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Voltammetric studies on poly(*para* phenylene) films obtained by electroreduction

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Summary

Voltammetric studies were carried out on poly(para phenylene) PPP thin films obtained by electroreduction of dibromobiphenyl. Both oxidation and reduction were observed in the same medium (solvent + salt) with PPP deposits on various substrates (ITO, glassy Carbon...). The difference between the oxidation and reduction thresholds agrees well with the optical bandgap 2.8 - 2.9 eV. At these potentials prepeaks show up which may be interpreted in terms of compensation of remnant charges of the opposite sign.

Introduction

A large amount of work has been done for the last ten years on electroactive polymers (1). Poly(para phenylene), PPP, is one of those polymers which retains scientist attention because of both theoretical interest and potential applicability. Many authors have already published on PPP chemical (2) and electrochemical (3) synthesis, however very recently we reported on the first electrochemical synthesis of PPP by electroreduction of dibromobiphenyl leading to either powder or film according to experimental conditions (4).

Spectroelectrochemical data show a major change in the optical absorption spectra upon oxidation and reduction of these PPP films (5). In this paper we present voltammetric studies carried out in the same medium for both oxidation and reduction processes.

Experimental

PPP films were synthesized according to the method already published (4). They were grown under argon atmosphere onto various substrates : glassy carbon, ITO (indium tin oxide), metals... and were rinsed thorougly with THF after electrochemical synthesis. They were then transferred into the voltammetric cell and the experiment was run under inert gas in order to prevent side reactions.

The solvent was either acetonitrile (polarography grade, Carlo Erba) used as received or propylene carbonate (Janssen) carefully distilled and collected on activated alumina ; the supporting salts ($LiBF_4$, NBu_4BF_4, NBu_4ClO_4...) were vacuum dried with great care in an oven prior to use.

A three electrode cell was used in the experiment and the potential applied to the working electrode (PPP film deposited on glassy carbon or ITO electrode) was monitored by a PAR model 173 potentiostat equiped with a model 175 programmer. The counter electrode was a platinum grid or plate and the reference a silver wire immersed in the electrolyte or a Ag/Ag^+ 0.1 M reference electrode.

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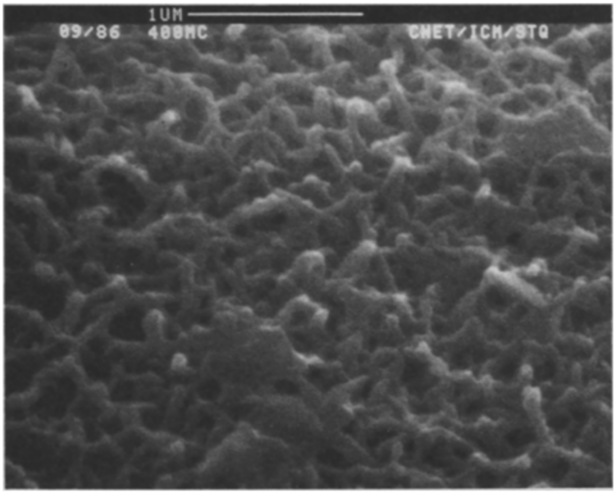

Fig. 1 :

Morphology of PPP film showing the fibrillar nature of the material with a large specific area

(bar : 1 micrometer).

Results

Morphology of PPP films is shown in figure 1 where the fibrillar character of such films is well represented. Fibrils, loosely arranged, 500 to 1000 Å in diameter, allow a large exchange between the material and the medium. This type of morphology was already described in the case of KOVACIC PPP (6) but is quite surprising for a film of electroactive polymer obtained by electrosynthesis as most of them show normally a compact surface. This morphology is therefore very convenient to carry out electrochemical experiments in order to get a better knowledge of the PPP behavior.

Voltammetry upon reduction and oxidation of PPP films deposited on glassy carbon electrode (7 mm^2) in acetonitrile (sweep rate 100 mV/s) was carried out. It is to be noted that no clear peak appears in either domain for complete oxidation or reduction of the material, but when the potential is swept back, a peak shows up which is the signature of reduction (oxidation) of the oxidized (reduced) species. Data concerning the potential at which these maxima occurs are collected in table I.

Table I

Potentials for oxidation and reduction of PPP films in different media (glassy carbon 7 mm^2 ; sweep rate 100 mV/s ; supporting salt : 0.1 M).

Medium Solvent/Salt	E_{red}/V (1) maximum of the backward peak	E_{ox}/V (1) maximum of the backward peak
Acetonitrile/NBu_4ClO_4	- 2.8	+ 0.6
Acetonitrile/NBu_4BF_4	- 2.75	+ 0.65
Propylene Carbonate/NBu_4ClO_4	- 2.75	+ 0.65

(1) versus Ag/Ag^+

There is no evidence of any influence of the medium on voltammogram shape when operating at constant sweep rate (100 mV/s). However, the point is that if the sweep rate is lowered, E_{ox} and E_{red} move closer to each other to some extent until the potential difference between these two peaks reaches a constant value. Similar observations were registered with ITO electrodes, but indium tin oxide being a less conducting material the sweep rate has to be restricted to low values (5 or 10 mV/s) in order to get a nice voltammogram.

It was thus interesting to sweep the whole domain from reduction to PPP oxidation in the same electrolyte with film deposited on various substrates and to clarify the role of external parameters on PPP film behavior. This was done with deposits on glassy carbon or ITO, immersed in different electrolytes : propylene carbonate or acetonitrile with tetraethyl (or butyl) ammonium perchlorate (or tetrafluoroborate).

In figure 2 are reproduced voltammograms of a sample on glassy carbon (2 cm^2) with an electrolytic solution of acetonitrile NEt_4BF_4. The same general behavior was observed with PPP films on 2 cm^2 ITO electrodes as long as slow sweep rates were used (5 or 10 mV/s). From this figure, the following features may be drawn :

- prepeaks appear at the oxidation or reduction threshold and their intensity increases with the number of cycles at the beginning (The maximum of the cathodic prepeak moves to lower potential as the number of cycles is increased until it reaches a constant value with tetraethyl cation).

- the cathodic prepeak is often absent at the first cathodic sweep (or very tiny) when one starts with the neutral film just washed after synthesis.

- the prepeak intensity is enhanced as the potential limit is shifted to larger values in the opposite domain. Furthermore, the more pronounced the electrochemical reaction in one domain, the larger the prepeak intensity is the other. Experiments performed under the same conditions indicate that when the potential is held in the cathodic as well as the anodic

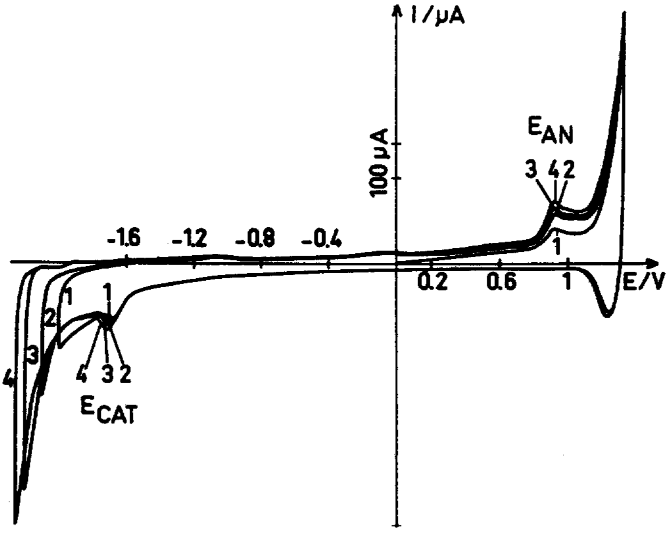

Fig. 2 :

Voltammograms of PPP films showing first cycles in both domains : reduction and oxidation carried out in the same medium Acetonitrile, NEt_4BF_4 0.1 M. Sweep rate 50 mV/sec. Potential are given against Ag wire.

domain at a value beyond that of the prepeak maximum, charges are accumulated into the material and at the next reverse sweep the opposite prepeak grows strongly. But it is to be noted that only a part of the charges passed through the sample can be recovered. In other experiments several cycles limited to potentials higher than the prepeak maxima but however lower than oxidation or reduction of PPP, indicate that their intensity remains stable as long as the cycle limits are within this range.

Discussion

An analogy exists between these two new peaks which appear only when the potential applied to a sample is driven through the whole domain of PPP electroactivity. Each of them is irreversible, depends strongly on what happened in the opposite domain and disappears upon cycling within the limits of the corresponding domain, either cathodic or anodic.

Such observations were reported very recently on disubstituted poly (fluorene) (7) and were explained in terms of remnant charges in the polymer after dedoping. The scheme represented in figure 3 tries to describe the process which is the following : PPP films are grown cathodically on various substrates at a potential quite close to the PPP reduction threshold. The films thus obtained should be neutral, but a very light

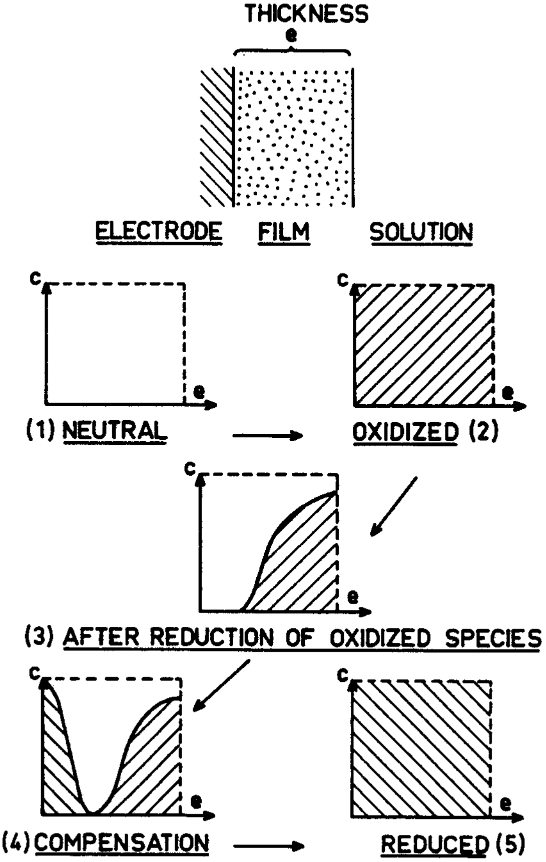

Fig. 3 :

Schematic representation of a PPP film with charge in-depth profiles following its status : neutral to oxidized to fully reduced through compensation of remnant charges.

doping cannot be avoided. When the film is taken from quasi neutral to an anodic potential (cycle 1 in figure 2) charges isolated far from the interface film-electrode may be compensated as soon as the material becomes conducting. This indeed occurs at the very beginning of oxidation and shows up as a small prepeak E_{AN} located at the oxidation threshold. Upon anodic cycling this prepeak disappears. Further potential increase leads to a completely oxidized PPP film 2 (figure 3) and a peak - signature of the reduction of oxidized species - appears on the voltammogram on the reverse sweep. This reduction occurs first at the interface film-electrode building thus an insulating layer which hinders further charge removal 3 (figure 3). As the potential is still lowered the PPP reduction takes place and develops from the same interface a newly conducting layer to the expense of the insulating one previously formed : this phenomenum allows compensation of remnant charges 4 (peak E_{CAT} on figure 2). The process continues through complete reduction of the film 5 and oxidation of the reduced species and in the next sweep (cycle 2 in figure 2) the prepeak intensity E_{AN} is enhanced as compared to the first cycle one coming from the synthesis as mentioned above.

Table II

Potentials for oxidation, reduction, prepeaks of PPP films under different experimental conditions (glassy carbon : 7 mm^2 (100 mV/s) ; ITO : 2 cm^2 (5 mV/s) ; supporting salt 0.1 M)

The experiments were carried out in different cells and there was no attempt to use the same reference electrode as we were only interested in the difference between the potentials for the discussion and not in the absolute value of peak potentials.

Sample : Substrate/Solvant /Salt		ITO (1) Acetonitrile/ NBu_4BF_4	Glassy C/ (2) Acetonitrile/ NBu_4ClO_4	Glassy C/ (2) Acetonitrile/ NBu_4BF_4
E_{ox}/V		+ 1.4	+ 0.7	+ 0.7
E_{AN}/V	foot	+ 1.1	+ 0.45	+ 0.4
	max	+ 1.3	+ 0.65	+ 0.6
E_{red}/V		- 2.2	- 2.75	- 2.8
E_{CAT}/V	foot	- 1.7	- 2.45	- 2.4
	max	- 1.8	- 2.75	- 2.6
DIFFERENCE/V (FOOT POTENTIAL) $E_{AN}-E_{CAT}$		2.8	2.9	2.8

(1) versus Ag wire ; (2) versus Ag/Ag$^+$

The PPP film behaves in the same way whatever the first scan direction, the only difference comes from the occurence of the first prepeak and its interpretation. As stated before, in the first anodic scan E_{AN} is a consequence of the electro-synthesis ; but in the first cathodic scan, starting with a neutral film just washed after synthesis, the prepeak E_{CAT} - very tiny if not absent - may arise from complete reduction of organo nickel species located on one end of PPP chains (4). These species are not destroyed during the transfert to voltammetric cells as everything is carried out under inert gas. Therefore the first cathodic prepeak may be accounted for by this reaction. The subsequent prepeaks are explained in this same way as before in terms of remnant charges after dedoping.

This picture seems to hold in any case, whatever the substrate of film deposit or the electrolytic medium. In table II, are collected some data on prepeaks and backward peaks registered at the required sweep rate (5 or 10 mV/s for ITO ; 50 or 100 mV/s for glassy carbon electrodes). It must be pointed out that the potential difference between anodic and cathodic prepeaks remains almost constant whatever the experimental conditions. A small shift up to 0.2 V occurs sometimes with supporting salts other than NBu_4BF_4 ; this might be due to differences in ion mobilities. Anyway, this difference in potential seems to be correlated with an intrinsic property of PPP and may be compared favourably with the energy of optical absorption threshold (5) found in such films, 2.8 to 2.9 eV.

The existence of prepeaks at the very beginning of oxidation and reduction processes reveals that under these conditions all the charges accumulated into PPP film cannot be recovered in the reverse sweep but it allows to know with a better accuracy the energy gap of this type of electroactive polymers.

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