

Biologically Derived Water Soluble Conducting Polyaniline

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Abstract

An enzymatic, polyelectrolyte (matrix) assisted polymerization of aniline that directly leads to the formation of water soluble, electrically conducting polyaniline is reported. This new biological route is advantageous in that it offers a mild (pH 4-5), benign, one pot synthesis where the desired product requires minimal purification prior to processing. UV-vis-near-IR spectroscopy, FTIR, GPC and conductivity measurements all confirm that the electroactive and conducting form of polyaniline, similar to that which is traditionally chemically synthesized, is formed.

Keywords: Polyaniline and derivatives, Coupling reactions, UV-Vis-NIR absorption, Solution processing

1. Introduction

Polyaniline (PANI) has received considerable attention over recent years as a promising material for a host of technological applications [1]. Polyaniline is typically synthesized by oxidizing aniline monomer either chemically [2] or electrochemically [3]. Commercial use of polyaniline has remained limited however because of harsh or cost prohibitive chemical synthetic procedures, electrical instability, poor processability and environmental incompatibility. A variety of new synthetic routes have been investigated to address these limitations such as modification of the polymer with various ring or N-substitutes [4], post treatment of the polymer with fuming sulfuric acid [5], polyelectrolyte assisted polymerization [6], self-doped methods [7] and polydispersions [8]. To date however, although much progress has been made towards commercialization of PANI, there still exists a need for a more practical synthetic alternative.

Enzymatic polymerization of aniline is promising as a more facile, efficient and environmentally benign synthetic approach. Peroxidases, such as horseradish peroxidase (HRP), in the presence of hydrogen peroxide are known to efficiently catalyze the polymerization of phenol and aromatic amines to produce high molecular weight polymers [9-10]. These reactions however are both ortho and para directed and result in highly branched polymers which have limited solubility and poor electrical conductivity.

In this study a new enzymatic approach for the polymerization of aniline that minimizes the parasitic branching and results in a water soluble, conducting form of polyaniline is reported [11]. This approach involves the polymerization of aniline using the enzyme, HRP, in the presence of a polyelectrolyte. Here the polyelectrolyte serves several important functions. The first is as a type of matrix within which the aniline monomers preferentially organize and polymerize in a primarily para-directed

mechanism to form a more linear, extended chain conformation. Figure 1 shows a schematic of the comparison of the types of polyaniline structures obtained enzymatically in the absence of and in the presence of the polyelectrolyte, poly(sodium 4-styrenesulfonate) (SPS).

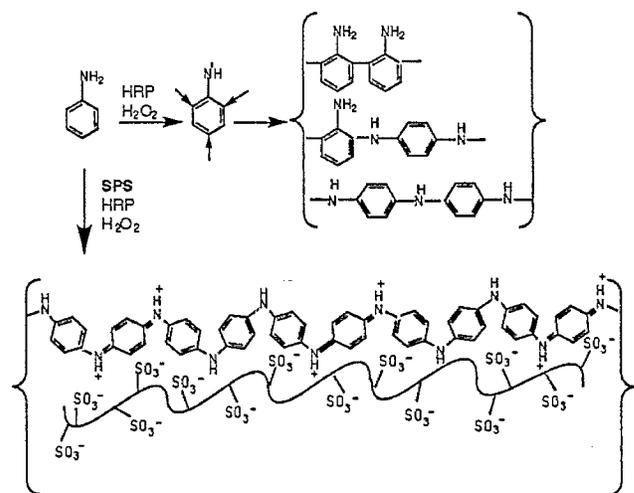


Figure 1. Representation of the branched structures for the traditional ortho-para directed enzymatic polymerization of aniline versus enzymatic polymerization of aniline (at pH 4.3) in the presence of SPS.

Also, the polyelectrolyte matrix acts as a large molecular counterion which is integrated and essentially locked to the polyaniline chains to provide electrical conductivity and stability. Lastly, the matrix serves to provide water solubility of the final complex and allows for tunability of the mechanical integrity of the complex through judicious choice of the polyelectrolyte. This paper will discuss this new biological approach for the synthesis of water soluble, conducting polyaniline.

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2. Experimental

Materials: Aniline and the polyelectrolyte, poly(sodium 4-styrenesulfonate) (MW 70 kD), used in this study were purchased from Aldrich Chemicals Co. Inc., Milwaukee, WI and used as received. The enzyme, horseradish peroxidase (HRP) (EC 1.11.1.7, 200 unit/mg) was purchased from Sigma Chemicals Co., St. Louis, MO, with RZ>2.2. A stock solution of the HRP consisting of 10 mg/ml in pH 6.0, 0.1M phosphate buffer was prepared and used as needed. The activity of the HRP was determined according to the Sigma method using pyrogallol as a substrate by monitoring the increase of absorbance at 420 nm in the first 20 seconds. All other chemicals and solvents used were also commercially available, of analytical grade or better and used as received.

Polymerization: The polymerization reactions were carried out in 0.1M sodium phosphate buffered aqueous solutions with the pH ranging from 4.0 to 10.0 (pH 4.3 was found to be the optimum pH to obtain the emeraldine salt form). Typically, aniline was dissolved in concentrations ranging from 6mM to 100mM with an equimolar amount of polyelectrolyte (based on the molecular repeat unit). A catalytic amount of HRP was then added, followed by incremental addition of a stoichiometric amount of hydrogen peroxide under continuous stirring to initiate the reaction. The reaction was then left stirring for at least one hour and the final solution was dialyzed (cutoff molecular weight of 2000) against deionized water overnight to remove any unreacted monomer, oligomers and phosphate salts. Figure 2 shows a schematic of this polymerization reaction.

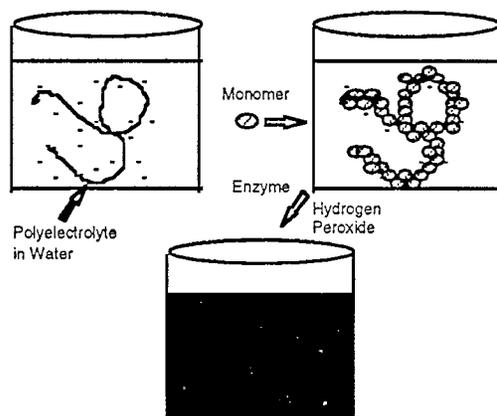


Figure 2. Schematic of the enzymatic, polyelectrolyte assisted polymerization showing monomer alignment along the polyelectrolyte matrix and polymerization upon addition of enzyme and hydrogen peroxide.

Precipitated PANI/SPS for FTIR studies was prepared by polymerizing a solution which contained an excess amount of aniline (4 times the molar ratio of SPS). Hydrogen peroxide was slowly added until dark green precipitates formed and fell out of solution, leaving behind a colorless supernatant. The precipitate was collected, washed with distilled water and then vacuum dried for 24 hours for further characterization studies.

Characterization: Absorption studies were recorded using a Perkin-Elmer Lambda 9 UV-vis-near-IR spectrophotometer. FTIR measurements were carried out on a Perkin Elmer 1760X FTIR spectrometer. GPC studies were done on a Waters LC Module I (Milford, MA) with two linear ultrahydrogel columns connected in series. Conductivity was measured using the four-point probe method with a Keithley 619 electrometer/multimeter.

3. Results and Discussion

A series of control experiments were first investigated to determine the role of the SPS polyelectrolyte during enzymatic polymerization. Figure 3 shows the absorption spectra of the enzymatic polymerization of aniline in an 85% dioxane/15% water mixture with no SPS; an aqueous pH 4.3 buffered solution with no SPS and an aqueous pH 4.3 buffered solution with SPS. The dioxane mixture was chosen since this is a commonly used solvent system for enzymatic polymerization to obtain higher molecular weight polymers. Upon polymerization, the two solutions which did not contain SPS turned an immediate purple color which darkened with time and eventually precipitated. The SPS containing solution however turned a deep green color and no precipitation was observed. The absorption of the solutions without SPS, prior to precipitation, show absorption at approximately 460 nm which is indicative of multiple branched polymeric structures [12]. The SPS containing solution however shows a spectrum which is consistent with the emeraldine salt form of polyaniline [13]. This is evidence that the SPS serves to promote a more linear and para-directed polymerization, provides the necessary counterions for formation of the emeraldine salt form of PANI and complexes to the PANI to maintain water solubility.

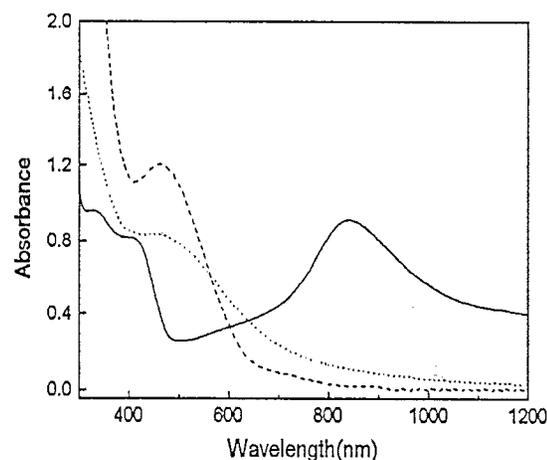


Figure 3. UV-vis absorption of the PANI formed in (...) pH 4.3 phosphate buffer, (---) dioxane/water mixture, (—) pH 4.3 phosphate buffer with SPS.

The pH of the reactant solution is also important in controlling the type of polyaniline complex that is formed. Figure 4 shows a comparison of the visible absorption of aniline enzymatically polymerized in the presence of SPS (1:1 molar ratio) with the pH ranging from 4.0 to 8.0. As shown, at low pH (<5.50), the polymer has strong absorption bands at 800-1060 nm and 410-420 nm which are due to polaron transitions [14]. As the pH of the reactant solution increases, the intensity of these bands

decreases and a new peak emerges at 440-460 nm which is again due to the formation of branched polymer structures.

This behavior may be explained by weaker electrostatic adsorption and/or poorer alignment of the aniline monomer with the anionic sulfonate groups of the SPS under higher pH conditions. Since the pK_a of aniline is 4.60, a pH of 4 is sufficient to provide a majority of cationic charges for preferential alignment and reaction of the monomer and salt formation of the PANI with the SPS. As the pH of the reactant solution increases above the pK_a , electrostatic interaction and preferred integration of the monomer with the SPS decreases and a more random, branched form of polyaniline results.

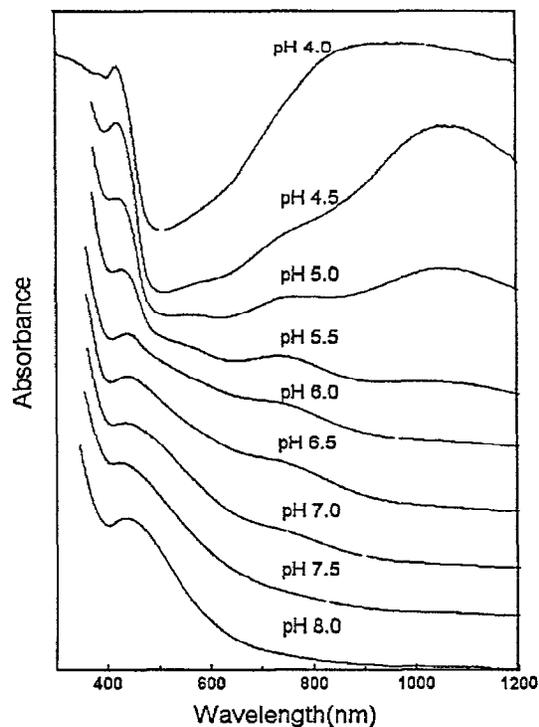


Figure 4. UV-vis spectrum of PANI/SPS complex with varying pH of the reactant solution.

From these results it is expected that as the pH of the reactant solution increases, the degree of branching increases and consequently the conductivity of the complex will decrease. Figure 5 is a plot of conductivity of PANI/SPS complex versus pH of the reactant solution. As shown, the conductivity of the complex decreases substantially from approximately 10^{-3} S/cm at pH 4-5 to 10^{-7} S/cm at pH 7-8. These results show that it is possible to control both the structure and electrical properties of polyaniline through enzymatic polymerization in the presence of a polyelectrolyte matrix. Moreover, a water soluble, conducting form of polyaniline may be prepared at substantially higher pH's and under milder conditions than is currently done chemically.

The reduction/oxidation reversibility of the PANI/SPS complex prepared at pH 4.3 is shown in Figure 6. Figure 6a shows that as the pH is increased from 3.5 to 11, the absorption peaks shift to shorter wavelengths which correspond to known changes in the protonation levels of the polyaniline backbone [15]. The reverse behavior is observed in figure 6b as the pH is adjusted back to 3.5. This pH induced redox reversibility confirms the presence of

the electroactive form of polyaniline in the enzymatically synthesized complex.

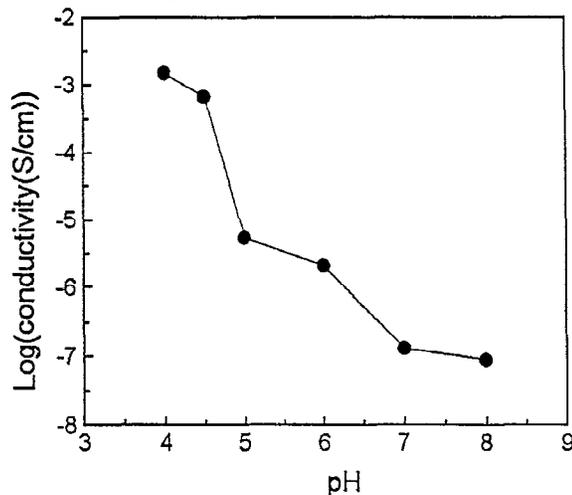


Figure 5. Plot of conductivity of PANI/SPS complex versus pH of the reactant solution.

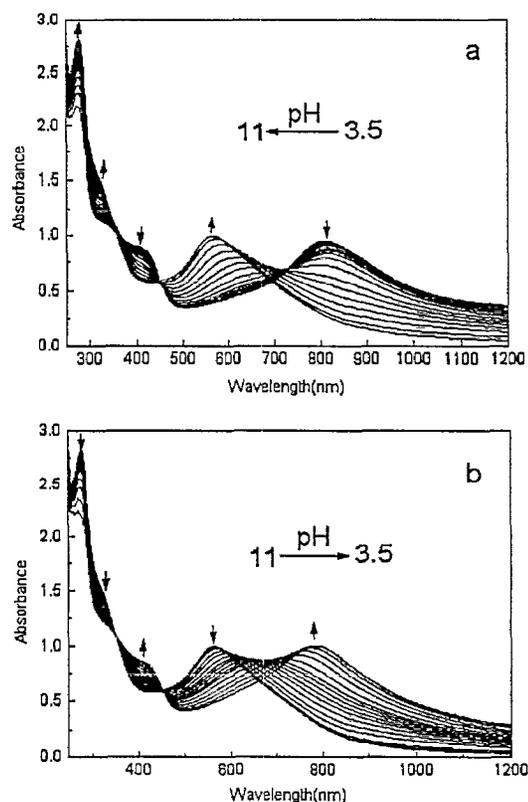


Figure 6. UV-vis spectra of PANI/SPS prepared at pH 4.3 with a) increasing pH (by titrating with 1N NaOH) and b) decreasing pH (by titrating with 1N HCl).

FTIR spectroscopy of both a solution cast film and a precipitated sample of the PANI/SPS complex (KBr pellet) prepared at pH 4.3 was carried out (spectra not shown). These spectra were found to be similar to each other and are in good agreement with spectra obtained from chemically synthesized PANI. Absorption bands found at 1584 and 1484 cm^{-1} are assigned to quinone and benzene ring

deformation [16] and a band at 1310 cm^{-1} is assigned to C-N stretching of a secondary aromatic amine [17]. The C-H out of plane bending located at 830 cm^{-1} is due to a para-substitution pattern, indicating that a head to tail coupling of aniline occurs during the polymerization. No other bands due to meta or ortho substitution patterns are observed. In addition, the presence of asymmetric and symmetric S=O stretching bands at 1034 and 1008 cm^{-1} confirms the presence of SPS in both samples.

Molecular weight studies of the PANI/SPS complex were investigated using GPC. Since it is difficult to differentiate the molecular weight of just the PANI in the PANI/SPS complex, the trend in the chromatographs with progress of the reaction was studied to project complex formation and extent of polymerization. For this experiment, a series of samples was prepared from a solution of 3:1 molar ratio of aniline to SPS. After the reaction was initiated with hydrogen peroxide, samples were withdrawn from the reaction media at 20, 40, 60, 80, 100, 120 and 140 minutes respectively. Each sample was dialyzed against distilled water to remove any low molecular weight material and buffer prior to GPC. To minimize aggregation, 1% (W/V) of LiBr was added to each sample before running. The results are shown in Figure 7. At the onset of polymerization, only one peak is observed which is similar to that observed for SPS only. As the reaction continues however, a shoulder begins to emerge at 14.3 minutes. This bimodal distribution has been reported previously for PANI in N-methyl-2-pyrrolidinone (NMP) and is attributed to aggregation [18]. In all cases, the peaks are observed to shift sequentially to shorter retention times and higher molecular weights. This is direct evidence that polymerization is occurring and proceeding with time of the reaction. These results also show that the PANI/SPS behaves as one complexed system, rather than two separate species.

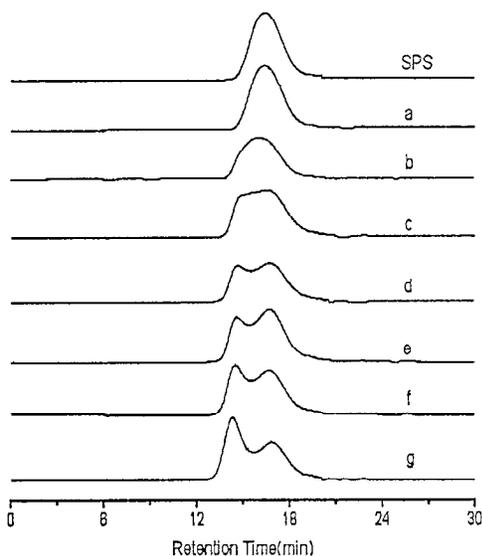


Figure 7. GPC of PANI/SPS complexes during different stages of polymerization.

The effect of the concentration of SPS on the electrical conductivity of the PANI/SPS was also investigated. To determine this a series of solution cast films were prepared from solutions of varying molar ratios of aniline to SPS (PANI/SPS from 0.6 to 2.2). In each case the conductivity of the pure complex was measured and then the same film

was exposed to HCl vapor for additional doping. As expected the conductivity of the complex was observed to increase almost four orders of magnitude with increasing concentration of PANI to a maximum value of 5×10^{-3} S/cm. Exposure to HCl increased the conductivity in each case another 1-2 orders of magnitude to a maximum value of approximately 0.5 S/cm.

4. Summary. A new biological route for the direct synthesis of water soluble, electrically conducting polyaniline is described. This approach is advantageous in that it is simple, biochemically mild and requires minimal separation and purification. The final polymer structure and electrical properties may be optimized by simply varying the pH, polyelectrolyte concentration and time of reaction. This process is general in that numerous anilino-functional comonomers and polyelectrolytes may be employed to produce new electroactive polymers. Furthermore, it is anticipated that suitable immobilization of the enzymes used with this approach could potentially lead to a facile, reusable, cost effective and environmentally friendly approach for large scale production of processable polyaniline.

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5. References

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