Highly Active Mg(II) and Zn(II) complexes for the ring opening polymerisation of lactide

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A range of simple ethylenediamine based Zn(II) and Mg(II) complexes have been prepared and their structures determined via NMR spectroscopy and X-ray crystallography. Preparation of these complexes was also demonstrated to be scalable, with 25 g of Zn(II) being readily produced. These complexes were trialed for the ring opening polymerisation (ROP) of lactide under industrial relevant conditions. Their reactivity has been related to their structure in solution. Incredibly high activity is achieved in the majority of cases including low catalytic loading and high temperatures, at industrially relevant conditions (180 °C 10,000:1:100 [LA]:[Zn]:[BnOH]), with high conversion achieved within 10 minutes and TOFs in excess of 100,000 hr⁻¹ achieved. The performance of these initiators for polymer production is supported by GPC, DSC and IR spectroscopy which all highlight the excellent control achieved.

Introduction

The production of bioplastics is currently a hot topic in light of the environmental burden associated with petrochemically derived materials. Polymers, such as poly(lactic acid) (PLA), are widely researched as a viable commodity plastic, being both renewably sourced and biodegradable. PLA is suitable for a range of applications, including use in food packaging and for in vitro surgical tools.¹⁻⁷ The production of PLA, from ring opening polymerisation (ROP) of the lactic acid dimer, lactide (LA), has received considerable interest both industrially and in academia.⁸ Current research is generally motivated by a desire to improve the initiators used for production of PLA, maintaining high activity, and control while avoiding the use of toxic heavy metals. A diverse library of metal complexes has been explored, particularly with the aim of controlling polymer microstructure.⁹⁻¹³ Aluminium has received considerable attention in the literature.¹⁴⁻²³ In particular, (ONNO)Al(III) complexes have been shown to be stereoselective in the ROP of rac-LA, albeit often with poor activity and subject to severe air/moisture sensitivity. For the ROP of rac-LA, strong isotactic bias has often been observed by such complexes, the most notable examples from Spassky,²⁴⁻²⁵ Feijen²⁶⁻²⁷ and Nomura.²⁸⁻⁴ⁱ In(III) analogues have been explored as initiators for ROP.¹⁷,⁴²⁻⁴⁷ Typically, greater activity is achieved at the cost of reduced stereocentrol as a consequence of a larger metal cation. Mehrkhodavandi and co-workers have investigated a range of amino/iminophenolate systems.⁴³⁻⁴⁵ Recently, this group has reported an air and moisture stable indium salan system.⁴⁶ A range of lanthanide initiators have also been applied to the ROP of rac-LA;⁴³⁻⁴⁷ in particular Williams and co-workers have demonstrated highly active Y(III) and Lu(III) systems amenable to the preparation of isotactic and heterotactic PLA.⁴³⁻⁴⁴, ⁴⁷ Group IV metal complexes have also garnered interest, due to their high activity and robustness,⁴⁸⁻⁵⁰ with both isotactic and heterotactic PLA being achieved with Zr(IV).⁵¹⁻⁵⁴ Whilst the majority of these are solution based studies there is a need for catalysts with earth abundant and benign metals that work under challenging melt conditions as these are the industrial conditions.

Zinc complexes have also been successfully applied to the ROP of lactide, generally being highly active under solution conditions.⁶⁶⁻⁸³ Early work by Coates and co-workers employed a β-diminate based Zn(II) complex which demonstrated a high degree of heterotacticity in solution.⁸⁴ Highly active zinc catalysts in solution have been examined by Williams and co-workers.⁸⁵⁻⁸⁶ The most recent work utilises dinuclear macrocyclic zinc complexes which show high TOFs (up to 60,000 hr⁻¹) at room temperature, in solution, as well as immortal polymerisation characteristics. Currently, the most isoselective Zn(II) complex has been reported by Ma and co-workers in solution at -40 °C.⁸⁷ These aminophenolate complexes were also found to be suitable for solvent-free polymerisation under immortal conditions. Magnesium complexes have also attracted attention for the ROP of LA.⁸⁸⁻¹⁰⁰ Often, such complexes are isostructural to their Zn(II) analogues. In the case of the β-diminate Mg(II) complex, the heteroselectivity observed with the Zn(II) analogue was not replicated.⁶⁶ However, Chisholm and co-workers have demonstrated several Mg(II) complexes for the production of heterotactic PLA.⁷¹, ¹⁰¹

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Results and Discussion

Synthesis

All ligands were prepared via a simple condensation to afford the respective Schiff base, which were characterised by multinuclear NMR spectroscopy and mass spectrometry. For 2H and 3H, the 1H NMR spectra is observed to be broad and suggestive of multiple species in solution. This could be explained by an intramolecular ligand cyclisation reaction, which has been reported for similar types of systems in the literature. Complexes of Zn(II) and Mg(II) were prepared in toluene and reported for similar types of systems in the literature. This journal is © The Royal Society of Chemistry 20xx

Complexes of Zn(II) and Mg(II) were prepared in toluene and purified by hexane recrystallisation or via washing (Scheme 1).

Scheme 1. Ligands and their complexation to Zn(II) and Mg(II).

For Mg(2), the crystal structure revealed a phenoxy bridged dimeric complex with cyclisation of one ligand to form a 5 membered ring. This is likely related to the fluxionality observed for the ligand via 1H NMR spectroscopy. The magnesium centres displayed a distorted octahedral geometry in this structure (Mg(2): O(1)-Mg(1)-N(3) = 168.40(6)°) (see ESI).

Complexes based upon ligands 5-7H have no chiral centres. Zn(5) is observed to be five coordinate in the solid-state, with one amine group being directed at the zinc centre but sufficiently separated as to not be considered as a formal bonding interaction (Zn(1)-N(4) = 2.744 Å). Due to this, the geometry at the metal centre has a strong preference for square based pyramidal (t5 = 0.01). Zn(6) also shows preference for a five coordinate complex in the solid-state. In this instance, the pendant arm and amine centre is rotated away from the metal centre. This is likely due to the absence of phenyl substituents, which would otherwise hinder this movement. Zn(6) also shows a strong preference for a square based pyramidal geometry (t5 = 0.05). Chen et al report the para-only bromo substituted Zn(II) complex. This structure is four coordinate with the pendant amine groups directed towards the metal centre but this cannot be considered a formal bonding interaction (Zn(1)-N(3) = 2.573 Å). The geometry and bond lengths at the metal centre are similar to Zn(5). Mg(5) are observed to have a pseudo octahedral geometry despite the methylation of the amine. For Zn(1), and Mg(1), the -CH3 resonances are observed as four discrete multiplets and a broad quartet is also observable for the NH proton. In contrast, Zn(2) yield 1H NMR spectra in which the -CH3 resonances appear as two broad resonances at room temperature in CDCl3. This observation could be an indication of greater fluxionality in solution caused by the lability of the pendant amine. At 233 K, the spectrum of Zn(2) is more resolved, having four discrete...
resonances for the CH₂ protons, suggesting the “locking” of geometry under these conditions (see supporting information). Both ¹H and ¹³C(¹H) NMR spectra for Mg(2)₃ indicates the two ligands are equivalent at the metal centre suggesting the presence of the homoleptic imino complex in solution rather than the dimeric cyclised structure observed in the solid-state. It is anticipated that the tridentate imino coordination mode would be favored over the bidentate cyclised system. For Mg(2/3)₆, the ¹H NMR spectra consist of 5 broad resonances for the –CH₂– and NH protons while the aromatic and methyl resonances are sharp. The ¹H NMR spectrum for Zn(5)₂ shows the greatest resolution, with splitting patterns of the –CH₂– groups observable at room temperature. The signals due to the methyl group attached to the amine are split into two discrete resonances suggesting inequivalence of these protons on coordination. This spectrum implies the two ligands around the metal are equivalent and locked in their coordination suggesting a different coordination mode to the solid-state (presumably 6 coordinate). The appearance of the ¹H NMR spectra for Zn(6/7)₂ is comparable to the analogous Zn(2/3)₂ spectra. However, for each methylated complex, there is resolution of one of the methylene groups to indicate a broad triplet at room temperature. This resolution could imply a lesser degree of fluxionality compared to Mg(2/3)₆. Diffusion ordered spectroscopy (DOSY) NMR was performed on the zinc complexes. For each sample, there is one main species as indicated by the diffusional correlation peaks. The magnitude of the diffusion coefficients correlates with the bulk of the aryl and nitrogen substituents (see supporting information).

Polymerisation

All polymerisations were carried out under industrially preferred conditions, without solvent at elevated temperatures. The lactide monomers were not rigorously purified but used after a single recrystallisation. Benzyl alcohol was added as a co-initiator in the majority of cases. For all initiators, the polymerisation of rac-LA afforded atactic PLA (Pᵣ ~ 0.50) with the exception of Zn(5)₂ which demonstrated a slight heterotactic preference (Pᵣ = 0.66). With L- or D-LA, no epimerisation was observable, even at high temperatures, as shown by the ¹H(¹H) NMR spectra of the methine region which yields a single iii resonance (see supporting information). At 130 °C, polymerisation is observed to be very rapid for Zn(1,4,5,7)₅ with high conversion being achieved within minutes ([LA]:[Init]:[BnOH] = 300:1:1) (Table 1). In contrast, for Zn(2,3,6)₅, polymerisation performance is observed to be much poorer with 30 - 60 minutes being required to achieve high conversion. The reduction in activity for Zn(5/6)₂ compared to Zn(1/2)₅ which have the same aryl substituents is likely due to the increased steric bulk of the methylated amine. For this subseries increasing aryl sterics increase rate and the addition of a methyl group to the amine centre reduces the rate.

In contrast, Zn(7)₅ is observed to be more active than the secondary amine analogue Zn(3)₂ (R¹ = R² = Cl). In this case, the combination of both aryl substituents and methylated amine likely cause a change of coordination around the metal centre. Similar relationships of activity are observed for polymerisation with the Mg(II) complexes under these conditions (Table 2); both Mg(1,5)₅ achieve a high conversion of LA in one minute compared to Mg(2,3,6)₂ which require significantly more time. Mg(7)₅ is observed to be more active compared to Mg(3)₂ requiring 10 minutes to reach high conversion. The difference in activity displayed by these complexes is contrary to what would be expected based purely on the steric contribution of the substituents. While a six coordinate metal centre is indicated in the solid-state structure (with the exception of Zn(5/7)₂), the coordination in solution is fluxional. There is, however, a correlation between the distinct nature of the methylene resonances and activity towards polymerisation; the more active complexes {M(1,4,5)₂} have a greater number of – CH₂– resonances with discrete splitting patterns being observed. For the less active complexes {M(2,3,6)₅} these resonances appear as two broad signals at room temperature. It is suggested that this broadness is due to fluxionality at the metal centre due to the lability of the pendant amine which hinders polymerisation. In essence activity is superior for the systems where the ligands are “locked” in solution.

For the majority of initiators, under these conditions, the molecular weight control is observed to be moderate, with broad dispersities (D = 1.05 – 1.86). These complexes were also capable of polymer degradation through transesterification reactions and this may be responsible for the poor molecular weight control. For Zn(1,4,5)₅, the reduced control could also be due to the short reaction time in which polymerisation conditions were not homogenous leading to sub-optimal initiation.
For Zn(1)$_2$, similar results are achievable without the use of benzyl alcohol albeit with an increase of dispersity (D = 1.86). Initiation in this case could either be due to impurities in the monomer or initiation by the ligand. Zn(6/7)$_2$ provide the narrowest dispersity, however, the molecular weights are much lower than expected. MALDI-ToF analysis of the polymer derived from both initiators show a series consistent with the molecular weight from GPC (however the data is weak/poor likely due to the high molecular weight). In both cases BnO- and –H are indicated as the polymer end groups (see ESI). An improvement in molecular weight control can be achieved by decreasing the concentration of initiator, which is also favourable for industrial PLA production. At 10000:1:100, the polymerisation of L-LA reaches high conversion after just 5 minutes for Zn(1)$_2$ (TOF = 99,600 hr$^{-1}$, Table 3). Excellent molecular weight control is demonstrated under these conditions, (M$_n$ = 12050 Da; M$_{n,\text{theo}}$ = 12850 Da). The distribution of polymer chain lengths is also observed to be narrow (D = 1.09). MALDI-ToF analysis of this polymer revealed one series (M$_n$ = 10362.9 Da) with a peak spacing of 144 Da indicating the complete absence of transesterification side reactions. The expected end groups of BnO- and H- are also confirmed. These improvements are undoubtedly due to a decrease in initiator concentration which increases reaction time allowing for a more homogenised polymerisation and reduces the extent of side reactions. A further consequence of the reduced metal content is the isolation of colourless polymer prior to purification (see ESI).

Theoretical molecular weight based on conversion and co-initiator added ([(M$_\text{LA}$ × 3×%conv) + M$_{\text{BnOH}}$]). Molecular weight via GPC analysis (in THF). A correction factor of 0.58 has been applied. 128

Table 2. Immortal polymerisation of L-lactide at 130°C with Zn(II) complexes.

| Init. | [LA]:[I]:[BnOH] | Time / min | Conv % | M$_{n,\text{theo}}$ | M$_n$ | D$^*$ | Conditions: L-LA, solvent free (130 °C) * Determined via $^1$H NMR spectroscopy. a Theoretical molecular weight based on conversion and co-initiator added ([(M$_\text{LA}$ × 3×%conv) + M$_{\text{BnOH}}$]). Molecular weight via GPC analysis (in THF). A correction factor of 0.58 has been applied. b for Zn(1)$_2$ is most likely related to the increase in steric bulk of 4H and 5H. Good control of molecular weight and dispersity is maintained by these complexes (D = 1.04 – 1.05). MALDI-ToF analysis of polymer from Zn(4)$_2$ and Zn(5)$_2$ reveals one symmetrical series with a peak spacing of 144 Da indicating the absence of side reactions. There is a good agreement between measured molecular weight with the theoretical value (for Zn(4)$_2$, M$_n$ = 9930 Da; M$_{n,\text{theo}}$ = 9750 Da) and the residual peak mass is consistent with BnO- and H- end groups. The magnesium analogues, Mg(1/5)$_2$, display a much reduced activity under analogous conditions, requiring 20 minutes to achieve 45 and 23 % conversion respectively. A good agreement of theoretical and measured molecular weight is observed for both initiators. MALDI-ToF of polymer derived from Mg(1/5)$_2$ identifies the end groups as BnO- and H-. However there is a minor series which has a separation of 72 Da indicative of transesterification side reactions.

Zn(1,4,5,7)$_2$ and Mg(1,5)$_2$ were also tested for polymerisation activity at higher temperatures (180 °C) (Table 4). Under these conditions, reduced metal loading was necessary due to the high activity of the initiators. For Zn(1/4)$_2$, high conversion is achieved within 4 minutes ([LA]:[Init]:[BnOH] = 10000:1:100). For these polymers, there is a reasonable agreement between molecular weight with the theoretical value (for Zn(1)$_2$, M$_n$ = 16100 Da; M$_{n,\text{theo}}$ = 13050 Da, TOF = 180,000 hr$^{-1}$). However, the GPC trace has a shoulder towards high molecular weight. As a consequence, the chain dispersity is increased relative to 130 °C (for Zn(1)$_2$, D = 1.47). For comparison, commercially available Sn(Oct)$_2$ and Zn(OAc)$_2$H$_2$O were also tested under these conditions. Polymerisation of L-LA with Sn(II) was observed to be comparable to Zn(1)$_2$ (3 minutes, 95 %, M$_n$ = 16100 Da, D = 1.54). Zn(OAc)$_2$H$_2$O performed less well, (10 minutes, 27 %) demonstrating the need for ligated complexes. The production of higher molecular weight was also demonstrated with Zn(1)$_2$ ([LA]:[Init]:[BnOH] = 10000:1:133) within the same timeframe (M$_n$ = 42500 Da; M$_{n,\text{theo}}$ = 40700 Da, TOF = 188,000 hr$^{-1}$). Reasonable conversion and high molecular weight is also achieved at 10000:1:15 after 5 minutes (63 %; M$_n$ = 66400 Da, D = 1.47). There is good agreement of measured and theoretical molecular weight (M$_{n,\text{theo}}$ = 60600 Da). The molecular weight achieved is comparable to that of commercially available PLA (1.80)

Table 3. Immortal polymerisation of L-lactide at 130°C with Zn/Mg(II) complexes.

| Init. | [LA]:[I]:[BnOH] | Time / min | Conv % | M$_{n,\text{theo}}$ | M$_n$ | D$^*$ | Conditions: L-LA, solvent free (130 °C) * Determined via $^1$H NMR spectroscopy. b Theoretical molecular weight based on conversion and co-initiator added ([(M$_\text{LA}$ × 3×%conv) + M$_{\text{BnOH}}$]). Molecular weight via GPC analysis (in THF). A correction factor of 0.58 has been applied. 128

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NatureWorks, 6202D: $M_n = 44350 \text{ Da}, D = 2.00$, see ESI).\textsuperscript{109} This system was also found to achieve relatively high molecular weight in the absence of co-initiator (3 minutes, 38 %; $M_n = 48950 \text{ Da}, D = 1.29$). In this case the dispersity is found to be lower and it is suggested that the polymerisation pathway without benzyl alcohol leads the observed shoulder in the GPC trace. Conversion can be increased by extension of the polymerisation time (15 minutes, 73 %), however this is achieved with a broadening of the dispersity due to increased viscosity and poor mixing. The molecular weight achieved is industrially applicable ($M_n = 82400 \text{ Da}, D = 1.64$), being comparable to that of commercial PLA samples (NatureWorks, 40430: $M_n = 61,900 \text{ Da}, D = 1.98$ / NatureWorks, 25000HP: $M_n = 71900 \text{ Da}, D = 1.62$).\textsuperscript{109}A similar result is observed for Zn(1), in the absence of benzyl alcohol. Zn(5) requires more time to reach higher conversion, which is consistent with the previous experimental conditions. However, this initiator facilitates a more controlled ROP with excellent agreement between experimental and theoretical molecular weight values and a narrow dispersity ($M_n = 11550 \text{ Da}, M_{n,\text{theo}} = 11350 \text{ Da}; D = 1.08$). Polymerisation without co-initiator affords negligible conversion within the same timeframe and this is undoubtedly the reason for enhanced control. Zn(5) is therefore more resistant to lactide impurities or stable towards insertion of the complex-ligand bonds into the lactide carbonyl. Zn(7) also facilitated polymerisation under these conditions with good control being maintained despite 1 hour at high temperature ($M_n = 11650 \text{ Da}, M_{n,\text{theo}} = 8600 \text{ Da}; D = 1.06$). In the absence of co-initiator, the polymerisation activity is suppressed, similar to Zn(5).

The magnesium complexes activity is not enhanced at 180 °C with similar conversions being achieved in the same time frame. However, reasonable molecular weight control is maintained. MALDI-ToF analysis of these polymers confirms the expected benzyl alcohol groups. A greater degree of transesterification reactions is also indicated and this is more pronounced for polymer derived from Mg(1).

**Mechanistic Studies**

The stability of these complexes, with respect to lactide, has been investigated on an NMR scale at room temperature in CDCl\textsubscript{3} (see supporting information). The addition of L-LA to Zn(4,5)\textsubscript{2} caused no change of the resonances originating from the complexes. From these NMR spectra, there is also evidence of lactide coordination through an upfield shift of methine resonances. Further to this, conversion of the lactide is observed over the course of a week to give oligomers without the addition of an exogenous alcohol. As the complexes appear to be unchanged by addition of the LA or PLA, it is likely that an activated monomer mechanism is in operation facilitated by impurities in the monomer.\textsuperscript{110-111} Stability was also assessed under melt conditions: 5 equivalents of L-LA were added to Zn(1) at 180 °C and stirred for 1 minute. The resultant material was analyzed by \textsuperscript{1}H NMR to reveal complete conversion of lactide (see ESI). The majority of the complex is shown to be intact, albeit with broadened resonances. There are new resonances in the aromatic region suggesting some decomposition, although the resonances are minor (~ 5%); the material was also analyzed by ESI-MS which showed the presence of oligomers. The mass of which was consistent with lactide being ring-opened by the ligand rather than lactic acid or water. It was observed that Zn(1) was capable of initiating the ROP of lactide in the absence of a co-initiator and this evidence suggests this is achieved through insertion of the ligand. This would generate a new species which is capable of facilitating the coordination-insertion ROP. With the loss of a ligand, the lower coordinate zinc centre could be predicted to be more active. The operation of a second active species would also explain the high molecular weight shoulder in the GPC trace. It is hypothesised that it is the amine group which inserts into the lactide rather than the phenoxide as this explains the inactivity of Zn(5,7) in the absence of co-initiator. In the presence of co-initiator the predominant ROP pathway is presumably an activated monomer mechanism.

**Kinetics**

An investigation into the kinetics of the most active initiators was carried out via \textit{in situ} IR spectroscopy measurements. These experiments were conducted on a 15 g scale (L-LA) to immerse the IR probe fully in the lactide melt. For each initiator (Zn(1,4,5)\textsubscript{2}), the observed activity on this scale is consistent with the smaller scale polymerisation in a sealed tube (Table 5). Rate data is extracted from the first 2-3 minutes of reaction. After this period, the increased viscosity leads to a second linear regime with a reduced rate. Zn(1) was shown to have the highest rate constant ($k_{\text{app}} = (6.86 \pm 0.36) \times 10^{-3} \text{ s}^{-1}$, TOF = 114,000 hr\textsuperscript{-1}) Zn(4)\textsubscript{2} and Zn(5)\textsubscript{2} were shown to have slightly reduced rates of polymerisation ($k_{\text{app}} = (6.28 \pm 0.31) \times 10^{-3} \text{ s}^{-1}$ and (6.05 ± 0.26) \times 10^{-3} \text{ s}^{-1} with TOFs 112,800 and 54,000 hr\textsuperscript{-1} respectively), although within experimental error. Under these
conditions, polymerisation with Zn(1/4) leads to polymer with a relatively broad dispersity and this is once again attributed ligand initiated polymerisation. However, Zn(5) maintains the excellent control previously seen (Đ = 1.05). All molecular weights observed are slightly higher than expected and this could be due to loss of benzyl alcohol from the melt mixture. All isolated polymer from these studies were colourless powders prior to purification (see supporting information). DSC analysis was carried out on the PLLA derived from Zn(1); under these challenging large scale conditions to determine the extent of epimerisation. For this sample, a melt temperature of 171 °C was observed highlighting once again the excellent control of this initiator (see ESI).

Stereocomplexation

The ability to control the polymerisation of L-LA, with the absence of epimerization or transesterification at 180 °C massively widens the applications of these initiators. The production of isotactic stereoblock PLA is an important goal, due to the increasing interest for non-petroleum derived, biodegradable materials. A particular challenge is to achieve this under industrially relevant conditions, in the absence of solvent. Using Zn(1), this has been achieved through an initial polymerisation of L-LA at 180 °C with a ratio of 1500:1:10 followed by the addition of an equivalent amount of D-LA (total ratio 3000:1:10). Best results were achieved using overhead stirring to ensure the polymerisation remained mobile. High conversion was achieved after 5 minutes and a clear film like polymerisation was observed for the least fluxional complexes. Excellent control and activity was achieved under industrially relevant conditions of high temperature and low catalyst loading, with the resultant PLA having no colouration. Kinetic data under these conditions was recorded via IR spectroscopy, further demonstrating and quantifying the activity of these complexes, with TOFs in excess of 100,000 hr⁻¹, which are undoubtedly at the forefront of the field. Due to the ease of epimerisation, solvent-free stereoblock formation was also achieved through sequential monomer addition.

Table 5. IR kinetics for polymerisation of L-lactide at 180°C with Zn(II) complexes.

| Init. | Time / min | Conv % | \( M_{\text{theo}} \) \( g \) | \( M_n \) | \( Đ \) | \( k_{\text{app}} \times 10^{-3} \) \( s^{-1} \) |
|-------|------------|--------|----------------|-------------|-----|----------------------|
| Zn(1); | 5 | 95 | 13700 | 14500 | 1.63 | 6.86 ± 0.36 |
| Zn(4); | 7 | 94 | 13650 | 16100 | 1.41 | 6.28 ± 0.31 |
| Zn(5); | 8 | 72 | 10450 | 12750 | 1.05 | 6.05 ± 0.26 |

Conditions: L-LA (15 g), [LA]:[I]:[BnOH] = 10000:1:10, solvent free (180 °C) → Determined via 1H NMR spectroscopy. Room theoretical molecular weight based on conversion and co-initiator added \( (M_{\text{LA}} \times \text{Conv}) + M_{\text{BnOH}} \). Molecular weight via GPC analysis (in THF). A correction factor of 0.58 has been applied.\(^{108}\)

Conflicts of interest

There are no conflicts to declare

Acknowledgements

We are grateful to the EPSRC for funding (EP/P016405). We would also like to thank PURAC/CORBION for generous donation of D-Lactide. NatureWorks are also thanked for generous donation of commercial PLA samples. We also acknowledge the EPSRC (EP/L027267/1) for analysis facilities at the University of Bath.

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