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Redox controlled polymerization of lactide catalyzed by bis(imino)pyridine iron bis(alkoxide) complexes

Ashley B. Biernesser, Bo Li, and Jeffery A. Byers*

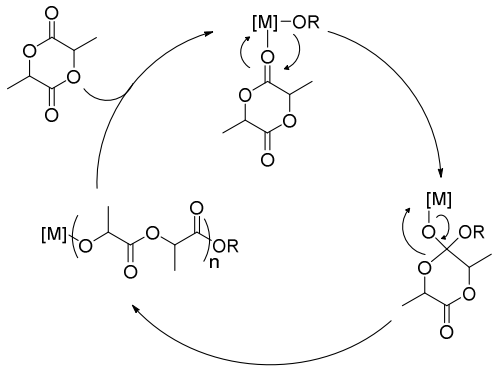
Eugene F. Merkert Chemistry Center, Department of Chemistry, Boston College, 2609 Beacon Street, Chestnut Hill, Massachusetts, 02467

ABSTRACT: Bis(imino)pyridine iron bis(alkoxide) complexes have been synthesized and utilized in the polymerization of *(rac)*-lactide. The activities of the catalysts were particularly sensitive to the identity of the initiating alkoxide with more electron donating alkoxides resulting in faster polymerization rates. The reaction displayed characteristics of a living polymerization with production of polymers that exhibited low molecular weight distributions, linear relationships between molecular weight and conversion, and polymer growth observed for up to fifteen sequential additions of lactide monomer to the polymerization reaction. Mechanistic experiments revealed that iron bis(aryloxide) catalysts initiate polymerization with one alkoxide ligand, while iron bis(alkylalkoxide) catalysts initiate polymerization with both alkoxide ligands. Oxidation of an iron(II) catalyst precursor lead to a cationic iron(III) bis-alkoxide complex that was completely inactive towards lactide polymerization. When redox reactions were carried out during lactide polymerization, catalysis could be switched off and turned back on upon oxidation and reduction of the iron catalyst, respectively.

INTRODUCTION

Millions of tons of largely biologically inert polymeric materials are produced and disposed of annually.[1a] The growing amount of waste created by this practice has generated concern about the environmental impact that results from releasing large quantities of slowly degrading materials into the environment. In response to these concerns, recent research efforts have been devoted to the development of biodegradable alternatives to the useful engineering polymers used today. A leading candidate in this regard is poly(lactic acid). Derived from renewable resources such as corn starch, polylactic acid (PLA) can degrade via hydrolytic cleavage of the ester bonds of the polymer backbone. This property has been exploited for several applications including textiles, fibers, packaging, and for a variety of medical materials.[1]

The majority of PLA is produced by the ring opening polymerization of lactide, a cyclic dimer of lactic acid (Scheme 1). This process is typically catalyzed or initiated by Lewis acidic metal alkoxide complexes of tin,[2] zinc,[2a,3] aluminum,[4] or the rare-earth metals.[5] There are also several excellent nucleophilic organocatalysts, specifically those that involve N-heterocyclic carbenes.[6] Compared to several other transition metal catalysts, the biocompatibility and low toxicity of iron complexes makes them ideal as catalysts for this process, especially when the products are used for food packaging or as biodegradable devices in the biomedical industry.[7] Additionally, the redox activity of iron complexes is unique compared to other catalysts typically used for lactide polymerization. Considering recent reports demonstrating how lactide polymerization can be controlled by the electronic nature of the catalyst,[8-10] the ability to modulate the electronic properties of the catalyst through redox reactions at the metal center provides an additional dimension for the design of active and selective catalysts. Despite these advantages, there are only a few reports documenting iron catalysts for lactide polymerization,[11] none of which address the sensitivity of the polymerization reaction to the oxidation state of iron.



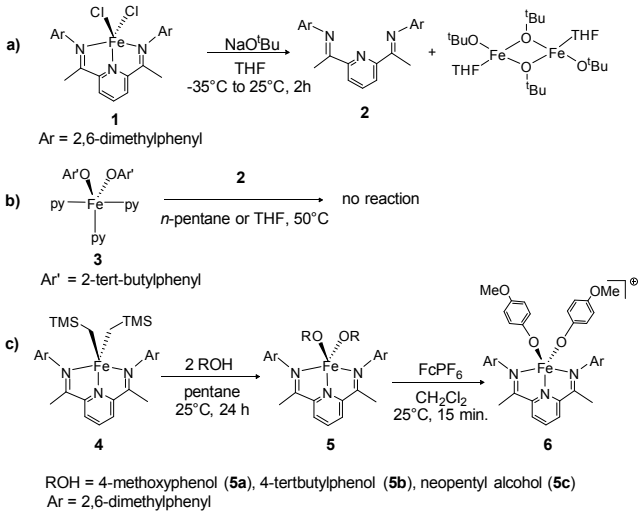
Scheme 1. Ring opening polymerization of lactide

Considering that iron bis(imino)pyridine complexes have the ability to catalyze a wide variety of transformations including ethylene polymerization and oligomerization,[12] hydrogenation and hydrosilation of alkenes,[13] and intermolecular [2+2] cycloadditions of alkenes,[14] we reasoned that they would also be good candidates as lactide polymerization catalysts. Due to their ability to stabilize multiple oxidation states, we also reasoned that bis(imino)pyridine complexes would be ideally suited to investigate the sensitivity of lactide polymerization to iron oxidation state. However, to date no transition metal complex containing bis(imino)pyridine ligands had ever been used as a catalyst for the ring opening polymeriza-

tion of lactide or any other cyclic ester. Herein, we report the synthesis of iron(II) bis(imino)pyridine alkoxide complexes and, for the first time, the application of a transition metal catalyst for lactide polymerization that contains this versatile class of ligand.

RESULTS AND DISCUSSION

Synthesis of Bis(imino)pyridine Iron Alkoxides. The majority of lactide polymerization catalysts are metal alkoxide complexes that produce polymer by a coordination-insertion mechanism for the enchainment of lactide monomers (Scheme 1). Initiation typically occurs from a metal alkoxide precursor that acts simultaneously as a Lewis acid to activate the lactide monomer and as a nucleophile to initiate ring opening.[1] Due to this precedence, we targeted bis(imino)pyridine iron bis(alkoxides) as useful precatalysts for lactide polymerization. We initially envisioned that these complexes could be synthesized through salt metathesis reactions between a bis(imino) pyridine iron dichloride complex[12b] (**1**) and alkaline or alkaline earth alkoxides. However, these reactions typically lead to loss of the bis(imino)pyridine ligand and the formation of bridging alkoxide species (Scheme 2a). We also attempted to synthesize bis(imino) pyridine iron bis(alkoxide) complexes through ligand substitution reactions between the known iron alkoxide complex **3**[15] and free bis(imino)pyridine ligand (**2**) (Scheme 2b). To our surprise, **3** was found to be largely inert to ligand substitution reactions even after prolonged heating (24 h) at 50 °C in *n*-pentane or THF.



Scheme 2. Synthesis of iron bis(imino)pyridine alkoxide complexes **5** and **6**.

Ultimately we discovered that bis(imino)pyridine iron(II) alkoxide complexes (**5**) could be obtained by protonolysis reactions of the dialkyl complex **4** with various alcohols (Scheme 2c). The protonolysis reaction was general for a variety of aromatic and aliphatic alcohols producing bis(alkoxide) complexes **5** in high yields (86-96%). Attempts to crystalize **5** were unsuccessful, but some insight into the structure of the new complexes could be obtained by following the progress of the protonation reactions using ^{1}H NMR spectroscopy. Titration of an alcohol such as neopentyl alcohol into a C_6D_6 solution of iron dialkyl **4** lead to the clean formation of a new paramagnetic complex after two equivalents of alcohol were added (Figure 1). Diagnostic peaks appeared at -174 ppm, -20 ppm, and 60 ppm (shifted from -149 ppm, -17 ppm, and 58 ppm, respectively). Concomitant with the appearance of this new species was the formation of tetramethylsilane that resulted from the protonolysis reaction (not shown in Figure 1). Integration of the tetramethylsilane relative to the *m*-pyridine protons of the bis(imino)pyridine ligand revealed that two equivalents of tetramethylsilane were liberated upon addition of two equivalents of alcohol. These results suggested that the new species was a bis(imino)pyridine iron bis(alkoxide) iron complex **5c**. Solution magnetic moment measurements using Evans' method were in line with a high spin iron(II) complex (μ_{eff} = 5.2 μ_B).

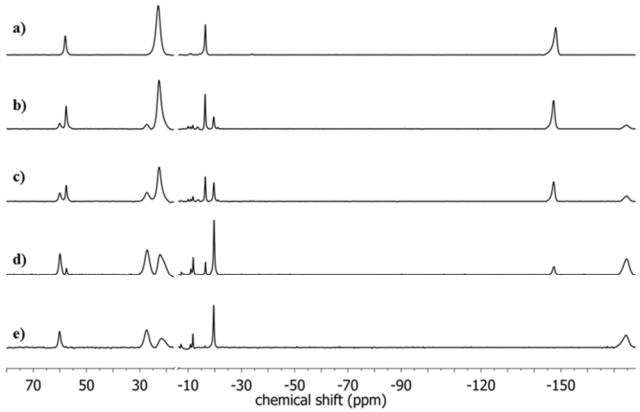


Figure 1. ^{1}H NMR spectra from: a) bis(imino)pyridine iron bis(alkyl) **4**, b) **4** + 0.5 equiv. neopentyl alcohol, c) **4** + 1 equiv. neopentyl alcohol, d) **4** + 1.5 equiv. neopentyl alcohol, e) **4** + 2 equiv. neopentyl alcohol (**5c**). The region of the NMR spectra between -10 and 20 ppm is omitted for clarity (See Figure S1 for entire spectrum).

To unambiguously determine that an iron bis(alkoxide) complex was being formed during the protonation reaction, oxidation of the iron(II) alkoxide **5a** was performed with ferrocenium (Fc) hexafluorophosphate (Scheme 2c). This reaction proceeded cleanly to give a cationic iron(III) species (**6**), which could be crystallized from benzene to give X-ray quality crystals. The crystal structure of this complex appears in Figure 2 and provides indirect evidence that monomeric bis(alkoxide) iron(II) complexes are being synthesized upon addition of alcohols to the iron(II) bis(alkyl) precursor. The iron(III) bis(alkoxide) is a five coordinate iron species that is best described as a distorted trigonal bipyramidal complex where the imine moieties comprise the axial positions of the trigonal bipyramid. The iron atom is distorted away from the ideal trigonal bipyramidal structure by being displaced out of the imine-pyridine-imine plane by 0.413 Å. The ligand bond distances and angles are typical for neutral bis(imino)pyridine and anionic phenol ligands, which suggests that oxidation occurred at the iron center rather than at one of the two potentially redox active lig-

ands.[16] This assignment was supported by the magnetic moment of the complex, which was measured at 5.9 μ_B, a typical value for a high spin iron(III) complex.

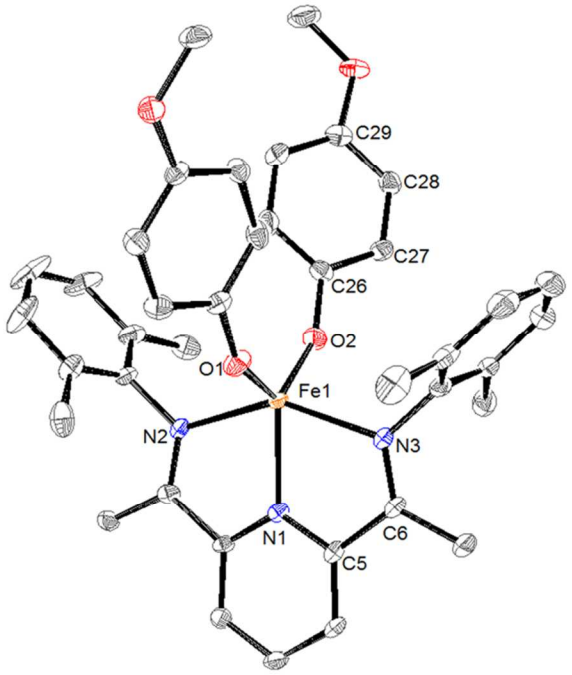


Figure 2. X-ray structure of **6** with thermal ellipsoids represented at the 50% probability level. Hydrogen atoms, solvent (benzene), and the counter ion (PF_6) are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe_1-N_1 = 2.089(3), Fe_1-N_2 = 2.172(3), Fe_1-N_3 = 2.197(3), Fe_1-O_1 = 1.816(3), Fe_1-O_2 = 1.820(3), N_3-C_6 = 1.275(5), C_5-C_6 = 1.487(5), O_2-C_{26} = 1.350(5), C_{26}-C_{27} = 1.385(6), C_{27}-C_{28} = 1.378(5), C_{28}-C_{29} = 1.385(6), N_2-Fe_1-N_3 = 147.05(11), N_2-Fe_1-N_1 = 71.73(11)

Lactide polymerization. Iron bis(imino)pyridine bis(alkoxide) complexes were then investigated for their catalytic activity toward the polymerization of (*rac*)-lactide. At a monomer to catalyst ratio of 50:1, iron(II) bis(alkoxide) complex **5a** was active for the polymerization of lactide at room temperature, giving 93% conversion of lactide after 3 hours. The polymer obtained from this reaction was analyzed by gel permeation chromatography (GPC), and, relative to polystyrene standards, revealed a number average molecular weight (M_n) of 6.8 kg/mol and a narrow polydispersity (entry 1, Table 1).

In addition to the preformed catalysts, active catalyst species could also be formed *in situ* by pretreating **4** with two equivalents of the appropriate alcohol. For example, when **4** (2 mol%) was treated with 4-methoxyphenol (4 mol%) and exposed to lactide, similar results were obtained compared to the preformed catalyst species (cf. entry 1 to entry 2, Table 1). This result suggests that the bis(alkoxide) could be successfully formed *in situ*.

Increasing the monomer to catalyst ratio resulted in polymers with increased molecular weights, but at the expense of slower monomer conversion. Efficient reactions could still be obtained at a monomer to catalyst ratio of 100:1 (entry 3, Table 1), but further increasing the ratio to 200:1 lead to reactions that were too slow to be practical at room temperature (entry 4, Table 1).

As is common for lactide polymerization reactions, the efficacy of the polymerization was sensitive to the identity of the initiating species.[1,2c,17] For polymerizations catalyzed by the iron bis(alkyl) complex **4**, high molecular weight polymer was obtained but the reaction was sluggish (entry 5, Table 1). This result could be explained with slower initiation rates and/or lower concentration of the active species in the reaction mixture.

Table 1. (*rac*)-Lactide polymerization catalyzed by iron bis(imino)pyridine complexes.[a]

Entry	*cat.*	*[LA]: [cat.][b]*	*M_n (kg/ mol)*	*M_w (kg/ mol)*	*PDI[c]*	*conv. (%)*
1	**5a**	50:1	6.8	7.9	1.16	93
2	**4**[d]	50:1	6.2	7.3	1.18	88
3[e]	**4**[d]	100:1	9.6	10.4	1.09	62
4[e]	**4**[d]	200:1	1.9	2.0	1.06	5
5[e]	**4**	50:1	15.6	22.9	1.45	14

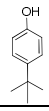
[a] Reactions were performed in dichloromethane (0.25M) for 3 h at room temperature. Conversion was determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard. Molecular weights were determined by GPC relative to polystyrene standards. [b] LA = lactide. [c] PDI = M_w/M_n [d] Reaction was carried out in the presence of 2 equivalents 4-methoxyphenol relative to **4**. [e] Reaction was carried out for 24 h.

Because the catalytically active bis(alkoxide) species could be generated *in situ*, the sensitivity of the polymerization to the identity of the initiator for lactide polymerization was investigated (Table 2). These studies revealed that the initiator has a dramatic effect on the activity of the polymerization catalyst. Electron donating phenols were found to serve as better initiators (entries 1-3), while electron withdrawing initiators resulted in little to no activity (entries 4-5). Aliphatic alcohols were tolerated in addition to phenols (entries 6-8). In fact, neopentyl alcohol was found to be the most efficient initiator of all that were studied (entry 6), although this initiator resulted in significantly lower molecular weight polymer. End group analysis of all of the polymers revealed alkyl or aryl ester end groups even for polymerizations initiated by neopentyl alcohol where formyl end groups may be expected as a result of β-hydride elimination and initiation by an iron hydride (See Supporting Information Figures S2-S3).

Identity of the active species. In order to get a better understanding of the mechanism for the polymerization reactions and to help identify the active species, we decided to carry out a time course study on the polymerization of lactide. Treatment of **1** (2 mol%) with 4-methoxyphenol (4 mol%) generated **2a** as a pre-catalyst, which was subsequently exposed to a 0.25 M solution of lactide in dichloromethane. A plot of the number average

molecular weight (M_n) versus conversion was linearly correlated, which suggests that the polymerization reaction is a living polymerization (Figure 3). However, the polydispersities observed in the reactions, while narrow, are slightly broader than what is typically observed for living polymerization reactions. Nevertheless, the linear plots of M_n vs. conversion and the narrow polydispersities observed for the polymerization demonstrate good control over molecular weight and are consistent with very few termination or transesterification events. The living characteristics of the reaction are further highlighted by the sequential addition of lactide to the polymerization, which lead to a linear increase in molecular weight for up to fifteen sequential additions (Figure 4). High molecular weight polymer (>75 kg/mol) could be obtained in this fashion with little loss in molecular weight control as is evidenced by the low polydispersities of the polymer (Figure 4).

Table 2. Lactide polymerization using **4** as the catalyst in the presence of various alcohol initiators.[a]

Entry	*Initiator*	*time (h)*	*M_n (kg/mol)*	*M_w (kg/mol)*	*PDI[b]*	*Conv. (%)*
1		3	6.2	7.3	1.18	88
2		24	7.2	8.4	1.18	95
3		24	6.2	7.5	1.21	93
4		24	1.1	1.4	1.27	6
5		24	--	--	--	0
6		2	4.1	5.2	1.27	96
7		24	4.0	5.4	1.33	96
8		24	3.6	4.7	1.21	88

[a] Reactions were performed in dichloromethane (0.25M) at room temperature with 2 mol% **4** and 4 mol% initiator. Conversion was determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard. Molecular weight was determined by GPC relative to polystyrene standards. The average of three trials is reported. [b] PDI = M_w/M_n.

Extrapolation of the M_n vs. conversion plot to zero conversion did not go through the origin (Figure 3), which is consistent with several possibilities including: a) small amounts of impurity in the lactide that promote chain transfer, b) inefficient initiation of the polymerization, or c) significant amounts of polymer backbiting resulting in unexpectedly low molecular weight at high monomer conversion.[11c] We can rule out this last possibility because little broadening in the polydispersity of the polymer was observed at high monomer conversion (cf. entries 2 to 1 and 7 to 6, Table 2). This observation is consistent with minimal transesterification reactions, which are more prevalent at high monomer conversions.[1] This property of the catalyst is particularly noteworthy because many lactide polymerization catalysts suffer from competing transesterification reactions at high monomer conversions.[11e] It is likely that the bulky 2,6-dimethyl-aryl substituted bis(imino)pyridine ligand restricts access to the transition metal center for extended chain ester moieties on the polymer but are accessible to the sterically less encumbered cyclic monomer unit.

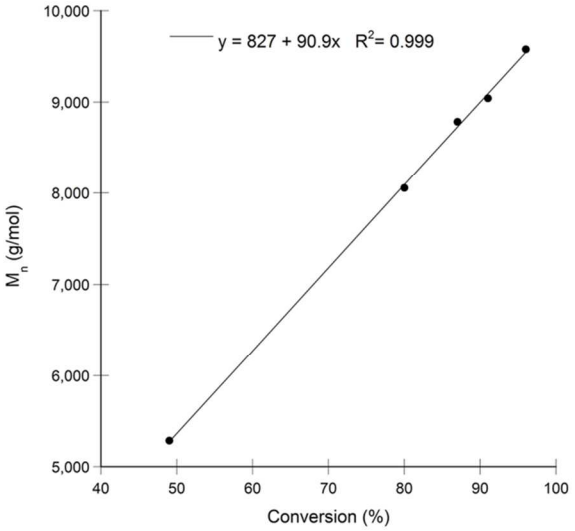


Figure 3. Number average molecular weight (M_n) versus conversion for lactide polymerizations catalyzed by **4**/4-methoxyphenol.

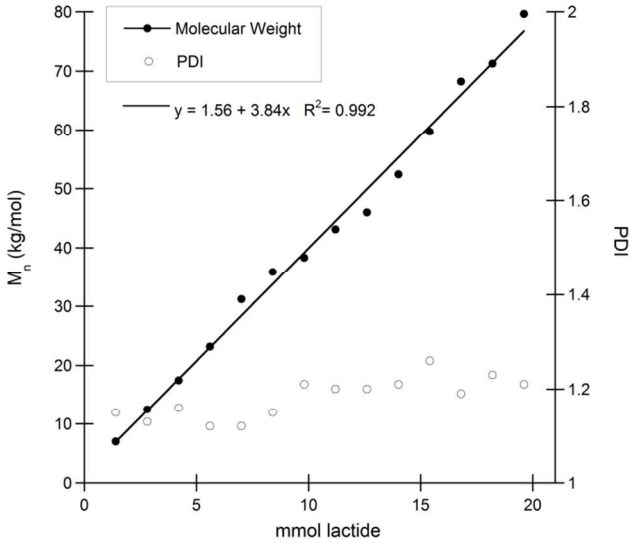


Figure 4. Sequential addition of lactide to give polymers with increased molecular weight. PDI = M_w/M_n.

Considering the propensity for iron alkoxides to form multinuclear species with expulsion of the bis(imino) pyridine ligand (*vide supra*), we considered the possibility

that the bis(imino) pyridine iron alkoxide complexes were precursors to multinuclear iron alkoxides that form under the polymerization conditions. To determine whether the bis(imino)pyridine ligand remained coordinated to iron during the polymerization reaction, we compared polymerizations initiated by **4** and 4-methoxyphenol to those initiated by $Fe(py)_2(CH_2SiMe_3)_2$ and 4-methoxyphenol. We anticipated that if the tridentate bis(imino)pyridine ligand in **4** was being replaced by alkoxide ligands to form multinuclear alkoxide species, a similar phenomenon would occur for the substitutionally more labile monodentate pyridine ligands in $Fe(py)_2(CH_2SiMe_3)_2$. Consequently, similar reaction rate, polymer molecular weight, and polydispersity would be observed for both catalyst compositions. In the event, much slower and less reproducible reaction rates were observed for $Fe(py)_2(CH_2SiMe_3)_2$ /4-methoxyphenol (k_{obs} = 0.73 x 10^{-4} ± 0.6 x 10^{-4} s^{-1}) than with **4**/4-methoxyphenol (k_{obs} = 1.66 x 10^{-4} ± 0.08 x 10^{-4} s^{-1}) (Figure 5). Additionally, the molecular weight of the polymer for reactions catalyzed by $Fe(py)_2(CH_2SiMe_3)_2$/4-methoxyphenol was lower (M_n = 4.9 kg/mol) compared to **4**/4-methoxyphenol (M_n = 6.2 kg/mol). These results demonstrate that the catalytically active species in $Fe(py)_2(CH_2SiMe_3)_2$/4-methoxyphenol is different compared to **4**/4-methoxyphenol, and suggests that the bis(imino)pyridine ligand remains coordinated to iron during polymerization reactions catalyzed by **4** with various alcohol initiators.

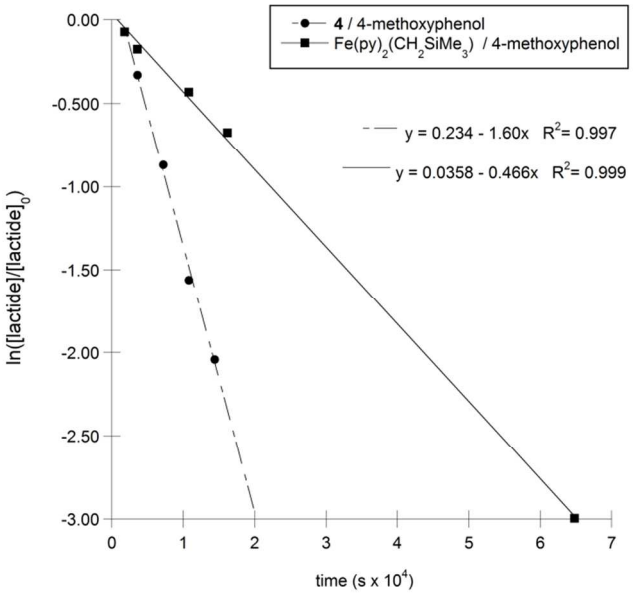


Figure 5. Reaction rate comparison between lactide polymerizations catalyzed by **4**/4-methoxyphenol (■) and $Fe(py)_2(CH_2SiMe_3)_2$/4-methoxyphenol (●).

To further characterize the identity of the active species, we addressed the issue of whether one or both alkoxide ligands can act as initiators for lactide polymerization. The dramatic effect that the identity of the initiator has on the catalyst activity suggests that only one alkoxide is involved in lactide polymerization while the other remains as an ancillary ligand for the catalyst. However, assuming the bis(imino)pyridine remains tridentate, this possibility would involve an unusual six-coordinate iron complex containing a bis(imino)pyridine ligand. As an alternative explanation, the identity of the alkoxide may affect the initiation rate without significantly altering propagation rates.

To gain some insight into this issue, we analyzed the molecular weight data that resulted from the polymerization reactions. Since the molecular weight of the polymer increases linearly with conversion, a theoretical M_n can be predicted given the conversion of the reaction, the monomer to catalyst ratio, and the number of initiating alkoxides.[11c] If one alkoxide were initiating the polymerization reaction carried out by **4**/4-methoxyphenol, a theoretical M_n of 6.8 kg/mol is expected. This compares favorably with the observed M_n of 7.2 kg/mol and suggests that only one phenol is used as an initiator in the polymerization reaction (Figure 6). A similar conclusion can be made for lactide polymerizations initiated by **4**/4-*tert*-butylphenol. In contrast, the theoretical M_n predicted for polymerization reactions initiated by one alkoxide in **4**/neopentyl alcohol would be 6.9 kg/mol whereas the observed M_n was 4.0 kg/mol. The observed M_n is much closer to the theoretical M_n predicted by a catalyst that uses two initiating alcohols (M_n = 3.5 kg/mol). Therefore, it appears that for the phenols, one initiating alkoxide is used during the polymerization reaction whereas for the aliphatic alcohols, both alkoxide ligands are used as initiating species (Figure 6).

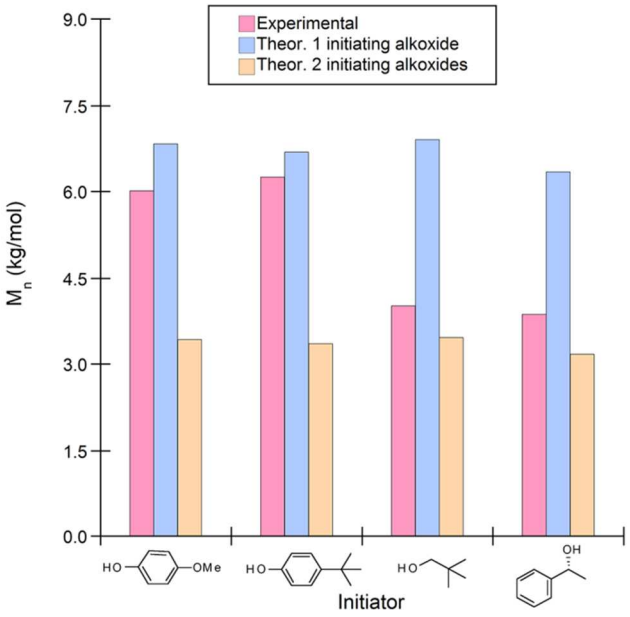


Figure 6. Comparison of experimental and theoretical molecular weights with one initiating alkoxide or two initiating alkoxides per iron center.

These results can be rationalized by realizing that the identity of the propagating species is electronically more similar to neopentyl alcohol as compared to 4-methoxyphenol. For example, the pK_a for neopentyl alcohol and the alcohol of lactic acid is ~16 and 18, respectively, whereas the pK_a for *p*-methoxy phenol is 10.2,

which is considerably more acidic. Thus, when a lactide monomer coordinates to a catalyst containing neopentoxide and a growing polymer chain, due to their similar nucleophilicities, insertions from the neopentoxide ligand occur at about the same rate as insertions from the growing polymer chain (pathway b, Figure 7). In contrast, lactide insertion for a catalyst containing an aryloxide ligand and a growing polymer chain favors insertion from the growing polymer chain because the aryloxide ligand is significantly less nucleophilic than the propagating polymer chain (pathway a, Figure 7).

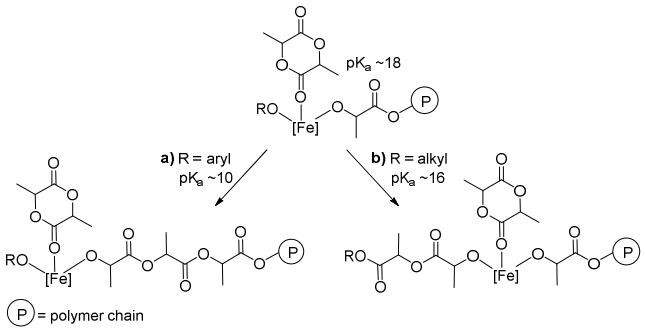


Figure 7. Polymer propagation with a) one polymer chain and one spectator alkoxide (R = aryl) and b) two polymer chains per metal center (R = alkyl).

To further assess whether one or two alkoxide ligands are involved in the polymerization reaction, we carried out the polymerization of lactide initiated by the chiral secondary alcohol (*R*)-1-phenylethanol. We reasoned that if both alkoxides were being used in the polymerization of lactide, the propagating species would be similar to the reactions carried out with neopentyl alcohol. As such, we predicted that there would be little difference in tacticity for the resulting polymer. However, if one alkoxide remains as an ancillary ligand during the polymerization, then a difference in tacticity might be observed for the reactions initiated with (*R*)-1-phenylethanol compared to neopentyl alcohol due to different amounts of stereoinduction resulting from enantiomorphic site control.[18] Analysis of the polymer tacticity from polymerizations initiated by both (*R*)-1-phenylethanol and neopentyl alcohol were found to produce atactic polymer (P_r = 0.49 and 0.51) with nearly the same relative concentrations of stereoerrors (See Supporting Information Figures S4-S5).[3b,19] This result provides further support that both alkoxides bound to iron are initiating lactide polymerization. The low stereoselectivity observed in the polymerization reactions regardless to the identity of the initiating alcohol species is noteworthy (e.g. P_r = 0.50 when 4-methoxyphenol is used as the initiator). This outcome is to be expected for a catalyst that contains an achiral ancillary ligand such as the bis(imino)pyridine ligands when there is very little stereoinduction from chain-end control. Therefore, under the reaction conditions investigated, it appears that the chiral polymer chain end has very little stereochemical influence on subsequent insertions of lactide monomer when bis(imino)pyridine ligands are used as ancillary ligands on iron.

Sensitivity of (rac)-lactide polymerization to the oxidation state of the metal. Finally, since we had access to the iron(III) bis(alkoxide) complex **6**, we decided to investigate its competency as a lactide polymerization catalyst. Previous studies have shown the ability to control lactide polymerization by oxidation and reduction reactions of ferrocene ligands attached to metals such as titanium,[8] indium,[9] or cerium.[10] The activity of the catalyst can be "switched" off and on by reversibly oxidizing or reducing the ferrocene ligands. Less common are examples where lactide polymerization is controlled by oxidation and reduction of the metal that is also the active site for polymerization, although there are two reports detailing examples of this using cerium as the metal catalyst.[10] Despite the fact that many iron(II/III) redox processes are accessible and reversible, redox switchable lactide polymerization has never been demonstrated before for an iron catalyst. In fact, a direct comparison between iron(II) and iron(III) lactide polymerization catalysts with the same ancillary ligand set has never been performed. Despite the enhanced Lewis acidity of **6** compared to **5a**, complex **6** did not show any activity for lactide polymerization after 24 hours at room temperature. This result was somewhat expected due to the acute electronic dependence observed for the iron(II) complexes where an electron-donating initiator was required for enhanced catalytic activity (*vide supra*). Oxidation of the neutral iron(II) bis(alkoxide) **5a** to the cationic iron(III) bis(alkoxide) **6** results in a significantly less electron rich metal center, so much so that lactide polymerization is completely thwarted. The reversibility of the redox reactions were demonstrated with stoichiometric reactions followed by ^{1}H NMR spectroscopy (Figure S6). Although low signal to noise complicated quantitative electrochemical analysis of **5a**, reversible redox behavior was identifiable in the cyclic voltammogram of **5a** in dichloromethane (Figure S7) with **5a** demonstrating a redox potential of approximately -0.71 V relative to Fc/Fc^+.

Considering the reversibility of the redox reaction and the complete inactivity of the iron(III) complex **6**, we then decided to see if our lactide polymerization catalysts could be controlled by changing the oxidation state of the metal center (Figure 8). The polymerization was performed with catalyst **5a** (2 mol%) until 25% conversion had been achieved. At this point, ferrocenium hexafluorophosphate (2 mol%) was added to the reaction mixture to oxidize the complex to the iron(III) species (**6**) *in situ*. The polymerization was completely shut down and no further conversion or change in polymer molecular weight (Figure 8) or molecular weight distribution (Figure S8) was observed until cobaltocene ($CoCp_2$, 2 mol%) was added to the reaction mixture to reduce the catalyst back to iron(II). At this point, the polymerization resumed with a comparable rate to that initially observed for catalyst **5a** (k_{obs} = 1.5 x 10^{-4} s^{-1} before addition of $FcPF_6$ and 2.2 x 10^{-4} s^{-1} after addition of cobaltacene). The veracity of the redox switching capabilities was further demonstrated by performing multiple redox switching without decreasing catalyst activity and with minimal impact on the polymer molecular weight distribution (Figure S9). These results

demonstrate the reversible nature of the redox event occurring at the iron center and the sensitivity of the lactide polymerization to the oxidation state of the metal center.

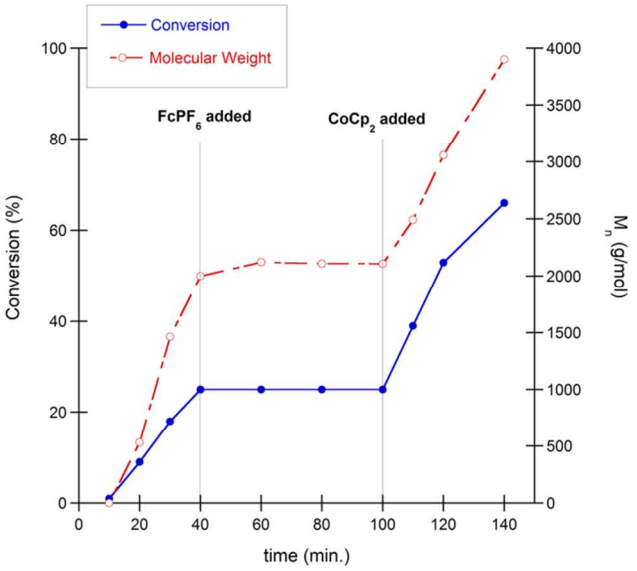


Figure 8. Polymerization of (*rac*)-lactide in the presence of **4**/4-methoxyphenol over time. At the time points labeled 40 min. and 60 min., ferrocenium hexafluorophosphate and cobaltacene were added to the reaction to oxidize and reduce the metal center, respectively.

The bis(imino)pyridine iron catalyst system provides some distinct advantages compared to other catalysts that have demonstrated redox switchable polymerization. First, catalysis is completely shut down upon oxidation of the iron center to iron(III), whereas some redox switchable catalysts demonstrate only a lowering in reaction rate upon catalyst oxidation.[8] Second, the bis(imino)pyridine ligands used in this report are easier to synthesize and modify compared to the ferrocene-based ligands that are commonly employed for redox switchable polymerization,[8,9] Finally, among the catalysts where redox switching occurs upon oxidation and reduction at the active site of polymerization,[10] the bis(imino)pyridine iron complexes display the most control over molecular weight. Whereas the cerium complexes reported by Diaconescu and coworkers demonstrate some broadening in molecular weight distribution upon redox switching,[10a] **5a** resulted in polymer with the same molecular weight and molecular weight distribution whether or not redox switching was employed.

CONCLUSIONS

Synthesis of iron(II) bis(alkoxides) supported by bis(imino)pyridine ligands was achieved by treating the bis(alkyl) iron(II) complex **4** to a variety of aliphatic and aromatic alcohols. A cationic iron(III) bis(alkoxide) complex **6** was also synthesized and structurally characterized by oxidation of **5a** with ferrocenium hexafluorophosphate.

The iron(II) complexes were found to be effective catalysts for the polymerization of (*rac*)-lactide both as the discrete iron(II) bis(alkoxide) species or via *in situ* activation from **4** and the appropriate alcohol. Activity for lactide polymerization was found to be very sensitive to the identity of the initiating alcohol with electron rich alcohols initiating lactide polymerization much more efficiently than the electron poor alcohols. Poly(lactic acid) with narrow molecular weight distributions was obtained within a few hours at room temperature, and the catalysis demonstrated several hallmarks of a living polymerization system such as the linear dependence of M_n on conversion, narrow molecular weight distributions, and linear polymer growth upon sequential addition of lactide monomer. Mechanistic experiments revealed that only one alkoxide ligand serves as an initiator for lactide polymerizations initiated by aromatic alcohols whereas both alkoxide ligands participate as initiators for catalysts initiated by aliphatic alcohols.

Finally, the iron(III) bis(alkoxide) complex **6** was completely inactive for lactide polymerization. However, the lactide polymerization reaction could be "switched" on and off by reversibly reducing and oxidizing the metal center, respectively. It is our belief that the versatility of this catalyst system is due in large part to the special properties of iron complexes supported by bis(imino) pyridine ligands. While we have no evidence for the participation of the known redox activity of the bis(imino) pyridine ligands in the polymerization of (*rac*)-lactide, we believe that the electronic and steric flexibility provided by these ancillary ligands will be useful for a variety of polymerization and copolymerization reactions.

ASSOCIATED CONTENT

Supporting Information. Experimental section, CIF file for complex **6** (CCDC 945620), characterization data for new compounds and polymers, additional polymerization data, and electrochemical characterization of **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

* Tel: 617-552-6725, Email: jeffery.byers@bc.edu

Notes

The authors declare no competing financial interest.

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Table of Contents