J. Braz. Chem. Soc., Vol. 21, No. 2, 312-318, 2010.
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0103 - 5053 $6.00+0.00

Article

pH Effects on the Ohmic Properties of Bromophenol Blue-Doped Polypyrrole Film

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A resposta ôhmica durante medidas de resistência *in situ* de filmes de polipirrol (ppy) dopados com azul de bromofenol (BPB) foi analisada para se estudar o efeito do pH nas propriedades analíticas dos filmes. As moléculas de BPB foram inseridas na matriz polimérica através de síntese eletroquímica sobre eletrodos digitalizados de ouro. Os filmes de ppy-BPB não apresentaram diminuição da resistência ôhmica linear com relação ao aumento do pH do meio, no intervalo de 1,5 a 11, sendo observado um aumento da resistência do filme após imersão em pH 7,5. O comportamento não linear é uma desvantagem para a aplicação do ppy-BPB como sensor de pH, no entanto, importantes informações sobre a interação entre o dopante e o polímero conjugado podem ser obtidas deste sistema. O comportamento ôhmico do filme de ppy-BPB pode ser explicado em termos da variação no equilíbrio entre as formas neutra e aniônica do corante preso na matriz de ppy. O estudo neste trabalho contribui para o desenvolvimento de sensores eficientes baseados em polímeros condutores.

The ohmic response of bromophenol blue (BPB) doped polypyrrole (ppy) films obtained by *in situ* resistance measurements was studied to evaluate the pH effect on their analytical properties. BPB molecules were inserted into the ppy matrix by electrochemical synthesis onto digitized gold electrodes. Ppy-BPB films do not present decrease in the linear ohmic resistance when increasing pH values over the pH range 1.5-11.0, displayed by an increase in resistance after immersion in pH 7.5. The nonlinear behavior is a disadvantage for the application of the ppy-BPB film as pH sensor, however, meaningful information about the interaction between the dopant and the conjugated polymer can be obtained from the system. The ohmic behavior of the ppy-BPB films are explained in terms of the equilibrium between neutral and anionic dye species embedded in the ppy matrix. This work brings important contributions to the development of efficient conducting polymer-based sensors.

Keywords: polypyrrole, bromophenol blue, ohmic properties, doped films

Introduction

Conducting polymers are well known materials with interesting optical, magnetic and electrical properties.[1-3] The oxidation process in the electronic structure of a heterocyclic conjugated polymer, such as polypyrrole (ppy),[4,5] leads to the formation of polaron and bipolaron states. These energy states are related to remarkable properties of conjugated polymers that take place with the introduction of anion dopants into the polymer matrix to stabilize those charges (polaron and bipolaron) formed during oxidation.[6] The dopant used during the polymer synthesis can directly affect the electrical and structural properties of the conjugated polymer.[2,7,8] Study of the interaction between polymer and dopant is meaningful for the comprehension and applications of these materials.[9]

The literature have demonstrated the application of electroactive conjugated polymers in the solar cells development,[10,11] organic light-emitting devices,[12,13] and electrochromic and electrochemical devices.[14-17] Among this applications, the use of electroactive conducting polymers in pH sensing technology has been the focus of many studies in the last decade.[18,19] Ppy is one of the most studied conjugated polymers and has been widely applied in chemical sensors.[20-24] Despite the plethora of work published in this area, it still lacks some understanding of the interaction between conjugated polymer and counter ions, and its direct relation to the electrical film properties. Conjugated polymers conductivity depends on several parameters, such as chain structure, polymerization

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mode and medium, as well as the pH medium.[25] As one of its inherent properties in the oxidized state, ppy is a polyradical cation and electrostatically attracts anions into the polymeric matrix. In addition, the ppy film presents both pore size and charge distributions, making possible certain anion recognition functionality, as well. Furthermore, these steric requirements (pore size and charge distribution) may control possible interferences from other ions.[26]

In this work, we present a pH-sensitive material obtained by doping ppy with a pH indicator, bromophenol blue (BPB).[27-29] Each component is pH sensitive, presenting different pKa (3.9 to BPB[30] and 8.6 to ppy[31]). The analytical properties of the ppy-BPB film were investigated by studying the pH effect on the ohmic properties of the film toward the comprehension of the interaction between ppy and the dopant. The films were assembled by electrodepositing ppy-BPB onto digitized gold substrates separated by a 10 μm gap. This type of electrode was used to increase the contact surface between the electrodes coated with polymer and the solution to analyze. In addition, it offers some advantages in chemical sensor applications as high sensitivity, small sensitive area allowing development of miniaturized devices, which can be integrated with the emerging *lab-on-chip* area.[32]

Experimental

Chemicals

Pyrrole (Aldrich) was double distilled and stored under N_2. Bromophenol blue (BPB), sodium perchloride (Reagen), sodium phosphate monobasic, sodium phosphate dibasic, sodium pyrophosphate decahydrate (Aldrich), sodium hydroxide, phosphoric acid (Merck), sodium chloride (Synth), sodium nitrate (Vetec), sodium bisulfite and potassium phosphate monobasic (Nuclear) were used as received. All solutions were prepared using Milli-Q® water.

Apparatus and synthesis procedure

Electrochemical polymerization and electrochemical characterization of the BPB-doped ppy film was carried out using an Autolab model Pgstat30 galvanostat/potentiostat. A three-electrode electrochemical cell was equipped with a platinum wire as counter-electrode, a saturated calomel electrode (SCE) as reference and as working electrode a digitized gold (Au) substrates (assembled by using conventional photolithography procedure)[32] with *ca.* 10 mm^2 area was used, separated by a 10 μm gap, (provided by Escola Politécnica da Universidade de São Paulo). Ppy-BPB films were potentiodinamically synthesized from 0.05 mol L^{-1} pyrrole and 0.4 mmol L^{-1} pH indicator solutions at controlled temperature (10 °C), with synthesis potential ranging from –0.3 to 1.3 V at a scan rate of 0.02 V s^{-1}. The synthesis temperature was controlled by a Tecnal TE184 thermostated bath. Upon synthesis, the ppy-BPB film was dried at 45 °C for 2 h and then kept under vacuum. The 0.2 mol L^{-1} phosphate buffer solution (PBS) was calibrated in a Hanna Instruments, model HI 9321 pHmeter. Film thickness was measured using a Veeco perfilometer, model Dektak 3. The resistance measurements were carried out by connecting a Keithley programmable electrometer, model 617, to a digitized electrode immersed in PBS, at different pHs. All measurements were carried out at room temperature (*ca.* 25 °C).

Results and Discussion

Cyclic voltammetry

At first, the electrochemical characteristics of the polymeric films were established in order to verify their redox behavior after synthesis. Cyclic voltammetry (CV) experiments were then carried out for ppy-BPB films synthesized onto the digitized electrodes. The ppy-BPB film was analyzed from –0.6 to 0.9 V (the same potential range was used during the electrochemical synthesis), at a scan rate of 5 mV s^{-1}. Figure 1 shows the CVs of ppy-BPB films using $LiClO_4$ 0.1 mol L^{-1} as electrolyte.

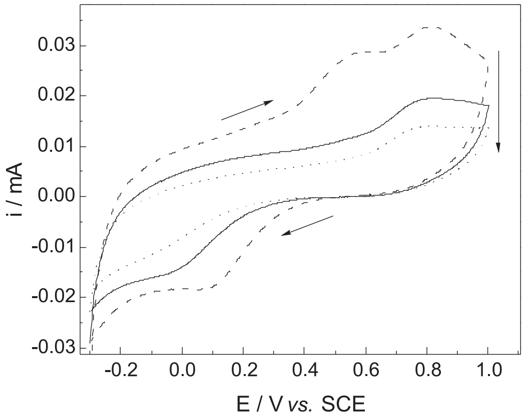

Figure 1. Cyclic voltammograms of ppy-BPB in $LiClO_4$ 1 mol L^{-1}. (---) first scan; (—) second scan; (···) third scan. Scan rate = 5 mV s^{-1}.

An interesting behaviour observed in the cyclic voltammograms, presented in Figure 1, is the considerable decreasing of current with the number of scans. Additionally, an intense anodic peak appears only in the first scan. This peak can be related to the overoxidation of ppy.[33] The literature shows a current rising with the number of cycles observed for electroactive conjugated polymers, indicating that the potential to reach a certain oxidation current decreases after each successive scan.[34] However, in our experiment a very different behaviour was observed: the increasing resistance of the polymeric film and the structural change of the conducting polymer during overoxidation[35] produces a decrease in the current (Figure 1).

Ohmic response of ppy-BPB films

The signal output (resistance) of the ppy-BPB films was converted to percentual sensitivity (S%) using equation 1, where R_x is the resistance measured after immersion of the film in buffered solution and R_0 is the baseline resistance (measured before immersion).[36] The film was kept in the solution long enough for resistance stability.

$$S\% = \left[\frac{(R_0 - R_x)}{R_0}\right] \times 100 \qquad (1)$$

Figure 2 shows S% as a function of pH. The sensitivity increased after conditioning the film at acid-to-neutral medium, which, according to equation 1, results in a film resistance decrease. This behavior is expected, since the concentration of negative charges increases steadily from pH 1.5 to pH 7.5.[37] However, the sensitivity starts to decrease after pH 7.5, dropping steadily up to pH 11.

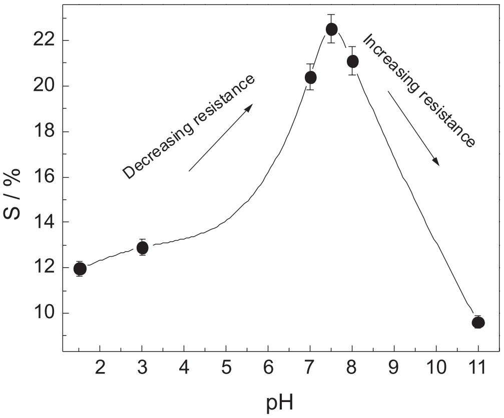

Figure 2. pH ohmic sensitivity of a ppy-BPB film deposited onto a digitized gold electrode in phosphate buffer solution.

In order to explain the atypical pH sensitivity presented by ppy-BPB, two considerations should be taken into account: *i*) the interaction between electroactive conjugated polymer and dopant and, *ii*) the overoxidation process during the synthesis of ppy-BPB (Figure 1).

Spectrophotometric measurements of the ppy-BPB film showed a pKa shift from 3.0-4.0 (dye BPB in solution) to 7.7 (matrix-embedded dye),[3] although this film presented UV-vis spectra similar to the ones of BPB (without ppy). This behavior occurs due to a synergic effect resulting from the interaction between dopant (BPB) and conjugated polymer (ppy). This interaction affects the dissociation equilibrium of BPB (Figure 3). One should bear in mind that, at acid pH, the concentration of neutral BPB form is higher than the anionic form.

According to the literature, the ohmic resistance of the ppy film increases linearly with the pH of the medium.[18,38] However in our system an unexpected behavior was observed. In more alkaline media, BPB equilibrium shifts and the concentration of the anionic form increases, resulting in a higher doping level and conductivity increase of the ppy-BPB film. According to this rationale, one would expect a linear behavior for sensitivity *versus* pH (Figure 2). However, at pH 7.5, an inversion point is observed and the sensitivity starts to decrease. This behavior can be explained considering the breaking of N−H bonds, resulting in deprotonation of ppy in alkaline medium.[39] The deprotonation decreases the π-conjugation length, leading to "carrier loss", and therefore to a decrease in the film conductivity (increase in resistance), followed by a dedoping process. In fact, during the measurements at alkaline pH, we could actually see the dye leaving the film to the nearby solution. Indeed, the anion concentration increased in the more alkaline medium. However, deprotonation and dedoping prevented the film from reaching higher conductivity than that obtained at pH 7.5.

The overoxidation of ppy may interfere in the ions insertion and extraction in the ppy matrix, affecting the pH sensitivity of ppy-BPB film. To elucidate this hypothesis, were compared the pH sensitivity of overoxidized ppy-BPB film to overoxidized ppy film

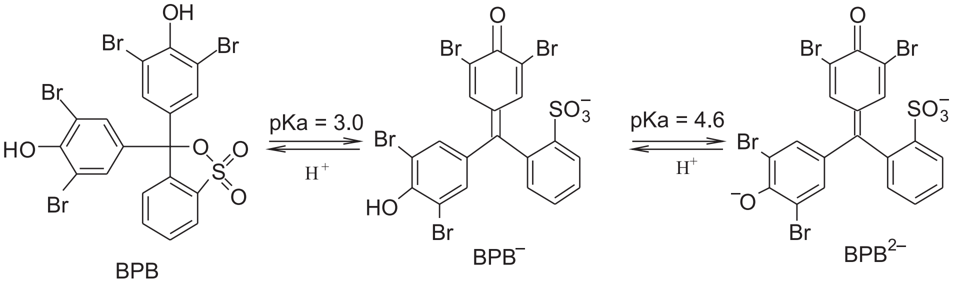

Figure 3. Dissociation equilibrium of the pH indicator Bromophenol Blue (BPB).

(without the dye). According to the literature,[18] ppy films electrochemically synthesized by cyclic voltammetry method sweeping from 0 to +3 V, presented linear pH sensitivity (increasing resistance as pH increases), differently from the ppy-BPB studied in this work. Therefore, despite the relative high oxidation potential applied during the synthesis (+1.3 V), leading to overoxidation of ppy,[18] we can assume that the nonlinear ohmic behavior observed from ppy-BPB is related to the interaction between ppy and BPB.

At this point it is also interesting to mention the film thickness influence on pH sensitivity of ppy. According to the literature,[18,26,40] thinner films usually appeared to present better pH sensitivity than thicker ones. This observation has been explained considering the morphology and molecular organization of the polymeric films.[41] Thin ppy films comprised mainly ordered molecular strands anchored directly on the electrode surface, while thick films are amorphous structures. As result, the diffusion of ions in thin films should be faster than in thick films. However, when ppy film is too thin, it will not give the best response. This occurs due to the electrode covering, that is not complete and the morphology shows nodules with different sizes. In our work, we have used ppy-BPB films thickness thinner enough to create a contact in the gap of the digitized electrode. The thickness obtained for ppy-BPB (*ca.* 560 nm) is close to the best responses to pH previously reported for ppy (400 nm) in the literature.[18]

Response time

The ppy-BPB film response time to pH changes was measured by monitoring the resistance *versus* time in alkaline and acidic media. For these measurements, the ppy-BPB film was immersed in a pH 8.0 solution for 40 s and then immersed in acidic medium (pH 3.0). A very interesting result is the short response time obtained from this system, when compared to values in the literature.[42-44] The changes in resistance from acid to alkaline media, and the other way around, were observed in less than 10 s. A short response time was expected, since the diffusion of ions in thin films is fast. The obtained response time is comparable to those of efficient polymer-based pH sensors. Grant and Glass[42,43] worked with sol-gel encapsulation of pH-sensitive self-referencing dye seminaphthorhodamine-1 carboxylate, which resulted in a response time of 15 s. Response times from 3 to 5 min were obtained for electrochemically synthesized polymer-based pH sensors, such as ppy and PAni (polyaniline).[44] The response time of other ppy electrochemically synthesized on platinum electrodes[45] was shorter than 1 s.

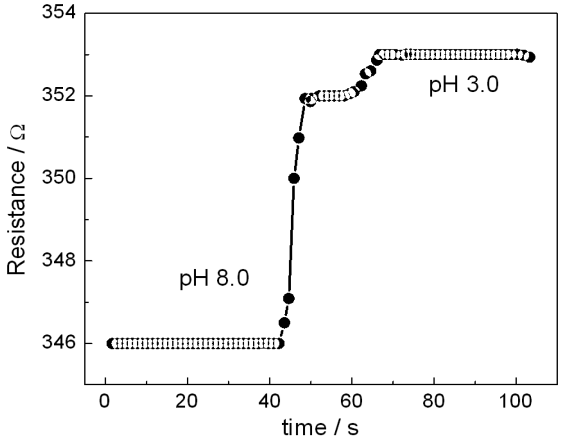

Figure 4. Dynamic ohmic response of ppy-BPB to pH changes from alkaline (pH 8.0) to acid media (pH 3.0).

Ohmic reproducibility and reversibility

Figure 5 presents the reproducibility and reversibility results for the ppy-BPB film. In this measurement, the same film was successively immersed into solutions with pH 1.5 (not shown), 3.0, 7.0, 7.5 (not shown) and 8.0 (pH 1.5 and 7.5 present the same behavior that pH 3.0 and 7.0, respectively). A conditioning time of 5 min was set before resistance measurement. The film was then rinsed with Milli-Q® water and immersed in the next pH buffered solution. A dramatic drop in resistance associated with the conditioning time was observed in the beginning of the measurements.[46] Apparently, this time is necessary for the charge distribution homogenization in the polymeric matrix. The incorporation of ions into the polymeric matrix, in addition to the dissociation shift equilibrium of BPB (Figure 3), stabilizes the charge carriers, contributing to their mobility, resulting in the increase of conductivity.

After the conditioning time, the films were reversible and reproducible (between the 25th and the 59th measurements). The ppy-BPB was dried for 24 h between the 59th and the 60th measurement in order to evaluate if, after drying, the film kept its ohmic properties. The results indicate a reproducible behavior, as the system returned to its initial resistance. However, the resistance of the films in acidic and neutral pH was more reversible than those of the films immersed in a pH 8.0 buffer solution. These results are very interesting, mainly considering that reproducibility is not the best characteristic of conducting polymers.[47] Indeed, the system studied here presents very good reproducibility and reversibility. The properties of the ppy-BPB film are affected by the BPB embedded in the polymeric matrix, which could explain its unusual reversibility.

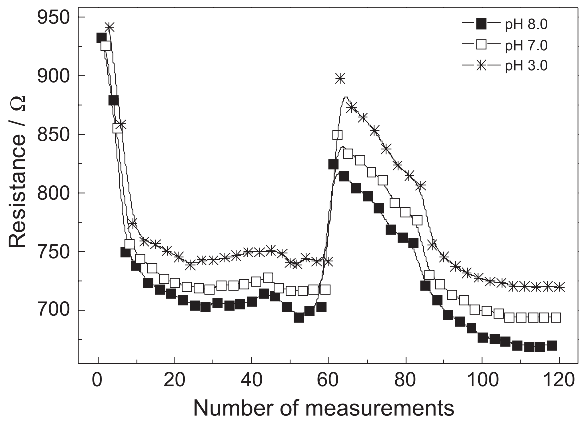

Figure 5. Reproducibility and reversibility of ppy-BPB in phosphate buffer solutions at pH 3.0, 7.0 and 8.0.

Influence of interferants on the ohmic properties of the ppy-BPB film

The effect of ions on the ohmic properties of the ppy-BPB film was studied by adding 0.01 and 0.15 mol L^{-1} of pyrophosphate ($P_2O_7^{4-}$), chloride (Cl^-), potassium (K^+), nitrate (NO_3^-) and sulfite (HSO_3^-) ions to the buffer solution. Aiming the normalization of the obtained values, equation 2 was used. The coefficient of interference *(C.I.)* was calculated from the resistance of the ppy-BPB film immersed in buffer solution with interferant (R_i) compared to the resistance from ppy-BPB in PBS without interferant (R_x). Therefore, *C.I.* values close to zero mean an irrelevant interference. The results are shown in Table 1.

$$C.I.(\%) = \frac{|(R_i - R_x)|}{R_x} \qquad (2)$$

According to Table 1, the ohmic response of the ppy-BPB film was affected only by bisulfite and nitrate (0.01 and 0.15 mol L^{-1}) solutions, respectively. In fact, this interference was very small when compared to literature values.[39] These changes may be related to reducing and oxidizing properties of these ions, respectively, since they may modify the oxidation level of ppy, and thus, the resistance of the film.

Indeed, chloride and potassium ions did not affect the film response significantly. Considering that these ions are usually present in milk, serum and salt water, ppy-BPB may be applied to analyze such kinds of samples. In addition, given the small effect of the interferant concentration on *C.I.,* one might suggest that the ionic strength of the solution does not interfere significantly on the ohmic response of ppy-BPB films. These results are in agreement with *C.I.* values of 0.16 and 0.18 found in interference studies of ppy in the presence of heavy metals.[39] The interference of 0.15 mol L^{-1} NaCl, LiCl, and $NaClO_4$ was investigated for sensors based on poly(o-methoxyaniline), and *C.I.* values of 0.01, 0.13 and 0.31 were obtained, respectively.

Effect of the temperature

Figure 6 shows the relative resistance of the ppy-BPB film in solution at pH 1.5, 3.0, 7.0, 7.5 and 8.0 as a function of temperature (15, 25, and 35 °C). The resistance decreases as the temperature increases and the curves present similar slopes. As ppy is a semiconductor, raising the medium temperature also increases the number of thermo excited states, contributing to the interchain mobility of charge carries (hopping) and increased conductivity.[48-49]

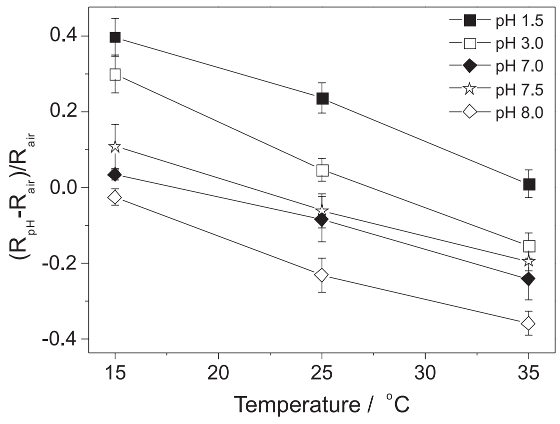

Figure 6. Effect of the temperature on the resistance of ppy-BPB film in phosphate buffer solution at pH 1.5, 3.0, 7.0, 7.5 and 8.0.

Table 1. Coefficient of interference of ppy-BPB for 0.01 and 0.15 mol L^{-1} interferants in the phosphate buffer solution

	0.01 mol L^{-1}					0.15 mol L^{-1}				
pH	$P_2O_7^{4-}$	Cl^-	K^+	NO_3^-	HSO_3^-	$P_2O_7^{4-}$	Cl^-	K^+	NO_3^-	HSO_3^-
1.5	0.00	0.04	0.06	0.05	0.07	0.00	0.03	0.10	0.15	0.17
3.0	0.01	0.00	0.01	0.06	0.08	0.00	0.00	0.01	0.08	0.15
7.0	0.00	0.04	0.00	0.03	0.08	0.00	0.02	0.01	0.12	0.10
7.5	0.00	0.00	0.07	0.01	0.13	0.01	0.08	0.09	0.08	0.18
8.0	0.00	0.02	0.05	0.02	0.10	0.00	0.04	0.11	0.15	0.17

A distinct behavior was expected, since the alkaline medium affects the polymeric chain due to the deprotonation process. However, the polymeric chain is still partially doped, therefore, it has polaronic bands, allowing electrons to migrate from the bonding to the antibonding bands. The effect of the temperature on the pH sensitivity of ppy-BPB and ppy films are the same,[48,51,52] as the BPB equilibrium is not dependent on the temperature, in the range studied in this work.

Conclusions

This work demonstrates that the equilibrium among anionic species of a dopant embedded in the polypyrrole matrix can affect the electrical properties of the polymer. The unexpected increase in conductivity of the ppy-BPB with the pH of the medium, confirmed the contribution of the BPB anionic species to the conductivity of the film. In addition, the nonlinear ohmic behavior of the ppy-BPB film in different pH media was explained in terms of deprotonation process and agrees with the literature.

Acknowledgments

The authors acknowldge the financial support by the Brazilian agencies, CAPES and CNPq. We also thank Prof. F. Josepetti Fonseca, Escola Politécnica da Universidade de São Paulo, for the fabrication of the digitized gold substrates and Prof. Liliana Micaroni, Universidade Federal do Paraná, for the thickness measurements.

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Received: February 25, 2009
Web Release Date: November 26, 2009