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8-Quinolinolato Gallium Complexes: Iso-selective Initiators for *rac*-Lactide Polymerization

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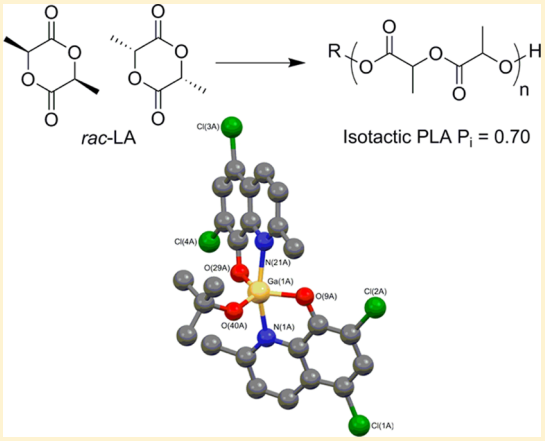
Supporting Information

ABSTRACT: The synthesis and characterization of a series of 8-quinolinolato gallium complexes is presented, and the complexes are analogous to a series of aluminum complexes previously reported. The complexes have been shown to be active initiators for the ring-opening polymerization of *rac*-lactide. High degrees of polymerization control are demonstrated, as exemplified by the linear evolution of molecular weight as the polymerization progresses, narrow polydispersity indices, and molecular weights corresponding to those predicted on the basis of initiator concentration. Some of the initiators show iso-selective polymerization of *rac*-lactide, with P_i = 0.70. The polymerization rates have been monitored, and the pseudo first-order rate constants are compared to those of analogous aluminum compounds. The 8-quinolinolato gallium initiators show rates approximately 3 times higher than those of the series of aluminum compounds, while maintaining equivalently high iso-selectivity (P_i = 0.70) and polymerization control.



INTRODUCTION

As the demand and usage of polymers increases, so do issues associated with the sustainability of their source materials, their end of life fates, and costs. Economic and environmental concerns have driven the quest to replace some petroleum-derived materials with alternative polymers sourced from renewable raw materials and with improved end of life options.[1] Polylactic acid (PLA) is one such material: it is efficiently prepared from starch and after use can be either composted or recycled. Although current production is around 100 000 t/a, growth in manufacture is predicted, and its properties make it suitable for applications spanning packaging, fibers, composites, and medical devices. PLA is manufactured by the ring-opening polymerization (ROP) of lactide (LA) (Figure 1), a process that is initiated by Lewis acidic metal alkoxide complexes.[1b,2] Quite a range of metals have precedent for initiating ROP, and for further details on the scope of this catalysis, the reader is referred to several comprehensive reviews.[1b,2,3] There has been a long-standing academic interest in aluminum-based initiators, due to the excellent control conferred by this metal and the potential for some Al complexes to enable stereocontrolled ROP of *rac*-lactide.[4] From the materials property perspective, the production of stereoblock or stereocomplex PLA, via the iso-selective ROP of *rac*-LA, remains a high priority target. Such polymers exhibit significantly improved thermal-mechanical properties as compared to isotactic PLA; for example, the T_m for isotactic PLA is 170 °C, whereas that for stereoblock/stereocomplex PLA has been reported from 170 to 230 °C.[5] Such improvements in thermal stability could enable higher-value applications for PLA.

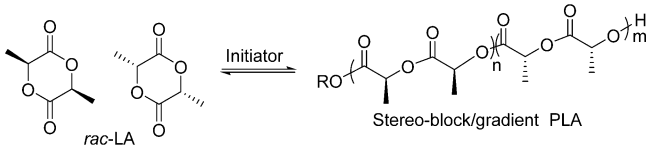


Figure 1. The isoselective ring-opening polymerization of *rac*-LA producing stereoblock PLA.

Aluminum initiators have a strong track record in the production of stereoblock/complex PLA from *rac*-LA. So far, the most iso-selective catalysts reported have been aluminum salen complexes. These are important academic targets, but the very slow rate of polymerization and high catalyst loadings required are significant drawbacks to these systems. Recently, several groups have reported improved activity and good iso-selectivities using indium catalysts.[6] For example, Mehrkhodavandi and co-workers reported the dinuclear complex, **A** (Figure 2), which polymerized 200 equiv of *rac*-LA in 30 min (298 K, methylene chloride, ~0.5 M in [LA], 90% conversion, P_i = 0.62).[6a] This is a marked increase in rate as compared to the Al salen systems, which typically take hours to achieve high conversions and require increased temperatures.[4a−c,e−g] Recently, the same group has extended the study of dinuclear and mononuclear indium complexes, resulting in efficient catalysis with a moderate-good isotactic bias (P_i = 0.77) in the best

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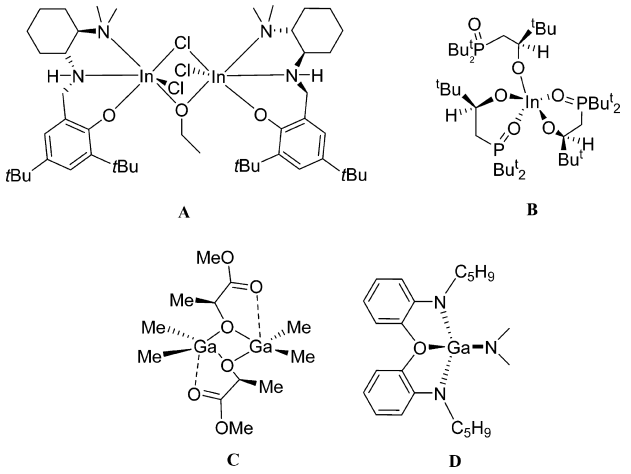

Figure 2. Examples of the structures of some stereoselective In and Ga initiators for *rac*-LA ROP.

cases.[6a−c] During the past 6 years, various other researchers have also reported promising indium-based catalysts, showing good rates and control.[6e,7] One attractive system was reported by Tolman and Hillmyer, where $InCl_3$, in the presence of an equivalent each of an alcohol and triethylamine, polymerized *rac*-LA quite rapidly and with high heteroselectivity (P_s = 0.97, 1:100 [I]:[LA], 5 h).[8] Another example of an interesting indium complex was a racemic homoleptic species, **B** (Figure 2), reported by Okuda and Arnold, which was found to induce a slight isotactic bias (P_i = 0.63).[6d]

Given the significant potential for Al and In initiators, it was somewhat surprising to discover that Ga complexes have been far less investigated in the ROP of LA. The first report of a dialkyl gallium alkoxide complex, **C** (Figure 2), demonstrated the potential of this group 13 congener for fast, controlled polymerization catalysis.[9] A recent comparative study of aluminum and gallium complexes, with the structures represented by compound **D** (Figure 2), showed that the Ga catalysts were faster and equally well controlled as the Al counterparts (Ga >99% conversion, 100 equiv of LA, 353 K, toluene 1 h, versus Al 45% conversion under the same conditions).[10] Despite the difference in rate, the change in metal center did not affect the polymerization stereoselectivity, with moderate iso-selectivity being observed for both the Al and the Ga initiators (P_i = 0.70).

We have previously reported a series of bis(8-quinolinolato) aluminum ethyl complexes, which, in the presence of iso-propyl alcohol, were efficient, iso-selective initiators (P_i = 0.76), for the ROP of *rac*-LA.[11] In this Article, the preparation and application of a series of gallium complexes, with some of the same 8-quinolinato ligands, is presented.

RESULTS AND DISCUSSION

Two 8-hydroxyquinoline ligands, **1** and **2**, were selected for investigation as ancillary ligands for gallium polymerization initiators (Figure 3). The ligands were selected as both are commercially available compounds, an attractive feature if polymerization activity of the initiators can be increased. Furthermore, the aluminum complexes of **1** and **2** showed distinct differences in polymerization activity with the halide substituents of ligand **2** enhancing activity and iso-selectivity.

Ga Complex Synthesis. Pro-ligands **1** and **2** were reacted with gallium(III)chloride, in toluene at 298 K, to form bis(8-

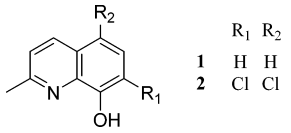

Figure 3. The structures of the pro-ligands, **1** and **2**.

quinolinolato) gallium chloride compounds, **1a** and **2a** (Figure 4). The compounds were isolated as yellow crystalline solids, in

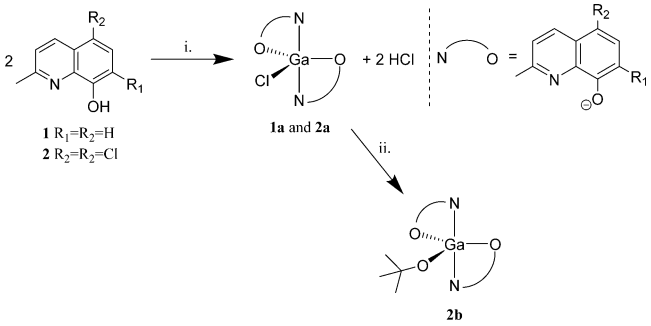

Figure 4. The preparation of compounds **1a**, **2a**, and **2b**. Reagents and conditions: (i) $GaCl_3$, toluene, 298 K, 12 h, **1a** (51%), **2a** (53%); (ii) KO*t*Bu, benzene-d_6, 298 K, 24 h, product not isolated.

moderate yields. The completion of the complexation reaction was confirmed by ^{1}H NMR spectroscopy where the resonances assigned to the quinolinolato protons were at higher chemical shift as compared to the pro-ligands, due to the Lewis acidic Ga center deshielding the nuclei. For each complex, the stoichiometry was further confirmed by elemental analysis and mass spectrometry. For compound **2a**, single crystals suitable for X-ray diffraction experiments were obtained from a saturated toluene solution.

Compounds **1a** and **2a** were tested as initiators for the ROP of *rac*-LA (1 M solution of LA in THF, 298 K, 20 h) but showed no activity. This is in line with the findings of other researchers that metal halide complexes are rarely effective initiators, presumably due to the high M−Cl bond strength (481 kJ mol^{-1} versus 285 kJ mol^{-1} for Ga−O).[12] To prepare active initiators, the gallium chloride complexes were reacted further to generate new alkoxide and amide complexes. Thus, various salt metathesis reactions, with the relevant potassium salts (Figure 4), were attempted. The reactions of either compound **1a** or **2a** with potassium *tert*-butoxide, potassium ethoxide, or potassium bis(trimethylsilyl)amide all resulted in a mixture of products. As an illustrative example, the reaction between **2a** and potassium *tert*-butoxide yielded a yellow powder whose ^{1}H NMR spectrum indicated the presence of the desired alkoxide complex **2b** (vide infra) together with another complex, showing only resonances for the quinolinate ligands. This second product was isolated and characterized by X-ray crystallography. The product was determined to be the oxo-bridged dimeric complex $[(L_2Ga)_2(\mu\text{-}O)]$, which formed due to undesired oxidation of the target alkoxide complex (see the Supporting Information). The oxygen/moisture necessary for such a degradation reaction is presumed to have arisen from residual oxygen/water in the reaction/NMR solvents. It should be noted that the same solvents were applied successfully for the isolation of aluminum and gallium alkyl complexes, without any such degradation, illustrating the high sensitivity of the alkoxide derivatives. The pure alkoxide complex **2b** was

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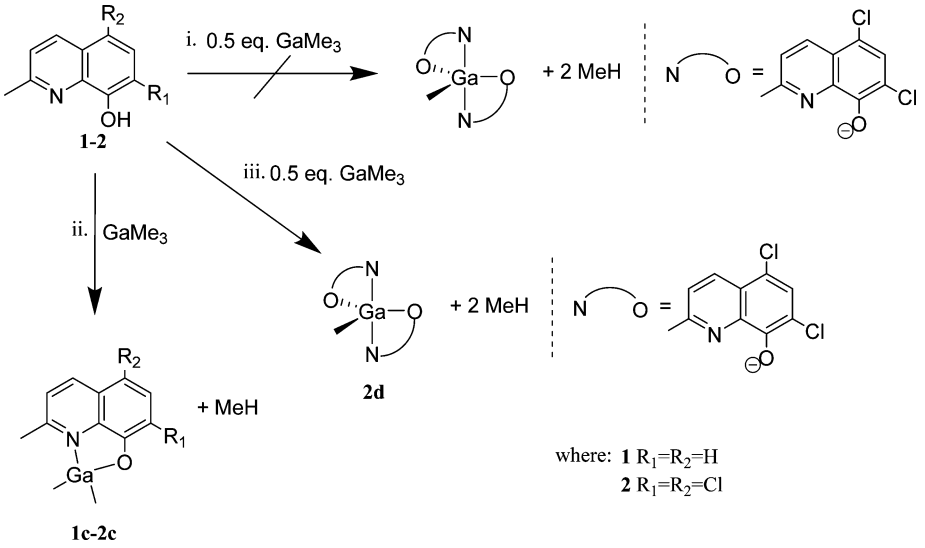

Figure 5. Synthetic routes attempted for the preparation of bis(8-quinolinolato) gallium methyl compounds, and the synthesis of compounds **1c**, **2c**, and **2d**. Reagents and conditions: (i) 0.5 equiv of $GaMe_3$, toluene, 298 K; (ii) $GaMe_3$, toluene, 298 K (**1c** 74%, **2c** 87%); (iii) 0.5 equiv of $GaMe_3$, toluene, 393 K (25%).

prepared by an NMR scale reaction, in a Young's tap NMR tube with centrifugation to remove the KCl byproduct (Supporting Information Figure S1). The ^{1}H NMR spectrum shows that all of the quinolinate resonances are shifted to lower field, and furthermore the singlet at 1.17 ppm, with a relative integral of 9, confirms the presence of the *tert*-butyl alkoxide. The low intensity signal at 1.05 ppm corresponds to residual *tert*-butyl alcohol. Crystals suitable for X-ray diffraction analyses (vide infra) were grown by addition of hexane to this solution.

As an alternative route to gallium alkoxide complexes, gallium alkyl complexes [L_2GaR] (R = alkyl) were targeted as suitable precursors for further reaction, via protonolysis, with various alcohols. The reaction of 2 equiv. of the pro-ligands, **1** and **2**, with trimethylgallium resulted only in the formation of the monoligated complexes **1c** and **2c** [$LGaMe_2$] together with the residual pro-ligands. It is relevant that the reaction was conducted under the same conditions as had previously enabled the isolation of the bis-ligated aluminum ethyl complexes [L_2AlEt].[11] Changing the conditions, for example, by using more polar solvents such as THF or pyridine, resulted solely in the formation of the same monoligated product. It was only possible to form some of the desired bis-ligated gallium complexes, by refluxing the solutions in toluene for 24 h. Even under such forcing conditions, complex **2c** was only partly converted, in low yield (25%), to the desired bis-ligated product **2d**.

Given the preferential formation of monoligated complexes, these species were themselves directly targeted. Complexes **1c** and **2c** were prepared in high yields (74% and 87%, respectively) by reaction between equimolar quantities of trimethylgallium and the appropriate pro-ligands (Figure 5). The complex formation was confirmed by ^{1}H NMR spectroscopy, where characteristic shifts in the quinolinolate resonances were observed. A singlet peak was observed between 0 and 0.1 ppm, with a total relative integral of 6, due to the two gallium coordinated methyl groups.

X-ray Crystallography. Crystals suitable for X-ray crystallographic analysis were isolated for compounds **2a** and **2b** from toluene and benzene-d_6/hexane solutions, respectively. Both compounds crystallized in centrosymmetric (i.e., racemic) space groups. The structure of **2a** has C_2 symmetry about an axis that passes through the gallium and chlorine atoms (Figure 6), while the structure of **2b** contains two crystallographically

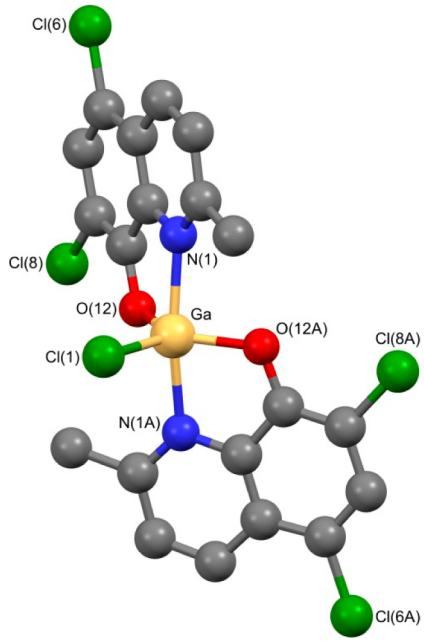

Figure 6. The molecular structure of the C_2-symmetric complex **2a**. Selected bond lengths (Å): Ga–Cl(1) 2.1915(6), Ga–N(1) 2.1073(10), Ga–O(12) 1.8680(10).

independent complexes, **2b-A** (shown in Figure 7) and **2b-B** (shown in Supporting Information Figure S4). All three molecules have pentacoordinate gallium centers with similar distorted trigonal bipyramidal coordination geometries, the τ values being 0.69, 0.57, and 0.57 for **2a**, **2b-A**, and **2b-B**, respectively. The greater deviation of **2b-A** and **2b-B** from the trigonal bipyramidal geometry is due to the steric bulk of the *tert*-butoxide coligand. As with the aluminum complexes, in every case the only geometric isomer observed has the nitrogen

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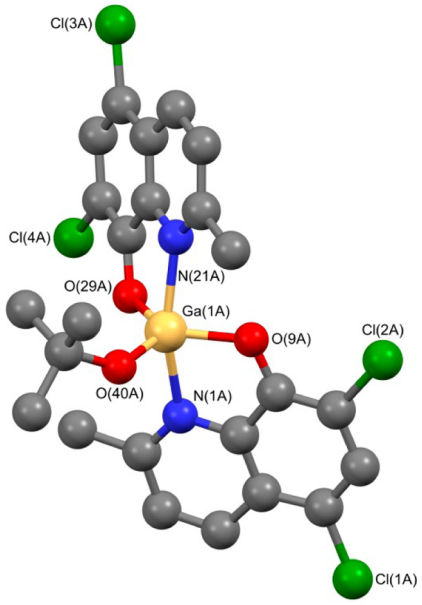

Figure 7. The structure of one (**2b-A**) of the two independent complexes present in the crystals of **2b**.

atoms of the ligand coordinated trans to one another in the axial positions. The O-donors, from the quinolinolate rings, are coordinated at equatorial sites, with the remaining site being occupied by a chloride or alkoxide coligand, for **2a** and **2b**, respectively. The Ga−O and Ga−N bond lengths to the quinolinolato ligand differ between **2a** and **2b** (**A** and **B**) significantly; in the case of **2a**, all of the Ga−O and Ga−N bonds are shorter than those in **2b-A** and **2b-B**. Again, this can be attributed to the larger *tert*-butoxide group versus chloride (Figure 6 and Table 1). In both cases, the Ga−N and Ga−O bonds of the ligand are longer than the Al−N and Al−O bonds previously observed for the aluminum quinolinolate complexes.[11]

Polymerization of *rac*-LA. Compounds **1c**, **2b−d** were tested as initiators in the ROP of *rac*-LA (Table 2). Polymerizations were conducted under a standard set of conditions: using a 1 M solution of lactide in toluene, at 348 K with an initiator concentration of 10 mM. In the case of compounds **1c** and **2c**, an equivalent (vs initiator) of isopropyl alcohol was added so as to enable generation of the active gallium alkoxide species in situ. The polymerizations were monitored by taking aliquots at regular time intervals, which were analyzed using ^{1}H NMR spectroscopy, to determine the LA conversion, and by GPC-MALLS (gel permeation chromatography-multiangle laser light scattering), to determine the number average molecular weight, M_n, and the polydispersity index, PDI. In each case, the polymerization rate was compared by determination of the pseudo-first-order rate constant, k_{obs}, which is the gradient of the linear plots of $\ln([LA]_0/[LA]_t)$ versus time. The tacticity of the PLA obtained using compound **2b** was determined by integration of the methyne region of the homonuclear decoupled NMR spectrum. The normalized integrals were compared against the values predicted using Bernoullian statistics to give the probability of isotactic linkages, P_i.[13] The polymerization results are summarized in Table 2.

Because of the previously discussed problems with the isolation of compound **2b**, the compound was synthesized in situ at a known concentration in toluene. The potassium chloride salt was removed by centrifugation, and the stock solution was added to the polymerization mixture. At this point, it is worth highlighting that the stoichiometric salt metathesis reaction proceeds to full conversion, as observed in the ^{1}H NMR experiments. We can therefore eliminate the possibility of any excess potassium *tert*-butoxide salt, a known active initiator for the ROP reaction, initiating the polymerization. The initiator, **2b**, was moderately active in the ROP of *rac*-lactide, with the polymerization proceeding to high conversion in excess of 50 h. Such rates are typical for discrete group 13 initiators, and indeed the polymerization occurs at a rate similar to that of the previously reported bis(8-quinolinolato) aluminum ethyl initiators.[9a,10,11] The initiator gives rise to PLA with a moderate degree of isotactic enchainment, with a P_i value of 0.70 consistent with a bias toward a stereoblock microstructure (Supporting Information Figure S8). There are only two other examples of iso-selective gallium initiators: compound **D** (Figure 2, P_i = 0.70) and a dimethyl gallium *N*-heterocyclic carbene complex, reported by Horeglad and co-workers, where a P_i value of up to 0.78 was claimed.[9b,10]

The initiator bis(5,7-dichloro-2-methyl-8-quinolinolato) gallium *tert*-butoxide, **2b**, is analogous to the bis(5,7-dichloro-2-methyl-8-quinolinolato) aluminum ethyl initiator, where the active alkoxide initiator is formed in situ by reaction with isopropyl alcohol during the course of the ROP reaction.[11] Initiator **2b** is significantly faster than its aluminum analogue, with around a 3 times higher k_{obs} value (1.3×10^{-5} s^{-1} for **2b** vs 5.0×10^{-6} s^{-1} for the Al analogue) (Figure 8). This finding is in line with the only other comparison between Ga and Al complexes, in that case using κ^3-*N,O,N*-{$(C_6F_5N{-}C_6H_4)_2O$}-$MNMe_2$-type complexes.[10] The increased activity of the gallium compounds is tentatively attributed to the reduced Lewis acidity of Ga resulting in a weaker or more labile gallium alkoxide bond. In addition to the beneficial increase in rates, the Ga complex also shows high iso-selectivity and good polymerization control (equaling those observed with the Al analogue). This is particularly relevant as studies comparing Al and In catalysts have been hampered by a reduction in stereocontrol for the indium congeners.[7a]

Initiator **2d** has the same ancillary ligand as bis(5,7-dichloro-2-methyl-8-quinolinolato) aluminum ethyl. The proposed active alkoxide complex is formed in situ during the polymerizations by reaction between **2d** and the equivalent of alcohol. It was therefore somewhat surprising that complex **2d** completely failed to polymerize *rac*-LA, even in the presence of an equivalent of isopropyl alcohol. Dagorne et al. used a κ^3-*N,O,N*-{$(C_6F_5N{-}C_6H_4)_2O$}GaMe initiator, in the presence of

Table 1. Comparative Selected Bond Lengths (Å) for the Two Independent Complexes Present in the Crystals of 2b

bond length	2b-A	2b-B	bond length	2b-A	2b-B
Ga(1)−N(1)	2.1274(15)	2.1232(15)	Ga(1)−O(29)	1.8881(12)	1.8863(13)
Ga(1)−O(9)	1.8871(13)	1.8868(13)	Ga(1)−O(40)	1.7904(13)	1.7844(15)
Ga(1)−N(21)	2.1310(16)	2.1493(16)			

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Table 2. Polymerization Data Using Initiators 1c, 2b−d

initiator (I)	$[LA]_0/[i\text{PrOH}]/[I]^a$	time (h)	conversion (%)^b	$k_{obs} \times 10^5$ (s^{-1})^c	M_n (exp) (g mol^{-1})^d	M_n (calcd) (g mol^{-1})	PDI^d	P_i^e
1c	1/1/100	45	92	1.8	11 300	13 200	1.24	0.5
2b	1/0/100	51	91	1.3	14 600	13 100	1.25	0.70
2c	1/1/100	38	96	2.6	15 200	13 800	1.19	0.5
2d	1/1/100		0					
AlL_2Et[11] $R_1{=}R_2{=}Cl$	1/1/100	137	91	0.5	9900	13 100	1.11	0.72

[a]Polymerization conditions: toluene, 348 K, 1:1:100 [I]:[*i*PrOH]:[LA], 1 M [LA]. [b]Determined by integration of the methine region of the ^1H NMR spectrum (LA 4.98−5.04 ppm; PLA 5.08−5.22 ppm). [c]Determined from the gradients of the plots of $\ln\{[LA]_0/[LA]_t\}$ versus time, where the average errors = 9−10% (determined using initiator **1c**). [d]Determined by GPC in THF, using multiangle laser light scattering (GPC-MALLS). [e]Determined by analysis of all of the tetrad signals in the methine region of the homonuclear decoupled ^1H NMR spectrum.

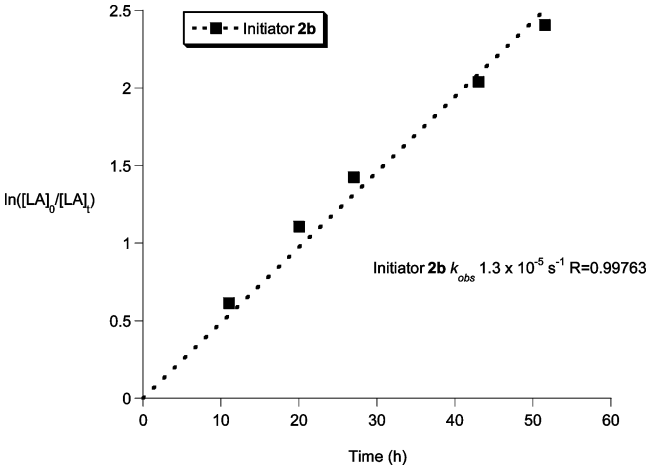

Figure 8. Plot of $\ln([LA]_0/[LA]_t)$ versus time of initiator **2b**. Conditions: $[LA]_0$ 1 M, 1:100 [I]:[LA], toluene, 348 K.

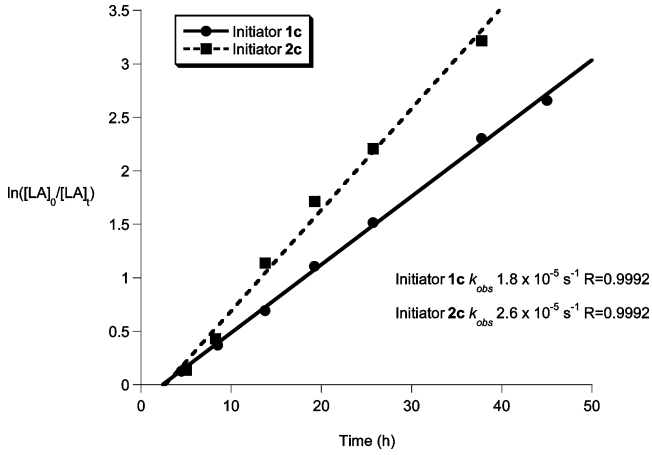

Figure 9. Plot of $\ln([LA]_0/[LA]_t)$ versus time of initiator **1c** and **2c**. Conditions: $[LA]_0$ 1 M, 1:1:100 [I]:[*i*PrOH]:[LA], toluene, 348 K.

an equivalent of alcohol; this system was also completely inactive toward the ROP of *rac*-LA.[10] This was in contrast to the analogous aluminum complex, which showed moderate activity under the same conditions. The lack of reactivity of compound **2d**, in the presence of iso-propyl alcohol, can be attributed to the failure to form the active alkoxide initiating species. An NMR scale experiment between **2d** and a slight excess of iso-propyl alcohol, heated at 348 K for 24 h in toluene-d_8, showed no conversion to the desired alkoxide product.

In contrast, monoligated compounds, **1c** and **2c**, were active initiators for the ROP of LA, in the presence of 1 equiv of isopropyl alcohol. The polymerizations using **1c** and **2c** are marginally faster than those using initiator **2b**, with k_{obs} values of 1.8 and 2.6 × 10^{-5} s^{-1}, respectively (Figure 9). Thus, the halide ligand substituents increase the rate of polymerization, in line with previous structure−activity studies using Al complexes.[11] In both systems, an initiation period of approximately 2−3 h was observed (note such initiation periods are not observed using the gallium alkoxide complex **2b**). Once again, the alcoholysis reaction was studied using compound **2c**, which was heated at 348 K in toluene with 1−10 equiv of iso-propyl alcohol for 72 h. This experiment failed to result in any formation of a gallium alkoxide complex, leaving only compound **2c** unreacted. The lack of reactivity of compound **2c** toward alcoholysis indicates that the ring-opening polymerization may be likely to proceed via a different mechanism to the usual coordination insertion route. A possible reaction pathway could be via an activated monomer mechanism; such a mechanism does not require any formation of a gallium alkoxide species. Instead, the Lewis acidic gallium metal center acts as a nucleophile, activating the lactide monomer unit to attack by uncoordinated iso-propyl alcohol. Such a mechanism has been previously proposed for a series of (phenoxy-imine)indium complexes, which were also shown to be inert to alcoholysis reactions.[6e] Furthermore, invoking this mechanistic pathway could rationalize the lack of polymerization activity observed with compound **2d**, which would be expected to have a lower Lewis acidity than **1c**/**2c** due to its higher coordination number (penta- vs tetracoordinate Ga). Thus, **2c** might be insufficiently Lewis acidic to activate the lactide, a key step in the activated monomer polymerization pathway.

Analysis of the homonuclear decoupled $^1H\{^1H\}$ NMR spectrum showed the formation of atactic PLA for **1c** and **2c**, consistent with the reduced steric influence of the hydroxyl-quinoline ligands in monoligated complexes. All of the initiators display a high degree of polymerization control, showing a linear evolution of the M_n with % conversion (Supporting Information Figures S9 and S10) and M_n values that are close to those predicted on the basis of the initiator concentration (Table 2). The monomodal molecular weight distribution, observed with all initiators, is especially relevant for **2b** as it provides further support for the lack of any additional initiating species, such as KO*t*Bu, in the polymerization system. All of the PDIs are also narrow throughout the course of the polymerizations, below 1.25 in all cases, indicative of limited transesterification side reactions. The end groups of the polymers formed by initiators **1c** and **2c** were analyzed by MALDI-ToF mass spectrometry, which confirmed that the chains were end-capped with iso-propyl ester groups

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(Supporting Information Figure S11). The peaks were separated by 144 amu. However, there is also a series of low molecular weight peaks that correspond to the formation of cyclic PLA (Supporting Information Figure S12).

CONCLUSIONS

A series of gallium complexes featuring one or two 8-quinolinolato ligands have been synthesized with either chloride, *tert*-butyl alkoxide, or methyl coligands. The new complexes were fully characterized, and in two cases X-ray crystallographic data were obtained. Some of the complexes were tested as initiators (**2b**) or as part of initiating systems, with exogenous alcohol (**1c**, **2c**) for the polymerization of *rac*-LA. Both the initiator and the initiating systems displayed moderate rates and excellent polymerization control. It is tentatively proposed that compounds **1c** and **2c** operate by an activated monomer mechanism, due to their lack of reactivity with exogenous alcohol. The complexes were all more active than the aluminum counterparts.

Interestingly, initiator **2b** yielded stereoblock PLA, with a P_i value of 0.70, from *rac*-LA. This is an unusual example of a gallium complex capable of exerting iso-selectivity and yielding the higher value stereoblock PLA. Of particular note is that the complex exhibits equivalent good stereocontrol to an aluminum analogue but operates at approximately 3 times the rate. It is clear that further improvements to the rate and stereocontrol are desirable and could be achieved by rational ligand design.

EXPERIMENTAL SECTION

Materials and Methods. All reactions were conducted under an inert nitrogen atmosphere, using a nitrogen-filled glovebox or standard Schlenk techniques. All solvents and reagents were obtained from commercial sources, and triethyl aluminum was obtained from Strem. Toluene was distilled from sodium, degassed, and stored under nitrogen. Isopropyl alcohol was heated to reflux over CaH_2, distilled onto fresh CaH_2 and further refluxed, then distilled, degassed, and stored under nitrogen. Benzene-d_6 was distilled from sodium, and toluene-d_8 and $CDCl_3$ were dried over CaH_2; all of the NMR solvents were degassed and stored under nitrogen. *rac*-Lactide was obtained from Purac Plc. and was purified by recrystallization (dry toluene) and sublimation (three times).

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Av400 spectrometer operating at 400 MHz for ^{1}H, and 100 MHz for $^{13}C\{^1H\}$ spectra. Solvent peaks were used as internal references for ^{1}H and ^{13}C chemical shifts (ppm). Higher resolution $^1H\{^1H\}$ NMR (homodecoupled spectroscopy) experiments were performed on a Bruker Av500 spectrometer and also a DRX 400 spectrometer. Spectra were processed and analyzed using Mestrenova software. Elemental analyses were determined by Mr. Stephen Boyer at London Metropolitan University, Science Centre, 29 Hornsey Road, London N7 7DD, UK. GPC-MALLS measurements were conducted on a Polymer Laboratories PL GPC-50 instrument at 35 °C, using two Polymer Laboratories Mixed D columns in series and THF as the eluent, at a flow rate of 1 mL min^{-1}. The light scattering detector was a Dawn 8, Wyatt Technology, and data were analyzed using Astra V version 5.3.4.18. The refractive angle increment for polylactide (dn/dc) in THF was 0.042 mL g^{-1}.[14]

Bis(2-methyl-8-quinolinolato)gallium Chloride ***1a.*** 8-Hydroxy-2-methylquinoline (0.45 g, 2.8 mmol) in toluene (10 mL) was added dropwise, with stirring, to a solution of gallium(III)chloride, in toluene (0.25 g, 4.4 mmol) at 273 K. The reaction was stirred for 12 h, after which time a pale green solid precipitated from the reaction. The precipitate was filtered and dried in vacuo. The solid was then crystallized from THF, at low temperature, to yield a pale yellow, microcrystalline, air-stable solid (0.30 mg, 0.71 mmol, 51%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.24 (s, 6H, CH_3), 7.15 (dd, 2H, C*H*, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.0 Hz), 7.22 (dd, 2H, C*H*, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.0 Hz), 7.50 (m, 4H, C*H*), 8.31 (d, 2H, C*H*, $^3J_{HH}$ = 8.0 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 23.3 (CH_3), 112.8 (CH), 114.2 (CH), 124.3 (C^{IV}), 127.0 (CH), 129.0 (CH), 136.9 (C^{IV}), 139.8 (CH), 155.6 (C^{IV}), 156.9 (C^{IV}). Anal. Calcd ($GaC_{10}H_{16}N_2O_2Cl$): C, 56.99; H, 3.83; N, 6.65. Found: C, 56.89; H, 3.9; N, 6.58. m/z (LSIMS): 422 (M^+, 15%), 385 (M^+ − Cl, 45%).

Bis(5,7-dichloro-2-methyl-8-quinolinolato)gallium Chloride ***2a.*** 5,7-Dichloro-8-hydroxy-2-methylquinoline (0.65 g, 2.8 mmol) in toluene (15 mL) was added dropwise with stirring to a solution of gallium(III)chloride (0.25 g, 1.4 mmol) in toluene (10 mL) at 273 K. The reaction was left to stir for 12 h at 298 K, after which time the solvent was removed in vacuo. The yellow solid was then recrystallized from toluene to yield yellow crystals (391 mg, 0.70 mmol, 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.25 (s, 6H), 7.59 (s, 2H), 7.60 (d, 2H, $^3J_{HH}$ = 8.4 Hz), 8.59 (d, 2H, $^3J_{HH}$ = 8.4 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 23.3 (CH_3), 117.1 (C^{IV}), 118.0 (C^{IV}), 123.6 (C^{IV}), 125.1 (CH), 128.2 (C^{IV}), 129.2 (CH), 137.5 (CH), 150.7 (C^{IV}), 159.4 (C^{IV}). Anal. Calcd ($GaC_{20}H_{12}O_2N_2Cl_5$): C, 42.95; H, 2.16; N, 5.01. Found: C, 43.09; H, 2.08; N, 4.92. m/z (LSIMS): 560 (M^+, 40%), 523 (M^+ − Cl, 25%).

Bis(5,7-dichloro-2-methyl-8-quinolinolato)gallium tert-Butoxide ***2b.*** Bis(5,7-dichloro-2-methylquinolinato)gallium chloride (0.10 g, 0.18 mmol) was added portion-wise over 30 min to a suspension of potassium *tert*-butoxide (20 mg, 0.18 mmol) in benzene-d_6 (4 mL). The reaction was allowed to stir at 298 K for 24 h. The orange precipitate was removed by centrifugation, and ^{1}H NMR spectroscopy of the solution revealed complete conversion to the product.

^{1}H NMR (400 MHz, benzene-d_6) δ (ppm): 1.17 (s, 9H, $OC(CH_3)_3$), 3.16 (s, 6H, CH_3), 6.50 (d, 2H, C*H*, $^3J_{HH}$ = 8.8 Hz), 7.41 (s, 2H, C*H*), 7.79 (d, 2H, C*H*, $^3J_{HH}$ = 8.8 Hz).

^{1}H NMR Data of the Degradation Product of ***2b.*** ^{1}H NMR (400 MHz, toluene-d_8) δ (ppm): 3.23 (s, 6H, CH_3), 6.10 (d, 2H, C*H*, $^3J_{HH}$ = 8.6 Hz), 7.26 (s, 2H, C*H*), 7.49 (d, 2H, C*H*, $^3J_{HH}$ = 8.6 Hz).

(2-Methyl-8-quinolinolato)dimethyl Gallium ***1c.*** Trimethylgallium (108 mg, 0.94 mmol) in toluene (3 mL) was added dropwise to a solution of 5,7-dichloro-8-hydroxy-2-methylquinoline (0.15 g, 0.94 mmol) in toluene (10 mL). The solution was stirred at 298 K for 16 h, after which time a yellow precipitate had formed. The solid was isolated by filtration and dried in vacuo to yield a yellow solid. The volume of the filtrate was reduced, and further product was isolated (0.18 g, 0.70 mmol, 74%).

^{1}H NMR (400 MHz, benzene-d_6) δ (ppm): 0.10 (s, 6H, CH_3), 1.97 (s, 3H, CH_3), 6.27 (d, 1H, C*H*, $^3J_{HH}$ = 8.4 Hz), 6.73 (dd, 1H, C*H*, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz), 7.29 (t, 1H, C*H*, $^3J_{HH}$ = 7.8 Hz), 7.34 (dd, 1H, C*H*, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.38 (d, 1H, C*H*, $^3J_{HH}$ = 8.4 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): −6.0 (CH_3), 22.4 (CH_3), 110.3 (C^{IV}), 111.6 (CH), 114.7 (CH), 122.2 (CH), 130.6 (CH), 139.0 (C^{IV}), 139.8 (CH), 153.6 (C^{IV}), 162.0 (C^{IV}). Anal. Calcd ($GaC_{12}H_{14}NO$): C, 55.87; H, 5.47; N, 5.43. Found: C, 55.96; H, 5.51; N, 5.57.

(5,7-Dichloro-2-methyl-8-quinolinolato)dimethyl Gallium ***2c.*** Trimethylgallium (0.20 g, 1.8 mmol) in toluene (3 mL) was added dropwise to a solution of 5,7-dichloro-8-hydroxy-2-methylquinoline (0.40 g, 1.8 mmol) in toluene (15 mL). The solution was stirred at 298 K for 16 h, after which time the solvent was removed in vacuo to yield a yellow solid (0.50 g, 1.53 mmol, 87%).

^{1}H NMR (400 MHz, benzene-d_6) δ (ppm): 0.00 (s, 6H, CH_3), 1.82 (s, 3H, CH_3), 6.15 (d, 1H, C*H*, $^3J_{HH}$ = 8.4 Hz), 7.47 (s, 1H, C*H*), 7.82 (d, 1H, C*H*, $^3J_{HH}$ = 8.4 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): −6.1 (CH_3), 22.3 (CH_3), 113.9 (C^{IV}), 119.1 (C^{IV}), 122.7 (CH), 124.4 (C^{IV}), 130.6 (CH), 137.1 (CH), 138.9 (C^{IV}), 155.3 (C^{IV}), 156.9 (C^{IV}). Anal. Calcd ($GaC_{12}H_{12}NOCl_2$): C, 44.10; H, 3.70; N, 4.29. Found: C, 44.13; H, 3.74; N, 4.35.

Bis(5,7-dichloro-2-methyl-8-quinolinolato)methyl Gallium ***2d.*** Trimethylgallium (50.8 mg, 0.44 mmol) in toluene (3 mL) was added dropwise to a solution of 5,7-dichloro-8-hydroxy-2-methylquinoline (0.20 g, 0.88 mmol) in toluene (15 mL). The solution was heated at reflux for 24 h, after which time the solvent was removed in

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vacuo to yield a yellow solid. The product was isolated by washing with hot hexane to remove the side products, yielding a pale yellow solid (60 mg, 0.11 mmol, 25%).

^{1}H NMR (400 MHz, benzene-d_6) δ (ppm): 0.16 (s, 3H, Ga−CH_3), 2.83 (s, 6H, CH_3), 6.45 (d, 2H, CH, $^3J_{HH}$ = 8.8 Hz), 7.44 (s, 2H, CH), 7.82 (s, 2H, CH, $^3J_{HH}$ = 8.8 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): −4.9 (Ga−CH_3), 22.9 (CH_3), 115.5 (C^{IV}), 117.5 (C^{IV}), 124.0 (CH), 124.0 (C^{IV}), 129.2 (CH), 135.9 (CH), 138.8 (C^{IV}),153.9 (C^{IV}), 157.5 (C^{IV}). Anal. Calcd ($GaC_{21}H_{15}N_2O_2Cl_4$): C, 46.80; H, 2.81; N, 5.20. Found: C, 46.72; H, 2.87; N, 5.15.

General Polymerization Procedure. In a glovebox, a Young's tap ampule was loaded with *rac*-lactide (432 mg, 3 mmol) and (2-methyl-8-quinolinolato) **1c** (7.7 mg, 0.03 mmol). Toluene (2.9 mL) and iso-propyl alcohol (0.03 mmol) were injected into the reaction, such that the overall concentration of lactide was 1 M and of initiator was 10 mM. The ampule was removed from the glovebox and placed in an oil bath at 348 K. Aliquots were taken from the reaction, under an nitrogen atmosphere. Aliquots were quenched with hexane (1−2 mL), and the solvent was allowed to evaporate. The crude product was analyzed by ^{1}H NMR and homonuclear decoupled ^{1}H NMR spectroscopy and GPC-MALLS. The conversion of LA to PLA was determined by integration of the methine proton peaks of the ^{1}H NMR spectra, δ 5.00−5.30. The P_i value was determined by integration of the methine region of the homonuclear decoupled ^{1}H NMR spectrum, δ 5.1−5.24.[13] The PLA number-averaged molecular weight, M_n, and polydispersity index (M_w/M_n; PDI) were determined using gel permeation chromatography equipped with multiangle laser light scattering (GPC-MALLS).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR spectra, crystallographic data and structures, MALDI-TOF spectra, and references. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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