Poly(alkylthiophene) with Pendant Dianiline Groups via Postpolymerization Functionalization: Preparation, Spectroscopic, and Spectroelectrochemical Characterization

K. Buga, K. Kepczynska, I. Kulszewicz-Bajer, and M. Zagórska*

Faculty of Chemistry, Warsaw University of Technology, 00-664 Warszawa, Noakowskiego 3, Poland

R. Demadrille and A. Pron

DRFMC, UMR 5819-SPrAM (CEA-CNRS-Univ. J. Fourier-Grenoble I), Laboratoire de Physique des Métaux Synthétiques, 38054 Grenoble Cedex 9, France

S. Quillard and S. Lefrant

Institut des Matériaux Jean Rouxel, 2 rue de la Houssinière, B.P. 32229,
44322 Nantes Cedex 3, France

Received July 15, 2003; Revised Manuscript Received November 28, 2003

ABSTRACT: Using postpolymerization functionalization, we have prepared a new solution-processable electroactive polymer combining electrochemical properties of poly(thiophene)s and oligoanilines. The elaborated procedure consists of three steps. First, 3-octylthiophene and ethyl 3-thiopheneacetate are copolymerized to give poly(3-octyl-2,5-thienylene-*co*-3-methylene-ethylcarboxylate-2,5-thienylene)—the precursor polymer. The precursor is then hydrolyzed, and in the last step, aniline dimer is attached to it via amidation reaction. UV−vis−NIR and Raman spectroelectrochemical studies combined with cyclic voltammetry show that, as expected, both poly(thienylene) main-chain and dianiline side groups can be oxidatively doped, the latter adopting, upon oxidation, the structure of semiquinone radical cation.

Introduction

Facile functionalization of poly(thiophene)s, i.e., polymers with the 2,5-thienylene repeat unit, stimulated extensive research on poly(thiophene)-based solution-processable conjugated polymers with tunable physicochemical properties.[1] The principal strategy consists, in this case, of branching side functional groups modifying electron density on the conjugated main chain and influencing in this manner not only electronic but also electrochemical properties of the polymer such as its oxidative or reductive doping potentials and others.[2−4] In the overwhelming majority of poly(thiophene) derivatives studied, the redox process of doping takes place in the π-conjugated system of the main chain whereas the substituent groups remain intact. In this perspective it seems interesting to branch electroactive side groups to the conjugated main chain. If, in addition, these side groups contain basic centers, spectroscopic, electrical, and electrochemical properties of such polymers can be tuned not only by the doping of the redox type but additionally by interactions of acid−base type. In the search for such polymers we have recently synthesized random copolymers of 3-alkylthiophene and thiophene functionalized with oligoanilines at the 3-position.[5] In this case long alkyl side groups ensure solution processability whereas the oligoaniline side chains introduce new electrochemistry. Unfortunately, the copolymerization route to these polymers is not convenient and introduces severe limits with respect to the content of 3-oligoaniline-2,5-thienylene units in the polymer chain. In particular, the obtained copolymers are only partially soluble, and the soluble high molecular weight fractions contain at the most one 3-oligoaniline-2,5-thienylene unit per 10 3-alkylthiophene units.

For this reason we have focused on the elaboration of an alternative procedure for the preparation of random copolymers containing oligoaniline pendant groups via postpolymerization functionalization which ensures significantly higher content of the oligoaniline side groups while retaining the solution processability of the polymer. This approach has already been used with success for branching other than oligoaniline side groups to conjugated polymers of poly(thiophene) family.[6−10] Our procedure developed in the course of this research can be briefly described as follows. We first copolymerize 3-alkylthiophene with thiophene functionalized with an acetate group at the 3-position. Ester side groups, present in the resulting copolymer, are then hydrolyzed to give carboxylic groups, and in the final step, oligoaniline groups are attached to the main poly(thiophene) chain via amidation reaction. The described reaction strategy is similar to that used by Welzel et al.,[11] who first obtained copolymers of 3-methylthiophene and thiophene-3-acetic acid using electrochemical oxidation and then postfunctionalized it with an amine containing long alkyl substituents via amidation reaction.

Contrary to the case described in ref 5, the oligoaniline side groups studied in this research are not in conjugation with the poly(2,5-thienylene) main chain because they are separated from it by a methylene amide group. Thus, both electroactive polymer segments may undergo oxidative doping separately. The advantage of the proposed system is based on the fact that the oligoaniline side chains constitute an inherent part

---

* Corresponding author: Tel 48-22-660 5584; e-mail zagorska@chemix.ch.pw.edu.pl.

10.1021/ma034997c CCC: $27.50

of the conductive polymer matrix which percolates and facilitates the electrochemical processes in the side groups even if they are not in conjugation with the conductive main chain.

In the paper we report on the preparation, spectroscopic characterization, and the UV−vis−NIR and Raman spectroelectrochemical behavior of solution-processable random copolymer containing dianiline side groups which are attached to the polymer main chain via postpolymerization functionalization. We limit ourselves to the redox chemistry of these new polymers; its acid−base behavior will be the subject of another publication.

Experimental Section

Reagents and Chemicals. 3-Octylthiophene was prepared from 3-bromothiophene by Grignard coupling as described elsewhere.[12] Ethyl 3-thiopheneacetate (98%, Aldrich) was vacuum distilled (66 °C, 2 mmHg) prior to its use. *N*-Phenyl-1,4-phenylenediamine (98%, Aldrich) was crystallized from water in the presence of $Na_2S_2O_5$. THF (pure, POCh Gliwice (Poland)) was dried over sodium and then vacuum distilled. CH_3NO_2 (97%, ROTH) and CCl_4 (pure for analysis. POCh Gliwice (Poland)) were dried over $CaCl_2$ and then distilled.

$FeCl_3$ (anhydrous, 98%, Fluka), 4-(dimethylamino)pyridine (abbreviated as DMAP) (99% Aldrich), *N*,*N*′-dicyclohexylcarbodiimide (abbreviated as DCC) (99%, Fluka), HCl (35−38%, pure for analysis), POCh Gliwice (Poland)), NaOH (pure for analysis POCh Gliwice (Poland)), and CH_3OH (pure for analysis POCh Gliwice (Poland)) were used as received.

Characterization Techniques. Both the precursor copolymer, i.e., poly(3-octyl-2,5-thienylene-*co*-3-methylene-ethylcarboxylate-2,5-thienylene), and the final copolymer containing aniline dimer side groups were identified by ^{1}H NMR and FTIR. In the latter case the elemental analysis was additionally performed. NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer with chloroform-*d* ($CDCl_3$) solvent.

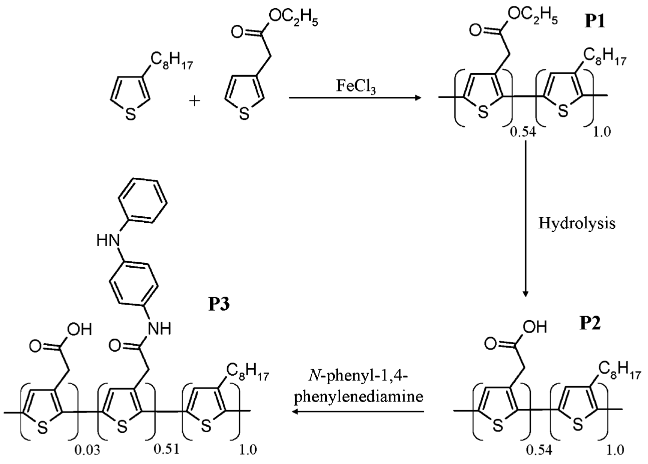
FTIR spectra of the synthesized polymers were recorded on a FTIR Bio-RAD FTS 165 spectrometer (wavenumber range: 400−4000 cm^{-1}; resolution: 2 cm^{-1}) either on free-standing films cast from chloroform or using the KBr pellet technique. UV−vis−NIR spectra of thin solid films or solutions in chloroform were recorded on a UV−vis Perkin-Elmer Lambda 2 spectrometer.

Molecular weight determinations of the synthesized polymers were measured using size exclusion chromatography (SEC) on a Shimadzu LC-10 AD chromatograph equipped with a Nucleogel M-10 column, using refractometric detection by RID-6A refractometer. THF was used as the eluent. The column temperature and the flow rate were fixed to 35 °C and 1 mL min^{-1}, respectively. The column was calibrated using polystyrene standards provided by Polymer Standards Service.

For cyclic voltammetry investigations a thin layer of the polymer was deposited on a platinum electrode by casting from chloroform solution. The experiments were carried out in a single compartment electrochemical cell using a Pt counter electrode and an Ag/0.1 M $AgNO_3$ in acetonitrile reference electrode. A 0.1 M solution of tetrabutylammonium tetrafluoroborate solution in acetonitrile was used as the electrolyte. The same electrolyte as well as the reference and counter electrodes were used in the case of UV−vis−NIR and Raman spectroelectrochemical studies. In the former case a thin polymer film was deposited on an ITO transparent working electrode whereas in the latter one on a platinum electrode. The UV−vis−NIR spectra were measured on a Lambda 2 Perkin-Elmer spectrometer whereas the Raman spectra were obtained using a FT Raman Bruker RFS 100 spectrometer with the near-IR excitation line (1064 nm).

Synthesis of Copolymers. The sequence of reactions, applied for the preparation of the functionalized polymers studied in this research, is depicted in Scheme 1. First, 3-octylthiophene and ethyl-3-thiopheneacetate are copolymerized to give poly(3-octyl-2,5-thienylene-*co*-3-methylene-ethylcarboxylate-2,5-thienylene) **P1**. Subsequent hydrolysis of the ester groups in **P1** yields **P2** which after grafting of *N*-phenyl-1,4-phenylenediamine via amidation reaction is converted into **P3**, i.e., a polymer in which the main chain consists of 2,5-thienylene groups to which alkyl and aniline dimer side groups are attached.

Scheme 1



The precursor polymer **P1** was obtained from 3-octylthiophene and ethyl-3-thiopheneacetate via oxidative polymerization using anhydrous $FeCl_3$ as the oxidizing/polymerizing agent using the procedure similar to that described in ref 13. In all preparations a 1:1 comonomer molar ratio was used. Typically 300 mg (1.76 mmol) of ethyl 3-thiopheneacetate and 345 mg (1.76 mmol) of 3-octylthiophene dissolved in 35 mL of CCl_4 were placed into a reaction flask. In a separate flask a solution of 2.28 g (14.08 mmol) of $FeCl_3$ in 15 mL of nitromethane was prepared. This solution was then slowly added, over the period of 15 min, to the comonomers solution, by means of a syringe. After the addition of the oxidant the reaction mixture turned black. The reaction was carried out for 1.5 h and was terminated by precipitation of the polymer in methanol. The resulting rubbery product was repeatedly washed with methanol until the filtrate was colorless. As formed, crude polymer always contains residual dopants of frequently unknown chemical nature and requires careful dedoping. The dedoping was carried out in an ammonia solution in methanol (1:5) for 2 h and was followed by soaking the polymer in pure methanol for 24 h. Finally, the dedoped polymer was dried until constant mass yielding 390 mg of the product (61% reaction yield).

P1 was then hydrolyzed to give the corresponding polyacid, **P2**. The applied hydrolysis procedure was a modification of the method described in ref 14. In the reaction 250 mg of the precursor polymer was added to 50 mL of 2 M aqueous NaOH solution. The mixture was then heated to the boiling temperature, and the reaction was carried out for 66 h under reflux. The product in a form of red suspension was separated by filtration on a Buchner funnel, stirred in 1 M HCl for few hours, and finally vacuum-dried. In each preparation a small part of poly(3-octyl-2,5-thienylene-*co*-3-methylene-ethylcarboxylate-2,5-thienylene) did not hydrolyze which was manifested by the presence of rather large black particles in the red suspension of the hydrolyzed product. These particles could however be relatively easily separated from the suspension.

The reaction of aniline dimer grafting was carried out under a dry nitrogen flow using a procedure frequently applied to the esterification or amidation reactions.[15] 78 mg of the hydrolyzed polymer was dissolved in 45 mL of dry THF. Then a solution of 84 mg (0.46 mmol) of aniline dimer in 5 mL of dry THF, 80.5 mg (0.66 mmol) of DCC, and 9.5 mg (0.08 mmol) of DMAP were consecutively added. The reaction was stopped after 18 h. Side reaction product in a form of dispersed red precipitate was separated from the reaction mixture by filtra-

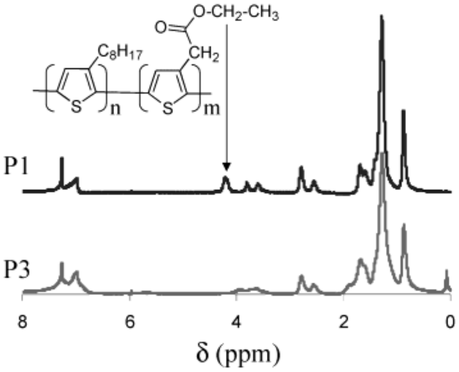


Figure 1. ^{1}H NMR spectra of the precursor polymer **P1** (upper spectrum) and the polymer with aniline dimer side groups **P3** (lower spectrum).

tion. In the next step THF was removed on a rotary evaporator, and the remaining polymer was repeatedly washed with methanol until the filtrate was colorless. Finally, the obtained polymer powder was dried in a vacuum line until constant mass.

Copolymerization of 3-octylthiophene with ethyl 3-thiopheneacetate, using 1:1 comonomer ratio, leads to a copolymer which is enriched in 3-alkylthiophene-2,5-thienylene units with respect to 3-methylene-ethylcarboxylate-2,5-thienylene ones. This is clearly evidenced in the ^{1}H NMR spectrum of the copolymerization product (see Figure 1). The copolymer composition can be, in this case, conveniently determined by the ratio of the integrated signals at 0.88 and 4.18 ppm. The former corresponds to the methyl group in the alkyl substituent whereas the latter to the methylene group adjacent to oxygen in the ester substituent. The ratio of the integral values for both signals is 180.7 to 64.8, which corresponds to the ratio of the octyl groups to the ester groups of 1 to 0.54. On the basis of the ^{1}H NMR data the formula of **P1** is presented in Scheme 1.

The enrichment in the 3-octyl-2,5-thienylene units with respect to the 3-methylene-ethylcarboxylate-2,5-thienylene ones in **P1** (1:0.54), as compared to the initial ratio of both comonomers in the reaction mixture (1:1), can be rationalized by the mechanism of the polymerization of thiophene and its derivatives. The active species in the initiation and propagation steps is, in this case, the thiophene radical cation. Since 3-octylthiophene is more easy to oxidize than ethyl-3-thiophene acetate, the concentration of the radical cations originating from the former should be higher in the reaction mixture, leading to a higher content of the 3-octyl-2,5-thienylene units in the resulting polymer chain. Note that the signal corresponding to the aromatic protons in the 2,5-thienylene unit (at ca. 7 ppm), which is a clear singlet in regioregular poly(3-alkylthiophene) homopolymers, is split, in the case of our copolymer, into several strongly overlapping lines. This is caused by slightly different chemical shift of the aromatic proton in both comonomers as well as by a random nature of the copolymer which inevitably leads to structurally nonequivalent sequences. The reactions of the hydrolysis of **P1** followed by grafting of aniline dimer to give **P3** are nearly quantitative as judged from the elemental analysis and ^{1}H NMR data. First, comparing the NMR spectra of **P1** and **P3**, it can be noticed that the signal at 4.18 ppm, characteristic of the presence of the ester group, essentially disappears upon the hydrolysis−aniline dimer grafting sequence of reactions (compare spectra in Figure 1). Second, the elemental analysis of **P3** can be reasonably well fitted assuming 100% hydrolysis of **P1** and 95% of the hydrolyzed sites participating in the grafting. This leads to the **P3** formula presented in Scheme 1.

It should be noted that acceptable fit of the elemental analysis can be obtained only if one assumes that the hydrophilic substituents in the above formula are solvated with two water molecules (calcd: % C = 68.77, % H = 7.36, % N = 3.83, % S = 12.95; found: % C = 67.48, % H = 7.33, % N = 3.48, % S = 11.76).

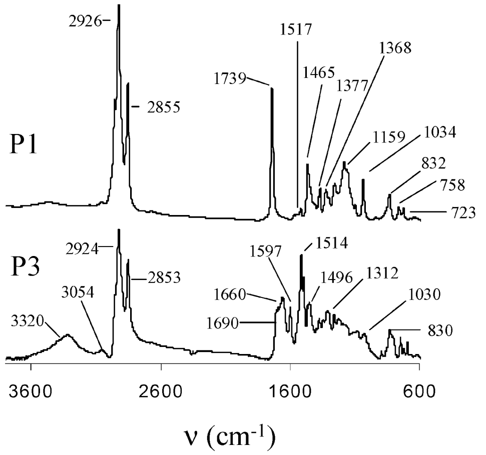


Figure 2. FTIR spectra of the precursor polymer **P1** (upper spectrum) and the polymer with aniline dimer side groups **P3** (lower spectrum).

In Figure 2, IR spectra of the precursor polymer **P1** (upper spectrum) and the polymer containing dianiline pendant groups **P3** (bottom spectrum) are compared. To a first approximation, the spectrum of **P1** can be considered as a superposition of the IR spectra of the corresponding homopolymers, i.e., poly(3-octyl-2,5-thienylene) and poly(3-methylene-ethylcarboxylate-2,5-thienylene). In particular, the bands at 1517, 1465, 1377, 832, and 723 cm^{-1} are due to the presence of 3-octyl-2,5-thienylene subunits.[16] The subunits with ester substituents give rise to the following bands unobserved in poly(3-octyl-2,5-thienylene): 1739, 1368, 1159, 1034, and 758 cm^{-1}. The bands in the spectral range 2850−2950 cm^{-1} are characteristic of C−H stretching deformations in saturated systems and originate from the aliphatic groups present in both subunits.

Grafting of aniline dimer to the conjugated backbone via the amidation reaction between the hydrolyzed form of **P1** and *N*-phenyl-1,4-phenylenediamine to give **P3** results in a significant change of the IR spectrum (compare spectra in Figure 2). The presence of the dimer is manifested by several bands characteristic of aromatic amines. At 3320 cm^{-1} a rather broad band ascribed to N−H stretching deformations appears which is accompanied by a band of lower intensity at 3054 cm^{-1} attributed to C−H stretching in the aromatic ring. Other important changes corroborating the grafting of aniline dimer involve the appearance of the band at 1597, 1514, and 1496 cm^{-1}. In the same time the bands characteristic of the ester group virtually disappear. A shift of the band corresponding to C=O stretching deformations from 1739 to 1660 cm^{-1} confirms the transformation of the ester type carbonyl group into the amide type one. The band at 1660 cm^{-1} is accompanied by two peaks of small intensity at 1690 and 1704 cm^{-1}, which can be ascribed to residual carboxylic groups originating from incomplete aniline dimer grafting.

Molecular weights of the precursor copolymer **P1** and the copolymer with dianiline pendant groups **P3** were measured using size exclusion chromatography with polystyrene standards. The number-average (M_n) and the polydispersity coefficient (D) determined for **P1** are 14.3 kDa and 5.52, respectively. This is not unexpected since large polydispersity is characteristic of poly(alkylthiophene)s obtained by chemical oxidative polymerization.[17] M_n of **P3** is only slightly lower (13.3 kDa), but the polydispersity coefficient is significantly lower (D = 3.78). Evidently in the sequence of the reactions (hydrolysis + dimer grafting) some fractionation of the copolymer occurs. It should be stressed here that the molecular weight determination by SEC using polystyrene standards must be treated only as a rough approximation. It is known that, in the range of molecular weights studied here, the SEC method usually overestimates the real M_n value by a factor of ∼2.[18,19]

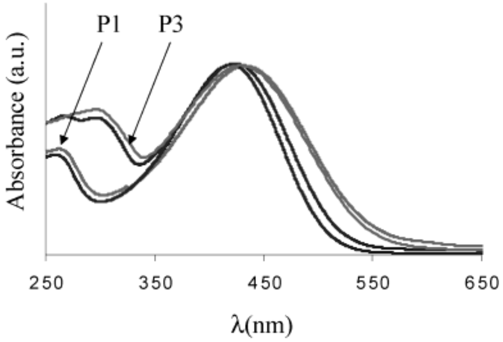


Figure 3. Solution ($CHCl_3$ solvent) and solid-state UV−vis spectra of the precursor polymer **P1** and and the polymer with aniline dimer side groups **P3**: black line, solution spectra; gray line, solid-state spectra.

Results and Discussion

Aniline dimer is an electrochemically active chromophore group. For this reason its grafting to the 2,5-thienylene backbone should modify spectroscopic, voltammetric, and spectroelectrochemical properties of the resulting polymer. In the subsequent discussion we will describe these changes.

In Figure 3 solution ($CHCl_3$ solvent) and solid-state spectra of **P1** and **P3** are compared. In the solution spectra of both copolymers a common absorption is observed at 421 and 423 nm, respectively, associated with the $\pi-\pi^*$ transition in the 2,5-thienylene ring. This band is hypsochromically shifted not only with respect to the analogous band in regioregular poly(3-alkylthiophene)s[20] but also with respect to regiorandom poly(3-alkylthiophene) obtained by oxidative polymerization.[21] Evidently the ester and the aniline dimer substituents lower the conjugation in the copolymer main chain. This observation is also consistent with a rather small solvatochromic effect observed in the case of **P1** and **P3**. Solvatochromism is a common phenomenon in poly(thiophene) derivatives and is caused by chain conformation changes toward lower planarity occurring upon the dissolution of the polymer.[22] It is spectroscopically manifested by a hypsochromic shift of the band originating from the $\pi-\pi^*$ transition when going from the solid-state spectra to the solution ones. It is obvious that more conjugated and by consequence more planar, in the solid state, chains should undergo more pronounced conformational changes upon the dissolution of the polymer and by consequence exhibit stronger solvatochromism. This is indeed the case since the strongest solvatochromic effect is observed for regioregular poly(3-alkylthiophene)s.[23] In both cases (**P1** and **P3**) the solvatochromic shift is small, of the order of 10 nm—the value which is even lower than that measured for regiorandom poly(3-alkylthiophene)s obtained by oxidative polymerization. In the solid-state spectra, for both **P1** and **P3**, the maximum of the $\pi-\pi^*$ transition band, ascribed to the conjugated polymer backbone, is located at 435 nm. This value is only slightly higher than the corresponding value recorded for poly(3-acetic acid-2,5-thienylene) homopolymer (425 nm) or its esters.[24] Thus, it is clear that ester or aromatic amine substituents significantly lower the polymer backbone planarity even in the case where they are grafted to only $^1/_3$ of the thienylene rings.

In the case of **P3**, the dimer grafted to the polymer chain is in its reduced state. Thus, in the spectral range investigated, only one electronic transition is expected for this chromophore, i.e., the $\pi-\pi^*$ transition in the aromatic ring.[25] The absorption band originating from this transition peaked at 300 nm and is clearly seen in the solution spectrum of **P3** and is accompanied by a band at 268 nm, present also in the spectrum of **P1**. In the solid-state spectrum both bands fuse into one broad, unsymmetric band (see Figure 3).

The extent of the chain torsion and by consequence the extent of the p-orbitals overlap influence not only the optical properties of the conjugated polymers but also their electrochemical properties and in particular the potential of their oxidative (p-type) or reductive (n-type) doping. In the case of homopolymers obtained by polymerization of thiophene derivatives two factors influence their voltammetric behavior to the largest extent, namely the chemical nature of the subsituent and its distribution along the polymer chain. The latter is closely related to the regioregularity of the macromolecules under investigation. Since **P1** can be considered as a random copolymer of poly(3-octyl-2,5-thienylene) and poly(3-methylene-ethylcarboxylate-2,5-thienylene), it is instructive to compare its voltammetric properties with those reported for the corresponding homopolymers. In regioregular head to tail−head to tail poly(alkylthiophene)s (>96% of HT−HT couplings), i.e., poly(3-alkylthiophene)s, the onset of the oxidative doping is manifested by a steep increase of the anodic current at the potential of ca.0.10 V vs Ag/Ag^+ reference electrode.[26] The onset of the oxidative doping in poly(alkylthiophene)s of the same stoichiometry but of different regioregularity, i.e., head to head−tail to tail (HH−TT) coupled poly(4,4′-dialkyl-2,2′-bithiophene)s, is shifted toward higher potential values by ca. 0.40 V.[21] The latter are more twisted, show much lower conjugation length, and by consequence are more difficult to oxidize. It was demonstrated in ref 26 that if a series of poly(3-alkylthiophene)s, with decreasing regioregularity, are tested in identical experimental conditions, the potential of the onset of the oxidative doping shifts toward higher E values when the fraction of HT−HT couplings decreases. In other words, the introduction of different than HT−HT coupling sequences lowers the conjugation and makes the oxidative doping more difficult. In the same time the slope of the anodic current at the onset of the doping decreases, which results in a broadening of the anodic peak.

In Figure 4a a typical cyclic voltammograms of **P1** is presented. It should be noted that the polymers described here exhibit a so-called “memory effect”, first described by Odin and Nechtschein,[27] which is manifested by a shift of the oxidative doping peak recorded during the first scan as compared to the same peak registered for the consecutive scans. This phenomenon is of kinetic nature and originates from slow chain relaxation processes accompanying the doping and dedoping of the polymer. The memory effect can be eliminated by the electrode pretreatment procedure consisting of few doping−dedoping cycles. In the case of **P1** the memory effect was efficiently eliminated since the two consecutive scans presented are essentially identical in their anodic part. We also notice that in its shape the voltammogram of **P1** is similar to that recorded for poly(3-methylene-ethylcarboxylate-2,5-thienylene) homopolymer.[28] It consists of two overlapping anodic peaks and one broad cathodic peak. The maxima of the anodic peaks (at $E = 0.41$ V and $E = 0.64$ V) are shifted toward significantly lower

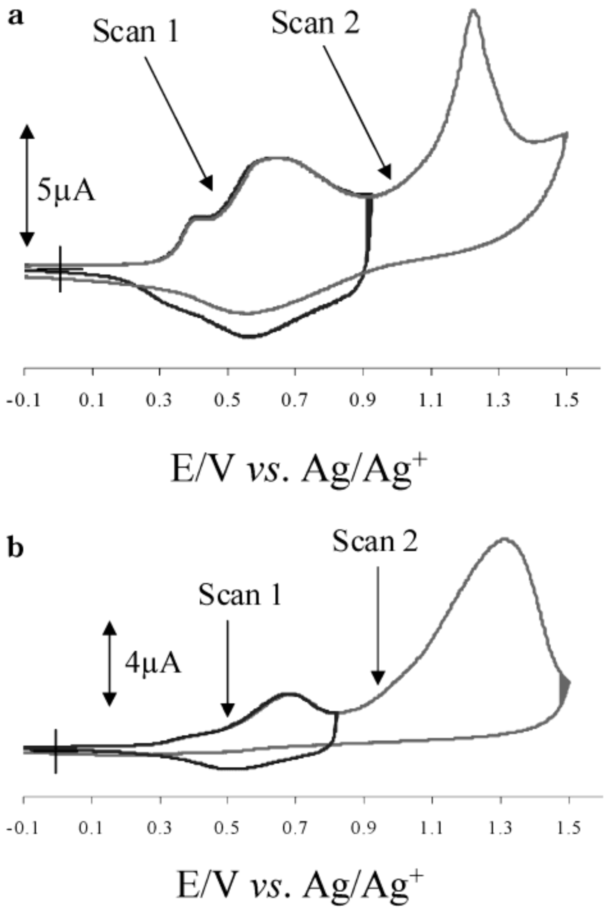
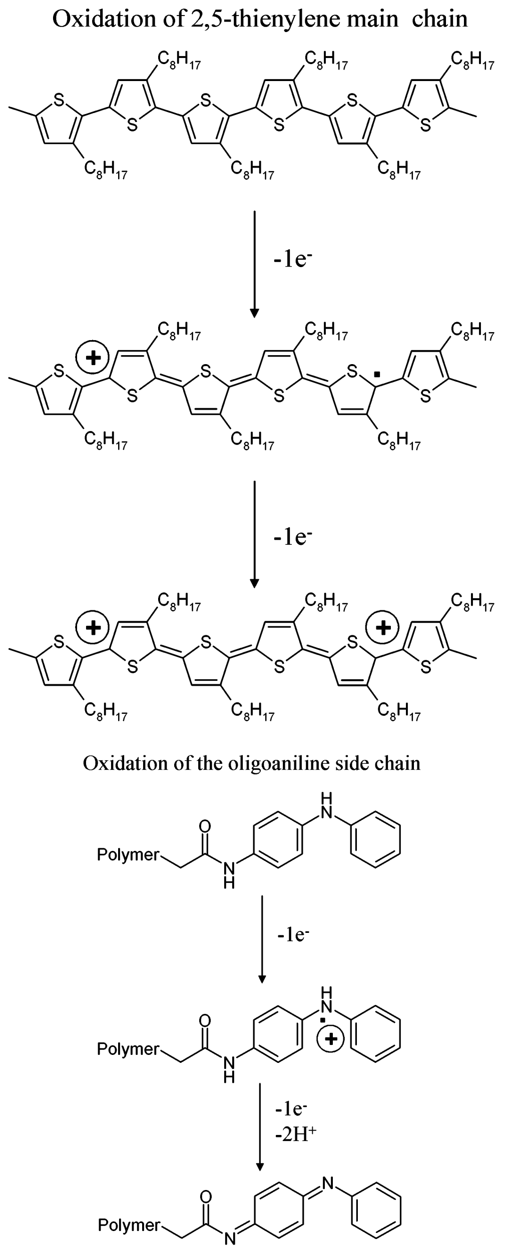


Figure 4. Cyclic voltammograms recorded in 0.1 M solution of Bu_4NBF_4 in acetonitrile, E vs Ag/Ag^+ reference electrode, scan rate 50 mV/s: (a) the precursor polymer **P1**; (b) the polymer with aniline dimer side groups **P3**.

Scheme 2



potentials, as compared to the case of poly(3-methylene-ethylcarboxylate-2,5-thienylene) homopolymer, by 0.19 and 0.10 V, respectively. In fact, as expected for the random copolymer, the positions of the observed peaks are intermediate between those reported for poly(3-methylene-ethylcarboxylate-2,5-thienylene) homopolymer and poly(octylthiophene) homopolymer of poor regioregularity.

The replacement of the ester groups with the dianiline ones leads to some modifications in the resulting voltammogram (Figure 4b). **P3** starts to oxidize at slightly lower potentials as compared to **P1** (0.20 vs 0.26 V). However the maximum of the first oxidation wave is not clearly defined due to its lower intensity and a strong overlap with the second one. Thus, the first oxidation process is characterized by a prepeak extending from 0.2 to 0.55 V with a poorly defined maximum. A clear maximum of the second peak is slightly shifted toward higher potentials (0.69 V) as compared to the case of **P1**. It should be noted here that **P3** contains two types of electrochemically oxidizable units−2,5-thienylene groups and dianiline side groups. During the potential scan the former is being oxidized to radical cations (polarons) and then to spinless dications (bipolarons) whereas the latter to a semiquinone type radical cation and then eventually to a spinless dication which, upon the release of two protons, is transformed into a base (see Scheme 2). In conducting polymer science the above-depicted process is termed "oxidative doping"; thus, it can be stated that in **P3** both the main chain units and the lateral oligoaniline units are being doped. The potentials of the oxidation of "free" aniline dimer, i.e., the dimer which is not attached to the poly(2,5-thienylene) chain, are reported in ref 29 as 0.64 and 0.82 V vs saturated calomel electrode (SCE). Since the potential of our reference electrode, measured vs SCE, is +0.34 V, these values correspond to $E = 0.30$ V and $E = 0.48$ V in our experiments. One may expect that branching of aniline dimer to the poly(2,5-thienylene) chain should not affect its oxidation potential to a large extent since both electroactive components are not in conjugation. Thus, it can be postulated that the dianiline side chains undergo oxidative doping in the potential range of the cyclic voltammetry prepeak. This postulate requires however spectroelectrochemical verification (vide infra).

If the potential scan is extended to potentials significantly exceeding the potentials of the oxidative doping, an overoxidation of the polymer occurs. The term "overoxidation" is used for an irreversible electrochemical process which, if studied by cyclic voltammetry, gives rise to a strong anodic peak at potentials which are more positive than those of the oxidative doping. Since this process is irreversible in both electrochemical and chemical senses, the anodic overoxidation peak has no cathodic counterpart.[30] Electrode polarization to potentials characteristic of the overoxidation leads to the destruction of the polymer conjugated backbone and by consequence total loss of its electrochemical activity. The overoxidation processes in polythiophene and its derivatives depend strongly on the composition of the electrolytic solution. They are facilitated by the presence of even minute amounts of water or other nucleophiles and proceed via nucleophilic attack on the radical cations present in the oxidatively doped polymer chains. Typical overoxidation processes may result in the formation of thiophene monoxide (sulfoxide), thiophene dioxide (sulfone) units in the polymer, heterocyclic ring scission, or even chain scission via the formation of hydroxyl, carbonyl, or carboxylic groups.[31]

The overoxidation peaks are clearly observed in the second scan as anodic peaks of strong intensity with maxima at 1.23 and 1.31 V for **P1** and **P3**, respectively. In the case of **P3** the overoxidation irreversibly destroys its electroactivity. Note that **P1** is more resistant toward the overoxidation. The ratio of integrated intensity of the overoxidation peak to the integrated intensity of the oxidative doping peaks is smaller in this case (compare parts a and b of Figure 4). Moreover, the polymer retains some residual electroactivity on the consecutive scan in the potential range from −0.25 to 1.50 V. This is consistent with the reported high electrochemical stability of the corresponding homopolymer.[28]

As it has already been stated, to clarify the problem of the sequence of dopings of the side chains and the main chain in **P3**, we have undertaken Raman and UV−vis−NIR spectroelectrochemical investigations of both **P1** and **P3** since in both methods doping-induced spectroscopic changes can be monitored separately for the thienylene and dianiline groups. It should be however stressed that the results of cyclic voltammetry and both UV−vis−NIR and Raman spectroelectrochemical investigations should be compared with caution. Cyclic voltammetry is a dynamic method in which the potential is swept at a constant rate whereas in spectroelectrochemical studies carried out in this research the spectra were recorded step by step at fixed potentials in “quasi-static” conditions, i.e., when anodic current is stabilized at a negligibly low level. Nevertheless, as in many other conjugated systems, the results of the spectroelectrochemical investigations could be correlated with cyclic voltammetry.

UV−vis−NIR spectroelectrochemical data registered for **P1** and **P3** are compared in Figure 5 and Figure 6. It is convenient to discuss the spectroelectrochemical behavior of **P1** in two potential intervals: (i) from $E = -0.20$ V to $E = 0.65$ V, i.e., from the potential at which the polymer is fully reduced to the potential slightly exceeding the second oxidative doping peak maximum, and (ii) from $E = 0.65$ V to $E = 1.00$ V, i.e., to the potential of the onset of the oxidative degradation.

In the first range of potentials the doping is characterized by a gradual bleaching of the band corresponding to the $\pi-\pi^*$ in the 2,5-thienylene ring (at 431 nm) with simultaneous growth of the two peaks in the near-infrared part of the spectrum associated with the formation of polaronic and/or bipolaronic states. In Figure 5a only the higher energetic band, peaked at ca. 780 nm, is clearly seen together with the onset of the second less energetic one. Thus, the observed spectral changes manifest the transition from the neutral state to the doped polaronic (bipolaronic) state. Note that the intensity of the first doping induced band reaches its maximum at the potential which almost coincides with the potential of the maximum of the second oxidative doping peak in the cyclic voltammetry. Above $E = 0.65$ V this first doping-induced band decreases in intensity and, for higher potentials, is transformed into a broad absorption tail extended toward the near-infrared (Figure 5b). These changes are characteristic of the transition from the bipolaron state to the quasi-metallic state.[32]

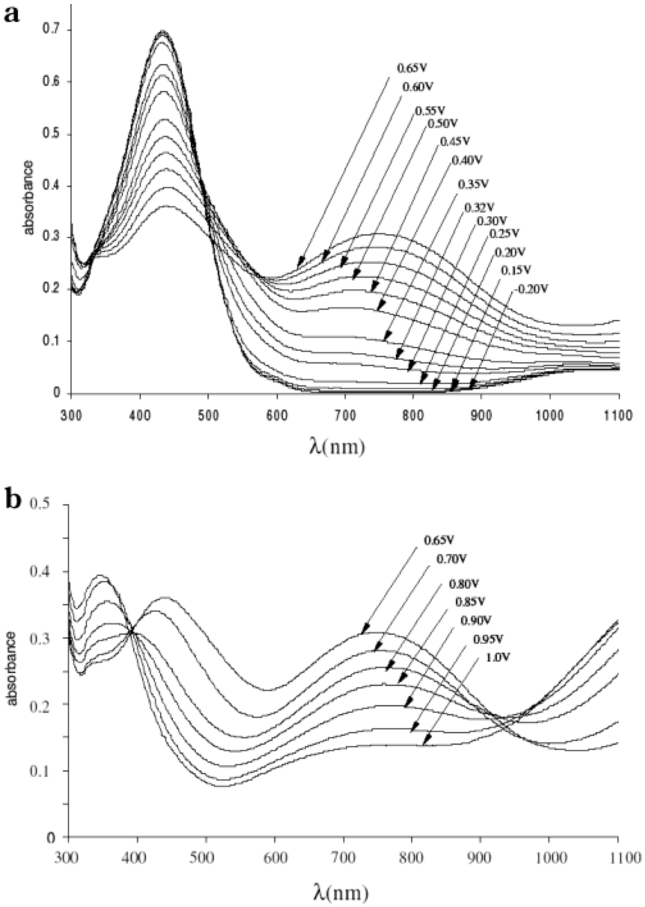


Figure 5. UV−vis−NIR (to 1100 nm) spectra, registered with increasing electrode potentials, for the precursor polymer **P1**. Electrolyte 0.1 M solution of Bu_4NBF_4 in acetonitrile, *E* vs Ag/Ag^+ reference electrode. (a) Potential range from −0.20 to +0.65 V. (b) Potential range from +0.65 to +1.00 V.

Before discussing the UV−vis−NIR spectroelectrochemical behavior of **P3**, it is instructive to describe the doping-induced spectral changes in a “free” aniline dimer, i.e., the dimer which is not attached to the poly(thienylene) main chain. The phenyl-capped dimer in its fully reduced state shows one absorption at 302 nm, whereas in its fully oxidized base form it exhibits an additional absorption band at 440 nm.[25] In its semioxidized doped form (semiquinone radical form) it shows two bands at 387 nm and ca. 700 nm.[25] Since, in **P3**, the dimer is not in conjugation with the main chain, one may expect that the positions of the bands in the “free” and “branched” dimers should be similar. This is rather unfortunate because, apart from the band at 302 nm, all other peaks typical of the dimer more or less coincide with the bands characteristic either of neutral

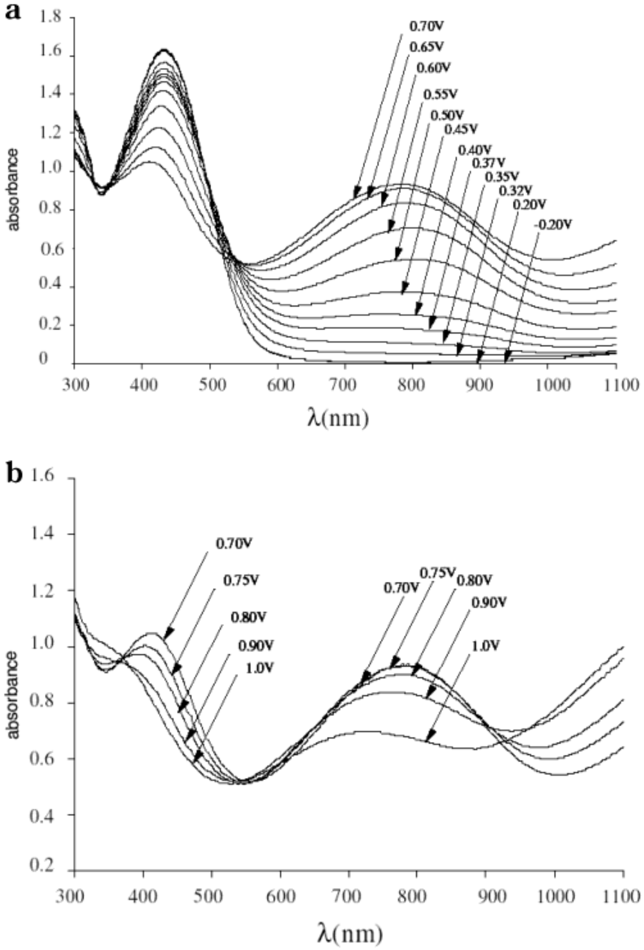


Figure 6. UV–vis–NIR (to 1100 nm) spectra, registered with increasing electrode potentials, for the polymer with aniline dimer side groups **P3**. Electrolyte 0.1 M solution of Bu_4NBF_4 in acetonitrile, E vs Ag/Ag^+ reference electrode. (a) Potential range from −0.20 to +0.70 V. (b) Potential range from +0.70 to +1.00 V.

or of doped poly(thienylene) chain. Thus, UV–vis–NIR spectroelectrochemistry is of limited use for the studies of the oxidative doping of the side groups in **P3**. Nevertheless, despite these limitations, some interesting information can be extracted from the evolution of the UV–vis–NIR spectra of **P3** induced by increasing electrode potential. Again, as in the case of **P1**, it is convenient to discuss the spectral changes in two potential intervals: from $E = -0.20$ V (fully reduced state) to $E = 0.70$ V (potential slightly exceeding the maximum of the oxidative doping peak in the cyclic voltammogram) and from $E = 0.70$ V to $E = 1.00$ V (the onset of oxidative degradation) (Figure 6a,b). First we notice that the oxidation starts at slightly higher potentials as compared to **P1** studied in the same experimental conditions and is manifested by simultaneous bleaching of the bands corresponding to the $\pi-\pi^*$ transitions in the thienylene ring of the main chain and in the phenylene ring of the aniline dimer. Note that for the latter only the low-energy part of the $\pi-\pi^*$ transition band is registered because of the spectral cut of the ITO electrode. The spectral changes corresponding to the oxidation of the poly(thienylene) main chain are rather clear and mimic those observed for **P1** (vide supra). The first doping-induced polaronic (bipolaronic) band reaches its maximum at the electrode potential higher by 50 mV with respect to the corresponding

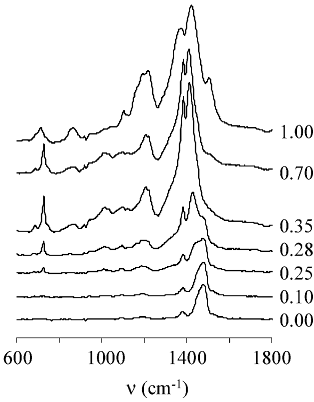


Figure 7. FT Raman spectra ($\lambda_{exc} = 1064$ nm), registered with increasing electrode potentials, for the precursor polymer **P1**. Electrolyte 0.1 M solution of Bu_4NBF_4 in acetonitrile, E vs Ag/Ag^+ reference electrode.

potential recorded for **P1**. This means that branching of aniline dimer slightly impedes the oxidation of the main chain despite the fact that both are not in conjugation. Analogously, as in the case of **P1**, at $E > 0.70$ V the first doping induced band is gradually transformed into an absorption tail extending toward the near-infrared part of the spectrum which is characteristic of the quasi-metallic state. One can however notice few signatures of the aniline dimer doping. First, a broad band is superimposed on the absorption tail with a maximum at ca. 700 nm, which can be ascribed to the dimer in the semiquinone radical (doped) form. Second, a shoulder in the vicinity of 350–380 nm is also characteristic of this form of the dimer.

The results of the UV–vis–NIR spectroelectrochemistry seem to indicate that both the main chain and the side chains are oxidatively doped at potentials exceeding the potential of the maximum of the second anodic peak in the cyclic voltammetry. We were tempted to verify this hypothesis using Raman spectroelectrochemistry since doped forms of both constituents of the polymer give very characteristic bands.

To clearly identify the lines originating from the doping of aniline dimer side chains, it is convenient to compare Raman spectroelectrochemical behavior of **P1** and **P3**. As expected, spectral changes in **P1**, imposed by increasing electrode potential, are very similar to those observed for poly(3-alkylthiophene)s, indicating that the ester group remains inert during the oxidative doping. **P1** in its neutral state is out of resonance for the excitation line used in these experiments ($\lambda_{exc} = 1064$ nm) since the value of the absorbance in this region of the spectrum is negligible (see Figure 5a). The following attributions can be proposed for the neutral polymer, i.e., at $E = 0.00$ V (see Figure 7).[33,34] The bands at 1522 and 1480 cm^{-1} are ascribed to $C_\alpha-C_\beta$ antisymmetric and symmetric stretchings in the 2,5-thienylene ring, respectively. The band at 1379 cm^{-1} originates from $C_\beta-C_\beta$ stretching whereas a weak and broad band in the vicinity of 1200 cm^{-1} can be considered as a superposition of two bands corresponding to $C_\alpha-C_{\alpha'}$ (inter-ring) antisymmetric and symmetric stretching deformations. As has already been stated, the undoped form of the polymer is out of resonance with the used excitation line. The resonant conditions improve, however, in the course of the doping since the absorbance at 1064 nm increases with increasing electrode potential (see Figure 5). This implies that the vibrations originating from the doped form should be detected even if the doped segments constitute only a small fraction of the polymer. This seems to be the case for **P1**. The doping-induced spectral changes start at $E = 0.25$ V. At this potential the anodic current in the cyclic voltammogram is still negligible (compare Figure 7 and Figure 4a). The most pronounced feature of the doping is a bathochromic shift of the band corresponding to $C_\alpha - C_\beta$ symmetric stretching vibrations by ca. 70 cm^{-1}, i.e., to 1410 cm^{-1}. This shift is usually interpreted in terms of the doping-induced bond order lowering with simultaneous transformation of the aromatic sequence of bonds to the quinoid type one. Note that in the potential range between $E = 0.25$ V and $E = 0.35$ V the $C_\alpha - C_\beta$ symmetric stretching bands originating from the undoped and doped polymer segments coexist. Beginning from $E = 0.35$ V only spectral features typical of the doped polymer can be detected despite the fact that, as judged from the cyclic voltammetry and UV−vis−NIR spectroelectrochemistry (see Figures 4a and 5a), the doping is not yet completed. Evidently, the bands originating from the doped segments dominate the spectrum because of the resonance effects, whereas the bands ascribed to the undoped segments are “invisible”. The spectrum remains essentially unchanged from $E = 0.35$ V to $E = 1.00$ V. Another significant spectral change, induced by the doping, is a relative increase of the bands originating from $C_\alpha - C_{\alpha'}$ inter-ring stretching with respect to all intra-ring stretching bands. As it has already been stated, for the copolymer studied two $C_\alpha - C_{\alpha'}$ interring bands are expected due to symmetric and antisymmetric stretchings. For the neutral state these bands are extremely weak: for example, at $E = 0.00$ V they strongly overlap to give one broad peak at 1200 cm^{-1}, whereas at $E = 0.10$ V two relatively well separated peaks of low intensity can be distinguished at 1186 and 1200 cm^{-1}. In the doped polymer both peaks not only grow in intensity but also undergo a hypsochromic shift to 1206 and 1220 cm^{-1}, consistent with the change of the bond sequence from aromatic to quinoid.[34] Note that, similarly as in the case of the $C_\alpha - C_\beta$ symmetric stretchings, in the potential range from $E = 0.25$ V to $E = 0.35$ V, bands originating from the undoped segments and the doped ones coexist. Finally, the band at 725 cm^{-1}, ascribed to $C_\alpha - S - C_\alpha$ ring deformations,[33,34] increases in intensity with increasing electrode potential. At $E = 1.00$ V the spectral lines broaden and, in almost all cases, change their position. This can be taken as an evidence of the beginning of irreversible oxidative degradation, especially in view of the fact that the cyclic voltammetry indicates the onset of the overoxidation peak at this potential.

In Figure 8 the results of the Raman spectroelectrochemical studies of **P3** are presented. First we notice that the doping-induced changes in the Raman bands originating from the 2,5-thienylene structural units are qualitatively the same as those observed during the electrochemical oxidation of **P1**. However, we notice that the onset of the doping process, as probed by Raman spectroscopy, occurs at $E = 0.35$ V, i.e., at the potential which is ca. 100 mV higher than the potential of the onset of the oxidative doping of **P1**. This is consistent with the results of and UV−vis−NIR spectroelectrochemistry and shows that the grafting of the aniline dimer side groups somehow impedes the oxidation of the polymer main chain. We also observe that at the potentials corresponding to the polymer neutral state, i.e., $E < 0.35$ V, only bands corresponding to the thienylene main chain are present with no trace of the peaks ascribed to the grafted aniline dimer. This is surprising since, as shown by ^1H NMR and elemental analysis, the aniline dimer is grafted to a third of the thienylene rings. Moreover, both constituents are out of resonance for $\lambda_{exc} = 1064$ nm. Thus, the origin of the thienylene bands enhancement with respect to those of aniline dimer is not clear at the present time. The bands characteristic of the aniline dimer appear as soon as the doping starts, i.e., at $E = 0.35$ V. Four most characteristic bands ascribed to the aniline dimer are as follows: 1329, 1570, 1584, and 1614 cm^{-1}. The evolution, with increasing potential, of the three latter is shown in more detail in the inset of Figure 8. The band at 1614 cm^{-1} is ascribed to C−C stretchings in the terminal ring of the dimer which is aromatic in character. Two bands at 1584 and 1570 cm^{-1} are characteristic of the para-substituted ring, which in the doped state has a semiquinone radical structure. It should be noted that in the Raman spectrum of the “free” phenyl-capped dimer, studied in ref 25, the last band is absent in the Raman spectrum and is registered only in the IR spectrum. This is a clear consequence of the exclusion rule because the molecule studied there is centrosymmetric. Our dimer attached to the poly(thienylene) main chain is not centrosymmetric, and as a result the mode at 1570 cm^{-1} is also active in Raman. Another indication of the semiquinone radical structure in the doped dimer is the presence of a clear band at 1329 cm^{-1} which, being intermediate in energy between the C=N stretchings of imine nitrogens and C−N stretchings in amine nitrogens, is usually attributed to C−N stretchings in the semiquinone radical unit.[35−37] The Raman spectroelectrochemical behavior is very consistent with the results of aniline dimer oxidation reported in ref 29 and proves that the oxidative doping of the side dianiline groups occurs within the potential range of the oxidation prepeak in the cyclic voltammetry, as postulated (vide supra).

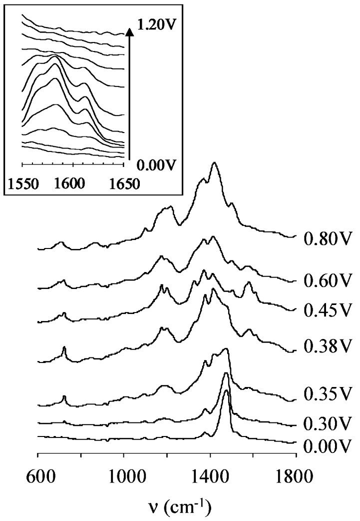


Figure 8. FT Raman spectra ($\lambda_{exc} = 1064$ nm), registered with increasing electrode potentials, for the polymer with aniline dimer side groups **P3**. Electrolyte 0.1 M solution of Bu_4NBF_4 in acetonitrile, E vs Ag/Ag^+ reference electrode.

One can notice that the bands characteristic of the doped dimer in the oxidation state of semiquinone radical cation grow in intensity up to $E = 0.45$ V, then they decrease, and finally disappear totally at

$E = 0.80$ V. There are two possible explanations of this behavior. First, one may expect that semiquinone radical cation is further oxidized to spinless dication which upon release of two protons gives fully oxidized form of the dimer in its base state (see Scheme 2). This form does not give rise to any absorption band in the NIR part of the spectrum and being out of resonance remains "invisible" if $\lambda_{exc} = 1064$ nm is used. An alternative explanation is based on the fact that the spectrum of **P3** at $E = 0.80$ V is essentially indistinguishable from the spectrum of **P1** recorded at $E = 1.00$ V. Since the latter exhibits features of partially overoxidized polymer (vide supra), it may be postulated the disappearance of the bands originating from the dimer is caused by the overoxidation effects. This means that although **P3** starts to dope at higher potentials than **P1**, it is more sensitive to overoxidation. This conclusion is fully consistent with the results of the cyclic voltammetry.

Conclusions

To summarize, by postfunctionalization grafting of aniline dimer on poly(3-octyl-2,5-thienylene-*co*-3-methylene-ethylcarboxylate-2,5-thienylene), we have prepared a new solution-processable polymer combining electrochemical activity of poly(thiophene)s and oligoanilines. In particular, both the poly(thienylene) main chain and dianiline side groups can be oxidatively doped as demonstrated by UV−vis−NIR and Raman spectroelectrochemistry.

Acknowledgment. This work was supported by the Committee of the Scientific Research in Poland (KBN Grant 4T09A 082 22).

References and Notes

(1) Roncali, J. *Chem. Rev.* **1992**, *92*, 711−738.
(2) Groenendaal, B. L.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481−494.
(3) Goldenberg, L. M.; Levesque, I.; Leclerc, M.; Petty, M. C. *J. Electroanal. Chem.* **1998**, *447*, 1−3.
(4) Zhu, S. S.; Kingsborough, R. P.; Swager, T. M. *J. Mater. Chem.* **1999**, *9*, 2133−2131.
(5) Dufour, B.; Rannou, P.; Travers, J. P.; Pron, A.; Zagorska, M.; Korc, G.; Kulszewicz-Bajer, I.; Quillard, S.; Lefrant, S. *Macromolecules* **2002**, *35*, 6112−6120.
(6) Bauerle, P.; Hiller, M.; Scheib, S.; Sokolowski, M.; Umbach, E. *Adv. Mater.* **1996**, *8*, 214−218.
(7) Besbes, M.; Trippe, G.; Levillain, E.; Mazari, M.; Le Derf, F.; Perepichka, I.; Derdour, A.; Gorgues, A.; Salle, M.; Roncali, J. *Adv. Mater.* **2001**, *13*, 1249−1252.
(8) Lowe, J.; Holdcroft, S. *Macromolecules* **1995**, *28*, 4608−4616.
(9) Zhai, L.; Pilston, R. L.; Zaiger, K. L.; Stokes, K. K.; McCullough, R. D. *Macromolecules* **2003**, *36*, 61−64.
(10) Lanzi, M.; Paganin, L.; Costa Bizzarrri, B.; Della Casa, C.; Fraleoni, A. *Macromol. Rapid Commun.* **2002**, *23*, 630−633.
(11) Welzel, H.-P.; Kossmehl, G.; Stein, H.-J.; Schneider, J.; Plieth, W. *Electrochim. Acta* **1995**, *32*, 577−584.
(12) Tamao, K.; Kodama, S.; Nakajima, S.; Kumada, M.; Minato, A.; Suzuki, A. *Tetrahedron* **1982**, *38*, 3347−3354.
(13) Costa Bizzarri, P. C.; Andreani, F.; Della Casa, C.; Lanzi, M.; Salatelli, E. *Synth. Met.* **1995**, *75*, 141−147.
(14) Kim, B.-S.; Chen, L.; Gong, J.; Osada, Y. *Macromolecules* **1999**, *32*, 3964−3969.
(15) Neises, B.; Steglich, W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 522−523.
(16) Garreau, S.; Leclerc, M.; Errien, N.; Louarn, G. *Macromolecules* **2003**, *36*, 692−697.
(17) Zagorska, M.; Kulszewicz-Bajer, I.; Pron, A.; Firlej, L.; Bernier, P.; Galtier, M. *Synth. Met.* **1991**, *45*, 385−393.
(18) Liu, J. S.; Loewe, R. S.; McCullough, R. D. *Macromolecules* **1999**, *32*, 5777−5785.
(19) Izumi, T.; Kobashi, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2003**, *125*, 5286−5287.
(20) McCullough, R. D.; Tristam-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910−4911.
(21) Lapkowski, M.; Zagórska, M.; Kulszewicz-Bajer, I.; Koziel, K.; Pron, A. *J. Electroanal. Chem.* **1991**, *310*, 57−70.
(22) See, for example: Inganäs, O. In *Hanbook of Organic Conductive Molecules and Polymers*; Nalwa, H., Ed.; Wiley & Sons: New York, 1997; Vol. 3, p 785.
(23) Trznadel, M.; Pron, A.; Zagorska, M.; Chrzaszcz, R.; Pielichowski, J. *Macromolecules* **1998**, *31*, 5051−5058.
(24) Royappa, A. T.; Rubner, M. F. *Langmuir* **1992**, *8*, 3168−3177.
(25) Boyer, M. I.; Quillard, S.; Louarn, G.; Froyer, G.; Lefrant, S. *J. Phys. Chem. B* **2000**, *104*, 8952−8961.
(26) Skompska, M.; Szkurłat, A. *Electrochim. Acta* **2001**, *46*, 4007−4015.
(27) Odin, C.; Nechtschein, M. *Phys. Rev. Lett.* **1991**, *67*, 1114−1117.
(28) Li, F.; Albery, W. J. *J. Electroanal. Chem.* **1991**, *302*, 279−284.
(29) McCoy, C. H.; Lorkovic, I.; Wrighton, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 6934−6942.
(30) Krische, B.; Zagórska, M. *Synth. Met.* **1989**, *28*, C257−C262.
(31) Barsch, U.; Beck, F. *Electrochim. Acta* **1996**, *41*, 1761−1771.
(32) Chung, T. C.; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phys. Rev. B* **1984**, *30*, 702−710.
(33) Louarn, G.; Trznadel, M.; Buisson, J. P.; Laska, J.; Pron, A.; Lapkowski, M.; Lefrant, S. *J. Phys. Chem.* **1996**, *100*, 12532−12539.
(34) Trznadel, M.; Zagórska, M.; Lapkowski, M.; Louarn, G.; Lefrant, S.; Pron, A. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1387−1393.
(35) Boyer, M. I.; Quillard, S.; Cochet, M.; Louarn, G.; Lefrant, S. *Electrochim. Acta* **1999**, *44*, 1981−1987.
(36) Lapkowski, M.; Berrada, K.; Quillard, S.; Louarn, G.; Lefrant, S.; Pron, A. *Macromolecules* **1995**, *28*, 1233−1238.
(37) Colomban, P.; Folch, S.; Gruger, A. *Macromolecules* **1999**, *32*, 3080−3092.

MA034997C