

Kinetic Studies of Polypyrrole Formation in DMF

T.F. Otero

Universidad del País Vasco, Facultad de Química, Dpto. de Ciencia y Tecnología de Polímeros, Laboratorio de Electroquímica, Apdo. 1072, 20080 San Sebastián, Spain

A.H. Arévalo*

Universidad Nacional de Río Cuarto, Facultad de Ciencias Exactas Fisico, Química y Naturales, Dpto. de Química y Física, Estafeta No 9, 5800 Río Cuarto, Argentina

Received: April 4, 1994; September 2, 1994

Apesar das dificuldades apontadas na literatura, filmes espessos de polipirrol podem ser obtidos sobre platina a partir de soluções de NaClO₄ em dimetilformamida (DMF). A velocidade de polimerização a potencial constante aumenta entre 900 mV e 2400 mV (SCE), diminuindo a potenciais mais anódicos. Quando a temperatura diminui, a velocidade de polimerização aumenta, indicando uma alta energia de ativação de reações paralelas de passivação durante a polimerização. A partir de microgravimetria *ex-situ* e de checagem do peso reduzido do polímero, a cinética empírica foi determinada.

$$R_p = k [\text{pyrrole}]^{0.5} [\text{ClO}_4^-]^{1.3}$$

Propõe-se um ataque nucleofílico do solvente no polímero carregado positivamente, o que promove uma passividade do filme. A partir da capacidade dos filmes de armazenar mudanças elétricas, obtida a partir de voltogramas de controle, deduziu-se que um aumento de [ClO₄⁻] causa um atraso dos ataques nucleofílicos ao polímero durante a polimerização.

In spite of the difficulties indicated in the literature, thick polypyrrole film can be obtained on platinum from NaClO₄-dimethylformamide (DMF) solutions. The polymerization rate at a constant potential increases between 900 mV and 2400 mV (SCE), decreasing at more anodic potentials. When the temperature decreases the polymerization rate increases, indicating a high activation energy of parallel passivation reactions during polymerization. The empirical kinetics were obtained from *ex situ* microgravimetry and measuring the reduced polymer weight.

$$R_p = k [\text{pyrrole}]^{0.5} [\text{ClO}_4^-]^{1.3}$$

A nucleophilic attack of the solvent on the positively charged polymer is proposed promoting the passivity of the film. A delay in nucleophilic attacks on the polymer during polymerization when [ClO₄⁻] increases is deduced from the capacity to store electrical charges in films, obtained from control voltammograms.

Keywords: kinetic studies, polypyrrole, dimethylformamide

Introduction

In recent years, the electrochemical polymerization of pyrrole has been studied in different solvents¹⁻⁶. The formation of the polymeric film and electrical and physical properties of the resulting films are strongly affected by the preparation conditions⁷⁻¹². In particular, the solvent has a very strong influence on the outcome of the electropolym-

erization reaction. If the nucleophilic character of the solvent is great, film formation is minimized⁴.

A simple mechanism was proposed by Genies *et. al.*¹ which explains the electropolymerization of pyrrole as a process initiated by the aromatic radical cation, generated by the initial loss of an electron from the monomer⁴, followed by polymerization by a stepwise coupling reaction which involves electrophilic aromatic substitution or radi-

cal coupling. In both, the polymerization reaction proceeds via the radical cation intermediate. This radical cation can be attacked by the nucleophilic solvent, promoting a shorter conjugation length, a decrease in the film conductivity, and lower polymerization rates when the film grows¹³.

In previous studies, a very fragile and powdery polymer was obtained on the electrode from DMF solutions⁴. A nucleophilic attack of the solvent on the polymeric radical-cation was proposed to explain the loss of polymer production in this medium¹³. In our laboratory, an effort is being made to search for models of interfacial reactions according to empirical kinetics and electrochemical studies of electrogenerated polymers. The simultaneous presence of an electropolymerization process, a proton catalyzed polymerization reaction, passivation processes and side reactions to generate non-polymeric products during current flow has been proposed^{14,15}.

The aim of this work is to evaluate some of the aspects related to the electrogeneration of polypyrrole (ppy) from DMF solutions: the formation and growth of films, the kinetic studies and the electrochemical properties of the films in spite of the strong nucleophilic character of the solvent.

Experimental

The monomer Pyrrole (Py) (Jansen), was distilled at 59 °C under vacuum. The electrolyte used, anhydrous sodium perchlorate (Merck), was kept in an oven at 100 °C and used without prior purification. Dimethylformamide (DMF) (Pancreac, synthetic grade) was kept in molecular sieves warranting a water content lower than 0.1% by weight, measured by the Karl-Fischer method.

A conventional three compartment electrochemical cell was used. A Pt sheet with a surface area of 1 cm² was used as the working electrode, and a Pt wire with a surface area of 4 cm² in spiral form was used as the counter electrode. The reference electrode was an aqueous saturated calomel electrode. Special care was taken to maintain anhydrous conditions. All the experiments were performed under inert Argon atmosphere.

The electrochemical experiments were carried out using a M273 PAR potentiostat-galvanostat. For the microgravimetric determinations, a 4504 MP8 Sartorius microbalance (precision: 10⁻⁷ g) thermostated at 15 °C, was used.

Results and Discussion

When a platinum electrode was submitted to a potential sweep in a 0.2 M Py and 0.2 M NaClO₄-DMF solution, the voltammogram shown in Fig. 1a was obtained. On the anodic hemicycle, a very low current flows through the electrode until a potential of 900 mV is reached. From there, the current densities increase, first to a maximum of 1200 mV, and later to a minimum of 1300 mV. Above

1300 mV a new oxidation process occurs giving increasing current densities at increasing anodic potentials. On the cathodic hemicycle a shoulder at 300 mV is observed.

To determine the influence of the potential related to the maximum on the production of the polymer, as well as on the polymer properties, polymeric films were obtained on the electrode by polarization for 30 s at different anodic potentials. In every case, the electrode was polarized at -300 mV in the presence of the monomer for 5 s, and then the potential was stepped to the chosen anodic value for 30 s. Then, the potential was again stepped to -300 mV. The correlative chronoamperograms were recorded on a microcomputer.

One of the most important differences among the films generated from other solvents is their morphology. A homogeneous yellow film initially coats the electrode, and irregular blue-black formations and a corrugated texture later appear on the film.

These films formed at different anodic potentials were studied in the background solution by cyclic voltammetry in the -300 to 500 mV range at 20 mV.s⁻¹. The results are used as control voltammograms.

After this control was established, each polymeric film was reduced in this solution, at -300 mV until a constant (close to zero) current was reached. The coated electrode was then rinsed with methanol, dried at 40 °C and weighed

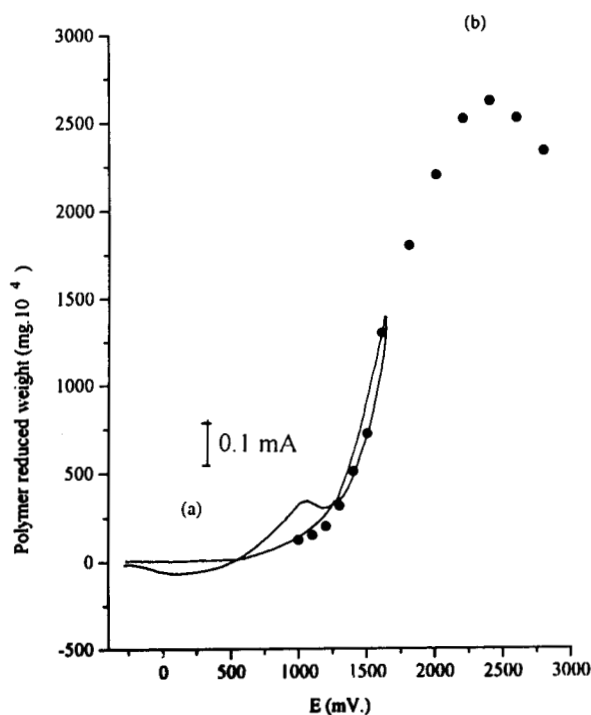


Figure 1. a) Voltammogram obtained using a Pt electrode in 0.2M Py and 0.2 M NaClO₄-DMF solution at a scan rate of 20 mV.s⁻¹. b) Weight of the reduced films obtained from PPY films carried out at different potentials for 30 s. in 0.1 M Py and 0.2 M NaClO₄-DMF solution, submitted to a reduction potential (-300 mV) in 0.2 M NaClO₄-DMF solution, dried and weighed.

using a microbalance (precision of 10^{-7} g). The polymer was dried and weighed several times to achieve a constant weight. The electrode was cleaned by burning the polymer in a reduction flame, and weighed before the initiation of a new experiment in a fresh solution for a new polarization time. The experimental results are shown in Fig. 1b. An increase in the polymerization rate occurs when the electric potential rises from 900 to 2400 mV from the increase of the polymer weight generated at a constant polarization time. At greater overpotentials a decrease of the polymerization rate is observed.

By the integration of each chronoamperogram we obtained the electric charge consumed during each electropolymerization. The ratio between the weight of each reduced polymer film and the corresponding polymerization charge consumed to generate the film gives us the **charge productivity (CP)** (as $\text{mg}\cdot\text{mC}^{-1}$). The polymerization charge used to calculate CP is $Q_{a,p} - Q_{c,p} - Q_{a,c}$, where $Q_{a,p}$ is the anodic polymerization charge, $Q_{c,p}$ is the cathodic polymerization charge and $Q_{a,c}$ is the anodic control charge.

Table 1 shows the decrease of the CP when the potential rises. The obtained decrease in productivity seems to indicate the presence of faster and faster side reactions, giving non-polymeric products at increasing potentials. Through the integration of the cathodic voltammograms of control, the electrical charge stored in the film was obtained. The ratio between this charge and the weight of the reduced polymer film gives the **capacity to store electrical charge (CSEC)** (storage capacity).

Up to 1500 mV, an increase of the CSEC (mC of charge per mg of polymer) is observed on the electrogenerated polymer, indicating that the side reactions do not affect the polymer structure, or in any case, promote a decrease of nucleophilic attack on the polymer. At higher anodic potentials the storage capacity begins to decrease, pointing to the presence of a nucleophilic attack on the conjugated structure, parallel to the electropolymerization process, and the subsequent passivation process. Taking into account the increase of the CP when the polarization potential decreases, the increase of the polymerization rate and CSEC

when the generation potential increases, we chose the potential of 1300 mV to generate the polymer.

Temperature influence

To state the influence of temperature on obtaining the polymer, we generated polymeric films by potential steps ranging from - 300 mV to 1300 mV in $\text{Py}\text{-ClO}_4^-$ solutions at different temperatures and with a polarization time of 60 s; this time corresponds to the average kinetic experiment time. These films were then controlled by cyclic voltammetry experiments in a monomer-free solution, and then reduced to - 300 mV. The electrodes thus modified were washed with methanol, dried at 40 °C and then weighed until a constant weight was obtained. The results are shown in Table 2. The weight of the polymer film obtained, the CP and the CSEC increase when the temperature decreases.

The rates of most of the chemical and electrochemical reactions increase when the temperature increases. In electroinitiated polymerizations, passivation processes occur

Table 1. Productivity of the consumed electrical charge during polymerization at different potentials and capacity to store electrical charge (measured by cyclic voltammetry in the background electrolyte) in the polymer. Polymerization in 0.1 M Py-0.2 M NaClO_4 -DMF. T = 20 °C. Polarization time: 30 s.

Polymerization Potential (mV)	Productivity of the Charge ($\text{mg}\cdot\text{mC}^{-1}$) $\times 10^{-4}$	Capacity to Store Electrical Charge ($\text{mC}\cdot\text{mg}^{-1}$) $\times 10^{-2}$
1000	106.75	0.08
1100	27.49	0.16
1200	6.49	1.12
1300	5.61	1.54
1400	4.90	1.67
1500	4.57	2.02
1600	4.09	1.66
2000	3.42	1.36
2400	2.90	0.72
2800	1.78	0.40

Table 2. Productivity of the consumed electrical charge during polymerization at different temperatures, weight of the generated films and capacity to store electrical charge. Films generated by polarization at 1300 mV. Polymerization in 0.2 M Py-0.2 M NaClO_4 -DMF. Polarization time: 60 s.

Temperature °C	m $\text{mg}\cdot 10^4$	Productivity of the Charge ($\text{mg}\cdot\text{mC}^{-1}$) 10^4	Capac. to Store Electric. Charge ($\text{mC}\cdot\text{mg}^{-1}$) 10^{-2}
-10	183	4.40	2.65
0	167	4.27	2.64
10	92	3.40	2.12
20	79	2.97	2.19
30	73	2.83	2.16

simultaneously with polymer growth. One of these degradation-passivation processes could be the source of the observed influence of temperature.

To check this hypothesis, two similar films were electrogenerated at $-10\text{ }^{\circ}\text{C}$. One of the films was then transferred to the background solution at $-10\text{ }^{\circ}\text{C}$. There it was alternatively submitted to control cyclic voltammograms followed by polarizations at 1300 mV for different times. Figure 2 shows the change of the electrical charge needed to oxidize the polymer film after the different polarization times. CSEC decreases linearly with the increasing polarization times. The second film was submitted to a similar treatment in the background solution, but at $30\text{ }^{\circ}\text{C}$. The decrease of the CSEC is faster, as can also be seen in the Fig. 2.

The polymeric degradation seems to be due to a nucleophilic attack on the oxidized polymeric chains, promoting the opening of double bonds and the formation of the new bonds with oxidized solvent or residual water^{15,16}. As such, the weight of the partially degraded polymer when reduced is a little greater than the weight of the initial reduced film (i.e. 0.0586 mg and 0.0544 mg).

Kinetics at different concentrations of monomer

Polymeric films were electrogenerated in $0.2\text{ M NaClO}_4\text{-DMF}$ solutions having different monomer concentrations at $-10\text{ }^{\circ}\text{C}$ by a square wave of potential from -300 mV to 1300 mV , where it was kept during the polymerization time and reduced at -300 mV to a constant current (close to zero) under inert atmosphere.

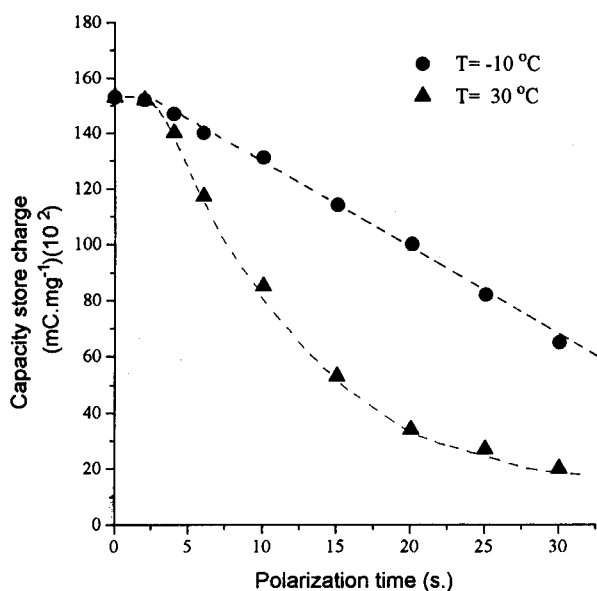


Figure 2. Evolution of the capacity to store electrical charge (mC.mg^{-1}) after subsequent polarizations at 1300 mV . Film weight 0.0544 mg . Both films were treated in $0.2\text{ M NaClO}_4\text{-DMF}$ solution: a) $-10\text{ }^{\circ}\text{C}$, and b) $30\text{ }^{\circ}\text{C}$ and checked in the same solution at $-10\text{ }^{\circ}\text{C}$ between -300 mV and 500 mV at 20 mV.s^{-1} .

The experimental kinetics were followed by *ex situ* microgravimetry. A polymer film was generated by polarization in a monomer solution during a polarization time. The coated electrode was then checked in the background solution by cyclic voltammetry at 20 mV.s^{-1} and by potential steps for 60 s at each potential, both between -300 mV and $+500\text{ mV}$. The coated electrode was then reduced at -300 mV to constant current, rinsed with methanol, dried and weighed several times to constant weight. The experimental kinetics obtained are shown in Fig. 3a, where kinetics related at different concentrations of monomer are depicted. Well defined straight variations of the reduced polymer weight were obtained. Each slope represents the **polymerization rate (Rp)** because it is derived from the polymer weight produced per unit of polarization time under each set of experimental conditions. An increase of the polymerization rate is observed when the concentration of monomer increases in the solution. The different experimental results can be summarized in the equation:

$$Rp_i = [\delta m / \delta t]_i \propto [M]_i^a$$

where Rp_i represent the polymerization rate, i represents the set of experimental conditions, $[M]$ the concentration of monomer, a the empirical order of dependence, m the mass of the polymer, and t the polymerization time. The

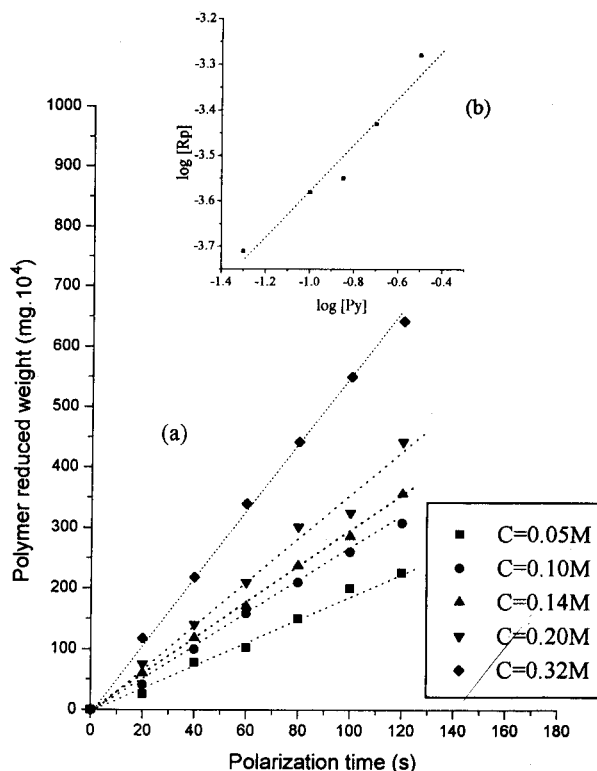


Figure 3. a) Evolution of reduced PPY film weight with polymerization time for different Py concentrations. Solution: Py- $0.2\text{ M NaClO}_4\text{-DMF}$, $T = -10\text{ }^{\circ}\text{C}$. $E_{\text{polym.}} = 1300\text{ mV}$. b) Determination of the empiric order of reaction related to Py concentration.

empirical reaction order can be obtained from a bilogarithmic representation of Rp_i versus $[M]_i$ (Fig. 3b). The straight line has a slope of 0.5, thus:

$$Rp \propto [Py]^{0.5}$$

The experimental results related to polymer production and control for polymeric films generated by polarization for 40 s are summarized in Table 3.

There, we recovered the electrical charge consumed during polymerization and obtained the integration of each chronoamperogram, the electrical charge related to the polymer reduction in the solution of polymerization (step Ep to -300 mV), the anodic and cathodic charges obtained from the control voltammograms in the background solution, the weight of the reduced polymer film, the CP and the CSEC.

In general, it can be stated that higher current densities flowing through the solution promote greater CP and lower CSEC. This tendency seems to agree well with the models of interfacial reactions proposed by our laboratory for other similar systems^{5,14,15}.

High current densities promote a strong acidification around the electrode. An acid catalyzed chemical polymerization in a homogeneous phase occurs at the same time as the electrochemical polymerization. A portion of the chemically generated polymer interacts with the electrode surface and precipitates at the same time that electrogeneration takes place. As a consequence, the same charge produces more polymer when consumed at high current densities. Nevertheless, the acid catalyzed polymer is a hydrogenated polymer. The conjugation is low, therefore, its electroactivity does not work during the electrochemical control of the film. This is the reason for the decrease in CSEC when the concentration of monomer increases.

Kinetics at different concentrations of electrolyte

The kinetics were subsequently followed at different concentration of $NaClO_4$: 0.2, 0.3, 0.4, 0.5 and 0.63 M in 0.1 M Py-DMF solutions. The experimental procedure was similar to that used when the concentration of the monomer was changed. A linear increase of the reduced polymer weight obtained at each concentration of electrolyte was

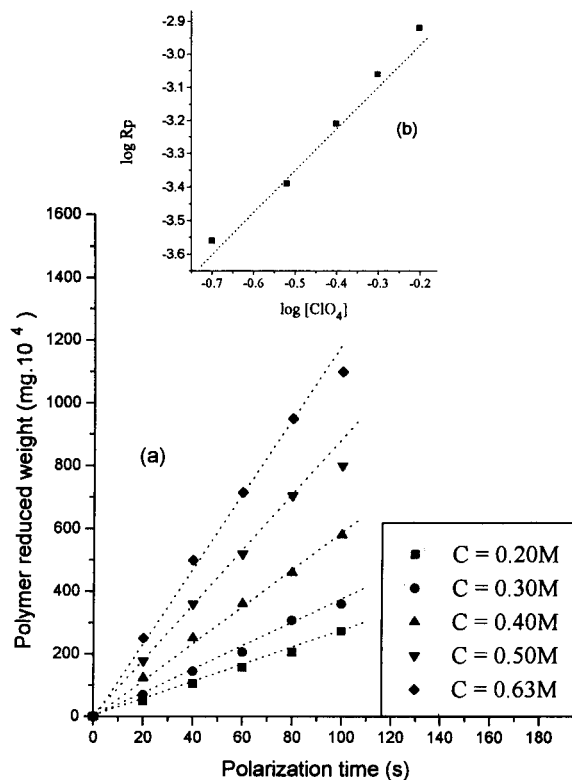


Figure 4. a) Evolution of reduced PPY film weight with polymerization time for different electrolyte concentrations. Solution: 0.1 M Py- $NaClO_4$ -DMF, $T = -10^\circ C$. $E_{polym.} = 1300$ mV. b) Determination of the empiric reaction order related to electrolyte concentration.

observed. Increasing slopes were obtained for increasing concentrations (Fig. 4a). Each slope represents a polymerization rate, as above, and different straight lines can be represented by:

$$Rp_i = [\delta_m / \delta_t] \propto [ClO_4^-]^b$$

If the polymerization reactions follow such empirical kinetics, the order of dependence, b , can be obtained from the slope of the double logarithmic representation of Rp vs. $[ClO_4^-]$. Figure 4b shows a straightforward variation whose slope, 1.3, is the empirical reaction order:

$$Rp \propto [ClO_4^-]^{1.3}$$

Table 3. Productivity of the consumed electrical charge during polymerization of Py at different monomer concentrations. Anodic and cathodic charges related to the control voltammogram. Weight of the reduced films and capacity to store charge. Films generated by at 1300 mV. Polymerization in 0.2 M $NaClO_4$ -DMF. $T = -10^\circ C$. Polarization time: 40 s.

[Py] mo.l ⁻¹	Polymerization		Control		Weight Red. Pol. mg.10 ⁴	Produc. Charge (mg.mC ⁻¹)10 ⁴	Capacity Store Charge (mC.mg ⁻¹)10 ⁻²
	Anodic Charge mC	Cathod. Charge mC	Anodic Charge mC	Cathod. Charge mC			
0.05	34.95	3.33	1.72	1.08	80	2.68	2.15
0.10	35.01	3.40	2.17	1.37	108	3.67	2.01
0.14	26.54	2.92	1.86	1.24	130	5.97	1.43
0.20	38.42	3.97	2.85	2.00	151	4.78	1.89

This high order dependence related to the electrolyte suggests the direct participation of the anions in the polymerization mechanism.

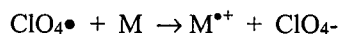
Different modes of participation are possible. One is through the conductivity of the solution. According to the Arrhenius expression, only a 1/2 dependence should be expected.

A second mode for ClO_4^- participation in the polymerization mechanism can be the stabilization of the monomeric cation radical, once it is formed:



favoring the stability of the radical, and allowing interaction with a new monomeric radical.

Finally, a mode was proposed in the literature¹⁷⁻²³, through the direct discharge of ClO_4^- on the electrode, metal or polymer,



The non-integer number for the order of dependence points to a complex participation, probably through various modes.

From the set of electrical and gravimetric data, some of them depicted in Table 4, a direct participation of ClO_4^- in the mechanism can be deduced. At increasing concentrations of electrolyte higher CP are obtained without any defined effect on CSEC. This means that the charge has a higher efficiency for producing the polymer without significant influence from the chemical polymerization.

Conclusions

The electrogeneration of ppy from NaClO_4 -DMF solutions takes place at anodic potentials greater than 800 mV vs. SCE. The polymerization rate increases when the potential rises, and reaches a maximum at 2400 mV. A strong influence of solvent attacks seems to be the source of this maximum, as was deduced from the decrease of the storage capacity of films generated at high anodic potentials. In contrast to other solvents, a non-uniform film is obtained.

At lower overvoltages a yellow film coats the electrode, and blue-black, irregular formations grow on the yellow base. A bilayer structure seems to be present. The polymerization rate increases when the temperature decreases. This fact seems to be due to the quick increase of the degradation processes in the polymer to give non-electroactive lakes, as was studied by polarizations and controls in the background solutions. The empirical kinetics was obtained by *ex-situ* microgravimetry

$$R_p = [\text{Py}]^{0.5}[\text{ClO}_4^-]^{1.3}$$

obtaining a higher dependence from the electrolyte than from the monomer. From the storage efficiencies, it could be deduced that the increase of monomer concentration favors nucleophilic attacks, as those attacks are delayed when the concentration of electrolyte rises.

Acknowledgments

This work was supported by the Basque Government, *Amerika eta Euskaldunak* program. Authors also wish to thank the Universidad Nacional de Río Cuarto, Argentina, for allowing Dr. Arévalo to develop this work at the Universidad del País Vasco.

References

1. E.M. Genies, G. Bidan and A.F. Diaz, *J. Electroanal. Chem.* **149**, 101 (1983).
2. S. Asavapiriyantont, G.K. Chandler, G.A. Gunawardena and D. Pletcher, *J. Electroanal. Chem.* **177**, 229 (1984).
3. I. Rodríguez, M.L. Marcos and J. González Velazco, *Electrochim. Acta* **32**, 1181 (1987).
4. A.F. Diaz and J. Bargon, *Handbook of Conducting Polymers* **88** (T.A. Soktheim, ed., M. Dekker, N.Y., 1986).
5. T.F. Otero and C. Santamaría, *Electrochim. Acta* **37**, 369 (1992).
6. T.F. Otero and E. Angulo, *J. Appl. Electrochem.* **22**, 369 (1992).
7. X. Bi, Y. Yao, M. Wan, P. Wang, K. Xiao, Q. Yang and R. Qian, *Makromol. Chem.* **186**, 1101 (1985).

Table 4. Electrical and gravimetric parameters related to films generated at different electrolyte concentrations. Polymerization in 0.1 M Py- NaClO_4 -DMF. Polarization potential 1300 mV. T = - 10 °C. Polarization time: 60 s.

[NaClO ₄] mo.l ⁻¹	Polymerization		Control		Weight Red. Pol. mg.10 ⁴	Produc. Charge (mg.mC ⁻¹)10 ⁴	Capacity Store Charge (mC.mg ⁻¹)10 ⁻²
	Anodic Charge mC	Cathod. Charge mC	Anodic Charge mC	Cathod. Charge mC			
0.2	61.49	5.69	3.42	2.20	168	3.21	2.04
0.3	62.79	6.38	4.56	2.97	213	4.11	2.14
0.4	102.33	6.85	8.90	6.04	379	4.38	2.35
0.5	153.16	16.34	16.41	9.41	536	4.45	3.06
0.63	150.02	17.10	9.75	9.75	605	5.09	2.31

8. T.F. Otero and E. de Larreta-Azelain, *Polymer* **29**, 1522 (1988).
9. T. Osaka, K. Naoi, S. Ogano and S. Nakamura, *J. Electrochem. Soc.* **134**, 2096 (1987).
10. T.F. Otero and E. de Larreta-Azelain, *J. Chimie Phys.* **86**, 131 (1989).
11. D.S. Madison and J. Unsworth, *Synth. Met.* **30**, 47 (1989).
12. T.F. Otero and J. Rodríguez, *Synth. Met.* **55-57**, 1418 (1993).
13. K. Imanishi, M. Satoh, Y. Yasuda, R. Tsushima and S. Aoki, *J. Electroanal. Chem.* **242**, 2831 (1991).
14. T.F. Otero, J. Rodríguez, E. Angulo and C. Santamaría, *Synth. Met.* **43**, 2831 (1991).
15. T.F. Otero and J. Rodríguez, *J. Electroanal. Chem.* **310**, 219 (1991).
16. M. Ogasawa, K. Funahashi, T. Demurta, T. Hagiwara and K. Iwata, *Synth. Met.* **14**, 61 (1986).
17. J. Prezja, I. Lundstrom and T.A. Skotheim, *J. Electrochem. Soc.* **128**, 1685 (1982).
18. J.E. Leonard, P.C. Scholl, T.P. Steckel and M. Mozogachi, *Tetrah. Let.* **1867**, (1980).
19. S.N. Bhadani, Y.K. Prasad and S. Kundu, *J. Polym. Sci.* **15**, 1819 (1977).
20. B.L. Funtand and V. Hornof, *J. Polym. Sci.* **9**, 2171 (1971).
21. G.S. Shapovai, *J. Macromol. Sci. Chem.* **A17(3)**, 453 (1982).
22. G. Pistoia and O. Bagnorelli, *J. Polym. Sci.* **17**, 1001 (1979).
23. S.K. Samal and B. Nayak, *J. Polym. Sci.* **A26**, 1035 (1988).