White light emission PMMA fibre co-doped with 1,4-Bis(2-methylstyryl) benzene and Rhodamine B for new optical applications

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ARTICLE INFO

Keywords:

Optical properties
Fibers
Spectroscopy

ABSTRACT

The article presents the white light emission poly (methyl methacrylate) cylindrical fibre fabricated by co-doping by organic luminescent dyes. The used composition of aromatic hydrocarbon 1,4-Bis(2-methylstyryl) benzene Bis(MSB) and xanthene dye Rhodamine B (RhB) assures covering the emission in the range 370–700 nm under 355 nm excitation (Nd-YAG, third harmonic). The chosen complexes, according to the wide emission bands in the visible spectrum range and relatively large spectral shift of emission Bis(MSB) and absorption bands of RhB complexes, reduce the spectrum shape modification in the polymeric fibre structure and can be effectively used for lightning applications. The fabrication process and characterization of luminescent properties (emission spectrum, chromaticity CIE 1931 coordinates) vs. fibre length (0.5 m) are presented and discussed.

1. Introduction

The co-doped luminescent fibers offers covering of new fields in optoelectronic applications. The well-known technology of additive color mixing technique can be successively used for white light generation in fluorescent materials. This technique is commonly used in color displays, white color LED's, and medical, decorative and stage lighting [1–8]. The different color emission can be successively obtained in the structure of polymeric optical fibers by doping using luminescent complexes [9–12]. There are several methods of luminescent polymers fabrication based mainly on doping by organic complexes [13–15], lanthanides [16,17], nanocrystals [18], and quantum dots [19,20]. Typically, the direct and solvent-based polymerization processes is used for the incorporation of dyes and lanthanide complexes in the polymer structure. The use of optical fibre technique for mixing the light from different semiconductor emitters (typically SLED) is commonly used in the thick polymer optical fibre illumination systems [21]. The using of single excitation light source and active (co-doped) fibers is especially attractive for new light sources for endoscope constructions, sensors and other compact light sources [22]. The light propagation in the active optical fibre structure modify the luminescence profile mostly by energy transfer, reabsorption processes and spectral attenuation of a polymer matrix and was investigated in the previous works [23]. The poly (methyl methacrylate) PMMA is the most commonly used polymer for the fabrication of core of the polymer optical fibers. The advantages of PMMA: high

transparency, good mechanical properties, and processing technology are attractive for developing new optical fibre constructions (special profile of refractive index, photonic and functionalized e.g. luminescent, photochromic, thermochromic fibers) [24–27]. The Bis(MSB) is a highly fluorescent aromatic hydrocarbon (quantum yield efficiency 0.93 in cyclohexane solution) [28]. The UV range absorption and emission in the blue fluorescence make it useful for wavelength shifter materials in liquid and solid-state scintillators and UV detectors [29,30]. Moreover, some photochromic properties based on the isomerization phenomena (rotation around the double C bond) are investigated in the Bis(MSB) molecules [31]. Rhodamine B belongs to the group of xanthenes. They are widely used for fluorescence microscopy, luminescent tracers and dye lasers [32–34]. The Rhodamine B luminescent properties (quantum yield 0.65 in basic ethanol) were intensively studied in the solvent and polymer host environment [35]. Presented in the paper PMMA co-doped with 1,4-Bis(2-methylstyryl) benzene and Rhodamine B is a new proposition of fluorescent white light emission fibre.

2. Material and methods

The co-doped PMMA were fabricated using Methyl methacrylate (MMA), Benzoyl Peroxide (BP), sodium hydroxide (NaOH, for removing

Table 1

The concentrations of Bis(MSB) and Rhodamine B used in experiment.

Sample	1,4-Bis(2-methylstyryl) benzen mM/L	Rhodamine B mM/L
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Received 18 November 2019; Received in revised form 20 March 2020; Accepted 23 March 2020 0272-8842/ © 2020

Published by Elsevier Ltd.

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E-mail address: p.miluski@pb.edu.pl (P. Miluski). <https://doi.org/10.1016/j.ceramint.2020.03.227>

A	0.69	0
B	0.70	0.18
C	0.71	0.31
D	0.69	0.54
E	0	0.50

the monomer stabilizer), Rhodamine B (RhB), and 1,4-Bis(2-methylstyryl) benzene Bis(MSB). The materials were supplied by SigmaAldrich except for Bis(MSB) - Tokyo Chemical Industry and used without additional purification. The used concentrations of complexes are presented in Table 1. The direct doping technique was used for the incorporation of fluorescent complexes in the PMMA. The polymerization process was realized at 65–80 °C for 28h. The fabricated specimens had good transparency with no visible defects. The PMMA fiber preform specimens were prepared by cutting and polishing 3.2 mm-thick discs with a diamond cutting and a polishing machine. The co-doped fiber (diameter 1.2 mm) was fabricated using optical fiber drawing tower (furnace temperatures $T = 160\text{--}190\text{ }^{\circ}\text{C}$, preform feeding 0.5 cm/min, drawing speed 50–80 cm/min). The excitation spectrum was measured using Horiba Fluorolog 3 spectrofluorometer and Xenon arc lamp. The luminescence spectra were recorded using a Nd-YAG Qswitched laser systems Continuum Minilite 1 (third harmonic 355 nm) and Stellarnet Green Wave spectrometer (one end excitation and cut back method). During the fibre spectral attenuation measurement, the deuterium halogen Stellarnet SL5 source was used.

3. Results

The analysis of spectroscopic properties for specimens A-E shown that the excitation spectrum, recorded for monitoring at 567 nm, corroborates the Bis(MSB) and RhB incorporation in the PMMA matrix (Fig. 1a). The wide excitation spectrum with the local maxima corresponding to Bis(MSB) (300–380 nm) and RhB (over 450 nm) are noticeable. The wide excitation is important for effective excitation of fluorescent fibre and gives a possibility of emission color tuning by using different excitation wavelengths. The luminescence spectrum of co-doped specimens consists of Bis(MSB) and Rhodamine B emission bands (Fig. 1b). The energy transfer from Bis(MSB) and Rhodamine B is limited due to the relatively large shift of the maximum of emission of Bis(MSB) and excitation of Rhodamine B complexes.

Fig. 1. a) The normalized excitation spectrum of sample D, monitoring at 567 nm (inset: specimens A-E under 365 nm excitation light using a mercury vapor black light illuminator), b) the luminescence spectra of samples at excitation 355 nm.

The concentrations of Bis(MSB) and Rhodamine B as for specimen D were used for optical fibre fabrication. The luminescence spectra recorded vs. the fibre length are presented in Fig. 2a. The emission profile (370–700 nm, FWHM = 210 nm) gives a possibility to obtaining highquality white light since the color rendering index CRI is typically significantly higher for broadband emission sources (e.g. halogen bulbs) in comparison with narrow spectral emission sources (e.g. discharge light bulbs or RGB LEDs) [36–38]. The analysis of fluorescence spectra confirms the multipeak emission characteristic for Bis(MSB) in the range 200–520 nm (maxima at 396 nm, 420 nm, 495 nm and barely visible 448 nm) and RhB 570 nm. Moreover, it is noticeable that the spectrum shape changes vs. fibre length. The light-guiding in optical fibers allows observing the reabsorption on a significantly longer distance than polymer slices. Moreover, the spectral attenuation additionally changes the luminescence spectrum profile. Due to the reabsorption process, the 396 nm peak is relatively fast absorbed and for fibre length greater than 40 cm is not observed in the luminescence spectrum. The reabsorption process also changes the emission profile of RhB as presented in Fig. 2b. The redshift emission effect is much higher for RhB dye (from 572 nm to 596 nm at slope 0.8 nm/cm).

The CIE 1931 coordinates presented in Fig. 3a corroborate the white color of luminescence (inset, Fig. 1a). In the range 13–40 cm the x, y coordinates are close to the cold white light region of CIE diagram and slowly towards the red emission. Due to the relatively large shift of emission Bis(MSB) and absorption bands of RhB complexes, low spectrum shape modification is observed in the range 13–40 cm (the intensity ratio of a maximum of Bis(MSB) to RhB emission in the range 1.9–2.0) and the white light emission can be easily obtained.

The minimum of spectral attenuation of commercial PMMA core optical fibers is typically observed for the visible (VIS) spectrum range for optical windows near to the 570 nm and 650 nm [39]. Due to the air cladding optical fiber construction the high attenuation level (12.3–15.7 dB/m in the range 500–850 nm) is noticeable in Fig. 3b for codoped fibre. The minimum of attenuation of 12.3 dB/m PMMA occurs for 655–696 nm. The local maximum at 732 nm (15.1 dB/m) is also noticeable. Typically, the PMMA fibers have high attenuation since structure of $(C_5H_8O_2)_n$ causes Rayleigh scattering for short wavelengths. The molecular absorption is more important for longer wavelengths of the optical spectrum. The absorption bands observed in the fibre attenuation spectrum refers to the carbon–hydrogen (CH)

a)

a)

b)

b)

Fig. 2. a) The luminescence spectra vs. fibre length at excitation 355 nm, b) the wavelength of fluorescence peaks vs. fibre length.

Fig. 3. a) The CIE1941 chromaticity coordinates vs. fibre length at 355 nm excitation, b) the spectral attenuation of fabricated fibres (inset: white light side emission at 355 nm excitation).

stretching vibrations. The harmonics of CH vibration have been marked in Fig. 3b (n - vibrational quantum number, d - IR bending vibration) [40]. Additionally,

the undoped PMMA fibre spectral attenuation is presented. The higher attenuation slope for the spectral range up to 650 nm is observed due to the Rhodamine B absorption spectrum. The white light emission obtained from co-emission of Bis(MSB) and RhB can be successively used for new compact light source constructions.

4. Conclusions

The luminescence characterization of poly (methyl methacrylate) fibre co-doped with 1,4-Bis(2-methylstyryl) benzene Bis(MSB) and Rhodamine B (RhB) was presented. The wide emission in the range 370–700 nm under 355 nm excitation was obtained. The luminescence spectra and CIE 1931 coordinates vs. fibre length were investigated. The thermal temperature is close to the cold white emission. Small dimensions, flexibility, wide emission band are attractive for optoelectronics applications in the displays illuminators and compact light sources for sensors and micro illuminators.

Acknowledgments

This work was supported by project no. S/WE/3/2018.

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