

Optoelectrochemical properties of the copolymer of 2,5-di(4-methylthiophen-2-yl)-1-(4-nitrophenyl)-1H-pyrrole monomer with 3,4-ethylenedioxythiophene

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Received 18 September 2007; received in revised form 28 December 2007; accepted 9 January 2008

Available online 26 January 2008

Abstract

Copolymer of 2,5-di(4-methylthiophen-2-yl)-1-(4-nitrophenyl)-1H-pyrrole (MTNP) with 3,4-ethylene dioxythiophene (EDOT) was electrochemically synthesized and characterized via cyclic voltammetry, Fourier Transform Infrared spectroscopy, Scanning Electron Microscopy, conductivity measurements. Spectroelectrochemical investigations showed that resulting copolymer film has distinct electrochromic properties. It has five different colors (dark purple, red, light grey, green, blue). At the neutral state λ_{\max} due to the π - π^* transition was found to be 500 nm and E_g was calculated as 1.71 eV. Double potential step chronoamperometry experiment shows that copolymer film has good stability, fast switching time (1.1 s) and high optical contrast (30%).

Electrochromic device based on P(MTNP-co-EDOT) and PEDOT was constructed and characterized. Oxidized state of the device shows dark purple color with a blue color reduced state. At interval potentials device has good transparency and colors of the device are yellow and grey. Maximum contrast and switching time of the device were measured as 23% and 1.1 s at 650 nm.

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Keywords: Conducting polymers; Electro-optical effects; Thin films; Copolymerization; Spectroelectrochemistry

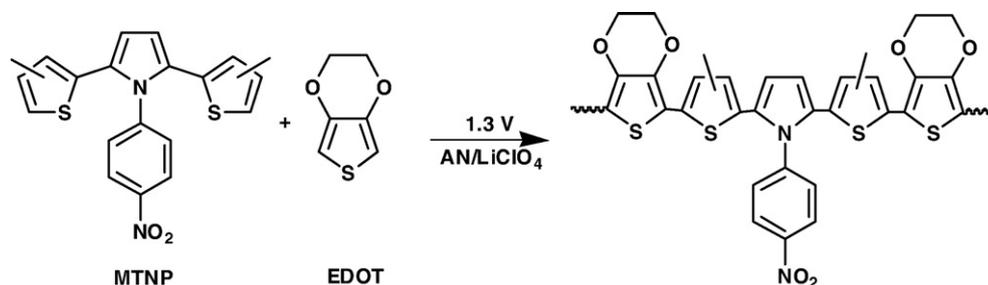
1. Introduction

In the last few decades, conducting polymers (CPs) have been very actively pursued [1]. Several discoveries brought the CPs to full commercialization with applications in electrochromic rear-view mirrors [2,3], windows [4,5], thin-film transistors [6], displays [7], sensors [8], polymer light-emitting diodes [9,10], photovoltaics [11], and electrochromic devices [12–15]. More recently, research on CPs has mostly focused on their optical properties in the visible [16–17] and near infra-red (NIR) [18–21] spectral regions. Poly(thiophene) derivatives have been the most studied materials since they exhibit fast switching times, out-

standing stability and high contrast ratios in the visible and NIR regions. The earliest electrochromic materials in the visible region were the inorganic tungsten trioxide (WO₃) and iridium dioxide (IrO₂) [22]. Due to the increased versatility of organic materials (viologens, metallophthalocyanines, and conducting polymers) [23,24], these compounds have recently received the brunt of attention for potential electrochromic applications [25]. Among organic materials, conjugated polymers have several advantages over small molecules and inorganic solids; these are, outstanding coloration efficiency, fast switching times [26,27], multiple colorations with the same material [17], fine-tunability of the band gap (and the color) [28], high stability [12,14], thin film flexibility and cost effectiveness.

For conducting polymers, the electrochromism is related to doping–undoping process. The doping process modifies the polymer electronic structure, producing new electronic states in the band gap, causing color changes. Electronic absorption shifts

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Scheme 1. Copolymerization reaction.

bathochromically upon doping, and the color contrast between the undoped and doped states is related to the polymer band gap [29]. A major focus in the study of electrochromic polymeric materials has been that of controlling their colors by main-chain and pendant group structural modification and copolymerization. Copolymerization of distinct monomers or homopolymerization of hybrid monomers containing several distinct units can lead to an interesting combination of the properties observed in the corresponding homopolymers. Indeed, it has been observed that the color of copolymers based on carbazole, thiophene and pyrrole derivatives can be controlled by altering the ratio of the respective monomers [30].

For that matter, we synthesized a copolymer of 2,5-di(4-methyl-thiophen-2-yl)-1-(4-nitrophenyl)-1H-pyrrole (MTNP) with EDOT. EDOT is a popular choice as a substituted monomer since it produces a low band gap polymer with high stability and good conductivity [31]. EDOT can give rise to noncovalent intramolecular interactions with adjacent thiophenic units and thus induce self-rigidification of the π -conjugated system in which it is incorporated [32–34]. The resultant copolymers were characterized via cyclic voltammetry, SEM and conductivity measurements. The optoelectrochemical and electrochromic properties, such as the relative luminance, change of color upon redox switching, and long-term switching stability of the copolymer were determined. We also constructed and character-

ized dual-type electrochromic devices based on P(MTNP-co-EDOT) and PEDOT. Devices were assembled in sandwich configuration of electrochromic materials deposited ITO glass electrodes and a gel electrolyte. For the construction of devices, PEDOT was used as the cathodically coloring, P(MTNP-co-EDOT) were used as the anodically coloring materials. Device has four different colors at different applied potentials.

2. Experimental

2.1. Chemicals

Acetonitrile (ACN) (Merck), LiClO_4 (Aldrich), EDOT (Aldrich), poly(methyl methacrylate) (PMMA) (Aldrich), propylene carbonate (PC) (Aldrich) were used without further purification. (MTNP) was previously synthesized in our group [35].

2.2. Instrumentation

A Voltalab PST50 model potentiostat was used for the CV and chronocoulometry studies. FTIR spectra were recorded on a Nicolet 510 FTIR spectrometer. Surface morphologies of the homopolymer films were investigated by using JEOL JSM-6400 scanning electron microscope (20 KV). Varian Cary 5000

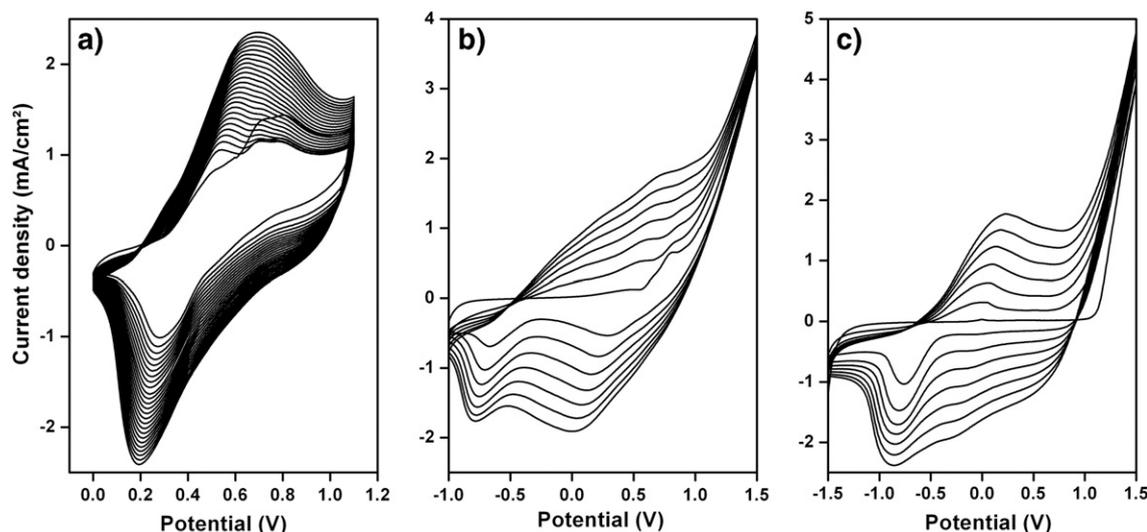


Fig. 1. Cyclic voltammograms of a) MTNP, b) MTNP and EDOT, c) EDOT.

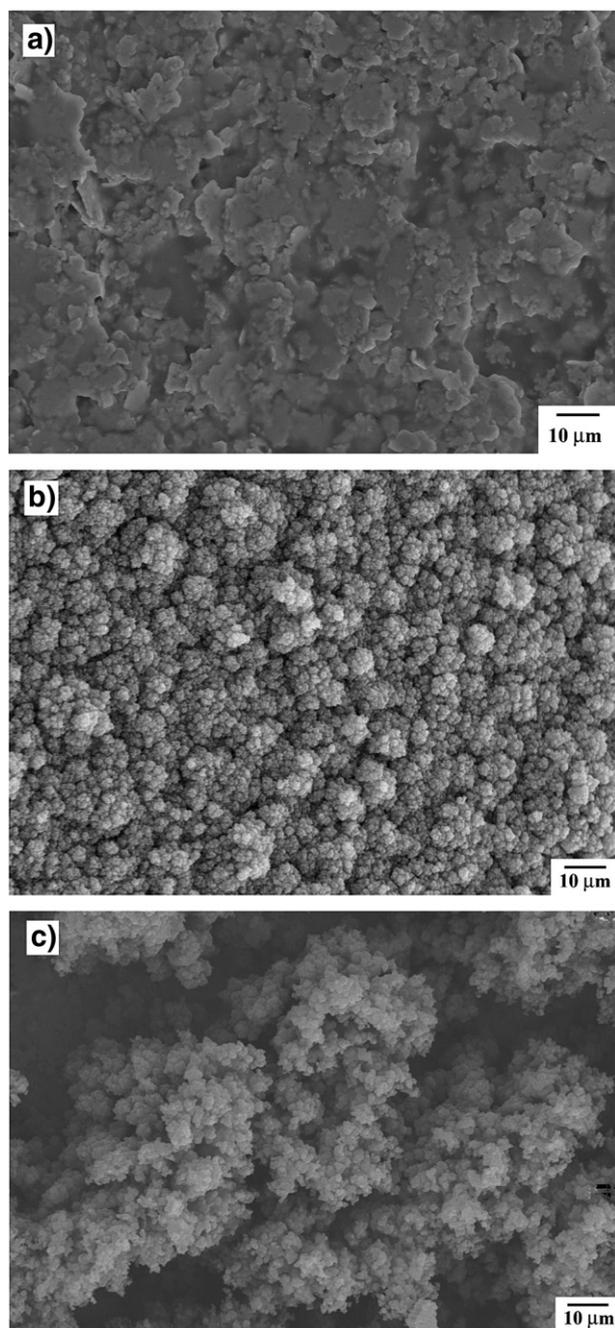


Fig. 2. SEM micrographs of a) MTNP, b) EDOT, c) P(MTNP-co-EDOT).

UV–vis spectrophotometer was used in order to conduct the spectroelectrochemical experiments and to characterize the devices. Colorimetry measurements were done via Minolta CS-100 spectrophotometer.

2.3. Electrochemistry

The oxidation reduction behaviors of monomer in the presence of EDOT were investigated by CV. The voltammograms were recorded in ACN/ LiClO₄ (0.1 M) solvent–electrolyte couple using a system which has a potentiostat and a CV cell consisting of Pt foil working and counter electrodes, and a Ag/Ag⁺ reference

electrode. The electrochemistry experiments were carried out at room temperature under nitrogen atmosphere.

2.4. Synthesis of copolymer

The potentiodynamic polymerization of MTNP with EDOT was carried out in a solution containing 0.01 M MTNP and 0.01 μL EDOT in LiClO₄ (0.1 M)/ACN solvent–electrolyte couple by constant potential of 1.3 V for 10 min under nitrogen atmosphere. After electrolysis, the film was washed with ACN to remove the excess supporting electrolyte and the unreacted monomer. (Scheme 1)

For the spectroelectrochemical studies, copolymer was synthesized in the same solvent–electrolyte couple system on an ITO-coated glass slide using a UV–cuvette as a single-compartment cell equipped with Pt counter electrode, and a Ag/Ag⁺ reference electrode. The electrochromic measurements, spectroelectrochemistry, and switching studies of the polymer film deposited on ITO-coated glass slide were carried out in the same media in the absence of monomer.

2.5. Preparation of the gel electrolyte

The gel electrolyte for electrochromic device was prepared using LiClO₄:ACN:PMMA:PC in the ratio of 3:70:7:20 by weight. After the dissolution of LiClO₄ in ACN, poly(methyl methacrylate) (PMMA) was plasticized by 1,2-propylenecarbonate in order to form a highly transparent and conductive gel.

2.6. Construction of electrochromic devices

ECD's were prepared by sandwiching the gel electrolyte between ITO's which were deposited by conducting polymers. While constructing the device, one of the polymers was kept in the oxidized, the other in neutral state. To improve the optical stability during redox process, balancing the charge on the electrodes is an important point before the construction of devices. In order to match the redox charges of the two complementary polymer films (to keep a balanced number of redox sites for switching),

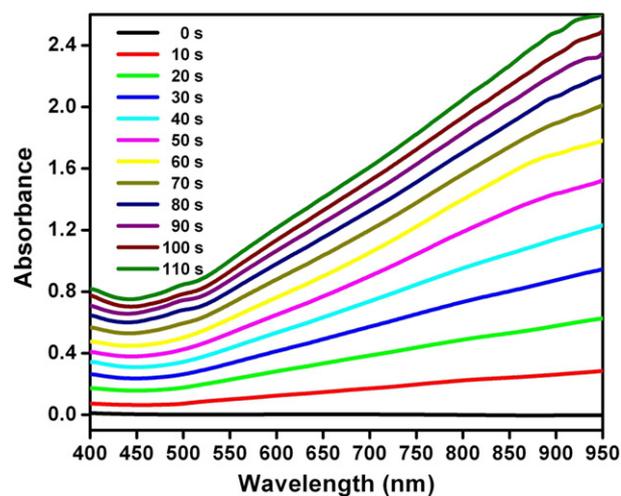


Fig. 3. In situ electrochemical copolymerization of MTNP with EDOT.

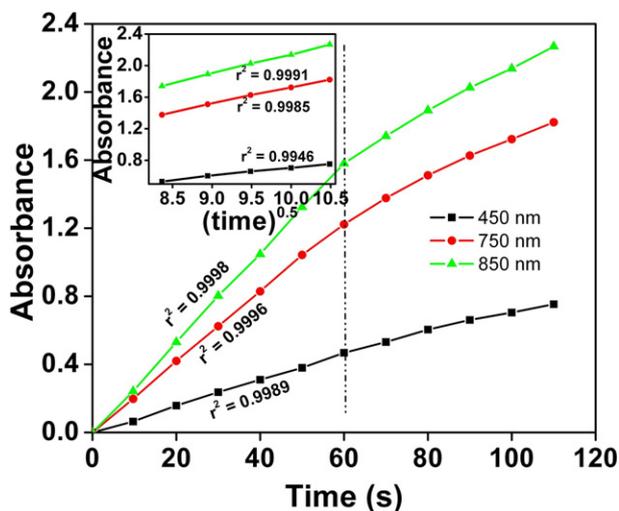


Fig. 4. Absorbance recorded at different wavelengths during the polymerization. Inset figure represents absorbance changes recorded with the square root of the time at different wavelengths (between 60 and 120 s).

chronocoulometry was used. The gel electrolyte was spread on the polymer-coated sides of the electrodes and the electrodes were sandwiched under atmospheric conditions. To construct electrochromic devices, PEDOT was used as the cathodically coloring material and P(MTNP-co-EDOT) as the anodically coloring material. PEDOT was potentiostatically deposited on ITO working electrode by applying +1.3 V in AN/LiClO₄ (0.1 M) solvent–electrolyte. P(MTNP-co-EDOT) was also obtained by constant polymerization method at +1.3 V in the presence of EDOT in AN/LiClO₄ (0.1 M). In order to obtain the complementary operating conditions, anodically coloring polymer was fully reduced and the cathodically coloring polymer was fully oxidized. The characterization of the ECDs' optical properties was performed. Electrochromic switching and open circuit stability of the devices were also investigated.

3. Results and discussion

3.1. Cyclic voltammetry

Cyclic voltammetry experiments were carried out in ACN/LiClO₄ solvent electrolyte system on bare Pt electrode with a 250 mV/s scan rate. When redox behavior of MTNP was investigated via cyclic voltammetry, an electrochromism between yellow and blue colors was observed, while a greenish cloud was formed around the electrode due to the partial dissolution of linear oligomers. First run of the cyclic voltammogram of MTNP in ACN showed two oxidation peaks at +0.55 and +0.76 V and a reduction peak at +0.28 V. After subsequent runs electroactivity increases with increasing scan number. The peak at 0.76 V decreases as a result of monomer consumption in the diffusion layer (Fig. 1a).

In order to investigate the CV behavior of the copolymer, we performed CV studies in the presence of EDOT under same experimental conditions. There was a drastic change in the voltammogram, both the current increase between consecutive cycles and the oxidation potential of the material were different

than those of MTNP and EDOT, which, in fact, could be interpreted as the formation of copolymer (Fig. 1b and c).

3.2. Infrared spectra

FTIR spectrum of MTNP showed the following absorption peaks: 3093 cm⁻¹ (aromatic C–H stretching), 1513 cm⁻¹ (asymmetric ArNO₂ stretching), 1338 cm⁻¹ (symmetric ArNO₂ stretching), 840 cm⁻¹ (C–N stretching for Ar–NO₂), 3020 cm⁻¹ (C–H_α stretching of thiophene), 1494–1340 cm⁻¹ (aromatic C=C, C–N stretching due to pyrrole and benzene), 1035 cm⁻¹ (C–H in plane bending of benzene), 773 cm⁻¹ (C–H_α out of plane bending of thiophene).

FTIR spectrum of electrochemically synthesized P(MTNP-co-EDOT) showed the characteristic peaks of the monomer. The dominant peaks at around 1340 cm⁻¹ and 1520 cm⁻¹ due to Ar–NO₂ stretching remain unperturbed. The peaks related to C–H_α stretching of thiophene disappeared completely. This is an evidence of the polymerization from 2,5 positions of thiophene moiety of the monomer. On the other hand, evolution of a new peak was observed at 1354 cm⁻¹, which is attributed to

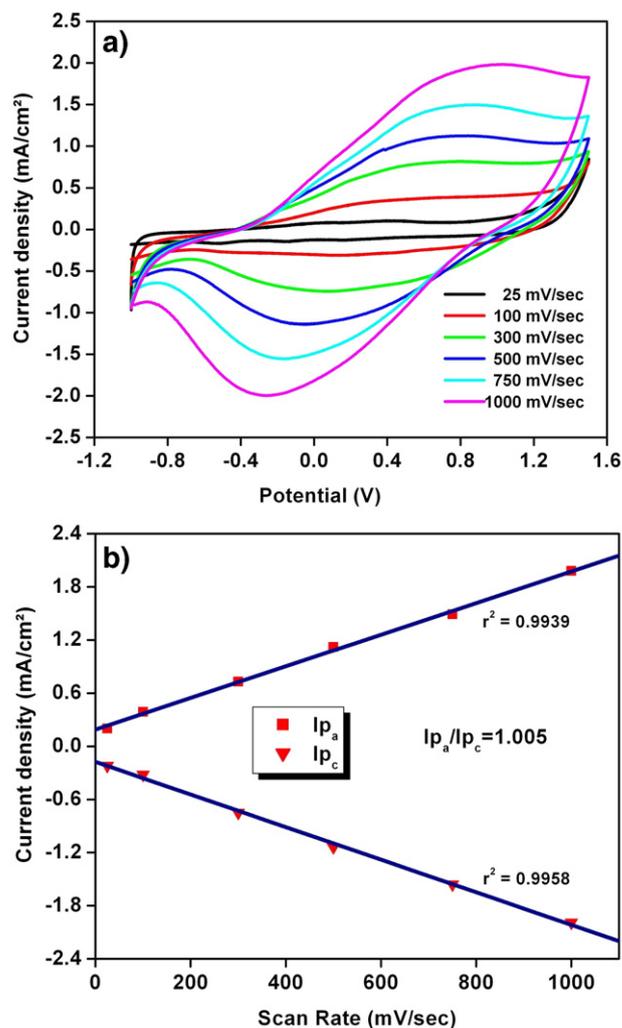


Fig. 5. a) CV of copolymer at different scan rates b) Peak current vs scan rate graph.

the aromatic ethylenedioxy group belonging to EDOT. The strong absorption peak at 1197 cm^{-1} was attributed to the incorporation of ClO_4^- ions into the polymer film during doping process. Results of the FTIR studies clearly indicated the copolymerization of the MTNP with EDOT.

3.3. Surface morphologies

Surface morphologies of P(MTNP), P(MTNP-co-EDOT) and PEDOT were examined employing SEM. Micrograph of polymers designates the excellence of their film formation ability. Wrinkled topography observed on P(MTNP) film (Fig. 2a). The film also exhibited homogeneous and compact structure. As far as the SEM micrograph of copolymer of MTNP with EDOT is concerned (Fig. 2.c), the copolymer film differs from SEM micrograph of PEDOT (Fig. 2.b) and P(MTNP), considerably. Sponge-like structures were observed on P(MTNP-co-EDOT) film; whereas the topology of PEDOT revealed globules.

3.4. Conductivity of the copolymer film

The conductivity of electrochemically prepared P(MTNP-co-EDOT) was measured as $4.2 \times 10^{-3}\text{ S/cm}$ via four probe technique.

3.5. In situ electrochemical polymerization

In situ electropolymerization of MTNP and EDOT was carried out in a solution containing 0.01 M MTNP and 0.01 M

EDOT in LiClO_4 (0.1 M)/ACN solvent-electrolyte couple by constant potential of 1.3 V. During the electrolysis, UV–vis spectra were taken for every 10 s time interval (Fig. 3).

It can be concluded from Fig. 3 that there is a linear increase in absorbance with time until a certain time (0–60 s). After this time, linearity continues with the square root of the time due to polymerization rate becomes controlled by diffusion because of the consumption of monomer at the electrode double layer (Fig. 4).

3.6. Scan rate dependence of the peak currents

P(MTNP-co-EDOT) film prepared via constant potential electrolysis (1.3 V) was washed with AN and its redox switching in monomer-free electrolyte showed a single, well-defined redox process (Fig. 5a). The current response was directly proportional to the scan rate indicating that the polymer film was electroactive and adhered well to the electrode. The scan rate for the anodic and cathodic peak currents shows a linear dependence as a function of the scan rate as illustrated in Fig. 5b. This demonstrates that the electrochemical processes are not diffusion limited and reversible even at very high scan rates.

3.7. Spectroelectrochemical studies of copolymers obtained from different feed ratios of 3,4-ethylenedioxythiophene

By changing the amount of PEDOT in the copolymer composition, spectroelectrochemistry studies were performed in order to see the differences in λ_{max} . Polymers were obtained by

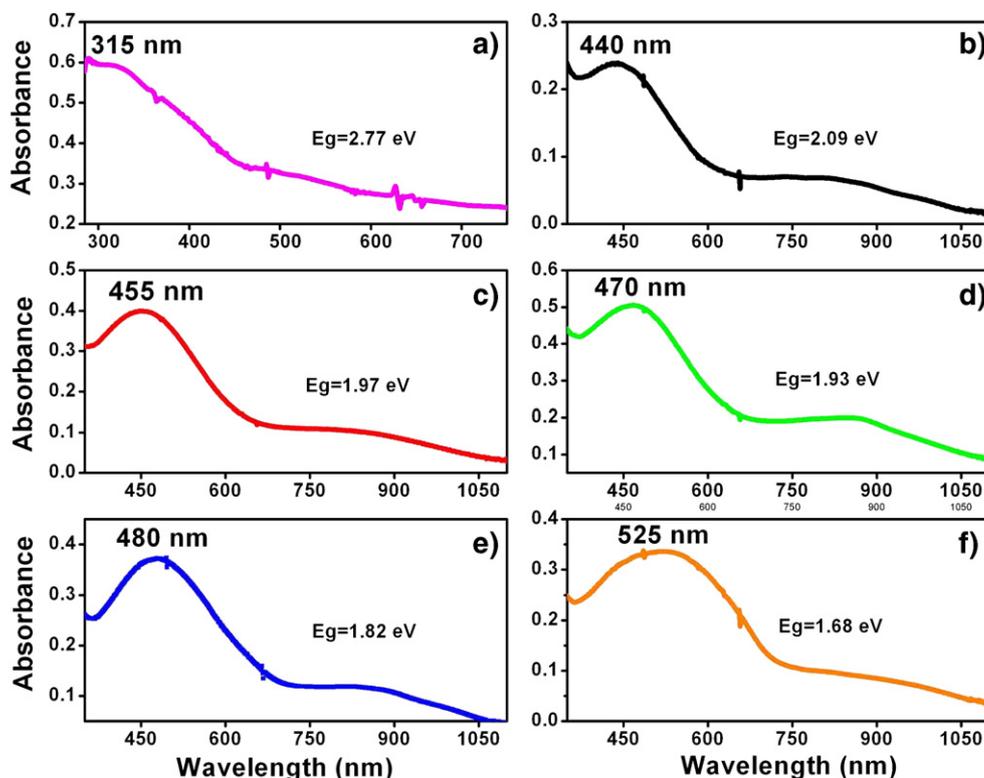


Fig. 6. Optoelectrochemical spectra of copolymers synthesized a) 1:0 b) 1:0.25 c) 1:0.4 d) 1:0.6 e) 1:0.8 f) 1:1.2 MTNP:EDOT feed ratios.

constant potential polymerization in the presence of AN/LiClO₄ solvent–electrolyte couple by varying the potential between 0.8 V and 1.5 V. Knowing that the λ_{\max} of the homopolymer is 315 nm and that of the PEDOT is 600 nm, maximum absorption wavelength values were obtained in this range. It was also noticed that as the amount of PEDOT in the copolymer composition increases, band gap (E_g) of the copolymer decreases and λ_{\max} of the copolymer shifts and becomes closer to 600 nm (Fig. 6). The following table is a good summary of comparison of the homopolymer, PEDOT and copolymers prepared with different feed ratios of EDOT. Maximum wavelengths of the copolymers are between those of the PEDOT and the homopolymer. As seen from Table 1, introduction of EDOT to the polymer chain led to a tremendous decrease in the band gap. These numerical values also support the copolymerization phenomenon.

3.8. Electrochromic properties of copolymer

The best way of examining the changes in optical properties of conducting polymers upon applied voltage is spectro-electrochemistry. It gives not only information about the electronic structure of the polymer such as band gap (E_g) but also on the intergap states that appear upon doping.

P(MTNP-co-EDOT) film was potentiostatically synthesized at 1.3 V on ITO electrode in electrolyte solution composed of 0.01 M MTNP, 0.01 M EDOT and ACN/LiClO₄ (0.1 M). The spectroelectrochemical and electrochromic properties of the resultant copolymer were studied by applying potentials ranging between -0.4 V and $+1.0$ V in monomer free ACN medium. At the neutral state λ_{\max} due to the π - π^* transition of the copolymer was found to be 500 nm and E_g was calculated as 1.71 eV. Upon applied voltage, reduction in the intensity of the π - π^* transitions and formation of charge carrier bands were observed. Thus, appearance of peaks around 750 nm and >1100 nm could be attributed to the evolution of polaron and bipolaron bands respectively (Fig. 7).

The colors of the electrochromic materials were defined accurately by performing colorimetry measurements. CIE system was used as a quantitative scale to define and compare colors. Three attributes of color; hue (a), saturation (b) and luminance (L) were measured and recorded. The P(MTNP-co-EDOT) film has distinct electrochromic properties. It shows 5 different colors ranging from its neutral state to oxidized state.

Table 1

λ_{\max} and E_g values of copolymers prepared with different EDOT feed ratios			
[MTNP]:[EDOT]		λ_{\max} (nm)	E_g (eV)
1	0	315	2.77
1	0.25	440	2.09
1	0.4	455	1.97
1	0.6	470	1.93
1	0.8	480	1.82
1	1	500	1.71
1	1.2	525	1.68
0	1	600	1.60

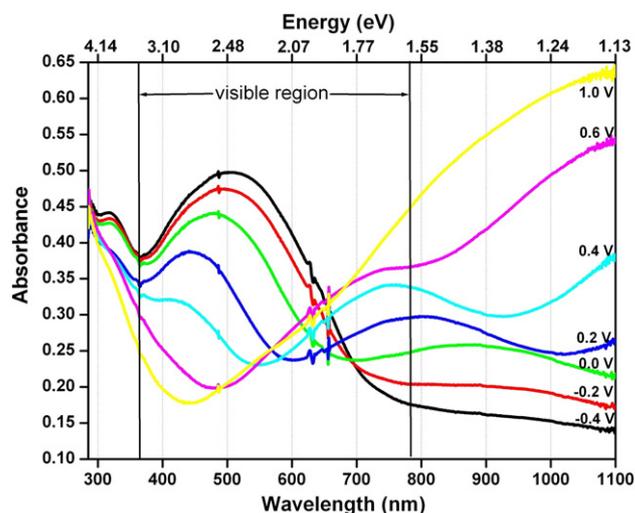


Fig. 7. Optoelectrochemical spectra of P(MTNP-co-EDOT) film at applied potentials between -0.4 and $+1.0$ V.

These colors and corresponding L*a* b values were given in Table 2.

3.9. Electrochromic switching

Electrochromic switching studies were performed to test the ability of a polymer to switch rapidly and the ability to exhibit striking color change. The experiments carried out by spectro-electrochemistry showed the ability of P(MTNP-co-EDOT) to switch between its neutral and doped states with a change in transmittance at a fixed wavelength. During the experiment, the percent transmittance (%T) of the polymer was measured using a UV–vis spectrophotometer at 500 nm. The polymer film was synthesized on ITO-coated glass slides and switched between -0.4 V and $+1.0$ V. The contrast was measured as the %T difference between the reduced and oxidized forms of copolymer. It is noted as 30% for 500 nm. As seen in Fig. 8 copolymer has reasonable stability and switching time (1.1 s).

3.10. Spectroelectrochemistry of the electrochromic device

A dual-type ECD consists of two electrochromic materials (copolymer as the anodically coloring, PEDOT as the cathodically coloring layer) deposited on transparent ITO,

Table 2

Colorimetry properties of copolymer and device

Material	Potential (V)	Color	L	a	b
Copolymer Films	-0.4	dark purple	52	26	-19
	0.0	red	76	16	15
	$+0.15$	light gray	81	1	8
	$+0.3$	green	86	-14	16
	$+1.1$	blue	64	-4	46
Copolymer/PEDOT	$+1.8$	dark purple	45	39	-12
	$+0.7$	green	76	-17	0
Device	$+0.3$	light gray	74	0	2
	-1.8	blue	55	-20	-32

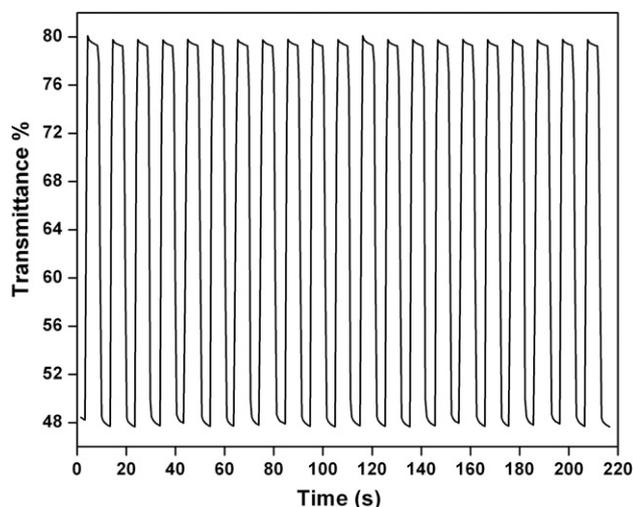


Fig. 8. Electrochromic switching, optical absorbance change monitored at 500 nm for P(MTNP-co-EDOT) between -0.4 V and $+1.0$ V.

placed in a position to face each other and a gel electrolyte was applied in between. The anodically coloring polymer film P (MTNP-co-EDOT) was fully reduced and the cathodically coloring polymer (PEDOT) was fully oxidized prior to construction of electrochromic devices (ECD).

Optoelectrochemical spectra of the dual type ECD as a function of applied potential (between -1.8 V and $+1.8$ V) are given in Fig. 9. Maximum absorption at around 470 nm reveals the π - π^* transition upon application of negative voltages. At that state, PEDOT did not reveal an obvious absorption at the UV–vis region of the spectrum and device showed dark purple color. A new π - π^* transition was observed at 620 nm due to PEDOT layer reduction while the intensity of π - π^* transition peak of anodically coloring P(MTNP-co-EDOT) was decreasing (Fig. 9). At 0.3 V intermediate light gray state and at 0.7

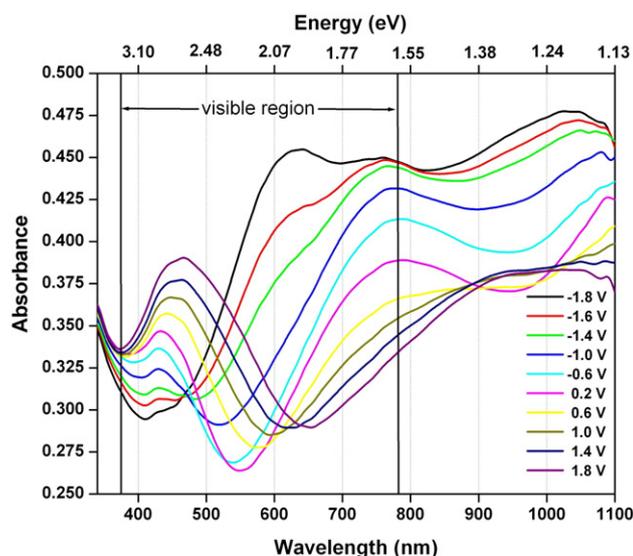


Fig. 9. Spectroelectrochemical spectra of the device with applied potentials -1.8 V and $+1.8$ V.

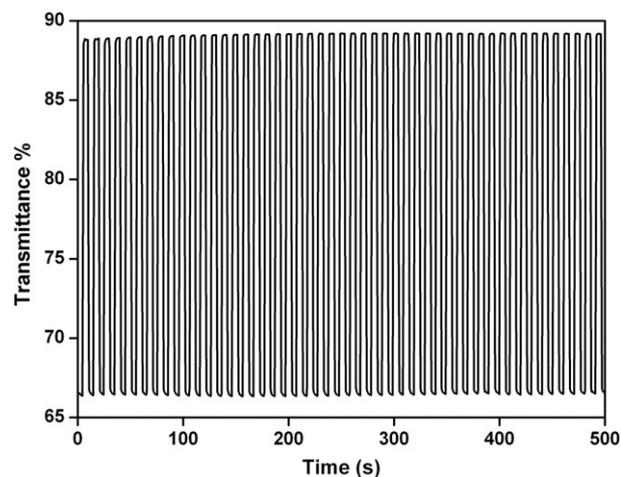


Fig. 10. Electrochromic switching, optical absorbance change monitored at 650 nm for device between -1.8 V and $+1.8$ V.

intermediate light green state were observed. $L^* a^* b$ values of P(MTNP-co-EDOT)/PEDOT ECD are given in Table 2.

3.11. Switching of electrochromic device

One of the most significant characteristics of electrochromic device is the response time. It is defined as the time needed to perform a switching between two states. Chronoabsorptometry was performed to estimate the response times of the device and its stability during consecutive scans.

Switching properties and optical contrast ($\% \Delta T$) of P(MTNP-co-EDOT) /PEDOT device at the wavelength of maximum contrast (650 nm) were measured (Fig. 10). Switching square wave potentials between -1.8 and $+1.8$ V with a residence time of 5 s, the optical contrast ($\% \Delta T$) at 650 nm were found as 23% and it was calculated that the ECD switches rapidly in about 1.1 s to reach the total transmission change.

4. Conclusion

Synthesis of a copolymer based on MTNP and EDOT was successfully achieved in ACN/LiClO₄ (0.1 M) solvent-electrolyte couple. Copolymer was characterized by CV, SEM, conductivity and FTIR studies. The scan rate for the anodic and cathodic peak currents shows a linear dependence as a function of the scan rate indicating that the polymer film was electroactive and adhered well to the electrode. Spectroelectrochemical studies and electrochromic characterization methods showed that copolymerization with EDOT not only decreases the band gap (E_g) but also enhanced the electrochromic properties such as optical contrast and switching time. It was also noticed that as the amount of PEDOT in the copolymer composition increases, band gap (E_g) of the copolymer decreases and λ_{\max} value of the copolymer shifts and becomes closer to 600 nm (λ_{\max} for PEDOT).

Spectroelectrochemical analyses revealed that the copolymer has an electronic band gap of 1.71 eV. The contrast is measured as the difference between $\%T$ in the reduced and oxidized forms and noted as 30% at 500 nm.

In the second part of the study, dual-type complementary colored polymer ECD were assembled with a configuration of ITO/P(MTNP-co-EDOT) || gel electrolyte || PEDOT/ITO and its characteristics were examined. Electrochromic switching study results showed that optical contrast ($\% \Delta T$) and switching time were 23% and 1.5 s at 650 nm. In addition, the device has good environmental and redox stability.

Acknowledgements

The authors gratefully thank the DPT-2005K120580, DOSAP program METU.

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