



Influence of CN Moieties Linked to the Backbone on Kinetics of PPV-like Polymers Formation

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Abstract A series of copolymers formed by four DCN-PPV:PPV monomer ratio were prepared. These polymers were obtained in a water/acetonitrile 1:1 mixture and purified by dialysis. The influence on kinetics of polymer formation was obtained by the spectroscopic study of the thermal conversion of the polyelectrolyte obtained. The final polymers were also characterized by ¹H NMR, EA, GPC and CV. The results indicated that the copolymers were formed by blocks of PPV and DCN-PPV and that the DCN-PPV blocks are obtained in the conjugated form due to the high velocity of the elimination process in the units linked to the CN groups.

The uses of PPVs type polymer like emitting layer in light emitting diodes (LEDs) have attracted a lot of attention through the last ten years. This interest resulted in a development of commercial projects by important companies, just like DuPont, Kodak, Philips and others^[1,2]. Despite this technological development, some difficulties on the positive and negative charge injection on PPV-type polymers were yet founded. Problems like that have stimulated the searching for materials with appropriate injection and conductive properties. For these reasons PPV-like polymers with CN moieties connected to the backbone is justified by the diminishment of the electron injection barrier and by the improvement in the electron mobility in the polymer matrix. Nevertheless the syntheses of this kind of materials, principally for that with the CN group linked to the aromatic ring are complicated and, frequently, the obtained polymer showed bad mechanical properties^[3]. Facing these difficulties, the objective of this work is to study the influence of the CN moieties on the kinetics of the polymerization process of PPV-like polymers. The polymers were prepared following a modified Wessling methodology and it was obtained a series of copolymers with different ratios of PPV and a PPV-like polymer with CN groups attached to the position 2,5 on aromatic ring (DCN-PPV).

The formation of the copolymers was performed in a 1:1 water/acetonitrile mixture where four different DCN-PPV:PPV monomer ratios were dissolved: 1:9, 3:7, 5:5 and 7:3 (w:w). The polymerization was achieved with slow addition of ca. 8,5 mmol of NaOH into the reaction mixture. After that, the solution was neutralized and the polymer was purified using a dialysis membrane with 14,000 – 16,000 DA molecular weight cut off. It was obtained a light orange solution for the 1:9 DCN-PPV:PPV mixture that was turned to dark orange for 7:3 DCN-PPV:PPV monomer ratio. The kinetics aspects of the thermal conversion of the polyelectrolyte into the conjugated polymer was studied by UV-Vis, Fluorescence and FTIR spectroscopic measurements of the materials submitted to different thermal treatments. The obtained copolymers were also characterized by ¹H NMR, elemental analysis (EA), gel permeation chromatography (GPC) and cyclic voltammetry (CV).

The spectroscopic results obtained for the materials submitted to thermal conversion in different temperatures indicated that, even in low temperatures (60 °C and 100 °C), the copolymers presented a higher conjugation degree and that this conjugation degree increased for higher DCN-PPV proportions. This observation is consistent with the fact that the polyelectrolyte solution obtained in the polymerization process presented a light orange color for the 1:9 DCN-PPV:PPV ratio and a dark orange color for 7:3 DCN-PPV:PPV monomeric ratio. This fact was assigned to a fast elimination process for the monomeric unit linked to the CN moieties. The FTIR, UV-vis, EA, GPC and CV characterizations results showed that the copolymers films presented a low conjugation defects degree, a high molecular mass and a ratio of PPV and DCN-PPV unit proportional to the monomeric ratio used in the polymerization process.

References

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