

Article

Luminescent Properties of Oxazine 170 Perchlorate Doped PMMA Fiber

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Abstract: The article presents fabrication and luminescent properties of poly(methyl methacrylate) (PMMA) fiber doped by Oxazine 170 perchlorate. The bright fluorescence of polymeric fiber (at molar fluorescent organic dye concentration 4.3×10^{-5}) was characterized in terms of spectrum and signal attenuation vs. the fiber length. The significant changes in fluorescence spectrum (λ_{\max} red shift average slope 4.6 nm/cm and Full Width at Half Maximum (FWHM) increasing slope 6.7 nm/cm) have been noticed for the length of the fiber (0.02–0.08 m) which corresponds to a high overlapping region of absorption and emission spectra of used dye. The red shift of λ_{\max} (c.a. 80 nm) was presented in fabricated polymeric fiber at distance 0.85 m. The obtained characteristics can be used for luminescent properties optimization of fluorescent organic-dye-doped PMMA fiber.

Keywords: polymer optical fiber; poly(methyl methacrylate); Oxazine 170 perchlorate; fluorescence

1. Introduction

The organic electronics became an alternative for inorganic based light generation technology since the reliability of organic based devices has been significantly improved [1]. The main issue of the organic light emitting devices is instability of their properties in terms of environmental factors [2]. Organic materials can react with oxygen and OH^- ions (humidity) and create modified structures, quenching the luminescence. Additionally, the photobleaching effects can occur when exposed to high-intensity radiation. Moreover, the UV and temperature degradation of the organic host also limit their applications [3]. Nevertheless, the much higher quantum efficiency and low energy consumption of organic dyes based devices is a significant advantage. Low-cost processability and environmentally friendly technology are attractive for high volume production. In fact, the energy saving displays and light sources based on Organic Light Emitting Devices (OLED) technology are the most promising candidates for future commercial applications [4]. Luminescent organic technology can be also successfully applied in optical fiber applications. The limitation of polymeric fibers is high attenuation (an order of 180 dB/km at 650 nm) in comparison with silica based fibers (below 0.2 dB/km at 1550 nm). In fact, high signal attenuation limits the polymeric optical fiber (POF) applications to short distance communication, compact light sources and optical sensors [5,6]. There are reported numerous constructions of POFs based optical sensors for liquids and gasses monitoring [7–10]. In addition, the possibility of incorporation of luminescent dopants significantly extends the application field of optical fiber devices [11–15].

Unlike silica optical fibers, POFs are mostly fabricated as multimode fibers. Moreover, the using of much thicker fibers (significantly higher flexibility of polymeric materials) allows easy and efficient connection to light sources and detectors and makes it proper solution for inexpensive data transmission applications and sensors [7]. There are reported several constructions of POFs fibers: well-known core-cladding (step and gradient index profile) and sophisticated (single-mode,

non-linear, photonic band gap, and microstructured) polymer optical fibers [16–21]. Additionally, the waveguiding properties of optical fibers give an opportunity to radiative energy conversion or amplification. Optical fiber fabrication (drawing technique or extrusion) is mostly based on well developed textile fiber technology [21]. In fact, the low thermal conductivity of polymers limits drawing technology to the laboratory and low-level scale production. The high volume production of polymeric optical fibers is based on extrusion technique of acrylic thermoplastic granules or direct in process polymerization [22–24]. So far, the poly(methyl methacrylate), well known as organic glass, is the most frequently used one in optical fiber technology as it assures low absorption in visible spectrum range, excellent mechanical and processing properties and low cost. The PMMA was developed in the 30s of the 20th century and now is commercially used in numerous optical application (lenses, LEDs, light sources covers and optical fibers) [25–27]. Unfortunately, its structure $(C_5H_8O_2)_n$ causes Rayleigh scattering for short wavelengths part of the optical spectrum and molecular absorption for longer wavelengths. In such circumstances, the lowest attenuation is observed for visible spectrum range for four optical windows 465, 525, 565 and 650 nm. The lowest attenuation (c.a. 40 dB/km) is observed for window 525 nm [28]. Significantly higher attenuation in the red part of VIS and IR range comes from the absorption of carbon-hydrogen overtone bond vibration. The telecommunication windows typically fall in the near infra-red region (850–1550 nm). In such circumstances, polymer technology exhibits significant limitation but, the infrared spectrum of acrylic polymers can be modified by hydrogen atoms substitution. The replacement of hydrogen with a heavier atom causes the fundamental vibration of a C–X to shift into longer wavelengths (the attenuation is determined by higher vibration overtones). Several atoms were investigated so far: carbon-deuterium C–D, carbon-fluorine C–F, and carbon-chlorine C–Cl can be successfully applied to reduce attenuation in desired telecommunication spectrum range. Unfortunately, the atom substitution process is very expensive and limits practical application of modified polymers. The reasonable cost-performance effect was obtained using fluorinated polymers since they have yielded the lowest minimum losses (10 dB/km at 1000 nm) so far [29,30]. The incorporation of luminescent dopants in polymeric optical fibers gives the opportunity to new construction development and exhibits new applications fields in optical fiber technology. Among the numerous applications, the most important are light sources, amplifiers, and sensors [31,32]. Polymeric chain structure allows directing incorporation of luminescent complexes or guest-host doping mechanism. The several techniques, described below, can be applied for efficient luminescent structures fabrications.

1.1. Organic Dyes Doping

The idea of laser wavelength converters based on solvent and organic dyes mixtures can be successfully applied in a rigid polymer host. Organic dyes assure efficient luminescence at low excitation power which has to be limited as the melting temperature is c.a. 80–110 °C in most of the thermoplastic polymers. In fact, the organic host also leads to a direct and solvent-based doping mechanism possibility. Moreover, the luminescence some of them can be modified since their properties strongly depend on the environmental conditions (temperature, solvent acidity, and polarity) [33]. The solvent-free technique is strongly desired for optical fiber drawing technique since the impurities and solvent residues cause the main problems (e.g., volume bobbling) during heating the preform. In addition, the organic dye-doped polymers provide interesting fluorescence properties as they assure high doping level, efficient luminescence in visible and near infrared spectrum and high quantum yield despite a short lifetime of the excited state (typically few ns) [34–36]. The disadvantage of using organic luminescent markers is photobleaching effect, especially for high energy excitation radiation. The most efficient luminescence of organic dyes is observed for xanthenes group. In fact, the highest quantum yield is reported for Rhodamine 6G (0.95) and Fluorescein (0.90) [33]. Oxazine chromophore can be obtained by replacing the xanthenes central carbon atom by nitrogen. Additionally, atom substitution is the π -electron source; the red shift of luminescence spectrum (c.a. 80 nm) can then be observed [33]. In such conditions, the emission in the red part of the visible spectrum can be easily

obtained. In opposite to oxazines, one of the most efficient laser dyes in the VIS shorter wavelengths (blue and green) range can be obtained by coumarins. Their fluorescence properties (absorption and fluorescence spectra) strongly depend on the solvent polarity. The highly efficient fluorescence was observed in numerous 7-Aminocoumarins compounds [37,38].

1.2. Organometallic Lanthanide Complexes

The lanthanide ions are very attractive due to their well defined multi-peak luminescence spectrum, long excited state lifetime and stable emission properties. The numerous rare earth ions (Nd^{3+} , Sm^{3+} , Tb^{3+} , Eu^{3+} , Dy^{3+} , Yb^{3+} , Pr^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+}) can be used for luminescent applications [39]. Unfortunately, the directly doped polymers exhibit weak luminescence since absorption spectrum of lanthanide ions is very narrow. The improving of luminescence efficiency can be obtained by chelation of lanthanide ions (Ln^{3+} complexes). Antenna effect is used then for energy transfer from organic ligand (wide absorption band) to luminescent rare earth ion. The β -diketones, carboxylic acid derivatives, terphenyl ligands, and proteins sensitization were reported in the literature [39–44]. Additionally, the luminescence of most of the lanthanide complexes is quenched by organic groups in the polymeric host, especially for the NIR-emitting ions and efficient luminescence in the visible spectrum of PMMA host is reported only for europium Eu^{3+} and terbium Tb^{3+} organometallic complexes [45].

1.3. Lanthanide Ions-Doped Inorganic Nanoparticles

Nowadays, the remarkable progress can be noticed in luminescent nanocomposites. The luminescence quenching by the polymeric host can be reduced by the controlled low phonon energy local environment of luminescent centers. Phonon energies of some common inorganic materials (e.g., chalcogenide or fluoride glass, CaF_2 , LaF_3 , LaCl_3 crystals) allows obtaining efficient luminescence since the reduction of non-radiative transitions occurs [46–49]. The several types of core-shell structures with enhanced luminescence properties of nanocrystals were investigated. In such circumstances, they have potential as optical active structures where nanoparticles are dispersed in a polymeric host. The promising telecommunication spectrum ranges of polymeric active waveguides have been investigated using Nd^{3+} (1320 nm) and Er^{3+} (1536 nm) nanoparticles [47].

1.4. Oxazine 170 Perchlorate Doped PMMA

The organic dyes typically can be easily incorporated in PMMA matrix using solvent-free technique preserving its high fluorescence efficiency. Beside the xanthenes, the oxazines are one of the most frequently used laser dyes for the VIS (red) and near-IR [33]. The Oxazine 170 perchlorate main absorption band is situated at 621 nm since the emission spectrum, according to mirror symmetry, is situated at 648 nm as presented in Figure 1.

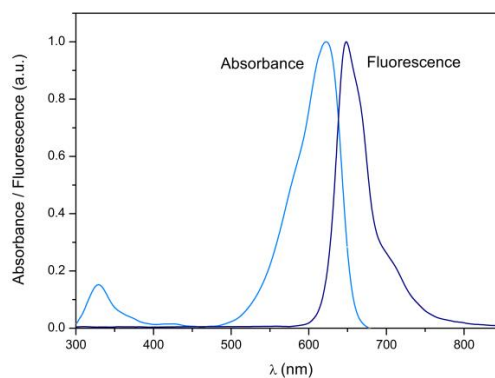


Figure 1. Measured normalized absorbance/fluorescence spectra of Oxazine 170 perchlorate in ethanol, fluorescence measured at excitation 593.5 nm.

Under such circumstances, the oxazines are promising laser dyes for 650 nm PMMA optical window which is the most interesting since there are available low-cost laser diode sources (InGaAs) and high sensitivity silicon photodiodes. The polymeric host typically slightly shifts (a few nm) the emission spectrum into the longer wavelengths. Moreover, the high quantum yield (0.63, CH₃OH) and melting temperature c.a. 260 °C make it a proper candidate for optical fiber drawing technology [33,50]. It is worth to note that in the visible range the highest attenuation of PMMA core optical fibers (typically 610–640 nm) is noticeable for maximum absorption of Oxazine 170 perchlorate. The high PMMA absorption of excitation radiation can be overcome by using shorter wavelength excitation since the pump radiation affecting length can be significantly longer than in bulk samples. In such case, the excitation pump radiation wavelength can be shifted into the 525 nm transmission window observed in the step index profile of PMMA fiber [28] where Nd:YAG, the second harmonic wavelength (532 nm) laser radiation can be used. In fact, the high quantum yield of organic laser dyes allows efficient light amplification on the short distances (tenths of cm) in comparison with lanthanide ions doped silica amplifiers (tenths of m) [31]. Moreover, the big core diameter and high optical aperture of PMMA fluorinated cladding fibers allow effective coupling of optical radiation with co-working electronic devices (light sources and detectors).

2. Materials and Methods

The raw materials: Methyl Methacrylate (MMA), Benzoyl Peroxide (BP), and Oxazine 170 perchlorate were supplied by Sigma-Aldrich (St. Louis, MO, USA). The stabilizer agent has been removed from the monomer before free radical polymerization process of preform fabrication (48 h at 67–80 °C). The PMMA doping was performed directly during the polymerization process (Ox170 molar concentration 4.3×10^{-5}) and 15 mm outer diameter preform was obtained. No visible polymerization defects were observed in the preform. The fiber (1.6 mm diameter, presented in Figure 2) was fabricated using computer controlled optical fiber tower. The process parameters were as follows: furnace temperatures $T = 160\text{--}185$ °C, preform feeding 0.3 cm/min, drawing speed 32–62 cm/min. Chosen fiber diameter assures high fluorescence signal at low excitation laser power density which has to be limited since glass transition temperature of PMMA is c.a. 105 °C.

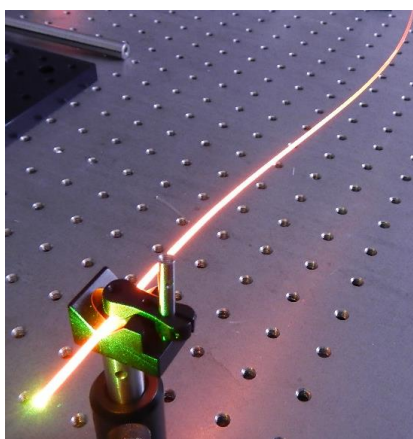


Figure 2. The photo of Oxazine 170 perchlorate doped PMMA fiber under 532 nm excitation.

The one end excitation and fiber cutback methods were used for fluorescence spectra measurements. The luminescence signal was collected from the end of the fibre. The solid state, diode pumped laser (532 nm, FWHM = 10 nm) was used as excitation source. All spectra were measured using an optical fiber-coupled Stellarnet Green Wave spectrometer in the range of 500–850 nm at a resolution of 0.5 nm.

3. Results

Under the 532 nm excitation, the intense lateral fluorescence can be noticed (Figure 2). The measured effective pumping length was 50 mm (at 1% initial power criterion). The used excitation radiation power (37 mW) has to be limited due to the fact of low damage threshold of PMMA. The luminescence spectrum shift can be noticeable due to reabsorption of luminescence signal in PMMA fibre. The maximum of excitation spectrum, presented in Figure 3, is situated at 615 nm. The used laser diode (532 nm) allows an intense fluorescence due to the effective excitation of Ox170. The longer wavelength shift effect expected in organic dye-doped fibers is also noticeable in Figure 2.

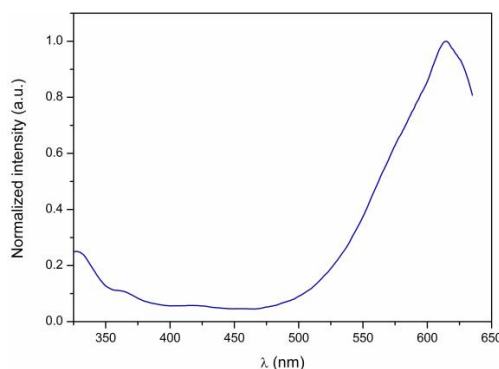


Figure 3. The normalized excitation spectrum of Ox170 perchlorate doped PMMA.

The laser source used for fibre excitation has significantly shorter wavelength than Ox170 maximum excitation spectrum (615 nm, as presented in Figure 3). In such circumstances, the wider fluorescence signal range of can be observed vs. the fiber length.

In fact, the combination of the long affecting length of excitation radiation, reabsorption properties of organic dye and spectral attenuation of PMMA host change the fluorescence spectrum shape in polymeric fiber. The measured normalized fluorescence spectra for different lengths of the fibre are presented in Figure 4. The significant spectral shape modification and so-called “red shift” effect can be noticed. Moreover, the monotonic λ_{\max} increasing tendency is clearly visible. The maximum of the luminescent peak for Ox170 can be observed in the range from 619 up to 697 nm as presented in Figure 5a. The further analysis allows to observe that significant change of λ_{\max} (average slope 4.6 nm/cm) can be noticed for fiber length 0.02–0.10 m and corresponds to the overlap spectral region (620–655 nm) of absorbance and fluorescence spectra of Ox170 (Figure 1). Outside this range, the reabsorption is much weaker and the characteristic average slope is lower (c.a. 0.56 nm/cm) for fiber length 0.10–0.85 m.

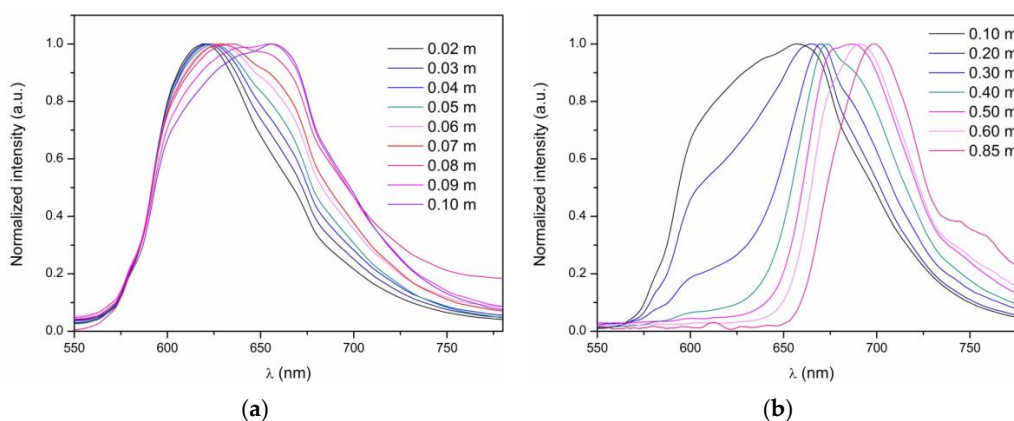


Figure 4. The normalized fluorescence spectra of Ox170 doped fiber: (a) 0.02–0.10 m; (b) 0.10–0.85 m.

The full width at half maximum (FWHM) of recorded spectra is presented in Figure 5b. The chosen excitation wavelength is shorter than the maximum of the absorption spectrum of Oxazine 170 perchlorate and FWHM fast increasing can be noticed then (slope 6.7 nm/cm). Moreover, the broadening of luminescence spectrum is the result of the more efficient excitation of organic molecules since luminescence peak shifts (λ_{\max}) are observed in the maximum of excitation spectrum of Ox170. The FWHM maximum (105 nm) is observed for fiber length 0.08 m and corresponds to the fluorescence λ_{\max} of Ox170 (650 nm). The monotonic decreasing tendency of FWHM is observed for distances longer than 0.08 m ($\lambda_{\max} > 650$ nm) and is resulted by reabsorption of fluorescence radiation in dye-doped polymeric fiber. The nearly linear dependence can be noticed for fiber length longer than 0.3 m since the luminescence wavelength is situated on the right tail of Ox170 fluorescence spectrum. The decreasing of spectrum width is expected then as the absorption plays a significant role in the final luminescence spectrum shape.

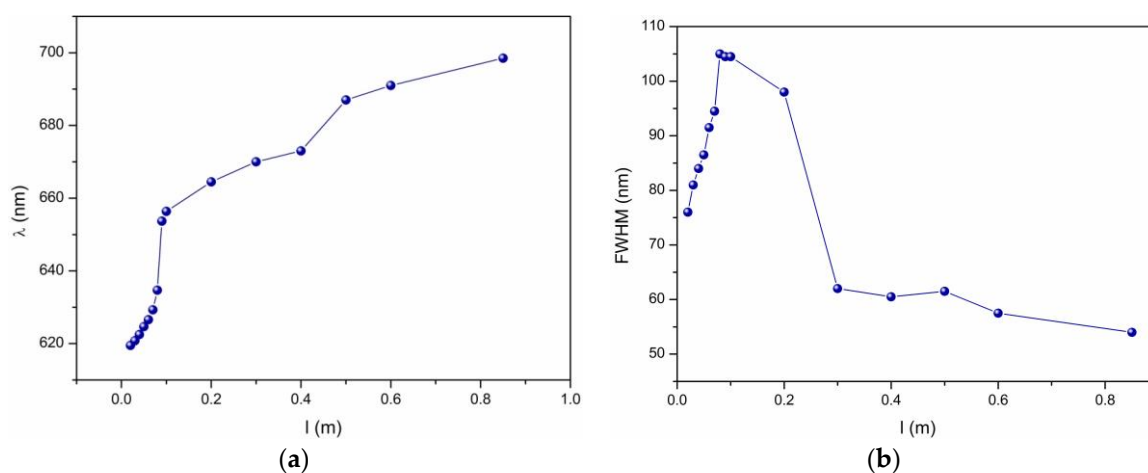


Figure 5. (a) The λ_{\max} shift vs. fiber length; (b) The FWHM of luminescence spectrum vs. fiber length.

The absorption of Ox170 molecules causes strong signal attenuation. The significant spectrum shape modification (λ_{\max} and FWHM) can be observed then. Measured attenuation for fluorescence signal (λ_{\max}) slope equals 18.5 dB/m and is presented in Figure 6. High attenuation of fluorescence signal limits the useful fiber length. In fact, the organic dyes doped polymeric luminescent fibers length is limited to tenths of centimeters. The measured fluorescent properties of Ox170 doped PMMA fiber strongly correspond to spectroscopic properties of the used dye. The λ_{\max} and FWHM of fluorescence spectra can be directly interpreted using absorption and emission spectra of Ox170. Moreover, the possibility of fluorescent spectrum shape modification can be used in numerous optical applications and desired fluorescence spectrum can be obtained using optimized POFs. The significant red shift of λ_{\max} c.a. 80 nm can be obtained at distance 0.85 m in presented polymeric optical fiber. The bright fluorescence of Ox170 in PMMA fiber can be used for specific light conversion. Moreover, the presented interesting properties of dye-doped PMMA fiber can be used in new optical fiber applications since the advantages of polymeric optical fibers (high flexibility at big core diameter, high numerical aperture) are often desired in new compact light sources [51].

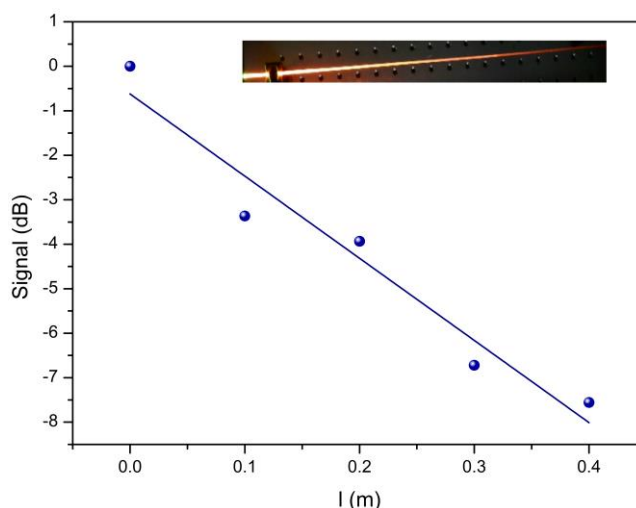


Figure 6. The luminescence signal attenuation vs. fiber length.

4. Conclusions

Luminescent polymers are promising materials for photonic applications. The well-developed technology of POFs and several techniques of host doping mechanisms make them a good alternative for silica-based optical fibers. In fact, a new class of organic-inorganic materials can be obtained by polymer host doping. The core-shell structures and co-doped photonic materials can be also investigated. Moreover, low processing temperatures of acrylates allow optical fibre drawing for a wide range of dopants (organic and inorganic). In the article, the incorporation of Oxazine 170 perchlorate in PMMA host process and fabricated fiber was presented. The bright fluorescence of polymeric fiber was obtained under 532 nm excitation. Remarkable luminescence parameters changes (λ_{\max} red shift; average slope: 4.6 nm/cm; FWHM increasing slope: 6.7 nm/cm) can be noticed for the overlapping region of absorption and emission spectra of used dye. In fact, the total λ_{\max} shift c.a. 80 nm was obtained in presented polymeric fiber (0.85 m). The obtained results can be used for new optical radiation conversion applications.

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