

Electrochemical Modulation of the Thickness of Polypyrrole Films by Using Different Anionic Dopants

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The tailoring of key characteristics of conducting polymers (e.g., thickness, conductivity, degree of oxidation, color and morphology) is desirable for specific applications. We present results on the regulation of the thickness of polypyrrole films electrochemically grown on glassy carbon by potentiodynamic and potentiostatic techniques at circumneutral pH in the presence of selected aqueous dopant anions (i.e., I⁻, NO₃⁻, Br⁻, Cl⁻, ClO₄⁻, SO₄²⁻ and F⁻). In this manner, a supporting electrolyte containing KI yields relatively thick and highly conductive films whereas KF produces little conductive, very thin films. Other electrosynthesis parameters (i.e., applied potential range, number of cycles, time) also play a key role. For example, one can obtain insulating films by applying potentials in the region required for overoxidation of the film.

Keywords: (alphabetically): anionic dopants; cyclic voltammetry; polymer electrosynthesis; overoxidation; polypyrrole.

1. INTRODUCTION

Interest in conducting polymers has grown considerably due to their applications in microelectronic, electrochromic, and biomedical devices, rechargeable batteries, anticorrosion films, chemical and biochemical sensors, protection against electromagnetic radiation, antistatic packaging

and the like [1-14]. Modern developments of new custom-designed polymers that partially or completely replace classical materials abound [16-18]. This is especially true in the field of conductive polymers like polypyrrole, which can be produced both chemically and electrochemically [14, 15]. Electrochemical polymerization leads to the formation of a polymer film on the surface of a working electrode. It offers several advantages including the controllability of its thickness, morphology, and conductivity [14, 19]. Since its seminal electrochemical preparation in 1968, polypyrrole (PPy) has been one of the most extensively studied and used conductive polymers [15, 20].

The nature of the solvent and electrolyte used during the electrochemical synthesis of PPy greatly influence its final properties [20]. In the present study we use a variety of doping anions in aqueous solution that become incorporated in the polymeric matrix and are known to affect the electropolymerization process itself, the charge-discharge process, the ensuing conductivity, and the final morphology [20-23]. For example, the electrical conductivity of PPy has been reported to be quite sensitive to the counter ion and may span over 5 orders of magnitude; it has not yet been established whether this effect is due to an electronic interaction between the polymer chains and the anions or to differences in film morphology resulting from its growth in different electrolytic solutions [12, 20, 22].

The potential applied during electrosynthesis is also of the paramount importance. The anodic potential must be high enough to oxidize the pyrrole units but also low enough to avoid the (irreversible) overoxidation of the polymer formed in the preceding cycle, since it would lead to important mass and electrical activity losses of the polymer film [24-27]. Since the early times in PPy history, overoxidation has been reported at potentials higher than 0.6 V vs. SCE [27], and some analytical applications concern electronically non-conductive overoxidized PPy membranes (OPPy) [28]. Evidently, the electrical properties and polymer stability during the electrochemical processes are crucial for various applications [29-31]. We now present a study aimed at offering data for the tailoring of PPy thickness.

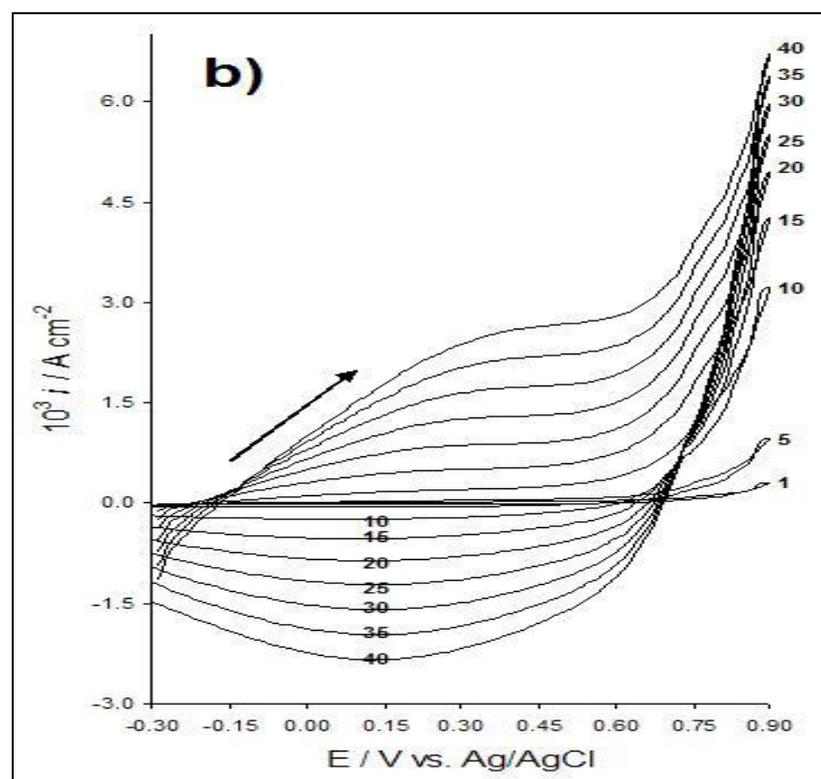
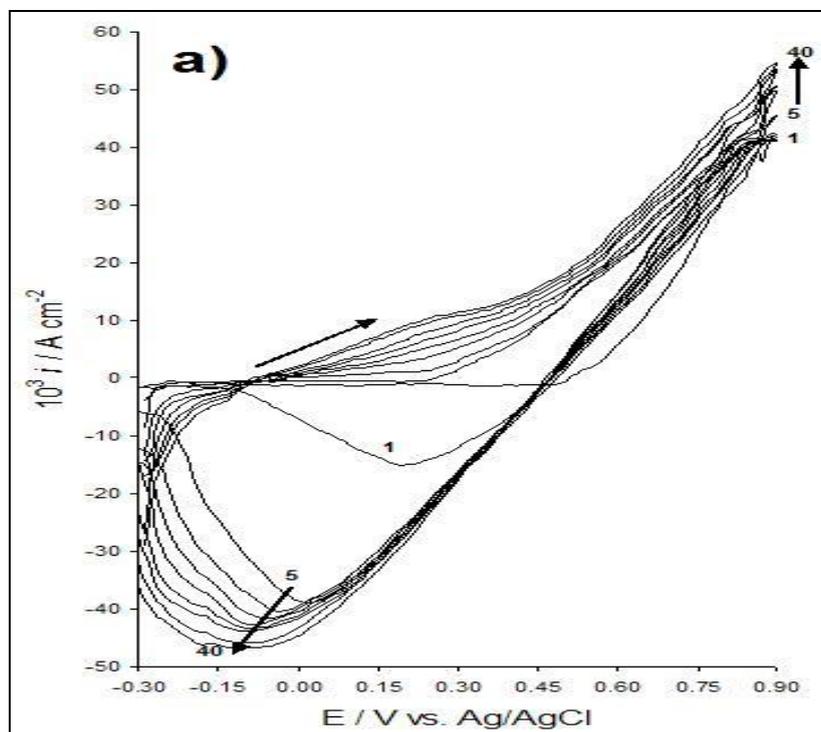
2. EXPERIMENTAL PART

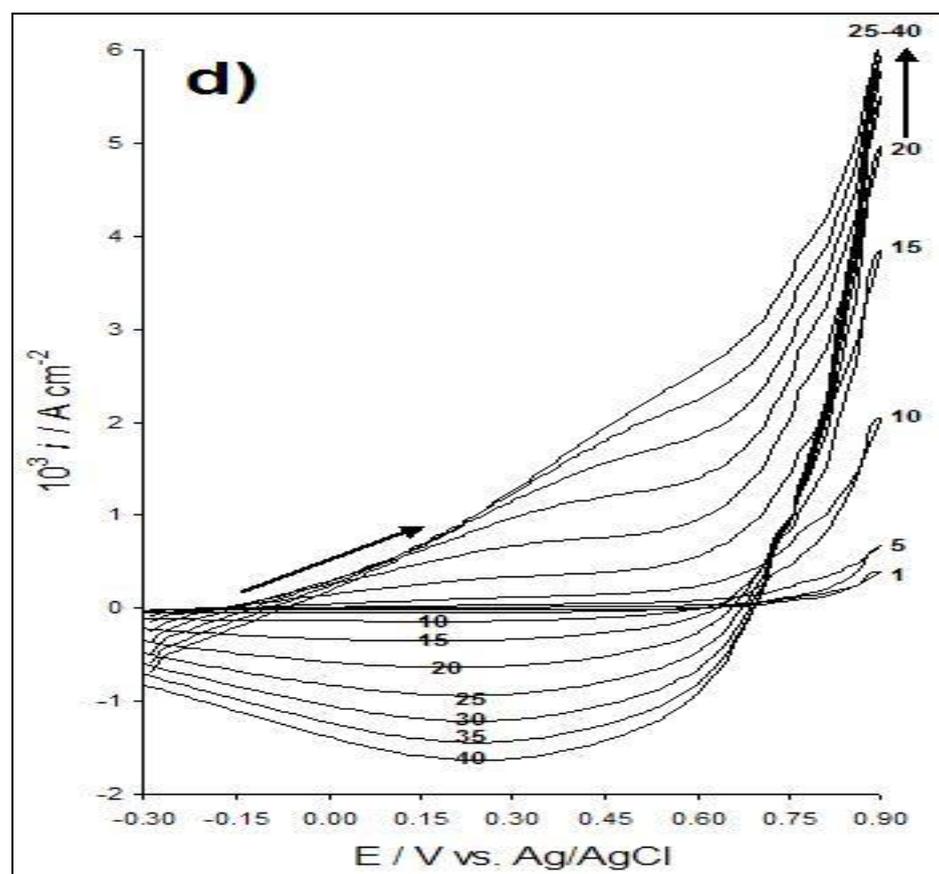
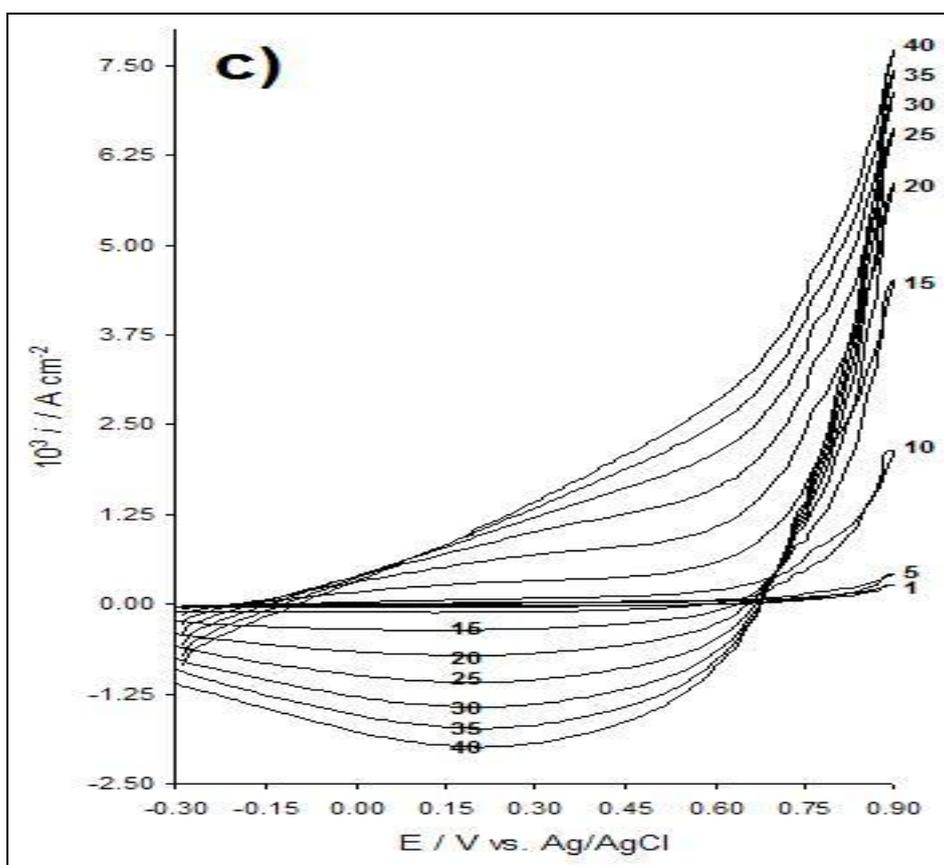
Electrochemical formation of PPy films was achieved by potentiodynamic and potentiostatic methods. A vitreous carbon disk (Bioanalytical Systems, 0.07 cm²) was used as working electrode. Prior to each experiment, the surface of the working electrode was mechanically polished with 0.10, 0.05 and 0.03 μm alumina and ultrasonicated for 10-15 min. A Pt wire (0.75 mm, 99.99+%, Aldrich) was used as the auxiliary (counter) electrode. All potentials are referred to a Ag/AgCl_(sat) reference electrode (Bioanalytical Systems, Model MF-2052). All the experiments were performed with a BAS potentiostat (Bioanalytical Systems, Model CW50W). The electrolytes were 0.1 M aqueous solutions of KI, KNO₃, KBr, KCl, KClO₄, K₂SO₄ or KF (all J. T. Baker, reagent grade), in 0.1 M pyrrole (Py, Aldrich, reagent grade). In all cases the solutions were prepared with Millipore water (18 MΩ cm) and deaerated during 10-15 min with nitrogen (Praxair, 99.97%) before performing the experiments.

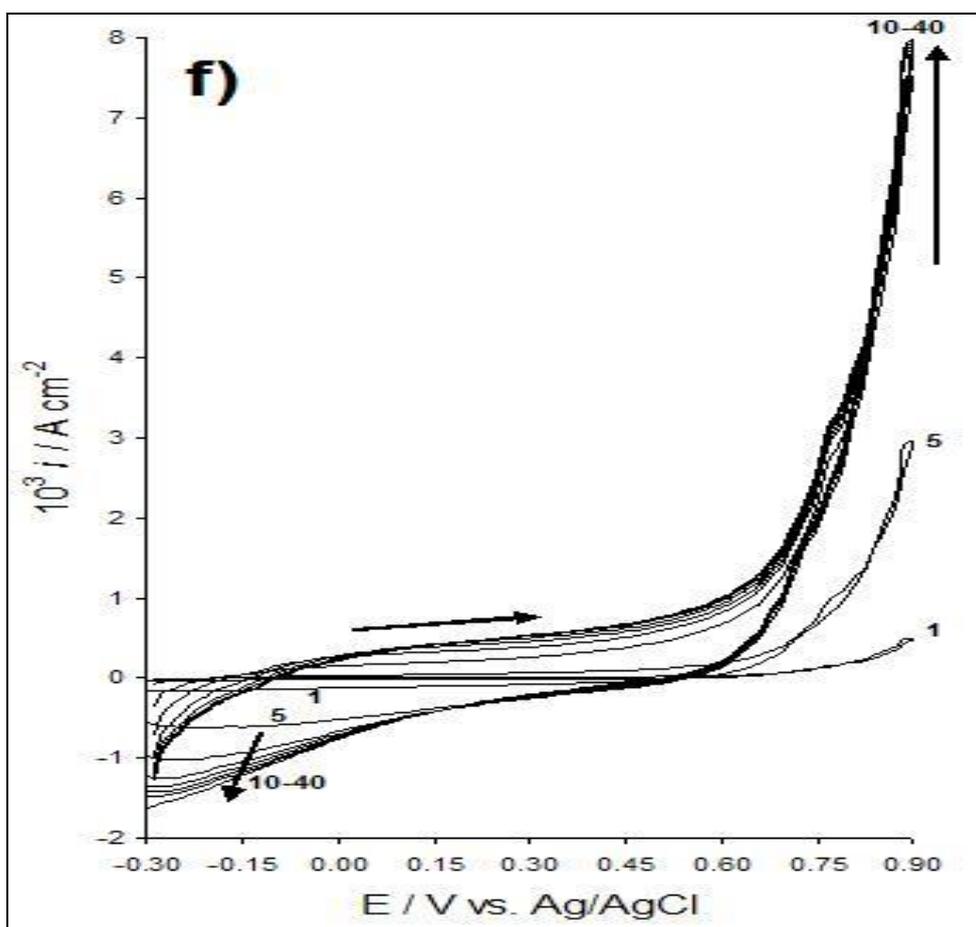
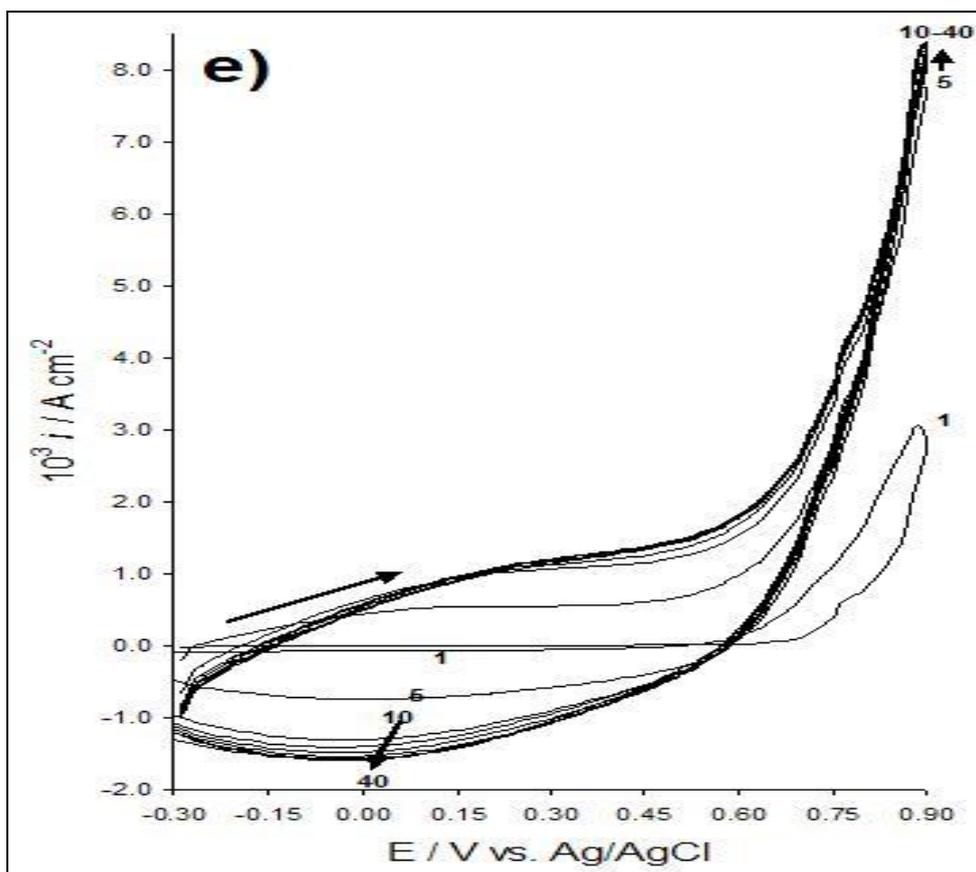
3. RESULTS AND DISCUSSION

a) Potentiodynamic modulation of PPy properties

PPy was potentiodynamically grown in solutions of I^- , NO_3^- , Br^- , Cl^- , ClO_4^- , SO_4^{2-} or F^- . Each film was obtained after 40 cycles in the potential range: -0.30 to +0.90 V vs. Ag/AgCl [32].







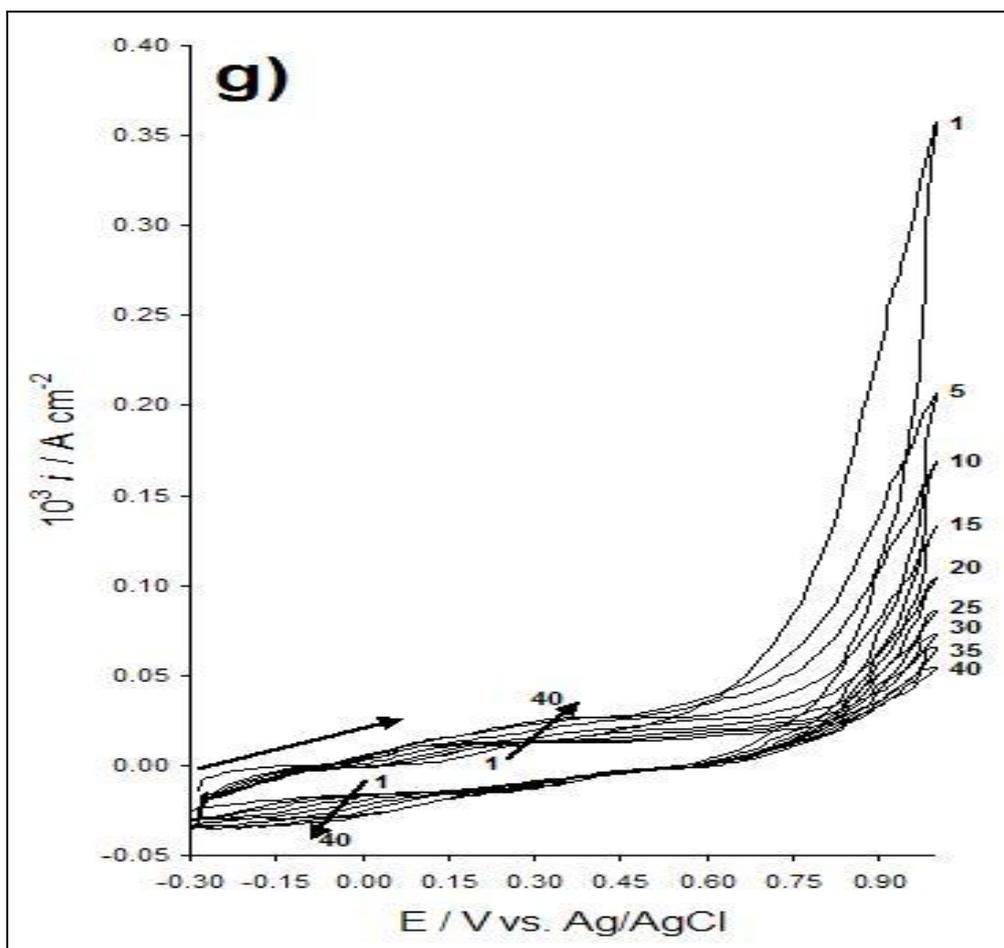


Figure 1. Cyclic voltammetry of the electropolymerization of PPy films in 0.1 M Py on a glass carbon electrode in aqueous medium (neutral pH) in the presence of different anions (0.1 M): a) KI, b) KNO_3 , c) KBr, d) KCl, e) KClO_4 , f) K_2SO_4 , and g) KF. The voltammograms are obtained for 40 cycles, between -0.3 to 0.9 V vs. Ag/AgCl, at a scan rate of 0.1 V/s.

The resulting voltammograms are shown in Figures 1a-g. The peaks between -0.10 V and +0.25 V during polymerization in KI (Figure 1a) correspond to the charge and discharge of the PPy film [14, 32] together with the reduction/oxidation of the $\text{I}_2/2\text{I}^-$ couple [35- 37]. The cathodic response indicates that an important amount of iodine species becomes trapped within the polymeric matrix. This electrochemical polymerization is catalyzed by the $\text{I}_2/2\text{I}^-$ couple [35] and the electrochemical oxidation of the Py starts at 0.6 V. This catalytic phenomenon explains the large currents obtained with this system (ca. $\pm 50 \text{ mA cm}^{-2}$) compared to those that follow. It is also noteworthy that the currents do not change considerably during the last ca. 80% of the 40 cycles.

Figures 1-b, c, and d show the polymerization cycles in KNO_3 , KBr and KCl, respectively. The PPy grown between +0.15 and +0.45 V results in peak currents of similar magnitude (derived from charge/discharge successive cycles). A steady increase in the anodic response with cycle number is observed for each series. In agreement with earlier reports [12, 22] these four anions (I^- , NO_3^- , Br^- and Cl^-) show a gradual current increase towards the positive potential limit. We show below that this increase is related to the progress of electropolymerization which results in larger film thicknesses.

The situation is significantly different when using KClO_4 and K_2SO_4 . Figures 1-e and 1-f show that the first 10 cycles involve substantial polymer growth that considerably decreases in the remaining cycles (see Table 1). This dramatic change in film growth dynamics may be attributed to the loss of conductivity in the polymer caused (at least partially) by its overoxidation [24, 28].

Table 1. Values of $I_{p,\max}$ obtained at the polymerization potential of 0.9 V vs. Ag/AgCl (cyclic voltammetry).

	KI	KNO_3	KBr	KCl	KClO_4	K_2SO_4	KF
$I_{p,\max}$ (mA/cm ²)	55.1 (54.6)	6.7	7.7	6.1	8.4 (8.0)	7.9 (7.52)	0.3 (0.05)
No. of cycles	39 (40)	40	40	40	26 (9)	40 (10)	1 (40)

Figure 1-g shows the corresponding voltammograms in KF. These reveal that the incorporation of the anion in the PPy matrix is rather scant, as judged by the very small peak currents obtained (below $\pm 0.02 \text{ mA cm}^{-2}$). Contrary to all of the experiments reported above, the anodic currents decrease with the number of cycles (see Table 1). This is consistent with earlier reports that ascribe this observation to the initial oxidation of the monomer immediately followed by oxidation of the PPy produced and adsorbed on the substrate, yielding a current decrease [36]. Such a decrease continues during the subsequent cycles that correspond to the oxidation of species between the bulk of the solution and the substrate (which becomes passivated). This outcome provides a method for the production of passivated PPy thin films upon demand [1, 9, 10].

To further explain this, Auger spectroscopy has shown that the controlled diffusion of dopant anions in electrochemically synthesized PPy films in a ClO_4^- electrolyte is spontaneous - upon immersion - between the original dopant and other anions subsequently placed in a fresh solution [20]. In contrast, no exchange occurs with PPy films grown in a KF solution, even after long immersion periods. This lack of anionic mobility provides further explanation to the scant growth of PPy in this electrolyte and reinforces the observation that the nature of the anion plays a key role in the final characteristics of the film.

The influence of the anion is also evidenced in the rate of PPy growth, reported to be much faster in the presence of electrolytes with large anions (e.g., polystyrenesulfonate) than with small ones (e.g., Cl^-), as larger anions are more strongly adsorbed on the electrode surface and facilitate the initial stage for electropolymerization [14].

Also noteworthy is the signal-crossing in the initial cycles observed in the oxidation zone of the voltammograms of Figures 1a-g, which agrees with previous reports [37, 38]. This has been interpreted as the result of polymer nucleation and growth on the electrode surface, analogous to the electrodeposition of many metallic species [39, 40].

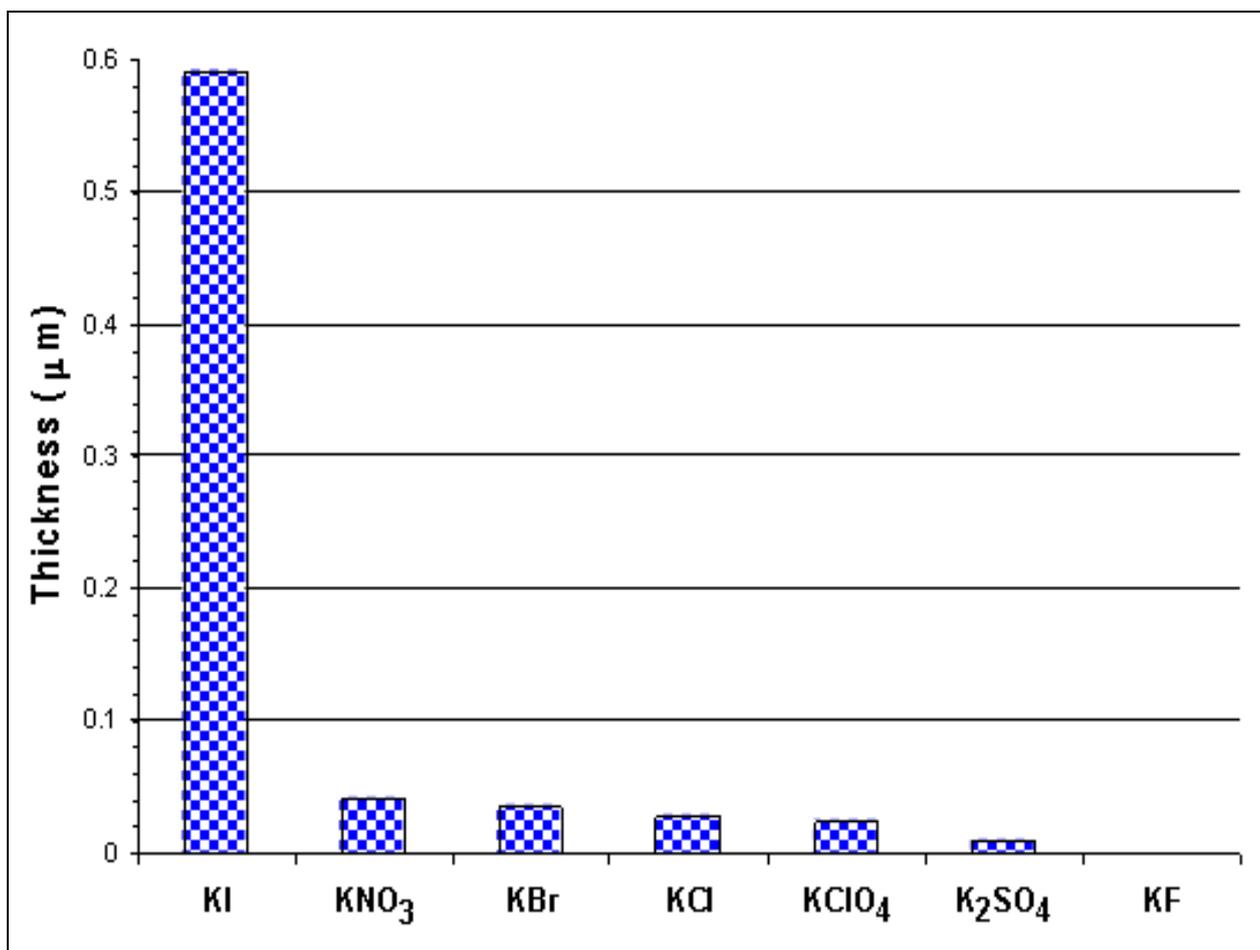


Figure 2. PPy film thickness vs. dopant anion (calculated for the voltammograms in Figure 1).

A summary of the thicknesses of our PPy films, calculated by a standard coulometric technique [14], is given in Table 2. It is again clear that the thickest films are formed in KI, whereas the thinnest correspond to KF. An important finding here is that one does not need to perform 40 cycles to obtain the thickest films with every anion. For instance, in KClO₄ only nine cycles are needed, whereas in KF one cycle is enough. This may result in considerable time and energy savings in the production of specific films. The area under the curve for the PPy synthesis in the presence of each anion gives the charge passed during polymer formation; a summary is given in Table 2 for cycles 2 and 40. From here one can estimate the film thickness based on previous findings which show that a charge of 1 C cm⁻² is approximately equivalent to a thickness of 2.5 μm in the PPy film [41-43]. The films formed in KF show a loss in current and charge upon cycling (e.g., cycle 2 corresponds to 0.11 mC cm⁻² and cycle 40 to only 0.03 mC cm⁻²). Even this ultrathin film may protect the substrate in specific cases.

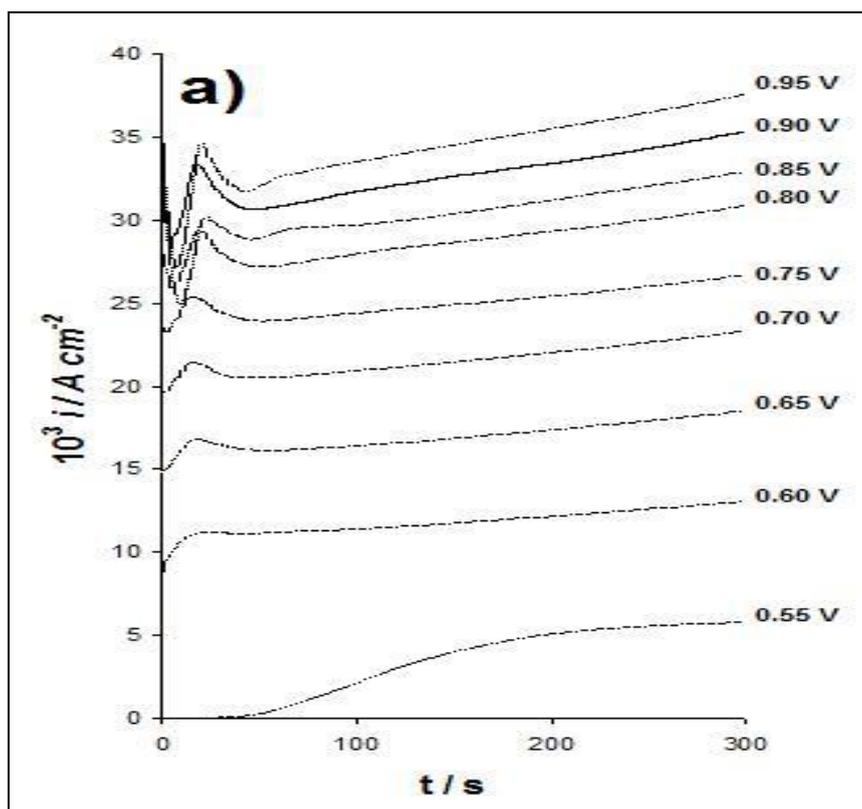
Figure 2 shows that the film thicknesses obtained potentiodynamically (at 40 cycles, scan rate = 0.1 V/s) follow the order: I⁻ > NO₃⁻ > Br⁻ > Cl⁻ > ClO₄⁻ > SO₄²⁻ > F⁻. These results support the proposal that PPy films of different thickness can be custom-designed. For example, thick films can be obtained in KI (ca. 0.6 μm) whereas thin films can be produced in KF (< 0.0001 μm).

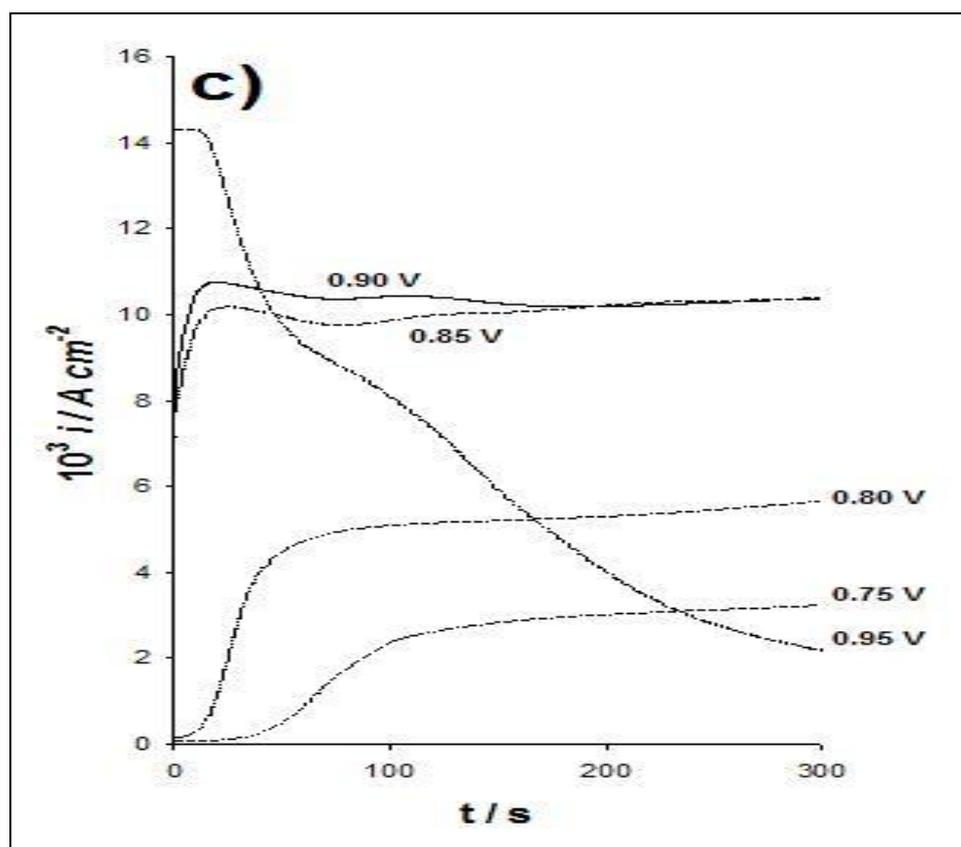
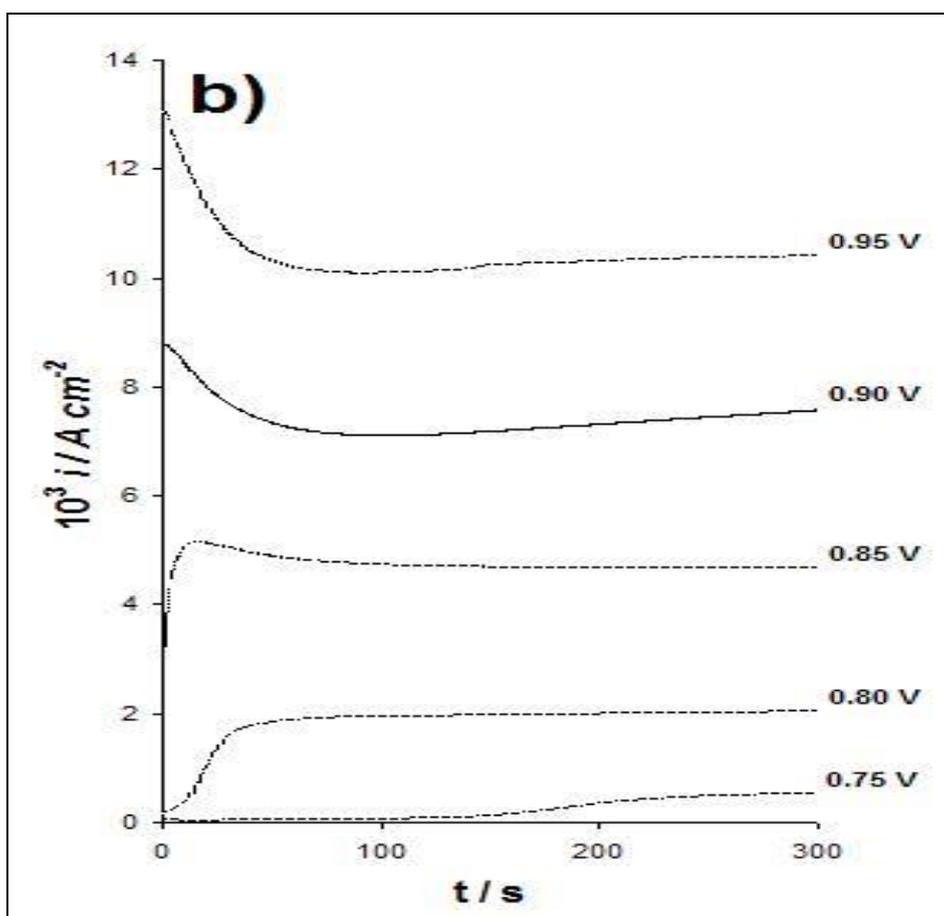
Table 2. PPy film thickness and charge passed, calculated from the voltammograms obtained during the electrosynthesis of PPy films in cycles 2 and 40, at a scan rate of 0.1 V/s, in the range: -0.30 V to 0.90 V vs. Ag/AgCl.

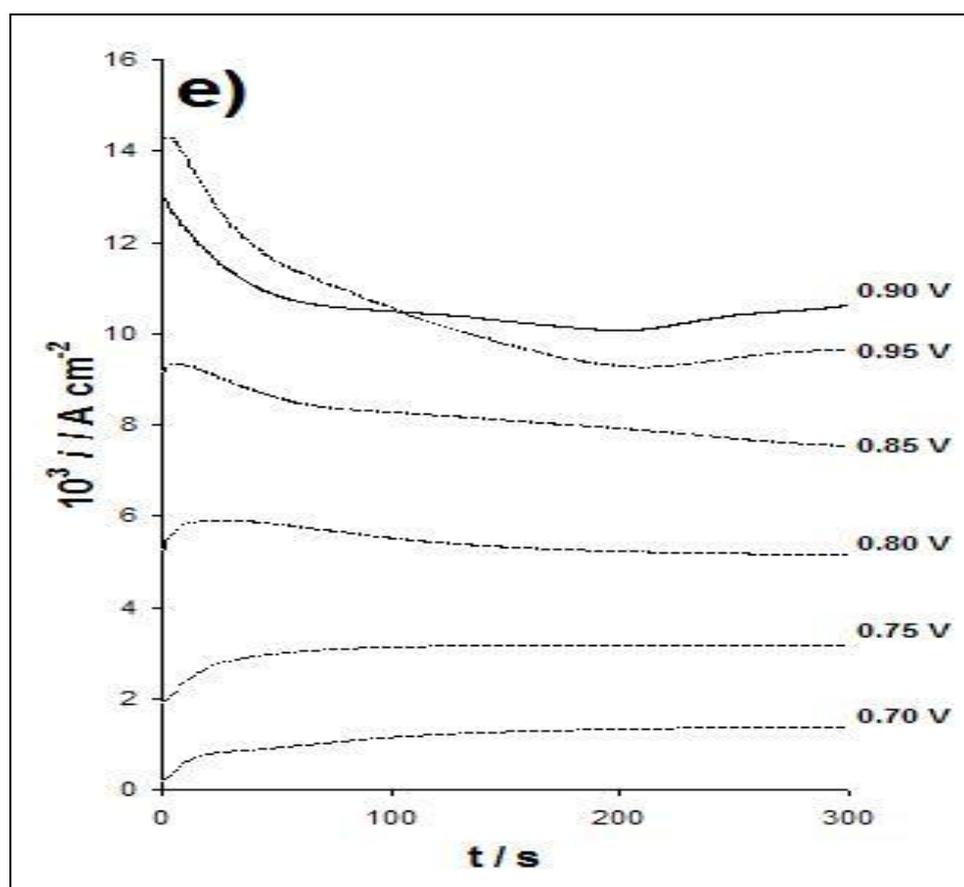
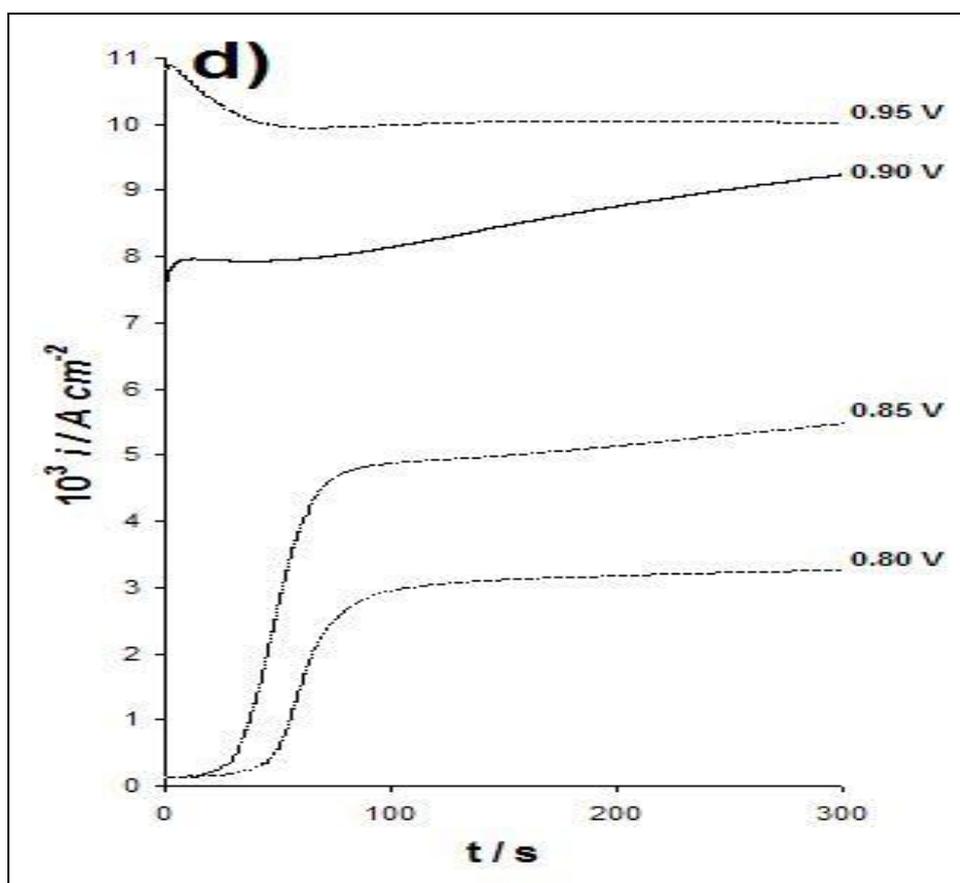
Electrolyte (0.1 M)	CYCLIC VOLTAMMETRY			
	Cycle 2		Cycle 40	
	Charge (mC/cm ²)	Thickness (μm)	Charge (mC/cm ²)	Thickness (μm)
KI	107.02	0.267	236.57	0.591
KNO ₃	0.18	0.00045	16.68	0.041
KBr	0.19	0.00048	14.51	0.036
KCl	0.17	0.00043	11.20	0.028
KClO ₄	1.36	0.00034	9.54	0.024
K ₂ SO ₄	0.23	0.00057	3.77	0.009
KF	0.11	0.00028	0.03	0.00007

b) *Potentiostatic modulation of PPy properties*

In order to evidence what happens to the films after the maximum thickness is reached when the cycling continues, we switched to the potentiostatic regime for PPy preparation in the potential range of +0.55 to +0.95 V. Figure 3 shows the resulting chronoamperometric curves in different electrolytes. These curves are characteristic of phase formation processes on electrode surfaces.







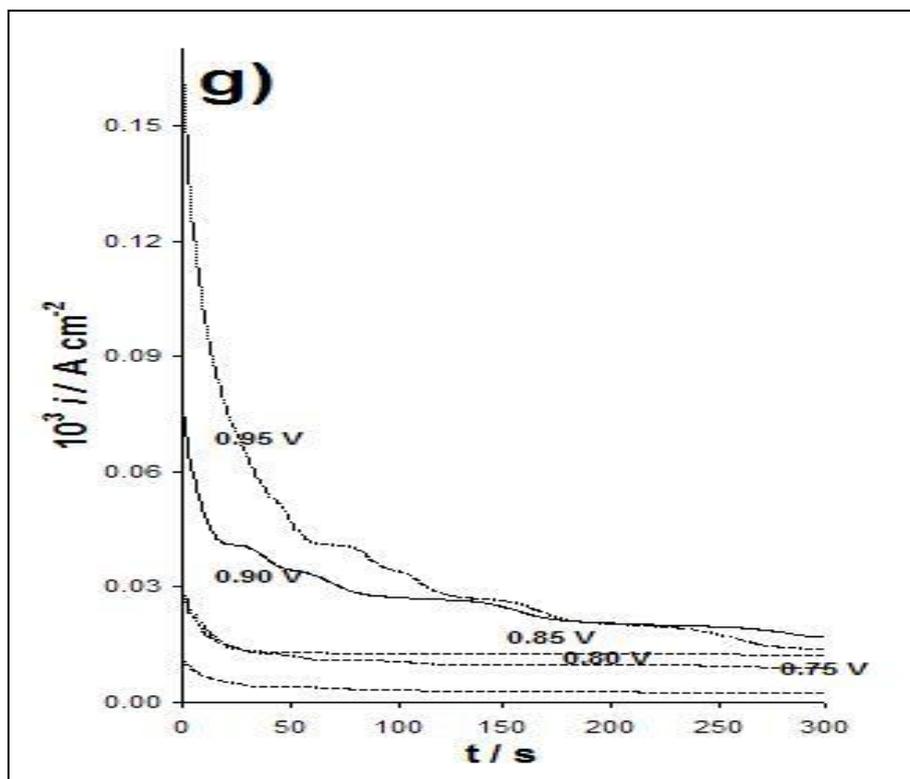
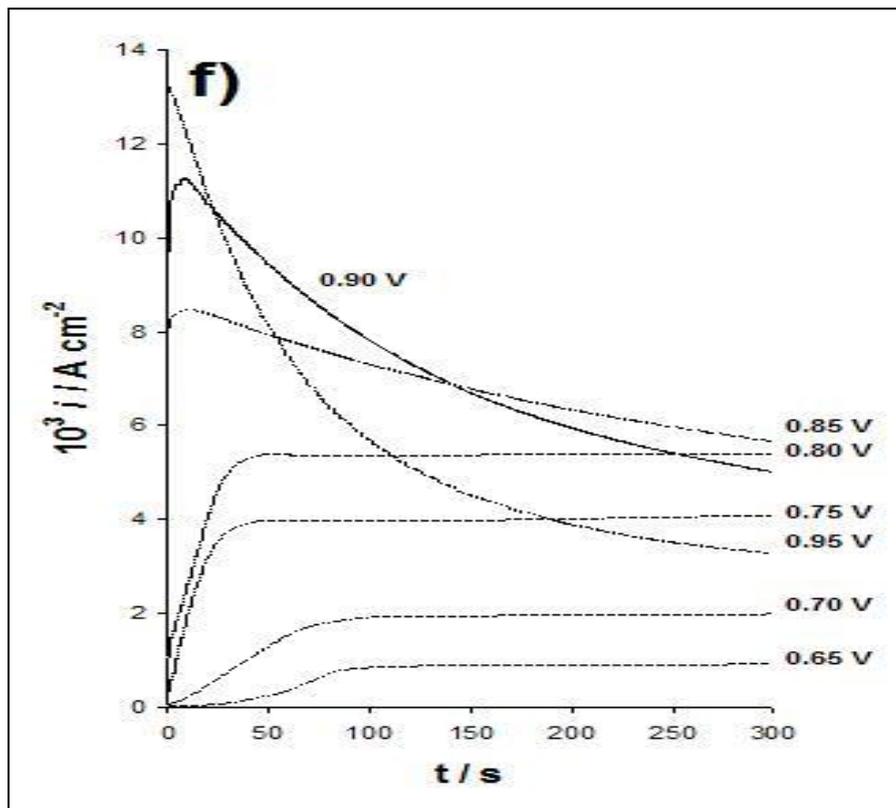


Figure 3. Current vs. time curves obtained during the constant potential electropolymerization of PPy in 0.1 M Py on a glass carbon electrode in aqueous medium (circumneutral pH) in the presence of salts of different anions (0.1 M): a) KI, b) KNO_3 , c) KBr, d) KCl, e) KClO_4 , f) K_2SO_4 and g) KF, at 0.9 V vs. Ag/AgCl during 300 s.

If the growth of the film were controlled by the diffusion of pyrrole through the electrolyte, then one would expect that at the large overpotentials required to observe PPy growth on the electrode surface, the currents should merge into a common procession at sufficiently long times [44]. After an initial decay, there is an ascending portion related to the nucleation processes associated to the incipient formation of the PPy nuclei [34, 45, 46]. Then, current decays again, signaling the existence of a process that limits the rate of PPy growth. This growth involves the formation of radical cations through oxidation and reaction with Py monomers, followed by fast oxidation and the loss of two protons to recover a one-unit longer, neutral PPy chain. Thus the population of polarons remains low during PPy growth and a low conductivity is obtained [38, 45].

Most of the syntheses were performed at potentials between 0.75 and 0.95 V vs. Ag/AgCl (except in KI, performed at 0.55 to 0.95 V). No current decay vs. time is observed in the curve at 0.90 V when using KI or KCl (see Figures 3-a, 3-d), while the contrary occurs for the other anions at the same potential. Such decay becomes more pronounced with synthesis potential and it can be ascribed to the overoxidation of the polymer.

Given the importance of the stability issue, this irreversible overoxidation has been the subject of numerous studies [25-27] and it is associated to the formation of hydroxyl (-OH) and carbonyl (-C=O) groups in the pentacycle, arising from reactions of the aqueous solvent with charge-carrying species [30]. This breaks the electronic conjugation, perturbing the conduction of charge carriers. In extreme conditions this effect can completely annihilate the electroactive capacity of PPy. This can be used to advantage since overoxidized PPy displays transport selectivity for certain ions [47]. The dramatic current exponential decay observed in Figures 3-c (at 0.95 V), 3-f (at 0.95 V) and 3-g (at 0.90 and 0.95 V) is an evidence of this overoxidation [47].

The polymerization mechanism resulting from potentiostated synthesis is similar to that in the potentiodynamic regime in the sense that the rate of film growth seems to be repressed with time at these high potentials. In the case of KF this occurs very early in the process since even after the first cycle the current response decreases (as discussed earlier, see Figure 1-g).

As an indirect measure of stability, the currents at 20 s and 300 s are now compared for the different anions utilized. Figure 4 shows that current *increases* with time for example for KCl and KI (14% and 6%, respectively) whereas for KBr and KF it *decreases* 3% and 75%, respectively. This clearly demonstrates that synthesis time can be used to modulate the final conductivity of the polymer film.

Table 3 shows the charge passed and film thicknesses. Charge is obtained from the area under the curve for films prepared at $E = 0.90$ V during 20 and 300 s, and the thickness is calculated as discussed above.

Figure 5 compares film thicknesses obtained potentiostatically at 0.90 V for 20 s and 300 s. A similar trend is observed in both cases compared to the potentiodynamic syntheses (except in the cases of KNO_3 and KClO_4), as film thicknesses are: $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{F}^-$. The origin of the resulting charges is probably a combination of the growth and overoxidation processes. It is clear that overoxidation does not occur to the same degree with all anions. Longer synthesis times do not necessarily lead to thicker or more conductive films.

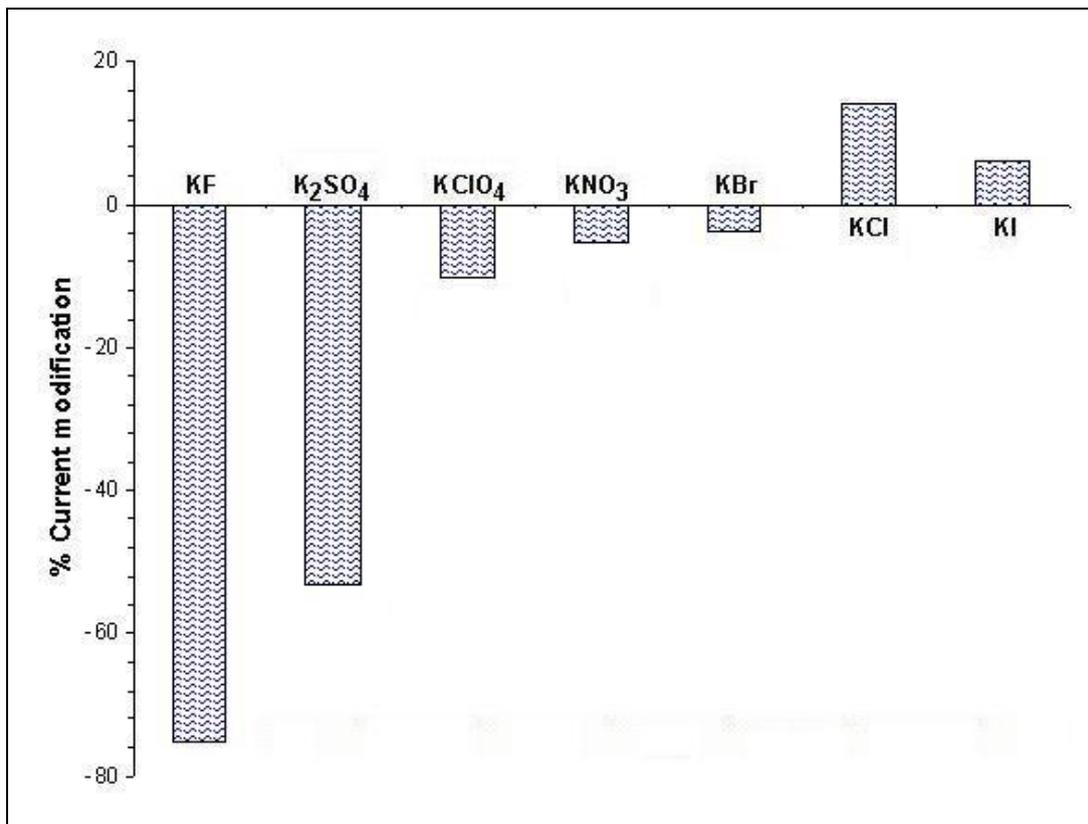


Figure 4. Percentages of current decrease or increase when using an electroynthesis growth time of 300 s at a constant potential (0.90 V vs. Ag/AgCl), as compared to the current obtained after 20 s in selected electrolytes.

Interestingly, for some applications (e.g., chromium (VI) reduction [48]), overoxidized PPy films show very low efficiencies. This is a case in point where tailoring the oxidation stage of the films can be used to great advantage. Non-overoxidized films are reported at high efficiencies by an adequate choice of anions and of electroynthesis time [48].

Table 3. PPy film thickness and charge passed, calculated from the current vs. time graphs obtained from electroynthesis at 0.90 V vs. Ag/AgCl, at 20 s and 300 s.

Electrolyte (0.1 M)	CONSTANT POTENTIAL			
	t = 20 s		t = 300 s	
	Charge (mC/cm ²)	Thickness (µm)	Charge (mC/cm ²)	Thickness (µm)
KI	774.28	1.935	10142.86	25.357
KNO ₃	133.28	0.333	2228.57	5.571
KBr	86.28	0.215	3171.43	7.928
KCl	60.57	0.151	2557.14	6.392
KClO ₄	116.28	0.290	3278.57	8.196
K ₂ SO ₄	123.14	0.307	2171.43	5.428
KF	0.89	0.002	8.35	0.020

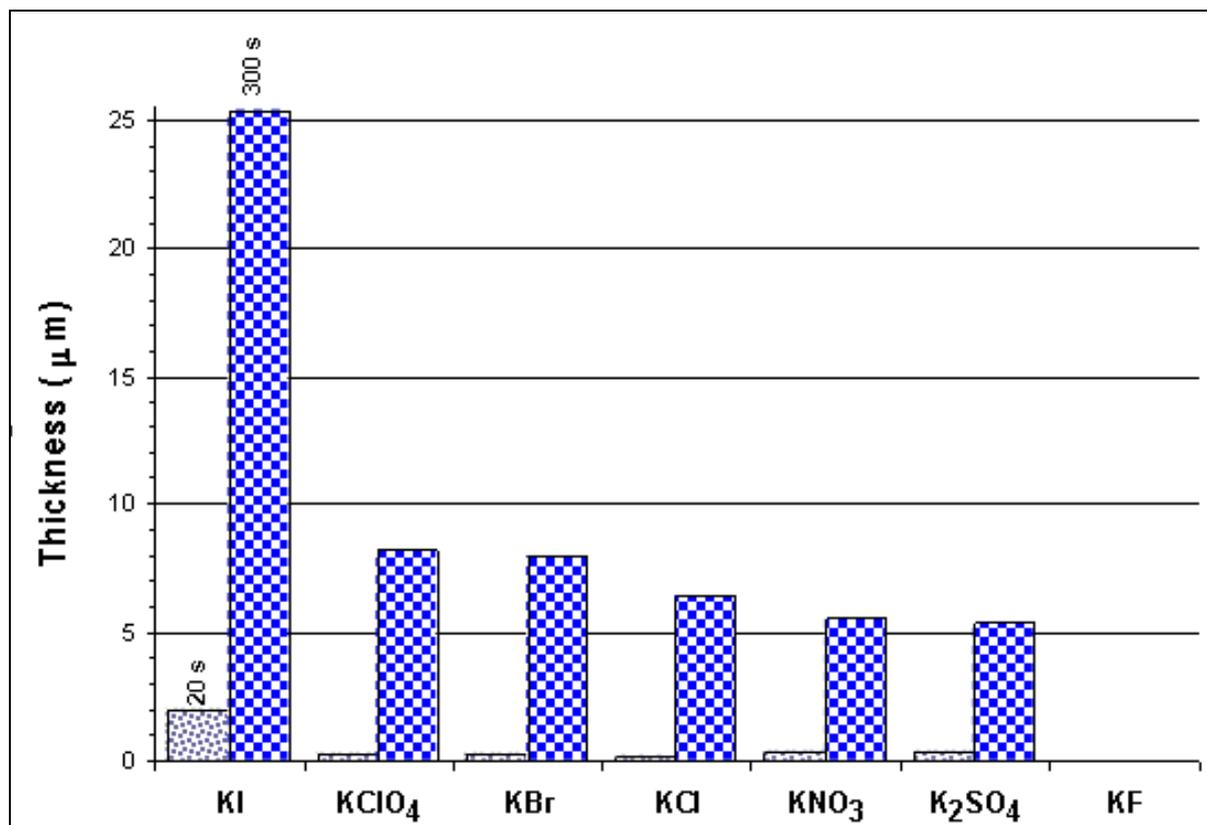


Figure 5. PPy film thickness vs. dopant anion, calculated for electrosynthesis at a constant potential of 0.90 V vs. Ag/AgCl at 20 s and 300 s.

4. CONCLUSIONS

PPy films with controllable properties can be achieved by modulating selected parameters during their electrosynthesis. Several properties are related to the nature of the anion (dopant) used during film preparation. In all cases, the PPy film thickness decreases in the following order: $I^- > Br^- > Cl^- > SO_4^{2-} > F^-$. Thicker films are produced when the electrosynthesis is performed at constant potential. At higher potentials, polymer films display a tendency to overoxidize with a concomitant conductivity loss. The overoxidation potential ranges as well as the onset times for overoxidation are firmly related to the nature of the anion as well. Our findings provide the basis for the preparation of PPy films with varying thickness for diverse purposes.

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