

Optical Properties of Poly(3-octylthiophene) Partially Dedoped.

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Introdução

In this work poly(3-octylthiophene) (P3OT) films were synthesized electrochemically in non-aqueous media through the oxidation of the monomer, (3-octylthiophene), using a standard three-electrode cell in acetonitrile with 0.05 mol L⁻¹ LiClO₄ or 0.05 mol L⁻¹ Et₄NBF₄. The polymeric films were deposited on fluorine tin oxide (FTO). The partial dedoping was obtained in NH₄OH solution and providing a good chemical stability of the formed material. The films obtained through this method have been characterized by Fourier-transform infrared spectroscopy (FT-IR), Electron Paramagnetic Resonance (EPR), UV-Vis absorption and photoluminescence (PL) spectroscopy. The FT-IR and EPR spectra together gave the results that led to characterization of two structures (benzene and quinone forms) as forming the P3OT polymer chain. These results were associated with the stabilization of pristine chains (benzene form) and mixed chains (composed of benzene and quinone structures) in the polymeric film. Their band in the PL spectra is wide and asymmetric and its adjustment by Gaussian functions was necessary. This was the main indication that there are two distinct contributions to the emission spectra. These two contributions are attributed to the emission by mixed chains (Gaussian centered at higher energy) and by pristine chains (Gaussian of lower energy) present in the formed polymeric material.

Resultados e Discussão

The free radical for the P3OT prepared with both supporting electrolytes (LiClO₄ and (C₂H₅)₄NBF₄), doped and partially dedoped, presented the following values of the g-factor: 2.003 and 2.004, respectively. An interesting result of the EPR spectrum was the fact it shows sign of a line, related to the free radical for partially dedoped P3OT, demonstrating that the polymer is not really totally dedoped; in other words, it still presents chains formed by quinonic structures, besides the benzenic structures. With the objective of characterizing the changes in chemical nature of the material produced by the electrochemistry synthesis and subsequent deprotonation, FT-IR spectroscopy was used. It was possible to observe that the bands obtained in the FT-IR spectra of the partially dedoped P3OT films resembled those of the pristine P3OT spectrum, indicating the occurrence of the polymerization. It is plausible to suppose that the feature at 1431, 1104, 1059 and 1102 cm⁻¹ can be related with the similar stretching and deformation modes due to the presence of the quinonic ring in the polymeric structure of the electrochemically

generated film, as it happens in other polymeric systems.¹ Through UV-Vis spectra it was possible to observe the instability of partially dedoped P3OT, which had been prepared with LiClO₄. For that, the spectra were registered soon after the formation of the polymeric film and again sixty days later. The absorption band changed from 436 nm to 450 nm, showing the dominant effect of natural dedoping with time. The values obtained for the PL bands are different from those observed by other groups that studied P3OT obtained by chemical synthesis. In literature, the PL spectra of P3OT have bands centered at 645 nm. Wang *et al.*² present a PL spectrum where, besides the main band at 642 nm, a small band appears at 575 nm, and its origin was not explained. The spectra of samples of partially dedoped P3OT prepared with LiClO₄ in our work show emission bands centered very close to 575 nm, similar to the band that appears in the spectrum presented by Wang. The spectra of P3OT prepared with (C₂H₅)₄NBF₄ displays the bands centered in intermediate values, between 575 and 640 nm. Due to the apparent contradiction found in the literature and of the fact the PL spectra present a great width at half height, an adjustment was made through Gaussians, trying to obtain the best adjustment for such spectra.

Conclusões

To explain the PL spectra of P3OT a fitting model was built with Gaussians for results of FT-IR and EPR spectroscopies, where identified the presence of two structures (benzenic and quinonic forms) that constitute the polymeric chains. Those chains were denominated mixed chains (formed by benzenic and quinonic structures) and pristine chains (formed exclusively in the benzenic form). So, through the adjustment of the proposed model it can be observed that the PL spectra are formed by two main contributions: the emission of the mixed chains (Gaussian of smaller wavelength) and the emission of the chains in the pristine form (Gaussian of larger wavelength). Also, the PL spectra bands for P3OT prepared with (C₂H₅)₄NBF₄ are moved for smaller energies in relation to P3OT prepared with LiClO₄, which can be caused by the formation of a smaller number of mixed chains in P3OT prepared with (C₂H₅)₄NBF₄.

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¹ de Santana, H.; Matos, J. R.; Temperini, M. L. A. *Polym. J.* **1998**, 30, 315.

² Wang, G.; Yuan, C.; Lu, Z.; Wei, Y. *J. Lumin.* **1996**, 68, 49.