

# Electrochromic Properties and Electrochromic Device Application of Copolymer of *N*-(4-(3-Thienyl methylene)-oxycarbonylphenyl)maleimide with Thiophene

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**ABSTRACT:** A new copolymer of *N*-(4-(3-thienyl methylene)-oxycarbonylphenyl)maleimide (MBThi) with thiophene [P(MBThi-co-Th)] was synthesized electrochemically in the presence of tetrabutylammonium tetrafluoroborate as the supporting electrolyte, in acetonitrile/borontrifluoride ethylether solvent mixture (80 : 20, v/v). Spectroelectrochemical analysis of the resulting copolymer reflected electronic transitions at 440, 730, and ~1000 nm, revealing  $\pi$ - $\pi^*$  transition, polaron, and bipolaron band formation, respectively. Switching ability was evaluated by a kinetic study via measuring the transmittance (%T) at the maximum contrast. Dual-type polymer

electrochromic devices (ECDs) based on P(MBThi-co-Th) and poly(ethylene dioxythiophene) (PEDOT) were constructed. Spectroelectrochemistry, switching ability, and stability of the devices were investigated by UV-vis spectroscopy and cyclic voltammetry. These devices exhibit low switching voltages (between 0.0 and +2.0 V) and short switching times with reasonable switching stability under atmospheric conditions. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4500–4505, 2006

**Key words:** electrochemical polymerization; conducting copolymers; electrochromic devices

## INTRODUCTION

An electrochromic material is the one that changes color reversibly by an electrochemical reaction and the phenomenon is called electrochromism.<sup>1</sup> 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 bathochromically upon doping, and the color contrast between the undoped and doped states is related to the polymer band gap.<sup>2</sup> 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. Polyheterocycles have proven to be of special interest for this because of their environmental stability under ambient conditions and in use conditions.<sup>3</sup>

Three major strategies of color control are used for electrochromic properties. The polymer's band gap is directly related to the relative energies of the HOMO and the LUMO. Via substitution on the polymer's repeat unit, the electrochromic properties can be

controlled by the induced steric and electronic effects. These substituents determine the effective conjugation length and the electron density of the polymer backbone.

Blends, laminates, and composites offer a second method for combining the electrochromic properties of several systems. The use of two polymers covering different color regions is a simplest way to achieve multicolor electrochromism.<sup>4</sup>

Copolymers offer a third means of controlling the electrochromic properties of the conducting polymers. 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.<sup>5</sup> 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.<sup>6</sup>

The main application of these materials is electrochromic devices, which are essentially electrochemical cells in which the electrochromic electrode is separated by a suitable solid or liquid electrolyte from a charge-balancing counter electrode. The color changes occur by charging and discharging. Possible applications for such devices include car rear-view mirrors, displays, or smart windows.<sup>7</sup>

In this study, we constructed dual-type electrochromic devices based on copolymer of *N*-(4-(3-thienyl methyl-

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ene)-oxycarbonylphenyl)maleimide (MBThi) with thiophene and poly(3,4-ethylenedioxythiophene) (PEDOT). Devices were assembled in sandwich configuration of electrochromic materials deposited on ITO glass electrodes. For the construction of devices, PEDOT was used as the cathodically coloring material and P(MBThi-co-Th) was used as the anodically coloring material.

## EXPERIMENTAL

### Materials

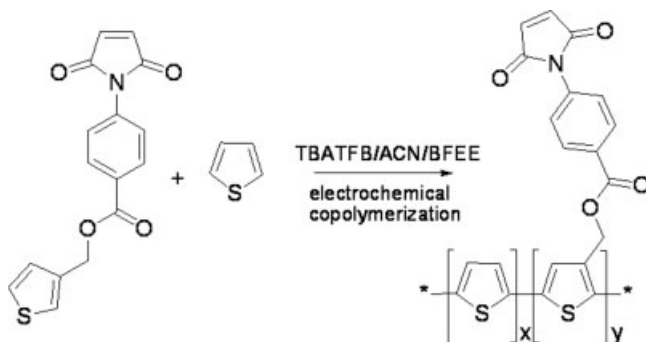
Propylene carbonate (PC), tetrabutylammonium tetrafluoroborate (TBAFB), and poly(methylmethacrylate) (PMMA) were purchased from Aldrich and used without further purification. Borontrifluoride ether (BFEE) was purchased from Sigma (Taufkirchen, Germany). Acetonitrile (AN) (Merck, Dormstadt, Germany) and thiophene (Th) (Aldrich) were distilled prior to use. 3,4-Ethylenedioxythiophene (EDOT) was purchased from Aldrich and used as received. *N*-(4-(3-Thienyl methylene)-oxycarbonylphenyl)maleimide was synthesized as reported previously.<sup>8</sup>

### Equipment

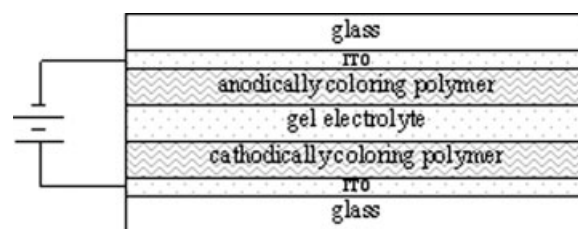
All electrochemistry was performed using a Solartron 1285 potentiostat/galvanostat. Spectroelectrochemical studies were carried out on a Agilent 8453 UV-vis spectrophotometer. Colorimetry measurements were obtained by a Coloreye XTH Spectrophotometer (GretagMacbeth). The IR spectrum was recorded on a Nicolet 510 FTIR spectrometer.

### Synthesis of copolymer of MBThi with thiophene P(MBThi-co-Th)

Polymerizations were performed in the presence of 50 mg MBThi and  $8.2 \times 10^{-3}$  mol L<sup>-1</sup> thiophene in 0.1 mol L<sup>-1</sup> TBAFB/AN/BFEE in a cell equipped with Pt working and counter electrodes and Ag wire pseudo reference electrode. Electrodeposition of co-



**Scheme 1** The synthesis of P(MBThi-co-Th) by electrochemical method.



**Scheme 2** Schematic representation of device.

polymer films were performed potentiodynamically between 0.0 and 2.0 V at a scan rate of 500 mV s<sup>-1</sup> (Scheme 1). The free-standing films which were grown on the electrode surface were peeled and vigorously washed with AN to remove unreacted monomers.

### Electrochemistry

A three-electrode cell containing ITO-coated glass slide as the working electrode, a platinum foil as the counter electrode, and a silver wire as the pseudoreference electrode were used for electrodeposition of polymer films by potentiodynamic methods.

### Gel electrolyte preparation

The gel electrolyte for electrochromic device based on PMMA was plasticized by 1,2-propylenecarbonate to form a highly transparent and conductive gel. A high vapor pressure solvent, AN was used to dissolve the PMMA and to allow an easy mixing of the gel components. The composition of casting solution (by weight AN:PC:PMMA:TBAFB) was 70 : 20 : 7 : 3.

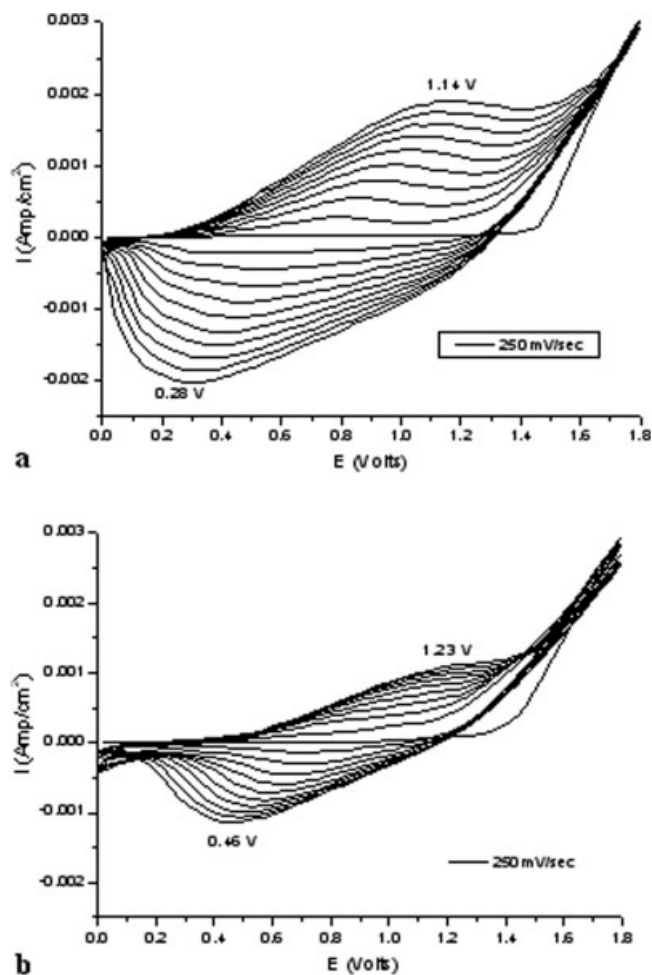
### Construction of ECD

Both anodically and cathodically coloring polymers were electrochemically deposited onto the ITO-coated glass from a 0.2M TBAFB/AN electrolyte. The redox sites of these polymer films were matched by stepping the potentials between 0.0 and +1.8 V for P(MBThi-co-Th) and -1.2 and +1.2 V for PEDOT. Electrochromic devices (ECD) were built by arranging two electrochromic polymer films (one doped, the other neutral) facing each other separated by a gel electrolyte. The construction of an absorption/transmission type device is depicted in Scheme 2.

## RESULTS AND DISCUSSIONS

### Cyclic voltammetry

To investigate the CV behavior of the copolymer, we performed CV studies in the presence of thiophene. A three-electrode cell containing ITO-coated glass slide as the working electrode, a platinum foil as the counter electrode, and a silver wire as the pseudo reference



**Figure 1** Cyclic voltammogram of (a) pure polythiophene (b) MBThi in the presence of thiophene in 0.2M TBAFB AN/borontrifluoride ethyl-ether (8 : 2, v/v). Potentials versus Ag wire.

were used. There was a drastic change in the voltammogram, both the increase in the increments between consecutive cycles and the oxidation potential of the material was different than those of pure thiophene, which in fact could be interpreted as the formation of copolymer, which needs to be supported by other means of characterization (Fig. 1).

### FTIR analysis

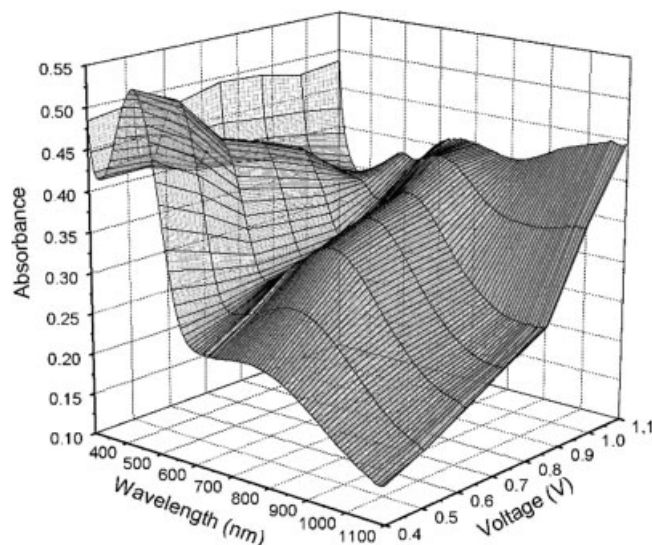
The FTIR spectrum of the monomer showed the usual features of substituted thiophenes. The absorption bands at 3170 and 3107  $\text{cm}^{-1}$  correspond to the aromatic C—H stretching originating from the benzene ring and thiophene moiety, the bands at 2955  $\text{cm}^{-1}$  corresponds to the aliphatic substituents (methyl group) of the monomer. The presence of the intense peak at 1718  $\text{cm}^{-1}$  was attributed to C=O stretching vibrations and the bands in the region of 1100–1213  $\text{cm}^{-1}$  were attributed to C—O—C (ester group)

stretching vibrations. The bands at 1605 and 1513  $\text{cm}^{-1}$  related to the C=C units of benzene ring and thiophene, the bands at 1389 and 1280  $\text{cm}^{-1}$  to the C—N vibrations of the maleimide group respectively. Thiophene moiety of the monomer was further characterized by the presence of the bands at 767 and 832  $\text{cm}^{-1}$  (C—H $_{\alpha}$  and C—H $_{\beta}$  stretching respectively).

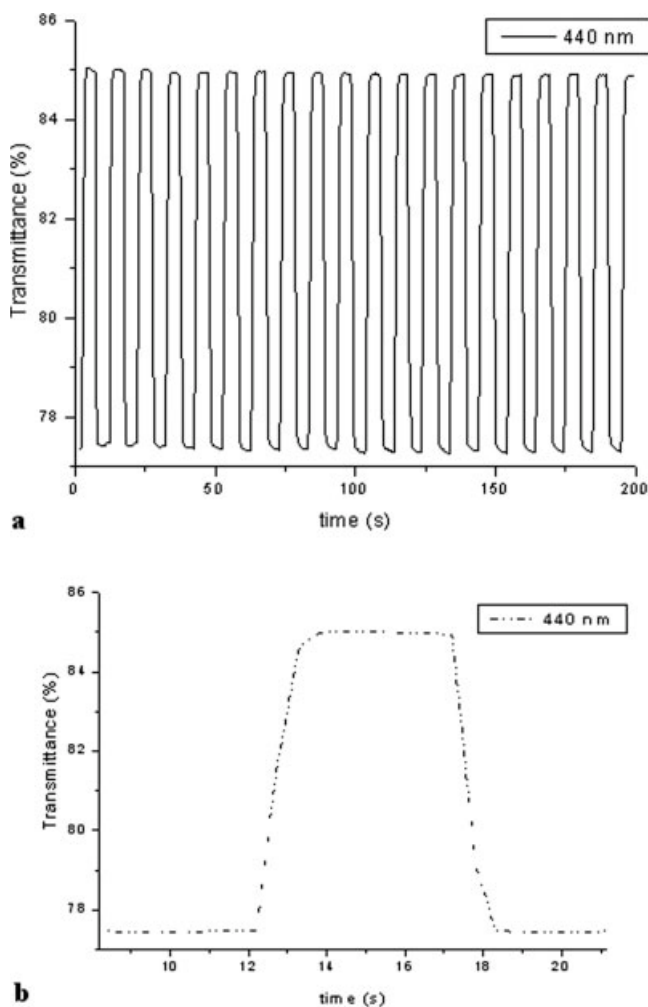
The FTIR spectrum of electrochemically synthesized copolymer revealed the presence of C=O, C—O—C and C=C stretching vibrations at 1711, 1115, and 1510  $\text{cm}^{-1}$  due to ester and phenyl groups of the monomer respectively. Besides, 2945  $\text{cm}^{-1}$  is due to C—H stretching vibrations of methyl group, the peak at 1395  $\text{cm}^{-1}$  are due to C—C and C—N stretching vibrations. The bands at 767 and 832  $\text{cm}^{-1}$  indicating C—H $_{\alpha}$  and C—H $_{\beta}$  stretching of the thiophene group of the monomer disappeared completely, whereas evolution of a new absorption peak at 840  $\text{cm}^{-1}$  (2,3,5-trisubstituted thiophene) was observed. The peaks around 1078 and 1611  $\text{cm}^{-1}$  indicated the presence of dopant anion and polyconjugation.

### Electrochromic properties of the copolymer

The redox switching of conjugated polymers is accompanied by changes in electronic transitions upon doping and dedoping, which is reason why the conjugated polymers are useful in electrochromic applications such as, smart windows, mirrors, etc.<sup>9</sup> Spectra were recorded while the polymer was oxidized by stepwise increasing the potential. To investigate the spectroelectrochemical behavior of the copolymer, films were deposited onto ITO-coated glass slides in TBAFB/AN/BFEE potentiodynamically between 0.0 and 1.8 V. Spectroelectrochemical properties were



**Figure 2** Spectroelectrochemistry of P(MBThi-co-Th) at applied potentials between 0.4 and +1.1 V in 0.2M TBAFB/AN.



**Figure 3** (a) Electrochromic switching, optical absorbance change monitored at 440 nm for P(MBThi-co-Th) between 0.0 and 1.1 V. (b) One step of the electrochromic switching.

studied in the same but monomer free solution. The  $\lambda_{\max}$  value for the  $\pi-\pi^*$  transitions in the neutral state of copolymer was found to be 440 nm, revealing light orange color which are all significantly different than pure polythiophene ( $\lambda_{\max} = 495$  nm). The electronic band gap defined as the onset energy for the  $\pi-\pi^*$  transition was found to be 1.74 eV. Upon increase in the applied voltage, the evolution of a new absorption band at 730 nm was observed due to evolution of charge carriers (Fig. 2), which was accompanied by gradual decrease in the intensity of the bands at  $\lambda_{\max}$ . At 1.1 V the extreme oxidation was achieved, where color of the copolymer was blue.

The switching time of the copolymer was determined by monitoring the %T change at 440 nm through switching the applied potential in a square wave form between 0.4 and 1.1 V with a residence time of 5 s. Applied potentials, which corresponds to the extreme states of the polymer, were obtained from the spectroelectrochemistry studies. As seen in

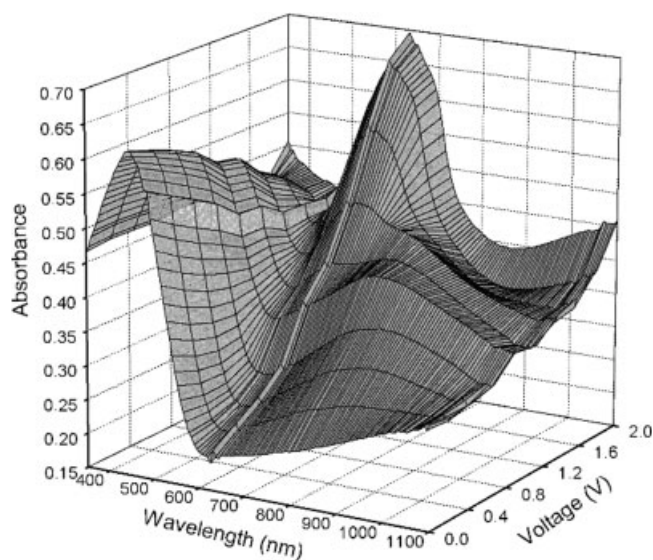
Figure 3(a,b), copolymer has good stability and fast switching time.

### Electrochromic properties of the device

In this study, we constructed the dual transmissive/absorptive type device of copolymer and PEDOT using transparent ITO electrodes. The anodically coloring polymer, namely P(MBThi-co-Th) was coated on ITO potentiodynamically in the presence of 0.2M TBAFB acetonitrile/borontrifluoride ethyl-ether (8 : 2, v/v). PEDOT, cathodically coloring polymer, was synthesized at 1.5 V in 0.1M TBATFB/AN on ITO electrodes. Prior to construction, the charge capacities of the electrochromic layers were balanced to achieve complete electrochromic reaction and eliminate the residual charge formation during the coloring/bleaching processes.

### Spectroelectrochemistry and switching

Spectroelectrochemical studies of the ECD were performed to examine the spectral changes that occur during redox switching. Optoelectrochemical spectra of the dual-type P(MBThi-co-Th)/PEDOT ECD as a function of applied voltage are shown in Figure 4. At 0.0 V the device revealed a maximum absorption at 450 nm and its color was light orange. At this stage the copolymer was in its neutral state revealing light orange color and PEDOT was in its oxidized form (highly transparent) revealing on significant absorption at the visible region. Upon incremental increase in the applied potential, oxidation of the copolymer layer, which was signified with the decrease in the intensity of the peak due to  $\pi-\pi^*$  transition was



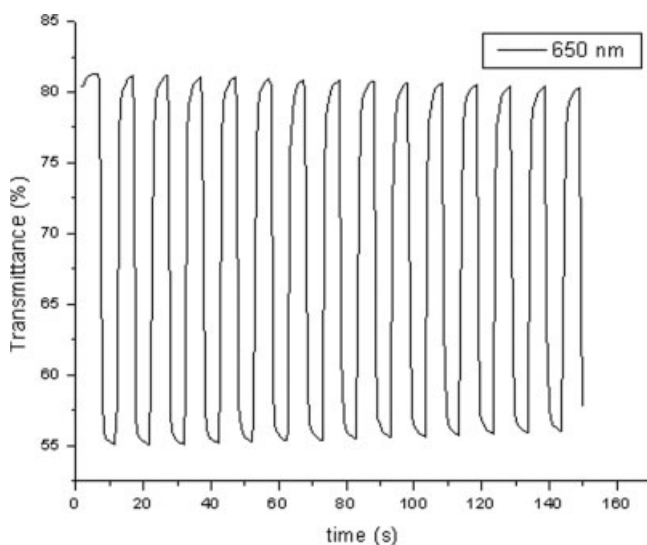
**Figure 4** Spectroelectrochemistry of P(MBThi-co-Th)/PEDOT device at applied potentials between 0.0 and 2.0 V.

observed. Beyond 2 V evolution of the new peak around 650 nm ( $\pi$ - $\pi^*$  transition of PEDOT itself) was observed, due to reduction of this layer. At 2 V the spectra of the device is very similar to pure PEDOT, indicating that the PEDOT and copolymer were in their fully neutral and oxidized states, respectively.

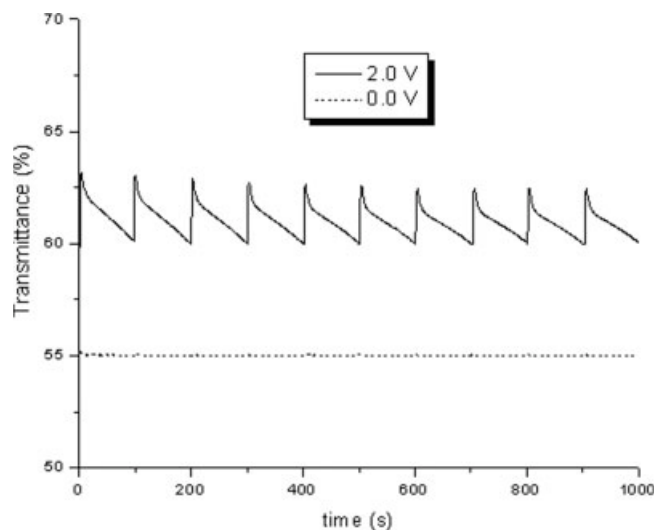
The time required to change the color of the device from 0.0 and 2.0 V was determined by kinetic studies, while applying the potential step square wave form. Figure 5 demonstrates the transmittance change at 650 nm (where the maximum contrast was observed). During the experiment, potentials were stepped between 0.0 and 2.0 V with a residence time of 5 s. Results showed that time required to reach 95% of ultimate % $T$  was 1.6 s. This value is comparable with that of polythiophene which is 1.7 s.<sup>6</sup>

#### Open circuit memory and stability of the device

The color persistence in the electrochromic devices is an important feature since it is directly related to aspects involved in its utilization and energy consumption during use.<sup>10</sup> This was done by polarizing the device in the colored/bleached states and following the optical spectrum as a function of time at open circuit conditions. Figure 6 represents the changes in the transmittance at the open circuit conditions after polarizing at 0.0 and 2.0 V, respectively. The transmittance was nearly invariant for 1000 s for the light orange colored state and showed a decreasing trend from 63% to 60% during 200 s for the blue colored state. This implies that light orange colored state has higher optical stability. Operational stability of the device was investigated by applying continuous potentiodynamic scans (references and counter electrode



**Figure 5** Electrochromic switching, optical absorbance change monitored at 650 nm for P(MBThi-co-Th)/PEDOT device between 0.0 and 2.0 V.

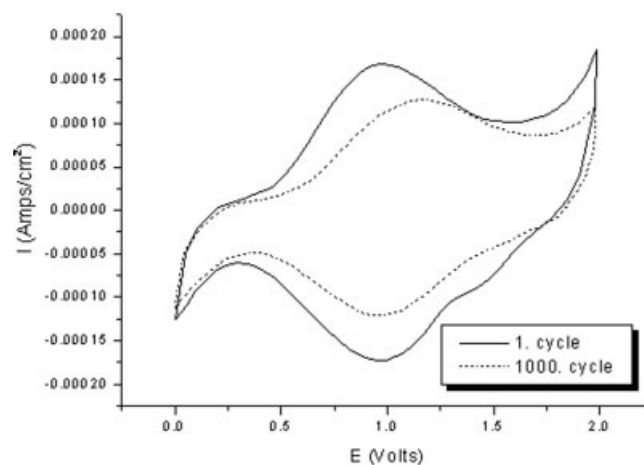


**Figure 6** Open Circuit memory of a P(MBThi-co-Th)/PEDOT/ECD monitored by single-wavelength absorption spectroscopy at 650 nm. 2.0 and 0.0 V pulses are applied for 1 s every 200 s to recover the initial transmittance.

are short circuited) between 0.0 and 2.0 V at a scan rate of 500 mV s<sup>-1</sup>. Results indicated the reasonable stability of the device under atmospheric conditions, where there is only limited decrease in current response after 500 cycles (Fig. 7).

#### Colorimetry

Colorimetry analysis has become an important technique for the electrochromic polymers, allowing the accurate measure of the color.<sup>11</sup> Color is made up of three attributes; hue (a), saturation (b), and luminance (L), and color systems such as the often-used CIE system are used as a quantitative scale to define and compare colors. Results of Colorimetry studies are given in Table I.



**Figure 7** Cyclic voltammogram of electrochromic device as a function of repeated scans 500 mVs<sup>-1</sup>: after one cycle (—), after 1000 cycles (---).

**TABLE I**  
**Electrochromic Properties**

Electrochromic device	Color	<i>L</i>	<i>a</i>	<i>b</i>
P(MBThi- <i>co</i> -Th)/PEDOT	Blue (oxidized state)	49.6	-4.6	-22.7
	Light orange (neutral state)	77.2	7.9	40.0

### CONCLUSIONS

A new copolymer of *N*-(4-(3-thienyl methylene)-oxy-carbonylphenyl)maleimide(MBThi) with thiophene [P(MBThi-*co*-Th)] was synthesized electrochemically. Electrochromic properties and switching ability of resulting copolymer was investigated. ECD was assembled with a configuration of ITO/Conducting Copolymer||Gel Electrolyte||PEDOT/ITO and characterized for their performance. Device exhibits low switching voltages (-0.0 to 2.0 V) and switching time with reasonable switching stability in atmospheric conditions.

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