

Electrochromic Properties of a Copolymer of 1-4-Di[2,5-di(2-thienyl)-1H-1-pyrrolyl]benzene with EDOT

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ABSTRACT: Homopolymer of 1-4-di[2,5-di(2-thienyl)-1H-1-pyrrolyl]benzene and its copolymer with 3,4-ethylenedioxythiophene (EDOT) were electrochemically synthesized and characterized. Resulting homopolymer and copolymer films have distinct electrochromic properties. At the neutral state, homopolymer has λ_{\max} due to the π - π^* transition as 410 nm and E_g was calculated as 2.03 eV. The resultant copolymer revealed multichromism through the entire visible region, displaying red-violet, brownish yellow green, and blue colors with the variation of the applied potential. For the copolymer, λ_{\max} and E_g were found to be 450 nm and 1.66 eV, respectively. Double potential step chronoamperometry experiment shows that

homopolymer and copolymer films have good stability, fast switching times, and high optical contrast in NIR region as 41 and 30%, respectively. Copolymerization with EDOT not only decreases the band gap, E_g , but also enhances the electrochromic properties. Hence, electrochemical copolymerization is considered to be a powerful tool to improve the electrochromic properties of N-substituted 2,5-di(2-thienylpyrrole) derivatives. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1082–1087, 2009

Key words: electrochemical polymerization; conducting polymer; electrochromism; multichromism; copolymerization; optical contrast

INTRODUCTION

Several chemical materials exhibit redox states with different electronic (UV/visible) absorption spectra. When the switching of redox states generates new or different visible bands, the material is said to be electrochromic.^{1–4} Color changes in an object give visual signals that can be used to convey useful information for an observer.¹ Electrochromism is the reversible change in optical properties that can occur when a material is electrochemically oxidized (loss of electron(s)) or reduced (gain of electron(s)).^{5,6} Many chemical species can be switched between redox states that have distinct electronic absorption spectra. Such spectra arise from either a moderate energy internal electronic excitation or an intervalence optical charge transfer where the chemical species has two centers of differing valence or oxidation states.^{7–11} It is important, however, to realize that while many types of chemical species exhibit electrochromism, only those with favorable electrochromic

performance parameters² are potentially useful in commercial applications.

Conducting polymers are of interest as electrochromic materials because of their ease of chemical and electrochemical synthesis, environmental stability, and processability. Conjugated polymers are used as electroactive layers in electrochromic devices because of their ease of color tuning properties, fast switching times, and high contrast.^{6,12–14}

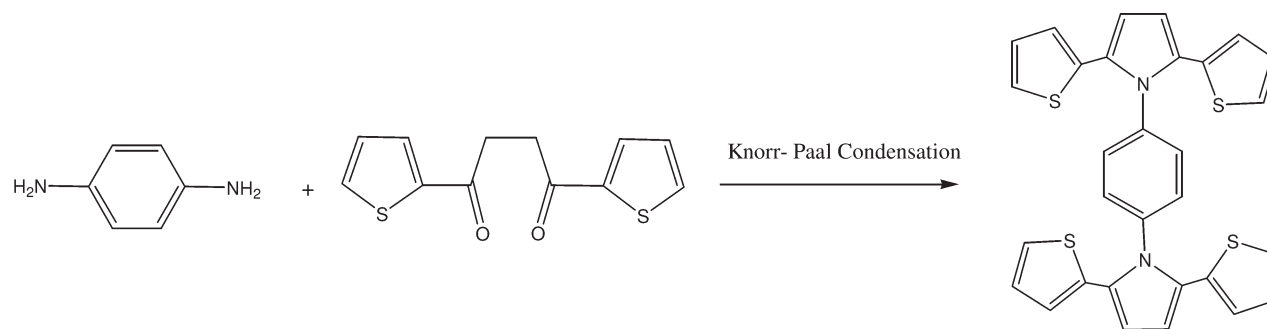
For that matter, we synthesized a novel copolymer of 1-4-di[2,5-di(2-thienyl)-1H-1-pyrrolyl]benzene (DTPB) with 3,4-ethylenedioxythiophene (EDOT). EDOT is a popular choice because it produces a low band gap polymer with high stability and good conductivity.¹⁵ EDOT can give rise to noncovalent intramolecular interactions with adjacent thiophenic units and thus induce self-rigidification of the conjugated system in which it is incorporated.^{16–18}

In the present work, synthesis of DTPB was achieved. Spectral methods, such as ¹H NMR, ¹³C NMR, Fourier transform infrared (FTIR), were used to analyze the structure of the material. Electrochemical polymerization of DTPB was achieved in dichloromethane (DCM) using tetrabutylammonium tetrafluoroborate as the supporting electrolyte. The resulting polymer was analyzed by cyclic voltammetry (CV), FTIR, and scanning electron microscopy (SEM). Second part of the study was devoted to investigate the optoelectrochemical behavior and

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Scheme 1 1,4-Di[2,5-di(2-thienyl)-1H-1-pyrrolyl]benzene(DTPB).

switching ability of the homopolymer and copolymer together with the colorimetry measurements.

EXPERIMENTAL

Materials

AlCl_3 (Aldrich, Taufkirchen, Germany), thionyl chloride (Aldrich), DCM (Merck, Darmstadt, Germany), toluene (Sigma), propionic acid (Aldrich), benzylamine (Aldrich), methanol (Merck), acetonitrile (AN) (Merck), tetrabutylammonium tetrafluoroborate (TBAFB) (Aldrich), and 3,4-ethylenedioxythiophene (EDOT) (Aldrich) were used without further purification.

Equipments

A Voltalab 50 potentiostat was used for the CV studies. Bruker Spectrospin Avance DPX-400 Spectrometer was used to record ^1H and ^{13}C NMR spectra in CDCl_3 . Chemical shifts are given in ppm downfield from tetramethylsilane. The FTIR spectra were recorded on a Varian Cary FTIR 1000 spectrometer. The surface morphology of the homopolymer film was analyzed using JEOL JSM-6400 scanning electron microscope. Solartron 1285 potentiostat/galvanostat was used to supply a constant potential during electrochemical synthesis. Spectroelectrochemical and kinetic studies of the polymers were performed on Varian Cary 5000 UV-Vis-NIR spectrophotometer. Colorimetry measurements were done via Minolta CS-100 chromameter.

Cyclic voltammetry

The electroactivity of the monomer and the polymer was investigated via CV. The system consists of a potentiostat and a CV cell containing Pt working electrode, platinum wire counter electrode, and Ag wire pseudo reference electrode. The measurements were carried out in tetrabutylammonium tetrafluoroborate (TBAFB) (0.1M)/DCM solvent-electrolyte couple at room temperature under nitrogen atmosphere.

Synthesis of 1,4-Di[2,5-di(2-thienyl)-1H-1-pyrrolyl]benzene

1,4-Di[2,5-di(2-thienyl)-1H-1-pyrrolyl]benzene was synthesized according to a previously reported method (Scheme 1.¹⁹ δ_{H} (DMSO-d_6) 6.57 (4H, s, pyrrolyl), 6.72 (4H, J = 3.6, 1.1 Hz, 3-thienyl), 6.96 (4H, J = 3.6, 5.1 Hz, 4-thienyl), 7.44 (4H, J = 1.1, 5.1 Hz, 5-thienyl), 7.46 (4H, s, phenyl).

Synthesis of homopolymer of DTPB

For the spectroelectrochemical analyses, the poly(DTPB) films were prepared potentiodynamically ($-0.5 \text{ V} \leq E \leq +1.2 \text{ V}$) on ITO/glass electrodes, using 0.03M monomer in a solution containing TBAFB and DCM. A platinum wire was used as the counter electrode against a Ag wire pseudo reference electrode. Electrochromic measurements, spectroelectrochemistry, and switching studies of the polymer film deposited on ITO-coated glass slide were done using a UV-cuvette with three-electrodes placed in the sample compartment of a spectrophotometer.

Synthesis of copolymers of DTPB with EDOT

EDOT was used as the comonomer for the synthesis of conducting copolymer of DTPB. DTPB (50 mg) was dissolved in 5 mL of DCM and 10 μL of EDOT were introduced into the electrolysis cell. TBAFB was used as the supporting electrolyte. Films were prepared potentiodynamically scanning the potential between -0.5 and $+1.0 \text{ V}$ on ITO/glass electrodes.

Spectroelectrochemistry

To carry out the spectroelectrochemical experiments, copolymer films were deposited on ITO-coated glasses. They were used both for the spectroelectrochemistry and electrochromic measurements in AN/TBAFB.

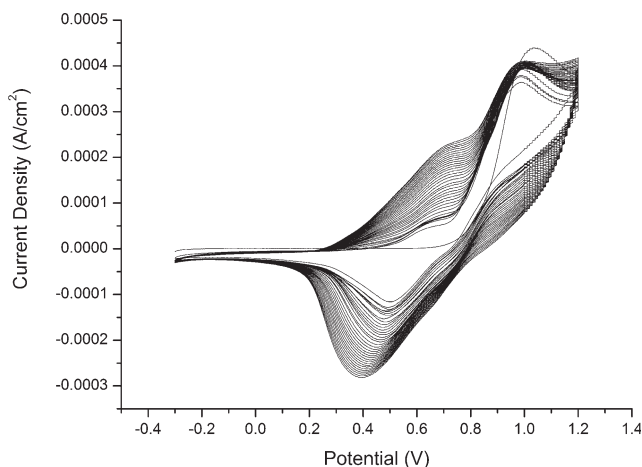


Figure 1 Cyclic voltammogram of monomer DTPB in 0.1M DCM/TBAFB on Pt working electrode with 100 mV s⁻¹ scan rate.

RESULTS AND DISCUSSION

Cyclic voltammetry

Electrochemical behavior of DTPB was examined in DCM with 0.1M TBAFB as the supporting electrolyte. Figure 1 shows the cyclic voltammogram of DTPB performed between -0.5 and 1.2 V at a scan rate of 100 mV s⁻¹. DTPB exhibited a broad oxidation peak at 1.0 V due to the irreversible oxidation of the monomer. Upon repeated scanning, a reversible redox couple develops at 0.68 and 0.38 V signifying the formation of the electroactive polymer. To investigate the CV behavior of the copolymer, we performed CV studies in the presence of EDOT under same experimental conditions. Figure 2 shows the cyclic voltammogram of such a system where the first cycle represents both the oxidation of DTPB (broad anodic wave) and EDOT (steady increase of current beyond

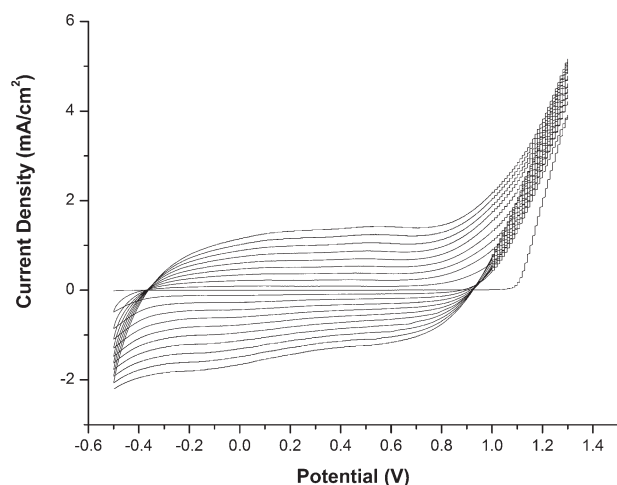


Figure 2 Cyclic voltammogram of copolymer of DTPB with EDOT in 0.1M DCM/TBAFB on Pt working electrode with 100 mV s⁻¹ scan rate.

1.1 V). As the number of cycles increased, new anodic (0.70 V) and cathodic (0.43 V) peaks were observed due to the evolution of the copolymer on electrode. 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 DTPB (Fig. 1) and EDOT (Fig. 3), which, in fact, could be interpreted as the formation of copolymer. The effect of scan rate variation on the copolymer film was also investigated. Results showed a linear relationship between the peak current and the scan rate exists which indicates the presence of an electroactive polymer film which is well adhered on the electrode and the redox processes were nondiffusion limited.²⁰

FTIR spectra

FTIR spectrum of the DTPB shows the following absorption peaks: 3085 cm⁻¹ (aromatic C-H), 3035 cm⁻¹ (C-H_α stretching of thiophene), 1560-1340 cm⁻¹ (aromatic C=C, C-N stretching due to pyrrole and benzene), 771 cm⁻¹ (C-H_α out of plane bending of thiophene). The homopolymer revealed most of the characteristic peaks of the monomer where the peaks related to C-H_α stretching of thiophene disappeared and the presence of the new peaks at around 1635 and 1081 cm⁻¹ were attributed to polyconjugation and dopant anion, respectively. Similar spectra were observed in case of the copolymer where the presence of EDOT moieties were signified by new peaks around 2850, 2872, and 1148-1050 cm⁻¹ due to the aliphatic, C-O-C stretchings, respectively.

Scanning electron microscopy

Surface morphologies of copolymer were investigated by scanning electron microscope. SEM micrograph of P(DTPB-co-EDOT) was different than those

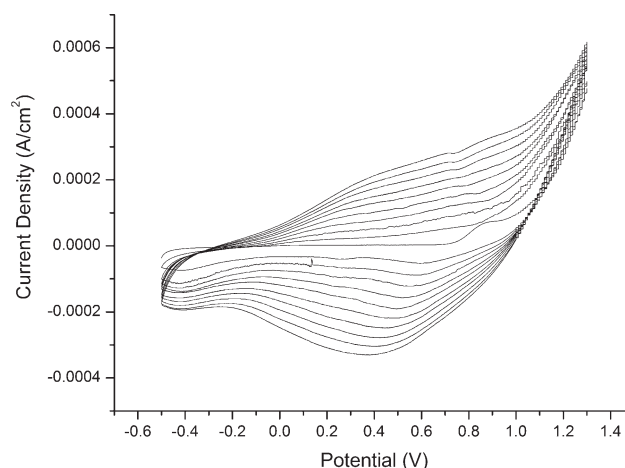


Figure 3 Cyclic voltammogram of EDOT in 0.1M DCM/TBAFB on Pt working electrode with 100 mV s⁻¹ scan rate.

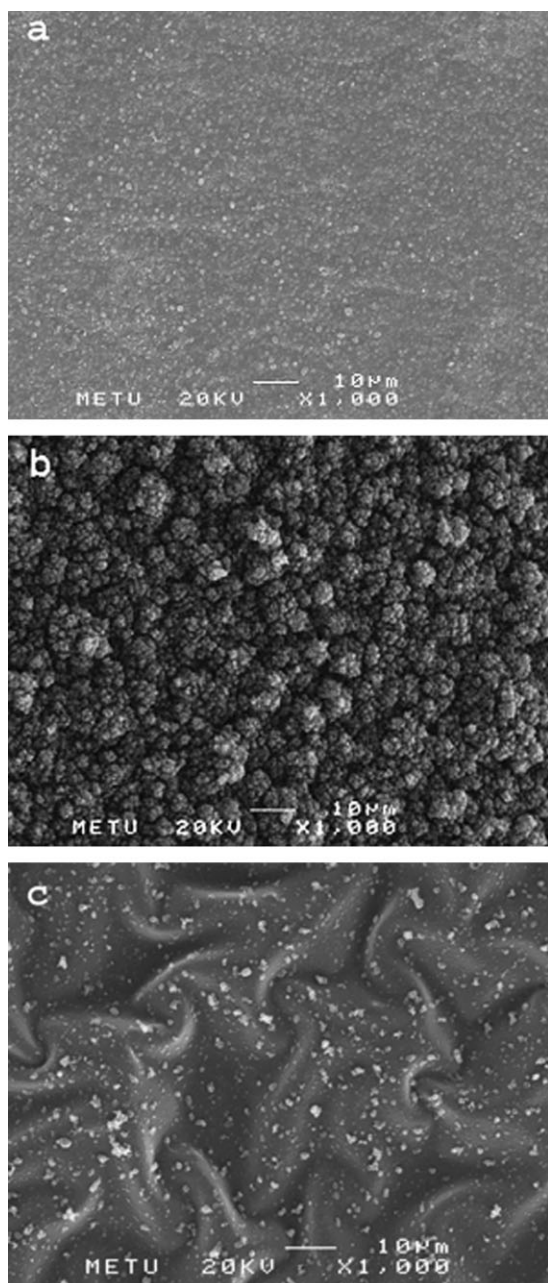


Figure 4 SEM micrographs of (a) P(DTPB), (b) PEDOT, (c) P(DTPB-co-EDOT).

of P(DTPB) which has a smooth morphology and PEDOT which exhibits a cauliflower structure (Fig. 4). The different morphology of the copolymer proves that a copolymer is formed rather than a mixture of homopolymers where a cauliflower structure dominates.

Spectroelectrochemistry

Spectroelectrochemical analyses were performed to examine the change in optical properties that originate from the redox switching of conjugated poly-

mers and to assess the basic properties of conjugated polymers, such as band gap (E_g) and the intergap states that appear upon doping. Figure 5 presents the spectroelectrochemistry of P(DTPB) revealing π - π^* transition in the neutral state which fades upon increasing the applied voltage. The electronic band gap, defined as the onset energy for the π - π^* transition, was found to be 2.03 eV ($\lambda_{\max} = 410$ nm). Upon application of the potential, reduction in the intensity of the π - π^* transition and formation of charge carrier bands were observed. Thus, appearance of peaks around 650 and 1250 nm were attributed to the evolution of charge carrier bands. The polymer displayed yellow (x: 0.37, y: 0.43) and blue (x: 0.28, y: 0.31) color in its neutral and doped states.

Assessment of the spectroelectrochemical behavior of the copolymer and the evaluation of the differences of the spectral signatures of the material to those of the respective homopolymers reveal the most compelling evidence of copolymerization.²¹ Hence, the spectroelectrochemical and electrochromic properties of the resultant copolymer were studied by applying various potentials in monomer free electrolytic medium. P(DTPB-co-EDOT) film was synthesized potentiodynamically between -0.5 and $+1.0$ V on an ITO electrode. At neutral state, λ_{\max} (due to the broad π - π^* transition of the copolymer) was found to be 455 nm and E_g was calculated as 1.7 eV. The optical properties of PEDOT have been thoroughly investigated in the literature. PEDOT reveals π - π^* transition centered at 610 nm and has a band gap of 1.6 eV. Thus, λ_{\max} and E_g of the copolymer is considered to be in agreement with the expectations compared to parent polymers. At 0.4 V copolymer presents a weakened (and shifted) π - π^* transition at

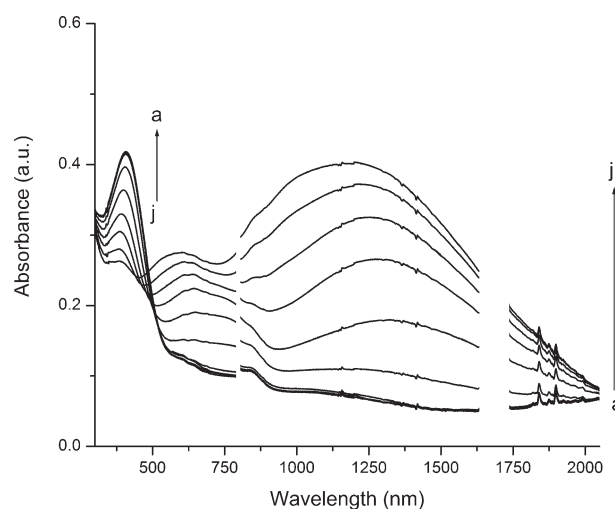


Figure 5 Spectroelectrochemical spectrum of P(DTPB) with applied potentials between -0.5 and $+1.2$ V in AN/TBAFB (0.1M); (a) -0.3 , (b) -0.5 , (c) 0, (d) 0.2, (e) 0.5, (f) 0.6, (g) 0.7, (h) 0.8, (i) 0.9, (j) 1.

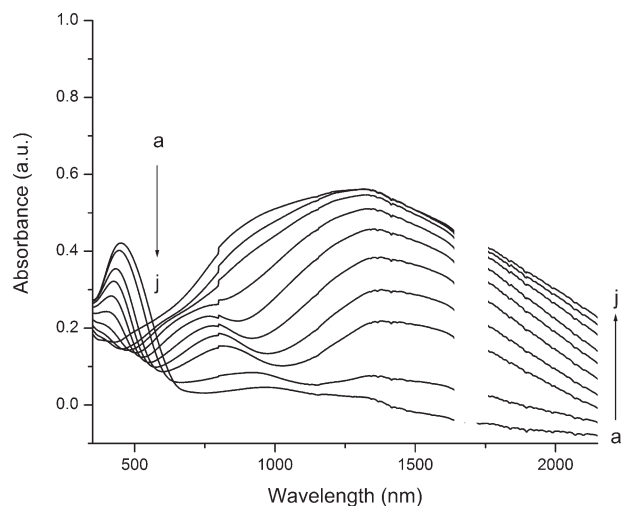


Figure 6 Spectroelectrochemical spectrum of P(DTPB-co-EDOT) with applied potentials; (a) 0, (b) 0.2, (c) 0.4, (d) 0.5, (e) 0.6, (f) 0.7, (g) 0.8, (h) 0.8, (i) 1.0, (j) 1.2.

432 nm and yet a new transition around 805 nm originates due to the charge carrier bands. Further doping resulted in the further shift of λ_{\max} along with a decay in its intensity (Fig. 6). Potentials beyond 0.7 V enhanced the formation of bipolaron bands signified by the broad transition beyond 1000 nm. Hence, doping of the copolymer not only results in a decrease in the intensity of $\pi\text{-}\pi^*$ transition (which is common in most of the conducting polymers) but also a decrease in the peak width with a shift in λ_{\max} , all of which has a significant effect on displayed color. This particular trend clarifies the underlying reason of perceived distinct multichromism where the polymer displayed red-violet, brownish yellow, green, and blue color (Fig. 7) at 0.0, -0.4 , 0.6, 1.2 V, respectively.

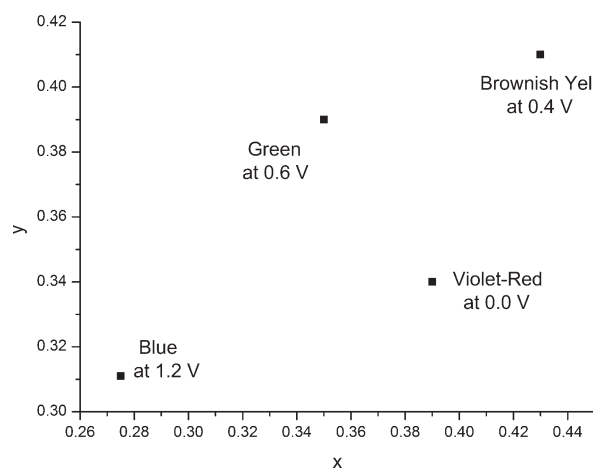


Figure 7 Color space values of the copolymer at various potentials.

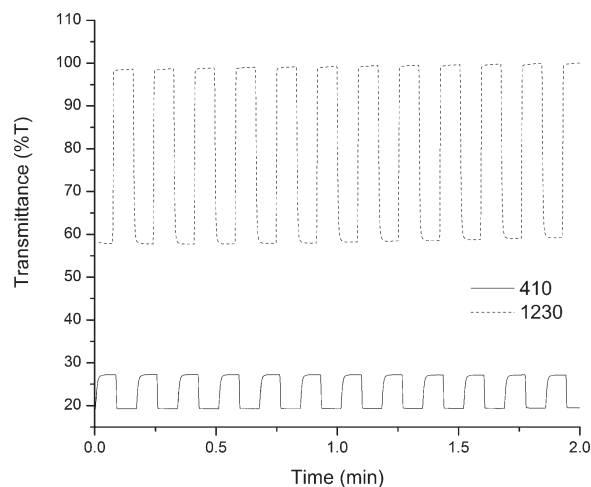


Figure 8 Electrochromic switching, optical absorbance change monitored at 410 and 1230 nm for poly(DTPB) in 0.1M TBAFB/AN.

Electrochromic switching

The ability of a polymer to switch immediately and exhibit a color change is significant for electrochromic applications. Hence, electrochromic switching studies are performed to examine properties like

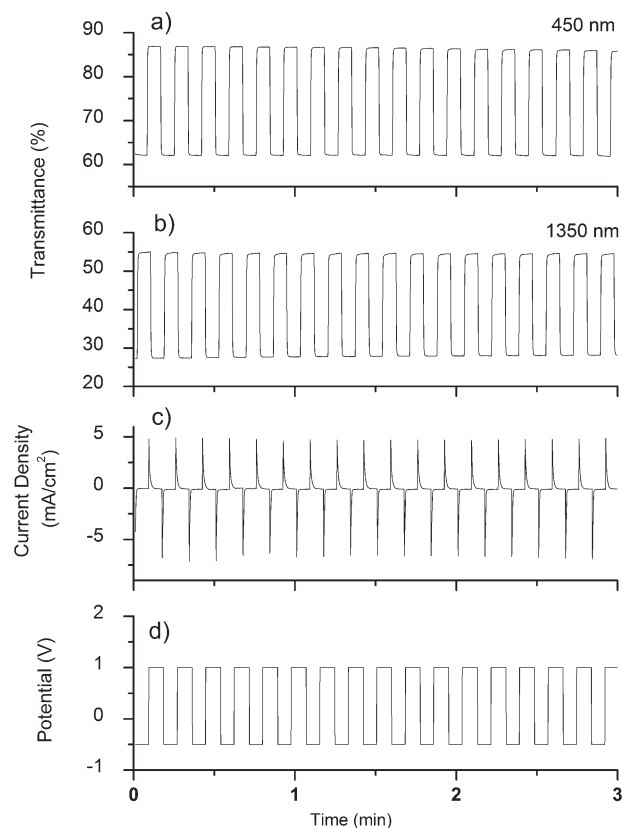


Figure 9 Electrochromic switching, optical absorbance change monitored at 450 (a) and 1350 nm (b) for P(DTPB-co-EDOT) in 0.1M TBAFB/AN. Current densities (c) and potentials (d) during switching studies.

switching time and optical contrast. Within the light of spectroelectrochemistry studies, the ability of both P(DTPB) and P(DTPB-co-EDOT) to fully switch between their neutral and doped states at certain potentials were confirmed. Homopolymer film was synthesized on ITO-coated glass slides and its percent transmittance (%T) was monitored at selected wavelengths while the polymer was switched between -0.5 and 1.2 V. The optical contrast was measured as the difference between %T in the neutral and oxidized states and noted as 8 and 41% at 410 and 1230 nm, respectively, (Fig. 8). Homopolymer exhibits a switching time of 0.7 s and displayed enhanced optic contrast in NIR range. The copolymer on the other hand revealed optical contrasts as 25 and 30% both in the visible and NIR region, respectively (Fig. 9). Hence, the copolymerization was found to enhance the optical contrast at the expense of the increase in switching time (switching time of copolymer was also found to be 4.2 s).

CONCLUSIONS

Synthesis of a new homopolymer and its copolymer with EDOT were successfully achieved. The resulting copolymer displayed distinctive multichromism where the color of the polymer changes between red-violet, brownish yellow, green, and blue color upon oxidation. In addition to structural characterization techniques, electrochromic properties and switching ability of the polymers were investigated via spectroelectrochemistry, kinetic, and colorimetry studies. Studies showed that copolymerization with EDOT not only decreases the band gap, E_g , but also enhances the electrochromic properties such as optical contrast. In conclusion, electrochemical copolymerization is considered to be a powerful tool to

improve the electrochromic properties of the N-substituted 2,5-di(2-thienylpyrrole) derivatives, which were previously explored through the synthesis of its numerous derivatives.

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