"In Situ" Raman Spectroelectrochemical Studies of Poly(3,3′-dibutoxy-2,2′-bithiophene)

A. Pron,[†,⊥] **G. Louarn,***[‡] **M. Lapkowski,**[§,∥] **M. Zagorska,**[⊥]
J. Glowczyk-Zubek,[⊥] **and S. Lefrant**[‡]

Department of Materials Science and Ceramics, Academy of Mining and Metallurgy, Mickiewicza 30, 30059 Cracow, Poland, Laboratoire de Physique Cristalline, Institut des Matériaux, 2 rue de la Houssinière, 44072 Nantes Cedex 03, France, Institute of Physical Chemistry and Technology of Polymers, Silesian Technical University, 44100 Gliwice, Poland, Department of Textile Engineering and Environmental Sciences, Technical University of Lodz, Bielsko-Biala Campus, 43300 Bielsko-Biala, Plac Fabryczny, Poland, and Department of Chemistry, Technical University of Warsaw, Noakowskiego 3, 00664 Warsaw, Poland

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ABSTRACT: Raman "in situ" spectroelectrochemical studies have been carried out in order to elucidate the electrochemical doping of poly(3,3′-dibutoxy-2,2′-bithiophene). Raman spectra registered at different potentials strongly depend on the position of the excitation line with respect to the electronic spectrum of the polymer. In particular, blue (458 nm) and red (676 nm) excitation lines are very insensitive toward the oxidative doping of the polymer and independently of the electrode potential always give spectra characteristic of the unoxidized segments of the chain. To the contrary, the infrared excitation line (1064 nm) allows for detailed monitoring of the oxidative doping. The changes in the spectra occurring upon increasing potential of the electrode are consistent with the doping-induced transformation to the quinoid structure. The proposed assignments of the observed Raman bands have been confirmed by the vibrational analysis involving the calculation of the force field and frequencies via Fourier's dynamical matrix.

I. Introduction

Significant research interest, in the recent 14 years, has been devoted to the polythiophene family of compounds. This interest is stimulated by the fact that polythiophene belongs to the so-called "conducting polymers", i.e., the compounds which undergo an insulator to conductor transition as a result of electrochemical or chemical doping of the oxidative type.[1] Unsubstituted polythiophene, although highly conductive, after doping exhibits several drawbacks from both basic research and technological points of view:

(i) Both electropolymerization and chemical polymerization of unsubstituted thiophene are not regiospecific since in addition to α,α′-linkages a substantial amount of α,β′-bonds is created. These statistically occurring coupling defects make detailed characterization of the polymer more difficult.

(ii) Polythiophene undergoes oxidative doping at relatively high potentials. As a result doped polythiophene has a tendency to self-discharge phenomena which may be disadvantageous in several applications.

(iii) Unsubstituted polythiophene is infusible and insoluble. It cannot be therefore processed into technologically useful forms.

This last disadvantage of polythiophene can be easily removed by substitution of hydrogen in the 3-position of the thiophene ring by a long flexible alkyl group. Poly(3-alkylthiophenes) first synthesized by Elsenbauer et al.[2] are soluble in common organic solvents. They also retain their electroactivity and can be rendered conductive via oxidative doping.

However, it must be stressed here that poly(3-alkylthiophenes) are not regioregular which is caused by the geometrical nonequivalence of the coupling positions in the thiophene ring. Being predominantly "head-to-tail" coupled, they contain a significant amount of coupling defects involving "head-to-head" and "tail-to-tail" coupling.[3–5]

Regioregular poly(3-alkylthiophenes) can be obtained by the polymerization of 2-bromo-3-alkylthiophenes as demonstrated by McCoullogh et al.[6] In these polymers, virtually 100% of coupling are head-to-tail ones.

Regioregular polythiophenes with an alternative coupling pattern (pure head-to-head–tail-to-tail) can obtained by electrochemical or chemical polymerization of 4,4′-dialkyl-2,2′-bithiophenes[3,4,7] or 3,3′-dialkyl-2,2′-bithiophenes.[5] Unfortunately, poly(4,4′-dialkyl-2,2′-bithiophenes) and poly(3,3′-dialkyl-2,2′-bithiophenes) exhibit even higher oxidation potentials than the corresponding poly(3-alkylthiophenes).[7] In addition, UV–vis-near-IR and UPS spectroscopies[8] showed that a significant nonplanarity exists in these polymers due to strong steric interactions between alkyl substitutents in the head-to-head coupled rings. This nonplanarity if reduced upon doping, but the system does not become totally planar even for the highest doping level. As a result, for comparable doping levels, the conductivity of poly(4,4′-dialkyl-2,2′-bithiophenes) is *ca.* 1 order of magnitude lower than that of poly(3-alkylthiophenes).

One of the methods to resolve the high oxidation potential and nonplanarity problem in substituted polythiophenes is to introduce a strongly electrodonating alkoxy side group instead of an alkyl one. It has been demonstrated by Dietrich and Heinze et al.[9] that the interactions of the alkoxy side group with the conjugated π system of the polythiophene backbone lead to effective lowering of the oxidation potential in poly(3,3′-dimethoxy-2,2′-bithiophene) as compared to the corresponding poly(3-alkylthiophene).

[†] Academy of Mining and Metallurgy.
[‡] Institut des Matériaux.
[§] Silesian Technical University.
[∥] Technical University of Lodz.
[⊥] Technical University of Warsaw.
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In a series of papers, Leclerc and his co-workers[10-13] studied electronic and spectroscopic properties of various poly(3-alkoxythiophenes). In particular, they showed that in poly(3,3′-dibutoxy-2,2′-bithiophene) the absorption band due to $\pi-\pi^*$ transition is red shifted with respect to this band in other polythiophenes. The doping of poly(3,3′-dibutoxy-2,2′-bithiophene) results in the appearance of the bands in the near-infrared region of the spectrum. Since in all conducting polymers the doping causes bleaching of the $\pi-\pi^*$ band, the polymer becomes nearly transparent in the conductive state. Thus, poly(3,3′-dibutoxy-2,2′-bithiophene) is extremely attractive from the application point of view, owing it to its high transparency and wide range of potentials of electrochemical stability in the doped state.

In this paper we present a detailed Raman spectroelectrochemical study of poly(3,3′-dibutoxy-2,2′-bithiophene). Raman spectroscopy has proven to be an extremely useful probe for studying doping phenomena in conjugated polymers.[14-16] Although Raman spectra are complicated by resonance effects in essentially all conjugated polymer systems, the use of different excitation lines may provide spectroscopic and chemical information unobtainable by other spectroscopic methods.

II. Experimental Section

Synthesis of 3,3′-Dibutoxy-2,2′-bithiophene. 3,3′-Dibutoxy-2,2′-bithiophene was prepared from 3-butoxythiophene via a metalation reaction followed by dimerization with $CuCl_2$. For the preparation of 3-butoxythiophene the procedure published in ref 17 was used, whereas 3,3′-dibutoxy-2,2′-bithiophene was prepared using a modification of the method described in ref 3. The synthesis can be briefly described as follows:

(a) Metalation of 3-Butoxythiophene. 3-Butoxythiophene (8.5 g, 54 mmol) was mixed with butyllithium (44 mL, 15% solution in hexane) in the presence of tetramethylethylenediamine (6.8 g dissolved in 110 mL of dry ether). The reaction mixture was then heated at the boiling temperature for 2 h under a backcondenser.

(b) Dimerization. The reaction mixture prepared as described above was cooled to −78 °C using the methanol−dry ice bath. Then 7.3 g of $CuCl_2$ was added. The mixture was then allowed to warm up to the ambient temperature and additionally kept at room temperature for 15 h. At the end of the reaction 100 mL of 2 M HCl was added. The mixture was then washed four times with water and once with a saturated $NaHCO_3$ solution, again four times with water, and finally dried over $MgSO_4$. The solvent was removed in a rotary evaporator, and the crude product was purified chromatographically.

^1H NMR ($CDCl_3$): δ 7.1 (d, 2H) 6.84 (d, 2H), 4.1 (t, 4H), 1.84 (m, 4H), 1.57 (m, 4H), 0.99 (t, 6H). Elem Anal. Calcd for $C_{16}H_{20}O_2S_2$: C, 61.93; H, 7.09; S, 20.67. Found: C, 61.52; H, 7.16; S, 21.09.

Polymerization of 3,3′-Dibutoxy-2,2′-bithiophene. Poly(3,3′-dibutoxy-2,2′-bithiophene) was prepared by voltammetric polymerization of 3,3′-dibutoxy-2,2′-bithiophene. The polymerization reaction was carried out in a three-electrode cell using a platinum working electrode, a platinum counter electrode, and an Ag wire as a pseudo reference electrode. The anodic and cathodic parts of the cell were separated with a dense frit. The polymerization was carried out in a 0.1 M Bu_4NBF_4/acetonitrile electrolyte. The concentration of 3,3′-dibutoxy-2,2′-bithiophene was always in the range of $10^{-2}-10^{-3}$ M. In Figure 1, the first 13 cycles registered during the polymerization of 3,3′-dibutoxy-2,2′-bithiophene are presented. Irreversible oxidation leading to oxidative polymerization starts in this case at *ca.* 650 mV vs Ag, i.e., at significantly lower potentials than for 4,4′-dibutyl-2,2′-bithiophene studied in the same experimental conditions.[7] It should be stressed here that the polymerization yield is rather low since only the first redox couple shown in Figure 1 corresponds to the doping and dedoping of the polymer deposited on the electrode. The remain redox couples at higher potentials are due to oxidation and reduction of thiophene oligomers which are removed during the washing of the electrode. The deposited polymer, reduced on the electrode, washed with pure acetonitrile, and dried, is soluble in common organic solvents such as chloroform, methylene chloride, or THF. The FT-IR spectrum of poly(3,3′-dibutoxy-2,2′-bithiophene) is shown in Figure 2. As expected, the spectrum shows the bands characteristic of a three-substituted thiophene ring similar to those in the case of poly(3-alkylthiophenes).[18] A strong band at 1054 cm^{-1} due to the presence of C−O−C linkages which is absent in poly(3-alkylthiophenes) can be seen.

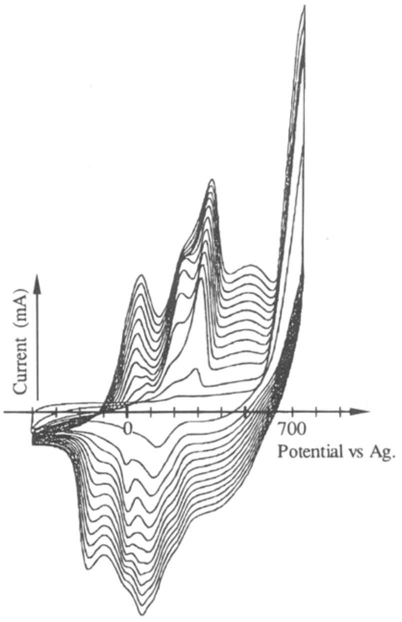


Figure 1. Voltametric synthesis of poly(3,3′-dibutoxy-2,2′-bithiophene) (potential range, −400 to +700 mV measured vs Ag; sweep rate, 50 mV/s).

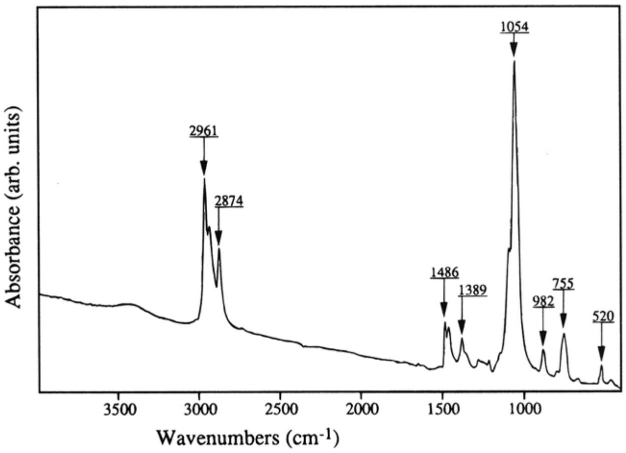


Figure 2. FT-IR spectrum of reduced poly(3,3′-dibutoxy-2,2′-bithiophene).

Cyclic Voltammetry. Cyclic voltammograms were recorded in a 0.1 M Bu_4NBF_4−acetonitrile solution using the same cell which was applied for the voltammetric polymerization. Poly(3,3′-dibutoxy-2,2′-bithiophene) was carefully washed with pure acetonitrile prior to voltammetric studies.

UV−Vis−Near-IR "in Situ" Spectroelectrochemical Studies. UV−vis−near-IR spectroelectrochemical studies were carried out using poly(3,3′-dibutoxy-2,2′-bithiophene) deposited on an ITO electrode with a Pt counter electrode and a Ag pseudo reference. The concentration of the electrolyte was the same as that in the voltammetric studies.

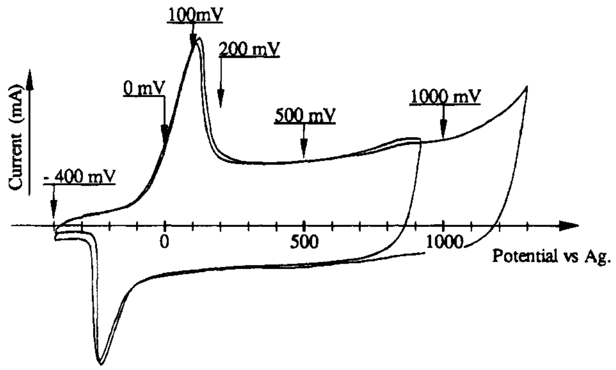


Figure 3. Cyclic voltametric curves of poly(3,3′-dibutoxy-2,2′-bithiophene) obtained in a 0.1 M solution of Bu_4NBF_4 in acetonitrile (potential scanning rate, 25 mV/s).

Raman Spectroelectrochemical Studies. Raman spectra were recorded for the polymer deposited on the platinum electrode using the same electrolytic solution as in other studies. The details concerning the construction of the electrochemical cell used for this study can be found elsewhere.[19] The potentials were measured vs Ag pseudo reference electrode. Three excitation lines were used: 458, 676, and 1064 nm. The spectra obtained for the excitation lines from the visible range were recorded on a multichannel Jobin-Yvon T64000 spectrometer connected to a CCD detector. For the IR excitation (1064 nm) a FT-Raman Bruker RFS 100 was used. The scattering signal was collected at 90° for the visible excitation lines. In FT-Raman experiments a backscattering configuration was used.

III. Results and Discussion

Typical voltammograms of poly(3,3′-dibutoxy-2,2′-bithiophene) are shown in Figure 3. In the potential range of −400 to +1300 mV one redox couple is observed associated with oxidative doping and reductive dedoping of the polymer. The oxidation peak with a maximum at 140 mV is relatively narrow similar to those in the case of regioregular poly(4,4′-dialkyl-2,2′-bithiophenes).[7] If the range of potential scanning is extended to 1600 mV, a second oxidation peak appears. However, the second redox process is not totally reversible and leads to a partial degradation of the polymer. Such behavior is characteristic of the majority of conducting polymers.[20] It must be, however, stressed here that poly(3,3′-dibutoxy-2,2′-bithiophene) exhibits an unusually wide range of electrochemical stability in the doped state since its oxidation potential of doping is much lower than that in poly(3-alkylthiophenes), whereas the oxidative degradation occurs roughly at the same potentials as those in poly(3-alkylthiophenes). These results are in good agreement with those reported by Faïd et al.[10] Similarly, a high electrochemical stability of the doped form has been found by Dietrich and Heinze et al.[9] for poly(3,3′-dimethoxy-2,2′-bithiophene).

The type of substituent and its distribution pattern along the polythiophene chain strongly influence the electronic properties of substituted polythiophenes. For example, in regioregular poly(4,4′-dialkyl-2,2′-bithiophenes) the conjugation length is significantly reduced as compared to those of unsubstituted polythiophene or poly(3-alkylthiophenes). This is caused by strong steric interactions between the alkyl substituents in the head-to-head coupled thiophene rings. As a result the $\pi-\pi^*$ transition is blue shifted.[3] Weaker steric interactions between −OBu groups in poly(3,3′-dibutoxy-2,2′-bithiophene) and their interaction with the π-system of the polythiophene backbone cause a significant red shift of the $\pi-\pi^*$ transition with respect to the analogous transition in unsubstituted polythiophene.

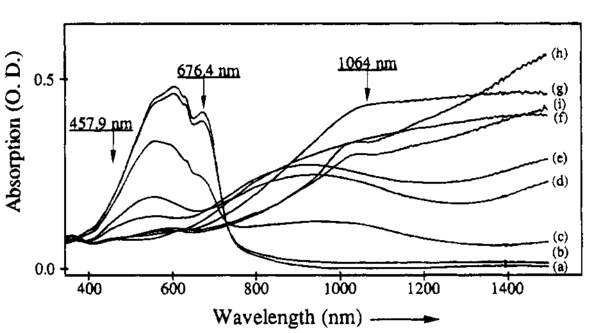


Figure 4. "In situ" UV−vis absorption curves of poly(3,3′-dibutoxy-2,2′-bithiophene) recorded for selected potentials of the electrode (vs Ag): (a) −400, (b) 0, (c) 50, (d) 100, (e) 200, (f) 500, (g) 1000, (h) 1400, (i) 1600 mV. The arrows indicate the positions of the excitation lines used in Raman with respect to the given spectra of poly(3,3′-dibutoxy-2,2′-bithiophene).

In Figure 4 UV−vis−near-IR spectra of poly(3,3′-dibutoxy-2,2′-bithiophene) registered for increasing electrode potentials are presented. The reduced (undoped) sample ($V = -400$ mV) exhibits a strong absorption band with a maximum at 610 nm. Electrochemical oxidation of the sample results in a gradual decrease of the band due to the $\pi-\pi^*$ transition with a simultaneous increase of the absorption in the near infrared. These changes well coincide with the onset of the oxidation peak in cyclic voltammetry (compare Figures 3 and 4); thus, an increase of the potential from −400 to 0 mV does not result in any significant change of the UV−vis−near-IR spectrum. The oxidation manifested by a decrease of the intensity of the $\pi-\pi^*$ transition starts at 0 mV, i.e., at the onset of the oxidation peak. A further increase of the potential (to 200 mV) results in essentially the total disappearance of the $\pi-\pi^*$ band at 610 nm with a simultaneous increase of the band at 900 nm. At $V = 500$ mV the absorption in the near infrared becomes monotonic, efficiently hiding the 900 nm peak. Such an absorption tail extended into the near infrared is characteristic of free carriers in polymers of high conductivity. A decrease of the near-infrared absorption at 1400 mV coincides with the oxidative degradation peak in the cyclic voltammetry and can be taken as spectroscopic proof of the degradation of conductivity.

In Raman spectroelectrochemical studies of conjugated polymers two effects must be taken into consideration:

(i) The position of a particular Raman line may depend on the excitation wavelength. This is associated with a distribution of conjugated lengths usually occurring in conducting polymers which causes, depending on the excitation line energy, different segments of the polymer to be in resonance.

(ii) The intensity of a particular Raman line may also depend on the energy of the excitation line. Oxidative doping of conjugated polymers drastically changes the resonance conditions, leading to selective enhancement or the disappearance of selected lines. For this reason, the spectra recorded at the same electrode potential but using different excitation lines may differ.[21,22]

The study of electrochemical doping of conjugated polymers requires therefore the registration of Raman spectra not only for different potentials covering the whole voltammogram but also for different excitation lines from the spectral region in which electronic transitions characteristic of the polymer occur.

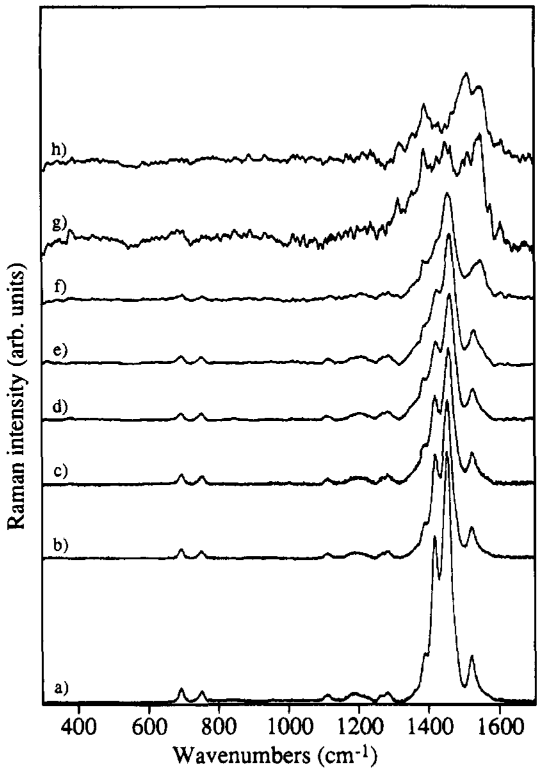


Figure 5. Raman spectra with λ_{exc} = 457.9 nm of poly(3,3′-dibutoxy-2,2′-bithiophene) recorded during the oxidation process. Selected electrode potential (vs Ag): (a) −400, (b) 0, (c) 50, (d) 100, (e) 200, (f) 500, (g) 1000, (h) 1400 mV.

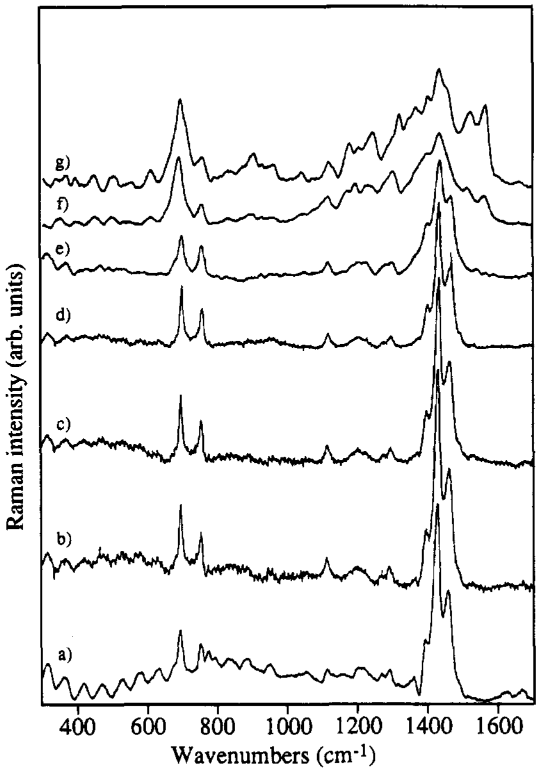


Figure 6. Raman spectra with λ_{exc} = 676.4 nm of poly(3,3′-dibutoxy-2,2′-bithiophene) recorded during the oxidation process. Selected electrode potential (vs Ag): (a) −400, (b) 0, (c) 100, (d) 200, (e) 500, (f) 1000, (g) 1400 mV.

Table 1. Refined Set of the Main In-Plane Force Constants of Polythiophene, Poly(3-decylthiophene), and Poly(3,3′-dibutoxy-2,2′-bithiophene)

force constant (mdyn/Å)	F_t^2	$F_{t'}^2$	$F_{t''}^2$	F_R^2	F_S^2
polythiophene	6.2	7.5	7.5	5.0	4.9
poly(3-decylthiophene)	6.5	7.5	7.4	5.3	5.0
poly-(3,3′-dibutoxy-2,2′-bithiophene)	5.8	7.6	7.1	4.9	5.1

The positions of the excitation lines used in this research with respect to the electronic spectrum of poly(3,3′-dibutoxy-2,2′-bithiophene) are indicated in Figure 4 by arrows. Both 458 and 676 nm excitation lines are located within the absorption band characteristic of the undoped poly(3,3′-dibutoxy-2,2′-bithiophene) and should resonantly enhance the undoped segments of the polymer. To the contrary, the IR excitation line (1064 nm) should reveal the presence of the oxidized (doped) segments since it is located well within the doping-induced band. Raman spectra recorded for the excitation line of 458 nm are presented Figure 5. In the reduced state (V = −400 mV) the spectrum is dominated by bands originating from the thiophene ring vibrations. There are, however, some differences between this spectrum and the one characteristic of unsubstituted polythiophene. The band at 1523 cm^{-1} can unambiguously be assigned to C_α=C_β antisymmetric vibration.[23,24] However, in the region of C_α=C_β symmetric vibrations two peaks are present which dominate the spectrum. Since the first peak at 1449 cm^{-1} occurs roughly at the same wavenumbers as in the case of unsubstituted polythiophene, it can be assigned to C_α=C_β–(H) group vibration, whereas the peak at lower wavelength (1415 cm^{-1}) must be due to C_α=C_β–(OBu) deformation. Two peaks of lower intensity at 695 and 750 cm^{-1} can be ascribed to S–C–S deformation (symmetric and antisymmetric respectively) in the thiophene ring. The bands due to C_β–C_β and C_α–C_α (inter-ring) in the vicinity of 1300 and 1200 cm^{-1} are broad and poorly defined. It should be stressed here that λ_{exc} = 458 nm is extremely insensitive to the oxidative doping process and reveals only the nondoped segments of the polymer. With increasing potential the intensity of the spectrum decreases but its essential features remain the same. At V = 1000 mV an abrupt degradation of the polymer occurs manifested by the appearance of a large number of poorly defined peaks.

Very similar behavior can be noted if λ_{exc} = 676 nm (Figure 6). Again the spectrum is practically independent of the electrode potential up to 1000 mV; then the degradation processes began to occur. The only striking difference between the spectrum recorded for λ_{exc} = 458 nm and that recorded for λ_{exc} = 676 nm is the inversion in the intensities between the bands due to C_α=C_β–(H) and C_α=C_β–(OBu), the last being strongly enhanced. Since the introduction of the butoxy group causes a red shift of the electronic spectrum, it is reasonable to assume that the vibration due to the presence of this group will be enhanced if longer excitation lines are used.

In order to confirm these assignments, we have performed a vibrational analysis. The method used has been described in our earlier paper[25] and can be briefly outlined as follows. The calculations of the force field and frequencies were carried out using Fourier's dynamical matrix. The calculation starts from a minimum basis set of force constants expressed in terms of the internal coordinates of the chain and defined by:

$$F_{RR'} = \left(\frac{\partial\phi}{\partial R\, \partial R'}\right)_0$$

where ϕ, R, and R' are the harmonic potential energy and two coordinates, respectively.

Table 2. Experimentally Observed Raman Modes in Polythiophene, Poly(3-decylthiophene), and Poly(3,3′-dibutoxy-2,2′-bithiophene)[a]

polythiophene								
A_g & B_{3g}		B_{1u} & B_{2u}		poly(3-decylthiophene)		poly(3,3′-dibutoxy-2,2′-bithiophene)		
expt	calcd	expt	calcd	expt	calcd	expt	calcd	assignment
				3055				C_β–H stretching
				2956		2961		C–H stretching of alkyl or butoxy groups
				2923		2920		
				2884		2874		
1520	1527		1512	1515	1511	1522	1512	C_α=C_β stretching
1444	1447					1451	1456	
			1435	1438	1436	1415	1401	
1361	1375			1385	1384	1290	1300	C_β–C_β stretching
		1370	1367	1375	1373			
1210	1208		1210	1200	1207	1190	1201	C_α–C_α stretching + C_β–H bending
1186	1147		1144	1160	1148	1170	1163	
1014	1010		1002	1018	1015		1004	ring deformation
				1091	1082	1112	1108	C_β–C_{subs} stretching
985	984	872	892					
720	715			725	716	754	757	
		741	735		562	699	676	S–C deformation
542	558		585				523	

[a] For comparison calculated Raman modes are presented.

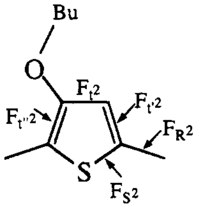
In our model, we assumed that certain force constants can be transferred among molecules and polymers of a chemically similar series like thiophene, oligothiophenes, polythiophene, and poly(3-alkylthiophenes). In this way, the number of independent constants are drastically reduced, and in our case this number is much lower than the number of observed frequencies. The force constants are determined and adjusted from the experimental frequencies with a least-squares root process by minimizing the quantity:

$$X = \left[\frac{1}{N}\sum_{i=1}^{N}(\omega^{i}_{\text{exp}} - \omega^{i}_{\text{cal}})^2\right]^{1/2}$$

in which ω^i_{exp} and ω^i_{cal} are respectively the experimental and calculated frequencies, whereas N is the number of experimental frequencies.

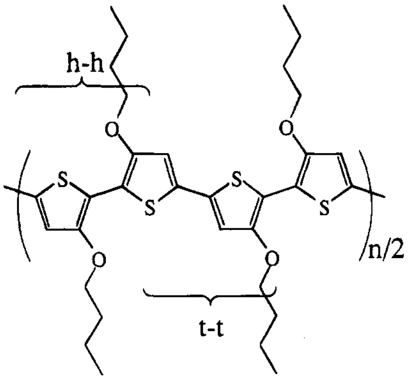
Geometrical parameters used in the calculation are taken from the work of Thémas et al.[26] We assume that the polymeric chains are infinite, have no defects, and are planar, especially for the ring (local planar symmetry in order to separate in-plane and out-of-plane vibrations).

The five parameters which reflect the electronic structure of the backbone are $F_t{}^2$, the force constant relative to the C_β–C_β bond, $F_{t'}{}^2$, the force constant relative to the C_α=C_β bonds, $F_{t''}{}^2$, the force constant relative to the C_α=C_β bonds with butoxy group substituted C_β, $F_R{}^2$, the force constant relative to the C_α–C_α bonds, $F_S{}^2$, the force constant relative to the C_α–S bonds according to the following scheme:



These main force constants are presented in Table 1 and in ref 23. The butoxy-substituted ring is characterized by an important decrease of C_α=C_β constants (with butoxy group substituted C_β): from $F_{t'}{}^2$ = 7.5 mdyn/Å in the polythiophene ring to $F_{t''}{}^2$ = 7.1 mdyn/Å in the butoxy-substituted ring. These values are in good agreement between calculated and observed frequencies within a reasonable limit, taking into account experimental errors, the hypothesis of ring planarity, and anharmonicity effects. Experimental and calculated frequencies are presented on Table 2 for polythiophene, poly(3-decylthiophene), and poly(3,3′-dibutoxy-2,2′-bithiophene). We have also added the assignment of IR and Raman vibrational modes.

As it has been already mentioned, the use of the 458 and 676 nm excitation lines does not lead to significant changes in the Raman spectra upon oxidation of the polymer. Interesting doping-induced changes can, however, be observed in Raman spectra if the infrared excitation line is applied (λ_{exc} = 1064 nm). For the reduced state (V = −400 mV) the spectrum resembles that obtained with λ_{exc} = 676 nm (compare Figures 6a and 7a). However, the increase of the potential to the onset of the oxidative doping (0 mV) results in drastic changes in the Raman spectrum. In order to clearly explain these changes, it is instructive to sketch the chain of poly(3,3′-dibutoxy-2,2′-bithiophene):



Since the chain of regioregular poly(3,3′-dibutoxy-2,2′-bithiophene) consists of a sequence of head-to-head and tail-to-tail coupled thiophene rings, two types of nonequivalent C_α–C_α inter-ring linkages are expected: these between h–h coupled rings and those between t–t coupled rings. Similarly two types of C_α=C_β are expected due to the presence of unsubstituted C_β and butoxy group substituted C_β. To the contrary, only one type of C_β–C_β bond is expected.

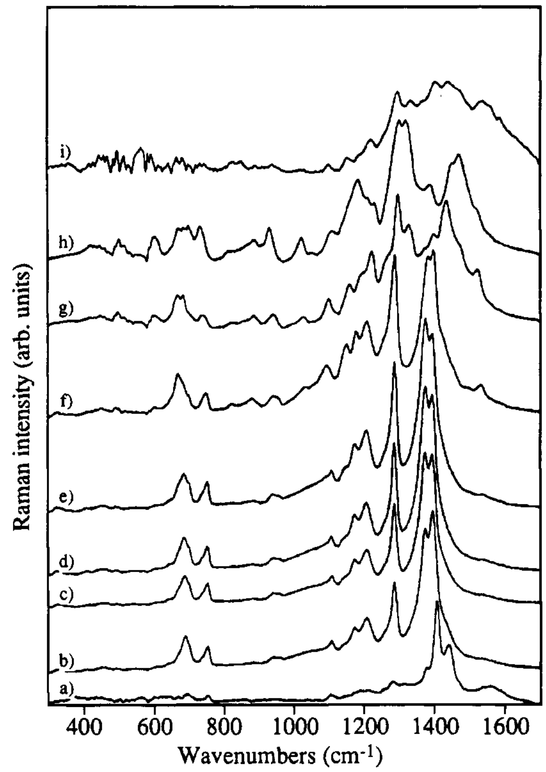


Figure 7. Raman spectra with λ_{exc} = 1064 nm of poly(3,3′-dibutoxy-2,2′-bithiophene) recorded during the oxidation process. Selected electrode potential (vs Ag): (a) −400, (b) 0, (c) 50, (d) 100, (e) 200, (f) 500, (g) 1000, (h) 1400, (i) 1600 mV.

Oxidative doping causes a redistribution of charge within the polymer backbone due to the formation of the domains with quinoid types of bonds. In Raman spectra of unsubstituted polythiophene it is manifested by a shift of $C_\alpha{=}C_\beta$ toward lower wavenumbers observed for those excitation lines which are in resonance with the oxidized units.[22] These phenomena are also observed in the case of poly(3,3′-dibutoxy-2,2′-bithiophene). The doping causes a shift of both lines ascribed to $C_\alpha{=}C_\beta{-}H$ and $C_\alpha{=}C_\beta{-}OBu$ to 1398 and 1377 cm^{-1}, respectively. Moreover, these lines characteristic of the quinoid structure appear and grow with increasing potential, namely: at 1288 cm^{-1} assigned to $C_\beta{-}C_\beta$ and two lines at 1209 and 1177 cm^{-1} due to two nonequivalent $C_\alpha{-}C_\alpha$ linkages. Thus, all changes observed upon doping are consistent with the doping-induced formation of quinoid segments. Again the degradation of the polymer above V = 1000 mV is clearly seen in Raman spectra.

IV. Conclusion

To summarize, we carried out detailed Raman spectroscopic studies of electrochemical doping of regioregular poly(3,3′-dibutoxy-2,2′-bithiophene). The obtained results allow for the formulation of the following conclusions:

Raman spectra registered at different potentials strongly depend on the position of the excitation line with respect to the electronic spectrum of poly(3,3′-dibutoxy-2,2′-bithiophene). In particular:

(1) Blue (458 nm) and red (676 nm) excitation lines are insensitive toward the oxidative doping of the polymer and reveal the presence of unoxidized segments independently of the electrode potential.

(2) The use of an infrared (1064 nm) excitation line allows for an unambiguous monitoring of electrochemical doping, showing at the same time the formation of quinoid segments in the polymer chain. This last observation is consistent with the generally accepted mechanism of doping in the polythiophene family of compounds.

(3) Raman spectroscopy studies show that significant degradation of the polymer occurs already at V = 1000 mV vs ECS, although in cyclic voltammetry the oxidative degradation peak starts at higher potentials.

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