

Biomimetic Synthesis of a Water Soluble Conducting Molecular Complex of Polyaniline and Lignosulfonate

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A new biomimetic route for the synthesis of a conducting molecular complex of polyaniline (Pani) and a natural polyelectrolyte, lignosulfonate (LGS) is presented. A poly(ethylene glycol) modified hematin (PEG–hematin) was used to catalyze the polymerization of aniline in the presence of LGS to form a Pani/LGS complex. UV–vis, FTIR, conductivity and TGA studies for the LGS–polyaniline complex indicate the presence of a thermally stable and electrically conductive form of polyaniline. Also the presence of LGS in this complex, an inexpensive byproduct from pulp processing, provides a unique combination of properties such as electronic conductivity, processability and biodegradability. The use of this conductive complex for corrosion protection is also proposed.

Introduction

Polyaniline (Pani) has been extensively studied as a conducting polymer and has received considerable interest over several decades.¹ Recent investigations have been focused on exploring methods to augment the electrical properties, processability and environmental compatibility of this polymer for numerous technological applications. Several chemical^{2–5} and electrochemical⁶ methods have been reported for obtaining the polymer in both a conducting and processable form. More recently, polymeric protonating agents^{7,8} and polymeric templates^{9,10} have also been used for the synthesis of soluble, electroactive Pani. However, these more traditional polymerization routes often involve more tedious chemistry or harsh reaction conditions. To address some of these limitations, the use of biocatalysts was investigated. The enzyme horseradish peroxidase (HRP) has been extensively used for the oxidative polymerization of phenols and anilines in the presence of hydrogen peroxide.¹¹ Also aniline monomers containing hydrophilic substituents^{12,13} or photodynamic azobenzene groups¹⁴ have been enzymatically polymerized to yield a wide range of soluble polyanilines. An extension of this work then included a template-assisted, HRP-catalyzed polymerization of aniline to synthesize a water-soluble and processable form of conducting polyaniline under environmentally mild conditions.^{15–17} In this case, the polyelectrolyte provides a preferential local environment that facilitates the para-directed coupling of the monomer, provides the counterions for doping the polyaniline, and remains complexed to the polyaniline, imparting water solubility.

Although HRP is a promising biocatalytic approach to the synthesis of Pani, there exists a need to develop a cost-effective and more robust “synthetic enzyme” catalyst alternative for peroxidase in these reactions. Synthetic porphyrin complexes and their possible applications in catalysis have 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.¹⁸ Hematin, however, was soluble in water only at very high pH and thus was not effective in the low to neutral 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 hematin was carried out resulting in a porphyrin conjugate bearing pendant polymer chains of PEG as a flexible and hydrophilic linker. This poly(ethylene glycol) modified hematin (PEG–hematin),¹⁹ developed in our group could effectively act as a “peroxidase mimic” and proved to be a promising and versatile alternative for the polymerization of various anilines and phenols.²⁰

A wide range of polyelectrolytes have been investigated in this template-assisted biocatalytic approach including such common polyelectrolytes as sodium (poly-4-styrene sulfonate) to even more delicate biological macromolecules such as DNA and RNA. Lignin is one of the most abundant biopolymers in nature, second only to cellulose.²¹ Lignosulfonate (LGS), an inexpensive byproduct from pulp processing industries, has become increasingly valuable for its versatility in performance for petroleum derived chemicals like resins, plastics and fillers.^{22–24} This aromatic network polymer has found applications in numerous industrial arenas because of its versatile dispersing, binding, complexing, and emulsifying properties. Graft copolymers of acrylic acid and calcium LGS

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are used as drilling additives for providing superior rheological control and stability against flocculation.²⁵ In this paper, we report the biomimetic polymerization of aniline in the presence of LGS to yield a conducting, water-soluble Pani that is doped by LGS. The use of LGS as a polymeric template for the synthesis of Pani was inspired by its high water solubility and relative abundance as a byproduct from the pulp processing industry, with the added advantage of being extremely inexpensive. The LGS–Pani complex also provided a unique combination of properties for the polyaniline including electrical conductivity, processability, corrosion protection, and biodegradability.²⁶

Experimental Section

Materials. Hematin was purchased from Sigma Chemical Co. (St. Louis, MO). Aniline monomer (purity 99.5%), poly(ethylene glycol) (PEG), and hydrogen peroxide (30%) were purchased from Aldrich Chemicals Inc., Milwaukee, WI and were used as received. The commercial grade sample of lignosulfonate (LGS, Lignosol SFX-65, Code No. M12E-10A, sulfur content 6.45%) was obtained from Lignotech USA, Rothschild, WI, and was used as received. All other chemicals were of reagent grade or better. PEG–hematin was synthesized according to the procedure previously published.¹⁸

Polymerization Reaction. The polymerization of aniline in the presence of LGS was catalyzed by PEG–hematin at 25 °C in the presence of hydrogen peroxide under ambient conditions. A 5.2 mg sample of LGS was dissolved in 10 mL of sodium phosphate buffer (100 mM) maintained at pH values ranging from pH 1.0–4.0. This range of pH was required to supply the essential ionic environment needed to promote head to tail coupling of the aniline and for subsequent salt formation with the LGS. This was followed by the addition of 180 μ L (1.975 mmol) of aniline and 5 mg of PEG–hematin to this solution. To commence the polymerization, 200 μ L of 0.03% hydrogen peroxide was added in increments. The reactants were stirred for 12 h to complete the polymerization followed by precipitation of the polyaniline/LGS complex. The precipitate obtained was thoroughly washed with acetone to remove unreacted monomer and any oligomeric products. The final purified polymer complex was dried overnight and the gravimetric yield was determined to be approximately 71%.

Characterization. All UV–vis spectra were obtained using a Perkin-Elmer Lambda 9 UV–vis–near-IR spectrophotometer. The FT-IR measurements were carried out using a Perkin-Elmer FT-IR spectrophotometer in the form of KBr pellets. Conductivity measurements were performed on pellets using the four point probe method with a Keithley 619 electrometer/multimeter. Thermogravimetric analysis (TGA) was performed using TA instruments, Hi-Res 2950 Thermogravimetric analyzer. Cyclic voltammograms were recorded at room temperature by using a three-electrode cell with a platinum wire as a counter electrode, an Ag/AgCl electrode as the reference electrode and a platinum foil (1 \times 1 cm²) with a cast film of the Pani/LGS complex as the working electrode. The cyclic voltammogram was obtained

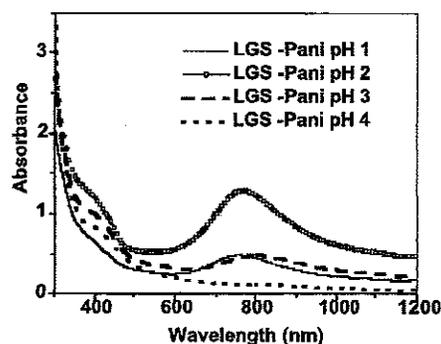
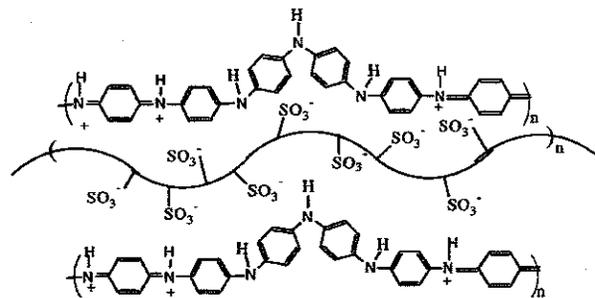


Figure 1. pH dependent UV–vis absorption spectra of the Pani/LGS complex.

Scheme 1. Proposed Schematic for the Formation of the Molecular Complex Pani/LGS



at room temperature in a 1.0 M HCl electrolyte solution by scanning between 0.0 and 1.0 V at a scan rate of 20 mV/min.

Results and Discussion

The schematic of the polyaniline synthesized in the presence of the LGS is shown in Scheme 1 wherein LGS acts as the template and the polymerization was catalyzed by using PEG–hematin.

Effect of pH. The local environment in the vicinity of the template has been known to have a profound effect on the ability to charge and preferentially align the monomers on the template prior to polymerization.¹⁶ Therefore, the pH of the reaction medium dictates the extent of dissociation of the template polyelectrolyte and influences the solubility as well as the nature of the polyaniline formed in the reaction. To study the effect of pH, the polymerization was carried out at different pH conditions ranging from pH 1 to 4. The absorption spectra of the Pani/LGS complex synthesized using PEG–hematin in this pH range is given in Figure 1. The polyaniline formed at each pH showed typical absorption bands at around 400 and 760 nm due to the well-known polaron transitions.²⁷ The extended absorption observed until 1200 nm was indicative of the presence of extended conjugation in the Pani backbone. Observation of the intensity of the polaron band at 770 nm suggests that the extent of polymerization was highest at pH 2.0 (maximum intensity) and least at pH 4.0 (minimum intensity) during the same time period. This behavior was quite different from the LGS/Pani complex formed by peroxidase²⁸ catalyzed polymerization carried out at pH 4.3 wherein precipitation and degradation was observed over a time period of 7 days.

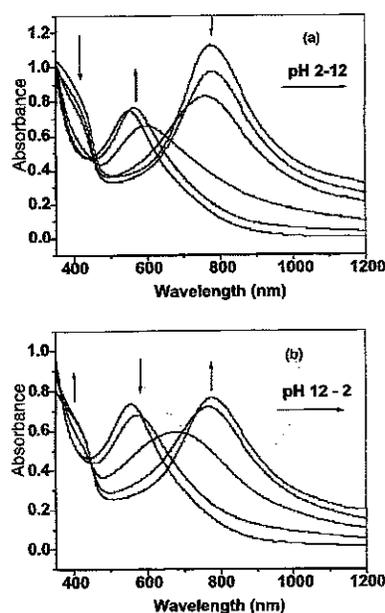


Figure 2. UV-vis spectra change of the Pani/LGS complex during titration with (a) 1 N NaOH and (b) 1 N HCl.

The peroxidase synthesized Pani evidently had limited stability accompanied by the green polyaniline being altered to yellow, which was verified by the disappearance of the polaron bands at 800 nm in the UV-vis spectra (not shown).

These results thus show that the LGS-templated polymerization of aniline is strongly pH-dependent in this case, wherein an optimal pH is needed to provide the emeraldine conducting form of polyaniline. The higher stability of the PEG-hematin catalyst provided an advantage of being able to carry out the synthesis at a lower and optimal pH of 2, which was not possible with the peroxidase. Thus, it could be concluded that PEG-hematin was an efficient and advantageous catalyst for the synthesis of a more stable LGS/Pani complex.

The reversible redox behavior of the Pani/LGS complex prepared at pH 2.0 was studied with varying pH. The shift in the absorption spectra of the complex on titration with 1 N NaOH (de-doping) and 1 N HCl (re-doping) is shown in Figure 2. As the pH is increased from pH 2.0, the polaron bands at 760–780 nm gradually disappear with the emergence of a new peak at 550–600 nm due to exciton transitions, which is also accompanied by a color change in the complex from green to blue (emeraldine base) and finally to a purple color (Figure 2a).^{26c} Also the Pani/LGS complex could be de-doped and subsequently re-doped by titrating with 1 N HCl (Figure 2b) to again yield the green form. This pH induced redox reversibility was indicative of the presence of the electroactive form of polyaniline in the Pani/LGS complex.

The yields of Pani/LGS complex synthesized at pH 1, 2, and 3 were 56%, 61%, and 52% respectively. The molecular weight of these polymer complexes may not provide any additional information on the molecular weight of the polyanilines complexed with the LGS. MALDI-TOF analysis and light-scattering experiments were attempted to obtain the molecular weight of the Pani/LGS complexes, which

Table 1. Results from Elemental Analysis of LGS-Polyaniline Synthesized at Various pH Values

element	composition (%)			
	LGS	Pani/LGS pH 1	Pani/LGS pH 2	Pani/LGS pH 3
carbon	41.88	56.65	57.73	52.35
hydrogen	4.46	4.89	4.89	4.99
nitrogen	<0.1	6.00	5.51	3.45
sulfur	6.45	3.95	3.98	4.61

however proved to be difficult since the complexity of LGS structure prevents the accurate determination of the molecular weight of Pani/LGS complex. The MALDI experiments were unsuccessful because of the presence of the negatively charged polyelectrolyte LGS system which inhibits precise mass measurements. Moreover, sample preparation for light-scattering measurements precludes the analysis of large and bulky structure such as the LGS/Pani. Further, GPC measurements also proved to be unattainable because standards similar to the complex LGS/Pani were not available. Finally, it is important to emphasize that a precise molecular weight assessment of the complex LGS/Pani does not and cannot specify any molecular weight for the solitary Pani.

Elemental Analysis. The complexity of the structure of LGS prevents the accurate estimation of concentration ratios for LGS and aniline. To obtain an estimate of the relative ratios of Pani to LGS in Pani/LGS complex synthesized at pH 1, 2, and 3, elemental analysis was carried out. The results are presented in Table 1. It is evident from Table 1 that the Pani/LGS complex synthesized at pH 1 contains the maximum ratio of polyaniline with respect to LGS, as indicated by the highest relative content of nitrogen with respect to sulfur. Although the gravimetric yield has been observed to be higher in the case of Pani/LGS synthesized at pH 2, the conductivity of the complex was observed to be lower as compared to the one synthesized at pH 1. These results again signify that a lower pH favors the synthesis of the electrically conducting form of polyaniline. On the basis of this ratio of nitrogen to sulfur obtained, the ratio of aniline unit to LGS unit in the Pani/LGS complex at pH 1.0 was calculated to be 1:2.5, which thus implied that approximately one repeat unit of aniline complexed with every 2.5 repeat units of LGS.

FT-IR. The Pani formation was also confirmed by comparison of the FTIR spectrum of the polymeric complex Pani/LGS and LGS (Figure 3). The ring stretch of the Pani quinoid form was observed as a broad band between 1590 and 1650 cm^{-1} , while the ring stretch of the benzenoid form appeared as a significantly broad band centered around 1490 cm^{-1} , shifted to lower wavenumbers from 1500 cm^{-1} . This observed ring stretch shift to lower wavenumbers was attributed to the interaction of Pani with LGS. The peak at 1140 cm^{-1} was attributed to the C–N stretching in secondary amines, that at 730 cm^{-1} was due to the NH deformation in secondary amines, and the appearance of a 900 cm^{-1} peak corresponding to 1,4-disubstituted aromatics, in the Pani/LGS spectrum, confirms Pani formation.²⁹ Furthermore, the peaks at 1180 and 512 cm^{-1} , due to the S=O stretching and SO₂ scissoring respectively, in both the LGS and the LGS/Pani spectra, confirmed the presence of the template in the complex.

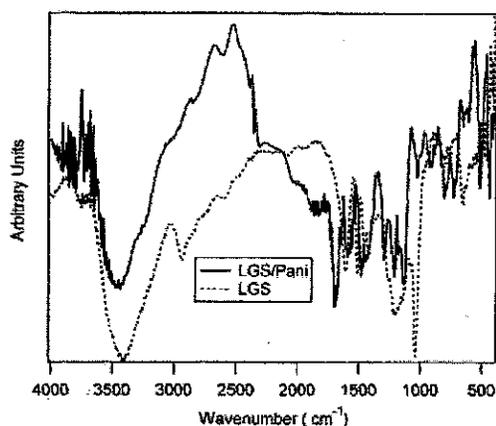


Figure 3. FTIR spectra of the LGS and Pani/LGS complex.

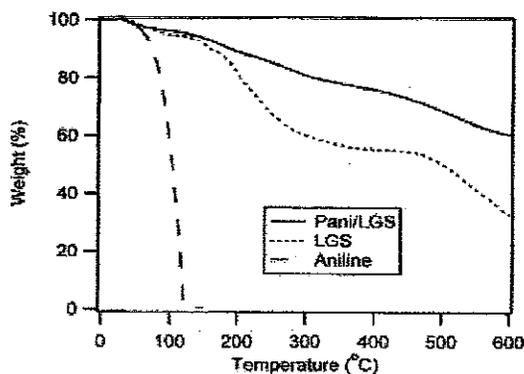


Figure 4. TGA curves of LGS, aniline monomer and Pani/LGS complex.

Thermal Analysis. The TGA curve of the Pani/LGS complex presented in Figure 4 showed a trend in weight loss around 200 °C similar to previous reports³⁰ of TGA curves for HCl doped Pani, which showed about 5% weight loss around 200 °C and which was attributed to loss of HCl and traces of water. It was also reported that weight loss, caused by thermal degradation, commenced around 300 °C and approximately 38% weight loss was observed before a temperature of 575 °C was reached.

In the TGA curve of the LGS, the degradation was observed to start around 175 °C and almost 40% weight loss occurred at 300 °C. Thus, in comparison, the TGA curve of the Pani/LGS complex clearly demonstrated the increased thermal stability on the complexation of Pani with the polyelectrolyte, which in turn offers thermal processing advantages.

Conductivity. Electrical conductivity of Pani/LGS, synthesized at pH 1.0, and formed into pellets, was determined to be of the order of 10^{-3} S/cm without addition of any external dopants. Moreover, since the primary dopant in this system is the large LGS polyelectrolyte, the electrical stability of the Pani/LGS is expected to be greater than that of other polyanilines that have smaller dopants.

Cyclic Voltammetry. Cyclic voltammetry was carried out to determine the electrochemical nature of the Pani/LGS complex. The cyclic voltammogram of a cast film of the complex is shown in Figure 5. Two well-resolved sets of peaks were observed with the complex corresponding to two

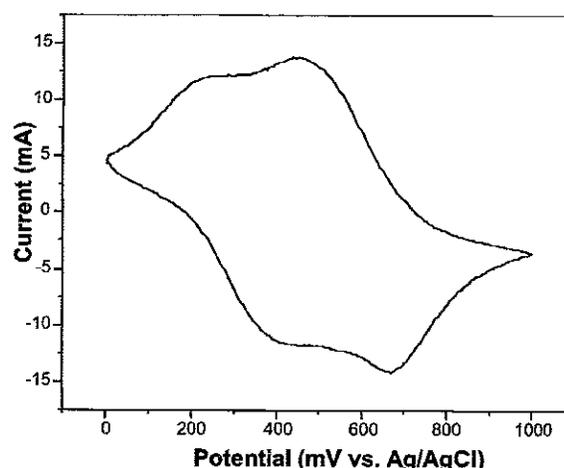


Figure 5. Cyclic voltammogram of a solution cast film of Pani/LGS in 1 M HCl with a scan rate of 20 mV/s.

reversible redox processes at 0.56 and 0.30 V vs SCE at a scan rate of 20 mV/s over a potential window of 0.0–1.0 V. This behavior is similar to the previous reports indicating the redox behavior of polyaniline.³¹

Conclusions

The synthesis of an electroactive polymer, polyaniline, templated to a natural polymer, liginosulfonate has been accomplished using an environmentally friendly process. The biomimetic PEG–hematin-catalyzed Pani synthesis has been efficiently carried out with LGS to improve solubility and processability of the conducting polymer. The versatility and robustness of the “synthetic enzyme” PEG–hematin has also been demonstrated by the ability of this “synzyme” to carry out the polymerization reaction at various pH conditions. This provides a distinct advantage over similar reactions with the native enzymes. This method thus provides the flexibility to synthesize Pani complexed with a natural polyelectrolyte with varying conductivity and solubility. This approach could be utilized to impart electrical conductivity to some of the extensively used natural polyelectrolytes similar to LGS, which could further widen the scope of their application. This Pani complex can also be used for corrosion protection and studies are under way to further tune this material in this area.

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