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Anion exchange influence on the electrochemomechanical properties of polyaniline

Leonardo Lizarraga, Estela María Andrade, Fernando Victor Molina *,[1]

INQUIMAE and Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, UBA, Ciudad Universitaria, Pabellón II, C1428EHA Buenos Aires, Argentina

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Abstract

The anion influence on the volume changes of polyaniline (PANI) thick films (∼200 μm) during redox switching was studied using voltammetric experiments with simultaneous microscopical observation. The area occupied by the polymer film in the microscope images was measured and used to compute the film volume and its variations. It is found that the electrolyte anion has a definite influence on the film volume changes. When a film equilibrated with perchloric acid is transferred to sulphuric acid, fully reduced and relaxed and afterwards subject to voltammetric cycling, a net volume increase is observed, spanning several potential cycles until a stationary profile is reached. This change is not reversed when the film is transferred back to perchloric medium, and in this electrolyte the response shows a faster evolution. Exchanges with hydrochloric acid show behaviour more similar to $HClO_4$. IR measurements show that anion exchange is complete before the voltammetric cycling is started, indicating that anion ingress/exchange alone is not the only cause for PANI volume changes. The results are interpreted in terms of polymer backbone conformational changes and polymer/anion interactions.
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1. Introduction

Aryl amine polymers such as polyaniline (PANI) have received great attention since its rediscovery by Shirakawa et al. [1]. One of the key features is its wide range of proposed applications, including presently fields such as actuators [2,3], electrochromic and photovoltaic devices [4–6], secondary batteries [7], fuel cells [8], supercapacitors [9,10], ionic sensors [11,12], biosensors [13–15], electrocatalysis [16] and corrosion protection [17,18] among many other ones [19–21]. Due to their potential applications and interesting characteristics, the electrochemistry of aryl amine polymers has been intensively studied in the past years [22–26]. The insulator/conductor transition observed during the oxidation from the fully reduced form leucoemeraldine (LE) to the oxidized one emeraldine (EM) (redox switching) has been extensively studied ([23,27–29] and references therein), but its details are not fully known yet. The dimensional changes in PANI, on the other hand, are comparatively less studied. In the case of polypyrrole, there is already a body of work relating its dimensional changes and their applications for actuators, artificial muscles, etc. [30–34].

Dimensional changes in the oxidation of LE to EM in PANI have been observed by several authors, using electrogravimmetry [35], ellipsometry [36–39], linear displacement experiments [40–42], scanning probe microscopy [43] and microscopical observation [44,45]. It was proposed the use of PANI for mechanical actuators [46–49], but it has not received as yet the same degree of attention as polypyrrole. Volume and length changes have been generally attributed to proton/anion exchange (i.e., doping/dedoping) either in electropolymerized films [33,36] or in chemically synthesised PANI films and fibres, both in aqueous [40,41,47,50,51] and in nonaqueous solution [52]. Electrochemical quartz crystal microbalance (EQCM) studies [53,54] indicate, however, that water movement exists and can play a significant role in the process.

In our previous work [44] the volume changes of thick PANI films with potential in the absence of stress were studied. It was

* Corresponding author. Fax: +54 11 4576 3341.
E-mail address: fmolina@qi.fcen.uba.ar (F.V. Molina).
[1] ISE member.

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found that two stages are distinguishable in the volume–charge response, each one comprising about half the charge spent in the LE–EM oxidation. More recently [45], it was confirmed that the film volume follows the charge, showing an expansion during the second half of the LE–EM oxidation. A model was presented assuming the existence of a relatively stable intermediate, protoemeraldine (PE), with a formal potential distribution for the PE–EM reaction. This assumption is also supported by EPR measurements [55,56], and recent photoluminescence research [57]. The volume change was modelled statistically considering contributions from mixing, polymer deformation and electrostatic charge. The model has shown very good agreement with the experiments indicating that, in the conditions studied, the deformation contribution dominates the volume changes, due to the changes in the dihedral angles caused both by amine–imine transformation and protonation changes in the PE–EM oxidation.

The study of mechanical deformations of aryl amine polymers, besides its own interest is also useful because it should aid to gain insight into the electrochemical switching process. In this paper, we present a study of the anion effect on the volume changes (or electrochemomechanical deformations [51]) of relatively thick PANI films caused by switching between leucoemeraldine and emeraldine forms. Different acidic media (H_2SO_4, $HClO_4$ and HCl) were employed. The response caused by anion exchange during the subsequent voltammetric cycling was studied. The volume changes were measured with the aid of an image capture and processing system. In order to obtain additional information on the anion/polymer interactions, ex situ FTIR measurements of PANI films in its base form before and after the exchange of the different acids employed were conducted.

2. Materials and methods

2.1. Polymerization

PANI films were synthesized electrochemically from a 0.5 M aniline solution in a 1.5 M sulphuric + 1.5 M perchloric acid mixture, by potential cycling at a scan rate of 0.05 V s^{-1} between 0.1 and 1.0 V. The process was monitored through the anodic charge under the first anodic peak (between 0.3 and 0.5 V), Q_a, and it was stopped when $Q_a = 0.5$ C cm^{-2}. About 45 cycles were needed for the electrosynthesis. A three-electrode cell suitable for microscopical observation was employed for the microscopy experiments as described below; a standard three-electrode cell was employed for the electrosynthesis of polymers for FTIR measurements. The reference electrode used was a reversible hydrogen electrode (RHE) in the same solution. Potentials are reported in the results in the standard hydrogen electrode scale. A platinum foil was used as counterelectrode. A Teq HP (S. Sobral, Buenos Aires, Argentina) potentiostat/galvanostat under computer control was employed in all the electrochemical measurements; potentials were accurate to 1 mV. The working electrode for the microscopy experiments was a platinum disk of 0.5 mm diameter, whereas for the FTIR measurements it was a 10 mm Pt disk, in both cases inserted into a PTFE holder. The electrodes were polished with alumina, washed in an ultrasonic bath and rinsed carefully.

The reagents were all analytical grade; aniline was vacuum distilled under reducing conditions shortly before use; all other were used as received. Ultra pure water from a Millipore MilliQ system was used throughout.

2.2. Electrochemical and microscopic measurements

These experiments were conducted in a cell with top and bottom optical windows allowing a side view microscopical observation of the polymer film. The inset of Fig. 1 shows schematically the cell; for further details see Ref. [44]. The cell was placed on the stage of a Leica DM-RX microscope, equipped with a CCD camera coupled to an image acquisition board, in turn inserted in the computer controlling the potentiostat; the software set-up allowed synchronization between electrochemical potential scan and image capture within 0.1 s. Images were processed for length and area measurements using Scion Image software [58]. After polymerization, the working electrode was extracted from the cell, carefully rinsed with high purity water and reinserted into the cell with fresh support electrolyte. Electrochemical experiments with simultaneous image capture were performed both in potentiostatic and linear potential scan conditions. In both cases, image capture and processing was conducted as follows.

Fig. 1 summarizes the characteristics of microscopic measurements. The inset at the top left of Fig. 1a is a schematic of the cell employed. The images obtained (see Fig. 1b and c) are side view projections of the polymer film on top of the electrode; the dark pixels correspond to the polymer whereas the clear ones to the background. Fig. 1b shows the images obtained at the cathodic (top) and anodic (middle) limits in 1 M $HClO_4$. The bottom image of Fig. 1b is the difference (pixel to pixel) between the two above; here dark pixels represent pixels which are dark at the anodic limit (middle image) and clear at the cathodic one (top image), that is they show the expansion of the film upon oxidation. Using standard image processing operations and appropriate calibration, the area occupied by the polymer film projection on the video images is obtained. Also, length measurements were conducted. Calibration was attained by taking images of a reference scale; the spatial resolution was equal or less than 2 μm; area measurement is accomplished in the Scion Image software [58] by pixel count; the main source of error is the exact determination of the dark zone in the images; the accuracy or the area is estimated to be better than 0.1%. Note that due to the inherent integration, area measurement is more accurate than length measurement. Fig. 1c shows results similar to Fig. 1b in 1 M HCl. In Fig. 1a typical area versus potential curves obtained (as discussed below) in 1 M $HClO_4$ are shown: the star and dot show the points where the images presented in Fig. 1b were obtained.

At the beginning of each experiment, the potential was held at the cathodic limit until the polymer was fully reduced (i.e., its anodic voltammetric charge did not increase with further holding) and relaxed (the peak shape did not change with further holding) [59]. After the holding time, the image of the fully

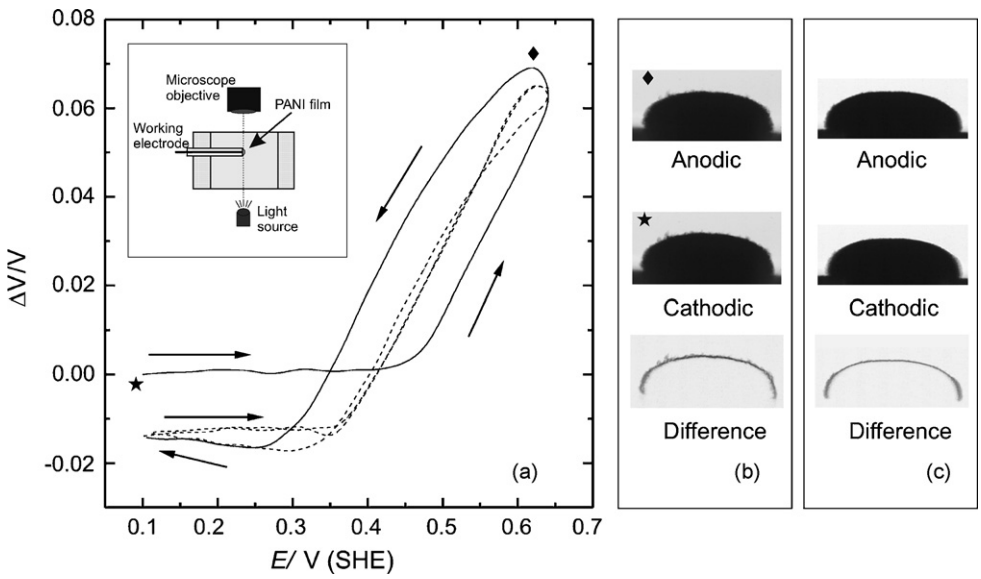

Fig. 1. Scheme of the volume change experiments: (a) typical $\Delta V/V$ vs. E curve obtained from the area measured in the video images with Eq. (2); 1 M $HClO_4$, Continuous line: first cycle; dotted line, stationary cycle. 12 mV s^{-1}. Inset: cell for lateral observation employed in the experiments; (b) video images obtained during the experiment depicted in (a); top, cathodic limit; middle, anodic limit; bottom, pixel to pixel difference between the two above showing the film expansion upon oxidation; (c) same as (b) in 1 M HCl.

reduced and relaxed polymer film was captured and its processing yielded the initial area value A_0. The subsequent images yielded the corresponding area values A_E, at different potential values and at regular intervals. From the images captured, the relative changes in the observed area, $\Delta A/A = (A_E - A_0)/A_0$ can be computed.

2.2.1. Quasi-equilibrium chronoamperometric measurements

These experiments were performed at different potentials between 0.1 and 0.65 V, both in increasing and decreasing steps, as it was conducted in Ref. [45]. In each case the potential was held till the current reached a stationary, nearly zero value (90 min approximately). Then, video images were recorded, yielding the corresponding area values A_E. The initial area at the cathodic limit (0.1 V) is the reference value A_0. Apart from this, charge values at each potential were obtained by integrating the current transients. Care was taken to verify that the results obtained with increasing and decreasing steps were coincident for most of the potential range; for details of the procedure see Ref. [45].

2.2.2. Potential scan experiments

In order to study the anion exchange effect on volume changes, solutions of perchloric, sulphuric and hydrochloric acids all 1 M were employed. In each experiment, two of these solutions (thereafter referred as A and B) were employed. In each experimental run, the cell was filled with solution A and voltammetric cycling was performed between 0.1 and 0.65 V at 0.012 V s^{-1} till a stationary profile was reached. Afterwards, solution A was replaced by solution B, holding the potential at the cathodic limit for about 60 min to fully reduce and relax the polymer [44,59]. At this point, cyclic voltammetry measurements were started with simultaneous recording of video images, and this recording was extended for six full cycles in order to study the evolution of the film response in electrolyte B. Following, the cell was again filled with solution A, the potential was held again for 60 min at the cathodic limit, and the simultaneous voltammetric and video recordings were done again. These exchange experiments were performed about five or six times with the same polymer film in order to study the overall evolution of the film.

2.3. IR spectra recording

The IR spectra were recorded ex situ with both thin and thick films. In the first case PANI films of about 1 mC cm^{-2} were employed using the diffuse reflectance technique in a Nicolet 510P FTIR spectrophotometer, equipped with a Spectra Tech Baseline Diffuse Reflectance accessory. See Andrade et al. [60,61] for details. The exchange experiments were conducted as described above (see Section 2.2.2). The spectra were recorded:

(i) when the polymer was completely reduced just before starting the scan in the new electrolyte, and
(ii) after a stationary voltammogram was reached.

Then the polymer was stabilized in the new electrolyte, potential held, and steps (i) and (ii) repeated. In all cases, the electrode was removed from the cell at the cathodic limit ($E = 0.1$ V) with applied potential, carefully rinsed and dried with air at about 45 °C. Hydroxylamine was added to the rinse water in order to keep the film in its reduced state. The electrode was placed in the diffuse reflectance accessory and the spectra were recorded.

Thick PANI films as obtained in Section 2.1 showed excessive absorption to be studied by the above technique. Thus, these films were mechanically removed from the electrode, resulting

in a powder, which was pressed with KBr into pellets following usual procedures in order to obtain the corresponding IR spectra. The experimental steps were the same as described above but in this case a new film was used for each pellet, as the procedure is obviously destructive.

3. Results

3.1. Volume change measurements

The films obtained are similar to those prepared in our previous papers [44,45]; these films are considerably swollen, with about 65% electrolyte in volume [45]. As shown in Fig. 1b and c (and Ref. [44]), the film expansion is approximately isotropic in either direction. Measurements of the maximum diameter D, and height (at the film centre) h, at the anodic (D_A, h_A) and cathodic (D_0, h_0) limits result for both ratios in

$$\frac{D_A}{D_0} = \frac{h_A}{h_0} = f = 1.03 \quad (1)$$

within experimental error, thus confirming the isotropy of the film expansion in the experimental conditions employed here. In the reduced state, the films employed had a thickness, h of 180–200 μm and diameter, D of about 700–800 μm. Because of the isotropy, the ratio $\Delta V/V$ can be calculated from $\Delta A/A$ assuming cylindrical symmetry [44] by

$$\frac{\Delta V}{V} = f^3 - 1 = \left(\frac{\Delta A}{A} + 1\right)^{3/2} - 1 \quad (2)$$

In the following, results will be presented as relative volume changes computed form the measured $\Delta A/A$ using Eq. (2). Also, due to the isotropy, the linear strain $\Delta l/l$ can be straightforwardly obtained from $\Delta V/V$ as

$$\frac{\Delta l}{l} = \sqrt[3]{1 + \frac{\Delta V}{V}} - 1 \quad (3)$$

3.1.1. Quasi-equilibrium results

In order to have a reference to analyze the effects of anion exchange, the volume changes in several acids under quasi-equilibrium conditions were studied as described in Section 2.2.1. Fig. 2 shows the volume changes observed for PANI films in 1 M H_2SO_4 and $HClO_4$. In the first case it is observed a constant volume up to $E \approx 0.25$ V and afterwards the volume increases reaching about 8% increase at $E = 0.65$ V. In the presence of perchloric acid, however, an initial decrease is observed, reaching a minimum at $E \approx 0.3$ V and then increasing up to 5% increase at $E = 0.65$ V. It should be remarked that this behaviour is observed under stationary (potentiostatic) conditions in both increasing and decreasing potential sequences, so it should not be due to the dynamics of polymer/solution ion exchange, and should be attributed to different polymer–anion interactions.

3.1.2. Potential scan results

In the following, the results obtained for volume changes under cyclic voltammetry, for several conditions, are shown. The reference volume V_0 is in all cases the volume of the polymer just before starting the potential scan, so that the initial $\Delta V/V$ value is 0.0. The corresponding voltammograms are also shown; in all cases investigated, no significant influence of the previous electrolyte has been found in the j/E response, where j is the current density.

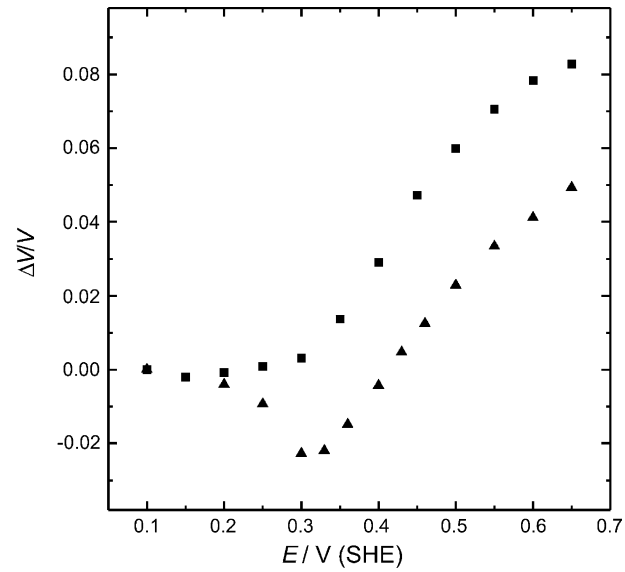

Fig. 2. Relative volume changes of PANI (0.5 C cm^{-2}) film under quasi-equilibrium conditions in the presence of 1 M H_2SO_4 (■) and 1 M $HClO_4$ (▲).

Fig. 3 shows the volume changes observed in the presence of $HClO_4$ as a function of electrode potential, along with the corresponding cyclic voltammograms, when the PANI films have been stabilized previously by repeated potential cycling in different electrolytes. Fig. 3a shows the volume variations when the polymer has been previously stabilized in the same electrolyte (1 M $HClO_4$), whereas Fig. 3d shows the corresponding cyclic voltammograms. The solid line is the curve obtained in the first cycle, the dashed line is the curve for the last (stationary) cycle, and the dotted lines are the intermediate cycles. It is observed that in the first cycle there is no volume change up to $E \approx 0.45$ V, afterwards the volume increases steadily up to about 6% at the anodic limit, then decreases below the initial value (showing a noticeable hysteresis) reaching a minimum at $E \approx 0.25$ V and finally increases somewhat till the cathodic limit. It should be noted that the volume increase starts after the voltammetric peak (that is, when a considerable amount of charge has passed), and the minimum volume is found at a potential more cathodic than the polymer reduction peak. A net decrease of about 1.5% is observed after the first cycle. In the following cycles, the start of volume increase moves cathodically up to $E \approx 0.3$ V, the position of the minimum volume also moves to $E \approx 0.3$ V and there is no net volume variations compared with the first cycle. Thus, the hysteresis observed in the first cycle almost disappears after about 5–6 cycles. In contrast, the voltammetric response does not show changes after the second cycle.

Fig. 3b and c shows the corresponding responses when the polymer has been previously stabilized in 1 M H_2SO_4 and HCl, respectively. In the first cycle, the overall features are similar, but the net volume increase is somewhat smaller, mainly with HCl

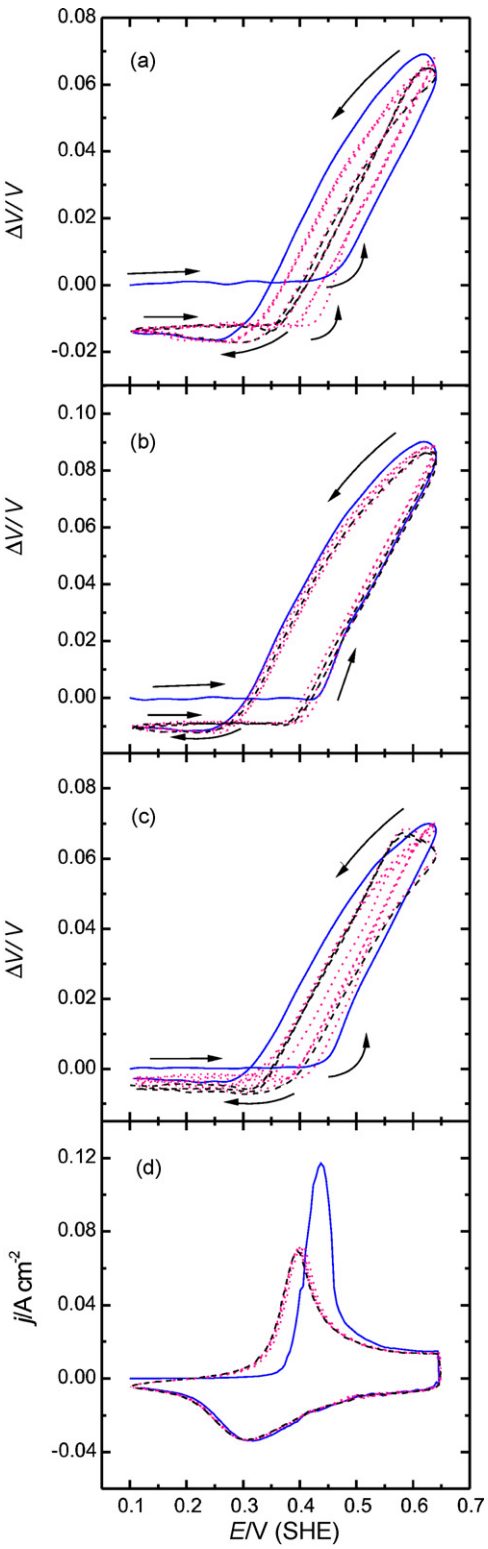

Fig. 3. Relative volume changes of a PANI film (0.5 C cm^{-2}) in 1 M $HClO_4$ under cyclic voltammetry (12 mV/s), after holding for 90 min the potential at the cathodic limit. The film was previously cycled until stationary conditions in: (a) 1 M $HClO_4$, (b) 1 M H_2SO_4, (c) 1 M HCl. In (d) the corresponding current/potential voltammograms are shown. Continuous line: first cycle; dotted line: intermediate cycles; dashed line: last cycle.

as previous electrolyte. In the subsequent cycles, the hysteresis does not diminish as when the polymer has been stabilized in the same electrolyte. As noted above, it is observed in all cases that the volume increase starts past the voltammetric peak, as previously observed [44].

Comparing with the quasi-equilibrium measurements, the most noticeable difference is, apart form hysteresis, that the volume decrease observed in Fig. 2 is noticeably less pronounced under cyclic voltammetry conditions, and only seen in the cathodic scan.

Fig. 4 shows the corresponding results for PANI films in 1 M H_2SO_4. Fig. 4a–c shows the results when the film has been previously stabilized in H_2SO_4, $HClO_4$ and HCl, respectively. The shapes are similar to those found in Fig. 3, but several differences are noticed. In all cases, no significant volume decrease below the initial value is observed during the potential cycling, as it is found in the quasi-equilibrium behaviour (Fig. 2). When the PANI film has been previously cycled in H_2SO_4, there is no noticeable net volume change after the first cycle, and the hysteresis observed in the first cycle decreases considerably in the following cycles, comparable to that observed in Fig. 3a. When the polymer has been stabilized in other acid, a net volume increase after the first cycle is observed, and also a slow evolution towards higher volumes is noticed (note the increasing volumes at the cathodic limit); this behaviour is more marked when the previous electrolyte was $HClO_4$. The hysteresis shows in these cases little decrease along the cycles recorded. In all cases, the volume increase starts in the first cycle at about 0.45 V, almost coincident with the voltammetric peak (Fig. 4d); in the following cycles that point moves cathodically as observed in $HClO_4$. Again, the profile shows changes during several cycles whereas the voltammetric profile is almost stabilized in the second cycle.

Fig. 5a–c shows the volume changes in 1 M HCl when the polymer has been previously stabilized in HCl, H_2SO_4 and $HClO_4$, respectively and Fig. 5d the corresponding voltammograms. The behaviour in this case appears to be intermediate between the two previous electrolytes, but more similar to $HClO_4$: there is a small volume decrease around 0.35 V, but little or none net volume change.

The anion exchange experiments were usually conducted 5–6 times with the same film, and checked with at least duplicate films; no significant differences between similar experiments were found, only a small decrease of the total volume variations with successive exchanges for a given film is observed.

3.2. Infrared spectra

Fig. 6 summarizes the results obtained with PANI films, whereas Fig. 7 those with PANI pellets. In both cases the sequence shown is as follows: the polymer has been initially stabilized by repetitive cycling in H_2SO_4, where spectrum a was obtained. Then the film was transferred to $HClO_4$ solution, and the potential held at the cathodic limit as described before, for about 90 min for a thick film and about 15 min for a thin one. After the appropriate time, the electrode was removed before the start of the potential cycling and spectrum b was recorded. Following, the electrode was cycled in $HClO_4$ solu-

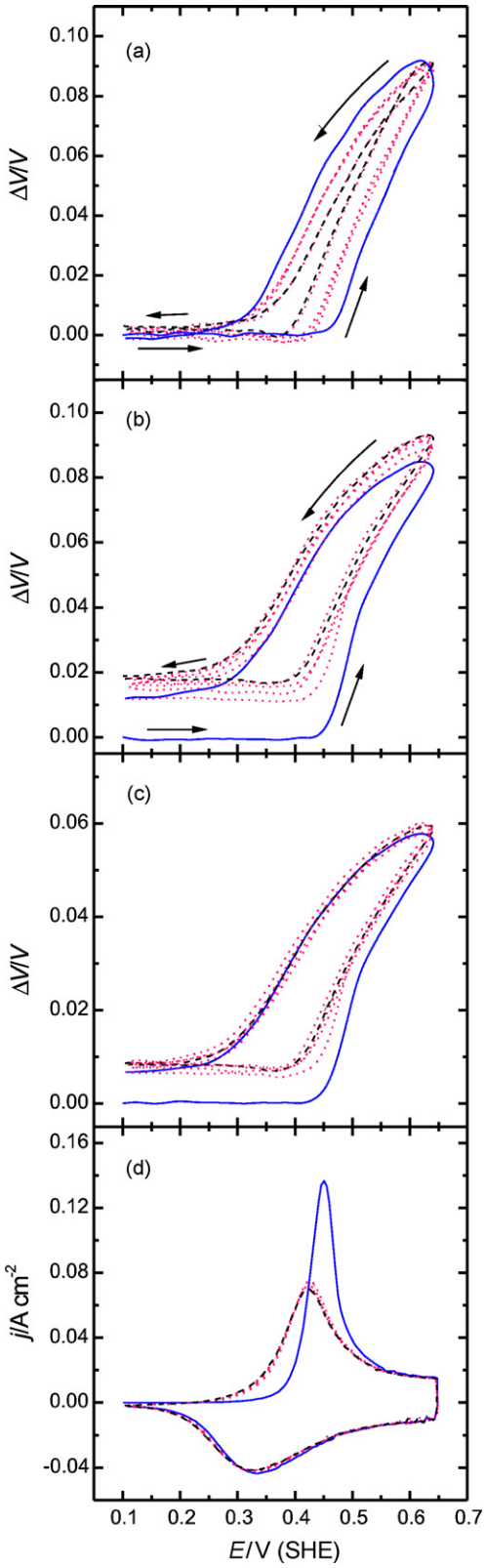

Fig. 4. Relative volume changes of a PANI film (0.5 C cm^{-2}) in 1 M H_2SO_4 under cyclic voltammetry (12 mV/s), after holding for 90 min the potential at the cathodic limit. The film was previously cycled until stationary conditions in: (a) 1 M H_2SO_4, (b) 1 M $HClO_4$, (c) 1 M HCl. In (d) the corresponding current/potential voltammograms are shown. Continuous line: first cycle; dotted line: intermediate cycles; dashed line: last cycle.

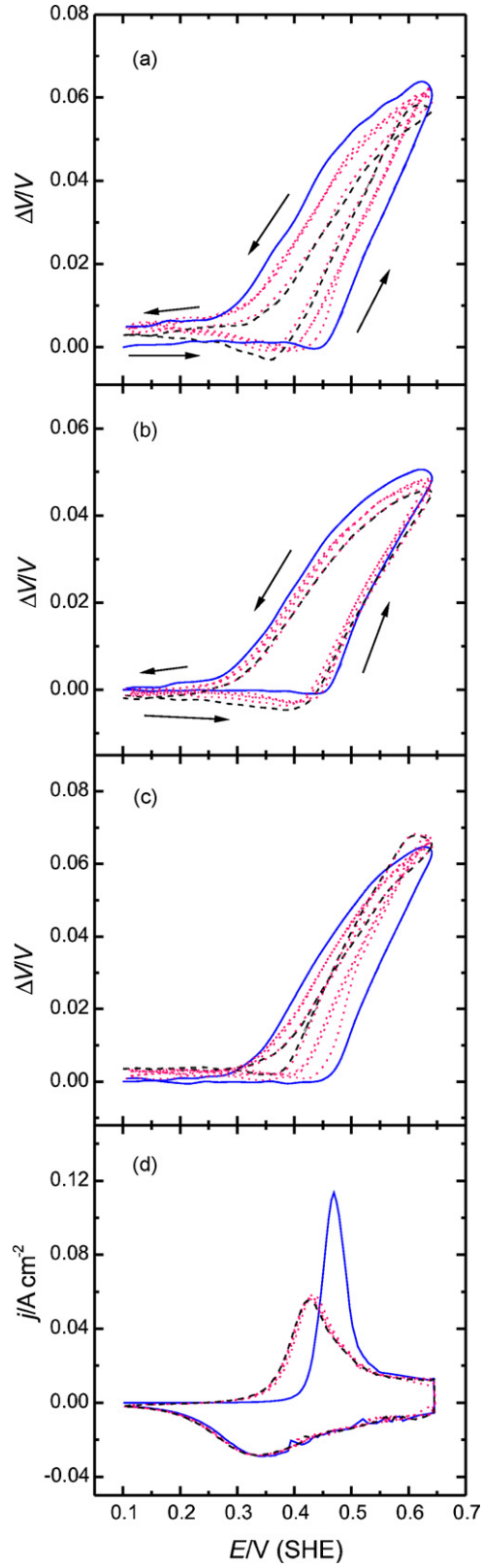

Fig. 5. Relative volume changes of a PANI film (0.5 C cm^{-2}) in 1 M HCl under cyclic voltammetry (12 mV/s), after holding for 90 min the potential at the cathodic limit. The film was previously cycled until stationary conditions in: (a) 1 M HCl, (b) 1 M H_2SO_4, (c) 1 M $HClO_4$. In (d) the corresponding current/potential voltammograms are shown. Continuous line: first cycle; dotted line: intermediate cycles; dashed line: last cycle.

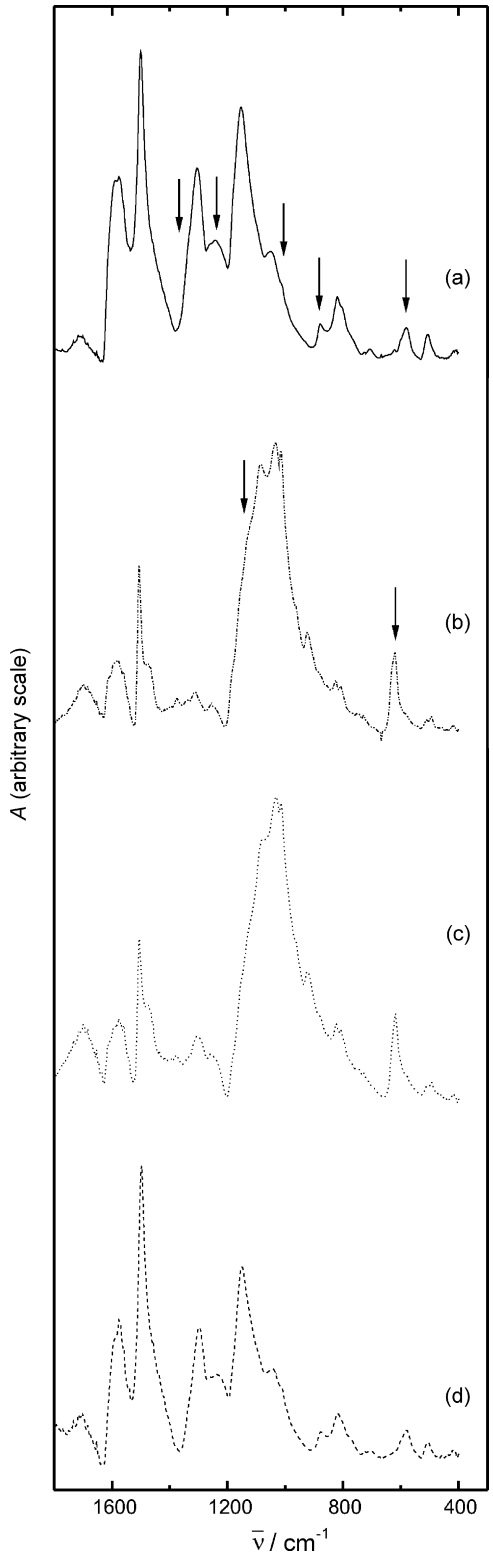

Fig. 6. Diffuse reflectance FTIR spectra of PANI films (10 mC cm^{-2}) on Pt surfaces. (a) The film stabilized by repetitive cycling in 1 M H_2SO_4; (b) the same film after removing from H_2SO_4, immersed in 1 M $HClO_4$ and waiting 90 min at the cathodic limit, no cycling; (c) after repetitive cycling in 1 M $HClO_4$; (d) after removing from 1 M $HClO_4$, immersed in 1 M H_2SO_4 and waiting 90 min at the cathodic limit, no cycling.

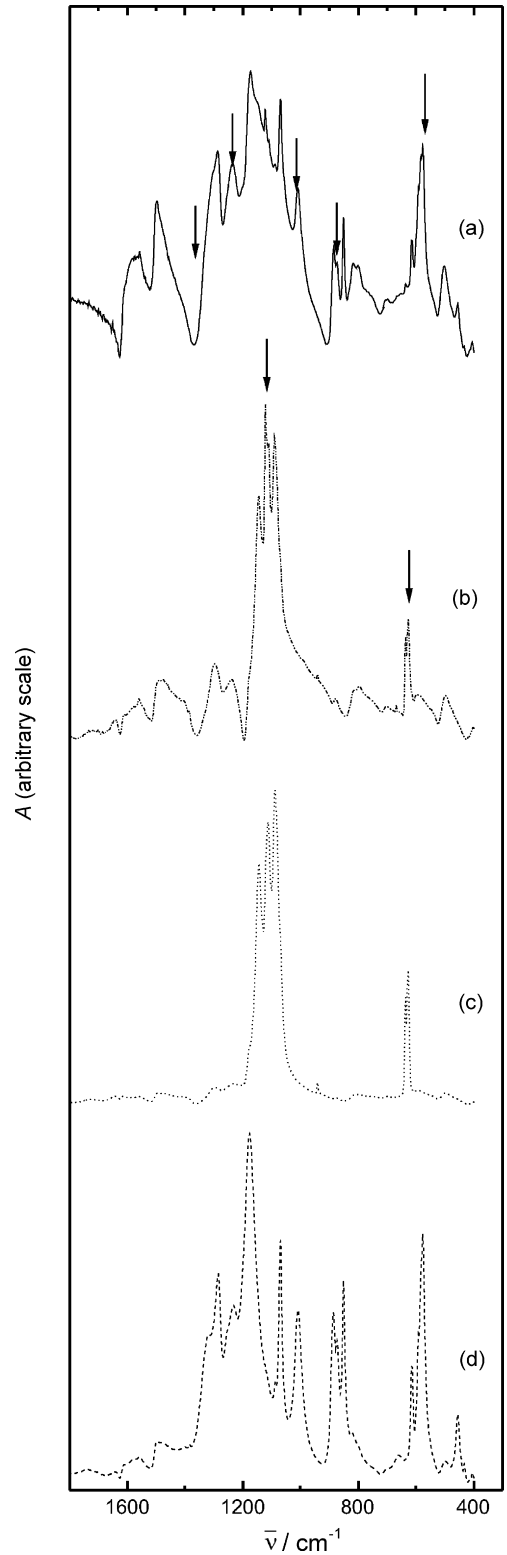

Fig. 7. Transmittance FTIR spectra of PANI films (0.5 C cm^{-2}) in KBr pellets. (a) Film stabilized by repetitive cycling in 1 M H_2SO_4; (b) film treated as in (a), then removed from H_2SO_4, immersed in 1 M $HClO_4$ and waiting 90 min at the cathodic limit, no cycling; (c) film treated as (b) and repetitive cycling in 1 M $HClO_4$; (d) film treated as (c) then removed from 1 M H_2SO_4, immersed in 1 M $HClO_4$ and waiting 90 min at the cathodic limit, no cycling.

tion till a stationary voltammogram was observed, and spectrum c recorded. Finally, the film was transferred again to H_2SO_4, potential holding was performed and the spectrum d recorded before cycling.

In the presence of H_2SO_4 (Figs. 6a and 7a), bands of the HSO_4^- ion show up at 570, 880, 1020, 1240 and 1340 cm^{-1} (marked with arrows, some of them as a shoulder); this wavenumbers are similar to those of the HSO_4^- in aqueous solution [62,63]. After the film is transferred to the $HClO_4$ solution and cathodized but not cycled (Figs. 6b and 7b), these bands disappear and, instead, it is observed the presence of the two IR active bands of the ClO_4^- ion at 1120 cm^{-1} and 625 cm^{-1} (marked with arrows) [64], showing the presence of these anions in the film. These results indicate that during the film reduction anion exchange is completed (at least to the extent detectable in these measurements) and no cycling is necessary. The spectra shown in Figs. 6c and 7c correspond to the films stabilized by cyclic voltammetry in $HClO_4$; as it is observed, they are similar (as far as the anion bands are concerned) to Figs. 6b and 7b, respectively, showing that no further changes in anion content occur. When the film is transferred back to H_2SO_4 medium and reduced potentiostatically without cycling (Figs. 6d and 7d) the perchlorate bands disappear and the HSO_4^- bands are observed again. Thus, it can be concluded that anion exchange is completed, in our experiments, before potential cycling is started. Furthermore, because the results of Figs. 6 and 7 are very similar, this behaviour is independent of the film thickness.

4. Discussion

The main aspects of the experimental results indicate that the volume/potential (*V*/*E*) response of PANI films in 1 M acids shows a dependence not only on the anion of the acid electrolyte, but also on the anion which has been in contact with the film previously, as follows:

(1) When the voltammetric scan is started from a reproducible, fully reduced and relaxed state [59], the *V*/*E* profile shows an evolution through several cycles, more important when the electrolyte is H_2SO_4.
(2) The *V*/*E* response is dependent on both the anion of the current electrolyte and the anion present before the film was fully reduced. When the film is cycled in 1 M H_2SO_4 having been cycled before in 1 M $HClO_4$ or HCl the volume shows a net increase along several cycles. This is not observed with the other acids.
(3) The electrochemical response (that is, the voltammetric profile) does not show a significant dependence on the previous anion. Regarding the evolution mentioned in 1, the *j*/*E* profile only shows a difference between the first cycle and those following (first cycle effect, see [59] and references therein).
(4) The IR measurements show that the anions are fully exchanged during the full film reduction, so that when cycling is started the previous electrolyte anion is no longer present. For example, comparing Fig. 5a and b (PANI in 1 M H_2SO_4), the volume response is different when the film has been previously cycled in $HClO_4$, and the response evolves with a net volume increase through several cycles, even when the ClO_4^- anion has been already fully replaced by HSO_4^-.

In order to analyze these results, we start considering the PANI redox behaviour. The LE–EM redox switching of PANI has been studied by several authors [23,27–29], and is generally accepted to be described by two steps which, in the acidic media employed here, can be written as

$$[\text{–B–NH–B–NH–B–NH–B–NH–}]_n(\text{H}^+)_{4\alpha_{\text{LE}}n} \rightleftharpoons [\text{–B–NH–B–NH–B–N}^\bullet\text{–B–NH–}]_n(\text{H}^+)_{(3\alpha_{\text{LE}}+\alpha_{\text{PE}})n} + ne^- + n(1+\alpha_{\text{LE}}-\alpha_{\text{PE}})\text{H}^+ \quad (4)$$

$$[\text{–B–NH–B–NH–B–N}^\bullet\text{–B–NH–}]_n(\text{H}^+)_{(3\alpha_{\text{LE}}+\alpha_{\text{PE}})n} \rightleftharpoons [\text{–B–NH–B–NH–B–N} = \text{Q} = \text{N–}]_n(\text{H}^+)_{(2\alpha_{\text{LE}}+2\alpha_{\text{EM}})n} + ne^- + n(1+\alpha_{\text{LE}}+\alpha_{\text{PE}}-2\alpha_{\text{EM}})\text{H}^+ \quad (5)$$

where –NH– represents amine groups, B benzenoid rings, Q quinoid rings and B–N•–B stands for the radical cation (polaron) protoemeraldine state; α_{LE}, α_{PE} and α_{EM} stand for the fraction of protonated amine, radical cation and imine N atoms, respectively. In highly acidic media an important fraction of these sites are expected to be protonated, but to a different extent. Also, because the PANI film contains an important fraction of electrolyte [45], Donnan equilibrium between the internal and external media should be considered [42,70]. Several authors have reported pK_a values for the leucoemeraldine, pK_{aLE}, and emeraldine, pK_{aEM} forms of PANI. Orata and Buttry [65], analyzing EQCM measurements reported a pK_{aLE} value of about −0.3 and a pK_{aEM} value of about 3; however, these values were deduced neglecting water transport during the redox conversion. Chiang and MacDiarmid [66] performing ex situ analysis reported a pK_{aLE} of 0–1 (pH dependent); their interpretation, however, has been questioned [67]. Menardo et al. [68,69] based on titration experiments, found $pK_{aLE} = 2.5$ and $pK_{aEM} = 5.5$; this last value is in agreement with that reported by Asturias et al. [70], considering the Donnan equilibrium between the polymer film and solution. Other authors [71,72] have reported higher values for pK_{aEM} based on UV–vis measurements, but they do not consider the membrane properties of PANI films. In any case, there is consensus in that $pK_{aEM} > pK_{aLE}$, based also in structural considerations [23]. Also, it should be pointed out that these pK_a values should be considered average ones, because interactions along the polymer chain would cause a spreading of pK_a values among different sites, as it is observed with formal redox potentials [45,73–75].

The intermediate radical cation state has been considered a transient state; however, in recent studies [44,45,56] it has been treated as a relatively stable species, protoemeraldine (PE), successfully interpreting the quasi-equilibrium volume response of PANI films. This is consistent with the work by Glarum and Marshall [55], who found an increased EPR signal at potentials compatible with the PE state (see [45] for details). Also, recent

EPR stationary measurements (with samples contained in tubes prepared in Ar atmosphere and sealed under vacuum) by Petr et al. [56], show a high EPR response for PANI when 25% of the aromatic rings are oxidized (i.e., half way between LE and EM); this response being higher than both LE and EM signals. Thus, the intermediate state protoemeraldine can be considered as stable, at least in the time scale of the experiments reported here. Its pK_a has been estimated to be similar to pK_{aLE} [45].

At the pH of the present study, it is thus expected that quinoid N atoms will be fully protonated whereas the other N types will, in principle, have $\alpha < 1$. Of course, anions will be also present in the internal medium in order to satisfy electroneutrality. Reactions (4) and (5) will liberate protons (otherwise it would be required an unlikely combination of values for the α's) and thus require ionic transport between the internal and external media. There is presently consensus in that both H^+ and anions move during the redox switching, but water movement has been also observed [35,53,65,76–78]. In a recent careful EQCM study of PANI in 1 M $HClO_4$ by Hillman and Mohamoud [54], the results are described by a mechanism involving proton exit in the first part of the LE–EM conversion and anion entry in the latter part, with water ingress over all the oxidation process. This is in agreement with probe beam deflection studies [76].

The electrochemomechanical behaviour of conducting polymers has been mainly attributed to ion exchange, with the volume increase upon oxidation attributed to anion ingress [33,34,41,49]. However, in the present results the volume response of PANI films show, upon electrolyte exchange, a slow evolution spanning several cycles, whereas the IR measurements indicate that the anions have been fully exchanged prior to potential cycling. Also, our films are highly swollen with electrolyte. Thus, anion ingress could not be considered the only cause for the volume increase. Furthermore, as reported in Ref. [44], the volume/charge slope for the rising part of the volume/charge profile (not shown here) gives values of 400–500 $cm^3\,mol^{-1}$, which in turn correspond to about 21–26 water molecules per anion. These values (in qualitative agreement with Hillman and Mohamoud [54]) are higher than typical anion hydration shells and suggest that there is water transport independently of ion movement. On the other hand, the slow relaxation found along several cycles, independent of ion transport, appears to be similar to that found by Rodriguez Presa et al. [59] in electrochemical relaxation experiments, and Inzelt [29] in combined chronoamperometric/EQCM studies. We attribute this relaxation to slow polymer backbone conformational changes. Upon redox switching, there is a change in the bond angles of the N atoms as illustrated in Fig. 8. There, the configurations around the protonated N atoms in the three PANI forms are schematized; a molecular geometry calculation using the AM1 method [45] resulted in the value of 65° for the angles θ_{LE} and θ_{PE}, and of 50° for θ_{EM}. As expected, the EM form of PANI has a more elongated structure, which was shown to be consistent with the quasi-equilibrium volume changes in the statistical model presented in [45].

According to these results and those by Hillman [54] we explain the behaviour observed in the *V*/*E* profiles as follows. During the first part of the anodic scan reaction (4) is the main process, which does not cause significant changes in the backbone conformation (i.e., bond angles around N atoms); protons are expulsed and anions and water ingress to the film, with a net result of proton expulsion; volume changes are small. Afterwards, reaction (5) starts, with changes in the bond angles which lead to a more rigid structure of the polymer chains; ingress of anions and water and egress of protons are also produced, but the amount of water entering the film is considerably higher in this stage (see also [54]). A noticeable volume increase is produced here, which is thus attributed to the polymer conformation changes. The higher amount of water entering the film is assumed to be a consequence of such expansion and not the cause, because the amount entering is higher than what the anion hydration would justify. The hysteresis observed is attributed to the slow relaxation of the polymer film at the macroscopic scale (due to cross-linking and/or entanglements), and not to the ion exchange dynamics. It should be noted that test experiments conducted in this study at scan rates one order of magnitude lower (not shown) showed essentially the same *V*/*E* profiles. The EQCM studies by Hillman and Mohamoud show similar characteristics (see Fig. 2 of Ref. [54]). The net volume decrease consistently observed in $HClO_4$ is attributed to this slow relaxation (with, possibly, incomplete reaction), preventing the return of the film to its original value in the time scale of the potential cycling.

Although a number of researchers have studied the PANI dimensional changes, to the best of our knowledge it was always by linear displacement measurements under stress (load hanging or force/strain), and most frequently using stretched films and fibres. Thus, a direct comparison is difficult. Desilvestro et al. [35] conducted gravimetric measurements in situ using a high area Pt grid electrode hanging from a digital balance, in HCl, $HClO_4$ and H_2SO_4 media; volumes were determined indirectly using electrolyte solutions of different density. They found a volume increase upon oxidation, ranging from 6% in H_2SO_4 to about 14% in HCl, and assigned the total mass changes (in strongly acidic media, with Hammet acidity function values < -1) to H^+ expulsion combined with water entry. Note that the volume change is not related to the ion balance; it is possible, however, in view of more recent studies [54,76], that the balance between proton expulsion in the first part of the redox switching and anion entry in the second part is some net proton expulsion. The volume changes are of the same order of magnitude

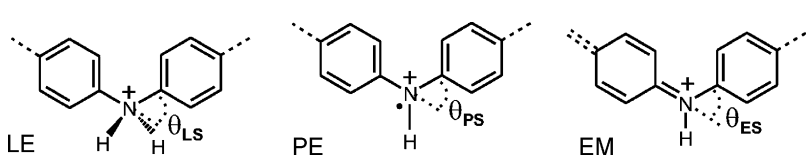

Fig. 8. Scheme of the bond angles around N atoms in the leucoemeraldine (LE), protoemeraldine (PE) and emeraldine (EM) forms of PANI.

as those found here, albeit higher for HCl and $HClO_4$; however, this work is concerned with mass changes and the volume changes are not discussed. Herod and Schlenoff [40] studied the elongations of both unstretched and stretched PANI films, vertically mounted and spring clamped at the bottom end in acidic media. They found anisotropy for stretched films and isotropy for unstretched ones; in this last case, a total elongation of about 2% between reduced and oxidized states in H_2SO_4 was found; also it was observed some evolution with cycling towards higher elongation, in qualitative agreement with the present results. In that work, oxidation and reduction were conducted galvanostatically, which prevented the film to be fully reduced; this fact would explain the small elongation range observed. Kaneto et al. [41,42,47,51] also employed films under mechanical stress, by hanging a load at the bottom of a vertically mounted film. Most of their work was conducted using stretched films which showed anisotropy; for unstretched films in 1 M HCl, an evolution of the elongation was found over some cycles, with total elongations of the order of 3–4%, in agreement with that found here. More recently, Smela et al. ([49] and references therein) studied PANI fibres and films, both stretched, by force/strain measurements. They found strains of the same order of ours (∼2%), and also some evolution in the first cycles is observed, mostly due to the replacement of a large anion (coming form the synthesis) by Cl^-; however, the potential range included the pernigraniline state, which is known to undergo degradation in aqueous media, and consequently film break was observed. No anion effect was reported.

The presence of evolution in H_2SO_4 after cycling in an other electrolyte (Fig. 4b and c) indicates that the polymer electrochemomechanical behaviour does not adjust to the HSO_4^- anion immediately but relaxes during several potential cycles. This behaviour when the electrolyte is exchanged would suggest the presence of some sort of "memory effect". Memory effects upon doping in electroactive polymers (also known as "size memory effects") have been subject of interest for several years [79–85]. It has been proposed [83] that a given anion leaves, during polymerization, pores or cavities which can only be occupied by anions of similar or smaller size. Such sort of size selectivity has been observed and even applied in other polymers such as polypyrrole [86]. In the case of PANI, however, the existence of such size memory effect is in disagreement with recent measurements [84]. Even when both are very similar in size (0.221 nm HSO_4^- versus 0.225 nm ClO_4^-) several researchers (see [84]) consider that perchlorate promotes a compact polymer structure whereas bisulphate (and also chloride) promotes an open one. In the experiments reported here, both HSO_4^- and ClO_4^- anions were present during polymerization; if the anion size were the relevant parameter, the anion exchange experiments would show similar results for both anions, which is not observed. Besides, measurements (not shown) with films synthesized in 3 M $HClO_4$ (with no HSO_4^- present in the polymerization) gave results essentially equal in the anion exchange experiments. Moreover, when the polymer is immersed in H_2SO_4 after being cycled in another acid, the response changes along several cycles indicating a slow relaxation of the film towards a stationary volume cycle in the new electrolyte. In the case of HCl an evolution, albeit considerably less marked, is also observed. The IR results indicate that the anion exchange (obviously ClO_4^-/HSO_4^- exchange, as Cl^- is IR inactive) is complete before the potential scan begins, so that slow anion exchange is not the cause. Thus, we attribute the evolution observed to slow conformational changes of the polymer film, related to anion/polymer interaction. As reported previously [44], IR measurements indicate relatively strong interaction of both Cl^- and HSO_4^- with the polymer, and a weak interaction in the case of ClO_4^-. Strongly interacting anions (HSO_4^-) would alter the conformation of the polymer chain, with a relatively slow process of macroscopic conformational relaxation taking several oxidation/reduction cycles. On the other hand, weakly interacting anions (ClO_4^- and, intermediately, Cl^-) would be relatively neutral towards polymer conformation, thus little or no relaxation is observed. Thus, the slow evolution observed would not be due to a memory of the previous anion but to a slow conformational adjustment to the new one, when this new anion (HSO_4^- in this study) shows strong interactions with the polymer. The nature of these interactions is very difficult to establish at the present time; presumably, HSO_4^- anion form hydrogen bonds with the NH^+ and NH_2^+ groups.

5. Conclusions

The following conclusions stem from this work:

(1) When thick PANI films are immersed in a new acid after being stabilized in another one, the volume changes show dependence on the anion of the previous electrolyte during several potential cycles.
(2) The HSO_4^- anion shows a behaviour different form Cl^- and ClO_4^-.
(3) The anions are completely exchanged during polymer reduction in the new electrolyte before cycling starts.

The observed behaviour is attributed to conformational changes of the polymer backbone at a macroscopic level, due to geometrical changes of the nitrogen atoms upon oxidation.

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