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Redox Control within Single-Site Polymerization Catalysts

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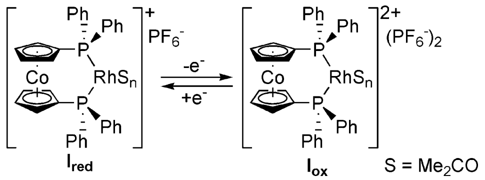
Incorporation of a redox-active functionality within a ligand framework potentially allows the reactivity and selectivity of complexed metal centers to be modulated through either chemical or electrochemical switching of the redox center(s).[1] A pioneering demonstration of this concept was described by Wrighton et al., who showed that the hydrogenation of cyclohexene catalyzed by the diphosphino-cobaltocene stabilized rhodium complex, $\mathbf{I}_{red}$, is approximately 16-fold faster than with its dicationic cobaltocenium analogue $\mathbf{I}_{ox}$ (Scheme 1).[2] This observation was rationalized on the basis of the more electron-rich Rh center of $\mathbf{I}_{red}$ being better able to promote the oxidative addition of H_2.

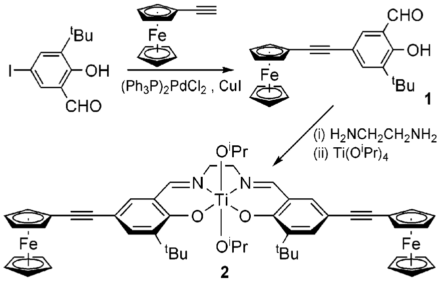
Scheme 1



To date, the application of redox switchable catalysts in single-site polymerization catalyst technology has not been demonstrated, yet it offers a number of attractive and potentially technologically useful advantages. For example, oscillating a catalyst through oxidized and reduced forms should allow the activity of the active site to be modulated, by changes to the electrophilicity of the active centers, and thereby facilitate "selectivity switching" between different monomers during the polymerization process. Rather unusual micro-block copolymer materials might be anticipated from combinations of two or more monomers, where the block lengths will be dependent upon the frequency of oscillation of the catalyst between its reduced and oxidized forms. Here, we describe "proof of concept" findings which show that activity can indeed be varied by redox switching of a ferrocenyl unit contained within the ligand backbone of a lactide polymerization catalyst. A key component of such a catalyst is a substitutionally inert redox-active ligand.

A ligand class which has enjoyed widespread usage in polymerization catalysis is the bis(iminophenoxide) (salen) family, and we therefore rationalized that a ferrocenyl-functionalized derivative would be a suitable candidate for this study—the chemistry of ferrocene and its derivatives is well-established[3−9] with the electronic (redox) properties often playing an important role.[10,11]

Scheme 2



The ethynylferrocene-substituted salicylaldimine **1** was synthesized via the $PdCl_2(PPh_3)_2$/CuI-catalyzed coupling of 3-*tert*-butyl-5-iodosalicylaldehyde[12] with ethynylferrocene[13] (Scheme 2). Red crystals of **1** were grown from diethyl ether/pentane solution, and the molecular structure[14] is shown in Figure 1. The ferrocenyl-substituted salen ligand was then prepared by treatment of **1** with ethylenediamine, and its subsequent reaction with $Ti(O^iPr)_4$ cleanly afforded the titanium complex **2** in 88% yield. Solution NMR data are consistent with the planar *trans* structure commonly found in Ti(salen) alkoxide complexes.[15]

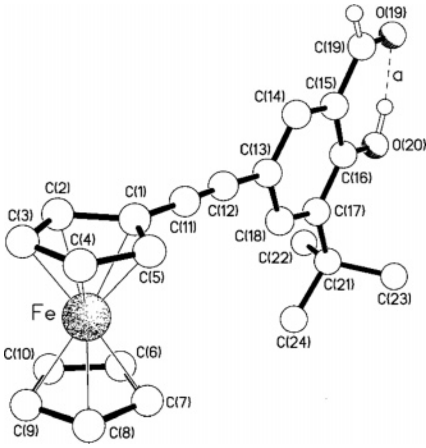


Figure 1. Molecular structure of **1**.

To identify a suitable chemical oxidant and reductant for the redox switch, we determined the standard half electrode potential $E_p^{1/2}$ of **2**. This was found to be 0.08 V (vs Fc/Fc^+); we therefore selected AgOTf as a suitable one-electron oxidant ($E_p^{1/2} = 0.43$ V vs Fc/Fc^+) since the silver metal byproduct is relatively inert and readily removed. Reaction of **2** with 2 equiv of AgOTf (in order to oxidize both ferrocene substituents) in CH_2Cl_2 resulted in a color change from orange to brown with concomitant precipitation of Ag^0; subsequent filtration and removal of solvent afforded the dicationic complex **3** (Scheme 3). Though broadened by the presence of the paramagnetic ferrocenium substituents, the ^{1}H NMR resonances of the salen component of **3** are clearly assignable.[14] Decamethylferrocene was chosen as a suitable reductant for **3** not only for its standard potential[16] ($E^{1/2} = -0.59$ V vs Fc/Fc^+) but also due to its compatibility with the system: the products of reduction will be **2** and 2 equiv of $[Cp^*_2Fe]^+[OTf]^-$. The reaction of **3** with Cp^*_2Fe resulted in a change from a brown back to the pale orange/brown color of **2**, a transformation confirmed by the reappearance of the resonances attributable to the ferrocenyl substituents in the ^{1}H NMR spectrum.[14]

The ring-opening polymerization of *rac*-lactide (LA) was initially investigated by dissolving 0.025 mmol of both **2** and **3** in 5 mL of toluene in separate glass ampules. The initiators may also be conveniently prepared from the in situ reaction of (ferrocenyl salen)-H_2 with $Ti(O^iPr)_4$ followed by stringent removal of the volatile

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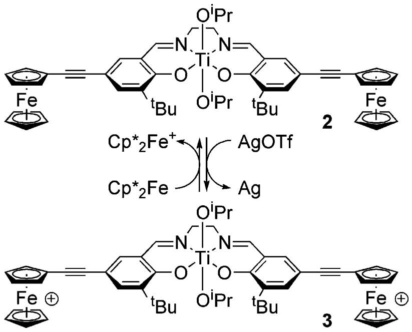
Scheme 3



components to ensure that no residual ^{i}PrOH remained. After addition of 100 equiv of LA, the ampules were sealed and placed in a preheated oil bath at 70 °C. Samples were then removed at timed intervals and immediately cooled and exposed to air in order to terminate the propagation process.

Analysis of the conversion data (Figure 2) clearly shows that the non-oxidized ligand supports a substantially more rapid polymerization (k_{app}[**2**]/k_{app}[**3**] $\approx$ 30). This is consistent with our recent study of a variety of other salen−titanium initiators, which showed that electron-withdrawing substituents within the salen framework afford a slower rate of propagation for lactide monomer[17] (contrasting salen Al-based lactide initiators for which activities increase with electron-withdrawing substituents).[18] The longer reaction times required for **3** may lead to a small amount of catalyst decomposition as suggested by the tailing off in the conversion versus time plot (Figure 2) after ca. 250 h. Nonetheless, in accord with Wrighton's Rh-catalyzed hydrogenation system,[2] the redox-active ligand backbone is clearly shown to relay an electronic effect to the titanium center.

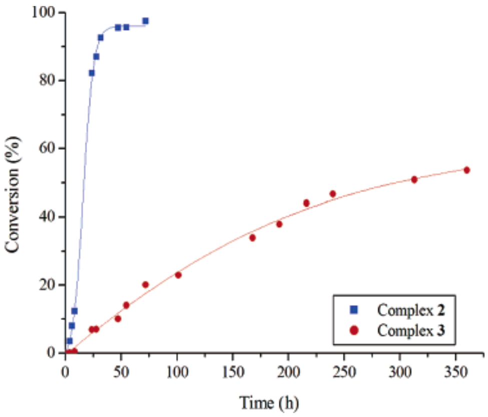


Figure 2. A plot of LA consumption versus time for **2** and **3** (toluene, 70 °C, $[LA]_0/[Ti] = 100$).

The molecular weight distributions of the PLA samples are <1.2, suggesting a well-controlled propagation process, mostly free from undesired termination processes. Both **2** and **3** behave in a manner similar to that of other salen−titanium initiators, affording a single atactic CO$_2$^{i}Pr-terminated chain per metal center and with an induction period prior to propagation.[17]

To demonstrate a genuine switching effect, it is necessary to show the reversible nature of the redox event. The polymerization of LA (100 equiv, 70 °C) was therefore repeated using complex **2**. After 8 h, a conversion of ca. 18% had occurred (Figure 3). At this point, 2 equiv of AgOTf were added, affording a brown solution and a precipitate of Ag metal. The conversion of monomer slowed markedly. After a further 20 h, 2 equiv of Cp*$_2$Fe was added, and the re-formation of the reduced (neutral) ligand was accompanied by a corresponding increase in activity (Figure 3). Significantly, neither AgOTf nor Cp*$_2$FeOTf afforded any polymerization activity under comparable conditions. The return in activity to approximately the same magnitude as that observed prior to oxidation ($k_{app} = 4.98 \times 10^{-6}$ s^{-1}, cf. $k_{app} = 4.73 \times 10^{-6}$ s^{-1} before oxidation) confirmed the redox switch.

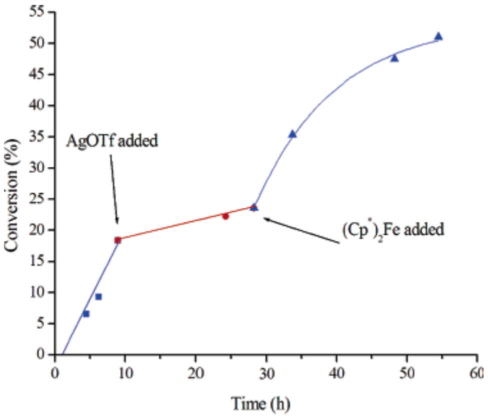


Figure 3. A plot of conversion versus time for the polymerization of *rac*-LA during the in situ oxidation and reduction of complex **2**/**3** (toluene, 70 °C, $[LA]_0/[Ti] = 100$).

In conclusion, these results demonstrate that remote redox-active ligand substituents may be exploited to control the activity of single-site polymerization initiators. Moreover, the redox switch can be used to oscillate a catalyst between sites of differing activities. The potential application of such redox-switchable initiators to the polymerization of mixed monomer pools and thereby providing access to unusual micro-block copolymer materials is now a realistic possibility, as is the potential for electrochemical modulation of electrode-attached catalysts. These, along with investigations into other catalyst/monomer combinations, will form the focus of future work.

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Supporting Information Available: Full experimental details, including crystallographic and polymerization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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