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Synthesis and Characterization of an Electrochromic Copolymer Film Bearing Two Different Donor-Acceptor-Donor Type Electrochromes

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Abstract: Two donor-acceptor-donor type monomers (**EC** and **TB)** were selected to grow a copolymer via electrochemical techniques. **EC** monomer contains 3,4-ethylenedioxythiophene as the donor and carbazole as the acceptor units, while **TB** monomer includes thiophene and benzothiadiazole as the donor and the acceptor, respectively. The resulting copolymer film was investigated in terms of its electrochemical and optical properties and compared with the homopolymers of **EC** and **TB**. The copolymer film exhibited different electrochromic properties from their corresponding homopolymers. The neutral state faded-orange color of the polymer of **EC** and magenta color of the polymer of **TB** possesed a brownish color of the copolymer in the neutral state, with having a broader absorption band in the visible region by covering the characteristic absorption bands coming from both homopolymers. The physico-chemical properties, energy gaps, optical contrasts and coloring efficiencies for the homopolymers and for copolymer were systematically studied.

***Keywords**:* Electrochromic polymer, Electropolymerization, Copolymerization.

İki Farklı Elektron Verici-Alıcı-Verici Tip Elektrokrom İçeren Bir Elektrokromik Kopolimerin Sentezi ve Karakterizasyonu

Özet: İki farklı elektron verici-alıcı-verici tip monomer (**EC** ve **TB)** kullanılarak, elektroanalitik yöntemler ile elektrokromik bir kopolimer sentezlenmiştir. **EC** monomeri, elektron verici grup olarak 3,4-etilendiyoksitiyofen ve elektron alıcı grup olarak karbazole içerirken, **TB** monomeri elektron verici ve alıcı olarak sırasıyla tiyofen ve benzotiyadiyazol birimleri içermektedir. Elde edilen kopolimer, elektrokimyasal ve optiksel özellikleri bakımından incelenmiş ve bu özellikler **EC** ve **TB** homopolimerleri ile karşılaştırılmıştır. Kopolimer film, ilgili homopolimerlerden farklı özellikler göstermiştir. Nötral halde soluk turuncu olan **EC** polimeri ile morumsu renkteki **TB** polimeri, kopolimere dönüştüğünde iki polimerden gelen daha geniş bir bant aralığını kapatarak kahverengine dönüşmüştür. Homopolimerler ve kopolimerin fiziko-kimyasal özellikleri, enerji aralıkları, optik zıtlıkları ve renklenme verimleri sistematik olarak incelenmiştir.

***Anahtar kelimeler**:* Elektrokromik polimer, Elektropolimerizasyon, Kopolimerizasyon.

1. Introduction

Electrochromic polymers are conjugated systems that have an ability to change their colors upon an applied potential. Upon oxidation or reduction, electronic absorption spectra of the polymer film amend due to the occurance of intermediate states. The

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corresponding color change is reversible and for this reason, electrochromic polymers have been getting more attention in smart applications such as displays, [1-4] smart windows, [5, 6] car rear views [7] and other electrochromic or optoelectronic applications [8-16].

By modifying the molecular structure of a conjugated compound, it is possible to achieve a coarse and fine tuning in the electrochemical and optical properties. Altering the energy gaps, oxidation and reduction rates, de-doped and doped state colors or coloring efficiency make these materials prefferable to their inorganic counterparts [17].

Structural modification of an organic semiconductor can be performed in distinct ways. The most preffered way is the combination of an electron donor with an electron acceptor in the same monomer structure, in order to extend the conjugation and decrease the band gap. This method is widely used in conjugated polymer synthesis and called donor-acceptor-donor (DAD) approach. [18, 19] Furthermore, different alkyl, alkoxy or cyclic groups can be substituted on the donor-acceptor structure, in order to achive a fine-tuning in the optical properties [20, 21] or increase the solubility of the resulting polymer [22, 23].

Copolymerization of different conjugated units is the other way of structural modification. Copolymerization can be performed either chemically [24, 25] or electrochemically. On the other hand, electrochemical polymerization technique is a quick process for obtaining a copolymer as a thin film on the working electrode, with the usage of relatively less amount of monomer. With having these advantages, various studies were reported about the synthesis of such copolymer films using electrochemical methods [26-32]. On the other hand, the widely used comonomer in such studies is 3,4-ethylenedioxythiophene (EDOT) unit, since EDOT posses excellent photoelectric and electrochemical properties.

Besides all, electropolymerization of two different DAD type electrochromes have not been investigated in the literature so far, except a recently published study by us. [33] Combination of two different DAD units in the same polymer chain resulted in a broader UV-Visible absorption with having a multichromic behavior.

Herein, a different copolymer film synthesis including two DAD type monomers was reported. The main aim of this study is to monitor the change in the electrochemical and optical properties when two DAD type monomers combined in the same polymer backbone.

2-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-7(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)-9H-carbazole (**EC**) and 4,7-di(thiophen-2-yl)benzo[c]]1,2,5]thiadiazole (**TB**) were used to obtain a copolymer film. Different from our previous study of [33], **EC** contains 3,4-ethylenedioxythiophene (EDOT) unit as a donor unit. **EC** and **TB** and properties of their homopolymers were already examined by us, previously. [34, 35] In this study, copolymerization of these monomers were investigated. Both monomers show extended conjugation when compared to their bare donors (3,4-ethylenedioxythiophene (E_{ox}: 1.55 V) and thiophene (E_{ox}: 2.20 V)). For better comparison, the homopolymers (**P(EC)** and **P(TB)**) were re-prepared in the same electrolytic conditions. Moreover, the copolymer properties were also compared with the other DAD containing copolymer in [33] and the effect of EDOT moiety in one of the comonomer were discussed.

2. Material and Methods

All the chemicals used in this study were from Sigma Aldrich. **EC** monomer had been synthesized before for a different study and used as it is. [34] **TB** monomer was commercially available from Derthon Chemicals, China. The major solvents; acetonitrile (ACN) and dichloromethane (DCM) were purified by distillation prior to use. An electrolytic solution of 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) in ACN-DCM (10-1) was used for the monomer characterizations. Polymerizations were carried out via cyclic voltammetry (CV), both on Pt disc (vs Ag/AgCl reference electrode, active working electrode area of 0.02 cm^2) and ITO-glass (vs Ag wire pseudo reference electrode, using active working electrode area of 1.75 cm^2) working electrodes. ITO-glass electrodes were commercially available from Delta Tech. (8-12 Ω, 0.7 cm × 5 cm). **EC** and **TB** monomers were mixed in one to one ratio to obtain a copolymer. All monomers were used in 0.016 M concentration and the same number of repetitive cycling were applied on the same active electrode area for each polymerization. Spectroelectrochemical investigations were performed in ACN - $TBABF_4$ blank electrolyte couple using a combined system of “Carry 60 model UV-Visible spectrometer” and a “Gamry PCI4-300 electrochemical station”.

3. Results

Figure 1 a shows the fluorescence and UV-Vis spectra of **EC** and **TB** monomers**,** collected in DCM as the solvent. The maximum of the electronic absorption for **EC** was observed at 364 nm, while that of **TB** is at 445 nm. In emission, **EC** exhibited two bands with maximum at 394 nm and 415 nm (excitation at 340 nm) and **TB** revealed one emission band having maximum at 568 nm (excitation at 430 nm). **TB** exhibited a wider Stoke’s shift as 122 nm, when compared with that of **EC** (30 nm), indicating a better intramolecular charge transfer of **TB** in the excited state. [36] This may be due to relatively weak donor-acceptor interaction in **EC** monomer, since carbazole is not a strong acceptor unit. Moreover, optical absorption ranges of **EC** and **TB** were measured at 312 - 406 nm, and 350 - 530 nm, respectively, indicating that the resulting copolymer is expected to have a wider absorption band by covering these two absorption regions. The colors of the monomer solutions in DCM under daylight and UV light were also shown in Figure 1 b and 1 c.

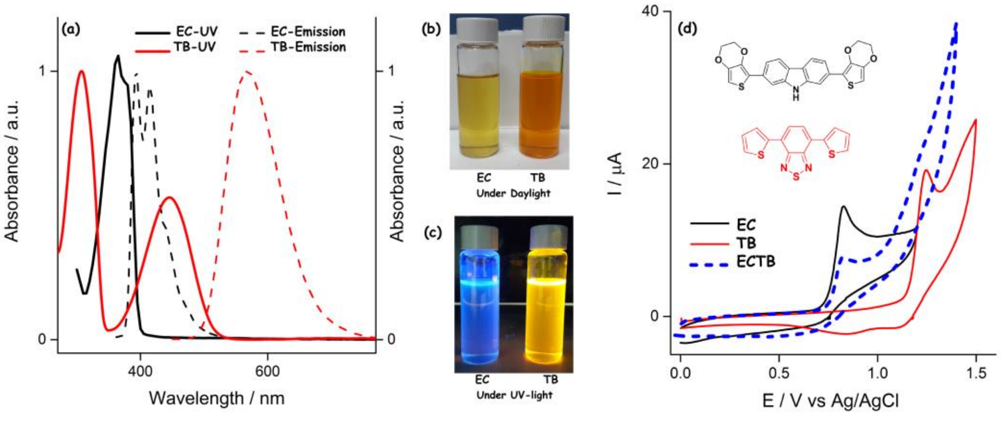

Figure 1. a) Optical absorption and emission behaviors of the monomers, **EC** and **TB**, in DCM. Color visions of the monomers under daylight (**b**) and ultraviolet light (**c**). **d)** CVs of the monomers, **EC**, **TB** and the monomer mixture (**ECTB**) measured at 100 $mV.s^{-1}$ scan rate and in the electrolytic condition of 0.1 M $TBABF_4$ – ACN/DCM. Inset of (**d**): The chemical structures of **EC** (black) and **TB** (red).

Cyclic voltammograms of the monomer mixture (**ECTB**) and of the bare monomers, **EC** and **TB** were performed in the anodic region and given in Figure 1 d (The chemical structures of the monomers were demonstrated in the inset of Figure 1 d). **EC** was scanned between 0.0 V and 1.1 V and the onset of the oxidation potential appeared at 0.74 V. The oxidation of **EC** reached its maximum at 0.83 V. For **TB** (scanned between 0.0 V and 1.50 V), oxidation onset was measured at 1.16 V and the peak point was recorded at 1.25 V. This indicates the easier oxidation of **EC** monomer. **EC** (0.016 M) and **TB** (0.016 M) then were mixed in a same electrolytic solvent in one to one ratio. Resulting monomer mixture (**ECTB)** started to oxidize at 0.75 V and showed a peak maximum at 0.83 V following by a shoulder at 1.23 V. The former oxidation might be due to **EC**, and latter may belong to **TB**. According to CVs in Figure 1 d, working range for the copolymerization was determined as 0.0 V and 1.35 V.

The electropolymerizations were then carried out on Pt disc working electrode by performing 10 repetitive cycling between the predetermined potential ranges. Resulting cyclic voltammograms were shown in Figure 2. During electropolymerization, increasing the current intensities for homopolymerizations (Figure 2 a and b) and for copolymerization (Figure 2 c) at each redox cycle indicated the polymer growth. After obtaining the polymer films, **P(EC)**, **P(TB)** and **P(ECTB)**, CVs of the polymers were collected in monomer free electrolyte solution containing ACN-TBABF$_4$. Oxidation and scan rate behaviors were revealed with these films on Pt disc electrode. Oxidation for **P(EC)**, **P(TB)** and **P(ECTB)** started at the potentials of 0.15 V, 0.85 V and 0.47 V, respectively. As expected, oxidation onset of **P(ECTB)** was recorded before **P(TB)** due to the existence of **EC** unit in the copolymer. Moreover, the maximum of the oxidation peaks of polymers appeared at 0.69 V for **P(EC)** and at 1.1 V for **P(TB)** and **P(ECTB)**, indicating the incorporation of **TB** unit in the copolymer structure.

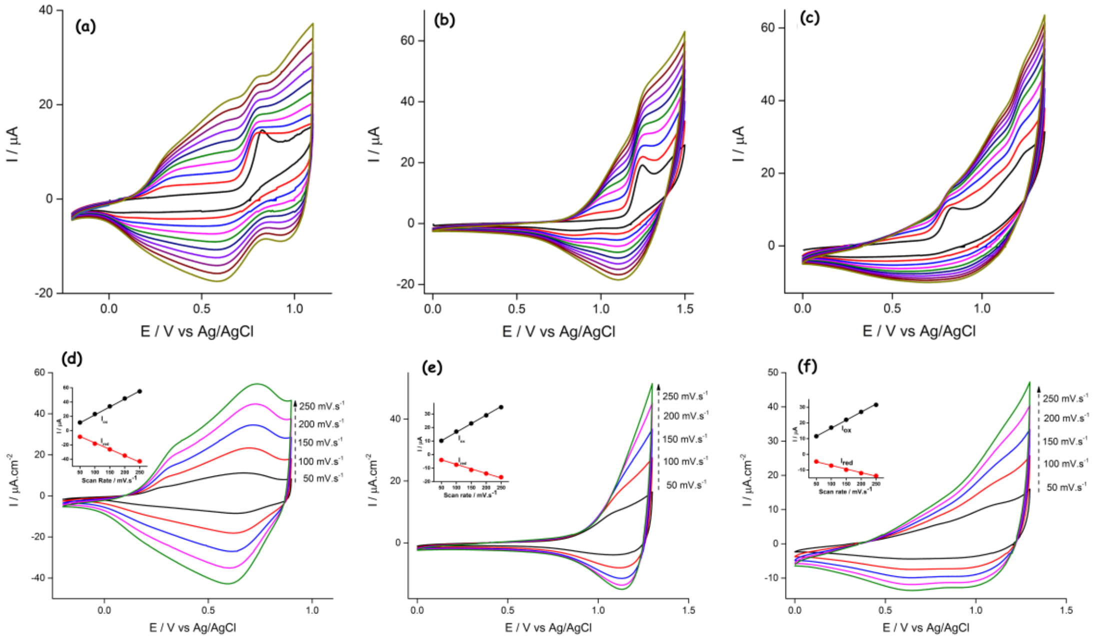

Figure 2. Repetitive CVs of **EC** (**a**), **TB** (**b**), **ECTB** (**c**) on Pt disc working electrode vs Ag/AgCl at a scan rate of 100 mV.s^{-1}. CVs of the resulting polymer films, **P(CE)** (**d**), **P(TB)** (**e**), **P(ECTB)** (**f**) with increasing scan rates from 50 to 250 mV.s^{-}. Insets of **d**, **e** and **f**: Relationship of anodic and the cathodic peak currents as a function of scan rate.

Scan rate dependency is an important parameter in order to see the ability of effective charge injection-rejection process for the polymer film even at high scan rates. For this aim, the polymer films on Pt disc working electrodes exposed to subsequently increasing scan rates from 50 to 250 mV.s^{-1} and the resulting CVs were demonstrated in Figure 2 d, e and f. As seen from the insets of figures, all the polymer films exhibited a linear correlation between the current intensity and the scan rate, indicating a nondiffusional redox process. Moreover these results showed the well adherence of the polymer films on the working electrode surface. Another result can be extracted from the scan rate study that, the capacitance property of **P(EC)** positively contributed to the copolymer, by showing more square-type CVs than that of **P(TB)**.

Copolymer and the homopolymer films must be obtained on a transparent working electrode for revealing the spectrochemical properties. For this aim, polymers were collected on ITO-glass electrode via five anodic cyles. Film thickness of the polymer films could not be measured because of lack of the realated instrument. On the other hand, same number of repetitive cycling was applied on the same concentrations of monomer solutions (0.016 M) for each polymerization. Moreover, the active working electrode area was adjusted to be same by keeping the equal height of the solvent in the electrochemical cuvette. Thus, the similar thicknesses was tried to be obtained. Figure 3 a shows the related voltammograms. Copolymer **P(ECTB)** gave its oxidation onset at 0.37 V, which is 250 mV later than **P(EC)** and 260 mV earlier than **P(TB)**, which indicates that the copolymer oxidation potential is between the other two homopolymers. Same behavior was also seen in the current magnitudes. Smaller magnitude of current was measured in **P(ECTB)** according to **P(EC)** and larger according to that of **P(TB)**. These results indicate that the the copolymer bears the properties coming from both homopolymers**.**

Optical absorption spectra of **P(EC)**, **P(TB)** and **P(ECTB)** films were depicted in Figure 3 b. The absorption maximum of the homopolymers were measured at 482 nm for **P(EC)** and at 308 – 565 nm for **P(TB)**. For **P(ECTB)**, maximum of the optical absorption band measured at 315 nm and 502 nm. Moreover, **P(ECTB)** has an additional absorption peak with a maximum at about 593 nm, indicating the existence of **TB** unit in the copolymer structure. In other words, the optical absorption spectrum of **P(ECTB)** showed the optical characteristics of both **P(EC)** and **P(TB)**, with having a wider absorption range.

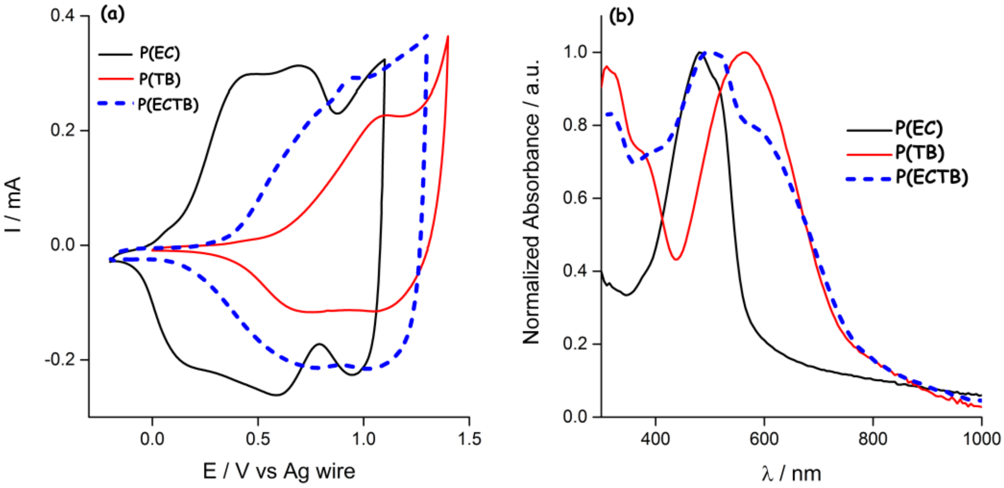

Figure 3. (a) CVs of **P(EC), P(TB), P(ECTB)** on ITO-glass working electrode at a 50 mV.s^{-1} scan rate. **(b)** Absorbance behaviors of the polymer films at their neutral states.

Electronic absorption spectra of the polymer films were followed during the slow oxidation of the polymer films, in order to observe the optical tunings in the polymers (Figure 4). During the electrochemical doping of each of the polymers, the magnitude of the neutral absorption band lost its intensity along with the generation of the new bands. Figure 4 a, b and c shows these appearences. The new bands can be interpreted as the appearence of the charge carriers or polarons. [37] The maximum of the attributed polaron bands for **P(EC), P(TB)** and **P(ECTB)** were measured at 630, 820 and 700 nm, respectively. When the doping continued, newer bands (beyond 900 nm for **P(EC)**, 1000 nm for **P(TB)** and 950 nm for **P(ECTB)**) were observed for each polymer, possibly evaluated as the appearence of bipolarons. [38] Optical energy gaps, E_g, for the polymers were calculated using the onset of their higher wavelength absorption ends. For **P(EC)**, E_g was measured as 2.13 eV. On the other hand, E_g's of **P(TB)** and **P(ECTB)** were found to be same, 1.64 eV. The copolymer exhibited a lower E_g according to that of homopolymer **P(TB)**, since the absorption band of the copolymer was widered as a result of participation of both of **EC** and **TB** units in the copolymer structure.

The colors of the polymer films also changed by altering the electronic absorption spectra. Faded-orange **P(EC)** film showed multichromic property and transformed into orange-brown and then bright-blue during a completed doping. **P(TB)** was purplish or bright-magenta color and became bright-cyan in the doped state. The copolymer, **P(ECTB)**, exhibited brown color in its neutral form, which is the result of the absorption region coming from both **EC** and **TB** units. During the oxidation of dark-brown film of **P(ECTB)**, the various color changes were observed and the corresponding colors appeared as grayish, faded blue and faded-cyan, respectively. The pictures of the polymer films in their neutral and oxidized states were depicted in Figure 4 d, e and f.

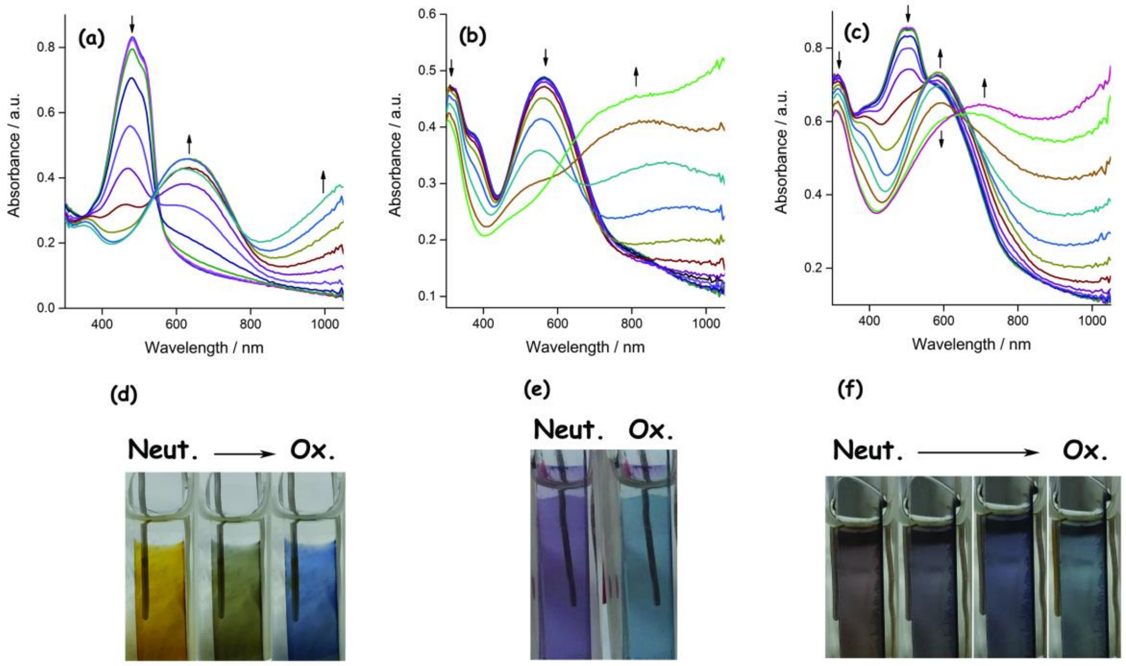

Figure 4. Spectrochemical behaviors of **P(EC)** (**a**), **P(TB)** (**b**), **P(ECTB)** (**c**), as a function of applied potential. The pictures of **P(EC)** (**d**)**, P(TB)** (**e**)**, P(ECTB)** (**f**), at their neutral and oxidized states. (Applied potentials: From -0.2 V to 1.1 V for **P(EC)**; from 0.0 to 1.4 V for **P(TB)** and -0.2 V to 1.3 V for **P(ECTB),** at a scan rate of 20 mV.s^{-1})

For performing a further optical investigation on the polymers, kinetic study was carried out by applying square wave input of potentials where the polymers oxidized and reduced. The change in the transmittance behavior as a function of time was monitored. With the resulting plots of this study, the optical contrast (T %) between oxidized and reduced states of the polymer films were clarified. The kinetic study was performed at the maximum of the absorption wavelengths of corresponding polymers. At 483 nm, **P(EC)** exhibited 37.2 % optical contrast. On the other hand, T % of **P(TB)** at 563 nm was found to be 16.6 %, while that of **P(ECTB) (**at 490 nm) was 18.5 %. The T % of the copolymer was found to be close to that of **P(TB)**, due to color mixing resulted in a darker color. In order to observe the ability of saving T % at higher oxidation-reduction times, the polymer films were switched in 10 s, 5s, 3s, 2s and 1 s intervals, For **P(EC)**, only 2 T % lost was observed even in 1s switching interval. On the other hand, 37 % T lost was observed in **P(TB)**, due to its time need for oxidation. As expected, **P(ECTB)** was affected by the oxidation resistance of **P(TB)** and showed 22 % T lost in 1s switching interval.

Table 1. Electrochemical and spectrochemical parameters of the polymer films

Polymers	**P(EC)**	**P(TB)**	**P(ECTB)**
λ_{max} (nm)	482	565	502 / 593
$E_{g\text{-}optical}$ (eV)	2.13	1.64	1.64
Neutral/oxidized colors	Pale orange / blue	Magenta / cyan	Brown / blue / cyan
t_{ox} / t_{red} (s)	0.52 / 0.34	2.45 / 0.46	1.90 / 0.56
T %	37.2 at 483 nm	16.6 at 563 nm	18.5 at 490 nm
CE (cm^2/C)	564	133	157

Coloration efficiency (CE) explains the correlation between the optical absorbance alteration and charge / discharge intensity needed for a complete switch at a certain wavelength. CE value of each polymer was calculated according to the equation in [39] and depicted in Table 1. According to CE results, contribution of **EC** enhanced the coloration efficiency of the copolymer when compared to that of **P(TB)**.

The switching ability of the polymer films were also measured from the kinetic data and time need for oxidation (t_{ox}) and reduction (t_{red}) was measured. **P(EC)** has rapid response times in subsecond scale as 0.52 s (in oxidation) and 0.34 s (in reduction). For **P(TB)**, response to oxidation was 2.45 s while for reduction is found to be 0.46 s, pointing a relatively slow oxidation and rapid reduction. The copolymer, **P(ECTB)** completed its oxidation in 1.9 s and reduction in 0.56 s. These results showed that the copolymer film oxidizes faster than **P(TB)** and slower than **P(EC)**. This is expected due to the wider working potential range used for the oxidation and reduction in the copolymer, which may exhaust the copolymer and results in a slower de-doping according to so for homopolymers. All transmittance and switching time values were specified at 95 % of the full optical contrast and/or response. All the electrochemical and optical properties of the polymers were summarized in Table 1.

The electrocopolymerization of **P(TB)** with another DAD unit have also reported recently by our group. [33] The difference from the previous study is; 3,4-ethylenedioxythiophene (EDOT) unit is used as the donor group here, while 3,4-propylenedioxythiophene (Prodot) derivative was used in [33]. Changing the donor unit from Prodot to EDOT resulted in an expected red-shifted optical absorption for the resulting copolymer, accompanying the change in the hues of colors of the polymer films in the neutral and oxidized states. The optical band gaps of the copolymers in both study were found to be almost equal to each other due to incorporation of same thiophene-benzothiadiazole containing comonomer into the polymer matrix. Moreover, the copolymer in this study revealed faster switching times due to the existence of EDOT moiety in one of the comonomers.

4. Conclusion and Comment

Electro-synthesis of a new copolymer film was introduced. DAD type monomers were used for the copolymerization. Carbazole based homopolymer **P(EC)** has a wider optical energy gap (2.13 eV) but excellent switching ability. **P(TB)** has narrower optical energy gap (1.64 eV) but poorer switching response in oxidation. The resulting copolymer (**P(ECTB)**) revealed synergetic properties with having a narrower band gap of 1.64 eV and relatively better switching times. Moreover, the copolymer depicted a wider visible-optical absorption by covering the characteristic absorption bands coming from both homopolymers. The electrochemical and optical properties of the copolymer were found to be better than **P(TB)** (faster switching times, band gap lowering and easier oxidation ability). The copolymer film was also found to have multichromic property. Furthermore, **P(ECTB)** saved its optical stability even at high switching rates.

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