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# Fast switching, high contrast multichromic polymers from alkyl-derivatized dithienylpyrrole and 3,4-ethylenedioxythiophene

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# ABSTRACT

In this report we disclose the synthesis and characterization of optoelectronic properties of a novel conducting polymer based on 1-(2-ethyl-hexyl)-2,5-di-thiophen-2-yl-2,3-dihydro-1H-pyrrole, (SNS-HE). Additionally, copolymers based on SNS-HE and 3,4-ethylenedioxythiophene (EDOT) were electrochemically synthesized and characterized. Cyclic voltammetry, FTIR, spectroelectrochemistry analyses confirmed that the resulting polymers were true copolymers having distinct electrochromic properties from that of the parent homopolymers. Depending on the synthesis conditions, the SNS-HE based polymers exhibited optical band gaps ranging from 2.32 to 1.70 eV and the copolymers displayed multichromism within a wide range of the visible spectrum. The copolymers revealed shorter switching times (around 0.5 s) and higher optical contrast (around 36%). Our studies have shown that color of the copolymers could be easily tuned by controlled increase in copolymerization potential. Moreover, a prototype of the all solid state poly(SNS-HE-EDOT)/PEDOT complementary electrochromic device was fabricated in order to investigate the utilization of these polymers. These devices exhibited short switching times with reasonable open circuit memory under atmospheric conditions.

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# 1. Introduction

Conducting polymers are a class of polymer which generally joins the typical properties of conventional polymers with those of electronically conducting materials [1]. Utilization of these materials in numerous applications including, biosensors [2], actuators [3] and electrochromic devices [4] has been proposed. Therefore remarkable effort has been performed for achieving new polymers which meet the criteria for commercial applications. Generally, tuning of polymer properties goes through specific structural changes in the polymer, like use of different polymer backbones or modification of polymers through utilization of specific functional groups [5].

In recent years an emerging class of conducting polymer, poly(2,5-dithienylpyrrole) derivatives (SNS) has been investigated for their electrochromic properties by several groups. In literature there are studies in which various SNS derivatives containing substituted phenyl derivatives [6–13], aryl derivatives [14,15], BODIPY [16], 1,10-phenanthrolinyl [17], anthraquinone [18] have been investigated. Among those, especially substituted phenyl derivatives revealed soluble conducting polymers upon chemical

polymerization. Due to monomers' low oxidation potentials their electrochemical polymerizations were easily accomplished. However, to our best knowledge, in literature there is only a single study [19] involving an amine functionalized alkyl substituted SNS derivative. It is known that introduction of an alkyl group into a conducting polymer could be used to manipulate the electrochromic properties of the polymer, due to inductive electronic effects and interchain interactions between the chains [20], Keeping this in mind, in this study we investigated electrochemical and electrochromic properties of ethyl-hexyl functionalized SNS derivative.

Besides chemical tailoring, copolymerization also provides an effective method for controlling of properties of conducting polymers. Contrary to synthetic approach, copolymerization is an easy, facile method to combine the electrochromic properties of the parent polymers [21]. In literature there are several studies that investigate copolymerization and tune the color of the conducting polymers via copolymerization. Among those utilization of 3,4-ethylenedioxythiophene (EDOT) has dominated literature owing to EDOT's rapid switching ability and high stability. Since most of the conducting polymers display color variations simply between two colors, it is crucial for potential applications to obtain a multichromic conducting polymer with short switching time and high stability.

In the present work, 1-(2-ethyl-hexyl)-2,5-di-thiophen-2-yl-2,3-dihydro-1H-pyrrole (SNS-HE) (Scheme 1) was synthesized

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Scheme 1. The synthetic route of SNS-HE.

and its structure was analyzed by several methods (<sup>1</sup>H, <sup>13</sup>C NMR, FTIR, mass spectroscopy). Electrochemical polymerization of SNS-HE was achieved and the resultant homopolymer was investigated for its electrochromic properties. Then a novel multicolored electrochromic copolymer based on SNS-HE and EDOT was achieved by electrochemical copolymerization. The resultant copolymer films exhibit four different colors with the variation of the applied potential with enhanced switching time and optical contrast together with precisely adjustable band gap. Moreover, utilization of the copolymers on electrochromic devices was performed through construction of absorption/transmission type electrochromic devices.

# 2. Experimental

#### 2.1. General

All chemicals were purchased from Aldrich, Merck Chemical as analytical grade. Lithium perchlorate (LiClO<sub>4</sub>) was electroanalytical grade and thiophene, succinyl chloride, 2-ethyl-1-hexylamin, 3,4-ethylenedioxythiophene (EDOT) were used as received. Acetonitrile (ACN) was distilled over calcium hydride and kept on 4 Å molecular sieves. The gel electrolyte [22] was prepared according to previously reported methods.

#### 2.2. Equipments

NMR spectra were recorded with a Bruker Spectrospin Avance DPX-400 Spectrometer at 400 MHz for <sup>1</sup>H NMR and 100 MHz for <sup>13</sup>C NMR. Chemical shifts ( $\delta$ ) were given relative to tetramethylsilane (TMS) as the internal standard. Mass spectroscopy (MS) was performed on DP-MS 5973 HP quadruple MS. The FTIR spectra were recorded on a Brucker Tensor 27 spectrometer. Ivium stat potentiostat/galvanostat was used to supply a constant potential during electrochemical synthesis and cyclic voltammetry. Spectroelectrochemical and kinetic studies of the polymers were performed on Varian Cary 100 UV-vis spectrophotometer. Colorimetry measurements were recorded on a Minolta CS-100A Chroma Meter in a proper box having D-50 illumination. Measurements were performed with a 0/0 (normal/normal) viewing geometry as recommended by CIE.

#### 2.3. Synthesis of

# 1-(2-ethyl-hexyl)-2,5-di-thiophen-2-yl-2,3-dihydro-1H-pyrrole (SNS-HE)

1,4-di(2-thienyl)-1,4-Butanedione was synthesized according to literature starting from thiophene and 1,4-dichlorobutanedione

[23]. FT-IR (KBr, cm<sup>-1</sup>): 3101, 2919, 1733, 1654, 1514, 1353, 1316, 1191, 1057, 953, 860, 788, 741, and 633. MS calculated for C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>S<sub>2</sub> (*m*/*z*) calculated: 250.34, found: 250.3. SNS-HE was synthesized according to literature [19] by refluxing 1,4-di(2thienyl)-1,4-butanedione (2 mmol, 0.5 g), 2-ethyl-1-hexylamine (3.2 mmol, 0.52 mL) and 0.2 g propanoic acid in toluene (20 mL) for 24 h under N<sub>2</sub> atmosphere. The solvent was evaporated and later it was purified on a silica gel column (eluting with dichloromethane/hexane, 3/1) to yield title compound (1-(2-ethylhexyl)-2,5-di-thiophen-2-yl-2,3-dihydro-1H-pyrrole) as a vellow oily (45%). FT-IR (KBr, cm<sup>-1</sup>): 3104, 3070, 2958, 2929, 2870, 2860, 1460, 1422, 1380, 1305, 1200, 1040, 840, 760 and 695 cm<sup>-1</sup>. <sup>1</sup>H NMR (in CDCl<sub>3</sub>) ( $\delta$ /ppm): 7.21 ppm (d, 2H), 6.96 ppm (t, 4H), 6.23 ppm (s, 2H), 4.02 ppm (d, 2H) 1.33 ppm (m, 1H), 0.97 ppm (m, 2H), 0.85 ppm (m, 6H), 0.67 ppm (t, 3H) and 0.47 ppm (t, 3H).<sup>13</sup>C NMR (in CDCl<sub>3</sub>) ( $\delta$ /ppm): 134.59, 128.10, 126.15, 124.95, 124.10, 109.81, 48.2, 38.5, 29.3, 27.2, 21.7, 12.9, 22.5 and 9.4 ppm. MS calculated for C<sub>20</sub>H<sub>25</sub>N<sub>1</sub>S<sub>2</sub> (*m*/*z*) calculated: 343,5, found: 343,4.

#### 2.4. Synthesis of homopolymer (poly(SNS-HE))

Poly(SNS-HE) films were prepared potentiodynamically on ITO electrodes, using 0.01 M monomer in a solution containing LiClO<sub>4</sub> in acetonitrile (ACN). A platinum wire was used as the counter electrode and Ag/Ag<sup>+</sup> electrode calibrated against ferrocene was used as the reference electrode. During the electrochemical process, the color of the solution in the vicinity of working the electrode dark-ened progressively. However, as the polymerization proceeded, part soluble oligomers became insoluble and deposited on the working electrode. Electrochromic measurements; spectroelectrochemistry, and switching studies of the polymer films deposited on ITO (both the homopolymer and the copolymer) were performed using a UV-cuvette with three-electrodes placed in the sample compartment of a spectrophotometer. In these studies platinum and Ag wires were used as the counter and reference electrodes respectively due to geometrical restrictions.

#### 2.5. Synthesis of copolymers (poly(SNS-HE-EDOT))

EDOT was used as the comonomer for the synthesis of conducting copolymer of SNS-HE. SNS-HE (50 mg) was dissolved in 5 ml of ACN and 5  $\mu$ L of EDOT was introduced into the electrolysis cell having the same electrode system utilized in homopolymers synthesis. The films were either prepared potentiodynamically scanning the potential between 0.0 V and 1.3 V or potentiostatically at 1.1–1.4 V on ITO glass electrodes.

#### 2.6. Construction of electrochromic device (ECD)

Both anodically poly(SNS-HE-EDOT) and cathodically (PEDOT) coloring polymers were electrochemically deposited onto the ITO-coated glass slide in 0.1 M LiClO<sub>4</sub>/ACN electrolyte solution at 1.2 V. The redox sites of these polymer films were matched by stepping the potentials between 0.0 V and +1.8 V for the copolymer and -1.2 to +1.2 V for PEDOT. ECDs were built by arranging two electrochromic polymer films (one doped, the other neutral) facing each other separated by a gel electrolyte.

# 3. Results and discussion

# 3.1. Monomer synthesis

1-(2-Ethyl-hexyl)-2,5-di-thiophen-2-yl-2,3-dihydro-1Hpyrrole (SNS-HE) was synthesized by two-step synthetic route, as shown in Scheme 1. The first step involves synthesis of 1,4-di(2-thienyl)-1,4-butanedione through thiophene and 1,4dichlorobutanedione and the second step includes a Paal–Knorr reaction between 1,4-di(2-thienyl)-1,4-butanedione and 2-ethyl-1-hexylamine in toluene. Structural investigation of monomer was performed via <sup>1</sup>H, <sup>13</sup>C NMR, FTIR and MS analyses. The monomer is yellow oil at room temperature.

# 3.2. Electrochemical polymerization

Typical successive cyclic voltammogram (CV) of the monomer during the process of electrochemical polymerization is shown in Fig. 1a The monomer revealed an irreversible oxidation at around 1.0V, signifying the formation of radical cation of the monomer through its SNS moiety and the increase in the redox wave currents implied that the amount of the polymer on the electrode was increased. Such behavior is in accordance with the previous studies based on other SNS derivatives [19]. During potential scanning, homogeneous, adherent thin film coating on the electrode was observed by the naked eye and the color of the solution close to the working electrode changed probably due to dissolved oligomers.

Additional proof of homopolymerization was achieved via comparison of FTIR spectra of the monomer and the polymer. FTIR spectra of SNS-HE revealed typical signals at 3104–3070 cm<sup>-1</sup>, 2958–2860 cm<sup>-1</sup> due to C–H stretching of aromatic and aliphatic moieties. The stretching of C=C, C–C and C–N, C–S bonds was signified by the appearance of peaks at 1577–1422 cm<sup>-1</sup> and 1340 cm<sup>-1</sup>, 695 cm<sup>-1</sup>, respectively. Upon homopolymerization most of the characteristic peaks were maintained, except the peaks regarding C–H stretching of thiophene moiety which indicated that the polymerization mainly proceeds through 2,5 positions of the monomer [24]. In addition, the broad band centered at 1645 cm<sup>-1</sup> and the intense band at 1085 cm<sup>-1</sup> revealed formation of polyconjugation and presence dopant anion, respectively.

Copolymerization is often used to achieve novel polymers having different properties that are expected to embody the advantages of both of the parent polymers, widen the application fields and display better electrochromic properties. In literature copolymerization of EDOT with other monomers such as 3-methylthiophene [25], N-ethylcarbazole [26], N-methylpyrrole [27], 5-cyanoindole [28], pyrene [29], SNS derivatives [11,30,31] has been reported. Hence, we attempted to incorporate the EDOT with in SNS-HE units through electrochemical copolymerization in order to enhance the film forming ability of SNS-HE. Since the electrochemical copolymerization of the monomers is expected to be based on already known coupling reactions of radical cations, it is necessary to achieve the reactive radical cations of each comonomer within the same potential window.



Fig. 1. Potentiodynamic electropolymerization of (a) SNS-HE, (b) SNS-HE and EDOT, (c) EDOT in 0.1 M LiClO<sub>4</sub>/ACN at a scan rate of 100 mV s<sup>-1</sup> vs Ag/Ag<sup>+</sup>.

Fig. 1b and c displays potentiodynamic scans of the monomer in the presence of EDOT and pure EDOT in  $LiClO_4/ACN$  system with ITO working electrode at a scan rate of  $100 \text{ mV s}^{-1}$ , respectively. During potentiodynamic scan the anodic peaks of the copolymer appeared at 1.0 V and 0.67 V. As seen redox potentials of copolymer are noticeably different from PEDOT and poly(SNS-HE) which could be interpreted as a proof for the formation of a true copolymer. Moreover, FTIR spectrum of the copolymer revealed presence of a new peak at 1199–1109 cm<sup>-1</sup> due to asymmetric and symmetric C–O–C stretching of etheric units that stem from comonomer EDOT, respectively. In addition, the broad band centered at 1653 cm<sup>-1</sup> and the intense band at 1085 cm<sup>-1</sup> revealed the formation of polyconjugation and presence dopant anion, respectively. Thus, existence



Fig. 2. Cyclic voltammograms of the copolymer on ITO electrode in 0.1 M LiClO<sub>4</sub>/ACN at various scan rates vs Ag/Ag<sup>+</sup>.

of these distinctive peaks confirms the formation SNS-HE-EDOT copolymer [32,33].

The electroactivity of the copolymer sample (synthesized at 1.3 V) was studied in monomer free supporting electrolyte system. Cyclic voltammograms and plots of wave current density vs potential scan rate are illustrated in Fig. 2. As seen both the anodic and cathodic current densities of the copolymer show a linear dependence with the scan rate, having an anodic and cathodic regration fit of R = 0.999; R = 0.999, respectively. On the contrary, current density vs square root of the scan rate (not given) revealed an anodic regration fit of R = 0.992 and cathodic regration fit of R = 0.992. The linearity of the wave currents with potential scan rate is a characteristic of mass transfer in the electroactive film on the electrode. Such observation indicates that migration of the electroactive species is not diffusion controlled, the electroactive polymer is well adhered and electrode supported [34].

#### Table 1

Electrochromic properties of the copolymers and the device.



Applied potentail during copolymerization.

<sup>b</sup> For the neutral polymer films.

<sup>c</sup> Band gap, estimated from the optical absorption band edge of the films.

<sup>d</sup> The switching time of the copolymers at  $t_{100}$ : 100%,  $t_{95}$ : 95%,  $t_{90}$ : 90% of ultimate contrast.

<sup>e</sup> Colorimetry study results at n: neutral, i: intermediate, o: oxidized states.



Fig. 3. Spectroelectrochemistry of poly(SNS-HE) film on an ITO coated glass slide in monomer-free 0.1 M LiClO<sub>4</sub>/ACN electrolyte solution (a) 0.6 V, (b) 1.0 V, (c) 1.2 V, (d) 1.3 V. (e) 1.4 V and (f) 1.5 V vs Ag wire.

#### 3.3. Electrochromic properties

Spectroelectrochemical analyses of poly(SNS-HE) were performed in order to elucidate the electronic transitions and changes in optical properties upon redox switching. The spectral behavior (Fig. 3) of the poly(SNS-HE) was investigated by UV-vis spectrophotometer in a monomer-free electrolyte system while incrementally increasing the applied potential between 0.0 and 1.5 V. In the neutral state, poly(SNS-HE) showed a single broad absorption peak at 360 nm, which corresponded to the  $\pi$ - $\pi^*$  inter band transition ( $E_g = 2.32 \text{ eV}$ ) and the polymer appeared yellow in color. At 1.5 V the homopolymer appeared in bluish gray color revealing two absorptions at around 360 and 602 nm, indicating that the polymer film could not be fully oxidized. Hence, upon several redox switching the polymer lost their electroactivity and did not display color change.

On the other hand, poly(SNS-HE-EDOT), synthesized at 1.2 V, revealed maximum absorption at 492 nm (Fig. 4) with a band gap of 1.70 eV. Upon increase in the applied potential, the peak height of the interband transition was suppressed and simultaneously a new absorption peak appeared at around 773 nm due to charge carrier band formations. Beyond 0.8 V the spectrum was overwhelmed by the broad transition entailing to the NIR region most probably indicating bipolaron formation. The copolymer displayed distinct multichromism (Fig. 4), revealing reddish brown, yellowish green and blue colors in neutral, mid and highly oxidized states. Hence, we can infer that incorporation of EDOT units with in SNS-HE chain allowed us to overcome the limitations of poly(SNS-HE).

In order to explore the effect of polymerization potential on electrochromic properties, several copolymers were synthesized at different (1.1, 1.2, 1.3, 1.4V) applied potentials without changing the comonomer feed ratio and solvent-electrolyte system. All the polymers revealed similar spectral features (not given) having



**Fig. 4.** Spectroelectrochemistry of poly(SNS-HE-EDOT) film on an ITO coated glass slide in monomer-free 0.1 M  $LiClO_4/ACN$  electrolyte solution at applied potentials (a) -0.2 V, (b) 0.0 V, (c) 0.2 V, (d) 0.3 V, (e) 0.4 V, (f) 0.6 V, (g) 0.7 V, (h) 0.8 V, (i) 1.2 V and (j) 1.6 V vs Ag wire.

a strong band in the visible region at their neutral state and a broad band extending into the NIR in their doped state. Fig. 5 represents the normalized spectra of the neutral copolymers. As seen, all the copolymer films exhibited a broad transition showing significant shift of peak maxima between 450 nm and 522 nm (Table 1) with the increase in polymerization potential from 1.1 V to 1.4 V. The positions of these bands define the color of the copolymers, which range from reddish brown to violet (results of the colorimetric measurement as also provided) upon variation of polymerization potential. In accordance with the literature [21,30,31,35] this indicates that the composition of the copolymer changes with the change in polymerization potential. The higher the applied potential, the more EDOT units are incorporated into the copolymer film.

The switching ability of the copolymers was evaluated by monitoring the changes in the percent transmittance of the polymers as a function of time. Fig. 6a–c represents the percent transmittance change, applied potential profile and the current density of the copolymer (synthesized at 1.4V) as a function of time. As seen the optical contrast was calculated to be 36.43% at 522 nm and the



Fig. 5. Normalized UV-vis spectrum of copolymers (in neutral state) synthesized at different polymerization potentials.

device revealed continual, regular current alternations upon repetitive cycling. Such persistent and uniform redox behavior could be considered as a sign of high stability. The switching time of the copolymer was measured at 90% of ultimate contrast and it



Fig. 6. (a) Transmittance (%), (b) current density, (c) applied potential, during repetitive electrochromic switching, (d) transmittance (%) of a single switch of the copolymer deposited at 1.4 V on ITO electrode, monitored at 522 nm in 0.1 M LiCIO<sub>4</sub>/ACN.



**Fig. 7.** Optoelectrochemical spectra of poly(SNS-HE-EDOT)/PEDOT ECD at applied potentials of (a) -0.2 V, (b) 0.0 V, (c) 0.2 V, (d) 0.4 V, (e) 0.6 V, (f) 0.8 V, (g) 0.9 V, (h) 1.0 V, (i) 1.1 V, (j) 1.2 V, (k) 1.3 V, (l) 1.4 V and (m) 1.5 V.

was found to be 0.4 s. Such definition was proposed [36] due to limitation of human eye to perceive any variations beyond this limit. Moreover, we have also investigated the switching ability of the other copolymer (Table 1) films synthesized under different polymerization potentials. It was observed that all the copolymers presented fast switching times with parallel coloring and bleaching processes.

#### 3.4. Electrochromic device (ECD) application and characterization

Nowadays the scientific community is committed to the development of electrochromic devices since it is operational under a wide range of viewing angles and lighting conditions with low-power requirements. Therefore, we fabricated a prototype of the all solid state complementary electrochromic device in order to investigate the electrochromic performance of SNS-HE based polymers in ITO/poly(SNS-HE-EDOT)/PEDOT/ITO configuration. Fig. 7 shows the spectroelectrochemistry study of such ECD between -0.2 and 1.5 V bias to copolymer layer. At -0.2 V a well defined transition at 461 nm was observed and the device revealed brown color owing to the copolymer film that is in neutral state. Since this is a dual type device at this point PEDOT layer is expected to be in its oxidized state showing no significant transitions in visible region. Upon stepwise increase in the applied potential copolymer layer started oxidize and a new peak at 605 nm emerged due to neutralization of PEDOT layer. Upon further amplification of the potential (beyond 1.0V), the spectrum was overwhelmed by the  $\pi$ - $\pi$ <sup>\*</sup> transitions of PEDOT and the device displayed blue color. Moreover, switching time and optical contrast of the device were evaluated (Fig. 8) in the case of



**Fig. 8.** Electrochromic switching, transmittance (%) change monitored at 605 nm for poly(SNS-HE-EDOT)/PEDOT ECD between 0.0 V and 1.5 V.



Fig. 9. Open circuit memory of poly(SNS-HE-EDOT)/PEDOT device monitored at 605 nm and 461 nm while a pulse of 1.0 V and -0.2 V was applied for 1 s every 200 s to recover respectively.

polymers while applying the potential in square wave form (between 0.0 V and 1.5 V) with a residence time of 5 s. The optical contrast of the device, measured as the difference between T% in the extreme forms, was found to be 26.6%. The time required to reach 95% of ultimate T% was 0.44 s.

Open circuit memory (also called optical memory) is described as the time at which an electrochromic material maintains its color after the removal the applied electric field [22]. After polarizing the device in one color and removing the electric field; the device is expected to reveal color persistence at the induced state. In order to evaluate such property, we applied 1 s pulse of 1.0 V (for blue) or -1.2 V (for brown) and then kept the device under open-circuit condition for 200 s while simultaneously probing the percent transmittance as a function of time. As seen in Fig. 9 the optical properties of the device remained almost the same for extended periods of time for the brown state of the device where the copolymer layer is in neutral and PEDOT is in its oxidized state. However this is not eligible for the case of blue colored state.

#### 4. Conclusions

Herein, we reported the synthesis and characterization of a alkyl substituted SNS derivative namely,1-(2-Ethyl-hexyl)-2,5di-thiophen-2-yl-2,3-dihydro-1H-pyrrole (SNS-HE). Poly(SNS-HE) was grafted on ITO electrode via electrochemical polymerization and the homopolymer displayed yellow-gray transition upon switching. Additionally, electrochemical copolymerization of SNS-HE and EDOT was achieved in 0.1 M LiClO<sub>4</sub>/ACN system under different potentiostatic conditions. Investigation of electrochromic properties of the both the homopolymer and the copolymers were performed via spectroelectrochemistry and kinetic studies. The resultant copolymer revealed enhanced optic contrast, switching time compared to parent polymer and multichromism throughout the entire visible region, displaying violet, yellow, green, and blue colors upon variation of the applied potential. Moreover, we successfully established the utilization of poly(SNS-HE-EDOT) in dual type electrochromic devices. The device exhibited short switching time with reasonable optical memory under atmospheric conditions. To sum up, our studies have shown that we could tune the color of the polymers by changing the polymerization potential and SNS-HE based polymers are promising candidates as electrochromic materials.

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2011.11.079.

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