Effect of Working Conditions on the Morphology of Electrosynthesized Polyfuran

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ABSTRACT: The influence of electrolyte and deposition potential on polyfurane doped/undoped electrogenerated films was analyzed by potentiodynamic profiles and current–time transients. The films were formed on platinum electrodes from the monomer and tetrabutylammonium hexafluorophosphate, tetrabutylammonium tetrafluoroborate, or tetraethylammonium perchlorate in acetonitrile. Results were also discussed with the aid of X-ray photoelectron spectroscopy (XPS), electron probe microanalysis (EPMA), and primarily by scanning electron microscopy (SEM). It was shown that there is some oxygen contamination not only after ClO_4 doping. However, it was shown by XPS and EPMA that C—O—C bonds are present in the films, which confirmed that there was no destruction of the furan ring during electropolymerization. SEM study showed film morphology evolution with monomer concentration, and with the electrolyte or the dopant used. The undoping effect was also visualized, showing that doped polyfuran was more homogeneous than the respective undoped deposits. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1346–1354, 2004

Key words: conjugated polymers; heteroatom-containing polymers; electrochemistry; scanning electron microscopy; X-ray photoelectron spectroscopy

INTRODUCTION

In recent years, the electrochemical synthesis and properties of conducting polymers have been studied, primarily because of their technological interest. In particular, polypyrrole, polythiophene, and its derivatives have been the subject of several studies[1,5]; polyfuran (PFu), however, has not received similar attention.

Electrochemically generated conducting PFu was first reported by Tournillon and Garnier.[6] They showed the electrochemical oxidation of various heterocycles, such as thiophene, furan, and the like, leading to the formation of new organic conducting polymers. They can be obtained either as thin films or as thick deposits, with a very high reproducibility of structures, chemical composition, and conducting properties. These compounds are very stable in the air and under vacuum, and they afford a large range of conductivities depending on monomer structures.[6]

Pons and Hinman[7] pointed out the necessity of high positive potentials for growing films from furan derivatives, attributed to their insulating character. Other authors[8] have also remarked on the difficulty of

PFu film formation by electroreduction because films obtained in this way are insulators.

The low electrical conductivity of PFu films was attributed to the short length of their conjugated chains or to the restriction of carrier migration resulting from the existence of alternate regions of high and low conductivity.[9] Carrillo et al.[10] reported the synthesis of perchlorate doped polyfuran films, with reproducible electrochemical behavior, by constant potential electrolysis. Conducting polyfuran films were obtained at three different applied potentials and ring opening during polymerization was also observed.[10]

Potentiostatic synthesis and potentiodynamic study of PFu films were reported by González-Tejera et al.[11] Both methods are important to promote their technological applications, as has been performed with polypyrrole and polythiophene.[12,13] Importantly, the electroactivity of these polymeric materials increases with cycling, which is very useful for technological applications.

Another study[14] shows the results of electrochemical polymerization of furan and 2-methylfuran. The effect of different electrolytes on the conductivities of the polymer and the effect of temperature on the electrochemical polymerization were analyzed. The electronic spin resonance spectrum of furan obtained during electrolysis indicated that a radical cation formed after electron transfer couples, immediately followed by elimination of H^+. The resulting spectrum could be assigned to a radical cation of dimer and/or a radical
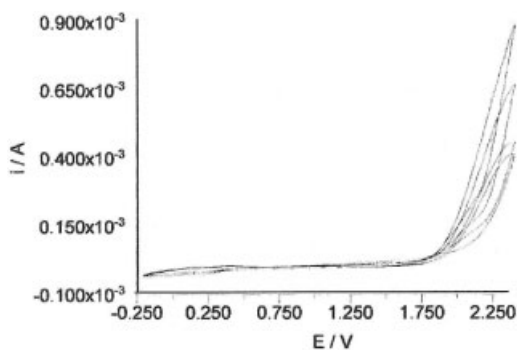
Figure 1 Potentiodynamic profiles of furan from cycle 1 to cycle 4 between -0.20 V and 2.40 V in CH_3CN. Interface: Pt/0.10M furan $+$ 0.10M Bu$_4$NPF$_6$. Scan rate: 0.100 V s^{-1}.

stabilized in the polymer chain, indicating that furan polymerization occurs by an α-β mechanism.

We believe that these different results can be the consequence of the comparison of deposits obtained under different working conditions, leading to polymers with diverse properties, because it has been demonstrated that parameters such as electrochemical perturbation, potential, electrolyte, and solvent, for example, significantly modify the morphology and structure of the deposits.[15–17]

In this article we report the results obtained in the electropolymerization of furan on Pt using CH_3CN media with Bu$_4$NPF$_6$, Bu$_4$NBF$_4$, and Et$_4$NClO$_4$ as electrolytes. The electrochemical techniques used were cyclic voltammetry and potential step. Films were also characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and electronprobe microanalysis (EPMA).

EXPERIMENTAL

All the experiments reported were carried out in a conventional three-compartment cell. A polycrystalline nonannealed Pt disc (geometrical area 0.7 cm^2) and Ag/AgCl in tetramethylammonium chloride[18] were used as working and reference electrodes, respectively. The reference electrode was placed in a compartment separated from the working electrode by a Luggin capillary. The counterelectrode was a Pt gauze, separated from the working electrode by a fine glass frit.

Before each experiment the working electrode was polished with alumina slurry (particle size 0.3 μm) on soft leather and afterward washed with deionized water and anhydrous acetonitrile. Before all the experiments, solutions were purged with high-purity argon and an argon atmosphere was maintained over the solution during measurements.

Acetonitrile (HPLC grade; Aldrich, Milwaukee, WI) was stored in a dry argon atmosphere and over a

generous amount of molecular sieve (4 Å). To ensure minimum water content, the solvent was manipulated by syringe. The same procedure was applied to furan (Merck, Darmstadt, Germany) and all the solutions used. Tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$), tetrabutylammonium tetrafluoroborate (Bu$_4$NBF$_4$), and tetraethylammonium perchlorate (Et$_4$NClO$_4$) were used as supporting electrolytes. These salts were dried in vacuum for several days before use.

Electrochemical polymerization and deposition of furan was carried out from solutions containing 0.1M monomer and 0.05 to 0.1M background electrolyte. Doped polymer was obtained by applying a potential between 2.10 and 2.9 V versus saturated calomel electrode (SCE) for 1 h and the undoped polymer was prepared by applying a potential of -0.1 V versus SCE to the doped polymer immersed in a solution containing only the electrolyte.

Electron microprobe analysis (PGT-IMIX PTS model, JEOL, Tokyo, Japan) was used to determine the composition of the films. For the observation of their surface and cross section morphology, a JEOL-type JSM 6400F scanning electron microscope (SEM; JEOL) was used.

XPS measurements were carried out with a Leybold LHS-12 spectrometer (XPS analyses were carried out at the University of Nantes, CNRS). XPS data were obtained with magnesium-source radiation (1253.6 eV) operating at 10 kV and 10 mA and the pass energy was set to 50 eV. High-resolution scans with a good signal-to-noise ratio were obtained in the C1s, N1s, O1s, P2p, and F1s regions of the spectrum. Quantitative analysis was based on the determination of the C1s, N1s, O1s, P2p, B1s, Cl2p, and F1s peak areas with 0.2, 0.36, 0.6, 0.31, 0.1, 0.58, and 1 as sensitivity factors. The vacuum in the analysis chamber was about 10^{-6}
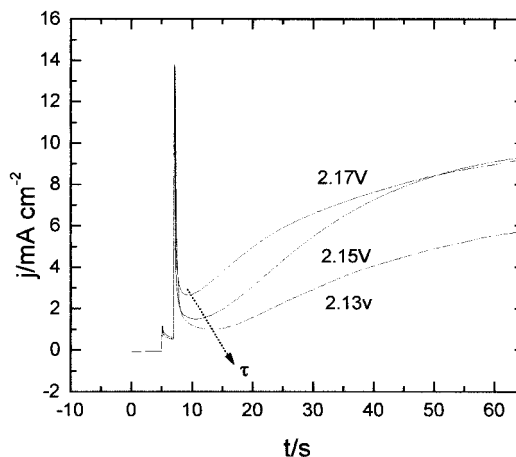

Figure 2 Current–time transients during furan electrooxidation at potentials between 2.13 and 2.17 V in CH_3CN. Interface: Pt/0.10M furan $+$ 0.10M Bu$_4$NPF$_6$.

TABLE I
XPS Peaks of PFu Obtained on a Pt Surface (from the Monomer and TBAPF$_6$ in Acetonitrile)

C–C	C–O–C C–OH	COOH	C1sN$^+$	N1s		O1s F1sF
				M–O	C–O–C	
		Binding energy (eV)				
285	285.6	288.8	404	530	532.5	686.6
		Relative atomic percentage				
33	66	1	100	7	93	100

Pa. All the spectra were recorded under identical conditions. Decomposition of XPS peaks into different components and the quantitative interpretations were performed after subtraction of the background using the Shirley method.[19] The developed curve-fitting programs allowed variation of the parameters, such as the Gaussian–Lorentzian ratio, the full width at half maximum, the position, and the intensity of the contribution. These parameters were optimized by a curve-fitting program.

RESULTS AND DISCUSSION

Electrochemical study

It is important to mention at first that it is possible to obtain PFu electrodeposits only by working in an absolutely anhydrous medium, which was also observed during the electrodeposit processes of others polymers such as polythiophene and polyselenophene.[16]

Concerning the electrode substrate no electropolymerization was attained on steel, whereas on gold the electrochemical response was totally irreversible, leading to a deposit with very low adherence. Considering

this behavior the study was continued on platinum because on this substrate the best results were obtained and the influence of the electrode substrate on the quality of the deposit was demonstrated.

Figure 1 shows the potentiodynamic I/E profile corresponding to the first four cycles during furan electrooxidation on a platinum disk electrode in the electrolytic medium mentioned above. Potential limits correspond to those previously established as optima under those working conditions: below that limit neither deposit formation nor a current increase was observed after successive cycles. On the other hand, above that limit the deposit degraded as a consequence of its overoxidation. Thus, the anodic charge can be attributed to the PtO monolayer formation process, the electrooxidation of furan, and its polymerization and doping processes.

As successive cycles were completed the current increased and it was clearly observed that the electrode became covered by a compact dark film of polyfuran. This observation suggests that the conducting nature of the polymeric film formed on the working electrode surface. Nevertheless these minor current
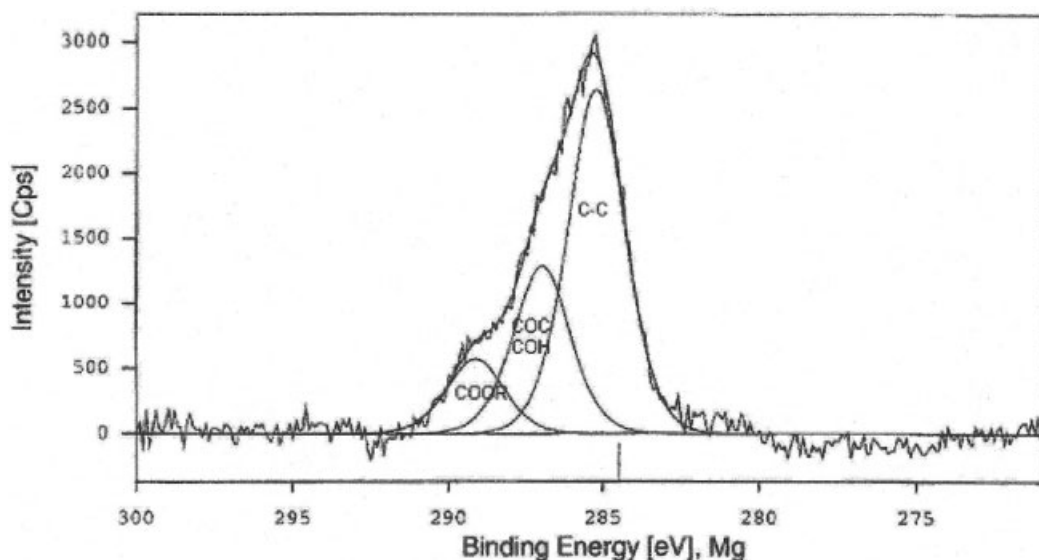

Figure 3 C1s core level spectra of PF$_6^-$ doped polyfuran films. The features through the data correspond to the fitting with Gaussian functions.
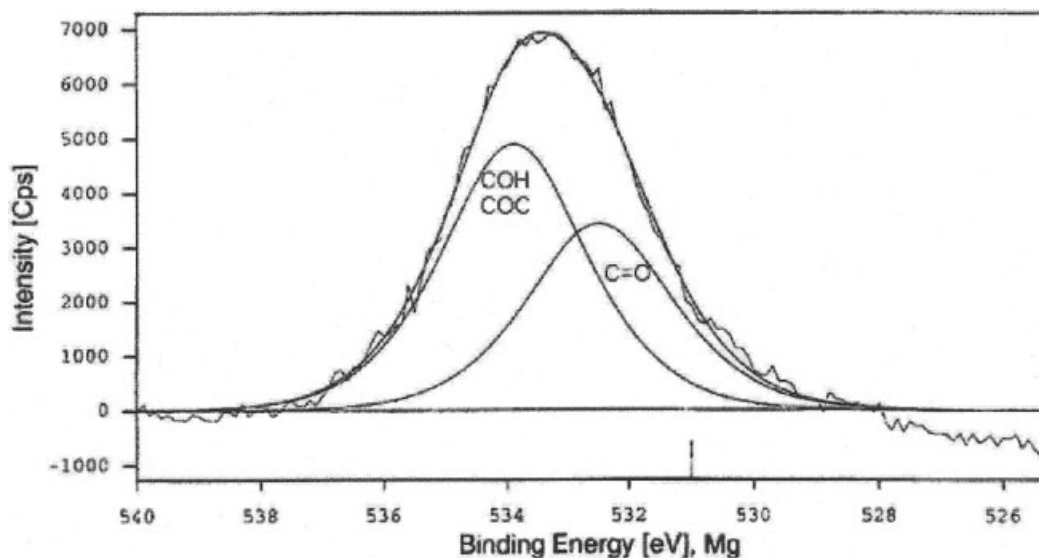
Figure 4 O1s core level spectra of PF_6^- doped polyfuran.

values suggest that conductivity should be smaller than that of polythiophene obtained under identical experimental conditions.[17]

Upon reversal potential scan direction no significant current was observed, indicating an irreversible process for PFu. Only the small current observed near −0.1 V versus SCE corresponded to the undoping process, indicating that the undoping charge is smaller than the doping charge. This process was confirmed both by the potential and the charge involved along with microanalysis results, which revealed that release of anions during the undoping process was not complete.

To register current–time transients (Fig. 2) a potentiostatic pulse program was applied to the interface and the corresponding polarization potentials (nucleation and growth potentials, E_{NG}) were selected in the range where the conducting film is formed (2.13–2.17 V). Once the double layer had previously charged, monomer oxidation began and the current reached a minimum after an induction time, $\tau < 10$ s, it increased again and some current variations were observed as a consequence of different contributions of nucleation and growth to the whole polymerization process.

Moreover, a small induction time would indicate that the nuclei formed are oligomers. Therefore, the deposit was produced from the first shorter-chain nuclei of PFu generated. This behavior can be explained by the electronegativity and the heteroatom size, de-
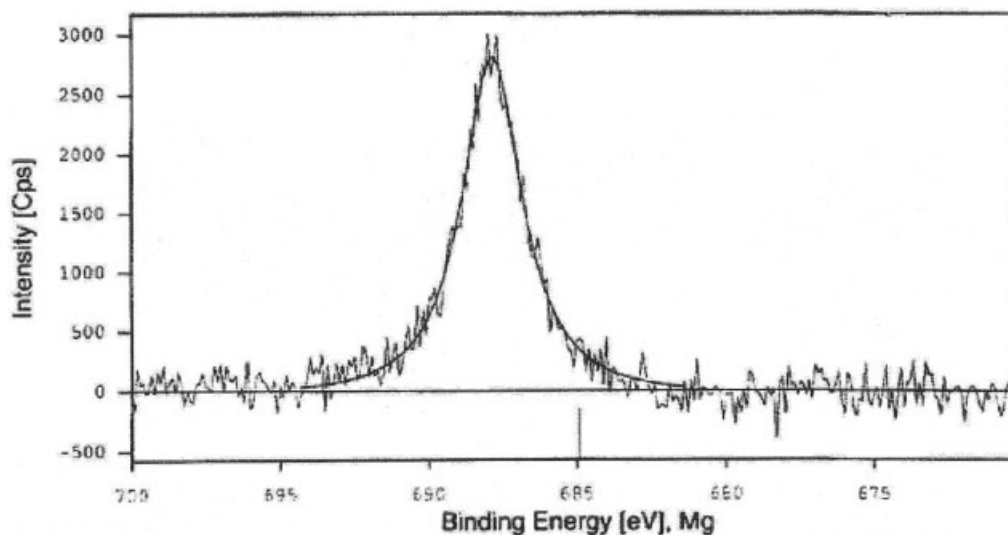

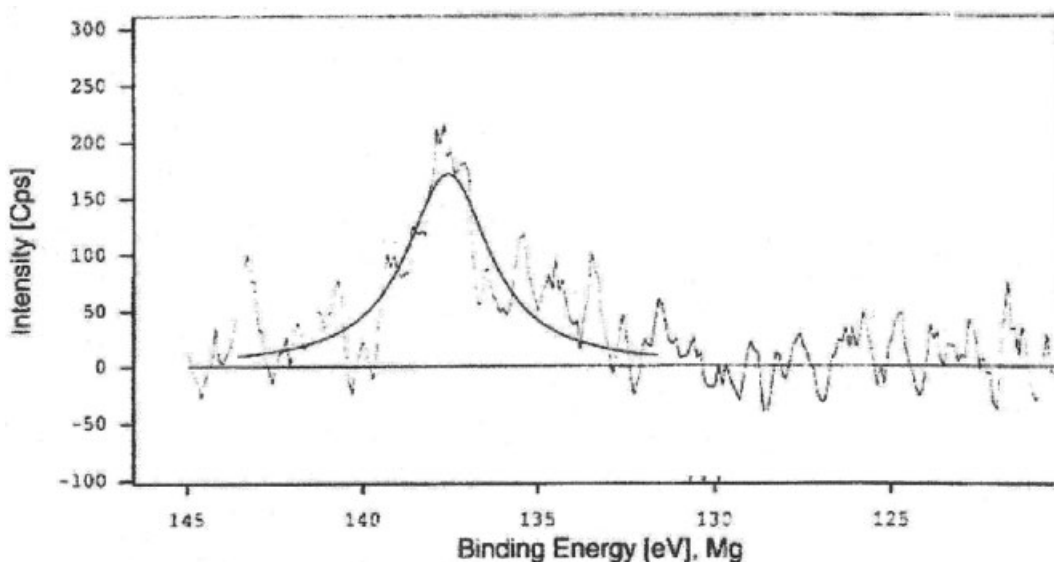**Figure 5** F1s core level spectra of PF_6^- doped polyfuran.

Figure 6   P2p core level spectra of PF_6^- doped polyfuran.

termining the morphology and the nucleation and growth mechanism of the deposit.

We also attempted to produce a polyfuran electrodeposit under analogous conditions but using CH_2Cl_2 as the solvent, although no deposit was obtained after prolonged electrolysis time (>30 min), even though oxidation of the monomer was observed. The explanation for this phenomenon is the greater solubility of oligomers in this solvent, thus requiring a longer chain for their precipitation onto the electrode surface. However, this phenomenon does not occur because we can observe that these species diffuse into the electrolyte bulk instead of precipitate within the electrolysis period studied. This phenomenon is a fur-

ther evidence of the previously proposed electropolymerization model.[16,17]

XPS study

Deposits obtained by the potentiostatic method, on a platinum electrode from $0.1M$ monomer solution in acetonitrile and between 0.05 and $0.1M$ supporting electrolyte, were characterized by XPS. The most relevant results using Bu_4NPF_6 (Table I) as supporting electrolyte are the following.

Carbon peak C1s can be decomposed in three components; the first one situated at 285 eV corresponds to C—C bonds and will be used as reference.[20] The sec-
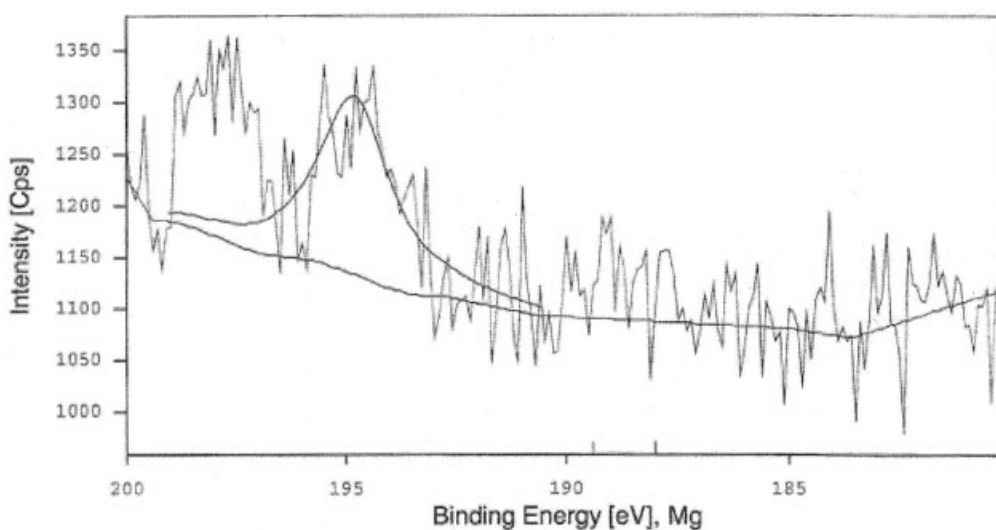

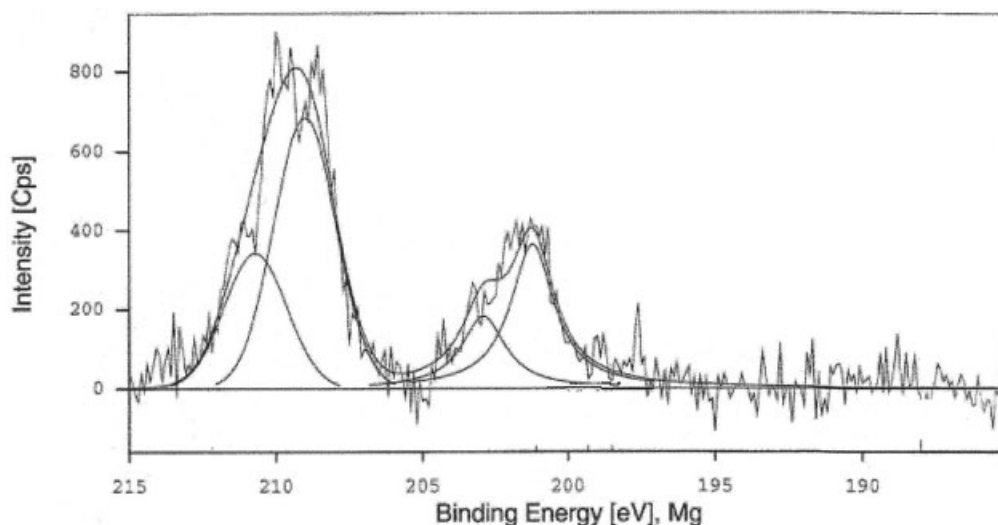**Figure 7**   B1s core level spectra of BF_4^- doped polyfuran.

Figure 8 Cl2p core level spectra of ClO_4^- doped polyfuran.

ond contribution, located at 285.6 eV, can be assigned to C—O—C of the furan cycle and, at least partly, to positively charged carbon. This C^+ is formed by polymer doping. Moreover other contributions cannot be excluded such as C—OH related to surface contamination. The third at 288.8 eV can be assigned to COOH.

Some fluorine is also present, which corresponds to the dopant counterion PF_6^-.

Oxygen O1s peak can also be decomposed into two components. The one situated at 530 eV can be assigned to a substrate contribution (M—O bonds), whereas the second component at 532.5 eV corresponds to O1s of the furan ring. Therefore, decomposition of C1s and O1s peaks shows the presence of C—O—C bonds, which confirm that furan rings are not destroyed during the electrochemical polymerization process, corroborated by EPMA.

Analysis of XPS spectra shows peaks corresponding to the elements C1s, O1s, F1s, P2p, B1s, and Cl2p from polyfuran and different supporting electrolytes; $N(Bu)_4PF_6$, $N(Bu)_4BF_4$, and $N(Et)_4ClO_4$ are clearly visible (Figs. 3–8). These data confirm the presence of PF_6^-, BF_4^-, and ClO_4^- ions in the deposit prepared in the doped form. The XPS results also show that the counterion is always present, and that no positive charge is located on an atom. This charge should thus be delocalized on the polymeric chain.[6]

EPMA study

Results from EPMA study corresponded to homogeneous parts of the samples, which were simultaneously corroborated by SEM visualization. The average values obtained for different electrodeposition conditions are reported in Table II. It can be seen that the O/C ratio is about 0.34 ± 0.05, which means there is a systemic oxygen excess, given that the theoretical ratio is 0.25.

This increase in oxygen amount confirms that the samples might be contaminated, even in the case of ClO_4^- doping, when $TEAClO_4$ is used as support electrolyte, which can be a source of oxygen in the polymer.

Microanalysis results for the various electrolyte anions in Table III agree with a polymer structure of polyfuran containing 19 monomeric units per counterion when the electrolyte anion is PF_6^-, five monomeric
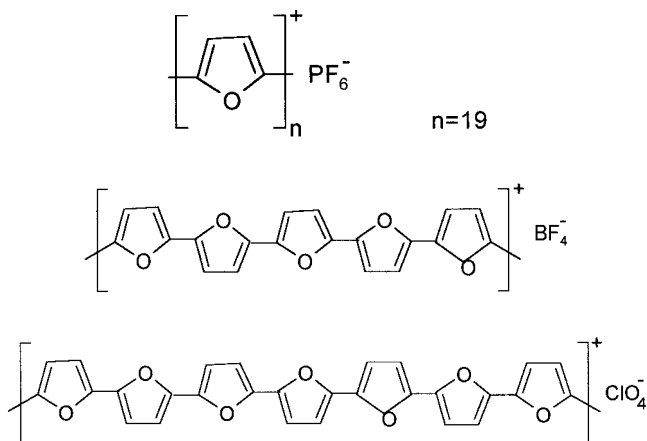
TABLE II
Averaged EPMA Analysis of PFu Obtained Under Different Experimental Conditions

Electrolyte anion (dopant)	Doping	Monomer concentration [M]	Electrolyte concentration [M]	Atomic ratio (O/C)
PF_6^-	doped	0.10	0.10	0.34
	undoped	0.10	0.10	0.35
BF_4^-	doped	0.10	0.05	0.35
	undoped	0.10	0.05	0.29
ClO_4^-	doped	0.10	0.10	0.36
	undoped	0.10	0.10	0.39

TABLE III
Oxidation Potential (E_{ox}) and Microanalysis of PFu Obtained from Solutions Containing Various Electrolytes

Electrolyte anion	E_{ox}/V	Normal wt %					
		C	O	F	P	B	Cl
PF_6^-	2.10	54.36	24.15	6.20	1.95		
BF_4^-	2.90	50.46	23.16	6.81		2.61	
ClO_4^-	2.53	50.69	27.82				5.77

units per counterion when the electrolyte anion is BF_4^-, and seven monomeric units per counterion when the electrolyte anion is ClO_4^-. These data led us to propose the following structures for polyfuran obtained using different support electrolytes:

$$\left[\begin{array}{c}\text{furan ring}\end{array}\right]_n^+ PF_6^- \quad n=19$$

$$\left[\begin{array}{c}\text{furan rings}\end{array}\right]^+ BF_4^-$$

$$\left[\begin{array}{c}\text{furan rings}\end{array}\right]^+ ClO_4^-$$

Data in Table III confirm that the monomer oxidation potential changes considerably depending on the electrolyte anion. This behavior can be explained considering the basic character of the anion: if it is greater, proton extraction (which is the determining step in the oligomerization process) will be easier,[16] thus a lower E_{ox} is necessary.

SEM study

Scanning electron micrographs of doped and undoped polyfuran films obtained in the presence of PF_6^- (Fig. 9), BF_4^- (Fig. 10), and ClO_4^- (Fig. 11) show a wide variation of surface morphology of these films, thus emphasizing the influence of the nature of the electrolyte anion, and monomer or electrolyte concentration on polymer growth. Electropolymerization produces regions in the films with different growth rates. Similar growth behavior has been observed in the case of polythiophene[21,22] and polyselenophene,[23] which are now discussed.

Doping effect

Results obtained using $0.1M$ furan and $0.1M$ TBAPF$_6$ are illustrated in Figure 9(a) and (b), which corre-

spond to the doped (E = 2.13 V) and undoped (E = −0.1 V) polymer, respectively. It is observed that both polymers show a similar morphology, with a regular and homogeneous surface. Notice that the doped polymer presents a more swollen structure, as expected for a polymer doped with PF_6^-.

Figure 10(a) and (b) illustrate the behavior of polyfuran obtained from solutions containing $0.1M$ in furan and $0.05M$ TBABF$_4$, doped (E = 2.9 V) and undoped (E = −0.1 V), respectively. Different morphologies are observed with a certain degree of swelling in the doped polymer, indicating the presence of BF_4^- as the dopant ion. On the other hand, the undoped polymer shows a homogeneous structure with holes, indicating the release of the dopant.

a
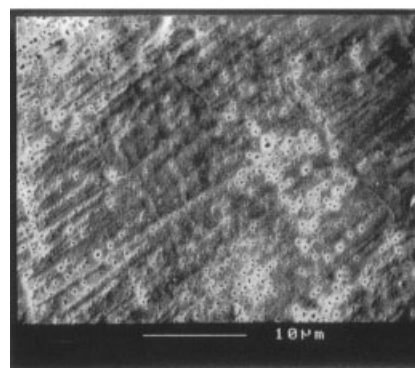
b

Figure 9 Polyfuran potentiostatically obtained from $0.10M$ furan + $0.10M$ Bu$_4$NPF$_6$ in CH$_3$CN: (a) doped, E = 2.13 V; (b) undoped, E = −0.1 V.
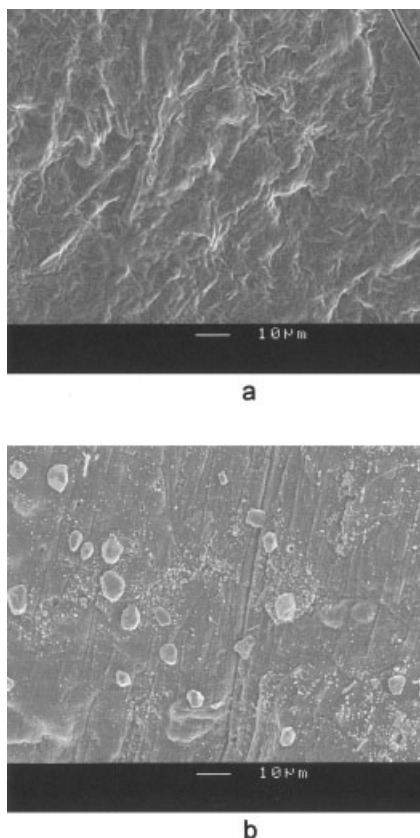
Figure 10 Polyfuran potentiostatically obtained from $0.10M$ furan $+ 0.05M$ Bu$_4$NPF$_6$ in CH$_3$CN: (a) doped, $E = 2.9$ V; (b) undoped, $E = -0.1$ V.

Figure 11(a) and (b) show the behavior of the polymer prepared from solutions containing $0.1M$ in furan and $0.1M$ TEAClO$_4$, doped ($E = 2.53$ V) and undoped ($E = -0.1$ V), respectively. It may be observed that the doped polymer shows a higher degree of swelling, which becomes evident as expected after the doping process with ClO$_4^-$ anions. The undoped polymer presented a porous texture this can be attributed to the "memory" of the polymer.

In all cases the doped polymer shows a degree of swelling higher than that of the undoped polymer. The presence of holes in the latter case is the consequence of the release of the anion confirming the "memory" of the polymer. The films had a rough appearance attributed to different growing layers. Confirmation of these phenomena is provided by nucleation and growth mechanism studies currently under way.

It is also important to notice that the nature of the electrolyte cations does not affect the obtained deposit because it is a *p*-doping polymer. It was demonstrated by comparing polyfuran obtained from solutions containing $0.10M$ tetramethylammonium tetrafluoroborate with polyfuran obtained from solutions containing $0.10M$ Bu$_4$NBF$_4$, because no difference was ascer-

tained in either voltammetric or in potentiostatic profiles or in microphotographs.

Similar studies have been done on other polymers such as polythiophene (PTh).[22] If we compare the results obtained for PTh to those obtained in the present work, it can be seen that under analogous conditions the current in voltammograms is always lower for furan, which means that PFu is less conductive than PTh. These experimental results are in agreement with the results obtained by Tournillon.[6]

Under the experimental conditions used to register the current–time transients during furan electropolymerization through potentiostatic pulses, the contribution of several nucleation and growth mechanisms becomes evident and their dependency with analyzed variables is analogous to that previously described for thiophene.[22]

CONCLUSIONS

As previously described for other polyheterocycles attainment of polyfuran strongly depends on the electrode substrate and on the working conditions used during monomer electrooxidation, particularly the absence of water in the electrolytic medium. These con-
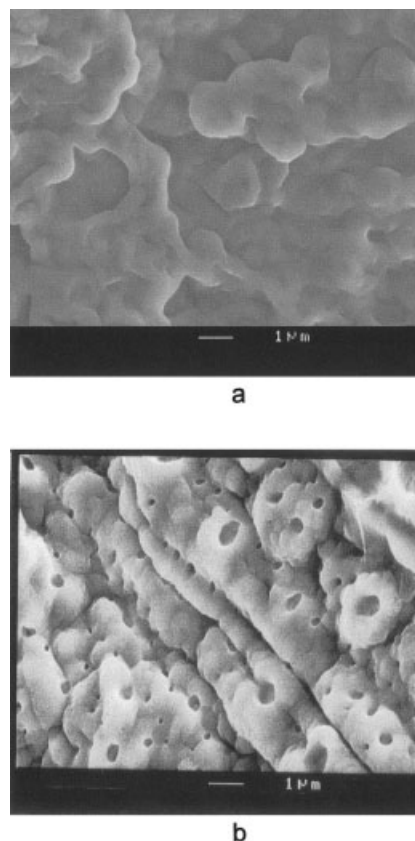

Figure 11 Polyfuran potentiostatically obtained from $0.10M$ furan $+ 0.10M$ Bu$_4$NClO$_4$ in CH$_3$CN: (a) doped, $E = 2.53$ V; (b) undoped, $E = -0.1$ V.

ditions induce a change in its morphology and, consequently, in its macroscopic properties. Therefore, if the variables are not carefully controlled during the electrodeposition process very different properties will be obtained. This explains the production of polymers with diverse properties, even though they are obtained from the same monomer.

Thus, it is possible to confirm the variables that control the electropolymerization process (potential, concentration, electrolyte, etc.) to determine the quality of the deposit and the morphology of the polymeric film.

Scanning electron micrographs of doped and undoped polyfuran show an important surface morphology variation, emphasizing the influence of the nature of the electrolyte anion on polymer growth. Electropolymerization produces regions in the films with different growth rates, corroborated by the current nucleation and growth mechanism study now under way.

The doped polymer exhibits a degree of swelling and the undoped polymer shows holes on the polymeric surface.

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