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Reactive groups on polymer coated electrodes 10. Electrogenerated conducting polyalkylthiophenes bearing activated ester groups

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Abstract

Three new thiophene derivatives containing different activated ester groups covalently attached to the thiophene ring via a linear undecyl spacer have been synthesized. Electropolymerization of these monomers in acetonitrile led to stable electroactive polymers, while activated functional groups withstand the polymerization conditions and were correctly incorporated in the resulting polymers. These polymers show the characteristic electrochemical behavior of poly(3-alkylthiophene)s with the reversible redox transition in the range of 0.7–0.9 V. UV/Vis spectra of them exhibit an absorption maximum at around 460 nm. Conductivity measurements on oxidized films of these polymers by means of the two-probe method gave values in the range of 10^{-3}–10^{-2} S cm^{-1}. The reactivity of the pendant activated ester groups was demonstrated by the reaction with butylamine, (4-amino-2-oxabutyl) ferrocene and 2-aminoanthraquinone. Spectroscopic studies and electrochemical characterization confirmed that the immobilized amino compounds are covalently bound to the polymer surfaces. These results suggest that the obtained new polymers can be used as electrically conducting carrier materials for the immobilization of biochemically interesting molecules.

Keywords: Conducting polyalkylthiophene; Electropolymerization; Activated ester

1. Introduction

In previous work [1], we reported two new thiophene derivatives functionalized with epoxy and cyclic carbonate groups. Their electro-oxidative homopolymerization and copolymerization with 3-methylthiophene led to highly electroactive materials, while the functional groups remain intact during the electropolymerization or copolymerization processes. The electrochemical and spectroscopic data indicate that these resulting polymers deposited on electrodes possess an extended conjugated π-electron system with comparable electrical and electrochemical properties to non-functionalized polyalkylthiophenes. Using butylamine and 2-aminoanthraquinone as model compounds, it was found that amino compounds can easily react with pendant functional groups on these polymer surfaces, suggesting that the new type of electrically conducting polymers could be used as an interface for the immobilization of biocompounds for the development of biosensors. In oder to explore new electroactive polymers with anchoring sites suitable for the covalent attachment of large and sensitive biomolecules, we describe in this article another type of such materials, which bear easily replaceable leaving activated ester groups (see Scheme 1).

It is well known that activated esters are widely used in peptide synthesis. The related synthesis is characterized by rapid reaction of activated ester groups with amines under very mild conditions to form corresponding amides in high yields [2]. Taking advantage of this profitable feature, Willner and Katz reported many reactive electrodes by chemical adsorption of the bifunctional agent dithio-bis-(succinimidylalkanote), where disufide as anchor group was chemically attached to the electrode surface and the pendant succinimido groups served as functional groups for further electrode surface modification [3,4]. Recently, this concept was extended to electrogenerated conducting

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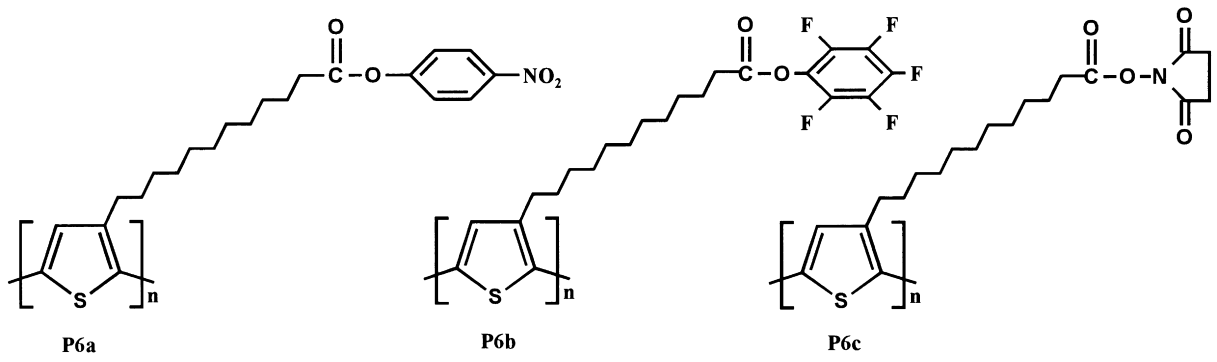


Scheme 1. Conducting polythiophenes bearing activated ester groups.

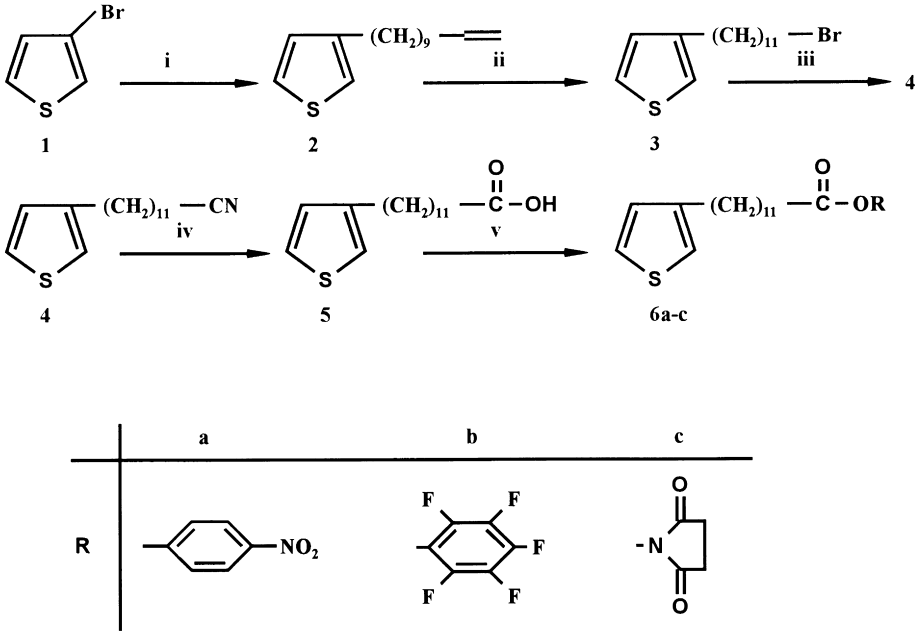
polymers. By the introduction of activated ester groups into conjugated polymer backbones novel electrically conducting polymer interfaces were designed. Ryder reported the synthesis and electropolymerization of pentafluorophenyl pyrrole-3-acetate [5]. More recently, thiophene based activated esters were described by Bäuerle, which led to redox active polymers by electrosynthesis [6,7]. In this respect, we have also reported two types of such materials by the copolymerization of pentafluorophenyl thiophene-3-acetate as well as *N*-succinimido thiophene-3-acetate with 3-methylthiophene [8]. As expected, it was found that these electrically conducting polymers with pendant activated functional groups could easily and rapidly react with amino compounds to form modified electrodes [5,8].

In this work, three new thiophene derivatives substituted by activated ester groups were synthesized, which are characterized by different terminal ester groups and a long flexible alkylene spacer unit (undecylene) between the thiophene ring and the functional groups. This article deals with the synthesis of these monomers, their electropolymerization, and the characterization of the resulting electroactive polymers.

2. Experimental

2.1. Chemicals and reagents

3-Bromothiophene (Lancaster), pentafluorophenol (Fluka), 4-nitrophenol (Fluka), *N*-hydoxysuccinimide (Fluka), *N*,*N*′-dicyclohexylcarbodiimide (DCC, Merck), 2-aminoanthraquinone (Fluka) and bis-(diphenylphosphino-



i): CH_2=CH-$(CH_2)_9$-MgBr / Ni(dppp)Cl_2, ether, 50°C; ii): HBr / UV light; iii): KCN, ethanol / water, 90°C; iv): KOH, ethanol /water, 100°C; v): corresponding hydoxy compound, DCC, CH_2Cl_2, RT.

Scheme 2. Synthesis of the monomers **6a**–**6c**.

1,3-propane)nickel dichloride (Ni(dppp)Cl_2, Aldrich) were reagent grade and used as received. 10-Undecyl bromide was obtained from 10-undecenol (Fluka) according to the reported procedure in Ref. [9]. For the control experiment, (4-amino-2-oxabutyl) ferrocene was prepared [6]. All solvents used in the synthesis were distilled prior to use.

For electroanalysis in this work electrochemical grade acetonitrile (J.T. Baker) and tetrabutylammonium perchlorate (TBAP, Fluka) was used. Before each electrochemical experiment acetonitrile was once distilled over CaH_2 and the supporting electrolyte salt, TBAP, was dried in vacuo at 100°C.

2.2. Synthesis of the monomers **6a**–**6c**.

The new thiophene derivatives **6a**–**6c** were synthesized according to Scheme 2. The conversion from 3-bromothiophene (**1**) to carboxyl functionalized intermediate **5** was performed according to the method described in the literature [10,11]. The general procedure for the preparation of the monomers **6a**–**6c** from carboxyl functionalized thiophene **5** is as follows: 10 mmol 3-(11-carboxyundecyl)thiophene **5** and the corresponding phenol (pentafluorophenol, 4-nitrophenol or *N*-hydoxysuccinimide) were dissolved in 50 ml CH_2Cl_2 containing 3,6 ml pyridine. After 10 min electromagnetic stirring in an ice bath, 12 mmol DCC was added to this mixture. The reaction medium was kept for 24 h further at ambient temperature. Then, the white precipitate was filtered off and the filtrate was washed in turn with 3% HCl, 8% $NaHCO_3$ solution and water, and dried over $MgSO_4$. After the removal of the solvent under reduced pressure the crude product was collected. The purification was followed by silicagel column chromatography using hexane/ethyl acetate mixture as eluent.

4-Nitrophenyl 11-(3-thienyl)undecanecarboxylate (**6a**): colorless solid; yield: 90%; m.p. 64–65°C. ^{1}H n.m.r. ($CDCl_3$, ppm): 8.25 (dd; 2H, H-3″, H-5″), 7.25 (dd; 2H, H-2″, H-6″), 7.20 (m; 1H, H-5′), 6.92 (s; 1H, H-2′), 6.88 (d; 1H, H-4′), 2.56 (m; 4H, H-2, H-12), 1.72 (m; 2H, H-11), 1.60 (m; 2H, H-3), 1.28 (s, 14H, H4–H10). ^{13}C n.m.r. ($CDCl_3$, ppm): 171.21 (C-1), 155.48, 145.18, 143.14, 128.21, 125.09, 124.97, 122.36, 119.69 (C1″–C6″, C2′–C5′), 34.87, 43.26, 30.48, 30.27, 29.48, 29.35, 29.25, 29.14, 28.98, 25.41, 24.67 (C2–C12). MS (EI, *m*/*e*): 403 (M^+), 265 ($C_{16}H_{25}OS^+$), 111 ($C_6H_7S^+$), 97 ($C_5H_5S^+$). Anal. calcd for $C_{22}H_{29}O_4NS$ (403.3): C, 65.51; H, 7.19; S, 7.95. Found: C, 66.00; H, 7.16; S, 7.99.

Pentafluorophenyl 11-(3-thienyl)undecanecarboxylate (**6b**): colorless solid; yield: 67%; m.p. 34–35°C. ^{1}H n.m.r. ($CDCl_3$, ppm): 7.22 (m; 1H, H-5'), 6.92 (s; 1H, H-2′), 6.88 (d; 1H, H-4′), 2.60 (m; 4H, H-2, H-12), 1.96 (m; 2H, H-11), 1.60 (m; 2H, H-3), 1.28 (s; 14H, H4–H10). ^{13}C n.m.r. ($CDCl_3$, ppm): 169.56 (C-1), 143.22, 141.39, 139.28, 137.15, 135.82, 128.25, 124.99, 119.73 (C1″–C6″, C2′–C5′), 34.92, 33.30, 30.53, 30.26, 29.49, 29.42, 29.33, 29.09, 28.83, 25.45, 24.75 (C2–C12). MS (EI, *m*/*e*): 448 (M^+), 265 ($C_{16}H_{25}OS^+$), 111 ($C_6H_7S^+$), 97 ($C_5H_5S^+$). Anal. cald for $C_{22}H_{25}O_2F_5S$ (448.3): C, 58.94; H, 5.58; S, 7.15. Found: C, 58.74; H, 5.27; S, 6.79.

N-Succinimido 11-(3-thienyl)undecanecarboxylate (**6c**): colorless solid; yield: 75%; m.p. 72–73°C. ^{1}H n.m.r. ($CDCl_3$, ppm): 7.22 (m; 1H, H-5′), 6.92 (s; 1H, H-2′), 6.88 (d; 1H, H-3′), 2.80 (s; 4H, H-3″, H-4″), 2.60 (m: 4H, H-12, H-2), 1.72 (m; 2H, H-11), 1.60 (m; 2H, H-3), 1.26 (s; 14H, H3 – H10). ^{13}C n.m.r. ($CDCl_3$, ppm): 169.16 (C-1), 168.63 (C3″, C4″), 143.19, 128.23, 124.96, 119.68 (C2′–C5′), 30.86, 30.48, 30.19, 29.43, 29.35, 29.24, 28.99, 28.69, 25.51, 24.48 (C2–C12). MS (EI, *m*/*e*): 379 (M^+), 265 ($C_{16}H_{25}OS^+$), 111 ($C_6H_7S^+$), 97 ($C_5H_5S^+$). Anal. calcd for $C_{20}H_{29}O_4NS$ (379.3): C, 63.33; H, 7.65; S, 8.45. Found: C, 63.76; H, 7.49; S, 8.04.

2.3. Apparatus and procedure

For the electrochemical characterization of the monomers **6a**–**6c**, a three-electrode one compartment cell was employed. The working electrode was a platinum disc electrode (about 16 mm^2) polished with diamond paste before each experiment. A platinum wire was used as counter electrode, and Ag/AgCl electrode was chosen as reference.

The polymers were synthesized in the above-described three-electrode cell from a reaction medium involving 0.2 mol dm^{-3} corresponding monomer and 0.1 mol dm^{-3} TBAP in acetonitrile by successive scanning in the range of 0.0–1.9 V. The solutions were degassed by argon bubbling prior to polymerization which was performed at ambient temperature under an argon atmosphere. After the polymerization, the polymer modified electrode was rinsed with acetonitrile and transfered in another three-electrode cell containing monomer free electrolyte for characterization. All cyclovoltammetric experiments were carried out with a HEKA PG 28 potentiostat connected to a programmable function generator.

For spectroscopy analysis, a platinum sheet (about 7 cm^2) was used in preparative electrolyses. FTIR spectra were recorded with a Nicolet 800-FTIR spectrometer. SEM were taken on SEM 4000.

3. Results and discussion

3.1. Synthesis of the monomers

The synthetic route to obtain thiophene derivatives with different activated ester groups **6a**–**6c** is presented in Scheme 2. Firstly, according to the method described by Kumada et al. [10], an important central basic intermediate for the preparation of functionalized thiophenes, 3-(10-undecenyl)thiophene (**2**), was synthesized by the reaction of 3-bromothiophene (**1**) with the corresponding Grignard reagent in the presence of catalyst (Ni(dppp)Cl_2). Then, **2** was converted to 3-(11-bromoundecyl)thiophene (**3**) by anti-Markovnikov addition of HBr under UV light in

Table 1
Oxidation potentials of the monomers **6a-c** and electrochemical and spectroscopic data of the resulting polymers **P6a-c**

E_p^{oxd}(V)[a]						
Polymer	Monomer	Polymer	E_p^{red}(V)[b]	Q^{ord}/Q^{red} [c]	σ (S cm^{-1})[d]	λ (nm)[e]
P6a	1.96	0.74	0.64	1.03	0.02	468
P6b	1.96	0.90	0.84	1.08	0.008	465
P6c	1.95	0.86	0.80	1.03	0.003	457

[a] E_p^{oxd}: peak oxidatioin potential.
[b] E_p^{red}: peak reduction potential.
[c] Q^{oxd}/Q^{red}: ratio of the charge exchanged during oxidation and reduction process.
[d] σ: electrical conductivity measured by means of two-probe method
[e] λ: absorption maximum in UV/vis spectrum.

practically quantitative yield. The conversion of **3** to the carboxylic acid **5** was accomplished in two steps according to the procedure reported by Bäuerle et al. [11]: the reaction of **3** with potassium cyanide leading to the 3-(11-cyanoundecyl)thiophene **(4)** and subsequent saponification of the latter resulting in carboxylic acid **5**. The desired thiophenes functionalized with activated ester groups **6a**–**6c** were directly obtained from carboxylic acid **5** by reaction with the corresponding hydroxy compound in the presence of pyridine and DCC.

In this respect, Bäuerle described three analogous compounds [6,7]: *N*-[6-(3-thienyl)hexanoyloxy]pyrrolidine-2,5-dione, *N*-[6-(2,2′-bithien-3-yl)hexanoyloxy]-pyrrolidine-2,5-dione and *N*-[6-(2,2′:5′,2″-terthien-3-yl)hexanoyloxy]pyrrolidine-2,5-dione. Compared to these compounds, the synthesized monomers **6a**–**6c** are

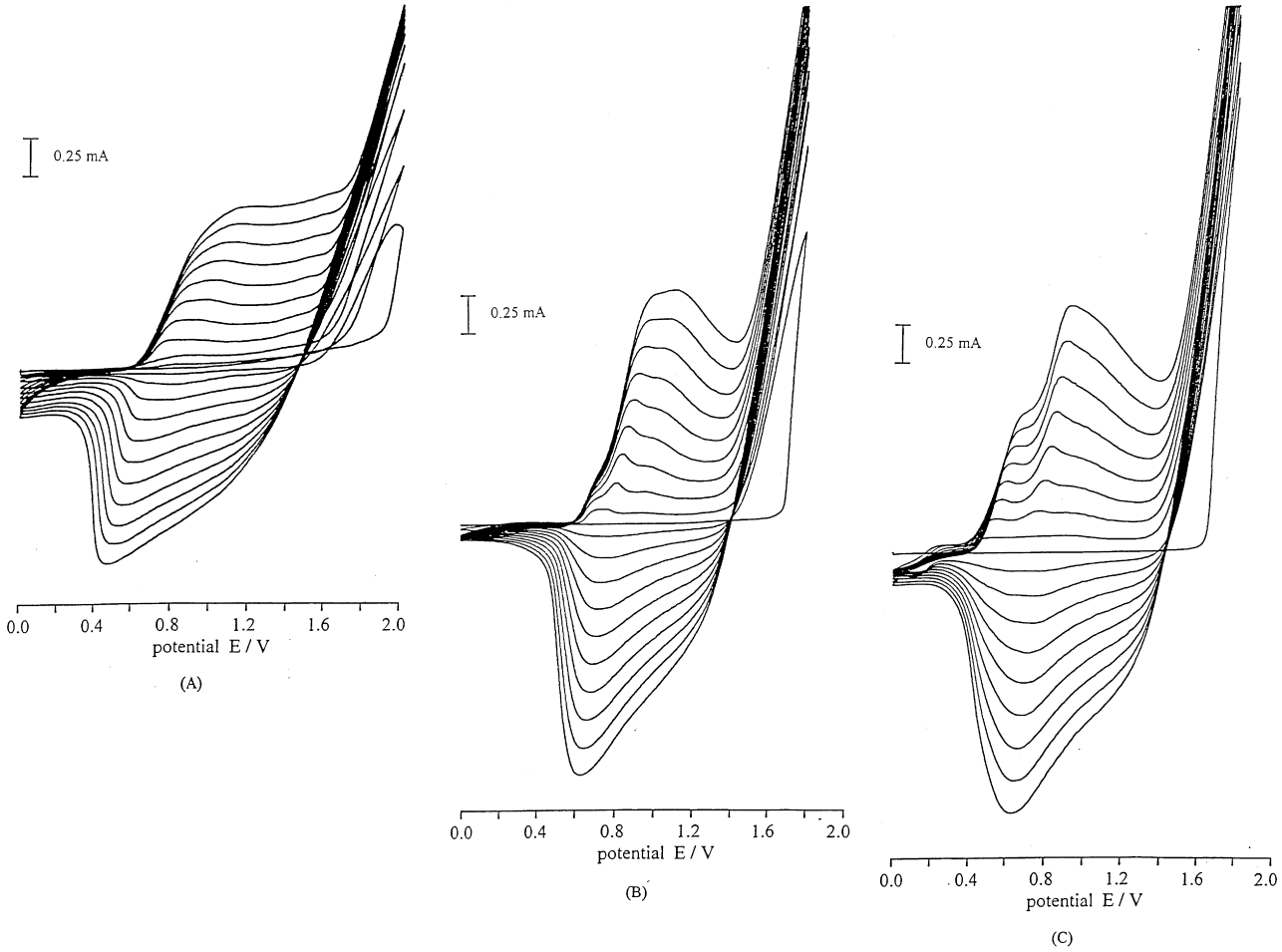


Fig. 1. Cyclic voltammograms recorded from a reaction medium involving 0.2 mol dm^{-3} monomer and 0.1 mol dm^{-3} TBAP in acetonitrile at a scan rate of 100 mV/s. (A) **6a**; (B) **6b**; and (C) **6c**.

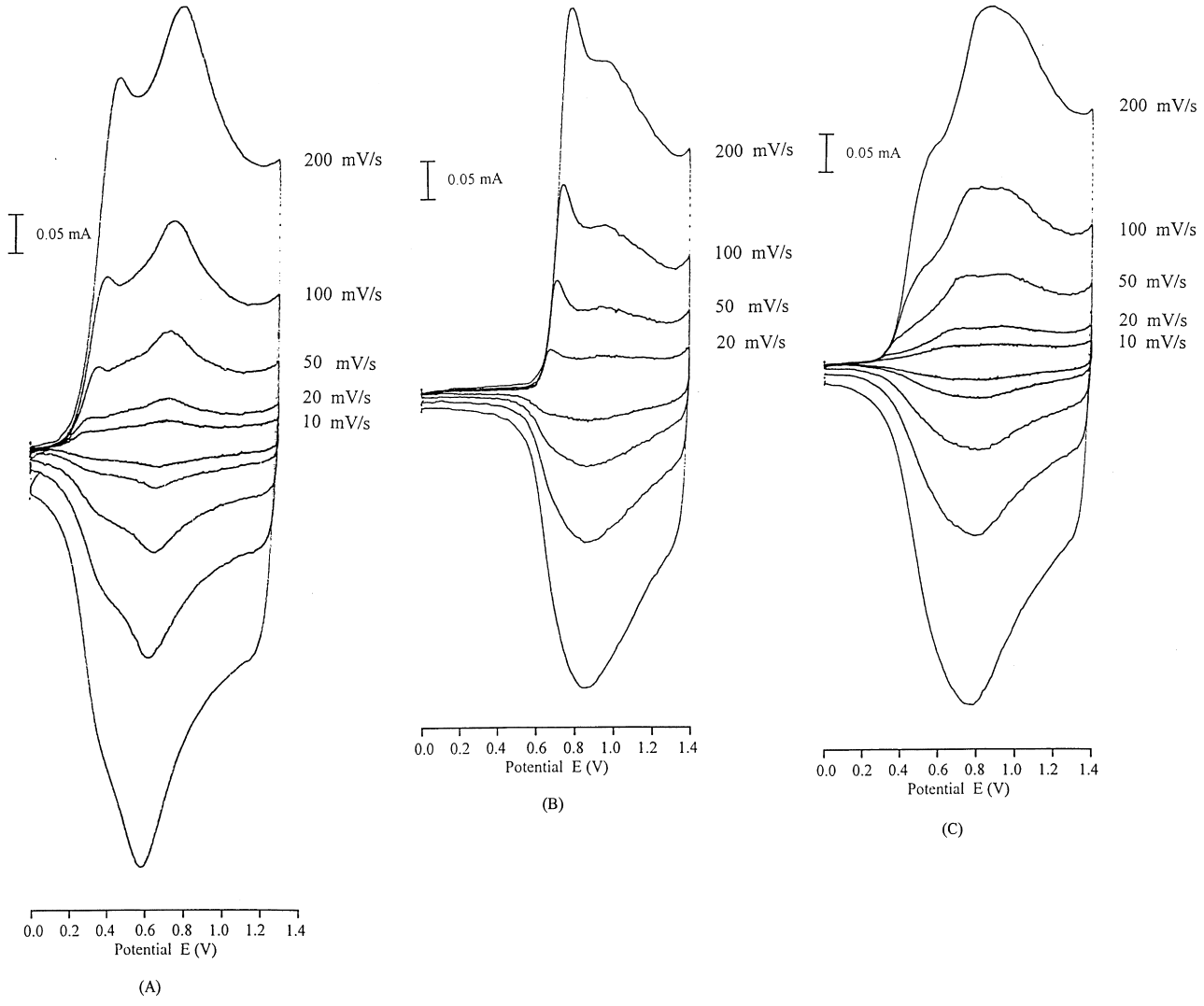


Fig. 2. Cyclic voltammograms of the obtained polymers in a monomer-free electrolytic medium at different scan rates. (A) **P6a**; (B) **P6b**; and (C) **P6c**.

characterized by different terminal activated ester groups and a longer spacer between the thiophene ring and the functional groups. Therefore, the polymeric materials electrogenerated from these monomers (with a longer spacer) should be favorable for the immobilization of big biomolecules and for the retention of their activity [12,13].

3.2. Electrochemistry

The oxidation potentials of the new synthesized monomers **6a**–**6c** were determined by cyclovoltammetry in acetonitrile containing 0.1 mol dm^{-3} TBAP. Low monomer concentration (0.001 mol dm^{-3}) was used in order to prevent the occurrence of polymerization. As expected, the electrochemical characterization of **6a**–**6c** reveal irreversible oxidation peaks in the cyclic voltammograms (CVs). Table 1 lists the oxidation potentials of **6a**–**6c**. A comparison of these values shows that due to the long alkylene spacer between the thiophene ring and the activated ester groups, no electrical effect of the functional groups on thiophene ring is observable. All monomers possess the same oxidation potential (see Table 1), comparable to those of non-functionalized alkylthiophenes [14].

In previous work [8], we reported the synthesis of two analogous monomers with a shorter spacer: pentafluorophenyl thiophene-3-acetate and *N*-succinimido thiophene-3-acetate. The electrooxidative polymerization of these monomers resulted in only non-electroactive polymeric films on the surfaces of working electrodes, suggesting that the coplanar conjugated polymer chains necessary for the electroactivity of polythiophene were not formed as a result of the steric hindrance of the bulky substituents.

In the cases of the synthesized new monomers **6a**–**6c**, however, this hindrance to form conjugated polymer chains was reduced by the introduction of a long flexible spacer containing eleven methylene groups between each functional group and the thiophene ring. As a consequence, their electropolymerization led to stable electoactive

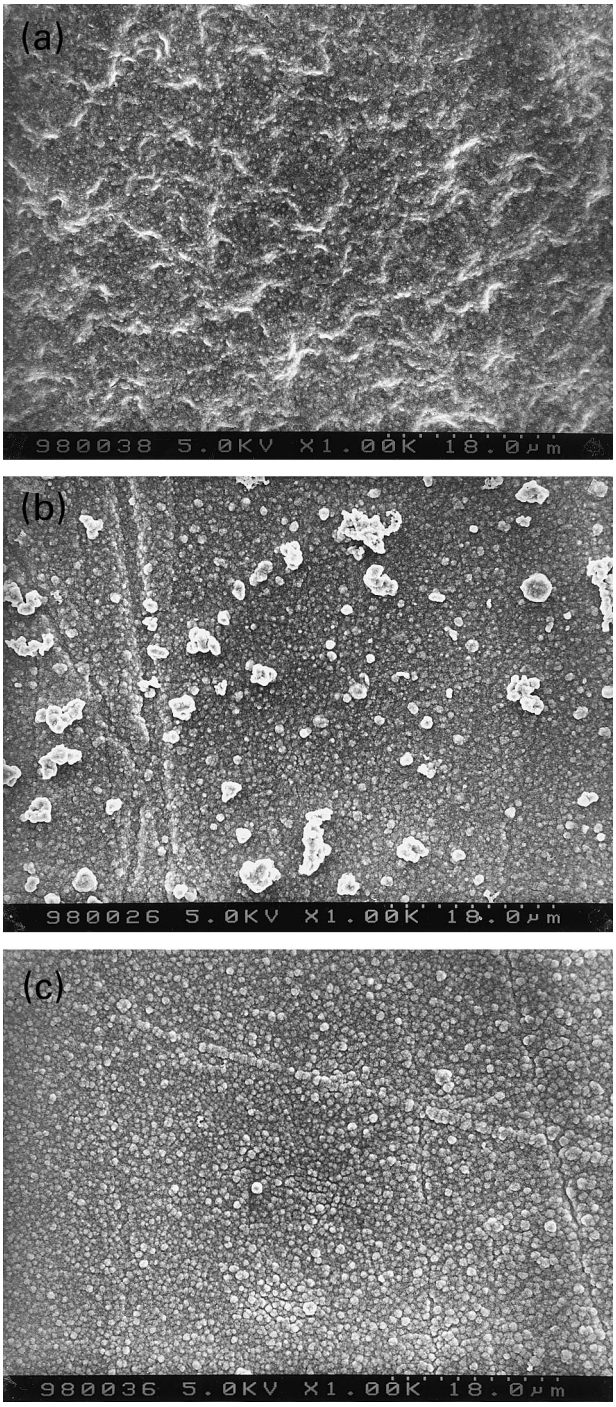


Fig. 3. SEM photographs of the resulting polymers: (a) **P6a**; (b) **P6b**; and (c) **P6c**.

polymers. Fig. 1 shows the multisweep cyclovoltammograms recorded from the reaction medium involving 0.2 mol dm^{-3} corresponding monomer and 0.1 mol dm^{-3} TBAP in acetonitrile. Upon successive potential scans, both anodic and cathodic waves in a potential lower than the oxidation potential of the corresponding monomer occurred, pointing out that the new redox material emerged on the working electrode surface. The steady increase of the current peaks with increasing cyclic number indicate that the conductivities of the deposited polymer **P6a**–**P6b** (**P** refers to polymer) are high enough to sustain the electropolymerization processes. Two oxidation components (0.6–0.8 V) were observed in the anodic waves in the cases of **6b** and **6c**, the latter becoming predominant upon repetitive cycling. This behavior is especially obvious in the cases of **6c**. The same phenomenon was also noticed in the electropolymerization of other functionalized thiophene derivatives. It was suggested that conformational changes in polythiophene backbone result in different conjugation lengths and hence, distinct oxidation peaks [6,15].

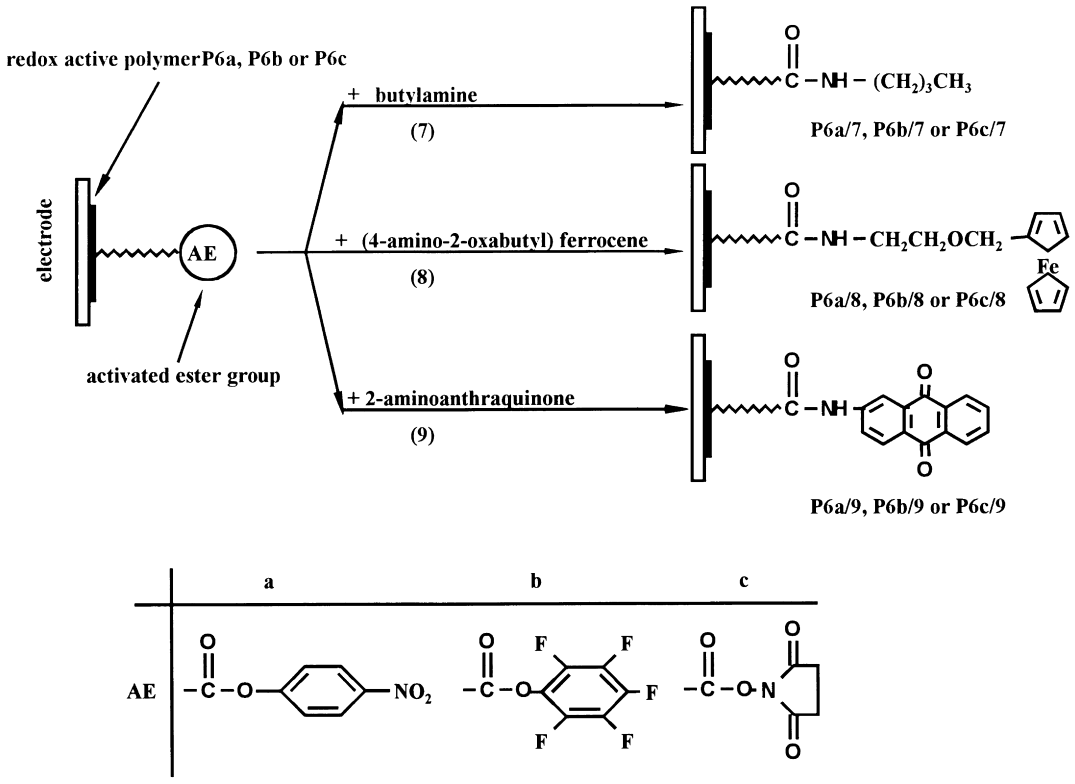
Fig. 2 displays the cyclovoltammograms of the resulting polymers **P6a**–**P6c** in a monomer-free electrolytic medium at different scan rates. As observed during polymerization process, besides a main anodic peak a shoulder appeared in all cases, which was explained in the literature for the presence of different effective conjugation lengths resulted from conformational changes in polymer main chains of deposited materials [6,15]. The reversible redox transitions of obtained new polymers **P6a**–**P6c** occurred in the potential range of 0.7–0.9 V, comparable to those of poly(3-decylthiophene) (1.03 V/SCE) [14]. As typical property of conjugated polyheterocycles, a strong electrochromism was observed for the polymers **P6a**–**P6c**. When the polymers are transferred to their oxidized form, the color of the polymer layers changes from dark brown (neutral form) to dark blue (oxidized form).

For both anodic and cathodic waves the peak currents change linearly with scan rates (see Fig. 2), indicating that the redox active species of the polymers **P6a**–**P6c** are affixed onto the electrode surfaces and the related reactions are not limited by diffusion [11,16]. The calculation from the coulometric data give the doping level of the polymers **P6a**–**P6c** in the range of 0.16–0.17, which is in very good agreement with the values obtained on polyalkylthiophenes. Further analysis of the charge passed in both oxidation and reduction processes of all synthesized polymers **P6a**–**P6c** led to the ratio of C_{oxd} to C_{red} in the range of 1.03–1.08. This value close to 1.0 indicates that the polymers **P6a**–**P6c** are highly electroactive materials.

Conductivity measurements on films of the polymers **P6a**–**P6c** in their oxidized forms by means of two-probe method gave values in the range of 10^{-3}–10^{-2} S cm^{-1} (see Table 1). Taking into account the fact that two-probe measurements gives usually lower values than four-probe technique [15], the obtained results indicate that polymer **P6a**–**P6c** possess a comparable conductivity with that of non-substituted polythiophene. UV/Vis spectroscopic characterizations of these polymers (neutral forms) deposited on ITO-electrode revealed the absorption maximum at around 460 nm (see Table 1).

3.3. Morphology

The morphology of obtained polymers **P6a**–**P6c** was



Scheme 3. Modification of polymers **P6a**–**P6b** with amino compounds.

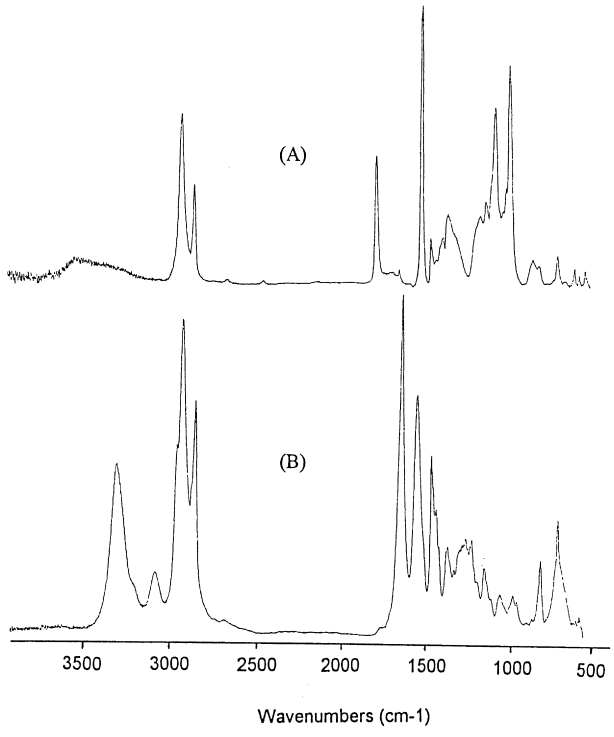


Fig. 4. FTIR spectra of polymer **P6b**: (A) freshly deposited on Pt; (B) after treatment with 0.1 mol dm^{-3} butylamine in acetonitrile for 3 min.

examined by SEM. Fig. 3 displays the SEM photographs of these polymers. It can be clearly seen that the electropolymerization of the monomers **6a**–**6c** produced a rather compact, homogeneous polymer surface. In the case of polymer **P6b**, however, scattered deposited particles on smooth polymer surface were observed.

3.4. Reactions on polymer surfaces

The correct incorporation of activated ester groups in the corresponding polymer films was proved by the FTIR method. In FTIR spectra of the polymers **P6a**–**P6b**, besides the absorption bands of long alkylene chain ($\nu = 2960$–$2850\ cm^{-1}$) and the thiophene system ($\nu = 1500$–$1400\ cm^{-1}$), the characteristic absorption of three carbonyl groups in polymer **P6c**, the nitro group in polymer **P6a** and the pentafluorophenyl group in polymer **P6b** were observed. These characteristic absorptions correspond to the IR bands of the corresponding monomers and are located at $\nu_{C=O} = 1735$, 1778 and $1812\ cm^{-1}$ (for polymer **P6c**); $\nu_{NO_2} = 1530$ and $1350\ cm^{-1}$ (for polymer **P6a**), and $\nu_{C-F} = 1004\ cm^{-1}$ (for polymer **P6b**).

The goal in our work lies in the development of new electroactive polymers with suitable anchoring sites for the covalent attachment of biomolecules. Therefore, using butylamine (**7**), (4-amino-2-oxabutyl) ferrocene (**8**) and 2-aminoanthraquinone (**9**) as model compounds, the activities of the pendant functional groups on polymers **P6a**–**P6b**

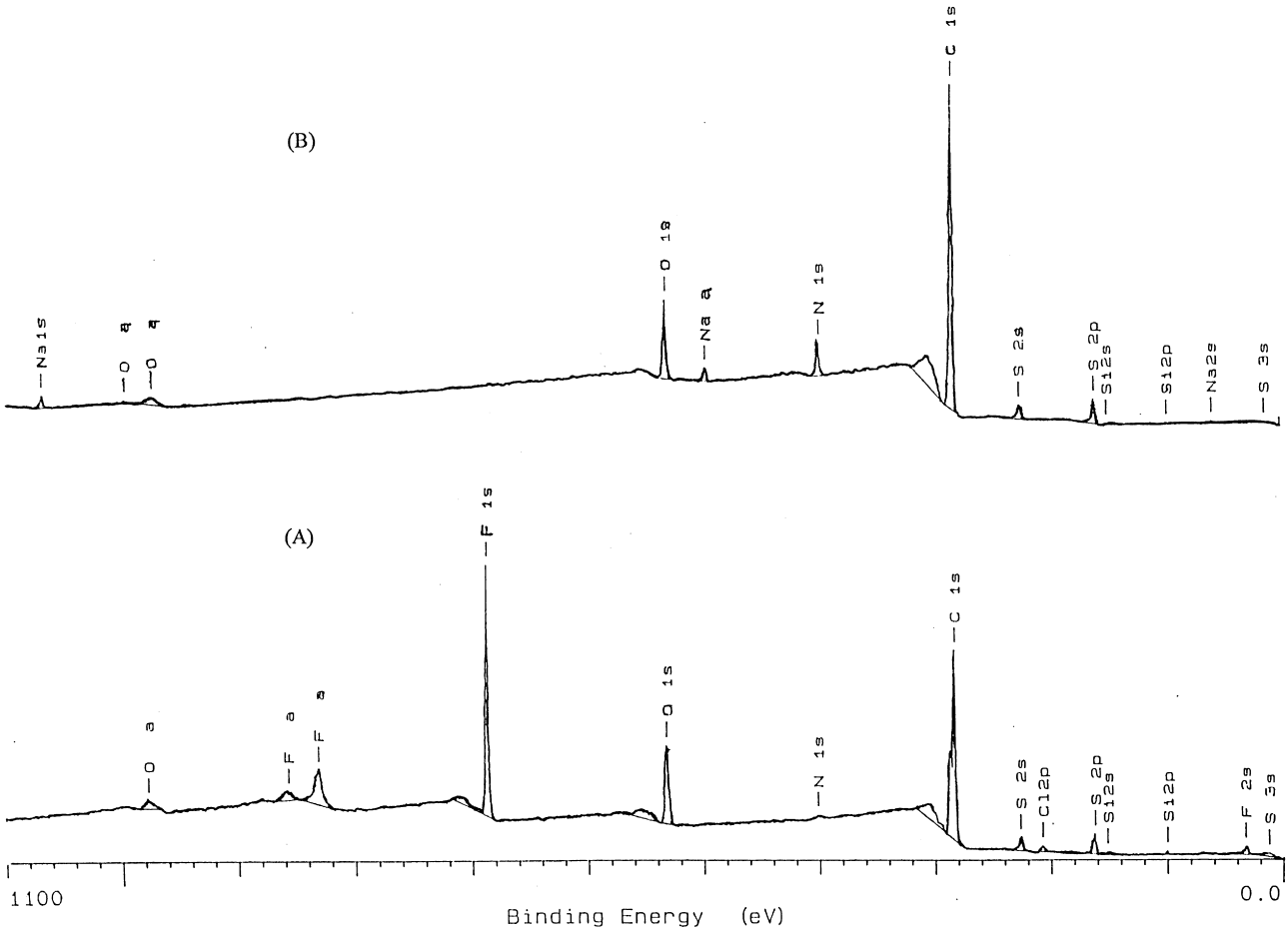


Fig. 5. ESCA spectra of polymer **P6b**: (A) freshly deposited on Pt; (B) after treatment with 0.1 mol dm^{-3} butylamine in acetonitrile for 3 min.

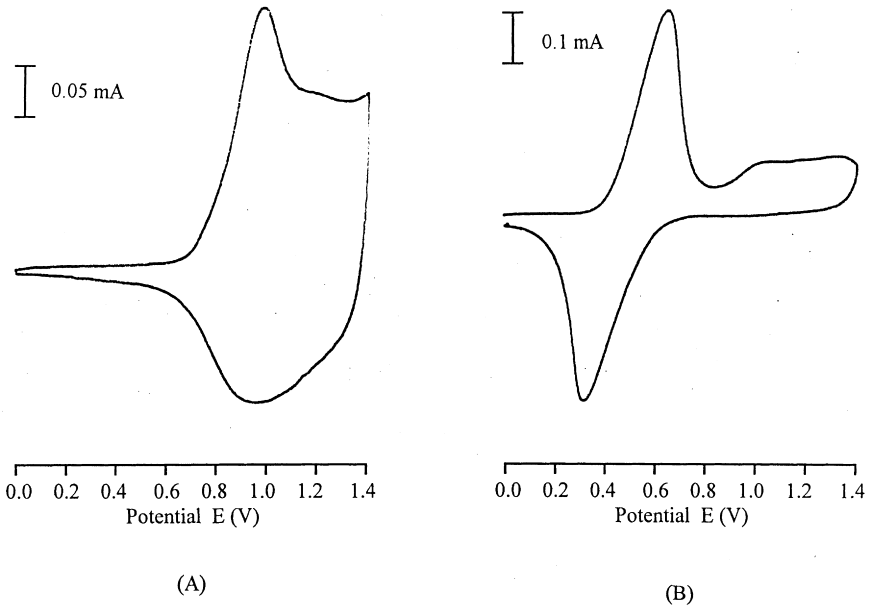


Fig. 6. Cyclic voltammograms of polymer **P6b** in acetonitrile/TBAP (0.1 mol dm^{-3}) at a scan rate of 100 mV s^{-1}: (A) freshly deposited polymer; (B) sample after modification with ((4-amino-2-oxabutyl)ferrocene) (3 min) in an acetonitrile solution (0.1 mol dm^{-3}).

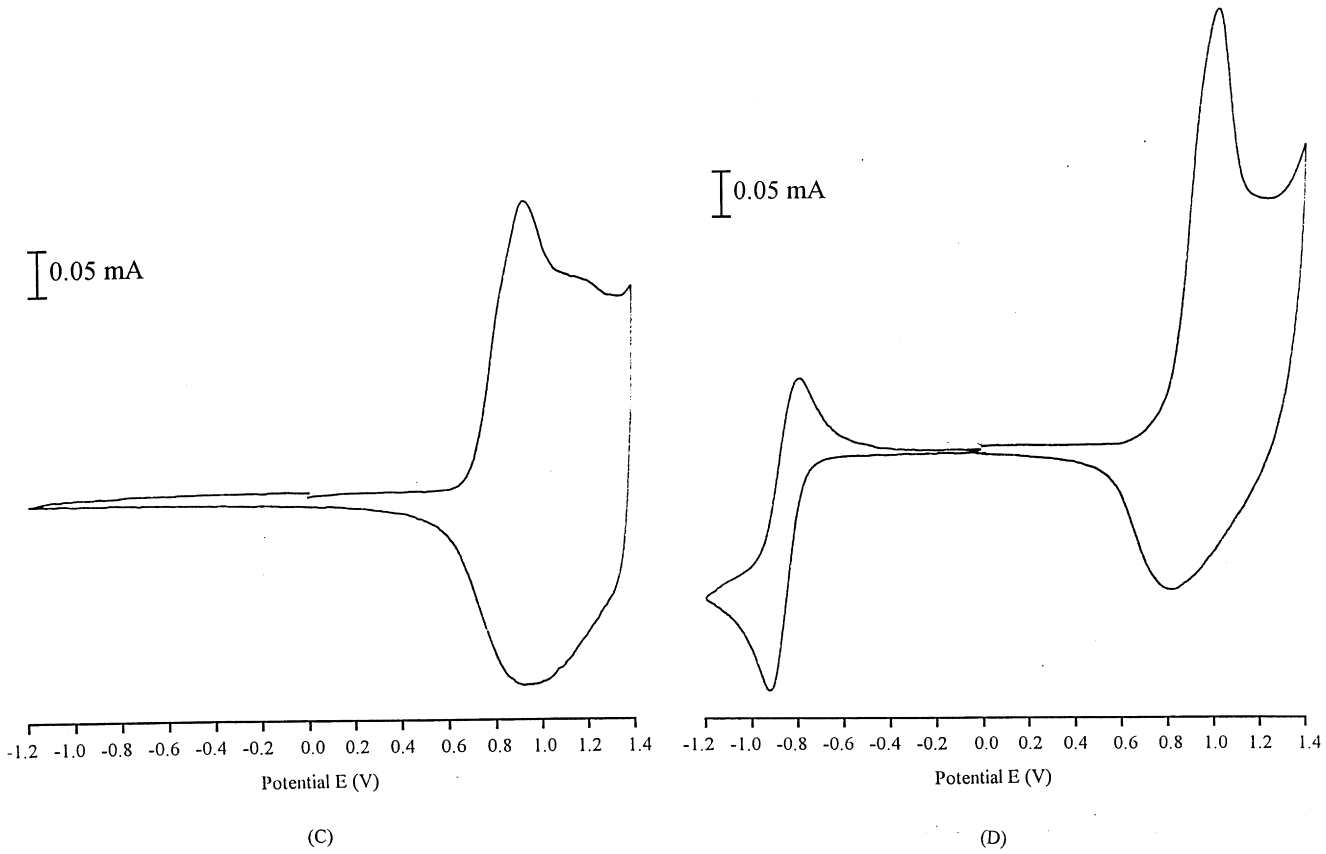


Fig. 7. Cyclic voltammograms of polymer **P6b** in acetonitrile/TBAP (0.1 mol dm^{-3}) at a scan rate of 100 mV s^{-1}(C): (A) freshly deposited polymer; (B) sample after modification with 2-aminanthraquinone (3 min) in an acetonitrile solution (0.1 mol dm^{-3}).

were examined and the related reactions were monitored by FTIR and ESCA methods.

In the proceeding experiments (see Scheme 3), we found that amino compounds react very easily with these pendant-activated ester groups and can be covalently attached onto polymer surfaces. This result is in agreement with the observations in literature [5,7]. As an illustrative example, Fig.4 shows the FTIR spectra of polymer **P6b** before (Fig. 4(A)) and after (Fig. 4(B)) treatment with 0.1 mol dm^{-3} acetonitrile solution of butylamine. By comparison of both spectra Fig. 4(A) and (B), it can be clearly seen that after the treatment the carbonyl stretching band was shifted from 1792 to 1641 cm^{-1} ($\nu_{C=O}$) and new absorption band at 3306 cm^{-1} (δ_{NH}) appeared, which is consistent with the formation of an amide bond. Also the complete loss (at least on the surface) of the pentafluorophenoxy group from polymer **P6b** was evidenced by the disappearance of the characteristic band at 1004 cm^{-1} (ν_{C-F}) from spectrum. Using the same reaction conditions (0.1 mol dm^{-3} acetonitrile solution of butylamine and 3 min reaction time), FTIR spectra of treated polymer **P6c** reveal a disappearance of the carbonyl bands of the ester and the succinimidooxy group ($\nu_{C=O} = 1735$, 1778 and 1812 cm^{-1}) and an appearance of new bands at 1640 and at 3306 cm^{-1} due to amide formation. In the case of polymer **P6a**, similar results were also observed.

The reactivity of the pendant activated ester groups as suitable sites for the covalent immobilization of amino compounds onto polymers **P6a**–**P6b** was also proved by ESCA spectra. As an illustrative example, in Fig. 5 the ESCA spectra of the samples **P6b** used for FTIR characterization are displayed. It clearly revealed that, after the treatment of polymer **P6b** with butylamine, fluorine (688.2 eV) completely disappeared and the signal of nitrogen atom from butylamine (396.8 eV) appeared, which is in good agreement with the results of FTIR studies.

As in the case of butylamine, the formation of amide bonds between the polymer backbones and the ferrocene groups as well as anthraquinone groups (see Scheme 3) was also confirmed by spectroscopic studies. These results were further proved by electrochemical characterization of the attached redox active ferrocene as well as quinone group. In Fig. 6(A) and (B) the electrochemical behavior of the freshly deposited **P6b** and the modified form **P6b/8** is displayed. It is clearly visible that there are two redox active subunits in CV of this modified polymer: the conjugated polythiophene backbone and the bound ferrocene group. The redox transition of the bound ferrocene occurred at the potentials: $E_p^{oxd} = 0.63$ V, $E_p^{red} = 0.30$ V, comparable to those of ferrocene detected by bare Pt-electrode. However, the bound redox groups exhibit a rather broad

peak separation: $\Delta E = 0.33$ V, which is much higher than that of free ferrocene (detected by bare Pt-electrode $\Delta E = 0.07$ V) [8]. This phenomenon was also observed in the literature and attributed to the kinetic limitation of the involved electron transfer process through the polymer layer [6]. The multi-sweep experiments showed that the modified polymer possesses a good electrochemical stability. After a small loss of the electroactivity of ferrocene signal from the first to the second scan, practically no change was observed in the following scans. This result also clearly indicates that the ferrocene groups are not physically adsorbed, but covalently bound.

A similar result was also achieved by using redox active 2-aminoanthraquinone (**9**) as model compound. After the immobilization of this compound to the synthesized polymers **P6a**–**P6b**, two electroactive subunits (the fixed quinone group in negative potential range and the polythiophene backbone in positive potential range) appeared in the CVs of the modified polymers **P6a/9**–**P6c/9**. Fig. 7(A) and (B) exhibit the representative CVs of the freshly deposited polymer **P6c** and the modified sample **P6c/9** in the potential range from −1.2 to +1.4 V. In comparison with the attached ferrocene group, whose redox active response occurred in the first scan cycle, however, several cyclic potential sweeps were required to access the redox activity of the bound quinone group. In the literature, this so-called 'break in' process was also observed by the investigation on both traditional polymer (polystyrol) and conducting polypyrrole bearing redox active groups [17,18]. The main reason responsible for this phenomenon was believed to be that the polymers have high electrical resistance. Taking into account the fact that polythiophene is conductive in its oxidized state, but semiconductive in its neutral form, our observed result with the attachment of ferrocene as well as anthraquinone groups is in good agreement with this explanation. This result also clearly point out that the polymers **P6a**–**P6c** are very suitable materials not only as conducting matrices, but also as normal insulated polymer matrices for the immobilization of redox active amino compounds.

4. Conclusions

Three new thiophene derivatives — 4-nitrophenyl 11-(3-thienyl)undecanecarboxylate; pentafluorophenyl 11-(3-thienyl)undecanecarboxylate; *N*-succinimido 11-(3-thienyl)undecanecarboxylate — have been synthesized. Electro-oxidative polymerization of these monomers in acetonitrile led to stable electroactive polymers, while the activated functional groups withstand the used polymerization conditions and were incorporated unchanged in the corresponding polymers. These polymers show the characteristic electrochemical behavior of poly(3-alkylthiophene)s with the reversible redox transition in the range of 0.7–0.9 V. UV/Vis characterization exhibit an absorption maximum at around 460 nm. Conductivity measurements on films of these polymers in their oxidized forms gave values in the range of 10^{-3}–10^{-2} S cm^{-1}. As expected, the pendant activated ester groups of these polymers react very easily with amino compounds to form modified electrodes. These results suggest that the synthesized new polymers could be used as electrically conducting carrier materials for the immobilization of biochemical interesting molecules.

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