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Synthesis and characterization of fluorescent nitrobenzoyl polythiophenes



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ABSTRACT

Two thiophene derivatives named 4"-nitrobenzoyl (thiophene-3'-yl)-1-ethylate (**NTh**) and 3",5"dinitrobenzoyl (thiophene-3'-yl)-1-ethylate (**DNTh**) were synthesized and characterized. Both monomers were electrochemically polymerized onto platinum or glassy carbon electrodes by potentiodynamic method in 0.1 mol L⁻¹ TBABF₄/CH₂Cl + boron trifluoride diethyl etherate (**BFEE**) (1:1, v/v). These monomers were also successfully polymerized by chemical oxidation using FeCl₃/CHCl₃. Spectroscopic and electrochemical properties of the monomers and polymers were investigated. Films of both polymers showed well-defined reversible redox system at the anodic branch (1.0 V vs. Ag/AgCl, KCl (sat.)), attributed to thiophene doping/dedoping process; and another redox process at the cathodic branch (**PNTh**) (or two redox processes for **PDNTh**) was attributed to the reduction of the 4-nitrobenzoyl or 3,5dinitrobenzoyl substituent groups. The THF solutions of monomers and polymers are fluorescent, with emission bands at λ_{max} = 488 nm (**NTh**), 511 nm (**DNTh**), 440 nm (**PNTh**) and 546 nm (**PDNTh**). The monomers are also fluorescent in the solid state.

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1. Introduction

The synthesis and characterization of novel π -conjugated polymers have attracted a great deal of interest, mainly because of their properties: electrical conductivity, electrochromism, electroluminescence, nonlinear optical characteristics and chemical sensing [1], which are useful for a wide range of applications, including electrochromic devices [2,3], organic light emitting diodes (OLEDs) [4], organic solar cells (OSCs) [5], organic field effect transistors (OFETs) [6], energy storage [7] and biosensors [8]. All these applications usually require the rational design and modification of the monomer structure. Therefore, the creative design and strategies to synthesize new derivatives of conjugated polymers can lead to materials with enhanced performance.

Some of the conjugated polymer properties are assigned to their ability on changing the electronic and spectral features, upon the modification of their chemical structure, *i.e.*, the tailoring of the band gap (E_g) of these polymers allows the shift of the absorption and emission wavelengths [9], or even in the electrochemical response [10]. Therefore, the properties can be adjusted by

modification of the monomer structure by attaching different functional groups, such as, electron-donating and/or electronwithdrawing, n-dopable, or fluorescent substituents [10-13]. For instance, the appendage of a nitro group on the monomer structure would make the resulting polymers amenable for use in sensors or electrochemical capacitors [14,15].

The presence of nitro groups in conjugated polymers may provide interesting applications: i) during the redox process of corresponding conjugated polymers, the nitro group can be reduced, ii) the NO₂ group can be reduced to NH₂ at less negative potential, and iii) the introduction of the nitro groups in the conjugated polymer structure can provide a post-functionalization approach, *e.g.*, reduction of NO₂ into NH₂ [16]. In addition, polymers bearing nitro groups have not been extensively investigated.

The presence of the electron-withdrawing nitro group in the monomer structure usually leads to a higher oxidation potential, culminating in poor polymer film quality or no electropolymerization [16–18]. The nitro group can stabilize the radical cation intermediates, allowing its diffusion away from the electrode that prevents the polymerization on the anode surface [19,20]. Therefore, its preparation still remains as a challenge.

Thiophene and pyrrole electropolymerizations has been largely studied, and follow the same reaction mechanism. The pyrrole



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oxidation potential (~1.2 V vs. Ag/AgCl) is lower than the thiophene oxidation potential (~1.6 V) that can reach 2.4 V, depending on the substituent group; thus, thiophene electropolymerization is very difficult to be carried out in aqueous medium. Polypyrrole is more susceptible to oxidation than polythiophene, leading to the carbonyl group formation at the position 3 and breakup of the conjugation. Polythiophene presents a better thermal stability than polypyrrole, and the conductivity of both polymers can vary (10^{-3} to 10^3 S cm⁻¹) according to the substituent, dopant and experimental conditions of electropolymerization [21,22]. Therefore, numerous applications can be associated to intrinsic characteristics and properties of these polymers.

A series of polypyrrole and polythiophene derivatives bearing nitro- and dinitro- substituents have been synthesized and characterized by our research group aiming their application in electrochromic devices (ECDs) [3,23–25], fluorescent layers [26] or as material for energy storage [14]. In an earlier study, Welzel et al. [19] synthesized two thiophene derivatives substituted with nitro- and dinitro- groups and tried to electropolymerize these derivatives under standard conditions (such as TBAP/CH₃CN), but they were not successful. According to their results, the high potential (up to 2.3 V vs. Ag/AgCl) necessary for the monomers oxidation caused an overoxidation process destroying the aromatic structure of the thiophene units.

The replacement of the usual organic media (CH₃CN) by a Lewis acid, such as boron trifluoride diethyl etherate (BFEE) is a good strategy to prepare good-quality conjugated polymer films bearing electron-withdrawing substituents [17,23]. BFEE solution has been widely used as catalyst to electropolymerize aromatic monomers. such as thiophene and its derivatives, selenophene and pyrene [27–29]. In the presence of BFEE, the monomer oxidation occurs at a lower potential, rather than in CH₃CN, by virtue of the interaction between the Lewis acid and the aromatic monomer [30]. It occurs because the strong electrophilic nature of BFEE catalyzes the deprotonation of aromatic compounds, decreasing the oxidation potential of such compounds [31,32]. In the specific case of thiophene derivatives, the formation of π -complexes with BFEE suppresses the resonance stability of the thiophene ring, thus facilitating the loss of electrons from the ring [33]. So the catalytic effect of BFEE enables the formation of high quality polymer films.

In the present work, we report a new synthetic route for the preparation of two thiophene derivatives bearing nitro- and dinitro- groups: 4"-nitrobenzoyl (thiophene-3'-yl)-1-ethylate (**NTh**) and 3",5"-dinitrobenzoyl (thiophene-3'-yl)-1-ethylate (**DNTh**), improving the previous route proposed by Welzel et al. [19]. Polymer films of **PNTh** and **PDNTh** were successfully electropolymerized by direct anodic oxidation of the monomers onto platinum or glassy carbon electrodes by using a mixed electrolyte containing $TBABF_4/CH_2Cl_2$ and BFEE (1:1, v/v). The electrochemical and spectroscopic properties of the monomers and polymers were investigated in details.

2. Experimental

2.1. Chemicals and equipments

Most chemicals and solvents were purchased and used without further purification. The solvents CH_3CN , $CHCl_3$ and CH_2Cl_2 were dried and then distilled before the use, the first two under P_2O_5 and the last one under CaH_2 [34]. The starting materials 3-(2'-Bromoethyl) thiophene and 3-(2'-Iodoethyl) thiophene were synthesized according to the previous literature [35]. The monomers **NTh** and **DNTh** were obtained as described below. BFEE was distilled and freshly used. Tetrabutylammonium tetrafluoroborate (TBABF₄) was dried under high vacuum at 100 °C for 3 h before use.

NMR spectra (¹H, ¹³C and Cosy NMR) were obtained in a Varian spectrometer (Unity Plus, 300 and 400 MHz) using CDCl₃ as solvent. Infrared spectra were registered using a Bruker FTIR (IFS66, 1% sample KBr pellets) and ATR Varian FTIR (640-IR, film electropolymerized on Pt foil) spectrometers. Melting points were determined on Electrothermal equipment (Mel-Temp, analogic mode). Elemental analyses were performed in a Carlo Erba (EA 1110) and a Perkin-Elmer (CHN 2400) equipment. Gas chromatograms were carried out in a Varian (CP-3380) $(30 \text{ m} \times 0.25 \text{ mm})$ \times 0.25 µm DB-5 capillary column) using a 60-200 °C temperature range $(10 \circ C \min^{-1})$. Gas chromatograms/mass spectra were carried out in a Shimadzu (GC/MS-QP5050A), using the same column and temperature ramp. UV-Vis spectra of the monomers and polymers, both solubilized in THF solvent, were carried out in a Perkin Elmer spectrophotometer (Lambda 650, double beam). Excitation and emission fluorescence spectra were recorded in a Shimadzu spectrofluorophotometer (RF-5301PC). All electrochemical experiments were carried out using an Autolab potentiostat/ galvanostat PGSTAT30 (NOVA software v.1.10).

2.2. Synthesis of the monomers

2.2.1. 4"-Nitrobenzoyl (thiophene-3'-yl)-1-ethylate - NTh

3-(2'-Iodoethyl) thiophene (0.712 g, 3.0 mmol), 4-nitrobenzoic acid (0.500 g, 3.0 mmol) and proton-sponge[®] (1.280 g, 6.0 mmol) were stirred for 5 hours in dry CH₃CN (10 mL) at 75 °C. In the first hour of reaction, a white solid precipitated (proton-sponge iodine). This solid was removed by filtration and rigorously washed with diethyl ether. The reaction solution was rotaevaporated for diethyl ether extraction, and the reaction was continued until its completeness to be confirmed by GC. The remaining proton-sponge iodine precipitate was filtrated and washed with ethyl ether. The resulting solution (orange color) was rotaevaporated and the crude product was extracted with 0.01 mol L⁻¹ HNO₃/ CHCl₃ (1:1) biphasic solution (2 × 50 mL, each extraction). The organic phase was dried with anhydrous Na₂SO₄ and rotaevaporated/



NTh: $R^1 = H$; $R^2 = NO_2$ **DNTh**: $R^1 = NO_2$; $R^2 = H$

hexane mixture (3:7), and precipitated at -10°C. The isolated product (Scheme 1) was recrystallized using the same procedure above, and dried under high vacuum for 3 hours.

Pale yellow solid, 60% yield (500 mg). M.p. 78-80 °C; ¹H NMR (300 MHz, CDCl₃) δ = 8.29 (d, *j* = 9.0 Hz, 2H, -ArH), 8.18 (d, *j* = 9.0 Hz, 2H, -ArH), 7.31 (dd, *J* = 4.9, 2.9 Hz, 1H, -ThH), 7.09 (ddd, *J* = 3.0, 1.4, 0.8 Hz, 1H, -ThH), 7.02 (dd, *J* = 4.9, 1.3 Hz, 1H, -ThH), 4.59 (t, *j* = 4.0 Hz, 2H, -CH₂), 3.14 (t, *j* = 6.0 Hz, 2H, -CH₂); ¹³C NMR (75 MHz, CDCl₃) δ = 164.6, 150.5, 137.5, 135.5, 130.7, 128.1, 125.9, 123.6, 121.8, 65.7, 29.5; IR (KBr) cm⁻¹: 3105, 3081, 2925, 2861, 1718, 1606, 1527, 1455, 1350, 1270, 1100, 1010, 951, 870, 834, 783, 717, 690, 630, 582 and 505; Anal. calcd. for C₁₃H₁₁NO₄S (%) (277.3005 g mol⁻¹): C, 56.31; H, 4.00; N, 5.05; S 11.56. Found: C, 56.19; H, 3.92; N, 4.97; S, 10.98. MS, *m/z* (relative intensity): 150 (14), 111 (15), 110 (100), 104 (18), 97 (26), 76 (23), 53 (14), 50 (25), 45 (35).

2.2.2. 3",5"-Dinitrobenzoyl (thiophene-3'-yl)-1-ethylate - DNTh

The same **NTh** synthetic procedure was carried out for the **DNTh** monomer (Scheme 1), employing the following amounts: 3-(2'-iodoethyl) thiophene (0.579 g, 2.4 mmol), 3,5-dinitrobenzoic acid (0.508 g, 2.4 mmol) and proton-sponge[®] (1.01 g, 6.8 mmol). The mixture, initially orange, turned purple in few minutes. After extracted from the organic layer (2×50 mL of 0.01 mol L⁻¹ HNO₃/CHCl₃ (1:1)), the crude product was eluted with CHCl₃ in a silica gel column (70-230 Mesh) to eliminate the purple dye. After this procedure, the precipitation, recrystallization and drying steps were performed according to the **NTh** synthetic procedure.

Pale green solid, 45% yield (348 mg). M.p. 107-109 °C; ¹H NMR (300 MHz, CDCl₃) δ = 9.21 (t, *j* = 3.0 Hz, 1H, -ArH), 9.12 (d, *j* = 3.0 Hz, 2H, -ArH), 7.32 (dd, *j* = 4.9, 2.9 Hz, 1H, -ThH), 7.11 (dt, *j* = 2.9, 1.0 Hz, 1H, -ThH), 7.03 (dd, *j* = 4.9, 1.3 Hz, 1H, -ThH), 4.67 (t, *j* = 9.0 Hz, 2H, -CH₂), 3.19 (t, *j* = 6.0 Hz, 2H, -CH₂); ¹³C NMR (75 MHz, CDCl₃) δ = 162.6, 149.0, 137.3, 134.2, 129.6, 128.2, 126.4, 122.6, 122.2, 66.8, 29.8; IR (KBr) cm⁻¹: 3095, 1731, 1630, 1540, 1457, 1440, 1342, 1276, 1174, 1074, 976, 924, 833, 804, 775, 725, 698, 593, 511 and 425; Anal. calcd. for C₁₃H₁₀N₂O₆S (%) (322.2984g mol⁻¹): C, 48.45; H, 3.13; N, 8.69; S, 9.95. Found: C, 48.64; H, 3.31; N, 8.61; S, 9.13. MS, *m/z* (relative intensity): 149 (10), 111 (11), 110 (100), 97 (41), 75 (23), 53 (13), 45 (30).

2.3. Chemical polymerization

A typical poly-condensation reaction was used to obtain the polymers **PNTh** and **PDNTh** (Scheme 2). Dry FeCl₃ (~100 mg, 0.6 mmol), used as oxidant, was suspended in dry CHCl₃ (2 mL) and stirred for 20 min under N₂. To the dark green solution formed, it was slowly dropwise added (during 30 min) the monomer solution of NTh (50 mg, 0.18 mmol) or DNTh (50 mg, 0.16 mmol), both dissolved in dry CHCl₃ (2 mL) and kept previously under N₂ for 20 min. The mixture was stirred and purged overnight with N₂ at room temperature. Each insoluble oxidized polymer was then filtered off, washed with water, and reduced in a mixture of aqueous hydrazine (25%)/ethyl acetate (1:9), under stirring for 3 h [26]. The neutral polymers were filtered off and washed with water and ethyl acetate. Then, the purified polymers were dried under high vacuum for 24 h. The polymers presented low solubility in common organic solvents, such as acetonitrile, chloroform, DMF, DMSO and acetone.

2.3.1. NTh polymer - P NTh

A reddish brown solid was obtained in 35 mg (70%) for **PNTh**. IR (KBr) cm⁻¹: 3105, 2957, 2919, 2854, 1723, 1603, 1524, 1456, 1346, 1269, 1169, 1106, 1010, 973, 964, 829, 778, 714 and 500; Anal. calcd. for $C_{13}H_9NO_4S$ (%) (275.2847 g mol⁻¹): C, 56.72; H, 3.30; N, 5.09; S, 11.65. Found: C, 55.95; H, 3.29; N, 4.77; S 11.62.

2.3.2. DNTh polymer - PDNTh

A reddish brown solid was obtained, 38 mg (74%) for **PDNTh**. IR (KBr) cm⁻¹: 3095, 1730, 1626, 1543, 1456, 1340, 1269, 1157, 1072, 978, 916, 825, 770, 717, 656, 507 and 457; Anal. calcd. for C₁₃H₁₀N₂O₆S (%) (320.2826 g mol⁻¹): C, 48.75; H, 2.52; N, 8.75; S, 10.01. Found: C, 48.47; H, 2.94; N, 8.58; S, 10.60.

2.4. Electrochemical measurements

Electropolymerizations (**NTh** and **DNTh** monomers) and redox behavior of monomers and polymers were carried out in onecompartment cell containing a glassy carbon (GC) or platinum (Pt) disk electrode (both with φ = 3 mm), platinum wire and Ag/AgCl, KCl (sat.) as the working, counter and reference electrodes, respectively. Before every assay, the working electrode was



NTh: $R^1 = H$; $R^2 = NO_2$ **DNTh**: $R^1 = NO_2$; $R^2 = H$

PNTh or PDNTh

carefully polished in a felt-pad soaked with aqueous alumina slurry ($0.3 \mu m$) and rinsed with plenty of distilled water, followed by acetone and, then, dried in a soft paper. Compartments with sintered glass walls were used to keep the reference and counter electrodes separated from the monomer solutions. The electrolytic medium for electropolymerizations was a mixture (1:1, v/v) of 0.1 mol L^{-1} TBABF₄/CH₂Cl₂ and freshly distilled BFEE. The polymers were electrosynthesized from that medium, containing 10 mmol L^{-1} monomer, via cyclic voltammetry in a potential range from 0.00 V to +1.90 V vs. Ag/AgCl, KCl (sat.), at a scan rate of 20 mV s⁻¹. Immediately after obtaining the films, they were rinsed thoroughly with CH₂Cl₂ and transferred to another cell containing 0.1 mol L⁻ TBABF₄/CH₂Cl₂ supporting electrolyte. The redox behavior of the polymers was monitored during 10 cyclic voltammetric scans at 20 mV s⁻¹, between the neutral and doped states, which also served as a pre-treatment step. The same electrolytic medium was employed to study the cathodic behavior of the monomers. All experiments were carried out after degassing for 10 min, maintaining the system at 20 °C - 22 °C under argon atmosphere.

3. Results and Discussion

3.1. Chemical syntheses of monomers and polymers

The **NTh** and **DNTh** monomers were synthesized through a simple two-step route (Scheme 1), giving an overall yield of 60% and 45%, respectively, and gave satisfactory elemental, mass spectral and spectroscopic analyses. Firstly, the thiophene halogenated precursor 3-(2'-iodoethyl) thiophene was obtained, followed by esterification reaction with 4-nitrobenzoic or 3,5-dinitrobenzoic acid in presence of proton-sponge[®] (1,8-bis (dimethylamino) naphthalene) (Scheme 1). The sterically hindered base, proton-sponge[®], was alternatively employed in the place of triethylamine to avoid the by-product formation (3-vinylthiophene), formed by HI elimination, [23]. The structures of both compounds were fully characterized by routine analysis techniques (melting point, ¹H and ¹³C NMR, FTIR, GC/MS, and elemental analysis).

The polymers were synthesized by using FeCl₃ as oxidant agent in dry CHCl₃ medium (Scheme 2), employing a Fe³⁺/monomer 4:1 molar ratio, 16 hours reaction time, room temperature and argon atmosphere. Pure neutral polymers were obtained by exhaustive washes with methanol and water, followed by reduction with hydrazine, exhaustive washes with water and ethyl acetate, and dried under high vacuum for 24 hours. The products **PNTh** (70%) and **PDNTh** (74%) were obtained in good yields. The dedoping process was investigated by elemental analysis of the polymers, showing CHNS data very close to calculated values.

3.2. Redox behavior of monomers

Fig. 1 shows cyclic voltammograms of $3.0 \text{ mmol } \text{L}^{-1}$ **NTh** and **DNTh** monomer solutions ($0.1 \text{ mol } \text{L}^{-1}$ TBABF₄/CH₂Cl₂) on GC disk electrode, in two potential windows: 0.0 V to -1.5 V and 0.0 V to 2.5 V vs. Ag/AgCl, KCl (sat.). One irreversible peak was observed in the anodic branch, related to oxidation (one electron) of the thiophene group for both compounds (**NTh**:E_{pla'} = 2.25 V, Fig 1(a); **DNTh** E_{plIa'} = 2.30 V, Fig. 1(b)). The high oxidation potential is in agreement to data described in literature [19], and no polymerization is observed. Thus, the anodic sweep was also carried out in the presence of BFEE ($0.1 \text{ mol } \text{L}^{-1}$ TBABF₄/CH₂Cl₂ + BFEE (1:1, v/v), where it can be observed a small shift on the oxidation peak potentials (**NTh**: E_{pla'} = 1.96 V, inset of Fig. 1(a); **DNTh**: E_{plIa'} = 2.07 V, inset of Fig. 1(b)), allowing the electropolymerization process at higher ($10.0 \text{ mmol } \text{L}^{-1}$) monomer concentration (Fig. 2). As already



Fig. 1. Cyclic voltammograms of 3.0 mmol L^{-1} **NTh** (a) and **DNTh** (b) monomers on GC electrode vs. Ag/AgCl, KCl (sat.), $\nu = 20$ mV s⁻¹. Sweeps were carried out in 0.1 mol L^{-1} TBABF₄/CH₂Cl₂. Inset: anodic sweeps were carried out in 0.1 mol L^{-1} TBABF₄/CH₂Cl₂ + BFEE (1:1, v/v).

described [26], the presence of the pendant nitrobenzoyl moieties does not interfere in the oxidation process. In addition, BFEE is a volatile compound, and the variation on its concentration can result on slight shifts of the thiophene E_{pa} . Commonly, the E_{pa} decreases with the BFEE ratio increasing [27,35].

It is important to highlight that in the presence or absence of BFEE the onset oxidation potential remains the same (Table 1), while the oxidation peak potential is shifted to lower potentials in the presence of BFEE, confirming the catalytic effect of this reagent [27,35].

At the cathodic branch (Fig. 1), the sweep was carried out in the absence of BFEE (0.1 mol L^{-1} TBABF₄/CH₂Cl₂) due to the reactivity of the reduced species generated. It was observed a one electron reduction process, concerning the nitro group reduction (aprotic medium) for both monomers, identified by the two pairs of peaks I_c/I_a (4-nitrobenzoyl moiety) and II_c/II_a (3,5-dinitrobenzoyl moiety), Eqs. (1) and (2), respectively, Table 1.

$$(\text{COOR})-\text{Ar-}(\text{NO}_2)+1 \quad e^- \rightleftharpoons (\text{COOR})-\text{Ar-}(\text{NO}_2)^{-1} \tag{1}$$

$$(\text{COOR})-\text{Ar-}(\text{NO}_2)_2 + 1 \ \text{e}^- \rightleftharpoons (\text{COOR})-\text{Ar-}(\text{NO}_2)_2^{-\cdot}$$
(2)

The electron transfer process of soluble nitrocompounds is quasi-reversible [36,37], as observed here from the anodic to the cathodic peak potential separations (**NTh**: $E_{pla} - E_{plc} = 130 \text{ mV}$; **DNTh**: $E_{plla} - E_{plc} = 110 \text{ mV}$). Besides, it can be observed a second electron transfer process in **DNTh** molecule ($E_{pllc''} = -1.18 \text{ V/}E_{plla''} = -1.07 \text{ V}$), normally assigned to the nitro radical anion reduction, giving the respective dianion intermediate (Eq. (3)) [36]. However, a recent work involving ESR-spectroelectrochemistry and



Fig. 2. Cyclic voltammograms of the potentiodynamic electrodeposition of (a) **NTh** and (b) **DNTh**,both 10.0 mmol L⁻¹, in 0.1 mol L⁻¹ TBABF₄/CH₂Cl₂ + BFEE (1:1, v/v), on Pt electrode vs. Ag/AgCl, KCl (sat.), $\nu = 20$ mV s⁻¹, 10 scans.

quantum chemical studies about the methyl 3,5-dinitrobenzoate reduction have indicated to a rare biradical dianion formation (Eq. (4)) [37]. These intermediate species are strong bases that can react in the presence of water (or electrophilic species), generating the respective nitro reduction product, hydroxylamine [36,37].

$$(\text{COOR})-\text{Ar-}(\text{NO}_2)_2^{-.}+1 \quad e^- \rightleftharpoons (\text{COOR})-\text{Ar-}(\text{NO}_2)_2^{2-}$$
(3)

$$(\text{COOR})-\text{Ar-}(\text{NO}_2)_2^{-\cdot}+1 \text{ e}^- \rightleftharpoons (\text{COOR})^{-\cdot}-\text{Ar-}(\text{NO}_2)_2^{-\cdot}$$
(4)

3.3. Electrochemical polymerization of NTh and DNTh

Unlike similar nitrobenzoyl pyrrole derivatives synthesized and recently described [26], the electropolymerization of **NTh** and **DNTh** required the use of BFEE as catalyst, 1:1 (v/v) in 0.1 mol L⁻¹ TBABF₄/CH₂Cl₂ solution. Fig. 2 shows successive cyclic voltammograms carried out for the electropolymerization of both 10.0 mmol L⁻¹ monomer solutions, on Pt disk electrode. It can be seen that the onset oxidation potential of **NTh** and **DNTh** are 1.78 V and 1.86 V vs. Ag/AgCl, KCl (sat.), respectively, in the presence of BFEE (Table 1),



Fig. 3. Cyclic voltammograms of **PNTh** (red) and **PDNTh** (black and dashed dot line) films onto Pt disk electrode vs. Ag/AgCl, KCl (sat.), in 0.1 mol L⁻¹ TBABF₄/CH₂Cl₂, $\nu = 20 \text{ mV s}^{-1}$. **PNTh** and **PDNTh** films were obtained according to Fig. 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

while unsubstituted thiophene polymerizes at 1.3 V [27]. The higher oxidation potential of substituted thiophene monomers may be associated to the steric hindrance and/or electronic density decrease of the ring. The electropolymerization of thiophenes substituted with strong electron withdrawing groups, directly attached to β positions has already been reported and assigned to the high reactivity of the corresponding radical cation [34].

Electropolymerization of both monomers (**NTh** and **DNTh**) can be accomplished by sweeping the potential between 0.6 and 1.9 V in the presence of BFEE. On the first scan, the anodic current increases at around 1.8 V and a typical current loop can be clearly seen between 1.8 and 1.9 V when the scan is reversed (Fig. 2). The presence of this loop is indicative of a nucleation process, as reported in the literature [38]. Upon subsequent scans, a reversible peak, typical of adsorbed polythiophene films [34] can be observed between 0.7 V and 1.0 V with a continuous growth of the peak current intensity, indicating the formation and growth of a polymeric film. The redox couples, $E_{plc''} = 0.84 \text{ V/E}_{pla''} = 0.87 \text{ V}$ for **PNTh** and $E_{pllc'''} = 0.90 \text{ V/E}_{plla'''} = 0.94 \text{ V}$ for **PDNTh**, can be attributed to the p-doping/dedoping processes of polythiophene films [35].

The redox behavior of **PNTh** and **PDNTh** was also investigated. Fig. 3 shows cyclic voltammograms of the polymer films (obtained after 10 cycles on Pt disk electrode) in a monomer and BFEE free solution $(0.1 \text{ mol } \text{L}^{-1} \text{ TBABF}_4/\text{CH}_2\text{Cl}_2)$. At the anodic region, it can be observed a reversible peak centered at around 1.00 V ($\text{E}_{\text{pla}^{\text{cr}}}$ = $0.99 \text{ V}/\text{E}_{\text{pla}^{\text{m}}}$ = 1.02 V for **PNTh** and $\text{E}_{\text{plIc}^{\text{cr}}}$ = $0.97 \text{ V}/\text{E}_{\text{plIa}^{\text{m}}}$ = 1.01 V for **PDNTh**), which corresponds to the oxidation/reduction of the polythiophene backbone. At the cathodic region it appears a quasireversible peak at E_{plc} = $-0.97 \text{ V}/\text{E}_{\text{plIa}}$ = -0.74 V for **PNTh**, and E_{plIc} = $-0.72 \text{ V}/\text{E}_{\text{plIa}}$ = -0.54 V for **PDNTh**, which are assigned to the reduction of 4-nitrobenzoyl and 3,5-dinitrobenzoyl moieties, respectively [37]. When the sweep is carried out to more negative potential (-1.5 V) a small irreversible cathodic peak is observed ($\text{E}_{\text{plIc}}^{\text{cr}}$ = -0.97 V), and the film becomes electro inactive at the

Table 1

Electrochemical data, E^{HOMO}, E^{LUMO} levels and E_g^{ec} for NTh and DNTh monomers, PNTh and PDNTh polymers in 0.1 mol L⁻¹ TBABF₄/CH₂Cl₂.

entry	comp.	E _{pc} (V)	E _{pa} (V)	E _{pa} . (V)	E _{ox} onset (V)	$E_{Th}^{HOMO}(eV)$	E _{red} ^{onset} (V)	$E_{\varphi - NO2}^{LUMO}$ (eV)	E_g^{ec} (eV)
1	NTh	-0.83	-0.70	2.25/1.96 ^a	1.78/1.78 ^a	-6.18/-6.18 ^a	-0.64	-3.76	2.42
2	DNTh	-0.79	-0.68	2.30/2.07 ^a	1.85/1.86 ^a	-6.25/-6.26 ^a	-0.62	-3.78	2.47
3	PNTh	-0.97	-0.74	1.01	0.90	-5.30	-0.67	-3.73	1.57
4	PDNTh	-0.72	-0.54	1.02	0.93	-5.33	-0.50	-3.90	1.43

^a 0.1 mol L⁻¹ TBABF₄/CH₂Cl₂ + BFEE (1:1, v/v).

cathodic region. Therefore, the second electron transfer enables the generation of very reactive species (dianion or diradical dianion, Eqs. (3) and (4), respectively), which can react with organic functional groups (or other species) present in the film.

In the PNTh film, the 4-nitrobenzoyl moiety electron transfers occur at more negative potentials (-0.97 V/-0.74 V, $E^{\circ} = -0.86 \text{ V}$), compared to the respective **NTh** monomer $(-0.83 \text{ V}/-0.70 \text{ V}, \text{ E}^{\circ} = -$ 0.76 V), meaning that the redox process becomes more difficult to occur on the film/electrode interface than for monomer/electrode surface. When analyzing the corresponding data for the **PDNTh** film $(-0.72 \text{ V}/-0.54 \text{ V}, \text{ E}^{\circ} = -0.63 \text{ V})$ and **DNTh** monomer $(-0.79 \text{ V}/-0.54 \text{ V}, \text{ E}^{\circ})$ 0.68 V, E° = -0.73 V), it can be observed the opposite effect, *i.e.*, the electron exchange occurs at less negative potential in the PDNTh film/electrode than for the DNTh monomer/electrode surface. These potential shifts can be attributed to the structural differences between 4-nitrobenzoyl and 3,5-dinitrobenzoyl moieties, as well, the electron transfer mechanisms involved into the film. It is known that the electrochemical potentials for these reactions are strongly dependent on the nitro group structural position in the aromatic system [36,39], and also on the structural changes occurring during the electron transfer processes [40,41]. Therefore, in a general way, the electron-withdrawing effect of the additional nitro group in the 3,5-dinitrobenzoyl moiety can make the PDNTh film electrochemically more accessible than DNTh monomer, during the first electron transfer process.

Welzel et al. [19] described the preparation of eight thiophene derivatives, including the NTh and DNTh monomers described in this work, but did not observe the electrochemical homopolymerization of these monomers in acetonitrile medium. Thus, electrochemical copolymerizations of NTh and DNTh were carried out in the presence of 3-methylthiophene, furnishing stable copolymers with characteristic redox properties of polythiophene. The cathodic behavior of these copolymers was not described. In turn, Li et al. [42] described the preparation of two similar monomers (3-thiophene acetic acid-4-nitrobenzyl ester and 3thiophene acetic acid-4-(4-nitrophenyl) butyl ester), which were electropolymerized in acetonitrile and high monomer concentration $(0.2 \text{ mol } L^{-1})$. The polymer films presented a well-defined redox behavior for the polythiophene backbone (anodic region), as well, a distinct redox behavior for the nitrophenyl moiety (cathodic region).

The electropolymerization of the **NTh** and **DNTh** monomers employing BFEE can be carried out at small concentrations (10.0 mmol L⁻¹) of monomers and improve the quality of the resulting polymer films (**PNTh** and **PDNTh**), showing a welldefined redox couple, R-NO₂/R-NO₂⁻⁻, for both 4-nitrobenzoyl and 3,5-dinitrobenzoyl moieties into the polymeric films. Thus, the electroactivity of pendant groups in conducting polymers should depend not only on the monomer structure but also on the experimental conditions employed during the electropolymerization process [18,26].

Fig. 4 shows the behavior and stability of the nitro group redox process in the **PNTh** film (prepared after 10 scans, on Pt disk electrode), using 0.1 mol L^{-1} TBABF₄/CH₂Cl₂ as electrolyte solution. After consecutive scans, it can be observed a drop on the oxidation/ reduction currents of the 4-nitrobenzoyl moiety of the film, until they are no longer observed. At the anodic branch, in turn, the redox activity of the polythiophene backbone was maitained, showing a positive shift of the anodic peak associated to a small increase of the current. The cathodic peak of the polythiophene backbone remains unaltered. These results contrast with the data described by Li et al. [18], which showed a complete lost of the charge/discharge capability of the polymer after two scans in such wide potential range.

The cyclovoltammograms of **NTh** and **DNTh** monomers (Fig. 1) show a characteristic propertie of nitro groups, which can be easily



Fig. 4. Successive four cyclic voltammograms of the polymer **PNTh** in 0.1 mol L⁻¹ TBABF₄/CH₂Cl₂, $\nu = 20$ mV s⁻¹. Film obtained from 10 scans (0.0 to 1.85 V), from 10 mmol L⁻¹ monomer solution in 0.1 mol L⁻¹ TBABF₄/CH₂Cl₂ + BFEE (1:1, v/v) on Pt electrode vs. Ag/AgCl, KCl (sat.), $\nu = 20$ mV s⁻¹.

reduced/oxidated without affecting other functional groups [43]. As described above, the electroactivity of the nitrobenzoyl moiety in **PNTh** and **PDNTh** disapears after 5 scans, but does not affect the conjugated π -electron system of the polymeric chain (Fig. 4), which remains electroactive. The study of similar nitrobenzoyl substituted polypyrroles (poly-4"-nitrobenzoyl(pyrrol-1'-yl)-1-propylate and poly-3",5"-dinitrobenzoyl(pyrrol-1'-yl)-1-propylate) [26], showed an irreversible reduction system for the nitro moieties, which become inactive after the first scan, decreasing the polypyrrole backbone electroactivity. Therefore, the polythiophene is more stable than polypyrrole films in the presence of the nitrobenzoyl reduced species.

To investigate the electroactivity and stability of the polymers, **NTh** (Fig. S1a) and **DNTh** (Fig. S1b) were electropolymerized by 3 cycles on Pt disk electrode. Cyclic voltammograms were monitored between neutral and oxidized states at scan rates from 20 mV s^{-1} to 200 mV s^{-1} in a monomer and BFEE free electrolyte. The scan rate (ν) dependence with the anodic (I_{pa}) and cathodic (I_{pc}) peak currents is linear, evidencing that the redox process is non-diffusional in the range studied and the electroactive films are well adhered on Pt electrode surface.

3.4. Spectroscopic properties of monomers and polymers

3.4.1. FTIR measurements

The FTIR spectra of both monomers (**NTh** and **DNTh**) and respective polymers (**PNTh** and **PDNTh**, obtained via chemical polymerization) were carried out and revealed characteristic bands, in agreement to the proposed structures (experimental section). Fig. 5 shows the FTIR spectra of the **NTh** monomer (Fig. 5a) and respective polymers, chemically (**PNTh** powder, Fig. 5b) and electrochemically (**PNTh** film, Fig. 5c) synthesized. These spectra presents similar major bands, such as carbonyl C=O stretching at 1718 cm⁻¹; asymmetric and symmetric Ar-NO₂ stretching at 1527 cm⁻¹ and 1350 cm⁻¹, respectively; aromatic C-H in-plane vibration at 1270 cm⁻¹; ester C-O stretching at 1100 cm⁻¹; symmetric aromatic C-H vibration at 717 cm⁻¹. The bands around 3104–2861 cm⁻¹, related to thiophene and benzene aromatic rings symmetric/asymmetric stretching are not observed in ATR mode (Fig. 5c), probably due to the low penetration depth of photons in these region.

3.5. UV-Vis measurements

As shown in Scheme 2, the **NTh** and **DNTh** monomers present thiophenyl, 4-nitrobenzoyl and 3,5-dinitrobenzoyl chromophores



Fig. 5. FTIR spectra of (a) **NTh**, (b) **PNTh** prepared from oxidation with FeCl₃, and (c) **PNTh** prepared by electropolymerization on Pt electrode (ATR mode) in 0.1 mol L⁻¹ TBABF₄/CH₂Cl₂ + BFEE (1:1, v/v).

(Table 2). In THF, these monomers present absorption bands at $\lambda_{max} = 232$ nm that correspond to π - π^* primary electronic transition of the thiophene ring (Fig. 6). An overlapping band was observed for the **DNTh** monomer at 238 nm, related to the 3,5-dinitrobenzoyl chromophore. The absorption band at $\lambda_{max} = 278$ nm correspond to the 4-nitrobenzoyl chromophore of the **NTh** monomer.

The same absorption bands (λ_{max} = 232 nm and 278 nm, respectively) were observed for the chemically synthesized polymer, **PNTh**, with an additional broad band at λ_{max} = 410 nm related to the polythiophene band (π - π * transition). The **PDNTh** UV-Vis absorption spectrum presented a different behavior, the π - π * electronic transition (λ_{max} = 239 nm) of the 3,5-dinitrobenzoyl chromophore was improved, and additional bands at 277 nm and 427 nm can be observed, which also corresponds to the polythiophene band.

3.6. Electro-optical properties of monomers and polymers

As described in a previous work [26], the cyclic voltammetry was used to estimate the relative position of HOMO (E^{HOMO}) and LUMO (E^{LUMO}) energy levels of conjugated polymers [9,44]. These levels, as well as the electrochemical band gap energy (E_g^{ec}), were calculated from the onset oxidation potential (E_{ox}^{onset}) and reduction potential (E_{red}^{onset}), respectively, for the monomers (**NTh** and **DNTh**) and polymers (**PNTh** and **PDNTh**), according to relationships proposed by Bredas et al. (Eqs. (5) to (7)) [45,46]:

$$E^{HOMO} = -(E_{ox}^{onset} + 4.40) \text{ eV}$$
 (5)

$$E^{LUMO} = -(E_{red}^{onset} + 4.40) \text{ eV}$$
 (6)

$$E_{g}^{ec} = (E^{LUMO} - E^{HOMO}) \text{ eV}$$
⁽⁷⁾



Fig. 6. UV-Vis absorbance spectra of **NTh** and **DNTh** monomers and **PNTh** and **PDNTh** dedoped polymers in THF. The polymers were synthesized from oxidation with FeCl₃. Inset: **PNTh** and **PDNTh** backbone bands.

where, the -4.40 eV energy correspond to the HOMO/LUMO energy levels of the reference ferrocene/ferricenium redox pair (*vs.* Ag/ AgCl, KCl (sat.)), as described in the literature and used as external standard [47].

Normally, the calculated E_g^{ec} (Eq. (7)) corresponds to the optical band gap energy (E_g^{opt}) of the polymeric chain. For **PNTh** and **PDNTh**, it does not occur because the nitrobenzoyl moiety reduction potential is higher than the reduction potential of the conjugated polymeric chain (polythiophene). That is, both oxidation and reduction occur in distinct moieties of the monomer or polymer, and cannot be associated to the optical band gap. The electrochemical behavior of the studied substances (**NTh**, **DNTh**, **PNTh** and **PDNTh**) should take into account the electron transfer processes as separated phenomena, as specified in the Scheme 3. Therefore, the E_g^{ec} corresponds to energy difference between two distinct moieties (thiophene/polythiophene HOMO and nitrobenzoyl LUMO) separated by a non-conjugated bridge (ethyl group).

At the same time, the UV-Vis optical absorption spectroscopy is a well-known technique to evaluate the band gap of materials, which can be associated to HOMO/LUMO electronic transitions caused by absorption of electromagnetic energy. These electronic transitions $(n-\pi^*, \pi-\pi^*)$ normally occur in chromophores present in the molecule, which E_g^{opt} can be estimated from the onset absorption wavelength (λ_{onset}) of the chromophore electronic transition (Scheme 3) [9,44–47].

3.6.1. Electrochemical measurements

The E^{HOMO} and E^{LUMO} (Eqs. (5) and (6)) were determined by cyclic voltammetry in 0.1 mol L⁻¹ TBABF₄/CH₂Cl₂, $\nu = 20$ mV s⁻¹ (Table 1). For the monomers **NTh** and **DNTh**, the E^{HOMO} calculated from E_{ox}^{onset} of the thiophene moieties are $E_{Th}^{HOMO} = -6.18$ eV and -6.25 eV, respectively. With addition of BFEE the onset reduction potential of the thiophene moieties remains the same $E_{ox}^{onset} = 1.78$ and 1.85 V, respectively; and the estimated molecular orbital energy values are $E_{Th}^{HOMO} = -6.18$ eV and -6.26 eV. The E^{LUMO}

Table 2

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Absorbance and Eg^{opt} data for thyophene, nitrobenzoyl and dinitrobenzoyl chromophores present in **NTh** and **DNTh** monomers, **PNTh** and **PDNTh** polymers (THF).

		Absorbance φ -NO ₂ chromophore			Absorbance thyophene chromophore		
entry	comp.	λ_{max} (nm)	$\lambda_{onset} (nm)$	$E_{g}^{opt}(eV)$	λ_{max} (nm)	$\lambda_{onset} (nm)$	$E_{g}^{opt'}(eV)$
1	NTh	278	307	4.03	232	243	5.10
2	DNTh	238	284	4.36	232	243	5.10
3	PNTh	278	307	4.03	232, 410	498	2.49
4	PDNTh	239	304	4.07	277, 427	510	2.43

* Assuming the same value for **NTh**. E (eV) = 1239 (eV nm)/ λ (nm).



Scheme 3. HOMO/LUMO energy levels and related electrochemical and optical electron transfers for NTh or PNTh.

calculated from E_{red}^{onset} of the 4-nitrobenzoyl ($E_{\varphi-NO2}^{LUMO} = -3.76 \text{ eV}$) and 3,5-dinitrobenzoyl ($E_{\varphi-NO2}^{LUMO} = -3.78 \text{ eV}$) moieties presented a small variance. The E_{red}^{onset} of **DNTh** is less cathodic due the second nitro substituent on the benzoyl group. Thus, the E_g^{ec} values were calculated according to Eq. (7) for **NTh** (2.42 eV) and **DNTh** (2.47 eV) monomers. The E^{HOMO} and E^{LUMO} calculated for the respective polymers

The *E*^{HOMO} and *E*^{LUMO} calculated for the respective polymers followed the same procedure described above, allowing the determination of E_g^{ec} for **PNTh** (1.57 eV) and **PDNTh** (1.43 eV), which show a decrease on the electrochemical gap energy values when compared to monomers data (Table 1). This behavior is caused by decreasing on the E_{ox}^{onset} of the polythiophene moiety due to the formation of the conjugated polymeric chain, which correspond to an increasing of the HOMO energy (**PNTh**, E_{Th} $H^{OMO} = -5.30 \text{ eV}$ and **PDNTh**, E_{Th} $H^{OMO} = -5.33 \text{ eV}$) for both polymers. On the other hand, at the cathodic branch it can be observed almost the same values for LUMO energies (**PNTh**, $E_{\varphi-NO2}^{LUMO} = -3.90 \text{ eV}$).

3.6.2. Optical measurements

The corresponding band gap energies of the electronic transitions for thiophene (E_g^{opt}) and nitrobenzoyl (E_g^{opt}) chromophores were determined from λ_{onset} (E (eV) = 1239 (eV nm)/ λ (nm)) of the respective absorption bands as already explained in Scheme 3, either to monomers as to polymers, and are described in Table 2.

According to the $E_g^{opt'}$ calculated for thiophene (5.10 eV, **NTh**, and 5.10 eV, **DNTh**) and polythiophene chromophores (2.49 eV, **PNTh**, and 2.43 eV, **PDNTh**), it was observed a drop on the band gap energy after the polymerization process, as expected. Normally, the polymeric chain gives rise to π - π^* electronic transitions occurring at lower HOMO/LUMO energy gap [42]. The E_g^{opt} calculated values for the nitrobenzoyl chromophore of monomers and polymers studied are between 4.03 eV and 4.36 eV (Table 2).

3.6.3. Fluorescence measurements

Fig. 7a shows the excitation and emission spectra for the monomer/polymer pair **NTh/PNTh**, while Fig. 7b shows the spectra

for **DNTh**/**PDNTh**, both in THF medium. When excited at 421 nm (**NTh**, Fig. 7a) and 430 nm (**DNTh**, Fig. 7b), both monomers show emission bands at λ_{max} = 488 nm and λ_{max} = 511 nm, respectively, with Stokes shifts of 67 nm for **NTh** and 81 nm for **DNTh**.

The **PNTh** solution was excited at three different wavelengths (262 nm, 314 nm or 371 nm, Fig. 7a), in which an emission band was observed only at λ_{max} = 440 nm, with Stokes shift of 69 nm for the maximum intensity of emission. **PDNTh** also was excited at different emission wavelengths (Fig. 7b): at 355 nm, it was observed an emission band at λ_{max} = 530 nm and Stokes shift of 175 nm. When exciting **PDNTh** at 519 nm, it was observed an elevated intensity emission at λ_{max} = 546 nm and a corresponding Stokes shift of 27 nm.

For the **NTh/PNTh** pair, the red shift of the monomer emission band, if compared to the respective polymer emission band (Fig. 7a), shows an opposite behavior than typical fluorescent conductive polymers, in which the monomer absorbs and emits light at lower wavelengths than the polymer, *i.e.*, higher energy is necessary to excite the monomer than polymer [45,46]. The different behavior of **PNTh** can be associated to electronic distribution, structure or fluorescence mechanism of the polymer. On the other hand, the **PDNTh** polymer can be excited at shorter and longer wavelengths than its corresponding **DNTh** monomer.

The fluorescence mechanism of the related compounds must be associated to a photoinduced electron transfer process [48]. The monomer molecules are free in solution and can rotate via -CH₂bond, hindering the formation of the excimer that allows the electron transfer between nitrobenzoyl and thiophene moieties, thus, the excitation process occurs at shorter wavelengths. The



Fig. 7. Excitation and emission spectra in THF for: (a) **NTh** and **PNTh**; (b) **DNTh** and **PDNTh**. Inset: Color of polymers (left) and monomers (right) under ambient light (up) and irradiated with UV light at 256 nm (down).

same photoinduced electron transfer should occur in the polymeric chain; however, at lower energy since thiophene and nitrobenzoyl groups are arranged in a rigid chain. Therefore, the fluorescence mechanism of the monomers and polymers should be deeply studied in due course, and will be reported in a future paper.

4. Conclusion

Two nitrobenzoyl thiophene compounds (**NTh** and **DNTh**) and respective polymers (**PNTh** and **PDNTh**) were synthesized, characterized, and their electro-optical properties were investigated. The band gap energy values (E_g^{ec}, E_g^{opt} and $E_g^{opt'}$) determined for the monomers and polymers are distinct, corroborating the proposed model in Scheme 3, in which optoelectronic transitions (E_g^{opt} and $E_g^{opt'}$) occur separately in each chromophore, and the value E_g^{ec} is not specifically associated to the π - π * electronic transition occurring on the polymeric chain. An interesting fluorescence effect was observed for all monomers and polymers studied and should be more deeply studied.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. electacta.2015.08.006.

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