

X-Ray Diffraction and Ultraviolet–Visible Absorption Studies on Electrochemically Synthesized Poly(thiophene-3-methanol) Films

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To investigate the effect of the CH₂OH substituent on the energy gap of polythiophene, and to study the possible long-range order in this polymer, *ex situ* optical absorption and X-ray diffraction measurements were performed on electrosynthesized polythiophene-3-methanol (PTOH) films. In addition, the evolution of the optical absorption of PTOH as a function of applied potential was followed *in situ*. The diffraction pattern of PTOH is similar to that of liquid thiophene and bithiophene with only one broad peak at $Q=1.4 \text{ \AA}^{-1}$, indicating that despite the two-dimensional deposition process of PTOH, its structure is exceptionally disordered. The optical absorption spectrum of PTOH shows maximum absorption at 3.05 eV, which corresponds to a conjugation length of only 5–6 monomer units. Nevertheless, the evolution of the optical spectrum upon oxidation is characterized by similar features as observed for polythiophenes of higher degree of conjugation, namely by a decrease in the intensity of the absorption due to valence to conduction band transition and a simultaneous appearance of a new broad absorption band at 1.65 eV. However, only low doping levels are obtained for PTOH. These results are discussed on the basis of the C–O–C coupling in PTOH.

The study of substituted polythiophenes is an active research area in the fields of electronically conducting polymers. Substitution provides various possibilities to modify the structure of the thiophene backbone and thereby tailor its properties. A large number of different polythiophene structures have already been synthesized and characterized. Light emitting diodes,^{1,2} transistors³ and modified electrodes for electrocatalysis and electroanalysis^{3–5} appear as their most promising applications.

The electropolymerization of thiophene bearing a CH₂OH substituent in the β -position leads to an interesting material, polythiophene-3-methanol (PTOH). The unique properties of PTOH are due to the nucleophilic OH function. It provides an alternative coupling path for the monomers during the electropolymerization. Therefore PTOH films always contain both C–C and C–O–C coupled monomer units, the proportion of which is a strong function of the synthesis conditions.^{6,7} With careful control of these conditions electroactive PTOH films can be prepared.

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In previous studies we have characterized the redox processes of PTOH in detail.^{8,9} Because C–O–C coupling lowers the degree of conjugation in PTOH, it is natural that even when prepared under optimized conditions PTOH exhibits lower conductivity and electrochemical activity than its alkyl counterpart poly(3-methylthiophene).¹⁰ On the other hand PTOH films are very compact and adhere strongly to the electrode surface. These aspects are important in applications like corrosion protection and microelectronics.

We have previously shown that the early stages of the electrosynthesis of PTOH fit the model of instantaneous nucleation followed by two-dimensional layer-by-layer growth.⁶ Therefore in this work we wanted to study if any signs of long-range order were found in PTOH by X-ray diffraction measurements. To investigate the effect of the CH₂OH substituent on the energy gap of polythiophene UV–VIS spectra were registered from PTOH films. In addition, the evolution of the optical absorption of PTOH as a function of its anodic polarization was followed *in situ*. The results obtained for PTOH have been compared with those obtained for chemically syn-

thesized poly(3-octylthiophene) (POcT) and those obtained earlier¹¹ for electrochemically synthesized polythiophene (PT).

Experimental

The electrosynthesis of the PTOH films studied *ex situ* was carried out in a conventional three electrode system on ITO electrodes (Planar International, Inc., Finland). The reference electrode against which all potentials in this paper are quoted was a Ag/Ag⁺(0.01 M) electrode in 0.1 M Bu₄NClO₄ in acetonitrile. A platinum grid served as a counter electrode. The electrodes were vertically positioned in the one-compartment glass cell. The reference electrode was separated from the rest of the cell with a Bu₄NClO₄ (0.1 M in acetonitrile) salt bridge. All PTOH films were synthesized in a glove box filled with nitrogen (99.999%).

A potential step programme was used for the deposition of PTOH on ITO. The thin (of order 10⁻⁸ m) films used for the *ex situ* absorption measurements were synthesized by stepping the potential to 2.4 V for 4 s, after which the polymer was reduced at 0.2 V for 15 min (it must be noted that because of the large area of the poorly conducting ITO electrodes¹³ and the high resistivity of the growing polymer⁶ the potential experienced by the reactant monomer is likely to be much lower than that set by the potentiostat). The microphotograph registered from PTOH on ITO glass shows a fine, homogenous structure (Fig. 1). The *ex situ* spectra were recorded from dry undoped ITO/PTOH electrodes ($A \approx 1 \text{ cm}^2$) and corrected for ITO background. The samples for the *in situ* absorption measurements were synthesized similarly, but in a sandwich type spectroelectrochemical cell consisting of a ITO working electrode ($A = 0.79 \text{ cm}^2$), a Pt counter electrode and an Ag/Ag⁺(0.01 M) reference electrode. Before transferring the cell into the glove box for the synthesis, a blank UV-VIS spectrum was regis-

tered from the cell filled with acetonitrile. After the synthesis the cell was carefully washed with acetonitrile and filled with a solution of the supporting electrolyte only. It was then transferred out of the glove box for the registration of the UV-VIS spectra of ITO/PTOH as a function of applied potential. The measured blank spectrum was subtracted from each *in situ* spectrum registered for ITO/PTOH. To control the electrochemical state of the PTOH film a voltammogram was recorded from the polymer electrode before and after the absorption measurements.

The XRD measurements were performed from a thick (of order 10⁻⁵ m) free-standing PTOH film peeled off from ITO surface. The thick film was synthesized with a multistep programme in which the potential was stepped to 2.35 V for 4 s several times. After each polymerization step the as-grown polymer was reduced for a few seconds at 0.2 V, and at the end of the synthesis the film was reduced at this potential for 15 min. PTOH adheres very strongly to the ITO surface, and thus it is very difficult to separate the polymer from the substrate. To remove the PTOH film from the ITO substrate the electrode was dipped in HNO₃, soaked in ion-exchanged water for 1 h and finally dried in vacuum for 1.5 h. In this connection it must be noted that Kreja *et al.*¹² have recently observed that nitration of polyalkylthiophenes takes place in nitric acid. However, their experiments were carried out on a highly dispersed polymer sample and with longer reaction times and at higher temperatures than used in our HNO₃ treatment, and thus it is likely that the amount of nitration occurring during our peeling process is negligible.

The solutions used for polymerization contained 0.5 M thiophene-3-methanol monomer and 0.1 M Bu₄NClO₄ in acetonitrile. Prior to use the Bu₄NClO₄ salt (Fluka AG, purum >98%) was dried under vacuum at 50 °C overnight, and thiophene-3-methanol (Aldrich Chem. Co.) was distilled under reduced pressure. Acetonitrile purchased under nitrogen (Aldrich, anhydrous 99+%, H₂O < 0.005%) was used as received. All chemicals were stored in a glove box.

The poly(3-octylthiophene) (POcT) used as a reference compound was chemically synthesized by Neste Ltd., Finland. POcT thin films were prepared from chloroform solution by spin-coating (500 r.p.m.) on glass substrates. UV-VIS spectra were registered from undoped POcT in chloroform and as a solid film.

The potential was controlled by a Pine Instrument Co. type RDE4 potentiostat connected to a HI-TEK PP RI waveform generator. For the registration of the micrographs an Olympus BH-2 optical microscope was used. The X-ray diffraction patterns were measured with a computer-controlled diffractometer LOFTE, using graphite 002 monochromatized Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$, Siemens M18XHF-SRA rotating anode operating at 8 kW) and θ - 2θ transmission geometry. *Ex situ* optical absorption measurements were performed with a Cary 5 UV-VIS-NIR spectrophotometer, and the *in situ*

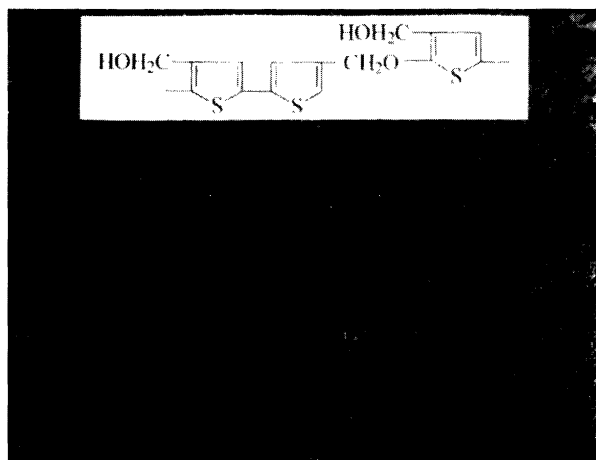


Fig. 1. Microphotograph of undoped electropolymerized PTOH film on ITO glass (500 \times magnification). Insert: C-C and C-O-C coupled monomer units in the PTOH chain.

absorption measurements with a Hewlett Packard 8452A diode array spectrophotometer. All experiments were carried out at room temperature.

Results and discussion

X-Ray diffraction from free-standing PTOH. The diffraction pattern of the free-standing PTOH film is shown in Fig. 2. For comparison the diffraction profile obtained in Ref. 11 for electropolymerized polythiophene (PT) is presented in the same figure. The pattern obtained for the PTOH film is dominated by one broad peak at $Q = 1.4 \text{ \AA}^{-1}$ (marked A in Fig. 2). This broad halo, also seen for PT, is related to amorphous (liquid-like) packing of the polythiophene chains, and has been observed for all thiophene based polymers studied so far.¹⁴⁻²⁰ However, in the case of PTOH this peak is wider than observed for other electrochemically or chemically synthesized polythiophenes.

In this Q -range PT shows two amorphous peaks at large Q values (peaks B and C in Fig. 2). Similar broad peaks have also been detected in the X-ray patterns of polyalkylthiophenes and are believed to be related to repetition along the main chain, i.e. to intrachain structure.^{16,17} It is surprising that for PTOH no such well defined peaks are observed, but only a broad shoulder at $Q = 2.8 \text{ \AA}^{-1}$ (near position B). This suggests that the chain structure of PTOH is very disordered. In addition, PTOH completely lacks the sharp Bragg-like reflections found for some partially crystalline polythiophenes.¹⁴⁻¹⁶

Polythiophenes all pack with a varying degree of disorder, but PTOH seems to be exceptionally disordered, approaching a 'perfect amorphous material'. The diffraction pattern of PTOH is actually very similar to those of liquid thiophene and bithiophene, which also show only one broad peak at $Q = 1.4 \text{ \AA}^{-1}$.²¹

It has been shown that in many cases electrochemically prepared polythiophenes are more disordered containing more cross-linking than the corresponding chemically

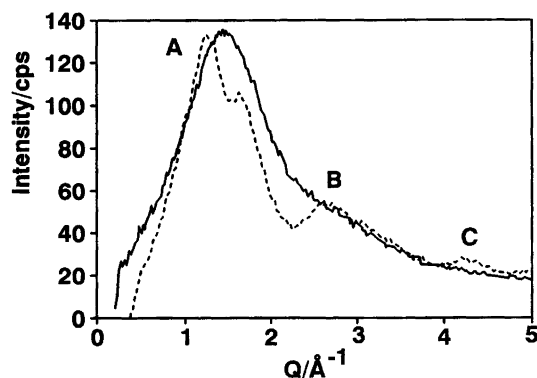


Fig. 2. X-Ray diffraction patterns obtained from free-standing electropolymerized polythiophene-3-methanol (full line) and polythiophene (dashed line; data from Ref. 11) films. The intensity is plotted as a function of the scattering vector Q ($Q = 4\pi \sin(\theta)/\lambda$, where 2θ is the scattering angle and $\lambda = 1.5418 \text{ \AA}$).

synthesized materials.¹⁸⁻²⁰ However, as the degree of disorder in PTOH is considerably higher than that in other electrochemically synthesized polymers, it is evident that the polymerization method alone cannot account for the highly amorphous nature of PTOH. We believe that the main factor determining the structure of this polymer is the OH function of the CH_2OH substituent. Owing to this nucleophilic group some of the monomers couple via C-O-C bonds.^{7,10} Such structures are much more flexible than thiophene rings coupled through C-C bonds, and thus dramatically increase the conformational freedom of the polymer chains. In addition, it has previously been shown by FTIR⁹ that C-O-C crosslinking takes place between adjacent PTOH chains, which can also introduce more conformational disorder in the film.

The initial stages of the electrochemical polymerization of PTOH have been interpreted by a model of two-dimensional layer-by-layer growth.⁶ However, no signs of a layer structure can be seen in the XRD pattern of the PTOH bulk film. This suggests that in the later stages of the polymerization the two-dimensional growth is strongly disturbed by the reactions of the OH function, and thus no well defined layer structure is being formed.

Ex situ UV-VIS absorption measurements from ITO/PTOH. The UV-VIS absorption spectrum of an undoped PTOH film on ITO glass substrate is shown in Fig. 3. For comparison the spectra of

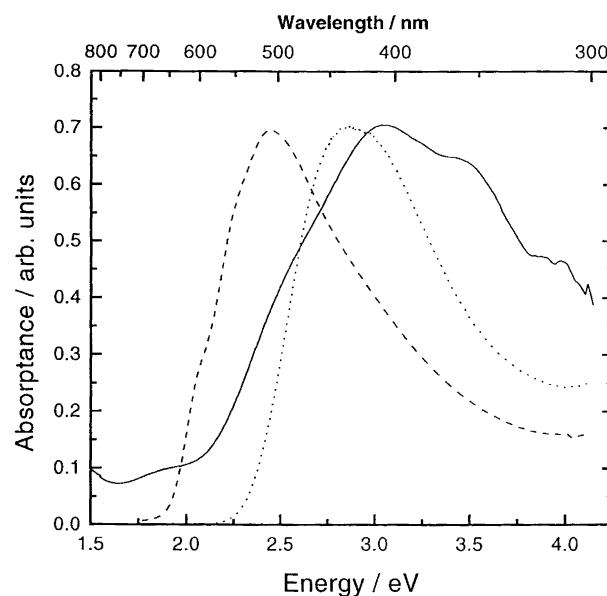


Fig. 3. UV-VIS absorption spectrum of undoped PTOH on ITO-glass (solid line), and undoped poly-3-octylthiophene (POCt) in chloroform (dotted line) and as a solid film on glass substrate (dashed line). Maximum absorption is found at 3.05, 2.9 and 2.4 eV for PTOH film, dissolved POCt and POCt film, respectively. The spectrum of PTOH is corrected for an approximated ITO background without interference. All curves have been rescaled to about the same intensity maximum.

poly(3-octylthiophene) (POcT) in solution and as a solid film are presented in the same figure. The maximum absorption of PTOH occurs at 3.05 eV (corresponding to 407 nm) indicating a high energy gap. The colour of neutral PTOH is yellow–brown, which also suggests a large bandgap for this polymer. On the basis of the absorption data obtained for thiophene oligomers the energy of maximum absorption of PTOH corresponds to a conjugation length of only 5–6 monomers.^{22–24} This low degree of conjugation is not surprising, for as discussed earlier two competing coupling paths exist for the thiophene-3-methanol monomer units (C–C and C–O–C). Already a 17–20% probability of C–O–C coupling would reduce the average conjugation length to 5–6 monomers. Additionally, owing to the increased possibility of cross-linking induced by the OH function, the structure of PTOH is likely to be twisted. Twisting decreases chain planarity, which lowers the effective conjugation in the PTOH chains. In fact the absorption maximum of PTOH is close to that of poly(3-butyl-co-3,4-dibutylthiophenes)²⁵ and stereoregular poly(3,3'-dioctyl-2,2'-bithiophene),²⁶ in which the thiophene rings are twisted out of plane because of the large size of the substituents.

Solid non-twisted polyalkylthiophenes (PATs) show thermochromism, i.e. a blue shift in the position of the absorption maximum as the temperature is increased.²⁷ The spectra of a dissolved PAT at room temperature and that of the same polymer as a film at high temperature are similar. Furthermore, the thermochromism shows an isobestic behaviour, indicating that solid PAT may be described as a system consisting of two different molecular species, both of which have an absorption spectrum of their own. We have constructed a model²⁸ suggesting that these species represent two different phases, namely a restricted, planar phase of high degree of order and a relaxed, disordered phase. For the latter phase the model gives an average twist angle of 30°, which is in good agreement with the twist of 32–34° found by electron diffraction and theoretical calculation for bithiophene molecules in vapour phase.^{29,30} As the absorption maximum of PTOH is close to that of dissolved POcT (cf. Fig. 3) and as the X-ray pattern of PTOH in Fig. 2 is reminiscent of that of liquid thiophene and bithiophene, the structure of PTOH can be considered to be as disordered as that of the relaxed forms (solutions and high-temperature films) of PATs.

The apparent fine structure of the spectrum of PTOH is due to an interference phenomenon in the ITO layer,¹³ since similar effects were also observed for pure ITO glass. This interpretation was verified by inclining the sample in the beam path and thus altering the effective thickness of the ITO layer. The thickness of the ITO deposit could be determined from these measurements and was found to be ca. 450 nm.

In situ UV–VIS absorption measurements from ITO/PTOH during anodic polarization. The main charge

carriers in polythiophenes are polarons and/or bipolarons, the formation of which results in new quantum states in the energy gap. Thus new transitions become possible and the charging of conjugated polythiophenes is accompanied by dramatic changes in their optical absorption spectra.²³

The evolution of the spectra of PTOH upon doping are characterized by similar features as observed for many polythiophenes of higher degree of conjugation.^{3,31} As the doping proceeds the intensity of the absorption due to valence to conduction band transition (i.e. interband transition) around 400 nm decreases, and a new broad absorption band appears at around 750 nm (1.65 eV) (Fig. 4a). This new absorption band is assigned to transitions related to the (bi)polaron states in the energy gap. This is consistent with our previous FTIR results,⁹ which showed that despite the C–O–C coupling that breaks the conjugation, (bi)polaron type charge carriers are formed in PTOH upon oxidation. The anodic charging of PTOH is also manifested by a colour change from yellow–brown to dark blue.

For p-doped polythiophenes of high degree of conjugation^{3,31} the intensity of the (bi)polaron band with respect to that of the interband absorption is much higher than the corresponding ratio observed for PTOH in Fig. 4. This indicates that only low doping levels are obtained for PTOH (voltammetric results give 6–9 mol% as calculated from sweeps similar to that in Fig. 4).⁹ When the PTOH film is discharged its colour turns back to yellow–brown, the band at 750 nm gradually disappears and the intensity of the interband transition increases (Fig. 4b).

As mentioned in an earlier chapter the energy of the interband absorption of PTOH corresponds to a conjugation length of only 5–6 monomer units. This suggests that polarons are the main charge carriers in PTOH, as the work of Horowitz *et al.*²³ on dissolved thiophene oligomers has shown that for chains of short conjugation length (<9–11 monomer units) polarons are the most stable charge carriers. The low doping levels obtained for PTOH further supports this idea (several authors^{32,33} have reported that at doping levels <10 mol% the charge conduction in polythiophenes is dominated by polarons).

A polythiophene film is typically a mixture of chains of different conjugation lengths. As the degree of effective conjugation is the key factor determining the absorption and redox properties of the polymer, the experimental data recorded from the polymer film displays a superposition of the responses of all the differently conjugated segments the film includes.^{3,31} The ill defined shape of the voltammetric peak in Fig. 5 and the width of the bands in the optical absorption spectra in Figs. 3 and 4 suggest that in PTOH the distribution of chain lengths is rather wide.

The segments of highest conjugation are oxidized first,³¹ which explains why the peak of the interband transition in Fig. 4a is gradually shifted from 3.00 eV (413 nm) to 3.15 eV (394 nm) when increasing the potential from 0.2 to 0.6 V. Anodic discharging takes place in

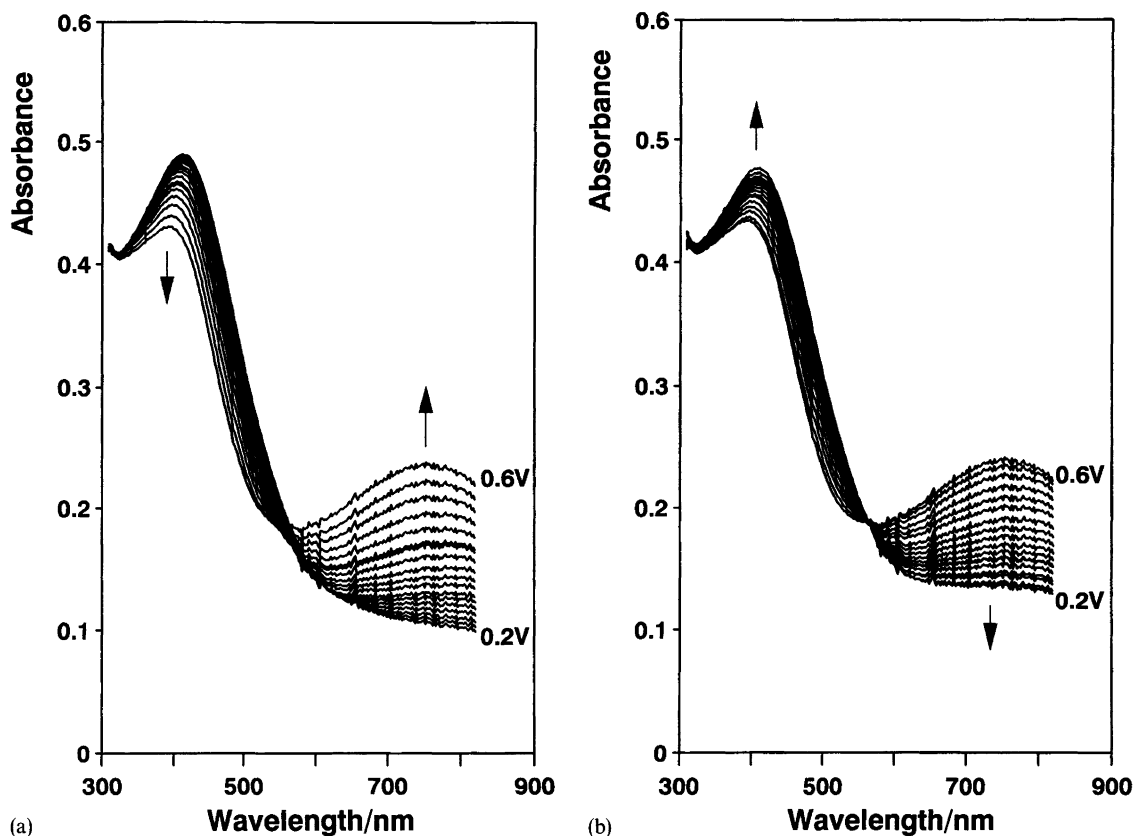


Fig. 4. The evolution of the UV-VIS absorption of PTOH on ITO glass during anodic (a) charging and (b) discharging in 0.1 M Bu_4NClO_4 in acetonitrile. The potential was varied from 0.2 to 0.6 V and back to 0.2 with 25 mV steps, and at each potential a spectrum was recorded after a hold time of 30 s.

reverse order, i.e. the segments of lowest conjugation are reduced first and thus the interband transition peak is shifted from 3.15 eV (394 nm) to 3.04 eV (408 nm), Fig. 4b. It must be noted that the peak does not return to its initial value (3.00 eV). As only intensity changes are observed in the spectra when the film is further reduced at 0 V, it seems likely that the small shift in the energy of the interband transition is related not to incomplete reduction of the film, but to the fact that the structure of PTOH is somewhat modified during its anodic polarization. This structural modification also lowers the electrochemical activity of PTOH as seen from the voltammograms in Fig. 5. This is in accordance with our previous studies, which have shown that the oxidation of PTOH follows an EC type of mechanism (E stands for electrochemical step, C for chemical step), the C step of which is irreversible (the attack of the free OH groups in the film on the charged sites of the polymer backbone).^{8,9}

Conclusions

Electrosynthesized PTOH films have been characterized by X-ray diffraction and optical absorption measurements. The diffraction pattern of PTOH shows only one broad peak at $Q=1.4 \text{ \AA}^{-1}$, which indicates that even

though polythiophenes all pack with a varying degree of disorder, PTOH seems to be exceptionally disordered. Despite the fact that the initial stages of electropolymerization of PTOH follow the model of two-dimensional-type nucleation and growth,⁶ the X-ray diffraction pattern does not give any evidence of a layered structure. It is possible that some kind of layers exist in PTOH, but that the layers are of such dimensions that they cannot be detected by XRD. However, it seems more probable that in the later stages of polymerization the two-dimensional growth is strongly disturbed by the reactions of the OH function, leading to intra- and interchain C–O–C bonds, and thus to high degree of disorder.

In the *ex situ* optical absorption spectrum the maximum absorption of undoped PTOH is seen at 3.05 eV. This indicates a high energy gap for PTOH, and corresponds to a conjugation length of only 5–6 monomers.^{22–24} The low degree of conjugation can be explained by considering that in PTOH chains part of the monomer units are coupled via C–O–C bonds.⁷ Additionally, increased crosslinking occurs due to the OH function,⁹ which causes out-of-plane twisting of the PTOH chains.

Upon oxidation of PTOH the intensity of the interband absorption decreases and a new broad band appears at around 1.65 eV. The appearance of this new band shows

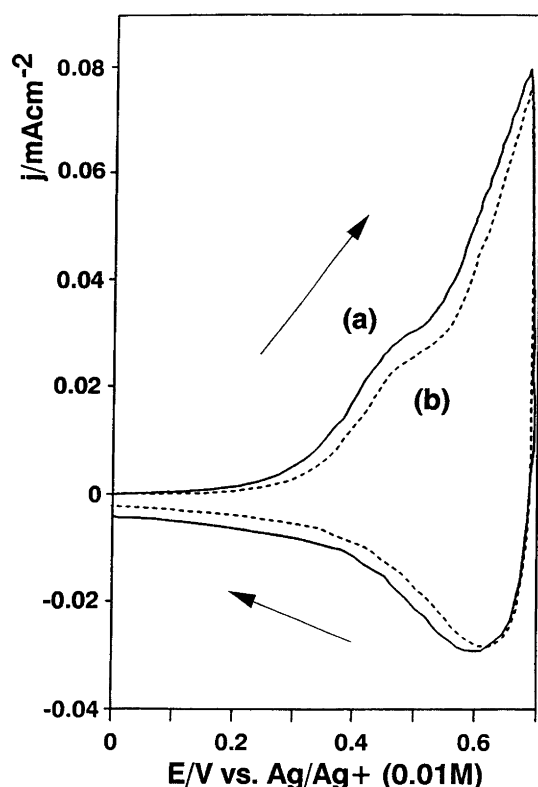


Fig. 5. Cyclic voltammograms of PTOH on ITO glass in 0.1 M Bu_4NClO_4 in acetonitrile (a) before and (b) after the measurements of Fig. 4 ($\nu = 10 \text{ mV s}^{-1}$). Prior to each cycle the film was reduced at 0 V for 15 min.

that new states are formed in the energy gap of PTOH during oxidation. The low conjugation length of PTOH suggests that these new states are more likely related to polarons than bipolarons.²³ Only low doping levels are obtained for PTOH, as indicated by the low intensity of the band at 1.65 eV compared to that of the interband transition.

To conclude, we can state that electropolymerized PTOH is an example of an electroactive 'perfectly amorphous' polythiophene with a high energy gap.

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