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HAL Id: jpa-00222617
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Submitted on 1 Jan 1983

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ELECTROOPTICAL PROPERTIES OF THIN FILMS OF POLYHETEROCYCLES

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Résumé - Des films minces de polymères conducteurs préparés par polymérisation électrochimique d'hétérocycles changent de couleur reversiblement lorsqu'on les soumet à des cycles d'oxydation-réduction. Par exemple le polypyrrrole synthétisé sous une forme oxydée passe du brun au jaune lorsqu'il est réduit, les potentiels à appliquer à l'électrode étant respectivement 0 et -0,7 volt par rapport à une électrode de référence au calomel. D'autres couleurs peuvent être obtenues avec d'autres hétérocycles tels les thiophènes. Cette propriété peut trouver des applications dans le domaine de la visualisation. Les propriétés électrochimiques de quelques polyhétérocycles ont été déterminées et les caractéristiques densité optique, temps de réponse, durée de vie sont comparées à celles des autres matériaux électrochromes.

Abstract - Some conducting polyheterocycles prepared by electroinitiated polymerization as thin films on electrodes change color reversibly when they are electrochemically cycled. As an example, polypyrrole is synthesized in an oxidized form and may be reduced reversibly between 0 and -0.7 volt vs SCE. The modified electrode changes from brown to yellow during the cycling of the potential. Other colors may be obtained with other heterocycles. The electrochemical properties of some polyheterocycles have been determined and their characteristics-optical density, switching speed, ageing effects - are compared to those of other electrochromic organic materials.

INTRODUCTION

Chemically or electrochemically doping or undoping of conducting polymers induces a modification of their physical properties such as electrical conductivity and absorption spectrum. Conductivity may be controlled through electrochemical doping and this property allows the use of conducting polymers in rechargeable batteries (1). Optical absorption spectrum depends on the extent of doping and changes in the visible range have been observed for all the conducting polymers: polyacetylene (2), polyparaphenylene (3), polypyrrole (4); the doping process may be chemical or electrochemical. Materials in which a colour change is induced by the passage of a charge are called electrochromic and some of them have been proposed for applications in displays. One of the first properties which are required for an electrochromic material is the ability to form uniform thin films on electrode. Electrochemically initiated polymerization is an attractive method to deposit films and has been used to make films of conducting polypyrroles (5). The films are obtained in the oxidized state and may be reversibly reduced with a colour change from brown to yellow. Polypyrrole and N substituted polypyrroles have been proposed as electrochromic materials (6). In a previous paper the electrochemical polymerization of other heterocycles was described: thiophene, furan, indole, azulene and the physicochemical and conducting properties of the polymers were given (7). We investigated other electrochemically polymerized thiophenes and in this paper we report the electrochemical and electrooptical properties of thin films of these polymers and we compare them to those of polypyrrole films.
**FILMS PREPARATION**

Electrochemical polymerization was carried out in a single compartment cell from deaerated solutions containing 0.05 M monomer in acetonitrile. The monomers were purified by distillation, chromatography and/or recrystallization. Acetonitrile was used as received or after distillation. Tetraethylammonium tetrafluoroborate ($\text{Et}_4\text{NBF}_4$) was used as supporting electrolyte in a concentration of 0.1 M. The working electrode was a unpolished platinum foil or Sn O$_2$ coated glass and the counter-electrode was a platinum foil or a platinum wire. All potentials were measured with respect to a calomel reference electrode (SCE).

The films were prepared at constant current density (150 $\mu$A/cm$^2$) or at constant potential. After polymerization the working electrodes were removed from the cell, rinsed with acetonitrile and dried with argon. The film thicknesses were determined from measurements using a Sloan Dektak profiler.

**MEASUREMENTS ON THE FILMS**

Electrochemical measurements on the films were made in the cell described before and in 0.1 M ($\text{Et}_4\text{NBF}_4$) - CH$_3$ CN. Cyclic voltammetry and chronoamperometry were carried out using Tacussel apparatus. Spectra were recorded with a Perkin Elmer spectro photometer.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Oxidation potential of monomer V vs SCE</th>
<th>Polymer</th>
<th>Growth rate $\text{A/mm}$ (1)</th>
<th>Oxidation potential V vs SCE</th>
<th>Reduction potential V vs SCE</th>
<th>Conductivity $\Omega^{-1}\text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH</td>
<td>0.8</td>
<td></td>
<td>210</td>
<td>- 0.12</td>
<td>- 0.29</td>
<td>$10^2$ a</td>
</tr>
<tr>
<td>N</td>
<td>0.8</td>
<td></td>
<td>250</td>
<td>0.46</td>
<td>0.39</td>
<td>$10^{-4}$ a</td>
</tr>
<tr>
<td>S</td>
<td>1.6</td>
<td>(2)</td>
<td>1.12</td>
<td></td>
<td>0.75</td>
<td>10 b</td>
</tr>
<tr>
<td>S</td>
<td>1.1</td>
<td></td>
<td>250</td>
<td>1.02</td>
<td>0.6</td>
<td>$10^{-4}$ b</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>1.4</td>
<td>(2)</td>
<td>0.9</td>
<td></td>
<td>0.4</td>
<td>$10^2$ b</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>1.35</td>
<td>(3)</td>
<td>1.1</td>
<td></td>
<td>0.77</td>
<td>50 b</td>
</tr>
</tbody>
</table>

(1) current density 150 $\mu$A/cm$^2$. Electrolyte salt $\text{Et}_4\text{NBF}_4$ 0.1 M  
(2) non uniform films  (3) not measured  

a thin films  b pressed pellets
Conductivity measurements were made on films or pressed pellets at room temperature by a four probe technique using a Keithley current source and a Keithley electrometer.

RESULTS AND DISCUSSION

Polymer deposition

Six monomers were polymerized; they are listed in table 1 where electrochemical data of the polymers are given. The films were deposited at potential slightly higher than the oxidation potential of the corresponding monomer. Uniform films were obtained except for thiophene and 3 methylthiophene, the oxidation potential of which being the highest. The growth rate for the uniform films was a few 100 Å/min. The films had good adhering properties when the thicknesses were lower than a few microns.

The polymers are conducting but their conductivities depend on the nature of the monomer.

Cyclic voltammetry

All the films exhibit cyclic voltammetric responses and this behavior is illustrated in figure 1 where typical voltammograms are represented. It is interesting to compare the electrochemical responses of films grown from similar monomers: poly (2 2' bithiophene) voltammogram is different from this of polythiophene: the wave in the anodic region is sharper and there are two not clearly defined waves in the cathodic region which are not well understood. Poly (3,4 dimethylthiophene) and poly(3 methylthiophene) possess two waves in the cathodic region. The peaks are very broad in the case of poly (3 methylthiophene). It can be seen that except for polypyrrole the reduction and the oxidation of the polymers occur at potentials which are in the positive range versus SCE.

![Typical cyclic voltammograms of films of electrochemically polymerized heterocycles on Pt in 0.1 M Et4 N BF4/CH3CN solutions: a) pyrrole b) N methyl pyrrole c) thiophene d) 2 2' bithiophene e) 3 methyl thiophene f) 3,4 dimethylpyrrole.](image)

Fig. 1 - Typical cyclic voltammograms of films of electrochemically polymerized heterocycles on Pt in 0.1 M Et4 N BF4/CH3CN solutions: a) pyrrole b) N methyl pyrrole c) thiophene d) 2 2' bithiophene e) 3 methyl thiophene f) 3,4 dimethylpyrrole.

The anodic and cathodic peak currents have not exactly the same value except for poly N methyl pyrrole. They are proportionnal to the thickness and to the scan rate up to 0.2 V/s. But when the scan rate increases the anodic wave is shifted toward higher potentials.

Film thickness has an influence: the redox waves become broader and the peak to peak separation increases when the thickness increases.

The quantities of electricity consumed in the oxidation and in the reduction are almost equal. They are given by the areas under the 2 peaks and they vary linearly with the thickness of the film showing that the electroactive sites are uniformly distributed in the film. The value of the charges represent only a fraction of the charge consumed for the synthesis: 20 % for poly (2 2' bithiophene) and 6 % for polypyrrole. The charge was independant of the scan rate.
Spectroelectrochemical studies

The absorption spectra for all the films have been measured in the oxidized and in the reduced state (figure 2). The two pyrrole films have similar spectra with a strong absorption band in the U.V.-blue range for the reduced state. The oxidized states are slightly different. Poly (3 methylthiophene) and poly (2,2' bithiophene) are characterized by a band peak at 470 nm in the reduced state and a very broad band in the red range in the oxidized state. Poly thiophene is very similar.

Fig. 2 - Absorption spectra of polyheterocycles

- a) poly (N methyl pyrrrole) (≈ 0.3 μm)
- b) polypyrrole (≈ 0.1 μm)
- c) poly (2,2' bithiophene) (≈ 0.1 μm)
- d) poly (3 methylthiophene)

--- reduced state

--- oxidized state

Spectrum of poly (3,4 dimethylthiophene) does not change very much under oxidation or reduction. In table 2 are listed the observed color changes for the monomers which polymerize in uniform films.

Chronoamperometry

Figure 3 shows the typical current response when a step of potential is applied to the electrode. The voltage pulse depends on the polymer and was deduced from the electrochemical study: $-0.7 \rightarrow 0$ V for poly(pyrrole), $0 \rightarrow 0.8$ V for poly(N methylpyrrrole) and $0 \rightarrow 1.3$ V for poly(2,2' bithiophene). The oxidation was found to be slower than the reduction process. The response times defined as the times required for current to fall to 10% of its maximum, depend on the nature of the film and on its thickness (see figure 4).
Table 2
Electrooptical data

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Color change</th>
<th>Oxidized state</th>
<th>Reduced state</th>
<th>Absorption coefficient (cm⁻¹)</th>
<th>Electrochromic efficiency (AOD/(mC/cm²))</th>
<th>Response time (ms)</th>
<th>Lifetime (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N)ₙ</td>
<td>brown yellow</td>
<td></td>
<td></td>
<td>4.10⁴ (1)</td>
<td>0.1</td>
<td>100</td>
<td>2.10⁴</td>
</tr>
<tr>
<td>(N)ₙ(CH₃)</td>
<td>brown orange</td>
<td></td>
<td>red yellow</td>
<td>1.10⁴ (1)</td>
<td>0.05</td>
<td>100</td>
<td>10³</td>
</tr>
<tr>
<td>(S)ₙ(S)ₙ(CH₃)₂</td>
<td>blue grey</td>
<td></td>
<td>red</td>
<td>8.10⁴ (2)</td>
<td>0.05</td>
<td>100</td>
<td>10³</td>
</tr>
<tr>
<td></td>
<td>deep blue</td>
<td></td>
<td>blue</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

(1) measured at 500 nm in the oxidized state
(2) measured at 470 nm in the reduced state

Fig. 3 - Chronoamperometry typical curves for polyheterocycle films subjected to square wave potential pulse.

Fig. 4 - Response time-thickness dependence for polypyrrole (a) and poly (2,2'-bithiophene) (b) films.
Electrochromic properties

The thicknesses of the films which give a sufficient contrast on platinum foils were found to be about 0.1 \( \mu \text{m} \). In these conditions the optical density change is between 0.1 and 0.3 and a few mC/cm\(^2\) have to be injected in order to obtain this value. The ratio of the optical density change to the consumed charge is an indication of the sensitivity of the material and is called the electrochromic efficiency. The values of this parameter are given in table 2 for the most interesting polymers. There is a factor 2 between the efficiencies of polypyrrroles and poly(2,2'-bithiophene) but the absorption coefficient of this last polymer is higher.

Two other parameters characterize electrochromic displays: response time and life time. Response time was lower than 150 ms on platinum electrodes which were used in these experiments. Life time was defined as the number of oxidation-reduction cycles with 0.5 second pulse duration which caused a 50 \% decrease in the current peak height. The values are listed in table 2.

Electrochromic parameters of polyheterocycles may be compared to those of other electrochromic materials such as tungstene oxide, irridium oxide, lutetium diptylodicyanine (8), electroactive polymers obtained by attaching an electrochromic molecule (tetrathiafulvalene) to a linear polymer chain (9) or polyelectrolyte complexes (10) (11). For these polymeric materials the electrochromic efficiency is in the range 0.05 to 0.160 (mC/cm\(^2\))-1, the response time is a few 100 ms and the life time is 10\(^4\) cycles.

CONCLUSION

As polypyrroles, electrochemically polymerized thienophenes are electroactive polymers and undergo color changes when they are switched between the oxidized state and the reduced state. The blue to red color change which may be observed is more attractive than the brown to yellow color change obtained with polyppyrrrole. Electrooptical measurements on these two kinds of polymers deposited on unpolished platinum foils showed that, even not optimized thin films exhibit good switching speeds (< 200 ms) compared to other electrochromic materials. Life time is lower (10\(^3\) cycles) for polythiophene than for polyppyrrrole (2.10\(^4\) cycles). Recent studies show that these two parameters may be improved allowing these polymers to be good candidates for electrochromic displays.

ACKNOWLEDGMENT

This work was supported in part by the Delegation Generale à la Recherche Scientifique et Technique.

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