SEVEN publicações acadêmicas

EM PARCERIA COM:

NANOMETER PPV FILMS/SYNTHETIC DYES CONVERTED AT LOW TEMPERATURES: *AZOCHROMOTROPIC SULFANIC ACID*; *INDIGO CARMINE; ORANGE 2 SODIUM SALT; METHYL ORANGE* AND *NITRAZINE YELLOW*

L. C. Poças[1] and M. A. T. da Silva[2]

ABSTRACT

Light-emitting polymers, like conjugated polymers, are attractive for fundamental physics and technological applications. Poly(p-phenylenenovinylene) (PPV) is an excellent choice for electroluminescent and photovoltaic devices, although it presents challenges due to its insolubility in organic solvents. A conventional route to obtain PPV involves a thermal process at high temperatures, but with increased structural defects. An innovative alternative, with lower temperature and treatment time, was proposed using synthetic dyes instead of DBS without compromising the properties of PPV.

Keywords: Conjugated polymers. PPV.

INTRODUCTION

Light-emitting polymers can be processed in the form of thin and ultra-thin films at a low cost, which makes them attractive both from a technological point of view and from a fundamental physics point of view[1,2,3,4]. In this class, conjugated polymers are found that have in their atomic structure alternations of double and single bonds between carbons. In particular, poly(p-phenylenylene (PPV) presents itself as a promising candidate for application as an active layer in electroluminescent devices, such as polymer light-emitting diodes (PLEDs)[5,6,7,] and photovoltaic devices 8,9,10,11. PPV is not soluble in organic solvents, however, it can be processed into thin film form using a water-soluble precursor, polyxylidophene tetrahydrophylophene chloride (PTHT). After being processed, the films are subjected to a thermal step to eliminate the tetrahydrothiophene side group of the PTHT, with treatment for up to 6 hours, at temperatures above 200 ºC, under vacuum, to obtain PPV[12]. However, using this conventional conversion route, there is an increase in the number of intrinsic structural defects.[7] Marletta et al· [13,14,15] developed an alternative route, at low temperature, which consists of replacing the Cl- counterion of PTHT with the salt of sodium dodecylbenzenesulfonated acid (DBS); allowing the conversion to PPV to be performed at lower temperatures (~100°C) and with shorter time intervals (~30 min.), without compromising the properties of PPV.

---

[1] Federal Technological University of Paraná – UTFPR – Londrina – Paraná
luizc@utfpr.edu.br
[2] Federal Technological University of Paraná – UTFPR – Londrina – Paraná

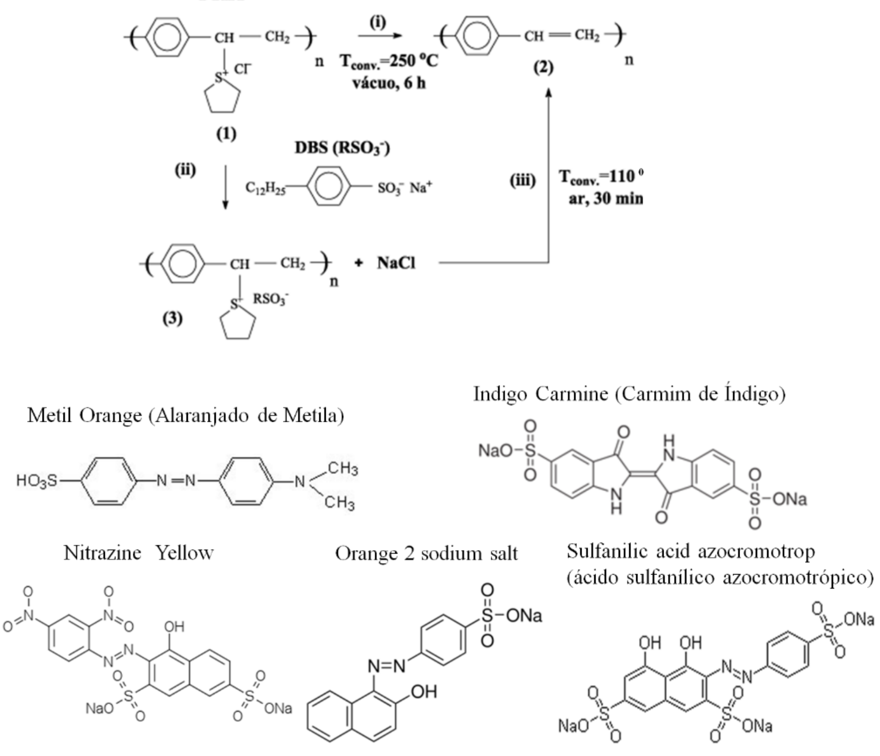
OBJECTIVE

In this work, the alternative route of PPV synthesis was used, through the replacement of the Cl- counterion of PTHT by synthetic dyes instead of DBS, to investigate the effects of reducing the temperature and heat treatment time of PPV.

METHODOLOGY

Figure 1 shows a scheme of the PPV conversion routes and the chemical structures of the various substituting elements (dyes) used in this work.

Figure 1 – Thermal conversion process of PPV and as a counter-ion of PTHT and chemical structure of the various dyes used as counter-ion of the precursor polymer, PTHT: *Methyl Orange*, *Indigo Carmine*, *Orange 2 sodium salt, Sulfanilic acid azocromotrop, and Nitrazine Yellow.*



DEVELOPMENT

To investigate the process of thermal conversion at low temperature in PPV+dye samples, absorption and photoluminescence (PL) measurements were performed at room temperature (Figure 2). The PPV+dye samples present, in general, a good spectral definition in the *bandgap* region, with the maximum absorption around 440 nm, demonstrating an efficient film conversion process under these conditions and for these dyes. The absorption curves have very similar shapes and intensities. Figure 2 also shows the emission spectra obtained at room temperature for all samples. It is possible to observe in all samples (except PPV+Nitrazine) the presence of vibranic structures with almost the same spectral shape and with the peak emission of zero phonon almost in the same position, around 520 nm. These emission spectra, therefore, confirm that the thermal conversion process of the PPV has been achieved. The peaks of LP located in the lowest energy region are related to the transition of phonon replicas.[16.17]

Emission efficiency is an indirect measure of the quantum yield of the sample, i.e., a ratio between the absorption and emission of the film. This analysis, based on the absorption and PL spectra of Figure 2, shows that the PPV+Acido film presents slightly better than the other films, although the emission efficiency of all films has the same order of magnitude (Table 1).

Figure 2 - Absorption and PL spectra of *casting films*: a) PPV+Sulfanic Acid Azochromotropic (PPV+Acido); b) PPV+Indigo Carmine (PPV+Indigo); c) PPV+Orange 2 sodium salt (PPV+Orange); d) PPV+Methyl Orange (PPV+Methil) and e) PPV+Nitrazine Yellow (PPV+Nitrazine).

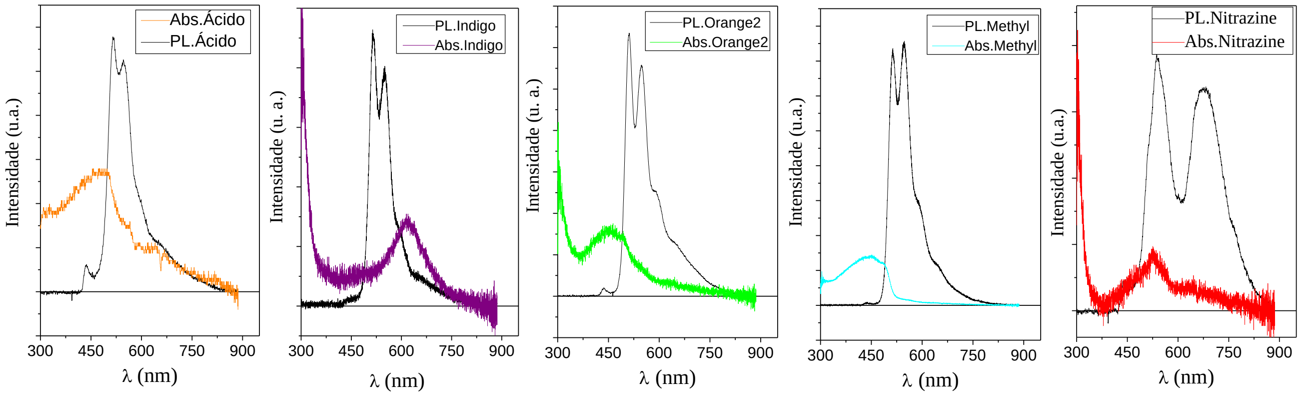


Table 1 – Peak absorption, pot, PL, and relative efficiency (PL/Pot) of casting films.

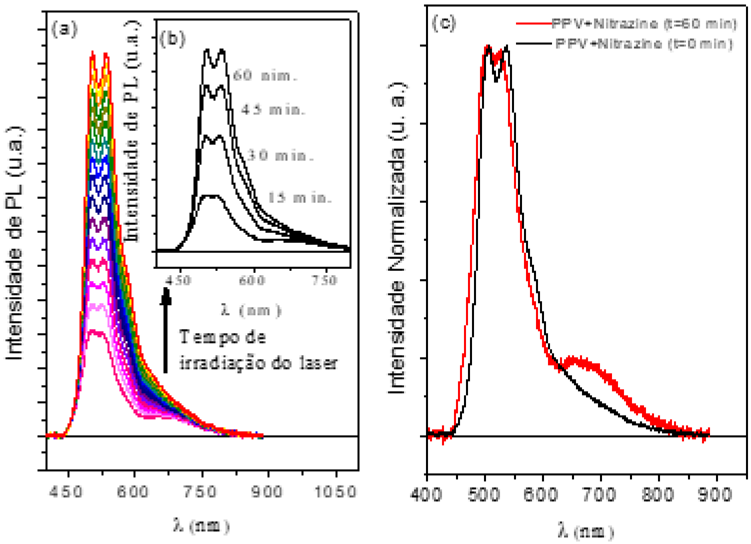
Sample	**Abs (405-800 nm)**	**Pot = 1-10$^{-\|ABS\|}$**	**PL**	**η**
PPV+Methyl	0,603	0,7505	34.98x105	4,661x106
PPV+Orange2	0,0860	0,1796	6,220x105	3,463x106
PPV+Indigo	0,0540	0,1169	1,925x105	1,647x106
PPV+Acid	0,0260	0,05810	3,140x105	5,410x106

These results are a consequence of the low incorporation of defects (carbonyl groups) during the conversion to low temperature7 and confirm that the use of these dyes, associated with the low temperature conversion process, can be used efficiently and with reduced thermal degradation of the PPV.

Figure 3 shows PL spectra of a self-assembled PPV+Nitrazine film, subjected to polarized laser irradiation with a wavelength of 405nm, for a relatively long time. There was an increase of approximately 4 times in the intensity of the PPV emission band in an irradiation time of 60 min. In the region of longer wavelength (dye emission), however, there is a relative reduction in emission when compared to the increase presented by PPV emission [see Figure 3(b)].

This behavior of the PPV+Nitrazine film is subtly similar to that observed in a sample of PPV+CR[18], where the results were explained by a process of degradation of the azo-dye molecules (*Congo red*) that occurs with photo-irradiation. The observed changes in the spectrum are correlated with the combined effect of energy transfer between the light emitted by the PPV and the azo-dye molecules, the degradation of the dye, and possible conformational changes in the chain and in the conjugation length of the PPV, with an increase in the irradiation time.

Figure 3 - (a) PL spectra of the self-assembled PPV+Nitrazine film as a function of the irradiation time of the polarized laser. The *inset* (b) shows the spectra obtained with times of 15, 30, 45, and 60 min. (c) Normalized LP spectra, with irradiation time of 0 min. and 60 min.



FINAL CONSIDERATIONS

The analysis of the emission efficiency of PPV+dye casting films shows that PPV+Acido film presents subtly better than other films, although all samples present with the same order of magnitude. Through photo-irradiation with polarized laser, a significant increase in the PL intensity of the PPV and a concomitant reduction in the fluorescence of the azodye molecules were observed. We credit these results to some combined effects, such as the energy transfer between the PPV and the azo-dye, changes in the structure conformation of the PPV+Nitrazine film, and degradation effects of the dye molecules that occur with *polarized* laser irradiation.

REFERENCES

1. Melo, R. M., et al. (2003). *Química Nova, 26*, 177.
2. Gong, H., et al. (2024). *Polymer Chemistry, 15*, 3176-3183.
3. Wan, Q., et al.. (2023). *Journal of the American Chemical Society, 145*(22), 11914–11920.
4. Xu, J., Du, K., Peng, F., et al. (2024). Highly conductive polymer electrodes for polymer light-emitting diodes. *npj Flexible Electronics, 8*, 38.
5. Grimsdale, A. C., et al. (2009). *Chemical Reviews, 109*, 897.
6. Akcelrud, L. (2003). *Progress in Polymer Science, 28*, 875.
7. et al. (2000). *SID Symposium Digest of Technical Papers, 31*(1), 1076-1079.
8. Günes, S., et al. (2007). *Chemical Reviews, 107*, 1324.
9. Masuda, K., et al. (2010). *Applied Materials Interfaces, 2*, 236.
10. Ma, J., et al. (2021, October). *Optical Materials, 120*, 111486.
11. Susarova, D. K., et al. (2011). *Journal of Materials Chemistry, 21*, 2356-2361.
12. Bradley, D. D. C. (1987). *Journal of Physics D: Applied Physics, 20*, 1389.
13. Marletta, A., et al.. (2000). *Advanced Materials, 12*, 69.
14. Marletta, A., et al.. (2000). *Macromolecules, 33*, 5886.
15. Marletta, A., et al. (2002). *Macromolecules, 35*, 9105.
16. Yu, J., et al. (1994). *Synthetic Metals, 66*, 143.
17. Yu, J., et al. (1996). *Synthetic Metals, 82*, 159.
18. Laureto, E., et al. (2011). *Synthetic Metals, 161*, 87.