

Renewable polyether polyols via the hydrogenation of polyesters [†]

Bernhard M. Stadler ¹, Sandra Hinze ¹, Sergey Tin ¹ and Johannes G. de Vries ^{1,*}

¹ Leibniz Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Straße 29a, 18055 Rostock, Germany; bernhard.stadler@catalysis.de (B.M.S.); sandra.hinze@catalysis.de (S.H.); sergey.tin@catalysis.de (S.T.)

* Correspondence: johannes.devries@catalysis.de

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Abstract: Polymers are involved in countless products ranging from high-tech materials used in aero-space industry, car parts, electronics to simple consumer goods such as clothing, sports gear, carpets, and various packing materials. As a result, humankind currently produces a previously unmatched amount of plastic waste. A lot of this waste is currently dumped in landfills or “mismanaged”. In order to counter-act the pollution of the environment as well as to conserve natural resources several strategies have been proposed and developed for the recycling of polymeric materials depolymerization and mechanical recycling being the most applied. Both approaches have in common that it is very difficult for them to be cost competitive with the production of the virgin polymers. A solution to this dilemma could be “chemical upcycling”. In this approach a polymer is converted to a higher value new material. In the case of polyesters, we could show that in the presence of a homogenous ruthenium catalyst and Lewis acids polyesters can be hydrogenated to polyether polyols. The type of Lewis acid and its ratio with respect to the ruthenium were proven to be crucial. Based on mechanistic investigations it was shown that this reaction proceeds via a tandem hydrogenation/etherification process. The obtained polyether polyols are in the right molecular weight range for the use in adhesives.

Keywords: polymers; hydrogenation; ruthenium; waste prevention; sustainable chemistry

1. Introduction

A lot of plastic waste is currently dumped in landfills or “mismanaged”. The latter term describes the uncontrolled dumping of waste by organizations or individuals. Due to natural erosion phenomena this waste is transported by rivers and from there to the oceans,[1] where it forms “islands” that can reach three times the size of France.[2] Additionally, plastics are directly dumped from ships to the waters.[3] There it causes great harm to aquatic life and in the form of micro plastic makes its way into the animal and human food sources.[4] The estimate of the amount of plastic marine debris circulating in 2020 ranges from 50 to 150 million tons.[1] The damage to the ecosystem and the possible negative health effects for humans led to the development of various concepts for solving this problem.

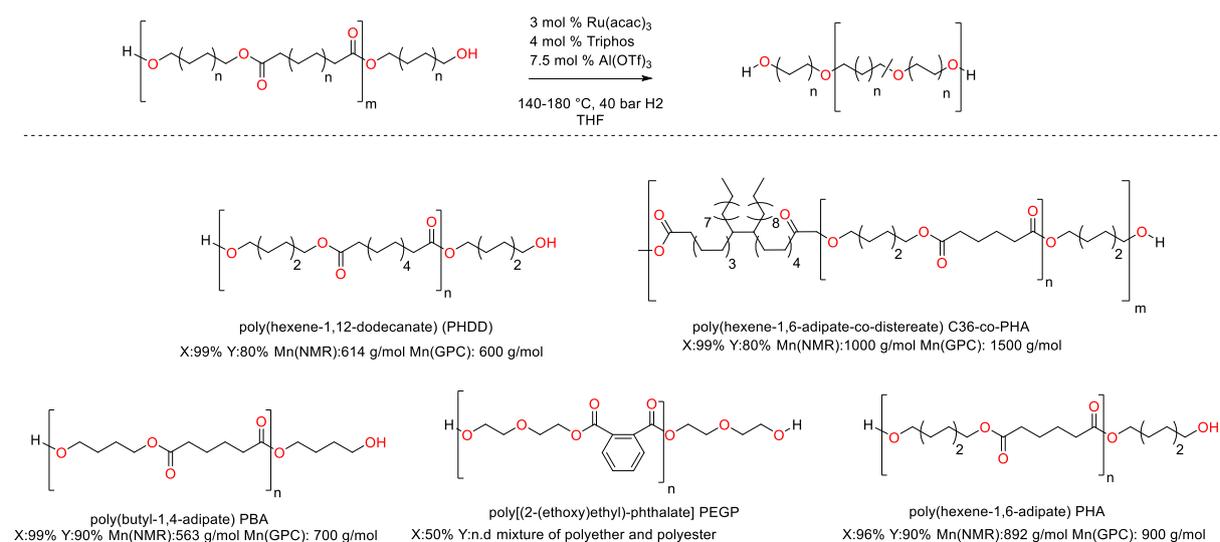
The most applied concepts are mechanical recycling and depolymerization. In many examples this has been implemented on industrial scale.[5] However, only 8% of the produced plastic is currently recycled.[6] This is mainly due to economic reasons. In the case of mechanical recycling an extra input of energy and resources is needed to obtain a product that often has inferior properties due to degradation or cannot be used in food contact applications due to an unknown content of potential toxic compounds. Depolymerization on the other hand usually results in monomers that

can be used to produce virgin grade polymers. However, this approach is still precluded by cumbersome collection and separation processes. As a result, it is very difficult for these monomers to be cost-efficient with their virgin counterparts made from petrochemical feedstocks, at least at the moment.

A possible solution to this dilemma could be the chemical upcycling of plastic waste to higher valuable products. To contribute to this, we developed a homogenous hydrogenation protocol in the presence of Lewis acids that enables the synthesis of polyether polyols from polyesters.

2. Results

For the hydrogenation of esters to ethers an acid has to be present.[7,8] The few exceptions of homogenous hydrogenation catalysts active under acidic conditions are combinations of ruthenium[9,10] or cobalt[11] with a triphos ligand and bipyridine complexes[12,13] of iridium and rhodium. Using an *in-situ* system of Ru(acac)₃, triphos ligand and a Lewis acid it was possible to reduce ester to ether bonds.[14] The nature of the Lewis acid as well as the ratio to the ruthenium catalyst was found to be crucial for the selective formation of ether bonds. Monitoring of the reaction progress revealed that the reaction proceeds via a hydrogenation/etherification sequence. The developed protocol was successfully used to reduce various polyester to the corresponding polyether polyols. (Scheme 1). Interestingly, the average molecular weight of the obtained polyether polyols is in the right range for the use in two-component adhesives and the synthesis of polyurethanes.



Scheme 1: Scope and limitation of the reduction of polyesters to polyether polyols. X refers to the conversion of carboxylic acid ester groups. Y to the yield of ether groups in the product oligomer.

3. Conclusions

It is possible to reduce polyester using cheap and abundant hydrogen to polyether polyols using ruthenium in combination with a triphos ligand. This concept can be applied in the prevention of plastic waste via upcycling. Additionally, it could serve as a means to obtain polyethers that are otherwise not possible to obtain using state of the art polymerization techniques such as ring opening polymerization.

Author Contributions: B.M.S. designed and performed the experiments. B.M.S. and S.T. wrote the manuscript. The project was conceived by S.H. and J.G.d.V. All authors contributed to discussions and reviewed the manuscript

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