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Review

Modern mass spectrometry in the characterization and degradation of biodegradable polymers

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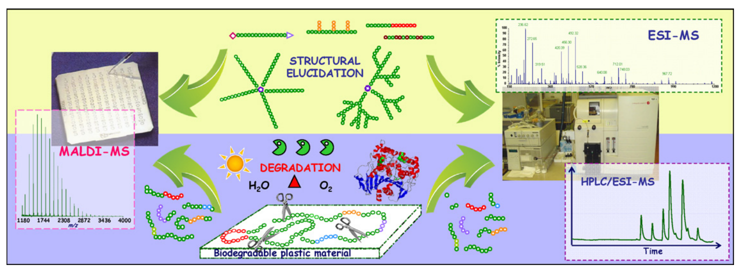
HIGHLIGHTS

- Recent trends in the structural characterization of biodegradable polymers by MALDI and ESI MS are discussed.
- MALDI MS as a noteworthy tool to follow the synthetic polymerization route of biodegradable materials is evidenced.
- Elucidation of degradation mechanisms by modern MS techniques is examined.
- ESI MS and HPLC–ESI MS are highlighted as highly suitable methods for structural and quantitative analysis of water-soluble biodegradation products.
- Novel MS methods developed ad hoc and new MALDI matrices for biodegradable polymers are reviewed.

GRAPHICAL ABSTRACT



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ABSTRACT

In the last decades, the solid-waste management related to the extensively growing production of plastic materials, in concert with their durability, have stimulated increasing interest in biodegradable polymers. At present, a variety of biodegradable polymers has already been introduced onto the market and can now be competitive with non biodegradable thermoplastics in different fields (packaging, biomedical, textile, etc.). However, a significant economical effort is still directed in tailoring structural properties in order to further broaden the range of applications without impairing biodegradation. Improving the performance of biodegradable materials requires a good characterization of both physico-chemical and mechanical parameters. Polymer analysis can involve many different features including detailed characterization of chemical structures and compositions as well as average molecular mass determination. It is of outstanding importance in troubleshooting of a polymer manufacturing process and for quality control, especially in biomedical applications. This review describes recent trends in the structural characterization of biodegradable materials by modern mass spectrometry (MS). It provides an overview of the analytical tools used to evaluate their degradation. Several successful applications of MALDI-TOF MS (matrix assisted laser desorption ionization time of flight) and ESI MS (electrospray mass spectrometry) for the determination of the structural architecture of biodegradable macromolecules, including their topology, composition, chemical structure of the end groups have been reported. However, MS

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methodologies have been recently applied to evaluate the biodegradation of polymeric materials. ESI MS represents the most useful technique for characterizing water-soluble polymers possessing different end group structures, with the advantage of being easily interfaced with solution-based separation techniques such as high-performance liquid chromatography (HPLC).

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Contents

Paola Rizzarelli was born in Catania (Italy) on October 16th, 1972. She graduated in Chemistry in 1996. In 2001 she got a Ph.D. in Chemical Sciences at the University of Catania under the supervision of Professor Giorgio Montaudo. Since October 2001, she is CNR Researcher at the Institute of Chemistry and Technology of Polymers. Her research interests concern the synthesis, characterization and degradation of biodegradable polymeric materials. Her scientific activity involves the application of modern mass spectrometry in the characterization of polymers, the investigation of photo-, thermo-oxidation, and thermal degradation mechanisms and products by MALDI MS, and in the analysis of fragmentation mechanisms of synthetic polymers by tandem MS.

Sabrina Carroccio received a Ph.D. degree at the University of Catania in 2002 under the supervision of Professor Giorgio Montaudo. Since 2001, she is a researcher at the Institute of Chemistry and Technology of Polymers of the National Research Council (CNR) in Catania. She has authored 30 peer reviewed international papers and 2 book chapters. Her research interests on degradation include characterization of macromolecules by Mass Spectrometry (MS) techniques, pyrolysis, thermo and photo oxidation mechanisms of polymers. Particularly, she has worked on the development of modern MS as a new method for studying deterioration mechanisms of polymeric materials.

1. Introduction

In the last century, astonishing progress in material science and technologies made our daily life more and more comfortable and self-confident. A variety of synthetic polymeric materials have been developed and used as synthetic fibers, plastics, and rubbers in place of the traditional natural ones. Nowadays, synthetic polymers play an important role in the development of controlled delivery devices for a variety of applications correlated to drugs, food-related bioactive ingredients, and genes. Synthetic polymers with a wide range of mechanical properties, durability, performance and cost, are extensively employed in the daily needs of contemporary society, ranging from simply packaging to construction, electronic devices and medical appliances, etc. Plastics have been playing an important role in the improvement and quality of life since they were invented. In 2011 about 280 million tons of plastics were produced all over the world, with an increase of about 4% from 2010. Most of these plastics are of petroleum origin; consequently, the higher and higher production of plastic materials results in the increase of oil consumption. Additionally, due to their persistence in the environment, polymeric materials contribute seriously to the environmental pollution. The worldwide augment in plastics waste has involved a great deal of strategies aimed at minimizing the negative impact of the increasing production and consumption of polymeric materials. The depletion of fossil resources and the waste accumulation problems have stimulated an increasing interest in biodegradable polymers.

Biodegradable polymers are defined as degradable materials in which the degradation results from the action of microorganisms and ultimately the material is converted to water, carbon dioxide (in the case of aerobic degradation) and/or methane (in the case of anaerobic degradation) and a new cell biomass. The biodegradation of plastics is usually a heterogeneous process. Because of a lack of water-solubility and the size of the polymer molecules, microorganisms are unable to transport the polymeric material directly into the cells where most biochemical processes take place; rather, they must first excrete extracellular enzymes which depolymerize the polymers outside the cells. As a consequence, if the molar mass of the polymers can be sufficiently reduced to generate water-soluble intermediates, these can be transported into the microorganisms and fed into the appropriate metabolic pathways.

The idea of degradable plastics, which would return to the earth in a mineralized state after they are discarded, is very appealing also because such materials might require less energy to be produced than conventional plastics. Since the issue of biodegradable polymers caught wide notion in the early 1970s, biodegradable polymers have received extensive investigations from academia and industry and experienced several important stages of improvement.

Biodegradable polymers can be classified into four major categories: natural polysaccharides and other biopolymers; polyesters produced by microorganisms; synthetic polymers from bio-derived monomers; polyesters from fossil-based monomers [1]. Synthesis [1–3], properties, processing and applications [1,3,4] of biodegradable plastic materials have been recently reported. Most of the biodegradable polymers belong to the polyester group (Fig. 1). This is due to the ester-containing covalent bond with a reactive polar nature. It can be broken down easily by the hydrolysis

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