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Optical pH sensitive material based on bromophenol blue-doped polypyrrole

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ABSTRACT

Optical pH sensitive materials have been developed using electrochemically synthesized polypyrrole (Ppy) film doped with bromophenol blue (BPB). The results have shown that the system Ppy–BPB color derives from a synergistic effect, where the sensitive pH range of the resulting film is larger than the individual species. The material is suitable for the optical determination of pH between 1.5 and 11.0 and is stable (more than 300 h), reproducible, and reversible. The results in saline solution show potential application of the Ppy–BPB film on physiological samples. However, Ppy–BPB films undergo irreversible spectral changes assigned to irreversible reduction when exposed to pH 11.0.

1. Introduction

Polypyrrole (Ppy), one of the best-known conducting polymers, has been intensively studied as an electroactive material for several years [1–3]. It has been applied in various important devices such as batteries [4], gas separating membranes [5], sensors [6–8], microelectronic devices [9], coatings [10], composite materials [11]. All these devices have interesting optical, mechanical, and electrical properties that allow their use when inorganic materials are not suitable. Polypyrrole has especially promising commercial applications because of its good environmental stability, facile synthesis, and high conductivity, comparatively to those of many other conducting polymers. The electrochemical polymerization of pyrrole in aqueous solution allows the use of a large number of anions as dopants [12,13], including indicators [14,15].

pH has a significant effect on chemical reactions; therefore, its measurement and control is very important in chemistry, biochemistry, clinical chemistry, and environmental science. It is routinely measured using glass electrodes. Nevertheless, in some circumstances, the determination of pH using optical sensors (optodes) is desirable [16,17]. Examples of applications include physiological pH measurement [18], sea-water pH monitoring [19,20], industrial process control [21], and others [22,23]. In these cases, pH optodes offer advantages due to some of their favorable characteristics, such as intrinsic safety, small size, immunity to electrical interference, no need of a reference sensor, remote-sensing capacity, and other features [24,25].

Despite the advantageous characteristics of optodes, an inherent limitation is their narrow pH range due to the indirect measurement of pH, usually through the concentration of an indicator dye in either acidic or basic form. Therefore, the pH measurement depends on the pK_a of the dye and the pH range is restricted to about 3–4 pH units. Thus, efforts have been made to extend optode pH ranges. The use of organic dyes such as phenol red [19,26], bromothymol blue and their derivatives [27], bromophenol blue [19], and cresol red [28] as absorbent pH indicators has been reported.

Numerous dye immobilization materials have been evaluated, including sintered and controlled-porosity glass [29], hydrophobic polymeric materials [22], and hydrophilic materials such as acetylcellulose [30], polyacrilamide [31] and cross-linked poly(vinyl alcohol) [32]. Dye covalent binding to suitable matrices seems to be the most efficient immobilization method, since membranes are almost free of dye leaching [17,26,29]. Although good results have been obtained with most pH optodes, they require a long and tedious preparation method involving matrix treatment and dye immobilization.

Conductive polymers that change their color as a function of pH offer the possibility of developing optodes with extended pH ranges [33] as they are basically polyelectrolytes with multiple pK_a values. Recently, conducting polymers, such as polypyrrole, have been used to prepare optical sensors [34].

In order to obtain a pH-sensitive material, we have doped polypyrrole (Ppy) with some indicators. The results of bromophenol blue (BPB), which interacts with polypyrrole synergically, are reported in this paper. Other indicators used in our research, such as thymol blue, bromothymol blue, and indigo carmine resulted in systems in which the optical characteristics are just a sum of their individual properties without any synergistic effect. Ppy–BPB

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optode presented an optical response as a function of its visible absorption characteristics.

2. Experimental

2.1. Reagents

Pyrrole was double distilled and stored under N_2, sodium phosphate monobasic, sodium phosphate dibasic and sodium pyrophosphate decahydrate (Aldrich), bromophenol blue (Reagen), sodium chloride (Synth), sodium nitrate (Vetec), sodium bisulfite and potassium phosphate monobasic (Nuclear), sodium hydroxide (Merck), and phosphoric acid (Merck) were used as received. All solutions were prepared with Milli-Q water. Conducting fluorine-doped tin oxide glass (FTO-glass, 20 Ω cm^{-2}) was purchased from Flexitec Ltd. (Brazil).

2.2. Apparatus and synthesis procedure

The electrochemical polymerization of the indicator-doped polypyrrole film was carried out using a galvanostat/potentiostat Autolab model Pgstat30. The electrochemical cell was equipped with a conducting FTO-glass used as working electrode, a platinum wire as counter-electrode, and a saturated calomel electrode (SCE) as a reference. Ppy–BPB films of 1 cm^2, were potentiodynamically synthesized at a scan rate of 0.02 V s^{-1} in a 0.05 mol L^{-1} aqueous solution of pyrrole containing 0.4 mmol L^{-1} of indicator. The synthesis potential was scanned from −0.3 to +1.3 V and back,

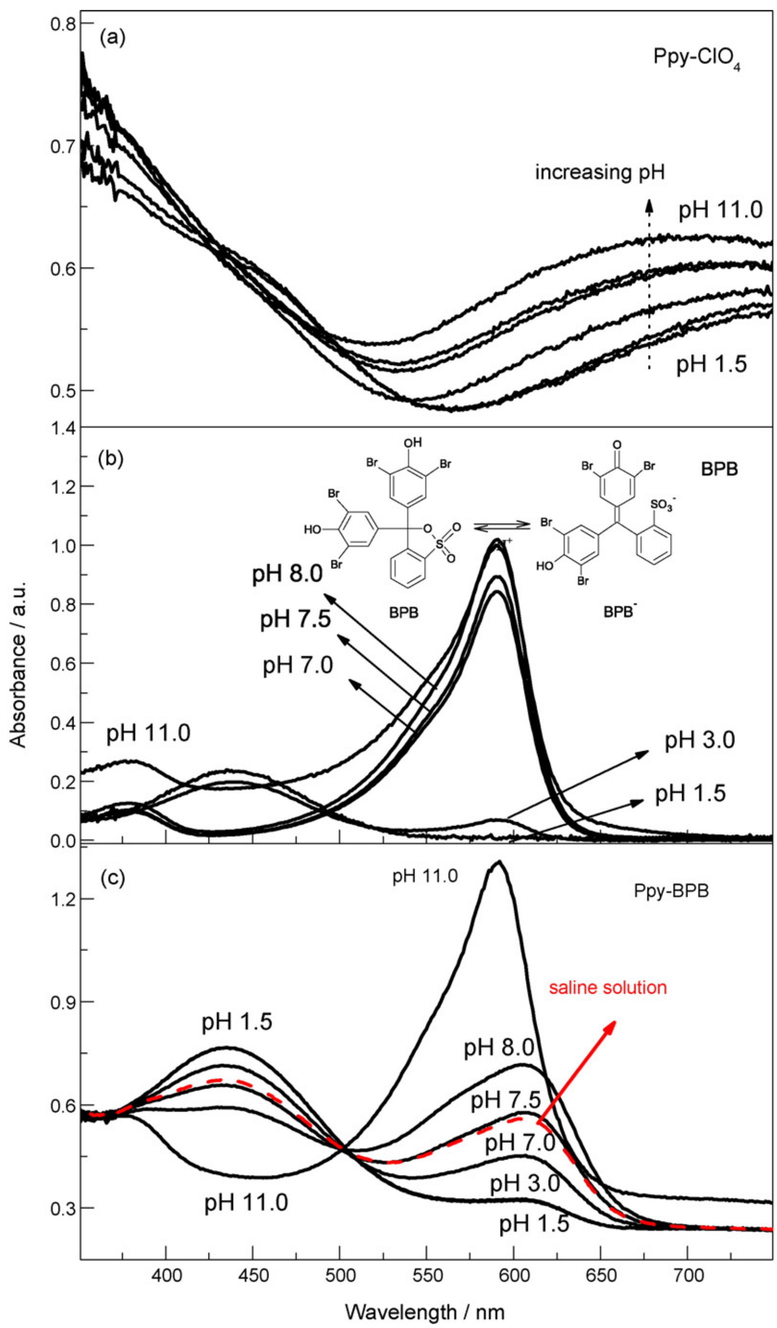

Fig. 1. Absorption spectra of (a) PPy–ClO_4 film, (b) BPB solution, and (c) Ppy–BPB film in PBS at pH 1.5, 3.0, 7.0, 7.5, 8.0 and 11.0 carried out at room temperature. The red dashed line is related to Ppy–BPB in saline solution. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)