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A multielectrochromic copolymer based on pyrrole and 3,4-ethylenedioxythiophene

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Abstract – In this study, an electrochromic copolymer bearing pyrrole and 3,4-ethylenedioxythiophene (EDOT) was electrosynthesized on working electrode. Coating conjugated copolymer on working electrode and its electrochemical/optical characterization were studied with cyclic voltammetry method and in-situ spectroelectrochemistry. Monomers (pyrrole and EDOT) feeding ratio for effective copolymerization was reported and its electrochemical and spectroelectrochemical behavior were discussed. For comparisons sake, EDOT and Pyr were also electrochemically polymerized and their homopolymers were also electrosynthesized. In the same conditions, electrochemical, spectroelectrochemical and electrochromic properties of PPyr, PEDOT and Poly(Pyr-co-EDOT) were also analyzed and compared. The experimental results showed that copolymer had better electrochromic properties than that of PPyr. This proves that the entrance of EDOT unit into chain enhances optical and electrochemical performance of the polymer chain. Copolymer, Poly(Pyr-co-EDOT) exhibited better electrochromic performance than that of PPyr. The copolymer had a λ_{\max} value at 450 nm with a band gap of 2.05 eV. Poly(Pyr-co-EDOT) had a multielectrochromic property, which contains five colour transitions upon oxidation. these colors are yellowish-brown, reddish brown, brown, green and dark cyan. The experiments showed that optical contrast ($\Delta T\%$) and switching time (t_{sw}) of Poly(Pyr-co-EDOT) copolymer were 11.3 % ; 1.7 s at 450 nm and 36 % ; 4.0 s at 850 nm, respectively. It is thought that this study will form a basis for pyrrole-edot based electrochromic copolymer studies.

Keywords –Pyrrole, Copolymer, Electrochromism, 3,4-ethylenedioxythiophene, Conjugated Polymer

I. INTRODUCTION

Today's conditions and technological developments lead human beings to new and easily synthesized materials. Unfortunately, the prices of fossil fuels used in renewable energy technologies and the expensive elements used for this purpose, which are gradually decreasing in the world, are unfortunately hurting [1]. Conductive polymers, which are one of materials used for many applications, have attractive electrical behaviors similar to inorganic semiconductors [2]. Conductive polymers are used in many applications, some of which are electrochromic applications [3-4], capacitors [5-7] (with the role of counter electrode or dye material in dye-sensitized solar cells [8-10]

in LEDs [11], biosensors [12-13] and in countless applications. According to the application areas of the conductive polymers, the chemical structure of the monomer or monomers that make up the chemical structure of the conductive polymers can be changed just like a puzzle in order to achieve the desired electronic and optical properties. Electrochromic applications, one of the application areas of such materials, are one of the most popular areas where conductive polymers are used. Electrochromic applications, one of the application areas of such materials, are one of the most popular areas where conductive polymers are used [14]. Playing with the structure of the monomer used is sometimes not enough to achieve the required

property [15]. In this case, the work is done by using the copolymerization technique of two or more monomers. There are many conjugated monomers (thiophene, pyrrole, fluorene, carbazole, aniline and etc.) for this purpose. Among them, EDOT is one derivation monomer of thiophene and its homopolymer, for example, is mostly used for electrochromic applications [16]. Its polymer, PEDOT, has some advantages like stability, easy processability and possessing good electrochromic parameters such as coloration efficiency (CE), optical contrast (ΔT %) and switching time (t_{sw}) besides low band gap (~ 1.65 eV). For this, EDOT was used as couple during copolymerization with other conjugated monomers. While doped state of PEDOT is almost transparent in the visible region, polymer is dark blue in the neutral state. For that reason, PEDOT is an important conjugated polymer for its cathodically coloring electrochromic polymer in device applications. The incorporation of EDOT unit into pure other conjugated monomers can lead to huge alternations on the electrochemical and optical properties of the resulting copolymer formations [17].

Pyrrole is also another conjugated monomer was used for polymerization. However, polypyrrole (PPyr), itself has poor electrochromic properties [18]. The quality of PPyr films is also another problem and the electrodeposition conditions (substrate, solvent, mass transport, supporting electrolyte) were tried to be analysed by many research groups [19-23]. Many groups tried to make copolymers of it with other dyes. For example, Saraç and co-workers [24] made electrochemical synthesis and structural analysis of PPyr, PEDOT and Pyrrole-EDOT based copolymer carbon fibre microelectrodes. Kadac et al. [25] electrosynthesized a copolymer of EDOT and pyrrole and studied on its electrochemical properties without its electrochromic behaviours. To the best of our knowledge, there is no report on the electrochromic properties of pyrrole-EDOT based copolymer in literature.

In this study, electrochemical and spectroelectrochemical properties of copolymer of pyrrole and EDOT monomers were reported and its electrochromic properties were investigated in detail. Homopolymers of pyrrole and EDOT were also electrosynthesized for comparisons sake. The related characterizations were done by using

methods such as cyclic voltammetry and in-situ UV-vis spectroscopy.

II. MATERIALS AND METHOD

All chemicals were used as received from Aldrich Chemical without further purification. Pyrrole (Pyr) and 3,4-ethylene dioxothiophene were dissolved in 0.1 M tetrabutylammonium hexafluorophosphate (TBPF₆) and acetonitrile (ACN) and uniequivalent monomer conditons (1:1) were used for monomers. Three electrode system was used for electropolymerization and electrochemical and optical characterizations. For electroanalytical studies, Indium tin oxide coated glassy electrode) ITO electrode, Pt wire and Ag wire as working, counter and reference electrodes, respectively. For spectroelectrochemical studies, An UV cuvette was used as solution container and a square teflon cape with three holes for insertion of electrodes were used. Cyclic voltammetry (CV) and transient methods were used for electropolymerization and electrochemical/optical characterizations. Obtained Electrochromic copolymer was characterized in monomer free medium and switched between its redox states via transient method at constant potentials. Ivium Compactstat brand device was used during potenstiostatic analysis. Spectroelectrochemical analysis was done with a Specord S600 spectrometer. With the same device, the color space data was taken by the International Commission of Illumination with luminance (L), hue (a), and intensity (b). FTIR spectra were carried out with Bruker Equinox 55 with an attenuated total reflectance (ATR).

III. RESULTS AND DISCUSSIONS

A. ELECTROSYNTHESIS OF PPYR /PEDOT AND POLY(PYR-CO-EDOT)

Electropolymerization of pyrrole/ EDOT and their copolymer, (Poly(Pyr-co-EDOT) were electrosynthesized in the medium of 0.1 M TBAPF₆ /ACN medium with a scan rate of 100 mVs⁻¹. It is crucial to find suitable polymerization potential range for a copolymer formation. Thus, the onset potentials of both monomer structures were determined in the same conditions. The onset oxidation potentials of Pyr and EDOT monomers was found as 0.95 V and 1.05 V, respectively (Figure 1a and b). This small potential difference indicates that the copolymer formation can be

suitable. From these results, 0.0125 M Pyr and 0.0125 M EDOT were mixed in 0.1 M TBAPF₆/ACN solution and its electropolymerization studies were achieved for 10 cycles as seen in Figure 1c. As the cyclic voltammograms for in the electrochemical polymerization of EDOT and Pyr monomers, it was observed that both anodic and cathodic current intensities increased in each new cycle for the mixture. This shows that the polymer film was successfully coated on the ITO working electrode. All conjugated polymer coated homopolymers (PPyr and PEDOT) and copolymer (Poly(Pyr-co-EDOT)) were rinsed into DCM in order to get rid of unwanted monomeric and oligomeric species.

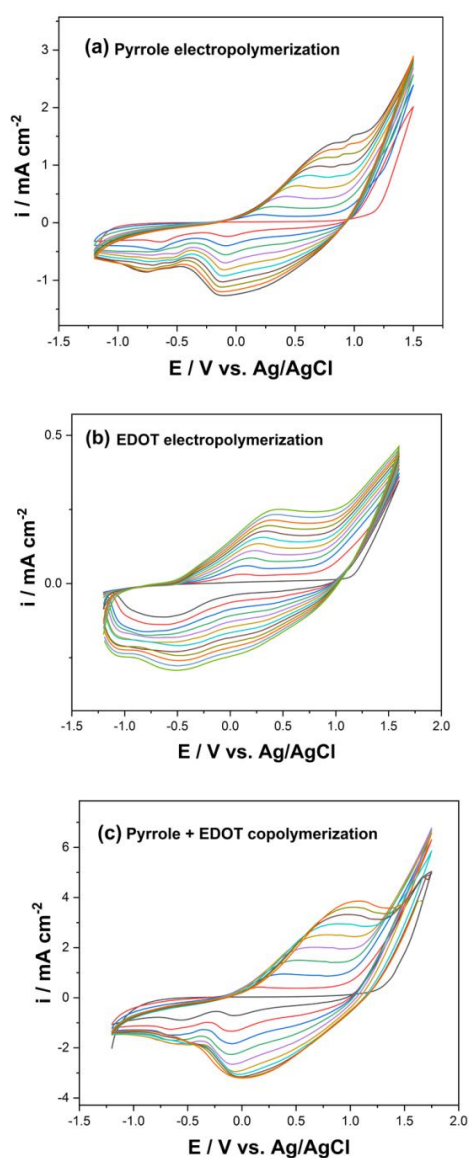


Fig. 1 Electropolymerization studies for (a) Pyr (b) EDOT monomers and Pyr:EDOT (1:1) mixture with a scan rate of 100 mV s⁻¹ on ITO electrode in the medium of 0.1 M TBAPF₆/DCM solution

B. ELECTROCHEMICAL CHARACTERIZATIONS OF POLY(PYR-CO-EDOT)

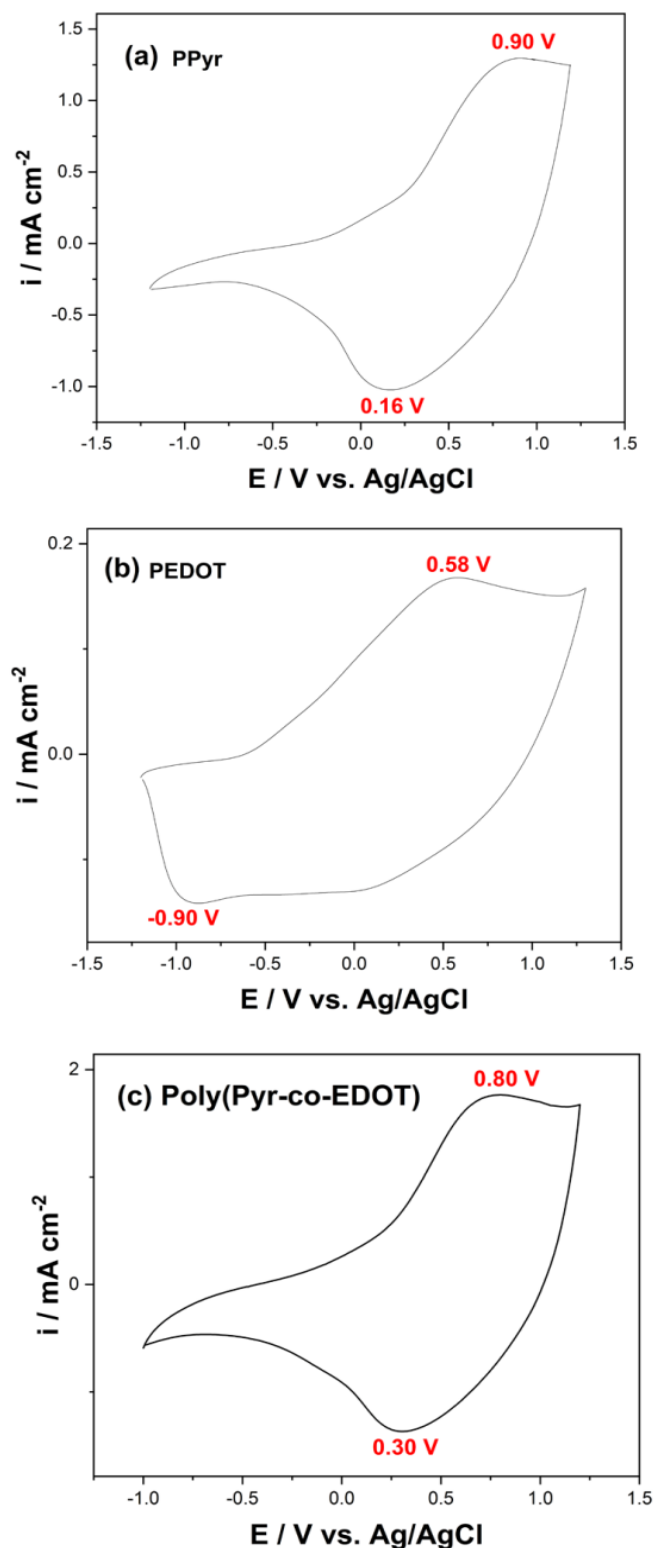


Fig. 2 Electrochemical behaviour of (a) PPyr (b) PEDOT homopolymers and (c) Poly(Pyr-co-EDOT) copolymer in the medium of 0.1 M TBAPF₆/DCM solution

Electrochemical characterizations of homopolymers and copolymer were achieved in the medium of 0.1 M TBAPF₆/ACN medium. Polymer coated ITO working electrodes were immersed in the monomer free electrolyte solution in their proper potential ranges and their doping dedoping properties were investigated. As seen in Figure 2a and 2b, PPyr and PEDOT gave redox couples (doping/dedoping) at 0.90 V/ 0.16 V and 0.58 V / -0.90 V, respectively. When Poly(Pyr-co-EDOT) was scanned at a scan rate of 100 mV s⁻¹ in the monomer free medium like homopolymers, the doping potential changes to 0.80 V and a dedoping potential was observed at around 0.30 V. This proves a new copolymer formation on ITO electrode (Figure 2c).

C. SCAN RATE DEPENDENCY EXPERIMENTS FOR POLY(PYR-CO-EDOT)

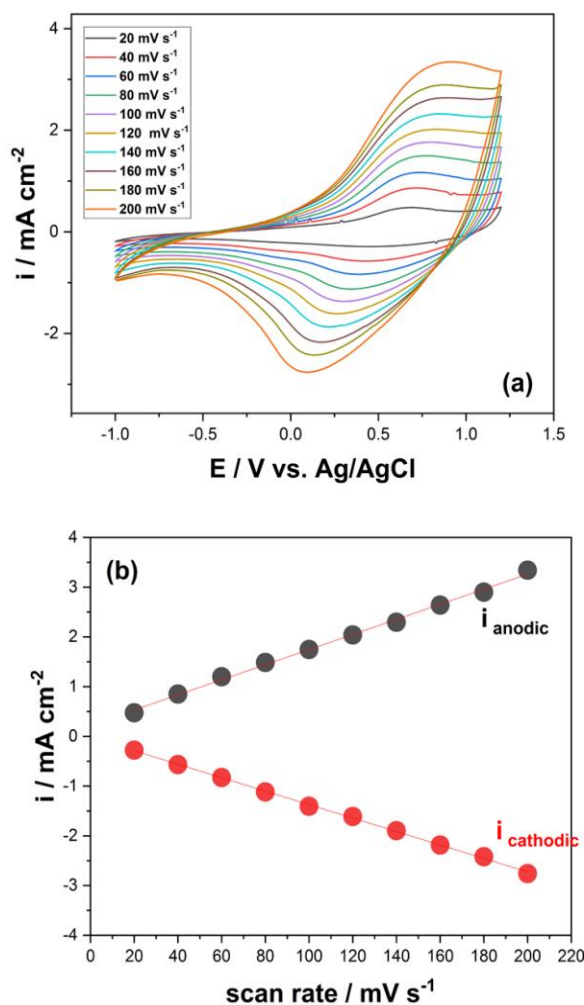


Fig. 3 Scan rate dependency studies of (a) Poly(Pyr-co-EDOT) with different scan rates between 20 mV s⁻¹ and 200 mV s⁻¹ with an increments of 20 mV. (b) Relationship of anodic and cathodic currents with scan rate.

Scan rate dependency experiments of Poly(Pyr-co-EDOT) were analysed in monomer free medium. Scan rates were chosen with an increment of 20 mV differences in 1 s. Starting from 200 mV s⁻¹ to 20 mV s⁻¹, the electrochemical behaviour of the copolymer was examined (Figure 3a). The related experiments showed that anodic and cathodic peak current intensities increase and decrease linearly as the scanning rates rise (Figure 3b). This indicates that Poly(Pyr-co-EDOT) coated on ITO electrode behaves nondiffusionally in terms of redox behaviour in the monomer free medium. Furthermore, Copolymer film was successfully well coated on working electrode.

D. ELECTROCHROMIC PROPERTIES OF OF PPYR AND PEDOT AND POLY(PYR-CO-EDOT)

Homopolymers of PEDOT, PPyr and copolymer, Poly(Pyr-co-EDOT) were synthesized on ITO working electrode in order to investigate electro-optical properties. Each polymer coated ITO electrodes were immersed into monomer free medium and in-situ UV-vis spectrometers data were achieved (Figure 4). The maximum absorption intensities (π - π^* transitions) were observed for PEDOT, PPyr and Poly(Pyr-co-EDOT) at 400 nm, 600 nm and 450 nm, respectively (Figure 4a, 4b, 4c). The polymer films were scanned between their proper potential windows as given in Figure 3. The results show that the absorption bands intensities of given π - π^* transition bands decrease upon oxidations and new charge carriers (polaron) were formed at longer wavelengths. The band gap was calculated as 2.18 eV, 1.65 eV and 2.05 eV for PEDOT, PPyr and Poly(Pyr-co-EDOT), respectively. As seen from results the values and spectroelectrochemical behaviour of homopolymers were different than that of Poly(Pyr-co-EDOT). This proves that the new intramolecular charge formations between EDOT and Pyr units. It is noteworthy that the band gap of the Poly(Pyr-co-EDOT) copolymer is between that of PPyr and PEDOT polymer. This shows that the electron-rich EDOT monomer is in the copolymer chain, and the HOMO level of PPyr raises. Figure 3c already supports this situation.

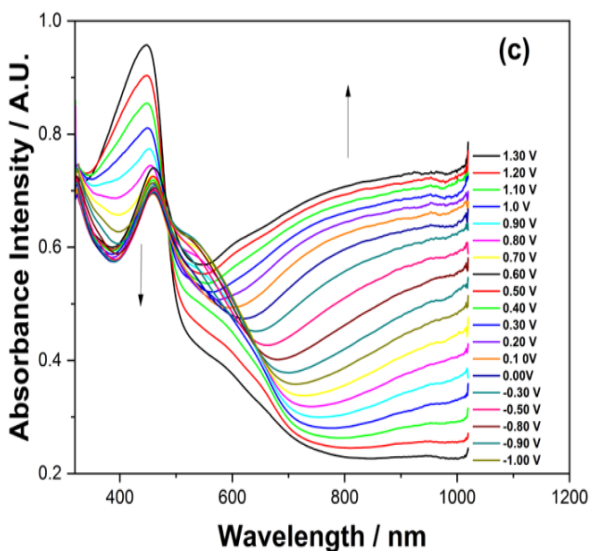
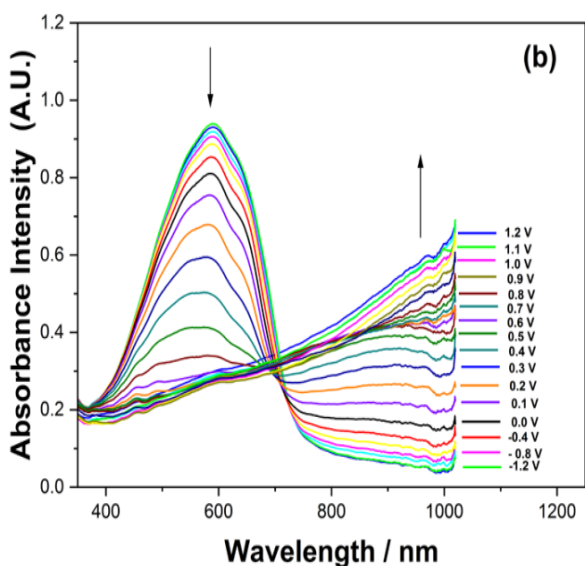
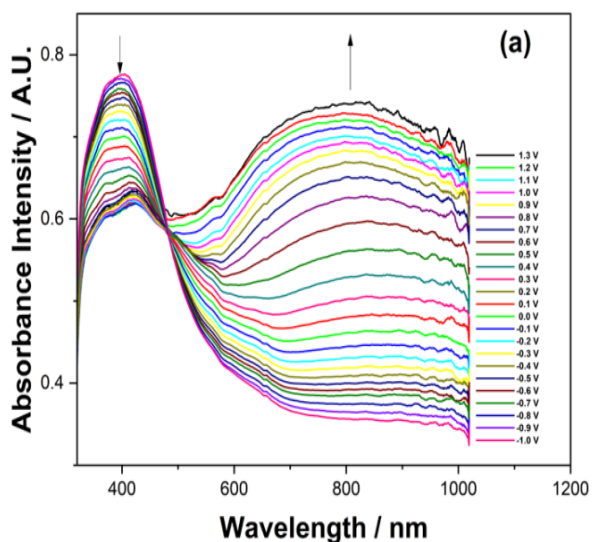


Fig. 4 Spectroelectrochemical studies for (a) PPy (b) PEDOT homopolymers and (c) Poly(Pyr-co-EDOT) copolymer on ITO electrode in the medium of 0.1 M TBAPF₆ /DCM solution

Table 1. A summary of observed and calculated color changes for PPy, PEDOT and Poly(Pyr-co-EDOT)

Polymer	Color Changes			
	Observed		Calculated L/a/b	
	Neutral	Oxidized	Neutral	Oxidized
PPyr			 56.12/5.24/12.2	 53.7/3.01/5.79
PEDOT			 89.5/3.95/-17.12	 97.3/1.48/-9.4
Poly (Pyr-co-EDOT)	-1.0 V		 66.96/-0.59/30.23	
	-0.5 V		 63.00/1.18/14.92	
	0.0 V		 61.72/3.32/10.03	
	0.5 V		 61.62/-3.44/4.32	
	1.0 V		 58.65/-3.36/0.5596	

Table 2. A summary of electrochromic properties of PPy, PEDOT and Poly(Pyr-co-EDOT)

Polymers	PPyr	Poly(Pyr-co-EDOT)	PEDOT
E_g^{opt} (eV)	2.18	2.05	1.65
$\lambda_{max}(nm)$	400	450	600
$\Delta T \%$	7 (400 nm) 31 (800 nm)	11.3 (450 nm) 36.0 (850 nm)	56 (600 nm)
$t_{95\%}^c$	2.5 (400 nm) 3.8 (800 nm)	1.7 (450 nm) 4.0 (850 nm)	0.8 (600 nm)

The color changes upon oxidation for homopolymers and copolymer were also analyzed. The experiments showed that PPy and PEDOT polymers gave color transitions (neutral to oxidized) brownish-green to brownish blue and dark blue to transparent blue, respectively. The copolymer, Poly(Pyr-co-EDOT) show multielectrochromic property upon oxidation. The observed colour

changes and observed color changes were given in Table 1. More color changes Poly(Pyr-co-EDOT) for than that of homopolymers proves also different optical behaviour of Poly(Pyr-co-EDOT) copolymer. Electrochromic properties of polymers can be specified with regard to CIE 1976 (L, a, b) color space with daylight (Standard Illuminant D65/10 as illuminant and 10°). L, a and b are interrelated with the parameter of the lightness, red-green and yellow-blue balances, respectively.

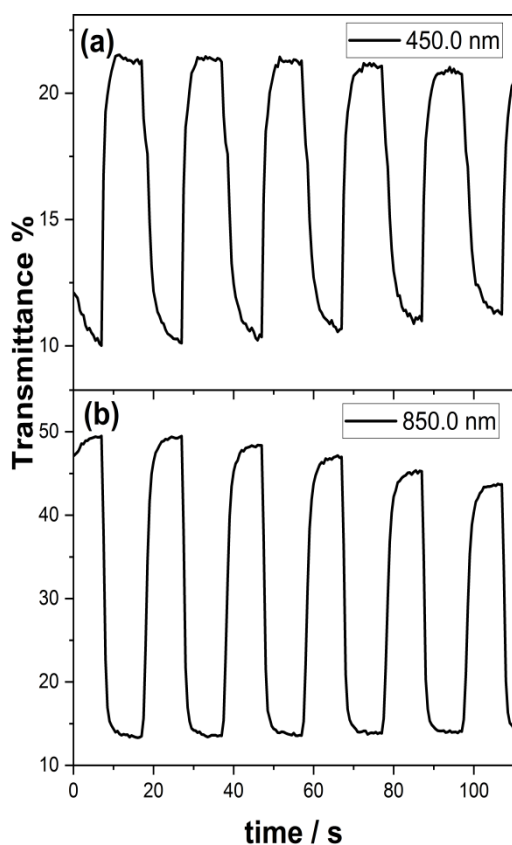


Fig. 5 Kinetic studies for Poly(Pyr-co-EDOT) copolymer film

Kinetic studies related were also observed as seen in Figure 5 and summarized in Table 2. Some electrochromic parameters are important in order to describe the electrochromic performance of polymers. These are coloration efficiency (CE), switching time (t_{sw}) and optical contrast ($\Delta T\%$). The data was investigated between the neutral and oxidized states of polymers. Conjugated polymer was switched between its states. The copolymer performance was chosen at 450 nm and 850 nm, as seen in Figure 5. From the results, $\Delta T\%$ and t_{sw} were calculated. $\Delta T\%$ values were found as 11.3 % at 450 nm and 36.0 % at 850 nm for Poly(Pyr-co-EDOT). t_{sw} values were found as 1.7 s at 450 nm and 4.0 s at

850 nm. It can be said that these properties were improved when EDOT entered the copolymer chain.

IV. CONCLUSION

In this study, electrochemical and optical properties of a multielectrochromic copolymer were discussed. For comparison reasons, each component of copolymer was homopolymerized in the same conditions with Poly(Pyr-co-EDOT). The experimental results showed that copolymer has multielectrochromic behaviour and had a different color perspective when compared with that of homopolymers (PPyr and PEDOT). Electrochromic properties of copolymer for Poly(Pyr-co-EDOT) was calculated from kinetic studies during switching between its neutral and oxidized states. The results showed that Poly(PPyr-co-EDOT) had better optical and electrochemical performance when compared its properties with PPyr. This study shows that the copolymer has the potential to be used in electrochromic devices and energy-saving smart glass applications.

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