

Electrochemical bandgaps of a series of poly-3-*p*-phenylthiophenes

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Abstract The change of the UV-Vis optical absorption of electropolymerized substituted poly-3-*p*-X-phenylthiophenes ($X = -H, -CH_3, -OCH_3, -COCH_3, -COOC_2H_5, -NO_2$) has been followed in situ as a function of applied electrode potential in an electrolyte solution of tetraethylammoniumtetrafluoroborate Et_4NBF_4 in acetonitrile. The UV-Vis spectra show features between 300 and 900 nm similar to those observed with many other polythiophenes having a high degree of conjugation. During stepwise oxidation of the poly-3-*p*-X-phenylthiophene films, the intensity of the absorption due to the $\pi \rightarrow \pi^*$ -transition around 450–566 nm decreases, and a new broad absorption band associated with (bi)polaron states appears around 730–890 nm. On the other hand, during the oxidation (*p*-doping) of the poly-3-*p*-X-phenylthiophene films, a blue (hypsochromic) shift is observed for both absorption bands. This is explained by taking into account that a polymer contains a distribution of chain lengths, and the longest polymer chains (the absorption of which occurs at lower energies) start to oxidize at the relatively lowest potentials. The electrochemical bandgaps of poly-3-*p*-X-phenylthiophenes have been estimated based on results of cyclic voltammetry. Bandgaps obtained this way have been found to be generally higher than optical bandgaps; the actual discrepancy was found to depend on the mode of evaluation.

Introduction

Numerous conjugated polymers have been synthesized, since the discovery in 1977, that polymers can conduct electricity when doped [1]. In particular, substituted regioregular polythiophenes [2] are prominent as some of the most promising members of the conjugated polymers family because they are stable and processable, they show very high charge carrier mobilities [3] and they become highly conducting upon doping [4]. Thus, the polythiophenes constitute a class of conjugated polymers that has been incorporated in electroluminescent devices such as polymer light emitting diodes [5], microcavities [6], solar cells [7] and recently, optically pumped lasers [8].

Cyclic voltammetry has been recognized as an important technique for measuring bandgaps, electron affinities, ionization potentials and work functions on various conjugated polymers [9]. The oxidation process corresponds to the removal of an electron from the highest occupied molecular orbital (HOMO) energy level, whereas the reduction corresponds to the electron addition into the lowest unoccupied molecular orbital (LUMO). If the oxidation/reduction processes can be measured using the same electrolyte/solvent system and if the redox processes involve the same functional moiety of the studied compound, one may expect that the difference between the two onset potentials should closely follow the optical bandgaps.

Johansson et al. [10] have determined the bandgaps $E_{g,EC}$ from electrode potentials for redox conversions of 30 different polythiophenes, which are both *n*- and *p*-dopable. The *n*-doping of polythiophenes with alkyl or alkoxy groups at position 3 or at positions 3 and 4 of the thiophene ring has usually turned out to be difficult [11]. Phenyl substitution at position 3 of the thiophene ring yields *n*-dopable polymers without exceptions. On the other hand,

Dedicated to Piero Zanello on the occasion of his 65th birthday in recognition of his numerous contributions to inorganic electrochemistry.

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they found that the electrochemical bandgaps are in general larger than optical bandgaps. The poor agreement and the lack of standards in reporting and translating redox potentials suggest that the well-established procedure of evaluating HOMO and LUMO positions in cyclic voltammograms may be a misleading method.

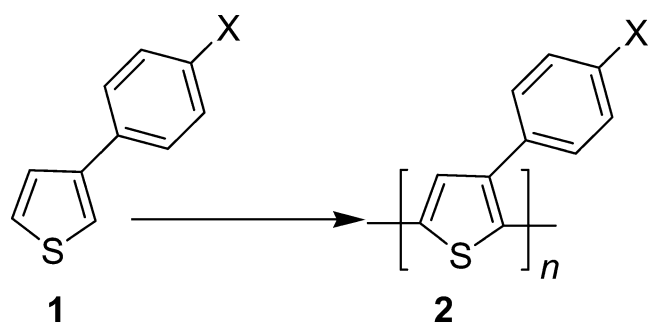
Greve et al. [12] have studied the effect of substituents on the redox properties of three novel-3-substituted polythiophenes. As a result of their study, they found that, although the differences in oxidation potential are significant, the electrochemical bandgap remains more or less constant because the reduction potential increases along with the oxidation potential, whereas the electronic levels of the highest occupied molecular orbitals and the lowest unoccupied molecular orbitals may vary over 0.5 eV. Moreover, they demonstrated that the optical bandgaps are smaller than the electrochemical bandgaps.

Beaupré et al. [13], Zheng et al. [14] and Morgado et al. [15] have studied different polymers, and they also demonstrated that the electrochemical bandgaps in general are higher than optical bandgaps.

In this paper, we report on the optical properties of a series of poly-3-*p*-X-phenylthiophenes ($R = -H, -CH_3, -OCH_3, -COCH_3, -COOC_2H_5, -NO_2$; see Fig. 1). Their electrochemical bandgaps were calculated from cyclic voltammograms and correlated with optical bandgaps.

Experimental

In situ UV-Vis spectra of the monomers (1a–f) and polymers (2a–f; Fig. 1) were recorded with a Shimadzu



1	X	2
a	-H	a
b	-CH ₃	b
c	-OCH ₃	c
d	-COOC ₂ H ₅	d
e	-COCH ₃	e
f	-NO ₂	f

Fig. 1 Studied 3-*p*-X-phenylthiophenes

model UV-2101PC spectrometer (resolution 0.1 nm). Spectroelectrochemical experiments were done in a 1-cm path length quartz cuvette with an indium-doped tin oxide (ITO)-coated glass electrode with a specific surface resistance of about 10–20 Ω/square, installed perpendicular to the light path. A platinum wire was used as a counter electrode. A non-aqueous Ag/AgCl electrode filled with the supporting electrolyte solution (tetraethylammoniumtetrafluoroborate Et₄NBF₄ in acetonitrile) and saturated with AgCl connected via salt bridge served as reference electrode. All the potentials in this work are reported with respect to the same Ag/AgCl electrode used in measurements (0.045 V vs an aqueous SCE). The blank cuvette contained a solution of supporting electrolyte and uncoated ITO electrode. UV-Vis spectra for monomers were recorded with their acetonitrile solutions with the same spectrometer.

Anodic electropolymerization was used to prepare polymers by applying a constant electrode potential [1.77, 1.76, 1.48, 1.91, 1.92 and 2.10 V for monomers 1a, 1b, 1c, 1d, 1e and 1f, respectively (Fig. 1)]. After each polymerization process, the film was washed with acetonitrile to remove any traces of oligomers. All electrochemical experiments

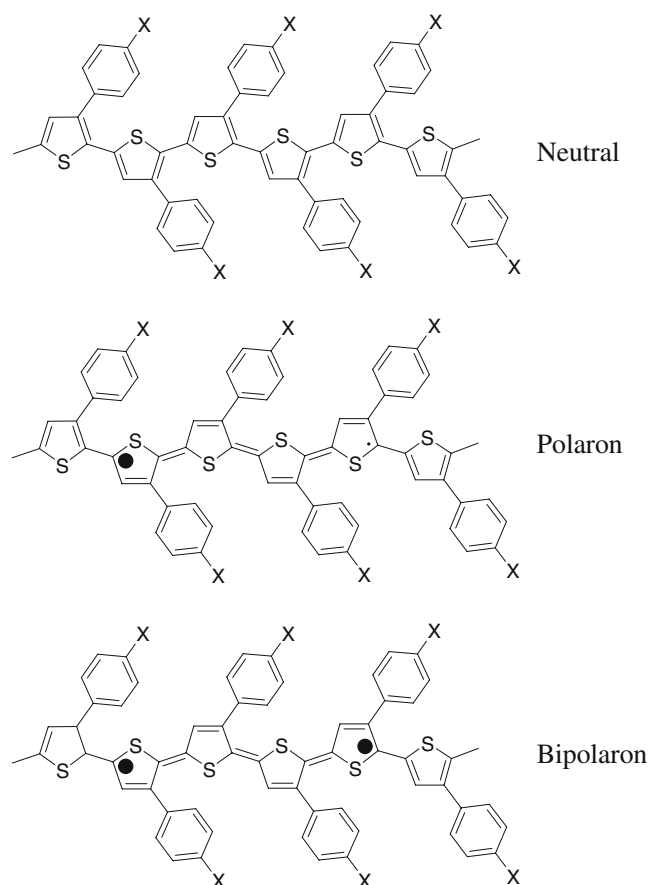


Fig. 2 Simplified representative structural formulas of poly-3-*p*-X-phenylthiophenes in their neutral, radical cation (polaron) and dication (bipolaron) states

Table 1 Oxidation, reduction peaks, absorption maxima (wavelengths), electrochemical and optical bandgaps for polymers (2a–f)

Polymer	Ox. E_{pa}/V	Ox. E_{pc}/V	$E_{0,ox}/V$	Red. E_{pc}/V	Red. E_{pa}/V	$E_{0,red}/V$	$E_{g,EC}^a/eV$	UV-Vis λ_{max}/nm	$E_{g,opt}/eV$
2a	1.459	0.971	1.215	-1.845	-1.586	-1.716	2.93	530	2.35
2b	1.291	0.998	1.150	-2.043	-1.602	-1.823	2.98	566	2.20
2c	1.281	0.987	1.134	-2.080	-1.634	-1.857	2.99	523	2.36
2d	1.382	0.929	1.156	-2.043	-1.361	-1.702	2.86	459	2.71
2e	1.330	1.029	1.180	-1.996	-1.377	-1.686	2.87	450	2.76
2f	1.505	1.091	1.298	-2.147	-0.890	-1.519	2.82	453	2.74

$$^a E_{g,EC} = (E_{pa}^{ox} + E_{pc}^{ox})/2 - (E_{pc}^{red} + E_{pa}^{red})/2$$

Fig. 3 UV-Vis spectra of polymers (2a–f) coated on ITO glass electrodes, obtained at different electrode potential values

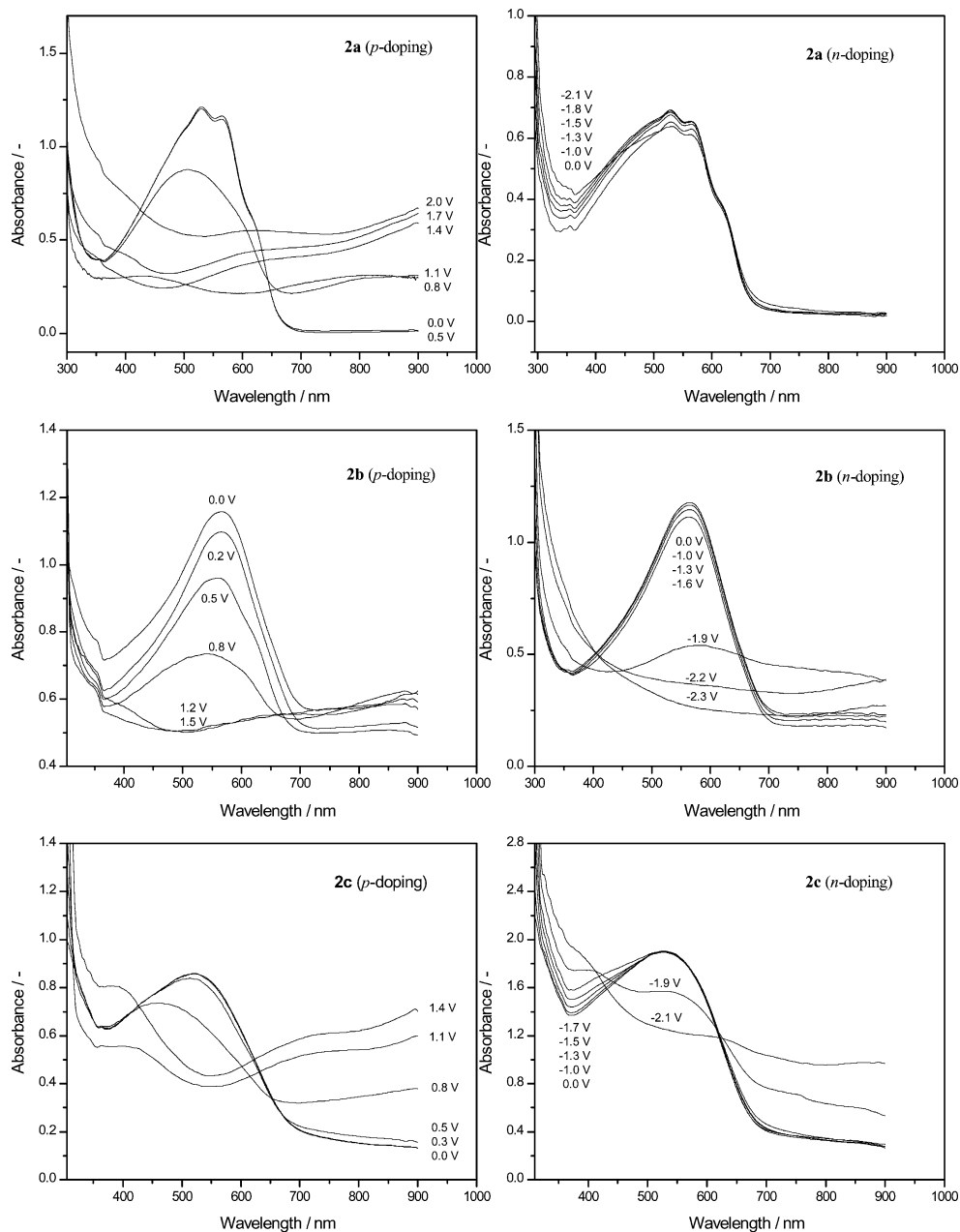
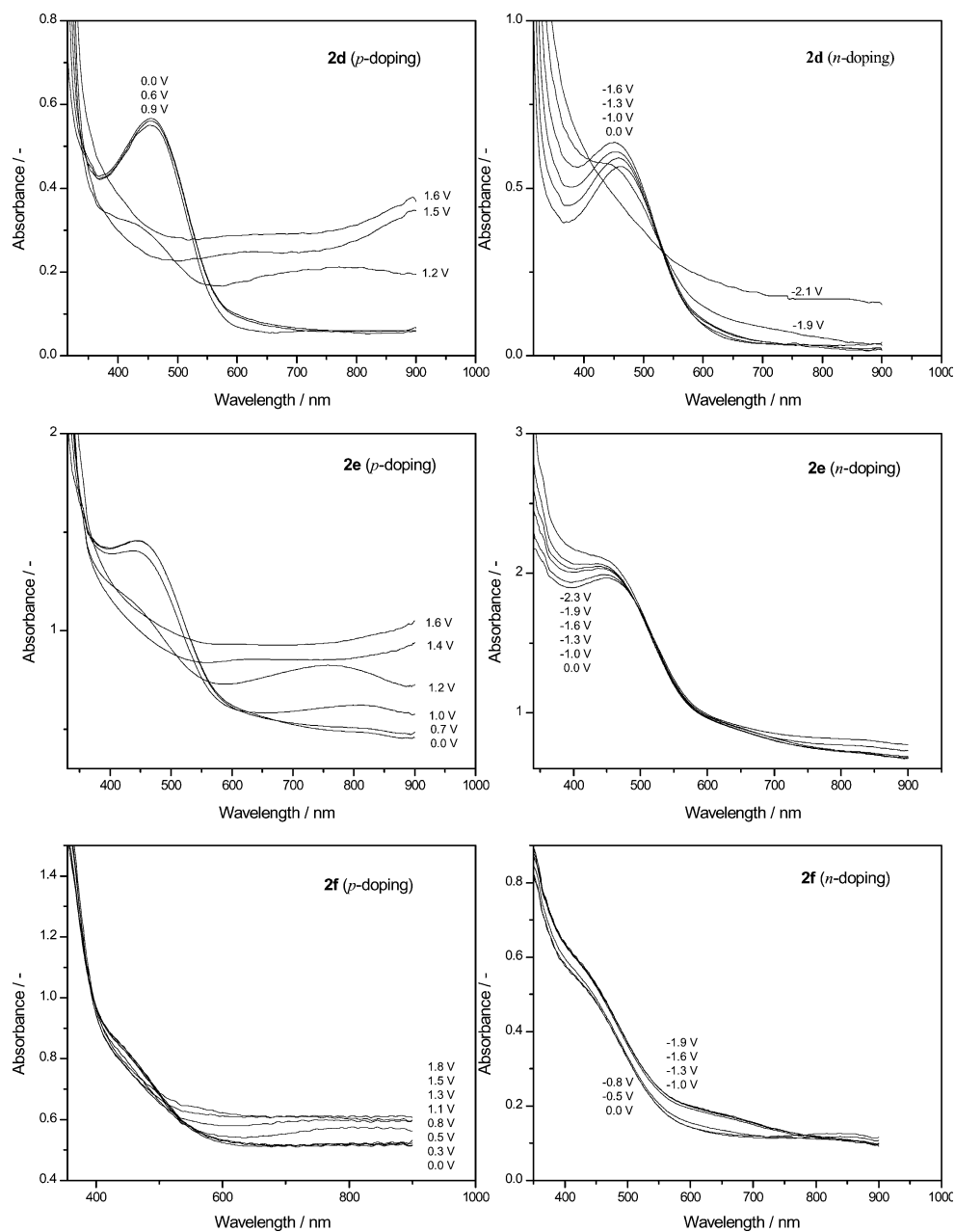


Fig. 3 (continued)



were carried out at room temperature with nitrogen-purged solutions.

A custom-built potentiostat interfaced with a standard PC via an ADDA-converter card operating with custom developed software was used.

Results and discussion

According to in situ UV-Vis absorption measurements obtained during anodic polarization, the main charge carriers in polythiophenes are polarons and/or bipolarons,

as schematically shown in Fig. 2,¹ associated with the formation of new quantum states in the energy gap. New optical transitions become possible and the charging of conjugated polythiophenes is accompanied by dramatic changes in their optical absorption spectra [16].

The evolution of the spectra of poly-3-*p*-X-phenylthiophene (2a–f) upon doping is characterized by similar

¹ The regioregularity depicted in Fig. 2 cannot be proven with, e.g. NMR spectroscopy because of the insolubility of the products obtained in this study; it cannot also be deduced from electrochemical results. The theoretical considerations discussed below make such a structure very likely nevertheless.

features as observed for many polythiophenes with a high degree of conjugation [17–23]. During stepwise oxidation of the poly-3-*p*-X-phenylthiophene films, the intensity of the absorption due to the $\pi \rightarrow \pi^*$ transition around 450–566 nm decreases, and a new broad absorption band related to (bi)polaron states appears around 730–890 nm (see Table 1 and Fig. 3).

During the oxidation (*p*-doping) of the poly-3-*p*-X-phenylthiophene (2a–f) films, a blue/hypsochromic shift is observed for both absorption bands. A similar feature has been observed for poly-3-methylthiophene by Visy et al. [19] and for poly(thiophene-3-methanol) by Lankinen et al. [21]. The explanation is based on the assumption that a polymer contains a distribution of chain lengths, and the

longest polymer chains (the absorption of which occurs at lower energies) are first oxidized at lower potentials [24, 25]. As the electrode potential of the poly-3-*p*-X-phenylthiophene is increased to higher values, the intensity of the absorbance maximum around 730–890 nm starts to decrease, and the blue shift becomes more pronounced (see Fig. 3). Thus, it seems probable that some of the species absorbing at around 730–890 nm are oxidized further at these higher positive potentials, and that their oxidation products are not absorbing in the wavelength range studied (but instead in the near-infrared range). The decrease of the (bi)polaron absorbance is not necessarily due to overoxidation (not investigated in this study) but also to formation of other types of charge carriers. This

Fig. 4 UV-Vis spectra of monomers (1a–f) with acetonitrile as solvent and polymer (2a–f) films deposited on an ITO glass electrode

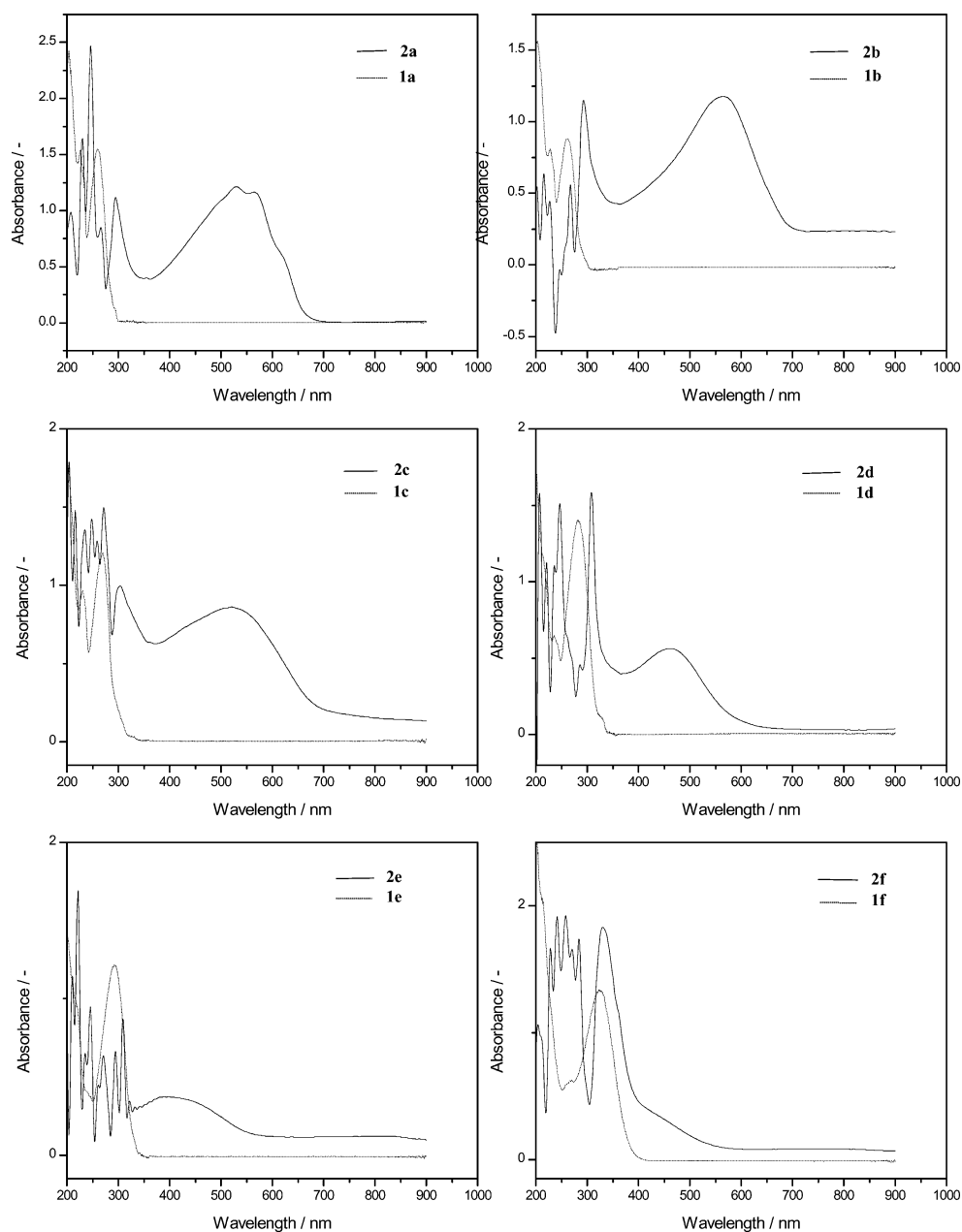


Table 2 Oxidation and reduction onset peaks and electrochemical onset bandgaps for polymers (2a–f)

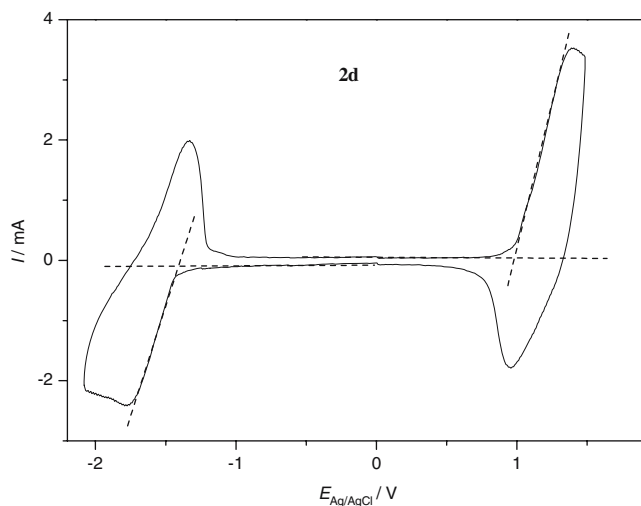
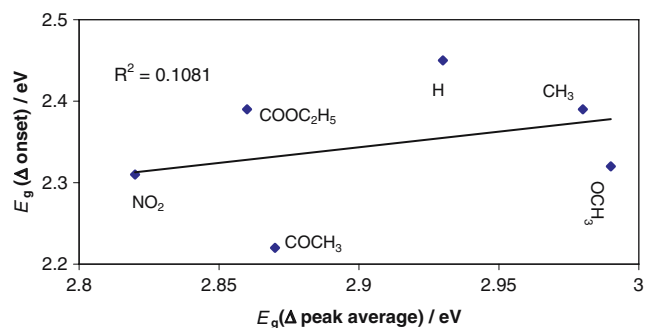
Polymer	$E_{\text{onset}}^{\text{ox}}/\text{V}$	$E_{\text{onset}}^{\text{red}}/\text{V}$	$E_{\text{g,EC onset}}/\text{V}^{\text{a}}$
2a	0.76	-1.69	2.45
2b	0.86	-1.53	2.39
2c	0.85	-1.47	2.32
2d	0.98	-1.41	2.39
2e	0.86	-1.36	2.22
2f	1.02	-1.29	2.31

$$^{\text{a}}E_{\text{g,onset}} = E_{\text{onset}}^{\text{ox}} - E_{\text{onset}}^{\text{red}}$$

observation combined with the low degree of conjugation observed for poly-3-*p*-X-phenylthiophenes and the low doping levels obtained supports the previous suggestion that at lower potentials, where no overoxidation occurs, the charge carriers observed are polarons rather than bipolarons [21, 22]. On the other hand, Fig. 4 illustrates differences between the UV-Vis spectra of the monomers (1a–f) and the UV-Vis spectra of the polymers (2a–f).

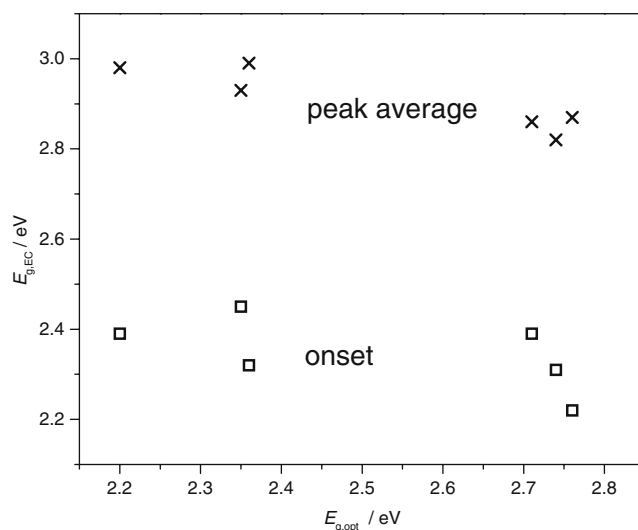
During the reduction (*n*-doping) of the poly-3-*p*-X-phenylthiophene films, a bathochromic/red shift is observed for the $\pi \rightarrow \pi^*$ transition peak for polymers 2b, c. On the contrary, a blue shift is observed for polymer 2d, and no shift is observed for polymers 2a, e and f. These differences may be ascribed to the nature of the substituent or to degradation of the polymers.

For poly-3-*p*-X-phenylthiophene (2a), a more complex structure of the spectra showing several bands and shoulders changing as a function of electrode potential can be observed. The various peaks and shoulders can be associated with a few predominating lengths of conjugation. The longest segments are oxidized most easily; correspondingly, the respective absorptions disappear first, whereas shorter segments of conjugated units, which are harder to oxidize, are converted last (e.g. at $E_{\text{Ag}/\text{AgCl}} = 1.1$ V).

**Fig. 5** Cyclic voltammogram of polymer 2d at $dE/dt = 100 \text{ mV} \cdot \text{s}^{-1}$ **Fig. 6** Electrochemical bandgaps, E_{g} , evaluated from onset and peak average, respectively

A summary of cyclic voltammetry data for polymers (2a–f) is given in Tables 1 and 2. By varying the nature of the substituent on the backbone of poly-3-*p*-X-phenylthiophene, the oxidation potential $E_{0,\text{ox}}$ and the reduction potential $E_{0,\text{red}}$ can be increased or decreased depending on the nature of the substituent (whether it is electron withdrawing or electron donating). We have used $E_{0,\text{ox}} = (E_{\text{pa}}^{\text{ox}} + E_{\text{pc}}^{\text{ox}})/2$ and $E_{0,\text{red}} = (E_{\text{pc}}^{\text{red}} + E_{\text{pa}}^{\text{red}})/2$ for the calculation of $E_{\text{g,EC}}$ (see Table 1). The onset potentials for the oxidation $E_{\text{onset}}^{\text{ox}}$ and reduction $E_{\text{onset}}^{\text{red}}$ processes are given in Table 2 together with the resulting $E_{\text{g,EC onset}} = E_{\text{onset}}^{\text{red}} - E_{\text{onset}}^{\text{ox}}$. The onset potentials were determined from the intersection of the two tangents drawn at the current rise and background charging current of the CVs as illustrated in a typical example in Fig. 5 (see [26] and [27] for the CVs of polymers 2a–f).

The dependency of $E_{0,\text{ox}}$ and $E_{0,\text{red}}$ on the various substituents is significant, whereas the electrochemical as well as the onset bandgaps show only small absolute changes (up to remain 170 and 230 mV, respectively) because the respective potentials for *p*- and *n*-doping shift in the same direction.

**Fig. 7** Electrochemical vs optical bandgap of polymers (2a–f), [electrochemical bandgap evaluated by onset (squares) and by peak average (crosses)]

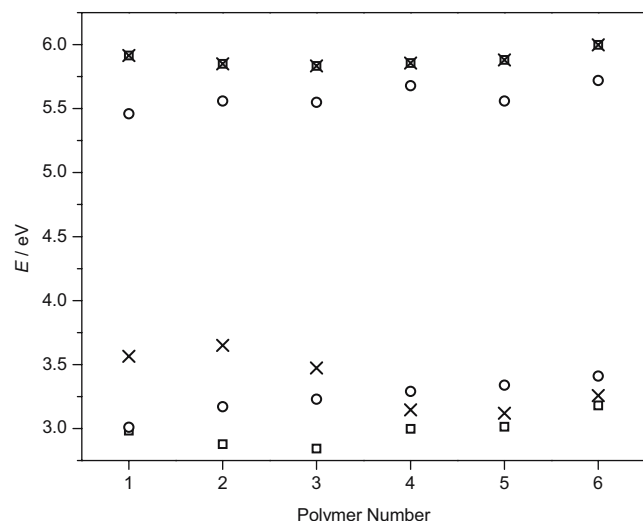


Fig. 8 Energies of the HOMO and LUMO for the polymers evaluated by different procedures: HOMO and LUMO from peak potential averages (squares); HOMO and LUMO from onset potentials (crosses); LUMO calculated from HOMO (taken from peak potential average, $E_{0,ox}$) and optical absorption maximum (circles)

In Fig. 6, we compare the two alternative evaluation techniques by plotting the electrochemical bandgaps $E_{g,EC}$ obtained from the values of $E_{0,ox}$ and $E_{0,red}$ vs band gaps $E_{g,EC\ onset}$ obtained from onset potentials. As expected, the onset gives a lower bandgap. This comes as no surprise because the onset potentials approach more closely the situation also encountered in optical spectroscopy. Around the onset potential, charge is injected into the neutral polymer (e.g. the empty LUMO during reduction); any subsequent charge transfer affects an already charged material, thus requiring more energy (a higher overpotential) resulting in the observed larger bandgap. No correlation was observed; this is in agreement with previous studies [10, 12–15, 28–30].

In Fig. 7, values of $E_{g,EC}$ are plotted vs the optical bandgap $E_{g,opt}$, obtained from the optical absorption maxima at 0 V (this potential was chosen, as the value of $E_{g,opt}$ may change subsequently at higher potentials due to conceivable degradation of the polymer films) of thin films prepared by deposition on an ITO electrode. With all the studied polymers, the value of the bandgap derived from

optical spectroscopy is smaller than that derived from electrochemical measurements. This again is not unexpected. As pointed out, only $E_{g,EC\ onset}$ approaches charge injection into a neutral state of the polymer, thus resembling optical excitation. In addition, it has to be considered that the final state of charge transfer (whether oxidation or reduction) is a charged one, whereas optical excitation results in a neutral species (bound excitons). This will certainly affect the respective energies. The same discrepancy has been observed for other polythiophenes [10, 12, 31], poly(phenylene vinylene)s [15, 28] and copolymers thereof [14], poly(quinoxaline vinylene)s and poly(pyridopyrazine vinylene) [29, 30] and for fluorene-based copolymers [13].

Brédas et al. [32] used the valence-effective Hamiltonian method to calculate the ionization potential E_i and electron affinity E_{ea} corresponding to the energies of the HOMO and LUMO levels, respectively, for different oligomer and polymer systems. They were related to the respective electrode potentials: $E_i = E_{onset}^{ox} + 4.4\text{ eV}$; $E_{ea} = E_{onset}^{red} + 4.4\text{ eV}$ (wherein E_{onset}^{ox} and E_{onset}^{red} are the onset potentials of the oxidation and reduction peaks, respectively). Moreover, E_i and E_{ea} are used to estimate the energy barriers for the injection of both holes and electrons into the polymer.

Figure 8 shows a plot of the energies of the HOMO and LUMO levels calculated both from peak average ($E_{g,EC}$) and onset red/ox potentials ($E_{g,EC\ onset}$) for the investigated polymers (see also Table 3). The energy levels were calculated on the basis of the assumption that the standard hydrogen electrode, SHE, is found at 4.5 eV vs vacuum [33, 34]. The difference between the reference electrode used in this study and the SHE ($E_{Ag/AgCl}^0(a_{Cl^-} = 1) = 0.22\text{ V vs SHE}$) has been taken into account as well. Thus, the energy of the HOMO is obtained by adding 4.72 V to the measured value of E_{ox} (which gives values between 5 and 6 eV for most of the polymers studied in this paper) and the energy of the LUMO by adding 4.72 V to E_{red} (giving values between 3 and 4 eV).

The onset bandgaps converted this way into HOMO/LUMO energies (Table 3) are closer to those calculated from absorption spectra than bandgaps ($E_{g,EC}$) calculated from peak averages. Calculated values of the (UV-Vis) LUMO energy obtained from the HOMO energy (taken

Table 3 HOMO and LUMO calculated from peak average, onset and UV-Vis spectroscopy for polymers (2a–f)

Polymer	Peak average/eV		Onset/eV		Optical/eV	
	HOMO	LUMO	HOMO	LUMO	HOMO ^a	LUMO
2a	5.915	2.984	5.460	3.010	5.915	3.565
2b	5.850	2.877	5.560	3.170	5.850	3.650
2c	5.834	2.843	5.550	3.230	5.340	3.474
2d	5.856	2.998	5.680	3.290	5.856	3.146
2e	5.880	3.014	5.560	3.340	5.880	3.120
2f	5.998	3.181	5.720	3.410	5.998	3.258

^a HOMO values calculated from peak potential average

from redox peak averages), and the optical bandgap (taken from the absorption maxima) have also been included in Fig. 8 (see also Table 3). It was observed that the electronic levels of the highest occupied molecular orbitals and lowest unoccupied molecular orbitals vary by about 0.5 eV.

Conclusions

A blue (hypsochromic) shift observed during the oxidation (*p*-doping) of the poly-3-*p*-X-phenylthiophene films for both absorption bands ($\pi \rightarrow \pi^*$ -transition around 450–566 nm and the band associated with (bi)polaron states around 730–890 nm) can be explained by taking into account that a polymer contains a distribution of chain lengths, and the longest polymer chains (the absorption of which occurs at lower energies) start to oxidize at the relatively lowest potentials.

Values of the polymer bandgap calculated from the electrode potentials of redox conversions have been found consistently to be higher than those derived from optical measurements. Obviously, the frequently used method of deriving HOMO and LUMO levels from cyclic voltammetry may be misleading; this conclusion is found to be in agreement with previous studies.

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