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

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This set of questions is appropriate for a junior/senior level course. The number of questions selected would be appropriate for about an hour. Feel free to remove/add questions as you see fit! Three categories of questions exist - introductory, characterization, and mechanistic. This is an excellent article that ties in the concepts of organometallic synthesis and characterization, catalysis, mechanistic studies, and polymer chemistry. An excellent LO for faculty looking to incorporate polymer chemistry into the inorganic curriculum, in light of ACS standards for certification.

**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. Living polymerization
   4. Polydispersity index (PDI)
   5. *M*n
   6. *M*w
2. In the general mechanism for polymerization reactions, there are a series of steps that occur: initiation, propagation, termination. As we will see in this paper, the authors’ data support that the observed reaction is a *living polymerization*. What is a living polymerization and what are the key characteristics for a living polymerization? (For more background on living polymerization and polymerization topics see: <https://www.cmu.edu/maty/crp/features.html>, <http://www.polyacs.org/725.html> )
3. What is meant by “biologically inert polymeric materials”? Provide an example of a biologically inert polymer and an application.
4. Draw the structure for lactic acid and denote any chiral centers. How is this compound converted to make the monomer lactide?
5. Why is the polymerization of lactide being studied? What are some advantages of poly(lactic acid) over many other commonly used polymers?
6. Why is iron an interesting metal to investigate for use as a catalyst in lactide polymerization? List some potential benefits.

**Characterization Questions**

1. 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.

|  |  |
| --- | --- |
| **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. (You will need to use other sources to answer this questions.)
   1. Describe the Evans’ method and how it can be used to get information about the spin state of a metal center.
   2. What other technique could be used to obtain the same information?
2. 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.
   1. How are these spectra different from those typically observed for diamagnetic complexes (look at Figure 1)?
   2. 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**?
3. Use the CBC method to classify the ligands coordinated to the iron center in complexes **4** and **5** as L, X, or Z.

**Mechanistic Questions**

1. The authors investigated the mechanism of the polymerization reaction and provided evidence for their suggestion that the reaction was a *living polymerization*.
   1. What evidence supported the suggested classification?
   2. What evidence was not consistent with this classification?
2. The paper mentions that Lewis acid metal complexes and NHCs are good catalysts to polymerize lactide.
   1. What features in catalyst design (*why do these complexes serve as catalysts in this reaction*) are necessary to initiate lactide polymerization?
   2. Looking at Scheme 2, address why the authors were targeting complex 5.
3. Coordination insertion is one mechanism used to make polymers using transition metal complexes. Find an example in the literature of ethylene polymerized via this mechanism.
4. An important term in catalysis chemistry is mol %, which is used to describe the catalyst loading. A lower value can indicate and more efficient catalyst.
   1. Write the equation for mol%.
   2. Determine the value for mol% when the authors used a 50:1 ratio of lactide monomer:Fe complex.
5. Assuming that all of the lactide is converted to polymer what would be the maximum *Mn* observed in the polymerizations using 50 monomer equivalents **(This assumes a perfectly living polymerization and 1 alkoxide initiating)**. How does the % conversion change this value? Determine the expected *Mn* values for entries 1-4 in Table 1 taking into consideration the conversions are less than 100%.
6. 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**?
7. A study was conducted to evaluate if one or two alkoxides present on iron are able to initiate polymerization. The authors discovered that the identity of the initiator was important to observing whether one or two alkoxides initiated polymerization.
   1. What were the findings described in the paper?
   2. Why is this important in terms of living polymerization and the reaction mechanism?
8. One cool thing the authors discovered is the catalysis is “switchable”, which means the catalysis can be switched on and off. It was noted that the oxidation state of iron is critical to observing polymerization.
   1. What oxidation state for iron is necessary to turn on catalysis and what oxidation state for iron is not active for polymerization?
   2. To study the switchable catalysis the authors add ferrocenium (Fc+) hexaflurophosphate and cobaltocene (Cp2Co). Identify which of these oxidizes **5a** and which reduces **5a**. Explain the graph shown in Figure 8.