Electrochemical and spectroscopic characterization of poly (bithiophene + 2-methylfuran) copolymer

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A B S T R A C T

In this work, Poly(bithiophene + 2-methylfuran) copolymer was successfully synthetized by an electrochemical polymerization of two monomers, bithiophene and 2-methylfuran in acetonitrile containing lithium perchlorate. The obtained copolymer was characterized via cyclic voltammetry, impedance spectroscopy, UV–visible, scanning electron microscope, conductivity and photocurrent measurements. The cyclic voltammetry study showed two redox couples characteristic of Poly (bithiophene + 2-methylfuran) copolymer. The impedance spectroscopy study revealed that the resistance of the copolymer film increases with the addition of 2-methylfuran. The photocurrent measurement showed good photoelectrochemical properties, making this copolymer an ideal candidate for photovoltaic cell applications.

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1. Introduction

Polymers based on aromatic compounds containing heteroatoms such as oxygen (O), nitrogen (N) or sulphur (S) have attracted significant interests due to their extraordinary properties. In physics, for instance, conducting polymers are of great scientific and technological importance because of their electrical, electronic, magnetic and optical properties [1,2]. The research for organic conducting polymers was started in the 1970's and largely was focused on polythiophene, polypyrole, polyfuran, polycarbazole, and their derivatives [3]; due to their potential applicability in solar cells (SCs) [4,5], organic light emitting diodes (OLEDs) [6], organic field effect transistors (OFETs) [7] and electroluminescent devices (ECDs) [8]. In addition, polythiophene and its derivatives has been extensively studied for their fascinating properties such as low band gaps, good environmental stability and swift changes of color with potential and fast response time [9]. Furthermore, polythiophene (PTh) shows a high environmental stability in both doped and undoped states. Its structural versatility led to multiple developments aimed to applications such as conductors, electrode materials and organic semiconductors [10]. Among these

derivatives, the polybithiophene (PBTh) has attracted considerable attention owing to its easy electrosynthesis: the oxidation potential of the monomer is lower than those unsubstituted or even the 3-methyl-substituted thiophenes [11]. Moreover, thiophene can be a good candidate for copolymerization with monomers such as furan [12,13], pyrrole [14], fluorine [15], benzanthrone [16] and benzothiophene [17]. However, Furan has received less attention compared to pyrrole, thiophene, aniline …. etc., because of its high oxidation potential [18,19]. Oligofurans and their derivatives exhibit several unique properties: they are highly fluorescent and electron-rich. Also, they exhibit tighter ringbone solid-state packing, greater rigidity, better solubility, smaller overlap integrals and lower polarizability than oligothiophenes [20]. Many researchers have overcome this difficulty by changing the deposition conditions [21–28].

The copolymerization is an important method of synthesis, which allow modifying various properties of polymers [29] such as electrochemical, photoelectronic, electroluminescence and electrochromic properties [30–32]. So far, copolymers of furan with 3-methyl thiophene [33], benzodithiophene with alkylsulfanyl-bithiophene [34] and benzothiophene with thiophene [17], have been prepared successfully by direct electrochemical oxidation by mixing the corresponding monomers. The electrochemical copolymerization can produce a variety of conducting materials with different electrical, optical and morphological properties.

Copolymer materials with a high conductivity and a good film-ability have been reported in literature [35].

In this work, the electrochemical copolymerization was used to synthesis bithiophene (BTh) and 2-methylfuran (MeFu). The co-polymers were studied by cyclic voltammetry (CV), electrochemical impedance (EIS), UV–visible spectroscopy; scanning electron microscopy (SEM) coupled with dispersive X-ray (EDX) analysis and conductivity measurements. The modification of PBTh proprieties by addition of MeFu was reported to enhance the performance of this photovoltaic device.

2. Experimental

2.1. Materials

The monomers used are bithiophene and 2-methylfuran (Aldrich products). Their chemical structures are shows in Fig. 1. The supporting electrolyte used for the electrochemical and pho-toelectrochemical characterization is the lithium perchlorate ($LiClO_4$, Fluka) which is a pure salt suitable for analysis purposes, dissolved in acetonitrile solvent CH_3CN (Aldrich). This electrolyte was preferred than others due to its solubility in organic and aqueous solutions as well as its electrochemical stability in a large potential range.

2.2. Preparation and characterization of the film

The electrochemical polymerization of bithiophene and 2-methylfuran was carried out in a one-compartment cell relied to Potentiostat/Galvanostat (PGZ-401 Voltalab 40) coupled with a computer equipped with software (voltamaster 4) which makes it possible to select the electrochemical technique and to fix the desired parameters. The reference electrode was a saturated calomel electrode (SCE). The working electrode used for the cyclic voltammetry experiments was a platinum disc (with a diameter of 1 mm) and indium tin oxide (ITO, SOLEMS with a resistivity of 50 Ω/cm^2 and a thickness of 100 nm) and the counter electrode was a platinum plate.

The analysis of the copolymer was carried out by cyclic vol-tammetry (cycling) in solvent/supporting electrolyte system ($CH_3CN/LiClO_4$ 10^{-1} M solution), containing 10^{-2} M as the mono-mer (BTh) and 2-methylfuran with different concentrations (10^{-4}; 5×10^{-4}; 10^{-3}; 5×10^{-3} and 10^{-2} M), between 0 and 2 V/SCE, at the scan rate of 50 mV/s. After polymerization, the film was rinsed with acetonitrile in order to remove any trace left from the monomers or the oligomers.

The electrochemical impedance spectroscopy measurements were carried out under alternating voltage of 10 mV, in the 100 kHz and 50 mHz frequency range. The cell used during the impedance measurements was a traditional cell containing $CH_3CN/LiClO_4$ 10^{-1} M solution without the monomer.

The polybithiophene, poly (2-methylfuran) and P(BTh + MeFu) films, deposited on a transparent ITO electrode, were characterized by UV–vis absorption spectroscopy, using a Shimadzu UV 1800 – PC spectrophotometer. The photocurrent measurements were recorded 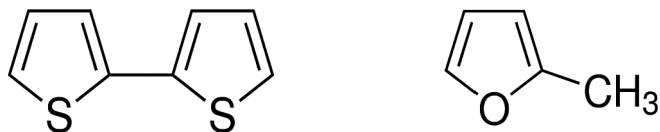with a 500-W halogen lamp as a polychromatic light source and the illumination intensity was 100 mW/cm^2. The morphology of the deposited layers was observed by scanning electron microscopy (SEM) model: JEOL, JSM-7001F microscope operating and the electrical conductivity measurements were performed on 1 nm thick pellets using a Keithley model 2400 Lucas Labs Pro 4.

3. Results and discussion

3.1. Electropolymerization of bithiophene (BTh)

Fig. 2 shows the cyclic voltammograms (repetitive cycling) corresponding to the electrochemical polymerization of bithio-phene (10^{-2} M) dissolved in $CH_3CN/LiClO_4$ electrolyte solution. These voltammograms were recorded in the potential range be-tween 0 and 2 V/SCE with scan rate of 50 mV/s. There was an anodic peak at 1.22 V and a second one at 1.54 V/SCE which appears only at the first scan; representing the first and the second oxidation of the monomer (BTh) to its radical cation [36]. It should be noted that the working electrode surface was covered by a polymer film upon the first cycle and was accompanied by a color-reversible change from the red at the oxidation to blue at the reduction. In the reverse scan, a cathodic peak was obtained at 0.88 V/SCE corresponding to the reduction of the formed polymer film.

The anodic and the cathodic peaks, respectively, refer clearly to the oxidation and the reduction of the polybithiophene. With the cyclic voltammetry scans, the generation of a new redox couple and an increase in the current intensity of the oxidation and the reduction peaks, is a clear evidence indicating the deposition of the polymer film on the electrode surface [37].

3.2. Electropolymerization of (bithiophene +2-methylfuran) copolymer

The cyclic voltammograms corresponding to the ($CH_3CN/LiClO_4$ 10^{-1} M) solution, containing BTh (10^{-2} M) and MeFu for different concentrations (10^{-4}, 5×10^{-4}; 10^{-3}; 5×10^{-3} and 10^{-2} M), recording at v = 50 mV/s, between 0 and 2 V/SCE, are represented in Fig. 3. The electrode (Pt) was cleaned before each recording and the solution was slightly stirred for homogenization before each experiment.

The obtained cyclic voltammograms show during the positive scan potential, an anodic peak at 1.6 V, preceded by others at 1.40 V and 0.7 V/SCE which were characteristic to the oxidation of the two monomers (bithiophene and 2-methylfuran) present in the solu-tion. During cathodic scan potential, there was a peak at 0.8 V/SCE corresponding to the reduction of the copolymer. The overall oxidation peaks and waves were recombined into a single oxidation peak potential at 1.45 V/SCE. In addition, the oxidation peaks and wave current intensities decrease slightly with the increase in MeFu concentration. Consequently, the electrode inhibition results in oxidation products of 2-methylfuran among, and ring opening products may be produced [38] due to the MeFu molecule fragility (resonance energy = 16 kcal) [39]. These products are strongly adsorbed on the electrode and inhibit it. They are therefore, involved in the design of a less conductive copolymer which is obtained from the single bithiophene.

As previously reported [40], the mechanism of the electro-polymerization of conducting polymers and polyheterocycles occurred by the coupling via α-α bonding of monomer radical cation after its oxidation at the electrode. However, the MeFu has just one free, α position, the other is occupied by the methyl group. In the case of the radical cations coupling, resulting from the two monomers (BTh and MeFu), the electropolymerization reaction can lead to the formation of oligomers consisting of n bithiophene
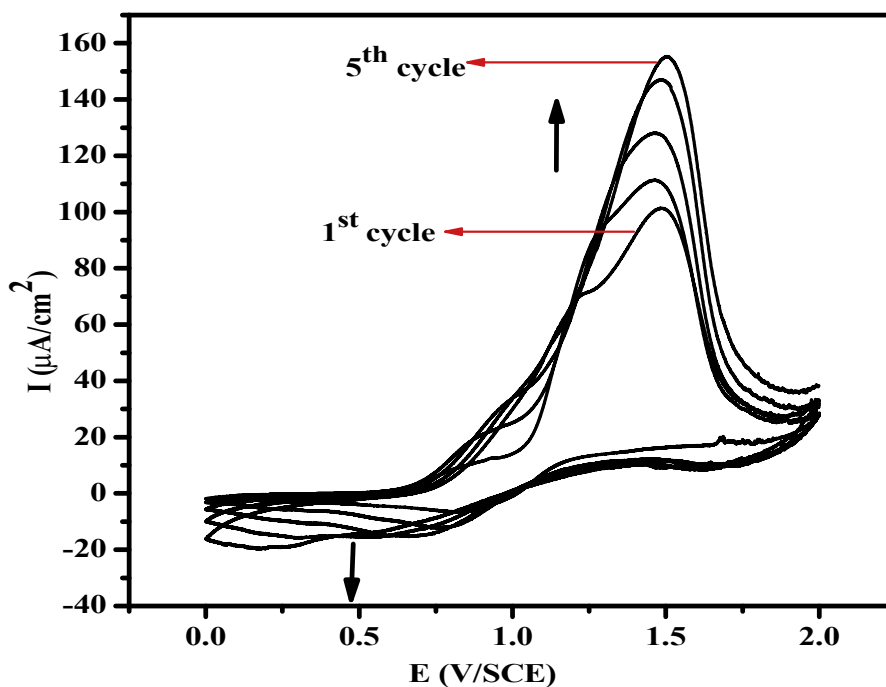

Fig. 1. Chemical structure of bithiophene (BTh) and 2-methylfuran (MeFu).

Fig. 2. Cyclic voltammograms (repetitive cycling) corresponding to the bithiophene 10^{-2} M in $CH_3CN/LiClO_4$ (10^{-1} M) solution, recorded between 0 and 2 V/SCE, at a scan rate of 50 mV/s, on a Pt electrode (Ø = 1 mm).

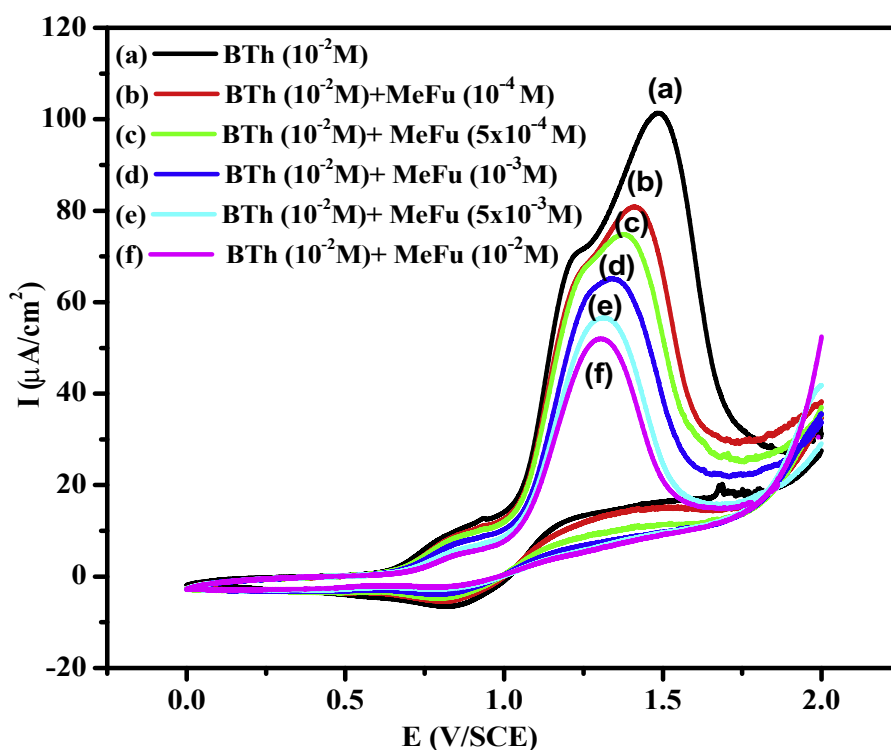**Fig. 3.** Cyclic voltammograms relating to a solution of BTh (10^{-2} M) dissolved in $CH_3CN/LiClO_4$ (10^{-1} M), obtained for different concentrations of MeFu (10^{-4}; 5×10^{-4}; 10^{-3}; 5×10^{-3} and 10^{-2} M), recorded between 0 and 2 V/SCE with v = 50 mV/s.

closed at the extremities by 2-methylfuran ring. Thus, the comonomer formation starts with the monomer which has lower oxidation potential. In this present work, BTh has a lower oxidation potential than MeFu, therefore the MeFu-(BTh)$_n$-MeFu copolymer (with n ≥ 1) (Scheme 1) can be formed on the electrode surface. On the other hand, the possibility of ring opening products formation
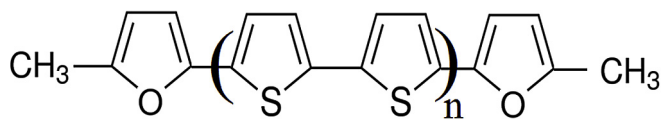
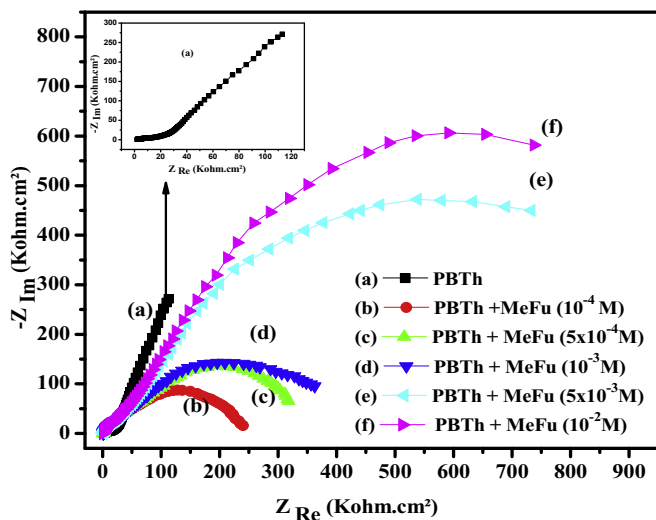**Scheme 1.** Mechanism of bithiophene and 2-methylfuran copolymerization.

Fig. 4. Nyquist diagrams corresponding to the copolymer film of P(BTh + MeFu), recorded on a frequency range between 100 kHz and 50 mHz and obtained for different concentrations of MeFu.

during the electropolymerization process of 2-methylfuran is not excluded. B. Demirboğa [25] has electropolymerized 2-methylfuran in acetonitrile and the obtained polymer film was found to include a large amount of saturated rungs and ring opening components. The same results were in fact confirmed in our previous study [38].

3.3. Electrochemical impedance spectroscopy measurements (EIS)

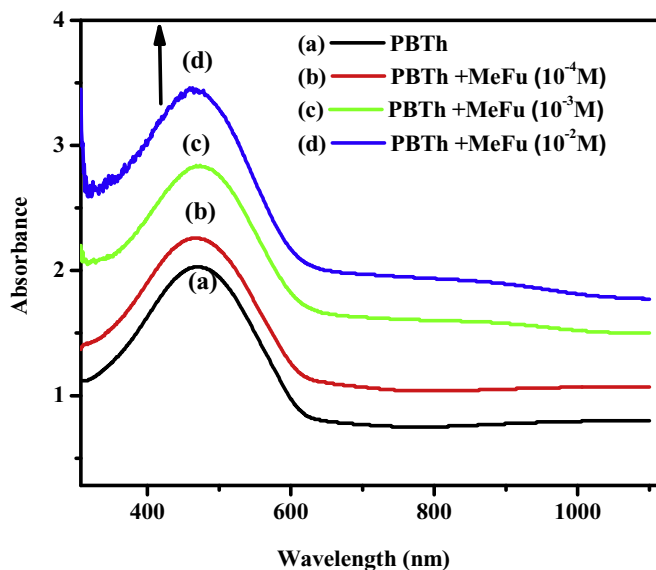The electrochemical impedance spectroscopy response (Nyquist

Fig. 5. UV–vis absorption spectra of PBTh and copolymer P(BTh + MeFu), obtained for different concentrations of MeFu.
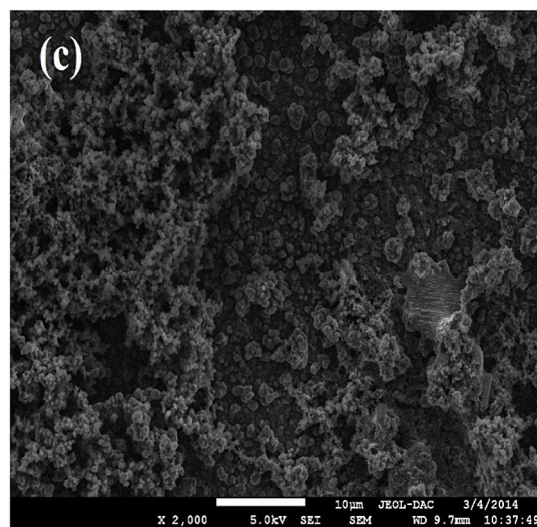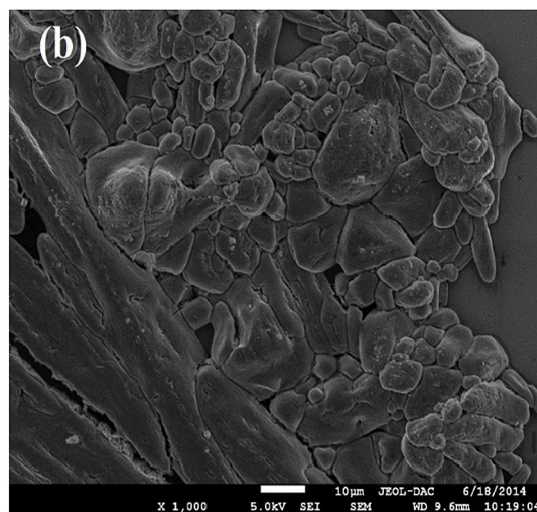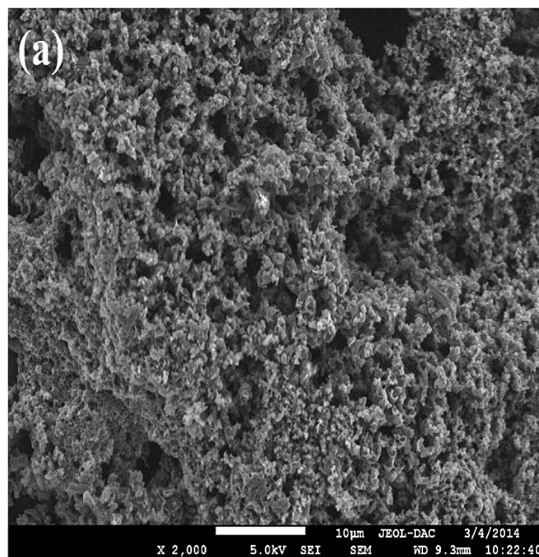

Fig. 6. Scanning electron microscopy (SEM) of PBTh, PMeFu and P(BTh + MeFu) copolymer films.

diagrams) of PBTh and P(BTh + MeFu) copolymer, obtained with solvent/electrolyte system ($CH_3CN/LiClO_4$ 10^{-1} M), in a frequency range between 100 kHz and 50 mHz are shown in Fig. 4. In the case of PBTh, a semicircle was observed at high frequencies and a straight line at low frequencies region [41] corresponding, respectively, to the charge transfer and diffusional process. In the case of the copolymers, the EIS diagrams were represented by two consecutive arcs; one at high and the other at low frequencies, which are both characteristics of two processes of charge transfer, the first arc remains practically unchanged. The diameter of the second semi-circle of (BTh + MeFu) copolymer increases with the increase in MeFu concentration suggesting an augmentation in the resistance and thus a decrease in the conductivity of P(BTh + MeFu) film.

3.4. UV–visible spectroscopy of copolymer film

The UV–vis absorption spectra of PBTh and P(BTh + MeFu) copolymer films deposited on ITO blade are shown in Fig. 5. The polybithiophene exhibits a maximum absorption at 471 nm in the neutral state. This broad absorption band corresponds to the π-π* transition of the conjugated polymer main chain. The width implies the coexistence of both long and short effective conjugation lengths. In the case of the copolymer, the absorption band shifts to a high wavelength value (low energy) and a bathochromic displacement of the maximum absorption with a significant

Table 1
Conductivity measurement results of PBTh, and P(BTh + MeFu) copolymer films.

Samples	Conductivity (S/cm)
PBTh	4.60×10^{-2}
PBTh + MeFu (10^{-4} M)	4.10×10^{-2}
PBTh + MeFu (10^{-3}M)	3.69×10^{-2}
PBTh + MeFu (10^{-2}M)	3.04×10^{-2}

decrease in the gap [42].

3.5. Morphology

The morphology of PBTh, PMeFu and P(BTh + MeFu) copolymer films deposited on ITO electrode, was examined using scanning electron microscope SEM. The photographs, in Fig. 6, show the polymer film in the three cases electrodeposited in a uniform way on the electrode surface but the film morphology was different. In the case of PBTh (Fig. 6a), the film was formed into small grains, whereas, in the case of PMeFu, the grains (Fig. 6b) were coarser. The surface morphologies of P(BTh + MeFu) copolymer films are intermediate between those of PBTh and PMeFu, as shown in Fig. 6c.

3.6. Electrical conductivity measurement

The electrical conductivity of PBTh and P(BTh + MeFu) thin films were measured via four-probe technique at room temperature. The conductivity of the copolymers was measured and summarized in Table 1.

Usually, conducting polymers show conductivity over a wide range i.e., from 10^{-11}–10^2 S/cm. The conductivity values of PBTh and P(BTh + MeFu) films obtained from different concentrations of MeFu, were 4.60×10^{-2}; 4.10×10^{-2}; 3.69×10^{-2} and 3.04×10^{-2} S/cm respectively, showing that the conductivity of PBTh is more important compared to that of the copolymers. This is related to the difference in the conjugation lengths of tow polymers [43]. The conductivity decreases when the MeFu is added, this result is in good agreement with that obtained by EIS, where an increase of the semi-circle diameter was observed, suggesting a decrease of the film conductivity.

3.7. Photoelectrochemistry

Fig. 7 shows the current density variation with time for PBTh and P(BTh + MeFu) deposited by cycling on ITO in $CH_3CN/LiClO_4$

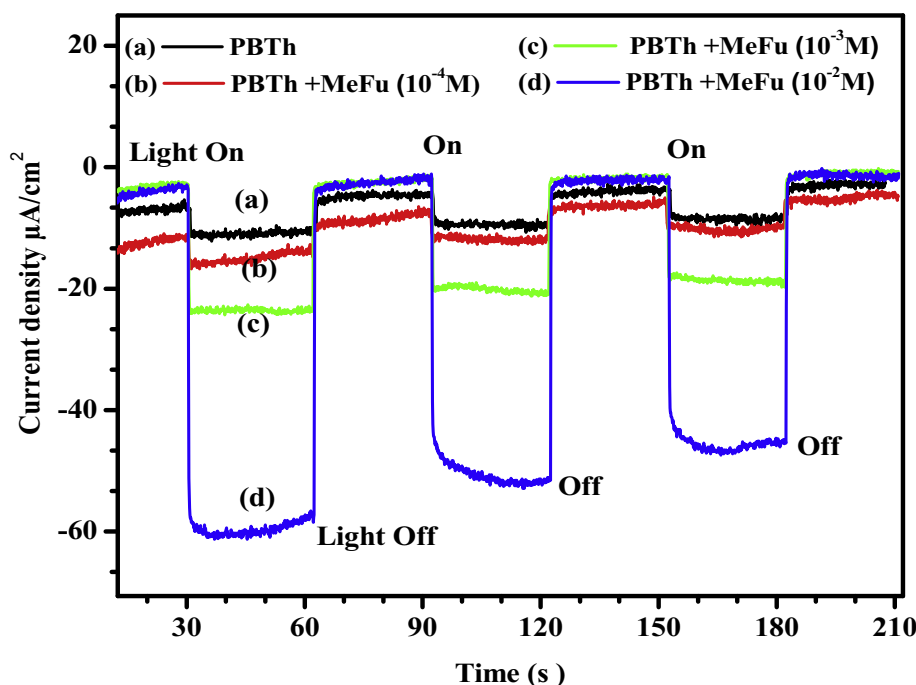**Fig. 7.** Photocurrent density–time for PBTh/ITO and P(BTh + MeFu)/ITO electrodes, obtained for different concentrations of MeFu, in ($CH_3CN/LiClO_4$ 10^{-1} M) solution, observed upon switching the light on and off.

10^{-1} M, with an imposed potential of -1000 mV, excited by polychromatic light every 30 s. The photocurrent was observed to increase with the addition of MeFu to the BTh film.

As shown, the copolymer film presents a cathodic peak of photocurrent immediately after irradiation. This response indicates that the recombination process was occurring in the film because of the presence of charge carriers in the bulk polymer, mainly due to the structural disorder of the copolymer (the copolymer-like behavior of p-type polymers, as observed by F. Habelhames et al.) [44,45].

4. Conclusion

Polybithiophene and Poly (bithiophene + 2-methylfuran) have been prepared by cyclic voltammetry (cycling) method and the physicochemical properties of the obtained copolymers were studied by different electrochemical and spectrometric methods. The analysis of the obtained film shows anodic and cathodic peaks characteristics of the oxidation and the reduction of the formed copolymer. The morphological analysis of the surface of the films by SEM shows that the presence of MeFu modifies the electrochemical properties and the morphology of the polybithiophene. It is also observed that the optical properties indicate that the copolymer film reveals the corresponding transitions which lead to a bathochromic shift of the maximum absorption with a significant decrease in the gap. The copolymer photocurrent increases the copolymer-modified electrodes to be used in photovoltaic cells.

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