Exploring Biocatalyzed Lactone Building Blocks Toward Biobased Polyesters

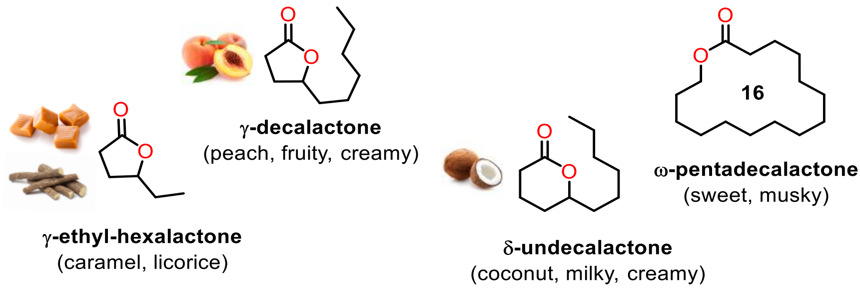
CHAPTER 10

Valorization addendum

10.1 Potential markets for lactones synthesized using biocatalysts

In this thesis, the biocatalyzed synthesis of (alkyl substituted) lactones was demonstrated. Several sectors have been identified that are relevant for the industrial development of lactones, in particular when they are obtained from biotechnological routes. Potential markets for (biobased) lactones prepared using biocatalysts include flavors & fragrances (F&F), as well as specialty polymers.

- **Flavors, fragrances and cosmetic ingredients.** This market was estimated to 26 billion dollars in 2017.[1] Examples of lactones that are relevant for this market are given in Scheme 10.1. In this sector, natural ingredients obtained from natural processes such as fermentation or biocatalyzed processes have a commercial added value. Additionally, biocatalysis is advantageous because it is enantioselective, meaning that it can enable the production of pure enantiomers. This is especially needed for lactones for which one enantiomer differs in intensity or in character. The market value of ingredients in F&F is estimated to less than 15 € kg^{-1}.[2]



Scheme 10.1. Examples of lactones used in flavors & fragrances with corresponding fragrances.

- **Additives in dispersions, emulsions, and inks.** So far, the vast majority of lactones used as precursors for polymers that are reported in the literature are synthesized chemically. As a consequence, the normal or proximal lactones are typically obtained. Thanks to the selectivity of enzymes, new structures of lactones can be produced. These lactones may give rise to polymers with novel properties. In addition, lactones synthesized using biocatalysis are seen as more sustainable or greener (although the environmental benefit of biocatalysis is not applicable to all processes by default and has to be proven on a case-to-case basis). As such, the corresponding additive polymers could be used as dispersing agents, emulsifiers, and encapsulators of added market value.

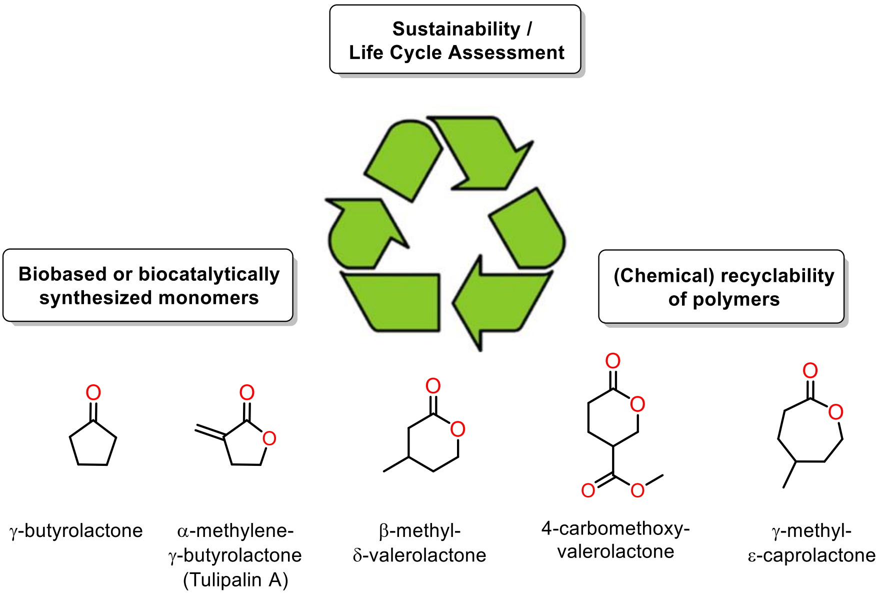
10.2 Transition to a more sustainable chemical industry: recyclable polymers

In 2016, 8.4 million tons of plastics were recycled in Europe while 60 million tons were produced, with a total of 335 million tons plastics produced worldwide.[3] The recyclability of polymers is crucial for a circular economy. In fact, plastic recycling addresses the mismatch between the long lifetime of plastics and their short use, which results in massive amounts of plastic waste.

There are several ways to recycle a polymer, depending on the goal that is to be achieved with recycling. **Mechanical recycling** is used to reshape polymers. It can however lead to lowered mechanical properties due to potential degradation of the polymer upon recycling. Similarly, **biological degradation**, or biodegradability, does not allow recovering the starting building blocks. As such, **chemical recycling** has appeared to be an emerging recycling strategy.[4] It consists of the depolymerization of polymeric materials under controlled conditions to recover either the starting monomers, or to upgrade them to new building blocks. Chemical recycling typically includes pyrolysis, thermodynamic recycling, and solvolysis.[5]

Because ring opening polymerization (ROP) is a thermodynamically-driven type of polymerization, polymers prepared from lactones are particularly relevant for chemical recycling. This type of recycling allows recovering the lactones as starting materials, which is considered as one of the most sustainable ways to recycle them. Bioprocesses and the integration of life cycle assessment (LCA) have both been identified as key green research areas.[6] As such, the use of biocatalysis to synthesize monomers, the chemical recyclability of the corresponding polymers and a sustainability assessment of the processes are correlated as shown in Scheme 10.2. Although biocatalysis adheres in principles to the rules of green chemistry, its environmental benefits have to be proven on a case-to-case basis as was mentioned earlier.[6-7]

The chemical recyclability of polymers from γ-butyrolactone was among the first one to be demonstrated.[8-9] Recycling is achieved either by non-catalyzed thermal processes or by using a catalyst at room temperature. Polymers obtained from the ROP of the functionalized α-methylene-γ-butyrolactone (Tulipalin A), which is biobased, can also be chemically recycled upon heating.[10] This is due to the extremely low ceiling temperature of this monomer (T_c = - 52 °C at 5 M), which means that the polymer is thermodynamically prone to depolymerization. β-Methyl-δ-valerolactone is another example of a monomer that is obtained from biomass whose polymers can be chemically recycled. This



Scheme 10.2. Relationship between chemical recyclability of polymers, biobased origin or use of biocatalysis and sustainability.

monomer is particularly relevant because its preparation by fermentation has been established, and is currently being commercially exploited by the company Valerian Materials.[11-12] Examples of polymers produced from this monomer include recyclable cross-linked elastomers from polyesters[13] and flexible polyurethane foams.[14]

Two other relevant monomers are functionalized ε-caprolactone derivatives. The first one is γ-methyl-ε-caprolactone, which can be obtained using biocatalysis.[15] In addition, the techno-economic feasibility of its production from *p*-cresol (biobased platform chemical from lignin) was established for a potential industrial production of several kiloton per year.[16] The monomer can be recovered from the cross-linked polyester by recycling *via* enzymatic hydrolysis.[17] The second one, γ-carbomethoxy-ε-caprolactone is a monomer produced from malic acid which is a "top added-value chemical". The corresponding polymer was shown to be chemically recycled using tin octanoate as catalyst.[18]

In conclusion, lactones and polymers therefrom have potential for commercialization in multiple markets. Together with a production from renewable resources and using bio-technology, their environmental advantage must be demonstrated to make them fully competitive in tomorrow's biobased economy.

10.3 References

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