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Review

# The Closure of the Cycle: Enzymatic Synthesis and Functionalization of Bio-Based Polyesters

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**The polymer industry is under pressure to mitigate the environmental cost of petrol-based plastics. Biotechnologies contribute to the gradual replacement of petrol-based chemistry and the development of new renewable products, leading to the closure of carbon circle. An array of bio-based building blocks is already available on an industrial scale and is boosting the development of new generations of sustainable and functionally competitive polymers, such as polylactic acid (PLA). Biocatalysts add higher value to bio-based polymers by catalyzing not only their selective modification, but also their synthesis under mild and controlled conditions. The ultimate aim is the introduction of chemical functionalities on the surface of the polymer while retaining its bulk properties, thus enlarging the spectrum of advanced applications.**

## Trends

Different integrated biotechnological advances are gradually replacing petrol-based chemistry and contribute to the development of new chemicals and plastics. Some biobased polymers, such as PLA, are chemically synthesized and are already available on an industrial scale.

A long-term contribution to the production of renewable building-blocks and monomers is expected from biotechnology research on the bioconversion of $CO_2$ and microbial electrocatalysis.

Advanced applications of polymers are obtainable by introducing chemical functionalities on the surface of the polymer while retaining its bulk properties. Such modifications can change the superficial hydrophobicity as well as introduce a 'pendant' as anchoring point or for successively chemical modifications. These possibilities are of key importance, especially for biomedical applications.

Biocatalyzed polymerization is not yet economically competitive. The conventional process configurations and reactors used in chemical synthesis do not respond to the complexity of the biocatalytic systems. Thus, the need to improve mass transfer while preserving the integrity of the biocatalyst still requires a specific tailored solution.

Robust enzyme immobilization, as well as thin film conditions or ionic liquids, are some of the solutions proposed for overcoming such limitations.

## Introduction

For several decades, the demand for polymers and plastics derived from fossil fuels has grown at a faster rate than for any other group of bulk materials, and expectations are that this trend will continue until 2020 [1]. With the worldwide increase in demand, the amount of plastic material released to the environment has become a significant problem because such material does not biodegrade easily or quickly, if at all, leading to ecological problems such as the formation of plastic patches in the ocean or in rivers [2]. The UN Environmental Programme estimated that the overall natural capital cost of plastic use in the consumer goods sector each year is US$75 billion, representing financial impacts resulting from issues such as pollution of the marine environment or air pollution caused by incinerating plastic. Of the natural capital costs of plastic, 30% are due to greenhouse gas emissions from raw material extraction and processing [3].

Biotechnology research has responded to the need to mitigate the environmental impact of plastics with research and technological innovations that now enable the biotechnological production of bio-based monomers from **renewable** carbon (see Glossary) on an industrial scale [4].

Among polymers, polyesters are a widely used class with applications ranging from clothing to food packaging and from the car industry to biomedical applications. The possibility to synthesize polyesters from bio-based monomers is demonstrated by PLA, currently the most important bio-based polyester in terms of volume, with a capacity of approximately 180 000 tons/y. Renewable polyesters can be also biosynthesized by microorganisms through complex regulatory pathways responding to external stimuli, including poly(hydroxyalkanoate)s (PHAs), which

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are **biodegradable** microbial polyesters commercially produced via fermentation, although we do not discuss them here [5].

Research aiming at developing the next generation of bio-based polyesters must not only address their sustainability, but also pursue their competitiveness in terms of their superior technological and functional properties. Biocatalysis goes a step further by enabling the synthesis of structured, functionalized, and biodegradable polyesters through highly selective and benign synthetic processes. Moreover, biocatalysts enable targeted hydrolyses and modifications of polyesters that are not possible with conventional chemical strategies [6,7]. Here, we illustrate how polymer chemistry is already benefitting from a range of biotechnological advances that enable the environmentally sustainable production of high-quality polyesters with new functional properties. Innovations in the field of bio-based polyesters are a paradigm of the increasingly intimate integration between biotechnologies and sustainable chemistry, which responds to the pressing challenges of a circular economy [8].

## Bio-based Monomers and Polyesters

The percentage of chemical production based on biotechnology is estimated to increase from less than 2% in 2005 to approximately a quarter of all chemical production by 2025 [9,10]. The largest contribution will come from the conversion of renewable carbon into chemicals via biotechnological routes. Factors boosting the integration between biotechnology and chemistry include the expected decrease in petroleum production and concerns about $CO_2$ emissions; however, there is also the need to improve public confidence in the chemical industry. Although only 7% of worldwide petroleum consumption is currently used for chemical production, bio-based processes leading to platforms of chemical building blocks will create higher added-value compared with current biofuel production processes [4].

By 2030, the market value of bio-based building blocks is expected to reach €3.2 billion, whereas the demand for fermentation-based chemical building blocks was less than €700 million in 2013[i].

Such building blocks could either be produced from renewable carbon through green chemical conversion routes or via microbial conversions. The incorporation of fermentative production of basic building blocks as unit operations in integrated **biorefineries** [4] is dependent on intense research activities ranging from microbial strain development and engineering to fermentation and down-stream processing optimization. Different critical analyses of research advances for enhancing the commercial potential of specific building blocks have been extensively reviewed elsewhere [11,12].

Strong research efforts are also currently directed towards the bioconversion of $CO_2$ into chemical building blocks by designing artificial metabolic routes or through microbial electrocatalysis. However, intense fundamental research is still needed before consumers will benefit from the practical applications of such technologies [12].

One of the key end uses for bio-based building blocks is expected to be in the production of bio-based polymers, with a projected market value for renewable plastic of €5.2 billion by 2030 [10]. Recent industrial analysis (November 2015) suggested that worldwide production capacity will triple from 5.7 million tons in 2014 to nearly 17 million tons in 2020[ii]. The most relevant monomers already available for use in fermentation technologies or in chemical processes and that are already tested in the synthesis of polyesters are detailed in Table 1.

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