Preparation and Spectroscopic and Spectroelectrochemical Characterization of Copolymers of 3-Alkylthiophenes and Thiophene Functionalized with an Azo Chromophore

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ABSTRACT: New polythiophene derivatives containing a nonlinear optical chromophore were prepared via copolymerization of 3-alkylthiophene and 2-[*N*-ethyl-*N*-[4-[(4-nitrophenyl)azo]phenyl]amino]ethyl 3-thienylacetate. The presence of chromophore groups in the copolymer chain was confirmed by ^{1}H NMR, ^{13}C NMR, and FTIR spectroscopies as well as by elemental analysis. The introduction of azo dye as a side group to the conjugated polythiophene backbone significantly alters electrochemical and spectroelectrochemical behavior of these compounds as compared to poly(3-alkylthiophene) homopolymers. In particular, two redox processes are observed by cyclic voltammetry. The first anodic peak at lower potentials corresponds to the oxidative doping of the polymer whereas the second one is associated with the oxidation of the chromophore side group to a radical cation. Electrochemical oxidation of the copolymers results in a gradual bleaching of the absorption peak ascribed to the $\pi-\pi^*$ transition in the polyconjugated system. At the same time the absorption peak characteristic of the chromophore undergoes a bathochromic shift from 485 to 516 nm. Thus, in the spectra of the oxidatively doped copolymers an additional peak unobserved in poly(3-alkylthiophene) homopolymers is present in addition to the doping-induced absorption in the near-infrared part at the spectrum. This additional peak has an important influence on the Raman spectroelectrochemical behavior of the prepared copolymers as probed by the green ($\lambda_{\max} = 514$ nm) excitation line. Electrochemical oxidation significantly worsens the resonance conditions for the vibrations of the conjugated backbone whereas it improves the resonance conditions for the vibrations associated with the chromophore side groups. As a result at lower potentials only the lines characteristic of the 2,5-disubstituted thienylene ring are registered, and at higher potentials, lines due to the chromophore dominate the spectrum.

Introduction

Polythiophenes are very unique among other polyconjugated systems for two principal reasons:

i. Their functionalization is relatively easy as compared to polypyrrole, polyacetylene, poly(*p*-phenylene), and other conjugated polymers.

ii. The attachment of substituents as side groups (through β carbons) has relatively little impact on electronic and electrochemical properties of the conjugated polythiophene backbone.

Thus, by synthesizing 3- and/or 4-substituted polythiophenes, one can produce new materials which combine physical properties characteristic of the polyconjugated backbone with specific properties of a given substituent. Such an approach to polythiophene chemistry has been very popular in the past decade, and several successful attempts of polythiophene functionalization were reported. For example, substitution at the 3 position with sufficiently long alkyl groups leads to soluble (i.e., processible) poly(3-alkylthiophenes).[1] Similarly the introduction of alkoxy side chains not only improves the processibility of polythiophenes but also significantly lowers their oxidative doping potential which, in turn, results in a better stability of the oxidized (i.e., conductive) form of the polymer.[2,3] Functionalization of the backbone of polythiophenes with crown ethers[4] or calixarenes[5] combined with their electroactivity led to the fabrication of new types of modified electrodes capable of metal complexing. Polymer modifications have also been achieved by introducing side chains bearing redox-active groups,[6−8] photochromic groups,[9] or mesogenic groups.[10]

In this research we have undertaken the task of the preparation of polythiophenes functionalized with azobenzene-type chromophores. Such materials are very interesting for several reasons:

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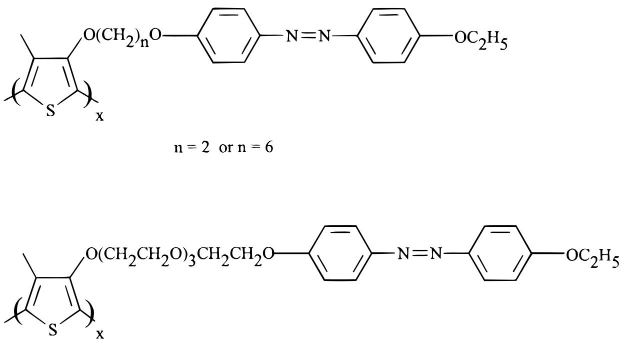
Chart 1



i. Polyconjugated systems exhibit interesting third-order nonlinear optical (NLO) behavior.[11] From this point of view it is interesting to functionalize polythiophene with an appropriate second-order NLO chromophore. Such functionalization allows one to combine second- and third-order NLO properties in one material.

ii. Azobenzene derivatives are photochromic. Moreover, these photochromic properties are retained to a large extent in azobenzene derivatives grafted to the polythiophene backbone as demonstrated recently by Levesque and Leclerc.[12]

iii. Azobenzene chromophore substituted polythiophene should exhibit a very interesting electrochemical behavior, that is, the combination of the electroactivity of the conjugated backbone and the electroactive groups of the side chain.

iv. Because of this dual electroactivity, an azobenzene chromophore modified polythiophene differs distinctly in its spectroelectrochemical behavior as compared with other polyconjugated systems. This difference should be detected not only in UV−vis−near-infrared (NIR) spectroelectrochemical studies but also in Raman spectroelectrochemistry.

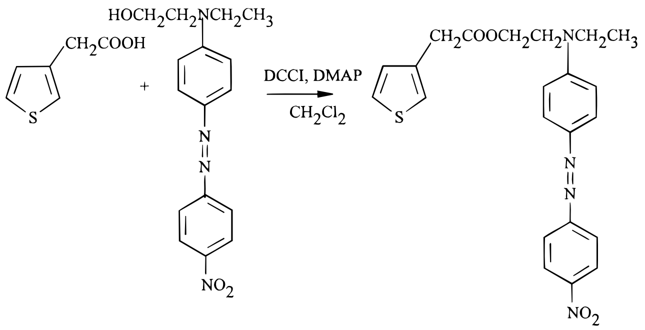
A few reports on the derivatization of polythiophene with an azobenzene chromophore have already been published. For example, Levesque and Leclerc[12] reported on the synthesis of an azobenzene-substituted polythiophene of the type shown in Chart 1. These authors concentrated on the studies of the novel dual photochromism observed in their polymer and demonstrated that the photoactive substituents not only modify their own UV−vis absorption but also induce the spectral features associated with the conjugated backbone of the polymer.

We have selected a different chromophore for the functionalization of polythiophene, namely, 4-nitro-4′-[*N*-ethyl-*N*-(2-hydroxyethyl)amino]azobenzene, commercially known as Dispersed Red 1 (DR1). This aminoazobenzene is one of the NLO chromophores most frequently attached to classical polymers such as, for example, poly(methyl methacrylate). However, attached to a conductive polymer such as polythiophene, aminoazobenzene should exhibit, in addition to NLO properties, some electroactivity due to the presence of an amino group.

DR1 has already been introduced to polythiophene by Chittibabu et al.[13] They prepared a DR1 derivative containing vinyl groups, which served as a photo-cross-linking agent between two poly(alkylthiophene) chains.

Our approach to obtain DR1-functionalized polythiophene was totally different. First we have reacted 3-thiopheneacetic acid with DR1 using an estrification procedure.[14] Then by copolymerization of the obtained chromophore-functionalized thiophene monomer with 3-alkyl-substituted thiophenes, we have produced a relatively well-soluble material which was able to form thin films of good optical quality.

Scheme 1



As already stated, the prepared materials should exhibit NLO and photochromic properties. These studies will be the subject of a separate publication. In this paper we focus on the preparation and chemical and spectroscopic characterization of the newly synthesized copolymers. We put special emphasis on new electrochemical and spectroelectrochemical features which originate from a combination of main-chain and side-chain electroactivity. We also report new resonant Raman spectroelectrochemical features unobserved in other derivatives of polythiophene which cause the enhancement of main-chain Raman modes for low electrode potentials and the enhancement of side-chain Raman modes for higher potentials.

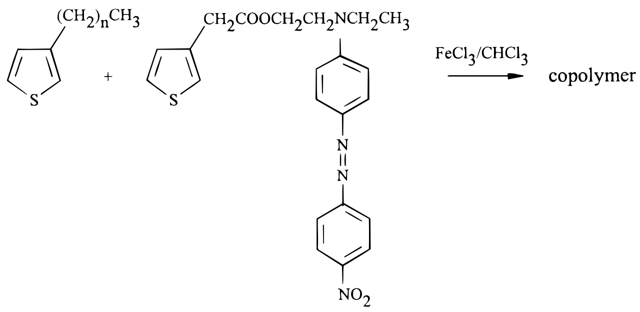
Experimental Section

1. Synthesis of 3-Alkylthiophene. 3-Butylthiophene (3-BuT), 3-octylthiophene (3-OcT), and 3-decylthiophene (3-DeT were prepared by Grignard coupling of the appropriate alkylmagnesium bromide with 3-bromothiophene in the presence of a [1,3-bis(diphenylphosphine)propane]nickel(II) chloride catalyst.[15]

2. Synthesis of 2-[*N*-Ethyl-*N*-[4-[(4-nitrophenyl)azo]phenyl]amino]ethyl 3-thienylacetate (3-DRT) (Scheme 1). A total of 2 g (14 mmol) of 3-thiopheneacetic acid (Fluka) and 3.77 g (12 mmol) of 4-nitro-4′-[*N*-ethyl-*N*-(2-hydroxyethyl)amino]azobenzene (Aldrich, recrystallized in isopropyl alcohol) were dissolved in 80 mL of dry CH_2Cl_2. Then 2.59 g (13 mmol) of dicyclohexylcarbodiimide (Aldrich) and 0.22 g (1.8 mmol) of (dimethylamino)pyridine (Aldrich) were added to the vigorously stirred solution. The stirring was continued for 24 h. The mixture was then filtered, and the solvent was removed by rotary evaporator under vacuum. The product was purified on silica gel using methylene chloride (yield 60%, red crystals). Mp: = 118 °C. Anal. Calcd for $C_{22}H_{22}N_4SO_4$: C, 60.26; H, 5.06; N, 12.78; S, 7.31; O, 14.59. Found: C, 60.26, H, 5.02, N, 12.57; S, 6.55. UV (λ_{max}, $CHCl_3$, nm): 472, 286. IR (KBr, cm^{-1}): 3101 (w), 2983 (w), 2960 (w), 2910 (w), 1732 (s), 1598 (s), 1585 (s), 1515 (s), 1410 (s), 1388 (m), 1360 (m), 1332 (s), 1310 (m), 1246 (m), 1159 (m), 1135 (s), 1103 (m), 1077 (w), 1028 (m), 862 (m), 824 (m), 789 (w), 768 (m), 756 (w), 723 (w), 690 (w), 629 (w), 607 (w). ^1H NMR ($CDCl_3$, 500 MHz, ppm): 1.21 (t, 3H), 3.45 (q, 2H), 3.66 (s, 2H), 3.67 (t, 2H), 4.33 (t, 2H), 6.77 (d, 2H), 7.00 (dd, 2H), 7.12−7.13 (m, 2H), 7.28 (dd, 2H), 7.87−7.93 (m, 4H), 8.31 (d, 2H). ^{13}C NMR ($CDCl_3$, 500 MHz, ppm): 12.17, 35.67, 45.52, 48.60, 61.75, 111.38 (2C), 122.60 (2C), 123.04, 124.63 (2C), 125.89, 126.20 (2C), 128.35, 133.05, 143.76, 147.35, 151.15, 156.68, 170.98.

3. Synthesis of Copolymers of 3-Alkylthiophene and 2-[*N*-Ethyl-*N*-[4-[(4-nitrophenyl)azo]phenyl]amino]ethyl 3-Thienylacetate [Poly(3-AlkT-*co*-3-DRT)] (Scheme 2). The polymerization was carried out in a three-neck flask under constant flow of dry argon. In a typical preparation a solution

Scheme 2



of 1.8 g (11.1 mmol) of $FeCl_3$ in 25 mL of chloroform and 6 mL of nitromethane was placed into the reactor. Then a solution of 0.3 g (0.7 mmol) of 2-[*N*-ethyl-*N*-[4-[(4-nitrophenyl)azo]-phenyl]amino]ethyl 3-thienylacetate in 6 mL of chloroform was added in one portion. In the next step a solution of 0.4 g (2 mmol) of 3-octylthiophene in 12 mL of chloroform was added dropwise. The polymerization was carried out at room temperature for 4 h with constant stirring, and then it was terminated by the addition of 200 mL of methanol. The precipitated polymer was then separated and washed repeatedly with methanol. Since the crude polymer is partially doped, it was treated with a mixture of NH_3(aq)/MeOH for 1 h in order to dedope it. The neutral polymer was washed with methanol in a Soxhlet apparatus and finally dried to constant mass.

4. Spectroscopic Studies. FTIR spectra were measured on a Biorad FTS 165 spectrometer in a transmission geometry. Thin films of the polymer were deposited on the surface of pressed KBr pellets by casting from chloroform solutions.

Raman spectra were recorded on a multichannel Jobin−Yvon T 64000 spectrometer connected to a CCD detector with an excitation line of 514.4 nm.

UV−vis−NIR spectra were recorded on a Perkin Elmer Lambda 2 spectrometer.

^1H and ^{13}C NMR spectra of the copolymers were recorded at 298 K on a Varian Unity 300 spectrometer operating at 299.35 and 75.144 MHz, respectively. The spectra of the comonomers were recorded on a Varian Unity 500 spectrometer operating at 500.60 and 125.88 MHz, respectively. In all experiments $CDCl_3$ was used as a solvent and tetramethylsilane as the internal standard.

5. Cyclic Voltammetry. For cyclic voltammetry thin layers of the polymers were deposited on a platinum working electrode by casting from chloroform solutions. Ag/AgCl was used as a reference and a Pt foil as a counter electrode. The voltammograms were recorded in 0.1 M Bu_4NBF_4/acetonitrile or 0.1 M Bu_4NClO_4/acetonitrile electrolytes using Autolab Electrochemical Instrument (Eco Chemie).

6. UV−Vis−NIR and Raman Spectroelectrochemistry. For UV−vis−NIR spectroelectrochemical measurements the polymers were deposited on indium−tin oxide (ITO) transparent electrodes by casting from chloroform solutions. In the case of Raman spectroelectrochemistry, Pt working electrodes were used. The electrolyte composition was the same as that in the case of cyclic voltammetry studies.

Results and Discussion

Although chromophore-substituted thiophene copolymerizes with 3-alkylthiophenes in the presence of $FeCl_3$, all attempts to obtain homopolymer of 3-DRT at the same reaction conditions were unsuccessful. Similar difficulties were reported before in the case of electropolymerization of spironaphthoxazine-functionalized thiophene.[9] Two possible explanations for the inhibition of the homopolymerization process given by the authors[9] can also be postulated in our case. The first one is connected with high steric interactions induced by bulky substituents, which can hinder coupling of thiophene rings. On the other hand, the presence of a redox-active group in the side chain can promote the reactions competing with the polymerization process. This last explanation seems convincing since Levesque and Leclerc[12] do not report any difficulties in the synthesis of homopolymers (Chart 1) whose side group chromophores are much less electroactive.

Table 1. Results of Elemental Analysis of the Copolymer of 3-Decylthiophene (3-DeT) and 2-[*N*-Ethyl-*N*-[4-[(4-nitrophenyl)azo]phenyl]amino]ethyl 3-Thienylacetate (3-DRT)

$[(3\text{-DeT})_{8.1}(3\text{-DRT})]_x$	% C	% H	% S	% N
calcd	72.72	8.87	13.03	2.50
found	72.32	8.92	12.60	2.40

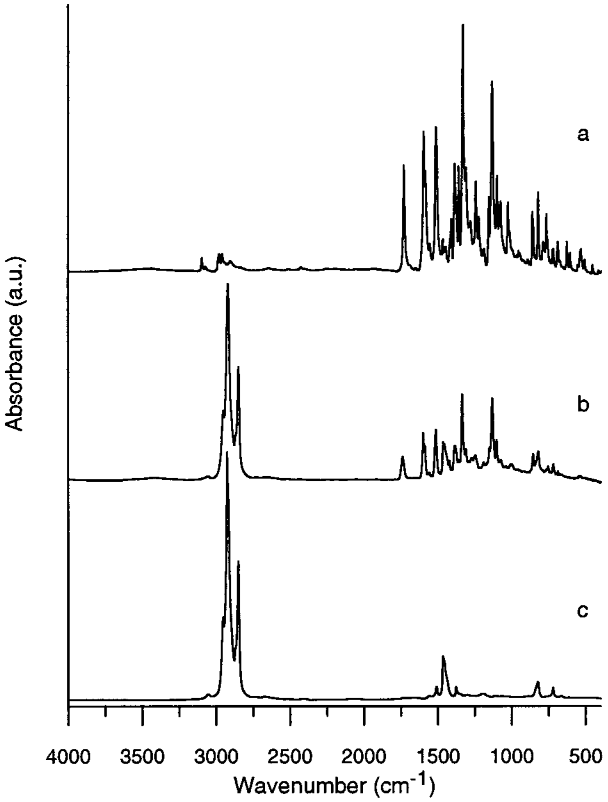


Figure 1. FTIR spectra of 2-[*N*-ethyl-*N*-[4-[(4-nitrophenyl)-azo]phenyl]amino]ethyl 3-thienylacetate (a), the copolymer of 3-decylthiophene and 2-[*N*-ethyl-*N*-[4-[(4-nitrophenyl)azo]-phenyl]amino]ethyl 3-thienylacetate (b), and poly(3-decylthiophene) (c).

All obtained copolymers of 3-DRT and 3-alkylthiophenes are partially soluble in such organic solvents as chloroform or toluene. The solubility of the product depends on the length of the alkyl group, as can be expected. The insoluble part of the polymer is significantly enriched in 3-DRT units as compared to the soluble fraction.

The ratio of 3-DR-2,5-thienylene units to 3-alkyl-2,5-thienylene units in the $CHCl_3$ fraction varies from 1:5 to 1:13 depending on slight differences in the copolymerization procedure and on the alkyl substituent size. The composition of the copolymer can be determined from the analytically measured N/S ratio. Typical elemental analysis data are listed in Table 1. Analytical results are in very good agreement with the chemical compositions of copolymers estimated on the basis of ^1H NMR measurements.

IR Spectroscopy. In Figure 1a the IR spectrum of 3-DRT is shown whereas in Figure 1b the corresponding

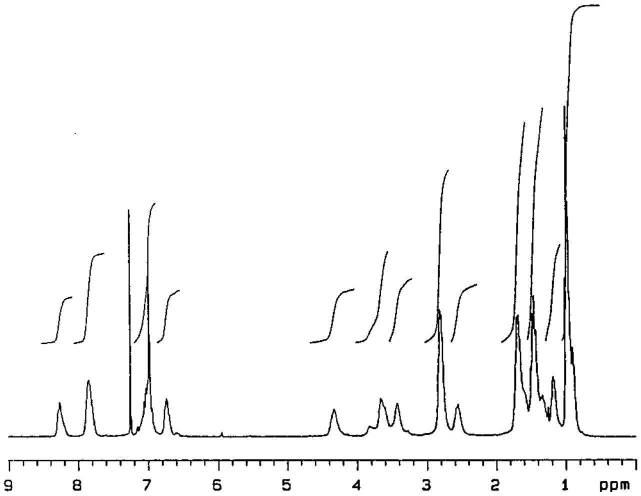


Figure 2. ^{1}H NMR spectrum of the copolymer of 3-butylthiophene and 2-[*N*-ethyl-*N*-[4-[(4-nitrophenyl)azo]phenyl]amino]-ethyl 3-thienylacetate.

spectrum of the copolymer of 3-decylthiophene and 3-DRT is presented. For comparison, the spectrum of poly(3-decylthiophene) is shown in Figure 1c. Spectral features of the ester derivative of DR are clearly seen in the copolymer spectrum, in particular the band at 1740 cm^{-1}, which can be ascribed to C=O stretching. In the region of 2000−600 cm^{-1} the bands originating from the chromophore dominate the spectrum (1600, 1515, 1387, 1338, 1135, and 824 cm^{-1}). The copolymerization process is manifested by the disappearance of the band at 768 cm^{-1}, which is characteristic of C−H deformation in a monosubstituted thiophene ring (compare parts a and b of Figure 1). It should be mentioned that few bands ascribed to the polythiophene backbone strongly overlap with those originating from the chromophore. For example, the band at 1515 cm^{-1} nearly coincides with the band at 1516 cm^{-1} in 3-DRT, and the band at 824 cm^{-1} corresponding to α−α′-coupled 3-alkylthiophene is very close to the band at 823 cm^{-1} present in the spectrum of 3-DRT.

NMR Spectroscopy. The ^{1}H NMR spectrum of the copolymer of 3-DRT with 3-butylthiophene is presented in Figure 2. On the basis of the comparison with the spectrum of the comonomer, we assigned the following lines corresponding to the protons of the chromophore: 1.19 ($-CH_3$), 3.44 ($-CH_2-CH_3$), 3.68 ($-CH_2-N$), 3.84 (CH_2-COO-), 4.34 ($-O-CH_2-$), 6.73, 7.85, and 8.28 ppm (protons of phenylene groups). The lines assigned to the butyl group are as follows: 0.99, 1.46 1.69 2.57, and 2.83 ppm. The line corresponding to the aromatic proton of the thiophene ring is located at 6.98 ppm. The last line probably consists of few, not well-resolved signals originating from nonregioregularity of the thiophene chain. Different types of couplings of thiophene rings (head-to-head as well as head-to-tail couplings) are always observed when the polymerization is performed via oxidation of β-substituted thiophene with $FeCl_3$.[16−19] Also as a result of nonregioregularity, two peaks (at 2.83 and 2.57 ppm) ascribed to the α-CH_2 group of the alkyl side chain are observed in the polymer spectrum. The dominant peak is shifted downfield with respect to the α−CH_2 peak of the monomer whereas the second peak of lower intensity is shifted upfield as previously reported.[16] Because of the same effect, the signal at 3.84 ppm assigned to the aryl methylene group of the chromophore-substituted thienylene ring appears at lower field than that in the monomer. The satellite peak probably overlaps with that associated with the $-CH_2-N$ group at 3.68 ppm.

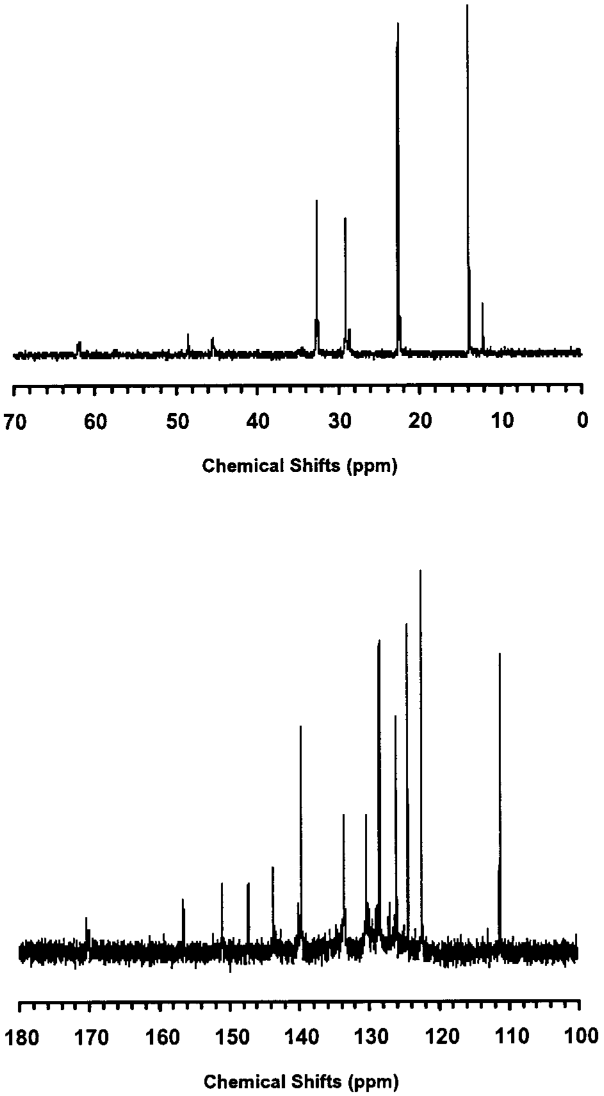


Figure 3. ^{13}C NMR spectra of the copolymer of 3-butylthiophene and 2-[*N*-ethyl-*N*-[4-[(4-nitrophenyl)azo]phenyl]amino]-ethyl 3-thienylacetate.

The integration of the lines originating from the protons of the DR substituent and the lines corresponding to the butyl group leads to the following composition of the polymer: poly(3-BuT-*co*-3-DRT) 5:1, which is in fairly good agreement with the composition determined from the elemental analysis.

The ^{13}C NMR spectrum of the copolymer is shown in Figure 3. Using INEPT-pulse sequence, we were able to distinguish the proton-bonded carbons from all other carbons present in the molecule. On the basis of the comparison with the spectra of 3-DRT and poly(3-alkylthiophene) homopolymers, we proposed the following assignments:

i. The line at the lowest field (170 ppm) corresponds to the carbon of the ester group.

ii. The lines at 156.47, 150.93, 147.19, 143.64, 126.04, 124.41, 122.41, and 111.20 ppm are assigned to the aromatic carbons in the DR moiety.

iii. The remaining four lines (at 139.64, 133.49, 130.29, and 128.43 ppm) originate from the carbons of the thiophene ring and can be attributed to C3, C5, C2, and C4, respectively.

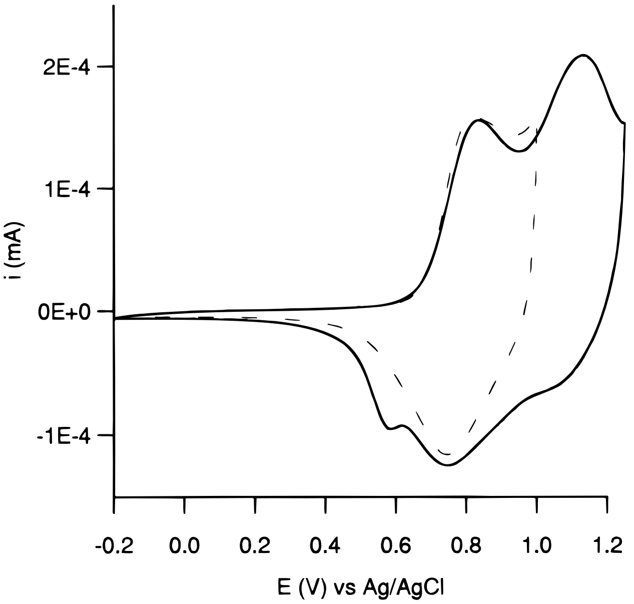


Figure 4. Cyclic voltammetry of a thin film of the copolymer of 3-butylthiophene and 2-[*N*-ethyl-*N*-[4-[(4-nitrophenyl)azo]phenyl]amino]ethyl 3-thienylacetate in a 0.1 M Bu_4NClO_4/acetonitrile solution. Scan rate: 0.05 V/s.

In the aliphatic part, the lines of low intensity at 12.17, 35, 45.43, 48.44, and 61.75 ppm correspond to the DR substituent whereas those of higher intensity (13.79, 22.48, 28.97, and 32.48 ppm) correspond to the carbon of the butyl group. Again the nonregioregularity of the system is manifested by the presence of the satellite lines in addition to the main peaks.

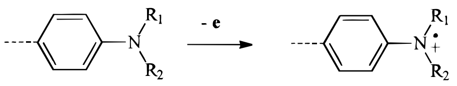
It should be noted at the end that the results of ^1H NMR, ^{13}C NMR, and IR spectroscopic studies are very consistent (vide supra).

Cyclic Voltammetry. Two types of electrochemical activities are expected for the obtained copolymers; first, electrochemical oxidative doping and reductive dedoping of the polyconjugated system; second, the oxidation of the azo dye. For these reasons it is instructive to compare the electrochemical behavior of the poly(3-alkylthiophene) homopolymer with that of the copolymers containing the electroactive dye.

The cyclic voltammogram of the copolymer cycled up to 1 V (Figure 4, broken line) closely resembles the one observed for poly(3-butylthiophene)[18] with an oxidation peak at 0.81 V and a reduction peak at 0.72 V vs Ag/AgCl. When the copolymer is oxidized further (Figure 4, solid line), an additional peak appears at higher potential (E_{pa} = 1.1 V vs Ag/AgCl). This second redox couple is not as reversible as the first one since after a few cycles the intensity of the peak decreases. We ascribed this redox couple to the oxidation of the chromophore side chain.

There are a few reports on the electrochemical oxidation of azo dyes. For example, Fasani et al.[20] studied the electrochemical behavior of a series of differently substituted *N*,*N*-dialkylamino azo dyes. These authors observed a reversible redox couple characteristic of one-electron transfer. As they found out, in the oxidative part of the cyclic voltammetry the dye is oxidized to the radical cation according to Scheme 3. In the reductive part the dye is reduced to the neutral state. The radical cation formed upon electrochemical oxidation is stable for several days. In our experiments with 2-[*N*-ethyl-*N*-[4-[(4-nitrophenyl)azo]phenyl]amino]ethyl 3-thienylacetate, we have observed similar electrochemical behavior (see Figure 5). To a first approximation, we can therefore treat the observed cyclic voltammetry of the copolymer as a superposition of the cyclic voltammogram of poly(alkylthiophene) and a dye.

Scheme 3



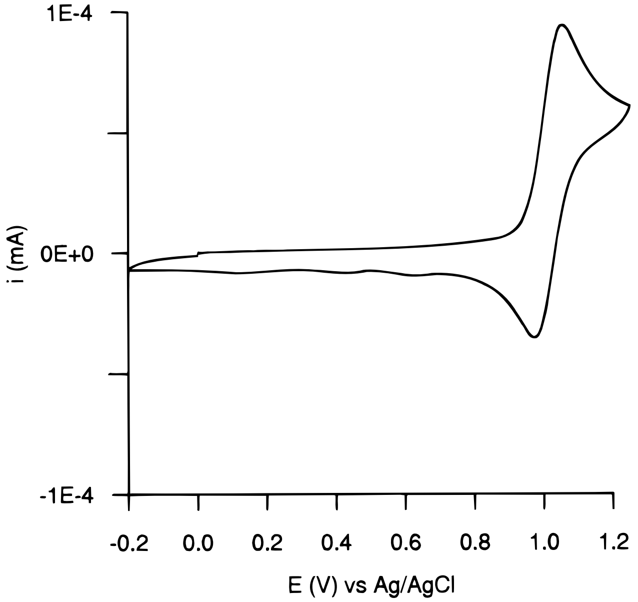


Figure 5. Cyclic voltammetry of 10^{-4} M 2-[*N*-ethyl-*N*-[4-[(4-nitrophenyl)azo]phenyl]amino]ethyl 3-thienylacetate in a 0.1 M Bu_4NClO_4/acetonitrile solution. Scan rate: 0.2 V/s.

Table 2. UV–Vis Data for Selected Poly(3-alkylthiophene) Homopolymers and Copolymers of 3-Alkylthiophenes and 2-[*N*-Ethyl-*N*-[4-[(4-nitrophenyl)azo]phenyl]amino]ethyl 3-Thienylacetate

	λ_{max} (nm)	
compound	solid state	$CHCl_3$ solution
PBuT homopolymer	494	440
P(3-BuT-*co*-3-DRT) (8:1)	455	446
P(3-BuT-*co*-3-DRT) (5:1)[a]	457	446
POcT homopolymer	494	440
P(3-OcT-*co*-3-DRT) (13:1)[a]	483	445
P(3-OcT-*co*-3-DRT) (7.6:1)[a]	477	
PDeT homopolymer	498	440
P(3-DeT-*co*-3-DRT) (8.4:1)[a]	481	447
3-DRT	485[b]	472
DR 1	495[b]	481

[a] Copolymer composition determined from ^1H NMR spectra and from elemental analysis. [b] Measured in a poly(methyl methacrylate) matrix.

UV–Vis–NIR Spectroscopy. UV–vis–NIR spectroscopic data for poly(alkylthiophene) homopolymers and the copolymers containing DR side groups are listed in Table 2. For comparative reasons, at the end of the table, spectroscopic data for 3-DR-thiophene (the comonomer used in the copolymerization) and DR1 (the dye used in the synthesis of the comonomer) are included.

Neutral poly(3-alkylthiophene) homopolymers exhibit one strong absorption peak ascribed to the π-π^* transition in the polyconjugated backbone. In the solid state this absorption peak is located at 494–498 nm, and it is very little dependent on the size of the alkyl substituent. Poly(3-alkylthiophenes) are solvatochromic;[21,22] i.e., upon dissolution the maximum of their absorption peak is blue shifted by ca. 55 nm.

The DR1 chromophore and its thienyl derivative (the comonomer used in polymerization) exhibit a very similar absorption spectrum peaked at 495 and 485 nm, respectively, in the solid state. The introduction of DR1 into poly(alkylthiophenes) results in a hypsochromic shift of their optical absorption registered for the solid state. Moreover, this blue shift increases with increasing chromophore content (see Table 2). This observation suggests that the bulky substituents tend to decrease the average conjugation length in the polythiophene backbone. It should also be noted that the solution spectra of the copolymers are much more similar to those of the corresponding homopolymers, which means that with increasing DR1 content the solvatochromic shift decreases (see Table 2).

The presence of the chromophore side group significantly alters spectroelectrochemical behavior of the copolymers as compared with the corresponding poly(3-alkylthiophene) homopolymers (Figure 6a). In Figure 6b spectroelectrochemical data are presented for the copolymer of 3-octylthiophene with 2-[*N*-ethyl-*N*-[4-[(4-nitrophenyl)azo]phenyl]amino]ethyl 3-thienylacetate.

The spectroelectrochemical behavior of the homopolymer has been described in several papers.[23−25] Oxidative doping, occurring when the electrode potential is raised from $E = 0$ V to potentials exceeding $E = 0.5$ V, results in a bleaching of the $\pi-\pi^*$ band with a simultaneous growth of two absorption bands in the NIR part of the spectrum. These two bands are associated with the formation of bipolaronic states in the doped polymer. Complete bleaching of the $\pi-\pi^*$ band takes place at $E = 1.0$ V. In our spectra only the first bipolaronic peak is registered because of the limits of the spectrometer used.

This gradual bleaching of the $\pi-\pi^*$ absorption is also observed upon electrochemical oxidation of the copolymers. However, in this case the band characteristic of the chromophore side group does not disappear but undergoes a small bathochromic shift to 516 nm. At potentials corresponding to the complete oxidative doping of the polymer, the band characteristic of the DR1 chromophore is clearly visible because it is no longer obscured by the $\pi-\pi^*$ transition of the polymer. The bathochromic shift of the chromophore absorption band seems to corroborate the conclusions drawn from the cyclic voltammetry studies that in the copolymers two types of electrochemical activities can be distinguished—electrochemical oxidative doping of the polyconjugated backbone and electrochemical oxidation of the chromophore.

Raman Spectroelectrochemistry. On the basis of the differences in the UV−vis−NIR spectra of the copolymer and the corresponding homopolymer observed for higher electrode potentials, one may expect different Raman spectroelectrochemical behavior of both systems. It should be stated here that Raman spectroelectrochemical studies of polythiophenes are usually complicated by strong resonance phenomena. As a result the Raman spectra of these polymers depend not only on the electrode potential but also on the energy of the excitation line.[24−26] The green excitation line ($\lambda_{exc} = 514$ nm) is located rather close to the maximum of the $\pi-\pi^*$ electronic transition band in neutral poly(3-octylthiophene) homopolymer. As a result, the bands originating from the neutral (undoped) segments of the polymer are resonantly enhanced and the oxidized (doped) segments of the polymer remain "invisible". Thus, in the Raman spectra no significant changes are observed with the increasing potential. The positions of the dominant bands at 1512 ($C_\alpha-C_\beta$ antisym), 1450 ($C_\alpha-C_\beta$ sym), and 1376 cm^{-1} ($C_\beta-C_\beta$ sym) remain unchanged. The only effect of the oxidative doping is manifested by a gradual decrease of the overall intensity of these peaks and their broadening with increasing electrode potential.[24] Raman spectroelectrochemical behavior of poly(3-octylthiophene) as studied with the use of the green excitation line unequivocally indicates that the neutral form is in resonance with the energy of the excitation line but the oxidized (doped) form is not.

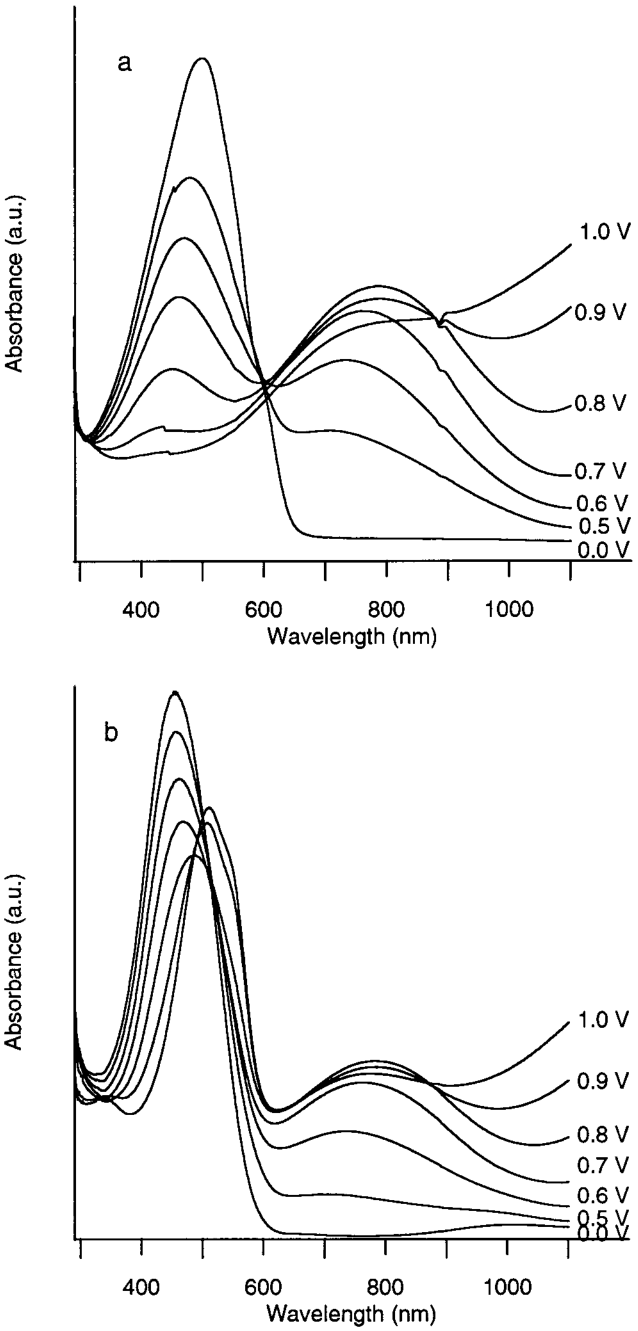


Figure 6. UV−vis−NIR spectra of poly(octylthiophene) (a) and of the copolymer of 3-octylthiophene and 2-[*N*-ethyl-*N*-[4-[(4-nitrophenyl)azo]phenyl]amino]ethyl 3-thienylacetate (b) recorded in a 0.1 M Bu_4NClO_4/acetonitrile solution at different potentials.

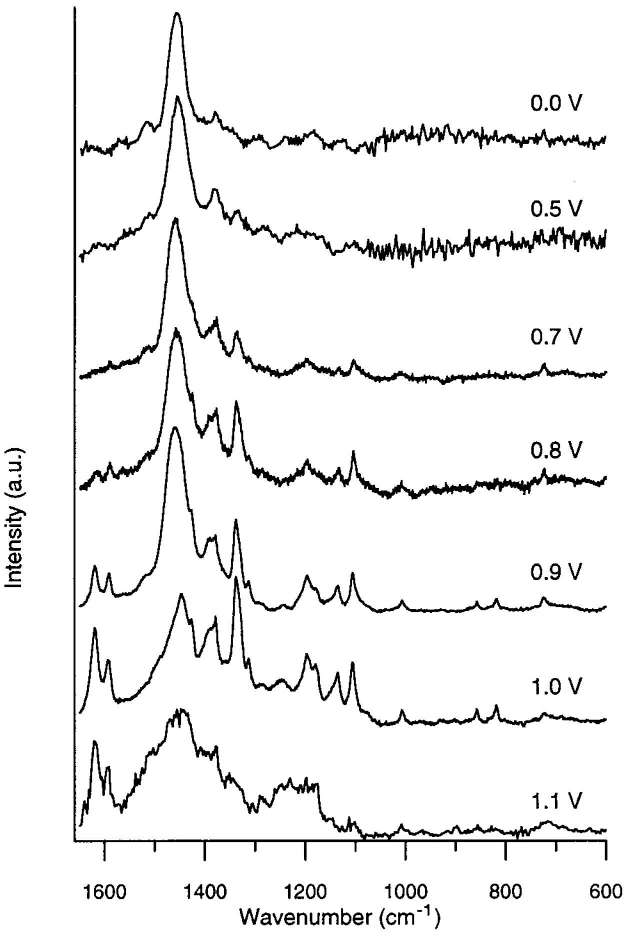


Figure 7. Raman spectra of the copolymer of 3-octylthiophene and 2-[*N*-ethyl-*N*-[4-[(4-nitrophenyl)azo]phenyl]amino]ethyl 3-thienylacetate in a 0.1 M Bu_4NBF_4/acetonitrile solution at different potentials.

The introduction of dispersed red–chromophore side chains drastically changes the resonant conditions for the oxidized form of the polymer. In neutral films of the copolymer, two dominant transitions, i.e., the $\pi-\pi^*$ transition in the thienylene chain and the transition characteristic of the neutral chromophore moiety, essentially coincide, being located at 483 and 485 nm for poly(3-octylthiophene-*co*-3-DRT). So, the resonant conditions for the Raman scattering are almost identical for both the polymer backbone and the chromophore side group. In the Raman spectrum registered at 0 V, three lines characteristic of the neutral conjugated polymer backbone can be distinguished at 1514, 1457, and 1378 cm^{-1} (Figure 7). It should be noted here that two Raman bands characteristic of the chromophore substituent are located in close vicinity to the polythiophene bands, i.e., 1446 (assigned as the N=N stretch[27]) and 1391 cm^{-1} (assigned as the phenyl–N stretch[27]). Thus, they can contribute to some broadening of the polythiophene bands observed at the potential of 0 V.

As in the case of poly(3-alkylthiophene) homopolymers, the resonance conditions for Raman scattering associated with the polyconjugated backbone worsen with increasing electrode potential. In contrast, the oxidation improves resonant conditions for the chromophore since upon oxidation the maximum of its spectrum shifts from 482 to 516 nm (vide supra). This latter maximum nearly coincides with the energy of the excitation line (514 nm). Thus, with increasing potential, Raman bands due to the polymer backbone weaken and the lines characteristic of the chromophore increase in intensity because of the improved resonance conditions. At $E = 0.5$ V, i.e., at the onset of the oxidative doping as determined from cyclic voltammetry, the strongest band ascribed to the chromophore is clearly visible at 1335 cm^{-1} (assigned as the NO_2 sym stretching mode[27]) despite the fact that in the copolymer studied by Raman spectroscopy only 1 out of 13 thiophene rings is functionalized with the chromophore.

With a further increase of the electrode potential, Raman bands ascribed to the chromophore functional group grow in intensity at the expense of the bands associated with the polymer backbone (Figure 7). At $E = 0.9$ V almost all of the lines originating from the vibrations of the chromophore can be easily distinguished: 1591 (ring stretching mode[27]), 1423, 1391, 1338, 1105, 857, and 818 cm^{-1}. The line at 1447 cm^{-1} contributes to the broadening of the 1457 cm^{-1} line of the polymer ($C_\alpha-C_\beta$ sym). The most significant spectroscopic manifestation of the chromophore oxidation is the appearance of a new band at 1619 cm^{-1}, which grows in intensity with increasing electrode potential. Because this is the region of C–C stretching of the aromatic ring, it can be postulated that the oxidation of the chromophore side group to the radical-cation type of structure significantly changes the vibration properties of the phenylene ring adjacent to the nitrogen atom being oxidized.

At $E = 1.0$ V the bands of the chromophore dominate the spectrum (Figure 7). No lines characteristic of the neutral chain are observed, which means that the oxidative doping of the polymer is completed at this potential.

In addition to the peaks originating from the chromophore vibrations, two peaks at 1197 and 1181 cm^{-1} are present at high electrode potentials. Such peaks usually appear in the Raman spectra of oxidatively doped polythiophenes. They can be ascribed to $C_\alpha-C_\alpha$ inter-ring stretching in the polythiophene chain, and their presence is usually interpreted as a manifestation of the formation of a quinoid-type bond structure upon oxidative doping.[24,28] It should be noted that at 1196 cm^{-1} a Raman peak of small intensity is registered for Disperse Red 1 and chromophore substituted thiophene. This peak can, therefore, contribute to the intensity of the observed band. At $E = 1.1$ V (Figure 7) oxidative degradation of the copolymer occurs, leading to a poorly resolved, essentially structureless Raman spectrum.

Conclusions

To summarize, we have synthesized new soluble polythiophene-based copolymers containing azo dye side groups. These new copolymers combine electrochemical and spectroelectrochemical properties of the polythiophene conjugated chain and the chromophore. The introduction of the chromophore significantly alters the resonant conditions for Raman scattering. As a result Raman spectroelectrochemical behavior of the copolymers probed with the green excitation line is different from that in the case of the corresponding poly(3-alkylthiophene) homopolymers.

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