

# Hemoglobin-biocatalysts synthesis of a conducting molecular complex of polyaniline and sulfonated polystyrene

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## Abstract

A new biocatalyst route for the synthesis of a conducting polyaniline (PANI)/sulfonated polystyrene (SPS) complex is presented. Hemoglobin (Hb) is used to polymerize aniline in the presence of a polyanionic template SPS. The synthesis is simple, and the conditions are mild in that the polymerization may be carried out in lower pH (1.0–4.0) buffered aqueous solution, with a stoichiometric amount of hydrogen peroxide and a catalytic amount of Hb. UV–Vis absorption, FT-IR, elemental analysis, and conductivity measurements, cyclic voltammetry (CV), thermogravimetric analysis (TGA), fluorescence spectra and XRD studies all confirm that the electroactive form of PANI, similar to that which is traditionally chemically synthesized, is formed and complexed to the SPS. Cyclic voltammetry studies show three sets of redox peaks over the potential range of –0.2 to 1.0 V, and the formation of peak does not change at a series of scanning 20 times, which suggests that the PANI/SPS complex is more stable. The PANI complexes produced at different pH show the different conductivity. This biomimetic approach offers unsurpassed ease of synthesis, processability, stability, and environmental compatibility.

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## 1. Introduction

Polyaniline (PANI), one of the most extensively studied conducting polymers, has attracted considerable attention over recent years due to environmental compatibility as well as its electrical properties for many technological applications [1–5]. Several chemical [6,7] and electrochemical [8] methods have been reported for obtaining the polymer in both a conducting and processable form in strong acid medium. However, the main disadvantages of these traditional polymerization routes often involve more tedious chemistry or harsh reaction conditions. Recently, the use of enzymes as biological catalysts in the synthesis of PANI has also attracted great interest since enzymes can offer environmentally benign reaction conditions, a higher degree

of control over the kinetics of the reaction, and a higher yield of product. Akkara et al. investigated the enzyme horseradish peroxidase (HRP) used for the oxidative polymerization of phenols and anilines in the presence of hydrogen peroxide [9]. A major limitation of the enzymatic oxidation of anilines and phenols from aqueous solutions however has been that as soon as polymer begins to form, it precipitates out, and only very low molecular weight polymers are produced. To address this and improve processability, a variety of modified enzymatic polymerizations have been investigated including solvent mixtures, modified monomers in aqueous solutions, micelles, reverse micelles, and polymerizations at the air-water interface [10,11]. It was found, however, that, although these polymers are of higher molecular weight, they are typically a mixture of at least two structurally different types of PANIs. Therefore, although dramatic improvements have been made regarding the molecular weight, organization, and processing of these polymers, the bulk electrical and optical properties of enzymatically

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synthesized polymers are still not sufficient for commercial applications.

Recently a new enzymatic approach was developed to synthesize water-soluble conducting PANI in the presence of sulfonated polystyrene (SPS) under mild, aqueous pH 4.3 buffer conditions [12]. In this case, the polyelectrolyte (SPS) will emulsify the aniline monomer prior to the polymerization, and help to dope and dissolve the synthesized polymer. Most importantly, the polyelectrolyte molecules such as SPS will serve as template to promote a head-to-tail coupling during polymerization of aniline, which is necessary for the formation of conducting PANI [12].

Unfortunately, HRP shows low activity toward aniline and low stability at pH below 4.5, i.e. at the same pH interval where the polyelectrolyte complex between PANI ( $pK_a$  of aniline is 4.63) and negatively charged polymeric templates may be formed. For improvement of the enzymatic synthesis, Sakharov and co-workers reported the enzymes laccase and palm tree peroxidase used for synthesis of polyelectrolyte complex of PANI and SPS at the pH of 3.5 [13–15]. Although laccase and palm tree peroxidase are promising biocatalytic approaches to the synthesis of PANI, there exists a need to develop a cost-effective and more robust mimetic enzyme catalyst alternative for peroxidase in these reactions. Synthetic porphyrin complexes and their possible applications in catalysis has been the subject of intense research over the past few decades. Recently the hydroxy ferriprotoporphyrin compound hematin was reported as a cost-effective catalyst for the polymerization of ethyl phenol by Akkara et al. [16]. Some metalloporphyrins show similar catalytic function as peroxidase [17]. Hemin has been used as a substitute for peroxidase. However, because metal porphyrin lacks the three-dimensional structure, the activity was largely inhibited by competing substrates. Hematin was soluble in water only at very high pH and thus was not effective in the low pH aqueous conditions required for the template-assisted enzymatic polymerization of aniline. To address this issue and enhance the aqueous solubility, the chemical modification of the hemin was carried out resulting in a porphyrin conjugate bearing pendant polymer chains of poly(ethylene glycol)/ $\beta$ -cyclodextrin as a better substitute for native peroxidase. However, the catalytic activity was still much less than that of peroxidase [18–21].

Hemoglobin (Hb) is the major heme protein of red blood cells and is responsible for the transport of oxygen to the tissues. Hb has oxidant activities and it has been proved that Hb can effectively act as mimetic peroxidase [21,22]. Since Hb has a quaternary structure which consists of four polypeptide subunits (two  $\alpha$ ,  $\beta$  protomers) and each subunit contains a heme (iron-porphyrin) as the active center. Hb shows remarkable advantages in the synthesis of conducting PANI compared to the commonly used enzymes such as HRP, laccase and palm tree peroxidase due to its high activity and stability under wider range of pH acidic conditions and its low-cost. We expected it to be a promising and versatile alter-

native for the polymerization of various anilines and phenols in the presence of hydrogen peroxide.

In the present work, the Hb-catalyzed polymerization of aniline is investigated in the presence of the anionic polyelectrolyte, SPS. The details of the synthesis and characterization of the biomimetic synthesis of PANI/SPS complex are discussed.

## 2. Experimental

### 2.1. Materials

Hb (bovine) was purchased from Shanghai Institute of Biochemistry, Shanghai, China. The concentration of Hb stock solution was 10 mg/mL. Poly (sodium 4-styrenesulfonate) (MW 70,000) was obtained from Aldrich Chemical Co. Inc., Milwaukee, WI, and used as received. Aniline monomer (purity 99.5%) and hydrogen peroxide (above 30 wt.%) were purchased from Shanghai Chemical Agent, Shanghai, China. Commercial aniline was purified by distillation before use. All other chemicals and solvents were of analytical grade or better, and used as received.

### 2.2. Polymerization reaction

Hb catalyzed the polymerization of aniline in the presence of SPS and hydrogen peroxide under ambient conditions. The reactions were carried out in a 30 mL, 0.2 M  $\text{Na}_2\text{HPO}_4$ -citric acid buffered solution maintained at pH 1.0–4.0 which contained a 1:1 molar ratio of aniline (6 mM) to SPS (6 mM based on the monomer repeat unit). A 37-mg sample of SPS was added first to the buffered solution, followed by addition of aniline with constant stirring. To the solution, 0.34 mL of Hb stock solution (10 mg/mL) was then added. The reaction was initiated by the addition of a stoichiometric amount of  $\text{H}_2\text{O}_2$  up to 20 mM. To avoid the inhibition of Hb due to excess  $\text{H}_2\text{O}_2$ , diluted  $\text{H}_2\text{O}_2$  was added dropwise over 1.5 h. After the addition of  $\text{H}_2\text{O}_2$ , the reaction was left stirring for 12 h to complete the polymerization, and then the final solution was dialyzed (cutoff molecular of 2000) against correspondent pH 1.0–4.0 HCl aqueous solution overnight to remove any unreacted monomer, oligomers, and phosphate salts. The unreacted aniline concentration in the dialysis solution was determined by measuring the absorbance at 251 nm ( $\epsilon = 151$ ) [10] in 1.0 M HCl. The resulting solutions were dried in oven under vacuum at 50 °C for 24 h for further characterization.

### 2.3. Characterization instrumentation

All UV-Vis spectra were obtained using a TU-1800PC UV-Vis spectrophotometer (Purkinje General Instrument Co. Ltd., Beijing, China). The FT-IR measurements were carried out using a Thermo Nicolet 360 FT-IR spectrophotometer in the form of KBr pellets. Elemental Analysis were carried out using TND-5000B automatic voltage regulatory

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