CONFORMATIONAL CHANGES DURING THE REDOX SWITCHING OF ELECTROACTIVE POLYMERS

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Dedicated to Professor Dr. A.J. Arvia on occasion of his 75th Anniversary

Abstract

In this work experimental results published and unpublished, showing conformational changes and swelling of electroactive polymers, in contact with an external electrolyte or during its redox switching, are reported. Thus, voltammetric results showing relaxation effects, both at room temperature and in the range 200- 300 K, Rotating Ring Disk Electrode monitoring of the ingress/egress of protons from the polymer after electrochemical relaxation, volume changes monitored by image capture and AFM and changes in the UV-Vis spectra following relaxation are shown. These experiments show that either as a consequence of relaxation or the change of the composition of the external medium the polymers undergo conformational changes and swelling. A simple model based on Polyelectrolyte theory is proposed to rationalize these findings.

Resumen

En este trabajo se muestran resultados experimentales publicados e inédtos, que evidencian cambios conformacionales e hinchamiento de polímeros electroactivos cuando éstos son puestos en contacto con un medio electrolítico o cuando se los somete a una conmutación redox. Así, se presentan experimentos voltamétricos que muestran efectos de relajación a temperatura ambiente y en el rango entre 200 y 300K, experimentos con electrodos de disco y anillo rotantes que muestran el egreso e ingreso de protones luego de la relajación electroquímica, cambios de volumen de los polímeros observados por métodos de captura de imagen y Microscopía de Fuerza Atómica y los cambios en los espectros de absorción UV-vis luego de la relajación. Esos resultados muestran que como consecuencia de la relajación o de la variación en la composición del medio electrolítico que contacta el polímero, éste sufre cambios conformacionales o de hinchamiento. Se propone y desarrolla un modelo basado en la Teoría de Polielectrolitos que permite explicar los resultados experimentales.

Introduction

Among the electroactive polymers, and according to their charge transport capabilities two big groups are considered. They are the called Redox Polymers (RP) such as polyvynil M bipyridyl, (M = Ru, Os, Co, Fe, etc.), poly(*o*- aminophenol) (POAP), poly(*o*-phenylenediamine) (POPD), poly(bencidine) (PB), etc. and the Conducting Polymers (CP) such as poly(pyrrole) (Ppy), poly(thiophene) (PT), poly(aniline) (Pani), poly(*o*- toluidine) (POT), poly(*o*- anisidine) (POA), etc. Besides, among the Pani family there might be three forms of polymers: Ring substituted, N- substituted and copolymers with other ring substituted amines.

CP such as aryl amine derived polymers, mainly Pani and its derivatives, have been proposed for different applications, such as mechanical actuators [1], electrochromic devices [2], as materials for batteries [3,4], sensors, membranes and anti- static covers [5].

It is precisely due to their interesting characteristics, that the electrochemistry of the arylamine polymers has been intensively studied [6-10]. They show three oxidation states; leucoemeraldine (LE), emeraldine (E), and pernigraniline, going from the most reduced state to the most oxidized one. The marked differences in their electrical conductivity and optical properties are well known. However, the mechanical properties associated to the redox switching are much less studied.

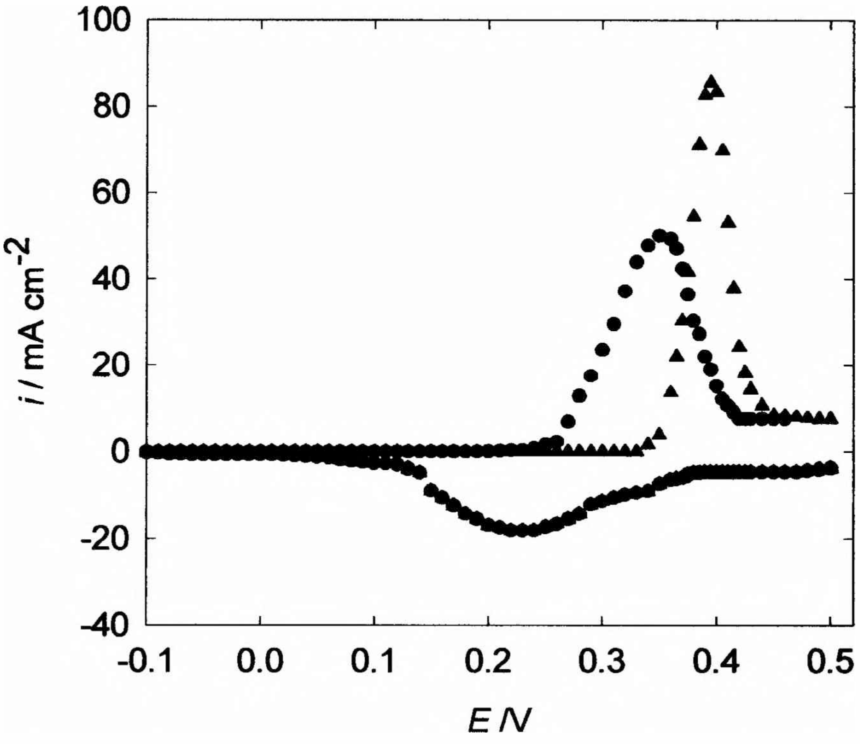

***Figure 1**: Voltammetric response of POT film (Q_T = 84 mC cm^{-2}) in 3.7 M H_2SO_4, v = 0.1 V s^{-1}. (•) steady state profile, (Δ) first cycle after a wait time, t_w = 2400s, E_w = -0.1 V.*

One of the interesting features of the voltammetric response of the CP is the occurrence of the so-called 'slow relaxation', 'first cycle effect' or 'memory effect' [10-

20]. The fact is that, when the polymer is poised at a potential value in its insulating state for some time, the voltammetric profile during the first positive going half cycle differs from the steady-state profile. The peak features, potential, E_p, peak width at half current, $\Delta E_{1/2}$, and current, i_{pa}, depend on the time spent at the insulating state. This is a general effect observed in most conducting polymers and some electroactive polymers [21]. Polymers of the family of the arylamines, such as Pani, POT and POA show relaxation; ladder polymers such as POAP, POPD and PB do not show relaxation. Several models have been proposed to explain the relaxation effect [15,16,19,22-30].

Not only the voltammetric profile changes after relaxation [31] but also other properties such as the spin number [13,14], the polymer volume [32,33], the number of proton ejected [34] and the UV-Vis spectra [35]. In our laboratories we have been studying the changes in several polymer properties after relaxation. Electroactive polymers are polyelectrolytes and this fact has not been properly recognized. From this point of view, these polymers shall share all properties of polyelectrolytes: polymer swelling, elasticity, Donnan equilibrium with an external electrolytic solution, etc.

In what follows we will briefly review our work, show other results yet unpublished and sketch a rationale that explains many of the experimental findings during the redox switching of these electroactive polymers.

Results

In the first two sections we summarize some experimental results obtained in our laboratories that point out to the possibility that the relaxation effect is due to conformational changes of the polymer when this is maintained at negative potentials.

a. *The effect of the polymer thickness and the external electrolyte nature and concentration in the reduction and relaxation of POT.*[31]

In this work we have studied the effect of the polymer thickness and the external electrolyte nature and concentration in the reduction and relaxation of POT. The electrolytic media studied in this work were: 3.7 M $HClO_4$; 1 M $HClO_4$; 1 M $HClO_4$ + 2.7 M $NaClO_4$; 3.7 M H_2SO_4; 1 M H_2SO_4; and 2.35 M H_2SO_4 + 1.35 M Na_2SO_4. The last mixture corresponds to one that is 1 M in H^+, 3.7 M in HSO_4^- and 2.7 M in Na^+ ions.

The complete reduction of the polymer is a relatively slow process, which depends on the external proton concentration and the film thickness. The rate of this process should be related to slow proton entrance into the film and the subsequent ionic equilibrium within the polymer phase.

Like other polymers derived from aryl and ring-substituted aryl amines, POT exhibits a relaxation effect when it is maintained at potentials corresponding to the reduced state. In Figure 1 we show both the steady state cyclic voltammogram and that obtained after relaxation. Whether it is completely reduced or not, the polymer undergoes relaxation. For completely reduced polymers the relaxation time depends on the external acid concentration and the film thickness but it is independent of the ionic strength of the external medium. The wait-time, t_w, is the main factor governing the polymer relaxation and it is in agreement with the laws reported for Pani [18] in different experimental conditions. In the range from -0.1 to 0.2 V *vs.* SCE the relaxation does not depend on potential. Current transients measured during the relaxation show no indication of diffusional control. Since during the relaxation of the polymer, after the current transient, there is only a small background current we conclude that this process should be due to structural rearrangements in the polymer.

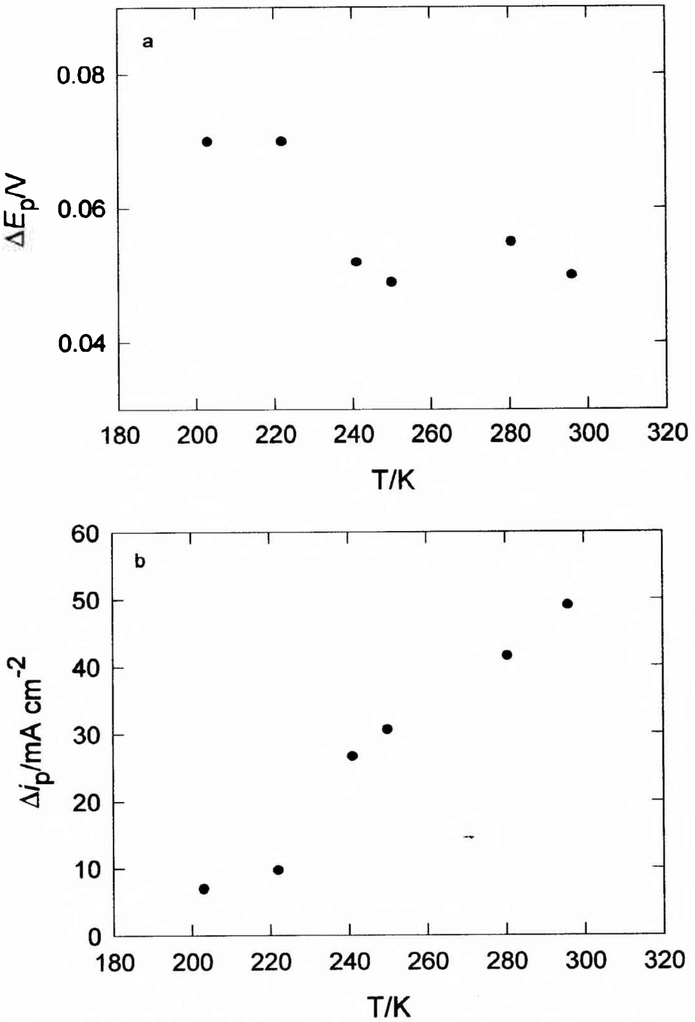

***Figure 2**: Temperature dependence of (a) ΔE_p, and (b) Δi_p, of POT in 3.7 M H_2SO_4.*

Experiments carried out with medium exchange show that, once the polymer is fully reduced and relaxed, its state (degree of reduction, protonation and ion incorporation) is independent of the composition and concentration of the electrolyte in which this particular state was obtained. Furthermore, these experiments show that the shape of the voltammetric oxidation profile depends exclusively of the composition and concentration of the electrolyte in which the polymer is being oxidized. In turn, this means that the effect of the solution composition and concentration manifests itself through the participation of protons and anions in the mechanism of oxidation of the polymer and not through the modification of the initial state by previous protonation equilibrium and / or anion exchange with the solution.

b. Low Temperature effects on the relaxation of Pani .[36]

We have also studied the effect of temperature on the relaxation of PANI and POT in 3.7 M $HClO_4$ and 3.7 M H_2SO_4. The temperature range studied was 200 - 300K. In these experiments it is observed that, as the temperature decreases, the peak potential shifts in the positive direction whereas the change in the peak current after relaxation decreases. Figure 2 shows these results for POT in 3.7M H_2SO_4. This means that the relaxation is hindered as the temperature is decreased.

In a previous work on the temperature dependence of the voltammetric behavior of these polymers [37,38], we explained the change of the voltammetric parameters with temperature invoking Feldberg's model for the oxidation of CP's [39]. According to Feldberg, during the oxidation of these polymers, besides the faradaic charge, there is also a current contribution due to the charging of the oxidized polymer. As the temperature is lowered, this contribution is hindered and the voltammetric current decreases as the temperature is decreased.

We found that the voltammetric behavior at low temperature can be *formally* accounted by introducing lateral interaction between the redox centers in Feldberg's model. Then, the relaxation can be accounted for considering that, after relaxation, the interaction parameters change. For the relaxation to occur the interaction parameter $r_O = r_{OO} - r_{OR}$ must be negative and the parameter $r_R = r_{RR} - r_{OR}$ must be positive and bigger than $|r_O|$. This means that the interactions between the oxidized redox centers must be repulsive and that, those between the reduced ones must be attractive. This implies that either the reduced centers are closer after relaxation or that the oxidized ones are more distant after relaxation or both. This conclusion points toward structural changes in the polymers during relaxation.

With these ideas in mind the temperature dependence of the relaxation can be explained ion terms of a smaller values of the interaction parameters as the temperature is decreased. In turn, this would mean that as the temperature is decreased the polymers relax less that at room temperature. This is reasonable since conformational changes should be hindered as the temperature is decreased.

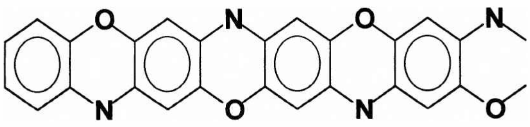

***Figure 3**: Scheme of the proposed ladder structure of POAP.*

c. *Effect of the polymer structure in the electrochemical relaxation* [40]

In order to investigate the effect of the polymer structure we studied the electrochemical relaxation effect on polymers electrosynthesized from monomers of ring-substituted amines. Among these types of polymers we have mentioned POAP, PB and POPD. In these polymers, no relaxation effect occurs when the potential is held a negative values, only a very small relaxation is observed when the potential is held at positive values. It is well known that these polymers have a "ladder" structure as that depicted on Figure 3. It is clear that such structure will prevent such polymers from suffering conformational changes during the potential holding.

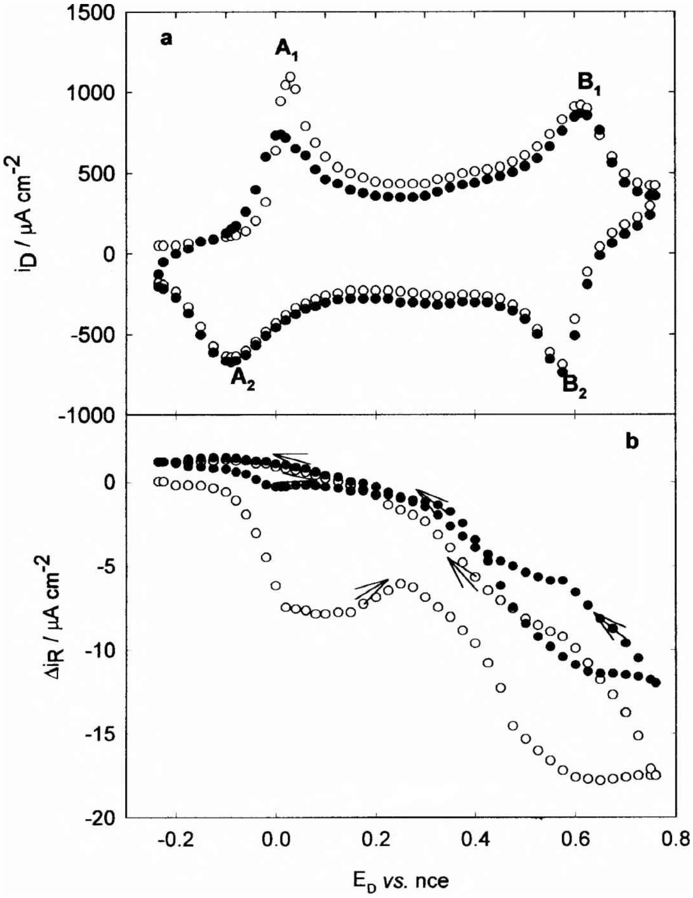

Figure 4: (a) Voltammetric response, i_D vs. E_D, of a Pani film in 1 M $HClO_4$ at the disk electrode, $\Omega = 523.6$ rad s^{-1}, $v = 0.05$ V s^{-1}. (b) Simultaneous recording of the current changes at the ring electrode, Δi_R vs. E_D. The ring potential was set to about -0.3 V vs. NCE. Arrows indicate the potential sweep direction. (○) First sweep. (●) Second sweep.

d *Proton exchange during the relaxation of Pani film electrodes* [34]

It is well known that during the redox switching of electrodes modified with Pani, and other aryl amine derived polymers, ion exchange with the surrounding electrolytic media occurs. Anion exchange has been measured by several methods such as radiotracers [41,42], electrochemical quartz microbalance (EQMB) [43-47], *ex- situ* IR [48], Electrochemical Tunneling Microscope [49] and Probe Beam Deflection (PBD)

[50,51]. These experiments show that during the positive half- potential cycle, anion insertion takes place. The anion insertion lags the electrochemical current showing that it starts after the polymer has begun being oxidized. PBD experiments also show that prior to anion insertion, protons begin to be ejected from the film, but this technique is unable to separate both contributions. Unfortunately, no measurements of anion exchange after polymer relaxation has been reported.

We have measured the differences between proton exchange at steady state cycling and after relaxation. This was done with a technique of Rotating Ring Disk Electrode similar to that proposed by Albery and Calvo [52]. The experimental results show (Figure 4) that during the positive going potential sweep the amount of protons ejected is about ten times greater after relaxation as compared to that expelled during the steady state. This means that during relaxation protons enter into the film. However, we have shown that this is not the rate-controlling step (see section a). Therefore proton entrance is the consequence of other process, which at this stage we postulate as slow-conformational changes in the reduced polymer.

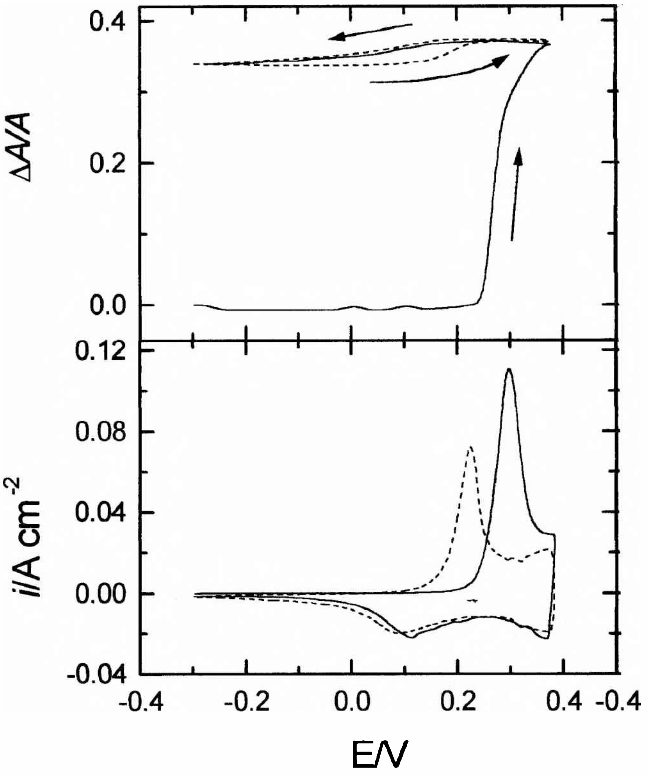

***Figure 5**: Relative area changes (a) and cyclic voltammograms (b) as a function of electrode potential for a 350 mC cm^{-2} POT film in 1 M H_2SO_4. (—) First cycle after complete reduction and relaxation at the negative limit; (···) Steady state voltammograms. Sweep rate v = 0.025 V s^{-1}.*

e. *Volume changes during the relaxation of POT and Os(BPPVP).*[32,33,53]

Recently we have developed a technique by which the volume changes during the redox switching of electroactive polymers can be done [33]. In the first version of these experiments [32] only the relative change of area could be measured and for this reason we will show the relative changes of area. This technique is essentially based on capturing the microscopic image of a very thick polymer film on top an electrode of *c.a.* 0.5mm diameter. In Figure 5 the relative changes of the projected area of the polymer is shown together with the voltammetric response for steady state cycling (dashed line) and after relaxation (full line) in sulfuric acid. It is clear that during relaxation the area, and therefore the volume, of the polymer has decreased substantially. These experiments have been extended to Pani in different electrolytic media [33].

Preliminary experiments have been performed during the redox switching of Os(BPPVP). Although not so marked as in the case of POT [53] also volumes changes have been observed.

f. *Swelling of Os(II)(BPPVP) as a function of the pH of the external medium* [54]

As a part of other work, we have measured the effect of the external electrolyte on the swelling of Os(II)(BPPVP), that is, on the reduced form of this polymer. This polymer can be cast on solid substrates in different forms. One of then consist simply in depositing a drop of the complex solution on a convenient substrate and allowing the solvent to evaporate. In this way a globular deposit is obtained. The thickness of the film increases as the pH of the solution decreases. A curve of the dependence of the film thickness on the pH of the external medium is shown in Figure 6. It is interesting to point out that the swelling of the polymer also depends on the nature of the anion of the electrolyte in the external medium. Further work in this direction is in progress at the time being.

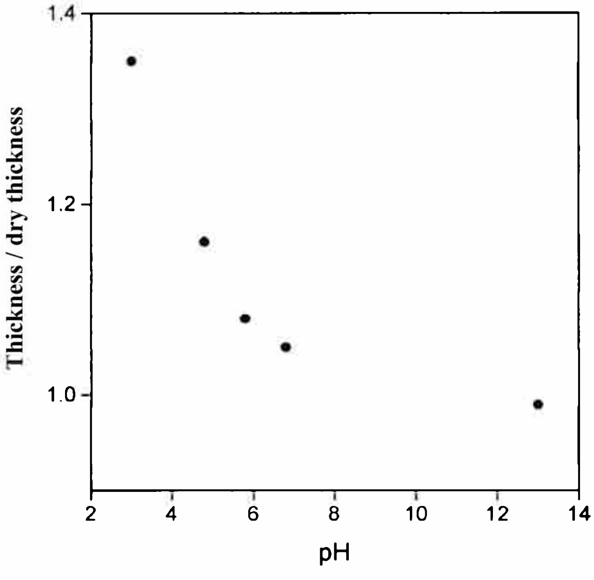

***Figure 6**: Os(II) (PBPVP) film thickness as a function of the pH of the external medium.*

g. *Changes of the "in- situ" UV-Vis spectral response of Pani during relaxation.* [35]

In this work, employing an *in situ* technique similar to that described in [55], we measured the absorbance changes of Pani and POT, in different electrolytic media during the polymer relaxation. The spectrum of POT in 3.7 M H_2SO_4 in steady state, that is at $t_w = 0$, is shown in Figure 7. There are observed two complex bands centered at around 220 and 255 nm. They are associated with the π electron system of benzene. In Figure 8 are shown the difference spectra of POT in 3.7 M H_2SO_4, with respect to that obtained at $t_w = 0$, obtained at different waiting times, t_w, while the polymer is relaxing at E_w = -0.1V. There, it can be seen that, as the polymer progressively relaxes, the absorption bands at 220 and 255 increase in intensity, the first one shifts to the red and the complex band centered at 255 nm does not shift during the relaxation process. Also, during the relaxation show up a third band at around 330 nm that increases in intensity during the process. One of the reasons invoked in the bibliography, to explain these spectral changes, is the occurrence of conformational changes in the macromolecule. To verify this hypothesis we have made some semiempirical ZINDO- HF calculations employing different conformation of polymeric units, formed by four polymer monomer units. The results of these calculations show that the spectral transitions undergo substantial changes, similar to those reported above, during the conformational changes. So that, at least in vacuum, conformational changes would explain the spectral changes observed during the relaxation process. This opens several experiments to make.

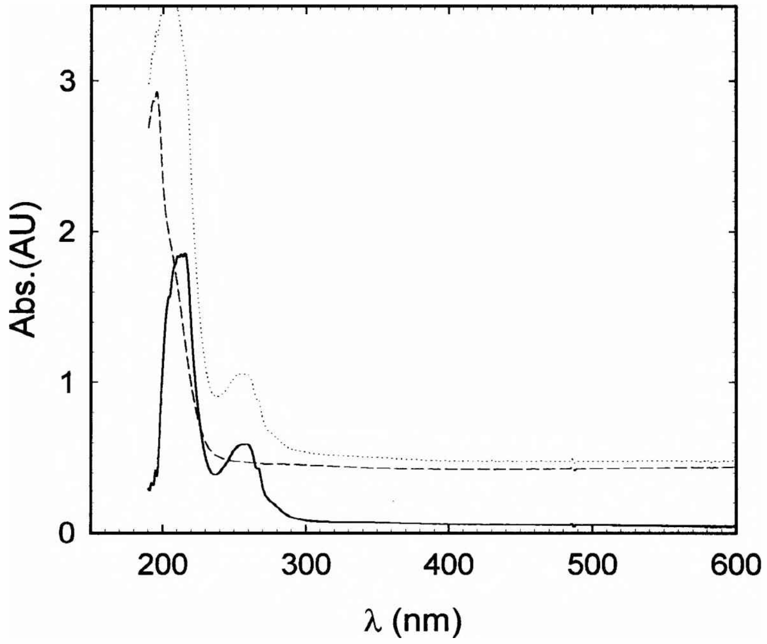

***Figure** 7: Spectra of: (a) (---) 3.7 M* H_2SO_4*; (b) (····) POT in 3.7 M* H_2SO_4 *in the steady state,* (t_w*= 0) and (c) (—) Difference spectrum.*

Discussion

In what follows we sketch the basis of a very general model that allows explaining the experimental findings on the basis of what is already known from the physical chemistry of macromolecules. Moreover, this model would allow us to explain what happens during the redox switching of electroactive polymers. Details of this model as well as the results of some calculations, made from the experimental results of the volume changes during the redox switching and the relaxation will be published elsewhere [62]. This model is heavily based on another much more simpler already published [56].

Before describing the model, and for the sake of completeness, we will briefly describe the mechanism of the first couple of the redox switching of Pani- like polymers.

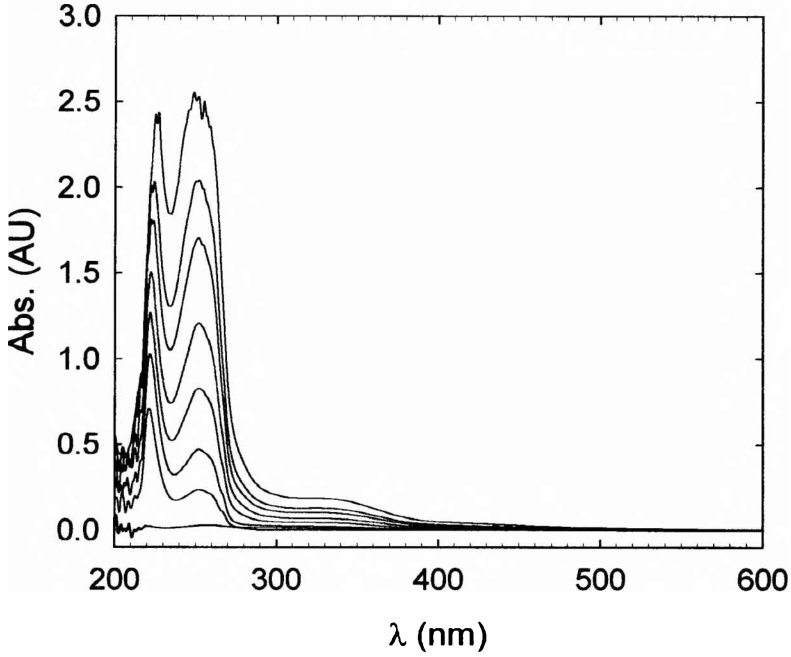

***Figure 8**: Difference spectra, recorded at different waiting times $t_0 < t_w < 240$ min, while the POT film is relaxing at $E_w = -0.1$ V, in 3.7 M H_2SO_4.*

The reduced form of Pani is the Leucoemeraldine form (LE, insulator). When it is submitted to a convenient positive potential it is oxidized to the Emeraldine form (EM, conductor) according to reaction (1):

$$(\text{-B-NH-B-NH-B-NH-B-NH-})_n \leftrightarrow (\text{-B-NH-B-NH-B-N=Q=N-})_n + 2nH^+ + 2ne \qquad (1)$$

where -NH- represent non protonated amine groups, -N= non protonated imino groups, B represents benzoic rings and Q quinonic rings. Both forms, LE and EM are protonated to different degrees leading to LH^+ and EMH^+ forms [57]. The polymer, in both oxidation states, also contains different amount of anions, according to its oxidation degree, in order to maintain the charge compensation [42-44,46,50,58,59].

Both, the reduced form (LE) and the half-oxidized form (E) of these polymers constitute a net of partially charged polyelectrolyte chains. When such a polyelectrolyte is brought in contact with an electrolytic solution the following contributions to the free energy of the polymer, should be considered [60,61]:

(*i*) When the polymer interacts with the solvent, changing its conformational structure and incorporating solvent molecules (swelling), the free energy involved in the process will have a term of free energy of mixture, ΔA_m, plus, and as a consequence of the swelling, a term of free energy of deformation of the polymer. Since this last contribution is purely entropic, we will call it: $-T\Delta S_d$.

(*ii*) As the polymer bears a net charge, there will also be a free energy of a counterion ionic atmosphere formation, ΔA_{el}.

(*iii*) The polymer also undergoes a binding equilibrium process due to the possibility of exchanging protons with the solution. This process depends on the chemical potential of the protons in solution and so there will be a bonding free energy involved in the process, ΔA_{bind}.

Expressions for these contributions have been worked out and can be found in the literature (see for instance [60,61]).

We will consider the polymer as a separate phase. It is in contact, on one side with a solution, the external solution. On the other side it is in contact with a metallic conductor capable of providing holes or electrons for the polymer to be oxidized or reduced. We will consider an electrochemical process by which a reduced electroactive polymer is converted into an oxidized one. The polymer contains N_{ox} and N_{red} redox centers, the total number of them, $N = N_{ox} + N_{red}$, is constant. The conversion of Red to Ox occurs through the reaction 2:

$$\mathrm{Red} \leftrightarrow \mathrm{Ox}^+ + \mathrm{e} \tag{2}$$

We will also consider that the polymer in its reduced state to consist of $N_{2,r}$ chains each containing, on the average, $M_{2,r}$ monomer units. The total number of units being $M_r = N_{2,r}\, M_{2,r}$. Similarly, for the oxidized form of the polymer we define $N_{2,o}$ and M_o. respectively. Furthermore, in (at) any state of oxidation, the polymer forms a network of entangled or cross- linked chains. This network is in contact with an external solution, and in electrochemical equilibrium with the solvent molecules and with the different ionic species present there.

The polymer is bound to solvent molecules through an osmotic equilibrium. We will denote the number of bound solvent molecules as N_{1r} and N_{1o} to the reduced and oxidized polymer, respectively. For simplicity, we will consider that the molar volume of each monomer unit is of the order of magnitude of the molar volume of the solvent, v_0. The volume fractions of polymer, ϕ_2, of each type of polymer are: $\phi_{2,r} = M_r /(M_r + N_{1r})$ and $\phi_{2,o} = M_o /(M_o + N_{1o})$. In a similar way are defined the volume fractions for the solvent. Obviously, $\phi_{2,o} + \phi_{1,o} = 1$ and $\phi_{2,r} + \phi_{1,r} = 1$.

As the polymer is oxidized it is converted into another polymer with a different chemical entity. For simplicity, we will assume that this different polymer does not interact with each other; that is, their chemical nature do not change during oxidation. During oxidation the amount of the reduced one decreases and the amount of the oxidized one increases. These amounts can easily be related to the charge employed to oxidize the polymer. Under these assumptions, it is easy to obtain expressions for the different contributions of the free energy terms to the chemical potentials of the reduced and oxidized forms. Thus the different contributions to the chemical potentials of the reduced and oxidized forms results [62]:

$$\mu_{\text{bind}} = (\partial \Delta A_{\text{bind}}/\partial M)_{\phi 2} = kT\{\ln(1\text{-}f) + f \ln [f/q(1\text{-}f)]\} \tag{3}$$

$$\mu_{\text{el}} = (\partial \Delta A_{\text{el}}/\partial M)_{\phi 2,f} = kT\{z_{\text{ad}}^2\ \phi_2^2 f^2/2\ v_0\ I\} \tag{4}$$

$$\mu_{\text{m}} = (\partial \Delta A_{\text{m}}/\partial M)_{\phi 2} = kT\{(N_1/M) \ln \phi_1 + \chi[1+(N_1/M)]\ \phi_1\phi_2 \tag{5}$$

$$= \{[(1\text{-}\phi_2)/\phi_2] \ln (1\text{-}\phi_2) + \chi\ (1\text{-}\phi_2)\} \tag{6}$$

$$\mu_{\text{d}} = (\partial \Delta A_{\text{d}}/\partial M)_{\phi 2} = \nu\ kT\{[\ln \phi_2 + 3(\phi_2^{-2/9} - 1)]\} \tag{7}$$

where f is the fraction of occupied binding sites, χ is the interaction parameter of the polymer with the solvent, I is twice the ionic strength and v is the number of chains participating in the deformation; the other symbols have already been defined. Note that all these chemical potentials result independent of M, depending only on ϕ_2. This is logical since it has been assumed that the chemical nature of the polymer does not change.

Obviously, the chemical potential of each kind of polymer is the sum of all the contributions:

$$\mu_{\text{pol}} = \mu_{\text{bind}} + \mu_{\text{el}} + \mu_{\text{m}} + \mu_{\text{d}} \tag{8}$$

In order to find the electrode potential we proceed as before [56] by writing the expression of the differential of free energy of the system and differentiating with respect to the number of electrons, N_{elec}.

$$\text{d}A = \mu^*_{\text{ox}}\ \text{d}N_{\text{ox}} + \mu^*_{\text{red}}\ \text{d}N_{\text{red}} + \mu^*_{\text{elec}}\ \text{d}N_{\text{elec}} + \mu_{\text{pol,ox}}\ \text{d}M_{\text{pol,ox}} + \mu_{\text{pol,red}}\ \text{d}M_{\text{pol,red}} \tag{9}$$

where μ^*_{ox}, μ^*_{red} and μ^*_{elec} are the *electrochemical* potentials of the redox centers and of the electrons. We have shown before that the electrode potential, E, (a difference of a constant, C, that depends on the reference electrode) can be written as:

$$F(E + C) = (\partial A/\partial N_{\text{elec}})_{N,N\text{ox},\text{T}} \tag{10}$$

Considering that the number of redox centers can be related to the number of units $M_{ox} = \alpha\, N_{ox}$ and $M_{red} = \alpha\, N_{red}$ [56] we can write all the differentials in terms of N_{elec}. So, the electrode potential results:

$$F(E + C) = \mu_{ox} - \mu_{red} + \mu_{elec} + \alpha\,(\mu_{pol,ox} - \mu_{pol,red}) \tag{11}$$

Where μ_{ox} , μ_{red} and μ_{elec} are the *chemical* potentials of the redox centers and the electrons. Defining the fraction of oxidized centers as $\theta = N_{ox}/N$ and replacing the chemical potentials of the redox centers written as $\mu_{ox} = \mu^0{}_{ox} + RT \ln \theta$ and $\mu_{red} = \mu^0{}_{red} + RT \ln (1-\theta)$, we obtain:

$$F(E + C) = \mu^0{}_{ox} - \mu^0{}_{red} + \mu^0{}_{elec} + \alpha\,(\mu_{pol,ox} - \mu_{pol,red}) + RT \ln [\theta/(1-\theta)] \tag{12}$$

All the constant chemical potentials can be lumped in a formal apparent standard potential, $FE^{0'} = \mu^0{}_{ox} - \mu^0{}_{red} + \mu^0{}_{elec} + \alpha\,(\mu_{pol,ox} - \mu_{pol,red})$, so that:

$$F(E + C) = FE^{0'} + RT \ln [\theta/(1-\theta)] \tag{13}$$

This is the relation between the potential and the charge. To obtain the current/ potential relationship it would suffice to take the derivative of this relation. Within the approximations made in this model the characteristics of the polymer enter only in the apparent formal potential. According to this, the interaction of the polymer with the solvent, the effect of the ionic strength and of the concentration of binding ions should be reflected on $E^{0'}$. It is observed experimentally that the formal apparent potential depends on this variables

The ingress /egress of solvent molecules can be easily explained with this model. Let us assume that the volume fraction of the units of the reduced form, $\phi_{2,r}$ is smaller than that of the oxidized form. Then, as the reduced form is converted into the oxidized form some solvent molecules must come in into the polymer. In a similar way it can be explained the ion ingress/ egress during the redox switching. Now, we will assume that the degree of protonation of the reduced form is smaller than that of the oxidized form. Then, as the polymer is oxidized some ions must ingress in order to maintain the electroneutrality of the polymer. Also, if the degree of protonation of the reduced polymer is smaller than that of the oxidized one, some protons must ingress into the polymer. However, it should be taken care at this point since the oxidation reaction of the polymer also produces protons. In this case, the net result will be the difference between the protons produced by the electrochemical reaction and those necessary to produce the changes in proton binding.

Conclusions

We have presented evidences that electroactive polymers do swell and, that during its redox switching they change the state of swelling and its conformation. It is clear that when the polymer is oxidized it becomes other chemical entity and therefore its interaction with the external medium must change and, as a consequence of this, its conformational state. A simple model is presented that takes into account these changes within the framework of the theory of polyelectrolytes.

Acknowledgments

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