Probing speciation inside a conducting polymer matrix by \textit{in situ} spectroelectrochemistry

Jacqueline Ferreira\textsuperscript{a}, Alexandre G. Brolo\textsuperscript{b,\,*}, E.M. Girotto\textsuperscript{c}

\textsuperscript{a} Instituto de Química e Geociências, Universidade Federal de Pelotas, 96010-900, P.O. Box 354, Pelotas, Rio Grande do Sul, Brazil
\textsuperscript{b} University of Victoria, Department of Chemistry, P.O. Box 3065, V8W 3V6, Victoria, British Columbia, Canada
\textsuperscript{c} Universidade Estadual de Maringá, Av. Colombo 5790, 87020-900 Maringá, Paraná, Brazil

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\textbf{Abstract}

The interactions between polypyrrole and an embedded bromophenol blue (BPB) dye at different oxidation levels and pHs were investigated. Cyclic Voltammetry, \textit{in situ} UV–vis and Raman spectroelectrochemistry were used to detect electrochemical and optical changes in the BPB-doped ppy films. The acid–base equilibrium of the embedded dye was observed to be highly dependent on the applied potential and on the pH conditions. The intensities of the vibrational bands characteristic of the acidic and basic forms of the species inside the film clearly showed a potential dependent shift of the dissociation equilibrium of BPB, which is effectively controlled by the oxidation level of ppy. This type of information provides some insights into the effect of the environment on the chemical behavior of acid–base pairs embedded in polymeric matrices.

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1. Introduction

The ability to change color in response to environmental or external stimulus makes conducting polymers an excellent material for applications in optical devices [1,2]. Although some of these properties, such as electrochromism [1–4], thermochromism [3,5], solvatochromism [6] or piezochromism [7] are intrinsic characteristics of the polymer, hybrid materials with color-changing properties can be easily fabricated by incorporating organic dyes to the polymer film. Many dyes have poor solubility in water, but acidic dyes, with solubility-enhancing groups such as sulfonates, have been used as dopants (ionic species that enable the polymer conductivity [2,8,9,17]). The large conjugated system of dyes can interact with the \(n\)-system of polymers, such as polypyrrole (ppy), leading to hybrid systems [10–12]. The influence of the nature of the dopant ions on the optical, electrochemical and structural characteristics of these hybrid systems has been widely investigated [2,13,17].

Despite of the large amount of research on the influence of dopants and ions on the optical and electrochemical properties of conducting polymers, there are no reports on the direct identification of the speciation inside the polymer matrix during redox. In this work, we will use \textit{in situ} Raman and UV–vis spectroelectrochemistry to obtain this type of molecular level information. The main objective is to directly observe how the oxidation state (doping level) of the polymer affects the acid-base chemistry of the embedded dye. The redox of conducting polymers leads to conformational changes, which can be readily probed \textit{in situ} by Raman spectroelectrochemistry [14–20]. Polypyrrole is one of the most studied conducting polymers [21,22–24] and bromophenol blue (BPB) is a well known pH indicator (the chemical structure of BPB, its protonated forms and their pK\(_a\) values are presented in \textbf{Scheme 1}) [25–27]. The ppy/BPB system provides then a good model to the proposed investigation, since it was early demonstrated that the dissociation equilibrium of BPB affects the electrical properties of polypyrrole [28] in addition to a shift in the pK\(_a\) due to interactions between polymer and dopant at different pH [29]. Therefore shifts in the pK\(_a\) of the embedded dye are expected, driven by the conditions of charge neutrality inside the polymer matrix. The results reported here help the understanding of the effect of the environment inside the polymer on the chemistry of the dopant, providing insights that might be useful to the further development of polymer-based optoelectronic devices.

2. Experimental

2.1. Materials and reagents

Pyrrrole (Aldrich) was double distilled and stored under N\(_2\). Bromophenol blue (BPB from Reagen), sodium phosphate monob-
The polypyrrole film doped with bromophenol blue (ppy/BPB films) was potentiodynamically synthesized using a 0.05 mol L\(^{-1}\) aqueous solution of pyrrole and 0.4 mmol L\(^{-1}\) of BPB. A three-compartment electrochemical cell was used for both the synthesis and electrochemical investigations. Gold slides were used as working electrodes, Ag/AgCl(Cl\(_{sat}\)) was the reference electrode, a Pt wire was the counter electrode. The potential range for electrolysis was from −0.3 to 1.3 V at a scan rate of 0.02 V s\(^{-1}\). The same electrochemical procedure was used to synthesize the film in the absence of BPB (referred thereafter simply as ppy films), but in those cases the 0.4 mmol L\(^{-1}\) of BPB was replaced by 0.1 mol L\(^{-1}\) NaClO\(_4\) solution. The electropolymerization and all the electrochemical measurements were carried out with an Autolab PGSTAT 30 potentiostat/galvanostat. The surface coverage of the films, determined by analyzing the electric charges under the voltammetry, was 2.5 × 10\(^{-8}\) mol/cm\(^2\) for ppy and 6.8 × 10\(^{-9}\) mol/cm\(^2\) for the ppy/BPB. These coverages were obtained considering 100% of electrochemical efficiency for the film formation. SEM/EDX analysis of the ppy/BPB film for nitrogen (present in the pyrrole ring) and bromine (present in the BPB molecule) was carried out to estimate the concentration of BPB on the polymeric matrix. The results indicated that, on average, the ppy/BPB films contain about 9 molecules of ppy for each BPB molecule.

A three-electrodes cell was filled with phosphate buffer solutions (PBS) of different pHs and mounted on a microscope stage for all spectroelectrochemical measurements. The working electrode was optically accessed through a 0.2 mm glass window. The pHs of the PBS solutions were determined using an Orion Instruments model 420A plus pH-meter. The systems were allowed to reach the equilibrium, by observing the stabilization of the current at a given potential, before each spectrum (either Raman or reflection-absorption spectroscopy) was recorded. The reflectance-absorption experiments were recorded on a USB2000 miniature fiber optic spectrometer (Ocean Optics) attached to the ocular of an Olympus BHSM microscope. This spectrometer is optimized for fluorescence measurements; therefore, it contains a cut-off filter for wavelengths shorter than 450 nm. A 50 W halogen lamp from the microscope provided the required broad band light source. The output of the halogen lamp was focused on the ppy film using a long working distance 50× Olympus microscope objective (NA = 0.55) and the reflectivity was recorded for all applied potentials. The Raman spectra were obtained at the same microscope using a He–Ne laser (Melles Griot—632.8 nm) as an excitation source. The Raman microscope system operates in back-scattering mode, and the same objective is used for both excitation and collection. The collected scattered light was filtered using a Kaiser super notch filter to remove the contributions from the excitation. The remaining radiation was directed through a Kaiser Holospec f/1.4 spectrograph coupled with an Andor CCD detector (model DV-401-BV).

### 3. Results and discussion

The objective of this work is to study the behavior of ppy films doped by a dye in situ using spectroscopy. As a first step, however, it is important to establish the electrochemical characteristics of the doped and undoped systems in order to determine the appropriate range of applied potentials for the spectroelectrochemical measurements. Cyclic voltammograms (CVs) experiments were then carried out for both ppy and ppy/BPB films synthesized on gold slides. The potential range for the CV measurements was between −0.6 and 0.9 V, the scan rate was 0.02 V s\(^{-1}\). Fig. 1 shows representative CVs for ppy (Fig. 1a) and ppy/BPB (Fig. 1b) films at pH values equal to 3.0 and 7.5. Ppy presented an electrochemical behavior dependent on the pH, with higher conductivity at lower pH values (notice the higher current for the CV at pH 3.0 in Fig. 1a). This dependence has been reported before [30] and it was ascribed mainly to ppy deprotonation in alkaline solutions, which decreases the doping level. In other words, the anionic counter-ion moves away from the polymer matrix following this deprotonation, leading to lower conductivity. On the other hand, in acidic solutions, the ppy chains are highly protonated, allowing the counter-ion to move easily into the polymer matrix to restore charge neutrality [31–33]. Another interesting feature in Fig. 1a is the decrease in the oxidation potential of ppy as the film is conditioned in more alkaline media, moving from +0.0 V (pH 3.0) to −0.3 V (pH 7.5). This shift is indicated by a dashed arrow in Fig. 1a. During the oxidation process, anions from the nearby electrolyte migrate into the polymer matrix for charge stabilization [33], and the higher activity of OH\(^−\) ions in alkaline solution might give an extra contribution for the stabilization of the oxidized form of ppy. Similar trends, a decreasing in oxidation potential as the pH increased, were observed for (poly(3-carboxymethyl pyrrole)), which is a ppy self-doping system [34].

Fig. 1b shows that ppy/BPB present a different electrochemical behavior than pure ppy (Fig. 1a). At low pH, a redox pair at 0.7/0.6 V (highlighted in the figure) was evident in the CV of the ppy/BPB film. CVs of BPB solutions at pH 3.0 (not shown) also presented a reversible pair at ca. 0.7/0.6 V, therefore, that feature in the film...
The UV–vis-absorption spectra of BPB and its deprotonated forms (BPB$^-$ and BPB$^{2-}$) in aqueous solution were collected at different pH-values (Fig. 2). The absorption spectra of the dye in solution presented two pH-dependent absorption bands at 435 and 580 nm and also a shoulder at ca. 525 nm (Fig. 2). The assignment of these bands has been discussed in the literature [36–40]. BPB buffered at different pH shows different colors in the visible spectrum. The 435 nm-band dominates at pH 1.5 but it vanishes at pH > 4.81. This band is then assigned to the double protonated form of the dye (BPB, yellow solution). The strong 580 nm-band appears more intense for more alkaline medium and it is assigned to the BPB$^{2-}$ form (blue solution). Finally, the BPB$^-$ (red solution) is characterized by a shoulder at ca. 525 nm that is evident at pH 7.0 (see Fig. 2).

Fig. 3 shows the in situ reflection–absorption spectroelectrochemical measurements for the ppy/BPB system at pH 1.5, 3.0, 7.5 and 11.0. All the in situ spectroelectrochemical measurements were carried out between –0.4 and +0.4 V. According to the CVs presented in Fig. 1b, this is a potential range within the redox window for ppy and where BPB is not expected to be electrochemically active. The similar data set for ppy was published elsewhere [41,42]. The spectra present two main broad peaks at ca. 600 and 700 nm. The 700 nm-band is assigned to the transition from the bonding polaron state to the antibonding polaron states in ppy [43]. The 600 nm-band is related to the double charged form of the dye (BPB$^{3-}$), but also contains contribution from the ppy. Unfortunately, we were not able to probe the region between 400 and 500 nm due to instrument limitations (our spectrometer contains a cut-off filter for wavelengths shorter than 450 nm that could not be removed). At pH 1.5 and 3.0 (Fig. 3a and b) the absorption band at 600 nm increases as the potential is made more anodic; the absorption at 700 nm is also potential dependent in acid medium; increasing its intensity as the oxidation level of ppy increases. At pH 1.5, the ppy-band at 700 nm is always more intense than the BPB$^{2-}$ band (at 600 nm); however, at pH 3.0, the band with contributions from the dye (at 600 nm), becomes more intense than the ppy-band (at 700 nm) in the potential range between –0.4 V and +0.2 V. A band at 525 nm is also observed at pH 3.0, and it can be assigned to a combination of the transition from the valence band to the antibonding polaron state in ppy [43] and the mono charged form of the dye (BPB$^-$). Compared to acid medium, dramatic changes in the optical behavior of the films were observed around neutral and basic conditions, as shown in Fig. 3c and d. The
absorption at 600 nm, which have a strong contribution from the BPB$^{2-}$ form of the dye, is now very strong and the band related to the ppy matrix appears as a shoulder at ca. 700 nm. Although both of these bands present some potential dependence, the band at 600 nm does not change as much as at the lower pH (Fig. 3a and b). The potential dependence of the UV–vis spectra of ppy/BPB at pH 7.0; 8.0 (not shown) follows the same trend; i.e., the absorption attributed to the dye at ca. 600 nm shows a weak potential dependence. The series of peaks in the long wavelength that appears in a regular interval of ∼25 nm is probably an interference pattern due to the reflection of the light from the top (in contact with the solution) and the bottom (in contact with Au) of the film. Although aromatic dyes are known to form dimers at relatively high concentration, we haven’t observed any clear signature for dimerization due to the reflection of the light from the top (in contact with the solution) and the bottom (in contact with Au) of the film. Although aromatic dyes are known to form dimers at relatively high concentration, we haven’t observed any clear signature for dimerization from the spectra in Fig. 3.

The reflectance measurements presented in Fig. 3 provide insights into the interaction between the dye and the polymer matrix that could not be obtained from the CVs. Specifically: it is possible to notice a stronger potential dependence at the 600 nm region at more acid solutions. The absorption at 600 nm might contain contributions characteristic of the BPB$^{2-}$ form of the dye. This is a surprising result, since at low pH the equilibrium favours protonated species, such as BPB. However, even at pH 1.5 and 3.0 (Fig. 3a and b), the absorption at 600 nm (with contributions from the charged form of the dye) increases as the potential is stepped towards positive values. We rationalize these observations by considering that as the ppy undergoes oxidation, the charged BPB species in the film (BPB$^+$ and BPB$^{2-}$) must act as counter-ions, stabilizing the positively charged polymer chain. Hence, the ppy oxidation directly affects the dissociation equilibrium of the dye (Scheme 1), increasing the concentration of the specie BPB$^{2-}$. This suggestion is consistent with the CV data that shows a negative shift in the oxidation potential of ppy to −0.2 V in the ppy/BPB film. The demand for co-counter-ions to stabilize the polymer chain is well known. For instance, quartz micro-balance studies have showed that anions from the nearby electrolyte solution must diffuse into the polymer matrix in order to keep the conditions for electroneutrality [44,45]. The CV and UV-vis results show that charged deprotonated species (BPB$^{2-}$ in this case) are acting as counter-ions, and; therefore, the equilibrium in Scheme 1 is no longer valid for the dye inside the film. The dye equilibrium already favours the BPB$^{2-}$ forms at higher pHs, leading to a high absorption at 600 nm, as shown in Fig. 3c and d. Moreover, OH$^-$ ions, which deprotonate the ppy chain, are also present and significantly contribute to further stabilize the positive charges after the oxidation of the film. The BPB$^{2-}$ band at 600 nm is then not significantly affected by the applied potential at pH values larger than 7.

Nath et al. [41] have studied the dependence of the local pH in the interior of ppy/BPB microtubules to the applied potential. They assumed that a monomer solution containing a concentration of BPB $\leq 8 \times 10^{-4}$ mol L$^{-1}$ yields a film with CV characteristics similar to the pure ppy film. In other words, the presence of BPB in the microenvironment did not affect the redox process of the polymer film. These observations contrast to our results (see Fig. 1), which show a clear effect of the dye on the redox behavior of the polymer film on a gold surface (a monomer solution of 0.05 mol L$^{-1}$ with $4 \times 10^{-4}$ mol L$^{-1}$ BPB was used in our case).

Although the reflectance–absorption data (Fig. 3) hinted that deprotonated forms of BPB are present inside the film even at very acidic conditions, the broad absorption bands, inherent of electronic transitions overlaps with the absorption from the ppy, and our instrumental limitations restricted the detection of all the BPB-species. Raman spectroscopy is a vibrational technique, which provides molecular-specific information that is not accessible by electronic spectroscopy. We then decided to search for the species embedded in the film using in situ Raman spectroelectrochemistry. A limitation to this approach, however, is that the Raman spectra of the film is expected to be dominated by the ppy features [2,20,46]. These are broad vibrational bands that changes with the oxidation level. A survey of the Raman spectrum of the ppy/BPB film, however, showed that new features (compared to the Raman of pure ppy) are present in the spectral region around 900 cm$^{-1}$. Therefore, we decided to concentrate our attention to that region.

The in situ Raman spectra of ppy/BPB films at low pH, in the region between 750 and 1000 cm$^{-1}$, are presented in Fig. 4b for

![Fig. 3. Reflection–absorption spectra of ppy/BPB film in PBS at (a) pH 1.5, (b) pH 3.0, (c) pH 7.5 and (d) pH 11.0.](image-url)
different applied potentials. The spectra of the pure ppy film at different applied potentials are also shown in Fig. 4a for comparison. Both Fig. 4a and b were obtained in PBS at the same pH. Previous work from our group has demonstrated that the oxidation level of ppy films is related to the relative intensities of the bands at ca. of 930 and 985 cm\(^{-1}\) [20]. The 930 cm\(^{-1}\)-band, assigned to a C–H deformation mode, is dominant on the oxidized form of the polymer, and the 985 cm\(^{-1}\) is characteristic for the reduced (neutral) oxidation state of ppy. In acidic media, the spectrum of the ppy/BPB film at +0.4 V (ppy is highly oxidized) is similar to the pure oxidized ppy film [20,47] (Fig. 4), since it is dominated by a band at the 930 cm\(^{-1}\) region. The intensity of this band decreases as the potential is switched to the negative direction. The 987 cm\(^{-1}\)-band, assigned to ppy in the reduced state, becomes more intense than the 932 cm\(^{-1}\)-band when potential values more negative than 0.0 V are reached. In addition, a comparison between Fig. 4a and b indicates the spectra of ppy/BPB in this spectral region present some interesting differences relative to the spectra of pure ppy at the same conditions of pH and potential. First of all, the band around 932 cm\(^{-1}\) is present as a defined peak in the ppy/BPB spectra (Fig. 4), since it is dominated by a strong peak at 990 cm\(^{-1}\) [49,50]. Considering that the reflection-absorption data, shown in Fig. 3, presented an increase in the absorption due to BPB\(^2-\) as the ppy film was reduced, we tentatively assigned this band to a deformation mode of the ring of the BPB\(^2-\) anion. It is important to point out that the laser excitation used in the Raman measurements (632.8 nm) is within the absorption band of BPB\(^2-\) (Fig. 2). This leads to resonance Raman effects [51], which can increase the Raman cross section for this species. It is important to point all that all measurements were done with films adsorbed on top of smooth gold surfaces. Therefore, significant contributions to the overall signal due to surface-enhanced Raman scattering (SERS) is not expected (SERS is only significant operative when the metal surface contain nanostructures or roughness). The demand for negative charges in the polymer matrix affects the acid–base equilibrium inside the ppy matrix, decreasing the concentration of the protonated species within the film during oxidation. This potential dependent speciation corroborates our previous UV–vis–reflectance analysis where it was shown that the dye in the charged form acts as counter-ion, interacting with the oxidized polymer chain.

Fig. 5 presents the Raman data of the ppy and ppy/BPB films at pH 8.0. First of all, it is interesting to observe the behavior in the absence of the dye, provided by Fig. 5a, where the 989 cm\(^{-1}\)-band, characteristic for the reduced form, is only dominant at −0.4 V, and this band is immediately replaced by a new peak at −920 cm\(^{-1}\) when the potential becomes as positive as −0.2 V. This is a direct evidence of the facile oxidation of the ppy matrix at higher pH values, in accordance to the CV observations presented in Fig. 1. In contrast, the ppy/BPB films at higher pH (Fig. 5b) present several features that are not observed in pure ppy. Fig. 5b shows the 989 cm\(^{-1}\)-band at −0.4 V assigned to the reduced form of the ppy matrix. However, as the potential is stepped to −0.2 V, a new band at 950 cm\(^{-1}\) is recorded, and the feature characteristic to the oxidized form of the ppy (at −920 cm\(^{-1}\)) is only apparent at the most positive potentials (+0.4 V). Strong features at 860 and 893 cm\(^{-1}\) are also observed in the oxidized matrix (notice in Fig. 5b that all these fea-
tures are weak at $-0.4$ V, when the reduced form is predominant, as indicated by the strong 893 cm$^{-1}$-band. The 860 cm$^{-1}$ band is less sensitive to the applied potential than the band at 893 cm$^{-1}$, which decreases intensity as the potential becomes more positive. Our analysis of Fig. 4 concluded that the oxidized form of the ppy matrix is favoured by the presence of anionic, unprotonated, species inside the film (in accordance to the CV and reflectance data shown in Figs. 1 and 3). In that case, the 860 cm$^{-1}$-band was correlated to the complete deprotonated, form of the dye (BPB$^{2-}$). This assignment was done in the discussion of Fig. 4b, and this species is even more relevant at higher pH values. The fact that the magnitude of this 860 cm$^{-1}$-band does not change significantly with the applied potential is expected, based on the results presented in Fig. 3c and d. The feature at 950 cm$^{-1}$ in Fig. 5b is assigned to the oxidized form of ppy, and the shift from its position in the absence of BPB (920 cm$^{-1}$ in Fig. 5a) suggests a strong interaction between the ppy matrix and the dye. However, phosphate ions (PO$_4^{3-}$) also present a strong band in solution at $-940$ cm$^{-1}$. Although PO$_4^{3-}$-ions are expected to become the dominant species only at very basic pH ($pK_a$ of phosphoric acid is equal to 12.1); our experimental data so far demonstrates that the conditions inside the film favours deprotonation of the species relative to the bulk, leading to a more basic environment than the solution. In that case, the Raman peak of the oxidized matrix at $-920$ cm$^{-1}$ would basically be buried under a strong phosphate background, and it only emerges as a significant spectral feature at more positive potentials. Phosphoric acid is the only phosphorus species with a strong band at $-893$ cm$^{-1}$ [49]. However, the presence of fully protonated phosphoric acid in the film is unlike (in solution, H$_3$PO$_4$ is only dominant at pH $< 2$). Therefore, we assign the 893 cm$^{-1}$-band to an unprotonated form of BPB, probably BPB$^-$. Our results suggest that at pH $> 7$, the presence of anionic forms trapped in the polymer matrix holds the film at an oxidized level, independent of the applied potential. These results suggest a decrease in ion uptake from the electrolyte. Similar results from the observed in Figs. 4 and 5 were observed for different pHs, making the behavior at pHs 3 and 8 representative of the response of the system in both the low and high pH limits.

The effect of ions and ions transport on the performance of the sensors based on conducting polymers is a great concern in that field [52,53]. The study presented here brings a new perspective regarding the stability of species inside the polymer, providing useful insights towards the development of efficient sensor. Our results indicated that the demand for ions transported from the solution might be alleviated by the dominant charged forms of the dye embedded into the polymer matrix.

4. Conclusions

We have demonstrated a detailed investigation on the interaction between an embedded dye and its polymeric host. The redox of the dye-doped polymer depends on the pH and the acid–base equilibrium of the dye was affected by the applied potential. The BPB dissociation equilibrium is perturbed to compensate for the positive charges generated by oxidized ppy. Even the speciation inside the film is significantly altered. Systems like the one investigated in this work could be used to minimize the interference caused by ions present in the electrolyte, decreasing the uptake of ions from the electrolyte solution. Additionally the understanding of the environment inside the polymer on the chemistry of the dopant provides new insights to development of polymer based pH sensors.

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