

Synthesis and Characterization of Water-Soluble Conducting Polyaniline by Enzyme Catalysis

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ABSTRACT: Enzymatic synthesis of a water-soluble, conducting polyaniline (PANI) was studied, using horseradish peroxidase as the biocatalyst and H_2O_2 as the initiator, in the presence of a poly(vinylsulfonic acid, sodium salt) (PVS) polyanion template. The effects of the buffer, concentration of H_2O_2 , and the molar ratio of aniline to PVS on the polymerization were particularly investigated. The products were characterized by UV-vis/near-IR and FTIR spectroscopy, thermogravimetric analysis, and four-point probe conductivity measurement. The results showed that PVS could

be chosen as a new template in the synthesis of PANI. The proper conditions of polymerization were obtained as follows: pH of the buffer was pH 4.0–5.0, the concentration of H_2O_2 was around 20 mM, and the molar ratio of PVS to aniline was 1–1.5. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 814–817, 2005

Key words: enzymes; catalysis; conducting polymers; water-soluble polymers; poly(vinylsulfonic acid) (PVS)

INTRODUCTION

Enzymatic polymerization of aniline can be accomplished by horseradish peroxidase (HRP) in the presence of hydrogen peroxide.¹ A major drawback of the enzymatic oxidation of anilines and phenols from aqueous solutions, however, has been that as soon as the polymer begins to form, it precipitates out, and only very low molecular weight polymers (oligomers) are produced.² Recently a template-guided enzymatic approach was developed to address and resolve these limitations. It involves the polymerization of aniline using the enzyme HRP in the presence of a polyanion template. This approach inherently minimizes the parasitic branching and promotes a more *para*-directed, head-to-tail polymerization of aniline and produces a water-soluble, conducting high molecular weight polyaniline (PANI). So far, polyelectrolytes such as sulfonated polystyrene (SPS),³ poly(vinylphosphonic acid) (PVP),⁴ lignosulfonates (LGS),⁵ and DNA (or RNA)⁶ have been demonstrated as “good templates” for enzymatic synthesis of conducting polyaniline.

We report here a detailed study on the enzymatic polymerization of aniline in the presence of a new anionic polyelectrolyte, poly(vinylsulfonic acid, sodium salt) (PVS). The reaction was carried out in a

mild, aqueous buffered solution. The characterization of the product is also presented.

EXPERIMENTAL

Materials

Horseradish peroxidase (HRP; BE 1841/100 mg, with RZ 3) was purchased from Sino-American Biotechnology Co. (Beijing, China). Aniline (99.5%) was obtained from Shanghai Wulian Chemical Engineering Co. (China). Poly(vinylsulfonic acid, sodium salt) (PVS, 25 wt %) was purchased from Aldrich Chemicals (Milwaukee, WI) and used as received. Hydrogen peroxide (30 wt %) was purchased from Zhejiang Lin'an Lanling Chemical Engineering Co. (China). All other chemicals were of reagent grade or better.

Polymerization

The enzymatic polymerization of aniline was carried out at room temperature in a 30 mL, 0.1M sodium phosphate buffer solution of pH 3–7, which contained a 1 : 1–1 : 2M ratio of aniline (6 mM) to PVS (6–12 mM, based on the monomer repeat unit). PVS was added first to the buffered solution, followed by addition of the aniline with constant stirring. To the solution, 2 mg HRP was then added. The reaction was initiated by the addition of a stoichiometric amount of H_2O_2 under vigorous stirring. To avoid the inhibition of HRP arising from excess H_2O_2 , diluted H_2O_2 (20 mM) was added dropwise, incrementally, over 2 h. After the

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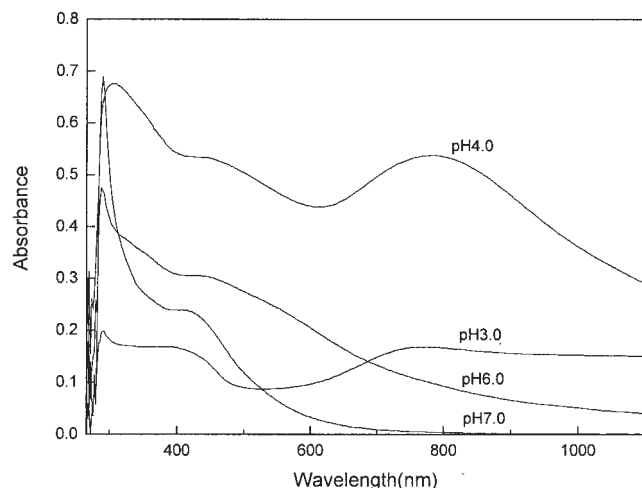


Figure 1 UV-vis spectrum of PANI/PVS complex with varying pH values of the reactant solution.

addition of H_2O_2 , the reaction was stirred for about 3 h, and then the final solution was precipitated by 1 : 1 acetone/deionized water solution for the removal of unreacted aniline monomer, oligomers, and phosphate salts. The precipitate was then dried in a vacuum oven at 60°C for 48 h and used for further characterization.

Characterization

The UV-vis/near-IR spectra were recorded on a Ultrospec[®] 3300 pro UV-vis/near-IR spectrophotometer (Amersham Biosciences, Piscataway, NJ). FTIR measurements were carried out using a Nicolet 560 FTIR spectrophotometer (Nicolet Instrument Technologies, Madison, WI). Conductivity measurements were obtained on PVS-PANI pressed pellet samples using an SZ Digital four-point probe. The conductivity values reported are the average of several readings at different regions and sides of the disk. Thermogravimetric analysis (TGA) was performed using a Pyris 1 thermogravimetric analyzer (Perkin Elmer Cetus Instruments, Norwalk, CT). The TGA of all samples were carried out in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Effect of pH

The pH at which the enzymatic polymerization is carried out is very important in determining what type of polyaniline is ultimately formed (electroactive or insulating). The absorption spectra of PANI, enzymatically synthesized with PVS at pH values ranging from 3.0 to 7.0, are given in Figure 1. All reactions were carried out under identical conditions (30 mL phosphate buffer with a 1 : 1.5M ratio of aniline to

PVS), so that only the pH of buffer was varied in each case. In the following discussion, the absorption band at approximately 800–1200 nm (attributed to polaron transition^{7–10}) is compared as a signature of the formation of conducting polyaniline. At pH 4.0, the polymer shows strong absorption bands at 800 nm. The intensity of the polaron bands at 800 nm decreases at pH 3.0 and almost disappears when the pH is >6.0 . It is known that in the enzymatic polymerization of aniline, only the initiation step of generating aniline radicals is enzyme dependent. The following radical-radical coupling and radical transfer steps are controlled exclusively by radical and solvent chemistry.¹ Therefore, one would expect that a low pH medium is also necessary for the synthesis of conducting polyaniline by enzymatic catalysis once the aniline radicals have been generated. Zemel and Quinn¹¹ showed that the pH of the reaction media for enzymatic polymerization of aniline must be sufficiently acidic to cause protonation of the aniline monomer and yet high enough to preserve as much of the bioactivity of the enzyme as possible; thus the pH of the buffer should be controlled around 4.0–4.5.

Effect of H_2O_2 concentration

To determine the effect of H_2O_2 concentration ($C_{\text{H}_2\text{O}_2}$) on the polymerization, three different $C_{\text{H}_2\text{O}_2}$ concentrations (200, 20, and 2 mM) were investigated. All the other conditions were the same as presented earlier in the experimental section. After 30 min of the addition of H_2O_2 , the UV-vis/near-IR spectra of these solutions were recorded, as shown in Figure 2. It is observed that, only when $C_{\text{H}_2\text{O}_2}$ is 20 mM (line b), the absorption band at around 800 nm is distinct. Although the concentration of H_2O_2 is too high (line a), the bioactivity of HRP is restrained because of the strong ox-

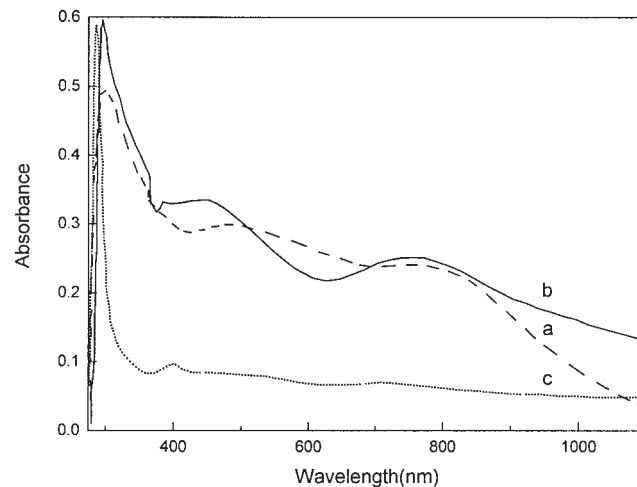


Figure 2 Effect of H_2O_2 concentration on polymerization: (a) $C_{\text{H}_2\text{O}_2} = 200$ mM; (b) $C_{\text{H}_2\text{O}_2} = 20$ mM; (c) $C_{\text{H}_2\text{O}_2} = 2$ mM.

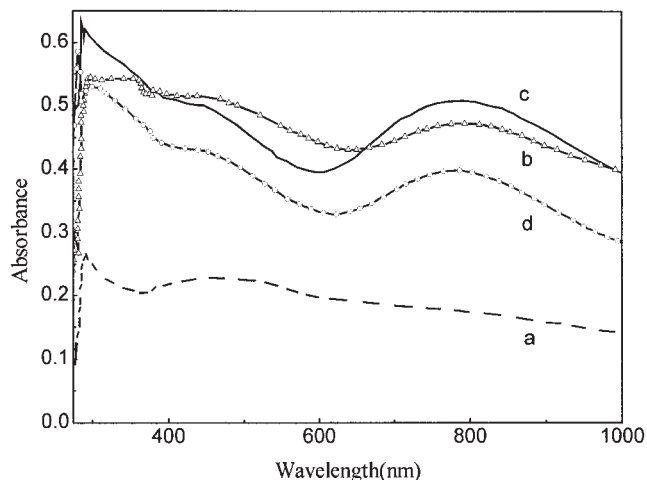


Figure 3 Effect of molar ratio (r) of aniline to PVS on polymerization: (a) $r = 1 : 0$; (b) $r = 1 : 1$; (c) $r = 1 : 1.5$; (d) $r = 1 : 2$.

dizability of H_2O_2 , and so the synthesized polymer is obviously decreased. Even though the concentration of H_2O_2 is too low (line c), there is no polymer produced because of insufficient oxidization; thus the concentration of initiator H_2O_2 should be 10–20 mM.

Effect of molar ratio of aniline to PVS

The molar ratio (r) of aniline to PVS in the solution also affects the type of polymer formed in the reaction. Figure 3 shows the absorption spectra of the PANI/PVS complex synthesized with 6 mM aniline and various PVS concentrations. It is observed that the ab-

sorption band of the solution without PVS (line a) is at about 550 nm, which is indicative of oligomers. The PVS containing solution (lines b–d), however, shows absorption at about 800 nm, which shows that the PVS serves to promote a more linear and *para*-directed polymerization, and ultimately a conducting polyaniline is formed. From Figure 3 (lines b–d), we can see that the optimum of r is around 1 : 1.5, with respect to which the absorption at 800 nm is the most obvious.

FTIR

Figure 4 shows FTIR spectra of the PANI/PVS complex. The bands at around 1590 and 1510 cm^{-1} are attributed to quinone and benzene ring deformation, and the band at 1310 cm^{-1} is assigned to C—N stretching of a secondary aromatic amine. The two bands appearing at 1030 and 1000 cm^{-1} are attributed to the asymmetric and symmetric stretching of SO_3^{2-} , indicating the presence of PVS in the sample. The presence of the PVS as dopant in the synthesized polyaniline is further confirmed by the strong C—H vibration band appearing at around 2920 cm^{-1} .

Thermal analysis

The TGA thermograms of aniline, PVS, and PANI/PVS complex are shown in Figure 5. The initial 6–10% weight loss in the PANI/PVS complex and PVS up to 100°C is attributed to the loss of water. For PVS, we notice a gradual weight loss in the range of 130–450°C, attributed to the condensation of sulfonic groups activated by water loss. Weight loss resulting

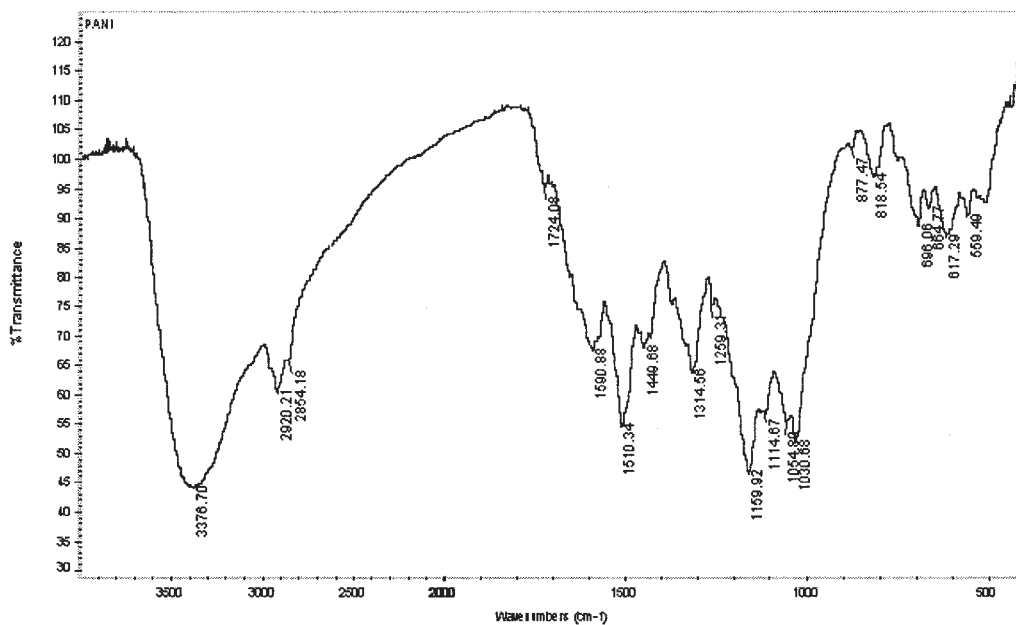


Figure 4 FTIR spectra of PANI/PVS complex.

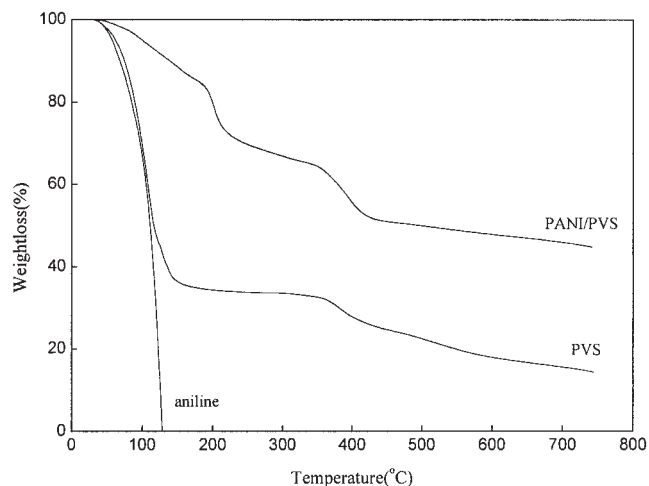


Figure 5 TGA curves of aniline, PVS, and PANI/PVS complex.

from degradation starts at around 375°C. Almost 80% of the sample by weight is lost at about 700°C. The PANI/PVS complex shows a similar degradation pattern that becomes much less pronounced at higher temperatures, and more than 55% of the weight is retained even at 700°C.

Conductivity of PANI/PVS complex

Conductivity of the PANI/PVS complex, dried in a vacuum oven at 60°C for 48 h, was determined to be 4.78×10^{-1} S/cm.

CONCLUSIONS

The enzymatic synthesis of a water-soluble conducting polyaniline using a new template, PVS, is presented. The polymerization could be accomplished at room temperature in an aqueous buffer at pH 4.0–5.0, the molar ratio of PVS to aniline was 1–1.5, and the concentration of H₂O₂ was around 20 mM. The selection of PVS as the polyelectrolyte for the polymerization of aniline has extended the scope of polyanion templates.

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