Spectroelectrochemistry of pyrrole oligomers in the presence of acrylamide

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Abstract: Soluble pyrrole oligomers were characterized during electropolymerization of pyrrole in the presence of acrylamide (in acetonitrile) which stabilizes radical cations of pyrrole allowing the reaction to be followed by spectroscopic and spectroelectrochemical means. The role of the applied electrical conditions and the effect of the presence of pyrrole oligomers on the formation of pyrrole oligomers in solution, and on the resulting polymer on an electrode surface (both Pt and indium tin oxide), were investigated. The soluble and insoluble products were characterized using UV-visible and FTIR spectroscopy, cyclic voltammetry and a four-point probe technique. Polypyrrole and poly(pyrrole-acrylamide) free-standing films had conductivity values of about 90 and 1 S cm⁻¹, respectively. Spectroscopic, cyclovoltammetric and conductivity results support the incorporation of acrylamide into intermediate species that may have useful application in industry. © 2002 Society of Chemical Industry

Keywords: pyrrole oligomers; polypyrrole; acrylamide; copolymer; spectroelectrochemistry

INTRODUCTION
Polypyrrole (PPy) is one of the most widely studied conducting polymers due to its ease of synthesis, stability in the oxidized form and electrical and optical properties useful for technological applications. Many reports have explored the effect of oxidation conditions, such as solvent, electrolyte, additives, functional substituents and electrode potential, on the properties of the polymer. One of the problems encountered is that conducting polymers are difficult to dissolve in any solvent because of their delocalized π electronic and crosslinked structures, which have the same molecular characteristics that give rise to the properties necessary for practical applications. To overcome the solubility problem of PPy, pyrrole has been polymerized oxidatively in the presence of anionic polymers using various oxidizing agents. However, another avenue of research is observation and characterization of the soluble intermediates during the polymerization of pyrrole. Because the soluble intermediates will help us to understand the polymerization mechanism of pyrrole due to their ease of characterization by electrochemical and spectroscopic means, a series of oligomers from bipyrrrole to heptapyrrole was prepared and studied in acetonitrile.

Electropolymerization involves many experimental variables, such as solvent, monomer concentration, electrolyte type, temperature, electrode materials and applied electrical conditions. The polymers are deposited under potentiostatic or galvanostatic conditions or by cyclic potential sweeps. The electrical conditions applied affect both the structure and properties of electrogendated PPy films and the rate of polymer production. For example, a decrease in oxidation potential produces an increase in conductivity correlated with a bathochromic shift of the absorption maximum of the polymer, indicative of an extension of conjugation (less crosslinking), longer chain length and fewer structural defects. High monomer concentrations are generally used to avoid competitive reactions of radical cations or of the oxidized polymer with nucleophiles in the medium, but this parameter generally depends on the oxidation potential of the monomer. If the monomer is easily oxidized like pyrrole, the competition of parasitic reactions is less important so that even millimolar concentrations may be used for efficient polymerization. In our previous study, we reported the effect of the presence of a co-monomer, acrylamide at high concentrations, on the polymerization of pyrrole, and the presence of acrylamide at high concentrations which led to stable oligopyrrole intermediates in the solution during the polymerization reaction of pyrrole. In the light of this approach, in this study, we report effects of the presence of acrylamide on both the formation of the soluble pyrrole oligomers in the electrolyte solution and on the insoluble polymer on the electrode surface, and possible interactions between the oligomers and acrylamides, depending on the applied electrical conditions.

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