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Assessing and Optimizing the Performance of Photoredox-Mediated Metal-Free Ring-Opening Metathesis Polymerization in Batch and Flow Reactors

By

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Chapter 5

Polymer Chemistry for the General Public

Section 0: Who's this chapter for, and why is science communication important?

This chapter is meant for anyone interested in learning more about chemistry and what chemists do! The preceding chapters of my thesis that describe my research are written with chemists as the audience, so there are various technical, chemistry terms thrown around which make it harder for non-chemists to follow these chapters. In this chapter, I'll describe my research (mainly from dissertation chapters 1 and 4) for **anyone** that's interested but doesn't want to be slowed down by scientific jargon.

Describing one's own research so that a wide audience can follow is a huge skill called science communication, and I've worked hard to develop this skill over the course of my graduate schooling. Science communication is a vital skill for any scientist, because at some point we hope that non-scientists will be able to use our research. This means we need to explain the motivation behind our research and how to use our research to people that are interested in listening.

Science communication is also important to me as an educator. Students that take general chemistry and organic chemistry (usually not because the students want to but because their major requires it), walk away never wanting to look at chemistry again. This is a problem that educators need to address. We see chemistry as a beautiful, logical science, but we still have trouble motivating learning students that don't see the full picture yet. I strive to describe my science in interesting (but still accurate) ways because when I eventually teach science, I want everyone to have the opportunity to love chemistry just as much as I do.

Section 1: What are polymers, how do you make them, and why are they important?

The word "polymer" comes from the Greek words "poly" (meaning many) and "mer" (meaning parts). A polymer is a molecule formed by stringing together smaller molecules called monomers ("mono" meaning single in Greek). You can make a polymer by taking a molecule and then combining it with itself over and over again.

Making polymers is like using LEGO building blocks at the molecular level (see Figure 1 on the next page for an illustration of this analogy). You can combine these different little pieces and make them into a variety of structures to achieve a multitude of material and chemical properties. The length, sequence, and structure of the polymer can greatly affect its characteristics, and the ability to combine these molecules in many different ways to create many different properties is why we frequently encounter polymers in everyday life. Plastics, spandex, rubber, Kevlar, tree bark, and even DNA—these are all examples of polymers!

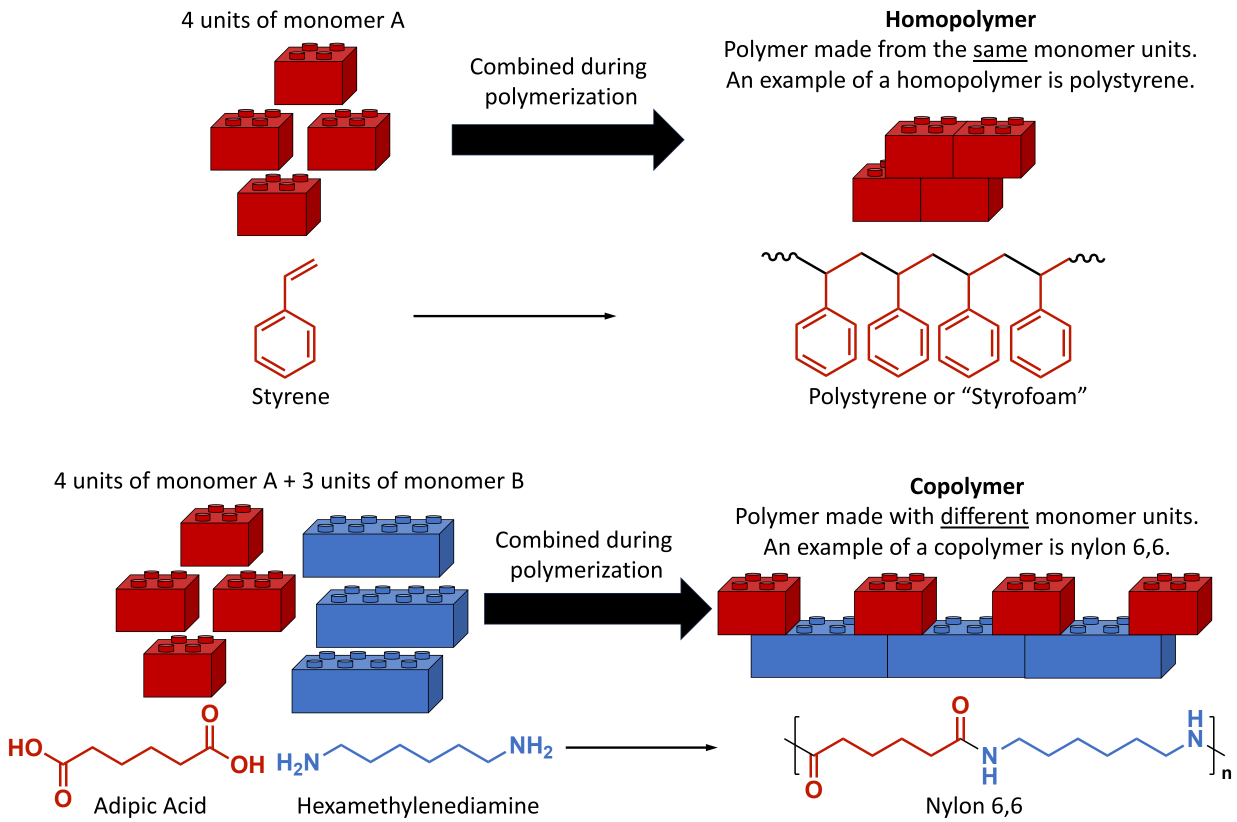

Figure 1. Comparing polymers to LEGOs. Polymers are very similar to LEGOs—both are made from smaller units and can be combined in different ways to make a multitude of different products. Shown is an example of a homopolymer ("homo" meaning same) and copolymer ("co" meaning together). The homopolymer consists of the same one monomer combined over and over again, while the copolymer consists of many different monomers combined together. Polystyrene, (commonly called Styrofoam, the material frequently used for coffee cups) is a homopolymer. Nylon 6,6 (the clothing material) is a copolymer made from the monomers adipic acid and hexamethylenediamine. Fun fact: LEGOs are actually made from the copolymer ABS (acrylonitrile butadiene styrene, a polymer made with 3 different monomer units).

Section 2: What's the role of a polymer chemist, and what are the problems they solve?

Polymer chemists have this really interesting job. We make polymers, study their properties, and figure out ways to more easily manufacture them. To study polymers, we use different types of equipment to determine molecular properties (like how long each polymer is) and physical properties (like how strong the polymer is). We then try to figure out how these different properties are related so we can design polymers with specific properties.

The polymer chemistry field also has a challenging problem: we need to make enough polymers to meet the ever-growing demand for polymer products, which is projected to reach over one billion tons by 2050, but we also need to do this sustainably, because we don't want plastic trash everywhere, and we want to make sure our polymers aren't environmentally toxic.

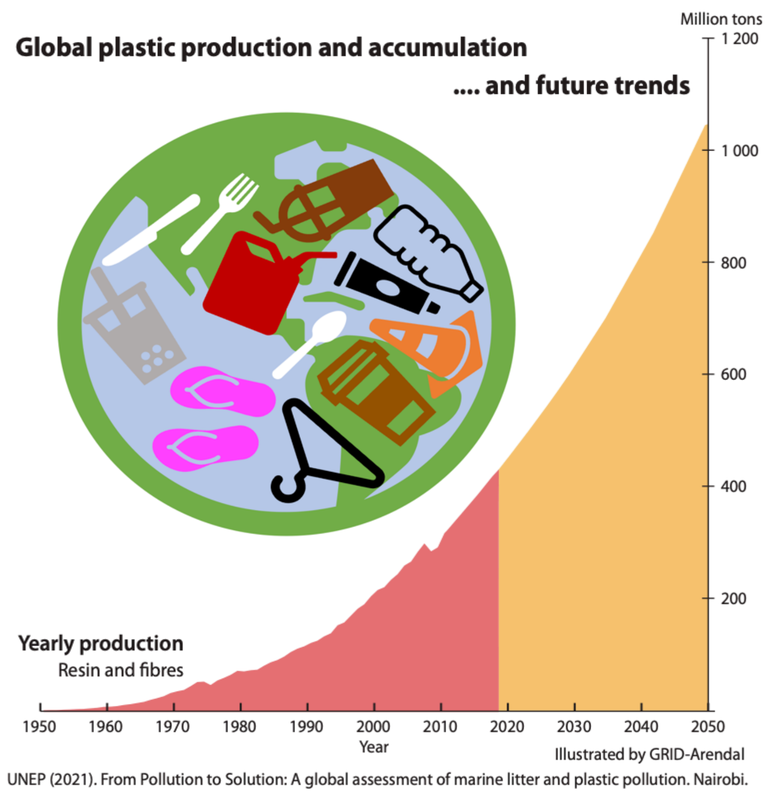

Figure 2. Plastic production forecast through 2050. Red area represents measured data, orange area represents forecasted data. Reproduced from Grid-Arendal UNEP (2021).

Section 3: What research are you working on, and how are you solving these polymer sustainability problems?

My primary research goal is to prepare a polymerization performed in a small-scale university laboratory for a large-scale industrial laboratory or factory. I optimize the polymerization process by testing different reactor setups making it safer, greener, and more efficient. For example, I may take a product stirred in a small glass jar the size of a thumb, and mix it in an even bigger glass jar the size of a refrigerator. Or if you don't need to stir it, I can run the reaction mixture through something called a flow reactor, which is just some tubing that allows your reaction to occur (a flow reactor is similar to a water faucet except instead of water coming out of the faucet, the polymer product comes out). In flow reactors, scaling up production just requires faster flow speeds (like turning the faucet on higher) instead of larger reactor volumes. But the specific polymerization that I'm studying is a bit trickier to make efficient.

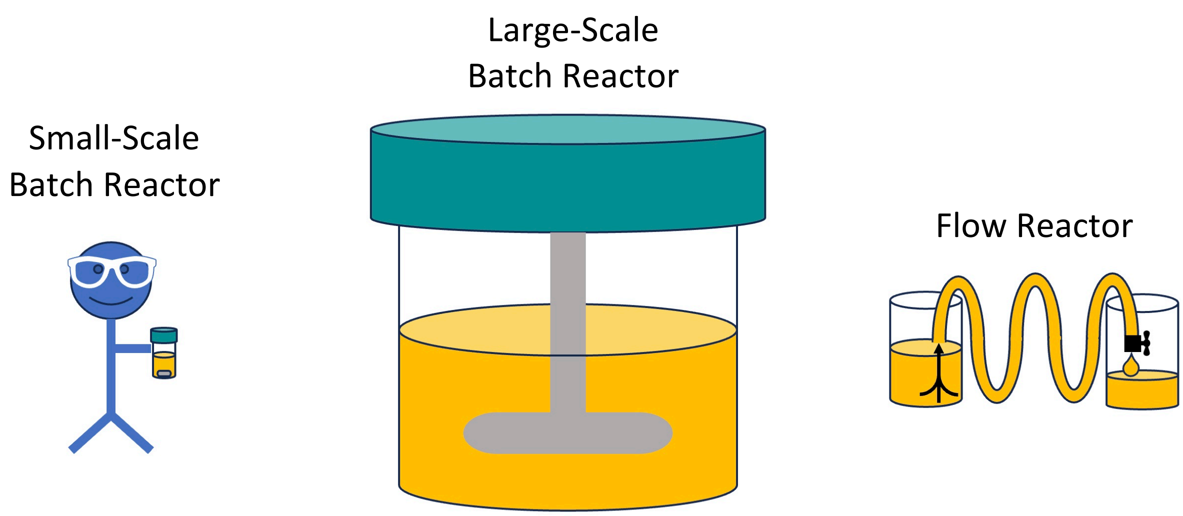

Figure 3. Graphic of small-scale batch, large-scale batch, and flow reactor setups. Approximately to scale.

I'm studying a polymerization where the building blocks are molecular rings and the polymer is made by breaking open these rings and stitching them to the next ring. Normally, the rings are hard to break apart, like opening a nut with only your hands. Fortunately, we can use molecular nutcrackers—reactive, toxic metals—to crack open up the donuts. After these rings are opened, the metal also stitches them together. But since we use toxic metals in the polymerization, (1) you can't use these polymers in any biological applications and (2) discarding them becomes an environmental hazard (this ring-opening chemistry is so effective and efficient that it won the 2005 Nobel Prize for Chemistry). To avoid using these reactive metals, my research group found an alternative way to open these rings: we use visible light to crack them! Now that we use light instead of metals for the polymerization, we can use these polymer products for any application we want, and it's safer for the environment.

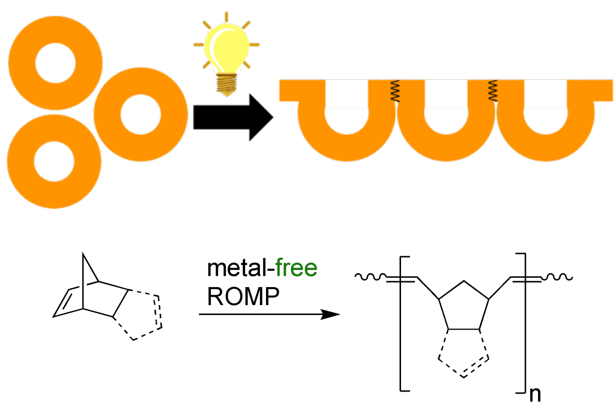

Figure 4. My polymerization of focus. It's called metal-free ring-opening metathesis polymerization (MF-ROMP), which is the scientific way to describe that the polymerization involves opening up molecular rings! The product polymer can be used as sound-proofing material, car plastic, clothing padding, or even oil-spill cleanup material.

However, using light adds an obstacle towards scaling up the polymer production. How we make the polymer is by stirring a liquid in a small glass vial and then shining a bright blue LED on it. But if we try using a bigger glass jar, the light isn't strong enough and won't reach the center of the jar. (You can think about it like trying to use a flashlight on a faraway object at night—even when you use a laser pointer, your light can't reach the moon!). This is problematic because then the polymerization will only occur on the exposed side of the reactor, making the process really inefficient.

Another alternative to a bigger batch reactor is using an unstirred flow reactor. In this case, the tubing is usually narrow enough so light penetration isn't an issue, but now the reaction is inefficient for a different reason. Since we can't stir the reaction solution, the only mixing that occurs comes from diffusion (the natural tendency of liquids to mix themselves, try dropping food dye in water and watching it mix itself), which creates a significant amount of inconsistency in the polymerization process. It's like adding all the ingredients of cake into an oven without mixing it—you won't make a very good cake!

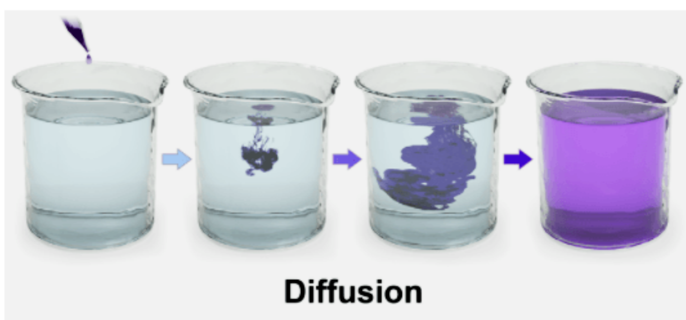

Figure 5. Graphic of diffusion using purple food dye in water. The leftmost image shows the water right before the food dye was added. The adjacent images show how the dye mixes into the water via diffusion over time until the dye looks evenly distributed within the water (Even at this last point diffusion occurs, but we can no longer observe it because it no longer produces a color change). Graphic from BruceBlause CC By 3.0 via Wikimedia Commons.

So we can't achieve an efficient polymerization using a large-scale batch reactor (because of light penetration) or a conventional flow reactor (because of mixing issues). So I looked at ways the scientists get better mixing in flow reactors, and found something interesting… There's a reactor design where you mix a flow reactor! It's called droplet flow, and you pump liquid and gas through your flow reactor at the same time. This forms liquid droplets sandwiched between gas, and doing this actually causes your droplets to mix themselves. **Figure 7** shows this droplet flow reactor in use; you can see the yellow reaction solution sandwiched between the gas. Even after discovering this reactor setup, the polymerization wasn't efficient yet—I had to figure out what gas, temperature, light, and amounts work best. Let's think about cakes again. To make a great cake recipe, you need to know exactly how much of each ingredient to add, what oven temperature to use, and how long to cook your cake. You figure this out by comparing to others' cake recipes, learning from your past attempts, and harnessing your baker's intuition. This is basically how I came up with the final reactor optimizations!

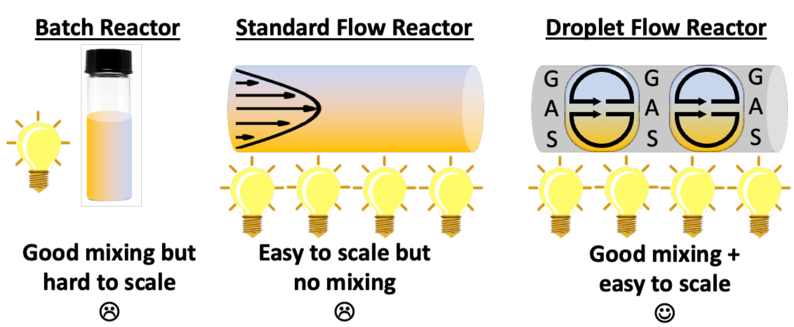

Figure 6. Comparison of the different reactor setups specifically for a polymerization that uses light.

Section 4: What excites you about this research project? What are the results of your research?

Throughout this research project, I worked on the cutting edge of polymer science, photoredox chemistry, and reaction engineering, and I got to learn new strategies and techniques every day. I'm also proud that this is the most efficient setup to make polymers this way as of 2023. You can reach 95% polymer conversion (the percentage of donuts that become polymer), and you can actually make a few pounds of polymer a month this way! I've been in contact with a company that's interested in adopting my reactor setups to help make their polymers more sustainable.

Figure 7. Image of the droplet flow reactor in use.

Section 5: Acknowledgments

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