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Co-polymers of oligolactic acid and tetrasubstituted thiacalix[4]arenes as a new material for electrochemical sensor development

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ABSTRACT

New derivatives of oligolactic acid (OLA) have been obtained by cross-esterification with carboxylated thiacalix[4]arene derivatives in *cone*, *paco* and *1,3-alternate* configurations. The products of the reaction characterized by NMR ^{1}H, FTIR-ATR spectroscopy, MALDI-TOF mass spectroscopy and elemental analysis have been applied for surface modification of glassy carbon electrode (GCE). Electrochemical characterization with redox probes (ferricyanide ion and Methylene blue (MB)) showed predominant influence of electrostatic interactions influencing the flux of the charge carriers over the diffusion control. The role of a macrocycle moiety on the surface morphology and sensitivity toward measurement conditions has been established. The electrodes covered with new materials were applied as transducers in sensing specific DNA interactions and acetylcholinesterase (AChE) based hydrolysis of acetylthiocholine. This made it possible to distinguish factors affecting the DNA structure (MB intercalation, oxidative DNA damage, thermal denaturing) whereas immobilization of the AChE on the silver dendrites deposited in the inner volume of the polymers allowed recording the signal of thiocholine oxidation at extremely low working potential (0 mV vs. Ag/AgCl).

1. Introduction

During the last decades, there was an enormous increase in the interest toward sensors and their applications [1–3]. Physical, chemical and biochemical sensors are intended for provision of information on the environment that is highly required for establishment of safety conditions for human life and for the support of industrial processes and technologies [4]. Besides many others, two areas of sensor applications are mostly considered, i.e., environmental monitoring and medical diagnostics. The appropriate devices mainly detect and quantify environmental pollutants, food additives, metabolites, disease biomarkers and many other species [5,6]. Taking into account autonomous operation and compact design as main requirements to the chemical and biochemical sensors, complex solutions covering the formation of sensing layer, its mechanical protection, transduction of receptor binding sites with the transducer are needed, especially on the stage of sensor manufacture, testing and routine use [7].

Functionalized polymers are considered as one of the tools that allow reaching the topics of sensor development mentioned above [8]. Particularly, in electrochemical sensors polymers are commonly used as mechanical support and inert matrix for entrapment of the synthetic and biochemical receptors and auxiliary agents [9–11]. Introduction of functional groups or material processing are able also to establish some specific properties offering new opportunities in sensor assemblies. Thus, ion-exchanging materials and polymer with molecular imprints discriminate the transfer of low-molecular compounds in accordance with their charge and size [12–14]. Polymeric composites have been proposed for prevention of the electrode fouling [15]. If available, commercial materials and polymeric membranes produced for use in electrophoresis and protein/DNA purification can be used. Teflon® [16], nylon [17] and cellulose derivatives [18–20] are often reported in such sensors. In other cases, polymeric layers onto transducer can be obtained by electropolymerization [21], sol-gel polycondensation [22] or casting from solutions in organic solvents. The latter protocol being universal, can be applied for the majority of polymers but has some limitations related to low solubility of certain materials and lesser

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