Synthesis of biobased monomers and polymers

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The project aim is to develop sustainable synthetic reaction pathways for the synthesis of monomers of biological origin and, consequently, the development of polymers of biological origin. Vegetable originated substrates deriving from the agri-food sector are of particular interest. The intent is to transform waste materials characterized by low cost and wide availability into high added value products.

In accordance with the growing environmental awareness of the scientific community, all synthetic procedures will be environmentally sustainable. All procedures will be optimized to have excellent atom economy and reduced waste production, to avoid the use of toxic reagents and solvents, and will be conducted under environmentally sustainable conditions with reduced energy input, such as low temperature and pressure. The so-produced monomers and polymers will undergo characterization by their chemical and mechanical properties.

Particular focus will be put on the production of vinyl monomers (olefins) which will then be employed in atom transfer radical polymerization (ATRP) processes. The ATRP technique relies on the establishment of a reversible activation/deactivation equilibium between dormant species and growing chains mediated by a complex of a transition metal, which is usually copper. Furthermore, it allows to retain control over the molecular weight distribution by altering the reaction conditions. The so-produced polymers are pseudo-living, giving the possibility of producing alternating block copolymers. ATRP processes take place under mild reaction conditions and require minimal amounts of catalyst in order to function, making them environmentally bening.

ATRP was chosen since our research group has an been studying it on styrene for years and we would be interested in expanding its application to other vinyl monomers. Moreover, at the current state olefins are almost entirely of petrochemical origin, with a limited number of publications focusing on their production which do not involve the use of sensitive and/or toxic reagents and handling techniques that are incompatible with industrial applications.

An interesting aspect of the production of vinyl monomers from biological substrates is their molecular architecture. Biobased substrates often have complex molecular architecture, bearing various functional groups. Consequently, the deriving vinyl monomers will be bear more functional groups than their petrochemical analogues despite structural similarities, and so the corresponding polymers will. The difference in structure has two consequences. First, the deriving polymers will have additional properties compared to their analogues. Second, those polymers could undergo further transformations involving their functional groups once the polymerization processes have ended, allowing the production of high added value materials. As so, the topic of polymer derivatization will be studied as well during the course of this PhD project.

Another research topic that will be pursued in this PhD project is bisphenol A (BPA) replacement in the production of epoxy resins. BPA has been banned all across Europe as it is an endocrine disruptor and its use is currently prohibited in the construction sector, which relies on epoxy resins in mortar production. Therefore, there is a need for developing a less toxic alternative to BPA and bisphenols, in general. Research efforts will be directed towards substrates bearing a aromatic rings and hydroxyl mieties, which will be condensed to afford a BPA-like structure and functionalized accordingly to bear the epoxy moiety.