

PHYSICOCHEMICAL AND MORPHOLOGICAL PROPERTIES OF NOVEL COPOLYMERS FOR APPLICATION IN PHOTOVOLTAIC ENERGY

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ABSTRACT

We present in this work, the synthesis and characterization of a novel copolymer from bithiophene and methylfuran, the properties of the copolymer layers were studied by electrochemical method (cyclic voltammetry), UV-vis spectroscopy and photocurrent measurements, scanning electron microscopy (SEM), conductivity measurement and photocurrent measurement techniques.

The cyclic voltammogram showed one redox couple characteristic of the oxidation and reduction states of the produced copolymer. The copolymer covering the surfaces was confirmed by the scanning electron microscopy and the energy dispersive X-ray analysis. The morphological analysis of the film surfaces showed spherical structures formed by agglomerated particles. The photocurrent measurement shows good photoelectrochemical properties of this copolymer makes it ideal candidates for photovoltaic cells applications.

Mots Clés: *Polybithiophene, Polymethylfuran, electrochemical characterisation, Photocurrent.*

1. INTRODUCTION

During the past two decades, electrically conducting conjugated polymers such as polyaniline, polythiophene, polypyrrole and polyacetylene have received considerable attention because of their remarkable electronic, magnetic and optical properties [1]. These properties are favorable to its applications in the areas such as organic transistors [3], light-emitting diodes (LEDs) [4], solar cells [5], actuators [6], and electrochromic windows [7].

Many copolymers of thiophene with different conjugated units have been synthesized and the application in polymers solar cells showed promising photovoltaic properties. Therefore, bithiophene can be a good candidate for copolymerization with pyrrole, furan and aniline. The main motivation for preparing copolymer composites lies in the possibility that these materials overcome the limitation of the rareness of new conjugated p-bond-containing monomers [8]. In this study, we report on the morphological evolution, optical and structural properties of poly (bithiophene-co-methylfuran) prepared by electrochemical method. The characterizations of samples were carried out by cyclic voltammetry (CV), UV vis spectroscopy and photoelectrochemical analyses by photocurrent measurements. Scanning Electron Microscopy SEM.

2. EXPERIMENTAL

2.1. Materials

Bithiophene and the methylfuran, (Aldrich) was used after distillation under reduced pressure. The supporting electrolyte used is the lithium perchlorate (LiClO₄, Fluka) in the acetonitrile solvent CH₃CN (Aldrich).

2.2. Film characterization

Cyclic voltammograms (CV) of copolymer on ITO substrate were obtained with VOLTALAB potentiostat/galvanostat model PGS 401 interfaced to a personal computer controlled with a Voltmaster programme. Photocurrent measurements were carried out with a 500 W Halogen lamp as polychromatic light source (intensity of 100 mW/cm²).

The optical absorption spectra of prepared composite films deposited on ITO substrate was measured using a Shimadzu UV 1800 –PC. The morphologies of the polymers and copolymers films were analyzed by using a scanning electron microscope (SEM) model: JEOL, JSM-7001F microscope operating.

3. RESULTS

3.1. Optical properties

The UV–vis spectra of polybithiophen, polymethylfuran and copolymers are shown in Fig. 1. It should be noted that the spectra of PBT film shows a wide and strong absorption peak at 474 nm, while polymethylfuran shows a broad peak at 382 nm, this broad absorption band corresponds to the $\pi - \pi^*$ transition [9]. However, the maximum absorption peak of the obtained copolymers is at 475. The strong and absorption peaks of the copolymers suggest the presence of long conjugated sequences and a wide conjugated chain length distribution in the backbone [10].

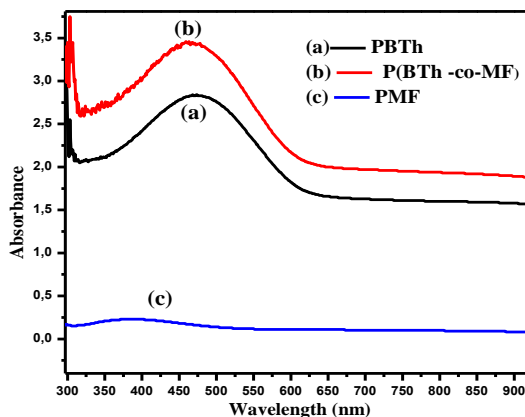


FIGURE 1 .UV–vis spectra of PBTh, PMF and their copolymers

3.2. Electrochemical polymerization

Fig. 2 shows the anodic polarization curves of PBTh, PMF and copolymer in CH₃CN/LiClO₄ (10⁻¹ mol/ l) solution, carried out in the potential range between 0 and 2 V/SCE, with scan rate of 50 mV/s. We observed the oxidation and reduction of the PBTh at 1.55 and 0.8 vs. ECS respectively. For the PMF we observed when a

positive sweep potential, an anodic peak at 1.7 V/SCE. During negative scanning potential, we observe a cathodic peak at 0.8 V/SCE, corresponding to the oxidation and reduction of PMF (Fig.2.b)

The CV of the synthesis of P(BTh-co- MF) copolymer films (Fig. 2c) shows an anodic peak a 1.5 V and a cathodic peak at 0.7 V, characteristic of the oxidation and the reduction of the copolymer formed. We observed electrochemical stability of copolymer (PBTh-co-PMF) is in good agreement with composite voltammograms given in the literature [11].

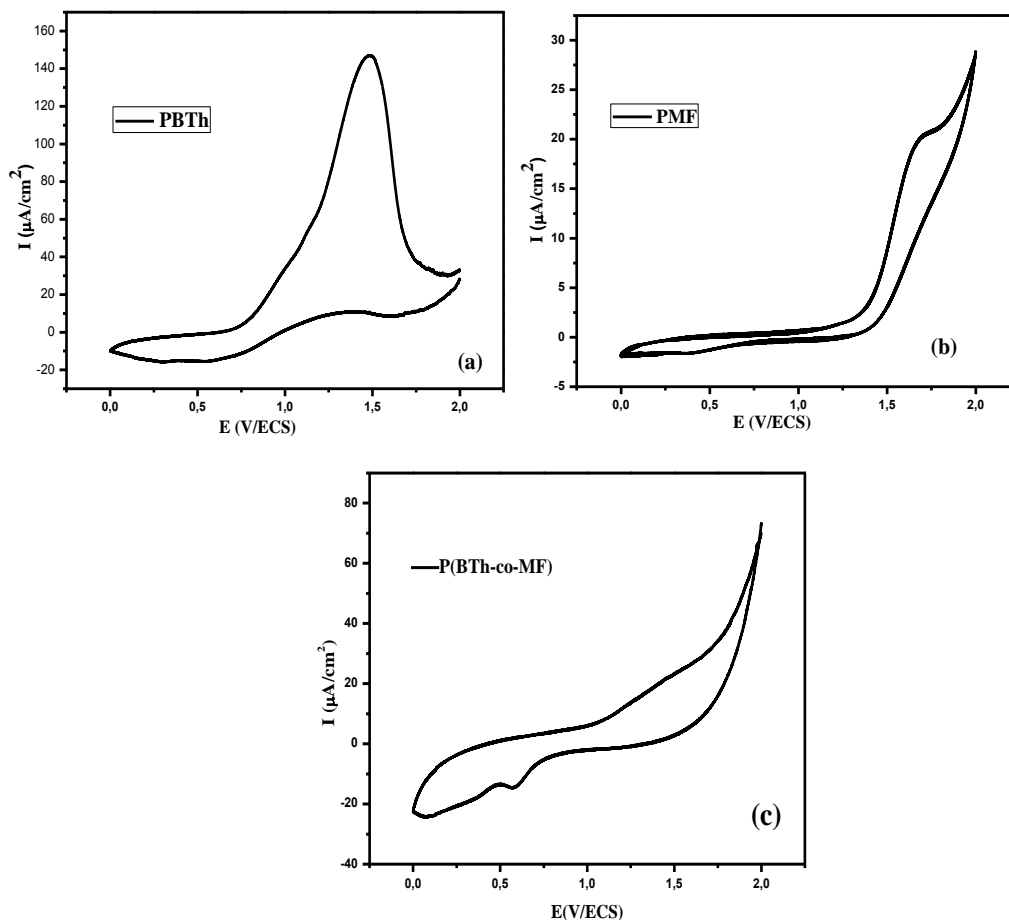


FIGURE 3. Voltammograms of polymers and copolymers: (a) PBTh, (b) PMF and (c) poly(BTH –co- MF)

3.3. Morphology

SEM morphology of PBTh, PMF and copolymers of PBTh –co- PMF are shown in Fig. 3, respectively. From the SEM image of PBTh film in Fig. 3a, it can clearly be observed that the film is formed small grains and is electrodeposits in a uniform way on all surfaces. In the case of the MF, the grains are coarser is show in Fig.3b, the PFu film is compact with some granules, and porous PFu/CIO4⁻ [12]. During the copolymerization process the poly (BTh -co- MF) SEM image (Fig. 3c), the copolymer micrograph suggests that the addition of MF to the solution consequently modifies the morphology of the film significantly.

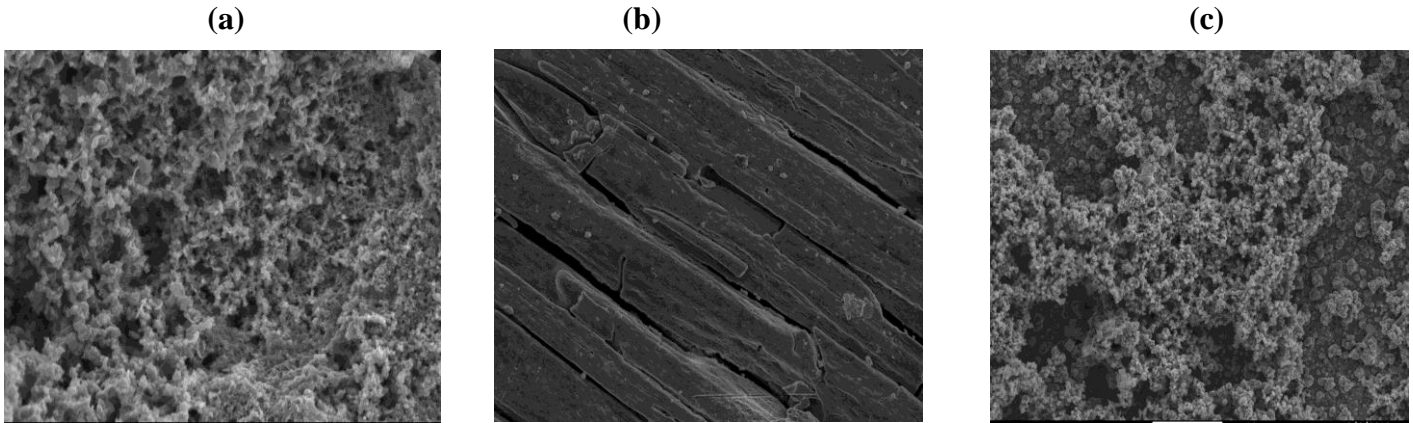


FIGURE 3. SEM micrographs of a: PBTh, b: PMF, and c: PBTh-co- PMF

3.4. Photocurrent

Fig.4. show the variation of the density of current according to the time of PBTh and P(BTh-co-MF) deposited by cycling on ITO in $\text{CH}_3\text{CN}/\text{LiClO}_4$ 10^{-1} M with a potential imposed of - 1000 mV with an excitation by the light polychromatic each 30 seconds. As shown, the copolymer film presents a cathodic peak of photocurrent immediately after irradiation. This response indicates that recombination processes is occurring in the film, due to the presence of charge carriers in the polymer bulk, mainly due to structural disorder of copolymer , the copolymers behavior of p-type polymers, this resultants observed by F. Habelhames et al. [13].

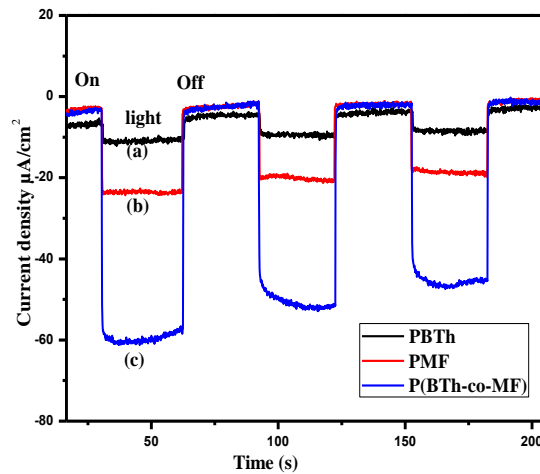


FIGURE 4. Photocurrent density-time dependencies obtained with PBTh/ITO, PMF/ITO and P(BTh-co-MF)/ITO electrode.

4. CONCLUSIONS

The electrochemical and photophysical properties of alternating PBTh, PMF and copolymer A copolymer P(BTh-co-MF) was synthesized and its spectroelectrochemical properties were studied. The films of the copolymer was carried out electrochemically in a solution (CH₃CN/LiClO₄ 10⁻¹ M) by voltammetry cyclic method. The films of polymers and copolymers obtained were characterized by SEM measurements and photocurrent. Analysis of the film obtained by cyclic voltammetry shows anodic and cathodic peaks characteristics of the oxidation and reduction of the copolymer formed. The copolymers prepared from the mixtures show both the good properties, such as good redox activity, capacitive property and electrical conductivity. The photocurrent of the copolymers increased the copolymer modified electrodes have been applying in photovoltaic cells.

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