

# Electropolymerization of a New 4-(2,5-Di-2-thiophen-2-yl-pyrrol-1-yl)-Tetra Substituted Nickel Phthalocyanine Derivative

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**ABSTRACT:** A new tetrakis 4-(2,5-di-2-thiophen-2-yl-pyrrol-1-yl) substituted nickel phthalocyanine (NiPc-SNS) was synthesized and characterized by elemental analysis, Fourier Transform Infrared (FT-IR), and UV-vis spectroscopies. The electrochemical polymerization of this newly synthesized NiPc-SNS was performed in dichloromethane (DCM)/tetrabutylammonium perchlorate (TBAP) solvent/electrolyte couple. An insoluble film was deposited on the electrode surface, both during repetitive cycling and constant potential electrolysis at 0.85 V. Resulting polymer film, P(NiPc-SNS), was characterized utilizing UV-vis and FT-IR spectroscopic techniques and its electrochemical behavior was investigated via cyclic voltammetry (CV). Spectroelectrochemical behavior of the polymer film on

indium tin oxide (ITO) working electrode was investigated by recording the electronic absorption spectra, *in situ*, in monomer-free electrolytic solution at different potentials and it is found that the P(NiPc-SNS) film can be reversibly cycled between 0.0 and 1.1 V and exhibits electrochromic behavior; dark olive green in the neutral and dark blue in the oxidized states with a switching time of 1.98 s. Furthermore, the band gap of P(NiPc-SNS) was calculated as 2.27 eV from the onset of  $\pi$ - $\pi^*$  transition of the conjugated backbone. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1293–1299, 2011

**Key words:** phthalocyanines; spectroelectrochemistry; electrochemical polymerization

## INTRODUCTION

Phthalocyanines and their metal complexes have attracted great interest because of their unique physical properties arising from delocalized  $\pi$ -electronic structure of the macrocyclic aromatic system. Some of these interesting properties, like relatively high hole mobility, rich redox chemistry, stability, and high extinction coefficient around 700 nm, make them find many application areas including electrochromic displays, organic solar cells, and electrode modifications.<sup>1–4</sup> More interestingly, introduction of phthalocyanine groups along a polymer matrix will not only impart these unique properties to the polymers but also enhance the properties of the resulting hybrid material in terms of sensor and electronic device applications. Therefore, one might expect better performance characteristics and higher thermal/chemical stability in phthalocyanine containing polymers than phthalocyanine complexes.<sup>5</sup> On the other hand, their lower solubility prevents film formation

which is the most important necessity for polymeric phthalocyanines in their applications, especially in the field of organic electroluminescent devices. To overcome this difficulty vacuum deposition is usually used to prepare thin films of porphyrins and phthalocyanines. Electrochemical polymerization, on the other hand, is much practical way of preparing phthalocyanine films when there exists a suitable substituent in the peripheral benzene rings of phthalocyanines. This technique will not only allow the easy control of thickness but also allow easy modification of electrode for making use of electrocatalytic behavior of phthalocyanines. Although, pyrrole, thiophene, or amino substituted phthalocyanines or porphyrins were used for this purpose,<sup>6–12</sup> we have recently reported the electrochemical synthesis of polymeric phthalocyanines containing 4-(2,5-di-2-thiophen-2-yl-pyrrol-1-yl) (SNS) substituent.<sup>13</sup> This substituent, SNS, consists of two external thiophenes and a central pyrrole ring and exhibits relatively lower oxidation potential and usually yields soluble polymers with electrochromic and fluorescence properties.<sup>14–18</sup> Furthermore SNS moiety has the advantage of being easily functionalized via central pyrrole unit and opens new routes for synthesizing new hybrid materials. In our previous study we have investigated the electrochromic properties of two new phthalocyanine containing polymers and

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found that they both exhibit reversible electrochromic changes. Since it is found that incorporation of metal ion enhances coloration efficiency, we have synthesized a new nickel ion containing derivative to investigate the effect of different central metal ions present in the phthalocyanine ring. In the present work, the synthesis and characterization of this new nickel phthalocyanine complex containing 4-(2,5-di-2-thiophen-2-yl-pyrrol-1-yl) (SNS) substituent is described. The electrochemical polymerization of this monomer containing phthalocyanine macrocycle was investigated using potentiodynamic or potentiostatic techniques. Furthermore, electrochemical and optical properties of the corresponding polymer films were also elaborated.

## EXPERIMENTAL

### Chemicals

All chemicals were purchased from Aldrich and Merck and used without any further purification. The 4-(2, 5-di-2-thiophen-2-yl-pyrrol-1-yl)-phthalonitrile (SNS-PN) was synthesized by utilizing 1,4-di(2-thienyl)-1,4-butadione<sup>19</sup> and 4-aminophthalonitrile<sup>20</sup> via Knorr-Paal Reaction.<sup>21</sup> Details of the synthesis route were reported previously.<sup>22</sup>

### Electrochemistry

Prior to electrochemical polymerization, redox behavior of NiPc-SNS was investigated using cyclic voltammetry (CV) in 0.1M tetrabutylammonium perchlorate (TBAP)/dichloromethane (DCM) electrolyte-solvent couple. The monomer was successfully electropolymerized via potentiodynamic or potentiostatic methods using three-electrode system containing a platinum disc ( $d = 1.6$  mm), a platinum wire as working and counter electrodes, respectively, as well as Ag wire as a pseudo-reference electrode (calibrated externally using a solution of ferrocene/ferrocenium couple). Electrochemical behavior of corresponding polymer films, coated on working electrode, was investigated in monomer-free electrolytic medium. For electro-optical studies, indium-tin oxide (ITO, Delta Tech. 8–12  $\Omega$ , 0.7 cm  $\times$  5 cm) electrodes were coated by the polymer film and the coated electrode was dipped into a UV cuvette with 1.0-cm path length together with Pt wire and Ag wire as counter and reference electrodes, respectively. Prior to spectroelectrochemical investigations, the polymer film was switched between neutral and doped states several times to equilibrate its redox behavior in monomer-free electrolytic solution. *In situ* spectroelectrochemical studies were performed using Hewlett-Packard 8453A diode array spectrometer. Electroanalytical measurements were performed using

a Gamry PCI4/300 potentiostat-galvanostat. Fourier Transform infrared spectroscopy (FT-IR) spectra were recorded on Bruker Vertex 70 Spectrophotometer, respectively.

### Synthesis of tetrakis 4-(2,5-di-2-thiophen-2-yl-pyrrol-1-yl) substituted nickel phthalocyanine (NiPc-SNS)

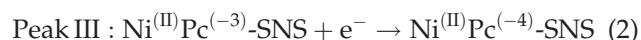
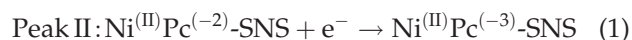
SNS-PN (0.28 mmol) and nickel (II) chloride (9.1 mg) were dissolved in *n*-hexanol (3 mL) under nitrogen in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.05 mL) and heated with stirring at 140°C for 2 days. The mixture was then cooled to room temperature and the product was precipitated by adding the reaction mixture dropwise into ethanol. The green crude product (Scheme 1) was purified using silica gel column chromatography with DCM-hexane (ratio 2 : 1) as the eluting solvent.

Green solid, Yield 40%. Elemental analysis (%), calcd. for C<sub>80</sub>H<sub>44</sub>N<sub>12</sub>S<sub>8</sub>Ni: C 64.55, H 2.98, N 11.29, S 17.23; found: C 64.41, H 3.11, N 11.49, S 16.95.

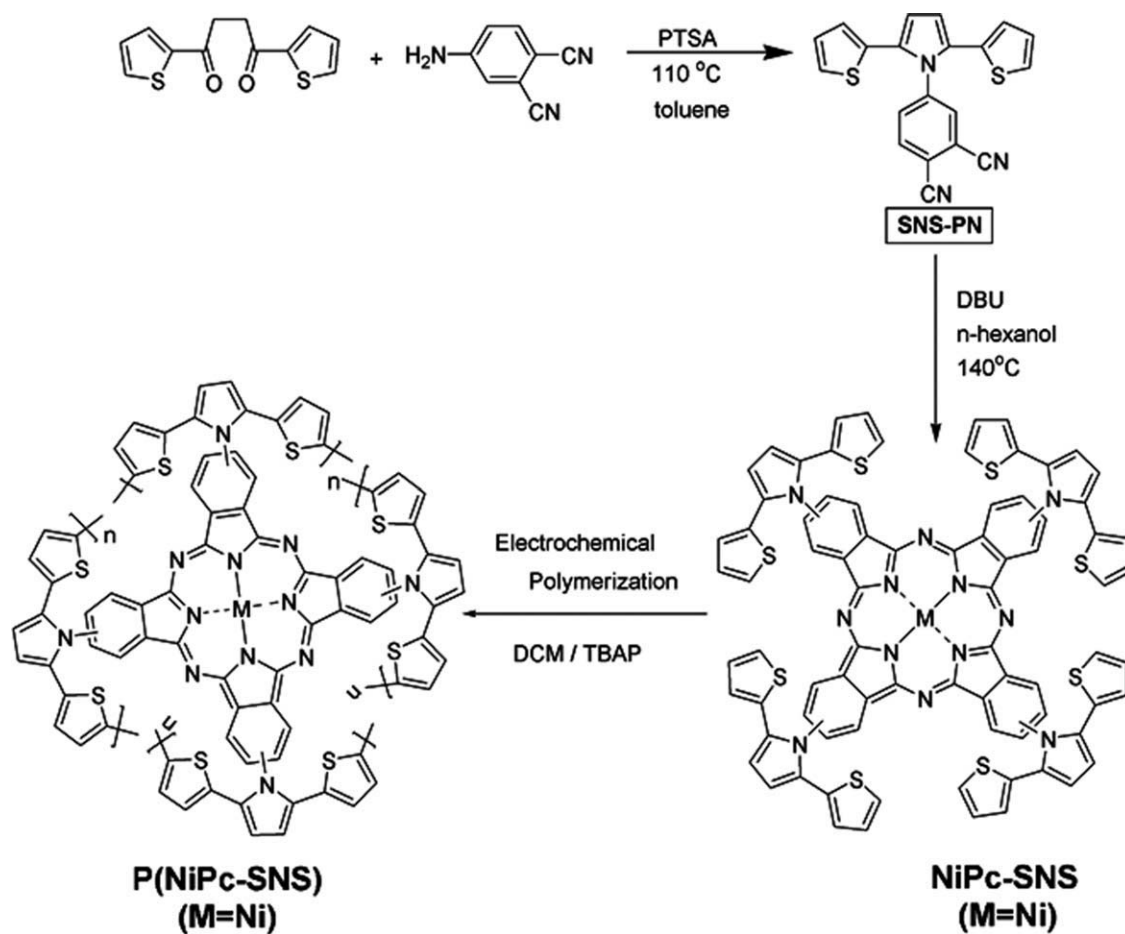
## RESULTS AND DISCUSSION

### Electrochemical polymerization of NiPc-SNS

Electrochemical behavior of NiPc-SNS was investigated in 0.1M TBAP/DCM, electrolyte/solvent couple utilizing CV and differential pulse voltammetry (DPV), before the synthesis of the polymer and results are depicted in Figure 1(a,b), respectively. As seen from Figure 1(a), NiPc-SNS complex displays two reversible reduction couples upon negative potential scan, II (−0.59 V) and III (−0.82 V) versus Ag/AgCl at a scan rate of 100 mV s<sup>−1</sup>, due to ring-based processes<sup>13</sup> as shown in the eqs. (1) and (2):



On the other hand, there exists an irreversible oxidation peak at about 0.88 V versus Ag/AgCl. For comparison sake, all of the potential values and assignments of the phthalocyanine complexes are summarized in Table I. A close inspection of Table I reveals that the irreversible oxidation peak obtained at 0.88 V for NiPc-SNS is very close to the previously reported values<sup>13</sup> clearly indicating the loss of electron from the dithienylpyrrole unit of the phthalocyanine complex. In the case of reversible peaks (II and III), the peak potentials are very close to the one(s) obtained for metal-free derivative. On the other hand they show positive shifts in comparison to zinc containing derivative due to the metal center differences.



Scheme 1 Synthetic route of 4-(2,5-di-2-thienyl-1H-pyrrol-1-yl)phthalonitrile and of NiPc-SNS complex.

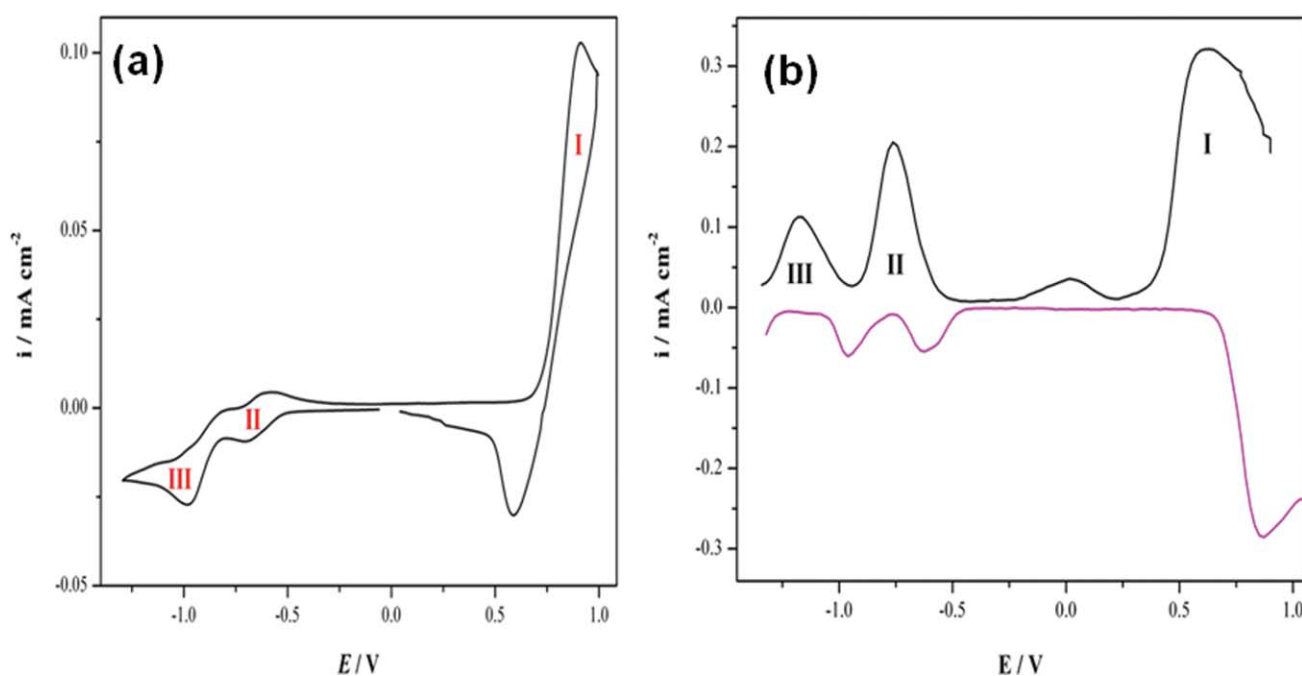


Figure 1 (a) Cyclic voltammogram of NiPc-SNS on a Pt disc electrode at 100 mV s<sup>-1</sup> and (b) DPV of NiPc-SNS in 0.1M TBAP/DCM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

**TABLE I**  
**Summary of the Redox Potentials ( $E_{1/2}$  vs Ag/AgCl) of the Pc Complexes in 0.1M TBAP Dissolved in DCM**

Complex	(II) $Pc^3/Pc^{2-}$	(III) $Pc^{4-}/Pr^{3-}$	SNS unit
$H_2Pc$ -SNS	$-0.570 \pm 0.001V$	$-0.930 \pm 0.001V$	$0.820 \pm 0.001V$
$ZnPc$ -SNS	$-0.840 \pm 0.001V$	$-1.190 \pm 0.001V$	$0.840 \pm 0.001V$
$NiPc$ -SNS	$-0.590 \pm 0.001V$	$-0.820 \pm 0.001V$	$0.880 \pm 0.001V$

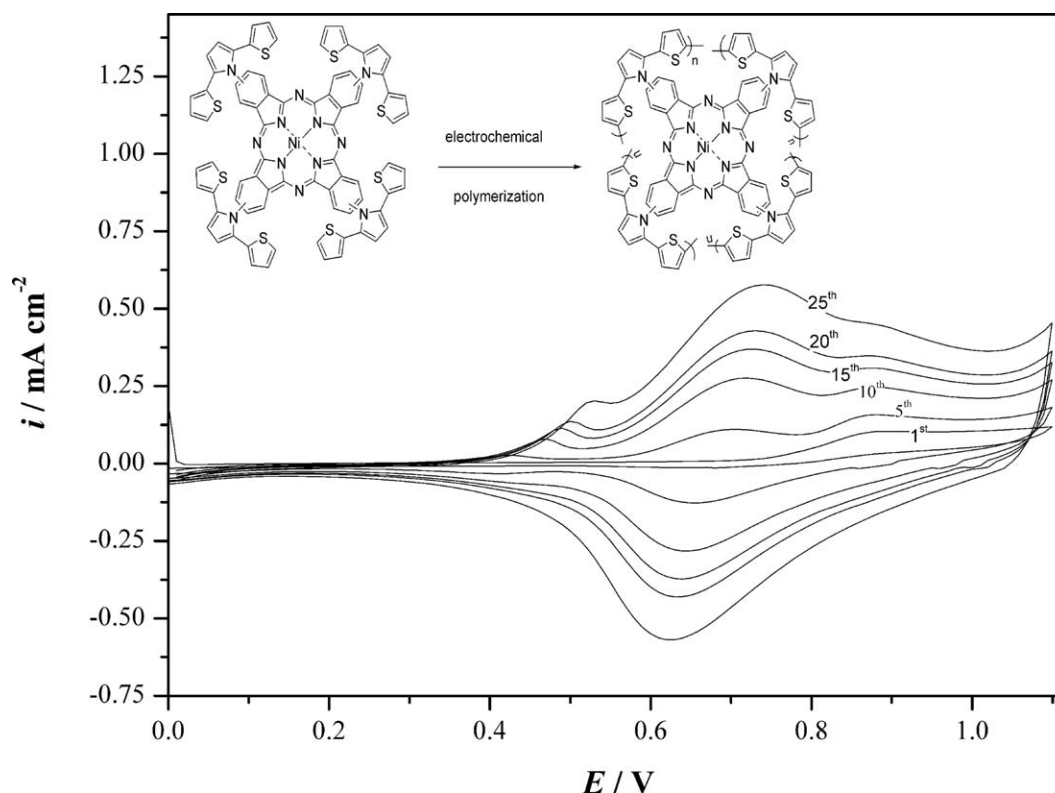
Next, we focused on the electropolymerization of NiPc-SNS. Electrochemical polymerization was performed utilizing CV by scanning in the potential ranges 0.0–1.1 V in 0.1M TBAP/DCM, electrolyte/solvent couple. During the first anodic scan, a single and irreversible monomer oxidation peak was observed at 0.88 V which is attributed to the oxidation of dithienylpyrrole unit [Fig. 1(a)]. Upon repetitive cycling, a new reversible redox couple with a concomitant increase in the current intensities after each cycling was observed, indicating the formation of conducting polymer film, P(NiPc-SNS) on the surface of the Pt disc working electrode (Fig. 2). Thus, the new redox couple can be ascribed to the reversible doping (0.79 V) and dedoping (0.65 V) of the polymer film. After several anodic scans another intensifying peak at about 0.56 V versus Ag/AgCl was also noted which might be due to phthalocyanine-based oxidation.

The electrochemical behavior of the polymer film obtained from NiPc-SNS after 25 successive scans

is also investigated in the monomer free electrolytic solution. The polymer films coated on the working electrode was cycled between its neutral and oxidized states at various scan rates to elucidate the scan rate dependence of the anodic ( $I_{ac}$ ) and cathodic ( $I_{cc}$ ) peak currents [Fig. 3(a)]. It is found that both anodic and cathodic peak currents increase linearly with increasing scan rate, indicating that the redox process is nondiffusional and the polymer film is well adhered to the working electrode surface [Fig. 3(b)].

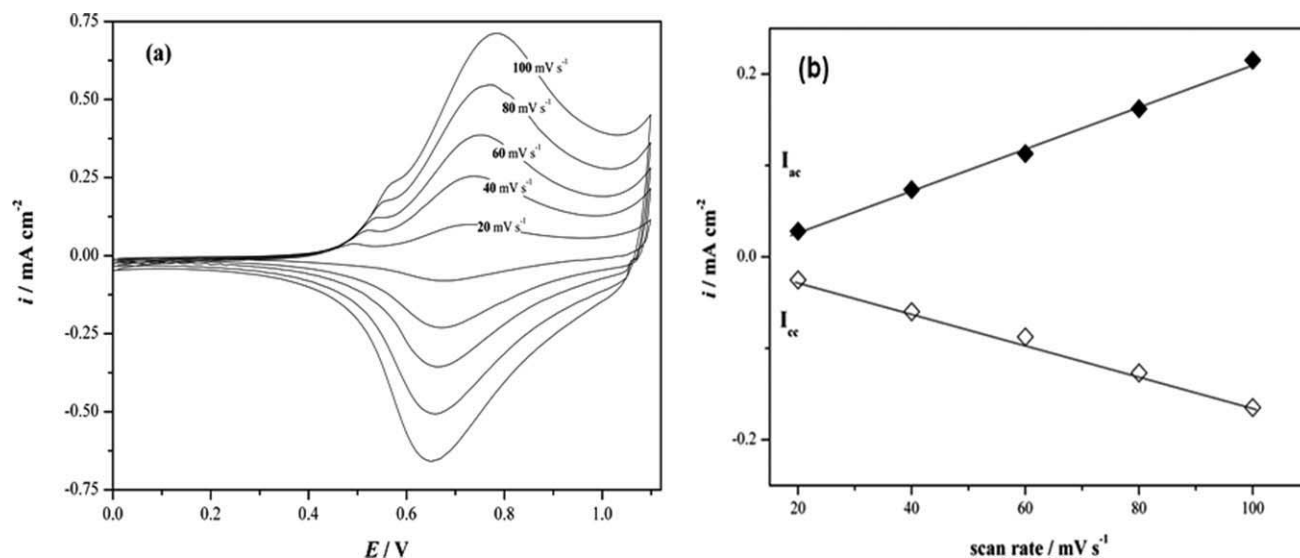
#### Spectroscopic characterization of NiPc-SNS and P(NiPc-SNS)

Figure 4(a) depicts the FT-IR spectrum of NiPc-SNS and its starting material SNS-PN for comparison reasons. The peaks at  $688\text{ cm}^{-1}$  (for  $\alpha$ -hydrogens of thiophene rings),  $765\text{ cm}^{-1}$  (for  $\beta$ -hydrogens of pyrrole ring), and  $836\text{ cm}^{-1}$  (for  $\beta/\beta'$ -hydrogens of thiophene rings) confirms the presence of 4-(2,5-di-2-



**Figure 2** Repeated potential scan electropolymerization of 1 mM NiPc-SNS on a Pt disc electrode at  $100\text{ mV s}^{-1}$  in 0.1M TBAP/DCM.





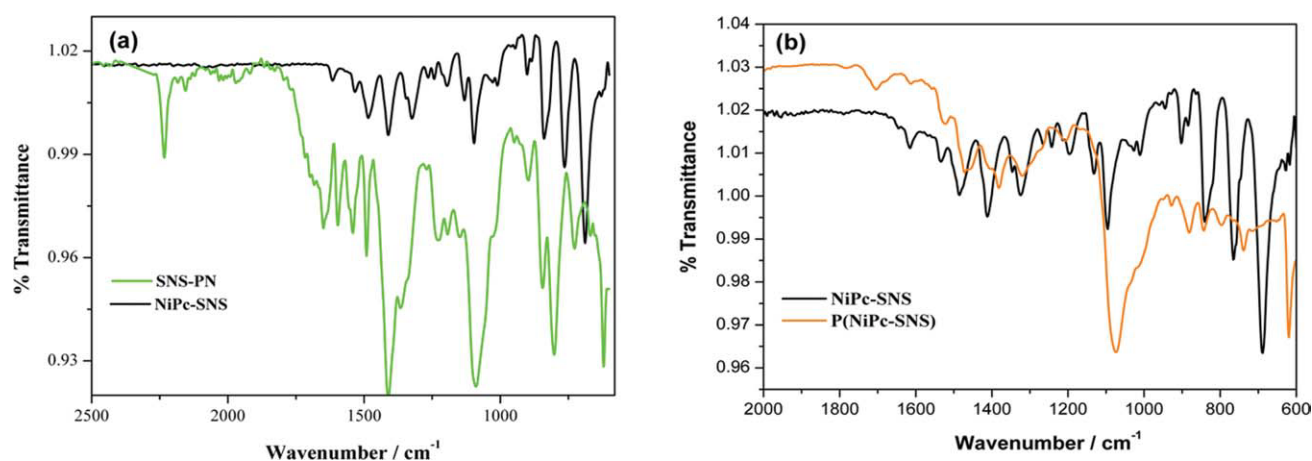
**Figure 3** (a) Scan rate dependence of P(NiPc-SNS) film ( $25 \text{ mC cm}^{-2}$ ) on a Pt disc electrode in  $0.1 \text{ M TBAP/DCM}$  at different scan rates between  $20$  and  $100 \text{ mV s}^{-1}$ . (b) Relationship of anodic ( $I_{ac}$ ) and cathodic ( $I_{cc}$ ) current peaks as a function of scan rate.

thiophen-2-yl-pyrrol-1-yl) substituent through the benzene ring of phthalocyanine.<sup>23</sup> Furthermore the characteristic nitrile ( $\text{C}\equiv\text{N}$ ) stretch at  $2240 \text{ cm}^{-1}$  of SNS-PN disappears upon formation of the phthalocyanine complex. In the FT-IR spectrum of P(NiPc-SNS) [Fig. 4(b)], characteristic vibration bands of phthalocyanine skeleton at  $1196$ ,  $935$ ,  $890$ , and  $760 \text{ cm}^{-1}$ ,<sup>24</sup> remain unchanged upon polymerization. The peak at  $688 \text{ cm}^{-1}$  in the monomer spectrum loses its intensity, as expected, in the spectrum of the P(NiPc-SNS), which confirms the formation of linear polymer chains via  $\alpha$ - $\alpha'$  linkages. The peaks at  $1070$  and  $620 \text{ cm}^{-1}$  in the polymer spectrum are due to the presence of  $\text{ClO}_4^-$  dopant.

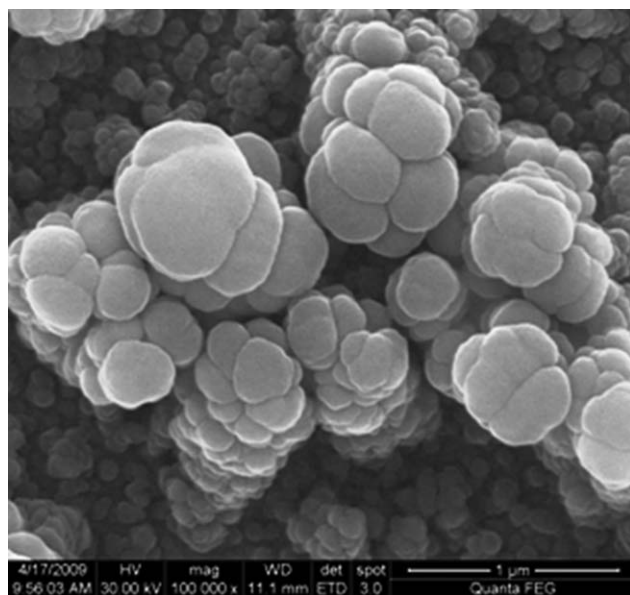
Since UV-vis spectroscopy is a suitable technique to monitor the presence of phthalocyanine groups, their substituents and interactions between them, the

electronic spectrum of the NiPc-SNS complex was also recorded in dimethylsulfoxide (DMSO). The main and most characteristic feature of the absorption spectra of phthalocyanines is the presence of very intensive two bands; one in the visible region ( $600$ – $800 \text{ nm}$ ) called the Q-band and a weaker band in the UV region ( $300$ – $500 \text{ nm}$ ) called B or the Soret band.<sup>25,26</sup> The complex shows typical B band at  $330 \text{ nm}$  and a split of Q band at  $635$  and  $673 \text{ nm}$  which confirms the features of phthalocyanine complexes. The substituent SNS groups also shows absorption band at about  $320 \text{ nm}$  which overlaps with the B band of phthalocyanine.

Morphology of P(NiPc-SNS) film was also investigated by recording the scanning electron microscope (SEM) micrograph. The solution side of the polymer film, depicted in Figure 5, reveals a



**Figure 4** (a) FT-IR spectra of SNS-PN and NiPc-SNS. (b) FT-IR spectra of NiPc-SNS and P(NiPc-SNS). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]



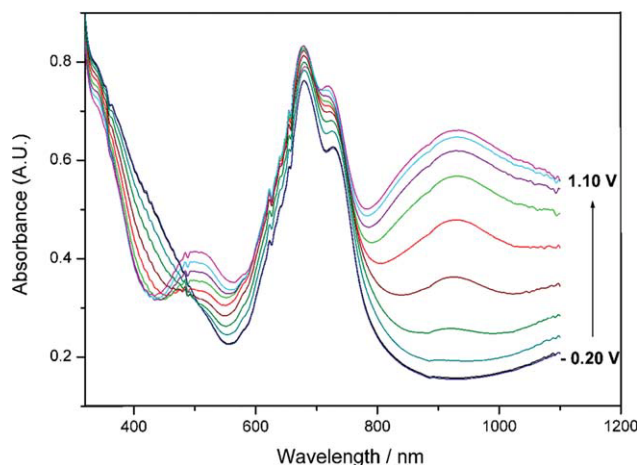
**Figure 5** SEM micrograph of solution side of P(NiPc-SNS).

cauliflower-like micro-spherical grains of less than 1  $\mu\text{m}$  diameter. This structure is characteristic for most conducting polymers and might be due to the difficulty of intercalation of dopant ions into the polymer chain.<sup>27</sup>

### Spectroelectrochemical properties of P(NiPc-SNS)

For spectroelectrochemical investigations, P(NiPc-SNS) film was electrodeposited on to ITO electrode via constant potential electrolysis at 0.85 V (25  $\text{mC cm}^{-2}$ ). When the electropolymerization was over, the electrodes were rinsed with DCM to remove the traces of unreacted monomers or electrolyte and then transferred into monomer free electrolytic solution.

Spectroscopic changes were recorded, *in situ*, during the potential scan from  $-0.2$  to  $1.1$  V with a voltage scan rate of  $100 \text{ mV s}^{-1}$  and the results are depicted in Figure 6. An inspection of Figure 6 reveals that P(NiPc-SNS) film, in its neutral state, exhibits three absorption bands at 340, 680, and 720



**Figure 6** Electronic absorption spectra of P(NiPc-SNS) on ITO ( $25 \text{ mC cm}^{-2}$ ) in  $0.1\text{M TBAP/DCM}$  solution during anodic oxidation of the polymer film. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

nm. By the commencement on the low energy end of the  $\pi\text{-}\pi^*$  transitions at 340 nm, the bang gap ( $E_g$ ) of the P(NiPc-SNS) is found as 2.27 eV which is not much different than previously reported values for other SNS derivatives.<sup>13–17</sup> Upon increasing the potential, the P(NiPc-SNS) film shows a decrease in the absorption at 340 nm due to  $\pi\text{-}\pi^*$  transition. The originally hidden band due to metal to ligand charge transfer becomes visible at about 500 nm as the 340-nm band loses its intensity. Furthermore, a new intensifying absorption band at about 930 nm was also noted, which may be attributed to electronic transitions within the polaron energy band that develops as the P(NiPc-SNS) film becomes electrically conductive. These changes are accompanied with a color change from green to blue. The slight changes observed in the characteristic Q-bands during potential scan from  $-0.2$  to  $1.1$  V may indicate a ring-based process accompanying the doping process.

The switching ability of the polymer film P(NiPc-SNS) between neutral and doped states in the electrolytic solution was investigated and it was

**TABLE II**  
Voltammetric and Spectroelectrochemical Data for P(NiPc-SNS) Recorded in DCM Containing  $0.1\text{M TBAP}$

$\lambda/\text{nm}$ at charge $25\text{mC}/\text{cm}^2$	$T_{\text{bleached}}$	$T_{\text{colored}}$	$\Delta\%T$	$\Delta\text{OD}$	CE ( $\text{cm}^2/\text{C}$ )	Reduced state	Oxidized state
340	23.16	28.63	5.47	0.092	71.9		
500	39.84	49.98	10.14	0.099	86.71		
676	18.86	31.08	12.22	0.217	162.43		



observed that the polymer film exhibits electrochromic behavior. The change in electro-optical response was recorded *in situ* while switching between 0.0 and 1.1 V with a residence time of 10 s. The optical density change ( $\Delta OD$ ) and the coloration efficiency (CE) of the polymer film was calculated using the eqs. (3) and (4)<sup>28,29</sup> and the results are depicted in Table II.

$$CE = \Delta OD / Q_d \quad (3)$$

$$\Delta OD = \log(\%T_{\text{bleached state}} / \%T_{\text{colored state}}) \quad (4)$$

Values are commonly reported at 90% of a full switch, beyond which the naked eye can not sense the difference. The percent transmittance changes,  $\Delta\%T$ , between the neutral and oxidized states were found to be 5.47% for 340 nm, 10.14% for 500 nm, and 12.22% for 676 nm in the visible region. The time required to attain 90% of the total transmittance difference was found to be 1.98 s for fully oxidized at 676 nm. The CE of the P(NiPc-SNS) was found to be 71.9, 86.71, and 162.42  $\text{cm}^2 \text{C}^{-1}$  for 340, 500, and 676 nm, respectively. It is interesting to note that these CE values are higher than P(H<sub>2</sub>Pc-SNS) and P(ZnPc-SNS) films<sup>13</sup> which makes it a candidate for optical displays and electrochromic devices. Since CE values depend to some extent on electrode preparation,<sup>30</sup> the differences can be attributed to different doping levels of phthalocyanine polymers.

## CONCLUSION

In this study, synthesis, characterization, and electrochemical polymerization of a new type of phthalocyanine complex bearing 4-(2,5-di-2-thiophen-2-ylpyrrol-1-yl) (SNS) was reported. Electrochemical and spectroelectrochemical properties of the polymer film P(NiPc-SNS) was investigated via *in situ* spectroelectrochemical and cyclic voltammetry techniques in monomer-free electrolytic medium. The polymer was found to exhibit a well defined and reversible redox process accompanied by electrochromic changes which make the polymer a candidate for electrochromic material applications. The polymer film can be successfully cycled and switched between dark blue colored oxidized state and dark olive green colored neutral state. The band gap  $E_g$  of the polymer was

found to be 2.27 eV from the electronic absorption spectrum of the neutral form of the film.

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