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Redox Switchable Copolymerization of Cyclic Esters and Epoxides by a Zirconium Complex

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ABSTRACT: A zirconium precatalyst, (salfan)Zr(O^{t}Bu)$_2$ (salfan = 1,1'-di(2-*tert*-butyl-6-*N*-methyl-methylenephenoxy)ferrocene), shows activity for the redox controlled block copolymerization of L-lactide and cyclohexene oxide. The role of the oxidant is examined and several diblock (AB, BA) and triblock copolymers (ABA and BAB) were synthesized and characterized.

Introduction

Synthetic polymers are ubiquitous in today's world. Their applications range from everyday items such as molded car interiors and plastic utensils to specialty objects like absorbable medical sutures and drug delivery materials.[1] Most plastics are derived from petroleum feedstocks and are non-biodegradable, but there is a growing sector of bio-sourced and biodegradable materials that is beginning to replace environmentally hostile substances.[2] Aliphatic polyesters and polyethers are particularly appealing because they can be prepared in a highly controlled fashion by the ring-opening polymerization of bio-derived lactones, lactides, and epoxides.[1a, 2a] In general, the properties of polyesters and polyethers formed from only one monomer (homopolymers) are not as diverse as those of polymers made from multiple monomers (copolymers).[1c, 3] Various copolymer

structures exist and can be envisioned, ranging from a random sequence of monomers (A and B) to precisely controlled positions along the polymer chain.[4]

AB diblock and ABA triblock copolymers have emerged as some of the most common types of copolymers due to the number of methods available for their preparation. Living polymerization mechanisms such as atom transfer free radical polymerization, reversible addition fragmentation chain transfer, coordination-insertion, and anionic or cationic ring opening polymerization combined with step-growth techniques such as telechelic polymerization,[5] end-group modification,[6] and multi-functional initiators[7] have allowed a greater degree of control over polymer block lengths than ever before.

However, few methods exist that do not require additional modification steps in order to achieve a precise control of the copolymer structure.[8] Our group's aim is to design catalyst systems that can create block copolymers[8b, 9] by selectively polymerizing monomers in different oxidation states.[9a, 9b, 10]
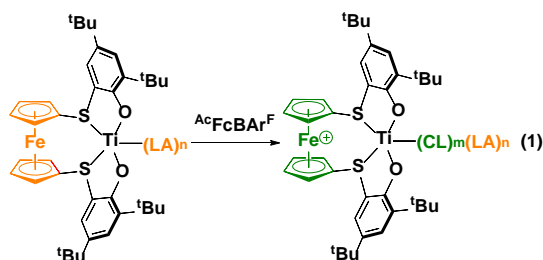
Recently, we reported the first example of switching in situ between the reduced ((salfan)Zr(O^{t}Bu)$_2$, salfan = 1,1'-di(2-*tert*-butyl-6-*N*-methylmethylenephenoxy)ferrocene) and oxidized ([(salfan)Zr(O^{t}Bu)$_2$][BAr$^F_4$]) forms of a metal complex that resulted in a change in the rate of polymerization of L-lactide (LA) and ε-caprolactone (CL), respectively.[8b] One-pot copolymerization of the two monomers (Eq 1) to give a block copolymer was also achieved by using a titanium

complex, (thiolfan*)Ti(O^{i}Pr)$_2$ (thiolfan* = 1,1'-di(2-*tert*-butyl-6-thiophenoxy)ferrocene). Unfortunately, the activity was low and the incorporation of ε-caprolactone was only about 17% before both monomers were polymerized at comparable rates by the oxidized catalyst. Herein, we report the redox switchable copolymerization[8b, 11] of L-lactide or β-butyrolactone (A) and epoxides (B) and the formation of ABA or BAB type copolymers by using a zirconium alkoxide complex supported by a ferrocene-based ligand, (salfan)Zr(O^{t}Bu)$_2$. The synthesis of diblock PLA/PCHO copolymers using a bis(imino)pyridine iron complex was recently reported by using a redox switch at the metal performing the polymerization reactions.[11]

Results and discussion

The synthesis of (salfan)Zr(O^{t}Bu)$_2$ was reported previously.[8b] While studying the influence that the solvent has on polymerization activity, we noticed that [(salfan)Zr(O^{t}Bu)$_2$][BAr$^F_4$] can polymerize THF (Figure S1). Therefore, we reasoned that [(salfan)Zr(O^{t}Bu)$_2$][BAr$^F_4$] may also ring-open polymerize other cyclic ethers (Table 1). Cyclohexene oxide stood out as a highly active orthogonal partner for L-lactide since no conversion is observed with (salfan)Zr(O^{t}Bu)$_2$ after 24 h (Table 1, entry 7), while [(salfan)Zr(O^{t}Bu)$_2$][BAr$^F_4$] polymerizes 95% of it in 1.5 h (Table 1, entry 8). Although in low conversion, propylene oxide (Table 1, entry 10) and oxetane (Table 1, entry 12) showed slightly higher activity with [(salfan)Zr(O^{t}Bu)$_2$][BAr$^F_4$] than (salfan)Zr(O^{t}Bu)$_2$. A similar selectivity to that previously reported for L-lactide[8b] (Table 1, entry 1) was observed for β-butyrolactone: (salfan)Zr(O^{t}Bu)$_2$ polymerizes 96% of the monomer (Table 1, entry 3), while [(salfan)Zr(O^{t}Bu)$_2$][BAr$^F_4$] converts only 11% of it (Table 1, entry 4). Almost no reactivity was observed toward succinic anhydride in the presence of either precatalyst (Table 1, entries 5-6).

Several studies were conducted to probe the possibility of carrying out redox switchable copolymerizations. Conversion studies were carried out to determine CHO and LA's potential for a controlled redox switchable copolymerization. The reversibility of the CHO polymerization was demonstrated by an "on-off-on" polymerization (Figure S109), where the polymerization was turned "off" by the addition of a reductant ($CoCp_2$) and turned back "on" by the addition of an oxidant ($^{Ac}FcBAr^F$). The corresponding LA "on-off-on" polymerization was previously reported.[8b] Since living polymerizations are important toward controlling the molecular weight and structure of multi-block copolymers, the living character of LA and CHO homopolymerizations was determined by plotting M_n versus percent conversion. The polymerization of LA by (salfan)Zr(O^{t}Bu)$_2$ was found to be living (Figure S110), while the polymerization of CHO by [(salfan)Zr(O^{t}Bu)$_2$][BAr^F] was not (Figure S111). Furthermore, while probing the effect that the presence of the other monomer has on polymerization rates, it was found that the polymerization of LA is faster in the presence of CHO (Figure S112), while the polymerization of CHO is faster in the absence of LA (Figure S113).

Table 1. Polymerization of different monomers with (salfan)Zr(O^{t}Bu)$_2$ (red) and [(salfan)Zr(O^{t}Bu)$_2$][BAr$^F_4$] (ox).

Entry	Catalyst	Monomer	Time	Conversion[a]
1	red	LA	3 h	93%
2	ox	LA	24 h	0
3	red	BBL	24 h	94%
4	ox	BBL	24 h	11%
5	red	SA	24 h	<5%
6	ox	SA	24 h	0
7	red	CHO	24 h	0
8	ox	CHO	1.5 h	95%
9	red	PO	24 h	0
10	ox	PO	24 h	16%
11	red	OX	24 h	0
12	ox	OX	24 h	10%

Conditions: monomer (0.50 mmol), initiator (0.005 mmol), oxidant (^{Ac}FcBAr^F, 0.005 mmol, 5.5 mg), 100 °C, C_6D_6 as a solvent (0.5 mL), 1,3,5- trimethoxybenzene as an internal standard. LA = L-lactide, BBL = β-butyrolactone, PO = propylene oxide, OX = oxetane, SA = succinic anhydride, CHO = cyclohexene oxide, SO = styrene oxide.

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

Table 2. One-pot copolymerization of two different monomers by (salfan)Zr(O^{t}Bu)$_2$ (red) or [(salfan)Zr(O^{t}Bu)$_2$][BAr$^F_4$] (ox).

Entry	Monomer 1	Monomer 2	Catalyst	Conversion[a]	M_n[b]	PDI[c]	Figures
1	BBL	CHO	red	78%-0%	4.8	1.22	S14, S114
2	BBL	CHO	red-ox	86%-92%	4.2	1.44	S15, S115
3	BBL	CHO	ox	0%-97%	8.3	1.51	S16, S116
4	BBL	CHO	ox-red	69%-97%	9.7	1.55	S17, S117
5	LA	PO	ox	9%-trace	-	-	S18
6	LA	PO	ox-red	95%-trace	16.4	1.65	S19, S118
7	LA	OX	ox	9%-trace	-	-	S20
8	LA	OX	ox-red	88%-trace	14.1	1.66	S21, S119
9	LA	CHO	red	45%-0%	8.0	1.13	S22, S120
10	LA	CHO	red-ox	45%-75%	7.6	1.29	S23, S121
11	LA	CHO	ox	trace-54%	5.5	1.54	S24, S122
12	LA	CHO	ox-red	85%-70%	12.3	1.44	S25, S123

Notes. Conditions: monomer (0.50 mmol), initiator (0.005 mmol), oxidant ($^{Ac}FcBAr^F$, 0.005 mmol, 5.5 mg), 100 °C, solvent (4 : 1 benzene-d_6: 1,2-difluorobenzene), 1,3,5-trimethoxybenzene as an internal standard. LA = L-lactide, BBL = β-butyrolactone, PO = propylene oxide, OX = oxetane, CHO = cyclohexene oxide, SO = styrene oxide.

In order to determine whether the orthogonal behavior would persist in a polymerization with both monomers present, we evaluated several combinations of epoxides and L-lactide or β-butyr-olactone (Table 2). For example, the combination of L-lactide with propylene oxide or oxetane showed similar activity in the presence of the two monomers as their individual polymerizations, incorporating small percentages of the epoxide and L-lactide during the oxidized phase, and poly-merizing L-lactide rapidly in the reduced state (Table 2, entries 5-8).

Since the polymerization of the cyclic ethers was low, no significant change in molecular weight was observed compared to the polymerization of just L-lactide. Importantly, β-butyrolactone with cyclohexene oxide demonstrated significant conversions by ^{1}H NMR spectroscopy. The oxidized catalyst polymerized 100 equivalents of cyclohexene oxide in about 1 hour (Table 2, entry 3). Once reduced, the catalyst polymerized the same number of equivalents of β-butyrolactone overnight (Table 2, entry 4). The copolymerization rate for β-butyrolatone was slower than the homopoly-merization rate, decreasing from 94% in 20 hours to 69% in 24 hours. A similar trend was found for cyclohexene oxide in the presence of L-lactide (Table 2, entries 1-2). Although polymer weights might be expected to increase with each redox switch, GPC data only indicated an increase in pol-ymer weight from the oxidized state to the reduced state, i.e., when incorporating additional LA but not CHO (see below for discussion). It is important to mention that a unimodal distribution was observed by GPC, consistent with the formation of block copolymers (Figures 1 and S114-S123).
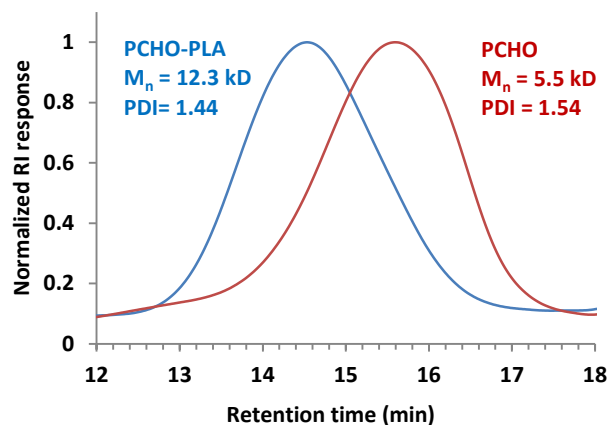
Figure 1. Comparison of GPC traces for a PCHO homopolymer (Table 2, entry 11) and a PCHO-PLA copolymer (Table 2, entry 12). The PCHO homopolymer sample was obtained from a PCHO-PLA copolymerization without employing the switch.
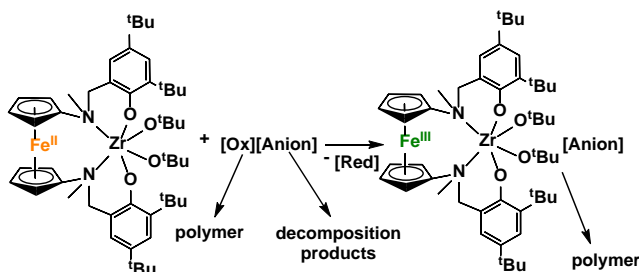
Scheme 1. Possible side reactions during the oxidation of (salfan)Zr(O^{t}Bu)$_2$ in the presence of CHO.

The decreased rate of CHO incorporation after an in situ oxidation of the catalyst could have resulted from an incomplete oxidation of the catalyst and/or activity of the oxidant with CHO. Although the former reason would prevent an increase in polymer molecular weight, the latter is in line with control experiments that show that ^{Ac}FcBAr^F polymerized CHO quickly at room tem-

perature (Figure S26, Table 3). Therefore, we evaluated the activity of the oxidant (Scheme 1) toward cyclic ethers.[12] Screening a number of oxidants led to disappointing results. NOBF$_4$ has a higher oxidation potential than ^{Ac}FcBAr^F, but its oxidation of the catalyst was not reversible (Table 3, entry 2). AgOTf was not very active with CHO and it oxidized (salfan)Zr(O^{t}Bu)$_2$ reversibly, but the oxidized catalyst was inactive toward CHO polymerization (Table 3, entry 3), likely because OTf coordination inhibited its activity. The addition of NaBAr^F to the mixture initiated CHO polymerization. However, as sodium compounds have been known to initiate ring-opening polymerization of epoxides,[13] it was tested separately (Table 3, entry 4). Like ^{Ac}FcBAr^F, NaBAr^F rapidly polymerized CHO. To determine whether the combination of silver and weakly coordinating borate ions could yield a competent oxidant, several silver borate salts were synthesized and tested. Unfortunately, the larger borates AgBPh$_4$ and AgBAr^F did not oxidize the catalyst and, in the latter case, led to some decomposition of the catalyst (Table 3, entries 6 and 7). The oxidation with Ag[B(C$_6$F$_5$)$_4$] was also not clean (Table 3, entry 8). Other solvents that were utilized to assess the solubility of (salfan)Zr(OtBu)$_2$ were dichloromethane and chlorobenzene. The former decomposed the catalyst after 1 h at ambient temperature, while the latter did so after 1.5 h at 100 °C (Figures S53-S54).

Control experiments were performed for the polymerization of CHO with ^{Ac}FcBAr^F (Figures S55, S131) and [H$_2$(salfan)][BAr^F] (Figures S56, S130) in order to compare the resulting polymers with those obtained when (salfan)Zr(O^{t}Bu)$_2$/^{Ac}FcBAr^F was used. For ^{Ac}FcBAr^F, the polymerization proceeded rapidly and reached completion in less than a half hour at room temperature. The molecular weight of the resulting polymer, M$_n$ = 111400 Da, was extremely large. Although this molecular weight is not comparable to that of the polymers obtained in the presence of (salfan)Zr(O^{t}Bu)$_2$/^{Ac}FcBAr^F (bimodal distribution described above), it is still possible that some of the polymer was generated by ^{Ac}FcBAr^F since ^{Ac}FcBAr^F would be present in different concentrations

in the two reactions, i.e., in the presence and absence of (salfan)Zr(O^{t}Bu)$_2$. The polymerization of CHO by [H$_2$(salfan)][BAr^F] was slower than that by [(salfan)Zr(OtBu)$_2$][BAr^F], requiring 4.5 h to reach 69% conversion. This experiment is also inconclusive since the electronic properties of iron in [(salfan)Zr(OtBu)$_2$][BAr^F] and [H$_2$(salfan)][BAr^F] are different.

Table 3. Screening of oxidants for in situ switching between (salfan)Zr(O^{t}Bu)$_2$ and [(salfan)Zr(O^{t}Bu)$_2$][BX$_4$].

Entry	Oxidant	Polymerization of CHO (initial 20 °C)	Polymerization of CHO (1 h at 100 °C)	Reversible oxidation	Polymerization of CHO by [(salfan)Zr(O^{t}Bu)$_2$][BR$_4$]
1	[^{Ac}Fc][BAr$^F_4$]	90%+	-	yes	yes
2	NOBF$_4$*	-	-	irreversible	-
3	AgOTf	0%	0%	yes	no
4	NaBAr^F	14%	83%	-	-
5	AgBF$_4$	1%	13%	irreversible	-
6	AgBPh$_4$*	0%	2%	no reaction	-
7	Ag[BAr$^F_4$]*	0%	70%	no reaction	-
8	Ag[B(C$_6$F$_5$)$_4$]	90%+	-	irreversible	-
9	AgNO$_3$	0%	0%	decomposition	-

* The reaction was performed in o-F$_2$C$_6$H$_4$ instead of a 4 : 1 C$_6$D$_6$: o-F$_2$C$_6$H$_4$ mixture.

Table 4. Formation of block copolymers by redox switchable catalysis using (salfan)Zr(O^{t}Bu)$_2$ (red) or [(salfan)Zr(O^{t}Bu)$_2$][BAr$^F_4$] (ox).

En try	Monomer 1	Monomer 2	Monomer 3	Cata-lyst	Conver-sion[a]	Time (h)	M_n[b]	PDI[c]	Fig-ures
1	LA	CHO	-	red-ox	91-89	4-18	11.4	1.32	S57, S124
2	LA	CHO	LA	red-ox-red	91-92-99	4-18-8	16.9	1.25	S58, S125
3	CHO	LA	-	ox-red	94-99	3-12	13.8	1.66	S59, S126
4	CHO	LA	CHO	ox-red-ox	94-80-82	3-12-8	13.3	1.53	S60, S127
5	CHO	LA	PO	ox-red-ox	91-99-trace	3-12-5	8.9	1.51	S61, S128
6	LA	CHO	BBL	red-ox-red	99-97-30	4-18-15	9.0	1.53	S62, S129

Notes. Conditions: monomer (0.50 mmol), initiator (0.005 mmol), oxidant (^{Ac}FcBAr^F, 0.005 mmol, 5.5 mg), 100 °C, solvent (4 : 1 benzene-d$_6$: 1,2-difluorobenzene), 1,3,5-trimethoxybenzene as an internal standard. LA = L-lactide, BBL = β-butyrolactone, PO = propylene oxide, CHO = cyclohexene oxide.

In order to avoid a competition between CHO polymerization and the oxidation of (salfan)Zr(O^{t}Bu)$_2$, sequential monomer additions were employed for the formation of block copolymers that did not start with the oxidized catalyst (Table 4). In this way, the concomitant presence of the oxidant and CHO can be avoided. Although these methods limit the applicability of our system for one-pot reactions, this limitation might be overcome by employing electrochemical switches, an avenue we are currently researching, or by finding different chemical oxidants. Furthermore, the principle of synthesizing block copolymers by using redox switchable catalysis still applies. Solubility issues with the oxidant and oxidized species were corrected with the addition of 1,2-difluorobenzene. The polymers were purified by precipitation in methanol and characterized by ^{1}H NMR spectroscopy and gel permeation chromatography (GPC).

Copolymers composed of three different monomers were also synthesized and characterized (Table 4, entries 5 and 6). PCHO-PLA-PPO contained a small amount of PO, as reflected in a similar molecular weight to that of the PCHO-PLA diblock polymer (Table 4, entry 5). The composition of PLA-PCHO-PBBL determined by ^{1}H NMR spectroscopy indicated that 30% of the initial BBL amount was incorporated in the last block after 15 h, although the homopolymerization of BBL proceeded to 94% conversion with (salfan)Zr(O^{t}Bu)$_2$ in 24 hours (Table 1, entry 3). We noticed

that after the polymerization of the first monomer, each subsequent oxidation/reduction and monomer addition proceeded more slowly. For L-lactide and CHO, a similar pattern was found: the time required for high conversion increased after the first block was synthesized.

In the case of LA and CHO, the molecular weight of the corresponding triblock copolymer, PLA-PCHO-PLA, increased after reduction and LA monomer addition (i.e., from 11.4 for PLA-PCHO to 16.9 kDa for PLA-PCHO-PLA, Table 4, entries 1 and 2). However, the same trend was not observed following chemical oxidation and CHO addition, i.e., the molecular weights for PCHO-PLA and PCHO-PLA-PCHO are similar (13.8 and 13.3 kDa, respectively, Table 4, entries 3 and 4). The same observation was made by Byers et al. with respect to the molecular weight of diblock copolymers.[11] To help determine the composition of the copolymers, a comparison was drawn between the poly-mers obtained by homopolymerization and copolymerization reactions (Table S1). As mentioned above, despite the percentage of conversion indicated by ^{1}H NMR spectroscopy, the molecular weight measurements by GPC only increased after each reduction and subsequent LA addition. Oxidations followed by CHO addition gave polymers of the same or slightly decreased weight.

The lack of bimodal distribution in GPC traces (Figures S124-S129) suggests that only one type of polymer is present and that the oxidant did not create a separate polymer chain. Furthermore, the molecular weights of PLA-PCHO and PCHO-PLA diblock copolymers that were obtained from high conversions of each monomer were similar (Table S1, entries 2 and 5) even though they repre-sented a decrease or increase from their previous homopolymer blocks (Table S1, entries 1 and 4). In addition, ^{1}H NMR spectra of the purified polymers indicate an increased ratio of LA to CHO from PLA-PCHO to PLA-PCHO-PLA (Table S1, entries 2 and 3). Likewise, from PCHO-PLA to PCHO-PLA-PCHO, the percentage of protons corresponding to CHO increased (Table S1, entries

5 and 6). The triblock copolymers PLA-PCHO-PLA and PCHO-PLA-PCHO had reversed compositions, as expected: PLA-CHO-PLA had 69% PLA to 31% PCHO, while PCHO-PLA-PCHO had 66% PCHO to 34% PLA.

Inspired by the selective precipitation procedures developed by Byers and coworkers to remove homopolymer fragments from the copolymeric material,[11] we applied these methods to our PLA/PCHO diblock and triblock copolymers synthesized by sequential addition (Tables S2-S5, Figures S67-82, S132-141). There was one rather notable difference that was found during the sequential polymerization procedure. The copolymers developed by Byers et al. were largely composed of PLA, even when sequential monomer addition was used. In their sequential precipitations, their copolymers were easily dissolved into acetone and precipitated in hexanes. This was reflected in the mass balance of their experiments, where most of the copolymer mass was found in the acetone filtrate and the hexanes precipitate. Compared to the iron system developed by Byers and coworkers, our catalyst incorporated a greater percentage of PCHO into its copolymers. Therefore, the copolymer was largely insoluble in both solvents. The mass balance reflects this fact, with most of the copolymer being found in the acetone and hexanes precipitates. In contrast to the copolymers studied by Byers and coworkers, there is a small loss of PCHO and even a smaller loss of PLA during the precipitation procedures, suggesting that most of the PCHO and PLA sequences are part of the copolymer rather than of individual homopolymeric chains. The resulting GPC traces showed, in general, higher molecular weights after successive precipitation processes, but no significant change in PDI values. The copolymers achieved by sequential addition are therefore likely predominantly block copolymers.

DOSY experiments[14] of the homopolymers and copolymers provided further evidence of copolymer formation. A mixture of PLA and PCHO homopolymers gave a distinct spectrum with PCHO diffusing at a slightly slower rate than PLA (Figure 2a). Their respective values (1.27×10^{-10} m²/s and

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1.53 x 10⁻¹⁰ m²/s) were similar to those obtained by Byers and coworkers in a recent report.[11] In contrast, the diblock copolymers exhibited higher diffusion rates and altered diffusion patterns. The PLA block of PLA-PCHO (D = 1.76 x 10⁻¹⁰ m²/s) diffused more slowly than the PCHO block, possibly due to its attachment to PCHO and the OᵗBu end group (Figure 2b). The PCHO and PLA blocks of PCHO-PLA (D = 1.57 x 10⁻¹⁰ m²/s) diffused at the same rate (Figure 2d). The corresponding triblock copolymers, PLA-PCHO-PLA (D = 1.18 x 10⁻¹⁰ m²/s) and PCHO-PLA-PCHO (D = 1.31 x 10⁻¹⁰ m²/s), shared similar patterns to their diblock precursors and showed a decrease in diffusion rate (Figure 2c and 2e, respectively). Neither diblock nor triblock copolymers contained traces of the homopolymer blocks, indicating the formation of only one type of polymeric species.

Since end group analysis could not be accurately obtained due to the overlap between the OᵗBu methyl peaks and PCHO methyl peaks, low molecular weight copolymers were synthesized and analyzed by ¹H NMR spectroscopy (Table 5). The low integration of protons corresponding to junctions or to the ends of blocks is consistent with a block[15] and not a random[16] copolymer structure (Figures S63-66). 2D Heteronuclear multiple bond correlation (HMBC) and heteronuclear single quantum coherence (HSQC) ¹H-¹³C experiments were utilized to assign some of these peaks. For a PLA-PHB copolymer, low incorporation of BBL was observed, in line with BBL's low reactivity with (salfan)Zr(OtBu)₂ in sequential addition copolymerizations. It was previously reported that PHB methylene protons are sensitive to BBL-LA junctions.[16] In the case of LA₈-BBL₁₀ obtained by us, integrations of the BBL methylene protons in a BBL-LA environment (2.70 ppm) versus a BBL-BBL environment (2.50 ppm) indicated that despite using a sequential addition of the monomers, there was some competitive behavior between the leftover LA and the newly added BBL with the reduced catalyst. Correlations of BBL methylene ¹H peaks to LA methine ¹³C peaks, as well as LA methine ¹H peaks to BBL carbonyl ¹³C peaks, also presented evidence of BBL-LA heterosequences (Figures S83-S86).

Copolymers with PCHO were more difficult to interpret due to PCHO's broad signals. BBL's methylene protons in BBL$_3$-CHO$_{25}$ did not show a third set of peaks outside the 2.50 ppm region (BBL methylene protons in a PHB homopolymer sequence) or correlations to CHO, suggesting a lack of heterosequences. Small peaks, which are proposed to be related to junctions or end groups, were analyzed. The proton peaks near 4.10 ppm were assigned as BBL methine ^{13}C peaks by HSQC and correlated to BBL methine ^{13}C peaks by HMBC. Small alkyl peaks near the broad regions of 1.00-1.50 ppm could not be assigned definitively to BBL, CHO, or the O^{t}Bu end group (Figures S87-S90).

The diblock PLA$_{13}$-PCHO$_7$ copolymer had several small LA methine proton signals (5.17, 4.98, and 4.34 ppm) located near the main PLA methine signal (5.15 ppm). The signals at 5.17 ppm and 4.98 ppm were correlated to the bulk LA methyl ^{13}C signal at 16.7 ppm, suggesting that these are the methines of the LA units closest to the bulk of the PLA polymer. The LA methine signal at 4.98 ppm is related to the LA methyl peak at 1.70 ppm and a doublet at 1.46 ppm. The LA methine proton peak at 4.34 ppm is correlated to the LA methyl peak at 2.68 ppm and a doublet at 1.49 ppm (possibly corresponding to an adjoining LA methyl group). The O^{t}Bu proton peak at 1.44 ppm can be correlated to a methyl ^{13}C peak at 27.9 ppm and a quaternary ^{13}C peak at 82.3 ppm, however, neither of these peaks correlates to any other peaks. Although there was no definitive evidence of direct correlations by 2D NMR spectroscopy, these LA monomer units show a relationship to the main PLA signals yet altered microstructures. Therefore, we propose that the peaks at 4.98 and 4.34 ppm, along with their related peaks, most likely correspond to the LA monomer units closest to the junction with PCHO and O^{t}Bu, respectively (Figures S95-98).

The diblock CHO$_{17}$-LA$_8$ showed similar peaks as PLA-PCHO, with a few additional small peaks at 4.77, 4.50, 4.20, and 4.10 ppm, which were identified as being related to LA and CHO methine ^{13}C peaks by HSQC. HMBC, however, was only helpful in identifying the peaks at 4.50, 4.20, and

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4.10 ppm as being nearby LA methine ^{13}C peaks (Figures S91-94). The presence of numerous small peaks between 4.00 - 5.00 ppm may be due to differences in the junction environment (i.e., PCHO-PLA has an ester linkage, while PLA-PCHO has an ether linkage).

The low weight copolymer LA_5-CHO_{20}-PHB_3 showed little incorporation of BBL (around 2 monomers per initiator). The BBL's methylene peaks showed correlations with LA's methine ^{13}C peaks exclusively, indicating that the "third block" of the copolymer was in reality a heterosequence of BBL and leftover LA in solution. Like CHO_{17}-LA_8, a number of small peaks were present on the HSQC and HMBC maps, but none of them could be identified definitively as junction protons (Figures S99-102).

Reexamination of the ^{1}H NMR spectra for the larger block copolymers in this light yields some information on the microstructure of these copolymers. For LA/CHO copolymers, some of the small peaks present in the ^{1}H NMR spectra between 3.76-5.15 ppm and 1.85-3.37 ppm could now be identified as LA monomer units closest to the end groups or junctions. Their relatively low integration (less than 3 protons in most cases) compared to the bulk polymer peaks (100-300 protons), indicates few junctions or heterosequences. For the LA/CHO/BBL copolymers, given the number of heterosequences found in the low weight polymers with LA and BBL, it is likely that the BBL block is heavily contaminated with LA monomers, thus not forming a true block copolymer in this case. We have tentatively assigned some of these peaks in Figures S63-66.

Table 5. Formation of low weight block copolymers by redox switchable catalysis using (salfan)Zr(O^{t}Bu)$_2$ (red) or [(salfan)Zr(O^{t}Bu)$_2$][BAr$^F_4$] (ox) and sequential monomer addition.

Entry	Mono- mer 1	Mono- mer 2	Mono- mer 3	Catalyst	Conver- sion[a]	Composi- tion[b]	Figures

1	LA	BBL	-	red	92-65	8:10	S83-86
2	BBL	CHO	-	red-ox	70-90	3:25	S87-90
3	CHO	LA	-	ox-red	96-95	17:8	S91-94
4	LA	CHO	-	red-ox	92-87	13:7	S95-98
5	LA	CHO	BBL	red-ox-red	92-88-50	5:20:3	S99-102

Notes. Conditions: monomer (0.25 mmol), initiator (0.010 mmol), oxidant (^{Ac}FcBAr^F, 0.010 mmol, 5.5 mg), 100 °C, solvent (4 : 1 benzene-d_6 : 1,2-difluorobenzene), 1,3,5-trimethoxybenzene as an internal standard. LA = L-lactide, BBL = β-butyrolactone, CHO = cyclohexene oxide. Samples could not be analyzed by GPC due to their low molecular weight.

[a] Conversion calculated by integration of polymer peaks versus internal standard in crude mixture. The first number indicates conversion of Monomer 1, while the second number indicates conversion of Monomer 2, etc.

[b] Conversion calculated by integration of polymer peaks versus internal standard in purified polymer. The first number indicates the estimated number of units of Monomer 1 per polymer chain, while the second number indicates the estimated units of Monomer 2, etc.
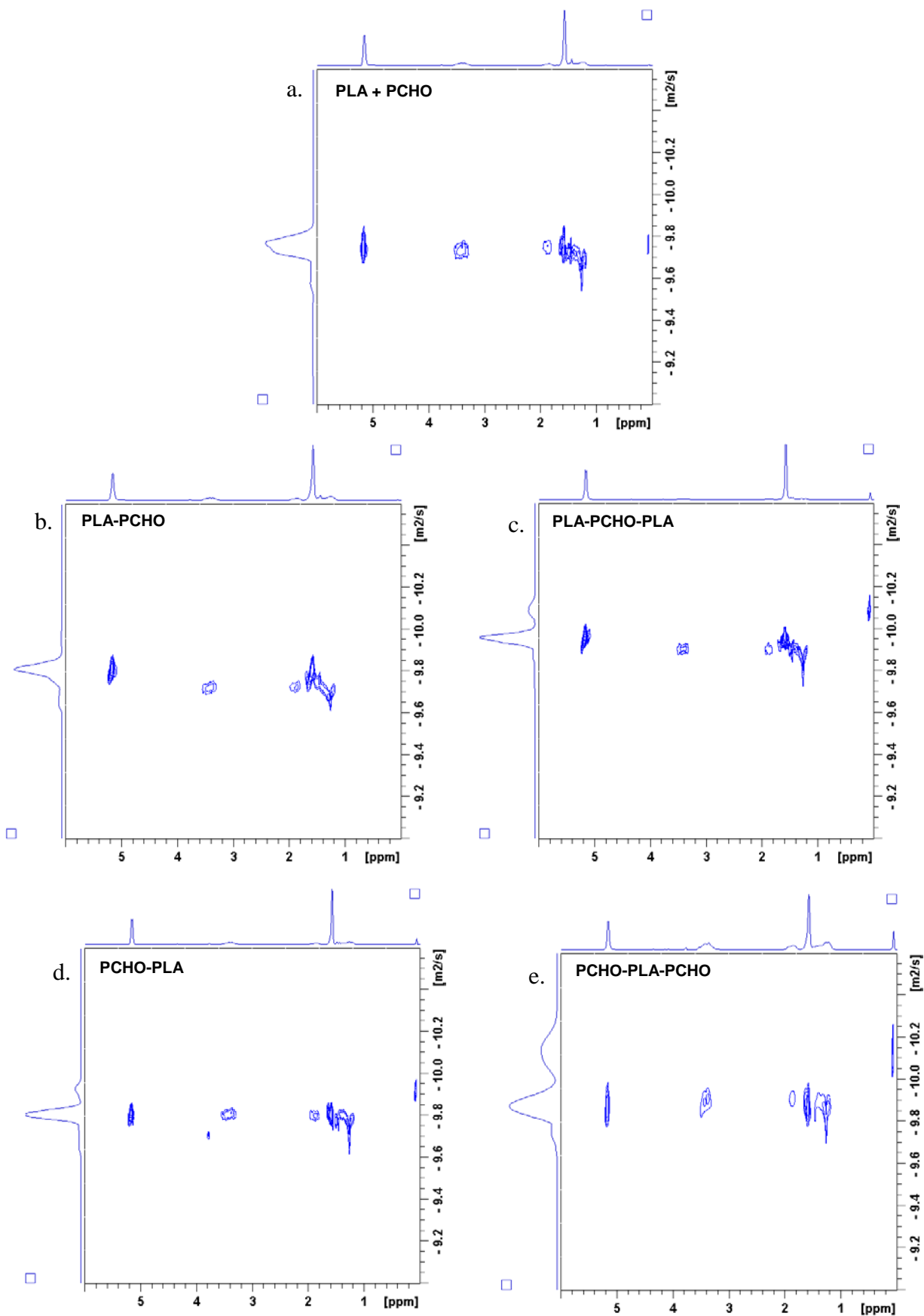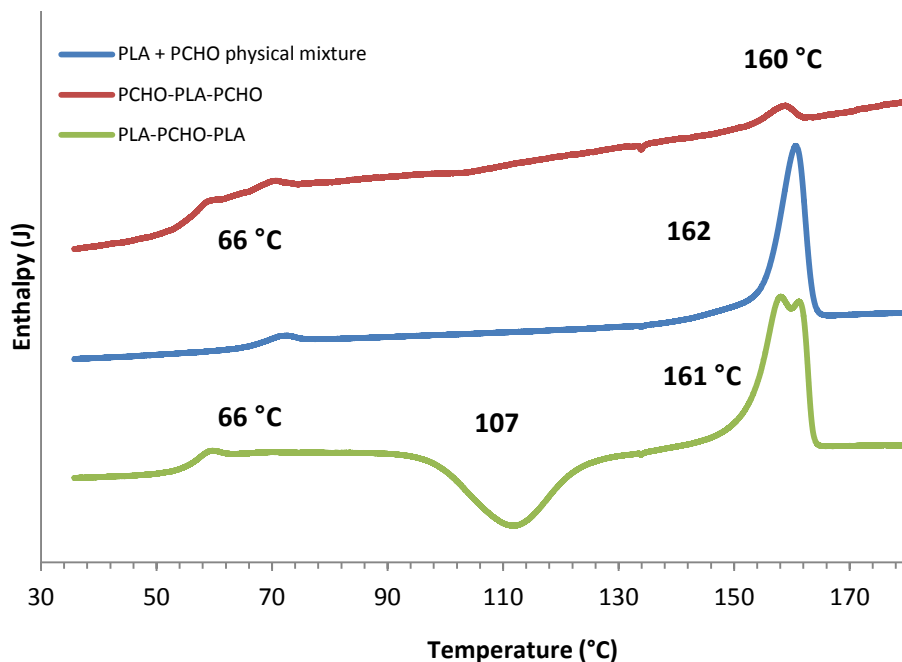
Figure 2. DOSY map of a mixture of PLA and PCHO homopolymers (a); DOSY maps of PLA-

PCHO diblock copolymer (b) and subsequent PLA-PCHO-PLA triblock copolymer (c); and DOSY

maps of PCHO-PLA diblock copolymer (d) and subsequent PCHO-PLA-PCHO triblock copolymer (e).

Furthermore, thermogravimetric and differential scanning calorimetry (DSC) analysis of the PLA-PCHO copolymers showed behaviors in between those corresponding to the homopolymers PLA and PCHO. For example, the decomposition of pure PLA starts at 160 °C and the polymer completely degrades by 225 °C.[17] PCHO's decomposition curve ranges from 350 °C to 407 °C.[18] A diblock PLA-CHO copolymer began decomposing at 200 °C and continued until 375 °C (Figure S142). A comparison between the decomposition behavior of PLA-PCHO-PLA (Figure S143) and PCHO-PLA-PCHO (Figure S145) was consistent with an increased content of PCHO of the latter (Figure 4). Similarly, analysis by DSC (Figures S146-152) indicates that the profiles of the copoly-mers are different than those of PLA (Figure S146)[19] and PCHO (Figure S147)[18] or of a physical mixture of the two homopolymers (Figure 4). A 3 : 1 mixture of PCHO to PLA (a higher amount of PCHO was used because the glass transition temperature of PCHO is often a small, broad peak)[20] showed a melting point (T_m) of 162 °C for PLA, a glass transition temperature (T_g) of 66 °C for PCHO and a crystallization temperature (T_c) of 107 °C for PLA. The DSC trace of PLA-PCHO-PLA showed a smaller T_g peak for the PCHO block (66 °C) compared to the T_m of the PLA blocks (161 °C). PCHO-PLA-PCHO showed a decreased T_m (162 °C) peak for the PLA block compared to PLA-PCHO-PLA (161 °C, Figures S150, S152).

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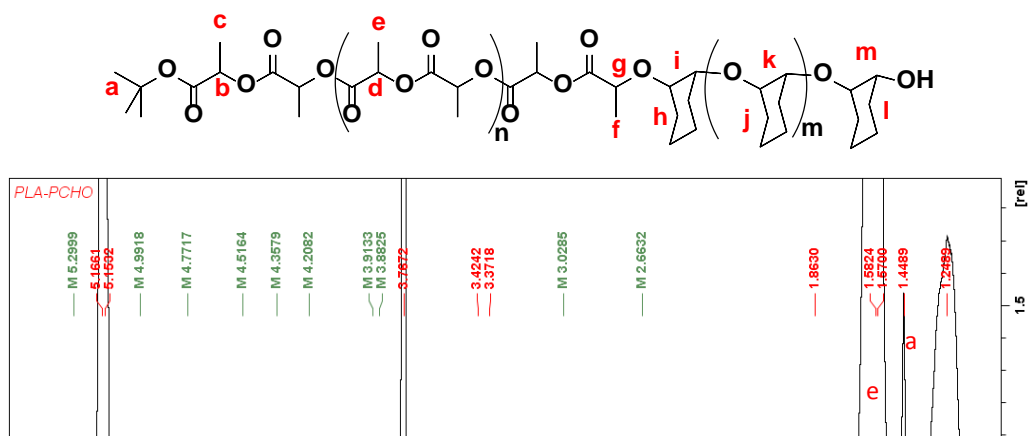
Figure 3. Selected region of the ¹H NMR (300 MHz, 25 °C, C_6D_6) spectrum of the purified PLA-PCHO polymer obtained by polymerization of 100 equivalents of cyclohexene oxide and L-lactide monomers added sequentially, using catalyst redox switch "red-ox". Peaks were magnified to show the suggested assignment of the protons corresponding to the junction between blocks. The peak at 3.76 ppm corresponds to TMB (internal standard). Labels j, h, and l refer to the broad peaks from 1.86 to 1.24 ppm. Unlabeled peaks could not be assigned by HSQC or HMBC. M denotes peaks that were manually picked.

Figure 4. DSC analysis of a PLA-PCHO-PLA copolymer obtained by sequential addition (top), a 1:3 physical mixture of PLA and PCHO homopolymers (middle), and a PCHO-PLA-PCHO copolymer obtained by sequential addition (bottom).

Conclusions

We achieved the redox switchable copolymerization of L-lactide/β-butyrolactone and cyclohexene oxide both in one pot and by sequential additions. Difficulties in achieving multiple redox switches in a one-pot polymerization underscored the necessity of choosing an effective yet otherwise innocent oxidant. The complex role of the oxidant was revealed through chemical oxidant screenings. Sequential monomer additions were employed to achieve multi-block copolymers. GPC analysis indicated an increase in the hydrodynamic volume of the copolymers after the addition of a PLA block and a decrease after the addition of a PCHO block. However, sequential precipitations, 2D NMR experiments, and DOSY experiments confirmed the formation of block copolymers and indicated that no significant homopolymer impurities are present. In addition, a clear decrease in the diffusion coefficient of the diblock to the triblock copolymers was observed.

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TGA and DSC analyses were also used to characterize these novel copolymers. Small changes in the decomposition, glass transition temperature, and melting temperature were observed, consistent with a change in the copolymer's properties compared to those of a combination of homopolymers.

Experimental

General considerations

All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glovebox. Solvents were purified using a two-column solid-state purification system by the method of Grubbs[21] and transferred to the glove box 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 internal solvent, 7.16 ppm (C_6D_6) and 7.26 ppm ($CDCl_3$) for ^{1}H NMR spectra. All 2D NMR spectroscopy was performed on a Bruker 500 MHz spectrometer. The target block copolymer (10 mg) was dissolved in $CDCl_3$ (ca. 0.5 mL). Spectra were acquired with the ledbpgp2s pulse program from the Bruker topspin software. The gradient strength was logarithmically incremented in 32 steps from 2% up to 95% of the maximum gradient strength.[14] Liquid monomers and 1,2-difluorobenzene were distilled over CaH_2 and brought into the glove box 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. $Na[BAr^F_4]$, $[^{Ac}Fc][BAr^F_4]$, $Ag[BAr^F_4]$,[22] $AgB(C_6F_5)_4$,[23] and $(salfan)Zr(O^tBu)_2$[8b] were synthesized following previously published procedures. Molecular weights of the polymers were determined by GPC (Gel Permeation Chromatography) at MRL Shared Experimental Facilities in UCSB that is supported by the MRSEC Program of the National

Science Foundation under award NSF DMR 1121053; a member of the NSF-funded Material Research Facilities Network. GPC uses an Agilant liquid chromatograph equipped with a Waters Alliance HPLC System 2690 Separation Module and autosampler, two Agilent PLGEL 5 µm MIXED-D, 300 x 7.5mm columns, a Waters 2410 Differential Refractometer and Water 2998 Photodiode Array Detector. The column temperature was set at 25 °C. A flow rate of 1.0 mL/min was used and samples were dissolved in chloroform with 0.25% triethylamine. GPC results were calibrated to narrow molecular weight polystyrene standards. Where indicated, molecular weights were also determined by 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 8mm linear columns, Wyatt DAWN HELEOS-II and 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. dn/dc values were calculated for PLA and PCHO by creating 5 solutions of increasing concentration (0.1 - 1.0 mg/mL), directly injecting them into the RI detector sequentially, and using the batch dn/dc measurement methods in the Astra software. The dn/dc value for PLA and PCHO were calculated to be 0.024 mL/g and 0.086 mL/g over three trials. TGA was obtained using a Perkin Elmer Pyris Diamond TG/DTA instrument under nitrogen. The method used was to increase the temperature from 150 to 450 °C at 10 °C/min, held 450 °C for 5 minutes then decreased back to 150 °C at 50 °C/min. DSC was obtained using a Perkin-Elmer DSC model 8500 heat flow system with Intracooler II. The method used was to increase the temperature from 20 to 200 °C at 10 °C/min, held 200 °C for 2 minutes, then decreased back to 20 °C at 30 °C/min for two cycles.

Decomposition study of (salfan)Zr(O^{t}Bu)$_2$ in CH$_2$Cl$_2$. To a J-Young NMR tube, a solution of (salfan)Zr(O^{t}Bu)$_2$ (4.6 mg, 5 µmol) in C$_6$D$_6$ (0.15 mL) was added, followed by 0.5 mL of CH$_2$Cl$_2$. After 20 min, the volatiles were removed under reduced pressure and the solid was analysed by ^{1}H NMR spectroscopy.

Decomposition study of (salfan)Zr(O^{t}Bu)$_2$ in C$_6$H$_5$Cl. To a J-Young NMR tube, a solution of (salfan)Zr(O^{t}Bu)$_2$ (4.6 mg, 5 μmol) in C$_6$D$_6$ (0.15 mL) was added, followed by 0.5 mL of C$_6$H$_5$Cl. After heating for 1 hour at 100 °C, the volatiles were removed under reduced pressure and the solid was analysed by ^{1}H NMR spectroscopy.

Procedure for determining the reversibility of (salfan)Zr(O^{t}Bu)$_2$ oxidation. To a C$_6$D$_6$ (0.15 mL) solution of (salfan)Zr(O^{t}Bu)$_2$ (4.6 mg, 5 μmol) in a J-Young NMR tube, a solution of 1,3,5-tri-methoxybenzene (16.8 mg, 50 μmol) in C$_6$D$_6$ (0.15 mL), 0.10 mL of F$_2$C$_6$H$_4$, and a solution of [^{Ac}Fc][BAr^F$_4$] (5.5 mg, 5 μmol) in F$_2$C$_6$H$_4$ (0.10 mL) were added and the reaction was left at room temperature for 2 h. The reaction was monitored by ^{1}H NMR spectroscopy. A solution of CoCp$_2$ (5.5 mg, 5 μmol) in C$_6$D$_6$ (0.10 mL) was then added and the reaction was left at room temperature for another 2 h. The reaction was monitored by ^{1}H NMR spectroscopy.

General polymerization procedures

General procedure for polymerization of one monomer by (salfan)Zr(O^{t}Bu)$_2$. To a J-Young NMR tube, a solution of (salfan)Zr(O^{t}Bu)$_2$ (4.6 mg, 5 μmol) in C$_6$D$_6$ (0.15 mL) was added, followed by a solution of 1,3,5-trimethoxybenzene (16.8 mg, 50 μmol) in C$_6$D$_6$ (0.15 mL), 0.10 mL of C$_6$D$_6$, and 0.10 mL of F$_2$C$_6$H$_4$. The solution was shaken. 0.5 mmol monomer was added. The reaction was monitored to completion or for 24 hours.

General procedure for polymerization of one monomer by [(salfan)Zr(O^{t}Bu)$_2$][BAr^F$_4$]. To a J-Young NMR tube, a solution of (salfan)Zr(O^{t}Bu)$_2$ (4.6 mg, 5 μmol) in C$_6$D$_6$ (0.15 mL) was added, followed by a solution of 1,3,5-trimethoxybenzene (16.8 mg, 50 μmol) in C$_6$D$_6$ (0.15 mL), 0.10 mL of C$_6$D$_6$, and 0.10 mL of F$_2$C$_6$H$_4$. The solution was shaken. 0.10 mL of a [^{Ac}Fc][BAr^F$_4$] solution (5.5 mg, 5 μmol) was added. After 2 h, 0.5 mmol monomer was added. The reaction was monitored to completion or for 24 h.

General procedure for the polymerization of two monomers by (salfan)Zr(OtBu)₂ or [(salfan)Zr(OᵗBu)₂][BArᶠ₄] with one redox switch (one pot)

Copolymerization of LA and CHO by (salfan)Zr(OᵗBu)₂ (red-ox). To a C_6D_6 (0.15 mL) solution of (salfan)Zr(OᵗBu)₂ (4.6 mg, 5 µmol) in a J-Young NMR tube, a solution of 1,3,5-trimethoxybenzene (16.8 mg, 50 µmol) in C_6D_6 (0.15 mL), 0.10 mL of $F_2C_6H_4$ and a C_6D_6 (0.10 mL) solution of cyclohexene oxide (49.0 mg, 0.5 mmol) and L-lactide (72.0 mg, 0.5 mmol) were added. The reaction was heated to 100 °C and periodically removed from the oil bath every 30 min to be analyzed by ¹H NMR spectroscopy. A solution of [ᴬᶜFc][BArᶠ₄] (5.5 mg, 5 µmol) in $F_2C_6H_4$ (0.10 mL) was added. After two hours, the reaction was heated to 100 °C again and removed from the oil bath every hour to be analyzed by ¹H NMR spectroscopy. At the end, the reaction mixture was dissolved in CH_2Cl_2 and poured into cold methanol; a white solid precipitated briefly and was filtered.

Copolymerization of LA and CHO by (salfan)Zr(OᵗBu)₂ (ox-red). To a C_6D_6 (0.15 mL) solution of (salfan)Zr(OᵗBu)₂ (4.6 mg, 5 µmol) in a J-Young NMR tube, a solution of 1,3,5-trimethoxybenzene (16.8 mg, 50 µmol) in C_6D_6 (0.15 mL), 0.10 mL of $F_2C_6H_4$ and a solution of [ᴬᶜFc][BArᶠ₄] (5.5 mg, 5 µmol) in $F_2C_6H_4$ (0.10 mL) was added. After two hours, a C_6D_6 (0.10 mL) solution of cyclohexene oxide (49.0 mg, 0.5 mmol) and L-lactide (72 mg, 0.5 mmol) was added. The reaction was heated to 100 °C and removed from the bath every 30 min to be analyzed by ¹H NMR spectroscopy. A solution of CoCp₂ (0.95 mg, 5 µmol) in C_6D_6 (0.10 mL) was added. The reaction was heated to 100 °C again and removed from the oil bath every hour to be analyzed by ¹H NMR spectroscopy. At the end, the reaction mixture was dissolved in CH_2Cl_2 and poured into cold methanol; a white solid precipitated briefly and was filtered.

General procedure for the sequential polymerization of LA and CHO by (salfan)Zr(OᵗBu)₂ or [(salfan)Zr(OᵗBu)₂][BArᶠ₄] with two redox switches (sequential addition of monomers)

Copolymerization of LA and CHO by (salfan)Zr(O^{t}Bu)$_2$ (red-ox-red). To a C$_6$D$_6$ (0.15 mL) solution of (salfan)Zr(O^{t}Bu)$_2$ (4.6 mg, 5 μmol) in a J-Young NMR tube, a solution of 1,3,5-trimethoxybenzene (16.8 mg, 50 μmol) in C$_6$D$_6$ (0.15 mL), 0.10 mL of F$_2$C$_6$H$_4$ and L-lactide (72.0 mg, 0.5 mmol) were added. The reaction was heated to 100 °C and removed from the oil bath every 30 min to be analyzed by ^{1}H NMR spectroscopy. A solution of [^{Ac}Fc][BAr$^F_4$] (5.5 mg, 5 μmol) in F$_2$C$_6$H$_4$ (0.10 mL) was then added and the reaction was left at room temperature for 2 h. A solution of cyclohexene oxide (49.0 mg, 0.5 mmol) in C$_6$D$_6$ (0.10 mL) was added. The reaction was heated to 100 °C and removed from the oil bath every 30 min to be analyzed by ^{1}H NMR spectroscopy. A solution of CoCp$_2$ (5.5 mg, 5 μmol) in C$_6$D$_6$ (0.10 mL) was then added and the reaction was left at room temperature for 2 h. L-lactide (72.0 mg, 0.5 mmol) was added. The reaction was heated to 100 °C and removed from the oil bath every 30 min to be monitored by ^{1}H NMR spectroscopy until completion. At the end, the reaction mixture was dissolved in CH$_2$Cl$_2$ and poured into cold methanol; a white solid precipitated briefly and was filtered. Yield: PLA-PCHO, 174 mg, 81.8%; PLA-PCHO-PLA 350 mg, 96.8%.

Copolymerization of LA and CHO by [(salfan)Zr(O^{t}Bu)$_2$][BAr$^F_4$] (ox-red-ox). To a C$_6$D$_6$ (0.15 mL) solution of (salfan)Zr(O^{t}Bu)$_2$ (4.6 mg, 5 μmol) in a J-Young NMR tube, a solution of 1,3,5-trimethoxybenzene (16.8 mg, 50 μmol) in C$_6$D$_6$ (0.15 mL), 0.10 mL F$_2$C$_6$H$_4$ and a solution of [^{Ac}Fc][BAr$^F_4$] (5.5 mg, 5 μmol) in F$_2$C$_6$H$_4$ (0.10 mL) was added and the reaction was left at room temperature for 2 h. A solution of cyclohexene oxide (49.0 mg, 0.5 mmol) in C$_6$D$_6$ (0.10 mL) was added. The reaction was heated to 100 °C and removed from the oil bath every 30 minutes to be analyzed by ^{1}H NMR spectroscopy. A solution of CoCp$_2$ (5.5 mg, 5 μmol) in C$_6$D$_6$ (0.10 mL) was then added and the reaction was left at room temperature for 2h. L-lactide (72.0 mg, 0.5 mmol) was added. The reaction was heated to 100 °C and removed from the oil bath every hour to be analyzed by ^{1}H NMR spectroscopy. A solution of [^{Ac}Fc][BAr$^F_4$] (5.5 mg, 5 μmol) in F$_2$C$_6$H$_4$ (0.10 mL)

was then added and the reaction was left at room temperature for 2 h. A solution of cyclohexene oxide (49.0 mg, 0.5 mmol) in C_6D_6 (0.10 mL) was added. The reaction was heated at 100 °C and removed from the oil bath every hour to be analyzed by ^{1}H NMR spectroscopy until completion. At the end, the reaction was dissolved in CH_2Cl_2 and poured into cold methanol; a white solid precipitated briefly and was filtered. Yield: PCHO-PLA, 211 mg, 93.9%. PCHO-PLA-PCHO, 280 mg, 91.3%.

Procedure for CHO conversion study with two redox switches. To a J-Young NMR tube, a solution of (salfan)Zr(O^{t}Bu)$_2$ (4.6 mg, 5 µmol) in C_6D_6 (0.15 mL) was added, followed by a solution of 1,3,5-trimethoxybenzene (16.8 mg, 50 µmol) in C_6D_6 (0.15 mL), and a solution of [^{Ac}Fc][BAr$^F_4$] (5.5 mg, 5 µmol) in $F_2C_6H_4$ (0.10 mL). The mixture was left at room temperature for 2 h. 1.00 mL of C_6D_6 was layered on top followed by 0.20 mL of a cyclohexene oxide (98 mg, 1.0 mmol) solution in C_6D_6. The tube was shaken to mix the contents and a timer was started. NMR spectra were taken two minutes apart until 50% conversion was reached. The tube was brought back to the glovebox and a solution of CoCp$_2$ (5.5 mg, 5 µmol) in C_6D_6 (0.10 mL) was added. The reaction was monitored for 15 minutes by ^{1}H NMR spectroscopy then brought back into the glovebox and 0.10 mL of a [^{Ac}Fc][BAr$^F_4$] solution in $F_2C_6H_4$ (5.5 mg, 5 µmol) was added. Polymerization was monitored by ^{1}H NMR spectroscopy every 2 minutes until 90% conversion was reached.

Procedure for CHO conversion study with and without LA. To two J-Young NMR tubes, a solution of (salfan)Zr(O^{t}Bu)$_2$ (4.6 mg, 5 µmol) in C_6D_6 (0.15 mL) was added, followed by a solution of 1,3,5-trimethoxybenzene (16.8 mg, 50 µmol) in C_6D_6 (0.15 mL), 0.10 mL of C_6D_6, 0.10 mL of $F_2C_6H_4$ and a solution of [^{Ac}Fc][BAr$^F_4$] (5.5 mg, 5 µmol) in $F_2C_6H_4$ (0.10 mL). The resulting solution was shaken. To one J-Young NMR tube, L-lactide (72 mg, 0.5 mmol) was added. To both NMR tubes, a solution of cyclohexene oxide (49.0 mg, 0.5 mmol) in C_6D_6 (0.10 mL) was added. NMR tubes were monitored every 5 minutes until one of them reached over 90% conversion.

Procedure for LA conversion study with and without CHO. To two J-Young NMR tubes, a solution of (salfan)Zr(O^tBu)$_2$ (4.6 mg, 5 µmol) in C$_6$D$_6$ (0.15 mL) was added, followed by a solution of 1,3,5-trimethoxybenzene (16.8 mg, 50 µmol) in C$_6$D$_6$ (0.15 mL), 0.10 mL of C$_6$D$_6$, and 0.10 mL of F$_2$C$_6$H$_4$. The solution was shaken. To one J-Young NMR tube, a solution of cyclohexene oxide (49.0 mg, 0.25 mmol) in C$_6$D$_6$ (0.10 mL) was added. To both NMR tubes, L-lactide (72.0 mg, 0.5 mmol) was added. NMR tubes were heated to 100 °C. The reactions were removed from the oil bath and analyzed every 15 minutes by ^{1}H NMR spectroscopy until one of them reached over 90% conversion.

Procedure for conversion versus Mn study. To 4 J-Young NMR tubes, a solution of (salfan)Zr(O^tBu)$_2$ (4.6 mg, 5 µmol) in C$_6$D$_6$ (0.15 mL) was added, followed by a solution of 1,3,5-trimethoxybenzene (16.8 mg, 50 µmol) in C$_6$D$_6$ (0.15 mL), 0.10 mL of C$_6$D$_6$, and 0.10 mL of F$_2$C$_6$H$_4$. The resulting solution was shaken. To all NMR tubes, L-lactide (72.0 mg, 0.5 mmol) was added. NMR tubes were heated to 100 °C in an oil bath and a timer was started. An NMR tube was taken out every 15 minutes and the polymerizations were monitored until 40% conversion. The contents of the first tube were poured into a vial of cold methanol. Spectra were taken every 15 minutes afterward. Once significant changes in conversion were observed (about 10% more than the previous data point), the contents of the tube were poured into a vial of cold methanol. Conversion vs. Mn studies for CHO were conducted at room temperature and at half the concentration for LA to slow down polymerization times.

Procedure for polymerization of CHO by [H$_2$(salfan)][BAr^F]. To a J-Young NMR tube, a solution of H$_2$(salfan) (3.4 mg, 5 µmol) in C$_6$D$_6$ (0.15 mL) was added, followed by a solution of 1,3,5-trimethoxybenzene (16.8 mg, 50 µmol) in C$_6$D$_6$ (0.15 mL), 0.10 mL of C$_6$D$_6$, 0.10 mL of F$_2$C$_6$H$_4$, and a solution of [^{Ac}Fc][BAr$^F_4$] (5.5 mg, 5 µmol) in F$_2$C$_6$H$_4$ (0.10 mL); the mixture was left at room temperature for 2 hours. A solution of cyclohexene oxide (49.0 mg, 0.5 mmol) in C$_6$D$_6$ (0.10 mL) was added. The reaction was monitored to completion or for 24 h.

Procedure for polymerization of CHO by $^{Ac}FcBAr^F$. To a J-Young NMR tube, a solution of [^{Ac}Fc][BAr^F] (5.5 mg, 5 μmol) in $F_2C_6H_4$ (0.10 mL) was added, followed by a solution of 1,3,5-tri-methoxybenzene (16.8 mg, 50 μmol) in C_6D_6 (0.15 mL), 0.10 mL of C_6D_6, and 0.10 mL of $F_2C_6H_4$. The solution was shaken. A solution of cyclohexene oxide (49 mg, 0.5 mmol) in C_6D_6 (0.10 mL) was added. The reaction was monitored to completion.

Modifications for the synthesis of low weight diblock and triblock copolymers. The same polymerization procedures as above were followed, but with the following modifications. Quantities of (salfan)Zr(O^{t}Bu)$_2$, 1,3,5-trimethoxybenzene and [^{Ac}Fc][BAr$^F_4$] were doubled from 5 μmol to 10 μmol. Quantities of monomer were halved from 0.50 mmol to 0.25 mmol, with the exception of BBL, which was otherwise difficult to observe by ^{1}H NMR spectroscopy.

Procedure for precipitation of homopolymers from copolymers. A polymerization reaction mixture was dissolved in minimal CH_2Cl_2 and poured into 10 mL of cold methanol. The mixture was centrifuged and the supernatant was poured off. The resulting crude polymer was dried, dissolved in minimal CH_2Cl_2, and precipitated in 10 mL cold methanol two more times. To isolate the copolymer from any resulting homopolymer fragments selectively, 100 mg of the crude polymer was dissolved in minimal CH_2Cl_2 and poured into 10 mL of cold acetone. The mixture was centrifuged and filtered through a 0.20 micron FTPE filter. The isolated precipitate was dried, dissolved in minimal CH_2Cl_2 and poured into 10 mL of cold hexanes. The mixture was centrifuged and then filtered through a 0.20 micron FTPE filter. Filtrates and precipitates from each precipitation were dried, weighed, and analyzed by ^{1}H NMR spectroscopy and GPC.

ASSOCIATED CONTENT

Supporting Information. Synthetic details, NMR spectra, GPC, TGA, and DSC data. This material is available free of charge via the Internet at http://pubs.acs.org.

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SYNOPSIS TOC. Several diblock (AB, BA) and triblock polymers (ABA and BAB) were synthesized

and characterized by using redox-switchable catalysis.