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Guanidine Carboxy Zinc Complexes for the Chemical Recycling of Renewable Polyesters

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Dedicated to Prof. Wolfgang Beck on occasion of his 90th birthday.

Our previously published non-toxic guanidine carboxy Zn catalysts, suitable for lactide ring opening polymerisation (ROP) under industrially preferred melt conditions, have been tested towards the alcoholysis of renewable polyesters. A structure-reactivity relationship has been found for the methanolysis of PLA in anhydrous THF, dependent on the substituents introduced at the ligand backbone. Using the unsubstituted "TMGasme" catalyst **C2**, a polyester conversion of 41% was reached after 5 h at 60 °C. Introducing an electron density donating -NMe$_2$ group at the ligand (**C3**) caused and increase in catalyst activity, resulting in a PLA conversion of 72%. Hence, **C3** was further tested, stressing the industrial applicability of PLA chemical recycling. Catalyst recycling, process scale up as well as solvent free alcoholysis, with full degradation in the PLA melt after 1 h, were demonstrated, allowing for the implementation of a circular (bio)plastics economy promoted by these catalysts.

Introduction

Renewable, biodegradable plastics such as polylactide (PLA) are often stated as a solution to overcome the environmental pollution caused by petroleum based, non-degradable plastics.[1] However, biodegradation cannot be the only answer, as it requires certain controlled conditions such as defined temperature or pH value.[2] Efficient biodegradation of PLA can therefore only be achieved at industrial composting sites in about 60 days.[3] In natural soil full degradation is extended to about a year,[4] whereas almost no biodegradation of PLA occurs in a marine environment.[5] Aside from that, toxic impurities such as tin octanoate (Sn(Oct)$_2$), the catalyst currently used in industrial PLA production via ring opening polymerisation (ROP) of lactide, can be released from the polymer during degradation.[6] Hence, accumulation of these substances in landfills can be a further threat to the environment. Extensive research has been made towards non-toxic metal catalyst as an alternative to Sn(Oct)$_2$.[7] Catalysts based on Fe,[8] Al,[8b,9] Mg,[10] Ge,[11] Sc,[9c,12] Zn[9a,13] and group 4 metals[14] have been reported most of which require highly purified monomer or solvents for the best performance, hindering the use in industry. Nevertheless, robust and highly active Zn based catalyst show a great potential for industrially preferred ROP in the polymer

melt.[10,13e,j,k] Recently, Herres-Pawlis et al. presented a Zn guanidine catalyst, drastically outperforming the industry catalyst under such conditions.[15] However, the majority of these examples states biodegradation as the only end of life option for PLA. Recently the focus in literature shifted towards different recycling strategies for PLA. Mechanical recycling, while a promising method for a direct product-to-product recycling, often involves a loss of polymer quality due to contamination or mixed a plastics feed.[16] Chemical recycling methods, such as alcoholysis, can be used to selectively degrade PLA from polymer mixtures. In this process, the polymer is broken down into smaller molecules.[17] Various alkyl lactates are thus accessible from PLA via alcoholysis.[18] These can be used directly as green solvents (ethyl lactate),[19] as starting materials[18,20] or cyclized back to the monomer lactide.[17] Using recycled lactide in PLA production can reduce the overall cost, since most of the process costs in traditional PLA production is caused by the fermentation of starchy plants to lactic acid, which is subsequently transformed into the monomer, making the chemical recycling beneficial for industry.[21] Furthermore, such efficient recycling can drastically reduce the environmental impact of PLA and its degradation products. Various examples have been presented in literature involving ionic liquids,[22] organocatalysts[18,20,23] and even simple metal salts[24] as catalyst for PLA alcoholysis.[25] While omnipresent in lactide ROP, non-toxic metal based catalysts recently started to emerge in PLA alcoholysis as demonstrated in the works of Jones or Mazzeo.[26]

In this study we investigated our previously published, non-toxic and robust guanidine carboxy Zn chloride ROP catalyst towards their activity in the polylactide alcoholysis. These catalysts, based on the "TMGasme" ligand system are well suitable for lactide ROP under industrially preferred melt conditions and thus fulfil vital requirements to substitute Sn(Oct)$_2$ as the catalyst for industrial PLA production. Facile

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ligand synthesis gives quick excess to various ligands. The ROP activity of the respective Zn catalyst is therefore tuneable via the introduced substituents in backbone of the "TMGasme"-ligand.[13j,k] Activity of three "TMGasme"-type Zn complexes (Figure 1) to form methyl lactate (MeLa) from PLA, using mild reaction conditions was proved, following a structure-reactivity relationship, dependent on the introduced substituents at the ligand backbone.

The fastest catalyst was subsequently tested towards an application in industry, showing promising results and further demonstrating the overall industrial relevance of these catalyst class as an all-round tool for PLA production and recycling.
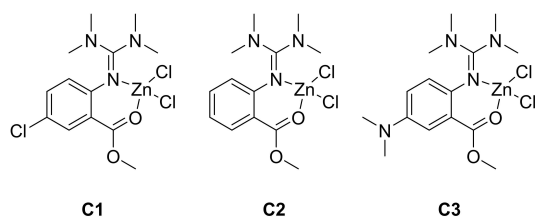

Figure 1. Chemical structure of the used "TMGasme"-type guanidine Zn chloride catalysts: [ZnCl$_2$(TMG5Clasme)] (**C1**), [ZnCl$_2$(TMGasme)] (**C2**), [ZnCl$_2$(TMG5NMe$_2$asme)] (**C3**).[13j,k]

Table 1. Results of polyester alcoholysis.[a]

#	cat	t [h]	polyester conversion [%][b]	product selectivity [%][b]	product yield [%][b]	k_{obs} [$\times 10^{-1}$ h^{-1}][c]
1[d]	C1	5	35 (78)	14 (42)	5 (33)	0.84
2[d]	C2	5	41 (89)	17 (54)	7 (33)	1.08
3[d]	C3	5	72 (100)	32 (86)	23 (86)	2.65
4[e]	C3	5	21	7	1	0.47
5[f]	C3	5	13	10	1	0.27
6[g]	C3	20	98 (100)	85 (88)	83 (88)	n.d.
7[h]	C3	24	98 (75)	86 (33)	85 (25)	n.d.
8[i]	C3	5	59	23	14	1.79
9[j]	C3	5	87	46	40	4.02
10[k]	C3	5	86	46	40	3.99
11[l]	C3	5	90	54	49	4.52
12[m]	C3	72	21	100	21	0.03
13[n]	C3	5	88	91	80	n.d
14[o]	C3	24	n.d.	n.d.	n.d.	n.d.
15[p]	C3	1	100	98	98	n.d.

[a] Standard procedure: Schlenk tube at 60 °C and THF, 260 rpm, catalyst loading of 1 mol% (regarding the polymer ester bond), MeOH loading of 7.1 eq, 250 mg PLA. [b] from ^{1}H NMR spectroscopy according to literature. [c] from ln(polyester$_0$/polyester$_t$) vs. t. [d] results after 24 h in brackets. [e] with n-BuOH. [f] with i-BuOH. [g] scaled up, in Schlenk flask, in brackets results for small scale experiment [h] catalyst recycling, using the standard small-scale procedure, results for second run in brackets. [i] with 1.0 eq PET (regarding the PET ester bonds), 1 mol% **C3** regarding the PLA ester bonds. [j] with each 0.5 equiv. PLA and PET (regarding the respective ester bonds), 1 mol% **C3** regarding all ester bonds. [k] with 0.25 equiv. PLA and 0.75 equiv. PET (regarding the respective ester bonds), 1 mol% **C3** regarding all ester bonds. [l] with PLA-PCL blend, with 5.96 w/w **C3**, regarding the polymer weight. [m] with PCL, 1 mol% **C3** regarding the PCL ester bonds. [n] solvent free at 60 °C, 1 mol% **C3** regarding the PLA ester bonds. [o] solvent free at room temperature, 1 mol% **C3** regarding the PLA ester bonds, PLA conversion product selectivity and yield not determined due to mostly undissolved PLA (see Figure S16, almost no reaction has taken place). [p] solvent free at 150 °C, 1 mol% **C3** regarding the PLA ester bonds.

Results and Discussion

To introduce a tool for efficient chemical recycling and enable a circular (bio)plastics economy, three "TMGasme"-type Zn chloride catalysts were resynthesised (Figure 1) and tested towards the methanolysis of polylactide (single use cup $M_n = 54.600$ gmol^{-1}) to form methyl lactate (MeLa) at 60 °C in anhydrous THF.[13j,k] All catalysts were active towards the formation of MeLa, with **C3** showing the highest activity (Table 1, entry 1–3). The activity decreases if the unsubstituted catalyst **C2** was used and was even further reduced by introducing an electron density withdrawing group to the ligand backbone (**C1**).

Although different reactions in itself, a similar structure-reactivity relationship is found for PLA methanolysis and lactide ROP comparing the unsubstituted catalyst **C2**, with **C3**, which shows the highest activity in both cases. The increase in activity for **C3**, caused by the electron density donating -NMe$_2$ group introduced at the ligand, is most likely due to a stabilizing effect caused by the increased electron density at the ligand. For **C1** in contrast to lactide ROP, the opposite effect is observed in the methanolysis, a decrease of activity. The electron density withdrawing chlorido group at the ligand lowers the electron density at the ligand. In lactide polymerisation, this leads to an increased activity compared with the unsubstituted catalyst **C2**.[13j,k] The structure-reactivity relationship found for the three tested "TMGasme" catalysts in the PLA methanolysis is therefore most likely to correlate with catalyst stability. During the reaction, the formation of PLA oligomers was observed (Figure 2). Therefore, random chain scission of the polymer occurs and the formation to MeLa is following a two-step consecutive reaction, consistent with literature.[26a,b]

Herein, PLA is first degraded into oligomers, that are then transformed to MeLa in an equilibrium reaction. Thus, the degradation of PLA can be described using a pseudo first order rate law. The observed reaction rate constant k_{obs} was determined for different catalyst loadings, as shown in Figure 3 for **C1** (for **C2** and **C3** see Supporting Information, Figures S1/2).

Using the obtained results, the reaction rate constant of the PLA degradation k_{dp} was determined from the slope of the resulting plot of k_{obs} vs. catalyst loading (Figure 4). The obtained k_{dp} values further support the structure-reactivity relationship
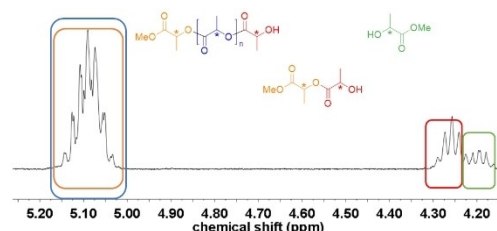

Figure 2. Exemplary ^{1}H NMR spectrum (CDCl3, 400 MHz) of PLA alcoholysis into methyl lactate after 2 h reaction time (250 mg PLA; 1 mol% **C3** & 7.1 eq MeOH, regarding the polymer ester bonds) with assignment of the methine signals used for the kinetic evaluation according to literature (blue: polylactide, orange: α-end, red: Ω-end, green: methyl lactate).[26a]
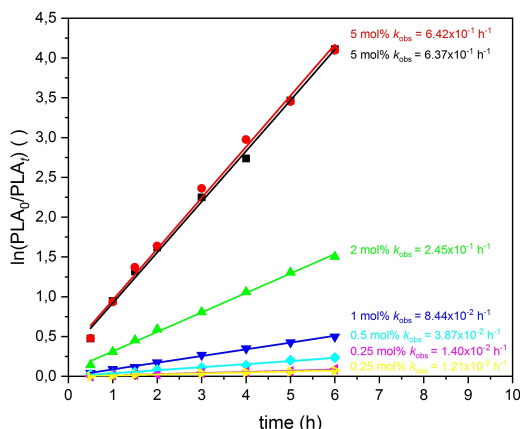
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Figure 3. Semilogarithmic plots of $\ln(PLA_0/PLA_t)$ vs. t for PLA alcoholysis into methyl lactate at 60 °C in THF using different loadings of **C1**.
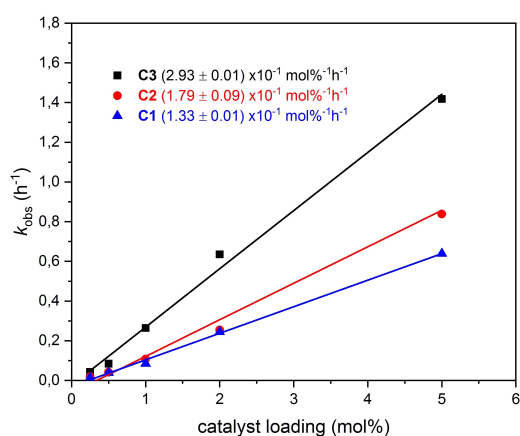

Figure 4. Plot of k_{obs} vs. catalyst loading for **C1** (blue triangles) **C2** (red dots) and **C3** (black rectangles).

concept with **C3** (2.93×10^{-1} mol%$^{-1}$ h^{-1}) being twice as active as **C1** (1.33×10^{-1} mol^{-1} h^{-1}).

Since PLA alcoholysis is still of upcoming interest, no benchmark experiments are yet established and inconsistent reaction parameters, such as catalyst or alcohol loading, are used throughout literature. This makes a direct comparison of the catalyst's activity difficult. Regarding the works of Jones, the tested "TMGasme"-catalysts show a promising mid-range activity towards MeLa formation and should therefore be further investigated.[26a,c–e] Hence, the fastest catalyst **C3** was closely examined, by first extending the alcohol scope. *n*-BuOH and *iso*-BuOH were used to study the influence of a bulkier alcohol on the PLA alcoholysis. The formation of the respective lactates was confirmed using NMR spectroscopy (Supporting Information, Figures S3/5).[27] Compared to MeOH, the PLA degradation is reduced almost by half, indicating that the chain scission is dependent on the steric demand of the used alcohol (Table 1, entries 4/5). In anticipation of a possible application in an industrial PLA chemical recycling process, the scale-up of the reaction was tested, using a factor of 1:10. Herein, a PLA conversion of 95% and a MeLa yield of 60% was achieved after

20 h of reaction time, which is in very good agreement with the small-scale results (Table 1, entry 6). Recycling of the catalyst and the solvent as well as product separation are important factors to consider for an industrial process. Removal of the liquid components in vacuo was chosen as a quick separation method. Distillation might later be applied to further separate MeLa from THF. NMR spectroscopic analysis of the solid residue confirmed the catalyst recovery. Traces of MeLa, unreacted PLA and oligomers were still present in the residue (Supporting Information, Figure S9). However, fresh solvent, alcohol and PLA were added to the recycled catalyst. Compared to the first run, the PLA conversion was decreased to 75% (Table 1, entry 7). A continuous process might therefore be the better choice for industry, rather than a batch process.

The catalyst should further promote a selective PLA degradation from a mixed plastics feed. Different amounts of PET were added to the PLA feed, as it is the most commonly used petroleum-based polyester and might be present in post-consumer PLA waste. If the same amount of PET, regarding the ester bonds, is added to the reaction, k_{obs} of the PLA degradation drops to 1.7×10^{-1} h^{-1} (Table 1, entry 8). However, no PET degradation to dimethyl terephthalate was observed. Thus, the loss towards the activity of PLA degradation is caused by a diffusion limitation resulting from the poor solubility of PET in THF. The experiment was repeated, reducing the total amount of PLA and PET ester bonds back to the previous PLA methanolysis. This resulted in an increased activity towards the MeLa formation (Table 1, entry 9), which is to be expected due to the increased ratio of catalyst to PLA ester bonds. A similar effect was observed using a PLA to PET ratio of 1:4, applying the same reaction conditions. Herein, a further increase in MeLa formation, compared to the previous experiment stayed out. This is, due to diffusion limitations, caused by the poor solubility of PET in THF (Table 1, entry 10). Hence, **C3** tolerates a mixed plastics feed and promotes selective PLA degradation. To further stress this finding, the methanolysis of a PLA-PCL-blend was studied. Likewise, to the PET experiments, selective PLA degradation, with enhanced k_{obs} was observed (Table 1, entry 11). Nevertheless, the activity of **C3** towards the meth-anolysis of PCL ($M_n = 45.000$ gmol^{-1}) into methyl 6-hydroxyhex-anoate was investigated. Using NMR spectroscopy, formation of methyl 6-hydroxyhexanoate was confirmed and a PCL con-version of 21% was detected after 72 h reaction time (Support-ing Information, Figure S12).[28] This gave a k_{obs} value of 3.3×10^{-3}, almost 100 times slower than for the PLA methanolysis (Table 1, entry 12). Considering the green chemistry principles, the use of solvents is to be reduced, which can further cut the overall process cost and should be targeted in an industrial application.[29] Hence, **C3** was tested towards PLA methanolysis in the absence of THF. Compared to the methanolysis in solution, an increased activity was observed, with a PLA conversion of 88% after 5 h, using a catalyst loading of 1 mol% at 60 °C (Table 1, entry 13). Note, that the reaction mixture was slightly clouded, indicating the presence of undissolved PLA. Further, a drastic reduction of PLA oligomer formation was observed, resulting in an increased MeLa selectivity (91%) and yield (80%), compared to methanolysis in THF (Supporting

Information, Figure S14). This trend is consistent with the findings of Mazzeo.[26b] Therefore, the solvent free reaction was further studied, utilizing PLA methanolysis at room temperature as well as in the PLA melt at 150°C. Almost no PLA conversion was detected at room temperature, with large quantities of undissolved PLA still visible after 24 h reaction time, emphasizing PLA dissolution as a key factor for successful alcholysis (Supporting Information, Figure S15). However, selective MeLa formation was also observed (Supporting Information, Figure S16). As to be expected, a drastic increase in the catalyst activity was observed with increased temperature. After just 1 h of reaction time full PLA conversion was achieved at 150°C in the polymer melt, proving once more the industrial relevance and applicability of **C3** in a PLA chemical recycling process (Table 1, entry 15).

Conclusion

Three of our previously published guanidine carboxy Zn chloride lactide ROP catalysts were resynthesised and for the first time tested towards the methanolysis of polylactide to form methyl lactate at 60°C in anhydrous THF. Using a catalyst loading of 1 mol%, regarding the PLA ester bonds, all complexes were active under these mild reaction conditions. The reaction rate constant of the polymer degradation k_{dp} was determined for all catalyst with **C3** being the most active catalyst (2.93×10^{-1} mol%$^{-1}$h^{-1}). An electron density donating group causes an increase in methanolysis activity, whereas an electron density withdrawing group lowers the activity, compared to the unsubstituted catalyst. A tuneable reactivity can therefore be achieved in both, PLA formation and chemical recycling, making this non-toxic and robust catalyst a beneficial alternative to the industrially used toxic Sn catalyst. To further proof the industrial relevance of guanidine carboxy Zn catalyst, an in-depth analysis towards industrial requirements was performed with the fastest catalyst **C3**. Herein scale up of the methanolysis as well as catalyst recycling and stability towards mixed plastics feed could be demonstrated. Alcoholysis of PCL into 6-hydroxyhexanoate was achieved and the product scope was broadened towards different lactates, illustrating the diverse opportunities to form value added products via chemical recycling. Further, full methyl lactate yield was achieved for methanolysis in the PLA melt, within 1 h, demonstrating once more the industrial relevance of the catalyst in a green chemistry context without the use of an additional solvent. Guanidine carboxy Zn catalyst can hence be a vital tool to bridge the gap between end of life PLA and its production, and to form a circular (bio)plastics economy.

Experimental Section

General procedure for the polyester alcoholysis

In a glovebox, a Young tube was charged with the respective catalyst and THF (4.0 ml). Polylactide (250 mg, 3.47 mmol regarding

the ester bond, 1.0 equiv.) was added thereto under a flow of N$_2$. The polymer was fully dissolved, using external heating and the tube was placed in an oil bath, preheated to 60°C using a stirrer speed of 260 rpm. The respective alcohol (24.7 mmol, 7.1 equiv.) was added under a flow of N$_2$ and the reaction monitoring was started. Aliquots of the reaction were taken after time increments appropriate to the catalyst's activity. NMR spectroscopy was used to determine the PLA conversion. Out of this the product yield, selectivity and the observable reaction rate constant were determined according to literature.[26a]

Further experimental details, analytics as well as kinetic evaluation of all polyester alcoholysis experiments are listed in the Supporting Information.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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RESEARCH ARTICLE

Old but gold: Three lactide ROP guanidine carboxy Zn catalysts were resynthesised and tested in the chemical recycling of renewable polyesters towards value added lactates. A tuneable activity, dependent on the ligand backbone has been found. With the fastest catalyst fulfilling industrial requirements these catalysts are well suited to promote a circular (bio)plastics economy.
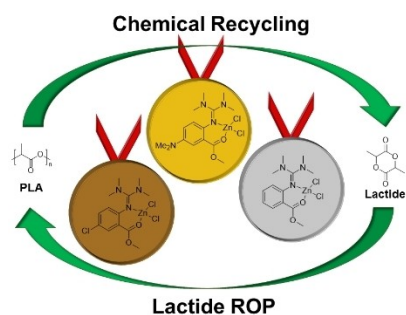
M. Fuchs, M. Walbeck, E. Jagla, Dr. A. Hoffmann, Prof. Dr. S. Herres-Pawlis*

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Guanidine Carboxy Zinc Complexes for the Chemical Recycling of Renewable Polyesters