# Reimagining Plastic: New Approaches to Making and Recycling One of the World's Most Useful and Problematic Materials

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Plastics are familiar. If you look around the space you are in right now, there is almost certainly something plastic in your view—plastics are simply all around us. Things of course were not always this way. Over the past century, plastic has transformed human spaces and day to day activities in many positive ways. Our societal reliance on plastic also poses challenges.

Initially, plastics were synthesized in order to replace hard-to-obtain natural products. Examples of early plastics included a material that was made to replace ivory in billiard balls and another that was made to replace shellac, which is a natural resin that comes from the excrement of the lac insect. The development of plastics provided opportunities to synthesize useful materials where and when they were needed.

The first plastics were synthesized in the mid-1800s, though this was certainly not the time they entered mainstream society. In the 20th century, plastics became more and more prevalent, and the plastic industry emerged during World War II. Nylon was an early material that was first made in bulk during World War II in order to replace silk fibers and found especial use in parachutes. After World War II, the new plastic industry that had suddenly grown in order to support the war effort began to introduce plastics as a commodity to the general public.

The etymology of the word "plastic" from ancient Greek and Latin relates to molding, forming, or shaping. Chemically, plastics are polymers, long molecules made from many repeating units called monomers. Notably, in addition to controlling the chemical identity of the polymers that comprise plastic materials, chemists could also control the three-dimensional shapes of the resulting materials. Compared to natural solid materials such as metals or wood, the development of plastic manufacturing increased the tunability and ease of three-dimensional material control. What made plastics distinct was not this polymeric chemical structure, for there are many naturally occurring polymers, including DNA, wool, and silk. But plastics were polymers that were synthetically produced, meaning that these non-natural materials were synthesized in a lab, either on a research scale or an industrial scale.

As plastics were becoming more and more mainstream, the chemist Victor Yarsley wrote to a colleague in 1941, "Let us try to imagine a dweller in the 'Plastic Age.' This 'Plastic Man' will come into a world of color and surfaces . . . a world in which man, like a magician, makes what he wants for almost every need."[1] I imagine many polymer chemists over the last century sincerely sought to do good for the world by inventing these new materials, and in fact these chemists have done good things for the world. They invented robust materials; these days we use these plastic materials for applications that include water pipes and gas pipes, which are conventionally made of polyvinyl realize by reflecting on the last time you had blood drawn or the last time you got a vaccine; plastics facilitate these activities. Plastics permeate the toy industry and are components of electronics. Because plastics are affordably manufactured and easily tailorable, they are useful in a wide array of applications. Plastics have been a major part of heralded technological developments, and society has come to embrace these materials.

Despite these positive attributes of plastics, their story undoubtedly also has ugly sides. The enormous scale at which plastics are produced and their manufacture from fossil fuel sources results in a costly environmental burden. In addition, at end-of-use, plastic waste often enters the environment as pollution and conventional plastic recycling processes cannot sustainably manage plastic waste on the scale it is continually being generated. Given our societal dependence on these materials, chemists are working to reimagine plastics for a more sustainable future.

## CHANGING HOW WE MAKE PLASTICS

In any chemical reaction that is done on a significant scale, it is worth considering the chemical origin of the starting materials. If I were, for example, to complete a polymerization reaction in my research laboratory, the precursor materials would come from the chemical storage cabinets in my lab or from the department stockroom. Before that, they would have been ordered from a chemical company. But this is not where they originated. Plastics are polymers made mostly of carbon atoms, so where did those carbon atoms come from? To find out, we must evaluate the reaction pathway that leads from the natural source of carbon to the final product. In the language of chemistry, this is accomplished by analyzing the retrosynthetic pathway, which traces the lineage of a complex molecule from its chemical precursors.

For example, let's consider nylon, the material produced for those World War II parachutes. In one form of nylon, nylon 66, 1,6-hexanediamine and sebacoyl chloride combine to create the endless repeating units that form the long molecules of nylon (Figure 1a). But what is the chemical origin of 1,6-hexanediamine? Retrosynthesis shows that 1,6-hexanediamine comes from butane (Figure 1b), which is naturally sourced from the fossil fuel natural gas.

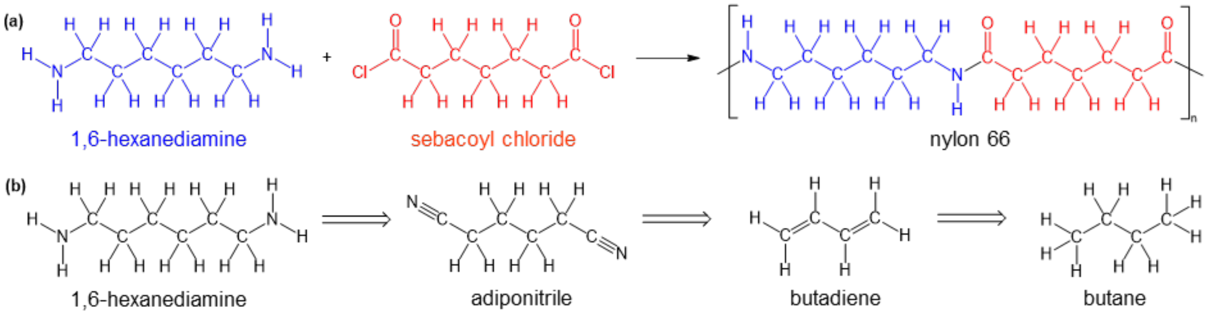


Figure 1. (a) Chemical synthesis of nylon 66 from 1,6-hexanediamine and sebacoyl chloride. (b) Retrosynthesis of 1,6-hexanediamine showing that butane is the carbon source of this material.

In fact, the carbon source of all major plastic materials is natural gas. The natural gas from which that nylon polymer was made may have been sourced from a fracking site, maybe one nearby to Juniata College in central Pennsylvania. The production of that natural gas likely has impacted the local economy in some positive and some negative ways. That natural gas may have passed through a natural gas pipeline, which likely disturbed the local ecosystem. And processing that natural gas certainly contributed to climate change. As is the case in the energy industry, the success of the fossil fuel industry is entangled in the success of the plastic industry.

The tools of research chemistry can help to address these problems. Recently, chemists have considered methods to source plastics from more-renewable carbon sources. Figure 2 shows a polymerization reaction in which one of the carbon sources is carbon dioxide, as renewable a carbon source as we can find. It is surely exciting to discover a chemical reaction like this one, but researchers didn't stop there. They can do much more in order to optimize the chemical reaction so that it produces the desired product in high yields, in short reaction times, and at low temperatures. One way to optimize a chemical reaction is by introducing a catalyst, which is a molecule that causes the chemical reaction to proceed faster and at lower temperatures. To do this, chemists need to understand how a particular catalyst functions in the specific chemical reaction. For example, researchers have shown that several different catalysts, including molecules that contain earth-abundant metals such as iron and aluminum, can improve the chemical reaction shown in Figure 2 with respect to its yield and reaction temperature. This produces higher quality plastic in terms of the length and uniformity of the polymer chains.

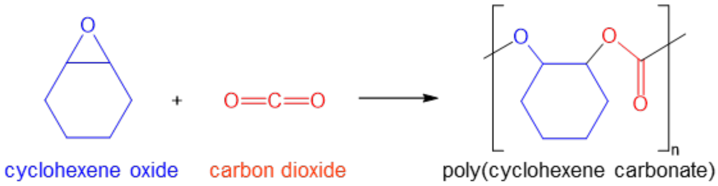


Figure 2. The chemical reaction of cyclohexene oxide and carbon dioxide, which results in poly(cyclohexene carbonate).

In my own research, I was motivated by reports showing that iron-containing catalysts could accomplish this chemical reaction.[2] However, as I read the literature, I recognized an opportunity for more systematic study of these catalysts. The catalysts that had been studied included molecular appendages, and these appendages apparently significantly influenced the reactivity.[3] However, the researchers often changed multiple variables at once and because of this, the influence of each controllable variable was unclear.

Therefore, my undergraduate research students and I have been working to make chemical compounds like the catalysts that were used in these studies, but we have systematically changed one molecular appendage at a time in order to measure the impact of each change. The results so far show that our changes influence their properties in ways that we anticipate would measurably change their performance in polymerization reactions. We are working to finalize and share details of this study so that these results help others further improve these iron-containing catalysts and therefore more efficiently synthesize polymers that are less reliant on fossil fuel carbon sources.

## NEW APPROACHES TO PLASTIC WASTES

The tools of research chemistry are also at work to solve a second major problem: plastic waste management. In addition to the readily identified plastic waste that can be seen floating in oceans and blowing across landscapes, plastics also break down in the environment to microscopic scales, creating microplastic pollution. These microplastics are consumed by organisms low in the food chain and accumulate through the food chain, leading to a host of biological challenges.

One challenge of plastic waste management is the massive scale. Humans globally generate about 300 million tons of plastic annually, which is an enormous amount of waste to responsibly manage. What happens to all this waste? Current estimates report that about 9 million tons are released into the environment as pollution.[4] The remaining plastic waste stream is treated in varied ways. The vast majority of it goes into landfills. Another component of the waste plastic is burned, releasing carbon dioxide into the atmosphere, and the heat of combustion is used to generate electricity. Only a small portion of plastic waste is recycled; in 2018 the portion of U.S. plastic waste that was recycled amounted to just 9 percent.[5]

Perhaps you have a conventional view in mind when you think about plastic recycling. You put plastic waste into a big bin and bring it to the curb each week. A truck picks it up and takes it to a recycling center, where it is sorted based on the number it is marked with. (Each different numbered plastic has a different chemical formula.) Once it is sorted, it is cleaned, melted, and then new things are made from the resulting material. In fact, I have presented exactly this scenario to my four-year-old, and he most definitely thinks that recycling is cool.

Unfortunately, plastic recycling is more complicated than this. For the most part, when plastic waste is recycled, it is turned into new plastic products. But what typically happens is a process called downcycling, where something of greater value produces something of lesser value. One familiar way we experience downcycling is in paper recycling, where new high-quality white paper is recycled to make cardboard or tissue paper. The reason downcycling occurs is because plastic recycling is a purely mechanical process; the plastic waste is ripped to bits, heated up, and cooled down, but the chemical structure of the polymer is unchanged. This process weakens the material properties of the plastic—for example making it softer or more brittle—so each time the plastic is recycled, its properties diminish. Because of this, plastic materials can be recycled between one and five times and then are finally used in terminal applications, in which the material properties of the plastic are less important. One example of a terminal application of plastics is carpet fibers. After such use, the plastics become trash and are likely landfilled. I recall elementary school lessons in which I learned about recycling as a circular process, but plastic recycling is in fact a linear process; sometimes it is linear with diversions in it, but for all plastics, chemicals that are mined from the ground and reacted to form robust materials eventually are converted to waste.

There is even more disappointing news about plastic recycling. As it turns out, not all plastic waste we place in our curbside bins is ultimately recycled. Before 2017, much of the plastic waste that was collected curbside in the U.S. was being shipped internationally. China, for example, accepted waste from all around the world, recycled what they could, and sent the rest to landfills. Most of the countries the U.S. formally partnered with in this way have now ended these programs. Meanwhile, in the U.S. we have failed to develop a robust enough plastic recycling system of our own to facilitate recycling of all of our waste plastic; therefore, much of what is intended for recycling is landfilled. This is driven by simple economics: for almost all plastic materials, the cost of recycling exceeds the cost of sourcing new materials.

Given these issues surrounding plastic recycling, we must adopt alternative approaches to plastic waste management. These strategies include biodegradation, upcycling, and an approach called chemical recycling to monomer.

Biodegradable and compostable plastics may be familiar to some readers. They are often synthesized from renewable carbon sources and can decompose to environmentally safe non-polymer forms given the proper conditions: sunlight, water, and non-extreme temperatures. The most popular of these biodegradable materials is called polylactic acid, or PLA. In the life cycle of polylactic acid, the carbon is sourced from plants, which are refined in a fermentation extraction process, and then processed and manufactured to make a plastic material. Following use, PLA can biodegrade so long as it is exposed to aerobic conditions (this is not the case in a landfill, where an anaerobic environment stops the biodegradation process). When broken down, PLA releases carbon dioxide, which is in turn reabsorbed by other plants, resulting in a truly circular process. In theory, this approach to plastic waste management is very attractive, though the material properties of polylactic acid present a major challenge. PLA is not a hard plastic; it can be used to make single use drinking cups, but cannot be used to replace the materials that Legos or pipes or syringes are made from.

Another approach to plastic waste management is called upcycling. Whereas downcycling is taking something of higher value and turning it into something of lesser value, upcycling involves taking something of lesser value and turning it into something of greater value. Some recently reported progress in plastic waste management is the conversion of plastic waste to fuel. For example, in one recently reported study, shards of polyethylene underwent chemical reactions to produce diesel, gasoline, and other fuels.[6] While exciting, it is perhaps worth noting that this upcycling example is a linear process; carbon-containing chemicals are mined from the ground, turned into usable plastic materials, then, at end-of-life of the plastic, are turned into a usable fuel, then finally emitted to the environment as waste carbon dioxide.

An approach to plastic waste management that especially interests me is the concept of chemical recycling to monomer. This process is identical to conventional recycling except that it is truly circular. Recall that plastics are synthetic polymers, which are long chains of repeating monomer units. In contrast to conventional recycling, the process of chemical recycling to monomer is not simply a mechanical process of ripping apart the polymer and reforming it into a new shape. Instead, this process chemically breaks the bonds that hold the polymer together, deconstructing the polymer to its constituent monomers. Those monomers can then be used to build new polymers, which can then be converted back to monomers. Because the monomers have no memory of where they came from, they can be repeatedly rebuilt into plastics with properties that match the quality of the virgin material.

In order for chemical recycling to monomer to be feasible, the polymerization reaction used to synthesize the plastic material must be able to occur in both directions (monomer to polymer as well as polymer back to monomer). Many chemical reactions are reversible and can occur in either direction (reactant to product or product to reactant) depending on the reaction conditions. However, some chemical reactions, including some polymerization reactions, are irreversible. This is because some monomers have such an energetic driving force to become polymers that once they are polymeric, the reaction cannot be reversed. Plastics that cannot depolymerize to form monomers include polyethylene, polypropylene, and polyvinyl chloride (PVC). But other polymers can be guided back to monomers by adjusting the conditions. I previously described that to form polymers from monomers, chemists usually use compounds called catalysts. With the help of well-designed catalysts, some polymers can also depolymerize to produce monomers. For example, this approach is theoretically achievable for polystyrene, which is the polymer Styrofoam is made of, and for which there are no other good waste management strategies, and for polyethylene terephthalate (PET), which is a polymer that is often used to make plastic bottles.

Researchers have increasingly advocated that depolymerization should be a focus of polymer research, and that chemists should be thinking about depolymerization catalysis distinctly from polymerization catalysis.[7] My research students and I are entering this field of depolymerization catalysis by considering a class of polymer materials called polylactones, which include a chemical commonality called an ester linkage. Some of these polylactones have useful thermal properties and some have been shown to be capable of depolymerization. We are using published research to understand the polymerization reactions of polymers of this type as we work to establish reaction conditions that result in depolymerization. We anticipate this research will help to demonstrate depolymerization catalyst design principles that can be applied to plastic waste management through the strategy of chemical recycling to monomer.

Current approaches to plastic manufacturing and plastic waste management are troubling because plastics are sourced from fossil fuels and because of insufficient recycling strategies. But alternative approaches are possible, and I am continuously motivated by the energy my undergraduate research students bring in their efforts to contribute to solutions to these problems. Still, chemists will not reimagine plastic alone. Solutions to challenges posed by our societal reliance on plastic will require the interest, imagination, and dedication of the chemical research community, public policy makers, and engaged citizens.

NOTES

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