

Electrochemical synthesis and redox processes of poly(paraphenylene vinylene)

An in situ FTIR-attenuated total reflectance and electrochemical quartz crystal microbalance study

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Abstract

The electrochemical synthesis and the redox reactions of poly(paraphenylene vinylene) (PPV) have been studied by in situ Fourier transform infrared (FTIR) spectroscopy using the attenuated total reflection method and by the electrochemical quartz crystal microbalance, EQCM, technique. The polymer material has been synthesized by electrochemical reduction of $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*p*-xylene on a Pt-electrode in dimethylformamide or acetonitrile using tetraethylammoniumtetrafluoroborate or tetraethylammoniumtosylate as electrolyte salts. The IR spectra of the doped conducting state show a very large broad absorption band starting at 1700 cm^{-1} and extending to 5000 cm^{-1} . Additional changes in the spectra can be seen in the region between 1700 and 700 cm^{-1} where new absorption bands appear. The intensity for these infrared active vibrations (IRAV) increase with increasing *n*-doping level. The reversible charging–discharging reaction is characterized by the growth in intensity of the IRAV during charging and diminish during discharging of the PPV film. Results from FTIR spectroscopy obtained from the charging–discharging reaction are consistent with the results obtained from the EQCM experiments, which show movement of counter cations during *n*-doping. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Poly(paraphenylene vinylene); Electrochemical synthesis; In situ FTIR-ATR spectroscopy; EQCM

1. Introduction

Poly(*p*-phenylene vinylene) (PPV) is a quite extensively studied member of the group of conjugated polymers [1–4]. Since the first report on electroluminescence from conjugated polymers observed when using PPV as the active layer in a LED structure [5], the number of reported works on the electronic properties of this material has strongly increased [4]. The transition from semiconducting (undoped) into a conducting (doped) state can be performed chemically or electrochemically. For PPV with a nondegenerate ground state, polarons and bipolarons are proposed to be responsible for the electronic properties in the doped state [6]. Spectroscopic investigations in the infrared range can give information not only about structural properties of the polymer chain but also of electronic properties of the material. In situ infrared spectroscopy with attenuated total reflection

(ATR) allows observation of structural and electronic changes taking place in the polymer during electrochemical reactions [7,8]. Charging reactions in polyconjugated materials give rise to strong doping-induced infrared active vibrations (IRAV) which are generally due to a large electron–phonon coupling within the molecule [9,10]. The characteristics of the bands from IRAV in the doping spectra are dependent on the effective conjugation of the macromolecule, i.e. the delocalization of the doping induced quasiparticle excitations such as polarons, etc. The quartz crystal microbalance technique in combination with electrochemistry (EQCM) has been used to monitor in situ the mass changes in the film during electrochemical synthesis and subsequent changing of the polymer film between insulating and conducting states [11]. Several studies on different conducting polymers with EQCM have revealed more details of both the counterion movement and the simultaneous movement of the solvent and the salt [12].

In this work, PPV films are prepared by electrochemical reduction of $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*p*-xylene [13]. The

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influence of the polymerization conditions (polymerization potential, solvent, electrolyte salt and addition of water to the polymerization solution) on the film formation and electrochemical behavior will be studied by in situ infrared spectroscopy by the ATR technique and by EQCM.

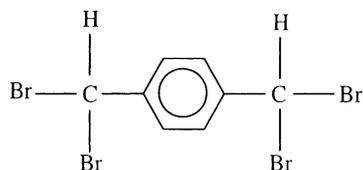
2. Experimental

2.1. Chemicals

Electrochemical polymerization of PPV was performed in a 0.05 M solution of the monomer material $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*p*-xylene (**1**, Tokyo Kasei) containing also 0.1 M tetraethylammoniumtetrafluoroborate (TEABF₄, Aldrich) or tetraethyl-ammonium-4-toluolsulfonate (TEATOS, Aldrich) in dimethylformamide (DMF, Lab-Scan) or acetonitrile (ACN, Aldrich). The monomer material, **1** (structure shown in Scheme 1), was used as received. The electrolyte salts, TEABF₄ and TEATOS were dried at 80°C for 1 h under vacuum conditions before use. The ACN was distilled over calciumhydride. Before usage, both solvents, ACN and DMF were purified by drying over activated aluminum oxide (Al₂O₃, Aldrich). In some experiments, the solvents were also used with addition of 0.2% of water.

2.2. Apparatus

The infrared spectra were recorded with a FTIR spectrometer (Bruker, IFS66S) using a MCT detector. The spectroelectrochemical measurements were carried out in a small-size ATR-spectroelectrochemical three-electrode flow cell made from Teflon[®]. The experimental set-up for the in situ FTIR-ATR technique has been described earlier [7,8]. The reflection element, a germanium crystal coated with a thin evaporated layer of platinum, served as the working electrode and a Pt foil was used as the counter electrode. The electrochemically active area of the germanium reflection element was 0.63 cm². A silver wire coated with silver bromide was used as the pseudo reference electrode (the redox potential of ferrocene, $E_{\text{redox}} = (E_{\text{ox}} + E_{\text{red}})/2$ was measured at +0.47 V versus this reference electrode). All the potentials are referred to this reference electrode unless differently stated. The polymer films studied by FTIR spectroscopy were polymerized electrochemically directly on the surface of the reflection element



Scheme 1.

in the spectroelectrochemical cell using a Jaisille potentiostat (IMP 88 PC) connected to a sweep generator (Prodis 1/14I).

For EQCM measurements, a 12 mm diameter AT-cut quartz crystal with 8.99 MHz resonant frequency from Gamma (Budapest, Hungary) was used. The crystal was sandwiched between two vacuum deposited platinum electrodes by using a standard keyhole electrode configuration. The electrochemical electrode area was 0.33 cm². A thin layer of chromium was used to improve adhesion between the platinum electrode and the underlying quartz substrate. A detailed description of the quartz crystal balance has been described elsewhere [14]. A platinum wire was used as the counter electrode and a silver wire coated with silver bromide was used as the pseudo reference electrode. Changes in the resonance frequency of the quartz crystal were measured using a Hewlett-Packard frequency counter connected by an IEEE-488 interface bus to a personal computer. An Electroflex EF 451 N° three-electrode potentiostat/galvanostat, connected through an AD-DA converter to a computer was used in the cyclic voltammetric experiments. Oxygen was removed from the solutions by purging with dry nitrogen several minutes before the measurements. During polymerization a stream of dry nitrogen was passed over the solutions.

2.3. Procedure

In the in situ FTIR experiments, PPV was synthesized potentiodynamically by scanning the electrode potential between +1.2 and -2.3 V or between 0 and -2.3 V versus Ag/AgBr. The effect of addition of 0.2% of water to the polymerization solution was also studied. The scan rate was 30 mV/s and FTIR spectra were recorded during nine successive scans. After deposition of PPV at the surface of the reflection element in the spectroelectrochemical cell, the cell was flushed with monomer-free electrolyte solution and the redox reaction of the film was studied. Infrared spectra of the redox process were recorded in situ during slow potential scans, 5 mV/s, in the potential range from -500 to -2100 mV (*n*-doping). Each spectrum, calculated from 32 co-added interferograms with a resolution of 4 cm⁻¹, covers a range of about 80 mV in the redox experiments and 600 mV during polymerization. The spectra are related to a reference spectrum, chosen at -1500 mV where the polymer still is in its neutral state. In studying the electrochemical polymerization process of PPV, the reference spectrum was taken at open circuit potential after the cell was filled with the electrolyte. Thus, only spectral changes (difference spectra) during polymerization or charging-discharging reactions are shown. In these difference spectra, vibrational bands pointing upwards correspond to compounds appearing during the process, whereas bands pointing downwards are related to compounds that are consumed during the electrosynthesis.

In the EQCM experiments, PPV films were electrochemically deposited onto the platinum covered faces of the

quartz crystal by potential cycling between 0 and -2.3 V (7 scans). A scan rate of 30 mV/s was used in all polymerization experiments. The electrolyte solution, containing also 0.05 M of the monomer material **1** was 0.1 M TEABF₄ in DMF. The redox behavior of the films was characterized in monomer-free electrolytes. In the redox experiments, the potential cycling was made between -500 and -2100 mV (*n*-doping) using a scan rate of 5 mV/s. Changes in mass were calculated from the changes in resonance frequency by using the Sauerbrey equation [15].

3. Results and discussion

3.1. In situ infrared studies on the electrochemical polymerization and redox process of PPV

3.1.1. Influence of the potential range used during polymerization

Polymerization of substance **1** by potential cycling was studied spectroscopically by taking in situ IR spectra at different stages of the polymerization process. The electrolyte was a 0.05 M solution of monomer in 0.1 M TEABF₄-DMF. During the first reductive scan, a big current peak was observed in the cyclic voltammogram but IR absorption peaks characteristic for PPV were not yet observed in the spectra. Obviously, during the first scan only soluble oligomers are formed by the electrochemical polymerization reaction. When the chain length of the oligomers in the solution phase increases, their solubility decreases and they start to precipitate at the electrode surface [16]. Changes in the spectrum, characteristic for PPV were observed during the second potential scan. Spectra from the second cycle

between 0 and -2.3 V during polymerization are shown in Fig. 1. The increase in the intensity of the bands due to the formation of the neutral form of PPV can be seen in Fig. 1. The absorption band at 966 cm⁻¹ is characteristic of an out-of-plane bending vibration of the vinyl group in trans configuration [17,18]. The band at 3024 cm⁻¹ is due to the transvinylene C–H stretching mode. The band at 838 cm⁻¹ is assigned to phenylene ring C–H out of plane bending and the bands at 1517 cm⁻¹ and 1424 cm⁻¹ (weak) to C–C ring stretching [18]. The wavenumbers of the peaks observed in Fig. 1 of the electrochemically polymerized PPV are in good agreement with those reported for chemically polymerized PPV [19,20]. The negative peaks at 1063 , 1090 , 1260 , 1386 , 1667 , 2857 and 2930 cm⁻¹ originate from the solvent, DMF [21]. The decrease in the intensity of the solvent absorbance peaks is due to growing of the PPV film on the electrode surface.

The cyclic voltammogram in the potential range from -500 to -2100 mV of a PPV film, infrared spectra shown in Fig. 1, on the Ge reflection element is shown in Fig. 2. The inset in Fig. 2 shows the cyclic voltammogram in the same potential range of a PPV film but obtained on a Pt electrode with an electrochemically active area of 0.07 cm². The PPV films were polymerized in a 0.05 M monomer solution in 0.1 M TEABF₄-DMF by potential cycling between 0 and -2.3 V (7 scans). As can be seen in Fig. 2, the two cyclic voltammograms are rather similar indicating that the substrate has a minor influence on the electrochemical property of the PPV film formed. Fig. 3 shows the difference spectra recorded during the electrochemical *n*-doping process of the PPV film. The reference spectrum was taken approximately at -1460 mV. As can be seen in Fig. 3, new strong absorption bands appear during the reduction process. These bands

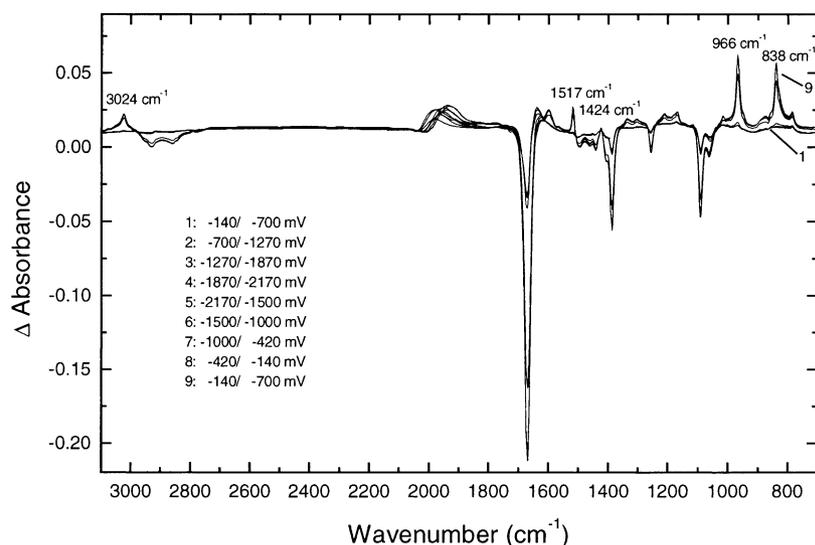


Fig. 1. Changes in the in situ ATR-FTIR spectra obtained during polymerization of $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*p*-xylylene during the second reduction scan in the wavenumber region 3100 – 700 cm⁻¹. The potential cycling was performed between 0 and -2.3 V (7 scans) in a 0.05 M solution of the monomer in 0.1 M TEABF₄-DMF. The inserted potential ranges indicate the potential values where each spectrum during the second reduction cycle was recorded.

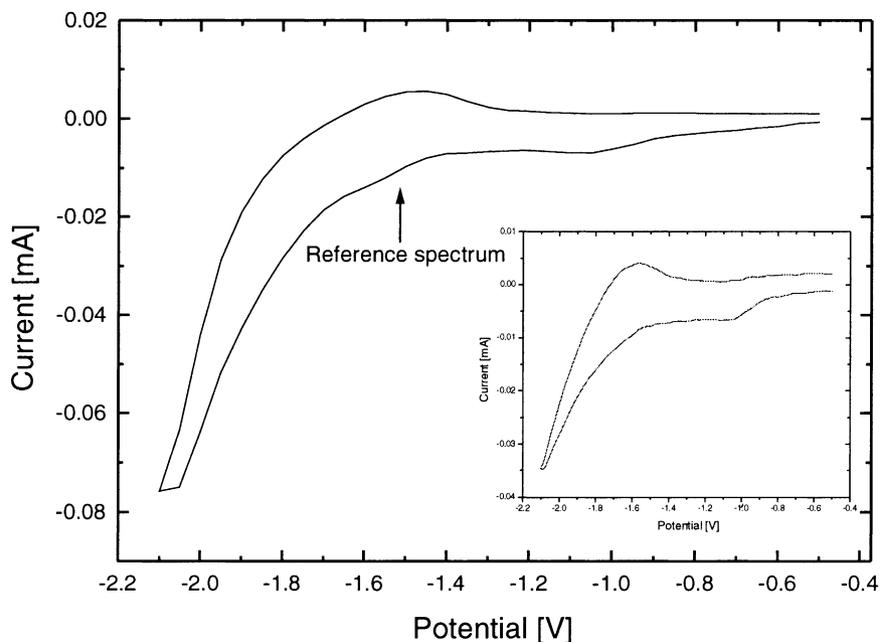


Fig. 2. Cyclic voltammogram obtained during the charging–discharging reaction of an electrochemically polymerized PPV film on the Ge reflection element in the potential range from -500 to -2100 mV. A 0.1 M TEABF₄-DMF solution was used as electrolyte and the scan rate was 5 mV/s. The polymerization was performed as for the PPV film in Fig. 1. Inset: current/voltage curve obtained during the charging–discharging reaction of an electrochemically polymerized PPV film on a Pt electrode. 30 mV/s was used as scan rate.

have no counterparts in the spectrum of the neutral form of PPV and the intensity of the peaks increase with the increasing level of reduction (n -doping). The broad absorption band, extending from 2100 cm^{-1} up to $>5000\text{ cm}^{-1}$, can be explained by electronic transitions due to the formation of free carriers in the polymer chain. This broad and intense absorption band is found in most conjugated polymers in

their conducting form. For a detailed discussion on these transitions, see e.g. [22]. The wavenumber range $1800\text{--}700\text{ cm}^{-1}$ of the spectra in Fig. 3 is shown in an enlarged scale in Fig. 4.

The n -doping induced IRAV bands that grow in intensity with the degree of reduction of the PPV film are listed in Table 1. In Fig. 4, the negative bands at 967 and 838 cm^{-1}

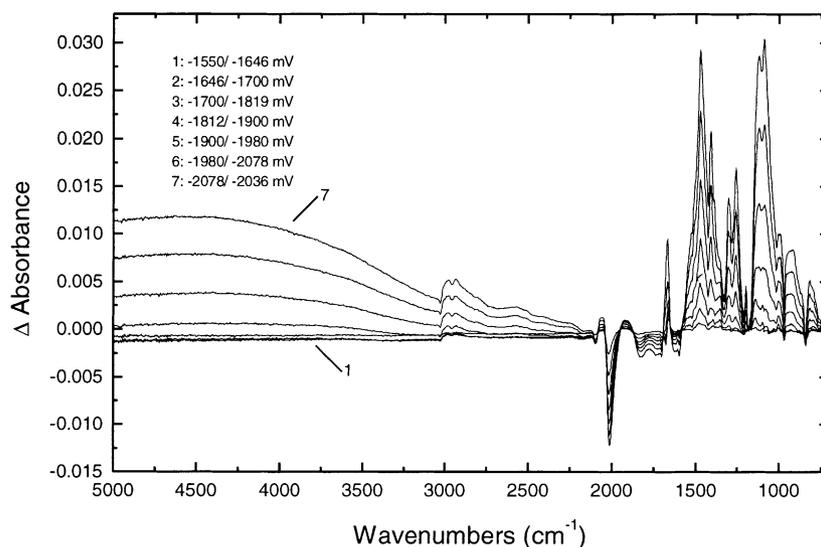


Fig. 3. In situ ATR-FTIR difference spectra recorded during the charging reaction of an electrochemically polymerized PPV film in 0.1 M TEABF₄-DMF solution in the wavenumber region $5000\text{--}700\text{ cm}^{-1}$. The inserted potential ranges indicate the potential values where each spectrum was recorded and refer to the cyclic voltammogram in Fig. 2. The reference spectrum was recorded at -1460 mV.

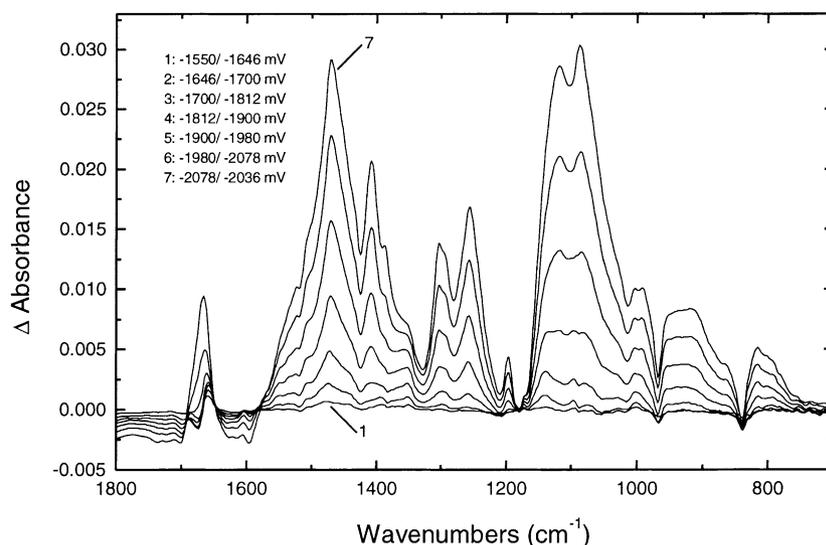


Fig. 4. An enlargement from Fig. 3, showing the absorption features in the wavenumber region $1800\text{--}600\text{ cm}^{-1}$ during the first charging cycle of the PPV film.

are connected with the loss of PPV in its neutral form. At 1667 cm^{-1} , a positive band from the solvent can be seen. It is probably caused by diffusion of solvated ions into the film during the reduction process. The rest of the peaks from the electrolyte are overlapped by the IRAV bands. During dedoping of the PPV film, the doping induced absorption bands progressively vanish and reappear during the following reduction cycle, which shows that the charging–discharging process is reversible.

When potentiodynamic polymerization of PPV was made in an extended potential range, i.e. from $+1.2$ to -2.3 V , the characteristic peaks of PPV in the IR spectra were of much lower intensity when compared to the results obtained in Fig. 1. After several potential cycles, the reflection element was covered only with a small amount of polymer material. As reported earlier [13] just a small current response could be obtained in the cyclic voltammogram during the doping reaction of a PPV film prepared in such a way. During

n-doping of this film, no spectral changes due to IRAV bands were obtained with in situ FTIR spectroelectrochemistry.

3.1.2. Influence of the type of solvent and water content in the polymerization solution

The effect of the content of water in the polymerization solution on the rate of the reaction in the initial state of polymerization has been studied earlier by the EQCM technique and presented in [14]. The faster film formation in presence of water can be explained by the lower solubility of the oligomers formed in the initial stages of the polymerization reaction. In the present study in DMF, we found that in presence of 0.2% water characteristic peaks of PPV could already be seen during the first potential scan from 0 to -2.3 V . However, during the subsequent potential cycles, a slow decrease in the intensity of the peaks characteristic for PPV was observed. This indicates that water has a negative effect on the quality of the final film. With in situ FTIR spectroscopy during reduction (*n*-doping) of a polymer film produced in water-containing polymerization solution, the broad band, extending from 1700 cm^{-1} to the near infrared, could not be seen. Also the IRAV bands in the wavenumber range 1700 and 700 cm^{-1} were smaller in comparison to experiments in waterfree conditions.

When ACN was used as solvent, only small spectral changes were observed during electrochemical polymerization of substance **1**. The poor film growth in ACN can be explained by the low solubility of the monomer material in this solvent [13]. During the reduction process of this film no spectral differences originating from the charging–discharging reaction could be obtained.

3.1.3. Influence of electrolyte salt

When 0.1 M TEATOS was used as the electrolyte in the polymerization solution, changes in the spectra due to

Table 1
Comparison of absorption bands from *n*-doping of electrochemically and *p*-doping of chemically made PPV

<i>n</i> -doping (cm^{-1})	<i>p</i> -doping (cm^{-1}) ²³
1604	1618
1506	1510
1470	1486
1407	1417
1304	1319
1257	1282
1195	1205
1124	1153
1088	1118
991	1002
938	960
866	876

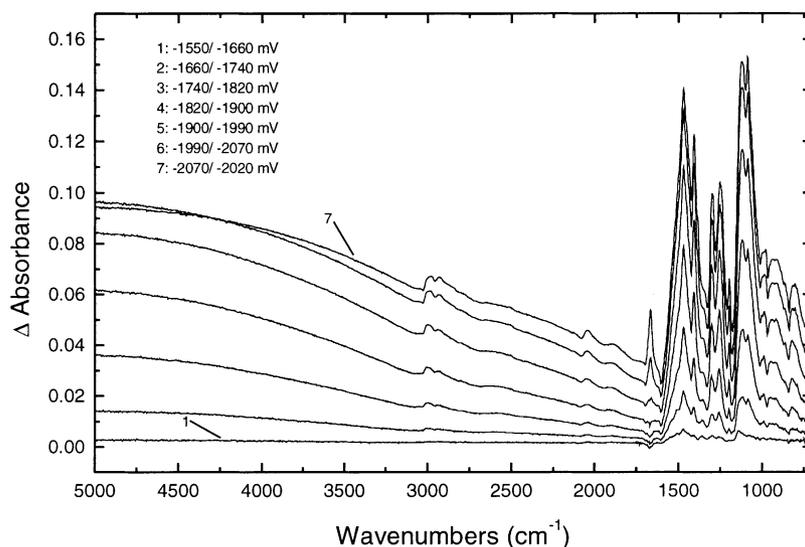


Fig. 5. In situ ATR-FTIR difference spectra obtained in the wavenumber region $5000\text{--}700\text{ cm}^{-1}$ during the charging of a PPV film in contact with an 0.1 M TEATOS-DMF electrolyte solution. The charging–discharging of the film was performed by potential cycling between -500 and -2100 mV using 5 mV/s as scan rate. The reference spectrum was recorded at -1450 mV . The film was polymerized in a 0.05 M monomer solution with 0.1 M TEATOS-DMF by potential cycling between 0 and -2.3 V .

formation of a PPV film could be observed already during the first potential scan from 0 to -2.3 V . As already reported [14], the electrolyte salt affects the polymerization mechanism and the morphology of the polymer film. The infrared spectra obtained during charging of a PPV film in 0.1 M TEATOS-DMF solution is shown in Fig. 5. The film was polymerized in a 0.05 M monomer solution in 0.1 M TEATOS-DMF by potential cycling between 0 and -2.3 V (7 scans). The other experimental conditions were identical to those previously described for the redox process of the PPV film in Fig. 3. When comparing Figs. 3 and 5, no distinct differences can be observed in the wavenumbers of the bands in the region between 1800 and 700 cm^{-1} . However, the absorbance of the broad band at wavenumbers higher than 1700 cm^{-1} is almost 10 times larger in Fig. 5 than in Fig. 3, showing that it is easier to create charge carriers in the PPV film prepared in presence of TOS^- than in presence of BF_4^- .

3.1.4. Comparison between infrared bands obtained during *p*-doping of chemically and *n*-doping of electrochemically polymerized PPV film

Table 1 shows the absorption bands obtained by in situ ATR-FTIR spectroscopy from *n*-doping of an electrochemically polymerized PPV film and from *p*-doping of a chemically made PPV film at similar doping level [23]. In the *n*-doping case, the peaks are taken from the spectrum recorded at -2078 mV with the spectrum at -1460 mV as the reference spectrum. In the *p*-doping case, the peaks are from the spectrum recorded at 1060 mV and the spectrum taken at the beginning of the potential sweep, i.e. at 500 mV versus SCE is the reference spectrum. As can be seen in

Table 1, the absorbance peaks for both types of doping appear approximately at the same wavenumbers. However, the maxima of the bands are shifted to lower wavenumbers in the case of *n*-doping. Influences on the absorption maxima have been explained by the Coulomb energy associated with charge carriers in [24], where it was found that the energy related to negative charged carriers is higher than for positive charged ones.

3.2. In situ EQCM studies on mass changes during doping of a PPV film

In the EQCM experiments, the PPV film was polymerized as described in the procedure section. In the EQCM experiments, the frequency change during the oxidation or reduction of a polymer film is caused by changes in the mass of the film due to transport of cations, anions and solvent species into or out of the film [25]. The changes in mass and the current during *n*-doping of a PPV film cycled in 0.1 M $\text{TEABF}_4\text{-DMF}$ solution between -1100 and -2100 mV (scan rate 5 mV/s) are shown in Fig. 6. As can be seen in Fig. 6, the mass increases during reduction and decreases during oxidation of the film. The mass increase is related to the transport of TEA^+ cations into the film during reduction in order to maintain the charge neutrality in the polymer film. Similar to many other conjugated polymers, the first cycle in cyclic voltammetric experiments with PPV shows a different behavior compared to subsequent cycles. This behavior is due to differences in the conformational reorganization of the polymer material during the first charging–discharging cycle [26,27]. The consecutive cycles are reproducible and the potentials where the mass increase and

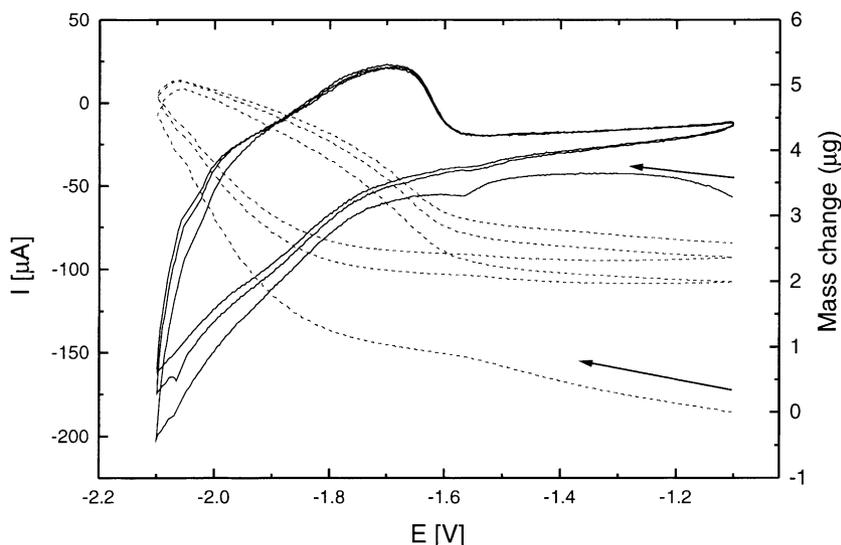


Fig. 6. Current (—) and mass (---) changes during charging and discharging (*n*-doping) of a PPV film cycled in 0.1 M TEABF₄-DMF solution between -1100 and -2100 mV. The film was made by potential cycling between 0 and -2.3 V in a 0.05 M monomer-0.1 M TEABF₄-DMF solution.

decrease take place coincide well with the potentials where Faradaic current due to the redox process are observed.

4. Conclusions

In this paper, the preparation of PPV by electrochemical reduction of compound **1** and the redox reactions of the polymer film have been investigated by in situ internal reflection FTIR spectroscopy and EQCM experiments.

The IR spectra obtained during electrochemical polymerization of compound **1** using DMF as solvent show the characteristic bands of PPV. During electrochemical charging–discharging processes of the PPV film doping induced IRAV bands were observed in the infrared spectra in the wavenumber range 1700–700 cm⁻¹. In addition to these bands, a broad absorption band extending from 1700 cm⁻¹ up to near infrared also appears during the charging reaction. This indicate the change of the polymer from its neutral to the conducting form. These results were obtained regardless of using TEATOS or TEABF₄ as electrolyte salt in the polymerization solution. When comparing the absorption bands obtained during the charging–discharging reaction (*n*-doping) of the electrochemically polymerized PPV film to the ones obtained during *p*-doping of a chemically polymerized PPV film the same kind of spectral pattern was obtained. When changing the solvent used during electrochemical polymerization of compound **1** to ACN a poor film growth was obtained. For this film no spectral changes could be obtained during the charging–discharging reaction. It was found from the EQCM experiments during the charging–discharging reactions of the PPV film that the mass of the film changes due to transport of ions into/from the polymer film in order to maintain charge neutrality.

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