Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, the director of the Wisconsin Initiative for Science Literacy (WISL) encouraged all Ph.D. chemistry candidates to include a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, state legislators, and members of the U.S. Congress.

Ten Ph.D. degree recipients have successfully completed their theses and included such a chapter, less than a year after the program was first announced; each was awarded $500.

WISL will continue to encourage Ph.D. chemistry students to share the joy of their discoveries with non-specialists and also will assist in the public dissemination of these scholarly contributions. WISL is now seeking funding for additional awards.

Wisconsin Initiative for
Science Literacy

The dual mission of the Wisconsin Initiative for Science Literacy is to promote literacy in science, mathematics and technology among the general public and to attract future generations to careers in research, teaching and public service.

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INFORMATION-RICH INVESTIGATIONS INTO CATALYTIC OLEFIN POLYMERIZATION: TECHNIQUE DEVELOPMENT AND MECHANISTIC STUDIES

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Chapter 1:

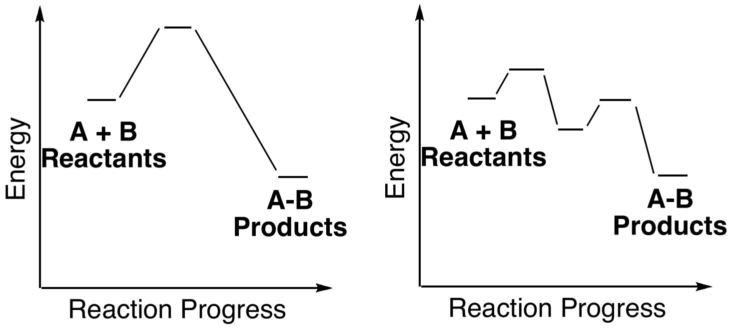
An Introduction for My Parents

Chapter 1.1. Catalysis in Modern Life

Although the general public is typically unaware of it, chemical discoveries made over the past two centuries are responsible for nearly all aspects of modern life. Non-natural materials such as plastics are today both widespread and cheap, due to industrial processes which have been developed over the past century.[1] Generations of chemists in the pharmaceutical industry worked to develop cheap and efficient chemical syntheses that produce commonplace drugs such as aspirin and antibiotics. Most transportation – including cars and airplanes – rely upon petroleum derivatives, which are only accessible due to crude oil processing techniques. Chemists are also responsible for developing the forensic techniques seen today on shows such as *CSI*.[2] Despite this, science coverage by the mainstream media focuses primarily on discoveries by physicists and biologists, while ignoring most developments in the chemical world.[3]

Many desirable chemical reactions are very slow at room temperature, while others are inaccessible due to the massive amounts of energy required for them to occur. For example, incomplete combustion in internal combustion engines produces carbon monoxide (CO), a poisonous gas and a contributor to smog. The reaction of carbon monoxide with oxygen (O_2) is energetically favorable (that is, it releases energy), but does not occur rapidly at room temperature. There are two ways chemists can force this reaction and others like it to occur. First, we can use more harsh conditions – higher temperatures and gas pressures – to “drive” a reaction to the desired product. This, however, requires significant amounts of energy which in this case not only introduces engineering difficulties but inevitably enhances production of other pollutants such as nitrogen oxides (NO_x). A better way, however, is to use a *catalyst* – a substance that increases the rate of a chemical reaction (allowing it to occur under comparatively mild conditions) without being itself consumed. Catalysts work by reducing the overall energy required for a chemical reaction by providing an alternative reaction pathway (Scheme 1.1). Catalytic converters, which are found on all modern automobiles, contain a catalyst that turns carbon monoxide into carbon dioxide much faster than would otherwise occur.

Scheme 1.1. Reaction pathway without catalyst (left) and with catalyst (right).



Catalysis is responsible for a large number of industrial processes that are very important to the modern world. For example, ammonia – a key component of fertilizer – is produced largely through the Haber-Bosch process, which uses an iron catalyst to react nitrogen (N_2) and hydrogen (H_2) to form ammonia.[4] The Haber-Bosch process is said to be responsible for supporting up to a third of the world's current population. The development of nitrogen fixation won Fritz Haber the Nobel Prize in Chemistry in 1918.[5]

Ideal catalysts will meet a number of basic criteria. For example, most – but not all – catalysts contain one or more metals. Ideally, those metals should be inexpensive and readily available (e.g. iron). (Unfortunately, many of the most expensive metals – such as platinum and rhodium – also seem to make the best catalysts.) Additionally, catalysts should be both efficient and active – that is, a single catalyst should be able to catalyze a large number of reactions ("turnovers") rapidly without decomposing. The best catalysts are also selective, in that they produce the desired product without any byproducts. Natural catalysts, known as *enzymes*, typically meet all these criteria but are not easily applied to most industrial applications. One of the many challenges faced by chemists today is to develop highly effective catalysts which can be used on a massive scale to perform desirable reactions, such as the use of solar energy to convert water into hydrogen or other fuel sources, the selective synthesis of various important pharmaceutical drugs, or the degradation of waste materials into fuels such as methanol, methane, and hydrogen.

Chapter 1.2. Reaction Kinetics and Mechanisms

One way to design more effective catalysts is by improving preexisting ones. This process is much easier if the catalyst's behavior is first fully understood. Once the catalyst has been characterized and researchers have established how it functions, chemists can often selectively alter the catalyst composition to improve it.

The study of the way that catalysts work is part of a subspecialty of chemistry known as *mechanistic chemistry*. Basically, mechanistic chemists focus on elucidating the *reaction mechanism* – or series of individual steps – that governs a chemical reaction. An example of a simple reaction mechanism – the decomposition of ozone (O_3) in the atmosphere to form oxygen (O_2) – is shown in Scheme 1.2. This process occurs in two steps. In the first step, a single molecule of ozone dissociates to form a molecule of oxygen (O_2) and a single oxygen atom. In the second step, the oxygen atom reacts with another molecule of ozone to form two molecules of molecular oxygen (O_2).

Scheme 1.2. Example of a reaction mechanism: the natural decomposition of ozone in the atmosphere.

$$\begin{array}{l} \text{1.)} \quad O_3\,(g) \rightarrow O_2\,(g) + O\,(g) \\ \text{2.)} \quad O_3\,(g) + O\,(g) \rightarrow 2\,O_2 \\ \hline \textbf{Total:} \quad 2\,O_3\,(g) \rightarrow 3\,O_2\,(g) \end{array}$$

Mechanistic chemists rely upon a number of tools to study chemical reactions. One of those tools is another subspecialty of chemistry known as *kinetics*. Chemical kinetics refers to the study of rates of chemical reactions. By determining the ways that reaction rates vary in response to altered reaction conditions, chemists can deduce the important steps in the reaction mechanism.

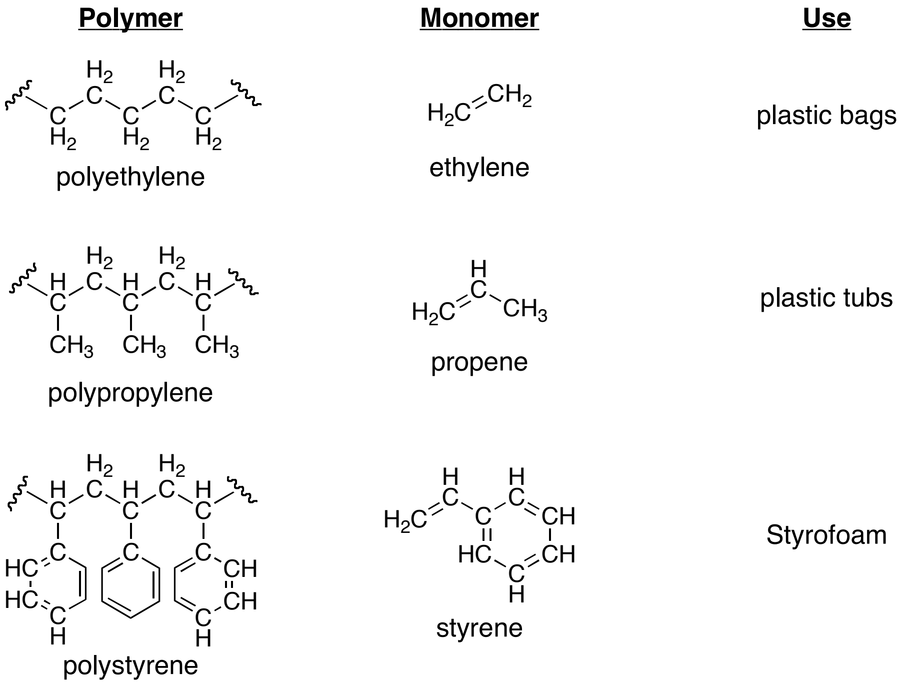
For a reaction rate to be determined, a chemist must establish how the concentrations of starting material and product change as a function of time. One way to do this is by ending ("killing") a reaction at various timepoints before it is completed and then measuring the ratio of starting materials to products. This technique is effective but often tedious and requires large amounts of starting material. More efficient techniques allow chemists to deduce the concentrations of starting material and product over the reaction timecourse without stopping the reaction (*in situ* studies). This may require special devices known as *spectrometers*, which can measure the way solutions absorb or emit electromagnetic radiation. For example, if a starting material is bright red while the final product is clear, the concentration of the starting material (and, by deduction, the final product) can be determined as a function of time by monitoring the intensity of the color of the solution. This allows researchers to collect multiple datapoints from a single reaction. In practice, my group typically uses a specific technique known as Nuclear Magnetic Resonance (NMR, a method closely related to MRI) to study reactions *in situ*. This technique lets us quantify the concentrations of all species in solution as a function of time with a high degree of accuracy.

Reaction rates should vary predictably in response to changes in the reaction condition depending upon the exact reaction mechanism. For example, a one-step reaction mechanism may require starting materials A and B to react to form the product C. Based upon this mechanism, we can predict that, if the concentration of A is doubled, the reaction rate should also double. If this does not happen – if, for example, changing the concentration of A has no effect on the reaction rate – then the reaction mechanism is probably wrong.

Chapter 1.3. Catalytic Alkene Polymerization

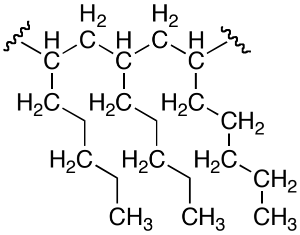
One field in which catalysts and mechanistic studies are important is the field of *catalytic alkene polymerization*. Polymerization is the process by which polymers, or plastics – which are long molecular chains made out of units called *monomers* – are made. There are many kinds of polymers (Scheme 1.3), but the kind that my research group studies are called *polyolefins*.

Scheme 1.3. Examples of some popular polymers, together with some of their applications. The wavy lines at the end represent that the structures are only a fraction of the actual length of the molecule. Unmarked vertices signify carbon atoms, bearing (in this case) one hydrogen atom each.



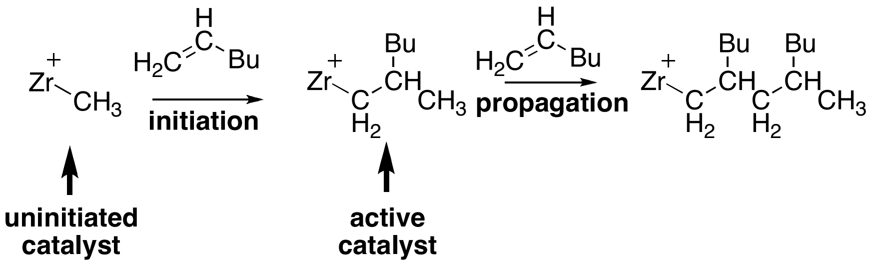
Polyolefins are among the most common kinds of polymer, and are produced on a multi-billion ton scale annually. There are many kinds of polyolefins, but the ones the public is most familiar with are polyethylene (found in trash bags and plastic milk bottles) and polypropylene (found in plastic tubs and other materials). The types of polyolefins that are studied in academia are often different than those that are used by industry. For example, I have worked with polyethylene, but the polymer I study most frequently is polyhexene (Scheme 1.4). Polyhexene is not frequently used in industry but is a good model for more industrially relevant polyolefins and is much more readily handled because it is soluble (will dissolve) at room temperature.

Scheme 1.4. The structure of polyhexene. Unmarked vertices indicate carbon atoms bearing (in this case) two hydrogen atoms each.



Polyolefins are synthesized industrially through a number of methods. The method that I study is called *homogeneous catalytic* polymerization. This means that the process is aided by a catalyst, and that everything involved in the reaction is in the same (liquid) phase. In the past, my research group has studied in detail the mechanism by which homogeneous catalytic olefin polymerization occurs (Scheme 1.5). The *catalytic cycle* controlling olefin polymerization can be broken down into multiple steps. In the first step, the starting catalyst "grabs" a monomer unit (or "link" on the polymer chain) and inserts into it, connecting it to an *endgroup* which was bound to the catalyst. This is called *initiation*, and it is typically very slow. In the next step, the newly formed polymer-bearing (or chain-bearing) catalyst "grabs" more monomer units and connects them to the newly formed chain. This step is known as *propagation* and occurs very quickly. Other steps involved in polymerization are different kinds of *chain transfer* – steps in which the chain bound to the catalyst "breaks" away and the catalyst start to generate a new polymer chain. These steps are much slower than propagation, so the polymer chains formed by the catalysts I study are typically quite long (hundreds of monomer "links").

Scheme 1.5. Two of the steps in catalytic olefin polymerization. Note that the catalyst contains other components, known as *ligands*, which have been omitted from this image. Bu = butyl = $CH_2CH_2CH_2CH_3$.



Now that we have overviewed the process of catalytic olefin polymerization, it is possible to discuss the specific details about some of the research I performed over the past five years.

Chapter 1.4. My Work

Over the past five years, I have tried to develop ways to address a single question: how do we monitor the nature of the catalyst (the catalyst *speciation*) during polymerization? As seen in Scheme 1.5, the catalyst can assume many forms during polymerization. Because the first step of polymerization (*initiation*; the initial chain "grabbing") is slow, some of the catalyst may not have reacted, especially during the beginning of the polymerization. Alternately, some catalyst could get lost during the chain transfer step or through other processes we do not know about. If the nature of the catalyst cannot be determined in solution, then accurate kinetics are not possible and the reaction mechanisms we have proposed may be incomplete.

I have developed multiple strategies to address this question. One way to determine catalyst speciation is by studying the products of polymerization. Remember that, during catalyst initiation, the first monomer "link" is bound to an endgroup which was previously attached to the catalyst. If we use an endgroup that can be detected later, then we can "count" the number of catalyst centers which initiated during the reaction. Specifically, with the help of Dr. Bolin Zhu, my group designed a labeled catalyst and used it to synthesize polyhexene. Then we injected the polyhexene into an instrument which *fractionates* (separates) the polymer chains based on chain length. One of the detectors at the end of the instrument detects all polymer that comes out (*elutes*) from the instrument, while another detects only the polymer label. This is the first time this strategy has been used to "count" the amount of active catalyst, and a paper describing our research was recently accepted by a prestigious journal.

Another way to determine catalyst speciation is by following the polymerization *in situ* using analytical techniques such as NMR spectroscopy. Typically, NMR spectroscopy monitors all species in solution at the same time. This is an easy approach, but it makes it very hard to detect species in low concentrations (such as the catalyst) when other species in solution (such as the monomer and polymer chains) have high concentrations. Researchers can compensate for the lack of sensitivity, but only by purchasing extremely expensive equipment or by reducing the number of data points collected during a single experiment. My innovation was to separate the method we use to monitor low-concentration species from the way we monitor high-concentration species and to rapidly switch between these two methods. This has allowed us to monitor faster reactions and has also let us detect several previously unnoticed steps during reactions.

These new methods will be useful during future investigations into catalytic olefin polymerization and other catalytic processes that are of interest. Hopefully, the insights offered through these investigations will help chemists in the future to improve the catalytic processes which have already contributed so much to society.

Chapter 1.5. References

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