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Upcycling commodity polymers: critical advances and future opportunities

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Abstract

The vast majority of commodity plastics do not degrade and permanently pollute the environment. Currently, less than 20% of post-consumer plastic waste in developed countries is recycled, predominately for energy recovery or repurposing as lower-value materials by mechanical recycling. Chemical recycling offers an opportunity to revert plastics back to monomers for repolymerization to virgin materials without altering the properties of the material or the economic value of the polymer. For plastic waste that is either cost-prohibitive or infeasible to mechanically or chemically recycle, the nascent field of chemical upcycling of plastics promises to use chemical or engineering approaches to place plastic waste at the beginning of a new value chain. Here we highlight state-of-the-art methods for upcycling plastic waste into value-added performance materials, fine chemicals, and specialty polymers. By identifying common conceptual approaches, we critically discuss how the advantages and challenges of each approach contribute to the goal of realizing a sustainable plastics economy.

Introduction

Plastics are the largest synthetic consumer product in the world, with an annual production that reached 359 million metric tons in 2018.[1] Plastics are the material-of-choice for applications as diverse as packaging, construction materials, electronics, biomedical devices, and energy storage because of their light weight, low cost, easy processability, and diverse properties. Despite these considerable advantages, the end-of-life management of plastic waste has not advanced at a rate proportionate to their production; the resulting accumulation of plastic waste that does not degrade represents a Faustian bargain which negatively affects the environment. Developing strategies to reduce, reuse, and recycle plastic waste is therefore a pressing scientific and societal challenge, not only to decrease the amount of discarded plastics contaminating the environment, but also to reduce the greenhouse gas emissions caused by the manufacturing of virgin plastics.

The majority of discarded plastics is landfilled or incinerated. Incineration partially recovers the energy stored in plastic waste in the short-term but does not create economic value or mitigate resource depletion of the materials in the long-term, while releasing carbon dioxide and other harmful gasses that further contribute to climate change.[2–4] Large scale recycling strategies to repurpose plastics have been implemented over the past 30 years in western countries, but even today only 32.5% of the collected plastics from municipal solid waste (MSW) in Europe (2019)[1] and 8.7% in the United States (2018)[5] is recycled. According to the World Bank, these numbers are even worse in Africa and South Asia where only 65% and 46 % of the MSW, respectively, are collected, with recycling rates below 5%.[6] The plastics currently recycled are almost universally mechanically recombined and limitations in sorting techniques means that additives, contaminants, mis-sorted polymers or multilayer products found in plastic waste streams lead to significant deterioration of properties during and after reprocessing. Therefore, mechanical recycling of post-consumer plastics too often leads to what is called *downcycled* materials that demonstrate diminished quality and/or utility. Additional purification, such as the *Creasolv*© or *PureCycle*© processes, can aid the realization of virgin grade recycled materials but requires solvent-based extractions and adds steps to the industrial processes. Chemical recycling is emerging as an alternative to mechanical compounding, where discarded plastics are transformed into high purity monomers for the repolymerization to the same material. Indeed, solvolysis,[7] enzymatic,[8] or catalytic recycling[9] are successful industrial processes for some plastics,[10] and chemical recycling is currently being commercialized by companies such as Eastman[11], Ioniqa[12] or Loop Industries[13]. However, using existing technologies, only a small subset of commodity plastics could be chemically recycled in an energy-efficient and cost-effective manner.

The challenges inherent to both mechanical and chemical recycling arise from the technical-grade products that result from these processes being more expensive or more energy intensive than homologues synthesized from petroleum, making broader uptake and implementation unfavorable. An alternative approach is to consider plastic waste as a chemical feedstock, thus positioning it at the beginning of the value chain instead of at its end. Under such a framework, post-consumer plastic waste becomes a low cost and abundant starting material for the synthesis of materials or molecules. Finding solutions for transforming post-consumer plastics into materials with an added economic value remains a grand challenge with complex and interrelated chemical, economic, and environmental questions to answer. New concepts are emerging, which that target high value markets in the circular economy for plastics, sometimes referred to as *upcycling*.

Value considerations: defining the upcycling of plastic waste

The term *upcycling* was first employed by Gunter Pauli in 1999 in the book of the same name to refer to any process that transforms byproducts, undesired, unwanted or waste products into new materials of higher value.[14] While the "waste products" Pauli described did not explicitly refer to discarded plastics, the current imbalance between increasing production and limited end-of-life solutions makes plastic waste a compelling target for upcycling. Within the plastic field, the concept *upcycling* can be interpreted as "the use of plastic waste, postindustrial or postconsumer, as a feedstock for the synthesis of value-added products, being polymers, molecules, or materials" and considered complementary to chemical and mechanical recycling. (**Figure 1**)

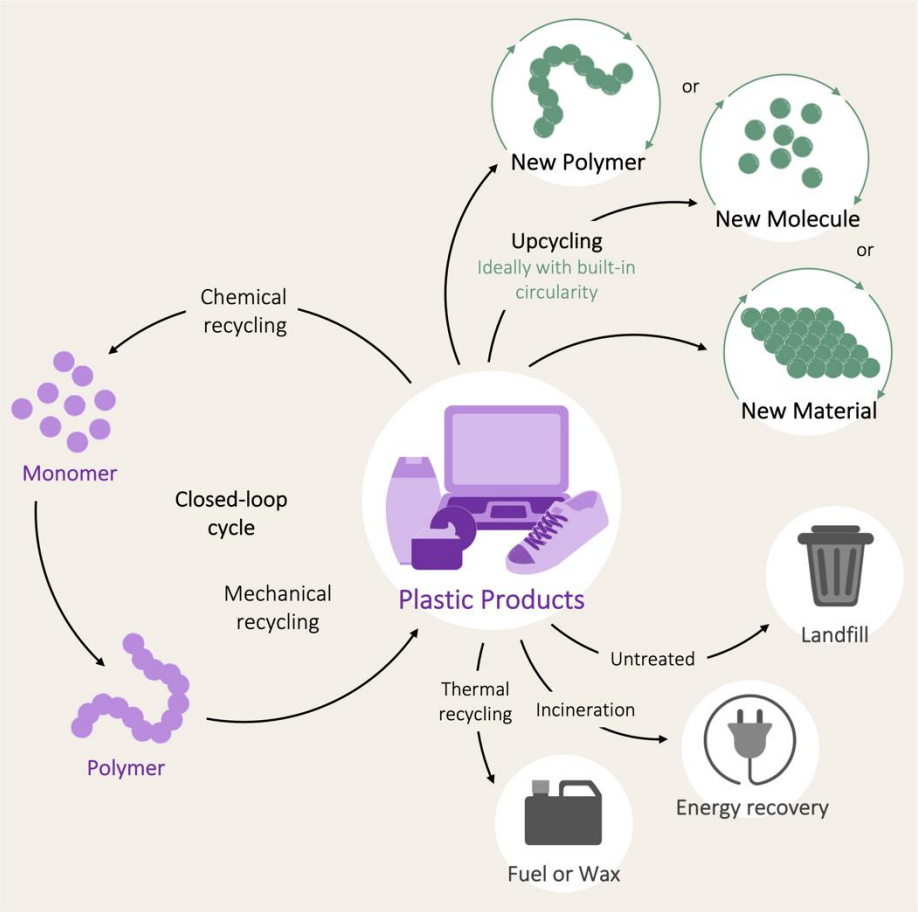

***Figure 1**. Positioning the concept of upcycling in the life cycle chain of plastics.*

Upcycling methodologies seek to repurpose waste plastics into products with increased 'value'. The concept of 'value' in a sustainable plastics economy is broader than economic value, but the many external, personal, and sociological considerations that contribute to 'value' encourage a more holistic, but difficult to quantify, approach to plastic waste solutions Therefore, in this review we focus on the concept of sustainable substitution. Substitutability means that the upcycled product needs a degree of functional equivalence with alternative products for a specific end use, without precluding the generation of alternative products with unknown potential. A significant challenge for mechanical recycling, for example, is that application areas are limited for recyclates and current markets cannot absorb more low value materials, which results in low prices.[15] The limited substitution potential of mechanical

recyclates, therefore, diminished the perception of value. Vadenbo *et al.* introduced important factors for substitutability including technical properties, user perceived value, and market size, among others.[16] Following this framework, a substituted product should preferably outperform the product derived from primary resources when considering environmental and/or economic criteria. If the upcycled product is capable of sustainable substitution, there will be an increased perception of value because the product is functionally equivalent but is derived from a waste stream. Quantifying sustainable substitutability requires considering the manufacturing of the substituted material in terms of energy efficiency and environmental impact compared to the material that it is replacing, as well as the potential of the upcycled material to be recycled and/or upcycled.

Guiding principles: Environmentally friendly, Economically attractive, Industrially relevant

According to this definition of 'value', we believe a polymer upcycling approach should ideally be economically beneficial, environmentally benign, and industrially relevant towards sustainable substitution. Efforts made towards upcycling technologies will be critically described considering these three aspects of the overall methodology. (**Figure 2**)

***Figure 2**. Guiding principles for the design of an optimal upcycling methodology*

First, the upcycling approach employed should observe as much as possible the 12 principles of green chemistry and green engineering put forward by Anastas, Warner and Zimmerman respectively in 1998[17] and 2003[18]. Particularly, the atom efficiency of the reaction as well as the final isolated yield should be maximized while the use or production of toxic compounds should be limited. The impact of the upcycling method on the environment should be minimized, and ideally, Life Cycle Assessment (LCA) or similar holistic assessments should be used to quantify the overall environmental impact of the process – which could be compared against current plastics manufacturing to calculate the positive impact on the supply chain.[19] LCA covers a wide range of impact categories, usually with a focus in the circular economy for plastics towards greenhouse gas (GHG) emissions and resource depletion, including petrochemical resources and water demand. The entire cost incurred by the upcycling

technology (collection, sorting, eventual purification, deconstruction) should be balanced by the value of the final upcycled product and should demonstrate an economic advantage compared with the same product obtained by other means. The targeted product (material, polymer, or molecule) produced as a result of the upcycling procedure should be a sustainable substitute for a targeted application or demonstrate performance-advantaged properties. Finally, the methodology should employ technologies and reactions that could be scaled-up for implementation at an industrial level.

Our aim in this review is to highlight a selection of the latest innovations in upcycling concepts and methods. Advances in chemical recycling have been reviewed elsewhere.[20–25] Upcycling approaches will be discussed by the type of product obtained following the three aforementioned categories (polymer, molecule, material). A critical analysis of the different upcycled processes will be provided where the actual added 'value' or sustainable substitution potential will be examined according to the definition and judgment criteria of upcycling outlined above. The ultimate goal of this Review is to communicate complementary approaches to mechanical and chemical recycling of plastic waste and to provide a guide to academic and industrial research on chemical upcycling approaches. More than options to manage plastic waste and solve the problem of their end-of-life, this review attempts to propose uncommon routes to reveal the new feedstock potential of plastic waste.

1. Polymer-to-polymer

Polymer-to-polymer upcycling results in the direct transformation of discarded plastics into a compositionally distinct polymer that is more economically valuable than the parent material. The use of some plastic waste to design next-generation materials could reduce our current reliance on petrochemical resources to produce these plastics, thus improving the sustainability of their production. Two approaches stand out in this paradigm: (1) the transformation of plastic waste into a new polymer through the synthesis of innovative building blocks and, (2) the post-functionalization of plastic waste to obtain new materials with enhanced properties.

Depolymerization–Repolymerization

A first strategy for repurposing discarded plastics into a polymer of higher value consists of its depolymerization into differentiated building blocks for their subsequent polymerization into a different material. As opposed to polyolefins, most of the oxygen or nitrogen-containing polymers possess reactive functional groups that provide opportunities for targeted deconstruction and subsequent reconstruction into new plastics.

The most well-studied example for depolymerization is reaction of the ester groups of poly(ethylene terephthalate) PET, which provide an intrinsic retrosynthetic handle for transesterification into oligomeric fragments prior to repolymerization into different polymers, including block copolyesters, polyurethane (PU) coatings, or polyisocyanurate foams.[26–28] More recently, PET has also been repurposed into fiberglass reinforced plastic (FRP) through depolymerization and subsequent polymerization with bio-derived esters and acids.[29] (**Figure 3A**) Combining bio-sourced monomers and recycled PET, the optimized material outperforms the comparative standard petroleum-based FRP in terms of mechanical properties (storage moduli), while consuming less energy and emitting less GHGs. Moreover, the supply chain energy calculated using the material flow industry (MFI) tool demonstrated that the described technology performed more efficiently than the conventional mechanical

recycling of PET and traditional FRP synthesis, 10 Megajoule (MJ)/US$, compared to 40 and 22 MJ/US$, respectively. This strategy is a very good example of a sustainable substitution in which economically added value can be created whilst producing a material with improved mechanical properties via a less energetically demanding pathway.

Bisphenol A-based polycarbonate (BPA-PC) is another widely produced thermoplastic (>6 million tons in 2019) that has been investigated for depolymerization–repolymerization repurposing.[30] An elegant strategy demonstrated the transformation of discarded BPA-PC into poly(aryl ether sulfone) (PSU), a high-performance polymer commonly used for reverse osmosis water purification membranes and medical equipment.[31] In a one-step reaction, the BPA obtained from depolymerization of BPA-PC reacts with a sulfonated BPA derivative to obtain PSU. The absence of side reactions and quantitative conversion theoretically make this methodology a better candidate than the conventional polycondensation leading to PSU, but the molecular weights achieved were 5 times lower than conventional polymerization. In a similar fashion, bis(hydroxyethyl ether) derived from depolymerized BPA-PC was repolymerized with a naturally occurring bicyclic diol in the presence of diphenyl carbonate to obtain a PC with controlled mechanical properties.[32] (**Figure 3B**) Indeed, depending on the BPA-PC/bicyclic diol ratio, the PC obtained exhibits various mechanical behaviors, from ductile to brittle. However, if these polymers are aiming to replace petroleum-based BPA-PC, no clear directions are specified in terms of application targeted or destination market for such material.

While numerous studies on BPA-PC depolymerization reclaim the major component of BPA-PC, *i.e.,* the BPA unit, the carbonate moiety (C=O) is lost during the depolymerization process. In order to capitalize on the CO present in BPA-PC, a recent communication demonstrated that depolymerizing BPA-PC in the presence of 1,3-propanediol and 1,5-pentanediol enables the upcycling of C=O into linear carbonate-containing diols together with BPA.[33] These monomers have been repolymerized into aliphatic PCs which show promise as solid electrolytes for energy storage applications. Nevertheless, the moderate yields and the need for flash column chromatography to purify the monomers diminish the potential of industrialization. Apart from using alcohols, the aminolysis of BPA-PC leads to carbamates while maintaining the C=O functionality and the BPA moiety. In an atom economic process, BPA-PC oligomers have been prepared using different diamines for their incorporation into PUs.[34] Indeed, the importance of depolymerization conditions including solvent selection or polymer/amine ratio on the selective transformation of BPA-PC into carbamates was thoroughly investigated to reduce undesirable side reactions and to increase reaction yields and avoid energy-intensive purification processes. It should also be noted that although the depolymerization of BPA-PC is a well-studied topic, its implementation at larger scale would require the deployment of structures to appropriately collect and sort BPA-PC wastes, which is not currently the case in Europe or the US.

Another option to upcycle plastic waste into new polymers is to leverage the unique ability of enzymes and microbes to mediate depolymerization and subsequent repolymerization processes, as recently reviewed elsewhere.[35] In line with this, bio-mediated transformations of discarded PET,[36–38] polystyrene (PS),[39] and mixed plastic waste,[82] into polyhydroxyalkanoates (PHAs) have been reported. PHAs are particularly appealing on account of their facile biodegradation for sustainable packaging materials.

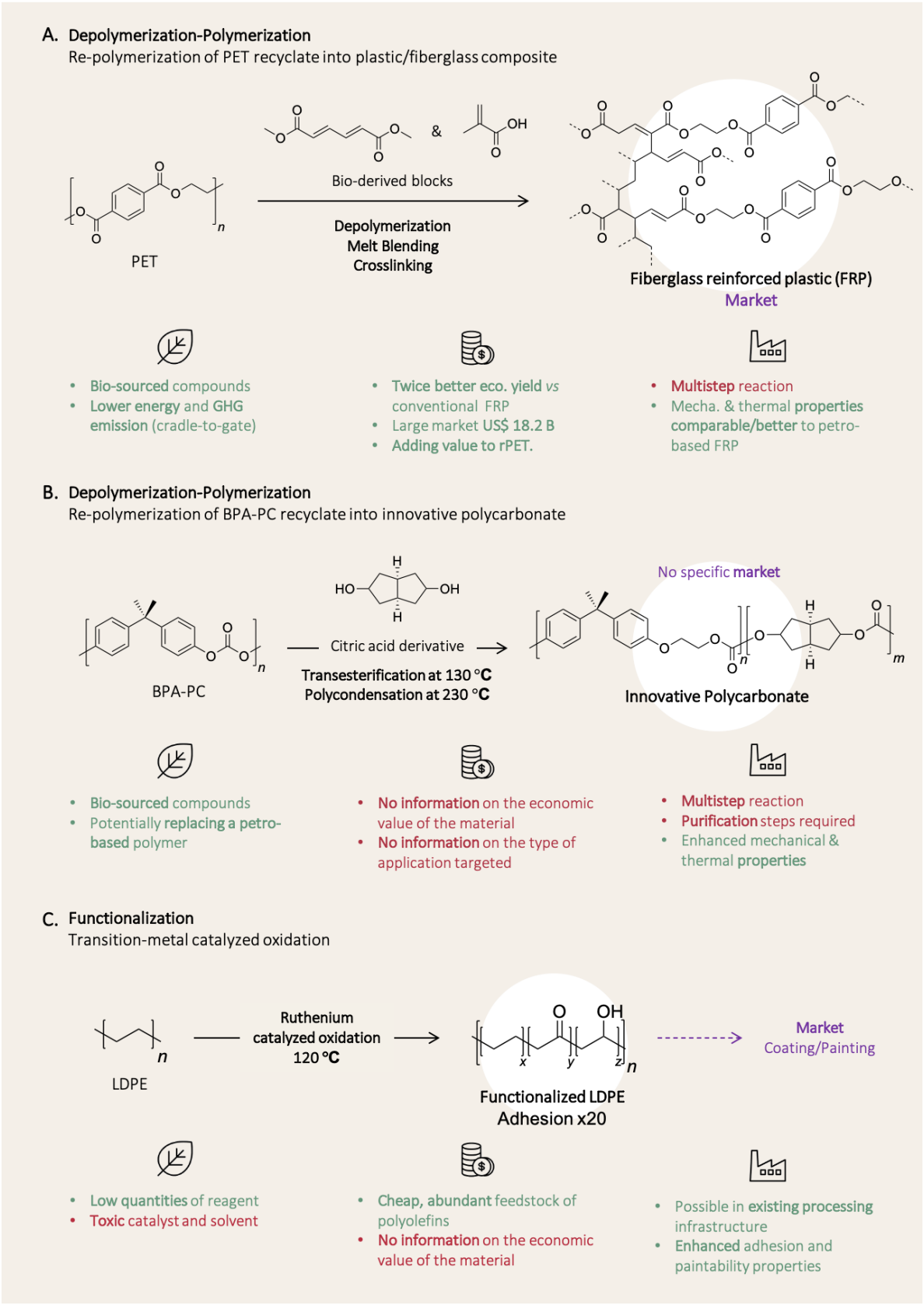

Figure 3. *Treatment of plastic waste through polymer-to-polymer transformations employing depolymerization-repolymerization methods,* ***A.*** *Repolymerization of PET recycle into FRP.* ***B.*** *Repolymerization of BPA-PC recycle into innovative polycarbonate.* ***C.*** *Functionalization – transition-metal catalyzed oxidation. Markets in the figure are global markets.*

However, to become a relevant process, a systematic evaluation of bioreactors and the influence of waste purity on performance is required to meet the growing challenge of plastic waste. Current possibilities and limitations of biotechnology on plastic recycling have been commented on elsewhere.[41]

Functionalization

Polymer functionalization, also known as post-polymerization modification, is a common industrial approach to differentiate the properties of virgin plastics. Compared to chemical recycling, polymer functionalization is an attractive approach for vinylic polymers because of the high enthalpic barrier for their depolymerization and the lack of inherent functionality. High- and low-density polyethylene (HDPE or LDPE), polypropylene (PP), poly(vinyl chloride) (PVC), and PS represent 67% of the plastic waste generated in MSW – if fibers are not included.[42] However, in the US for example, the recycling rate of such materials does not exceed 10 % for HDPE, 4.5 % for LDPE and less than 1 % for PS, PP or PVC.[43] Thus, C–H functionalization has emerged as an attractive approach to enhance the value of commodity materials while retaining the beneficial attributes of the parent material.[44]

Upcycling of polyolefins through polymer functionalization has demonstrated recent commercial success through the DeltaMax™ class of PP performance additives introduced by Milliken & Company in 2018. DeltaMax™ initiates radical coupling between PP and ethylene copolymer additives that enhance the impact and melt-flow properties of post-consumer plastic waste, thus circumventing the typical performance deterioration observed during mechanical recycling of PP. Recent academic reports take a similar approach by developing creative catalysts and reagents to overcome the selectivity challenges of peroxide initiated polyolefin functionalization to install hydroxyl,[46–48] xanthate,[49,50] or other polar functional groups[51] without concomitant chain scission. The resulting materials have enhanced paintability and adhesive properties, from 0.3 MPa for the unmodified PE to 6 MPa for the functionalized version in lap shear test, indicating their promise as additives.[52] (**Figure 3C**) Additionally, singlet carbenes generated from *bis*-diazirine precursors have been shown to provide efficient crosslinking of linear and branched polyolefins, which represented a long-standing challenge that yields materials with enhanced mechanical strength and thermal stability. A disadvantage of this method is that the resulting polyolefin thermosets are not reprocessable and, thus, cannot be further recycled. In a more recent example, maleimides bearing dioxaborolane functionalities were grafted onto HDPE to enable the conversion of this high volume commodity polymer into a vitrimer with built-in reprocessability.[54] These polymers demonstrate enhanced creep resistance and stress relaxation due to a combination of molecular bond-exchange and macrophase separation.

A number of these emerging methods have demonstrated success for polymer functionalization in the melt (*i.e.,* without solvent), a key criterion for conducting such chemistry in an environmentally and economically efficient manner. The potential to perform these polymer functionalization reactions in an extruder indicates that they can 'drop in' to the current plastics manufacturing and recycling infrastructure, indicating their ability to be performed on significant scale. Despite the established success and emerging technology applicable to polyolefin functionalization, the volume of polyolefin waste (>150 million metric tons annually) is much larger than the market for even a combination of these functionalized materials. This mismatch in volume, however, does not obviate the potential benefits of upcycling by functionalization. Developing high-value markets for functional polyolefin materials can provide economic incentives to drive progress in complementary technologies

that enhance sustainability, such as better polymer collection and sorting technology or next-generation polymer processing and characterization techniques.

Other high-volume commodity polymers including acrylics, aromatic polymers, and condensation polymers have been transformed into new materials such as densely functional macromolecules and low surface-energy materials through functionalization.[55–57] Despite the success of these approaches on virgin quality plastics, leveraging C–H functionalization as a solution for polymer waste upcycling will be enhanced by (1) the development of methods that proceed under mild and environmentally friendly conditions, (2) the preservation of the thermomechanical properties of the polymer, (3) the application of the methodology to mixed waste streams, and (4) the synthesis of final products that enter into a closed-loop plastics economy.

2. Polymer-to-molecule

The upcycling of discarded plastics into small molecules can provide an economical and sustainable substitution of synthetic chemicals that are otherwise labor-intensive or cost-prohibitive to produce. With plastic waste as an abundant starting material, chemical transformations that target synthetic chemicals through selective depolymerization have the potential for high-volume production. In this section, upcycling approaches that lead to molecules different from the polymer parent monomer(s) will be examined, considering their final applications as new monomers, fine chemicals, or additives.

Polymer to monomers

The depolymerization of plastic wastes into new monomers is an exciting field of research. Polyesters, and most notably PET, has been widely studied as a substrate for depolymerization into small molecules, mainly due to the presence of a chemically labile ester group and the better-established collection and sorting system already existing for this plastic. Solvolysis of PET is a well-developed recycling approach and is currently being implemented industrially.[13,58,59] A complementary option is the aminolysis for the production of terephthalamides, a valuable family of building blocks, which are commonly prepared using phosgene or derivatives, that can be prepared by aminolysis of PET up to 92 % of yields without purification in minutes. They can be utilized as monomers for various materials, including novel polymers such as polybenzoxazines or polyionenes. These materials exhibit interesting properties, depending on the functionality, and they are reclaimed in a myriad of high added value applications which includes strong adhesives,[60] materials for the treatment of nosocomial and mycobacterial infections,[61] antimicrobial and antifungal materials,[62–64] and elastomeric self-healing materials.[65] Some of these technologies employ highly energetic reactions (high temperature and/or pressure) and includes purification steps, making the scaling up of these methodologies difficult, but the conventional route to synthesize terephthalamides is based on highly toxic compounds,[66] which thus provides a sustainable advantage of the PET-to-terephthalamide route.

BPA-PC is a high-volume engineering polymer whose depolymerization serves as a feedstock for the synthesis of cyclic carbonates and carbamates.[67–69] (**Figure 4A**) This approach leverages plastic waste for the preparation of cyclic carbonates considered valuable building blocks for the preparation of aliphatic PCs or poly(hydroxyurethane)s, which are emerging materials with applications in energy storage, microelectronics, and biomaterials.[70,71] This strategy has an additional benefit of obviating the need for using toxic phosgene in cyclic carbonate

preparation, which further enhances its environmental benefits. The main drawbacks of these methodologies are the need for higher yields and simplified purification routes, which are hurdles to be overcome towards industrial implementation.

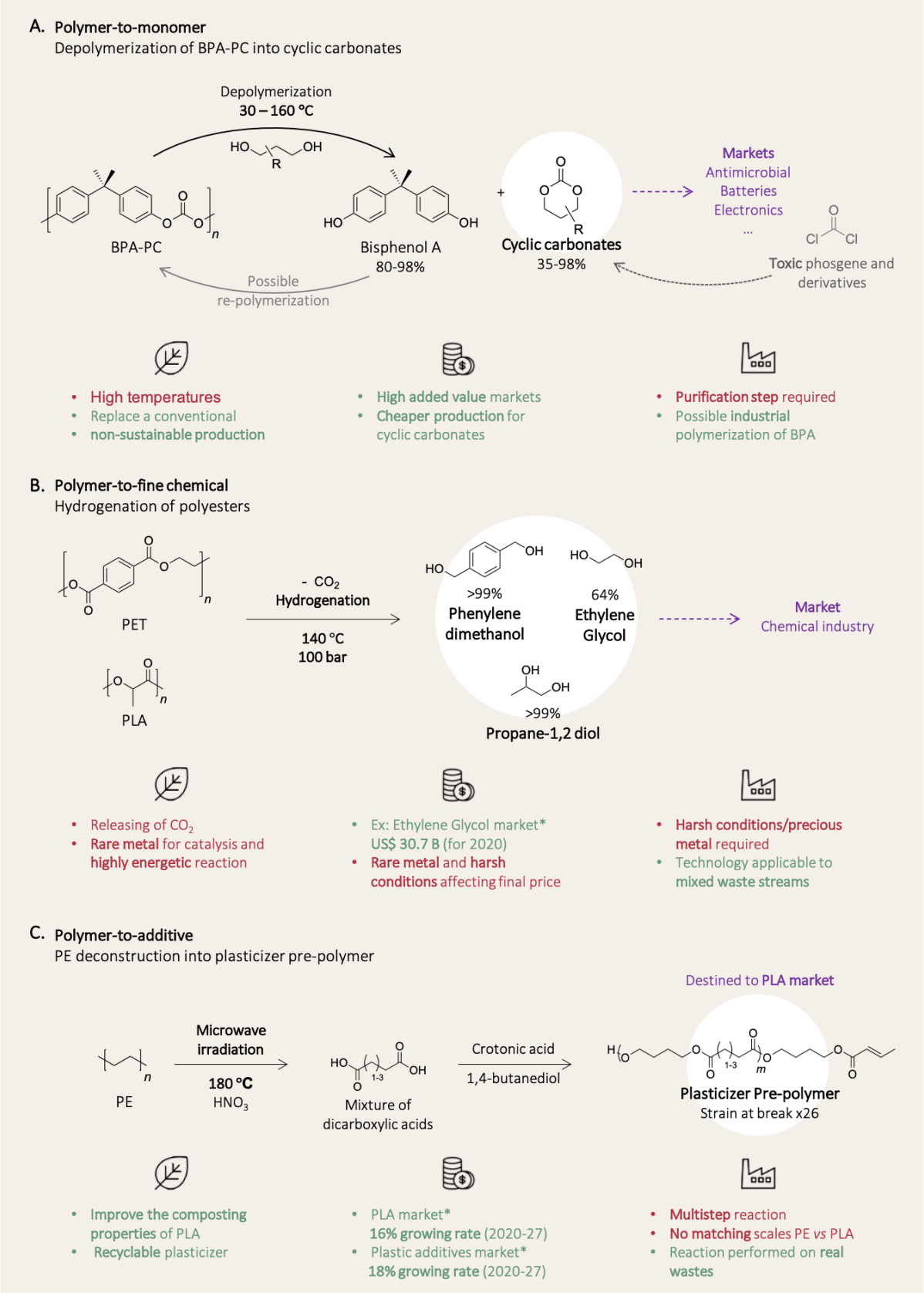

*Figure 4. Treatment of plastic waste through polymer-to-molecule transformations into **A.** monomers – Depolymerization of BPA-PC intro cyclic carbonates, **B.** fine chemicals – Hydrogenation of polyesters, and **C**. additives – PE depolymerization intro plasticizer for PLA. Markets in the figure are global market*

It should be noted here that while the use of post-consumer plastics for the preparation of monomers is an attractive approach, its advantage compared to the preparation of analogous molecules from petrochemical resources is not systematically clear. In addition, the market for most of these emerging materials is not developed, making their current substitution potential still relatively small compared to the large volume of plastic waste. Future studies should define the environmental and economic advantages of these methods through LCA and techno-economic analysis (TEA) studies as well as developing chemistry that is tolerant to the impurities found in post-consumer waste streams (AMD, dyes, mis-sorted polymers, multilayer products) must still be considered.

Polymer to fine chemicals

Fine chemicals are another attractive target for the upcycling of commodity polymer waste. Transition metal catalyzed hydrogenation and hydrosilation of polyesters and polycarbonates yields multifunctional small molecules (64-99% yield) with developed markets as solvents and reagents in the chemical industry.[72,73] (**Figure 4B**) The studies demonstrated that the functional group tolerance of these late transition metals made them applicable to impure post-consumer waste streams, showing promise for their use under conditions that are relevant to the waste coming from MSW. However, a disadvantage of these approaches is their reliance on precious metals (Ruthenium or Iridium complexes) and harsh conditions (100 bar, 140 °C), which will require further catalyst development and engineering optimization to yield a more environmentally friendly and cost-effective process.

The use of enzymatic and microbial transformations to convert plastic waste into small molecules is an emerging area of research.[8,74] The biological valorization of PET into different aromatic derivatives using enzymatic conditions (30 °C, neutral pH, etc.) is a clear advantage compared to some other recycling methods.[75] For example, muconic and gallic acids, obtained at 92 and 85% yield, respectively, are important reagents for the food and pharmaceutical industry, which could provide an economic added value to the process, although such molecules are not synthesized at scale comparable to PET production. Nevertheless, these enzymatic transformations concern the terephthalic acid obtained from a preceding chemical depolymerization of PET which requires high temperature and microwave irradiation, which could compromise the overall economy and sustainability of the technology.

Polymer to additives

Even pristine polymeric materials often exhibit inadequate physical properties for real-world applications and additives must be incorporated into the polymer to improve its processability and applicability. As a result, the global thermoplastic additives market has reached US$ 2.7 B in 2019;[76] meanwhile, an increase in environmental awareness is driving this market from petroleum to sustainable sources. In line with this trend, the upcycling of discarded polymers into additives for enhancing the properties of other commodity or sustainable polymers is receiving significant interest.

A few procedures have been reported to deconstruct polyolefins into different additives as an example of upcycling. The depolymerization of LDPE from real waste bags and HDPE from a discarded container) has been carried out through microwave assisted oxidative degradation to yield different carboxylic acids, *i.e.,* succinic, glutaric, and adipic acids.[77] (**Figure 4C**) These

molecules were reacted with crotonic acid to design a macro-plasticizer and subsequently grafted to PLA through reactive extrusion.[78] The resulting plasticized PLA demonstrated enhanced mechanical toughness compared to virgin PLA, *i.e.*, 26-times higher strain at break and 2.5-times lower stress at break. Moreover, increased biodegradation at 60 °C was observed for the PLA plasticized films while the plasticizer was proven to be recyclable after the controlled hydrolytic degradation.

Similarly, the use of rubber from waste tires has been explored to prepare telechelic polyisoprene oligomers of defined length by metathesis. These oligomers are key intermediates in the synthesis of compatibilizers and thermoplastic elastomers while also representing a cost-effective and efficient way of recycling waste items for the tire industry.[79] However, while these additives may enhance the properties of single-use plastics, their impact on the recyclability of the resulting material must be taken into consideration when evaluating their ultimate benefit.

3. Polymer-to-material

Commodity polymers or inseparable mixtures thereof represent a compelling starting material for the production of next-generation materials for applications in nanomaterials, energy storage, and composites. This section will discuss the conversion of polymers to materials through two strategies: thermal treatment to yield carbon-based materials and compatibilization to achieve polymeric blends. The realization of materials with similar or even enhanced properties compared to those made by *de novo* synthesis has the potential to both lessen the use of petrochemical resources and divert waste back into the market.

Polymer to nanomaterial

With hydrocarbons representing more than 64% of non-fibers commodity plastics[42], their conversion to carbon-based nanomaterials for energy generation and storage is an attractive approach toward advanced materials with an enhanced economic value. In this context, the transformation of polyolefin waste into carbon-based nanomaterials was practiced before the term upcycling was defined. Applications pursued using a thermal degradation procedure include the production of nanomaterials useful for supercapacitor, photovoltaic, catalysis, and energy storage applications, among other high value ventures. However, the challenge with such thermolysis procedures, *i.e.*, gasification, low-temperature carbonization or pyrolysis,[81–83] for plastic waste is that the value of the final product is not sufficient to offset the energy required and the environmental impact of the concurrent release of GHGs.[84] These methodologies have recently been reviewed in detail, proposing necessary improvements of increasing the carbonization yield in the presence of additives or impurities and the efficiency of catalysts upon re-use.[80,85]

Modern advances have controlled the formation of hollow carbon spheres from mixed plastic waste, suggesting the potential generality of thermolysis methods.[86] A complementary workflow includes performing polymer functionalization prior to thermolysis, which was demonstrated through the sulfonation of wastes LDPE bags and subsequent thermolysis to yield anionic carbonaceous materials capable of lithium ion storage, useful for lithium battery technology.[87,88] (**Figure 5A**) Thermolysis approaches are typically resource- and energy-intensive, requiring high temperatures and transition metal catalysts. Recent progress has been made to repurpose the high carbon content within waste polymers into carbon-based nanomaterials using methods that mitigate the cost and environmental impact of pyrolysis,

such as using boron-assisted catalytic graphitization or co-pyrolysis with zinc dust to obtain graphite from PET.[89,90]

However, a persistent challenge with the polymer-to-nanomaterial approach is one of scale. While many of the proposed applications are high value with the global nanomaterials market size was valued at US$ 8.5 billion in 2019 and carbon nanotubes accounting for 27% of that value, the quantity demanded by the market is a small volume (~2 500 tons) compared to the 338 million metric tons of plastic waste produced annually.[5] Moreover, pure waste streams are required to achieve defect-free nanomaterials; the impact of additives, colorants or catalysts will need further investigations to allow non-pure waste streams to become a feedstock for such applications.

Polymer to blend compatibilizers

The valorization of mixed plastic waste is a huge challenge for any recycling processes, mechanical or chemical. In this context, a strategy to derive additional value from plastic waste mixtures is highly desired. One promising option is blend compatibilization, which lowers the interfacial tension between disparate polymer phases and leads to properties that represent a synergistic combination of the two materials.[91]

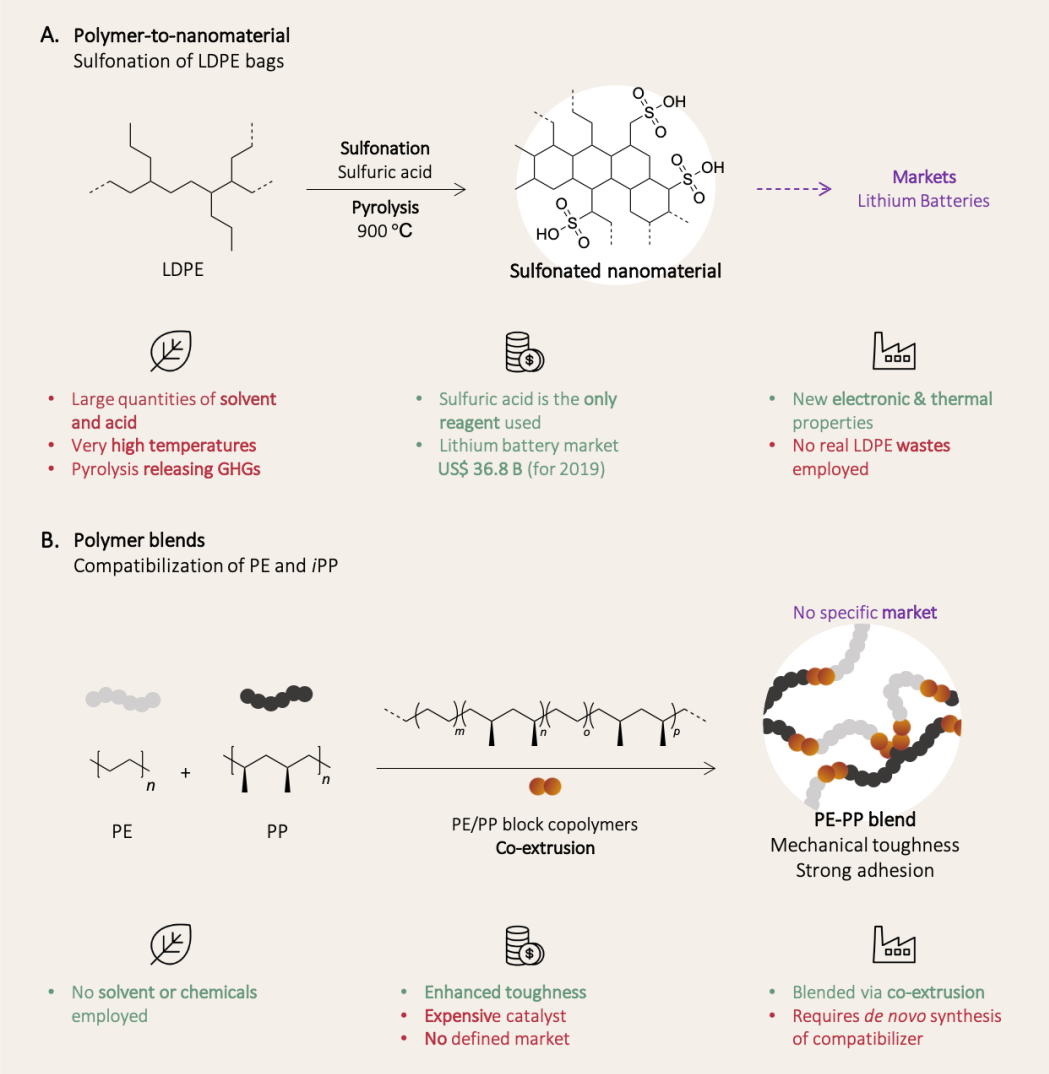

*Figure 5. Treatment of waste plastics through polymer-to-material transformations and examples for the synthesis of **A.** nanomaterials and **B.** polymeric blends. Markets in the figure are global market*

The most common approach to upcycle blends via compatibilization is through the addition of a copolymer compatibilizer, which generally results in an enhancement of phase dispersion and mechanical properties of polymer blends.[92] Plastic waste mixtures of PET, PE, and PP have been compatibilized using non-reactive copolymers, such as ethylene–propylene–diene monomer rubber (EPDM), styrene–ethylene–butylene–styrene (SEBS), and other polyolefin copolymers. These compatibilized blends enhance the overall mechanical properties of the compounded material, as observed through tensile and flexural testing. [93–97] In a specific case study, post-industrial polyolefin waste contaminated with PET was compatibilized through co-extrusion in the presence of EPDM or SEBS additives to induce morphological changes.[98] The compatibilized blend demonstrated three times better flexural modulus and impact strength compared to the uncompatibilized blend. Recent work demonstrated that block copolymers of PP and PE are effective additives for compatibilizing polymer mixtures that reflected the complicated composition of polyolefin waste.[99,100] (**Figure 5B**) Only 0.2 weight % of the copolymer was required to achieve value-added properties, indicating the efficiency of this strategy. Nevertheless, this exogenous compatibilizer approach includes two drawbacks for a universal implementation of such procedures: the synthesis of a specialty copolymer is mandatory for each different waste stream and a relatively pure binary post-consumer polymer mixture is needed.[101,102]

Instead of adding a copolymer to a mixed waste stream, reactive compatibilization promotes the formation of compatibilizing macromolecules or domains through *in situ* polymer functionalization and/or coupling.[103] In head-to-head comparisons, reactive compatibilization has been demonstrated to outperform compatibilization by a copolymer.[104,105] For polymer functionalization, the most common reactive compatibilization approach includes the addition of a small percentage of a polymer precursor that is compatible with one phase and reacts with a functional group in the complementary phase, thus generating graft or block copolymers *in situ*.[93] Additionally, interphases can be generated by the addition of radical initiators and comonomers during polymer processing.[106] For example, reactive compatibilization was accomplished on agricultural polyolefin waste using dialkyl peroxides as reactants and liquid polybutadienes as lubricants to improve the particle dispersion and tensile impact strength of the commingled waste.[107] While reactive compatibilization holds tremendous promise, a host of challenges must be addressed to realize a general method toward mixed waste upcycling. These include controlling the polymer morphology, limiting irreversible crosslinking or degradation reactions, and developing chemistry that occurs in the polymer melt at time scales commensurate with thermal polymer processing.

Blending dissimilar plastics into high-value materials that can be repeatedly reprocessed solves a persistent problem in the short term, but it may exacerbate challenges with sorting polymers into pure feedstocks in the long term. Therefore, technology that can disentangle mixtures of plastics into pure feedstocks would enhance the value proposition of upcycling generally, creating opportunities to exploit polymer mixtures for both high-performance blends and deconstructing those blends into value-added feedstocks.

Quantifying the sustainability of upcycling

The environmental impact of any of the discussed upcycling methods should ideally be minimized and evaluated by means of LCA or similar holistic methods and circular economy indicators. As an example, we provide insights from carbon footprint calculations of three upcycling cases, namely (1) re-polymerization of PET recyclates into plastic/fiberglass

composites ('polymer-to-polymer' upcycling), (2) depolymerization of BPA-PC into cyclic carbonates ('polymer-to-molecule' upcycling), and (3) sulfonation of LDPE bags ('polymer-to-nanomaterial' upcycling). The impact of the upcycling processes is compared to a benchmark scenario in which the plastic materials would be incinerated with energy recovery and the applications that are substituted by the recycled materials would be fulfilled with virgin materials. (**Figure 6A**) The analysis includes energy and other resource consumption required for the upcycling processes. To compare the upcycling processes to mature virgin production, assumptions regarding the applied process models and upscaling calculations are made, including aspects such as solvent recovery and residue treatment (details in Supplementary Materials). Based on the carbon footprint of the upcycling processes and the potential CO_2 savings made by avoiding incineration and production of virgin polymers, the net impact is calculated. (**Figure 6B**)

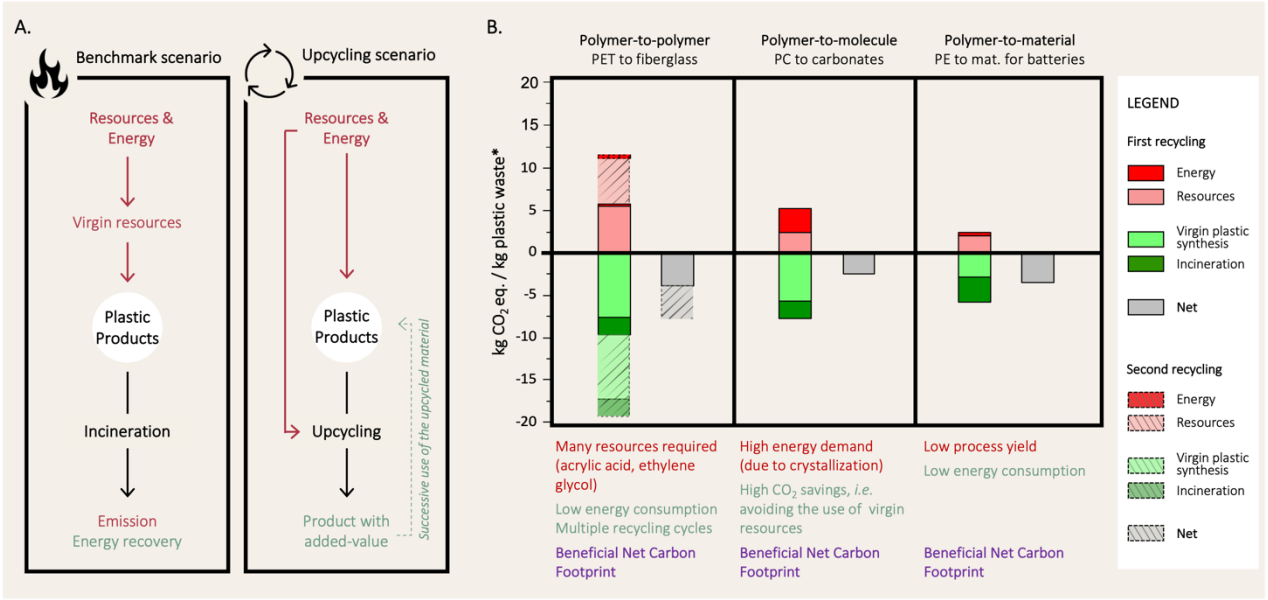

*Figure 6. **A.** Schematic comparison between the benchmark and upcycling scenario and **B.** Indicative assessment of the environmental friendliness of upcycling plastic waste as a strategy to substitute virgin resources for three technologies: the repolymerization of PET recyclates into FRP[29], the depolymerization of BPA-PC intro cyclic carbonates[69], and the sulfonation of wastes LDPE bags into carbonaceous materials for battery electrodes[88]. *carbon footprint data are extracted from Ecoinvent database*

Results demonstrate that, in each of the three different upcycling scenarios, an environmental benefit is feasible as indicated by a net negative value for the net impact balance. The transformation of PET waste into FRP composites shows the most beneficial environmental balance. An important assumption in the analysis is that the properties of the upcycled polymer have at least a comparable quality to their virgin counterparts. Based on the performed analysis, 3.92 kg CO_2 eq. emission/kg waste plastics can be avoided by performing the upcycling process analyzed in this case. Furthermore, the upcycled polymer can in theory be recycled again, which would increase this benefit. For the polymer-to-molecule (recycling of BPA-PC into cyclic carbonates) and polymer-to-nanomaterial (sulfonation of LDPE bags waste) scenarios, an assumption is made that the waste material can substitute virgin resources only once and, thus, less carbon emission can be avoided compared to polymer-to-polymer upcycling. However, these upcycling routes still have a positive environmental balance of 2.43 and 3.47 kg CO_2 eq./kg waste plastics, respectively. Although the carbon footprint is calculated for three specific processes for which multiple assumptions are made,

the obtained results indicate that polymer upcycling has potential to create a beneficial impact for the environment and can reduce overall carbon dioxide emissions, which is a major contributor to global climate change.

Assessing circular economy developments such as upcycling by holistic methods is complex, and a recognition of the strengths and limitations of these LCA is required to accurately assess and steer developments in plastic upcycling. For example, a large scale application of upcycling can induce shifts in a particular market[108–110], but the traditional attributional LCA is not always able to correct such shifts with respect to the scale at which a particular product is introduced. The recent development of consequential LCAs better articulate the environmental friendliness of upcycling by incorporating the ability to predict the market response based on the production of a particular item. Additionally, the aspect of quality is important to consider in upcycling assessments. Many LCAs assume a one-to-one substitution with virgin resources. The quality of the recycled material, however, can be lower compared to this of virgin plastics, which suggests that a correction should be made to the environmental saving of the recycling process. For mechanical recycling, some developments have recently been made in this respect, but for upcycling processes the inclusion of quality in LCA remains somewhat unexplored.[111,112]

LCAs are not built to evaluate all aspects related to sustainability, and emerging studies suggest linking LCA with circular economy indicators to improve their overall predictive power. For example Moraga *et al*. suggest that functions, products, components, materials, and embedded energy of the targeted substitution in the circular economy strategy can be assessed at different scopes.[113] This might involve quantifying aspects not traditionally assessed in LCA, such as the accounting for lifetime of a product, assuming that single/short use applications with quality degradation are inherently less sustainable, or assessing the societal need of certain products or functions. Finally, the recyclability of the substituted product itself should be taken into account, as a second upcycling cycle. More complex analysis should include how the structure and properties of the upcycled product influences consecutive cycles, or the consumer behavior. This, together with more detailed frameworks to assess upcycling in a holistic way, are needed to develop meaningful policies which can further stimulate sustainable upcycling developments.

Outlook and Perspective

The multifaceted challenges that need to be solved to advance a sustainable plastics economy are daunting in their scale and complexity. In this review we have elaborated on the concept of upcycling. The nascent state of this field and lack of a clear definition of the term led us to propose upcycling as “the use of plastic waste as a feedstock for the synthesis of value-added products, being polymers, molecules, or materials”. To focus this emerging field and provide benchmarks for further development, we propose to focus upcycling on the sustainable substitution of *de novo* synthetic products. Such a substitution can be guided by six principles, which are built around environmental impact, industrial relevance, and economic value. These principles allow a comparison of different upcycling strategies, as well as benchmarking polymer upcycling approaches as a sustainable and complementary strategy to mechanical and chemical recycling in the long term. Applying these principles on a compilation of recent research leads to three broad conclusions about the current state of polymer upcycling.

First, benchmarking the current state of the field with the guiding principles makes clear that polymer upcycling is in its infancy and faces considerable challenges before it will be suitable

for widespread implementation. The central challenge is that plastics are designed to be chemically stable, so the development of selective and scalable transformations on plastic materials remains difficult. Hence, future research is required to accurately understand and control the complex chemical mechanisms that lead to selective polymer deconstruction at a molecular level. Reaction development should focus on the design of more efficient catalysts or reagents to (1) minimize the energy required for upcycling, (2) enhance the selectivity in transforming the plastic waste to the targeted product and, (3) be sufficiently robust to operate on mixed and contaminated plastic waste streams. These motivating factors have not typically been at the forefront of academic research, which has often presented methods that transform virgin polymers that do not contain the additives and impurities found in real-world samples. While fundamental research and proof-of-principle studies are vital to develop new technologies, the importance and complexity of translating such methods to real plastic waste needs to become an equally important facet of technology development.

A second critical area for development includes incorporating aspects such as material performance, sustainability metrics (LCA, TEA), material flow analysis (MFA)), and market volumes of the upcycled product earlier in the research pipeline. Undoubtedly, a challenge for upcycling is the scale of the waste input compared to the substitution potential of the product. In most cases, however, upcycling should be considered as part of a suite of solutions to address the challenges of reclaiming plastic waste. For example, upcycling a high-volume plastic to a variety of low volume, high value applications may provide at least part of the economic justification to support upcycling to high volume chemicals and materials. Even a small-scale upcycling process may provide an economic benefit sufficient to offset a cost intensive recycling process – thus leading to greater levels of recycling overall. Of course, these substitutions should also be sustainable, implying that holistic comparisons that incorporate sustainability metrics and cost drivers will need to become routine to quantify the value of upcycling. Ultimately the question to ask could be “why should we use waste-plastic-derived feedstocks over other feedstocks?” and tools such as LCA, TEA or MFA need to serve as tools to help answer this question by evaluating upcycling approaches. Applying these approaches consistently during the development phase will encourage researchers to consider the economic and environmental cost as well as the market volume in which the upcycled product could be employed. However, these approaches should not limit fundamental research, which will remain critical to reimagine what is possible and identify the boundary conditions for future development.

Third, the end-of-life fate of upcycled products needs to be considered during the technology development process. Ideally upcycling not only extends the useful lifetime of a plastic, but also installs chemical functionality that can render the plastic more recyclable.[114,115] An emerging approach with considerable promise is to transform plastics into a value-added material with built-in intrinsic recyclability. One example of this is the production of poly(dicyclopentadiene), a commercial thermoset, with a degradable main-chain monomer incorporated through copolymerization. Including the degradable units in the main chain of the polymer enabled depolymerization into soluble products and subsequent polymerization into products with targeted properties. Another approach is to create innovative materials that can demonstrate closed-loop upcycling. A proof-of-concept strategy reported the production of aliphatic polyesters, wherein a mixture of two homopolymers can be converted into a sequence-defined copolymer that, relative to the homopolymers, demonstrated enhanced thermal stability and full chemical recyclability.[116] In a complementary closed-loop

upcycling of thermosets, depolymerization and repolymerization with a different selection of building blocks yielded materials with differentiated properties while remaining fully recyclable.[117]

Plastics remain the best materials to protect food, purify water, store, or generate energy, reduce infections, and create performance materials. Given their essential role in the global economy, a holistic and sustainable plan to manage plastics at end of their life is required. Chemical upcycling of polymers holds promise for a paradigm shift from traditional ways of treating waste plastics by transforming and repurposing them into feedstocks for higher-value products. This is reaffirmed by both the recent U.S. Department of Energy report on "Chemical Upcycling of Polymers"[114] and the Royal Society of Chemistry report on "Science to Enable Sustainable Plastics"[118] that emphasize the importance and challenges for innovating in the areas of waste treatment by chemical modification to create products comparable or superior to modern commodity polymers. The nascent work in the area of upcycling demonstrates the significant opportunities to transform discarded plastics into higher-value specialty polymers, functional molecules, or high-performance materials. Continued innovations with a focus on using plastic waste to generate materials that are both of high value and high recyclability as a result of the chemical modification is an aspirational goal that will play an important role in the shift toward a more sustainable plastics economy.

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