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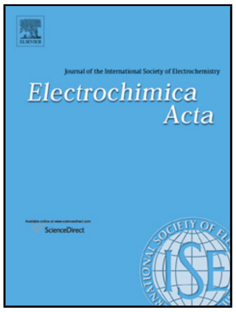

Title: In situ UV-visible spectroelectrochemistry in the course of oxidative monomer electrolysis

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ACCEPTED MANUSCRIPT

In situ UV-visible spectroelectrochemistry in the course of oxidative monomer electrolysis as a tool to characterize the molecular structure of poly(Mg(II)porphine)

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Abstract

Novel method to characterize the macromolecuar structure of an electroactive polymer deposited via electrooxidation of the corresponding monomer on the electrode surface has been proposed. It is based on experimental determination of the number of electrons spent for oxidation of an initially solute monomer species which is used to calculate the number of covalent bonds linking each monomer unit with neighboring units inside the polymer. The former parameter is found by tracing simultaneously the variations of instantaneous values of the solute monomer concentration and of the passed charge in the course of the monomer oxidation electrolysis. This monomer concentration is established with the use of its UV-visible absorbance in the vicinity of the monomer band(s) during this process on the basis of an original procedure to separate the absorbances due to the monomer and solute oxidation products for each instantaneous spectrum. Correctness of the proposed method (including its theoretical principles, home-made installation and experimental realization) has been examined for the polypyrrole deposition, with the conclusion on its (mostly) chain structure, which is in conformity with previous evidences. Then, our approach has been applied to the electrooxidative polymerization of (non-substituted) Mg(II) porphine, for which an indirect experimental information of its molecular structure has only been available earlier. The spectroelectrochemical method has resulted in the conclusion that the oxidation product, poly(Mg(II)porphine), consists of chains of single-bonded monomeric porphine macrocycles, with a relatively small number of interchain bonds.

Keywords

Electroactive materials, electropolymerization, unsubstituted porphine, redox equivalent, conjugated polymer, solute oligomers

1. **Introduction**

Electroactive materials containing the porphine macrocycle in their structure are actively studied [1,2] in view of their applied prospects in electrocatalysis [3-7], photocatalysis [8], sensors [9,10], solar energy conversion [11-13], non-linear optics [14,15], etc. Another research direction is oriented to synthesis of catalytic metal (M) containing centers of the MN_4 type on the surface of carbon support for their application as platinum-free catalysts of oxygen reduction for fuel cells [4, 7, 16–19].

Porphine unit is present in most systems as a pendant group of a polymer chain. There are a few examples of copolymers possessing a well-defined molecular structure of alternating porphyrin and (hetero)aromatic units which are mostly synthesized by organometallic catalysis, see e.g. refs [20-24]. On the contrary, molecular structures of polymer films deposited by direct oxidation of substituted porphyrins on electrode surface were not studied [25-28].

Our team succeeded in synthesis of the first homopolymer (pMgP-I) on the basis of non-substituted Mg(II) porphine (MgP, Fig. 1a) [29]. This polymer has been characterized by combination of methods of electrochemistry, spectroscopy and

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