



# The effect of cycling on the nanoscale morphology and redox properties of poly[2,2'-bithiophene]

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## ABSTRACT

The changes in the redox behavior and nanoscale morphology of poly[2,2'-bithiophene] deposited onto highly oriented pyrolytic graphite substrates upon repeated doping–undoping were studied. It was shown that repeated cycling resulted in very particular changes in the voltammetric response of the polymer films as well as their nanoscale morphology. Specifically, when the cycling was performed to relatively low anodic potentials, the overall doping–undoping charge did not change; however, the shape of voltammograms was consistently changing showing broadening of the voltammograms and reducing of the doping peak height in the anodic scan, as well as broadening and deterioration of the undoping peak in the reverse scan. Furthermore, a remarkable feature was observed that all voltammogram traces intersected at several characteristic potentials producing quasi-isosbestic points. With an increase in the anodic scan potential limit, the overall doping–undoping charge starts to decrease showing irreversible degradation of the polymer; however, the general pattern of the peak broadening could be still observed. Atomic force microscopic (AFM) studies of the polymer films cycled to various anodic limits showed that repeated cycling resulted in a gradual decrease in the degree of crystallinity, as revealed by AFM phase imaging, and an increase in the degree of disorder. Coupled with the changes in the redox behavior, these findings suggested the formation of more flexible and open polymer nanostructure that enables easier penetration of the dopant ions and solvent. However, at the same time, an increase in the degree of disorder reduced the interchain interactions and inhibited the formation of extended electronic states delocalized across neighboring polymer chains. This occurred at first without irreversible degradation of the polymer and a decrease in the overall doping–undoping charge. Cycling to higher anodic potentials resulted in irreversible degradation accompanied by profound changes in the polymer morphology.

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## 1. Introduction

The problem of degradation and stability of organic electron conducting polymers due to their overoxidation in solution has been addressed repeatedly in the literature [1–7]. At the same time, much less attention has been paid to the morphological changes that occur in polymer films during repeated doping–undoping cycles, beyond the well documented swelling–deswelling of the polymer films due to uptake and release of the solvent [8–12]. In most cases, the analysis concerned either the changes due to overoxidation, or the so-called memory effect (the difference in the position and height of the principal doping peak in the first and subsequent doping cycles, see, e.g., a recent review [13]). A number of other papers [7,14–17] did analyze the evolution of

the voltammetric responses with cycling but, unfortunately, presented no or very little microscopic and structural data, which made it more difficult to understand the observed changes in the redox behavior. Furthermore, such studies were limited almost exclusively to polypyrrole. In our recent paper [18], we have demonstrated that variations in the nanostructure of the poly[2,2'-bithiophene] (PBT) films obtained using different polymerization methods gave rise to significant differences in their charge storage capacity and stability toward repeated redox cycling. In this work, we analyze in detail the evolution in the redox responses of the polymer films upon repeated doping–undoping and demonstrate that these changes correlate well with the evolution in the nanoscale morphology of the polymer films observed by atomic force microscopy (AFM) and its extension, AFM phase imaging (PI-AFM). Taken together, our data support our earlier findings [18] that degradation of the polymer films and a decrease in their redox activity and charge storage capacity may be related to nanoscale structural factors rather than simple overoxidation of the polymer material.

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## 2. Experimental

### 2.1. Preparation of polymer samples

Poly[2,2'-bithiophene] (PBT) samples were prepared by galvanostatic electropolymerization. The electropolymerization was performed using a specially designed three-electrode Teflon cell mounted on top of the HOPG working electrode (the electrode surface area exposed to the solution was  $0.28 \text{ cm}^2$ ). The substrate in all cases was highly oriented pyrolytic graphite (HOPG) (NTMDT, ZYB quality). Silver and platinum wires were used as pseudo-reference and counter electrodes, respectively. The potential of such a pseudo-reference electrode was controlled using the  $\text{Fc}/\text{Fc}^+$  standard and was found to be  $+0.05 \text{ V}$  vs. SCE. All potentials are given in the text with respect to this pseudo-reference electrode. To improve stability and consistency, between measurements the reference electrode was stored in a solution of supporting electrolyte of the same concentration as during measurements.

The electropolymerization solution was a  $0.005 \text{ M}$  solution of 2,2'-bithiophene in acetonitrile containing  $0.1 \text{ M}$  tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) as a supporting electrolyte. 2,2'-Bithiophene (Aldrich) was purified through vacuum sublimation and tetrabutylammonium hexafluorophosphate (Aldrich, 98% purity) was used as received. Acetonitrile was purified using an in-house SPS-400-5 solvent purification system (Innovative Technology) using columns packed with activated alumina and copper catalysts. The water content was less than  $10 \text{ ppm}$ . A Princeton Applied Research (PAR) Model 263A potentiostat/galvanostat controlled with version 2.8 Corrware/Corrview electrochemistry software (Scribner) was utilized. The monomer and supporting electrolyte salt were stored in vacuum desiccators over silica gel to prevent moisture accumulation.

All samples were prepared under galvanostatic conditions at a current density of  $1 \text{ mA cm}^{-2}$  for  $50 \text{ s}$ . After the deposition, the PBT films were reduced in the synthesis solution at a potential of  $0.0 \text{ V}$  for  $100 \text{ s}$  in order to convert them into a neutral/undoped state. The samples were then rinsed three times with pure acetonitrile. After rinsing, the synthesis solution was replaced with a solution of  $\text{TBAPF}_6$  in acetonitrile without the monomer. The samples were then subjected to 50 or 100 doping and undoping cycles at a scan rate of  $100 \text{ mV s}^{-1}$  from  $0.0 \text{ V}$  to specific anodic potential limits chosen for each sample; however, the CVs presented in this paper were only recorded after every 5 cycles. These potential limits were:  $1.3 \text{ V}$ ,  $1.4 \text{ V}$ ,  $1.45 \text{ V}$  and  $1.5 \text{ V}$ . As control, several cyclic voltammograms were also recorded for other scan rates and the peak currents showed good linear dependence on the scan rate. After cycling, the samples were rinsed again three times with pure acetonitrile and dried in a vacuum desiccator at room temperature for at least 3 days to prevent the effect of residual solvent on the AFM measurements. In addition to the cycled samples, non-cycled, as-prepared PBT samples were also made under the same conditions and characterized as control. Therefore, whereas drying may have changed slightly the morphology and other properties of the films as characterized by cyclic voltammetry, we could still compare correctly the effect of cycling on the nanoscale morphology of the films. The thicknesses of all films presented in this work were determined to be ca.  $90 \text{ nm}$  using AFM as described below.

The cyclic voltammograms and AFM images presented in this paper are typical ones selected from at least three independently prepared samples and in the case of the AFM images, also from at least three different areas of the sample.

### 2.2. AFM measurements of films on HOPG

The atomic force microscopy (AFM) images were obtained under ambient conditions using a Multimode atomic force microscope

(Veeco Metrology) equipped with a Nanoscope IV controller (Veeco). The phase imaging measurements were performed in the tapping mode using Pointprobe n-doped Si probes (Nanoworld, force constant  $20 \text{ N/m}$ , resonant frequency  $300 \text{ kHz}$ ). In this configuration, more positive phase values correspond to more dense/crystalline regions of the polymer. The topography images presented in the paper were subjected to manual first-order plane fit and the phase images were offset. The thicknesses of all deposited films were determined directly using AFM by selectively removing a portion of the film with a contact AFM probe (DDESP, Nanoworld, force constant  $40 \text{ N/m}$ ) by repeated scanning with high force reference over a certain area until the substrate surface is reached. The size of the area was typically several  $\mu\text{m}^2$  and was selected to be much greater than the size of typical polymer morphological features. The film thickness was then determined from corresponding topography cross-sections measured over areas with and without the polymer. The procedure was repeated several times at different areas of the sample and an average value was calculated. The thickness values determined in this way at different areas of the sample typically did not differ by more than several nanometers indicating that the films were quite uniform. For instance, the results of such measurements at different areas for one of the films were  $90 \text{ nm}$ ,  $92 \text{ nm}$ ,  $97 \text{ nm}$ ,  $94 \text{ nm}$ ,  $93 \text{ nm}$ ,  $90 \text{ nm}$ , which gives an average value of  $93 \pm 3 \text{ nm}$  (confidence level 95%).

## 3. Results

### 3.1. Changes in the redox behavior of PBT films in the course of potential cycling

Fig. 1a–d shows representative cyclic voltammograms of PBT films of the same thickness deposited onto the surface of a HOPG electrode. The films were subjected to 50 doping and undoping cycles to anodic potentials limits of (a)  $1.3 \text{ V}$ , (b)  $1.4 \text{ V}$ , (c)  $1.45 \text{ V}$ , and (d)  $1.5 \text{ V}$ . The CVs were recorded after every fifth cycle during the scanning process.

One can see that all CVs show a remarkable feature that all voltammogram traces intersect around several specific points, which we will call quasi-isosbestic points, by analogy with the isosbestic points defined in molecular spectroscopy [19]. Specifically, we can define the following quasi-isosbestic points in Fig. 1a–d:

- Fig. 1a: two quasi-isosbestic points are observed on the reverse scan denoted as “B” at ca.  $0.8 \text{ V}$  and “C” at ca.  $0.6 \text{ V}$ . There is an indication of an isosbestic point on the direct scan around  $1.25 \text{ V}$ ; however, it is not well pronounced due to its closeness to the anodic scan limit.
- Fig. 1b: three well pronounced quasi-isosbestic points are observed at potentials of ca.  $1.1 \text{ V}$  (“A”, direct scan), ca.  $0.75 \text{ V}$  (“B”, reverse scan) and ca.  $0.55 \text{ V}$  (“C”, reverse scan). However, the quasi-isosbestic point “B” occurs only for the first 20 cycles (see Fig. 1b inset).
- Fig. 1c: the isosbestic point at ca.  $0.8 \text{ V}$  on the reverse scan is no longer observed; however, the isosbestic points “A” on the direct scan at a potential of ca.  $1.1 \text{ V}$  and “C” on the reverse scan at ca.  $0.55 \text{ V}$  are still well pronounced. We still denote the potential of  $0.75 \text{ V}$  as a special point “B” for the sake of discussion.
- Fig. 1d: the quasi-isosbestic points “A” and “C” are still seen but their position now change slightly from  $1.1 \text{ V}$  to ca.  $1.0 \text{ V}$  and from  $0.55 \text{ V}$  to ca.  $0.5 \text{ V}$ , respectively. Again, as in Fig. 1c, we retain a special point “B” at  $0.75 \text{ V}$  for the sake of discussion.

Generally, by analogy with molecular spectroscopy, the occurrence of an isosbestic point on a cyclic voltammogram should

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