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Electrochromic Properties of 'Trimeric' Thiophene-pyrrole-thiophene Derivative Grown from Electrodeposited 6-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)hexan-1-amine and its Copolymer

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A centrosymmetric polymer precursor, namely 6-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)hexan-1-amine (TPHA), was synthesized via a Knorr–Paal reaction using 1,4-di(2-thienyl)-1,4-butanedione and hexane-1,6-diamine. The resultant monomer was characterized by Nuclear Magnetic Resonance (^{1}H-NMR). Electroactivity of TPHA was investigated via cyclic voltammetry. The electronic structure and the nature of electrochromism in P(TPHA) and its copolymer with EDOT, (P(TPHA-co-EDOT)), were examined via spectroelectrochemistry studies. P(TPHA) switches between claret red neutral state and blue oxidized state. Optical response times for coloring and bleaching processes of the P(TPHA) and P(TPHA-co-EDOT) were found as 2.1 s and 1.6 s, respectively.

The copolymer of TPHA was used to construct dual type polymer electrochromic devices (ECDs) against poly(3,4-ethylenedioxythiophene) (PEDOT). Spectroelectrochemistry and electrochromic switching out of the devices were investigated.

Keywords: conducting polymers; electrochromism; electrochromic devices; electrochemical copolymerization

1 Introduction

Discoveries in the last two decades brought conjugated polymers to full commercialization with applications in electrochromic rearview mirrors (1–3), windows (4–6), thin-film transistors (7), displays (8, 9)), sensors (10, 11), polymer light-emitting diodes (12), photovoltaics (13), and electrochromic devices (14). As the new century commences, the science of conducting polymers remains vibrant, with development of new molecules, phenomena, experimental techniques, and technologies.

The earliest electrochromic materials in the visible region were the inorganic tungsten trioxide (WO_3) and iridium dioxide (IrO_2) (15). Due to the increasing versatility of organic materials (viologens, metallophtalocyanines, and conducting polymers), these compounds have recently received the brunt of attention for potential electrochromic applications. Among organic materials, conjugated polymers have several advantages over small molecules and inorganic solids; these are, outstanding coloration efficiency, fast switching times (16, 17), multiple colorations with the same material (18), fine-tunability of the band gap (and the color) (19, 20), high stability (21), thin film flexibility and cost effectiveness.

For conducting polymers, electrochromism is related to a 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 (22). A major focus in the study of electrochromic polymeric materials has been on the control of colors by main-chain and pendant group structural modification and copolymerization. Copolymerization can lead to an interesting combination of the properties.

This study comes in two parts. In the first part, 6-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)hexan-1-amine (TPHA) was

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synthesized via a Knorr–Paal reaction using 1,4-di(2-thienyl)-1,4-butanedione and hexane-1,6-diamine. This route is convenient for the preparation of 'trimeric' thiophene-pyrrole-thiophene derivatives substituted at the N atom of the pyrrole ring (23−25). This strategy yields centrosymmetric polymer precursors and seeks to minimize the steric influence of the central substituent through the addition of the thiophene spacers. Thus, electrochemical polymerization of TPHA could easily be achieved and the polythiophene paradox (26) could be solved. Electrochemical polymerization of TPHA was carried out using $LiClO_4$ as the supporting electrolyte in acetonitrile (AN). Electrochromic and spectroelectrochemical behavior of the homopolymer were studied.

In the second part of the study, copolymer of TPHA was synthesized electrochemically with 3,4-ethylenedioxy thiophene (EDOT) and its electrochromic properties were investigated. While P(TPHA) has only two colors in its oxidized and neutral states, its copolymer exhibits multichromic properties with four different colors. Also, a dual-type electrochromic device (ECD), based on P(TPHA-co-EDOT) and poly(3,4-ethylenedioxy thiophene) (PEDOT), was constructed and characterized. ECD was assembled in sandwich configuration of electrochromic materials deposited on ITO glass electrodes. For the construction of the device, PEDOT was used as the cathodically coloring and P(TPHA-co-EDOT) was used as the anodically coloring material. The ECDs showed claret red color in its oxidized states and blue color in reduced state.

2 Experimental

2.1 Materials

$AlCl_3$ (Aldrich), dichloromethane (Merck), thiophene (Aldrich), succinylchloride (Aldrich), hydrochloric acid (Merck), $NaHCO_3$ (Aldrich), $MgSO_4$ (Aldrich), propionic acid (Aldrich), hexane-1,6-diamine (Aldrich), toluene (Sigma), propylene carbonate (PC), acetonitrile (AN) (Merck), $LiClO_4$ (Aldrich), polymethylmetacrylate (PMMA) and 3,4-ethylenedioxy thiophene (EDOT) were used as received.

2.2 Equipment

^{1}H-NMR spectrum of TPHA was recorded on a Bruker-Instrument-NMR Spectrometer (DPX-400) using $CDCl_3$ as the solvent. Voltalab PST 50 potentiostat/galvanostat was used to supply a constant potential during electrochemical synthesis and cyclic voltammetry experiments. Spectroelectrochemical studies of polymers and characterization of the ECD were performed by a Varian Cary 5000 UV-Vis spectrophotometer.

2.3 Synthesis of 6-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-hexan-1-amine (TPHA)

The starting material, 1,4-di(2-thienyl)-1,4-butanedione, was synthesized according to the procedure reported previously

(27). To a suspension of $AlCl_3$ (16 g, 0.12 mol) in CH_2Cl_2 (15 ml), a solution of thiophene (9.61 ml, 0.12 mol) and succinyl chloride (5.51 ml, 0.05 mol) in CH_2Cl_2 was added dropwise. The mixture was stirred at room temperature for 4 h. This was then poured into an ice-concentrated HCl (5 ml) mixture. The dark green organic phase was washed with concentrated $NaHCO_3$ (3×25 ml) and brine, and then dried over $MgSO_4$. After evaporation of the solvent, a blue green solid was suspended in ethanol. Filtration and washing with ethanol yielded the 1,4-di(2-thienyl)-1,4-butanedione, **(I)**.

The monomer (TPHA) **(II)** was synthesized from 1,4-di(2-thienyl)-1,4-butanedione and hexane-1,6-diamine in the presence of catalytical amounts of propionic acid. A round-bottomed flask equipped with an argon inlet and magnetic stirrer was charged with the 1,4-di(2-thienyl)-1,4-butanedione (5 mmol, 1.25 g), 0.97 g (8 mmol) hexane-1,6-diamine, 0.01 g (0.13 mmol) propionic acid and 20 ml of toluene. The resultant was stirred and refluxed for 24 h under argon. Evaporation of toluene, followed by flash column chromatography (SiO_2 column, elution with dichloromethane) afforded the desired compound as a brown solid. The synthetic route to TPHA is shown in Scheme 1.

2.4 Cyclic Voltammetry (CV)

The electroactivity of the polymer were investigated using cyclic voltammetry. The oxidation-reduction peak potentials of the monomer were also obtained. The system consists of a potentiostat, an XY recorder, and a CV cell containing Pt working electrode, platinum wire counter electrode and Ag wire as a pseudo reference electrode. Measurements were carried out in $LiClO_4$ (0.1 M)/AN solvent-electrolyte couple at room temperature under nitrogen atmosphere.

The oxidation/reduction behavior of the copolymer was investigated via cyclic voltammetry in the presence of $LiClO_4$ (0.1 M)/AN solvent-electrolyte couple.
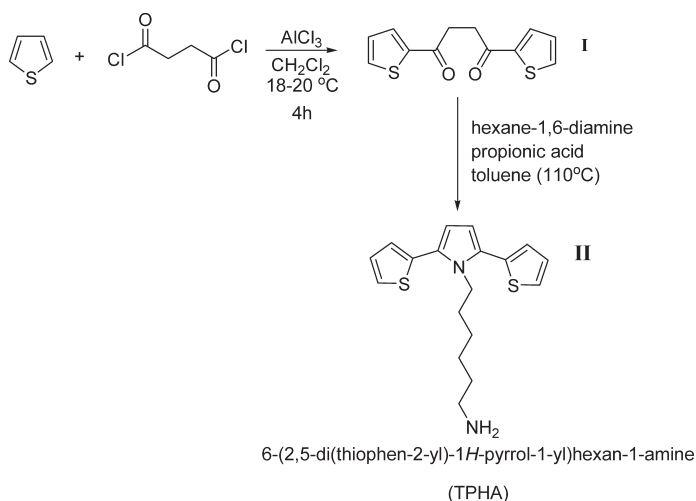
Sch. 1. Synthetic route of the monomer.
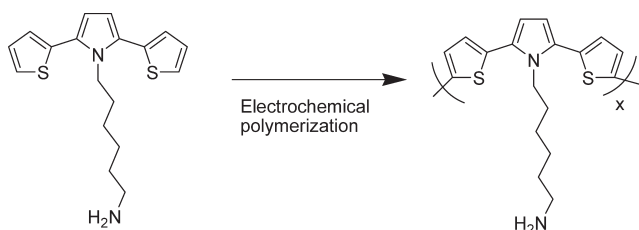
2.5 Electrochemical Polymerization of TPHA

Electrochemical polymerization of TPHA was carried out by sweeping the potential between 0.0 V and +1.4 V at 250 mV. s^{-1} in the presence of 8×10^{-3} M (TPHA) in LiClO$_4$ (0.1 M)/AN (Scheme 2). A three-electrode cell assembly was used where the working electrode was an ITO-coated glass, the counter electrode was a platinum flake and a Ag wire was used as the pseudo reference electrode. P(TPHA) was washed with AN in order to remove excess LiClO$_4$ and unreacted monomer after the potentiodynamic electrochemical polymerization.
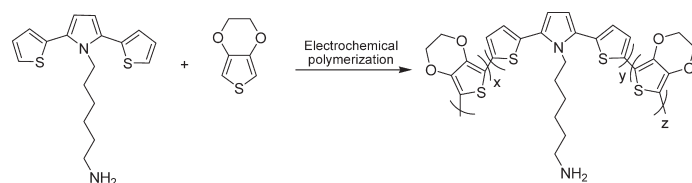
2.6 Electrochemical Copolymerization of TPHA with EDOT

The synthesis of the conducting copolymer P(TPHA-co-EDOT) was achieved in the presence of EDOT (Scheme 3). 1.3×10^{-3} M of TPHA was dissolved in 0.1 M LiClO$_4$ in AN and 1.3×10^{-3} M of EDOT were introduced into a single compartment electrolysis cell. A three-electrode cell assembly was used with the same electrodes previously described. The copolymer was potentiodynamically deposited on ITO.

2.7 Preparation of the Gel Electrolyte

A gel electrolyte was prepared by using LiClO$_4$: AN:PMMA:PC in the ratio of 3:70:7:20 by weight. After LiClO$_4$ was dissolved in AN, PMMA was added into the solution. In order to dissolve PMMA, vigorous stirring and heating was required. Propylene carbonate (PC), as the plasticizer, was introduced to the reaction medium when PMMA was completely dissolved. The mixture was stirred and heated until the highly conducting transparent gel was produced (28).

Sch. 2. Electrochemical polymerization of TPHA in LiClO$_4$ (0.1 M)/AN.

Sch. 3. Electrochemical copolymerization of TPHA with EDOT.

2.8 Construction of Electrochromic Device

An electrochromic device was constructed by sandwiching a gel electrolyte between two ITO coated glass slides, where P(TPHA-co-EDOT) was electrochemically deposited on one of them, and complementary cathodically coloring polymer (PEDOT) was deposited on the other. P(TPHA-co-EDOT) was potentiodynamically deposited on ITO in 0.1 M LiClO$_4$ in AN at −1.0 V and 1.4 V. PEDOT layer was prepared at +1.5 V in the same electrolyte-solvent couple. Chronocoulometry was employed to match the redox charges of the two complimentary polymer films to maintain a balanced number of redox sites for switching. The redox sites of these polymer films were matched by stepping the potentials between − 1.0 and +1.4 V for P(TPHA-co-EDOT), -1.0 V and +1.5 V for PEDOT. ECDs were built by arranging two electrochromic polymer films (one oxidized, the other neutral) facing each other separated by a gel electrolyte.

3. Results and Discussion

3.1 H-NMR spectrum of TPHA

^{1}H-NMR spectrum of monomer was investigated on a Bruker-Instrument-NMR Spectrometer (DPX-400) monomer with CDCl$_3$ as the solvent and chemical shifts (δ) are given relative to tetramethylsilane as the internal standard.

^{1}H-NMR spectrum of monomer (m.p:180°C) (Figure 1): C$_{18}$H$_{22}$N$_2$S$_2$, δ_H (CDCl$_3$): 7.2 (d; 2H), 6.95 (dd; 2H), 6.9 (dd; 2H), 6.25 (s, 2H), 3.95 (t; 2H), 2.0 (m; 2H), 1.35 (m; 2H), 1.2 (m, 8H).

3.2 Cyclic Voltammetry

Redox behavior of TPHA was investigated via cyclic voltammetry while the polymer film switched between blue and claret colors. First run of the cyclic voltammogram of TPHA in AN revealed an oxidation peak at +0.80 and two reduction peaks at +0.6 and 0.9 V. After subsequent runs, electroactivity increases with increasing scan number. On the other hand, the height of the peak at 0.6 V decreases
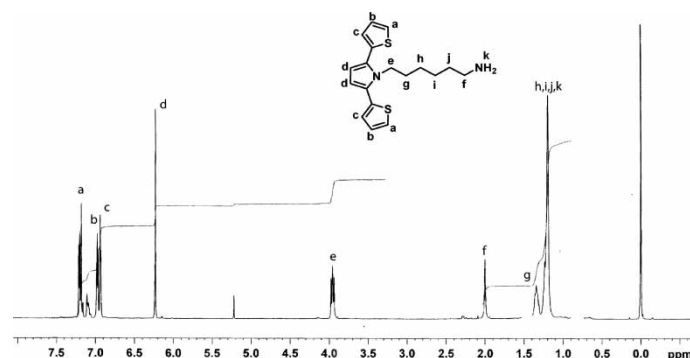

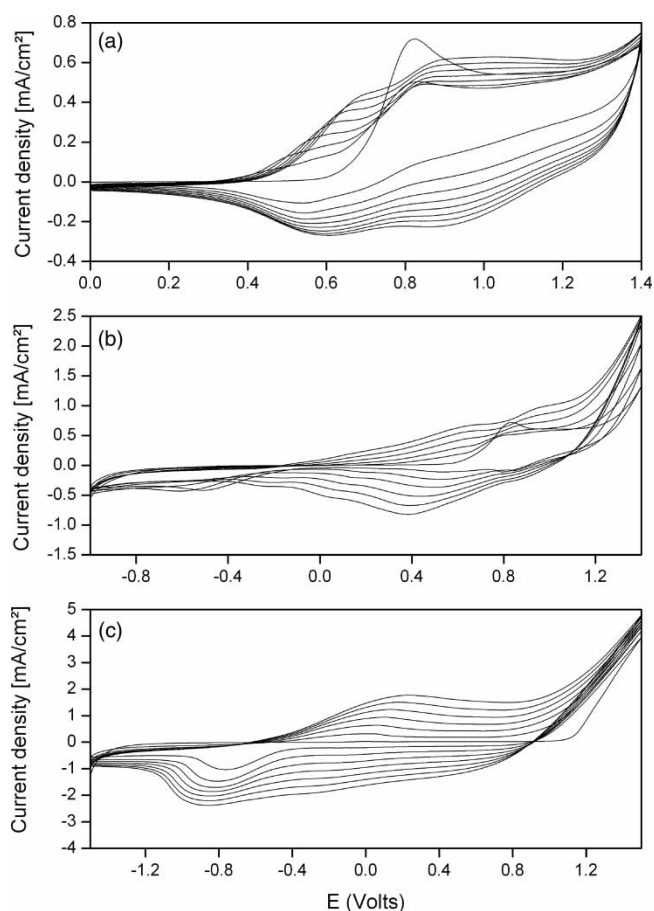
Fig. 1. 1H-NMR spectrum of TPHA.

due to reduction of the monomer concentration in the diffusion layer (Figure 2a).
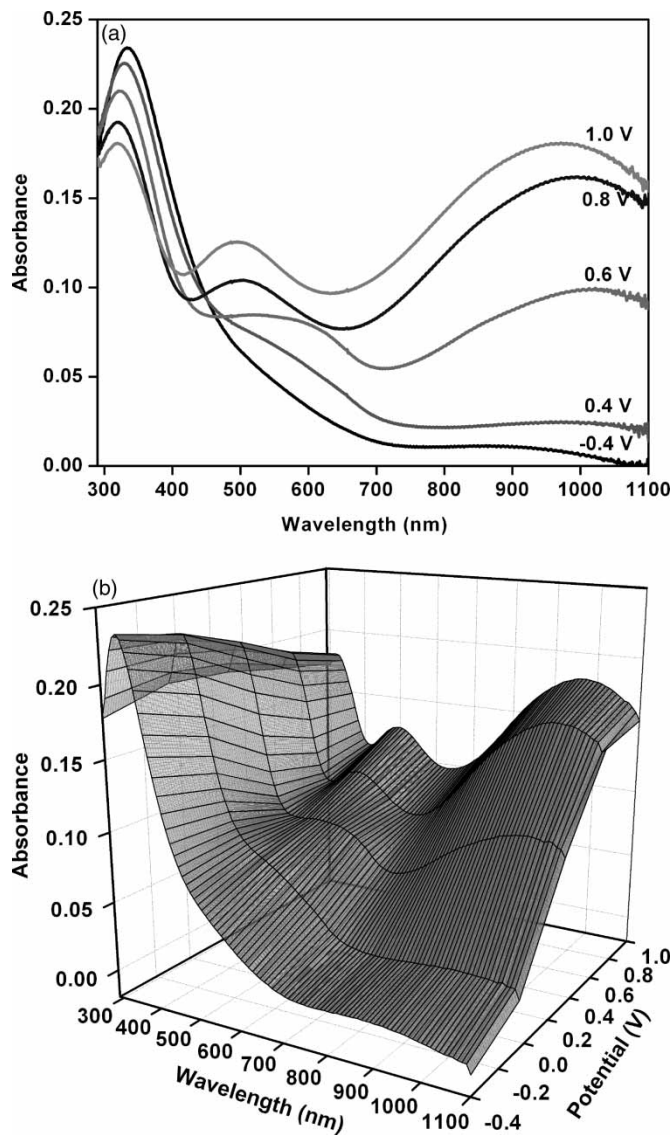
In order to investigate the redox behavior of the copolymer, cyclic voltammetry studies under same experimental conditions with homopolymer was performed. There was a drastic change in the voltammogram, both the increase in the increments between consecutive cycles and the oxidation potential of the material was different than those of from TPHA and EDOT, which could be interpreted as the formation of the copolymer (Figures 2b and c).

3.2 Spectroelectrochemistry of P(TPHA) and its Copolymer with EDOT

The electronic structure and the nature of electrochromism for P(TPHA) and its copolymer with EDOT were examined via spectroelectrochemistry studies. For the examination of the optical properties of TPHA, the polymer was electrodeposited onto ITO-coated glass slides via sweeping the potential between 0.0 V and +1.4 V with a 250 mV . s^{-1} scan rate. A series of spectra were collected at various potentials ranging from −0.4 V to + 1.0 V as shown in Figure 3.

Fig. 3. Optoelectrochemical spectrum of P(TPHA) in the presence of 0.1 M LiClO$_4$ in AN (a) 2D, (b) 3D.

P(PTHA) switches between claret red neutral state and a blue oxidized state. At the applied potential of −0.4 V, P(PTHA) has a peak absorbance at 334 nm (λ_{max}) and a band gap (Eg) of 2.27 eV (defined as the onset of the π-π* transition of the neutral polymer). As seen from the spectroelectrochemical series, the π-π* transition decreases upon doping while the polaron (470 nm) and bipolaron (970 nm) peaks increase. The change in optical properties which result from the redox switching of copolymer was investigated via spectroelectrochemical analysis. Figure 4 shows the π-π* transition in the neutral state (−0.6 V, claret red) displaying a maximum at 501 nm. The electronic bandgap, calculated from the onset of the π-π* transition is 1.73 eV. Upon oxidation, the π-π* transition is depleted at the expense of a peak at 752 nm, corresponding to the charge carrier (radical cations) bands revealing a blue color at 1.0 V.

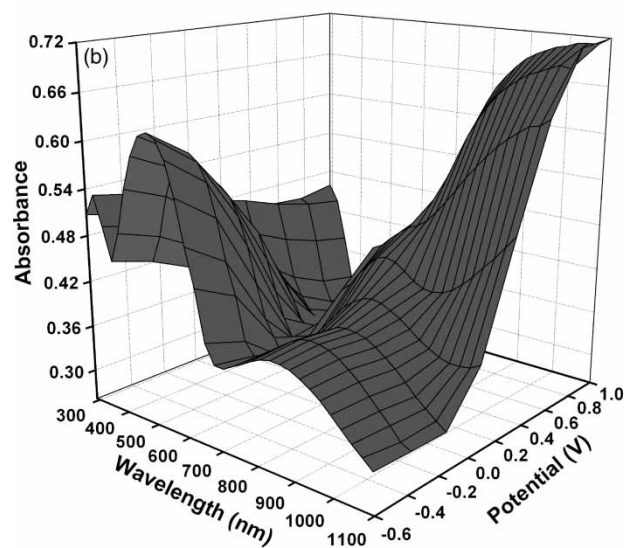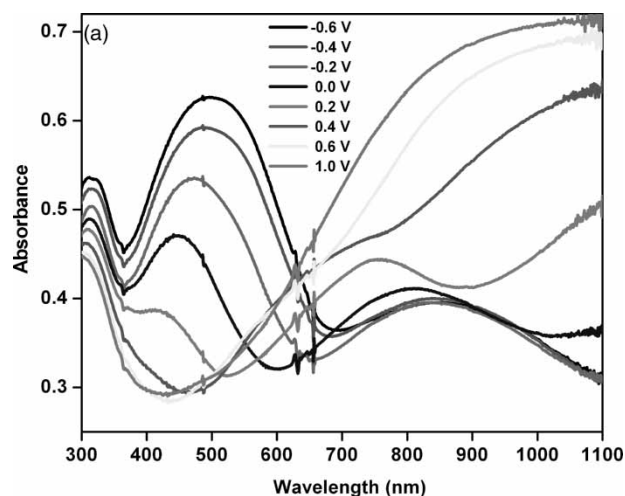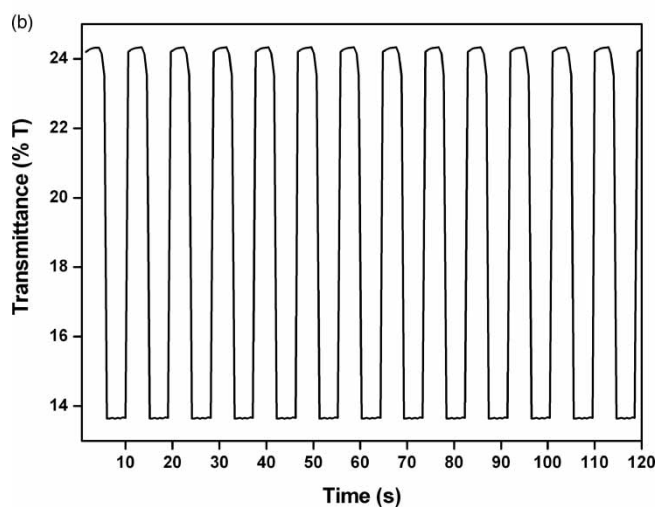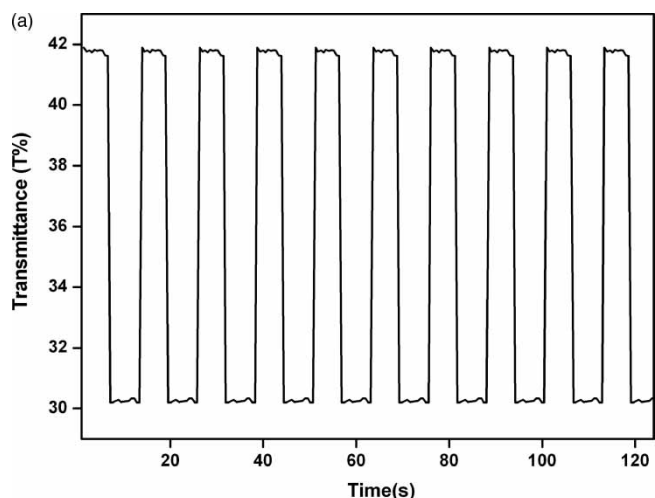

Fig. 2. Cyclic voltammogram of (a) P(TPHA), (b) P(TPHA-co-EDOT) and, (c) PEDOT in 0.1 M AN/LiClO$_4$ on ITO electrode with 250 mV . s^{-1} scan rate.

Fig. 4. Optoelectrochemical spectrum of P(TPHA-co-EDOT) (a) 2D, (b) 3D.

Fig. 5. Electrochromic switching, optical absorbance monitored for (a) P(TPHA), (b) P(TPHA-co-EDOT) in the presence of 0.1 M LiClO$_4$ in AN.

3.3 Switching Properties of P(TPHA) and its Copolymer P(TPHA-co-EDOT)

Figure 5 reveals the optical response time for coloring and bleaching processes of the P(TPHA) and its copolymer with EDOT. To evaluate the response time of P(TPHA) film a double potential step chronoabsorptometry experiment was done simultaneously with the measurement of the percent transmittance (%T) at 332 nm (Figure 5a). In this double potential step experiment, the potential is set at 1.0 V for 5 s period of time, and it was stepped to −0.4 V for 5s period of time, before being switched back to the initial potential. Percent transmittance of the pristine polymer film was found to be 11%. The response time to full contrast was 2.1 s. It is observed that the copolymer shows faster switching speed than the homopolymer. Switching speed is reported as the time required for the coloring/bleaching process of an electrochromic material. For the copolymer time required

for maximum optical contrast is 1.6 s. These results suggest that the EDOT induces a morphology change in the pristine polymer film that causes differences in the optical response.

3.4 Scan Rate Dependence of the Peak Currents

P(TPHA) and P(TPHA-co-EDOT) films prepared via constant potential electrolysis were washed with AN and their redox switching in monomer-free electrolyte revealed a single, well-defined redox process. Figures 6(a and b) show cyclic voltammograms of P(TPHA) and P(TPHA-co-EDOT) at different scan rates. The current responses were directly proportional to the scan rate indicating that the polymer films were electroactive and adhered well to the electrode. The scan rates for the anodic and cathodic peak currents show a linear dependence as a function of the scan rate as illustrated in Figures 7(a and b) for P(TPHA) and P(TPHA-co-EDOT), respectively. This
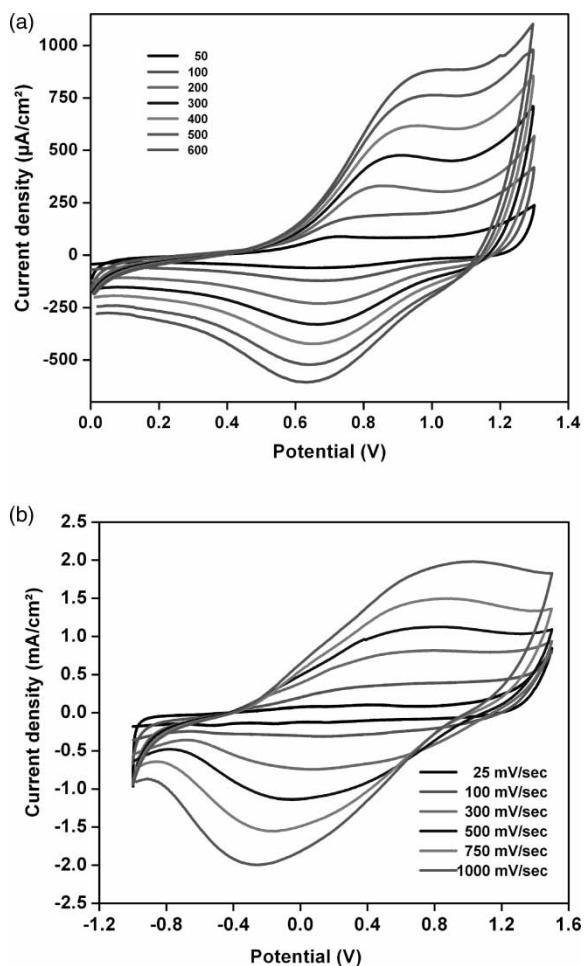
Fig. 6. Cyclic voltammograms of a) P(TPHA) and b) P(TPHA-co-EDOT) at different scan rates.

Fig. 7. Peak current vs. scan rate for a) P(TPHA), b) P(TPHA-co-EDOT).

demonstrates that the electrochemical processes are not diffusion limited and reversible even at very high scan rates.

3.5 Relative Luminance Changes for P(TPHA-co-EDOT) with Applied Potential

In this study, light transmission (luminance) of EC polymers was studied in detail. The luminance of a polymer film is a quantity that is highly dependent on the light source and is usually written as relative to the background luminance of a standard light source (29). Relative luminance studies are unique and valuable since, unlike chronoabsorptometry experiments that monitor a single wavelength, they allow the examination of the spectral changes across the entire visible region for a polymer film. In a typical experiment, the polymer, immersed in a monomer-free electrolyte solution inside a quartz cuvette, is placed in front of a standard light source (D65) inside a specially designed light booth that excludes all external light. Potential is stepped (200 mV steps) from the fully neutral state to the fully oxidized state while the luminance (L) is measured with a
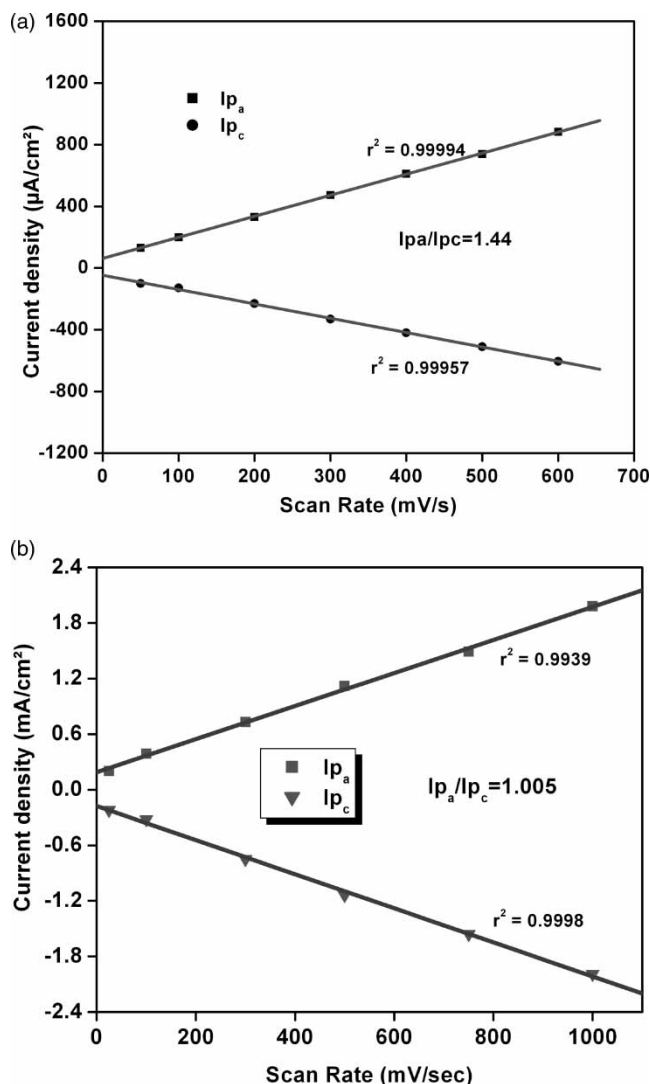
colorimeter as shown in Figure 8. A background measurement is also taken using a blank ITO slide in the same electrolyte solution. When the polymer is held in its neutral state, it is very absorptive and does not permit much of the light to pass through to the colorimeter. However, upon oxidation, firstly the polymer becomes more transmissive and a large amount of light reaches the colorimeter and than becomes less transmissive. Using the difference between the absorptive and transmissive state a total change in luminance, (%T) can be calculated and used as a tool to compare EC polymers and draw conclusions on the effect of polymer structure on percent contrast.
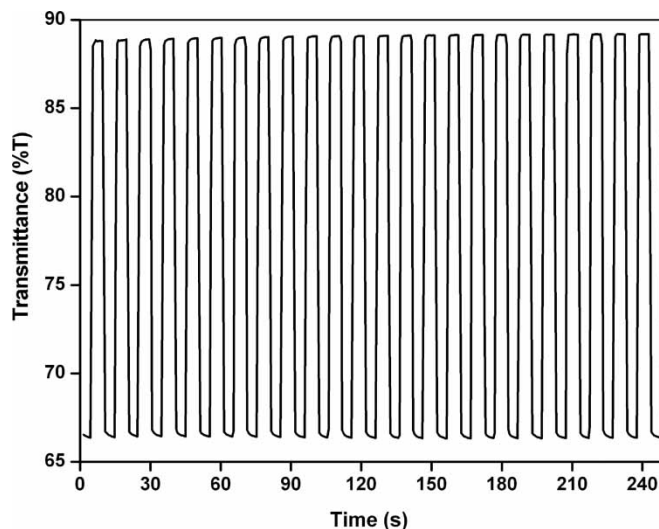
3.6 Spectroelectrochemistry of P(TPHA-co-EDOT)/ PEDOT ECD

Dual polymer electrochromic device was fabricated and evaluated to examine the optical changes that occur
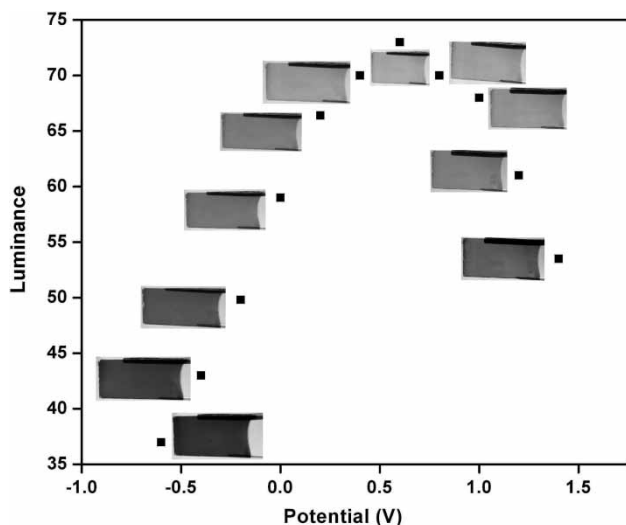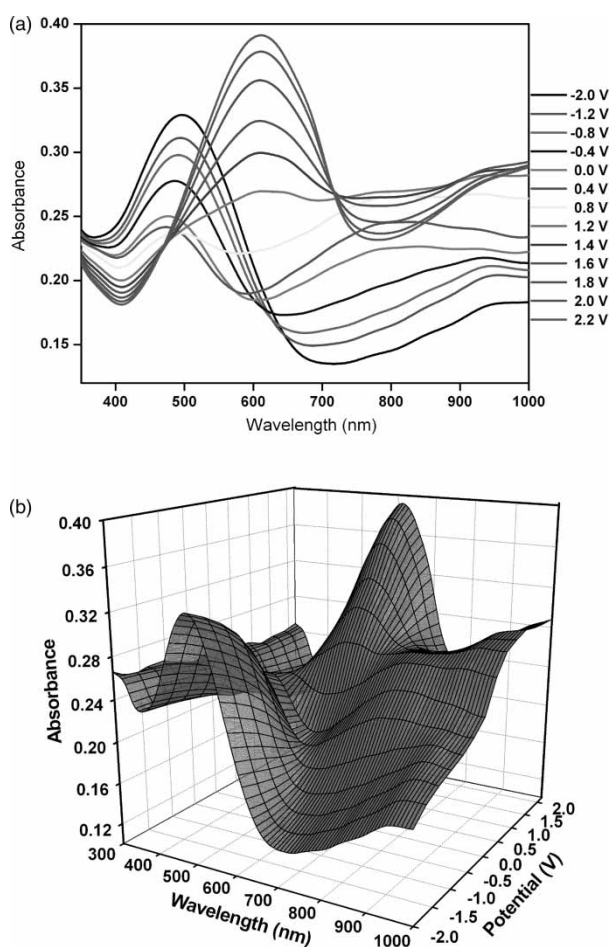
Fig. 8. Relative luminance change of P(TPHA-co-EDOT) film with applied potential.

Fig. 9. Series of UV-Vis-NIR absorbance spectra of the P(TPHA-co-EDOT)/PEDOT device under various applied voltages (a) 2D, (b) 3D.

Fig. 10. Electrochromic switching, optical absorbance monitored for P(TPHA-co-EDOT)/PEDOT.

upon doping or dedoping processes. Figure 9 shows a series of UV-Vis-NIR absorbance spectra of P(TPHA-co-EDOT)/PEDOT device under various applied voltages. When a negative voltage (-2.0 V) was applied to P(TPHA-co-EDOT) layer, the polymer film had an absorptive cleared red color at 501 nm. When the voltage was increased stepwise to $+2.2$ V, P(TPHA-co-EDOT) layer started to get oxidized and intensity of peak at 611 nm increased. At this voltage, the PEDOT layer was reduced revealing a transmissive blue color. This results in the bleaching of the device where color changes from claret red to blue.

3.7 Switching Properties of P(TPHA-co-EDOT)/EDOT Device

Response time, one of the most important characteristics of electrochromic devices, is the time needed to perform a switching between the two states. Chronoabsorptometry was performed to estimate the response time of the device and its stability during consecutive scans. Switching between square wave potentials -2.0 V and 2.2 V with a residence time of 5 s, the optical contrast ($\Delta T \%$) at 611 nm was found 23% with 1.2 s switching time by UV-Vis spectrophotometer (Figure 10).

4 Conclusions

In this study, 'trimeric' thiophene-pyrrole-thiophene derivatives substituted at the N atom of the pyrrole 6-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)hexan-1-amine (TPHA) was successfully synthesized. Free standing, stable and electrically conducting polymer of TPHA was obtained. The resulting polymer was characterized by CV, spectroelectrochemical studies,

electrochromic switching and colorimetry studies. The observed band gap value was found to be 2.27 eV at 334 nm via spectro-electrochemical studies.

The synthesis of conducting copolymers of TPHA with EDOT was achieved in the presence of acetonitrile/LiClO$_4$ (0.1M) solvent-electrolyte couple system via potentiodynamic electrolysis. The resulting copolymer displayed color changes between claret red, lilac, gray and blue upon applied potential. Electrochromic properties and switching ability of resulting copolymer was investigated via spectro-electrochemistry, kinetic studies.

The dual type complementary colored polymer ECDs were constructed. The percentage transmittance change at 611 nm was found to be 23% for P(TPHA-co-EDOT)/PEDOT.

5   Acknowledgments

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