SEM Study of the Growth of Electrochemically Obtained Polythiophene Thin Films: Effect of Electrolyte and Monomer Concentration in Acetonitrile

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ABSTRACT: The initiation of the electrochemical growth of polythiophene thin films was studied by X-ray photoelectron spectroscopy (XPS), electron probe micro analysis (EPMA), and mainly by scanning electron microscopy (SEM). The films were deposited on SnO_2-coated glass in a classical three-electrode cell. Depositions were done under pure argon atmosphere. Two electrolytes were tested, tetrabutyl ammonium hexafluorophosphate (Bu_4NPF_6) and tetramethylammonium hexafluorophosphate (Me_4NPF_6) in anhydrous acetonitrile. The effect of the electrolyte, and monomer and electrolyte concentration, on the film properties were visualized. These results are discussed with the help of the other characterization techniques. It is shown that for optimum concentration ($0.05M$ monomer and $0.05M$ electrolyte), two processes are active, one three-dimensional (3D) and one two-dimensional (2D). When the monomer concentration is increased, a third 3D contribution is presently active. When the electrolyte concentration increases, there is some electrolyte crystal precipitation on the synthesized polymer films. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1799–1809, 2002; DOI 10.1002/app.10291

Key words: polythiophene; electrochemistry; scanning electron microscopy; electrodeposit; electrooxidation

INTRODUCTION

In comparison with other chemical and electrochemical syntheses of conducting poly(heterocycles), the anodic electropolymerization presents several distinct advantages, such as absence of catalyst, direct grafting of the doped conducting polymer onto the electrode surface (which is of particular interest for electrochemical application), easy control of the film thickness by the deposition charge, and the possibility of performing a first *in situ* characterization of the growing process of the polymer by electrochemical techniques.

The electropolymerization of five-membered heterocycles involves many experimental variables, such as the solvent, reagent concentration, nature and shape of the electrodes, and applied electrical conditions. As a consequence of the diversity of these parameters and of the complexity

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of the electropolymerization pathways, electrosynthesis conditions determine to a large extent the structure and properties of the resulting polymer. However, because of the interdependence of many of the experimental variables, the analysis of the effects of an individual parameter and hence the optimization of electrosynthesis conditions constitutes a complex problem.[1]

In recent years, a number of articles involving aspects related to the preparation, characterization, and possible applications of conducting polymers have been published. In particular, polythiophene (PTh) and its derivatives were the subject of several studies.[2–5] Despite detailed studies concerning the physical, chemical, electronic, and electrochemical properties of PTh, PTh derivatives, and other conducting polymers, relatively few studies on the nucleation and growth mechanism (NGM) during the anodic electropolymerization of these polymers can be found in the literature, although the current response in a potential step experiment may be conveniently used to monitor and elucidate the kinetics of deposition. Despite the fact that the observation of characteristic deposition details are important for the understanding of the structure, quality, and properties of the film, these aspects are not yet fully recognized. Schrebler et al.[6] studied the nucleation and growth mechanisms of polythiophene, reporting the effect of electrolyte and monomer concentration in dichloromethane. The results in this work confirm the stated principles of how the global process of NG of PTh over Pt occurs. Parameters such as applied potential, monomer concentration, and nature and concentration of electrolyte media used, as well as the time considered in the analysis of the results, clearly have an effect over the different contributions present in
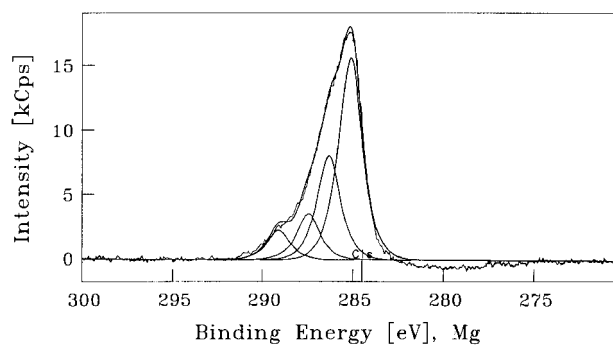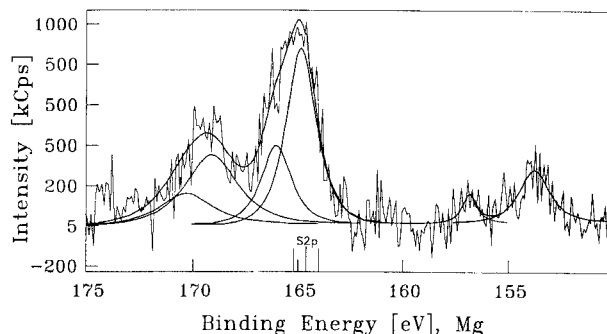

Figure 2 S2p core level spectra of PF_6^- doped polythiophene.

the electropolymerization process. The IN3D contribution, in all situations analyzed, is the prevailing mechanism. However, the other two contributions [charge transfer control with a two-dimensional, IN2D, and a progressive nucleation with three-dimensional (3D) growth mechanism under diffusion control, PN3D) could be made more or less important depending upon conditions which would make it possible to correlate them with the structure or morphology of the polymer to be obtained.[6]

The present study is related to the study of the growth mechanism of polythiophene by scanning electron microscopy (SEM). Some results of X-ray electron spectroscopy (XPS), electron microprobe analysis (EPMA), and X-ray diffraction studies are also discussed.

We report the results obtained in the electropolymerization of PTh on SnO_2 (conductor glass) electrode by using acetonitrile media with electrolytes such as Bu_4NPF_6 and Me_4NPF_6. Although the electropolymerization technique used was cyclic voltammetry, it was in general terms compared with the behavior obtained in the potentiostatic method.[6]

EXPERIMENTAL

Electrochemical Techniques, XPS, SEM, EPMA

The setup for cyclic voltammetry was described previously.[7] A SnO_2 (geometrical area, 2 cm²) and an Ag/AgCl in tetramethylammonium chloride (Me_4NCl)[8] were used as working and reference electrodes, respectively. The potentials with respect to the latter were corrected to that of the saturated calomel electrode (SCE). A Pt gauze, separated from the working electrode compart-
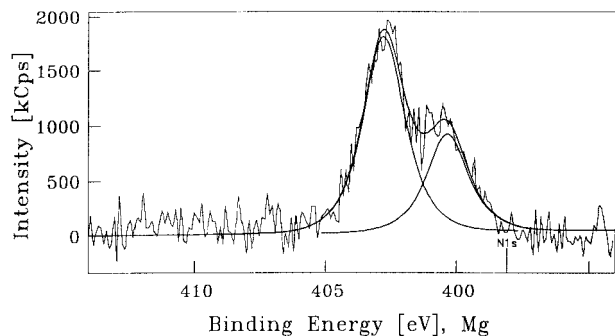

Figure 1 C1s core level spectra of PF_6^- doped polythiophene films. The features through the data correspond to the fitting with Gaussian functions.

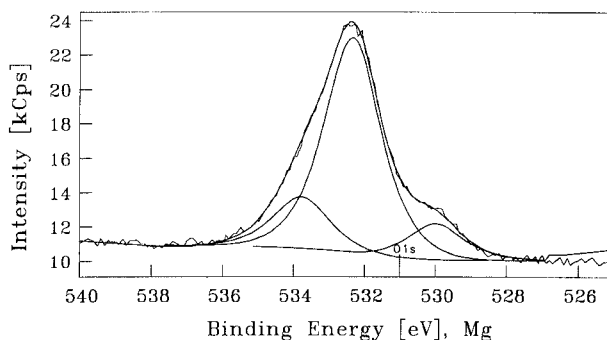**Figure 3** N1s core level spectra of PF_6^- doped polythiophene.

Figure 5 O1s core level spectra of PF_6^- doped polythiophene.

ment by a fine glass frit, was used as a counter electrode.

Before each experiment, the working electrode was cleaned with a mixture of acetone, ammonium, and H_2O_2, with application of heat. Prior to all the experiments, solutions were purged with high-purity argon and an argon atmosphere was maintained over the solution during the measurements.

Anhydrous acetonitrile (Aldrich, HPLC grade) was stored in an atmosphere of dry argon and over a generous amount of molecular sieves (4 Å). To ensure a minimum water content, the solvent was manipulated by syringe. The same procedure was applied to thiophene (Aldrich) and all the solutions employed. The background electrolytes were tetrabutyl ammonium hexafluorophosphate (Bu_4NPF_6) and tetramethyl ammonium hexafluorophosphate (Me_4NPF_6), supplied by Aldrich. The electrochemical polymerization and deposition of PTh was carried out from solutions containing $0.05–0.1M$ monomer and $0.05–0.1M$ background electrolyte. Polymerization was achieved by cyclic voltammetry (potentials between 0.00 and 2.00 V at 10 mV·s^{-1}).

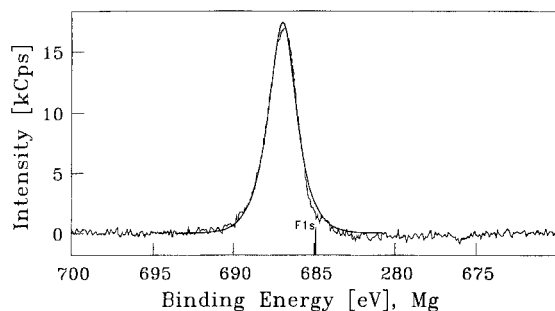Electron microprobe analysis (PGT-IMIX PTS model) was used to determine the composition of the films. For the observation of their surface and cross-section morphology, a JEOL-type JSM 6400F SEM was employed.

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, S2p, N1s, O1s, P2p, and F1s regions of the spectrum. The quantitative analysis was based on the determination of the C1s, S2p, N1s, O1s, P2p, and F1s peak areas with 0.2, 0.44, 0.36, 0.6, 0.31, and 1 as sensitivity factors. The vacuum in the analysis chamber was about 10^{-6} Pa. All the spectra were recorded under identical conditions. The decomposition of the XPS peaks into different components and the quantitative interpretation were performed after substration of the background by using the Shirley method.[9] The developed curve-fitting programs allow the variation of parameters, such as the Gaussian-Lorentzian ratio, the full width at half-maximum (FWHM), the posi-

Figure 4 F1s core level spectra of PF_6^- doped polythiophene.

Table I   XPS Quantitative Analysis of a SnO_2 Underlayer after Scratching of the Electrochemically Deposited Polythiophene

SnO_2	Relative Atomic (%)				
	Sn	O	P	F	N
Before etching	5.5	38.5	5.5	45.5	5
After 1 min of etching	26	50	6	14	4

Table II   Averaged EPMA Analysis

Thiophene Concentration	TMAPF$_6$ Concentration	Number of Cycle	At. Ratio S/C
[0.05]	[0.05]	3	0.21
[0.05]	[0.05]	4	0.22
[0.05]	[0.1]	4	0.23
[0.05]	[0.1]	5	0.24
[0.1]	[0.05]	3	0.22
[0.1]	[0.05]	4	0.22

Thiophene Concentration	TBAPF$_6$ Concentration	Number of Cycle	At. Ratio S/C
[0.05]	[0.1]	2	0.22
[0.05]	[0.1]	5	0.20
[0.1]	[0.05]	2	0.21
[0.1]	[0.05]	5	0.24
[0.1]	[0.1]	3	0.21

tion, and the intensity of the contribution. These parameters were optimized by the curve-fitting program.

To check the surface contamination, some etching was done. Sputtering was accomplished at pressures of $< 5 \times 10^4$ Pa, a 10-mA emission current, and a 3-kV beam energy using an ion gun. With these experimental conditions, all the surface of the samples were sputtered.

RESULTS AND DISCUSSION

Some properties are more or less similar for all the samples studied; therefore, they will first be presented and then more specific results will be discussed separately for each sample.

XPS Study

As said above, the aim of the present work was to contribute to the study of the nucleation and
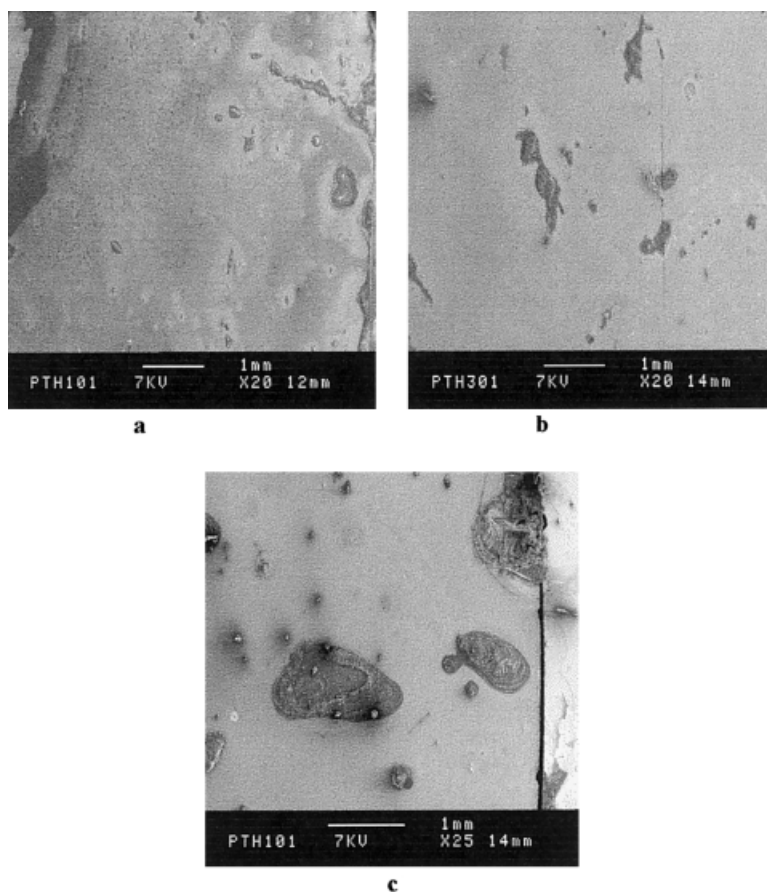

Figure 6   Effect of the voltammetric cycle number (small enhancement). Electrochemical conditions: [thiophene]/[TBAPF$_6$] : [0.05/0.05]M, cycle number: (a) 1 cycle; (b) 3 cycles; and (c) 10 cycles.
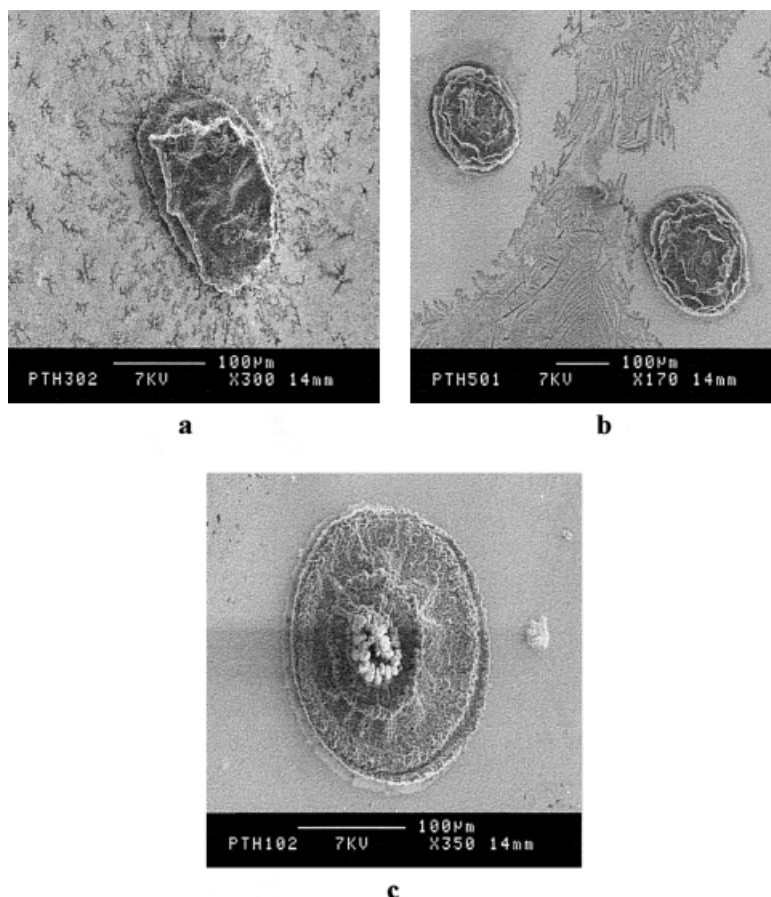
Figure 7 Visualization of nucleus surrounded by thin growing arborescence. Electrochemical conditions: [thiophene]/[TBAPF$_6$] : [0.05/0.05]M, acetonitrile, SnO$_2$, cycle number: (a) 3 cycles; (b) 5 cycles; and (c) 10 cycles.

growth of polythiophene. Therefore, the samples were studied after a few voltammetric cycles (1–10) and the films were far from covering the whole substrate surface, which means that the surface analyzed by XPS corresponds not only to the polymer surface but also to the substrate surface. Therefore, surface quantitative analysis does not correspond to polymer composition, while the peak decomposition should be used very carefully. The example developed here corresponds to polymer obtained after 10 voltammetric cycles (i.e., the maximum number of cycles used in the present work) to obtain the higher substrate coverage.

The carbon peak C1s can be decomposed in four components (Fig. 1); the first one situated at 285 eV corresponds to C—C bonds and will be used as reference.[10] In fact, because the binding energy of the C—S bonds is only 0.3 eV greater than that of C—C, the resolution of the decompo-

sition software is not accurate enough to discriminate between C—C and C—S bonds.

The second contribution situated at 286.15 eV can be assigned, at least partly, to positively charged carbon. This C$^+$ is formed by polymer doping. However, as shown below by EPMA, the relative dopant concentration cannot explain the high relative percentage of this contribution (27 at. % of the C bonds), and therefore, some other contribution should be present, such as C—OH, related to surface contamination. The two other contributions are also related to contamination. The third at 287.3 eV can be assigned to C=O bonds, whereas the fourth at 289 eV corresponds to COOH.

The decomposition of the S2p core-level spectrum (Fig. 2) leads to two doublets (S2p$_{3/2}$, S2p$_{1/2}$). The first one with binding energies lying at 164.6 and 165.8 eV for S2p$_{3/2}$ and S2p$_{1/2}$, respectively, corresponds to covalent sulfur in the ring carbon
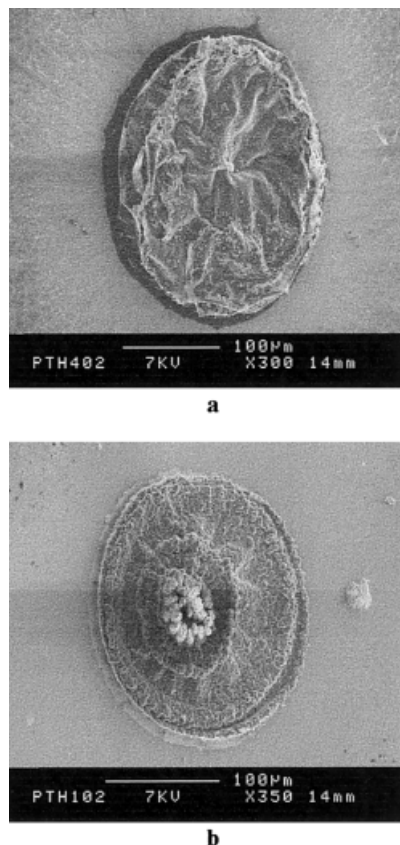
Figure 8 Visualization of specific nucleus: Electrochemical conditions: [thiophene]/[TBAPF$_6$] : [0.05/0.05]M, acetonitrile, SnO$_2$, cycle number: (a) 4 cycles; and (b) 10 cycles.

atoms. The second small doublet with 168.9 and 170.1 eV as binding energies can be assigned to positively charged sulfur. However, it cannot correspond to a positive charge induced by doping because the binding energy shift related to covalent sulfur is more than 4 eV, which corresponds to highly oxidized sulfur. After an etching of 1 min, this oxidized contribution disappears, which means that it corresponds only to a surface phenomenon.

A small percentage of nitrogen was detected and the nitrogen should be decomposed in two contributions (Fig. 3). The first one situated at 400.1 eV corresponds to covalent nitrogen and could be attributed to air contamination or (more probably) to some solvent contamination of the film.

The second contribution at 407.5 eV corresponds to positively charged nitrogen and could correspond to the presence of some electrolyte salt in the films. Some fluor is also present (Fig. 4); it corresponds to the dopant counter ion PF$_6$.

The oxygen O1s peak also can be broken down into three components (Fig. 5). The one situated at 530 eV corresponds to SnO$_2$,[11] which is logical because the substrate is only partly covered by the electrochemically synthesized polythiophene. The second component at 532.4 eV can be assigned at C=O bonds, whereas the third component situated at 533.8 eV corresponds to C—OH bands.

It should be noted that after scratching off the deposited polymer, XPS analysis of the SnO$_2$ underlayer shows that there is a strong contamination of the surface by PF$_6$ ions (Table I) (i.e., there is an oxidation of the SnO$_2$). It can be seen in Table I that before etching there is not only a strong oxygen contamination but also some nitrogen and PF$_6$ ions. Even after etching, although the ratio of Sn/O $\cong$ 1/2, which is the expected value, the contamination by N and PF$_6$ ions stays significant. This means that before thiophene polymer deposition there is oxidation of the substrate, which is in good agreement with previous studies.[12]

EPMA Study

The results discussed correspond to homogeneous parts of the samples; the results will be exposed simultaneously with SEM visualization.

The averaged values obtained for different electrodeposition conditions are reported in Table II. It can be seen that the ratio of S/C is about 0.22 $\pm$ 0.02, which means that there is systemically a small sulfur deficiency because the theoretical ratio is 0.25. This small deficiency and the detection of 2–4 at. % of N and O confirms that the samples are contaminated by some solvent, electrolyte salt, oxygen compounds, and others.

Moreover, some fluorine and phosphor are also detected (3 < F at. % < 10); they are present in the atomic ratio [F]/[P] $\cong$ 6. It is interesting to note that the F/P ratio in Table I is about 2.3 after 1 min of etching and 8.3 before etching. When the number that belongs to the contamination (after etching) is subtracted from that obtained before etching, the F/P ratio of exactly 6.0 is obtained, which corresponds to the dopant counter ion.

Therefore, after XPS and EPMA analysis measurements, it can be said that polythiophene was synthesized electrochemically and a description of the nucleation and growth (NG) study by SEM will be developed below.
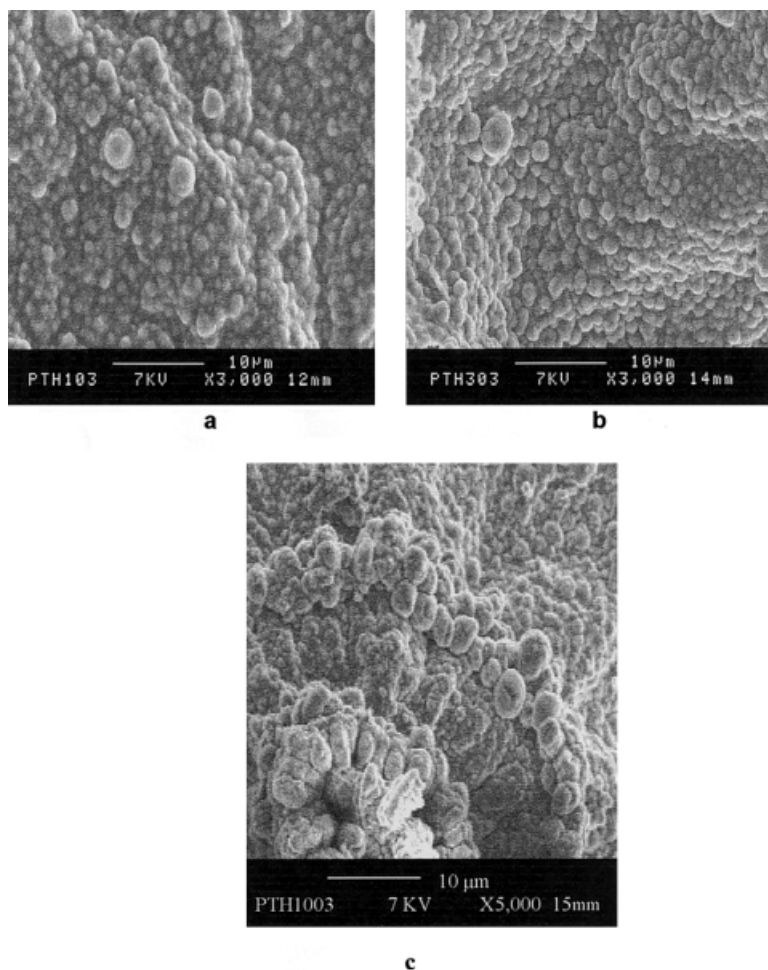
Figure 9   Effect of the cycle number (large enhancement). Electrochemical conditions: [thiophene]/[TBAPF$_6$] : [0.05/0.05]M, acetonitrile, SnO$_2$, cycle number: (a) 1 cycle; (b) 3 cycles; and (c) 10 cycles.

SEM Study

Effect of the Number Voltammetric Cycles

For thiophene monomer and TBAPF$_6$ electrolyte concentration of [0.05]M during the first cycles, there is polymer growth on nucleation sites randomly distributed on the SnO$_2$ underlayer (Fig. 6). It should be noted that the surface of the SnO$_2$ films is quite rough. All these rugosities have been shown to be nucleation sites for the upper layer.[13] This induces a strong interaction between the SnO$_2$ layer and the growing polymer at a microscopic scale, which induces nucleation on activated SnO$_2$ sites. These sites are activated during oxidation cycles, because it was shown by XPS that the SnO$_2$ surface is oxidized by PF$_6$ ions at the deposition initiation (Table I). When the number of cycles increases, the nucleus size increases and the nucleus coalesce. However, as shown Figure 7, the nuclei corresponds to more than one form. Around the more or less circular and thick nucleus appears thin arborescence. Although the central nucleus appears 3D (Fig. 8), the arborescence looks like a two-dimensional (2D) process.

It should be noted that whatever the nucleus size is, the large enhancement allows us to see that the polymer exhibits the same well-known cauliflower-like appearance of polythiophene (Fig. 9).[14] When the number of cycles increases, upper structures appear which corroborate the 3D NG.

It should be noted that the results discussed above were obtained with TBAPF$_6$ as electrolyte salt. Similar results are obtained with TMAPF$_6$ as electrolyte salt. The nucleation on preferential
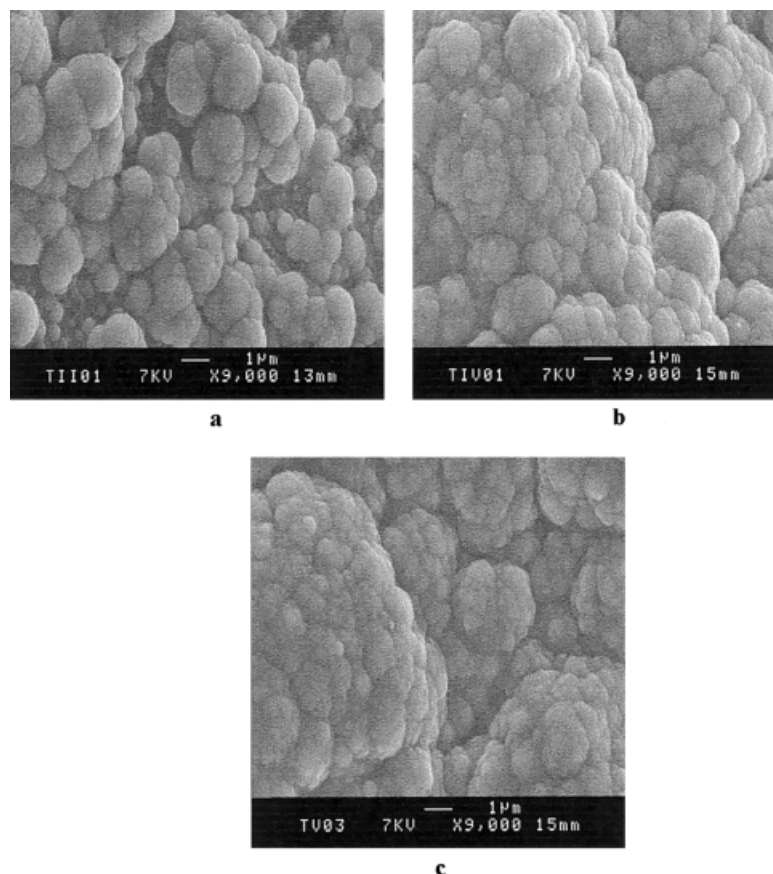
Figure 10   Visualization of films obtained with TMAPF$_6$ as electrolyte. Electrochemical conditions: [thiophene]/[TBAPF$_6$] : [0.05/0.05]M, acetonitrile, SnO$_2$, cycle number: (a) 2 cycles; (b) 4 cycles; and (c) 5 cycles.

site randomly distributed on the SnO$_2$ underlayer followed a nucleus growth in a 3D arrangement (Fig. 10), the cauliflower appearance being also systematical. However, arborescence is less numerous. Therefore, the influence of the electrolyte will appear more clearly through the study of the effect of electrolyte and monomer concentration.

Effect of Electrolyte and Monomer Concentration

We will first describe the films obtained with TBAPF$_6$ electrolyte. If the microphotograph of Figure 11, corresponding to the [0.05M/0.05M] concentrations, is used as reference, it can be seen that no sensible modification was introduced by increasing the electrolyte concentration (Fig. 11, [0.05M]/[0.1M]). An increase of the monomer concentration modifies the aspect of the polymer surface (Fig. 11, [0.1M]/[0.05M]). It seems that a new upper layer progressively covers the cauliflower-like structures. Although after five cycles, some structures with nest shape appear randomly distributed at the surface, after 10 cycles, these structures appear to cover nearly the whole underlayer.

When both concentrations (monomer and electrolyte) were increased, the films appear quite different: an underlayer constituted of small grains is covered with a small amorphous-like thin layer.

The results obtained with TMAPF$_6$ as electrolyte salt are summarized in Figure 12. Here also the microphotograph of the sample obtained with the concentration, [monomer][electrolyte] = [0.05M]/[0.05M], is used as a reference to discuss the other concentrations.

An increase of the electrolyte concentration ([0.05M]/[0.1M]; Fig. 12) induces the visualization of smooth crystallites in opposition with the cauliflower-like aspect of the polythiophene.
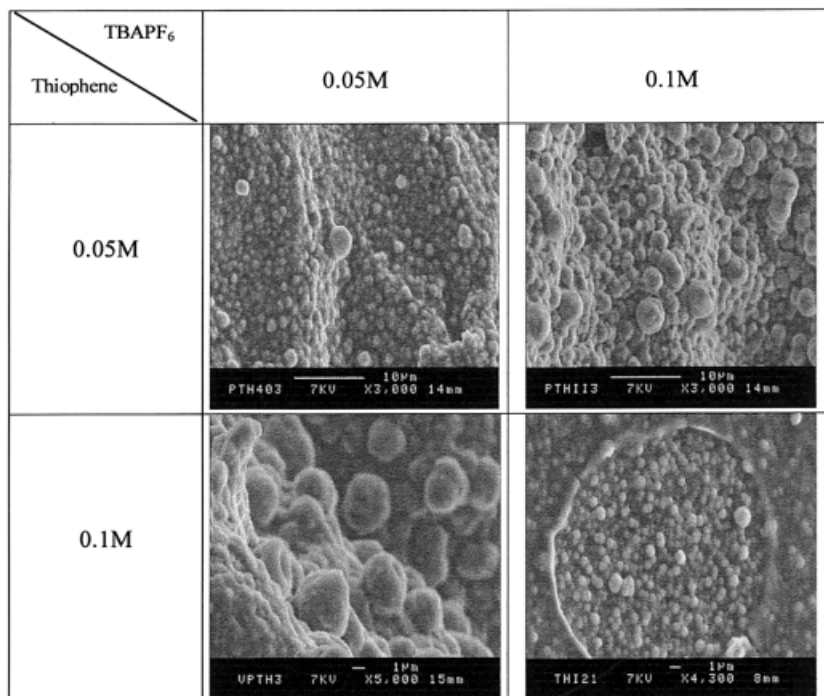
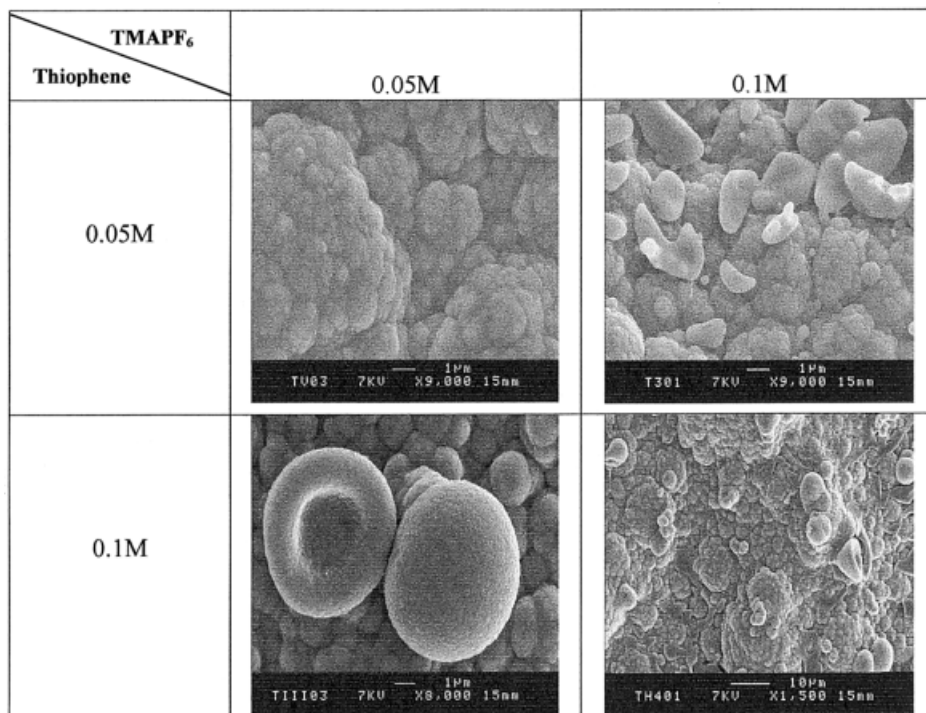**Figure 11**   Effect of the monomer and electrolyte concentrations [TBAPF$_6$].

Figure 12   Effect of the monomer and electrolyte concentrations [TMAPF$_6$].
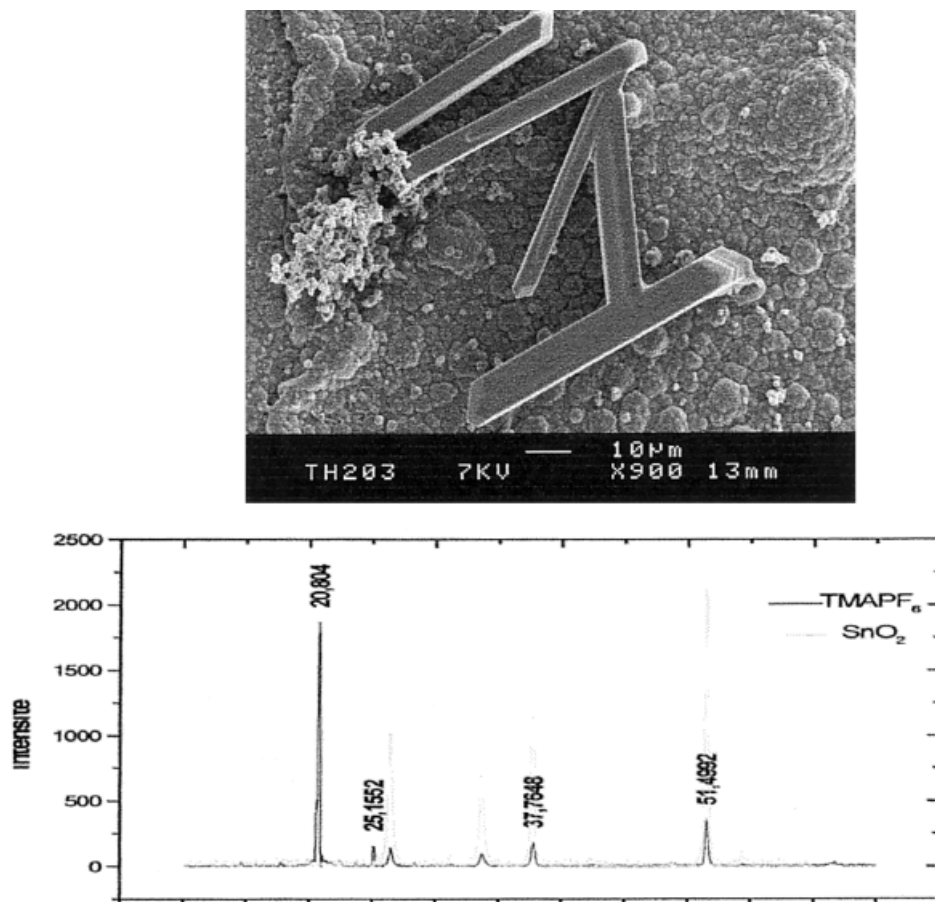
Figure 13 SEM and XRD of polythiophene. Electrochemical conditions: [thiophene]/ [$TBAPF_6$] : [0.1/0.1]M, cycle number: 2 cycles, acetonitrile; SnO_2 (work electrode), v = 500 mV/min, E = 2.00 V.

An EPMA study of such smooth structures gives a very high concentration of P and F and, what is more, an atomic ratio $\cong$ 1/6. This means that probably these crystallites correspond to electrolyte deposit.

A study by X-ray diffraction of this sample was performed. The diffractogram obtained (Fig. 13) exhibits not only the peaks of the SnO_2 under-layer but also a peak situated at 20.804 Å° which is typical of the electrolyte $TMAPF_6$ crystallized in the tetragonal structure (JCPDS 38-1729) fiche JCPDS structure,[15] which corroborates the fact that some electrolyte has crystallized at the sur-face of the polythiophene film. In $TBAPF_6$, the same phenomenon is observed.

When the monomer concentration increases, we can see in Figure 12 [0.1M]/[0.05M] that above the classical polythiophene matrix some cuplike features are visible. They have the same cauli-flower-like morphology as the polymer but with this specific cuplike shape. EPMA on such struc-tures shows that they correspond to polythio-phene. However, these cuplike structures have a sulfur concentration higher than in whole-poly-mer matrix, which means that they are not so contaminated as the other parts of the sample. These features show that a new NG process oc-curs in such experimental conditions. In the case of an increase of both concentrations (Fig. 12; [0.1M]/[0.1M]), the two families of perturbations are visible.

Discussion of the NG

NG mechanisms were studied by using another electrochemical technique (potential step).[6] The re-sults obtained presently for a function of cycle num-ber which can be considered similar to the electrol-ysis time of the reference study and for similar concentrations are very coherent (i.e., the morpho-

logical study confirms the contribution of more than one NG mechanism to the thin film growth, which is in complete agreement with preceding electrochemical studies on these materials).[6,16] It can be seen that in both these studies, the main contribution is tridimensional, below the control of carrier transfer and, when the deposition time increases, a new contribution appears below the control of diffusion, which can correspond to initial arborescence and then cauliflower-like structures.

The IN2D contribution, possibly associated with the deposition of short-chain oligomers (5 to 12 monomers units)[17,18] or to a strong interaction of the monomers with the electrode surface,[19] appears notably diminished in CH_3CN. This fact can be attributed to a stronger adsorption of CH_3CN molecules on the surface because of its higher polarity than of CH_2Cl_2 molecules, which produces a decrease of the monomers or short-chain oligomers adsorption, favoring the formation of a 2D ad-layer.[16]

CONCLUSION

It appears that in the present work optimum electrochemical synthesis conditions are achieved for concentrations [monomer]/[electrolyte]: [0.05M]/[0.05M]. The visualization of the films after 1, 2, 3, . . . , 10 cycles allows us to see that at least two NG processes, one 3D and one 2D. When the monomer concentration increases, a new NG process appears, a 3D. When the electrolyte concentration increases, there is a contamination of the film by salt crystals. This has been directly confirmed in the case of $TMAPF_6$.

The different parameters analyzed have a distinct effect on the contributions involved in the electropolymerization process and might become more or less important depending on these parameters, which would make it possible to correlate the structure and morphology of the obtained polymer. It is very important to consider these effects, especially that of the monomer or the electrolyte concentration. In the present work, it has been shown that a control of these variables is determinant for the obtainment of one kind or another of morphology.

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