. The average distance between energy exchanging molecules  $R_0$  is called Förster distance (in Å) and can be described by [35, 36]:

$$R_0^6 = \frac{9000(\ln 10)Q_D\kappa^2}{128\pi^5Nn^4} \int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda \approx \approx 9.78 \cdot 10^3 [\kappa^2 n^{-4} Q_D J(\lambda)]^{\frac{1}{6}}, \quad (1)$$

where:  $\kappa$  is the dipole molecules orientation factor,  $n$  is the refractive index,  $Q_D$  is the fluorescence quantum yield of the donor,  $J(\lambda)$  is degree of spectral overlap between the donor emission and the acceptor absorption:

$$J(\lambda) = \frac{\int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda}{\int_0^\infty F_D(\lambda)d\lambda}, \quad (2)$$

$R_0$  is average distance for 50 % of energy transfer efficiency. In many cases the dipole orientation factor is unknown value but the Förster distance can be calculated using experimentally obtained equation [39]:

$$R_0 = \frac{7.35}{([A]_{1/2})^{1/3}}, \quad (3)$$

where:  $[A]_{1/2}$  is the half quenching concentration which can be obtained under the condition of double reduction of fluorescence intensity of the donor caused by acceptor presence:

$$\frac{I_{0d}}{I_d} = 2, \quad (4)$$

where  $I_{0d}$  is fluorescence intensity of donor,  $I_d$  is fluorescence intensity of donor in the presence of acceptor. The total energy transfer between dyes can be calculated using:

$$\eta = 1 - \frac{I_d}{I_{0d}}. \quad (5)$$

### 3. Research methodology

The specimens of PMMA were fabricated using conventional free radical polymerization method [37, 38]. The monomer of methyl metacrylate, organic dyes and polymerization initiator were supplied by Merck Millipore

Chemicals with standard degree purity above 99 %. The set of specimens with varied concentration of Rhodamine B ( $15\text{--}20 \cdot 10^{-4}$  mol/l) and constant concentration of Fluorescein at  $57 \cdot 10^{-4}$  mol/l were fabricated. The detailed concentration ratios are presented in Table 1.

Table 1. The concentrations of dyes used in experiment

Specimen	Fluorescein concentration $10^{-4}$ [mol/l]	Rhodamine B concentration $10^{-4}$ [mol/l]
a	0	0
b	57	0
c	57	15
d	57	17
e	57	18
f	57	20
g	0	20

The concentration of organic dyes was kept low enough to obtain transparent specimens after polymerization process. The polymer rods were cut and polished before the measurements. The specimens diameter was 13.0 mm and the thickness 3.2 mm. The specimens under VIS and UV radiation are presented in Fig. 1. The measurements were done in room temperature (295 K). The system was prevented from ambient sources of light. During experiment, 3 W LED diodes 405 nm and 460 nm and FWHM 20 nm were used as excitation sources. The absorption spectra were measured using Stellarnet Green Wave spectrometer and deuterium-halogen source of light Stellarnet SL5.

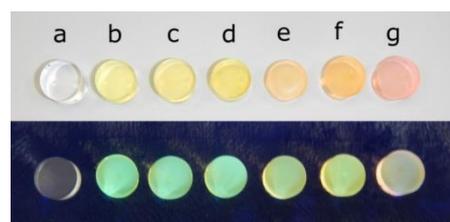


Fig. 1. The photo of fabricated specimens under VIS (upper) and (lower) UV radiation

The spectra were recorded using Stellarnet Green Wave spectrometer in the range of 350–1150 nm and 0.5 nm resolution. The LED sources were thermally stabilized using 40 W Peltier module and temperature controller FOX-1004. The obtained absorbance spectra are presented in Fig. 2. The results show that reference specimen - base polymer has low absorption for short VIS wavelength. This is necessary to effective excitation of Fluorescein doped PMMA, especially in optical fiber constructions. The presented spectra shows that co-doped PMMA has wide absorption spectrum range and the optimization of dyes concentration ratio allows to modify this

characteristic. In that case the absorption range for Fluorescein - Rhodamine B concentration ratio respectively  $57 \times 10^{-4}$  mol/l and  $20 \times 10^{-4}$  mol/l equals 400 up to 580 nm (Fig. 2f). Optimized wide range of absorption spectrum has been used to control the luminescence properties of polymer matrix.

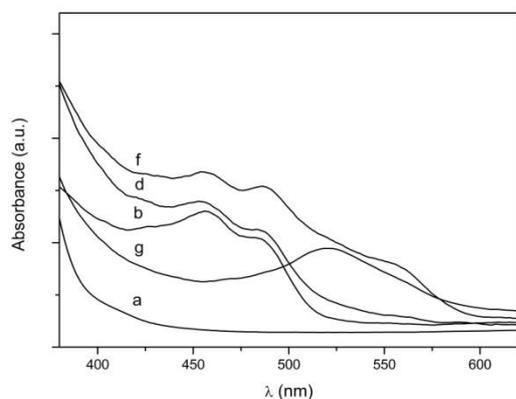


Fig. 2. The absorbance spectra of selected specimens

The luminescence spectra of specimens under excitation of 405 nm and 460 nm are presented in Fig. 3. It is noticeable that the ratio of donor – acceptor concentration causes high impact to luminescence spectra. Moreover, the quenching effect of donor luminescence is clearly visible in a presence of increasing of acceptor concentration.

The scope of the investigation was to obtain energy transfer in co-doped PMMA. Discussing that luminescence results the Forester radius was calculated for half quenching concentration ( $74 \text{ \AA}$ ). The value  $R_0$  shows that the non-radiative transfer is involved in the dye mixture. The total energy transfer efficiency was calculated using  $I_{0d}/I_d$  of Stern-Volmer plot (Fig. 5) and its value changes from 17 % up to 55 % for 405 nm and from 21 % up to 56 % for 460 nm excitation LED source. Using this feature with optimization of dyes concentration ratio it is possible to control the luminescence spectrum of co-doped polymer matrix.

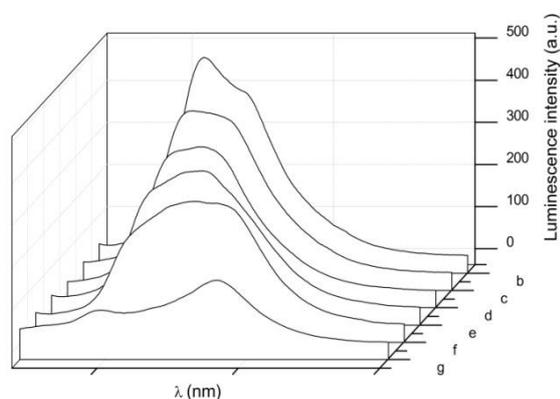


Fig. 3. The luminescence intensity vs. wavelength for excitation using LED 405nm

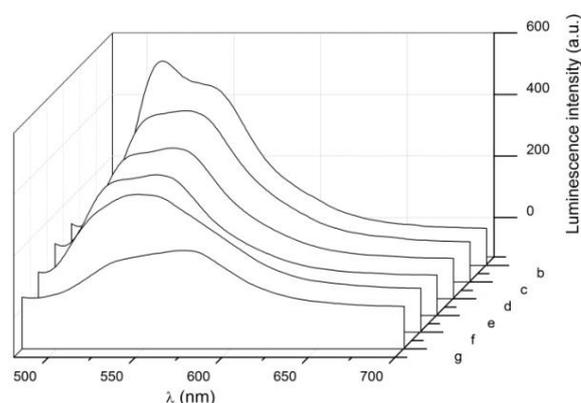


Fig. 4. The luminescence intensity vs. wavelength for excitation using LED 460nm

The wide emission spectrum ( $\lambda_{FWHM} = 490\text{--}620 \text{ nm}$ ) was obtained for specimen (Fig. 2f) and excitation 405 nm.

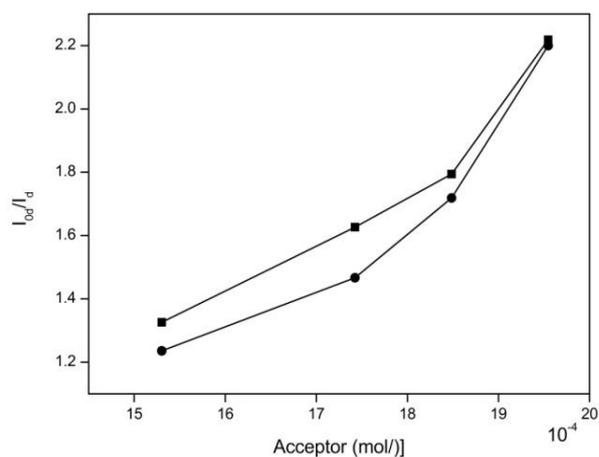


Fig. 5. The obtained Stern-Volmer plot for the presented energy transfer system, excitation ● 405nm and ■ 460nm

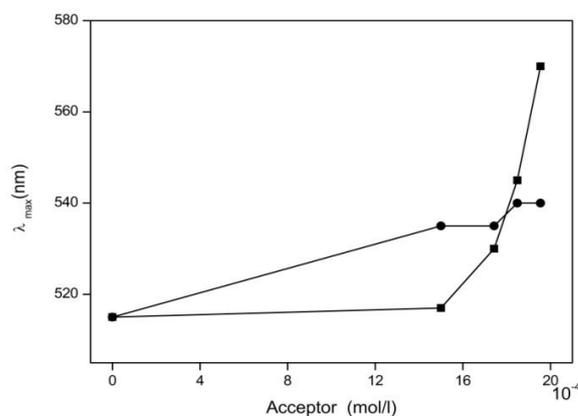


Fig. 6. The wavelength of emission peak vs. concentration of Rhodamine B in PMMA for excitation: ■ 405nm and ● 460nm

The nearly Gaussian distributions of luminescence intensity was obtained. The wavelength value corresponds to maximum of emission spectrum also changes for different dyes concentration. The results are presented in Fig. 6. emission in the range from 515 up to 570 nm was obtained for 405 nm excitation. The energy transfer efficiency corresponds to overlapping factor of excitation source with donor absorption spectrum.

The advantages of fabricated polymers: high optical transmission and luminescence intensity, electrical isolation, low weight and cost, high environmental compatibility causes this kind of materials can be used in special sources of light and sensor technology. The application of co-doped polymers allows to increase sensitivity and selectivity of sensors. This is desired in many applications in science, medicine and environmental hazards detection.

#### 4. Conclusions

The fabrication process and measurement of fluorescence resonant energy transfer phenomenon for 405 nm and 460 nm excitation wavelength in double doped organic dyes PMMA matrix was presented. The Fluorescein and Rhodamine B dyes were used as donor and acceptor respectively. The calculated  $R_0$  value show that the non-radiative process occurs during excitation of co-doped specimens. The obtained total energy transfer efficiency values varied from 17 % up to 56 %. The tunable emission was obtained for different excitation wavelength and dyes concentration with emission peak from 515 nm up to 570 nm and FWHM=130 nm. The polymer host advantage is possibility of fabrication wide range of waveguide structures using solvent based thin film technology and cylindrical optical fibres. The absorption and emission spectra exhibit potential application of presented materials for low dimensions and tunable sources of light and sensor applications.

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