

EFFECTS OF DOPING ON THE ELECTROCHEMICAL AND ELECTRICAL PROPERTIES OF POLY(2,5-DI(2-THIENYL)PYRROLE)

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The electropolymerization of 2,5-di(2-(thienyl)pyrrole) (SNS) on a Pt electrode from ethanolic solution with LiClO₄ or LiCl as electrolyte has been studied by cyclic voltammetry (CV) and chronoamperometry (CA). In both media, a quasi-reversible process has been indicated by CV, reversing the scan at low oxidation potentials. Under these conditions, reducible positive charges formed in both oxidized polymers are compensated by the entrance of anions from solution. Elemental analysis reveals that polymers generated at a low oxidation potential by CA contain a 21.03% (w/w) of ClO₄⁻ or a 9.56% (w/w) of Cl⁻. The poly(SNS) doped with Cl⁻ presents higher proportion of reducible positive charges, higher polymerization charge and lower productivity. A much higher electrical conductivity, however, has been found for the poly(SNS) doped with ClO₄⁻. Both polymers are soluble in DMSO, acetone and methanol. The dimer, trimer, tetramer and pentamer have been detected as soluble and neutral linear oligomers by mass spectrometry-fast atom bombardment. The analysis of polymers by infrared spectroscopy confirms the predominant formation of linear molecules with α - α linkages between monomeric units. A condensation mechanism involving one-electron oxidation of all electrogenerated linear and neutral polymeric chains is proposed to explain the SNS electropolymerization.

Key words: 2,5-Di(2-thienyl)pyrrole; Electropolymerization; Cyclic voltammetry; Oligomers; Chronoamperometry; Conductivity; Pyrroles; Thiophenes.

Conducting polymers derived from thiophene and pyrrole can be generated by electropolymerization on a platinum anode¹⁻¹¹. Polymers obtained that way have a salt structure because they are doped by anions from the electrolyte. Anions act as counterions which compensate positive charges

(polarons) formed by the subsequent oxidation of polymeric chains. Doped polyheterocycles exhibit higher values of conductivity compared to undoped polymer.

Most of investigation in the field of conducting polymers have been carried out with polypyrroles. Electropolymerized pyrroles doped with perchlorate ions are reported^{1-4,7} to have conductivities from tens to hundreds of $S\text{ cm}^{-1}$ at room temperature, depending on the medium and the electrosynthesis conditions, however, still substantially lower than metals, with values above 10^6 S cm^{-1} . The crosslinking of chains in polypyrroles seems to be responsible for their moderate conductivity, while higher values are expected for extended linear π -systems⁶. Following this idea, the electrochemical, electrical and optical properties of polymers electro-synthesized from monomers with three heterocycles linked in α -position (with respect to heteroatom) have been studied some time ago^{6,8-11}. The use of triheterocycles increases the probability of formation of long linear molecules with α -bonds between the rings and thus higher conductivity of resulting polymer can be expected. In fact, the modest conductivities of about 10^{-4} – 10^{-5} S cm^{-1} have been found⁸⁻¹¹ apparently due to high proportion of soluble linear oligomers produced by the electropolymerization.

In our previous works^{8,10,11}, we have reported that anodic oxidation of 2,5-di(2-thienyl)pyrrole (SNS) in 0.1 M LiClO_4 + acetone solution (Fig. 1), yields an adherent polymer which is in oxidized state doped with perchlorate counterions. The polymer is soluble in common organic solvents and can be completely electro-dissolved by cathodic reduction in the same electrolyte.

The aim of our present work is to study the effect of two doping ions, Cl^- and ClO_4^- , on electrochemical and electrical properties of poly(SNS). Ethanol has been chosen as a solvent where the two salts, lithium chloride and perchlorate, are sufficiently soluble. The electrochemical behaviour of oxidized poly(SNS) doped with Cl^- or with ClO_4^- has been comparatively stud-

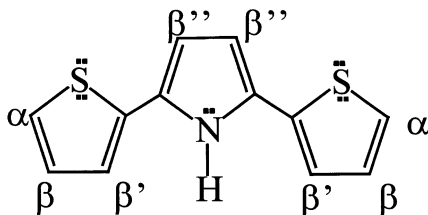


FIG. 1
Structure of 2,5-di(2-thienyl)pyrrole (SNS) and designation for hydrogen atoms

ied by cyclic voltammetry (CV). Both forms have been synthesized by chronoamperometry (CA) to determine their density and conductivity. The composition and structure of these materials have been characterized by elemental analysis, mass spectrometry-fast atom bombardment (MS-FAB) and IR.

EXPERIMENTAL

Reagents

The monomer SNS was synthesized using reagents of HPLC quality supplied by Aldrich, Panreac and Merck. Solutions for the electrochemical trials were prepared in absolute ethanol (99.8%) of HPLC quality from Panreac. Both anhydrous lithium perchlorate and anhydrous lithium chloride were of analytical grade (Aldrich) and dried at 80 °C before use in electrochemical experiments.

Instrumentation

The electrochemical study of SNS and the electrogeneration of its oxidized polymers were carried out with a PAR 273A potentiostat-galvanostat. The weigh W_{ox} of poly(SNS) films was determined on a Sartorius 2405 ultramicrobalance with a precision of 10^{-6} g. The density of collected polymers was obtained by the flotation method and their electrical conductivity was determined by a Philips PM 2518 X/01-11 multimeter. The ^1H NMR spectrum for the synthesized monomer was measured using a Varian 300 spectrometer. The mass spectrum was measured on a Hewlett-Packard HP 5988 analyzer and MS-FAB spectra using a Fisons VG Quattro triple quadrupole mass spectrometer with a cesium gun operating at potential energy of 10 V. Infrared spectra were determined on a Perkin-Elmer 1600 FTIR, using KBr pills as sample supports. Elemental analysis was carried out with a Carlo Erba NA 1500 CHNS-O elemental analyzer. The content of chlorine in each polymeric material was determined by standard ion chromatography after reduction of the sample with carbon. Kontron 600 HPLC liquid chromatograph filled with a Waters IC-Pak anion column working at 30 °C equipped with a Wescan conductometric detector was used.

SNS Synthesis

The monomer was synthesized according to the method described by Wyndberg and Metselaar¹². An improvement in its yield and purity was reached when the oil product from the final Paal-Knorr reaction was chromatographed using a column filled with 60 g of compact silica gel (60 Å) and 3 : 2 dichloromethane-hexane mixture as eluent. After several elutions, thin layer chromatogram of the solution showed one sole spot related to the monomer. The solvent was then evaporated and a pale yellow solid crystallized in flakes (m.p. 82–83 °C), was collected. The yield of pure SNS was 59%. Elemental analysis: for $\text{C}_{12}\text{H}_9\text{NS}_2$ (231) calculated: 62.33% C, 3.89% H, 6.06% N, 27.73% S; found: 62.49% C, 3.76% H, 6.12% N, 27.45% S. Mass spectrometry, m/z : 231 (100, M^+). ^1H NMR (CDCl_3 , 300 MHz): δ 6.403–7.132 (m, aromatic hydrogens). Once prepared, the pure monomer was maintained in dark under nitrogen atmosphere.

Electrochemical System

All electrochemical experiments were performed in a three-electrode two-compartment cell under a nitrogen atmosphere at 25 °C. Working and counter electrodes were Pt sheets of 1 cm² area. Before each trial, both electrodes were cleaned by heating in a flame and cooled down by immersion into ethanol. This procedure was necessary to prevent the appearance of interferences during the electrochemical analysis of the monomer. A reference Ag/AgCl electrode containing saturated aqueous NaCl solution was connected to the anodic compartment through a salt bridge filled with the background electrolyte.

For the cyclic voltammetry of the monomer, the anodic compartment of the cell was filled with 25 ml of a 5 mM SNS solution in 0.1 M LiClO₄ + ethanol or in 0.1 M LiCl + ethanol. A 5 ml aliquote of the corresponding electrolyte solution was placed in the cathodic compartment. The cell was always maintained in dark to avoid the slow photopolymerization of substrate.

The oxidized poly(SNS) doped with ClO₄⁻ or Cl⁻ was generated by CA in the same cell. Samples for analysis were obtained by scratching the deposits from the working Pt electrode, rinsed with water on a filter and dried under vacuum for 24 h.

Measuring of Conductivity

For the conductivity measurement, an amount of 20 mg of dry polymer was compressed into a disk form by applying a pressure of 8 000 kg cm⁻² using hydraulic press. The resulting pills with a diameter of 13 mm and a height of about (100 ± 1) μm were fixed between two metallic disks of the same diameter and held together by two plastic screw clips. Finally, the resistance was measured between the two metallic disks using a digital multimeter.

RESULTS AND DISCUSSION

CV Study of SNS Oxidation

The poly(SNS) was generated electrochemically by CV from 5 mM monomer solution in ethanol using two different electrolytes: 0.1 M LiClO₄ or 0.1 M LiCl. A dark-blue polymeric deposit formed on the working electrode at potentials $E \geq 0.58$ V for LiClO₄ and $E \geq 0.54$ V for LiCl. All CV measurements started at -0.50 V to observe clearly electrochemical oxidation of the monomer. Figures 2 and 3 show the respective cyclic voltammograms recorded in 0.1 M LiClO₄ + ethanol and 0.1 M LiCl + ethanol at scan rates $v = 100$ mV s⁻¹ (curves 1), $v = 50$ mV s⁻¹ (curves 2) and $v = 20$ mV s⁻¹ (curves 3).

As can be seen in Fig. 2, three consecutive peaks of SNS oxidation appear during the positive scan in 0.1 M LiClO₄ + ethanol. The height of all anodic peaks increases linearly with the square root of the scan rate, as expected for diffusion-controlled processes¹³. In addition, their anodic peak potentials (E_p^a) shifted to more positive values with raising v , indicating a quasi-reversible or irreversible behaviour¹³. Figure 2 evidences that the third anodic peak is irreversible, due to the absence of any reduction peak

on the reverse scan. To clarify this point for the first anodic peak, several cyclic voltammograms were recorded reversing the scan before second oxidation process appeared. Figure 4 shows the reduction peak between 0.2 and 0.3 V, associated apparently with the first anodic peak with E_p^a 0.72–0.89 V for the scan rate raising from 20 to 100 mV s^{-1} . This redox couple behaves as a quasi-reversible, since the difference between anodic and cathodic peak potentials increases gradually with raising ν (ref.¹³). Moreover, a greenish colour formed at working electrode during the reverse scan indicates the partial dissolution of oligomers present in poly(SNS).

The differences between anodic and cathodic currents shown in Fig. 4 can be explained^{9–11} as follows: The polymer formed in the first oxidation process is subsequently oxidized at the same potential. Positive charges (polarons) compensated with ClO_4^- counterions are neutralized during further reduction with the loss of ClO_4^- . The neutral species yielded in this reaction can dissolve partially in the medium (electroreduction). For this reason, the anodic current of the peak couple in Fig. 4 is much higher than its corresponding cathodic part. The fact, that the reduction peak related to the first oxidation process is not exhibited when the potential is reversed after the third anodic peak (Fig. 2), suggests the existence of degradative re-

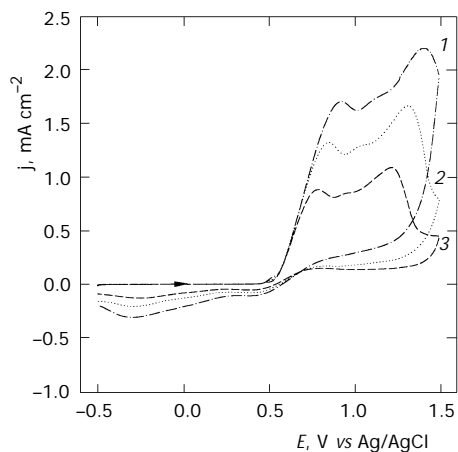


FIG. 2

Cyclic voltammograms of the oxidation of $5 \cdot 10^{-3}$ M SNS solution in 0.1 M LiClO_4 + ethanol on a Pt electrode of 1 cm^2 area. Initial and final potentials -0.500 V; reversal potential 1.500 V. Scan rates: 1 100, 2 50, 3 20 mV s^{-1} . Temperature 25°C

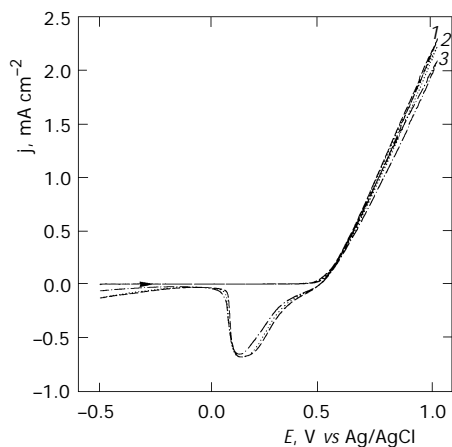


FIG. 3

Cyclic voltammograms of the oxidation of $5 \cdot 10^{-3}$ M SNS solution in 0.1 M LiCl + ethanol on Pt. Initial and final potentials -0.500 V; reversal potential 1.035 V. Scan rates: 1 100, 2 50, 3 20 mV s^{-1} . Temperature 25°C

actions in second and third oxidation processes. More oxidized and cross-linking molecules are formed where polarons can not be further reduced.

In 0.1 M LiCl + ethanol, the CV behaviour is different. A growing oxidation current, practically independent on the scan rate, can be seen in Fig. 3. Once the scan is reversed at 1.035 V, well-defined reduction peak appears at about 0.2 V, similar to Fig. 4 for LiClO₄. The reduction of the dark-blue polymer doped with Cl⁻ is accompanied by its partial dissolution, as indicated by a greenish colour at the electrode. The fact, that the reduction peak current does not depend on scan rate suggests that the proportion of reducible polarons in the polymer is unchanged. The SNS oxidation in 0.1 M LiCl + ethanol solution seems to involve complex transport mechanism because the anodic current is not controlled by the diffusion of the monomer. Effects of polymer doping by Cl⁻ were studied by CV at lower SNS concentrations in saturated LiCl solution. The voltammetric curves, however, were similar to those reported in Fig. 3 which indicates that the oxidation process is not limited by the transport of Cl⁻ to compensate polarons in oxidized poly(SNS).

Electrogeneration of the Oxidized Poly(SNS)

Polymers doped with ClO₄⁻ or Cl⁻ were synthesized by CA from 0.1 M monomer solution in ethanol. In this process the salt concentration influences the doping and the polymer solubility. As the solubility of oxidized poly(SNS) becomes lower in medium with higher salt content, an electrolyte of 0.2 M LiClO₄ or 0.2 M LiCl was used to avoid the solubilization of once deposited polymer. The constant potential of 0.7 V chosen to prevent

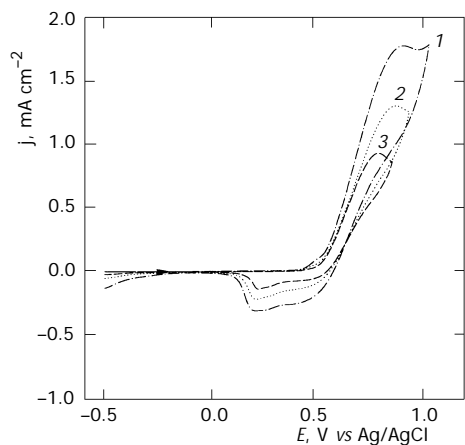


FIG. 4

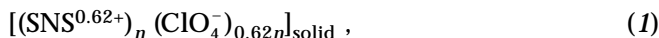
Cyclic voltammograms corresponding to the first oxidation process of a $5 \cdot 10^{-3}$ M SNS solution in 0.1 M LiClO₄ + ethanol on Pt. Initial and final potentials -0.500 V; reversal potentials: 1 0.860, 2 0.940, 3 1.000 V. Scan rates: 1 100, 2 50, 3 20 mV s⁻¹. Temperature 25 °C

possible crosslinking reactions was applied for 360 s of SNS electropolymerization. Under these conditions, good adherent film was obtained. At longer times deposits loosened their consistency and greenish colour formed at the working electrode evidenced the material loss by dissolution.

The electropolymerization charge Q_{pol} consumed in each process directly calculated from chronoamperogram was 122 mC cm^{-2} for LiClO_4 and 163 mC cm^{-2} for LiCl solution, respectively. The polymer-coated electrodes were rinsed with water, dried in air and weighted until constant mass was reached. The weight W_{ox} of the film was determined as the weight difference between the coated and uncoated electrode. From these data, the ratio $W_{\text{ox}}/Q_{\text{pol}}$ was found to be $1.4 \cdot 10^{-3} \text{ mg mC}^{-1}$ for LiClO_4 and $7.4 \cdot 10^{-4} \text{ mg mC}^{-1}$ for LiCl solutions. The higher Q_{pol} for the poly(SNS) doped with Cl^- indicates higher content of oxidized molecules.

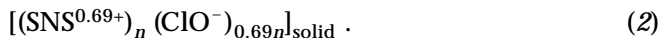
Elemental Analysis of Poly(SNS)

The elemental analysis of oxidized poly(SNS) generated by CA from 0.2 M LiClO_4 + ethanol solution revealed 7.49% (w/w) of Cl, corresponding to 21.03% (w/w) of ClO_4^- counterions. This confirms the salt resembling structure of this material containing 0.62 perchlorate ions per monomeric unit. Its formula can be written as follows:



where $(\text{SNS}^{0.62+})_n$ represents a polymeric molecule composed from n units of SNS. Each monomer molecule of oxidized polymer possesses an average positive charge of 0.62 compensated by 0.62 ClO_4^- ions. Note that similar content of perchlorate has been determined for the poly(SNS) electro-synthesized from 0.1 M LiClO_4 + acetonitrile solution¹¹.

For the poly(SNS) produced from 0.2 M LiCl + ethanol solution, 9.56% (w/w) of Cl was found by elemental analysis, indicating the presence of 0.69 Cl^- ions per each monomeric unit. The resulting formula is:



Comparing both formulae it can be concluded that the polymer contains more reducible positive charges when it is doped with Cl^- . This finding is consistent with higher Q_{pol} value obtained for the electrochemical preparation of this material, as pointed out above.

Solubility, Density and Conductivity of Poly(SNS)

Both oxidized poly(SNS) forms were soluble in DMSO, acetone and methanol, but insoluble in water and carbon tetrachloride. Their densities were further determined by flotation from bromoform-carbon tetrachloride mixtures in which they were insoluble. A value close to 1.5 g cm^{-3} was found for both forms which, however, showed differences in their electrical conductivity. For poly(SNS) doped with ClO_4^- a conductivity of $2.1 \cdot 10^{-5} \text{ S cm}^{-1}$ was found, whereas the polymer doped with Cl^- showed substantially lower value of $1.5 \cdot 10^{-6} \text{ S cm}^{-1}$. These results can be explained by the formation of higher proportion of shorter molecules in 0.2 M LiCl solution. On contrary, an increase in conductivity is expected when long highly π -conjugated molecules are formed⁶.

Detection of Oligomers by MS-FAB

The MS-FAB ionization technique operates at room temperature using liquid matrix to avoid high molecular fragmentation typical for other mass spectroscopic methods, such as EI and CI. Since the method is limited by the solubility of oligomers in liquid matrix, saturated solutions of both polymers in DMSO were prepared and further mixed with a thioglycerol. Figure 5 shows the MS-FAB spectra recorded in positive ionization mode under above mentioned conditions. The spectra display molecular ion peaks of 460, 689, 918 and 1 148 a.u. related to the dimer, trimer, tetramer

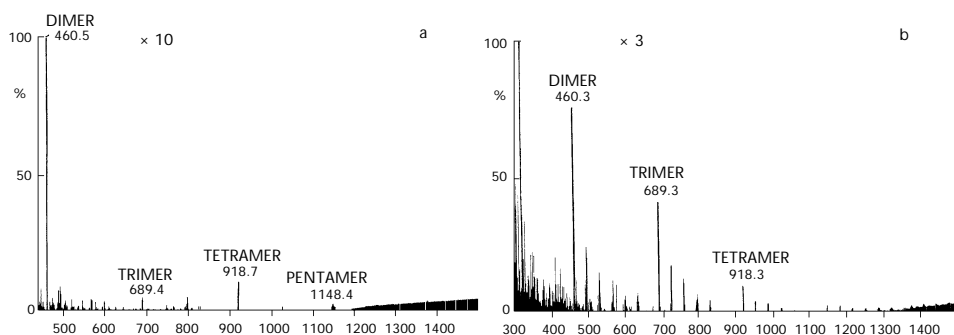


FIG. 5

MS-FAB positive ionization mode for the saturated solution of oxidized poly(SNS) in DMSO using a thioglycerol matrix, the doping counterion a ClO_4^- , b Cl^- . Each polymer was electrogenerated on a 1 cm^2 Pt electrode from 0.1 M SNS solution in ethanol containing 0.2 mol l^{-1} of corresponding lithium salt by applying 0.700 V for 360 s. Temperature $25 \text{ }^\circ\text{C}$.

and pentamer. In fact, the maximum mass peaks for these soluble and neutral linear oligomers correspond to M^+ or $(M+1)^+$ active ions, where M is the molecular mass of the oligomer $(M)_n$ calculated from the expression:

$$(M)_n = nA - (2n - 2), \quad (3)$$

where A denotes the molecular mass of SNS (231 a.u.) and n 2, 3, 4 or 5 is the number of monomeric units in the oligomer $(M)_n$. The term $(2n - 2)$ can be related to the number of hydrogen atoms lost during the electropolymerization yielding the oligomer.

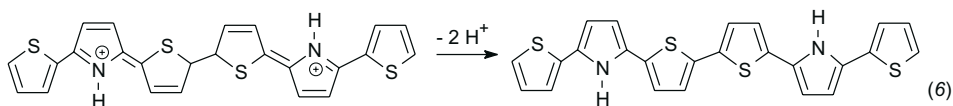
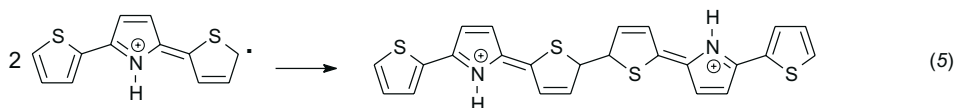
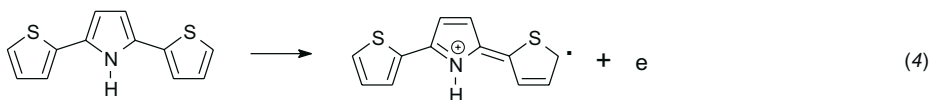
Although no quantification of the relative content of soluble oligomers is possible from spectra given in Fig. 5, the decrease in peak intensity with increasing molecular mass indicates that dimer is formed to much higher extent than the other species. Note that oxidized molecules doped with ClO_4^- or Cl^- were not detected by MS-FAB. Consequently, this technique only allows to identify undoped and linear oligomers in solution.

IR Analysis of SNS and Poly(SNS)

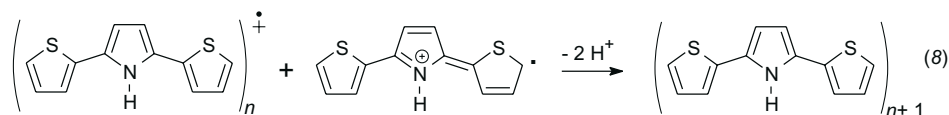
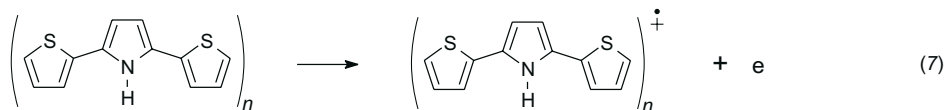
A comparative IR analysis for the monomer and electrogenerated polymers within the wavelength region 1 200–600 cm^{-1} was carried out in an attempt to elucidate their structure. The IR spectrum for solid SNS (Fig. 6a) shows three strong bands centered at 692, 778 and 841 cm^{-1} with relative intensities of 1.30 : 1.25 : 1, which can be ascribed⁶ to the absorption of the C–H out-of-plane bending modes of α -H, β'' -H and $\beta + \beta'$ -H atoms of SNS (see Fig. 1). These bands are much weaker for the poly(SNS) doped with ClO_4^- (Fig. 6b), than for the polymer doped with Cl^- (Fig. 6c). In addition, Fig. 6b exhibits other two strong bands at 1 122 and 637 cm^{-1} related to the Cl–O bonds of ClO_4^- dopant. The nature of links between two monomeric units of the polymer is difficult to determine from this spectrum, since positive charges and perchlorate counterions modify significantly the absorbance of different C–H bending modes. In the case of poly(SNS) doped with Cl^- relative intensities of 1.10 : 2.10 : 1 were found (Fig. 6c) for the respective bands C–H(α) : C–H(β'') : C–H($\beta + \beta'$). Comparison with the monomer allows us to conclude that the relative intensity of the C–H(α) out-of-plane bending mode is lower in polymeric chains. This result may be explained by the predominance of α - α linkages due to majority of linear molecules.

Electropolymerization Mechanism

The presence of short linear oligomers detected by MS-FAB supports the expectation that SNS electropolymerization follows at low potentials condensation mechanism^{2,14}. The process is initiated by one-electron oxidation of the monomer at the electrode, followed by coupling of resulting radical cation to dication. This species further loses two protons to give neutral dimer (SNS)₂ adsorbed on the electrode. The electrodimers can be described by the following scheme.



Here oxidation of the dimer (SNS)₂ in one-electron step is followed by condensation with the monomeric radical cation, yielding trimer (SNS)₃ after losing two protons. The polymer chain then continues to grow by consecutive oxidation and condensation reactions expressed for a molecule with *n* monomeric units in the following form.



The condensation reactions are presumed to proceed *via* α - α links between thiophene rings of each reactant. This mechanism explains the formation of the linear and soluble oligomers detected by MS-FAB. In addition, the electrogenerated neutral molecules are subsequently oxidized to produce polarons balanced by counterions (ClO_4^- or Cl^-) from solution.

CONCLUSIONS

It has been demonstrated that the monomer SNS can be electropolymerized on a Pt electrode in ethanolic solutions of LiClO_4 or LiCl as electrolytes. The CV study of the oxidation of 5 mM SNS solution has shown three con-

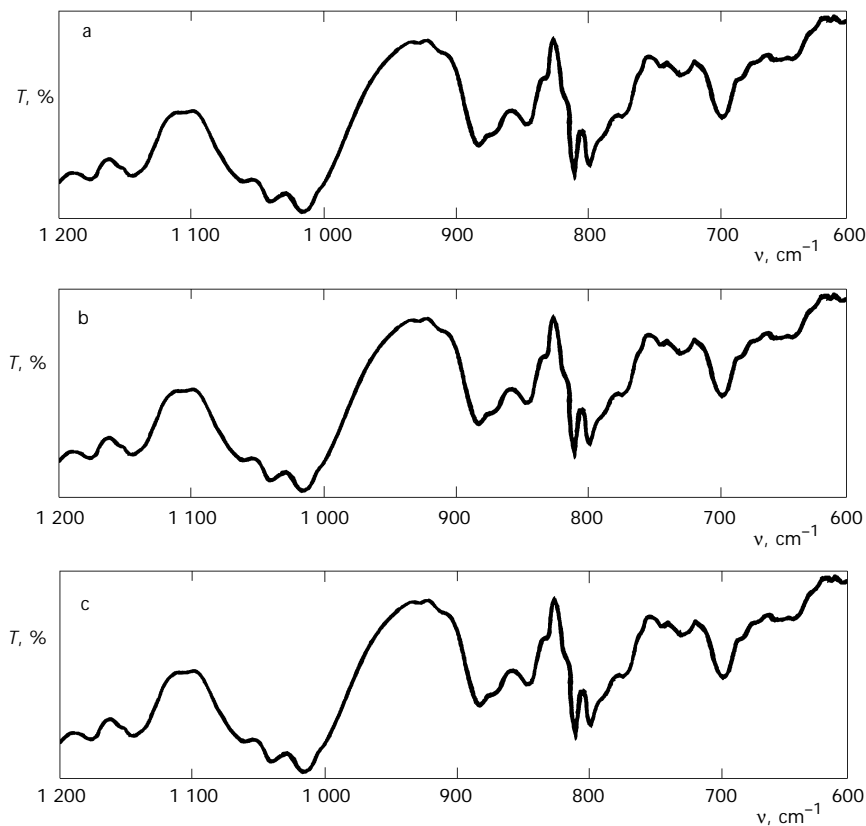


FIG. 6
IR spectra obtained in KBr for a pure SNS, b oxidized poly(SNS) doped with ClO_4^- , c oxidized poly(SNS) doped with Cl^- . Each polymer was synthesized as reported in Fig. 5

secutive anodic peaks in 0.1 M LiClO₄, while just a steep increase of anodic current was found in 0.1 M LiCl. When the scan was reversed at low oxidation potentials, well-defined peak related to the reduction of polarons was observed. These positive charges are balanced by anions from the solution. Adherent and stable deposits of both oxidized forms have been formed at -0.700 V by CA from 0.1 M monomer solution either in 0.2 M LiClO₄ + ethanol or in 0.2 M LiCl + ethanol. Elemental analysis revealed the composition of polymers 21.03% (w/w) of ClO₄⁻ or 9.56% (w/w) of Cl⁻. The poly(SNS) doped with Cl⁻ then represents a form with more polarons than the polymer doped with ClO₄⁻, in agreement with its higher polymerization charge. Both polymers had a density of ca 1.5 g cm⁻³ and were soluble in DMSO, acetone and methanol. A substantially higher electrical conductivity found for poly(SNS) doped with ClO₄⁻ can be assigned to the presence of long π -conjugated molecules in the polymer. MS-FAB spectra of saturated solutions of both forms in DMSO mixed with a thioglycerol matrix indicated that the dimer is the main soluble oligomer. Other undoped linear oligomers, such as trimer, tetramer and pentamer, have also been detected. This technique, however, is unable to identify doped oligomers. The IR analysis of polymers has confirmed the predominant formation of linear molecules with α - α linkages between monomeric units during SNS electropolymerization at low potentials. A condensation mechanism involving the one-electron oxidation of all electrogenerated linear and neutral polymeric chains is proposed to explain the SNS electropolymerization.

REFERENCES

1. Díaz A. F., Kanazawa K. K., Gardini G. P.: *J. Chem. Soc., Chem. Commun.* **1979**, 19, 635.
2. Geniè E. M., Bidain G., Díaz A. F.: *J. Electroanal. Chem.* **1983**, 149, 101.
3. Satoh M., Kaneto K., Yoshino K.: *Synth. Met.* **1986**, 14, 289.
4. Roncali J., Garnier F., Lemaire M., Garreau R.: *Synth. Met.* **1986**, 15, 323.
5. Yumoto Y., Morisihita K., Yoshimura S.: *Synth. Met.* **1987**, 18, 203.
6. Ferraris J. P., Hanlon T. R.: *Polymer* **1989**, 30, 1319.
7. Otero T. F., Rodríguez J.: *Synth. Met.* **1992**, 51, 307.
8. Brillas E., Otero T. F., Figueras A., Carrasco J.: *Synth. Met.* **1993**, 61, 253.
9. Cava M. P., Joshi M. V., Helmer C., Cain J. L., Bakker M. G., McKinley A. J., Metzger R. M.: *J. Chem. Soc., Perkin Trans. 2* **1993**, 1081.
10. Brillas E., Otero T. F., Figueras A., Carrasco J.: *J. Electroanal. Chem.* **1994**, 370, 231.
11. Brillas E., Otero T. F., Figueras A., Carrasco J., Urpí F.: *J. Electroanal. Chem.* **1995**, 392, 55.
12. Wyndberg H., Metselaar J.: *Synth. Commun.* **1984**, 14, 1.
13. Lund H., Baizer M. M. (Eds): *Organic Electrochemistry. An Introduction and a Guide*, 3rd ed., Chaps 2 and 3. Dekker, New York 1991.
14. Guyard L., Hapiot P., Neta P.: *J. Phys. Chem.* **1997**, 101, 5698.