Aluminum salen and salan complexes in the ring-opening polymerization of cyclic esters: Controlled immortal and copolymerization of rac--butyrolactone and rac-lactide

Citation for published version:

Digital Object Identifier (DOI):
10.1002/pola.26476

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Early version, also known as pre-print

Published In:
Journal of Polymer Science Part A - Polymer Chemistry

Publisher Rights Statement:
Copyright © 2012 Wiley Periodicals, Inc. All rights reserved.

General rights
Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.
Aluminum salen and salan complexes in the ring-opening polymerization of cyclic esters: Controlled immortal and copolymerization of rac-β-butyrolactone and rac-lactide**

Edward D. Cross,1 Andreas Decken2 and Michael P. Shaver3*

[1] Department of Chemistry, University of Prince Edward Island, 550 University Ave., Charlottetown, PE, C1A 4P3, Canada.

[2] Department of Chemistry, University of New Brunswick, P.O. Box 6600, Fredericton, NB, E3B 5A3, Canada.

[3] EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

[1*] Corresponding author; e-mail: michael.shaver@ed.ac.uk

[**] The authors thank the Natural Sciences and Engineering Research Council of Canada (NSERC), Innovation PEI, Canadian Foundation for Innovation (CFI), Atlantic Canada Opportunities Agency and University of Prince Edward Island for funding.

Supporting information:
1H{1H} NMR spectra, kinetic and molecular weight plots for 1 and 4, 1H NMR spectra of poly(rac-LA-co-rac-β-BL) polymers and X-ray crystallography data. Available online at http://dx.doi.org/10.1002/pola.26476

Abbreviations:
ROP, ring-opening polymerization; PLA, poly(lactic acid); PHB, poly(3-hydroxybutyrate); β-BL, β-butyrolactone; PCL, poly(ε-caprolactone); NMR, nuclear magnetic resonance; DSC, differential scanning calorimetry.

Keywords:
Ring-opening polymerization, living polymerization, immortal polymerization, copolymerization, biodegradable polymers, poly(3-hydroxybutyrate), β-butyrolactone, poly(lactic acid), lactide, poly(ε-caprolactone), ε-caprolactone, aluminum, homogeneous catalysis.
Graphical abstract

Synopsis

Aluminum-based salen and salan complexes mediate the living and immortal ROP of rac-b-butyrolactone and rac-lactide with a considerable degree of control over the polymerization, yielding polymers with controlled molecular weight and narrow PDIs. Copolymerization of these monomers to yield poly(rac-lactide-co-rac-β-butyrolactone) was successful under neat conditions at 120°C, presenting the first case where narrow PDIs were achieved. A strong bias for rac-lactide insertion over rac-β-butyrolactone was observed.

Abstract

Aluminum-based salen and salan complexes mediate the ring-opening polymerization (ROP) of rac-β-butyrolactone (rac-β-BL), ε-caprolactone and rac-lactide. Al-salen complexes displayed impressive control over the ROP of rac-β-BL, with narrow PDIs of < 1.15, while Al-salan complexes also showed superb control with PDIs of <1.05. All poly(3-hydroxybutyrate) (PHB) isolated using Al-salen and salan complexes contained an atactic microstructure. Kinetic studies of rac-β-BL ROP by 1H NMR spectroscopy revealed pseudo-first order polymerization kinetics and a linear relationship between molecular weight and percent conversion. Al-salen and salan complexes also mediated the immortal ROP of rac-β-BL and rac-lactide by addition of excess benzyl alcohol of up to 50 mol eq. with excellent control observed. Screening novel methyl/adamantyl substituted Al-salen complex showed improved control in the ROP of rac-lactide and rac-β-BL, yielding atactic PHB and highly isotactic PLA ($P_m = 0.88$). All complexes gave only modest control in the ROP of ε-caprolactone, with broadened PDIs. Control over the copolymerization of rac-lactide and rac-β-BL was achieved utilizing the Al-salan complex under neat polymerization conditions to produce poly(rac-LA-co-rac-β-BL) with narrow PDIs of < 1.10. 1H NMR spectra of the copolymers a strong bias for insertion of rac-lactide over rac-β-BL observed.
Introduction

Interest in the development of biodegradable polyesters, in particular poly(lactic acid) (PLA), poly(glycolic acid) (PGA), poly(ε-caprolactone) (PCL) and their copolymers, for biomedical devices has continued to increase.\textsuperscript{1-4} While these polymers remain at the forefront of research efforts in this field, other classes of biodegradable polyesters such as the poly(hydroxyalkanoates) (PHAs) have begun to attract greater focus in the past decade.\textsuperscript{5} Poly(3-hydroxybutyrate) (PHB), one of the more well-known PHAs, has been of particular interest as it is produced by bacteria with high isotactic stereoregularity producing semicrystalline PHB with a $T_g$ and $T_m$ of approximately 5°C and 180°C respectively, giving it properties similar to that of isotactic polypropylene.\textsuperscript{6} Alternatively, ring opening polymerization of $\beta$-butyrolactone ($\beta$-BL) by metal-based complexes has provided an additional route to this biodegradable polyester, gaining access to PHB with predictable molecular weight, narrow PDI and potentially alternative stereoregularity from the completely isotactic bacterial PHB. Rare-earth and group 3 complexes have been particularly proficient at mediating the ROP of rac-$\beta$-BL, while aluminum complexes which can polymerize this monomer in a controlled and stereoregular manner have remained relatively unexplored.\textsuperscript{7,8}

Once a catalyst system has been developed that can effectively control the ROP of cyclic esters, access to novel biodegradable materials can be achieved by the copolymerization of two or more monomers in the hopes of observing properties unique to the copolymer. In particular, reports of complexes which effectively mediate the ROP of rac-$\beta$-BL and rac-lactide in the copolymerization of these monomers remain scarce. It has been reported that tin alkoxides copolymerize (R)-$\beta$-BL and L-lactide, producing poly((R)-3-hydroxybutyrate)-co-poly(L-lactic acid) where the presence of (R)-$\beta$-BL and L-lactide in the copolymer correlated well with the initial monomer:catalyst feed ratio.\textsuperscript{9} However, these copolymers possessed considerably high PDIs of >1.7. When mediated by dibutylmagnesium, the copolymerization of rac-$\beta$-BL and L-lactide produced similar results to those of tin alkoxides - good correlation between the ratio of monomers in the feed to those observed in the resulting copolymer, but PDIs of > 1.6.\textsuperscript{10} Zirconium amine-tris(phenolate) complexes successfully copolymerized rac-$\beta$-BL and rac-lactide, again with broad PDIs of > 1.6, however, the authors noted that the rate of insertion of rac-$\beta$-BL was significantly higher than that observed for rac-lactide at 80°C in toluene when the polymerization was monitored by $^1$H NMR.\textsuperscript{11} Thus, the resulting copolymer was composed of two distinct blocks rather than the expected random or gradient copolymer. Only by utilizing a sequential addition of rac-$\beta$-BL followed by rac-lactide was a block-co-polymer of narrow PDI (<1.1) obtained. Finally, it was demonstrated that an aluminum half-salen complex which had similar observed rates in rac-$\beta$-BL and rac-lactide ROP at 90°C in toluene resulted in no rac-$\beta$-BL incorporation during the copolymerization, with only PLA formed, even after extended polymerization times.\textsuperscript{12}

In this study, we chose aluminum-based salen (salen = $N,N'$-bis(salicylaldimine)-1,2-ethylenediamine) and salan (salan = $N,N'$-bis(o-hydroxybenzyl)-1,2-diaminoethane) frameworks that were known to produce PLA
with narrow PDIs, to explore their ability to mediate the ROP of rac-β-BL. We then used these tetradeutate salen and salan aluminum complexes in the copolymerization of rac-β-BL and rac-lactide, comparing their activity to previously reported systems. In particular, we can generate poly(rac-LA-co-rac-β-BL) polymeric materials of controlled molecular weight and polydispersities. To support previous reports mentioned, we wished to observe similar preference for insertion of rac-lactide over rac-β-BL, and if these tetradeutate salen and salan complexes would provide increased control to access the targeted copolymers with narrow PDIs.

Experimental

Materials

All chemicals and solvents were obtained from Sigma Aldrich unless otherwise stated. 4-Methylphenol, 1-adamantanol (99%), tin(IV)chloride (97%), paraformaldehyde powder (95%), 1,2-diaminoethane (≥99%), N,N”-dibenzylethlenediamine (97%) and trimethylaluminum (2.0 M solution in heptane) were used as received. Triethylamine (≥99%) was dried over calcium hydride at ambient temperature overnight prior to vacuum transfer and was degassed by 3 freeze-pump-thaw cycles prior to use. Benzene-\(d_6\) (D, 99.5%) and toluene-\(d_8\) (D, 99.94%) were purchased from Cambridge Isotope Laboratory, dried over calcium hydride at reflux overnight prior to vacuum transfer and were degassed by 3 freeze-pump-thaw cycles prior to use. rac-β-Butyrolactone (≥98%) was dried over calcium hydride overnight at ambient temperature, distilled under vacuum and degassed by 3 freeze-pump-thaw cycles prior to use. PURASORB DL-lactide was obtained from PURAC Biochem by Gorinchem and sublimed 3 times under vacuum prior to use. ε-Caprolactone was dried over calcium hydride and distilled under inert atmosphere prior to use. Complexes 1\(^{13}\) and 2\(^{14}\), as well as 3-adamantyl-2-hydroxy-4-methylbenzaldehyde\(^{15,16}\) were prepared according to literature procedures.

Toluene and pentane were obtained from an Innovative Technologies glovebox equipped with an inline Solvent Purification System, consisting of columns of alumina and copper catalyst. The solvents were degassed by 3 freeze-pump-thaw cycles prior to use. All air-sensitive manipulations were performed in an MBraun LABmaster sp glovebox or using standard Schlenk techniques. \(^1\)H (300 MHz) and \(^{13}\)C\(^{\{1\}H}\) NMR (75 Hz) spectra were collected on a Bruker Avance Spectrometer. Gel permeation chromatography (GPC) analysis was carried out on a Polymer Laboratories PL-GPC 50 Plus integrated GPC system with two 300 × 7.8 mm Jordi Gel DVB mixed bed columns using HPLC grade THF at a flow rate of 1 mL per minute at 50°C utilizing a refractive index detector and poly(styrene) standards for molecular weight determinations.

Copolymers of rac-β-BL and rac-lactide were analyzed using a Wyatt Technology miniDAWN™ TREOS® multiple angle light scattering (MALS) detector operating at 658 nm and using dn/dc values for PLA and PHB of 0.050\(^{17}\) and 0.065\(^{18}\) respectively. DSC analyses were completed on a TA Instruments DSC Q100 in hermetically sealed aluminum pans. A nitrogen flow rate of 50 mL min\(^{-1}\) and heating parameters of 5°C min\(^{-1}\) for heating and cooling were employed.
Synthesis and characterization of 3: 3-Adamantyl-2-hydroxy-4-methylbenzaldehyde (0.869 g, 3.21 mmol) of was dissolved in of absolute ethanol (10 mL). To this solution, 1,2-diaminoethane (0.097 g, 1.61 mmol) was added followed by several drops of formic acid, and the mixture was refluxed for 4 hours with a yellow precipitate observed generally within the first 30 minutes. After 4 hours, heating was ceased, and the mixture was allowed to cool to room temperature. The yellow precipitate was filtered and washed with cold absolute ethanol. Yield: 0.663 g (73%). $^1$H NMR (300 MHz, CDCl$_3$, $\delta$, ppm): 13.67 (s, -OH, 2H), 8.34 (s, ArCH=N, 2H), 7.06 (s, ArH, 2H), 6.88 (s, ArH, 2H), 3.91 (s, N-C$_2$H$_5$C$_2$H$_2$-N, 4H), 2.17 (m, AdH and ArCH$_3$, 30H), 1.80 (bs, AdH, 15H) ppm. $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$, $\delta$, ppm): 167.8, 158.8, 137.7, 131.0, 129.9, 127.1, 118.7, 59.9, 40.7, 37.6, 37.4, 37.3, 29.5, 21.1 ppm. Anal. For C$_{38}$H$_{48}$N$_2$O$_2$ Calcd.: C, 80.81; H, 8.57; N, 4.96. Found: C, 81.12; H, 8.40; N, 5.10.

Synthesis and characterization of 4: 2-Adamantyl-4-methylphenol (2.25 g, 9.28 mmol) was dissolved in of absolute ethanol (10 mL). To this solution, N,N'-dibenzyl-1,2-diaminoethane (1.12 g, 4.64 mmol) was added followed by paraformaldehyde (0.96 g, 9.28 mmol), and the mixture was refluxed for 18 hours. After 18 hours, heating was ceased, and the mixture was allowed to cool to room temperature. A white precipitate formed and was filtered then washed with cold absolute ethanol. Yield: 2.45 g (35%). $^1$H NMR (300 MHz, CDCl$_3$, $\delta$, ppm): 10.36 (bs, -OH, 2H), 7.31 (m, ArH, 10H), 6.92 (s, ArH, 2H), 6.59 (s, ArH, 2H), 3.61 (s, PhCH$_2$N, 4H), 3.50 (s, PhCH$_2$N, 4H), 2.65 (s, ArCH$_3$, 6H) ppm. $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$, $\delta$, ppm): $\delta$ 154.4, 136.9, 129.8, 128.7, 127.7, 127.5, 126.9, 122.1, 59.0, 58.3, 49.8, 41.5, 40.6, 37.4, 37.3, 36.9, 29.4, 29.3, 21.0 ppm. Anal. For C$_{52}$H$_{64}$N$_2$O$_2$ Calcd.: C, 83.38; H, 8.61; N, 3.74. Found: C, 83.18; H, 8.44; N, 4.02.

Synthesis and characterization of 5: In a nitrogen filled glovebox, of 3 (0.900 g, 1.59 mmol) was dissolved in toluene (15 mL) in an oven-dried ampoule. With vigorous stirring, a 2.0 M solution of trimethylaluminum in heptane (0.552 g, 1.59 mmol) was added dropwise. Effervescence was observed, and the ampoule was sealed, removed from the glovebox and heated to 110°C for 24 hours. After 24 hours a yellow precipitate formed and the ampoule was allowed to cool to room temperature. The precipitate was filtered and washed with pentane. Yield: 0.414 g (43%). $^1$H NMR (300 MHz, C$_6$D$_6$, $\delta$, ppm): 7.33 (s, ArCH=N, 2H), 7.32 (s, ArH, 2H), 6.60 (d, ArH, 2H, $J$ = 1.8 Hz), 2.93 (q, N-CH$_2$CH$_2$-N, 2H, $J$ = 6.3, 12.3 Hz), 2.51 (br, AdH and N-CH$_2$CH$_2$-N, 14 H), 2.28 (s, ArCH$_3$, 6H) 2.18 (br, AdH, 6H), 1.87 (bm, AdH, 14H) -0.41 (s, AlCH$_3$, 3H). $^{13}$C{$^1$H} NMR (75 MHz, C$_6$D$_6$, $\delta$, ppm): 168.2, 165.4, 142.2, 138.2, 135.0, 131.3, 129.7, 126.0, 124.5, 120.1, 54.0, 41.5, 38.3, 38.0, 30.2, 21.7, 21.1 ppm. Anal. For C$_{39}$H$_{48}$AlN$_2$O$_2$ Calcd.: C, 87.45; H, 8.17; N, 4.63. Found: C, 77.72; H, 8.03; N, 4.39.

Synthesis and characterization of 6: In a nitrogen filled glovebox, 4 (0.815 g, 1.08 mmol) was dissolved in toluene (15 mL) in an oven-dried ampoule. With vigorous stirring, a 2.0 M solution of trimethylaluminum in heptane (0.358 g, 1.08 mmol) was added dropwise. Effervescence was observed, and the ampoule was sealed, removed from the glovebox and heated to 110°C for 24 hours. After 24 hours a white precipitate formed and the ampoule was allowed to cool to room temperature. The precipitate was filtered and washed with pentane.
Yield: 0.564 g (66%). ¹H NMR (300 MHz, C₆D₆, δ, ppm): 7.23 (s, ArH, 2H), 7.05 (m, ArH, 10H), 6.49 (s, ArH, 2H), 4.10-3.52 (br, ArCH₂ and ArCH₂N, 6H), 2.50 (m, AdH, 14H), 2.34 (s, ArCH₃, 6H), ¹³C{¹H} NMR (75 MHz, C₆D₆, δ, ppm): 157.5, 140.0, 132.8, 129.7, 129.2, 129.1, 120.9, 41.2, 38.1, 37.9, 30.4, 21.5 ppm. Anal. For C₅₃H₄₅AlN₂O₂ Calcd.: C, 80.67; H, 8.30; N, 3.55. Found: C, 80.52; H, 8.13; N, 3.48.

General conditions for the living ROP of cyclic esters: An example of a typical polymerization procedure is as follows: In a nitrogen filled glovebox, 2 (0.0366g, 0.0546 mmol) and benzyl alcohol (6.0 μL, 0.055 mmol) were dissolved in toluene (3 mL) and allowed to stir for 5 minutes. This was followed by the addition of rac-β-BL (0.500g, 5.46 mmol). The ampoule was sealed, removed from the glovebox and heated at 70°C for 6 h. The ampoule was cooled to room temperature and methanol (0.5 mL) was added, and the solution was left to stir for 30 minutes at ambient temperature. The solution was then precipitated into cold methanol (100 mL). The white precipitate was filtered and dried under vacuum to constant weight.

General conditions for the immortal ROP of cyclic esters: An example of a typical polymerization procedure is as follows: In a nitrogen filled glovebox, 2 (0.0084 g, 0.0138 mmol) and benzyl alcohol (7.5 μL, 0.069 mmol) were dissolved in toluene (3 mL) and allowed to stir for 5 minutes. This was followed by the addition of rac-lactide (1.00 g, 6.94 mmol). The ampoule was sealed, removed from the glovebox and heated at 70°C for 24 h. The ampoule was cooled to room temperature, a crude sample was removed for ¹H NMR spectroscopic analysis and 1% conc. HCl/methanol solution (v/v, 0.5 mL) was added. The solution was then precipitated into cold methanol (100 mL). The white precipitate was filtered and dried under vacuum to constant weight.

General conditions for the copolymerization of rac-β-BL and rac-lactide: An example of a typical polymerization procedure is as follows: In a nitrogen filled glovebox, rac-lactide (0.500 g, 3.46 mmol), rac-β-BL (0.299 g, 3.46 mmol), 2 (0.0219 g, 0.0346 mmol) and benzyl alcohol (3.6 μL, 0.035 mmol) were added to an ampoule. The ampoule was sealed, removed from the glovebox and heated at 120°C for 6 h. The ampoule was cooled to room temperature and the residue was dissolved in a 10:1 mixture of CH₂Cl₂:MeOH. After stirring for 30 minutes at ambient temperature, a sample was removed for ¹H NMR spectroscopic analysis. The solution was then precipitated into cold methanol (100 mL). The precipitate was filtered and dried under vacuum to constant weight.

Results and Discussion

Al-salen complex 1 and Al-salan complex 2 were chosen as the representative complexes to be examined in this study (Scheme 1) due to their ease of synthesis and their ability to mediate the ROP of rac-lactide with great control over PDIs and high polymer tacticity. Moreover, we synthesized novel Al-salen and salan complexes with methyl and adamantyl substitutions on the phenolate rings that were inspired by other ortho-
substituted adamantyl phenoxide ligands (Scheme 1). Treatment of 3 and 4 with trimethylaluminum in toluene at 110°C for 24 h allowed access to pure 5 and 6 in moderate isolated yields due to the high solubility of the complexes in a variety of solvents. Single crystals of 5 were grown by slow evaporation of a concentrated solution of 5 in toluene (Figure 1). The Al centre exists in a distorted square pyramidal coordination environment, evident by the O(1)-Al(1)-O(2), N(1)-Al-N(2), O(1)-Al(1)-C(1) and N(1)-Al(1)-C(1) angles of 94.54(4), 76.50(5), 117.58(6) and 93.04(6) respectively. This system’s bond lengths and angles are comparable to other sterically hindered Al-based salen systems.

Scheme 1. Al-salen (1) and salan (2) complexes previously employed in the ROP of rac-lactide including the synthesis of complexes 5 and 6 through ligands 3 and 4.
The ability of complexes 5 and 6 ability to mediate the living ROP of rac-lactide was examined at 70°C in toluene to compare to similar systems. These ligand frameworks represent a modest change in steric bulk and electronics due to the decreased bite-angle of the ligand when comparing salen complexes 1 and 5, but a significant change in both steric and electronics when comparing 6 to 2. It has been shown that bulky dialkyl substituted Al-salan complexes exhibited poor activity in the ROP of rac-lactide, and thus a similar trend was expected. This was confirmed as only trace amounts of PLA oligomers were isolated after 24 h at 70°C in toluene using 6 (Table 1, Entry 4). In contrast, 5 was effective in mediating the living ROP of rac-lactide (Table 1, Entries 1-3). Experimental molecular weights correlated well with theoretical values and narrow PDIs were obtained. H{H} NMR spectra of the resulting PLA showed 88% isotactic enchainment of lactide monomer (Figure S1), the highest isospecificity reported for salen complexes with an ethylene bridge. Furthermore, increasing the [M]/[Al] ratio produced the corresponding PLA of higher molecular weight (Figure S2). Previous reports have shown that Al-salen complexes may mediate the ROP of rac-lactide by an “immortal” mechanism through the addition of excess alcohol to serve as a chain-transfer agent. This immortal mechanism was first proposed by Inoue et al. using Al-porphyrin systems for epoxides and β-lactones. While several different systems have been shown to operate quite efficiently under this immortal mechanism, Al-salen and salan systems operating under an immortal mechanism have not been fully studied with regards to the upper limits of monomer and catalyst loadings before control over the polymerization was lost. To this end, Al-salen and salan systems 1, 2 and 5 were further examined in depth as mediators of immortal ROP of rac-lactide (Table 1).

Table 1. Ring-opening polymerization of rac-lactide utilizing 5 and 6.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>[M]:[Al]:[BnOH]</th>
<th>Time (h)</th>
<th>Mn</th>
<th>Mn,th</th>
<th>PDI</th>
<th>% Conv.</th>
<th>Pm/Pf</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>100:1:1</td>
<td>12</td>
<td>6100</td>
<td>7000</td>
<td>1.07</td>
<td>49</td>
<td>0.88 (m)</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>250:1:1</td>
<td>18</td>
<td>26200</td>
<td>28200</td>
<td>1.04</td>
<td>78</td>
<td>0.89 (m)</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>500:1:1</td>
<td>24</td>
<td>33600</td>
<td>40400</td>
<td>1.04</td>
<td>56</td>
<td>0.88 (m)</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>100:1:1</td>
<td>24</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>&lt;5</td>
<td>---</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>500:1:2</td>
<td>24</td>
<td>28300</td>
<td>31200</td>
<td>1.14</td>
<td>87</td>
<td>---</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>500:1:5</td>
<td>24</td>
<td>15600</td>
<td>14400</td>
<td>1.20</td>
<td>99</td>
<td>---</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>500:1:10</td>
<td>24</td>
<td>7400</td>
<td>6900</td>
<td>1.16</td>
<td>94</td>
<td>---</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>1000:1:10</td>
<td>24</td>
<td>17900</td>
<td>12400</td>
<td>1.06</td>
<td>85</td>
<td>0.86 (m)</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>500:1:2</td>
<td>24</td>
<td>11400</td>
<td>15600</td>
<td>1.03</td>
<td>43</td>
<td>---</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>500:1:5</td>
<td>24</td>
<td>3800</td>
<td>4600</td>
<td>1.04</td>
<td>31</td>
<td>---</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>500:1:10</td>
<td>24</td>
<td>2900</td>
<td>2900</td>
<td>1.05</td>
<td>39</td>
<td>---</td>
</tr>
<tr>
<td>12</td>
<td>2</td>
<td>1000:1:10</td>
<td>24</td>
<td>7300</td>
<td>8100</td>
<td>1.03</td>
<td>56</td>
<td>0.76 (r)</td>
</tr>
<tr>
<td>13</td>
<td>5</td>
<td>500:1:2</td>
<td>24</td>
<td>20100</td>
<td>30400</td>
<td>1.09</td>
<td>84</td>
<td>---</td>
</tr>
<tr>
<td>14</td>
<td>5</td>
<td>500:1:5</td>
<td>24</td>
<td>7300</td>
<td>12400</td>
<td>1.02</td>
<td>86</td>
<td>---</td>
</tr>
<tr>
<td>15</td>
<td>5</td>
<td>500:1:10</td>
<td>24</td>
<td>5000</td>
<td>6900</td>
<td>1.07</td>
<td>95</td>
<td>---</td>
</tr>
<tr>
<td>16</td>
<td>5</td>
<td>1000:1:10</td>
<td>24</td>
<td>4800</td>
<td>5700</td>
<td>1.07</td>
<td>39</td>
<td>0.88 (m)</td>
</tr>
</tbody>
</table>

*Polymerizations were conducted in 3 mL of toluene and 0.058 mmol of Al complex at 70°C using benzyl alcohol to generate the active alkoxide and function as the chain transfer agent where applicable. Calculated
by SEC(GPC) using polystyrene standards with a conversion factor of 0.58 for PLA. Calculated by $([M]/[Al]) \times MW(\text{monomer}) \times (% \text{ conv.}) + MW(\text{endgroup})$. Determined by gravimetric analysis after drying under vacuum to constant weight. Probability of a meso or racemic linkage determined by examination of the methine region of selective $^1H\{^1H\}$ NMR spectra.

In the immortal ROP of rac-lactide mediated by 1, 2 and 5 using benzyl alcohol as the chain transfer agent, experimental molecular weights agreed well with theoretical molecular weights when the ratio of benzyl alcohol was increased from 2 to 10 with respect to a constant [M]/[Al] ratio of 500. Moderate conversion was observed in 2, while 1 and 5 showed much higher conversion after 24 hours at 70°C in 3 mL of toluene. No significant loss of control was observed, as shown by the lack of broadening in PDIs. Increasing the initial monomer feed to 1000 relative to a 10:1 ratio of benzyl alcohol:complex to test the behavior of the system at higher loadings resulted in well controlled behavior, a similar observation for a related aluminum-based salen complex under these conditions. A slight decrease in tacticity was observed for each of the Al-salen complexes 1 and 5, but a more significant decrease was observed for Al-salan complex 2 where a $P_r$ of 0.94 was measured for living conditions. It was observed that after 1000 mol equivalents of monomer were added to the initial polymerization mixture that no polymerization was observed upon workup, likely due to the high concentration of monomer coordinating to the aluminum center which would effectively render the complex inactive. Thus up to these loadings, benzyl alcohol serves as an excellent chain transfer agent for this system, and supports previously mentioned reports that these systems would serve as effective complexes in immortal ROP of rac-lactide.

While Al-based salen complexes have not previously been employed in the ROP of rac-β-BL, bis-Al-salen complexes have been utilized, and have generally shown that ROP of rac-β-BL only produced low molecular weight oligomers even after prolonged polymerization times. Contrasting these reports, we have found that Al-salen and salan complexes 1, 2 and 5 are excellent catalysts for the ROP of rac-β-BL. Narrow PDIs <1.15 were observed for 1 and 5, but while calculated molecular weights correlated well to theoretical molecular weights for 1, increasing the [M]/[Al] for 5 did not produce PHB of the corresponding increased molecular weight (Table 2, Entries 15 and 16). The control over molecular weight and PDIs for 1 and 2 was greater than for similar aluminum “half” salen complexes. When 2 was utilized for ROP of rac-β-BL narrow PDIs of <1.05 were observed, and an increase in [M]/[Al] gave PHB of the corresponding increased molecular weight (Table 2). While polymerizations mediated by 1 at 120°C were marked by faster rates and a significant increase in PDI, identical conditions when employing 2 displayed no loss of control (Table 2). Upon investigation of the methylene and the carbonyl region in $^{13}C\{^1H\}$ NMR spectra of the isolated PHB, confirmed no stereocontrol was observed regardless of solvent or temperature, 1, 2 and 5 produce solely atactic PHB. A living polymerization character was observed for 1, 2 and 5 through kinetic experiments obtained via $^1H$ NMR spectroscopy at 70°C in benzene-$d_6$. Pseudo-first order reaction kinetics with respect to
monomer were observed in plots of $\ln([M_0]/[M])$ versus time, however, a slight delay of approximately 15 minutes was introduced due to the time required to heat the polymerization to 70°C prior to the collection of spectra. Additionally, a plot of $M_n$ versus percent conversion revealed a linear relationship with excellent agreement between measured and theoretical values (Figure 2, S3 and S4). Signals in the $^1$H NMR spectrum corresponding to a benzyl ester endgroup were observed at 5.2 ppm for each of the complexes, with no evidence of carboxyl or crotonate endgroups. These results suggest that the ROP of rac-$\beta$-BL by 1, 2 and 5 proceeded by a standard coordination-insertion mechanism with 2 exhibiting the greatest reported control over molecular weight and PDIs shown by an Al-based complex for living ROP of rac-$\beta$-BL.

Table 2. Polymerization of rac-$\beta$-BL.$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>[M]/[Al]</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>$M_n^b$</th>
<th>$M_{n,th}^c$</th>
<th>PDI$^b$</th>
<th>% conv.$^{d,e}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>100</td>
<td>Neat</td>
<td>70</td>
<td>3</td>
<td>5900</td>
<td>5100</td>
<td>1.08</td>
<td>58</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>100</td>
<td>Toluene</td>
<td>70</td>
<td>6</td>
<td>5100</td>
<td>5100</td>
<td>1.06</td>
<td>58</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>100</td>
<td>Toluene</td>
<td>120</td>
<td>6</td>
<td>7400</td>
<td>7100</td>
<td>1.35</td>
<td>82</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>250</td>
<td>Toluene</td>
<td>70</td>
<td>18</td>
<td>16600</td>
<td>20300</td>
<td>1.14</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>500</td>
<td>Toluene</td>
<td>70</td>
<td>36</td>
<td>25800</td>
<td>35400</td>
<td>1.09</td>
<td>82</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>100</td>
<td>Neat</td>
<td>25</td>
<td>24</td>
<td>6200</td>
<td>6400</td>
<td>1.03</td>
<td>73</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>100</td>
<td>Toluene</td>
<td>25</td>
<td>48</td>
<td>6400</td>
<td>4800</td>
<td>1.03</td>
<td>58</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>100</td>
<td>THF</td>
<td>25</td>
<td>48</td>
<td>6400</td>
<td>6600</td>
<td>1.03</td>
<td>75</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>100</td>
<td>Neat</td>
<td>70</td>
<td>3</td>
<td>6100</td>
<td>6300</td>
<td>1.04</td>
<td>72</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>100</td>
<td>Toluene</td>
<td>70</td>
<td>6</td>
<td>8600</td>
<td>8600</td>
<td>1.03</td>
<td>99</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>100</td>
<td>THF</td>
<td>70</td>
<td>6</td>
<td>8200</td>
<td>7800</td>
<td>1.03</td>
<td>89</td>
</tr>
<tr>
<td>12</td>
<td>2</td>
<td>100</td>
<td>Toluene</td>
<td>120</td>
<td>2</td>
<td>7400</td>
<td>8300</td>
<td>1.05</td>
<td>94</td>
</tr>
<tr>
<td>13</td>
<td>2</td>
<td>250</td>
<td>Toluene</td>
<td>70</td>
<td>10</td>
<td>19600</td>
<td>17500</td>
<td>1.03</td>
<td>81</td>
</tr>
<tr>
<td>14</td>
<td>2</td>
<td>500</td>
<td>Toluene</td>
<td>70</td>
<td>20</td>
<td>35700</td>
<td>38800</td>
<td>1.04</td>
<td>90</td>
</tr>
<tr>
<td>15</td>
<td>5</td>
<td>100</td>
<td>Toluene</td>
<td>70</td>
<td>12</td>
<td>2400</td>
<td>3600</td>
<td>1.05</td>
<td>28</td>
</tr>
<tr>
<td>16</td>
<td>5</td>
<td>250</td>
<td>Toluene</td>
<td>70</td>
<td>18</td>
<td>8800</td>
<td>4900</td>
<td>1.04</td>
<td>41</td>
</tr>
</tbody>
</table>

$^a$ Polymerizations were conducted with 0.058 mmol of Al complex in 3 mL of solvent where applicable using benzyl alcohol to generate the active alkoxide. $^b$ Calculated by SEC(GPC) using polystyrene standards with a conversion factor of 0.68 for PHB.$^{26}$ $^c$ Calculated by $([M]/[Al]) \times MW(rac-\beta$-BL) $\times$ (% conv.) + MW(endgroup). $^d$ All PHB isolated possessed an atactic microstructure confirmed by $^{13}$C {$^1$H} NMR spectroscopy. $^e$ Determined by gravimetric analysis after drying under vacuum to constant weight.
Figure 2. Plot of $\ln([M_i]/[M_f])$ vs time (min) (top) and $M_n$ vs percent conversion (bottom) (solid line = $M_{n,th}$) for ROP of rac-$\beta$-BL by 2 at 70°C in benzene-$d_6$ with [M]/[Al] = 100.

Following our study using 1, 2 and 5 for living ROP of rac-$\beta$-BL, we sought to investigate the versatility of these complexes by introducing an excess of benzyl alcohol, and entering an immortal ROP mechanism. Experimental molecular weights agreed with theoretical molecular weights when the ratio of benzyl alcohol was increased from 2 to 50 with respect to a constant [M]/[Al] ratio of 500 for 1 and 2 (Table 3). Monomer conversion of >80% was observed after 24 hours at 70°C in toluene. No significant loss of control was observed in comparison to polymerizations conducted under living conditions, as shown by the lack of broadening in PDIs. Thus, benzyl alcohol serves as an efficient chain transfer agent for this system at these loadings. However, when the monomer loading was increased to 1000 mol eq., no polymerization was observed due to similar reasons mentioned in the immortal ROP of rac-lactide. 1 gave similar control to 2 in the immortal ROP of rac-$\beta$-BL with PDIs of <1.09, but was significantly slower to reach comparable conversion of monomer. Additionally, a plot of molecular weight versus [rac-$\beta$-BL]/[BnOH] ratio showed a linear increase with a slope that correlated well to the molecular weight of the monomer at lower ratios of [rac-$\beta$-BL]/[BnOH], with some deviation observed at higher ratios (Figure 3 and S5). Slight deviation was when 1 was employed compared to 2. These results represent the greatest control and highest ratio of chain-transfer agent:complex achieved in an immortal type ROP of rac-$\beta$-BL with an Al-based complex. 27,28
Table 3. Immortal ring opening polymerization of rac-β-BL by 1 and 2.a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>[M]:[Al]:[BnOH]</th>
<th>(M_n)</th>
<th>(M_{nth}^c)</th>
<th>PDI</th>
<th>% conv.d</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>500:1:2</td>
<td>8100</td>
<td>8700</td>
<td>1.07</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>500:1:5</td>
<td>4540</td>
<td>6000</td>
<td>1.06</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>500:1:10</td>
<td>2100</td>
<td>2500</td>
<td>1.08</td>
<td>57</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>500:1:25</td>
<td>1100</td>
<td>1400</td>
<td>1.07</td>
<td>75</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>500:1:35</td>
<td>800</td>
<td>700</td>
<td>1.09</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>500:1:50</td>
<td>900</td>
<td>600</td>
<td>1.08</td>
<td>61</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>500:1:2</td>
<td>16300</td>
<td>19800</td>
<td>1.05</td>
<td>92</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>500:1:5</td>
<td>7500</td>
<td>7400</td>
<td>1.03</td>
<td>85</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>500:1:10</td>
<td>3200</td>
<td>3600</td>
<td>1.11</td>
<td>82</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>500:1:25</td>
<td>1600</td>
<td>1500</td>
<td>1.08</td>
<td>84</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>500:1:35</td>
<td>1200</td>
<td>1300</td>
<td>1.05</td>
<td>98</td>
</tr>
<tr>
<td>12</td>
<td>2</td>
<td>500:1:50</td>
<td>800</td>
<td>1000</td>
<td>1.10</td>
<td>98</td>
</tr>
<tr>
<td>13</td>
<td>2</td>
<td>1000:1:50</td>
<td>1500</td>
<td>1800</td>
<td>1.04</td>
<td>99</td>
</tr>
<tr>
<td>14</td>
<td>5</td>
<td>500:1:2</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>&lt; 5</td>
</tr>
</tbody>
</table>

a All polymerizations were conducted with 0.058 mmol of Al complex in 3 mL of toluene at 70°C for 24 h using benzyl alcohol to generate the active alkoxide and function as the chain transfer agent. b Determined by SEC (GPC) using polystyrene standards with a conversion factor of 0.68 for PHB and 0.58 for PLA. c Calculated by ([M]/[Al]) \(\times\) MW(monomer) \(\times\) (% conv.) + MW(endgroup). d Determined by gravimetric analysis after drying under vacuum to constant weight.

Figure 3. Plot of \(M_n\) vs \([rac-β-BL]/[BnOH]\) for immortal ROP of rac-β-BL at 70°C in toluene utilizing 2.

Ratios of \([rac-β-BL]/[BnOH]\) were corrected based upon the percent conversion of monomer. Deviation from ideal monomer molecular weight attributed to the data being collected over a significantly large range of chain-transfer agent loadings along with the high monomer loading.

While aluminum salen\textsuperscript{12,23,29-31} and salan\textsuperscript{32} complexes had been previously employed in both homo and copolymerizations of ε-caprolactone, the complexes employed in this study had not been utilized in polymerizations of this monomer. When the ROP of ε-caprolactone was attempted using complexes 1, 2 and
5, they were unable to provide a significant degree of control over the molecular weight of the PCL, and exhibited substantially broadened PDIs (Table S1). Manipulation of the monomer concentration, temperature or solvent did not produce any noteworthy improvement in control over the molecular weight or PDI for any of the complexes. It was also observed that the polymerizations progressed at a surprisingly slow rate given the higher reactivity of ε-caprolactone monomer.

With optimized protocols for the living and immortal ROP of rac-β-BL and rac-lactide, we surveyed the copolymerization of these monomers to establish if controlled copolymerization could be achieved. As a comparator, Sn(Oct)$_2$, well known for its use in the production of high molecular weight PLA on an industrial scale, was used as the initial probe for the copolymerization of rac-lactide and rac-β-BL to serve as an additional benchmark to our studies utilizing the Al-salen and salan complexes. With Sn(Oct)$_2$, only atactic PLA was isolated until polymerizations conducted at 120°C in neat monomer were employed. In this case, an atactic-PLA-co-atactic-PHB polymer was isolated with a high PDI of approximately 1.8. Using conditions of 70°C in benzene-$d_6$, no polymerization was observed as monitored by $^1$H NMR spectroscopy. Polymerizations were then conducted in neat monomer at 120°C and showed that 1, 2 and 5 produce poly(rac-LA-co-rac-β-BL) copolymers. Poor control was observed using 1 and 5 as evidenced by the broad PDIs of > 1.5 comparable to previous reports mentioned regarding tin, magnesium, group 4 and aluminum complexes. However, utilizing the Al-salan complex 2 in the copolymerization gave excellent control and narrow PDIs (Table 4).

**Table 4.** Copolymerization of rac-β-BL and rac-lactide by 2.$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>[LA]:[β-BL]</th>
<th>PLA:PHB$^b$</th>
<th>$M_n$$^c$</th>
<th>$M_{n,th}$$^d$</th>
<th>PDI$^e$</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:1 (100:100)</td>
<td>3.5:1</td>
<td>20100</td>
<td>14900</td>
<td>1.09</td>
<td>32.0</td>
</tr>
<tr>
<td>2</td>
<td>2:1 (100:50)</td>
<td>9:1</td>
<td>29400</td>
<td>16700</td>
<td>1.05</td>
<td>43.6</td>
</tr>
<tr>
<td>3</td>
<td>4:1 (200:50)</td>
<td>19:1</td>
<td>18900</td>
<td>27000</td>
<td>1.07</td>
<td>35.5</td>
</tr>
<tr>
<td>4</td>
<td>6:1 (300:50)</td>
<td>39:1</td>
<td>29400</td>
<td>23000</td>
<td>1.07</td>
<td>39.3</td>
</tr>
<tr>
<td>5</td>
<td>1:2 (50:100)</td>
<td>1:1</td>
<td>15800</td>
<td>13600</td>
<td>1.07</td>
<td>17.7</td>
</tr>
<tr>
<td>6</td>
<td>1:4 (50:200)</td>
<td>1:1.6</td>
<td>17100</td>
<td>23900</td>
<td>1.07</td>
<td>13.6</td>
</tr>
<tr>
<td>7</td>
<td>1:6 (50:300)</td>
<td>1:2</td>
<td>14600</td>
<td>17300</td>
<td>1.05</td>
<td>11.4</td>
</tr>
</tbody>
</table>

$^a$ Polymerizations were conducted neat at 120°C and with 0.035 mmol of Al complex using benzyl alcohol to generate the active alkoxide.$^9$ Calculated by $^1$H NMR by integration of methyl signals associated with each polymer unit.$^5$ Calculated by ($[M]/[Al] \times MW(rac-β-BL) \times (\% \text{ conv.}) + ([M]/[Al] \times MW(rac-lactide) \times (\% \text{ conv.}) + MW(endgroups))$. $^d$ Calculated by SEC(GPC) / MALS in THF at 50°C.

Further study of the copolymerization was carried out by manipulation of the initial polymerization feed ratios of rac-β-BL and rac-lactide. From an initial feed ratio of 100:100 (1:1), near complete conversion of rac-
lactide was observed while rac-β-BL conversion was significantly lower. After precipitation, the resulting copolymer possessed a 3.5:1 ratio of PLA:PHB as observed by $^1$H NMR spectroscopy. Moreover, signals typical of highly heterotactic PLA were observed indicating the presence of long sequences of PLA in the copolymer. Further increasing the excess of rac-lactide in the initial feed of the polymerization to 300:50 (6:1) resulted in a copolymer possessing a 39:1 PLA:PHB ratio after precipitation. Again, in this case, a strong presence of heterotactic PLA was observed. Increasing the excess of rac-β-BL to 200:50 (4:1) saw a loss of the long PLA sequences, as evidenced by the greater representation of PHB in the copolymer (1:1.2) and the loss of characteristic signals in the $^1$H NMR spectrum for heterotactic PLA (Figure S6). A further excess of 300:50 (6:1) rac-β-BL saw a 1:2 ratio of PLA:PHB in the copolymer after precipitation. Examination of the filtrates in each of the polymerization by $^1$H NMR spectroscopy showed no evidence of any PLA or PHB homopolymers, and therefore some inconsistencies in rac-β-BL conversion in comparison to the $M_n$ of PHB observed in the copolymer were attributed to potential decomposition of the monomer under these harsh conditions. $^1$H NMR kinetic experiments were conducted to monitor the formation of PHB and PLA in toluene-$d_8$ at 85°C when the copolymerization was mediated by 2 and 5 (Figure 4). The results show that there is a faster rate of rac-lactide insertion with respect to the rate of insertion for rac-β-BL. A slight induction period was observed for the ROP of rac-lactide in this case, as all of the lactide monomer was not dissolved until t = 30 minutes, and in conjunction with a 15 minute time from monomer addition to the collection of the first $^1$H NMR spectrum, gave rise to the non-zero intercepts of each of the linear regressions. These results support that in the copolymerization of rac-β-BL and rac-lactide there is a preference for incorporation of the rac-lactide monomer rather than rac-β-BL, even when the rate of homopolymerization of rac-β-BL is greater than that for rac-lactide.

![Figure 4](image)

**Figure 4.** Plots of ln([M]₀/[M]ₜ) vs time (min) for the copolymerization of rac-β-BL and rac-lactide by 2 (left) and 5 (right) at 85°C in toluene-$d_8$ with [rac-β-BL]:[rac-lactide]:[Al] of 50:50:1.

Analysis of the phase transitions of these materials by differential scanning calorimetry (DSC) showed no phase separation between PLA and PHB segments of the copolymers even with the presence of lengthy
heterotactic PLA segments. The DSC thermograms show only a single glass transition temperature was observed by DSC ranging from 11.4°C for a poly(rac-LA-co-rac-β-BL) copolymer containing a 2:1 ratio of PHB:PLA to 43.6°C for a poly(rac-LA-co-rac-β-BL) copolymer containing 1:9 PHB:PLA. As expected, increased PLA content of the resulting copolymer increases the $T_g$ while increased PHB content lowers the $T_g$. No melting or crystallization temperature was visible in any of the copolymer samples, confirming that each of the copolymers were amorphous in nature.

**Conclusions**

We have shown that aluminum-based salen and salan complexes can efficiently mediate the immortal ROP of rac-lactide up to 10 mol equivalents of benzyl alcohol chain transfer agent and up to 1000 mol equivalents of monomer before control is lost. Moreover, we have shown that these complexes are also able to form high molecular weight PHB by the ROP of rac-β-BL, where previous reports of the ROP of rac-β-BL aluminum salen complexes were only able to access low molecular weight oligomers. The aluminum salan complexes demonstrated particular efficacy at controlling the ROP of rac-β-BL under a variety of polymerization conditions. Each of the complexes operated under the expected living coordination-insertion mechanism. The complexes also facilitated the immortal ROP of rac-β-BL up to an excess of 50 mol equivalents of benzyl alcohol before the system became less behaved. When employed in the copolymerization of rac-lactide and rac-β-BL, the aluminum salen complexes were unable to provide control under the thermally demanding conditions, the aluminum salan complex allowed access to gradient poly(rac-LA-co-rac-β-BL) copolymers where a narrow polydispersities of $< 1.1$ was achieved – an unprecedented result that to the best of our knowledge. The copolymer composition strongly favoured the insertion of rac-lactide over rac-β-BL as previously observed in the literature, with long segments of PLA formed until a 4:1 excess of rac-β-BL:rac-lactide was present in the initial monomer feed. The initial thermal studies of these materials showed a single $T_g$, indicating that no phase separation was occurring between the segments of PLA and PHB.
References


