

On the “soft template” effect of an enzymatic oligomerization reaction

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The oxidation of the aniline dimer, *p*-aminodiphenylamine (PADPA), with *Trametes versicolor* laccase and molecular oxygen was studied in aqueous solution at pH = 3.5. Depending on the experimental conditions used, oligomeric products are obtained, which originate from enzymatic as well as non-enzymatic follow-up reactions. The presence of dispersed anionic interfaces – also called “templates” – in the reaction mixture can have a significant and positive effect on the course of the reaction as with such templates products can be obtained which resemble the conductive emeraldine salt form of polyaniline (PANI-ES) [1-3]. Without templates, these products do not form. The effect of three different templates under their respective optimal conditions was investigated and compared in a systematic way by using UV/vis/NIR, EPR and Raman spectroscopy measurements, as well as an HPLC-MS analysis. The templates used were sulfonated polystyrene (SPS), micelles from sodium dodecylbenzenesulfonate (SDBS) – previously used by Shumakovich *et al.* [4] – and vesicles from sodium bis(2-ethylhexyl) sulfosuccinate (AOT). Although all three templates carry a sulfonate group and yield PANI-ES-type products, there are clear differences in the properties of the product mixtures obtained. Reasons for these differences are discussed.

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References: [1] Junker, K., Luginbühl, S., Schüttel, M., Bertschi, L., Kissner, R., Schuler, L., Rakvin, B., Walde, P. *ACS Catalysis*, **2014**, *4*, 3421. [2] Janošević Ležaić, A., Luginbühl, S., Bajuk-Bogdanović, D., Pašti, I., Kissner, R., Rakvin, B., Walde, P., Ćirić-Marjanović, G. *Sci. Rep.*, **2016**, *6*, 30724. [3] Luginbühl, S., Bertschi, L., Willeke, M., Schuler, L. D., Walde, P. *Langmuir*, **2016**, *32*, 9765. [4] Shumakovich, G., Streltsov, A., Gorshina, E.; Rusinova, T., Kurova, V., Vasil'eva, I., Otrokhov, G., Morozova, O., Yaropolov, A. *J. Mol. Catal. B: Enzymatic*, **2011**, *69*, 83.