An electrochemical approach to aluminum-based redox switchable ring opening polymerization

Zachary C. Hern,[†] Amy Lai, Ramzi N. Massad, Paula L. Diaconescu*

Department of Chemistry and Biochemistry, University of California Los Angeles, Los Angeles, California 90095-1569, United States

ABSTRACT: We report the electrochemically switchable reactivity of (salfen)Al(O^iPr) (salfen = 1,1′-di(2,4-bis-*tert*-butyl-salicylimino)ferrocene) toward the ring opening polymerization of various cyclic esters, ethers, and carbonates. Using a recently developed electrochemical system comprised of an H-cell and glassy carbon working electrode, an applied potential can alternate between two redox states of the catalyst and alter monomer incorporation during ring opening polymerization. We discuss differences in activity and control under electrochemical conditions compared to previously studied chemical redox methods and discuss the necessity of a redox switch during certain copolymerization reactions.

INTRODUCTION

New techniques to control polymerization reactions have recently been developed to provide precision over monomer placement. This precise placement of monomers can lead to unique and tunable thermal, mechanical, and degradation properties.[1-10] One way to control such monomer sequence is switchable polymerization,[11-18] where a single, active catalyst can be toggled between

two states that show orthogonal reactivity for various monomers. In particular, for redox switchable reactions,[19-40] sequential redox switches can lead to block copolymers with tunable block compositions and lengths. Recently, electrochemistry has been used to facilitate these redox switches,[41-47] which circumvents the need for repeated redox reagent additions and allows switching through the use of an automated potentiostat.

We reported an electrochemical system that is capable of producing tri- and tetrablock copolymers by altering the redox state of a ferrocene-based redox-switchable zirconium catalyst, (salfan)Zr(O^{t}Bu)$_2$, (salfan = 1,1′-di(2-$tert$-butyl-6-N-methylmethylenephenoxy)ferrocene).[44] This system was able to produce ABC triblock and ABAB tetrablock copolymers of L-lactide (LLA), cyclohexene oxide (CHO), and β-butyrolactone (BBL). We hypothesized that this approach would be generally applicable to other redox switchable metal complexes that exhibit unique activities toward a large monomer scope. We set out to determine if the electrochemical conditions (i.e., solvent, supporting electrolyte, electrodes) affected other redox switchable polymerization reactions. Here, we study a previously reported aluminum complex, (salfen)Al(O^{i}Pr) (salfen = 1,1′-di(2,4-bis-$tert$-butyl-salicylimino)ferrocene),[28] and its electrochemically controlled ring-opening polymerization activity. (salfen)Al(O^{i}Pr) bears only one alkoxide initiating group, which we hypothesize will lead to a greater diffusion constant and more facile electron transfer at the electrode surface compared to the previously studied (salfan)Zr(O^{t}Bu)$_2$.[44] A comparison of polymers produced from redox switchable reactions using chemical redox reagents and electrochemical switching is also discussed.
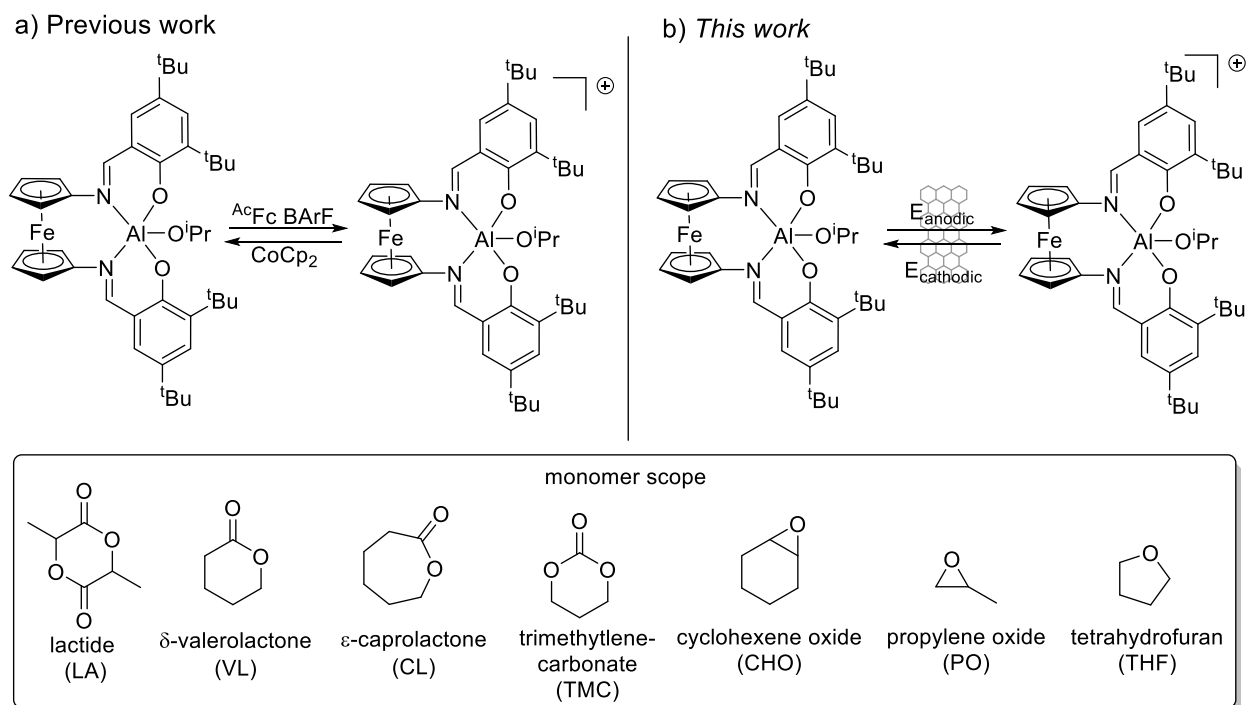
Figure 1. a) Previous work using chemical redox reagents. b) This work using electrochemical switches to produce homo and diblock copolymers. Bottom: monomer scope of cyclic esters, ethers, and carbonates investigated.

RESULTS AND DISCUSSION

The cyclic voltammogram of (salfen)Al(O^{i}Pr) under bulk electrolysis conditions (75 mM tetrapropylammonium bistriflimide (TPANTf$_2$) in 1,2-difluorobenzene) exhibits a single, reversible electron transfer process with an E$_{1/2}$ = 0.99 V versus Ag/Ag$^+$ (Figure 2). When a larger potential window is used (> 1.0 V), an additional electron transfer process is observed (Figure S1); this cyclic voltammogram is largely unchanged compared to using TPABArF$_{24}$ (BArF$_{24}$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) as the electrolyte,[28] indicating the change of anion imparts no appreciable difference in the electrochemical electron transfer behavior of (salfen)Al(O^{i}Pr). An oxidative potential of no more than +1.1 V (versus Ag/Ag$^+$) was applied during bulk electrolysis reactions to avoid secondary oxidations.
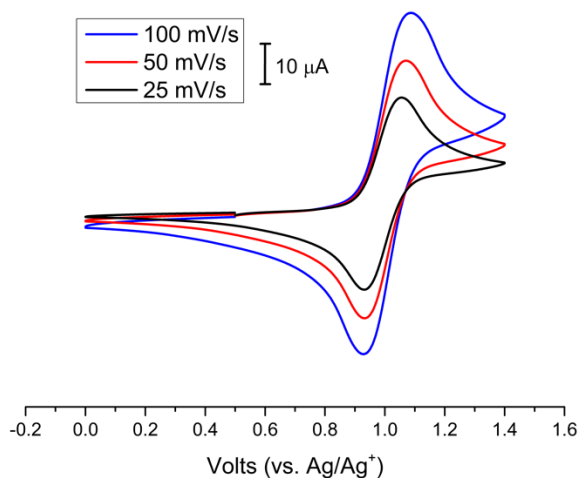
Figure 2. Cyclic voltammogram of 2.5 mM (salfen)Al(O^{i}Pr) in 100 mM TPANTf$_2$ in 1,2-difluorobenzene.

We set out to investigate if our electrochemical reaction conditions had an effect on homopolymerization reactions catalyzed by (salfen)Al(O^{i}Pr). We previously reported that in C$_6$D$_6$, LA and TMC polymerization proceeded with (salfen)Al(O^{i}Pr) in the reduced state but not the oxidized state, while CHO exhibits the opposite reactivity. δ-Valerolactone (VL) and ε-caprolactone (CL) showed activity in both oxidation states.

First, homopolymerization reactions of LA and TMC were carried out with (salfen)Al(O^{i}Pr) in the reduced state in the presence of TPANTf$_2$ in 1,2-difluorobenzene. We found that both reactions became slower under these electrochemically relevant conditions. Specifically, LA polymerization proceeded at 100 ºC, reaching a conversion of 37% in 24 hours (compared to 64% in 24 hours when using previously reported conditions). A similar reaction, using 1,2-difluorobenzene as the solvent and excluding the electrolyte, showed 40% conversion in 24 hours at 100 ºC, suggesting the presence of electrolyte did not have an effect on the reaction rate and, instead, the solvent choice was responsible for activity differences. Similarly, TMC homopolymerization proceeded

more sluggishly at room temperature, reaching 73% conversion in 3.5 hours (compared to 98% in only 2.5 hours). Both VL and CL showed similar trends of slower reactions rates (Table 1, entries 5 and 7, respectively). Expectedly, no cyclic ethers (CHO, PO, THF) were polymerized with (salfen)Al(O^{i}Pr) in the reduced state (Table 1, entry 9).

We next moved to the polymerization activity of the electrochemically generated oxidized form of (salfen)Al(O^{i}Pr). The first major difference was the rapid polymerization of TMC, which reached nearly a full conversion in under 15 minutes, compared to no activity for the chemically generated counterpart. Since this activity is unusual, we decided to find out whether it is due to the change in solvent, and/or the presence of TPANTf$_2$. When the results of using a chemical oxidant in 1,2-difluorobenzene were similar to those obtained with the electrochemically generated species, a new batch of (salfen)Al(O^{i}Pr) and carefully purified ^{Ac}FcBArF$_{24}$ were employed. These experiments showed that indeed, [(salfen)Al(O^{i}Pr)][BArF$_{24}$] has similar activity toward TMC as the electrochemically generated species.

Both oxidation states, regardless of how they were generated, produced TMC polymers with a bimodal trace at high conversions as determined by size exclusion chromatography (SEC). When TMC loading was increased to 200 equivalents, the polymer produced by the reduced state at moderate conversion (< 60%) resulted in a unimodal trace with a narrow dispersity. However, as conversion increased (> 80%), the trace became bimodal, suggesting a loss of control at higher conversion—a phenomenon that has been reported previously.[48] LA showed no conversion in the oxidized state, while both CL and VL did, both faster than in the reduced state. Lastly, cyclic ethers were surveyed and showed a drastic different compared to when using chemical redox reagents. Specifically, the homopolymerization of CHO generated electrochemically reached 80% conversion in 21 hours (Table 1, entry 10), in comparison to 99% in only 0.1 hours for the

chemically controlled reaction. Additionally, the process seemed to be better controlled, producing a polymer with a dispersity of 1.26 (compared to 1.45).

Table 1. Electrochemical homopolymerization reactions of various monomers.

entry	mon.	cat.	conv.[a]	time (h)	M_n (kDa)[b]	Đ
1	LA	red	37%	24	4.5	1.1
2	LA	ox	NR	24	--	--
3	TMC	red	73%	3.5	7.2	1.3
4	TMC	ox	94%	0.2	11.8	1.5
5	VL	red	72%	5.5	14.1	1.1
6	VL	ox	> 95%	0.2	14.5	1.1
7	CL	red	87%	5	11.7	1.1
8	CL	ox	77%	4	20.2	1.4
9	CHO	red	NR	24	--	--
10	CHO	ox	74%	20	12.4	1.3

Conditions: 75 mM solution TPANTf₂, 1.5 mL 1,2-difluorobenzene. 0.01 mmol precatalyst, 100 equivalents monomer, unless otherwise noted; all polymerizations were carried out at room temperature except for LA, which was carried out at 100 ºC; red = (salfen)Al(O^{i}Pr); ox = [(salfen)Al(OiPr)][NTf₂]; [a] determined by ^{1}H NMR spectroscopy by integrating polymer to monomer peaks; [b] determined by SEC.
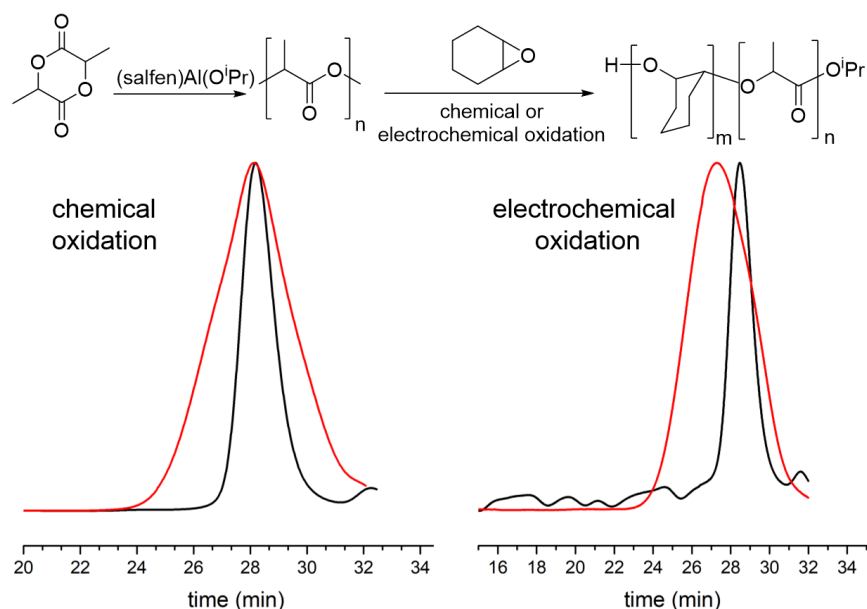
Figure 3. Comparison of PHCO-b-PLA block copolymers produced by (salfen)Al(O^{i}Pr) via a chemical redox switch (left) and an electrochemical switch (right).

Next, we moved our attention to how electrochemistry affects copolymerization reactions. First, we set out to determine if the slower reaction times and lower dispersity of CHO polymerization carried over to simple diblock copolymerization reactions. Two PCHO-b-PLA copolymers were synthesized, one using an electrochemical switch and the other a chemical switch. For a direct comparison, the chemical redox switch was performed using electrochemical conditions (e.g., 75 mM solution of TPANTf$_2$ in 1,2-difuorobenzene), but with a chemical oxidant (AcFcNTf$_2$, AcFc = acetylferrocenium) in place of electrochemistry. The initial LA polymerization by the reduced complex proceeded as usual, however, the incorporation of CHO in the second block proceeded more quickly, reaching 72% conversion in 2.5 h (compared to 67% in 16 h). The diblock copolymer produced chemically exhibited a broad SEC trace with a dispersity of 1.7 (Table 2, entry 1). Additionally, the peak of the SEC trace remained at the same retention time, and only broadened (both to greater and smaller retentions times), indicating the process was less controlled

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and only a minority of polymer chain ends incorporated CHO. On the other hand, when the oxidation was performed electrochemically, CHO incorporation occurred more slowly and the final copolymer exhibited a lower molecular weight with a narrower dispersity of 1.2 (Table 2, entry 2). Additionally, the peak of the SEC trace decreased in retention time indicating the majority of the polymer chains increased in molecular weight.

Table 2. Electrochemical copolymerization reactions with (salfen)Al(O^{i}Pr).

entry	mon. 1	mon. 2	cat.	conv. (%)[a]	time (h)	M$_n$ (kDa)[b]	Đ
1[c]	LA	CHO	red-ox	41 – 72	24 – 2.5	19.7	1.7
2	LA	CHO	red-ox	37 – 67	22 – 16	13.5	1.2
3	TMC	CHO	red-ox	56 – 77	2.5 – 18	26.1	1.4
4	TMC	CHO	ox-ox	97 – 46	0.2 – 3	11.6	3.0
5	LA	TMC	red-ox	59 – 5	24 – 24	N.D.	N.D.
6	LA	TMC	red-red	59 – 9	24 – 24	N.D.	N.D.

Conditions: 75 mM solution TPANTf$_2$, 1.5 mL 1,2-difluorobenzene. 0.01 mmol precatalyst, 100 equiv monomer 1 and 200 equiv monomer 2; red = (salfen)Al(O^{i}Pr); ox = [(salfen)Al(O^{i}Pr)][NTf$_2$]; [a] determined by ^{1}H NMR spectroscopy by integrating polymer to monomer peaks and reported as conversion of that monomer; [b] determined by SEC; [c] using chemical redox agents.
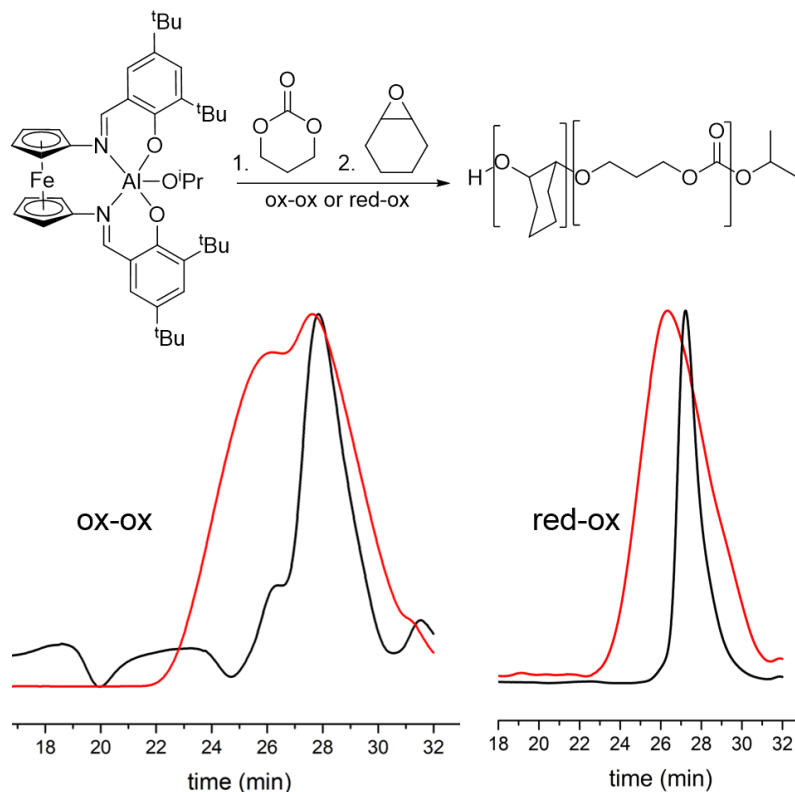
Figure 4. SEC traces of a TMC and CHO copolymerization reaction using an ox-ox redox switch (left) and a red-ox redox switch (right). Black trace represents the first polymerization step and the red trace represents the second step.

Since the polymerization of TMC proceeded with (salfen)Al(O^{i}Pr) in both the reduced and oxidized state, we set out to determine if the oxidation state had an effect on copolymers containing a TMC block. First, PCHO-b-PTMC copolymers were synthesized using both an oxidized-oxidized catalyst state and a reduced-oxidized catalyst state. The reduced-oxidized catalyst switch proceeded with 56% and 77% TMC and CHO conversion, respectively, and yielded a diblock copolymer with a unimodal SEC trace, a molecular weight of 26.1 kDa and a dispersity of 1.4 (Fig. 4). On the other hand, because TMC polymerization in the oxidized state proceeds rapidly and uncontrolled, the diblock polymer had a bimodal SEC trace (similar to that of the PTMC trace)

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with a dispersity of 3.0, suggesting either both PTMC polymeric species chain extended during the second polymerization step or a mixture of homopolymers was produced.

Attempts to synthesize PTMC-b-PLA block copolymers, both by a reduced-reduced and a reduced-oxidized (generated electrochemically) catalyst state afforded mostly PLA homopolymers with less than 10% TMC conversion. ^{1}H NMR spectra of the isolated polymers also indicated little TMC incorporation. This result was expected as TMC incorporation after LA polymerization is rare in the literature.[49-51]

CONCLUSIONS

In conclusion, (salfen)Al(O[i]Pr) exhibits similar reactivity when using an electrochemical switch compared to a chemical redox switch. In the reduced state, lactide, lactones, and TMC are polymerized with good control, while cyclic ethers show no activity. In the electrochemically generated oxidized state, CHO is polymerized relatively slowly and with better control than when using a chemical oxidant. Both lactide and cyclohexene oxide were the only two monomers that exhibit orthogonal reactivity (LA in the reduced state and CHO in the oxidized state) and both lactones (VL and CL) and TMC are ring opened in both oxidation states. The necessity of a redox switch is shown when producing well controlled diblock copolymers, namely PCHO-b-PLA and PCHO-b-PTMC.

ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge.

Experimental and characterization data (PDF)

AUTHOR INFORMATION

Corresponding Author

Paula L. Diaconescu – Department of Chemistry and Biochemistry, University of California Los Angeles, Los Angeles, California 90095-1569 United States; email: pld@chem.ucla.edu

Present Addresses

† HRL Laboratories, Malibu, CA

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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