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Chemical and biological catalysis for plastics recycling and upcycling

Lucas D. Ellis[1,5], Nicholas A. Rorrer[1,5], Kevin P. Sullivan[1,5], Maike Otto[2], John E. McGeehan[3], Yuriy Román-Leshkov[4], Nick Wierckx[2] and Gregg T. Beckham[1] ✉

Plastics pollution is causing an environmental crisis, prompting the 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 reaction engineering are needed to overcome kinetic and thermodynamic limitations of plastics deconstruction. Either chemical and biological catalysts will need to 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 incentivize improved plastics reclamation and reduce the severe global burden of plastic waste.

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 tonnes 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 natural environment is a global pollution crisis, with an estimated 4.8–12.7 million metric tonnes 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, which will not only provide a means to abate pollution from plastics, but could reduce greenhouse gas emissions associated with plastics manufacturing and virgin materials production[4]. From a fossil feedstock perspective, it is estimated that plastics manufacturing alone will consume ~20% of global petroleum use by 2050 (ref. [5]).

Today, primary (post-production) 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, by 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 re-use[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 recycling approaches cannot enable a fully circular plastics economy as there are not sufficient economic incentives and technologies, whether mechanical or otherwise, for the recycling of waste plastics. Most recycling today can therefore be considered downcycling 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 to convert them into another material (open-loop recycling generally, or open-loop upcycling if the final product is of higher value)[8]. This approach of using catalysis to convert plastic waste to circular material streams is distinctly different from the conversion of plastics to fuels or energy recovery. Chemical recycling enables potential generation of value-added products far beyond the scope of mechanical recycling. Such strategies will be key to developing a new model 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 connected by covalent bonds, which are typically not accessible for depolymerization by biological or abiotic means in landfills or the natural environment. As an example, polyethylene and polypropylene exhibit only aliphatic C–H and sp^3 C–C bonds that are difficult to cleave, especially in a solid, high-molecular-weight polymer. In addition, plastics also exhibit crystallinity or are formulated with other components, including other polymers, providing further barriers to natural decomposition at appreciable rates. 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 past half-century. Thus,

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[1]Renewable Resources and Enabling Sciences Center, National Renewable Energy Laboratory, Golden, CO, USA. [2]Institute of Bio- and Geosciences—Biotechnology (IBG-1) and Bioeconomy Science Center (BioSC), Forschungszentrum Jülich, Jülich, Germany. [3]Centre for Enzyme Innovation, School of Biological Sciences, Institute of Biological and Biomedical Sciences, University of Portsmouth, Portsmouth, UK. [4]Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA. [5]These authors contributed equally: Lucas D. Ellis, Nicholas A. Rorrer, Kevin P. Sullivan. ✉e-mail: gregg.beckham@nrel.gov

biological systems for breaking down synthetic plastics have not yet 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 catalysing 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 technologies that can enable closed-loop or open-loop recycling and upcycling. To this end, this Review highlights challenges and opportunities in developing processes that employ chemical and biological catalysts for plastics recycling and upcycling. Besides other polymers, plastics commonly contain additives, including metals, dyes, pigments, fillers, antioxidants, 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 is 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 accessibility can be achieved through polymer solubilization, allowing for volumetric processes where the rates of depolymerization scale as a function of the solution volume. However, when substrates remain in solid form, interfacial catalysis methods will be required, where reaction performance will scale proportionately with feedstock surface area. 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 tonnes per year[1]. Polymers 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 (Fig. 1a) and polymers with C–N and C–O inter-monomer linkages (Fig. 1b)[4]. The materials within each class are further ordered by their global annual consumption amounts, in millions of metric tonnes per year (MMT yr^{-1})[4]. For simplicity, we include polymers here with annual global market sizes exceeding 2.5 MMT yr^{-1}.

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 molecular identity and arrangement, crystallinity, and molecular weight. Generally, the monomer identity influences the final application of the polymer by dictating many properties, such as the glass transition temperature (T_g)[12]. As the T_g represents a softening of the material, it is a prime factor in determining the final polymer application. Flexible molecules in the backbone, which can relax faster, may result in low-T_g materials with applications such as polyethylene bags or rubber (that is, polybutadiene)[13]. Meanwhile, rigid molecules or molecules 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 T_g characteristic of their amorphous region, semi-crystalline polymers will also exhibit concomitant melting behaviour 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 material and reduce the permeability of liquids and gases. Co-monomers (for example, 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 (for example, increasing molecular weight leads to higher T_g, modulii, and so on). 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 power of 3–3.5 ($\eta = {\sim}MW^{3-3.5}$) 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 cross-linking) also contributes to the macroscopic properties, influencing both polymer processing and end use. In the case of polyethylene, 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 be processed after polymerization, materials that become covalently cross-linked (that is, infinitely branched) during polymerization lose their ability to flow and be reprocessed. These materials are routinely classified as thermosets and include polyurethanes, epoxies, and rubber materials[19].

Even though plastics are often thought of as chemically homogenous on a molecular level, commercial plastics are rarely a single component or formulation. Polymers are often melted together to make blends, combined with small-molecule additives, or physically or chemically bound to other plastics. Polymer blends, or complex copolymer matrices, are used to introduce higher-order phases that may enable improved performance. Acrylonitrile–butadiene–styrene is an illustrative example of a copolymer and a polymer blend. Namely, the rubbery nature of suspended polybutadiene domains dissipates 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, antioxidants, 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 recovered easily. Aside from chemical blends, polymeric materials also often contain a physical mixture of components. For example, textiles are often woven from polypropylene, PET, nylon, and cotton fibres; most food packaging comprises layers of different plastics (often including thin metal layers); and thermosets commonly contain filler (for example, carbon black, calcium salts, and other inorganic fillers) or reinforcement (for example, tyre cord, glassfibre, or carbon fibre) 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.

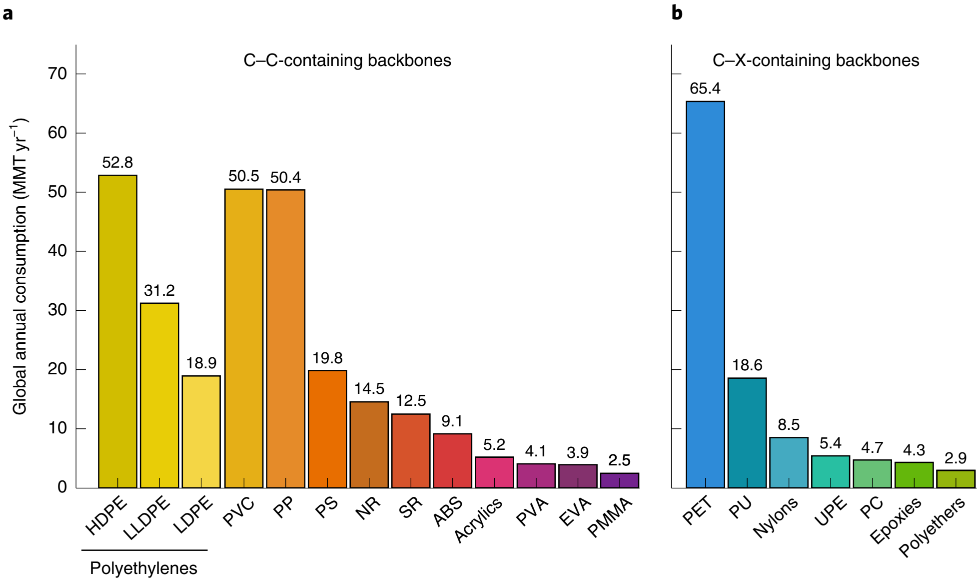

Fig. 1 | Annual global market size of commodity plastics in MMT yr^{-1}. **a**, Polymers linked by C–C bonds: polyethylenes (including HDPE, LDPE, and linear LDPE (LLDPE)), PVC, polypropylene (PP), polystyrene (PS), natural rubber (NR), synthetic rubber (SR), acrylonitrile–butadiene–styrene (ABS), acrylics, poly(vinyl acrylate) (PVA), ethylene-vinyl acetate (EVA), and poly(methyl methacrylate) (PMMA). **b**, Polymers linked by C–N and C–O bonds: PET, polyurethanes (PU), nylons, unsaturated polyesters (UPE), polycarbonate (PC), epoxies, and polyethers. All polymers included here have global annual market sizes that exceed 2.5 MMT yr^{-1} (ref. [4]).

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 both 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 (MWD), melting point (T_m), and crystallinity), as well as reaction conditions (pH, temperature, substrate loadings, stirring rate, and so on) are critical to ensure reproducibility. At this nascent stage in the plastics 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 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], among other forms. Both amorphous and biaxially oriented films are transparent compared with crystalline PET, which is often white and translucent. This morphological difference in feedstocks can result in differences in catalyst performance; thus, the substrate must be defined clearly. This definition, including substrate source, shape, and processing, should be a minimum 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 MWD, weight-averaged molecular mass (M_w), and number-averaged molecular mass (M_n), for all catalytic transformations. One should also report the relevant phase behaviour of the polymer feedstock. For interfacial catalysis, the T_g for all polymers and T_m/degree of crystallinity for semi-crystalline 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, such as antioxidants, flame retardants, or other fillers that could inhibit specific catalyst systems, should also be documented[26]. Additionally, thermogravimetric analysis 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, such as 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 or size exclusion chromatography 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 the conversion extent. Analysis of the MWD is beneficial for

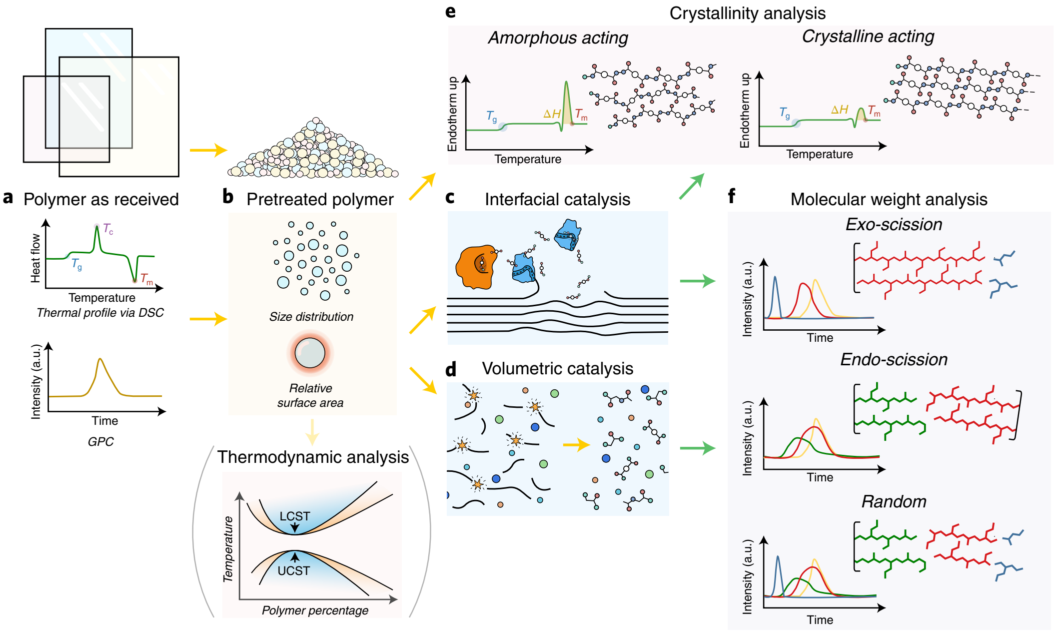

Fig. 2 | Substrate characterization flowchart. Polymer substrates should be used that are commercially and widely available for benchmarking catalyst and process performance. **a**,**b**, Substrates should be characterized as received (**a**), as modified (**b**), and after catalytic deconstruction, as changes to the thermal history and molecular weight profile will aid in elucidating catalytic mechanisms. **c**,**d**, The implemented characterization technique will depend on the catalyst mode of action (that is, interfacial (**c**) versus volumetric (**d**)). **e**, For interfacial catalysis, the polymer's thermal history should also be characterized, 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. **f**, For all catalysis experiments, MWD and chain conformation should be confirmed and will provide insights into the mechanisms of polymer cleavage. DSC, differential scanning calorimetry; GPC, gel permeation chromatography; LCST, lower critical solution temperature; UCST, upper critical solution temperature.

understanding the mode of action of a catalyst. As an example, if the MWD evolves into a multimodal distribution, a catalyst is stochastically cleaving internal bonds of the polymer chain (endo-acting); however, if the MWD broadens towards lower molecular weights, reducing the higher-molecular-weight chains, the reactivity will be on chain ends (exo-acting). Moreover, the MWD can reveal whether a process is reaching a plateau, and is unable to work on certain regions of a polymer, such as the regions near chain entanglements (Fig. 2). MALDI-TOF[27] is also an effective augmentation to the characterization of both 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 cross-links 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), an 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 the 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 the degree of crystallinity can demonstrate which fraction of the polymer is more susceptible to deconstruction (for example, an increase in crystallinity can imply degradation of the amorphous phase of a polymer) (Fig. 2). These thermal properties can be readily obtained via differential scanning calorimetry or alternative techniques such as dynamic mechanical analysis, rheology, and X-ray diffraction for T_g, T_m, and the 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 (that is, colour, shape, size, and so on) 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 dynamic light scattering or static light scattering, which are especially important for interfacial catalysis. Here, the wet contact angle may also be a useful tool before and after treatment as it is an accessible measurement that 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, ideal polymeric feedstocks remain complex and contain chemical additivities, including residual chemicals from synthesis, functional additives (plasticizers, flame retardants, ultraviolet stabilizers, lubricants, curing agents, biocides, antioxidants, antistatic agents, and so on), colourants (pigments and dyes),

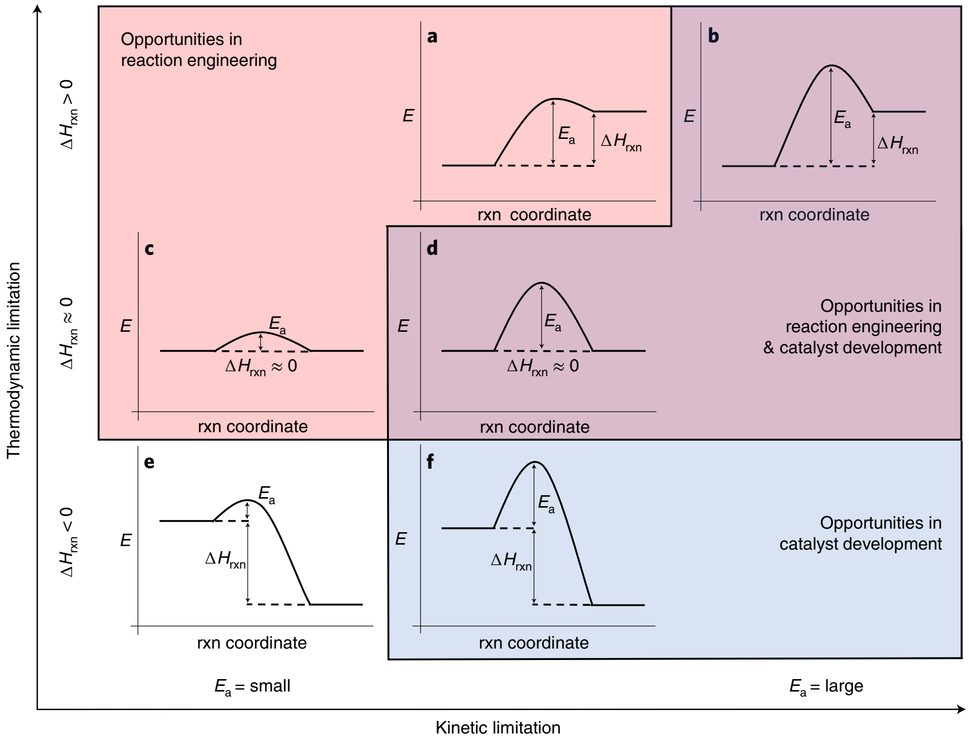

Fig. 3 | Simplified model to illustrate thermodynamic and kinetic control in polymer upcycling. a–f, Graphs of E versus reaction coordinates for $\Delta H_{\mathrm{rxn}} > 0$ (**a** and **b**), $\Delta H_{\mathrm{rxn}} = {\sim}0$ (**c** and **d**) and $\Delta H_{\mathrm{rxn}} < 0$ (**e** and **f**) and for small E_a (**a**, **c**, and **e**) versus large E_a (**b**, **d**, and **f**). Opportunities in chemical catalysis in plastics depolymerization centre around high-barrier reactions (**b**, **d**, and **f**). However, highly endothermic processes or even some near-isoenthalpic reactions with high reaction barriers will remain difficult (**b** and **d**) due to competing side reactions of lower energy; thus, these catalytic processes will require coupled reaction engineering innovations. Some processes will only require unique reactor configurations due to lower reaction barriers (**c**) or moderate barriers that cannot be significantly lowered due to highly endothermic processes (**a**); thus, these processes represent opportunities for reaction engineering innovation.

and fillers (mica, talc, calcium carbonate, and so on)[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], Fourier-transform infrared spectroscopy (FTIR) spectroscopy[32], and elemental analysis. NMR spectroscopy (one-dimensional ^{1}H and ^{13}C) is the preferred technique for the structural characterization of polymers, as it is capable of measuring the presence of co-monomers, degree of branching, and identity of organic additives. However, prevalent polymers (namely, polyethylene and polypropylene) 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 ultraviolet–visible 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 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 differential scanning calorimetry and X-ray diffraction results[34]. The additional benefit of small-angle X-ray scattering is that for volumetric studies, it can elucidate whether 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 thermogravimetric analysis[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 now describe several key challenges when selecting desired reaction pathways for conversion technologies. Chemical recycling of plastics will require the design of both catalysts and reactor configurations. From a reaction chemistry perspective, plastics deconstruction and upcycling transformations can be viewed in light of both thermodynamics and kinetics, as illustrated in Fig. 3. This simplified, qualitative model is not intended to represent exact reaction energetics and will not focus on all pertinent thermodynamic properties needed for scale-up, but rather offers a framework to discuss opportunities in designing 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 favourable ($\Delta G_{\mathrm{rxn}} < 0$). 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 a reaction over all temperatures, whereas the ΔH_{rxn} varies widely depending on target chemistry. In this simplified model, catalysts lower the E_a for a given polymer and target chemistry, while the ΔH_{rxn} remains constant (Fig. 3b versus Fig. 3a, Fig. 3d versus Fig. 3c, or Fig. 3f versus Fig. 3e). In other words, 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 alternative mechanism to the product. Similarly, the thermodynamic favourability of the depolymerization of a polymer can be tuned by selecting lower-energy-state products (Fig. 3a versus Fig. 3d versus Fig. 3f), thus making ΔH_{rxn} more exothermic (and ΔG_{rxn} more exergonic).

With fixed reactants and products, a universal means to favour depolymerization is to increase the 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 favoured to depolymerize. However, simply because depolymerization is thermodynamically favoured 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, reactor selection and engineering can manipulate the favourability of a reaction (that is, the thermodynamic limitation), while catalysts can enable targeted reactions to occur at appreciable rates (that is, the kinetic limitation).

There will be certain polymer transformations where a catalyst is not needed (Fig. 3a,c), thus requiring only reaction engineering innovations. For example, although poly(methyl methacrylate) depolymerization to methyl methacrylate is endothermic, yields of up to 97% have been reported without a catalyst; this chemistry mirrors the profile in Fig. 3a (see also ref. [36]). Other processes will require new catalysts, likely enabled by relatively simple reactor configurations, to address heat and mass transfer limitations (see Fig. 3f). As an example, radical-based oxidation of polyethylene and polystyrene 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 Fig. 3 will probably be the most challenging to realize—namely, those that require simultaneous catalyst and reaction engineering innovations (Fig. 3b,d). Successful examples of such processes to date include the endothermic catalytic cracking of polyethylene and polyethylene/polypropylene mixtures to benzene, toluene, and xylenes (BTX), which requires acidic zeolite catalysts (for example, Ga-ZSM-5 or Zn-ZSM-11) and unique reactor configurations to obtain high yields (Fig. 3b)[38,39]. Similarly, examples of isoenthalpic transformations, such as the catalytic depolymerization of polyacetals with homogenous acids and biomass-derived diols to cyclic acetals[40] or the depolymerization of PET using nitrogen-based organocatalysts[41], allow for a high-barrier scenario such as that shown in Fig. 3d to become a lower-barrier process such as that shown in Fig. 3c. 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 that the ideal combination of catalyst and process are selected to favour the desired reaction pathways with a low reaction barrier, while preventing undesired pathways from becoming favourable or having appreciable rates.

Reaction 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 (for example, 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 its own distribution of products[42]. Mixtures of polymer feedstocks exaggerate this selectivity issue, in part to due to differing depolymerization mechanisms. Polyethylene and polypropylene, for example, mainly thermally decompose by random chain scission; polystyrene decomposes through a mixture of random chain scission and zipper scission; PVC degrades via branched-chain scission; and PET and polycarbonate break down through C–O and 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 the depolymerization of polyethylene, polypropylene, and polystyrene have been reported across incredibly broad ranges of 163–303, 83–285, and 83–323 kJ mol^{-1}, 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 a reaction can impede selective transformations. Relative to common substrates for solution or gas-phase reactions, 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 the surface area to the volumetric concentration of available bonds, are critical to consider.

Counterintuitively, the complex phase phenomena of certain polymer/solvent combinations can result in temperature-, concentration- and/or molecular weight-dependent demixing behaviour, 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 reaction engineering approaches have already been developed—in both waste plastics and biomass conversion—to overcome this scaling challenge. For example, various non-catalytic reaction engineering strategies, such as co-reactant addition (for example, steam), the use of microwave-assisted pyrolysis, the use of supercritical solvents, solubilization of the polymer in oil (for example, vacuum gas oil) or solvent (for example, tetralin, decalin or 1-methylnaphalene) before pyrolysis, or dilution of the solid substrate in a non-reactive heat transfer agent (for example, 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. Reaction media, including supercritical fluids[48], ionic liquids[49–54], and deep eutectic solvents (DESs)[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 behaviour 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, photocatalytic reactor systems may be inhibited by dyes and light stabilizers, and enzymes can be deactivated through active site inhibition, degradation induced by additives, or non-productive binding to non-target components. Two primary approaches can be used to overcome the challenges resulting from additives—either via the development of robust catalysts and processes that are insensitive to additives, or using 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 and fractionation in biomass conversion, enabling comparisons from process concepts and lessons learned through decades of study[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]. Recent 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 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 polypropylene, 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 the synthesis of virgin materials, must be clear. Process, economic, life-cycle, and supply-chain modelling tools are thus critical in the development of realistic, scalable systems for catalytic plastics 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 to 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 12 principles of green chemistry[61]. One accessible process metric used to assess the environmental impact of a process is the environmental 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 (for example, 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. Although 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.[65] reported an electrochemical method to perform pyrolysis coupled with electrolysis, generating C1–C5 products from polypropylene under milder conditions than in conventional pyrolysis. Notably, the thermal energy inputs were all provided by solar thermal energy, substantially reducing the energetic cost of the process.

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 ultraviolet 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 ultraviolet light[68]. One challenge in the use of TiO_2, however, is the tendency to over-oxidize the substrates, generating CO_2. Care must be taken to optimize the process to favour 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) into H_2 and small organic molecules, including acetate and formate[69]. Although 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 for combining advances in catalysis with advances in reaction engineering that has been explored 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 and lower temperature, and with greater selectivity. For example, microwave-assisted catalysis enabled complete glycolytic PET depolymerization in 5 min under conditions that were otherwise the same, instead of 4 h using 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 using dimethylaminopyridine as a catalyst and acetic anhydride as a stoichiometric reagent. These reactions proceeded with up to 74% yield in 15 min. The isolated monomers could then be transformed into 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, although 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 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 (that is, homogeneous, heterogeneous, or 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 behaviour. 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 re-use[80]. Creative strategies 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 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 centre with the ligand[83]. Certain catalysts, such as those that are highly unstable in the presence of trace water, sulfides, and so on 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, and 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 the 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 polyethylene, 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 with polymers linked by heteroatoms (as discussed below), *sp*^{3}-hybridized C–C-linked polymers, exemplified by polyethylene, polypropylene, and polystyrene, present 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 has emerged as a central need. 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, olefin intermediate, or alkyl radical) that can ultimately enable C–C cleavage. Although 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: increasing the robustness and reusability of highly selective catalysts such as organometallic catalysts for C–C cleavage; and 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 polyethylene, polypropylene, polystyrene, and mixtures thereof[42,45,90–93]. Catalytic cracking utilizes highly acidic zeolites such as ZSM-5, H-Y, H-β, AL-SMA-15, HUSY, and many others to abstract a hydride from the polymer backbone, resulting in a reactive carbocation intermediate with mixtures of olefins/paraffins or liquid aromatics as products[94]. By tuning the catalyst acid strength, acid type (that is, the ratio of Lewis acids to Brønsted acids), and process configurations, mixtures of olefins/paraffins or aromatics (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 unfavourable products requires higher reaction temperatures, precise process configurations, and catalysts to provide for maximum selectivity and yield of products. Although further process analysis is needed, we suspect that olefin production is probably not a viable long-term strategy from polyolefins due to energy demands, competition with less expensive feedstocks such as 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 potential advantage of this process is the ability for such an approach to work on a mixture of polyolefin feedstocks.

To make cracking more thermodynamically favourable 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 bifunctional hydrocracking catalysts. These bifunctional catalytic systems, operating under high hydrogen pressures, provide a means to crack then hydrogenate polyethylene[96–101], polypropylene[101], and polystyrene[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]. A series of catalysts, including carbon-supported ruthenium, porous silica-coated supported platinum, and a complex atomic layer deposition platinum on a perovskite support, have all been leveraged as hydrogenolysis catalysts capable of converting polyethylene into alkane mixtures in a solvent-free system[103–105]. 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[106]. 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 the inspiration of coordination polymerization catalysts such as Ziegler–Natta, Phillips, or metallocene catalysts[107,108]. Additional opportunities exist to apply certain depolymerization strategies such as hydrogenolysis to other polymer feedstocks, including heteroatom-linked polymers. For example, molecular hydrogenolysis catalysts have been leveraged for depolymerization of mixed chain-growth polymers[109,110], 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 (Fig. 4)[111], 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 polyethylene, 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 such as 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 polyethylene at high conversion to low-molecular-weight alkanes at 175 °C in 4 d[88], while a heterogeneous version of this system was able to provide a 73% reduction in the molecular weight of a HDPE feedstock at 200 °C in only 15 h[111]. 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 of pulling metabolites through a highly endothermic reaction step by utilizing a series of coupled reactions. Biological metabolism could be a source of inspiration for tandem or cascade chemistries when dealing with thermodynamically unfavourable reaction steps. One excellent example of such a tandem chemistry is the combination of aromatization and hydrogenolysis using a supported platinum catalyst to yield aromatic surfactants from polyethylene at relatively mild operating conditions[112].

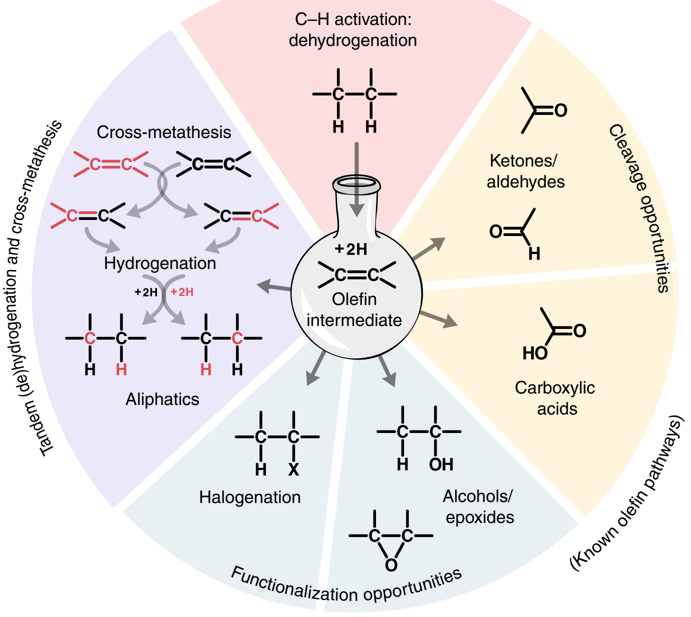

Fig. 4 | Opportunities in polyolefin upcycling via the olefin-intermediate process. The sp^3 C–C backbone of polyolefins provides a significant challenge for low-temperature selective deconstruction. The olefin-intermediate process[111] can be utilized as a means to activate polyolefins at modest temperatures, but this tandem chemistry requires a reaction capable of being paired with equilibrium-limited dehydrogenation 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 polyethylene to alkanes using dehydrogenation and cross-metathesis[88,111]. Considering the well-known chemistries available for olefin cleavage and functionalization, this process will probably play an important role in the deconstruction and upcycling of polyolefins and other C-C-linked polymers. In addition, such C=C activating chemistries can be applied directly to the olefinic backbone of elastomers as well.

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 (although the work by Zhang et al.[112] is exceptionally similar in nature to an olefin-intermediate process) (Fig. 4). We predict that there are many transformations that are possible with an olefin intermediate. The challenge in such a system is twofold: (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 catalyst 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, such as catalytic cracking, oxidation, hydrogenolysis, metathesis, and more[113,114]. For example, metathesis catalysts have been utilized in the depolymerization of polybutadiene to various olefinic products such as cyclic macrocycles, smaller rings (cyclopentene/cyclohexene), or even terminal olefins[115].

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 such as polyethylene, polypropylene, polystyrene, 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 that 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 such as nitrogen oxides and bromine compounds have been utilized to begin this reaction path[37,75,116]. 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[117]. Non-selective catalysts such as nitrogen oxides can produce nitrated products[37]; thus, more selective catalysts are needed in this field. Through catalyst design and reaction engineering, waste plastics could potentially be selectivity oxidized to valuable products at relatively mild operating conditions.

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[118–122]. 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, probably making it a challenge to directly adapt them to depolymerization, which requires catalysts that are cheap, recoverable, and stable. For instance, many metal-catalysed C–C cleavage strategies outlined in the literature rely on the energy released from breaking strained rings, or on heteroatoms directing groups to bind to the metal centre 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- and C–N-linked polymers

Depolymerization reactions for polymers that contain heteroatom backbones linked by C–O and C–N bonds (for example, PET, polyamides, and polyurethanes) typically exhibit relatively low reaction barriers and near-neutral reaction free energies (Fig. 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 Fig. 5.

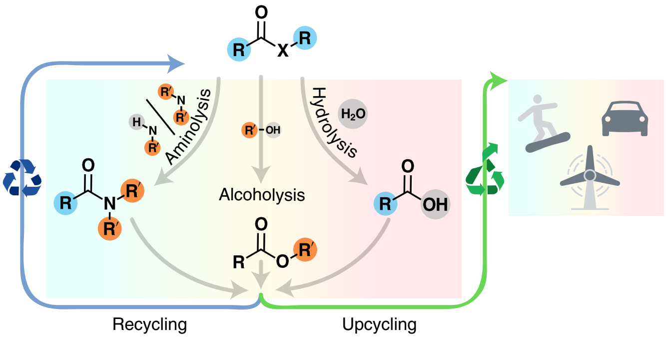

Fig. 5 | Depolymerization of C–N- and C–O-linked polymers for closed-loop recycling or open-loop upcycling. These methods are commonly achieved via the use of a nucleophile, which reacts with the carbonyl and generates cleaved products. Blue spheres represent the polymer backbone, whereas orange spheres represent the small-molecule nucleophile. Deconstruction of C–O-/C–N-backbone polymers presents a more readily accessible path to regenerate monomer species (shown in the blue pathway as recycling) than in C–C-backbone polymers, as the monomers are often more well-defined and stable. Opportunities also exist for developing new pathways to value-added products separate from a return to monomeric species (shown in the green pathway as upcycling). Because of its relative ease, research into depolymerization of these monomers has focused on recycling to monomer species, but creative approaches to developing strategies for simultaneous depolymerization and functionalization to create new upcycled materials with unique properties represent an exciting area of investigation.

Solvolysis is a primary means to achieve depolymerization of heteroatom-linked plastics. It employs nucleophilic solvents, which 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 reviewed extensively[123]. Although many strategies have been explored in this space, opportunities in solvolytic depolymerization continue to emerge. For example, ionic liquids have been used to facilitate depolymerization in polymers such as nylon 6 (ref. [49]), nylon 6,6 (ref. [50]), PET[51], polycarbonate[52], fibre-reinforced plastics[53], and even rubber tyres[54]. Ionic liquids exhibit a remarkable range of tunable properties, including good solubilization capacity for polymers, and can simultaneously catalyse their depolymerization. A recent example employed tetraalkylammonium ionic liquids to stabilize a zinc oxide catalyst, enabling solvolytic depolymerization of polycarbonate to monomeric products with glycerol[124]. Despite their benefits, however, the cost of ionic liquids necessitates recovery of the solvent for re-use, which remains an opportunity for innovation. DESs are similar to ionic liquids, but exhibit hydrogen-bonding interactions in addition to ionic interactions, and have the advantage of being less costly and generally less toxic than ionic liquids[125]. A recent study demonstrated significant enhancement in the glycolysis of PET with urea/metal DES relative to ionic liquids. The authors showed that the increased activity results from the presence of hydrogen bonding between the DES and ethylene glycol, demonstrating simultaneous solubilization and catalytic enhancement capabilities[126].

Significant enhancements in the activity of solvolytic depolymerization can be achieved through the use of catalysts. Catalytic strategies to depolymerize chain-growth polymers have also been reviewed[7,127]. 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, although several other metals have been explored[128]. Interesting hybrid acid–base pair catalytic systems have been developed, including one study that showed high activity for PET depolymerization using the Lewis acid zinc acetate to activate the carbonyl and various organic amine bases to activate the nucleophile, resulting in synergistic enhancement of the depolymerization rate[129]. Another promising strategy utilizes differing organometallic ruthenium complexes capable of reductively depolymerizing a variety of polymers, including PET[109], polycarbonate[109], polylactic acid[109], polyamides[130], or polyurethanes[131], with certain systems even maintaining performance in the presence of additives and colourants[109]. Depolymerization of heteroatom-linked polymers continues to be a very active research area with consistent catalyst innovations.

Certain plastics with heteroatoms in their backbones are unsuitable for deconstruction 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[132,133]. 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 (for example, PET or polyurethanes) than for C–C backbone plastics (for example, polyethylene or polypropylene), many current depolymerization approaches for heteroatom-linked polymers result in 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 glassfibre-reinforced resins[134].

Opportunities 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 polymers in a one-pot depolymerization/condensation reaction, leading to the direct synthesis of polyester materials[135]. 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[136,137]. Such one-pot processes are highly desired throughout the chemical disciplines, as they eliminate costly separations[138]. 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 reaction engineering, rather than solely via breakthroughs in fundamental science, especially compared with depolymerization of C–C-linked polymer systems. Creative strategies to merge highly active catalytic systems with innovative reactive systems, 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 the deconstruction of polymers

In addition to chemical catalysts, biocatalysts (enzymes and microbes) offer the potential to contribute to energy-efficient polymer deconstruction and upcycling[139]. Successful biological catalysts typically target enthalpically neutral or modestly exothermic processes, where the reaction barrier can be lowered (Fig. 3d,c). Biological plastics deconstruction will probably 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, enzymes secreted from whole-cell biocatalysts, or displays on cell surfaces[140,141]. 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 probably occur primarily in water or in aqueous mixtures with other solvents. 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[140,142]. 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[143]. Instead, it has conceptual parallels to heterogeneous catalysis, where reactants and products exist in a different phase than the catalyst. Indeed, recent approaches to kinetic treatments of interfacial biocatalysis have leveraged well-known kinetics concepts from the heterogeneous catalysis literature[144]. In particular, Westh et al. derived formalisms and developed accessible assays for enzymes acting on polymers that enable the determination of steady-state rates while incorporating key parameters including surface-site inhibition[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 probably 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.[156] reporting the discovery of a bacterium that secretes a two-enzyme system (PETase and MHETase) for PET hydrolysis inspired many entrants into this field and, as a result, structural, kinetics, engineering, and evolution studies are now rapidly emerging[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 the 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, for example, PET hydrolases. Moreover, high-solids loading will probably 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[164,165]. 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 the addition of stabilizing glycans through eukaryotic expression[171]. A recent example was reported by Tournier et al.[168] wherein a cutinase was engineered to deconstruct micronized PET to >90% depolymerization extent in ~10 h at an enzyme loading of 1 mg leaf compost cutinase per gram of PET substrate. 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 past 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 probably 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 versus (semi-)aromatic polyesters; thus, questions in terms of the natural substrates remain to be addressed. While PET hydrolases 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, whether PET hydrolases act on polymer chains in an exo- or endo-acting fashion, and whether 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 the 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 probably synergistic. Most importantly, for a fundamental understanding of enzymatic biocatalysis for plastics upcycling, the relationship between the polymer properties (for example, crystallinity, molecular weight, surface area, and so on) and the enzyme performance represents the ultimate objective in terms of harnessing enzymes for the deconstruction of synthetic polymers. Even for PET, little work has been done to date to correlate detailed polymer properties to enzyme performance (see below).

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 bonds represent 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]. Polyurethanes are a common target for the environmental microbiology community and, at least for polyurethanes that employ ester bonds, esterases will probably find utility, but cross-linking considerations in polyurethane thermosets will be critical to consider as well[178]. From an evolutionary perspective, in contrast with biopolymers such as 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 with the chemical catalysis sections above (Fig. 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 probably 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 polyethylene degradation[179]. Oxidoreductase action on C–C-bonded polymers has been reported as an example of a biological catalyst lowering the barrier for a highly exothermic reaction (Fig. 3f,e), 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 whether 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[181,182]. Especially when plastics depolymerization yields a mixture of monomers and contaminants (for example, from polyurethanes or mixed plastic waste streams), microbial catalysis provides a promising alternative by funnelling these plastics-derived intermediates into central metabolism to produce value-added chemicals. This concept of biological funnelling is well established in the conversion of lignin-derived monomers and likely to be useful for plastics upcycling as well[183]. This same concept could apply to the development of synergistic microbial consortia that are specialists at consuming particular substrates[184]. Alternatively, isolated plastic monomers can also be transformed into functionalized derivatives with retention of more complex chemical structures[185].

In essence, biological plastics upcycling requires three catalysis steps: (1) production of the depolymerization enzyme (or catalyst); (2) deconstruction of the polymer; and (3) conversion of the plastic hydrolysate to the final product. Analogous to biomass conversion, several process options are available (Fig. 6). Separate depolymerization and conversion (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 probably play a prominent role[186,187]. When depolymerase enzymes are secreted by a microbe (or a consortium of microbes)

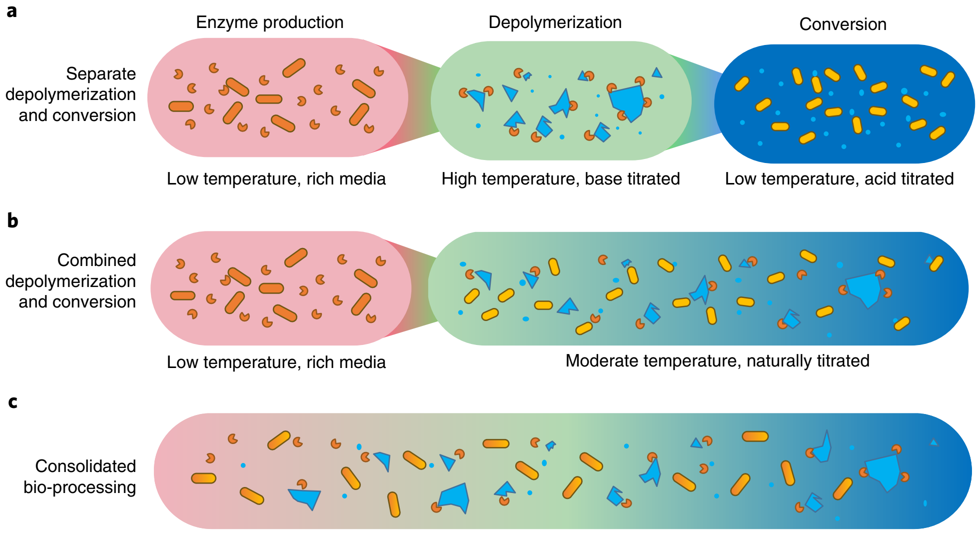

Fig. 6 | Opportunities in biological processes for deconstruction and upcycling of polymers. The conversion of plastics can be achieved through multiple processing strategies in which chemistry and biology can either be decoupled or coupled. **a**, The separate development of enzyme production, depolymerization, and conversion enables each biocatalyst to operate at its optimum temperature, pH, and nutrient regimen, but will potentially require both acid and base titration. **b**, The combination of depolymerization and conversion operations reduces the severity of titration and may prevent the accumulation of inhibiting intermediates. **c**, The consolidated bio-processing (CBP) model can be further extended through the cellular production of depolymerization enzymes, enabling a one-pot process. Despite these advantages of CBP, further development will be required to operate efficiently in physical constraints amenable to all processes.

that also harbours catabolic capacity for the released deconstruction products, this one-pot biological processing is termed consolidated bio-processing (CBP) in the biomass conversion field[188]. Parallels to CBP have been discovered in natural microbes, most prominently by Yoshida et al.[156], 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 carbon and energy sources. 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 (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 from the global biochemistry, metabolic engineering, and synthetic biology communities[189,190]. Specifically for plastics upcycling in CBP-like concepts (Fig. 6), microbes must be capable of enzyme expression and secretion at concentrations sufficient for effective extracellular depolymerization. In addition, if deconstruction and upcycling are 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 (for example, 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[191]. Certainly, much can be learned from the industrial composting of biodegradable polymers such as poly(lactic acid) and polycaprolactone.

For microbial uptake and biological upcycling of plastics-derived intermediates (which can be obtained from either biological or chemical catalysis), discovery and engineering of transporters and catabolic enzymes will probably 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[192]. Polymers such as polyurethanes, which contain more complex monomers, will require additional pathway discovery efforts[193]. 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 plastic-derived 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 engineered microbes 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[194]. Some polyurethane-derived diamines such as methylenedianiline and toluene diamine are extremely toxic[195]. Also, many additives will inhibit microbes and enzymes, including antimicrobials added to avoid the decay of, for example, polyurethane foams. For some of these high-value/high-toxicity monomers, efficient extraction processes will need to be developed to recover them before microbial conversion[57,184]. Amelioration of toxic effects from plastic-derived chemicals can also potentially be gained via solvent-tolerant strains[196].

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.

Conclusions

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, offers 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 Review, we highlight key challenges and opportunities to realize catalysis-enabled chemical circularity for today's polymers. Given the range of polymers used, this will probably require a battery of catalysis-driven technology options. Moreover, opportunities exist to use and combine biological and chemical catalysis to generate commodity chemicals and alternative materials, ideally at lower-energy inputs, greenhouse gas emissions, and costs than virgin polymer manufacturing[4]. These efforts could be synergistic with the development of alternative materials with better end-of-life functionalities that increase their amenability to catalytic deconstruction. Through the 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 waste problem.

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Author contributions

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Competing interests

The authors declare no competing interests.

Additional information

Correspondence should be addressed to G.T.B.

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