

ENZYMATIC AND BIOMIMETIC SYNTHESIS OF ELECTROACTIVE POLYMERS AND THEIR OPTICAL AND ELECTRONIC PROPERTIES

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ABSTRACT

Electroactive polymers as a class of advanced materials have attracted considerable interest during last two decades. Typically these materials are synthesized chemically or electrochemically under harsh conditions such as extremely low pH, using toxic catalysts and yield undesirable byproducts. New enzymatic and biomimetic approaches have been developed for the synthesis of electroactive polymers such as, Polyaniline, Polyazophenols, Polypyrrole and Polythiophene. These enzymatically-synthesized polymers show interesting optical and electronic properties.

INTRODUCTION

Peroxidase-catalyzed oxidation of phenols and anilines has been extensively investigated due to its importance in the synthesis of electronic and photoactive polymer in an environmentally benign way {1-3}. In the presence of H₂O₂, peroxidase, such as horseradish peroxidase (HRP) can oxidize phenols and anilines to generate corresponding radicals. These radicals may couple together through radical coupling and radical transfer to form dimers, trimers, tetramers and oligomers and finally polymers etc. In a suitable solvent system, polymers such as polyanilines and polyphenols with modest molecular weight may be realized.

Typically, the enzymatically-synthesized polyanilines (in both organic and aqueous solutions) are not electrically active due to the low molecular weight and presence of branched structure. Recently a new enzymatic approach was developed to synthesize water-soluble conducting polyaniline under mild conditions using sulfonated polystyrene (SPS) as a template {3}. The properties of this polyaniline/SPS complex are comparable to previously reported chemically synthesized and self-doped sulfonated polyaniline. The use of the anionic polyelectrolytes as templates in peroxidase-catalyzed polymerization of aniline leads to the first enzymatic synthesis of conducting polyaniline, and opens the door for the synthesis of electrically active conducting polymers through biological approach.

Peroxidase-catalyzed synthesis involves a reaction mechanism that results in a direct ring-to-ring coupling of phenol and aniline monomers. The resulting polymers may have an aromatic backbone structure, with interesting electrical and optical properties. By using chromophore functionalized phenols or anilines as substrates, phenol-based (or aniline-based) macromolecular dyes with interesting optical or electrical properties (depending on chromophores) may be synthesized. This approach offers the possibility to build in substantial chromophore density in the polymers. For example, by using azo functionalized phenol and aniline as monomer, photo active polyaniline and polyphenol have been enzymatically synthesized by our group {4}. These biologically derived azopolymers have almost 100% dye content. Since both 'ortho' and 'meta' couplings occur through the phenol ring, a high articulated nanostructured macromolecular dye is realized, leading to large free volume and poor packing of the azo chromophores. Since enzymes tend to be expensive and tend to lose their activity relatively easily, biomimetic approaches which mimic the enzyme

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HRP have been developed. These biomimetic approaches provide low cost alternatives to the enzymes and in some cases catalyze polymerization that is not possible for the enzyme to carry out.

EXPERIMENTAL

MATERIALS

Horseradish peroxidase (HRP) (EC 1.11.1.7) (200 unit/mg) was purchased from Sigma with RZ>2.2. A stock solution of 10 mg/ml in pH 6.0, 0.1M phosphate buffer was prepared. A biomimetic enzyme was prepared by attaching polyethylene oxide (PEO) oligomers to Hematin purchased from Aldrich. The 'para' substituted azophenol monomers were synthesized following typical procedures. All other chemicals and solvents used were commercially available, and analytical grade or better was used as received.

POLYMERIZATION OF ANILINE

The enzymatic polymerization of aniline was typically carried out at room temperature in a 30 ml, 0.1M sodium phosphate buffer solution of pH 4.3 which contained a 1:1 molar ratio of SPS to aniline, (6mM) SPS (based on the monomer repeat unit) and 6mM aniline. SPS was added first to the buffered solution, followed by addition of the aniline with constant stirring. To the solution, 0.2ml of HRP stock solution (10mg/ml) 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 due to excess H_2O_2 , diluted H_2O_2 (0.02M) was added drop wise, incrementally, over 1.5 hours. After the addition of H_2O_2 , the reaction was left stirring for at least one hour and then the final solution was dialyzed (cutoff molecular weight of 2000D) against pH 4.3 deionized water overnight to remove any unreacted monomer, oligomers and phosphate salts. PEO functionalized Hematin was also used to polymerize aniline. PEO-Hematin can tolerate much wider range of pH than HRP and can also polymerize Pyrrole as well as some Thiophene monomers.

ENZYMATIC POLYMERIZATION OF AZOPHENOLS

Enzymatic polymerization of 4-phenylazophenol was carried out at room temperature in a 100 ml, 50% acetone and 50% 0.01 M sodium phosphate buffer mixture, which contained 2.0 g of 4-phenylazophenol. To this solution, 2.0 ml of HRP stock solution was added. The reaction was initiated by the addition of H_2O_2 . To avoid the inhibition of HRP due to excess H_2O_2 , a diluted stoichiometric amount of H_2O_2 (0.2 M) was added incrementally under vigorous stirring over a three hour time period. After the addition of H_2O_2 , the reaction was left stirring for one more hour. The yellow precipitates formed during the reaction were then collected with a Buchner funnel, washed thoroughly with the mixed solvent of 20% acetone and 80% water (v/v) to remove any residual enzyme, phosphate salts and unreacted monomers and then vacuum dried for 24 hours. Similar experimental conditions were used for $-CH_3O$, $-NO_2$ and $-CN$ substituted azophenols.

Polymerization of the sulfonated and carboxylic substituted monomers was carried out in a mixture of 80% phosphate buffer / 20% acetone and the other conditions are similar to that described previously. In these reactions, no precipitates were formed and the resulting polymers were solubilized in the reaction media. The polymer solutions were dialyzed against deionized water for 24 hours using a dialysis bag (SPECTRUM®) with a molecular weight cut off of 3000 to remove unreacted monomer and phosphate salts. The resulting dialyzed solution was then condensed and dried in a vacuum oven at 50 °C. The enzymatic polymerization of 4-hydroxypyrene was performed as a similar procedure as described above for the azophenols in the solution of 50% ethanol and water mixture. The synthesized polymers were formed as precipitates, and purified by centrifuging and washing. These polymerization reactions can also be carried out by PEO functionalized Hema tin.

SURFACE RELIEF GRATING FORMATION

Surface relief gratings (SRG) were holographically recorded by a simple two-beam interference apparatus at 488 nm from an argon ion laser under ambient conditions with a typical laser intensity of 300 mW/cm². The formation process of the grating was probed by monitoring the first order diffraction of a lower power He/Ne laser beam at 633 nm, at which the absorption is negligible. After the holographic gratings were recorded, the surface relief structures of the gratings on the polymer films were imaged by atomic force microscopy under ambient conditions. A 100 nm scanner in the contact mode under a scan rate of 1 Hz was used in these measurements.

RESULTS AND DISCUSSION

ENZYMATICALLY SYNTHESIZED CONDUCTING POLYANILINE.

The enzymatic polymerization of aniline in SPS solution is performed as shown schematically in Figure 1. This approach is based on preferential electrostatic alignment of aniline monomer onto an anionic template to minimize branching and promote a linear polyaniline chain growth. Since aniline has a pK_a of 4.63, it is primarily positively charged at pH 4.3.

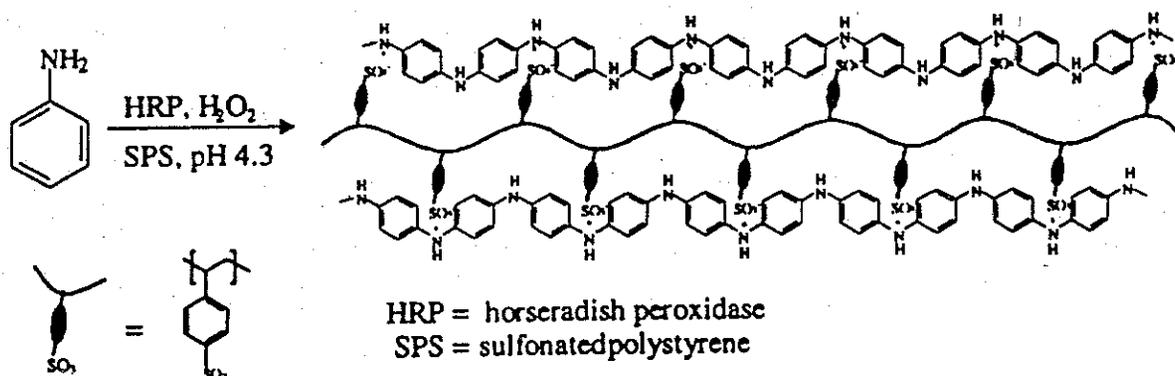


Figure 1 : Enzymatic Polymerization of Aniline

Conversely, the sulfonate groups on the SPS are negatively charged (SPS is a strong polyelectrolyte that will totally dissociate in almost the entire pH range). Therefore it is believed that the aniline monomer interacts with the SPS electrostatically and preferentially complexes with the template prior to and during the reaction. 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 polyaniline and SPS complex. The PANI/SPS complex can be reversibly doped and dedoped by changing the pH range from 3.5 to 11. The reversible redox behavior of the PANI/SPS complex can be monitored by absorption measurements in the visible. The PANI can be complexed with a number of polyelectrolytes such as DNA and Poly (vinyl phosphonic acid).

Enzymatically synthesized polyazophenols Peroxidase-catalyzed polymerization of azophenols is schematically shown in Figure 2. FTIR, FT-Raman and NMR (¹H, ¹³C) spectroscopy show that the coupling reaction occurs primarily at the 'ortho' positions with some coupling at the 'meta' positions of the phenol ring of the monomer as well (data not shown in this paper). This results in the formation of a branched polyphenylene backbone with pendant azo functionalities on every repeat unit of the macromolecules. The enzymatic polymerization of 4-phenylazophenol was studied using UV-Vis spectroscopy. Figure 3 shows the absorption spectra of solutions of the monomer and polymer in dioxane. The monomer spectrum of 4-phenylazophenol is similar to that known for other azo-benzene derivatives where a maximum absorption at 355 nm, characteristic of *trans* 4-phenylazophenol and a weak broad peak at about 440 nm due to *cis* 4-phenylazophenol are present.

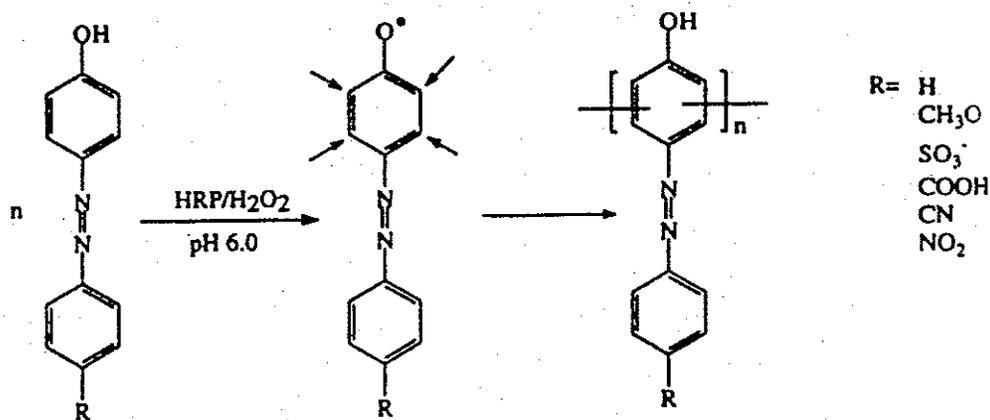


Figure 2 : Peroxidase Catalyzed Polymerization of Azophenols

Comparison of these solution spectra shows that a significant absorption change occurs as a result of polymerization. The trans absorption at 355 nm in the monomer, blue shifts to 345 nm in the polymer, and the cis absorption at 440 nm becomes stronger in the polymer.

One of the applications of these enzymatically synthesized macromolecular dyes is photo-induced fabrication of Surface relief structures. Taking advantage of the good solubility of these polymers, optical quality films may be fabricated by spin coating the polymer solution onto glass slides. Surface relief gratings were optically inscribed on these polymer films at room temperature.

This photofabrication process is a simple, one step process that doesn't require any subsequent post processing. As an example, a three-dimensional view of the SRG written on the methoxy substituted polyazophenol film is shown in Figure 4. A SRG with surface modulation around 0.4 μm was formed on this film.

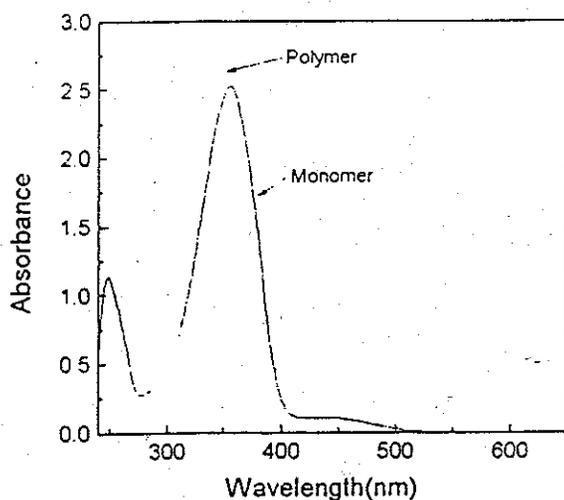


Figure 3. UV-vis spectra for the polymer and monomer of 4-phenylazophenol in dioxane.

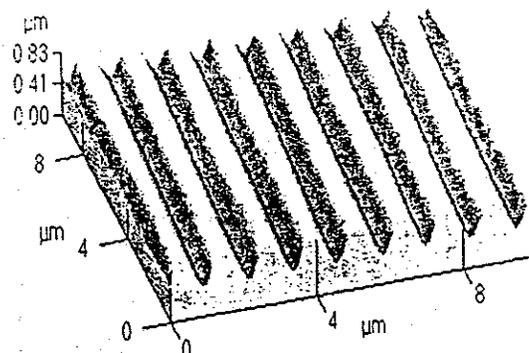


Figure 4. AFM image of SRG formed on enzymatically synthesized polyazophenol thin film.

CONCLUSION

Electroactive polymers such as Polyaniline, Polyazophenols Polypyrrole and Polythiophene were synthesized by peroxidase as well as biomimetic "synzyme" catalyzed polymerization. These polymers show interesting electronic and optical properties.

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