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Electrochemical overoxidation of poly(3,4-ethylenedioxythiophene)—PEDOT studied by means of in situ ESR spectroelectrochemistry

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Abstract

Electrochemical doping and dedoping processes in poly(3,4-ethylenedioxythiophene)—PEDOT have been studied by in situ ESR spectroelectrochemistry with an aim to investigate the behaviour of charge carrying species, generated and annihilated in these processes, with changing potential. As an extension of earlier studies, we investigated the behaviour of PEDOT at high oxidation potentials, beyond the limit of electrochemical stability of the polymer located at ca. 1.6 V. Past this limit, a sudden and irreversible drop in the concentration of spins together with narrowing of the ESR signal is observed. Changes in the spectroscopic response of the film are irreversible as evidenced by the course of the subsequent reduction process, which by no means resembles the reduction process of the polymer recorded within the potential window in which the polymer is stable. Supplemented by results of electrochemical studies, it is concluded that direct overoxidation of the polymer chain most probably leads to a decrease in the conjugation length of the polymer's delocalised π-bond, through cross-linking of the polymer chains. Consequently, the remaining spins become trapped in isolated packets where they behave more like oligomer type radicals.

Keywords: Charge carriers; PEDOT; ESR spectroscopy; Overoxidation; Polymer films

1. Introduction

Since the development of poly(3,4-ethylenedioxythiophene)—PEDOT in the late 1980s by scientists at Bayer A.G. [1], this polymer to date received an ever-accelerating scientific interest of scientists throughout the world. Today PEDOT is being investigated in a many research fields starting from basic polymer science [2] through material science [3], electrochemistry [4], electronics [5] and optoelectronics [6–8], photovoltaics [9–11], corrosion protection [12], novel cell systems [13] down to biosensors [14] as one of future prospects. The reasons for such widespread interest are its much sought for properties like high conductivity, interesting electrical and spectrochemical properties associated with its low band gap, electrochromic and antistatic properties and good stability all of which paved this polymer way into numerous important applications [15,16]. These properties originate from the high regularity of the polymer backbone, which are purely α–α′ coupled, thanks to the blocking of unfavourable β positions by the cyclic 3,4-dioxy substituent. The two oxygen atoms bonded directly to the thiophene backbone enrich the conjugated π-bond with electrons, lowering the oxidation potential of the polymer, while the cyclic character of the ethylenedioxy substituent curbs the disorder that otherwise linear side groups could introduce into the polymer structure. A review of the state of development of PEDOT's chemistry and contemporary applications together with a rich list of references has been given by Groenendaal et al. [3].

The electronic properties of a conductive polymer can be altered through doping. Nowadays it is widely accepted that depending upon the doping level two different charge carrying species can prevail i.e., polarons and bipolarons both of which can propagate the electrical current along the polymer chain [17–19]. Polarons carry a magnetic moment and can therefore be observed and distinguished from diamagnetic bipolarons by means of ESR spectroscopy. Their spectroscopic response is sensitive however to the chemical environment they reside in and since bipolarons constitute a

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part of that environment, the spectroscopic response of polarons will be influenced by the presence of bipolarons as well as any other paramagnetic species in the polymer material. This influence will be evident not only at high doping levels where polarons become oxidised to bipolarons but also at intermediate doping levels where both species coexist together [20]. The influence of the doping level on such properties of PEDOT as conductivity and carrier mobility has been already studied [21]. Recently our group has published results on the ESR spectroelectrochemical studies of PEDOT during doping and subsequent dedoping [22,23]. These results revealed some interesting information about the behaviour of paramagnetic species during these processes like the hysteresis of the potential dependence of concentration of spins, strong interactions between polarons at intermediate doping levels and the presence of an ESR signal in the dedoped polymer. Some of these features of PEDOT have been already observed by Kvarnström et al. by means of in situ IR and EQCM [24].

One of the features of PEDOT is its extraordinary stability towards different ageing factors both physical and chemical. One of the first stability studies of PEDOT concerned its thermal stability with respect to such properties as conductivity [16,25,26]. It was found that PEDOT could withstand temperatures just above 100 °C, without notable loss of conductivity for considerable lengths of time. Rannou and Nechtschein have studied the kinetics of conductivity decay at higher temperatures [27], while Winter et al. have studied the structural changes taking place in PEDOT upon its thermal treatment [28]. When the electrochemical approach towards synthesis of PEDOT has been applied, investigations of electrochemical stability of this polymer have also been initiated. Studies of PEDOT and other thiophene polymers in such ‘extended’ potential windows past the potential of electrochemical stability of the polymer have been reported in several papers throughout the last years. Heinze and co-workers reported that overoxidation of PEDOT up to 3.0 V leads to evolution of a strong double and irreversible oxidation peak [29]. Such treatment led to inactivation of electrochemical properties of the material. Kvarnström et al. have evaluated the onset of degradation potential at 1.9 V [24]. Comparing this value with a boundary at ca. 1.4 V for other polythiophenes [30] it can be seen that PEDOT is indeed an electrochemically stable material. The effect of high oxidation potentials on other properties of PEDOT has also been investigated. Lapkowski and Pron have demonstrated a finite potential window of conductivity of PEDOT [31], while Du and Wang have reported in a recent study the effect of polymerisation potential on PEDOT’s conductivity and ESR response [32]. Also recently, a detailed study of electrochemical dissolution of polythiophene has been presented by Aoki and co-workers [33]. Their work gives some insight into the degradation mechanisms that could be involved in the degradation of an electroactive polymer such as PTh upon its overoxidation. The course of the degradation of polythiophene main chain studied through identification of its fragmentation products may be an indication as to what happens to the main polymer chain of PEDOT upon its electrochemical degradation. Since to date there have been no reports concerning the intrinsic behaviour of charge carriers at high oxidation potentials, we decided to take a more detailed look at the ESR spectroscopic behaviour of PEDOT at potentials past the stability boundary. Our aim was see if the spectroscopy results of PEDOT’s overoxidation studies can add anything or better still provide new evidence to help elucidate the degradation mechanism of this polymer.

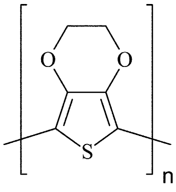
We are aware that the degradation process is a very complex one, being a sum of several parallel reactions and depends on numerous variables, some of which may be elusive and immeasurable and thus difficult to reproduce. Therefore any conclusions have to be taken cautiously as they may only apply to degradation conditions studied. Nevertheless, knowledge of the behaviour of charge carriers beyond normal application regimes is necessary not only for a complete characterisation of the redox properties of the material but may also shed some light on the changes taking place in the polymer matrix at these extreme conditions.

2. Experimental

2.1. Electrochemistry

Cyclic voltammetry experiments and measurements were done on AUTOLAB model PGSTAT20 potentiostat–galvanostat (EcoChemie, Netherlands) under the control of a PC class computer. The following electrodes were used: platinum wire (Ø = 1 mm) sealed using Teflon^{TM} tape leaving a geometric area of ca. 0.10 cm^2 was used as working electrode. Ag wire was used as a quasireference electrode. Platinum coil wound around the two electrodes served as an auxiliary electrode. All potentials are given versus the Ag quasireference electrode used. By measurement of the potential of ferrocene couple versus this electrode, its potential was estimated at +0.6 V versus SCE.

Poly(3,4-ethylenedioxythiophene) (PEDOT) was synthesised through electropolymerisation on platinum electrode from 0.01 M solution of monomer in 0.1 M $(Bu)_4NPF_6$ in CH_3CN. Cyclic voltammetry was employed with additional control of maximum oxidation current of the monomer. For a given electrode area, the current value at which the oxidation half-cycle was reversed, did not exceed 4.0×10^{-4} A. Thanks to such optimised procedure we were able to synthesise polymer films having similar CV responses each time.



poly(3,4-ethylenedioxythiophene)
PEDOT