Aluminum Salen and Salan Complexes in the Ring-Opening Polymerization of Cyclic Esters: Controlled Immortal and Copolymerization of *rac*-β-Butyrolactone and *rac*-Lactide

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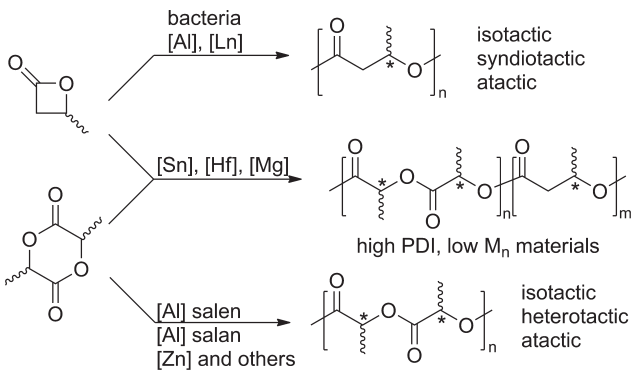
ABSTRACT: Aluminum-based salen and salan complexes mediate the ring-opening polymerization (ROP) of *rac*-β-butyrolactone (β-BL), *rac*-lactide, and ε-caprolactone. Al-salen and Al-salan complexes exhibit excellent control over the ROP of *rac*-β-butyrolactone, yielding atactic poly(3-hydroxybutyrate) (PHB) with narrow PDIs of <1.15 for Al-salen and <1.05 for Al-salan. Kinetic studies reveal pseudo-first-order polymerization kinetics and a linear relationship between molecular weight and percent conversion. These complexes also mediate the immortal ROP of *rac*-β-BL and *rac*-lactide, through the addition of excess benzyl alcohol of up to 50 mol eq., with excellent control observed. A novel methyl/adamantyl-substituted Al-salen system further improves control over the ROP of *rac*-lactide and *rac*-β-BL, yielding atactic PHB and highly isotactic poly(lactic acid) ($P_m = 0.88$). Control over the copolymerization of *rac*-lactide and *rac*-β-BL was also achieved, yielding poly(lactic acid)-*co*-poly(3-hydroxybutyrate) with narrow PDIs of <1.10. ^{1}H NMR spectra of the copolymers indicate a strong bias for the insertion of *rac*-lactide over *rac*-β-BL. © 2012 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 1137–1146

KEYWORDS: biodegradable; copolymerization; ring-opening polymerization; *rac*-β-butyrolactone; *rac*-lactide

INTRODUCTION Interest in the development of biodegradable polyesters, in particular poly(lactic acid) (PLA), poly(glycolic acid), poly(ε-caprolactone) (PCL), and their copolymers, has continued to increase,[1–4] finding application in nanotechnology, thermoplastic, commodity, and biomedical industries.[5–8] Although these polymers remain at the forefront of research efforts in this field, other classes of biodegradable polyesters such as the poly(hydroxyalkanoate)s have begun to attract greater focus in the past decade.[9] Poly(3-hydroxybutyrate) (PHB) has been of particular interest as it is produced with high isotactic stereoregularity by bacteria, resulting in 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.[10] Alternatively, ring-opening polymerization (ROP) of β-butyrolactone (β-BL) using metal-based initiators has provided an additional route to this biodegradable polyester,[11] allowing access to PHB with predictable molecular weights, narrow polydispersity indecies (PDIs), and different stereoregularity to the isotactic bacterial PHB. Although rare-earth complexes have been shown to be proficient at mediating the stereoselective ROP of *rac*-β-BL,[12] and some studies on group 4,[13] Sn,[14–18] and Cr[19] systems have been reported, aluminum complexes that can polymerize this monomer in a controlled and stereoregular manner have remained relatively unexplored.[20]

Although homopolymerizations of these monomers remain important, access to novel biodegradable materials can be achieved by the copolymerization of two or more judiciously chosen monomers, targeting a material with unique properties. In particular, complexes that effectively mediate the ROP of both *rac*-β-BL and *rac*-lactide, and are effective in the copolymerization of these monomers, remain scarce (Scheme 1). It has been reported that tin alkoxides copolymerize (*R*)-β-BL and L-lactide, producing poly((*R*)-3-hydroxybutyrate)-*co*-poly (L-lactic acid) where the incidence of PHB and PLA in the copolymer correlated well with the initial monomer feed ratio.[21] However, these copolymers possessed substantially broadened PDIs of >1.7. The copolymerization of *rac*-β-BL and L-lactide mediated by dibutylmagnesium produced similar results, with good correlation between the ratio of monomers in the feed and the composition of the resulting

Additional Supporting Information may be found in the online version of this article.



SCHEME 1 Biodegradable polyester materials.

copolymer and PDIs of >1.6.[22] Hafnium amine-*tris*(phenolate) complexes also successfully copolymerized *rac*-β-BL and *rac*-lactide, again with broad PDIs of >1.6. The authors also noted that the rate of insertion of *rac*-β-BL into the copolymer was significantly slower than that observed for *rac*-lactide when the polymerization was monitored by ^{1}H NMR spectroscopy,[13] producing a copolymer composed of two distinct blocks rather than the expected random or gradient copolymer. Narrow PDIs (<1.1) were obtained only when using sequential addition of *rac*-β-BL followed by *rac*-lactide. In terms of group 3 complexes, it was demonstrated that an aluminum half-salen complex that had similar observed rates in *rac*-β-BL and *rac*-lactide ROP at 90 °C in toluene was unsuccessful at mediating the copolymerization. There was no incorporation of *rac*-β-BL during the copolymerization with only PLA formed, even after extended polymerization times.[23]

For this study, we used aluminum-based salen (salen = *N*,*N*′-*bis*(salicylaldimine)-1,2-ethylenediamine) and salan (salan = *N*,*N*′-*bis*(*o*-hydroxybenzyl)-1,2-diaminoethane) complexes **1** and **2** (Fig. 1),[24,25] known to produce well-controlled PLA with narrow PDIs,[24,26–30] and explored their ability to mediate the ROP of *rac*-β-BL. We then used these tetradentate salen and salan aluminum complexes in the copolymerization of *rac*-β-BL and *rac*-lactide, comparing their activity to previously reported systems and targeting poly(lactic acid)-*co*-poly(3-hydroxybutyrate) materials of controlled molecular weights and narrow polydispersities. We also wished to investigate whether these aluminum systems display a preference for the insertion of *rac*-lactide over *rac*-β-BL, in the hopes of generating gradient materials.

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*′-dibenzylethylenediamine (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 three 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 Laboratories, were dried over calcium hydride at reflux overnight prior to vacuum transfer, and were degassed by three 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 three freeze–pump–thaw cycles prior to use. PURASORB DL-lactide was obtained from PURAC Biochem by Gorinchem and sublimed three times under vacuum prior to use. ε-Caprolactone was dried over calcium hydride and distilled under inert atmosphere prior to use. Complexes **1**[24,31] and **2**[25] as well as 3-adamantyl-2-hydroxy-4-methylbenzaldehyde[15,16] were prepared according to literature procedures.

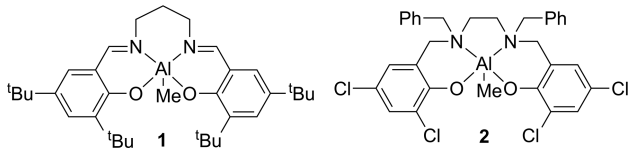


FIGURE 1 Al-salen complex **1** and Al-salan complex **2**, previously reported as efficient and stereoselective mediators for the ROP of *rac*-lactide.

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 three freeze–pump–thaw cycles prior to use. All air-sensitive manipulations were performed in an MBraun LABmaster sp glovebox or on a dual manifold vacuum line using standard Schlenk techniques. ^{1}H (300 MHz) and ^{13}C{^{1}H} NMR (75 MHz) spectra were collected on a Bruker Avance 300 spectrometer. Gel permeation chromatography (GPC) was performed on a Polymer Laboratories PL-GPC 50 Plus integrated GPC system with two 300 × 7.8 mm^2 Jordi Gel divinylbenzene mixed bed columns, using HPLC grade tetrahydrofuran (THF) at a flow rate of 1 mL min^{-1} at 50 °C, using a refractive index detector and poly (styrene) standards for molecular weight determinations, with conversion factors of 0.58 and 0.60 for PHB and PLA, respectively.[32] 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 d*n*/d*c* values for PLA and PHB of 0.050[17] and 0.065,[18] respectively. Differential scanning calorimetry (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 used.

Synthesis and Characterization of 3

3-Adamantyl-2-hydroxy-4-methylbenzaldehyde (0.87 g, 3.2 mmol) was dissolved in absolute ethanol (10 mL). To this solution, 1,2-diaminoethane (0.10 g, 1.6 mmol) was added, followed by several drops of formic acid before the mixture was heated to reflux, with a yellow precipitate observed after 30 min. After 4 h, 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: 0.66 g (73%).

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 13.67 (s, —O*H*, 2H), 8.34 (s, ArC*H*=N, 2H), 7.06 (s, Ar*H*, 2H), 6.88 (s, Ar*H*, 2H), 3.91 (s, N—CH_2CH_2—N, 4H), 2.17 (m, Ad*H* and ArCH_3, 30H), 1.80 (bs, Ad*H*, 15H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ, 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 $C_{38}H_{48}N_2O_2$ 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, 9.3 mmol) was dissolved in absolute ethanol (10 mL). To this solution, *N*,*N*′-dibenzyl-1,2-diaminoethane (1.12 g, 4.6 mmol) was added, followed by paraformaldehyde (0.96 g, 9.3 mmol) before the mixture was heated to reflux. After 18 h, heating was ceased and the mixture was allowed to cool to room temperature. A white precipitate formed and was filtered and washed with cold absolute ethanol. Yield: 2.45 g (35%).

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 10.36 (bs, —O*H*, 2H), 7.31 (m, Ar*H*, 10H), 6.92 (s, Ar*H*, 2H), 6.59 (s, Ar*H*, 2H), 3.61 (s, ArCH_2, 4H), 3.50 (s, PhCH_2N, 4H), 2.65 (s, ArCH_3, 6H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ, ppm): δ 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 $C_{52}H_{64}N_2O_2$ 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, **3** (0.90 g, 1.6 mmol) was dissolved in toluene (15 mL) and added to an oven-dried ampoule. With vigorous stirring, a 2.0 M solution of trimethylaluminum in heptane (0.55 g, 1.6 mmol) was added dropwise. Effervescence was observed, and the ampoule was sealed, removed from the glovebox, and heated to 110 °C. After 24 h, a yellow precipitate formed and the ampoule was allowed to cool to room temperature. The precipitate was filtered and washed with pentane. Yield: 0.41 g (43%).

^{1}H NMR (300 MHz, C_6D_6, δ, ppm): 7.33 (s, ArC*H*=N, 2H), 7.32 (s, Ar*H*, 2H), 6.60 (d, Ar*H*, 2H, J = 1.8 Hz), 2.93 (dd, N—CH_2CH$_2$—N, 2H, J = 6.3, 12.3 Hz), 2.51 (br, Ad*H* and N—CH$_2$CH_2—N, 14 H), 2.28 (s, ArCH_3, 6H) 2.18 (br, Ad*H*, 6H), 1.87 (bm, Ad*H*, 14H) −0.41 (s, AlCH_3, 3H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, δ, 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 $C_{39}H_{49}AlN_2O_2$ Calcd.: C, 77.45; H, 8.17; N, 4.63. Found: C, 77.27; H, 8.03; N, 4.39.

Synthesis and Characterization of 6

In a nitrogen filled glovebox, **4** (0.82 g, 1.1 mmol) was dissolved in toluene (15 mL) and added to an oven-dried ampoule. With vigorous stirring, a 2.0 M solution of trimethylaluminum in heptane (0.36 g, 1.1 mmol) was added dropwise. Effervescence was observed, and the ampoule was sealed, removed from the glovebox, and heated to 110 °C. After 24 h, a white precipitate formed and the ampoule was allowed to cool to room temperature. The precipitate was filtered and washed with pentane. Yield: 0.56 g (66%).

^{1}H NMR (300 MHz, C_6D_6, δ, ppm): 7.23 (s, Ar*H*, 2H), 7.05 (m, Ar*H*, 10H), 6.49 (s, Ar*H*, 2H), 4.10–3.52 (br, ArCH_2 and ArCH_2N, 6H), 2.50 (m, Ad*H*, 14H), 2.34 (s, ArCH_3, 6H), ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 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 $C_{53}H_{65}AlN_2O_2$ 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 living polymerization procedure is as follows: in a nitrogen filled glovebox, **2** (0.0366 g, 0.055 mmol) and benzyl alcohol (6.0 μL, 0.055 mmol) were dissolved in toluene (3 mL) and allowed to stir at ambient temperature for 5 min. This was followed by the addition of *rac*-β-BL (0.500 g, 5.46 mmol). The ampoule was sealed, removed from the glovebox, and heated at 70 °C for 6 h. The ampoule was then cooled to room temperature and methanol (0.5 mL) was added, and the solution was left to stir for 30 min at ambient temperature. The solution was then precipitated into cold methanol (100 mL) before the white precipitate was filtered and dried under vacuum to constant weight.

General Conditions for the Immortal ROP of Cyclic Esters

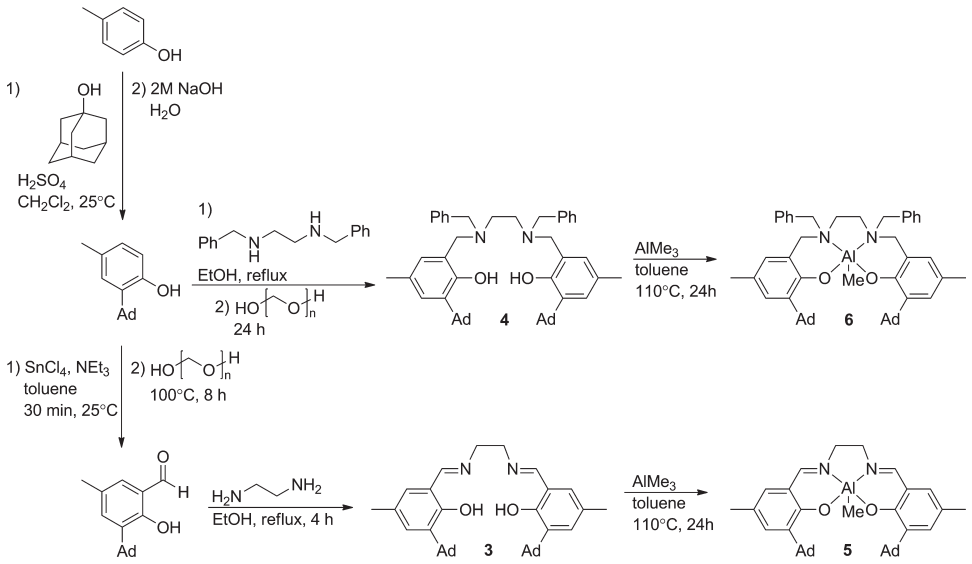
An example of a typical immortal polymerization procedure is as follows: in a nitrogen filled glovebox, **2** (0.0084 g, 0.014 mmol) and benzyl alcohol (7.5 μL, 0.069 mmol) were dissolved in toluene (3 mL) and allowed to stir for 5 min. This was followed by the addition of *rac*-lactide (1.00 g, 6.94 mmol). The ampoule was sealed, removed from the glovebox, and heated at 70 °C for 24 h. The ampoule was then cooled to room temperature, a crude sample was removed for ^{1}H NMR spectroscopic analysis and 0.5 mL of a solution comprising 1% conc. HCl in methanol (v/v) was added. The solution was then precipitated into cold methanol (100 mL) before 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 copolymerization 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, 0.035 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 then cooled to room temperature and the residue was dissolved in a 10:1 (v/v) mixture of CH_2Cl_2:MeOH. After stirring for 30 min at ambient temperature, a sample was removed for ^{1}H NMR spectroscopic analysis. The solution was then precipitated into cold methanol (100 mL) before the precipitate was filtered and dried under vacuum to constant weight.

RESULTS AND DISCUSSION

Al-salen complex **1** and Al-salan complex **2** (Fig. 1) were chosen as representative complexes to be used in this study due to their facile synthesis and ability to mediate the ROP of *rac*-lactide with both excellent control over molecular weights and PDIs and high polymer tacticity.[24,25] We extended this study by targeting novel Al-salen and Al-salan complexes with methyl and adamantyl substitutions on the phenolate rings (**5** and **6**, Scheme 2), inspired by other



SCHEME 2 Synthesis of novel adamantyl-substituted complexes **5** and **6** via ligands **3** and **4**.

ortho-substituted adamantyl phenoxide ligands,[33,34] anticipating that **5** would give us improved tacticity control. 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 (Fig. 2). The Al center 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. The bond lengths and angles for **5** are comparable to other sterically hindered Al-salen systems.[31]

The ability of complexes **5** and **6** to mediate the living ROP of *rac*-lactide was examined at 70 °C in toluene to allow comparison with 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**[31] and **5**, but a significant change in both sterics and electronics when comparing salan complexes **2**[25] and **6**. It has already been shown that bulky dialkyl-substituted Al-salan complexes exhibit poor activity in the ROP of *rac*-lactide,[25] and thus a similar trend was expected. This was confirmed, with only trace amounts of PLA oligomers 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 the theoretical values and narrow PDIs were obtained. $^1H\{^1H\}$ NMR spectra of the resultant PLA showed 88% isotactic enchainment of lactide monomer (Supporting Information Fig. S1), the highest isospecificity reported for a salen complex with an ethylene bridge. Furthermore, increasing the [M]/[Al] ratio produced PLA of correspondingly higher molecular weight (Supporting Information Fig. S2). Previous reports have shown that Al-salen complexes may also mediate the ROP of *rac*-lactide by an "immortal" mechanism through the addition of excess alcohol to serve as a chain-transfer agent.[35–38] This immortal mechanism was first proposed by Inoue and coworkers using Al-porphyrin systems for epoxides and β-lactones.[39] Although several different systems have been shown to operate quite efficiently via this immortal mechanism,[40] Al-salen and salan systems have not been fully studied with regard to the upper limits of monomer and catalyst loadings, maintaining control over the polymerization. To this end, Al-salen and salan systems **1**, **2**, and **5** were examined in depth as mediators of the immortal ROP of *rac*-lactide (Table 1, Entries 5–16).

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

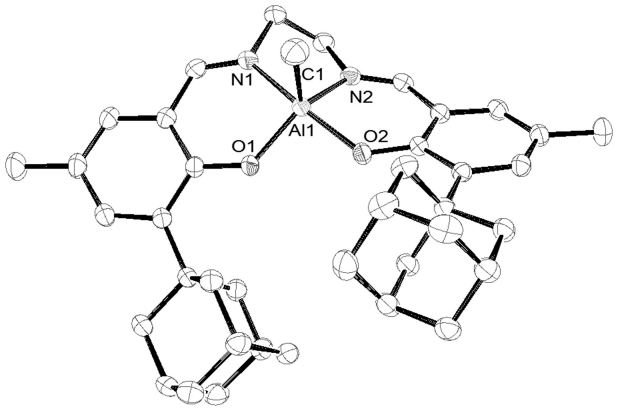


FIGURE 2 Molecular structure of **5** with thermal ellipsoids drawn at 50% probability and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) include: Al(1)—O(1), 1.8215(9); Al(1)—O(2), 1.8321(9); Al(1)—C(1), 1.9728(15); Al(1)—N(1), 2.0351(11); Al(1)—N(2), 2.0391(11); O(1)—Al(1)—O(2), 94.54(4); O(1)—Al(1)—C(1), 117.58(6); O(1)—Al(1)—N(1), 87.92(4); O(1)—Al(1)—N(2), 127.78(4).

TABLE 1 Living ROP of *rac*-Lactide Using 5 and 6 and Immortal ROP of *rac*-Lactide Using 1, 2, and 5[a]

Entry	Complex	[M]:[Al]:[BnOH]	Time (h)	% Conv.[b]	$M_{n,th}$[c]	M_n[d]	PDI[d]	P_m/P_r[e]
1	**5**	100:1:1	12	49	7,000	6,100	1.07	0.88 (*m*)
2	**5**	250:1:1	18	78	28,200	26,200	1.04	0.89 (*m*)
3	**5**	500:1:1	24	56	40,400	33,600	1.04	0.88 (*m*)
4	**6**	100:1:1	24	<5	–	–	–	–
5	**1**	500:1:2	24	87	31,200	28,300	1.14	–
6	**1**	500:1:5	24	99	14,400	15,600	1.20	–
7	**1**	500:1:10	24	94	6,900	7,400	1.16	–
8	**1**	1,000:1:10	24	85	12,400	17,900	1.06	0.86 (*m*)
9	**2**	500:1:2	24	43	15,600	11,400	1.03	–
10	**2**	500:1:5	24	31	4,600	3,800	1.04	–
11	**2**	500:1:10	24	39	2,900	2,900	1.05	–
12	**2**	1,000:1:10	24	56	8,100	7,300	1.03	0.76 (*r*)
13	**5**	500:1:2	24	84	30,400	20,100	1.09	–
14	**5**	500:1:5	24	86	12,400	7,300	1.02	–
15	**5**	500:1:10	24	95	6,900	5,000	1.07	–
16	**5**	1,000:1:10	24	39	5,700	4,800	1.07	0.88 (*m*)

[a] Polymerizations were conducted in 3 mL of toluene with 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.
[b] Determined by gravimetric analysis after drying under vacuum to constant weight.
[c] Calculated by ([M]/[Al]) × MW (monomer) × (% conv.) + MW (end group).
[d] Obtained from SEC (GPC).
[e] Probability of a *meso* or *racemic* linkage determined by examination of the methine region of $^1H\{^1H\}$ NMR spectra.

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 using **2**, whereas **1** and **5** showed much higher conversion after 24 h at 70 °C in 3 mL of toluene. No significant loss of control was observed when increasing the amount of chain-transfer agent, 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 polymerizations, similar to those reported for a related aluminum-based salen complex under these conditions.[38] A slight decrease in tacticity was observed for Al-salen complexes **1**[24] and **5** under immortal conditions, but a more significant decrease was observed for Al-salan complex **2**, where a P_r of 0.94 was reported under living conditions[25] but a P_r value of only 0.76 was obtained under immortal conditions. It was observed that at monomer to catalyst ratios of greater than 1000:1, no productive polymerization occurred. This was most likely due to the high concentration of lactide, which resulted in coordination of the monomer to the aluminum center, effectively rendering the complex inactive. However, up to these loadings, benzyl alcohol serves as an excellent chain-transfer agent for the Al-salen and Al-salan systems and supports previous reports[35–38] that these systems serve as effective catalysts in the immortal ROP of *rac*-lactide.

Although Al-based salan complexes have not previously been studied in the ROP of *rac*-β-BL, *bis*-Al-salen complexes have been used,[41–43] although only low molecular weight oligomers were produced 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 under a range of conditions (Table 2). The control over molecular weight and PDIs for *rac*-β-BL polymerizations mediated by **1**, **2**, and **5** was significantly improved over those using related aluminum "half" salen complexes.[23] Both bulk and solution polymerizations at 70 °C mediated by **1** and **2** resulted in excellent control over molecular weights and PDIs, with slightly narrower PDIs observed for the solution polymerizations, even when a coordinating solvent was used (Table 2, Entries 1 and 2 for **1** and Entries 9–11 for **2**). Although polymerizations mediated by **1** at 120 °C exhibited faster rates and a significant broadening in PDI compared to polymerizations at 70 °C, the use of higher temperatures when using **2** did not result in a loss of control (Table 2, Entries 2 and 3 for **1**; Entries 10 and 12 for **2**), illustrating the versatile nature of the Al-salan system. When **2** was used for the ROP of *rac*-β-BL, narrow PDIs of <1.05 were observed, at temperatures ranging from 25 to 120 °C (Table 2, Entries 6–12), and an increase in [M]/[Al] gave PHB of the corresponding increased molecular weight (Table 2, Entries 10, 13, and 14). Narrow PDIs of <1.15 were observed for *rac*-β-BL polymerizations mediated by Al-salen catalysts **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, cf. Entries 2, 4, and 5 for **1**).

Upon investigation of the methylene and the carbonyl region in $^{13}C\{^1H\}$ NMR spectra of the isolated PHB, no stereocontrol

TABLE 2 Polymerization of *rac*-β-BL Using Al-salen and Al-salan Complexes 1, 2, and 5[a,b]

Entry	Complex	[M]/[Al]	Solvent	Temp. (°C)	Time (h)	% conv.[c]	$M_{n,th}$[d]	M_n[e]	PDI[e]
1	**1**	100	Neat	70	3	58	5,100	5,900	1.08
2	**1**	100	Toluene	70	6	58	5,100	5,100	1.06
3	**1**	100	Toluene	120	6	82	7,100	7,400	1.35
4	**1**	250	Toluene	70	18	94	20,300	16,600	1.14
5	**1**	500	Toluene	70	36	82	35,400	25,800	1.09
6	**2**	100	Neat	25	24	73	6,400	6,200	1.03
7	**2**	100	Toluene	25	48	58	4,800	6,400	1.03
8	**2**	100	THF	25	48	75	6,600	6,400	1.03
9	**2**	100	Neat	70	3	72	6,300	6,100	1.04
10	**2**	100	Toluene	70	6	99	8,600	8,600	1.03
11	**2**	100	THF	70	6	89	7,800	8,200	1.03
12	**2**	100	Toluene	120	2	94	8,300	7,400	1.05
13	**2**	250	Toluene	70	10	81	17,500	19,600	1.03
14	**2**	500	Toluene	70	20	90	38,800	35,700	1.04
15	**5**	100	Toluene	70	12	28	3,600	2,400	1.05
16	**5**	250	Toluene	70	18	41	8,800	4,900	1.04

[a] Polymerizations were conducted with 0.058 mmol of [Al] in 3 mL of solvent, where applicable, using 1 eq. benzyl alcohol to generate the active alkoxide.
[b] All PHB isolated possessed an atactic microstructure, determined by $^{13}C\{^1H\}$ NMR spectroscopy.
[c] Determined by gravimetric analysis after drying under vacuum to constant weight.
[d] Calculated by ([M]/[Al]) × MW (*rac*-β-BL) × (% conv.) + MW (end group).
[e] Obtained from SEC (GPC).

was observed regardless of solvent or temperature, confirming that catalysts **1**, **2**, and **5** produce solely atactic PHB. Kinetic experiments performed at 70 °C in benzene-d_6 confirmed that **1**, **2**, and **5** mediate living ring-opening polymerization of *rac*-β-BL. Pseudo-first-order reaction kinetics with respect to monomer were observed in plots of $\ln([M]_0/[M]_t)$ versus time, although a slight delay of approximately 15 min was introduced due to the time required to heat the polymerization to 70 °C prior to the collection of spectra. Plots of M_n versus percent conversion revealed a linear relationship with excellent agreement between experimental and theoretical molecular weight values (Fig. 3, Supporting Information Figs. S3 and S4). Signals in the ^1H NMR spectra corresponding to a benzyl ester end group were observed at δ 5.2 ppm for polymers produced by each of the complexes, with no evidence of carboxyl or crotonate end groups. These results suggest that the ROP of *rac*-β-BL by **1**, **2,** and **5** proceeds via a standard coordination-insertion mechanism, with **2** exerting the best control over molecular weights and PDIs by an Al-based complex for the living ROP of *rac*-β-BL reported to date.

Following our study using **1**, **2**, and **5** for the living ROP of *rac*-β-BL, we sought to investigate the versatility of these complexes by introducing an excess of benzyl alcohol and entering an immortal ROP regime. Experimental molecular weights agreed well with theoretical molecular weights when the ratio of catalyst to benzyl alcohol was increased from 2 to 50 with respect to a constant [M]/[Al] ratio of 500

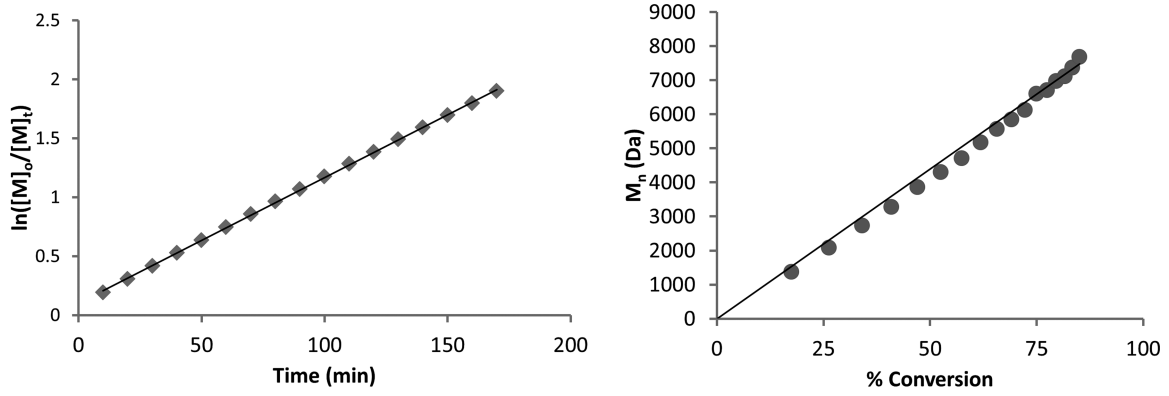


FIGURE 3 Plot of $\ln([M]_0/[M]_t)$ versus time (min) (left) and M_n versus percent conversion (right) (solid line = $M_{n,th}$) for ROP of *rac*-β-BL by **2** at 70 °C in benzene-d_6 with [M]/[Al] = 100.

TABLE 3 Immortal Ring-Opening Polymerization of *rac*-β-BL by 1, 2, and 5[a]

Entry	Complex	[M]:[Al]:[BnOH]	% conv.[b]	$M_{n,th}$[c]	M_n[d]	PDI[d]
1	**1**	500:1:2	40	8,700	8,100	1.07
2	**1**	500:1:5	70	6,000	4,540	1.06
3	**1**	500:1:10	57	2,500	2,100	1.08
4	**1**	500:1:25	75	1,400	1,100	1.07
5	**1**	500:1:35	50	700	800	1.09
6	**1**	500:1:50	61	600	900	1.08
7	**2**	500:1:2	92	19,800	16,300	1.05
8	**2**	500:1:5	85	7,400	7,500	1.03
9	**2**	500:1:10	82	3,600	3,200	1.11
10	**2**	500:1:25	84	1,500	1,600	1.08
11	**2**	500:1:35	98	1,300	1,200	1.05
12	**2**	500:1:50	98	1,000	800	1.10
13	**2**	1,000:1:50	99	1,800	1,500	1.04
14	**5**	500:1:2	<5	–	–	–

[a] All polymerizations were conducted with 0.058 mmol of [Al] 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 gravimetric analysis after drying under vacuum to constant weight.
[c] Calculated by ([M]/[Al]) × MW (monomer) × (% conv.) + MW (end group).
[d] Obtained from SEC (GPC).

for **1** and **2** (Table 3). No significant loss of control was observed in comparison with 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 the Al-salen and Al-salan systems at these loadings. However, when the monomer loading was increased above 1000 mol eq., no polymerization occurred, as was observed in the immortal ROP of *rac*-lactide. Al-salen complex **1** resulted in similar control to Al-salan complex **2** in the immortal ROP of *rac*-β-BL, with PDIs of ≤1.09, but was significantly slower to reach comparable conversions. Monomer conversion of >80% was observed after 24 h at 70 °C in toluene for **2**, whereas **1** was noticeably slower, reaching conversions of 40–75% in the same timeframe. Complex **5** was inactive under these conditions, presumably because of the high monomer concentration.

Plots of molecular weight versus [*rac*-β-BL]/[BnOH] ratio were linear for **1** and **2** (Fig. 4, Supporting Information Fig. S5), with a slope that correlated well with the molecular weight of the monomer at lower ratios of [*rac*-β-BL]/[BnOH]. Some deviation was observed at higher ratios and this was attributed to the data being collected over a significantly large range of chain-transfer agent loadings, along with the high monomer loading. Slight deviation occurred when **1** was used compared to **2**. However, these results represent the best control and highest ratio of chain-transfer agent:-complex achieved in an immortal ROP of *rac*-β-BL with an Al-based complex reported to date.[44,45]

Although various aluminum salen[23,42,46–48] and salan[49] complexes have previously been used in both homopolymerizations and copolymerizations of ε-caprolactone, Al-salen **1** and Al-salan **2** have not been studied. 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 (Supporting Information Table S1). Manipulation of the monomer concentration, temperature, or solvent did not produce any noteworthy improvement in control over the molecular weights or PDIs. It was also observed that the polymerizations progressed at a surprisingly slow rate, given the higher reactivity of the ε-caprolactone monomer, with solution polymerizations only reaching about 70% conversion after 6 h in toluene, whereas neat polymerizations reached 75% after 7 h at 70 °C.

With optimized protocols determined for the living and immortal ROP of *rac*-β-BL and *rac*-lactide using **1**, **2**, and **5**, we investigated the copolymerization of these monomers to see if our systems could produce high molecular weight, controlled copolymer materials. As a comparison, $Sn(Oct)_2$, well known for its use in the production of high molecular weight PLA on an industrial scale,[50] 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 using the Al-salen and salan complexes. With $Sn(Oct)_2$, only atactic PLA was isolated unless the copolymerizations were conducted under bulk conditions at 120 °C. In this case, an atactic-poly(lactic acid)-*co*-atactic-poly(3-hydroxybutyrate) was isolated with a broad PDI of approximately 1.8. Polymerizations conducted in neat monomer at 120 °C using **1**, **2**, and **5** also resulted in the formation of poly(lactic acid)-*co*-poly(3-hydroxybutyrate). Poor control was observed for copolymers synthesized using **1** and **5**, as evidenced by the broadened PDIs of >1.5, making these catalysts comparable to previous copolymerizations using tin,[21] magnesium,[22] group 4,[13] and aluminum[23] complexes. However, using the Al-salan complex **2** in the bulk copolymerization gave excellent control over molecular weights and narrow PDIs of ≤1.09 (Table 4).

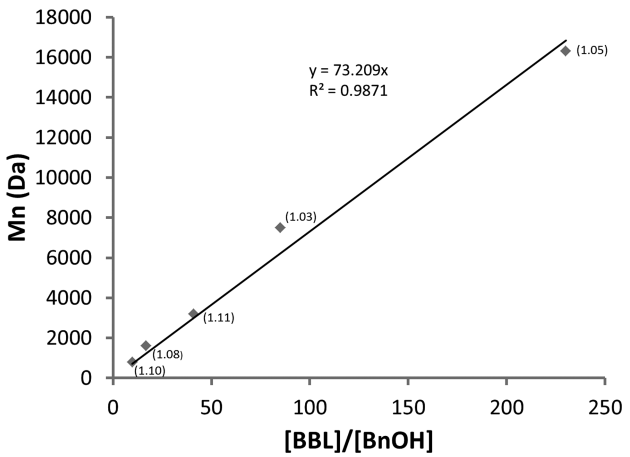


FIGURE 4 Plot of M_n versus [*rac*-β-BL]/[BnOH] for immortal ROP of *rac*-β-BL at 70 °C in toluene using **2**. Ratios of [*rac*-β-BL]/[BnOH] were corrected based upon the percent conversion of monomer.

TABLE 4 Bulk Copolymerization of *rac*-*β*-BL and *rac*-Lactide Using 2[a]

Entry	[LA]:[β-BL]	PLA:PHB[b]	$M_{n,th}$[c]	M_n[d]	PDI[d]	T_g[e] (°C)
1	1:1 (100:100)	3.5:1	14,900	20,100	1.09	32.0
2	2:1 (100:50)	9:1	16,700	29,400	1.05	43.6
3	4:1 (200:50)	19:1	27,000	18,900	1.07	35.5
4	6:1 (300:50)	39:1	23,000	29,400	1.07	39.3
5	1:2 (50:100)	1:1	13,600	15,800	1.07	17.7
6	1:4 (50:200)	1:1.6	23,900	17,100	1.07	13.6
7	1:6 (50:300)	1:2	17,300	14,600	1.05	11.4

[a] Polymerizations were conducted neat at 120 °C and with 0.035 mmol of [Al] using 1 eq. benzyl alcohol to generate the active alkoxide.
[b] Ratio of PLA to PHB calculated using ^{1}H NMR spectroscopy through integration of methyl signals associated with each polymer unit.
[c] Calculated by ((([M]/[Al]) × MW (*rac*-*β*-BL) × (% conv.)) + ((([M]/[Al] × MW (*rac*-lactide) × (% conv.)) + MW (end groups).
[d] Obtained from SEC (GPC)/MALS.
[e] DSC run with nitrogen flow rate of 50 mL min^{-1} and heating parameters of 5 °C min^{-1} for heating and cooling.

Further study of the copolymerization was performed by manipulating the initial monomer feed ratios of *rac*-*β*-BL and *rac*-lactide. From an initial feed ratio of 1:1 (100 eq. of each monomer), 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 calculated from the ^{1}H NMR spectrum. Moreover, signals typical of highly heterotactic PLA were observed, indicating the presence of long sequences of PLA in the copolymer. As the amount of *rac*-lactide in the initial feed was increased, the ratio of PLA:PHB in the copolymer increased disproportionately. For example, using a *rac*-lactide to *rac*-*β*-BL initial feed ratio of 6:1 (Table 4, Entry 4) resulted in a copolymer possessing a 39:1 PLA:PHB ratio. Again, a strong presence of heterotactic PLA was observed. Increasing the proportion of *rac*-*β*-BL in the initial feed to four times the *rac*-lactide concentration (*rac*-LA:*rac*-*β*-BL = 50:200, Table 4, Entry 6) resulted in greater PHB incorporation into the copolymer (1:1.2 ratio) and a loss of the long PLA sequences, as evidenced by the loss of the characteristic heterotactic PLA signals in the ^{1}H NMR spectrum (Supporting Information Fig. S6). A further increase in *rac*-*β*-BL concentration, to a ratio of 6:1 (Table 4, Entry 7), resulted in a 1:2 ratio of PLA:PHB in the copolymer after precipitation. Regardless of initial monomer feed ratios, the copolymerizations remained very well controlled, with PDIs consistently below 1.09. After copolymer work-up, examination of the filtrates by ^{1}H NMR spectroscopy showed no evidence of PLA or PHB homopolymers, and therefore some inconsistencies in *rac*-*β*-BL conversion, in comparison to the molecular weights of the PHB observed in the copolymer, have been attributed to potential decomposition of the monomer under these harsh, high temperature conditions.

Solution copolymerizations were successful at 85 °C for complexes **2** and **5**, although **1** yielded poorly controlled (PDIs ca. 1.4) homopolymers of PLA and PHB under these conditions. ^{1}H NMR spectroscopic kinetic experiments were conducted to monitor the formation of the copolymer in toluene-d_8 at 85 °C in reactions mediated by **2** and **5** (Fig. 5). These data 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 the lactide monomer took about 30 min to dissolve fully at this lower temperature and, in conjunction with a 15-min delay between monomer addition and the collection of the first ^{1}H NMR spectrum, gave rise to the non-zero intercepts of each of the linear regressions. These results indicate that the copolymerization of *rac*-*β*-BL and *rac*-lactide, mediated by these Al-salen and Al-salan complexes, displays a preference for the incorporation of *rac*-lactide over *rac*-*β*-BL, even when the rate of homopolymerization of *rac*-*β*-BL is significantly greater than that of *rac*-lactide.

Analysis of the phase transitions of these poly(lactic acid)-*co*-poly(3-hydroxybutyrate) materials by 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 (T_g) ranging from 11.4 °C for a

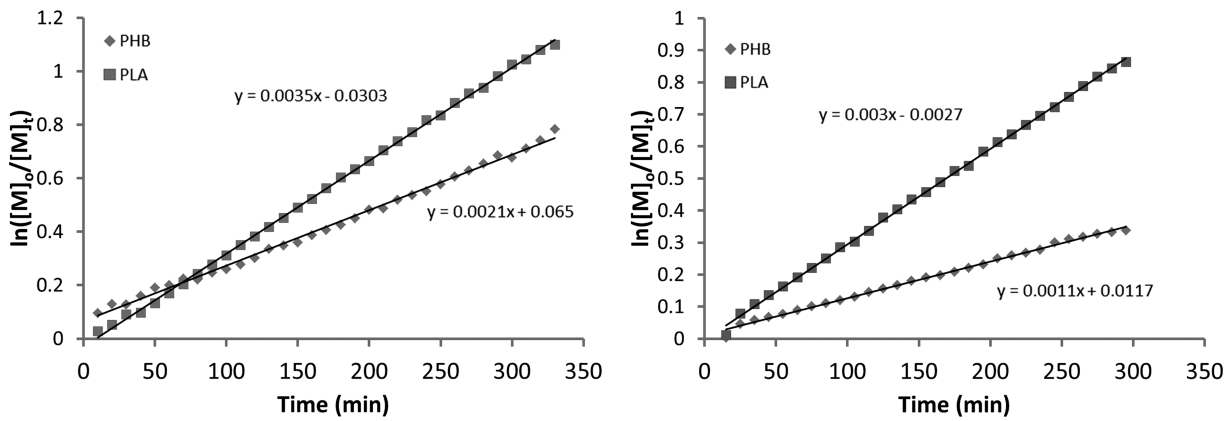


FIGURE 5 Plots of ln([M]$_0$/[M]$_t$) versus time (min) for the copolymerization of *rac*-*β*-BL and *rac*-lactide by **2** (left) and **5** (right) at 85 °C in toluene-d_8 with [*rac*-*β*-BL]:[*rac*-lactide]:[Al] of 50:50:1.

poly(lactic acid)-*co*-poly(3-hydroxybutyrate) copolymer with a 1:2 ratio of PLA:PHB to 43.6 °C for a poly(lactic acid)-*co*-poly(3-hydroxybutyrate) copolymer containing a 9:1 ratio of PLA:PHB. As expected, increased PLA content in the copolymer results in an increase in the T_g, whereas increased PHB content lowers the T_g (Table 4). No melting or crystallization temperatures were 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 **1**, **2**, and **5** efficiently mediate the immortal ROP of *rac*-lactide up to 10 mol eq. of benzyl alcohol chain-transfer agent and up to 1000 mol eq. of monomer. Moreover, we have shown that these complexes are able to form high molecular weight PHB by the ROP of *rac*-β-BL, whereas previous reports of *rac*-β-BL ROP using aluminum salen complexes were only able to access low molecular weight oligomers. The aluminum salan complex **2** demonstrates particular efficacy at controlling the ROP of *rac*-β-BL under a variety of polymerization conditions. Complexes **1** and **2** also facilitate the immortal ROP of *rac*-β-BL up to an excess of 50 mol eq. of benzyl alcohol before any loss of control is observed. When used in the copolymerization of *rac*-lactide and *rac*-β-BL, the aluminum salen complexes **1** and **5** were unable to provide control under thermally demanding conditions; however, the aluminum salan complex **2** allowed access to gradient poly(lactic acid)-*co*-poly(3-hydroxybutyrate) copolymers with narrow polydispersities of <1.1, to the best of our knowledge, an unprecedented result. Complexes **5** and **2** also mediate the formation of well-controlled poly(lactic acid)-*co*-poly(3-hydroxybutyrate) at 85 °C in toluene. The copolymer composition strongly favors the insertion of *rac*-lactide over *rac*-β-BL, with long segments of PLA formed unless at least a fourfold excess of *rac*-β-BL is present in the initial monomer feed. The initial thermal studies of these poly(lactic acid)-*co*-poly(3-hydroxybutyrate) materials show a single T_g, indicating that no phase separation occurs between the segments of PLA and PHB. Current efforts in the group look to expand the monomer scope to other hydroxyalkanoate polymers with larger hydrophobicity differences to PLAs to generate phase separated gradient materials.

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