Materials Chemistry and Physics 293 (2023) 126916

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Electrochromic properties of a polydithienylpyrrole derivative with N-phenyl pyrrole subunit

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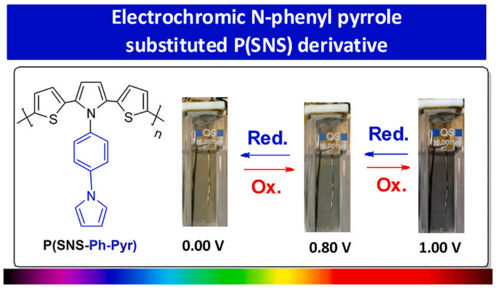
HIGHLIGHTS

- A SNS trimeric unit bearing a pyrrole substituent was synthesized.
- Electrochemical polymerization of SNS-Ph-Pyr was successfully achieved.
- P(SNS-Ph-Pyr) film exhibits multiple colors depending on the applied potential.
- P(SNS-Ph-Pyr) films presented good chromatic contrast and stability during switching.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
2,5-dithienylpyrrole
Poly(2,5- dithienylpyrrole)
Conjugated polymer
Electrochromic polymer

ABSTRACT

In this report, a new N-phenyl typed 2,5-dithienyl pyrrole compound bearing pyrrole unit was successfully synthesized and its conjugated homopolymer, poly(1-(4-(1H-pyrrol-1-yl)phenyl)-2,5-di(thiophen-2-yl)-1H-pyrrole) (P(SNS-Ph-Pyr)), was obtained in the medium of 0.1 M $TBAPF_6$/DCM via electroanalytical methods. Cyclic voltammetry and FTIR studies proved that monomer SNS-Ph-Pyr was synthesized and polymerized electrochemically and its corresponding polymer film, P(SNS-Ph-Pyr)) has a well reversible redox peaks at about 0.70/0.50 V vs. Ag/AgCl reference electrode in monomer free solution with a long term reversible redox behavior. The in situ UV–visible spectroelectrochemical studies of polymer film exhibited that electrochromic P(SNS-Ph-Pyr)) film had a color transition between yellow (at reduced state (0.0 V)) to grayish blue (at oxidized state (1.0 V)) with a intermediate color (green at 0.70 V). Moreover, electrochromic switching studies displayed that polymer film (coated with a thickness of 100 mC/cm^2) had average optical contrast values (15.6% (383 nm), 19.5% (650 nm) and 41.7% (900 nm) but high coloration efficiency values (220 cm^2/C (383 nm), 264 cm^2/C (650 nm) and 384 cm^2/C (900 nm).

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https://doi.org/10.1016/j.matchemphys.2022.126916
Received 17 August 2022; Received in revised form 12 October 2022; Accepted 13 October 2022

1. Introduction

It is known that conjugated conductive polymers have attracted attention in recent years, especially in energy and technological applications, with their superior optical and electrochemical properties [1,2]. The most widely used applications of conjugated polymers, are as follows: energy storage [3], bio-and other sensors [4], solar cells [5], batteries [6], transistors [7], light emitting devices [8], super capacitors [9] and electrochromic materials [10–12]. Especially, electrochromic polymers have taken great attention in electrochromic applications due to their low cost, easy processing/color control and alternative options of their copolymerization technique [13,14]. Looking at the literature, it is possible to see a large number of conductive electrochromic polymers functionalized with familiar conjugated organic molecules (thiophene, pyrrole, aniline, furan, fluorene, carbazole etc.).

Among electrochromic conjugated polymers, polythiophene and polypyrrole derivatives are two classes of widely used conjugated polymers with their high conductivity and stability. However, the conductivity and processability decreases gradually, when bulky units were functionalized from starting monomer; thiophene or pyrrole chemical units. In order to avoid this problem, many solutions were suggested. Interconnecting α positions of thiophene and pyrrole was an effective one and a new trimeric structure, namely, 2,5-di(thienyl)pyrroles (SNS) was introduced into literature by Ferraris et al. [15,16]. Since then, most scientists have synthesized a large number of new electrochromic P (SNS) derivatives and their copolymers. Moreover, many homopolymers of SNS structures were electrochemically synthesized and their copolymers with 3,4-ethylenedioxythiophene were synthesized in such a wide range that the bonds to the N group of pyrrole in SNS polymer structure were classified (N- alkyl-, phenyl-, amine/amide-, heterocyclic-, and crosslinked substituted derivatives) [17,18]. Among them, N-phenyl substituted P(SNS) derivatives take great attention by most of scientists because of easy monomer functionalization along phenyl bridge of SNS unit as well as their excellent electrochromic properties. Furthermore, intermediate phenyl ring bonded to SNS trimeric structure causes a pronounced resonance effect over the main chain and increase electron donating ability [19–39]. For example, Wu research group introduced two different electrochromic P(SNS) polymer containing a phenyl and furan units [28,29]. The results show that both polymer films exhibited high percent transmittance difference in near IR region with multichromic properties. On the other hand, Cihaner research group studied on a N-heterocyclic substituted P(SNS) polymer and directly incorporate a 1,1-bipyrrole unit into SNS structure. The experimental studies revealed that the corresponding polymer average reversible redox stability and solubility properties with yellow emission [40]. Although there are many examples of N-functionalized SNS derivatives, there is no report based on incorporation of a phenyl pyrrole unit into a P(SNS) polymer.

In the light of this information, a novel SNS derivative, SNS-Ph-Pyr was synthesized using Paal-Knorr pyrrole condensation reaction and characterized with NMR, FTIR, UV–vis spectrophotometer and fluorescence spectroscopy. Its polymer ((P(SNS-Ph-Pyr)) was electrosynthesized and investigated for its electrochromic properties in detail for any potential application in the field of display technology.

2. Material and method

All chemicals were purchased from Aldrich Chemical and used without purification. For electranalytical studies, an electrolyte medium was prepared with tetra butyl ammonium hexa fluoro phosphate (TBAPF$_6$) dissolved in dichloromethane (DCM, distilled over CaH$_2$). Pt disc (0.02 cm^2) and wire were used as working and counter electrodes for electroanalytical studies, respectively. An Ag/AgCl in 3 M NaCl (aq) solution was used as reference electrode. The monomer was electropolymerized with an electrolyte medium containing 2 mM monomer concentration. Repetitive cyclic voltammetry and constant potential electrolysis techniques were used in order to obtain electrosynthesized. For spectroelectrochemical studies, a Pt wire (as counter electrode) and an indium tin oxide-coated quartz glass slide (ITO, Delta Tech. 8–12 Ω, 0.7 cm × 5 cm) (as working electrode) with Ag wire as a pseudo reference electrode were used in an UV cuvette. After electrochemical polymerization, the polymer films coated on working electrodes were rinsed into DCM solvent in order to get rid of monomeric/oligomeric species on electrodes. Potenstiostatic sudies were achieved with a marked of Ivium Compactstat potenstiostat galvanostat. NMR and FTIR spectra were recorded on a Bruker NMR spectrometer and Bruker Equinox 55 with an attenuated total reflectance (ATR) spectrophotometer. Spectroelectrochemical and fluorescence studies were achieved in a Specord S600 UV–vis spectrometer and Varian Cary Eclipse Fluorescence spectrophotometer, respectively. The color space given by the International Commission of Illumination with luminance (L), hue (a), and intensity (b) was also analyzed with Specord S600 UV–vis spectrometer.

2.1. Synthesis of compounds

2.1.1. Synthesis of 1-(4-(1H-pyrrol-1-yl)phenyl)-2,5-di(thiophen-2-yl)-1H-pyrrole (SNS-Ph-Pyr)

First of all, 1,4-di(thiophen-2-yl)butan-1,4-dione and 4-(1H-pyrrol-1-yl)aniline(1)was synthesized in the presence of Cu catalyst. 1,4-di(thiophen-2-yl)butan-1,4-dione was synthesized according to reference given in the literature [19]. Then, desired molecule (1-(4-(1H-pyrrol-1-yl)phenyl)-2,5-di(thiophen-2-yl)-1H-pyrrole (SNS-Ph-Pyr))was obtained by the reaction between compound **1** and 1,4-di(thiophen-2-yl)butan-1,4-dione. This reaction gives the **SNS-Ph-Pyr** in 80% yields (Scheme 1).

2.1.1.1. Synthesis of 4-(1H-pyrrol-1-yl) aniline (1). 4-Iodoaniline (1000 mg, 4.5 mmol) was stirred in DMF (10 mL) under argon gas K$_2$CO$_3$ (2131 mg, 10 mmol), CuI(174 mg, 9.1 mmol), dimethylethylenediamine (DMEDA) (321 mg, 3.6 mmol) and pyrrole (612 mg, 9.1 mmol) were added sequentially. The mixture was stirred at 110 °C for 24 h, product formation was controlled by TLC. Then 20 mL of distilled water was added and the water phase was washed with 3 × 50 mL of ethyl acetate. The organic phase was dried with MgSO$_4$ and filtered. Column chromatography with hexane/ethylacetate (19:1) yielded 50%, 361 mg of target product. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.18 (d, $J = 8.6$ Hz, 2H), 6.98 (t, $J = 2.2$ Hz, 2H), 6.72 (d, $J = 8.5$ Hz, 2H), 6.31 (t, $J = 2.2$ Hz, 2H).

2.1.1.2. Synthesis of SNS-Ph-Pyr. The resulting 4-(1H-pyrrol-1-yl)aniline (1) was used in the synthesis of 1-(4-(1H-pyrrol-1-yl)phenyl)-2,5-di (thiophen-2-yl)-1H-pyrrole (SNS-Ph-Pyr). 1,4-di(thiophen-2-yl)butan-1,4-dione (0.38 mmol) was dissolved in toluene (10 mL) under argon gas. P-toluene sulfonic acid (PTSA, 0.058 mmol) and 4-(1H-pyrrol-1-yl) aniline (0.5056 mmol) were added sequentially. The mixture was stirred at 110 °C for 5 days and product formation was controlled by thin layer chromatography (TLC). After toluene was removed under low vacuum, it was purified with hexane/ethylacetate (50:1) by column chromatography using silica gel and the targeted product was obtained with 117 mg (80% yield). ^{1}H NMR (500 MHz, CDCl$_3$) 7.43 (d, $J = 8.7$ Hz, 2H), 7.33 (d, $J = 8.7$ Hz, 2H), 7.16 (d,$J = 2.2$ Hz, 2H), 7.05 (dd, $J = 5$ 0.05: 1.05 Hz, 2H), 6.81 (m, 2H), 6.58 (m, 2H), 6.53 (s, 2H), 6.37 (t, $J = 2.2$ Hz, 2H). ^{13}C NMR (500 MHz, CDCl$_3$) δ141.1, 135.6, 135.0, 131.4, 130.4, 127.2, 124.7, 124.4, 120.4, 119.3, 111.4, 110.2.

3. Result and discussion

3.1. Synthesis and characterization of SNS-Ph-Pyr

1,4-di(thiophen -2-yl)butan-1,4-dione and 4-(1H-pyrrol-1-yl)aniline (1) were intermediate materials for the synthesis of SNS-Ph-Pyr monomer. Firstly, thiophene and succiniyl chloride were reacted in order to get 1,4-di(thiophen-2-yl)butan-1,4-dione in the presence of $AlCl_3$ dissolved in DCM at 0 °C. Compound 1 was obtained from a mixture of pyrrole and 4-iodoaniline with the gradual addition of K_2CO_3, CuI and DMEDA in DMF. The monomer were obtained from a reaction of 1,4-di(thiophen-2-yl)butan-1,4-dione and 1 through Paal-Knorr condensation reaction in the presence of PTSA catalyst in dry toluene as shown in Scheme 1. All the products were purified by using column chromatography in order to get solid products. Monomer, SNS-Ph-Pyr, was characterized on the basis of ^1H NMR, ^{13}C NMR and FTIR analysis, which firmly proved the proposed chemical structures.

Optical properties of SNS-Ph-Pyr (1×10^{-5} M) were recorded in the medium of ACN. UV–vis and fluorescence spectra were shown in Fig. 1. The absorption band of the monomer gives rise to a strong absorption band at 200 nm and a two slight absorbance peaks at 265 nm and 365 nm. As it is known from literature, SNS unit, itself, had two broad bands at around 230 nm and 330 nm in chloroform [41]. Pyrrole gives an absorption peak at around 205 nm [42]. From this knowledge, the first strong band at 200 nm corresponds to pyrrole rings, which are populated in the structure. The other bands at 230 and 265 nm most probably belong to SNS ring and phenyl part of the monomer structure. SNS-Ph-Pyr had one emission peak at about 416 nm (excited at 265 nm) that was attributed to blue color emission. SNS moiety give an emission band at around 425 nm in chloroform [41]. Depending on solvent and functional unit from SNS structure, this band shifts for SNS derivatives. In literature, there are also other blue light emitted SNS monomers [41, 43–45].

3.2. Electrochemical polymerization of SNS-Ph-Pyr

SNS-Ph-Pyr monomer was potentially scanned between 0.0 V and 1.20 V versus Ag/AgCl containing 0.1 M $TBAPF_6$ and DCM. Monomer was oxidized at about 0.8 V, which exhibits the formation of radicalic cation forms at/around the working electrode surface and shows similar oxidation potential values like its SNS analogues as seen in Table 3. During the second scan, a new oxidation and reduction couple peaks were observed at 0.6 V and 0.55 V, respectively. After next repetitive cycles, new radical-monomer or radical-radical monomer couplings were formed and new oligomeric/polymeric species were formed because there is a shift of redox potential and monomer oxidation current increase during potential cycling (Fig. 2). These all indicates the formation of an electroactive polymer on the working electrode surface (25 successive scans). During the polymer formation, the anodic current

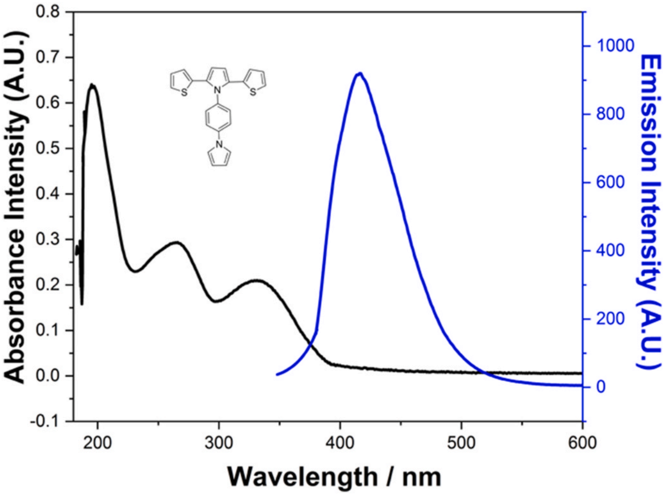
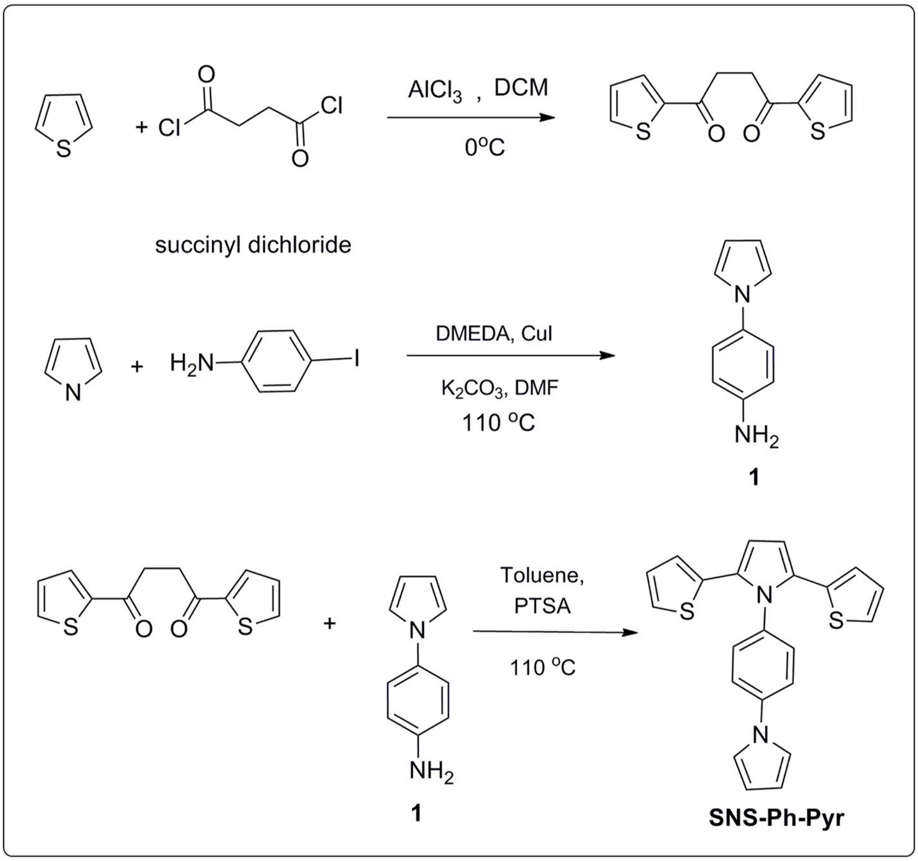


Fig. 1. Absorption and emission spectra of SNS-Ph-Pyr (1×10^{-5} M) in ACN.



Scheme 1. Synthesis procedures for compounds 1 and SNS-Ph-Pyr.

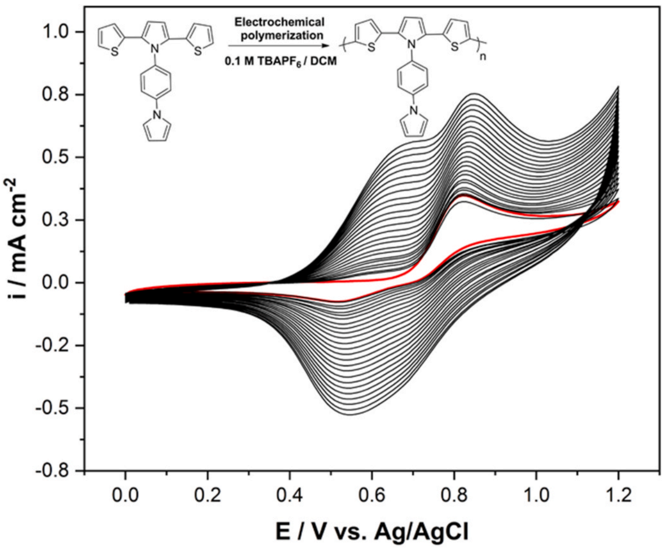


Fig. 2. Repetitive cyclic voltammogram (total numbers of cycle: 25) of SNS-Ph-Pyr in 0.1 M TBAPF$_6$/DCM on Pt disc electrode with 100 mV s^{-1} scan rate.(red line:1st cycle of monomer). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

at about 0.67 V and 0.82 V continued to increase together. While the current increase of the first potential at about 0.67 V is an expected situation related to the formation of classical electropolymerization process, the current increase for latter indicates some radicalic cation formations originating from monomers or oligomers in the diffusion layer of the system.

3.3. Electrochemical behavior of P(SNS-Ph-Pyr)

After electropolymerization step, Pt disc coated with polymer film (P(SNS-Ph-Pyr)) was taken out of monomer solution. After washing with DCM solvent, the polymer film coated on the working electrode was immersed in a monomer-free solvent electrolyte medium. A single and prominent reversible redox couple ($E_{pa} = 0.7$ V, $E_{pc} = 0.5$ V vs. Ag/AgCl with a scan rate of 100 mVs^{-1}) were appeared when potentially scanned between 0.0 V and 1.0 V) (Fig. 3a). When the last cycle of Fig. 2 was examined, it was seen that double oxidation peaks obtained were decreased to one in Fig. 3a. There are P(SNS) polymer derivatives showing the same characteristic in the literature [21,25,40]. This may be due to the oligomeric species that migrate to the washing solvent after the polymer coated with the electrode is washed. This was also scan rate effect on the potential for polymer behavior in the monomer free medium. When the polymer film is scanned at very low scan rates (20 mVs^{-1}), two anodic peaks are observed. This potential peak becomes gradually less dominant and disappears during higher scan rates.

The polymer film coated on Pt disc electrode (25 cycled) was switched between its redox states at different scan rates in order to see the scan rate dependency of anodic (i_{anodic}) and cathodic (icathodic) peak currents (Fig. 3a). The experimental results showed that both redox (anodic and cathodic) peak currents increase with growing scan rates (between 20 mVs^{-1} to 250 mVs^{-1}). As can be seen from Fig. 3b, upon amplification of the scan rate P(SNS-Ph-Pyr) film revealed a proportional incline ($R^2 = 0.99737$ for anodic fitting), $R^2 = -0.99912$ for cathodic fitting) in the current intensity. This indicates that this doping and dedoping redox process is nondiffusional and polymer film is adhered very well to the Pt disc electrode (Fig. 3b).

Electrochemical stability of polymer between neutral and oxidized states or a potential range is important for technological applications. For that reason, P(SNS-Ph-Pyr) film (25 cycled) was switched between 0.0 V and 1.0 V with a scan rate of 200 mVs^{-1} for 1000 cycles in monomer free electrolytic solution and anodic and cathodic current and charge data were recorded after each 100 cycles (Fig. 4). According to results, P(SNS-Ph-Pyr) film saved 78% (charge) and 75% (current) of its electroactivity after 1000 cycles.

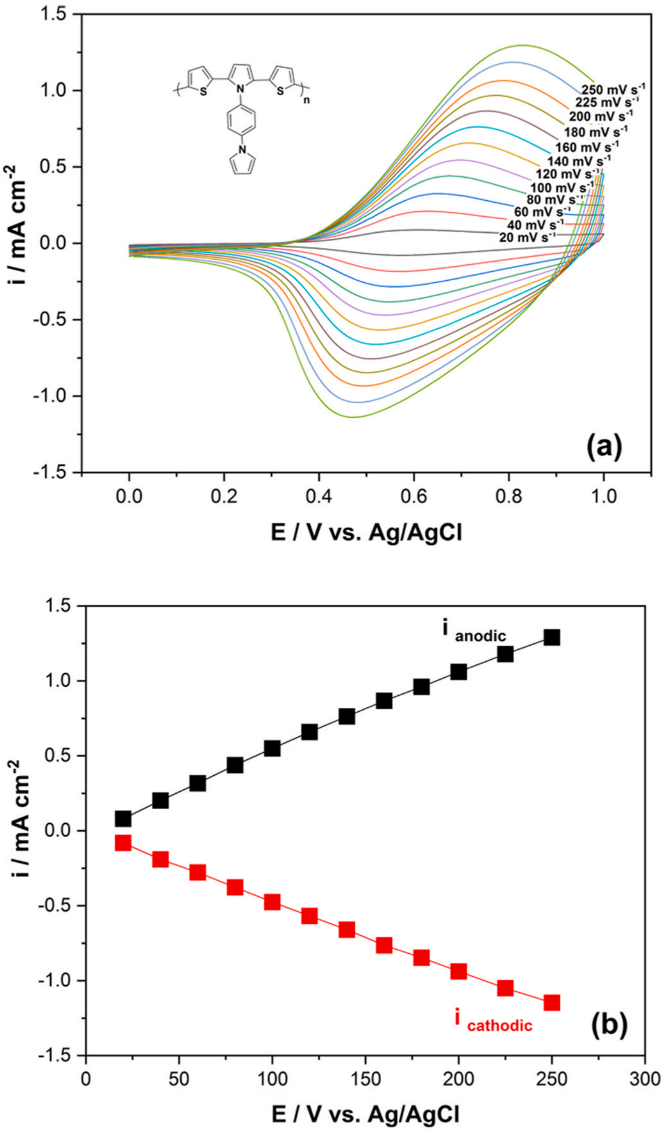


Fig. 3. (**a**) Cyclic voltammograms of polymer film at various scan rates from 20 mV s^{-1} to 250 mVs^{-1}, (**b**) Anodic/cathodic current intensity vs. scan rate dependency plot for the polymer film.

3.4. In situ spectroelectrochemical behavior of P(SNS-Ph-Pyr)

For spectroelectrochemical investigations, polymer film was electrodeposited on ITO electrode at various thicknesses (50/75/100 mC/cm^2) via constant potential electrolysis (0.8 V). Each has same spectroelectrochemical behaviors with different absorbance intensities. Among them, spectroelectrochemical behavior of polymer film with 75 mC/cm^2 thicknesses was chosen and spectroscopic changes were recorded in situ as seen in Fig. 5 during the oxidation potential scan between 0.0 V and 1.0 V (with a scan rate 30 mV s^{-1}). In its neutral state, polymer has an absorption band at around 383 nm, which corresponds to π-π* transition of P(SNS-Ph-Pyr). The band gap of polymer film was found as 2.32 eV (similar band gap value like other P(SNS) derivatives (Table 3)) with other by the commencement of the low energy end at 383 nm. Upon oxidation at about 0.4 V, the absorption intensity of π-π*

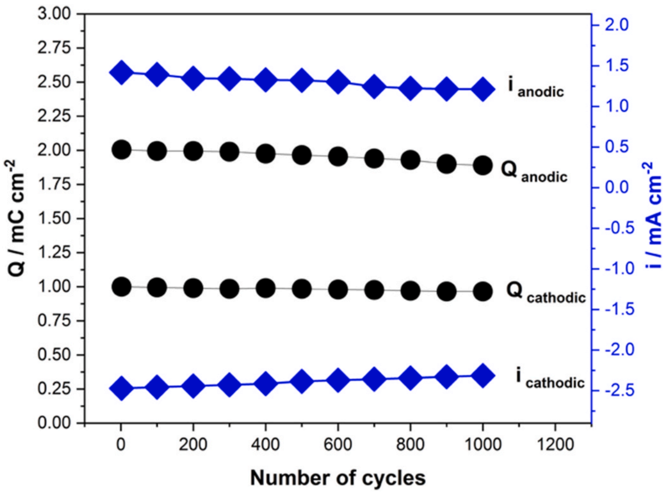


Fig. 4. Electrochemical stability test for polymer film (25 cycled) in the medium of 0.1 M TBAPF$_6$/DCM.

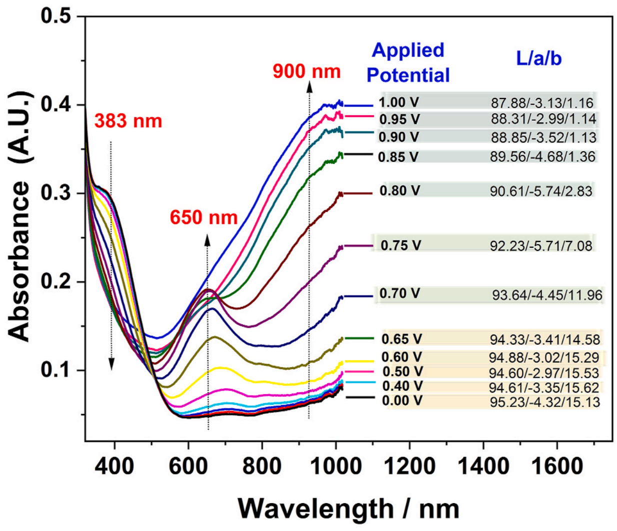


Fig. 5. Spectroelectrochemical behavior of polymer film in the medium of 0.1 M TBAPF$_6$/DCM. (The colors and corresponding L/a/b values of polymer film (with a thickness of 75 mC/cm^2) were depicted in each line of spectra). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

transition decreases and new charge carrier, polaron, formed at 650 nm. After applied potentials at 0.85 V, while the amplitude of absorption band at 650 nm stays almost the same, bipolaron charge carrier at about 900 nm starts to become more apparent.

3.5. Electrochromic properties of P(SNS-Ph-Pyr)

P(SNS-P-Pyr) exhibits electrochromic behavior, which is a remarkable and underestimated property. Upon oxidation, polymer film reveals various colors; grayish blue at 1.0 V, green at 0.70 V and yellow at 0.0 V. While experimenting with in situ UV–vis absorbance changes, the colors that the polymer should theoretically have and the corresponding L/a/b values of these colors are given in the inset of Fig. 5. In fact, it has been proved by photographing that the polymer film coated on ITO gives the same colors experimentally at each potential applied as seen in Table 1.

Electrochromic properties of polymer film can also be monitored by observing switching properties of polymer film. The rapid response and color change of a polymer between redox states is very important for electrochromic applications. For this purpose, the polymer film is switched in its neutral and oxide states and electrochromic parameters such as optical contrast (percentage transmittance change) (%ΔT), switching time (t$_{sw}$) and coloration efficiency (CE) give important information about the properties of the electrochromic polymer. The optical density (ΔOD) and CE can be calculated using the following equations:

$$\Delta OD = log\frac{T_{colored}}{T_{bleached}} \quad \text{and} \quad CE = \frac{\Delta OD}{Q_d}$$

where $T_{colored}$ and $T_{colored}$ are transmittance values in the oxidized and neutral states, respectively. Q_d is charge value difference during redox state change. In this study, 95% of total transmittance change was chosen in order to find CE and t$_{sw}$ because human eye can't detect the color change 100% with the naked eye.

A square-wave potential step method is coupled with UV–vis spectroscopy, which is called chronoabsorptometry. In this double potential step method, polymer film is switched between starting potential to initial oxidation potential for a set of period and then again, within a certain period of time, it goes on a potential way in the opposite direction and returns to the potential it was first applied to. This switching event continues in this way by repeating as many times as desired. The wavelengths at which switching will be selected are chosen by finding the wavelengths at which spectroelectrochemical events show the maximum absorbance change. According to Fig. 5, three wavelengths were selected and polymer film (with a thickness of 100 mC/cm^2) switched between their redox states as shown in Fig. 6 Switching data were shown at 383 nm, 650 nm and 900 nm in Fig. 6a, **b** and **6c** respectively. As seen in Fig. 6d, polymer film successfully switched between 0.0 V and 1.0 V during kinetic data taken.

The electrochromic properties of polymer films coated at different thicknesses are summarized in Table 2 at various wavelengths. The dynamic changes of the transmittance during a single cycle for the polymers with different thicknesses were given in Figure SI-2a, b and c at different wavelengths ((See Figure SI-2). Accordingly, while the amount of coated charge increased, the optical contrast value and coloration efficiency of the polymer film also increased depending on the wavelength values but there are no improvements (faster response

Table 1
Experimental colors of electrochromic polymer film at different applied potentials in the medium of 0.1 M TBAPF$_6$/DCM (with a thickness of 75 mC/cm^2 coated polymer film).

Applied Potential	0.00 V	0.40 V	0.60 V	0.70 V	0.80 V	0.90 V	1.00 V
Colors							

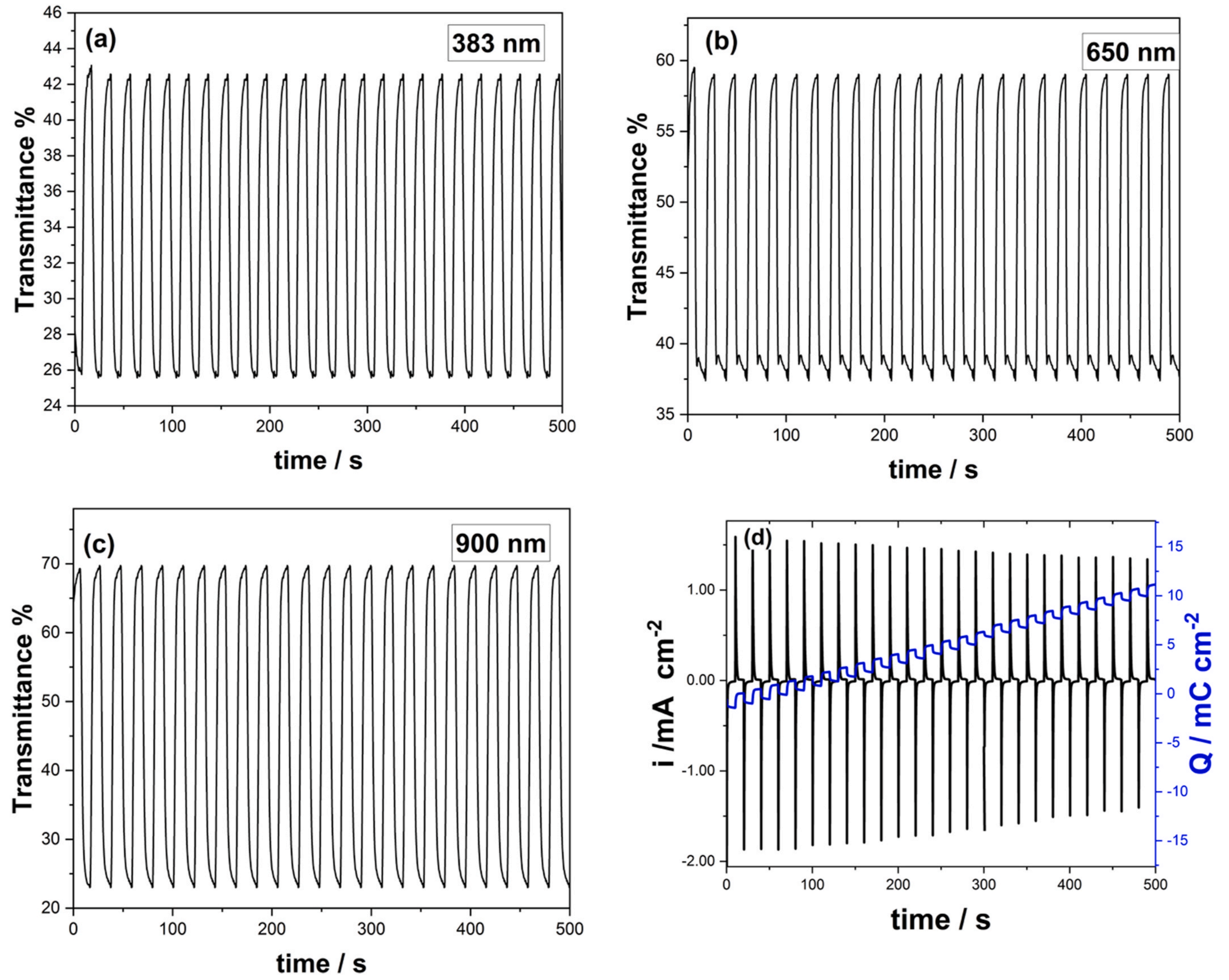


Fig. 6. Electrochromic switching and optical absorbance change monitored during switching at (a) 383 nm (b) 650 nm (c) 900 nm and (d) chronoamperometry experiments for P(SNS-Ph-Pyr) in 0.1 M TBAPF$_6$/DCM for (with a thickness of 100 mC/cm^2 coated polymer film).

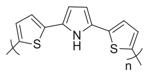
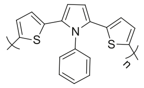
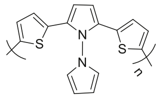
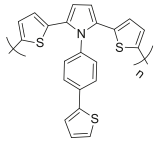
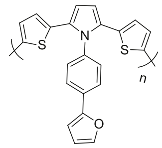
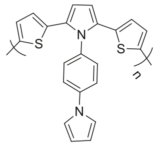
Table 2
A summary of electrochromic properties for P(SNS-Ph-Pyr) film at different thicknesses.

Thickness (mC/cm^2)	$t^c_{95\%}$ (s)	$t^b_{95\%}$(s)	ΔT %	CE (cm^2/C)
50	2.2(383 nm)	1.7 (383 nm)	10.6 (383 nm)	58 (383 nm)
	1.1 (650 nm)	3.1 (650 nm)	17.5 (650 nm)	188 (650 nm)
	1.4 (900 nm)	5.1 (900 nm)	27.4 (900 nm)	91 (900 nm)
75	1.8 (383 nm)	1.8 (383 nm)	11.8 (383 nm)	97 (383 nm)
	1.8 (650 nm)	1.8 (650 nm)	18.4 (650 nm)	216 (650 nm)
	4.7 (900 nm)	3.6 (900 nm)	30.4 (900 nm)	209 (900 nm)
100	2.7 (383 nm)	4.6 (383 nm)	15.6 (383 nm)	220 (383 nm)
	2.7 (650 nm)	1.8 (650 nm)	19.5 (650 nm)	264 (650 nm)
	3.8 (900 nm)	3.7 (900 nm)	41.7 (900 nm)	384 (900 nm)

time) related with switching times of polymer films. From this table, it cannot be said that the polymer film always responds quickly to switching according to the polymer film thickness and the preferred wavelength. For example, while colored and bleached switching times of polymer film at 1.8 s and 1.8 s at 650 nm, respectively, response time for color change generally increase as polymer thicknesses increase as seen in Table 2. A thicker polymer layer on ITO electrode may lead to longer diffusion distances and causes slower response time depending on the morphology of polymer film. Considering the stability tests during 1000 s switching, it was concluded that the polymer film of 100 mC/cm^2 thicknesses was stable and lose its 17% loss electroactivity at 900 nm after 1000s (See Figure SI-1).

The spectroelectrochemical data of P(SNS-Ph-Pyr) and its analogues was summarized in Table 3. According to Table 3, all polymers show higher ΔT % values in the near IR region than that in the visible region [16,19,28,29,40]. While studies on CE values were not done for most polymers, it can be concluded that the polymers of the existing studies had lower CE values than that of P(SNS-Ph-Pyr) (384 cm^2/C). Again, most polymers show a yellow color change in the reduced state and bluish in the oxidized state, while most have different intermediate colors. It has been observed that P(SNS-Ph-Pyr) has a slow or average response times when coated with different thicknesses.

Table 3
A summary of electrochemical and spectroelectrochemical data of P(SNS-Ph-Pyr) and its some analogues.

Polymer	E^{ox}_{m}(V)[a]	E_{gap}[b] (eV)	$t_{sw(s)}$[c]	ΔT %	CE (cm^2/C)	EC colors[d]
 [16]	0.87* vs. Ag/Ag+	2.61	-	-	-	yellow orange (0.20 V) dark blue (0.82 V)
 [19]	0.45 vs. Ag/Ag$^+$	2.2	1.7 (413 nm) (for 95%)	27 (413 nm)		yellow (−0.2 V) green (1.0 V)
 [40]	0.98 vs. Ag/AgCl	2.21	–	18 (444 nm) 33 (661 nm) 45 (1000 nm)	–	orange (n) violet (ox)
 [28]	~0.9 vs. Ag/AgCl	2.24	t^c (s):1.74 (409 nm) 2.40 (572 nm) 1.68 (970 nm) (for 90%) t^b (s):1.60 (409 nm) 0.85 (572 nm) 1.77 (970 nm) (for 90%)	18.1 (409 nm) 10.1 (572 nm) 36.7 (970 nm)	303.84 (970 nm)	yellowish-green (n) bluish purple (i) deep bluish violet(ox)
 [29]	0.74 vs. Ag/AgCl	2.26	t^c (s): 1.91 (590 nm) 1.90 (1320 nm) (for 90%) t^b (s): 1.99 (603 nm) 1.97 (1320 nm) (for 90%)	6.2 (590 nm) 22.7(1320 nm)	181.8 (1320 nm)	saffron yellow (0.0 V) yellowish-gray (1.0 V) light purple (1.2 V) bluish-purple (1.4 V)
 this study	0.8 vs. Ag/AgCl	2.32	*details given in Table 2*	*details given in Table 2*	*details given in Table 2*	yellow (0.0 V) green (0.75 V) grayish blue (1.0 V)

[a] All polymerization conditions (solvent electrolyte couple, working and reference electrodes used, scan rates etc. wre given references related.

[b] Optical band-gaps as calculated from the onset of the π-π* transition of the neutral-state polymer. were.

[c] t_{sw}: switching time, t^c: coloring time,t^b: bleaching time, *predicted data from reference given.

[d] Colors (n) neutral state, (i) intermediate state, (ox) fully oxidized state. given in the references given in Table.

3.6. *Chemical structure analysis of P(SNS-Ph-Pyr)*

In order to prove that polymerization of monomer SNS-Ph-Pyr occurred though the α-H of thiophene unit of SNS trimeric structure, FTIR spectra of monomer and its corresponding polymer were compared as seen in Fig. 7. Some peaks of monomer were obtained at 3100 cm^{-1} (aromatic C–H stretching), 2923 cm^{-1} (C–H stretching of thiophene), 1457-1329 cm^{-1} (C═C, C–N stretchings of aromatic units). Furthermore it had three main peaks at 699 cm^{-1} (α-H of thiophene rings), 760 cm^{-1} (β-H of pyrrole ring) and 836 cm^{-1} (β-H of thiophene rings). While most of the peaks for polymer spectrum remained same, the peak at 699 cm^{-1} disappeared due to α-coupling of external thiophene rings [16]. Besides, a new peak appears at 796 cm^{-1} due to β-H of coupling of thiophene rings. Moreover, the peaks at 731 cm^{-1}, 1005 cm^{-1} and 3104 cm^{-1} are related with α-H of pyrrole ring, which indicates that pyrrole substituted from N-phenyl SNS unit didn't proceed through polymerization from coupling of pyrrole ring [40,45].

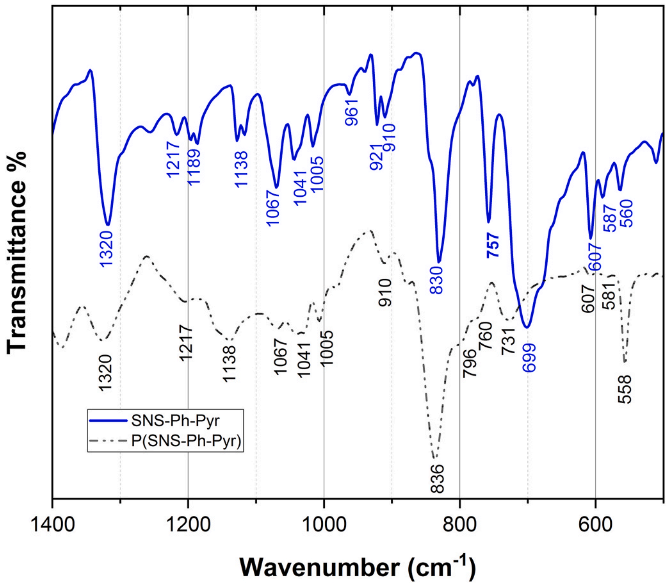


Fig. 7. FTIR spectra of SNS-Ph-Pyr and P(SNS-Ph-Pyr).

4. Conclusions

In conclusion, the pyrrole functionalized N-phenyl derivative SNS monomer was synthesized and its polymer was successfully electrochemically synthesized and characterized. P(SNS-Ph-Pyr) exhibited stable and reversible redox property as well as superior electrochromic behavior. It had a color change between yellow (neutral) and grayish blue (oxidized) with a green intermediate color, which makes polymer a feasible nominee in any necessary usage area for technological applications since these colors are important for full color electrochromic display applications. Work along this line currently underway in our laboratories.

CRediT authorship contribution statement

Buket Bezgin Carbas: Conceptualization, Data curation, Formal analysis, Writing –- original draft, Revising the manuscript critically for important intellectual content, Approval of the version of the manuscript to be published. **Nurseli Mislina Ergin:** Synthesis of molecule, Formal analysis. **Huseyin Bekir Yildiz:** Conceptualization, Data curation, Formal analysis, Writing –- original draft, Revising the manuscript critically for important intellectual content, Approval of the version of the manuscript to be published. **Arif Kivrak:** Synthesis of molecule, Formal analysis. **Atif Emre Demet:** Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

Acknowledgement

We thank the Scientific and Technological Research Council of Turkey (TUBITAK Grant Number 121G114) for its financial support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matchemphys.2022.126916.

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