



Synthesis and characterization of new materials derived from 4-methoxy-aniline

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Abstract – Development of novel functionalized polymers are important for many applications as biosensors construction and catalysis. The monomer 4-methoxy-aniline, despite the few references in literature, is a candidate for this purpose. Electropolymerization of 4-methoxy-aniline was performed in acid (pH 0.1) and basic (pH 12.0) media. The polymer was extracted, dried and analyzed through Fluorescence spectroscopy and FT-IR. The polymer prepared in acid medium presented fluorescence intensity due to electronic delocalization pointing a great number of segments combined of the material. The FT-IR studies indicate presence of bands related to secondary aromatic amines, suggesting that the mechanism of electropolymerization is similar to the aniline.

The use of electrodes modified with polymers for sensors applications is well known [1-3]. The substrate acts as link to biological components through the chemical groups on the modified electrode surface. The monomer 4-methoxy-aniline (4MA) is an aniline derivative. The presences of amine and methoxy groups ease the electropolymerization process. Despite the few papers in literature [4,5], poly(4MA) can be formed. The spectroscopic characterization may give us information about the structure of the formed film and the direct use as substrate for biological sensors.

The electropolymerization was performed in graphite bar as work electrode and as auxiliary electrode. The potentials are referred to an Ag/AgCl (KCl 3mol.L⁻¹) electrode. Aqueous solution of sulphuric acid was the supporting electrolyte and the solution pH was adjusted with an aqueous solution of sodium hydroxide. Cyclic voltammetry was performed in a potentiostat of the CH Instruments model 420A. The polymers were prepared in pH 0.1 (+0.20 and +0.90V), and pH 12.0 (-0.40 and +0.48V). The difference in the potential range comes from the difference in the protonation of the amino groups at acid media and deprotonation at basic media, easing the electronic transference in the structure and decreasing its oxidation potential. Therefore it is expected different materials over the electrode surface.

An extraction process with acetonitrile was performed after the polymerization. The materials were analyzed using FT-IR spectrophotometer Shimadzu, model Prestige 21 and Fluorescence Spectrophotometer Hitachi, model F-4500. The IR spectrum, from the monomer, showed differences with the two polymers mainly in respect with the vibrations of the nitrogen atom. The typical two bands related to the N-H asymmetric and symmetric stretchings at 3421 and 3346 cm⁻¹ and a low intensity harmonic at 3224 cm⁻¹ of primary aromatic amines disappear giving rise to one single band at 3447 (polymer prepared in acid medium) and 3436 cm⁻¹ (polymer prepared in basic medium) related to secondary aromatic amines.

A great difference between the polymers comes from the UV-visible and fluorescence data. The monomer presents two electron donators auxochromic groups and the UV-visible spectra shows three well-defined bands (202, 240 and 307nm). In the poly(4MA) prepared in acid medium is observed a hipsochromic shift of those bands and the appearance of more three bands with the broader one ranging from 450 to 608nm related to an important electronic delocalization, pointing a great number of segments combined of the polymer. However, for the poly(4MA) prepared in basic medium, is observed a bathochromic shift and no additional bands but a broadening of the last one ranging from 366 to 402nm and with low intensity, suggesting lower electronic conjugation.

The fluorescence spectra confirmed these observations. The monomer presents two excitation bands, but they are related to one species whereas the emission spectra showed only one band at the same wavelength. The poly(4MA) prepared in acid medium presents one band of fluorescence, but the polymer prepared in basic medium not presented any. This result is in accordance with the data from the UV-Visible spectra, related to the conjugation of the materials. These results suggest that the polymerization could be similar of the aniline, with the first attack going through the nitrogen atom.

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