

## **ORIGINAL PAPER**

## Preparation of aqueous polyaniline–vesicle suspensions with class III peroxidases. Comparison between horseradish peroxidase isoenzyme C and soybean peroxidase

<sup>a</sup>Katja Junker, <sup>b</sup>Ivan Gitsov, <sup>c</sup>Nick Quade, <sup>a</sup>Peter Walde\*

<sup>a</sup>Department of Materials, ETH Zürich, Wolfgang-Pauli-Str. 10, CH-8093 Zürich, Switzerland

<sup>b</sup> The Michael M. Szwarc Polymer Research Institute &Department of Chemistry, State University of New York, College of Environmental Science & Forestry, Syracuse, New York 13210, USA

<sup>c</sup>Department of Biology, ETH Zürich, Schafmattstr. 20, CH-8093 Zürich, Switzerland

Received 13 July 2012; Revised 28 September 2012; Accepted 22 October 2012

Aniline was polymerised enzymatically in aqueous solution at pH = 4.3 and  $25 \,^{\circ}C$  in the presence of submicrometer-sized vesicles formed from sodium bis(2-ethylhexyl)sulphosuccinate (AOT). H<sub>2</sub>O<sub>2</sub> served as oxidant and the enzyme used was either horseradish peroxidase isoenzyme C (HRPC) or soybean peroxidase (SBP), both being class III peroxidases. From previous studies with HRPC, it is known that stable vesicle suspensions containing the emeraldine salt form of polyaniline (PANI-ES) can be obtained within 1–2 days with a 90–95 % yield, provided that optimal reaction conditions are applied. Unfortunately, HRPC becomes inactivated during polymerisation. In the present study, a linear dendritic block copolymer was added to HRPC, resulting in higher operational enzyme stability; the stabilising effect, however, was too small to afford a substantial decrease in the required amount of enzyme. Moreover, replacing HRPC with SBP was of no advantage, although SBP is known to be more stable towards inactivation by H<sub>2</sub>O<sub>2</sub> than HRPC. By contrast, SBP was found to be much slower in oxidising aniline, and complete inactivation of SBP occurred before all the aniline monomers were oxidised, leading to low yields and the formation of over-oxidised products. The same was observed for HRP isoenzyme A2. Reactions without vesicles indicated that peroxidase inactivation was probably caused by PANI-ES.

© 2013 Institute of Chemistry, Slovak Academy of Sciences

Keywords: emeraldine salt, enzyme, peroxidase, polyaniline, template, vesicles

## Introduction

In 1998, Samuelson and collaborators reported that horseradish peroxidase (HRP), with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as oxidant, could successfully be applied as catalyst in the polymerisation of aniline to obtain polyaniline (PANI) in its conducting emeraldine salt form (ES) in an aqueous solution at pH = 4.3 containing sulphonated polystyrene (SPS) (Samuelson et al., 1998). The negatively charged SPS assists the polymerisation by in some way pre-organising the reacting monomers and intermediates and by acting as counter ions (dopants) through the formation of a soluble complex with the positively charged PANI (Liu

et al., 1999b). For this enzymatic polymerisation, the reaction conditions are less harsh than in the conventional chemical synthesis of conductive PANI, which usually is carried out with ammonium peroxydisulphate as oxidant at pH < 3 (Chiang & MacDiarmid, 1986; Geniès et al., 1990; Stejskal & Gilbert, 2002; Wallace et al., 2009). Therefore, the HRP/H<sub>2</sub>O<sub>2</sub>catalysed, SPS-assisted synthesis of conducting PANI appears promising for the development of an environmentally friendly aniline polymerisation process

<sup>\*</sup>Corresponding author, e-mail: peter.walde@mat.ethz.ch