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Redox Control of Group 4 Metal Ring-Opening Polymerization Activity toward L-Lactide and ε-Caprolactone

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Supporting Information Placeholder

ABSTRACT: The activity of several group 4 metal alkoxide complexes supported by ferrocene-based ligands was controlled using redox reagents during the ring-opening polymerization of L-lactide and ε-caprolactone. Switching in situ between the oxidized and reduced forms of a metal complex resulted in a change in the rate of polymerization of each monomer. Opposite behavior was observed for each monomer used. One-pot copolymerization of the two monomers to give a block copolymer was also achieved.

~~Temporally switchable polymerization processes have received increased attention because they hold the promise of mimicking the selectivity exhibited by natural systems.[1-2] Allosteric,[3] chemical,[4] electrochemical,[5] photochemical,[6] and mechanochemical[7] control have been employed to turn on/off various polymerizations.[1] In the realm of chemical control, processes involving metal complexes containing redox-switchable groups are especially interesting because these groups provide a way to alter selectivity without the need for further, extensive synthetic steps to achieve ligand modification.[8] The first example using a metallocene redox switch in order to influence catalytic selectivity was reported by Wrighton's group in 1995.[9] In that seminal work, the authors showed that a rhodium complex containing cobaltocene (reduced form) is a better catalyst for the hydrogenation of olefins than the complex incorporating cobaltocenium (oxidized form). The reverse trend was observed for the hydrosilylation of acetone. Since then, several groups have reported switchable catalysts using redox-active substituents.~~Temporally switchable polymerization processes have received increased attention because they hold the promise of mimicking the selectivity exhibited by natural systems.[1-2] Allosteric,[3] chemical,[4] electrochemical,[5] photochemical,[6] and mechanochemical[7] control have been employed to turn on/off various polymerizations.[1] In the realm of chemical control, processes involving metal complexes containing redox-switchable groups are especially interesting because these groups provide a way to alter selectivity without the need for further, extensive synthetic steps to achieve ligand modification.[8] The first example using a metallocene redox switch in order to influence catalytic selectivity was reported by Wrighton's group in 1995.[9] In that seminal work, the authors showed that a rhodium complex containing cobaltocene (reduced form) is a better catalyst for the hydrogenation of olefins than the complex incorporating cobaltocenium (oxidized form). The reverse trend was observed for the hydrosilylation of acetone. Since then, several groups have reported switchable catalysts using redox-active substituents.[3-4, 10-18] However, Wrighton's report is still the only example in which both the oxidized and reduced forms of a catalyst show activity and selectivity toward different substrates. Herein, we report a class of group 4 metal alkoxide complexes supported by ferrocene-based ligands that show switchable selectivity toward L-lactide and ε-caprolactone in the oxidized and reduced forms for the corresponding ring opening polymerization processes. One-pot copolymerization of the two monomers to give block copolymers is also discussed.

In the area of switchable polymerization reactions,[~~19-22~~19-22] Long et al reported first that the rate of ring-opening polymerization of *rac*-lactide could be altered by changing the redox state of a ferrocenyl unit in a titanium salen bis(*iso*-propoxide) catalyst.[~~4~~4] We recently reported a similar behavior using a yttrium alkoxide.[~~18~~18] In both cases, a decrease in reactivity toward lactide was observed after the oxidation of the ferrocene group. However, a change from yttrium to indium brought to light the opposite behavior: while the yttrium complex loses its activity toward trimethylene carbonate upon oxidation, the corresponding indium complex showed increased activity toward the same substrate.[~~18~~18] A cerium(III)/(IV) redox switch ~~showed~~presented analogous behavior to the yttrium system and allowed us to study it using DFT calculations.[~~17~~17] Based on those results, we interpret the difference between the two oxidation states to be the result in large changes of the binding profile to the two oxidation states, i.e., for early transition metals, cationic complexes make stronger bonds with the polar substrates of interest than the neutral complexes. Guided by these results, we decided to turn to ~~zirconium~~group 4 metal complexes in order to test whether a better balance between the oxidized and reduced complexes exists, such that the cationic/oxidized states would still show activity toward polar substrates.

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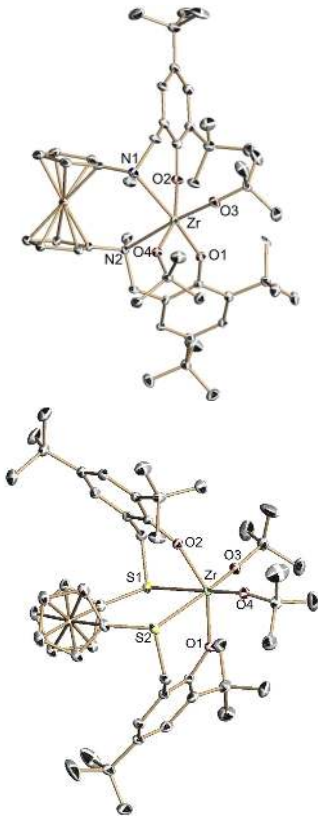
Chart 1. New supporting ferrocene-based pro-ligands.

Given the success of [OEEO]-type (E = N, O) bis(phenolato) ligands in ~~zirconium catalysis,[23-25]~~group 4 metal catalysis,[23-25] we focused on the following ~~two~~three classes of pro-ligands (Chart 1): H_2(salfan) (1,1'-di(2,4-di-*tert*-butyl-6-*N*-methylmethylenephenol)ferrocene~~) and~~), H_2(thiolfan) (1,1'-di(2,4-di-*tert*-butyl-6-thiomethylenephenol)ferrocene~~). The corresponding zirconium bis(*t*-butoxide) complexes were~~), and H_2(thiolfan*) (1,1'-di(2,4-di-*tert*-butyl-6-thiophenol)ferrocene). Compounds (salfan)Zr(O^tBu)$_2$ (**1**^{red}), (thiolfan)Zr(O^tBu)$_2$ (**2**^{red}), and (thiolfan*)Ti(O^iPr)$_2$ (**3**^{red}) were synthesized from the reaction of Zr(O^tBu)$_4$ or Ti(O^iPr)$_4$ and each of the respective pro-ligands. ~~Complexes (salfan)Zr(O^tBu)$_2$ (**1**^{red}) and (thiolfan)Zr(O^tBu)$_2$ (**2**^{red}) were~~ All three metal complexes were characterized in the solid state by single-crystal X-ray diffraction (~~Figure 1~~Figures S69-72). The two ~~*t*-butoxide~~alkoxide ligands coordinate cis to each other in ~~both~~all metal complexes; however, a difference between the two zirconium complexes is observed: both *t*-butoxide ligands are found trans to a sulphur donor in (thiolfan)Zr(O^tBu)$_2$, but, in (salfan)Zr(O^tBu)$_2$, one of them is trans to a nitrogen, while the other is found cis to both nitrogen donors. This relatively small difference in the zirconium coordination environments may cause some of the differences observed in their reactivity behavior (see below).



~~Figure 1.~~ ~~Thermal-ellipsoid (50% probability) representation of (salfan)Zr(O^tBu)$_2$ (left) and (thiolfan)Zr(O^tBu)$_2$ (right) with hydrogen atoms omitted for clarity.~~

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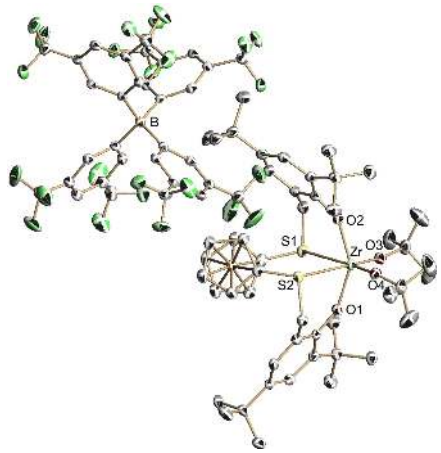
Electrochemical studies performed with ~~both~~ (salfan)Zr(O^{t}Bu)$_2$, (thiolfan)Zr(O^{t}Bu)$_2$, and (thiolfan~~)Zr(O^{t}Bu*)~~Ti(O^{i}Pr)$_2$ ($E_{1/2}$ = -0.57~~ and,~~ 0.1~~7~~07, and 0.02 V vs. ferrocene, respectively) indicated that ferrocenium salts might oxidize the ferrocene backbone in ~~the two complexes.~~these compounds. Indeed, the addition of one equivalent of acetyl ferrocenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (^{Ac}FcBAr^F) in C_6D_6 resulted within minutes in dark colored products, [(salfan)Zr(O^{t}Bu)$_2$][BAr^F] (**1^{ox}**~~) and~~), [(thiolfan)Zr(O^{t}Bu)$_2$][BAr^F] (**2^{ox}**), and [(thiolfan*)Ti(O^{i}Pr)$_2$][BAr^F] (**3^{ox}**), respectively (Eq. 1). The ^{1}H NMR spectra of these compounds indicated the formation of paramagnetic species, as expected. ~~Both compounds~~Each paramagnetic product could be reduced to the respective starting material, (salfan)Zr(O^{t}Bu)$_2$~~,~~ (thiolfan)Zr(O^{t}Bu)$_2$, and (thiolfan~~)Zr(O^{t}Bu)$_2$, respectively, within minutes in C$_6$D$_6$*)~~Ti(O^{i}Pr)$_2$, through the addition of one equivalent of CoCp$_2$ (see the supporting information for details). Compound [(thiolfan)Zr(O^{t}Bu)$_2$][BAr^F] was characterized by single-crystal X-ray diffraction (Figure ~~2~~S73).



~~**Figure 2.** Thermal-ellipsoid (50% probability) representation of [(thiolfan)Zr(O^{t}Bu)$_2$][BAr^F] with hydrogen atoms omitted for clarity.~~

Once the ferrocene and ferrocenium-based compounds were characterized, the polymerizations of L-lactide (LA) and ε-caprolactone (CL) were attempted. At 100 °C in C_6D_6, (salfan)Zr(O^{t}Bu)$_2$ polymerizes 100 equivalents of L-lactide in 2 h with 90% conversion, while less than 5% conversion was observed in the presence of [(salfan)Zr(O^{t}Bu)$_2$][BAr^F] under the same conditions. This difference in reactivity is maintained at various temperatures (80, 90, 100 °C, Table S1~~, entries 1-6). Similarly,~~). A similar trend was observed for (thiolfan)Zr(O^{t}Bu)$_2$ ~~polymerizes 100 equivalents of lactide in 8 h with~~, which achieves 93% conversion in 8 h, and (thiolfan*)Ti(O^{i}Pr)$_2$, which leads to 82% conversion in 60 h, while less than 5% conversion was observed in the presence of [(thiolfan)Zr(O^{t}Bu)$_2$][BAr^F] ~~under the same conditions~~or [(thiolfan*)Ti(O^{i}Pr)$_2$][BAr^F], respectively (Table 1).

Table 1. Reactivity of oxidized and reduced complexes toward L-lactide (LA) and ε-caprolactone (CL).

Initiator	monomer	time (h)	conversion	M_n (GPC)	M_n (calc)	PDI
1^{red}	LA	2	90%	7.31	~~7.20~~6.77	1.16
1^{ox}	LA	2	<5%	-~~-~~	-~~-~~	-~~-~~
2^{red}	LA	8	93%	7.83	~~7.20~~6.70	1.10
2^{ox}	LA	8	<5%	-~~-~~	-~~-~~	-~~-~~
3^{red}	LA	60	82%	4.49	5.90	1.14
3^{ox}	LA	36	<5%	--	-	
1^{red}	CL	24	<5%	-~~-~~	-~~-~~	-~~-~~
1^{ox}	CL	24	98%	6.95	5.~~70~~59	1.06
2^{red}	CL	1.5	57%	- -	- -	- -
2^{ox}	CL	1.5	92%	8.26	5.~~70~~24	1.14
3^{red}	CL	2	<5%	-	-	-
3^{ox}	CL	4	48%	3.20	2.70	1.12

Conditions: Monomer (0.50 mmol), initiator (0.005 mmol), oxidant (0.005 mmol, 5.5 mg), d_6-benzene as solvent (0.5 mL), 1,3,5-trimethoxybenzene as an internal standard. All experiments were performed at 100 °C, except for those corresponding to entries ~~5~~7 and ~~6~~8, which were performed at 25 °C; M_n are reported in 10^3 g/mol; PDI = M_w/M_n~~. Theoretical~~;

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theoretical M_n values were calculated by assuming ~~100% conversion of the monomer with~~ dual propagation chains; dn/dc values: PLA, 0.044 mL/g, PCL, 0.075 mL/g.

On the other hand, the activity toward ε-caprolactone shows the opposite trend: at 25 °C in C_6D_6, (salfan)Zr(O^tBu)$_2$ converts less than 5% of 100 equivalents in 24 h, while 98% conversion was observed in the presence of [(salfan)Zr(O^tBu)$_2$][BAr^F] under the same conditions (Table 1). As with L-lactide, this difference in reactivity is maintained at various temperatures with only a slight decrease in selectivity (80, 90, 100 °C, Table S2~~, entries 3-8). Similarly, (thiolfan)Zr(O^tBu)$_2$ polymerizes 100 equivalents of ε-caprolactone in 1.5 h with 57% conversion, while 92% conversion was observed in the presence of [(thiolfan)Zr(O^tBu)$_2$][BAr^F]~~). Similarly, [(thiolfan)Zr(O^tBu)$_2$][BAr^F] or [(thiolfan*)Ti(O^iPr)$_2$][BAr^F] show higher activity toward ε-caprolactone than their reduced counterparts (Table 1).

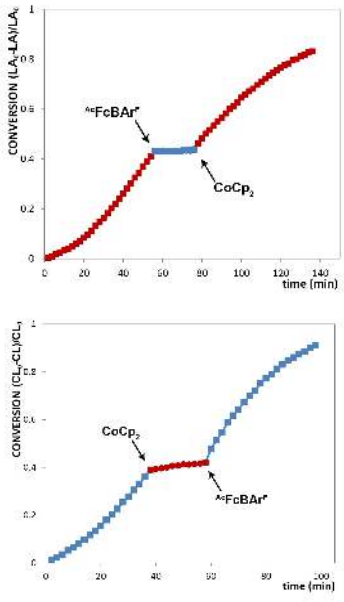
Since (salfan)Zr(O^tBu)$_2$ showed better activity and selectivity toward the two substrates, we decided to focus our selectivity studies~~–~~ on this compound. Switching in situ between the oxidized and reduced forms of (salfan)Zr(O^tBu)$_2$ was ~~studied~~examined in the presence of both monomers (Figure ~~3~~1). After 54 min at 95 °C, the polymerization of L-lactide by (salfan)Zr(O^tBu)$_2$ reached 43% conversion. Upon oxidation with $^{Ac}FcBAr^F$, the polymerization halted. Once $CoCp_2$ was added to the reaction mixture, the polymerization resumed with the same rate as before the switch was performed (see the supporting information for details, Figure ~~S47~~S56). In the case of ε-caprolactone (Figure ~~S49~~S58), starting with [(salfan)Zr(O^tBu)$_2$][BAr^F], the polymerization reached 39% conversion~~,~~ after 38 min at 80 °C. Upon reduction with $CoCp_2$, the polymerization almost stopped; once $^{Ac}FcBAr^F$ was added to the reaction mixtures, the polymerization resumed with a rate similar to that before the switch was performed ~~(Figure S49).~~. In addition, in situ switching was performed 3 consecutive times; it was found that there was minimal change in the rate of the reaction before or after changing the iron oxidation states (see the supporting information for details, Figures ~~S48~~S57 and ~~S50~~S59).

The polymers obtained from the above reactions were characterized by gel permeation chromatography (GPC). The molecular weights ~~correlate well with~~are close in value to the corresponding theoretical molecular weights and the PDIs (PDI = M_w/M_n) are ca. 1.1-1.2; this data indicates a controlled polymerization process in all cases (Table 1). End-group analysis of lactide polymerization (Figure ~~S42~~S44) indicates that this reaction proceeds through a coordination-insertion mechanism. Unfortunately, a similar study could not be performed for the polymerization of ε-caprolactone because of overlap between the *t*-butyl peaks and the alkyl peaks of ~~poly-CL.~~polycaprolactone. GPC analysis of the polymers produced from L-lactide or ε-caprolactone by switching in situ between (salfan)Zr(O^tBu)$_2$ and [(salfan)Zr(O^tBu)$_2$][BAr^F] shows that the polymerization is also controlled when using redox agents, ~~since the molecular weights correlate well to the corresponding theoretical molecular weights and the PDIs are 1.08-1.20~~with PDIs in the 1.08-1.20 range (Tables 2, S3).

Table 2. In situ switching during the polymerization of L-lactide (1.0 M in benzene) with (salfan)Zr(O^tBu)$_2$.

complex	time (min)	conversion	M_n	PDI
(salfan)Zr(O^tBu)$_2$	40	57%	4.68	1.08
add $^{Ac}FcBAr^F$	20	56%	4.24	1.09
add $CoCp_2$	40	92%	7.68	1.15

Conditions: Monomer (0.50 mmol), initiator (0.005 mmol), oxidant (0.005 mmol, 5.5 mg), 100 °C, d_6-benzene as solvent (0.5 mL), 1,3,5-trimethoxybenzene as an internal standard, experiments were performed individually; M_n are reported in 10^3 g/mol; dn/dc values: PLA, 0.044 mL/g, PCL, 0.075 mL/g; PDI = M_w/M_n.



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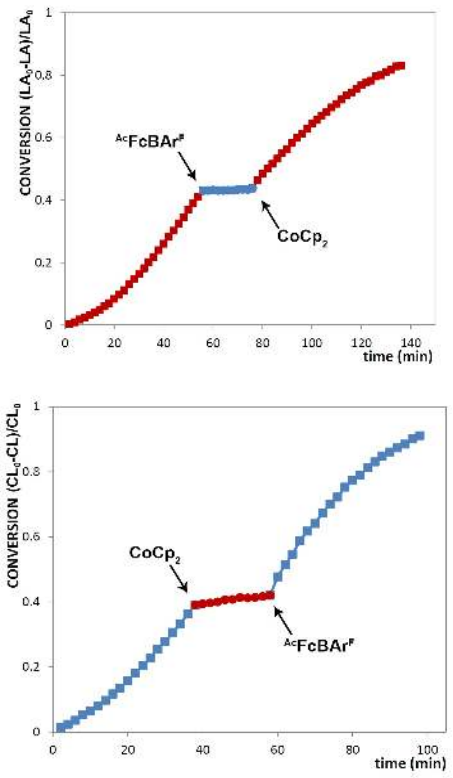
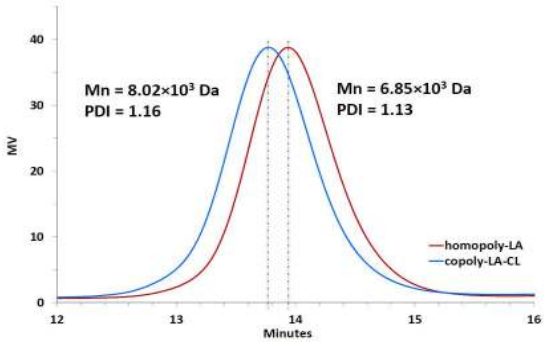


Figure 31. Plot of conversion vs. time for the polymerization of L-lactide (50 equivalents, 0.5 M) starting with (salfan)Zr(O^{t}Bu)$_2$ (top) and ε-caprolactone (100 equivalents, 1.0 M) starting with [(salfan)Zr(O^{t}Bu)$_2$][BAr^F] (bottom) in C_6D_6 using in situ oxidation and reduction with ^{Ac}FcBAr^F and $CoCp_2$, respectively.

As a proof of concept, one-pot copolymerization of L-lactide and ε-caprolactone by in situ switching the redox states of the initiator was attempted. Although L-lactide was polymerized by the reduced form of (salfan)Zr(O^{t}Bu)$_2$, polymerization of ε-caprolactone did not occur upon addition of the oxidant. We attribute this lack of reactivity to a strong coordination of L-lactide to the oxidized zirconium complex. (see below). We reasoned that athe titanium analoguecomplex might alleviate this problem since its complexes are less electrophilic than the corresponding zirconium counterparts. Unfortunately, several trials of synthesizing the direct titanium analogue of (thiolfan)Zr(O^{t}Bu)$_2$ failed, probably due to its smaller radius than that of zirconium.[26] Therefore, a similar pro-ligand, H$_2$(thiolfan*) (Chart 1), was synthesized by removing the methylene group between sulfur and the phenoxy substituent and its titanium alkoxide complex, (thiolfan*)Ti(O^{i}Pr)$_2$, successfully isolated.

Compound (thiolfan*)Ti(O^{i}Pr)$_2$ shows similar selectivity toward the individual polymerization of L-lactide and ε-caprolactone (Tables S1, S2) as its zirconium counterpart. Gratifyingly, the one-pot copolymerization of L-lactide and ε-caprolactone catalyzed by (thiolfan*)Ti(O^{i}Pr)$_2$ was successful (Eq. 2): L-lactide was first polymerized with 58% conversion at 100 °C for 36 h by the reduced form of the initiator, while almost no conversion was observed for ε-caprolactone at this stage. After addition of the oxidant at room temperature, ε-caprolactone was then polymerized with 18% conversion at 100 °C for another 2 h, while almost no conversion was observed for L-lactide during this step (Figure S43S48). The resulting block copolymer was isolated and characterized by ^{1}H NMR spectroscopy and GPC that indicate that the copolymer is best described as poly[block(LA-minor-CL)-block(CL-minor-LA)], i.e. some incorporation of the monomer that is not predominantly converted was still observed. The protons corresponding to the juncture of the two blocks could be identified by ^{1}H NMR spectroscopy (Figure S44S53), while the polymer chain extension was clearly demonstrated by comparing its GPC trace with that of the L-lactide homopolymerpolymer obtained with the same initiator before the oxidation event (Figure 42). At the same time, the PDIs of both polymers are narrow (1.13 for the homopolymer and 1.16 for the copolymer), indicating that the copolymerization process is well controlled. Attempts to increase the amount of ε-caprolactone by increasing the reaction time led to a decrease in selectivity and higher incorporation of L-lactide (Table S4).



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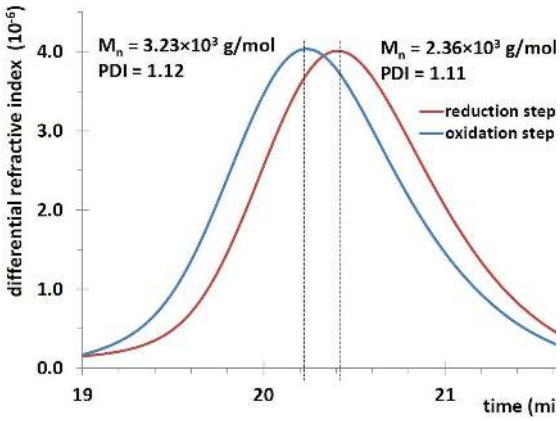

Figure 42. GPC traces of the LA-CL copolymer produced by redox switching copolymerization (blue) and the ~~LA homopolymer~~polymer produced before switching (red) using (thiolfan*)Ti(O^{i}Pr)$_2$.

We propose that the lack of copolymerization activity observed with the oxidized zirconium complexes stems from the higher Lewis acidity of zirconium compared to that of titanium that increases the bond strengths of all intermediates for the cationic compound.[17] As mentioned in the introduction, a softer Lewis acid is likely to balance this effect.[18] In addition, the reaction of a cationic yttrium complex (obtained from the oxidation of a ferrocene-based ligand) and one equivalent of L-lactide showed that the product did not react with another equivalent of L-lactide,[18] presumably because L-lactide could not open the 5-membered ring formed after the ring opening of the first molecule (compound B in Scheme S1, see also Figures S45-47 for further studies).

In conclusion, we described the first example of substrate selectivity by using redox control of a zirconium precatalyst in the ring opening polymerization of L-lactide and ε-caprolactone. The reduced forms, compounds (salfan)Zr(O^{t}Bu)$_2$~~,~~ (thiolfan)Zr(O^{t}Bu)$_2$, and (thiolfan~~)Zr(O^{t}Bu*)Ti(O^{i}Pr)$_2$,~~ showed higher activity toward lactide, while the oxidized counterparts, [(salfan)Zr(O^{t}Bu)$_2$][BAr^F~~] and~~], [(thiolfan)Zr(O^{t}Bu)$_2$][BAr^F], and [(thiolfan*)Ti(O^{i}Pr)$_2$][BAr^F] showed higher activity toward caprolactone. The precatalysts based on salfan had higher activity and selectivity toward both substrates and were studied for in situ redox switching experiments, which could be repeated three times. Individual experiments and GPC data indicate controlled polymerization processes. In addition, the one-pot copolymerization of the two monomers to give a block copolymer was also achieved by using ~~a~~the titanium analogue. Further copolymerization studies and mechanistic investigations are currently ongoing.

ASSOCIATED CONTENT

Supporting Information. Synthetic details, NMR spectra, data from kinetics, electrochemistry, and crystallographic studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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SYNOPSIS TOC

The activity of several zirconium alkoxide complexes supported by ferrocene-based ligands was controlled using redox reagents during the ring-opening polymerization of L-lactide and ε-caprolactone. Switching in situ between the oxidized and reduced forms of a specific zirconium complex resulted in a change in the rate of polymerization of each monomer. A different behavior was observed depending on the monomer used. The one-pot copolymerization of the two monomers to give a block copolymer was also achieved by using a titanium analogue.

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