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Electrochromic Properties of Copolymer of Terephthalic Acid Bis-(thiophen-3-yl-methyl) Thioester with Pyrrole

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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. This 3-functionalized thiophene monomer was polymerized in the presence of pyrrole (Py) upon constant potential application. Spectroelectrochemistry experiments reflected a π to π^* transition with a band gap energy of 2.4 eV for the copolymer. A dual type electrochromic device (ECD) of P(TTMT-co-Py) and poly(3,4-ethylenedioxythiophene) (PEDOT) was constructed. The device switches between greenish yellow and blue upon application of -2.4 V and $+0.8$ V, respectively. Optical contrast was calculated as 17.5%, whereas switching time was found as 1.6 s at maximum contrast point.

Keywords: conducting polymers; electrochromic device; thiophene derivative; copolymer with pyrrole

1 Introduction

Chemical and electrochemical polymerization of various organic aromatic molecules such as pyrrole, aniline, thiophene, furan, carbazole, etc. produces novel electronically conducting polymers (CPs) (1). The electrochemical technique has received wider attention both because of the simplicity and the added advantage of obtaining a conductive polymer being simultaneously doped. Free-standing as well as self-supporting conductive polymer films of desired thickness or geometry can be obtained (2).

In electrochemical doping, the electrode supplies the redox charge to the conducting polymer, while ions diffuse into (or out of) polymer structure from the nearby electrolyte to compensate the electronic charge. The doping level is determined by the voltage between the conducting polymer and the counter electrode; that voltage precisely determines the doping level at electrochemical equilibrium. Thus, doping at any level can be achieved by setting the electrochemical cell at a fixed applied voltage and simply waiting as long as necessary for the system to come to electrochemical equilibrium (3). The p-doping was explained as partial oxidation of the π -backbone of an organic polymer; whereas, the n-doping was defined as partial reduction of the backbone π -system of an organic polymer (4).

Electrochromism can be defined as the persistent change of optical properties of a material induced by reversible redox process. The doping process modifies the electronic structure of CPs, producing new electronic states in the band gap and causing color changes. Electronic absorption shifts to higher wavelengths with doping, and the color contrast between doped and undoped forms is related to the polymer band gap energy (5).

The colors of conducting polymers can be 'tuned' by choosing a suitable aromatic substituent (6), as well as copolymerization. Based on that fact and very well known properties of thiophene, functionalized thiophenes and their homopolymers, as well as copolymers (7–11), were widely synthesized in recent years with the purpose of enhancing diversity of electrochromic materials.

For practical electrochromic device (ECD) investigations, a simple two-electrode circuit is used with a solid (often polymeric), gel or liquid electrolyte being sandwiched between the primary electrochromic electrode and a charge-balancing secondary electrode, in what is essentially a rechargeable electrochemical cell. Color switching of the ECD takes place on charge/discharge by application of an appropriate electrical potential (12).

In this study, a 3-functionalized thiophene monomer, terephthalic acid bis-(thiophen-3-yl-methyl) thioester (TTMT) (13) was electrochemically copolymerized with pyrrole. P(TTMT-co-Py) was characterized with Fourier transform infrared spectroscopy (FTIR), cyclic voltammetry (CV), scanning electron microscopy (SEM) and conductivity measurements. Moreover, electrochromic properties of the

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copolymer and its dual type electrochromic device (ECD) constructed with P(TTMT-co-Py) (anodically coloring polymer) and poly(3,4-ethylenedioxythiophene) (PEDOT) (cathodically coloring polymer) were investigated.

2 Experimental

2.1 Materials

Pyrrrole (Aldrich), tetrabutyl ammonium tetrafluoroborate (TBAFB) (Aldrich), 3,4-ethylenedioxythiophene (EDOT) (Aldrich) were used without purification. The gel electrolyte was prepared by blending polymethylmethacrylate (PMMA) (Aldrich), TBAFB, acetonitrile (AN) (Merck), and propylene carbonate (PC) (Aldrich).

2.2 Equipment

Cyclic voltammetry measurements were carried out in AN using TBAFB as the supporting electrolyte in a cell equipped with ITO (indium tin oxide) coated glass working, Pt wire counter electrodes and a Ag/Ag⁺ reference electrode, at room temperature and under nitrogen atmosphere. The cyclic voltammograms were recorded on a Bank Wenking POS 2 potentiostat. 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 Ag/Ag⁺ as the reference electrode, at room temperature and under nitrogen atmosphere. The IR spectra were recorded on a Nicolet 510 FTIR spectrometer. Scanning electron microscopy (SEM) studies were performed by a JEOLJSM-6400. Conductivity of the polymer film was measured by a four-probe technique. Spectroelectrochemical and kinetic studies were performed on a Solatron 1285 potentiostat/galvanostat hyphenated with a Agilent HP8453A UV-Vis spectrophotometer, in addition to a VoltaLab PST050 potentiostat coupled with a Varian Cary 5000 UV-Vis-NIR spectrophotometer in a cell furnished with ITO coated glass working, Pt wire counter electrodes and a Ag/Ag⁺ reference electrode at room temperature. For colorimetry measurements, a Konica Minolta CS-100 A chromameter was used.

2.3 Electrochemical Synthesis of P(TTMT-co-Py)

Copolymerization of TTMT with Py was accomplished via constant potential electrolysis for 40 min in a two compartment cell furnished with Pt working, Pt counter, Ag reference electrodes, in the presence of 0.05 M TBAFB (supporting electrolyte), 10 mg TTMT, 70 μ L Py in AN at +1.2 V. The free standing polymer film was washed with AN in order to get rid of unreacted monomer. A similar procedure was applied for the synthesis of P(TTMT-co-Py) onto ITO glass working electrode in the AN medium containing 0.10 M TBAFB, 5 mg TTMT, and 2 μ L Py.

2.4 Preparation of Gel Electrolyte

The fully transparent and highly conducting gel electrolyte was prepared by plasticization of PMMA with 1,2-propylene-carbonate in a 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.

2.5 P(TTMT-co-Py)/PEDOT Device Construction

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

3 Results and Discussion

3.1 Characterization of P(TTMT-co-Py)

3.1.1 Cyclic Voltammetry Measurements

Oxidation–reduction behavior of TTMT in the presence of Py was investigated via cyclic voltammetry and a reversible electroactivity different than that of Py was observed (Figure 1). In the cyclic voltammogram of PPy shown in Figure 1(a) –0.18 V and +0.25 V were observed as the reduction and oxidation peaks respectively; on the other hand, Figure 1(b) revealed that P(TTMT-co-Py) had –0.13 V as the reduction and –0.4 V as the oxidation potential.

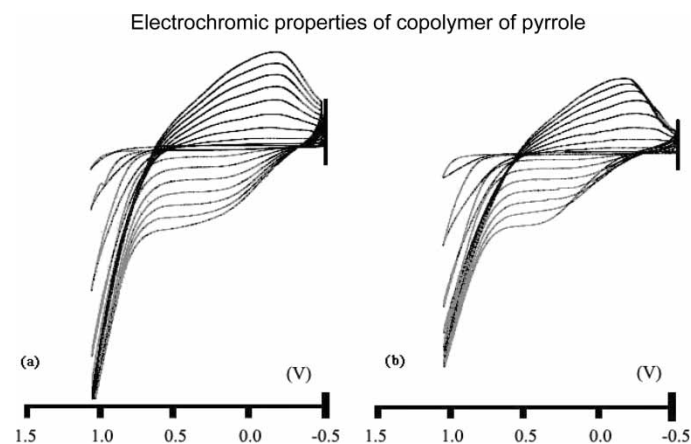


Fig. 1. Cyclic voltammograms of (a) PPy (b) P(TTMT-co-Py).

3.1.2 FTIR Spectra

In the FTIR spectrum of monomer, the following absorption peaks have been already identified (13): 3098 cm^{-1} (aromatic proton bands C-H stretching), 1495 cm^{-1} (aromatic C=C stretching vibration), 1107 cm^{-1} (cyclopentadienyl C=C stretching vibration), 2921 cm^{-1} and 2851 cm^{-1} (aliphatic methylene stretching vibration), 1202 cm^{-1} (C-C stretching vibration arising from carbonyl bonded to an aryl group), 903 cm^{-1} (C-S stretching vibration due to carbonyl bonded to sulfur), 1657 cm^{-1} (C=O stretching vibration arising from carbonyl sandwiched between an aryl group and sulfur). The absorption bands at 784 cm^{-1} and 838 cm^{-1} were due to the vibrations of C-H_α and C-H_β of thiophene rings, respectively. The FTIR spectrum revealed that electrocopolymerization of TTMT with Py was successfully realized. The peak monitored at 838 cm^{-1} indicating C-H_β of the thiophene ring disappeared completely upon polymerization. The peaks observed at 1513 cm^{-1} and 1158 cm^{-1} were due to pyrrole N-H and C-N stretching vibrations, respectively and they showed the presence of pyrrole in the polymeric matrix. In addition, the new peaks formed at 1034 cm^{-1} , 878 cm^{-1} , 1117 cm^{-1} were attributed to N-H and C-H deformation vibrations of three neighboring H atoms of 2-substituted pyrrole. The strong peak observed at 1082 cm^{-1} was the characteristic BF₄⁻ dopant ion peak. The medium and broad peak monitored at 1647 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.

3.1.3 Conductivity Measurements

Room temperature (20°C) conductivity of P(TTMT-co-Py) was measured via a four-probe technique and determined as 0.60 S cm^{-1} . On the other hand, the conductivity of the pure polypyrrole film, which was synthesized at the same conditions, was measured as 1.1 S cm^{-1} . The fact that the conductivity of the copolymer film was less than that of the pure polypyrrole film can be explained by the weakening of conjugation through TTMT units and considered as a proof of copolymerization.

3.1.4 Morphology of P(TTMT-co-Py)

Solution side of P(TTMT-co-Py) film showed a granular structure whereas electrode side had a rough surface (Figures 2(a) and (b), respectively). Both SEM micrographs were different than those for pure polypyrrole films. The solution side of PPy film has a more defined shaped cauliflower like structure; with a smooth surface on the electrode side.

3.1.5 Spectroelectrochemistry of P(TTMT-co-Py)

The best way to examine optoelectronic properties upon change in voltage is spectroelectrochemistry. TTMT was potentiostatically copolymerized with Py onto an ITO coated glass electrode in AN containing 0.10 M of TBAFB as the supporting electrolyte. The copolymer deposited ITO glass was put in a monomer

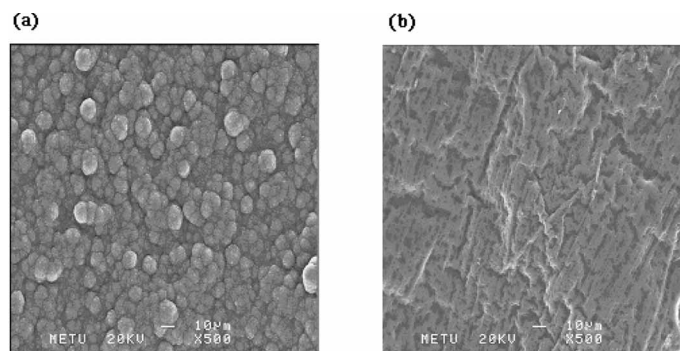


Fig. 2. SEM pictures of P(TTMT-co-Py) (a) solution side (b) electrode side.

free environment and spectroelectrochemical properties were determined in order to elucidate electronic transitions, band gap energy (Figures 3 and 4). At the reduced state, λ_{max} due to π to π^* state transition was found to be 375 nm and band gap energy was calculated as 2.4 eV. The appearance of peaks around 725 nm and 930 nm could be attributed to the evolution of polaron and bipolaron bands, respectively.

3.1.6 Colorimetry of P(TTMT-co-Py)

Colorimetry analysis, which enables numeric determination of color, is considered a valuable method for electrochromic applications. The commonly utilized scale was set by La Commission Internationale de l'Eclairage (CIE). In the CIE system, luminance or brightness, hue and saturation, symbolized with L, a, b, respectively, are determined to qualify color. At the fully reduced state, the color of the polymer

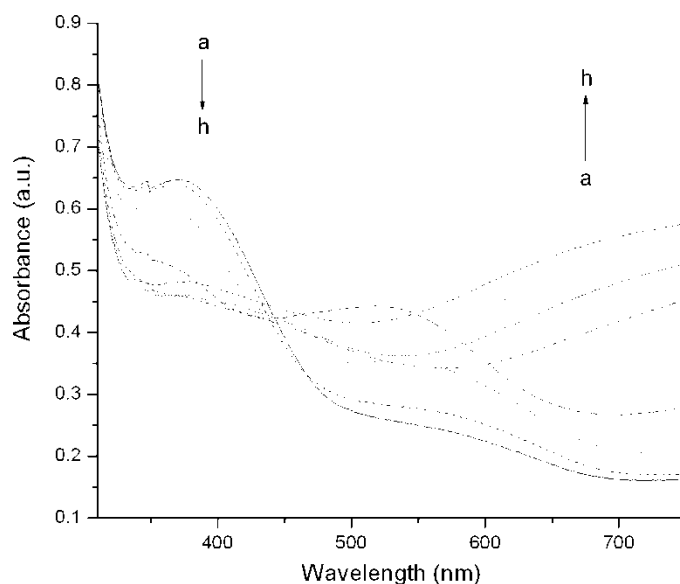


Fig. 3. Spectroelectrochemistry of P(TTMT-co-Py) as a function of wavelength (300 nm–700 nm) at applied potentials between -0.6 and $+0.8\text{ V}$: (a) -0.6 V , (b) -0.4 V , (c) -0.2 V , (d) 0.0 V , (e) $+0.2\text{ V}$, (f) $+0.4\text{ V}$, (g) $+0.6\text{ V}$, (h) $+0.8\text{ V}$.

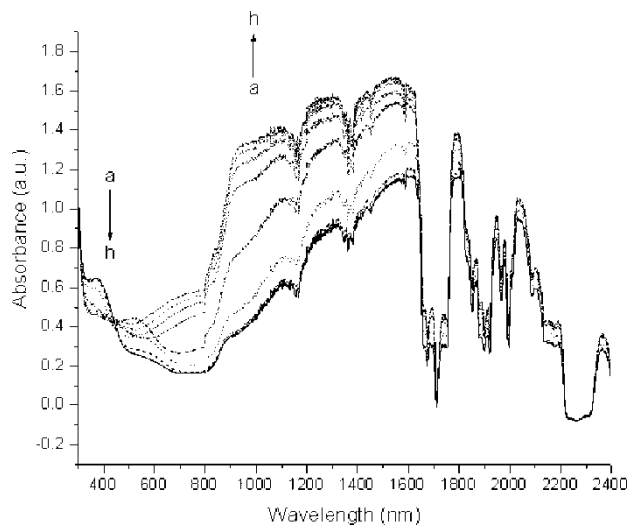


Fig. 4. Spectroelectrochemistry of P(TTMT-co-Py) as a function of wavelength (300–2500 nm) at applied potentials between -0.6 V and $+0.8$ V: (a) -0.6 V, (b) -0.4 V, (c) 0.0 V, (d) $+0.2$ V, (e) $+0.4$ V, (f) $+0.6$ V, (g) $+0.8$ V.

was greenish yellow ($L = 74$, $a = -10$, $b = 89$), at 0.0 V the color of the polymer turned to pale violet red ($L = 68.4$, $a = 16.0$, $b = -7.1$); on the other hand, at the fully oxidized state, the film has a greenish blue color ($L = 40.3$, $a = -16.2$, $b = -16.1$).

3.1.7 Kinetic Studies of P(TTMT-co-Py)

Kinetic studies were performed to test the ability of a polymer to switch rapidly between the colors of doped and undoped state. During the experiment, the copolymer electrochemically coated onto ITO glass was switched between -0.6 V and $+0.8$ V (Figure 5), in other words between undoped and doped states, respectively, for five seconds. For P(TTMT-co-Py), optical contrast ($\% \Delta T$) and switching time were calculated as 4.6% and 1.65 s, respectively at the given λ_{\max} . However, the maximum contrast in the visible range was found as 13% at 725 nm, at that wavelength switching time was calculated as 1.45 s.

3.2 Characterization of P(TTMT-co-Py)/PEDOT Device

3.2.1 Spectroelectrochemistry of the Device

With the aim of examining optical changes of the ECDs occurring upon application of different potentials spectroelectrochemical studies were carried out. The optoelectronic spectra of P(TTMT-co-Py)/PEDOT device at voltages varying between -2.4 V and $+0.8$ V was shown in Figure 6. Upon a stepwise increase of the applied potential from -2.4 V to $+0.8$ V, alternation of the color from yellow to blue was observed. A maximum absorption due to $\pi-\pi^*$ transition of P(TTMT-co-Py) was observed at 380 nm, and the color of the device was dominated by the copolymer. With the application of $+0.8$ V, P(TTMT-co-Py) was fully

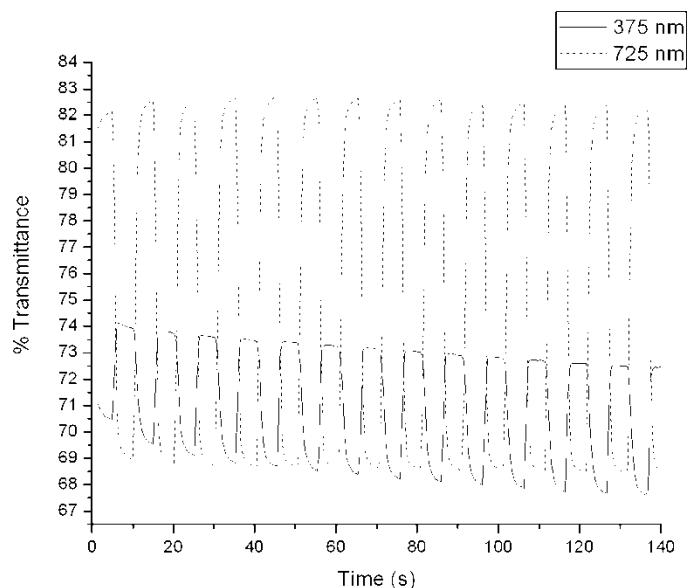


Fig. 5. Electrochromic switching, percent transmittance change monitored at 375 nm (solid line) and 725 nm (dashed line) for P(TTMT-co-Py) between -0.6 V and $+0.8$ V.

oxidized whereas PEDOT was completely reduced, $\pi-\pi^*$ transition of PEDOT was monitored at 580 nm, and thus, at this voltage the color of the ECD was blue.

3.2.2 Colorimetry of the Device

When 0.0 V bias applied to the anodically coloring polymer layer, the ECD has a violet red color ($L = 74.4$, $a = 5.2$,

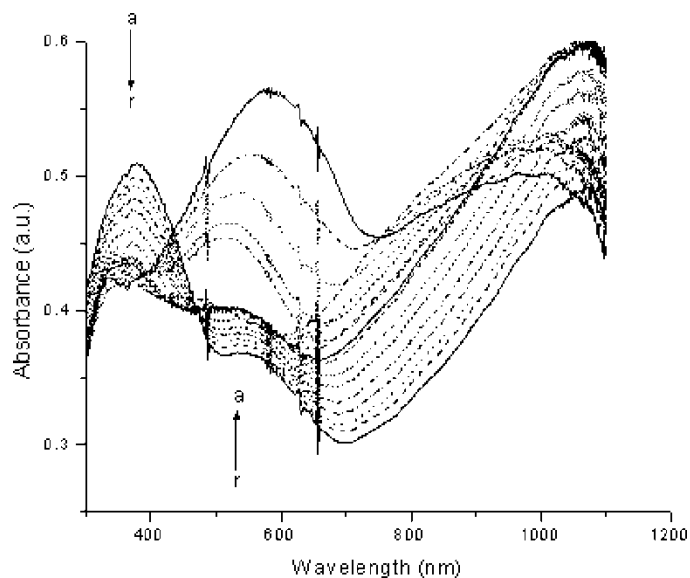


Fig. 6. Spectroelectrochemistry of P(TTMT-co-Py)/PEDOT ECD as a function of wavelength at potentials between -2.4 V and $+0.8$ V: (a) -2.4 V, (b) -2.2 V, (c) 2.0 V, (d) -1.8 V, (e) -1.6 V, (f) -1.4 V, (g) -1.2 V, (h) -1.0 V, (i) -0.8 V, (j) -0.6 V, (k) -0.4 V, (l) -0.2 V, (m) 0.0 V, (n) $+0.2$ V, (o) $+0.4$ V, (p) $+0.6$ V, (r) $+0.8$ V.

$b = -9.9$). Upon application of -2.4 V, a yellow color ($L = 73.7$, $a = -9.7$, $b = 20$) was observed. With the application of $+0.8$ V, the polymer was completely oxidized, whereas the PEDOT layer was fully reduced; at this potential, the color of the device was blue ($L = 59$, $a = -2.5$, $b = -28.3$).

3.2.3 Electrochromic Switching of the Device

To investigate switching characteristics of the ECDs, a percent transmittance change at the maximum contrast wavelength was monitored while stepping potential between -2.4 V and $+0.8$ V during 140 s. For the device, maximum contrast ($\% \Delta T$) and switching time were measured at 580 nm, and found as 17.5% and 1.6 s, respectively (Figure 7).

3.2.4 Open Circuit Memory of the Device

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 (14). The optical memory of an electrochromic material is defined as the time during which this material retains its color without applying potential (15). In the experiment, the ECD was polarized in the yellow/violet red/blue states by an applied pulse -2.4 V/ 0.0 V/ $+0.8$ V, respectively for 1 s, and then kept under open circuit conditions for 199 s, while the optical spectrum at 580 nm as a function of time was monitored (Figure 8). As seen in the figure mentioned, upon application of 0.0 V at the end of each 199 s no significant change in the percent transmittance (60.4%) was observed.

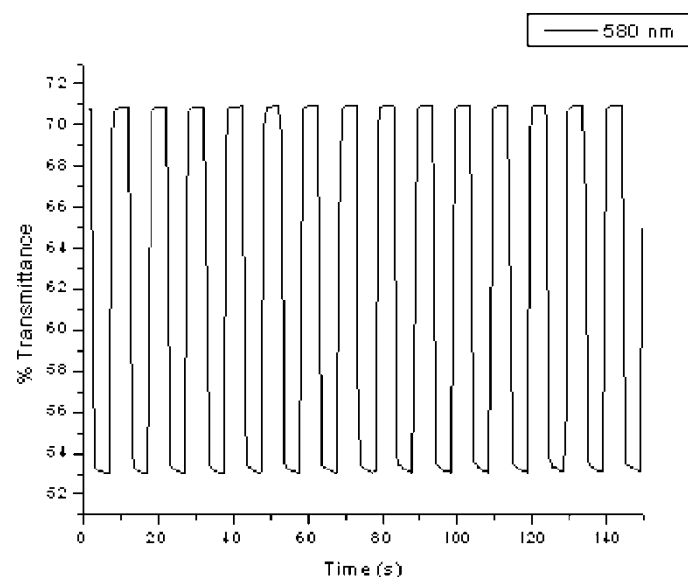


Fig. 7. Electrochromic switching, percent transmittance change monitored at 580 nm for P(TTMT-co-Py)/PEDOT ECD between -2.4 V and $+0.8$ V.

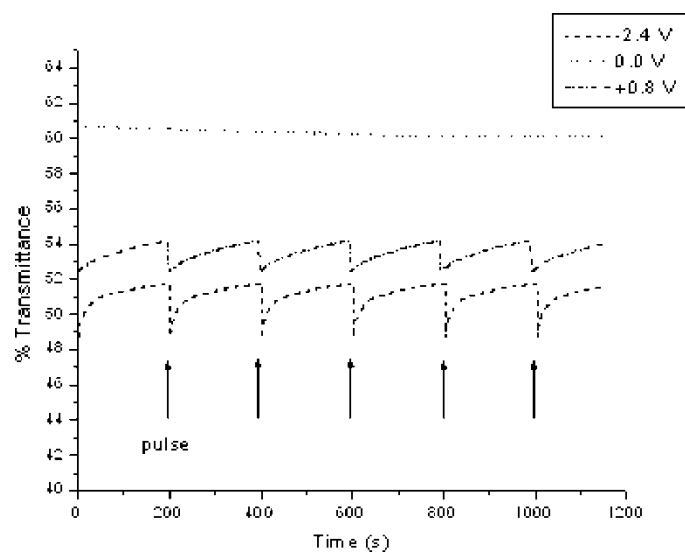


Fig. 8. Open circuit memory of P(TTMT-co-Py)/PEDOT ECD monitored at 580 nm, pulses are applied for 1 s every 200 s to recover the initial transmittance.

When polarized upon application of $+0.8$ V in the blue colored state, $\%T$ abruptly changed to 52.5%, whereas during 199 s the ECD tried to reach 54% transmittance; on the other hand, upon application of -2.4 V $\%T$ changed to 49%, whereas during 199 s the ECD tried to reach 51.6% transmittance, in other words, it was able to remember its color.

3.2.5 Stability of the Device

Construction of ECDs with long life times is targeted in electrochromic applications. In order to evaluate redox stability of

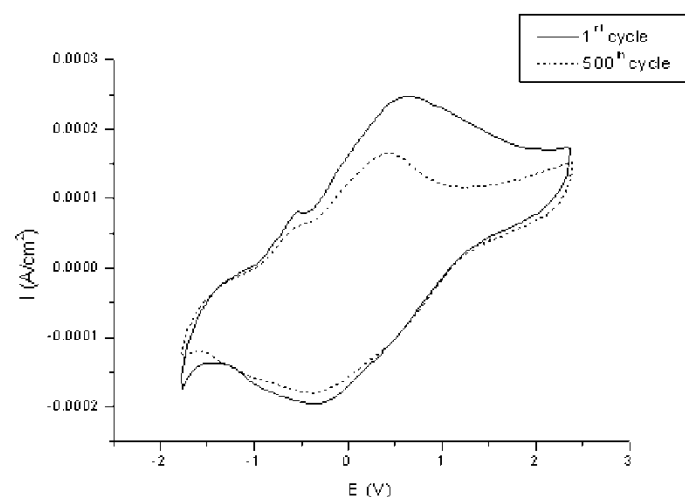


Fig. 9. Cyclic voltammogram of P(TTMT-co-Py)/PEDOT ECD as a function of repeated scans 500 mV/s: after 1 cycle (solid line), after 500 cycles (dashed line).

the device under atmospheric conditions, cyclic voltammetry was utilized. The voltage of the device was continuously swept between -2.0 V and $+2.5$ V with 500 mV/s scan rate and cyclic voltammetry was monitored (Figure 9). As seen in the figure mentioned, P(TTMT-co-Py)/PEDOT could be repeatedly switched up to 500 cycles retaining most (79%) of its electroactivity.

4 Conclusions

Electrochemical synthesis of the copolymer terephthalic acid bis-(thiophen-3-yl-methyl) thioester (TTMT) with pyrrole was successfully accomplished. Optoelectronic and switching properties of P(TTMT-co-Py) were investigated. Spectroelectrochemistry experiments showed that π to π^* transition, polaron and bipolaron band formations occurred at 375 nm, 725 nm, 930 nm, respectively. Furthermore, band gap energy was calculated as 2.4 eV. P(TTMT-co-Py)/PEDOT electrochromic device was assembled in sandwich configuration: ITO coated glass/anodically coloring polymer [P(TTMT-co-Py)]/gel electrolyte/cathodically coloring polymer (PEDOT)/ITO coated glass. The device has three different colors, yellow, violet red, and blue upon application of different potentials. The switching voltages were -2.4 V and $+0.8$ V, switching time and optical contrast were found as 1.6 s and 17.5%, respectively. The ECD showed optimal redox stability and optical memory under atmospheric conditions.

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