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Investigation of a Zirconium Compound for Redox Switchable Ring Opening Polymerization

Ruxi Dai[a] and Paula L. Diaconescu*[a]

A zirconium compound, (salfen)Zr(O^{i}Pr)$_2$ (salfen = N,N'-bis(2,4-di-*tert*-butylphenoxy)-1,1'-ferrocenediimine), was tested as a redox switchable catalyst for the ring opening polymerization of cyclic esters and epoxides. Different activities were observed in the reduced and oxidized state, and an orthogonal switch on monomer activities could be achieved. Diblock and triblock copolymers were synthesized using an *in situ* redox switch of the catalyst oxidation state.

1. Introduction

Polymers are playing an important role in our society's everyday life, their applications ranging from plastic bags to smart phone screen protectors, and from artificial tissues to electronic wire covers.[1-4] As the polymer consumption increases every year, the "white pollution" is becoming a more and more serious environmental issue in the world.[5-8] Biodegradable polymers, as a promising alternative to the plastics in use now, have been researched intensely in the past few decades.[9-13] Poly-lactide (PLA) is an example of a material that has been proved to be environmentally friendly.[14,15] However, the properties of the homopolymers are not as diverse as those of its possible copolymers.

Block copolymerization is a method to regulate the properties of copolymers, and it is considered one of the most feasible approaches among the large number of methods available.[16-18] Although anionic or atom transfer radical polymerization can be used for the synthesis of block copolymers, these methods require additional modification steps, for example, end group modification and bifunctional initiators, especially when different types of monomers, such as LA (lactide) and CHO (cyclohexene oxide), need to be combined.[19-21] Therefore, researching methods to build block copolymers with few or no additional modification steps is necessary.

Switchable catalysis is a promising method for the construction of sequence controlled block copolymers.[22-29] In such reactions, an external trigger, such as electron transfer,[30-36] chemical reagents,[37-43] or light,[43-45] is used to toggle between two or more catalyst states, which each show orthogonal reactivity toward different monomers. In redox switchable

catalysis, the oxidation state of the catalyst can be changed by using electron transfer; different polymer blocks are synthesized by the different oxidation states of the catalyst. This method has been best applied to the ring opening polymerization of cyclic esters and ethers.[30-36,46-50]
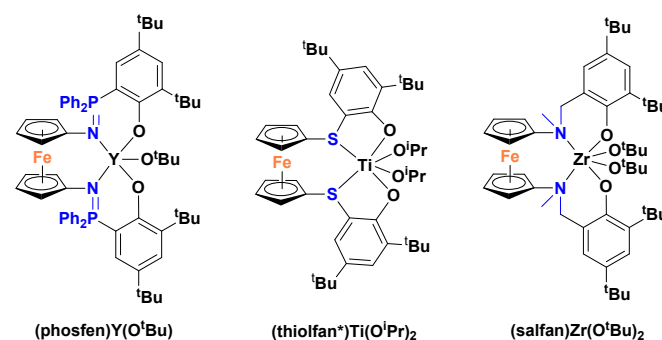

Figure 1 Previously reported metal complexes supported by ferrocene chelating ligands that perform redox switchable ring opening polymerization.

The first example of a redox controlled ring opening polymerization was first reported in 2006 by N. Long and coworkers,[51] who showed that a titanium Schiff base complex, featuring ferrocene groups appended at the periphery of the molecule, has a different activity in the polymerization of *rac*-lactide depending on the oxidation state of the ferrocene units. In 2011, our group reported a complementary study, showing that while a yttrium complex, (phosfen)Y(O^{t}Bu) (phosfen = 1,1'-di(2-*tert*-butyl-6-diphenylphosphiniminophenoxy)ferrocene, Figure 1), mimicked the results observed with the previous titanium complex, an indium analogue showed the opposite activity.[48] Further, in 2014, we reported the first example of a redox switchable polymerization system, where reversible oxidation and reduction could be done on a single precatalyst, (salfan)Zr(O^{t}Bu)$_2$ (salfan = 1,1'-di(2-*tert*-butyl-6-N-methylmethylenephenoxy)ferrocene, Figure 1), and each oxidation state could polymerize different monomers.[36] A copolymerization study based on this redox switchable system

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was reported in 2016, demonstrating an orthogonal monomer selectivity under different precatalyst oxidation states.[35] The precatalyst, (salfan)Zr(O^{t}Bu)$_2$ (Figure 1), had a ferrocene unit in the ligand backbone such that iron could be reduced and oxidized *in situ*, while the zirconium center showed a different ring opening polymerization activity depending on the monomer of choice. Mechanistic studies were reported in 2017.[33] Based on those results, we became interested in whether a compound featuring a fully conjugated ligand, (salfen)Zr(O^{i}Pr)$_2$ (salfen = N,N'-bis(2,4-di-*tert*-butylphenoxy)-1,1'-ferrocenediimine),[52] could behave similarly in redox switchable polymerization. Herein, we report its redox properties and polymerization behavior toward cyclic esters and ethers.

2. Experimental Section

2.1 General considerations

All experiments were performed in an Mbraun inert gas glovebox or under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were purified with a two-state solid-state purification system by the method of Grubbs and transferred to the glovebox inside a Schlenk flask 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 500, or Bruker 600 spectrometers at room temperature in C$_6$D$_6$. Chemical shifts are reported with respect to the residual solvent peaks, 7.16 ppm (C$_6$D$_6$) 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, and CoCp$_2$ were purchased from Sigma-Aldrich and used as received. ^{Ac}FcBAr^F (^{Ac}Fc = acetylferrocene, BAr^F = tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate)[53] and (salfen)Zr(O^{i}Pr)$_2$[52] were synthesized following previously published procedures. Molar masses of polymers were determined by size exclusion chromatography using a SEC-MALS instrument at UCLA. SEC-MALS uses a Shimazu Prominence-i LC 2030C 3D equipped with an autosampler, two MZ Analysentechnik MZ-Gel SDplus LS 5 μm, 300 × 8 mm linear columns, a Wyatt DAWN HELEOS-II, and a Wyatt Optilab T-rEX. The column temperature was set at 40 ^{o}C. A flow rate of 0.70 mL/min was used and samples were dissolved in THF. The number average molar mass and dispersity values were found using the known concentration of the sample in THF with the assumption of 100% mass recovery to calculate dn/dc from the RI signal. Cyclic voltammograms were acquired with a CH Instruments CHI630D potentiostat and recorded with CH Instruments software (version 13.04). All potentials are given with respect to the ferrocene-ferrocenium couple. CHN analyses were performed on an Exeter Analytical, Inc. CE-440 Elemental Analyzer.

2.2 Isolation of [(salfen)Zr(O^{i}Pr)$_2$][BAr^F] ([Zr]^{ox})

(salfen)Zr(O^{i}Pr)$_2$ (25.7 mg, 0.03 mmol) and ^{Ac}FcBAr^F (32.7 mg, 0.03 mmol) were each dissolved in 5 mL diethyl ether. ^{Ac}FcBAr^F was added to (salfen)Zr(O^{i}Pr)$_2$ dropwise. A dark red solution was generated instantly, then the mixture was stirred at room temperature for 1 hour. The solution was filtered through a Celite plug and concentrated under a reduced pressure. Hexanes was layered on the top of the diethyl ether solution, and the mixture was kept in the freezer for 18 hours (overnight). The top layer was removed, leaving a dark colour viscous liquid at the bottom of the vial as the product. The oil was dried under a reduced pressure for 2 hours to remove the volatiles; the product was still an oil-like, viscous liquid after drying. Yield: 49.8 mg (97%). Crystals feasible for elemental analysis were grown from benzene/hexanes solutions. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 ^{o}C), δ, ppm: 8.40 (s, 8H, *m*-C$_6$H$_3$, BAr^F), 7.68 (s, 4H, *m*-C$_6$H$_3$, BAr^F), 7.95 (s, 2H, N=C*H*), 7.82 (s, 2H, *m*-C$_6$H$_2$), 7.11 (s, 2H, *m*-C$_6$H$_2$), 4.34 (br, 8H, C$_5$H$_4$), 4.02 (s, 6H, CH(C*H$_3$*)$_2$), 3.53 (s, 6H, CH(C*H$_3$*)$_2$), 1.78 (s, 2H, C*H*(CH$_3$)$_2$), 1.62 (s, 18H, C(C*H$_3$*)$_3$), 1.25 (s, 18H, C(C*H$_3$*)$_3$). Elemental analysis for C$_{78}$H$_{76}$N$_2$O$_4$FeZrBF$_{24}$, Calcd: C, 54.49%, H, 4.45%, N, 1.63%; Found: C, 54.50%, H, 3.81%, N, 1.23%.

2.3 NMR scale polymerizations with (salfen)Zr(O^{i}Pr)$_2$ ([Zr]^{red})

Under an inert atmosphere, (salfen)Zr(O^{i}Pr)$_2$ (4 μmol), the monomer, C$_6$D$_6$ (0.6 mL), and an internal standard (hexamethylbenzene) were added to a J-Young NMR tube. The reaction mixture was left at room temperature for 5 minutes while being shaken occasionally. 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. When the reaction was done, CH$_2$Cl$_2$ was added to the mixture and then the resulting solution was poured into 10 mL of cold methanol to precipitate the polymer. The mixture was centrifuged 3 x 5 minutes, decanted, and dried under a reduced pressure to give the final polymer product.

2.4 NMR scale polymerizations with [(salfen)Zr(O^{i}Pr)$_2$][BAr^F] ([Zr]^{ox})

Under an inert atmosphere, (salfen)Zr(O^{i}Pr)$_2$ (4 μmol), C$_6$D$_6$ (0.3 mL), and an internal standard (hexamethylbenzene) were added to a J-Young NMR tube. The ^{Ac}FcBAr^F solution (0.1 mL, 40 mM in 1,2-difluorobenzene) was added and the NMR tube was shaken for 5 minutes before adding the monomer. The tube was sealed and brought out of the glovebox and left at room temperature. The NMR tube was monitored periodically by ^{1}H NMR spectroscopy. When the reaction was done, CH$_2$Cl$_2$ was added to the mixture and then the resulting solution was poured into 10 mL of cold methanol to precipitate the polymer. The mixture was centrifuged 3 x 5 minutes, decanted, and dried under a reduced pressure to give the final polymer product.

2.5 General procedure for copolymerizations

2.5.1 Redox switchable polymerization starting with [Zr]^{red}

Under an inert atmosphere, (salfen)Zr(O^{i}Pr)$_2$ (4 μmol), the monomer, C$_6$D$_6$ (0.6 mL) and the internal standard (hexamethylbenzene) were added to a J-Young NMR tube. The reaction mixture was left at room temperature for 5 minutes while being shaken occasionally. 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 monitored periodically by ^{1}H NMR spectroscopy. After the first block of the copolymer was made, the NMR tube was brought back into the glovebox. An ^{Ac}FcBAr^F solution (0.1 mL, 40 mM in 1,2-difluorobenzene) was added and the NMR tube was shaken for 5 min before adding the second monomer. The tube was sealed and brought out of the glovebox, left at room temperature and monitored periodically by ^{1}H NMR spectroscopy. When the reaction was done, CH$_2$Cl$_2$ was added to the reaction mixture and then the solution was poured into 10 mL cold methanol to precipitate the polymer. The mixture was centrifuged for 3x5 minutes, decanted, and dried under a reduced pressure to give the final polymer product.

2.5.2 Two redox switches starting with [Zr]^{red}

Under an inert atmosphere, (salfen)Zr(O^{i}Pr)$_2$ (4 μmol), the monomer, C$_6$D$_6$ (0.6 mL) and the internal standard (hexamethylbenzene) were added to a J-Young NMR tube. The reaction mixture was left at room temperature for 5 minutes while being shaken occasionally. 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 monitored periodically by ^{1}H NMR spectroscopy. After the first block of the copolymer was made, the NMR tube was brought back into the glovebox. An ^{Ac}FcBAr^F solution (0.1 mL, 40 mM in 1,2-difluorobenzene) was added and the NMR tube was shaken for 5 min before adding the second monomer. The tube was sealed and brought out of the glovebox, left at room temperature and monitored periodically by ^{1}H NMR spectroscopy. After the second block was made, the NMR tube was brought back into the glovebox. A CoCp$_2$ solution (0.1 mL, 40 mM in C$_6$D$_6$) was added to the reaction mixture and the third monomer was added. The reaction mixture was left at room temperature for 5 minutes while being shaken occasionally. 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 monitored periodically by ^{1}H NMR spectroscopy. When the reaction was done, CH$_2$Cl$_2$ was added to the reaction mixture and then the solution was poured into 10 mL cold methanol to precipitate the polymer. The mixture was centrifuged for 3x5 minutes, decanted, and dried under a reduced pressure to give the final polymer product.

2.6 Cyclic voltammetry studies of (salfen)Zr(O^{i}Pr)$_2$

Cyclic voltammetry studies were carried out in a 20 mL scintillation vial with electrodes fixed in position by a rubber stopper, in a 0.10 M TPABAr^F (TPA = tetra-n-propylammonium) solution in 1,2-difluorobenzene. A glassy carbon working electrode, a platinum reference electrode, and a silver-wire pseudoreference electrode were purchased from CH Instruments. Before each cyclic voltammogram was recorded, the working and auxiliary electrodes were polished with an aqueous suspension of 0.05 μm alumina on a Microcloth polishing pad.

3. Results and Discussion

3.1 Redox properties of (salfen)Zr(O^{i}Pr)$_2$

Compound (salfen)Zr(O^{i}Pr)$_2$ ([Zr]^{red}) was synthesized according to the reported procedures.[52] It can be oxidized *in situ* by ^{Ac}FcBAr^F (^{Ac}Fc = acetylferrocene, BAr^F = tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate) to give [(salfen)Zr(O^{i}Pr)$_2$][BAr^F] ([Zr]^{ox}) and then reduced back cleanly by CoCp$_2$ (Scheme 1, Figure S2). Cyclic voltammetry experiments were carried out, with 1,2-difluorobenzene as the solvent and TPABAr^F (TPA = tetra-n-propylammonium) as the electrolyte, showing that the compound has a redox potential of $E_{1/2}$ = 0.10 V vs ferrocene (Figure 2). When the chemical oxidation reaction was done on a 25 mg scale, a dark-red oil was collected and characterized to be [(salfen)Zr(O^{i}Pr)$_2$][BAr^r]. Such an observation of the viscous oil-like liquid appearance is consistent with several previous reports on similar ionic compounds.[32,36,54] Attempts were made to grow crystals of [(salfen)Zr(O^{i}Pr)$_2$][BAr^F] from benzene/hexanes, but single crystals could not be obtained.
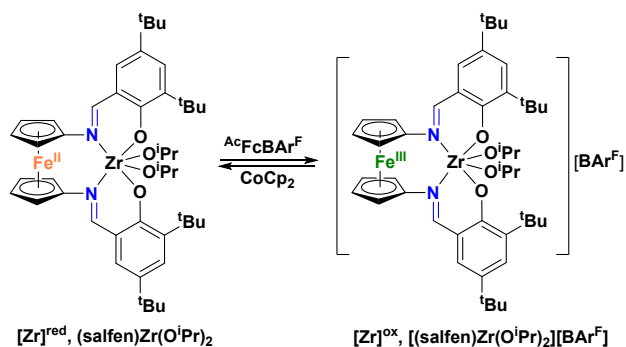
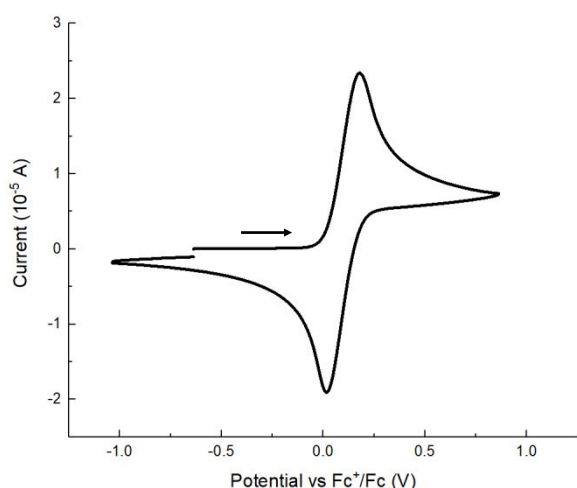**Scheme 1** Redox interconversions between [Zr]^{red} and [Zr]^{ox}.

Figure 2 Cyclic voltammogram recorded at a glassy carbon electrode at 100 mV/s in 1,2-difluorobenzene, 0.10 M TPABArᶠ containing 5.0 mM (salfen)Zr(OⁱPr)₂.

3.2 Homopolymerizations

The activity of five different cyclic esters in the presence of (salfen)Zr(OⁱPr)₂ ([Zr]ʳᵉᵈ) or the *in situ* generated oxidized species ([Zr]ᵒˣ) was tested. LA (L-lactide) and VL (δ-valerolactone) could be polymerized by [Zr]ʳᵉᵈ but not by [Zr]ᵒˣ (Table 1, entries 1-4). When [Zr]ʳᵉᵈ was added to 100 equivalents of VL, 39% conversion was achieved after heating at 100 °C for 24 hours (Table S1, entry 3). However, the polymer product could not be precipitated out with methanol, as was done in the PLA (poly-L-lactide) work up. Increasing the monomer feeding to 250 equivalents gave a higher conversion of 64%, resulting in a product that could be precipitated out from methanol as a white powder (Table 1, entry 3). TMC (1,3-trimethylene carbonate) worked with both the reduced and oxidized species (Table 1, entries 5-6). PC (propylene carbonate) and BL (β-butyrolactone) did not work with either the reduced nor oxidized species (Table 1, entries 7-10).

With regard to epoxide homopolymerization, both CHO and PO (propylene oxide) showed no conversion with [Zr]ʳᵉᵈ. However, CHO polymerization went very fast upon adding [Zr]ᵒˣ, similarly to the CHO homopolymerization catalyzed by [(salfan)Zr(OᵗBu)₂][BArᶠ].[35] PO polymerization was not as fast, 100 equivalents of monomer led to a 51% conversion after 24 hours (Table S1, entry 15), but these results indicate a higher activity of (salfen)Zr(OⁱPr)₂ than (salfan)Zr(OᵗBu)₂ toward PO.[35] Unlike PCHO, PPO (poly-propylene oxide) is usually a liquid[55,56] and could not be precipitated from methanol as a solid product. Therefore, an increased feeding of PO (1000 equivalents, Table 1, entry 14) was used and, after 24 hours at room temperature, the reaction mixture was quenched with methanol, stirring with activated carbon for 3 hours. The mixture was then filtered through Celite and the volatiles were removed under a reduced pressure, giving a viscous liquid as the product. The molecular weight obtained was much lower than the theoretical value, and the SEC (size exclusion chromatography) measurement (Figure S21) showed multiple traces, indicating that the polymerization process was not controlled.

A direct comparison with (salfan)Zr(OᵗBu)₂ (Figure 1) in order to determine the effect that the change in the supporting ligand has on polymerization activity is not possible since the alkoxide groups are different. However, we note that LA was polymerized faster (3 hours) while CHO and PO were polymerized slower with (salfan)Zr(OᵗBu)₂ (4 hours for CHO and 24 hours for PO)[35] than (salfen)Zr(OⁱPr)₂.

Table 1 Homopolymerization of different monomers with [Zr]ʳᵉᵈ and [Zr]ᵒˣ.[a]

Entry	Monomer[d]	cat.	Time (h)	Conv. (%)	Mn[e] (10⁻³ Da)	Đ
1	LA	red	24	71	6.4	1.02
2	LA	ox	24	<3	--	--
3[b]	VL	red	24	64	10.8	1.13
4	VL	ox	24	<3	--	--
5	TMC	red	24	92	10.0	1.29
6	TMC	ox	24	88	8.7	1.13
7	PC	red	24	<3	--	--
8	PC	ox	24	<3	--	--
9	BL	red	24	<3	--	--
10	BL	ox	24	<3	--	--
11	CHO	red	24	<3	--	--
12	CHO	ox	0.2	100	22.0	1.23
13	PO	red	24	<3	--	--
14[c]	PO	ox	24	88	1.8	1.62

[a] All polymerization reactions were carried out with 4 μmol precatalysts, 0.6 mL of C₆D₆ as the solvent and hexamethylbenzene as an internal standard. 100 equivalents of monomer was used unless otherwise mentioned. All reactions with [Zr]ʳᵉᵈ were done at 100 °C and all reactions with [Zr]ᵒˣ were done at 25 °C. [b] 250 equivalents of monomer was used. [c] 1000 equivalents of monomer was used. [d] VL stands for δ-valerolactone, TMC stands for 1,3-trimethylene carbonate, BL stands for β-butyrolactone, PC stands for propylene carbonate and PO stands for propylene oxide. [e] Molar masses were derived from SEC measurements.

3.3 Copolymerizations with redox control

Based on the results of the monomer screening, LA, TMC, and CHO are the three active monomers that could be used for a copolymerization study. VL was not chosen due to a too low conversion in a relatively long time. PO was not chosen because of the uncontrollable polymerization process. A diblock-copolymer, PCHO-PLA, and a triblock-copolymer, PLA-PCHO-PLA, were prepared. LA was first polymerized with [Zr]ʳᵉᵈ, and then ᴬᶜFcBArᶠ was added to the solution to give [Zr]ᵒˣ, after which, CHO was added and the PCHO-PLA copolymer was formed after an hour. The reaction time for the second block, PCHO, was much shorter than that for the previously reported system of (salfan)Zr(OᵗBu)₂ (17 hours).[35] A sequential addition was needed because the oxidant, ᴬᶜFcBArᶠ, can also polymerize CHO. Therefore, in each oxidation reaction, only 0.97 equivalents of ᴬᶜFcBArᶠ with respect to [Zr]ʳᵉᵈ was added to avoid an excess of oxidant. A discussion on the roles of the oxidant was reported by us previously.[35] Both PLA-PCHO diblock-copolymers and PLA-PCHO-PLA triblock-copolymers

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were characterized by SEC and DOSY NMR spectroscopy to confirm that their copolymeric nature (DOSY NMR spectra showed in Figures S13, S14; SEC traces in Figures S23 and S25). A mixture of PLA and PCHO homopolymers (from Table 1, entry 1 and entry 12, respectively) was also characterized by SEC and DOSY NMR spectroscopy. The SEC trace of this mixture showed two peaks and the DOSY NMR spectrum showed two species with different diffusion rates (Figures S24 and S15, respectively). Those characterizations further supported that the aforementioned PCHO-PLA and PLA-PCHO-PLA were copolymers and not mixtures of homopolymers. A comparison between SEC traces of PLA, PCHO-PLA, PLA-PCHO-PLA is shown in Figure 3.

TMC and LA is another possible combination for a copolymerization study. When TMC was polymerized first, followed by the addition of LA (Table 2, entry 3), the PLA-PTMC copolymer was formed as expected. But when LA was polymerized first followed by adding TMC to the system, TMC showed no conversion over 24 hours. Such results were consistent with previous reports that TMC cannot open the ring formed by the metal-lactide coordination-insertion intermediate.[57-61] Since TMC could be polymerized by either $[Zr]^{ox}$ or $[Zr]^{red}$, attempts were made to form the PTMC block by $[Zr]^{ox}$ (Table 2, entry 5), but the experiment did not go as expected, with the TMC conversion still 0%. These results demonstrated that the Zr-LA coordination is strong and that TMC could not be incorporated into the polymer.
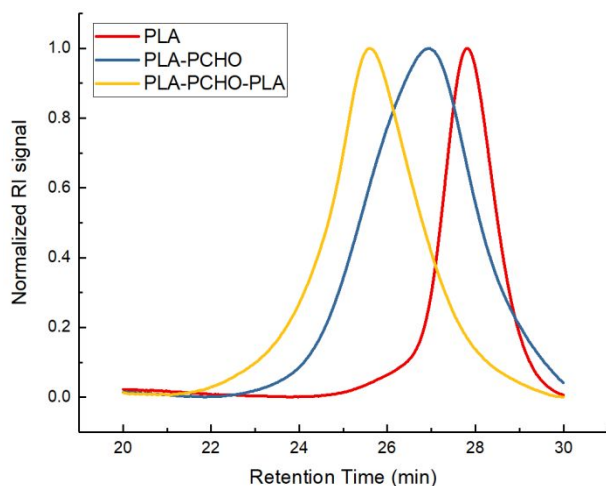

Figure 3 SEC traces of PLA homopolymer, PLA-PCHO diblock and PLA-PCHO-PLA triblock copolymers.

Table 2 Redox controlled copolymerization studies.[a]

Entry	Monomer	Catalyst[b]	Conv. (%)	Time (h)	Đ
1	LA-CHO	red-ox	70-100	24-1	1.37
2	LA-CHO-LA	red-ox-red	66-100-88	24-1-16	1.55
3	TMC-LA	red-red	60-87	16-24	1.09
4	LA-TMC	red-red	70-0	24-24	--
5	LA-TMC	red-ox	70-0	24-24	--

[a] All polymerization reactions were carried out with 4 μmol precatalyst, 0.6 mL of C_6D_6 as a solvent and hexamethylbenzene as an internal standard. 100 equivalents of monomer were used unless otherwise mentioned. All reactions with the reduced species, $(salfen)Zr(O^iPr)_2$, were done at 100 °C and all reactions with the oxidized species, $[(salfen)Zr(O^iPr)_2][BAr^F]$, were done at 25 °C. [b] "red" means that $[Zr]^{red}$ was used as a precatalyst, "ox" means that $[Zr]^{ox}$ was generated *in situ*.

4. Conclusions

Compound $(salfen)Zr(O^iPr)_2$ was tested as a redox switchable precatalyst for the ring opening polymerization and copolymerization of cyclic esters and ethers. Different monomers were tested for homopolymerization reactions with the oxidized and reduced states of the precatalyst. LA, VL, and TMC could be polymerized by $[Zr]^{red}$, while CHO, PO could be polymerized by $[Zr]^{ox}$. A PCHO-PLA diblock copolymer and a PLA-PCHO-PLA triblock copolymer were prepared and characterized by SEC and DOSY NMR spectroscopy. The preparation of PLA-PTMC copolymers was attempted but it was not successful.

In comparison to the two oxidation states of $(salfan)Zr(O^tBu)_2$, LA homopolymerization was slower with $(salfen)Zr(O^iPr)_2$, while PO and CHO homopolymerizations were faster with $[(salfen)Zr(O^iPr)_2][BAr^F]$. Such difference was more significant when carrying out a PLA-PCHO copolymerization, when with $(salfan)Zr(O^tBu)_2$ the PLA block was finished in 3 h and the CHO block in 17 h, while with $(salfen)Zr(O^iPr)_2$ the LA block was prepared in 24 h and the CHO block in 1 h. We are currently studying other catalyst modifications in order to understand further the effect that the supporting ligand has on redox switchable catalysis.

Conflicts of interest

There are no conflicts of interest.

Acknowledgments

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TOC graphic:
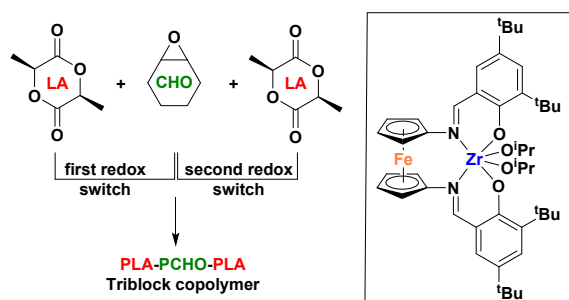
TOC sentence: Redox switchable catalysis with a ferrocene Schiff base zirconium complex allowed the synthesis of diblock and triblock copolymers.