Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Polyfurfural Film Synthesized by Electrochemical Reduction of Furfural on Bright Platinum Electrode

Alzira Maria Serpa Lucho[a]; Reinaldo Simões Gonçalves[a]
[a] Instituto de Química da Universidade Federal do Rio Grande do Sul, Porto Alegre/RS, Brazil

To cite this Article Lucho, Alzira Maria Serpa and Gonçalves, Reinaldo Simões(2005) 'Polyfurfural Film Synthesized by Electrochemical Reduction of Furfural on Bright Platinum Electrode', Journal of Macromolecular Science, Part A, 42: 6, 791 — 799

To link to this Article: DOI: 10.1081/MA-200058663

URL: http://dx.doi.org/10.1081/MA-200058663

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry, 42:791–799, 2005

ISSN 1060-1325 print/1520-5738 online
DOI: 10.1081/MA-200058663

Polyfurfural Film Synthesized by Electrochemical Reduction of Furfural on Bright Platinum Electrode

ALZIRA MARIA SERPA LUCHO AND REINALDO SIMÕES GONÇALVES

Instituto de Química da Universidade Federal do Rio Grande do Sul,
Porto Alegre/RS, Brazil

The electroreduction of furfural (2-furancarboxaldehyde) was confirmed on bright platinum electrode in acetonitrile solutions. The product synthesized was an organic film with good adherence and electrical conductivity. Three electrochemical methods such as CV, chronopotentiometry and chronoamperometry were used in this process. SEM photographs were conclusive to confirm the presence of the film on the electrode surface. The IR and ^{13}C NMR spectra of the resin obtained galvanostatically suggest a complex structure with the presence of the furfural and organic solvent molecules.

Keywords furfural, platinum, non-aqueous solutions, electropolymerization

Introduction

Conducting polymers are regarded as potential materials for the electronic industries. The possibility of combining the properties of organic polymers and the electronic properties of semiconductors in these new materials has been the driving force for various applications. Conducting polymers can be prepared via chemical (1–3) or electrochemical polymerization (4). Films of electronically conducting polymers generated by electrochemical polymerization are generally deposited onto a supporting electrode surface by different electrochemical techniques including potentiostatic (constant-potential), galvanostatic (constant current) and potentiodynamic (cyclic voltammetry).

The characterization of the electrochemical doping-undoping processes of polyheterocyclic polymers is then a matter of great interest. Electrical conductivity is achieved in the conducting polymer film by oxidation (p-doping) or reduction (n-doping), followed respectively by the insertion of anionic or cationic species. As recently pointed out, polypyrrole (4) and polyaniline (5) are probably the most intensively studied conducting polymers. To date, on the other hand, much less attention has been devoted to the electropolymerization of polyfurans (6), probably because of their

Received September 2004, Accepted January 2005

Address correspondence to Reinaldo Simões Gonçalves, Instituto de Química da Universidade Federal do Rio Grande do Sul, Caixa Postal 15049, CEP 91501-970 Porto Alegre/RS, Brazil. E-mail: reinaldo@iq.ufrgs.br

theoretical less well-defined structures and poor stability. Furfuryl alcohol polymerization is a well-known homogeneous acid catalysis process (2). However, the major structural features of the acid catalyzed furfuraldehyde resins were proposed by pyrolysate composition analysis involving thermal degradation techniques (7). The authors suggest a complex network structure with participation of furan ring and ring-opened sequences.

Furfural is an electrophore and can be reduced into furfuryl alcohol, or oxidized into furoic acid (8).

Recently, we found that Polyfurfural (PFY) films can be deposited onto a platinum platinized electrode by different electrochemical methods in acetonitrile solution (9). The mechanism was described as involving the oxidation of the monomer at the surface of the electrode until the final polymer product via others reactions.

Here, we report an organic film formed on the bright platinum electrode from electroreduction of furfural in the same medium with excellent adherence. The synthesis of the films occurs from cathodic reduction of the monomer by three different electrochemical methods. The morphology of the film was characterized by Scanning Electron Microscopy (SEM). A probable polymer structure was discussed from IR and ^{13}C NMR spectroscopic analysis.

Experimental

A standard glass three-electrode electrochemical cell was used. The reference was a saturated Ag/AgCl, and the auxiliary electrode was bright platinum. Bright platinum was also used as a working electrode. The setup for electrochemical tests were a potentiostat Autolab/EcoChemie PGSTAT 30 system and a Tectrol source, model TCM 1000-005. SEM photographs were made with a JSM microscope model 5800. The polymer was analyzed with an IR spectrophotometer Shimadzu model 8300. The characterization of the polymer structure was proposed from NMR spectrum takes from a VARIAN model INOVA-300.

All solutions were prepared in pure acetonitrile with Lithium Chloride ($5.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$) as supporting electrolyte. Pure furfural ($1.0\,\mathrm{mol\,L^{-1}}$) was added to the electrolysis solutions.

Results and Discussion

In this paper, an experimental strategy was adopted in order to confirm the possibility of electropolymerization of furfural by three different electrochemical methods. In this sense, the data were organized as presented below.

Galvanostatic Reductive Electropolymerization of Furfural

The electroreduction of furfural was performed galvanostatically by applying a current density of $5.0\,\mathrm{mA\,cm^{-2}}$, during different polarization times. The working electrode was connected to the negative pole of a DC power and partially immersed into the electrolysis solution. The presence of the film on the electrode surface was visible after 500 s of electrolysis. The SEM photography presented in Figure 1 shows the immersed side of platinum wire covered with the organic film formed on the electrode surface after galvanostatic electrogrow. The morphology of the film was not compact, but mainly porous.

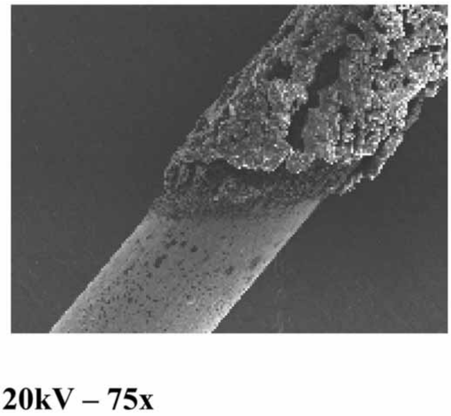


Figure 1. SEM photograph of the platinum electrode recovered with the organic film synthesized galvanostatically at $j = 5\,mA/cm^2$, $t = 500\,s$.

Despite the visible changes of the electrode surface, some chronoamperometric experiments were made in order to confirm the electrochemical behavior modification. The recovered electrode was transferred to another solution without furfural. The potential of the working electrode was shift to $-2.0\,V$ (Ag/AgCl) and the curves I(t) for two conditions were recorded as is shown in Figure 2. The chronoamperogram of the bare electrode is also presented. At this potential the cathodic current values obtained should be associated with electrochemical reduction processes. The effect of the presence of the organic film on the charge transfer processes at this potential is visible. The current values decreases proportionally to the electrolysis time suggesting dependence on the film thickness.

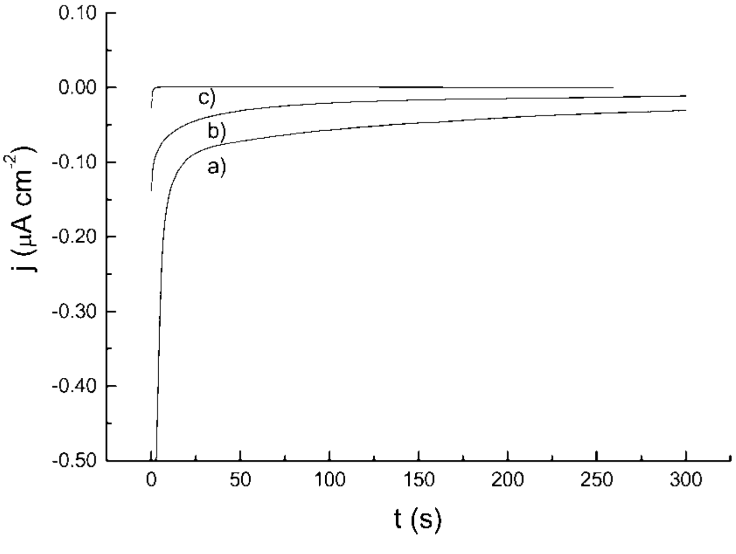


Figure 2. Chronoamperograms of the platinum electrode recorded at $-2.0\,V$(Ag/AgCl): a) bare electrode, b) 5 min and, c) 60 min after galvanostatic synthesis of furfural resin on the electrode surface.

Potentiostatic Reductive Electropolymerization of Furfural

In order to drive the reductive electropolymerization of furfural in the direction of better control of the polymer structure and porosity, the influence of the potential control was investigated. These experiments were performed in the same electrolysis solution as previously described. The working electrode was partially immersed and kept at −7.0 V (Ag/AgCl) during different times. The presence of the organic film was completely visible after 3600 s of electrolysis. The SEM micrograph exhibits a more compact film in Figure 3.

Despite the visible presence of the organic film on the electrode surface, the same strategy was adopted in order to confirm electrochemical behavior changes of the electrode. The modified electrode was transferred to another solution containing lithium chloride ($5.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$) in acetonitrile without furfural. Cyclic voltammograms from −2.0 V (Ag/AgCl) to 0.25 V (Ag/AgCl) were recorded at $0.020\,\mathrm{Vs^{-1}}$, as shown in Figure 4. The (E) curve of the bare electrode is also given in the same figure. The effect of the presence of the polymer film on the electrochemical behavior changes of the working electrode is significant. The charge transfer processes in all potential range were significantly inhibited by the presence of the organic film, as is noticeable by comparing both voltammograms.

Reductive Electropolymerization of Furfural by the CV Method

In these experiments, the organic film was deposited on the immersed platinum electrode by cycling the potential consecutively from −7.0 V (Ag/AgCl) to −6.0 V (Ag/AgCl) at $0.020\,\mathrm{Vs^{-1}}$ in the same electrolysis solution described previously. The presence of the organic film was completely visible after 100 cycles. Figure 5 presents the SEM photograph of the electrode surface covered with the organic film. Similarly, the film formed on the electrode surface was not as thick as that obtained by the galvanostatic method. The morphology of the organic film also seems highly porous.

However, the presence of the organic film was confirmed by comparing the voltammograms of the working electrode recorded at $0.020\,\mathrm{Vs^{-1}}$ in another solution containing lithium chloride ($5.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$) in acetonitrile without furfural (Figure 6). In all

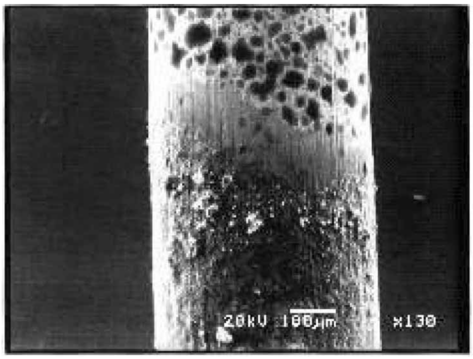


Figure 3. SEM photograph of the platinum electrode recovered with the organic film synthesized potentiostatically at −7.0 V (Ag/AgCl) during 3600 s.

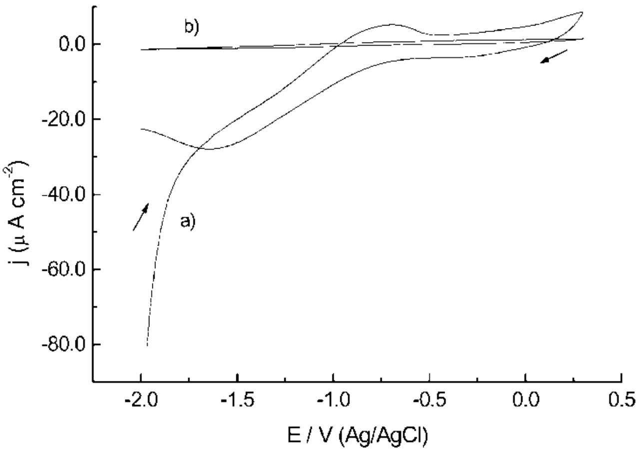


Figure 4. Cyclic voltammograms of platinum electrode recorded at 0.02 V/s in acetonitrile without furfural: a) bare electrode and b) recovered with furfural resin synthesized potentiostatically at −7.0 V (Ag/AgCl) during 3600 s.

potential ranges, the current density values decreases dramatically by comparing both voltammograms.

The films synthesized by different electrochemical methods were clearly dissimilar as judged visually. The thicknesses of the organic film formed on the electrode surface were dependent of the electrochemical method as is shown in Table 1. These differences should be related with the polymerization rate (10), electropolymerization time (11) or, with the molecular weight of the polymer synthesized (12).

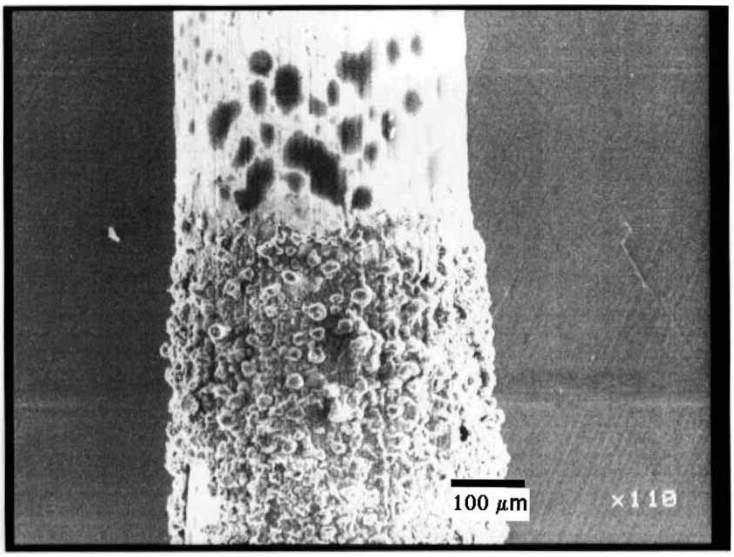


Figure 5. SEM photograph of the platinum electrode recovered with the organic film synthesized by CV from −7.0 V to −6.0 V (Ag/AgCl) at 0.020 Vs^{-1} after 100 cycles.

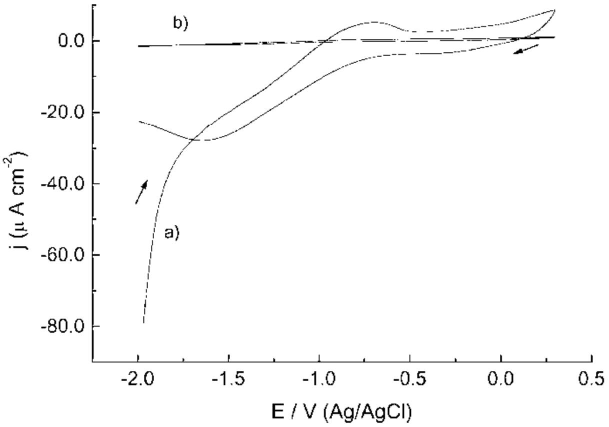


Figure 6. Cyclic voltammograms of platinum electrode recorded at 0.02 V/s in acetonitrile without furfural: a) bare electrode, and b) recovered with furfural resin synthesized by CV between −7.0 V (Ag/AgCl) and −6.0 V (Ag/AgCl) at 0.02 V/s after 100 cycles.

Electrical Conductivity Properties o Polyfurfural

In these experiments, the film samples were obtained galvanostatically and collected from the electrode surface. Conductivity measurements were carried out applying a constant current (50 μA) to the samples in a four-probe arrangement (12). The polymeric film with a 0.02 cm thickness showed an electrical conductivity around 400 mS cm^{-1}. This value is much higher in magnitude than polyfuran film synthesized chemically (-10^{-13} S cm^{-1}) (13). This property allowed us to consider polyfurfural as a polymer with conjugated π-electron backbones as observed in conducting polymeric film (14). All the films obtained from this method showed good adhesion to the platinum surface.

IR and ^{13}C NMR Spectroscopy Analysis

The IR spectrum of the polymer was made with 1 mg of the film synthesized galvanostatically and prepared with KBr discs. Figure 7 shows the IR spectrum of the compound, and the most relevant bands are presented. Two bands at 1800–1600 cm^{-1}

Table 1

Thickness values determined from SEM photographs of the organic films formed on the electrode surface from the three electrochemical methods

Method	Experimental	Thickness
Galvanostatic	5 mA/cm^2 t = 60 min	107 μm
Potentiodynamic	100 cycles	23 μm
Potentiostatic	−7.0 V t = 60 min	12 μm

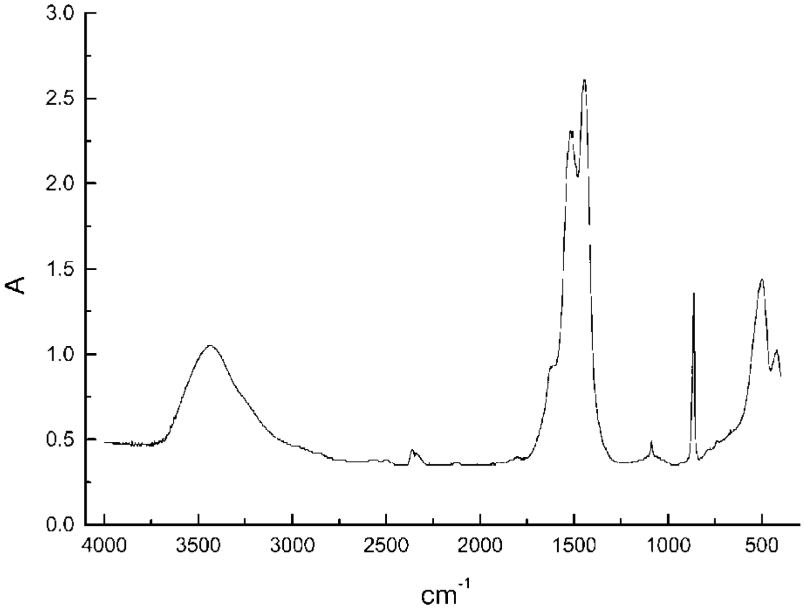


Figure 7. IR spectrum of the furfural resin synthesized galvanostatically on the electrode platinum surface.

should be associated with the carbonyl group. One band at 3100 cm^{-1}, corresponds to the C—H stretching in the carbon sp$_2$, thus suggesting a content of aromatic units in the polymer, and one small band at 2300 cm^{-1} regarding to the C═N group. Also, the ^{13}C NMR spectrum (Figure 8) agrees with the proposed structure. Indeed, on the basis of the signals obtained, a new structure may be suggested as shown in Figure 9. It is clear that the molecule of the solvent should be involved in the polymer structure formation.

The comparisons between both spectra allow us to consider polyfurfural as a product formed according to the two paths presented in Scheme 1.

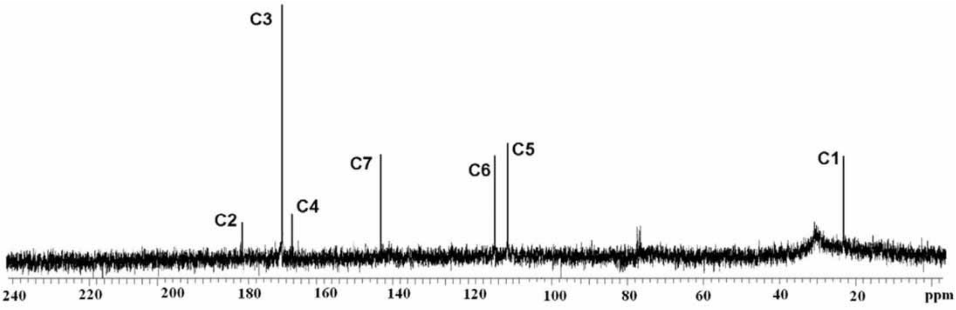


Figure 8. ^{13}C NMR spectrum of the furfural resin synthesized galvanostatically on the electrode platinum surface.

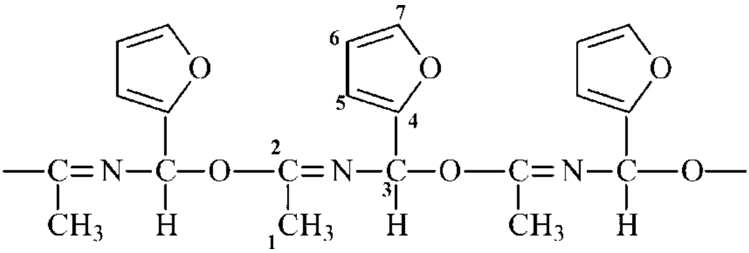
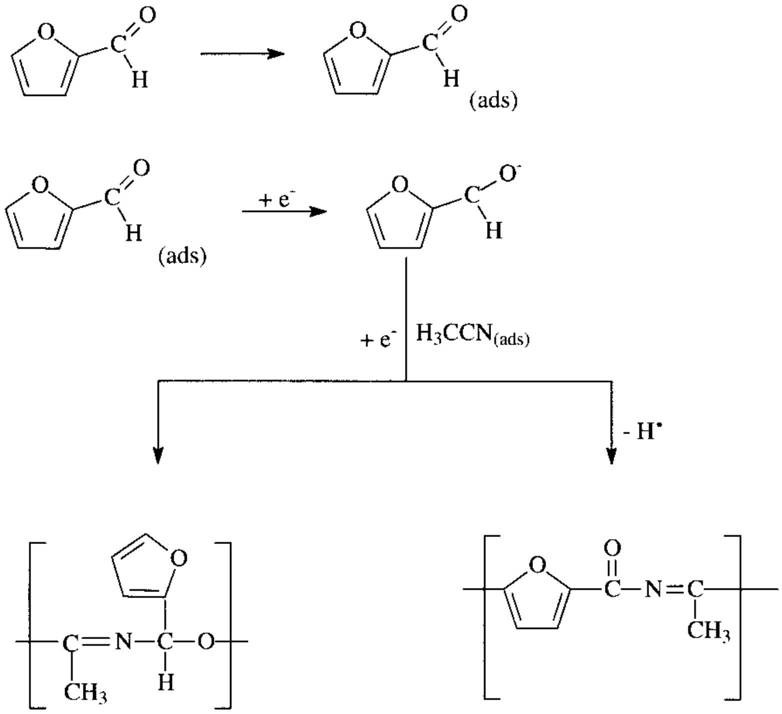


Figure 9. Corresponding structure visualized from the ^{13}C NMR spectrum of the furfural resin.

We are considering both possibilities since that the presence of carbonyl group and C=N group were unequivocally detected. It should be reasonable to accept both structures on the electrode surface.

Conclusions

The electroreduction of furfural (2-furancarboxaldehyde) was confirmed on a bright platinum electrode in acetonitrile solutions. The synthesized product was an organic film with good adherence and electrical conductivity. Three electrochemical methods such as CV, chronopotentiometry, and chronoamperometry were used in this process.



Scheme 1. Mechanisms of electropolymerization of furfural on platinum electrode.

SEM photographs were conclusive in confirming the presence of the film on the electrode surface. The IR and ^{13}C NMR spectra of the resin obtained galvanostatically suggest a complex structure with the presence of the furfural and organic solvent molecules. Despite the visible presence of the polymer, some CV and chronoamperometric experiments were made to visualize the changes on the electrochemical behavior of the platinum electrode.

References

1. Gonzalez, R., Rieumont, J., Figueroa, J.M., Siller, J., and Gonzalez, H. (2002) Kinetics of Furfuryl Alcohol Polymerization by Iodine in Methylene Dichloride. *European Polymer Journal*, 3: 281–286.
2. Batista, P.S. and Souza, M.F. (2000) Furfuryl Alcohol Conjugated Oligomer Pellicle Formation. *Polymer*, 41: 8263–8269.
3. Gonzalez, E., Gonzalez, M., Gonzalez, R., Ortiz, P., and Rieumont, J. (2000) The Resinification of 2-Ethenylfuran Catalyzed by Trifluoroacetic Acid in Water-Chloroform Mixtures. *Polymer*, 41: 2491–2498.
4. Sadki, S., Schottland, P., Brodie, N., and Sabouroud, G. (2000) The mechanism of Pyrrole Electropolymerization. *Chem. Soc. Rev.*, 29: 283–293.
5. Pekmez, N. and Yildiz, A. (1995) Electropreparation of Polyaniline in the Presence of Anhydrous Cuprous Ions In Acetonitrile. *J. Electroanal. Chem.*, 386: 121–126.
6. Tediar, F. (1985) Électropolymérisation du furanne-1 Obtention des produits sur différents substrats. *Eur. Polym. J.*, 21: 317–319.
7. Sánchez, R., Hernandez, C., and Keresztury, G. (1994) Structural Analysis of Acid Catalyzed Furfuraldehyde Resins by Thermal Degradation Techniques. *Eur. Polym. J.*, 30: 43–50.
8. Chamoulaud, G., Floner, D., Moinet, C., Lamy, C., and Belgsir, E.M. (2001) Biomass Conversion II: Simultaneous Electrosyntheses of Furoic Acid and Furfuryl Alcohol on Modified Graphite Felt Electrodes. *Electrochim. Acta*, 46: 2757–2760.
9. Lucho, A.M.S., Hallal, J.L.J., and Gonçalves, R.S. (2003) Evidence of a Polymeric Film Formation from Furfural Electrooxidation on Platinum Platinized Electrode in Acetonitrile. *J. Macrom. Sci., Part A-Pure and Applied Chemistry*, A40: 933–946.
10. Dyreklev, P., Granström, M., Inganäs, O., Gunaratne, L.M.W.K., Senadeera, G.K.R., Skaarup, S., and West, K. (1996) The Influence of Polymerization Rate on Conductivity and Crystallinity of Electropolymerized Polypyrrole. *Polymer*, 37: 2609–2613.
11. Carrillo, I., Sánchez de la Blanca, E., and González-Tejera, M.J. (2001) Influence of the Electropolymerization Time on the Nucleation Mechanism, Structure and Morphology of Polyfurane/Perchlorate Doped Films. *Polymer*, 42: 9447–9453.
12. Heffner, G.W., Dahman, S.J., Pearson, D.S., and Gettinger, C.L. (1993) The Effect of Molecular Weight and Crystallinity on the Conductivity of a Conducting Polymer. *Polymer*, 34: 3155–3159.
13. Benvenuti, F., Galletti, A.M.R., Carlini, C., Sbrana, G., Nannini, A., and Bruschi, P. (1997) Synthesis, Structural Characterization and Electrical Properties of Highly Conjugated Soluble Poly(furan)s. *Polymer*, 38: 4973–4982.
14. Kroschwitz, J.I. ed. (1988) *Electrical and Electronic Properties of Polymers: A State-of-the-Art Compendium*; John Wiley & Sons: N.Y., 56–101.