# Theoretical and experimental studies on the electronic, optical, and structural properties of poly-pyrrole-2-carboxylic acid films

Mauricio Foschini [a], Hugo Santos Silva [a], Raigna A. Silva [a], Alexandre Marletta [a,b], Débora Gonçalves [b,*]

[a] Instituto de Física, Universidade Federal de Uberlândia, Av. João Naves de Ávila, Postcode 593, Uberlândia, MG 38400-902, Brazil
[b] Instituto de Física de São Carlos, Universidade de São Paulo, Av. Trabalhador São-carlense 400, Postcode 369, São Carlos, SP 13560-970, Brazil

ABSTRACT

A theoretical approach is used here to explain experimental results obtained from the electrosynthesis of polypyrrole-2-carboxylic acid (PPY-2-COOH) films in nonaqueous medium. An analysis of the Fukui function (reactivity index) indicates that the monomer (pyrrole-2-carboxylic acid, PY-2-COOH), and dimers and trimers are oxidized in the C4 or C5 positions of the heterocyclic ring of the PY-2-COOH structure. After calculating the heat of formation using semiempirical Austin Model 1 post-Hartree–Fock parameterization for dimer species, both C4 and C5 positions adjacent to the aromatic rings of PPY-2-COOH were considered the most susceptible ones to oxidative coupling reactions. The ZINDO-S/CI semiempirical method was used to simulate the electronic transitions typically seen in the UV–VIS–NIR range in monomer and oligomers with different conjugation lengths. The use of an electrochemical quartz crystal microbalance provides sufficient information to propose a polymerization mechanism of PY-2-COOH based on molecular modeling and experimental results.

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## 1. Introduction

Conducting polymers such as polyaniline, polythiophene, and polypyrrole have been studied in recent years mainly because of a variety of applications found for these materials in energy storage devices, electrochromic displays, and sensors [1–3]. Polypyrrole (PPY) films, in particular when electrochemically prepared, have been used as relatively stable matrices for enzyme immobilization, yielding selective biosensors for environmental monitoring and analysis [4–6]. However, PPY/enzyme-based biosensors, such as PPY/glucose oxidase, are not economically competitive compared to traditional biosensors, due to their relatively low detection sensitivity ($10^{-4}$ to $10^{-2}$ mol L$^{-1}$) and short lifetimes (7–21 days) [3,7–10]. Alternatively, functionalized PPY films have been explored for use as biosensors with enhanced efficiency after immobilizing enzymes as bio-receptors [11,12].

Polypyrrole-2-carboxylic acid (PPY-2-COOH) has proved to be an electroactive material with interesting properties for using in amperometric biosensors [13]; however, its polymerization route has not been investigated systematically. We have experimentally demonstrated the influence of water, added intentionally to the solvent, acetonitrile, on the properties of PPY-2-COOH films produced by cyclic voltammetry [13]. However, even after these re-sults, topics such as the electropolymerization mechanism, electronic and structural properties, and degrees of conjugation of intermediate species formed after the oxidation of PY-2-COOH have so far not been addressed. In this study, we performed semi-empirical simulations to predict species formed in the early stages of PY-2-COOH oxidation. The reactivity of the monomer, PY-2-COOH, was estimated by calculating the Fukui reactivity indices of a set of neutral, anionic and cationic forms of monomer and dimer structures. Theoretical and experimental data are compared, aiming to come up with a proposal for the mechanism of formation of PPY-2-COOH.

## 2. Computational details

The geometrical structures of oligomers formed in the early stages of polymerization of PY-2-COOH were predicted by ab initio Density Functional Theory (DFT) using B3LYP level of theory calculations. The double-zeta basis set with the Orca 2.8 package was used to verify the various stages of the semiempirical method, beginning the routine only after verifying the structural parameters. The geometrical structures were obtained with the semiempirical Austin Model 1 (AM1) methodology, and optimized using the tight convergence criteria (root mean square, RMS, gradient $\leqslant 0.05$) in the Mopac2009 package. The heats of formation ($\Delta H$, kcal mol$^{-1}$) were calculated for isolated oligomers formed after oxidative coupling in different positions of the aromatic rings

* Corresponding author. Tel.: +55 16 33739825.
E-mail address: gdebora@if.sc.usp.br (D. Gonçalves).

of PY-2-COOH. When compared to DFT, semiempirical approach was preferentially chosen because it allowed us to take into account nonlocal, dispersion interactions. Restricted open-shell wave function formalism was considered for performing open-shell calculations and preventing spin-contamination. The external potential perturbations were calculated using the condensed Fukui function for different types of attacks: electrophilic (Eq. (3)), nucleophilic (Eq. (4)), and radical (Eq. (5)) [14].

$$f_k^- = [q_k(N) - q_k(N-1)] \qquad (1)$$

$$f_k^+ = [q_k(N+1) - q_k(N)] \qquad (2)$$

$$f_k^0 = \frac{f_k^+ + f_k^-}{2} \qquad (3)$$

where $f_k$ is the Fukui reactivity index, $q_k$ is the Mulliken charge for neutral ($N$), oxidized ($N+1$) or reduced ($N-1$) states, and $N$ is the number of electrons.

Unrestricted Hartree–Fock (UHF) calculations are often evaluated independently, for both spin-up and spin-down states, but this method usually modifies the values of Mulliken charges due to the effects of spin contamination [14]. In this case, the restricted open-shell Hartree–Fock (ROHF) method has become the most common choice to avoid these effects. Our previous investigations [14] indicated that the ROHF method can be employed to estimate active sites present in conjugated oligomers [11]. The electronic transitions for $n$-conjugated oligomers ($n \leqslant 18$) were calculated in the UV–VIS–NIR range of energy using the Zerner's Intermediate Neglect of Differential Overlap method, and spectroscopic parameterization configuration interaction (ZINDO-S/CI) [15] via ArgusLab program [16]. Lorentzian line-shapes (FWHM = 25 nm) were used to envelope individual transitions, thus allowing further comparison with experimental results from the absorbance curves.

## 3. Experimental

Pyrrole-2-carboxilic acid (PY-2-COOH) and tetramethylammonium tetrafluoroborate (TMABF$_4$) were dried under vacuum, and kept under vacuum when not in use.

PPY-2-COOH films were prepared by cyclic voltammetry using a PAR/EG&G 283 potentiostat/galvanostat from −0.2 to 1.6 V vs Ag/AgCl at a scan rate of 50 mV s$^{-1}$. Fluorine-tin-oxide (FTO) (13 Ω cm$^{-2}$) plates were used as the working electrodes. A solution containing 0.1 mol L$^{-1}$ PY-2-COOH and 0.1 mol L$^{-1}$ TMABF$_4$ in acetonitrile (ACN) was used for the electropolymerization procedures. ACN containing 32 ppm of water (labeled value) was dried under molecular sieves (4 Å) and then, treated at 300–400 °C during 4 h. PPY-2-COOH films were also prepared by chronoamperometry at fixed potential of 1.6 V at $t$ = 120 s using a Stanford electrochemical quartz-crystal microbalance (EQCM) (QCM200).

A homemade two-compartment Teflon cell was used for the EQCM measurements with Ag/AgCl as the reference electrode and a Pt plate (2 cm$^2$) as the counter electrode. In this case, the working electrode was a 5 MHz AT-cut quartz crystal substrate coated with polished Au layers on both sides.

UV–VIS–NIR spectra were recorded in situ using a Hitachi U-2001 spectrophotometer for the PPY-2-COOH films obtained on FTO substrates. A homemade three-compartment electrochemical parallel-face cell was used for these measurements in a monomer-free solution containing 0.1 mol L$^{-1}$ TMABF$_4$ in ACN, and by applying fixed potentials, which varied from −0.6 V to 0.8 V vs Ag/AgCl.

## 4. Results and discussion

The geometrical structures of dimer species possibly formed as intermediates after the electropolymerization of PY-2-COOH were optimized using semiempirical approaches, solved by validation with Density Functional Theory (DFT). The heats of formation, ΔH, were calculated for two heterocyclic rings bonded in the C5–C5, C5–C4, C5–C3, C4–C4, C4–C3, and C3–C3 positions, whose geometries were optimized (Table 1).

From the data in Table 1, it can be inferred that the most stable structures are the ones formed in the C5–C4 and C4–C4 positions of the heterocyclic ring of PY-2-COOH. For a realistic proposal of polymerization mechanism, it can be assumed that different isoenergetic structures can be obtained; however, C5–C4 seems to be the most probable position that can be formed to yield a polymer with a higher degree of conjugation. After increasing the number of heterocyclic structures coupled at the C4–C5–C4–C5 sites, and optimizing the geometries, a planar geometry can be predicted with a torsion angle of about 74° between adjacent planes. The C4 and C5 positions of the heterocyclic ring of PY-2-COOH (Fig. 1a) proved to be the most susceptible to oxidation, yielding the dimeric species illustrated in Fig. 1b. Fig. 1c depicts our proposed oligomeric structure of 16 conjugated rings formed after the oxidation of PY-2-COOH. The darker atoms in this figure indicate the most reactive sites in a relatively long oligomeric structure, with a dihedral angle of 51° between each pair of heterocyclic rings typically originated from a chemical defect, which can disrupt the conjugated backbone.

Note that the differences obtained in the values of ΔH could not be meaningfully compared when one takes into consideration the thermal energy and, therefore, translational and rotational degrees of freedom, which may increase these values. On the other hand, a preferential bonding in the C5–C4 sites is clearly evident from these values, and it can be confirmed by calculating the Fukui reactivity indices from Eqs. (1)–(3) (results shown in Table 2).

The energies involved in electronic transitions commonly found in aromatic compounds were calculated in the UV–VIS range using the configuration-interaction (CI) method. To determine the absorption intensities, the statistical weights of the electronic states were calculated by considering the oscillator strengths in each transition. The curves in Fig. 2 shows an intense band at 3.6–3.8 eV (344–326 nm) typically assigned to the HOMO → LUMO transition, and a band at 6.7–6.8 eV (185–182 nm), which shifts to lower energies as the degree of conjugation increases, disappearing completely after $n$ = 2. Above $n$ = 6, the main band seen in these spectra, at 3.6 eV, shifts to higher energies as a result of a torsion disorder for shorter oligomers with $n < 6$. The absorbance curves of oligomers with $n > 16$ exhibit two overlapping bands at 3.7 eV and 3.5 eV, which can be assigned to the in-plane and out-of-plane $\pi \to \pi^*$ transitions commonly seen in aromatic rings [17–19].

Fig. 3 shows the absorbance spectrum of a very thin PPY-2-COOH film, which was experimentally obtained after only one voltammetric cycle, aiming to generate well-defined bands in the absorbance spectrum. For purposes of comparison, Fig. 3 shows a

**Table 1**
Heat of formation, ΔH, of possible dimeric structures formed after the electropolymerization of PY-2-COOH.

| Dimeric structures (coupling positions) | ΔH (kcal/mol) |
| --- | --- |
| C5–C4 | −103.38 |
| C4–C4 | −103.29 |
| C5–C3 | −101.92 |
| C5–C5 | −101.32 |
| C4–C3 | −100.42 |
| C3–C3 | −52.28 |