Vibrational signatures of electrochemical p- and n-doping of poly(3,4-ethylenedioxythiophene) films: an in situ attenuated total reflection Fourier transform infrared (ATR-FTIR) study [☆]

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Abstract

The vibrational spectroscopic properties of electrochemically synthesized poly(3,4-ethylenedioxythiophene) (PEDOT) films were studied with in situ Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy. PEDOT films were p-doped (oxidized) and n-doped (reduced) electrochemically. The doping induced infrared absorption spectra (IRAV spectra) during p- and n-doping of PEDOT films were studied comparatively. The results are discussed within the framework of a stronger localization of charges in the case of n-doping compared to p-doping. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Conducting poly(3,4-ethylenedioxythiophene), PEDOT (structure shown in the inset in Fig. 2), has properties like high stability [1,2], high electrical conductivity [3,4] and a low optical band gap of approximately 1.6 eV [5] making this material a candidate for many industrial applications in the conducting polymer family. As antistatic material, PEDOT is already being used industrially in large scale [6]. Among electrically conducting polymers,

PEDOT has been shown to have one of the lowest redox potentials for p-doping. In organic electrolytes (acetonitrile-TBAPF$_6$) a redox potential, $E_{redox} = (E_{ox} + E_{red})/2$, of -200 mV (vs Ag/AgCl) for p-doping is reported for electrochemically made PEDOT films [7]. A similar redox potential was also found for films electrochemically cycled in aqueous electrolytes containing poly(styrene sulfonate) [8]. Cyclic voltammetric results from n-doping of PEDOT films was first reported by Inganäs et al. [3]. Results from UV–VIS measurements during p-doping [9,10] and n-doping [11] of PEDOT in organic solvents showed the well-known bleaching of the $\pi \rightarrow \pi^*$ transition and the occurrence of in-the-gap states due to polaronic quasi-particle excitations as in other polythiophenes. Recently it was reported that polymers from derivates of 3,4-ethylenedioxythiophene

are n-dopable [12]. As such this material is one of the very few examples within the conjugated conducting polymer family which is both p- and n-dopable. Combined with the high stability of this material, applications such as all polymer secondary batteries, which need both types of doping, are now within practical scope.

The vibrational spectra of conjugated, conducting polymers show strong unusual effects during doping (redox) processes, due to strong electron–phonon coupling within these quasi-one-dimensional solids [13–15]:

1. First, there is a "frequency dispersion" for few Raman lines in a continuous and smooth way by changing the effective conjugation length of the conjugated polymers whereas the infrared spectra does not show this effect. The infrared spectra, however, show an "intensity dispersion" by changing the conjugation length.
2. Upon doping, the infrared spectrum is dominated by new very strong doping induced infrared bands, the so-called infrared active vibration (IRAV) bands.
3. The intensity of the IRAV bands increases smoothly with increasing doping level.
4. The doping induced infrared absorption of stretch oriented samples is highly anisotropic along the chain axis of the molecules.

A first attempt to explain these observations listed above has been presented by Horovitz et al. [16,17]. The Horovitz theory considers the charge density wave, which exists in the dimerized form of *trans*-polyacetylene with the fact that π-electrons are coupled to the motion of the polymer backbone. The "pinning parameter" is used as a measure of localization. Zerbi et al. showed the correlation of the IRAV bands with the infrared activation of totally symmetric modes which contain a contribution by the "effective conjugation coordinate". This coordinate basically describes the changes of geometry from the ground state to the excited electronic state of the polymer along the so-called δ-coordinate. The smaller the value of the "effective conjugation force constant" the larger the "effective conjugation" of the polymer backbone [14]. Recently, Ehrenfreund and Vardeny established a link between the doping induced electronic states within the semiconducting $\pi \rightarrow \pi^*$

energy gap and the IRAV bands of the doping induced infrared spectrum [18]. Their model is based on a linear response theory by Soos and coworkers [19]. Furthermore, there are theoretical descriptions unifying these models [20,21].

In all the descriptions, there is a strong link between the effective conjugation of the macromolecule, effective delocalization of the doping induced (or photo-induced) quasi-particle excitations such as polarons, solitons etc. and the signatures of the IRAV bands in the doping induced infrared spectrum. Thus, in a system which is p- and n-dopable, i.e. supporting quasi-particle excitations of both signs, it should be possible to investigate these doping induced IRAV bands comparatively and to get information on the electronic effects by analyzing the infrared spectra. Especially, an in situ experiment, where p- and n-doping are carried out in one setup on the same sample, is a clean way of performing these comparative studies.

In this work we show that PEDOT is a conducting polymer that can reversibly be doped of both p- and n-type electrochemically in an organic electrolyte. In situ attenuated total reflection (ATR) Fourier transform infrared spectroscopy (FTIR) is used to study the spectroelectrochemical behavior and the doping induced IRAV absorption bands arising upon electrochemical p- and n-doping of PEDOT films. The results show the stronger pinning of the negatively charged quasi-particles (polarons) as compared to the positively charged ones. Furthermore, differences in IRAV frequencies are observed for different signs of doping.

2. Experimental

Acetonitrile (J.T. Baker) was freshly distilled over calcium hydride and purified by drying over superactive alumina, 70–230 mesh (Merck) prior to measurement. Tetrabutylammoniumhexafluorophosphate (TBAPF$_6$), tetraethylammoniumhexafluorophosphate (TEAPF$_6$) and tetrabutylammoniumperchlorate (TBAClO$_4$, all from Fluka) were dried under vacuum before use. The monomer 3,4-ethylenedioxythiophene was used as obtained from Bayer AG. Great caution was taken in order to protect the electrolyte from atmospheric oxygen and water throughout the experiments.
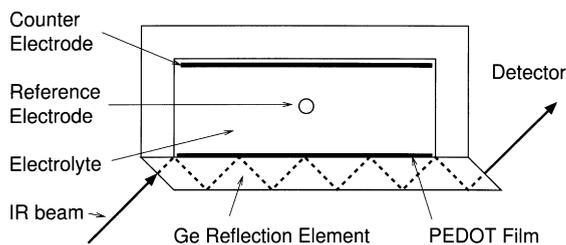
Fig. 1. Setup of the spectroelectrochemical cell.

The instrumental setup and the technique of spectroelectrochemical ATR-FTIR measurements, described in general, have been published elsewhere [22–24]. The three-electrode spectroelectrochemical cell is shown in Fig. 1.

The working electrode consisted of a reflection element of germanium coated with a thin layer of platinum. A platinum sheet and a silver wire coated with silver chloride were used as counter and reference electrodes, respectively. All potential values in the paper refer to the Ag/AgCl reference electrode. The electrochemistry was controlled by a Jaissle potentiostat and the FTIR spectra were recorded using a Bruker IFS66S spectrometer with an MCT detector.

FTIR spectra with a resolution of $4 \, cm^{-1}$ were recorded consecutively during slow potential sweeps. To obtain specific spectral changes during individual electrochemical reaction processes, a spectrum just before the considered reaction was chosen as the reference spectrum. The subsequent spectra were related to that spectrum, showing only the spectral differences to this reference state. For each spectrum 32 interferograms were coadded covering a range of about 90 mV in the cyclic voltammogram.

3. Results and discussion

The cyclic voltammetric response of a PEDOT film in monomer free solution can be seen in Fig. 2(a) and (b). The film was synthesized by potential scanning between −1000 and +1200 mV in 50 mM EDOT in 0.1 M TBAClO₄-acetonitrile. The potential range between −900 and +600 mV was cycled for p-doping and the range between −900 and −1975 mV for n-doping.

The redox behavior of PEDOT during p-doping has been described earlier [7]. In general, the cyclic voltammetric response from p-doping usually shows several redox peaks during the charging–discharging cycle. The main oxidation (p-doping) peak is between 0 and +200 mV and the main re-reduction (dedoping) peak between −400 and −500 mV depending on the film thickness.

The redox response of the film during n-doping can be seen in Fig. 2(b). A small peak occurs with a maximum at −1750 mV, at more negative potentials the current increases and during the reverse scan a re-oxidation (dedoping) from this process can be seen immediately after the scan direction is reversed. A re-oxidation current corresponding to the first reductive process at −1750 mV was not found in the cyclic voltammogram. However, when slower scan rates are used (5 mV/s), a small re-oxidation peak is seen at −1550 mV.

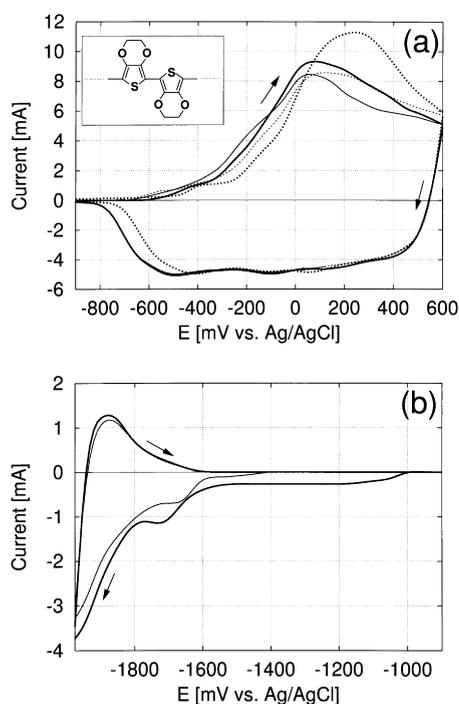The cyclic voltammetric behavior of p-doping after

Fig. 2. Cyclic voltammograms of a PEDOT film on a Pt electrode cycled in 0.1 M TBAClO₄-acetonitrile solution at a scan rate of 100 mV/s. Thick lines: first cycle; thin lines: second cycle. (a) p-doping of a fresh film (solid lines), p-doping after n-doping (dotted lines); (b) n-doping between the p-doping experiments. Inset: structure of PEDOT.
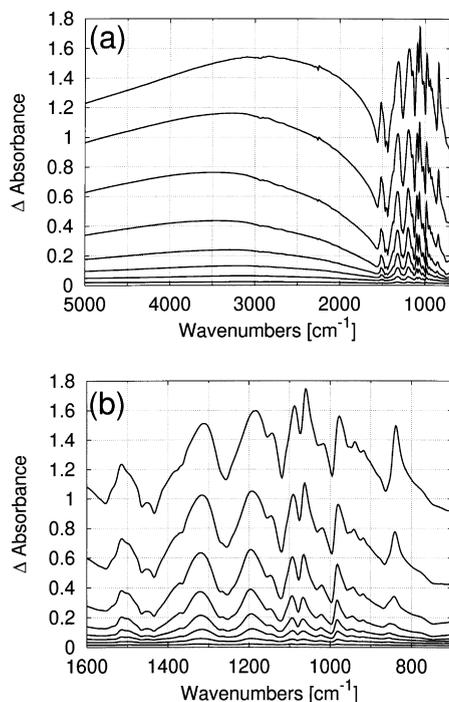
Fig. 3. In situ FTIR-ATR difference spectra of a PEDOT film in 0.1 M TEAPF$_6$-acetonitrile solution during anodic potential sweep (p-doping) between -900 and $+600$ mV; scan rate 5 mV/s; reference spectrum at -900 mV. (a) full spectral region; (b) enlargement of (a) in the region 1600–700 cm^{-1}.

Fig. 5. In situ FTIR-ATR difference spectra of a PEDOT film in 0.1 M TBAClO$_4$-acetronitrile solution during cathodic potential sweep (n-doping) between -900 and -1900 mV; scan rate 5 mV/s; reference spectrum at -1500 mV. (a) full spectral region; (b) enlargement of (a) in the region 1600–1700 cm^{-1}.

previous n-doping is shown in Fig. 2(a) (dashed curves), where the film was cycled two times in anodic direction (p-doping) after n-doping/dedoping. The anodic peak potential of the first cycle is shifted
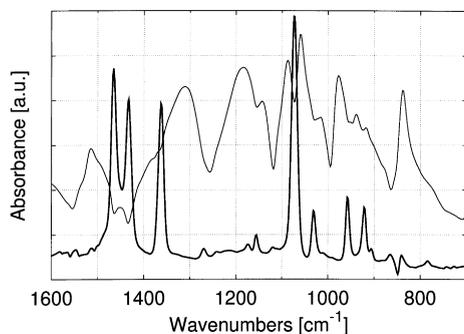

Fig. 4. In situ spectrum of a neutral PEDOT film at -900 mV (thick line, reference spectrum: filled cell without polymer), and the spectrum of a p-doped film at $+500$ mV (reference spectrum at -900 mV). The spectra are separated and scaled individually.
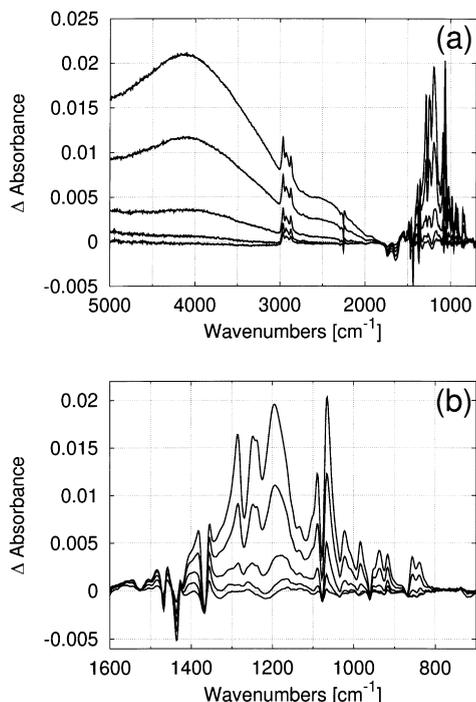
with 200 mV in the positive direction in that case. In general, the charge involved in the redox processes during n-doping is always smaller than the charge involved in p-doping.

The in situ ATR-FTIR difference spectra from the p- and n-doping of PEDOT are displayed in Figs. 3 and 5. In Fig. 3 the spectra are gathered during p-doping at a scan rate of 5 mV/s. The frequency region 5000–700 cm^{-1} is seen in Fig. 3(a) and the region 1600–700 cm^{-1} in Fig. 3(b).

The development of the doping induced bands in the IR spectra starts at a potential that coincide well with the potential at which the first Faradic current can be detected in the cyclic voltammogram (-500 mV). Bands at 1513, 1319, 1195, 1090, 1060, 980 and 849 cm^{-1} grow in during the oxidation process, all of which are absent in the spectrum of a neutral film. The spectrum of a p-doped film recorded at $+500$ mV and of a neutral PEDOT film obtained in situ when applying -900 mV are compared in Fig. 4.
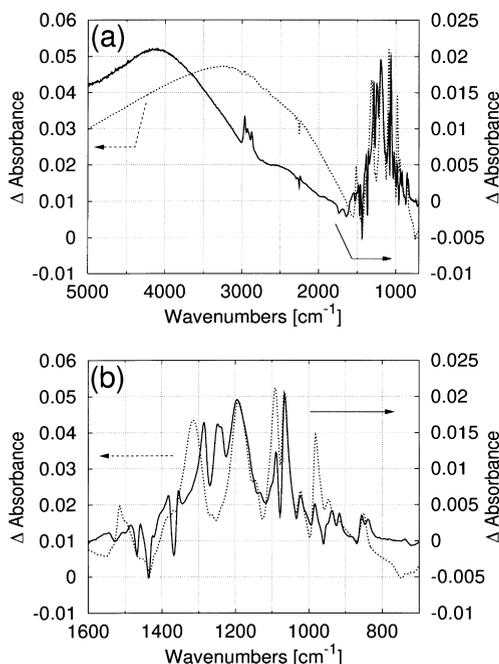
Fig. 6. Comparison of in situ FTIR-ATR difference spectra of p-doped and n-doped PEDOT with similar doping levels in 0.1 M TBAClO$_4$-acetonitrile solution. Solid line: n-doped, spectrum at −1800 mV, reference spectrum at −1500 mV; dashed line: p-doped, spectrum at −300 mV, reference spectrum at −900 mV. (a) full spectral region; (b) enlargement of (a) in the region 1600–700 cm^{-1}.

The spectra are scaled individually for clear comparison. The intensities of the p-doping induced IRAV bands are about 20–30 times higher than the bands of the neutral form.

The p-doping induced IRAV effects are fully reversible. The spectral feature above 2700 cm^{-1} shows the electronic absorption related to the formation of charge carriers typical for conducting polymers [25]. The maximum of the absorbance is shifted to just below 3000 cm^{-1} upon maximum p-doping, i.e. at +600 mV. In Fig. 5(a) and (b) difference spectra during n-doping of a PEDOT film are shown. Before spectra were recorded the film was kept at −900 mV for several minutes in order to reach the neutral form. At −1670 mV some spectral features from the neutral film are bleached, simultaneously new bands start to develop. The main growth of the n-doping induced IRAV bands takes place in the potential region between −1780 and −1900 mV, i.e. the potential

where the strong increase of the Faradic current in the cyclic voltammogram occurs. The main bands during n-doping appear at 1285, 1245, 1195, 1090 and 1060 cm^{-1}. The maximum of the free carrier absorption can be seen above 4000 cm^{-1}. The spectral features in the range of the aliphatic C–H vibrations at 2800–3000 cm^{-1} are due to the incorporation of TBA$^+$ ions into the film, which balance the negative charges of the n-doped polymer chain (during p-doping, the spectral response of the analogous incorporation of ClO$_4^-$ ions is hidden by the intense IRAV band at 1090 cm^{-1}).

Since the amount of n-doping in our experiments was much less than during p-doping, the spectrum of the n-doped form is compared with the spectrum of a p-doped form of similar doping level in Fig. 6(a) and (b). The doping level was around 2.5% calculated from the electrochemical charge ratio to fully p-doped PEDOT, which is assumed to be 25% as usually found in thiophene based conjugated polymers [26]. Besides differences in the relative intensities, the IRAV bands at vibrational energies below 1200 cm^{-1} are similar for the p- and the n-doped structures. Above 1200 cm^{-1} differences in the p- and n-doped forms are observed:

1. The band at 1513 cm^{-1} is missing in the n-doped form.
2. Instead of the band at 1315 cm^{-1} in p-doping two new bands at 1285 and 1245 cm^{-1} are seen in n-doping.
3. The maximum of the electronic absorbance is found at just above 4000 cm^{-1} for n-doping instead of around 3000 cm^{-1} for p-doping.
4. The relative intensities of the bands are different in the two differently charged forms.
5. The intensities of the bands in n-doping are generally lower than the intensities of fully p-doped material.

The same film can be switched between n-type and p-type charging and the doping induced IRAV bands for both signs of doping are reproducible. No spectral differences or changes in the cyclic voltammetric behavior due to degradation products were observed (up to six scans in the spectroelectrochemical studies, up to 20 scans in cyclic voltammetric experiments).

The origin and behavior of doping induced IRAV bands can be described in the framework of the

effective conjugation coordinate model presented by Zerbi and coworkers. The IRAV bands correspond to totally symmetric Raman active vibrational modes, which couple to the π-electron system. The vibrations become infrared active due to symmetry breaking and are strongly enhanced, because the charge distribution in the formed polaronic state causes high dipole moment changes during vibration. In general, in the frequency range between 1600 and 800 cm^{-1} four A_g modes exist in polythiophene, which give rise to an absorption pattern of three strong bands in the photo-induced absorption spectrum [27] and in the doping induced absorption spectrum [28] as well as to three Raman bands [29] in unsubstituted polythiophenes. Although the force field calculated for polythiophene [14] may not be directly applicable to substituted polythiophenes, the pattern of three main bands (1319, 1195, doublet at 1090 and 1060 cm^{-1}) is also observed during p-doping of PEDOT. Additional bands at 1513 and 980 cm^{-1} at p-doping may be related to the oxygen containing substitution of the PEDOT rings.

For n-doping, the nature of the charge carriers are different. The IRAV bands at comparable doping level are smaller, and the band pattern looks different. A direct correlation to the calculated force field of poly-thiophene could not be obtained. A different behavior of the infrared absorption features of p- and n-doped conjugated polymers with nondegenerate ground state was also reported by Kim et al for poly(paraphenylene–vinylene) [30]. The lower intensities of the IRAV bands together with the maximum of the electronic absorption at higher energies indicate a higher localization of the doping induced charge carriers and a smaller effective conjugation in n-doped PEDOT.

4. Conclusions

Electrochemically synthesized PEDOT films have been p- and n-doped several times without any spectral indication due to degradation. A lower degree of n-doping compared to p-doping has been obtained. The doping induced IRAV-bands arising from p- and n-doping are not identical, indicating that the material exhibits different electronic structures by positive and negative charging. The charge carriers are more localized in the case of n-doping. If extrapolated to other members of functionalized poly-thiophenes this finding has important consequences for the design and performances of optoelectronic devices such as light emitting diodes and solar cells.

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