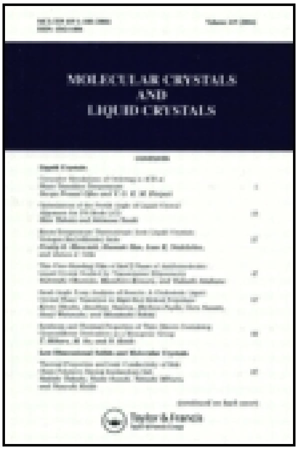

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 31 Aug 2012.

To cite this article: F. O. F. Bergamaski , Y. Galvão Gobato & E. C. Pereira (2008): Photoluminescence Intensity Enhancement in Poly(3-thiopheneacetic Acid) Films Induced by Laser Irradiation, Molecular Crystals and Liquid Crystals, 485:1, 780-788

To link to this article: http://dx.doi.org/10.1080/15421400801918070

Mol. Cryst. Liq. Cryst., Vol. 485, pp. 32/[780]–40/[788], 2008
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400801918070

Photoluminescence Intensity Enhancement in Poly(3-thiopheneacetic Acid) Films Induced by Laser Irradiation

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In this work, we have reported an enhancement of the photoluminescence intensity in Poly(3-thiopheneacetic acid), PTAA, films irradiated by laser in air. This effect depends on the laser intensity, exposure time and sample thickness. It was observed an increase of the luminescence intensity up to 110% without any significant shift in PL peak position. Our results suggest that a partial degradation process occurs in the sample, which confines the charge carriers in a narrower region of the film increasing the probability of radioactive decay.

Keywords: laser irradiation; photoluminescence; poly(3-thiopheneacetic acid)

INTRODUCTION

Photoluminescence (PL) [1–3] and electroluminescence (EL) properties [2,4] of conjugated polymers have been under investigation due to its potential application as optical-electronic devices. Poly(*p*-phenylenevinylene) (PPV) [5–9] polymer is the most studied material. Other conjugated polymers, such as polythiophene derivatives, have similar properties [10–14] and were less investigated [10–13] in the literature.

The improvement in polymer stability is of fundamental importance for device applications. Many studies have revealed that conjugated polymers degrades when they are exposed to optical radiation in air,

The authors would like to acknowledge the financial support from CNPq, CAPES and FAPESP (05/02845-1, 03/09933-8).

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resulting in a PL quenching [7] and/or increase of PL intensity [9,17,18]. The PL intensity behavior for PPV films under light irradiation has been assigned to the formation of carbonyl groups during illumination in air due to the chain scission of the vinyl double bond from the polymer backbone. The polymer chain is damaged through the photochemical reaction with active oxygen especies, causing a reduction in the average conjugation length by the formation of "defects" such as carbonyl groups [7,9,14–16]. These effects have been explained by the chain shortening process which change the energy gap between lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) states [9,17].

The PL enhancement in PPV was explained by the successive formation of an energy gradient causing the transfer of excitons to a non-degraded region in the sample, where carrier are confined, resulting in an enhancement of the recombination rate. This energy profile can favor the deactivation of excited states by a fast Förster-type energy transfer process from the higher degraded regions, shorter segments, to a less degraded, one longer segments, further inside the sample before recombination [9,17,22]. Although the chemical composition of PTAA is different from PPV and the defects formed during its degradation upon laser irradiation could be different, an enhancement in its emission under laser irradiation was also observed for PTAA-PVA blends [15–19]. In order to understand in a more complete way the blend behavior, we steped back, and characterized the emission behavior of pure PTAA films.

In this work, we study the enhancement and quenching of the PL intensity in poly(3-thiopheneacetic acid), PTAA, films induced by laser irradiation. This phenomenon was investigated by using absorption, emission and FTIR techniques. We show that this PL enhancement depends on the laser excitation conditions and on the film thickness.

EXPERIMENTAL

The 3-thiopheneacetic acid monomer (Aldrich), was previously recrystallized from 1:1 hexane-ether mixture. The schematic representation of the monomer is shown in Figure 1. The poly(3-thiopheneacetic acid) was synthesized chemically by an oxidative-polymerization route using $FeCl_3$ in chloroform as oxidizing agent with a monomer-oxidizing agent molar ration of 1:5. The polymerization was carried out for 1 h at room temperature (25°C) under stirring and dried under nitrogen atmosphere. The reaction was finished by methanol addition. The resulted mixture was filtered to obtain a brown-red PTAA powder. Soon after, the PTAA was treated with concentrated HCl for total removal of the iron ions. The solutions used for film preparation were

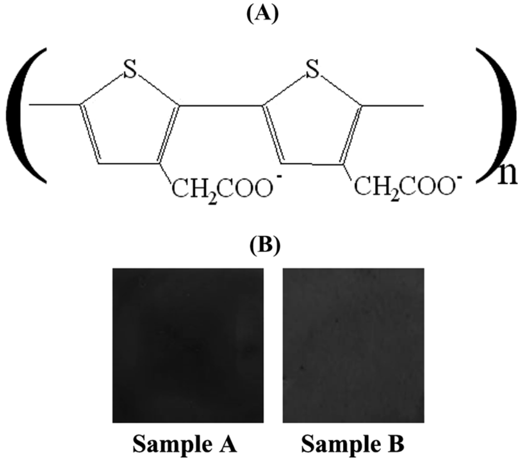

FIGURE 1 (A) Schematic representation of the monomer 3-thiopheneacetic acid. (B) Photograph of the films prepared PTAA-cast, 5 μm thick, named sample A, and spin-coating film, estimated ~1 μm, named sample B.

obtained by dissolving 0.3 g of PTAA in 20 mL of 0.1 M NH_4OH. Figure 1 shows a photograph of the films prepared. PTAA-cast (5 μm thick), Sample A, and spin-coating film (estimated ~1 μm), Sample B, were photo-irradiated using a 458 nm Ar ion laser at intensities 50 or 250 mW/cm^2. The absorption spectra were recorded by a Varian Cary 5 G UV-visible-near-IR spectrophotometer, whereas the PL spectra were recorded by a Spex 500 M single spectrometer. A coherent Ar ion laser beam was used as excitation source and the PL signal was detected by a photocounting system connected to a thermoelectrically cooled R5108 Hamamatsu photomultiplier. All measurements were performed in air and 298 K. The FTIR Fourier-transform infrared (FTIR) measurements were performed by a FTIR spectrometer Bruker equinox 55 using PTAA-cast film prepared on silicon substrate (9 μm thick), Sample C.

RESULTS AND DISCUSSION

Figure 2 shows both the absorption and emission spectra for sample A. The absorption curve is characterized by one peak at 410 nm which is generally attributed to the $\pi \rightarrow \pi^*$ transition for polythiophene films [24]. The emission spectra is also characterized by one wide band peaked at 587 nm and then the Stokeś shift is of 804 meV. A small increase the energy absorption peak is observed after the sample was irradiated by using 50 mW/cm^2 of laser intensity for 195 min.

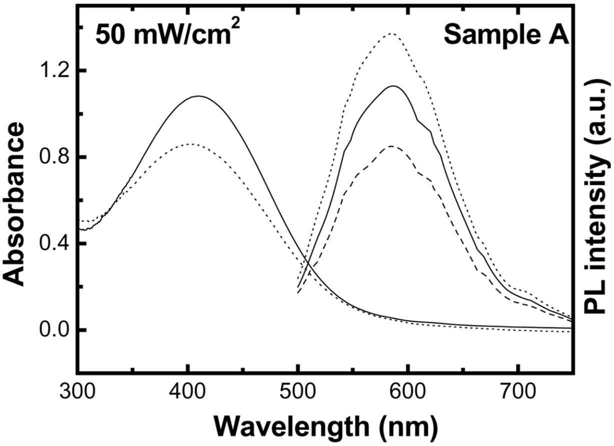

FIGURE 2 Absorption and PL spectra for sample a before and after photo-irradiation with 458 nm Ar$^+$ laser at 50 mW/cm^2. (——) 0 min., 20 min. (- - - -) and 195 min (·····).

After photo-irradiation, the absorption peak is positioned at 402 nm while the emission peak has no change in the energy. The Stokes´shift is of about 817 meV. Considering that these experiments were performed at 298 K the variation in the Stokes shift is lower than kT (where is the Boltzmann constant) and it can be disregarded.

A different behavior emerges by analyzing the intensities of absorption and emission spectra before and after laser irradiation. The decrease of absorption intensity indicates that the density of the cromophores groups responsible for this process had a decrease in their number. Otherwise, one can observe an important increase in the emission band intensity after 195 min irradiation. In this case, the explanation is not so straighforward as those proposed for the absorption, once different mechanisms could explain such results [9,17,18] as will be discussed later. Another important result is that for shorter laser irradiation times, under these experimental conditions, the emission decreases as function of time, pointing that the effect of laser irradiation on the optical properties of this samples is complex. Friend *et al.* [23] suggested that the incorporation of oxygen and/or water into the polymer film can explain this effect. This incorporation could lead to a highly non planar polymer which quenches the emission.

Figure 3 shows the time dependence of PL integrated intensity for the sample A. It is observed an initial decrease in the emission intensity followed by an important increase (for irradiation times

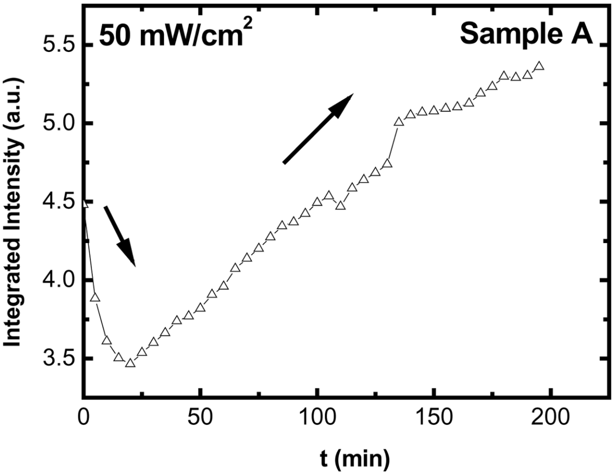

FIGURE 3 Time dependence of integrated PL intensity for sample A irradiated at 50 mW/cm^2.

higher than 20 min) which appears to saturate after 200 min of laser irradiation. Comparing the minimum intensity value, at 20 min of irradiation, the increase in the emission intensity is of about 57%.

Figure 4, shows the time dependence of integrated PL intensity for sample B for two irradiation intensities (50 mW/cm^2 and 250 mW/cm^2). The sample B, is very thin and its thickness can not be measured by using high precision micrometer. However, the absorption spectra can be used to estimate their relative thickness. Considering that the sample A presents an initial absorption peak of 1.2 and its thickness is 5 μm (±1 μm) and that sample B has an initial absorption peak of 0.33, the relative thickness between than is about four times and then it is about 1 μm. This value is within the experimental error of the equipment used for thicknesses determination. An enhancement of PL intensity is clear observed when the sample is irradiated by using 50 mW/cm^2 of laser intensity. In this case, the initial decreased is also observed but the minimum emission occurs at 5 min. The increase in the integrated photoluminescence intensity is of about 110% and a decrease is observed for irradiation times higher than 45 min. The absorption and emission spectra (not shown in this article) present the same behavior observed in Figure 2, i.e., there is no important displacement in the peak position of absorption and emission spectra. A different picture emerges when a 250 mW/cm^2 laser intensity irradiation is performed. In this case,

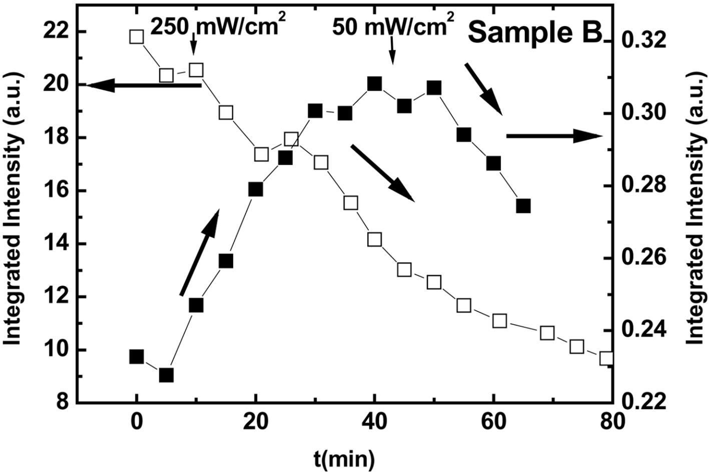

FIGURE 4 Time dependence of integrated PL intensity for sample B at 50 mW/cm^2 (black square) and 250 mW/cm^2 (white square).

we observe that the PL intensity decrease as function of irradiation time (of about 41% of its initial value), indicating an important degradation of the optical properties in our sample. This decrease of PL intensity is accompanied by important effects in the absorption and emission spectra as shown in Figure 5. We observed a strong blue for both absorption and emission spectra. Besides, a decrease in the absorption intensity is also observed. This effect could be interpreted as a decrease in the conjugation length of the polymer chains [8,9].

In order to explain the results observed in Figures 2–5, we performed IR measurements for sample C, shown in Figure 6. We present the IR spectra before and after 205 min laser irradiation. Due to the detection limit of our experimental equipment, a very thick sample (9 µm) was prepared. Then, we choose the laser irradiation intensity adequate to reproduce a similar behavior observed in Figure 2. The inset of Figure 6 shows the integrated PL intensity as function of time for sample C for 250 mV/cm^2 laser intensity irradiation. The important peaks to our purposes are those related to the C=C (1560 cm^{-1}) and C=O (1720 cm^{-1}) bonds which can be tentatively correlated to the axial deformation in aromatic rings and axial deformation of the carboxilic acid. We measured the IR spectra before and after the laser irradiation and observed an important decrease in the 1560 cm^{-1} band which could be related to a decrease in the number of C=C bonds. Considering that the results of PL enhancement (results for

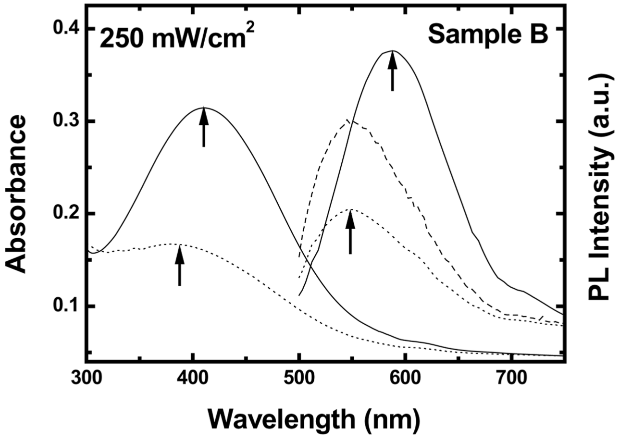

FIGURE 5 Absorption and PL spectra for sample B before and after photoirradiation with 458 nm Ar$^+$ laser at 250 mW/cm^2. (———) 0 min., 36 min. (- - - -) and 79 min (·····).

Sample A and C), shows a decrease in the number of chemical species which have an $\pi \rightarrow \pi^*$ transition and also that the C=C bond is necessary to that kind of transition does exist, we conclude that both data

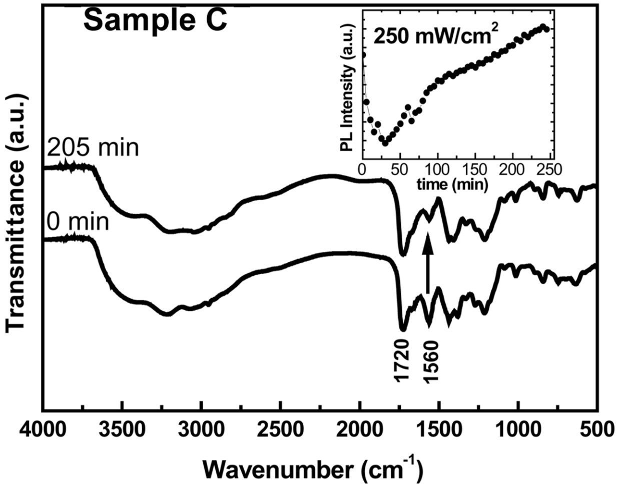

FIGURE 6 FTIR spectra before and after photoirradiation with 458 nm Ar$^+$ laser at 250 mW/cm^2 during 205 min. The inset shows the time dependence of integrated PL intensity.

agree. In other words, there is a decrease in the number of C–C bonds in the polymeric chains which indicates that part of the polymer was degraded. We suggest that only a small portion of the polymer was degraded once there is not any blue shift or change in the Stoke shift for the data presented for Sample A and C. These ideas could explain the changes observed in the absorption spectra after laser irradiation.

To explain our results of PL enhancement in Poly(3-thiopheneacetic acid) films (Figs. 2, 3 and 6) we have considered a similar process proposed for PPV [9] films under laser irradiation. The explanation could be associated to a non uniform degradation on the polymer film considering that the light penetration length, λ_o, is smaller than the sample thickness, d. In this case, the degraded polymer region is non uniform, i.e., there is a defect concentration profile formed across the film following the laser intensity profile with different polymer segment lengths. As a consequence, an inhomogeneous profile of PTAA segments of different sizes from the air/polymer interface into the film is formed. The difference in the segments lengths leads to an increase in the energy gap between $\pi \rightarrow \pi^*$ states [25]. The energy profiles and the strong overlap of vibrational states enable the carriers to relax the energy efficiently through Förster transfer mechanism [8,26,27], resulting in the transfer to a non degraded region in the polymer. The confinement of the carriers, i.e., an increase in the carrier density in the non degraded region increase the efficiency of the radioactive decay. This proposition is corroborated by both using high intensity laser irradiation or exposing very thin PTAA films which lead only to a decrease in the emission intensity.

CONCLUSIONS

We have investigated the photoluminescence of PTAA films upon laser irradiation. Different time dependence of the integrated emission was observed. For very high laser intensity, a decrease in the PL intensity was observed. Otherwise, for 5 mm thick films, we have observed an increase in the PL intensity followed by no changes in the PL and Absorption peak positions. For 1 mm thick films, we have observed an initial increase followed by a sharp decrease by using 50 mW/cm^2 of laser intensity. The same sample irradiated with 250 mWcm^2 shows only a PL intensity decrease. Our results can be explained by considering a partial degradation of the polymer film, which leads to a carrier diffusion to a non-degraded region which results in an increase of the probability of radioactive decay.

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