



Preparation and characterization of “clickable” polyaniline derivatives on graphene modified electrodes

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ABSTRACT

The electrochemical polymerization of 2- and 3-ethynylaniline and copolymers with aniline was investigated. It is found that 3-ethynylaniline is more reactive than 2-ethynylaniline and, in the presence of aniline it electropolymerizes. The effect of the electrode material on the electropolymerization of 3-ethynylaniline and its copolymers with aniline was studied and graphene-modified electrodes show very good performance for the formation of a PANI-like polymer, as demonstrated by FTIR and Raman measurements. The graphene layer thickness also appears to influence the polymerization, the best results obtained for the thinnest films used. Finally, copolymers of aniline and 3-ethynylaniline were chemically prepared at room temperature. These copolymers display PANI-like structure with alkyne grafted groups and showed good electrochemical response, slightly different to that of the parent PANI with lower electrical conductivity. Preliminary tests indicate that the PANI derivative can be successfully clicked to poly(ethylene glycol) by a thiol-yne click reaction.

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1. Introduction

Polyaniline (PANI) is one of the most important conducting polymers and has been intensively studied over the last three decades due to its easy preparation, good environmental stability, interesting redox properties and good electrical conductivity in its doped form, making it a great candidate for applications in several areas [1–6]. Nowadays, most of the aspects concerning the basic science behind PANI are well known and research is currently aimed towards the improvement of the performance of PANI-like materials for specific applications, either with PANI derivatives or hybrids with other high-performance materials like carbon nanotubes or graphene [7]. However, due to low processability, for most applications PANI must be modified with different functionalities [8–10]. This has been attempted by post-modification reactions [11,12], homopolymerization of derivatives of aniline and their copolymerization with aniline [13–16].

Generally, the synthesis of derivatives of PANI has been performed with the aim to furnish PANI with specific groups directed to a given application, and limited to sulfonic/carboxylic acid to prepare self-doped PANI [15–17], alkyl [18,19], and alkoxy [20–22], among others. However, a derivative of PANI that permits its functionalization with a wide variety of groups in a simple reaction is still to be discovered. In other words a method that allows a general modification of PANI has never

been proposed. A potentially interesting PANI derivative allowing functionalization of the polymer with a wide range of functionalities would be one with grafted alkyne groups. These moieties are very active and widely employed in general reactions known as “click chemistry”.

Click chemistry encompasses a series of coupling reactions whose principal characteristics are, among others, that they are wide in scope and easy to perform, use only readily available reagents, are insensitive to oxygen and water and are orthogonal to functional groups other than the involved in the click reaction [23–27]. In particular, of this type of reaction the copper catalyzed azide–alkyne cycloaddition (CuAAC) has been the most widely employed to date [23–25]. And comprises the stoichiometric coupling of one alkyne moiety with an azide group in the presence of Cu(I). Other useful click reactions involve the coupling of thiol radicals to unsaturated bonds, like alkenes (thiol-ene) or alkynes (thiol-yne). Therefore, providing PANI with alkyne groups will greatly increase the number of PANI-based materials that can be prepared, some of them not achievable otherwise.

In this paper I study the preparation a PANI derivative having pendant alkyne groups by means of polymerization of ethynylaniline isomers and copolymerization with aniline. I explore different parameters including the ethynylaniline isomer employed, the type of polymerization (chemical or electrochemical) and the electrode material. Alkyne moieties can react with many molecules with a wide range of functional groups that would improve the possibilities of applications of PANI in sensing target compounds. In this work, in a preliminary demonstration of the strategy, PANI with grafted alkynes is clicked to poly(ethylene glycol) by a thiol-yne click reaction.

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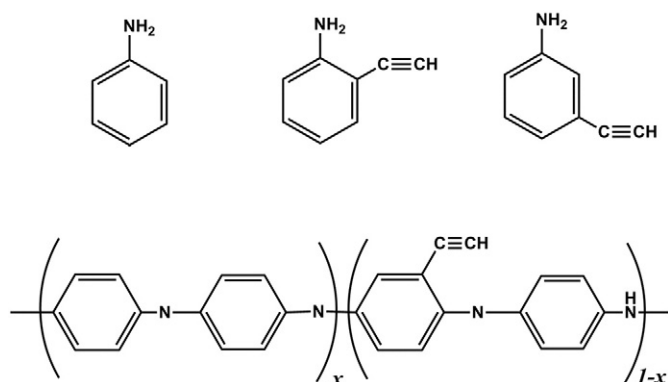


Fig. 1. Chemical structures of the monomers used in this study and the copolymer of ethynylaniline isomers with aniline.

2. Experimental part

2.1. Electrochemical synthesis

All electropolymerization reactions were conducted in a $\mu\text{Stat}400$ potentiostat from Dropsens. The polymers were prepared in 1 M HCl solutions using screen printed electrodes consisting of a carbon or Pt working electrode, a silver reference electrode and high area carbon counter-electrode. The anodic potential employed was varied from 0.8 V to 1.2 with the aim to obtain a stable solid on the working electrode surface. A scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$ was employed in all cases. In the case of graphene modified electrodes, the working Pt electrodes were modified by drop-casting specific amounts of graphene from dispersions in 1-methyl-2-pyrrolidone (NMP). Briefly, a graphite working electrode was intercalated by double potential step experiments in a conventional one- three-electrode electrochemical cell, where a normal

hydrogen electrode (NHE) was employed as the reference electrode (RE), and a piece of large surface area carbon served as the counter electrode (CE). A potential of 0 V was initially applied for 10 s, so it may be assumed that at zero time no faradaic reactions took place on the surface of the electrode. A perturbation potential of -1 V was then imposed for 20 min. The intercalated graphite electrode was treated for 5–10 s at a nominal power of 800 W under argon atmosphere, producing expanded graphite. Finally, graphene dispersions of around $0.8 \text{ mg} \cdot \text{mL}^{-1}$ were prepared by treatment of the expanded graphite in NMP with an ultrasonic probe for 5 min. Subsequently, specific amounts of graphene were drop-cast onto the working Pt screen printed electrodes.

2.2. Chemical polymerization

PANI and copolymers with 3-ethynylaniline (3Ethy) were prepared by the following procedure: ammonium peroxodisulfate (0.11 mol) was added to 100 mL of aniline (ANI) solution (0.1 M) in 1 M HCl at room temperature. The polymerization was conducted over 3 h at room temperature and the solid polymers were filtered and washed with abundant 1 M HCl and water. In the case of copolymerizations, the feed ratios ANI/3Ethy were 10/90 and 50/50.

2.3. Thiol-yne click reaction

For the click reaction of PANI-3Ethy with poly(ethylene glycol) dithiol (PEG2SH, Aldrich $M_n = 8000 \text{ g} \cdot \text{mol}^{-1}$), 200 mg of the PANI derivative were dispersed in 50 mL of NMP. Subsequently, 650 mg (0.08 mmol) of PEG2SH was added and treated with ultrasound. Finally 200 mg (1.15 mmol) of the radical initiator, azobisisobutyronitrile (AIBN) was incorporated and the mixture maintained overnight under nitrogen atmosphere at 70°C with magnetic stirring. The solid product

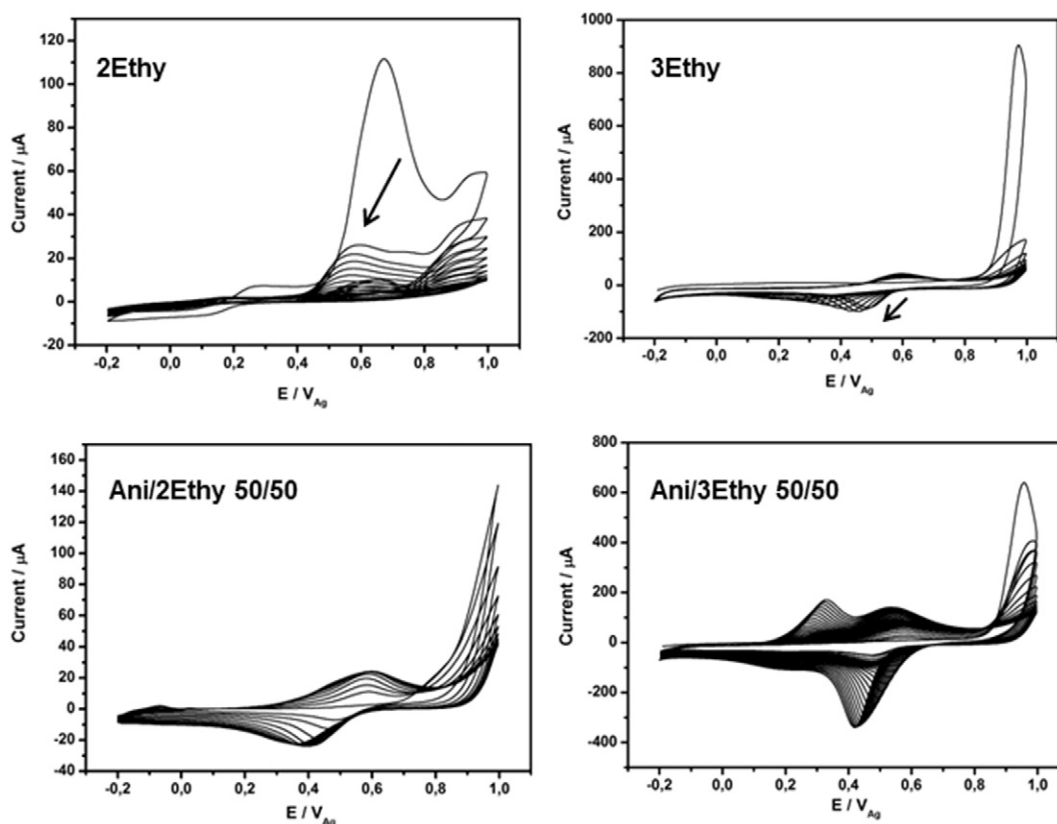


Fig. 2. Cyclic voltammograms of the oxidation of 2Ethy and 3Ethy and their mixtures with aniline in a 50/50 feed ratio, in 1 M HCl. Scan rate = $100 \text{ mV} \cdot \text{s}^{-1}$.

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