

ELECTROPOLIMERIZATION, ELECTRODISSOLUTION, ELECTRODEPOSITION AND CROSSLINKING OF POLY(SNS).

T.F. Otero*^a, S. Villanueva^a, E. Brillas^b, J. Carrasco^c

^a Universidad del País Vasco, Facultad de Química, Laboratorio de Electroquímica, P.O. 1072, 20080 San Sebastián (Spain) ^b Departament de Química Física, Universitat de Barcelona, Martí i Franqués 1, 08028 Barcelona (Spain)

^c Departament d'Enginyeria Química i Metal·lúrgia, Universitat de Barcelona, Martí i Franqués 1, 08028 Barcelona (Spain)

SUMMARY

The aim of this work is to check that the poly 2,5-di-(2-thienyl)pyrrole, poly(SNS), is a linear polymer which behaves, from an electrochemical point of view as an organic metal. Like inorganic metals poly(SNS) oxidizes, reduces, dissolves and deposits electrochemically. The polymeric films can be electrodissolved by flow of a cathodic current and are able to be electrodeposited again by flow of an anodic current through a solution containing soluble reduced polymer.

Keywords: Electropolymerization, electrodi dissolution, electrodeposition, poly 2,5-di-(2-thienyl)pyrrole.

INTRODUCTION

The technological and industrial applications of conducting polymers have been limited by their low processability. Until now, conducting polymers can be electrogenerated as metals but they don't have one of their most interesting properties, electrodi dissolution. The processability of conducting polymers increases when they become soluble. To obtain soluble conducting polymers it is necessary to find linear polymers non degraded or crosslinked. The ionic and molecular polymeric units should have strong interaction with the solvent molecules. Only linear polymers with low molecular weight are able to have these properties. Two ways are being developed in order to improve processability: the synthesis of soluble oligomers using monomers with lateral chains [1] and the formation of lineal chains from heteroaromatic monomers (SNS, SSS and SOS) [2]. In our laboratory we are working from several years ago trying to get, using polyconjugated materials, those flexible electrochemical methods of processability. In order to attain those aims we focused on heteroaromatic monomers [3,5]. We improved the method of synthesis of 2,5-di-(2-thienyl)pyrrole [6], named SNS in order to get several grams per synthesis. The aim of this work is to explain the new electrochemical properties of this polymer, poly(SNS).

EXPERIMENTAL

The monomer SNS was synthesised as reported previously. Acetonitrile from Lab Scan, HPLC grade, was directly used as solvent. The Lithium perchlorate salt Aldrich, A.C.S. reagent, was dried in an oven at 80 °C prior to be used.

All the electrochemical studies were performed in a one-compartment thermostated three-electrode cell. Two platinum sheets of 1 and 4 cm² surface area were used as working and counter electrodes, respectively. Both electrodes were cleaned by immersion in sulfochromic mixture and rinsed with distilled water and then with acetonitrile before each electrogeneration. The reference electrode was an Ag/AgCl electrode. The chronoamperometric and chronopotentiometric measurements were carried out using a PAR 273A potentiostat-galvanostat connected to a personal computer and controlled through a PAR M270 program.

Each solution was deoxygenated by bubbling nitrogen, once presaturated with acetonitrile, for 15 min prior to each experiment. The polymer weight was obtained by "ex-situ" microgravimetry. Each film was dried in hot air, rinsed several times with acetonitrile, dried again and weighed until constant weight. The weight of the electrodes and polymer films was determined with a Sartorius 4504 MPS ultramicrobalance, having a precision of 10⁻⁷g.

RESULTS

Electropolymerization process

The electropolymerization, also named electrogeneration, is initiated by the electrochemical oxidation of the monomer, SNS, giving a solid film coating the electrode ahead poly(SNS). When an anodic current density of 0.5 mA cm⁻² flows through a 5 mM SNS + 0.1 M LiClO₄ acetonitrile solution, a polymeric film is generated on the electrode. This film is soluble in some organic solvents, DMSO, acetone and methanol, partially soluble in acetonitrile and insoluble in aqueous solutions [7].

A microgravimetric study of the polymerization kinetic has been done. As table 1 shows, a linear variation (Equation 3.1) of the polymer weight with the charge is obtained.

Table 1: Poly(SNS) weight obtained for the anodic polymerization of a 5 mM SNS + 0.1 M LiClO₄ acetonitrile solution on a Pt electrode flowing an anodic current density of 0.5 mA cm⁻² during different times.

Poly(SNS) weight/ mg	Time/ s	Charge/ mC
0.0149	10	5
0.0259	20	10
0.0350	30	15
0.0436	40	20
0.0582	50	25
0.0682	60	30

$$W_{\text{oxid}} = K_{\text{pol}} \times Q_{\text{pol}} \quad (3.1)$$

There W_{oxid} is the oxidized polymer weight generated on the electrode, Q_{pol} is the consumed charge during the process and K_{pol} is the productivity of the charge consumed during the process: electropolymerization, 2.1×10^{-3} mg mC⁻¹.

The electropolymerization is a faradaic process, the generated polymer weight is proportional to the charge consumed during the process.

Electrodissolution process.

Oxidized or reduced states of poly(SNS) have very different solubilities in acetonitrile. The solubility of the oxidized polymer drops to zero when a salt, like LiClO₄, is dissolved in acetonitrile, keeping the reduced polymer a high solubility. This fact allows the polymeric dissolution of the oxidized films, their electrodisolution.

When potentials lower than 0.2 V were applied to poly(SNS) electrogenerated films, a yellow cloud appears around the electrode and the electrodisolution process takes place. As above, a microgravimetric study of the electrodisolution process has been done. A film of weight 0.0685 mg, was electropolymerized applying an anodic current density of 0.5 mA cm⁻² during 60 s through a 5 mM SNS + 0.1 M LiClO₄ acetonitrile solution. Once obtained the film, a cathodic current density of 0.2 mA cm⁻² was applied, in the background solution, during different times. Table 2 shows the variation of the polymer weight with the injected cathodic charge.

Table 2: Poly(SNS) dissolved weight (mg) obtained when a cathodic current density of 0.2 mA cm⁻² is applied during different times on a covered electrode. Cathodic charge (mC) consumed during the electrodisolution process. The weight of the used film was 0.0685 mg. It was electrogenerated from a 5 mM SNS + 0.1 M LiClO₄ acetonitrile solution.

Poly(SNS) dissolved weight/ mg	Time/ s	Charge/ mC
0.0098	5	1
0.0143	10	2
0.0283	20	4
0.0455	30	6
0.0603	40	8
0.0655	50	10

The poly(SNS) dissolved weight increases linearly with the charge, in agree with the follow expression (3.2),

$$W_{\text{dissolved}} = K_{\text{cat}} \times Q_{\text{cathodic}} \quad (3.2)$$

Where the $W_{\text{dissolved}}$ is the polymer weight dissolved obtained by difference of weight between the covered electrode before and after applying the cathodic charge, K_{cat} is the productivity of the

electrodissolution process and in this case has a value of $7.2 \times 10^{-3} \text{ mg mC}^{-1}$, for each mC of consumed charge, $7.2 \times 10^{-3} \text{ mg}$ of polymer are dissolved, finally Q_{cathodic} is the consumed charge during the process.

Electrodeposition process.

In this process an oxidized and insoluble poly(SNS) film is obtained by the oxidation of the reduced and dissolved polymeric molecules present in the electrolytic solution. This film keeps its solubility in organic solvents, or can be dissolved by electrochemical reduction. A microgravimetric study of the deposited polymer weight has been done, by flow of an anodic current density of $8 \mu\text{A cm}^{-2}$ during different times through 6 ml of a 0.25 M LiClO_4 acetonitrile solution in which 0.25 mg of reduced polymer have been previously dissolved. With these results we can say that electrodeposition is also a faradaic process because the poly(SNS) deposited weight on the electrode is proportional to the consumed charge. However the productivity of this process, $7.2 \times 10^{-4} \text{ mg mC}^{-1}$ is much lower than the productivity of the electrodisolution process, $7.2 \times 10^{-3} \text{ mg mC}^{-1}$. This fact is due to the parallel reactions that take place during the electrodeposition that consume charge without any polymeric deposition [8]. The electrodeposited polymer can be only partially electrodisolved. This fact is due to the presence of crosslinking reactions during the deposition. To check the presence of crosslinking reactions, poly(SNS) films with the same weight were electropolymerized, then polarized in the background solution at a potential of 550 mV (same potential as the deposition takes place) during different polarization times and finally submitted to a cathodic current density (figure 1).

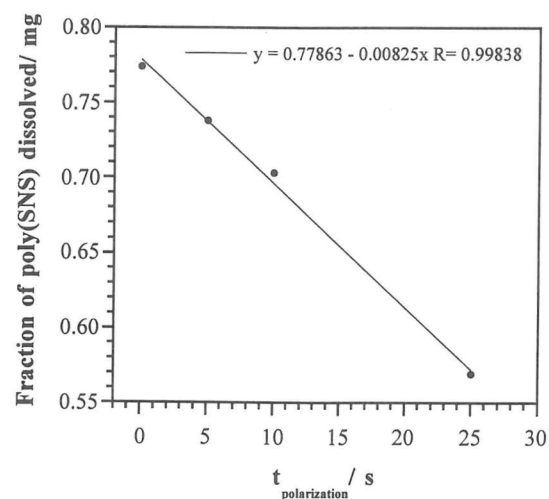


Figure 1: Poly(SNS) weight dissolved after polarization in the background solution at 550 mV, during different times. These films were electrogenerated by flow of an anodic current density of 0.5 mA cm^{-2} during 60 s through a 5 mM SNS + 0.1 M LiClO_4 acetonitrile solution.

This figure shows the evolution of the dissolved poly(SNS) weight with the polarization time. When the polarization time increases, the fraction of the dissolved polymer decreases. The influence of the crosslinking process is higher when the polarization time increases.

CONCLUSIONS

The flow of an anodic current through a solution of SNS gives a film, poly(SNS). The electropolymerization process is a faradaic process. The polymeric film can be electrodisolved by flow of a cathodic current in acetonitrile solution. The electrodisolution is also a faradaic process. Poly(SNS) films can be electrodeposited by oxidation of the reduced molecules dissolved in the background solution. These films are soluble in organic solvent and can be partially electrodisolved. The fact that these films can't be completely electrodisolved is due to the presence of crosslinking reactions during the electrodeposition process. So electropolymerization, electrodisolution and electrodeposition processes can be performed using conducting polymers. Electrodisolution and electrodeposition mimic similar processes with inorganic metals.

REFERENCES

- [1] M.Sato, S. Tanaka, K. Kaeriyama, J. Chem. Soc., Chem. Commun., 873 (1986).
- [2] J.P. Aimé, in H.S. Nalwa, (ed.), Handbook of Organic Conductive polymers: Vol. 3 Conductive Polymers: Spectroscopy and Physical properties. Wiley and Sons, Chichester, 5, (1997), 219.
- [3] J. Carrasco, T.F. Otero, E. Brillaas, M. Montilla, J. Electroanal. Chem. 418 (1996) 115.
- [4] E. Brillas, M. Montilla, J. Carrasco, T.F. Otero, J. Electroanal. Chem., 418 (1996) 123.
- [5] E. Brillas, G. Anton, T.F. Otero, J. Carrasco, 445 (1998) 125.
- [6] J. Carrasco, A. Figueras, T.F. Otero, E. Brillas, Synth. Met, 61 (1993) 253.
- [7] E. Brillas, J. Carrasco, A. Figueras, F. Urpí, T.F. Otero, J. Electroanal. Chem., 55 (1995) 392.
- [8] T.F. Otero, S. Villanueva, E. Brillas, J. Carrasco, Acta Polym., 49 (1998) 433.

Received, May 17, 1999
Revised, July 30, 1999