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# Synthesis, Characterization and Electrochromic Properties of Copolymer of Terephthalic Acid Bis-(thiophen-3-yl-methyl) Thioester with Thiophene

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*Terephthalic acid bis-(thiophen-3-yl-methyl thioester) (TTMT) was synthesized via the reaction of thiophen-3-yl methanethiol with terephthaloyl dichloride. Nuclear magnetic resonance (<sup>1</sup>H-NMR) spectroscopy and Fourier transform infrared (FTIR) spectroscopy were utilized for the characterization of the monomer. Electrochemical copolymerization of TTMT with thiophene in acetonitrile/boron trifluoride diethyl etherate (AN/BFEE) (8 : 2, v/v) solvent mixture was realized by using tetrabutylammonium tetrafluoroborate (TBAFB) as the supporting electrolyte. The resulting copolymer was characterized via cyclic voltammetry (CV), FTIR, differential scanning calorimetry (DSC), scanning electron microscopy (SEM), four-probe technique conductivity measurement and UV-Vis spectroscopy. Spectroelectrochemical analysis of the copolymer, P(TTMT-co-Th), reflected  $\pi$  to  $\pi^*$  transition at 476 nm and band gap was calculated as 2.03 eV. Kinetic studies were carried out upon measuring the percent transmittance (%T = 16%) at the maximum contrast point and switching time (1.25 s). A dual type electrochromic device (ECD) of P(TTMT-co-Th) and poly(3,4-ethylenedioxythiophene) (PEDOT) was constructed. Spectroelectrochemistry, switching ability, open circuit memory and stability of the device were examined by UV-Vis spectroscopy and cyclic voltammetry. The device switches between brown and blue, exhibits 0.0 V and 2.6 V as the switching voltages and short switching time (1.03 s).*

**Keywords** conducting polymers, electrochromic device, functionalized thiophenes, electrochemical polymerization

## Introduction

Conducting polymers offered the promise of achieving a new generation of polymers: Materials, which exhibit the electrical and optical properties of metals or semiconductors which retain the attractive mechanical properties and processing advantages of polymers (1). Conducting polymers may be synthesized via various techniques including chemical

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polymerization and electrochemical polymerization. Chemical polymerization occurs in the bulk of the solution in the presence of strong chemical oxidants, and the resulting polymers precipitate as insoluble solids (2). Electrochemical polymerization is normally carried out in a single or dual-compartment cell by adopting a standard three-electrode configuration in a supporting electrolyte, both dissolved in an appropriate solvent (3). An important feature of the electrochemical polymerization technique involves the direct formation of conducting polymer films, which are suitable for use in electronic devices (4).

Electrochromic devices (ECDs) could be effectively constructed with conducting polymers thanks to their ability to change color upon application of different potentials, in other words, their electrochromic behavior. An electrochromic material is the one that changes color in persistent but reversible manner by an electrochemical reaction and the phenomenon is called electrochromism. Electrochromism is the reversible and visible change in transmittance and/or reflectance that is associated with an electrochemically induced oxidation-reduction reaction (5).

All conducting polymers, such as the polypyrroles, polyanilines, and polythiophenes, are latently electrochromic in thin-film form. Redox switching gives rise to new optical absorption bands accompanied by a transfer of electrons and counter anions. In their oxidized states, conducting polymers are "doped" with counter anions ("p-doping") and contain a delocalized  $\pi$ -electron band structure. The energy band gap between the highest occupied  $\pi$ -electron band (valence band) and the lowest unoccupied band (the conduction band) determines the intrinsic optical properties. Reduction of conducting polymers with concurrent counter-anion exit, removes the electronic conjugation to give the "undoped" (neutral) electrically insulating form (6).

The colors of conducting polymers can be "tuned" by choosing a suitable aromatic substituent (7), as well as copolymerization. Based on that fact and very well known properties of thiophene, functionalized thiophenes and their homopolymers, as well as copolymers (8–15) were widely synthesized in recent years with the purpose of enhancing the diversity of electrochromic materials.

An ECD consists of two conducting polymer coated transparent electrodes sandwiched with a gel electrolyte in between, which provides the electron exchange. One of the electrodes is oxidized, while the other is being reduced upon externally applied potential, leading to a device switching between a combination of the neutral color of one film and the oxidized color of the other film, and vice versa (16). The requirements for high performance electrochromic devices are: a) high electrochromic efficiency; b) short response time; c) good stability; d) optical memory, defined as the color stability under open circuit conditions; e) optical contrast, also called write-erase efficiency; and f) color uniformity (17).

In this study, a new 3-functionalized thiophene monomer, terephthalic acid bis-(thiophen-3-yl-methyl) thioester (TTMT) was synthesized via esterification reaction of thiophen-3-yl methanethiol and terephthaloyl chloride. 3-Methyl thiophene was brominated with the use of N-bromosuccinimide (NBS) (18) and the resultant product, 3-bromomethyl thiophene, was converted to thiophen-3-yl methanethiol via the synthesis route proposed by Denise and Paul Cagniant (19). A copolymer of TTMT with thiophene (Th) was electrodeposited onto Pt or indium tin oxide (ITO) coated glass electrodes in the presence of acetonitrile/boron trifluoride diethyl etherate (AN/BFEE) and tetrabutylammonium tetrafluoroborate (TBAFB). BFEE was used since it facilitates electrochemical polymerization by lowering the aromatic resonance energy and promoting the abstraction of an electron from the  $\alpha$ -position of heterocycle ring (20). The resultant products were characterized by nuclear magnetic resonance ( $^1\text{H-NMR}$ ), Fourier transform infrared spectroscopy

(FTIR), cyclic voltammetry (CV), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) and conductivity measurements. Moreover, electrochromic properties of the copolymer and its dual type electrochromic device (ECD) constructed with P(TTMT-co-Th) (anodically coloring polymer) and poly(3,4-ethylenedioxythiophene) (PEDOT) (cathodically coloring polymer) were investigated.

## Experimental

### Materials

3-Methyl thiophene (Aldrich), N-bromosuccinimide (NBS) (Fluka), benzoyl peroxide (Sigma), carbon tetrachloride (Riedel-de Haen), thiourea (Sigma), methanol (Merck), sodium hydroxide (Aldrich), sulfuric acid (Merck), benzene (Merck), magnesium sulphate (Aldrich), triethylamine (TEA) (Aldrich), dichloromethane (Merck), terephthaloyl dichloride (Acros), hydrochloric acid (Merck), distilled water, sodium sulphate (Aldrich), ethanol (Merck) were used as received in the synthesis of terephthalic acid bis-(thiophen-3-yl-methyl) thioester. Boron trifluoride diethyl etherate (BFEE) (Aldrich), tetrabutyl ammonium tetrafluoroborate (TBAFB) (Aldrich) were used without purification. Thiophene (Th) (Aldrich) was distilled before use.

3,4-Ethylenedioxythiophene (EDOT) (Aldrich) was used with no further purification. The gel electrolyte was prepared by blending polymethylmethacrylate (PMMA) (Aldrich), TBAFB, acetonitrile (AN) (Merck), and propylene carbonate (PC) (Aldrich).

### Equipment

NMR spectra of the monomer were recorded on a Bruker-Instrument-NMR Spectrometer (DPX-400) with  $\text{CDCl}_3$  as the solvent and chemical shifts ( $\delta$ ) were given relative to tetramethylsilane as the internal standard. The cyclic voltammetry measurements were carried out in a AN/BFEE solvent mixture using TBAFB as the supporting electrolyte in a cell equipped with ITO (indium tin oxide) coated glass working, Pt wire counter electrodes and a  $\text{Ag}/\text{Ag}^+$  reference electrode, at room temperature and under nitrogen atmosphere. The cyclic voltammograms were recorded on Solartron 1285 potentiostat/galvanostat. Electrolyses were done using a Wenking POS 73 potentiostat in a two compartment cell containing two Pt foils as the working and counter electrodes and a  $\text{Ag}/\text{Ag}^+$  as the reference electrode, at room temperature and under nitrogen atmosphere. The IR spectra were recorded on a Nicolet 510 FTIR spectrometer. Thermal studies were achieved with Du Pont 2000 DSC. Scanning electron microscopy (SEM) studies were performed by JEOLJSM-6400. Conductivity of the polymer film was measured by a four-probe technique. Spectroelectrochemical and kinetic studies were performed on Solartron 1285 potentiostat/galvanostat and a HP8453A UV-Vis spectrophotometer. For colorimetry measurements, Coloreye XTH Spectrophotometer (Gretag-Machbeth) was used.

### Synthesis of Terephthalic Acid Bis-(thiophen-3-yl-methyl) Thioester (TTMT)

To obtain 3-bromomethyl thiophene, 3-methyl thiophene (10 mL, 0.100 mol), NBS (18 g, 0.100 mol) were refluxed for 6 h in 30 mL carbon tetrachloride containing 0.08 g (0.003 mol) of benzoyl peroxide. After cooling in an ice-bath, the unreacted NBS was removed by filtration, the reaction medium was washed with carbon tetrachloride and

the solvent was evaporated. The remaining oily substance was distilled in vacuum and 5.13 g (0.028 mol) of 3-bromomethyl-thiophene were obtained. The product was immediately refluxed with equimolar thiourea for 2 h in 30 mL of methanol. The liquid product was left to solidify for 24 h in cold. 6.2 g (0.025 mol) of isothiuronium salt were obtained. The resulting salt was dissolved in 30 mL of methanol and refluxed for 2 h with 0.049 mol of sodium hydroxide. Methanol was evaporated and the medium was acidified until pH 7.00. After extracting with benzene, water present in the organic layer was trapped with magnesium sulphate. Subsequent to filtering magnesium sulphate and evaporating benzene, thiophen-3-yl-methanethiol synthesis was completed and 2.11 g (0.016 mol) of the substance were obtained. Thiophen-3-yl-methanethiol was dissolved in 15 mL of triethylamine and 30 mL of dichloromethane. 1.62 g (0.008 mol) of terephthaloyl dichloride were dissolved in 30 mL of dichloromethane and added dropwise to the first solution with continuous stirring. The final reaction was carried out for 24 h in an ice-bath and under nitrogen atmosphere. The resulting substance was washed with 1% hydrochloric acid solution and with water. Extraction was done with dichloromethane, the organic layer was dried over sodium sulphate, and then filtered; the solvent was removed via rotaevaporatory. The target material, terephthalic acid bis-(thiophen-3-yl-methyl) thioester (TTMT) (0.32 g, 0.001 mol) was obtained by twice recrystallization in ethanol. The synthesis route is shown in Scheme 1.

#### **Synthesis of Copolymer of TTMT with Thiophene [P(TTMT-co-Th)]**

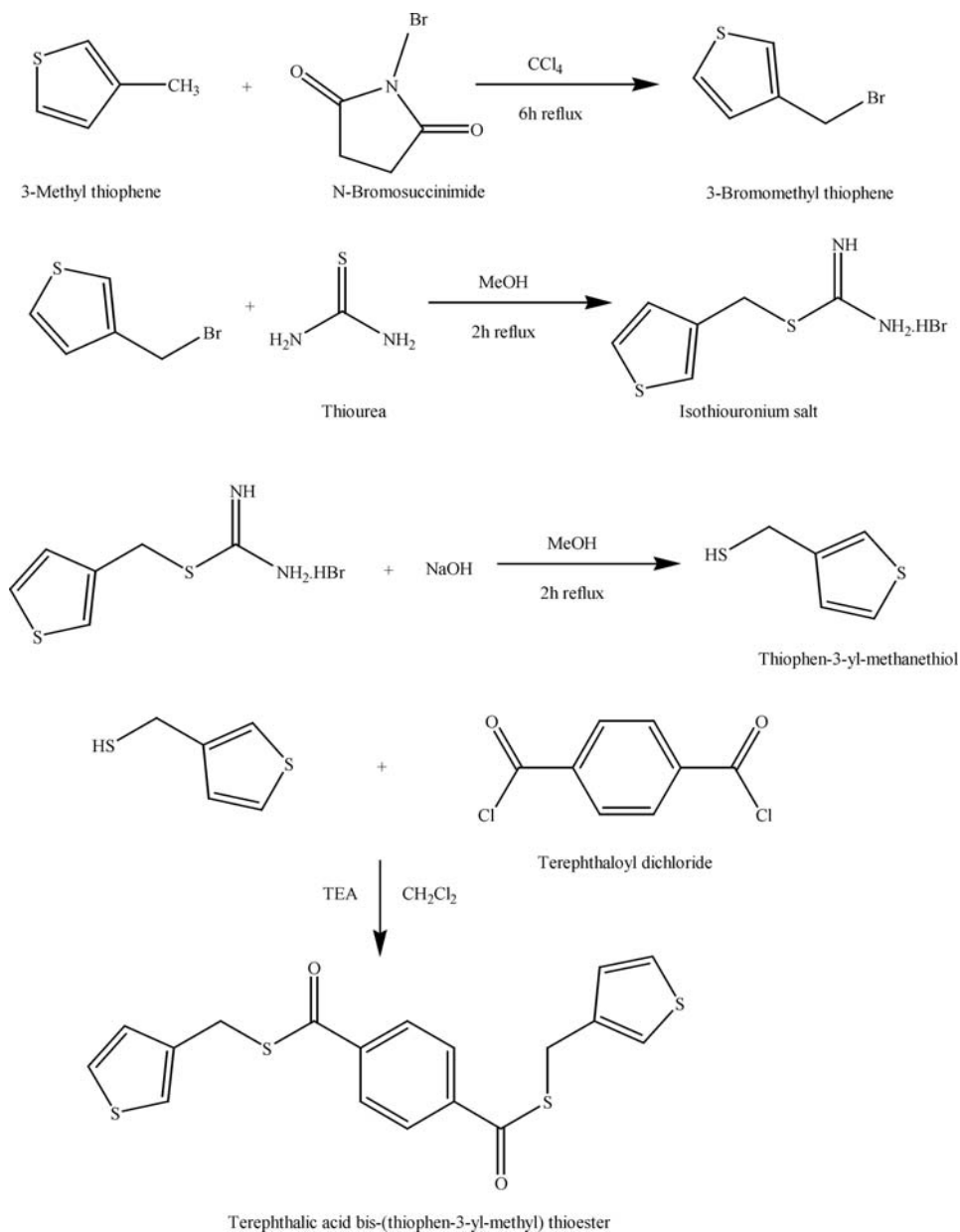
Copolymerization of TTMT with Th was accomplished via constant potential electrolysis for 40 min in a two compartment cell furnished with Pt working, Pt counter, Ag/Ag<sup>+</sup> reference electrodes, in the presence of 0.05 M TBAFB (supporting electrolyte), 10 mg TTMT, 80  $\mu$ L Th in AN/BFEE (8:2, v/v) at 1.5 V. The freestanding polymer film was washed with AN in order to get rid of the unreacted monomer. A similar procedure was applied for the synthesis of P(TTMT-co-Th) onto ITO glass working electrode in the AN/BFEE (8:2, v/v) medium containing 0.10 M TBAFB, 5 mg TTMT, 5  $\mu$ L Th.

#### **Preparation of Gel Electrolyte**

The fully transparent and highly conducting gel electrolyte was prepared by plasticization of PMMA with 1,2-propylenecarbonate in TBAFB/AN medium. The blend was heated at 70°C and continuously stirred until gel formation. The ratio of the composition of TBAFB/PMMA/PC/AN was 3:7:20:70.

#### **Electrochromic Device (ECD) Construction and Characterization**

Electrochromic devices were constructed by sandwiching the gel electrolyte between anodically and cathodically coloring polymers, which were electrochemically deposited onto ITO coated glass electrodes. Cathodically coloring polymer, P(TTMT-co-Th), was coated onto ITO glass from AN/BFEE (8:2, v/v) containing 0.10 M TBAFB, 5  $\mu$ L Th, and 5 mg TTMT. Anodically coloring polymer PEDOT was deposited from 0.10 M TBAFB/AN electrolyte containing 3  $\mu$ L EDOT. The redox sites of the two polymer films were matched by the employment of chronocoulometry so as to attain effective switching. The P(TTMT-co-Th) and PEDOT coated electrodes were polarized at 0.0 V and 1.5 V respectively in monomer free TBAFB/AN supporting electrolyte-solvent system before assembling ECDs.

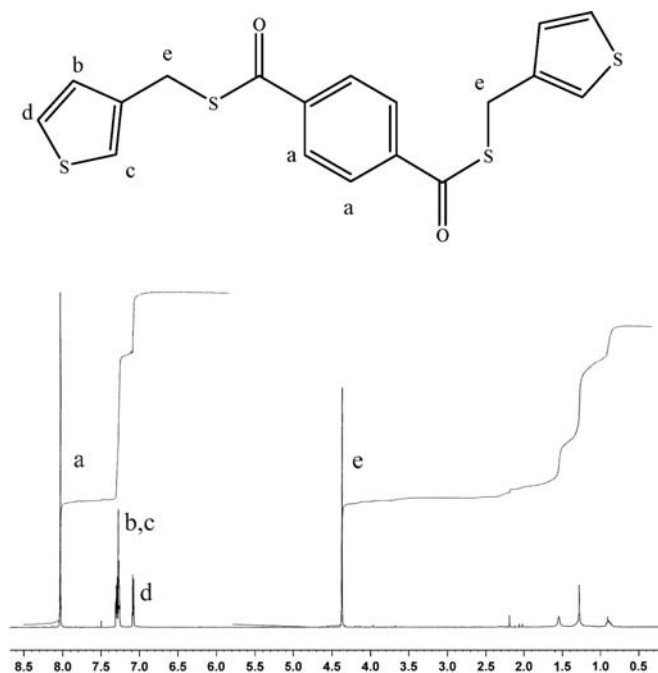


Scheme 1. Synthesis route of TTMT.

## Results and Discussion

### <sup>1</sup>H-NMR and FTIR Spectra

The structure of the monomer was confirmed by <sup>1</sup>H-NMR and IR spectral analysis. <sup>1</sup>H-NMR ( $\delta$ , ppm) data (Figure 1) for TTMT: 8 (s, 4H) from benzene ring, 7.3–7.1 (m, 6H) from 2, 4, 5 positions of thiophene ring, 4.4 (s, 4H) from COSCH<sub>2</sub>.



**Figure 1.**  $^1\text{H-NMR}$  spectra of TTMT.

In the FTIR spectrum of monomer, the following absorption peaks were identified:  $3098\text{ cm}^{-1}$  (aromatic proton bands C–H stretching),  $1107\text{ cm}^{-1}$  (cyclopentadienyl C=C stretching vibration),  $2921\text{ cm}^{-1}$  and  $2851\text{ cm}^{-1}$  (aliphatic methylene stretching vibration),  $1202\text{ cm}^{-1}$  (C–C stretching vibration arising from carbonyl bonded to an aryl group),  $903\text{ cm}^{-1}$  (C–S stretching vibration due to carbonyl bonded to sulfur),  $1657\text{ cm}^{-1}$  (C=O stretching vibration arising from carbonyl sandwiched between an aryl group and sulfur). The absorption bands at  $1495$ ,  $652$ ,  $784\text{ cm}^{-1}$  were due to the vibrations of C–H and C=C bonds of thiophene rings.

The FTIR spectrum revealed that electrocopolymerization of TTMT with Th was successfully realized. The peak monitored at  $784\text{ cm}^{-1}$  indicating cis C–H wagging of the thiophene ring and the band at  $652\text{ cm}^{-1}$  due to deformations of C–H out of plane of the thiophene ring disappeared completely upon polymerization. In addition, evolution of a new peak at  $838\text{ cm}^{-1}$  indicated the formation of 2,3,5-trisubstituted thiophene structure. The strong peak observed at  $1086\text{ cm}^{-1}$  was the characteristic  $\text{BF}_4^-$  dopant ion peak. The medium and broad peak monitored at  $1633\text{ cm}^{-1}$  was the C=O stretching vibration arising from carbonyl sandwiched between an aryl group and sulfur and the intensity of that peak was relatively low when compared to the intensity of the carbonyl peak of the monomer.

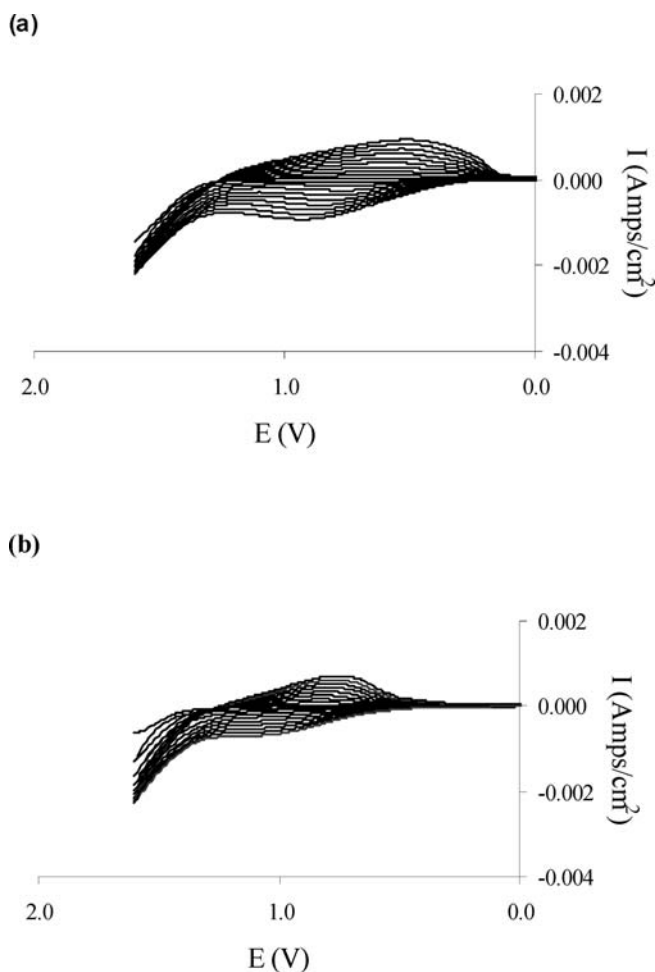
### Cyclic Voltammetry

Oxidation-reduction behavior of TTMT was investigated via cyclic voltammetry. Cyclic voltammograms taken in AN/TBAFB, AN/BFEE/TBAFB and BFEE/TBAFB media revealed that the monomer was not electroactive since it was lacking any redox peaks.

Upon addition of thiophene into a AN/BFEE/TBAFB medium containing the monomer, a reversible electroactivity different than that of Th was observed (Figure 2). In the cyclic voltammogram of PTh shown in Figure 2(a) 0.5 V and 0.9 V were observed as the reduction and oxidation peaks respectively; on the other hand, Figure 2(b) revealed that P(TTMT-co-Th) had 0.75 V as the reduction and 1.1 V as the oxidation potential.

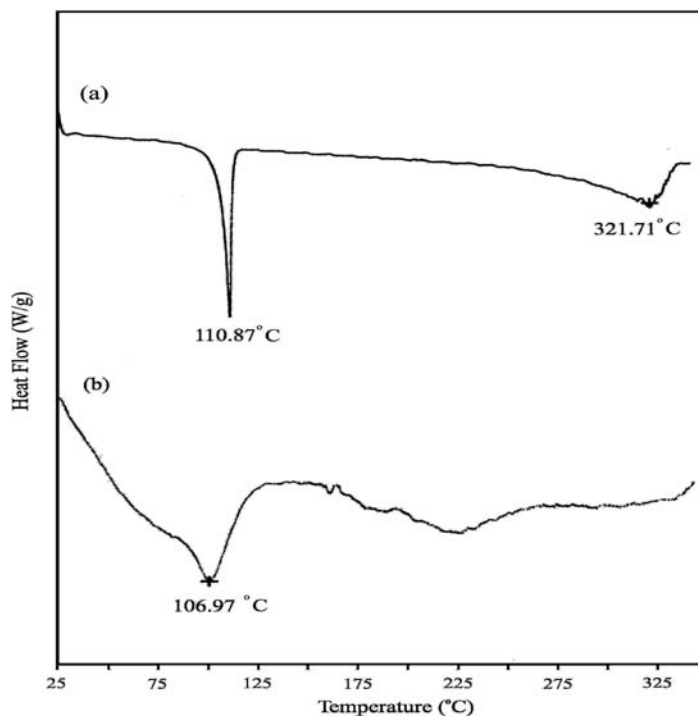
### Thermal Properties

DSC thermograms were examined in the range of 25–350°C at a heating rate of 10°C per minute. From the DSC thermogram of the monomer shown in Figure 3(a); 110.87°C was read as the melting temperature and 321.71°C as the decomposition temperature. In the case of the copolymer, a single thermal event was viewed at 106.97°C (Figure 3(b)).



**Figure 2.** Cyclic voltammograms of (a) PTh, (b) P(TTMT-co-Th).

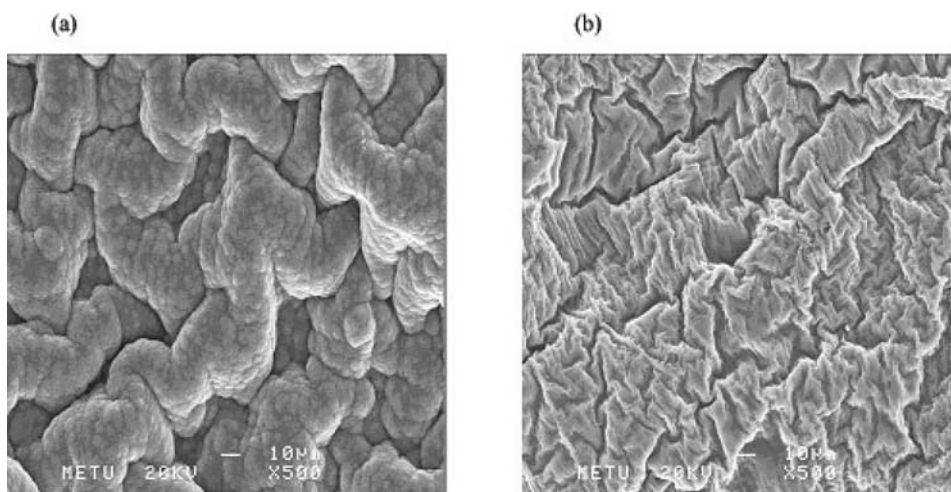




**Figure 3.** DSC thermograms of (a) TTMT, (b) P(TTMT-co-Th).

### *Morphology of the Film*

The solution side of P(TTMT-co-Th) film showed a worm-like structure, whereas the electrode side had a rough surface (Figure 4(a) and (b), respectively). Both SEM



**Figure 4.** SEM micrographs of (a) solution side of P(TTMT-co-Th) and (b) electrode side of P(TTMT-co-Th).

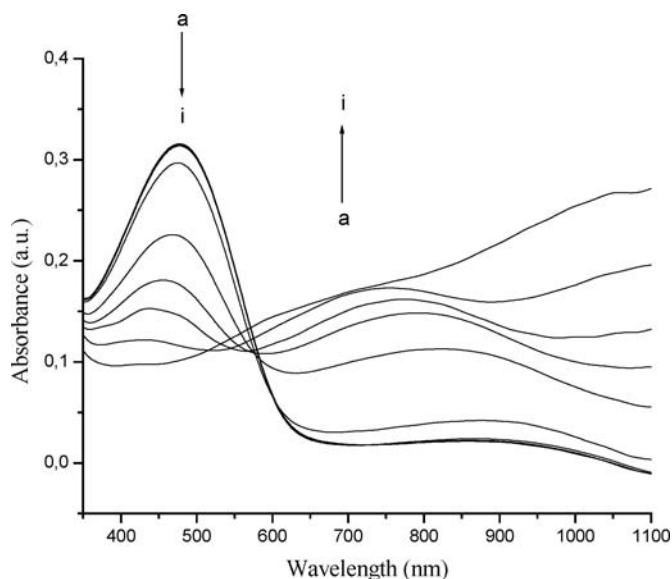
micrographs were different than those for pure polythiophene films. The solution side of the PTh film has a very characteristic cauliflower-like structure with a smooth surface on the electrode side.

### Conductivity of the Film

Room temperature (20°C) conductivity of P(TTMT-co-Th) was measured via a four-probe technique and determined as  $1.1 \times 10^{-2} \text{ S cm}^{-1}$ . On the other hand, the conductivity of the pure polythiophene film, which was synthesized at the same conditions, was measured as  $3.3 \text{ S cm}^{-1}$ . The fact that the conductivity of the copolymer film was less than that of the pure polythiophene film can be explained by weakening of conjugation through TTMT units and considered as proof of copolymerization.

### Spectroelectrochemistry of P(TTMT-co-Th)

TTMT was potentiostatically copolymerized with Th onto an ITO coated glass electrode in AN/BFEE (8:2, v/v) containing 0.10 M of TBAFB as the supporting electrolyte. The copolymer deposited ITO glass was put in a monomer free environment and spectroelectrochemical properties were determined. Spectroelectrochemical analyses of the P(TTMT-co-Th) were done with the purpose of elucidating electronic transitions and change in optical properties upon redox switching. Spectroelectrochemical spectra of the copolymer as a function of applied voltage are given in Figure 5 revealing  $\lambda_{\text{max}}$  as 476 nm with a band gap of 2.03 eV. The absorptions observed at around 750 and 820 nm were attributed to the evolution of polaron and bipolaron bands, respectively.



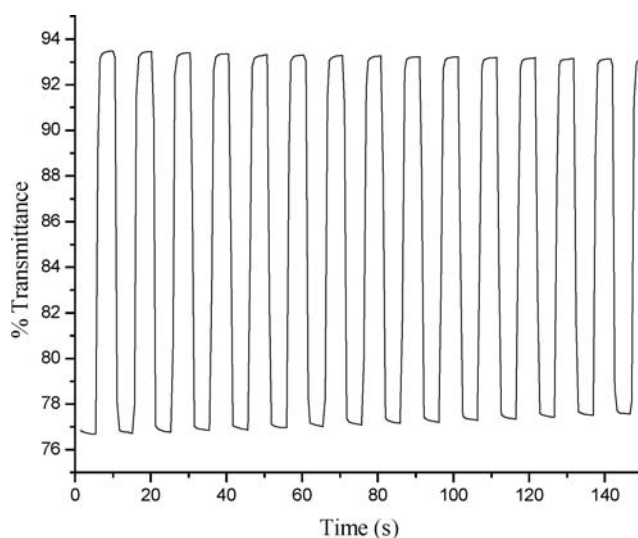
**Figure 5.** Spectroelectrochemistry of P(TTMT-co-Th) as a function of wavelength at applied potentials between 0.0 and +1.2 V: (a) 0.0 V, (b) +0.2 V, (c) +0.4 V, (d) +0.6 V, (e) +0.7 V, (f) +0.8 V, (g) +0.9 V, (h) +1.0 V, (i) +1.2 V.

### Electrochromic Switching of P(TTMT-co-Th)

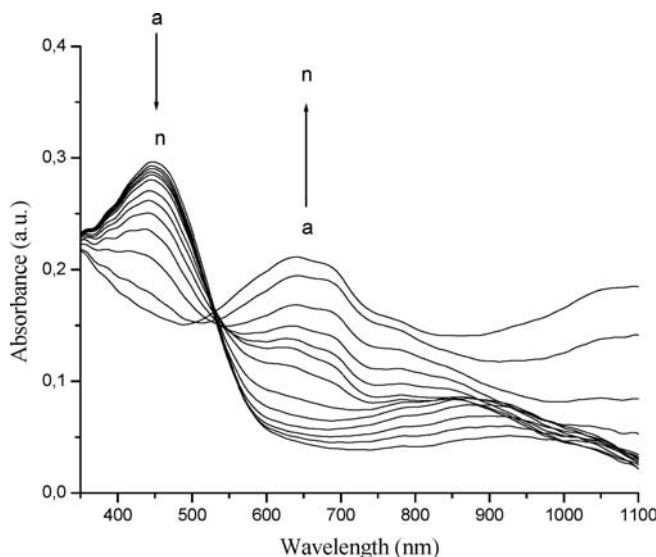
A remarkable color change and the switching ability between the two colored states of the polymer are crucially important for electrochromic applications. A square-wave potential step method, coupled with optical spectroscopy known as chronoabsorptometry, is used to probe switching time and contrast. During the experiment, the copolymer coated onto ITO glass was switched at the wavelength of maximum contrast between its neutral and doped states by the application of 0.0 V and 1.2 V, respectively, for five seconds and % transmittance (%T) was measured. For P(TTMT-co-Th), optical contrast (% $\Delta T$ ) and switching time were calculated as 16% and 1.25 s, respectively at 476 nm. Figure 6 shows transmittance-time profiles of the copolymer recorded during the experiment.

### Spectroelectrochemistry of P(TTMT-co-Th)/PEDOT Device

With the aim of examining optical changes of the ECDs occurring upon doping and dedoping, spectroelectrochemical studies were carried out. Figure 7 shows the spectra of P(TTMT-co-Th)/PEDOT device at voltages varying between 0.0 V and +2.6 V. Upon a stepwise increase of the applied potential from 0.0 V to 2.6 V, alternation of the color from brown to blue was observed. When 0.0 V bias was applied to the P(TTMT-co-Th), anodically coloring polymer layer, brown color was observed. There was a maximum absorption at 446 nm due to  $\pi$  to  $\pi^*$  electronic transition. At this potential, the PEDOT layer was in oxidized state, revealing a transparent sky blue color and the color of the ECD was dominated by the copolymer which was in its neutral state. At potentials beyond +0.8 V, the PEDOT starts to dominate and evaluation of a new peak at around 636 nm due to  $\pi$  to  $\pi^*$  transition was monitored. With the application of +2.6 V, the copolymer was fully oxidized whereas, the PEDOT layer was in its neutral state, and thus, at this voltage the color of the ECD was blue.



**Figure 6.** Electrochromic switching, optical absorbance change monitored at 476 nm for P(TTMT-co-Th) between 0.0 V and +1.2 V.



**Figure 7.** Spectroelectrochemistry of P(TTMT-co-Th)/PEDOT device as a function of wavelength at applied potentials between 0.0 and +2.6 V: (a) 0.0 V, (b) +0.2 V, (c) +0.4 V, (d) +0.6 V, (e) +0.8 V, (f) +1.0 V, (g) +1.2 V, (h) +1.4 V, (i) +1.6 V, (j) +1.8 V, (k) +2.0 V, (l) +2.2 V, (m) +2.4 V, (n) +2.6 V.

### *Electrochromic Switching of P(TTMT-co-Th)/PEDOT Device*

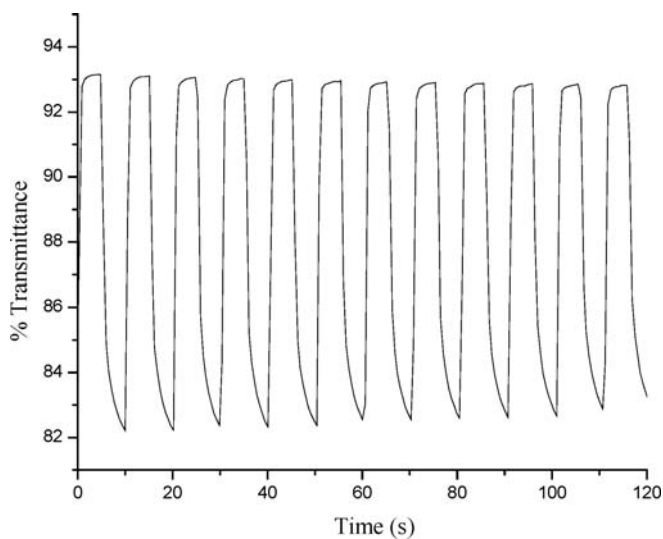
The response time needed to perform switching between the two colored states and the optical contrast were determined for the P(TTMT-co-Th)/PEDOT device. In this double potential step experiment, the potential was stepped between 0.0 V and 2.6 V with a residence time of 5 s at each potential. The optical contrast, monitored at 636 nm, was measured as 11% and the switching time was calculated as 1.03 s at 95% of the maximum transmittance. Figure 8 shows transmittance-time profiles of the ECD recorded during the experiment.

### *Open Circuit Stability of the ECD*

As stated by Girotto et al., the color persistence in the ECDs is an important feature since it is directly related to aspects involved in its utilization and energy consumption during use (21). The optical memory of an electrochromic material is defined as the time during which this material retains its color without applying potential (22). In the experiment, the ECD was polarized in the brown/blue states by an applied pulse (0.0 V/2.6 V, brown/blue colored states, respectively) for 1 s, and then kept under open circuit conditions for 200 s, while the optical spectrum at 636 nm as a function of time was monitored (Figure 9). When polarized upon application of 2.6 V in the blue colored state, % T abruptly changed to 83%, whereas during 200 s the ECD tried to reach 85% percent transmittance, in other words it was able to remember its color.

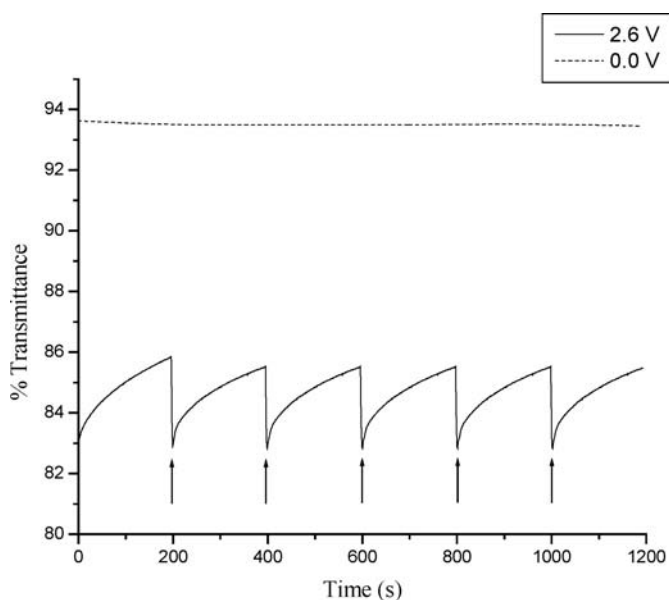
### *Stability of the ECD*

Construction of ECDs with long life times is targeted in electrochromic applications. In order to evaluate redox stability of the device under atmospheric conditions, cyclic

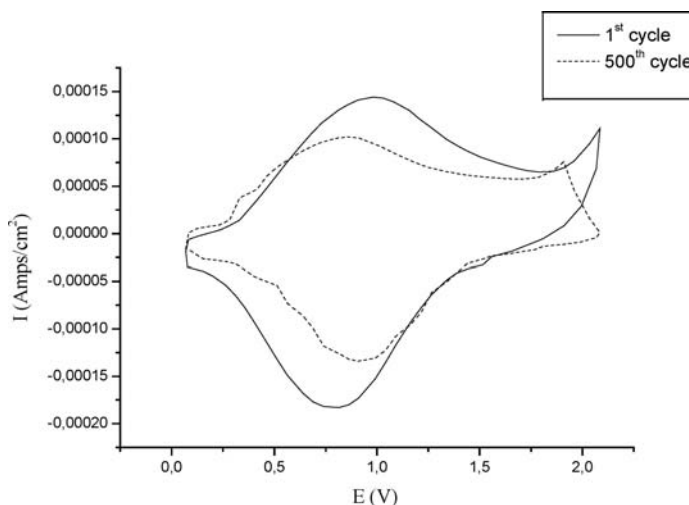


**Figure 8.** Electrochromic switching, optical absorbance change monitored at 636 nm for P(TTMT-co-Th)/PEDOT device between 0.0 V and +2.6 V.

voltammetry was utilized. The voltage of the device was continuously swept between 0.0 V and 2.6 V with 500 mV/s scan rate and cyclic voltammetry was monitored (Figure 10). As seen in the figure mentioned, P(TTMT-co-Th)/PEDOT could be repeatedly switched up to 500 cycles retaining most (70%) of its electroactivity.



**Figure 9.** Open circuit memory of P(TTMT-co-Th)/PEDOT device monitored by single-wavelength absorption spectroscopy at 636 nm. 0.0 V (dashed line) and +2.6 V (solid line) pulse are applied for 1 s every 200 s to recover the initial transmittance.



**Figure 10.** Cyclic voltammogram of P(TTMT-co-Th)/PEDOT ECD as a function of repeated scans 500 mV/s: after 1 cycle (solid line), after 500 cycles (dashed line).

### Colorimetry

Colorimetry analysis is considered as a valuable method for electrochromic materials since it enables numeric determination of color. The commonly used scale was set by La Commission Internationale de l'Eclairage (CIE). According to the CIE system, three values are determined to describe color, those are luminance or brightness, hue and saturation symbolized with L, a, b respectively. L, a, b values of the film and the device were measured when the copolymer is at the fully oxidized and fully reduced states and data were listed in Table 1. At the fully reduced state the color of the copolymer was brown ( $L = 45$ ,  $a = 17$ ,  $b = 29$ ); on the other hand, at the fully oxidized state the film has a blue color ( $L = 57$ ,  $a = -4$ ,  $b = 4$ ). When 0.0 V bias was applied to the P(TTMT-co-Th), anodically coloring polymer layer, the copolymer was completely reduced and the ECD has brown color ( $L = 49$ ,  $a = 5$ ,  $b = 25$ ). With the application of +2.6 V, the copolymer was entirely oxidized whereas the PEDOT layer was in its neutral state, at this voltage the color of the ECD was blue ( $L = 52$ ,  $a = 0$ ,  $b = -28$ ).

**Table 1**  
Electrochromic properties of P(TTMT-co-Th) and P(TTMT-co-Th)/PEDOT ECD

Material	$E_g$ (eV)	Color (red) <sup>a</sup>	Color (ox) <sup>a</sup>	L	a	b
P(TTMT-co-Th)	2.03	Brown	Blue	(ox) 57 (red) 45	-4 17	4 29
P(TTMT-co-Th)/PEDOT		Brown	Blue	(ox) 52 (red) 49	0 5	-28 25

<sup>a</sup>Reduced state (red), oxidized state (ox) of P(TTMT-co-Th).

## Conclusions

Synthesis of terephthalic acid bis-(thiophen-3-yl-methyl) thioester (TTMT), and its copolymer with thiophene were successfully accomplished. Switching properties of P(TTMT-co-Th) were investigated. Spectroelectrochemistry experiments showed that  $\pi$  to  $\pi^*$  transition, polaron and bipolaron band formations occurred at 476 nm, 756 nm, 817 nm respectively. Furthermore, band gap energy was calculated as 2.03 eV. P(TTMT-co-Th)/PEDOT electrochromic device was assembled in sandwich configuration: ITO coated glass/anodically coloring polymer [P(TTMT-co-Th)]//gel electrolyte//cathodically coloring polymer (PEDOT)/ITO coated glass. The device color changed between brown and blue upon application of potential. The switching voltages were 0.0 V and 2.6 V, switching time and optical contrast were found as 1.03 s and 11%, respectively. The ECD showed optimal redox stability and optical memory under atmospheric conditions.

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