

Nanoreactors for the enzymatic synthesis of conducting polyaniline

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Abstract

The mechanistic role of template in the enzymatic synthesis of conducting polyaniline has been investigated using micelles and DNA as ionic templates. These studies show the existence and importance of a molecular local environment where the pH and charge density near the template molecule is different from that of the bulk solution. This local environment serves as a type of “nanoreactor” that ultimately controls the type of polyaniline that is produced enzymatically. When DNA is used as the template, an electro-responsive polyaniline/DNA complex is formed where the conformation of the DNA may be controlled through the electronic state of the polyaniline.

Keywords: Polyaniline, Conductivity.

1. Introduction

Recently a new enzymatic approach was developed to synthesize water-soluble conducting polyaniline in the presence of sulfonated polystyrene (SPS) under mild; aqueous pH 4.3 buffered conditions.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. The SPS in this approach serves three critical functions. One is to provide the necessary counterions for doping of the synthesized polyaniline to the conducting form. The second is to maintain water solubility of the final PANI/SPS complex for facile processing. These first two functions are well understood and are not discussed. The third function is to serve as a template that preferentially organizes the aniline monomers prior to polymerization and promotes the head to tail coupling. Although it is known that the resulting polymer complex is in fact, the linear benzenoid-quinoid form of polyaniline, the mechanistic role of how the template directs the chain growth of the conducting polyaniline has not been completely understood. To gain insights into this mechanism, aqueous micelles and DNA were used as templates in the synthesis.

2. Experimental Sections

Materials. Horseradish peroxidase (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 10 mg/ml in pH 6.0, 0.1M phosphate buffer was prepared. Aniline (99.5%), poly(sodium 4-styrenesulfonate)(SPS) 70KD, sodium salt; sodium dodecylbenzenesulfonic acid (99%, SDBS) and benzenesulfonic acid sodium salt (99%, SBS) were obtained from Aldrich Chemicals Co. Inc., Milwaukee, WI and

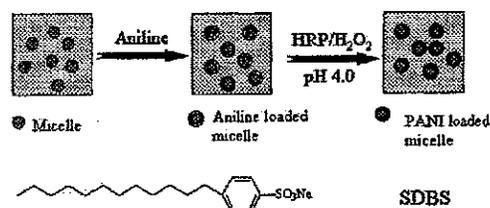


Fig. 1. Schematic of enzymatic synthesis of micellar polyaniline.

used as received. All other chemicals and solvents used were commercially available, of analytical grade or better and used as received.

Polymerization using Micellar Templates. Enzymatic polymerization of aniline in an aqueous micelle template system is shown schematically in Figure 1. The aqueous micelle solutions were prepared by dissolving surfactants into 30 ml of a 0.1M, pH 4.3 phosphate buffer to a concentration over the CMC (critical micellar concentration) with continuous stirring. Typically the concentration used was 10 mM, where the known critical micellar concentration (CMC) of SDBS is 1.6 mM. An equivalent molar amount of aniline was then added and stirred until dissolved. To this solution, 0.2 ml of HRP stock solution (10 mg/ml) was added and the reaction was then initiated by the addition of diluted H₂O₂ (0.02M). After drop wise addition of a stoichiometric amount of H₂O₂ under vigorous stirring for 1.5 hours, the reaction was left to stir for at least one more hour.

3. Results and Discussion

Aqueous micellar systems offer several interesting variations with which one may probe the roles of the template in these enzymatic reactions. The local environment created by this micellar aggregation of strong

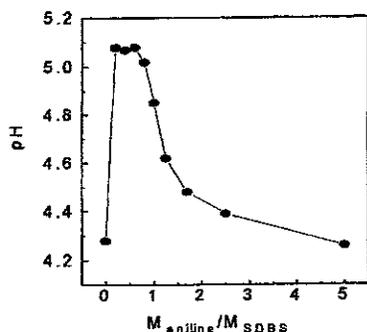


Fig. 2. The pH changes of the bulk solution. Two stock solutions, 0.2 M SDBS and aniline at the same pH were mixed together with different molar ratio ratios of aniline to SDBS. The bulk pH of the mixed solution is measured and plotted as function of the molar ratio of aniline to SDBS.

acid surfactant molecules is similar to that of strong acid polyelectrolytes. Each of these systems can form electrical double layers in which counterions such as H^+ may be condensed and can form hydrophobic pockets within which the monomers may associate.

To obtain the conducting polyaniline, both chemical and electrochemical polymerization of aniline must be carried out in strong acid media. It is expected that a low pH medium is also necessary for the synthesis of conducting polyaniline by enzymatic catalysis. The presence of the lower pH local molecular environment of the aqueous micelle is demonstrated by the bulk pH change of the solution during the process of loading aniline monomer with the micelles (Figure 2). An interesting jump of the bulk pH from 4.3 to 5.1 is observed with the addition of aniline to the SDBS micelle solution. The loading of aniline with the micelle is a process driven by electrostatic and hydrophobic interactions. The co-micelles or complexes of aniline and SDBS are formed spontaneously when the two stock solutions, SDBS micelles and anilines were mixed together. No chemical reaction is involved in this mixing process. Thus the bulk pH change may be explained by inhomogeneous distribution of the protons in the media; were protons are somehow trapped in the local molecular environments formed by aqueous micelles. Therefore, a necessary lower pH microenvironment for the growth of conducting polyaniline is provided by aqueous micelles. The bulk pH returns to 4.3 as the molar ratio of aniline to SDBS increases due to the dominance of aniline in the system.

More insight regarding the role of the template is provided by carrying out the enzymatic polymerization in the presence of the aqueous micelle system. Figure 3 shows the visible absorption spectra for the polyaniline formed in the presence of SPS (macromolecule), SDBS (above the CMC) and SBS (non-aggregating molecule). A comparison of these spectra shows that the polymer formed in the SDBS micelle system strongly absorbs from 800 to 1200 nm and is similar to that observed in the SPS system. The polyaniline formed in the micellar system is also water-soluble and in its doped state due to the presence of SDBS molecules. These results show that the micelles formed by the SDBS are suitable templates for the enzymatic synthesis of conducting polyaniline. However, the spectrum of the polyaniline

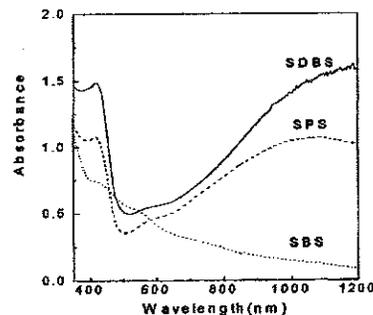


Fig. 3. UV-vis-near-IR spectra of polyaniline produced in 10mM SDBS, SPS and SBS solution.

is significantly different when the reaction is carried out in the presence of the non-aggregating molecule, SBS. In this case, the absorption peak is observed at much shorter wavelengths, near 500 nm, and is indicative of a more branched, insulating form of polyaniline. Since the concentration of SO_3 groups is the same for the SDBS and SBS, the primary difference in these systems is the formation of micelles with the SDBS.

The necessity of this local "micelle" environment was further investigated by carrying out the reaction in SDBS systems under conditions where micelle formation would be limited (with SDBS below the CMC and over the CMC but in the presence of 50% acetone, respectively). It was expected that under these conditions the SDBS molecules would be dispersed in the reaction media with minimal aggregation. The resulting polyaniline spectra (data not shown) show that under these poor micelle-forming conditions, the emeraldine salt form of polyaniline is not as readily obtained with the SDBS. These results suggest that the aqueous micelles formed by the SDBS serve as a nanoreactor that provides the necessary lower pH and hydrophobic local environment for the formation of conducting polyaniline.

Since the reaction conditions in this enzymatic approach are so mild, an extension of this work has included the use of DNA as the template. It was found that DNA could also provide this requisite nanoreactor environment and promote the formation of conducting polyaniline. A polyaniline/DNA complex is formed where the conformation of the DNA may be reversibly controlled through the oxidation state of the polyaniline. This binding of an electroactive polymer to a biological template and the ability to control the conformation of the template opens new possibilities for the fabrication of biosensors, diagnostic tools and a new ways to probe the fundamental properties of biological systems. In addition, the use of "nanoreactors" for polymer synthesis in general, may offer some yet unexplored opportunities towards new electronic and photonic materials.

References

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