Available online at www.sciencedirect.com
ScienceDirect
European Polymer Journal 42 (2006) 2352–2360
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

A soluble and multichromic conducting polythiophene derivative

Serhat Varis, Metin Ak, Cihangir Tanyeli,
Idris Mecidoglu Akhmedov, Levent Toppare *

Department of Chemistry, Middle East Technical University, 06531, Ankara, Turkey

Received 10 April 2006; received in revised form 2 May 2006; accepted 12 May 2006

Abstract

A new soluble polythiophene derivative was synthesized by both chemical and electrochemical oxidative polymerization of 1-4-nitrophenyl-2,5-di(2-thienyl)-1*H*-pyrrole ($SNSNO_2$). Chemical method produces a polymer which is completely soluble in organic solvents. The structures of both the monomer and the soluble polymer were elucidated by ^1H and ^{13}C-NMR and FTIR. The average molecular weight has been determined by GPC to be $Mn = 6.3 \times 10^3$ for the chemically synthesized polymer. P($SNSNO_2$) was also synthesized via potentiostatic electrochemical polymerization. Characterizations of the resulting polymer were performed by cyclic voltammetry CV, FTIR and UV–Vis spectroscopy. Four-probe technique was used to measure the conductivities of the samples. Moreover, the spectroelectrochemical and electrochromic properties of the polymer film were investigated. In addition, dual type polymer electrochromic devices ECDs based on P($SNSNO_2$) with poly3,4-ethylenedioxythiophene (PEDOT) were constructed. Spectroelectrochemistry, electrochromic switching and open circuit stability of the devices were studied. They were found to have good switching times, reasonable contrasts and optical memories.

Keywords: Soluble conducting polymer; Electrochromic device

---

1. Introduction

The study of conductive polymers is a rapidly growing area in polymer chemistry. Since conductive polymers have special properties such as conductivity, electrochromism [1–4], electrochemomechanical properties [5], and porosity that change over several orders of magnitude, in a continuously reversible and controlled way upon doping [6], they are used in a wide variety of technological applications. The technological expectations developed by these facts are restricted by two main limiting features: low stability and low processability of the material. A great effort has been made in order to overcome both technological limitations [7]. The low processability due to the insolubility or infusibility of the conducting polymers has been overcome by the synthesis of soluble oligomers using side group substituents [8,9], or soluble precursors

---

[*] Corresponding author. Tel.: +90 3122105148; fax: +90 3122101280.
E-mail address: toppare@metu.edu.tr (L. Toppare).

doi:10.1016/j.eurpolymj.2006.05.011

[10], or generating sequence block copolymers [11,12]. A special case of block copolymers is the chemical generation of dimers or trimers having two or more heteroaromatic rings derived from thiophene, furan and pyrrole [13,14]. In this way, we synthesized 1-4-nitrophenyl-2,5-di(2-thienyl)-1*H*-pyrrole ($SNSNO_2$) via Knorr–Paal reaction using 1,4-di(2-thienyl)-1,4-butanedione and *p*-nitroaniline. In common with several other research groups, this route is convenient for the preparation of 'trimeric' thiophene-pyrrole-thiophene derivatives substituted at the N atom of the pyrrole ring [15–18]. This strategy yields centrosymmetric polymer precursors and seeks to minimize the steric influence of the central substituent through the addition of the thiophene spacers. Thus, chemical and electrochemical polymerization of ($SNSNO_2$) can easily be achieved. Its electrochemical polymerization was carried out by using $NaClO_4$/$LiClO_4$ as the supporting electrolyte. The resultant products were characterized via several techniques such as cyclic voltammetry CV, nuclear magnetic resonance ^1H NMR. Fourier transform infrared FTIR spectroscopy, scanning electron microscopy SEM and conductivity measurements. Electrochromic and spectroelectrochemical behaviors of the polymer were also studied. Finally, we utilized dual type ECDs where P($SNSNO_2$) was used as the anodically coloring and PEDOT as the cathodically coloring electrochromic materials.

2. Experimental part

2.1. Materials

$AlCl_3$ (Aldrich), succinyl chloride (Aldrich), dichloromethane DCM (Merck), propionic acid (Aldrich), 4-nitroaniline (Sigma), toluene (Sigma), nitromethane (Aldrich), methanol (Merck), ferric chloride (Aldrich), acetonitrile AN (Merck), NaOH (Merck), $LiClO_4$ (Aldrich), $NaClO_4$ (Aldrich), propylene carbonate PC. (Aldrich) and polymethyl methacrylate (PMMA) (Aldrich) was used without further purification.

2.2. Equipments

NMR spectra of the monomers were recorded on a Bruker-Instrument-NMR Spectrometer DPX-400 by using $CDCl_3$ as the solvent. The FTIR spectrum was recorded on a Nicolet 510 FTIR spectrometer. Mn was measured by gel permeation chromatography PL220. The surface morphologies of the copolymer films were analyzed by using JEOL JSM-6400 scanning electron microscope. Solartron 1285 potentiostat/galvanostat was used to supply a constant potential during electrochemical synthesis and cyclic voltammetry experiments. Varian Cary 5000 UV–Vis spectrophotometer was used in order to perform the spectroelectrochemical studies of polymer and the characterization of the devices. Colorimetry measurements were done via Minolta CS-100 spectrophotometer.

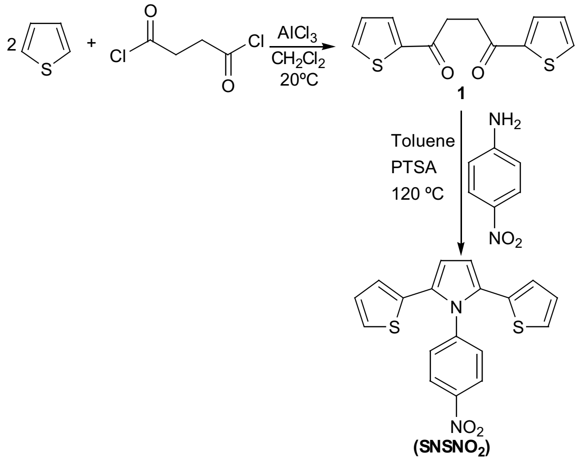
2.3. Synthesis of 1-4-nitrophenyl-2,5-di(2-thienyl)-1H-pyrrole ($SNSNO_2$)

The starting material, 1,4-di(2-thienyl)-1,4-butanedione, was synthesized according to literature procedure [13]. To a suspension of $AlCl_3$ 16 g, 0.12 mol in CH_2Cl_2 15 ml, a solution of thiophene 9.61 ml, 0.12 mol and succinyl chloride 5.51 ml, 0.05 mol in CH_2Cl_2 was added dropwise. The red mixture was stirred at room temperature for 4 h. This was then poured into ice and concentrated HCl 5 ml mixture. The dark green organic phase was washed with concentrated $NaHCO_3$ 3 × 25 ml and brine, and then dried over $MgSO_4$. After evaporation of the solvent a blue-green solid remained, which was suspended in ethanol. Filtration and washing with ethanol yielded the 1,4-bis-2-thienyl-butane-1,4-dione.

The monomer ($SNSNO_2$) was synthesized from 1,4-di(2-thienyl)-1,4-butanedione and 4-nitroaniline in the presence of catalytical amount of *p*-toluenesulphonic acid PTSA [23]. A round-bottomed flask equipped with an argon inlet and magnetic stirrer was charged with the 1,4-di(2-thienyl)-1,4-butanedione 5 mmol, 1.25 g, 0.97 g 7 mmol 4-nitroaniline, 0.1 g 0.58 mmol PTSA and 20 ml of toluene were added. The resultant mixture was stirred and refluxed for 24 h under argon. Evaporation of the toluene followed by flash column chromatography SiO_2 column, elution with dichloromethane afforded the desired compound as pale brown powder. The synthetic route of the monomer is shown in Scheme 1.

2.4. Chemical polymerization of ($SNSNO_2$) with Iron(III)chloride

A typical chemical polymerization of ($SNSNO_2$) was achieved using iron(III)chloride as the oxidant. To carry out the oxidative polymerization,



Scheme 1. The synthetic route of the monomer.

(SNSNO$_2$) 1×10^{-3} M was dissolved under a blanket of N$_2$ in nitromethane 15 ml. A solution of ferricchloride 2×10^{-3} M in nitromethane 5 ml was dropwise added to the monomer solution. The reaction was carried out for 5 min with constant stirring. The dark blue oxidized polymer was first washed with methanol, filtered, compensated with 30% NaOH, and dried under vacuum for ^{1}H NMR analyses.

2.5. Cyclic voltammetry CV

The oxidation/reduction behavior of polymer was investigated by CV using NaClO$_4$ 0.1 M and LiClO$_4$ 0.1 M/AN solvent-electrolyte couple. Experiments were carried out in an electrolysis cell equipped with indium/tin oxide ITO-coated glass plate as the working, Pt wire counter and Ag/Ag$^+$ 10^{-2} M reference electrodes. The measurements were carried out at room temperature under nitrogen atmosphere.

2.6. Electrochemical polymerization of (SNSNO$_2$)

Electrochemical polymerization of (SNSNO$_2$) was carried out by sweeping the potential between 0.4 V and +0.98 V with 500 mV/s scan rate, in the presence of 50 mg (SNSNO$_2$) in NaClO$_4$ 0.1 M and LiClO$_4$ 0.1 M/AN electrolyte-solvent couple. The working and counter electrodes were Pt wire and the reference electrode was Ag/Ag$^+$ 10^{-2} M P(SNSNO$_2$) was washed with AN in order to remove excess NaClO$_4$/LiClO$_4$ and unreacted monomer after the potentiodynamic electrochemical polymerization. Similar method was used to synthesize the polymer on an ITO coated glass plate.

2.7. Preparation of the gel electrolyte

Gel electrolyte was prepared by using NaClO$_4$:-LiClO$_4$:AN:PMMA:PC in the ratio of 1.5:1.5:70:7:20 by weight. After NaClO$_4$/LiClO$_4$ was dissolved in AN, PMMA was added into the solution. In order to dissolve PMMA, vigorous stirring and heating was required. Propylene carbonate PC, as a plasticizer, was introduced to the reaction medium when all of the PMMA was completely dissolved. The mixture was stirred and heated until the highly conducting transparent gel was produced.

3. Results and discussion

3.1. Synthesis

For the synthesis of 1,4-di(2-thienyl)-1,4-butanedione, the double Friedel–Crafts reactions proposed by Merz and Ellinger [13] was chosen. However, we found that the reaction time can be considerable reduced, the reaction mixture being refluxed at 18–20 °C for 4 h (instead of 24 h stirring at ambient temperature) without loss of yield (75%). The monomer, 1-4-nitrophenyl-2,5-di(2-thienyl)-1*H*-pyrrole (SNSNO$_2$) was synthesized via Knorr–Paal reaction using 1,4-di(2-thienyl)-1,4-butanedione and *p*-nitroaniline.

The chemical polymerization of the monomer takes places with a quantitative yield by using iron (III) oxide as the oxidant. Electrochemical polymerization on the other hand yields free standing film on the ITO electrode to be further used for spectroelectrochemical studies.

3.2. Cyclic voltammetry

Cyclic voltammogram of (SNSNO$_2$) in AN/LiClO$_4$–NaClO$_4$ solvent/electrolyte couple indicated two consecutive oxidation peaks at 0.88 V and 1.10 V and a reduction peak at 0.66 V. When the range between –0.3 V and +1.3 V was studied (Fig. 1), it was seen that the electroactivity increased with increasing scan number. This process promotes an electrochromic change of the film to a yellow-orange color, while a greenish cloud is formed around the electrode due to the partial dissolution in the medium of neutral linear oligomers of low molecular weight present in the reduced

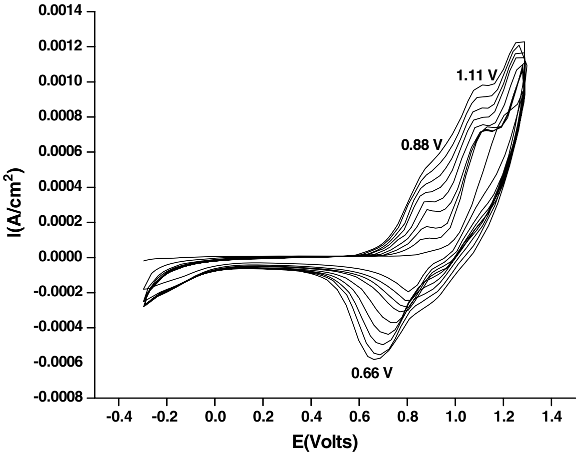


Fig. 1. Cyclic voltammogram of ($SNSNO_2$).

$P(SNSNO_2)$. More positive potential limits than 0.98 V promoted lower adherence of deposits, because of the oxidation and degradative crosslinking of polymer at 1.11 s anodic peak. Potentials lower than 0.88 V, seem to be most useful in obtaining insoluble, adherent and electroactive films. Under these conditions, the monomer gives a polymer, which is subsequently oxidized at the same potential to produce polarons balanced with ClO_4^- counterions. Further reduction of this polymer at 0.4 V peak involves the neutralization of polarons with loss of ClO_4^- and the resulting short linear species are dissolved [19–22]. Hence, in order to obtain uniform, adherent and dark-blue deposit of oxidized $P(SNSNO_2)$, the potential was swept between 0.4 V and 0.98 V.

3.3. NMR spectra of ($SNSNO_2$) and $P(SNSNO_2)$

^1H NMR spectrum of monomer Fig. 2: Pale orange crystals, mp 188 °C. $C_{18}H_{12}N_2O_2S_2$, δ_H $CDCl_3$: 6.46 s, 2H, pyrrolyl, 6.47 dd, 2H, d, $J = 1.00$ Hz, 3.60 Hz, 3-thienyl, 6.77 dd, 2H, $J = 3.60$ Hz, 4.98 Hz, 4-thienyl, 7.05 dd, 2H, $J = 1.0$ Hz, 4.98 Hz, 5-thienyl, 7.30 dd, 2H, $J = 2.20$ Hz, 9.18 Hz phenyl, 8.13 dd, 2H, $J = 2.20$ Hz, 9.18 Hz, phenyl.

^{13}C-NMR spectrum of the monomer Fig. 3: ^{13}C-NMR δ, ppm: Ca: 111.5, Cb: 124.3, Cc: 133.8, Cd: 129.7, Ce: 130.1, Cf: 127.2, Cg: 147.3, Ch: 125.7, Ci: 125.2, Cj: 147.3.

^1H NMR spectrum of polymer Fig. 3. $CDCl_3$: 6.3–6.5 2H, broad s, pyrrolyl, 6.50–6.75 2H, s, 3-thienyl, 6.75–7.00 2H, broad s, 4-thienyl, 7.10–7.50 2H, broad s, phenyl, 8.20–8.40 2H, broad s, phenyl. Broadening of the peaks and the tremendous decrease in the intensity of 5-thienyl proton confirm the polymerization (Fig. 4).

GPC data revealed $Mn = 6.3 \times 10^3$ for $P(SNSNO_2)$ prepared by chemical polymerization.

3.4. FTIR spectra

FTIR spectrum of the ($SNSNO_2$) shows the following absorption peaks: 3103 cm^{-1} aromatic C–H stretching, 1521 cm^{-1} asymmetric $ArNO_2$ stretching, 1349 cm^{-1} symmetric $ArNO_2$ stretching, 840 cm^{-1} C–N stretching for $ArNO_2$, 3020 cm^{-1} C–H_α stretching of thiophene., 1494–1340 cm^{-1} aromatic

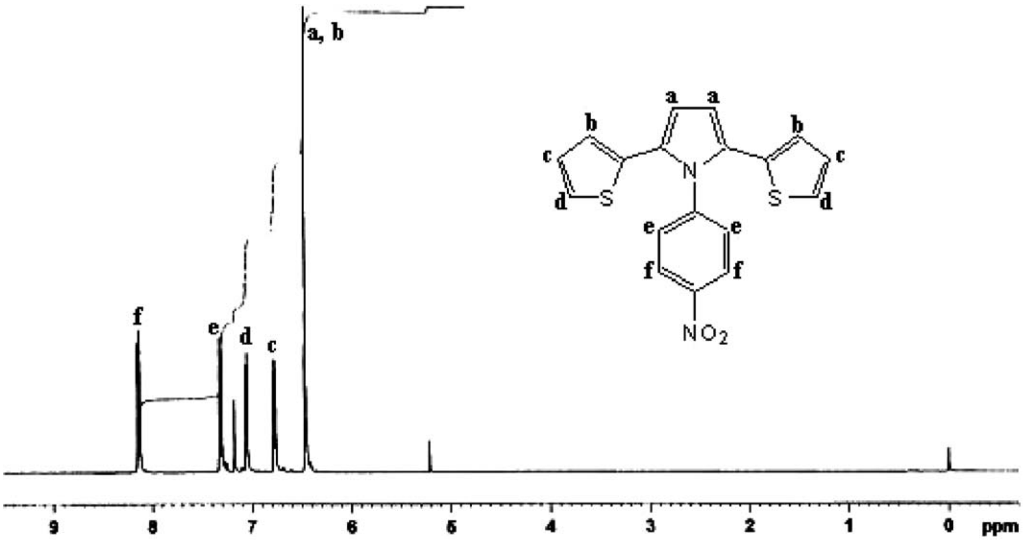


Fig. 2. ^1H NMR spectrum of monomer in $CDCl_3$.

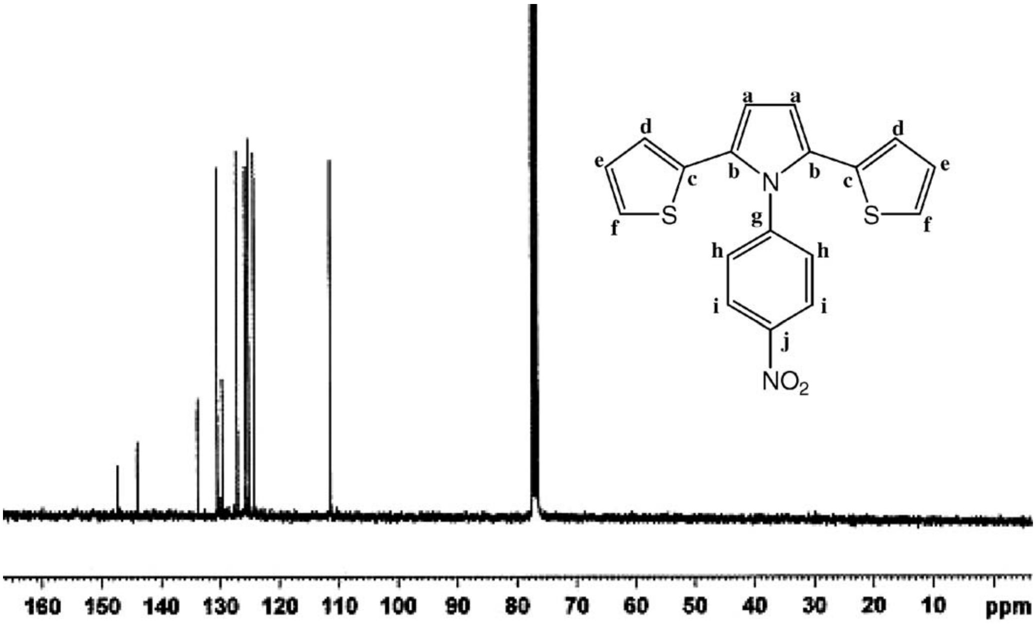


Fig. 3. ^{13}C-NMR spectrum of monomer in $CDCl_3$.

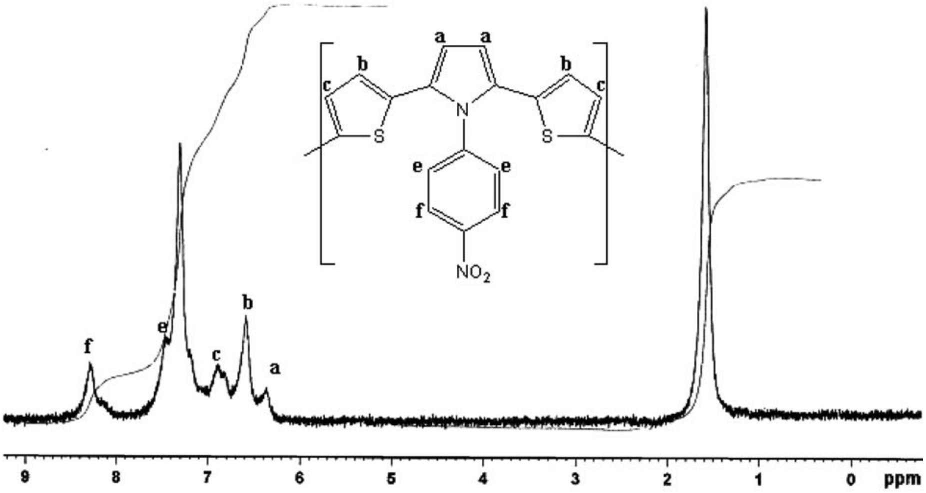


Fig. 4. ^{1}H NMR spectrum of polymer in $CDCl_3$.

C=C, C–N stretching due to pyrrole and benzene, 1035 cm^{-1} C–H in plane bending of benzene, 773 cm^{-1} C–H$_\alpha$ out of plane bending of thiophene.

Most of the characteristic peaks of the monomer ($SNSNO_2$) remained unperturbed upon polymerization by chemical polymerization. The intensity absorption bands of the monomer at 3020 cm^{-1} and 774 cm^{-1}arising from C–H$_\alpha$ stretching of thiophene moiety, respectively, disappeared completely. This is an evidence of the polymerization from 2,5 positions of thiophene moiety of the monomer. Whereas, two new bands related to C–H$_\beta$ out-of-plane bending of 2,5 disubstituted thiophene and C–S stretching appeared at 779 and 632 cm^{-1}, respectively. The broad band observed at around 1649 cm^{-1} proves the presence of polyconjugation and the new peak at 696 cm^{-1} indicates the presence of the dopant ion Cl^-.

FTIR spectra of electrochemically synthesized ($SNSNO_2$) showed the characteristic peaks of the monomer. The peaks related to C–H_α stretching of thiophene disappeared completely. The new broad band at around 1640 cm^{-1} was due to polyconjugation. The strong absorption peak at 1113, 1087 and 620 cm^{-1} were attributed to the incorporation ClO_4^- ions into the polymer film during doping process. Results of the FTIR studies clearly indicated the polymerization of the monomer.

3.5. Conductivities of the films

The conductivities of electrochemically and chemically prepared P($SNSNO_2$) were measured as 6.0×10^{-4} S cm^{-1} and 4.0×10^{-5} S cm^{-1} respectively via four probe technique.

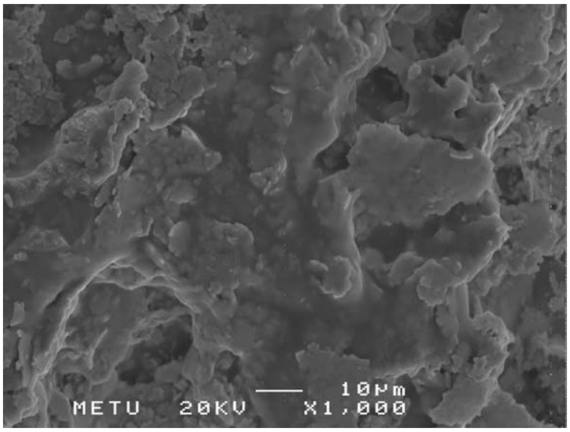


Fig. 5. SEM micrographs of P($SNSNO_2$).

3.6. Scanning electron microscopy SEM

Surface morphologies of polymer were investigated by scanning electron microscope Fig. 5. SEM micrographs of P($SNSNO_2$) imply that the synthesized monomer is good in film forming, exhibiting homogeneous and compact structure.

3.7. Electrochromic properties of conducting polymer

The best way of examining the changes in optical properties of conducting polymers upon voltage change is spectroelectrochemistry. It also gives information about the electronic structure of the polymer such as bandgap E_g and the intergap states that appear upon doping. P($SNSNO_2$) film was potentiodynamically synthesized on ITO electrode in the presence of 0.01 M $SNSNO_2$, while the potential was swept between 0.4 V and 0.98 V in AN/$NaClO_4$/$LiClO_4$ 0.1 M. The spectroelectrochemical and electrochromic properties of the resultant polymer were studied by applying potentials ranging between +0.2 V and +1.0 V in monomer free AN/$NaClO_4$/$LiClO_4$ 0.1 M medium. At the neutral state λ_{max} value due to the π–π* transition of the polymer was found to be 400 nm and E_g was calculated as 2.15 eV Upon applied voltage, reduction in the intensity of the π–π* transitions and formation of charge carrier bands were observed. Thus, appearance of peaks around 635 nm and 860 nm could be attributed to the evolution of polaron and bipolaron bands respectively Fig. 6.

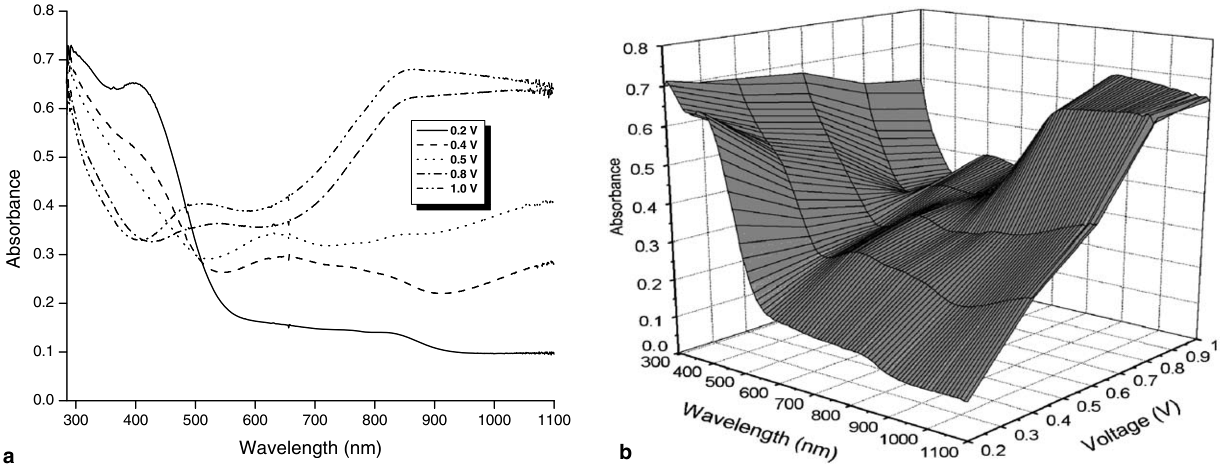


Fig. 6. Spectroelectrochemical spectrum of P($SNSNO_2$) as applied potentials between 0.2 and +1.0 V in AN/$NaClO_4$/$LiClO_4$ 0.1 M. (a) 2D, (b) 3D.

Table 1
L, *a* and *b* values of the P(SNSNO$_2$) film at different applied potentials in AN/NaClO$_4$/LiClO$_4$ 0.1 M and those of the device at different applied potentials

Material	Applied potential (V)	*L*	*a*	*b*
P(SNSNO$_2$)	0.2	78	−5	39
	0.4	66	−9	26
	0.6	70	−3	3
	1.0	59	11	−12
P(SNSNO$_2$)/PEDOT device	−0.8	55	2	20
	0.5	25	−2	23
	1.6	39	−1	−16

The colors of the electrochromic materials were defined accurately by performing colorimetry measurements. CIE system was used as a quantitative scale to define and compare colors. Three attributes of color, hue *a*, saturation *b* and luminance *L* were measured and recorded. The P(SNSNO$_2$) film shows different colors in the fully reduced state 0.2 V, half reduced state 0.4 V, half oxidized state 0.6 V and fully oxidized state 1.0 V (Table 1).

3.8. Electrochromic switching

Electrochromic switching studies were performed to test the ability of a polymer to switch rapidly and the ability to exhibit striking color change. The experiments carried out by spectroelectrochemistry showed the ability of P(SNSNO$_2$) to switch between its neutral and doped states with a change in transmittance at a fixed wavelength. During the experiment, the percentage transmittance %T at 400 and 860 nm of the polymer is measured using a UV–Vis spectrophotometer. The polymer film is synthesized on ITO-coated glass slides. The %T is then monitored at $\lambda_{\max}$ while the polymer is switched from +0.2 V to +1.0 V The contrast is measured as the difference between %T in the reduced and oxidized forms and is noted as 13 and 23%T for 400 and 860 nm respectively. As seen in Fig. 7, polymer has reasonable stability and switching time less than 2 s.

3.9. Spectroelectrochemistry of electrochromic devices ECDs

While constructing the electrochromic device, the anodically coloring polymer film P(SNSNO$_2$) was fully reduced and the cathodically coloring polymer PEDOT was fully oxidized. Upon application of a voltage, one of the polymer films is oxidized, whereas the other is neutralized, resulting in a color change. The observed colors with the colorimetry parameters *L*, *a*, *b* values are shown in Table 1.

Spectroelectrochemistry experiments were performed to investigate the changes of the electronic transitions of the ECD, with the increase of applied potential. Fig. 8 represents the absorption spectrum of the ECD, recorded by application of different voltages between −0.8 V and 1.6 V At −0.8 V the polymer layer was in its neutral state, where the absorption at 400 nm was due to π–π^* transition of the polymer. At this potential, PEDOT was in oxidized state showing no pronounced absorption

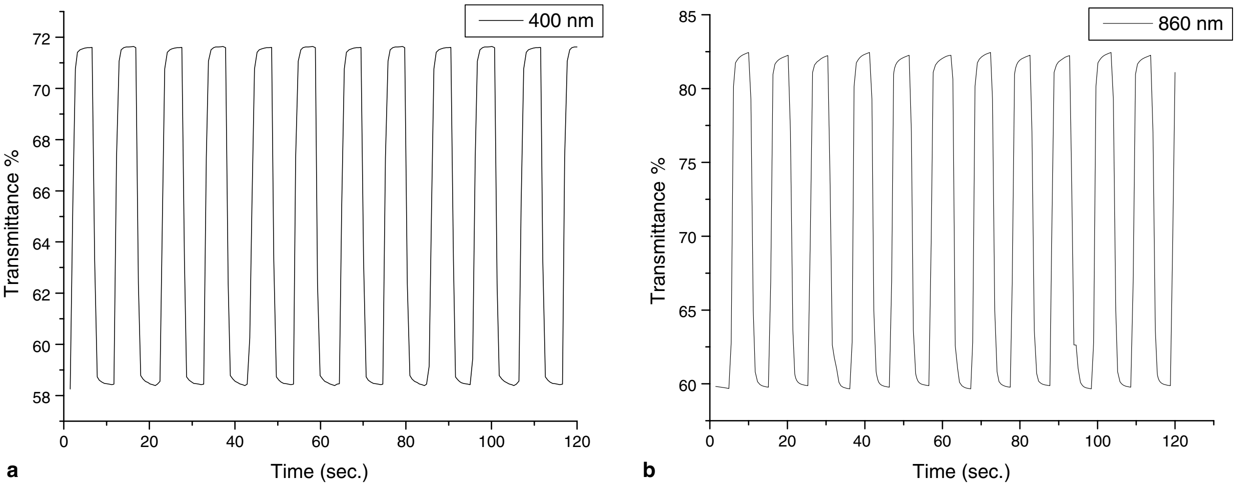


Fig. 7. Electrochromic switching, optical absorbance change monitored at 400 nm (a) and 800 nm (b) for P(SNSNO$_2$) between 0.0 V and 1.0 V.

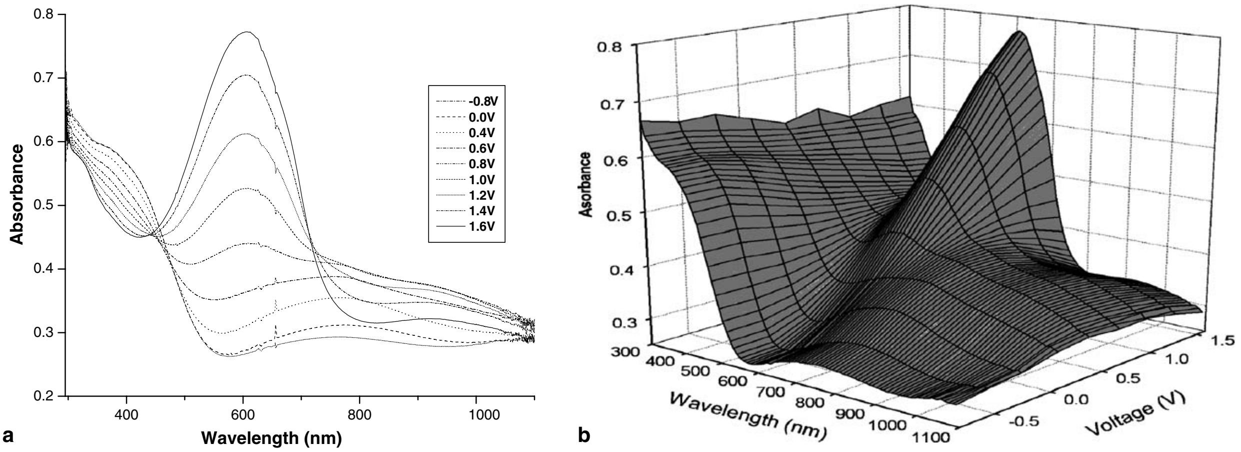


Fig. 8. Spectroelectrochemical spectrum of the device as applied potentials between −0.8 and +1.6 V in AN/$NaClO_4$/$LiClO_4$ 0.1 M. (a) 2D, (b) 3D.

at the UV–Vis region of the spectrum, thus the color of the device was yellow. As the applied potential was increased the polymer layer started to get oxidized, and a decrease in the intensity of the absorption was observed. Meanwhile, PEDOT layer was in its reduced state, which was followed by the appearance of the new absorption at 600 nm and dominated the color of the device was blue.

3.10. Switching of ECDs

To investigate switching characteristics of the ECD's the transmission and the response time at the maximum contrast wavelength was monitored during repeated redox stepping experiments. For the device, maximum contrast %T at 400 and 600 nm was measured as 6 and 30% by stepping potential between −0.8 V and +1.6 V with a residence time of 5 s (Fig. 9).

3.11. Stability of ECDs

Redox stability is an important requirement for production of reliable electrochromic devices with long lifetimes. Main reasons for device failure are different applied voltages and environmental conditions. Cyclic voltammetry was employed by monitoring current alterations to visualize the long

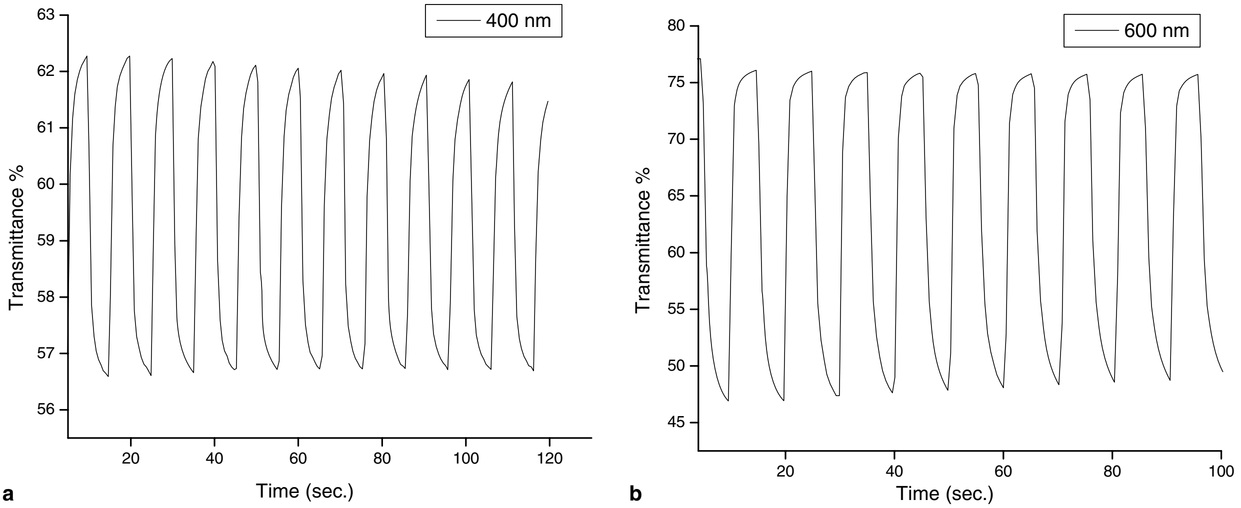


Fig. 9. Electrochromic switching, optical absorbance change monitored at 400 nm (a) and 600 nm (b) for device between −0.8 V and 1.6 V.

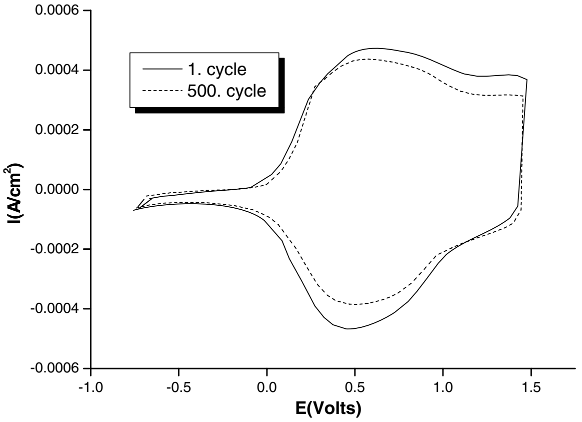


Fig. 10. Cyclic voltammogram of the device as a function of repeated scans 500 mV/s: after 1st cycle plain, after 500 cycles dash.

term stability of the ECD. The voltage was continuously swept between −0.8 V and 1.5 V with 500 mV/s scan rate. After 500 cycles, almost all initial electroactivity was maintained proving that ECD has reasonable environmental and redox stability (Fig. 10).

4. Conclusions

The synthesis of a new monomer, 1-4-nitrophenyl-2,5-di(2-thienyl)-1*H*-pyrrole $SNSNO_2$ was successfully achieved. $P(SNSNO_2)$ has been synthesized by both chemical and electrochemical oxidative polymerizations. Chemically synthesized polymer of $(SNSNO_2)$ can be dissolved in common organic solvents. This property provides several applications. Conducting polymer of $P(SNSNO_2)$ was synthesized potentiodynamically in AN/$NaClO_4$/$LiClO_4$ 0.1 M solvent-electrolyte couple. Spectroelectrochemical analyses revealed that the polymer of $(SNSNO_2)$ has an electronic bandgap of 2.15 eV. The contrast is measured as the difference between %T in the reduced and oxidized forms and is noted as 13 and 23%T at 400 and 860 nm respectively.

In the second part of the study, dual-type complementary colored polymer ECD made up of $P(SNSNO_2)$/PEDOT was constructed and their characteristics were examined. A potential range from −0.8 V to 1.6 V was found suitable for operating the device. The color changes were distinctive and aesthetically pleasing. Good switching time and optical contrast values were obtained. In addition, the device showed good environmental and redox stability. Considering these results, polymers of $SNSNO_2$ monomer is feasible candidate for electrochromic layers in ECDs.

Acknowledgements

Authors are gratefully thank to DPT2002K120510-IM-4, to DPT-2005K120580, BAP2005-01-03-06 and TUBA grants.

References

[1] Hyodo K. Electrochimica Acta 1994;392:265.
[2] Ak M, Cirpan A, Yılmaz F, Yağcı Y, Toppare L. Eur Polym J 2005;415:967.
[3] Kerman I, Toppare L, Yilmaz F, Yagci Y. J Macromol Sci Pure Appl Chem 2005;42:509.
[4] Sahin E, Camurlu P, Toppare L, Mercore V, Cianga I, Yagci Y. Polym Int 2005;54:1599.
[5] Sansinena JM, Olaza'bal V, Otero TF, Polo da Fonseca CN, De Paoli MA. Chem Commun 1997:2217.
[6] Otero TF. Nalwa HS, editor. Handbook of organic conductive molecules and polymers, vol. 4. Chichester: Wiley; 1997. p. 517.
[7] Skotheim TA, Reynolds JR, Pomerantz M. Electroresponsive molecular and polymeric systems. New York: Marcel Dekker; 1991. p. 187.
[8] Elsenbaumer RL, Jen KY, Oboodi R. Synth Met 1986;15:169.
[9] Dellacasa C, Bertienelli F, Bizzarr PC, Salatelli E. Adv Mater 1995;7:1005.
[10] Edwards JH, Feast WJ, Bott DC. Polymer 1984;25:395.
[11] Aime JP. Nalwa HS, editor. Handbook of organic conductive polymer, vol. 3. Chichester, UK: Wiley; 1997. p. 219.
[12] Sahmetlioglu E, Yuruk H, Toppare L, Cianga I, Yagci Y. Polym Int 2004;5312:2138.
[13] McLeod GG, Mahboubian-Jones MGB, Pethrick RA, Watson SD, Truong ND, Galin JC, et al. Polymer 1986;27(455):10.
[14] Ferraris JP, Hanlon TR. Polymer 1989;30:1319.
[15] Ferraris JP, Andrus RG, Hrncir DC. Chem Commun 1989;18:1318.
[16] Meeker DL, Mudigonda DSK, Osborn JM, Loveday DC, Ferraris JP. Macromolecules 1998;31:2943.
[17] Von Kieseritzky F, Hellberg J, Wang XJ, Inganas O. Synthesis 2002;9:1195.
[18] Raimundo JM, Blanchard P, Brisset H, Akoudad S, Roncali J. Chem Commun 2000;11:939.
[19] Niziurski-Mann RE, Scordilis-Kellev C, Liu TL, Cava MP, Carlin RT. J Am Chem Soc 1993;115:887.
[20] Cava MP, Joshi MV, Helmer C, Cain JL, Bakker MG, McKinley AJ, et al. J Chem Soc Perkin Trans 1993;2:1081.
[21] Brillas E, Otero TF, Figueras A, Carrasco J, Urpi F. J Electroanal Chem 1995;392:55.
[22] Brillas E, Carrasco J, Oliver R, Estrany F, Vilar J, Morlans JM. Electrochim Acta 2000;45:4049.
[23] Just PE, Chane-Ching KI, Lacaze PC. Tetrahedron 2002;58:3467.