

In Situ FTIR Spectroscopy Study of the Break-In Phenomenon Observed for PPy/PVS Films in Acetonitrile

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The in situ Fourier transform infrared (in situ FTIR) technique was used for the first time to investigate the break-in phenomenon observed for polypyrrole/poly(vinyl sulfonate) (PPy/PVS) films in acetonitrile containing 0.1 M LiClO₄. Consecutive potential scans provided a continuous increase of the infrared band intensities, simultaneous to an increase observed in the charge involved in the voltammetric peaks, suggesting a rise in the number of the polymeric chains participating in the infrared signal at the same time as the electroactive participants increase in the redox process. Moreover, in situ FTIR spectra evidence that the new infrared-activated chains in each voltammetric cycle adopt the same polymeric structure achieved by the chains activated in the initial cycles. However, if we achieve a cathodic potential limit of -2.1 V (vs Ag/AgCl), a restructuring of the polymeric morphology is observed. In situ FTIR spectra obtained for PPy/ClO₄ films under the same conditions pointed to a steady-state behavior from the very early voltammetric scans. Moreover, the intensities of FTIR bands obtained for PPy/ClO₄ films in the early voltammetric cycles are much higher than those obtained for PPy/PVS films after several potential scans. Only when high cathodic and high anodic potential limits were used for the consecutive cycles did the FTIR band intensities from PPy/PVS become similar to those obtained from PPy/ClO₄, indicating that in both films a similar number of polymeric chains were infrared active. Polarization at a high anodic potential ($+1.3$ V vs Ag/AgCl) produced overoxidation of the polymer appearing characteristic 1725 cm^{-1} band assigned to the formation of carbonyl groups. Furthermore, the $\sim 1540\text{ cm}^{-1}$ band shifted to higher wavenumbers, indicating that overoxidation reduced the length of conjugated chains in the polypyrrole.

1. Introduction

Polypyrrole (PPy) is one of the most widely studied conducting polymers from numerous points of view, including its synthesis, characterization, and technological applications, through several experimental techniques and theoretical methods.^{1–3}

Infrared absorption^{4–12} and Raman^{13–18} spectroscopy combined with theoretical calculations^{19–25} of vibrational spectra have been used to study the structure, chemical bond distribution, inter- or intrachain interactions, and so forth, of the conducting polymers, such as PPy. Moreover, the in situ Fourier transform infrared (in situ FTIR) technique has been widely used to study the molecular restructuring of the PPy during the doping process, completing the information obtained by classical electrochemical methods.^{8–12} Christensen and Hamnett⁹ reported an in situ ellipsometry and FTIR spectroscopy study of PPy/ClO₄ in aqueous solution, observing two kinds of species during the oxidation of the polymer film, which were identified as polarons and bipolarons. Later, Mostany et al.¹¹ observed a double band potential-dependent in the region around 1200 cm^{-1} for PPy/NO₃ films in aqueous solution. Deconvolution of this double peak produced two Gaussian bands, closed to 1186 and 1222 cm^{-1} , enabling a follow-up of the evolution of the populations of the radical cations (polarons) and dications (bipolarons) as the potential increased. Investigations of the overoxidation processes of polypyrrole films in aqueous^{5,9–11} and organic^{5,8,10} solvents were also reported.

The vibrational spectra of conjugated, conducting polymers have been reported to show strong unusual effects during doping processes, due to strong electron–phonon coupling.^{9,11,22,25–27} The doping of a conducting polymer, such as PPy, produces new very strong infrared bands in the infrared spectrum, the so-called infrared active vibration (IRAV) bands. The origin and behavior of doping induced IRAV bands have been described by Zerbi et al.^{22,25} by the effective conjugation coordinate model. The IRAV bands correspond to totally symmetric Raman active modes, which become infrared active due to symmetry breaking and are strongly enhanced because the charge distribution in the oxidized polymer causes high dipole changes during vibrations. Therefore, there is a strong link between the effective conjugation of the polymer, the effective delocalization of the doping induced quasi-particle excitations, such as polarons, and the signatures of the IRAV bands in the doping induced infrared spectrum.^{11,25–27} Furthermore, the intensity of the IRAV bands increases with the increment of the doping level.^{11,25,26} However, previous works have considered that the conducting polymer FTIR spectra are not affected by the doping species.^{11,25}

On the other hand, it has been observed for different conducting polymers that for freshly synthesized films several voltammetric cycles were required for the films to become fully electroactive. This behavior, called the break-in phenomenon, has been attributed to the incorporation of ions and solvent molecules into the polymer matrix during the potential cycling and to the potential-dependent morphological changes.^{28–30}

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Recently, our group has studied a similar behavior observed for the PPy/poly(vinyl sulfonate) (PVS) films in an acetonitrile (AN) medium using energy-dispersive X-ray spectrometry (EDXS) and cyclic voltammetry.³⁰ In this case, Li^+ cations were incorporated in the early cycles, probably with AN molecules, and stabilized inside the polymer by the ion pairs formed with the sulfonated groups of the PVS, producing an increment of the mass inside the polymer and a restructuring of the polymeric chains with the cycling. This fact provided perchlorate interchange during the redox process of PPy/PVS film in a 0.1 M LiClO_4/AN medium.

In the present work, we analyze the break-in phenomenon for PPy/PVS films in a 0.1 M LiClO_4/AN medium using in situ FTIR spectroscopy for the first time. The in situ FTIR spectra confirm the voltammetric results obtained for PPy/PVS films in ref 30. A continuous increase of FTIR bands was obtained with the voltammetric cycling, suggesting a rise of the electroactive participants involved in the redox process. This produced a higher number of infrared active polymeric chains, which preserve the structure of the chains activated during the initial cycles. Moreover, infrared activation of polymeric chains in PPy/PVS films increased more quickly, with a parallel restructuring of the polymeric chains, as it was observed by FTIR, when a strongly cathodic potential limit was reached in the voltammetric cycles. In situ FTIR spectra registered for the PPy/ ClO_4 films under analogous conditions produced similar IRAV bands to those obtained for PPy/PVS films; however, the intensities of the bands were much higher from the first cycle and a steady-state behavior was obtained from the very early cycles. Only when some voltammetric cycles were performed on a PPy/PVS film using strong cathodic and anodic potentials, the intensities of in situ FTIR spectra of this film became comparable to those for PPy/ ClO_4 films. On the other hand, overoxidation of the PPy/PVS film provided the appearance of a peak at 1725 cm^{-1} , which was attributed to the formation of carbonyl groups in the pyrrole rings, and the $\sim 1540\text{ cm}^{-1}$ band shifted to higher wavenumbers, suggesting that the conjugation length of the PPy was reduced.

2. Experimental Section

Pyrrole monomer (Fluka, >97%) was distilled under vacuum before use. Sodium poly(vinyl sulfonate) (Aldrich), LiClO_4 (Fluka), and AN (Merck, with a water content <0.005%) were used as received. Millipore water with a resistivity >18 M Ω cm was used.

PPy/PVS and PPy/ ClO_4 films were generated by electrochemical oxidation on Pt disk electrodes at +0.8 V versus Ag/AgCl in aqueous solutions of 0.1 M pyrrole and 0.05 M PVS-Na or 0.1 M LiClO_4 . The polymerization charges were $94 \pm 5\text{ mC/cm}^2$ for PPy/PVS and PPy/ ClO_4 films. After being generated, the films were washed with water and AN and dried by N_2 flow. A three-electrode conventional cell used, which was composed of a Pt working electrode, an Ag/AgCl reference electrode and a Pt wire as the auxiliary electrode. All solutions were purged with N_2 gas for 15 min.

In situ FTIR studies were performed in a three-electrode spectro-electrochemical all-glass cell. The working electrode was the modified Pt disk, which was pressed against a CaF_2 window trapping a thin layer of electrolyte. A Pt wire, surrounding the working electrode, was used as a counter electrode. A Ag/AgCl electrode located in a different compartment and connected to the main cell through a salt bridge was used as reference, preventing characteristic FTIR bands corresponding to water molecules from the reference electrode. A Bruker IFS 66v

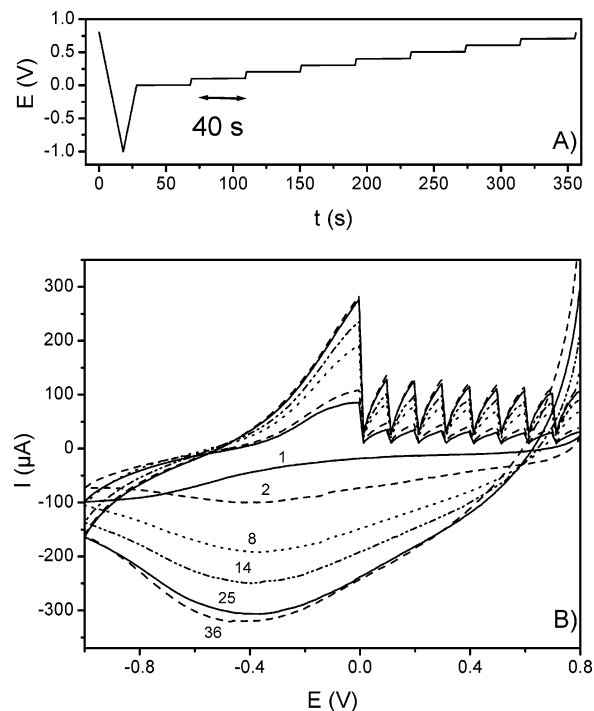


Figure 1. (A) Potential–time curve registered during a voltammetric cycle from $E_i = +0.8\text{ V}$ and $E_f = -1.0\text{ V}$ with the potential stops at 0.0, +0.1, +0.2, +0.3, +0.4, +0.5, +0.6, and +0.7 V to obtain the FTIR spectra. (B) Current–potential curves registered under the same conditions for different voltammetric cycles, which are marked on the curves. Scan rate: 0.1 V/s.

spectrometer with an angle specular reflectance accessory (incidence angle of 65°) was used. All of the beam path was under vacuum, and a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector was used. A KRS-5 infrared polarizer was placed in the optical path before the beam was reflected in the cell. All measurements were performed using a purged acetonitrile 0.1 M LiClO_4 solution, and the three-electrode system was controlled by a Quiceltron potentiostat/galvanostat.

The in situ FTIR spectra were obtained at the desired potentials in the course of a cyclic voltammogram; the scans were stopped for 40 s for registering a spectrum. Each spectrum resulted from the coaddition of 128 interferograms, which were achieved after 5 s to permit potential equilibrium, at 4 cm^{-1} resolution and using p-polarized radiation. The reference spectrum was that recorded with a clean working electrode in a 0.1 M LiClO_4/AN solution previous to the polymer deposition.

This method allows us to achieve the spectra at a constant potential and to observe the voltammetric changes together with the spectrochemical modifications. Parts A and B of Figure 1 show the potential–time and potential–current curves, respectively, obtained during spectro-electrochemical measurements. As can be seen in Figure 1B, the result is that of typical cyclic voltammograms with potential stops in 0.0, +0.1, +0.2, +0.3, +0.4, +0.5, +0.6, and +0.7 V, where the spectra are performed. In these figures, the initial potential (E_i) was +0.8 V, the final potential (E_f) was -1.0 V , and the scan rate was 0.1 V/s.

3. Results and Discussion

In situ FTIR spectra of the PPy/PVS film in 0.1 M LiClO_4/AN obtained at 0.1 V intervals between 0.0 and +0.7 V are shown in Figure 2. This figure displays the ring stretching region, where the IRAV bands of the polymer backbone are observed.^{8,11,22,25–27} As has been previously reported, IRAV bands show increasing intensities for rising oxidation potentials.

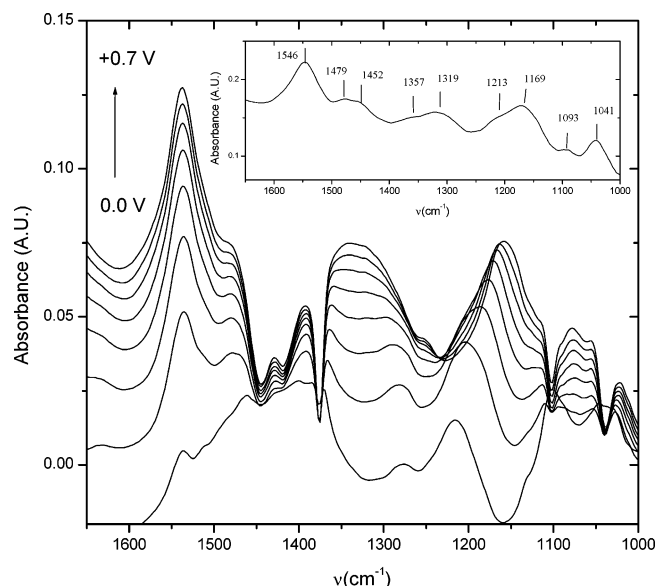


Figure 2. In situ FTIR spectra obtained for a PPy/PVS film in 0.1 M LiClO₄/AN solution at 0.1 V intervals between 0.0 and +0.7 V. The voltammetric cycle was performed between +0.8 and −1.0 V with a scan rate of 0.1 V/s. Inset: Ex situ FTIR spectra for a PPy/PVS film registered by pressing the polymerized working electrode against the F₂Ca windows on the air.

In this figure, five main upward peaks (IRAV bands) are observed at 1537, 1479, 1250–1355, 1110–1250, and 1077 cm^{−1}. Moreover, downward peaks attributed to the interference of AN or perchlorate on the polymer in situ FTIR spectra are present: the broad band at 1470–1357 cm^{−1} and the peak observed at 1040 cm^{−1} are assigned to the AN molecules,^{31,32} while the peak at 1101 cm^{−1} has been reported as being due to perchlorate anions.^{8,10} Since AN and perchlorate vibration signals mask part of the polymer in situ spectra, the ex situ FTIR spectrum of the PPy/PVS film as synthesized under analogous experimental conditions has been included in the inset of Figure 2 as a comparative reference. Thus, features at 1546, 1479, 1452, 1357, 1319, 1213, 1169, 1093, and 1041 cm^{−1} are observed in this spectrum, which are similar to those already reported for PPy synthesized with different anions.^{4,6,7,9,11,22}

All of the peaks observed in Figure 2 show increasing intensities when the film is polarized at more anodic potentials. However, while the 1537, 1479, and 1077 cm^{−1} peaks keep constant wavenumbers, the bands obtained at 1355–1250 and 1250–1110 cm^{−1} show a dispersion of their peak frequencies with the oxidation depth of the polymer for increasing potentials in the same potential cycle.

IRAV bands at 1538, 1483, 1345–1250, and 1250–1118 cm^{−1} were obtained from PPy/ClO₄ films under similar experimental conditions. Although the wavenumbers of these bands are very close to those of PPy/PVS films, their intensities are much higher. Figure 3 displays an in situ FTIR spectra of PPy/ClO₄ film in 0.1 M LiClO₄/AN obtained at 0.2 V intervals between −0.9 and +0.5 V, during a voltammetric cycle performed between $E_i = +0.7$ V and $E_f = -1.0$ V. As can be seen, the AN–perchlorate downward bands were observed again. In this case, spectra recorded between −0.9 and −0.3 V did not show any IRAV bands, confirming that the IRAV bands are not present in a reduced polymer.^{22,25,27}

On the other hand, our group has recently reported the voltammetric behavior of PPy/PVS compared with PPy/ClO₄ films in 0.1 M LiClO₄/AN solution.³⁰ Increasing charges

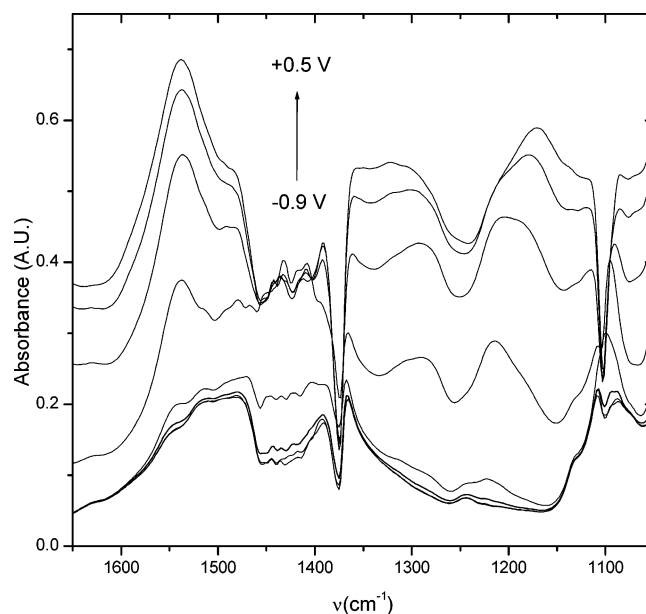


Figure 3. In situ FTIR spectra obtained for a PPy/ClO₄ film in 0.1 M LiClO₄/AN solution at 0.2 V intervals between −0.9 and +0.5 V. The voltammetric cycle was performed between +0.7 and −1.0 V with a scan rate of 0.1 V/s.

participate on the consecutive voltammograms obtained from PPy/PVS films, suggesting a rise in the number of electroactive species involved in the redox process. However, voltammograms obtained for PPy/ClO₄ films pointed at steady-state behavior from the very early cycles, confirming that all of the electroactive species included in this kind of films participate in the voltammetric peaks nearly from the beginning, due to the quick interchange of the perchlorate anions.

In good concordance with those results, now in situ FTIR spectra obtained at the same potential of polarization from consecutive voltammetric cycles applied to PPy/PVS films in 0.1 M LiClO₄/AN show increasing intensities of the IRAV bands (Figure 4). Figure 4A shows in situ FTIR spectra performed at +0.5, +0.6, and +0.7 V for different voltammetric cycles between $E_i = +0.8$ V and $E_f = -1.0$ V. Moreover, the baseline corrected ~1540 cm^{−1} peaks obtained at +0.7 V for different cycles are shown in Figure 4B, where the peak area increase was clearly observed with the number of cycles. The voltammograms registered simultaneously to the Figure 4 spectra, which show the increase of voltammetric peaks, are displayed in Figure 1B (see also Figure 2 in ref 30).

Note in Figure 4 that the FTIR bands present, at the same oxidation potential, constant peak frequencies, indicating the same chemical nature and polymeric structure of the involved oxidized chains in consecutive voltammetric cycles. However, the intensities of the FTIR bands increase with the number of cycles. This behavior indicates that the number of infrared active chains increases with the cycling, while the chains activated in each cycle adopt the same polymeric structure achieved by the fraction of polymer activated during the previous cycles.

Both parallel results, voltammetric peaks and FTIR bands increasing with cycling, are attributed to a slow penetration of solvated Li⁺ cations inside the polymeric matrix during the reduction process. Each new cycle provides the penetration of a new amount of Li⁺ cations into the polymer, reaching more internal polymeric chains and increasing the fraction of the polymeric material participating in the subsequent reduction/oxidation process. It must be remembered that the IRAV bands correspond to totally symmetric Raman modes, and they become

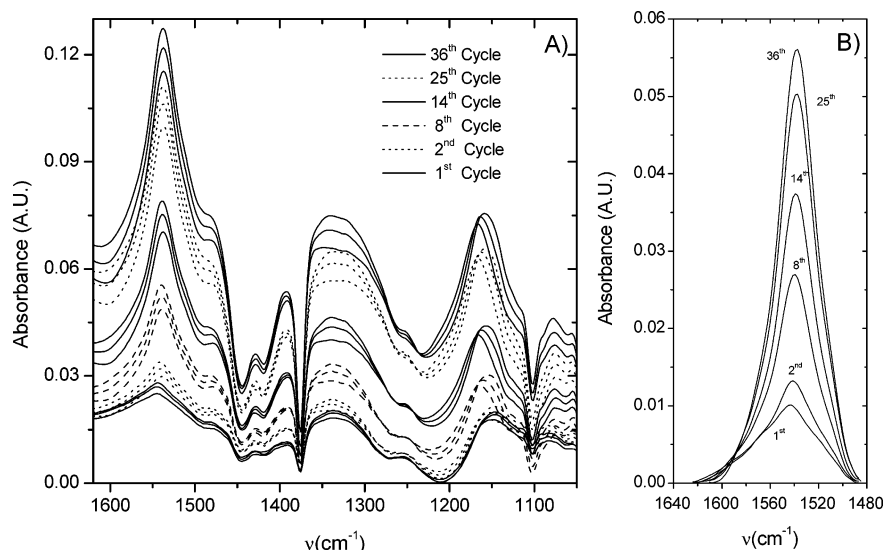
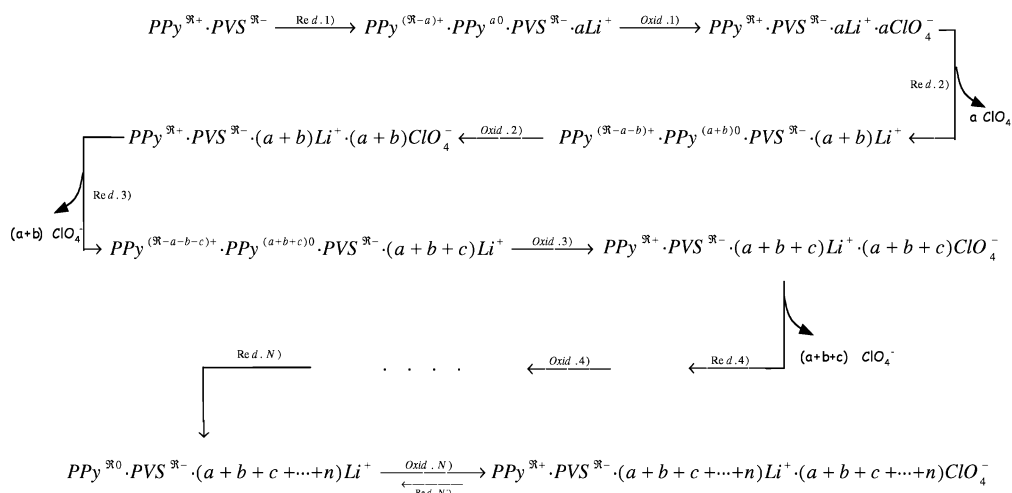


Figure 4. In situ FTIR spectra of a PPy/PVS film in 0.1 M LiClO₄/AN solution registered at +0.5, +0.6, and +0.7 V (bottom to up curves) for different cycles (A). The baseline corrected ~1540 cm⁻¹ peaks obtained at +0.7 V for different cycles (B). The number of cycles is indicated in the figure. The voltammetric cycles were carried out as in Figure 2.

SCHEME 1: Evolution of the Redox Process of a PPy/PVS Film from the 1st to the *n*th Voltammetric Cycle in a 0.1 M LiClO₄/Acetonitrile Medium^a



^a PPy^{*R*+} symbolizes the PPy initially synthesized, where the oxidation charge is *R*+. PVS^{*R*-} symbolizes the PVS macroanion incorporated into the polymer during the electropolymerization. *a*, *b*, *c*, ..., *n* correspond to the number of positive charges of the PPy reduced in the cathodic branch of the 1st, 2nd, 3rd, ..., *N*th voltammetric cycles, respectively, and not reduced in previous cycles. *R* = *a* + *b* + *c* + ... *n*.

infrared active due to symmetry breaking. The entrance of Li⁺ cations inside the polymeric matrix generates Li–PVS ionic pair formation, providing the stabilization of Li⁺ inside the polymer and forcing the interchange of perchlorate anions on the consecutive cycles to neutralize the positive charges on the polypyrrole chains. Only in this polymeric fraction, where the Li–PVS ionic pairs have been formed forcing a prevalent interchange of perchlorate anions under potential scan, the symmetry of the Raman modes is broken, producing active FTIR bands. Thus, in each cycle, the intensities of these bands will increase due to the rise in the polymeric fraction participating in the reduction/oxidation process.

This process is illustrated by Scheme 1. Initially, the as grown PPy/PVS film stores *R* positive charges on the PPy chains, which are compensated by *R* negative charges of the PVS chains. During the first cathodic scan, *a* electrons are injected into the material, reducing *a* positive charges on the PPy⁺ chains, generating PPy⁰, and forcing the entrance of *a* Li⁺ cations to balance the negative charges remaining now free on the PVS chains. A part of the material remains compact and nonacces-

sible to the redox process, keeping (*R* – *a*) positive charges on the PPy. During the anodic branch of the first cycle, the PPy⁰ will be oxidized to PPy⁺ but the Li⁺ cations remain inside the polymer, forming ion pairs with the sulfonate groups of the PVS, forcing the entrance of *a* ClO₄⁻ anions for the charge balancing. These anions are expelled from the material during their reduction in the second voltammetric cycle by injection of *a* electrons, but this process consumes an extra amount of *b* electrons. Consequently, simultaneous to the expulsion of *a* ClO₄⁻ anions from the material, *b* Li⁺ cations will move inside the polymer balancing the free *b* sulfonate groups on PVS chains. At the end of this cathodic scan, the material contains (*a* + *b*) Li–PVS ion pairs and PPy^(*a*+*b*) neutral chains. During the oxidation of the second cycle, all of the reduced PPy^(*a*+*b*) chains were oxidized requiring the penetration of (*a* + *b*) ClO₄⁻ anions for positive charge balancing. After the third reduction scan, (*a* + *b* + *c*) positive charges of the PPy chains were reduced, forming now (*a* + *b* + *c*) Li–PVS ion pairs in the polymer matrix. During the third oxidation branch, (*a* + *b* + *c*) ClO₄⁻ anions were incorporated inside the material.

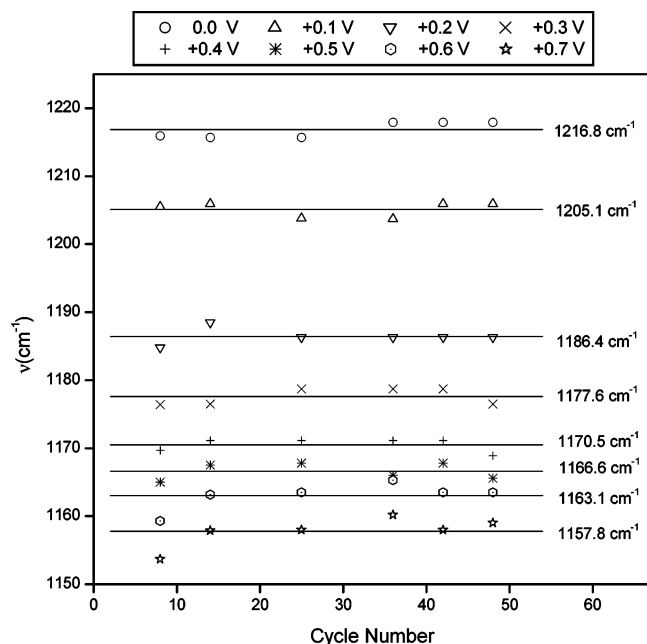


Figure 5. Evolution with the oxidation potential applied of the wavenumbers of the 1250–1110 cm^{-1} band for PPY/PVS film in different cycles. The frequencies shown inside the figure indicate the average values obtained for each oxidation potential. Voltammetric cycles were carried out from $E_i = +0.8$ V to $E_f = -1.0$ V (8th, 14th, 25th, and 36th cycles), to $E_f = -1.5$ V (42th cycle), and to $E_f = -1.8$ V (48th cycle). Scan rate: 0.1 V/s.

Thus, every new cycle incorporated a new polypyrrole fraction into the electroactive material, involving a greater charge. After N cycles, all of the PPY chains from the material were reduced and the reduced material contains R (being $R = a + b + c + \dots n$) Li–sulfonate couples. Any subsequent cycle involves R electrons and the interchange of $R \text{ ClO}_4^-$ anions. Hence, after the first cycle, a small fraction of the PPY, involving a charge, a , became electroactive and also infrared active, due to the symmetry breaking of the Raman active modes by ion-pair formation and anionic interchange. The active fraction (electrochemical and IR) increases in the consecutive cycles involving increasing charges ($a + b + c + \dots n$). Consequently, the voltammetric peaks and the in situ FTIR bands increase continuously in the consecutive voltammetric cycles.

It should be noted that the “free” Li^+ cation interchange has not been considered in the redox process of Scheme 1 due to the small quantities of this kind of species.³⁰ Thus, most of the Li^+ cations are stabilized inside the polymer forming Li–PVS ion pairs, and knowing that the ClO_4^- anion transport is predominant during the oxidation/reduction process to compensate the charge on PPY, the Li– ClO_4 interactions inside the polymer are not significant enough to be included in this scheme.

An alternative explanation for those rising peaks can be found on a distribution of the polymeric chains perpendicular to the electrode surface during potential cycling. Under those conditions and using p-polarized light, those vibration modes with a transition dipole perpendicular to the electrode surface will become active and enhanced. However, a similar increase of the IRAV bands with the cycling was obtained by using s-polarized light.

Besides the increase of the FTIR band intensity, a red shift of the 1250–1110 cm^{-1} band for increasing oxidation potentials was observed (Figure 2). However, this band increases without any shifting when the spectrum is obtained at the same oxidation potential for consecutive potential cycles (Figures 4 and 5).

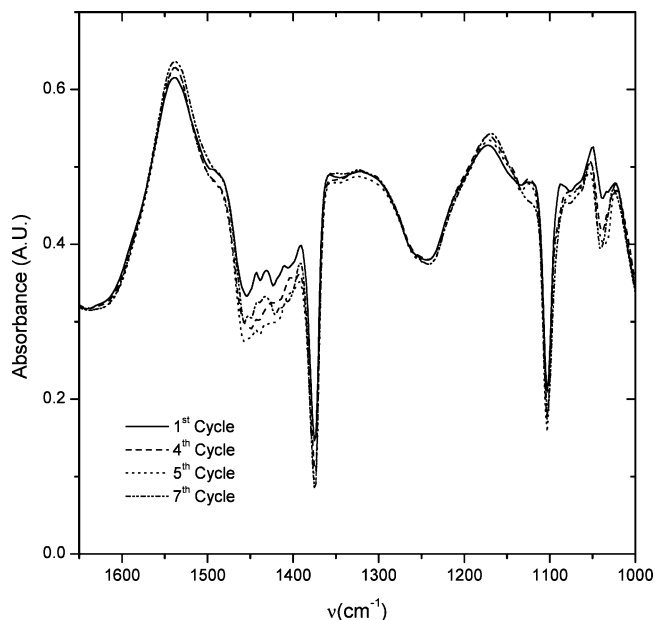


Figure 6. In situ FTIR spectra obtained for a PPY/ ClO_4 film in 0.1 M LiClO_4/AN solution at +0.5 V for different cycles. The spectra have been translated to compare better. The voltammetric cycle was performed between +0.7 and -1.0 V with a scan rate of 0.1 V/s.

These results point to a correlation between the oxidation depth and the frequency of the band maximum: spectra obtained from the same oxidation state (the same potential) show the same frequency regardless of the active material fraction. This fact is obtained for a large range of voltammetric cycles, confirming that the portion of polymer infrared activated in each cycle adopts the same morphology in consecutive cycles and as a consequence the band frequencies can be used as a probe for the oxidation state for the polymer. The observed shift for increasing oxidation potential during a cycle can be due to the diminution of the radical-cation species (polarons) by the formation of dication species (bipolarons) at more anodic potentials, according to Mostany et al. results.¹¹

It should be noted that Figure 5 depicts FTIR frequencies obtained at 0.0, +0.1, +0.2, +0.3, +0.4, +0.5, +0.6, and +0.7 V from a film submitted to different potential cycles and, some of them, performed to different cathodic potential limits (E_f). The potential is scanned from $E_i = +0.8$ V to $E_f = -1.0$ V (8th, 14th, 25th, and 36th cycles), or to $E_f = -1.5$ V (42th cycle) and to $E_f = -1.8$ V (48th cycle). However, when a high cathodic limit such as -2.1 V was reached, the frequencies obtained for this band changed quite a lot with regard to the results indicated in Figure 5, in good accordance with the voltammetric behavior. Reaching -2.1 V, a shift of the oxidation voltammetric peaks toward more positive potentials has been observed,³⁰ and at the same time, a shift of the 1250–1110 cm^{-1} FTIR band toward lower frequencies (from 5 to 15 cm^{-1} depending on the oxidation potential) has been obtained, confirming that an irreversible reorganization of the polymeric structure is produced in this case, as was previously reported.³⁰ We will come back to this subject later.

The IRAV bands observed from PPY/ ClO_4 films in 0.1 M LiClO_4/AN appeared at similar wavenumbers but were much more intense than those obtained from PPY/PVS films under similar experimental conditions. However, while the intensity of in situ PPY/PVS FTIR bands increased with the cycling, the spectra for PPY/ ClO_4 were stable from the very early cycles (Figure 6). Furthermore, the intensities of the peaks obtained

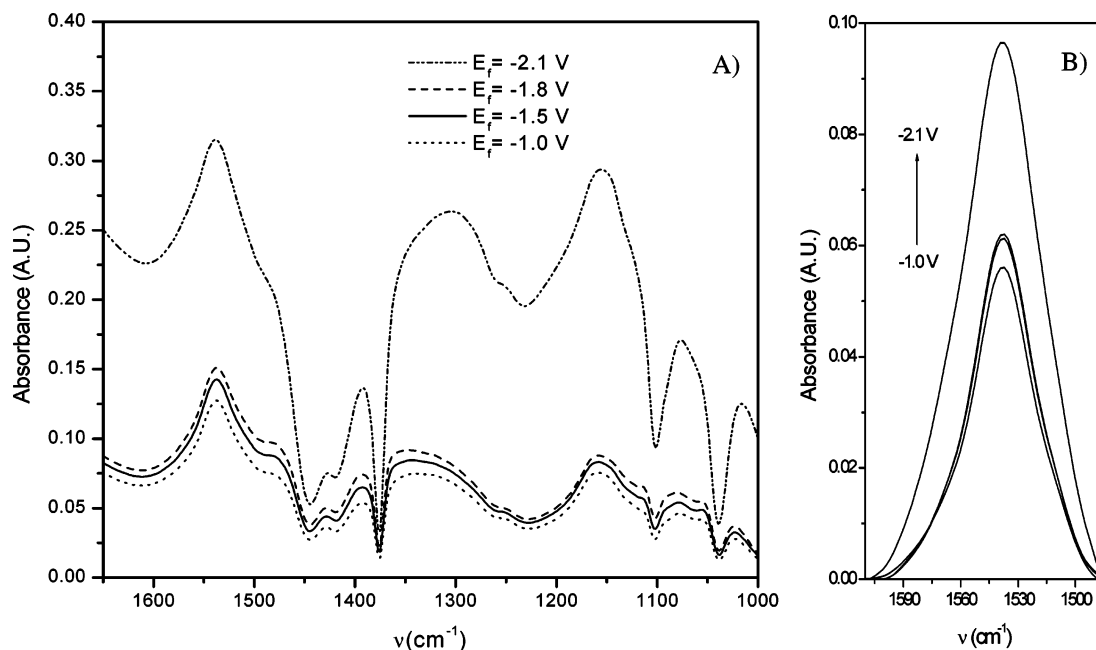


Figure 7. In situ FTIR spectra of a PPy/PVS film in 0.1 M LiClO₄/AN solution registered at +0.7 V changing the final potential of the voltammetric cycles (A). The baseline corrected $\sim 1540\text{ cm}^{-1}$ peaks obtained at +0.7 V for different E_f values (B). The E_i value was always adjusted to +0.8 V.

for PPy/ClO₄ films were much higher than those obtained from PPy/PVS films, even after 36 consecutive cycles.

3.1. In Situ FTIR Spectra Obtained Extending the Voltammetric Potential Range. We have mentioned above that FTIR spectra signals depend on the potential range used for the voltammetric cycles. Thus, when more negative potential limits were reached, noticeable increases of FTIR spectra intensities were observed. Figure 7 shows the FTIR spectra of PPy/PVS film recorded at +0.7 V when different cathodic potential limits were attained during the potential cycle: -0.8 , -1.5 , -1.8 , and -2.1 V, always keeping the same anodic limit of $E_i = +0.8$ V. A drastic enhancement of infrared bands was obtained when -2.1 V was reached, indicating that a higher number of polymeric chains intervene in the redox process, probably as a result of the massive entry of the Li⁺ cations at such a negative potential. The increment of the intensity is clearly observed in Figure 7B, where the baseline corrected $\sim 1540\text{ cm}^{-1}$ bands are shown. However, no shift is observed for this band.

Moreover, simultaneous to FTIR band increment, an increase of the charge in the voltammetric peaks with the more negative cathodic limit was observed. The charges measured by integration of the anodic peaks were $6.52\text{ mC}\cdot\text{cm}^{-2}$ for the last cycle performed using $E_f = -1.0$ V and $8.29\text{ mC}\cdot\text{cm}^{-2}$ for the third cycle with $E_f = -2.1$ V. Figure 8 depicts the voltammograms obtained in the spectro-electrochemical cell for PPy/PVS film in 0.1 M LiClO₄/AN solution, registered from $E_i = +0.8$ V to different cathodic limits. As can be seen, the anodic peak increased and shifted to a more positive potential with cycling, when a -2.1 V final potential was used. Furthermore, small more cathodic redox peaks were observed together with the main redox peaks, as was reported previously.³⁰ It should be noted that all of the in situ FTIR spectra and voltammograms were carried out in the spectro-electrochemical cell, with the working electrode pressed against the CaF₂ window, and the electrode was never separated from the window. That is the reason the voltammogram shapes in Figure 8 are slightly different from those performed in a conventional electrochemical cell,³⁰ where the working electrode was positioned in the bulk of the electrolyte solution. If the electrode is separated from the CaF₂

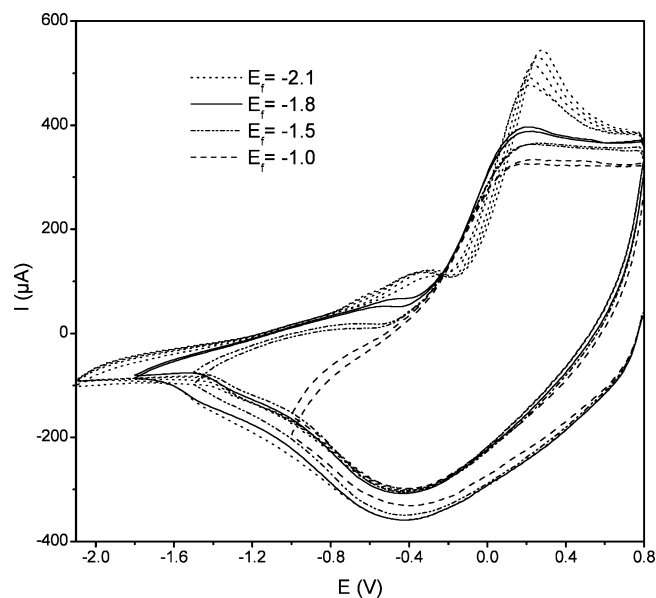


Figure 8. Voltammetric behavior of a PPy/PVS film in 0.1 M LiClO₄/AN solution changing the final potential (E_f). The E_i value was always adjusted to +0.8 V. The voltammograms were obtained diminishing E_f in the following order: -1.0 V (---), -1.5 V (- · - · -), -1.8 V (—), and -2.1 V (···). Scan rate: 0.1 V/s .

window, the voltammetric waves quickly tend to adopt similar shapes to those observed by us in ref 30.

The shift of the oxidation peaks with the cycling when a -2.1 V final potential is used in voltammograms has been explained as being due to a restructuring of the PPy/PVS polymeric chains during cycling, producing a more compact structure and making a higher overpotential necessary to flatten the more tilted chains.^{29,30,33} Furthermore, the prepeak observed on the oxidation scans was attributed to the irreversible changes of the polymeric films produced by massive incorporation of counterions and solvent molecules during the voltammetric cycles.^{30,34}

In this way, an increase of the FTIR bands of PPy/PVS film with the cycling will be related to the slow restructuring of polymeric matrix. Reaching a strongly negative potential (-2.1

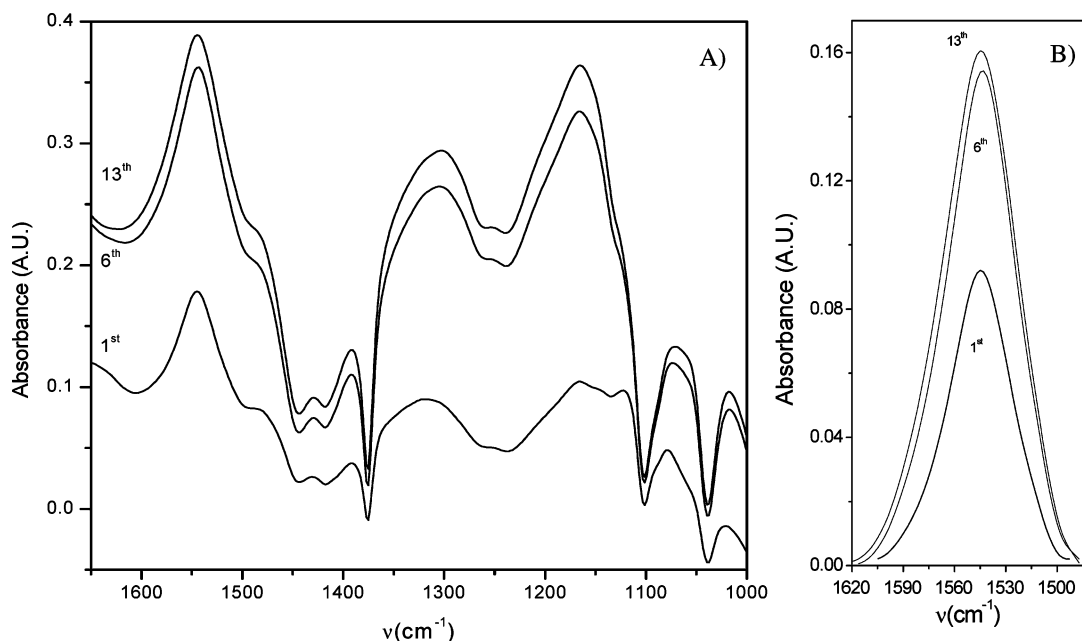


Figure 9. In situ FTIR spectra of a PPy/PVS film in 0.1 M LiClO₄/AN solution registered at +0.7 V for different cycles. The voltammetric cycles were carried out between +0.8 and -2.1 V, from the first cycle (A). The baseline corrected ~ 1540 cm⁻¹ peaks obtained from part A (B). The E_i value was always adjusted to +0.8 V.

V), the FTIR bands are enhanced due to massive incorporation of ion and solvent molecules inside the polymer, promoting a fast increase of the electroactive part of the polymer, which becomes infrared active. Furthermore, this reorganization of the polymer is confirmed by the shift obtained when $E_f = -2.1$ V is used with respect to $E_f = -1.0$ V: the 1250–1110 cm⁻¹ band shifted from 5 to 15 cm⁻¹ toward lower frequencies, and the 1355–1250 band shifted toward higher frequencies, as can be observed clearly in Figure 7.

Moreover, when -2.1 V was used as the final potential of the voltammetric cycles from the first cycle, only 13–15 cycles were required to reach steady-state FTIR spectra for PPy/PVS films, in accordance with the voltammetric behavior.³⁰ Figure 9 shows in situ FTIR spectra for PPy/PVS film registered at +0.7 V for the 1st, 6th, and 13th cycles, with $E_i = +0.8$ V and $E_f = -2.1$ V. Figure 9B depicts the baseline corrected ~ 1540 cm⁻¹ peaks from the FTIR spectra of the specified cycles, and the increment of the band intensities is evidenced again. Furthermore, the intensity in 13th cycle is higher than that observed in Figure 7; however, this peak is lower than those obtained for PPy/ClO₄ film after 7 cycles (Figure 6), evidencing that although the number of polymeric chains participating in the redox process has been increased, part of the polymeric film is still infrared inactive.

Zhou et al.²⁹ reported that during the potential scan in monomer-free solution the PPy(II) structure approached its final steady state faster when higher oxidation potentials were reached. Moreover, as can be seen in Figure 8 using $E_f = -2.1$ V, the voltammetric anodic peak shifted to a more positive potential with the cycling, requiring a more positive oxidation potential than +0.8 V to be reached in order to oxidize an increasing fraction of polymeric chains. Thus, we decided to extend the oxidation potential above +0.8 V, voltammetric cycles were performed between +1.3 and -2.1 V, and then FTIR spectra were obtained as above during the anodic branch for PPy/PVS film. Once again, the intensities of in situ FTIR spectra increased with respect to spectra registered at the same potential but reaching +0.8 V as the maximum oxidation potential (compare Figure 10 with previous figures), although

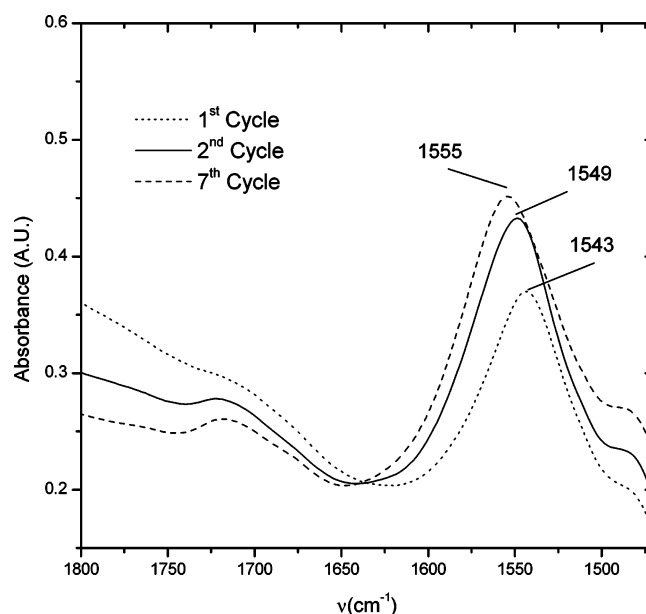


Figure 10. In situ FTIR spectra of a PPy/PVS film in 0.1 M LiClO₄/AN solution registered at +0.7 V for different cycles (1st, 2nd, and 7th) with $E_i = +1.3$ V and $E_f = -2.1$ V, after 13 cycles between $E_i = +0.8$ V and $E_f = -2.1$ V. The values indicate the peaks frequencies in cm⁻¹. The spectra have been translated to compare better.

the charges included in the oxidation voltammetric peaks maintained their values or diminished slowly. After three voltammetric cycles, the FTIR spectra reached stable intensities. Now, the in situ FTIR spectra of PPy/PVS films obtained starting the voltammetric cycle at +1.3 V show similar intensities to those obtained from PPy/ClO₄ films. Thus, the area measured from the ~ 1540 cm⁻¹ peaks obtained at +0.5 V, for the PPy/ClO₄ film in the seventh cycle and for the PPy/PVS film obtained during the third cycle with $E_i = +1.3$ V, produced values of 12.02 and 12.65 (arbitrary units), respectively. Hence, we observed that a very similar amount of polymeric chains was infrared active from both oxidized films when the steady state was reached.

On the other hand, when the PPy/PVS film was cycled between +1.3 and -2.1 V in a 0.1 M LiClO₄/AN solution, a new FTIR peak appeared at ~1720 cm⁻¹ (Figure 10), which has been attributed to the formation of carbonyl groups on pyrrole units.^{5,8-11,35} Hence, overoxidation of PPy/PVS film, until +1.3 V, will produce irreversible oxidation of the polymeric chains with conjugation loss. Probably, the origin of these CO groups is the nucleophilic attack of OH⁻ ions on the residual water in AN. The resulting overoxidized PPy contains β -C=O groups formed by keto-enol tautomerism according to Beck et al.,⁵ which interrupt the C=C conjugation in the polymeric chains. This behavior has also been reported by Novak et al.⁸ for PPy and Tsai et al.³⁵ for polythiophenes in AN medium.

Moreover, overoxidation of PPy/PVS films provided shorter conjugated chains of PPy, as confirmed by the shift of the ~1540 cm⁻¹ peak toward higher frequencies with the cycling between +1.3 and -2.1 V (Figure 10). This shift indicates a diminution of the π -electron delocalization or, in other words, a reduction of the chain conjugation length, according to the dispersion of the ~1540 cm⁻¹ peak toward lower wavenumbers observed by Zerbi et al.^{25,36} for increasing pyrrole units in oligopyrroles. As can be seen in Figure 10, this dispersion occurs simultaneously with the appearance of the CO FTIR peak. The reduction of the chain conjugation length could explain the low diminution of the charge included in the voltammetric peaks; however, the FTIR bands increased due to the rise in the amount of the infrared active modes.

4. Conclusions

In situ FTIR investigations of the doping processes of the PPy/PVS films in acetonitrile containing 0.1 M LiClO₄ during voltammetric cycles provided a continuous increase of the IRAV band intensities with the cycling, suggesting a rise in the number of the polymeric chains participating in the infrared signals. At the same time, the increase of the voltammetric peaks indicated the increment of electroactive participants in the redox process. This behavior has been interpreted by the slow incorporation of solvated Li⁺ cations inside the polymeric matrix, which were stabilized by forming Li-PVS ionic pairs, forcing the interchange of perchlorate in the subsequent redox processes (Scheme 1). Only the polymer fraction where the Li⁺ cations were incorporated during the previous cycles will produce IRAV bands which increase their intensities with the amount of polymer participating in the reduction/oxidation process.

In situ FTIR spectra have confirmed that the infrared active PPy chains maintain the same structure, at a constant oxidation potential, after polarization at -1.0 V, whatever the fraction of electroactive material. However, after polarization at -2.1 V, a restructuring of the polymeric chains was observed.

On the other hand, in situ FTIR spectra obtained for PPy/ClO₄ films, reaching -1.0 V as the cathodic potential limit under similar conditions, pointed to a steady-state behavior from the very early voltammetric scans, in good agreement with voltammetric results. Moreover, the intensities of the FTIR bands obtained for the PPy/ClO₄ films from the early voltammetric cycles are much higher than those obtained for the PPy/PVS films after several potential scans, suggesting that in the PPy/ClO₄ films all of the polymeric chains were infrared active. Only when high cathodic and anodic potential limits were used for the consecutive cycles did the FTIR band intensities of PPy/PVS reach a steady-state behavior, becoming similar to those of the PPy/ClO₄ films, indicating that a similar number of polymeric chains were infrared active.

The use of a strong anodic potential limit (+1.3 V) produced the formation of carbonyl groups and reduced the length of conjugated chains in the polypyrrole.

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