Developing an Electrochemically Redox Switchable System for Polymer Synthesis

Miao Qi

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Miao Qi

Advisor: Jeffery A. Byers

Abstract This dissertation discusses the development of an electrochemically switchable system for copolymer synthesis as well as surface modifications. In Chapter one, the usage of electrochemistry to control polymerization reactivities is introduced. In Chapter two, an electrochemically redox switchable polymerization for lactide and cyclohexene oxide will be presented. In Chapter three, a surface modification method based on the electrochemically redox switchable catalysis is discussed. The surface-anchored catalyst responds to applied electrochemical potentials towards two different ring-opening polymerizations to generate binary polymer patterns in one step. The method represents a facile way to generate polymer coatings on surfaces. In Chapter four, a discussion on the detailed kinetic analysis of an iron-catalyzed epoxide polymerization will be presented, the study allows us to unveil the importance of entropy-controlled reactions. In Chapter five, future perspectives on the electrochemically redox switchable catalysis will be discussed.

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ABBREVIATIONS

ΔE	quadrupole splitting (Mössbauer)
ΔG	change in Gibbs free energy
ΔH	change in enthalpy
ΔS	change in entropy
δ	chemical shift (NMR); isomer shift (Mössbauer)
Å	angstrom
А	ampere
Ar	aryl
ATR	attenuated total reflection
ATRP	atomic transfer polymerization
BArF	tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
Bu	butyl
СНО	cyclohexene oxide
CL	ε-caprolactone
conv	conversion
COPASI	Complex Pathway Simulator
Ср	cyclopentadienyl
CTA	chain transfer agent
CV	cyclic voltammetry
equiv	equivalents(s)
D	diffusion constant
DME	dimethoxyl ethane
DOSY	diffusion-ordered spectroscopy
E _{1/2}	half-wave potential or redox potential

Et	ethyl
eATRP	electrochemically mediated atomic transfer polymerization
eRAFT	electrochemically mediated reversible addition-fragmentation
	polymerization
Fc	ferrocene
FTIR	fourier transform infrared spectroscopy
g	gram(s)
GC	gas chromatography
GPC	gel permeation chromatography
h	hour(s)
i	current
i_{pa}	anodic peak current
ipc	cathodic peak current
iPr	isopropyl
L	liter(s)
Μ	molarity (mol/L)
Me	methyl
Med	redox mediator
Mes	2,4,6-trimethylphenyl
Min	minute(s)
M _n	Number average molecular weight
mol	mole(s)
$M_{ m w}$	Weight average molecular weight
NMR	nuclear magnetic resonance
р	para
PDI	Pyridyl diimine

Ph	phenyl
PLA	poly(lactic acid)
P _n	polymer with n repeating unit
PVDF	poly(vinylidene difluoride)
Q	charge
RAFT	reversible addition-fragmentation polymerization
RI	refractive index
ROP	ring opening polymerization
SAM	self-assembled monolayer
SPS	solvent purification system
STEM	scanning tunneling electromicroscopy
TBA	tetrabutyl ammonium
tBu	tert-butyl
THF	tetrahydrofuran
TMS	trimethylsilyl
TGA	thermalgravimetric analysis
V	volt(s)

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1. Chapter 1. Electrochemistry for Polymer Synthesis

1.1 Introduction to electrochemistry and bulk electrolysis.

Redox processes are common in many bond forming reactions. Electrochemistry has been used as an innovative way to replace toxic and expensive chemical redox reagents.^{1,2} In most cases, electrolysis doesn't require harsh reaction conditions and provides versatility where the charge input can be extended to a wider window of redox potentials. Additionally, changing electrochemical parameters can be highly automatic and programmable.^{2–4} With the increasing interest in electrochemically facilitated organic transformations,^{2,5–7} polymerization is no exception.

There has been a long history of using electrochemistry to initiate polymerization reactions.⁸ More recently, electrochemically mediated or controlled polymerization has shown many interesting features and scientists have shown increasing interest in developing electrochemistry methods for developing polymerization systems due to above-mentioned advantages.^{9,10} The ability to selectively oxidize the reactant to appropriate oxidation states. For example, in radical-initiated polymerization reactions initiated from redox events, the reactive free radical species often lead to undesired side reactions. Electrochemistry can precisely control the generation of desired radical species to prevent side reactions.¹¹ In the following part of this section, the engineering aspect of the electrolysis cell will be introduced to

In a typical bulk electrolysis cell, a working electrode and a counter electrode are connected to a power source to enable the electron transfer of the species on the surface of the working electrode (Figure 1a).¹² In the electrolyte, charges are transported by the movement of ions. The observed over potential on the working electrode is measured by referencing a stable, constant electrochemical reaction on the reference electrode.

In an electrolysis cell, the charge of the overall reaction must be balanced. When an anodic oxidation happens on the working electrode, the charge imbalance must be eliminated through the reduction reaction on counter electrode.^{10,11,13} Often times, the reaction at the counter electrode for example, the decomposition of electrolyte, will cause many undesired reactions. In this case, either a divided cell set-up or a sacrificial counter electrode can be used to improve the cell performance and avoid deleterious side reactions.^{14,15} In a divided cell, the counter electrode and the working electrode are separated by a semi-permeable membrane, normally a cation permissive membrane.^{16,17} Common examples for such materials include organic polymers¹⁶ and ceramics¹⁷. The charge balance can be completed by the movement of cations through the membrane, and the working electrode can be isolated from the undesired side reactions. Sacrificial counter electrodes, on the other hand, often consist of reactive metals, instead of decomposing the substrate and electrolyte, the charge imbalance can be compensated by the oxidation of the metal or deposition of the metal cation. Sacrificial counter electrodes can be used directly in undivided cells (Figure 1b).^{18,19}



Figure 1.1. Electrolysis cell set-up a) three electrode set-up; b) two electrode set-up, where a sacrificial counter electrode is used to balance the charge. RE: reference electrode, WE: working electrode, CE: counter electrode.

In heterogeneous electron transfer processes, mass transport plays an important role in determining the reaction rate.¹¹ It is especially important for polymerizations as the polymer product is high in molecular weight and thus has a low diffusion rate. In this case, increased

surface area for the electrode is often required. Carbon based electrodes, including carbon fibers,^{20,21} and vitreous carbon foam^{22,23} have been applied to various electrosynthesis methods, due to their light weight, high stability and low cost. Carbon fibers are tough and robust and easy to modulate, however, carbon fibers often suffer from the capillary effect and must be attached to a conducting rod to avoid the loss of materials into the fibers themselves.²⁴ Carbon foam and carbon paper are very fragile, difficult to handle and unsuitable for reactions requiring high stirring rates. At the same time, polymer products can be absorbed onto the porous carbon electrode surface and analyzing the product from the electrochemically controlled polymerizations can be challenging and the deposited polymer mass also needs to be considered. In electrochemistry for a dissolved analyte, the relationship between current and diffusion constant is described with the Cottrell equation, $i = nFAc_i^0 \sqrt{D} / \sqrt{\pi t}$, where n is number of electrons, F is the Faraday constant, A is the surface area of electrode and c_i^0 is the initial concentration of the analyte.¹¹ As shown in the equation, the current increases linearly with the square root of the diffusion constant. In other words, charge transfer will be more sluggish for compounds that have smaller diffusion constants. This effect is particularly important for electrochemically facilitated polymerizations, if the redox-active species are macromolecules, they will diffuse slower and will take longer for the reaction to occur as polymerization proceeds.¹⁰

1.2. Redox-mediated electron transfer processes

Mediated electron transfer processes are hybrids between homogeneous electron transfer and direct bulk electrolysis.¹ Instead of directly reducing/oxidizing the substrates on the electrode surface, a redox mediator is firstly converted, followed by the homogenous electron transfer from the reactive intermediate to the substrate (Scheme 1.1). Normally, redox

mediators diffuse faster to the electrode surface and the electron transfer is more efficient. Only a catalytic amount of the redox mediators is needed as they are quickly regenerated on the electrode. This mediated electron transfer shares a lot of similarities with photoredoxsystems where photo-catalysts act as electron shuttles to facilitate electron transfer to the substrate.^{14,26,27}



Scheme 1.1. Redox-mediated electron transfer process

With the addition of redox mediators, the kinetic inhibition of the heterogeneous electron transfer between electrode and substrate can be eliminated, which means that overpotentials can be avoided, and that reactions can be accelerated.^{14,15} When the direct electrochemical conversion causes passivation of the electrode, the employment of a mediator can be helpful, since direct interaction of the substrate with the electrode surface is avoided. Since the electrolysis is conducted at potentials lower than the redox potential of the starting material, the reaction can be carried out under milder conditions and side reactions can be prevented. This can be particularly significant when sensitive functional groups, which are not intended to react, are present.

A good application of mediated electron transfer process is the controlled radical polymerizations. Free radical species are highly reactive but have poor selectivity; free radical polymerizations often lead to chain terminations and disproportionation. In the mid-1990s,

efforts were aimed at developing polymerization with living characteristics, where the initiation is much faster than the chain propagation and no chain termination or chain transfer are happening.²⁸ This type of polymerization allows the easy control of the degree of polymerization with low molecular weight distributions.²⁹ Those examples show similar concept of reversibly activating/deactivating the radical propagating species. Transition metal complexes, in this case, have been widely applied in controlled radical polymerization reactions including atom transfer radical polymerization (ATRP).^{30–33} In ATRP. activation happens when initiators first undergo halogen abstraction by a lower oxidation state metal complex to generate a free radical with the metal complex being oxidized to form a metalhalide bond (scheme 1.2). Monomer can sequentially be added to radical propagating species to elongate the chain. Deactivation happens with the metal halide complex recombines with the radical propagating species to terminate the chain growth, while itself returns to its lower oxidation state. Deactivation happens a lot faster than activation, such that very reactive radical concentration remains low in the reaction media to suppress side reactions, e.g. chain termination from radical recombination. In ATRP, the one electron transfer happening at the metal center is essential for the establishment of the dynamic equilibrium.

n [M]ⁿ + P_n-Br
$$\xrightarrow{activation}$$
 n [M]ⁿ⁺¹Br₂ + P_n $\xrightarrow{Propagation}$

Scheme 1.2. Activation/deactivation equilibrium in atomic transfer radical polymerization

Since electron transfer plays an important role in controlling the reactivity in ATRP, electrochemistry methods have been applied to various radical polymerization systems to control the multiple equilibrium steps to achieve temporal control of the polymerization steps.

A notable example of such a system is electrochemically mediated atom transfer radical polymerizations (*e*ATRP) (Scheme 1.3).^{34–36}



Scheme 1.3 Electrochemically mediated atomic transfer polymerizations, the Lazarus switch brings the inactive Cu(II)-halide complex back to its active Cu(I) oxidation state. Electrochemistry keeps the activation/deactivation equilibrium constant in order to initiate the polymerization and keep its living characteristics.

Electrochemical transformations are used for a twofold purpose: 1) to alter the equilibrium between reduced complexes (e.g copper(I)) that activate alkyl halides for ATRP and oxidized species (e.g. copper(II)) that deactivate propagating chains towards ATRP, and 2) to continuously reduce the oxidized form of the catalyst so as to mitigate unwanted chain termination events by maintaining a steady state of oxidized and reduced species (Scheme 1.3). Without continuous reduction, chain termination from radical coupling or radical disproportionation alters the equilibrium of the oxidized and reduced species leading to a gradual loss in activity. Since controlling the equilibrium between the active and inactive state of the catalyst relies on electrical input, a switchable polymerization system requires continuous application of reducing or oxidizing potentials As the reaction equilibrium needs some time to establish, an induction period is often observed in the *e*ATRP systems.³⁶



Figure 1.2 On/off switch of *e*ATRP of methyl methacrylate with tris(2-aminoethyl)amine copper (II) complex, when the application of reducing potential results in polymerization. Recreated from Ref. 36.

The similar principle has also been applied to the reversible addition fragmentation polymerization (RAFT).³⁷ In RAFT, the reversible chain transfer of the active polymer chain end to the chain transfer agent (CTA) facilitates the activation/deactivation equilibrium of the polymerization. In this type of polymerizations, redox events are not happening. In order to control the activation/deactivation equilibrium of RAFT radical polymerization electrochemically, a radical species much be formed through the fragmentation of the bond by an electrochemical reduction. However, electrochemical reduction of the CTA did not lead to any polymerization activities.³⁸ It was found that the electroreduction of the thiocarbonate CTA underwent a two-electron process and irreversibly cleaved the C-S bond without producing the radical propagating species (scheme 1.4).



Scheme 1.4 Two-electron reduction of phenylcarbonothioylthio)pentanoic acid (chain transfer agent) on the electrode.

Although using electrochemistry was not successful in controlling the reactivity of RAFT radical polymerizations, several examples demonstrated that RAFT cationic polymerization systems can be controlled by electrochemistry. Yan and coworkers reported that electrochemistry can be used to switch the reactivity of vinyl ether polymerizations with electrochemistry.³⁸ As shown in Figure 1.3, 2,3-dicholor-5,6- dicyano-1,4-benzoquinone (DDQ) was used as the redox catalyst to control the concentration of the propagation chain end. Like the ATRP, the activation/deactivation equilibrium is key to the reactivity in this system. The oxidized form of the catalyst (DDQ) can react with the "capped" dormant chain end and generate the propagating cation species. Upon applying an oxidizing potential, the dormant chain end can be reactivated to propagate; without the potential input, the cationic chain end recombines with the DDQ^{2-} and the reaction stalls as the equilibrium strongly favors the deactivation side. Different from *e*ATRP, an oxidizing potential is required to reactivate the polymerization process,





Figure 1.3 *e*RAFT cationic polymerization of isobutyl vinyl ether (iBVE) controlled by electrochemistry. Revolution of monomer conversion over time. The "off" state indicate no oxidizing potential applied. Recreated from ref. 38.

Fors and coworkers reported a similar but more complicated electrochemically switchable cationic polymerization system, where they used two mediators at the same time (Scheme 1.5).³⁹ (2,2,6,6-tetramethyylpiperidin-1-yl)oxyl (TEMPO) acts as the redox charge transfer mediator and a dithiocarbamate chain transfer agent (CTA) was used to mediate the charge transfer in the polymerization equilibrium. As shown in Scheme 1.6, with the application of an oxidizing potential, oxidized TEMPO reacts with the dormant chain end to generate the propagating cationic chain end and a thiocarbonate radical. However, it was unclear what the role of TEMPO is in this polymerization system. Without the addition of TEMPO, the direct oxidation of the RAFT CTA led to non-living characteristics due to the irreversible charge transfer as describe earlier. It was proposed that through the addition of TEMPO as an electron shuttle, the reversible redox reactions can happen with the thiocarbonate CTA. They have also demonstrated that through the application of the reducing current, the reaction equilibrium can be shifted more rapidly, and no induction period was observed for the polymerization of vinyl ethers.



Scheme 1.5 Proposed catalytic cycle of the TEMPO mediated polymerization of vinyl ethers. Recreated from ref. 39.

*e*ATRP has been extended to copolymer synthesis as well as surface modifications. Polymer brushes can be constructed on electrode surfaces using *e*ATRP by anchoring the radical initiator on the electrode surface, the polymer chain grows off the surface (Figure 1.4).⁴⁰ Interestingly, as diffusion of catalyst onto electrode surface now plays an important role, by tilting the electrode, a gradient polymer brush can be formed; where the shorter chains formed on the area where the substrate is far from the working electrode and longer chains formed on the places where the silicon substrate is closer to the working electrode. This example combines the temporal control of the *e*ATRP and the diffusion properties in electrolysis.



Figure 1.4 Polymer brushes grafting on electrode with eATRP. a) When the substrate is placed in parallel with the working electrode, polymer brush with identical chain lengths is formed; b) when the electrode is tilted, a gradient brush is formed.

Overall, electrochemistry has been used to mediate various equilibrium-driven polymerization processes, serving the purpose of shifting the reaction equilibrium towards propagation and reactivating dormant species. In these systems, concentration of mediators and charge transfer rate is essential for establishing polymerizations with living characteristics. These electrochemically controlled polymerizations can be robust, and the unique features of such system can be used to synthesize polymers with interesting patterns. So far, electrochemistry has only been used to mediate polymerizations that proceed by ATRP and RAFT cationic mechanisms, and the polymers synthesized are limited to polyolefins with carbon-carbon backbones.

1.3 Electrosynthesis of conducting polymers



Scheme 1.6 Electropolymerization of conducting polymers.

Despite the recent examples of electrochemically mediated polymerizations with temporal control, there is a long history of the use of electrochemistry in polymer synthesis. More than 150 years ago, first example of electropolymerization was reported by Letheby,⁴¹ where he observed the formation of a dark and shiny insoluble powder when applying anodic oxidation to an aniline solution. Electrochemical synthesis represented one of the earliest examples of conducting polymers. In the 1980s, modern synthetic methods of conducting polymers was developed, scientists found out that using anionic polymerization techniques, polyacetylene can be formed, and the iodine doped polyacetylene (PA) displayed metal-like optical properties and electron conductivity.^{42,43}

The exact mechanism of electropolymerization of conjugated polymers remains unclear.⁴⁴ It is generally believed that the reaction undergoes a step growth mechanism where first there is formation of soluble oligomers, followed by nucleation and propagation producing polymeric materials. In most cases, as polymerization propagates, the polymer product becomes less soluble and sometimes will deposit onto the electrode. After deposition, the solid-

state polymerization can still proceed and lead to the formation of polymer networks on the electrode surface.

The most important electrochemical method of preparing conducting polymers is the anodic oxidation of monomers. Potentiostatic (constant potential),⁴⁵ potentiodynamic,⁴⁶ or galvanostatic (constant current) techniques have been used to synthesize conducting polymers.⁴⁷ The potentiodynamic experiment, where the applied potential is swept for cycles, similar to cyclic voltammetry experiments, not only leads to polymerization activities, but also provides information on the reaction process. As shown in figure 1.5, in the first cycle, only the redox wave from the monomer can be observed. As the polymerization proceeds, the appearance of a new species indicates the formation of polymer, and the increased peak current indicates the increase in polymer concentration.





It is believed that the first step in the anodic polymerization involves the formation of the oligomer intermediate.⁴⁷ It was determined later that the oligomer intermediate (Oligomer⁺) undergoes a comproportionating reaction with another equivalent of monomer to generate the charged monomer (monomer⁺) which reenters the catalytic cycle (Scheme 1.7).⁴⁸ This autocatalytic mechanism indicates the oligomer⁺ acts as redox mediators to facilitate further chain elongation.



Scheme 1.7 The proposed autocatalytic cycle in anodic polymerization of conducting polymers.

Deprotonation was believed to be a fast step in the cycle as it re-established the aromaticity in dimers and oligomers.⁴⁸ Interestingly, several studies found out that the proton elimination step is not spontaneous and will not occur without an applied potential higher than the oxidation peak potential of the oligomers. The proton elimination is slower to occur with extended conjugation systems in oligomers. Consequently, the polymerizations proceed much faster in wet solvent.

Due to the above-mentioned complexities, the electrosynthesis of conjugated polymers often produces polymers with inconsistent chemical and physical properties.⁴⁹ Factors

including temperature, stir rate, and solvents impact the polymerization outcome. Moreover, the influence of electrolyte cannot be ignored, as the size of the electrolyte greatly affect the subsequent charging/discharging properties, and the morphology of the polymers. After the formation of the deposited solid material on the electrode, the conductivity of electro-generated polymers is affected by counterions.^{48,49} For example, in the case of PEDOT and derivatives, the *in situ* conductivity decreases with the anion sequence $ClO_4^- > BF_4^- > CF_3SO_2^- > PF_6^{-.49}$

Electrosynthesis of conducting polymers offers an elegant and easy strategy for the immobilization of metal complexes on the surface of electrodes.^{50,51} An easy strategy is to electropolymerize metalloporphyrin containing monomers.⁵⁰ Such materials have been used to study enzymatic processes, combining the molecular nature of the metal sites and the powerful electrochemical analytical tools. The metal porphyrin films have also been applied to heterogeneous catalysis such as CO₂ reductions.^{50,51}

Nanopatterns of conducting polymers can be directly written onto substrates using scanning electrochemical microscopy (SECM).⁴⁴ An ultramicroelectrode (UME) was scanned across a solid substrate immersed into a monomer containing solution⁵² and the electrochemical response of the modified surface can be easily detected by the electrode tip as well. For example, constant anodic oxidation allowed the formation of a polythiophene film on the substrate (Figure 1.6). The UME tip locally oxidizes the mediator ruthenium (Ru(bipy)₃Cl₂) in the aqueous solution, which then oxidized the spin-coated insoluble thiophene monomer on the substrate surface. This method allows the formation of polythiophene patterns with a resolution as low as 15 µm.⁵²



Figure 1.6 Locally deposited polythiophene films forms with SCEM

1.4 Conclusion

There is a long history of using electrochemistry to facilitate various polymerizations. The unique advantages of using electrochemistry provide many opportunities. For example, the high programmable nature of electrochemistry can benefit the formation of complex polymer architectures, both in solution and on heterogeneous surfaces. At the same time, in the heterogeneous systems, the diffusion-affected process can open new possibilities, such as to affect polymer molecular weight distributions. Electrochemistry can also be beneficial for reactions where high pressure is required, for example, polymerization of gaseous monomers. With the renaissance of electrochemistry in organic transformations, electrochemistry is more widely adopted in controlling polymerization reactions. Combining the powerful tools of electrochemical characterization, new reactivities might be discovered in an efficient and programmable manner. In the following chapters, efforts towards developing an electrochemically redox switchable polymerization system will be discussed. The unique properties of electrochemical redox reaction allowed us to generate sophisticated polymer architectures.

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2. Chapter 2. E-Switchable Ring-Opening Polymerization of Lactide and Epoxide

2.1 Introduction

Efforts have been dedicated to investigate the structure-property relationship of synthetic polymers.^{1,2} While methods to synthesize biological macromolecules, such as peptides^{3,4} and DNA,⁵ have been developed that result in sequence selective syntheses with high automaticity, achieving sequence control for other synthetic polymers remains challenging. In the past decades, significant advances have been made to change the primary structure of synthetic polymers.^{2,6–12} Elegant methods involving step growth polymerization reactions have been developed to construct block copolymers with control over composition, molecular weight, and comonomer sequence.¹³ However, many of these methods are dictated by the inherent reactivity of monomers, which limits the ability to incorporate monomers in particular sequences,^{10,14} requires precise control over the monomer feed ratio,^{15,16} or results in non-uniform distribution of monomers in copolymers synthesized from a single monomer feed.^{17–20}

Switchable catalysis,^{21–24} in which the reactivity of a catalyst can be altered in situ with application of an external stimuli, provides an attractive alternative to control polymer sequence (Figure 2.1). These catalysts are reminiscent of allosteric enzymatic processes where an enzyme responds to external stimuli so as to alter its reactivity accordingly.^{25,26} Various stimuli have been used to effect changes in reactivity in switchable polymerization catalysts.²³ Particularly effective have been switchable catalysts that utilize redox chemistry, which provides a facile and efficient way to vary the active state of a catalyst.^{27,28,36,29–31,31–35} While reports for switchable catalysts exist for the controlled polymerization of various monomers, such methods have been applied to great affect for the ring-opening polymerization of lactones and epoxides because catalyst oxidation state drastically alters the Lewis acidity of the metal

complexes that are important to facilitate the ring-open processes.^{37–39} Since their original discovery by the Gibson group for redox-controlled lactide polymerization,⁴⁰ many efforts have been dedicated to control ring-opening polymerization processes by varying the oxidation states of metal complexes that either contain redox non-innocent ligand moieties (e.g. ferrocene-containing ligands)^{17,41,42} or directly inducing redox reactions on the metal center that is also the active site for polymerization.^{43–45}





Over the past years, we have been investigating a switchable polymerization system based on iron alkoxide complexes bearing bis(imino)pyridine ligands.^{45,46} In these catalysts, iron(II) is the active form of the catalyst for lactide polymerization, but upon one electron oxidation to formally iron(III), the species becomes dormant. Sequential addition of chemical redox reagents (e.g. ferrocenium and cobaltocene) provided a means to activate and deactivate the catalyst towards lactide polymerization.⁴⁴ We have subsequently shown that the catalyst exhibits complementary reactivity for epoxide polymerization, being active when in the formally iron(III) oxidation state and inactive when in the iron(II) oxidation state. We have subsequented block copolymers¹⁴ and

cross-linked polymer networks.¹⁵ In this chapter, an extension of this chemistry to include an electrochemical method to afford the redox equivalents needed for switching (Scheme 2.1b). Through careful design of the electrochemical cell and altering the conditions of the electrochemical reactions, a method for rapid switching was developed for the polymerization of lactide and epoxides. This method was used to control block copolymer syntheses wherein the sequence of the polymerization reaction was dictated by the electrochemical potential applied.



Figure 2.2. A switchable polymerization system based on iron alkoxide complexes bearing bis(imino)pyridine ligands

As discussed in chapter 1, while most reports that utilize redox chemistry to control chemical reactivity in polymerization reactions use chemical redox reagents,^{22,23} few reports utilize electrochemical means to affect the needed redox processes.⁴⁷ A notable method that uses electrochemistry to alter chemical reactivity in polymerization catalysts are

electrochemically mediated atom transfer radical polymerizations (*e*ATRP).^{48–50} In this chapter, we reveal an alternative way to use electrochemistry to control polymerization reactions. Instead of serving as a means to control equilibrium concentrations, the electrochemistry will be used to toggle between two different oxidation states of an iron-based catalyst that has complementary reactivity for ring opening polymerization of lactide and epoxides (Scheme 2.1b). A significant difference with this new e-switchable polymerization system compared to eATRP is that polymerization does not require continuous electrical input because its role is to provide the stoichiometric oxidizing or reducing equivalents needed to alter the oxidation state of the catalyst so as to achieve switchable catalysis.



Scheme 2.1 e-switchable ROP uses electrochemistry to control the reactivity towards different polymerization reactions

2.2. Cell design

Before a redox-switchable polymerization reaction could be achieved using electrochemistry, it was first necessary to characterize the redox characteristic of the iron-based catalyst.^{44,51} Therefore, cyclic voltammetry was conducted using iron(II) species 2 (Scheme in dichloromethane (5 mM) and 2.1) dissolved using tetrabutylammonium hexafluorophosphate (nBu₄NPF₆, 100 mM) as the supporting electrolyte. A glassy carbon electrode was used as the working electrode, a platinum wire was used as the counter electrode, and a lithium ribbon separated from the bulk electrolyte by a selective ion permeable membrane served as the reference counter electrode. As can be seen in Figure 2.1a, the CV exhibits a welldefined redox peak at ca. 2.9 V (vs Li⁺/Li), the cathodic and anodic waves of which correspond to Fe(III) \rightarrow Fe(II) and Fe(II) \rightarrow Fe(III) conversions, respectively. The redox behavior agrees with our previous discovery that the iron catalyst can be chemically oxidized and reduced by reacting with ferrocenium hexaflurophosphate (FcPF₆) and cobaltacene (Cp₂Co), respectively,⁴⁴ and is consistent with the 0.8 V (vs Fc/Fc⁺) redox potential we previously reported.44,51 Notably, no other redox features are observed in the CV data within the measurement window (2.3 to 3.7 V vs. Li⁺/Li). The clean redox behavior of the system provided an opportunity to reliably convert the catalyst between the reduced and oxidized forms without worrying about parasitic chemical reactions, such as iron over-reduction (or over-oxidation). To provide precise control over the chemical potential, potentiostatic reduction/oxidation was employed throughout.



Figure 2.3 (a) Cyclic voltammogram at a scan rate of 25 mV/s using Fe(II) complex **2.1**; (b) Modified divided electrochemical cell used for bulk electrolysis needed for e-switchable polymerization (5 mL total). Counter electrode side: fine glass fritted tube coated with poly(vinylidene) difluoride (PVDF) membrane saturated with Bu₄NPF₆ was used to isolate a sacrificial lithium wire counter electrode suspended in dimethoxyethane (DME, 2 mL) and using LiClO₄ (100 mM) as the supporting electrolyte; working electrode side: high surface area carbon fiber (2.5 g) suspended in dichloromethane (5 mL) using Bu₄NPF₆ (100 mM) as the supporting electrolyte.

Next, the electrochemical cell design was modified for bulk electrolysis (Fig. 1b). A primary concern during the design of this cell was to compensate for the charge imbalance incurred by interconverting the neutral iron(II) complex **2.1** with the cationic formally iron(III) complex **2.2**. In control experiments, lithium salts were found to exhibit no influence on either the polymerization of lactide or epoxides (See experimental section), so these salts were used to balance charge and to make the medium conductive. Additionally, the glassy carbon electrode used for CV experiments was replaced with a high surface area carbon fiber, which was found to be necessary in order to enable rapid conversion of the iron-based catalyst. The

counter electrode was replaced by a lithium ribbon, separated from the working electrolyte by an ultrafine grade (<1.4 μ m) glass frit coated with a poly(vinylidene fluoride) (PVDF) membrane soaked in nBu₄NPF₆ to enhance conductance. PVDF has been shown as an effective solvent impermeable quasi-selective ion transport membrane.⁵² In this set-up, Li metal acts as a sacrificial electrode to bring electrolysis to completion.

2.3 Controlling the reactivities of lactide and cyclohexene oxide polymerization with bulk electrolysis

Using the optimized electrochemical cell shown in Figure 2.1b, (*rac*)-lactide polymerization was triggered by applying a reduction potential of 2.3 V (vs. Li/Li⁺) to a rapidly stirring solution containing the formally iron(III) complex **2.2** (Figure 2.2). When the catalyst loading was 1 mol%, electrolysis took approximately 40 min to reach full conversion as indicated by the dissipation of current to near zero values. Satisfyingly, the living characteristics of the lactide polymerization was retained after the electrochemical reduction as is evidenced by the linear increase in molecular weight with conversion that was observed (Figure 2.2). The polymerization behaved similarly to a reaction triggered by a chemical reductant leading to molecular weights that were close to theoretical molecular weights (e.g. at 75% conversion, $M_n(expt) = 9.6$ kg/mol and $M_n(theor) = 10.8$ kg/mol) and with only small increases in molecular weight distributions (i.e. M_w/M_n) compared to the reactions triggered by chemical reductants (Figure 2.2).



Figure 2.4 Left: Evolution of conversion and molecular weight during (rac)-lactide polymerization triggered by applying 2.3 V for 40 min to a solution containing 1 mol% of **2.2** as a catalyst precursor; M_w/M_n was shown in the third y-axis; right: GPC traces of time points indicated in the left graph. grey bar indicates the time period where the electrochemical potential is applied.

The ability to switch the polymerization "ON" and "OFF" was next demonstrated by cycling between electrochemical reduction at 2.3V and oxidation at 3.7 V, respectively (Figure 2.3). Satisfyingly, after activating the formally iron(III) complex **2.2** with electrochemical reduction, electrochemical oxidation after 30% conversion led to full deactivation of the catalyst with minimal increase in conversion and molecular weight (c.f. point *a* to *b*, Figure 2.3). As was observed with the chemical oxidation and reduction reactions,⁴⁴ the catalyst remained dormant after electrochemical oxidation with no change in polymer molecular weight or molecular weight distribution over six hours. At this point, the reaction mixture was once again subjected to electrochemical reduction, which led to reactivation of the catalyst that propagated at a similar rate as initial activation (i.e. $k_0 \rightarrow a = 3.5 \times 10^{-5} \text{ s}^{-1}$ and $k_e \rightarrow g = 3.2 \times 10^{-5} \text{ s}^{-1}$) and led to molecular weights slightly higher than theoretical molecular weights (e.g. at 55%)

conversion, $M_n(expt) = 8.7$ kg/mol and $M_n(theor) = 7.9$ kg/mol). These data indicate full reactivation of the iron-based catalyst for polymerization.



Figure 2.5. Left: evolution of conversion and molecular weight during an electrochemical redox-switchable polymerization of (rac)-lactide achieved through sequential electrolysis at different applied potentials (grey bars); with 1 mol% of **2.2** as a catalyst precursor; right: GPC traces of time points acquired

While activity and molecular weight increased as expected upon sequential catalyst oxidation and reduction, the molecular weight distributions (i.e. M_w/M_n) for the reactions did not remain constant with 1 mol% catalyst loading. The molecular weight distribution was narrow after initial reduction of the catalyst, but for every subsequent oxidation or reduction event, an increase in molecular weight distribution was observed increasing from 1.3 to 1.5 after electrochemical oxidation (time points *a* to *b*, Figure 2.3) and again from 1.5 to 1.9 after the second electrochemical reduction (time points d to e, Figure 2.3). Interestingly, the molecular weight distribution changes were only observed during electrochemical oxidation or reduction; the molecular weight distribution remained constant after the electrochemical redox events. This trend was particularly striking after the second electrochemical reduction, which

activated the catalyst for polymerization and resulted in a linear increase in molecular weight while maintaining the $M_w/M_n = 1.9$ that resulted after electrolysis (time points *e* to *g*, Figure 2.3). Paralleling this change was the shape of the GPC traces, which were only altered during the electrolysis events and remained relatively unaltered with subsequent polymerization (Figure 2.3).

These results are reminiscent of recent results from Fors and coworkers, who were able to achieve similar molecular weight control with tailored molecular weight distributions with the slow addition of radical initiators in nitroxide-mediated radical polymerizations⁵³ and anionic polymerization reactions. ⁵⁴ Due to these similarities, we hypothesized that the broadening in the molecular weight distributions that occurred during the electrolysis events were due to mass transport-controlled redox reactions. Mass transport limitations are commonly observed during bulk electrolysis because electrochemical redox reagents require the substrate to diffuse to the surface of the working electrode.⁵⁵ In the context of the switchable catalysis, if the rate of iron diffusing to the surface of the electrode is similar to the polymerization rate, then not all of the iron catalyst will be activated simultaneously. As a result, during electrochemical reduction some of the catalyst is activated for polymerization before all of the iron in solution can be fully reduced. Polymer chains attached to iron complexes that are activated early on during electrolysis lead to polymers with higher molecular weights than those activated near the end of electrolysis, which results in molecular weight distributions that are broadened during electrolysis. However, after electrolysis is complete, polymerization proceeds without significant contributions from transesterification or termination and the molecular weight distributions established during electrolysis are maintained as the reaction proceeds. A similar diffusion limitation exists upon catalyst deactivation during electrochemical oxidation of the catalyst, which once again leads to a broadening in molecular weight distribution.



Figure 2.6 a) Plot of anodic peak current versus the square root of scan rate in cyclic voltammetry; b) calculated diffusion constant (D) versus molecular weight. IPA: anodic peak current, *v*: scan rate.

Cyclic voltammetry is a powerful tool to determine diffusion constants. According to Cottrell equation, $i = \frac{n\mathbb{P}Ac_{j}^{0}\sqrt{D_{j}}}{\sqrt{nt}}$ (F is the Faraday constant, A is the area of the electrode, c_{j}^{0} is the concentration of the analyte, D is the diffusion constant), the peak current for a redox reactive species correlates linearly with the square root of the diffusion constant. As proposed earlier, the iron-containing polymer will have a slower mass transport rate to the electrode surface; as shown in the Figure 2.3, complex 2.2 was added to different equivalence of lactide; as expected, longer PLA chain length led to smaller peak current. The smaller electrochemical response indicated a slower mass transport rate.

In principle, these effects can be utilized to control molecular weight and dispersity in a similar fashion as Fors and coworkers have demonstrated, but utilizing the electrochemical redox reactions in this way is beyond the scope of this communication. Instead, we focused on developing an electrochemically redox-switchable polymerization reaction that can be utilized in copolymerization reactions. For this application, electrochemical switching without large increases in molecular weight distribution are preferable. To achieve this goal, we explored methods that reduced electrolysis time. Since the time needed for bulk electrolysis is directly proportional to the amount of redox active substrate in solution (not its concentration),⁵⁵ the most straightforward way to reduce electrolysis times is to lower catalyst loadings. Therefore, reactions were explored at 0.5 mol% catalyst loading for more efficient switching. Due to the polymerization reaction being first order in iron, significantly slower polymerization rates may be expected when using this method to reduce electrolysis time. However, since the reaction is also first order in lactide,⁴⁴ the lactide concentration could be increased commensurately with the catalyst loading being decreased so as to maintain similar reaction rates. Under these conditions, switchable catalysis could be carried out with more efficient switching times and at approximately the same polymerization rate as was observed with 1 mol% catalyst loading.



Figure 2.7. left: evolution of conversion and molecular weight during an electrochemical redox-switchable polymerization of lactide achieved through sequential electrolysis at different applied potentials (grey bars) with 0.5 mol% Fe loading; right: GPC traces of time points acquired

As expected, reducing the formally iron(III) catalyst **2.2** loading to 0.5 mol% led to a significant decrease in the time needed for full electrolysis time from approximately 45 minutes to 10 minutes (Figure 2.4). Once again, polymerization commenced upon application of electrical current for reduction of the catalyst. After allowing the lactide to polymerize to 30% conversion, oxidative electrolysis was carried out for approximately 10 minutes to fully oxidize the Fe(II) catalyst, which resulted in complete deactivation of the catalyst without increase in lactide conversion or molecular weight. Satisfyingly, only a minimal increase in dispersity was observed from 1.25 to 1.30 (Figure 2.4). After allowing the reaction to stir in the deactivated state for five hours without any change in conversion or molecular weight, a second reductive potential was applied. As anticipated, lactide polymerization was reactivated with polymerization occurring at a similar rate indicating that catalyst decomposition neither occurred during the electrochemical reactions nor when the catalyst is in its dormant state. Molecular weight increased as before and importantly only a small increase in dispersity from 1.30 to 1.50 was observed.

Table 2.1 Cycling experiment where the reaction mixture was allowed to toggle between 2.3 V and 3.7 V for 4 cycles and followed by electrochemical reduction of complex 3 to its Fe(II) oxidation state.

$\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $					
	Time (min)	Conv ^a (%)	Mn(theo) (kg/mol)	M _n (expt) ^b (kg/mol)	$M_{ m w}/M_{ m n}^{ m b}$
4 cycles of 2.3 V/3/7 V electrolysis, ^c followed by 2.3 V					
а	90	12	4.3	-	-
b	210	29	8.4	10.1	1.64
c	420	45	13.0	14.1	1.83
d	600	57	16.4	18.1	1.91
e	1020	81	23.3	22.9	2.05

^aConversion was determined from ¹H NMR by integrating the methine peaks of the remaining lactide (5.0 ppm) versus the methyl peak of ⁿBu₄NPF₆(1.0 ppm); ^bObtained from GPC (RI detector);^c each electrolysis took around 10 min to finish.

In order to test the reproducibility of the redox switch, we carried out multi-step electrolysis with multiple redox switches, we cycled the cell with redox electrolysis for 5 times and studied the subsequent polymerization reactions. To our delight, the reaction proceeds with living characteristics with experimental molecular weight close to the theoretical molecular weight, although a broad molecular weight distribution was observed. The reaction still remains first order with respect of lactide conversion, which suggested the iron complex remains equally active after 5 cycles of on/off switch.



Figure 2.8. First order kinetic plot of lactide polymerization during (rac)-lactide polymerization triggered by applying 2.3 V after toggling between 2.3 V and 3.7 V for 4 cycles.

With a switchable lactide polymerization in hand, we next turned towards developing an electrochemical switch to control chemoselectivity in polymerization reactions of cyclohexene oxide. As expected based on our previous findings,⁴⁵ when the iron(II) complex **2.1** was exposed to cyclohexene oxide in the electrochemical cell, no reaction occurred. However, cyclohexene oxide polymerization could be triggered by applying an oxidative potential of 3.7 V (vs Li⁺/Li) for 35 minutes to convert 2 into the formally iron(III) complex **2.2**. As was the case with lactide, minimal conversion of the epoxide was observed during electrolysis and conversion continued to increase after electrolysis was over (Figure 2.4). The complementary reactivity of the iron complexes towards epoxide polymerization was demonstrated by applying a reducing potential of 2.3 V to the polymerization reaction for 10 minutes, which reverted **2.2** back to **2.1** and completely stopped the epoxide polymerization reaction. Thus, the iron complexes demonstrated similar switching capabilities for epoxide polymerization as they did for lactide polymerization, but with complementary reactivity, being "ON" in the oxidized state and "OFF" in the reduced state.



Figure 2.9 Evolution of conversion and molecular weight during an electrochemical redox-switchable polymerization of cyclohexene oxide through sequential electrolysis at different applied potentials (grey bars) with 0.1 mol% of 2.1 as a catalyst precursor. [cyclohexene oxide] = 1.4 M in dichloromethane.

2.4 Block copolymer synthesis with an electrochemical redox switch

As electrolysis proved to be a reliable way to switch between oxidation states of the iron complex that demonstrated orthogonal reactivity for lactide and epoxides, block copolymerizations triggered by electrochemical reactions were conducted starting from a mixture of lactide and cyclohexene oxide in the same cell (Figure 2.5). Learning from our previous experiences in chemically triggered copolymerizations,⁴⁵ a 1:5 mixture of lactide to

cyclohexene oxide was used to maximize incorporation of the epoxide. Using these conditions and starting with a 0.5% loading of the iron(II) complex **2.1** (with respect to lactide), polymerization of lactide occurred exclusively from the mixture of lactide and cyclohexene oxide without any evidence for incorporation of the epoxide. After three hours and 50% lactide conversion, oxidative electrolysis at 3.7 V was applied. Analysis of the reaction mixture immediately after electrolysis revealed that the epoxide polymerization began (10% conversion) with only a small increase in lactide conversion (9%) being observed during electrolysis (Figure 2.5a). Subsequent stirring of the reaction mixture for eight additional hours led to an increase in conversion of the epoxide (50%) without any further increase in lactide conversion. Notably, the molecular weight of the polymer increased over the entire course of the reaction, which is consistent with the formation of a block copolymer (vide infra).



Figure 2.10 (a) Lactide/epoxide conversion and MW increase for block copolymerization reaction with an Fe(II) to Fe(III) electrochemical redox switch, one pot; with

0.5 mol% Fe loading relative to lactide, 5:1 [lactide]:[epoxide]; final polymer composite PLA: polyether = 3: 1; potential of 3.7 V was applied to the cell for around 63 min (b) Lactide/epoxide conversion and MW increase for block copolymerization reaction with an Fe(III) to Fe(II) electrochemical redox switch, one pot; with 0.5 mol% Fe loading relative to lactide, 5:1 [lactide]:[epoxide]; final polymer composite PLA: polyether = 3: 1; potential of 2.3 V was applied to the cell for around 65 min.

In addition to an iron(II) to iron(III) redox switch, an iron(III) to iron(II) redox switch was developed in which cyclohexene oxide was polymerized first (Figure 2.5b). Exposing the same 5:1 mixture of cyclohexene oxide to lactide to 0.5 mol% (with respect to lactide) of the formally iron(III) complex **2.2**, led to exclusive formation of epoxide, reaching 30% conversion after 3 hours. Application of a 2.3 V potential led to reduction of the iron complex and complete switching of the chemoselectivity of the catalyst from epoxide to lactide. Further reaction after electrolysis led to full conversion of the lactide without any further conversion of the epoxide. As was the case with the iron(II) to iron(III) switch, the iron(III) to iron(II) switch resulted in monotonous increase in molecular weight of the polymer over the entire course of the reaction, which once again suggested the formation of block copolymers as opposed to a mixture of homopolymers.



Figure 2.11 DOSY-NMR of block copolymer generated from Fe(III) to Fe(II) switch reported in Figure 2.5b.

Three additional pieces of data indicated that copolymers were formed in the electrochemical redox-switchable polymerization experiments as opposed to mixtures of homopolymers. Firstly, as we had disclosed previously, the polymers isolated had solubility properties that were different from either homopolymer.⁴⁵ The poly(lactic acid) rich copolymer show similar solubility to the pure poly(lactic acid) samples, they are soluble in acetone and insoluble in hexanes. Poly(cyclohexene oxide) homopolymer is only soluble in hexanes and not soluble in acetone. The polymers collected were precipitated in toluene to remove the insoluble electrolyte Bu₄NPF₆, and the solvent in the filtrate was precipitated in hexanes to collect the precipitate. The solid was precipitated acetone again to collect the filtrate.





Secondly, the polymer isolated from the reaction mixtures from formally iron(III) to iron(II) and iron(II) to formally iron(III) switching were subjected to analysis by diffusion ordered nuclear magnetic resonance spectroscopy (Figure 2.6 and Figure 2.7, respectively). In both polymerization reactions, a single peak in the DOSY-NMR spectrum was observed with resonances that were assigned to both poly(lactic acid) and polyether protons, which supports the formation of block copolymers during the electrochemically switchable copolymerization reactions.

In order to assess the homogeneity of the transfer between ester and ethers in the copolymerization reactions, ¹³C NMR spectra of polymers were obtained from electrochemical

switchable copolymerization reactions between lactide and cyclohexene oxide. The simplified stereochemistry of copolymers involving L-lactide and cyclohexene oxide resulted in ¹³C NMR spectra that could be readily analyzed and assigned. Analysis of the carbonyl region of the ¹³C NMR spectra from the copolymers obtained from electrochemical redox switching copolymerization experiments revealed the repeat unit for poly(L-lactic acid) and the appropriate end group for the particular electrochemical switch. Analysis of the carbonyl region of the ¹³C NMR spectrum from poly(L-lactic acid) (168-176 ppm) led to assignment of peaks ascribed to repeat units as well as initiating and terminating end groups (Figure 2.8). Substitution of 4-methoxyl phenyl group has a shielding effect on the neighboring carbonyl carbon,⁵ so the signal at 169.20 ppm was assigned to the initiating lactic acid with a benzoate end group (Figure 2.8). In contrast, the hydroxyl end group has a deshielding effect, which led to the assignment of the signal at 175.16 ppm to the terminating lactic acid unit with a hydroxyl end group (Figure 2.8).



9.5 179.0 178.5 178.0 177.5 177.0 176.5 176.0 175.5 175.0 174.5 174.0 173.5 173.0 172.5 172.0 171.5 171.0 170.5 170.0 169.5 169.0 168.5 168.0

Figure 2.13 ¹³C-NMR of poly(L-lactic acid) obtained from polymerization of L-lactide with 2 mol% Fe(II) complex **2.1**.

A unique resonance was observed for the carbonyl carbon *c* that appears at 170.71 ppm for copolymer synthesized from Fe(II) to Fe(III) redox switch (Figure 2.9). This resonance was assigned to the carbonyl group that bridges the polyester with polyether blocks because an alkoxide group has a deshielding effect. In addition to evidence for the initiating lactic acid with a benzoate end group at 169.23 ppm, an additional unexpected resonance was observed at 175.21 ppm. This resonance is very similar to the lactic acid terminating group with hydroxyl end group, which is consistent with a small amount of homo poly(lactic acid) that couldn't be separated from precipitation. However, DOSY analysis of the copolymer does not have evidence for a significant amount of homo poly(lactic acid).



Figure 2.14 ¹³C-NMR of block copolymers obtained from e-switchable copolymerization of lactide and cyclohexene oxide, Fe(II) to Fe(III) redox switch

Copolymer synthesized from Fe(III) to Fe(II) redox switch also contained resonances that could be assigned to the end groups and contained unique resonances for the polymer

(Figure 2.10). It is noteworthy that the polymer produced from an Fe(II) to Fe(III) switch has a different group that bridges the polyester and polyether. Once again, the resonance at 175.2 is consistent the lactic acid terminating group with a hydroxyl end group. This species resonance is expected from termination of the poly(lactic acid) at the end of the reaction. In contrast, the initiating lactic acid with benzoate end group was observed. The absence of this resonance is consistent with the copolymer chemical structure. Four signals from carbonyls bridging carbon *d* appeared slightly upfield of the primary carbonyl resonance for poly(lactic acid). The four resonance observed were explained by diastereomeric stereo sequences arising from the last two cyclohexene oxide units inserting prior to the conversion to the polyester resonances (i.e., [ether/ether]-(ester) stereocenters = [RR/SS]-(S), [RR/RR]-(S), [SS/RR]-(S), [SS/SS]-(S).



178.0 177.5 177.0 176.5 176.0 175.5 175.0 174.5 174.0 173.5 173.0 172.5 172.0 171.5 171.0 170.5 170.0 169.5 169.0 168.5 168.0 167.5 f1 (ppm)

Figure 2.15 ¹³C-NMR of block copolymers obtained from e-switchable copolymerization of lactide and cyclohexene oxide, Fe(III) to Fe(II) redox switch.

2.5 Electron self-exchange

Previously, when the iron(III) complex 2.2 was reduced with partial equivalence of cobaltocene and mixed with lactide, non-living characteristics was observed with slow reaction rate and broad molecular weight distributions (Figure 2.16). Another interesting feature of the polymerization is that the observed molecular weight of the polymers is smaller than the theoretical molecular weight calculated from the equivalences of the reduced complex. The difference between the theoretical molecular weight is more significant when the equivalences of the added $CoCp_2$ is smaller (0.25, 0.5). This observation is very interesting, because a lower observed molecular weight suggested the amount of the active species is more than what has been reduced through the addition of the reductant.

If we calculate the amount of the iron complex that has been reduced based on the observed molecular weight, when 0.25 eq of CoCp₂ was added to the reaction solution, 67% of the iron was active in catalyzing the lactide polymerizations; and if we define the calculated amount of the active iron complex in the solution based on the observed molecular weights and plotted against the equivalence of the CoCp₂ that was added, it is clear that the curve (black) deviates greatly from the theoretical (orange) and get closer when higher equivalence of the CoCp₂ was added (Figure 2.16). We hypothesized that this observation may come from the electron self-exchange when both iron(II) and iron(III) complexes exist at the same time and the electron transfer rate is comparable with the polymerization rate. The active chain end, which is coordinated to the iron(III) center, can be deactivated after it transfer an electron to a nearby iron(III) complexes; the iron(III) complex is now reduced and can initiate another polymer chain. The dormant iron(III) chain end can be reactivated to polymerize again. Under this circumstance, the observed molecular weight can be smaller than the theoretical molecular weight, as more of the iron complexes have participated in the polymerization reaction. If the electron transfer is indeed the reason for this interesting polymerization outcome, ideally, we

can use the molecular weight information from the obtained complexes to estimate the electron transfer rate in this solution with iron complexes that have mixed valences. The measurement of electron transfer rate is difficult to obtain using any other existing method.



Figure 2.16 Trends in reduction efficiency observed during the partial reduction of **2.2** in the presence of lactide at varying equivalents of reductant.

As discussed in the previous section, distinct signals from the bridging carbonyl carbons can be found in the ¹³C-NMR of block copolymers, and only one bridging unit was observed for both block polymers, from Fe(III) to Fe(II) switch or Fe(II) to Fe(III). This result indicated that the redox events only happened once on each metal center. If electron self-exchange is happening between the Fe(II) and Fe(III) complexes and is affecting the polymerization rate, both ester to ether and ether to ester bridging units should be observed in the block copolymer center. In these reactions, the electrolysis took a long time (30 min) to fully convert the complexes to another oxidation state, and there was a long period of time in the reaction cell that both Fe(II) and Fe(III) complexes exist at the same time. This observation contradicts the results in Figure 2.16, when partial equivalences of $CoCp_2$ was added to the reaction mixture.

There are several noticeable differences in this electrolysis cell system. First, the reduction process was dynamic, where the iron(III) complex was reduced gradually. Second, there was a distribution of iron(II) concentration in the electrolysis cell where most of the reduced species remained closer to the electrode surface, and the iron(III) complex needs to diffuse to the electrode to be reduced. The diffusion is another factor needs to be included. Third, the electrolysis happened in a concentrated solution of the electrolyte, nBu₄NPF₆, the electron transfer process is very different in a salt solution than in the pure organic solvents.⁵⁵ At this stage, we are not able to identify if the electron self-exchange is happening between the iron(II) complex,

2.6 Conclusion

In summary, a redox-switchable polymerization reaction was developed in which electrochemical potential was used to toggle between the reactivity of an iron-based complex for lactide and epoxide polymerization. The switchable system was made possible by utilizing a two-compartment electrochemical cell design where high surface area carbon fiber was used as the working electrode and lithium was used as a sacrificial counter electrode. An important feature of the cell was the high surface area carbon fiber, which was combined with low catalyst loadings to minimize the effect of mass transport. Under these conditions an electrochemical switchable polymerization reaction could be achieved with minimal impact on molecular weight and molecular weight distributions during the electrochemical switching event. As a result, polymerization reactions could be carried out with precise control over activity and selectivity. This property was exploited for the synthesis of block copolymers starting from a mixture of monomers in which the polymer sequence was dictated by the electrochemical potential applied. Although this e-switchable polymerization shares some similarities with eATRP, the two reactions use electrochemistry in fundamentally different ways. As a result of these differences, continuous application of electrical current is not necessary for e-switchable polymerization as is the case in eATRP. Additionally, altering the redox potential changes the reactivity of the catalyst, which cannot be achieved in eATRP and allows for the synthesis of block copolymers starting from a single monomer feed.

The e-switchable polymerization method has some notable advantages compared to similar reactions carried out with the addition of chemical redox reagents. Firstly, electrochemical methods obviate the need for stoichiometric quantities (with respect to the catalyst) of chemical reagents for every electrochemical switch, which simplifies polymer purification. They also provide a convenient means to change oxidation states of the catalyst by varying the redox potentials in situ, which makes syntheses more easily programmable. Moreover, electrochemical methods provide access to a wider range of potentials with more precise control over the redox potentials, making the method more versatile for catalysts with multiple redox states. Finally, electrochemical methods can be applied in circumstances where addition of chemical redox reagents is difficult (e.g. when a reaction is under pressure), which can be beneficial for polymerization reactions that utilize gaseous reagents. In the future, these advantages will be exploited for the development of e-switchable polymerization reactions that incorporate a wider variety of monomers in a controlled and programmable manner.

Experimental Section

General Considerations. Unless stated otherwise, all reactions were carried out in oven-dried glassware in argon or nitrogen-filled glove box. Nuclear magnetic resonance (NMR), ¹H NMR spectra were recorded at ambient temperature (unless indicated otherwise) on spectrometers operating at 500 or 600 MHz; ¹³C NMR spectra were recorded at ambient temperature (unless indicated otherwise) on spectrometers operating at 125 MHz. Gel permeation chromatography (GPC) was performed on an Agilent GPC220 in THF at 40 °C with three PL gel columns (10 μ m) in series. Molecular weights and molecular weight distributions were determined from the signal response of the RI detector relative to polystyrene standards; a light scattering detector was also used to determine molecular weight of copolymer samples. Polymer products were separated using a Beckman Coulter J2-MC Centrifuge with Rotor 17.0 at 2500 RPM operating at 4°C for 20 minutes. Mark-Houwink parameters and refractive index increment (dn/dc) used were obtained from literature.

Bis(imino)pyridine iron bisphenoxide complex 2.1 and 2.2 were synthesized following literature procedures.² Solvents (dichloromethane, benzene, dimethoxyethane (DME)) were used after passage through alumina columns under a blanket of argon or distilled over calcium hydride to remove water and then degassed briefly by exposure to vacuum. N-Methyl-2pyrrolidone (NMP), methanol, hexanes, and acetone was purchased from Fisher Scientific and used without further purification. (*rac*)-Lactide were obtained from Purac Biomaterials; and Llactide was purchased from Natureworks. Racemic and enantiomerically enriched lactide were recrystallized from ethyl acetate followed by recrystallization from hot toluene and dried *in vacuo* over P_2O_5 prior to polymerization. Cyclohexene oxide was purchased from Acros Organics and distilled from calcium hydride prior to its use. Cyclic voltammetry and bulk electrolysis were carried out on potential station Biologic VMP3. High surface area carbon fiber was provided by Zoltek and was sonicated in a saturated sodium bicarbonate solution, followed by acetone then dichloromethane for 15 min respectively then heated to 160 °C for 24 hours to remove excess solvent prior to its use in bulk electrolysis. Glassy carbon obtained from CHInstrument was used as working electrode for cyclic voltammetry experiment. Platinum wire, tetrabutylammonium hexafluorophosphate (>99%), lithium perchlorate (>99.99%), bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, 99.95%), poly(vinylidene fluoride (PVDF) and lithium metal ribbon (>99.9%) were purchased from Aldrich. The hollow cylinder with a fine frit was repurposed from a gas dispersion tube (cylinder is approximately 12mm O.D. x 20mm long, overall length is approximately 10 inches), which was purchased from Chemglass. The glass vessel used for electrochemical bulk electrolysis was repurposed from a female type glass cap with a 24/40 outer joint.

Preparation of Li/PVDF coated fritted cylinder tube. LiTFSI (1.00 g) and PVDF, (3.00 g) were mixed with a mass ratio of 1:3, and dissolved in NMP (10.0 mL) to form a uniform gel. The porous glass-frit was then coated with a thin film of the gel and the solvent was removed under house vacuum at 100 °C for two hours. The above process was repeated six times until a conformal coverage was obtained. Around 0.2 g of polymer was deposited as a result of the coating process. The resulting LiTFSI/PVDF solid solution coated on the glass-frit served as the solid electrolyte to conduct lithium ions as well as a physical barrier to prevent mixing of the catholyte and anolyte solutions.

Procedure for CV measurements. Cyclic voltammetry was conducted with a 3electrode configuration, where a glassy carbon rod was used as the working electrode, a platinum wire was applied as counter electrode, and a lithium ribbon separated by a PVDF coated porous glass frit tube was used as the reference electrode. **2.1** (0.005 g, 0.007 mmol) was dissolved in a 0.1 M ⁿBu₄NPF₆ solution in dichloromethane (5 mL). The open circuit potential was measured to be 2.65 V. The cyclic voltammogram shown in Figure 1a was scanned in the electrochemical window between 2.30 V and 3.70 V. The scan rate was 25 mV/s.

Cell assembly for bulk electrolysis. In an argon-filled glovebox, high surface area carbon fiber (2.5 g) was bundled together with a piece of platinum wire (used for electrical contact) and placed in the cell. A lithium rod was placed in the hollow fritted cylinder tube and a 0.1 M LiClO₄ solution in DME (2 mL) was added to the tube. The top of the lithium rod was affixed to the tube with Teflon tape, and the glass tube was inserted into a 24/40 joint rubber septum. The platinum wire was let aside the rubber septum. The septum was affixed to the electrochemical cell, and electrical connection to the potentiostat was established through alligator clips affixed to the platinum wire attached to the carbon fiber working electrode and the lithium counter electrode.

Procedure for the e-polymerization of (*rac*)-lactide with 1.0 mol% 2.2. In an argonfilled glove box, iron(III) bis(alkoxide) complex 2.2 (0.007 g, 0.010 mmol) was dissolved in 0.1 M "Bu₄NPF₆ dichloromethane solution (2.00 mL) in a 7-mL vial. The solution was added to the cell containing (*rac*)-lactide (0.144 g, 1.00 mmol) dissolved in a 0.1 M "Bu₄NPF₆ dichloromethane solution (2.00 mL). The vial originally containing the iron complex was washed with an additional aliquot of 0.1 M "Bu₄NPF₆ dichloromethane solution (1.00 mL), and then the cell was sealed for electrolysis. A reductive potential of 2.3 V was applied to the cell, and the progress of the electrolysis was monitored by measuring the current in the cell. After the electrolysis was complete (10-15 min, when capacity of 0.27 mA ·h was applied), the reaction was allowed to stir 24 hours at room temperature. Aliquots (0.3 mL) were removed periodically from the reaction mixture to measure conversion (by ¹H NMR) and polymer molecular weight (by GPC). Lactide conversion was determined from the ¹H NMR by comparing the relative integration of the methine peaks of the remaining lactide (q, 5.0 ppm) to the methine peaks of poly(lactic acid) (q, 5.2 ppm). The polymerization was terminated by exposure to air outside of the glovebox. To ensure that all of the polymer and unreacted monomer was collected, the carbon fiber was washed three times with dichloromethane. The dichloromethane fractions were combined and the solvent was removed under reduced pressure to afford a solid mixture containing poly(lactic acid) polymer, unreacted monomer, and ⁿBu₄NPF₆. To purify the polymer, the mixture was dissolved in dichloromethane (1.0 mL) and precipitated in methanol (100 mL) with stirring. Lactide conversion was determined from the ¹H NMR by comparing the relative integration of the methine peaks of the remaining lactide (q, 5.0 ppm) to the methine peaks of poly(lactic acid) (5.2 ppm). The reaction mixture was analyzed by GPC to determine molecular weight and molecular weight distribution of the polymers.

Procedure for the e-polymerization of (*rac*)-lactide with 0.5 mol% 2.2. A similar procedure was carried out as was done with 1 mol% catalyst except iron(III) bis(alkoxide) complex 3(0.005 g, 0.007 mmol) was added to the reaction.

Procedure for the e-switchable polymerization of lactide. In the glove box, iron(III) bis(alkoxide) complex **2.2** (0.005 g, 0.007mol) was added to a 7 mL vial and a 0.1 M ⁿBu₄NPF₆ dichloromethane solution (2.00 mL) was added to dissolve the catalyst. The solution was added to the cell containing (*rac*)-lactide (0.202 g, 1.40 mmol) dissolved in 0.1 M ⁿBu₄NPF₆ dichloromethane solution (2.0 mL). The vial originally containing the iron complex was washed with an additional aliquot of 0.1 M ⁿBu₄NPF₆ dichloromethane solution (1.0 mL), and then the cell was sealed for electrolysis. A reductive potential of 2.3 V was applied to the cell, and the progress of the electrolysis was monitored by measuring the current in the cell. After the electrolysis was complete (10 min, when capacity of 0.19 mA·h was applied), the reaction was allowed to stir for five hours at room temperature. An oxidative potential of 3.7 V was applied to the cell, and the progress of the electrolysis was complete (15 min, when capacity of 0.17 mA·h
was applied), the reaction was allowed to stir for five hours at room temperature. A reductive potential of 2.3 V was applied to the cell, and the progress of the electrolysis was monitored by measuring the current in the cell. After the electrolysis was complete (10 min, when capacity of 0.15 mA·h was applied), the reaction was allowed to stir for 12 hours at room temperature Aliquots (0.3 mL) were removed periodically from the reaction mixture and terminated by exposure to air outside of the glovebox to measure conversion (¹H NMR) and polymer molecular weight (GPC). Lactide conversion was determined from the ¹H NMR by comparing the relative integration of the methine peaks of the remaining lactide (q, 5.0 ppm) to the methine peaks of poly(lactic acid) (q, 5.2 ppm). Each aliquot was also analyzed by GPC (RI) to determine molecular weight and molecular weight distribution of the polymers. Significant amount of the solution was removed for sampling purposes, so final yield of the polymerization wasn't calculated here.

General procedure for the e-polymerization of cyclohexene oxide. In the glove box, iron(II) bis(alkoxide) complex 2.2 (0.006 g, 0.007 mmol) was dissolved in a 0.1 M ⁿBu₄NPF₆ dichloromethane solution (2.00 mL) in a 7-mL vial. The solution was added to the cell cyclohexene 7.00 containing oxide (0.700)g, mmol) dissolved in 0.1Μ ⁿBu₄NPF₆ dichloromethane solution (2.00 mL). The vial originally containing the iron complex was washed with an additional aliquot of 0.1 MⁿBu₄NPF₆ dichloromethane solution (1.00 mL), and then the cell was sealed for electrolysis. An oxidative potential of 3.7 V was applied to the cell, and the progress of the electrolysis was monitored by measuring the current in the cell. After the electrolysis was complete (30-55 min, when capacity of 0.19 mA h was applied), the reaction was allowed to stir 24 hours at room temperature. Aliquots (0.3 mL) were removed periodically from the reaction mixture and terminated by exposure to air outside of the glovebox to measure conversion (¹H NMR) and polymer molecular weight (GPC). Epoxide conversion was determined from the ¹H NMR by integrating the methine peaks of the polyether signal (m, 3.2-3.5 ppm) versus the methyl peak of ⁿBu₄NPF₆ (t, 1.0 ppm). The carbon fiber was washed three times with dichloromethane to collect all the polymer and unreacted monomers. To purify the polymer, the dichloromethane fractions were combined and the solvent was concentrated under reduced pressure to afford a solid mixture containing polyether and ⁿBu₄NPF₆. The solid was re-dissolved in hexanes (10.0 mL) and filtered to remove nBu₄NPF₆. The reaction mixture was analyzed by GPC (RI) to determine molecular weight and molecular weight distribution of the polymers. Significant amount of the solution was removed for sampling purposes, so final yield of the polymerization wasn't calculated.

General procedure for the e-switchable copolymerization of lactide and cyclohexene oxide, Fe(II) to Fe(III) redox switch. In an argon-filled glove box, iron(II) bis(alkoxide) complex 2.1 (0.005 g, 0.007 mmol) was dissolved in a 0.1 M ⁿBu₄NPF₆ dichloromethane solution (2.00 mL) in a 7-mL vial. The solution was added to the cell containing cyclohexene oxide (0.700 g, 7.00 mmol) and lactide (L or rac, 0.202 g, 1.40 mmol) dissolved in a dichloromethane solution containing 0.1 M ⁿBu₄NPF₆ (2.00 mL). The vial originally containing the iron complex was washed with an additional aliquot of 0.1 M ⁿBu₄NPF₆ dichloromethane solution (1.00 mL), and then the cell was sealed for electrolysis. Reaction was allowed to stir for three hours, then an oxidative potential of 3.7 V was applied until complete conversion of Fe(II) to Fe(III) was observed. After the electrolysis was complete after 63 min, when capacity of 0.19 mA h was applied. Aliquots were periodically removed from the reaction mixture to determine conversion (¹H NMR) and molecular weight (GPC). Lactide and epoxide conversions were obtained as previously described in the homopolymerization reactions. The polymers were analyzed by GPC to determine molecular weight and molecular weight distribution after each step of the reaction. The ratio of polyester to polyether ([poly(lactic acid):[polycyclohexeneoxide]] of the reaction mixtures were determined by ¹H NMR by integrating the methine polyether peak (m, 3.2-3.6 ppm) and comparing it to the integration of the methine polyester peak (q, 5.2 ppm). The reaction was allowed to stir for 12 h and then was removed from the glove box and quenched with 1 drop of water. The polymer was purified according to a procedure adapted from our previously reported procedure:⁴ The remaining volatiles were removed *in vacuo*, and the reaction mixture was dissolved in a minimal amount of dichloromethane (2 mL) and precipitated into stirring methanol (100 mL). After stirring one hour, the turbid mixture was centrifuged and poured through a 0.02 µm polypropylene (PP) filter membrane. The process was repeated again to fully remove unreacted lactide and nBu₄NPF₆ in solution and collect polymer mixture in the precipitate. After drying under reduced pressure, the precipitate collected was dissolved in minimal dichloromethane (2 ml) and precipitated into stirring acetone (100 mL) to remove homopolyether in the precipitate. After evaporating the solvent from the filtrate under reduced pressure, the polymer was dissolved in a minimal amount of dichloromethane (1 ml) and precipitated into stirring hexanes (100 mL). After stirring one hour, the mixture was centrifuged and poured through a 0.02 µm polypropylene (PP) filter membrane to collect the copolymer in the precipitate. The final copolymer composite was characterized by ¹H-NMR and DOSY-NMR (Figure S6) to verify the formation of block polymer. To assess the homogeneity of the ester to ether transfer, copolymers obtained using L-lactide were also characterized by ¹³C NMR spectroscopy (vide infra, Figure S8). ¹H NMR (CDCl₃): 5.0-5.2 ppm (1H, methine peaks of lactic acid unit) 3.2-3.5 ppm (1H, cyclohexane), 1.2-2.0 ppm (5H, cyclohexane), 1.4 ppm (3H, d, methyl signal of lactic acid unit), ¹³C NMR (with rac-lactide, CDCl₃): 5.0-5.2 ppm (1H, methine peaks of lactic acid unit) 3.2-3.5 ppm (1H, cyclohexane), 1.2-2.0 ppm (5H, cyclohexane), 1.4 ppm (3H, d, methyl signal of lactic acid unit) Yield: 0.213 g, 23.6%. To demonstrate chemoselectivity, lactide polymerization was purposely stopped before reaching full conversion, yield was calculated based on partial conversion of both monomers. Isolated copolymer: 86%.

General procedure for the e-switchable copolymerization of lactide and cyclohexene oxide, Fe(III) to Fe(II) redox switch. In an argon-filled glove box, iron(III) bis(alkoxide) complex 2.2 (0.006 g, 0.007 mmol) was dissolved in a 0.1 M Bu₄NPF₆ dichloromethane solution (2.00 mL) in a 7-mL vial. The solution was added to the cell containing cyclohexene oxide (0.700 g, 7.00 mmol) and lactide (L or rac, 0.202 g, 1.40 mmol) dissolved in a dichloromethane solution containing 0.1 M ⁿBu₄NPF₆ (2.00 mL). The vial originally containing the iron complex was washed with an additional aliquot of 0.1 M ⁿBu₄NPF₆ dichloromethane solution (1.00 mL), and then the cell was sealed for electrolysis. Reaction was allowed to stir for three hours, then an oxidative potential of 3.7 V was applied to convert Fe(II) to Fe(III). The electrolysis was complete in 58 min, when capacity of 0.19 mA·h was applied, Aliquots were periodically from the reaction mixture to determine conversion (¹H NMR) and molecular weight (GPC). Lactide and epoxide conversions were obtained as previously described in the homopolymerization reactions. The polymers were analyzed by GPC to determine molecular weight and molecular weight distribution after each step of the reaction and each precipitation. The ratio of polyester to polyether was determined by ¹H NMR in the same way as described for the iron(II) to iron(III) switch. The reaction was allowed to stir for 12 h and then the solution was removed from the glove box and quenched with one drop of water. The polymer was purified according to a procedure adapted from our previously reported procedure:⁴ The remaining volatiles were removed in vacuo, and the reaction mixture was dissolved in a minimal amount of dichloromethane (2 mL) and precipitated into stirring methanol (100 mL) to remove unreacted lactide and "Bu4NPF6. After stirring one hour, the turbid mixture was centrifuged and poured through a 0.02 µm polypropylene (PP) filter membrane to remove unreacted lactide and ⁿBu₄NPF₆ in solution and collect polymer mixture in the precipitate. After drying in vacuo, the precipitate collected was redissolved in minimal dichloromethane (2 ml) and precipitated into stirring acetone (100 mL)

to remove homopolyether in the precipitate. After drying the filtrate, the material was redissolved in minimal dichloromethane (1 ml) and precipitated into stirring hexanes (100 mL). After stirring one hour, the mixture was centrifuged and poured through a 0.02 µm polypropylene (PP) filter membrane to collect the copolymer in the precipitate. The final copolymer composite was characterized by ¹H-NMR and DOSY-NMR (Figure S6) to verify the formation of block polymer. To assess the homogeneity of the ether to ester transfer, copolymers obtained using L-lactide were also characterized by ¹³C NMR spectroscopy (vide *infra*, Figure S8). ¹H NMR (with *rac*-lactide, CDCl₃): 18 ppm (methyl peaks of lactic acid unit) 22-25ppm (1H, cyclohexane), 72 ppm (methane peaks of lactic acid unit), 175 ppm (carbonyl of lactic acid unit), Yield: 0.330 g, 23.6%. To demonstrate chemoselectivity, epoxide polymerization was purposely stopped before reaching full conversion, yield was calculated based on partial conversion of epoxide. ¹³C NMR (with rac-lactide, CDCl₃): 5.0-5.2 ppm (1H, methine peaks of lactic acid unit) 3.2-3.5 ppm (1H, cyclohexane), 1.2-2.0 ppm (5H, cyclohexane), 1.4 ppm (3H, d, methyl signal of lactic acid unit), Yield: 0.330 g, 23.6%. To demonstrate chemoselectivity, epoxide polymerization was purposely stopped before reaching full conversion, yield was calculated based on partial conversion of epoxide.Isolated copolymer: 88%.

Procedure for Diffusion Constants measurement with Cyclic Voltammetry For degree of polymerization equals to 200: In an argon-filled glove box, iron(II) bis(alkoxide) complex 2.1 (0.006 g, 0.007 mmol) was dissolved in a 0.1 M $^{n}Bu_4NPF_6$ dichloromethane solution (2.00 mL) in a 7-mL vial. The solution was added to the cell containing lactide (*L* or *rac*, 0.202 g, 1.40 mmol) dissolved in a dichloromethane solution containing 0.1 M $^{n}Bu_4NPF_6$ (2.00 mL). For lower degree of polymerizations, the lactide concentration was kept constant, increased amount of complex 2.1 was added to the solution (0.024 g, 0.24 g and 0.60

Cyclic voltammetry was conducted with a 3-electrode configuration, where a glassy carbon rod was used as the working electrode, a platinum wire was applied as counter electrode, and a platinum rod separated by a capillary tube was used as the reference electrode. The open circuit potential was measured to be around 0.05 V. The cyclic voltammogram shown were scanned in the electrochemical window between -1.1 V and -0.2 V. The scan rate was varied from 25 mV/s to 500 mV/s.

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3. Chapter 3. Electrochemically Switchable Polymerizations from Surface-Anchored Molecular Catalysts

3.1 Introduction

Modifying surface properties including surface wettability, corrosion resistance, thermal and electrical conductivity and is tremendously useful in electronic coatings and sensors.^{1,2} From anti-fouling paints^{3,4} to conformal coatings on electronics,^{5,6} many of these applications rely on forming layers of organic polymers on the inorganic substrates. The organic coatings can be readily prepared through surface-initiated polymerization, where polymers grow directly from solid substrates from surface-anchored initiators, which has gained its popularity in recent years.⁷⁻¹¹ Surface-initiated polymerizations not only provide stronger adhesion of the organic layer to the solid support compared to traditional coating strategies which rely on physical interactions only, properties of the coatings can be tuned readily with the ease of controlling the primary structures of polymers.^{1,12} Thus far, many types of polymerizations that operate with distinct mechanisms, including radical,¹³ anionic,^{14,15} cationic,^{16–18},metathesis,^{19–23} and ring-opening polymerizations^{24–29} have been applied to generate polymer brushes on various surfaces supports.⁹ Forming patterns of polymers with drastically different physical properties requires laborious lithography methods to form patterns of covalently anchored initiators on the support. It is common that more than 5 steps are required even just to form a binary polymer pattern.²⁴

With the recent advances in the photoswitchable surface-initiated radical polymerizations, arrays of polymer brushes can be generated with photolithography methods either from micropatterned initiators with photomask to activate/deactivate polymerization on certain area of the solid substrate.^{9,11,32,24–31} However, existing patterning methods have only are limited to polymers with hydrocarbon backbones, for instance, surface-initiated

polyacrylates³³ or polynorbornenes^{21,34}. A facile patterning method for ring-opening polymerizations can open up new possibilities to form materials with unique surface properties for a variety of applications. Redox-switchable, ring-opening polymerization catalysis can be used to expand the scope of surface-initiated polymerization reactions and to provide an alternative and more efficient way to create surfaces with varied chemical composition.

As mentioned in the previous chapter, continuous effort from our group has been dedicated to constructing a redox-switchable polymerization system, where a redox-active bis(imino)pyridine iron bisalkoxide complex can toggle between catalyzing the lactide or epoxides polymerizations in respond to either redox reagents^{38,39} or electrochemical potentials.⁴⁰ In this chapter, we extend the system to surface-initiated polymerizations to introduce this concept as a way for facile surface modifications. We envision that switchable catalysis will enable in situ generation of different polymer patterns upon application of an applied stimulus. Iron complexes previously used for the redox-switchable polymerization of lactide and epoxides were anchored to TiO₂ nanoparticles. The reactivity of the anchored complex for catalyzing lactide polymerization was maintained as well as its ability to undergo redox-switching and a change in chemoselectivity to epoxide polymerization upon catalyst oxidation. The Fe(II)-TiO₂ can be oxidized into the Fe(III)-TiO₂ structure with both chemical oxidant and electrochemistry. The immobilized complex show similar polymerization reactivities compared to the molecular iron complexes, the Fe(II)-TiO₂ only catalyzed the lactide polymerization and Fe(III)-TiO₂ only active for epoxide polymerizations. An electrode with porous TiO₂ layer on conducting FTO support electrode was constructed to spatially control the growth of polyester and polyether on a single electrode surface with a pattern of binary conducting channels. The system presented a facile surface modification method to spatial control the polymer coatings.

3.2 Synthesis and structural characterization of the iron containing nanoparticles

In order to achieve our goal of developing a redox-switchable surface-initiated polymerization reaction, we first needed a method to anchor the polymerization catalyst onto the surfaces. Previously, protonolysis reactions between the bis(imino)pyridine iron(II) bisalkyl precursor (complex **3.1**) and various organic alcohols were found to be reliable to synthesize molecular, monomeric iron alkoxide complexes.^{38,39,41–44} Surface hydroxides in metal oxide nanoparticles are ubiquitous, which we hypothesized would be suitable surrogates for the alcohols. TiO₂ P25 nanoparticles were first treated with UV light to introduce more surface hydroxyl groups followed by heating at 150 °C for 16 hours under high vacuum (1 x 10⁻⁵ torr) to remove physiosorbed water. Thermogavimetric analysis (TGA) demonstrated the efficacy of removing water with this procedure (Figure 3.1). Physiosorbed water can be removed at temperature lower than 150 °C, and a 1.7% weight loss higher than 350 °C is attributed to the removal of chemosorbed water. We estimate the surface hydroxyl concentration of 0.46 mmol/g, which is consistent with literature reports.⁴⁵



Figure 3.1. TGA of TiO₂ nanoparticles after UV/water treatment.

Subjecting the treated nanoparticle with an iron bisalkyl precursor was used to covalently anchor the molecular iron catalyst onto the nanoparticle surface. The resulting iron containing titania powder appeared light purple. Analysis of the resulting purple powder by ICP-OES indicating the weight percent of iron is 2.1 wt%, which suggested that all of the surface hydroxyl group has been modified with iron, if a similar structure has formed with one iron center bond to two -OH groups on the surface, similar to the molecular iron complexes.³⁹



Scheme 3.1. Protonolysis allowed the covalent bound iron complex on titania nanoparticles.

Several analytical methods were used to gather structural insight into the iron containing nanoparticles. Scanning Tunneling Electromicroscopic (STEM) elemental mapping images showed that the iron atoms and nitrogen atoms are evenly distributed across the scanned window without the evidence for the formation of iron nanoparticles.⁴⁶ Iron element resides on the TiO₂ particles (Figure 3.2), indicating the iron centers have been attached to the nanoparticles with nitrogen containing ligand remained close to the metal center. Moreover, the strong spatial correlation between iron and nitrogen in the STEM is consistent with the metal complexes being deposited on the surface rather than the complexes serving as a precursor for deposition of elemental iron. Mössbauer spectroscopy provided further evidence that the molecular identity of the iron complex was maintained when supported on the TiO₂ surface



Figure 3.2. STEM-elemental mapping of the Fe(II)-TiO₂ powder.

The Mössbauer spectrum revealed the presence of two iron-containing species. The major species (81%) had an isomer shift of $\delta = 1.09$ mm/s and a quadrupole splitting of $|\Delta E_Q| = 2.37$ mm/s, while the minor species (19%) had $\delta = 0.42$ mm/s and $|\Delta E_Q| = 0.89$ mm/s. The molecular bis(imino)pyridine iron(II) bisphenoxide complex has Mössbauer parameters ($\delta = 0.94$ mm/s, $|\Delta E_Q| = 2.19$ mm/s)⁴⁴ similar to the major species observed on the functionalized nanoparticle. Importantly, the isomer shift of the precursor **3.1** is 0.25 mm/s⁴⁷, which is too low to be either species observed in the functionalized nanoparticle.



Figure 3.3 Anchoring the bis(imino)pyridine iron complex onto the TiO2 nanoparticle surface. a) the Mössbauer spectroscopy of the Fe(II)-TiO2 powder; b) the Fe(III)-TiO2 powder obtained through the oxidation with FcPF6.

Reacting the nanoparticles with an excess of ferrocenium hexafluorophosphate (FcPF₆) produced a light brown solid. Analysis of these particles by Mössbauer spectroscopy revealed once again the presence of two species, but this time the major signal (75%) was a new iron species with $\delta = 0.49$ mm/s and $|\Delta E_Q| = 0.85$ mm/s (Figure 3b). These parameters are similar to those obtained for the major species observed in the Mössbauer spectrum of the molecular cationic Fe(III) bisalkoxide complex, which exhibit $\delta = 0.45$ mm/s and $|\Delta E_Q| = 0.85$ mm/s (Figure S8). Further corroborating the experimental findings were Mössbauer parameters computed for a cationic iron(III) bistitanoxide model complex (Table S1, $\delta = 0.46$ mm/s, $|\Delta E_Q|$ = 0.98 mm/s), which are similar to the major species found in the iron(III)-functionalized nanoparticles from the starting material, indicating the successful formation of the ironalkoxide bond around the metal center. Taking a closer look at the Mössbauer spectra of the supported iron complexes, it is worth mentioning that the minor species in the Mössbauer spectrum of the Fe(II)-modified nanoparticles has similar parameters to the major species in the Mossbauer spectrum of the Fe(III)-modified nanoparticles; vice versa. While it may be a coincidence of the preparation method that some impurities were introduced to the supported complexes, we proposed several other possible reasons here: 1) the incomplete oxidation of Fe(II) to Fe(III), and the light responsive titania nanopowder might act as a photoanode to oxidize some of the Fe(II) metal centers; 2) It is also worth pointing out that the commercial P25 TiO₂ are 80% in rutile phase and 20% in anatase phase, which might explain the distribution of iron-containing species on the surface.⁵⁸

 Table 3.1 Calculated and observed Mössbauer parameters of homogeneous iron

 complexes and analogous model complexes

complex	δ (mm/s)	ΔE _q (mm/s)	δ (mm/s)	ΔE _q (mm/s)
	Observed	Observed	calculated	calculated
5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	0.94	1.73	0.926	1.938
CTT -	1.10 (major)	2.39 (major)	1 041	2 110
3.2a	0.42 (minor)	0.89 (minor)	1.011	2.110
- 2 b kk	1.10 (major)	2.39 (major)	1 094	2 256
3.2b	0.42 (minor)	0.89 (minor)	1.084	2.330
	0.37	0.68	0.453	0.698
	0.37	0.68	0.455	0.980

Although we were able to convince ourselves that the major species found in both iron(II) and iron(III)-TiO₂ nanoparticles have similar Mössbauer parameters of their molecular complex analogues, the identities of the minor species observed remained unclear. It is possible that one iron center can bind to either one or two surface hydroxyl groups. We hypothesized that computational tool set can help us answer this difficult question. DFT calculations with ORCA program^{59,60} were carried out with both complex **3.2** & **3.3**. To limit the computational expense, analogues iron(II) and iron(III) titanoxide complexes were modeled to resemble the bonding nature on the nanoparticle surface. As listed in table 3.1, ORCA calculated Mossbauer parameters of complex 3.2 & 3.3 are similar to the experimental data ($\delta = 0.926$ mm/s and $|\Delta E_Q| = 1.938$ mm/s). Complex **3.2a** and **3.2b** were constructed to resemble the coordination environment around the iron centers on the surfaces, in which the iron center binds to either one or two titanium hydroxyl groups. Unfortunately, the results came out that 3.2a and 3.2b have similar Mössbauer parameters and are both similar to the the molecular complex **3.2**. At this stage, we are not able to rule out the possible surface structures of the iron-containing nanoparticles; combining more synthetic and analytical techniques, this questions should be able to be answered, these experiments were not performed due to the COVID-19 crisis.

3.3 Polymerization studies with the iron containing TiO₂ nanoparticles

When exposing the Fe(II)-TiO₂ particles with lactide solutions with an internal standard, 67% lactide conversion was observed with NMR spectroscopy. Thermal gravity analysis (TGA) of the grafted PLA show a 61% weight loss at 285 °C which is in the range of the decomposition temperatures of PLA (Figure 3.5b).⁴⁸ In order to analyze the resulting polymer product with routine techniques used by polymer chemists (NMR, GPC, etc), a facile cleaving method is

required to solubilize the product in organic solvents. Such a method should not involve harsh conditions, such as strong acidic²² or basic conditions²³ used previously to dissolve metal oxide nanoparticles. Such conditions will lead to the decomposition of poly(lactic acid) due to hydrolysis of the ester repeating unit. We found that the surface-grown polymers could be cleaved from the nanoparticles by treating the particles with iodomethane. This method was found to be efficient in removing most of the surface-grown PLA from the particle surface. Before iodomethane treatment, characteristic IR signals from PLA can be observed from the particle surface, but after the treatment, the signals disappeared (Figure GPC 3.5c). GPC analysis of the cleaved poly(lactic acid) (Figure 3.5) revealed a polymer with molecular weight of $M_n = 6.04$ kg/mol and a dispersity of $M_w/M_n = 1.47$. The polymer cleaved from the nanoparticle was methylated at the ester chain end only, as evidenced by ¹H NMR spectroscopy (Figure 3.4d), with the hydroxyl chain end remained unreacted, which further supports the formation of covalent linkage of the polymer and the titania surface. The polymer molecular weight agreed with the predicted molecular weight of 5.31 kg/mol, which was calculated from the conversion of the reaction, the iron loading, and the assumption that only one polymer chain is initiated per iron center. This assumption is based on our previous results for reactions initiated from iron alkoxides derived from alcohols with acidity $(pK_a < 10)^{42}$ similar to Ti-OH.⁵⁴ The good match between the measured and predicted molecular weights suggested that most of the deposited iron centers are active for lactide polymerization.



Figure 3.4 Lactide polymerization with Fe(II)-TiO2 particles. a) Reaction scheme of surface-initiated lactide polymerization catalyzed with Fe(II)-TiO2 particles; b) TGA analysis of the PLA-modified TiO2 particles; c) ATR spectrum of the PLA-modified TiO₂ particles

before and after MeI treatment; d) ¹H-NMR spectra of PLA cleaved off TiO₂ particles with MeI treatment. End groups are assigned according to literature reported values.

The method described above to remove surface-initiated polymers from the support is uncommon in the literature.⁵⁵ The technique not only enables polymer composition to be unambiguously identified, but it also provides a valuable mechanistic tool that can be used to better understand the surface-initiated polymerization reaction. A time course investigation of the polymerization reaction was carried out. The conversion of lactide monomer over time was analyzed by ¹H NMR spectroscopy, polymer molecular weight information was obtained with GPC after cleaving the polymer off the insoluble TiO₂ nanoparticle support. Using this combination of techniques, molecular weight, molecular weight distribution, and conversion could be monitored over time (Figure 3.6). This study revealed a linear increase of molecular weight with conversion, which suggested that the surface initiated lactide polymerization had living characteristics. This behavior was similar to lactide polymerization catalyzed by the homogeneous molecular iron complex 3.2.41 However, different from the homogeneous reactions were slower reaction rates and broader molecular weight distributions. Examining the conversion versus time plots revealed a possible explanation. At lower conversions (<40%), the reaction rate was fast and followed first order reaction kinetics. Molecular weight distributions were also narrower than observed at the end of the reaction. At higher conversion, however, the reaction deviated from first order kinetics reaching an ultimate conversion of 65%. Coincidentally, the molecular weight distribution became broader as the reaction proceeded. The slower reaction rates and higher dispersity at high conversions is consistent with mass transport becoming more prominent as the polymerization proceeds. While beyond the scope of this article, this mechanistic insight will be invaluable for future reaction design.



Figure 3.5 . Kinetic analysis of lactide polymerization catalyzed by Fe(II)-TiO2 powder. Left: first order kinetic plot of the reaction process; right: conversion versus molecular weight plot.

The Fe(III) TiO₂ powder gave 33% conversion of cyclohexene oxide, similarly, treating of the surface-initiated polyether with MeI successfully cleave the titanium alkoxide linkage, yielded a polymer product with molecular weight around 11.6 kg/mol and broad distribution of 3.08 (Figure 3.6). The molecular weight distributions for both surface-initiated poly(lactic acid) and polyether are notably broader than the polymers produced from homogeneous catalysts, which can be a result of insufficient mass transport for heterogenized catalysts. The isolated polymer has a decomposition temperature at 316 °C, which is close to the decomposition temperature of the PCHO. The iodomethane treatment worked well in removing the PCHO off the surface as well, the IR signals from PCHO disappeared after the treatment (Figure 3.6c).



Figure 3.6 Cyclohexene oxide polymerization with Fe(II)-TiO₂ particles. a) Reaction scheme of surface-initiated cyclohexene oxide polymerization catalyzed with Fe(III)-TiO₂ particles; b) TGA analysis of the PCHO-modified TiO₂ particles; c) ATR-FTIR spectrum of the

3.3 Cyclic voltammograms of Fe(II)-TiO₂ particles

With the successful anchoring of the reactive iron complexes on the TiO_2 surfaces and their redox-switching capabilities demonstrated, we then moved to test the polymerization reactions on conductive surfaces so that electrochemical potential could be used to affect redox-switching. To prepare the supported Fe(II)-TiO₂ electrode, a Ti mesh was first coated with a layer of TiO₂ (50 nm) through atomic layered deposition (ALD). The coated Ti mesh was soaked into a solution of the iron(II) alkyl precursor (complex 1). Cyclic voltammetry of the Fe(II)-TiO₂ electrode was carried out with platinum wire as the counter electrode and a lithium ribbon as reference electrode. The Fe(II)-TiO₂ electrode was found to have a half-wave potential at $E_{1/2} = -0.4$ V vs Fc/Fc⁺, which corresponds to a reversible redox interconversion between iron(II) and iron(III) oxidation states. Compared to the molecular bisphenoxide complex 2 with $E_{1/2} = -0.8$ V vs Fc/Fc⁺, the redox potential of the Fe(II)-TiO₂ electrode shifted positively around 300 mV, indicating the iron center is more electron deficient than the molecular iron phenoxide complex.^{38,39} This result is consistent with the less electron donating capability of the inorganic metal-oxide ligand compared with organic phenoxide ligand. The peak separation does not increase when varying the scan rates from 20 mV/s to 500 mV/s in contrast to the molecular iron-bisphenoxide complex 3.2, which suggested the electron transfer process is no-longer diffusion-limited, as the center of electron transfer is immobilized on the surface. Although in the ideal scenario, for surface-anchored complex, peak separation should not be observed with the anodic and cathodic peaks on top of each other.⁴⁹ The peak separation of 200 mV observed with the Fe(II)-TiO₂ plate was probably a result of the large resistance of the thick semiconducting TiO₂ layer. Furthermore, a linear dependence of peak current versus scan rate is found, suggested the redox-active center was on the surface.⁵⁰



Figure 3.7 a) Cyclic votammetry of Fe(II)-TiO₂-Ti mesh electrode with varying scan rate, working electrode: titanium mesh, counter electrode platinum wire, reference electrode: platinum wire; b) Cyclic voltammetry of 0.35 mM molecular bis(imino)pyridine iron bisphenoxide complex with varying scan rate; working electrode: glassy carbon, counter electrode platinum wire, reference electrode: platinum wire c) relationship between scan rates

versus cathodic peak current. Supporting electrolyte: 0.1 M tetrabutylammonium hexafluorophosphate in CH₂Cl₂.

3.4 Altering surface-initiated polymerization reactivities with electrochemistry

To maximize the yield of surface grafted polymers for the ease of characterization, we constructed an electrode with P25 TiO₂ nanoparticles as the active material and fluorine doped tin oxide (FTO) as the conductive substrate. For this purpose, we modified a procedure that has worked well for the fabrication of electrodes in dye-sensitized solar cells. A porous titania electrode was constructed. A slurry of TiO₂ nanopowder in a mixture of Triton X-100, acetylacetone and water was pasted onto an FTO glass electrode.⁵¹ Similar to the nanoparticles, anchoring of the iron complex onto the electrode was performed by reacting the plate with a solution of bis(imino)pyridine iron bisalkyl precursor **3.1**. Cyclic voltammograms of the supported complex show a semi-reversible redox active species with a redox potential at 2.9 V vs Li/Li⁺.



Figure 3.8 Cyclic voltammetry of Fe(II)-TiO₂ plate prepared with P25 nanoparticle; a) before lactide polymerization; b) after lactide polymerization. Supporting electrolyte: 0.1 M tetrabutylammonium hexafluorophosphate in CH₂Cl₂.

Potentiostatic electrolysis was used to oxidize the surface attached Fe(II)-TiO₂ electrochemically. A two-electrode set-up was used with the Fe(II)-TiO₂ was used as the working electrode, Li fritted/PVDF tube as the reference electrode and the counter electrode.⁴⁰ The isolated sacrificial lithium electrode was used to avoid side reaction happening on the counter electrode. An oxidizing applied potential of 3.7 V vs Li/Li⁺ was applied to the Fe(II)-TiO₂ plate electrode. The charge transfer appeared to be sluggish with the current decrease rapidly before achieving full oxidation, probably due to the large resistance of the TiO₂. The electrolysis was stopped after an hour, when the current dropped below 1 µA. Open-circuit potential of the electrochemical set-up changed from 2.6 V to 3.1 V, usually suggested a transformation of the charge in the capacitor, and here, the oxidation states of the iron species.⁴⁹ Soaking the Fe(II)-TiO₂ electrode plate with lactide solution led to monomer consumption and the appearance of an IR absorption band in the same region as the C=O stretching in dropcasted poly(lactic acid). A broad band peaked at 1610 cm⁻¹ was observed in the surface-initiated polymerization sample only. The broad band may due to the interaction of covalently attached polymer brush to the electrode surface. Interestingly, an increase of lactide conversion from around 20% to 30-40% was observed when a stirring rate of 300 rpm was applied. Stirring obviated the mass transport issue with the heterogeneous catalysis. Fe(II)-TiO₂ electrode plate does not consume cyclohexene oxide, as shown in Figure 3.8b.



Figure 3.9 Altering the reactivities of the surface-initiated polymerization by a redox switch. a) surface-initiated poly(lactic acid) can be formed from Fe(II)-modified TiO2 glass electrode; b) Fe(III) -modified TiO₂ glass electrode can be oxidized with electrochemically trigger surface-initiated poly(cyclohexene oxide); c) selective polymerization of surface-initiated polymers from a solution mixture of monomers based on the oxidation states of the iron centers on the TiO₂ glass electrode.

When we carried out the cyclic voltammetry experiment from the PLA-modified electrode. We hypothesized that the redox-active iron center would propagate away from the

electrode surface during the polymerization process (Figure 3.8b). Diffusion would affect the electron transfer process on the working electrode after the polymerization as the iron center will no-longer be attached to the electrode surface. Cyclic voltammetry shows that before polymerization, when the iron complex is attached to the electrode surface, no increase in peak separation was observed with increased scan rates (from 20 mV/s to 500 mV/s); and the peak separation increase was only observed with the Fe(II)-PLA-TiO₂ plate, indicating the electron transfer process redox active center was diffusion limited. It was noted that the anodic peak current is significantly larger than cathodic peak current, which might be a result of the capacitor behavior of the mesoporous TiO₂. However, such effect is more pronounced at the anodic reaction and less obvious for the cathodic wave. This observation might reveal some interesting configuration of the polymer.

As discussed in the previous section, based on the calculation of the molecular weight of the obtained PLA from the supported catalyst, each iron center only initiated one chain of PLA, in this case, the other side of the titanium hydroxyl ligand will stay coordinated to the metal center so the iron center will remain bound to the particle surface. However, it contradicts the CV experiment, which the peak separation increase indicated the iron center no longer remain close to the electrode surface. At this stage, we are not able to rule out the possible surface structures of the iron-containing nanoparticles; combining more synthetic and analytical techniques, this questions should be able to be answered, these experiments were not performed due to the COVID-19 crisis.

The electrochemically oxidized Fe(III)-TiO₂ plate was soaked into epoxide solution with stirring, 13% conversion of cyclohexene oxide was observed after 12 h. FTIR of the plate after polymerization step showed characteristic absorption bands of poly(cyclohexene oxide) (Figure 3.9b). However, a small amount of lactide conversion was observed when soaking the Fe(III)-TiO₂ plate into a solution of lactide. Where the signals from poly(lactic acid) C=O stretches could be observed on the Fe(II) plate, however, a small amount of PLA signals observed on the Fe(III)-TiO₂ plate after electrochemical oxidation (Figure 3.9c). This is likely due to the incomplete electrochemical oxidation with the charge transfer process happening through the semiconducting TiO₂ layer. Notably, when the chemically oxidized Fe(III)-TiO₂ electrode does not catalyze the lactide polymerization with no observation of PLA signals in the ATR-FTIR spectrum (Figure 3.11). It remained unclear what is the possible reason behind this incomplete oxidation behavior. It is worth mentioning that the highly porous TiO₂ nanoparticles can act as good capacitors for charge storage. Nevertheless, electrochemistry is found to be a reliable method that can alter the reactivities of the iron-containing electrodes towards different polymerizations in one step from a mixture of monomers.



Figure 3.10 Altering the reactivities of the surface-initiated polymerization by a redox switch. a) Raman spectroscopy of the binarily modified PLA and PCHO containing electrode surface; b) Raman mapping of the binarily modified PLA and PCHO containing electrode.

With the success of growing surface-anchored polymer brush with both PLA and PCHO with an electrochemical trigger, we then moved on to spatially discriminate polymer growth. Raman spectroscopy was used as a surface characterization technique. Similar to IR

study, we first examined the Raman spectroscopy of the surface-grown PLA on a Fe(II)-TiO₂ plate and surface-grown PCHO on Fe(III)-TiO₂ plate. As shown in Figure 3.10a, peaks at 820 cm⁻¹ and 880 cm⁻¹ were utilized to for mapping the signals from PLA and PCHO across the electrode surface. A sample area of 9,500 x 2,000 μ m² across the substrate was scanned, and the resulting two-dimensional map is shown in Figure 3.10d. Results illustrated that PLA and PCHO were primarily segregated to the reduced and oxidized sides of the plate, respectively. This observation is consistent with our expected reactivity of the iron-based complexes and illustrates the power of the technique to form differentially substituted surfaces on a single substrate from mixture of monomers. It is notable that the amount of PLA and PCHO was not evenly distributed over each side of the plate, with some areas of the reduced electrode and especially the oxidized electrode demonstrated evidence for deposition of PCHO and PLA (Figure 3.10b). This observation is likely due to a combination of factors. First, the poor resolution and low signal to noise of the peaks used to distinguish PLA from PCHO likely contribute to false positive indication of PCHO on the iron(II) side and PLA on the iron(III) side. Another reason that we observed signals from PLA on the iron(III) side could be from incomplete electrochemical oxidation of Fe(II) as discussed earlier in this article. A third reason for observing this "crossover" reactivity is due to mobility of the electrochemical signal during the switching due to imperfections incurred for the fabrication of the divided plate.



Figure 3.11 ATR-FTIR spectra of polymer-containing electrode surface when the iron(III) side was chemically oxidized.

To circumvent the complications associated with the simultaneous polymerization of lactide and epoxide, the electrode was sequentially exposed to the two monomers. One of the two electroactive strips on the electrode was oxidized by exposing it to an oxidizing potential. The plate was then first treated with a cyclohexene oxide solution (1.4 M) resulting in 19% monomer conversion. Next, the plate was treated with a lactide solution (0.35 M) resulting in 31% lactide conversion. The higher conversions observed in these reactions compared to the reaction where lactide and epoxide were both present were consistent with what we have previously observed in homogeneous reactions.^{42,43} We suspect that the lactide and epoxide monomers serve as competitive inhibitors for the iron(III) and iron(II) catalysts, respectively. Raman mapping of the resulting product shows distinct difference between the two strips with less undesired crossover of lactide polymerization on the iron(III) side and epoxide polymerization on the iron(II) side of the electroactive surface (Figure 3.10e). These results indicated that better compositional homogeneity could be achieved through sequential lactide and cyclohexene oxide polymerization rather than simultaneous lactide and cyclohexene oxide polymerization.

The bulk properties of the functionalized surfaces reflect the compositional differences between the two electrodes. For example, contact-angle measurements of the two surfaces revealed a significantly larger angle for the iron(II) side (19.3°) compared to the iron(III) side (14.7°), which is consistent with the more hydrophobic polyester compared to the polyether (Figure 3.12). The contact angles measured were significantly smaller than contact angles for drop casted polymer. These results reflect a more hydrophilic surface that is likely a consequence of the low Ti-OH density on the nanoparticles. To better visualize the differences between the surfaces, the polymer-modified electrodes were exposed to a solution containing cationic Rhodamine 6G dye. This experiment revealed significant differences between bare TiO₂, the iron(II) functionalized side, and the iron(III) functionalized side (Figure 10c). Whereas the bare TiO₂ plate did not adsorb significant amount of R6G, by comparison, the iron(II) functionalized side containing mostly PLA was dyed a pink color and the iron(III) functionalized side containing mostly polyether was bright red. This outcome reflects the high propensity for polyethers to bind cationic dyes and illustrates how application of electrochemical potential can alter the properties of surfaces through chemoselective polymerization reactions.



Figure 3.12. Contact angle measurements of the polymer-coated electrodes
3.5 Conclusions

In this chapter, we demonstrated an iron(II) complex was covalently anchored to a titania nanoparticle support in one step. Spectroscopic data supports the formation of iron oxide bonds with the bis(imino)pyridine ligand remaining coordinated to the metal center. The Fe(II)-TiO₂ can be oxidized to Fe(III)-TiO₂ with either chemical oxidant or electrochemistry. The immobilized complexes show similar polymerization reactivities compared to the molecular iron complexes, the Fe(II)-TiO₂ only catalyzed the lactide polymerization and Fe(III)-TiO₂ catalyzed epoxide polymerizations. An electrode with porous TiO₂ layer on conducting FTO support electrode was constructed to spatially control the growth of polyester and polyether on a single electrode surface with a binary pattern of two channels insulated from each other. Applying an oxidizing potential selectively to one of the channels, followed by polymerization from a mixture of both lactide and cyclohexene oxide allowed for the formation of a binary polymer pattern on a single electrode surface. FTIR and Raman mapping technique were used to determine the distribution of the chemical composition on the plate. The system presented a facile surface modification method with both temporal and spatial control of the polymer coatings. As the poly(lactic acid) and poly(cyclohexene oxide) have their unique physical properties, the material can be useful in many applications including the anti-fouling coatings on sea vessels combining the biodegradability of poly(lactic acid) and the antifouling effect of the polyethers. The polymer-coated electrode also responds to cations and water/oil droplets differently. While the ring-opening polymerizations can be extended to other type of monomers, the system has the potential to rapidly generate sophisticated patterns of multiple polymers with different chemical composition and physical properties, which can be attractive to constructing sensing materials that will not be formed using any other method.

We demonstrated here how redox-switchable ring-opening polymerization catalysis can be used to expand the scope of surface-initiated polymerization reactions and to provide an alternative and more efficient way to create surfaces with varied chemical composition. Within this context, we report three critical advances that are enabled through redox-switchable surface-initiated polymerization: 1) Altering the ability for an immobilized catalyst to polymerize different classes of monomers through application of electrochemical potential to a surface; 2) developing a method to pattern functional surfaces by using electrochemical potential to activate and deactivate polymerization reactions; 3) Utilize the orthogonal reactivity of switchable polymerization catalysts to create patterned surfaces functionalized with two different polymers.

Experimental Section

General Information. Unless stated otherwise, all reactions were carried out in ovendried glassware in an Ar or N₂-filled glove box. Bis(imino)pyridine iron bisalkyl complex 1 was synthesized following literature procedures.³⁹ Solvents (dichloromethane, diethyl ether, pentane) were used after passage through alumina columns under a blanket of argon⁵² or distilled over calcium hydride to remove water and then degassed briefly by exposure to vacuum. Methanol, hexanes, and acetone were purchased from Fisher Scientific and used without further purification. Titania P25 nanoparticle was purchased Sigma-aldrich. (rac)-Lactide were obtained from Purac Biomaterials; and L-lactide was purchased from Natureworks. Racemic and enantiomerically enriched lactide were recrystallized from ethyl acetate followed by recrystallization from hot toluene and dried in vacuo over P2O5 prior to polymerization. Cyclohexene oxide was purchased from Acros Organics and distilled from calcium hydride prior to its use. Cyclic voltammetry and bulk electrolysis were carried out on a potentiostat (Biologic VMP3). Glassy carbon obtained from CHInstrument was used as working electrode for cyclic voltammetry experiment. Pt wire, tetrabutylammonium hexafluorophosphate (>99%), lithium perchlorate (>99.99%), bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, 99.95%), poly(vinylidene fluoride (PVDF) and lithium metal ribbon (>99.9%) were purchased from Aldrich. The glass cylinder with a fine frit used to house the counter electrode was prepared from literature reported procedures.48

Characterization and Physical Measurements. Nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature (unless indicated otherwise) on spectrometers operating at 500 or 600 MHz for ¹H NMR and 125 MHz for ¹³C NMR. Gel permeation chromatography (GPC) was performed on an Agilent GPC220 in THF at 40 °C with three PL gel columns (10 μm) in series. Molecular weights and molecular weight distributions were

determined from the signal response of the RI detector relative to polystyrene standards. The Mark-Houwink parameters and refractive index increment (dn/dc) (0.042 mL/g for PLA and 0.085 mL/g for PCHO) used for GPC were obtained from literature.⁵³ Centrifugation used for polymer purification was carried out using a Beckman Coulter J2-MC Centrifuge with Rotor 17.0 at 2500 RPM operating at 4°C for 20 minutes. The Model 42 UVO-Cleaner (Jelight Company Inc.) was used to process the sample by UV irradiation. The atomic layer deposition (ALD) was conducted on Cambridge NanoTech (Savannah 100) system. The samples were imaged by transmission electron microscope (TEM) (JEOL, 2010F) at 200 kV. The Fy-Light 130K airbrush kit (Amazon, Fy-Light) was used to prepare TiO₂-FTO plates. Inductively Coupled Plasma - Reactive Ion Etching (ICP-RIE, Plasma-ThermVersaline LL ICP) instrument was used to make the patterned electrode.

Raman spectroscopy measurements was performed with Raman system (XploRA, Horiba) with a 532 nm laser excitation. ATR-FTIR spectra were recorded using a Bruker Vertex 70 FTIR spectrometer (Billerica, MA) equipped with an MCT detector (FTIR-16; Infrared Associates; Stuart, FL). The TiO₂ coated FTO glass slide was pressed on the ATR Si or ZnSe prism crystal.

Zero-field ⁵⁷Fe Mössbauer spectra were measured with a constant acceleration spectrometer (SEE Co, Minneapolis, MN) at 90 K. Isomer shifts are quoted relative to Fe foil at room temperature. Data were analyzed and simulated with Igor Pro 6 software (WaveMetrics, Portland, OR) using Lorentzian fitting functions. Samples were prepared by suspending 20–50 mg of compound in sufficient Paratone oil immobilizing by rapid freezing in liquid nitrogen.

All DFT calculations were performed with the ORCA program package.⁵⁴ The geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level of DFT.⁵⁵ Triple- ζ -quality basis sets TZVP

were performed with all atoms.^{56 57}Fe Mössbauer parameters (isomer shift δ and quadrupole splitting $|\Delta E_Q|$ were computed following the procedure reported by Neese *et al.*^{56,57}

Inductively coupled plasma optical emission (ICP-OES) spectrometry was recorded in an Agilent 5100 instrument that was calibrated using known concentrations of standard solutions to quantify Fe element. 1000 ppm Fe standard solution was purchased from Sigma-Aldrich. To digest iron-complex from Fe(II)-TiO₂, the powder/plate was soaked in 20 mL 1% nitric acid solution overnight before. Then the solution was subjected to centrifugation and used for ICP-OES test.

Calculating surface hydroxyl groups on the P25 TiO₂ **powder** The density of surface hydroxyl groups was calculated based on reported literature.⁵⁸ The temperature was first ramped up from 19 °C to 120 °C (T1) and held at 120 °C for 20 min to remove the physiosorbed water. The temperature was then increased from 120 °C to 500 °C (T2) at a rate of 20 °C/min to measure the weight loss from removing the surface hydroxyl groups. The calculation of the surface hydroxyl groups is done based on the hypothesis that the surface is free of hydroxyl groups at 500 °C

$$\# of \frac{\partial H}{mm^2} = 2 \times 0.625 \times (wt_{T1} - wt_{T2}) \times N_A / (SSA \times wt_{T1} \times MW_{H20})$$

The specific surface area of 50 m2/g was used to calculate the value. 0.625 is the calibration factor. wt_{T1} and wt_{T2} are the weight loss at 120 °C and 500 ° to calibrate the weight loss of chemisorbed water below 120 °C. MWH2O is the molecular weight of water, NA is the Avogadro constant.

Procedure for anchoring the iron complex onto P25 TiO₂ powder Prior to bring the plate into a nitrogen filled glovebox, the TiO₂ powder was heated under reduced pressure (lower than 10^{-4} torr) at 150 °C to remove the surface bound water. The powder (100 mg) was then mixed with a solution of bis(imino)pyridine iron bisalkyl complex **1** (50 mg, 0.08 mmol) in diethyl ether (4 mL) for overnight in the glovebox. The mixture was centrifuged to collect the powder. The powder was then washed with diethyl ether (2 mL × 3) and dichloromethane (2 mL) with centrifugation until the supernatant was colorless. The resulting powder was light purple in color. ICP-OES show 2.1 wt% iron loading. Yield: 85%.

Procedure for the surface-initiated polymerization of (*rac*)-lactide with the P25 Fe(II)-TiO₂ powder In a nitrogen-filled glove box Fe(II)-TiO₂ powder (100 mg) was suspended in the solution of (*rac*)-lactide (144 mg, 1.00 mmol) and 1,3,5-trimethoxy benzene (94.0 mg, 0.500 mmol) dissolved in a dichloromethane (2.00 mL). The mixture was allowed to stir vigorously at room temperature for overnight. The mixture was then centrifuged to separate the powder. The powder was washed with dichloromethane (5 mL) for 3 times in the glovebox. Lactide conversion was determined from the ¹H NMR by comparing the relative integration of the methine peaks of the remaining lactide (q, 5.0 ppm) to the methyl peaks of the internal standard (s, 3.8 ppm) in the supernatant.

Procedure for cleaving the polymer off the surface. The powder was then suspended in dichloromethane (2 mL) and precipitated in methanol (20 mL) to remove unreacted lactide monomer. The PLA-TiO₂ powder was collected with centrifugation, and suspended again in dichloromethane (5 mL). Iodomethane (0.2 mL, 3.21 mmol) was dissolved in dichloromethane (10 mL). The iodomethane solution (1 mL) was added to the suspension of the PLA-TiO₂ powder dropwise. The reaction mixture was allowed to stir at room temperature for 16 hours. The solvent was removed under vacuum. The remaining solid was then suspended in THF (10 mL) and centrifuged 3 times with extra THF (20 mL) to wash. The supernatant was collected and dried under vacuum for ¹H NMR and the molecular weight data was obtained from GPC. Yield: 63%.

Oxidizing the Fe(II)-TiO₂ with ferrocenium hexafluorophosphate (FcPF₆) In a nitrogen-filled glove box, Fe(II)-TiO₂ powder (100 mg) was suspended in dichloromethane (2 mL) and FcPF₆ (50 mg, 0.15 mmol) was dissolved in dichloromethane (5 mL). The FcPF₆ was then added to the suspension of the Fe(II)-TiO₂ powder, and the mixture was allowed to stir at room temperature for 30 min. The powder was separated using centrifugation, and washed with dichloromethane (5 mL × 3) with centrifugation, until the supernatant was colorless. The powder was then dried under vacuum, and appeared to be light brown in color. Yield: 71%.

Removing poly(cyclohexene oxide) from the surface of Fe(II)-TiO₂. On the bench, the solid product obtained from the surface-initiated polymerization of cyclohexene oxide was suspended again in dichloromethane (5 mL) in a 20-mL vial. Iodomethane (0.20 mL, 0.46 g, 3.2 mmol) was dissolved in dichloromethane (10 mL). The iodomethane solution (1.0 mL, 0.046g, 0.32 mmol) was added to the suspension dropwise. The reaction mixture was allowed to stir at room temperature for 16 hours. The solvent was removed under vacuum, and the remaining solid was suspended in hexanes (10 mL) and washed three times with THF (20 mL) following each was with centrifugation. The resulting solid was dried under vacuum and analyzed by ¹H NMR and GPC to get polymer composition and molecular weight, respectively. ICP-OES show 1.7 wt% iron loading, yield: 78%.

Preparation of TiO₂-FTO electrode. Preparation of TiO₂-FTO electrode was carried out following a previously reported method.¹⁵ commercial P25 TiO₂ nanopowder (1.5 g) was mixed with deionized H₂O (2.5 mL), acetylacetone (75 μ L) and Triton X-100 (2 drops) to make a uniform slurry. The slurry was then uniformly coated onto the FTO substrate (0.5 × 5 cm) by doctor blade method. Next, the plate was annealed at 450°C in air for 0.5 h. The plate was then treated under UV irradiation for 30 minutes. Such electrodes were used for the study of

electrochemical property of surface-anchored iron-complex and the following polymerizations. To get more uniform and thinner TiO_2 layer for better characterization by Raman spectrometer, the compressed air spraying method was also utilized to spray TiO_2 layer onto the FTO substrate. Dimensions of the plate are shown in Figure S1.

Anchoring complex 3.2 on TiO₂-FTO electrode. In a nitrogen-filled glove box, TiO₂-FTO electrode was soaked into a solution of bis(imino)pyridine iron bisalkyl complex 1 (50 mg, 0.080 mmol) in diethyl ether (4 mL) in a 7-mL vial overnight. The plate was removed from the reaction mixture and washed three times with diethyl ether (4 mL). The plate was purple in color after the treatment. The iron concentration remained difficult to determine as the full digestion of the entire glass-TiO₂ plate was not successful.

Preparation of the electrically discriminated two-strip TiO_2 -FTO electrode. To prepare electrically discriminated electrode for patterned polymerization, ICP-RIE instrument was used to etched out the middle an FTO layer into a 1mm width trench on FTO substrate (1 × 5 cm). As a result, two sides of the FTO electrode can be addressed separately by external electric potential. The TiO₂ layer was then coated on the etched FTO substrate by either doctor blade method or compressed air spraying method, following by anchoring iron complex 1 as described above.

Procedure for CV measurements. To prepare iron-functionalized electrodes for cyclic voltammetry study, ca. 10-50 nm TiO₂ layer was deposited on the titanium mesh according to previously reported method.¹⁶ CV of iron-complex anchored on ALD-TiO₂ was conducted using a three-electrode configuration, where the Fe(II)-TiO₂ was used as the working electrode, and two platinum wires served as the counter and reference electrodes. A solution of tetrabutylammonium hexaflurophosphate in dichloromethane (0.05 M) was used as the electrolyte. The scan rate was varied (20 mV/s to 500 mV/s) to study the diffusion process

on the electrode. For control experiment, iron-functionalized TiO₂-FTO electrodes made from P25 nanopowder were also used as working electrode to conduct similar CV study (Figure S9).

Cell assembly for bulk electrolysis. Following a previously reported procedure,⁴⁰ bulk electrolysis was carried out using a divided two-electrode configuration. All manipulations during the construction of the cell and the subsequent bulk electrolysis was carried out in an argon-filled glovebox. This cell used the iron(II) functionalized electrode as the working electrode and a lithium metal counter/reference electrode isolated from the working electrode by a Li⁺/PVDF membrane coated fritted tube. A 0.05 M solution of LiClO₄ in dimethoxy ether (1 mL) was added to the tube as the electrolyte. The top of the lithium rod was affixed to the tube with Teflon tape. For the working electrode chamber, a 0.05 M solution of Bu4NPF₆ in dichloromethane was used as the electrolyte. The electrical connection to the potentiostation was established by alligator clips affixed to the top of the Fe(II)-TiO₂ plate as the working electrode and the Li counter/reference electrode. An oxidizing potential of 1.0 V vs Fc/Fc⁺ was applied to the working electrode for at least one hour, until the current dropped below 3 μ A.

Oxidation of the iron(II) modified TiO₂-FTO electrode with FcPF₆. In a nitrogenfilled glove box, the iron(II) modified TiO2-FTO electrode plate was exposed to a solution of $FcPF_6$ (25 mg, 0.076 mmol) dissolved in dichloromethane (2 mL). The plate was removed from the solution and rinsed four times with diethyl ether (3 mL). The color of the plate was brown after the oxidation.

Surface-initiated polymerization of lactide on the iron(II) modified TiO_2 -FTO electrode. In an argon-filled glovebox, the iron(II) modified TiO_2 -FTO electrode plate was placed in a dichloromethane (10 mL) solution containing lactide (500 mg, 3.47 mmol) and 1,3,5-trimethoxy benzene (336 mg, 2.00 mmol) in a 20-mL vial. The mixture was stirred at 350 rpm at room temperature overnight. Lactide conversion (20%) was determined from the

¹H NMR by comparing the relative integration of the methine peaks of the remaining lactide (q, 5.0 ppm) to the methyl peaks of the internal standard (s, 3.8 ppm) in the supernatant.

Surface-initiated polymerization of cyclohexene oxide on the iron(III) modified TiO₂-FTO electrode. In an argon-filled glovebox, the iron(III) modified TiO₂-FTO electrode plate was placed in a dichloromethane (10 mL) solution containing cyclohexene oxide (1.37 g, 14.0 mmol) and 1,3,5-trimethoxy benzene (336 mg, 2.00 mmol) in a 20-mL vial. The mixture was stirred at 350 rpm at room temperature overnight. Cyclohexene oxide conversion (15%) was determined from the ¹H NMR by comparing the relative integration of the methine peaks of the remaining lactide (q, 5.0 ppm) to the methyl peaks of the internal standard (s, 3.8 ppm) in the supernatant.

Simultaneous surface-initiated polymerization of lactide and cyclohexene oxide on the electrically discriminated two-strip plate. The iron containing plate was washed three times with diethyl ether (4 mL), and then placed in a dichloromethane (10 mL) solution containing lactide (500 mg, 3.47 mmol), cyclohexene oxide (1.37 g, 14.0 mmol), and 1,3,5trimethoxy benzene (336 mg, 2.00 mmol) in a 20-mL vial. The reaction was allowed to stir at 350 rpm at room temperature overnight. Lactide conversion (21%) was determined from the ¹H NMR of the supernatant by comparing the relative integration of the methine peaks of the remaining lactide (q, 5.0 ppm) to the methyl peaks of the internal standard (s, 3.8 ppm). Cyclohexene oxide conversion (13%) was determined from the ¹H NMR by comparing the relative integration of the methine peaks of the remaining cyclohexene oxide (q, 3.0 ppm) to the methyl peaks of the internal standard (s, 3.8 ppm) in the supernatant.

Sequential surface-initiated polymerization of lactide and cyclohexene oxide on the electrically discriminated plate. The two-strip plate was placed in a dichloromethane (10 mL) solution containing lactide (500 mg, 3.47 mmol) and 1,3,5-trimethoxy benzene (336 mg, 2.00 mmol) in a 20-mL vial. The reaction was allowed to stir at 350 rpm at room temperature for 12 h. Lactide conversion (31%) was determined from the ¹H NMR of the supernatant from the first step by comparing the relative integration of the methine peaks of the remaining lactide (q, 5.0 ppm) to the methyl peaks of the internal standard (s, 3.8 ppm) in the supernatant. The plate was rinsed with dichloromethane (5 mL) and then placed in a dichloromethane (10 mL) solution of cyclohexene oxide (1.37 g, 14.0 mmol) and 1,3,5-trimethoxy benzene (336 mg, 2.00 mmol). The reaction was allowed to stir at 350 rpm at room temperature for 12 h. Cyclohexene oxide conversion (19%) was determined from the ¹H NMR of the supernatant from the second step by comparing the relative integration of the methine peaks of the remaining cyclohexene oxide (q, 3.0 ppm) to the methyl peaks of the internal standard (s, 3.8 ppm) in the supernatant.

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4. Chapter 4. A Mechanistic Investigation of Epoxides Ring-opening Polymerizations

4.1 Introduction

Iron-based catalysts have played an important pioneering role in the evolution of transition metal-based catalysts used for epoxide ring-opening reactions. In the 1950s, Baggett and Pruitt of Dow Chemical developed iron-based catalysts for the isospecific polymerization of propylene oxide.^{1–3} The combination of iron(III) chloride and propylene oxide yielded an ill-defined mixture of iron-containing products that was nevertheless active for polymerization. Subsequently, a variety of iron hydrates with and without additional ancillary ligands have been used for epoxide polymerization.^{4,5} Despite industrial application of iron-based catalysts for epoxide polymerization, there has been much debate regarding the polymerization mechanism. Through the hydrolysis of products from studies combining iron halide and alcohols, Borkovec and Colclough have shown that iron alkoxides are likely the active species for these polymerization reactions.^{6,7} However, the exact structure of the active site still remains unclear, monomeric, bimetallic, trinuclear, and even polymeric multimetallic species have all been proposed to be the key intermediate in the reaction.^{8–9}

Epoxides represent one of the most important building blocks for the assembly of small molecules^{10–13} and as monomers⁵ or crosslinking agents^{14,15} for the construction of macromolecules^{16–18} Transition metal-catalyzed processes have been developed that proceed through coordination-insertion mechanisms commonly requiring multiple metal centers to facilitate epoxide ring-opening.^{19,20} Unraveling the mechanistic features of these processes has led to some of the most useful transition metal-catalyzed reactions that have emerged in the past two decades, including hydrokinetic resolution of epoxides,¹² the regioselective

cyclization of epoxy alcohols,²¹ the stereoselective polymerization of epoxides,²² and the copolymerization of epoxides with carbon dioxide.^{23–25}

In 2016, we reported that complex **4.2a** facilitated the rapid polymerization of epoxides.^{26,27} As discussed in Chapter 2, during the course of our investigation into the redox-switchable nature of the polymerization catalyst, we observed some puzzling features of the epoxide polymerization reaction catalyzed by **4.2a**: 1) extremely fast reaction rates were observed early in the reaction but the reactions never reached full conversion, 2) addition of a second aliquot of epoxide to polymerization reactions that reached their ultimate conversion led to the rapid consumption of epoxide at similar rates as initial polymerization but that once again failed to reach full conversion, and 3) predominately block copolymers (as opposed to mixtures of homopolymers) were isolated from redox-switchable copolymerization reactions with lactide despite the fact that the epoxide polymerization reaction proceeded without good control over molecular weight and produced polymer with broad molecular weight distributions. Our desire to improve catalyst performance and to develop a better understanding of the redox-switchable nature of **4.2a**, and its complementary reactivity with **4.1a**, prompted us to pursue a detailed mechanistic investigation into the polymerization of epoxides catalyzed by **4.2a**.



Scheme 4.1. Reversible oxidation and reduction between 4.1a and 4.2a

4.2 Coordination-insertion mechanism

Previously,²⁷ the work done by Dr. Kayla Delle Chiaie have established a hypothesis that the epoxide opening polymerization catalyzed by **4.2a** undergoes a coordination-insertion mechanism based on three observations: 1) the ability to use redox chemistry to turn the reaction off and on. For anionic or cationic polymerizations, adding reductant to the reaction will not quench the reactive ionic species to terminate the conversion. 2) the regio-irregular and stereoregular nature of the polymerization with (*R*)-propylene oxide, while the (*R*)propylene oxide polymerizations that undergo strictly through cationic mechanism (catalyzed by ferrocenium salts or BF₃ etherate) produced regio-irregular and stereo-irregular polymers 3) 2^{nd} order kinetic behavior with epoxide monomers, where in epoxide polymerization that undergo cationic pathways, the reactions appear exclusively 1st order in epoxide.

Taking a closer look into the kinetic features of this polymerization reaction (Figure 4.1), we found that this reaction has a relatively slow initiation rate, fast reaction kinetics at intermediate times and the inhibition step became more apparent towards the end of the reaction that it never reached full epoxide conversion. We attributed that the slow initiation and the long inhibition in the polymerization reaction to several metal-mediated pre-equilibrium steps. Later, Dr. Kayla Delle Chiaie carried out kinetic analysis and found out that the polymerization reaction is first-order in the iron-based catalyst and is suggestive of a reaction that is second-order in epoxide. However, the kinetic data do not rigorously rule out the possibility for an active bimetallic intermediate facilitated by irreversible aggregation of the iron catalyst prior to epoxide coordination and insertion.



Figure 4.1 Evolution of cyclohexene oxide conversion over time.

4.3 Complex synthesis and kinetic analysis

It was assumed that changing the steric and electronic properties of the iron complex would affect the pre-equilibrium steps and promote a polymerization with living characteristics. Working with a previous member of our group, Dr. Kayla Delle Chiaie, we constructed a library of cationic bis(imino)pyridine iron(III) bisalkoxide complexes in order to gain some insights into the reaction mechanism. A summary of the polymerization results can be found in Scheme 4.2.

We found that although changing the ligand structure drastically affects the rate of the polymerization reactions, the molecular weight properties of the polymer products are very similar to each other, with M_w/M_n around 2 for all of the cases. It is worth mentioning that, for all the aromatic imine arm equipped ligands, only the ones with 2,6-substituted groups display fast reaction rate with the exception of **4.2e** and **4.2f**. 4-substituted **4.2e**, show slow rate of cyclohexene oxide conversion, which suggests that electronic effect and steric effect at *para* position on the aromatic arm largely affect the reaction rate. The electron-rich complex **4.2f** does not show any cyclohexene oxide conversion, suggesting electronic features of the complex also contributed to the reaction rate. It is puzzling to us that the 3,5-substituted

complex (**4.2j**) show fast reaction rate, suggesting the steric at 3,5-position is important to consider, too. Unfortunately, through changing the ligand structure of the complexes, we could not find a complex that catalyzed the polymerization of cyclohexene oxide with living characteristics.



Scheme 4.2 Results of cyclohexene oxide polymerization with different bis(imino)pyridine iron(III) BArF complexes

Although no apparent trend was observed with regard of ligand design versus reaction kinetics and polymerization outcome, a significant color difference was observed between the catalysts that consume cyclohexene oxide rapidly (complete in less than 200s) and those that are slow. Based on our previous observations, subtle changes in the steric and electronic environment are affecting the dimer/monomer equilibrium and/or facilitating dissociation of one imine arm of the bis(imino)pyridine iron complexes.¹⁴ The fast reacting catalysts are pale green, and the slower variants are dark purple (Figure **4.2**). In addition to a change in coordination number, which alters the ligand field of the complex, imine arm dissociation disrupts the extended π -conjugation of the bis(imino)pyridine ligand, which affects the ability for the ligand to serve as a π -accepting ligand. Such factors lead to changes in the UV-Vis spectrum that are manifested as a change in the color of the complex. We hypothesized that the complexes bearing bidentated ligands (where one imine arm dissociated from the iron center) are green and complexes bearing the tridentate ligands are purple.



Figure 4.2 UV-vis data for 4.2a and 4.2g at 0.53 M in dichloromethane

To mimic the coordination environment of the "arm-off" situation around the iron centers during the polymerization, complex **4.3a** (Figure 4.3) and **4.3b** (Figure 4.4) were synthesized and applied to epoxide polymerization reactions. The kinetics of complex **4.3a** and **4.3b**, both with strictly bidentate ligands, display fast reaction rates, which further supports that ligand arm dissociation to form a complex containing a bidentate ligand. **4.3a**, being incapable of becoming tridentate, was expected to be a superior catalyst for epoxide polymerization. Consistent with this expectation was a $k_{obs} = 4.40 \times 10^{-3} \text{ M}^{-1} \text{s}^{-1}$. obtained from the pale green complex **4.3a**, which was more than double the k_{obs} observed with the most reactive complex containing the formally tridentate bis(imino)pyridine ligand at -30 °C. As was the case with the

bis(imino)pyridine complexes, kinetic analysis for cyclohexene oxide polymerization catalyzed by **4.3a** was most consistent with a reaction that is second order in epoxide (Figure 4.3 b&c).

In contrast to **4.2a**, the order in catalyst obtained from the Burés method was 0.5 (Figure 4.3d). This result suggested a bimetallic mechanism is less probable because a bimetallic mechanism would have to require that the resting state of the bidentate complexes to be tetrameric. DOSY experiments, carried out by Dr. Kayla Delle Chiaie, suggested the complex **4.2a** and **4.3a** stay exclusively as monomeric form in solution.⁴⁷ The observation suggested that the resting state of the complex The capacity for **4.3a** to more readily dimerize is consistent with its more sterically open coordination environment in comparison to the bis(imino)pyridine ligands (e.g. **4.2a**).^{15,16} The reaction is 0.5 order in **4.3a** also suggests that the dimeric structure lies *off* the catalytic cycle and is inconsistent with a bimetallic mechanism. If the It is likely that an iron-based monomer/dimer equilibrium could be a contributing factor to the induction period observed during this reaction. A bimetallic mechanism is important to consider given the long history of epoxide opening reactions that require two metal centers to participate in the ring opening event.



Figure 4.3 Kinetic data and determination of the order in the catalyst for complex 4.3a with varying [**4.3a**].

Complex **4.3b**, equipped with a bulkier ligand, also appear to be pale green. The complex displays fast reaction rate with $k_{obs} = 2.20 \times 10^{-3} \,\mathrm{M}^{-1} \mathrm{s}^{-1}$. The reaction is also second order in epoxide and first order in [**4.3b**]. The reaction is slower compared to **4.3a**, which might be a result of slower epoxide binding rate compared with a bulkier coordination environment around the metal center. It is worth mentioning that the reaction has a molecular weight distribution $M_w/M_n = 2.3$ (0.2% catalyst loading) but the observed molecular weight ($M_{n,exp.} = 37.4 \,\mathrm{kg/mol}$) is close to the predicted molecular weight ($M_{n,theor.} = 46.55 \,\mathrm{kg/mol}$), and the molecular weight increases with decreased catalyst loading (Table 4.1).



Figure 4.4 Kinetic data and determination of the order in the catalyst for complex **4.3b** with varying **[4.3b]**.



Figure 4.5. Molecular weight of poly(cyclohexene oxide) catalyzed with varying [4.3b]. M_w/M_n shown as data labels

Based on the observation of rate laws with the ligand substitution effects, we have proposed a unified mechanism that has three off-cycle equilibrium steps, the first two of which predominate early on in the reaction: 1) monomer-dimer dissociation (K₁) 2) imine arm and anion dissociation, together with the binding of two epoxide monomers to the iron center (K₂) and 3) product inhibition that predominates at high conversion (K₅). The propagation steps involve simultaneous enchainment of two epoxide molecules (k_3) followed by rapid binding of two additional equivalents of epoxides (k_4) (Scheme 4.2). To simplify the model, we treated step 2 (K₂) as one equilibrium step but it is likely a conglomerate of equilibrium steps involving imine arm and anion dissociation along with epoxide coordination. Additionally, steps 3 and 4 are treated as irreversible steps due to the highly favored forward direction.



Scheme 4.3. Proposed mechanism for iron complex catalyzed epoxide polymerization

4.4 COPASI modeling

Based on the reaction kinetics data, we were not able to reach a conclusion on how the ligand structure affect the reaction features. The complicated pre-equilibrium step indicated that changing the coordina+tion environment will affect multiple steps in the reaction and it will be hard to isolate the contributions of the factors to design a living polymerization system without further analysis. To achieve a "living" epoxide polymerization with the iron complex, it is essential to study each step, reversible or irreversible, separately to distill the effects of such steps to the overall reaction. With the help of Complex Pathway Simulator (COPASI), which is a software designed for reaction kinetic simulations, we were able to look more closely at how the different ligands would affect the organization of the resting state of the complexes, some trends can be seen based on steric and electronic effect of the ligands. As shown in table 4.2, the steric hindrance is increased on the aryl substituent of the ligand from methyl to ethyl to isopropyl (4.2a, 4.2b, 4.2c), there is not a clear trend with regard of the equilibrium constants and the rate constants. Among the three of them, k_3 is the largest for 4.2a, which implies that the nucleophilic attack during this step is directional and dependent on the steric environment around the metal center. The other steps in the mechanism are not significantly affected by the sterics in these positions. Interestingly, when considering the 3,5-methylphenyl substituted ligand (4.2e), this complex would have a more open iron center which leads to a dramatic increase in the propagation rate constant (12.72). Additionally, having a more open metal center lowers K₁ because this complex can more easily adopt a dimeric structure and subsequently, K₅ increases due to more facile product inhibition.

Table 4.1. Summary of equilibrium and rate constants from COPASI fits for different bis(imino)pyridine ligands using 0.2 mol % of the complex in deuterated dichloromethane at 25°C. For full table see experimental section.

Complex	K ₁	K ₂	<i>k</i> ₃	k_4	K5	Standard Deviation
4.2a (Me)	0.927	0.999	8.37	9356	0.981	7.91×10^{-3}
4.2b (Et)	0.960	0.970	1.94	9240	1.360	1.20×10^{-1}
4.2c (iPr)	0.946	0.943	3.10	9175	1.181	2.67×10^{-2}
4.2d (2,6Me- 4-F)	0.0248	3.23	9.99	82557	365.0	1.23× 10 ⁻²
4.2e (Mes)	0.696	1.05	1.45	100.2	199.2	1.91×10^{-2}
4.2h (cy)	0.957	0.295	4.81	163.2	1044	6.27×10^{-2}
4.2j (3,5Me)	0.509	0.932	12.72	9133	13.24	1.39× 10 ⁻²
4.3a	0.971	0.889	126.50	3.484	9418.00	2.18×10^{-2}
4.3 b	3.101	0.014	77.19	0.105	100.37	1.16×10^{-2}

For complex **4.2d**, we hypothesized that the sterics at the 2,6 position on the aryl with an electron withdrawing group on the 4 position will accelerate the reaction for epoxide polymerizations. However, the **4.2d** is slower compared to **4.2a**. As shown in table 4.1, we see a large decrease in K_1 (strongly favoring dimeric structure) and increase in product inhibition (K₅). The epoxide opening step is not greatly affected due to this complex likely having a similar coordination sphere to complex **4.3a** while the epoxide coordination step is much more favored due to a more electronically deficient metal center.

Compared to complex 4.2a, complex 4.3a has a much higher rate constant for the propagation step (k_3) as well as a decreased rate constant for the epoxide coordination step (k_4) . It is likely that the more open metal center leads to this increased rate of propagation and perhaps the phenyl is in the directional path for the epoxide coordination, thus slowing this step. To further probe the mechanistic effects of a bidentate ligand, the more sterically encumbered isopropyl counterpart 4.3b was also synthesized and fit using COPASI. The relevant equilibrium and rate constants were then elucidated. Even though the reaction

appeared to be $\frac{1}{2}$ order in complex we saw that these complexes favored the monomeric species compared to the dimeric species at a ratio of 2:1 (K₁ = 3.1). This was unexpected since a half order reaction normally implies the reaction will favor the dimeric form of the catalyst. An alternative explanation for this could be that the resting state of the catalyst is actually I₅ from the product inhibition and this structure is dimeric which would also lead to an apparent halforder in catalyst. When directly comparing **4.3a** and **4.3b**, we saw similar trends based on steric as observed with the bis(imino)pyridine ligands. Drastically increasing the sterics from **4.3a** to **4.3b** lowers both the propagation and epoxide coordination rate constants ($k_3 = 0.10$ and $k_4 =$ 100) leading to a much slower reaction.

To summarize the kinetic analysis, the dimer-monomer and product inhibition equilibrium is affected by sterics and electronics and intermediate I_5 may be the actual resting state of the catalyst. The rate of epoxide opening is greatly affected by sterics around the iron-center but the overall ligand effect is complicated since it is difficult to improve the ligand sterics and electronics for one step of the catalytic cycle without affecting the other steps. This makes logical ligand design challenging in order to access a living polymerization.

Since COPASI allowed us to deconvolute each step in the reaction and extract the rate constants as well as equilibrium constants, we were able to use Van't Hoff analysis and Eyring analysis to study the entropic and enthalpic effect on each step of the reaction. As shown in Figure 4.5, using the relevant data, we were able to construct Eyring plots for k_3 . The Eyring plot revealed activation parameters of 4.36 kcal/mol for ΔH^{\ddagger} and -40 cal/(mol*K) for ΔS^{\ddagger} . The large value of entropy of activation tells us that the propagation step is entropically driven, which is reasonable because the propagation involves a highly organized transition state. The relatively small enthalpy gain is a result of the breaking C-O bonds compensated by the large ring strain of cyclohexene oxide. Through the analysis (Table 4.2 and Figure 4.6), we were able

to determine the thermodynamic parameters of the three equilibrium steps, in which the $|\Delta S|$ is much lower than the propagating steps in all three cases.



Figure 4.6. Eyring plots of k_3 . Reactions were performed at various temperatures with 0.2 mol% 4.2a.

The direction and sensitivity of the three equilibrium constants were validated with van't Hoff plots (Figure 4.6). Overall, for all the equilibrium steps, the Δ H and Δ S are relatively small, indicating a relatively small entropic and enthalpic contribution to the reaction kinetics and the equilibrium steps are less temperature dependent. For the complex's dimer/monomer equilibrium, it is noted that there are two phases, at lower temperatures (-40 °C to -20 °C), there is a large enthalpy contribution but the enthalpic effect is less pronounced above -20 °C, which suggested there might be a shift in rate-determining step with temperature.

 Table 4.2.
 Thermodynamic parameters of the equilibrium steps

	ΔH (kcal/mol)	$\Delta S (cal/mol*K)$
K ₁ (< -20°C)	2.080	6.80
K ₁ (> -20°C)	0.107	-0.387
K_2	0.172	0.577
K5	-1.58	-5.42



Figure 4.7. van't Hoff plots of $K_1(a)$; and $K_2(b)$ and $K_5(c)$. Reactions were performed at various temperatures with 0.2 mol% **4.2a**.

Through this kinetic analysis we have determined that the propagation steps are entropically controlled and the equilibrium steps are less dependent on entropic factors. In this case, changing the temperature we should be able to affect these steps while the off-cycle pre-equilibrium steps will be less impacted due to the first law of thermodynamics. We hypothesized that elevating the reaction temperature should lead to more comparable rates between initiation and propagation and result in a more living polymerization. To our delight, we were able to see a narrowing in dispersity from ~2.0 to ~1.5 when the temperature was raised from -30 °C to 40 °C, respectively (Figure 4.7). We believe elevated temperatures favor the monomer in the dimer/monomer equilibrium and reduce the induction period, getting one step closer to a living system.



Figure 4.8. Molecular weight distribution at various temperatures.

4.5 Conclusion

The study of epoxide polymerization by a family of cationic, bis(imino)pyridine iron(III) alkoxides presented above provides experimental evidence to support the proposed mechanism seen in **Scheme 4.2**. Notably, this is the first in-depth mechanistic investigation of iron-complex catalyzed epoxide polymerizations with a discrete catalyst. Through a combination of a stereochemical probe and the redox-switching capabilities of the reaction, a cationic initiated mechanism for the reaction could be ruled out in favor of an iron-catalyzed coordination-insertion type ring-opening polymerization mechanism. Kinetic analysis revealed an unusual second order dependency for the epoxide monomer and has a first-order dependence on the iron catalyst. Similar kinetic analysis of the related imino pyridine iron complex **4.3a and 4.3b** revealed a half-order dependence on the catalyst, which was explained by a dimer/monomer equilibrium that competes with propagation. These two factors led to the conclusion that the polymerization operates through a monometallic active species as opposed to a bimetallic

species as has been seen in many cobalt catalyzed polymerizations¹⁷ as well as chromium catalyzed hydrolysis reactions.¹⁸ Modelling of the kinetic data revealed a unified mechanism of the polymerization reaction and provided explanations for the dramatic influence that the identity of the bis(imino)pyridine had on the rate of the reaction. Overall, we have elucidated mechanistic details about iron-catalyzed epoxide polymerization and have proposed, to our best knowledge, a unique mechanism that is second order in monomer and first order in the catalyst. These findings reveal unique reactivity that is not available for classic coordination-insertion and cationic polymerization manifolds.

Experimental Section

General Considerations. Unless stated otherwise, all reactions were carried out in oven-dried glassware in nitrogen-filled glove box or using standard Schlenk line techniques. Solvents were used after passage through a solvent purification system under a blanket of argon and then degassed briefly by exposure to vacuum. Sigma-Aldrich, Oakwood Scientific, and Fisher Scientific supplied various anilines. Cyclohexene oxide was purchased from Sigma Aldrich, dried over calcium hydride and distilled. Nuclear magnetic resonance (NMR) spectra were recorded at ambient or cryogenic temperatures on a Varian spectrometer (¹H and 500 MHz, and ¹³C {¹H} 125 MHz) in CD₂Cl₂ and are referenced versus shifts of solvents containing residual protic impurities. NMR temperature was calibrated using a methanol standard. The line listing for the ¹H NMR spectra are reported as: chemical shift in ppm (peak width at half height). Infrared (IR) spectra were recorded on an OPUS ATR infrared spectrometer. High-resolution mass spectra were obtained at the Boston College Mass Spectrometry Facility using JEOL AccuTOF DART.

Gel permeation chromatography (GPC) was performed on an Agilent GPC220 in THF at 40 °C with three PL gel columns (10 μ m) in series and recorded with a refractive index detector. Molecular weights and molecular weight distributions were determined from the signal response of the refractive index (RI) detector relative to polystyrene standards.

General procedure of the synthesis of [Bis(imino)pyridine Fe Bis(alkoxide)⁺][BArF] complexes At room temperature, a solution of neopentyl alcohol (0.030 g, 0.34 mmol) and L-lactide (0.196 mg, 1.36 mmol) in toluene (5 mL) was added slowly to a solution of corresponding bis(imino)pyridine-iron-bis(trimethylsilyl)methyl complex (0.17 mmol, 0.090~0.121 g) in toluene (5 mL) in a 20-mL vial. The reaction mixture was allowed to stir for 2 hours. Ferrocenium BArF (0.357 mg, 0.34 mmol) was dissolved in dichloromethane (5 mL) and added to the reaction solution. The solvent was removed, and the resulting powder was

washed with n-pentane $(3 \times 5 \text{ mL})$ and dried in vacuo. Due to the synthetic challenges, which decomposition was observed after the oxidation with FcBArF, all complexes were pre-initiated with 4 equivalence of L-lactide prior to the oxidation step.

Bis(2,6-dimethylbenzeneamine)-*N*,*N'*-(2,6-pyridinediyldiethylidyne) iron-bis(lactic acid) complex **4.2**: yield 0.311g, 90%, ¹H NMR (C₆D₆): δ 38.5 (296), 7.0 (16.4), 6.7(19.4), 4.1 (280), 3.5 (29.1), 3.1 (9.22), 1.2 (37.0), 0.8 (19.4) ppm. IR(neat): 2363, 2340, 1755, 1655, 1455, 1354, 1276, 1122, 886, 839, 713, 682, 567 cm⁻¹.

Bis(2,6-dimethyl-4-fluorobenzene)-*N*,*N*'-(2,6-pyridinediyldiethylidynyl)-iron-bis(lactic acid) complex **4.2b**: yield: 0.324g, 92%, ¹H NMR (CD₂Cl₂): δ 29.8 (135), 9.7 (4.6) 8.3(23.4) 7.8 (12.21), 7.6 (9.8) 7.37 (2.7) 7.24(4.33) 7.18 (5.7) 6.92(5.14) 5.14 (19.9), 3.79 (8.7), 2.36 (3.5), 2.1(6.92), 1.52 (37.4) 1.16 (3.8) 0.95 (16.4) ppm. IR(neat): 2363, 2339, 1755, 1664, 1452, 1357, 1276, 1122, 884, 833, 713, 682, 664 cm⁻¹.

Bis(2,6-diisopropylbenzeneamine)-*N*,*N*'-(2,6-pyridinediyldiethylidynyl)-iron-bis(lactic acid) complex **4.2c**: yield 0.296 g, 81%, ¹H NMR (C₆D₆): δ 20.54(965), 7.78(11.8), 7.61(9.2), 7.37(2.7), 7.19(16.9), 5.18(9.5), 3.86(5.52), 3.80(10.34), 2.78(2.4), 2.27(13.8), 1.58(6.1), 1.17(21.7), 0.95(4.5)ppm. IR(neat): 3733, 2363, 2339, 1755, 1663, 1455, 1354, 1276, 1122, 886, 839, 769, 715, 682, 671 cm⁻¹.

Bis(2,6-diethylbenzeneamine)-N,N'-(2,6-pyridinediyldiethylidynyl)-iron-bis(lactic acid) complex **4.2d**: yield 0.288 g, 81%, ¹H NMR (C₆D₆): δ 22.53(218), 7.93(20.4), 7.85(12.4), 7.74(13.5), 7.67(9.9), 5.41(3.18), 5.17(10.3), 3.86(7.15), 3.82(8.7), 1.58(30.9), 1.02(3.18), 0.95(10.9) ppm. IR(neat): 2363, 2339, 1755, 1655, 1454, 1354, 1276, 1122, 888, 840, 713, 682, cm⁻¹.

Bis(3.5-dimethylbenzeneamine)-N,N'-(2,6-pyridinediyldiethylidynyl)-iron-bis(lactic acid) complex **4.2e**: yield 0.297 g, 86%, ¹H NMR (C₆D₆): δ 7.75 (11.56), 7.59 (8.3), 7.37(4.3),

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5.55(5.7), 5.17(9.5), 2.57(3.7), 2.10(4.4), 1.58(10.4), 1.57(5.32), 0.95(5.08). IR(neat): 2363, 2339, 1755, 1663, 1452, 1357, 1276, 1122, 884, 832, 713, 682, 667 cm⁻¹.

Bis(2,4,6-dimethylbenzeneamine)-*N*,*N*'-(2,6-pyridinediyldiethylidynyl)-iron-bis(lactic acid) complex **4.2f**: yield 0.285 g, 81%, ¹H NMR (C₆D₆): δ 28.5 (296), 6.6 (16.4), 6.3(19.4), 4.1 (280), 3.5 (29.1), 3.1 (9.22), 1.2 (37.0), 0.8 (19.4) ppm. IR(neat): 2363, 2339, 1755, 1663, 1453, 1355, 1278, 1122, 884, 832, 713, 682, 662 cm⁻¹.

Bis(4-fluorobenzeneamine)-*N*,*N'*-(2,6-pyridinediyldiethylidynyl)-iron-bis(lactic acid) complex **4.2g**: yield 0.261 g, 76%, ¹H NMR (CD₂Cl₂): δ 8.13(20.1), 7.73(13.5), 7.55(10.9), 6.93(12.7), 5.97(15.5), 5.19(20.3), 3.87(10.9), 2.57(10.8), 1.58(10.7), 0.95(7.4) ppm. IR(neat): 2363, 2339, 1755, 1663, 1452, 1354, 1276, 1122, 1088, 884, 832, 713, 682, 667 cm⁻¹. Bis(cyclohexylamine)-*N*,*N'*-(2,6-pyridinediyldiethylidynyl)-iron-bis(lactic acid) complex **4.2h**: yield 0.227 g, 67%, ¹H NMR (CD₂Cl₂): δ 18.51(150), 9.89(131), 8.46(3.3), 7.89(11.3), 7.73(7.05), 7.37(2.7), 7.25(3.7), 7.19(4.45), 6.91(4.18), 5.18(8.75), 4.16(2.6), 3.86(6.4), 2.35(3.4), 2.30(3.6), 2.22(2.8), 2.01(3.4), 1.56(5.6), 0.95(4.4) ppm. IR(neat): 2363, 2339, 1755,

1663, 1452, 1357, 1276, 1122, 884, 832, 713, 682, 667 cm⁻¹.

Bis(benzeneamine)-*N*,*N'*-(2,6-pyridinediyldiethylidynyl)-iron-bis(lactic acid) complex **4.2i**: yield 0.289 g, 86%, ¹H NMR (CD₂Cl₂): δ 8.00(13.9), 7.84(5.6), 7.74(10.8), 7.56(6.02), 7.37(2.8), 7.18(14.4), 6.03(18.0), 5.18(5.8), 2.56(25.8), 2.34(5.1), 1.58(9.34), 0.95(3.8).ppm. IR(neat): 2363, 2339, 1755, 1663, 1452, 1354, 1276, 1122, 884, 832, 713, 682, 667 cm⁻¹.

2,6-dimethyl-N-(1-(6-phenylpyridin-2-yl)ethylidene)aniline-iron complex **4.3**: yield 0.288 g, 86%, ¹H NMR (CD₂Cl₂): δ 15.83 (3787), 12.36 (251), 8.28 (4.6), 8.10 (5.8), 7.83 (11.51), 7.66 (7.7), 7.56 (6.0), 7.21 (6.7), 5.17 (7.9), 3.87 (23.6), 2.52 (6.0), 2.15 (4.3), 1.58 (7.24), 0.95 (4.69) ppm. IR(neat): 2363, 2339, 1755, 1663, 1452, 1357, 1276, 1122, 884, 832, 713, 682, 667 cm⁻¹.

General Procedure for the collection of kinetic data of epoxide polymerization reactions.

To a J. Young tube in the glovebox was added cyclohexene oxide (0.30 mL of a 0.527 M stock solution in CD_2Cl_2). This layer was frozen in the cold well that was cooled to -200°C using liquid nitrogen. The desired amount of catalyst (4.2a-I, 4.3a,b) was added to the tube in the cold well as a solution in CD₂Cl₂ so that the total volume of solvent in the NMR tube was 0.60 mL. This layer was frozen the J. Young tube was capped. The tube was quickly brought out and immediately submerged into a Dewar containing liquid nitrogen. (NOTE: Importantly, the NMR tube was transferred from the glovebox to the Dewar of liquid N₂ rapidly so that the two layers remained frozen and unmixed.) Immediately prior to collection of the kinetic data, the tube was brought to -78 °C in a Dewar containing dry ice/acetone. Once the tube reached the temperature where CD_2Cl_2 became a liquid, the tube was shaken vigorously to fully mix the two layers. The tube was resubmerged in the dry ice/acetone bath. With the NMR instrument thermostatic at the appropriate temperature, the tube was inserted and a preacquisition delay array was immediately started. (NOTE: The instrument was shimmed and locked on a sample containing CD_2Cl_2 and 4.2a.) Each acquisition was set to one scan and acquisition time per scan was 2 seconds. After collection of the initial data, acquisitions could be collected every 20 seconds. Subsequent spectra were integrated using VNMRJ software.

General procedures for COPASI modeling

Kinetic simulations were performed using the software package COPASI (Complex Pathway version 4.8 (build 35). This program available Simulator) is at http://www.copasi.org/tiki-view articles.php³⁴ In order to construct the computed output curves, all elementary chemical reactions, stoichiometry, initial reactant concentrations and individual rate coefficients were first entered and the program allowed solving the system of equations as a function of time.

The mechanistic model was introduced in the software according to the elements listed in scheme 4.2. All kinetic curves generated were plotted against the corresponding discrete concentration profiles obtained from experimental ¹H-NMR measurements of the polymerization reactions. The dataset of 3 experimental curves of varying **4.2a** were first loaded, Genetic Algorithm (default mode) was used to generate a predicted curve of concentration versus time until a good fit of the curve was observed. Unknown rate constants and equilibrium constants specified for each steps were determined via a parameter estimation (optimization) built-in routine. The results from varying **4.2a** was then used as a starting point for the calculation of all the other reactions (with defined range for unknown rate constants and equilibrium constants).

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5. Chapter 5. Future Perspectives on the Electrochemically Switchable Polymerization System

5.1 Controlling polymer molecular weight distributions

Molecular weight distribution of polymers is important for their macroscopic properties.^{1,2} While modern polymer chemistry has focused on developing polymers with narrow molecular weight distributions (polymer products with similar chain length), polymer of broadly distributed chain lengths can be superior in some applications. For example, polystyrene melts with broad molecular weight distributions are more processable. The shorter chains act as plasticizers to reduce the crystallinity of the polymer.³ Previously, Fors and coworkers have demonstrated that through controlling the addition rate of initiators, the shape of the molecular weight distribution pattern of the resulting polymer can be controlled.^{4–6}

As discussed in chapter 1, diffusion plays an important role in determining the charge transfer rate in a bulk electrolysis cell. An example in the literature by Liu and coworkers has demonstrated that changing the distance of the reactive substrate (surface-immobilized propagating polymer chain end) and the working electrode can affect the polymer chain length distribution on a surface.⁷ Other than this work, electrochemistry has not been applied to control the molecular weight distributions.

We plan on using the electrochemically switchable polymerization method (chapter 2) to control the polymer molecular weight distribution (Figure 5.1). Electrochemistry can be a powerful method to replace the usage of syringe pumps, due to the programmable nature of electrochemical set-up and the ability to be used under reaction conditions that are difficult for the addition of chemicals, for example, polymerization involving gaseous monomers, which often require increase pressure. However, there is some complexity that must be considered in the electrolysis set-up. First, the potentiostatic electrolysis used in chapter 1 is not ideal. This

is because the charge transfer process can be highly irreproducible. A minor change in the setup, including the temperature, inconsistent surface area of the electrodes, or even the placement of the electrodes can change the charge input rate. Therefore. galvanostatic electrolysis must be used to have a consistent, reproducible charge transfer rate. However, as constant charge input will inevitably lead to the shift in the potential applied on the working electrode and can lead to detrimental side reactions. Redox mediators can be used to facilitate the charge transfer process and protect the complexes from over-oxidation or reduction, as mentioned in chapter $1.^{8-10}$



Figure 5.1 Controlling the molecular weight distribution through programming the charge input rate

A unique advantage this system has is the ability to turn off the polymerization as well. Not only can we change the rate of activation, similar to the example reported by Fors and coworkers, we can control the rate of terminating the polymerization process. This would generate molecular weight distributions that are complementary to the activation process. We look forward to developing such methods to extend the existing examples to other polymerization reactions and bring more opportunities in this field.

5.2 Self-assembled monolayers

A disadvantage of the surface-initiated ring-opening polymerization system discussed in chapter 3 is the low grafting density of polymers. The low grafting density is a result of the low density of the iron metal centers on the surface after functionalization through the protonolysis reaction of the iron precursor and the hydroxyl group on the titania surfaces. A possible future direction for improving the grafting density is to utilize self-assembled monolayers to construct a covalently linked and density packed layer of hydroxyl function groups on the surface (Figure 5.2).^{11,12}

There are several self-assembled monolayers strategies that can be applied to our system. The first method is using the polymerization of the silane function groups on the hydroxide containing metal oxide surfaces.^{13–16} This method has been widely applied for anchoring radical initiators (halides) on surfaces. Subsequent ATRP polymerization has enabled the formation of polymer brushes on the surface. However, in terms of modifying hydroxyl containing surfaces, the hydroxyl functional groups might interfere with the bond forming reactions in the silane condensation polymerization. In this case, protection and deprotection of the hydroxyl groups is required and may bring some complexity in the fabrication steps (Scheme 5.1).¹⁷



Scheme 5.1 Self-assembled monolayer formation based on silane polymerizations

A second method of fabrication is adsorption of organothiol molecules on gold surfaces.^{18,19} This method has shown great versatility in generating various patterns of organic molecules on metal surfaces.²⁰ It has been shown that the existence of the hydroxyl group does not affect the monolayer formation.²¹ Compared with the silane method, the organothiol layer has significant advantages in terms of fabrication.

Overall, we are looking forward to using self-assembled monolayers to create a more reproducible surface-initiated polymerization system. These monolayers would enable the generation of more sophisticated surface patterns beyond the binary pattern we are able to create using current method (as discussed in chapter 3). At the same time, combining this redox-switchable surface-initiated polymerization method with other powerful surface-modification methods, e.g. dip-pen lithography,²² we should be able to generate advanced surface structures in all three dimensions.

5.3 Developing a photoswitchable polymerization system

A question that has been troubled us for a long time is whether our iron complexes can respond with photocatalysts to show similar redox switchability under to light irradiation. Titania nanoparticles are a type of photoanode which can generate photocurrent upon UV irradiation.^{23–25} Upon UV irradiation, an electron-hole pair can be generated and the holes at the valence band of TiO₂ have an oxidizing potential of + 2.6 V vs normal hydrogen electrode. The holes will migrate to the surface of the semiconducting electrode leading to oxidation reactions on the surface.²⁶



Figure 5.2. Schematic illustration of surface reactions on UV illuminated TiO2

We envision that the photocatalytic properties of the TiO₂ can be used to control our surface-initiated polymerizations, as discussed in chapter 3. Upon UV irradiation, the surface-bound iron(II) centers can be oxidized to the iron(III) oxidation state, and the surface reactivity can be tuned from lactide polymerization towards epoxide polymerization. Under dark conditions, the back electron transfer happens and the unreacted electrons at the conducting band will reduce the iron(III) centers back to the iron(II) oxidation state. Using photomasks, sophisticated surface patterns could potentially be generated on demand with high modularity.

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6. Appendix A. Control experiments and cell set-up details for chapter 1 &





Figure A. 1 Picture of the cell in chapter 1

Table A. 1. Lactide polymerization in the presence of LiClO₄

) O	O Cat. O 0.05 M LiClO ₄ in 1:1 CH ₂ Cl ₂ : D ME 5 h, r. t.	$\left(\begin{array}{c} 0 \\ - \end{array} \right)$		
Cat	Conv.(%) ^a	$M_{n(\text{theo})}{}^{b}$	M_n^{b}	M /M ^b	
Cat.		(kg/mol)	(kg/mol)	<i>W</i> W/ <i>W</i> n	
None ^c	0%	0	0	-	
2 mol% 2.1 °	68%	5.3	4.9	1.25	
2 mol% 2.1 ^d	70%	5.2	5.0	1.24	

^aConversion was determined from ¹H NMR by integrating the methine peaks of the remaining lactide (5.0 ppm) versus the poly(lactic acid) signal (m, 5.2-5.4 ppm); ^bObtained from GPC (RI detector), $M_{n(theo)}$ (theoretical molecular weight) = $1/[Cat.loading] \times Conversion \times 144.0$; ^c reaction was done in 0.05 M LiClO₄ in 1: 1 CH₂Cl₂/DME; ^d in CH₂Cl₂ without LiClO₄. [lactide] = 0.20 M

Table A. 2 Cyclohexene oxide polymerization in the presence of LiClO₄

	O	Cat. 0.05 M LiClO ₄ in 1:1 CH ₂ Cl ₂ : DME 5 h, r. t.	+~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~		
Cat	Conv.	$M_{n(\text{theo})}^{b}$	M_n^{b}	M/Mb	
Cal.	(%) ^a	(kg/mol)	(kg/mol)	<i>w</i> _w / <i>w</i> _n	
None ^c	2%	-	-	-	
2 mol% 2.2 ^c	38%	3.7	10.6	1.88	
2 mol% 2.2 ^d	35%	3.4	9.8	1.76	

^a Conversion was determined from ¹H NMR by integrating the methine peaks of the polyether signal (m, 3.2-3.5 ppm) versus the methyl peak of cyclohexne oxide(3.0 ppm); ^bObtained from GPC (RI detector), $M_{n(theo)}$ (theoretical molecular weight) = 1/[Cat.loading]×Conversion×98.1; ^creaction was done in 0.05 M LiClO₄ in 1: 1 CH₂Cl₂/DME; ^d in 1 : 1 CH₂Cl₂/DME without LiClO₄. [cyclohexene oxide] = 0.70 M

$\begin{array}{c} O \\ H \\ O \\$						
Cat	Conv.	M _{n(theo)}	M_n^{a}	M /M b		
Cal.	(%)	(kg/mol)	(kg/mol)	W _W /W _n		
None ^c	0%	0	0	-		
0.5 mol%	86%	24.7	24.0	1 25		
2.2 °	8070	24.7	24.9	1.20		
0.5 mol%	020/	26.4	28.0	1 10		
2.2 ^d	92%0	20.4	28.9	1.18		

Table A. 3 Lactide polymerization in 0.1 M nBu₄NPF₆ in CH₂Cl₂

^a Conversion was determined from ¹H NMR by integrating the methine peaks of the remaining lactide (5.0 ppm) versus the poly(lactic acid) signal (m, 5.2-5.4 ppm); ^bObtained from GPC (RI detector); ^c reaction was done in 0.1 M ⁿBu₄NPF₆ in CH₂Cl₂; [lactide] = 0.28 M; ^dReaction was done in pure CH₂Cl₂

	\sim	Cat. ^ nBuN ₄ PF ₆ (0.1 M), CH ₂ Cl ₂ , r. t., 18 h	()	
Cet	Conv.	M _{n(theo)}	M_n^{a}	A /A b
Cat.	(%)	(kg/mol)	(kg/mol)	M _w /M _n °
None ^c	0%	-	-	-
0.1 mol% 2.1 °	44%	37.2	11.6	2.06
0.1 mol% 2.1	42%	35.5	10.6	1.95

Table A. 4 Cyclohexene oxide polymerization in 0.1 M nBu₄NPF₆

^a Conversion was determined from ¹H NMR by integrating the methine peaks of the polyether signal (m, 3.2-3.5 ppm) versus the methyl peak of cyclohexne oxide(3.0 ppm); ^bObtained from GPC (RI detector); ^creaction was done in 0.05 M ⁿBu₄NPF₆ in 1: 1 CH₂Cl₂/DME; ^d in 1 : 1 CH₂Cl₂/DME without LiClO₄.
[cyclohexene oxide] = 1.4 M; ^dReaction was done in pure CH₂Cl₂

Electrolysis of preformed polymers



Scheme A. 1 Electrolysis of poly-L-(lactic acid) and poly(cyclohexene oxide) under applied potentials. No structural changes were observed.

Table A. 5 Evolution of conversion and molecular weight during (rac)-lactide polymerization triggered by applying 2.3 V for 40 min to a solution containing 1 mol% **2.2** as catalyst precursor. Time points are referenced as shown in Figure 2.2 of text. [Lactide] = 0.20

$ \begin{array}{c} & 1 \mod 8^{3} 2.3 \lor \\ & 1 \liminf 8^{3} 2.3 \lor \\ $						
	Time (min)	Conv ^a	M _n (theo)	M _n (expt) ^b	M /M b	
Time (min)	(%)	(kg/mol)	(kg/mol)	<i>W</i> _W / <i>W</i> _n		
35 min electrolysis						
а	35	5	-	-	-	
b	80	13	1.8	1.7	1.05	
c	160	29	4.2	3.5	1.18	
d	300	48	6.9	6.3	1.25	
e	4800	76	10.9	9.3	1.24	

^aConversion was determined from ¹H NMR by integrating the methine peaks of the remaining lactide (5.0 ppm) versus the methyl peak of ⁿBu₄NPF₆ (1.0 ppm); ^bObtained from GPC (RI detector)



Figure A. 2 First order kinetic plot of lactide polymerization during (rac)-lactide polymerization triggered by applying 2.3 V for 40 min, starting with 1 mol% cat. **2.1**.



Figure A. 3. First order kinetic plot of lactide polymerization during (rac)-lactide polymerization triggered by applying 2.3 V; a) after first electrolysis; b) after second electrolysis; starting with 1 mol% cat. **2.2**.

Table A. 6 Evolution of conversion and molecular weight during an electrochemical redox-switchable polymerization of lactide achieved through sequential electrolysis at different applied potentials with 1 mol% of **2.2** as a catalyst precursor. Time points are referenced as shown in Figure 2 of text. [Lactide] = 0.20 M in 0.1 M ⁿBu₄NPF₆ in CH₂Cl₂.

Time(min)		Conv. ^a	M _n (theo)	M _n (expt) ^b	M /M b
	l ime(min)	(%)	(kg/mol)	(kg/mol)	$M_{ m w}/M_{ m n}$ °
45 m	in electrolysis				
а	45	2%		-	-
b	105	8%	1.2	1.1	1.03
c	165	15%	2.2	2.3	1.17
d	255	27%	3.9	2.9	1.20
35 m	in electrolysis				
e	280	29%	4.2	3.2	1.48
f	340	29%	4.2	3.2	1.53
g	610	31%	4.2	3.2	1.58
30 m	in electrolysis				
h	640	32%	4.6	3.9	1.89
i	760	41%	5.9	7.5	1.89
j	850	53%	7.6	8.7	1.91
k	2080	78%	11.2	10.3	2.05

^a Conversion was determined from ¹H NMR by integrating the methine peaks of the remaining lactide (5.0 ppm) versus the methyl peak of ⁿBu₄NPF₆ (1.0 ppm); ^bObtained from GPC (RI detector)

 Table A. 7 Evolution of conversion and molecular weight during an electrochemical

 redox-switchable polymerization of lactide achieved through sequential electrolysis at different

 applied potentials (grey bars) with 0.5 mol% of 2.2 as a catalyst precursor. Time point

Time (min)		Conv. ^a	M _n (theo)	M _n (expt) ^b	1. /1. (h	
		(%)	(kg/mol)	(kg/mol)	$M_{\rm w}/M_{ m n}$ °	
10 min electrolysis						
а	10	3%	0.8	-	-	
b	160	17%	4.9	4.1	1.23	
c	310	29%	8.4	7.9	1.25	
10 min electrolysis						
d	320	29%	8.4	7.2	1.33	
e	470	30%	8.6	7.7	1.30	
f	620	30%	8.6	7.7	1.33	
15 min electrolysis						
g	635	31%	8.9	8.1	1.44	
h	785	46%	13.2	14.2	1.49	
i	935	56%	16.1	18.3	1.49	
j	2075	81%	23.3	21.6	1.59	

^a Conversion was determined from ¹H NMR by integrating the methine peaks of the remaining lactide (5.0 ppm) versus the methyl peak of ⁿBu₄NPF₆ (1.0 ppm); ^bObtained from GPC (RI detector)



Figure A. 4 First order kinetic plot of lactide polymerization during (rac)-lactide polymerization triggered by applying 2.3 V; a) after first electrolysis; b) after second electrolysis; starting with 1 mol% cat. **2.2**

E-polymerization of cyclohexene oxide



Figure A. 5 Evolution of conversion and molecular weight during cyclohexene oxide polymerization triggered by applying 3.7 V for 35 min to a solution containing 0.1 mol% of **2.1** as a catalyst precursor, in dichloromethane 1.4 M; (b) GPC trace of final polymer obtained

Table A. 8 Evolution of conversion and molecular weight during cyclohexene oxide polymerization triggered by applying 3.7 V for 35 min to a solution containing 0.1 mol% **2.3** as a catalyst precursor, in dichloromethane, [cyclohexene oxide] = 1.4 M.

$ \begin{array}{c} 0 \\ \hline \hline \hline \hline 0 \\ \hline \hline \hline \hline 0 \\ \hline \hline$						
	Time (min)	Conv.	$M_{n(\text{theo})}$	M_n^{a}	M /M b	
l ime (min)	(%)	(kg/mol)	(kg/mol)	$M_{\rm W}/M_{\rm n}$		
40 min electrolysis						
а	40	13%	12.7	8.1	1.46	
b	60	25%	24.5	8.1	1.42	
c	90	33%	32.4	7.6	1.57	
d	150	40%	39.2	9.1	1.63	
e	210	44%	43.1	8.7	1.65	
f	360	44%	43.1	9.3	1.65	

^a Conversion was determined from ¹H NMR by integrating the methine peaks of the the polyether signal (m, 3.2-3.5 ppm)versus the methyl peak of ⁿBu₄NPF₆ (1.0 ppm); ^bObtained from GPC (RI detector) **Table A. 9** Conversion and molecular weight data for rac-lactide/epoxide copolymerization reactions with an Fe(III) to Fe(II) electrochemical redox switch, one pot; with 0.5 mol% Fe loading relative to lactide, 1:5 [lactide]:[epoxide]; final polymer composite PLA:

Time	M ^b (kg/mol)	$M_{ m w}/M_{ m n}{}^{ m b}$	%Conv (Lactide) ^a	%Conv (epoxide) ^a		
0	0	0	0	0		
3	15.5	1.5	0	25		
58 min electrolysis						
4	14.3	1.8	13	27		
12	40.3	1.8	78	27		

^aConversion was determined from ¹H NMR by integrating the methine peaks of the the polyether signal (m, 3.2-3.5 ppm) or lactide (5.0 ppm) versus the methyl peak of ⁿBu₄NPF₆ (1.0 ppm); ^bObtained from GPC (LS detector);



Figure A. 6. Size and dimensions of the TiO_2 -FTO electrode (a) and TiO_2 -FTO AB electrode (b). in Chapter 3



Figure A. 7. Contact angle measurement of drop-casted PLA and PCHO

7. Appendix B NMR and Mössbauer spectra



Figure B. 1. ¹H-NMR(top) and ¹³C-NMR of block copolymers obtained from eswitchable copolymerization of lactide and cyclohexene oxide, Fe(II) to Fe(III) redox switch in Chapter 2



Figure B. 2. ¹H-NMR(top) and ¹³C-NMR of block copolymers obtained from eswitchable copolymerization of lactide and cyclohexene oxide, Fe(II) to Fe(III) redox switch in Chapter 2



Figure B. 3. Mössbauer spectroscopy of complex 3.3.



Figure B. 4. ¹H-NMR of complex 4.2b in CD₂Cl₂



Figure B. 5. ¹⁹F-NMR of complex 4.2b in CD₂Cl₂



Figure B. 6. ¹H-NMR of complex 4.2c in CD₂Cl₂



Figure B. 7. ¹⁹F-NMR of complex 4.2c in CD₂Cl₂



Figure B. 8. ¹H-NMR of complex 4.2d in CD₂Cl₂



Figure B. 9. ¹⁹F-NMR of complex 4.2d in CD₂Cl₂



Figure B. 10. ¹H-NMR of complex 4.2e in CD₂Cl₂


Figure B. 11. ¹⁹F-NMR of complex 4.2e in CD₂Cl₂



Figure B. 12. ¹H-NMR of complex 4.2f in CD₂Cl₂



Figure B. 13. ¹⁹F-NMR of complex 4.2f in CD₂Cl₂



Figure B. 14. ¹H-NMR of complex 4.2g in CD₂Cl₂



Figure B. 15. ¹⁹F-NMR of complex 4.2g in CD₂Cl₂



Figure B. 16. ¹H-NMR of complex 4.2h in CD₂Cl₂



Figure B. 17. ¹⁹F-NMR of complex 4.2h in CD₂Cl₂



Figure B. 18. ¹H-NMR of complex 4.2i in CD₂Cl₂



Figure B. 19. ¹⁹F-NMR of complex 4.2i in CD₂Cl₂



Figure B. 20. ¹H-NMR of complex 4.3a in CD₂Cl₂



Figure B. 21. ¹⁹F-NMR of complex 4.3b in CD₂Cl₂

8. Appendix C. ORCA calculation and COPASI modeling results

 Table C. 1. Calculated structures and selected bond angles and bond distances of a)

 Fe(II)-bistitanoxide complex S2 and complex S3



Complex	O1-Fe-O2 (°)	Ti-O3-Ti (°)	N1-Fe-N2 (°)	N2-Fe-N3 (°)	N1-Fe-N3 (°)			
3.1	100.8	118.1	81.2	77.3	158.2			
3.4	95.8	93.7	79.2	154.5	75.4			
	Fe-O(1) (Å)	Fe-O(2) (Å)	Ti(1)-O(3) (Å)	Ti(2)-O(3) (Å)	Ti(1)-Ti(2) (Å)	Fe-N1(Å)	Fe-N2(Å)	Fe-N3(Å)
3.1					3.316			
3.4	1.898	1.993	2.012	1.974	2.907			

Table C. 2 C	Cartesian	coordinates	for	the	model	Fe(II)-titanium	ester	complex	3.1
obtained from DFT ca	alculation	s.							

Element			
Fe	6.37015	13.06013	6.96409
0	5.67708	11.72103	8.33975
Ν	7.30990	14.49279	8.10599
Ν	4.93820	14.32392	7.32993
Ν	4.90675	12.19330	5.87735
С	6.99769	16.88521	9.07774
Н	8.06647	16.82124	9.35914
Н	6.40882	17.07774	9.99823
Н	6.88717	17.75103	8.38898
С	6.49007	15.63083	8.39588
С	5.23877	15.52985	7.97274
С	4.18597	16.60420	8.07317
С	2.90247	16.33154	7.32903
Н	2.13632	17.10150	7.32232
С	2.69435	15.18374	6.65609
Н	1.75920	15.06516	6.11865
С	3.74956	14.12761	6.61257
С	3.71185	13.01288	5.85975
С	2.52143	12.74592	4.95849
Н	2.64059	11.82658	4.35444
Н	2.39468	13.59004	4.24626
Н	1.59307	12.66696	5.56414
С	8.64702	14.46258	8.56201
С	9.69537	14.94694	7.75240
С	11.01634	14.86555	8.22701
Н	11.84366	15.20834	7.61901
С	11.27936	14.37555	9.50921
Н	12.29684	14.33086	9.87445
С	10.22961	13.99338	10.34432
Н	10.44659	13.67033	11.35508
С	8.90836	14.04189	9.88376
С	9.40960	15.62217	6.42861
Н	10.34665	15.83628	5.86979
Н	8.90406	16.58919	6.62531
Н	8.71433	15.05216	5.78462
С	7.77296	13.70006	10.81608
Н	7.11680	14.59169	10.93355
Н	8.13450	13.43418	11.83128
Н	7.16919	12.86413	10.41280
С	5.00070	10.94811	5.21339
С	4.16295	9.87193	5.60521
С	4.33266	8.61970	5.00646

H3.718467.781845.31214C5.293548.441724.01124H5.413047.471653.55180C6.099659.510313.61169H6.840769.371822.83793C5.9609310.757374.21852C3.1374310.025806.69607H3.6278410.514857.54381H2.712989.056937.02898H2.2846910.650786.38591O7.7293811.984526.05846H6.5932511.578833.90759Ti6.136869.666458.54601Ti8.897810.938887.22199O7.404489.727707.08155O4.685519.200829.83873C3.8139510.1588610.32670O6.563907.707968.71502C7.878557.343068.39371O10.5005912.112187.07082C10.5102112.623225.75595O9.735169.793745.81834C10.582238.860116.4894H3.1578210.592069.55844H4.3740310.8900010.92719H8.023456.278518.68290H8.625177.944128.94921H8.021347.378967.29708H11.628978.974866.08765H10.581098.99387.55111H<				
C 5.29354 8.44172 4.01124 H 5.41304 7.47165 3.55180 C 6.09965 9.51031 3.61169 H 6.84076 9.37182 2.83793 C 5.96093 10.75737 4.21852 C 3.13743 10.02580 6.69671 H 3.62784 10.51485 7.54381 H 2.71298 9.05693 7.02898 H 2.28469 10.65078 6.38591 O 7.72938 11.98452 6.05846 H 6.59325 11.57883 3.90759 Ti 6.13866 9.66645 8.54601 Ti 8.8978 10.93888 7.22199 O 7.40448 9.72770 7.08155 O 4.68551 9.20082 9.83873 C 3.81395 10.15886 10.32670 O 10.50059 12.11218 7.07082 C 10.51021 12.62322 5.75595 </td <td>Н</td> <td>3.71846</td> <td>7.78184</td> <td>5.31214</td>	Н	3.71846	7.78184	5.31214
H 5.41304 7.47165 3.55180 C 6.09965 9.51031 3.61169 H 6.84076 9.37182 2.83793 C 5.96093 10.75737 4.21852 C 3.13743 10.02580 6.69607 H 3.62784 10.51485 7.54381 H 2.71298 9.05693 7.02898 H 2.28469 10.65078 6.38591 O 7.72938 11.98452 6.05846 H 6.59325 11.57883 3.90759 Ti 6.13686 9.66645 8.54601 Ti 8.8978 10.93888 7.22199 O 7.40448 9.72770 7.08155 O 4.68551 9.20082 9.83873 C 3.81395 10.15886 10.32670 O 6.56390 7.70796 8.71502 C 7.87855 7.34306 8.39371 O 10.50059 12.11218 7.07082 <td>С</td> <td>5.29354</td> <td>8.44172</td> <td>4.01124</td>	С	5.29354	8.44172	4.01124
C 6.09965 9.51031 3.61169 H 6.84076 9.37182 2.83793 C 5.96093 10.75737 4.21852 C 3.13743 10.02580 6.69607 H 3.62784 10.51485 7.54381 H 2.71298 9.05693 7.02898 H 2.28469 10.65078 6.38591 O 7.72938 11.98452 6.05846 H 6.59325 11.57883 3.90759 Ti 6.13686 9.66645 8.5601 Ti 8.8978 10.93888 7.22199 O 7.40448 9.72770 7.08155 O 4.68551 9.20082 9.83873 C 3.81395 10.15886 10.32670 O 6.56390 7.70796 8.71502 C 7.87855 7.34306 8.39371 O 10.50059 12.11218 7.07082 C 10.51021 12.62322 5.75595 <td>Н</td> <td>5.41304</td> <td>7.47165</td> <td>3.55180</td>	Н	5.41304	7.47165	3.55180
H6.840769.371822.83793C5.9609310.757374.21852C3.1374310.025806.69607H3.6278410.514857.54381H2.712989.056937.02898H2.2846910.650786.38591O7.7293811.984526.05846H6.5932511.578833.90759Ti6.136869.666458.54601Ti8.897810.938887.22199O7.404489.727707.08155O4.685519.200829.83873C3.8139510.1588610.32670O6.563907.707968.71502C7.878557.343068.39371O10.5005912.112187.07082C10.5102112.623225.75595O9.735169.793745.81834C10.582238.860116.44894H3.1578210.592069.58844H4.3740310.8900010.92719H8.023956.278518.68290H11.628978.974866.08765H10.581098.990387.55111H10.581098.990387.55111H10.5300811.833034.98587H10.5300811.833034.98587H4.3337117.469648.61558	С	6.09965	9.51031	3.61169
C5.9609310.757374.21852C3.1374310.025806.69607H3.6278410.514857.54381H2.712989.056937.02898H2.2846910.650786.38591O7.7293811.984526.05846H6.5932511.578833.90759Ti6.136869.666458.54601Ti8.897810.938887.22199O7.404489.727707.08155O4.685519.200829.83873C3.8139510.1588610.32670O6.563907.707968.71502C7.878557.343068.39371O10.5005912.112187.07082C10.5102112.623225.75595O9.735169.793745.81834C10.582238.860116.44894H3.123479.6056111.00337H3.1578210.592069.55844H4.3740310.8900010.92719H8.023956.278518.68290H8.625177.944128.9421H10.581098.974866.08765H10.581098.974866.08765H10.581098.990387.55111H10.581098.990387.55111H10.5300811.833034.98587H4.3337117.469648.61558	Н	6.84076	9.37182	2.83793
C3.1374310.025806.69607H3.6278410.514857.54381H2.712989.056937.02898H2.2846910.650786.38591O7.7293811.984526.05846H6.5932511.578833.90759Ti6.136869.666458.54601Ti8.897810.938887.22199O7.404489.727707.08155O4.685519.200829.83873C3.8139510.1588610.32670O6.563907.707968.71502C7.878557.343068.39371O10.5005912.112187.07082C10.5102112.623225.75595O9.735169.793745.81834C10.582238.860116.44894H3.123479.6056111.00337H8.023956.278518.68290H8.023956.278518.68290H8.023956.278518.68290H11.628978.974866.08765H10.242707.829346.21248H10.581098.990387.55111H11.3699613.304315.59195H9.6056013.199355.58073H10.5300811.833034.98587H4.3337117.469648.61558	С	5.96093	10.75737	4.21852
H3.6278410.514857.54381H2.712989.056937.02898H2.2846910.650786.38591O7.7293811.984526.05846H6.5932511.578833.90759Ti6.136869.666458.54601Ti8.897810.938887.22199O7.404489.727707.08155O4.685519.200829.83873C3.8139510.1588610.32670O6.563907.707968.71502C7.878557.343068.39371O10.5005912.112187.07082C10.5102112.623225.75595O9.735169.793745.81834C10.582238.860116.44894H3.1578210.592069.55844H4.3740310.8900010.92719H8.023956.278518.68290H11.628978.974866.08765H10.242707.829346.21248H10.581098.990387.55111H11.6309613.304315.59195H9.6056013.199355.58073H4.3337117.469648.61558	С	3.13743	10.02580	6.69607
H2.712989.056937.02898H2.2846910.650786.38591O7.7293811.984526.05846H6.5932511.578833.90759Ti6.136869.666458.54601Ti8.897810.938887.22199O7.404489.727707.08155O4.685519.200829.83873C3.8139510.1588610.32670O6.563907.707968.71502C7.878557.343068.39371O10.5005912.112187.07082C10.5102112.623225.75595O9.735169.793745.81834C10.582238.860116.44894H3.123479.6056111.00337H3.1578210.592069.55844H4.3740310.8900010.92719H8.021347.378967.29708H11.628978.974866.08765H10.242707.829346.21248H10.581098.990387.55111H10.5300811.833034.98587H4.3337117.469648.61558	Н	3.62784	10.51485	7.54381
H2.2846910.650786.38591O7.7293811.984526.05846H6.5932511.578833.90759Ti6.136869.666458.54601Ti8.897810.938887.22199O7.404489.727707.08155O4.685519.200829.83873C3.8139510.1588610.32670O6.563907.707968.71502C7.878557.343068.39371O10.5005912.112187.07082C10.5102112.623225.75595O9.735169.793745.81834C10.582238.860116.44894H3.123479.6056111.00337H3.1578210.592069.55844H4.3740310.8900010.92719H8.023956.278518.68290H11.628978.974866.08765H10.581098.990387.55111H10.581098.990387.55111H9.6056013.304315.59195H9.6056013.19355.58073H10.5300811.833034.98587H4.3337117.469648.61558	Н	2.71298	9.05693	7.02898
O 7.72938 11.98452 6.05846 H 6.59325 11.57883 3.90759 Ti 6.13686 9.66645 8.54601 Ti 8.8978 10.93888 7.22199 O 7.40448 9.72770 7.08155 O 4.68551 9.20082 9.83873 C 3.81395 10.15886 10.32670 O 6.56390 7.70796 8.71502 C 7.87855 7.34306 8.39371 O 10.50059 12.11218 7.07082 C 10.51021 12.62322 5.75595 O 9.73516 9.79374 5.81834 C 10.58223 8.86011 6.44894 H 3.12347 9.60561 11.00337 H 3.15782 10.59206 9.55844 H 4.37403 10.89000 10.92719 H 8.02134 7.37896 7.29708 H 11.62897 8.97486 6.08765	Н	2.28469	10.65078	6.38591
H6.5932511.578833.90759Ti6.136869.666458.54601Ti8.897810.938887.22199O7.404489.727707.08155O4.685519.200829.83873C3.8139510.1588610.32670O6.563907.707968.71502C7.878557.343068.39371O10.5005912.112187.07082C10.5102112.623225.75595O9.735169.793745.81834C10.582238.860116.44894H3.123479.6056111.00337H8.023956.278518.68290H8.021347.378967.29708H10.581098.974866.08765H10.581098.990387.55111H9.6056013.199355.58073H4.3337117.469648.61558	0	7.72938	11.98452	6.05846
Ti6.136869.666458.54601Ti8.897810.938887.22199O7.404489.727707.08155O4.685519.200829.83873C3.8139510.1588610.32670O6.563907.707968.71502C7.878557.343068.39371O10.5005912.112187.07082C10.5102112.623225.75595O9.735169.793745.81834C10.582238.860116.44894H3.123479.6056111.00337H3.1578210.592069.55844H4.3740310.8900010.92719H8.023956.278518.68290H11.628978.974866.08765H10.581098.990387.55111H10.581098.990387.55111H9.6056013.199355.58073H4.3337117.469648.61558	Н	6.59325	11.57883	3.90759
Ti8.897810.938887.22199O7.404489.727707.08155O4.685519.200829.83873C3.8139510.1588610.32670O6.563907.707968.71502C7.878557.343068.39371O10.5005912.112187.07082C10.5102112.623225.75595O9.735169.793745.81834C10.582238.860116.44894H3.123479.6056111.00337H3.1578210.592069.55844H4.3740310.8900010.92719H8.023956.278518.68290H11.628978.974866.08765H10.581098.990387.55111H10.581098.990387.55111H9.6056013.304315.59195H9.6056013.199355.58073H4.3337117.469648.61558	Ti	6.13686	9.66645	8.54601
O7.404489.727707.08155O4.685519.200829.83873C3.8139510.1588610.32670O6.563907.707968.71502C7.878557.343068.39371O10.5005912.112187.07082C10.5102112.623225.75595O9.735169.793745.81834C10.582238.860116.44894H3.123479.6056111.00337H3.1578210.592069.55844H4.3740310.8900010.92719H8.023956.278518.68290H8.021347.378967.29708H10.581098.974866.08765H10.581098.990387.55111H11.3699613.304315.59195H9.6056013.199355.58073H4.3337117.469648.61558	Ti	8.8978	10.93888	7.22199
O4.685519.20829.83873C3.8139510.1588610.32670O6.563907.707968.71502C7.878557.343068.39371O10.5005912.112187.07082C10.5102112.623225.75595O9.735169.793745.81834C10.582238.860116.44894H3.123479.6056111.00337H3.1578210.592069.55844H4.3740310.8900010.92719H8.625177.944128.94921H8.021347.378967.29708H11.628978.974866.08765H10.581098.990387.55111H10.581098.990387.55111H10.5300811.833034.98587H4.3337117.469648.61558	0	7.40448	9.72770	7.08155
C3.8139510.1588610.32670O6.563907.707968.71502C7.878557.343068.39371O10.5005912.112187.07082C10.5102112.623225.75595O9.735169.793745.81834C10.582238.860116.44894H3.123479.6056111.00337H3.1578210.592069.55844H4.3740310.8900010.92719H8.023956.278518.68290H8.021347.378967.29708H11.628978.974866.08765H10.581098.990387.55111H9.6056013.304315.59195H9.6056013.199355.58073H10.5300811.833034.98587H4.3337117.469648.61558	0	4.68551	9.20082	9.83873
O6.563907.707968.71502C7.878557.343068.39371O10.5005912.112187.07082C10.5102112.623225.75595O9.735169.793745.81834C10.582238.860116.44894H3.123479.6056111.00337H3.1578210.592069.55844H4.3740310.8900010.92719H8.023956.278518.68290H8.021347.378967.29708H11.628978.974866.08765H10.581098.990387.55111H9.6056013.304315.59195H9.6056013.19355.58073H10.5300811.833034.98587H4.3337117.469648.61558	С	3.81395	10.15886	10.32670
C7.878557.343068.39371O10.5005912.112187.07082C10.5102112.623225.75595O9.735169.793745.81834C10.582238.860116.44894H3.123479.6056111.00337H3.1578210.592069.55844H4.3740310.8900010.92719H8.625177.944128.94921H8.021347.378967.29708H11.628978.974866.08765H10.581098.990387.55111H11.3699613.304315.59195H9.6056013.199355.58073H10.5300811.833034.98587H4.3337117.469648.61558	0	6.56390	7.70796	8.71502
O10.5005912.112187.07082C10.5102112.623225.75595O9.735169.793745.81834C10.582238.860116.44894H3.123479.6056111.00337H3.1578210.592069.55844H4.3740310.8900010.92719H8.023956.278518.68290H8.625177.944128.94921H11.628978.974866.08765H10.581098.990387.55111H11.3699613.304315.59195H9.6056013.193355.58073H10.5300811.833034.98587H4.3337117.469648.61558	С	7.87855	7.34306	8.39371
C10.5102112.623225.75595O9.735169.793745.81834C10.582238.860116.44894H3.123479.6056111.00337H3.1578210.592069.55844H4.3740310.8900010.92719H8.023956.278518.68290H8.625177.944128.94921H8.021347.378967.29708H11.628978.974866.08765H10.581098.990387.55111H11.3699613.304315.59195H9.6056013.19355.58073H10.5300811.833034.98587H4.3337117.469648.61558	0	10.50059	12.11218	7.07082
O9.735169.793745.81834C10.582238.860116.44894H3.123479.6056111.00337H3.1578210.592069.55844H4.3740310.8900010.92719H8.023956.278518.68290H8.021347.378967.29708H11.628978.974866.08765H10.581098.990387.55111H11.3699613.304315.59195H9.6056013.199355.58073H10.5300811.833034.98587H4.3337117.469648.61558	С	10.51021	12.62322	5.75595
C10.582238.860116.44894H3.123479.6056111.00337H3.1578210.592069.55844H4.3740310.8900010.92719H8.023956.278518.68290H8.625177.944128.94921H8.021347.378967.29708H11.628978.974866.08765H10.242707.829346.21248H10.581098.990387.55111H9.6056013.304315.59195H9.6056013.19355.58073H10.5300811.833034.98587H4.3337117.469648.61558	0	9.73516	9.79374	5.81834
H3.123479.6056111.00337H3.1578210.592069.55844H4.3740310.8900010.92719H8.023956.278518.68290H8.625177.944128.94921H8.021347.378967.29708H11.628978.974866.08765H10.242707.829346.21248H10.581098.990387.55111H11.3699613.304315.59195H9.6056013.199355.58073H10.5300811.833034.98587H4.3337117.469648.61558	С	10.58223	8.86011	6.44894
H3.1578210.592069.55844H4.3740310.8900010.92719H8.023956.278518.68290H8.625177.944128.94921H8.021347.378967.29708H11.628978.974866.08765H10.242707.829346.21248H10.581098.990387.55111H9.6056013.304315.59195H9.6056013.199355.58073H10.5300811.833034.98587H4.3337117.469648.61558	Н	3.12347	9.60561	11.00337
H4.3740310.8900010.92719H8.023956.278518.68290H8.625177.944128.94921H8.021347.378967.29708H11.628978.974866.08765H10.242707.829346.21248H10.581098.990387.55111H11.3699613.304315.59195H9.6056013.199355.58073H10.5300811.833034.98587H4.3337117.469648.61558	Н	3.15782	10.59206	9.55844
H8.023956.278518.68290H8.625177.944128.94921H8.021347.378967.29708H11.628978.974866.08765H10.242707.829346.21248H10.581098.990387.55111H11.3699613.304315.59195H9.6056013.199355.58073H10.5300811.833034.98587H4.3337117.469648.61558	Н	4.37403	10.89000	10.92719
H8.625177.944128.94921H8.021347.378967.29708H11.628978.974866.08765H10.242707.829346.21248H10.581098.990387.55111H11.3699613.304315.59195H9.6056013.199355.58073H10.5300811.833034.98587H4.3337117.469648.61558	Н	8.02395	6.27851	8.68290
H8.021347.378967.29708H11.628978.974866.08765H10.242707.829346.21248H10.581098.990387.55111H11.3699613.304315.59195H9.6056013.199355.58073H10.5300811.833034.98587H4.3337117.469648.61558	Н	8.62517	7.94412	8.94921
H11.628978.974866.08765H10.242707.829346.21248H10.581098.990387.55111H11.3699613.304315.59195H9.6056013.199355.58073H10.5300811.833034.98587H4.3337117.469648.61558	Н	8.02134	7.37896	7.29708
H10.242707.829346.21248H10.581098.990387.55111H11.3699613.304315.59195H9.6056013.199355.58073H10.5300811.833034.98587H4.3337117.469648.61558	Н	11.62897	8.97486	6.08765
H10.581098.990387.55111H11.3699613.304315.59195H9.6056013.199355.58073H10.5300811.833034.98587H4.3337117.469648.61558	Н	10.24270	7.82934	6.21248
H11.3699613.304315.59195H9.6056013.199355.58073H10.5300811.833034.98587H4.3337117.469648.61558	н	10.58109	8.99038	7.55111
H9.6056013.199355.58073H10.5300811.833034.98587H4.3337117.469648.61558	н	11.36996	13.30431	5.59195
H10.5300811.833034.98587H4.3337117.469648.61558	Н	9.60560	13.19935	5.58073
H 4.33371 17.46964 8.61558	Н	10.53008	11.83303	4.98587
	Н	4.33371	17.46964	8.61558

Energy = -4739.597229017931 A.U.

Element			
Fe	18.76896	5.77025	4.00585
0	18.44412	7.41859	3.12339
0	17.33529	5.98834	5.37325
Ν	20.39824	5.55728	2.83356
Ν	20.33666	6.16837	5.23134
Ν	17.85009	5.16195	2.14349
С	21.62659	5.66928	3.39469
С	22.78805	5.37423	2.65287
Н	23.77945	5.49042	3.05985
С	22.65611	4.83656	1.38033
С	20.24346	5.0613	1.59085
С	18.86894	4.82729	1.17539
С	16.49653	5.15702	1.6241
С	15.83285	3.90733	1.40181
С	14.55075	3.86483	0.83918
Н	14.04735	2.91654	0.70027
С	13.91785	5.02014	0.41521
Н	12.9307	4.96505	-0.02777
С	14.59027	6.22963	0.47155
С	15.88211	6.32011	1.02963
С	16.48733	2.57083	1.64916
Н	15.84331	1.90555	2.24953
Н	17.48998	2.65352	2.1135
Н	16.61787	2.06848	0.66545
С	16.58513	7.64292	0.83257
Н	16.78873	8.17164	1.76769
С	21.62923	6.00511	4.67028
С	22.88624	6.04605	5.51688
Н	22.65543	6.27969	6.57325
Н	23.35047	5.03581	5.51634
С	20.13592	6.83415	6.47764
С	20.52435	8.20892	6.58754
С	20.25698	8.91474	7.76963
Н	20.53471	9.95917	7.86877
С	19.61303	8.29299	8.83084
Н	19.40642	8.85494	9.73425
С	19.24409	6.95189	8.73621
Н	18,76159	6.49248	9.58762
С	19.50761	6.20813	7.57087
C	21,18161	8.96874	5.45135
H	22.17509	8.55703	5.20718
H	21.35197	10.03865	5.70383
H	20.54197	8.93236	4.54612
С	19.17259	4.74707	7.538
		-	

 Table C. 3. Cartesian coordinates for the model Fe(III)-titanium ester complex 3.4

 obtained from DFT calculations.

н	18,54354	4,47641	6.67534
Н	18.65452	4.42897	8.46573
Н	20.12292	4.18252	7.46908
Р	20.99881	1.73899	4.48982
F	21.10043	0.26118	3.62214
F	19.4175	1.32493	5.0178
F	20.89945	3.2125	5.35384
F	22.57891	2.16035	3.96297
F	21.66416	0.97483	5.87676
F	20.3312	2.50092	3.10639
С	18.6016	4.13649	-0.15378
Н	14.10242	7.09567	0.03533
Н	15.97945	8.34905	0.21794
Н	17.51791	7.4688	0.25024
Н	23.62198	6.78196	5.13876
Ti	17.3836	8.06983	4.74109
Ti	15.35984	6.10418	5.44258
0	15.6946	7.33273	3.9344
0	17.38567	9.90907	4.0873
С	18.05009	10.54364	5.15334
0	13.3789	6.21716	5.49135
0	15.06225	4.57929	4.25915
С	16.11937	3.71459	4.55025
0	16.37653	8.51304	6.45134
С	15.07021	9.00899	6.23983
Н	15.88574	2.69384	4.22936
Н	16.37565	3.68441	5.62647
Н	16.99309	4.07718	4.00798
С	13.00117	5.68391	6.7391
Н	12.12046	5.01679	6.61761
Н	12.74458	6.49849	7.4529
Н	13.82806	5.07911	7.17128
Н	14.80209	9.72839	7.04717
Н	14.31797	8.20626	6.31418
Н	14.97995	9.53492	5.27217
Н	17.39898	11.2051	5.75983
Н	18.94267	11.07197	4.7636
Н	18.44762	9.76761	5.83855
С	21.38207	4.66021	0.85083
Н	23.53484	4.51352	0.82398
Н	21.31457	4.17693	-0.10408
Н	19.52419	4.00589	-0.67978
Н	17.9383	4.73687	-0.74071
Н	18.15432	3.18095	0.02449

Energy = -5720.921268875836 A.U.

 Table C. 4. Full table of equilibrium and rate constants from COPASI fits for different

 bis(imino)pyridine ligands using 0.2 mol% of the complex in deuterated dichloromethane at

 25°C..

	[Fe] (mM)	T (°C)	k(obs)	K1(dimer)	K2(anion)	K5(pdtI)	k3	k4
4.2a	0. 527	-30	7.00E- 03	0.658	0.944	145.92	1.423	5450.00
4.2a	1.054	-30	1.80E- 02	0.658	0.944	145.92	1.423	5450.00
4.2a	2.108	-30	4.10E- 02	0.658	0.944	145.92	1.423	5450.00
4.3a	0. 527	-30	4.40E- 02	0.889	0.971	126.50	3.484	9418.00
4.2a	0. 527	-40	3.48E- 04	0.156	0.349	35063.00	0.036	5892.00
4.2a	0. 527	-20	1.06E- 01	0.669	0.944	1.63	1.540	7500.00
4.2a	0. 527	-10	2.56E- 01	0.669	0.962	1.31	3.185	7913.00
4.2a	0. 527	0	4.04E- 01	0.676	0.969	1.07	4.068	8954.00
4.2a	0. 527	10	4.04E- 01	0.729	0.995	1.12	5.279	9994.00
4.2a	0. 527	25	4.50E- 01	0.927	1.000	0.98	8.366	9356.00
4.2b	0. 527	25	7.72E- 02	0.960	0.970	1.36	1.943	9240.04
4.2c	0. 527	25	9.78E- 02	0.946	0.943	1.18	3.095	9175.25
4.2j	0. 527	25	3.44E- 02	0.509	0.932	13.24	12.720	9133.63
4.2e	0. 527	25	2.08E- 04	0.696	1.048	199.20	1.447	100.21
4.2h	0. 527	25	3.25E- 05	0.957	0.295	1043.75	4.809	163.17
4.2d	0. 527	25	2.85E- 01	0.025	3.233	364.98	9.986	82556.90
4.3b	0. 527	25	2.20E- 03	3.101	0.014	77.19	0.105	100.37
4.3b	1.054	25	2.70E- 03	3.101	0.014	77.19	0.105	100.37
4.3b	2.108	25	3.85E- 03	3.101	0.014	77.19	0.105	100.37

9. Appendix D GPC traces of all obtained polymers



Figure D 1. GPC traces of poly(lactic acid) produced from polymerization in the presence of LiClO₄ in Chapter 2



Figure D 2. GPC traces of polyether produced from polymerization in the presence of LiClO₄ in Chapter 2



Figure D 3. GPC traces of poly(lactic acid) obtained from a) lactide polymerization in 0.1 M ⁿBu₄NPF₆ in CH₂Cl₂ in the electrochemical cell without applied potential; b) lactide

polymerization in pure CH_2Cl_2 in the electrochemical cell without applied potential in chapter





Figure D 4. GPC traces of polyether obtained from a) cyclohexene oxide polymerization in 0.1 M Bu_4NPF_6 in CH_2Cl_2 in the electrochemical cell without applied potential; b) cyclohexne oxide polymerization in pure CH_2Cl_2 in the electrochemical cell without apCplied potential.



Figure D 5. GPC traces of a) poly-L-(lactic acid) and b) poly(cyclohexene oxide) before and after 30 min electrolysis in chapter 2.



Figure D 6. GPC traces of poly(lactic acid) obtained from cycling experiment where the reaction mixture was allowed to toggle between 2.3 V and 3.7 V for 4 cycles followed by electrochemical reduction of complex 2.1 to its Fe(II) oxidation state in chapter 2.



Figure D 7. GPC traces of polyether produced from an electrochemical redoxswitchable polymerization of cyclohexene oxide through sequential electrolysis at different applied potentials; obtained from RI detector in chapter 2.



Figure D 8. GPC trace of block copolymer generated from e-switchable copolymerization of lactide and cyclohexene oxide, Fe(II) to Fe(III) redox switch Table S10; a) 3 h; b) 4h; c) 12 h. Obtained from RI detector (chapter 2)



Figure D 9. GPC trace of block copolymer generated from e-switchable copolymerization of lactide and cyclohexene oxide, Fe(III) to Fe(II) redox switch Table S11; d) 3 h; e) 4 h; f) 12 h. Obtained from RI detector.



Figure D 10. GPC traces of poly(lactic acid) obtained from Fe(II-TiO₂ in chapter 3.



Figure D 11. GPC traces of poly(cyclohexene oxide) obtained from Fe(III)-TiO₂ in chapter 3.

10. Appendix E. COPASI fits in Chapter 3



Figure E. 1. COPASI fits for the time course experiments of cyclohexene oxide polymerization catalyzed by 4.2a



Figure E. 2. COPASI fits for the time course experiments of cyclohexene oxide polymerization catalyzed by 4.2b

Figure E. 3. COPASI fits for the time course experiments of cyclohexene oxide polymerization catalyzed by 4.2c



Figure E. 4. COPASI fits for the time course experiments of cyclohexene oxide polymerization catalyzed by 4.2d



Figure E. 5. COPASI fits for the time course experiments of cyclohexene oxide polymerization catalyzed by 4.2e



Figure E. 6. COPASI fits for the time course experiments of cyclohexene oxide polymerization catalyzed by 4.2h



Figure E. 7. COPASI fits for the time course experiments of cyclohexene oxide polymerization catalyzed by 4.2j



Figure E. 8 COPASI fits for the time course experiments of cyclohexene oxide polymerization catalyzed by 4.3a with varied [4.3a]



Figure E. 9. COPASI fits for the time course experiments of cyclohexene oxide polymerization catalyzed by 4.3b with varied [4.3b]