

Study of optical properties of selenophene's copolymers with polythiophene derivatives

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Introduction

Polythiophenes and its derivatives have interesting technological applications, such as photovoltaic cells, sensors and capacitors due their electrical and optical properties¹. These properties can be improved depending on the synthesis methodology. The Chemical oxidative coupling with FeCl₃ is the most popular synthesis method utilized to produce polythiophenes. However, this method produces polymers with irregular head-to-tail coupling. Then, it is expected that polymer chains contain certain degree of structural defects, hindering charge movement and interactions between chains. Synthesis methodologies used to produce regioregular polythiophenes, such as Grignard (GRIM), have as objective diminish these defects and improve electrical and optical properties¹.

Another conducting polymer that have attracted interesting are selenophenes. They are similar to polythiophenes in terms of structure. However, several theoretical studies have shown that, due to the selenium atom, it is expect that they have lower band gaps and stronger interaction between chains. Although, the lack of solubility and monomeric precursors, limits their application³. This problem can be solved by producing copolymers with polythiophene derivatives.

Results and Discussion

In this work we synthesized the poly(3-ethyl thiophene acetate) (PTAcEt-IR) and poly(3-ethyl thiophene acetate)-co-polyselenophene, containing 5% (Se-5%) and 10% (Se-10%) in mol ratio of the selenophene by chemical oxidative polymerization. The PTAcEt RR was obtained by GRIM method, being a regioregular polymer.

Figure 1 shows the absorption and emission spectrum of all polymers in solution of monochlorobenzene. The wavelength of maximum absorption (λ_{max}) ranges from 406 to 423 nm and it is related to interband transitions of unsaturated bonds in thiophene ring, π - π^* . Depending on the conjugation extension, this value can be shift to blue or red. Polymers with few defects tends to have this value red-shifted, as can be observed on PTAcEt RR, whose λ_{max} was equal to 423 nm. Moreover, solvents can also influence on λ_{max} . Se-10% presented the lowest λ_{max} value, 406 nm, which could be related to certain insolubility promoted by

the media due to presence of higher selenophene units in the copolymer structure. Se-5% has the second major λ_{max} , 310 nm, following by PTAcEt IR, λ_{max} = 308 nm. In this case, the presence of selenophene units contributed with the length of the conjugation.

The gap energy (E_g) was calculated based on absorption spectrum. Its values range from 2.46 eV to 2.32 eV. The lowest value, 2.32 eV, was found for PTAcEt RR. The others polymers have analogous E_g .

The wavelength of maximum emission intensity ($\lambda_{max\ em}$) ranges from 539 to 554 nm, being in the yellow's spectrum band. PTAcEt RR presented the highest value, 554 nm, while the rest of polymers have the same $\lambda_{max\ em}$ of 539 nm.

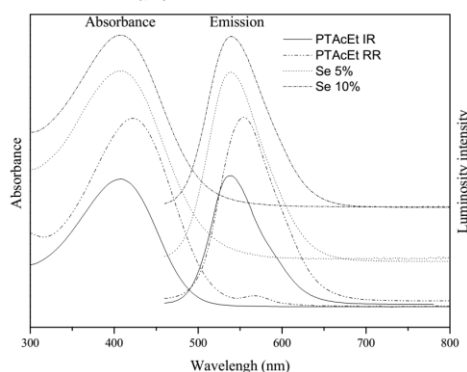


Figure 1. Spectrum of absorption (left) and emission (right) of the polymers and copolymers.

Conclusion

The present work has as objective to compare the optical properties, based on fluorescence and UV-vis spectroscopy, of PTAcEt IR, Se-5%, Se-10% and PTAcEt RR in solution. The results have shown that polymers with fewer defects in their structure, such as PTAcEt RR, have superior optical properties, including red-shift in the λ_{max} and lower gap energy. Moreover, small contents of selenophene units in the copolymer's structure has revealed a significant improvement in the optical properties, as can be seen in Se-5%.

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