Near-Infrared Emission of Nd-PSS Films

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Received on 4 April, 2005

We report a study of a new chemical synthetic route of polystyrene sulphonate (PSS) films doped with neodymium ion (Nd^{+3}) from a neodymium nitrate solution. The UV-Vis-NIR spectrum presents an intense characteristic electronic transition at 800 nm and the infrared spectrum presents low definition bands as a result of Nd^{3+} coordination with PSS molecule. Additionally, the spectrum of Nd-PSS film presents the same line shape profile of Nd^{3+} salt in aqueous solution. Selective luminescence spectroscopy measures shows that the incorporation of neodymium ion introduces a red shift bands and a better line shape definition in UV luminescence compared to PSS film, decreasing the interaction between PSS aromatic groups. The near-infrared emission was observed in the large spectrum region from 600 to 800 nm; it is associated with the Nd^{3+} complex of PSS monomer

Keywords: Polystyrene sulphonate, Neodymium ions and synthesis route

I. INTRODUCTION

Optical properties of polymeric matrix doped with rare earth ions are investigated in view of the technological applications in photonic devices [1-4]. Recently, electroluminescence of polymer light emission diodes was observed from polymeric blends of poly(dioctyfluorene-cobenzothiazole) and lissamine-functionalized terphenyl-based neodymium complex[1]. This metal complex like also present an emission on near-infrared (NIR) spectral region. This protocol presents new perspectives to incorporate the rare earth elements in polymeric matrix.

In this report we have addressed a study of the chemical synthesis route of polystyrene sulphonate (PSS) films doped with neodymium ions (Nd^{3+}). The techniques used to this were absorption and emission spectra in the region of UV-Vis-NIR and FTIR, which were performed to characterize the Nd ion incorporation into the host matrix. The spectral range of near-infrared emission observed for Nd incorporated in the Nd-PSS films is from 600 to 900 nm.

II. EXPERIMENTAL

The initial preceding to synthesize the Nd-PSS films was the conversion of the sodium polystyrene sulphonate (Na-PSS), M_w = 70000, into acid form (H-PSS). Scheme 1 shows this one using an Amberlite®IR-120. The film processing was performed using a precursor mixing aqueous solution of H-PSS and $Nd(NO_3)_3$ (neodymium nitrate) with a constant volume ratio, 6:1 (v:v), respectively. The concentration of $Nd(NO_3)_3$ was 0.7 mol.L^{-1} and of H-PSS was 0.15 mol.L^{-1}. Scheme 1 shows possible steps to ionic exchange reaction between H^+ and Nd^3. The initial solution containing H-PSS and $Nd(NO_3)_3$ was stayed overnight at 5 °C and the liquid phase was removed. Finally, the films were obtained after solvent evaporation under vacuum at room temperature.

Optical characterization of H-PSS and Nd-PSS films was performed using a HACH 4000 U spectrophotometer in UV-Vis-NIR region and a NEXUS 470 FTIR spectrophotometer in infrared region. The luminescence in UV-Vis-NIR region was carrier out using a Hitachi F-4500 spectrofluorimeter.

$$\text{Na-PSS}_{(aq)} \xrightarrow[\text{IR-120}]{\text{Amberlite}} \text{H-PSS}_{(aq)}$$

$$\text{H-PSS}_{(aq)} + \text{Nd}^{3+}{}_{(aq)} \longrightarrow \text{Nd-PSS}_{(s)} + \text{H}^{+}{}_{(aq)}$$

Scheme 1. Synthetic route of Nd-PSS films.

III. RESULTS AND DISCUSSION

Figure 1 displays the absorbance spectra in UV-Vis-NIR of H-PSS film, $Nd(NO_3)_3$ aqueous solution and the Nd-PSS film. We observe that the transitions present in the neodymium nitrate solution are present in the Nd-PSS film. For the spectra contain Nd, the mean difference is the intensity ratio between the transitions $^4I_{9/2} \rightarrow {}^4G_{5/2}+{}^2G_{7/2}$ (580 nm) and $^4I_{9/2} \rightarrow {}^4F_{5/2}+{}^2H_{9/2}$ (800nm). The increase in the absorbance spectra for Nd-PSS film above 400nm is due to the H-PSS matrix.

Figure 2 displays the FTIR spectra of H-PSS and Nd-PSS. In the case of H-PSS film, we observe the common bands of polystyrene sulphonate[5]: i) 1190 cm^{-1} - symmetric stretching of S=O, ii) 1000-1030 cm^{-1} - symmetric stretching of O-S-O, iii) 800 cm^{-1} - angular deformation of C-H of aromatic ring and iv) 3000-3900 cm^{-1} - symmetric stretching of O-H. For Nd-PSS film, the spectrum shows the same bands with an enlargement in all range. Sun and co-works[6] have seen a similar effect for poly(bithiazole-tetrathiapentalene) metal complex like. In this case, the result was correlated with the complex formation between the polymer and the ion. In our system seems the same coordination of Nd^{3+} with the sulfuric

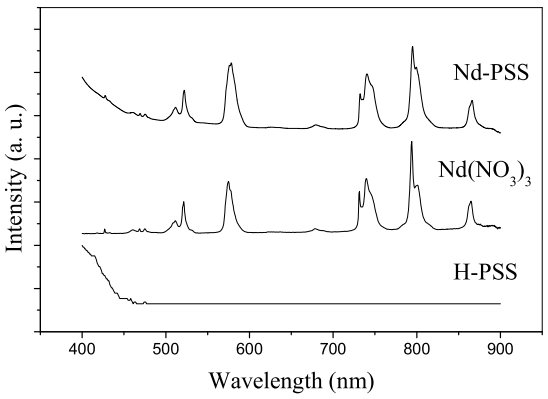

FIG. 1: Absorbance spectra of H-PSS film, aqueous solution of $Nd(NO_3)_3$ and Nd-PSS film in UV-Vis-NIR region.

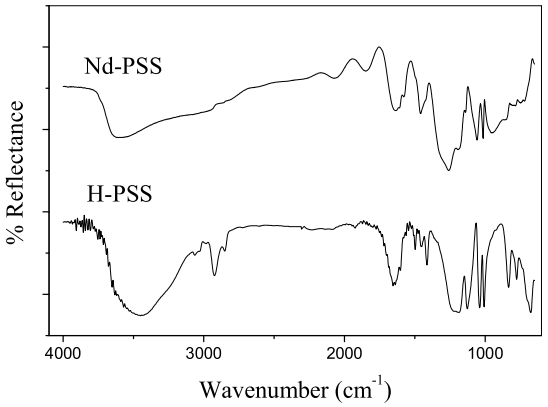

FIG. 2: FTIR spectra of Nd-PSS and H-PSS films.

groups of PSS monomers.

Figure 3 displays the PL for H-PSS and Nd-PSS films in the range between 450 and 900 nm. For high excitation energy (425 nm), both spectra can be considerably approximately equal. In this case the emission is preferentially due to the PSS excimers species. When the excitation energy (550 nm) decrease, the spectrum of Nd-PSS presents a considerable red shift as compared to H-PSS film. This result is in accordance to the result obtained FTIR measurement (Fig. 2). This is more perceptive in O-H band. Considering the complex formation of Nd^{3+} and the lateral chain of PSS (aromatic groups), the entanglement between adjacent polymer chains is expected to increase. Consequently, the new excimer species presents lower formation energy. This corroborates with the fact that H-PSS film is transparent in this excitation wavelength (Fig. 1).

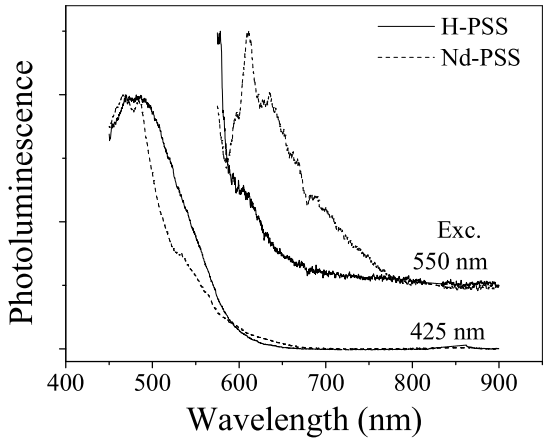

FIG. 3: Emission spectrum of H-PSS and Nd-PSS films as function of excitation wavelength.

IV. CONCLUSIONS

In summary, it has been demonstrated that Nd-PSS films can be obtained using H-PSS and neodymium nitrate. The study of absorbance in UV-Vis-NIR and IR region show the incorporation of Nd ion in the polymeric matrix without the significant changes in the internal Nd^{3+} electronic structure. The radiative transition in near-infrared region was attributing to complex metal like.

Acknowledgements

The authors acknowledge the financial support from FAPEMIG, CNPq, CAPES and IMMP/MCT (Brazil).

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