

Perchlorate Interchange during the Redox Process of PPy/PVS Films in an Acetonitrile Medium. A Voltammetric and EDX Study

A. J. Fernández Romero,* J. J. López Cascales, and T. Fernández Otero

Laboratory of Electrochemistry, Intelligent Materials, and Devices (CEMI), ETSII, Campus de Alfonso XIII, Universidad Politécnica de Cartagena, 30203 Cartagena, Spain

Received: July 30, 2004; In Final Form: October 13, 2004

Polypyrrole/poly(vinyl sulfonate) (PPy/PVS) films in acetonitrile containing 0.1 M LiClO₄ were studied by cyclic voltammetry. Consecutive voltammograms pointed to a continuous increase in the charge involved in the process, suggesting a rise in the number of the electroactive participants involved in the redox process. However, voltammograms obtained for the PPy/ClO₄ films in analogous conditions pointed to a steady-state behavior from the very early cycles. Theoretical studies based on the Nernst and Butler–Volmer equations indicated that perchlorate ions are involved during the oxidation/reduction process of the PPy/PVS films when the steady state is reached. This result was confirmed by “ex situ” energy-dispersive X-ray analysis of the films. In this regard, the electrochemical behavior of PPy/PVS polymers was similar to that of PPy/ClO₄ films when a high number of cycles were carried out. The exchange of ClO₄[−] during the redox reaction of the PPy/PVS films made it necessary to incorporate Li⁺ cations inside the polymer during the initial voltammetric cycles to compensate for the negative charges of PVS polyanions. Li⁺ cations are mainly stabilized inside the polymer by the ion pairs formed with the sulfonated groups of the PVS. An increase and shift of the voltammetric cycles indicated a restructuring of the polymeric chains with consecutive scans.

1. Introduction

Since the late 1970s, a great number of research groups have focused their interest on conducting polymers, such as polyacetylene, polypyrrole (PPy), polyaniline, and so forth, studying them from several points of view, including their synthesis, characterization, and technological application. PPy is one of the most widely studied conducting polymers because pyrrole is easily synthesized; furthermore, it is water-soluble, commercially available, and the most frequently used polymer in commercial applications. In addition, PPy shows good long-term stability of its electric conductivity, together with good redox properties and the possibility of forming polymeric blends with optimal mechanical properties.^{1–3}

PPy synthesis by electrochemical oxidation of pyrrole monomers is a well-known and well-controlled method. Anions of different sizes can be used to dope PPy during the polymerization process. Examples of these anions include (1) small anions, such as ClO₄[−], NO₃[−], Cl[−], and so forth; (2) huge anions, such as poly(styrene sulfonate) (PSS) or poly(vinyl sulfonate) (PVS); and (3) medium-sized anions, such as *p*-toluenesulfonate or benzenesulfonate. The resulting polymer will exhibit different conductive, mechanical, or electrochemical properties^{4–7} depending on the incorporated anion.

The ions interchanged with the solution during the redox switching are also influenced by the doping anion of the polymer.^{4–6} Various experimental techniques, such as cyclic voltammetry, electrochemical quartz crystal microbalance (EQCM), energy-dispersive X-rays (EDX), probe beam deflection, or electron paramagnetic resonance (EPR), have been used to determine the nature of ionic transport during its oxidation or reduction process.^{4–13}

Smyrl et al.^{5,6} reported that PPy films doped exclusively with small anions showed anion movement during the redox process, while in PPy films doped with PVS or PSS, cations were inserted and expelled from the polymeric matrix. The PPy films synthesized with medium-sized anions showed both cation and anion motion during the redox processes. Although this postulation is normally accepted, different or opposite behaviors to that proposed by Smyrl have frequently been reported.^{5,9,12,13–19}

According to the above, the nature of the ionic transport is affected by several factors. Both the anion incorporated in the film during the polymerization process and the one used as an electrolyte play important roles in the ion movement during the redox process as a result of factors such as the anion size, nature (univalent or divalent), or diffusion coefficient in solution and through the polymer. Similar observations have been made for electrolyte cations.^{14,16,20} Moreover, the nature of the solvent also plays an important role in the doping–dedoping process of PPy films.^{12,17,18,21,22} Solvent molecules can be transported inside the polymer during the redox process, and so, depending on the solvent–ion and solvent–polymer interactions, ionic transfer may be very different. Finally, anion or cation movement is strongly dependent on the structural disparities present in PPy films.¹³

In this work, we reveal that perchlorate interchange prevails in the PPy/PVS redox process in an acetonitrile (AN) medium, contrary to Smyrl’s predictions. Anomalous voltammetric behavior of this polymeric blend was observed in a 0.1 M LiClO₄/AN solution when compared with that of PPy/ClO₄ films. Thus, when a high number of cycles of a PPy/PVS film in AN were carried out, restructuring of the polymeric matrix was observed. On the basis of the Nernst and Butler–Volmer equations and EDX measurements, we confirm that the ClO₄[−] anions become the main mobile species during the redox process after cycling a PPy/PVS film many times. This fact can be

* Corresponding author. E-mail: antonioj.fernandez@upct.es.

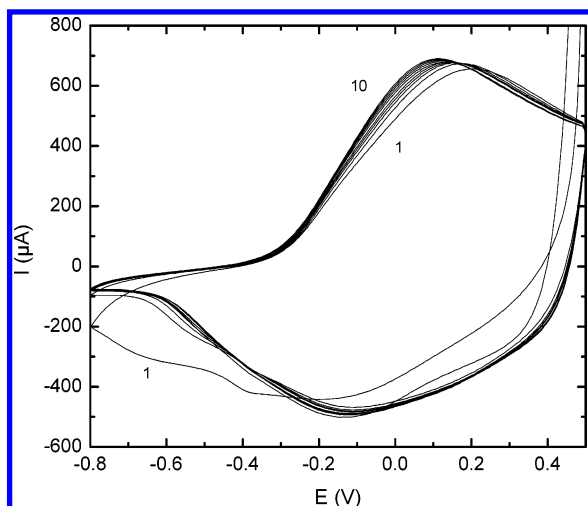


Figure 1. Cyclic voltammograms of PPy/ClO₄ polymer in a 0.1 M LiClO₄/AN solution. Scan rate: 0.1 V/s. Ten consecutive cycles are shown.

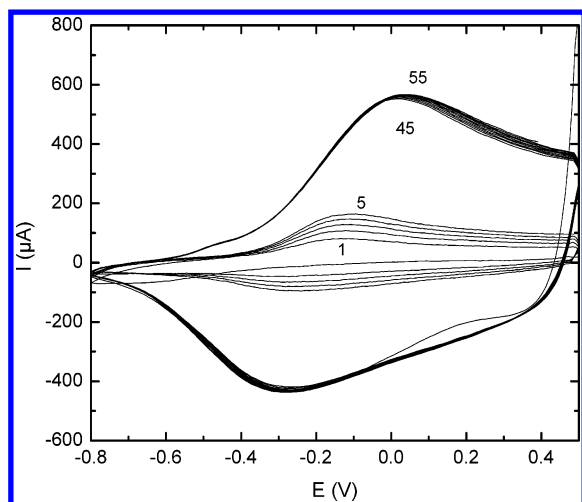


Figure 2. Cyclic voltammograms of PPy/PVS polymer in a 0.1 M LiClO₄/AN solution. The 5 initial and 10 final cycles are shown. Values indicate the scan numbers.

explained by stabilization of the cations inside the polymer to balance the negative charge associated with the PVS.

2. Experimental Section

Pyrrole monomer (Fluka, >97%) was distilled under a vacuum before use. Sodium poly(vinyl sulfonate) (PVS-Na; Aldrich), LiClO₄ (Fluka), NaClO₄ (Merck), and AN (Merck, with a water content < 0.01%) were used as received. Millipore water with a resistivity of > 18 MΩ cm was used.

PPy/PVS and PPy/ClO₄ films were generated by electrochemical oxidation on Pt-foil electrodes at +0.8 V (vs Ag/AgCl) in aqueous solutions of 0.1 M pyrrole and 0.05 M PVS-Na or 0.1 M LiClO₄. The polymerization charges were 86 ± 4 mC/cm² for the PPy/PVS and PPy/ClO₄ films depicted in Figures 1–5, but the charges were 320 ± 5 mC/cm² for the films used in Figures 6 and 7. After generation, the films were washed with water and AN and dried by a N₂ flow. A three-electrode cell composed of a Pt-modified working electrode, an Ag/AgCl reference electrode, and a Pt wire as the auxiliary electrode was used. All solutions were purged with N₂ gas for 15 min.

Cyclic voltammetry studies were performed in a similar three-electrode cell using a Quiceltron potentiostat/galvanostat. When

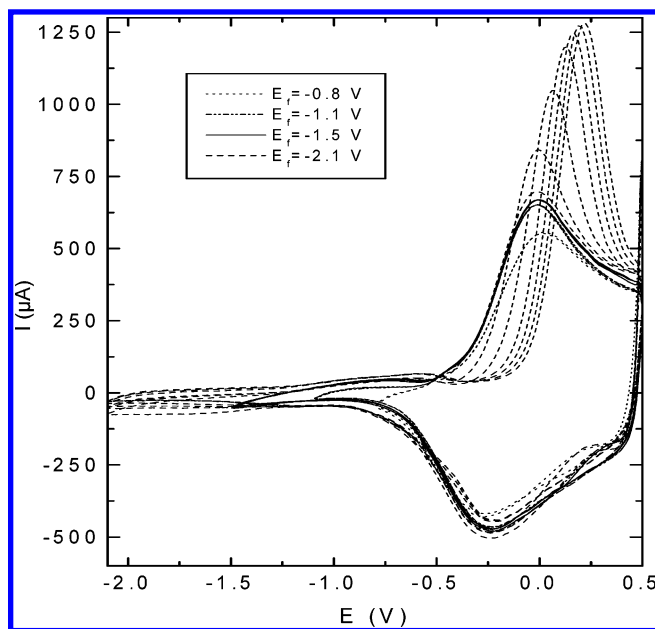


Figure 3. Voltammetric behavior of a PPy/PVS film in a 0.1 M LiClO₄/AN solution, changing the final potential (E_f). The initial potential (E_i) was always adjusted to +0.5 V. All scans were registered for the same film after a steady state had been reached by switching between +0.5 and -0.8 V. The voltammograms were obtained by diminishing E_f in the following order: -0.8 V (--- curve), -1.1 V (--- curve), -1.5 V (— curve), and -2.1 V (- · - curve). Scan rate: 0.1 V/s.

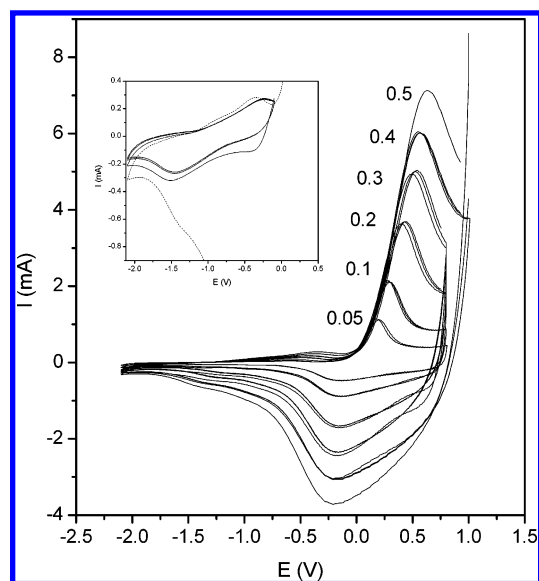


Figure 4. Voltammograms of a PPy/PVS film, varying the scan rate in a 0.1 M LiClO₄/AN solution. Scan rates in V/s are indicated. Inset: cyclic voltammetry for $E_i = -0.1$ V and $E_f = -2.1$ V. Scan rate: 0.6 V/s.

the AN solution was used, the reference electrode was placed in a separate compartment with the same electrolyte solution. Both cells were connected through a salt bridge, preventing water and ion contamination by the reference electrode.

EDX analysis was carried out with a scanning electron microscope (S-3500N). Thick PPy/PVS films were synthesized, using conductive carbon adhesive films, so that they could be pulled off of the Pt sheet easily. The EDX measurements performed with the polymeric film attached to the electrode produced a large peak of Pt, which masked the other peaks. PPy/PVS films were cycled in the electrochemical cell until

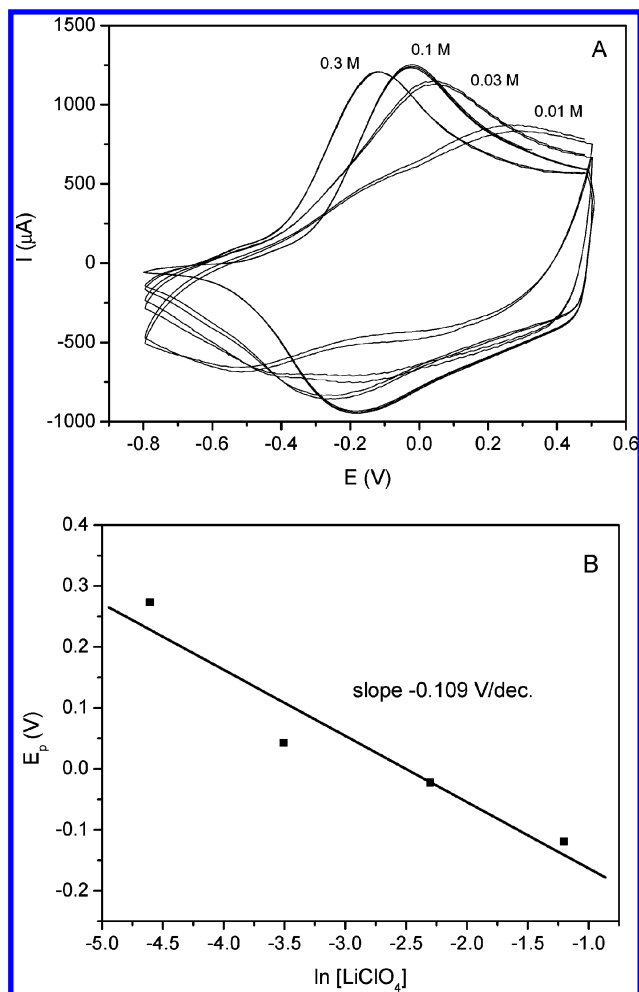


Figure 5. Voltammetric behavior of the PPY/PVS polymer in an AN solution, varying the LiClO_4 concentration. (A) Voltammograms for different concentrations, which are marked on the curves. Scan rate: 0.1 V/s. (B) Oxidation peak potentials as a function of $\ln [\text{LiClO}_4]$.

the voltammograms became steady and then were taken out of the solution, washed with AN, and dried. The oxidized or reduced films were obtained by stopping the last cycle at the desired potential.

3. Results and Discussion

3.1. Cyclic Voltammetry of PPY/PVS and PPY/ ClO_4 Films.

Figure 1 shows 10 consecutive voltammograms, from +0.5 to -0.8 V, performed on a PPY/ ClO_4 film in a 0.1 M LiClO_4/AN solution at a scan rate of 0.1 V/s. The first cathodic voltammogram showed an anomalous shoulder at -0.65 V, which is known as the first scan effect.^{12,18,22} In successive cycles, a cathodic peak was seen at -0.10 V. This peak gradually shifted toward lower potentials and stabilized at 0.075 V on the 10th cycle. The charge measured by integration of the anodic peak was 7.77 mC/cm^2 .

The voltammetric behavior of a PPY/PVS film in the same electrolyte solution and in the same potential range is shown in Figure 2. Despite the fact that similar polymerization charges were used to synthesize both films (PPY/ ClO_4 and PPY/PVS), the voltammetric behavior of the PPY/PVS film was quite different, although an anomalous cathodic peak was again evident. During the five initial cycles, the anodic charge was very small, measuring 1.39 mC/cm^2 for the 2nd cycle, and it increased to 7.07 mC/cm^2 for the 45th cycle, when it reached

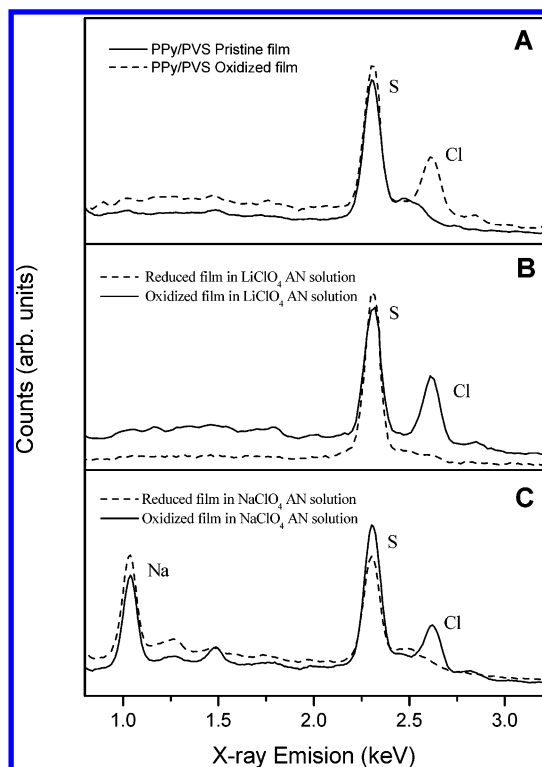


Figure 6. EDX spectra of free-standing PPY/PVS films. (A) The grown (solid line) and oxidized films (dashed line) at +1.0 V after cycling in a 0.1 M LiClO_4/AN solution, (B) the reduced film at -2.1 V (dashed line) and the oxidized film (solid line) at +0.5 V, both obtained after cycling in a 0.1 M LiClO_4/AN solution, and (C) the reduced film at -1.4 V (dashed line) and the oxidized film (solid line) at +0.5 V, both obtained after cycling in a 0.1 M NaClO_4/AN solution.

a voltammetric steady state. Moreover, a shift of the anodic-potential peak to higher potentials was observed for consecutive cycles.

It should be noted that the anodic charge for the PPY/PVS film after it reached the steady state (in the 45th cycle) was similar to the charge measured for the PPY/ ClO_4 film in the 10th cycle (and higher). When the previously calculated charges were normalized by their respective polymerization charges, very similar dimensionless values were obtained, 0.085 and 0.086 for the PPY/PVS and PPY/ ClO_4 films, respectively. Hence, we observed that the charge measured in the voltammetric peaks for PPY/PVS tended to resemble the PPY/ ClO_4 charge with an increasing number of cycles.

Similar increasing anodic peaks have been found when PPY/PBS {copoly[pyrrole-*N*-(butyl sulfonate)pyrrole]} films were cycled in a 0.1 M LiClO_4/AN solution.⁷ In this case, the increase was attributed to a replacement of the bulky $(\text{Bu})_4\text{N}^+$ cation by the small Li^+ cation. However, in our case, we did not use a bulky cation in the polymerization process of the PPY/PVS polymer.

Moreover, as has been reported previously,^{7,23,24} the value of the formal potential for the PPY/PVS voltammetric maximum is more negative than that of the PPY/ ClO_4 films. In addition, peak separation for PVS-based polymers increases with the number of voltammetric cycles to become even higher than that obtained for polymers doped with ClO_4^- when the steady state is reached. This result has been attributed to a slowing down of electrolyte motion in the polyanionic blend during charging-discharging.²⁵

In aqueous solution, the voltammetric response of a PPY/PVS film shows stable behavior from the second cycle onward,

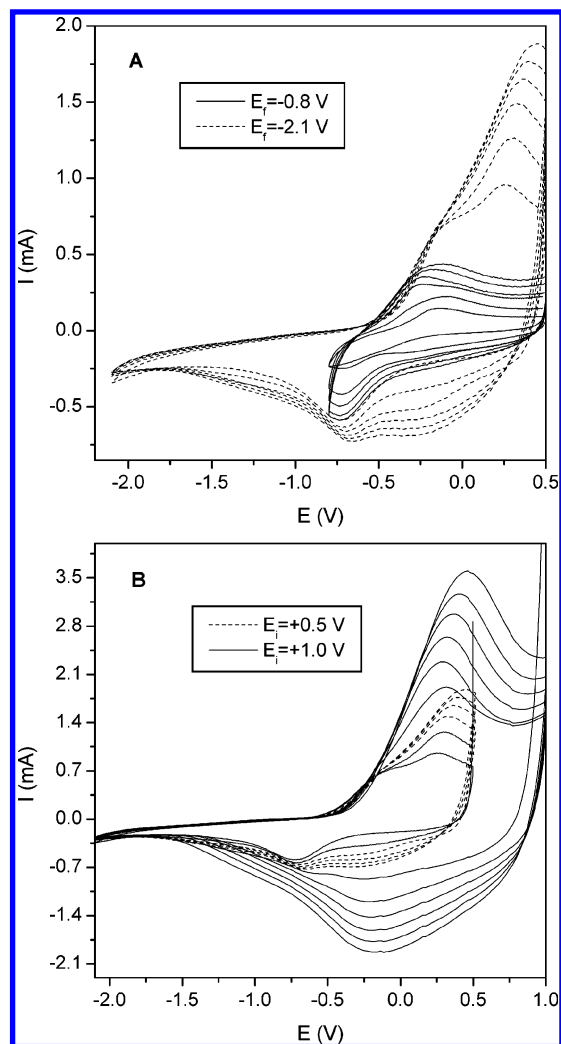


Figure 7. Voltammograms of a thick PPy/PVS film in a 0.1 M LiClO₄/AN solution. (A) The potentials range from $E_i = +0.5$ V to $E_f = -0.8$ V (— curve) and from $E_i = +0.5$ V to $E_f = -2.1$ V (--- curve). (B) The potentials range from $E_i = +0.5$ V to $E_f = -2.1$ V (--- curve) and from $E_i = +1.0$ V to $E_f = -2.1$ V (— curve). Scan rate: 0.1 V/s.

indicating that the AN solvent has a strong influence on the voltammetric behavior of PPy films, which has already been reported.^{7,10,12,13,18}

Continuing with the electrochemical behavior of PPy/PVS films in an AN medium, when more-negative potentials (−1.5 or −2.1 V) are reached, noticeable changes in their voltammograms are observed, with higher anodic peaks and greater anodic charges being obtained. Moreover, using −2.1 V as the cathodic potential limit, only 15 cycles were required to reach a steady voltammogram. Figure 3 illustrates the voltammetric behavior of a PPy/PVS film observed by changing the cathodic limit after stable peaks had been reached using −0.8 V as the final potential. The current in the anodic peak increased with increasing cathodic limits, with no change in the peak potential when the limits were −0.8, −1.1, and −1.5 V. However, when a strongly negative potential (−2.1 V) was reached, the anodic peak became sharper (the peak width at half-maximum moving from 0.432 to 0.240 V) and shifted to a higher potential (from $E_p = +0.015$ V to $E_p = +0.222$ V) with cycling. Moreover, the anodic charge also increased up to 9.61 mC/cm² for the last cycle. However, the cathodic branch maintained an invariant morphology under different cathodic potentials.

Similar anodic shifts and rising charges were observed in the anodic peak when PPy/ClO₄ films were cycled up to a final potential of −2.1 V. Surprisingly, the peak potential approached the value of $E_p = +0.222$ V in both films. These results again indicate a similar behavior for the PPy/PVS and PPy/ClO₄ films under these conditions.

The voltammetric behavior described above agrees with previous results reported by Zhou et al.,¹³ which showed an ever-increasing redox wave for the charging–discharging process of a PPy/PF₆ film in a 0.1 M TBAPF₆/AN monomer-free solution. These authors also observed a shift of the oxidation voltammetric peak to more-positive values by cycling from +1.6 to −2.0 V. This result was associated with a transition from the so-called PPy(II) to the PPy(I) structure, which has longer polymer chains. In the same study, PPy(II) has a more-negative oxidation potential than PPy(I), which, in turn, has a more-negative potential than the extrapolated value for a very long chain polymer. This fact was explained on the assumption that the PPy(I) structure has longer, more-cross-linked chains than PPy(II). Hence, the first structure needs a higher overpotential as a result of the additional energy required to flatten the tilted chains. Thus, the shift of the anodic peak in Figure 3 may be explained as being due to a restructuring of the PPy/PVS polymer during cycling, when the polymer will form a more-compact structure, making a higher overpotential necessary to flatten the more-tilted chains.

Furthermore, the same authors suggested that the evolution seen in the cyclic voltammograms might be the result of some solid-state reactions and ion movement during charging and discharging.²⁴ Similar results were obtained for PPy films that were prepared at low potentials and then cycled.^{26,27} The micromorphological changes during the consecutive cycling of PPy(II) were found to be coupled to the nature of the ion exchange, with the cation and anion exchange for the freshly prepared films [PPy(II)] being gradually replaced by the pure anion exchange at the end of cycling [when PPy(I) was formed].²⁸

In accordance with the above evidence, we consider that reorganization of the PPy/PVS polymeric matrix may be caused by cycling in an AN medium, producing a shift of the anodic peak. This restructuring may modify the kind of ionic transfer in the redox process, and hence the PPy/PVS film tends to behave more like PPy/ClO₄ as cycling progresses, the ClO₄[−] anions being the main mobile ionic species, which will be demonstrated below.

3.2. Evidence for Anionic Transport in an AN Medium.

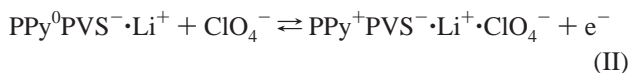
In addition to the above results, there is substantial experimental evidence pointing to a prevailing perchlorate interchange during the PPy/PVS redox process in an AN solution. For instance, a shift of the anodic voltammetric peaks to higher potentials was observed with increasing scan rates, while almost no variation was observed in the cathodic waves (Figure 4). Voltammetric peaks corresponding to the insertion of amobile ions have been considered to be more sensitive to the scan rate.⁸ Thus, the insertion of ionic species occurs in the anodic process. Considering the fact that Li⁺ insertion cannot be assumed in anodic voltammetric scans, there must be an uptake of ClO₄[−] anions during oxidation scans, producing a shift in the anodic peaks.

Further evidence supporting the anion interchange is based on a physical–chemical model developed by Otero et al.^{29–31} for electrochemical oxidation while under conformational relaxation control. In this case, when the PPy/PVS film was maintained at −2.1 V for 1 min, the subsequent step to an anodic potential produced a chronoamperogram, which showed a

maximum. This is only possible if ClO_4^- enters a compacted polymeric matrix at an anodic potential and it is expelled from the polymer to the solution at a cathodic potential.

3.2.1. Nernst and Butler–Volmer Treatment. As an initial hypothesis, we accept that, in these types of polymer/polyelectrolyte materials, it is not clear which prevailing species, cation or anion, is transferred during reverse redox processes. Three different possibilities exist: (1) there is a prevailing interchange of cations, (2) there is a prevailing interchange of anions, or (3) both cations and anions participate simultaneously in the oxidation/reduction process.

Considering that the polyelectrolyte remains fixed inside the polymeric material, two basic redox reactions for the prevailing interchange of cations or anions, respectively, can be proposed:



A combination of these two basic mechanisms for the charge balance describes the third possibility.

In the simplest approximation and considering an equilibrium condition, the electrochemical potential for these reactions could be described by the Nernst equation:

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{PPy}^+\text{PVS}^-][\text{Li}^+]}{[\text{PPy}^0\text{PVS}^-\text{Li}^+]} = E^\circ + \frac{RT}{nF} \ln \frac{[\text{PPy}^+\text{PVS}^-]}{[\text{PPy}^0\text{PVS}^-\text{Li}^+]} + \frac{RT}{nF} \ln [\text{Li}^+] \quad (1)$$

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{PPy}^+\text{PVS}^-\text{Li}^+\cdot\text{ClO}_4^-]}{[\text{PPy}^0\text{PVS}^-\text{Li}^+][\text{ClO}_4^-]} = E^\circ + \frac{RT}{nF} \ln \frac{[\text{PPy}^+\text{PVS}^-\text{Li}^+\cdot\text{ClO}_4^-]}{[\text{PPy}^0\text{PVS}^-\text{Li}^+]} - \frac{RT}{nF} \ln [\text{ClO}_4^-] \quad (2)$$

These equations describe the evolution of the redox potential as a function of the electrolyte concentrations. If cationic interchange prevails, the redox potential versus electrolyte concentration plots will show a semilogarithmic increase in the potential with the electrolyte concentration. On the contrary, a negative slope is predicted when the interchange of ClO_4^- anions prevails.^{8,9,15,19,32}

To describe kinetic processes, the Butler–Volmer formalism is more appropriate for the anodic branch of the voltammograms. In regard to the oxidation part of the general process, $\text{R} \rightleftharpoons \text{O} + n\text{e}^-$, the Butler–Volmer equation can be expressed by³³

$$i_a = nFAk^\circ C_R \exp[(1 - \alpha)n_f(E - E^\circ)] \quad (3)$$

or

$$E = E^\circ + \frac{1}{(1 - \alpha)n_f} \ln \frac{i_a}{nFAk^\circ} - \frac{1}{(1 - \alpha)n_f} \ln C_R \quad (4)$$

where E° , α , k° , n_s , and C_R are the standard potential, the transfer coefficient, the standard rate constant, the n value of the rate-determining step, and the reactive compound's con-

centration, respectively. For eq II, this equation can be expressed by

$$E = E^\circ + \frac{1}{(1 - \alpha)n_f} \ln \frac{i_a}{nFAk^\circ} - \frac{1}{(1 - \alpha)n_f} \ln [\text{PPy}^0\text{PVS}^-\text{Li}^+] - \frac{1}{(1 - \alpha)n_f} \ln [\text{ClO}_4^-] \quad (5)$$

So, the Nernst equation and Butler–Volmer formalism conclude that, for eq II, E is proportional to $-\ln [\text{ClO}_4^-]$. For eq I, both equations demonstrate a direct relationship between E and $+\ln [\text{Li}^+]$. Consequently, these equations offer a valuable tool for exploring which of the ionic species, cation or anion, prevails during the charge balancing of the electrochemical processes.

To know which ionic species intervenes in the redox process of PPy/PVS films in an AN solution, a voltammetric study was carried out by changing the electrolyte concentration. In this case, the anodic peak potentials in the cyclic voltammograms are considered to be the E potentials. Note that, although this approximation is not completely correct, the polarity of the slopes is the same when using peak potentials in eqs 1–5. Figure 5A shows that the anodic peak shifts toward lower potentials as the electrolyte concentration increases. This results in a negative slope when the peak potentials are plotted against $\ln [\text{LiClO}_4]$ (Figure 5B). Thus, these results confirm that the PPy oxidation is mainly governed by insertion of ClO_4^- anions.

3.2.2. EDX Analysis. According to the above information, it was expected that, after several voltammetric cycles, the electrochemical reaction of the PPy/PVS film could match that of eq II. In its reduced state, it was expected to contain neutral PPy, PVS, and Li^+ , while in its oxidized state, it was expected to be composed of oxidized PPy, PVS, Li^+ , and ClO_4^- . EDX analysis was performed on both reduced and oxidized PPy/PVS films in order to determine their ionic content (Figure 6). Figure 6A shows the EDX spectra of PPy/PVS as grown film after polymerization compared with that of an oxidized film at +1.0 V in a 0.1 M LiClO_4/AN medium. In the pristine film (solid line), only the S peak, caused by the sulfur of the sulfonate anions, is clearly observed, pointing to the presence of PVS inside the polymeric blend. The dashed line in Figure 6A shows a S peak and a Cl peak; the S peak indicates that PVS remains inside the polymer after cycling in a LiClO_4/AN solution, while the Cl peak (from chlorine) demonstrates that ClO_4^- anions have entered the oxidized film. Figure 6B shows reduced (solid line) and oxidized (dashed line) PPy/PVS films in a 0.1 M $\text{ClO}_4\text{Li}/\text{AN}$ solution. As can be seen, the oxidized film shows both the S peak and the Cl peak, indicating the presence of PVS and ClO_4^- inside the polymer. However, no Cl peak is detected in the reduced film after polarization at -2.1 V, indicating that the ClO_4^- anions have been expelled from the polymer by electrochemical reduction.

The presence of ClO_4^- anions inside the oxidized film indicates the simultaneous presence of cations. Because Li^+ cannot be detected by EDX analysis, a complementary EDX study was carried out after cycling the film in a solution of 0.1 M NaClO_4 electrolyte in AN (Figure 6C). In this case, the presence of S, Cl, and Na (from sodium) peaks associated with PVS, ClO_4^- , and Na^+ ions was detected in the oxidized film (solid line), demonstrating that Na^+ cations are maintained inside the oxidized film, probably forming couples with PVS anions. However, when the film was reduced in NaClO_4 in an AN solution, the Cl peak disappeared, although the Na peak remained in evidence, indicating that Na^+ cations are stabilized

inside the polymer and the ClO_4^- anions are interchanged in the redox process.

Hence, we can postulate that, after cycling in LiClO_4 , Li^+ cations will be stabilized inside the reduced PPy/PVS polymer, probably forming ion pairs and balancing the PVS negative charge; however, when the polymer is oxidized, they will remain inside the oxidized polymer as stable pairs, with the interchange of ClO_4^- prevailing to maintain the charge balance during the redox process.

The formation of analogous ion pairs in PPy/PSS films has already been reported by Ren and Pickup,⁸ who showed that the methylviologen dication (MV^{2+}) becomes immobilized in the composite after forming tight ion pairs with the sulfonate anions of PSS in the reduced PPy/PSS polymer. The authors added that oxidation of the resulting PPy/PSS/ MV^{2+} film resulted in ClO_4^- uptake and revealed similar ionic conductivities for both PPy/ ClO_4 and PPy/PSS/ MV^{2+} systems. This behavior is in good agreement with our results, which pointed to the tendency of PPy/PVS films to behave as PPy/ ClO_4 polymers as a result of forming Li^+ -PVS ion pairs and ClO_4^- uptake.

Finally, EDX analysis showed a peak of S, associated with PVS, in pristine, reduced, and oxidized polymeric films, which demonstrates that the polyelectrolyte does not participate in the ionic interchange during the redox processes.

3.3. Cation Contribution to the PPy/PVS Redox Process.

Although, as was observed above, the anion transport is predominant during the oxidation/reduction process, the participation of the cation motion cannot completely be ruled out. At the beginning of the voltammetric cycles, cations are necessarily incorporated into the polymeric matrix to reduce the initially oxidized polymer. The slow increase in voltammetric peaks in Figure 2 can be explained by the gradual incorporation of Li^+ into the polymer bulk. Previously, we remarked on the different voltammetric behaviors of PPy/PVS in AN and aqueous media, noticing a clear influence of the AN solvent on the PPy/PVS redox process. Considering that PVS anions are insoluble in an AN solution, the incorporation of AN molecules inside the PPy/PVS film will be hindered. However, Li^+ cations in an AN medium are solvated by four AN molecules.³⁴ As a result, the penetration of the solvated cations inside the polymer will be delayed and will, in fact, be a difficult process, which is the origin of the slowly increasing voltammetric peaks of Figure 2; in each cycle, a larger amount of solvated Li^+ will be incorporated into the polymer, reaching more internal chains, producing new Li^+ -PVS ion pairs to participate in the subsequent reduction/oxidation process, and, hence, increasing the charges of the voltammetric peaks. In relation to this, when a higher negative potential is reached from as early as the first cycle, a greater amount of solvated Li^+ will be forced to penetrate the reduced polymer, and therefore the anodic peak will shift and rapidly increase. In this way, increasing the cathodic limit leads to an irreversible reorganization of the polymeric structure, which can be seen by the shift and the current increase for the maximum in Figure 3.

On the other hand, the simultaneous participation of Li^+ interchange during the redox process cannot be entirely excluded. For PPy/ ClO_4 in an AN medium, Levi et al.¹⁵ found two voltammetric redox waves: small redox peaks at more-cathodic potentials, attributed to cation exchange, and the main redox peaks at more-positive potentials, associated with anion movement. Moreover, other authors have similarly described a split of anodic and cathodic voltammetry peaks for several PPy films.^{5,9,13–18}

The solid curve in Figure 7A depicts cyclic voltammograms from +0.5 to -0.8 V obtained with thick PPy/PVS films (polymerization charges of $320 \pm 5 \text{ mC/cm}^2$). These thick films present a principal cathodic wave at -0.7 V and an anodic peak at -0.2 V, peaks which increase in each cycle until a maximum charge value is reached. When the final potential is changed to -2.1 V and the same initial potential is maintained, other anodic/cathodic waves emerge at more-positive potentials (dashed lines in Figure 7A). Furthermore, the solid curves in Figure 7B depict how the positive waves increase strongly if +1.0 V is used as the initial potential, overlapping the more-cathodic redox waves, which remain almost unchanged.

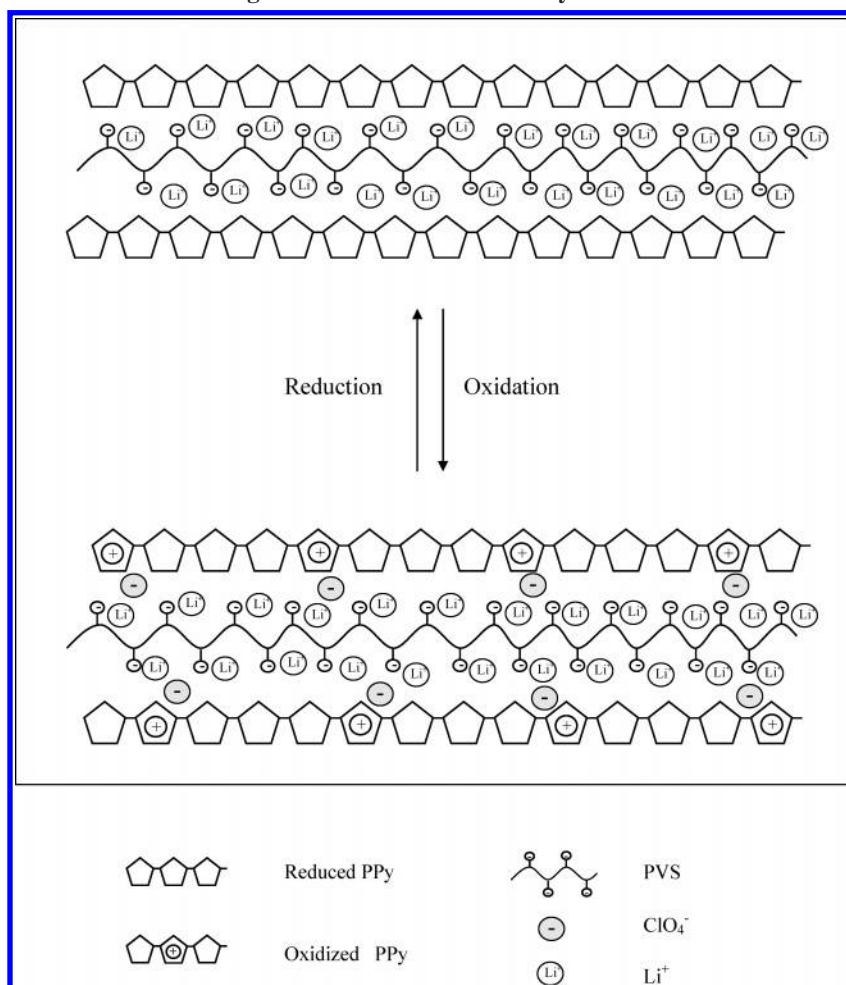
The small, more-cathodic processes can be attributed to cation movements, while the main peaks will correspond to anion movements. In this respect, EDX analysis has demonstrated that both cations and anions are embedded in the films at +0.5 and +1.0 V (Figure 6A,B). Hence, a small quantity of cations will move, corresponding to the more-negative process in Figure 7 and a high concentration of them being maintained inside the polymer at anodic potentials. It is necessary to maintain the electroneutrality inside the film; if anions penetrate at anodic potentials to compensate the oxidized PPy, PVS negative charges must be balanced by Li^+ cations. As a consequence, two different kinds of cations, "free" and "bound",¹⁵ will contribute to the charging-discharging process of PPy/PVS. In Figure 7, small cathodic waves will correspond to small quantities of "free" Li^+ cations, while the principal voltammetric peaks will be produced by massive incorporation of ClO_4^- anions, as a consequence of the great number of "bound" cations stabilized inside the polymer.

Splitting of the oxidation peaks can also be observed for a thin PPy/PVS film (Figure 4). Cyclic voltammograms of PPy/PVS in a 0.1 M LiClO_4/AN medium registered from -0.1 to -2.1 V produced small and complex anodic and cathodic peaks at more-negative potentials than those of the principal peaks (inset in Figure 4). This plot indicates that these peaks constitute an independent process. Visy et al.³⁵ revealed the appearance of a small prepeak, similar to ours, during the oxidation voltammetric scan for copolymers of 3-methylthiophene. These authors observed the massive incorporation of anion and solvent during the voltammetric cycles, leading to a gradual accumulation of mass inside the polymer during or between scans. This caused an irreversible change of the polymeric film behavior and led to the appearance of a prepeak on the oxidation scans. A similar increase in mass is to be expected for PPy/PVS during scans, producing an irreversible polymeric restructuring and the appearance of small cathodic prepeaks, as illustrated in Figure 4. However, in our film, cycling produces an accumulation of Li^+ cations and, probably, AN molecules inside the polymer.

4. Conclusions

We initially observed very different voltammetric behaviors for PPy/PVS and PPy/ ClO_4 polymers in an AN medium. However, the cycling of PPy/PVS in the same solution led to a similar behavior for both films. The small initial redox waves in PPy/PVS and their gradual increase can be explained by the difficulty that solvated Li^+ cations have in entering the polymeric matrix.

Voltammetric studies using the Nernst and Butler-Volmer equations indicated that perchlorate is the main mobile species during the redox process for PPy/PVS films. Furthermore, EDX analysis confirmed this perchlorate uptake as well as the fact that PVS was not replaced by smaller ClO_4^- during voltammetric scans. Interchanging of small anions has rarely been reported for this type of copolymer.

SCHEME 1: Model for Ion Insertion during the Redox Process of a PPy/PVS Film^a

^a Four pyrrole units involving one positive charge are considered in oxidized PPy.

The diffusion of ClO_4^- to and from a polymeric film necessitates an initial insertion of a Li^+ cation in the polymeric matrix and its stabilization inside the polymeric blend. Thus, Li^+ cations ensure electroneutrality in the negatively charged reduced polymer. The subsequent oxidation will produce ClO_4^- incorporation to compensate for the PPy positive charge. Consequently, Li^+ cations can form ion pairs with the sulfonated anions of PVS in the reduced polymer and become immobilized inside the composite. Scheme 1 shows this situation, where PPy has a neutral charge and Li^+ cations balance the negative charges of PVS in the reduced polymer. Afterward, when an anodic potential is applied, the majority of Li^+ cations are maintained inside the polymer, forming ion pairs with PVS, while ClO_4^- anions are taken up to balance the PPy positive charge. Four pyrrole units of PPy, carrying one positive charge, are represented.

On the other hand, the gradual increase of redox waves and the positive shift of anodic peaks with cycling support an irreversible restructuring of the PPy/PVS films. During voltammetric scans, the polymer will form a more-compact structure, where the polymeric chains will be more-cross-linked, necessitating a higher overpotential. This overpotential results from the additional energy needed to flatten the tilted chains. The increment of mass due to bound cations forming ion pairs and solvent molecules may also contribute to tilt and restructure the polymer chains.

Acknowledgment. The authors thank Dr. I. Ibarra and L. A. Alcolea from the Technological Instrumentation Service of the UPCT for their technical assistance in the EDX measurements. We are also grateful for financial support from the Spanish government (Grant BQU2001-0477) and from the Seneca Foundation (Project PI-25/00827/FS/01).

References and Notes

- (1) *Handbook of Conducting Polymers*; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998.
- (2) Otero, T. F. In *Modern Aspects of Electrochemistry*; White, R. E., Bockris, J. O'M., Eds.; Kluwer Academic: New York, 1999; Vol. 33, Chapter 3.
- (3) González, J.; Fernández, A. J.; Otero, T. F. In *Electronics and Optical Properties of Conjugated Molecular Systems in Condensed Phases*; Hotta, S., Ed.; Research Signpost: Kerala, India, 2003; Chapter 5.
- (4) Shimidzu, T.; Ohtani, A.; Yyoda, T.; Honda, K. *J. Electroanal. Chem.* **1987**, 224, 123–135.
- (5) Lien, M.; Smyrl, W. H.; Morita, M. *J. Electroanal. Chem.* **1991**, 309, 333–340.
- (6) Naoi, K.; Lien, M.; Smyrl, W. H. *J. Electrochem. Soc.* **1991**, 138, 440–445.
- (7) Bidan, G.; Ehui, B.; Lapkowski, M. *J. Phys. D: Appl. Phys.* **1988**, 21, 1043–1054.
- (8) Ren, X.; Pickup, P. G. *J. Phys. Chem.* **1993**, 97, 5356–5362.
- (9) Zhong, C.; Doblhofer, K. *Electrochim. Acta* **1990**, 35, 1971–1976.
- (10) Elliott, C. M.; Kopelove, A. B.; Alberty, W. J.; Chen, Z. *J. Phys. Chem.* **1991**, 95, 1743–1747.
- (11) Novák, P.; Kötz, R.; Haas, O. *J. Electrochem. Soc.* **1993**, 140, 37–40.

- (12) Lee, H.; Yang, H.; Kwak, J. *J. Electroanal. Chem.* **1999**, 468, 104–109.
- (13) Zhou, M.; Pagels, M.; Geschke, B.; Heinze, J. *J. Phys. Chem. B* **2002**, 106, 10065–10073.
- (14) John, R.; Wallace, G. G. *J. Electroanal. Chem.* **1993**, 354, 145–160.
- (15) Levi, M. D.; López, C.; Vieil, E.; Vorotyntsev, M. A. *Electrochim. Acta* **1997**, 42, 757–769.
- (16) Davey, J. M.; Ralph, S. F.; Too, C. O.; Wallace, G. G. *Synth. Met.* **1999**, 99, 191–199.
- (17) Slama, M.; Tanguy, J. *Synth. Met.* **1989**, 28, C139–C144.
- (18) Duffitt, G. L.; Pickup, P. G. *J. Chem. Soc., Faraday Trans.* **1992**, 88, 1417–1423.
- (19) Yang, H.; Lee, H.; Kim, Y. T.; Kwak, J. *J. Electrochem. Soc.* **2000**, 147, 4239–4246.
- (20) Tamm, J.; Hallik, A.; Alumaa, A.; Sammelselg, V. *Electrochim. Acta* **1997**, 42, 2929–2934.
- (21) Skaarup, S.; West, K.; Gunaratne, L. M. W. K.; Vidanapathirana, K. P.; Careem, M. A. *Solid State Ionics* **2000**, 136–137, 577–582.
- (22) Beck, F.; Dahlhaus, M. *J. Electroanal. Chem.* **1993**, 357, 289–300.
- (23) Shouji, E.; Okamoto, Y.; Ozaki, F.; Naoi, K. *Polym. Adv. Technol.* **1996**, 7, 177–181.
- (24) Zhou, M.; Heinze, J. *Electrochim. Acta* **1999**, 44, 1733–1748.
- (25) Zotti, G.; Zecchin, S.; Schiavon, G.; Louwet, F.; Gronendaal, L.; Crispin, X.; Osikowicz, W.; Salaneck, W.; Fahlman, M. *Macromolecules* **2003**, 36, 3337–3344.
- (26) Levi, M. D.; Lankri, E.; Gofer, Y.; Aurbach, D.; Otero, T. *J. Electrochem. Soc.* **2002**, 149, E204–E214.
- (27) Levi, M. D.; Aurbach, D. *J. Electrochem. Soc.* **2002**, 149, E215–E221.
- (28) Cohen, Y. S.; Levi, M. D.; Aurbach, D. *Langmuir* **2003**, 19, 9804–9811.
- (29) Otero, T. F.; Grande, H.; Rodríguez, J. *J. Electroanal. Chem.* **1995**, 394, 211–216.
- (30) Otero, T. F.; Grande, H. *J. Electroanal. Chem.* **1996**, 414, 171–176.
- (31) Otero, T. F.; Grande, H.; Rodríguez, J. *J. Phys. Chem. B* **1997**, 101, 3688–3697.
- (32) Takashima, W.; Pandey, S. S.; Kaneto, K. *Thin Solid Films* **2003**, 438–439, 339–345.
- (33) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd ed.; Wiley: New York, 2001; Chapter 3.
- (34) Izutsu, K. *Electrochemistry in Nonaqueous Solutions*; Wiley-VCH: Weinheim, Germany, 1998; Chapter 2.
- (35) Visy, C.; Kankare, J.; Kriván, E. *Electrochim. Acta* **2000**, 45, 3851–3864.