11th International Conference
on Advanced Materials

Rio de Janeiro Brazil
September 20 - 25

ICAM2009

Theoretical-study on the contribution of oxygen and chloroform to the sensibility of organic dosimeter

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Abstract – In this work we investigated the changes on the optical and structural behavior of poly(2-methoxy-5(2'-ethylhexyloxy)-*p*-phenylenevinylene) - MEH-PPV under the influence of blue-light radiation, which is used as phototherapy in the treatment of neonatal jaundice. It is observed changes from orange-red to yellow clearly, while its peak position emission shifts from around 570 nm to 450 nm with the radiation exposure time. The role of oxygen has been discussed. Finally, we have theoretically investigated a model for the degradation process of MEH-PPV based on structural models for MEH-PPV oligomers in vacuum and in chloroform.

Optical properties of luminescent polymers have been studied since the first report of electroluminescence in poly (p-phenylenevinylene) in 1990. However, the performance of the devices made from them is limited by high vulnerability to degradation processes which dramatically change the emission color and reduce the quantum efficiency and durability of their devices. The change in emission color and the reduction in photoluminescence and absorbance intensity, characteristic from these processes, caused by visible radiation, show the possibility to design dosimeters where the effects of these phenomena on the optical properties of conjugated polymers are more important than improving the durability of devices made from them. Moreover visible dosimetry is desired especially in medical applications where phototherapy is used for example in neonatal disease treatments where a strong relationship exists between the rate of decline in serum bilirubin level of infant's skin and the intensity and spectral qualities of the light source, as well as the distance between the light source and the neonates. In this work we investigated the changes on the optical behavior of poly(2-methoxy-5(2'-ethylhexyloxy)-*p*-phenylenevinylene) (MEH-PPV) solutions under the effect of blue-light radiation applied for neonatal hyperbilirubinemia (or jaundice) treatments, and we have theoretically investigated a model for MEH-PPV photodegradation based on structural models for MEH-PPV oligomers in vacuum and in solvent (chloroform). Solutions of this polymer in chloroform was exposed to a traditional phototherapy equipment (460 nm focus, 40 $\mu W/m^2/nm$), and the influence of this radiation on the optical properties of this system were investigated by photoluminescent and UV-Vis absorption spectra. FTIR and ^{13}C NMR measurements were carried out in order to investigate changes in chemical structure of MEH-PPV due blue-light irradiation. These results show that the radiation exposure causes the decrease of the polymer conjugation length probably due the oxidation of the vinylic bonds to give carbonyl groups (C=O) or the backbone scission and increase in conformational disorder of the polymer. All these effects may be responsible for the blue-shift observed in absorption and photoluminescence spectra of MEH-PPV solutions after blue-ligth radiation exposure. We investigated how the incorporation of oxygen and breaking of vinyl double bonds affect the absorption spectra. Our theoretical calculations were carried out on degradation structural models where the MEH-PPH vinyl bonds (C=C) are replaced by carbonyl (C=O) as a consequence of light exposure, which dramatically changes the polymer solution's color in the experiments. All calculations were carried out with semi-empirical methods using the PM3 Hamiltonian and ZINDO/S-CI (Zerner's Intermediate Neglect of Differential Overlap) codes. The results indicated that the inclusion of carbonyl within the polymeric chain can produce significant blue shifs in the absorption spectra, with associated decreasing in the intensity of the absorption spectra, which are in excellent agreement with the available experimental data. Because degradation is based on a photoreaction mechanism, the incorporation rate of carbonyl within the polymeric chain for the real polymer depends on its exposure time to blue-light radiation, which is very useful for the purposes of using the polymer as the basis for a dosimeter.

This work was sponsored by CNPq, FAPEMIG, CAPES and FAPESP.