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Novel photoconductive polyfluorophenol synthesized by an enzyme

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ABSTRACT

Poly(4-fluoro-2-methoxyphenol) has been synthesized using horseradish peroxidase biocatalyst in a buffer/1-butyl-3-methylimidazoliumtetrafluoroborate solvent mixture. Experimental observations indicate that the enzymatically synthesized polyfluorophenol is a suitable photoconductive material. The photocurrency obtained under 532 nm light intensity is about 0.82 W/cm^2. The work is relevant to the use of enzymes to produce polymeric materials with potential uses as components in photoelectronic devices owing to polymer characteristics in its mild and eco-friendly production process.

1. Introduction

Polyphenolic resins found applications in coatings, laminates, particle boards and bonding agents due to their high thermal stability and good mechanical strength [1,2]. Other envisaged uses of these materials include organic-based photoelectronics, components for non linear optics and sensors owing to the semi-conductivity and adequate optoelectronic properties of some polyphenol derivatives [3]. However, high-valent metal ions, such as copper complexes, and the presence of pyridine or formaldehyde solvents is involved in their commercial production [4,5]. Alternatively, plant oxidoreductases are able to biocatalyze in vitro the double-one-electron oxidation of phenolic monomers in buffer/organic solvent mixtures, thus generating free radicals that undergo radical transfer and coupling in mild conditions and with fast polymerization rates [3,6]. Then, oxidative polymerization of many phenol derivatives, containing alkyl or alkoxy groups, have been successfully achieved using horseradish peroxidase (HRP), soybean peroxidase (SBP) or laccases [7]. Among them, HRP has been extensively reported hitherto due to its availability at relatively low cost, catalytic efficiency and wide substrate specificity [8]. Nonetheless, oxidoreductase-mediated polyphenol and many polyphenol derivatives present poor conductivity. Therefore, the production of these materials by enzymatic means for photoelectronic devices is still challenging and reports in the open literature are scarce. Recently, Turac and Sahmetlioglu reported the use of HRP to attain poly(4-[(4-phenylazo-phenyimino)-methyl]-phenol) with molecular weight *ca.* 8000 Da. Their material showed an optical band gap of 3.36 eV, however, the polymer had low solubility in chloroform, THF and ethanol and was only soluble in 1,4-dioxane, DMF and DMSO [9]. In an earlier work, Liu et al. produced photoactive poly(4-phenylazophenol) films by HRP, which exhibited photoinduced absorption dichroism and large photoinduced birefringence with unusual relaxation behavior [10]. However, both materials are azopolymers, which are thermally unstable decomposing to free-radicals, which might restrict their applicability.

The present communication reports the successful HRP-mediated synthesis of a thermally stable and photoconductive polyfluorophenol, as shown in Fig. 1.

2. Materials and methods

2.1. Materials

Peroxidase Type II, from Horseradish (HRP), 4-fluoro-2-methoxyphenol, hydrogen peroxide (50 wt% in water) and 1-butyl-3-methylimidazolium tetrafluoroborate were supplied by Aldrich (US). Chloroform (HPLC grade) was supplied by JT Baker (Mexico). Dimethylsulfoxide and ethanol (Reagent grade) were supplied by Quimica Barsa SA de CV (Mexico). Deuterated chloroform containing 0.03% (v/v) of tetramethylsilane or trichlorofluoromethane was supplied by Aldrich (US). Technical grade methanol was purchased to Quimica Barsa SA de CV (Mexico).

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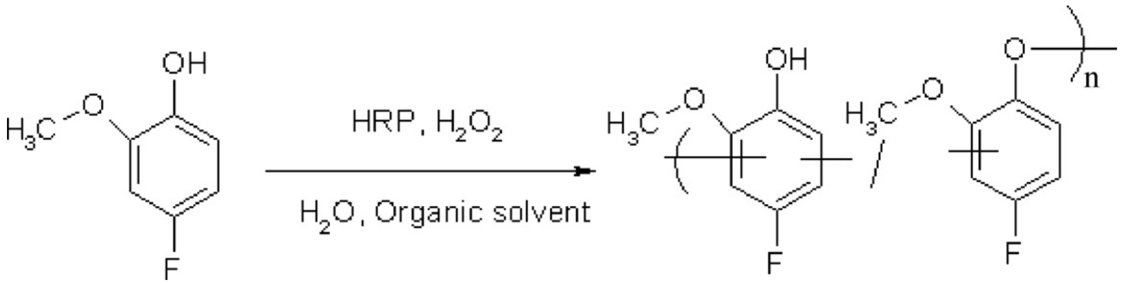

Fig. 1. Reaction scheme for de HRP-catalyzed polymerization of 4-fluoro-2-methoxyphenol.

2.2. Reaction procedure and characterizations

In a typical experimental procedure, 4-fluoro-2-methoxyphenol (0.55 g, 3.9 mmol) and HRP (1.5 mg) were dissolved in 25 mL of [BMIM][BF_4]/phosphate buffer (pH 5) (1:1). Reactions were carried out at 25 °C under stirring and H_2O_2 (5% aqueous; 3.2 mL) was added dropwise for 2 h. Then, reaction mixture was left stirring for 15–30 min and the contents were precipitated in 250 mL of cold methanol (5 °C), collected by filtration and dried under vacuum to give poly(4-fluoro-2-methoxyphenol) (PFMP) (0.18 g, 33%). Found C, 60.4%; H, 3.78%; O, 22.78%; F, 13.82%; $(C_7H_5O_2F)_n$ requires C, 60.21%; H, 3.57%; O, 22.86%; F, 13.57%. ^{1}H NMR (δ/ppm) 6.9–6.8, 6.7–6.6, 6.4–6.2 (bs,=CH, 3H); 3.9–3.7 (bs, O–CH_3). ^{13}C NMR (δ/ppm) 154.08 (C–F, d, $J^1{}_{C-F}$ = 368.1 Hz); 141.08–139.01 (bs,=C–O–R, 2C); 121.77, 107.64, 102.49 (bs,=C, 3C); 55.9 (s, O–CH_3). ^{19}F NMR (δ/ppm) −115.6 (d, $J^3{}_{F-H}$ = 2.25 Hz). Size-exclusion chromatography (SEC) was carried out using a Hewlett Packard HPLC pump (model 1050), a Hewlett Packard (model 1100) UV detector and a two Plgel 10 μm MixedDB LS 300 mm × 7.5 mm mounted in a Agilent (model 1200) column thermostat (25 °C). Columns were eluted with chloroform (HPLC grade) at 0.8 mL/min. Sample solutions were filtered through a Whatman WTP 0.45 μm filter before injection onto the columns, which were calibrated using Polymer Laboratories polystyrene standards. NMR spectra were obtained in Varian Unity Inova 100 MHz and 400 MHz spectroscopes using deuterated chloroform and referenced to TMS or $CFCl_3$. Infrared spectra were recorded between KBr disks in a Perkin Elmer 1605 FTIR spectrometer. Thermal analysis was carried out in a TA-Instruments (model Hi-Res 2950) between 25–350 °C (rate 10 °C/min) under nitrogen atmosphere. Titration procedure was conducted with PFMP samples (0.10 g) dissolved in dimethylsulfoxide containing 2.5% acetic anhydride (5.0 mL). Solution was kept at 95–100 °C for 1 h with gentle stirring. After cooling to room temperature, water (0.50 mL) was added to the reaction mixture, and the mixture was then again heated at 95–100 °C for 10 min. The solution was titrated with 0.2 M potassium hydroxide in ethanol in the presence of phenolphthalein as an indicator [11]. Optical absorption measurements were performed in Varian – Cary 5000 spectrophotometer under normal incidence reflectivity. Photoconductivity measurements were carried out on a home-made device with metallic contacts, charge transport in the samples was excited under a CW 532 nm all-solid state laser. Optical and electrical measurements were performed in pellets of 6 mm × 5 mm × 1.5 mm.

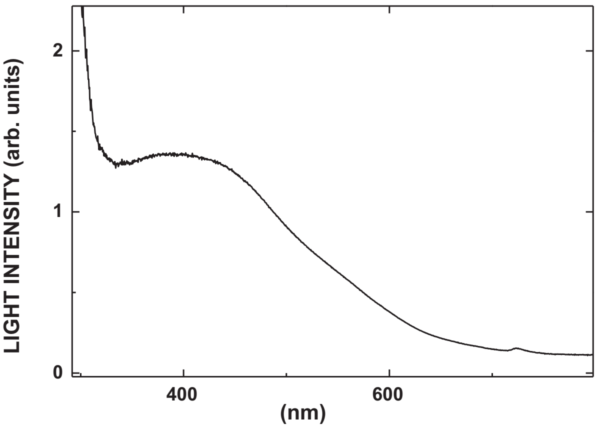

Fig. 2. Optical absorptions in the visible for PFMP.

3. Results and discussion

The optical absorptions in the visible for the enzymatically synthesized PFMPs are shown in Fig. 2, with the charge transfer absorption of phenyl unit [12] peaking about 400 nm.

Fig. 3 shows the comparative photocurrent intensity response of the fluorinated polymer. Dark conductivity i.e. when light is not applied, obtained for PFMP is five orders of magnitude greater that the current intensity for the blank sample, while increasing photocurrent with increase intensity of applied light is observed for the PFMP. This photocurrent was obtained under 532 nm light intensity of about 0.82 W/cm^2.

Poly(4-fluoro-2-methoxyphenol) (PFMP) (Fig. 1) molecular structure was corroborated by NMR spectroscopy (see supplementary data for ^{1}H, ^{13}C, ^{19}F and 2D NMR spectra and signal assignments). Three main broad signals of similar intensities were observed in the aromatic region of 1H NMR spectra, therefore oxyphenylene units were predominant in PFMP, resulting from random coupling of C3, C5 and C6 phenyl carbons to the oxygen atom from the deprotonated hydroxyl moiety. Infrared spectra of all PFMP samples were also consistent with the structure depicted

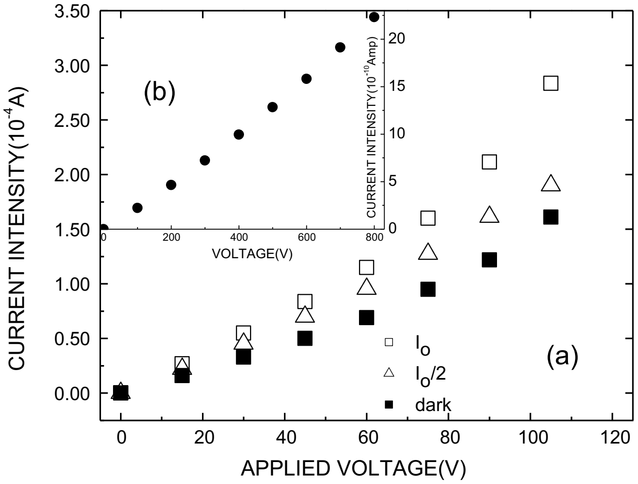

Fig. 3. (a) Photocurrent intensity of PFMP sample and inset above in the left (b) corresponds to blank sample. I_0 value was 0.82 W/cm^2.

in Fig. 1 (see supplementary data), and confirming the NMR data, with two bands at 1029 cm^{-1} and 1197.9 cm^{-1} assigned to symmetric and asymmetric stretching of an aromatic C-O-R group, respectively. A weak band in the 3650–3200 cm^{-1} region was observed which might be assigned to terminal repeat units with free hydroxyl moieties or the presence of phenylenyl linkages in low extension. In addition, the titration displayed a variation of phenylene/oxyphenylene unit ratio from 6/94 to 10/80 in the synthesized PFMP samples. The fluoropolymer presented good solubility in common hydrophobic organic solvents, such as chloroform and THF. TGA analysis displayed good thermal stability, with observed loss in weight of approximately 2–5% above 350 °C. The organic solvent employed in this work was the ionic liquid 1-butyl-3-methylimidazoliumtetrafluoroborate ($[\text{BMIM}][\text{BF}_4]$) [13,14]. PFMPs were achieved with narrow polydispersities (PDI < 1.3) and M_n ranged between 2.0 and 2.2×10^3 g/mol. Best result was achieved by 2 h dropwise addition of H_2O_2 to the reaction mixture with a buffer pH 5 [15]. Variation of buffer capacity to pH 4 or 7 resulted in dramatic decrease in polymer yields and its optimum content for this reaction was 50 v%. Control experiment conducted without enzyme or that without buffer gave no product, thus confirming that the presence of water and the enzyme are required to produce PFMP.

4. Conclusions

The present work is relevant to the use of enzyme biocatalysts in environmentally friendly process towards robust materials with potential uses as components in photoelectronics. The photophysical analyses reveal adequate photoconductive behavior for applications such as component of organic light emitting diodes or other devices. Further research is undergoing in order to establish the suitable conditions for the production of photoconductive prototypes using this novel enzyme-mediated polyfluorophenol.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcatb.2011.04.019.

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