

Energy conversion in 7-(Diethylamino)coumarin doped PMMA fluorescent fibre

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Abstract The article presents fabrication and spectroscopic characterization of 7-(Diethylamino)coumarin doped polymeric fibre. The poly(methyl methacrylate) (PMMA) was chosen as it assures direct doping possibility and excellent optical properties in fluorescence spectrum of used dye. The fabricated polymer exhibits an intense luminescence (at dye concentration 1.2×10^{-4} mol/l) in the range 505–537 nm (exc. 405 nm). Moreover, the coumarin doped PMMA fibre 600/1200 μm (doped core/cladding) fibre was fabricated and characterized. Presented fluorescence spectrum modification possibility can be used for new optical fibre construction optimization.

Keywords 7-(Diethylamino)coumarin · Polymeric optical fibre · Poly(methyl methacrylate) · Fluorescence · Organic dyes

Mathematic Subject Classification 160.4890 · 160.2540 · 160.5470

1 Introduction

Photoluminescent complexes are widely used in optical technology. The numerous applications of organic luminescent materials are well known in medicine (luminescent labeling, fluorescence-energy-transfer-based microscopy), environmental monitoring (water acidity and pollution) and numerous fields of scientific research (Resch-Genger et al. 2008; Basabe-Desmonts et al. 2007; Kasprzak et al. 2011; Lichtman and Conchello 2005; Lian et al. 2004; Merian et al. 2012; Rao et al. 2007). Fluorescent organic compounds (e.g. xanthenes, proteins, and polycyclic aromatic hydrocarbons) are widely used due to their bright luminescence in the visible spectrum range (Miluski et al. 2015a; Johansson 1991;

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Al-Hamdani et al. 2010). Moreover, their broadband absorption spectrum allows efficient excitation using arc lamp (Hg, Xe), semiconductor LEDs, and laser diodes. Fluorescent molecules can be often incorporated into polymer structure without significant change their luminescent properties. In such circumstances, the rigid organic host gives an opportunity for new applications in optical fibre technology. The organic dyes can be incorporated in optical fibers based on thermoplastic polymers due to low drawing temperatures (much lower than used in optical glass technology). In fact, the poly(methyl methacrylate) is the most frequently used polymer for optical applications (Miluski et al. 2015b; Bilro et al. 2012). High transparency and well-developed processing technology of PMMA make it a good candidate for low-cost optical components and optical fibres fabrication (Miluski et al. 2016a, b). The step/gradient index and microstructured optical fibers can be fabricated using PMMA host (Miluski et al. 2016b; Tama et al. 2010; Bundalo et al. 2014; Kailasnatha et al. 2008; Oliveira et al. 2015; Huang et al. 2004; Barton et al. 2004). Moreover, the guiding properties of optical fibres can be used to obtain some specific advantages: optical signal amplification, amplified spontaneous emission (ASE), and energy transfer (Karimi et al. 2004; Dorosz et al. 2012; Arrue et al. 2011; Ayesta et al. 2011; Nihei et al. 1996). The optical amplifiers, sensors, and lasers based on fluorescent organic complexes were reported so far (Dorosz et al. 2012; Arrue et al. 2011; Ayesta et al. 2011; Nihei et al. 1996). The Stoke shift, mirror symmetry of absorption and emission spectra, high quantum yield and short lifetime (few ns) were reported in PMMA host doped by coumarins (Johansson 1991; Al-Hamdani et al. 2010; Kailasnatha et al. 2008). In fact, the coumarin derivatives are commonly used for optical fluorescence microscopy, OLEDs, and dye lasers (Achamma et al. 2002; Bangar Raju 1995; Donovalova et al. 2012; Hrdlovic et al. 2010). The proposed 7-(Diethylamino)coumarin doped PMMA fibre fabrication and fluorescence properties characterization is shown. Moreover, the reabsorption effect observed in optical fibre structure can be used for fluorescence spectrum modification.

2 The fabrication of coumarin doped optical fibre

The raw materials: monomer methyl methacrylate (MMA), Benzoyl Peroxide (BP), Butanediol (BT), and Benzyl Benzoate (BEN) were supplied by Sigma-Aldrich and used without further purification. The 7-(Diethylamino)coumarin ($C_{13}H_{15}NO_2$ formula) was supplied by TCI Company (>98%). The stabilizer agent has been removed from the monomer before polymerization process. The free radical polymerization process was performed by 40 h at temperature 65–80 °C. The optical preforms (presented in Fig. 1a, diameter 12 mm) were fabricated as solid (A) and doped core/cladding structure (B). The used coumarin derivative concentration (1.2×10^{-4} mol/l) was verified to obtain efficient luminescence in the polymeric host. No polymerization defects (cracklings, intrusions or bubbles) were observed in fabricated preforms. The slightly dissolved boundary of cladding part (core/cladding preform) was noticed after the polymerization. The preforms were drawn into the fibers (0.4–2.0 mm diameter) using drawing tower. The step index (0.6/1.2 mm) fibre is presented in Fig. 1b.

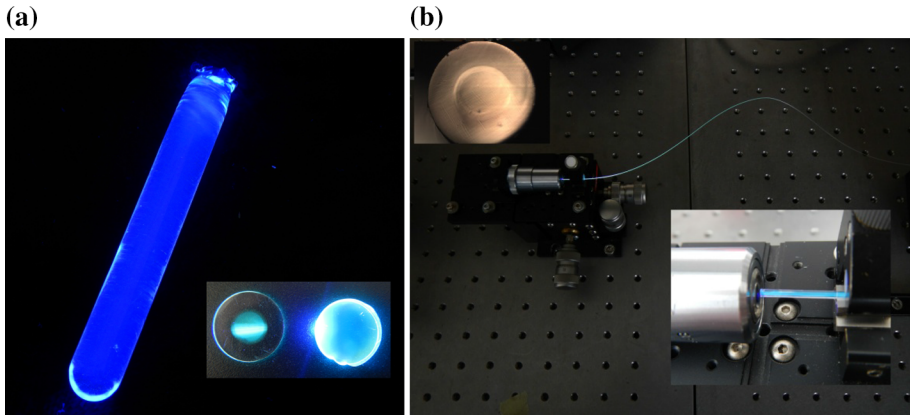


Fig. 1 The photo of fabricated: **a** preform A (at 365 nm excitation, mercury vapour black light), insertion: preform discs (from *left*: B and A, at exc. 405 nm), **b** optical fibre at laser 405 nm one end excitation, insertion: cross section of fibre, side emission of fabricated fibre

3 Measurements

The properties of 7-(Diethylamino)coumarin doped PMMA preforms (excitation and fluorescence spectra) and fibers (fluorescence, attenuation) were characterized. The specimens were cut and polished into the 2.0 mm thick preform discs. The refractive index (1.4925 and 1.4917 for core and cladding part respectively) was verified at 633 nm using optical refractometer (Metricon). The excitation spectrum was measured using Horiba Fluorolog 3 spectrofluorometer equipped with a Xenon arc lamp (450 W). The fluorescence spectra were recorded using Stellarnet Green Wave spectrometer in the range of 350–900 nm and 0.5 nm resolution. Additionally, the fluorescence of bulk specimens was measured using integrating sphere (120 mm diameter). The obtained excitation and fluorescence spectra are presented in Fig. 2. Efficient excitation can be obtained for 320–420 nm spectral range. The fluorescence spectrum of 7-(Diethylamino)coumarin (Fig. 2b) exhibits two peaks at 453 and 496 nm (FWHM = 110 nm).

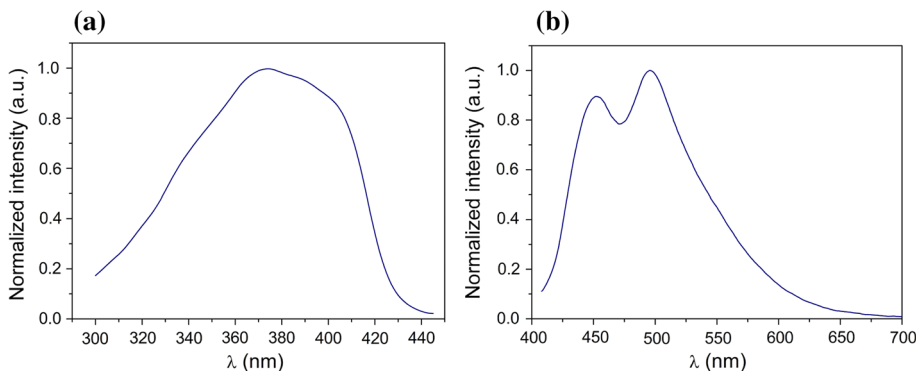


Fig. 2 The optical properties of 7-(Diethylamino)coumarin doped PMMA: **a** excitation spectrum, monitoring at 450 nm, **b** fluorescence spectrum, excitation at 405 nm

The laser diode (405 nm, 200 mW) was used for excitation of fabricated optical fibres. The polymeric fibres measurements were carried out using one end excitation and cutback method in the fibre length range 50–500 mm. Additionally, the dopant distribution profile was measured for preform disc (B) and is presented in Fig. 3. It is noticeable that dissolving process of core-cladding boundary determines the final dopant distribution profile.

The single luminescence peak (Fig. 4a) observed in optical fibres is resulted by reabsorption effect in optical fibre structure (the peak observed at 453 nm in bulk sample is strongly absorbed in optical fibre structure). Additionally, the fluorescence spectrum shows so-called “red shift” phenomenon versus the fibre length. The effective pumping length was estimated to 45 mm (at 2% initial power criterion). The reabsorption of coumarin dye leading to strong fluorescence signal attenuation (slope 16 dB/m, Fig. 4b) and limits the useful fiber length to few tenths of centimeters.

Additionally, the λ_{\max} and FWHM plots versus fibre length are presented in Fig. 5. The monotonic λ_{\max} increasing tendency is clearly visible (505–537 nm, average slope 0.7 nm/cm) for fibre length 50–500 mm (Fig. 5a). The increasing of FWHM (from 77 up to 108 nm) is possible since reabsorption effects are much weaker for the right tail of fluorescence spectrum.

The proposed 7-(Diethylamino)coumarin doped optical fibre exhibit interesting optical properties. The fluorescence (FWHM, λ_{\max}) can be optimized by the energy conversion process in polymeric optical fibre. The possibility of fluorescent spectrum shape modification can be used in new constructions of light sources based on direct energy conversion in polymeric optical fibres.

4 Summary

The 7-(Diethylamino)coumarin doped (1.2×10^{-4} mol/l) optical fibre was presented. The efficient luminescence was observed at 405 nm excitation. The measured absorbance and fluorescence spectra are presented. Moreover, the fluorescence spectrum shape parameters

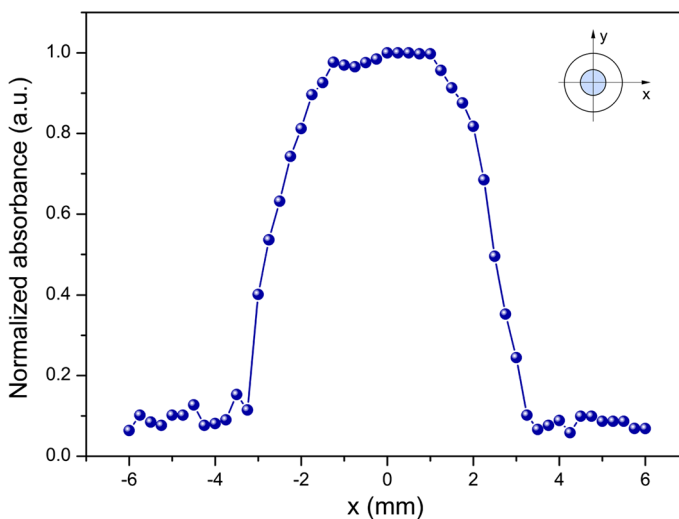


Fig. 3 Normalized absorbance profile of preform B measured at $\lambda = 405$ nm

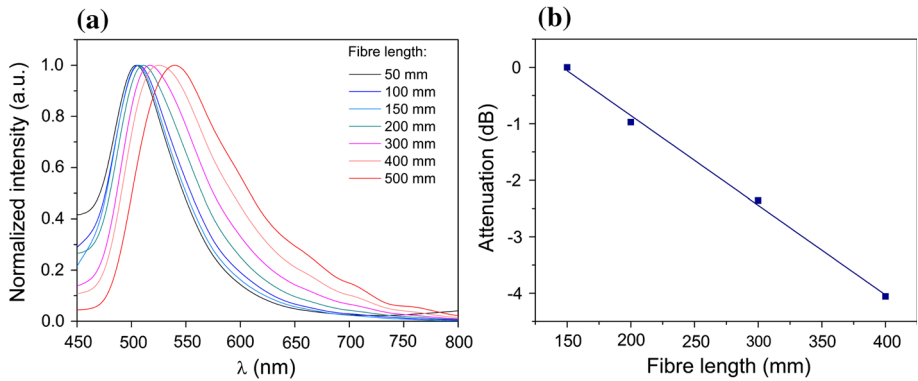


Fig. 4 **a** The fluorescence spectrum versus optical fibre length (B), at 405 nm, **b** fluorescence signal attenuation at λ_{\max}

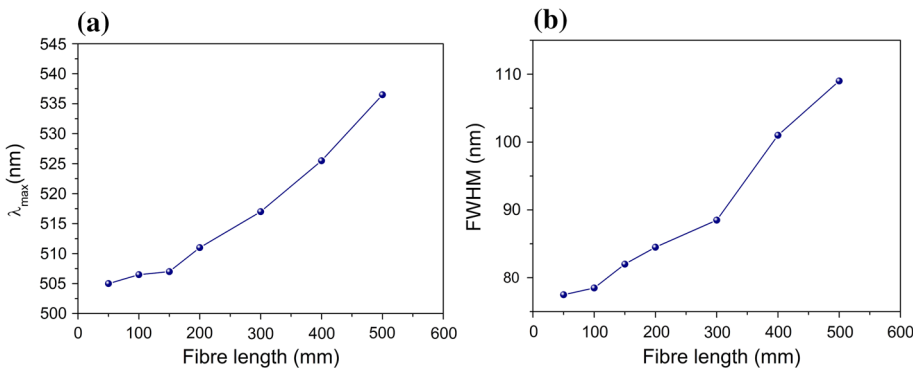


Fig. 5 **a** The λ_{\max} versus fibre (A) length, **b** The FWHM versus fibre (A) length, both graphs at 405 nm, 150 mW

(FWHM, λ_{\max}) were measured for fabricated optical fibre and the reabsorption effect in optical fibre is presented. The 7-(Diethylamino)coumarin doped PMMA optical fibre can be used for new fibre optic light sources and optical amplifiers investigations.

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