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COMMUNICATION

Group 4 salalen complexes for the production and degradation of polylactide†

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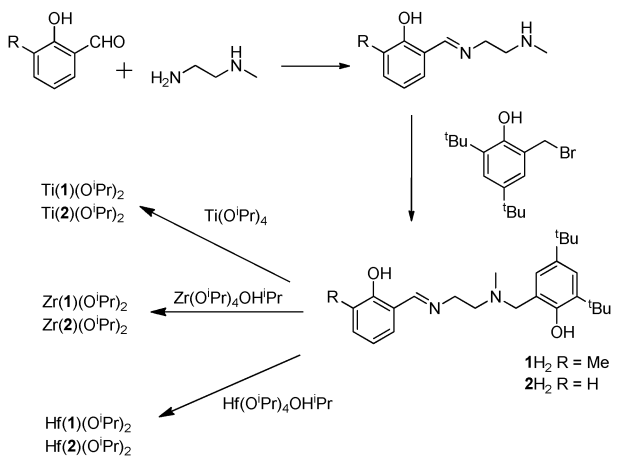
In this communication we report the preparation of highly active catalysts for the production of polylactide and the subsequent conversion of polylactide to methyl lactate. The use of these catalysts for potential recycling applications is discussed.

Unsurprisingly, polylactide (PLA) is receiving considerable attention in the literature due to its green credentials—namely being sustainable and biodegradable.[1] PLA is produced commercially by NatureWorks and Purac.[2] There are many examples of catalysts for this process based on groups 1–4,[3] lanthanides,[4] Al(III),[5] Zn(II)[3b,h,6] and organo-catalysts.[7] In this century remarkable advances have been made in this area, in particular in the stereoselective polymerisation of *rac*-lactide. For example, we have shown that it is possible to produce highly heterotactic PLA under melt conditions in only 10 min.[3l] Other groups have been able to prepare highly isotactic PLA under melt conditions, block and random copolymers of lactide with other cyclic esters.[5c,d] In the vast majority of examples the polymerisation is quenched by the addition of methanol to deactivate the catalyst and MeOH can also be used to remove any unreacted monomer.[3j,l,6a,8] However, on an industrial scale the monomer is typically removed by sublimation. One of the main obstacles in the wider implementation of PLA is the cost of the platform chemical itself (lactic acid). Lactic acid can be produced from batch fermentation of aqueous glucose under anaerobic conditions.[9] During the fermentation process approximately 1 tonne of gypsum ($CaSO_4$) is produced per tonne of lactic acid.[2] The crude lactic acid is purified by conversion to methyl lactate and then distilled and hydrolysed to form pure lactic acid.[2] The reversible equilibrium between polyesters and their starting materials can potentially be exploited for recycling of the polymer back into its building blocks. In a recent report by NatureWorks they state that chemical recycling of PLA could be a highly attractive approach.[10] Currently, this can be achieved by hydrolysis of the polymer with a strong acid at elevated temperatures akin to that used in the PET industry.[10] In the literature there have been various approaches to the scission of PLA or lactide.[11] Ohara has recently shown that the alcoholysis reaction can be performed under microwave irradiation at temperatures in excess of 130 °C.[11a] Phomphrai has also shown that it is possible to convert lactide into alkyl lactyllactates using group 1 metal amides.[11b] Also, the use of DMAP as a catalyst was able to successfully break down PLA under bulk conditions (135 °C).[11c] The depolymerisation/degradation of PLA films or scaffolds is an active research area, this is typically carried out using NaOH or HCl.[12] PLA can also be depolymerised *via* transesterification using Sn(II) octanoate or triazabicyclodecene as the catalyst at a temperature of 120 °C for 24 h.[13a] In this example PLA is dissolved in ethyl lactate and ethanol added. In a further patent example it is claimed that PLA is depolymerised to methyl lactate at 150 °C in the presence of H_2SO_4.[13b]

In this communication we report further preparation and characterisation of unsymmetrical group 4 complexes based on salalen ligands and their application for the conversion of PLA to methyl lactate at room temperature. There are many processes that use alcohols as chain transfer agents, but to the best of our knowledge this is typically used as a method of controlling the molecular weight.[3h]

The ligands prepared in this study are shown in Scheme 1 and adapted literature procedures were followed for their preparation.[14] The complexes were prepared from a 1 : 1 reaction of the appropriate ligand with the group 4 alkoxide.



Scheme 1 Ligands and complexes prepared in this study.

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† Electronic supplementary information (ESI) available: Full experimental details, representative NMR spectra, kinetic analysis and GPC traces are available as ESI. See DOI: 10.1039/c1cc13910j

Table 1 Solution polymerisation data[a,b]

Entry	Initiator	Time/h	T/°C	Conv./%[c]	M_n[d]	PDI[d]	P_r[e]
1	Zr(**1**)(O^{i}Pr)$_2$[a]	2	80	98	30 500	1.54	0.25
2	Zr(**2**)(O^{i}Pr)$_2$[a]	2	80	98	21 600	1.65	0.35
3	Hf(**1**)(O^{i}Pr)$_2$[a]	2	80	98	18 400	1.54	0.35
4	Hf(**2**)(O^{i}Pr)$_2$[a]	2	80	99	20 200	1.77	0.30
5	Zr(**1**)(O^{i}Pr)$_2$[a]	2	80	99	500	1.13	—
6	Zr(**2**)(O^{i}Pr)$_2$[a]	2	80	92	350	1.17	—
7	Hf(**1**)(O^{i}Pr)$_2$[a]	2	80	99	2950	1.39	0.30
8	Hf(**2**)(O^{i}Pr)$_2$[a]	2	80	97	2175	1.24	0.30
9	Zr(**1**)(O^{i}Pr)$_2$[a]	24	80	97	450	1.08	—
10	Zr(**2**)(O^{i}Pr)$_2$[a]	24	80	99	450	1.27	—
11	Hf(**1**)(O^{i}Pr)$_2$[a]	24	80	99	650	1.43	0.3
12	Hf(**2**)(O^{i}Pr)$_2$[a]	24	80	99	2150	1.23	—
13	Zr(**1**)(O^{i}Pr)$_2$[b]	6	25	99	2550	1.30	0.3
14	Zr(**2**)(O^{i}Pr)$_2$[b]	6	25	99	3500	1.39	0.3
15	Hf(**2**)(O^{i}Pr)$_2$[b]	6	25	96	2150	1.16	0.3
16	Hf(**2**)(O^{i}Pr)$_2$[b]	6	25	99	2150	1.21	0.3

[a] Solution polymerisation of *rac*-lactide. In all cases a 100 : 1 monomer-to-initiator ratio was employed, 0.7 g of monomer was used, toluene (10 ml) as the solvent. Entries 1–4 have not been quenched with MeOH. [b] Polymerisations performed in CH_2Cl_2. [c] Conversion as determined from ^{1}H NMR spectroscopy. [d] Determined from GPC analysis using THF as the solvent. [e] Determined from ^{1}H NMR homonuclear decoupled NMR spectroscopy. N.B. P_r values for Zr(**1**)(O^{i}Pr)$_2$, Zr(**2**)(O^{i}Pr)$_2$ and Hf(**2**)(O^{i}Pr)$_2$ could not be determined due to insufficient polymeric material being isolated.

The complexes have analogous NMR spectra to previously reported group 4 salalen complexes,[8,15] which have the common *fac-mer* geometry with the isopropoxides being *cis* oriented. Despite copious amounts of effort attempts to yield crystals suitable for X-ray diffraction where unsuccessful.

All complexes were trialled for the polymerisation of *rac*-lactide in solution (2 or 24 h) and under the industrially preferred melt conditions (130 °C) in the absence of solvent (Tables 1 and 2). All initiators were active for the ROP of *rac*-LA in solution at 80 °C for 24 h.

The kinetics of the polymerisation have been investigated with the complexes prepared from ligand **2**H$_2$. For Ti(**2**)(O^{i}Pr)$_2$ a k_{app} = 2.7 × 10^{-3} min^{-1} at 80 °C in $C_6D_5CD_3$ was found, which is similar to previously reported Ti(IV) species.[16] However, when both Zr(**2**)(O^{i}Pr)$_2$ and Hf(**2**)(O^{i}Pr)$_2$ were investigated the polymerisation was too fast at 80 °C to be monitored accurately, therefore the kinetics were investigated at 25 °C in $CDCl_3$. Both Zr(**2**)(O^{i}Pr)$_2$ (k_{app} = 11.2 × 10^{-3} min^{-1}) and Hf(**2**)(O^{i}Pr)$_2$ (k_{app} = 36 × 10^{-3} min^{-1}) were seen to be incredibly active for the ROP of *rac*-LA. However, repeatedly, we were unable to isolate high molecular weight polymeric material after our normal work-up produre, in stark contrast to previous results with similar initiators.[3l,o,8] On examination of the ^{1}H NMR spectrum taken after quenching it is clear that the major product was methyl lactate with a small amount of lactic acid, this was further confirmed by GC-MS analysis. If ethanol is utilised in the work-up then ethyl lactate is produced. Ethyl lactate is increasingly being promoted as an environmentally friendly solvent and is biodegradeable.[17]

Table 2 Melt polymerisation data[a]

Entry	Initiator	Time/h	Conv./%[b]	M_n[c]	PDI[c]	P_r[d]
1	Zr(**1**)(O^{i}Pr)$_2$	0.25	77	97 300	2.40	0.40
2	Zr(**2**)(O^{i}Pr)$_2$	0.25	82	271650	1.70	0.45
3	Hf(**1**)(O^{i}Pr)$_2$	0.25	91	49 700	2.24	0.45
4	Hf(**2**)(O^{i}Pr)$_2$	0.25	81	84 750	3.46	0.40
3	Zr(**1**)(O^{i}Pr)$_2$	0.25	99	1600	1.30	0.37
4	Zr(**2**)(O^{i}Pr)$_2$	0.25	99	3500	1.56	0.52
5	Hf(**1**)(O^{i}Pr)$_2$	0.25	99	5310	1.45	0.3
6	Hf(**2**)(O^{i}Pr)$_2$	0.25	99	750	1.05	0.30
7	Hf(**2**)(O^{i}Pr)$_2$	0.1	99	4800	1.76	0.40

[a] Melt polymerisation of *rac*-lactide. In all cases a 300 : 1 monomer-to-initiator ratio was employed, 2.0 g of monomer was used, T = 130 °C. Entries 1–4 have not been quenched with MeOH. [b] Conversion as determined from ^{1}H NMR spectroscopy. [c] Determined from GPC analysis using THF as the solvent. [d] Determined from ^{1}H NMR homonuclear decoupled NMR spectroscopy.

To investigate this conversion in more detail the polymerisation was repeated without quenching with methanol, and stopped by exposure to air, Table 1 entries 1–4 and Table 2 entries 1–4. High molecular weight PLA could be obtained, in solution and melt conditions, albeit the molecular weight control was poor. During the work up procedure it is clear that we are converting the polymer to oligomeric material and methyl lactate.

This phenomenon is only observed with these highly active salalen complexes and we have not observed this previously with any group 4 metal complex.[3l,o] Presumably, the addition of MeOH generates an (ONNO)Hf(OMe)$_2$ species and the polymer $C_3H_7O(C_6H_8O_4)_nOH$. In excess MeOH and in the presence of a highly active catalyst then depolymerisation *via* transesterification will occur. In the MALDI-ToF MS oligomeric products species with a methoxy end group are isolated.

Further kinetic investigations *via* NMR spectroscopy with both Hf(**1**)(O^{i}Pr)$_2$ and Hf(**2**)(O^{i}Pr)$_2$ have been carried out. CD_3OD was added during the polymerisation and the process was monitored *via* analysis of the methine region of the NMR spectrum, Fig. 1 for the mole fraction plot and supporting information for kinetic plots.† For Hf(**2**)(O^{i}Pr)$_2$ the methine resonance for the polymer decreased in a first order fashion, this was found to have k_{app} = 5 × 10^{-3} min^{-1}. This was also observed for Hf(**1**)(O^{i}Pr)$_2$ as the catalyst.† In this case the polymer decreased with a k_{app} = 10 × 10^{-3} min^{-1}. These results clearly show that these catalysts are not only capable of producing PLA but can also be used to recycle the polymer to lactic acid derivatives. We have taken PLA with low polydispersity indexes, prepared with our other catalysts,[3o] and added Hf(**1**)(O^{i}Pr)$_2$with MeOH. We observed conversion to methyl lactate, at room temperature. If the polymer is stirred in methanol (without catalyst) then we do not observe

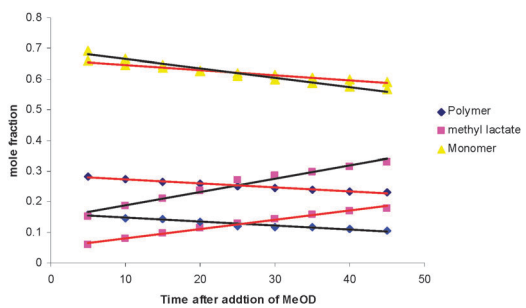

Fig. 1 Mole-fraction plots for the transesterification *via* depolymerisation of PLA and for the production of methyl lactate with Hf(**1**)(O^{i}Pr)$_2$ – black line and Hf(**2**)(O^{i}Pr)$_2$ red line.

such a conversion. We choose a series of PLA samples (0.35 g) with molecular weights (M_n) of 10 k, 20 k and 40 k and narrow PDIs and added Hf(**1**)(O^iPr)$_2$ (17 mg) in CH_2Cl_2 (5 ml) followed by 0.1 ml of methanol and observed conversion to methyl lactate regardless of molecular weight after 24 h. In all cases the molecular weight of the resulting oligomers were ~2000. For PLA samples of molecular weights (M_n) of 10 k, 40 k and 80 k in CH_2Cl_2 (2 ml) and 1 ml of MeOH added. Again we observed conversion to methyl lactate regardless of molecular weight.† In all cases the molecular weight of the resulting oligomers were ~3500. We have observed little difference between tacticities with either atactic or isotactic (the commercial forms of PLA) all being converted to methyl lactate. For example, from the kinetic polymerisation studies it is clear that both Hf(IV) catalysts produce strongly isotactic PLA† which upon addition of methanol is converted to methyl lactate. From the molecular weight studies atactic PLA is also converted. Significantly, we have also taken a commercial source of PLA (poly-*L*-lactide) with M_n ~ 200 000 and observed a 75% conversion to methyl lactate at room temperature in 24 h. Importantly, without the addition of Hf(**1**)(O^iPr)$_2$ no conversion to methyl lactate was observed, if the commerical sample was stirred in CH_2Cl_2 and MeOH.†

In conclusion we have prepared highly active group 4 initiators for the ROP of *rac*-lactide. However, upon quenching with MeOH the major product was methyl lactate. This work has the potential to be utilised for polymer recycling applications, as we have shown we can convert commercial PLA to methyl lactate. Attempts are on-going to optimise this system further. We wish to thank the University of Bath and Johnson Matthey for funding.

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