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Electrochemical Oxidation of Polyaniline in Nonaqueous Electrolytes: "In Situ" Raman Spectroscopic Studies

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Spectroscopic properties of poly(3-alkylthiophenes) and their 'head-to-head', 'tail-to-tail' coupled analogues poly(4,4'-dialkyl-2,2'-bithiophenes)

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Abstract

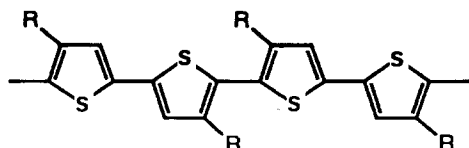
Electrochemical doping of new soluble conducting polymers, namely, poly(4,4'-dialkyl-2,2'-bithiophenes), has been studied *'in situ'* and *'ex situ'* by various spectroscopic methods. These compounds represent the 'head-to-head' and 'tail-to-tail' analogues of poly(3-alkylthiophenes). The $\pi \rightarrow \pi^*$ transition in poly(4,4'-dialkyl-2,2'-bithiophenes) is blue shifted with respect to that characteristic of poly(3-alkylthiophenes) suggesting a higher torsion angle between the adjacent substituted thiophene rings. The doping-induced bipolaronic bands (Vis-NIR) are, however, located in essentially the same positions as the doping-induced ones in poly(3-alkylthiophenes). This observation may suggest that during doping, more twisted poly(4,4'-dialkyl-2,2'-bithiophenes) adopt a structure more similar to that of doped poly(3-alkylthiophenes). The changes in FT-IR spectra are also consistent with the bipolaron model since all the five expected doping-induced modes appear with the onset of the oxidation peak and grow in intensity with increasing potential.

Introduction

Soluble poly(3-alkylthiophenes), synthesized a few years ago by different groups [1–4], have been the subject of growing interest in recent years [5–12], mainly due to their improved processability. More recently, a new group of soluble conducting polymers has been synthesized by electrochemical [13, 14] or chemical [15] oxidation of symmetrically disubstituted 4,4'-dialkyl-2,2'-bithiophenes.

These polymers exhibit interesting features as compared to classical poly(3-alkylthiophenes) which show the same stoichiometry. The main differences can be summarized as follows:

(i) The symmetry of the substrate forces regular coupling and the resulting chain is purely 'head-to-head' and 'tail-to-tail' coupled as schematically depicted below:



No coupling defects can be evidenced either by ^1H NMR [15] or by ^{13}C NMR [16]. To the contrary, poly(3-alkylthiophenes) in addition to predominant 'head-to-tail' coupling show a significant number of coupling defects involving 'head-to-head' and 'tail-to-tail' couplings [17, 18].

(ii) Close vicinity of alkyl groups in 'head-to-head' coupled thiophene rings results in a significant lowering of the conjugation length due to steric reasons. This decrease in conjugation is clearly manifested in the absorption spectra of poly(4,4'-dialkyl-2,2'-bithiophenes) and poly(3,3'-dialkyl-2,2'-bithiophenes) [19] which are blue shifted with respect to the spectra of the corresponding poly(3-alkylthiophenes).

Thus, poly(4,4'-dialkyl-2,2'-bithiophenes) are spectroscopically different to the corresponding poly(3-alkylthiophenes). It is therefore interesting to carry out a comparative study of both families of polymers which would involve different spectroscopic techniques such as UV-Vis-NIR absorption, Raman scattering, FT-IR, photoluminescence, etc. In addition, since both poly(3-

alkylthiophenes) and poly(4,4'-dialkyl-2,2'-bithiophenes) possess a non-degenerate ground state, their oxidative doping may result in two charge storage configurations: polarons or bipolarons. Oxidative doping gives rise to significant spectral changes in the region between 0.5 and 4 eV. The formation of polaronic (bipolaronic) states can therefore be monitored by studying doping-induced infrared active modes and doping-induced electronic transitions [20].

Experimental

Decylthiophene was prepared from 3-bromothiophene following the procedure already described [21]. 4,4'-Didecyl-2,2'-bithiophene was prepared from 3-decylthiophene in a two-step procedure involving lithiation of the monomer in the 5-position followed by oxidative coupling. The details of the preparation can be found elsewhere [15]. 3-Decylthiophene and 4,4'-didecyl-2,2'-bithiophene were then oxidatively polymerized with FeCl_3 to give poly(3-decylthiophene) and poly(4,4'-didecyl-2,2'-bithiophene), respectively [15]. Polymer films for all spectroscopic experiments were cast onto appropriate surfaces from saturated toluene solutions. Merck 'extra pure' toluene was used without further purification.

Resonance Raman scattering (RRS) spectra were recorded with standard equipment in a 90° scattering geometry and argon or krypton laser lines were used. An HG2S Ramanor (Jobin-Yvon) double monochromator was applied in all experiments. The signal was detected with a cooled GaAs photomultiplier coupled to a photon counting system. In order to avoid local degradation of the polymer, the light power was limited to 20 mW and the incident beam was defocalized ($\sim 3 \text{ mm}^2$). All experiments were performed at room temperature. IR spectra were measured on a Nicolet 20 SXC FT-IR spectrometer with a DTGS detector, whereas the UV-Vis-NIR spectra were obtained on a Cary 2300 spectrometer.

Doping-induced spectroscopic changes were monitored using spectro-electrochemical methods. Oxidative dopings were carried out electrochemically using 0.1 M LiClO_4 /acetonitrile electrolyte. Ag/AgCl was used as the reference electrode. An EG&G PAR 273 potentiostat-galvanostat was used for potential control. All electrochemical operations were done under dry argon.

For the registration of doping-induced IR modes, a specially designed cell equipped with an n-Si/Ti/Au electrode was used. Electrode structures containing a beam window of 5 mm diameter were fabricated by sputtering and lift-off photolithography. Before the experiment, the electrode surface was cleaned in 20%

HF solution, washed with deionized water and dried in a stream of nitrogen. Polymer layers were deposited in a glove bag filled with nitrogen to prevent the oxidation of silicon. In order to achieve quasi-equilibrium conditions of the redox reaction, the sample was kept under a given potential until current stability was achieved. After the measurement, the cell was carefully cleaned with acetonitrile and dried in a nitrogen flux. 1200 transmission interferograms were collected before conversion to FT-IR spectra. The same sample was used for all potentials studied.

In Vis-NIR studies, polymer films were deposited on an ITO transparent electrode. Before the deposition of the film, background spectra of the cell and electrolyte were recorded.

Results and discussion

In this section, we focus our attention only on poly(3-decylthiophene) and poly(4,4'-didecyl-2,2'-bithiophene), although compounds in the series of poly(3-alkylthiophenes) and poly(4,4'-dialkyl-2,2'-bithiophenes) (hexyl, octyl and decyl) have been simultaneously studied, but present similar results.

Undoped polymers

In Figs. 1(a) and (b), FT-IR spectra of undoped poly(3-decylthiophene) and poly(4,4'-didecyl-2,2'-bithiophene) are presented. Even in the wavenumber range $600\text{--}1600 \text{ cm}^{-1}$, spectra are dominated by the bands corresponding to aliphatic substituents in the thiophene ring (bands: $1464\text{--}1436$, 1377 and 720 cm^{-1}). The bands originating from the conjugated backbone vibrations are less intense (1511 , 1190 , 1120 , 824 and 746 cm^{-1}). In particular, the band at 824 cm^{-1} is characteristic of C-H out-of-plane deformations in position 3 of the substituted thiophene ring. The bands around 781 and 690 cm^{-1} , which correspond to two substituted (terminal) thiophene rings [22], are practically non-existent, which is consistent with the polymeric nature of the compound studied.

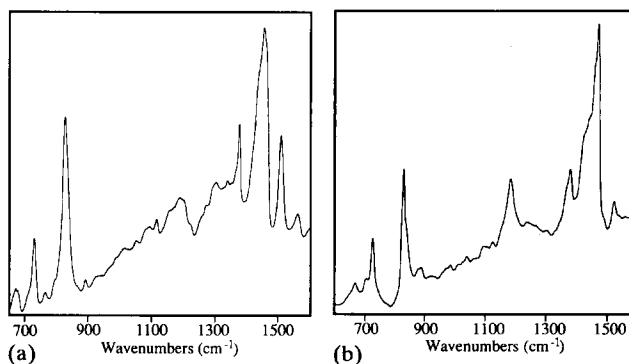


Fig. 1. FT-IR spectra of neutral thin films of (a) poly(3-decylthiophene) and (b) poly(4,4'-didecyl-2,2'-bithiophene).

Both poly(3-decylthiophene) and poly(4,4'-didecyl-2,2'-bithiophene) are photoluminescent. In the latter compound [23, 24], the fluorescence is about one order of magnitude stronger than in the former one (Figs. 2(a) and (b)). This strong fluorescence virtually excludes the recording of Raman spectra of poly(4,4'-didecyl-2,2'-bithiophene) with available laser line excitation. The Raman spectrum of poly(3-decylthiophene) obtained after subtraction of the band due to photoluminescence is shown in Fig. 2(c).

The observed features are in agreement with previously published data [25, 26] with main bands given in Table 1. It should be noted here that Raman spectra of 3-substituted polythiophenes are very similar to that of non-substituted polythiophene [27]. It is not unexpected since, under the conditions of the experiment (514 and 647 nm), we are in resonance (or close to it) with the $\pi \rightarrow \pi^*$ transition in the conjugated backbone. As a result, the bands originating from the backbone are strongly enhanced whereas those due to aliphatic substituents are practically invisible. One can notice one significant difference between the spectra of poly(3-alkylthiophene) and unsubstituted polythiophene. The band at 1375 cm^{-1} corresponding to $C_\beta-C_\beta$ stretching deformations is relatively strong in poly(3-decylthiophene) and very weak in polythiophene or thiophene oligomers [28]. In Table 1, the assignments of the

experimentally measured bands are listed and compared with theoretically predicted ones. In this Table, experimental and calculated results of poly(3-methylthiophene), which have been published previously [28], are given for comparison.

The vibrational analysis used can be briefly outlined as follows. The calculations of the force field and frequencies were carried out using the Fourier 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.

The optimization method used to refine these parameters is the usual least-squares fitting procedure. Geometrical parameters used in the calculations are taken from the work of Thémans *et al.* [29]. It is assumed that the unit cell symmetry is C_{2v} (which means 100% head-to-tail coupling) and that the chain is infinitely long. Under these geometrical conditions, the decomposition of the in-plane motions of the conducting backbone leads to 14 A_1 and 14 B_2 modes active in Raman and IR. Details of the calculations and assignments of the vibrational modes will be given in a forthcoming paper [30].

Doped polymers

Poly(3-alkylthiophenes) behave differently to poly(4,4'-dialkyl-2,2'-bithiophenes) in their oxidative doping. These differences are clearly manifested by the shape of their cyclic voltammograms (Figs. 3(a) and (b)). In poly(4,4'-didecyl-2,2'-bithiophene), the oxidative doping occurs at higher potentials as compared to the corresponding one in poly(3-decylthiophene) and over a very narrow potential range. The reduction part of the cycle is similar for both families of compounds. This means that, from the electrochemical point of view, the doping of poly(4,4'-dialkyl-2,2'-bithiophenes) is less reversible.

In Figs. 4(a) and (b), FT-IR spectra of poly(3-decylthiophene) and poly(4,4'-didecyl-2,2'-bithiophene) are shown for increasing potentials of doping. For both polymers, five new modes appear and grow in intensity with the increase of doping (1095 , 1171 , 1200 , 1343 and 1382 cm^{-1} in the case of poly(4,4'-didecyl-2,2'-bithiophene) and 1085 , 1162 cm^{-1} with a shoulder at 1200 , 1350 and 1390 cm^{-1} in the case of poly(3-decylthiophene)). It should be stressed that the doping-induced modes are better resolved in poly(4,4'-dialkyl-2,2'-bithiophenes), which is probably associated with a pseudo-centre of symmetry in these compounds.

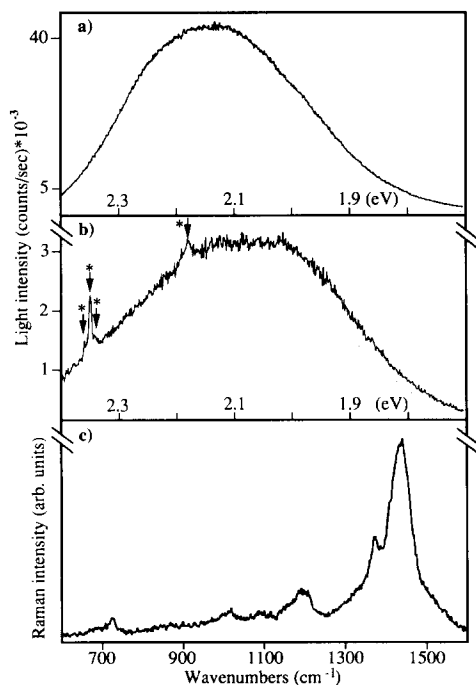


Fig. 2. Photoluminescence spectra recorded at 80 K with $\lambda_{\text{exc}} = 488.0\text{ nm}$: (a) poly(4,4'-didecyl-2,2'-bithiophene); (b) poly(3-decylthiophene). The asterisk indicates Raman lines superposed on the photoluminescence signal. (c) Raman spectrum of poly(3-decylthiophene) at 300 K with $\lambda_{\text{exc}} = 647.1\text{ nm}$.

TABLE 1. Experimental and calculated frequencies of Raman and infrared active modes for poly(3-decylthiophene) with results for poly(3-methylthiophene) given for comparison

Poly(3-methylthiophene)				Poly(3-decylthiophene)				Assignments
A ₁		B ₁		A ₁		B ₁		
Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	
						Exp.: 3055		C _β -H stretching
						Exp.: 2956		C-H stretching of alkyl groups
						2923		
						2884		
1520	1527		1512	1515	1511	1511	1510	C _α =C _β stretching
1444	1447		1435	1438	1436		1431	
1361	1375	1370	1367	1385	1384	1375	1373	C _β -C _β stretching
1210	1208		1210	1200	1107		1208	C _α -C _α stretching
1186	1147		1144	1160	1120		1143	C _β -H bending
1014	1010		1002	1018	1015		1008	ring def.
985	984	872	892	1091	1082		992	C _β -C _{subs} stretching
720	715	741	735	725	746		732	S-C deformation
542	558		585		562		589	
270	278				278			C _β -C _{subs} bending
	118				119			S-C-C _α deformation + C _β =C _α -C _α def. ang.

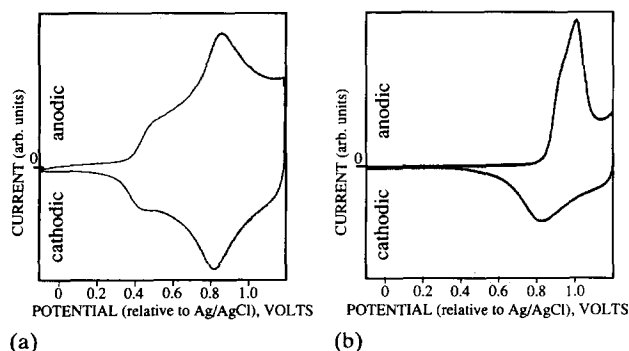


Fig. 3. Cyclic voltammograms of thin films on Pt recorded in 0.1 M LiClO₄/CH₃CN (sweep rate 20 mV/s): (a) poly(3-decylthiophene); (b) poly(4,4'-didecyl-2,2'-bithiophene).

It has been postulated previously [20, 31] that oxidative doping gives rise to four localized IR modes associated with bipolaron distortions of the polymer chain and made IR active through coupling to the uniform translation of the bipolaron. Usually, an additional absorption at higher wavenumbers, arising from an IR active localized mode associated with non-uniform translation of the bipolaron, is also observed.

Thus, the presented FT-IR results seem to suggest that, in poly(4,4'-dialkyl-2,2'-bithiophenes) as in poly(3-alkylthiophenes), the charge introduced to the chain is mainly stored in the form of bipolarons. This conclusion is further corroborated by UV-Vis-NIR spectroelectrochemical studies. The creation of bipolarons

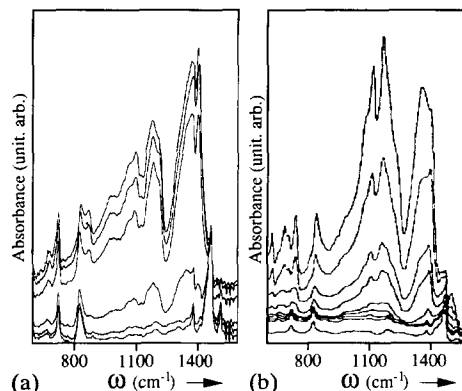


Fig. 4. Infrared spectra recorded during the oxidation process (in 0.1 M LiClO₄/CH₃CN): (a) poly(3-decylthiophene); (b) poly(4,4'-didecyl-2,2'-bithiophene).

should give rise to two allowed electronic transitions [32].

In Figs. 5(a) and (b), the electronic spectra recorded for increasing oxidative doping potentials are presented. It should be noted that for undoped polymers, the $\pi \rightarrow \pi^*$ transition in poly(4,4'-dialkyl-2,2'-bithiophene) is blue shifted showing lower conjugation caused by close vicinity of large alkyl substituents in the 'head-to-head' coupled thiophene rings. In both polymers, the oxidative doping results in gradual bleaching of $\pi \rightarrow \pi^*$ transition with the simultaneous growth of two subgap transitions, i.e. 1.6 and 0.8 eV for poly(4,4'-didecyl-2,2'-bithiophene), and 1.5 and 0.65 eV for

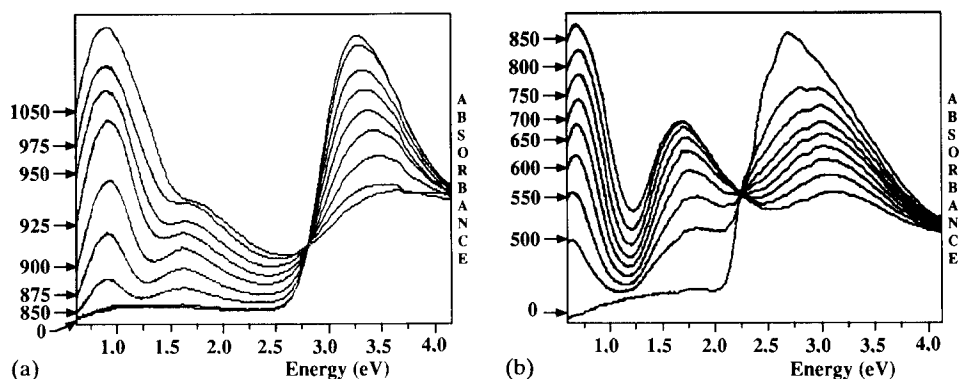


Fig. 5. 'In situ' UV-Vis absorption curves recorded during electrochemical doping with ClO_4^- : (a) poly(3-decylthiophene); (b) poly(4,4'-didecyl-2,2'-bithiophene). The applied voltages (vs. Ag/AgCl) are shown on the left side of the Figures.

poly(3-decylthiophene) in agreement with the bipolaronic model. A clear isosbestic point can be observed, consistent with the coexistence of only two optically different species.

The above-presented results are in excellent agreement with electrochemical spin response studies in poly(4,4'-dialkyl-2,2'-bithiophenes) and poly(3-alkylthiophenes) [33] which unequivocally show that charge injection during doping results in the formation of spinless bipolarons as dominating charge storage configurations.

Conclusions

We have studied spectroscopic properties of two types of soluble poly(alkylthiophenes) with different distribution patterns of substituents along the polymer chain, namely poly(3-alkylthiophenes) 'head-to-tail' coupled and poly(4,4'-dialkyl-2,2'-bithiophenes) 'head-to-head' and 'tail-to-tail' coupled. The results can be summarized as follows:

(1) Both families of compounds give practically the same infrared spectra consistent with an infinite chain of unsubstituted thiophene rings.

(2) Poly(4,4'-dialkyl-2,2'-bithiophenes) are strongly fluorescent and, due to this, the recording of their Raman spectra is impossible.

(3) In poly(3-alkylthiophenes), Raman bands associated with the conjugated backbone are enhanced due to resonance conditions whereas the bands due to aliphatic substituents are virtually invisible. The $\text{C}_\beta\text{-C}_\beta$ stretching vibrations occur with higher intensity than in unsubstituted polythiophene.

(4) The $\pi \rightarrow \pi^*$ transition in poly(4,4'-dialkyl-2,2'-bithiophenes) is blue shifted with respect to poly(3-alkylthiophenes) (3.25 eV versus 2.4 eV).

(5) Upon doping, five new IR active modes appear in both polymers; electronic and two subgap transitions occur at a similar energy in both polymers.

These last observations may suggest that poly(4,4'-dialkyl-2,2'-bithiophenes), during doping, modify their band structure towards that of classical poly(3-alkylthiophenes). Finally, these results are consistent with the formation of bipolarons upon oxidative doping in both families of polythiophenes.

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