Electrochemical Copolymerization of Bithiophene and 3, 4-Ethylenedioxythiophene

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The copolymerization of bithiophene (Bt) and 3, 4-ethylenedioxythiophene (EDOT) was realized electrochemically in electrolyte solution containing acetonitrile/hexafluorophosphate tetrabuthylammonium by direct anodic oxidation of the monomer mixtures on platinum electrode. As-formed copolymers own both the advantages of polybithiophene polyBt and poly 3,4-ethylenedioxythiophene polyEDOT, good electrochemical behavior, low band gap and important values in resistivity measurments. The corresponding polymers are characterized by cyclic voltammetry and UV-vis spectroscopy. The band gap values (E_g) of the polymers are found to be 1.56, 0.23 and 0.35 eV for PolyBt and PolyEDOT and copolymer, respectively.

Keywords: Electropolymerization, voltammetry cyclic, band gap; p-doping process, n-doping process.

1. INTRODUCTION

Upon copolymerization, conducting polymers show remarkable physical and chemical changes. This is accomplished by altering the nature of the monomers, their composition, and the structure of the resulting polymers (random, alternating, block, etc.) [1]. In this regard, Zhou et al. [2] Have successfully copolymerized butyl-3-thiophene and bromo-3-thiophene (luminous) on stainless steel electrodes. Furthermore, copolymers of pyrrole with bithiophene [3], thiophene with furan [4,5], thiophene with pyrrole [6], thiophene with fluorite [7], thiophene with benzanthrone [8], and thiophene with benzothiophene [9], were prepared by electrochemical oxidation of mixtures of two monomers. By electrochemically oxidizing a mixture of monomers, the corresponding copolymer can be produced. This is because the oxidation potentials of the monomers are close to each other.

Int. J. Electrochem. Sci., 17 **(2022)** Article Number: 220610

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The electrochemical copolymerization of furan and methyl-3lthiophene, at different polymerization potentials, for example, was carried out by Li et al. [2]. They used spectroscopy infrared to confirm that the methyl-3-thiophene units had been incorporated into the chain of copolymers and that the amount of these incorporated units increases with the potential of oxidation imposed. The quality of the deposited PFu was improved, and the opening of the cycle was reduced to a minimum by the introduction of a little pyrrole or thiophene in the matrix of polymer.

In the present work, Bt and EDOT were copolymerized succefully by electrochemical oxidation of the monomer mixtures

The electrochemistry of PolyBt, PolyEDOT and copolymers of Bt with EDOT were studied. In addition, spectroscopic properties and resistivity measurements of the copolymer were investigated in detail.

2. EXPERIMENTAL

2.1. Reagents and solvents

Commercially available EDOT (Aldrich), tetrabutylammonium hexafluorophosphate (Bu_4NPF_6), and acetonitrile (CH_3CN) were used without further purification. Bithiophene, on the other hand, was purified by recrystallization.

Electrolytic solution (Bu_4NPF_6 0.1 M in CH_3CN) was dried in presence of Aluminum oxide (Al_2O_3) previously heated at 450°C under vacuum during 24h and keep under argon atmosphere.

2.2. Electrochemical studies

Electrochemical experiments were performed under argon atmosphere using a Pt disk electrode (diameter 1 mm). The counter electrode was a vitreous carbon or platinum rod and the reference electrode was SCE. The three electrodes cell was connected to a Voltalab PGZ 301. Activated Al_2O_3 was added in the electrolytic solution to remove excess moisture. For a further comparison of the electrochemical and optical properties, all potentials are referred to the SCE electrode.

Following the work of Jenekhe [10], we estimated the electron affinity (EA) or lowest unoccupied molecular orbital (LUMO) and the ionization potential (IP) or highest occupied molecular orbital (HOMO) from the redox data. The LUMO and HOMO levels was calculated from the following empirical equations: $LUMO (eV) = - [E_{onset}^{red} (vs SCE) + 4.4]$ and the HOMO level from: $HOMO (eV) = - [E_{onset}^{ox} (vs SCE) + 4.4]$, based on an SCE energy level of 4.4 eV relative to the vacuum. The electrochemical gap was calculated from: $\Delta E^{el} = |HOMO-LUMO|$ (in eV).

For large scale polymer film production for the spectroscopic characterization, platinum or ITO glass electrodes with a larger surface area were employed as working electrodes and potensiostatic method at properly chosen potential was used.

2.3. Characterization

UV-Vis measurements were performed on a JASCO V-660 spectro-photometer, Optical band gap was calculated from the edge of the absorption spectrum using $\Delta E^{opt} = \frac{hc}{\lambda}$, that can be simplified in $\Delta E^{opt} = 1239.84/\lambda_{onset}$ with λ in nm.

The resistance of formed polymer films was measured by conventional four-probe techenique.

3. RESULTS AND DISCUSSION

3.1. Electrochemical copolymerization

In order to ensure the copolymerisation of Bithiophene with EDOT, the electrochemical experiments were classified into different groups on the basis of feed ratios of two monomers. According to the method of Kuwabata et al [11], the concentration of Bthiophene was chosen as 0.025M, while that of EDOT was 0.05M.

Figure 1 reports the cyclic voltammetry of the two monomers recorded in oxidation and in reduction. Interestingly, the oxidation of Bt monomer, recorded at 1.3 V, was observed to be less easy than that of EDOT (1.55 V). Furthermore, figure 1 shows, also, that the oxidation onset of the monomers is recorded at 1.2 V and 1.13 V (Fig.1A and 1B) respectively, which implies that the copolymerization is feasible.

The anodic curves of the monomers, as well as that of a mixture of these monomers, are shown in Figure 1. What is interesting about the data in this figure is the different anodic curve between the monomers and their mixture. Further, the oxidation onset of the mixture of two monomers is initiated at 1.4V, which is between Bt and EDOT. This may be partly due to some changes of the electrochemical environment caused by successive deposition of the two monomers during the anodic polymerization. Similar results of copolymer oxidation induced by Bt and EDOT have been reported in the literature [11–13]. Furthermore, the fact that the oxidation potential of the mixture of Bt and EDOT is between that of the two monomers suggests that the two monomers are oxidized alternately, and the copolymer chains are composed of alternate Bt and EDOT units, indicating the occurrence of copolymerization. The result found is quite comparable to that shown in the literature [14].

In the cathodic range, the three compounds exhibit irreversible reduction waves. -1.18 V for Bt,- 1.14 V, -1.17 V for EDOT and -1.17 V for copolymer (fig 1A, 1B, 1C). We can clearly see that the reduction and reduction onset of the mixture occur between Bt and EDOT.
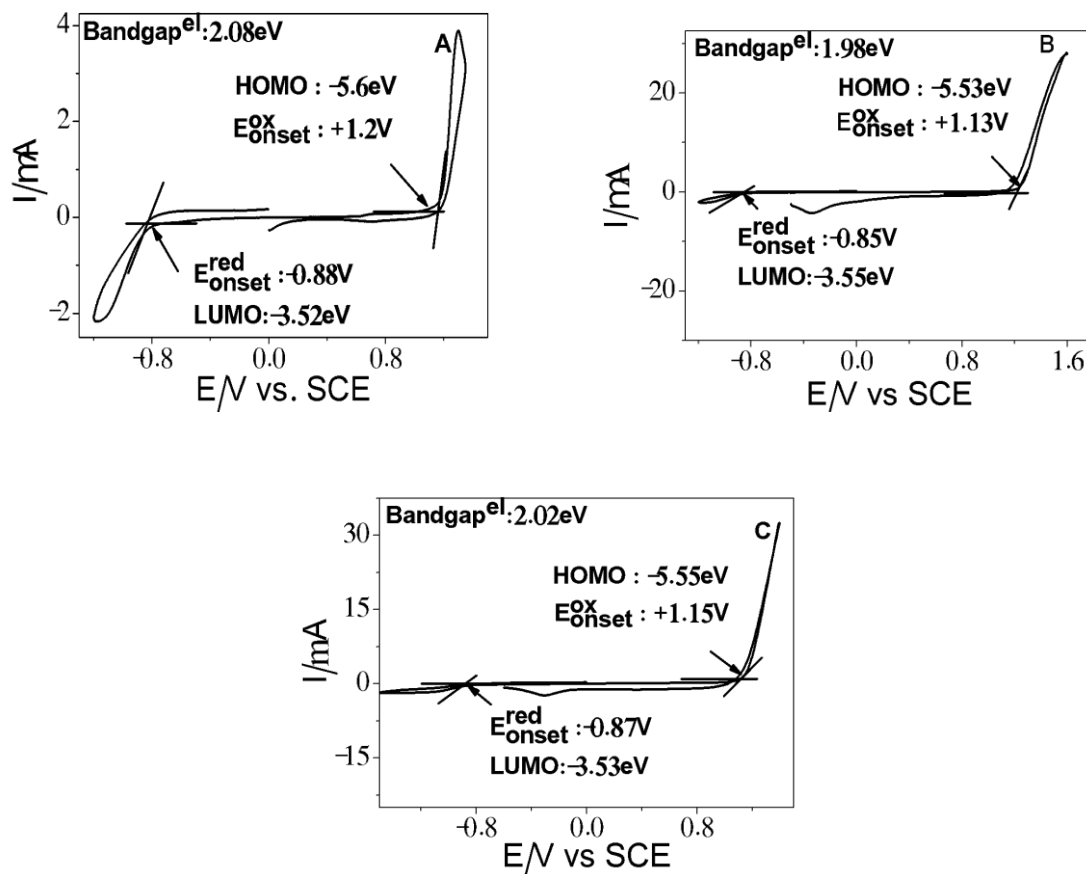
Figure 1. Cyclic voltammetry recorded in CH_3CN + 0.1 M Bu_4NPF_6 of (A) 0.025 M Bt, (B) 0.05 M EDOT and (C) 0.025 M Bt + 0.05 M EDOT, Sweep-rate: 100 mV/s, working electrode: platinum disk, diameter 1 mm.

From the onset of the first oxidation and reduction waves, HOMO and LUMO levels were calculated by Jenekhe format [10]. Bt with HOMO and LUMO levels calculated at -5.8 eV and -3.62 eV presents a lowest band gap (ΔE^{el} : 2.08 eV) than EDOT (HOMO: -5.53 eV, LUMO: -3.55 V and ΔE^{el} : 1.98 eV) And copolymer (HOMO: -5.55 eV, LUMO: -3.53 V and ΔE^{el} : 2.02 eV). Notably, the monomer EDOT is more easily oxidized and reduced than Bt, leading to a 0.1 eV contraction of the band gap from Bt to EDOT.

3.2. Electropolymerization processes of the monomers

For Bt, the intensity of the new redox systems, Ian (5 mA per cycle), is in the same range as the intensity recorded at $E1^{ox}$ during the first cycle (4.45 mA).

For EDOT, Ian at cycle 10 (25 mA), is as strong as the intensity at $E1^{ox}$ at cycle 1 (16 mA), and for the copolymer, the intensity of new redox systems Ian (20 mA at cycle 10) is less than the intensity recorded at $E1^{ox}$ in the first cycle (30.1 mA). This demonstrates that the polymerization process is much more efficient for EDOT than for Bt in the first cycle.
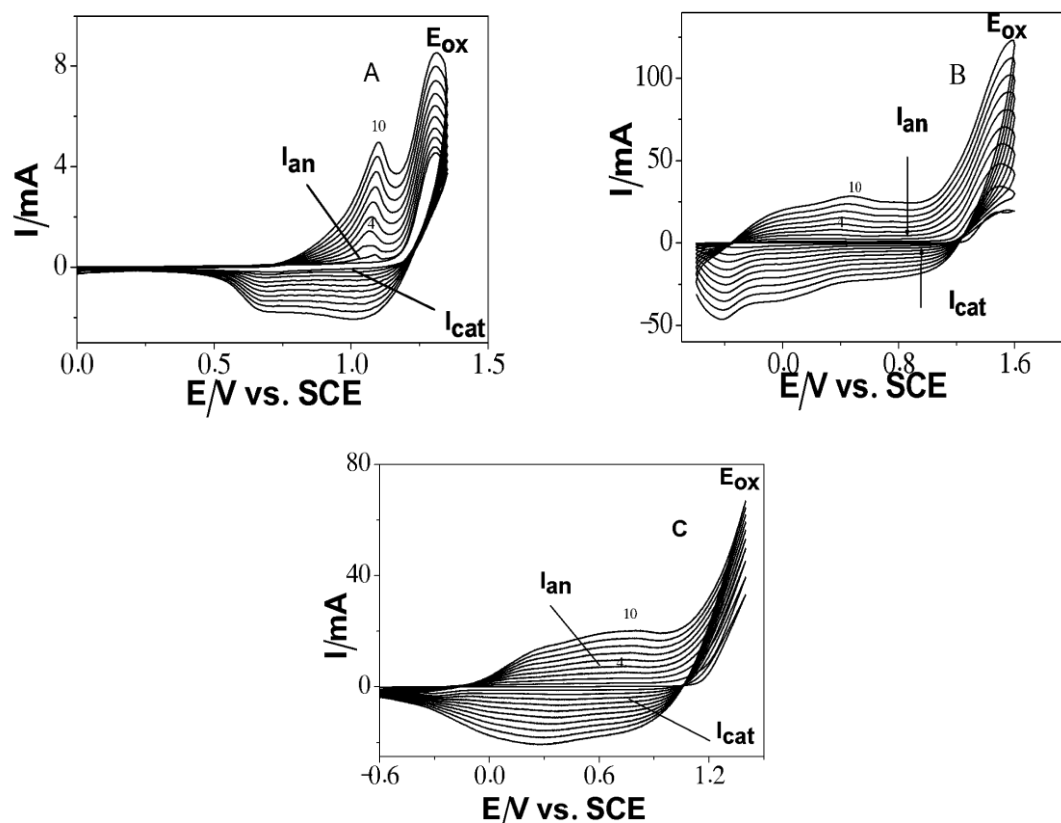
Figure 3. Cyclic voltammograms in CH_3CN/Bu_4NPF_6 0.1 M of Bt 0.025M, 10 sweeps between 0.0 and 1.4 V,of EDOT 0.05 M, 10 sweeps between -0.6 and 1.45 V and copolymer (0.025M Bt+0.05M EDOT) 10 sweeps between -0.6 and 1.4 V Scan rate: 100 mV.s^{-1}.

In order to obtain larger amount of polymer, for physicochemical analysis (UV, RESISTANCE…), electropolymerization of Bt, EDOT and copolymer was also performed with success along potentiostatic oxidation, at a potential slightly more positive than E^1_{ox} on working electrode of larger area (platinum, ITO glass electrodes).

As the polymers covering the electrode are insoluble in classical solvent, the study of their electrochemical behaviors was performed in a second electrochemical cell, in absence of monomer, using the previously modified platinum electrodes [22].

3.2. Electrochemical behaviour of the derived polymers

Figure 5 shows the modified electrodes were cycled repeatedly between their oxidized and reduced states without significant decomposition of the material, as shown by the stable recurrent cycles. As for their respective precursors BT, EDOT and copolymer, the cyclic voltammetries of the polymer allows calculating the HOMO, LUMO and electrochemical band gap of the derived polymers.

PolyBt with onset oxidation and reduction potentials at 0.81 V and -0.84 V respectively, has a HOMO/ LUMO energy levels at -5.21 eV/ -3.56 eV and therefore an electrochemical band gap ΔE^{el} of 1.56 eV.

PolyEDOT is oxidized at low potential values with onset oxidation at 0.13 V and is reduced at lower potential value with onset reduction at -0.1 V, leading to HOMO and LUMO levels at -4.53 eV and -4.3 eV respectively, and a band gap ΔE^{el} of 0.23 eV much less than the polyBt band gap.

The polyEDOT band gap contraction (1.33 eV) is 13 times bigger range than polyBt; this is due to the high conductivity of polyEDOT when oxidized and reduced.

For the copolymer formed with onset oxidation and reduction potentials at 0.15 V and -0.2 V, respectively, has its HOMO/ LUMO energy levels at -4.55 / -4.2 eV and therefore an electrochemical band gap ΔE^{el} of 0.35 eV. This values intervenient between polyBt and polyEDOT.
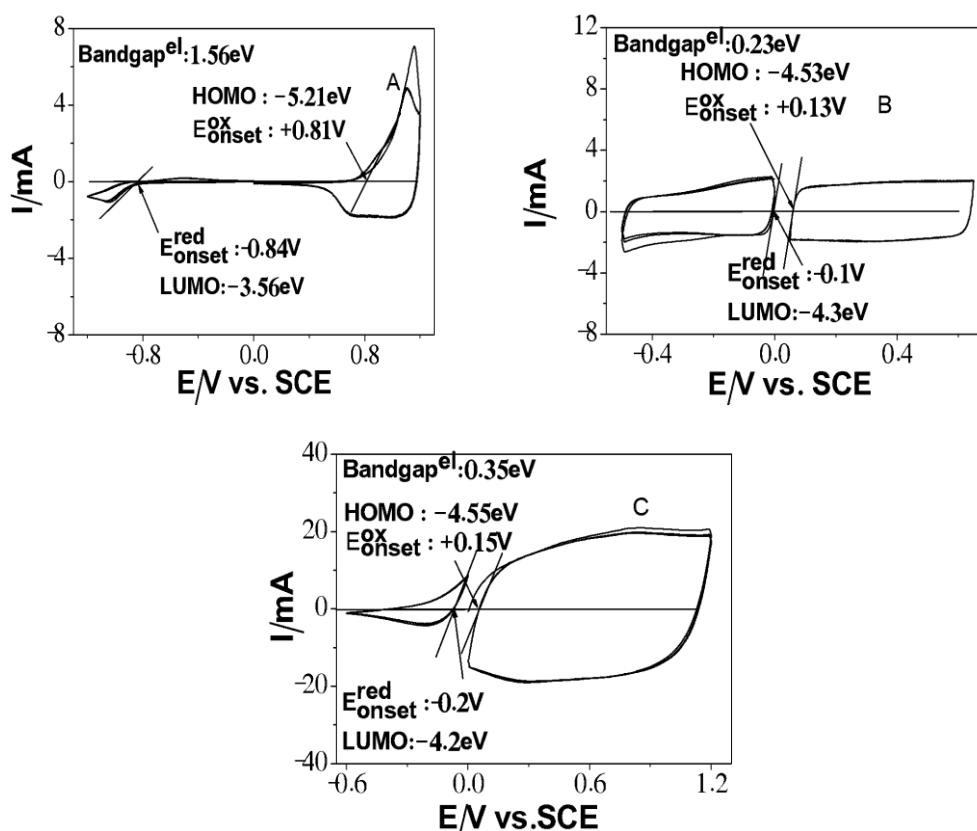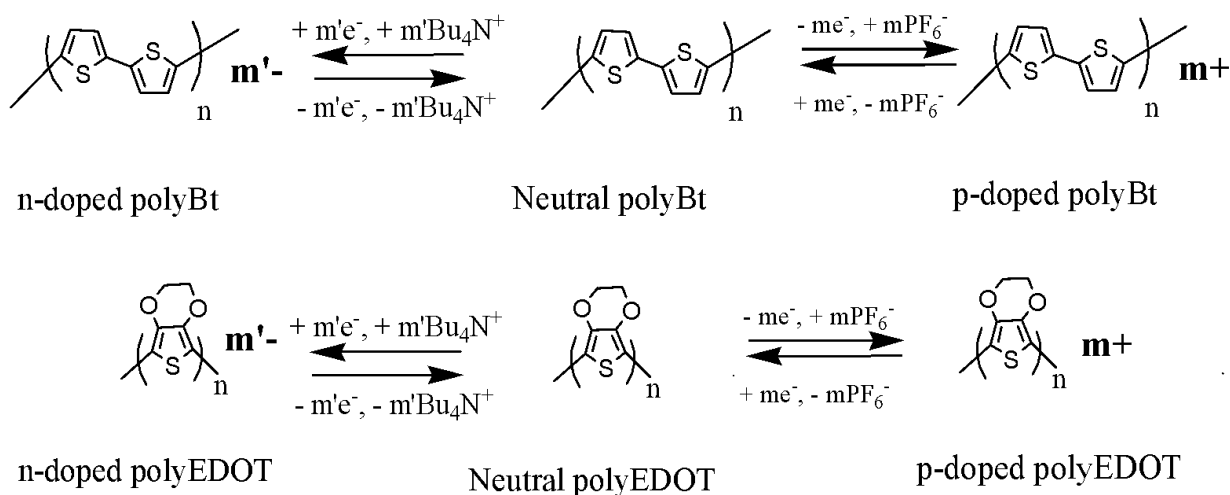

Figure 5. Voltammetric responses recorded in Bu_4NPF_6 0.1 M in CH_3CN between -1.2V and 1.3V for polyBt (A), between -0.5V and 0.5V for polyEDOT (B) between -0.6V and 1.2V for polyBt+ polyEDOT (C). Scan rate: 100 mV. s^{-1}.

The anodic and cathodic responses of the polymers are associated to the well-known p- and n-doping processes of electroactive polymers as presented in scheme 3. [15-22]

n-doped polyBt   **Neutral polyBt**   **p-doped polyBt**

n-doped polyEDOT   **Neutral polyEDOT**   **p-doped polyEDOT**

Scheme 3. Description of the p- and n- doping processes of polyBt and polyEDOT.

In oxidation, the p-doping process corresponds to an electron abstraction from the polymer backbone leading to the formation of holes; the electroneutrality of the p-doped polymer is obtained by insertion of the anion hexafluorophosphate (PF_6^-) in the polymer matrix. Under its p-doped state, mobility of holes is at the origin of the conductivity of the semi-conducting polymer. m, defined as the p-doping level, depends on the potential at which the polymer is oxidized, and the p-doping process is reversible if the polymer is not over-oxidized at too positive potential value. In reduction, the n-doping process corresponds to the reduction of the polymer matrix, leading to an excess of electrons in the polymer and accompanied by the insertion of the cation tetrabutylammonium (Bu_4N^+) for the electroneutrality. Under its n-doped state, the mobility of electrons is at the origin of the conductivity of the semi-conducting polymer. Here, m' is defined as the n-doping level and depends on the potential at which the polymer is reduced. The n-doping process is reversible since the potential does not reach the over-reduction process of the polymer. In the present study, processes appear reversible at the scale of the cyclic voltammetry between -0.2 V and 0.2 V for polyEDOT (B) and between -0.4 V and 0.6 V for poly (Bt+EDOT)(C), but for poly Bt is reversible just in oxidation at 1.0V(A) (see figure 5) [15-22].

3.4. Physical characterization of monomers and of their derived polymers
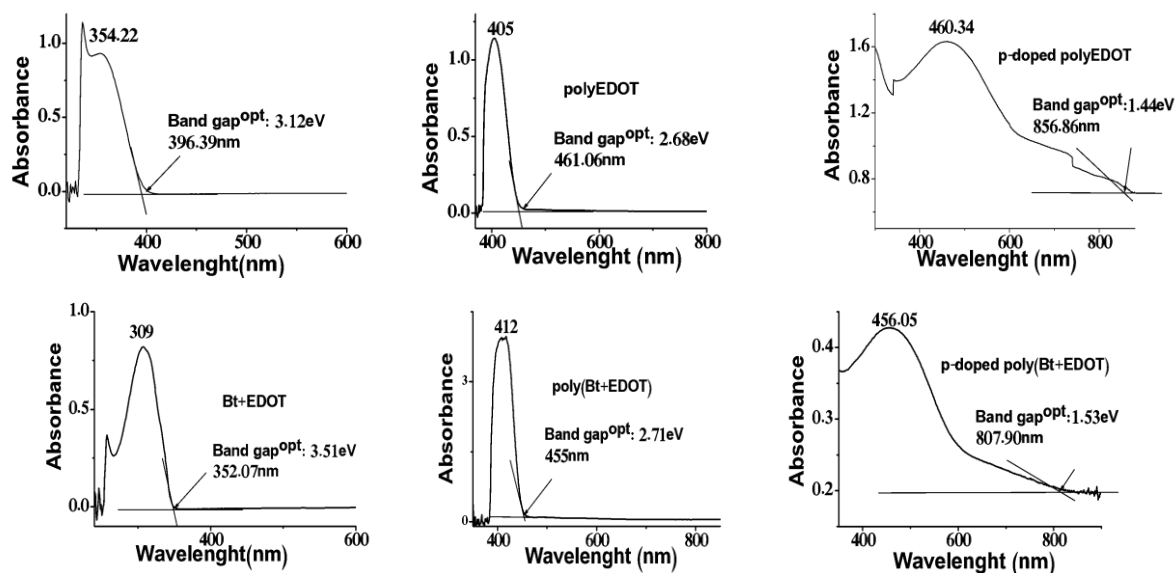
3.4.1. UV-visible spectroscopy
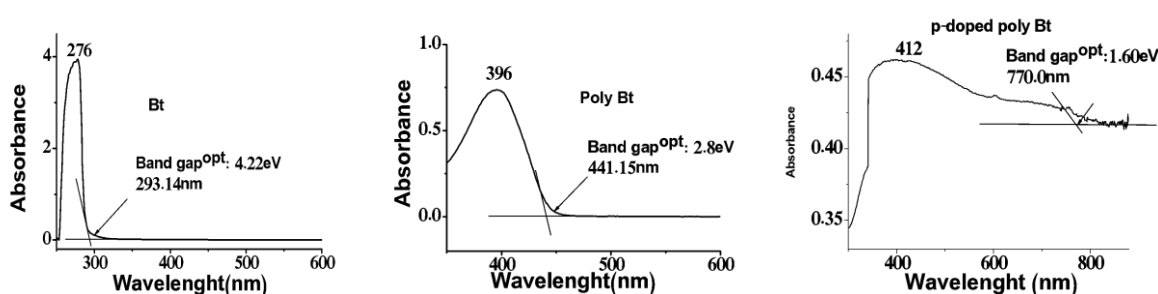
Figure 6. UV-visible spectra in DMSO of monomers and polymers

Figure 6 presents the UV-visible spectra recorded in DMSO of Bt, EDOT and Copolymer. All the monomer spectra present absorption bands centered at 278, 364.22 and 309 nm, respectively. Moreover, the calculated optical band gaps of Bt, EDOT and the copolymer is 4.22 eV, 3.12 eV and 3.51 eV, respectively.

We found that, the value of the measured gap is between That of BT and EDOT, and The difference of 1.2 eV between the two optical band gaps of BT and EDOT is lower than the one calculated from electrochemical studies (0.1 eV) [15-22].

After polymerization on a transparent glass electrode coated by a thin indium-tin oxide (ITO) layer, the UV spectra of the polymers in their p-doped states were recorded.

The spectrum of polyBt shows a main absorption band at 412 nm, but with a long tail up to 700 nm, showing an extension of the conjugation from the monomer to the polymer.

The optical band gap calculated from the onset absorption wavelength (770nm) is around 1.60 eV.

In the wavelength range used for this study, a spreading of the absorption band of the p-doped polymer is observed, which therefore exhibits a significant charge transfer character.

The UV spectrum of polyEDOT has a band at 460.34 nm with a long tail up to 850 nm.

The optical band gap calculated from the onset absorption wavelength (825.86 nm) is 1.44 eV,

For poly (BT+EDOT) his spectrum shows a band centered at 468.06 nm.

The optical band gap calculated from the onset absorption wavelength (807.90 nm) is 1.53 eV.

The spectrum of copolymer shows the characteristic absorption of both polyBt and polyEDOT.

After its synthesis as a thick film on a platinum electrode, we attempt to solubilise the polymer in DMSO. Figure 6 presents the UV-visible spectrum of the solubilised fraction of polymers obtained from Bt, EDOT and copolymer. From this spectrum we note a main absorption band centered at 396, 408 nm and 405nm, respectively. λ_{onset} around 441,461 and 455 nm leading to an optical band gap of

2.8, 2.68 and 2.71 eV. However, this band gap is in great accordance with the results calculated from electrochemical studies [15].

The obtained results are presented in and in Table 1.

Table 1. Optical and electrochemical band gaps of the polymers

Polymers	Λmax (nm)	Λonset (nm)	E_g^{opt} (eV)a	E_{onset}^{ox} (V)b	E_{onset}^{red} (V)c	EHOMO (eV)d	ELUMO (eV)e	E_g^{el} (eV)f
	412	770	1.6	0.81	-0.84	-5.21	-3.56	1.56
	460.34	856.86	1.44	0.13	-0.1	-4.53	-4.3	0.23
Copolymer	456.04	807.90	1.53	0.15	-0.2	-4.55	-4.2	0.35

[a] Energy of the band gap calculated from UV–vis spectroscopy, Eg opt= 1237.5/λonset.
[b] First oxidation potentials of the monomers and polymers from CV measurements.
[c] First reduction potentials of the monomers and polymers from CV measurements.
[d] Energy of the highest occupied molecular orbital calculated from E HOMO= (Eox onset+ 4.4).
[e] Energy of the lowest unoccupied molecular orbital calculated from E LUMO= (Ered onset+4.4).
[f] Energy of the band gap calculated from the difference between the energy of the HOMO and the LUMO.

3.4.1. Resistance measurement

The resistance of polyBt, polyEDOT and copolymer potentiotatically obtained from Bu_4NPF_6 0.1 M in CH_3CN solution containing 0.025M Bt and 0.05M EDOT are shown in table 2. Pure polyEDOT has the lowest resistance, which is up to 2 ohm, while the resistance of polyBt is about 8 ohm. It can be clearly seen from Table II the resistance of copolymer is between those of pure polyEDOT and Bt. This indicates that the insert of polyEDOT units into polyBt is helpful to improve the conductivity of polyBt [14].

Table 2. The resistance of polyBt, polyEDOT and copolymer

Polymer	Resistance (ohm)
PolyBt	8
PolyEDOT	2.28
Copolymer	5.5

4. CONCLUSION

In conclusion, the main electrochemical feature of the monomers, lower band gap for EDOT compared to Bt, is also observed in their respective polymers, lower band gap for polyEDOT compared to polyBt, the mixture of two monomers which has a low gap, lead to a copolymer whose gap is the average between the two compound, The most important result obtained in this work is the very low band gap (0.35 eV from electrochemical studies and 1.53 eV from optical studies).this very low band gap confers to this new copolymer a potential interest as p-semiconducting layer in BHJ solar-cells.

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