

An experimental study of the intrinsic fluorescence emission and Electrochemically Induced Ageing in poly-*o*-methylaniline films



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ABSTRACT

The intrinsic fluorescence emission of poly(*o*-methyl aniline) (*Pma*) films electrodeposited upon gold electrodes was studied. As this electrochemically active polymer becomes oxidized, the fluorescence diminishes as a consequence of the charge carriers injected into the film that act as quenchers of the excited states. Additionally, it is shown that the fluorescence emission can be employed to monitor the *Electrochemically Induced Ageing*, a characteristic phenomenon of this type of conducting polymers. The ageing rates of *Pma* films, in terms of the fluorescence intensity are compared with those determined from the voltammetric response for films of different thicknesses (ca. 0.3–3 μm). Similarities with *physical ageing* experiments are discussed.

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1. Introduction

Conducting polymers (CPs) are promising materials with several current and future applications in diverse technological fields [1,2]. One of most important properties of CPs is the electrochromism. Due to their particular electronic structure, the UV–vis spectrum noticeably changes with the oxidation degree. Between CPs, one of the most extensively studied in the last years is polyaniline (Pani) and its derivatives. The interesting optical properties of this type of polymers have led to a wide range of applications such as organic LEDs [3], smart windows [4], and energy conversion device [5]. It has been very fruitful the applications of Pani and its derivatives in different types of sensors, such as, optical gas sensors [6,7], ammonia sensors [8,9], biosensors [10], and pH optical sensors [11–13].

Despite the practical importance of Pani and its derivatives, the field of their photoluminescence has been much less studied. The first reports of photoluminescence of Pani films were published in 1989 [14]. Then, Thorne et al. carried out studies of time-resolved fluorescence of Pani in solution [15]. There are some works about Pani as emitting films in electroluminescent diodes [16], studies of Pani in different oxidation states by using fluorescence microscopy [17], and about the influence of torsion angle between adjacent rings [18] and chain length [19] on the emission

properties. More recently, Molina et al. have studied the fluorescence of films of Pani and some derivatives with applied potential, explaining the changes observed with film thickness, potential and copolymerization degree [20–23]. Finally, Mallavia et al. have shown that potentiodynamic measurements of fluorescence emission can provide very useful information about the charge transfer process and exciton dynamic in CPs [24–26].

On the other hand, some CPs, such as Pani and many of its derivatives, suffer a noticeable process of ageing when they are electrochemically reduced [27]. The modifications of the material during this process are complex and involve not only electrochemical transformations, but conformational and other physical changes too. In this sense, the ageing has several similarities with the well-known phenomenon of *physical ageing* in which amorphous materials, and among them most polymers, suffer slow structural modifications after being frozen below the glass transition temperature [28,29]. As a distinctive feature, many materials' properties (such as enthalpy specific volume and creep) change linearly with the logarithm of the ageing time [30–32]. This kinetic behaviour is also found in the ageing of CPs. Moreover, as in the *physical ageing*, the material's changes are reversible and so, this process must be distinguished from chemical ageing that leads to degradation [33].

In the literature, the process of ageing of CPs has received several names, such as, *slow relaxation* [34], *memory effect* [35], and *first cycle effect* [36]. However, we have proposed to use the term “*Electrochemically Induced Ageing*” (EIA) in order to enforce the idea that the condition at which the polymer ages is achieved by an electrochemical perturbation [37,38] as the *physical ageing* is driven by a thermal one [28].

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The EIA of CPs has been often studied by measuring the voltammetric peak parameters j_p and E_p during the first voltammetric scan (the *first cycle*) after the ageing [27,34,36–39]. This electrochemical response gives the characteristic kinetic behaviour in which the studied property (j_p or E_p) changes linearly with the logarithm of the ageing time, what indicates that the modifications of the voltammetric peak parameters are related to the changes that happen during the EIA.

Previously, it was published a model for the voltammetric response of CPs that allows explaining the changes in the voltammetric parameters during the EIA [37,40]. Although other techniques have been also employed to monitor de EIA, such as Electrochemical Impedance Spectroscopy (EIS) [41], UV–vis spectroelectrochemistry [42], ESR [43], and volume changes [44]; there is no previous reports on the use of fluorescence measurements related to this phenomenon in CPs.

Poly-*o*-methylaniline (or poly-*o*-toluidine, *Pma*) is one of the most studied Pani derivatives. Although it has been studied by several electrochemical [45–47] and spectroscopic techniques [6,48,49], there are not previous reports on fluorescence of *Pma* films. So, in this work it was studied the fluorescence response of *Pma* films electro synthesized on gold electrodes. The results reported show the dependence of the fluorescence emission on the applied potential and its changes during the EIA in acid electrolyte media. Additionally, the EIA has been monitored by voltammetry and these results are compared with those obtained from the fluorescence measurements.

2. Experimental

2.1. Synthesis of *Pma* films

All *Pma* films were electro synthesized by cyclic voltammetry between -0.2 and 0.65 – 0.7 V at 0.1 V s $^{-1}$ from 0.5 M *o*-methyl aniline (Fluka, >99.5%) in 3.7 M H $_2$ SO $_4$ (Baker, 98%) solutions upon an Au electrode of 1 cm 2 of geometric area. A conventional three electrodes electrochemical cell was employed, where a Pt foil was used as counter electrode and a Saturated Calomel Electrode (SCE) was the reference electrode. All potential values informed in this work are referred to this electrode. Milli-Q quality water was always employed.

2.2. Voltammetry of *Pma* films

The *Pma* films were studied by cyclic voltammetry in monomer-free 3.7 M H $_2$ SO $_4$ solutions. A PAR 273 potentiostat was employed for these measurements. The film thickness could be estimated from the voltammetric charge by using previously obtained ellipsometric correlations for Pani and other substituted arylamine polymers [50–52]. In this paper, the anodic integrated charge employed, denoted as Q_T , is that corresponding to the steady-state voltammogram recorded between -0.225 and 0.45 V at $\nu = 0.1$ V s $^{-1}$ in 3.7 M H $_2$ SO $_4$ solution. The charges of films studied in this work were in the range 6 mC cm $^{-2} < Q_T < 52$ mC cm $^{-2}$, and, by employing the equivalence given by Zerbino et al. for *Pma* films in acid media, $d/Q \approx 60$ nm mC $^{-1}$ cm 2 , the corresponding thickness result to be approximately 360 nm $< d < 3 \times 10^3$ nm [50]. However, as it was discussed recently [40], the presence of capacitive charge distorts the voltammogram so that the integrated charge not only depends on the faradaic charge but on the potential limits and the electrolyte composition as well. So, care must be taken when employing previous relationships between this charge and the film thickness, thickness calculated here must be considered just as a rough estimation.

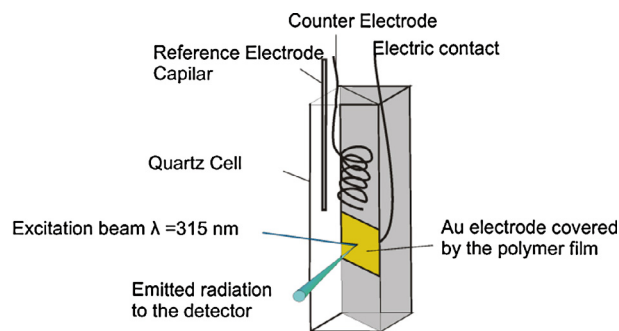


Fig. 1. Experimental set-up for the fluorescence measurements with applied potential.

2.3. UV–vis absorbance measurements

For these measurements, *Pma* films were electro synthesized onto Indium Tin Oxide (ITO) plates ($R_s = 5$ – 15 Ω cm, Delta Technologies). The exposed area of these electrodes was 1 cm 2 . The electro synthesis was carried out by cycling the potential at 0.1 V s $^{-1}$ between -0.2 V and a positive potential limit set at the beginning of the monomer oxidation (around 0.7 – 0.8 V). To improve the adherence and homogeneity of the film, after a few cycles the positive potential limit was decreased [53]. After the synthesis, the film was washed with pure water, cycled in the potential range comprised between -0.2 and 0.45 V, in 3.7 M H $_2$ SO $_4$ solution during some minutes and then introduced in the spectrophotometer cell. This was a square-section quartz cell (Spectrocell, 1 cm side) in which the electrode was inserted perpendicular to the light path. A small Pt plate served as the counter electrode. The reference electrode (SCE) was connected to the solution through a fine capillary.

Spectra were taken with an Agilent model 8453E diode array spectrophotometer in the spectral range comprised between 300 and 900 nm. In order to avoid effects of the EIA in these measurements, before starting the experiments the electrodes were polarized at -0.225 V during 20 min to completely age the polymer film. Then, the potential was increased in steps of 0.01 – 0.025 V and it was held for 3 min at the new potential value, before each spectrum was taken. Dynamic measurements were performed by measuring the absorbance at fixed wavelength while cycling the potential at low scan rates.

2.4. Fluorescence measurements

A Perkin Elmer LS 50B luminescence spectrometer coupled to a PAR 263A potentiostat was employed for the fluorescence emission studies. The Au plate of the working electrode was fixed to one of the faces of a triangular-base acrylic prism which was placed inside a commercial fluorescence quartz cell (Spectrocell) of 1 cm optical length (Fig. 1). In these measurements a Pt wire was employed as counter electrode. The area of these electrodes was about 1 cm 2 . The excitation wavelength was always 315 nm, and the emission was recorded between 325 and 600 nm.

3. Results and discussion

3.1. Voltammetry of *Pma* films

The voltammetric behaviour of *Pma* is very similar to that of Pani. The voltammetric peak corresponds to the redox commutation between the insulating reduced (leucoemeraldine) form and the conducting oxidized (emeraldine) form. Chemical structures of these two forms are presented in Fig. SI.1. The main difference of the voltammetric behaviour of these two polymer films is that

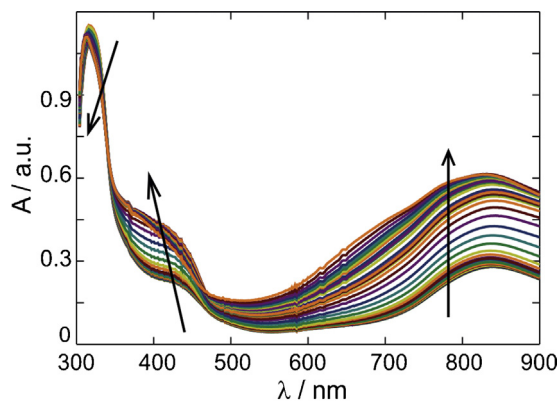


Fig. 2. Spectra of a *Pma* film in 3.7 M H_2SO_4 at several applied potentials between -0.2 and 0.45 V. Arrows indicate increasing potentials.

the *Pma* peaks appear at more positive potential than those of the *Pani*. This characteristic is mainly due to the steric effects of methyl group [27]. In Fig. SI.2 are shown the voltammograms of *Pma* films of different thickness in 3.7 M H_2SO_4 solutions, recorded at $\nu = 0.1 \text{ V s}^{-1}$. As it is found for *Pani*, the voltammetric response of *Pma* also shows capacitive currents at potentials corresponding to the oxidized (conducting) state. Recently, a formal representation of the anodic voltammetric wave for this kind of polymers was published [40]. The model takes into account not only the capacitive contribution but also the presence of interactions between redox centres, and allows satisfactorily fitting the experimental results for *Pani* films in acid media.

3.2. Absorbance and fluorescence of *Pma* films

To the end of characterizing the different features of the absorbance spectra this was studied as a function of the applied potential in the range -0.2 to 0.45 V. These are shown in Fig. 2.

These spectra show, three main characteristic bands in the wavelength range 300–900 nm. The band at 320 nm is attributed to the $\pi \rightarrow \pi^*$ transition characteristic of the benzenic ring units in the polymer. Also, it might be attributed to the band gap in the reduced polymer [54,55]. The position of the maximum also depends on the polymerization degree [56]. This band is the main one for the reduced form; besides a second broad and small band is observed at about 850 nm. As the polymer is oxidized, the band at 320 nm steadily decreases, a band starts growing at about 400 nm, and the band with a maximum at around 850 nm in the reduced state, shows a gradual increase and shift to 750 nm. These ones are attributed to the polarons and bipolarons associated to the formation of the quinonic units due to the oxidation of the amine to imine groups [56,57]. Fig. SI.3 shows absorbance changes of the different UV–vis bands as a function of the applied potential. The excitation wavelength employed in fluorescence studies corresponds to a maximum of the absorption spectra of these *Pani* derivatives (315–325 nm).

Fig. 3 shows the fluorescence spectra of a *Pma* film on gold at different applied potentials. The excitation wavelength employed in fluorescence studies corresponds to a maximum of the absorption spectra of these *Pani* derivatives (315–325 nm) in the reduced state. The fluorescence intensity, F , clearly depends on the applied potential, but the features of the spectrum remain at each potential. These results are consistent with those reported for *Pani* and poly-*o*-anisidine by other authors [20,21]. The fluorescence intensity diminishes as the potential is increased, and a drastic decrease is observed in the potential range of the oxidation peak.

The emission spectra show a peak at 374 nm and a shoulder at approximately 425 nm. Additionally, the fluorescence signal shows

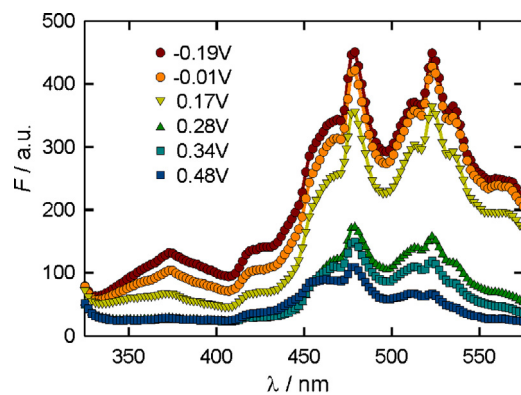


Fig. 3. Emission spectra of a *Pma* film 38 mC cm^{-2} thick in 3.7 M H_2SO_4 solution at several applied potentials, indicated in the graphic.

an important band between 450 and 550 nm, with several peaks that have been attributed to Raman dispersion [20], as they present Stokes shift [21]. In Fig. SI.4 the emission spectra of *Pani* and *Pma* are compared. Both spectra were taken at -0.2 V in the same electrolyte. These dispersion peaks appear at the same wavelengths. The same coincidence has been also reported for the comparison between *Pani* and poly-*o*-anisidine on a Pt electrode [20], although the peaks appear at different wavelength than those on Au substrates. Also *Pani* and *Pani-Cl* on FTO electrodes present dispersion peaks at the same wavelength, but the feature is different to that reported on Au and Pt [23]. So, it can be concluded that this dispersion peaks depend on the substrate but not on the presence of substituents (CH_3- , $\text{CH}_3\text{O}-$, $\text{Cl}-$) in the polymer backbone. However, the exact nature of this dispersion is not completely understood. Nevertheless, it is unimportant for this work as no spectral changes are observed for these peaks during the ageing (*vide infra*).

Fig. 4 shows the potential variation of fluorescence intensity of *Pma* film of different thicknesses. For comparison, the intensities were divided by the corresponding values at -0.2 V (F_a). At negative potentials (leucoemeraldine form) the fluorescence emission does not depend on the thickness. As the potential increases ($E > 0$ V), the relative fluorescence, F/F_a , starts depending on the thickness, it decreases more the thicker is the sample. Similar results have been reported for *Pani* and poly-*o*-anisidine films upon platinum electrodes [22].

Several explanations have been proposed for the attenuation of fluorescence as the polymer is oxidized. The time-resolved

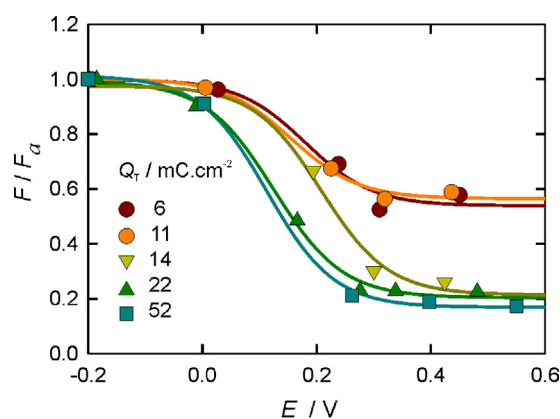


Fig. 4. Relative change of emitted fluorescence intensity at 374 nm as a function of the applied potential, for *Pma* films of different thicknesses ($Q_f/\text{mC cm}^{-2}$), indicated in the graphic. The intensity at -0.2 V, F_a , was taken as reference in each case. Lines are just eye-guiding.

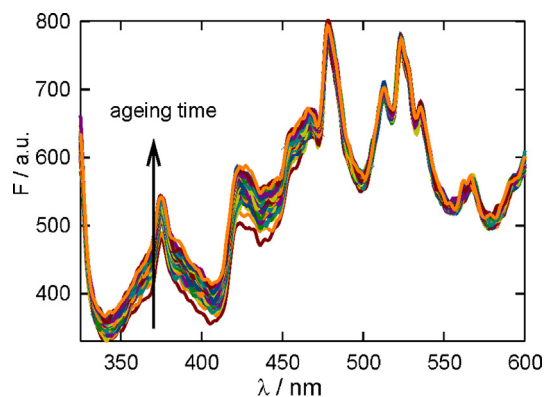


Fig. 5. Fluorescence spectra during the EIA at -0.2 V, of a *Pma* film 22 mC cm^{-2} thick, in $3.7 \text{ M H}_2\text{SO}_4$ solution.

fluorescence studies of Pani reported by Thorne et al. suggest the generation of charge quenchers that show one-dimensional migration [15]. Although some authors have obtained linear electrochemical Stern–Volmer plots for particular systems (other type of CPs in organic media) [24,25], the case for Pani derivatives is not so simple. There are two main reasons. According to Son et al. [14], the relation between free carriers concentration and fluorescence quenching is not linear but exponential, and high degree of quenching can be observed when just a little fraction of centres are oxidized because the charge carriers may have high effective size due to its mobility. Additionally, as discussed by Antonel et al. [21], even at high degree of oxidation, excitons could be isolated in non-conductive domains (far excitons) where quenching by free carriers is prevented. On the other hand, relation between faradaic (redox) charge and potential is not simple in CPs due to the presence of a non-negligible capacitive contribution [40]. Furthermore, there is a relatively wide apparent formal potential distribution in CPs whose origin can be thought to be due to coupling effects [58–60] or, alternatively, to different interactions between redox centres [40]. The dependence of the oxidation degree (and then fluorescence attenuation) on potential has been also explained by considering an intermediate species (protoemeraldine) whose formation occurs before the voltammetric anodic peak. This species would efficiently quench excited states even at low concentrations [21].

Beyond any particular model for the mechanism of the deactivation of the excited states, the present results support the idea that charge carriers injected to the film during the oxidation are responsible for the fluorescence quenching.

3.3. Electrochemically Induced Ageing in terms of fluorescence emission

In order to study the EIA of *Pma* films, the modified electrodes were cycled between -0.2 V and 0.45 V with a scan rate $\nu = 0.1 \text{ V s}^{-1}$ and, after reaching a steady-state voltammogram, the potential was held at -0.2 V. Then, fluorescence spectra were taken at different ageing times, t_a , during the EIA. Fig. 5 shows the successive spectra recorded during the ageing of a particular *Pma* film: 22 mC cm^{-2} thick, in $3.7 \text{ M H}_2\text{SO}_4$ solution. The intensity of fluorescence emission increases in the region 325 – 450 nm as a consequence of the EIA; the other spectrum features remaining practically constant. The difference spectra show peaks at 374 and 425 nm approximately. So, these wavelengths were chosen for monitoring the EIA. In Fig. 6 it is shown the semi-logarithmic time dependence of the fluorescence emission intensity at these two wavelengths during the EIA.

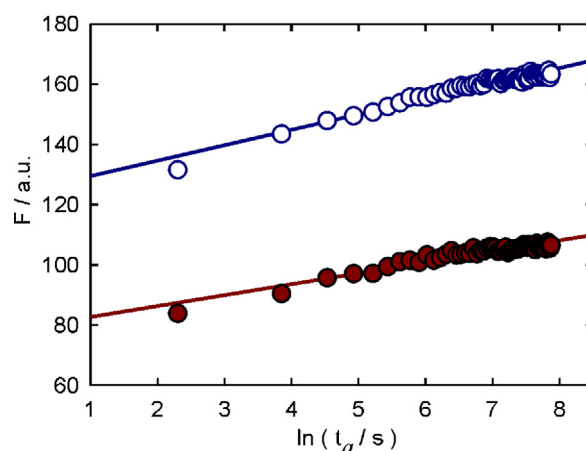


Fig. 6. Semi-logarithmic representation of the temporal variation of the fluorescence emission intensity during the EIA of a *Pma* film 38 mC cm^{-2} thick, at $E_a = -0.2$ V, in $3.7 \text{ M H}_2\text{SO}_4$ solution. Full circles: 374 nm ; empty circles: 425 nm .

In Fig. 7 fluorescence emission intensity at 374 nm is shown as a function of the logarithm of the ageing time for films of different thicknesses. For comparison, it is presented the variation of the fluorescence emission intensity relative to the initial value

$$F_r = \frac{F_a - F_{a,0}}{F_{a,0}} \quad (1)$$

where $F_{a,0}$ is the initial value for each one of the films.

As it can be seen, the variations of the fluorescence intensity are linear with the logarithm of the ageing time. As it was said at Section 1, this particular feature is also found in the analysis of different material properties during the physical ageing experiments [28]. For example, the specific volume linearly changes with the logarithm of the time during the physical ageing of amorphous solids. This kinetic behaviour has led to the definition of a particular ageing rate in physical literature as [28,31,32]

$$r_a^V = -\frac{1}{V_0} \frac{\partial(V)}{\partial \log(t_a)} \quad (2)$$

where V_0 is the initial specific volume of the amorphous solid. Although it is not a true rate in a kinetic sense, it results to be a parameter that allows characterizing and comparing the temporal evolution of the ageing by the changes in a particular property. The physical ageing of polymers has been also monitored by measuring the fluorescence emission of specific molecular probes introduced

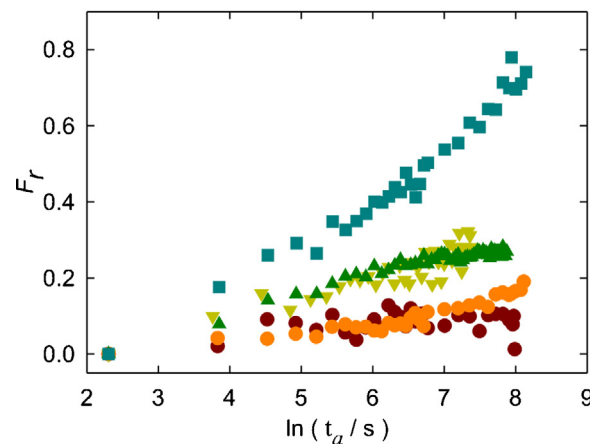


Fig. 7. Semi logarithmic plot of the relative change of fluorescence intensity, at 374 nm , during the EIA of *Pma* films of different thickness (Q_x). F_0 corresponds to the initial value.

within the polymer matrix [61,62]. In these cases, a similar ageing rate in terms of emitted fluorescence has been defined to quantify and compare the temporal behaviour of different samples under different conditions. Contrarily to the intrinsic fluorescence of *Pma* films studied here, when probes are employed to monitor the physical ageing, extrinsic fluorescence is measured [63]. Independently on the nature (intrinsic or extrinsic) of the fluorescence, the increase in its intensity during the physical ageing or the *EIA* allows defining an ageing rate as [32]

$$r_a^F = \frac{1}{F_{a,0}} \frac{\partial F_a}{\partial \ln(t_a)} = \frac{\partial F_r}{\partial \ln(t_a)} \quad (3)$$

Similar equations in terms of enthalpy [30], gas permeability [64], ellipsometric lengths [65], rheological [31] or dielectric properties [66] have been also employed to quantify the kinetic behaviour of physical ageing. According to the last equation, this ageing rate corresponds to the slope of the semi-logarithmic plots. As it can be seen in Fig. 7, the ageing rate is higher for thicker films.

The fluorescence emission was also studied in 1 M H₂SO₄ solution (Fig. SI.5). In this solution the emission spectrum is close similar to that in 3.7 M solution, with the same features. The temporal changes during the *EIA* are very similar in both media too (Fig. SI.6).

During the steady state potential cycling, the polymer commutes between the reduced state (*R*^{*}) and the oxidized (*Ox*) states [27]. The volume of the *R*^{*} form is smaller than that of the oxidized one. The existence of the *EIA* indicates that initially, when the polymer is held at a potential proper of the reduced form (state *R*^{*}), it is not at equilibrium, since many properties changes along time. The polymer tends to achieve the equilibrium state (*R*). The term *EIA* refers to the transition *R*^{*} → *R*. It is important to note that the changes during this transition take place without any variation of the external parameters (temperature, potential, etc.). In this sense, the *EIA* is quite similar to the *physical ageing*.

Particularly, its volume becomes smaller as the *EIA* progresses [67,68]. This indicates that conformational changes continue happening while the polymer tends to achieve its equilibrium form (*R*), which is more compact. Recent Electrochemical Impedance Spectroscopy studies support this idea [41]. Much the same as molecular probes are sensitive to the local density [69], it is expected that in *Pma*, a decrease of volume should lead to an enhancement of the fluorescence emission.

In the particular case of CPs, it is well-known that not only conformational changes but also ions and solvent injection/ejection occurs during the steady-state cycling and ageing [44,70]. As the *EIA* takes place, the polymer matrix becomes more rigid, solvent as well as counter ions go out the film and the non-radiative deactivation of fluorescence is probable to be less important, increasing the fluorescence yield.

3.4. Electrochemically Induced Ageing in terms of the peak current

The *EIA* was also studied by employing the peak current of the first cycle voltammogram after waiting some time at the ageing potential (−0.2 V). As it was previously reported, after ageing the anodic voltammetric features of the first cycle of potential change respect to those corresponding to the steady-state voltammogram [27]. The peak of anodic current shifts in the positive direction, it becomes higher and thinner (Fig. 8), and its changes depend linearly on the ageing time [37,38]. Fig. 9 shows the relative changes in the peak of anodic current, *j_r*, for the different *Pma* films studied in this work, as a function of the logarithm of the ageing time. Being

$$j_r = \frac{j_p - j_{p,0}}{j_{p,0}} \quad (4)$$

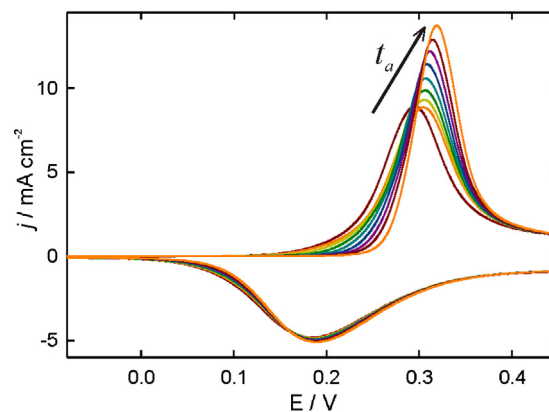


Fig. 8. Voltammetric response for the first cycle of potential after several ageing times, $t_a/s = 0, 6, 12, 24, 48, 96, 192, 384, 768$. *Pma* in 3.7 M H₂SO₄. $Q_T = 12 \text{ mC cm}^{-2}$. Arrow indicates increasing ageing times.

where *j_p* is the peak current density at the ageing time, *t_a*, and *j_{p,0}* is the peak current density corresponding to the steady-state voltammogram. The slope of these graphics corresponds to the ageing rate defined by the peak current, *r_a^j*. This kinetic behaviour is also observed in 1 M H₂SO₄ (Fig. SI.7).

In Fig. 10, the ageing rates defined by the fluorescence emission and the voltammetric peak current are presented as a function of the voltammetric charge. These values were obtained by linear fitting of the semi logarithmic plots. Whereas the *r_a^j* values do not practically depend on the film thickness, the ageing rate defined by the fluorescence emission increases as the film thickness increases. The same is found when analysing the effect of the acid concentration. The *r_a^j* values are similar, but *r_a^F* increases when passing from 3.7 M to 1 M H₂SO₄ (Figs. SI.5 and SI.6). The increase in ageing rate as the polymer film is thicker may be related to a different starting non-equilibrium state (*R*^{*}). Thus, thicker films may arrive to the ageing potential with a higher excess of free energy, that is, farther from equilibrium. This acts as a higher driving-force for the ageing process. Additionally, being farther from equilibrium, differences between *R*^{*} and *R* becomes higher and so, relative changes in fluorescence emission result to be higher.

It is important to remark some differences between fluorescence and voltammetric monitoring of *EIA*. In the first case, fluorescence is measured after the particular perturbation (potential scan) and during the ageing without altering the polymer dynamics. On the other hand, voltammetric experiments drastically alter the polymer film to gain some information from the distortion of the

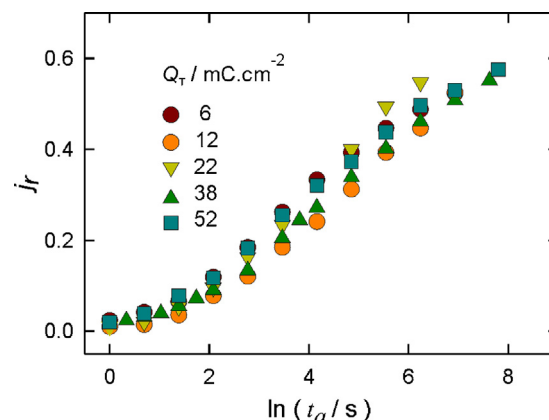


Fig. 9. Semi-logarithmic variation of the relative change in the peak current density, during the *EIA* of *Pma* films of different thickness (Q_T).

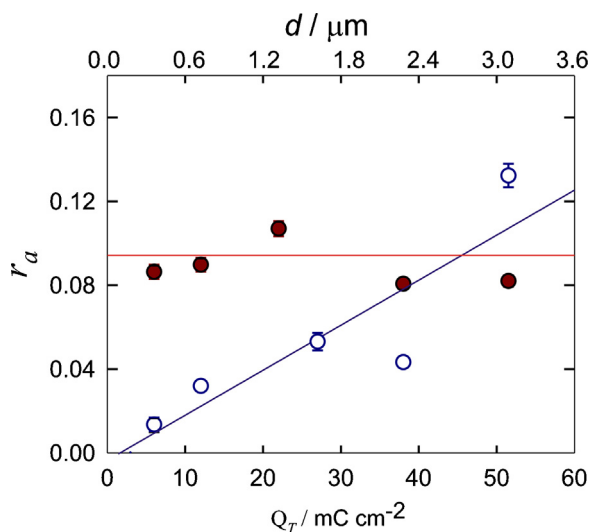


Fig. 10. Ageing rates defined by the fluorescence emission intensity, r_a^f (empty circles), and the peak current density, r_a^i (full circles), for different *Pma* films, as a function of their voltammetric charge (and film thickness) in 3.7 M H_2SO_4 . Lines are just eye-guiding.

voltammetric anodic wave as a consequence of changes produced after ageing to a certain degree (after a given time). So, cycles of steady-state switching, static polarization at the ageing potential and *first cycle* scan need to be performed for each ageing time. In this sense, fluorescence monitoring is similar to other non-altering methods to study the physical ageing of amorphous solids such as ellipsometry, or dielectric spectroscopy [65,66,71]. Voltammetry is more similar to differential scanning calorimetry experiments in which changes in enthalpy or heat capacity obtained from thermal scans after different ageing times are employed to infer some information about the material state as a consequence of ageing [30,32]. Thus, voltammetry (as well as calorimetric experiments in *physical ageing*) does not only give information about the state achieved after ageing but also about response of the aged material to the subsequent electrochemical (or thermal) perturbation. Unfortunately, deconvolution of these effects is not simple since some model for the electrochemical response is needed. A recent attempt in this direction involves considering both the capacitive contributions and formal potential distributions in CPs [37,38,40].

4. Conclusions

The fluorescence response of *Pma* films deposited on Au electrodes was studied in sulphuric acid media. The emission strongly depends on the applied potential as it was reported for similar polymers [20–22]. The creation of charge carriers as the polymer is oxidized is related with the fluorescence attenuation. So, a quenching of the excited states by the charge carriers seems to be a suitable description of the relation between the fluorescence intensity and the oxidation degree.

On the other hand, the intrinsic fluorescence emission has proved to be an interesting property for monitoring the *EIA* of CPs. As with other properties, a linear dependence with the logarithm of the ageing time was found in all analyzed cases. This allows defining an ageing rate in terms of fluorescence intensity that characterizes the temporal behaviour. This rate increases with film thickness, while the corresponding ageing rate defined in terms of the peak current (as it is traditionally monitored) does not sharply change. So, the fluorescence response results to be more sensitive to these experimental conditions. Nevertheless, the investigation of

the molecular basis of this deactivation is necessary to completely understand the origin of fluorescence increase during the *EIA*.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2013.07.170>.

References

- [1] M.E.G. Lyons, *Electroactive Polymer Electrochemistry*, Plenum, New York, 1996.
- [2] J. Heinze, B.A. Frontana-Uribe, S. Ludwigs, *Electrochemistry of conducting polymers—persistent models and new concepts*, *Chemical Reviews* 110 (2010) 4724.
- [3] G. Gustafsson, Y. Cao, G.M. Treacy, F. Klavetter, N. Colaneri, A.J. Heeger, *Flexible light-emitting diodes made from soluble conducting polymers*, *Nature* 357 (1992) 477.
- [4] R. Baetens, B.P. Jelle, A. Gustavsen, *Properties, requirements and possibilities of smart windows for dynamic daylight and solar energy control in buildings: a state-of-the-art review*, *Solar Energy Materials and Solar Cells* 94 (2010) 87.
- [5] T.-H. Lin, K.-C. Ho, *A complementary electrochromic device based on polyaniline and poly(3,4-ethylenedioxythiophene)*, *Solar Energy Materials and Solar Cells* 90 (2006) 506.
- [6] S.P. Surwade, S.R. Agnihotra, V. Dua, S.K. Manohar, *Nitrogen dioxide vapor detection using poly-o-toluidine*, *Sensors and Actuators B* 143 (2009) 454.
- [7] A. Airoudj, D. Debarnot, B. Bêche, F. Poncin-Epaillard, *Design and sensing properties of an integrated optical gas sensor based on a multilayer structure*, *Analytical Chemistry* 80 (2008) 9188.
- [8] A. Airoudj, D. Debarnot, B. Bêche, F. Poncin-Epaillard, *Development of an optical ammonia sensor based on polyaniline/epoxy resin (SU-8) composite*, *Talanta* 77 (2009) 1590.
- [9] J. Castellon-Urbe, M.E. Nicho, G. Reyes-Merino, *Remote optical detection of low concentrations of aqueous ammonia employing conductive polymers of polyaniline*, *Sensors and Actuators B* 141 (2009) 40.
- [10] L.R. Nemzer, A.J. Epstein, *A polyaniline-based optical biosensing platform using an entrapped oxidoreductase enzyme*, *Sensors and Actuators B* 150 (2010) 376.
- [11] P.T. Sotomayor, I.M. Raimundo, A.J.G. Zarbin, J.J.R. Rohwedder, G.O. Neto, O.L. Alves, *Construction and evaluation of an optical pH sensor based on polyaniline-porous vycor glass nanocomposite*, *Sensors and Actuators B* 74 (2001) 157.
- [12] T. Lindfors, S. Ervelä, A. Ivaska, *Polyaniline as pH-sensitive component in plasticized PVC membranes*, *Journal of Electroanalytical Chemistry* 560 (2003) 69.
- [13] M.M. Ayad, N.A. Salahuddin, M.O. Alghaysh, R.M. Issa, *Phosphoric acid and pH sensors based on polyaniline films*, *Current Applied Physics* 10 (2010) 235.
- [14] Y. Son, H.H. Patterson, C.M. Carlin, *Potential-dependent photoluminescence of conducting polymers: simple quenching model and experimental results for poly(aniline)*, *Chemical Physics Letters* 162 (1989) 461.
- [15] J.R.G. Thorne, J.G. Masters, S.A. Williams, A.G. MacDiarmid, R.M. Hochstrasser, *Time-resolved fluorescence of polyaniline*, *Synthetic Metals* 49 (1992) 159.
- [16] S.-A. Chen, K.-R. Chuang, C.-I. Chao, H.-T. Lee, *White-light emission from electroluminescence diode with polyaniline as the emitting layer*, *Synthetic Metals* 82 (1996) 207.
- [17] M.K. Ram, G. Mascetti, S. Paddeu, E. Maccioni, C. Nicolini, *Optical, structural and fluorescence microscopic studies on reduced form of polyaniline: the leucoemeraldine base*, *Synthetic Metals* 89 (1997) 63.
- [18] K. Harigaya, *Long-range excitons in conjugated polymers with ring torsions*, *Chemical Physics Letters* 281 (1997) 319.
- [19] P. Argyrakakis, M.V. Kobryanskii, M.I. Sluch, A.G. Vitukhnovsky, *The influence of conjugated polymer chain length on luminescence properties of ordered polymer films*, *Synthetic Metals* 91 (1997) 159.
- [20] P.S. Antonel, E.M. Andrade, F.V. Molina, *Potential and film thickness dependence of the photoluminescence of aryl amine polymers*, *Electrochimica Acta* 49 (2004) 3687.
- [21] P.S. Antonel, F.V. Molina, E.M. Andrade, *Fluorescence of polyaniline films on platinum surfaces. Influence of redox state and conductive domains*, *Journal of Electroanalytical Chemistry* 599 (2007) 52.
- [22] P.S. Antonel, E.M. Andrade, F.V. Molina, *Fluorescence of polyaniline films on electrode surfaces: thickness dependence and surface influence*, *Journal of Electroanalytical Chemistry* 632 (2009) 72.

- [23] P.S. Antonel, E. Völker, F.V. Molina, Photophysics of polyaniline: sequence-length distribution dependence of photoluminescence quenching as studied by fluorescence measurements and monte carlo simulations, *Polymer* 53 (2012) 2619.
- [24] F. Montilla, R. Mallavia, In situ electrochemical fluorescence studies of ppv, *Journal of Physical Chemistry B* 110 (2006) 25791.
- [25] F. Montilla, I. Pastor, C.R. Mateo, E. Morallón, R. Mallavia, Charge transport in luminescent polymers studied by in situ fluorescence spectroscopy, *Journal of Physical Chemistry B* 110 (2006) 5914.
- [26] F. Montilla, L.M. Frutos, C.R. Mateo, R. Mallavia, Fluorescence emission anisotropy coupled to an electrochemical system: study of exciton dynamics in conjugated polymers, *Journal of Physical Chemistry C* 111 (2007) 18405.
- [27] W.A. Marmisollé, D. Posadas, M.I. Florit, Electrochemical aging of poly(aniline) and its ring substituted derivatives, *Journal of Physical Chemistry B* 112 (2008) 10800.
- [28] L. Struik, *Physical Aging in Amorphous Polymers and Other Materials*, Elsevier, North-Holland, 1978.
- [29] L.C.E. Struik, The mechanical behaviour and physical ageing of semicrystalline polymers: 2, *Polymer* 28 (1987) 1534.
- [30] T.M. Murphy, D.S. Langhe, M. Ponting, E. Baer, B.D. Freeman, D.R. Paul, Enthalpy recovery and structural relaxation in layered glassy polymer films, *Polymer* 53 (2012) 4002.
- [31] G.M. Odegard, A. Bandyopadhyay, Physical aging of epoxy polymers and their composites, *Journal of Polymer Science Part B: Polymer Physics* 49 (2011) 1695.
- [32] J.J.M. Hutchinson, Physical aging of polymers, *Progress in Polymer Science* 20 (1995) 703.
- [33] H. Müstedt, Ageing of electrically conducting organic materials, *Polymer* 29 (1988) 296.
- [34] R. Mazeikiene, A. Malinauskas, A study into electrochemical slow relaxation of polyaniline, *Synthetic Metals* 129 (2002) 61.
- [35] C. Odin, M. Nechtschein, Memory effect in conducting polymers: electrochemical and esr studies on polyaniline, *Synthetic Metals* 43 (1991) 2943.
- [36] A. Malinauskas, R. Holze, Suppression of the “first cycle effect” in self-doped polyaniline, *Electrochimica Acta* 43 (1998) 515.
- [37] W.A. Marmisollé, M.I. Florit, D. Posadas, Electrochemically induced ageing of polyaniline monitored by the changes in its voltammetric response, *Journal of Electroanalytical Chemistry* 660 (2011) 26.
- [38] W.A. Marmisollé, M.I. Florit, D. Posadas, Effect of the potential on the electrochemically induced ageing of polyaniline films, *Journal of Electroanalytical Chemistry* 669 (2012) 42.
- [39] C. Odin, M. Nechtschein, Slow relaxation in conducting polymers, *Physical Review Letters* 67 (1991) 1114.
- [40] W.A. Marmisollé, M.I. Florit, D. Posadas, A formal representation of the anodic voltammetric response of polyaniline, *Journal of Electroanalytical Chemistry* 655 (2011) 17.
- [41] W.A. Marmisollé, M.I. Florit, D. Posadas, Electrochemically induced ageing of polyaniline. An electrochemical impedance spectroscopy study, *Journal of Electroanalytical Chemistry* 673 (2012) 65.
- [42] K. Koziel, M. Lapkowski, S. Lefrant, Spectroelectrochemical investigations of the memory effect in polyaniline, *Synthetic Metals* 69 (1995) 217.
- [43] F. Genoud, M. Guglielmi, M. Nechtschein, E. Genies, M. Salmon, ESR study of electrochemical doping in the conducting polymer polypyrrole, *Physical Review Letters* 55 (1985) 118.
- [44] L. Lizarraga, E.M. Andrade, F.V. Molina, Swelling and volume changes of polyaniline upon redox switching, *Journal of Electroanalytical Chemistry* 561 (2004) 127.
- [45] D.D. Borole, U.R. Kapadi, P.P. Mahulikar, D.G. Hundiwale, Electrochemical synthesis and characterization of conducting copolymer: poly(o-aniline-co-o-toluidine), *Materials Letters* 60 (2006) 2447.
- [46] M.J. Rodríguez Presa, R.I. Tucceri, M.I. Florit, D. Posadas, Constant phase element behavior in the poly(o-toluidine) impedance response, *Journal of Electroanalytical Chemistry* 502 (2001) 82.
- [47] J. Agrisuelas, C. Gabrielli, J.J. García-jaren, H. Perrot, F. Vicente, Kinetic and mechanistic aspects of a poly(o-toluidine)-modified gold electrode, *Journal of Physical Chemistry C* 116 (2012) 15620.
- [48] S. Bilal, A.-H.A. Shah, R. Holze, A correlation of electrochemical and spectroelectrochemical properties of poly(o-toluidine), *Electrochimica Acta* 54 (2009) 4851.
- [49] S. Bilal, A.-H.A. Shah, R. Holze, Raman spectroelectrochemical studies of copolymers of o-phenylenediamine and o-toluidine, *Vibrational Spectroscopy* 53 (2010) 279.
- [50] J. Zerbino, M. Florit, A. Maltz, Voltammetric and ellipsometric study of electrically conducting films of poly(o-toluidine) in different acid media, *Electrochimica Acta* 44 (1999) 1973.
- [51] J. Rishpon, A. Redondo, C. Derouin, S. Gottesfeld, Simultaneous ellipsometric and microgravimetric measurements during the electrochemical growth of polyaniline, *Journal of Electroanalytical Chemistry* 294 (1990) 73.
- [52] A. Redondo, E.A. Ticianelli, S. Gottesfeld, Ellipsometric studies of conducting polymers, *Synthetic Metals* 29 (1989) 265.
- [53] M. Pasquali, G. Pistoia, R. Rosati, Storage characteristics of polyanilines. An investigation by cyclic voltammetry and impedance spectroscopy, *Synthetic Metals* 58 (1993) 1.
- [54] J.E. Albuquerque, L.H.C. Mattoso, D.T. Balogh, R.M. Faria, J.G. Masters, A.G. MacDiarmid, A simple method to estimate the oxidation state of polyanilines, *Synthetic Metals* 113 (2000) 19.
- [55] D. Chinn, J. DuBow, M. Liess, M. Josowicz, J. Janata, Comparison of chemically and electrochemically prepared polyaniline. Films 1. Electrical properties, *Chemistry of Materials* 7 (1995) 1504.
- [56] A.A. Nekrasov, V.F. Ivanov, A.V. Vannikov, Analysis of the structure of polyaniline absorption spectra based on spectroelectrochemical data, *Journal of Electroanalytical Chemistry* 482 (2000) 11.
- [57] A. Neudeck, A. Petr, L. Dunsch, Of the ultraviolet–visible spectra of the redox states of conducting polymers by simultaneous use of electron-spin resonance and ultraviolet–visible spectroscopy, *Journal of Physical Chemistry B* 103 (1999) 912.
- [58] D. Posadas, M. Fonticelli, M.J. Rodríguez Presa, M.I. Florit, Redox potential distribution in the presence of mechanical stress. The case of electroactive polymers, *Journal of Physical Chemistry B* 105 (2001) 2291.
- [59] D. Posadas, M.I. Florit, The redox switching of electroactive polymers, *Journal of Physical Chemistry B* 108 (2004) 15470.
- [60] W.A. Marmisollé, M. Inés Florit, D. Posadas, The coupling among electron transfer, deformation, screening and binding in electrochemically active macromolecules, *Physical Chemistry Chemical Physics* 12 (2010) 7536.
- [61] J.S. Royal, J.M. Torkelson, Physical aging effects on molecular-scale polymer relaxations monitored with mobility-sensitive fluorescent molecules, *Macromolecules* 26 (1993) 5331.
- [62] R.D. Priestley, P. Rittigstein, L.J. Broadbelt, K. Fukao, J.M. Torkelson, Evidence for the molecular-scale origin of the suppression of physical ageing in confined polymer: fluorescence and dielectric spectroscopy studies of polymer–silica nanocomposites, *Journal of Physics: Condensed Matter* 19 (2007) 205120.
- [63] C.M. Evans, J.M. Torkelson, Determining multiple component glass transition temperatures in miscible polymer blends: comparison of fluorescence spectroscopy and differential scanning calorimetry, *Polymer* 53 (2012) 6118.
- [64] T.M. Murphy, D.S. Langhe, M. Ponting, E. Baer, B.D. Freeman, D.R. Paul, Physical aging of layered glassy polymer films via gas permeability tracking, *Polymer* 52 (2011) 6117.
- [65] L.A.G. Gray, S.W. Yoon, W.A. Pahnner, J.E. Davidheiser, C.B. Roth, Importance of quench conditions on the subsequent physical aging rate of glassy polymer films, *Macromolecules* 45 (2012) 1701.
- [66] Y. Huang, D.R. Paul, Effect of temperature on physical aging of thin glassy polymer films, *Macromolecules* 38 (2005) 10148.
- [67] E.M. Andrade, F.V. Molina, M.I. Florit, D. Posadas, Volume changes of poly(2-methylaniline) upon redox switching anion and relaxation effects, *Electrochemical and Solid-State Letters* 3 (2000) 504.
- [68] L. Lizarraga, E.M. Andrade, F.V. Molina, Anion exchange influence on the electrochemomechanical properties of polyaniline, *Electrochimica Acta* 53 (2007) 538.
- [69] R.D. Priestley, C.J. Ellison, L.J. Broadbelt, J.M. Torkelson, Structural relaxation of polymer glasses at surfaces, interfaces, and in between, *Science* 309 (2005) 456.
- [70] G. Ybarra, C. Moina, M.I. Florit, D. Posadas, Proton exchange during the redox switching of polyaniline film electrodes, *Electrochemical and Solid-State Letters* 3 (2000) 330.
- [71] J.S. Royal, J.M. Torkelson, Photochromic and fluorescent probe studies in glassy polymer matrices. 5. Effects of physical aging on bisphenol-a polycarbonate and poly(vinyl acetate) as sensed by a size distribution of photochromic probes, *Macromolecules* 25 (1992) 4792.