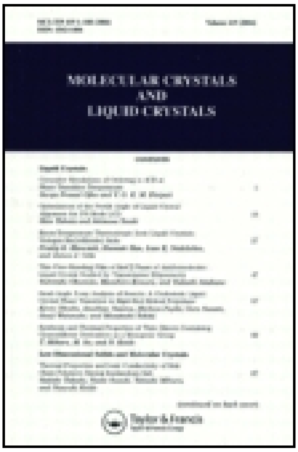

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Improvement of Photoluminescence Efficiency in Poly(p -Phenylene Vinylene) Induced by Laser Irradiation

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Improvement of Photoluminescence Efficiency in Poly(*p*-Phenylene Vinylene) Induced by Laser Irradiation

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In this work, we report a strong enhancement of photoluminescence (PL) intensity in PPV cast films upon laser irradiation in air, which competes with other quenching process related with formation of carbonyl groups. This increase of PL is dependent on laser intensity and film thickness. We observed that PL intensity increases up to 300% without significant changes in peak positions. This effect was accompanied by a blue shift of the absorption spectra and by the incorporation of carbonyl groups detected by infrared measurements.

Keywords: photoluminescence, enhancement, photodegradation, poly(*p*-phenylene vinylene).

INTRODUCTION

Semiconductor polymers have attracted interest due to their potential applications as active layers in electro luminescent devices as light-emitting diodes [1] and photoconductive devices [2]. The technological challenger of these new semiconductor devices is the improvement in the lifetime, when compared to conventional devices based on inorganic semiconductors, because the optical and electrical properties are degraded by photo-oxidative process. The operate lifetime in polymeric devices is high affected by photo-oxidation. This irreversible chemical reaction with oxygen induces the shortening in the conjugation length and a defects formation, such as carbonyl groups, acting as quenching sites [3-9]. There are few recent descriptions of PL enhancement via photoexcitation in conjugated polymers [8-10] which are not well discussed.

In the present work, we report an enhancement in the photoluminescence (PL) intensity as a new effect of photoexcitation on PPV cast films. This PL enhancement depends on the laser irradiation intensity and film thickness.

EXPERIMENTAL DETAILS

The poly(xylylidene tetrahydrothiophenium chloride) (PTHT) was synthesized following a precursor route described elsewhere [12]. PPV-cast films were photoirradiated using an Ar ion laser (line 458 nm) at several intensities. The absorption spectra were recorded by a Varian Cary 5G UV-visible-NIR spectrophotometer, whereas the spectra were recorded by a Spex 500M single spectrometer. A Coherent Ar ion laser was used as excitation source and the PL signal was detected by a photocounting using a thermoelectrically cooled R5108 Hamamatsu photomultiplier.

RESULTS

Fig. 1a shows emission spectra of a 3.0 μm thick PPV film before and after laser exposure at 1.27 W/cm^2 in air. Figure 1b shows the behaviour of the same sample measured under vacuum (10^{-5} mbar). A significant PL enhancement of 130% is observed after 60 min laser exposure in air without significant changes in peak positions and line shape. Otherwise, no enhancement was observed when the film was excited under vacuum (Fig. 1b), demonstrating that such PL enhancement practically does not occur in the absence of oxygen.

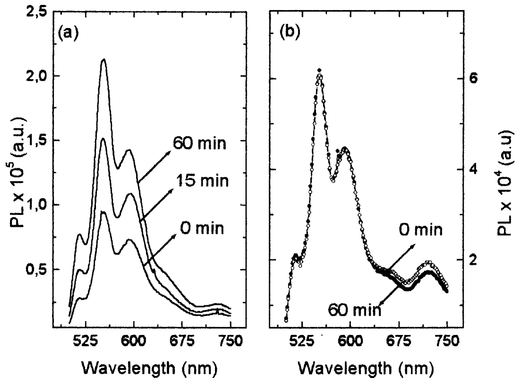

FIGURE 1. Room temperature photoluminescence spectra of a 3.0 μm PPV-cast film photoexcited by laser at 1.27 W/cm^2 in presence of air (a) and 10^{-5} mbar vacuum (b) for 60 min.

The increase of PL intensity was accompanied by a spectral blue shift in the absorbance and a decrease of 37 % in the density of states at the excitation wavelength (λ_{laser}=458 nm) after 46 min, as shown in Fig. 2. Similar absorption results were observed for conjugated polymers by other researches and were associated to the reduction in the average conjugation length produced by defects incorporated photochemically [5,10]. However, this chain shortening do not affects the PL spectra, as can be observed from the data in Fig. 1a. The same position of the zero-phonon line at 516 nm (2.4 eV) before and after irradiation is evidence that the PL emission is a characteristic of exciton recombination from conjugated PPV segments of at least 8-10 uninterrupted phenylenevinylene units [13]. In addition, we do not observe any increase of the vibronic progression in the PL spectra relative to the zero-phonon line, as a result of the increase of the amount of disorder [14,15] accounted for the carbonyl incorporation and/or chain shortening observed in the absorption.

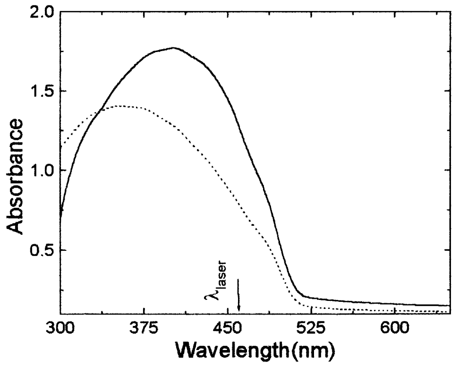

FIGURE 2. Absorption spectrum before (— 0 min) and after (---- 46 min) photoirradiation at 254 mW/cm^2 for 1.0 μm thick film in air.

Since the luminescence spectrum (shape and peak position) does not change significantly with exposure to laser irradiation, its integrated intensity was used to follow the enhancement process for different values of laser intensity and sample thickness. Figure 3 shows the normalized PL intensity of a 3.0 μm film as a function of the irradiation time. The luminescence steadily increases up to 300% for an excitation intensity of 127 mW/cm^2 and reaches saturation after 200 min of continuous excitation in air. However, if the sample thickness is reduced, a decrease of PL intensity is observed after certain period. This quenching process has been reported previously as being a result of the degradation of the organic structure near surface region. Based on the above results, we propose that the luminescence enhancement is due to a self-limited oxygen diffusion and spatial degradation produced by light intensity decay from the surface into the bulk, which builds an energy profile as a result of the conjugation length shortening. This process involves the formation of a dynamic energy gradient that increases and propagates into the film material and the charge/energy transfer to a non-degraded confinement layer, that confines and increases the formation and transition probability of excitons. This model explains well explain the enhancement of the PL intensity observed for the thick samples, as well as the quenching process in thin samples, that is a consequence of the change of the effective absorption and emission thickness and increase of the non-radiactive process via carbonyl centers. However, we are working on new experiments that would confirm the validity of the present model.

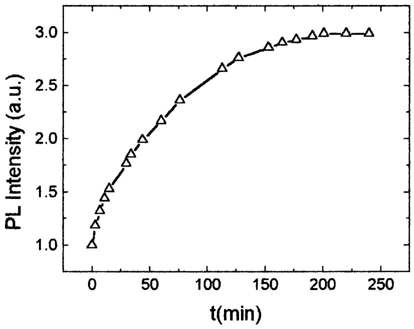

FIGURE 3. The time dependence of normalized PL integrated intensity for 1.27 W/cm^2 laser intensity for 3 μm PPV-cast film.

CONCLUSIONS

We report on the enhancement of photoluminescence (PL) intensity of PPV films induced by Ar ion laser in presence of air. The initial PL intensity increases up to 300% without significant changes in the spectral shape and position. This effect is accompanied by a blue shift in the absorption spectrum resulting in shortened effective conjugation length and by a formation of defects such as carbonyl groups.

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