

## METHYLENE - BLUE MODIFIED POLYPYRROLE FILM ELECTRODE FOR OPTOELECTRONIC APPLICATIONS

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Organic semiconductors have been the objects of considerable attention in recent years, both as electrodes and photoelectrodes in different applications. Radiation-induced and electrochemical modification of polypyrrole film by incorporating of large electro-active organic molecules is investigated in this paper. Introduction in the polypyrrole (PPy) of methylene blue as counterion has a strong effect on the electrochemical performance of PPy films. The UV - VIS spectra of the films (fitted with Gauss type function) are also evaluated. IR spectra are measured in order to proof the incorporation of MB into polypyrrole film.

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### 1. Introduction

The optoelectronics properties of films of organic semiconducting dyes are used in a wide range of devices (solar cells, photo-MOS transistors, vidicon television pickup tubes and xerographic detectors) [1-4].

The application of semiconductors electrodes to the construction of photochemical cells (PEC) has been reviewed.

In addition to fundamental studies of semiconductor/solute interface, investigations of such electrodes are concerned with the construction of efficient systems for the utilization of solar energy to produce electricity or chemical species.

The practical application of such devices depends upon the discovery of inexpensive and abundant materials, which are capable of stable operation in solution over an extended period. This fact has led to the investigation of a number of new semiconductor materials.

The electrochemistry of polypyrrole has been discussed in numerous review papers [5], from different points of view. Polypyrrole has been investigated owing to its properties, like: simple preparation procedure, good stability and appropriate range of applications.

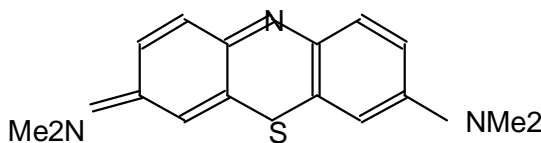


Fig. 1. The structure of methylene blue.

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In recent years a large number of papers have been published regarding the polypyrrole synthesis. In order to obtain films with good properties, modified polypyrrole films are prepared. The most convenient method is based on the fact that the anions can be incorporated into the polymer matrix as counter-ions during the process of polymerization to compensate the positive charge of the polypyrrole backbone [6].

Until now, there were only a few studies regarding the incorporation of large electro-active organic molecules into the polymer matrix, molecules which are expected to provide better properties than the standard inorganic anions used before. For example, polypyrrole films with methylene blue incorporated can facilitate the heterogeneous electron transfer of Cytochrome c [7] and indigo-carmin-modified polypyrrole film has been also obtained with good electro-activity and optical properties [8].

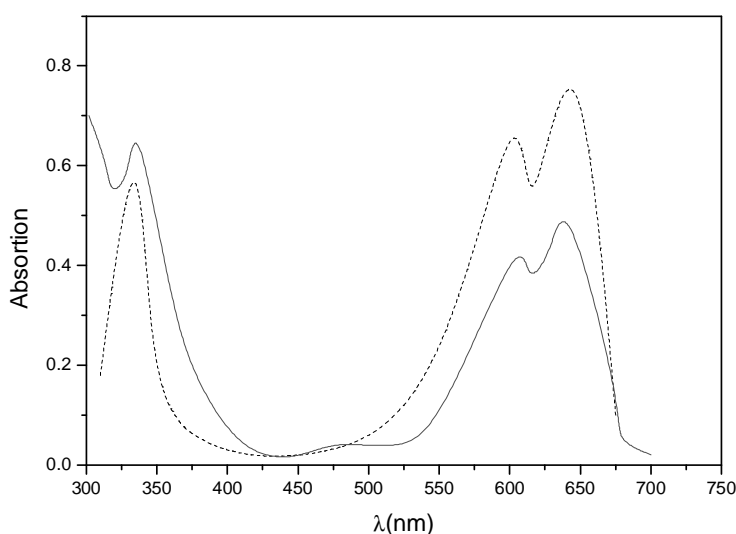


Fig. 2. The absorption spectra of MB(...) and PPy/MB (—) in water solution.

We report in this paper the preparation of polypyrrole films with methylene blue incorporated as counter-ions. The methylene blue indicator has a good electroactivity, which we also expect to find in the resultant film. The film was studied for its potential electrochromic and photoelectrochemical applications.

## 2. Experimental part

### 2.1 Apparatus

The voltammograms were obtained with a 5d Zahner system. A conventional three-electrode cell with Ag/AgCl/KCl (sat.) electrode as reference electrode and a platinum gauze as the auxiliary electrode was used. The working electrode was a platinum foil. UV-visible spectra were recorded with a SPECORD M 400 Carl Zeiss Jena spectrophotometer. A tin-oxide-coated glass substrate (ITO) was used as the working electrode for the spectroscopic measurements.

The electron and photon radiation beams were supplied by the 7.0 MeV Linear Accelerator of the National Institute for Lasers, Plasma and Radiations Physics, Romania.

The IR spectra were recorded on a SPECORD M80 Carl Zeiss Jena spectrophotometer with KBr pellets.

## 2.2 Reagents

Pyrrole (Aldrich) was distilled and stored in the dark before use. Methylene blue (Fluka), Fig. 1, was used as received. Doubly distilled water was used in all the experiments.

## 2.3 Preparation of modified electrodes

The platinum foil was polished with 0.3 and 0.05  $\mu\text{m}$  alumina powders and then washed thoroughly with water. The electro-polymerization was performed in aqueous solution with 0.1  $\text{mol dm}^{-3}$  pyrrole and 1  $\text{mmol dm}^{-3}$  methylene blue as supporting electrolyte. The electrode potential was held at 0.7 V for 5 min to obtain the polypyrrole films. After polymerization the films were washed with water. The same procedure was applied for the polymerization of polypyrrole /methylene blue films (PPy/MB) onto the ITO substrates. The ITO plate was washed with acetone and water before use [9].

Also, the same modified electrodes have been prepared by irradiation with electrons or photon beam (300R).

## 3. Results and discussion

### 3.1 Structural properties of PPy

PPy films thinner than 1  $\mu\text{m}$  have different spectral properties, depending on the conditions of synthesis and degree of polypyrrole oxidation, with the increasing degree, the color of the films changes from yellow to the blue and, ultimately, black [10].

The films have good adhesion to the substrate but at a thickness of over 10  $\mu\text{m}$  are relatively easy peeled off the electrode.

### 3.2 UV-visible and IR spectra of PPy/MB film

The absorption spectrum of MB (Fig. 2) shows a sharp peak at 664 nm ( $\alpha$  band) and a very slight shoulder at 610 nm ( $\beta$  band), which are assigned to the absorption bands of the monomeric and dimeric forms [10-13]. These two peaks can be observed in PPy/MB spectrum, too, where they shifted to 580 nm and 660 nm, indicating very clearly the incorporation of methylene blue in the polymer matrix. The shift of the peaks is due to the interaction between organic anions and polymer chains. Some cationic dyes undergo spectral changes in their absorption spectra with increasing concentration [11, 12]. This phenomenon has been ascribed to the formation of dimers or higher aggregate of these dyes in aqueous solution.

Fig. 3 shows the absorption spectrum of a PpyMB / ITO film together with the spectrum of methylene blue in aqueous solution of 0.2  $\text{mol dm}^{-3}$  HCl. It is a little difficult to observe the two peaks, which correspond to methylene blue, but the small shift of the peaks is noticed. Therefore further studies will be done.

This figure shows the absorption spectrum of the polypyrrole/methylene blue by radiative polymerization together with the spectrum of the blank solution. The peak at about 469 nm indicates the formation of the polymer with methylene blue incorporated.

The peaks from 611 nm and 665 nm are assigned to the absorption bands of monomeric and dimeric methylenic blue, respectively. The intensity of these bands decreased significantly by the incorporation of MB in the polymer matrix, Table 1.

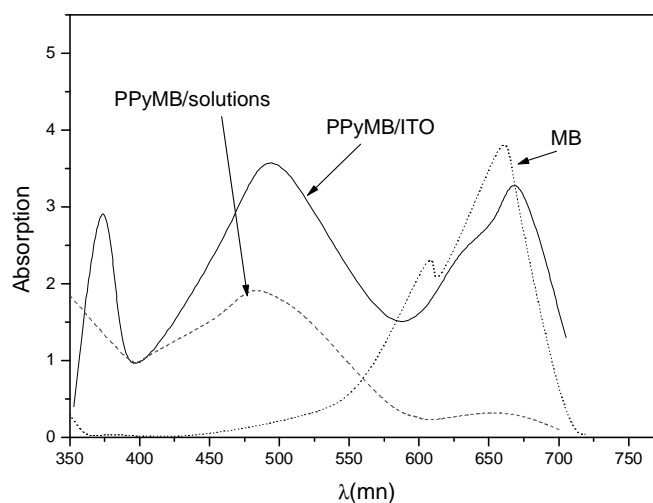


Fig. 3. The comparison between the absorption spectra of MB(...) in aqueous solution, PPyMB 0,2 M HCl aqueous solution (- - -) and PPy/MB/ITO (—).

Table 1. Correlation between the absorption peaks for PPy-MB film kept at different potential values and MB monomer and dimer concentrations.

Potential vs. SCE (V)	c (nm)	A	$C_m \times 10^6$ (M)	$C_d \times 10^7$ (M)
0.1	467	0.25	2.96	6.41
	521	0.238		
	678	0.26		
0.2	468	0.245	3.2	5.38
	523	0.223		
	672	0.24		
0.5	406	0.23	3.374	4
	491	0.21		
	674	0.21		
0.7	468	0.22	3.54	1.98
	519	0.195		
	666	0.205		

The IR spectra of the polypyrrole/methylene blue obtained either by radiation-induced polymerization or by electrochemical polymerization of pyrrole in aqueous solution, are quite similar, showing new specific bands at  $1000\text{ cm}^{-1}$  and  $1450\text{ cm}^{-1}$  (by comparison with pyrrole alone, where they are missed), both of them attributed to the polymeric chains of polypyrrole modified with MB. All the obtained results are based on previous experiments of our group [13].

### 3.3 Cyclic voltammograms of PPy/MB films

In another paper it was pointed out that an applied electrode potential more positive than 0.7 V for pyrrole polymerization leads to a simultaneously oxidation of the indicator used. That is why, next to the electrode surface a depletion layer will be formed which leads to a lower concentration of indicator in the polymer matrix [4].

Therefore, we used a potential of 0.7 V for pyrrole polymerization in order to obtain a film with more electro-active centers.

The PPy/MB film required a break-in period of several cycles to reach the steady state, which could be caused by the penetration of the electrolyte in the film, followed by some morphological changes.

Fig. 4 shows the cyclic voltammogram of PPy/MB film in  $0.2 \text{ mol dm}^{-3}$  HCl aqueous solution. The voltammogram was recorded between (-0.2 V) and (+0.6 V). Similar results were obtained for PPy/MB/ITO. As previously reported [3], the film changes its color reversibly with the change in the electrode potentials: it is transparent yellow green at 0.2 V to 0 V and blue at 0.3 V vs. SCE.

It is known that polypyrrole films have a porous structure; this is why the large background currents are regarded as capacitive currents [8].

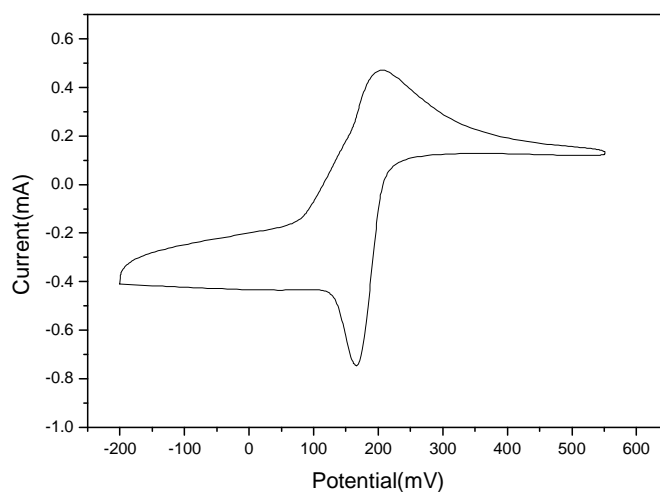


Fig. 4. The cyclic voltammogram of MB in 0.2M HCl aqueous solution.

The cyclic voltammogram is accompanied by a colour change from blue-green (in the oxide form) to a transparent film (in the reduced form). The redox peak couple is  $E_{PA} = 0.17 \text{ V}$  and  $E_{PC} = 0.05 \text{ V}$ .

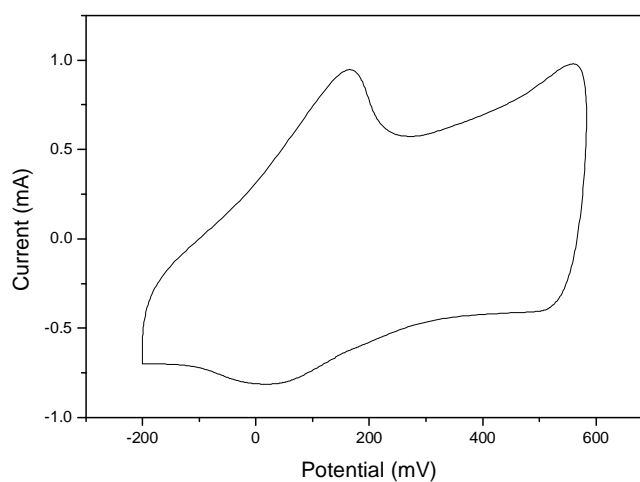


Fig. 5. The cyclic voltammogram of PPyMB film in 0.2M HCl aqueous solution.

The cyclic voltammogram of PPy/MB film was compared with the cyclic voltammogram of methylene blue in aqueous solution shown in Fig. 5. The redox waves correspond to reduction and oxidation of methylene blue/leucomethylene couple [7]. We suppose that redox couple observed in the voltammograms of PPy/MB film correspond to methylene blue/leucomethylene couple. The interaction between pyrrole and methylene blue is not clear, it needs some studies which will follow.

### 3.4. Stability of PPy/MB film

The film needs a break-in period where the PPy/MB film is cycled between -0.2 and 0.6 V. After this period the film can be cycled potentially between the same values for a longer period of time without any significant changes in the cyclic voltammograms. This means that the methylene blue molecules are irreversibly bound to the polymer matrix. One explanation of this stability of the film can be the interaction between the organic anions and polymer chains, Fig.6.

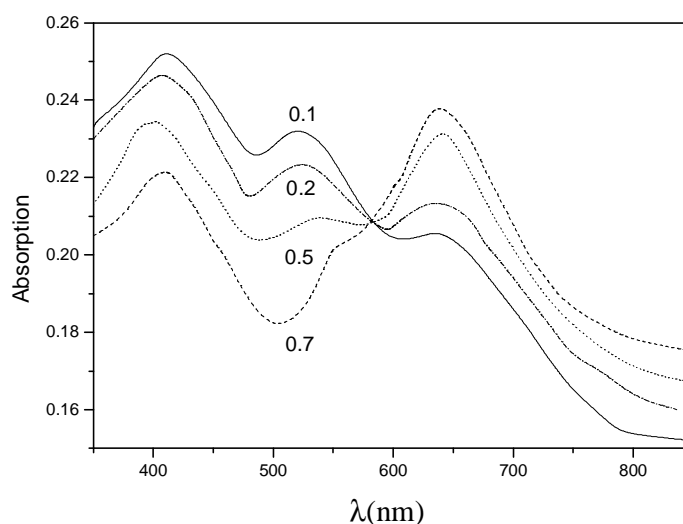


Fig. 6. The absorption spectra of ITO coated with a PPyMB film at four different potentials.

## 4. Conclusion

From the obtained results, it could be concluded:

- A sensitive modification of polypyrrole film with methylene blue could be achieved by radiation-induced method as a new and innovative method.
- The evidence of the new film, was proved by UV-VIS and IR spectroscopy;
- The cyclic voltammogram, for the prepared modified electrode, is accompanied by a color change from blue green to a transparent film.
- The new film has a strong stability due to the interaction between the organic molecules (MB) and the polymer chain of polypyrrole.
- The new proposed method for film preparation can find applications in optoelectronics.

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