Reduce, Reuse, Recycle:

Recovering 100% of Your Plastics by Refining Polymer Synthesis

Dr. Brooks Abel is an organic chemist and synthetic polymer researcher at UC Berkeley. After graduating in 2009 from the University of Southern Mississippi with a bachelors of science degree in polymer science, Dr. Abel worked at the National Institute of Standards and Technology and became a National Science Foundation Graduate Research Fellow in 2010. Dr. Abel obtained his Ph.D. in polymer science at the University of Southern Mississippi in 2016 and from 2017 to 2021, Dr. Abel worked as a postdoctoral researcher at Cornell University. Since 2021, Dr. Abel has worked as an assistant professor and researcher in the College of Chemistry at UC Berkeley.

With the Abel Research Group at UC Berkeley, Dr. Abel researches organic polymers, plastics, and their synthesis and selective catalysis. His research is motivated by finding solutions to sustainability and recycling issues with the end-of-life fates of synthetic materials and finding new polymerization and catalysis methods to meet those applications and solutions.

INTERVIEW WITH: BROOKS ABEL

BY: RIAN GRANT, ROHIT DIVEKAR, AND SANIA CHOUDHARY

BSJ: How did you get into research on plastic recyclability? And what prompted your research on, CRM, chemically recycling monomers[1], rather than, mechanically recycling or biodegradable plastics?

BA: I wanted to work on some big societal issue, so there was some actual impact potentially on the other side of what I was working on. Polymer plastics are a big picture in science, and the biggest problem in plastics is sustainability.[2] We're producing hundreds of millions of tons of plastic per year, and it's a linear lifespan. Essentially, only a small percentage of plastics, 10% or less, are actually recovered and reduced. Then you have a large percentage into the environment, and then the rest of it just goes in the landfill. From a synthetic polymer chemist point of view, the idea is we're making these existing plastics that were not designed to be recycled. They were designed because they have every property you could ever imagine. They're the perfect materials, until you get rid of them. So what do we do?

There's different ways you can approach recycling. One is the recycling you think of, mechanical recycling, in which case the plastic never gets back to its original application. Recycling facilities work to sort polymers out of trash to reuse, but there is always some contamination. So whenever you mechanically recycle plastics you can't get it back to its original application. Mechanical recycling is good for answering how we should handle the existing waste. The other option is biodegradability, something that you hear about a lot in compostables. Biodegradable polymers are challenging to recycle, but you can throw it out, grind it up and combine it with soil to compost it. Overall biodegradability had a good end of life, fate as it won't accumulate in the environment, but you still don't get plastics fully back.

The last strategy, that our group approaches, is called CRM, or chemically recycling to monomer. In CRM you depolymerize the plastics back to its original monomer.[3] The process requires a polymer that you can trigger the depolymerization of so that you have the option to distill off and recover the monomer. With the recovered monomer you can make the polymer over again. With CRM you recover all of the atoms that were in the original polymer without any impurities or additives, even if it was contaminated with other types of plastic.

BSJ: What makes a good candidate for these types of polymers, what are some challenges in choosing materials necessary to make CRMs?

BA: There's a thermodynamic component here.[4] If you want to form a polymer, it has to be thermodynamically favorable. But how do you depolymerize something that favors being a polymer? We have to make polymers that are in this sweet spot where there's enough driving force that the polymer wants to form, but not so

INTERVIEWS

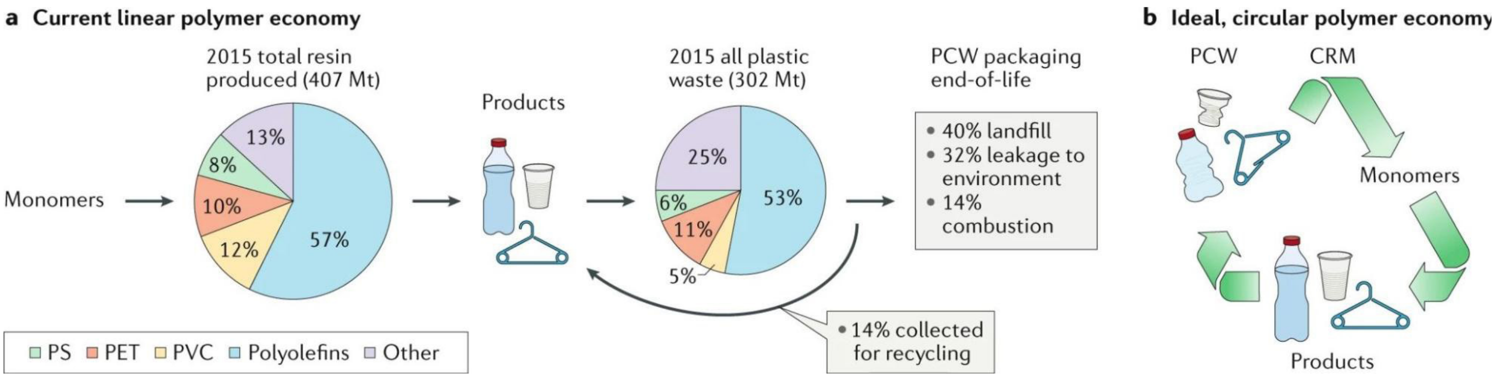

Figure 1: Comparing the Ideal Forms of Recycling. Under section a (left hand side) the linear polymer economy is shown along with a depiction of the percentages of recycled plastics that end up in landfills, leakage to the environment, combustion versus recycling. Under section b (right hand side) the goal cyclic polymer economy is shown.

much that you can't "unzip" the polymer.

We use this number called the ceiling temperature to describe the ability of polymers to depolymerize. Polymers generally want to depolymerize above their ceiling temperature, and they want to be polymers below the ceiling temperature. If you have a low enough ceiling temperature, you can heat the polymer up with an appropriate catalyst to trigger the depolymerization and it will go back to its monomer, so we design polymers that have low enough ceiling temperatures that we can access them.[5]

How else do you control the thermodynamics so there is just enough driving force to make the Polymer, but not so much that you can't undo it? You need heteroatoms in the backbone that can break down easily.[6] Those are going to be things with oxygen atoms and nitrogen atoms that have weak bonds.

Heterocyclic monomers check all these boxes. You can put the heteroatom functional group in an atomic ring, and pop open the ring during the polymerization step to create the chain.[7] Then we can control the thermodynamics of polymerization by using a five, six, or seven membered ring that is just strained enough to pop open in a polymer, but not so strained that it can't return to the ring monomer.

BSJ: How do you polymerize these heterocyclic rings?

BA: A polymer chain end has a reactive species on the end, that the monomers continually add to.[8] We describe the type polymerization based on what's on the end. Anionic polymerization means you have some negatively charged species on the system.[9] Polymerizations of things with these types of cyclic units are pretty well established, you can make all kinds of different molecular weights and lots of versions. But there's an entire world of really promising classes of monomers that can only be depolymerized by cation ring opening polymerization.[9] The reaction here involves some cationic species up against the polymer, that the monomer reacts with causing the monomer ring to pop open and form that same cation over again. The classes of monomers that can be heterocyclic and polymerized by cationic ring opening are a gold mine, if you're looking for ideal monomers and polymers for sustainability.

BSJ: Given the "gold mine" these monomers are, what are the challenges in actually getting to the "gold," or making the desired polymers?

BA: There's a difference between making a polymer and making a polymer well. Hexane, for example, is a volatile, flammable liquid. Its polymer is just all carbons connected together. At 18 carbons, you get something like wax or fatty acid chains. At a few 100 or a few 1000, you get polyester, which is fundamentally different. Both materials are just carbon atoms connected together, but they have different molecular weights and it drastically changes the properties. So aside from the chemical identity in the polymer, the next single, most important parameter is molecular weight. The issue with cationic heterocyclic ring-opening is that it is difficult to control the molecular weight. If you can't get high molecular weight polymers, they aren't that useful.

We want to be able to control the molecular weight. How do I do that? Well, you need a reaction that's so good, you repeat the reaction in the same molecule upwards of 10,000 times without screwing up once. There's a lot of issues with catalytic ring-opening where the catalysts tend to interact with the monomer in the wrong way. The catalyst's job is just to form the cation on the end of the polymer. That's the catalyst's only purpose in life, but the problem is these catalysts are Lewis acids.[10] Lewis acids love Lewis bases and heterocyclic polymers are great Lewis bases.[10] So the catalyst interacts with the heterocyclic monomer, when it's not supposed to, and starts creating random polymer chains. Or the catalyst shuts down by the monomer tightly surrounding and binding to it.

BSJ: How do you develop catalysts that will not shut down or produce these random polymer chains?

BA: What we're trying to do, fundamentally, is improve the catalysts. We are reopening a whole world of these amazing polymers that in the 1970s and 80s, when people weren't thinking about sustainability, were "left behind." Now we realize they can be really great, we just have to fine tune the chemistry.

How do you make a Lewis acid like certain Lewis bases and not like others? Lewis acids sort of pinpoint one little functional group that they activate, and we want them to do that 10,000 times in a row so we can get high molecular weight polymers. Where we're at now is working with special catalysts that are silicon based, creating silicon Lewis acids. We found one silicon catalyst, for example, that the silicon is bonded to a fluorine. The silicon to fluorine bond is very strong. And so what we do is we put a fluorine on the end of the polymer, and exploit the fact that silicon loves fluorine and will select to attack the fluorine instead of the other atoms that need to stay on

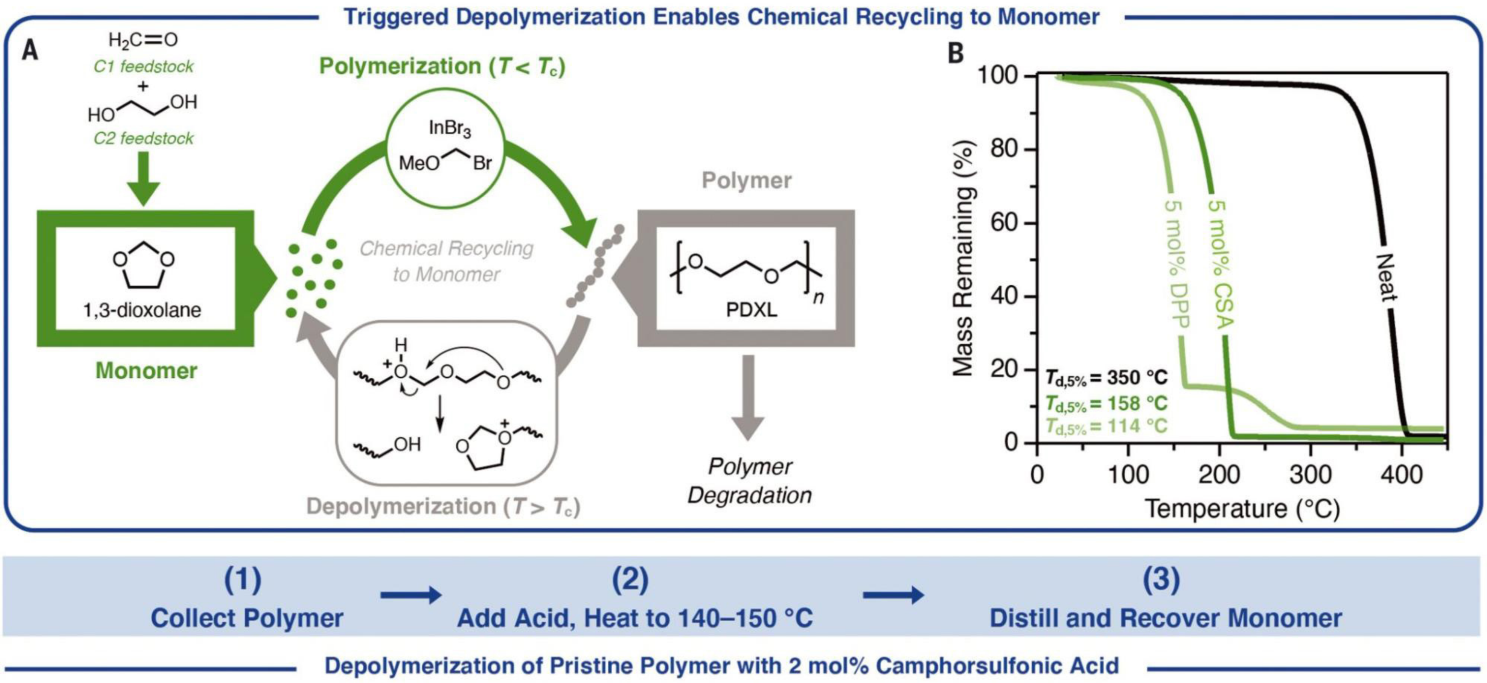

Figure 2: Reversible Reaction Scheme for Chemically Recycling to Monomer. The left hand side (A) depicts the general reversible reaction scheme for the monomer 1,3-dioxolane and its polymer PDXL. The Right hand side (B) shows the relationships between temperature and the remaining mass of the polymer. As the temperature increases beyond the temperature of degradation (higher than ceiling temperature Tc) the mass remaining approaches zero.

the monomer.

BSJ: When you are developing these highly selective catalysts, what are your main strategies?

BA: So we pursue different strategies. We have hydrogen bonding on our catalysts, where the leaving group is a phosphate, which are really good hydrogen bonding acceptors.[11] So the catalyst won't stick to the monomer because the hydrogen bond between the catalyst and the monomer is much weaker than the hydrogen bond between the catalyst and the phosphate. Halogens are also good leaving groups.[12] There's a lot of things out there that have a bromine or chlorine, or fluorine like the silicon example above. Then you need a catalyst that can pull off the halogen that is a hydrogen bond donor that selectively binds to halogens.

But each monomer is fundamentally different. Some monomers might bind to a catalyst more than others, and they might not be viable. Sometimes we choose a catalyst leaving group strategy that seems promising, and we just figure out which monomer it works for. Sometimes, I would want that specific monomer, and we figure out which catalyst works for that. So we build up libraries of catalysts and libraries of monomers, and we're always checking which works with which.

There's also the design and sustainability aspect of the catalyst itself. Once we figure out how and why a catalyst works, then we have a design principle for the next generation of catalysts. For example, I want to make catalysts lighter, more selective, faster. Another example could be that I want to use less catalyst. Or let's say you get some rare metal in your catalysts, that would not be very sustainable, you know? Well, maybe you could just use less of the metal. If you use a tiny amount of some rare earth kind of catalyst, then it's okay. Now you can make a kiloton of plastic with only a gram of catalyst. But I would say that's not necessarily our initial motivation when designing catalysts. Our initial motivation is to get anything to work, because it's so unprecedented to get control over these monomers, and then later figure out how to make it more sustainable.

BSJ: How do you come up with the inspiration or ideas behind these catalysts?

BA: We have to know the chemistry to be able to make these catalysts. We often make pre-existing molecules work for us. No one was originally designing these molecules as catalysts, but we use them as starting points because they already have a synthetic procedure and we don't have to invent a reaction. And then when we get a hit. We can spend a good six months trying to synthesize a catalyst, and you go run one reaction after another. I've done that. There was one epoxide synthesis I spent months and months and months on, and over 1000 reactions, trying to make work. So it's great to have a starting point someone else created. If an idea of ours isn't possible, and we're just making fancy crazy catalysts, we always keep it in storage in the freezer and maybe one day, 20 years from now, someone else is going to use it to create other molecules and/or catalysts that we never thought of.

BSJ: That's so funny, you're recycling this previous research to do research on recycling.

BA: Yeah, everything always comes back. And a lot of our research was opportunistic. We weren't originally trying to make recyclable polymers. We were trying to make polymer electrolytes for lithium ion batteries. We then asked, "how high molecular weight can I go?" Not that it was needed for the battery, but just to push the bounds of what we can do. Then we made a really high molecular weight, and the grad student I was working with, was like,"This is like polyethylene."[13] We were just trying to make 5000 grams per mole battery, but then we accidentally discovered cool properties in plastics.

BSJ: A bit of callback to when you discussed the importance of molecular weight control when making polymers: What else goes into controlling the molecular weight and fine tuning polymers besides having the perfect catalyst?

BA: Oftentimes we anthropomorphize polymers, so we call them living or dead. If the polymer chain can keep adding monomers, we say it's alive. If something happens, maybe a side reaction on the end of the polymer and it terminates, we say it's dead, they can't keep growing. To control weight we have to keep the chains alive. As long as they're alive, they keep reacting with monomers, and keep growing. There's lots of side reactions and types of termination that can happen and that are unique for each type of polymerization method. Within the catalytic type of polymerization method, polymers can terminate in certain ways that are unique to each monomer. We have to try to figure out, how do we prevent those side reactions from occurring so that my polymer chain doesn't die prematurely? We have to optimize the reaction conditions with the right solvent and temperature. For example, sometimes catalytic polymerizations have to be done at really low temperatures that freeze out, or lower the reaction rate of these side reactions.

Recently, we've developed something called immortal polymerizations. We've found ways in catalytic polymerizations to revive dead polymers. So imagine you have 100 polymer chains. They're all growing, and half of them terminate before they get to the desired point. We have strategies where we can have a growing chain transfer its cation to a dead chain and revive it. Essentially, now it doesn't matter if chains terminate during the reaction because they can be revived. Normally you would have to prevent every single termination event. But now it's a lot more forgiving.

These cation transfers, and transfer ability is another thing we pay attention to when modifying molecular weight. Sometimes the transfers happen on their own. Some polymers are inherently able to share their cations with the dead chains. It's a function of that particular monomer. It used to be considered a side reaction, but we realized it's actually a feature, not a flaw, and now we are hijacking this side reaction as a cation sharing mechanism. We use this feature to share a cation from a living chain to a dead chain and revive it so it can then reach the molecular weight we desire. The strategies we have to come up with beyond the catalyst development are primarily to suppress as many side reactions as we can. But if we can add immortality on top of it, then we can reach those molecular weights even easier.

BSJ: Once you've developed ideal catalysts, have found pathways to immortality, and overall created these fully recyclable plastics, how do you envision these CRMs being used in different real world applications?

BA: We figure out what its properties are, and then we predict what the application is. For example, we have a class of polymers called poly ortho esters, which are a very degradable functional group.[14] But what are the properties? No one's made a 1000 monomer unit poly ortho ester, and no one knew what the properties were. These polymer clusters that we made initially did not tell us much of their properties, some of them were grouped at 50k and even 80k and it wasn't until we got close to a couple 100,000 that

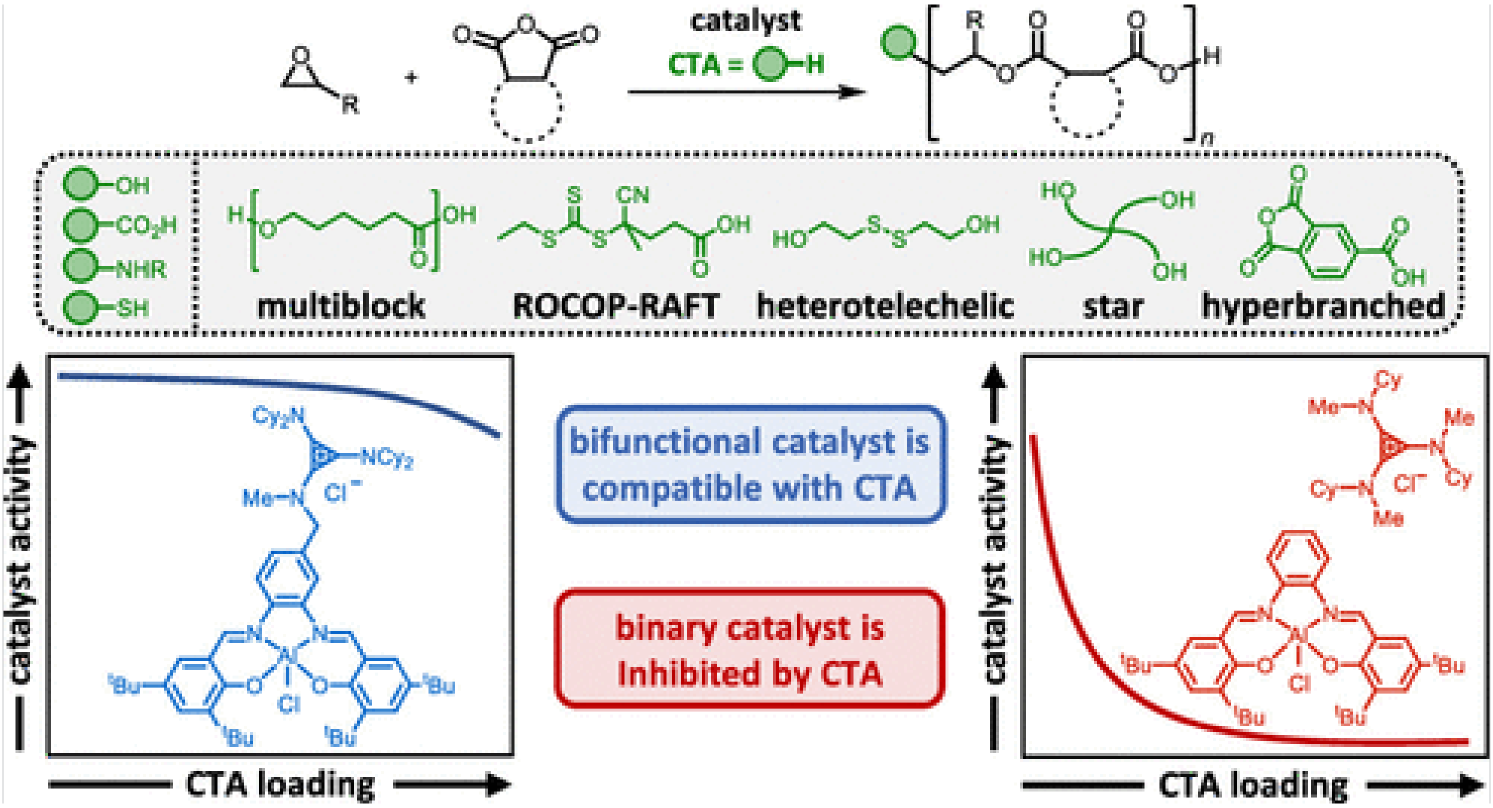

Figure 3: Multifunctional Catalyst. The bifunctional catalyst shown in the red and blue boxes is an example of the types of catalysts that chemists refine to control CRM mechanisms.

they started behaving like natural rubber. So then we realized, oh, we could use this as a recyclable version of natural rubber. A lot of times we know the polymer is going to get us some cool property. We don't know what it is, and then we kind of backtrack to figure out what the applications would be.

But if we ever had the application in mind, like, "I want to make the chemically recyclable version of polyethylene," we would have to go in with a lot better experimentation. Which of the 50 different monomers we have in our libraries is going to get me there? Once you get a hit, then we have to optimize its catalyst as much as we can. So there's a feedback loop there. Sometimes you choose the polymer application and you go after it. Sometimes we'll figure out what the properties are, and then dictate the application.

BSJ: What types of properties of polymers are most important to consider when judging their applications?

BA: When you talk about the properties, we like the idea of being able to make any molecular weight we want. With high molecular weight, polymers start to get stiffer and get harder to melt and process. The chains are enormous and tangled together, so you can't really melt the polymers. Instead they start to break and you can draw them into fibers. That's why many ultra high molecular weight polymers are made into high strength fibers. On the other hand, you don't need a water bottle that's eight times stronger than it is heavy, so you could target lower molecular weights for those polymers. So if we want a certain property, like a certain amount of toughness or rigidity, we use our data to determine at which molecular weight we can achieve that property through.

BSJ: All these applications of CRMs imply the introduction of these polymers into the plastics industry. What are the barriers of putting these out into the industry?

BA: Our big focus is to make something that depolymerizes, something that has interesting properties and checks all of those sustainability boxes. We have to consider, if you're making a "new plastic" that's going to be used on a 100 million metric scale, it is very important to think about the scalability of the polymers. We have pictures in our papers where we will have a giant chunk of polymer, and a small flask full of monomers that we made it from. These pictures serve to prove that one kilo of something we made in our academic lab is viable on an industrial scale.

Also, when you make something that wants to fall apart, you have to make sure it doesn't fall apart until it's supposed to. So it can't biodegrade on you too fast, and it can't depolymerize on you until it's time. For example, you wouldWn't want to use something acidic around polymers that are acid catalyzed, like pour tomato juice in it or store vinegar.

Another concern is lifespan, because biodegradable polymers can only be used in certain environments and for shorter time periods. One of the best applications of CRMs, is as a high volume, low value application, like single use packaging. How long is Amazon packaging used for? The product is put in a box. It's shipped to your house here in California, that's like hours, and then you throw it away, and/or you recycle it. So that packaging doesn't have to last for 10 years. That's exactly where CRMs would be great, when the thing is used for hours or days, not years. So that's where you're going to see the bulk of chemically recyclable polymers show up.

Another challenge with chemically recyclable polymers is, let's say you have a recycling facility and 1% of the polymers are chemically recyclable. You would have mixed acid with possibly millions of metric tons of plastic just to get 1% of it back. What do you do with all that plastic waste afterwards that you contaminated

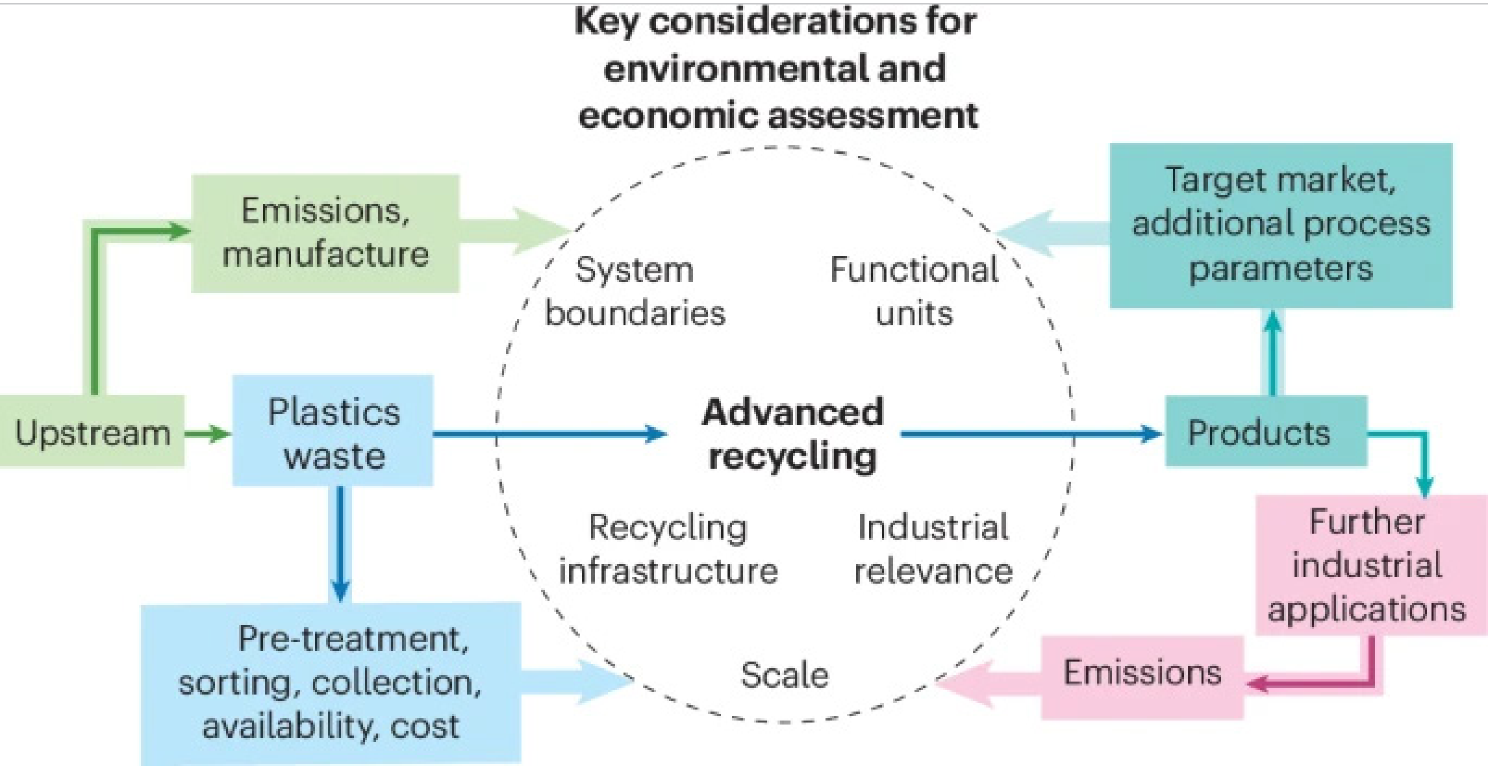

Figure 4: Considering Sustainability. Scientists and Policymakers have a complex web of considerations to weigh when determining the most environmentally friendly options. The above is only an example with some of the key considerations.

with acid? So there's also the issue of, how do you concentrate on what you isolate to be mostly chemically recyclable. So scale is important. If you're only making small amounts of material, it's not worth trying to recycle. So CRMs that actually get recycled need to be a high volume product, and there needs to be a good way to collect them. For example, current plastic like Coke bottles, you can save like, five cents by recycling. That's why that type of plastic is so highly recycled. Aluminum is also highly recycled, because there's a financial benefit in recycling it.

If 1% of the plastic that you've isolated is chemically recycled, it's not practical to isolate from all of that stuff. So there's a lot of policy making and implementation of infrastructure that would have to also come along with implementing CRMs successfully. How do you depolymerize something? We need a facility that does that. Every town can't have its own chemical recycling facility. You have to transport the polymer plastic to a place that does have chemical recycling facilities. Then you have to consider, does transporting that plastic have a higher carbon footprint than just making new plastic? One way we attempt to account for all these moving parts is to perform what are called Life Cycle Assessments, or techno economic analysis, where professionals actually go in and count what is the actual carbon footprint and what is the actual benefit for the environment of making this new plastic? Is it actually more sustainable?

Then another challenge with recycling is the plastic ends up in the consumers' hands. Recycling only works if people do the right thing, which is put it in a recycling bin. How do you convince the consumer to do the right thing? You cannot always rely on all people to do the right thing. So if you have a perfectly recycled material, if it doesn't go in the recycling bin, it does not matter, at least in the environment, you're never getting it back. If it goes in the trash, it's not even going to degrade.

There is so much to consider, it's really, really complicated. Sometimes the non intuitive solution is actually the better one. How do you educate your average consumer so they can make those decisions that are not intuitive?

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IMAGE REFERENCES

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