



# Saturation and degradation of the photoluminescent response of pyrromethene imbedded in a polymeric matrix; Comparison between films and optical fiber geometries



R. Narro-García<sup>a</sup>, L. Jaramillo-Ochoa<sup>b</sup>, M.A. Ocampo<sup>b</sup>, R. Quintero-Torres<sup>b,\*</sup>

<sup>a</sup> Universidad Autónoma de Chihuahua, Facultad de Ingeniería, Circuito Universitario S/N, 31125 Chihuahua, Chih., Mexico

<sup>b</sup> Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México, Boulevard Juriquilla 3001, Querétaro 76230, Mexico

## ARTICLE INFO

### Keywords:

Pyrromethene degradation  
High stability luminescence  
Polymer optical fiber  
Fiber light system

## ABSTRACT

In this work, poly(methyl methacrylate) (PMMA) thin films and a polymer optical fiber doped with pyrromethene (PM-567) were fabricated and characterized. The obtained films were uniform and homogeneous in its central zone and no aggregation of dye molecules were observed. UV–vis absorption, photoluminescence spectra, lifetime and photodegradation were measured for the fabricated films. Peak intensity and position of the photoluminescence spectra were dependent on the pyrromethene concentration. A resonant energy transfer mechanism is proposed as the main process associated with this behavior. Photodegradation results were well fitted by a gamma probability density function. While thin films were highly degraded under 405 nm excitation, the studied optical fiber displayed a much more stable behavior, presumably related with its construction design based on a transparent core and a thin PM-567 doped cladding.

## 1. Introduction

Organic luminescent dyes have been used for long time for multiple applications [1–3], including their use as a lasing active medium [4–7] and for fluorescent optical fibers [8]. Although advantageous, because of their commonly broad band emission in the visible region of the spectrum, their applications have been hindered by their chemical instabilities under moderate to high light irradiation or physicochemical environmental effects, which degrade them to non-fluorescent compounds, so inhibiting their function [9–11].

In a recent work, we studied a new fluorescent fiber construction made by adding Rhodamine 6G into the cladding material of a polymeric optical fiber with a transparent poly(methyl methacrylate) (PMMA) core [12], which on a preliminary basis seem to be much more stable than the common fibers made with a fluorescent core surrounded by a transparent cladding [13]. Since pyrromethene 567 (PM-567) has shown to be a more unstable system than rhodamine for fluorescent applications, in this work we study the stability of such a dye when used to make an optical fiber with the mentioned fluorescent-cladding-structure and compare it with the degrading behavior of PM-567 doped PMMA films. Having a high quantum yield for fluorescence, as high as 0.99 [14], and a broad emission band around 547 nm, the greater stability of PM-567 under the proposed structure deserves a great

interest as an alternative fluorescent optical fiber medium for the development of fiber light systems in which the optical fiber shows lateral and axial luminescence. One of the advantages of using this kind of fiber for the development of fiber light systems is that, unlike conventional lateral fiber light systems in which the lateral emission comes only from the pump radiation, the multicolor lateral or axial light emission of the presented fiber is a combination between the pump radiation and the dye molecule photoluminescence.

As a base for comparison, in this work, we first characterize the photodegradation of PM-567 doped PMMA films at four different concentrations as function of the pump intensity and then describe the photodegradation of the mentioned fiber.

## 2. Materials and methods

### 2.1. Thin film fabrication

Poly(methyl methacrylate) (PMMA) thin films doped with different concentration of Pyrromethene 567 (PM-567) were prepared by dissolving 50 mg of PMMA into 1 ml of chloroform under sonication for 10 min until a colorless homogeneous solution was obtained. PM-567 was added to the polymer solution at  $5 \times 10^{-5}$ ,  $10 \times 10^{-5}$ ,  $50 \times 10^{-5}$  and  $100 \times 10^{-5}$  mol/L concentrations. 350  $\mu$ l of this solution was

\* Corresponding author.

E-mail address: [rquintero@fata.unam.mx](mailto:rquintero@fata.unam.mx) (R. Quintero-Torres).

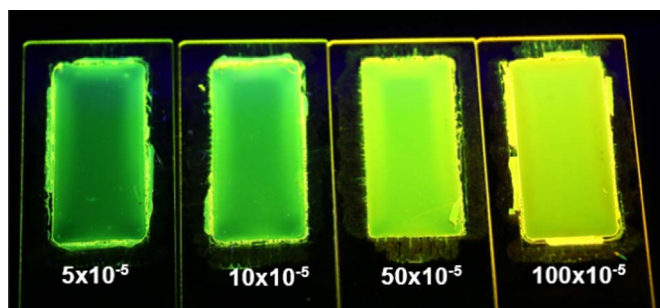


Fig. 1. Pictures of PMMA thin films doped with different concentration of PM-567 ( $5 \times 10^{-5}$ ,  $10 \times 10^{-5}$ ,  $50 \times 10^{-5}$ ,  $100 \times 10^{-5}$  mol/L).

further sonicated for another 10 min and then poured into a glass base rectangular mold. Finally, the so prepared samples were dried at room temperature for 24 h. Fig. 1 shows the four of the obtained films under UV light. The average thickness of the obtained films was 58  $\mu\text{m}$ . As observed, irregular edge films were obtained in most of the samples, however, their larger central parts, used for this study, were pretty uniform and homogeneous.

## 2.2. Preform and fiber fabrication

Besides the mentioned films, pyromethene doped cladding optical fibers were obtained by drawing a 25 mm diameter preform, made with a poly(methyl methacrylate) (PMMA) core and THV-Phyromethene567 cladding, (THV: fluorothermoplastic containing tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride from 3M-Dyneon). Fibers were drawn to a diameter of 0.4 mm at 200  $^{\circ}\text{C}$ . The described preform was obtained by multicoating a PMMA bar with a solution of PM-567 and THV in ethyl acetate. The used PMMA bar, with a molecular weight of 98,000 Da, and a polydispersity of 2.1, was obtained by a method described elsewhere [15]. For the coating, PM-567 was first diluted to saturation in HPLC grade ethyl acetate from Baker at room temperature. The saturated solution was then filtered with a 100 Rundfilter from Macherey-Nagel to separate not dissolved particles and then used to dissolve THV to make a concentrated solution of 150 g of this polymer per liter of solution. To make the preform, the obtained PMMA bar was machined to lower its diameter to 24 mm and then coated by applying several single coatings of the described solution over the bar mounted in a lathe at a speed of 200 rev/min. Each coating was applied under a flow of filtered air and subsequent coatings were applied until the previous one was dried to touch. In this way, an estimated thickness of 0.5 mm was obtained. The coated bar was then further dried at 90  $^{\circ}\text{C}$  for 40 h.

## 2.3. Photoluminescent characterizations

The UV–vis absorption spectra (300–750 nm) of the poly(methyl methacrylate) (PMMA) thin films were recorded in transmission mode with a spectrometer (Perkin Elmer Lambda 35) with 1 nm resolution. Thin films photoluminescence (PL) spectra were recorded by exciting the samples in front-face mode with a 404 nm CW laser diode. The photoluminescent response was measured by a fluorometer system in which the input signal is chopper modulated at the entrance of the monochromator (iHR320 from Horiba), feeding its exit to a H9307-02 photomultiplier tube and synchronously measured by introducing the photomultiplier output in a lock-in amplifier. Lifetime measurements were done on the surface of the thin films in front face mode. A 404 nm pulsed laser diode drove at 1 MHz with a pulse width lower than 2 ns was used as the excitation source. Intensity decays were collected by time-domain technique using a single photon detection module (ID100 model from IDQ) and an advanced time to digital converter (ID800 model from IDQ).

Thin films degradation was studied by monitoring the evolution of transmittance and photoluminescent response as a function of the irradiation time. In the case of the films transmittance measurements ( $T=I/I_0$ ), a probe beam centered at 514 nm was passed through the film while excited at 405 nm. The intensity of the probe beam was measured before ( $I_0$ ) and after ( $I$ ) passing the sample. For photoluminescent response, the pump beam, having a 1.2 mm of diameter, passes through the thin film and the photoluminescent response from the other side of the sample was measured by the fluorometer system.

To study the photodegradation behavior of the polymer fiber, the luminescence intensities of the polymer fiber were measured in dependence of the pump power and elapsed time. The polymer fibers were excited using a CW laser at 404 nm, able of delivering 200 mW, the laser is coupled into one end of the fiber using a lens of 5 cm focal length with anti-reflective film and the output signal from the end-face of the fiber is recorded by the fluorometer system.

Special care was taken to maintain the alignment of the setup and the sample position was stabilized and fixed to maximize the signal at the output in order to enable the comparison between the obtained signals for different pump powers. In this way intensity drifts not associated with the degradation were minimized.

## 3. Results and discussion

### 3.1. Optical characterization of thin films (low excitation power)

The absorption spectra of the thin films at different concentrations of PM-567 are shown in Fig. 2. Each spectrum has a strong band around 519 nm and a weak band around 370 nm. A linear relationship between the attenuation and dye concentration, as described by the Lambert-Beer law, was observed in the neighborhood of those peaks;

$abs = \log I_0/I = \alpha \cdot d \cdot \log(e)$ , in which  $d$  represents the film thickness and  $\alpha$  is proportional to the dye concentration. The four absorption spectra have the same shape, suggesting that no aggregation of dye molecules due to the increasing concentration of PM-567 in the studied samples was present.

Fig. 3 shows the photoluminescence spectra in the range of 475–700 nm for the different dye concentrations of the prepared films. All spectra exhibited one broad emission band but it is noted that both shape and spectra intensity are dye concentration-dependent. While peak intensity increases with increasing PM-567 concentration up to  $50 \times 10^{-5}$  mol/L, a further increase is not observed for a larger concentration (e. g. for  $100 \times 10^{-5}$  mol/L).

The luminescence saturation with the increase of the dye concen-

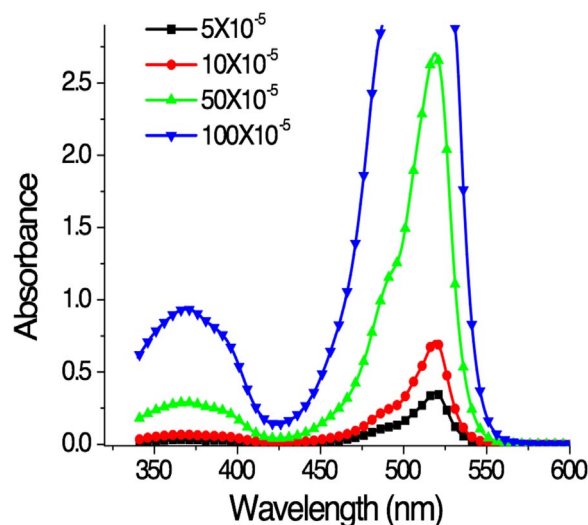


Fig. 2. Absorption spectra of PMMA thin films doped with different concentration of PM-567 ( $5 \times 10^{-5}$ ,  $10 \times 10^{-5}$ ,  $50 \times 10^{-5}$ ,  $100 \times 10^{-5}$  mol/L).

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