Enzyme Structure, Function and Utility in Room Temperature Ionic Liquids

by

Bilge Eker

An Abstract of a Thesis Submitted to the Graduate

Faculty of Rensselaer Polytechnic Institute

in Partial Fulfillment of the

Requirements for the degree of

DOCTOR OF PHILOSOPHY

Major Subject: Chemical and Biological Engineering

The original of the complete thesis is on file

In the Rensselaer Polytechnic Institute Library

Examining Committee:

Jonathan S. Dordick, Thesis Adviser

Robert J. Lindardt, Member

Ravi Kane, Member

Pulickel M. Ajayan, Member

Rensselaer Polytechnic Institute
Troy, New York

December, 2007
(For Graduation December 2007)

ABSTRACT

The use of enzymes in nonaqueous media successfully competes with conventional aqueous based biocatalysis by enabling synthesis of various water insoluble compounds with high industrial and pharmaceutical importance through inherent enantio-, chemo-, and regioselectivity with reduced byproducts and high product purity. In recent years, ionic liquids have emerged as novel solvents for nonaqueous biocatalysis, being recognized as green solvents owing to having negligible vapor pressure, odorless, and nonflammable properties. In general, enzymes exhibit low activity in ionic liquids, and it is important to generate methods to enhance enzyme functionality in ionic liquids to achieve optimum biocatalyst formulations. The overall focus of this thesis work is on improving enzyme functionality and utility through the design of enzyme formulations and solvent engineering methods to increase the potential for performing applications of enzymes in ionic liquids.

Catalyst formulation is a useful method to improve enzyme functionality such as enzyme activity, stability, and processibility in ionic liquids. In the course of this work, the simple adsorption of the bacterial protease, proteinase K, onto single-walled carbon nanotubes resulted in intrinsically high catalytic turnover. The high surface area and the nanoscopic dimensions of single-walled carbon nanotubes (SWNTs) offered high enzyme loading and low mass transfer resistance. Furthermore, the enzyme-SWNT conjugates displayed enhanced thermal stability in RTILs over the native suspended enzyme counterpart and allowed facile reuse. These enzyme-SWNT conjugates may therefore provide a way to overcome key operational limitations of RTIL systems.

Solvent engineering is another approach that has been used to optimize enzymatic reactions in ionic liquids by choosing the appropriate solvent system for the specific enzyme substrate combination. As a synthetically valuable model system, soybean peroxidase (SBP)-catalyzed oxidative polymerization reactions were performed in various aqueous ionic liquid solutions and different phenolic compounds were used as substrates for the synthesis of high molecular weight polymers. Higher molecular weight

polyphenols were synthesized in the solvent system having higher ionic liquid content, owing to high dissolution capacity of ionic liquids. Thermal analysis showed that those polyphenols are highly thermostable and they have thermosetting properties.