Spectroelectrochemical study of *N*-ethylcarbazole in the presence of acrylamide

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Abstract: Polymerization of *N*-ethylcarbazole (NECz) in the presence of acrylamide (AAm) has been investigated by *in situ* and *ex situ* UV–visible spectrophotometric measurements to obtain information about the reaction pathway, because NECz gives soluble oligomeric species allowing such measurements. A tentative mechanism is proposed in the light of these results. The redox properties of the new polymers have been studied for possible sensor application.

Keywords: *N*-ethylcarbazole; acrylamide; *in situ* spectroelectrochemical measurements

INTRODUCTION

N-Carbazole (NCz) is a prototypical organic molecule that has shown potential for technological applications. Polymers based on this molecule display good electro- and photoactive properties because of their high hole transporting mobility and strong absorption in the UV spectral region. The formation of this polymer is of interest in understanding charge transport, because it is highly π-conjugated compared to other known polymers.[1–3] At the same time, polycarbazole (PCz) derivatives have received attention in the study of polymer-modified electrodes.[4] The ability of these polymers to form coherent films depends greatly on the nature of the substituents. It is found that some substituents such as *N*-ethyl and *N*-phenyl do not allow the production of films in acetonitrile, whilst film formation is possible in $HClO_4$.[5]

The synthesis and modification of carbazole-based polymers to obtain polymers exhibiting outstanding and interesting thermal, electrical, photoelectrical, ion exchange and other physicochemical properties have been reviewed.[6,7] However, PCz has poor processing properties,[8] which need to be improved for practical applications.

In our previous studies,[9,10] conducting polymers such as PCz and polypyrrole (PPy) have been prepared in the presence of AAm to overcome their poor processability. Further studies on these copolymers showed that their use as thin films gives promising properties for electrodes, sensors and corrosion inhibition applications.[11] However, some points concerning the polymerization mechanism needs to be clarified. In this study, NECz was selected because it enables us to make model systems to explain the polymerization mechanism of AAm with NCz or NECz. *In situ* spectroelectrochemical measurements provide us with more details of the polymerization mechanism of carbazole derivatives in the presence of AAm. NECz was chosen to obtain soluble oligomers during polymerization. In the light of our previous studies, the redox properties of the newly prepared electrodes were also studied for possible sensor applications.

EXPERIMENTAL

Materials

N-Ethylcarbazole (NECz, Aldrich), acrylamide (AAm, Merck), tetraethylammonium perchlorate (TEAP, Fluka), acetonitrile (ACN, Carlo Erba, HPLC grade) and perchloric acid ($HClO_4$, Aldrich) were of reagent grade and used without further purification.

Instrumentation

Electrochemical measurements were carried out using a Wenking POS 73 potentiostat connected with a Kipp and Zonen X–Y recorder. FTIR spectra were recorded using a Mattson 1000 spectrophotometer and KBr pellets. UV–visible spectra measurements were performed with a Shimadzu 160 A recording spectrophotometer, which was also connected for spectroelectrochemical measurements.

Preparation of *N*-ethylcarbazole–acrylamide copolymers

The reaction media for the preparation of NECz–AAm copolymers was ACN. To compare *ex situ* FTIR measurements of the homopolymer and copolymer under the same conditions, it was necessary to use a mixture of solvents consisting of 50 vol% ACN and 50 vol% $HClO_4$ because NECz does not homopoly-

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