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**Journal of Physical & Theoretical Chemistry**  
**Islamic Azad University of Iran 2(4)**

(2006)

*Science and Research Campus*

ISSN: 1735-2126

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**New Synthesis of Polyaniline using a Peroxides Enzyme**

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**ABSTRACT**

A new method for the synthesis of water soluble Polyaniline (PANi) using Hemin Chloride (H.C) in the presence of hydrogen peroxide (H.P) is presented. Hemin chloride is an effective catalyst for the oxidative polymerization of aniline in the presence of hydrogen peroxide at room temperature. The UV- Vis absorption spectra of the product show a distinct absorption peak at 430 nm in pH 4.0 buffer solution, indicating the formation of Polyaniline. A new mechanism for polymerization of aniline in the presence of H.C and H.P is also presented.

**Keywords:** Polyaniline; Enzymatic Polymerization; Conducting polymer

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## 1. INTRODUCTION

Among conducting polymers Polyaniline has been a significant interest due to its electrical properties, which can be reversibly controlled by both charge transfer doping and premonition. The wide range of associated electrical, electrochemical and optical properties, coupled with good stability make Polyaniline potentially attractive for applications as an electronic materials [1-4]. Polyaniline can be synthesized by both electrochemical and chemical polymerization [5-9]. Recently there has been much interest in enzyme catalyzed polymerization as a new methodology for polymer synthesis. Enzymes such as peroxidase, lactase and lipase among others have been used for the synthesis of polymers and other specially chemicals. Enzyme catalyzed reactions are known as environmentally friendly processes and can be done at room temperature and pressure [10, 11].

Peroxides catalyzed polymerization of aniline has been utilized to produce controlled polymeric structures [12]. Recently Zhe Jin et al [13] reported the synthesis of Polyaniline with immobilized horseradish peroxides enzyme (HRP), using aqueous solution containing aniline, sulfonated polystyrene (SPS) and hydrogen peroxide. HRP is an oxidoreductase which catalyzes the radical polymerization of aniline in the presence of oxidizing agent such as hydrogen peroxide. Also recently, enzymatic polymerization has been used to synthesize water soluble analogue of aniline. In this report, we have extended the enzyme catalyzed polymerization using Hemin Chloride (H.C) as a peroxides enzyme to synthesize water soluble Polyaniline. The feasibility of Polyaniline synthesis with hemin chloride is studied at different conditions such as: different solution pH and varied aniline concentration, hemin chloride

concentration, hydrogen peroxide concentration and S.D.S. concentration.

## 2. EXPERIMENTAL

### 2.1 Materials and Apparatus

Aniline monomers, hydrogen peroxide, sodium dodecyl sulfate and Hydroin TM buffer reagents were purchased from Aldrich and Hemin Chloride was purchased from Merck. All aqueous solutions were prepared with deionised water. The hemin chloride and hydrogen peroxide solutions were freshly prepared whenever the experiments were performed. The spectral property of polymerization process was studied using a Perkin - Elmer Lambda 25 U V- Vis spectrometer.

### 2.2 Polymerization

The synthesis of Polyaniline (PANi) with Hemin Chloride (H.C) in the presence of hydrogen peroxide (H.P) was carried out in a one cm quartz cell at room temperature. Soluble PANi was prepared in a 3 cm<sup>3</sup> buffer solution containing 6.6 mM of freshly distilled aniline monomers, 0.008 mM hemin chloride and finally adding 75  $\mu$ L of hydrogen peroxide (with the concentration of 1.0 mM ) to the reaction vessel. A sharp absorption peak in 430 nm is appeared after adding H.P to the solution which is attributed to the bipolar on transition band of PANi [14, 15]. In Fig. 1, the structure of Hemin Chloride is presented.

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of solution pH

Fig. 2, shows the UV-Vis spectra of Polyaniline, prepared with the procedure discussed in section 2.2, except that the solution pH varied between 4 until 9. One strong absorption peak appears at 430 nm in pH 4.0. With increasing the solution pH

to 6.0 the intensity of this peak is decreased and in pH 9.0 disappears. So, electrically conductive PANi is obtained at a pH lowers than 6.0. The peak at 430 nm is attributed to the bipolar on transition band of Polyaniline [14, 15].

Catalytic reactions are sensitive to solution pH which can affect the reactants in solution such as premonition of aniline in acidic solutions can prevent the oxidation of aniline. Also in alkaline solutions the hemolytic cleavage of oxygen-oxygen bond in hydrogen peroxide in the presence of hemin chloride is very hard.

### 3.2 Effect of hydrogen peroxide concentration

Fig. 3 shows the UV-Vis spectra during Polyaniline synthesis at different hydrogen peroxide concentrations. The reactions were carried out as in section 3.1 except that the aniline concentration kept at 6.6 mM and hydrogen peroxide concentration varied between 1 and 30 mM. The UV-Vis spectra were recorded after 50 min.

With a concentration of 30 mM of hydrogen peroxide in the solution, a very weak absorption band is observed, indicating the very slow oxidative polymerization of aniline and there is a strong absorbance band at 430 nm in 1mM of hydrogen peroxide. When hydrogen peroxide concentration increases from 1 to 30 mM, the intensity of absorption peak at 430 nm increases, and shifts to 428 nm, which further demonstrates that Polyaniline is oxidized by hydrogen peroxide. Hydrogen peroxide not only oxidizes hemin to the reactive intermediate, which is necessary for catalytic oxidation of a substrate but also can inactivate hemin chloride. Therefore, reaction solution is very sensitive to hydrogen peroxide concentration. In concentrations above 10 mM of hydrogen peroxide, hemin is inactivated [16-19].

### 3.3 Effect of Hemin Chloride concentration

In catalytic reactions, the rate of reaction depends on enzyme concentration and increases with increasing the concentration of enzyme. Fig. 4 shows the effect of hemin chloride concentration on reaction rate. The hemin chloride concentration varied between 0.004 and 0.012 mM. The reactions were carried out as in section 3.2 except that the solution pH kept at 4.0 and hemin chloride concentration varied between 0.004 and 0.012 mM. The UV- Vis spectra were recorded after 50 min.

As it is shown in Fig. 4, the absorption at 430 nm increased with increasing the concentration of hemin chloride.

### 3.4 Effect of aniline concentration

Effect of aniline concentration in the polymerization rate was carried out as in section 3.3 except that the aniline concentration was varied between 6.6 and 50 mM. The UV-Vis spectra were reordered after 50 min.

Fig. 5 shows the UV-Vis spectra of the aniline concentration effect in Polyaniline synthesis in a pH 4.0 buffer solution containing 6.6 mM of SDS, 0.008mM of hemin chloride and different aniline concentrations varying from 6.6 to 50 mM. The intensity of the absorption peak at 430 nm is increased by increasing the aniline concentration.

### 3.5 Effect of reaction time

The effect of time to complete the reaction was studied at optimum condition of reaction containing aniline (6.6 mM), hydrogen peroxide (1.0 mM), hemin chloride (0.008 mM), SDS (6.6 mM) in pH 4.0 buffer solution and the time increased to 95 min.

In Fig. 6, the progress of reaction is shown. As it is shown from the curve the absorption at 430 nm becomes constant after 50 min, so the optimum time of reaction complete is 50 min.

#### 4. CONCLUSION

Hemin chloride is a porphyrin with an iron as a central atom, its structure (Fig.1.) is similar to peroxides enzymes, so can be used as an effective catalyst for Polyaniline synthesis. Oxidative polymerization of aniline in the presence of H.C & H.P is carried out successfully and yields a soluble Polyaniline. This method is simple, environmentally benign route for soluble Polyaniline synthesis.

#### ACKNOWLEDGMENT

The authors would be like to thank Islamic Azad University and Atomic Energy Organization of Iran for technical and economical supports.

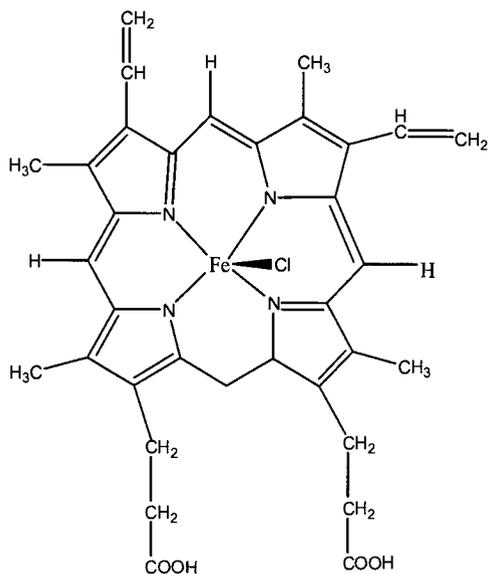


Fig.1, Schematic presentation of Hemin Chloride

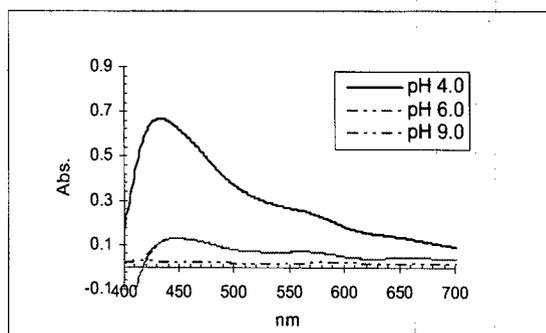


Fig. 2, UV-Vis spectra of Polyaniline recorded at different pH solution containing 0.008 mM hemin chloride, 6.6mM of aniline and SDS and 1mM of hydrogen peroxide.

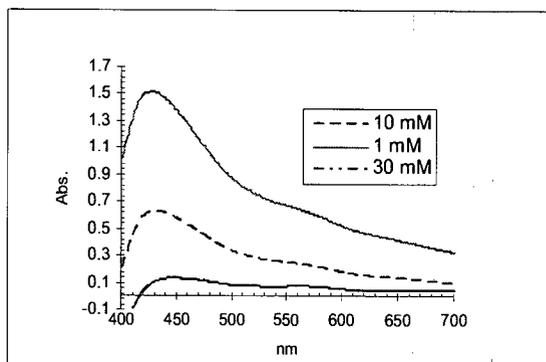


Fig. 3, UV-Vis spectra of Polyaniline recorded at different hydrogen peroxide concentrations in pH 4.0, 6.6mM of SDS & aniline and 0.008 mM of hemin chloride.

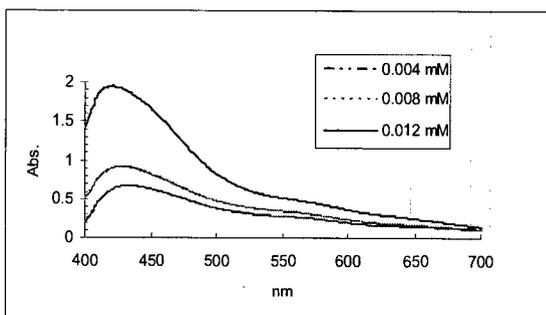


Fig. 4, UV-Vis spectra of Polyaniline recorded at different hemin chloride

concentrations in pH 4.0, 6.6mM of aniline & SDS, 1mM of hydrogen

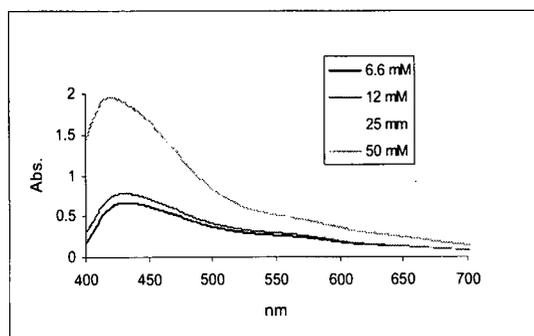


Fig. 5, UV-Vis spectra of Polyaniline recorded at different aniline concentrations in pH 4.0, 6.6 mM of SDS, 1mM of hydrogen peroxide and 0.008 mM of hemin chloride

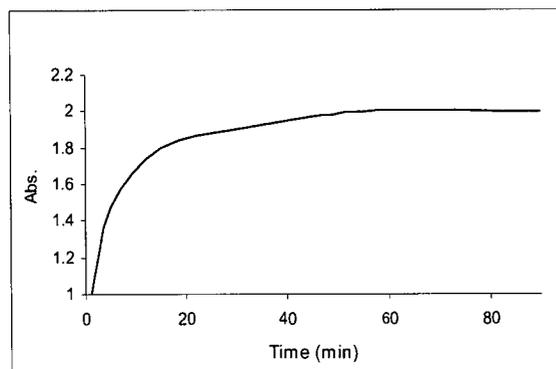


Fig. 6, Time effect in the reaction complement, at pH 4.0, 6.6mM of SDS & aniline, 0.008 mM of hemin chloride and 1mM of hydrogen peroxide.

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