Manganese catalyzed limonene epoxidation and ρ,α-dimethylstyrene radical polymerization

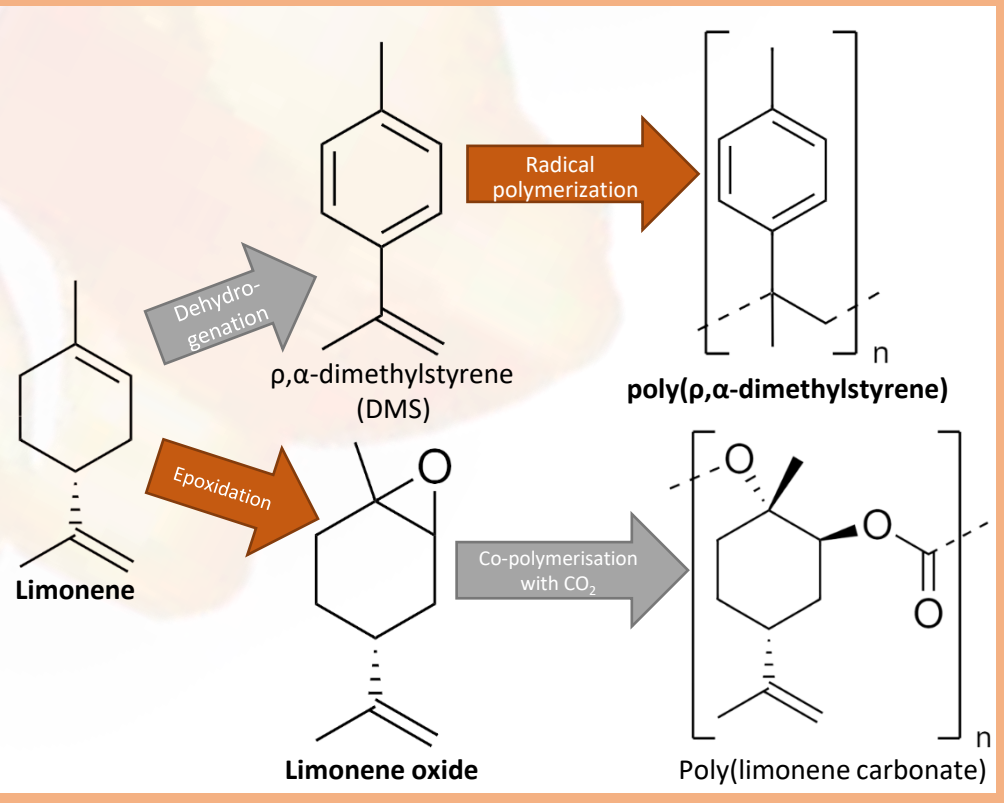
Introduction and goal of the project

Climate change and **resource scarcity** are one of the most current urging issues. The linear economy is one of the main causes of these problems, whereas the opposing **circular economy** provides solutions. For the chemical industry, this means moving away from fossil resources and towards **biobased resources**. Making use of biobased waste streams ties even more into the circular economy. Examples of such **waste streams** are rejected bananas, used coffee grounds, or orange peels. Various companies are treating these waste streams and as new resources. One of these companies is **PeelPioneers**, which currently processes orange peels to make new resources such as essential oils and fiber.

Limonene is the main component of the extracted essential oil. This compound is mainly used as a cleaning agent. However, it has the potential to be a resource for **biobased plastics**. In this research, two ways were explored to produce bioplastic from limonene. An overview can be seen in the flow scheme below. Poly(p,a-dimethylstyrene) and poly(limonene carbonate) are two potential bioplastics made from limonene. This research focusses on the **radical polymerization** of ρ,α-dimethylstyrene (DMS) **poly(ρ,α-dimethylstyrene)** and the **epoxidation** of limonene to **limonene oxide**.

The radical polymerization of DMS is build upon the work of my predecessor **Tycho Dings**, who explored limonene polymerization. This did not work, polymerization of the more stable DMS aims to solve this.

Epoxidation is done with a **manganese based catalytic system**, as proposed by Dong et al. (2012), which is a greener option as opposed to conventional ways. It is aimed to **scale up** the reaction tenfold. And also to determine the ***cis/trans* ratio** of the product, limonene oxide, which is important for further co-polymerization.



Limonene conversions and limonene oxide yields measured by GC

Epoxidation	Point of measurement	Limonene conversion	Limonene oxide yield
Long small scaled epoxidation	During reaction (t=0)	50,4%	0,3%
	During reaction (t=30)	77,8%	17,7%
	During reaction (t=60)	80,1%	20,2%
	During reaction (t=90)	88,5%	14,0%
	During reaction (t=120)	92,5%	15,7%
	During reaction (t=180)	92,5%	17,0%
	During reaction (t=240)	92,9%	17,0%
Upscaled epoxidation	Before cooling step	-4,2%	0,3%
	After cooling step	-45,6%	0,3%
	During reaction (t=0)	-26,2%	5,4%
	During reaction (t=30)	46,9%	36,3%
	During reaction (t=60)	52,1%	40,5%
	After extraction	69,4%	33,7%

Results and conclusions

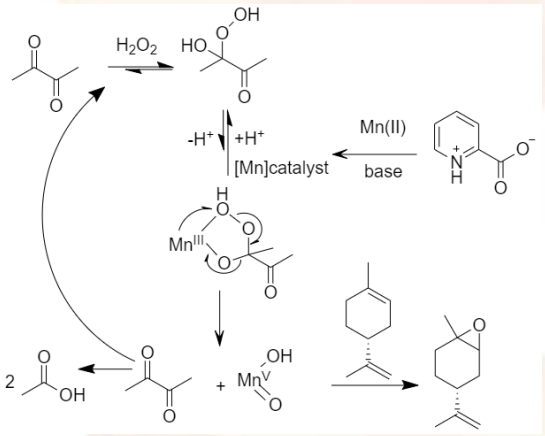
ρ,α-dimethylstyrene polymerization:

No poly(ρ,α-dimethylstyrene) was produced. It is possible that this is because of the stabilizers that are present in the monomer. Two different brands of DMS (with two different stabilizers) were used. DMS was purified by vacuum distillation and filtration over Al_2O_3.It is not proven by H^1 NMR or TLC if the stabilizers α-tocopherol or 4-tert-butylpyrocatechol were still present in DMS after purification steps, because they could not be detected. It is therefore not clear weather DMS polymerization with this method is not possible due to the presence of a stabilizer or that the monomer DMS is not suitable for radical polymerization, like limonene isn't either.

Limonene epoxidation:

Limonene epoxidation to limonene oxide using the method by Dong et al. was successfully replicated, proven by GC and GC-MS, although with lower yields than expected. First high limonene conversions were observed even before the start of the reaction, a change in the order of addition of reagents is hypothesized to fix this problem. A tenfold scale up of the epoxidation was successful. The cis/trans ratio was proven to be 65/35.

Proposed epoxidationreaction mechanism



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