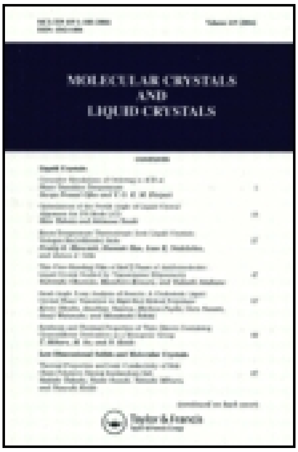

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Photoinduced Enhancement of Luminescence Intensity in Poly (Vinyl Alcohol)-Poly(3-Thiopheneacetic Acid) (PVA-PTAA) Blends

J. M. Souza [a], Y. Galvão Gobato [b], A. Vercik [b] & E. C. Pereira [a]
[a] CMDMC - LIEC - DQ, UFSCar, C.P. 676, São Carlos, SP, CEP 13565-905, Brazil
[b] DF, UFSCar, C.P. 676, São Carlos, SP, CEP 13565-905, Brazil

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Photoinduced Enhancement of Luminescence Intensity in Poly (Vinyl Alcohol)-Poly(3-Thiopheneacetic Acid) (PVA-PTAA) Blends

J. M. SOUZA[1], Y. GALVÃO GOBATO[2+],
A. VERCIK[2] and E. C. PEREIRA[1,*]

[1]*CMDMC - LIEC - DQ -UFSCar and*
[2]*DF-UFSCar and* +*-also from UFSC C.P. 676, CEP 13565-905,*
São Carlos -SP, Brazil

The photoluminescence (PL) behaviour of PVA-PTAA blends of different composition is investigated. It is observed that the interchain interaction have an important effect in this system leading to an unexpected decrease in the PL intensity as the PTAA content increase. An enhancement of the PL intensity as function of the time was also detected for all samples which were irradiated by laser. Using laser intensitiy of 18 W/cm^2 it was observed an increase of 93 % in PVA-PTAA 1wt% blend. Using this methodology it was possible to build an emission pattern.

Keywords: poly(3-thiopheneacetic acid), luminescence, blends, poly(vinyl alcohol)

INTRODUCTION

Conjugated polymers, such as poly(p-phenylene vinylene) (PPV) and polythiophene derivatives, in the non oxidized state, exhibit both

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* Corresponding author: decp@power.ufscar.br

electroluminescence (EL) and photoluminescence (PL)[1]. Many efforts have been made to describe the nature of the luminescence in these materials. The question about the role of the intrachain and/or interchain species in the excited state for luminescence quantum efficiency has been subject of great controversy[2]. This question has a practical motivation because from the understanding of these mechanisms it could be possible to improve the quantum yields of the conjugated polymers. When the polymer chains are isolated, as in a diluted solution, the photoexcitation produces only one single excited species namely intrachain exciton[3-5]. On the other side, in films or concentrated solutions it is expected that the photoexcitation generates interchain excited species at some extension[6]. Besides, the excited state wave function can overlap with that of the single-chain ground state[7,8]. Interchain interactions shifts the PL spectrum to the red region comparing to that of the single-intrachain exciton[2,7,8]. It is also expected that the luminescence quantum yield decreases with the increase of the interchain interactions due to the existence of a large number of non-radiative channels.

On the other hand, there are a few descriptions of PL enhancement in conjugated polymers. In this sense, the poly(3-alkyl thiophenes) exhibit a PL increase when the temperature is risen[9,10]. This anomalous temperature-PL relationship has been attributed to thermally induced conformational changes of the side groups.

This paper aims at the characterization the PL behaviour of PVA-PTAA blends upon laser irradiation.

EXPERIMENTAL

PTAA preparation was described elsewhere[11]. The PVA (MW 133000 and 99-100% hidrolyzed) (Mallinckrodt) was used as received. PVA-

PTAA blends were prepared by the addition of different amounts of PTAA salt to yield a 0.5wt%, 1 wt% or 10 wt% of PTAA in the blends. After that, diluted HCl was added drop wise into the solution until the pH was 3.0 to obtain the PTAA in the acid form. Flexible films of the blends were casting from this solution.The blends were photoirradiated using an Ar ion laser (line 457.9 nm) at 18 Wcm^{-2} intensity. The spectra were recorded using a Spex 500M single spectrometer. A Coherent Ar ion laser was used as excitation source and the PL signal was detected by a thermoelectrically cooled R5108 Hamamatsu photomultiplier.

RESULTS AND DISCUSSION

Figure 1 presents the PL spectra for different samples. It is observed that as the PTAA content is raised a decrease in the luminescence intensity occurs. A blue shift in the spectra is also observed. This decrease in the luminescence intensity is a unexpected result considering that the radioactive decay occur only in PTAA chains. Therefore, increasing the quantity of PTAA in the blend an enhancement in the luminescence could be anticipated. The results here could thus be associated with an modification of the interchain interaction among PTAA chains. These results are also confirmed by the differences observed between the behaviour when PTAA in salt form is used instead of PTAA acid form to prepare the blends[12]. Another interesting aspect of these blends is the raise in the luminescence spectrum upon laser irradiation. Figure 2 presents the results for PL intensity as function of the laser irradiation time.

In Figure 2 it is observed that the variation in the luminescence intensity increases 93 % and appears to saturate for time higher than

180 min. The curve can be fitted by a curve of the type (1 –exp (-t/τ)) giving the following value for τ = 80.40 min. The situation is very different when different laser irradiation are used. Using higher laser intensity a double process is observed: the PL increase is followed by a PL decrease which could be associated, therefore, to competitive processes [12]. Otherwise, using low laser intensities, stronger effects was observed. One possible application of the PL intensity variation is related to the possibility to build pattern emission. Figure 3 presents an example of this process. In this Figure, it was used a mask with the word "FAPESP".

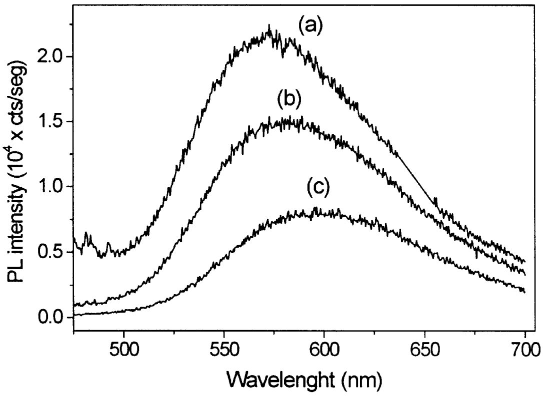

FIGURE 1: Emission spectra for different samples concentration: (a) PVA – PTAA: 0,5%; (b) PVA – PTAA 1,0%; (c) PVA – PTAA 10.0 %.

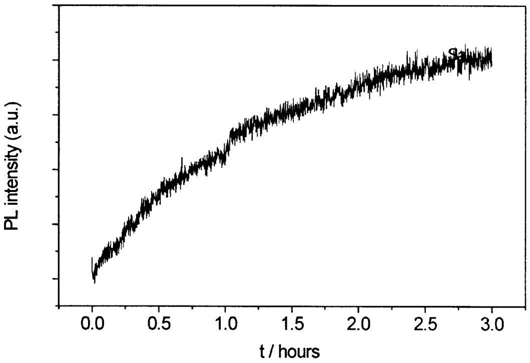

FIGURE 2: PL intensity as function of the time for PVA-PTAA 1 wt% at room temperature in the presence of air. Laser intensity= 18 W/cm^2.

FIGURE 3: Patterned luminescence from PVA-PTAA acid blend realized by photoirradiation. Photoirradiation realized under 22mW/cm^2 and 60 min.

CONCLUSIONS

The PL behaviour of PVA-PTAA blends are investigated. A decrease in the PL intensity as the content PTAA is increased it was detected which could be attributed to a modification in the interchain interaction. An increase in the PL intensity as function of the time was detected and, although its mechanism is not clear, we shown that the this effect could be used for practical applications.

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