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# Thermochromic Studies of MEH-PPV

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*In this work we studied the optical properties of Poly [2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) using polymeric blends with polystyrene. The photoluminescence spectrum of (MEH-PPV) present three characteristic peaks correlating to aggregate electronic transition at 608, 674 and 742 nm at 10° K. An addition of Polystyrene in MEH-PPV films induces a red shift in the absorption spectrum and the photoluminescence spectrum presents a new peak at high energy centred at about 572 nm at 10° K. It is attributed to intra band transition between localized intraband states.*

**Keywords:** MEH-PPV, Photoluminescence Spectrum, Absorption Spectrum.

## 1. INTRODUCTION

Polymer-based light-emitting diodes (PLEDs) have many attractive features such as low cost, easy fabrication using solution processing techniques, mechanical flexibility, easy color tuning, and applicability in flat panel displays. PLEDs are now approaching the brightness, efficiency, and lifetime to be commercially viable, offering significant advantages[1].

The electronic properties of conjugate polymers based on poly (*p*-phenylene vinylene) alkoxy derivatives are extremely sensitive to the chemical synthesis conditions, film processing and photo-oxidation effects. In solid-state films, these materials can aggregate and form excited interchain excitons, responsible for approximate 90% of optical excitations[2]. These lectronic species act as efficient quenching centres, decreasing the quantum luminescence yields[3]. The discovery that conjugated polymers, which are naturally disordered in the solid state, can also undergo temperature-dependent color changes that occurred in 1988 with substituted polythiophenes[4]. Polymers of this type form the bulk of the literature on thermochromic effects in conjugated polymers. A few [poly (phenylene vinylene) (PPV)] derivatives that display thermochromic properties have been reported[5,6]. However, these materials suffer from low contrast at practical temperature ranges, low reversibility, or phase changes that accompany the color change, rendering them impractical for many applications. The control of interchain interaction has been studied by changing molecular conformation in solutions and film processing[3].

The relative emission intensities and the fluorescence lifetimes of the donor showed that the miscibility of MEH-PPV and the copolymers is greater than that of MEH-PPV and polystyrene and this was confirmed by epifluorescence optical microscopy and scanning electron microscopy[7]. It posses a technological interest to enhance the electrical and

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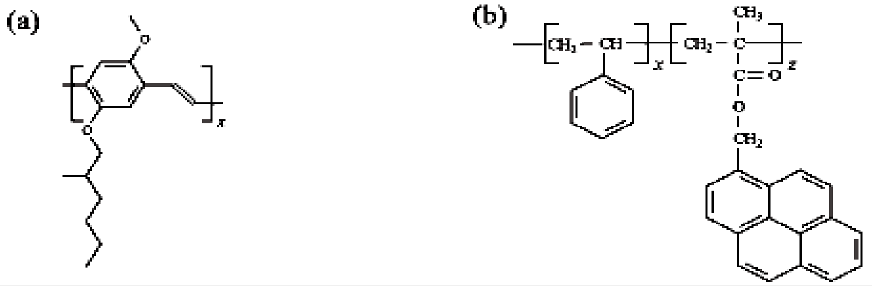
optical properties of polymeric light emission diodes. We report a study on the thermo chromic effects in the widely used light-emitting polymer (poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) and in two related copolymers, (poly [2-methoxy-5-(2- ethylhexyloxy)-1,4-phenylene-ethenylene-2,5-dimethoxy-1,4-phenylene-ethenylene) (M3EH-PPV)[6] and (poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-ethenylene-2, 5-dioctyloxy-1,4-phenylene-ethenylene) (MEH-DOOPPV )[6]. In this work we studied the optical properties of poly-[2-methoxy, 5-(2'-ethyl-hexyloxy) phenylene vinylene] (MEH-PPV) and Polystyrene blend films. The photoluminescence spectrum of blend films presents a new well-resolved peak at 572 nm, which is associated with intrachain-localized species. These methods allow for a local influence of the polymer properties, resulting in non-luminescent areas in the film. Polymer light emitting diodes (PLEDs) have suffered significant development since the first report of electroluminescence observation in conjugated polymers in 1990[8]. Conjugated polymers are nowadays used in several display applications[9], Many different electroluminescent conjugated polymers have been reported in literature, which cover the whole of the visible spectrum[10].

The results show the reduction of the interaction between adjacent MEH-PPV chains without energy and charge transfer.

## 2. EXPERIMENTAL

Fig. 1 shows the chemical structure of MEH-PPV synthesized by Wudl and Srdanov in 1993[11]. The MEH-PPV and the commercial polystyrene with molecular weight around 60,000 were used to prepare the blends films. Stock solutions of MEH-PPV (0.1 mg/mL) and polystyrene (0.1 mg/ml) in chloroform were mixed in the appropriate proportions (100%:0%, 20%:80% and 0%:100%, respectively) and stirred prior to casting onto glass substrates previously cleaned by the RCA procedure. The films were dried and stored at room temperature, protected from light to avoid photo degradation processes. Here we show morphology and miscibility studies of MEH-PPV blends with some optically inert polymers (host polymers): poly(styrene-*co*-2-ethylhexyl acrylate) (SEHAMA) with three different contents of 2-ethylhexyl acrylate units (0, 9 and 19 mol%) (Fig. 1). All these materials may exhibit emission in UV-range due to the presence of the phenyl moieties. However, this emission is not overlapped with the MEH-PPV absorption band. Because the NRET process requires a remarkable spectral overlap between the donor emission (SEAHMA) and the acceptor absorption band (MEH-PPV), we copolymerized the PS and its copolymers with 1-pynenyl moieties.



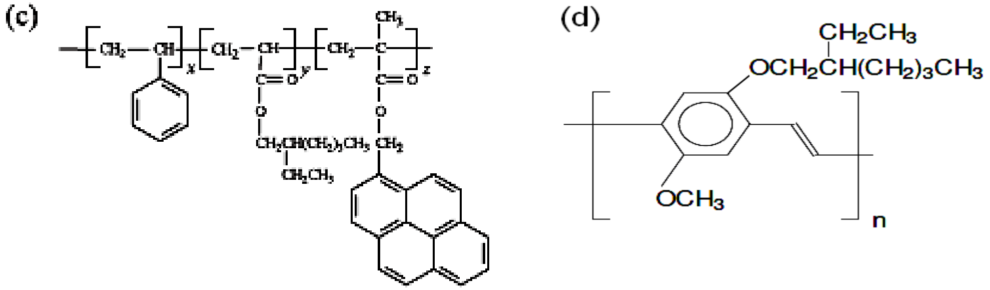


**Fig. 1:** Chemical Structures of the Conjugated Polymers
**(a)** MEH-PPV, **(b)** poly(styrene-*co*-1-methylpyrenyl methacrylate) (PS-*py*),
**(c)** poly(styrene-*co*-2-ethylhexyl acrylate-*co*-1-methylpyrenyl methacrylate)
(SEHAMA-*py*) and **(d)** MEH-PPV

Within the class of conjugated polymers, one widely studied is poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV) (Fig. 1a), which exhibits relatively high photoluminescence (PL) and electroluminescence efficiencies[12,13]. The UV-Vis absorption measurements were carried out with a Hitachi U-2001 spectrophotometer at room temperature (300° K). The photoluminescence spectra were recorded using a SPEX-750M monochromator equipped with a Jobin-Yvon CCD-detector (2000 x 800-3) in the range of temperature from 10° to 300° K. Excitation was performed with the 457.8 nm line of an $Ar^+$ laser. The samples were kept in a closed helium cryostat under vacuum of $10^{-4}$ torr.

## 3. RESULTS AND DISCUSSION

These results are consistent with the well understood mechanism for thermochromic effects in conjugated polymers first proposed in 1989[4]. In this model, the polymer sidechains become bulkier with heating. Stearic hinderance between in-plane sidechains forces twisting to occur in the polymer backbone. It is this conformational change in the polymer backbone that shortens the conjugation length and thus blueshifts the material absorption and photoluminescence[4,14]. The extent of this effect should depend both on the rigidity of the backbone itself and also on the relative bulkiness of the sidechains. Fig. 2 shows the absorbance spectra of MEH-PPV, MEHPPV: polystyrene blend and polystyrene cast films.The films that contain the active polymer present, above 350 nm, an extended band associated to non-localized states (HOMO-LUMO transitions). The addition of polystyrene in MEH-PPV films induce a red shift (5 nm) in the absorption spectrum, reproducing a solvating effect, reducing the interchain interaction and increasing the effective conjugation length of MEH-PPV main chain[2]. The photoluminescence spectrum of the MEH-PPV films present three characteristic peaks correlated to zero-phonon transition at 608 nm and two phonon-replicas at 674 and 742 nm at 10° K (Fig. 2). In this case, the zero -phonon transition is attributed to the interchain transition[3]. Following this absorption red shift, the PL spectrum for MEH-PPV: polystyrene film presents a new peak at high energy at about 572 nm (10° K), associated with intrachain electronic states[3]. The blends (MEH-PPV: polystyrene) present high thermal stability with weak electron-phonon coupling in the range of temperature from 10° to 300° K.

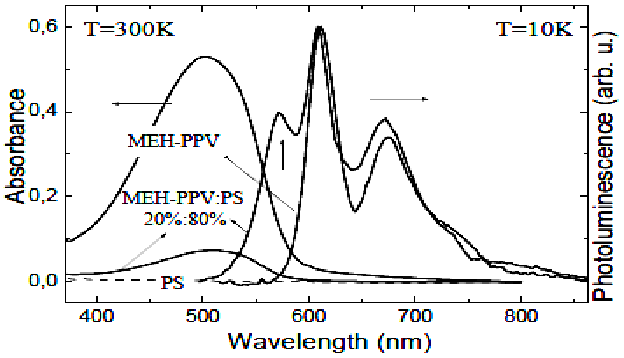


**Fig. 2:** Absorption MEH-PPV, MEH-PPV: PS Blend and PS Film at Room Temperature. The PL Spectra (10° K) of MEH-PPV and MEH-PPV: PS Blends Films

The well-resolved peak (Photoluminescence spectrum – Fig. 2) of MEHPPV: Polystyrene blends film was investigated as a function of excitation intensity (power). In Fig. 3 we show the evolution of the Photoluminescence spectra at 10° K. For excitation intensities being equal 1.2, 3.2, 12.7 and 124.6 $Wcm^{-2}$ the Photoluminescence intensity of the localized peak at 572 nm decreases due to a competition between two distinct radiative processes, or interchain and intrachain transitions. For the excitation intensity above 12.7 $Wcm^{-2}$, the line shape of emission spectra does not change and the emission is mainly due to interchain transition. This is coherent with the facility of non-localized electronic state formation via excited states for organic materials. In the case of conjugated polymer the wave function can delocalise among two or more adjacent chains.

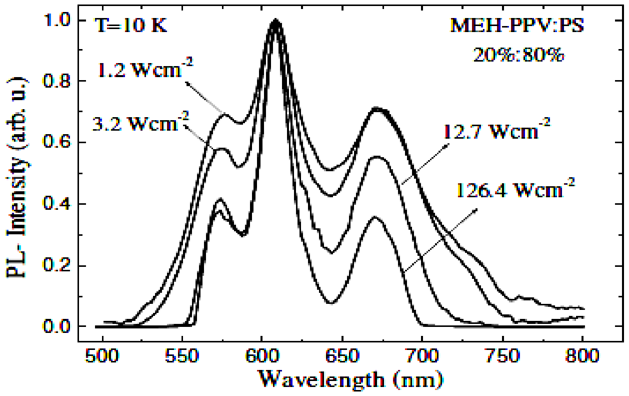


**Fig. 3:** Photoluminescence Spectra of MEH-PPV : Polystyrene Blends Films for Excitation Intensities 1.2, 3.2, 12.7 and 124.6 $Wcm^{-2}$

## 4. CONCLUSION

In conclusion, we have studied the thermochromic effects in films of the light-emitting polymer MEH-PPV and two related copolymers. MEH-PPV films exhibited a striking color change from red to yellow when heated from room temperature to 300 K.The MEH-PPV: PS blends films are a promissory alternative to minimizing the interchain interaction during the film processing. This is similar a solvating effect, increasing the effective conjugation length of MEH-PPV main chain and the intraband transition.

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