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# Impact of molecular weight, additives and copolymers on the chemical recycling of (bio)plastics using solid ruthenium-based catalysts

Marcus S. Lehnertz, [a] Sylvie Dufour, [b] Tabea Becker, [cd] Isabel Thiele, [e] Saskia Waldburger, [e] Jean-Marie Raquez, [b] Sonja Herres-Pawlis, [cd] Sebastian L. Riedel [f] and Regina Palkovits *[ag]

The production of polymers is rising ever since the 1950s. One of the emerging trends is the implementation of bioplastics, *i.e.*, polymers encompassing biodegradability and biosourcing. Even whether biodegradability is an interesting end-life option if plastic waste is mismanaged, the development of robust processes for direct chemical recycling is more appealing to create a real circular value chain. Furthermore, the direct recycling method of bioplastic reduces the competition of raw materials used for fabricating bioplastics with food production. In this study, the chemical recycling through hydrolysis of the bioplastics PLA and PHA is investigated. Ru/CeO$_2$ is applied as solid catalyst. The focus is placed on investigating the influence of molecular weight, the incorporation of additives such as reinforcement agents, and the implementation of copolymers in varying molar proportions. By comprehensively investigating the influence of polymer properties and additives, this study aims to contribute to the early identification of recycling challenges, enabling a forward-thinking approach to design efficient recycling processes, ensuring the sustainable integration of bioplastics into a truly circular economy.

### Sustainability spotlight

The contribution demonstrates the catalytic recycling of reinforced bioplastics by solid catalysts, therewith contributing to a circular plastics economy. In contrast to acid or base hydrolysis, using solid catalysts avoids salt formation providing a benign process strategy. In addition, the study addresses not only pure but reinforced plastics as important step towards industrial applicability. As important insight, we elucidated that tailored reinforcement can even facilitate recycling opening the path to plastics designed for recycling. For an even greener process, continuous operation and energy efficient separation should be targeted and are subject to our future studies. SDG 12 – Responsible Consumption and Production: valorising bioplastics such as PLA and PHA, the research reduces plastic waste and enhances resource efficiency. SDG 13 – Climate Action: closed-loop recycling processes reduces the reliance on fossil-based plastics and lowers greenhouse gas emissions associated with plastic production and disposal. SDG 9 – Industry, Innovation and Infrastructure: catalytic recycling strategies foster sustainable industrial innovation. SDG 2 – Zero Hunger: recycling (bio)plastics reduced the competition on land use for novel biomass production.

*[a]Institute of Technical and Macromolecular Chemistry, RWTH Aachen, Worringerweg 2, 52074 Aachen, Germany. E-mail: palkovits@itmc.rwth-aachen.de*

*[b]Laboratory of Polymeric and Composite Materials, Center of Innovation and Research in Materials and Polymers (CIRMAP), University of Mons, Place du Parc 23, Mons, 7000, Belgium*

*[c]Institute of Inorganic Chemistry, RWTH Aachen, Landoltweg 1a, 52074 Aachen, Germany*

*[d]Bioeconomy Science Center (BioSC), Forschungszentrum Jülich GmbH, Jülich, Germany*

*[e]Technische Universität Berlin, Institute of Biotechnology, Chair of Bioprocess Engineering, Berlin, Germany*

*[f]Department VIII – Mechanical Engineering, Event Technology and Process Engineering, Environmental and Bioprocess Engineering Laboratory, Berliner Hochschule für Technik, Berlin, Germany*

*[g]Institute for a Sustainable Hydrogen Economy (INW-2), Forschungszentrum Jülich, Marie-Curie-Str. 5, 52428 Jülich, Germany*

## Introduction

In modern life, plastic consumer goods are a constant source of supply and have become essential in various areas such as transportation, food, health and energy industries.[1,2] Thereby, polymers feature a beneficial range of material properties, which are influenced by the structure of the repeating units in the polymer chain. However, the cheap production of single-use plastics from mostly petroleum-based raw materials causes environmental pollution due to mismanaged waste streams and emits greenhouse gases.[3] To give an example, solely in Europe, plastic waste amounted to 29.1 Mt in 2019, whereof 67% ended up in landfills or incinerators.[4] These negative effects can be minimized by increasing bioplastics production and shifting from a linear towards a circular economy.[5–7] Thereby, commercially available, fossil-based plastics can be produced in

part from renewable resources and are sometimes classified as bioplastics. For example, well-known polyethylene (PE) can be replaced by bio-PE, retaining the properties of this material.[2] However, the definition of a material as a bioplastic also includes other variants: in addition to monomer production from bio-based raw materials, a bioplastic can also be fossil-based and biodegradable, or there is a material that combines both options, bio-based and biodegradable.[8] In this manuscript, the authors consider only the latter option as bioplastics.

Materials produced from biomass offer a significant benefit in terms of non-utilization of finite resources. However, compared to conventional fossil-based plastics, bio-based and biodegradable bioplastics still have disadvantages such as more cost-intensive production and lower manufacturing efficiency. Furthermore, in case of many bioplastics, additives are required to match the excellent material properties of conventional plastics. Another drawback is the possibility that the raw materials for bioplastics are in a competition with food production. This potential drawback can be minimized if recycling strategies are established, since closed-loop recycling reduces the acreage for the required raw materials as wells as refinery and production costs.[2]

Across all plastic classes, mechanical recycling is the most widely used method. 5 Mt of plastic waste are processed each year in Europe, driven by the cost effectiveness of this method.[9] However, mechanical recycling cannot be repeated infinitely, since many polymers tend to get altered under the applied shearing conditions.[10] Furthermore, mechanical recycling is mainly suitable for pure waste streams.[11,12] In order to establish an infinite loop, maintaining the plastic properties, and to deal with mixed waste streams, chemical recycling comes into play. Among others, chemical recycling methods range from gasification and pyrolysis to solvolysis.[11] In all these processes, the polymer backbone is broken down into its individual building blocks and sometimes even further into useful chemicals as new starting materials, such as synthesis gas. The higher temperatures often applied in chemical recycling in conjunction with the need to build-up the polymer from scratch often lead to higher energy consumption compared to mechanical recycling. However, the main advantage is the quality of the polymer, which is comparable to a first-use material.[10–12]

The tonnage of chemical recycling is expected to rise from currently almost zero to 3 Mt in the 2030s and 12 Mt in the year 2050.[9] To reach these expectations, research in the field of chemical recycling is necessary, especially to reduce the complexity and energy demand of these methods. This applies in particular to bioplastics, as these have a strongly growing market and in opposite to past trends, recycling should be ahead of the mass introduction of these polymers. In addition, chemical recycling can create a closed recycling loop without the complex recovery via diluted $CO_2$ streams in case of biodegradation.

Among the various chemical recycling approaches, the recovery of monomeric units such as lactic acid is particularly crucial to enable true circularity, as it allows direct re-polymerization without relying on new biomass feedstock. In contrast, reductive pathways that yield alcohols or other reduced compounds produce valuable chemicals but remove the material from the bio-polyester cycle.

## PLA

The bioplastic PLA is made from renewable raw materials, is established on the market and has a high potential to replace conventional materials owing to its polyester structure.[13,14] The lactic acid (LA) produced from sugar-rich biomass via fermentation is converted into the cyclic monomer lactide using a two-step mechanism. By subsequent metal-catalysed ring-opening polymerization, PLA is obtained.[8] The physical and mechanical properties such as hardness, stiffness and tensile strength can be adjusted via the crystallinity due to the chiral character of the polyester. Its physical properties make PLA suitable for use as packaging material.[15] Other applications include disposable cutlery, agricultural films or medical implants.[16–18] The latest market research reveals that the global production capacity for bioplastics is likely to increase significantly from 2.18 Mt in 2023 to 7.43 Mt in 2028, of which PLA accounts for the highest production capacity (31%).[7]

The enhancement of the mechanical properties of PLA through the incorporation of additives is an option to further increase the applicability and thereby the market share.[19,20] However, in the realm of eco-design, it is also crucial for a mechanical reinforcement to ideally support the degradation process.[21] Notably, chitin nanocrystals (NCh) within carbohydrates have demonstrated effective mechanical reinforcement in PLA,[22–25] along with notable biodegradability advantages.[26,27] The additional introduction of acid species, such as butyric acid and lactic acid derivates, as functionalization of the NCh nanocrystals, could facilitate biodegradation as well as recycling by initiating PLA hydrolysis. Encouraging outcomes have been observed with carbohydrate-based materials, such as natural fibers.[28,29]

Chitin is a structural polysaccharide derived from crustaceans and insects.[30] It is antimicrobial, inhibits the growth of fungi and improves the barrier properties of PLA.[23,31,32] The increasing popularity of nanochitin can be attributed to advanced extraction methods and surface functionalization, particularly owing to its enhanced mechanical performance when blended with matrices.[33] Recognized and catalysed by microorganism-derived enzymes, especially those of marine origin, chitin is acknowledged as a sustainable additive.[26,27,34]

Building on the discussion of PLA's properties and potential additives, the focus is now shifted to the exploration of recycling strategies for PLA, beginning with a general overview of its recyclability.

Hydrolysis of PLA in its solid state and hydrolytic degradation of PLA-based composites have been extensively studied.[35–42] Key parameters include water absorption and the diffusion coefficient of oligomers within the material as well as their solubility in the media. Trapped oligomers catalyse further bulk degradation (autocatalysis).[42]

Generally, PLA can be hydrolysed at any temperature, but its hydrolysis is particularly accelerated above the $T_g$, whether catalysed by an acid, a base or an enzyme. Indeed, acids or bases

may be added to accelerate the process, but are not necessarily needed due to autodegradation enabled by the emitted lactic acid.[43–47] However, studies by Fuji *et al.* focusing on hydrolysis at elevated temperatures between 120 and 250 °C reached lactic acid yields of up to 95%. Thereby, a correlation between lower temperatures and higher lactic acid yield was found.[48,49]

Besides neutral, basic or acid hydrolysis, transition metal catalysed hydrolysis is a promising and faster option to degrade PLA. A homogeneous Ru(II)-complex was applied by Enthaler *et al.* to perform a reductive depolymerization of PLA towards 1,2-propanediol (1,2-PD). A yield of 99% 1,2-PD was achieved at 140 °C under 45 bar hydrogen.[50] The system was also able to tackle real samples such as straws and cups. Klankermayer *et al.* reported equal success for real samples by applying a Ru–triphos catalyst at 140 °C under higher pressure of 90 bar and with addition of bistriflimidic acid.[51] Other Ru-complexes investigated by Krall *et al.* also demonstrated activity in the reductive depolymerization under the addition of potassium-*tert*-butanolate and in solvents such as anisole and tetrahydrofuran (THF).[52]

Further possible pathways have been investigated by Herres-Pawlis *et al.* applying zinc–guanidine complexes for the methanolysis of PLA and Feghali as well as Monsigny *et al.* for silanisation of PLA.[53–55] The activity of the reported zinc complexes started at 60 °C and ranged up to 150 °C, yielding 98% methyl lactate for the latter temperature, which can be used as green solvent.[53] The silanisation on the other hand leads to silanised propyleneglycol.[54,55] Moreover, Curely *et al.* described an economically viable polyester recycling process, in which mixed polyesters are methanolysed, and the resulting products are separated and purified, offering advantages over primary polymer production.[56] To the best of our knowledge, hydrolysis of PLA with a solid catalyst was not reported in scientific publications yet, apart from one mention in a mixed approach with PHB.[57] However, two patents hold by Japan Steelworks conclude that zinc oxide may have a catalytic effect at elevated temperatures of 200–400 °C.[58,59]

## PHA

A further class of bioplastics are polyhydroxyalkanoates (PHA). These linear polyesters rank second in bioplastic production capacity. However, by 2029, PHA is projected to close the gap, then reaching more than one-third of PLA's capacity.[60] PHAs are produced intracellular by various microorganisms, mainly under nutrient limitation or stress conditions and facilitate survival and robustness in nature as they serve as a carbon and energy storage.[61,62] Isolated, PHAs have properties like conventional fossil-derived polymers although they are bio-based and can be fully degraded into $CO_2$, water, and biomass aerobically or, in the case of anaerobic degradation, additionally to methane in many test environments, including seawater and soil.[63,64] Meanwhile, more than 160 different monomers are known, that are classified into short-chain-length (scl, 4–5 C-atoms) or medium-chain-length (mcl, 6–14 C-atoms) PHA monomers.[65] Polyhydroxybutyrate (PHB), the most studied PHA, is characterized by a melting temperature ($T_m$) of 170–180 °C and rapid thermal degradation from 190 °C, narrowing the

processability window besides being stiff and brittle due to its high crystallinity.[66] However, the incorporation of comonomers facilitates the modification of the copolymer properties depending on the length and ratio of the co-monomers. For example, poly(hydroxybutyrate-*co*-hydroxyvalerate) P(HB-*co*-HV), a scl–scl PHA, shows reduced $T_m$, improved flexibility and toughness. Even more pronounced effects are achieved by copolymerization with mcl monomers such as 3-hydroxyhexanoate (HHx). The obtained scl–mcl copolymers feature dramatically increased flexibility, ductility and reductions in melting temperature and crystallinity. Moreover, all these features can be modulated by the HHx proportion to control the material properties in order to cover a wide range of applications.[67–69] A current drawback are the high cost for PHAs. Therefore, research focuses on PHA metabolism,[70,71] metabolic strain engineering,[72] bioprocess development for tunable P(HB-*co*-HHx) production at high cell densities,[73] the use of biogenic waste streams as carbon feedstocks[74–76] and advanced downstream processing to reduce the overall high production costs of P(HB-*co*-HHx). Additionally, novel applications such as photocatalytic films for hydrogen production are being explored.[77] Nevertheless, the industrial importance of P(HB-*co*-HHx) is already demonstrated by the commercial production of packaging materials, shopping bags, coatings or straws and cutlery by companies such as Danimer Scientific, Kaneka Corporation and Bluepha.[78,79]

Due to the similar structure of PLA and PHA, the latter one is also susceptible to hydrolysis. This enables various circular application possibilities.[53,57,80–82] The degradation generally starts in the amorphous regions of the polymer and is significantly accelerated in acidic or basic media.[83,84] Thereby, the repetition unit 3-hydroxybutyric acid (3-HBA) is usually generated from PHB, or the respective monomers from P(HB-*co*-HV).[85] At elevated temperatures of 175–200 °C investigated by Strathmann *et al.*, crotonic acid (CA) as well as $CO_2$ and propene are generated at elongated reaction times besides 3-HBA for pure PHB as starting material.[86] The aminolysis of P(HB-*co*-HV) copolymer with methyl- and ethylamine represents another possibility to degrade the bioplastic. It was reported that a higher HV content leads to faster depolymerization since the addition of HV decreased the degree of crystallinity and thereby enhances the amount of amorphous regions.[87] However, it also has to be considered that a longer side chain length increases the steric hindrance and can therefore decrease the degradation rate. Since HV is still relatively short, this effect does not dominate here.[88] Perpendicular, this effect was observed for alkaline degradation at a pH value of 12.3 for P(HB-*co*-HHx), where the degradation rate decreased with increased HHx content.[69]

Homogeneously catalysed attempts have been made by Krall *et al.* with Ru-complexes. Compared to PLA, it was anticipated that the reductive depolymerization leads to the diol, in this case 1,3-butanediol (1,3-BD). In contrast to this expectation, BA came up as the main product.[52] Silanisation attempts conducted by Cantal *et al.* were not in line with the results for PLA and failed, too. Therefore, although PLA and PHAs show

a similar chemical structure, their reactivity differs significantly.[55]

To the best of our knowledge only two publications deal with the heterogeneously catalysed hydrolysis of PHB, whereas none is present for the recycling of P(HB-co-HHx), which will be subject to this study. Sun *et al.* applied Pd/C and Cu/Zn/Al catalysts under hydrogen atmosphere at 200 °C for the degradation of pure PHB. The latter catalyst generated BA with a yield of up to 70% and the follow up product of BA was identified to be butanol. CA was only significantly detectable when the reaction was conducted under nitrogen instead of hydrogen.[89] Furthermore, the group of Palkovits identified Ru on ceria to be the most promising option for PHB depolymerisation. A yield of up to 79% for 3 HBA, 20% BA and 1% CA was found for this catalyst under 100 bar hydrogen and after a reaction time of 110 min. The reaction showed to be relatively insensitive to pressure changes although hydrogen was needed in general to activate the catalyst. With ongoing reaction time, 3-HBA was suggested to transform into BA followed by conversion to gaseous products takes place.[57]

Despite their technical recyclability, bio-polyesters are currently not part of a dedicated, collected, and sorted waste stream. This challenge arises from their still limited market volume in packaging and the absence of large-scale recycling capacities, which in turn discourages separate collection.[90] The upcoming EU Packaging and Packaging Waste Regulation (PPWR) will most likely intensify the need for scalable recycling routes for all packaging materials, including bio-based and biodegradable polyesters.[91] In this context, technologies that can efficiently recycle bio-polyesters—either after improved sorting or even from mixed waste streams—will be crucial to establish economic incentives and close the circular loop.

Generally, in the broad topic of polymer recycling, many studies focus predominantly on the recycling process itself. However, this study has the intention to complement this knowledge by incorporating a more detailed analysis of polymer-derived factors. Therefore, this study aims to evaluate the influence of molecular weight, additives, and copolymer share on the catalytic hydrolysis of PLA and PHA using a Ru/$CeO_2$ catalyst. In this process, depolymerization occurs through water-mediated hydrolysis of the ester bonds, while hydrogen merely maintains the reduced, active state of the catalyst surface. Consequently, the reaction should be regarded as hydrolysis under hydrogen atmosphere rather than a true hydrogenolysis.

## Experimental

### Catalyst

The catalyst was prepared by wet impregnation. The respective amount of the precursor Ru(III)Cl$_3$·H$_2$O for a loading of 5 wt% Ru was dissolved in 20 mL of acetone. The respective amount of support was then added at once. For instance, in the case of Ru/$CeO_2$, 266 mg Ru(III)Cl$_3$·H$_2$O and 1900 mg of $CeO_2$ were used. The solution was stirred for 3 h followed by solvent removal under rotary evaporation (60 °C, 30 mbar, 1 h). The dried material was stored under Ar until reduction with molecular H$_2$.

The standard reduction was carried out in a glass tube using an oven (Heraeus instruments, type RO 4/50) at 300 °C for 3 h, with a heating rate of 5 °C min$^{-1}$ and a gas flow of 0.1 L min$^{-1}$. The catalyst is identical to the one applied by Palkovits *et al.*[57]

### Recycling approach

The reactions were conducted in 10 mL batch autoclaves (Parr Instruments Inc., Mirco Batch System 2500, Hastelloy C) equipped with a stirring bar. After the addition of the reaction components, *i.e.*, 1.6 mmol substrate, 5 mg catalyst, and 5 mL water as solvent, the system was flushed three times with H$_2$ and finally set to 5 bar H$_2$ pressure and placed in a pre-heated mantle. The reaction time was started immediately. The reactions were quenched by external cooling with ice water. After a cool-down period of 15 min, the pressure was released. The reaction solution was transferred to a glass vial using a syringe. An additional 1 mL of the respective solvent was used to rinse the autoclave. The as-obtained reaction solution was filtered with PA 45/20 filters (pore size 0.45 μm) to remove the catalyst particles and further product quantification by HPLC was carried out.

### HPLC

HPLC chromatograms were recorded with a Shimadzu LCMS-2020, equipped with a RI detector. The flow was set to 2.0 mL min$^{-1}$, and the eluent was a mixture of water and TFA with a concentration of 154 μL L$^{-1}$. The organic acid resin column with dimensions of 300 × 8 mm was delivered by CS-chromatography. The oven temperature was set to 40 °C.

### Production of PLA

The reactor was heated to 150 °C under vacuum and flushed three times with argon. All samples were prepared in the nitrogen filled glovebox. Lactide (8.00 g, 55.5 mmol) and the catalyst [Zn{(R,R)DMEG$_2$(1,2)ch}$_2$](OTf)$_2$ THF in the corresponding [M]/[I] ratio were weighed and homogenised in an agate mortar.[92] The reaction mixture was removed from the glovebox in a sealed glass vial. Under argon counter current, the lactide catalyst mixture was transferred to the preheated reactor and the stirrer (260 rpm) was turned on. The reaction time was set according to the [M]/[I] ratio. After the polymerisation was completed, the polymer was removed from the reactor. The polymer was dissolved in DCM (approx. 4 mL), precipitated in ethanol (200 mL) at room temperature and dried under reduced pressure. The molar mass of the dried polymer was determined by GPC.

### Production and characterisation of PHA

P(HB-co-HHx) with varying HHx contents was produced from canola oil and fructose during parallel 1.4 L bioreactor cultivations using the recombinant *Ralstonia eutropha* strain Re2058/pCB113 (ref. 93) and subsequent purification with chloroform and methanol.[69] Detailed material and abiotic biodegradation properties of the obtained PHA copolymers have already been described by Thiele *et al.*[69]

### PHB (commercial)

PHB was purchased from Sigma-Aldrich/Merck with the Article number 363502. This polymer with a melting temperature of 172 °C was applied as reference polymer for the P(HB-co-HHx) copolymers.

### PLA

PLA, which contains acid functional groups grafted onto the surface of the nanoreinforcements, was applied and may release acidic groups upon hydrolysis. Therefore, non-functionalised nanochitin (NCh-HCl), nanochitin functionalised with butyric acid (NCh-BA) and with lactic acid (NCh-LA) using the method developed by Magnani *et al.* in 2022 was synthesised.[94] As a negative control, nanocelluloses (CNC) was used as additive, which does not feature any hydrolysable functions on the surface and therefore cannot release acid species.

### PLA (commercial)

PLA 4032D for preparation of reinforced polymer were supplied by NatureWorks. According to the manufacturer, PLA 4032D contains 1.7% of D-lactide, with a number average molecular weight ($M_n$) of approximately 70 000 g mol$^{-1}$. The chloroform was of technical grade and was supplied by Sigma Aldrich. CNC was provided by Celabor SCRL (Wallonia, Belgium).

### Nanochitin synthesis

Non-functionalised nanochitins (NCh-HCl), BA and LA-functionalised nanochitins (NCh-BA and NCh-LA respectively) were prepared as described by Magnani *et al.* in 2022.[94] The length of NCh was measured by transmission electronic microscopy (TEM) analysis (Hitachi High-Tech SU8020), and the functionalisation was verified by Fourier-Transform InfraRed spectroscopy (FTIR).

### Solvent casting

In 30 mL chloroform, PLA4032D provided by NatureWorks ($M_n$ = 70 000 g mol$^{-1}$) and NCh (mixture = 1.8 g) were solubilised under magnetic stirring. The wt% of nanochitin was 1, 2 or 3%. After adequate dispersion of NCh (several hours), the solution was poured into a crystalliser (diameter 7 cm). A larger crystalliser was turned over. The whole setup was placed on two layers of paper towels to slow chloroform evaporation over 10 days. Subsequently, films were placed under vacuum at 40 °C, and the temperature was increased by 5 °C every hour until reaching 110 °C. The temperature is then reduced to room temperature under vacuum.

### GPC

The average molar mass of the used PLA was determined by gel permeation chromatography (GPC) on a Viscotek GPCmax VE-2001 applying a flow rate of 1 mL min$^{-1}$ at 25 °C with THF as the mobile phase. The device was equipped with a HPLC pump, two Malvern Viscotek T columns (porous styrene divinylbenzene copolymer) with maximum pore size of 500 and 5000 Å, a refractive index detector (VE-3580) and a viscometer (Viscotek

270 Dual detector). The software Omnisec – 5.12 was used for data acquisition. The results were evaluated using conventional calibration with Mark–Houwink correction factor of 0.58.[95,96]

## Results and discussion

### PLA

**Molecular weight.** The molecular weight ($M_n$) plays a critical role in the recycling of plastics. Therefore, the influence of the $M_n$ on the chemical recycling with solid catalysts is subject to this study. To exclude the effect of autodegradation, a blind experiment without catalyst was conducted (see SI Fig. S5). It is confirmed that the influence of thermally induced random chains scission is minor, since without catalyst, even after 60 min a yield of only 9% LA is present.

Three PLA samples with $M_n$ values ranging from ~8000 g mol$^{-1}$ to ~79 000 g mol$^{-1}$ were applied to the reaction system (Fig. 1). All PLA reactions were performed at 175 °C, *i.e.*, above the melting temperature of the investigated PLA grades ($\approx$150–165 °C). Therefore, the polymer was molten during reaction, and the kinetics are expected to be dominated by melt viscosity and mass transfer rather than by crystallinity. It is observed that the LA yield is lower for the highest $M_n$, whereas $M_n$'s up to 41 000 g mol$^{-1}$ seem to have no influence on the degradation. A lowered interaction between polymer and catalyst due to a greater expansion of the longer polymer chain may be excluded as reason, since the applied catalyst does not consist of a highly microporous system and features a low specific surface area of around 10 m$^2$ g$^{-1}$. The reason for the observation that lower yields are obtained with higher $M_n$ may at least partially be based on the applied analytical methods. A higher $M_n$ means longer chains are present, in this case approx. 106 repetition units for the lowest $M_n$ and 1093 repetition units for the highest $M_n$. Under the assumption that the polymer chain scissions by the catalyst are random, it is therefore statistically less favoured that a LA group is split of. However, since one of the main limitations of the HPLC method is that dimers and higher multimers are often not detectable, the results point at a lower performance of the catalyst based on the lower LA yield, even if the count of scissions may be equal for all investigated $M_n$. To sum up, the lower apparent lactic acid yield at higher molecular weights is not necessarily indicative of catalytic inhibition. Given that the HPLC method only quantifies low-molecular-weight species, higher-molecular-weight PLA requires more random chain scissions before detectable monomers are released. Thus, the apparent yield decrease reflects, to some extent, an analytical limitation rather than a reduction in catalytic activity.

To investigate this issue, GPC measurements after a specific reaction time have been conducted to evaluate the question if a higher $M_n$ indeed inhibits the catalytic process. The starting material, a PLA cup (cut up to approx. 0.5 × 1 cm pieces), was found to have a $M_n$ of 65 000 g mol$^{-1}$. After 10 min, the $M_n$ was already decreased to 45 000 g mol$^{-1}$. Afterwards, a sharp drop in molecular weight to 3000 g mol$^{-1}$ is observed at 20 min of reaction time. This equals a $M_n$ drop by 75%, whereas the yield of LA only increases by 10%. Furthermore, the polydispersity
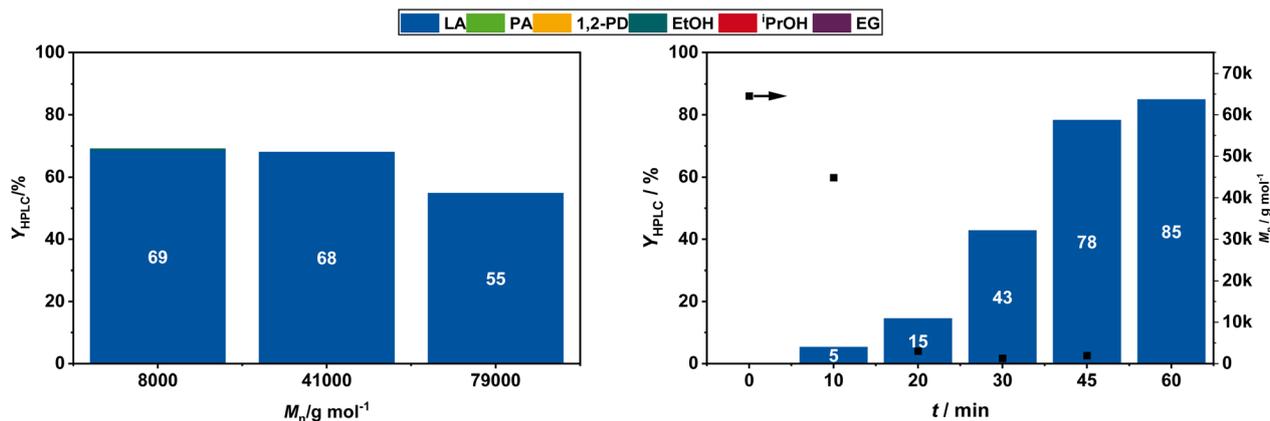
**Fig. 1** Chemical recycling results for (left) PLA with different molecular weights ranging from 8000 to 79 000 g mol$^{-1}$. Conditions: 5 mg Ru$_{5\ wt\%}$/CeO$_2$, 115 mg PLA, 175 °C, 5 bar H$_2$, 5 mL H$_2$O, 500 rpm, 0.5 h, 50 mL Hastelloy autoclave. (right) PLA after different reaction times ranging from 0 to 60 min. Black squares are attributed to the right $y$-axis $M_n$. Conditions: 5 mg Ru$_{5\ wt\%}$/CeO$_2$, 115 mg PLA, 175 °C, 5 bar H$_2$, 5 mL H$_2$O, 500 rpm, 0–1 h, 50 mL Hastelloy autoclave. Abbreviations: LA – lactic acid, PA – propionic acid, 1,2-PD – propionic acid, EtOH – ethanol, iPrOH – isopropanol, EG – ethylene glycol. Note: Species listed in the legend other than lactic acid (LA) were not detected under the applied conditions. They are included as potential degradation products for completeness.

index (PDI) is increased significantly from 1.8 to 2.2 over the same period. The results, especially based on the sharp $M_n$ drop between 10 and 20 minutes of reaction, support the hypothesis, that the chain splitting mechanism with the catalyst Ru/CeO$_2$ is based on random scissions. It must be emphasized that the quantification gap between HPLC and GPC introduces analytical uncertainty. While HPLC accurately detects only low-molecular-weight species such as lactic acid ($\approx 90$ g mol$^{-1}$), GPC provides reliable data only above $\approx 2500$ g mol$^{-1}$. Intermediate oligomers are therefore not captured by either method, which may lead to an underestimation of catalytic efficiency, particularly for high-$M_n$ PLA. Overall, it can be indicated that the lower yields for high $M_n$ PLA samples are at least partially attributed to the non-scission but monomer oriented analytical method of HPLC.

The practical effects of analytical restrictions must therefore be given greater consideration in future research, especially in the analytically challenging topic of polymer recycling. The results reveal that at least the indication of the molecular weight is useful in any study of polymer recycling to enable a better comparability.

in Fig. S6 (SI). In general, no side products besides the desired monomer LA could be identified.

Pure solvent casting PLA (S) was chosen as reference polymer presented on the far left of Fig. 3 yielding 11% LA, the lowest obtained yield in this comparison. For all reinforced polymers, the ones with a reinforcement proportion of 2% outperform those with either 1 or 3%. Therefore, a reinforcement grade of 2% seems to be ideal for the applied chemical recycling approach. The results indicate that pure solvent casting PLA is relatively resistant to the applied chemical recycling approach. The addition of functionalised reinforcing nanochitin (NCh) crystals not only increases the mechanical properties but also facilitates the direct chemical recycling. An optimal point seems to be reached with the addition of 2% nanocrystals. The reason for the beneficial effect of chitin nanocrystals could be the acid functionalisation. However, if the only reason would be the added acidity, there should be a correlation between proportion of nanocrystals as well as a correlation between strength of the functionalisation acid and the observed yields. Therefore, the experiment with 3 wt% NCh-LA reinforcement should reveal the
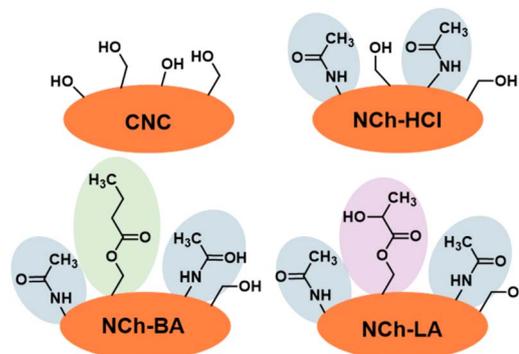
## Nanocrystal reinforcement

Besides the molecular weight of polymers, mechanical strength boosting additives such as cellulose nanocrystals (CNC) or nanochitin (NCh) can influence the biodegradation as well as recycling of the respective polymers.

To investigate their effect on chemical recycling in terms of catalysed hydrolysis, reinforced PLA was chosen as model substrate. The respective reinforcement agents and their functionalisation are illustrated in Fig. 2. Fig. 3 shows the results for nanochitin-reinforced PLA with either non-functionalised (NCh-HCl) as well as BA (NCH-BA) and LA functionalisation (NCh-LA). Results for CNC reinforcements with no acid functionalisation are applied as negative control and are displayed



**Fig. 2** Overview of the applied PLA samples, reinforced with cellulose (CNC) or chitin (NCh). NCh-type with functionalisations.
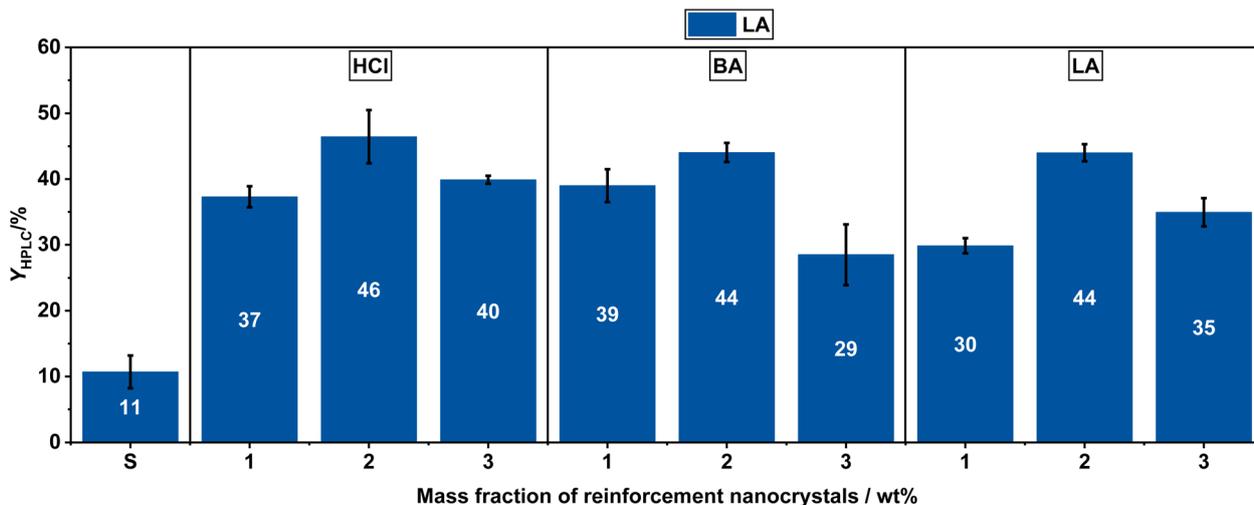
**Fig. 3** Chemical recycling results for a variety of reinforced PLA samples, except S denoted, in every case with addition of functionalised NCh reinforcement. Error bars determined by multiple measurements. Conditions: 5 mg Ru$_{5\ wt\%}$/CeO$_2$, 115 mg PLA, 175 °C, 5 bar H$_2$, 5 mL H$_2$O, 500 rpm, 0.5 h, 10 mL Hastelloy autoclave. Abbreviations: LA − lactic acid.

highest yield for LA, since the p$K_a$ of BA is 4.82 and the one of LA is 3.90. The results demonstrate that this correlation is not existent since the yields drop for 3% nanocrystals and are not higher for the LA functionalised samples. Therefore, the polymer properties themselves, influenced by the nanocrystals, must be of relevance, dominating the acidity influence and reducing the yields at high reinforcement rates of 3%. To investigate this issue, PLA reinforced with cellulose nanocrystals (CNC) was applied as negative control since these reinforcement agents feature no acid functionalisation at all. Depicted in the SI, Fig. S6, the sample with 1% CNC reinforcement reveals the highest LA yield of all samples measured with 57%, followed by 34 ± 5 and 31 ± 8% for reinforcement rates of 2 and 3%. The results indicate that a higher unmodified reinforcement rate decreases the degradation rate. This supports the hypothesis that at some point, the negative influence of the reinforcement agents on the recycling process surpass and dominate the positive effects of the acid functionalisation as discussed for the NCh reinforcements. The determination of the complex effect regarding the reinforcement agents are beyond the scope of this manuscript and are therefore subject to ongoing research. However, at higher reinforcement loadings, the nanocrystals may induce partial pore blockage or surface coverage on the solid catalyst, which can decrease the number of accessible active sites. In addition, chemical interactions between functional groups of the reinforcement (e.g., hydroxyl or amine moieties) and surface sites of the catalyst may locally alter acidity, potentially shifting the predominant degradation pathway.[97,98] These combined physical and chemical effects could therefore contribute to the observed reduction in recycling efficiency at higher reinforcement contents.

Moreover, a switch of the predominant reaction from PLA degradation to reinforcement degradation may slightly influence the results. Besides chemical reasons, practical reasons such as a changing viscosity of the molten polymer due to the incorporation of the reinforcement agents could also play a significant role. Elevated viscosity may limit both external and internal mass transport within the reaction mixture, thereby reducing the accessibility of the polymer chains to the active sites of the solid catalyst. Such effects are of particular practical relevance for process scaling, where efficient mass transfer is essential to maintain high recycling rates.

To quantify the influence of melt viscosity on degradation rates, future studies could combine *ex situ* rheology and kinetic/transport diagnostics. Melt viscosities of neat and reinforced PLA can be measured under inert atmosphere at elevated temperatures. By systematically varying viscosity through temperature or minor plasticization and correlating it with initial degradation rates obtained from GPC and HPLC, the impact of mass-transport limitations on catalytic performance could be evaluated. Complementary tests such as stirring-rate and catalyst-particle-size variation would further distinguish external from internal diffusion effects. Although such a detailed quantitative investigation would exceed the scope of the present work, this framework outlines a promising route for future studies to establish a direct correlation between viscosity and catalytic efficiency.

These results underscore the importance of designing bioplastics with optimal reinforcement levels to maximise recyclability without compromising material properties. Other crucial factors in the design of bioplastics include the processability within existing production and recycling infrastructures, as well as the specific performance requirements of the intended use case. These aspects jointly define the necessary balance between mechanical functionality, product lifetime, and sustainable end-of-life behaviour.

### PHA–P(HB-*co*-HHx)

**Investigation of various HHx copolymer proportions.** The build-up of copolymers from two or more different buildings blocks is another option to tune the properties of a polymer.

**Paper**

Fig. 4 shows the HPLC analysis results for P(HB-*co*-HHx) samples with increasing HHx proportion from left to right applied to the chemical recycling approach.

The applied catalytic system is able to depolymerise the HBA as well as HHx fraction of the copolymer. The observed 3-HBA yields for all samples with HHx is 3 to 7% lower than for the reference sample. The yields for the monomer 3-HBA are relatively stable around $30 \pm 2\%$. However, with increasing HHx content, the yields for the respective degradation products of the copolymer, 3-HHA and HA, increase to 8 and 3%, respectively. This general trend was interestingly also observed for BA with a yield of 9% for P(HB-*co*-HHx) with 14% of HHx. Overall, the trend for the follow-up products depicted in Fig. 4 (left) is aligned with the increase of their substrate amounts, thus HHx content. The increase in BA however indicates, that the hydrogenation ability of the catalyst somehow seems to positively correlate with an increasing HHx fraction. This is especially validated since CA, the non-hydrogenated counterpart of BA, is only present up to 6.81 wt% HHx.

For a deeper understanding, an attempt with increased reaction time to 3 h has been conducted with the 2.66 and 14.2% HHx samples, shown in the SI Fig. S2. The elongated reaction time was chosen to get more data in the range of full conversion. For the low HHx amount, 12% CA remain even close to full conversion, whereas no CA is detected for the 14.2% HHx sample. The results confirm that high HHx contents indeed seem to facilitate hydrogenation of CA to BA, which is obtained in yields of 14 and 24%, respectively. However, the sum of both C4-acids is $25 \pm 1\%$ in the case of both polymers. This trend may be explained by factors such as different viscosity of the polymers in the molten state and therefore variating contact with the catalyst. Different viscosities are relatively likely since the $T_m$ decreases from around 160 °C to 125 °C for 2.66 mol% to 14.2 mol%, respectively. Furthermore, varying proportions of two different catalytic mechanism may play a role – polymer splitting by hydrolysis *vs.* hydrogenation of CA to form BA. If the catalysed hydrolysis is generally favoured over the catalysed hydrogenation and the polymer with higher HHx content needs

longer to be hydrolysed due to a higher steric hindrance caused by longer side chains, the observation may be explained. However, there is no significant difference in total yield for high and low molar contents of HHx.

Overall, the increasing HHx content of PHA has no significant influence on the results of chemical recycling with solid catalysts compared to the homopolymer PHB. However, higher HHx content reduces the $T_m$ of the polymer (approx. 125 °C for 14.2% HHx *vs.* approx. 180 °C for PHB). Therefore, different $T_m$ for itself seem not to influence the reaction. This was expected since the reaction is carried out above the polymers $T_m$.[69,99] The same applies for the degree of crystallinity, which is reduced with increasing HHx content from 50 to 20% for the tested copolymers, but above $T_m$ the polymer should be in the molten state.[69] Therefore, promisingly, copolymers demonstrated to be no hindrance for chemical recycling approaches with solid catalysts.

**Evaluation of chemical recycling with solid catalysts for (reinforced) bioplastics.** Although some of the underlaying phenomena are not fully understood yet, chemical recycling *via* hydrolysis with solid catalysts appears to be a promising option to establish a closed loop for bioplastics. This could reduce the need for virgin biomass as feedstock and thereby minimises the biggest drawbacks of biobased chemicals – being partially in conflict with food production.

The demonstrated system is able to convert bioplastics over

- a broad range of molecular weights $M_n$
- with and without reinforcement agents
- as pure polymers or as copolymers

into valuable building blocks for a renewable chemical industry. Thereby, one of the biggest advantages is the synthesis of the respective building blocks in the pure form, thus without the generation of significant amounts of salts in case of acid/alkaline hydrolysis. Furthermore, the temperature range, although being higher than for some homogeneously catalysed approaches, is far below the temperatures of gasification or pyrolysis. Furthermore, the effort for downstream processing is
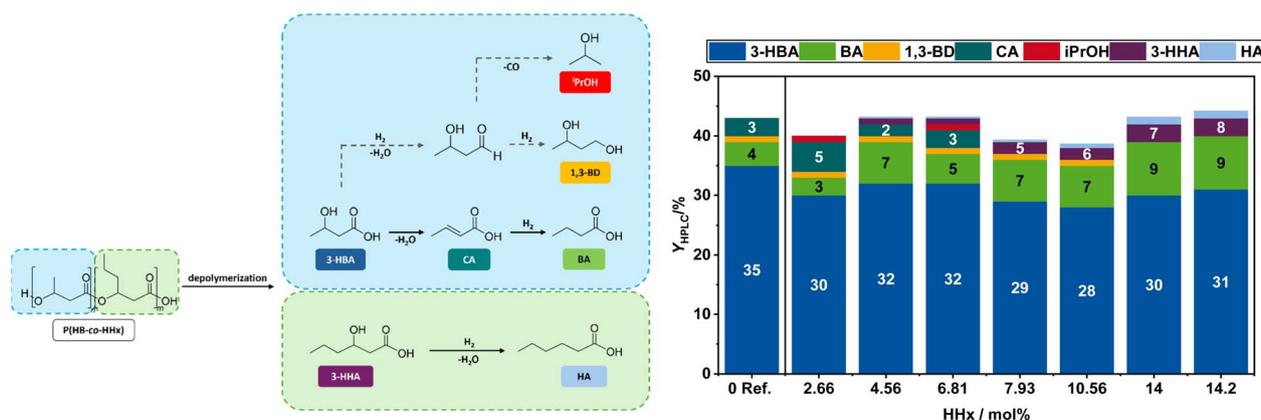


Fig. 4  (Left) Illustration of the copolymer P(HB-*co*-HHx) and the respective follow-up products. Abbreviations: 3-HBA – 3-hydroxybutyric acid, BA – butyric acid, 1,3-BD – 1,3-butanediol, CA – crotonic acid, iPrOH – isopropanol, 3-HHA – 3-hydroxyhexanoic acid, HA – hexanoic acid. (Right) Chemical recycling results for a variety of P(HB-*co*-HHx) samples. Conditions: 5 mg Ru$_{5\ wt\%}$/CeO$_2$, 138 mg PHA, 200 °C, 5 bar H$_2$, 5 mL H$_2$O, 500 rpm, 0.75 h, 10 mL Hastelloy autoclave.

reduced since fewer steps are necessary to build up functional chemicals.

Potential fields still to be explored are the catalysts prize as well as long term stability, the precise effect of different polymer characteristics on the underlying mechanism as well as the scale-up of the process. Equally important will be the efficient recovery and reuse of the Ru/CeO$_2$ catalyst, as catalyst retention and recyclability determine both the economic and environmental sustainability of noble-metal-based systems. Although CeO$_2$ proved catalytically active and mechanistically informative, it is not ideally suited for long-term operation due to its tendency to leach under acidic conditions (below a pH-value of 4).[57,100] Nevertheless, the structure–activity relationships identified for the Ru/CeO$_2$ catalyst provide valuable insights that can guide the development of more robust support materials for future applications.

In addition to catalytic activity and selectivity, the downstream processing and purification of the depolymerization products will be decisive for the overall process feasibility. The mild reaction conditions applied in this study help to suppress side reactions and formation of secondary products, which can facilitate subsequent separation steps. However, the efficient removal of unreacted polymer and soluble residues remains a critical challenge for scaling up chemical recycling. Furthermore, future research should extend to realistic waste mixtures originating from sorting streams, where impurities and compositional heterogeneity will test the robustness of the catalytic system.

If these fields are researched, chemical recycling by means of hydrolysis with solid catalysts can be a vital driving factor to boost the spread of biopolymers and contribute to the transition of the chemical industry from fossil based and linear to biobased and circular.

## Conclusions

The influence of molecular weight $M_n$, reinforcement agents and co-polymers on the chemical recycling with solid catalysts on bioplastics was investigated. A correlation between higher molecular weight ($M_n$) of PLA and lower product, thus LA yield was identified. Compared to conventional reactions where the product can be detected immediately after a catalytic cycle using typical methods such as HPLC or GC, polymer recycling involves multiple chain scissions before low-molecular-weight products, such as monomers, become detectable. This results in lower yields for polymers with higher $M_n$ at a given time. This may not be based on fewer catalytic events, but on the delayed detection of reaction intermediates. It is therefore important to differentiate between the actual number of chain scissions occurring and the detectability of low-molecular products. Mechanical strength-boosting additives such as cellulose nanocrystals (CNC) and nanochitin (NCh) can affect the biodegradation and recycling of PLA polymers. Reinforcement with 2% NCh turns out to be the optimal point in terms of recycling with the highest yields of LA among the polymers with functionalised additives. However, higher reinforcement rates (3%), independent if functionalised or not, decrease the degradation efficiency, possibly due to the interaction between the

reinforcements and the catalysts or changes in the viscosity. PHA copolymers, represented by P(HB-co-HHx), have only slight influence on the chemical recycling. The catalyst was able to degrade the entire PHA copolymer regardless of its HHx content. At elongated reaction time, total yields close to full conversion could be obtained. In summary, the chemical recycling of bioplastics by means of hydrolysis with solid catalysts represents a promising method, which can contribute to the establishment of a circular economy in the chemical industry.

## Author contributions

Marcus S. Lehnertz – conceptualisation, investigation, project administration, writing – original draft; Sylvie Dufour – investigation, writing – original draft; Tabea Becker – investigation, writing – original draft; Isabel Thiele – investigation, writing – original draft; Saskia Waldburger – investigation, writing – original draft; Jean-Marie Raquez – funding acquisition, writing – review and editing; Sonja Herres-Pawlis – funding acquisition, writing – review and editing; Sebastian L. Riedel – funding acquisition, writing – review and editing; Regina Palkovits – funding acquisition, writing – review and editing.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

HPLC and SEC data are available *via* the RADAR4Chem repository by FIZ Karlsruhe - Leibniz Institut für Informationsinfrastruktur and are published under an Open Access model (CC BY-NC-SA 4.0 Attribution-NonCommercial-ShareAlike): DOI: https://doi.org/10.22000/a5juqpkyz2xxzv7f.

Supplementary information (SI): includes a list of abbreviations, comprehensive reaction results from the different screening studies, as well as GPC chromatograms and FTIR spectra of the nanocrystals. See DOI: https://doi.org/10.1039/d5su00469a.

## Acknowledgements

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