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Effect Of Ultrasound Irradiation in Nucleation and Growth Mechanisms of Poly-*o*-Anisidine and Polyaniline

M. A. del Valle[1,*], *M. Romero*[1], *F. R. Díaz*[1], *F. Armijo*[1], *R. del Río*[1], *I. Núñez*[2], *E. A. Dalchiele*[2]

[1] Facultad de Química, Pontificia Universidad Católica de Chile, Av. V. Mackenna 4860, 7820436 Macul, Santiago, Chile
[2] Facultad de Ingeniería, Universidad de la República, Montevideo, Uruguay
[*]E-mail: mdvalle@uc.cl

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The current work studies the effect of ultrasound on nucleation and growth mechanisms (NGM) from the respective i-t transients obtained during the electro-polymerization of *ortho*-anisidine (OAN) and aniline (ANI), using a potentiostatic (potential step) approach. To this end, optimum electro-synthesis working conditions were searched for using cyclic voltammetry in the presence and absence of ultrasound radiation. The results revealed that ultrasonic disturbance has no effect on the oxidation potential of the starting units. In addition, i-t transients recorded at controlled potential are complex and their deconvolution revealed that both monomers studied herein consist of three contributions. However, it is noteworthy that when the system was irradiated with ultrasound, the respective NGM was not modified, since the same contributions are retained, only the time at which they are defined and the proportion with which each of them contributes to the total charge are altered. It was verified that the contribution most affected by ultrasound was that with diffusion-controlled growth, which is consistent with the morphology changes of the obtained polymeric deposits and the respective increase in the recorded currents during its electro-synthesis; this was explained by means of the proposed model of electro-polymerization based on oligomers solubility at the electrode/solution interface.

Keywords: poly(*o*-anisidine), polyaniline, electro-polymerization, nucleation and growth mechanisms, ultrasound irradiation.

1. INTRODUCTION

In recent years, conducting polymers have attracted considerable attention in the scientific ambit due to their versatility for diverse applications, *e.g.* rechargeable batteries, electro-catalysts, electro-chromic devices, photovoltaic cells, metal ion extraction, and so on. [1-6].

In each of these applications, the conductive polymer is supported on a substrate, which gives an advantage to electro-synthesis over other synthetic methods because enables obtaining the polymer directly on the electrode, without further treatment. In addition, it is important to understand, at molecular level, how the electro-deposition process takes place and to control the morphology of the electro-synthesized polymer. In reply to this challenge, our research group has been conducting a series of studies concerning the effect on the nucleation and growth mechanism (NGM) of experimental variables that govern the electro-polymerization process, *e.g.* applied potential, solvent, starting unity, monomer type and concentration, supporting electrolyte concentration and type, temperature [7-16]. Thereby, an electro-polymerization model was proposed, in which it is postulated that the determinant factor of this process is oligomer solubility at the electrode/solution interface: while the oxidation potential is applied, oligomers are generated at the interface; these oligomers will grow up to a critical chain length at which they become insoluble in the electrolytic solution and, consequently, they will precipitate onto the electrode surface, giving rise to nuclei that will carry on growing to afford the polymeric layer [7,11].

On the other hand, evidence exists regarding electrochemical synthesis of conducting polymers assisted by ultrasonic disturbance [17-23]. Pyrrole, thiophene or 3,4-ethylenedioxythiophene have been electro-synthesized by irradiating with high frequency ultrasound. A current increase during the respective potentiodynamic (cyclic voltammetry) and potentiostatic (potential step) syntheses was observed, being important to clarify that, by applying ultrasound to a system, the cavitation process is generated, which, in turn, leads to an increase in temperature of the system and thereby increase the speed of the processes involved in the electro-polymerization, being reflected in the current response obtained during the electro-synthesis, as previously reported [16]: it was pointed out that polymers synthesized under these conditions improve doping properties because the ultrasound irradiation increases the mass-transfer coefficient, producing polymer films with morphologies different than those obtained in the absence of ultrasound. The authors postulated that changes in the NGM at the early stages of electro-polymerization accounted for these morphological differences, although they did not make determination or systematic study of those mechanisms. Furthermore, it was established that ultrasound assisted electro-synthesis did not change the NGM since the same contributions found for i-t transients recorded during the potentiostatic synthesis in the absence of ultrasound persist. Only definition time of each contribution and its magnitude varies, leading to changes in the final morphology of the electro-synthesized polymer.

In order to contribute to the electro-polymerization model, contrasting this variable that obviously affects the solubility, a systematic study regarding the electro-polymerization of two monomeric units, poly(*o*-anisidine), POAN, and polyaniline, PANI, as a function of ultrasonic irradiation at constant temperature, is proposed. Thus, once electro-synthesis conditions are settled, the study would chiefly deal with the obtaining of i-t transients using potentiostatic method in the presence and absence of ultrasound, in order to analyze its effect on NGM and thereby, in its morphology to contrast, ultimately, the proposed electro-polymerization model that ascribes these changes to solubility at the interface [10,11].

2. EXPERIMENTAL

For the electro-polymerization a Metrohm electrochemical cell including a closed loop for circulating coolant (ethylene glycol: water = 50: 50) from a container through a filter and a thermostat-cryostat, which keeps the working temperature constant. A three-electrode assembly was employed: the working electrode was a 1 cm^2 geometric area sheet or a 0.07 cm^2 geometric area disk, both made of polycrystalline Pt. Ag|AgCl in tetramethylammonium chloride solution, whose concentration is adjusted so that its potential matches the potential of a saturated calomel electrode (SCE), was used as reference electrode [24]. Anyway, this electrode was removed from the work cell through a Luggin capillary, to avoid errors in the measurements recorded when ultrasound is applied. A large surface area, *c.a*. 10-fold greater than that of the working electrode, Pt coil was the auxiliary electrode. 3 $mol \cdot L^{-1}$ H_2SO_4 (Merck) solution in ultrapure water (resistivity 18.2 $M\Omega \cdot cm$) was utilized as supporting electrolyte. 0.05 $mol \cdot L^{-1}$ monomer solution of o-anisidine (OAN, Aldrich, $\geq$ 99% purity) and aniline (ANI, Aldrich, 99.5% purity) were prepared in the supporting electrolyte. To establish these conditions, a study in function of the concentration was perform, analyzing both the electrolyte concentration as monomer, finding that the maximum values of the currents recorded in potentiodynamic profiles were manifest when working under these conditions and also, an appreciable amount of polymer deposition is observed. Prior to each experiment, all solutions were flushed with high purity argon and, during the measurement an argon atmosphere was maintained above the working solution.

The optimum polymerization conditions (monomer and H_2SO_4 concentration and potential window) were determined by potentiodynamic method (cyclic voltammetry). This technique enables the optimum potentials at which nucleation and growth phenomena occur to be found. Electrochemical studies were performed on a Voltalab PGP200 potentiostat and three ultrasound sources were employed, namely one operating at 40 kHz frequency and 100 W ultrasonic power (Ultrasonic Cleaner YJ-120DT), another at 44 kHz and 140 W (Quantrex Q90 Ultrasonic Cleaning Systems) and, to generate high-frequency irradiation of 500 kHz and 1 W power, an "Olympus, immersion 0.5 MHz transducer, 1.00 inch diameter, coupled to an ENI 240L RF power amplifier (50 dB, 20 kHz-10 MHz)" was utilized.

The morphology of polymer films was analyzed by scanning electron microscopy (SEM) using a JOEL JSM-5900LV microscope, the deposits being supported on a 99% purity Pt foil.

3. RESULTS AND DISCUSSION

Fig. 1 shows the potentiostatic voltammetric profiles recorded during PANI and POAN synthesis with and without ultrasonic (U.S.) irradiation. Each step was performed keeping the temperature constant at 293 K to avoid cavitation phenomenon that may provoke an increase in the temperature of the system when subjected to ultrasound (40 kHz, and 100 W). Voltammetric profiles clearly highlight that there is no variation in the oxidation potential of the monomeric species since the oxidation peak observed in cycle one showed up at the same potential, with and without ultrasound

(950 mV for ANI and 670 mV for OAN), indicating this disturbance does not change the potential range within which the nucleation and growth phenomena take place.

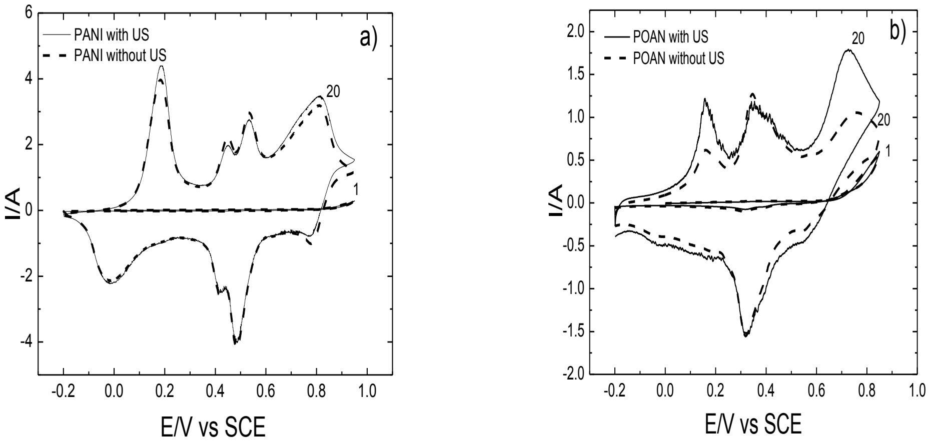

Figure 1. Potentiodynamic profiles recorded during the electro-oxidation of ANI and OAN with and without ultrasound irradiation, as shown in the insert. Interface: a) Pt| 0.05 mol·L^{-1} ANI + 3 mol·L^{-1} H_2SO_4; b) Pt| 0.05 mol·L^{-1} OAN + 3 mol·L^{-1} H_2SO_4. ν 100 mV·s^{-1}, T 293 K.

Similarly, it is noteworthy that a current increase was obtained in the voltammetric profiles when the electro-synthesis was carried out under high frequency ultrasound irradiation and is compared with profiles registered during the electrosynthesis in absence of U.S., after an equal number of successive cycles. This can be ascribed to the fact that U.S irradiation increases the mobility of the species, analogous to the phenomenon observed by Taouil *et al.* [17]; in a similar study, where doping properties were determined when the system was irradiated with ultrasound, they concluded that doping properties increased when this irradiation parameter was included, owing to an increase of the mass transfer coefficient that depends, precisely, on the diffusion layer thickness.

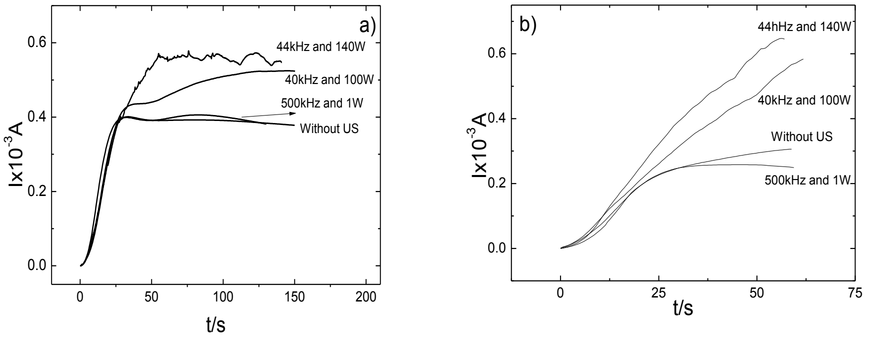

Figure 2. Effect of ultrasound on the i-t transients obtained during the electro-synthesis of a) PANI, Pt|0.05 mol·L^{-1} OAN + 3 mol·L^{-1} H_2SO_4, E 670 mV; b) POAN, Pt|0.05 mol·L^{-1} ANI + 3 mol·L^{-1} H_2SO_4, E 950 mV.

Figure 2 depicts the series of i-t transients recorded during PANI and POAN potentiostatic synthesis in the absence and presence of ultrasonic irradiation disturbances using different frequencies and powers, always at 293 K and within the potential range at which nucleation and growth of each monomer (determined from Fig. 1) occurs. Polymerization time was set until a steady current growth was observed. For OAN, this time cannot be longer than 70 s, because at longer times a second growth over the first polymeric layer takes place. This subject, however, is out of the scope of this study, because in the current work NGM in the early stages of the process will be established.

As seen in Fig. 2, when electro-synthesis is accomplished using high power and low frequency ultrasound irradiation, *e.g.* 40 kHz and 100 W and 44 kHz and 140 W, the obtained current is much higher that when synthesized in the absence of U.S., indicating that under these synthesis conditions U.S. has a very marked effect at the electrode/solution interface, increasing oligomers concentration in this region (the so called high-density oligomeric region, HDOR), making them to achieve critical chain length and concentration more quickly, favoring thus a more rapid oligomers precipitation upon the electrode surface.

Likewise, PANI and POAN were electro-synthesized under high frequency, low power U.S. irradiation (500 kHz and 1 W). The transients obtained were not significantly different from those recorded in the absence of U.S. This finding was attributed to lack of system cavitation at low power, since cavitation would be responsible for disrupting the electrode/solution interface that, in turn, would be reflected in the i-t response. This phenomenon was observed for both monomers.

The induction time, τ, the time required to achieve saturation of the HDOR (critical concentration and chain length), where oligomers are no longer soluble and precipitate on the electrode surface, generating the first nuclei and subsequent growth, are listed in Table 1. There, it is shown that for both monomers τ decreases slightly when operating at 40 kHz, 100 W and 44 kHz, 140 W, pointing out that under these conditions, the HDOR region saturates earlier and that is why deposits are generated faster than in the absence of U.S. irradiation. However, it was noted that synthesizing at 500 kHz and 1 W, τ exhibited a slight increase, revealing that high frequency U.S. emitted at low power levels has no bearing on the electro-deposition process.

Table 1. τ value during the electro-polymerization process illustrated in Fig. 2, as a function of U.S.

POAN (E 670 mV)		PANI (E 950 mV)	
US	τ /s	US	τ /s
without US	10.80 ± 0.25	without US	15.8 ± 0.2
500 kHz and 1 W	11.60 ± 0.15	500 kHz and 1 W	16.3 ± 0.1
40 kHz and 100 W	10.80 ± 0.25	40 kHz and 100 W	15.8 ± 0.2
44 kHz and 140 W	10.60 ± 0.30	44 kHz and 140 W	14.6 ± 0.3

As mentioned, to study further the effect of U.S. on the electro-polymerization, NGMs were determined from experimental i-t transients. To this purpose, the transient is considered from time □, whereby this value is taken as the origin of the curve i(0,0) and this portion of the plot is studied because this is the region that gives information concerning how nuclei are generated and their subsequent growth during the electro-polymerization [7-16].

Figure 3 shows i-t transients deconvolution recorded during the potentiostatic synthesis of PANI and POAN with and without ultrasound irradiation. As can be seen, transients are complex, as all reported to date [7-16], since its deconvolution revealed they are made up of more than one contribution along the electro-polymerization time. In the case of PANI electro-synthesized under the above conditions, it was found that the NGM consists of three contributions defined at different times. Initially, at short times, a two-dimensional nucleation with progressive growth (PN2D), responsible for the initial coating of the electrode surface that produces a compact polymer layer, is defined; subsequently, two contributions with progressive nucleation and three-dimensional growth, one charge transfer and the other diffusion controlled (PN3Dct and PN3Ddif, respectively) showed up.

As for POAN, alike to PANI, i-t transient deconvolution defined three contributions; namely, initially PN2D, followed by two nucleations with three-dimensional growth, one instantaneous and subsequently, another progressive. The growth is controlled by charge transfer and diffusion, respectively, *i.e.* $IN3D_{ct}$ and $PN3D_{dif}$.

Overall equations describing the current, *j*, response recorded during potentiostatic electro-synthesis of the corrected i-t transients for PANI and POAN, are represented by equations 1 and 2, respectively:

$$j = P_1 t^2[\exp(-P_2 t^3)] + P_3[1-\exp(-P_4 t^3)] + P_5 t^{-1/2}[1-\exp(P_6 t^2)] \qquad (1)$$

$$j = P_1 t^2[\exp(-P_2 t^3)] + P_3[1-\exp(-P_4 t^2)] + P_5 t^{-1/2}[1-\exp(P_6 t^2)] \qquad (2)$$

where P_1 and P_2 are the growth rate parameters for progressive nucleation with two dimensional growth (PN2D), P_3 and P_4 are the parameters of progressive and instantaneous nucleation with three-dimensional growth controlled by charge transfer (PN3Dct and IN3Dct)). P_5 and P_6 are the parameters of progressive nucleation with three-dimensional, diffusion-controlled growth (PN3Ddif). Expressions representing each of these parameters are as follows:

$$P_1 = \frac{\pi n F M H A N_0 K_g^2}{\rho} \qquad P_2 = -\frac{\pi A N_0 M^2 K_g^2}{3\rho^2} \qquad P_3 = nFK'_g$$

$$P_4 = -\frac{\pi M^2 K_g^2 A N_0}{3\rho^3} \qquad P_5 = \frac{ZFD^{1/2}C}{\pi^{1/2}} \qquad P_6 = -\frac{A N_0 \pi K D}{2}$$

where N_0 is the number of active surface sites, K_g rate constant of a nucleus, *A* nucleation rate constant (s^{-1}), *M* molar mass, ρ density of deposited material, *n* number of electrons transferred during electrodeposition, *F* Faraday constant, *h* height of the two-dimensional nuclei, *Z* charge of the deposited species, *K* and K'_g dimensionless constants of the deposited material, *D* diffusion coefficient and *C* monomer concentration.

This parameter values are different in each of the electro-synthesis conditions studied herein, indicating that the contributions present in the overall mechanism (NGM) of the process will be defined at different times and proportions. The values obtained for each of these parameters in Eqs. 1 and 2 in every synthesis condition are included in Tables 2 and 3, for PANI and POAN, respectively.

As seen in Fig. 3, where the continuous black line is the experimentally i-t transient obtained using potentiostatic electro-synthesis and the red dotted line the fitted simulated curve obtained from the deconvolution (the three mentioned contributions, whose addition makes up the respective NGM, are the ones that enable the accurate simulation of the experimental transient), the correlation between the experimentally obtained results and those derived from deconvolution is excellent, validating thus the obtained NGM such as in all previous studies [7-16].

Deconvolving each transients recorded during the respective electro-synthesis under ultrasound irradiation (500 kHz, 1 W, 40 kHz, 100 W, and 44 kHz, 140 W), it was found, just as in the absence of U.S., that the NGMs were maintained in all cases and only the time at which each contribution appeared and become defined were affected. This finding corroborates that U.S. irradiation does not modify the mechanisms, just affects nucleation and growth rate. It is noteworthy that this phenomenon was observed for both electro-obtained polymers (PANI and POAN), such as occurred for those previously reported [17-23].

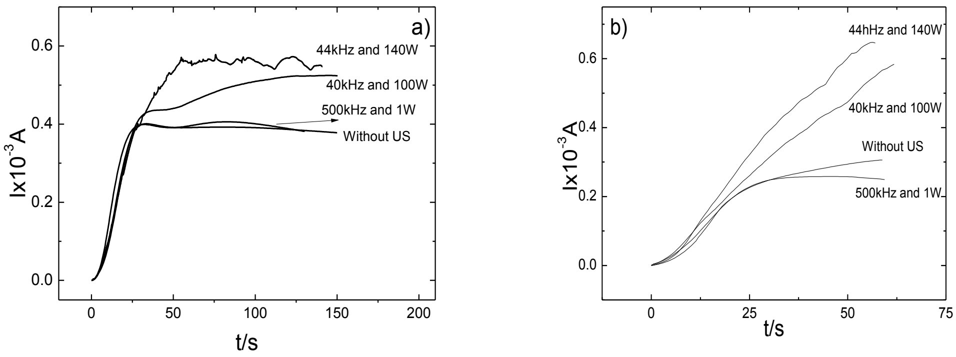

Figure 3. i-t transients deconvolution recorded during the electro-oxidation of a) ANI, at 293 K. Interface: Pt| 0.05 mol·L^{-1} ANI + 3 mol·L^{-1} H_2SO_4; b) OAN, at 293 K. Interface: Pt| 0.05 mol·L^{-1} OAN + 3 mol·L^{-1} H_2SO_4, under U. S. irradiation (44 kHz, 140 W).

Table 2. U.S. effect on Eq. 1 parameters (PANI NGM). Interface: Pt| 0.05 mol·L^{-1} ANI + 3 mol·L^{-1} H_2SO_4, at 293 K.

F/ kHz	P / W	P_1 / A·cm^{-2}·s^{-1}	-P_2 / s^{-3}	P_3 / A·cm^{-2}	-P_4 / s^{-3}	P_5 / A·s$^{1/2}$·cm^{-2}	-P_6 / s^{-2}	r^2
-	-	$1.08\cdot10^{-7}$	$2.35\cdot10^{-5}$	$2.94\cdot10^{-4}$	$2.30\cdot10^{-4}$	$1.00\cdot10^{-3}$	$3.38\cdot10^{-4}$	0.99892
500	1	$1.93\cdot10^{-7}$	$3.25\cdot10^{-5}$	$2.08\cdot10^{-4}$	$4.72\cdot10^{-4}$	$1.60\cdot10^{-3}$	$3.71\cdot10^{-4}$	0.99951
40	100	$4.69\cdot10^{-8}$	$4.08\cdot10^{-5}$	$3.69\cdot10^{-4}$	$3.01\cdot10^{-4}$	$1.90\cdot10^{-3}$	$1.52\cdot10^{-4}$	0.99865
44	140	$3.16\cdot10^{-7}$	$2.80\cdot10^{-4}$	$2.63\cdot10^{-4}$	$1.51\cdot10^{-4}$	$2.60\cdot10^{-3}$	$3.35\cdot10^{-4}$	0.99814

Figure 4 shows the effect of U.S. irradiation on the individual contributions making up the NGM obtained from i-t transients deconvolution recorded during PANI and POAN potentiostatic electro-synthesis. For both polymers it can be observed that PN2D presents a very noticeable difference when the process is subjected to the ultrasonic disturbance. When the process is performed under U.S. irradiation (44 kHz and 140 W), its definition is achieved at much shorter times than in the absence of the U.S. perturbation. As for PN3Dct, higher currents were obtained when the system was U.S. assisted and this trend increases as the power of U.S. generation does.

Table 3. U.S. effect on Eq. 1 parameters (POAN NGM). Interface: Pt| 0.05 mol·L^{-1} OAN + 3 mol·L^{-1} H_2SO_4, at 293 K.

F/ KHz	P / W	P_1 / A·cm^{-2}·s^{-1}	-P_2 / s^{-3}	P_3 / A·cm^{-2}	-P_4 / s^{-3}	P_5 / A·s$^{1/2}$·cm^{-2}	-P_6 / s^{-2}	r^2
-	-	$2.52\cdot10^{-7}$	$6.07\cdot10^{-5}$	$2.45\cdot10^{-4}$	$1.48\cdot10^{-3}$	0.8266	$6.00\cdot10^{-8}$	0.99976
500	1	$1.67\cdot10^{-7}$	$5.82\cdot10^{-5}$	$6.95\cdot10^{-5}$	$1.54\cdot10^{-3}$	0.7938	$3.68\cdot10^{-7}$	0.99947
40	100	$2.83\cdot10^{-7}$	$4.49\cdot10^{-5}$	$1.99\cdot10^{-4}$	$2.67\cdot10^{-3}$	1.5400	$1.00\cdot10^{-6}$	0.99970
44	140	$2.43\cdot10^{-8}$	$2.56\cdot10^{-5}$	$2.75\cdot10^{-4}$	$2.31\cdot10^{-3}$	2.6000	$1.11\cdot10^{-6}$	0.99946

The same behavior was evidenced for $PN3_{dif}$: highest current values are achieved when the system is U.S disturbed, corroborating that U.S. irradiation has a bearing on the electro-polymerization process rate, but with NGM change. This should be reflected in the morphology of the electro-coating, as reported by Taouil *et al*. [19] that electro-synthesizing polypyrrole under high frequency U.S. irradiation, found an increase of current values during both potentiodynamic (cyclic voltammetry) and potentiostatic (potential step) synthesis. Electro-deposits SEM morphological analysis revealed the films obtained under U.S. irradiation were more compact and homogeneous than those obtained under "soundless" (without ultrasound) conditions. These results were ascribed to NGM changes in the early stages of the electro-polymerization, but as already mentioned, they did not determine these NGM.

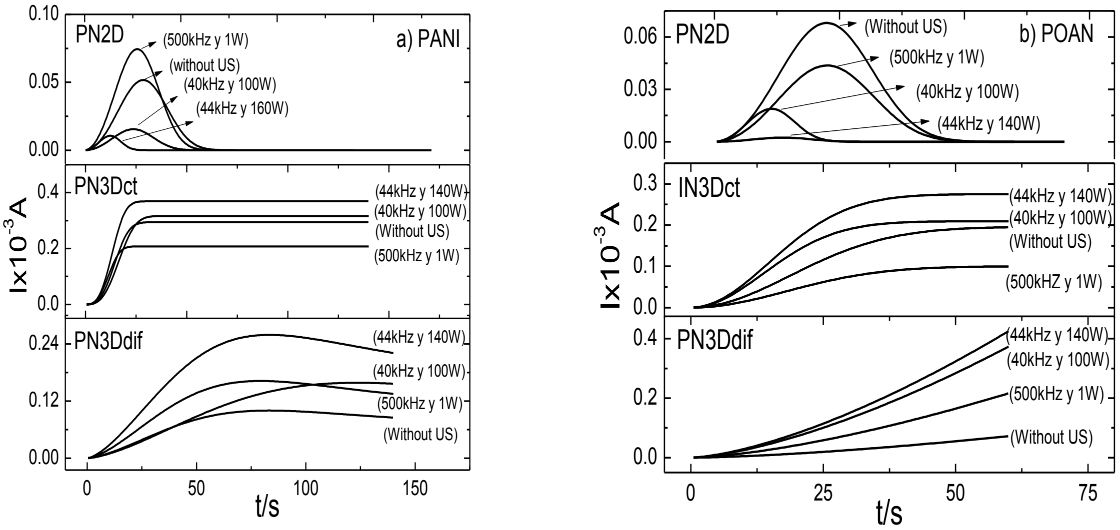

Figure 4. Effect of ultrasound on each NGM contribution of a) PANI. Interface: Pt| 0.05 mol·L^{-1} ANI + 3 mol·L^{-1} H_2SO_4, b) POAN. Interface: Pt| 0.05 mol·L^{-1} OAN + 3 mol·L^{-1} H_2SO_4, at 293 K.

In the current work it is corroborated that indeed U.S. does not modify the NGM, but rather the time at which each of these contributions are defined, moving forward the different involved processes, by increasing species mobility and thereby HDOR faster growth rate and shorter saturation time.

To confirm the effect of U.S. on the morphology of polymers electro-synthesized from the monomers studied in this survey, SEM was also performed to electro-synthesized polymer deposits obtained with and without U.S. irradiation (44 kHz and 140 W), in order to establish if a correlation exists with that predicted by the NGM determined herein.

Figure 5 exhibits SEM images of electro-synthesized PANI polymeric deposits at 293 K in the presence and absence of ultrasonic disturbance, 44 kHz and 140 W. As perceived there, the polymeric deposits obtained in the presence of U.S. are more compact and homogeneous compared to those produced in the absence of U.S., as in similar works reported elsewhere that utilized U.S. during the electrochemical synthesis from other monomers (pyrrole, thiophene, 3,4-ethylenedioxythiophene) [17-21]. As mentioned, these authors attributed the morphological differences to NGM changes at the early stages of the polymerization, but without studying it. However, in the current work it was demonstrates that ultrasonic irradiation does not change the NGM, only affects the rate at which each contribution is defined, which in turn is reflected in its morphology.

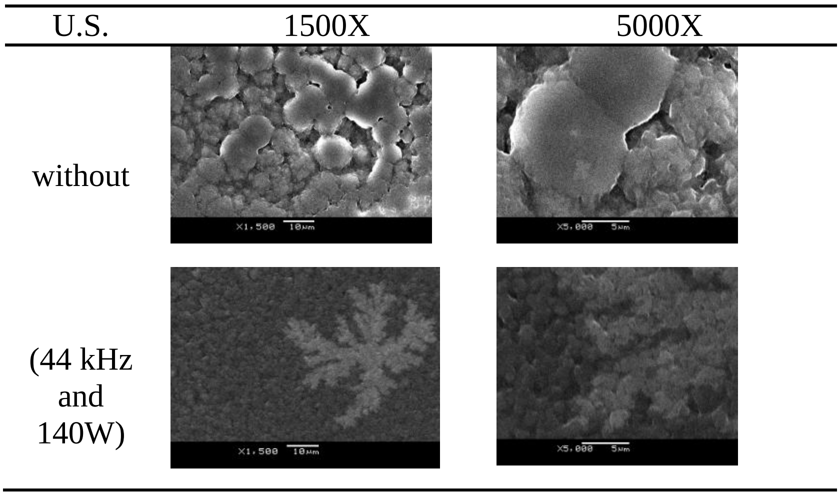

Figure 5. PANI SEM micrographs of a deposit obtained by potentiostatic electro-synthesis at 950 mV, in the presence and absence of ultrasonic irradiation at 293 K.

One explanation for obtaining more homogeneous and compact PANI deposits may be because in these electro-synthesis conditions many soluble oligomers are generated at the interface (HDOR), [25, 26], *i.e.* U.S. irradiation homogenizes this oligomeric region, reducing the size of the interface, causing precipitation of shorter oligomers, but of uniform size, which yields a more "orderly" deposit. This is consistent with the mechanism determined by deconvolution of i-t transients, since it is observed that after a few seconds of polymerization the first polymer layer was already defined, with two-dimensional growth, generating a compact film and, upon this, the three-dimensional growth carries on.

This same behavior was observed from SEM micrographs obtained for POAN deposits (Fig. 6) wherein it is seen that, similarly to PANI, U.S. irradiated electro-synthesis, generates more compact deposits, affording smaller nuclei, but in greater quantity that results in a more homogeneous morphology.

In both cases the presence of soluble oligomeric species exists at the electrode/solution interface during the electro-polymerization process, therefore, U.S. irradiation enhances HDOR saturation, favoring oligomers precipitation in a faster way and generating thus a greater quantity of nuclei (instead of isolated nuclei). This promotes its coalescence and growth toward the interface and results in a more compact coating.

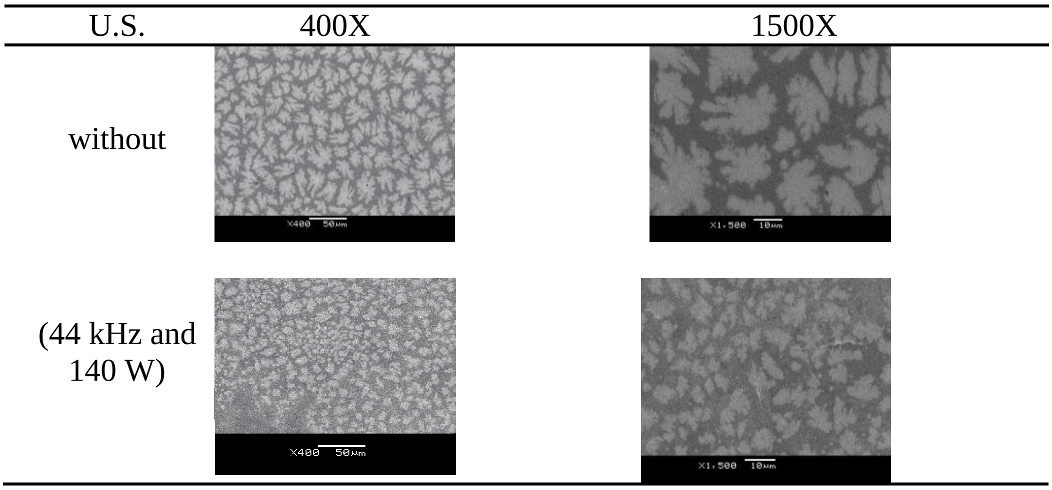

Figure 6. POAN deposits SEM micrographs obtained by potentiostatic electro-synthesis at 670 mV in the presence and absence of U.S., at 293 K.

4. CONCLUSIONS

Voltammetric profiles demonstrated that U.S. irradiation of the system generated a greater amount of polymeric film, as a result of an increase of oligomeric species concentration by decreasing HDOR thickness and, at the same time, U.S. irradiation does not affect the oxidation potential.

Similarly, the i-t transients recorded during ANI and OAN potentiostatic electro-oxidation using ultrasonic perturbation, exhibited a greater current response than when electro-polymerized in the absence of U.S., corroborating that this radiation favors the formation of larger amount of polymer film, since HDOR concentrates and homogenizes, generating a more compact and uniform deposit.

NGM determination demonstrated that U.S. irradiation does not change these mechanisms, just affects the rate at which each contribution to the overall process is defined; this fact is reflected and correlates with morphological differences found in SEM images when electro-polymerized in the absence and presence of U.S.

In conclusion, the PN2D contribution during the electro-polymerization carried out under ultrasound irradiation becomes defined at much shorter times, indicating the electrode is completely coated with a compact layer of polymer at shorter times. On the other hand, the three-dimensional growth contributions (PN3Dct and PN3Ddif; IN3Dct and PN3Ddif for PANI and POAN, respectively) are defined at shorter times and current values are greater when synthesized in the presence of U.S., resulting in larger quantity of electro-deposited material.

Finally, it should be pointed out that all these results corroborated the proposed electro-polymerization model, as ultimately they are explained as a function of the ultrasonic disrupting effect on solubility.

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