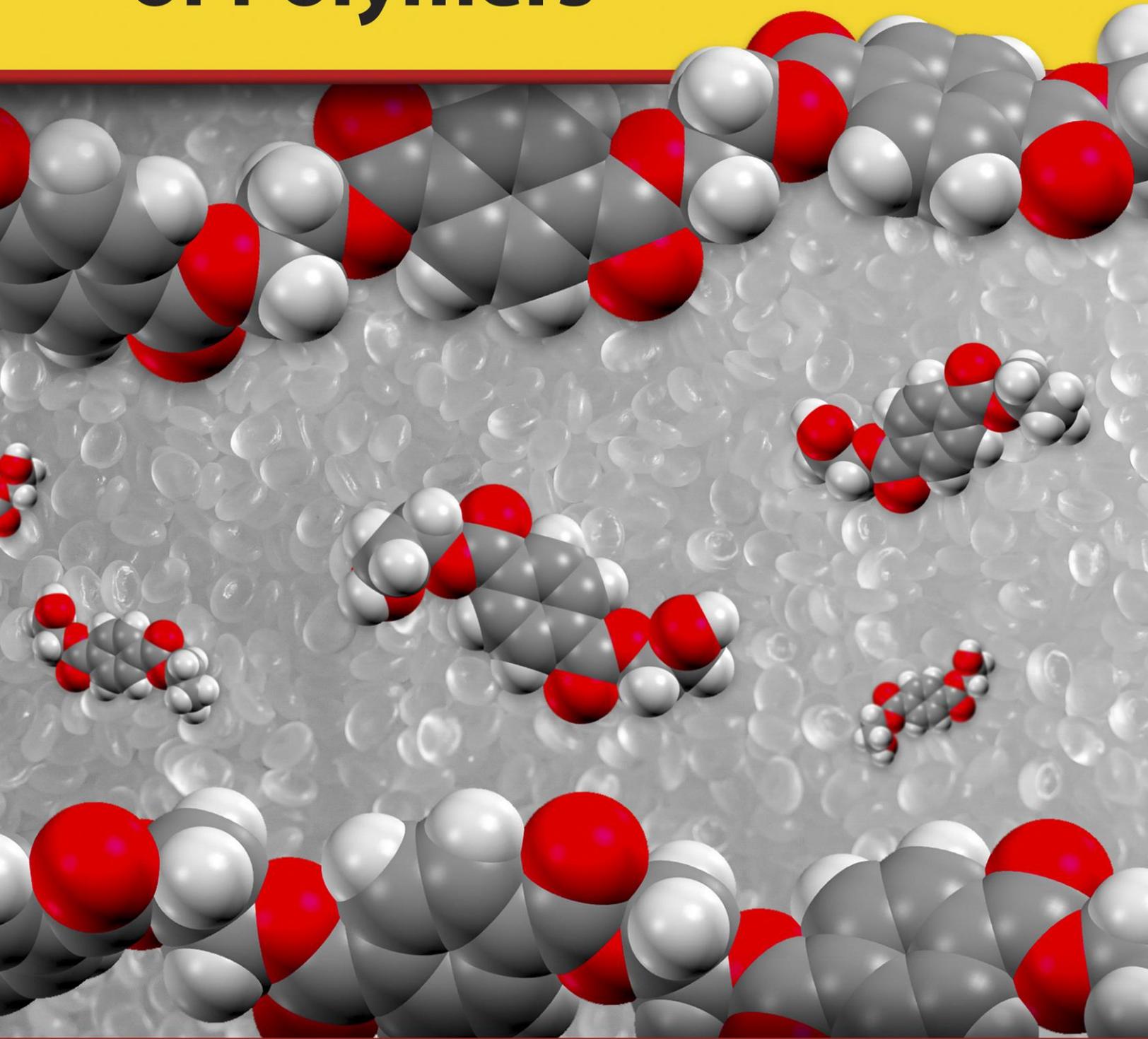


**Basic Energy Sciences Roundtable**

# **Chemical Upcycling of Polymers**



*Report of the Basic Energy Sciences Roundtable on  
Chemical Upcycling of Polymers  
April 30 – May 1, 2019*

The artwork on the cover depicts chemical upcycling of poly(ethylene terephthalate) (PET) (top) to bis(2-hydroxyethyl) terephthalate (middle) and repolymerization back to PET (bottom) to illustrate the vision of chemical circularity. The background image consists of polymer pellets.

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# Report of the Basic Energy Sciences Roundtable on Chemical Upcycling of Polymers

April 30–May 1, 2019  
Bethesda, Maryland

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Co-Chair: Geoffrey W. Coates, Cornell University  
Co-Chair: Karen I. Winey, University of Pennsylvania

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## Abbreviations, Acronyms and Initialisms

AIMD	ab initio molecular dynamics
AW	agricultural waste
BES	Basic Energy Sciences
BR	building reconstruction
CGMD	coarse-grained molecular dynamics
DFT	density functional theory
FTIR	Fourier-transform infrared
GC–MS	gas chromatography mass spectrometry
GPC	gel permeation chromatography
HDPE	high-density polyethylene
HFP	household food packaging
INS	inelastic neutron scattering
iPP	isotactic polypropylene
IR	infrared
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
MALDI	matrix-assisted laser desorption/ionization
MB	mass balance
MC	Monte Carlo
MCM	Mobil Composition of Matter
MD	molecular dynamics
MD–MC	molecular dynamics–Monte Carlo
ML	machine learning
MMA	methyl methacrylate
MS	mass spectrometry
MT	metric ton
MWC	mineral water containers
NMR	nuclear magnetic resonance
PC	polycarbonate
PDMS	polydimethylsiloxane
PE	polyethylene
PET	polyethylene terephthalate
PHASR	Pulse-Heated Analysis of Solid Reactions
PLA	polylactic acid
PMMA	poly(methyl methacrylate)
PP	polypropylene
PRO	Priority Research Opportunity
PS	polystyrene
PVC	polyvinyl chloride
RT	room temperature
SANS	small-angle neutron scattering
SAXS	small-angle x-ray scattering
T6HP	trans-hexahydrophthalide
$T_g$	glass transition temperature
UV	ultraviolet
WAXS	wide-angle x-ray scattering
XAS	x-ray absorption spectroscopy
ZSM	Zeolite Socony Mobil



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## Executive Summary

Plastics are ubiquitous in modern life. They are primarily made from synthetic carbon-based polymers—organic macromolecules made up of many repeating subunits called monomers—and are designed to be durable and resistant to degradation. Global plastics production has reached a rate of more than 400 million metric tons (MTs) per year, with more than 8 billion MTs produced in the past 50 years. Average production has increased by 36% in the past decade and is projected to grow to 700 million MTs in 2030—about 80 kg of plastics produced for every human on earth. Globally, 20% of discarded plastics are recycled (<10% in the United States), primarily using mechanical processes, and about 25% are incinerated for energy recovery. More than half are deposited into landfills or released into the environment. Thus, discarded plastics pose a long-term environmental challenge: For example, at the current rate of plastics production and disposal, the mass of plastics in the ocean is predicted to exceed the mass of fish by 2050.

Current approaches to reducing unwanted plastics are insufficient to address the growing accumulation of discarded plastics. Although incineration eliminates unwanted plastics and recovers some of the energy used to make them, it uses up the potential resource and creates unwanted byproducts. Mechanical recycling—which involves shredding, heating, and remolding of the plastics—is more efficient than making them from petroleum products, using less than half as much energy to generate new plastics. However, mechanical recycling generally degrades, or downcycles, the polymers. Chemical recycling involves deconstruction of polymers by chemical processes to monomers for conversion back into polymers or to molecular intermediates that can be used as fuel or feedstock by the chemical industry. However, present methods (e.g., pyrolysis—high-temperature decomposition in the absence of oxygen), are energy-intensive and require further processing to make products.

Chemical upcycling of polymers—the process of selectively converting discarded plastics into chemicals, fuels, or materials with higher value—holds the promise of changing the paradigm for discarded plastic from waste to valued resource. A significant opportunity exists for fundamental research to provide the foundational knowledge required to move toward a circular lifecycle for plastics, in which the chemical constituents of plastics are reformed into polymers or repurposed to give them another life.

To identify the fundamental challenges and research opportunities that could accelerate the transformation of discarded plastics to higher-value fuels, chemicals, and materials, the US Department of Energy, Office of Science, Office of Basic Energy Sciences sponsored a Roundtable on Chemical Upcycling of Polymers, which was held near Washington, DC, on April 30–May 1, 2019. This roundtable identified four Priority Research Opportunities to address the complex chemical transformations and physical processes underlying the upcycling of discarded plastics.

### Priority Research Opportunities for Chemical Upcycling of Polymers

#### Master the mechanisms of polymer deconstruction, reconstruction, and functionalization

The chemical stability and physical properties that make plastics valuable for various applications also make their chemical conversion to new products a grand challenge. Existing methods to transform the macromolecular structures of plastic are nonselective and energy-intensive. New energy-efficient catalysts, macromolecular transformations, and chemical processes are needed to more selectively deconstruct polymer chains in a discarded plastic into monomers or other intermediates that can be reconstructed into desirable products (e.g., chemicals, fuels, or new polymers) or directly convert discarded plastics into materials with new functions.

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## **Understand and discover integrated processes to upcycle mixed plastics**

Many plastic products are made from multiple polymers and contain additives (such as pigments and stabilizers), fillers, and residues. Physical separation of these complex mixtures to recover pure components is technically challenging. This effort presents an opportunity to develop new energy-efficient integrated chemical, catalytic, and separation approaches that address the chemical and physical challenges of mixed plastics and directly capitalize on their chemical complexity. These efforts will allow the transformation of mixed plastics to chemicals, fuels, and new materials.

## **Design next-generation polymers for chemical circularity**

Commercial plastics are generally not recycled in a closed-loop, circular manner, in part because methods to selectively deconstruct polymers back into their original monomers are not available. New plastics need to be intentionally designed for the desired properties and chemical circularity at the molecular level with the goal of closing the loop in plastics recycling and chemical upcycling. New monomer and polymer chemistries need to be developed that both deliver next-generation polymers with properties similar or superior to those of current polymers and enable circular life cycles using atom- and energy-efficient processes.

## **Develop novel tools to discover and control chemical mechanisms for macromolecular transformations**

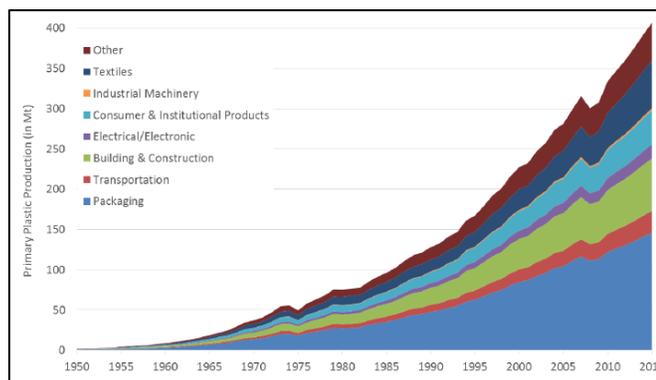
Deconstruction and reconstruction of polymers involves complex coupling of chemical and physical processes that span a wide range of length and time scales. This inherent complexity demands a new paradigm that integrates advanced experimental and computational approaches. When in situ and operando characterization methods are coupled with real-time computational modeling, simulations, and data analytics, the mechanisms and kinetics of deconstruction, reconstruction, and separations will be uncovered. These advanced multifaceted techniques will produce predictive insights into the design of new chemical transformations and processes for converting discarded plastics to desired products.

## 1. Introduction

Plastics have become an indispensable part of our global society and are used in a wide variety of applications, including packaging, building/construction, transportation, consumer products, textiles, medicine, and electronics. They are strong, lightweight, durable, chemically resistant, moldable, and low in cost and are used in thousands of products that add comfort, convenience, and safety to our everyday lives. For example, plastics are used in automotive airbags, child safety seats, seatbelts, and helmets that help keep us safe. They are used in carpets, flooring, roofs, sealants, and insulation to make our homes and buildings energy-efficient. They are used to make clothes, coats, pillows, blankets, and furniture that keep us comfortable. Plastics are used for beverage containers and for packaging to store food to keep it safe and fresh. They are used in computers, cell phones, televisions, and power cords that make our modern standard of life possible. With all their uses, the plastics industry is the third largest manufacturing sector in the United States and accounted for \$432 billion in shipments and 989,000 jobs in 2017, according to the Plastics Industry Association.<sup>1</sup>

Primarily made from fossil fuel feedstocks, plastics are synthetic-based organic macromolecules known as polymers; they are created by repeatedly linking together building blocks, called monomers. The first fully synthetic plastic, Bakelite, was produced in 1907 as a substitute for shellac, but large-scale use of polymers began in the 1940s when the military used nylon for parachutes and ropes, Plexiglas (poly[methyl methacrylate] [PMMA]) for airplane windows, and Government Rubber Styrene (poly[butadiene-*co*-styrene]) for tires. Then, in the 1950s, there was rapid worldwide growth and use of plastics. Over the next 65 years, the compound annual growth rate of plastics increased by 8.4%—roughly 2.5 times the growth rate of global gross domestic products during that period.<sup>2</sup>

Over the past two decades, global plastic production has more than doubled and the production rate in 2018 reached more than 400 million metric tons (MTs) per year (Figure 1). Single-use packaging accounts for approximately 40% of all plastics globally produced and contributes to 47% of the plastic waste produced.<sup>2,3</sup> China is the single largest producer of plastics (27.8%), followed by Europe (18.5%), the United States/Canada/Mexico (18.5%), the rest of Asia (16.7%), and the Middle East/Africa (7.3%).<sup>4</sup> Globally, 20% of discarded plastics are recycled, primarily using mechanical processes, and about 25% are incinerated for energy recovery. The remaining 55% of discarded plastics are deposited into landfills or released into the environment. Only 14% of plastic packaging is recycled globally, 40% is landfilled, and 32% is lost to the environment.<sup>3</sup> In the United States, recycling rates are much lower: 9% of discarded plastics are recycled, approximately 16% combusted for energy recovery, and 75% sent to landfills.<sup>5</sup> It is projected that annual global plastic production will grow to more than 700 million MTs by 2030—about 80 kg of plastics for every human on earth.<sup>6</sup> If the current trends continue, then by 2050, the plastics industry may account for 20% of the world's oil consumption, and the ocean may contain more plastic by weight than fish.<sup>7</sup>



**Figure 1.** Global plastics production (in millions of metric tons) according to industrial use sector as of 2015. Source: Geyer, R. et al. *Production, Use and Fate of All Plastics Ever Made*. *Sci. Adv.* 2017, 3, e1700782. Creative Commons License, <https://creativecommons.org/licenses/by-nc/4.0/>

The long-term energy and environmental challenges of plastics have been globally recognized, and there has been a public call to action in documents such as *The New Plastic Economy: Rethinking the future of*

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*plastics* (World Economic Forum),<sup>8</sup> *The New Plastic Economy: Catalysing action* (World Economic Forum in collaboration with the Ellen MacArthur Foundation),<sup>9</sup> and *Single-Use Plastics: A Roadmap for Sustainability* (United Nations Environmental Programme).<sup>3</sup> These challenges present an opportunity for fundamental research into chemical upcycling of polymers, where discarded plastics are selectively converted into higher-value products, as opposed to recycling, by which discarded plastics are converted into lower-value products or burned for energy recovery. Chemical upcycling has the potential to create a new paradigm in which discarded plastic is captured and becomes a valuable resource, enabling the efficient production of high-value chemicals, fuels, and new polymeric materials while reducing the accumulation of plastic wastes in the environment.

Plastic production currently competes for our finite stocks of oil and gas, a situation that will create a future energy challenge. Currently, plastic production consumes about 4–8% of the global gas and oil supply, with roughly half of that used for material feedstocks and half as fuel for the production process.<sup>8</sup> The energy used to produce plastics varies with the chemical composition and process. The energy consumed to produce a single 1 L polyethylene terephthalate (PET) bottle is approximately 1 kWh.<sup>10</sup> Since more than 480 billion PET bottles were sold globally in 2016,<sup>11</sup> PET production consumes approximately 1% of the world's crude oil supply.<sup>12</sup> Similarly, the energy consumed to make 12–14 single-use plastic shopping bags could drive a car for one mile.<sup>13</sup> Since it is estimated that at least 1 to 5 trillion plastic bags are consumed worldwide each year,<sup>3</sup> their production would consume enough energy for every registered vehicle in the United States to drive about 300–1,500 miles per year.<sup>14</sup> To save energy, discarded plastics can be recycled to make similar or new products rather than producing those products from virgin feedstocks (i.e., petroleum or natural gas). For example, recycling one ton of plastics saves about 130 million kJ of energy (ca. 22 barrels of oil);<sup>15</sup> therefore, recycling one-third of US plastic wastes annually could reduce total US energy consumption by about 1%. In addition, the dollar value of single-use plastic materials lost to the environment each year is estimated to be approximately \$80–120 billion.<sup>7</sup> Thus, there are economic, environmental, and energy benefits in chemical upcycling of discarded plastics.<sup>7</sup>

The vast majority of polymers (87%) are thermoplastics, or simply plastics, and fall into six categories described by the Society of the Plastics Industry codes 1–6, which were established to help sort materials for different recycling pathways to preserve their values, and a seventh code to cover all other plastics (Table 1). The largest class of polymers produced globally are polyolefins, which are used primarily in single-use packaging applications.<sup>2,3</sup> Thermosets, which make up more than 10% of the polymers produced globally, are cross-linked polymers—such as epoxies, polyurethanes, and vulcanized rubber—that currently cannot be recycled into new products. Biobased plastics made wholly or partially from renewable biological resources, such as polylactic acid (PLA) made from starch, account for only about 1% of the global production of plastics. Plastic resins, thermosets, and biobased plastics also contain additives such as plasticizers, fillers, flame retardants/heat stabilizers, antioxidants, colorants, and other materials that improve their properties, performance, stability, and appearance.<sup>2</sup>

Once discarded plastics have been collected and sorted at a materials recovery center, they are recycled to convert the plastics into useable products or to generate heat. Four different methods are currently used to recycle plastics, as detailed below.<sup>16</sup>

**Primary mechanical recycling** involves shredding, heating, and remolding the polymeric material. This method uses uncontaminated discarded plastic, such as process scrap or post-consumer waste of known origin, to make the same product without loss of properties and is often termed “closed-loop recycling.”

**Table 1.** Plastic resin identification codes and recycle rates.

Recycle code	Polymer	Major use	Common products	Global production <sup>a</sup>	Recycle rate (US) <sup>b</sup>
1 PET	Polyethylene terephthalate	Packaging	Drink bottles, cups, food carryout containers	10%	20%
2 HDPE	High-density polyethylene	Packaging	Grocery bags, detergent, bleach and shampoo bottles	16%	10%
3 PVC	Polyvinyl chloride	Building	Pipe, cables, siding, garden furniture, cling wrap	12%	0%
4 LDPE	Low-density polyethylene	Packaging	Plastic bags for food, trash bags, wrapping films	20%	5%
5 PP	Polypropylene	Packaging	Bottle caps, reusable food containers, shipping bags	21%	1%
6 PS	Polystyrene	Packaging/ building	Carryout containers, packaging peanuts, foam packaging, cups	8%	1%
7	Other (polyesters, polyurethane, acrylics, acrylonitrile-butadiene-styrene)	Various	Multilayer packaging, bottles, safety glasses, CDs, DVDs	13%	Varies

<sup>a</sup> From Geyer, R. et al. Production, Use and Fate of All Plastics Ever Made. *Sci. Adv.* **2017**, 3, e1700782.

<sup>b</sup> From Rahimi, A.; Garcia, J. M. Chemical Recycling of Waste Plastics for New Materials Production. *Nature Rev. Chem.* **2017**, 1, 0046.

**Secondary mechanical recycling** is the main industrial-scale process for recycling post-consumer plastics that contain contaminants, including discarded food, residues, and other plastics. This process is used to make new products that are typically different from those for which the original polymeric materials were manufactured. Mechanical recycling (primary and secondary) is more energy-efficient than making plastics from petroleum products and requires less than half the energy used to generate new plastics. However, the mechanical properties of the plastics typically degrade with secondary recycling as a result of cross-linking reactions and chain scission reactions caused by water, trace acids, heat or physical processing, and contamination with other (incompatible) polymers. Thus, secondary recycling of plastics is often called “downgrading” or “downcycling,” and the number of reprocessing cycles is limited by the degradation of the properties.

**Tertiary recycling** uses chemical processes, such as hydrolysis, pyrolysis, and gasification, to convert plastics to smaller molecules. These products include monomers; oligomers; and new chemical feedstocks, such as syngas (CO and H<sub>2</sub>), that can be used to synthesize new materials. These processes eliminate the need for fossil fuels to generate chemical feedstocks. However, many approaches (e.g., pyrolysis—high-temperature processing in the absence of oxygen) are energy-intensive and require further separations and processing to make sufficiently pure chemicals for reuse. Catalysts can be used to lower the temperature, increase selectivity, and increase the efficiency of deconstruction and reconstruction reactions.

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**Quaternary recycling** burns discarded plastics (thermoplastics, thermosets, and multilayered materials) to generate heat, which can be used to produce steam and electricity. This energy recovery process has the advantage of handling complex mixtures, such as multilayer packaging, but has the disadvantage that it recovers only about half the energy saved by mechanical recycling. For example, the heating value for plastics is only about 36 MJ/kg, whereas mechanical recycling conserves 60–90 MJ/kg.<sup>15</sup> Quaternary recycling also creates unwanted emissions, toxic byproducts, and CO<sub>2</sub>.

Biodegradation can also be considered a naturally occurring recycling method if it returns useful materials to the environment, while composting is a human-driven process in which biodegradation occurs under a specific set of conditions to provide desired products. Biodegradation of consumer plastics in landfills is very slow—taking centuries to degrade a plastic bottle—and can produce toxic chemicals such as polychlorinated biphenyls, phthalates, or bisphenol A. In addition to biodegradation, plastics and thermosets can be degraded in the environment by photodegradation, thermo-oxidative degradation, and hydrolytic degradation; but those processes are also slow, taking decades to decompose a piece of plastic. Although these natural processes can return resources to the environment, the energy and economic benefits of the discarded plastics are lost.

Overall, recycling discarded plastics has many benefits, but many fundamental scientific, technological, and economic challenges still need to be addressed.

**Chemical upcycling** of polymers is the process of selectively converting discarded plastics into chemicals, fuels, or higher-value products. Chemical upcycling has the potential to significantly reduce the use of fossil fuels, save energy, expand the types of plastics recycled (i.e., mixtures of plastics), and reduce the amount of plastics in the environment. The US Department of Energy, Office of Science, Basic Energy Sciences (BES) held a Roundtable on Chemical Upcycling of Polymers on April 30–May 1, 2019, outside Washington, DC, to identify the fundamental scientific challenges that must be addressed to enable the transformation of discarded plastics to higher-value products, including fuels, chemicals, and materials. The roundtable identified four Priority Research Opportunities (PROs) to accelerate this large-scale transition toward realizing a vision in which plastic never becomes waste (i.e., used once and discarded) and plastics production is decoupled from fossil fuels. These four PROs are detailed in the subsequent chapters of this report:

- Master the mechanisms of polymer deconstruction, reconstruction, and functionalization
- Understand and discover integrated processes to upcycle mixed plastics
- Design next-generation polymers for chemical circularity
- Develop novel tools to discover and control chemical mechanisms for macromolecular transformations

Advances in these PROs will provide the foundational knowledge needed to design new chemical reactions, catalysts, processes, and materials that enable efficient deconstruction, reconstruction, and functionalization of discarded plastics into higher-value products. These processes will use less raw material and energy to produce products from discarded plastics than from fossil fuels. Mechanistic insights gained from the deconstruction of pure polymers will be used to develop new approaches and processes for the deconstruction of mixed polymer streams. The integration of deconstruction and reconstruction schemes will provide unprecedented opportunities for the creation of new polymers to extend the useful lives of discarded plastics. New monomers and polymers will be designed and synthesized that will have properties similar or superior to those of current polymers and will exhibit circular life cycles. Nonrecyclable polymers, such as thermosets, will be recyclable through the design of reversible chemical reactions, such as dynamic covalent chemistry in which covalent bonds can be formed and broken reversibly under equilibrium conditions. These advances will require the integration of

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catalyst design with precise synthesis and detailed mechanistic studies using real-time characterization and analysis tools coupled to computational modeling, theory, and data science tools. Through fundamental research into the chemical upcycling of polymers, a new paradigm will emerge in which discarded plastic becomes a valuable resource that can be mined to enable the efficient production of chemicals, fuels, and new polymeric materials of higher value while reducing the accumulation of plastics in the environment and increasing chemical circularity. This ensures that resources and materials are continuously cycled to eliminate waste while increasing value across their life cycles.

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## 2. Priority Research Opportunities

### PRO 1: Master the Mechanisms of Polymer Deconstruction, Reconstruction, and Functionalization

**Key Question:** *How do we develop selective and integrated chemical processes to upgrade a discarded plastic into a desirable product?*

#### Summary

Discarded plastics have great potential value as precursors to fuels, chemicals, and new polymers. Many properties of plastics—such as chemical, thermal, and mechanical stability, which make them valuable for many applications—also make chemical conversions and recycling a challenge. Chemically, commercial plastics are typically long chains of identical, repeating, linked units (monomers), and only a few of the thousands of reactions that chemists have invented can selectively transform or cleave the links in these polymers. For example, polyolefins, the largest class of plastics, are the macromolecular analogues of hydrocarbons, which are notoriously resistant to selective chemical conversion. The challenge of transforming the strong bonds in polymers is exacerbated by their physical state. Even polymers joined by more reactive linkages, such as esters, become unreactive because of their semicrystalline structures and physical properties, including high melting point, high viscosity, and low solubility. For these reasons, new chemical reactions, catalysts, and processes need to be developed that can (1) selectively deconstruct plastics in an energy- and atom-efficient fashion to fuels, chemicals, or intermediates for higher-value products, (2) selectively couple deconstruction with reconstruction to generate new plastics, or (3) directly convert discarded plastics into future-generation materials.

#### Introduction

Plastics have a wide range of valuable properties, many of which derive from their thermal and mechanical stability and their resistance to most solvents and chemical reagents, and all of which make them challenging to upcycle. There has been some success in the chemical upcycling of polyesters, polycarbonates (PCs), and polyamides to produce high-purity small molecules that are adequate for subsequent polymerizations or other uses.<sup>17</sup> Microbial biocatalysts have also been used for the degradation of polyethylene (PE), polystyrene (PS), polyurethane, and PET,<sup>18</sup> but few studies have focused on recovery of the building blocks for reuse, except for PET.<sup>19</sup> The most abundant class of plastics is polyolefins, which are thermoplastics that consist solely of carbon-carbon and carbon-hydrogen bonds. Polyolefins are generally resistant to selective chemical or enzymatic transformations. Therefore, polyolefins and other thermoplastics are currently recycled by primary or secondary mechanical recycling, which involves shredding, heating, and forming by common techniques such as injection molding, blow molding, and extrusion. However, mechanical recycling eventually degrades the mechanical properties as a result of random chain cleavage or cross-linking. Although chemical recycling holds the promise of converting discarded plastics into higher-value products (i.e., upcycling), it is challenging to process solids with limited solubility, so chemical reactions must take place in the viscous melt or in the solid state, which reduces chemical reactivity. Thus, polymers containing more reactive functionality, such as ester or amide linkages, are more stable than their small-molecule analogues. Of the thousands of reactions invented by chemists over the centuries, in the solid or molten state, most are insufficient and ineffective to achieve polymer upcycling.

The thermodynamics of the polymerization and depolymerization reactions introduces another challenge. While polymerization reactions involving relatively weak carbon-carbon double bonds are exothermic (i.e., they release heat to their surroundings), depolymerization reactions involving cleavage of strong carbon-carbon single bonds are endothermic (i.e., they adsorb heat from their surroundings). Thus, depolymerization reactions must be driven by high temperatures. In many cases, it is difficult to

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selectively cleave the desired bonds in high yields, and the products formed will contain bonds that are more reactive than those of the starting polymer. Therefore, unwanted side reactions can occur if the products are not quickly removed from the reaction. This results in a need to develop new efficient catalysts, enzymes, reactions, and processes for the cleavage of the strong bonds found in plastics. These reactions also need to tolerate the additives (fillers, plasticizers, fire retardants, and colorants) typically used to improve and customize plastic resins. Alternatively, new chemical reactions could be developed to directly transform post-consumer plastic into higher-value materials, thereby avoiding the thermodynamic challenges imposed by polymer deconstruction.

To move toward chemical circularity, selective, integrated chemical processes must be developed to deconstruct and reconstruct discarded plastics into desirable, high-value products including monomers, small molecules, oligomers, and polymers. As a consequence of the complexity of mixed plastics, initial efforts should focus on investigating single plastics so that (1) detailed mechanistic insights can be gained from chemical and catalytic reactions of the polymer of interest without complication from other polymers or additives and (2) new research strategies, catalysts, and separations processes can be developed and applied toward more complex systems. These strategies also include tandem reaction sequences in which a polymer is initially activated by introducing a so-called *Achilles heel* or by exploiting a more reactive site within the polymer. Then, selective deconstruction reactions can generate products that can be directly fed into reconstruction reactions or separation processes to make higher-value products. This integration of deconstruction with reconstruction will lead to energy-efficient processes to enable a circular life cycle for plastics.

## Scientific Challenges

Plastics have been developed to exhibit useful properties in a variety of applications; to have appropriate mechanical properties over their anticipated operating temperatures; and to be environmentally persistent and resistant to solvents, oxygen, or other reagents. The majority of commodity plastics are semicrystalline thermoplastics with both crystalline and amorphous phases; the crystallites protect the reactive linkages, inhibiting deconstruction reactions or selective polymer-to-polymer transformations. The high-temperature conditions needed to dissolve or melt plastics for chemical transformations also facilitate unwanted reactions such as unselective homolytic bond cleavages, which increase in rate as the temperature increases. For example, the melting point of polyolefins is typically between 100 and 170 °C while that for PET is 260 °C. These physical and chemical features also vary with each plastic's molecular weight, molecular weight distribution, chemical functionality, and stereochemistry. Also, many commodity plastics contain additives (antioxidants, flame retardants, plasticizers, fillers) to improve their performance or environmental lifetimes. In combination, these properties and additives create significant challenges for the selective transformation of discarded plastics to higher-value products. For example, chemical reagents and catalysts need to be highly active and stable at the high temperatures required to melt the polymers so that the polymer chains are mobile and tolerant to additives. At the same time, the reactants should be effective at the lowest possible temperature to achieve selectivity over unwanted side reactions, such as homolysis, which reduces the polymer's molecular weight and degrades mechanical properties. Typically, catalysts have not been optimized for the unique reaction conditions needed to deconstruct commercial plastics. Thus, the challenges lie in the lack of reagents, catalysts, and enzymes, as well as processes and separations methods for the selective and energy-efficient conversion of plastics to higher-value products.

The following sections highlight some of the challenges associated with deconstruction of plastics by traditional methods (biochemical, pyrolysis, and catalytic pyrolysis) and emerging approaches (catalytic deconstruction and functionalization), as well as challenges imposed by the chemical heterogeneity of polymers.

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## Biochemical conversion

Polymers with hydrolysable chemical bonds in their backbones, such as PET or polyurethane, are more susceptible to biodegradation than polyolefins, PS, or polyvinyl chloride (PVC). Biodegradable plastics, which can be bio- or petroleum-based—including PLA, polyhydroxyalkanoate, poly( $\epsilon$ -caprolactone), or polybutylene succinate—can be degraded by microorganisms into a variety of products.<sup>20</sup> In contrast, most petroleum-based plastics are resistant to microbial degradation, and it is estimated that they remain in the environment for centuries. Thus, the biodegradation of recalcitrant plastics has become an area of active research.<sup>21</sup> The biodegradation of plastics is thought to occur by a combination of abiotic factors (ultraviolet [UV] radiation, temperature, oxygen, chemical oxidants) and biotic factors because the large, high-molecular-weight polymer chains cannot be transported across the cellular membranes of microorganisms. Thus, these polymer chains need to be depolymerized to smaller units (10–50 carbon atoms) by abiotic factors and microorganisms before they cross the cell membrane and become assimilated by the intracellular metabolism. The key characteristics responsible for plastics' resistance to biodegradation include hydrophobicity, degree of crystallinity, molecular size, structure, surface topography, and lack of favorable functional groups. Before the biochemical conversion of polyolefins and other recalcitrant polymers can become a reality, additional research is needed to identify new, highly active enzymes; and new knowledge is needed regarding the underlying reaction mechanisms to control selectivity to the desired products.

Inspiration can be gained on the biodegradation of recalcitrant polymers through a review of studies on the deconstruction of biomass, which is a recalcitrant biopolymer.<sup>22,23</sup> To overcome the difficulty associated with gaining access to the cell wall polymers, biochemical conversion typically uses low-severity thermochemical treatment (pretreatment) at temperatures between 100 °C and 200 °C to partially break down the cell walls and improve enzymatic accessibility. Many options exist for pretreatment of biomass, such as sulfuric acid, ammonia, water, or ionic liquids, all of which penetrate the cell wall and alter the chemistry and ultrastructure. This pretreatment step is typically followed by application of enzymes or microbes to convert the carbohydrates to soluble sugars, which can be isolated or upgraded to other chemicals or fuels. One of the challenges in this process has been to elucidate the physicochemical effects of the many possible pretreatments on subsequent hydrolysis and fermentation yields and products. A high-throughput screening method could be used to optimize pretreatment methods and search for an improved biocatalyst in the degradation of recalcitrant petroleum-based plastics.

## Pyrolysis and catalytic pyrolysis

One method to break strong carbon-carbon bonds in plastics into smaller higher-value products is by pyrolysis and catalytic pyrolysis. Lessons can be learned on how to control product selectivity and yields from the pyrolysis of other complex heterogeneous materials such as biomass<sup>24</sup> and coal<sup>25</sup> (as described in the factual document). Pyrolysis can produce high yields of liquid products (>80% for polyolefins and PS), in addition to gas and char. Unfortunately, the product selectivity is poor and a broad distribution of products is typically obtained, which is primarily dictated by the inherent chain scission events,<sup>26,27</sup> so additional separations are required to obtain the desired product.<sup>28</sup> Catalytic pyrolysis can reduce the reaction temperature, which saves energy, increases the yields of liquid products, and optimizes product selectivity. Gasification can be used to produce syngas (CO and H<sub>2</sub>), which can be used to make chemicals and fuels. The main challenge in plastic gasification is tar formation, which causes serious operational problems that lead to a reduction in the overall process efficiency. The novel strategy of pyrolysis with in-line reforming has the advantage of operating at lower temperatures and producing a H<sub>2</sub>-rich gas product free of tars.<sup>29</sup> Other thermal and catalytic deconstruction reactions, alone or coupled with functionalization steps, could yield valuable chemical intermediates, but such transformations require new chemical and catalytic approaches to increase selectivity and efficiency.

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## Catalytic deconstruction

The backbone of the most abundant classes of plastics—which include polyolefins, PVC, PS, PET, and polyurethanes—is composed of carbon-carbon, carbon-oxygen, and carbon-nitrogen bonds, along with the ubiquitous carbon-hydrogen bond. Selective transformation of these bonds by mild catalytic methods has been a long-standing challenge in the conversion of small molecules, including light alkanes, into complex products. Many of the reactions used to transform small molecules into products cannot be directly translated to the conversion of discarded plastics into more valuable products. Many reactions rely on directing groups or other stereoelectronic properties of the reactant to differentiate between reactive positions. The identical repeat units and highly uniform nature of most polymer chains obfuscate such differentiation between multiple sites. Furthermore, a preponderance of synthetic catalytic methods focuses on adding new organic functionality or creating carbon-carbon bonds, whereas fewer methods have been developed to break carbon-carbon bonds. Also, because polymer chains are long, a transformation at one position would unlikely increase or decrease the likelihood of a second activation at a remote location on the same chain. Finally, depolymerization must overcome the high enthalpic stability of polymers, which is sufficient to overcome the entropic penalty resulting from the combination of many monomers into a few macromolecules. In both depolymerization and deconstruction, entropy favors the formation of distributions of products or the highest number of small molecular species. Thus, reactions need to be developed to operate under kinetic control, which can be affected by catalysts or reagents, to obtain the required selectivity for polymer upcycling. However, many features of such kinetically controlled reactions for macromolecular conversions have yet to be established.

A potential new direction is to deconstruct plastics into small molecules by forming stronger bonds in the products. This could be enthalpically and entropically favored, as in hydrogenolysis, in which two element-hydrogen bonds are formed from H<sub>2</sub> and an element-element bond. For the selective cleavage of alkanes, hydrogenolysis and alkane metathesis are the most promising because they produce smaller hydrocarbons. Effective catalysts for both processes must be able to effect dehydrogenation followed by a carbon-carbon bond cleavage. These sequences are often, although not always, mediated by multiple catalytic sites operating in tandem, which creates an additional set of challenges.

## Catalytic functionalization

In addition to carbon-carbon bond cleavage, it is desirable to design new reactions that would create new functionality during bond cleavage to produce higher-value products and allow for further reconstruction. A possible approach could involve carbon-hydrogen bond activation and functionalization of discarded plastics to form new polymeric materials. However, plastics are composed of a large number of chemically indistinguishable repeating units so that the reaction of a specific carbon-hydrogen bond, the introduction of a functional group at a specific position, or the cleavage of the backbone at a defined location is currently beyond the capability of synthetic chemistry. Although oxidation reactions are often used to introduce functionality into hydrocarbons, these reactions suffer from poor selectivity. Moreover, the carbon-hydrogen bonds in the alcohol and ketone products are weaker than in the starting aliphatic hydrocarbon and are susceptible to hydrogen abstraction reactions, which can lead to unwanted radical reactions, such as carbon-carbon bond cleavage. New mild carbon-hydrogen functionalization reactions with even higher selectivity than current methods must be developed.

## Chemical heterogeneity

In addition to their large size and large number of atoms, polymers are generally a mixture of long chain molecules with a range of lengths and molecular weights (i.e., polydispersity). In addition, pendant groups hang from the polymer backbone, which imparts functionality. For example, low-density PE (LDPE) has a higher degree of short and long sidechains branching off the PE backbone, while linear LDPE (LLDPE) has many short branches. High-density PE (HDPE) has a much lower degree of

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branching than LDPE, which results in a higher degree of crystallinity. A small number of defects, such as branch points, stereoerrors, or functional groups from oxidation reaction, are also present, even in pure samples. Discarded plastics, even if appropriately sorted into their specific classes and cleaned of residues, will also contain variable amounts and types of additives and impurities, depending on their original intended use and sample history. This diversity can dictate or influence the pathways of subsequent depolymerization reactions critical to selective chemical upcycling. Moreover, these sparse features may be difficult to detect or accurately quantify or associate with a particular molecular weight chain. Thus, there is need to characterize discarded plastics to quantify their chemical distributions and to understand the reactivity of the distinct species. The development of in situ characterization tools and computational methods could dramatically accelerate the understanding of reaction mechanisms to optimize the reaction efficiency. These topics are discussed in more detail in PRO 4.

### Summary of Research Directions

There is a need to develop selective, integrated processes and catalysts for chemical upcycling of discarded plastics into monomers, chemical intermediates, or fuels, or to directly convert plastics into new materials with properties similar to or superior to current materials. Future research directions will address two scientific questions:

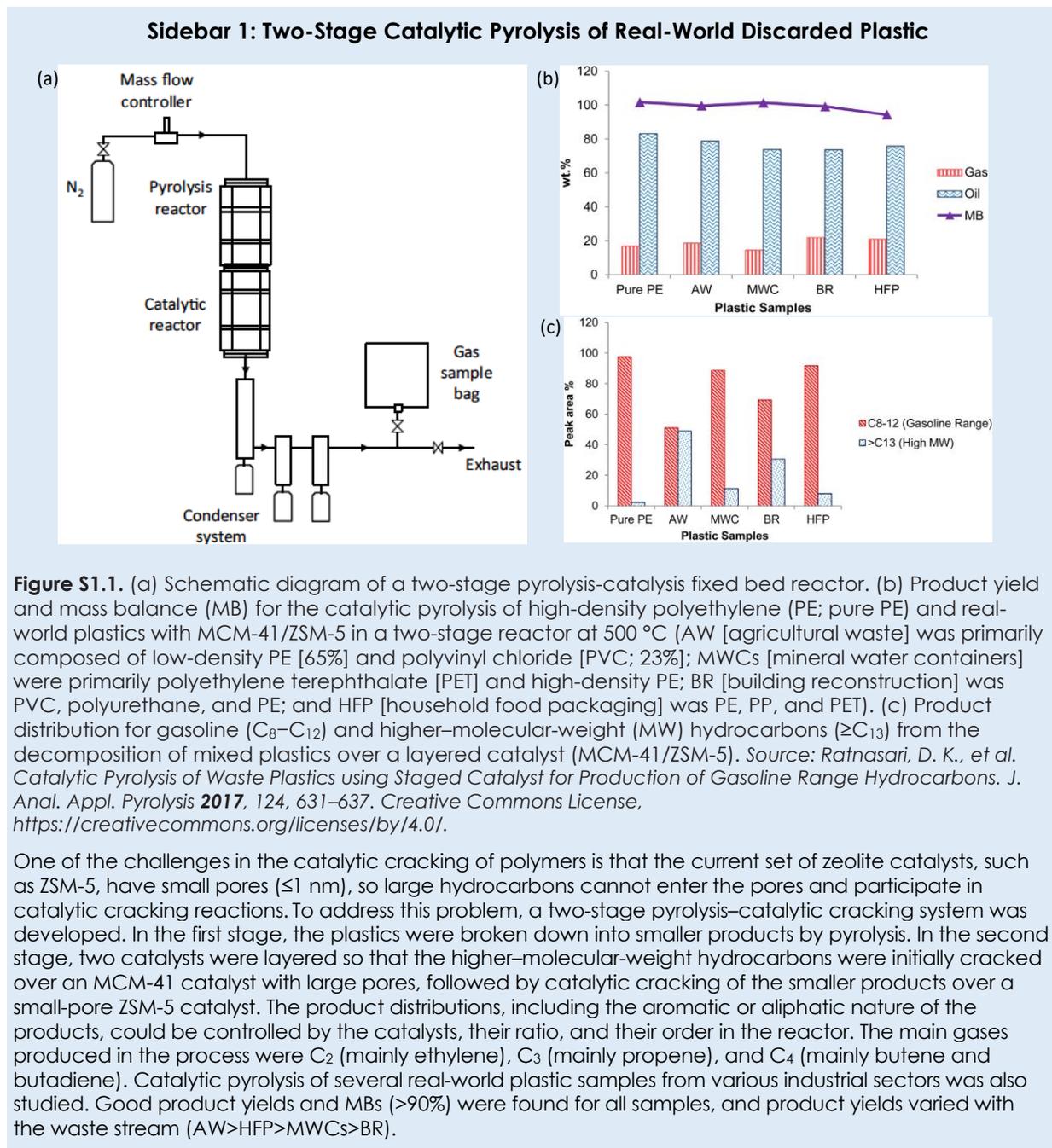
1. How do we create catalysts or reagents to efficiently react with the typically unreactive bonds in polymeric materials?
2. How do we develop efficient and selective chemical transformations of polymer chains that contain identical or nearly identical bonds into valuable smaller molecules?

### Create catalysts or reagents to efficiently react with unreactive bonds

Robust, recyclable catalysts, reagents, and processes are needed to operate under conditions that overcome the refractory physical and chemical properties of plastics and that also avoid long-lived intermediates, such as radicals, that lead to cross-linking or uncontrolled chain cleavage. Such chain scission reactions may occur spontaneously in the melt phase, such as during mechanical recycling or as side reactions in two-electron processes. Obviously, some plastics will inherently have more sensitivity to thermal side reactions than others. For example, tertiary carbons in polypropylene (PP) and PS stabilize radicals that could form via hydrogen abstraction, and the ensuing radical reactions complicate any attempts to recycle or catalytically upcycle these plastics at high temperatures. New catalysts must be developed to operate at lower temperatures and under conditions that avoid uncontrolled radical reactions. For example, electrochemical approaches, which can operate at room temperature and control the formation of reactive species by the applied potential, may be used to selectively generate products as discussed in PRO 3. Robust, acid-tolerant catalysts must also be developed for other abundant and hard-to-recycle plastics, such as PVC, which readily generates corrosive hydrochloric acid by an elimination reaction that leads to unwanted side reactions.

The past two decades have seen significant research into the catalytic conversion of discarded plastics, particularly polyolefins and PS, into transportation fuels.<sup>30</sup> Studies of reactions and mechanisms have been performed on individual polymer samples to gain insight into the relationships among activity, selectivity, and deactivation of the catalyst. These insights have been applied to the deconstruction of real-world plastic samples (see Sidebar 1).<sup>31,32</sup> There are three approaches to the catalytic pyrolysis of discarded plastics: (1) direct contact of catalyst and plastic, (2) thermal cracking followed by catalytic reforming, and (3) thermal cracking followed by hydrotreating. In the first approach, catalytic cracking typically proceeds over acid catalysts (zeolites, silica-alumina, clay, and mesoporous silicas) through a carbocation mechanism that leads to cracking, isomerization, cyclization, and aromatization reactions. This approach is challenged by the high viscosity of the plastic, which leads to mass and heat transfer constraints. Some of these problems are overcome by moving to fluidized bed reactors and away from

batch reactors, but the main drawback is the high amount of catalyst needed to achieve complete conversion. Also, impurities can lead to poisoning of the catalysts. In the second approach, some of these problems are overcome by initially thermally cracking the plastic to a lower-viscosity oil, followed by catalytic reforming. Impurities can be removed from the heavy oil before it comes into contact with the catalyst. In this approach, thermal cracking proceeds by a free radical mechanism and leads to linear hydrocarbon chains and olefins, which are upgraded over acid catalysts. In the third approach, the plastic is thermally cracked and the products are passed over a bifunctional catalyst that has both acidic and metal sites, under hydrogen pressure, to upgrade the products and reduce the olefin content. In these experiments, the acid sites are typically aluminosilicates (zeolites, Al-MCM-41, and amorphous SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>), and the supported metal catalysts are Pt, Pd, or Ni.

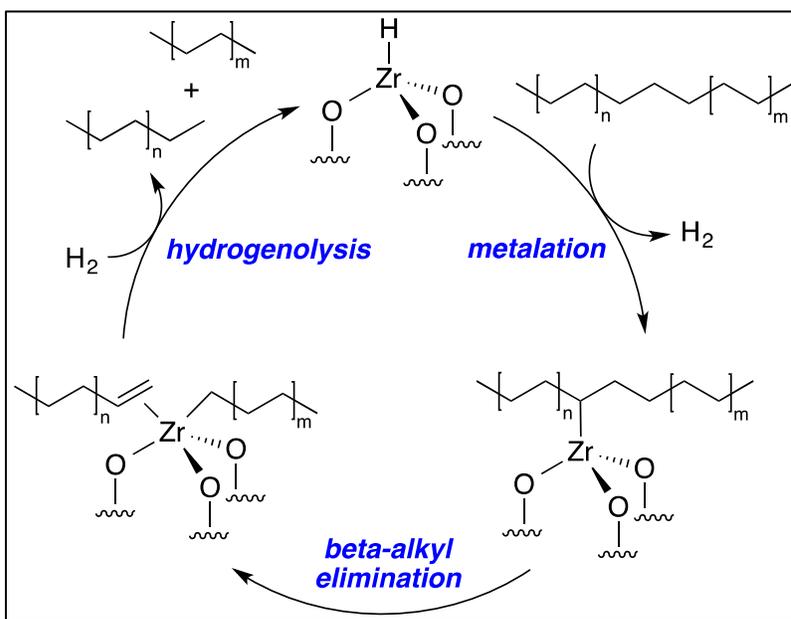


In all of these approaches, the acidity of the catalyst is critically important because it determines the activity and selectivity of the reactions. Deactivation of the catalyst is another key factor that depends on the acidity and the pore structure of the catalyst. As a consequence of the size and viscosity of the polymers, there are steric and diffusional constraints for the bulky polymer to enter the pores of the catalyst. Thus, there have been recent advances in the development of high-surface-area catalysts and hierarchical zeolites that have bimodal pore distribution, allowing high accessibility to the active sites. More research is needed to develop new stable catalysts with high accessibility to the active sites, which have high selectivity toward the desired products and can be easily regenerated.

Many of the catalysts for the synthesis of poly( $\alpha$ -olefins) operate at moderately high temperatures as a result of the exothermicity of olefin polymerization; new depolymerization catalysts may be developed based on the principles established for polymerization and hydrogenation catalysis. Some metal complexes are already sufficiently long-lived at high temperature to enable catalytic deconstruction of discarded polymers. These complexes contain polymeric ligands or metal alkylidenes used in ring-opening polymerization metathesis polymerization, or they contain robust, pincer-type metal alkyl compounds invoked as intermediates in dehydrogenation reactions. In an early example utilizing surface organometallic chemistry, a single-site aluminum-doped silica-supported zirconium hydride was reported to catalyze both polymerization of ethylene to PE and concurrent depolymerization and hydrogenation of PE into short hydrocarbon chains.<sup>33,34</sup> The depolymerization catalyst was proposed to operate through  $\beta$ -alkyl elimination from a zirconium polymeryl (Figure 2). The proposed mechanism of this transformation made use of well-known organometallic steps that were devised for small molecules, including hydrogenolysis,<sup>35</sup>  $\beta$ -alkyl elimination,<sup>36,37</sup> and dehydrogenative metalation. The depolymerization and hydrogenation reactions took place from 150 to 200 °C, the temperature regime most suitable for commercial polymerization, where unwanted free radical reactions are not possible. Thus, the catalysts had to resist homolytic cleavage of the metal-alkyl bond to grow chains by insertion, or they had to break chains by two-electron processes without engaging unselective one-electron chemistry. In the future, new, more selective catalysts are needed to process branched polyolefins such as LDPE, LLDPE, and HDPE in the polymer melt; furthermore, methods are needed to separate the desired products from the reaction.

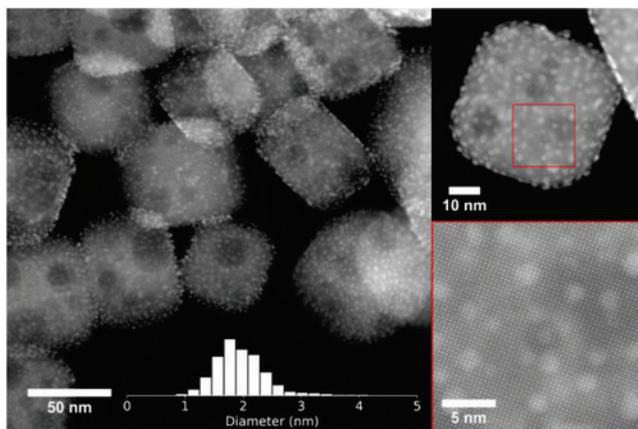
High-temperature regimes create new opportunities for other hydrogenolysis reactions. For example, Pt, Ir, and Rh nanoparticles supported on metal oxides catalyze the hydrogenolysis of small aliphatic hydrocarbons (e.g., C<sub>2</sub>–C<sub>8</sub>) above 300 °C.<sup>38,39</sup>

This approach can be extended to the deconstruction of polyolefins. In a recent example, platinum nanoparticles supported on strontium titanate (SrTiO<sub>3</sub>) were found to be effective for hydrogenolysis of PE at 300 °C



**Figure 2.** Possible mechanism for zirconium hydride-mediated hydrogenolysis. Dufaud, V.; Basset, J.-M. *Catalytic Hydrogenolysis at Low Temperature and Pressure of Polyethylene and Polypropylene to Diesels or Lower Alkanes by a Zirconium Hydride Supported on Silica-Alumina: A Step Toward Polyolefin Degradation by the Microscopic Reverse of Ziegler-Natta Polymerization*. *Angew. Chem. Int. Ed.* **1998**, *37*, 806–810. WILEY-VCH Verlag GmbH, D-69451 Weinheim, 1998. Adapted with permission.

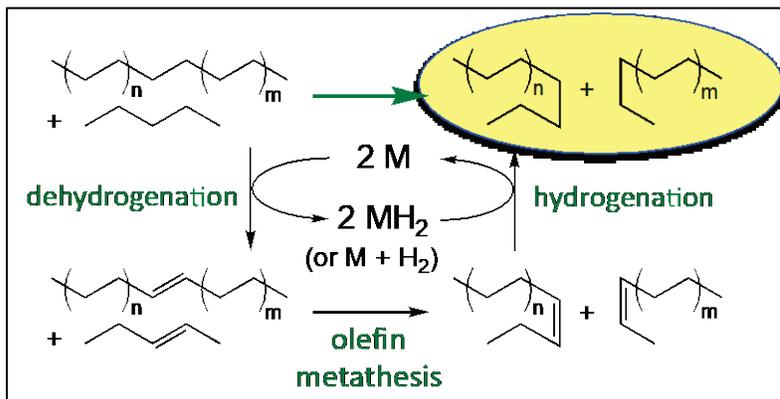
under H<sub>2</sub> to form high-quality liquid products characterized by a narrow distribution of oligomeric chains.<sup>40,41</sup> The platinum catalyst was stable and resisted sintering in a mixture of molten PE under hydrogen. The cube-on-cube epitaxy matched the face-centered cubic platinum nanoparticles and cubic SrTiO<sub>3</sub> to provide the necessary stabilization for the reaction (Figure 3). The hydrogenolysis reactions may also benefit from the interactions between the surface of the catalyst and the PE chain. Longer macromolecular chains are cleaved preferentially over short chains as a result of the more favorable surface binding of the former species, leading to a well-defined range of molecular-weight products that correspond to lubricant-grade liquids. In the future, the next generation of catalysts for hydrogenolysis (as well as for other transformations) must be designed to perform effectively and selectively at high temperature under solvent-free conditions.



**Figure 3.** Electron micrograph of platinum nanoparticles deposited on SrTiO<sub>3</sub> by atomic layer deposition for the selective hydrogenolysis of HDPE to waxes. Source: Celik, G., et al. *Upcycling Single-Use Polyethylene into High-Quality Liquid Products*. ACS Central Science **2019**, 5, 1795-1803. ACS AuthorChoice/Editors' Choice usage agreement.

the reaction. Because the polymer was insoluble in the solvent at room temperature (RT), high temperatures were needed to sufficiently dissolve the polymer and interact with both catalysts. This process, as well as the hydrogenation processes described previously, required long reaction times for the final product distribution to be accessed. Distribution of product molecular weights is also the result of cleavage reactions occurring stochastically across the chains. In the future, new catalytic transformation that employs alkane metathesis will require improved compatibility and synergism between the hydrogen transfer catalyst and the metathesis catalyst.

Alkane metathesis is also a useful process for breaking carbon-carbon bonds via a sequence in which alkanes are catalytically dehydrogenated, the intermediate olefins undergo metathesis to break and form carbon-carbon bonds, and then the new olefins are hydrogenated back to saturated hydrocarbons (Figure 4). In this way, large and small alkanes can be combined to give a distribution of saturated hydrocarbons. A few kinds of catalysts mediate these reactions, including early metal alkylidene-based compounds,<sup>42</sup> as well as a tandem, multisite combination of pincer iridium dehydrogenation and hydrogenation catalysts and rhenium oxide metathesis catalysts.<sup>43,44</sup> In the latter system, cross metathesis of high-molecular-weight and light hydrocarbons was used to deconstruct PE into a broad distribution of gases, liquids, and waxes.<sup>45</sup> In this case, the solvent consisted of short-chain hydrocarbons, which also served as the reagent for



**Figure 4.** Cross-alkane metathesis for an atom economical redistribution of short and long hydrocarbon chains. Image courtesy of Alan Goldman.

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## Develop efficient chemical transformations of polymer chains containing identical bonds

One challenge in the hydrogenolysis of polymers and in the cross-alkane metathesis reactions is that it provides a broad distribution of molecular weights of solids, liquids, and gas-phase products. Ideally, upcycling conversions should produce a single desired product or a well-defined range of products to avoid energy costs of separations, and new catalysts and chemical pathways are needed to increase the selectivity of the reactions. This challenge may be addressed with catalyst structures that combine the desired functionalization and/or cleavage events with molecular recognition, which influences chain conformations. Alternatively, the introduction of reactive functional groups (such as a hydroxyl group) at specific sites on the polymer backbone (such as at tertiary carbons) could provide molecular recognition sites on the polymer chain for subsequent reaction. Thus, reagents, catalysts, and electrochemical approaches are needed to selectively insert functionality into polymer chains while avoiding nonselective degradation resulting from long-lived reactive intermediates. This molecular recognition site should direct subsequent successive insertion of additional functionality, or it could provide sites for carbon-carbon bond cleavage. Such a transformation would produce oligomers of regular length that could be used as monomers or comonomers in subsequent polymerizations, or it would produce new functionalized polymers that could be easier to separate and purify for future applications.

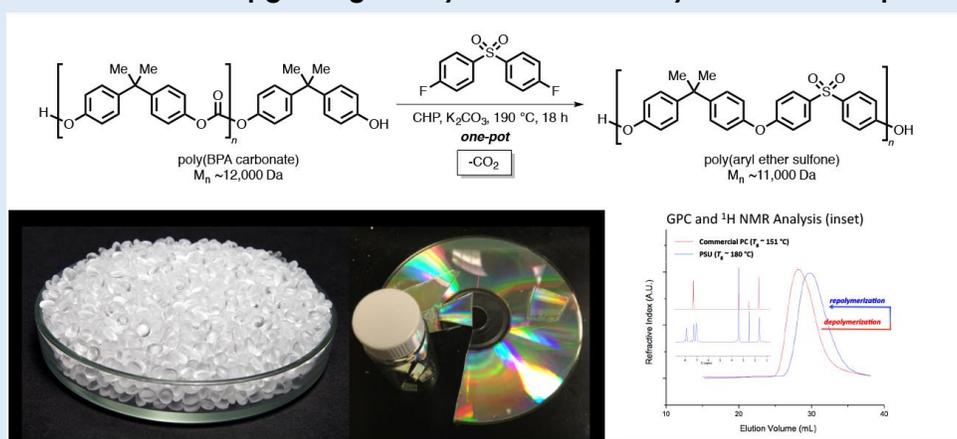
Some advances have been made in the development of catalysts and reagents that react with unconventional selectivity. For example, the primary carbon-hydrogen bonds in PP can be selectively hydroxylated via rhodium-catalyzed borylation followed by oxidation.<sup>46</sup> The borylation approach is advantaged by the versatility of boronate ester products but currently requires an expensive bis(pinacolato)diboron reagent. Although reactions have been observed at the stronger primary carbon-hydrogen bonds of PP rather than at the weaker tertiary carbon-hydrogen bonds, the extent of functionality was low because these bonds were hindered. In another example, it was reported that photochemical xanthylation resulted in the regioselective functionalization of branched polyolefins without coincident polymer-chain scission. Thus, secondary carbon-hydrogen bonds can be functionalized in the presence of primary and tertiary carbon-hydrogen bonds in hydrogenated polybutadiene and in several classes of PEs.<sup>47</sup> However, the reagent was expensive, and the process required solvent and light. Finally, the hydroxylation of PE has been reported with meta-chloroperbenzoic acid catalyzed by a nickel complex.<sup>48</sup> Although the reaction used a solvent and an oxidation agent that was more expensive than desired for large-scale conversion, the reaction was found to incorporate 2 to 5.5 functional groups (alcohols, ketones, or alkyl chloride) per 100 monomer units, and up to 88% selectivity for formation of alcohols. The selective introduction of functional groups through these approaches is a first step toward selective deconstruction or conversion to new products. New catalysts and reactions are needed to selectively introduce functionality at regular intervals in a polymer chain. For example, a catalyst could be used to oxidize a PE chain at every sixth carbon to make adipic acid for nylon production. This process could be accomplished using a template-based approach or molecular recognition to make new monomers or oligomers for the production of new plastics.

Another approach to providing new value to discarded plastics is to selectively depolymerize the polymer back to its monomer. For example, PMMA can be thermally depolymerized by an unzipping reaction to MMA in high yield (>90%). Subsequent repolymerization would provide identical or structurally modified products, or the monomers could be used in other chemical manufacturing processes. For example, discarded HDPE could be depolymerized to pure ethylene, which could then be repolymerized to LDPE. Polymers could also be depolymerized into different monomers. For example, PE could be converted into propylene or another  $\alpha$ -olefin, which would provide a way to make use of the valuable long carbon-carbon bonded chains in HDPE. These monomers could then be incorporated into reactions that give LLDPE or isotactic PP (iPP). Similarly, catalytic hydrogenation and hydrogenolysis reactions of polyesters, such as PET and PCs, can provide monomers for future reuse.<sup>49</sup> Polyesters can also be

deconstructed by reduction reactions involving carbon-oxygen bond cleavage and carbonyl reduction to provide diols.<sup>50</sup> This process has been demonstrated in a magnesium-catalyzed hydroboration of PLA.<sup>51</sup>

Selective transformation of discarded plastics into new high-value materials provides an appealing alternative to mechanical recycling. Currently, there are few integrated processes that exist for the direct conversion of a discarded plastic into the same polymer or a different polymer. Such processes would result in significant savings of energy, time, and cost, enabling the conversion of a discarded plastic to a useful product. As highlighted in Sidebar 2, the conversion of bisphenol A carbonate to polysulfone<sup>52</sup> illustrates the potential of this approach to upgrade a discarded plastic to a high-performance thermoplastic. Alternatively, polyesters can be reacted with amines to provide a route to polyamides.<sup>53</sup> Developing methods and disposable catalysts to perform these reactions in the solid state without a solvent could increase the efficiency of the reactions. Many related transformations can be envisaged that involve direct polymer-polymer conversions in the melt or in solution without deconstruction or processes that use tandem or multistage processes to sequentially functionalize and construct new high-value polymers with superior properties.

### Sidebar 2: Direct Upgrading of Polycarbonate to Polysulfone Thermoplastics



**Figure S2.1.** It is estimated that about 3 million tons of polycarbonates (PCs) are produced annually worldwide. Since PCs are not typically recycled, there is a need to design processes for the upcycling of discarded PCs. Instead of depolymerization back to monomers, PCs were transformed into poly(aryl ether sulfone)s, which are high-performance engineering thermoplastics commonly used for a variety of applications, including reverse osmosis and water purification membranes, as well as high-temperature applications. In this one-step process, PC was depolymerized followed by in situ polycondensation with bis(aryl fluorides) in the presence of carbonate salts. The poly(aryl ether sulfone)s were isolated at high purity and yield with the expected thermal properties. Mechanistic insights into the reaction mechanisms and the role of the carbonate salt were uncovered by density functional theory. By coupling computation with experimental studies, new insights can be gained in the depolymerization and repolymerization reactions, which will ultimately enable repurposing of spent polymeric materials. Source: (Left) iStock image; (center) Courtesy of Jeanette Garcia; (right) Jones, G. O., et al. Computational and Experimental Investigations of One-step Conversion of Poly(carbonate)s into Value-added Poly(aryl ether sulfone)s. *Proc. Natl. Acad. Sci. U.S.A.* **2016**, 113, 7722–7726. Preprinted with permission from PNAS.

To achieve efficient, selective, practical deconstruction, functionalization, and reconstruction of discarded plastics, there are varied and significant challenges to overcome. The reagents must be simple, and the catalysts should be selective, highly active, stable, and tolerant of impurities and additives. New catalysts need to be designed for catalytic pyrolysis reactions that have large assessable pores so that large polymer chains can access the active sites. New, highly active enzymes need to be discovered for the production of high-value chemicals. New catalysts and processes need to be developed for the circular life cycle of polymers (see PRO 3). For polymer functionalization, the catalysts may need to be left in the modified

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polymer, just as catalysts for polymer synthesis remain in the product. To reduce energy requirements, the reactions should be conducted in the polymer melt rather than in the solvents. As a consequence of the complexity and challenges in upcycling mixed discarded plastics, fundamental research is needed to gain more understanding of deconstruction and reconstruction reaction mechanisms on a single plastic waste stream to advance the development of new catalysts and processes. This knowledge can then be applied to convert more complex mixtures of discarded plastics into value-added chemicals, fuels, and materials (addressed in PRO 2).

### Science and Technology Impact

The invention of new methods to chemically upcycle polymers will require development of fundamentally new approaches to chemical synthesis and catalysis. In the case of hydrocarbon polymers such as polyolefins, PS, and acrylonitrile-butadiene-styrene, which comprise over half of all plastics by volume, chemists must develop new methods to selectively and efficiently cleave or functionalize the two most abundant bonds in organic molecules—namely aliphatic carbon-carbon and carbon-hydrogen bonds. These bonds are also the two linkages perhaps most resistant to the power of existing synthetic methods. The ability to break a specific carbon-carbon bond in a polymer and the strategies that introduce functional groups as a result of these cleavage reactions would dramatically advance polymer upcycling and would also disrupt current methods of producing small molecules. For example, the traditional hydrocarbon distribution obtained from Fischer–Tropsch or from nickel-catalyzed ethylene oligomerization might be more effectively transformed to desired products. One could even imagine, for example, that the cross-metathesis reactions created for polymer upcycling could also enable homologations of molecules in crude oil by reaction with natural gas components. The ability to use two or more catalysts operating in tandem could be used to effect dehydrogenation followed by olefin metathesis to achieve alkane metathesis, for example. More generally, polymer upcycling requires the ability to model and control complex reaction networks and the close coupling of catalysts and processes to enable integrated transformations, thereby presenting a broad range of challenges and opportunities.

For the upcycling of any class of plastics, even those with groups that are not considered unreactive in traditional systems (e.g., esters and amides), new methods to effect reactions in complex, refractory environments (e.g., semicrystalline or amorphous solids) must be developed. Doing so will expand controlled reaction chemistry beyond traditional gas and solution phases. The development of a fundamental understanding of molecular interactions in complex mixtures at multiple length scales across phases will be necessary. The upcycling target will drive the development of new approaches to separations science that target functional groups, molecular shapes, or other structural features, for direct isolation from the mixture or isolation after chemical derivatization. The approaches to these challenges may synergize with the development of new synthetic paradigms that will distinguish between identical or similar bonds in large molecules.

The direct technological impacts of new methods to chemically upcycle polymers will lead to a more energy-efficient economy in which post-consumer plastics realize their potential value as an organic resource for chemicals and fuels, as well as for their conversion back to valuable plastics as part of a circular materials economy. Moreover, the potential for spin-off technologies is abundant. The development of new methods for polyolefin transformations is obviously relevant to the conversion of hydrocarbons in petroleum refining, as well as the synthesis of artificial liquid fuels and the chemical synthesis of commodity and fine chemicals. Polymer functionalization holds tremendous promise for the development of new polymeric materials with many potentially valuable properties and applications. Insight gained from deconstruction and reconstruction of discarded plastics will provide a foundation to address the more complex challenge of chemical upcycling of mixed polymers that contain a variety of incompatible polymers and an array for functional groups as discussed in PRO 2.

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## PRO 2: Understand and Discover Integrated Processes to Upcycle Mixed Plastics

**Key Question:** *How can we directly transform mixed discarded plastics to desirable products?*

### Summary

Discarded plastics represent a large, untapped source of energy and chemicals. One of the challenges in processing this resource is the heterogeneous nature of discarded plastics, which contain a variety of incompatible polymers and multilayer polymer products, as well as additives (pigments, stabilizers, and plasticizers), fillers, and post-use contaminants. New energy-efficient and highly integrated chemical, catalytic, and separations approaches are needed to address the chemical and physical challenges of mixed plastics, which directly capitalize on their chemical complexity. New approaches are needed to characterize and predict the physical and chemical behaviors of solid mixtures. Integrated processes involving both separations and judicious combinations of chemocatalytic, biocatalytic, and thermal transformations are needed to address the diversity of components in these solid mixtures.

Additionally, opportunities exist to create entirely new kinds of materials by combining multiple polymers present in discarded plastics. To realize these goals, it will be necessary to provide new scientific understanding of the properties and reactivity of polymer mixtures so that new innovative chemical processes, catalysts, and separations methods can be designed to transform complex waste into high-value products.

### Introduction

One of the biggest challenges and opportunities in upcycling of plastic is to develop energy-efficient strategies for recycling mixed and contaminated feedstocks. Discarded plastics usually consist of a complex mixture of solids (Figure 5) containing a variety of polymers including PE, PP, PVC, PET, PS, and other polymers as well as additives and contaminants. Physical separation of these complex mixtures to recover the pure components is currently very challenging. Fiber-reinforced epoxies and multilayered packaging represent extreme cases of intrinsic incompatibility and



**Figure 5.** Most discarded polymer streams consist of compositionally nonuniform solid mixtures that include different classes of polymer materials containing additives and combined with other types of waste. Source: iStock image.

inseparability of distinct materials components. In these consumer waste streams, there are both macroscopic mixtures—milk and soda bottles, household products, packaging, and other products—and microscopic mixtures—multilayered materials, polymer blends, composites, additives, and contaminants. Manually sorting these materials to discard the multicomponent materials, followed by isolation of selected polymers, is labor-intensive, inefficient, and expensive.<sup>54</sup> Separation based on solubility or melting point tends to be problematic because the most widely used polymers are neither readily soluble<sup>55</sup> nor melt at low-temperature.<sup>56</sup> The high viscosity of most polymer melts represents another processing challenge, as discussed in PRO 1, because the melts are poorly suited to the well-established methods for separating mixtures of gases or low-viscosity liquids into their pure components. When the polymers are components of composite materials, such as fiber-containing thermosets or multilayered materials, even accessing the polymer component can be difficult.

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Instead of sorting polymers into their individual components, different polymers can be blended together to make new materials. However, most polymers are immiscible with one another because of the large unfavorable enthalpy of mixing. Thus, most polymer blends tend to macrophase separate, which leads to poor mechanical properties. If the phase behavior and morphology of polymer blends could be controlled, these immiscible blends could be turned into useful products. Traditionally, the interfacial properties of polymers are modified with compatibilizers, which are copolymers (block or graft) that are compatible with both phases and segregate preferentially to the interface. This approach ensures strong interfacial adhesion, good mixing, and improved properties. However, more flexible, robust, and cost-effective methods are needed for controlling the physical behaviors of mixtures of discarded plastics that account for the diversity and compositional variation of the feedstock.

## Scientific Challenges

Currently, few chemical processes exist to extract value from polymer mixtures, and almost no methods are available to predict how to design them. Key challenges for transforming mixtures of discarded polymers include (1) processing solid materials with different solubilities, chemical reactivities, and melting points; (2) characterizing the variable content of mixtures comprehensively and quickly; and (3) characterizing and managing impurities, which can poison catalysts and impact material properties. Addressing these challenges offers new research opportunities for building scientific understanding and new synthesis and processing routes for chemical transformations of mixed plastics to chemicals and fuels, as well as to new materials.

To address the challenges of integrating deconstruction reactions with chemical separations in the upcycling of mixed polymers, catalytic membranes could be designed to deconstruct plastics and selectively remove the products before unwanted side reactions occur. Products could also be removed based on size such that a range of product could be isolated, such as C<sub>5</sub>–C<sub>12</sub> hydrocarbons for fuel, or functionality such that aromatic hydrocarbons could be removed. Another more appealing (and energy-efficient) approach would be to develop selective chemical transformations to bypass complex and expensive separations. For example, chemical functionalization of polymers during upcycling could facilitate their solubilization or compatibilization with other polymers. Alternatively, low-temperature catalytic processes could be designed to react with the solid feeds directly. Since additives, such as colorants, plasticizers, antioxidants, and fire retardants, can poison conventional catalysts, there is a need for new catalysts or processes that resist poisoning.

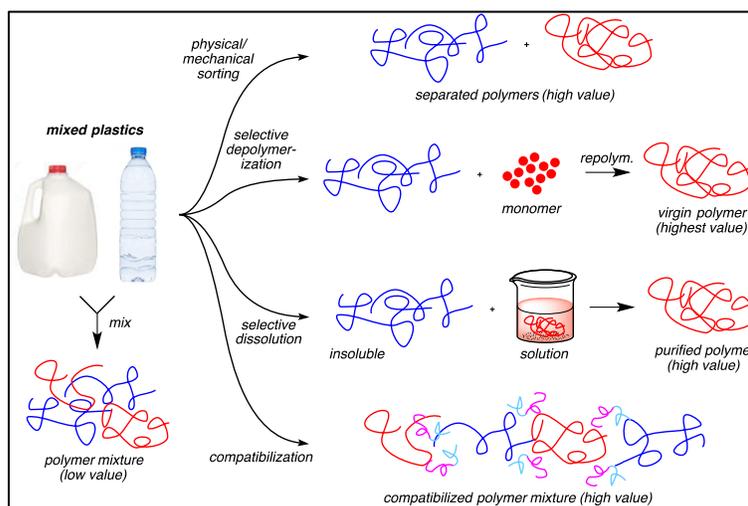
Another challenge in processing a heterogeneous mixture of plastics is designing catalysts or chemical processes that selectively transform an individual polymer or classes of polymers in a mixture into products. Potentially, tandem reactions could be designed to sequentially deconstruct mixed plastics to chemical feedstocks, or stimuli-responsive catalysts could be embedded into multilayer plastics to initiate the separation and deconstruction. Another approach could be to simultaneously deconstruct the mixed plastics into chemical intermediates that could be selectively reconstructed into new polymers or to deconstruct a subset of the polymers in a mixed plastic stream, such as polyolefins, into a versatile set of platform molecules, which could be used to make a variety of products. This approach would require the design of new catalysts and processes that work together to leverage the chemical heterogeneity of the mixed plastics. Finally, mixed plastics could be blended together with a compatibilizer to make new materials, which requires the design of copolymers that can preferentially segregate to the interface of immiscible polymers.

To avoid having to dissolve the mixed plastics in a solvent, it is desirable to develop methods to selectively transform solid polymer mixtures to products as discussed in PRO 1, which may require appropriate combinations of different approaches, such as cascading conversions that deploy microbial pathways, photocatalytic or electrochemical transformations, and thermocatalytic processes. In particular,

biological processes, which can remove organic degradable contaminants, could be integrated into processes for upcycling recalcitrant polymer mixtures. Theoretical methods can be combined with in situ characterization methods of catalysts, reaction intermediates, and products to predict and optimize chemical and catalytic transformations of polymer mixtures (discussed in PRO 4). Combining different conversion approaches with new polymer designs could lead to powerful new strategies for upcycling polymers.

## Summary of Research Directions

Discarded plastic mixtures can be viewed as an abundant, inexpensive, but diverse and unconventional chemical feedstock. The types of high-value products that could be extracted from discarded polymers range from new molecular building blocks, commodity and specialty chemicals, and fuels to new types of polymers and polymer blends with desirable physical properties. PRO 1 addresses converting discarded plastics containing primarily one polymer, and PRO 2 addresses the considerably more difficult and less-explored task of transforming mixed polymer systems into high-value products. Potential strategies for addressing mixed discarded plastics are summarized in Figure 6.



**Figure 6.** Overview of potential strategies to enhance the value of mixed plastics: physical sorting and mechanical recycling, selective deconstruction of a polymer in a mixture to monomer or chemical intermediates, selective separations of a polymer in a mixture by dissolution, and synthesis of polymer blends from a mixture of polymers using compatibilizers. Image courtesy of Geoffrey Coates.

## Develop catalysts for deconstruction of one component in a polymer mixture

One strategy for extracting value through catalytic transformation is selective functionalization or degradation of one polymer within a mixture or composite to separate and recover specific chemical components and facilitate recycling of the remaining polymers. Key requirements for such catalysts include the ability to selectively react with one polymer in a mixture and operate in demanding environments such as viscous melts, and resistance to poisoning by various trace contaminants or by the other polymer components. Some promising results have been obtained with textiles, specifically cotton/polyester blends. Such processes will ideally need to proceed with relatively low energy input, and optimally in a closed-loop fashion with efficient recovery of both catalyst and solvent (if a solvent is required). Examples include depolymerization of PET in mixtures with polyolefins (i.e., soda bottles)<sup>57</sup> or cotton (polyester/cotton blend fabrics)<sup>58,59</sup> (see Sidebar 3). Recent studies have used *E. coli* bacteria with polyester-based textiles and other woven products such as tents, bedspreads, and bandages to extract terephthalic acid for subsequent repolymerization to a product with upgraded quality.<sup>60</sup>

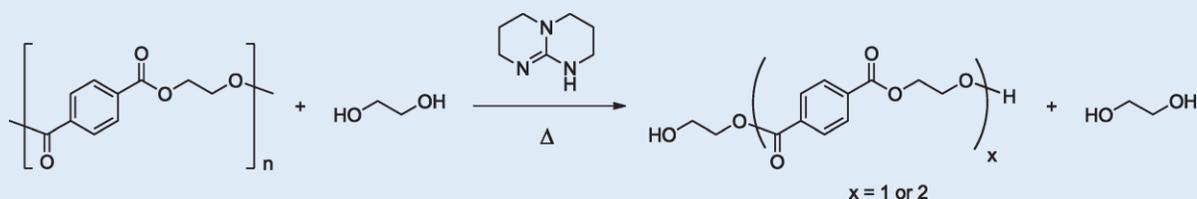
Chemical transformations of polymer mixtures should not be restricted simply to recovery of the original starting monomers. They should also provide new routes to existing commodity and specialty chemicals, or to an expanded range of new products that may be less readily accessible from existing starting materials. A recent study has shown that post-consumer PLA or propiolactone plastics containing polymeric and other impurities can be thermolytically converted to pure acrylic acid streams.<sup>61,62</sup>

### Sidebar 3: Integrated Chemical Recycling of Mixed Plastics: IBM's VolCat Process

IBM's VolCat process is one example of a chemical recycling process in which an organic catalyst selectively depolymerizes a polyester to monomer, leaving the impurities intact, and delivers "molecular sorting" (Figure S3.1). The methodology is applicable to separate polyolefin caps from polyester soda bottles by converting PET to bis(2-hydroxyethyl) terephthalate (BHET), a monomer that can be used to polymerize PET anew. In the VolCat process (Figure S3.2), a heterogeneous mixture of plastics containing PET is combined with a volatile organic amine catalyst and ethylene glycol (a compound commonly used as antifreeze), which can be recovered and reused. The product, BHET, is a soluble, small molecule building block that is readily separated from the unreacted (and insoluble) components of the mixture by simple filtration. The BHET is purified by recrystallization, which results in a building block that can be used to synthesize PET with the same physical, chemical, and mechanical properties as PET made from the petrochemical resources. Thus, VolCat is a fully integrated process that can efficiently transform complex mixtures of polyester and other polymers into a valuable monomer for the synthesis of new polyester.



**Figure S3.1.** The VolCat process. Source: <https://www.research.ibm.com/5-in-5/trash/>. Used with permission from IBM.



**Figure S3.2.** Glycolysis of polyethylene terephthalate catalyzed by 1,5,7-triazabicyclo[4.4.0]dec-5-ene. Source: Fukushima, K. et al. *Organocatalytic Depolymerization of Poly(Ethylene Terephthalate)*. *J. Polym. Sci. Part Polym. Chem.* **2011**, 49 (5), 1273–1281. Used by permission from Wiley Materials.

Another approach to selectively transform one polymer or class of polymers in a mixture is to use electrochemistry. Electrochemical approaches have the advantage that electron transfer processes, which form reactive species such as cation or anion radicals, are controlled by the applied potential and provide an efficient pathway for selective chemical transformations.<sup>63</sup> Electrochemical methods have been used to depolymerize and functionalize lignin under mild reaction conditions to yield small molecule products and aromatic monomers.<sup>64</sup> Thus, instead of using a catalyst and high temperatures, electrochemical methods could be developed for selective functionalization of carbon-hydrogen or carbon-heteroatom bonds, or depolymerize polymers by selective generation of radical intermediates under mild conditions.<sup>65</sup> Electrochemical methods have also been widely used in organic synthesis to prepare new compounds<sup>66</sup> and polymerize monomers to produce thin films of conducting polymers such as polythiophene and polypyrrole. Recently, electrochemical approaches have been developed for controlled radical polymerization reactions using atom transfer radical polymerization<sup>67</sup> or reversible addition-fragmentation chain-transfer polymerization reactions.<sup>68</sup> Thus, electrochemical methods can be used to deconstruct polymers and transform the chemical intermediates into higher-value products or new polymers.

Electrochemical synthesis is considered to be an efficient, scalable, environmentally friendly, and sustainable alternative to traditional, redox-based chemical methods. However, there are still challenges that need to be overcome using electrochemical methods for novel deconstruction and reconstruction of discarded plastics. Electrode composition and morphology need to be optimized to maximize current flow and kinetics and be highly resistant to fouling and corrosion processes. Solvent and electrolytes need to be

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tuned to optimize polymer solubility, kinetics, and reaction selectivity. Reaction cells and processes can be designed to overcome challenges such as over-reduction or over-oxidation at the electrodes and mass transport effect. Novel flow cells and separation methods can be used to extract products from the reaction mixture before unwanted side reactions occur. Mediators, which are soluble redox-active species, can be designed to alter reactivity, reduce overpotentials, and improve reaction kinetics.<sup>69</sup> By addressing these challenges, new opportunities arise for accessing unique selectivities and unconventional reaction pathways for bond formation and cleavage in discarded plastics.

### **Design strategies to facilitate blending of polymer mixtures**

There are two main approaches to blending immiscible polymers to make new materials: (1) addition of a compatibilizer, which is a block or graft copolymer that is compatible with the two phases and preferentially segregates to the interface upon melt mixing, and (2) reactive blending in which reactions occur between the polymers or additives to make copolymers at the interface during melt processing. By designing new polymeric compatibilizers for mixed discarded plastics, a variety of plastics could be blended together to produce new stable polymers with superior performance (see Sidebar 4).<sup>70</sup> Fundamental science challenges include the identification of molecular architectures and chemical compositions that quickly migrate to the polymer interface and provide strong interfacial adhesion. To be economically viable, compatibilizers with elaborate structures must be highly effective to reduce the quantity of compatibilizer needed. New compatibilizers should be as general as possible and function with a wide variety of polymers so that purification of postconsumer plastics will not be necessary to produce polymer blends with consistent properties.

Another approach to blending incompatible polymers involves reactive blending in which dissimilar polymer chains are covalently coupled during processing. For example, polymer chains terminally functionalized with complementary reactive groups, such as carboxylic acids, epoxides, cyclic anhydrides, and primary amines or hydroxyl groups, can undergo covalent reaction in the melt to form new block copolymers that stabilize the polymer blend.<sup>71</sup> The challenge with this method is to selectively functionalize the polymer chains with a reactive group (as described in PRO 1) and to have fast reactions at the temperature of the melt. An alternative approach involves solid-state shear pulverization in which mechanical processing leads to polymer chain scission and recombination reactions with neighboring chains to produce block-and-graft copolymers that act as compatibilizers.<sup>72</sup> Although the reaction can take place at low temperatures by cooling the extruder, the challenge is to selectively control the generation and reaction of the reactive (radical) species to control the formation of new materials. In this case, instead of mechanical recycling leading to downcycling, polymer degradation is controlled to produce improved compatibilization and improved properties. Coupling chemical functionalization with mechanical processing can also be used to improve the properties of discarded plastics. For example, the properties of polyamides from discarded carpeting were restored by properly designing chain extension agents (e.g., bis-oxazoline or bis-caprolactam derivatives), which were mixed with the polyamides in an extruder at very low concentrations (1–5 wt %). This approach significantly improved the materials' performance and addressed the embrittlement of polyamides.<sup>73</sup> Thus, there are many opportunities and challenges in blending incompatible polymers to generate new higher-value products from mixed discarded plastics.

To process and blend cross-linked polymers, such as thermosets, there has been significant interest in designing new polymers with reversible covalent linkages. Vitrimers are polymer networks that can change their topologies by associative exchange reactions and can be thermally processed in a liquid state without losing network integrity.<sup>74</sup> A wide array of vitrimer structures have been developed that show a viable approach to the repair, assembly, and alloying of mixed polymers and represent a potential solution to the recycling of plastics without the need to sort them. However, there are significant scientific

challenges that need to be overcome to design new polymers with covalent bonds that are reversible upon application of an external stimulus and have good mechanical properties, as described in PRO 3.

#### Sidebar 4: Upcycling Discarded Polymers by Design of Compatibilizers

The recycling of plastics is complicated by the comingling of many different types of polymeric materials (e.g., polyesters, polyolefins, polycarbonates, PVC). Separation can be achieved to a certain extent by exploiting differences in polymer densities; however, additives, such as glass or carbon fibers, can change the density of the plastic. Moreover, some polymers have very similar densities, which leads to significant contamination of one type of polymer with another. For example, PE and isotactic polypropylene (iPP) are similar in density and are mutually immiscible. Thus, mechanical recycling results in macrophase separation (e.g., oil and water) and the polymer blend has inferior mechanical properties compared with the original polymers.

The key to making stable polymer blends is in the design and synthesis of macromolecular additives, which can serve as compatibilizers for PE and iPP. For example, a block copolymer with four short, alternating segments of PE and iPP was synthesized with a transition metal catalyst with precise control over the length of each segment (Figure S4.1). This so-called tetrablock copolymer compatibilizes PE and iPP by spanning the interface between the immiscible polymers (Figure S4.2 A and B) and serves as a macromolecular suture to stitch the two polymers together. The mechanical properties of the blend are intermediate between PE and iPP and far superior to those of the uncompatibilized blend (Figure S4.2 C). Surprisingly, the diblock copolymer, which is composed of short PE-iPP chains, did not show a significant improvement in mechanical properties (Figure S4.2 C) compared with the tetrablock copolymer, which highlights the role of molecular architecture on mechanical properties. Although costly, the compatibilizer is only needed in very small quantities ( $\leq 1$  wt %) to improve the mechanical properties, making it possible to use this approach to transform a PE-iPP mixed polymer stream into a new value-added product.

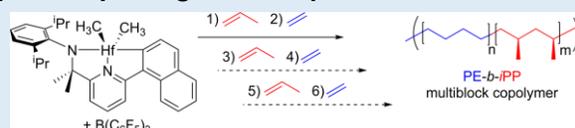


Figure S4.1. Synthesis of PE-iPP block copolymers.

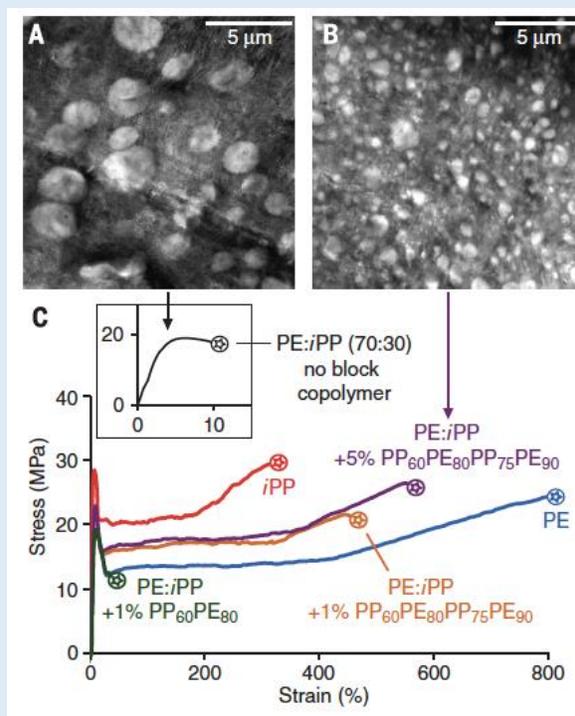


Figure S4.2. (A and B) Transmission electron microscopy images of PE-iPP blends show droplet morphology without block copolymers (A) and with 5 wt % tetrablock copolymers (B). (C) Materials melt blended at 190 °C without block copolymers (black, inset), with 1 wt % diblock (green), 1 wt % tetrablock (orange), and 5 wt % tetrablock copolymers (purple). Source: Eagan, J. M., et al. Combining Polyethylene and Polypropylene: Enhanced Performance with PE/iPP Multiblock Polymers. *Science* **2017**, 355, 814–816.

#### Design new catalysis for fuel and chemical recovery

One approach to extracting products of higher value from a mixture of plastics is to integrate catalytic transformations and separations for each type of polymer in a mixture. To achieve this goal, techniques are needed that can assess the overall composition of discarded plastics and rapidly identify their individual components (as discussed in PRO 4). Extracting higher-value products from solid polymers and viscous melts will require new process and reactor designs. Understanding molecular interactions in complex mixtures of macromolecules and catalysts will also be critical. The development of robust

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models validated by experimental data will allow a fundamental understanding of the structure–property relationships, as well as the molecular interactions and complex catalytic networks, for heterogeneous mixtures. That understanding will, in turn, enable control over reactivity and selectivity for the components present in mixed discarded polymers.

Although the chemical upcycling of mixed plastics is challenging, pyrolysis and catalytic pyrolysis methods have been developed over the past decades to convert mixed plastics into chemical products, such as fuels, in high yields, as discussed in PRO 1 (see Sidebar 1). One of the advantages of pyrolysis is that the mixed plastics need not be sorted, and PVC can be processed if the HCl is neutralized. Further advances in catalyst design are needed to improve the reactivities and selectivities for converting these streams to the desired targets. For instance, mixed plastics can be converted to hydrocarbons in the fuel range (C<sub>5</sub>–C<sub>12</sub>), and catalytic pyrolysis affords higher yields (76–96% vs 67%) of fuel-grade products at lower temperatures (240 °C) than thermal conversion (>450 °C) in the absence of a catalyst.<sup>75</sup>

A crucial challenge in the conversion of mixed discarded plastics to fuel is discerning whether the distribution of products is a function of the heterogeneity of the plastic mixture in the feed stream, or a consequence of impurities in the plastics that modulate or inhibit the catalytic sites. Additives are formulated to enhance the physicochemical properties of specific plastics, but they are potential catalyst poisons; and in mixed plastic streams, the different additives may prove deleterious to the quality of the recycled product.

Another issue is that the decomposition of many plastics can create harmful substances. Thermal degradation of PVC can release harmful chlorinated organic compounds, dioxins, and HCl. Therefore, research directions for upcycling of mixed plastics must thoroughly consider the dechlorination and deconstruction of PVC, a ubiquitous discarded plastic. For example, by mixing PVC with CaCO<sub>3</sub> before catalytic pyrolysis, the HCl liberated during PVC deconstruction can be trapped.<sup>76</sup> Operando treatment of catalysts with HCl leaching from PVC can poison catalytic sites; however, it could also increase the surface acidity of resistant catalysts. Such self-activating catalysts have not been explored in the area of polymer upcycling. Also, the HCl would be used as a catalyst for the hydrolysis of condensation polymers such as polyester, polyamides, and PC.

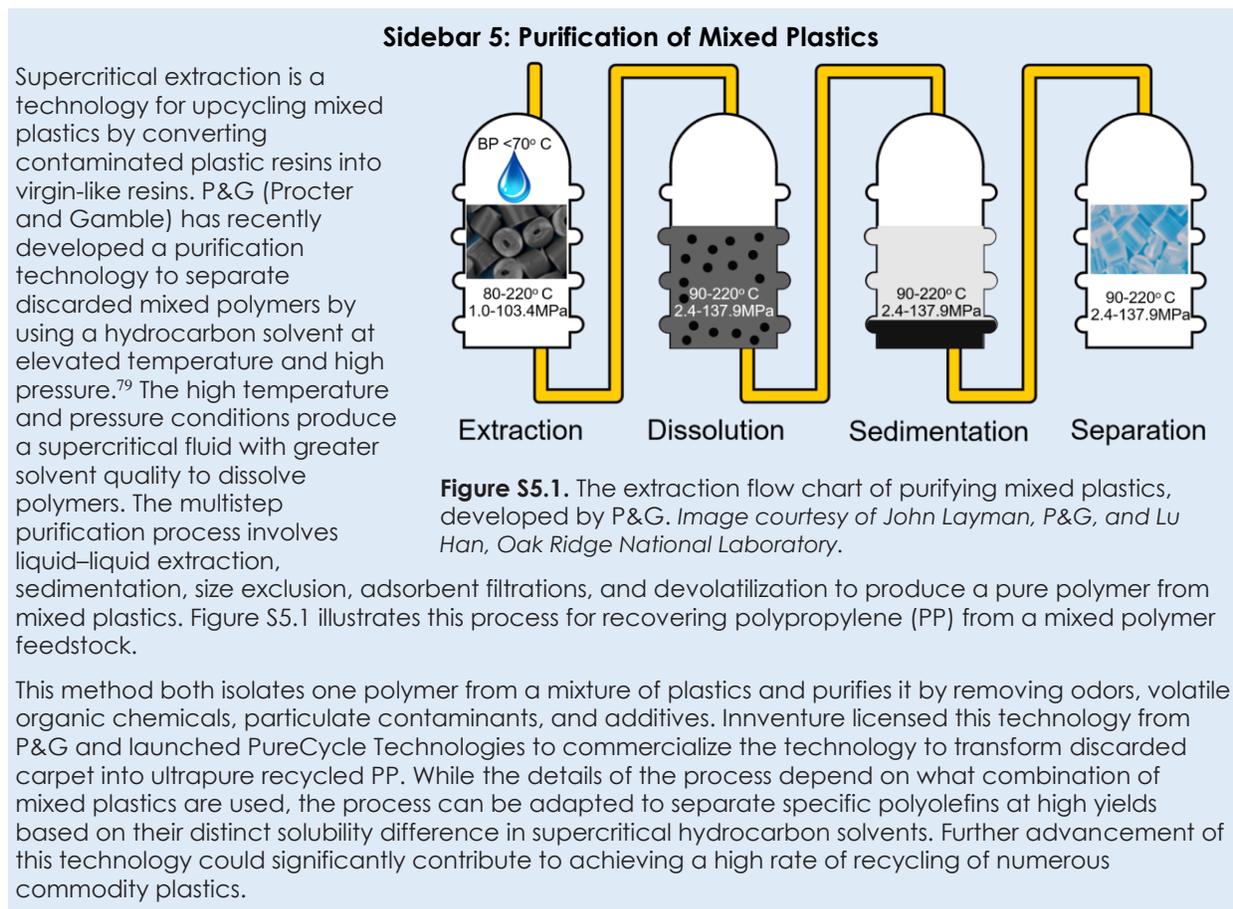
To design new catalyst and chemical processes to produce fuel and chemicals from mixed plastics, insights can be gained from the catalytic deconstruction of pristine plastics described in PRO 1. The fundamental understanding of the reaction mechanisms can be used to provide new insights into the factors that affect the conversion rates and selectivity in the deconstruction of mixed plastics. This understanding will also help guide the design of processes that take advantage of the chemical complexity of the products to make fuel and chemicals.

### **Develop physical or chemical separations followed by conversion to product**

Mixed discarded polymers—such as PET soda bottles contaminated by caps made from polyolefin (PP or HDPE)—could be more efficiently transformed if efficient separation processes could be integrated before the chemical recovery of intermediates. The selective dissolution of olefinic components offers new opportunities for the physical separation of minor or major components from discarded plastics (see Sidebar 5). With appropriate reactor design and solvent recovery, solvent-based separations can provide strategies for separating components in discarded textiles or post-consumer carpets containing polyolefin products.<sup>77</sup> Many new sustainable products for textiles, industrial yarns, and the fashion industry can be made from post-consumer plastics, particularly PET.

In designing chemical processing and separation strategies for mixed plastics, many factors need to be considered and optimized, including the selectivity, kinetics, energy requirements, solvent requirements, and tolerance to additives and impurities, as well as other factors. Since polymer upcycling is largely

motivated by energy, economic, and environmental factors, the processes need to be energy-efficient, inexpensive, and environmentally friendly. Many tools are available that can help guide the development of new sustainable processes. For example, life cycle analysis is a tool that quantifies the environmental impacts resulting from the production, use, and disposal of a product or process.<sup>78</sup> This tool and others can increase the awareness of green chemistry principles and aid the development of chemical products that account for the coproduction of undesirable chemicals and eventual end-of-life for new chemical and material products.



## Scientific and Technological Impact

Learning to upcycle mixed plastics will expand the molecular-level understanding of how molecular and mesoscale interactions and reactions impact macroscale properties, function, and products. Developing methods to process mixed polymers will enhance the ability to undertake transformations for many other types of solid mixtures (e.g., non-food biomass). It will lead to the design of new stable low-temperature catalysts, catalytic transformations involving the coupling of reactions and reaction networks, and concepts for the integration of separations with chemical transformations. It will also stimulate the investigation of new classes of materials based on polymer blends with unique properties.

Developing economical methods for the chemical upcycling of mixed plastics will enable single-stream waste recycling processes, thereby reducing the energy costs required for separating the plastics. It has the potential to generate new routes to existing products using a low-value feedstock. This development can also lead to an expanded product portfolio that includes polymer materials based on mixed feedstocks that cannot readily be derived directly from conventional resources.

## PRO 3: Design Next-generation Polymers for Chemical Circularity

**Key Question:** *How can we design new polymers that have the properties of today's polymers and enable simple reuse of the molecular building blocks?*

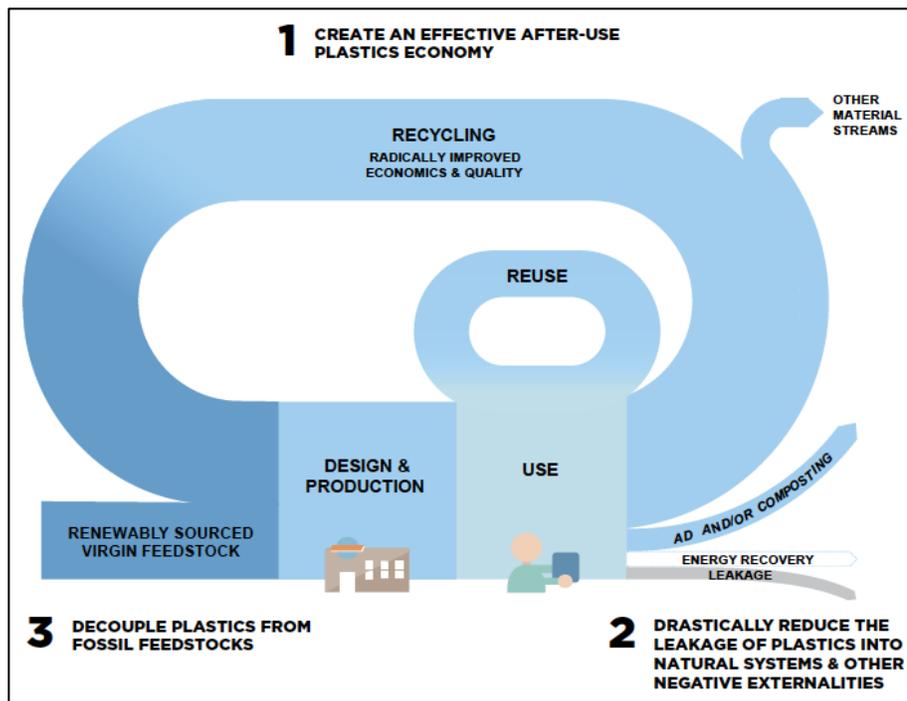
### Summary

In general, commercial plastics are not recycled in a closed-loop, circular manner, in part because methods to selectively deconstruct polymers back to their original monomers are absent, except for a few polymers such as PET, nylons, and—to a lesser extent—PMMA and PS. New plastics need to be intentionally designed to have a desired set of physical and mechanical properties, as well as to efficiently deconstruct at the molecular level into monomers or chemical intermediates that will be used to reconstruct plastics, with the goal of closing the loop in plastics recycling and chemical upcycling. New monomer and polymer chemistries need to be developed that both deliver next-generation polymers with properties similar or superior to those of current polymers and enable circular life cycles using atom- and energy-efficient processes.

### Introduction

The ability to create new plastics that have properties similar or superior to those of current materials, and that can at some later time be selectively deconstructed back into monomers or other intermediates for eventual reconstruction, will define a new paradigm for plastics. Acquiring this ability will require designing new chemistry and properties into plastics for circularity of construction—deconstruction and then reconstruction to create new plastics fabricated to have desired properties and circular life cycles. Circular plastics are highly

sought-after as renewable resources for a circular economy, which endeavors to decouple economic activity from the consumption of finite energy resources by designing out waste.<sup>7,80</sup> One vision of the circular life cycle of plastics was presented in the recent report, *The New Plastic Economy: Rethinking the future of plastics & catalysing action* (see Figure 7). In this vision, reliance on fossil fuels as chemical feedstocks is eliminated by focusing on renewable feedstocks, reuse, and recycling.<sup>7</sup>



**Figure 7.** Future vision of the circular life cycle of plastics. AD: anaerobic digestion. Source: Adapted image used courtesy of Ellen MacArthur Foundation, [https://www.ellenmacarthurfoundation.org/assets/downloads/publications/NPEC-Hybrid\\_English\\_22-11-17\\_Digital.pdf](https://www.ellenmacarthurfoundation.org/assets/downloads/publications/NPEC-Hybrid_English_22-11-17_Digital.pdf).

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Currently, conventional plastics are not recycled in a closed-loop, circular manner, in part because of the paucity of methods for chemical depolymerization back to their original monomers; the most notable exception is the chemical circularity demonstrated in PET recycling (see PRO 2 and Sidebar 3). Polyesters (e.g., PET) and polyamides (e.g., Nylon 66, Kevlar, Nomex) are prepared by condensation reactions that form ester or amide linkages, respectively. Those linkages can be reversibly cleaved, for example by hydrolysis; and these reactions will benefit from the design of new efficient catalysts (see PRO 1) and integrated processes that will create efficient routes to deconstruct these polymers. These developments could be adapted to PLA and Nylon 6, which also have ester and amide linkages, respectively, along the polymer backbone. To achieve chemical circularity, the monomers or intermediates produced during deconstruction will need to be purified to remove additives, such as colorants, fillers, or fire retardants, before reconstruction. The construction–deconstruction–reconstruction loop can then be completed to achieve polymer circularity for these two types of polymers.

Although it may be desirable to seek out strategies to depolymerize other commodity plastics with an eye toward achieving chemical circularity, chemical thermodynamics imposes limitations, particularly for polyolefins. As discussed in PRO 1, the origins of the stability of various grades of PEs and the driving force for polymerization of vinyl polymers—such as ethylene, propylene, styrene, vinyl chloride, and MMA—is the conversion of the weaker carbon-carbon  $\pi$ -bond to a stronger carbon-carbon  $\sigma$ -bond. From a thermodynamic perspective, the free energy of polymerization becomes less favorable as the temperature is increased and depolymerization back into monomers becomes the thermodynamically favored route. In principle, polymerization-depolymerization-repolymerization circularity could be achieved by conducting reactions at the appropriate temperatures. However, in many cases, at the high temperatures required for depolymerization, other reactions can compete with monomer formation and many products can be produced. For example, in the pyrolysis of PS in a fluidized bed reactor, the major product is the monomer styrene (up to 78%); but other products also are formed, including toluene, ethylbenzene,  $\alpha$ -methylstyrene, and a dimer and trimer of styrene.<sup>81</sup> Achieving the goal of closing the loop in plastics recycling requires that plastics be intentionally redesigned for chemical circularity at the molecular level.

Another factor that needs to be considered is the embodied energy for closed-loop upcycling of polymers, (i.e., the energy consumed by all the processes associated with the production of a material). Not all chemical upcycling processes are equivalent. Clearly, gasification or pyrolysis of mixed plastics to syngas and fuels, respectively, will use more energy than compatibilization. Chemical reactions (e.g., hydrolysis of esters, such as PET) require separations of products and solvent removal in addition to energy required to repolymerize the monomers back into a polymer. For polymer upcycling to be energy-efficient, the energy required to produce higher-value materials and chemicals from discarded plastics should be less than the energy required to produce the same products from fossil fuels.

Finally, it is currently estimated that 95% of the economic value of plastics, or \$80–120 billion annually, is lost to the environment after a single use.<sup>7</sup> Thus, there are economic, environmental, and energy benefits to addressing the scientific challenges of developing new monomers, polymers, and processes that deliver polymers with properties similar or superior to those of current polymers and enable circular life cycles. Thus, while chemical circularity is an important step toward sustainable solutions to the problems of discarded plastic, any new materials for plastic products will be extensively vetted against incumbent materials. It has taken decades to optimize today's commodity plastics for different products and uses, such as bottles, textiles, packaging, or construction. This optimization reflects a material's mechanical and chemical properties tied to end-use, processing requirements, cost, and aesthetics. Any disruptive innovation in circular plastics will require an equivalent but faster optimization effort. High-throughput experimental and computational methods, described in PRO 4, could be used to extract new correlations between the structure, properties, and processability of new materials. This will ensure value

is recaptured from discarded plastics in line with the fundamental and applied goals of chemical circularity.

### Scientific Challenges

To drive disruptive innovation in circular plastics, new monomers and polymerization chemistries need to be devised to yield polymers that confidently stand in as replacements for nonrecyclable polymers currently in use, but also offer scalable opportunities for resource recovery at end-of-life so that one-use plastics are intentionally designed out of the economy. Toward this goal, these questions arise: can new materials be designed that can be assembled into multi-material products of arbitrary complexity that can be expediently deconstructed by selective depolymerization (see Sidebar 6)? Can additives be efficiently separated from liberated monomers using atom- and energy-efficient chemical processes? Can the recovered products be reconstructed into new plastics with properties similar or superior to those of current plastics, enabling circular life cycles using atom- and energy-efficient processes? Can the number of processing steps needed to process discarded plastic be minimized to reduce the infrastructure and energy requirements?

If chemical depolymerization produces by-products, small molecules or oligomers that cannot be reused, valuable resources will continuously leak out into single-use waste streams. Thus, every component in a plastic needs to be designed with recovery and reuse in mind. Can monomers be recovered that are identical to those from which the plastic was originally derived? Can those monomers be recovered at sufficiently high purity that they can be immediately repolymerized into virgin-quality polymer resins for conversion into the next cycle of plastic products? It is critical that the research community address these scientific challenges by developing better materials, processes, characterization, and computational capabilities to further the understanding of, and control over, how polymers are manipulated at various stages in their life cycles. Only then will sustainability goals for resource recovery and management of material flow across interdependent partners in a circular ecosystem be realized.

The underlying chemistry of a plastic with a circular life cycle requires consideration of all aspects of the design, synthesis, processing, deconstruction, and reconstruction.

For example, there are challenges to the reprocessing of complex heterogeneous plastics, such as carpeting or multilayer packaging for foods and beverages. New materials with similar or superior properties must be developed with sorting and reprocessing in mind to overcome the current scientific and technical barriers. Chemical composition, structure, and morphology should be tuned to obtain the desired

#### Sidebar 6: Deconstruction of Multi-material Products



Innovative uses of polymers over the past decades have resulted in the complex construction of articles for everything from food packaging to footwear. In the food and beverage market, flexible packaging has evolved from single-material monolayer structures to laminates with more than seven layers. Each of these layers serves a unique function in the package to ensure that the quality of the product is maintained from manufacture to consumer use.

The ability to separate these individual layers and collect the materials after use remains a challenging obstacle to the industry, as discussed in PRO 2, since the packages are designed to provide the maximum benefit to the consumer and marketability for the brand. Simplification of design and the choice of the materials of construction will be critical to ensure that the material value is not lost and the materials can be upcycled. *Image used courtesy of DOW Inc.*

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properties so additives are not needed; or fillers, pigments, and additives should be designed so the components can be easily separated from the polymer matrix, recovered, and reused. Likewise, if comonomers are present, it should be easy to separate and recover them for circular plastics formulated with chemical heterogeneity. In the future, plastics need to be designed with their life cycles in mind, rather than solely for the material properties needed for a particular application. Doing so will require new fundamental knowledge and understanding of how chemical composition, structure, and morphology lead to desired processing and application properties and new monomers and chemical reactions to synthesize, process, deconstruct, and reconstruct new plastics for a circular economy.

In stride with chemical circularity, next-generation plastics designed with end-of-life in mind should ideally exhibit properties equal to or superior to those of current plastics (e.g., biological or chemical inertness, oxygen or moisture barrier, adhesion or flexural strength, resistance to crack propagation) if they are to succeed in the market. The challenge is to design new highly efficient bond-forming reactions or catalysts for the preparation of high-molecular-weight polymers that can be efficiently deconstructed. Efforts should also address the formation of both amorphous and semicrystalline thermoplastics. Additional effort should target new materials that have properties analogous to those of today's polyolefins, which represent 57% of all plastics globally produced (i.e., comparable glass transition temperatures [ $T_g$ ] and melting points in the range of PEs and PP).<sup>2</sup> Melt viscosities will also need to be tailored to allow for thermal processing, film blowing, injection molding, and other processes. To permit chemical upcycling, the deconstruction and degradation processes should not occur to a great extent either during processing or throughout the lifetime of the material in use. Upcycling could involve the complete chemical reversion of the polymer into monomer(s), or chemical modification with a co-reagent to convert the polymer into a new chemical species or into a new monomer (see Sidebar 3). These species could then be readily polymerized into macromolecules having desirable physical properties:  $T_g$ , melting point, crystallization temperature, and mechanical properties sufficient for a second application that could re-enter the chemical upcycling regenerative loop after use.

Likewise, for amorphous materials such as PMMA and PCs, duplicating the desired properties such as high  $T_g$  will require either designing clean chemical transformation steps to revert these materials to their respective monomers, or inventing new monomers and polymers that have the requisite properties, useful temperature, and optical performance. For an amorphous material with a sub-ambient  $T_g$  (polydimethylsiloxane [PDMS], natural and synthetic rubbers), clean chemical transformation steps need to be developed to revert the material to a monomer. That can be done practically in the case of PDMS by using base-catalyzed depolymerization to regenerate cyclic siloxane precursors to the polymer. For natural and synthetic rubbers, the presence of carbon-carbon double bonds along the backbone within each repeating unit provides a likely point for chemical transformation. Furthermore, it may be desirable to source circular plastics from sustainable resources of biological origin (i.e., biomass or bioproducts such as lactic acid) to remove reliance on fossil fuels.<sup>82</sup>

### Summary of Research Directions

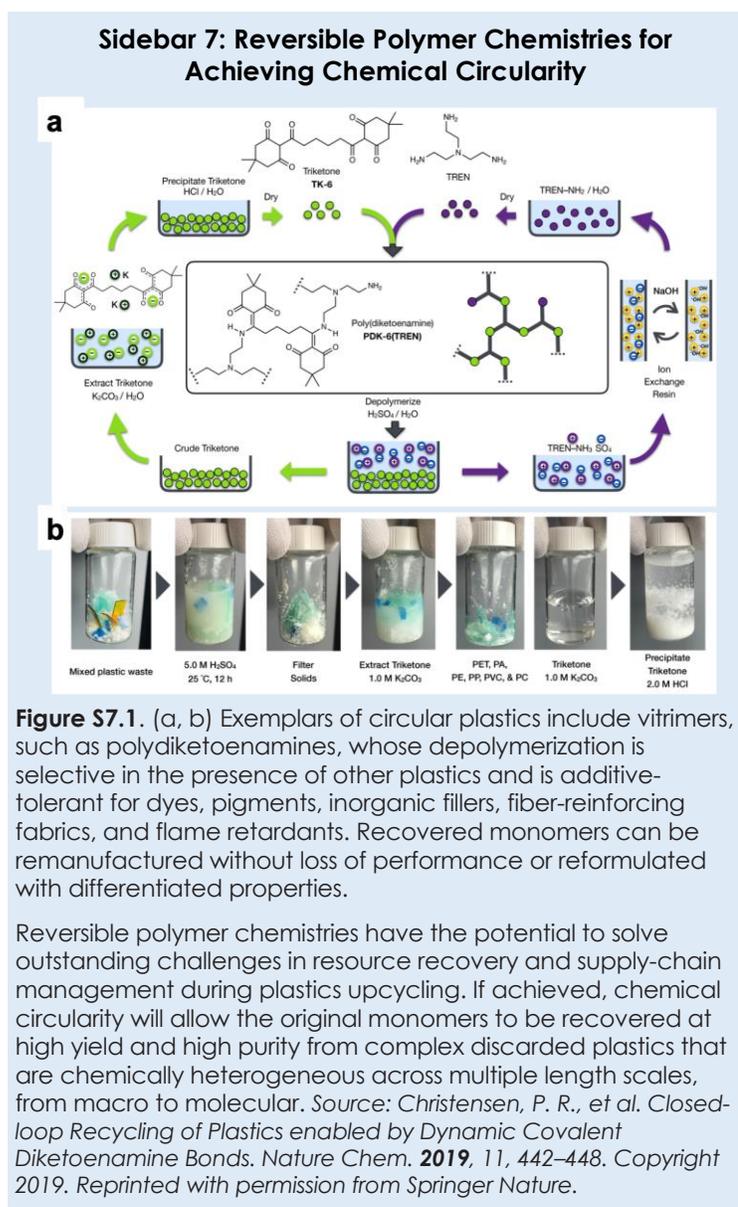
New monomers, catalysts, and processing strategies need to be designed and developed for construction of next-generation polymers that will enable a circular life cycle. These materials need to have the full gamut of physical, chemical, and mechanical properties, as well as processing capabilities to make them drop-in replacements for today's plastics. The goal is to either fully deconstruct these new polymers into virgin-grade monomers that can be made into the same plastic for use in the same or similar applications, or to modify them by adding or subtracting elements or blending with other polymers to afford new materials for reuse in different applications.

To avoid bottlenecks and inefficiencies, deconstruction, depolymerization, additive dissociation, monomer(s) recovery, and reconstruction should be thought of as a single integrated process. Furthermore, since discarded plastics are likely to be heterogeneous, any chemical processing step(s) implemented should be tolerant of a wide range of biological and chemical residues and other impurities (including other plastics). These chemical processes should be atom-efficient to minimize the energy resource requirements for processing. Any resources used or consumed at each stage of transformation ideally will be recoverable and reusable (e.g., catalysts, supported reagents, sorbents, solvents). The sustainability of the circular plastic cycle will also depend on the overall energy use and water requirements.

## Development of reversible polymer chemistries

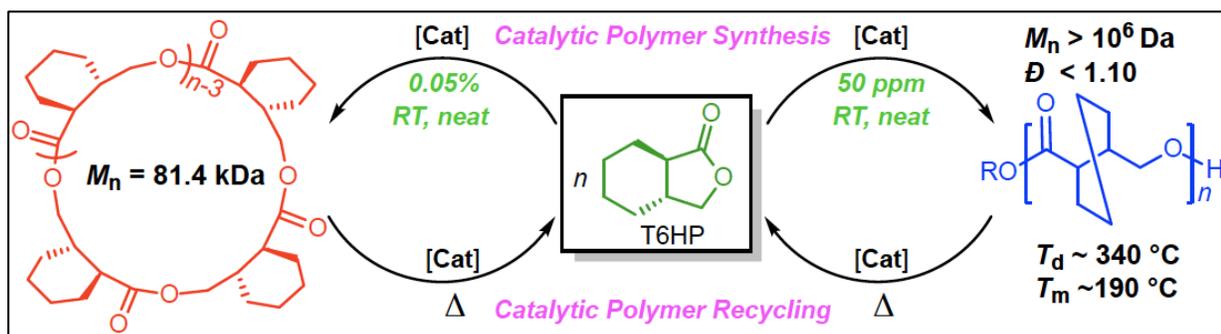
To meet the goal of chemical circularity, future research directions should seek to advance reversible polymer chemistries for post-consumer plastics upcycling that go beyond the current state of the art.<sup>83,84</sup> More specifically, while there are now many examples of dynamic polymer chemistries (e.g., covalent adaptable networks and vitrimers) that enable post-industrial recycling of thermosets by remolding,<sup>85</sup> it is not clear whether these chemistries or others are needed to return a resin to its original monomers at virgin quality when it is part of a multi-material item, contaminated with residues, or compounded with fillers, colorants, plasticizers, and/or UV stabilizers. Methods need to be developed for the selective depolymerization of a plastic in the presence of additives or other polymers, which will provide a pathway to upcycle mixed plastics (see Sidebar 7). One of the challenges of processing mixed plastics is developing selective catalysts that react with only one component of the mixture and efficiently isolating the products in sufficient purity for repolymerization.

In the future, reconstruction strategies for achieving chemical circularity should advance based on their selectivity, tolerance to impurities, and prospects for atom- and energy-efficient reversibility. These might be achieved by pairing condensation polymerization with solvolytic or hydrolytic depolymerization, ring-opening polymerization with ring-closing depolymerization, cyclopolymerization with retro-cyclodepolymerization,



supramolecular bond-forming polymerization with supramolecular bond-breaking depolymerization, and other chemistries with similar outcomes. Within each of these mechanistic classifications, variants harnessing covalent, dynamic covalent, or non-covalent chemistries may be envisioned and, on that basis, might provide unique opportunities for chemical circularity. Predictive design (e.g., by approaches based on high throughput, density functional theory [DFT], and data science) at all stages of development of plastics with circular life cycles could greatly accelerate the discovery process and would make a powerful accompaniment to experimental efforts, as described in PRO 4.

Strategies for reversible polymerization of linear and branched polymers (e.g., thermoplastics, thermoplastic elastomers) as well as to polymer networks (e.g., cross-linked elastomers, thermosets) should be explored. Moreover, new monomers may need to be designed for reversible polymerization to ensure scalability, energy-efficient reaction conditions, and practical rates of forward and reverse reaction; processability during manufacturing; and performance and stability throughout a plastic item's service life. One of the challenges in reversible polymer chemistry is that polymers that can be easily depolymerized into monomers typically require energy-intensive repolymerization conditions and lack the robust mechanical and physical properties required for common applications. For example, poly( $\gamma$ -butyrolactone) can be quantitatively depolymerized back to a monomer at 220–300 °C or by chemolysis at RT, but repolymerization requires energy-intensive conditions (–40 °C).<sup>86</sup> To overcome this problem, a trans-ring fusion strategy was developed to increase ring strain in  $\gamma$ -butyrolactone. Thus, a new monomer was synthesized in which a cyclohexyl ring was trans-fused to  $\gamma$ -butyrolactone at the  $\alpha$ - and  $\beta$ -positions, enabling polymerization to high-molecular-weight polymers at RT with linear or cyclic topology. The polymer properties were also enhanced, while complete recyclability back to a monomer by pyrolysis or chemolysis was preserved (Figure 8).<sup>87</sup>



**Figure 8.** A synthetic polymer system based on trans-hexahydrophthalide (T6HP) with endless reversibility of depolymerization and repolymerization. The catalyzed ring-opening polymerization of T6HP under room temperature (RT) and neat conditions produced high-molecular-weight polymers with linear or cyclic topology and robust properties of common plastics. The catalyzed depolymerization recovered the monomer in quantitative yield and high purity; the monomer can be directly and repeatedly repolymerized into the same polymer. Source: Adapted from Zhu, J. B. et al. A Synthetic Polymer System with Repeatable Chemical Recyclability. *Science* **2018**, 360 (6387), 398–403.

Integration of renewable feedstocks in monomer designs may also provide rich opportunities for sustainability, (e.g., by enabling the biodegradation of circular plastics into nutrients or benign compounds if they leak out of the ecosystem).<sup>88,89</sup> Although the most common biobased biodegradable polymers—such as PLA, polyhydroxyalkanoates, PET, succinate-derived polymers, and polysaccharides—have found applications in the market, there is a need to reduce the cost of biobased polymers through innovative chemistry and processing. There is also a need to develop new biobased materials with higher performance and value such as thermoplastic elastomers, engineering plastics, or composite materials.<sup>82</sup> An area of opportunity for renewable plastics is in packaging applications. Finally, in designing new biobased polymers, it is important to identify building blocks that can easily be prepared from abundant feedstocks and that do not compete for resources with food crops or alter the ecosystem.

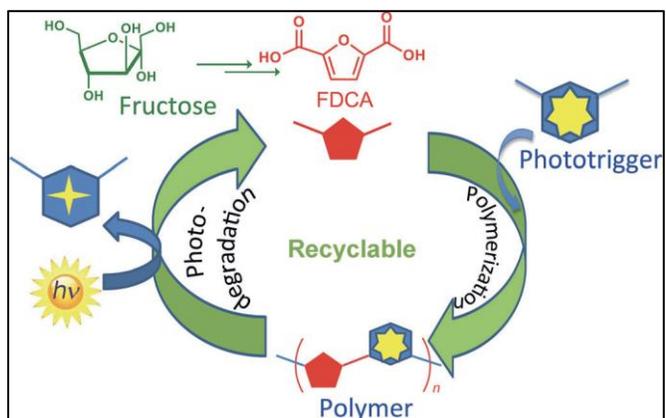
## Stimuli responsive deconstruction

Depending on the deconstruction or reconstruction mechanism, it may be necessary to identify and implement various catalysts, reagents, electrochemical, or physiochemical triggers (e.g., temperature or light) to enhance recovery and improve the overall efficiency of the closed-loop life cycle. For example, linear and cyclic poly(*o*-phthalaldehyde) has been shown to undergo mechanically triggered depolymerization back to a monomer.<sup>90</sup> Sonication was used as the mechanical driving force, and the obtained monomer was repolymerized by a chemical initiator back to the original polymer, completing the depolymerization-repolymerization cycle.

Light can also be used to induce chemical transformation in polymers so that they cleave, rearrange, or create chemical bonds.<sup>91</sup>

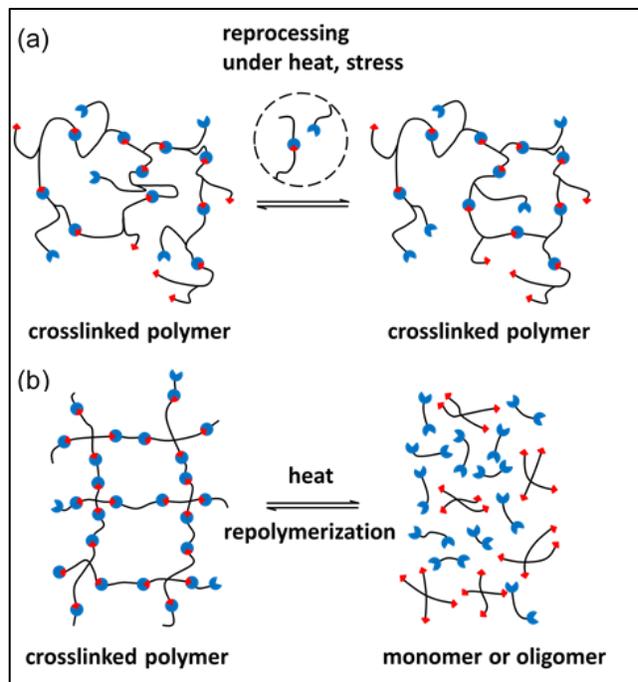
For example, photodimerization reactions by either a [2 + 2] (cinnamate, coumarin) or a [4 + 4] (anthracene) cycloaddition mechanism can be used to cross-link polymers and improve their mechanical properties.

Recently, a renewable polymeric material based on 2,5-furandicarboxylic acid containing built-in phototriggers (i.e., a nitrobenzyl chromophore) was synthesized and photodepolymerized under UV light back to a monomer (Figure 9) that could be used to resynthesize the polymer.<sup>92</sup> This strategy has the potential to build novel biobased plastics that are recyclable and photodegrade in the environment to biodegradable monomers.



**Figure 9.** Photodegradation of a biobased polymer derived from 2,5-furandicarboxylic acid. Source: Rajendran, S., et al. Programmed Photodegradation of Polymeric/oligomeric Materials Derived from Renewal Bioresources. *Angew. Chem. Int. Ed.* **2015**, 54, 1159–1163.

**Recyclable cross-linked polymers.** Cross-linked polymers (i.e., thermosets) make up more than 10% of all the polymers that are produced. They cannot be mechanical recycled, because they do not flow at elevated temperatures, or chemically recycled, because they are insoluble. Developing strategies to recycle cross-linked polymers without compromising their strength and chemical stability is a significant challenge. Reversible polymer chemistries—in particular, those based on dynamic covalent bonds, hydrogen bonds, or electrostatic interactions—yield polymeric materials with properties that may diverge from those of classical thermoplastics and thermosets.<sup>93</sup> For example, supramolecular polymers have plastic-like characteristics at low temperatures at which noncovalent interactions are strong and the persistence length of the macromolecule is long, and have molecular characteristics at high temperatures at which non-covalent interactions are weak and the persistence length is short. Similarly, vitrimers soften above their  $T_g$ , as would a thermoset; but they then flow as viscoelastic liquids at further elevated temperatures by associative exchange reactions, provided the temperature is also above the vitrimer's topology freezing temperature (Figure 10). The landscape of polymer properties for these materials is therefore dictated not only by polymer composition, morphology, and architecture but also by chemical dynamics, which have not been elucidated in sufficient detail to lay the groundwork for designing circular plastics for specific applications. Nevertheless, these characteristics are foundational to understanding and controlling their behavior during manufacturing (e.g., injection molding, extrusion, blowing, 3D printing), response to deformation, and physical aging. In this context, there is now an intensified urgency to understanding how these unique dynamic behaviors dictate their prospects for commercialization.



**Figure 10.** Illustration of reprocessable cross-linked polymers by (a) dynamic exchange reaction (i.e., vitrimers); (b) depolymerization and repolymerization, or dynamic dissociation and association. *Source: Adapted with permission from Fortman, D. J., et al. Approaches to Sustainable and Continually Recyclable Cross-linked Polymers. ACS Sustain. Chem. Eng. 2018, 6, 11145–11159. ACS Editors' Choice usage agreement.*

To resolve this gap in understanding the foundational properties of dynamic polymers, future research efforts should focus on the development of theoretical frameworks and, in turn, large-scale atomistic simulations of both structural and chemical dynamics in polymers in the condensed phase, capturing the evolution of structure and bonding in response to mechanical force (e.g., shear). In parallel, it is necessary to advance in situ characterization techniques, such as those based on coherent x-rays (e.g., x-ray photon correlation spectroscopy) and neutrons (e.g., neutron spin echo) to understand a polymer's equilibrium and nonequilibrium dynamics at relevant length and time scales with chemical specificity, capturing rare events associated with bonds undergoing transformation. It may also be possible for experimental high-throughput screening methods to determine the properties of circular plastics and thereby generate data sets of sufficient quality to serve as training sets for machine learning (ML) to more rapidly arrive at formulations with target specifications for applications of interest. ML is likely to be further useful in enhancing the atom- and energy-efficiency of both polymer processing and chemical deconstruction (see PRO 4).

## Scientific and Technology Impact

There is no greater paradigm shift in plastics than a transition from those in use today, with linear life cycles from production to end-of-life, to plastics that are repeatedly recirculated in the economy in a closed-loop manner, reducing energy needs and providing environmental benefits. While practical implementation of reversible polymer chemistries for circular plastics presents several key scientific challenges, fundamental research into new reversible polymer chemistries, catalysts, and processes will provide the foundation for developing a new class of materials with properties similar or superior to those of existing materials, and enable circular life cycles using atom- and energy-efficient processes. A significant challenge will be the development of new chemistries to replace, in part or in whole, the various grades of PEs, HDPE, LDPE, and LLDPE, and iPP. Progress has been made in recent years, but there are still significant challenges in the fundamental chemistry of deconstruction, separations, reconstruction, and (re)processing. Through the development of basic science programs in key areas spanning chemical and materials syntheses, chemical and mechanical characterization, and theory, plastics will be used as a renewable feedstock for the synthesis of new materials that move us closer to chemical circularity.

Plastics with circular life cycles offer a means to continually reuse plastics, reduce their environmental impact, and reduce the use of fossil fuels for their production. A significant opportunity exists for fundamental research to provide the foundational knowledge required to enable polymer upcycling, which holds the promise of changing the paradigm for discarded plastic from waste to valued resource by

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moving to a circular life cycle for plastics. Doing so would enable plastics to serve as renewable resources and would reduce our reliance on fossil fuels and reduce the accumulation of discarded plastics in the environment.

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## PRO 4: Develop Novel Tools to Discover and Control Chemical Mechanisms for Macromolecular Transformations

**Key Question:** *What experimental and computational tools are needed to elucidate the macromolecular transformations of plastics in complex, nonequilibrium media?*

### Summary

Deconstructing and reconstructing chemical bonds in polymers involve the complex coupling of chemical and physical processes that span a wide range of length and time scales. This inherent complexity demands a new paradigm that integrates advanced experiments and computation. The coupling of in situ and operando characterization with real-time computational modeling, simulations, and data analytics holds the promise of uncovering the mechanisms and kinetics of deconstruction, reconstruction, and separations will be uncovered. These advanced multifaceted techniques will produce predictive insights into the design of new chemical transformations and processes for converting discarded plastics into higher-value products and will enable a circular life cycle for plastics.

### Introduction

To make advances in the first three PROs, foundational knowledge is needed to design new chemical reactions, catalysts, processes, and materials that enable the efficient deconstruction, reconstruction, functionalization, and compatibilization of discarded plastics into higher-value products for a circular life cycle. This design effort will require integrating detailed kinetic and mechanistic studies using real-time characterization and analysis tools, including x-ray and neutron scattering and spectroscopy, coupled to computational modeling, theory, and data science tools. Additionally, insights into the structure, composition, and rheological properties of the reactive mixtures are needed to develop chemical and mechanical processes for deconstruction and reconstruction. Acquiring this insight requires developing in situ and operando experimental techniques and tools that are, ideally, nondestructive and capable of revealing and quantitating changes in polymer molecular weight, reaction intermediates, and products in real time with sufficient spatial and temporal resolution. Methods are also needed to follow the structure of the catalyst and its interaction with the polymer chains and to quantitate the fate of additives and impurities. Although analytical tools currently exist to study the synthesis and degradation of polymers, they do not provide in real time the detailed knowledge needed of kinetics and reaction mechanisms in the polymer melt or the solid state, or in reaction with mixed plastics. Moreover, detailed information is needed of the physicochemical properties and the physical, thermal, and mechanical properties to provide the scientific foundation needed to design new efficient and integrated deconstruction and reconstruction pathways to create higher-value products.

### Scientific Challenges

To address the inherent complexity in the chemical upcycling of plastics, a new paradigm is needed that integrates real-time computational and in situ and operando experimental data with data science approaches, which would create predictive science-based models that enable the understanding and control of chemical pathways to create new materials with desired properties, as discussed in PROs 1, 2, and 3. Capturing the complexity and heterogeneity of the reaction medium will provide more detailed kinetic and mechanistic insights into deconstruction, functionalization, and reconstruction reactions. It will also enable the design of new low-temperature atom-efficient catalysts to tune reaction pathways and selectivities in deconstruction and upcycling. High-throughput experiments and multiplexed experimental probes will provide the large data sets needed to take advantage of modern data science methods that will be used to extract new correlations with physical and chemical insights to drive new discoveries. This approach will accelerate the discovery of new materials (e.g., polymers, catalysts, additives) to enable chemical circularity.

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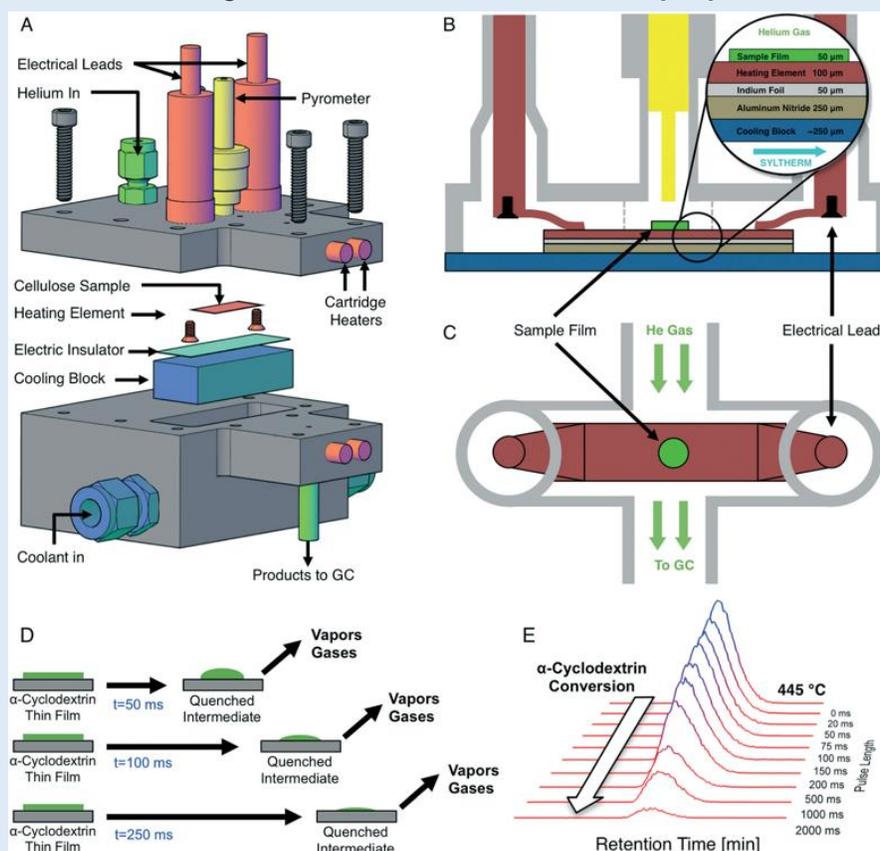
Plastics have a complex, heterogeneous macromolecular structure, which leads to many analytical and computational challenges. Many polymers, particular polyolefins, have limited solubility, so reactions must be studied in the solid state or in the viscous melt. During simple chain scission, the initial polymer and reaction intermediates have nominally the same chemical structure (and spectroscopic signature) and even changes in the concentration of end groups will be imperceptible until the polymers become quite low in molecular weight. Moreover, the reaction environments can evolve as polymer deconstruction proceeds, so in situ methods need to monitor reaction intermediates in the solid, liquid, and gas phases to probe how the reaction pathways evolve. Side reactions and impurities can occur in low concentrations, which are difficult to experimentally detect but can have a significant impact on product quality or the ability to purify the products. To simplify understanding the deconstruction reactions, smaller model systems are sometimes studied by standard analytical methods such as gas chromatography–mass spectrometry (GC–MS), high-performance liquid chromatography, nuclear magnetic resonance (NMR), infrared (IR) spectroscopy, and Raman spectroscopy. This is especially true for catalytic reactions so that the kinetics, mechanisms, and product selectivity can be clearly defined before moving to more complex polymeric systems. For studies of polymers, standard analytical tools can be used to study the deconstruction products and the polymer structure and properties, such as GC–MS, pyrolysis–GC–MS, gel permeation chromatography (GPC), electrospray or matrix-assisted laser desorption/ionization (MALDI) MS, solid-state NMR, x-ray and neutron scattering, differential scattering calorimetry, thermogravimetric analysis, viscometry, and optical spectroscopy. However, most of these tools are used ex situ, are time-consuming, and have limited sensitivity for large molecules and low concentrations of species. Discarded plastics are even more complex than polymers because they contain additives, colorants, antioxidants, and contaminants, including other plastics, which must be considered in the analysis.

Coal and biomass also have complex, heterogeneous macromolecular structures and contain varying concentrations (1–20 wt %) of inorganic materials, which leads to many analytical and computational challenges. Over the past few decades, progress has been made in analytical and computational methods to investigate the reaction mechanisms of coal<sup>94,95</sup> and biomass<sup>96,97</sup> deconstruction, which could be applied to the deconstruction of plastics. Many advances have been made in converting coal and biomass to higher-value fuels and chemicals, in addition to the co-pyrolysis of biomass with plastics,<sup>98</sup> based on new mechanistic understanding gained from model compound studies, and the developments in analytical and computational tools. For example, new large-scale reactors and processes were developed for fast pyrolysis of biomass, which involves heating samples to high temperatures (typically 400–600 °C) for short contact times (typically 1 s) to maximize the yield of liquid products.<sup>99</sup> To gain mechanistic understanding into the reactions under such unique conditions, new analytical tools were developed (e.g., pyrolysis molecular beam MS) to characterize the reaction products in real time.<sup>100</sup> Sidebar 8 highlights a new thin-film reactor developed to determine the kinetics and mechanisms of pyrolysis reactions under short contact time. This unique system can rapidly heat a sample without heat and mass transport limitations, allowing the sample's intrinsic chemistry to be determined.<sup>101</sup>

### Summary of Research Directions

In the deconstruction and reconstruction of plastics, it is important to recognize that the interactions and reactions between the polymer chains span over multiple length and time scales. At the atomic scale, fundamental bond-breaking and bond-making events occur, whereas at the nanoscale, interfaces among the polymer chains, catalysts, and fillers evolve. At the mesoscale, intra- and intermolecular interactions occur between the polymer chains, which determines the macroscale properties. These complex and dynamic interactions are poorly understood because of the multiphase and multiscale nature of these systems, and current experimental and computational approaches are inadequate for describing these systems.

### Sidebar 8: Pulse-Heated Analysis of Solid Reactions (PHASR): Thin-Film Reactor for Characterizing the Time-Resolved Evolution of Pyrolysis Products



**Figure S8.1.** To gain mechanistic insights into the pyrolysis of polymers without mass and heat transport limitations, a thin film reactor called PHASR was developed.<sup>101</sup> In this system ([A] exploded diagram, [B] side view, and [C] top view), a thin film (10–20  $\mu\text{m}$ ) of sample is placed on a heating element attached to electrical leads within a helium-flow chamber. (D) Films (in this case,  $\alpha$ -cyclodextrin) are heated with millisecond heating pulses followed by rapid quenching to produce product vapors and quenched intermediate samples. (E) Liquid chromatography was used to analyze the quenched intermediate samples reacted at 445  $^{\circ}\text{C}$  for sequential pulse lengths from 20 to 2000 ms. Kinetics of product formation and apparent activation energies were determined for glycosidic bond cleavage, providing new insights into the mechanisms of cellulose degradation. Investigation of thicker layers could provide new understanding of how heat and mass transfer alter product selectivity and yields. In polymer upcycling, this system could potentially quantitatively investigate the role of containments, such as additives, fillers, or other polymers, on the deconstruction kinetics, mechanisms, and products. It could also provide new insight into controlling the products from the pyrolysis of mixed plastics. Source: Zhu, C., *et al.* *Energetics of Cellulose and Cyclodextrin Glycosidic Bond Cleavage*. *React. Chem. Eng.* **2017**, 2, 201–214.

Novel tools and catalysts are needed to control and characterize the chemical reactions for macromolecular transformations to design new processes and materials. To address this challenge, this PRO focuses on the following scientific areas: (1) develop integrated experimental tools for parallel monitoring and characterization in heterogeneous chemical environments; (2) develop predictive computational methods for chemical transformations and thermophysical properties of macromolecules; and (3) integrate experiments and computations to understand, predict, and control polymer deconstruction and upcycling.

## Develop integrated experimental tools for parallel monitoring and characterization in heterogeneous chemical environments

Discovering reaction pathways in these inherently complex macromolecular systems requires the next generation of experimental protocols to capture and decipher the heterogeneous chemical environments. Current experimental approaches often characterize the products at the end of the reaction, which is insufficient for providing mechanistic details about the reaction pathways as the reaction medium evolves, particularly during deconstruction of mixed plastics (see PRO 2). Conducting high-throughput experiments with multimodal experimental probes instead of conducting one experiment at a time will tremendously accelerate knowledge generation and will map out the experimental variables. Lessons learned and progress made in high-throughput synthesis and screening in biology, drug discovery, and catalysis can be applied to high-throughput polymer synthesis and deconstruction.<sup>102</sup> This research will benefit from the creation of sufficiently large experimental data sets obtained from multimodal measurements that assess a broad range of reaction conditions to test and refine models involving multiple reaction pathways.

To elucidate the array of chemical transformations that occurs in plastic deconstruction and reconstruction, it is critical to identify and quantify the complex mixtures of reactants, intermediates, and products in real time. It is also necessary to understand how the evolving reaction environment impacts products and yields, how the reaction pathways and catalysts evolve over time, and how to separate the products from the reaction mixture. For example, in the pyrolysis of PE (Figure 11),<sup>103</sup> liquid products containing 5 to 40 carbons are formed, as well as gases with a range of functionalities including mono-olefins, *n*-paraffins, cycloalkanes, iso-paraffins, and aromatics. Sulfur and chloride could also be present, depending on the sources of the discarded plastics. Adding catalysts can tune the selectivity to a narrower distribution of products.<sup>104</sup> Gas- and liquid-phase chromatography with a variety of detectors can identify and quantitate low-molecular-weight products. GPC with multiple detectors (such as refractive index, light scattering, viscosity, UV-visible spectroscopy, and MS) can separate and quantitate the high-molecular-weight species and characterize the distribution of chain lengths. Two-dimensional chromatographic methods could be used to analyze reaction mixtures in real time, although such approaches would require significant research and development. Integration of chromatographic methods into the reactor is one approach to investigate plastic deconstruction by following changes in molecular weight, molecular weight distribution, and functional groups for kinetics analysis. The spectroscopic methods typically incorporated into in situ analysis—such as NMR, Fourier-transform IR (FTIR), and Raman—cannot provide molecular weight information until the products are quite small (fewer than ~25 backbone carbons), but they can provide information on the abundance of functional groups. Advances in soft ionization techniques for MS, including electrospray ionization and MALDI, can be used to follow the molecular weights of polymers; and instrumentation innovations have helped elucidate radical polymerization mechanisms.<sup>105</sup> However, these soft ionization techniques are not effective on hydrocarbon polymers. Functional groups introduced into a polymer chain to facilitate upcycling (i.e., the Achilles heel approach discussed in PRO 1) could also be valuable for labeling with fluorescent probes, for example, to track the polymer chains during deconstruction. As new analytic methods are developed that can effectively identify and quantitate product distributions over the course of a reaction, these data

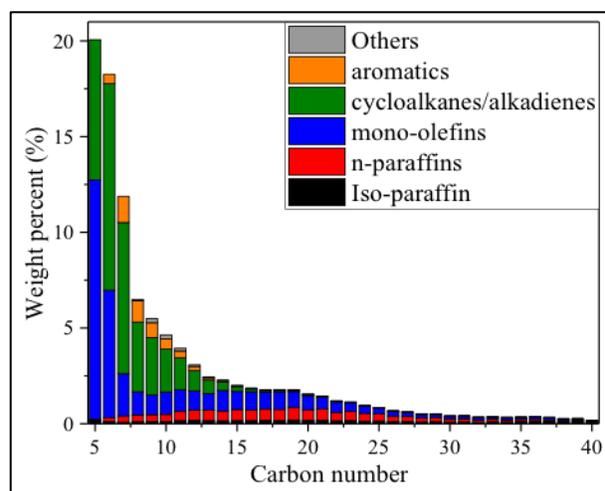


Figure 11. Liquid products from the pyrolysis of polyethylene. Image courtesy of George Huber.

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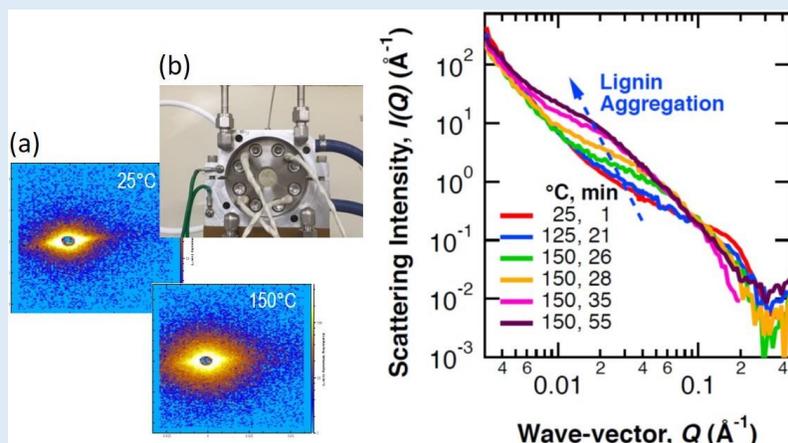
can be used to validate kinetic simulations and subsequently provide mechanistic information about the elementary steps making up the reaction network. Additionally, methods must capture the thermodynamic and kinetic features of reactions in which large molecules are being transformed into a distribution of smaller molecules or into a new large molecule. Entropy, which is not often calculated at high accuracy, plays an important role in these transformations, as discussed in PRO 1.

Spectroscopic tools, such as FTIR, Raman, and NMR, can provide unique quantitative insights in real time into macromolecular interactions; molecular connectivity; the presence and fate of functional groups; additives; and impurities.<sup>106</sup> For example, in situ IR spectroscopy has been used to measure the changes in functional group concentrations during catalytic conversion by inserting a probe directly into the reactors. Raman and UV–visible spectroscopy can also be used to measure functional group changes under reaction conditions in real time. Techniques such as these are valuable for determining the reaction pathways and selectivity toward one polymer in a mixture of polymers, as discussed in PRO 2. In situ methods must be developed to follow the deconstruction of cross-linked polymers, such as thermosets, covalent adaptive networks,<sup>85</sup> and vitrimers, as discussed in PRO 3.<sup>93</sup> Spectroscopic methods are also needed to detect additives, impurities, and defects that are in low concentrations and can impact the pathways of subsequent reactions critical to upcycling.

X-ray and neutron scattering and x-ray spectroscopy are ideally suited for studying the wide range of length and time scales that define the structure, dynamics, and properties of soft materials. Neutron scattering, when combined with molecular highlighting through selective deuteration, can enable the interrogation of these materials in ways that are impossible with other techniques. Small-angle neutron scattering (SANS)<sup>107</sup> is commonly used for studying soft matter systems. It can give structural information across multiple length scales (1 to ~100 nm) simultaneously, and is complementary to neutron reflectivity, which can be used to study thin films and interfaces. These techniques provide critical insight into the size, shape, and organization of polymers in plastics. Inelastic neutron scattering (INS) spectroscopy provides information on the vibrational spectrum of a material and is complementary to IR and Raman spectroscopy (see Sidebar 9).<sup>108</sup> The nondestructive and penetrating properties of neutrons enable time-resolved in situ studies of polymer processing, de novo synthesis, and deconstruction of plastics and related materials (see Sidebar 9 for a real-time analysis of biomass deconstruction). Neutron scattering can also simultaneously probe the structure and dynamics in soft matter systems. For instance, neutron spin echo spectroscopy studies the coherent collective dynamics in polymers that take place from nanoseconds to microseconds over length scales similar to those accessible by SANS and can provide information about the polymer conformational dynamics under processing-relevant conditions. Holistic time-resolved 4D models of polymer structure and dynamics may be needed to fully understand the behavior of these systems during synthesis and deconstruction. Approaches for integrating data from multiple techniques will be needed, as will approaches for developing new experimental and computational methods that can link information across length scales ranging from the atomic scale to mesoscale and can capture changes over time scales ranging from femtoseconds to seconds.

Small- and wide-angle x-ray scattering (SAXS and WAXS) can be used to probe the morphology and crystallinity of semicrystalline polymers over a range of length scales (0.1–100 nm). In synchrotron x-rays, the high power density and small beam divergence permit time-resolved SAXS and WAXS experiments and the use of very small samples. Thus, the polymer structure changes can be followed during deconstruction and reconstruction. For example, the effects of enzymatic hydrolysis on the structure of microcrystalline cellulose were studied using WAXS and SAXS, and it was determined that the enzymes act on the surface of cellulose bundles and cannot penetrate into the nanopores of wet cellulose to disrupt the crystallinity.<sup>109</sup>

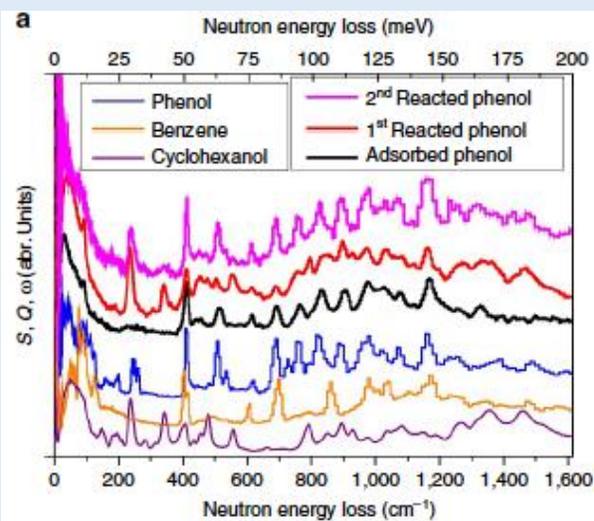
## Sidebar 9: Real-Time Neutron Scattering Analysis of Biomass Deconstruction



**Figure S9.1.** (a) 2D detector images of dilute acid pretreatment of biomass from the Bio-SANS instrument at Oak Ridge National Laboratory's High Flux Isotope Reactor. (b) High-temperature SANS reaction cell. (c) SANS data showing temperature dependence of structural changes in biomass during dilute acid pretreatment. Image courtesy of Sai Venkatesh Pingali, Oak Ridge National Laboratory.

The penetrating and nondestructive nature of neutrons allows interrogation of reactions under industrially relevant conditions. In this example, SANS was used to investigate dilute acid pretreatment of poplar wood in a time-resolved manner (Figure S9.1). Scattering profiles show that cellulose microfibrils aggregate and lignin rearranges to form aggregates as the pretreatment reaction proceeds. By following the evolution of a polymer's structure in real time and in situ during synthesis or deconstruction, transient processes can be revealed that would be otherwise unobserved, which can provide new insights into controlling the reaction products.

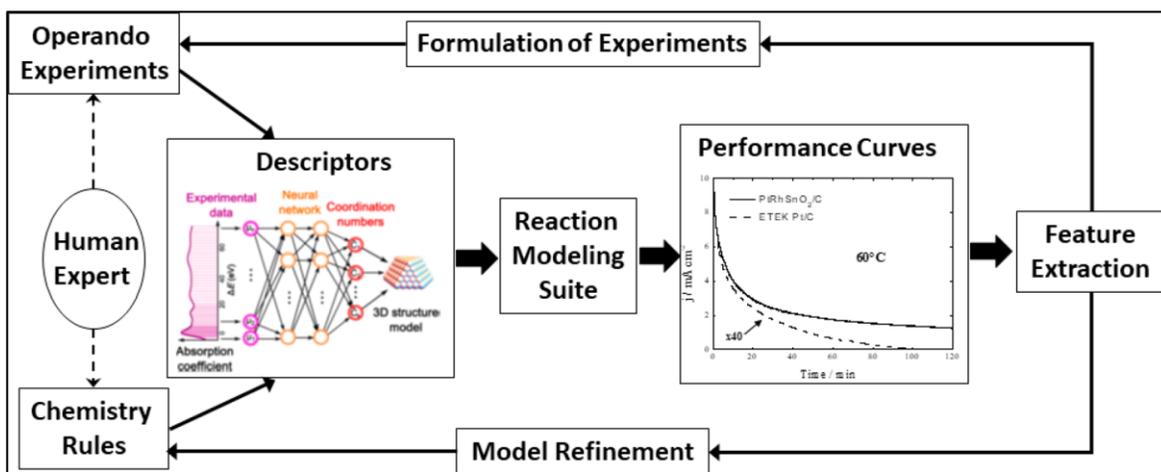
Inelastic neutron scattering (INS) spectroscopy provides information on the vibrational spectrum of materials that is complementary to infrared and Raman spectroscopy, except neutron scattering has no selection rules other than those resulting from variation in nuclear scattering lengths. Thus, INS offer the unique capability of providing sensitivity to hydrogen over all other atoms, including deuterium. Since the theory of neutron scattering is extensively developed, it permits direct comparison of theory with experiment without intervening approximations. INS can be used to provide unique insights into catalytic reactions. For example, in the study of the production of arenes by the direct hydrodeoxygenation of organosolv lignin over a porous  $\text{Ru}/\text{Nb}_2\text{O}_5$  catalyst, INS and density functional theory calculations confirm that the  $\text{Nb}_2\text{O}_5$  support was catalytically unique compared with other traditional oxide supports. The disassociation energy of aromatic–OH bonds in the phenolics was found to be significantly reduced upon adsorption on  $\text{Nb}_2\text{O}_5$ , resulting in its distinct selectivity to arenes (Figure S9.2).



**Figure S9.2.** Comparison of the INS spectra of the adsorbed and reacted phenol over  $\text{Ru}/\text{Nb}_2\text{O}_5$  in the catalytic hydrodeoxygenation of phenol. Source: Shao, Y., et al. *Selective Production of Arenes via Direct Lignin Upgrading over a Niobium-based Catalyst*. *Nature Commun.* **2017**, *8*, 16104. Creative Commons License, <https://creativecommons.org/licenses/by/4.0/>.

Another advantage of x-rays is their tunability over a range near the K or L edge of an element, which has made anomalous SAXS and WAXS a feasible approach for investigating the structure and morphology of a specific element in the presence of other elements. Moreover, x-ray absorption spectroscopy (XAS) is an element-specific method that is very sensitive to the local geometric and electronic properties of the metal atoms in catalysts and their surroundings; therefore, it can track catalyst structure modifications in

operando conditions. For example, an in situ sample cell was recently developed to measure time- and temperature-dependent XAS spectra in transmission mode to study solid–liquid heterogeneous catalytic reactions.<sup>110</sup> In this study, the conversion of an aryl nitrile (-CN) to an amide (-CONH<sub>2</sub>) on a TiO<sub>2</sub> catalyst could be followed by the change in the C and N K-edge XAS during the reaction in the presence of bulk liquid components (i.e., H<sub>2</sub>O [reactant] and EtOH [solvent]). This method could easily be expanded to mechanistic studies of catalytic plastic deconstruction. XAS can also be used to aid in catalyst discovery. Using supervised and unsupervised ML methods for XAS data analysis can disclose hidden relationships between the XAS spectrum and the descriptors of material's structure and/or the composition because of the sensitivity of ML methods to subtle variations in experimental data. By using ML-based methods, catalytic activity descriptors—such as the coordination number, number of free valences, interatomic distances, and crystallographic facets—can be identified and correlated with catalyst performance so new catalysts can be designed (Figure 12).<sup>111</sup>



**Figure 12.** Example of a catalyst design based on an active learning framework. Catalytic activity descriptors can be identified by extracting the attributes of the structure and electronic properties from the spectra and correlating them with catalyst performance. Source: Reprinted with permission from Timoshenko, J.; Frenkel, A. I. *Inverting X-ray Absorption Spectra of Catalysts by Machine Learning in Search for Activity Descriptors*. *ACS Catal.* **2019**, *9*, 10192–10211. Copyright 2019 American Chemical Society. Used by permission.

Finally, if a discarded plastic or its deconstruction products will be directly reprocessed into a new product, then the physical, mechanical, and rheological properties of the materials are needed to develop processes for upcycling. Thus, if a vitrimer is to be reprocessed, the temperature-dependent viscosity of the polymer must be understood and correlated with spectroscopic signatures of bond-making and bond-breaking. This allows the optimum processing conditions to be determined, which provides the desired viscosity and flow to form new shapes without decomposition. Also, if a mixture of plastics is blended with a compatibilizer, the polymer miscibility, rheological properties, compatibilizer diffusion in the polymer blend, and structure of the polymer interfaces must be understood, as discussed in PRO 3. Neutron scattering can provide insights into the entanglement of the polymer chains at the interface.

### Develop predictive computational methods for chemical transformations and thermophysical properties of macromolecules

The computational methods and simulation techniques needed to gain predictive insights into polymer deconstruction and reconstruction processes are currently not available in the standard computational toolbox. Computational approaches are needed to accurately describe the (1) ensemble structure and dynamics of a complex mixture of polymer chains at various stages of deconstruction and reconstruction, (2) energetics and kinetics of bond cleavage and formation processes, (3) spectroscopic signatures of reaction intermediates and products, and (4) properties of new polymers. Current DFT methods and

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computational power have advanced over the past two decades to the point that the reaction networks, energy landscapes, and rate constants for a few hundred reactions<sup>112</sup> are now feasible in a reasonable amount of time. DFT can reliably predict vibrational spectra for systems as large as a few hundred atoms, both using harmonic approximations<sup>113</sup> or based on molecular dynamics (MD) simulations.<sup>114</sup> Progress has also been made in the chemical kinetic modeling of heterogeneous catalysis, and qualitatively and quantitatively accurate predictions can be made on real-world systems.<sup>115</sup> In parallel, microkinetic models describing pathways of small gas-phase molecules are becoming routine. Nevertheless, the accuracy of DFT and kinetic models is still a challenge, as we currently do not have the capability to predict reaction kinetics to within a factor of 10 (error in  $\Delta G_{298} = 1.4$  kcal/mol), and techniques have only recently emerged to help understand errors and potentially reduce them.<sup>116</sup> Errors in computing complex structures and reaction environments with evolving interfaces are expected to be even larger. As discussed below, experimental data is needed to calibrate and improve the computational methods so that the chemical accuracy can be improved.

Modeling condensed phase reactions using DFT-based ab initio MD (AIMD), which can account for the dynamics of the environment, is emerging, but these calculations are too computationally demanding to accurately capture both the complexity of the polymer mixture and the nonequilibrium thermodynamics. This difficulty results from the computational limitations in simulating sufficiently long length and time scales. State-of-the-art AIMD simulations on massively parallel supercomputers using linear scaling techniques and related advances can simulate trajectories for thousands of atoms over nanoseconds;<sup>117</sup> however, the atomic-scale processes underlying a polymer system occur over angstroms to microns and over picoseconds to hundreds of nanoseconds, and even seconds. Moreover, the time to solution for AIMD simulations of chemical nonequilibrium cannot be reduced because of the inherently “serial” nature of time, since modern supercomputer power only increases by exploiting parallelism of the calculations. Because of these shortcomings, generating reaction mechanisms and kinetic models of macromolecular deconstruction and reconstruction is currently outside the realm of computational power for DFT-based simulations. The combinatorial nature of conformations that macromolecular systems can adopt during a reaction, the complex reaction environment, and the evolving solid interfaces and catalysts make the computational problem intractable for DFT-based investigation. During a reaction, the polymer’s structure, molecular weight, exposed interfaces, reaction sites, and properties change with time. Interfaces come into contact with catalysts and define the location of bond-breaking and bond-making, which controls the efficacy of a catalyst. Tracking of interfaces at the molecular level has generally been an elusive process until now. There is a clear need for developing scalable, predictive, and multiscale computations that can be used to provide mechanistic understanding and interpretation of experimental data in real time, as well as eventually design new selective and efficient catalyst and reaction pathways to higher-value products.

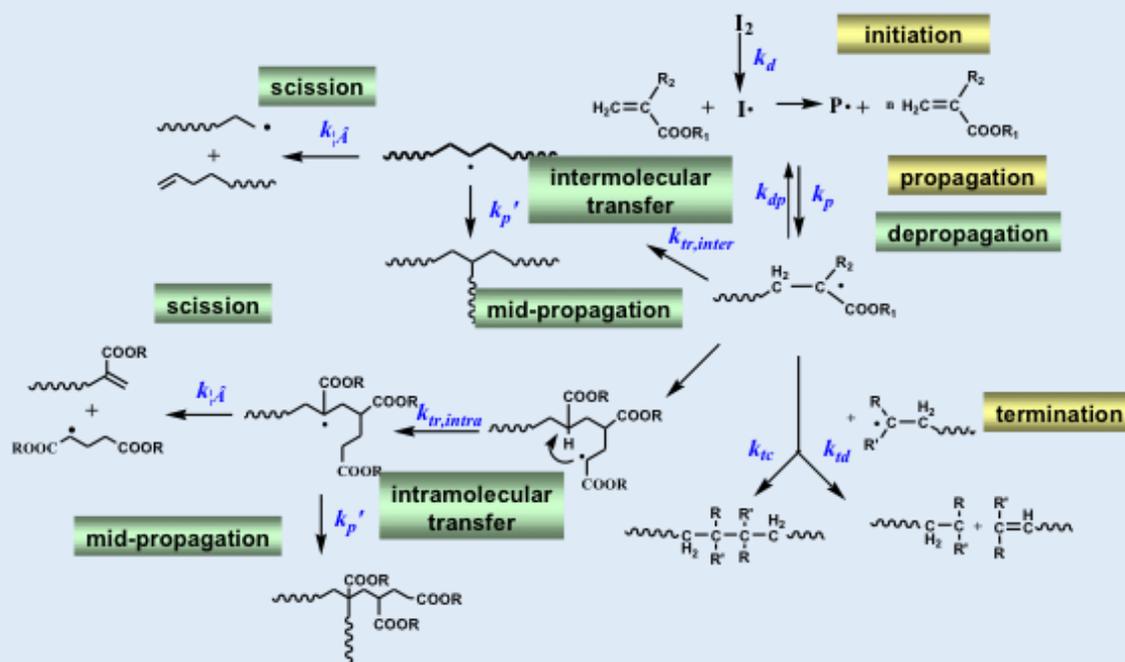
Reactive force fields, which can model bond-making and bond-breaking, could explore reaction mechanisms and optimize materials properties.<sup>118</sup> However, these methods must be enhanced using experimental data, first principles calculations, and data science tools to address the challenges in polymer upcycling. Furthermore, coarse-grained versions of these force fields, along with other acceleration methods such as metadynamics, will be necessary for performing dynamic calculations and predicting structure evolution and transport properties (e.g., diffusivity) in a melt.

ML tools have begun to emerge that can enhance simulation capabilities by allowing experimental and computational data to be used.<sup>119</sup> For example, ML can be used to conserve the fidelity of theoretical calculations across scales (e.g., tight binding to DFT, DFT to many-body) for automatic force field generation,<sup>120</sup> or it can be used as a computationally cheap surrogate for particular modeling levels<sup>121</sup> and to predict reaction pathways.<sup>122</sup> Moreover, ML is amenable to utilizing experimental data to calibrate and improve the computational methods and potentials so that the desirable chemical accuracy (<1 kcal/mol) can be achieved. These new classes of ML-potential models could enable high-fidelity dynamical and

statistical simulations of new polymer materials, and a way to understand the pathways and mechanisms of their deconstruction and reconstruction. These techniques are then envisioned to drive the construction of automated reaction network generation, enumerating all elementary steps for depolymerization and repolymerization with and without a catalyst. Since the full reaction network will be intractable because of its astronomic size, smart reaction networks need to be developed that actively learn the paths and that are self-parameterized to bound the explosion in computational cost and memory by accounting for only the important reaction paths. DFT, AIMD, ML, and experimental data can be leveraged to achieve this goal. Such an approach will build on earlier work that addressed building reaction networks on the fly<sup>123</sup> but should avoid a priori assumptions (Sidebar 10).<sup>124</sup>

### Sidebar 10: Multiscale Simulations of Plastics

Gradient copolymers provide an example of how multiscale simulations can combine quantum calculations and statistical models to describe a polymerization product. Quantum chemical calculations can provide rate constants for all elementary steps. For a large number of reactions, families of reactions are identified (below) and parameterized using semi-empirical methods, such as group additivity and Polanyi relations for thermochemistry and kinetics, respectively. Then, kinetic Monte Carlo models track the explicit sequence distribution in each chain rather than capturing a global average. Such multiscale approaches enable the construction of large reaction models to predict molecular weight and composition distributions within the product. To advance the fundamental understanding of the chemical transformations necessary for polymer deconstruction and reconstruction, new multiscale methods should focus on constructing models that capture the chemical heterogeneity and competing reactions within these systems and on making predictions for direct comparison with experiments.



**Figure S10.1.** Families of reactions for free radical polymerization. The rate constants for such families are parameterized using electronic structure calculations from a select number of reactions. Source: Cho, A. S.; Broadbelt, L. J. *Stochastic Modelling of Gradient Copolymer Chemical Composition Distribution and Sequence Length Distribution*. *Mol. Simul.* **2010**, *36*, 1219–1236.

Kinetic Monte Carlo (MC) methods will also be valuable in reaching even longer time and length scales with inputs from first principles or coarse-grained MD (CGMD) simulations.<sup>125</sup> Currently, the CGMD

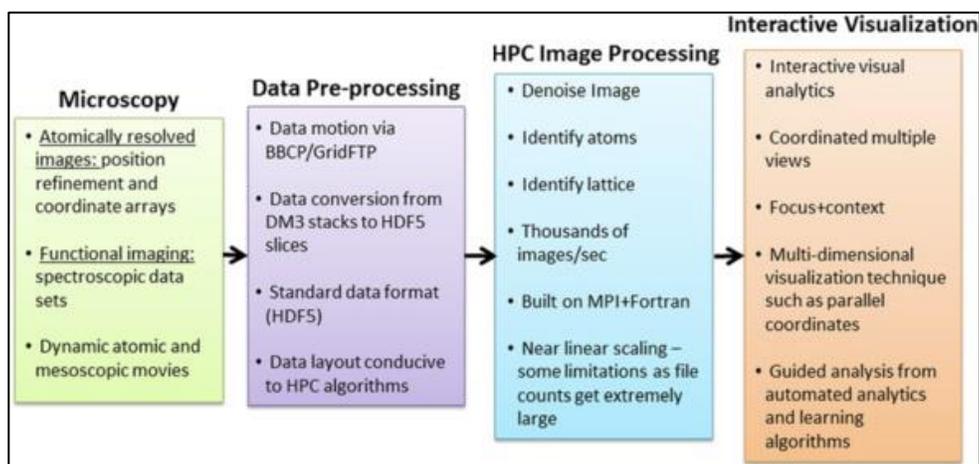
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methods use isotropic beads, and methods for the explicit inclusion of polarizability (permanent or transient) are needed. This new capability would greatly impact the field of polymer science. Hybrid simulation, such as MD–MC approaches, can provide robust models for dynamic covalent networks that accurately reflect the rheological properties due to the rapid relaxation behavior caused by bond exchange above the  $T_g$ . For example, the fast relaxation behavior of vitrimers can be simulated by explicit bond exchange and by using connectivity-altering atomistic MC to accelerate the equilibration of polymer melts. These approaches can help map out how the rate of vitrimer network topology rearrangement changes the dynamics and the bond exchange (see PRO 3).

### **Integrate experiments and computations to understand, predict, and control polymer deconstruction and upcycling**

Tremendous advances have been made in developing software, hardware, and theoretical methods that allow us to gain mechanistic information into reactions, understand the origins of selectivity, design new catalysts, and predict material properties. As discussed earlier, current computational methods do not have the accuracy or ability to handle the larger, complex, dynamic macromolecular systems found in polymer upcycling. A synergistic approach that blends experimental and computational data is needed to understand the underlying reaction pathways in the deconstruction and reconstruction of polymers.<sup>126</sup> This approach will allow computational methods to be improved and validated with experimental data and provide data for ML approaches to provide reliable predictive insights into controlling deconstruction and upcycling. One experimental challenge is that chemists rely on “piecemeal” data drawn from diverse analytical techniques—such as optical and vibrational spectroscopies, NMR, GC–MS, microscopies, scattering, and diffraction—to understand the reaction mechanisms and properties of a system. In the future, this problem will be compounded by the availability of high-throughput multimodal measurement techniques that will create large and disparate data sets. To integrate these data sets, lessons can be learned from advances made in combination of imaging data.<sup>127</sup> Electron microscopy data sets that provide high-resolution structural data detailing atomic positions, bond lengths, and angles, can be combined with functional imaging data sets from scanning probe microscopy that contain property information as a function of experimental variables, such as time, temperature, and external stimuli. Computational methods have been developed to visualize and analyze the multidimensional structural and functional data into chemically and physically relevant information (Figure 13).<sup>128</sup> A similar type of approach could be envisioned for merging multimodal data combined with data science approaches to gain new insights into polymer deconstruction and reconstruction. One of the challenges is the wide variation in chemical signatures and time and length scales probed by different experimental and computational techniques. Overcoming these challenges requires new approaches that integrate experimental, computational, and data science methods to effectively “fuse” partial information from multimodal experimental observations. The research community will benefit from computational tools and workflows that seek to transform the quality and quantity of information obtained from experiments.

Another challenge is understanding the structure, aggregation, and entanglement of polymer chains that can assume multiple conformations because of their flexible and dynamic nature. Doing so is important to understanding how polymer chains interact in compatibilization with small oligomeric chains (PRO 2); the reactivity and accessibility of polymer chains to the active site of a catalyst in the polymer melt (PRO 1); and the dynamic associative and dissociative interactions in dynamic covalent networks (PRO 3). The aggregation and crystallization of the polymer chains is also responsible for the mechanical and thermal properties of the polymers. Computationally, the degeneracy of polymer conformations and the long time scale to reach equilibrium makes computational simulation of polymers challenging even on today’s high-performance computers.<sup>129</sup>



**Figure 13.** High-performance computation (HPC) microscopy workflow for near-real-time analysis of large data sets from local imaging and spectroscopy experimental measurements. Source: Belianinov, A., et al. *Big Data and Deep Data in Scanning and Electron Microscopies: Deriving Functionality from Multidimensional Data Sets*. *Adv. Structural Chem. Imaging* **2015**, 1, 6.

### Scientific Impact and Technological Impact

Development of integrated experimental and computational tools can accelerate scientific discovery into understanding the chemical transformations and catalytic reactions in the deconstruction and reconstruction of plastics and provide insight into methods to control the selectivity of the reactions and properties of the final products. Opportunities abound for the development of in situ and in operando multiplex experimental methods and the analysis of large multicomponent data sets in real time. While the focus of this report is polymer upcycling, these next-generation methods will broadly accelerate research in materials science, catalysis, spectroscopy, analytical sciences, and data science. Methods that probe the reaction mechanisms and product evolution in complex, heterogenous systems and determine reactive intermediates in situ and in real time will be transformative for synthetic sciences.

Computational tools that can predict polymer structures, dynamics, and properties; deconstruction and reconstruction reactions; processing conditions; and feedstock composition to control the reaction pathways and products can tremendously accelerate the discovery of new processes and materials. Although there are significant challenges in processing complex solids, lessons learned and tools developed for other feedstocks—such as biomass and coal—can have a far-reaching scientific impact on understanding and controlling plastics deconstruction and upcycling. Overall, through fundamental research into the chemical upcycling of polymers, a new paradigm will emerge in which discarded plastic becomes a valuable resource that can be mined to enable the efficient production of chemicals, fuels, and new polymeric materials of higher value, while reducing the accumulation of plastic in the environment and increasing chemical circularity.

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## Appendix A. Workshop Agenda

### BES Roundtable on Chemical Upcycling of Polymers

Bethesda North Marriott Hotel & Conference Center

April 30 – May 1, 2019

#### Tuesday, April 30, 2019

- 7:00 - 8:00 AM     **Registration/Continental Breakfast – White Oak B**
- 8:00 – 8:15 AM     Welcome and Roundtable Charge  
Harriet Kung, Director, Basic Energy Sciences  
Bruce Garrett, Division Director, Chemical Sciences, Geosciences, and  
Biosciences
- 8:15 – 8:30 AM     Introduction of participants
- 8:30 – 8:45 AM     Roundtable Goals and Logistics  
Phil Britt, Oak Ridge National Lab
- 8:45 – 9:15 AM     Jeannette M. Garcia, IBM  
*Plastic Waste Depolymerization for Value-Added Materials*
- 9:15 – 9:45 AM     Maureen McCann, Purdue University  
*When Worlds Converge Exploiting Catalysis in Living Organisms for Energy-  
and Atom-Efficient Pathways to Polymers*
- 9:45 – 10:15 AM    Stephen A. Miller, University of Florida  
*Designing Polymers for Coherent Depolymerization*
- 10:15 – 10:30 AM   **Break**
- 10:30 – 11:00 AM   Summary of Homework Assignments  
Science needs (Geoff Coates)  
Crosscutting capability needs (Karen Winey)
- 11:00 – 11:30 AM   Discussion
- 11:30 – 11:45 AM   Instructions for breakout sessions
- Noon – 1:00 PM     **Working lunch** (grab lunch and convene in breakout room)
- 1:00 – 3:30 PM     *Breakout Session I*  
Panel 1: Depolymerization and deconstruction – Great Falls  
Panel 2: Upcycling – White Oak B  
Panel 3: Materials design – Oakley
- 3:30 - 4:00 PM     **Break**
- 4:00 – 5:00 PM     Continue Breakout Session I
- 5:00 – 6:00 PM     Plenary Session I – Report outs from each panel – White Oak B
- 6:00 – 7:30 PM     **Dinner on your own**
- 7:30 – 8:30 PM     Plenary Session II – Discussion and Identification of Potential Priority Research  
Opportunities (PRO's) – White Oak B

**Wednesday, May 1, 2019**

- 7:00 - 8:00 AM      **Continental Breakfast – chairs meet with panel leads**
- 8:00 – 10:30 AM    *Breakout Session III Development of PRO's*
- 10:30 – 11:30      Plenary III - Presentation of PRO's and Discussion– White Oak B
- 11:30 – noon        Closing Remarks/Adjourn  
Roundtable chairs
- Noon – 5:00 PM     **Working Lunch/writing (Chairs, and designated writers only)**

## Appendix B: Workshop Participants

### **BES Roundtable on Chemical Upcycling of Polymers** April 30 – May 1, 2019

#### **Invited Participants**

Phillip Britt, Oak Ridge National Laboratory  
Jeffrey Byers, Boston College  
Eugene Chen, Colorado State University  
Geoffrey Coates, Cornell University  
Bryan Coughlin, University of Massachusetts-Amherst  
Christopher Ellison, University of Minnesota  
Jeannette Garcia, IBM  
Alan Goldman, Rutgers University  
Javier Guzman, ExxonMobil  
John Hartwig, Lawrence Berkeley National Laboratory/University of California-Berkeley  
Brett Helms, Lawrence Berkeley National Laboratory  
George Huber, University of Wisconsin  
Cynthia Jenks, Argonne National Laboratory  
Jill Martin, Dow Chemical  
Maureen McCann, Purdue University  
Steve Miller, University of Florida  
Hugh O'Neill, Oak Ridge National Laboratory  
Aaron Sadow, Ames Laboratory  
Susannah Scott, University of California-Santa Barbara  
Lawrence Sita, University of Maryland  
Dion Vlachos, University of Delaware  
Karen Winey, University of Pennsylvania  
Robert Waymouth, Stanford University

## Invited Observers

Greg Beckham, National Renewable Energy Laboratory  
Chris Bradley, Office of Basic Energy Sciences  
Max Delferro, Argonne National Laboratory  
Nichole Fitzgerald, Energy Efficiency & Renewable Energy  
Bruce Garrett, Office of Basic Energy Sciences  
John Gordon, Los Alamos National Laboratory  
Gary Groenewold, Idaho National Laboratory  
Craig Henderson, Office of Basic Energy Sciences  
Linda Horton, Office of Basic Energy Sciences  
Wenyu Huang, Ames National Laboratory  
Charles (Will) James, Savannah River National Laboratory  
Harriet Kung, Office of Basic Energy Sciences  
Johannes Lercher, Pacific Northwest National Laboratory  
Andy Lovinger, National Science Foundation  
Michael Markowitz, Office of Basic Energy Sciences  
Raul Miranda, Office of Basic Energy Sciences  
Jim Murphy, Office of Basic Energy Sciences  
Jeffrey Neaton, Lawrence Berkeley National Laboratory  
Sara Orski, National Institute of Standards and Technology  
Christina Payne, National Science Foundation  
Mark Pederson, Office of Basic Energy Sciences  
Viviane Schwartz, Office of Basic Energy Sciences  
Leonid Sheps, Sandia National Laboratory  
Robert Stack, Office of Basic Energy Sciences  
Bobby Sumpter, Oak Ridge National Laboratory  
Suk-Wah Tam-Chang, National Science Foundation  
Thiyaga Thiyagaarajan, Office of Basic Energy Sciences  
Brian Valentine, Energy Efficiency & Renewable Energy  
Brenda Wyatt, Oak Ridge National Laboratory



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