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Open Loop Recycling – Guanidine Iron(II) Polymerization Catalyst for the Depolymerization of Polylactide

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Abstract: A previously reported non-toxic guanidine-iron catalyst active in the ring opening polymerization (ROP) of polylactide (PLA) under industrially relevant conditions was evaluated for its activity in the alcoholysis and aminolysis of PLA under mild conditions. Kinetic and thermodynamic parameters were determined for the methanolysis of PLA with [FeCl$_2$(TMG5NMe$_2$asme)] (**C1**) using ^{1}H NMR spectroscopy. A comparison with the Zn analog of **C1** showed that the metal center has a large impact on the activity for the alcoholysis. Further, the influence of different nucleophiles was tested broadening the scope of products from PLA waste. **C1** is the first discrete metal catalyst reported to be active in the selective aminolysis of PLA. Catalyst recycling, scale-up experiments and solvent-free alcoholysis were conducted successfully strengthening the industrial relevance and highlighting aspects of green chemistry. Moreover, the selective depolymerization of PLA in polymer blends was successful. **C1** is a promising catalyst for a circular (bio)plastics' economy.

Introduction

With increasing urgency to change the current, linear, fossil-based plastics economy to a more sustainable one, biodegradable and biobased plastics such as polylactide (PLA) are considered as sustainable solutions for the challenges the world is phasing right now.[1] Besides developing alternatives for commodity plastics the whole plastics economy needs to be remodeled. A circular approach – considering the end-of-life (EoL) of the plastics from the polymer design on – is a much-needed step towards a more sustainable future. Waste reduction, waste management, and proper recycling of plastic waste are as important as the implementation of sustainable polymers in the plastics market.[2]

PLA is biobased and completely degradable to CO$_2$ and water under industrial composting conditions.[3] Currently, PLA is produced in industry from lactide (LA) *via* a ring opening polymerization (ROP) using cytotoxic tin octanoate (Sn(Oct)$_2$).[4] The toxicity of Sn(Oct)$_2$ is especially relevant considering the degradation process during which tin could be accumulated and propose a danger to the environment. In the last years, new catalysts with benign metal centers such as Fe[5] or Zn[6] were proven to perform better than Sn(Oct)$_2$ under industrial conditions. With a circular approach for the plastics economy in mind, investigating the polymerization is not enough: The EoL of the polymer must be considered as well. PLA can be recycled in

several ways: biodegradation,[3, 7] mechanical recycling,[8] and chemical recycling.[8-9] Biodegradation to water and CO$_2$ leads to crop growth and therefore, to new biomass as monomer source but the expensive production of lactide limits the efficiency of this recycling strategy. Mechanical recycling is a good approach if the plastics waste is very pure. But these processes are often limited by the number of recycling cycles and impurities lead to a loss of polymer quality.[2a, 8, 10] Chemical recycling has the ability to either close the loop completely by turning plastic waste into new monomers without quality loss or to produce new value-added molecules in an open loop approach to a circular plastics economy.[2b, 6b, 11] The alcoholysis of PLA breaks the polymer into alkyl lactates such as methyl lactate (Me-LA) or ethyl lactate (Et-LA) which can either be transformed into LA[11k, 11p] or applied as green solvent.[12] Being able to use the same catalysts for the polymerization of LA and alcoholysis of the polyester can further lower the costs for PLA production. Several catalysts are reported to be active in the polymerization and alcoholysis including ionic liquids,[13] organocatalysts,[11f, 12c, 14] and, Sn,[11o] Zn,[11a-e, 11g, 11p, 15] Mg,[11e] and group 4 salalen complexes.[11a] Discrete iron complexes have not been reported to catalyse the alcoholysis of PLA, yet.

In this report, the activity of the guanidine Fe catalyst [FeCl$_2$(TMG5NMe$_2$asme)] (**C1**) for the selective alcoholysis and aminolysis of PLA under mild conditions is investigated. **C1** performs better than Sn(Oct)$_2$ in the ROP of LA and is therefore a promising candidate for industrial application in PLA polymerization (Figure 1).[5] A further advantage of "TMGasme"-type complexes is the approach to a benign catalyst design. A Zn complex with a TMGasme ligand was reported to be eco-toxicologically safe.[16] Thermodynamic parameters for the methanolysis of PLA and kinetic parameters for the alcoholysis in general with **C1** were determined and a comparison with its Zn analog was drawn up. The influence of different alcohols and their
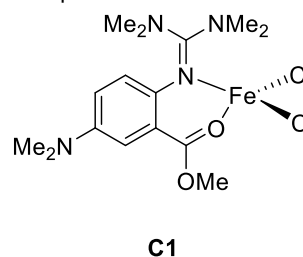

Figure 1. Molecular structure of [FeCl$_2$(TMG5NMe$_2$asme)] (**C1**).[5]

chain length was investigated. Further, selective aminolysis of PLA was conducted successfully for the first time.

Additionally, experiments such as the alcoholysis under solvent-free conditions, and catalyst recycling were conducted following a green chemistry approach. Studies towards industrial relevance were conducted by testing the catalyst stability towards impurities, isolating Me-LA, and scaling-up the reaction by factor 10. The selective depolymerization of PLA in polymer blends and the activity of **C1** for the alcoholysis of polyhydroxybutyrate (PHB), poly(3-hydroxybutyrate-*co*-3-hydroxyvakerate) (PHBV), polybutylene adipate terephthalate (PBAT) and polyethylene terephthalate (PET) were studied.

Results and Discussion

For a circular plastics economy, the EoL of any product needs to be considered from the start. Chemical recycling has the possibility to solve two problems at once: EoL plastics would no longer be one of the biggest contributors to the pollution of the environment but could be a new source for monomers or value-added chemicals. Using catalysts that show high activity in the polymerization of PLA for the depolymerization benefits this circular approach. The studied "TMGasme"-type Fe complex exhibits a high activity for the ROP of lactide to PLA. **C1** was chosen over other "TMGasme"-type guanidine Fe catalysts due to its higher activity for the ROP.[5] Further, a study of the structure activity relationship of three "TMGasme"-type Zn complexes showed that [ZnCl2(TMG5NMe2asme)] has the highest activity for the alcoholysis.[11j] After the resynthesis of **C1**,[5] the activity towards the methanolysis of PLA (PLA film produced by bio-mi Ltd. (Croatia), average molar mass: 49700 g mol^{-1}) in THF at 60 °C was investigated (Table 1, entry 2). Therefore, the conversion of internal methine groups (int) of PLA (X_{int}), the selectivity towards the product (S_{R-LA}) and the product yield (Y_{R-LA}) were calculated using ^{1}H NMR spectroscopy.[11c, 15b] A two-step transesterification mechanism is proposed for the alcoholysis of PLA.[9b, 11c, 11h, 15b, 17] First, the polymer is depolymerized to α- and Ω-oligomers through random scission of the polymer backbone. This irreversible step follows a pseudo first order mechanism. Subsequently, the oligomers are transformed to the corresponding lactate in an equilibrium reaction (Scheme 1).[9b, 11c, 11h, 15b, 17]
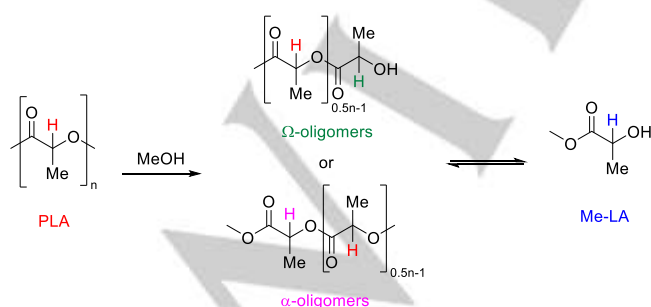
Scheme 1. Proposed two-step mechanism for the methanolysis of PLA.[11c, 11h, 15b]

This theory is supported by the analysis of the obtained ^{1}H NMR spectra during the methanolysis using 1 mol% **C1** at 60 °C: The

calculated PLA concentration decreases exponentially, whereas the oligomer concentration reaches a maximum and declines slowly during the reaction process. The Me-LA concentration starts to increase slightly delayed after oligomers have been formed (Figure S2).[11b] For a high-quality comparison of catalytic systems, the depolymerization rate constant k_{dp} of **C1** was determined from the slopes of k_{app} vs. the catalyst concentration (Figure 2). The obtained value of k_{dp} (0.0024±0.0001 mol%$^{-1}$ min^{-1}) (Figure S3) is lower than for its Zn analog [ZnCl2(TMG5NMe2asme)] (k_{dp} = 0.00488 mol%$^{-1}$ min^{-1}).[11j] This observation is contrary to the trend for the polymerization of PLA. Here, the Fe catalyst is more active than its Zn analog.[5, 18]
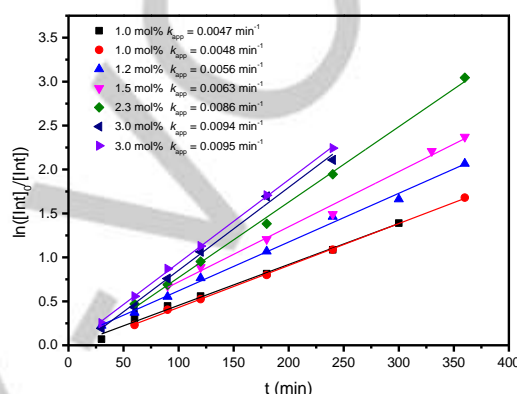
Figure 2. Semilogarithmic plots of ln([Int]0/[Int]t) vs. *t* for PLA methanolysis using different concentrations of **C1** in THF at 60 °C.

For a better understanding of these results, further experiments were performed to determine the activation energy E_a, the activation enthalpy ΔH, and the activation entropy ΔS.[11g, 15b, 19] The ethanolysis and methanolysis of PLA using **C1** were conducted at different temperatures (T = 40, 50, 60, 70 °C). The activation energy (75±6 kJ mol^{-1}) of the methanolysis is higher than for the methanolysis for known Zn systems (E_a = 45 kJ mol^{-1}).[15b] ΔH (72±6 kJ mol^{-1}) and ΔS (-109±19 J mol^{-1} K^{-1}) were calculated as well and can be used for comparisons with other discrete metal complexes (Figures S4 and S5).

Besides MeOH, EtOH, *i*-BuOH and *n*-BuOH were previously reported as nucleophiles active in the depolymerization of PLA following the same reaction mechanism as the methanolysis.[11g, 11j, 20] Using zinc catalysts, an impact of the chain length of the alcohol on the reaction process was reported: Increasing chain length leads to a lower k_{app}, a decreasing conversion of PLA and selectivity towards the product. MeOH seems to be easier activated than the longer chain alcohols using Zn catalysts.[11g, 11j] For **C1**, this trend was not observed. Comparing MeOH, EtOH, and *i*-BuOH shows no significant deviation for X_{int}, S_{R-LA}, and Y_{R-LA} of the different alcoholysis after 360 min under standard reaction conditions (Table 1, entries 2, 10 and 13). After 1440 min, the methanolysis yields 100 % Me-LA whereas the reactions with EtOH and *i*-BuOH show lower conversion and/or selectivity. The calculated k_{app} values are similar for MeOH and *i*-BuOH. The deviation of selectivity and yield of R-LA suggest that in the second reaction step the Me-LA formation is more favored than the formation of *i*-Bu-LA. The ethanolysis has the lowest k_{app} value and selectivity. *n*-BuOH shows the highest conversion of PLA and has the highest selectivity towards *n*-Bu-LA under standard reaction conditions after 360 min (Table 1, entry 12). These

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observations suggest a beneficial influence of the linear C4-chain of *n*-BuOH under standard reaction conditions. A trend concerning chain length and the investigated parameters could not be identified.

Table 1. Results of PLA alcoholysis.[a]

#	Nuc	T (°C)	t (h)	X_{int} (%)[b]	$S_{R\text{-}LA(M)}$ (%)[b]	$Y_{R\text{-}LA(M)}$ (%)[b]	k_{app} (min⁻¹)[c]
1	MeOH	50	6	49	30	14	0.0016
			24	95	79	75	
2	MeOH	60	6	73	55	40	0.0036
			24	100	100	100	
3[d]	MeOH	60	96	58	31	18	n.d.
4[e]	MeOH	60	6	96	77	74	0.0083
			24	100	100	100	
5[f]	MeOH	reflux	3	77	54	42	n.d.
6[g]	MeOH	60	24	100	100	100	n.d.
7[h]	MeOH	60	24	100	96	96	n.d.
8[i]	MeOH	150	1	99	100	99	n.d.
9	EtOH	50	6	58	41	24	0.0021
			24	91	71	65	
10	EtOH	60	6	74	54	40	0.0030
			24	100	75	75	
11[i]	EtOH	150	1	100	100	100	n.d.
12	*n*-BuOH	60	6	95	79	76	0.0076
			24	100	100	100	
13	*i*-BuOH	60	6	73	51	37	0.0035
			24	98	85	83	
14[j]	AllylOH	60	24	100	100	100	n.d.
15	BnOH	60	6	74	100	74	n.d.
			24	100	100	100	
16	BnNH₂	60	1	99	82	81	n.d.
			3	99	100	99	
17[k]	BnNH₂	60	1	81	23	19	n.d.
			3	100	75	75	

[a] Standard procedure: 250 mg PLA (bio-mi Ltd.), 1 mol% **C1** (regarding the PLA ester bonds), nucleophile (7 eq.), 4 mL THF, 60 °C, 260 rpm (further details can be found in the supporting information (SI)). [b] The conversion of internal methine groups of PLA (X_{int}), the selectivity towards the product ($S_{R\text{-}LA(M)}$), and the yield of the product ($Y_{R\text{-}LA(M)}$) were calculated from ¹H NMR spectroscopy according to literature. The results for the ethanolysis were calculated according to a new method (SI, Section 4). [c] Calculated from ln([Int]₀/[Int]ₜ). [d] experiment was performed using unpurified methanol and without Schlenk technique. [e] PLA from a cup from Huhtamäki was used. [f] Scaled up by factor 10: in Schlenk flask, 0.5 mol% **C1**, under reflux conditions. [g] 3 mol% **C1** (regarding the PLA ester bonds). [h] Catalyst recycling of Entry 4. [i] Under solvent free conditions. [j] Calculated using toluol as internal standard. The ¹H NMR data could not be analysed before complete Allyl-LA formation was obtained due to overlapping resonances of the α-oligomers and Allyl-LA (SI, Figure S13). [k] No catalyst. The easy activation of *n*-Bu-LA by **C1** promotes the Fe catalyst as a valuable and versatile tool on the path to a circular bioplastics' economy. *n*-Bu-LA is a key chemical for the industry due to its application as a solvent and as an additive.[11g, 21] Besides the chain length, the influence of the temperature was investigated for the methanolysis and the ethanolysis. The comparison of the results for the methanolysis at 50 °C (Table 1, entry 1) and the results at 60 °C (Table 1, entry 2) after 360 min shows a significant increase for all parameters with increasing temperature. The selectivity towards Me-LA increased by 25 percentage points. Like the methanolysis of PLA, using EtOH as nucleophile depolymerizes PLA to Et-LA (SI, Figure S1).[11g] The ethanolysis follows a similar trend as the methanolysis (Table 1, entry 9 and 10): A temperature increase of 10 °C leads to a 16 percentage points higher conversion after 360 min. The selectivity was impacted as well, increasing by 13 percentage points. Further, the apparent reaction rate constant increased significantly for both depolymerizations. At 50 °C, the ethanolysis proceeds faster than the methanolysis, whereas at 60 °C the methanolysis has a higher k_{app} and reaches a higher selectivity and a higher Me-LA yield than the ethanolysis after 24 h. Therefore, the temperature is a valuable parameter for controlling the alcoholysis of PLA.

Experiments with different nucleophile suggest that the Fe complex **C1** activates difficult nucleophiles to a higher extent than its Zn analog.[11j] Whereas [ZnCl₂(TMGNMe₂asme)] shows only 7 % respectively 10 % conversion of PLA using *n*-BuOH respectively *i*-BuOH, **C1** reaches higher X_{int} and $S_{R\text{-}LA}$ for both alcohols within 24 h (Table 1, entries 12 and 13) compared to different Zn catalysts.[11g, 11j] Therefore, a different transition state and mechanism for the first reaction step due to the metal centers could be plausible. These observations underline the importance of parameters such as the k_{dp} value for a high-quality comparison between catalytic systems and the need for a better understanding of the reaction process.[11j] Further, investigating the influence of the temperature on the aliphatic alcohols leads to a better understanding and a better tunability of the reaction process.

To broaden the scope of products that could be obtained from PLA waste further Allyl-OH, Bn-OH, and Bn-NH₂ were tested as nucleophiles for the depolymerization of PLA. The influence of a double bond neighboring the hydroxy group was investigated using allyl alcohol (Table 1, entry 14) and Bn-OH (Table 1, entry 15). Both alcohols were previously reported for the depolymerization of PLA using an organocatalyst.[14a] The double bond of the allyl lactate (Allyl-LA) could be used to functionalize the obtained product and Allyl-LA could be applied as a new monomer for polymer synthesis.[14a] **C1** depolymerizes PLA using Allyl-OH selectively to Allyl-LA within 24 h. Due to the overlap of the resonances of α-oligomers and Allyl-LA in the ¹H NMR spectra X_{int}, $S_{Allyl\text{-}LA}$, and $Y_{Allyl\text{-}LA}$. could not be determined until full conversion was observed after 24 h. This suggests no negative influence of the double bond on the catalyst activity and product selectivity of the reaction. Bn-OH was successfully applied for the alcoholysis of PLA as well. Here, the absence of oligomers was observed. This observation suggests a different reaction mechanism: Bn-OH attacks at the chain-end of the polymer and is transformed directly to benzyl lactate (Bn-LA) without formation of oligomers. This mechanism was proposed for the alcoholysis under solvent-free conditions by Mazzeo.[11h] Further, the conversion of internal methine groups of PLA is comparable with the results for the alcoholysis using aliphatic alcohols under standard reaction conditions.

To investigate the influence of the benzyl residue further and to proof that **C1** has a broad spectrum of applications, the aminolysis

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using benzyl amine was investigated (Figure 3). The selective aminolysis of PLA using a discrete metal catalyst has not been reported yet. Benzyl amine shows a high autocatalytic activity for the depolymerization of PLA to benzyl lactamide (Bn-LAM) (Table 1, entry 17). **C1** was able to reach complete selective aminolysis of PLA within 180 min (Table 1, entry 16) whereas without catalyst the depolymerization is slower and oligomers can still be detected after 360 min (Figure S16). Contrary to BnOH, the ^{1}H NMR spectra of the aminolysis showed resonances suggesting the presence of oligomers (Figure 3).
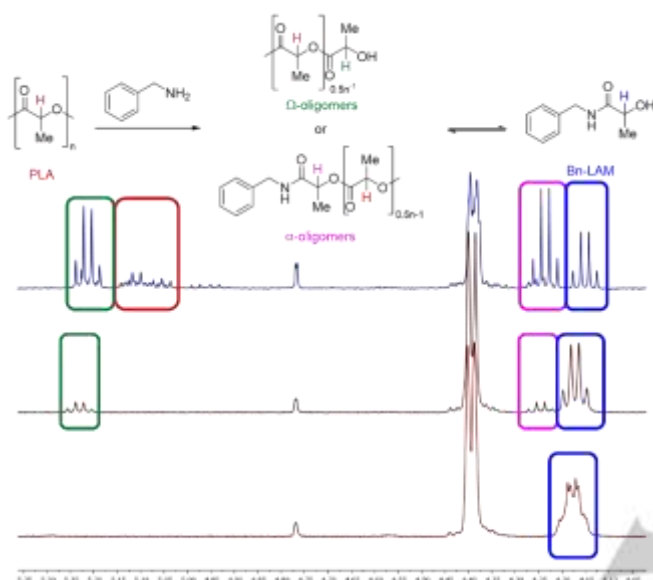
Figure 3. ^{1}H NMR spectra of the aminolysis of PLA using BnNH$_2$ with **C1** (1 mol% regarding PLA ester bonds) after 180 min (bottom), after 60 min (middle) and without catalyst (top) after 60 min (250 mg PLA, 7 eq. BnNH$_2$, 4 mL THF, 60 °C). The resonances are assigned to the protons of the internal methine group of PLA (red), α-oligomers (pink), Ω-oligomers (green), and Bn-LAM (blue) which were used for the calculations of X_{int}, S_{Bn-LAM}, and Y_{Bn-LAM}.

Therefore, besides the benzyl residue, other factors must be crucial for the mechanistic change during the alcoholysis of PLA using BnOH. The selective aminolysis of PLA with **C1** using Bn-NH$_2$ reaches complete depolymerization of PLA to Bn-LAM within 180 min under standard reaction conditions. For comparison: n-BuOH – the fastest alcohol – reaches a conversion of 85 % after 180 min. Therefore, besides alcohols, amines are a promising nucleophile class for the depolymerization of PLA.

Under the aspect of green chemistry, sustainability and industrial relevance further experiments were conducted: The methanolysis was performed under solvent-free conditions at room temperature, 60 °C and 150 °C. The absence of solvent facilitates the work-up, decreases the costs and increases the atom efficiency of the reaction.[22] At room temperature, no conversion of PLA was observed. An increase of the temperature to 60 °C led to a direct conversion of PLA to Me-LA. No resonances for oligomers are present in the ^{1}H NMR spectrum (Figure S20). These observations support the proposed mechanistic change under solvent-free conditions.[11h] At 150 °C, the methanolysis (Table 1, entry 8) and ethanolysis (Table 1, entry 11) under solvent-free conditions were successfully performed.[11j] After 60 min, complete selective depolymerization was observed. Reaching a Me-LA respectively Et-LA yield of 100 % (Figure S21). The methanolysis of PLA using **C1** was studied towards industrial relevance: The methanolysis was conducted using unpurified methanol and without the use of Schlenk technique. A significant

decrease in activity was observed (Table 1, entry 3). This is a disadvantage of **C1** compared to other catalytic systems that operate under more industrial relevant conditions.[11h] Further, a different PLA source was used to investigate the scope if different PLA sources impact the activity or might hinder the reaction. Table 3, entry 4 reports the results of the depolymerization of a commercially available PLA cup from Huhtamäki (Finland). The reaction proceeds significantly faster than using PLA from bio-mi Ltd. highlighting the importance of parameters such as k_{dp} for a high-quality comparison. After complete conversion, Me-LA was isolated by removing MeOH and THF at increased temperatures (69–150 °C) and could be obtained in a 68 % yield (Figure S17). Further, the methanolysis using standard conditions was scaled-up by factor 10 (Table 1, entry 5). The experiment was performed successfully. An additional scale-up experiments confirmed complete conversion of PLA to Me-LA within 17 h (Figure S18). Another important factor is the catalyst recyclability. Table 1, entry 7 displays the results of catalyst recycling experiments. The methanolysis of PLA was performed using 3 mol% **C1** regarding the ester bonds of PLA to assure complete conversion of PLA to Me-LA (Table 1, entry 6). The first depolymerization cycle was conducted under standard reaction conditions as described before. After complete conversion, the catalyst was isolated by removing all other components *in vacuo*. Subsequently, PLA and THF were added to the isolated catalyst and the second recycling cycle was conducted according to the general procedure for depolymerization experiments. The selectivity of **C1** dropped slightly after one recycling cycle but 100 % conversion is still reached within 24 h (Figure S19).

Another important aspect concerning the recycling of polymers is the separation of waste streams. Mixed plastic waste is a huge problem for chemical recycling; therefore, a catalyst selectively depolymerizing PLA under mild reaction conditions could be a huge advantage in the near future. PLA-PBAT and PLA-PCL blends were treated under similar reaction conditions as PLA using 6 wt% respectively 7 wt% **C1**. ^{1}H NMR spectroscopy showed selective depolymerization of PLA to Me-LA. PCL and PBAT were not degraded (Figure S22 and S23). Further, other (bio)plastics like PHB, PHBV and PET were treated under the same reaction conditions as the PLA blends. No signs of degradation could be observed for these polymers promising an easy separation of PLA from plastic waste.

Comparing **C1** with other catalytic systems active in the depolymerization shows that further investigation and optimization of the catalyst is needed. Schiff-base Zn catalysts show a higher activity for the methanolysis: Jones and Wood *et al.* reported a highly active Zn catalyst with a k_{app} value of 0.2 min^{-1}.[15b] Other Zn systems using guanidine ligands show k_{app} values between 0.037 and 0.034 min^{-1}.[6b] But, regarding nucleophiles, which are harder to activate such as n-BuOH or i-BuOH, **C1** shows comparable or higher k_{app} values than Zn based metal catalysts.[11g, 11j] As mentioned before, k_{app} is a valuable parameter for an estimation of the activity of the catalytic system. For a high-quality comparison, the calculation of k_{dp} is beneficial. Further, simple Zn catalyst such as Zn(OAc)$_2$ show a high turnover frequency (TOF = 45000 h^{-1}) for microwave assisted depolymerization of PLA under solvent-free conditions at 180 °C.[11o, 11p] Besides the activity, catalysator costs are an important topic. Compared to simpler catalytic systems, **C1** has higher costs but is comparable to other discrete metal catalysts. Due to its versatile applications: polymerization of different cyclic

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esters,[23] depolymerization with different nucleophiles, and its recyclability, the hybrid guanidine catalyst has a high potential.

Conclusion

A previously published N,O-hybrid guanidine Fe complex was resynthesized and its activity in the depolymerization of PLA was studied. **C1** depolymerized PLA in the presence of methanol completely and selectively to Me-LA under standard reaction conditions (250 mg PLA, 1 mol% catalyst, 60 °C, THF) within 24 h. Therefore, we report the first discrete Fe catalyst active in the alcoholysis of PLA. For a better comparison of catalytic systems, k_{dp} for the methanolysis using **C1** was determined (0.0024±0.0001 mol%$^{-1}$ min^{-1}). **C1** shows a lower k_{dp} than its Zn analog [ZnCl$_2$(TMG5NMe$_2$asme)]. This suggests that the metal center has a significant influence on the reaction. The observed trend is contrary to the one reported for the ROP using "TMGasme"-type Zn complexes.[5, 18] In the Zn complexes the more active complex in the polymerization is the more active one in depolymerization. In our case, **C1** shows a higher polymerization activity than the Zn analogous complex but the depolymerization activity is less pronounced.

Further, experiments using different nucleophiles for the depolymerization of PLA were conducted: Besides MeOH, EtOH, *i*-BuOH, *n*-BuOH, AllylOH, BnOH, and BnNH$_2$ were tested. All nucleophiles displayed high conversions of PLA and good selectivity towards the products under standard reaction conditions within 24 h. It has to be noted that this is the first time of an aminolysis reported for PLA with a discrete metal complex. These results show that PLA waste could be a new source for a variety of important molecules for industrial use including lactates and lactamides. Additionally, experiments investigating green chemistry aspects and studies towards the industrial relevance were conducted: The activity loss using unpurified MeOH has to be further investigated: optimizing the ligand design could lead to a more stable catalyst. Catalyst recycling was performed successfully and the methanolysis was scaled-up by factor 10. The methanolysis and ethanolysis were performed under solvent-free conditions at 150 °C within 60 min achieving 100 % yield of the corresponding alkyl lactate. **C1** selectively depolymerizes PLA in presence of other polymers such as PCL and PBAT and showed no impact on PHB, PHBV and PET facilitating downstream plastic waste separation.

The hybrid guanidine Fe catalyst **C1** is a versatile catalyst for the alcoholysis and aminolysis of PLA under mild conditions. **C1** can be used for the selective depolymerization of PLA with a broad variety of nucleophiles helping to take one more step towards a sustainable, circular plastics economy.

Experimental Section

General procedure of the PLA alcoholysis and aminolysis

A Young-type Schlenk tube was loaded with PLA (250 mg, 3.47 mmol regarding ester bonds, 1.00 eq.), **C1** (0.5-1.0 mol%) and THF (4 mL) in a glovebox. PLA and the catalyst were dissolved using an external heat source. The reaction flask was placed in a preheated oil bath (40-70 °C). The nucleophile (25 mmol, 7 eq.) was added under a stream of Ar. The reaction process was monitored by ^{1}H NMR spectroscopy. For the determination of k_{app}, small samples were taken after 30, 60, 90, 120, 180,

240, 360 and 1440 min and dissolved in CDCl$_3$ for the NMR spectroscopic measurement. The obtained data was used to determine X_{int}, S_{R-LA}, Y_{R-LA} and k_{app} according to literature.[15b] The results for the ethanolysis were determined using a new method described in the supporting information (SI, Section 4).

General procedure for catalyst recycling experiments

An experiment following the general procedure for the methanolysis of PLA using 3 mol% **C1** was conducted at 60 °C. After complete conversion, all volatile components were removed under reduced pressure (high vacuum). PLA (250 mg, 3.47 mmol regarding ester bonds, 1.00 eq.) and THF (4 mL) were added in a glovebox. All solid components were dissolved using an external heat source and the reaction flask was placed in a preheated oil bath (T = 60 °C). The reaction was started by adding MeOH (1.0 mL, 25 mmol, 7.1 eq.). A sample was measured using ^{1}H NMR spectroscopy after 23 h.

General procedure of the scale-up experiments

PLA (2.5 g, 35 mmol, 1.0 eq.) and **C1** (0.5 mol% regarding ester bonds) were equipped to a Schlenk flask in a glovebox. THF (40 mL) was added and PLA and **C1** was dissolved using an external heat source. MeOH (10 mL, 7.1 eq.) was added, and the reaction stirred at 260 rpm under reflux conditions. The reaction was monitored using ^{1}H NMR spectroscopy. After 3 d, the reaction was cooled to room temperature. All volatile residues were removed under high vacuum and collected in a cooling trap. THF and MeOH were removed under reduced pressure. Me-LA was obtained in an 80 % yield as a clear, colorless liquid.

General procedure of solvent-free alcoholysis

For the solvent-free alcoholysis, PLA (250 mg, 3.47 mmol, 1.00 eq.) and **C1** (15 mg, 3.5 µmol, 1.0 mol%) were equipped to a Young-type Schlenk tube. MeOH respectively EtOH (25 mmol, 7.1 eq.) was added. The reaction was placed in an oil bath at room temperature, 60 °C or 150 °C. Samples were taken, dissolved in CDCl$_3$, and measured with ^{1}H NMR spectroscopy. At 150 °C, the reaction flask was rapidly cooled to room temperature to stop the reaction process before a sample was taken.

Additional experimental details, analytics and evaluation of all conducted experiments can be found in the supporting information.

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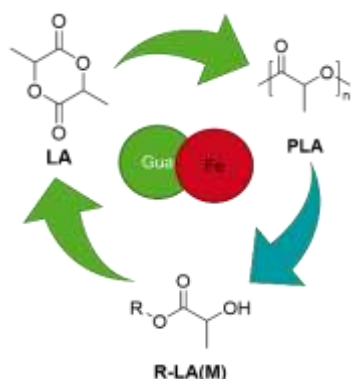
Versatile Allrounder: We report the first iron catalyst active in the selective alcoholysis and aminolysis of PLA using different nucleophiles. Having the increasing plastic waste problem and the acute danger imposed by climate change in mind solvent-free alcoholysis and catalyst recycling were investigated. Further, the successful selective methanolysis of PLA could facilitate the downstream separation of mixed plastic waste.

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