6112 *Macromolecules* **2002,** *35,* 6112−6120

Spectroscopic and Spectroelectrochemical Properties of a Poly(alkylthiophene)−Oligoaniline Hybrid Polymer

B. Dufour, P. Rannou, J. P. Travers, and A. Pron*

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

M. Zagórska, G. Korc, and I. Kulszewicz-Bajer

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

S. Quillard and S. Lefrant

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

Received January 7, 2002; Revised Manuscript Received May 16, 2002

ABSTRACT: By copolymerization of 3-octylthiophene with thiophene containing aniline tetramer in the 3-position we have prepared a hybrid copolymer, poly(3-octyl-2,5-thienylene-*co*-3-oligoaniline-2,5-thienylene), exhibiting very interesting spectroscopic and spectroelectrochemical properties. The UV−vis−NIR spectrum of this new hybrid copolymer, in addition to the band ascribed to the $\pi-\pi^*$ transition in the poly(2,5-thienylene) chain, shows two bands at 330 nm and ca. 580 nm which can be attributed to the transitions in the pendant oligoaniline groups, namely to the $\pi-\pi^*$ transition in the benzoid ring and to the excitonic-type transition between the HOMO orbital of the benzoid ring and the LUMO orbital of the quinoid ring. Electrochemical activity of poly(3-octyl-2,5-thienylene-*co*-3-oligoaniline-2,5-thienylene) was tested in nonaqueous electrolytes combining cyclic voltammetry, UV−vis−NIR spectroelectrochemistry, and Raman spectroelectrochemistry. All techniques unequivocally show that both the oligoaniline side chains and the poly(2,5-thienylene) main chain can be electrochemically doped. The doping starts by the oxidation of aniline tetramer substituents and is followed by the oxidation of the poly(2,5-thienylene) main chain. Because of strong resonance effect Raman spectroelectrochemistry turned out to be a very selective probe of the polymer doping. The blue excitation line probes selectively the vibrations originating from undoped segments of the poly(2,5-thienylene) main chain whereas the red one probes only the undoped and doped oligoaniline substituents. The infrared excitation line enhances resonantly signals due to vibration of the doped parts of the polymer and reveals the sequence of doping. Protonation of pending oligoaniline groups with diphenyl phosphate lowers the potential of the onset of the doping as revealed by cyclic voltammetry and UV−vis−NIR spectroelectrochemistry.

Introduction

Functionalized poly(thiophene)s constitute a large family of polymers with interesting electronic and electrochemical properties.[1] Nearly 16 years ago, it was demonstrated that poly(thiophene)s can be rendered soluble in the neutral (undoped) state by branching long flexible alkyl substitutents to the stiff polyconjugated 2,5-thienylene chain.[2] In the years which followed, soluble poly(alkylthiophene)s of different types of regioregularity were synthesized,[3−6] some of them showing, in the doped state, conductivities exceeding 10^3 S/cm.[7,8] Poly(alkoxythiophene)s were also extensively studied mainly because of the fact that the presence of the electrodonating group in side chains lowers the oxidation potential of the polymer and improves its stability in the doped state. Indeed poly(3,4-ethylenedioxythiophene) is one of the most stable conducting polymers, and for this reason it was commercialized by Bayer.[9]

Several other functional groups were attached to the poly(2,5-thienylene) backbone including side groups containing nonlinear optical (NLO) chromophores of nitroazobenzene type,[10,11] metal complexing groups such as crown ethers,[12] calixarenes,[13] porphyrins,[14] and others.

Inspired by this research directed toward the elaboration of multifunctional poly(thiophene)s, we have prepared a soluble copolymer consisting of 3-alkyl-2,5-thienylene units and 2,5-thienylene units functionalized with aniline tetramer. Several interesting spectroscopic and spectroelectrochemical features are expected for such a polymer. First, two types of strong chromophores are present in the system (2,5-thienylene and oligoaniline groups). Second, both chromophores can be electrochemically doped, and such doping results in significant changes of their electronic spectra. The doping can therefore be spectroscopically monitored in an appropriately designed UV−vis spectroelectrochemical experiment. Third, the electrochemical doping leads not only to chain geometry changes and force constants alteration but also to the modification of the resonance conditions for Raman scattering. Thus, Raman spectroelectrochemical response should, in this case, provide important information concerning the doping phenomenon, unobtainable by other spectroscopic methods.

There exists only one report on incorporation of aniline tetramer into the main chain of an electroactive

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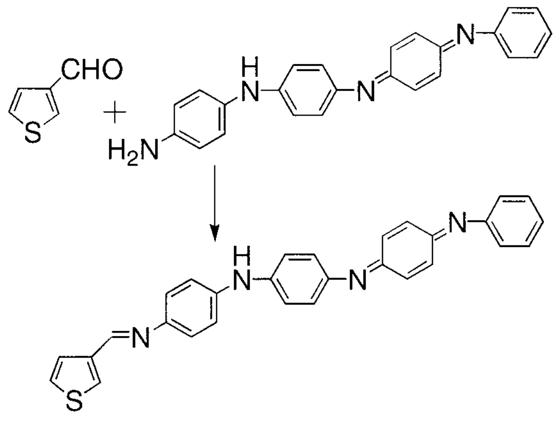
* Corresponding author. Telephone: 33-4-38784389. E-mail: pron@cea.fr.

10.1021/ma020003r CCC: $22.00

Scheme 1



The tetramer exists as a mixture of positional isomers. Here only one is shown for clarity.

polymer, namely poly(p-phenylene sulfide).[15] To our knowledge neither the preparation nor spectroelectochemical behavior of a hybrid poly(alkylthienylene) polymer with lateral oligoaniline groups has been reported to date. However, there exists one report on branching of oligoaniline side chains to conventional polymers such as poly(methacrylamides) and poly(methacrylates).[16]

Experimental Section

Synthesis of Comonomer. Thiophene functionalized with oligoaniline was prepared from 3-thiophenecarboxaldehyde and aniline tetramer according to Scheme 1.

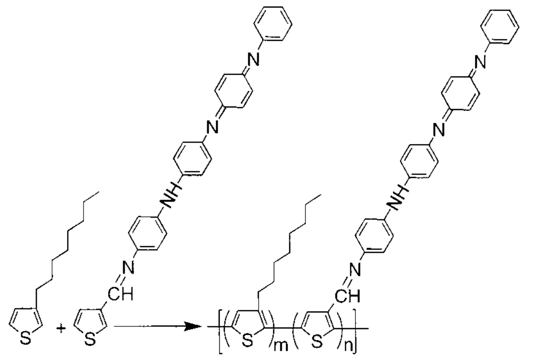
Aniline tetramer, in the oxidation state of emeraldine (4EB), which is not commercially available, was prepared using a modification of the method described in ref 17. In a typical preparation 7.28 g of the hydrochloric salt of N-phenyl-1,4-phenylenediamine ($C_{12}H_{12}N_2$·HCl) was dissolved in 600 mL of 0.1 M HCl with vigorous magnetic stirring. The solution was then transferred to a double-wall reaction vessel connected to a cooling unit and cooled to 0 °C. Then 17.84 g of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$ used as received from Aldrich) was dissolved at room temperature in 104 mL of 0.1 M HCl. The resulting yellowish solution was then cooled to 0 °C and then quickly added to the solution of dianiline hydrochloride. Immediately after its addition, the reaction mixture started to take a blue-greenish tint and quickly became pasty. The reaction was carried out for 4 h at 0 °C with vigorous mechanical stirring and constant monitoring of the temperature. The reaction product was then quantitatively transferred to a Buchner funnel, washed 20 times with 250 mL portions of 0.1 M HCl, and dried overnight. Still wet, as-synthesized 4EB·HCl cake was then suspended in deionized water for 2 h to ensure its good dispersion and finally deprotonated in 2500 mL of 0.1 M aqueous NH_3 for 48 h. Blue-violet dedoped 4EB was separated by filtration, additionally washed 20 times with 250 mL portions of 0.1 M aqueous NH_3 solution, and dried overnight. Finally it was pumped in a dynamic vacuum until constant mass giving typically reaction yields above 90%. It should be noted here that water is extremely strongly bonded to the tetramer and cannot be removed even by extended pumping at a pressure of 10^{-5} mbar. Spectroscopic studies as well as elemental analysis are consistent with the presence of one water molecule per tetramer unit.

Anal. Calcd for $C_{24}H_{20}N_4 \cdot 1H_2O$: C, 75.20; H, 5.78; N, 14.61; O, 4.41. Found: C, 75.86; H, 5.25; N, 14.54; O, 4.25.

Diffuse reflectance IR (cm^{-1}): 3389 (m), 3379 (m), 3300 (w), 3205 (w), 3080 (m), 3040 (m), 3030 (m), 1598 (s), 1518 (s), 1330 (s), 1167 (s), 1124 (m), 848 (s), 750 (s), 695 (s).

MS-ESI (H^+ mode): m/z calcd = 364.17; m_{H+}/z found = 365.30.

Scheme 2



For the preparation of thiophene functionalized with oligoaniline, 1.0 g (2.74 mmol) of aniline tetramer was first dissolved in 500 mL of anhydrous alcohol, and then, 0.6 g (5.36 mmol) of 3-thiophenecarboxaldehyde was added. The reaction was carried out for 12 h in air, at a temperature of ca. 78−80 °C with reflux. Then the insoluble part of the reaction mixture was separated by filtration and the filtrate was vacuum pumped in order to remove the solvent and other volatile components of the reaction mixture. Finally, the product was washed five times with 400 mL portions of distilled water and pumped in a vacuum line until constant mass.

Anal. Calcd for $C_{29}H_{22}N_4S \cdot 0.5H_2O$: C, 74.49; H, 4.96; N, 11.98; S, 6.85. Found: C, 74.30; H, 4.96; N, 11.96; S, 5.76.

^1H NMR (DMSO-d_6, 200 MHz, ppm): 8.59 (m, 1H), 8.44, 8.13, 8.06 (1H), 7.59 (m, 2H), 7.4−6.6 (m, 17H).

IR (KBr, cm^{-1}): 3381 (w), 3289 (w), 3193 (w), 3083 (w), 3027 (w), 1615 (m), 1590 (s), 1510 (m), 1495, 1315 (s), 1238 (w), 1212 (w), 1168 (m), 1104 (w), 1074 (w), 955 (w), 833 (m), 787 (w), 748 (w), 693 (w), 623 (w).

It should be noted here that IR fingerprinting corroborates the presence of all functional groups expected for the product. In particular the band at 1615 cm^{-1}, which is nonexistent in the spectra of the substrates, confirms the formation of a CH=N bond. The ^1H NMR and ^{13}C spectra of the product are complex. The presence of a quinoid ring in the oligoaniline unit results in rotational locking of this segment and introduces cis−trans isomerism, which in turn leads to at least four magnetically nonequivalent conformations. In addition, the reaction product exists as a mixture of positional isomers.[18,19] All these factors contribute to the complexity of the ^1H and ^{13}C NMR spectra. In the former one, the multiplets cannot be easily deconvoluted into well-defined components; in the latter one, the number of lines significantly exceeds that expected for one isomer of a well-defined conformation.

Synthesis of Copolymer. In our initial attempts, we tried to homopolymerize 3-oligoanilinethiophene. Neither chemical nor electrochemical polymerization of this monomer were successful, and each resulted in a mixture of the monomer and the dimer. 3-Oligoanilinethiophene can however be chemically copolymerized with 3-alkylthiophenes to give a polymer containing oligoaniline units as pending groups as depicted in Scheme 2.

In the copolymerization reaction, both comonomers were dissolved in a 50/50 mixture of dried $CHCl_3$ and CH_3NO_2. Then $FeCl_3$ dissolved in the same mixed solvent was slowly added. Typically the reaction was carried out at room temperature, in an atmosphere of purified argon, and the oxidizing agent was added dropwise over a period of ca. 4 h. After the addition of $FeCl_3$ had been completed the reaction mixture was vigorously stirred for additional 2 h. In the course of the reaction, only a minimal amount of an insoluble fraction was formed. This fraction was separated by filtration, and the remaining amount of copolymer was precipitated with methanol and then repeatedly washed with the same solvent. Following the recommendation given in ref 20, the dedoping was achieved by the treatment of the crude copolymer with 100 mL of 0.1 M aqueous NH_3 solution (repeated three times) which was then completed by a treatment with 100 mL of a 0.05 M solution of the ammonium salt of ethylenediaminetetraacetic acid (EDTA). In our initial experiments the molar ratio of 3-oligoanilinethiophene:3-octylthiophene in the reaction mixture was 1:4. However the resulting copolymer was enriched in 3-octylthiophene units as seen from the elemental analysis. For this reason in further experiments we used the molar ratio of the comonomers 3-oligoanilinethiophene:3-octylthiophene = 1:8, which gave a copolymer of similar composition as in the case of 1:4 ratio, improving however the reaction yield with respect to the comonomer containing aniline tetramer group. In this last case the following amounts of reagents were used: 1.376 g of 3-octylthiophene and 0.400 g of 3-olioganilinethiophene were dissolved in 160 mL of $CHCl_3/CH_3NO_2$ 50:50 mixed solvent, and 6 g of $FeCl_3$ was dissolved in 80 mL of the same mixed solvent.

The obtained copolymer can be extracted into four fractions with distinctly different content of 3-oligoaniline-2,5-thienylene units. This was done using the sequence of solvents (acetone, hexane, CH_2Cl_2, THF) recommended in ref 21. Consecutive extractions with acetone and hexane remove lower molecular weight fractions which in addition are little abundant. M_n and polydispersity, determined by SEC using PS narrow standards were 2800 Da equiv of PS and 1.31 for the acetone fraction and 8800 Da equiv of PS and 1.68 for the hexane fraction. These fractions were not further investigated. The fraction obtained during the extraction with CH_2Cl_2 was more abundant and showed higher molecular weight (M_n = 10300 Da equiv of PS, D = 1.89). Elemental analysis of this fraction gives the formula $[(3\text{-OT})_{12}(3\text{-TAT})]_n$, where 3-OT denotes an 3-octyl-2,5-thienylene unit and 3-TAT denotes a 2,5-thienylene unit containing aniline tetramer (calcd (found): C, 73.33 (73.36); H, 8.57 (8.81); N, 1.97 (1.95)). The content of N in the most abundant THF fraction (M_n = 11500 Da equiv of PS, D = 1.76) is small (in all cases below 0.32 wt %) which means that the units containing pendant oligoaniline group are very rare. The properties of this polymer are very little modified with respect to those of pure poly(3-octylthiophene). For all of the above-discussed reasons, in further studies we concentrated on the CH_2Cl_2 fraction.

Cyclic Voltammetry and UV−Vis and Raman Spectroelectrochemistry. All spectroelectrochemical and electrochemical experiments were carried out in the same electrolyte consisting of 0.1 M Bu_4NBF_4 solution in acetonitrile. For cyclic voltammetry and Raman spectroelectrochemistry investigations, thin polymer films were deposited by casting from a diluted chloroform solution on a platinum working electrode which was flame-treated prior to the film deposition. For UV−vis spectroelectrochemical investigations, the polymers were deposited on an ITO (indium−tin oxide) transparent electrode. With the goal to keep the same geometry, both cyclic voltammetry and UV−vis spectroelectrochemical investigations were carried out in the same electrochemical cell with working (platinum or ITO) and counter (platinum) electrodes of ca. 1 cm^2 surface area. Ag/AgCl wire electrode placed in the close proximity of the working electrode served as a reference. Its potential measured vs Ag/0.1 M $AgNO_3$ was −0.15 V. In such experimental setup the Ag/AgCl electrode can be considered only as a pseudo-reference electrode; however, its potential turned to be stable and the results of spectroelectrochemical experiments very reproducible.

The UV−vis spectra at a given potential were recorded in a Perkin-Elmer Lambda 2 spectrometer. At a given potential the spectra were taken when the current reached the low level "plateau" and no further changes in the absorbance were observed. It usually took 10−15 min.

Because of experimental limits, a slightly different geometry was used for the Raman spectroelectrochemical measurements. In this case, the surface area of the working electrode was ca. twice as small. The Raman spectra were obtained with three different excitation lines. In the case of the blue (457.9 nm) and the red (676.4 nm) lines Jobin-Yvon T64000 spectrometer connected to a CCD detector. For the near-IR excitation line (1064 nm) a FT Raman Bruker RFS 100 spectrometer was used.

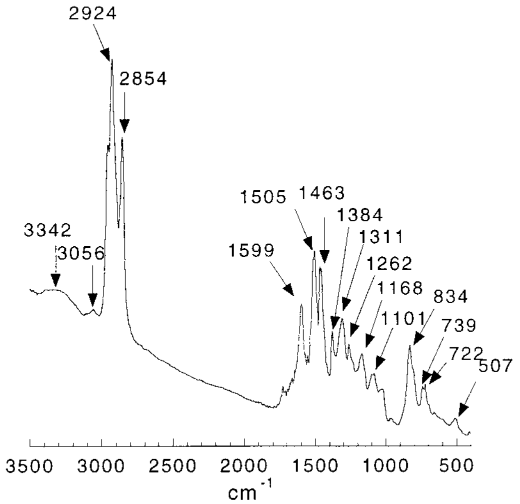


Figure 1. FTIR spectrum of poly(3-octyl-2,5-thienylene-*co*-3-oligoaniline-2,5-thienylene).

Results and Discussion

As has already been stated in the Experimental Section, attempts to homopolymerize 3-oligoanilinethiophene were unsuccessful independent of the method used (chemical or electrochemical polymerization). It is generally accepted[22,23] that the oxidative polymerization of thiophene involves the oxidation of the aromatic ring to a radical cation. Two such radical cations then couple to give a dication which after abstraction of two protons is transformed into a neutral dimer. The dimer is then oxidized to a radical cation at lower potentials than the monomer and the polymerization can proceed. Evidently, in the case of 3-oligoanilinethiophene, the reaction stops at the stage of monomer oxidation or at the stage of dimer oxidation since in the reaction mixture only monomer and dimer molecules were detected. In view of these difficulties, we have decided to copolymerize 3-oligoanilinethiophene with 3-octylthiophene, hoping that their coupling would be easier than the homocoupling of the oligoaniline-substituted molecules.

Indeed, thiophene functionalized with aniline tetramer copolymerizes with 3-octylthiophene. The presence of 2,5-thienylene units containing pendant aniline tetramer groups is clearly manifested in the FTIR spectrum of neutral copolymer in which IR bands due to the tetramer can be found together with bands characteristic of poly(3-alkylthiophene)s[24,25] (Figure 1). In particular, a weak band at 3056 cm^{-1} can be ascribed to C_β−H stretching in the thienylene ring whereas strong bands in the spectral range 2850−2950 cm^{-1} are related to C−H stretching in the octyl substitutent. Other IR absorption bands characteristic of the octyl group are as follows: 1463, 1384, and 722 cm^{-1}. The band at 808 cm^{-1}, strongly overlapping with the band at 834 cm^{-1}, is attributed to the C−H out of plane deformation in the thienylene ring. The band originating from C_α=C_β stretching deformations in the 2,5-thienylene unit, usually of weak intensity, is obscured by a strong band at 1505 cm^{-1} which is due to the presence of the aniline tetramer side group. Other bands characteristic of the oligoaniline substituent are a broad band in the vicinity of 3350 cm^{-1} and the bands at 1599, 1311, 1168, and 834 cm^{-1}.

Since aniline tetramer is a strong chromophore, its branching to the main chain, consisting of 2,5-thienylene repeat units, should give rise to new absorption

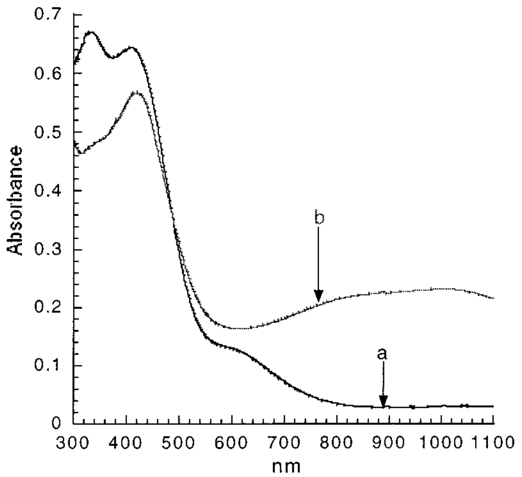


Figure 2. UV−vis−NIR spectrum of a solid thin film of poly(3-octyl-2,5-thienylene-*co*-3-oligoaniline-2,5-thienylene): (a) in contact with Bu_4NBF_4/acetonitrile electrolyte; (b) in contact with Bu_4NBF_4/acetonitrile electrolyte containing diphenyl phosphate as the protonating agent.

bands in the spectral region characteristic of visible radiation. Figure 2a shows UV−vis−NIR spectrum of the neutral copolymer deposited on ITO electrode and kept in Bu_4NBF_4/acetonitrile electrolyte, i.e., in the configuration used later for the spectroelectrochemical investigations. Before the interpretation of the spectral features of the copolymer containing pendant oligoaniline groups it is instructive to discuss the spectra of its constituents, i.e., aniline tetramer and poly(alkylthiophene). Aniline tetramer in the oxidation state of emeraldine base shows two absorption bands in the vicinity of 315 and 570 nm. The first is ascribed to the $\pi-\pi^*$ transition in the benzoid ring. The second one is due to excitonic-type transition in the oxidized (quinoid type) structural unit. Thus, it requires the presence of imine nitrogens and is not observed in totally reduced forms of oligoanilines.[26] In neutral poly(alkylthiophene)s, only one absorption band is observed associated with the $\pi-\pi^*$ transition in the 2,5-thienylene unit. The exact position of this peak strongly depends on the microstructure of the chain. In regioregular poly(alkylthiophene)s the $\pi-\pi^*$ band is strongly red-shifted and shows clear vibrational structure.[5,21] All discussed above bands can be found in the spectrum of the copolymer studied. The peak due to $\pi-\pi^*$ transition in the benzoid ring of aniline tetramer attached to poly(2,5-thienylene) main chain is red-shifted to 330 nm, i.e., by 15 nm as compared to the corresponding peak in "free" aniline tetramer. This shift indicates that the π-bonding systems of the oligoaniline side groups and the poly(2,5-thienylene) main chain cannot be considered as isolated π-systems but they are conjugated to some extent via CH=N linkages. The excitonic peak in the vicinity of 570−580 nm is also clearly visible; however, it strongly overlaps with the band characteristic of the 2,5-thienylene unit. The maximum of the latter is located at 430 nm, i.e., it is blue-shifted not only with respect to the corresponding band in regioregular poly(alkylthiophene)s but also with respect to the analogous band in poly(alkylthiophene)s obtained by oxidative polymerization. Moreover, no vibrational structure can be seen. Such spectral features are characteristic of poly(thiophene) derivatives of short chain or exhibiting low conjugation length.[3,4,6] Evidently, branching the oligoaniline side groups lowers the planarity of the main 2,5-thienylene chain as compared to poly(3-octylthiophene) homopolymer.

It should be underlined that the newly developed hybrid copolymer exhibits extremely interesting properties with respect to its application in plastic photovoltaic cells. This is due to the fact that it exhibits absorption covering a large range of the spectrum from UV to NIR (from 300 to 750 nm). This property combined with p-type charge carriers mobility make it a very promising material for organic photovoltaic cells of both double-layer and bulk heterojunction types.[27,28]

It is known that polyaniline or its oligomers can be protonated in nonaqueous solvents provided that appropriate acids are selected.[29] In the case when acetonitrile is used as the solvent, phosphoric acid esters such as, for example, diphenyl phosphate are especially suitable as protonation agents.[30] Their presence not only improves electrochemical response as evidenced by cyclic voltammetry but also changes spectral and spectroelectrochemical features of the system.[31] The changes of the spectrum of the neutral copolymer after the addition of diphenyl phosphate to Bu_4NBF_4/acetonitrile electrolyte, are shown in Figure 2b. It is clear that the aniline tetramer groups attached to the poly(2,5-thienylene) chain undergo protonation. In "free" aniline tetramer, in the oxidation state of emeraldine, the protonation is manifested by disappearance of both 315 and 570 nm bands with simultaneous growth of a peak at 435 nm and an extremely broad absorption which extends toward the near-IR All these protonation induced spectral changes occur also for the tetramer attached to the poly(2,5-thienylene) main chain and are clearly visible in the spectrum presented in Figure 2b. It should be noted here that although the disappearance of the 330 nm peak ($\pi-\pi^*$ transition in the benzoid ring of the oligoaniline substituent) is evident, the growth of the 435 nm peak is obscured by its coincidence with the poly(alkylthiophene) peak whose maximum is located at the same wavelength. The broad absorption extending toward the near-IR is also clearly seen.

For clarity, in the case of electrochemically active polymers, it is frequently advantageous to discuss UV−vis−NIR spectroelectrochemistry together with cyclic voltammetry. The results of spectroelectrochemical studies of the copolymer, carried out in Bu_4NBF_4/acetonitrile electrolyte, without the addition of diphenyl phosphate protonating agent, are presented in Figure 3, whereas its cyclic voltammogram registered in the same electrolyte is shown in Figure 5a. Neutral copolymer, deposited on a platinum electrode, gives the open circuit potential of 0.15 V vs Ag/AgCl. Lowering this potential to 0 V vs Ag/AgCl does not result in a reduction peak. This is in contrast to the case of polyaniline, which deposited on Pt electrode and studied in the same electrolyte is being reduced to leucoemeraldine in this potential range.[31] It can be therefore postulated that branching the aniline tetramer to the poly(2,5-thienylene) chain impedes its total reduction at least in the range of potentials studied in this research. As a result, the spectrum of the polymer with no potential imposed and that recorded at 0 V vs Ag/AgCl show only negligible differences. The presence of oxidized units in the tetramer substituent is clearly manifested by the presence of already discussed broad peak at 580 nm which does not disappear at the potential of 0 V vs Ag/AgCl, in agreement with the results of cyclic voltammetry. When the potential in the range between 0 and

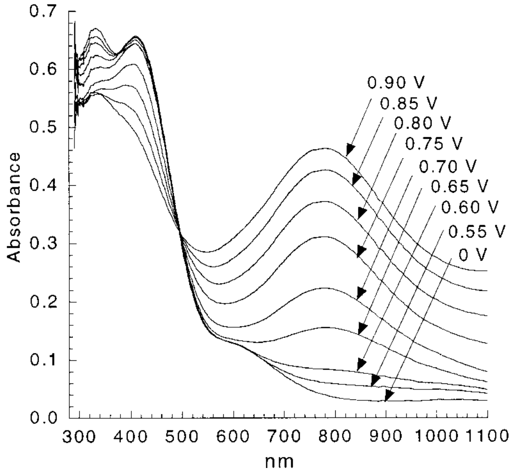


Figure 3. UV−vis−NIR spectroelectrochemical data of poly(3-octyl-2,5-thienylene-*co*-3-oligoaniline-2,5-thienylene) registered in Bu_4NBF_4/acetonitrile electrolyte. Potential vs Ag/AgCl.

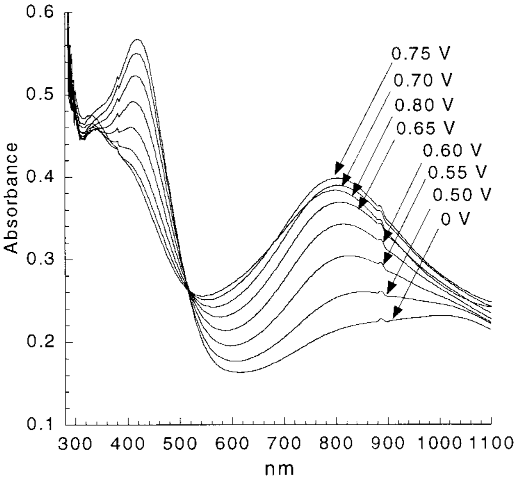


Figure 4. UV−vis−NIR spectroelectrochemical data of poly(3-octyl-2,5-thienylene-*co*-3-oligoaniline-2,5-thienylene) registered in Bu_4NBF_4/acetonitrile electrolyte containing diphenyl phosphate as the protonating agent. Potential vs Ag/AgCl.

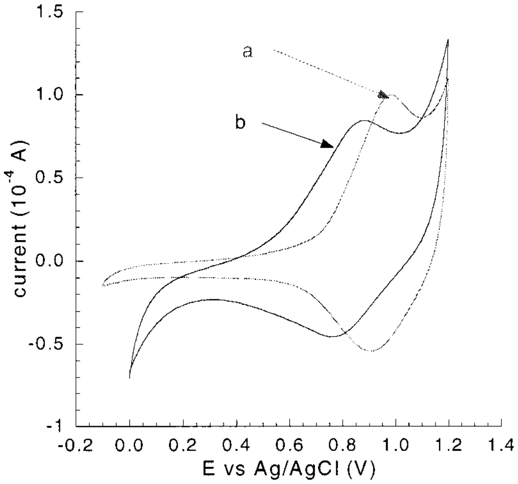


Figure 5. Cyclic voltammograms of poly(3-octyl-2,5-thienylene-*co*-3-oligoaniline-2,5-thienylene) (scan rate 50 mV/s) registered in (a) Bu_4NBF_4/acetonitrile electrolyte and (b) Bu_4NBF_4/acetonitrile electrolyte containing diphenyl phosphate as the protonating agent.

0.55 V vs Ag/AgCl is increased, no electrochemical oxidation takes place as judged from the cyclic voltammogram, and as a consequence the spectrum of the copolymer remains essentially the same. Further increase of the potential to 0.70 V results in a gradual decrease of the intensity of the peak at 330 nm ($\pi-\pi^*$ transition in the benzoid ring of the oligoaniline substituent) and the growth of a broad peak with a maximum around 800 nm, which is characteristic of the oxidative doping. In this potential range the peak characteristic of the $\pi-\pi^*$ transition in the thienylene ring with maximum at 430 nm does not change its intensity. This means that up to 0.70 V vs Ag/AgCl only amine groups in lateral oligoaniline chains are being oxidized and the main chain of the copolymer consisting of 2,5-thienylene units remains intact. Further increase of the potential results in the oxidative doping of the main chain, which is manifested by a gradual bleaching of the 430 nm peak with increasing potential. All these spectral changes can be correlated with the cyclic voltammogram of the copolymer. The oxidation of the lateral oligoaniline groups gives rise to an oxidation prepeak in the potential range 0.55−0.70 V whereas the onset of the oxidation of the main chain coincides with an abrupt increase of the anodic current above 0.70 V.

Spectroelectrochemical behavior of the copolymer changes upon the addition of the protonating agent (diphenyl phosphate) to Bu_4NBF_4/acetonitrile electrolyte (see Figure 4). First, the onset of the oxidative doping shifts to lower potentials, and as a result, spectral changes in the polymer layer can be noticed already at the potential of 0.50 V vs Ag/AgCl. Second, in the presence of diphenyl phosphate the aniline tetramer lateral groups are protonated (vide supra). For this reason the peak at 430 nm must be considered as a superposition of two bands which nearly coincide—the band originating from the $\pi-\pi^*$ transition in the thienylene unit and the band due to the protonation of the tetramer of aniline. It is therefore virtually impossible to differentiate between the oxidation of the lateral oligoaniline chains and the oxidation of the main chain. The above-described observations are consistent with the change in the cyclic voltammogram registered in acidified electrolyte. The addition of diphenyl phosphate results in a broadening of the oxidative doping peak accompanied by its shift toward lower potentials (compare parts a and b of Figure 5).

Raman spectroelectrochemisty is another method suitable for the investigation of the doping of electroactive polymers since this process may involve significant changes in the force constants of the functional groups of such polymers as well as the creation of new modes which are Raman inactive in the neutral (undoped) state of these polymers. One must be however aware of the fact that such studies in the copolymer discussed here, which contains two chromophores of different natures, can be very complex for several reasons. First, one may expect that the registered spectra should be dependent on the energy of the excitation line because, for a given λ_{exc}, different resonant enhancement is expected for different chromophores. Second, during the oxidative doping, the UV−vis−NIR spectrum of the polymer changes, which gives rise to different resonance conditions as compared to those characteristic of the neutral polymer. As a result, one can experience a complex spectrum evolution that is not easy to interpret. Under favorable conditions, it is however possible to selectively enhance nonelastic scattering in only one of the existing chromophores, which strongly simplifies the interpretation.

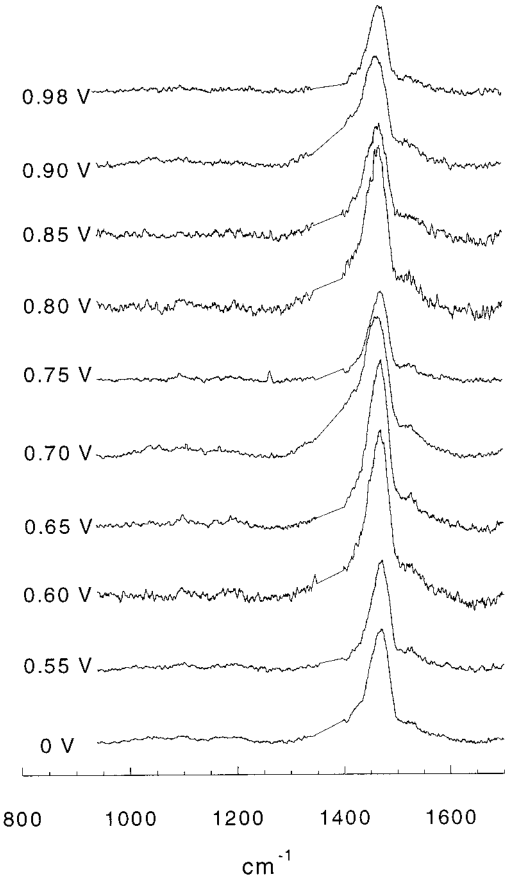


Figure 6. Raman spectroelectrochemical data of poly(3-octyl-2,5-thienylene-*co*-3-oligoaniline-2,5-thienylene) registered in Bu_4NBF_4/acetonitrile electrolyte (λ_{exc} = 457.9 nm). Potential vs Ag pseudereference electrode.

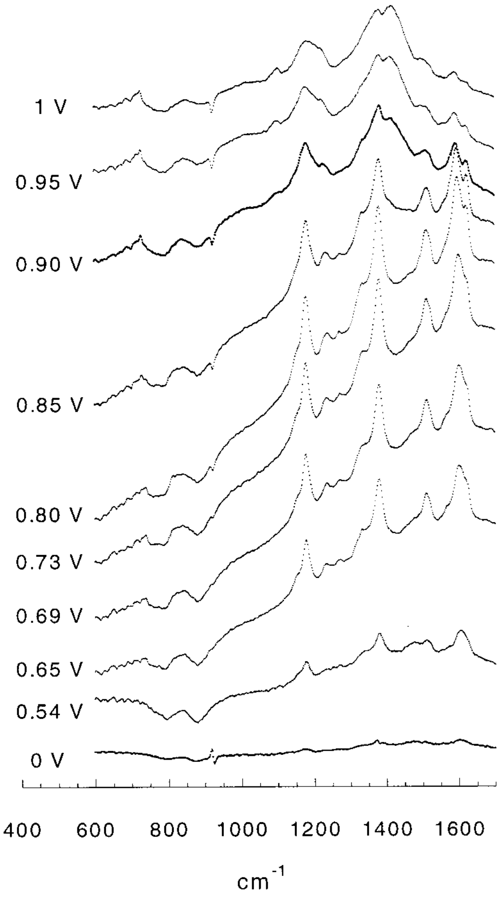


Figure 7. Raman spectroelectrochemical data of poly(3-octyl-2,5-thienylene-*co*-3-oligoaniline-2,5-thienylene) registered in Bu_4NBF_4/acetonitrile electrolyte (λ_{exc} = 1064 nm). Potential vs Ag pseudereference electrode.

It should be stressed here that in Raman spectroelectrochemical investigations we have used a Ag pseudoreference electrode. The potential of this electrode vs Ag/AgCl, measured in the same electrolyte as used for Raman spectroelectrochemistry, is ca. 0.15 V. Thus, in the case of all comparisons with cyclic voltammetry or UV−vis−NIR spectroelectrochemisty, etc., this correction should be taken into consideration. Three different excitation lines were used, namely the blue line (λ_{exc} = 457.9 nm), the red one (λ_{exc} = 676.4 nm), and the infrared one (λ_{exc} = 1064 nm). By selection of the blue line, we expected to probe the vibrations of the undoped main chain of our copolymer because its energy (457.9 nm) matches well the energy of the $\pi-\pi^*$ transition in undoped 2,5-thienylene unit (430 nm). Unfortunately, independent of the potential applied, the spectra were significantly obscured by fluorescence. Figure 6 shows the spectra obtained after the subtraction of the contribution from the fluorescence. Two most intensive peaks characteristic of undoped poly(3-octylthiophene)—at 1465 cm^{-1} ascribed to $C_\alpha-C_\beta$ symmetric stretching deformations and at 1378 cm^{-1} which is due to $C_\beta-C_\beta$ stretchings are clearly seen.[25,32] One should note that the second peak characteristic of the poly(2,5-thienylene) chain at 1378 cm^{-1} which is of much lower intensity coincides with one of the Raman bands of the solvent. This contribution must be subtracted in cases where bands due to the solvent are registered. Because of this procedure the line attributed to $C_\beta-C_\beta$ stretchings is hardly seen. No lines attributable to the aniline tetramer are detected. Thus, as expected, the blue excitation line enhances selectively the bands originating from the undoped segments of the main chain, leaving other Raman modes invisible. For this reason, it is not very diagnostic with respect to oxidative doping of the copolymer studied. It is evident that, independent of the potential applied, the Raman spectra are the same proving that in each case only undoped segments of the polymer main chain are probed. Of course the intensity of the spectrum decreases with increasing potential because undoped areas of the polymer diminish with increasing doping level. The blue excitation line is therefore oversensitive with respect to undoped segments. Its use corroborates however the attribution of the peaks in the UV−vis−NIR spectrum of the copolymer. The resonant enhancement of the peaks originating from $C_\alpha-C_\beta$ and $C_\beta-C_\beta$ stretchings in undoped segments of the main chain of the hybrid copolymer studied can occur only if the 430 nm peak in the spectrum shown in Figure 2a originates from the $\pi-\pi^*$ transition in the thienylene ring.

To the contrary for the infrared excitation line (1064 nm) one should expect the resonance enhancement only for the bands associated with the vibrations of doped (oxidized) chain segments because for the undoped polymer the absorbance is negligible in this spectral region. In Figure 7, FT Raman spectra (λ_{exc} = 1064 nm) recorded for the film of the copolymer, polarized at increasing electrode potentials, are presented. At the potential of 0 V in which the polymer exists in its reduced undoped form no spectrum with a reasonable signal-to-noise ratio can be recorded. Evidently no resonance conditions are achieved in this case. One must note here that electrochemically reduced polyaniline, studied in the same electrolyte, also produces a very poor spectrum which is impossible to interpret because of a bad signal-to-noise ratio. Since, as shown by UV−vis−NIR spectroelectrochemical studies, the onset of the oxidative doping results in a significant increase of the absorbance at $\lambda = 1064$ nm one may expect that the resonance conditions are being improved with increasing doping level. This is indeed the case. At 0.54 V weak Raman bands appear which, with the exception of one weak band, can all be attributed to the tetramer side group in the semiquinone radical oxidation state.[26,31,33] This can be considered as a clear manifestation of the resonant enhancement because the analytically determined ratio of thienylene rings with aniline tetramer substitutent to thienylene rings with octyl subsitutent is 1:12. Before the attribution of the observed bands, it is instructive to describe Raman spectra of principal forms of polyaniline. In leucoemeraldine only benzoid rings are present, therefore only one peak attributed to C−C stretching exists at 1622 cm^{-1}. In pernigraniline, two peaks at 1623 and 1580 cm^{-1} reflect the coexistence of benzoid and quinoid rings.[31] In the spectrum of the copolymer registered at $E = 0.54$ V only one peak is observed at 1602 cm^{-1}, i.e., at the position intermediate between those characteristic of the benzoid and quinoid structures. This can be taken as a spectroscopic evidence of the semiquinone radical structure resulting from the oxidation of the amine group in the aniline tetramer. Another spectroscopic feature characteristic of semiquinone radicals is the peak at 1375 cm^{-1} whose position is intermediate between the position of the band characteristic of C═N stretching in the quinoid at 1470 cm^{-1} and the position of the band ascribed to C−N stretchings in benzoid segments at 1235 cm^{-1}. The semiquinone radical band in polyaniline is usually located in the vicinity of 1320−1350 cm^{-1}; however in aniline oligomers where the delocalization is limited, it appears at higher wavenumbers,[34,35] usually between 1370 and 1400 cm^{-1}. In addition to bands characteristic of the oxidized form of aniline tetramer, a very weak band at 1465 cm^{-1} is present, which is the strongest band originating from the vibration of the thienylene ring (C_α−C_β stretchings). At $V = 0.63$ V, this band totally disappears, which means that beginning from this potential the infrared excitation line ($\lambda_{exc} =$ 1064 nm) probes only the oxidation of the tetramer substituents and no information concerning the main chain of the copolymer can be extracted. It should be noted that the registered spectrum closely resembles that observed for polyaniline in the same electrolyte and for similar potentials.

At potentials up to 0.85 V, apart from a remarkable increase of the intensity of the Raman bands, which is caused by increasing fraction of oxidized tetramer substituents being in resonance, only minor changes in the spectrum are observed. First, with increasing potentials the line at 1602 cm^{-1} splits into two lines at 1590 and 1602 cm^{-1}. This is indicative of the differentiation between the quinoid and benzoid units and can be interpreted as the oxidation of semiquinone radical structures (emeraldine oxidation state) to totally oxidized tetramer (pernigraniline oxidation state) followed by its deprotonation.

At $V = 0.90$ V the spectrum drastically changes. This may be taken as evidence that other than tetramer oxidation processes begin to take place. The principal spectral modifications can be described as follows. First, the bands characteristic of aniline tetramer start to decrease quickly with increasing potential; at $V = 0.95$ V, they become very weak. In the same potential range, new peaks appear which are characteristic of the oxidized poly(2,5-thienylene) main chain. In particular a strong band appears at 1413 cm^{-1}. It is known from Raman spectroelectrochemical studies of poly(3-decylthiophene)[25] that the oxidation of poly(2,5-thienylene) chain results in a red shift of the most intensive Raman mode (C_α−C_β stretchings) by 35−40 cm^{-1}. The observed phenomenon can therefore be interpreted in terms of the main chain oxidation since the C_α−C_β stretching peak in the undoped copolymer was located at 1465 cm^{-1}. This conclusion is further corroborated by the growth of the intensity of the peak in the vicinity of 1180 cm^{-1}, which always accompanies the shift in the position of the C_α−C_β stretching mode induced by the oxidation of the chain. From the above results, it is therefore clear that above $V = 0.85$ V the oxidized thienylene segments are in resonance. Since thienylene units are much more abundant in the copolymer as compared to aniline tetramer units, their Raman modes dominate the spectrum. One should add at the end that the results of Raman spectroelectrochemical studies with $\lambda_{exc} = 1064$ nm corroborate the conclusions drawn from UV−vis−NIR spectroelectrochemistry concerning the sequence of the doping. Both techniques show that the oxidation of the main chain starts at higher potentials as compared to the oxidation of oligoaniline lateral groups. In addition, taking into account the correction for the potential of Ag pseudoreference electrode (vide supra), the onset of the oxidation of the poly(2,5-thienylene) chain determined from Raman spectroelectrochemistry is in very good agreement with that extracted from cyclic voltammetry and UV−vis−NIR spectroelectrochemical data.

As it has already been stated neutral copolymer gives rise to two UV−vis bands associated with the oligoaniline substituent: i.e., at 330 nm and at 580 nm. Since the latter is rather broad, a significant absorbance value can still be measured at 676.4 nm, i.e., at the wavelength corresponding to the energy of the red excitation line. Thus, we believed that by the use of $\lambda_{exc} = 676.4$ nm we can resonantly enhance the bands originating from the neutral (undoped) tetramer subsitutent. Moreover, we hoped that we could also probe the doped polymer because the presence of doping induced bands also increase the absorbance in this spectral region (see Figure 3). Raman spectra obtained with $\lambda_{exc} = 676.4$ nm for increasing electrode potentials are presented in Figure 8. The spectrum recorded at 0 V vs Ag, i.e., ca. −0.15 V vs Ag/AgCl, can be interpreted as originating solely from the neutral (undoped) oligoaniline substituent since it shows a striking resemblance to the spectrum of neutral aniline pentamer consisting of four benzoid units and one quinoid unit.[36] This finding clearly confirms the conclusion derived from other spectroscopic studies (vide supra) that aniline tetramer if branched to poly(2,5-thienylene) chain cannot be totally reduced in the potential range studied. Therefore, the dominant peak at 1462 cm^{-1} can be ascribed to C═N stretching vibrations in the oligomer substituent. Alternatively this peak could be attributed to the band originating from the C_α−C_β stretching in the thienylene ring which gives rise to a Raman active mode at very similar wavelengths. We believe however that this is

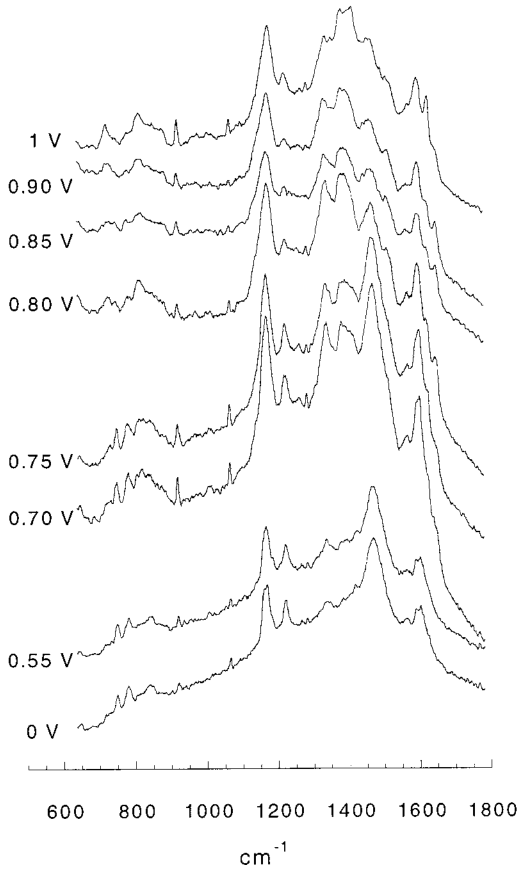


Figure 8. Raman spectroelectrochemical data of poly(3-octyl-2,5-thienylene-*co*-3-oligoaniline-2,5-thienylene) registered in Bu_4NBF_4/acetonitrile electrolyte (λ_{exc} = 676.4 nm). Potential vs Ag pseudereference electrode.

highly unlikely since at 676.4 nm no absorbance due to the $\pi-\pi^*$ transition in undoped thienylene ring can be measured, and for these reasons, no resonance effects are expected. The other observed bands originate from C−C stretchings in benzoid and quinoid rings (1615 and 1580 cm^{-1}), C−N stretching (1222 cm^{-1}), and C−H in plane bending deformation (1164 cm^{-1}) (vide supra). Up to $V = 0.6$ V, no changes in the spectra can be seen, consistent with UV−vis−NIR spectroscopic data and cyclic voltammetry, which indicate no oxidative doping in this potential range. Above this potential, the peaks due to the vibrations in the neutral tetramer substituent decrease in intensity indicating the worsening of the resonance conditions. The first step of the oxidation of the tetramer is manifested by the growth of two bands at 1340 and 1380 cm^{-1} which, for this excitation line, are usually ascribed to semiquinone radical cations. Contrary to the expectations, no oxidative doping of the poly(2,5-thienylene) chains can be monitored with the use of the red excitation line because at potentials corresponding to this process the spectra become very poor and difficult to interpret. Evidently no resonance conditions are achieved for the doped chain.

At the end it should be stated that due to the resonance effects Raman spectroscopy is remarkably selective in monitoring the oxidative doping of the hybrid copolymer developed in this research. The blue line probes only the undoped main chain and the red one the undoped oligoaniline substituent whereas the infrared one indicated consecutive dopings of the side chains and the main chain.

Conclusions

To summarize, we have demonstrated that by copolymerization of 3-octylthiophene with thiophene functionalized with aniline tetramer at the 3-position it is possible to obtain a polymeric system which combines spectroelectrochemical properties of polyaniline and poly(thiophene)s which is manifested by consecutive doping of the oligoaniline side chains and poly(2,5-thienylene) main chain.

Acknowledgment. M.Z., G.K., and I.K.-B. wish to acknowledge partial financial support from the Committee of the Scientific Research in Poland (KBN Grant No. 4T09A 082 22).

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MA020003R