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#### Redox-Controlled Polymerization of Lactide Catalyzed by Bis(imino)pyridine Iron Bis(alkoxide) Complexes

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In this article, Byers and co-workers investigate the use of bis(imino)pyridine iron bis(alkoxide) complexes as catalysts for the polymerization of lactide. The authors describe the synthesis of the iron complexes and the mechanistic studies done to elucidate the mechanism of the polymerization reaction. The following questions are intended to guide your reading of the article.

**Introductory Questions**

1. When discussing polymer chemistry, there are a number of important terms that are used to describe the mechanism of the polymerization reaction and the properties of the polymer. Please provide a definition for each of the terms (used in the article) that are listed below. You may need to consult other sources to find some of these definitions.
	1. Precatalyst
	2. Initiator
	3. *M*n
	4. *M*w
	5. Polydispersity or polydispersity index (PDI)
2. In the general mechanism for polymerization reactions, there are a series of steps that occur: initiation, propagation, termination. The authors suggest that the observed reaction is a *living polymerization*. What is a living polymerization reaction and how is it different from other types of polymerization reactions?
3. Why is the polymerization of lactide being studied? What are some advantages of poly(lactic acid) over many other commonly used polymers?
4. Why is iron an interesting metal to investigate for use as a catalyst in lactide polymerization? List some potential benefits that were mentioned in the article.

**Characterization Questions**

1. Use the CBC method to classify the ligands coordinated to the iron center in complexes **4** and **5** as L, X, or Z.
2. Both the iron(II) and iron(III) bis(alkoxide) compounds have unpaired electrons. Given μeff and the formula for the spin-only magnetic moment, determine the number of unpaired electrons (*n*) in each complex. $μ\_{eff}= \sqrt{n\left(n+2\right)}$

|  |  |
| --- | --- |
| **Complex** | **μeff** |
| iron(II) bis(neopentoxide) [**5c**] | 5.2 μB |
| iron(III) bis(4-methoxyphenoxide) [**6**] | 5.9 μB |

1. The authors use the Evans’ method to determine the Fe center is in fact high spin. Describe the Evans’ method and how it can be used to get information about the spin state of a metal center. What other technique could be used to obtain the same information? (You will need to use other sources to answer this questions.)
2. The article states that the iron has a distorted trigonal bipyramidal geometry. A square pyramidal structure is the other common geometry observed for five-coordinate complexes. For both complexes **5c** and **6**, fill the d-orbital splitting diagrams for each geometry in a way that is consistent with the number of unpaired electrons in each molecule.
3. In general, NMR is only useful to characterize organometallic species that are diamagnetic. However, the authors use NMR (Figure 1) to study conversion of dialkyl Fe complex **4** to the iron bis(alkoxide) complex **5**, which are both paramagnetic complexes. How are these spectra different from those typically observed for diamagnetic complexes?
4. What are key features observed in the NMR spectra (Figure 1) that confirm that the reaction of complex 4 with an alcohol produces complex **5**?

**Mechanistic Questions**

1. How do metal alkoxide catalysts typically catalyze lactide polymerization? Please explain how these properties lead to the catalytic cycle shown in Scheme 1.
2. The authors investigated the mechanism of the polymerization reaction and provided evidence for their suggestion that the reaction was a *living polymerization*. What evidence supported the suggested classification? What evidence was not consistent with this classification?
3. The authors mention that iron alkoxides could form in solution if dissociation of the bis(imino)pyridine ligand occurred under catalytic conditions and these iron alkoxides could initiate the polymerization reaction. Describe the findings and experiments conducted that support that the bis(imino)pyridine ligand remains coordinated during catalysis.
4. The active Fe species 5 can be generated *in situ* from complex 4. What does *in situ* mean and how did the authors generate 5 *in situ* from complex 4?
5. One cool thing the authors discovered is the catalysis is “switchable”, which means the catalytic reaction can be switched on and off by changing the oxidation state of iron center. What oxidation state for iron is necessary to “turn on” catalysis and what oxidation state for iron is not active for polymerization?
6. To study the switchable catalysis, the authors add ferrocenium hexaflurophosphate (Cp2Fe+) and cobaltocene (Cp2Co) to switch the oxidation state of the iron in the catalyst. Please determine the electron count around each metal center. Based upon these electron counts, explain why each compound displays the redox behavior described in the article.