



Electrosynthesis and comparative studies on carboxyl-functionalized polythiophene derivatives

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ABSTRACT

Electrochemical synthesis of a novel carboxylic acid functionalized polythiophene – poly(3-thiophene-butylric-acid), PTBA – has been realized. Its morphology, electrochemical, spectral and conducting properties have been compared to those of poly(3-thiophene-acetic-acid), PTAA, which is widely used to immobilise both bioactive molecules and inorganic nanoparticles. According to scanning electron microscopic (SEM) images, the difference in the real and geometric surface area of the modified electrodes is much more expressed in the case of PTBA. Both the symmetry of the cyclic voltammograms and the concurrent, sustained optical changes proved that this polymer possesses an improved and more stable redox activity. According to simultaneously performed *in situ* ac. impedance and UV–Vis measurements, both films could be uniformly transformed between the insulating and conducting forms, but PTAA exhibited some degradation. The development of the conducting state during the redox switching of both thiophene derivative polymers proved to be primarily connected to the formation of di-cationic species. The electrochemical quartz crystal microbalance (EQCM) results evidenced also differences between the two polymers, which difference can be interpreted by assuming the more expressed effect of the deprotonation-connected (self-) doping process in PTAA. The results confirm that the new conducting polymer, PTBA is much more convenient for being considered as the polymer matrix of practically applicable composites.

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1. Introduction

During the last two decades large-scale studies on conjugated polymers have been revealed their attractive properties, which can be utilized in numerous practical applications [1]. The most specific character of these materials is their electronic conductance, which makes them suitable to work as “organic” electrodes. Electronically conducting polymers offer perspectives in sensor applications either as the sensitive components or as matrices for immobilisation of specific substrates. From the wide sort of hybrids, the most intensively studied class of novel materials are the (i) biomolecule containing composites [2], and the (ii) polymer based nanocomposites, incorporating functional inorganic nanoparticles [3].

The possibility of using conjugated polymers for immobilising bioactive compounds in biosensors has been discovered already two decades ago [4]. In polymer based enzymatic biosensors the enzyme molecules are fixed in a polymer matrix, and the composite layer may function as an enzymatic electrode. The majority

of research studies on enzymatic biosensors gave account on the inclusion of glucose oxidase in polypyrrole or polyaniline for the determination of glucose concentration in blood, but fixation of other enzymes also been successfully realised [5–8]. The immobilisation has been performed [9–15] by applying different techniques such as adsorption and/or entrapment into polymer films or through their chemical bonding to the chain. Electropolymerization of a vitamin B12 bearing pyrrole derivative has been performed some years ago [16], although the presence of the bulky biomaterial restrained the formation of a well-conjugated polymer.

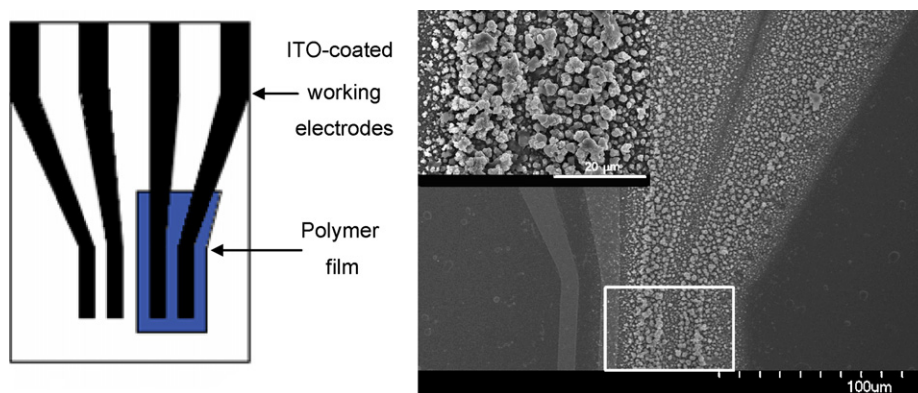
However, it is indisputable that chemical bond results a much more stable composite, which is much more resistant to bleaching. The other way to achieve this goal is when conducting films possess functional groups, and bonding of the targeted molecule or nanoparticle is achieved chemically before, during or after the polymerization. Different studies reported on the successful incorporation of nanosized iron-oxides such as magnetite (Fe₃O₄) [17,18] and titanium-dioxide (TiO₂) [19] into functionalized conjugated polymers.

From this point of view, carboxylate functional group bearing polymers are of prime importance, as they are able to create covalent bonds with both biologically active materials and inorganic nanoparticles. The electrochemical polymerization of 3-thiophene-

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Scheme 1. Schematic and scanning electron microscopic view of the PTAA coated special ITO electrode.

acetic-acid (TAA) and its co-polymers have been intensively studied with the aim to synthesize electroactive films [20–24]. The malonic acid thiophene derivative has been also polymerised very recently [25]. In spite of the successful realization of conducting films, there seems to be a restriction in connection with the length of the alkyl chain of the $-\text{COOH}$: acetyl group – being too short – may block the properly positioned embarking of the reactant. It can be predicted that even the polymerization of $-\text{COOH}$ substituted monomers is hindered, if the alkyl chain of the substituent is not long enough to insure the necessary flexibility during the chain propagation steps.

For this reason our aim was to study the electrochemical polymerization of two carbonic acid substituted thiophenes – TAA and 3-thiophene-butyric acid (TBA) – and to compare their polymers under exactly identical circumstances with the expectation that the longer alkyl chain between the hetero-aromatic unit and the carboxylate functional group in the case of PTBA makes possible an easier synthesis, and endows the layer with both a more extent and more stable redox activity that can be evidenced from the electrochemical and spectral behaviours.

2. Experimental

2.1. Materials

3-Thiophene-butyric-acid (TBA) (Rieke Metals Inc.) was used as received, 3-thiophene-acetic-acid (TAA) (Fluka), tetrabutylammonium tetrafluoroborate, Bu_4NBF_4 (Fluka), was dried at 60°C , in vacuum. Nitrobenzene, NB (Sigma–Aldrich) and acetonitrile, AN (Sigma–Aldrich) was dried by activated molecular sieves (Sigma–Aldrich, 3 Å). The water content of the solutions was controlled by coulometric Karl Fisher titration (Metrohm 684), and it was kept below 30 ppm.

2.2. Methods

All electrochemical measurements were performed on a PGSTAT 302 (Autolab) instrument, in a classical three-electrode electrochemical cell. The reference electrode was a $\text{Ag}/\text{AgCl}/3\text{ mol dm}^{-3}\text{ NaCl}$ electrode, having a potential 0.200 V vs. SHE, the counter electrode was a rectangular Pt in all cases. *In situ* UV–Vis–NIR spectroscopic measurements were carried out by using an Agilent 8453 UV–visible diode array spectrophotometer in the range of 380–1100 nm. The data obtained from ac impedance measurements at 130 Hz were analyzed by a lock-in amplifier (SR 830).

During basic electrochemical and spectro-electrochemical studies of the polymeric films the working electrode was a Au electrode ($A=0.0314\text{ cm}^2$), or an ITO-coated glass electrode (PGO, $A=0.70\text{ cm}^2$) respectively. The films were deposited galvanostatically

at $j=3\text{ mA cm}^{-2}$ with 100 mC cm^{-2} charge density in both cases.

Simultaneous ac impedance and *in situ* UV–Vis–NIR spectroscopic measurements were performed at an ITO-coated glass electrode (IAME, Abtech), consisting of four $10\text{ }\mu\text{m}$ wide and 3 mm long needles, forming gaps of $10\text{ }\mu\text{m}$ width between neighbouring electrode parts, of which two were used as the working electrode at once. When the polymer layer is forming on the ITO needle-shaped electrode, the film can grow over the gap, forming electrical contact between the parts, so that conductance can be measured [26]. This arrangement can be seen in Scheme 1, where the PTAA coated printed circuit electrode – covering partially the gap between two branches – is shown. PTAA and PTBA films were deposited potentiostatically at $E_{\text{PTAA}}=+2.5\text{ V}$ and $E_{\text{PTBA}}=+2.3\text{ V}$ potential from $0.1\text{ mol dm}^{-3}\text{ TAA}/0.1\text{ mol dm}^{-3}\text{ TBA}$ and $0.1\text{ mol dm}^{-3}\text{ Bu}_4\text{NBF}_4$ containing solution, in anhydrous NB.

EQCM measurements have been carried out by using a quartz crystal resonator and analyser EQCM type 5510 (Poland). The crystals ($f_0=10\text{ MHz}$) were gold coated, and had an overall diameter of 14.0 mm , while the piezoelectrically active area (identical with the geometric area) of the Au working electrode was 0.196 cm^2 . The EQCM system was calibrated by electrochemical silver deposition, using the standard procedure, and the value of -0.86 ng Hz^{-1} calibration constant was obtained.

Scanning electron microscopic (SEM) images (Hitachi S-4700 Field Emission Scanning Electron Microscope) were taken for the polymeric films deposited onto Au electrodes in order to investigate the morphology of the samples.

3. Results and discussion

3.1. Electropolymerization of TAA and TBA

In the first experiments, we synthesized both polymers galvanostatically with 3 mA cm^{-2} current density under identical conditions. The chrono-potentiometric curves are presented in Fig. 1 for the two polymers both on Au and ITO electrode. The figure demonstrates that, although the shape of the curves are very similar, the PTBA films could be deposited at lower potentials, than the PTAA films on both electrodes. The effect of the larger surface resistance of ITO can also be recognized.

3.2. Morphology of the polymeric layers

In order to study the morphology of the electrodeposited conducting polymer layers we have taken SEM images at different magnifications.

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