UV-Vis-NIR spectroelectrochemical and in situ conductance studies of unusual stability of n- and p-doped poly(dimethyldioctylquaterthiophene-alt-oxadiazole) under high cathodic and anodic polarizations†‡

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Combined CV studies and UV-Vis-NIR spectroelectrochemical investigations revealed an unusual stability of the p- and n-doped PMOThOD in the wide potential window of 4 V. The n-doping process occurs in this polymer down to −2.7 V (vs. Ag/Ag⁺) in a non-destructive way with the characteristic development of the ω3 transition as a function of the doping level. In situ electronic transport studies revealed a high conductivity of the n-doped polymer which implies high mobility of the negatively charged carriers in the freshly doped PMOThOD film electrodes. An increase in the cathodic polarization, long-term cycling of the film electrodes, especially of higher thickness, results in a growing contribution of the negatively charged carriers trapping to the redox properties of the PMOThOD. The trapping of the charged carriers reduces gradually the electronic conductance of the PMOThOD film, but its effect on the redox-capacity of the film (in a typical scan rates range up to 50 mV s⁻¹) is only minor.

Introduction

Gradual and controllable changes in the electrical, optical and chemical properties of conjugated polymers induced by their doping under mild conditions in appropriately designed electrochemical cells are often exploited in electrochemical sensors and actuators, electrochromic windows, in organic electronic elements and in many other new electrochemical devices.1 Unfortunately, degenerative oxidation and reduction of these materials which accompany the doping reactions, even at modest potentials, severely limit their utilization. Although polymers with improved n-doping stability have been studied,2–4 among them a new class of alternate low bandgap polymers,5 still much research is needed, focused on the preparation of new macromolecular compounds in which the p- and n-doping processes are not perturbed by side reactions of a degradative type. With the use of classical electroanalytical techniques, we have recently demonstrated that a new conjugated polymer, poly(dimethyldioctyl) quaterniophene-alt-oxadiazole (PMOThOD) (see Chart 1), exhibits unusually high stability both in the p- and n-doped states.6

However, classical electroanalytical techniques are phenomenological in nature. For this reason they should be accompanied by a combination of spectroscopic and in situ electronic conductivity studies which probe selectively the state of the electronic charge carriers appearing in the polymeric films during their doping. This, in turn, may shed more light on the origin of the observed unusual stability of the doped forms of the polymer.

We report here in detail UV-Vis-NIR spectroelectrochemistry and in situ conductance data, revealing clearly the specific behavior of the mobile charge carriers in an alternate, donor–acceptor type copolymer such as PMOThOD under high anodic and cathodic polarizations. These data are directly compared with those obtained for the parent (non-alternate) conducting polymer, namely poly(3-octylthiophene) (POThi). Stable n-doping, characterized by a variety of electroanalytical techniques, was recently reported for a new class of the low gap polymers based on 3,4-ethylenedioxythiophene-bis-substituted thiophenes,6 a new electroactive polymer based on oligothiophene substituted tetrazine, poly[bis[5-(2-20-bithienyl)]-s-tetrazene].7 The related anodic and cathodic polarizations did not, however, exceed 1 and −2 V (vs. Ag/Ag⁺), respectively. Recent thorough UV-Vis-NIR characterizations of a new family of poly(indolocarbazole-alt-bithiophene),8

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and poly(dipyrrolyl-ethylenes, -arylenes and -heteroarylenes) were limited to the p-doped state only at the highest anodic polarization of 1.1 V (vs. Ag/Ag⁺, or ~4.1 V vs. Li/Li⁺). With our new polymer, PMOThOD, the anodic polarization reached the potential of 1.6 V (vs. Ag/Ag⁺) whereas the cathodic polarization was extended down to ~2.6 V (vs. Ag/Ag⁺), or ~0.4 V vs. Li/Li⁺. We believe that the potential span of 4.2 V applied to the n- and p-doped PMOThOD conducting polymer is the highest ever reported in the literature for the conducting polymers. Moreover, both the spectro-electrochemical and electronic conductance features of the PMOThOD polymeric film, observed at the extremely high polarizations, were found to be linked together, demonstrating a unique behavior of the electronic charge carriers, appearing during the doping of this polymer.

Experimental

Synthesis of the monomer, 2,5-bis[5-(3′-octylthien-2′-yl)-3-methylthien-2-yl]-1,3,4-oxadiazole, has already been reported. The electropolymerization of this monomer on an ITO electrode was carried out similarly to that described for coating of a Pt electrode, except that instead of a galvano-static mode we used cyclic voltammetric deposition (5 cycles between 0 and 1.75 V vs. Ag/Ag⁺) in a one-compartment cell, containing 0.15 M TBAClO₄ in a 2:3 v/v mixture of methylene chloride and acetonitrile, with 0.005 M of the monomer. The deposited film was then finally neutralized at 0 V, washed and transferred to a hermetically closed spectroelectrochemical cell. The reference PTh film electrode was anodically deposited in a TBAPF₆ acetonitrile solution following the conventional procedure described in ref. 11. Platinum foil and Ag/0.015 M AgNO₃ in acetonitrile were used as a counter and a reference electrode, respectively. All potentials are quoted with respect to the reversible Ag electrode. Electrochemical and optical measurements were performed with the use of Autolab PGSTAT20 and Cary 500 (Varian company), respectively.

Spectroelectrochemical measurements were performed in 0.15 M TBAPF₆ in sulfolane. The optical absorption spectra were measured from neutral to the highly doped state using a strict sequence of preceding and following electrochemical steps (for details see the ESI). The measurements of the absorption spectra were performed at constant potentials after the preliminary polarization at the same potential for 50–150 s. After each spectroelectrochemical measurement the film was completely undoped, and its redox-behavior checked with cycling voltammetry (CV). The procedure was designed to provide constant monitoring of the redox-state of the polymer film as a function of the vertex potential, and allowed to qualitatively follow the transport characteristics of the charge carriers. These data were further compared with the results of the direct in situ electronic conductance measurements.

Conductance measurements were performed with the use of the interdigitated Pt array electrodes (purchased from Abtech Scientific (VA)). They were 5 μm wide and 3 mm long, separated by a 5 μm insulating gap from its adjacent elements (for more details see the ESI). The gap between two sets of arrays was bridged by a conducting polymer film which was deposited by anodic polymerization of the related monomeric species, as proposed in ref. 12. Simultaneous measurements of CV curves and in situ electronic conductance were performed using Autolab 20 supplied with a bipotentiostat module (Eco Chemie, Inc., The Netherlands) as described in ref. 13 and 14. The ohmic current was measured by applying a small potential difference of 5 mV. We report here (unless otherwise indicated) the absolute values of the conductance of the polymeric film deposited on the interdigitated electrode. Since the geometry of the film was not exactly known, only rough estimations of the conductivity can be made. From the stoichiomery of the polymerization reaction we estimated roughly the effective thickness of the film deposited onto an interdigitated electrode as ~5 μm.

Results and discussion

Spectroelectrochemical results

Fig. 1 shows the electronic spectra for the p- and n-doped PMOThOD and PTh film electrodes from neutral (nonconducting) to their heavily doped, conducting states. After each optical measurement at constant potential, the film was characterized by cyclic voltammetry (Fig. 2 shows the most representative curves for the whole potential domains). The characteristic wavelengths of the doping-induced absorption peaks (related to different electronic states) are listed in Table 1. The neutral state of the PMOThOD film electrode is characterized by a strong interband π–π⁺ transition with a maximum at 475 nm (2.61 eV) whereas the corresponding transition in the PTh film gives rise to a peak at 450 nm (2.76 eV). From these data, the difference in the optical band gaps of the two polymers is equal to 0.15 eV, which is identical to the band gap obtained from the CV curves (see the ESI, Fig. 1S† and clarification below).

Method for evaluation of band gaps in conducting polymers under quasi-equilibrium doping conditions. A common method of evaluation of band gaps in π-conjugated polymers is based on determination of differences in their p- and n-doping potentials, i.e. the potentials at which the current starts to grow. Since the kinetics of doping of practical film electrodes is not fast enough, it is sometimes difficult to get the relevant quantitative data. It was recently discussed that the difference in standard potentials of the same p- and n-doped polymer, readily obtained experimentally, is an accurate measure of its optical band gap. This appears to be perfectly correct if the voltammometric responses of both p- and n-doped films are close to equilibrium. Practically, redox switching of the polymer films from neutral to their doped states often results in a higher polarization compared to that for the reverse, undoping reaction.

A typical example is the CV response for the n-doped PTh film electrode (see Fig. 2d), with a poorly expressed cathodic peak. The resolution of the CV peak does not improve on diminution of the scan rate. In order to overcome this difficulty, we propose an approach based on determination of the undoping peak potential for the polymeric electrode under study, for its comparison with the peak potential obtained under similar conditions with a reference polymeric electrode.
(the band gap of which is known). The principle becomes clearer from consideration of the CV curves of the p- and n-doped PMOThOD film electrode, measured with different vertex potentials (see Fig. 3a and b, respectively). Whereas the anodic peak potential for the p-doped film electrode depends on the applied vertex potential (the relevant potential region is marked by the block arrow) and often on the cycling life, the related cathodic peak potential (marked by the vertical dotted line) is perfectly constant. This peak potential should be compared with the related peak potential of the reference polymeric electrode. Similar consideration should be applied for the anodic (re-oxidation) peak of the n-doped PMOThOD (see Fig. 3b). It is seen that independently of the number of the injected charge carriers during the n-doping, the related anodic potential is essentially constant. This peak potential should be compared with the similar peak potential for the reference film electrode, and taking into account the results for the p-doped film, the difference in the optical band gaps for the two polymers is thus accurately calculated (ESI, Fig. 1S).

We ascribe the difference in the band gaps of both polymers, \((E_{\text{POTh}} - E_{\text{PMOThOD}}) = 0.15\) eV to the presence of the electron-withdrawing oxadiazole species in the polymer chain of the PMOThOD film electrode. This finding is consistent with the widely accepted synthetic principles that the alternation of conjugated groups differing in their electron-withdrawing and electron donating properties results in a decrease of the band gap with respect to their corresponding homopolymers.\(^{2,5,15,16}\)

The features of the p-doped PMOThOD and POTH. Bleaching of the interband \(\pi-\pi^*\) transition, accompanied by the concomitantly appearing characteristic peaks at \(\omega_1\) in the NIR and at \(\omega_2\) in the visible part of the spectrum, occurs for both p-doped polymers. From comparison of Fig. 1a, b and 2a, b one can notice that the electronic spectra represented by the curves marked with the filled circles refer to the vertex potentials, for which CV curves reveal quasi-reversible behaviour: at these potentials the absorption peaks at \(\omega_1\) and \(\omega_2\) pass through maxima. This type of spectral evolution is consistent with the formation of polaronic species in the gap of the polymers.\(^{17,18}\)

It was of interest to correlate the changes in the electronic spectra and in the related CV curves as the vertex potentials exceeded the values typical for quasi-equilibrium charging described above, i.e. when going from the curves marked by the filled circles to the curves marked by the filled squares (see Fig. 1a, b and 2a, b). It is clear that the POTH film electrode is not stable in the related potential ranges. The intensity of the absorption peaks at \(\omega_1\) and \(\omega_2\) and the related CV peaks diminishes considerably. In addition, a new transition at \(\omega_3\) appears (tentatively ascribed to a bipolaron species) the intensity of which decreases with the increase in the doping level. Simultaneously, there is a blue shift and an increase in the intensity of the interband \(\pi-\pi^*\) transition (see Fig. 1b). This is very remarkable, implying, first, a gradual lowering of the conjugation length of the POTH film electrode,\(^{19}\) and, second, indicating a considerable decrease in its effective electronic conductivity after over-oxidation (see also the results of the in situ conductance measurements in the next section).

PMOThOD film electrodes behave quite differently. In the p-doped state the polaronic and bipolaronic species appear at wavelengths similar to that for the parent POTH film electrode.
However, the anodic stability of both polymers is drastically different. Only a few minor differences between the curves marked by the filled circles and squares can be noticed for the PMOThOD at high anodic polarizations (Fig. 1a). The enhanced stability of the PMOThOD film at high anodic polarizations, as compared to that of the P0T film electrode, can also be seen from the corresponding CV curves shown in Fig. 2a and b (see the curves marked by the filled squares).

The PMOThOD film electrode shows a very stable CV response accompanied by a gradual increase of the doping level as the vertex potential increases from 0.8 to 1.2 V (see Fig. 3a). There is only a minor modification of the initial branch of the anodic CV curve. The broad anodic and cathodic peaks in Fig. 3a consist actually of two separate peaks, as is evidenced from the highly resolved CV curves of the PMOThOD film electrode on a Pt foil, measured at small scan rates (see the right-hand curves in Fig. 4: the vertical lines mark the positions of the two redox-peaks involved). As the vertex potential increases up to 1.3 V, an additional (3d) redox-couple appears on the CV curve with the anodic and cathodic peaks at 1.19 and 1.02 V, respectively (see Fig. 5a). The effect of such a high anodic polarization on the shape of the CV curve is very remarkable: both branches of the curve shift towards more positive potentials, the doping level moderately decreases. The CV response around the highest potential limits of 1.6 V (marked by the dotted oval) shows a considerable decrease in current, which can be tentatively ascribed to complete valence band depletion. Based on our previous gravimetric estimations, the 3d oxidation peak can be ascribed to the formation of a triply charged species on a conjugation length equal to two repeat units of the polymer. A moderate increase in the intensity of the interband \( \pi-\pi^* \) transition and of the transition at \( \omega_2 \) is due to a loss of the electronic conductivity of the polymeric film (see next subsection), which may result in an essentially non-homogeneous character of the doping process. Indeed, assuming that the electronic conductivity of the film decreases after over-oxidation, the following cathodic scan may not completely neutralize (or completely oxidize the film, in the course of the subsequent oxidation) because of the dependence of the depth of discharge (charge) on the length of the conducting paths in

(see Fig. 1a and Table 1). However, the anodic stability of both polymers is drastically different. Only a few minor differences between the curves marked by the filled circles and squares can be noticed for the PMOThOD at high anodic polarizations (Fig. 1a). The enhanced stability of the PMOThOD film at high anodic polarizations, as compared to that of the P0T film electrode, can also be seen from the corresponding CV curves shown in Fig. 2a and b (see the curves marked by the filled squares).

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### Table 1

<table>
<thead>
<tr>
<th>Polymer</th>
<th>p-Doping</th>
<th>n-Doping</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \omega_1/\text{nm} )</td>
<td>( \omega_2/\text{nm} )</td>
</tr>
<tr>
<td>P0T</td>
<td>1540–1480</td>
<td>770</td>
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the film’s bulk. The fact that over-oxidation may create defects in the \( \pi \)-conjugation,\(^{19} \) resulting in excessive swelling of the film,\(^{20} \) or its mechanical fatigue,\(^{21} \) leads to a limited rate capability of the film electrode as reflected by the deterioration of its CV response. The spectroelectrochemical measurements were performed at quasi-stationary conditions; hence they are less sensitive to a direct loss of the electronic conductivity, but may reflect the phenomenon \( \text{via} \) the above mentioned non-homogeneous character of the doping process.

**Features of the n-doped POTh and PMOThOD.** Regarding the parent, n-doped POTh film electrode, one can see a typical development of the transitions at \( \omega_1 \) and \( \omega_2 \) when the film is slightly doped, followed by its drastic diminution as the cathodic polarization increases (see the curves marked by the filled circles and squares in Fig. 1d and 2d). In contrast, PMOThOD film demonstrates an unusually stable behavior: as is seen from Fig. 1c, after the development of the \( \omega_1 \) and \( \omega_2 \) transitions, the electronic spectra remain almost unchanged as the potential decreases from \(-2.3 \) to \(-2.6 \) V. The CV curves of the film on a Pt current collector (Fig. 3b, 5b and c) show clearly a decay in the current at such negative potentials, which should indicate a complete filling of the conduction band with electrons (and, hence, practical end of the n-doping process). This is in good agreement with the related electronic spectra in Fig. 1c. Moreover, in contrast to the behavior of the p-doped PMOThOD film electrode, the intensity of the interband \( \pi-\pi^* \)-transition in the n-doped film remains unchanged between \(-2.3 \) and \(-2.6 \) V (the curves marked by the filled circles and squares in Fig. 1c).

A unique feature of the absorption peak for the PMOThOD film at \( \omega_3 \) is that it appears at a very low doping level, and continues to grow up to the very end of the n-doping (note that this peak is absent in the spectra of the POTh film). The peak is red-shifted as the doping level increases, reaching saturation at \(-2.3 \) V. The related highly resolved slow scan rate \((v = 10 \text{ mV s}^{-1})\) CV peak passes through the last (3rd) reduction peak at this potential: see the left-hand curves in Fig. 4 (other details of this figure are discussed in the next subsection).

In order to understand the origin of the transition at \( \omega_3 \), the absorbance of the n-doped PMOThOD film electrode was plotted as a function of the doping level, \( X \) (scaled to the maximal doping level determined at 1.6 V) (see ESI, Fig. 2S).\(^{\dagger} \) The plot is linear, meaning that the transition at \( \omega_3 \), visible already from small doping levels, is, initially, due to reduction of the oxadiazole units (which are reduced more readily compared to the bithiophene units). At higher doping levels, reduction in the bithiophene units takes place; the resulting negatively charged species being in good \( \pi \)-conjugation with the oxadiazole-based species gradually change the characteristic frequency \( \omega_3 \). In addition, as was already mentioned, practical independence of the absorption spectra for the n-doped PMOThOD film electrode under high cathodic polarizations, implies good electronic conductivity of the heavily n-doped film. It was thus of interest to perform

![Fig. 3 Cyclic voltammograms of a p- and n-doped PMOThOD film electrode 0.5 \( \mu \)m thick on a Pt current collector measured with gradually increasing anodic and cathodic vertex potentials, respectively. The broken lines show the peak potentials of the undoping reaction which are practically independent of the related vertex potentials. The scan rate is indicated.](image)

![Fig. 4 Cyclic voltammograms of p- and n-doped PMOThOD film electrode 0.5 \( \mu \)m thick on a Pt current collector measured at 5, 10, 20, 50, and 10, 20, 50 mV s\(^{-1} \), respectively (the lowest and the highest scan rates are indicated near the curves). The small vertical lines mark the peaks potentials. Inset shows a double logarithmic plot of the n- and p-doping peak heights as a function of the scan rate (the slopes are 0.5 and 1.0, respectively).](image)
combined *in situ* conductivity and CV characterizations of the both polymeric films under consideration.

**In situ** electronic conductance measurements

Features of the n-doped PMOThOD. Since the electronic conductance of the n-doped PMOThOD film electrode was found to show a complicated dependence on the depth of discharge (i.e. on the vertex potential in the CV characterizations) and cycling life of the film electrode, we consider first potential dependences of the conductance of a fresh PMOThOD film, n-doped in a “narrow” potential window, *i.e.* between $-1.4$ and $-2.3$ V (see Fig. 6a). This limited potential range involves basically two reduction peaks marked by the vertical lines in the highly resolved CV curve for the n-doped film (see Fig. 4). The *in situ* conductance of the film deposited on the interdigitated array electrode measured simultaneously with the CV curve is shown at the bottom of Fig. 6a. Both forward and backward potential scans of the current and the conductance, $1/R$, are presented in this figure.

It is seen that $1/R$ drastically increases as the polymer undergoes the n-doping, reaching a flat maximum at $-2.3$ V. Reversal of the potential scan to $-1.4$ V reveals a well-defined, approximately symmetrical peak centered at *ca.* $-2$ V, *i.e.* in the vicinity of the major undoping peak (compare with the highly resolved CV curves in Fig. 3b, 5b and c). It is worth mentioning that the evaluated effective thickness of the polymeric coating on the interdigitated electrode was 5 $\mu$m, *i.e.* by an order of magnitude higher than that for the PMOThOD film on a Pt current collector. When the gaps between the interdigitated electrodes are bridged by electropolymerization, it is common that the local thickness of the film above the gap is lower than that on the interdigitated Pt electrodes. Hence for the purpose of a correct qualitative analysis, the potential dependences of the conductance should preferably be compared with the highly resolved CV curves for thin film electrodes on a Pt foil.

The conductance of the film is then presented as a function of the dimensionless doping level, $X$ (see Fig. 6b; the charge passed during the potential sweeping was normalized with
curs, or a partially reversible charge trapping takes place.23,24 For energetic reasons, either because some irreversible over-reduction occurs during film’s cycling, the conductance peak is a bit shifted along the abscissa from $X = 0.5$ a remarkable feature is that $1/R$ drops to very low values already at $X < 0.2$. The last result deserves careful consideration. In principle, if some irreversible changes occur during film’s cycling, the forward (doping) and the backward (undoping) branches of the conductance vs. charge curve may not coincide. The nature of these changes may be quite different, e.g. (i) the formation of cracks in the film due to an excessively fast rate of the potential sweeping, (ii) the decrease in the undoping rate due to a loss of the electronic conductivity of the film for two reasons: either because some irreversible over-reduction occurs, or a partially reversible charge trapping takes place.$^{23,24}$

The first possibility was rejected after examination of the deposit on the interdigitated electrode under an optical microscope at the end of the experiment, which did not reveal cracks. The involvement of the irreversible chemical changes of the polymer due to its over-reduction was excluded on the basis of the optical absorption measurements shown in Fig. 1c.

![Fig. 6](image_url)

**Trapping of the negatively charged carriers.** In this subsection evidence is furnished that the injected negatively charged species may be localized both on the bithiophene and the oxadiazole units of the alternate polymeric chains provided that a relatively high negative potential was applied, and the polarization time was sufficiently long. We define “trapping” as the phenomenon of charge occupation in hollow sites (in terms of site energy) on the polymeric chains, or within the polymeric fibrils, so that the mobility of the trapped charge carriers substantially decreases. The trapped charges may be completely or partially released under the driving force of the backward undoping process. Indeed, assuming that such trapping effect takes place, one can explain the peculiar shape of the conductance vs. $X$ curve due to an interplay between the concentration and the mobility terms in the expression of the conductance (i.e. the former term increases and counterbalances the decrease of the latter one). During the backward scan, the mobile charge carriers, and a part of the trapped charge carriers are oxidized (neutralized), so that the above interplay of the terms results in the conductance peak higher than that for the forward process. Then both the concentration and the mobility factors decrease the conductance. A part of the deeply trapped charges in the polymer chains may not be oxidized in the selected potential range, so this may explain the fact that the conductance becomes low at a relatively high doping level, $X = 0.2$.

The peak-shaped dependence of the conductance on $X$ together with a relatively low maximal conductivity of 85 mS cm$^{-1}$ may be considered in favor of the redox-type of the electronic conductivity, implying electron hopping between the neighboring redox centers.

In fact, the specific conductivity of a redox-type can be presented as a product of the electronic chemical diffusion coefficient and the differential redox-capacitance.25 Based on a Frumkin-type isotherm, typical for modeling the doping processes, it is easy to show that the specific conductivity, $\sigma$, is simply proportional to a product of the doping level, $X$, and the fraction of the neutral, yet not reduced species, $(1 - X)$:

$$\sigma \sim X(1 - X).$$

A plot corresponding to this simple statistical function, describing the probability of species movement along a 1-D lattice of sites, is shown in Fig. 6b for a comparison with experimental data.

For energetic reasons, the trapping effect becomes much more pronounced at higher cathodic polarizations, e.g. as the potential shifts towards $-2.5$ V (see Fig. 7a and b). The curve marked by the filled circles in Fig. 7a is the same as that presented in Fig. 6a, i.e. relates to the narrow potential range, down to $-2.3$ V. Then the vertex potential was shifted to $-2.5$ V in 50 mV steps. The potential dependence of the conductance for each 3rd scan is shown in Fig. 7b. It is remarkable that both conductance peaks (for the doping and undoping) decrease with shifting the vertex potential towards less positive values. Simultaneously, a transient increase of conductance appears at the end of the undoping process (marked with curly brackets in Fig. 7a and b). Fig. 7a compares the CV and the conductance-potential curves for the narrow and the wide range of the potential cycling. This figure clearly demonstrates the fact that the appearance of the transient increase of the conductance (marked by the curly brackets) corresponds to a rather broad peak on the CV in the same potential range, and that these both effects are due to the injection of charge between $-2.3$ and $-2.5$ V.

The above transient behaviour of the conductance at the end of the undoping process is very essential for understanding the trapping phenomenon. In order to have a better resolution of the transient behavior in terms of cyclic voltammetry, we performed a continuous cycling of the film with the gradually decreasing vertex potential (down to $-2.8$ V) with the use of a thin PMOTyOD film on a Pt foil (0.3 µm thick, see Fig. 5b and c). Fig. 5b shows that the increase of the number of the injected charge carriers results in a transient CV behaviour in...
The assumption of the redox-type conductance of the n-doped PMOThOD film seems to be in agreement not only with the shape of the $1/R$ vs. $X$ curves but also with the analysis of the CV peak heights as a function of the scan rate. Indeed, the highly resolved CV peaks in Fig. 4 were presented as a function of the scan rate in a double logarithmic plot (see inset to this figure). The $3^{\text{rd}}$ reduction peak (the highest reduction level) revealed a perfect slope of 0.50. The second, most prominent reduction peak gives a slightly higher slope of 0.64 (not shown in the figure) which, in any case, is closer to 0.50 than to 1.00 obtained for the peaks of the p-doped film (shown in the inset to Fig. 4). In general, the character of the dependence of the peak heights on the scan rate is similar to that reported for poly(bis[5-(2-20-bithienyl)]-s-tetrazine). The diffusional mechanism of the n-doping with a 0.5 slope means slow electron transport typical for the redox polymers, whereas absence of diffusion limitations and the characteristic slope of 1.0 imply fast charging rates and, in particular, a metallic type of conductivity in π-conjugated polymers. The intermediate value of the slope (0.64) for the second reduction peak at $-2.3\, \text{V}$ implies a mixed type of conductance, in agreement with a higher value of the $1/R$ at $-2.3\, \text{V}$ compared to that at $-2.5\, \text{V}$ (the $3^{\text{rd}}$ reduction peak), see Fig. 7b.

When the PMOThOD film is continuously cycled down to $-2.8\, \text{V}$ (see Fig. 5b and the left-hand curve in Fig. 5c), a kind of a steady-state is reached with a final, rather smeared, undoping peak. It is clear that the negatively charged carriers trapped on the hollow sites cannot be detrapped in the potential range typical of the n-doping/undoping reaction. For this reason, in order to observe the detrapping effect, we extended the potential windows to that typical of the p-doping of this electrode. The right-hand side of Fig. 5c compares three CV peaks: (i) the one measured with the fresh film prior to its n-doping; (ii) the first p-re-doping cycle after the continuous n-doping cycles, the latter resulting in accumulation of the trapped charges, and (iii) the second and the following p-re-doping cycles. This comparison shows quite clearly that all negatively charged, trapped carriers are released during the first p-re-doping cycle, resulting in a spectacular transient oxidation peak in the related CV curve. We reported earlier a similar phenomenon with pristine polythiophene films, which was accompanied by a transient increase in the conductance (for the first p-re-doping cycle only). A similar effect was observed for the regioregular alternate donor–acceptor type copolymer of dialkylthiophene and fluorenone. The present work does not focus on the changes that may remain in the film after the release of the trapped, negatively charged carriers. A comparison between the CV for the freshly p-doped film and that for the $2^{\text{nd}}$ and the following p-re-doping cycles (see the right-hand curves in

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Fig. 7 CV curves (the top) measured simultaneously with in situ electronic conductance (the bottom) for n-doped PMOThOD film electrode (panel “a”). The curve marked with filled circles relates to the $3^{\text{rd}}$ cycle measured in a narrow potential window, down to $-2.5\, \text{V}$. The following curves, marked with filled squares and triangles, relate to the $3^{\text{rd}}$ and the $10^{\text{th}}$ cycles measured down to the vertex potential of $-2.5\, \text{V}$. The wider potential window was achieved by gradual decreasing of the vertex potential between $-2.3\, \text{V}$ and $-2.5\, \text{V}$ with a $50\, \text{mV}$ step. The related electronic conductance-potential curves (the curves marked with filled circles, squares, triangles with their corners up and down, respectively) are shown in panel “b”. The potential scan rate was $20\, \text{mV}\, \text{s}^{-1}$.
Fig. 5c), shows a remarkable shift in the formal redox potential by 0.2 V, however, the redox-activity of the film does not seem to be deteriorated. This is another aspect of the exceptional stability of the n-doping process in the PMOThOD film electrodes, which, to our knowledge, has never been reported in the literature for any conducting polymer.

**Features of the p-doped PMOThOD.** The plot of the conductance vs. potential for the p-doped PMOThOD film is shown in Fig. 8a. With the vertex potential up to 1.0 V the curve of conductance has a characteristic sigmoid shape, reaching a very flat maximum of the conductivity, 200 mS cm$^{-1}$. However, as mentioned above, in contrast to the n-doped film, for the p-doped film, the related CV peaks are proportional to the scan rate, implying a metallic type of conductivity. The following consecutive cycling of the film in the same range of potentials does not change appreciably neither the shape of the CV nor the conductance curve (not shown in the figure).

The effect of the higher anodic polarizations on the conductance of the p-doped PMOThOD film is presented in the form of 1/$R$ vs. $X$ curves (see Fig. 8b). The value of the potential of 1.2 V is close to the potential of the 3d anodic peak for the p-doped film, responsible for the change in the shape of the CV curves described above (see Fig. 5a). From Fig. 8b one can conclude that approaching this high anodic potential leads to a decrease of the conductance, and this decrease is especially pronounced for the backward scan, i.e. immediately after the over-oxidation took place. Interestingly, the decrease in conductance is accompanied by a transform of the sigmoid to bell-shape dependence of 1/$R$ on $X$. There is no doubt that this decrease in the 1/$R$ is responsible for the gradual shift of the CV curves towards more positive potentials as the vertex potential increases (Fig. 5a). Concerning the effect of a decrease in the film’s conductance at high anodic potentials on the optical absorption spectra, we should repeat once again that spectroelectrochemistry (at stationary conditions) is less sensitive to the loss in conductance, but may reflect this phenomenon as it acquires the feature of a non-homogeneous doping process.

**Features of the p- and n-doped POTH.** The cyclic voltammetric curves together with the in situ conductance curves for the p- and n-doped POTH films are shown in Fig. 9a and b. Whereas the p-doping features of this film are qualitatively similar to that of the PMOThOD electrode (excluding high anodic polarizations), its maximal n-type conductance even in the fresh film is 6 times lower than that of the PMOThOD electrode. The 3d cycle (marked by the asterisk in Fig. 9b shows a drastic loss of both the polymer’s redox charge, and the conductance. Surely, the presence of the alternate
oxadiazole units in the PMOThOD chains stabilizes the n-doping, as is briefly discussed in the following subsection.

A brief comparison between the electroanalytical and conductance behavior of the PMOThOD and some low band gap polymers. The electron-withdrawing ability of oxadiazole unit is less strong compared to that of, e.g., pyrazine or 4-dicyanomethylene in 4H-cyclopentadithiophene units, which were recently proposed to alternate with the 3,4-ethylenedioxythiophene in order to gain the low band gap polymers.\(^5\) For this reason, the band gap of the PMOThOD film electrode (2.61 eV) is only 0.15 eV lower than that of the pristine homopolymer, POTh (2.76 eV). Thus the characteristic band gap of the PMOThOD film electrode is about twice higher than that of the low band polymers.\(^5\) The reduction peak in the PMOThOD film electrode is about twice higher than that of the pristine homopolymer, POTh (2.76 eV). Thus the characteristic band gap of the PMOThOD film electrode (2.61 eV) is only 0.15 eV lower than that of the pristine homopolymer, POTh (2.76 eV). This shift is due to the electron-donor effect of the octyl-bithiophene co-monomeric unit. Unfortunately, we could not check the general rule according to which band gap of the donor–acceptor type co-polymer can be calculated as a weighted average of the band gaps of the related homopolymers: the silicon-containing poly(1,3,4-oxadiazole) showed severe degradative oxidation at about 2 V.\(^29\)

The optical, and especially, in situ conductivity data obtained in this work suggest that the behavior of the PMOThOD film electrode, having some common features with that for the low band gap polymers, differs from them in several important aspects. Similar to the case of the low band gap polymers, the negatively charged species of the PMOThOD film electrode are localized on the electron-deficient units (here, oxadiazole units). However, in view of a lower electron-acceptor strength of the oxadiazole compared to the other groups under consideration, the extent of the electron localization on this unit is expected to also be lower, thus ensuring a faster electron transport (in this work it was proved by the in situ conductance measurements with the fresh PMOThOD films using moderate cathodic limiting potentials). This property of the oxadiazole has recently been exploited for the increase of the efficiency and lifetime of organic polymer light emitting devices (PLEDs).\(^30,31\)

The conductance peak’s width at the peak’s half-height (CW), and the bandwidth (BW), estimated as the width of the CV peak of the n-doped PMOThOD film electrode at its half-height, are both close to 0.30 V, which is similar to the values typical of low band polymers.\(^5\) For the fully p-doped PMOThOD film, the bandwidth was found to be 0.7–0.8 V whereas an estimation of the related CW was not possible due to a sigmoid shape of the conductance curve and a loss of the conductance at high anodic polarizations. If the origin of the much higher localization of the negatively charged carriers as compared to that of the positively charged carriers relates to intramolecular rather than intermolecular interactions,\(^6\) we may further suggest that the lower charge density of the bulky tetraalkylammonium cations as compared to a higher charge density of much smaller counter-balancing anions, is able to prevent π-dimerization of the negatively charged polaron, thus facilitating their localization on the polymeric chains.

Conclusions

Based on the combined CV studies and UV-Vis-NIR spectro-electrochemical investigations, we demonstrate an unusual stability of the n- and p-doped PMOThOD film electrodes. The extremely high potentials of the p- and n-doping used makes up the difference of about 4.0 V, i.e. well comparable with that typical of lithium-ion batteries. We show that the non-destructive n-doping of this film is accompanied by a characteristic development of the \(\alpha\rightarrow\beta\) transition as a function of the doping level (or electrode potential). We also demonstrate that the simultaneous in situ conductance measurements may provide more insight into the dynamics of the negatively charged electronic carriers during the n-doping process, revealing a crucial importance of such factors as the cycling life of the film electrode, the vertex potential of cycling, and the film’s thickness.

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References


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