

Synthesis and Characterization of a New Conducting Polymer Based on 4-(2,5-di-2-thiophen-2-yl-pyrrol-1-yl)-phthalonitrile

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ABSTRACT: A new conducting polymer was synthesized by electrochemical polymerization of 4-(2,5-di-2-thiophen-2-yl-pyrrol-1-yl)-phthalonitrile (SNS-PN). Electrochemical polymerization of SNS-PN was performed in acetonitrile/0.2M LiClO₄ solvent/electrolyte couple. Characterizations of the resulting polymer P(SNS-PN) were carried out by cyclic voltammetry, UV-vis, and Fourier transform infrared (FTIR) spectroscopic techniques. Spectroelectrochemical studies revealed that P(SNS-PN) has an electronic band gap

of 2.45 eV and exhibits electrochromic behavior. The switching ability of polymer was also monitored and the percentage transmittance change ($\Delta T\%$) was found as 24%. It is also found that P(SNS-PN) is fluorescent and its fluorescence intensity enhances in the presence of cations. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2685–2690, 2009

Key words: electrochemical polymerization; polythiophene; polypyrrole; electrochromism; fluorescence

INTRODUCTION

Since their discovery in the mid-1970s, conducting polymers still attract much interest for their fascinating properties, which allows their use in light emitting diodes (LEDs), electrochromic devices, solar cells, electrochemical supercapacitor, and field effect transistors.^{1–5} Although conducting polymers (polyaniline,⁶ polypyrrole,⁷ polythiophene,⁸ and polyfuran⁹) are well-known and intensively studied, among them polythiophenes are of growing interest because of their potential applications in the development of new materials such as photovoltaics,^{10–13} electrochromic devices,^{14,15} and energy storage.^{16–18} These applications usually require the modification of the properties of the polymers (electronic, optical, conductivity, etc.) with respect to desired applications. Functionalization of the monomer structure before polymerization, synthesis of copolymers, and association of the conducting polymer with other materials are widely used for this purpose. It is well-known that properties such as solubility, ionic conductivity and band gap energy are very much influenced by the present side group. An alternating sequence of donor-acceptor units along the polymer chain reduces the band gap⁸ and the presence of an alkyl or oligoether side chain enhances the solubility.^{19,20} A bulky substituent, on the other hand, may

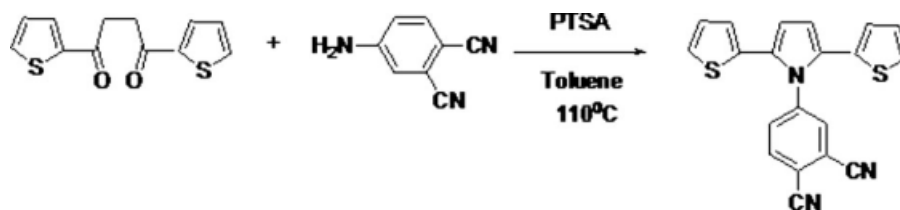
complicate the polymerization of monomer in question.²¹ To eliminate this problem, Jadamiec et al. suggested the use of terthiophenes in a way to dilute the number of substituents along the polymer chain.²¹ Polymerization of 2,4-di-(2-thienyl)-pyrrole (SNS) and 2,4-di-(2-thienyl)-furan was also investigated in this respect.^{22–24} Soluble conducting polymer formation from substituted SNS derivatives were recently reported by Toppare's research group.^{25–28} Cihaner et al. reported the formation of soluble polymers from several SNS derivatives exhibiting the electrochromic and fluorescence properties.^{29–31}

Herein, we report the electrochemical polymerization of a new monomer, 4-(2,5-di-2-thiophen-2-yl-pyrrol-1-yl)-phthalonitrile (SNS-PN) containing an acceptor group bonded to a high-spin donor. The corresponding polymer P(SNS-PN) was obtained electrochemically and its characterization was performed using cyclic voltammetry (CV) and Fourier transform infrared (FTIR) techniques. Electro-optical and electrochromic properties of the polymer film were investigated using in-situ spectroelectrochemical technique. Fluorescence measurements were also performed.

EXPERIMENTAL

All chemicals were purchased from Aldrich and Merck and used without any further purification. Before electrochemical studies, all solutions were degassed with N₂. The polymers were synthesized

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Scheme 1 Synthetic route of 4-(2,5-di-2-thiophen-2-yl-pyrrol-1-yl)-phthalonitrile (SNS-PN).

from an electrolytic medium containing 2.0 mM monomer and 0.2M LiClO₄ in acetonitrile via repetitive cycling at a scan rate of 100 mV/s or constant potential electrolysis at 1.0 V versus Ag wire. The polymer was coated on platinum (0.02 cm²) or indium-tin oxide (ITO, Delta Tech. 8–12 Ω, 0.7 × 5 cm²) working electrode. Since the polymer films, obtained on the ITO, were well-adhered on the working electrode surface it is not free standing. Any attempt to remove from the surface causes its fracture. In-situ spectroelectrochemical studies were performed using Hewlett–Packard 8453A diode array spectrometer. A Pt wire was used as a counter electrode, and a Ag wire as a pseudoreference electrode, which was calibrated externally using 5 mM solution of ferrocene/ferrocenium couple in the electrolytic solution. The transmittance and absorption spectra of P(SNS-PN) were recorded in-situ under various applied potentials. Also, square wave potential method was used to investigate the ability of switching of the polymer film between its neutral and doped states. Gamry PCI4/300 potentiostat-galvanostat was used for all electrochemical studies. FTIR spectra of the monomer and its polymer were recorded with a Bruker Vertex 70 spectrophotometer. NMR spectra were recorded on a Bruker NMR Spectrometer (DPX-400) in CDCl₃, and fluorescence measurements were recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer.

Synthesis of 4-(2,5-di-2-thiophen-2-yl-pyrrol-1-yl)-phthalonitrile (SNS-PN)

The monomer was synthesized by using 1,4-di(2-thienyl)-1,4-butadiene³² and 4-aminophthalonitrile³³ via Knorr-Paal Reaction (Scheme 1).^{25–31,34} 0.938 g (3.75 mmol) of the 1,4-di(2-thienyl)-1,4-butadiene (SOOS), 0.75 g (5.25 mmol) of the 4-aminophthalonitrile, and 0.075 g (0.435 mmol) of *p*-toluene sulfonic acid (PTSA) were dissolved in 40 mL of dry toluene. The mixture was stirred and refluxed for 120 h under argon atmosphere. Toluene was evaporated, and the product was separated by column chromatography on silica gel (eluent: dichloromethane/hexane (1:1)). Yellow solid, 80% yield. Elemental analysis (%) calcd. For C₂₀H₁₁N₃S₂: C 67.20, H 3.10, N 11.76, S 17.94; found: C 67.20, H 3.47, N 11.52, S

17.97. ¹H NMR (400 MHz, CDCl₃): δ/ppm: 7.68 (d, *J* = 8.27 Hz, 1H), 7.53 (d, *J* = 1.82 Hz, 1H), 7.45 (d, *J* = 1.96–1.80 Hz, 1H), 7.14 (d, *J* = 2.68 Hz, 2H), 6.8 (t, *J* = 4.29 Hz, 2H), 6.53 (d, *J* = 2.2 Hz, 2H), 6.47 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ/ppm: 142.82, 134.13, 134.10, 134.03, 133.04, 129.46, 127.36, 126.61, 126.07, 116.52, 115.19, 114.78, 114.42, 112.35.

RESULTS AND DISCUSSION

Electrochemical polymerization of SNS-PN

Electrochemical behavior of SNS-PN was investigated in 0.2 M LiClO₄/acetonitrile, electrolyte/solvent couple using cyclic voltammetry, before the synthesis of the polymers. Cyclic voltammogram of electrolytic solution containing 2.0 mM SNS-PN exhibits one irreversible oxidation peak at 0.92 V versus Ag wire in the first anodic scan. A new reduction peak was also noted during the reverse scan, which intensified upon successive scans in the potential range of 0.0–1.15 V. The formation of P(SNS-PN) can be easily seen with the increasing intensity of the reversible redox couple, indicating doping and dedoping of the polymer film [Fig. 1(a)]. Also, electrochemical behavior of the polymer film obtained from SNS-PN after 13 repetitive cycles was investigated in the monomer-free electrolytic solution. Figure 1(b) shows that polymer film exhibits a single and well-defined quasireversible couple ($E_{p,a} = 0.74$ V and $E_{p,c} = 0.61$ V) in 0.2 M LiClO₄/acetonitrile solution due to doping and dedoping of the polymer film. Since SNS-PN has two electron withdrawing cyanide groups per monomer unit, the oxidation potential of the monomer and first oxidation potential of the polymer are slightly higher than the reported values for various SNS derivatives.^{23,25–31} To see if these electron withdrawing cyanide groups can interact with any metal cation through nitrogen atoms cyclic voltammograms of the polymer film was also recorded after keeping the film in contact with a solution containing either tetrabutylammonium perchlorate (TBAClO₄) or sodium perchlorate (NaClO₄) for 5 min. The results are depicted in Figure 2. As seen from the figure, oxidation peak of the polymer film shifted anodically. This result clearly indicates an interaction between cyanide groups

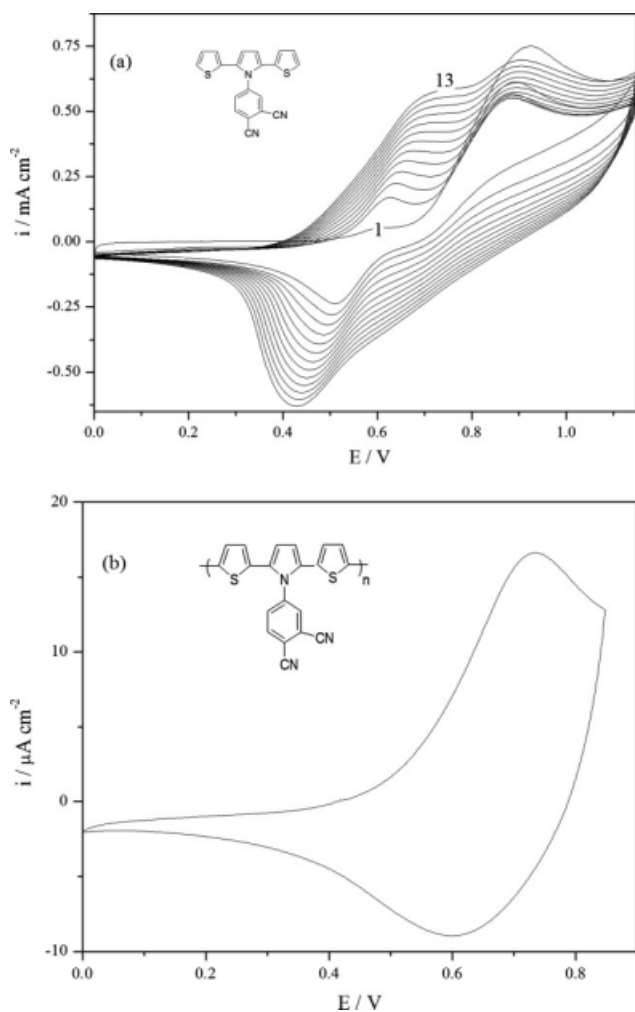


Figure 1 (a) Repeated scan electrochemical polymerization of $2.0 \times 10^{-3} M$ SNS-PN and (b) cyclic voltammogram of P(SNS-PN) film on a Pt disc electrode at 100 mV/s in acetonitrile solution containing 0.2 M LiClO₄.

present on the polymer chains and cations, thus reducing the electron withdrawing effect of these groups on the polymer film oxidation.

FTIR study

It is well-known that FTIR spectrum of unsubstituted SNS exhibits three strong bands centered at 692, 778, and 841 cm⁻¹ due to the C–H out of plane bendings of α -hydrogens of thiophene rings, β -hydrogens of pyrrole ring, and β/β' -hydrogens of thiophene rings, respectively.²³ The FTIR spectra of SNS-PN and its polymer P(SNS-PN) are presented in Figure 3. SNS-PN also exhibits these three strong peaks at 700 cm⁻¹, 765 cm⁻¹, and 840 cm⁻¹ due to the C–H bendings of α/β hydrogens of the five-membered aromatic rings. Furthermore, the peaks in the region of 1600–1420 cm⁻¹ are assigned skeletal vibrations of benzene ring and the peak at 2240 cm⁻¹ is due to the cyanide group. A close inspection

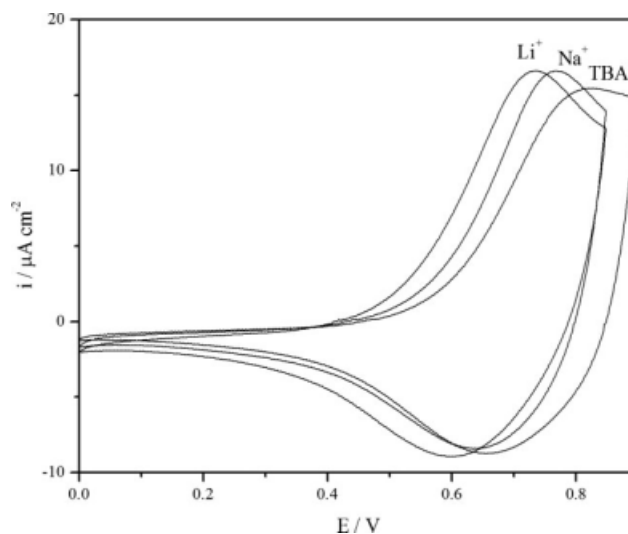


Figure 2 Cyclic voltammogram of P(SNS-PN) film (25 mC/cm²) on a Pt disc electrode in acetonitrile containing 0.2 M LiClO₄, NaClO₄, and TBAClO₄.

of Figure 3 reveals that all these peaks are also present in the FTIR spectrum of P(SNS-PN) except the peak at 702 cm⁻¹. This peak is due to α -hydrogens of external thiophene rings and its disappearance confirms the formation of linear polymer chains via α - α' linkages. The broad band observed at around 1650 cm⁻¹ proves the presence of polyconjugation²⁸ and the peaks at 1072 cm⁻¹ and 627 cm⁻¹ in the polymer spectrum are due to the presence of ClO₄⁻ dopant.²⁹

Spectroelectrochemistry of P(SNS-PN)

The transition between the doped and the neutral states results in important modifications of the absorption spectrum of the polymer. On the basis of these electro-optical properties, the use of the films as active element in smart windows and

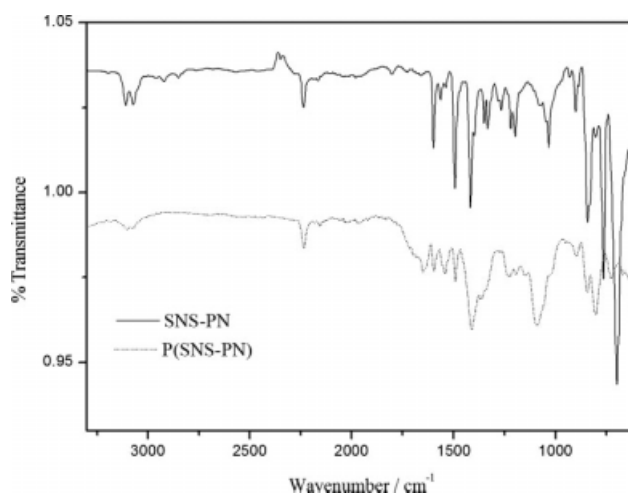


Figure 3 FTIR spectra of (a) SNS-PN and (b) P(SNS-PN).

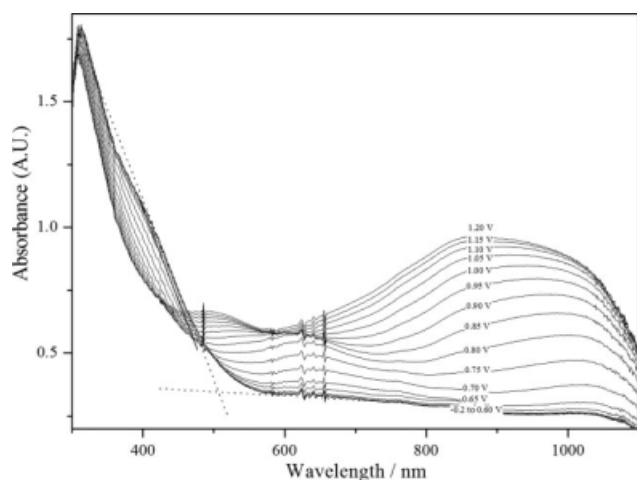


Figure 4 In-situ absorption spectra of P(SNS-PN) (55 mC/cm^2) recorded in acetonitrile containing 0.2 M LiClO_4 at various applied potentials.

electrochromic display devices is possible. For this aim, P(SNS-PN) film was deposited on ITO and its electrochemical behavior was studied in the monomer-free electrolytic solution containing 0.2 M LiClO_4 . After polymerization, the films were rinsed with acetonitrile to remove any unreacted monomer. Before spectroelectrochemical investigation, the polymer film on ITO was switched between neutral and doped states several times to equilibrate its redox behavior in monomer-free electrolytic solution. The changes in electronic absorption spectra recorded in situ at various applied potentials are depicted in Figure 4. As seen from the figure, the electronic absorption spectrum of the neutral form of the polymer film exhibits a band at about 389 nm due to $\pi\text{-}\pi^*$ transition and from its commencement on the low energy end the band gap (E_g) was found to be 2.45 eV .^{25–31,34} This value is slightly lower than the band gap of PSNS (2.6 eV),²³ and this difference might be attributed to the presence of electron withdrawing cyanide groups, which induce a decrease in the HOMO level.³⁵ Beyond 0.6 V , two new bands at 618 nm ($\sim 2.01 \text{ eV}$) and at 864 nm ($\sim 1.44 \text{ eV}$) start to intensify indicating the formation of polarons,¹⁸ and bipolarons, respectively. It is also noteworthy that P(SNS-PN) film can be reversibly switched between its neutral and oxidized states and exhibits electro-

chromic behavior; yellow in the neutral and blue in the oxidized state.

Switching times and optical contrast in the polymer film on ITO are determined with a change in transmittance at 389 , 618 , and 864 nm where the maximum transmittance difference between redox states was observed in the visible and near infrared region. For this aim, square wave potential step method was coupled with optical spectroscopy to investigate the switching ability of P(SNS-PN) between its neutral and oxidized states. The coloration efficiency (CE) for polymer is calculated from eq. (1) as described previously.^{36,37}

$$\text{CE} = \Delta\text{OD}/Q_d \quad (1)$$

where ΔOD is the change in optical density and Q_d is the charge (C/cm^2) passed during this process. ΔOD is determined from the percent transmittance ($\%T$) before and after a full switch and is calculated using eq. (2).

$$\Delta\text{OD} = \log \left(\frac{\% T \text{ of bleached state}}{\% T \text{ of colored state}} \right) \quad (2)$$

The charge passed at 95% of the optical switch was used to evaluate CE since beyond which the naked eye cannot sense the color difference. The polymer film coated on ITO (55 mC/cm^2) was switched between 0.0 V and 1.1 V versus Ag-wire and the time required to attain 95% of the total transmittance difference was found to be 1.7 s for fully oxidized state and 1.5 s for fully neutral state at 389 nm . Also, the average value of CE was found as $161 \text{ cm}^2/\text{C}$ (see Table I).

Fluorescence study

Since the electrochemically obtained P(SNS-PN) was found to be soluble in dimethylformamide (DMF) ($0.034 \text{ g}/100 \text{ mL}$) and partially soluble in dimethylsulfoxide (DMSO), the fluorescence property of both monomer and polymer was investigated in these solvents. Although the monomer exhibits a weak emission at about 400 nm , its polymer has a relatively intense emission band at the same wavelength when excited at 340 nm , corresponding to blue color (see

TABLE I
Voltammetric and Spectroelectrochemical Data for P(SNS-PN) Recorded in Acetonitrile Containing 0.2 M LiClO_4

λ/nm at charge	T_{bleached}	T_{colored}	$\Delta\%T$	ΔOD	CE (cm^2/C)	Neutral state	Intermediate state	Oxidized state
389	35.98	59.87	23.89	0.221	148			
618	45.46	69.71	24.25	0.186	108			
864	31.96	86.45	54.49	0.432	266			

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

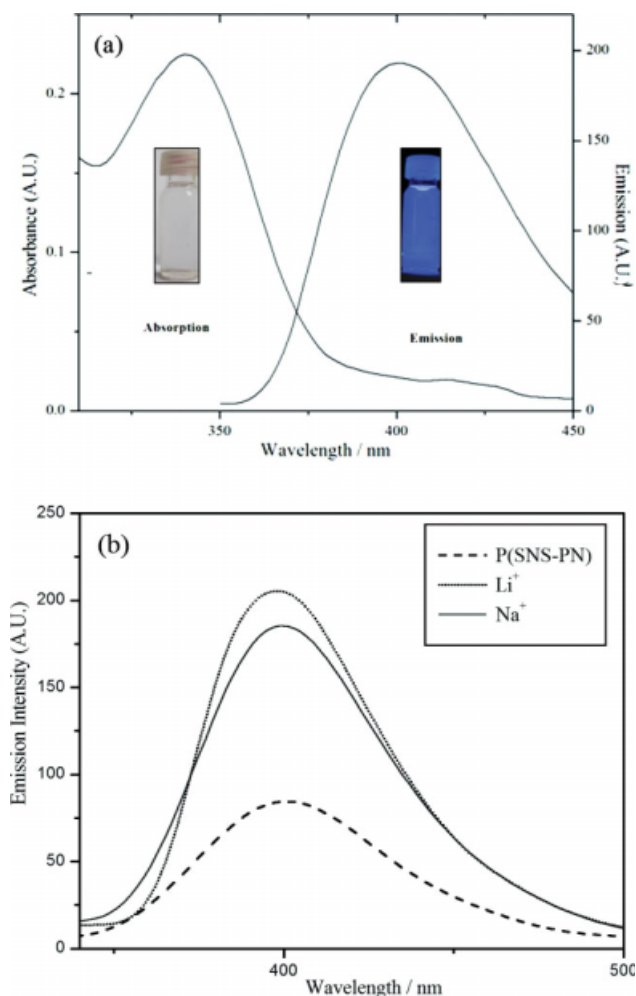


Figure 5 (a) Absorption and emission spectra of P(SNS-PN) recorded in DMSO and (b) emission spectra of P(SNS-PN) recorded in DMF in the absence and presence of 3.3×10^{-5} M LiClO_4 and NaClO_4 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Fig. 5a). These results indicate that this polymer is a blue light emitter and it may find applications in various fields, such as organic lasers and electroluminescent materials. It is noteworthy that the emission intensity increases in the presence of Li^+ and Na^+ cations, Figure 5(b). This observation also indicates the presence of an interaction between the cyanide groups of the polymer and the cations and is in accordance with the results obtained from CV studies.

CONCLUSIONS

In this study, the synthesis of a new monomer, SNS-PN, was successfully achieved via Knorr-Paal reaction. Its corresponding polymer was synthesized by electrochemical polymerization in LiClO_4 /acetonitrile electrolytic medium. Spectroelectrochemical analyses revealed that the polymer of SNS-PN has

electronic band gap of 2.45 eV. The time required to attain 95% of the total transmittance difference was found to be 1.7 s for P(SNS-PN). Optical contrast values were measured as 24%. The polymer film, besides exhibiting a well-defined and reversible redox process in acetonitrile, also exhibits stable electrochromic behavior: yellow in the neutral state and blue in the oxidized state with an average CE value of $161 \text{ cm}^2/\text{C}$. Soluble part of the polymer in DMSO has the fluorescent property emitting blue light. Moreover, the fluorescence intensity enhances in the presence of several cations, in DMF, due to the interactions between cyanide groups and cations. This result and the shifts in the oxidation potential of the polymer film makes P(SNS-PN) also a candidate in cation sensing, besides its use in organic lasers and electroluminescent materials.

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