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Rare earth metal ammonium tris(phenolate) catalysts for industrial poly(lactic acid) production

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Driven by the combined pressures of the climate crisis and increasing public and governmental consciousness of environmental contamination by petrochemical-derived plastic materials, demand for compostable, bio-based alternatives has increased dramatically in recent decades. Poly(lactic acid), prepared *via* the immortal catalytic ring-opening transesterification polymerisation of the cyclic monomer lactide, is the most widely commercialised of these alternative materials. The development of effective catalytic systems affording high rates of conversion, yet at loadings accommodating the stringency of food contact safety regulations, remains a high priority. Following our recent reports of both an industrially relevant zirconium-based system, and a related family of rare earth element-based catalysts able to dramatically out-perform the Zr species under mild conditions, this work examines the translation of the lanthanum- and yttrium-containing congeners to use under challenging, industrially relevant conditions (≤750 g-scale, 180 °C, solvent-free, commercial-grade lactide) *via* a simple benchmarking study. Kinetic data indicate that, in that setting, the La- and Y-based systems afford mutually similar rates when used at the same gravimetric metal loading. Polymer characterisation, including thermal stability studies, has revealed good catalytic control whilst affording a level of thermal stability of the final polymer sufficient for limited melt processing under commercially required temperatures without stabilisation to deactivate persistent catalyst residues. More sustained melt processing likely requires development of a suitable stabilisation protocol. While not out-performing the Zr-based system purely on kinetics, the catalysts assessed herein are credible candidates for application at-scale.

Introduction

Poly(lactic acid), PLA, is the most widely commercialised bio-based, compostable polymer, and is prepared industrially from carbohydrate feedstocks through a multi-step process culminating in the controlled catalytic, solvent-free ring-opening transesterification polymerisation (ROP) of lactide.[1–3] Lactide, the cyclic diester of lactic acid, is, in turn, prepared *via* the fermentative conversion of the carbohydrate substrate to lactic acid, followed by catalytic condensation (esterification) and purification.[3,4] ROP of a (purified) monomer that is a condensation product overcomes the limitations of a traditional polycondensation process, permitting materials to be readily produced of molecular weights sufficiently exceeding the entanglement threshold to ensure desirable thermoplastic properties.[5] Moreover, selection of an immortal ROP catalyst enables precise control of polymer molecular weight, simply through variation of the concentration of an alcohol chain transfer agent (co-initiator).[6–10] In the literature, tin- and titanium-based compounds such as tin(II) bis(2-ethylhexanoate), $Sn(Oct)_2$, are widely cited as the benchmark for bulk cataytic ROP of lactide and for production of polycondensates, such as polyurethanes from polyols and diisocyanates, due to their combination of remarkable activity and control.[11–13] In PLA synthesis, $Sn(Oct)_2$ further combines resistance toward undesirable side-reactions such as epimerisation with low cost, stability, ease of handling owing to being a liquid, and a relatively benign safety profile.[3,6,12,14–22] To ensure stability during further high-temperature processing of PLA produced in the presence of $Sn(Oct)_2$ it has been reported to be necessary to deactivate the catalytically-active metal centre after completion of the ROP step through chelation by a suitable stabiliser.[23–26]

The provision of alternative catalytic methods for the industrial synthesis of PLA is an enduring area of research interest, especially to access to a wider property window, for example through control of polymer topology, tacticity or dispersity. Despite innumerable metal-based catalyst systems having been reported over the past three decades, including examples exhibiting extremely high activity, only a handful credibly approach the requirements of an industrial system.[27–32] That is, combin-

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ing high activity and immortal kinetics at low loadings with good control, low cost, a favourable toxicological and safety profile, and robustness toward challenging industrial polymerisation conditions (typically ≥180 °C, solvent-free, with a significant concentration of acidic impurities). Notable examples include several robust and active guanidine-supported systems, and in particular iron- and zinc-based species,[27] reported by the groups of Herres-Pawlis[28,29] and Pellecchia,[30] respectively. Zn-based systems robust towards the use of unpurified monomer under solvent-free conditions have also been reported by Zhang, Wang and co-workers.[31]

Kol and co-workers have reported a zirconium alkoxide supported by a sterically demanding amine tris(phenolate) ancillary ligand, exhibiting remarkable robustness and activity in the ROP of lactide under industrially-relevant conditions, as well as enhanced control and selectivity.[33] This is consistent with inhibition of undesirable side-reactions and degradation pathways due to the highly constrained coordination environment about the metal centre.[6,34] More recently, we reported a next-generation zwitterionic catalyst system for the industrial polymerisation of lactide[6] comprising an easily-handled liquid formulation of an air-stable, homoleptic Zr ammonium tris(phenolate) complex, **1**, and an alcohol co-initiator.[6,35] The resulting system contained no exogenous solvents and exhibited extraordinary performance for the ROP of lactide under industrially relevant conditions and at near-negligible metal loadings (<20 ppm).[6,35] More recently, we have disclosed a wider family of closely related catalysts, based around both tetravalent [Hf(IV), Ce(IV)] and trivalent [La(III), Pr(III), Y(III), Yb(II)] metals.[34] The trivalent species all exhibited dramatically enhanced activity under laboratory conditions (recrystallised lactide, 120 °C, 50 wt% in PhCl, [LA] : [Cat.] : [ROH] = *e.g.* 1000 : 1 : 10) relative to the tetravalent comparators.[34] There was also an unambiguous correlation between metal size and polymerisation rate, with the largest congener, a lanthanum-based species, **2**, affording a rate that exceeded that of **1** by approximately a twentyfold ratio. Such extraordinary catalytic performance, combined with the low cost of La, relative to many other rare earth elements, makes that system an intriguing candidate for industrial application. However, as is commonplace in catalytic systems for the ROP of lactones and lactides, the high activity of **2** came at the expense of selectivity and control, and may also correlate with greater catalyst instability under more challenging conditions. Accordingly, it is conceivable that the smaller, yttrium-based system, **3**, (which was previously found to outperform **1** in terms of ROP rate by a factor of five) may possess more favourable characteristics for use at scale. We report here experiments in which the performance of the La- and Y-based catalysts, **2** and **3**, respectively, have been benchmarked under industrially relevant high temperature, solvent-free conditions.

Experimental

Catalyst synthesis was performed under an inert argon atmosphere using standard Schlenk line and glovebox techniques. Specific reagents, suppliers and methods are described in the Results and discussion section, below, and in the SI. Polymerisation reactions were undertaken under a nitrogen atmosphere in a jacketed (double-walled, heated) steel reactor, equipped with overhead mechanical stirring. Before heating was commenced, the reactor was purged with nitrogen after introduction of the monomer, which was of commercial polymer grade (TotalEnergies Corbion Lumilact®) and used without further purification. Once an internal temperature of 130 °C was attained, the polymerisations were initiated by transferring the required quantity of catalyst from a vial into the reactor, with several seconds of exposure to air, followed immediately by the co-initiator. The reactor was then re-sealed and heated to attain an internal temperature of 180 °C. Aliquots of the reaction mixture were periodically drawn for analysis.

Safety & hazards

While the metals used in this work are generally considered to be of low toxicity, all catalysts should be handled with care and regarded as hazardous (toxic) in the absence of evidence to the contrary. Metal alkoxide precursors may react violently with moisture and should be handled only using correct air-free techniques.

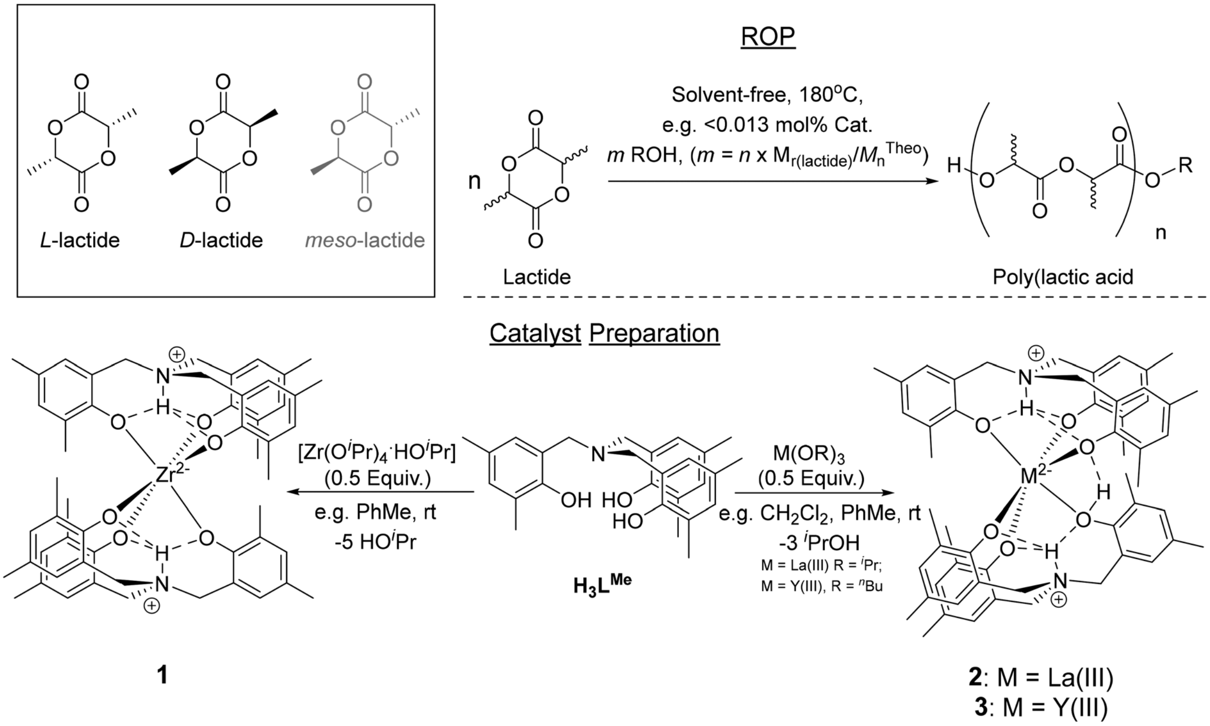
Results and discussion

Catalyst selection and preparation

La and Y complexes **2** and **3** were selected from the range of zwitterionic (homoleptic) ammonium tris(phenolate)-supported catalysts previously developed in our laboratory, due to their respective metals' relative abundance and correspondingly low cost, and distinct characteristics in relation to activity and stereoselectivity. The La complex, **2**, was synthesised *via* a high-yielding route from $La(O^iPr)_3$, as described previously,[34] whereas the Y complex, **3**, was prepared from a 0.5 M solution of $Y(O^nBu)_3$ in toluene (Scheme 1). To ensure industrial relevance, both species were subjected to minimal purification; though the Y complex was twice washed, sparingly, with commercially supplied anhydrous toluene to remove any residual $Y(O^nBu)_3$. While complex **2** was confirmed *via* ^1H NMR spectroscopy to be of high purity, complex **3**, obtained in 45% yield, was found to comprise ∼20 wt% pro-ligand tris(2-hydoxy-3,5-dimethylbenzyl)amine (H_3L^{Me}). This was accounted for, alongside residual solvent impurities, in all calculations of catalyst loadings and had no discernible effect on control in ROP (see below, and Fig. S1 and S2 in the SI).

Polymerisation reactions

Four polymerisation reactions (denoted R1–R4) were undertaken, in a jacketed steel reactor, on the 750–1000 g scale, with overhead mechanical stirring. These are described in Table 1. In each case, molten monomer was maintained at a temperature of 130 °C, prior to introduction of catalyst and co-initiator, after which the temperature was increased to 180 °C over



Scheme 1 Top: General scheme for the immortal, catalytic ROP of lactide under industrially relevant conditions with, inset left, stereoisomers of lactide. Bottom: General scheme for the synthesis of catalysts, variously, described and used in the current work.[6,34]

~30 min. Kinetic and other time-resolved data were collected *via* the periodic ejection of aliquots of the reaction mixture from the reactor, which were quenched on ice in an aluminium cup and retained for analysis. Initially the La-based catalyst, **2** (reaction R1), was applied to the ROP of polymer-grade L-lactide (1 kg TotalEnergies Corbion Lumilact®, [free acid] ≤ 10 mEq L^{-1} by titration) at a loading of 20 ppm La ([LA] : [**2**] : [ROH] ~ 48 000 : 1 : 140). However, this reaction progressed unsatisfactorily slowly, reaching only 30% conversion 170 min after introduction of the catalyst, at which time the reaction was terminated (Fig. 1). The viscosity of the reaction mixture was empirically very low, consistent both with the high remaining monomer concentration, and the presence only of very low-molecular weight polymeric material, as would be anticipated at low conversion for a system adherent to an immortal kinetic regime. Comparison of the observed rate constant, k_{obs}, for R1 with that afforded by the Zr-based catalyst, **1** (dosed as a formulation containing **1** and ROH in the molar ratio 1 : 150), reported previously under near-identical conditions ([LA] : [Zr] : [ROH] ~ 48 000 : 1 : 150), revealed that system to outperform **2** by a factor of three ($k_{\text{obs}}^{\text{La}} = 2.4 \times 10^{-3}$ min^{-1} and $k_{\text{obs}}^{\text{Zr}} = 7.8 \times 10^{-3}$ min^{-1}, for **2** and **1**, respectively).[6] Given the known capacity of **2** to dramatically out-perform **1** under laboratory conditions (higher metal loading and lower temperature, in chlorobenzene solvent),[34] such comparatively low activity of **2** under industrial conditions may be indicative of either: catalyst deactivation proliferating in R1, or **1** performing more favourably, relative to **2**, under industrial conditions than in solution, for example due to ligand conformation-related effects becoming less significant at high temperature. Significant catalyst deactivation is likely given the use of a commercial-grade monomer, which likely contains a higher concentration of acidic impurities than that used in previous laboratory studies, and the lower stability of **2** than **1** that we have observed on exposure of each species to ambient conditions. It is also inevitable that greater ingress of oxygen and moisture into the reaction vessel will have occurred under the conditions employed for this work, relative to previous small-scale polymerisation reactions, which were prepared and sealed in an argon-filled glovebox. Indeed, whereas **1** is extremely robust, and indefinitely stable on storage under air, **2** and the other trivalent congeners are less so, slowly decomposing under ambient atmospheric conditions.

The ROP of L-LA was subsequently assessed at a higher loading of 80 ppm La, introduced as **2** (reaction R2, 750 g L-LA, [LA] : [**2**] : [ROH] ~ 12 000 : 1 : 47). These conditions afforded a significantly enhanced rate, surpassing 50% conversion within 50 min and proceeding to >80% conversion after 6 hours. Comparison of the observed rate constant, $k_{\text{obs}}^{\text{La}} = 1.65 \times 10^{-2}$ min^{-1}, with that previously reported for **1** where [LA] : [Zr] : [ROH] = 12 000 : 1 : 200 (catalyst **1** introduced as a formulation wherein [ROH] : [Zr] = 200), $k_{\text{obs}}^{\text{Zr}} = 3.2 \times 10^{-2}$ min^{-1}, indicated that the magnitude of the rate discrepancy between the two systems was, broadly, retained. However, the approximately sevenfold increase in $k_{\text{obs}}^{\text{La}}$ observed on having increased the concentration of **2** by a factor of four, relative to

Table 1 Polymerisation conditions, polymer characterisation data and rate constants

Entry	Catalyst/ reaction	Monomer	[Cat.], ppm M/ mol%	[ROH], mol%	Duration, min	Conversion^c, %	k_{obs} ^{d}, min^{-1}	TOF^e, min^{-1}	M_n^{Theo} ^{f}, kg mol^{-1}	M_n^{GPC} ^{g}, kg mol^{-1}	$Đ_M$ ^{g}	[L units]^h, %	P_r ^{i}
1^a	**2**/R1	L-LA	20/2.1 × 10^{-3}	2.8 × 10^{-1}	170	30	2.4 × 10^{-3}	99	—	—	—	99	—
2^b	**2**/R2	L-LA	80/8.3 × 10^{-3}	3.8 × 10^{-1}	350	83	1.7 × 10^{-2}	153	31	39	1.44	96	—
3^b	**3**/R3	L-LA	80/1.3 × 10^{-2}	3.8 × 10^{-1}	350	80	1.4 × 10^{-2}	78	30	37	1.44	96	—
4^b	**3**/R4	*rac*-LA	70/1.1 × 10^{-2}	3.8 × 10^{-1}	350	92	1.0 × 10^{-2}	66	34	36	1.55	49	0.47

Conditions: solvent-free, 180 °C (catalyst and co-initiator introduced at 130 °C). [a] 1000 g LA. [b] 750 g LA. [c] Determined *via* gas chromatography. [d] Determined from the gradient of the empirically linear region of semi-logarithmic plots of $\ln([LA]_0/[LA]_t)$ *versus* time. [e] Calculated from the empirically linear region of plots of conversion ([PLA], wt%) *versus* time, *t*, corresponding to the first *n* minutes for reactions R1–R4, where *n* = 110, 35, 50 and 50, respectively; TOF = $([PLA]_{t=n}/[Cat]_0)/n$. [f] Theoretical molecular weight, $M_n^{Theo} = [PLA]_t \times M_{r,\ lactide} \times ([lactide]_0/[ROH]_0)$. [g] Determined *via* GPC in $CHCl_3$ using an evaporative light scattering detector calibrated against polystyrene standards of known molecular weight. [h] Determined *via* destructive methylation followed by chiral gas chromatography. [i] Determined *via* ^{1}H NMR spectroscopic analysis of the product, with homonuclear decoupling of the methine protons by broadband irradiation of the methyl region permitting resolution of discrete tetrad signals, $P_r = \sqrt{(2[sis])}$.[36,37]

reaction R1, is irreconcilable with a first-order rate dependency with respect to the catalyst, in the absence of significant catalyst deactivation. The large magnitude of the rate discrepancy is inconsistent, too, with the expected rate enhancement of R1, relative to R2, on the basis of the former having a higher molar [alcohol] : [catalyst] ratio ([LA] : [**2**] : [ROH] = 48 000 : 1 : 140 *versus* [LA] : [**2**] : [ROH] = 12 000 : 1 : 47).[6,8,34,38] Accordingly, it is likely that the unexpectedly high rate of R2 may arise from the combined effects of stoichiometric catalyst deactivation processes (occurring rapidly on introduction of the catalyst to the monomer melt) and viscosity effects associated with the difference in absolute alcohol concentration between R1 and R2 (for further discussion see the SI). Furthermore, given the fourfold reduction in [ROH] : [Catalyst] in the case of R2, relative to the Zr-based catalyst, **1**, under otherwise similar conditions, the two systems' catalytic performance may be considered quite comparable under industrially relevant conditions.

Control of polymer molecular weight in the presence of **2** was found to be excellent in R2 (Fig. 2), there being a linear relationship between theoretical and measured values (M_n^{Theo} and M_n^{GPC}) during progression of the polymerisation, and $Đ_M$ = 1.44 exhibiting little temporal variation. While values of M_n^{GPC} were generally somewhat higher than M_n^{Theo}, such that $M_n^{GPC} = 1.25 \times M_n^{Theo} - 1.45 \times M_n^{Theo}$, we note that when analysing truly isotactic PLLA *via* GPC using evaporative light scattering detection with polystyrene calibrants, it is typical to apply a correction factor of 0.58,[39,40] although this was not done in this case due to the presence of stereoirregularities (see below). Overall, these data are characteristic of a well-controlled, immortal catalytic ROP process, such as is desired for industrial PLA production. Furthermore, despite the known capacity of **2** to induce epimerisation of stereocentres along the PLA backbone in high-temperature, solvent-free polymerisations,[34] the extent of this was acceptably well-controlled: on termination of reaction R1, the product remained >98% stereopure, whereas in the case of R2, this value was 96%, while conversion was ∼82% (Table 1; Tables S1–S4 in the SI). The observed degree of stereoregularity remains within the range reported by others to be typical for commercial PLA.[24,39,41–43]

When the Y-based catalyst, **3**, structurally analogous to **2**, was applied to the ROP of L-lactide at the same gravimetric metal loading, and under similar conditions (reaction R3, 750 g L-lactide, 80 ppm Y; [LA] : [**3**] : [ROH] ∼ 7700 : 1 : 28), the rate was found to be only marginally lower than in R2 ($k_{obs}^{Y} = 1.43 \times 10^{-2}$ min^{-1} *versus* $k_{obs}^{La} = 1.65 \times 10^{-2}$ min^{-1}). Given the significantly greater (1.56×) molar concentration of **3** in R3, relative to **2** in R2, associated with the atomic mass difference between Y and La, this is somewhat consistent with our previous observation of **2** exhibiting a higher catalytic turnover frequency (TOF) than **3** (value calculated assuming no catalyst deactivation occurred).[34] However, the magnitude of the TOF discrepancy between the two systems in this case (∼2×) is smaller than the fourfold difference recorded under the laboratory conditions of the earlier report. Furthermore, the absolute concentration of the co-initiator was maintained

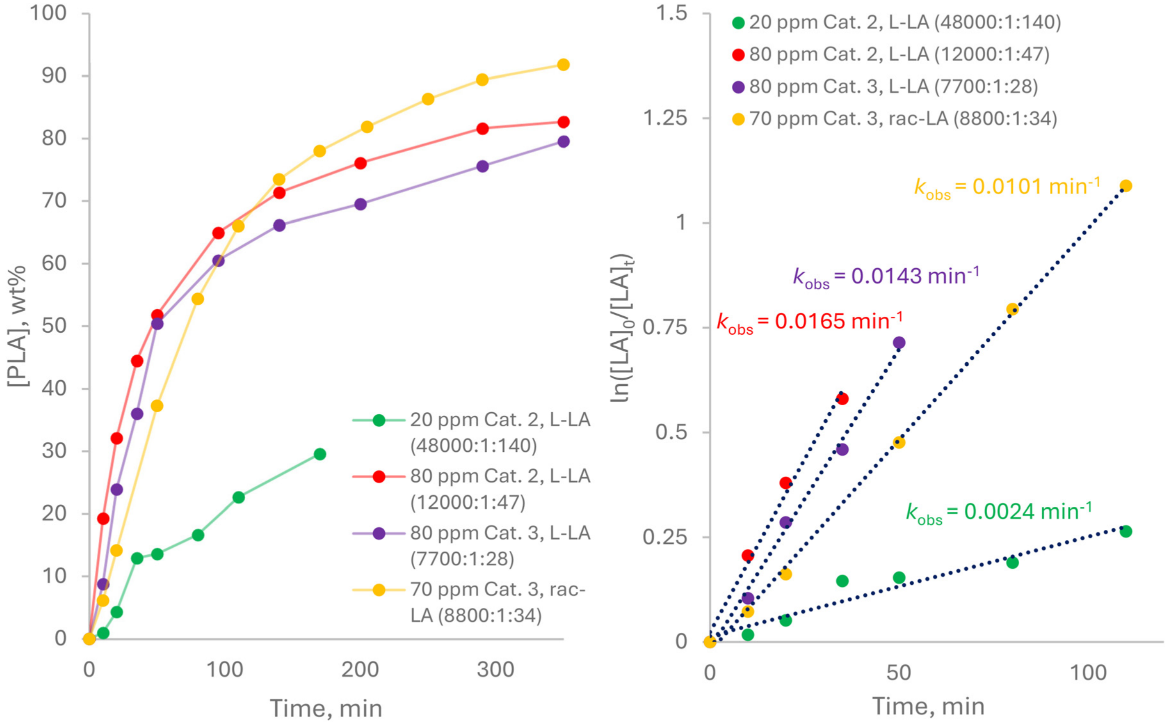


Fig. 1 Left: Plots of reaction conversion ([PLA], wt%) against time for the polymerisation reactions described herein and, right: semilogarithmic initial rate plots constructed from the same data for the determination of observed rate constants, k_{obs}.

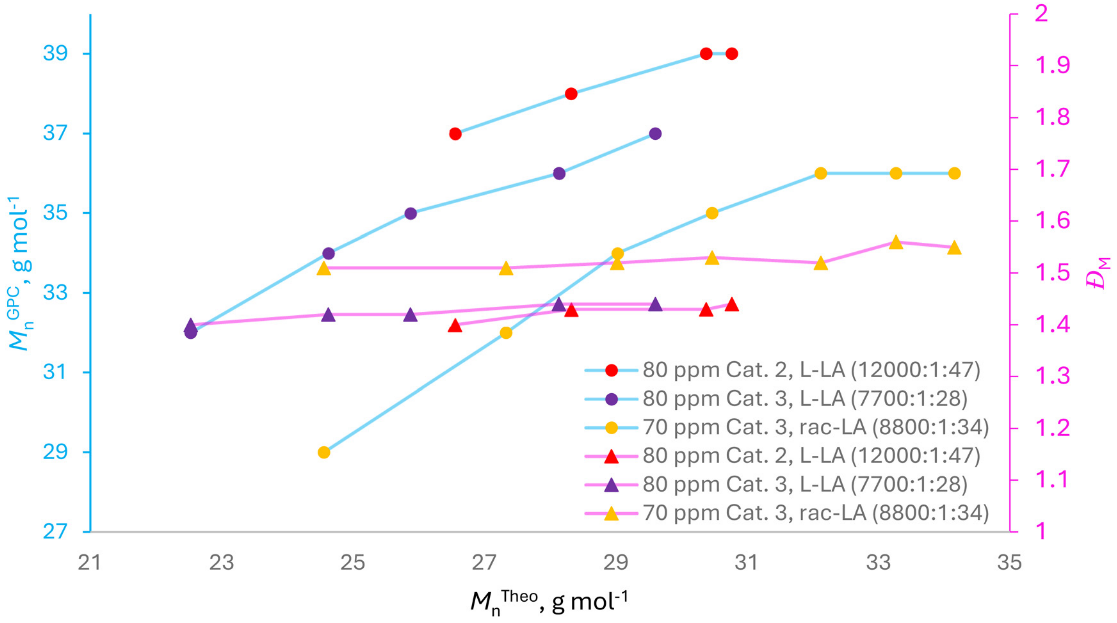


Fig. 2 Plots of the measured number average molecular weight, M_n^{GPC} (blue line), against theoretical molecular weight, M_n^{Theo}, with corresponding values of $Đ_M$ (magenta line) plotted on the secondary Y axis, for the latter portions of reactions R2, R3 and R4.

between reactions R2 and R3, to ensure similar viscosity and provide a product of consistent theoretical molecular weight, resulting in the molar [ROH] : [Metal] ratio being higher in the case of **2** (R2) than **3** (R3). Given the known rate-enhancing effect of increasing this ratio in catalytic systems of this type,[6,8,34,38] the small difference in catalytic activity between **2** and **3** is all-the-more surprising. It is, accordingly, plausible that, under such challenging conditions, the greater robustness of **3** in comparison to **2** is a significant determinant of catalytic performance. However, it is remains conceivable that under high-temperature, solvent-free conditions, metal size and the posited effect of ligand flexibility may no longer exert such a significant influence over the rate and selectivity of the polymerisation process as is the case in the presence of a solvent and at lower temperatures.[34] Both of these possibilities are consistent with the comparatively poorer performance of both **2** and **3** than **1** under similarly demanding conditions, given the known robustness and sterically congested ligand environment of **1**.[6,34]

Undertaking rigorous and quantitative mechanistic investigations, such as the determination of the propagation rate constant, k_p, for novel ROP catalysts at scale and under industrially relevant conditions is extremely challenging, for a variety of practical and economic reasons. Nevertheless, by approximating the reaction order with respect to the co-initiator to zero, and using the relative rates of reactions R1 and R2 to estimate the extent of stoichiometric catalyst deactivation as accounting for 1.05×10^{-3} mol% catalyst (given a polymerisation regime that is first-order with respect to the catalyst), rate constants $k'_{p,La} = 3.5 \times 10^{-3}\ s^{-1}\ mol^{-1}\ dm^3$ and $k'_{p,Y} = 1.8 \times 10^{-3}\ s^{-1}\ mol^{-1}\ dm^3$ have been calculated, for polymerisations catalysed by **2** and **3**, respectively. Discussion of the method used for determination of these values, and the calculation of modified TOF values that account for the estimated extent of catalyst deactivation (198 min^{-1}, 175 min^{-1} and 85 min^{-1} for reactions R1, R2 and R3, respectively), can be found in the SI.

The twofold difference between the calculated values of k'_p for La- and Y-mediated reactions under the current conditions remains smaller than that between the previously-reported relative rates afforded by **2** and **3** under mild, laboratory-scale, conditions in the presence of various (lower) concentrations of alcohol.[34] This is further reconcilable with the possibility, discussed above, that increased flexibility of the ligand scaffolds of both **2** and **3** towards helical inversion under high-temperature conditions, reduces the magnitude of any rate discrepancy arising from differences in the two systems' respective dynamic behaviour. Similarly, on comparison of calculated k_p values for high-temperature, solvent-free conditions, both systems (**2**, **3**) remain less active than the Zr-based formulation (containing **1**) that we have reported previously under comparable conditions.[6]

Catalyst **3** induced a similarly low degree of epimerisation in R3 to that arising from use of **2** in R2; the product comprised >95% L-lactyl units at 80% conversion. Gradient analysis of semilogarithmic plots of $\ln([LA]_t/[LA]_0)$ against time, t, across the whole reaction profile indicated little significant difference in catalyst longevity between R2 and R3 (see Fig. S3 in the SI), which may suggest that catalyst deactivation primarily occurs immediately following introduction to the monomer melt, rather than throughout the reaction duration (consistent with assumptions made in the determination of k_p values). Catalyst **3** also afforded similarly good molecular weight control to **2**, yielding comparable absolute values (M_n^{GPC} = 39 kg mol^{-1} at 83% conversion, and M_n^{GPC} = 37 kg mol^{-1} at 80% conversion for R2 and R3, respectively after 350 min), and the same dispersity ($Đ_M$ = 1.44). In addition to suggesting that the catalytic profiles of **2** and **3**, when used at the same gravimetric metal loading, are very similar under industrially relevant conditions, these observations also indicate that the presence of residual pro-ligand (at a concentration of $\sim 5 \times 10^{-4}$ mol kg^{-1} in the monomer melt in reaction R3) in the case of **3** does not have any significant or deleterious effect on that species' catalytic properties. The possibility that residual pro-ligand may have a stabilising effect on **3** was also considered as a potential contributing factor to that catalyst's unexpectedly high activity, relative to **2**, under industrial conditions. However, given the very low concentration of both species in the reaction mixture, and the much higher concentration of both the co-initiator and acidic impurities (by approximately two orders in both cases), this was considered unlikely.

Catalyst **3** was also applied to the ROP of racemic D,L-lactide (*rac*-lactide, *rac*-LA), at a loading of 70 ppm Y (reaction R4, [LA] : [Y] : [ROH] = 8800 : 1 : 34), under otherwise identical conditions to those used for the ROP of L-LA (R3, where the gravimetric Y loading was 80 ppm). In this case, a slightly lower rate was observed ($k_{obs}^{Y} = 1.01 \times 10^{-2}\ min^{-1}$) than might be expected based on the change in metal concentration and the marginally increased molar ratio of co-initiator to metal ([ROH] : [Y] = 34 : 1 in R4 *versus* 28 : 1 in R3). However, this may simply be due to variability in the concentration of acidic impurities between the L- and *rac*-lactide feeds. No significant stereoselectivity was detected by homonuclear decoupled ^1H NMR spectroscopic analysis of the product (P_r = 0.47, see Fig. S5 in the SI). This is in contrast to the observed slight heteroselectivity (*e.g.* P_r = 0.57) of **3** under laboratory conditions,[34] consistent with greater flexibility of the coordination environment and ligand geometry about the metal centre at high temperatures. Gradient analysis of semilogarithmic plots for the polymerisation reactions R3 and R4, of L-LA and *rac*-LA, respectively, in the presence of **3** indicated that, despite the slightly lower maximum rate, the activity of the catalyst was better sustained over the course of the reaction in the latter case (see Fig. S3 in the SI), with 92% conversion being reached after 350 min, and retention of excellent molecular weight control (after 205 min, M_n^{GPC} = 35 kg mol^{-1}, $Đ_M$ = 1.53 at 80% conversion, and after 350 min, M_n^{GPC} = 36 kg mol^{-1}, $Đ_M$ = 1.55 at 92% conversion). These observations may indicate reduced proliferation of side reactions, including catalyst decomposition processes. However, the absence of any heteroselectivity, but retention of fairly low dispersity, is more consistent with the high activity in R4 being well sustained due to a mixing effect arising from the lower melt viscosity of atactic poly(D,L-lactide) in R4 relative to near-stereopure isotactic PLLA in R3. Values of M_n^{GPC} were also slightly lower, relative to M_n^{Theo} for poly(D,L-lactide) samples from R4, than for PLLA prepared under comparable conditions in R3, and $Đ_M$ values were consistently slightly higher, which may further indicate that the *rac*-LA feed contained a higher concentration of protic contaminants than the L-LA.

Thermal analysis

PLLA of low dispersity has been produced in the presence of catalysts **2** and **3** (reactions R2 and R3, $Đ_M$ = 1.44 in both cases), with only very slight broadening of either molecular weight distribution with reaction progress, even at long reaction durations and low residual monomer concentrations (see SI). This is consistent with high selectivity for ROP, with effective suppression of inter-chain transesterification processes, commensurate with the known selectivity of **1**, reported previously, and likely arising from the highly enclosed nature of the coordination environment about the metal centre of the catalyst.[6,34] Such resistance towards undesirable side-reactions indicated that the materials produced in this work, and specifically in reactions R2 and R3, may be amenable to melt processing at elevated temperatures, without requiring removal or stabilisation of residual catalytically active metal centres.[26] This possibility was investigated *via* thermal characterisation, comprising thermogravimetric analysis (TGA), and exposure to high-temperature devolatilization conditions followed by rheological stability studies.

After removal of volatiles under mild, reduced-pressure devolatilization conditions (14 h, 110 °C, ~30 mbar, resulting in no significant degradation *via* GPC, see SI), TGA analysis (temperature ramp at 10 °C min^{-1} from 30–600 °C) revealed PLLA samples produced in reactions R2 and R3, in the presence of catalysts **2** and **3**, respectively, to exhibit mutually similar thermal stability. Both materials underwent degradation only at temperatures significantly exceeding the T_m of commercial PLA (Table 2 and Fig. 3),[42,44] but somewhat lower than that at which the onset of degradation of commercial PLLA occurred. Given the role that polymer chain ends are known to play in the catalytic thermal decomposition of PLA, however, it is possible that the relatively low molecular weight of the materials produced in this work, in comparison to commercial PLA, may have contributed to their reduced thermal stability.[4,43,45–49] The sample prepared in the presence of **3** underwent thermal degradation at a slightly lower temperature than was the case for **2**, while the residual mass of the latter sample, plotted against time, described a somewhat convex slope, empirically appearing consistent with two distinct decomposition processes occurring. Because of the variation in the decomposition profiles of the three materials, comparison of $T_{5\%}$, $T_{50\%}$ and $T_{95\%}$ is more instructive than T_{onset} regarding their relative thermal stability (Table 2).

Encouraged by the observation of thermal decomposition only occurring at temperatures significantly exceeding the T_m range of commercial PLA (T_m = 130–175 °C),[41,42] PLA samples from reactions R2 and R3 were also subject to isothermal thermogravimetric stability studies. Samples were heated at 10 °C min^{-1} to the target temperature, which was then maintained for one hour. The stability of each material was assessed at both 200 °C and 250 °C, with both samples appearing quite stable at 200 °C (≤4% mass loss), but undergoing more significant decomposition at 250 °C. In agreement with the results obtained in the standard temperature ramp TGA experiments, PLA from R3, prepared in the presence of **3**, decomposed more readily than that prepared in R2 using **2**, with a twofold difference in the two materials' measured rates of decomposition during isothermal TGA experiments at 250 °C (Table 2). Commensurate with the unexpectedly small difference in polymerisation rates afforded by **2** and **3** in reactions R2 and R3, and their rate discrepancy in relation to **1**, we suggest that the comparatively lower stability of the material prepared using **3** is due to the greater robustness of that catalyst, allowing more of it to persist, intact, in the polymer product after polymerisation. It is also plausible, given the use of consistent gravimetric metal loadings, that the greater molar quantity of the lighter congener, **3** (in PLA from R3), in comparison to **2** (R2), may contribute somewhat to the greater thermal instability of the product of reaction R3. The linearity of both isothermal thermogravimetric plots is, further, consistent with a degradation process that is *pseudo*-first order with respect to a species present in constant molar quantity. That species is, presumably, residual catalyst, given the presence of excess polymer, supporting the proposed role of catalyst survivability (robustness) in determining the thermal stability of the product. Alternatively, a *pseudo*-first order rate dependency on the concentration of polymer end groups was also considered, associated with a back-biting mechanism. However, that possibility was not readily reconcilable with the degradation rate difference between samples from reactions R2 and R3, respectively, given their similar M_n^{GPC} and $Đ_M$ values, and thus similar number of end groups.

Encouraged by the minimal degradation observed during 200 °C isothermal TGA experiments, the stability of the products of reactions R2 and R3 was also assessed after removal of volatiles at higher temperature (2 h, 190 °C, <1 mbar). Specifically, these conditions were anticipated to promote

Table 2 Thermogravimetric analytical data for PLA samples prepared from L-LA in the presence of 80 ppm La and Y, respectively, introduced as **2** and **3**, and a commercial PLA sample

Entry	Catalyst/reaction	T_{onset} [a], °C	$T_{5\%}$ [a], °C	$T_{50\%}$ [a], °C	$T_{95\%}$ [a], °C	M_{200} [b], %	M_{250} [b], %	dM/dT_{200} [c], % min^{-1}	dM/dT_{250} [c], % min^{-1}
1	**2**/R2	333	282	354	378	98	79	−0.03	−0.34
2	**3**/R3	307	275	337	370	96	56	−0.05	−0.72
3	Commercial sample	352	339	368	384	—	—	—	—

[a] Value determined *via* TGA experiment in which the temperature was increased at 10 °C min^{-1} from 30–600 °C; T_{onset} defined as the temperature at which the value of the tangent to the curve at its greatest negative gradient intersects y = 100%, $T_{n\%}$ is the temperature at which the sample mass loss has first exceeded n%. [b] Residual mass, %, after isothermal TGA experiment, wherein the isothermal temperature was reached *via* a temperature ramp at 10 °C min^{-1} and then maintained for 1 h. Isothemal temperature iT is denoted by the column label $M_{\text{i}T}$. [c] Rate of mass loss, in % min^{-1}, during isothermal TGA experiments. Isothermal temperature iT is denoted by the subscript number in the column label $dM/dT_{\text{i}T}$.

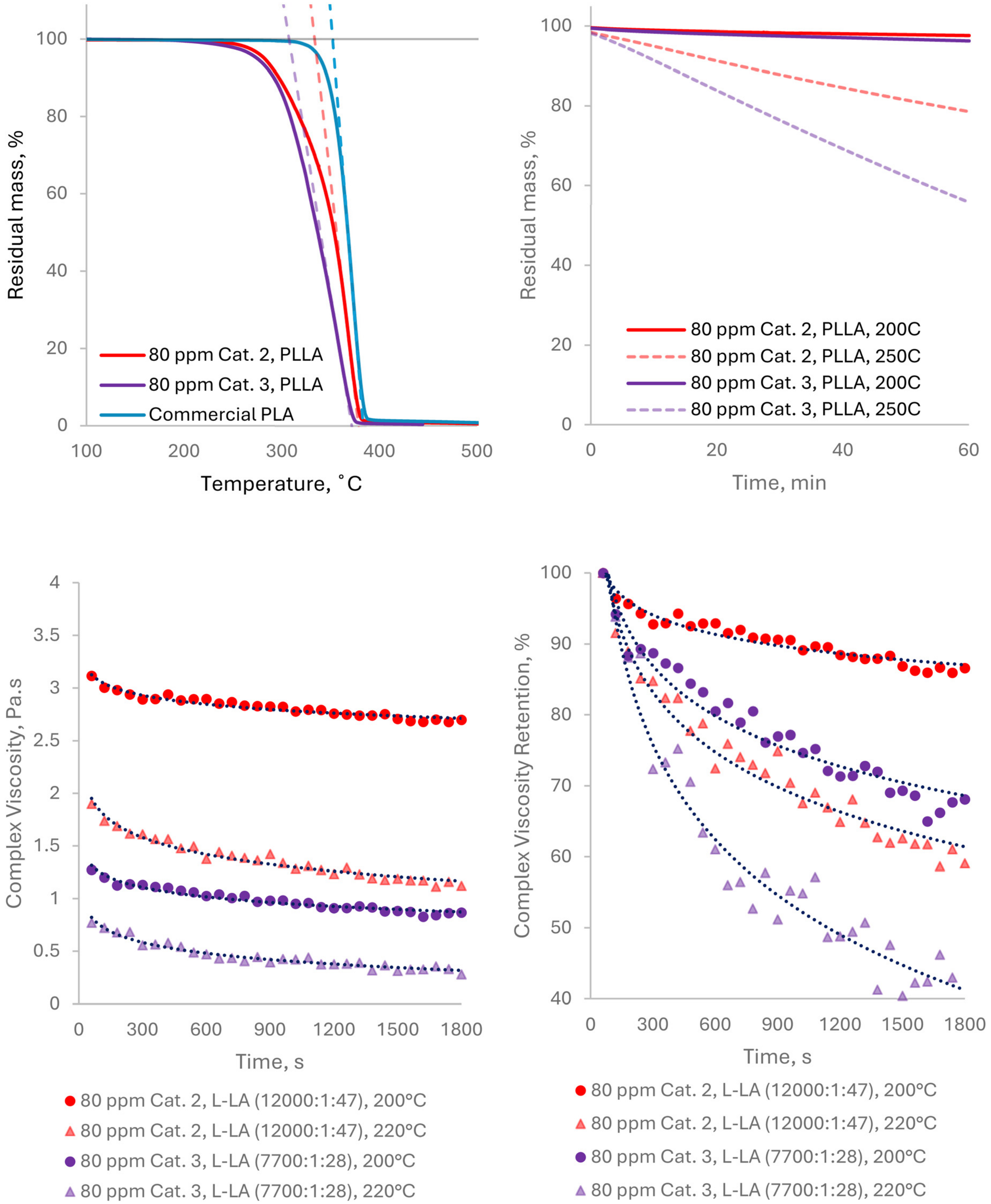


Fig. 3 Plotted thermogravimetric and rheological data, top left: thermogravimetric temperature ramp analysis of PLA samples from reactions R2 and R3 (100–500 °C shown only), and a commercial sample, top right: isothermal analysis of PLA from reactions R2 and R3 (isothermal region shown only), bottom left: complex viscosity of PLA samples from R2 and R3 after high-temperature devolatilization, against time at both 200 °C and 250 °C, and bottom right: complex viscosity retention (%) PLA samples from R2 and R3 against time at both 200 °C and 250 °C.

degradation *via* any lactide formation pathway that may exist, by excluding the moisture necessary for hydrolysis and encouraging evolution of the volatile monomer. Following devolatilisation, both samples were analysed *via* GPC and found to have experienced a very clear molecular weight reduction. This was most significant in the case of the Y-containing material, and concomitant with a large increase in dispersity, relative to the crude products (M_n^{GPC} = 19 kg mol^{-1}, $Đ_M$ = 2.42 and M_n^{GPC} = 12 kg mol^{-1}, $Đ_M$ = 2.63 for the products of R2 and R3, respectively after devolatilization, *versus* M_n^{GPC} = 31 kg mol^{-1}, $Đ_M$ = 1.44 and M_n^{GPC} = 30 kg mol^{-1}, $Đ_M$ = 1.44 for the corresponding crude materials). Additionally, GC analysis revealed that both materials contained high concentrations of lactide after devolatilization (7.4 wt% and 6.1 wt% respectively), whereas an appropriately stabilised commercial polymer, even with a high initial residual lactide concentration, may typically contain <1 wt% lactide after identical treatment. The region of the TGA curves describing the major mass loss event for samples that had undergone high-temperature devolatilisation described, in both cases, a near-identical profile to those devolatilised under mild conditions (see SI). Both of the samples that were devolatilised under high-temperature conditions, however, exhibited a gradual mass loss event beginning slightly above 100 °C, preceding the onset of more significant decomposition at >300 °C. This was not observed after devolatilisation using the lower-temperature protocol, and is consistent with sustained exposure to high-temperature devolatilisation conditions having increased the concentration of low-molecular weight species present. These observations are collectively characteristic of a catalytic degradation process, which may include a lactide-forming pathway (although we cannot exclude the possibility of pyrolytic degradation also occurring). They also indicate that a stabilisation protocol suitable for the current rare earth element-based catalysts should, necessarily, be implemented to achieve compatibility with such comparatively aggressive devolatilization conditions, or other sustained high-temperature processing. Although development of such a stabilisation protocol is beyond the scope of the present study it is considered achievable, drawing upon industry knowhow and the rich coordination chemistry of the rare earth elements.

Rheological analysis of the products of reactions R2 and R3 after high-temperature devolatilisation, consisting of 30-minute viscosity time sweeps at both 200 °C and 220 °C, further confirmed the greater instability of PLA prepared in the presence of catalyst **3** than of **2** (Fig. 3), with evidence of continued degradation occurring in both cases. Both higher temperature and the presence of catalyst **3** were associated with greater loss of viscosity over the course of the experiment, with the rate of viscosity change progressively decreasing in all cases throughout the analysis. These observations are reconcilable with degradation of the catalyst occurring at high temperature, particularly under ambient air. This is in contrast to the exclusion of air from polymerisation, TGA and devolatilization experiments. The absolute values of the complex viscosities of the two materials analysed were significantly lower than is typical for thermoplastic PLA at comparable temperatures.[5,50,51] However, this is attributable to their low molecular weights following degradation during devolatilisation. Indeed, given values of M_n^{GPC} were determined *versus* polystyrene calibrants without application of a correction factor, absolute M_n values will have fallen significantly below the entanglement threshold, above which much greater melt viscosity and thermoplastic properties are observed.[5] While PLA produced using catalysts **2** and **3** is likely compatible with some limited high-temperature processing in the absence of a stabiliser, applications in which more sustained or repeated melting is required are likely, nevertheless, to demand prior deactivation of the catalyst. The high-temperature devolatilization process assessed here, for example, represents prolonged exposure to challenging conditions, towards which these materials have been found to be insufficiently stable.

Conclusion

We have reported a series of simple experiments to assess the performance of two catalysts, based on Lanthanum and Yttrium, respectively, for the ring-opening polymerisation of lactides under industrially relevant conditions. While these catalysts do not out-perform a previously reported Zr-based system under those conditions, in notable contrast to their properties under milder conditions, they nonetheless exhibit performance broadly comparable to that system and similar to one another. Significantly, in contrast to earlier low-temperature, solution-phase studies, the Y-based system exhibits performance very similar to that of the La congener when used at consistent gravimetric metal loadings (k_{obs}^{Y} = 0.87 × k_{obs}^{La}). This is plausibly attributable to factors such as the greater robustness of the former and greater flexibility of both systems' ligand scaffolds under high-temperature conditions, indicating that they may be used interchangeably in an industrial setting. These findings also underscore the importance of understanding new catalyst candidates' robustness and performance profiles, specifically, under industrial reaction conditions. Indeed, the demonstration in the current work of the rare earth-based systems' poorer performance at very low loadings under industrial polymerisation conditions, in comparison to Zr, highlights both the remarkable robustness of the latter protocol, and the importance of benchmarking new catalyst candidates and other polymerisation technologies under conditions that appropriately replicate the intended process environment. The first examples of industrially viable lactide polymerisation catalysts based on the rare earth elements, the Y- and La-based species discussed herein also afford favourable control and selectivity in the production of PLA, and our thermal characterisation data indicate good stability of the resulting polymer in the absence of any exogenous stabiliser. The La-based system out-performs Y in this regard, which our data collectively suggest can be primarily attributed to greater degradation of the La catalyst occurring during polymerisation, thus reducing the persistence of active catalyst residues in the product. Overall, the findings described herein suggest that these systems represent a credible and much-needed addition to the limited pool of prospective alternative catalyst systems for the industrial production of PLA.

Conflicts of interest

The authors declare no conflicts of interest. Gerrit Gobius du Sart and Wilko de Lang are employees of TotalEnergies Corbion, a commercial producer of PLA.

Data availability

All experimental data is summarised in tabulated form in the manuscript and/or supplementary information (SI). Supplementary information: complete experimental procedures and analytical details. See DOI: https://doi.org/10.1039/d6py00368k.

Primary data is available upon reasonable request, where sharing it does not require commercially sensitive information to be disclosed.

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