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Investigation of redox switchable titanium and zirconium catalysts for the ring opening polymerization of cyclic esters and epoxides

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The synthesis and characterization of (thiolfan*)Zr(O^{t}Bu)$_2$ (thiolfan* = 1,1'-di(2,4-di-*tert*-butyl-6-thiophenoxide)ferrocene) is reported, as well as its activity toward the ring-opening polymerizations of L-lactide and ε-caprolactone. With the titanium analogue, (thiolfan*)Ti(O^{i}Pr)$_2$, diblock copolymers (AB and BA) and a triblock copolymer (ABA) were synthesized in a one-pot, redox-controlled process. Changing the metal center from titanium to zirconium has a profound influence on the reactivity profile of the corresponding reduced and oxidized catalysts in the switchable ring opening polymerization of cyclic esters and ethers.

Introduction

The use of plastics has increased twenty-fold in the past fifty years, and it is expected to double again in the next twenty years.[1] With the global increase in plastic waste, there has been an interest to create a new plastics economy, with efforts to decouple plastics from fossil fuel feedstocks by using biological sources,[2, 3] as well as creating new polymers that are biodegradable in order to decrease the amount of plastic waste ending up in our oceans.[1] In particular, both L-lactide and ε-caprolactone are cyclic esters that can be polymerized into biodegradable polymers,[4] which are used in a wide variety of applications like eco-friendly packaging,[5, 6] drug delivery,[7-9] and tissue engineering.[10] Synthesizing biodegradable polymers and copolymers in a controlled and selective manner[11] is useful because it can bring control over specific properties such as tensile strength, degradability,[12] and glass transition temperature.[13]

Many approaches[14-16] have been used to regulate the nature of polymerization reactions, such as allosteric,[17] chemical,[18-20] electrochemical,[21] photochemical,[22-25] and mechanochemical control.[26] Our group is focused on the use of chemical control via redox active systems[27-35] that switch between two stable oxidation states with different catalytic efficiencies.[36-43] Since one pre-catalyst is able to have two different active species, the cost of synthesizing two completely different metal complexes is eliminated. Catalytic selectivity can be achieved by simply oxidizing or reducing the catalyst to increase or decrease it activity toward a desired monomer. As a result, the microstructure of desired block copolymers[18, 44-50] can be tuned on a chemical basis. This approach can lead to the formation of new types of biodegradable materials[51] that will mimic, if not surpass, the properties of polymers like polystyrene or polypropylene, which are commonly being used today.

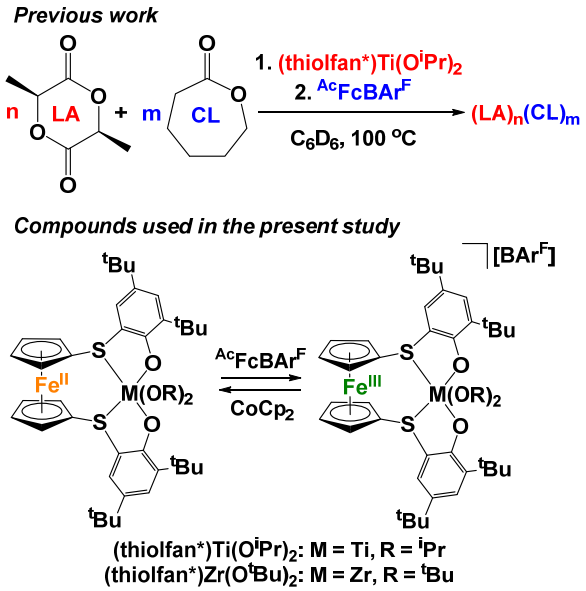

Figure 1. Copolymerization of L-lactide and ε-caprolactone by redox switchable catalysis mediated by (thiolfan*)Ti(O^{i}Pr)$_2$ (top) and drawings of (thiolfan*)Ti(O^{i}Pr)$_2$ and (thiolfan*)Zr(O^{t}Bu)$_2$ (bottom).

Previous research on this topic revealed a variety of different metal complexes that are capable of redox-controlled catalysis.[16, 30, 52] Our group was able to show that changing the oxidation state of iron in a ferrocene-based ligand modified the reactivity of a metal complex toward various monomers.[36-43] For example, (thiolfan*)Ti(O^{i}Pr)$_2$ (thiolfan* = 1,1'-di(2,4-di-*tert*-butyl-6-thiophenoxide)ferrocene), a titanium alkoxide complex supported by a ferrocene-based ligand, could catalyze the ring-opening polymerization of L-lactide (LA) in its reduced state and ε-caprolactone (CL) in its oxidized state ([(thiolfan*)Ti(O^{i}Pr)$_2$][BAr^F])

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(BAr^F = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate).[41] This was the first example showing that two forms of a catalyst have different activity and selectivity toward separate monomers, as well as demonstrating a one-pot copolymerization of two monomers to afford a block copolymer (Figure 1).

A related metal complex, (salfan)Zr(O^tBu)$_2$ (salfan = 1,1'-di(2-*tert*-butyl-6-N-methylmethylenephenoxy)ferrocene), also showed an ability to catalyze redox-switchable polymerizations toward L-lactide and ε-caprolactone,[41] and our group recently expanded its capabilities to synthesize block copolymers incorporating L-lactide, cyclohexene oxide, and ß-butyrolactone.[37] Since the use of a zirconium metal center showed promising results and an expanded substrate scope, we decided to investigate the compound analogous to (salfan)Zr(O^tBu)$_2$ supported by the thiolfan* ligand. Herein, we report the synthesis of (thiolfan*)Zr(O^tBu)$_2$ and its activity in the ring-opening polymerizations of L-lactide and ε-caprolactone. In addition, we investigate the substrate scope of (thiolfan*)Ti(O^iPr)$_2$ toward other monomers. In the original communication, the incorporation of ε-caprolactone in the PLA-PCL copolymer was only about 17%. We found out that after that point, the catalyst would polymerize both lactide and ε-caprolactone at the same rate, indicating a loss of selectivity in the catalyst. One of the goals in the present project is to probe the limitations of (thiolfan*)Ti(O^iPr)$_2$ and to polymerize ε-caprolactone further. Another goal was to expand the monomer scope of both reduced and oxidized forms of the titanium complex to form new block copolymers.

Results and Discussion

The compound (thiolfan*)Zr(O^tBu)$_2$ was synthesized by reacting H_2(thiolfan*) with Zr(O^tBu)$_4$, using a procedure similar to the synthesis of (thiolfan*)Ti(O^iPr)$_2$.[41] We found that the zirconium complex could be oxidized by ^{Ac}FcBAr^F and reduced by $CoCp_2$, both commonly used as redox agents in our group's previous studies.[36, 37, 41, 53] Since the analogous (thiolfan*)Ti(O^iPr)$_2$ was able to catalyze the ring-opening polymerization of L-lactide in its reduced state and ε-caprolactone in its oxidized state, we tested the same monomers with (thiolfan*)Zr(O^tBu)$_2$ to compare their reactivities (Table 1). A lower temperature was used to carry out polymerizations with the zirconium compound due to its tendency to decompose at high temperatures, as is discussed further below.

Table 1. Reactivity of L-lactide and ε-caprolactone towards (thiolfan*)Ti(O^iPr)$_2$ and (thiolfan*)Zr(O^tBu)$_2$.[a]

Entry	Cat.	Monomer	Time (h)	Temp (ºC)	Conv. (%)[b]	M_n	Đ
1	Ti^{red}	LA	60	100	90	8.4	1.45
2[c]	Ti^{ox}	LA	36	100	<5	-	-
3	Ti^{red}	CL	28	100	83	8.6	1.21
4	Ti^{ox}	CL	8	100	90	9.3	1.68
5	Zr^{red}	LA	60	70	95	3.5	1.45
6	Zr^{ox}	LA	20	50	12	-	-
7	Zr^{red}	CL	8	50	89	140	1.21
8	Zr^{ox}	CL	20	50	84	120	1.11

[a] Conditions: monomer (0.5 mmol), catalyst (0.005 mmol), oxidant (^{Ac}FcBAr^F, 0.005 mmol, 5.5 mg), solvent (4:1 benzene-d_6 : 1,2-difluorobenzene); hexamethylbenzene (0.025 mmol) or trimethoxybenzene (0.025 mmol) as an internal standard. Ti^{red} = (thiolfan*)Ti(O^iPr)$_2$, Ti^{ox} = [(thiolfan*)Ti(O^iPr)$_2$][BAr^F], Zr^{red} = (thiolfan*)Zr(O^tBu)$_2$, Zr^{ox} = [(thiolfan*)Zr(O^tBu)$_2$][BAr^F], LA = L-lactide, CL = ε-caprolactone. M_n are reported in 10^3 g/mol; $Đ = M_w/M_n$.
[b] Conversion was calculated by integration of polymer peaks versus those of an internal standard.
[c] Entry 2 was reported previously.[41]

Compared to (thiolfan*)Ti(O^iPr)$_2$, (thiolfan*)Zr(O^tBu)$_2$ showed a similar selectivity for L-lactide, with the reduced state (Table 1, entry 5) being more active than the oxidized state (Table 1, entry 6). However, its activity with ε-caprolactone was different from that of (thiolfan*)Ti(O^iPr)$_2$ (Table 1, entries 3, 4), and, in fact, showed the opposite selectivity. (thiolfan*)Zr(O^tBu)$_2$ in the reduced state (Table 1, entry 7) polymerized ε-caprolactone much faster than in the oxidized state (Table 1, entry 8), at a rate similar to the oxidized [(thiolfan*)Ti(O^iPr)$_2$][BAr^F] (Table 1, entry 4). To further analyze these results, experiments were performed to observe the conversion of L-lactide and ε-caprolactone over time with both catalysts (Figure 2).

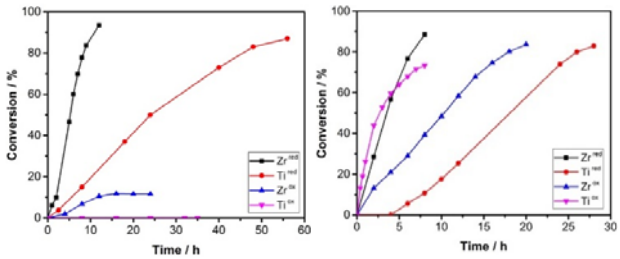

Figure 2. Conversion plots for the polymerization of L-lactide (left) and ε-caprolactone (right) with (thiolfan*)Zr(O^tBu)$_2$ (Zr^{red}), [(thiolfan*)Zr(O^tBu)$_2$][BArF] (Zr^{ox}), (thiolfan*)Ti(O^iPr)$_2$ (Ti^{red}), and [(thiolfan*)Ti(O^iPr)$_2$][BArF] (Ti^{ox}). Conversion was calculated by integration of polymer peaks versus those of an internal standard in the corresponding ^{1}H NMR spectra. The lines drawn are not a fit to the data, but rather a visual guide to illustrate the trend.

The polymerization of L-lactide with (thiolfan*)Zr(O^tBu)$_2$ was done at 100 ºC to compare its rate with that of (thiolfan*)Ti(O^iPr)$_2$, but it should be noted that (thiolfan*)Zr(O^tBu)$_2$ is unstable at 100 ºC, and it is ca. 50% decomposed after 6 hours when no substrate is present (Figure S14). Although (thiolfan*)Zr(O^tBu)$_2$ is stable at 70 ºC for over 47 hours (Figure S18), the polymerization of L-lactide is much slower, reaching 94% conversion after 60 hours (Figure S38). We observed that the polymerization of L-lactide was faster with the reduced compounds and much slower for the oxidized compounds (Figure 2, left). However, the polymerization of ε-caprolactone showed that (thiolfan*)Zr(O^tBu)$_2$ had a similar activity with the oxidized [(thiolfan*)Ti(O^iPr)$_2$][BAr^F]. Therefore, no obvious trends among the catalysts could be found. Although both titanium and

zirconium compounds share the same ligand, it is clear that the identity of the metal center and of the alkoxide group makes a difference in their activities towards different monomers.[42, 43] It was also observed from gel permeation chromatography that the polymers produced by the zirconium catalysts had very high molecular weights (Table 1, entries 7 and 8), possibly due to the propogation rate of the polymerization being faster than the rate of initiation.

Conversion studies were also carried out with L-lactide, ε-caprolactone and (thiolfan*)Ti(O^iPr)$_2$ to observe the living character of the polymerizations. Living polymerizations are desired in the synthesis of new materials, since the molecular weight and polydispersity can be controlled. We found that the polymerizations of both L-lactide and ε-caprolactone showed living characteristics (Figures S61-62).

Table 2. Reactivity of reduced and oxidized (thiolfan*)Ti(O^iPr)$_2$ toward different monomers.[a]

Entry	Cat.	Monomer	Time (h)	Temp (ºC)	Conv. (%) [b]	Mn (10^3)	Đ
1	Ti^{red}	CHO	24	100	<5	-	-
2	Ti^{ox}	CHO	2	25	99	4.6	1.46
3	Ti^{red}	VL	24	100	<5	-	-
4	Ti^{ox}	VL	12	100	50	3.1	1.18
5	Ti^{red}	BBL	16	100	<5	-	-
6	Ti^{ox}	BBL	48	100	95	5.4	1.03
7	Ti^{red}	TMC	24	100	<5	-	-
8	Ti^{ox}	TMC	22	100	91	1.4	1.12
9	Ti^{red}	OX	24	70	<5	-	-
10	Ti^{ox}	OX	4	50	95	7.4	1.08

[a] Conditions: monomer (0.5 mmol), initiator (0.005 mmol), oxidant (^{Ac}FcBAr^F, 0.005 mmol, 5.5 mg), solvent (4:1 benzene-d_6:1,2-difluorobenzene), hexamethylbenzene (0.025 mmol) as an internal standard. CHO = cyclohexene oxide, VL = δ-valerolactone, BBL = ß-butyrolactone, TMC = trimethylene carbonate, OX = oxetane.

[b] Conversion was calculated by integration of polymer peaks versus internal standard.

Since the incorporation of ε-caprolactone in the PLA-PCL copolymer was low with (thiolfan*)Ti(O^iPr)$_2$,[41] we explored its activity with other monomers to determine further possibilities for redox switchable polymerizations. Consequently, polymerizations of cyclohexene oxide, valerolactone, β-butyrolactone, trimethylene carbonate, and oxetane were attempted with the reduced and oxidized states of the titanium compound (Table 2).

All the monomers screened in this process showed almost no activity with (thiolfan*)Ti(O^iPr)$_2$ but considerable activity with [(thiolfan*)Ti(O^iPr)$_2$][BAr^F]. Overall, (thiolfan*)Ti(O^iPr)$_2$ and [(thiolfan*)Ti(O^iPr)$_2$][BAr^F] showed a similar activity toward L-lactide and CHO as the reduced/oxidized pairs of (salfan)Zr(O^tBu)$_2$[37] and (thiolfan*)Al(O^tBu)[36] and a clear difference when the activity toward VL, BBL, and TMC is considered. When we studied the mechanism of redox switchable polymerizations catalysed by (thiolfan*)Al(O^tBu),[36] we remarked that a possible reason why the reduced form is active toward L-lactide but not the oxidized form is the fact that a 5-member ring intermediate becomes too difficult to open when the catalyst is in a cationic form. We also had computational and experimental evidence showing that the mechanism of CHO polymerization is not cationic but it involves coordination-insertion, similar to the polymerization of cyclic esters. Given the divergent behavior of different catalysts toward VL, BBL, and TMC, it is difficult at the moment to explain the observed selectivity.

It is important to note that the oxidant used in these reactions, ^{Ac}FcBAr^F, can polymerize CL, VL (Table S1), and CHO[37] under the same conditions. In order to ensure that the polymers were generated from [(thiolfan*)Ti(O^iPr)$_2$][BAr^F] and not from ^{Ac}FcBAr^F, only 0.95 equivalents of ^{Ac}FcBAr^F relative to the catalyst was used to oxidize (thiolfan*)Ti(O^iPr)$_2$. Since [(thiolfan*)Ti(O^iPr)$_2$][BAr^F] is expected to have two active propagating groups, whereas ^{Ac}FcBAr^F is expected to have only one propagating group during ring-opening polymerization, the molecular weights of the polymers produced from the oxidized catalyst should be much smaller than of those produced from the oxidant when both reactions contained the same molar amount of monomer. For example, the molecular weight of PCHO produced by [(thiolfan*)Ti(O^iPr)$_2$][BAr^F] was 4,600 Da, whereas PCHO polymerized by ^{Ac}FcBAr^F gives an extremely large molecular weight of 111,400 Da, as previously reported.[37]

Based on the results from the monomer screenings (Table 2), we attempted the synthesis of different block copolymers with (thiolfan*)Ti(O^iPr)$_2$ and [(thiolfan*)Ti(O^iPr)$_2$][BAr^F] (Table 3). The in situ PLA-PCL copolymerization using the (thiolfan*)Ti(O^iPr)$_2$ red-ox switch was repeated (Table 3, entry 1) since the reaction was stopped at 17% conversion of ε-caprolactone previously.[41] However, this study only showed a slight improvement from the previous study. A closer look at this conversion profile showed that when the redox switch occurs at t = 30 hours, L-lactide polymerization halted for a period of 3 hours while ε-caprolactone was polymerized. Then, at t = 33 hours, L-lactide started polymerizing again, even while the oxidized catalyst was still present (Figure S63). A one-pot reaction with L-lactide, ε-caprolactone, and the reduced titanium species showed 86% PLA conversion and 42% PCL conversion in 60 hours (Figure S64). The same one-pot reaction with the oxidized species gave 62% PLA conversion and 36% PCL conversion in 14 hours (Figure S65). Even though the oxidized titanium species shows virtually no activity with L-lactide by itself (Table 1, entry 2, Table S2 and Figure S66), a significant activity was observed when L-lactide was in the presence of ε-caprolactone. This activity of the oxidized species towards L-lactide could offer an explanation for the increased polymerization of L-lactide at t = 33 hours in the red-ox switch experiment (Figure S63). Therefore, in a separate experiment, during the polymerization of ε-caprolactone, [(thiolfan*)Ti(O^iPr)$_2$][BAr^F] was switched back to the reduced form, (thiolfan*)Ti(O^iPr)$_2$, before L-lactide polymerized a considerable amount, and we were able to synthesize the corresponding triblock copolymer, PLA-PCL-PLA (Table 3, entry 4 and Table S3, entry 1a-c). The copolymer PCL-PLA was also attempted with an ox-red switch, but we observed the polymerizations of both monomers at a similar rate without suitable selectivity (Figure S65).

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Table 3. One pot copolymerization of different monomers using (thiolfan*)Ti(O^iPr)$_2$ (red) or [(thiolfan*)Ti(O^iPr)$_2$][BAr^F] (ox) by redox switchable catalysis.[a]

Entry	Monomer 1	Monomer 2	Monomer 3	catalyst	Time (h) [b]	Conversion (%) [c]	M_n (10^3)	Đ
1	LA	CL	-	reduced	30	71 - 11	7.24	1.02
				oxidized	3	77 - 44		
2	LA	CHO	-	reduced	16	90 - 0	11.8	1.17
				oxidized	4	90 - 99		
3	CHO	LA	-	oxidized	2	99 - 0	5.9	1.08
				reduced	9	99 - 74		
4	LA	CL	LA	reduced	36	60 - 20	8.5	1.01
				oxidized	4	68 - 34		
				reduced	7	88 - 35		

[a] Conditions: monomer (0.5 mmol), initiator (0.005 mmol), oxidant (^{Ac}FcBAr^F, 0.005 mmol, 5.5 mg), solvent (4:1 benzene-d_6:1,2-difluorobenzene), hexamethylbenzene (0.025 mmol) as an internal standard. CHO = cyclohexene oxide, VL = δ-valerolactone, BBL = ß-butyrolactone, TMC = trimethylene carbonate, OX = oxetane.

[b] Conversion times for each monomer appear in the order listed.

[c] Conversion was calculated by the integration of polymer peaks versus those of the internal standard. The conversions of each monomer appear in the order listed.

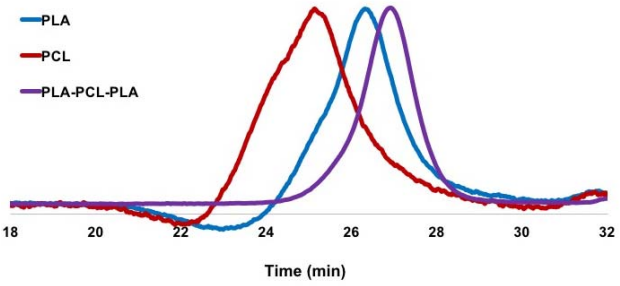

Figure 3. Comparison of homopolymer and copolymer GPC traces: blue line is the GPC trace for the polylactide homopolymer (Table 1, entry 1), red line is the GPC trace for the poly-caprolactone homopolymer (Table 1, entry 4), and the purple line is the GPC trace for the PLA-PCL-PLA block copolymer (Table 3, entry 4).

A PLA-PCHO diblock was synthesized in a one-pot reaction as well as the reversed diblock, PCHO-PLA (Table 3, entries 2, 3 and Table S3, entries 2a-b and 3a-b). Since L-lactide polymerizes at 100 ºC and cyclohexene oxide polymerizes at 25 ºC, the selectivity between the reduced and oxidized forms of (thiolfan*)Ti(O^iPr)$_2$ was enhanced further by this temperature difference.

GPC and DOSY experiments were used to determine that copolymers were formed rather than two separate homopolymers. The absence of a bimodal distribution in the GPC traces suggested that only one copolymer species was present (Figure 3 and S88) although the copolymers containing CHO show bimodal distributions (Figures S83 and S89) as was observed previously by us when employing (salfan)Zr(O^tBu)$_2$ and ^{Ac}FcBAr^F in one pot copolymerizations.[37] DOSY experiments of both homopolymers and copolymers gave further evidence that block copolymers were synthesized rather than mixtures of homopolymers. All block copolymers showed diffusion coefficients that could be clearly differentiated from those of the respective homopolymers (Figures S67-70).

Efforts to synthesize PLA-PCL copolymers with (thiolfan*)Zr(O^tBu)$_2$ were unsuccessful due to the lack of selectivity for L-lactide and ε-caprolactone between the reduced and oxidized forms of the catalyst. However, (thiolfan*)Zr(O^tBu)$_2$ showed a difference in conversion rates between L-lactide and ε-caprolactone (Figure 2), therefore, we attempted to synthesize PCL-PLA, expecting ε-caprolactone to polymerize first at 50 ºC with [(thiolfan*)Zr(O^tBu)$_2$][BAr^F], then L-lactide at 70 ºC with (thiolfan*)Zr(O^tBu)$_2$. However, we observed no polymerization of either monomer after 22 hours. Since this was an one-pot procedure, we propose that the coordination of L-lactide with [(thiolfan*)Zr(O^tBu)$_2$][BAr^F] is too strong to allow any additional monomer to insert and ring open. A similar hypothesis was proposed by us previously for (salfan)Zr(O^tBu)$_2$.[41] It should be also noted that decomposition experiments with [(thiolfan*)Zr(O^tBu)$_2$][BAr^F] in the

presence of L-lactide showed that the rate of decomposition increased in the presence of lactide (Figures S26, S33). This suggests that the coordination of L-lactide to zirconium plays a role in destabilizing the entire complex. Further studies are ongoing to determine the activity of (thiolfan*)Zr(O^tBu)$_2$ with other monomers and identify other potential substrates for copolymerization reactions.

Experimental Section

General considerations. All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or an Mbraun inert-gas glovebox. Solvents were purified with a two-state solid-state purification system by the method of Grubbs[54] and transferred to the glovebox without exposure to air. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed, and stored over activated molecular sieves prior to use. ^{1}H NMR spectra were recorded on Bruker 300, Bruker 400, or Bruker 500 spectrometers at room temperature in C_6D_6 or $CDCl_3$. Chemical shifts are reported with respect to the residual solvent peaks, 7.16 ppm (C_6D_6) and 7.26 ppm ($CDCl_3$) for ^{1}H NMR spectra. Liquid monomers and 1,2-difluorobenzene were distilled over CaH_2 and brought into the glovebox without exposure to air. Solid monomers and 1,3,5-trimethoxybenzene were recrystallized from toluene at least twice before use. 2,4-di-*tert*-butylphenol, *n*-BuLi, cobaltocene, and Zr(O^tBu)$_4$ were purchased from Sigma-Aldrich and used as received. ^{Ac}FcBAr^F,[55] H_2(thiolfan*),[36] and (thiolfan*)Ti(O^iPr)$_2$[41] were synthesized following previously published procedures. Molecular weights of polymers were determined by gel permeation chromatography using a GPC-MALS instrument at UCLA. GPC-MALS uses a Shimazu Prominence-i LC 2030C 3D equipped with an autosampler, two MZ Analysentechnik MZ-Gel SDplus LS 5 µm, 300 x 8 mm linear columns, a Wyatt DAWN HELEOS-II, and a Wyatt Optilab T-rEX. The column temperature was set at 40 °C. A flow rate of 0.70 mL/min was used and samples were dissolved in chloroform. The number average molar mass and dispersity values were found using the known concentration of the sample in chloroform with the assumption of 100% mass recovery to calculate d*n*/d*c* from the RI signal. CHN analyses were performed on an Exeter Analytical, Inc. CE-440 Elemental Analyzer.

Synthesis of (thiolfan*)Zr(O^tBu)$_2$. A toluene solution (5 mL) of Zr(OtBu)$_4$ (0.174 g, 0.455 mmol) was added drop-wise to a toluene (5 mL) solution of H_2(thiolfan*) (0.300 g, 0.455 mmol) at - 78 °C and the resulting mixture was stirred for 10 min. The reaction mixture was then warmed to ambient temperature and stirred for an additional hour. The volatiles were removed under reduced pressure, yielding the product as a yellow powder, which was dissolved in hexanes. A yellow crystalline solid was obtained after storing the solution in a -10 °C freezer. Yield: 0.300 g, 74%. ^{1}H NMR (300 MHz, 25 ºC, C_6D_6), δ (ppm): 1.282 (s, 18H, C(C*H*$_3$)$_3$), 1.380 (s, 18H, C(C*H*$_3$)$_3$), 1.772 (s, 18H, C(C*H*$_3$)$_3$), 3.697-3.710 (t, 4H, Cp*H*), 4.222 (s, 4H, Cp*H*), 7.593-7.602 (d, 2H, Ph*H*), 7.622-7.630 (d, 2H, Ph*H*). ^{13}C NMR (125 MHz, 25 ºC, C_6D_6), (ppm): 30.3 (CH(CH_3)$_2$), 32.1 (C(CH_3)$_3$), 33.1 (C(CH_3)$_3$), 34.7 (C(CH_3)$_3$), 36.3 (C(CH_3)$_3$), 70.7 (OCH(CH_3)$_2$), 78.7 (Cp-C), 90.3 (Cp-C), 119.9 (aromatic), 126.4 (aromatic), 131.0 (aromatic), 138.5 (aromatic), 141.1 (aromatic), 163.9 (aromatic). Anal. for $C_{46}H_{66}FeO_4S_2Zr\cdot(C_6H_{14})$: Calcd. C, 63.71; H, 8.23; N, 0.00. Found: C, 63.54; H, 7.96; N, 0.19.

Synthesis of [(thiolfan*)Ti(O^iPr)$_2$][BAr^F]. A toluene (5 mL) solution of (thiolfan*)Ti(O^iPr)$_2$ (30.2 mg, 0.037 mmol) and a 1,2-difluorobenzene solution (1 mL) of ^{Ac}FcBAr^F (40 mg, 0.037 mmol) were added to 5 mL of hexanes in a glass vial and stirred for 20 minutes at room temperature. Removing the volatiles under a reduced pressure yielded a dark brown oil, which was then washed 3 times with cold hexanes. The resulting oil was redissolved in benzene and was placed overnight in a -30 ºC freezer. The benzene was removed under a reduced pressure, yielding a dark brown powder as the final product. Yield: 20 mg, 41%. ^{1}H NMR (300 MHz, 25 ºC, C_6D_6), δ (ppm): -1.41 (s, 18H, C(C*H*$_3$)$_3$), -0.65 to -0.64 (d, 12H, (C*H*$_3$)$_2$CH)), 0.69 (s, 18H, C(C*H*$_3$)$_3$), 1.98 (s, 4H, Cp*H*), 3.49 (s, 4H, Cp*H*), 7.75 (s, 4H, B($F_6C_8H_2$*H*)$_4$), 8.24 (s, 8H, B(F_6C_8*H*$_2$H)$_4$), 10.43 (s, 4H, Ph*H*). Anal. for $C_{76}H_{74}BF_{24}FeO_4S_2Ti$ (1686.03 g/mol): Calcd: C, 54.14; H, 4.42. Found: C, 53.35%, H, 4.19.

Synthesis of [(thiolfan*)Zr(O^tBu)$_2$][BAr^F]. A toluene (5 mL) solution of (thiolfan*)Zr(O^tBu)$_2$ (51.5 mg, 0.05 mmol) and a 1,2-difluorobenzene solution (1 mL) of ^{Ac}FcBAr^F (62.9 mg, 0.05 mmol) were added to 5 mL of hexanes in a glass vial and stirred for 20 minutes at room temperature. Removing the volatiles under a reduced pressure yielded a dark brown oil, which was then washed 3 times with cold hexanes. The resulting product was dried under a reduced pressure and the vial was lightly tapped on the bottom to encourage formation of solids. A brown foam formed and was broken up into powder by a small metal spatula, giving the final product. Yield: 64.8 mg, 75%. ^{1}H NMR (300 MHz, 25 ºC, C_6D_6), δ (ppm): -1.28 (s, 18H, C(C*H*3)3), -0.75 (s, 18H, C(C*H*$_3$)$_3$), -0.49 (s, 18H, C(C*H*$_3$)$_3$), 7.75 (s, 4H, B($F_6C_8H_2$*H*)$_4$), 8.37 (s, 8H, B(F_6C_8*H*$_2$H)$_4$), 10.24 (s, 4H, Ph*H*), 0.5-1.5 (residual hexanes). Anal. for $C_{78}H_{78}BF_{24}FeO_4S_2Zr$ (1757.44 g/mol): Cald: C, 53.31, N, 4.47. Found: C, 52.50, H, 3.90.

Decomposition studies of (thiolfan*)Ti(O^iPr)$_2$ and (thiolfan*)Zr(O^tBu)$_2$. Under an inert atmosphere, a solution of the metal complex (5 µmol) in benzene-d_6 (0.2 mL), monomer (0.05 mmol), and a solution of the internal standard (either 1,3,5-trimethoxybenzene (0.2 equivalents to the monomer) or hexamethylbenzene (0.05 equivalents to the monomer)) in 1,2-difluorobenzene (0.1 mL) were added to a J-Young NMR tube and heated to the specified temperature using an oil bath. The NMR tube was taken out of the oil bath periodically and analyzed by ^{1}H NMR spectroscopy.

Decomposition studies of [(thiolfan*)Ti(O^iPr)$_2$][BAr^F] and [(thiolfan*)Zr(OtBu)2][BArF]. Under an inert atmosphere, a solution of the metal complex (5 µmol) in C_6D_6 (0.2 mL), a solution of ^{Ac}FcBAr^F (0.95 equivalents to the metal complex) in 1,2-difluorobenzene (0.1 mL), and internal standard (either 1,3,5-trimethoxybenzene (0.2 equivalents to the monomer) or hexamethylbenzene (0.05 equivalents to the monomer)) were added to a J-Young NMR tube. The reaction mixture was left to sit at room temperature for 30 minutes while being shaken occasionally. A small amount of monomer (0.05 mmol) was then added. The tube was sealed and brought out of the glovebox and heated to the specified temperature with an oil bath. The NMR tube was taken out of the oil bath and analyzed periodically by ^{1}H NMR spectroscopy.

NMR scale polymerizations with the reduced metal complex. Under an inert atmosphere, a solution of the metal complex (5 µmol)

in C_6D_6 (0.2 mL), a solution of the internal standard (either 1,3,5-trimethoxybenzene (0.2 equivalents to the monomer) or hexamethylbenzene (0.05 equivalents to the monomer)) in benzene-d_6 (0.2 mL) were added to a J-Young NMR tube. The reaction mixture was left to sit at room temperature for 30 minutes while being shaken occasionally. The indicated amount of monomer was then added with 0.1 mL of benzene-d_6. The tube was sealed and brought out of the glovebox and heated to the specified temperature with an oil bath. The NMR tube was taken out of the oil bath and analyzed periodically by ^{1}H NMR spectroscopy. The polymerization was stopped when the conversion reached a maximum amount. At that point, dichloromethane was added to the reaction mixture and poured into 10 mL of cold methanol to precipitate the polymer. The mixture was centrifuged for 1 hour, decanted, and dried under reduced pressure to yield the final polymer product.

NMR scale polymerizations with the oxidized metal complex. Under an inert atmosphere, a solution of the metal complex (5 µmol) in benzene-d_6 (0.2 mL), a solution of [^{Ac}Fc][BAr^F] (0.95 equivalents to the metal complex) in 1,2-difluorobenzene (0.1 mL), and a solution of the internal standard (either 1,3,5-trimethoxybenzene (0.2 equivalents to the monomer) or hexamethylbenzene (0.05 equivalents to the monomer)) in benzene-d_6 (0.2 mL) were added to a J-Young NMR tube. The reaction mixture was left at room temperature for 30 minutes while being shaken occasionally. The indicated amount of monomer was then added. The tube was sealed and brought out of the glovebox and heated to the specified temperature with an oil bath. The NMR tube was taken out of the oil bath and analyzed periodically by ^{1}H NMR spectroscopy. The polymerization was stopped when the conversion reached a maximum amount. At that point, dichloromethane was added to the reaction mixture and poured into 10 mL of cold methanol to precipitate the polymer. The mixture was centrifuged for 1 hour, decanted, and dried under reduced pressure to yield the final polymer product.

General procedure for conversion versus molecular weight studies. Under an inert atmosphere, a solution of the metal complex (5 µmol) in C_6D_6 (0.2 mL), a solution of the internal standard (hexamethylbenzene, 0.05 mmol) in benzene-d_6 (0.4 mL), and the monomer (300 equivalents to the metal complex) were added to a Schlenk tube equipped with a stir bar. For experiments involving the use of the oxidized metal complex, a solution of ^{Ac}FcBAr^F (0.95 equivalents to the metal complex) in 1,2-difluorobenzene (0.1 mL) was added to the metal complex 30 minutes prior to the addition of the monomer. The reaction mixture was then topped off with the appropriate amount of benzene-d_6 to bring the total volume to 2 mL. The tube was sealed and brought out of the glovebox and heated to the desired temperature while stirring. The Schlenk tube was brought into the glovebox periodically in order to take aliquots. For each aliquot, a small amount of the reaction mixture (about 0.2 mL) was removed, transferred to a vial, and quenched with hexanes. The volatiles were then removed under reduced pressure. The solids were redissolved in a small amount of chloroform-d and the solution was transferred to a clean NMR tube for analysis via 1H NMR spectroscopy. Following the NMR analysis, another 0.5 mL of chloroform (HPLC grade) was added to the NMR tube, and the solution was filtered through a 0.2 µm FTPE filter into a vial to be used for GPC analysis.

General procedure for polymerizations involving two monomers. Red-ox switch: Under an inert atmosphere, a solution of the metal complex (5 µmol) in C_6D_6 (0.2 mL) and a solution of the internal standard (either 1,3,5-trimethoxybenzene (0.2 equivalents to the monomer) or hexamethylbenzene (0.05 equivalents to the monomer)) in benzene-d_6 (0.2 mL) were added to a J-Young NMR tube. The reaction mixture was left to sit at room temperature for 30 minutes while being shaken occasionally. The indicated amount of monomer was then added in 0.1 mL of benzene-d_6. The tube was sealed and brought out of the glovebox and heated to the specified temperature with an oil bath. The NMR tube was taken out of the oil bath and analyzed periodically by ^{1}H NMR spectroscopy. After the specified amount of time, a solution of ^{Ac}FcBAr^F (0.95 equivalents to the metal complex) in 1,2-difluorobenzene (0.1 mL) was added. The reaction was monitored to completion by ^{1}H NMR spectroscopy.

Ox-red switch: Under an inert atmosphere, a solution of the metal complex (5 µmol) in benzene-d_6 (0.2 mL), a solution of ^{Ac}FcBAr^F (0.95 equivalents to the metal complex) in 1,2-difluorobenzene (0.1 mL), and a solution of the internal standard (either 1,3,5-trimethoxybenzene (0.2 equivalents to the monomer) or hexamethylbenzene (0.05 equivalents to the monomer)) in benzene-d_6 (0.2 mL) were added to a J-Young NMR tube. The reaction mixture was left at room temperature for 30 minutes while being shaken occasionally. The indicated amount of monomer was then added. The tube was sealed and brought out of the glovebox and heated to the specified temperature with an oil bath. The NMR tube was taken out of the oil bath and analyzed periodically by ^{1}H NMR spectroscopy. After the specified amount of time, a solution of $CoCp_2$ (5 µmol) in 1,2-difluorobenzene (0.05 mL) was added. The reaction was monitored to completion by ^{1}H NMR spectroscopy.

Red-ox-red switch: Under an inert atmosphere, a solution of the metal complex (5 µmol) in C_6D_6 (0.2 mL) and a solution of the internal standard (either 1,3,5-trimethoxybenzene (0.2 equivalents to the monomer) or hexamethylbenzene (0.05 equivalents to the monomer)) in benzene-d_6 (0.2 mL) were added to a J-Young NMR tube. The reaction mixture was left to sit at room temperature for 30 minutes while being shaken occasionally. The specified amount of monomer was then added in 0.1 mL of benzene-d_6. The tube was sealed and brought out of the glovebox and heated to the specified temperature with an oil bath. The NMR tube was taken out of the oil bath and analyzed periodically by ^{1}H NMR spectroscopy. After the specified amount of time, a solution of ^{Ac}FcBAr^F (0.95 equivalents to the metal complex) in 1,2-difluorobenzene (0.1 mL) was added under an inert atmosphere. The NMR tube was again heated to the desired temperature and monitored periodically by ^{1}H NMR spectroscopy. After another specified amount of time, a solution of $CoCp_2$ (5 µmol) in 1,2-difluorobenzene (0.05 mL) was then added under an inert atmosphere. The reaction was monitored to completion by ^{1}H NMR spectroscopy.

Conclusions

The present study allowed a direct comparison between the activity of titanium and zirconium metal complexes supported by the same ferrocene-containing ligand, thiolfan*. We described the synthesis and characterization of (thiolfan*)Zr(O^{t}Bu)$_2$, which can be oxidized and reduced with ^{Ac}FcBAr^F and $CoCp_2$, respectively. We also studied

its activity in the polymerizations of L-lactide and ε-caprolactone in both the reduced and oxidized forms. We found that L-lactide could be polymerized by both the reduced and oxidized forms of the zirconium compound, with the reduced form being much more active. The reduced compound was also more active towards ε-caprolactone compared to the oxidized compound. Overall, changing the metal center from titanium to zirconium has a profound influence on the reactivity profile of the corresponding reduced and oxidized catalysts in the switchable ring opening polymerization of cyclic esters and ethers.

Conversion studies were carried out in order to compare the activities of (thiolfan*)Zr(O^tBu)$_2$ and (thiolfan*)Ti(O^iPr)$_2$, but no clear trend could be found due to differences in selectivity with ε-caprolactone. Conversion versus molecular weight experiments were performed to verify that the polymerization processes showed living characterisitics. We were able to expand the monomer scope of (thiolfan*)Ti(O^iPr)$_2$ to other cylic esters and epoxides like cyclohexene oxide, oxetane, and ß-butyrolactone. We also synthesized copolymers containing L-lactide, ε-caprolactone, and cyclohexene oxide using a one-pot, redox switch process with (thiolfan*)Ti(O^iPr)$_2$. Homopolymers and copolymers were isolated and characterized by GPC and NMR spectroscopy. Experiments are ongoing to explore various monomer pairs as well as to probe further the selectivity of the different oxidation states of the titanium and zirconium complexes.

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References

1. *The New Plastics Economy – Rethinking the future of plastics*, World Economic Forum, Ellen MacArthur Foundation, McKinsey & Company, 2016.
2. D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388-2410.
3. G.-P. Wu, D. J. Darensbourg and X.-B. Lu, *J. Am. Chem. Soc.*, 2012, **134**, 17739-17745.
4. M. Vert, *Biomacromolecules*, 2005, **6**, 538-546.
5. V. Siracusa, P. Rocculi, S. Romani and M. D. Rosa, *Trends Food Sci. Technol.*, 2008, **19**, 634-643.
6. T. Iwata, *Angew. Chem. Int. Ed.*, 2015, **54**, 3210-3215.
7. N. Kamaly, B. Yameen, J. Wu and O. C. Farokhzad, *Chem. Rev.*, 2016, **116**, 2602-2663.
8. B. D. Ulery, L. S. Nair and C. T. Laurencin, *J. Polym. Sci. B Polym. Phys.*, 2011, **49**, 832-864.
9. C. Oerlemans, W. Bult, M. Bos, G. Storm, J. F. W. Nijsen and W. E. Hennink, *Pharm. Res.*, 2010, **27**, 2569-2589.
10. E. S. Place, J. H. George, C. K. Williams and M. M. Stevens, *Chem. Soc. Rev.*, 2009, **38**, 1139-1151.
11. J.-F. Lutz, M. Ouchi, D. R. Liu and M. Sawamoto, *Science*, 2013, **341**, 1238149.
12. H. Abe, Y. Doi, Y. Hori and T. Hagiwara, *Polymer*, 1998, **39**, 59-67.
13. J. Fagerland, A. Finne-Wistrand and D. Pappalardo, *New J. Chem.*, 2016, **40**, 7671-7679.
14. F. A. Leibfarth, K. M. Mattson, B. P. Fors, H. A. Collins and C. J. Hawker, *Angew. Chem. Int. Ed.*, 2013, **52**, 199-210.
15. A. J. Teator, D. N. Lastovickova and C. W. Bielawski, *Chem. Rev.*, 2016, **116**, 1969-1992.
16. S. M. Guillaume, E. Kirillov, Y. Sarazin and J.-F. Carpentier, *Chem. Eur. J.*, 2015, **21**, 7988-8003.
17. H. J. Yoon, J. Kuwabara, J.-H. Kim and C. A. Mirkin, *Science*, 2010, **330**, 66-69.
18. S. Paul, C. Romain, J. Shaw and C. K. Williams, *Macromolecules*, 2015, **48**, 6047-6056.
19. C. Romain and C. K. Williams, *Angew. Chem. Int. Ed.*, 2014, **53**, 1607-1610.
20. B. Liu, D. Cui and T. Tang, *Angew. Chem. Int. Ed.*, 2016, **55**, 11975-11978.
21. A. J. D. Magenau, N. C. Strandwitz, A. Gennaro and K. Matyjaszewski, *Science*, 2011, **332**, 81-84.
22. M. Tanabe, G. W. M. Vandermeulen, W. Y. Chan, P. W. Cyr, L. Vanderark, D. A. Rider and I. Manners, *Nat. Mater.*, 2006, **5**, 467-470.
23. B. P. Fors and C. J. Hawker, *Angew. Chem. Int. Ed.*, 2012, **51**, 8850-8853.
24. A. J. Teator, H. Shao, G. Lu, P. Liu and C. W. Bielawski, *Organometallics*, 2017, **36**, 490-497.
25. B. M. Neilson and C. W. Bielawski, *Chem. Commun.*, 2013, **49**, 5453-5455.
26. H. Mohapatra, M. Kleiman and A. P. Esser-Kahn, *Nat. Chem.*, 2017, **9**, 135-139.
27. I. M. Lorkovic, R. R. Duff and M. S. Wrighton, *J. Am. Chem. Soc.*, 1995, **117**, 3617-3618.
28. C. K. A. Gregson, V. C. Gibson, N. J. Long, E. L. Marshall, P. J. Oxford and A. J. P. White, *J. Am. Chem. Soc.*, 2006, **128**, 7410-7411.
29. C. Hermans, W. Rong, T. P. Spaniol and J. Okuda, *Dalton Trans.*, 2016, **45**, 8127-8133.
30. A. Sauer, J.-C. Buffet, T. P. Spaniol, H. Nagae, K. Mashima and J. Okuda, *ChemCatChem*, 2013, **5**, 1088-1091.
31. A. B. Biernesser, K. R. Delle Chiaie, J. B. Curley and J. A. Byers, *Angew. Chem. Int. Ed.*, 2016, **55**, 5251–5254.
32. A. B. Biernesser, B. Li and J. A. Byers, *J. Am. Chem. Soc.*, 2013, **135**, 16553-16560.
33. M. Chen, B. Yang and C. Chen, *Angew. Chem. Int. Ed.*, 2015, **54**, 15520-15524.
34. S. M. Shepard and P. L. Diaconescu, *Organometallics*, 2016, **35**, 2446–2453.
35. W. Huang and P. L. Diaconescu, *Inorg. Chem.*, 2016, **55**, 10013–10023.
36. J. Wei, M. N. Riffel and P. L. Diaconescu, *Macromolecules*, 2017, **50**, 1847-1861.
37. S. M. Quan, X. Wang, R. Zhang and P. L. Diaconescu, *Macromolecules*, 2016, **49**, 6768-6778.
38. M. Abubekerov, S. M. Shepard and P. L. Diaconescu, *Eur. J. Inorg. Chem.*, 2016, **2016**, 2634-2640.
39. X. Wang, J. L. Brosmer, A. Thevenon and P. L. Diaconescu, *Organometallics*, 2015, **34**, 4700–4706.
40. M. Abubekerov and P. L. Diaconescu, *Inorg. Chem.*, 2015, **54**, 1778–1784.

41. X. Wang, A. Thevenon, J. L. Brosmer, I. Yu, S. I. Khan, P. Mehrkhodavandi and P. L. Diaconescu, *J. Am. Chem. Soc.*, 2014, **136**, 11264-11267.
42. E. M. Broderick, N. Guo, T. Wu, C. S. Vogel, C. Xu, J. Sutter, J. T. Miller, K. Meyer, T. Cantat and P. L. Diaconescu, *Chem. Commun.*, 2011, **47**, 9897-9899.
43. E. M. Broderick, N. Guo, C. S. Vogel, C. Xu, J. Sutter, J. T. Miller, K. Meyer, P. Mehrkhodavandi and P. L. Diaconescu, *J. Am. Chem. Soc.*, 2011, **133**, 9278–9281.
44. V. Abetz and P. F. W. Simon, in *Block Copolymers I*, ed. V. Abetz, Springer Berlin Heidelberg, Berlin, Heidelberg, 2005, DOI: 10.1007/12_004, pp. 125-212.
45. W. Guerin, M. Helou, J.-F. Carpentier, M. Slawinski, J.-M. Brusson and S. M. Guillaume, *Polym. Chem.*, 2013, **4**, 1095-1106.
46. D. Mecerreyes, G. Moineau, P. Dubois, R. Jérôme, J. L. Hedrick, C. J. Hawker, E. E. Malmström and M. Trollsas, *Angew. Chem. Int. Ed.*, 1998, **37**, 1274-1276.
47. Y. Wang and M. A. Hillmyer, *Macromolecules*, 2000, **33**, 7395-7403.
48. I. Yu, T. Ebrahimi, S. G. Hatzikiriakos and P. Mehrkhodavandi, *Dalton Trans.*, 2015, **44**, 14248-14254.
49. D. C. Aluthge, C. Xu, N. Othman, N. Noroozi, S. G. Hatzikiriakos and P. Mehrkhodavandi, *Macromolecules*, 2013, **46**, 3965-3974.
50. Y. Zhu, C. Romain and C. K. Williams, *J. Am. Chem. Soc.*, 2015, **137**, 12179-12182.
51. A.-V. Ruzette and L. Leibler, *Nat. Mater.*, 2005, **4**, 19-31.
52. L. A. Brown, J. L. Rhinehart and B. K. Long, *ACS Catal.*, 2015, **5**, 6057-6060.
53. S. M. Quan and P. L. Diaconescu, *Chem. Commun.*, 2015, **51**, 9643 - 9646.
54. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518-1520.
55. D. Dhar, G. M. Yee, A. D. Spaeth, D. W. Boyce, H. Zhang, B. Dereli, C. J. Cramer and W. B. Tolman, *J. Am. Chem. Soc.*, 2016, **138**, 356-368.

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