Electrochemically Induced Volume Changes in Poly(3,4-ethylenedioxythiophene)

Xiwen Chen, Ke-Zhao Xing, and Olle Inganäs*

Department of Physics (IFM), Linköping University, S-581 83 Linköping, Sweden

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The electrochemical properties of poly(3,4-ethylenedioxythiophene) are studied using the bending beam method to detect volume changes during electrochemical transformations of the material. Thin films of poly(3,4-ethylenedioxythiophene) immersed in different supporting electrolytes first contract very rapidly and then expand on doping, while upon undoping they contract directly, or first expand and then contract, to their original positions. It is clearly observed that the oxidation or reduction of the polymer contains two steps, one due to a redox potential close to −0.5 V vs Ag/AgCl, and another potential around 0 V. We find that the volume changes cannot be understood as a simple consequence of ion transport but must be due to the structural change of the polymer between the different states. A hypothetical picture is that during the transition from the neutral to the polaron state, the polymer is slightly charged and thus contracted; on further doping to the bipolaron and to the metallic state, the coulomb repulsion between charged sites become stronger, and the polymer expands.

Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) is a new conducting polymer with high conductivity but also with high electrochemical and thermal stability.[1] Because of its very low bandgap around 1.5 eV,[1a] doping will move this absorption into the NIR region and make the polymer more transparent. PEDOT may therefore be used as a transparent electrode for electrochromic window.[2] The attractive electrical properties render it useful for metallization of insulator,[3] as antistatic packaging materials,[1e] and as a transparency anode in polymer light-emitting diodes.[4]

The electrochemical properties of alkoxy-substituted polythiophenes has been studied and are known to be complex.[5] A remarkable shift of the oxidation processes, compared to the parent polymer polythiophene, by more than 0.3 V to the cathodic side was observed,[6] and usually it was found that a broad main oxidation peak and a prepeak or a shoulder in the cyclic voltammetry,[1a,7] whose origin is still not completely clear.[8,9]

We know that a volume change usually occurs in conducting conjugated polymers during redox processes.[10] The bending beam method (BBM) has been shown to be an effective and sensitive method for detecting small volume changes in the active layer of bilayers,[11] where the active layer is a conjugated polymer. By this method it has been found that the

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volume changes in some conducting polymers are controlled by ion transport in the polymer matrix. As a sequel to ion injection or extraction, polymer chains slowly rearrange, a process that may explain the slow relaxation phenomena observed in conjugated polymer electrochemistry. The volume changes during these processes are on the order of a few percent, and ion transport through the material defines the rate of volume change. This bending method has also been developed into microdevices. Scaling down the geometry to build micromuscles, thin-film microelectrochemical mechanical devices on the 10−100 μm scale, give fast actuators. This technological approach allows the construction of self-assembling boxes of 30 μm dimension.[12]

However, the volume change in conducting polymers upon doping changes is not fully understood. Other bilayer structures have also been reported by other groups.[13] As an example, bending beam bilayers made of polyaniline/polyimide showed expansion from leucoemeraldine salt (LS) state to emeraldine salts (ES) state but contraction first and then expansion from ES to pernigraniline salt (PS).[13a]

We have sought to clarify the ion transport in PEDOT using the bending beam method, but we found that the volume changes in PEDOT is caused not only by ion migration. The other mechanism that could account for the volume change in PEDOT we label a structural transition induced by the doping/undoping process. If this mechanism is present also in other polymers, like the previously studied polypyrrole, revisions of the earlier conclusion from those studies may become necessary.

Experimental Section

Au/PE strips were prepared by coating polyethylene (LDPE, Neste DFDS-6430) films of 150 μm thickness with a 0.2 μm thickness gold layer by vacuum evaporation. A very thin chromium interlayer was used for better adhesion between the gold layer and the polyethylene substrate.[11] PEDOT was deposited onto the gold layer. The electropolymerization was conducted in the standard one-compartment three-electrode cell with a Pt foil counter electrode and a Ag/AgCl reference electrode. The polymerization potential was chosen between 1.0 and 1.2 V vs Ag/AgCl reference electrode (all potentials below are related to Ag/AgCl) so that the polymer can be deposited onto the substrate. It was also reported that low polymerization potential made polymer film adhesive.[14] A charge of 1.3 C/cm^2 was consumed for the polymerization, corresponding to a thickness of 10 μm. The thicknesses are confirmed by a Sloan Dektak 3030 surface profiler.

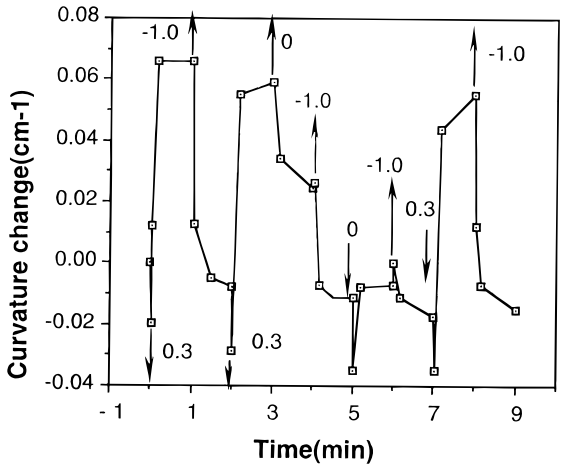

Figure 1. Curvature changes of PEDOT−$LiClO_4$(MeCN)/Au/PE strip under pulsed potentials in 0.1 M $LiClO_4$/MeCN solution, the numbers inside the figure indicate the applied potential (volt).

Chemically polymerized PEDOT was synthesized from 3,4-ethylenedioxythiophene and iron(III) tris-*p*-toluenesulfonate in *n*-butanol at 110 °C according to the literature method.[3] The resultant PEDOT film has a conductivity of ~300 S cm^{-1}. XPS results show that no iron can be detected, and according to the sulfur photoelectron spectroscopy the tosylate content is around 26%. X-ray powder diffraction shows that the material is partially crystalline. The films were formed on the gold surface of Au/PE bilayers for BBM(the thickness is around 10 μm).

Bending tests were conducted in a shallow cell equipped with a Ag/AgCl reference electrode and a Pt foil counter electrode. A bilayer was used as working electrode. A CCD camera was fixed above the cell to record the deflection of free end during the electrochemical redox of the PEDOT layer. Data were collected from a monitor screen to calculate the curvature change of the strips. This curvature change is directly related to the volume change in the active PEDOT layer. A curvature increase refers to volume swelling in the PEDOT layer. This experiment is run at room temperature.

XPS were performed in an instrument of custom design and construction with a UHV (<10^{-10} mbar). An unmonochromatized Mg Kα as XPS photon source. Its resolution, as determined from the width of the Au(4f7/2) line, is 0.9 eV.

Results

The BBM studies in different electrolytes and with PEDOT layers of different origins are reported below. We also report on the elemental composition of PEDOT after electrochemical reduction as studied by photoelectron spectroscopy.

1. PEDOT−$LiClO_4$/MeCN in 0.1 M $LiClO_4$/MeCN or in 0.1 M $LiClO_4/H_2O$. The change of curvature of a PEDOT film, electropolymerized in $LiClO_4$ acetonitrile (MeCN) solution, and characterized in monomer-free solution during doping and undoping, is shown in Figure 1. After equilibration at −1.0 V, doping is done at higher potentials. During doping at 0.3 V, the PEDOT film first contracts very rapidly, and then expands. If the doping potential is lowered to 0.0 V, then the film first contracts as much as at 0.3 V, but the subsequent expansion is much smaller than at 0.3 V. The same behavior is observed in 0.1 M $LiClO_4$ aqueous solution (Figure 2). If the doping potential is lowered to −0.3 V, the polymer mainly displays contraction, followed by an almost negligible expansion. Each undoping process returns the bending beam back, almost to the original

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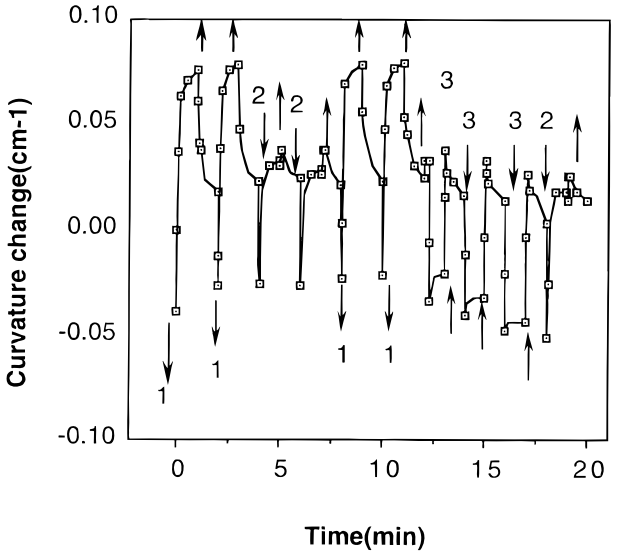

Figure 2. Curvature changes of PEDOT−$LiClO_4$(MeCN)/Au/PE strip under pulsed potentials in 0.1 M $LiClO_4$ aqueous solution. 1, 0.3 V; 2, 0.0 V; 3, −0.3 V; the up arrows indicate −1.0 V.

position. For the undoping process (Figure 1), it can be seen that the film contracts during undoping at −1.0 V. If the undoping potential is 0.0 V, the film also contracts, but it can be further undoped at −1.0 V. It is interesting that a very rapid expansion, followed by contraction to the original position, occurs in this case. This is more clear when undoping at −1.0 V, after doping at 0.0 V. The film first expands and then contracts. It appears that there are two steps: the first corresponding to a potential region between −1.0 and ≈−0.3 V, and the second above −0.3 V. Upon doping, the polymer contracts in the first step; in the second step the polymer expands. To estimate the corresponding volume changes for the two steps, we used the formula given by Pei and Inganäs,[11a] assuming that the polymer has a similar modulus. The doping induced volume changes of contraction and expansion in Figure 1 are −0.07% and 0.32%, respectively, from the curvature changes of −0.02 and 0.09 cm^{-1}.

2. PEDOT−Et_4NClO_4/MeCN in Et_4NClO_4/MeCN and in 0.1 M $BaCl_2$ Aqueous Solution. PEDOT films electropolymerized in Et_4NClO_4/MeCN after equilibration at −1.0 V first contracts and then expands upon doping in monomer-free solution (Figure 3). This is similar to the case of PEDOT−$LiClO_4$/MeCN. To observe the effect of cation size, we choose an aqueous solution, so that we can choose the big and divalent cation Ba^{2+}. This is to see if the initial contraction during doping is caused by cation diffusion out of the polymer. In 0.1 M $BaCl_2$ aqueous solution (Figure 4), it contracts at low doping potential, as low as −0.5 V, and then expands on further doping at higher potential.

3. PEDOT−PSSNa(aq) Film in PSSNa Aqueous Solution. Using poly(sodium styrene sulfonate) (PSSNa) as electrolytes for polymerization in aqueous solution, the resulting PEDOT should have an immobile anion and cations will exchange to keep the polymer neutral during the redox process. There is no way of transporting the PSS anions included with the PEDOT film or to inject more PSS polymer anions from the liquid electrolyte into the polymer electrode; therefore,

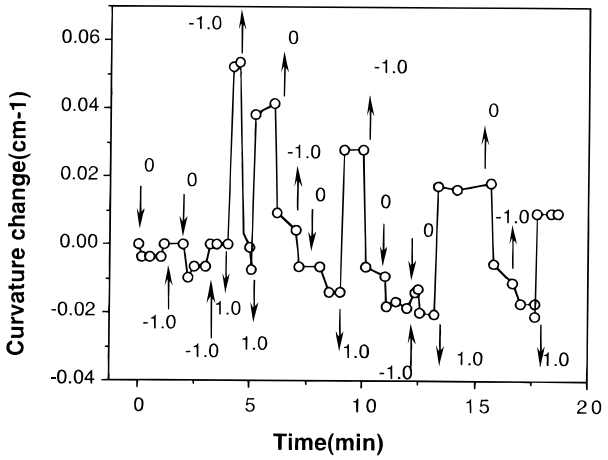

Figure 3. Curvature changes of PEDOT−Et_4NClO_4 (MeCN)/Au/PE strip under pulsed potentials in 0.1 M Et_4NClO_4/MeCN solution; the numbers inside indicate the applied potential (volt).

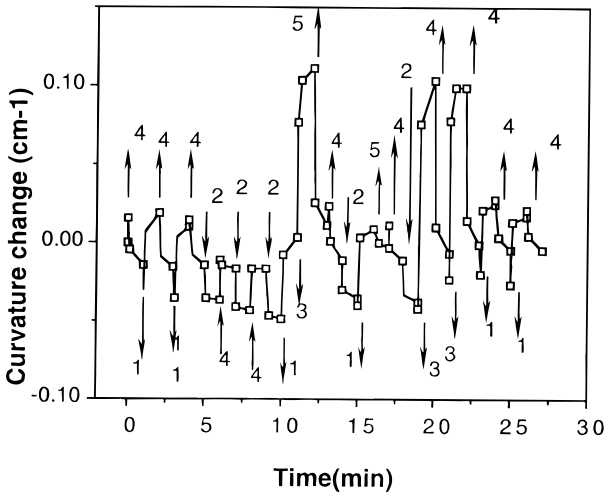

Figure 4. Curvature changes of PEDOT−Et_4NClO_4 (MeCN)/Au/PE strip under pulsed potentials in 0.1 M $BaCl_2$ aqueous solution. 1, 0.0 V; 2, −0.5 V; 3, 0.5 V; 4, −1.0 V; 5, −0.5 V.

all ionic transport should be due to cations. In 0.01 M PSSNa aqueous solution we can see that doping at lower potentials causes contraction of the PEDOT−PSSNa film, while at a high potential first contraction, and then a small expansion occurs (Figure 5). In 0.1 M $NaClO_4$ aqueous solution we observe a similar behavior. In the polymer complex PEDOT−(polymer anion), expansion during doping is much smaller than with PEDOT−(small anion).

4. cPEDOT(TsO) in 0.1 M $NaClO_4$(aq) and 0.1 M PSSNa(aq). In 0.1 M $NaClO_4$ aqueous solution (Figure 6) or in 0.1 M PSSNa aqueous solution, chemically polymerized cPEDOT films after equilibration at −1.0 V also first contract and then expand on doping. In this bulky polyanion electrolyte the expansion in the second step is also suppressed.

5. XPS Characterization of PEDOT Film at Reduced State. PEDOT−$LiClO_4$/MeCN film undoped at −1.0 V in 0.1 M $BaCl_2$ aqueous solution shows a very narrow binding energy peak for oxygen and almost no barium or chlorine by XPS spectra.

We found no Ba^{2+} cation, ClO^{4-}, or Cl^- in this neutral state by XPS. From UPS,[15] there is a significant difference between neutral and PSS- or TsO-doped

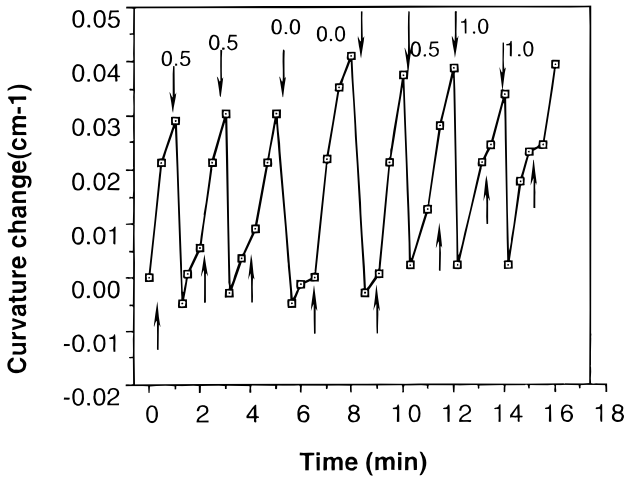

Figure 5. Curvature changes of PEDOT−PSSNa(aq)/Au/PE strip under pulsed potentials in 0.01 M PSSNa aqueous solution. The numbers inside indicate the doping potential (volt); the up arrows indicate −1.0 V.

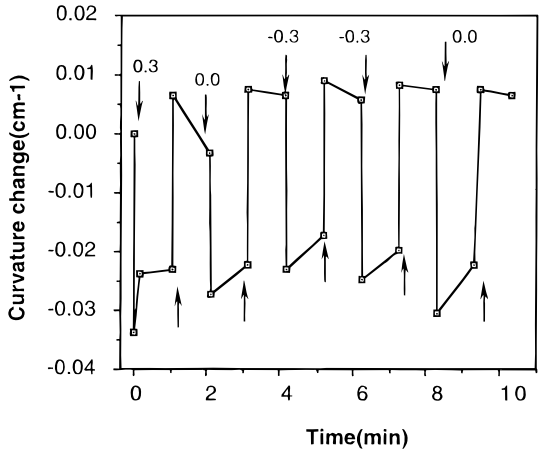

Figure 6. Curvature changes of PEDOT(TsO)/Au/PE strip under pulsed potentials in 0.1 M $NaClO_4$ aqueous solution. The numbers inside indicate the doping potential (volt); the up arrows indicate undoping potential at −1.0 V.

PEDOT. The experimental data are in very good agreement with the results of the quantum chemical calculation.

Discussion

From the BBM results, two oxidation processes can be clearly seen. The first redox potential is around −0.5 V, and the second at higher potential. To better understand this phenomena, we have studied their electrochemistry carefully. From spectroelectrochemical studies we found three steps corresponding to what is usually called polaron, bipolaron, and metallic states. These three steps of doping, however, can be found only in cyclic voltammetry with ultramicroelectrodes and at low temperature. The three redox potentials are around −0.5, 0, and 0.5 V. We have excluded other possibilities to account for these redox processes such as different conjugation lengths, the presence of both crystalline and amorphous phase, conformational changes, or resistance effect. We have thus concluded that there are three steps of redox transformation, from the neutral to the polaron state, from the polaron to the bipolaron state, and finally to the metallic state, each step involving a one electron transfer. This work is discussed in another paper.[16]

Whether cation or anion transport occurs during this process was tested by using the Ba^{2+} electrolyte. We can therefore exclude that ejection of the divalent barium cation is responsible for the volume decrease on doping of the polymer. In this case Cl^- must insert the polymer during doping and causes the polymer volume contraction. Since the direction of ion movement is opposite to that of volume change—the polymer contracts as ions are injected—it is probable that the electronic structure change from a neutral to polaron state causes the volume contraction. Solvents may contribute to the volume changes. With increase of doping levels the polymers increase their polarity, and solvent may swell the polymer. The ion movements may also include solvent molecules coordinated to ions. However this coordinated solvent will not be able to change the direction of volume changes, only the magnitude of the volume change. In films of cPEDOT-(TsO) and PEDOT−PSSNa there is also contraction and expansion on doping. In polyanion solutions there are no mobile anions that might transport in the material, and all films show expansion after the almost same initial contraction during doping. Thus this volume expansion is probably also due to a structural transition, as ion injection in these polymers will not explain the results. For all PEDOT films they show contraction first and expansion later at doping, regardless of whether a bulky cation or polyanion, immobile in the polymers, is available in the electrolyte.

Electrochemically prepared PEDOT is amorphous. Though chemically polymerized cPEDOT is partially crystalline, its CV on a macroelectrode is similar to that of electrochemically polymerized PEDOT (we were unable to make a thin film of cPEDOT on an ultramicroelectrode). We can thus assume that the observations from electrochemically polymerized PEDOT can also apply to chemically prepared PEDOT. The crystallinity may have some effect but does not play a role in the bending beam behavior.

We are thus forced to assume that the volume changes are caused not by the volume change due to injected ions but by its intrinsic structural change. In some cases during undoping process we can see that the film first expands and then contracts. The volume change for these undoping process does not go the reversible route as does the doping process. We think that in these cases the prior doping step does not complete and leaves both final oxidized products and intermediate. Due to their very fast undoping rates, it is not possible to distinguish the two undoping steps by BBM. As the amount of volume expansions for the polymers from different synthetic routes are not identical, the structures of different PEDOT with single counterion or polyanion may have a difference in morphology. In these cases there are also contributions for the volume changes from ion movement and solvent, which are not easy to distinguish in our studies.

It has been shown that the oxidized and reduced states of conducting polymers are structurally different;

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that is, upon oxidation one goes from an aromatic twisted to a quinoid-planar structure for nondegenerate conjugated polymer.[8c,17] For PEDOT in its polaron state it is only lightly charged and the interaction between charged main chain and its counterion is attractive, so from the neutral to the polaron state the polymer volume contracts. As the doping level increases, the polymer chain becomes filled with bipolarons and even more highly charged, and the coulomb repulsion between charged sites becomes stronger, forcing the polymer to expand. Similar behavior was found for iodine doping of polythiophene but not for those poly(3-alkylthiophenes) with long side chains (butyl or octyl) which are only swollen upon iodine doping.[18] Poly(3-octylthiophene) also increases its volume upon electrochemical doping.[11f] The volume changes by chemical doping or electrochemical doping agree with each other quite well. We suggest that for PEDOT, poly(3-methylthiophene), and polythiophene, the closely packed chains[19]—not diluted by side chains—may be responsible for this kind of volume change. Their structures may be also account for their properties such as high conductivity, high electrochemical switching rate, high tensile strength,[20] and insolubility.

In summary, we found that the volume changes in PEDOT contain two opposite components. By studies using different supporting electrolytes, however, we found that it is not controlled by counterion movement. We attribute it to electronically induced structural volume change.

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