ELECTRONIC AND STRUCTURAL MODIFICATIONS OF POLYSELENOPHENE DURING ELECTROCHEMICAL DOPING PROCESS OBSERVED IN SITU BY DISPERSIVE X-RAY ABSORPTION SPECTROSCOPY

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ELECTRONIC AND STRUCTURAL MODIFICATIONS OF POLYSELENOPHENE DURING ELECTROCHEMICAL DOPING PROCESS OBSERVED IN SITU BY DISPERSIVE X-RAY ABSORPTION SPECTROSCOPY

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ABSTRACT

The electronic and structural modifications of polyselenophene during the electrochemical doping have been studied by in situ dispersive X-ray absorption spectroscopy. XANES and EXAFS obtained at the C K-edge and the Se K-edge show that i) electrons are extracted from the π bonding band with a modification of the π band distribution, ii) the Se-C bond length increases from 1.885 Å (monomer) to 1.915 Å when the polymer is synthesized, iii) no variation in the C-C and C=C bond length value is observed when polyselenophene is doped in opposition with the bipolaron model and iv) the interaction between the Se atom and the dopant is observed which leads to a reordering of the polymeric chains.

RESUME

Les modifications structurales et électroniques du polyselenophène lors de son dopage électrochimique ont été étudiées in situ à l'aide de la spectroscopie d'absorption X en mode dispersif. Le XANES et l'EXAFS obtenus aux seuils K du carbone et du selenium montrent que i) des électrons sont extraits de la bande π liante avec modification de la distribution de la bande π antilienne, ii) la longueur de la liaison Se=C augmente de 1.885 Å (pour le monomère) à 1.915 Å lorsque le polymère est synthétisé, iii) aucune variation de longueur pour les liaisons C-C et C=C n'est observée lorsque le polymère est dopé contrairement à ce qui est prévu par le modèle bipolaron et iv) l'interaction entre l'atome de sélénium et le dopant entraîne une réorganisation des chaînes polymériques.

Among the class of conduction polymers, electrochemically synthetized polythiophene, polyselenophene and derivatives (1) are the first class of materials which are chemically stable in air and moisture in both doped and undoped states. However the conduction mechanism and the electronic structure of such polymers are not well known. Several models were proposed to explain the large modification of the conductivity during the doping : i) formation of localized positive bands in the gap (bipolaron theory) (2), ii) obtention of a degenerated semiconductor or iii) narrowing of the gap associated with a "metallic" like behavior. We have recently shown, by using XPS, UPS (3) and X-ray absorption spectroscopies (4), that electrons are extracted from the π bonding band when polythiophene and derivatives are doped. Consequently, a shift of the π and π bands towards the Fermi level is observed which finally results in a narrowing of the gap from 2.2 eV (undoped state) to ~ 0.3 to 0.4 eV (fully doped state).
These results are in agreement with the data already obtained by UV-V is and ESR spectroscopy and confirm the appearance of a "metallic" like behavior, in opposition with the bipolaron theory. Thus it was very important to check the validity of this model on other systems. We report in this paper investigation of polyselenophene at the C K edge and Se K edge.

Polyselenophene is electrochemically grafted on Pt or graphite electrode in CH₃CN = 5.10⁻¹ M N(Bu), SO₃CF₃ = 5.10⁻¹ M selenophene electrolytic medium. The electrode is anodically polarized at + 1.60 V/SCE (saturated calomel electrode) to obtain the doped film and cathodically polarized at + 0.1V/SCE to undoped the films. Two sets of spectra have been recorded:

- One ex-situ, at the CK edge on a 600 Å thick film deposited on Pt (electron detection mode in UHV).
- The second at the Se K edge on a 2 μm-thick film grafted on graphite.

Data were collected using the dispersive scheme. The high value of this edge (- 12658 eV) combined with the fast acquisition time of the dispersive method (5) allowed us to follow in-situ, the electronic modifications of the polymer under the electrochemical treatment.

1 - EXAFS ON Se K-EDGE

The $k^3$ weighted Fourier transforms of the monomer and the polymer are shown in Fig. 1 (analysis done using a 400 eV window).

- Two peaks at 1.5 Å and 2.45 Å (non corrected from the phase shifts) are observed for the monomer, which are assigned to the $\text{Se=C}$ and $\text{Se-C}$ bonds respectively.
- The same peaks are detected for the undoped and doped polyselenophene. The intensity of the second one, however, decreases by a factor two with the appearance of a new one at ~ 2.8 Å. The origin of these modifications is likely due to the $\alpha\alpha$ coupling of the monomeric units during the polymerization. Then interferences should occur between the $\text{Se=C}$ bond of one cycle with the $\text{Se-C}$ bond, C belonging to the next one. This should modify the intensity ratio of these two peaks.

During the oxidation of polyselenophene, a broad peak appears in the range 4-5.5 Å whose intensity increases with the doping level. The Fourier filtered curve of this peak is split in two domains (Fig. 2) with a characteristic beat mode in between. The low k oscillations could be associated to
a light element backscatter. Conversely, the oscillations over the node of the "beat" are relevant to high Z element which can be identified only as Se in this system.

These characteristics reveal that i) the dopant interacts with the Se atom which is consistent with the appearance of positive charge on the heteroatom and ii) the polymeric chains rearrange during the doping. However, we cannot decide if the Se-Se interaction comes from two adjacent monomeric units or from two different polymeric chains.

The fit of the Fourier filtered spectra reveals an increase of the Se-C bond length when the polymer is synthesized (1.915 Å instead of 1.885 Å for the monomer) and the number of neighbors remains constant. When the polymer is doped, no variation in the Se-C bond length is observed.

XANES

Five membered heterocycles (pyrrole, thiophene, selenophene) are planar molecules which have C\textsubscript{2v} symmetry with an in-plane axis containing the heteroatom. A LCAO calculation shows that the highest occupied orbital and the lowest unoccupied orbital correspond to pure π orbitals (6). No theoretical calculation is available for polyselenophene. However we expect the formation of a pure π bonding and π antibonding bands upon coupling as polypyrrole and polythiophene. Intramolecular resonance transitions are thus expected when a carbon or Se core electron is excited into these unfilled π bands.

C K EDGE

For an undoped thin polyselenophene film (Fig. 3), several peaks are observed at 283, 285, 291 and 301 eV. These peaks arise from the transition of the 1s electron to π band, σ(C-Se), σ(C-C) and σ(C=C) shape resonances (Table 1).

The same bound states and shape resonances are observed on a Cl\textsubscript{10} doped film, except an additional shoulder at 286 eV, and a decrease of the π transition intensity.

This decrease is directly linked to the extraction of electrons from the π\textsubscript{u} band and to the modifications of the π and π\textsuperscript{*} band distribution. In addition the

![Figure 3: XANES spectra at the CK edge of a thin polyselenophene film grafted on Pt a) undoped state b) fully doped](image-url)
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TABLE 1: Energies and proposed assignments of features in the carbon K spectra of polySelenophene PSe

<table>
<thead>
<tr>
<th>UNDOPED PSe</th>
<th>DOPED PSe</th>
<th>ASSIGNMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>E(eV)</td>
<td>E(eV)</td>
<td></td>
</tr>
<tr>
<td>283</td>
<td>283</td>
<td>o</td>
</tr>
<tr>
<td>285</td>
<td>285</td>
<td>o (C - Se)</td>
</tr>
<tr>
<td>291</td>
<td>291</td>
<td>o (C - C)</td>
</tr>
<tr>
<td>301</td>
<td>301</td>
<td>o (C - C)</td>
</tr>
</tbody>
</table>

Figure 4: Se K-edge XANES of polySelenophene.

a) selenophene, b) undoped, c) 2% doping level, d) 15%, e) 30%.

c (C - C) and c* (C - C) shape resonances are observed at the same energy for both doped and undoped states, which means that no variation in the C - C (or C = C) bond length value occurs in opposition with the bipolaron model where the initial aromatic structure should evolve to a quinoid like structure.

Se K EDGE

- The XANES spectra for the monomer (selenophene) and for the undoped polySelenophene are identical and characterized by a broad white line centered at ~ 12660 eV. This band arises from the excitonic transition of the 1s electron i) to the empty \( \pi \) orbital (selenophene) or to the empty \( \pi \) antibonding band (polymer and ii) to the \( \sigma \) shape resonances associated with the Se-C bond (1.885 Å).

- During the doping process, this white line is splitted into two components: one on the low energy side of the absorption edge and the other one at higher energy (~ 15 eV above this edge), the intensity of both transitions increasing with the doping level. These features should be due to the creation of empty states near the Fermi level and/or to the appearance of localized charge on the Se atom which modifies the potential barrier distribution near this atom.

Four conclusions can be drawn from this X-ray absorption study: i) the electrochemical polymerization mechanism agrees with the \( \alpha \alpha \) coupling of monomeric units, ii) during the doping electrons are extracted from the \( \pi \) bonding band with a modification of the \( \pi \) band distribution, iii) the aromatic structure does not evolve to a quinoid-like structure as expected with the bipolaron theory iv) the interaction between the Se atom and the dopant is detected by EXAFS, which induces a reorganization of the polymeric chains.

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