

Anodic Polymerization of ω -Diamines leading to Polyalkyleneimine : Mechanism, Properties and Applications.

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This study deals with the anodic oxidation of primary aliphatic non-conjugated ω -diamines. Recently it has been pointed out that an electrode passivation occurs when the anodic oxidation of an electrolyte composed with one salt dissolved in one pure ω -diamine is performed [1]. The electrode passivation only occurs with unsubstituted primary ω -diamines $H_2N-(CH_2)_n-NH_2$. The methods of choice for underlying this phenomenon are Electrochemical Quartz Crystal Microbalance coupled with Cyclic Voltammetry. The electropolymerization of ω -diamines occurs on different metallic or semiconducting electrodes such as gold, platinum, glassy carbon, p or n-type silicon, Fluorine Tin Oxide (FTO).

Several spectroscopic analysis such as InfraRed Attenuated Total Reflection (IR-ATR) or InfraRed Absorption Spectroscopy (IRAS), Raman and X-Ray Photoelectron Spectroscopy (XPS) were performed on the thin films obtained at the electrode surfaces [2]. The polymer synthesized during the anodic oxidation of an ω -alkyldiamine is a linear polyalkyleneimine. It was shown that ethylenediamine leads to linear polyethyleneimine (PEI) while 1,3-DAP yields linear polypropyleneimine (PPI). DETA, which is the dimer of EDA, induces PEI too.

The mechanisms of electropolymerization leading from diamines to polyalkyleneimines were obtained using *ab initio* calculations at the Hartree-Fock (HF) level of theory (Figure 1). So as to establish the polymerization mechanism, we performed these HF quantum-chemical calculations since they allow us to modelize short-lived or unstable intermediates and even transition states. So they can provide information about some intermediates which are difficult, and even impossible, to render evident through experiments. Thus thanks to quantum-chemical calculations of the energy in gas phase or in solution and of some thermochemical properties of the different intermediates, we established the successive steps of the polymerization mechanism of ω -diamines [3,4].

Platinum electrodes, modified by a coating of a thin linear PEI film, resulting from the anodic oxidation of pure ethylenediamine have been tested as pH sensors [5]. They exhibited potentiometric responses sensitive to pH changes in aqueous media. This response is linear, reversible and stable in time.

The potentiometric responses of the PEI films to $[NH_3]$ changes was also successfully tested. From these results we propose PEI to be used in analytical chemical sensors and in biosensors since we have also developed potentiometric enzymatic urea biosensors. More we made miniaturized pH sensors (Figure 2) so as to promote a commercial application using photolithography, sputtering and lift-off process so as to make interdigitated microarray electrodes [5]. Finally, we showed that olfactory cells can grow on electropolymerized PEI and PPI films previously coated on Fluorine doped Tin oxide (FTO) surfaces (Figure 3) since these polymers are biocompatible.

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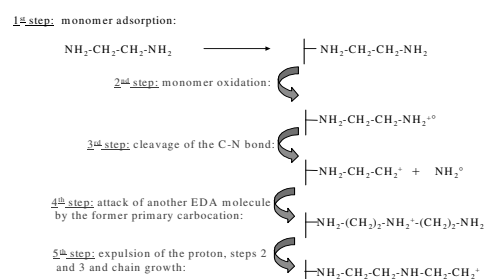


Figure 1 : Mechanism of Electropolymerization established using *ab initio* Calculations

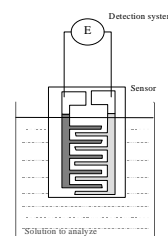


Figure 2 : Functioning Principles of the Chemical Microsystems

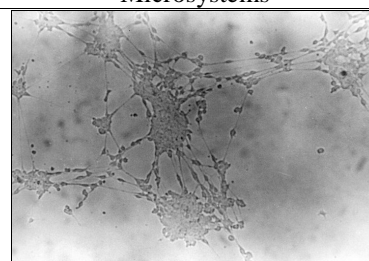


Figure 3 : Image of Olfactory Cells cultivated on a FTO Surface coated with a Polyethyleneimine Film