Chemical and biological catalysis for plastics deconstruction, recycling, and upcycling

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Abstract

Plastics pollution is causing an environmental crisis, prompting development of new approaches for recycling and upcycling. Here we review challenges and opportunities in chemical and biological catalysis for plastics deconstruction, recycling, and upcycling. We stress the need for rigorous characterization and use of widely-available substrates, such that catalyst performance can be compared across studies. Where appropriate, we draw parallels between catalysis on biomass and plastics, as both substrates are low-value, solid, recalcitrant polymers. Innovations in catalyst design and process engineering are needed to overcome kinetic and thermodynamic limitations of plastics deconstruction. Chemical and biological catalysts will need to either act interfacially, where catalysts function at a solid surface, or polymers will need to be solubilized or processed to smaller intermediates to facilitate improved catalyst-substrate interaction. Overall, developing catalyst-driven technologies for plastics deconstruction and upcycling is critical to incentive improved plastics reclamation and reduce the severe, global burden of plastic waste.

Introduction

Humankind has come to rely on fossil-derived plastics for many everyday uses. Up to 2015, it is estimated that a staggering 8.3 billion metric tons of plastics have been manufactured.[1] Given their incredible durability, synthetic polymers are predicted to persist in landfills for centuries to millienia.[2] Moreover, the leakage of plastics to the environment is a global pollution crisis, with an estimated 4.8 to 12.7 million metric tons of plastics entering the world's oceans each year.[3] In light of this looming environmental catastrophe, we urgently need to develop a more circular materials economy for plastics. Besides the potential for abating pollution from plastics, a more circular plastics economy could reduce greenhouse gas emissions associated with plastics manufacturing and virgin materials production.[4] From an fossil feedstock perspective, it is estimated that plastics manufacturing alone will consume ~20% of global petroleum use by 2050.[5]

Today, primary (post-industrial) and secondary (post-consumer) recycling are the main routes by which plastics are converted back to useful materials through mechanical recycling. Recycling rates vary by country, but the overall global recycling rate is low, at 16% in 2018, with 66% of plastics estimated to be landfilled or leaked to the environment.[4] When recovered, plastics are typically sorted by hand, density, or spectroscopically to fractionate them into single streams, where they are cleaned, mechanically processed to a desired particle size, and thermally processed into pellets for reuse.[6] For most thermoplastics, the mechanical properties of the recycled polymers are compromised, leading to lower value materials, which in most cases will ultimately still end up in landfills or the environment.[7] In nearly all cases, synthetic polymers are not inherently designed for recyclability. Because of this constraint, plastics that are unable to be mechanically recycled are typically landfilled. Overall, current mechanical recycling approaches do not represent a fully circular plastics economy as there are not sufficient economic incentives and technologies for the recycling of waste plastics. Most recycling today can therefore be considered down-cycling from both a material property and economic perspective.

To address this challenge, opportunities exist in chemical recycling (tertiary recycling), which depolymerizes plastics into intermediates that can either be used to synthesize the same plastic with virgin-like material properties (closed-loop recycling) or convert them into another material (open-loop recycling generally, or open-loop upcycling if the final product is of higher value).[8] In this review, we focus on the catalytic conversion of plastic waste to sustainable and circular material streams, as distinct from conversion to fuels or energy recovery. Chemical recycling thus enables potential generation of value-added products far beyond the scope of mechanical recycling. Such strategies will be key to developing a new paradigm in which the initial use of a plastic is only one step in the path of the useful lifetime of the material.

Plastics are long-lived because they are solid polymers with covalent bonds, which are typically not accessible for depolymerization by biological or abiotic means in landfills or the natural environment. In many cases, plastics also exhibit crystallinity or are formulated with other components, including other polymers. As an example, polyethylene (PE) and polypropylene (PP) exhibit only aliphatic C-H and sp^3 C-C bonds that are difficult to cleave, especially in a solid, high molecular weight polymer. This recalcitrance of synthetic polymers is analogous to that of lignocellulosic biomass in biofuels production.[9] Indeed, the plant cell wall is also a structurally and chemically heterogeneous composite solid that, despite millions of years of evolution, still requires years to biodegrade in many natural environments. Synthetic plastics, unlike biomass, have only been prevalent in the environment for the last half century. Thus, biological systems for breaking down synthetic plastics have not yet

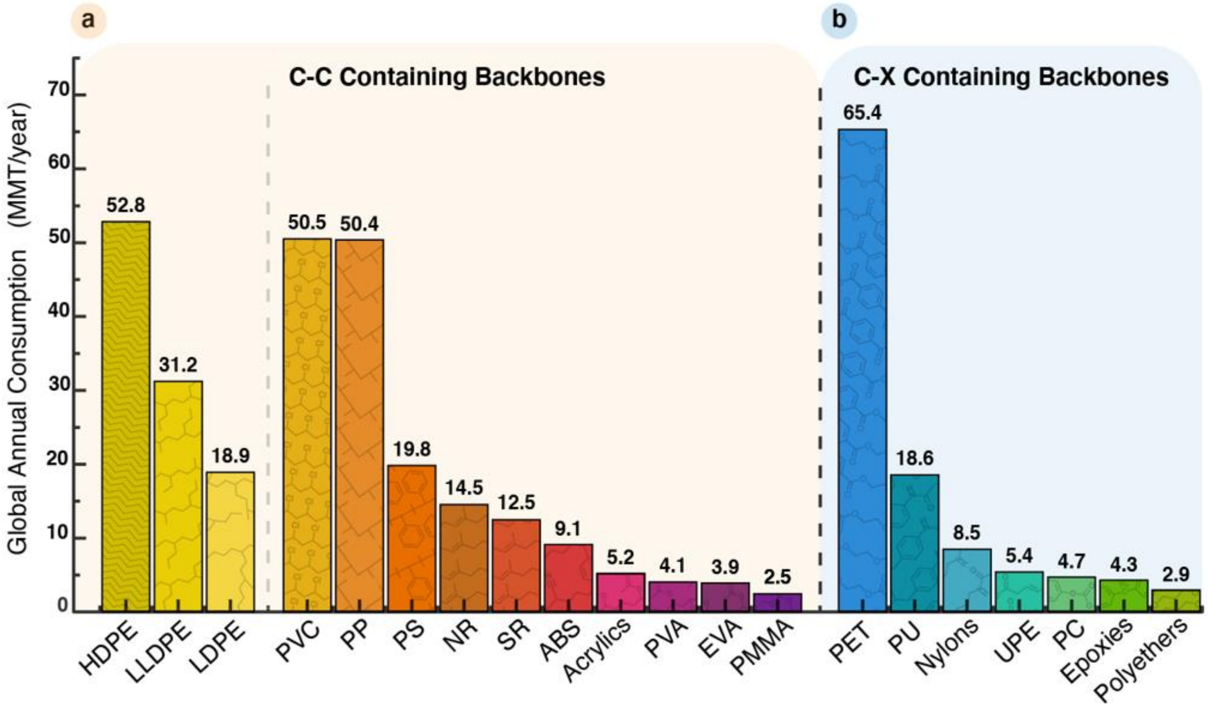

Figure 1. Annual global market size of commodity plastics in millions of metric tons per year (MMT/year). *(**a**) Polymers linked by C-C bonds: polyethylene (PE), including high-density PE (HDPE), low-density PE (LDPE), and linear low-density PE (LLDPE), poly(vinyl chloride) (PVC), polypropylene (PP), polystyrene (PS), natural rubber (NR), synthetic rubber (SR), acrylonitrile-butadiene-styrene (ABS), acrylics, poly(vinyl acrylate) (PVA), ethylene-vinyl acetate (EVA), and poly(methyl methacrylate (PMMA). (**b**) Polymers linked by C-N and C-O bonds: poly(ethylene terephthalate) (PET), polyurethanes (PU), nylons, unsaturated polyesters (UPE), polycarbonate (PC), epoxies, and polyethers. Polymers are included here that have global annual market sizes that exceed 2.5 MMT/year.*[4]

evolved optimized solutions, and abiotic factors, such as abrasion and light, tend to only reduce particle size with only minimal chemical degradation. Natural phenomena therefore tend to be very slow at catalyzing plastic depolymerization.[10]

Taken together, the lack of economic incentive for mechanical recycling, the inability to effectively recycle many plastics, and the urgency of the plastics pollution problem have prompted the research community to develop new technologies that can enable closed-loop recycling or open-loop upcycling. To that end, *this perspective highlights challenges and opportunities in developing processes that employ chemical and biological catalysts for plastics deconstruction, recycling, and upcycling*. Besides other polymers, plastics commonly contain additives, including metals, dyes, pigments, anti-oxidants, and plasticizers, and/or are contaminated with species that can act as catalyst inhibitors, thus catalyst robustness will be critical. Where applicable, we remark on the analogous challenges between plastics and lignocellulose, with the intention of accelerating development for catalytic plastics upcycling technologies by leveraging previous learnings in biomass conversion. The need for consistent substrates and analytical methods to assess catalyst and process performance are discussed. Given that plastics encompass a wide range of chemical functionalities, opportunities exist for developing robust catalytic processes able to conduct selective depolymerization and fractionation in mixed plastics streams, or catalytic processes able to convert multiple intermediates simultaneously. Catalyst acssibility can be achieved through polymer solubilization, however, when substrates remain in the solid form, interfacial catalysis methods will be required. Lastly, we discuss opportunities at the intersection of chemical and biological catalysis in hybrid process systems.[11]

A brief primer on plastics

Today, global plastics consumption exceeds 380 million tons per year.[1] Plastics are tailored for many specific consumer and industrial applications, resulting in a wide diversity of plastics present in waste streams. **Figure 1** shows the market sizes of the most prevalent synthetic polymers, categorized by polymers linked by C-C bonds (**Figure 1a**) and polymers with C-N and C-O inter-monomer linkages (**Figure 1b**).[4] The materials within each class are further ordered by their global annual consumption amounts, in millions of metrics tons per year (MMT/year).[4] For simplicity, we include polymers here with annual global market sizes exceeding 2.5 MMT/year.

At the molecular level, polymers are long chains in which the emergent material properties are dictated by the movement, arrangement, and interactions of these chains. Key factors that contribute to how the polymer chains move and rearrange are the monomer chemistry and arrangement, crystallinity, and molecular weight. Generally, monomer identity influences the final application of the polymer as it dictates the glass transition temperature (T_g).[12] Flexible monomers, which can relax faster, may result in low T_g materials with applications such as PE bags or rubber (i.e. polybutadiene).[13] Rigid monomers or monomers that result in stronger interchain interactions (and relax on longer timescales) can result in high T_g materials, ideal for reinforced applications. In general, when materials are at temperatures below the T_g, the polymer chains are kinetically arrested, exhibiting higher strengths. Even though monomer identity is often the largest contribution to T_g, it is not the only factor, as molecular weight,[14] tacticity,[15] and crystallinity[16] also contribute. While nearly all polymers exhibit a Tg characteristic of their amorphous region, semi-crystalline polymers will also exhibit concomitant melting behavior crystalline in their crystalline regions, making them semi-crystalline. Crystallinity has a direct impact on polymer properties, as increases in crystallinity augment the strength of the final product and reduce the permeability of liquids and gases. Co-monomers (e.g., isophthalic acid in poly(ethylene terephthalate) (PET)) are often used to lower or completely remove crystallinity to make polymers easier to process or more transparent.[17] Finally, molecular weight, and the distributions of molecular weights, have some effect on the thermomechanical polymer properties (e.g., increasing molecular weight leads to higher T_g, modulii, etc.). However, over a critical molecular weight, nearly all thermomechanical polymer properties are constant. The exception to this generalization is the viscosity of a polymer melt, which scales with the molecular weight to the 3-3.5 power ($\eta \sim MW^{3\text{-}3.5}$) and also encapsulates properties such as diffusivity. These factors together contribute to polymer recalcitrance by limiting polymer mobility and accessibility to chemical linkages, posing a challenge for catalytic plastics deconstruction.

While monomer identity plays a key role in the final polymer properties, the chain architecture of a polymer, specifically the degree of branching and/or crosslinking, also contributes to the macroscopic properties, influencing both polymer processing and end-use. In the case of PE, low-density polyethylene (LDPE) is ideal for bags and film applications because LDPE branches enable strain hardening during extensional or elongational flows, resulting in uniform film thickness.[18] Conversely, high-density polyethylene (HDPE) possesses minimal branching, leading to higher crystallinity and lower permeabilities, making it better-suited for storage applications. While most branched polymers maintain their ability to flow after polymerization, materials that become covalently cross-linked (i.e. infinitely branched) during polymerization lose their ability to flow and be reprocessed. These materials are routinely classified as thermosets and include polyurethanes (PU), epoxies, and rubber materials.[19]

Even though plastics are often thought of as chemically homogenous on a molecular level, commercial plastics are rarely monolithic. Polymers are often melted together to make blends, combined with small-molecule additives, or are physically or chemically bound to other plastics. Polymer blends, or complex co-polymer matrices, are used to introduce higher-order phases that may enable improved performance. Acrylonitrile-butadiene-styrene (ABS) is an illustrative example of a copolymer and a polymer blend. Namely, the rubbery nature of suspended polybutadiene domains dissipate mechanical stress, while the continuous acrylonitrile-styrene copolymer phase provides mechanical integrity.[20] Additives are ubiquitous in synthetic polymers as well, including plasticizers,[21] inorganic components, dyes, anti-oxidants, entrained polymerization catalysts, fire retardants, and antimicrobial agents.[21] Poly(vinyl chloride) (PVC) is a typical example of a modified polymer, in which plasticizers (and other additives) are used to modulate the T_g, enabling PVC applications to span from rigid tubing to flexible bags.[22] In principle, plasticizers and other additives may be recyclable, but they become deeply embedded in the polymer network and often cannot be easily recovered. Aside from chemical blends, polymeric materials also often contain a physical mixture of components. For example, textiles are often woven from PP, PET, nylon, and cotton fibers; most food packaging comprises layers of different plastics (often including thin metal layers); and thermosets commonly contain filler (e.g. carbon black, calcium salts, other inorganic fillers) or reinforcement (e.g. tire cord, fiberglass, or carbon fiber) additives.[23] Overall, the chemical and physical inhomogeneity of polymers contributes to their ability to take any size, shape, or material property that is desired, and these features must be considered for realistic, scalable, and economically viable end-of-life chemical recycling.

Considerations for substrates and characterization

Throughout this review, we will highlight common themes and lessons that can be shared between biomass conversion and plastics upcycling. A critical "lesson learned" from biomass conversion that is imperative for the field of plastics upcycling is the need for well characterized and widely-available feedstocks. In the biomass conversion field, researchers employ substrates across a wide-range of plant species that can vary substantially in cell wall composition and structure between, and within, species. Even with careful control of catalyst attributes and reaction parameters, differences in biomass substrates can hinder the reproducibility of experimental outcomes and complicate comparisons between studies. To address this challenge, the biomass community adopted standard analytical methods for quantitative substrate characterization, which are accessible in traditional laboratories.[24] Moreover, some commercial vendors have made standard and well-characterized biomass substrates available for purchase as standards. This is a model that should be replicated in the field of plastics upcycling. To do so, rigorous reporting of a polymer's chemical composition, physical properties, and structure (monomer identities, molecular weight distribution, melting point (T_m), and crystallinity), as well as reaction conditions (pH, temperature, substrate loadings, stirring rate, etc.) are critical to ensure reproducibility. At this nascent stage in the plastic upcycling field, researchers are presented with a superb opportunity to design and agree on standards for substrates, characterization methods, and catalyst performance metrics for the overall benefit of the community. The ability to quantitatively and reproducibly compare the expanding range of catalysts and processes being developed for the broad diversity of available feedstocks, with widely varying chemical composition and physical structure, will be critical to ensure efficient progression of the research field. Here we suggest some considerations for substrate sourcing and catalysis-focused characterizations.

Baseline polymeric substrates for upcycling studies should be obtained from commercial vendors that are widely-accessible, or obtained from well-described syntheses, to enable direct comparison between different studies. It is also important to indicate the processing that the material has undergone, if known, as this will affect the structure of the material. PET exemplifies the need for maintaining a consistent processing history, as PET can be obtained as either amorphous, crystalline, or biaxially-oriented films.[25] Both amorphous and biaxially-oriented films are transparent when compared to crystalline PET, which is often white and translucent. Accordingly, catalytic performance testing can result in different results for "PET" if the substrate is not clearly defined. This definition, including substrate source,

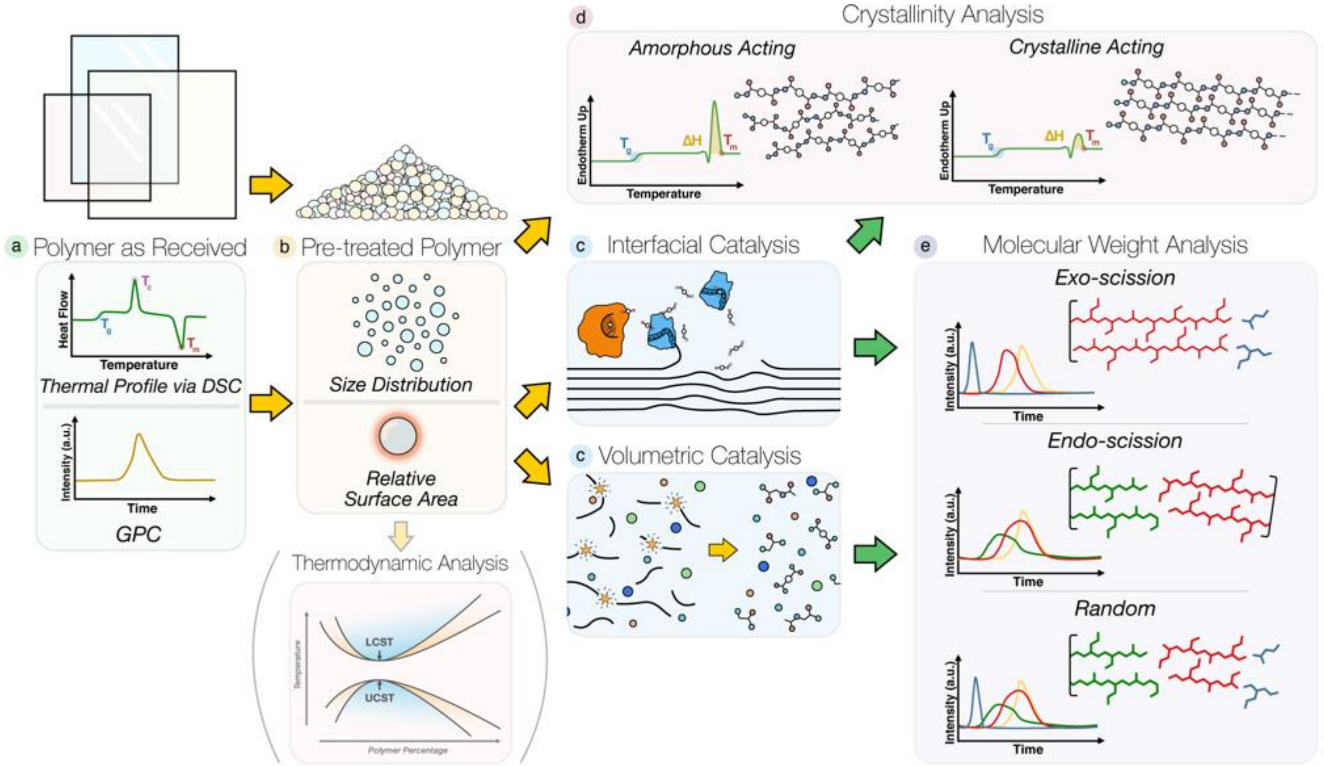

Figure 2. Characterization flowchart for substrate characterization. *Polymer substrates should be used that are commercially and widely available for benchmarking catalyst and process performance. Substrates should be characterized* ***(a)*** *as received,* ***(b)*** *as modified, and after catalytic deconstruction as changes to the thermal history and molecular weight profile will aid in elucidating catalytic mechanisms. The implemented characterization technique will depend on the* ***(c)*** *catalyst mode of action (i.e. interfacial vs. volumetric). (****d****) Non-volumetric catalysis should also characterize a polymer's thermal history to understand if the catalysis acts differently depending on the substrate domain. Techniques not depicted above, such as those for the polymer's structure and additives, will provide a strong supplement and further insight to catalytic action. For all catalysis experiments, (****e****) MWD and chain conformation must be confirmed and will provide insights into the mechanisms of polymer cleavage.*

shape, and processing, should be a minimal requirement for reproducible polymer deconstruction studies.

Even when substrates are obtained from a universally accessible source, they can still be poorly defined or provided with little to no characterization data. Thus, researchers should measure and report the molecular weight distribution (MWD), the weight-average molecular weight (M_w), and the number-average molecular weight (M_n), for all catalytic transformations. One should also report the relevant phase behavior of the polymer feedstock. For interfacial catalysis, the T_g for all polymers and T_m/degree of crystallinity for semicrystalline polymers should be reported; meanwhile, the solubility parameters and/or phase diagram between polymer and solvent should be reported for volumetric processes. Chemical additive content, like antioxidants, flame-retardants, or other fillers that could inhibit specific catalyst systems should also be documented.[26] Additionally, thermogravometric analysis (TGA) can also be leveraged to understand the degradation temperature of a polymer, T_D, as well as the presence of any volatile species.

Distilling the mixture of molecular weights of a polymer feedstock to a single number like M_w or M_n omits critical information in catalytic transformations. Richer information can be obtained by measuring the MWD for both volumetric and interfacial catalysis systems, before and as a function of conversion extent in a catalytic reaction. MWDs can be obtained via gel permeation/size exclusion chromatography (GPC or SEC) for thermoplastics as these are the only accessible techniques that will provide a comprehensive understanding of the evolution of the chain length distribution as a function of conversion extent. Analysis of the MWD is beneficial for understanding of the mode of action of a catalyst. As an example, if the MWD evolves into a multimodal distribution, a catalyst is acting either randomly on the polymer chain (endo-acting); however, if the MWD broadens towards lower molecular weights, reducing the higher molecular weight chains, the chain action will be on chain ends (exo-acting). Moreover, the MWD can reveal if a process is reaching a plateau, and is unable to work on certain regions of a polymer, such as the regions near chain entanglements (**Figure 2**). MALDI-TOF[27] is also an effective augmentation to both the characterization of polymer structure and size, as the fragmentation pattern can provide details about the MWD and the mass of specific oligomers/monomers that are evolving over the course of a reaction or being left behind in the polymer itself. In the case of thermosets, MWD cannot be obtained; however, when possible, the molecular weight between crosslinks can be obtained via shear rheology.

The phase of the polymeric feedstock during reaction will affect its reactivity, whether the polymer is a crystalline solid (ordered phase), amorphous solid (disordered phase), a mixture of crystalline and amorphous, or fully unfolded in a solubilizing solvent. For catalytic systems in which the polymer is not dissolved (requiring interfacial catalysis), the thermal properties will strongly dictate the operation of a catalyst, as well as its operation window. Below the T_g, the polymer will be kinetically arrested as the polymer chains are moving at a minimal rate, limiting accessibility of the catalyst. Above the T_g, chains exhibit a higher degree of mobility; however, if the polymer is semi-crystalline some chains will be crystalized and possibly inaccessible. Accordingly, the polymer properties will strongly dictate catalyst activity and performance. Additionally, changes in the thermal properties will help to elucidate the mode of action of a catalyst. Reductions in T_g may imply a high presence of small molecules or chain ends, while changes in degree of crystallinity can demonstrate which fraction of the polymer is more susceptible to deconstruction (e.g. an increase in crystallinity can imply the degradation of the amorphous phase of a polymer) (**Figure 2**). These thermal properties can readily be obtained via differential scanning calorimetry (DSC) or via alternative techniques such as dynamic mechanical analysis (DMA), rheology, and X-ray diffraction (XRD) for T_g, T_m, and degree of crystallinity, respectively.[28] For a volumetric system, in which the polymer unfolds into the solvent, the T_g, T_m, or degree of crystallinity will not strongly dictate catalyst performance. Instead, the dissolution of the polymer feedstock in the paired solvent will affect activity. Where possible, researchers should share solvent/polymer phase diagrams, demonstrating whether the reaction is a single phase, or remains biphasic. Additionally, physical details (i.e. color, shape, size, etc.) of the polymer feedstock, polymers mixed in solvents, and post-reaction mixtures, should be reported to ensure reproducibility, especially with interfacial catalysis where the surface area of the substrate will substantially impact the catalytic activity. When possible, researchers should also quantify the average particle size and relative surface area via techniques such as BET, microscopy, or light scattering (dynamic light scattering DLS) or static light scattering (SLS)), which is especially important for interfacial catalysis. Here, wet contact angle may also be a useful tool before and after treatment as it is an accessible measurement which will provide information about the hydrophobicity of a surface.[29]

In addition to describing the physical parameters of plastic feedstocks, it is important to understand and report their chemical compositions. Even with a washing step to remove chemical and organic contamination such as food waste or biofilms, ideal polymeric feedstocks remain complex and contain chemical additivities, including residual chemicals from synthesis, functional additives (plasticizers, flame retardants, UV stabilizers, lubricants, curing agents, biocides, antioxidants, antistatic agents, etc.), colorants (pigments and dyes), and fillers (mica, talc, calcium carbonate, etc.).[21] Low concentrations of certain additives, such as metal ions, sulfides, or antioxidants, may interfere with catalytic processes.[30] Where possible, researchers should attempt to identify and quantitate these additives using techniques including NMR spectroscopy,[31] FTIR spectroscopy,[32] and elemental analysis. NMR spectroscopy (1-D ^{1}H and ^{13}C) is the preferred technique for structural characterization of polymers, as it is capable of measuring the presence of co-monomers, the degree of branching, and the identity of organic additives. However, prevalent polymers, namely PE and PP, are not soluble in common NMR solvents at accessible temperatures (<100°C), necessitating the use of solid-state NMR spectroscopy[33] alongside other solid-state techniques such as FTIR spectroscopy, diffuse reflectance UV/vis spectroscopy, and elemental analysis. Elemental analysis should focus on identification of C, H, and N, as well as some of the common elements found in additives, including Br, Cl, or S. The aforementioned analyses should be performed for the polymeric substrate before and as a function of conversion extent.

In situ techniques, which may be less accessible for routine analyses, can be used to understand real-time kinetic phenomena. Small angle X-ray scattering (SAXS) can be implemented to understand the real-time changes to polymer morphology, including changes in the polymer crystalline and amorphous regions, and is the ideal technique to augment DSC and XRD results.[34] The additional benefit of SAXS is that for volumetric studies, it can elucidate if a chain is folded, unfolded, or partially unfolded in a given solvent system, revealing the "quality" of the solvent for a particular study and provide further insight into kinetics. Theoretically, volumetric studies should be conducted on polymers in their unfolded state to provide the greatest access to polymer chain segments. Real-time FTIR has provided understanding of polymerization kinetics for decades, as well as polymer deconstruction via TGA,[35] and can be used in addition to NMR spectroscopy and chromatographic techniques to track the formation of reaction products as well as intermediates.

Kinetics and thermodynamics of polymer deconstruction

Having reviewed the complexity of waste plastic feedstocks, we must take a global perspective of the fundamental challenges when selecting desired reaction pathways for conversion technologies. Chemical recycling of plastics will require both new catalysts and new processes. From a reaction chemistry perspective, plastics deconstruction and upcycling transformations can be viewed in light of both thermodynamics and kinetics, as illustrated in **Figure 3**. This simplified, qualitative model is not intended to represent exact reaction energetics and will not focus on all pertinent thermodynamic properties needed for technological scale-up of soft-matter feedstocks, but rather offers a framework to discuss opportunities in designing new catalysts and processes. In this model, any transformation from polymer to a desired product will exhibit a reaction barrier (E_a) and an enthalpy difference between the reactant and product (ΔH_{rxn}), dictating whether the free energy of a process is favorable ($\Delta G_{rxn} < 0$). We focus only on ΔH_{rxn}, instead of ΔG_{rxn}, since the entropy change of polymer deconstruction (ΔS_{rxn}) will almost always be positive, resulting in a more negative contribution to the free energy of reaction over all temperatures, whereas, the ΔH_{rxn} widely varies depending on target chemistry. In this simplified model, catalysts lower the reaction barrier (E_a) for a given polymer and target chemistry, while the ΔH_{rxn} remains constant (**Figure 3b** *vs* **Figure 3a**, **Figure 3d** *vs* **Figure 3c**, or **Figure 3f** *vs* **Figure 3e**). Otherwise stated, the thermodynamic difference between reactants and products cannot be changed with catalysts, but the rate of a reaction from one state to another can be modified by facilitating an alternate mechanism to the product. Similarly, the thermodynamic favorability of the depolymerization of a polymer can be tuned by selecting lower energy state products (**Figure 3a** *vs* **Figure 3d** *vs* **Figure 3f**), thus making ΔH_{rxn} more exothermic (and ΔG_{rxn} more exergonic).

With fixed reactants and products, a universal means to favor depolymerization is to increase temperature. In polymer synthesis, the ceiling temperature (T_c) of a polymer is the temperature at which the rate of depolymerization equals the rate of polymerization. At the T_c, the entropic penalty (ΔS) of polymer formation equals the exothermic enthalpy (ΔH) of polymer formation, so that $\Delta G_{polymerization} = 0$. Above T_c, polymers are thermodynamically favored to depolymerize. However, simply because depolymerization is thermodynamically favored does not mean it will occur at appreciable rates. Even at temperatures above T_c, there will be an associated reaction barrier for depolymerization (E_a). Thus, process selection and engineering can manipulate the favorability of a reaction (i.e. thermodynamic limitation), while catalysts can enable targeted reactions to occur at appreciable rates (i.e. kinetic limitation).

There will be certain polymer transformations where a catalyst is not needed (**Figure 2a, 2c**), thus requiring only process innovations. For example, though PMMA depolymerization to methyl methacrylate is endothermic, yields of up to 97% have been reported without a catalyst; this chemistry is illustrative of **Figure 2a**.[36] Other processes will require new catalysts, likely enabled by relatively simple process designs to address heat and mass transfer limitations (*vide infra*, **Figure 2f**). As an example, radical-based oxidation of PE and PS to carboxylic acids is exothermic, but the reaction exhibits a relatively high barrier of C-H activation to an alkyl radical. This transformation has been conducted in batch reactors with radical initiators such as nitrogen oxides.[37] The remaining categories illustrated in **Figure 3** will likely be the most challenging to realize, namely those that require simultaneous catalyst and process innovations (**Figure 3b**, **Figure 3d**). A successful example of such processes to date include the endothermic catalytic cracking of PE and PE/PP mixtures to benzene, toluene, and xylenes (BTX), which requires acidic zeolite catalysts, e.g., Ga-ZSM-5 or Zn-ZSM-11, and unique process configurations to obtain high yields (**Figure 3b**).[38,39] Alternatively, catalytic depolymerization of polyacetals with homogenous acids and biomass derived diols to cyclic acetals,[40] or the depolymerization of PET using nitrogen-based organocatalysts allows for a transformation of **Figure 3d** to a lower barrier process, like **Figure 3c**.[41] The challenges for enthalpically neutral (entropically dominant) processes are more focused on high conversion and facile separations, including catalyst recovery.

Ultimately, processes for polymer deconstruction and upcycling must consider these two key effects, namely, rate-limiting reaction barriers and the reaction thermodynamics, ensuring the ideal combination of catalyst and process are selected to favor *desired* reaction pathways with a low reaction barrier, while preventing *undesired* pathways from becoming favorable or having appreciable rates.

Process engineering for polymer deconstruction

Translation of processes from the laboratory to industry will require technologies capable of managing the inherent chemical and physical properties of a polymer feedstock. The chemical reactivity of waste plastics, for example, presents a unique challenge with high T_c values, such that non-selective thermal depolymerization processes (e.g., pyrolysis) can result in a complex network of competing, low barrier, and off-target reaction pathways, requiring precise unit operations to provide a high yield of useful products; these processes have been reviewed extensively.[42] The result of most thermal depolymerization processes, even for single-stream feedstocks, is a diverse product mixture of solids (char), liquids, and gases, with each phase containing their own distribution of products.[42] Mixtures of polymer feedstocks exaggerate this selectivity issue, in part to due to differing depolymerization mechanisms. PE and PP, for example, mainly thermally decompose by random chain scission, PS decomposes through a mixture of random chain scission and zipper scission, PVC degrades via branched-chain scission, while PET and polycarbonate (PC) break down through C-O & C-C homolytic cleavage.[43] Even if polymers are separated, decomposition studies have also reported wide variations in rates of depolymerization. Apparent activation barriers for depolymerization of PE, PP, and PS have been reported across incredibly broad ranges from 163-303 kJ/mol, 83-285 kJ/mol, and 83-323 kJ/mol, respectively.[44] Thus, designing processes with catalysts capable of selectively controlling the reactivity of each polymer system is critical.

Unfortunately, the variability in chemical reactivity is intertwined with the complexity of handling a solid feedstock, where poor management of the physical structure of the polymer during reaction can impede selective transformations. Relative to common solution or gas-phase reacting systems, polymers exhibit high viscosity and low thermal conductivity, such that heat and mass transfer can rapidly become the dominant reaction engineering challenge, highlighting the need for interfacial catalysis. Moreover, depolymerization processes wherein polymers are reacted in the solid phase result in kinetics that scale as a function of surface area, rather than volumetrically as soluble reactant concentration. Thus, either process designs that enable rapid kinetics on solid substrates, or processes capable of transforming reaction scaling from surface area to volumetric concentration of available bonds, are critical to consider.

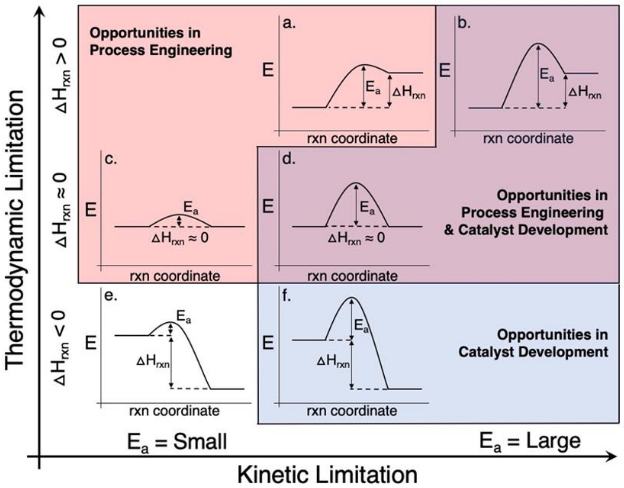

Figure 3. Simplified model to illustrate thermodynamic and kinetic control in polymer upcycling. *Opportunities in chemical catalysis in plastics depolymerization center around high barrier reactions (Panels **b**, **d**, and **f**). However, highly endothermic processes or even some near-isoenthalpic reactions, with high reaction barriers will remain difficult (Panels **b** and **d**), due to competing side reactions of lower energy; thus, these catalytic processes will require coupled process engineering innovations. Some processes will only require unique process configurations, due to lower reaction barriers (**c**), or moderate barriers that cannot be significantly lowered due to highly endothermic processes (**a**), and thus these processes represent opportunities in process engineering innovation.*

Counterintuitively, the complex phase phenomena of certain polymer/solvent combinations can result in temperature, concentration, and/or molecular weight dependent demixing behavior which provides a narrow window for solubilization. Optimizing the operating conditions of an upcycling technology for both catalyst activity and polymer solubility will be a non-trivial task. Fortunately, a variety of non-catalytic process engineering approaches have already been developed, in both waste plastics and biomass conversion, to overcome this scaling challenge. For example, various non-catalytic process engineering strategies, like co-reactant addition (e.g., steam), use of microwave-assisted pyrolysis, use of supercritical solvents, solubilization of the polymer in oil (e.g. vacuum gas oil) or solvent (e.g. tetralin, decalin, or 1-methylnaphalene) prior to pyrolysis, or dilution of the solid substrate in a non-reactive heat transfer agent (e.g., sand in a fluidized cracker), can drastically enhance product selectivities.[45–47] These examples of thermal deconstruction of polymers serve as a relevant indicator that polymer solubilization is critical to overcome heat and mass transfer limitations. Novel reaction media including supercritical fluids,[48] ionic liquids (IL),[49–54] and deep eutectic solvents (DES)[55] can be considered as potential reaction media to improve catalyst-substrate contact. Developing processes that allow for consistent and reliable accessibility of the polymer to a catalyst, or vice versa, will be a challenge at all temperature regimes, considering the complex phase behavior of polymers interacting with specific solvents.

Polymer additives may also impart challenges to polymer upcycling processes.[21] For example, antioxidants could impact the success of catalysts that employ radical initiators for depolymerization.[56] Similarly, photo-catalytic processes may be inhibited by dyes and light stabilizers, and enzymes can be deactivated through active-site inhibition, degradation induced by additives, or by non-productive binding to non-target components. Two primary approaches can be used to overcome challenges resulting from additives, namely either via development of robust catalysts and processes that are insensitive to additives, or pretreatment methods that can remove small-molecule inhibitory compounds, or some combination thereof.[57] The preprocessing of waste plastics for catalyst compatibility is analogous to pretreatment in biomass conversion, enabling comparisons from process concepts and lessons learned through decades of study in biomass pretreatment.[58]

Some plastic pretreatment methods are already well-established, especially via selective solvent extraction to remove low-molecular-weight additives.[57,59] These methods are able to effectively remove a wide variety of contaminants, but can require economically intractable solvent volumes.[57] New technologies have emerged to improve the efficiency of additive extraction relative to direct solvent extraction, including solvothermal processes and pressurized liquid-, supercritical fluid-, microwave-, and ultrasound-assisted extraction.[60] A comparative techno-economic analysis (TEA) was recently reported on several illustrative pretreatment methods to remove additives, which revealed that the feasibility of additive removal depends strongly on the additive, plastic, and extraction conditions, thus warranting further analysis.[57] For example, for dissolution-precipitation of PVC to be viable, 70% of the solvent must be recovered, but for PP, the process has been predicted to be viable even without solvent recovery.[57]

Ultimately, to realize viable catalytic processes to deconstruct and upcycle waste plastics, the economic and sustainability advantages of obtaining intermediates for upcycling via a depolymerization process, relative to synthesis of virgin materials, must be clear. Process, economic, life-cycle, and supply-chain modeling tools are thus critical in the development of realistic, scalable systems for catalytic plastic upcycling processes. In addition to the economic advantages, benefits in the relative environmental impacts of obtaining chemicals through reclamation of waste material rather than virgin synthesis can be assessed, and can help guide the selection process for viable systems, especially in cases where environmental regulations or subsidies may play a role in the feasibility of a process. In developing green processes, considerations such as atom economy, use of less hazardous solvents, and other key principles of green chemistry must also be considered, as outlined in the "twelve principles of green chemistry".[61] One accessible process metric used to assess the environmental impact of a process is the environmental factor (E-factor), which is defined as the ratio of the mass of waste per mass of product.[62] Additionally, plastics upcycling concepts must be built around viable economic targets, which will change with market fluctuations and policy. This volatility supports the need to develop multiple catalysis-enabled polymer upcycling strategies to provide for a robust ecology of processes, to ultimately provide market resilience. There are critical lessons to be learned from biomass conversion, where targeting low-value, high-volume products remains challenging, unless paired with higher-value co-products.[63]

Emerging approaches to accelerate polymer deconstruction

Additional strategies to design more efficient catalytic processes include the development of methods that employ alternative means of supplying energy to initiate the reactions (e.g. through photochemical or electrochemical means) relative to conventional thermal catalysis. Major advances in cost reductions for renewable electricity will undoubtedly lower the cost of renewable energy inputs and allow for the use of green electron sources in recycling and upcycling applications. Though electrochemistry has been widely explored in biomass valorization research,[64] applications to plastics degradation are scarce to date. Using electrical potential to drive chemical reactions is an effective way of utilizing cheap electricity to drive processes, and also enables reactions to occur under milder conditions. Recently, Jiang *et al*. reported an electrochemical method to perform pyrolysis coupled with electrolysis, generating C1-C5 products from PP under milder conditions than in conventional pyrolysis. Notably, the thermal energy inputs were all provided by solar thermal energy, significantly reducing the energetic cost of the process.[65]

Photocatalysis has been explored as a means to enable plastics depolymerization using the energy from photons.[66] Photochemical reactions can allow for milder reaction conditions, and enable selective chemistries where reaction barriers would be too high using conventional techniques. Titania (TiO_2) has been used in a variety of photocatalytic studies, owing to its ability to absorb UV light and generate highly reactive hydroxyl radicals.[67] In an example application, incorporation of TiO_2 into plastics has been shown to significantly enhance their rates of degradation by UV light.[68] One challenge in the use of TiO_2, however, is the tendency to overoxidize the substrates, generating CO_2. Care must be taken to optimize the process favor the selectivity to target products. Other examples of light-driven systems include the use of a carbon nitride/nickel phosphide catalyst to photoreform PET and poly(lactic acid) (PLA) into H_2 and small organic molecules including acetate and formate.[69] Though there are many opportunities in photocatalysis, there are also significant challenges for realistic use, including the ability of the light to penetrate into solutions, additives that may interfere with light absorption by the substrate or subsequent reactions, and reactor scalability.

A third method that has been explored that can combine advances in catalysis with advances in process conditions is microwave-assisted chemistry.[70] Substituting traditional heating with microwave-based heating allows for more uniform volumetric heating of the plastic material.[46,71–74] This results in a more consistent product distribution and a reduction in mass transfer limitations, allowing for reactions to occur at shorter timescales, lower temperature, and with greater selectivity. For example, microwave-assisted catalysis enabled complete glycolytic PET depolymerization in 5 minutes at otherwise the same conditions, instead of 4 hours using via conventional heating methods.[71] Another promising report outlines a method by which LDPE can be completely converted to various dicarboxylic acids in dilute nitric acid with microwave heating, in the presence of dioxygen.[75] Another exemplary study describes a microwave-assisted reaction in which nylon-6 was depolymerized to *N*-acetylcaprolactam by using dimethyl-aminopyridine as a catalyst and acetic anhydride as a stoichiometric reagent. These reactions proceeded with up to 74% yield in 15 minutes. The isolated monomers could then be transformed into new nylon-6, or into poly(*N*-vinylacetamide) materials.[76]

Mechanochemistry offers an additional strategy to facilitate deconstruction, in which mechanical force is applied to plastics, resulting in depolymerization typically through homolytic bond cleavage.[77] This is commonly achieved either by ball-milling or ultrasonication. In each case, the polymer molecular weight is reduced during the application of mechanical force, though chain scission rates decrease as the polymer chain length decreases. Mechanically stressing the backbone of a polymer lowers the energy barrier required to break the bonds, facilitating chemical transformations.[78] Applied mechanical force can be coupled with the addition of catalysts to create mechanocatalytic systems, which have been explored for lignocellulosic biomass depolymerization. As an example, solid acid catalysts have been added to cellulose in a ball-mill system, exhibiting catalytic enhancement of hydrolytic degradation significantly past what was achieved with ball milling alone.[79] A primary advantage of mechanocatalysis is the ability to perform these transformations in the absence of solvents and external heat, which could significantly reduce the cost and waste generation of such operations.

Overall, methodological innovations for plastics deconstruction will continue to create exciting new opportunities. Interfacing insights gained from conventional thermal catalytic processes with these aforementioned methods, among others, will enable creative strategies that are capable of generating more selective products under milder conditions.

Catalyst design for polymer deconstruction and upcycling

When systems involving catalysts of any sort (i.e., homogeneous, heterogeneous, biological) are employed, a primary challenge is catalyst stability and recoverability, as the process cost can be substantially affected by the catalyst price. Homogeneous catalysts have the significant advantages of, in general, being selective, efficient, and amenable to mechanistic study, enabling careful control of catalyst parameters and more facile determination of their mechanistic behavior. For applications in plastic degradation, they have the benefit of having increased access to the plastic substrate if the plastic is not fully solubilized. However, a primary challenge that prevents many homogeneous systems from being adopted in commercial applications is the difficulty in catalyst recovery and reuse.[80] Creative strategies for have been developed to address this challenge, including membrane separations[81] and thermomorphic solvents.[82] However, developing cost-effective homogeneous catalytic systems that include recovery and re-use of the catalysts represents both a significant challenge and an opportunity for innovation in the homogeneous catalysis research community.

In addition to recovery, catalyst stability in the presence of potential contaminants in the reaction mixture can significantly affect the process viability. Homogeneous catalysts decompose through a variety of mechanisms, including metal deposition, ligand decomposition, reaction with impurities (especially sulfur- and nitrogen-containing compounds), dimer formation, and reaction of the metal center with the ligand.[83] Certain catalysts, such as those that are highly unstable in the presence of trace water, sulfides, etc. may be more challenging to adapt for use towards plastic depolymerization, as the cost of pretreatment to remove the contaminants may be prohibitive.

For biological catalysis, enzymes are capable of rapid, selective chemical transformations, but generally are less tolerant to severe processing conditions and the presence of additives, as their activity is strongly dependent on preservation of the protein structure. Loss of activity can occur through denaturation of the enzyme from incompatible temperatures, ionic strengths, pH, or solvents.[84] Poisoning of the active site can also occur when incompatible compounds bind irreversibly, similar to decomposition of homogeneous organometallic catalysts. A wide variety of strategies for stabilizing enzymes have been developed, but heterogeneous substrate compositions such as those present in plastic waste streams make the development of stable enzymatic systems a substantial challenge.[85]

Heterogeneous catalysts are often considered to be advantageous in industrial applications as they are generally more tolerant to varying conditions than homogeneous catalysts. However, they are also susceptible to various deactivation modes, including blockage or poisoning of active sites, reduction in surface area from sintering or other means, leaching of catalytic species, among other challenges.[30] Heterogeneous catalysts are conventionally easier to recover and regenerate, which is an advantage over their homogeneous and biological counterparts. One approach to retain the activity and selectivity of homogeneous and biological catalysts while making the systems more stable is surface-immobilization of the catalysts.[86] As an example, homogeneous iridium pincer complexes have emerged as highly active catalysts for transfer dehydrogenation of alkanes. To enable recoverability and increase stability of the catalyst, these complexes were tethered to a heterogenous support.[87] A subsequent study incorporated rhenium onto the support and applied the resulting catalytic system for catalytic cross alkane metathesis of PE, producing light alkanes and waxes.[88] This process serves as a demonstration of how catalysts initially designed to be effective in homogeneous systems can be applied to plastics depolymerization. Enzyme immobilization on heterogeneous supports has also long been studied and employed as a means to recover biocatalysts after use, with one report showing resin-bound cutinase as a means to enhance PET biodegradation.[89]

Deconstruction catalysis for C-C linked polymers

In contrast to polymers linked by heteroatoms (discussed below), sp^3-hybridized C-C linked polymers, exemplified by the polyolefins PE, PP, and PS, present significant opportunities for advances in fundamental catalysis science, considering their abundance and the technical challenges to cleave C-C bonds. The resilience of C-C linked polymers has led to many efforts in non-catalytic, thermal processing. Of the catalytic approaches, C-H activation emerges as a central need in catalysis. While non-catalytic pyrolysis of polyolefins relies on C-C homolysis, resulting in reactive alkyl radicals, catalytic approaches tend to activate C-H bonds, creating a reactive intermediate such as a carbocation, surface stabilized adsorbate, stable olefin-intermediate, or an alkyl radical, that can ultimately enable C-C cleavage. Though there are a variety of catalytic means to depolymerize C-C linked plastics, we posit that there are two general themes in catalyst design that merit focus: 1) Increasing the robustness and reusability of highly selective catalysts like organometallic catalysts for C-C cleavage, and 2) enhancing the selectivity of highly robust and regenerable heterogenous catalysts for C-C cleavage.

The most studied catalysts to date in C-C bonded plastics depolymerization are those used in catalytic cracking, with examples in the literature for PE, PP, polystyrene (PS), and mixtures thereof.[42,45,90–93] Catalytic cracking utilizes highly acidic zeolites like ZSM-5, HY, H-BETA, AL-SMA-15, HUSY, or many others to abstract a hydride from the polymer backbone, resulting in a reactive carbocation intermediate with mixtures of olefin/paraffins or liquid aromatics as products.[94] By tuning the catalyst acid strength, acid type (i.e., the ratio of Lewis acids to Bronsted acids), and process configurations, mixtures of olefins/paraffins or aromatics (benzene, toluene, and xylenes (BTX) can be targeted.[94] Interestingly, there have been a significant number of publications seeking this endothermic transformation using non-catalytic, thermal processes,[90] but only a few catalytic approaches with this aim.[38,39] As discussed previously, selecting energetically unfavorable products requires higher reaction temperatures, precise process configurations, and catalysts to provide for maximal selectivity and yield of products. Although further process analysis is needed, we suspect that olefin production is likely not a viable long-term strategy from polyolefins due to energy demands, competition with less expensive feedstocks like ethane and propane, and the established capital infrastructure in small molecule olefin production. Conversely, mixed aromatic production performed on-site with a petroleum refinery could provide for a means to transform polyolefin waste into BTX feedstocks, a concept that is garnering commercial attention.[95] One significant advantage of this process is the ability for such an approach to work on a mixture of polyolefin feedstocks.

To make cracking more thermodynamically favorable and generate aliphatic products, the cracking strategy has also been paired with hydrogenation catalysts including metal sulfides,[96] nickel,[96–99] cobalt,[99] platinum group metals,[100,101] or combinations through alloying,[96,99] resulting in bi-functional hydrocracking catalysts. These bifunctional catalytic systems, operating under high hydrogen pressures, provide a means to crack, then hydrogenate polyolefin polymers, including PE,[96–101] PP,[101] and PS,[101], at lower temperatures than the cracking catalysts alone. Notably, noble metals provide an alternative pathway to the same aliphatic products through hydrogenolysis. For instance, aliphatic molecules adsorb to the surface of the platinum group metal, undergo dehydrogenation (through C-H activation of the backbone resulting in two carbon atoms adsorbed to a metal surface in a reactive state), C-C bond cleavage, and ultimately desorption.[102] Both carbon supported ruthenium and complex atomic layer deposition platinum on a perovskite support have been leveraged as hydrogenolysis catalysts capable of converting PE into alkane mixtures in a solvent-free system.[103,104] However, non-noble metals have also been employed, with various proposed mechanisms. For example, zirconium hydride supported on silica-alumina has been leveraged for such chemistry.[105] This system is thought to result in metal insertion into the C-C bond, after C-H activation with a reactive hydride. Uniquely, these catalysts are similar to Ziegler-Natta polymerization catalysts operating in reverse, an area that merits further attention. Indeed, there is significant opportunity from catalysts designed from inspiration of coordination polymerization catalysts like Ziegler-Natta, Phillips, or metallocene catalysts.[106,107] Additional opportunities exist to apply certain depolymerization strategies like hydrogenolysis to other polymer feedstocks, including heteroatom-linked polymers. For example, molecular hydrogenolysis catalysts have been leveraged for depolymerization of mixed chain-growth polymers,[108,109] resulting in alcohol products. Yet, there has not been demonstration to our knowledge of a single catalyst system capable of hydrogenolysis for mixtures of both polyolefins and heteroatom-linked polymers.

The adsorbed intermediate of hydrogenolysis is similar to what we recently dubbed the “olefin-intermediate process” (**Figure 4**),[110] which was originally developed with tandem dehydrogenation and cross metathesis with the use of organometallic catalysts.[88] The process relies on two chemistries, C-H activation through dehydrogenation to olefins and cross metathesis, which rearranges the chemical functionalities of two olefins. This process has been leveraged to produce a distribution of alkane products from PE, utilizing an iridium pincer dehydrogenation catalyst and a rhenium metathesis catalyst.[88] The heterogeneous C-H activation field, with much of its focus on producing small olefins like ethylene, propylene, and butenes from their alkane analogues, typically operates at temperatures above 450°C. This is due to the fact that non-oxidative C-H activation to olefins is an equilibrium-limited, endothermic process, requiring high temperatures to achieve high conversions. However, in this processing scheme, high conversion is not necessary. In fact, organometallic catalysts were able to depolymerize PE at high conversion to low molecular weight alkanes at 175°C in 4 days,[88] while a heterogeneous version of this system was able to provide a

73% reduction in the molecular weight of a high-density PE feedstock at 200°C in only 15 hours.[110] This is because the olefin is not the recovered product, but rather a reactive intermediate that can be consumed by another chemical reaction occurring simultaneously. This concept is similar to how biological systems are capable pulling metabolites through a highly endothermic reaction step, by utilizing a series of coupled reactions. Biological metabolism could be a source of inspiration for novel tandem, or cascade chemistries when dealing with thermodynamically unfavorable reaction steps. One excellent example of such a novel tandem chemistry is the combination of aromatization and hydrogenolysis using a supported platinum catalyst that yielded aromatic surfactants from PE at relatively mild operating conditions.[111]

To our knowledge, the tandem dehydrogenation and cross metathesis chemistry is the only example, but by no means the only opportunity, of such an “olefin-intermediate” process applied to plastics depolymerization (though, the work by Zhang *et al.*[111] is exceptionally similar in nature to an olefin-intermediate process) (**Figure 4**). We predict there are many transformations that are possible with an olefin-intermediate. The challenge in such a system is two-fold, 1) the catalyst systems must be compatible with one another, and 2) given that the dehydrogenation step produces an olefin and two hydrogen atoms, any process scheme has to manage the hydrogen and olefin. One research area for developing process and catalysts concepts for the olefin-intermediate process is in rubber depolymerization. Elastomer materials contain an olefinic bond within the polymer backbone, in essence, already existing as an ‘olefin-intermediate.’ A variety of processes have already been leveraged in elastomer depolymerization like catalytic cracking, oxidation, hydrogenolysis, metathesis, and more.[112,113] For example, metathesis catalysts have been utilized in the depolymerization of polybutadiene to various olefinic products like cyclic macrocycles, smaller rings (cyclopentene/cyclohexene), or even terminal olefins.[114]

As mentioned, polymer syntheses can serve as useful inspirations for deconstruction processes, such as coordination polymerization catalysts or free-radical synthesis approaches. Free-radical depolymerization has been leveraged in the production of oxidized products from polymers like PE, PP, PS, and even some chain-growth polymers. This free-radical process relies on initiation, propagation, and termination reactions, similar to some polymer syntheses, but using oxygen to react and generate highly reactive radical intermediates which result in C-C bond cleavage. These reactions are exothermic, typically operated at lower temperatures compared with other approaches and often include the use of radical initiators. Initiators like nitrogen oxides and bromine compounds have been utilized to begin this reaction path.[37,75,115] Challenges in this process concept include operating in a window of conditions that are sufficiently reactive to cleave C-C bonds, while avoiding full polymer combustion. These challenges have been overcome in the commercial production of adipic acid, where cyclohexane is ring-opened to a dicarboxylic acid through oxidation with nitric acid. Similarly, terephthalic acid is produced through C-H oxidation of *p*-xylene.[116] Non-selective catalysts like nitrogen oxides can produce nitrated products,[37] thus more selective catalysts are needed in this field. Through catalyst design and process engineering, waste plastics could potentially be selectivity oxidized to valuable products at relatively mild operating conditions.

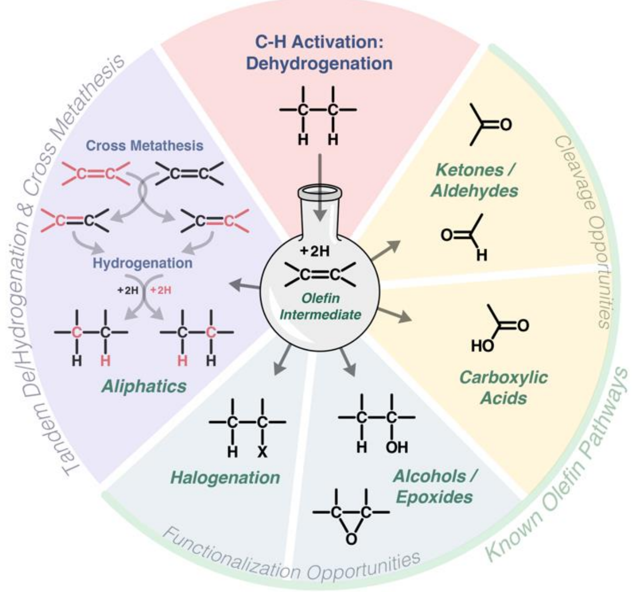

Figure 4. Opportunities in polyolefin upcycling via the olefin-intermediate process.[109] *Olefin intermediates can be utilized as a means to activate polyolefins, but this chemistry requires tandem reactions to rapidly convert low concentrations of olefin intermediates and the hydrogen atoms removed from the polymer backbone. Such a process has been leveraged to depolymerize PE to alkanes using dehydrogenation and cross metathesis. Considering the well-known chemistries available for olefin cleavage and functionalization, this process will likely play an important role in the deconstruction and upcycling of polyolefins and other C-C linked polymers. For example, such C=C activating chemistries can be directly applied to the olefinic backbone of elastomers as well.*

The above summary is not an all-inclusive list of the methods developed for C-C cleavage, as there are many additional catalysis opportunities available. Various examples of C-C cleavage catalysts have been reported in the homogeneous catalysis literature, and are the subject of many reviews.[117-121] These systems are often characterized by high conversions and selectivity, enabling synthesis of molecules with a range of functionalities. However, these systems are designed for specialized conditions and substrates, likely making it a challenge to directly adapt them to depolymerization, which requires catalysts that are cheap, recoverable, and stable. For instance, many metal-catalyzed C-C cleavage strategies outlined in the literature rely on the energy released from breaking strained rings, or on heteroatom directing groups to bind to the metal center and allow for the C-C cleavage to occur. These types of catalytic C-C cleavage systems may, in some cases, be less applicable for use in breaking bonds in polyolefins, as they rely on the presence of specific chemical moieties in the substrate that are not typically present in polymers. Chemical insight can still be obtained by studying these processes, but identification of these limiting issues is crucial in determining which systems may be useful for plastic depolymerization.

Deconstruction catalysis for C-O/C-N-linked polymers

Depolymerization reactions for polymers that contain heteroatom backbones linked by C-O and C-N bonds (e.g., PET, PA, PU) typically exhibit relatively low reaction barriers and near neutral reaction free energies (**Figure 3c-d**), compared with polyolefins, as C-O or C-N bonds are typically more labile than C-C or C-H bonds. Depolymerization of these types of polymers is typically achieved through the use of a nucleophile, which reacts with the carbonyl to generate products, as shown in **Figure 5**.

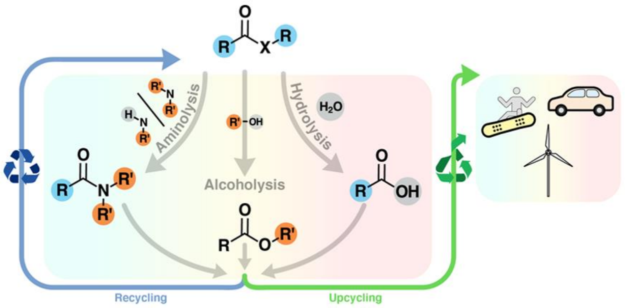

***Figure 5**. **Depolymerization of C-N and C-O linked polymers for closed-loop recycling or open-loop upcycling**. These methods are commonly achieved via use of a nucleophile, which will react with the carbonyl and generate cleaved products. Blue spheres represent the polymer backbone, and orange spheres represent the small molecule nucleophile.*

Solvolysis is a primary means to achieve depolymerization of heteroatom-linked plastics, which employs nucleophilic solvents that react with the carbonyls on the plastic to generate products containing both the monomer and the nucleophile. This method is effective for most heteroatom-linked polymers, and has been extensively reviewed.[122] Though many strategies have been explored in this space, new opportunities in solvolytic depolymerization continue to emerge. For example, ILs have been used to facilitate depolymerization in polymers such as nylon 6,[49] nylon-6,6,[50] PET,[51] PC,[52] fiber reinforced plastics,[53] and even rubber tires.[54] ILs exhibit a remarkable range of tunable properties, including good solubilization capacity for polymers, and can simultaneously catalyze their depolymerization. A recent example employed tetraalkylammonium ILs to stabilize a zinc oxide catalyst, enabling the solvolytic depolymerization of PC to monomeric products with glycerol.[123] Despite their benefits, however, the cost of ILs necessitates the recovery of the solvent for re-use, which remains an opportunity for innovation. DESs are similar to ILs, but exhibit hydrogen bonding interactions in addition to ionic interactions, and have the advantage of being less costly and generally less toxic than ILs.[124] A recent study demonstrated significant enhancement in the glycolysis of PET with urea/metal DES relative to ILs. The authors show that the increased activity results from the presence of hydrogen bonding between the DES and ethylene glycol, demonstrating simultaneous solubilization and catalytic enhancement capabilities.[125]

Significant enhancements in activity of solvolytic depolymerization can be achieved through the use of catalysts. Catalytic strategies to depolymerize chain-growth polymers have also been reviewed.[7,126] Catalytic systems include the use of Lewis acidic metals that associate the polymer carbonyl moieties, facilitating nucleophilic attack and depolymerization. Zinc salts are commonly employed for such strategies, though several other metals have been explored.[127] Interesting hybrid catalytic systems have been developed, including one study that showed high activity for PET depolymerization by using the Lewis acid zinc acetate to activate the carbonyl, and various organic amine bases to activate the nucleophile, resulting in a synergistic enhancement in depolymerization rate.[128] One promising example describes the use of a homogeneous ruthenium-based catalyst capable of depolymerizing PET, polylactic acid (PLA), and PC, even in the presence of additives and colorants.[108] Depolymerization of heteroatom-linked polymers continues to be a very active research area, with constant development of new catalysts.

Certain plastics with heteroatoms in their backbones are unsuitable for degradation via solvolysis, and require the use of alternative degradation strategies. For example, amine-cured epoxide resins are resistant to solvolysis, but an approach that involves oxidation of the amine, resulting in imide formation enables solvolysis to efficiently degrade the polymer in a subsequent step.[129,130] Creative approaches that employ sequences of reactions to achieve highly efficient depolymerization represent significant opportunities for advancements in this field.

Because it is generally easier to recover monomers from chain-growth polymers that contain heteroatoms in the backbone (e.g. PET or PU) than for C-C backbone plastics (e.g. PE or PP), many current depolymerization approaches for heteroatom-linked polymers result in the production of the same starting monomers that are used in the original polymerization.[41] If the yield of monomers is high and the cost low from these processes, closed-loop recycling may be viable, as the monomers can then be obtained from low-cost recycled materials instead of being produced from fossil-based resources. However, there are also opportunities for innovations in reactions that occur subsequent to, or in parallel with, the depolymerization reaction, combining depolymerization with the production of value-added molecules. As an example, we published a study detailing a method that converts reclaimed PET bottles to glycolyzed PET monomers and oligomers, followed by subsequent reaction with bio-derived olefinic acids to create high-value fiberglass-reinforced resins.[131]

Opportunities in catalysis related to process intensification lie in the ability to directly generate value-added products rather than passing through a separate monomer generation step. For example, one study describes the addition of adipic acid to a PET glycolysis system, resulting in the generation of new polymers in a one-pot depolymerization/condensation reaction, resulting in the direct synthesis of polyester materials.[132] Another exciting method is the generation of amide-based materials from PET by substituting alcohol-based nucleophiles such as ethylene glycol with amine-based nucleophiles. Aminolysis has been performed on PET with a variety of amine-containing substrates to generate amide-containing terephthalate-based monomers, which could then be used to make high-value amide-based polymers.[133,134] Such one-pot processes are highly desired throughout the chemical disciplines, as they eliminate costly separations.[135] These are representative examples of opportunities that should be sought in the valorization of waste chain-growth polymers, with the development of higher-value upcycled products from isolated monomers. Further developments in chemical depolymerization of heteroatom-linked polymers are expected through advances at the nexus of catalysis and process design, rather than solely via breakthroughs in fundamental science, especially compared to depolymerization of C-C linked polymer systems. Creative strategies to merge highly active catalytic systems with innovative processes, as well as continued development in strategies to directly upcycle heteroatom-linked polymers into value-added materials, will remain at the frontier of current research efforts.

Biological catalysis for deconstruction of polymers

In addition to chemical catalysts, biocatalysts (enzymes and microbes) offer the potential to contribute to energy efficient polymer deconstruction and upcycling.[136] Successful biological catalysts typically target enthalpically neutral or modestly exothermic processes, where the reaction barrier can be lowered (**Figure 3d** to **Figure 3c**). Biological plastics deconstruction will likely take place extracellularly, and we thus focus in this section on opportunities in enzymatic catalysis. Similar to approaches in biomass conversion, depolymerization enzymes can be envisioned in multiple contexts, including as freely-diffusing or complexed enzymes, immobilized enzymes, secretions from whole-cell biocatalysts, or displays on cell surfaces.[137,138] The use of multiple, synergistic enzymes in cocktails and in designer enzyme cascades is also likely to aid in the development of industrially-relevant biocatalytic plastics deconstruction.

Enzymatic biocatalysis for plastics deconstruction will likely occur primarily in water. Since most plastics are water-insoluble, depolymerization enzymes must react at a surface, via an interfacial mechanism. The natural parallel to this is well studied in the deconstruction of recalcitrant biopolymers such as cellulose and chitin.[137,139] The traditional Michaelis-Menten kinetics formalism used to describe enzyme kinetics is applicable for reactions with soluble substrates and products – akin to many applications of homogeneous chemical catalysts acting on small molecules. Interfacial biocatalysis, conversely, does not obey conventional Michaelis-Menten kinetics.[140] Instead, it has conceptual parallels to heterogeneous catalysis, where reactants and products exist in a different phase than the catalyst. And indeed, recent approaches to kinetic treatments of interfacial biocatalysis have leveraged well-known kinetics concepts from the heterogeneous catalysis literature.[140–142] In particular, Westh *et al*. derived new formalisms and developed accessible assays for enzymes acting on polymers that enable determination of steady-state rates while incorporating key parameters including surface-site inhibition,[143–145] which was recently applied to PET-degrading enzymes.[146] This work should be considered by researchers investigating interfacial enzyme kinetics for the development of structure-activity relationships and for the robust comparison of plastics-degrading enzymes.

Beyond interfacial biocatalysis, enzyme processes in non-aqueous media or low-water systems have also long been studied.[147] Biocatalysts adapted for action in harsh conditions, such as from halophilic or thermophilic environments, are often a viable source of enzymes for protein engineering and evolution efforts.[148] Moreover, enzyme immobilization on solid supports can also enable facile protein stabilization for reactions in non-aqueous or low-water environments.[149] The use of non-aqueous media that enables polymer solubilization, in parallel with enzyme stability improvements, will likely play a role in increasing the accessible surface area for enzymatic depolymerization to ultimately approach the traditional catalytic, volume-scaling rates associated with homogeneous or enzymatic catalysis of soluble substrates.

Work to date in synthetic polymer deconstruction with enzymes has primarily focused on PET conversion with hydrolases, which we use as a featured example (noting, however, that the same opportunities apply to other synthetic polymers). Because ester bonds are ubiquitous in natural biological molecules, including in cutin and suberin, cutinases and suberinases are an excellent starting point for sourcing enzymes that can depolymerize synthetic polyesters.[150] Early work focused on the discovery and engineering of thermophilic cutinases that have optimal activity near the T_g of PET. [151–155] The 2016 study from Yoshida *et al.* reporting the discovery of a bacterium that secretes a two-enzyme system (PETase and MHETase) for PET hydrolysis inspired many new entrants into this field, and as a result, new structural, kinetics, engineering, and evolution studies are now emerging in this field.[156–161]

Enzyme engineering strategies, (mostly with PET hydrolases) have borrowed concepts from polysaccharide-active enzymes to improve substrate turnover for plastics deconstruction. Work from Guebitz *et al*., among others, includes attachment of non-catalytic binding modules, such as carbohydrate-binding modules, PHA-binding domains, or hydrophobins to cutinases to improve their binding affinity to hydrophobic PET surfaces, thereby increasing the enzyme active site concentration at the substrate surface.[162] These additions have led to improvements in substrate turnover. Questions remain as to how to best employ non-catalytic binding modules in polymer deconstruction. Namely, the optimal binding affinity requirements are unclear, but are directly related to the mechanism of action of e.g. PET hydrolases. Moreover, high-solids loading will likely be a key cost driver in the use of enzymes for plastics recycling. As shown for cellulose depolymerization at high-solids loadings, the use of non-catalytic binding modules may not be universally beneficial due to shorter required distances to diffuse to a reactive surface after enzyme dissociation.[163] This question remains to be addressed for PET deconstruction. Additionally, it is currently unknown, to our knowledge, what the relative binding affinities of available non-catalytic binding proteins are to PET or other synthetic polymer surfaces – values that are experimentally accessible via biophysical techniques.

Enzyme complexes also offer potential strategies for biocatalytic plastics deconstruction. Cellulosomes, for instance, contain multiple enzymes tethered together via strong, non-covalent cohesin-dockerin modules.[165] These systems are effective in cellulose hydrolysis relative to freely-diffusing enzymes with only a single catalytic domain,[166] and they, like other multi-modular enzyme complexes in nature,[167] offer inspiration for engineering plastics-degrading enzyme complexes.

To date, structure-guided protein engineering of PET hydrolases has led to demonstrable improvements in enzyme performance. These efforts include engineering the active-site grooves to accommodate synthetic polymer substrates,[159,168,169] thermal stabilization,[170] and addition of stabilizing glycans through eukaryotic expression.[171] A recent example was reported by Tournier *et al.* wherein they engineered the leaf compost cutinase (LCC) to deconstruct micronized PET to >90% depolymerization extent in ~10 hours at an enzyme loading of 1 mg LCC/g PET substrate.[168] This *tour de force* study clearly demonstrates the ability of natural enzymes to be engineered towards industrially relevant activity on PET.

Despite considerable advances in the last decade, some aspects of the mechanistic action of PET hydrolases remain elusive.[172] While these questions are discussed here in light of PET hydrolysis, where the majority of work has been done, similar lines of inquiry will very likely apply for any newly reported plastics depolymerization enzyme. In terms of enzyme sourcing and discovery, most PET hydrolases are classified as cutinases, but little work has been done to definitively demonstrate cutin deconstruction across the known PET hydrolases. It is also noteworthy that suberin often contains aromatic moieties whereas cutin does not,[173] which is potentially related to the relative activity for aliphatic vs. (semi-)aromatic polyesters; thus questions in terms of the natural substrates remain to be addressed. While PET hydrolases likely employ the canonical two-step serine hydrolase reaction mechanism, how PET hydrolases interact with the solid synthetic substrates has not yet been reported.[174] Questions remain regarding whether these enzymes employ a processive or non-processive mechanism, if PET hydrolases act on polymer chains in an exo- or endo-acting fashion, and if and how they are inhibited by small molecules (including products and additives in plastics). For use in mixed waste streams, inhibition by non-productive binding, akin to cellulases binding to lignin, may be a concern.[175] Even for PET, there is potential that other enzymes in nature remain to be discovered with complementary and synergistic activities for PET hydrolases, akin to the discovery of lytic polysaccharide monooxygenase action on polysaccharides,[176] and various hydrolases themselves are likely synergistic. Most importantly, for a fundamental understanding of enzymatic biocatalysis for plastics upcycling, the relationship between the polymer properties (e.g., crystallinity, molecular weight, surface area, etc.) and the enzyme performance represents the ultimate objective in terms of harnessing enzymes for deconstruction of synthetic polymers. Even for PET, little work has been done to date to correlate detailed polymer properties to enzyme performance (*vide infra*).

Discovery and sourcing approaches that utilize natural diversity to find starting points for depolymerization enzymes targeted at polymers that contain similar C-O, C-N, and C-C represents a rich source for biocatalyst engineering and evolution. The literature contains reports of nylon oligomer degradation, for instance, that can serve as starting points for enzyme discovery and improvement.[177] PU is a common target for the environmental microbiology community, and at least for PUs that employ ester bonds, esterases will likely find utility, but cross-linking considerations in PU thermosets will be critical to consider as well.[178] From an evolutionary perspective, in contrast to biopolymers like cellulose for which interfacial biocatalysts have had hundreds of millions of years to evolve, anthropogenic plastics are an extremely young biological niche. Any enzyme found in nature will thus have only a sub-optimal moonlighting activity on anthropogenic polymers, and greater performance increases can therefore be expected from the directed evolution and engineering of plastics-degrading enzymes, especially for C-O and C-N bond cleavage.

In parallel to the chemical catalysis sections above (**Figure 3**), we posit that there is a clear path ahead for biocatalytic deconstruction of polymers linked by C-O and C-N bonds, and the coming years will likely see many exciting discoveries therein. Analogous to the challenges faced in the chemical depolymerization of polyolefins, applications of enzymes to efficiently deconstruct C-C bonded polymers will require fundamental breakthroughs to enable the controlled generation of industrially relevant products. For example, functional enzymes, microbes, and conditions have long been sought for PE degradation.[179] Oxidoreductase action on C-C bonded polymers has been reported, an example of a biological catalyst lowering the barrier for a highly exothermic process (**Figure 3f** to **Figure 3e**), but this has not been accompanied by appreciable substrate conversion. Organism-level studies have also been conducted, but with open questions remaining as to the enzymes responsible for deconstruction.[180] Sourcing microbes and enzymes from hydrocarbon-rich environments may be promising, and systems biology coupled with quantitative polymer deconstruction assays will be necessary to discover if there are indeed natural systems that could serve as a starting point for developing effective C-C-active depolymerases.

Biological catalysis for upcycling of polymers

In addition to depolymerase enzymes for plastics deconstruction, enzymes and/or whole-cell biocatalysts can also play a role in plastics upcycling.[181–183] Especially when plastics depolymerization yields a mixture of monomers and contaminants, e.g., from PU or mixed plastic waste streams, microbial catalysis provides a promising alternative by funneling these “plastic hydrolysates” into central metabolism and *de novo* produced value-added chemicals. This concept of biological funneling is well established in the conversion of lignin-derived monomers and likely to be useful for plastics upcycling as well.[184] This same concept could apply to the development of synergistic microbial consortia that are “specialists” at consuming particular substrates.[185] Alternatively, isolated plastic monomers can also be transformed into functionalized derivatives with retention of more complex chemical structures.[186,187]

In essence, biological plastics upcycling requires three catalysis steps: Production of the depolymerization enzyme (or catalyst), deconstruction of the polymer, and conversion of the plastic hydrolysate to the final product. Analogous to biomass conversion, several process options are available **(Figure 6).** Separate depolymerization and conversion (SDC, equivalent to separate hydrolysis and fermentation) is currently the most used approach because efficient chemical or enzymatic depolymerization methods are outside of typical microbial boundary conditions – this is a key area where hybrid chemo-catalytic deconstruction and biological upcycling will likely play a prominent role.[188,189] When depolymerase enzymes are secreted by a microbe (or a consortium of microbes) that also harbors catabolic capacity for the released deconstruction products, this one-pot biological processing is termed consolidated bioprocessing (CBP) in the biomass conversion field.[190] Parallels to CBP have been discovered in natural microbes, most prominently by Yoshida *et al.* wherein they reported that *Ideonella sakaiensis* 201-F6 is able to secrete a two-enzyme system for PET hydrolysis and consume the terephthalic acid and ethylene glycol breakdown products as a carbon and energy source.[156] The main advantages of this approach are the avoidance of product inhibition, toxicity, and costly base and acid additions through the immediate consumption of (acidic) monomers. However, current PET-based CBP suffers from low rates and co-substrates must be provided to support sufficient enzyme secretion. This could be amended by combined depolymerization and conversion (CDC, equivalent to simultaneous saccharification and fermentation), where enzyme production is performed separately but hydrolysis and conversion still take place in one pot.

Whole-cell biocatalysis or cell-free systems to upcycle plastics depolymerization products will undoubtedly leverage the foundational tools, learnings, and capabilities

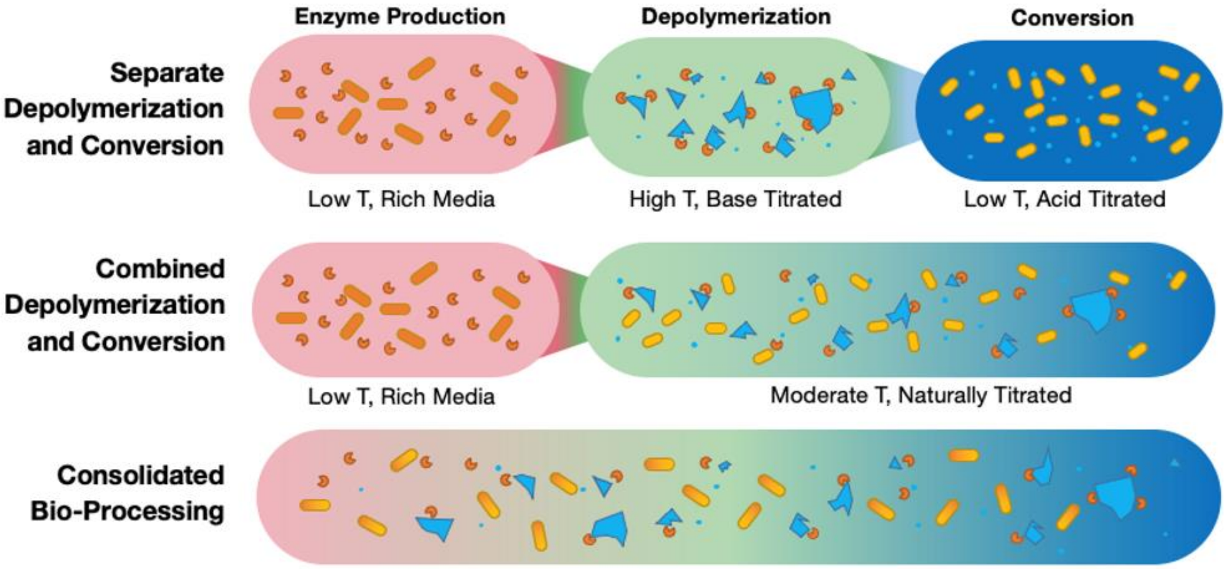

Figure 6. Opportunities in consolidated bioprocessing. *The separate development of enzyme production, depolymerization, and conversion enables each catalyst to operate in its optimal temperature, pH, and nutrient regime, but will require both acid and base titration; meanwhile, the combination of operations reduces the severity of titration and may prevent the accumulation of inhibiting intermediates. Despite these advantages of consolidated bioprocessing, further development will be required to operate efficiently in physical constraints amenable to all processes.*

from the global biochemistry, metabolic engineering, and synthetic biology communities.[191–193] Specifically for plastics upcycling in CBP-like concepts (**Figure 6**), microbes must be capable of enzyme expression and secretion at concentrations sufficient for effective extracellular depolymerization. In addition, if deconstruction and upcycling is conducted in a one-pot process, the enzyme and microbe must be compatible in terms of pH, temperature, and media. For plastics that are amenable to enzymatic deconstruction at temperatures achievable for thermophilic microorganisms (e.g., PET), the use of such thermophiles can be considered as a potential means for enabling one-pot processing, but work remains to be done to enable facile protein secretion and metabolic engineering therein.[194] Certainly, much can be learned from the industrial composting of biodegradable polymers like PLA and polycaprolactone.

For microbial uptake and biological upcycling of plastics-derived intermediates (which can be either obtained from biological or chemical catalysis), discovery and engineering of new transporters and catabolic enzymes will likely be necessary. Continuing with the example of PET, the primary intermediates from biological deconstruction are terephthalic acid and ethylene glycol, both of which have known catabolic pathways.[195] Polymers such as PU, which employ more complex monomers, will require additional pathway discovery efforts.[196] Additionally, the small molecules and co-monomers present in polymers represent critical targets to ensure high carbon conversion. Unlike sugars and lignin-derived aromatics, many of these molecules are not common in nature. As a result, their biodegradation may be limited to a few organisms in specific environmental niches. Leveraging enzyme and pathway discoveries from the environmental microbiology community via prospecting efforts, metagenomics, and systems biology approaches will enable the rapid discovery, optimization, and industrial use of enzymes and metabolic pathways for catabolism of plastics-derived intermediates.

Another complicating factor is posed by toxicity. Hydrophobic plastic depolymerization products such as styrene, octane, and octanol, perturb microbial membranes.[238,198] Some PU-derived diamines such as methylenedianiline and toluene diamine are extremely toxic.[199] Also, many additives will inhibit microbes and enzymes, including antimicrobials added to avoid decay of e.g. PU foams. For some of these high-value/high-toxicity monomers, efficient extraction processes will need to be developed to recover them prior to microbial conversion.[57,185,200] Amelioration of toxic effects from plastic-derived chemicals can also be potentially gained via solvent-tolerant strains.[198]

Much needs to be done to make bio-upcycling of plastics a reality, not only on the discovery and optimization of enzymatic depolymerases, but also on the discovery and optimization of metabolic pathways and microbial catalysts for the conversion of plastic monomers. When successful, plastic waste can be established as an abundant carbon-rich substrate for industrial biotechnology.[181] This would open up a broad spectrum of value-added products that can be produced by biotechnology, offering better end-of-life solutions for many unrecyclable plastics and plastic mixtures.

Conclusion

Plastic waste represents not only a global pollution problem, but also a carbon-rich, low-cost, globally available feedstock. Chemical recycling, enabled by catalysis advances, offer a much-needed complement to existing mechanical and solvent-based recycling approaches, towards a more holistic management strategy for these incredibly versatile materials. In this perspective, we highlight key challenges and opportunities to realize catalysis-enabled chemical circularity for today's polymers. Given the range of polymers used, this will likely require a battery of catalysis-driven technology options. Moreover, opportunities exist to use, and combine, biological and chemical catalysis to generate commodity chemicals and new polymers, ideally at lower energy inputs, GHG emissions, and cost than virgin materials manufacturing.[4] These efforts could be synergistic with the development of new polymers with better end-of-life functionalities that increase their amenability to catalytic deconstruction. Through development of commercially viable solutions, enabled by fundamental catalysis research and innovative integrated systems, the global catalysis community will undoubtedly play a critical role in solving the plastics upcycling problem and improve humankind's overall stewardship of the planet.

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