

On the Electrochemical and Spectroscopic Properties of a Soluble Polyaniline Parent Copolymer

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In common with other conjugated polymers, polyaniline is limited by poor thermal processability and solvent solubility, due to the stiffness of its backbone. Consequently, their post-synthesis processability is quite difficult, and a lot of work has been done recently to overcome this problem.

Improved solubility can be achieved by introducing bulky alkyl substituents into the polyaniline backbone, but limitations are then imposed on the conductivity of the polymer produced. The conductivity of polyaniline and the solubility of substituted polyanilines can be achieved by copolymerization. These copolymers of aniline and substituted anilines show improved solvent solubility, while maintaining high electrical conductivity which can be readily tailored by varying the composition of the copolymer.

In this paper, we report the preparation, by chemical and electrochemical methods, of some soluble copolymers of aniline and 2-ethylaniline.

Polyaniline (PANI), poly(2-ethylaniline) and poly(aniline-co-2-ethylaniline) films were electropolymerized onto Pt substrates by applying triangular potential sweeps (0.01Vs^{-1}) in the -0.25 to 0.75V (PANI films) and -0.25 to 0.85V (substituted PANI and copolymers) potential ranges. All potentials are referred to the Ag/AgCl electrode. The polymerization was carried out in a 0.5molL^{-1} monomer + 1molL^{-1} HCl electrolytic solution. In the case of the synthesis of the copolymers, the concentration of monomer was maintained constant and the proportion in moles of 2-ethylaniline/aniline was varied in the following form: 1:9, 3:7, 5:5, 7:3, and 9:1. The amount of electrodeposited material was controlled through the electrochemical charge passed, all films being grown until $4 \cdot 10^{-3} \text{Ccm}^{-2}$.

It was determined by ^1H NMR measurements and the molar fraction of 2-ethylaniline was calculated from the ratio of integrated area of the methylated protons and aromatic ones. By this way, it was found that the reactivity ratio, that is to say the ability of the monomer to enter to the copolymer chain, is higher in 2-ethylaniline than in aniline. So that, the molar composition of the copolymer is very different from that of the precursor solution. Specifically, in the case of poly(aniline-co-2-ethylaniline), it was found that when the amount of 2-ethylaniline in the feed solution (f_1) was greater than 40%, the composition of the copolymer is almost 100% poly(2-ethylaniline). Figure 1 shows the peak potential values (E_p) of both, the first and the second, oxidation peaks for copolymers cycled in *p*-toluene sulfonic acid electrolytic solution. As it can be seen, the increase of the first potential peak and the decrease of the second one, is gradual when f_1 varies from 0.0 to 0.4. From this point till $f_1 = 1.0$, the difference between the redox processes (ΔE_p) remains constant, indicating that the material is almost the same in all this range of feed solution composition. So, copolymers formed by electrochemical methods give the same behavior of those prepared by oxidative polymerization.

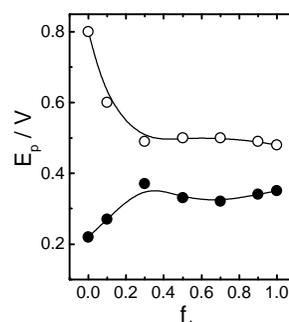


Figure 1: Peak potential as a function of the composition of feed solution (f_1). (●) leucoemeraldine/emeraldine redox couple and (○) emeraldine/permanganiline redox couple. Electrolytic solution 1molL^{-1} PTSA.

As it was mentioned above, the combination of good processability and high conductivity of these materials is the main goal of the synthesis and characterization of copolymers. Figure 2 shows the conductivity of the different homopolymers and copolymers measured by the two points method. As it can be seen from the figure, the conductivities vary in a range from 10Scm^{-1} (pure PANI) to $1 \cdot 10^{-3} \text{Scm}^{-1}$ (pure poly(2-ethylaniline)). It is very important to point out that the greater variation occurs in the range of $f_1 = 0.0$ to 0.3, in good agreement with the fact that the greater variation of copolymer composition takes place in this specific range. Another important feature regarding these results, it is the increase of the conductivity of the material in one order of magnitude by the addition of a small proportion of aniline units in the polymeric chains. Higher amounts of aniline will not change the conductivity until a proportion of 70% in the feed solution is reached.

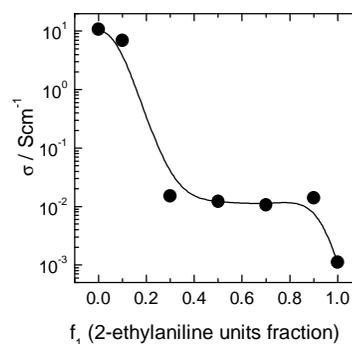


Figure 2

By electrochemical methods and Raman spectroscopy we have observed that the composition of the copolymeric chain differs from the precursor solution; copolymers formed from precursor solutions containing less than 30% (in moles) of 2-ethylaniline show intermediate properties between those of the homopolymers, and these properties vary gradually with the amount of 2-ethylaniline units in the copolymeric chain. This is an evidence of the formation of a new material, and not only a mixture of homopolymers. Those materials can be used for technological applications, due to some of their interesting properties: good conductivity, electrochromism, and solubility in some solvents, those properties are also reported in this paper.

Acknowledgements: Brazilian agencies CNPq and FAPESP (Proc. N° 98/7624-8) are gratefully acknowledged for financial support. A. L. S and L. M. L thank FAPESP (Proc. N° 98/14944-9) and CNPq respectively, for fellowships granted.