Towards carboxylic acid-functionalized aniline monomers: Chemical synthesis, electropolymerization and characterization

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A B S T R A C T

Polyaniline is one of the most studied conducting polymers because of its high stability and interesting combination of redox and proton doping properties. Moreover, it is possible to use the amino group of polyaniline to graft a substituent to obtain polyaniline derivatives. In the present study, aniline monomers were functionalized by an alkyl chain terminated by a carboxyl group at the N-position of the monomers in an attempt to obtain a series of carboxylic acid-functionalized polyanilines. The electro-oxidation of the modified aniline monomers was studied in HCl and H_3PO_4 acidic solutions with potentiodynamic and potentiostatic methods. The influence of the nature of the solvent and the length of the grafted alkyl chain on the thickness, morphological features and wettability of the carboxyl-functionalized polyaniline films was studied. In particular, the nature of the acid used strongly impacted the film properties leading to thinner, smoother, more hydrophilic, more adhesive and more homogeneous films when the electropolymerization was performed in phosphoric acid solutions.

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1. Introduction

Conducting polymers are a class of materials that have raised much interest because of their unique electronic, chemical and biochemical properties, making them suitable for numerous applications. Due to its simple synthesis, environmental stability, high degree of processability, simple acid-base doping-dedoping [1,2], and unique redox tunability [3,4] associated with its chain heteroatom, polyaniline (PANI) has been one of the most extensively studied electroactive conductive polymers during the last decades. Thus, polyaniline has demonstrated enhanced performance in applications such as corrosion protection [5,6], energy storage [7,8], electrochromic devices [9,10], (bio)sensors [11,12] or tissue engineering [13]. In particular, polyaniline is frequently used for biomedical applications or biosensing since its amino groups can be subjected to covalent immobilization because amide linkages are formed by the condensation reaction of the amino groups with carboxyl groups of the biochemical species (cells, enzymes, proteins) [11].

Polyaniline derivatives can also be prepared to improve or tune the chemical properties of polyaniline. Thus, several synthesis strategies have been used to obtain various polyaniline derivatives,

the main strategy consisting in the substitution of one or more hydrogen by an alkyl [14,15], an alkoxy [16,17], an acyl [18], or a sulfo group [19–21]. So, in this work, the grafting of an alkyl chain terminated by a carboxyl group on the N-position of the aniline monomers was performed in an attempt to significantly modify some properties (wettability, adhesion, morphology, roughness) of aniline monomers and keep the possibility of forming amide linkages using the carboxyl group. Then, the polymerization of the functionnalized aniline monomers was performed. The substituted polyanilines synthesized in this work contain carboxyl groups which can lead to the formation of amide linkages by the condensation reaction of the carboxyl groups with amino groups of chemical or biological species. This is an advantage with the aim of developing materials that could fix biological molecules such as proteins or biological cells, and with the aim of developing original sensors using substituted polyanilines as sensitive layers that could fix chemical analytes such as amines or enzymes.

The polymerization of aniline monomers into polyaniline films can be obtained by chemical oxidative reaction of aniline [22,23], electrochemical polymerization of aniline [1,2], or electroless autocatalytic oxidation of aniline [24,25]. However, electrochemistry is used here since the electrosynthesis of polyaniline provides several advantages such as easy polymerization processes together with a better control of film thickness and morphologies, as compared with other polymerization methods. So, the present study aimed at synthesizing a series of carboxylic acid-functionalized aniline
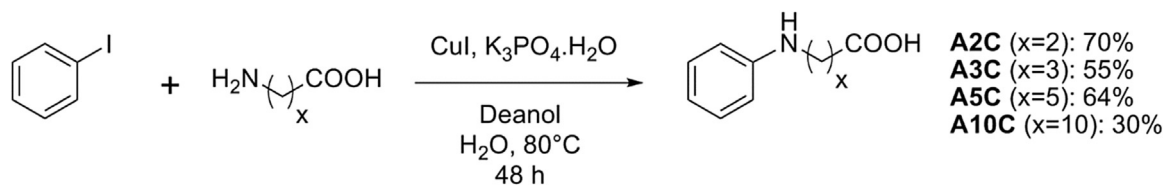
Fig. 1. Synthetic pathways towards monomers **A2C**, **A3C**, **A5C** and **A10C**.

monomers. Then, the solubilization and the electro-oxidation of the synthesized N-substituted anilines were studied in HCl and H_3PO_4 acidic solutions. In particular, the influence of the grafted alkyl chain length on the potentiodynamic and potentiostatic deposition, thickness, morphological features and wettability of the polymer films were investigated.

2. Experimental

2.1. Reagents

Analytical grade aniline was freshly distilled under reduced pressure and stored in the dark at low temperature (4 °C). Double deionized water (Milli-Q, resistivity 18 MΩ cm) and analytical grade hydrochloric acid and phosphoric acid were used to prepare the electrolyte solutions. All reagents were purchased from Acros and used as received.

2.2. Synthesis

Flash chromatography was carried out onto a Teledyne Isco Lumen Rf+ apparatus using silica gel column (80 g of adsorbent) and hexane/ethyl acetate mixtures. N-Phenylglycine (**A1C**) is commercially available. N-phenyl-3-aminopropanoic acid (**A2C**), N-phenyl-4-aminobutyric acid (**A3C**), N-phenyl-6-aminohexanoic acid (**A5C**) and N-phenyl-11-aminoundecanoic acid (**A10C**) were prepared according to the following general procedure [26]: to a mixture of iodobenzene (8.20 g; 40 mmol; 1 Eq.) and water (40 mL) were successively added the desired aminoacid (60 mmol; 1.5 Eq.), potassium phosphate monohydrate (18.41 g; 80 mmol; 2 Eq.) copper (I) iodide (0.76 g; 4 mmol; 0.1 Eq.) and N,N-dimethylethanolamine (12 mL). The reaction mixture was stirred at 80 °C for 48 h. After cooling to room temperature, the solution was poured onto crushed ice (250 g) and the pH adjusted to 5 by the dropwise addition of concentrated HCl. The aqueous layer was extracted with ethyl acetate (4 × 150 mL). Organic layers were combined, washed with brine (150 mL), dried over sodium sulphate and concentrated. The crude products were purified by flash chromatography. Their physical and spectral properties were in identical with those reported in the literature [26,27].

2.3. Electrochemistry

All electrochemical experiments were performed at room temperature with a VersaSTAT MC potentiostat/galvanostat from Princeton Applied Research. These experiments were done using a three-electrode setup with a Saturated Calomel Electrode (SCE) as reference electrode, a platinum sheet as counter-electrode, and either a platinum wire (area: 0.785 mm²) or a Fluorine doped Tin Oxide (FTO) substrate (R = 80 Ω/square) as working electrode. The platinum wire was used to perform electropolymerization of the synthesized monomers in HCl (1.2 mol L⁻¹) or H_3PO_4 (2 mol L⁻¹) aqueous solutions using cyclic voltammetry technique (5 potential scans were done at 50 mV s⁻¹). The FTO substrates (1.5 cm × 3.0 cm) were used to perform electropolymerization of the synthesized

monomers using chronoamperometry. Resulting coatings were used to perform the characterization of the electrodeposited polymer films.

2.4. Profilometry

Thickness and roughness of polymer films were estimated by profilometric measurements using a stylus-based mechanical probe profiler (Alpha-Step IQ, KLA Tencor). To determine the thickness of the samples, the films were scratched with plastic micropipet tips. Then, the stylus was moved perpendicularly to the scratch to obtain the height of the step corresponding to the thickness of the sample. To determine the average roughness (R_a) of the samples, the stylus was moved perpendicularly to the coating on a scan length of 4000 μm at a scan speed of 100 μm s⁻¹. For each electrodeposited film, 5 measurements were done at different positions of the coating. The average thickness and roughness values were calculated using these 5 measurements.

2.5. SEM

The morphological features of the polymer films were examined by high-resolution scanning electron microscope (SEM). Once electrodeposited and dried, the conductive polymer coatings were studied, without previous metallization, in a SEM Quanta 450 W from FEI with an electron beam energy varying from 10 to 25 keV.

2.6. AFM

The imaging of the surface topographies was performed, with a commercial atomic force microscope (AFM PicoSPM from Molecular Imaging, USA), in contact mode with gold-coated pyrex nitride probes. Pyrex-nitride probes (PNP TR probes, from Nano World) had silicon nitride triangular cantilevers (100 μm long) with low force constant (0.32 N m⁻¹) and integrated oxide sharpened, pyramidal tips with a height of 3.5 μm. The typical tip radius of curvature was below 10 nm. The experiments were done at the air and at room temperature.

2.7. Wettability

To examine the surface energy of the polymer films, water contact angles were measured using a contact angle analyzer (Digidrop, from GBX). The instrument is equipped with a CCD camera, a sample stage and a syringe holder. A 5 μL drop of ultrapure water was formed at the tip of a syringe needle and placed onto the sample surface by raising the sample until a contact was made. Then, an image of the drop was captured, and contact angles were determined by drawing the tangent close to the edge of the droplet. At least five drops were deposited on each electrodeposited film. The results were averaged over the five measurements.