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Comparative study of the electrochemical response of poly (alkyl thiophene) derivatives deposited on platinum and titanium electrodes

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Summary

A comparative investigation of the electrochemical response of poly(alkyl thiophene) derivatives (3-methylthiophene and 3-octylthiophene) on two different electrode materials (platinum and titanium) was performed using cyclic voltammetry. By analyzing the voltammetric data, a slight potential shift of the oxido-reduction peaks in polyoctylthiophene film deposited on titanium electrode compared to platinum has been observed. The calculated surface concentrations of the electroactive centers were found to decrease significantly in poly(octylthiophene) grafted onto titanium surface, while in poly(methylthiophene) these changes were negligible. The influence of the nature of the electrode material and the alkyl substituent length on the redox properties has been discussed. The reduced forms of the synthesized polymer films were characterized by FTIR spectroscopy. The FTIR spectra indicate decrease of the conjugation length, the degree of polymerization and the presence of defects (2,4 linkages and C=O groups) with the increase of the alkyl group length.

Introduction

Polythiophene (PT), as a representative of the conducting polymers, has received great scientific attention in the last twenty years, not only because of its interesting properties (good environmental and thermal stability), but also because of the wide application perspectives [1, 2, 3, 4].

Most of the studies devoted to this polymer were primarily focused on the polymerization mechanisms [5], the influence of the monomer concentration [6,7], as well as the influence of the supporting electrolyte nature on the quality of the conducting polymer [8]. Significant amount of the published literature was related to thiophene modifications in order to achieve better processibility of this material [9-11]. Numerous polyalkyl derivatives of thiophene have been synthesized so far by chemical and electrochemical approaches, resulting in conducting polymers with better solubility and very interesting properties [12,13].

Generally, the electrosynthesis of PT and its derivatives was performed on noble metals like Pt and Au in an organic medium such as acetonitrile, propylene carbonate or nitrometane [14,15]. Some less noble metals, such as Al, Fe, and Zn have been recently reported as electrode materials for electrochemical polymerization of thiophene in dichlormetane [16]. Wang et al. have reported that PT films could be also grafted on relatively reactive metals like copper from BF_3-diethyl ether solution [17].

The introduction of titanium electrodes is especially important in polymer electrochemistry due to their wide working potential window, when compared to many others. Deng et al. have described very unstable poly(methylthiophene) (PMT) films in the air, obtained by the electrochemical polymerization of 3-methylthiophene on Ti/TiO_2 electrode in acetonitrile [18]. In our previous paper we have followed the relaxation kinetics of polythiophene and its polyalkyl derivatives (poly-methylthiophene and polyoctylthiophene), deposited on platinum and titanium electrodes. It was found that the nature of the electrode material has considerable influence on the relaxation process in polythiophenes substituted with longer alkyl groups (octyl)[19].

The aim of this paper is to give a comparative view and to enhance the available data on the electrochemical behavior of the two poly(thiophene) derivatives (polymethyl and polyoctyl thiophenes), grafted on platinum and titanium electrodes in the same potential region. The influence of the nature of the electrode material on the redox properties, conjugation length, and the presence of defects will be also subject of discussion. Electrochemical response of unsubstituted polythiophene will be also given for comparison.

Experimental

Materials

Commercially available thiophene (T) was distilled using standard vacuum distillation procedure, while the other monomers, 3-methylthiophene (3MT) and 3-octylthiophene (3OT), products of *Across Organics*, were used as received, stored in a refrigerator in order to avoid noticeable decomposition. The other chemicals ($LiClO_4$ and acetonitrile) with very high purity were used without further purification.

The electrochemical polymerizations were performed in 0.1 M $LIClO_4$ solutions in acetonitrile and 0.1M concentrations of the corresponding monomers.

The electrochemical measurements were performed in classical three-compartment cell at room temperature. The polymer films were grafted on platinum and titanium working electrodes with areas of 0.785cm^2 and 0.196cm^2 respectively. Platinum foil with large surface was used as counter electrode, and saturated calomel as reference in both cases. The working electrodes were mechanically polished with diamond paste, ultrasonically cleaned, and finally rinsed with ethanol. The redox behaviour of the polymer films was examined in a monomer free acetonitrile solution, containing 0.1 M $LiClO_4$ at 100 mVs^{-1}, in order to avoid the formation of degradable products during the electrochemical potential cycling. Prior to the start of the electrochemical measurements, the system was blown by inert gas (argon) in order to release the oxygen, present in the electrolyte solution. The electrochemical measurements were performed on HEKA 488 potentiostat/galvanostat, connected to a personal computer.

FTIR Spectroscopy

FTIR measurements were recorded ex-situ, with a Perkin Elmer spectrophotometer, in the range between 4000 and 400 cm^{-1}. IR spectra were taken from the deposited polymer films in their neutral forms. The working electrode covered with polymer film was maintained at a potential of -0.2 V for 10 minutes and rinsed with acetonitrile.

Results and discussion

The investigated monomers were potentiodynamically polymerized at room temperature, with 10 performed cycles and a scan rate of 100 mVs^{-1} in the potential range between -0.2V and 1.8 V. In order to obtain more reliable electrochemical information of the redox behavior of the investigated polymers, CV measurements in electrolyte solution free of monomer were performed.

Platinum electrode

The cyclic voltammograms (CV's) obtained during the electrochemical polymerization of thiophene and its alkyl derivatives, deposited on platinium electrode, are presented in Figure 1 (1a, 1b and 1c).

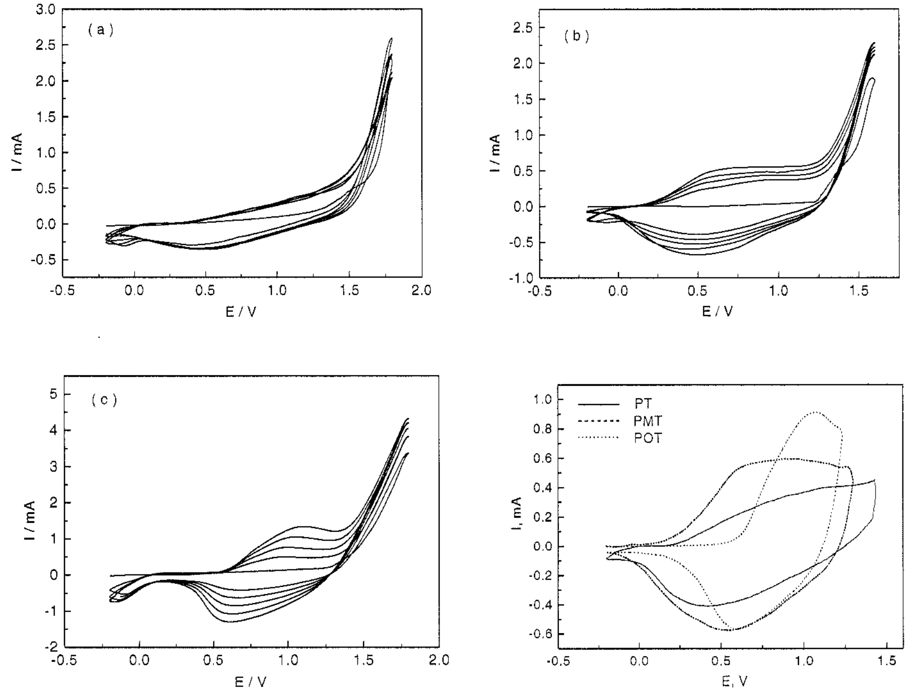

Figure 1. Cyclic voltammograms of the potentiodynamic polymerization (the first five cycles are presented) of **a)** thiophene **b)** methylthiophene **c)** octylthiophene, ν=100 mV s^{-1}, platinum electrode **d)** CV's of the investigated polymers in 0.1M LiClO4/acetonitrile solution free of monomer

The first oxidation cycles, presented within the same figures, show onset oxidation potentials of the monomers determined as 1.35, 1.29 and 1,39 V for T, MT and OT respectively. It could be seen that the three monomers have very similar onset oxidation potentials. The highest onset potential in OT may be explained by the actual lower concentration of the electroactive segment, if we take into account that the conjugated part in octylthiophene represents 57 $^{wt}/_{wt}$ % of its total molecular mass. From literature data it is well known that lower monomer concentrations shift the oxidation potentials to more positive values [20]. The electrochemical charging/discharging of the polymer films in a electrolyte solution free of monomer is presented in Figure 1d. Characteristic features of the presented CV curves for the three corresponding polymers (PT, PMT and POT) are the different oxidation potentials positioned at 0.82V, 0.64V, and 1.07V respectively. The decrease of the oxidation potential of the polymer by introducing the methyl group in the thiophene ring is obvious from the Figure 1d, but as soon as the methyl group is replaced with octyl, the potential increases again. It is well known that the decrease of the potential could be primarily due to the electron donor properties of the methyl group. In the case of poly(octylthiophene) this increased potential, is not likely due to the difference between the donor properties of the methyl and octyl groups, but more probable explanation could be the influence of the steric factor, similarly to ref. [21]. On the other hand, according to the literature data, the shift of the Ep_a in cathodic direction could suggest formation of longer conjugated segments in polythiophenes [22]. The highest E_{pa} in POT could be a proof of the presence of short conjugated segments, while in PMT longer conjugations could be assumed. This interpretation is supported by the FTIR spectra of the polymer films given below. The longer alkyl groups are usually responsible for hindering of the successive linking between the monomer units, thus taking coplanar configurations and resulting in shorter conjugation lengths [23]. The oxidation potential of PT lays in the middle between the E_{pa} of its derivatives. Since the width of the peaks is considerably large, the comment regarding the length of the conjugated segments must be taken with a great reserve.

The difference between the oxido reduction peaks ($\Delta E=E_a-E_c$), usually assigned as hysteresis in electrochemistry, is clearly defined at all three polymers (Table 1). The potential hysteresis is usually connected with a number of factors, including the diffusion of dopand anions, the thickness of the polymer layer, as well as the conformational relaxation of the polymer chains [24].

Table 1. Electrochemical characteristics of the deposited polymers obtained in electrolyte solution free of monomer

Sample	E_a (V)	E_c (V)	ΔE (V)	Q_a/Q_c	G mol cm^{-2}
Pt electrode					
PT	0.82	0.42	0.4	0.48	3.9 E-8
PMT	0.64	0.53	0.11	0.5	4.1 E-8
POT	1.07	0.58	0.24	0.99	3.2 E-8
Ti electrode					
PMT	0.68	0.58	0.10	0.45	4.9 E-8
POT	1.24	1.01	1.23	0.93	2.2 E-8

According to the presented data related to the anodic and cathodic amount of charges, it could be seen that the ratios Q_a/Q_c are about 0.5 and are approximately the same for PT and PMT, while this ratio in POT receives higher value (0.99). This could be an indication that the reversibility of the redox processes is more clearly defined in POT. The lower intensity value of 0.5 could indicate that the reversibility is very limited, and that some conformational changes occur during the oxido-reduction processes [25].

The calculated concentrations of the active surface centers (G) given in Table 1 are derived using the equation $G=Q_{red}/zFS$, where Q_{red} is the charge passed during the reduction of the polymer, z is the number of electrons involved in the reduction of one redox center ($z=1$), F is the Faraday constant, and S is the surface area of the working electrode. It is obvious that G has lowest value in POT and highest value in PMT. The concentration of surface active centers in PT is between these two values.

Titanium electrode

The cyclic voltammetric curves, corresponding to the electrochemically deposited materials onto titanium electrodes in the same potential region like in platinum electrode, are presented in Figure 2.

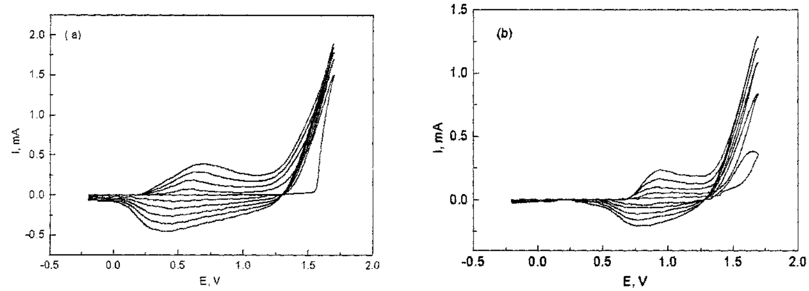

Figure 2. Cyclic voltammograms of potentiodynamic polymerization of **a)** methylthiophene **b)** octylthiophene v=100 mV s^{-1}, titanium electrode, the first five cycles are presented

Very similar in shape CV curves are seen when compared with the CV's for polymers deposited on Pt electrode. In must be pointed out that the oxido-reduction peaks are different, even though the electrodeposition was performed in the same potential region and the same monomer concentrations were used. PT is a material that could not be electrochemically deposited on bare titanium electrode. The electrochemical data corresponding to the titanium electrode obtained in electrolyte solution free of monomer are collected in Table 1. It could be noted that the oxidation potential in POT, grafted on titanium electrode, bears anodic shift (0.17 V compared to platinium electrode) that might be an indication of lower number of conjugated rings. Diaz et al. have shown that the reduction of the conjugation length from 10 to 5 thiophene rings causes an increase of the E_{pa} by about 0.18 V [26]. In PMT film, deposited on titanium electrode, the changes in oxido-reduction peaks are negligible. The FTIR spectra given below, could also support the hypothesis for the reduced number of conjugated rings in POT deposited on Ti electrode.

According to the estimated parameter G, this parameter does not change in PMT deposited on Ti electrode (G= 4.9 E-8 mol cm^{-2}, Ti electrode and 4.1 E-8 mol cm^{-2} Pt electrode). In POT film, deposited on Ti, changes in the G parameter are significant (3.2 E-8 mol cm^{-2}, Pt electrode and 2.2 E-8 mol cm^{-2} Ti electrode).

It could be concluded that the nature of the electrode material, as integral part of the electrochemical synthesis, plays a great role in the electrochemical behavior, especially in polymers with longer alkyl groups. The orientation of the polymer segments toward the surface of the electrode material might have a dominant role here. PMT segments probably take the same orientation when deposited on platinum and titanium electrodes, while POT probably takes different orientation on these two electrodes, producing different number of electroactive sites.

FTIR analysis

In order to analyze the influence of the substrate material on the quality of the polymer film, the presence of defects, the conjugation lengths and the degree of polymerization, FTIR spectra were taken from the neutral forms of the deposited polymer films. The characteristic FTIR spectra of the electrochemically deposited polymer films are given in Figure 3.

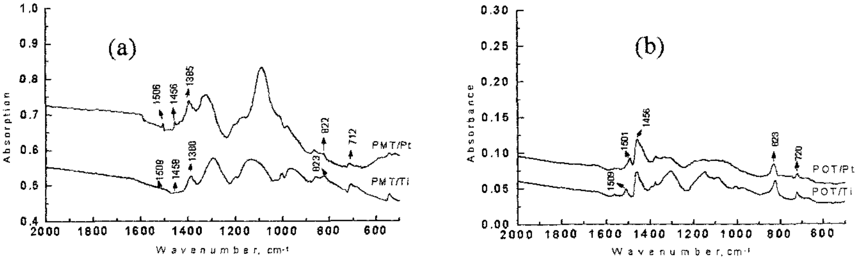

Figure 3. The FTIR spectra of polymethylthiophene **(a)**, polyoctylthiophene **(b)**

Table 2. Comparison of Infrared band positions (cm^{-1}) and their assignments for PMT and POT

Sample	electr.	arom C_β-H str	aliph C-H str	defects C=O	ring str	methyl def	arom C-H out-of-plane	2,4 links
PMT	Pt	3056	/	1643	1506 1456	1385	822	736
PMT	Ti	3056	/	1638	1509 1458	1380	823	734
POT	Pt	3055	2955 2923 2852	1638	1509 1458	1374	823	/
POT	Ti	3060	2954 2921 2850	1633	1490 1437	1377	821	/

Table 3. N_{dp}, N_c, $N_{C=O}$ features of the synthesized polymers

Sample	N_{dp}	N_c	(rings)	$N_{C=O}$
Pt electrode				
PMT	10.5	0.41	(> 6)	0.13
POT	9.45	1.31	(4-6)	/
Ti electrode				
PMT	8.11	0.46	(> 6)	0.1
POT	6.23	2.33	(3-4)	/

The principal absorption bands and their assignments are given in Table 2. The FTIR spectra for the two polymers deposited on Pt and Ti electrode are very similar. A slight shift of some of the absorption bands, and also some changes related to their intensities could be noticed.

The important spectral region for the symmetric and antisymmetric stretch C=C vibrations is between 1550 cm^{-1} and 1350 cm^{-1}. Following the previous analysis of the vibrational spectra of polythiophenes and their oligomers, the intensity ratio of symmetric to antisymmetric stretch band is indicative of the conjugation length in the polymer backbone [27]. The FTIR spectra of the PMT films deposited on platinum and titanium electrodes clearly show that the intensity ratios I_{sym}/I_{asym} have approximately the same values (0.41 and 0.46) that correspond to polymer chains containing more than six conjugated rings (Table 3).

In POT these ratios for both investigated electrodes have higher values, thus confirming presence of shorter conjugated segments (between 4 and 6 thiophene rings for a film deposited on Pt, and between 3 and 4 thiophene rings for a sample deposited on Ti), and are in close correlation with the presented CV's.

The degree of polymerization was estimated from the Furukawa et al. relationship:

$$N_{dp} = 2R_o/R + 2 \tag{1}$$

where R is a ratio of the integrated intensities of the two CH out of plane vibrations for monosubstituted and 2,5 disubstituted thiophenes, and R_o is a known value, derived for sexi-thiophenes [28]. The degrees of polymerization for both polymers are between 6.3 and 10.5, and are relatively lower when compared to those obtained for PT films electropolymerized in organic media [28]. The lower values are of course strongly dependent of the type of organic medium, but in our case we consider that the lower values are attributed to the more rigorous conditions of the electrochemical polymerization process. If we make a correlation between the number of conjugated thiophene rings and the degree of polymerization, such a correlation exists, but the longer conjugated segments not always mean a higher degree of polymerization.

The presence of C=O groups, attached to the thiophene ring, and the irregular 2,4 links between the monomer units, are usually assigned as defects of the polymer backbone. The occupied 3 rd position of the thiophene ring sometimes plays very preventive against formation of defects. In our previous paper [29], related to the chemically synthesized polythiophenes, it has been demonstrated that these defects are more pronounced in unsubstituted thiophene due to the free reactive sites in the 3rd position, while in polyalkylthiophenes these defects were negligible. Such a behavior is primarily a result of the steric reasons, and secondly of the substituted positions. Following this, the very slight presence of the absorption band, located at 740 cm^{-1} in PMT, could be explained by the fact that the 2,4 defects are possible in systems with shorter alkyl substituents. In POT the absorption band corresponding to the irregular 2,4 linking was missing. The presence of a band around 1630 cm^{-1} is characteristic for the C=O group. The intensity ratio of the C=O stretching mode, with respect to the intensity of the C-H out-of-plane bending mode, could give a rough measure of C=O defects in the polymer chain ($N_{C=O}$). According to the last $N_{c=o}$ parameter, the presence of C=O defects in these electrochemically deposited systems is negligible (Table 3).

Conclusions

Comparative investigation of the electrochemical behavior of two polyalkyl thiophene derivatives deposited on platinum and titanium electrodes was performed using CV and FTIR measurements. The following conclusions could be summarized:
In substituted polythiophenes with short alkyl group (CH_3), the nature of the electrode material does not have significant influence on the redox properties and characteristic parameters like the number of conjugated segments, degree of polymerization, and presence of defects. The electrode material has great influence on the redox properties and the quality of the polymer deposite in polyoctylthiophene, probably due to the different orientation of this system toward the electrode materials.
Due to the occupied 3'position of the thiophene ring in both investigated systems, the presence of 2,4 defects and C=O groups is very limited. The defects are more pronounced in polymers with short substituent (compared to polymers with long alkyl groups) mainly because of steric reasons.

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