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### Molecular level structure of biodegradable polymeric materials

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Despite of the constant improvement of the synthesis methods, synthetic polymers may show a structural heterogeneity related with topology (linear, cyclic, and branched), composition and comonomers composition distribution (different functional groups, sequence of monomers). This makes the structural and molecular analysis of synthetic polymers quite a complex analytical task. The knowledge of structure-property relationships is essential for the successful application of polymeric materials, especially in biomedical applications such as tissue engineering and delivery system of bioactive compounds and cosmetic modifications. Therefore, there is a continuous require for the development and detailed characterization of new polymeric materials. In this contribution our recent results concerned with application of ESI-MS and electrospray multistage mass spectrometry (ESI-MS<sup>n</sup>) techniques for advanced structural characterization of new biodegradable polymeric materials based on the aliphatic (co) polyesters will be reported. A new biodegradable polymeric materials with different architecture for potential application as biomaterials for medical and cosmetology purpose were synthesized via. anionic ring opening polymerization (ROP). Furthermore, application of mass spectrometry for monitoring the hydrolytic degradation process of the obtained homo and copolyester, which gave the detailed insights into the hydrolysis process and allowed on identification of the degradation products release from them into the water will be demonstrated.

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### Comparison of the MALDI and TiO<sub>2</sub>-assisted SALDI mass spectra of hormones and amino acids

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Surface-assisted laser desorption/ionization time of flight mass spectrometry (SALDI-TOF MS) have great potential to overcome poor reproducibility and high matrix-arising background in the low mass region, which commonly occur in the matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectra. In addition to a variety of highly abundant matrix-related ions in the low-mass range of the spectra, there are potential undesired polymerization reactions, which complicate the spectra, and in some cases, even prevent the detection of the ions of interests. In contrast, nanoparticles as substrates generate a lower number of background signals and low onset of fragmentation reactions in the gas phase. In this work, we compare the spectra of steroid hormones (estradiol, testosterone, progesterone), steroid medication (dexamethasone), amino acids (L-cysteine, L-alanine, L-methionine) and tripeptide (glutathione) acquired with traditional, organic matrices (DHB, 9AA, CHCA and THAP) with the spectra acquired with titanium dioxide (TiO<sub>2</sub>) nanoparticles of various shapes and dimensions, i.e. colloidal TiO<sub>2</sub> nanoparticles (TiO<sub>2</sub> NPs, average diameter ~5 nm), prolate nanospheroids (TiO<sub>2</sub> PNSs, length: 40–50 nm, the lateral dimension: 14–16 nm) and nanotubes (TiO<sub>2</sub> nanotubes, length: 100–150 nm, average diameter 11 nm). Various shapes and dimensions of substrates were used because it is well known that these factors determine the process of desorption and ionization. To compute repeatability (within day) and intermediate precision (between days) of MALDI and SALDI TOF techniques we used Excel tools (ANOVA test). In addition, homogeneity of the sample/matrix distribution on the target was also calculated and expressed as the coefficient of variation of a series of measurements. In summary, our results show that all three TiO<sub>2</sub> nanoparticles have great potential for the detection and analysis of steroid hormones and amino acids with good analytical parameters (all variations do not exceed 15%). Additionally, homogeneity of the sample/substrate mixture distribution on the target plate was satisfactory. Laser-induced ionization on nanostructures offers alternative ionization pathways through the formation of Na<sup>+</sup> and K<sup>+</sup> adducts with appreciable yield, in contrast to numerous matrix-adducts detectable in the MALDI spectra acquired with traditional matrices. All the examined molecules were detectable in the negative ion mode with TiO<sub>2</sub>, which was not the case with all other organic matrices and substrates. Other advantages of the application of TiO<sub>2</sub> nanoparticles as substrates for the analysis of low mass molecules are discussed.

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