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Catalytic conversion of biobased (poly)lactones into platform chemicals

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PURPOSE OF THE ABSTRACT

Global warming, caused by the expulsion of greenhouse gasses through consumption of fossil fuels for energy, base chemicals and specialized materials, is an ongoing concern. Therefore, science and technology has been focusing on alternative resources for several years. Polymer recycling could be a viable option, however, depending on the substrate often downgraded materials are obtained. Biomass on the other hand, offers a very promising sustainable solution for the production of platform chemicals as a renewable carbon source. These green and biobased materials generally contain high levels of oxygen compared to key industrial chemicals like alkenes and thus generally need deoxygenations. Our group has previously worked on the hydrodeoxygenation of (waste) polyols to mono alkenes as sustainable precursors for the polymer industry. [1,2] For these HDO reactions, phosphonium ionic liquids (ILs) were combined with an acid co-catalyst and used as dehydrating solvent in the presence of a homogeneous Ru hydrogenation catalyst, to convert biomass waste to biopropylene. The use of ILs as designer solvents was optimized for the desired application. Solubility differences of the products compared to the substrates allows for simple purification of the end-products, while simultaneously phosphonium ionic liquids showed high thermal stability in the acidic environment.

Here, we are extending the applicability of our system, tackling the (re)valorization of (poly)lactones to polymer precursors. These, often biobased, (poly)esters are nowadays already widely used in numerous consumer products. Poly(lactic acid) (PLA) is currently on the rise as biobased polymer. Unfortunately, biodegradability of this polymer is limited, as industrial facilities (60-70°C) are needed to have sufficient compost pace. In addition, recycling depolymerization to the respective lactide monomer proves to be very difficult. Therefore, we propose an alternative upcycling to a different polymer precursor: Acrylic Acid (AA). After optimization of the reaction parameters, we managed to improve the current state of the art from 24% [3] to >60% AA yield directly from (post-consumer) PLA. Similarly, poly(caprolactone) could be rearranged to hexenoic acids or, under the right conditions, decarboxylated to pentenes as drop-in polyolefin precursors. The discovery of controlled decarboxylation allows for the implementation of the same system on another biobased substrate mevalonolactone (MVL). In this way biobased isoprene can be produced, substituting the current fossil based production of synthetic rubbers. [4] It has been mechanistically proven that decarboxylation is the last and limiting step after a sequence of ring opening and dehydration.

With this work we provide a green solution to both recycling of plastic waste, as well as the conversion of biomass resources to valuable bulk chemicals for the polymer industry. The use of green, easily recyclable ionic liquids as both the catalyst and solvent makes this one of the most promising routes towards waste stream upcycling.

FIGURES

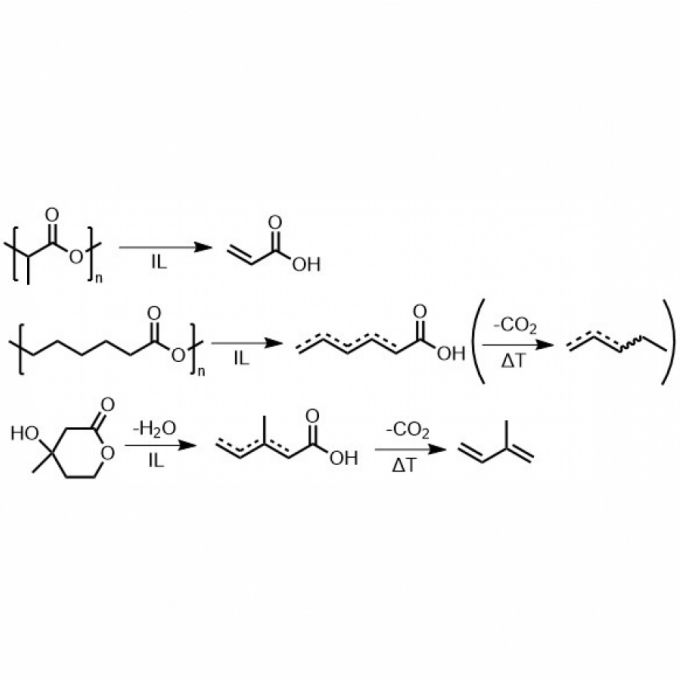

FIGURE 1

Valorization of biobased (poly)lactones

simplified reaction scheme for the valorization of 1) poly(lactic acid) to acrylic acid 2) poly(caprolactone) to hexenoic acids or pentenes 3) mevalonolactone to isoprene.

FIGURE 2

KEYWORDS

(waste) polymer recycling | poly(lactic acid) | biobased acrylic acid | biomass valorization

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