

100th anniversary of macromolecular science viewpoint

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100th Anniversary of Macromolecular Science Viewpoint: Towards Catalytic Chemical Recycling of Waste (and Future) Plastics

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ABSTRACT: The current global materials economy has long been inefficient due to unproductive reuse and recycling efforts. Within the wider materials portfolio, plastics have been revolutionary to many industries but they have been treated as disposable commodities leading to their increasing accumulation in the environment as waste. The field of chemistry has had significant bearing in ushering in the current plastics industry and will undoubtedly have a hand in transforming it to become more sustainable. Existing approaches include the development of synthetic biodegradable plastics and turning to renewable raw materials in order to produce plastics similar to our current petrol-based materials or create new polymers. Additionally, chemists are confronting the environmental crisis by developing alternative recycling methods to deal with the legacy of plastic waste. Important emergent technologies, such as catalytic chemical recycling or upcycling, have the potential to alleviate numerous issues related to our current and future refuse and, in doing so, help pivot our materials economy from linearity to circularity.

There is no doubt that the “age of plastics” has had a phenomenal impact on advancing most technologies, from food to transportation to communications. Plastics have been integral to the many impactful societal advancements of the 20th century which have greatly improved the quality of human life. However, our current portfolio of thermoplastic and thermoset materials is largely unsustainable, with environmental impacts growing as our production capacity and needs continue to increase. The phenomenal durability of commodity plastics have led to both their widespread use and accumulation in the environment, where they are incessantly persistent.¹ Alarming, as of 2015, it was estimated that of all post-consumer waste (PCW) plastic that has been generated only around 9% has been recycled and 81% existed in landfills or the environment (Figure 1).² Although a range of social and policy considerations will be crucial to addressing this mounting crisis, chemistry is envisioned to play a leading role. Polymer chemistry will lend pioneering solutions to reusing and/or repurposing PCW plastic and contribute with innovative sustainable materials to drive the transformation of our plastics economy.

For several decades, biodegradable plastics have been intensely studied in academic environments with the perpetual optimism to remedy our materials problem.³ Unfortunately, the commercial impact has been minimal (biodegradable, bio-sourced plastics represent << 1% of global plastic production)⁴, apart from a few polyesters such as poly(lactic acid) (PLA) or poly(hydroxy butyrate) (PHB). Beyond economic considerations, these plastics often possess inferior material properties to petroleum-based counterparts.⁵ Furthermore, there have been recent concerns about their real world degradability; for example, PLA is essentially non-degradable in sea water or a landfill even though it can be hydrolytically degraded in the laboratory and *via* industrial composting methods.⁶⁻⁷

The end-of-life biodegradation of these plastics also means that the material value is lost after service lifetime (which can be after just one use) and hence the overall carbon footprint– from production to environmental biodegradation– in these modes of use must be considered.⁸ Although further development of biodegradable plastics is vital, we must also address the legacy of our existing plastic infrastructure.

Although most commodity thermoplastics – such as polyethylene (PE), polypropylene (PP), or polyethylene terephthalate (PET) – are notionally physically recyclable, such efforts have massively underperformed with the causes largely placed around challenges relating to collection and sorting logistics.⁹ The majority of emerging economies have little to no recycling infrastructure in place leading to large amounts of inadequately disposed waste¹, but many developed economies with better waste management systems still struggle to recycle¹⁰ in their own right. For example, consumers can become confused and frustrated when disposing of various plastics since local or regional recycling authorities often have a degree of autonomy to set their own policies and requirements which can vary considerably. Moreover, mixed PCW plastic streams are plagued by a variety of issues including: 1) plastics that are difficult to sort (such as PE *versus* PP), 2) multi-component, or composite, plastics (for example, many food films are commonly composed of numerous layers of different plastics) and 3) the presence of numerous additives¹¹ (such as flame retardants, plasticizers, or coloring agents) and foreign debris that both reduce the overall quality of the end-recycled product and pose their own environmental problems. Together, these difficulties lead to the large environmental PCW losses – just 14% of plastic packaging is collected for recycling and only 2% is closed-loop recycled, *i.e.* collected and reprocessed for the same purpose.¹² Even if the aforementioned issues associ-

ated with current recycling schemes are addressed, we cannot escape the fact that

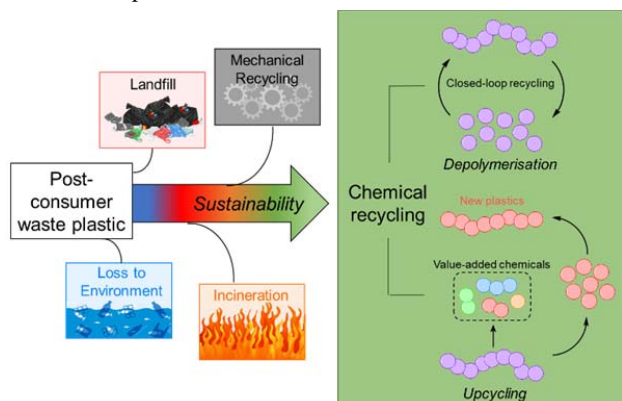


Figure 1. Overview of plastic waste treatment and emergence of chemical recycling.

each time a plastic is recycled, it deteriorates the virgin material (*via* chain scission reactions and other oxidative degradative processes) leading to a loss of mechanical integrity and performance in the recycled product.¹³ As such, physically recyclable plastics have a limited lifetime, even under the best of scenarios, and do not actually present a viable, long-term solution for sustainable materials use.

An evolving technological solution to the global plastics challenge is chemical recycling, a process in which polymers are transformed into small molecules that can either be recycled back into virgin polymeric material or upcycled into alternative chemical/material feedstocks (Figure 1).¹⁴ It is envisioned that the production of chemicals with intrinsic value (upcycling) from PCW plastic will be an important advancement toward a greener chemicals economy.¹⁵ For some plastics, the chemically depolymerized components may be economically unviable if they were to be repolymerized back into a polymer of the original constitution so transformation into a new “value-added material” could be advantageous in some instances. On the other hand, in a circular economy framework where materials are reused in a closed-looped process¹⁶, chemical recycling is an increasingly practical approach to address the key challenges associated with traditional recycling efforts.¹⁷ Nevertheless, chemical recycling of plastics remains an energy intensive endeavor, often requiring high temperature and/or pressure to achieve. Moreover, the various processes are often unselective, yielding mixtures of small molecules that can be dissimilar to the original monomer compositions due to off-target reactivity. A prime example of this would be the catalytic pyrolysis of polyolefins that yields complex mixtures of oils and waxes after depolymerisation.¹⁸⁻¹⁹ The development of low temperature and/or catalytic processes are crucial to enabling energy efficient transformations

to original monomer sources and/or targeted precursors for upcycling purposes. This should, in turn, endorse the circular economy framework that will be critical to future materials use.

When compared to the plethora of research on biodegradable materials, the chemical recycling of plastics is a nascent field. Although there are several informative reviews in associated areas²⁰⁻²⁴, there have been numerous advancements within the last few years as the field is rapidly expanding. There is also an excellent, up-to-date summary on chemical recycling to monomers with cyclic monomers.²⁵ This viewpoint aims to comment on emerging trends in the development of sustainable chemical recycling with focus on catalytic chemical recycling, particularly regarding methods that have lower energetic requirements and including opportunities for chemical upcycling. Moreover, we will examine most common plastic classes (categorized as polar or non-polar), but it is not intended to be an exhaustive account. We will instead highlight key contributions and contextualize their impact on the respective subfields while discussing prospective trends and offering opinion. The final section seeks to showcase unindustrialized materials and other promising strategies that may soon contend within the current (and future) plastics economy.

CHEMICAL RECYCLING OF COMMON COMMODITY PLASTICS

Most commodity plastics can be sorted into seven categories according to the Society of Plastics Industry recycling codes: PET (1), high density polyethylene (HDPE) (2), polyvinylchloride (PVC) (3), low density polyethylene (LDPE) (4), PP (5), polystyrene (PS) (6), and other (7). The last category defines all other potentially recyclable plastics not defined in the previous categories and includes important materials such as polycarbonate (PC), polyurethane (PU), polyamide (PA) and emerging bioplastics such as PLA or PHB. The biggest advancements in catalytic chemical recycling have been realized for polar plastics, specifically those containing carbonyl moieties in the polymer backbone – notably PET, PC and PU. This is perhaps not surprising since the significant polarity of the C=O bond avails it to nucleophilic attack, thus leading to well-controlled chain scission reactions of the backbone. However, the majority of new plastic production (estimated to be approximately 86% as of 2015²) and subsequent PCW plastic generation come from recycling categories 1-6, and polyolefins (PP and PEs) alone account for nearly two-thirds of the total plastic economy.²⁶ Unfortunately, this means that efforts to chemically recycle polar plastics only accounts for a small fraction of PCW plastic. Nevertheless, great strides have still been made in recent years concerning the controlled depolymerization of these types of plastics.

Polar Plastics (PET, PC, PU, PA). Although PET accounts for a minor fraction of total plastics production (10%), it has a high recovery rate.²⁷ The treatment of PET bottles is one of the most encouraging examples of responsible waste management where collection-to-recycle rates are approaching 30% in the US and 60% in the EU.¹² Sadly, most recovered PET (by volume) is actually fiber-based which is then downcycled for lower value textile applications (such as carpeting) as a consequence of the listed complications from physical recycling processes.¹³ These sorts of physical recycling schemes are effectively diversionary, simply prolonging the PCW generation process.

Chemical recycling offers a path to return PCW PET to virgin PET, although PET depolymerization is also being investigated in upcycling applications.²⁸⁻²⁹ For the former process, it is the most well-developed and studied polymer class. Typical approaches to depolymerizing PET into monomers for repolymerization involve the attack of nucleophiles at the carbonyl carbon to yield small molecule esters or amides (*i.e.* glycolysis, alcoholysis or aminolysis) that are suitable for subsequent polycondensation; however recently hydrogenation³⁰⁻³¹ or hydrogenolysis³²⁻³³ of PET with single-site metal catalysts has proven useful.

Nevertheless, the former depolymerization strategies remain prevalent but early examples usually required extremely high temperatures, pressures, or metal-based catalysts.³⁴ Although metal catalysts can be efficient, there are growing scarcity issues and environmental concerns related to their use. A breakthrough in the chemolysis of PET came from the development of ionic liquid-based (IL) catalysts³⁵ which are renowned for their green chemistry aspects including good recyclability and recoverability (Figure 2a).³⁶⁻⁴⁰ This was followed later by using highly active organic catalysts such as strong amine bases – amidines such as 1,8-diazabicyclo[5.4.0] (DBU) or guanidines such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (Figure 2a).⁴¹⁻⁴³ After repeated use, their activity often diminishes because of oxo-degradative side reactions or detrimental interactions with other reaction components. The most recent advancements for the depolymerization of PET are the implementation of amidine and guanidine-type eutectic salts (Figure 2a), which have greatly increased the efficiency of organic catalysts. DBU-based salts⁴⁴ and TBD-methanesulfonic acid complexes⁴⁵ retain the high catalytic activity observed for their respective free bases, but their thermal-oxidative stability is markedly improved leading to their recovery and reuse. Some organic salts also display great activity in step-growth polycondensations⁴⁶ and sometimes only require milder conditions than the preceding depolymerization step. Robust organic catalysts have the potential to greatly increase the commercial via-

bility of PET chemical recycling since they have the added benefit of often being colorless and can often remain embedded within the material formulation. In fact, the chemically recycled PET obtained from organobase eutectic salts was determined to be indistinguishable (chemically and thermally) from the initial feedstock, however the potential toxicity of leaving the catalyst embedded was not investigated.⁴⁵ The same principle of embedding the catalyst within new material formulation could also apply to any organocatalyzed PET that is mechanically recycled. Nevertheless, the presence of additives⁴⁷ in PET is a point of concern in the larger context of traditional plastics recycling infrastructure as they can contaminate PCW streams (and the environment) *via* leaching while ultimately impacting material properties of the recycled materials. Again, in this situation, the effects (*i.e.* toxicity and/or contamination) of using organocatalyzed processes are still largely unknown.

ILs⁴⁸⁻⁵¹ and organic bases⁵²⁻⁵⁴ have also been well studied for depolymerizations of bisphenol A (BPA)-PC waste.⁵⁵ The monomers obtained from alcoholysis often yield BPA and small carbonates that can be polymerized directly back to PC, however, carbon dioxide can be eliminated under by hydrolysis, precluding the return to an original material. A recent example converted waste PC into value-added polyarylether sulfones after hydrolytic degradation.⁵⁶ Due to growing concerns associated with BPA's toxicity, transforming waste BPA-PC into value-added materials, where the BPA can be sequestered, is attractive. A recent study described the transformation of BPA-PC into high-added-value six-membered cyclic carbonate monomers that are suitable for ring opening polymerization.⁵⁷

The chemolysis of PU, which is commonly produced from the polyaddition of polyols and isocyanates, is actually a rather mature and scalable technology.⁵⁸ Glycolysis is the most advanced method for PU waste treatment and it has been demonstrated in thermoplastics⁵⁹, elastomers⁶⁰⁻⁶¹ or foams⁶²⁻⁶⁵ materials to recover polyols, sometimes on commercial-level scales. Nevertheless, there still remains work to be done developing a more universal chemical recycling approach for PUs. This is partly due to the difficulty in selectively cleaving the C-N *versus* C-O bond in the urethane unit⁶⁶, but also due to the fact that commercial PU formulations are incredibly diverse in their monomer make-up, which leads to recovered resin streams that contain different polyols and/or additives. This can lead to costly purification processes and this issue hinders mechanical recycling efforts as well. Finally, PU production generally uses highly reactive isocyanate monomers, but they are not recoverable from traditional depolymerization

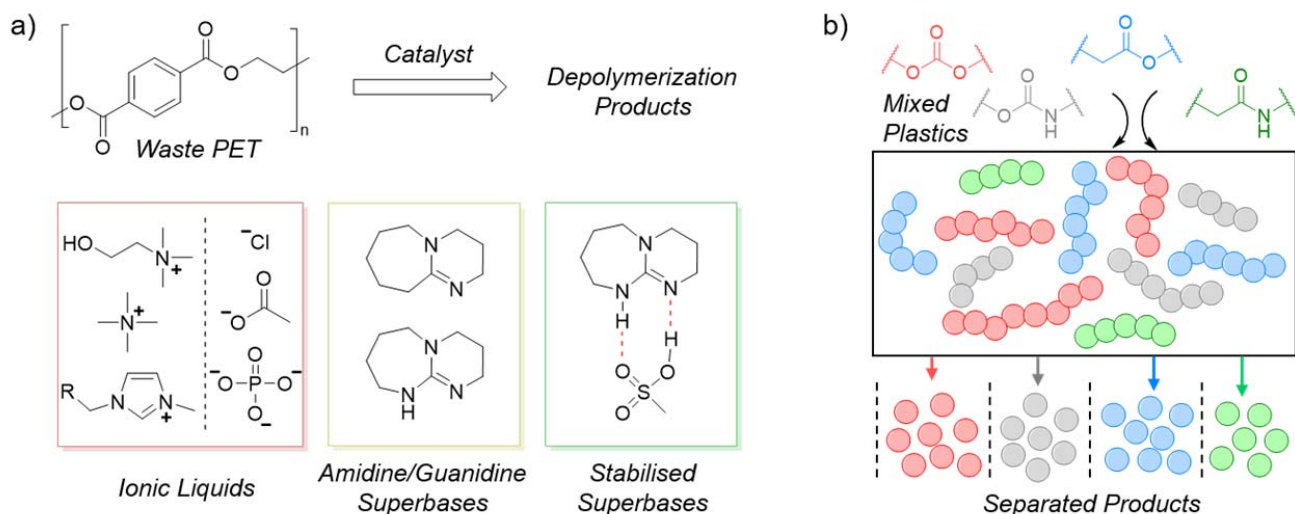


Figure 2. Depolymerization of polar plastics a) common organocatalysts for the chemolysis of PET and b) idealized mixed plastic recycling of polymers containing carbonyl groups

methods. However, more sustainable non-isocyanate PU production methods are being investigated and this will likely play an important role towards full chemical recycling of PUs.⁶⁷

Compared to other polar plastics, polyamides are more challenging to depolymerize due to the stability of the backbone amide bond, however this feature also renders them extremely strong and tough as materials. Polyamide 6 (PA-6) can be crudely depolymerized to aminocaproic acid (bifunctional amino-carboxylic acid) which is a reactive polycondensation monomer.⁶⁸⁻⁶⁹ However, the most important chemical recycling approach for PA-6 depolymerizes to the strained cyclic monomer, ϵ -caprolactam, which is an active monomer for ring-opening polymerization (ROP). This has previously been accomplished *via* supercritical protic solvents⁷⁰⁻⁷¹. Several catalytic IL methods have also successfully afforded ϵ -caprolactam from PA-6, albeit at high temperatures (*ca.* 300 °C).⁷²⁻⁷⁵ More pragmatic approaches to PA waste involve upcycling to feedstock chemicals such as ω -hydroxyalkanoic acids⁷⁶⁻⁷⁷ or 1,6-hexanediol and dimethyl adipate.⁷⁸ Scaling and further development of these strategies should enable better value recovery from PA waste.

Future aims should seek to lower reaction temperatures in order to ameliorate the costs of high energy inputs and detrimental side-reactions involving all reaction components; this will go hand-in-hand with catalyst improvements. Furthermore, developing conditions for single-batch, mixed-waste de(re)polymerizations (e.g. *via* selective amide, carbonate, urethane, and ester activation) should greatly increase the commercial viability by eliminating costly sorting mechanisms, but there has been little progress in this space to date (Figure 2b). A recent related example employed a one-pot depolymerization/polycondensation protocol for PET.⁷⁹

The development of more sophisticated catalysts that achieve greater selectivity under milder conditions is paramount to meeting these challenges. Porous nanostructured materials such as metal-organic frameworks (MOFs) offer an interesting opportunity. MOFs have been investigated in catalysis applications⁸⁰, including as polymerization catalysts⁸¹⁻⁸³, however they have not been investigated for depolymerization processes. This is surprising since they offer great structural diversity (e.g. multi-functionality for tandem catalysis) and are notable for their stability and efficiency (*i.e.* recyclability); these latter points seek to address environmental and scarcity concerns related to general metal use in catalysis. In addition, the incorporation of earth-abundant metals⁸⁴ (for example Al, Ti or Fe) into MOF catalysts⁸⁵⁻⁸⁸ should address scarcity issues as well. We believe the further development catalytic MOFs presents a spacious, untapped area for exploration in the chemical recycling of plastics.

Nonpolar Plastics (PE, PP, PS and PVC). Polyolefins are the most plentiful plastics (representing nearly two-thirds of all consumption), but they are largely chemically inert as synthesized. Their extreme durability renders them more suitable for physical recycling (especially for PE), but poses challenges for chemical recycling approaches regarding their PCW treatment. For chemical recycling, most progress has been realized for polar substrates, from a chemistry standpoint this should not be surprising. The carbon-heteroatom covalent bonds in such materials are inherently reactive due to their high polarity stemming from large electronegativity differences between atoms. Conversely, nonpolar plastics mainly feature sp^3 -hybridized C-C bonds in the polymer backbone and often require very forcing conditions to break the bonds along the polymer chain. It remains a grueling task to develop low-energy and selective depolymerization

strategies for polyolefins. However, research in this sector is accelerating and there have been many innovative examples in recent years.

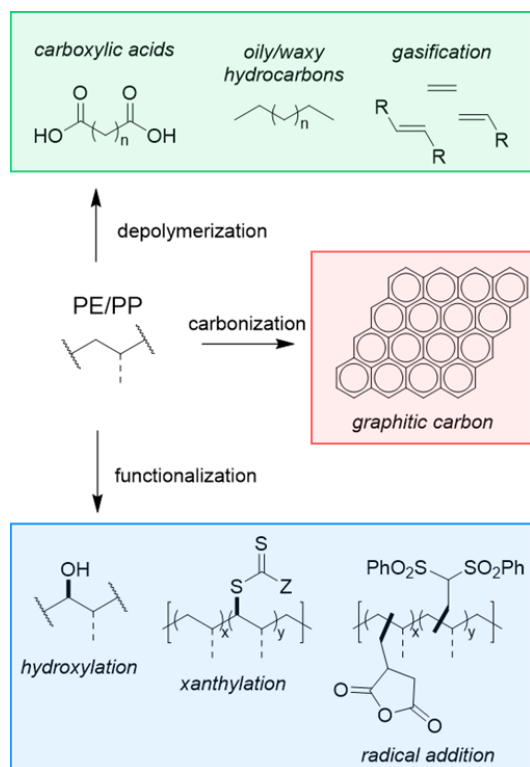


Figure 3. Primary methods for chemical modification of waste PE and PP.

Preceding methods to break-down polyolefins (PE and PP) featured uncontrolled, energy intensive ($T \geq 500\text{ }^{\circ}\text{C}$) catalytic pyrolysis methods that yielded complex mixtures of low-value oils and waxes.^{18-19, 89-93} These processes are harsh and, because of the homogeneity of the backbone, lead to a mixture of products with varying degrees of saturation and chain length. Recent catalyst development has afforded some notable improvements. A tandem catalytic approach was recently employed to furnish small molecule alkanes via cross-alkane metathesis (CAM) from waste PE.⁹⁴ Other examples also describe the gasification of PE into syngas which is a useful fuel in the energy industry.⁹⁵⁻⁹⁶ These down-cycling approaches are quite practical since they (1) address the environmental accumulation and (2) transform the plastics into materials that recover some net energy of the initial plastic production. Despite their obvious pragmatism, they ultimately promote damaging carbon emissions (*e.g.* CO_2). Furthermore, there is little to no recovery of any polymerizable monomer species so the process is still linear. Efforts to recover unsaturated monomers using gasification procedures are improving though and a recent report describes the zeo-

lite-catalyzed cold plasma (non-thermal pyrolysis) treatment of waste HDPE resulting in 22-25% ethylene recovery.⁹⁷ Similarly, ionization of PP using inductively coupled plasma gasifies the plastic, with up to 94% propylene recovery. Nevertheless, traditional approaches to chemical recycling are not imagined to be widely implemented for polyolefins due to the high ceiling temperatures (*i.e.* high energy cost) of these polymers which makes the process inherently inefficient.²⁵

On the other hand, there is growing interest to upcycle polyolefin waste into value-added materials (Figure 3). This can proceed by depolymerization to small molecules or *via* catalytic installation of functional groups along the polymer backbone. Recent highlights describe the chemoxidative depolymerizations of PE to yield graphitic carbon⁹⁸ or well-defined dicarboxylic acid small molecules (Figure 3).⁹⁹ Catalytic hydroxylation of polyolefins was initially demonstrated *via* a two-step borylation/oxidation¹⁰⁰⁻¹⁰², but recently the direct hydroxylation of PE and PP was accomplished using a straightforward nickel-catalyzed/*m*CPBA method.¹⁰³ Hydroxylated polyolefins have also been altered into carboxylic acids using elegant photocatalytic processes (Figure 3).¹⁰⁴⁻¹⁰⁵ Other polyolefin modification chemistries include the (chemo-)regio-selective xanthylation¹⁰⁶⁻¹⁰⁷ (which offers ample opportunity for further application/functionalization) and introduction of groups such as: phenylsulfonyls or esters (Figure 3).

Recently, the upcycling of PE waste into high-value linear alkanes with controllable and tunable size distributions was accomplished using well-defined Pt nanoparticles supported on SrTiO_3 -based perovskites.¹⁰⁸ Importantly, the process was conducted at relatively moderate conditions ($300\text{ }^{\circ}\text{C}$, 96 h) showing a distinct improvement on earlier benchmarks. Another promising example describes the efficient ($380\text{-}500\text{ }^{\circ}\text{C}$, 0.5-6 h, 23 MPa) liquification of PP into oil using supercritical water in a reactor.¹⁰⁹ These developments are encouraging, but energy requirements for depolymerization still need to be lowered further to make the processes more economical and successful translation of technology from bench to pilot scale will also be pivotal. Similar to earlier areas, primary gains will undoubtedly come from additional catalyst development. Transitioning to more earth abundant metals (such as manganese or iron¹¹⁰) in catalyst species will be equally crucial in any path to commercializing chemical recycling of polyolefins from both a cost and environmental impact basis. Again, MOFs could offer great opportunity in this sector.

The treatment of waste PS is severely underdeveloped, in fact it is primarily discarded as PCW immediately after use. In addition to its chemical inertness, PS comes in many different physical formulations which hinders its separation in waste streams. It is most recognizable as a foam, referred to as expanded polystyrene (EPS)¹¹¹, but it is

also produced in other higher density formulations. This creates a sorting problem for any recycling approach, leading to abysmal recovery rates.¹¹² Similarly to PE and PP, there are a number of chemical functionalization approaches to PS waste treatment such as: Friedel-Crafts acylation/alkylation, radical halogenation, metalation-electrophilic quenching and perfluoroalkylation, among others.¹¹³⁻¹¹⁵ Besides pyrolysis techniques, there are some older reports of chemical recycling to small molecules using catalytic solid acids or bases (*e.g.* metal oxides or silica) to depolymerize EPS into aromatic hydrocarbon mixtures.¹¹⁶⁻¹²⁰ Sulfonation of waste EPS was also used to afford high-value polyelectrolytes after depolymerization.¹²¹ However, a more recent clever approach to PS recycling transformed the EPS into a value-added thermoset derived from a renewable monomer.¹²² The EPS was dissolved in neat limonene (a renewable terpene) followed by photo-crosslinking of the resin mixture with a multifunctional thiol to afford a robust network material. This innovative approach showcases the promise of alternative chemical recycling methods. Yet, there has been little (translational) progress in the last two decades regarding PS waste treatment.

PVC is a convenient, high-performance polymer but its use is deeply problematic. The presence of plasticizing additives in PVC materials (notably, phthalates and dioxins) along with the propensity to undergo H-Cl elimination upon heat treatment preclude any physical recycling measures.¹²³ These problems can lead to contamination of mixed-plastic waste streams and corrode reprocessing reactors. The state-of-the-art approach to dealing with PVC waste (although not in a currently scalable manner) involves a costly de-chlorination step¹²⁴ (to inhibit formation of acidic decomposition products) followed by catalytic pyrolysis.¹²⁵ The comparatively weak C-Cl bonds in PVC theoretically provide an obvious reactivity point for chemical recycling methods. But, the current bottleneck to innovation is designing catalysts that can cleave the backbone (*e.g.* a CAM-type process⁹⁴) in the presence of substrates (*viz.* HCl) that can easily poison the metal centers. We envision that there could be many lessons and/or materials applied from current CO₂ capture technologies. Amine scrubbing (which offers an economical, reversible approach to capturing acidic products) and other sorbent technologies such as zeolites and MOFs could be useful since they are designed to operate in complex flue gas streams that can contain harsh contaminants such as NO_x and SO_x species.¹²⁶ Chemical recycling methods will undoubtedly play a role in developing solutions to this problematic material, because mechanical recycling is simply an unfeasible approach.

EMERGING MATERIALS

In this final section, we will highlight some promising areas of materials development, beyond traditional ther-

moplastics, that offer potential solutions in the future plastics economy (Figure 4). Thermoset materials (cross-linked *via* covalent networks) are critical in many engineering applications due to their high strength and elasticity. But, because of their permanent covalent networks, they are not amenable to physical recycling or solution processing and mechanical down-cycling (such as cutting/grinding a tyre into smaller pellets) is the optimal outcome for the majority of waste material. Recently, the potential to chemically recycle PCW thermosets has become more approachable as a result of the use of dynamic covalent chemistry in the network, which provides transient crosslinking in these materials and makes them responsive in nature.¹²⁷ A catchall term for materials displaying this reversible crosslinking is covalent adaptable networks (CANs) where the dynamic covalent bonds comprising the network can be controllably biased using specific reaction conditions such as light, heat, or pH (Figure 4a).¹²⁸⁻¹²⁹ More specifically, the dynamic bonds serve as exchangeable anchor points in the network, allowing the bulk material to be remolded or repaired, sometimes without stimulus (self-healing), or without loss of structural integrity (*i.e.* not melted).¹³⁰⁻¹³³ Although many dynamic bonds have featured in CAN materials, complete orthogonal depolymerization to the original monomer(s) is challenging and this complicates further material transformations in the overall recycling process. CANs based on carbonate¹³⁴, imine¹³⁵⁻¹³⁸, urea¹³⁹ ester¹⁴⁰ or thioester¹⁴¹⁻¹⁴² motifs have been depolymerized effectively to yield various oligomers and small molecules. Nevertheless, in a few instances original monomers have been recovered for networks connected employing chemistries such as: acetal¹⁴³, hemi-aminal¹⁴⁴⁻¹⁴⁶, boroxine¹⁴⁷ and olefin metathesis¹⁴⁸.

One of the most important advantages from chemical recycling is the possibility to decouple monomers from material additives; this is a feature that should greatly increase competitiveness in a future economy. Helms and coworkers recently developed an innovative and fully closed-loop recycling of a network plastic material using diketoenamine chemistry where starting monomers could be effectively captured and separated from dyes or fibers in the plastic (Figure 4a).¹⁴⁹ Increasing the overall sustainability of chemically recyclable thermosets is also a major challenge, but recent advancements include a biomass derived recyclable CAN¹⁵⁰ and a CAN featuring reversible imine bonds and biodegradable polyester units.¹⁵¹ Furthermore, there is the possibility to improve physical recycling process by improving the thermal and oxidative stability of materials. A sustainable super engineering plastic, with mechanical properties similar to polyphenylene sulfide (PPS) and polyether ether ketone (PEEK), based on starch-derived isosorbide showed minimal mass or performance loss after repeated melt recycling.¹⁵² The chemical recycling of rubbers and tires via metathesis¹⁵³ or

Diels-Alder¹⁵³⁻¹⁵⁶ chemistries offer interesting approaches beyond forcing devulcanisation methods. Moreover, inversely vulcanized polymers, commonly produced from the copolymerization of unsaturated monomers with excess elemental sulfur, offer an interesting materials platform for dynamically crosslinked materials¹⁵⁷⁻¹⁶¹ since sul-

fur is an abundant feedstock¹⁶² and this class of materials has even been produced on a kilogram scale¹⁶³. In a final example, crosslinked PU foam PCW, which was previously unrecyclable, was recently reprocessed (physically recycled) by adding an organometallic catalyst to enable dynamic carbamate exchange reactions.¹⁶⁴

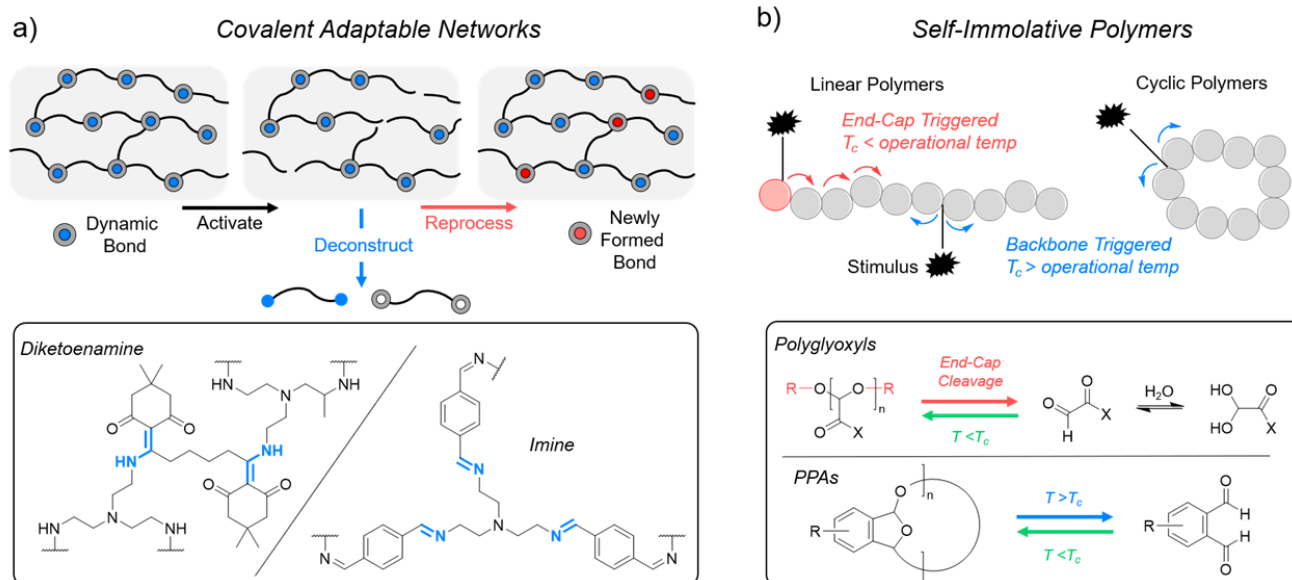


Figure 4. Emerging recycling strategies for next-generation materials a) covalent adaptable networks and b) self-immolative polymers

Self-immolative polymers (SIP) are attracting considerable interest in the materials community since they possess one of the most desirable properties in a consumer plastic – the ability to “trigger” complete depolymerization for on-demand material disposal (Figure 4b).¹⁶⁵ This would circumvent one of the main issues associated with current biodegradable polymers, where their end-of-life environment (especially moisture and temperature) can greatly impact the subsequent degradation kinetics or products. Although SIP degradation is often irreversible (more evocative of biodegradable polymers), it is potentially reversible (*i.e.* chemically recyclable) when monomeric units are recovered. Many reversible SIPs are based on polymers with low ceiling temperatures (T_c), meaning that the spontaneous depolymerization of the polymer begins to occur at or above this temperature, but below this temperature it is stable. The use of a cleavagable end-capping unit on the polymer can also provide adequate chain stability above the respective ceiling temperature which allows for polymers with extremely low ceiling temperatures (for example, $T_c < 20$ °C) to be practical. There are now several classes of reversible SIPs, including polybenzyl ethers (PBEs)¹⁶⁶, polyglyoxylates¹⁶⁷, polyglyoxylamides¹⁶⁸, and polyphthalaldehydes (PPA) (Figure 4b).¹⁶⁹ Furthermore, a growth area for SIPs is within composite materials due to their high recoverability after depolymerization processes.

Attention has also been directed at enhancing material toughness and strength since many non-composite SIPs display poor mechanical properties. Recently, McNeil and coworkers were able to finely modulate ceiling temperature by rational functionalization of the polymer backbone to afford a thermally robust PPA that is a promising thermoplastic material.¹⁷⁰ Additionally, a carbon fiber reinforced PPA composite was fully recycled with quantitative monomer recovery, thus showing that composite engineering will certainly be in play.¹⁷¹ A final important example in the area is a self-amplifying degradable polymer based on the degradation of a 3-iodopropyl acetal moiety.¹⁷² The novelty here is that a catalytic species prompts and accelerates chain cleavage (usually the triggering species is stoichiometric in nature) and each degraded monomer unit produces another equivalent of the same catalyst agent leading to an accelerating degradation event. New depolymerization triggers for SIPs, such as mechanical chain scission (*e.g.* sonication)¹⁷³⁻¹⁷⁴, should also open up interesting applications. We predict that SIPs will have a part in the shifting materials economy.

A final hurdle to achieving a more sustainable material economy is making new plastics that are actually competitive, in terms of thermomechanical properties, to existing commercial plastics. Many novel plastics simply fall short of commodity polymer properties which usually feature the following: low glass transition, high melting

temperature, great ductility, and high tensile strength. Nevertheless, there is progress to be made on this front and replacement materials are improving. Polycarbonates often possess robust thermomechanical properties and there is accelerating research to create them more sustainably, mainly using CO₂/epoxide copolymerization.¹⁷⁵⁻¹⁷⁶ In addition to chemical upcycling opportunities, organobase-promoted recycling to monomer has been demonstrated for sustainably sourced poly(limonene carbonate) (Figure 5).¹⁷⁷ Polyester bioplastics are also maturing as evidenced by the fully recyclable linear polyester reported by Chen and coworkers where they

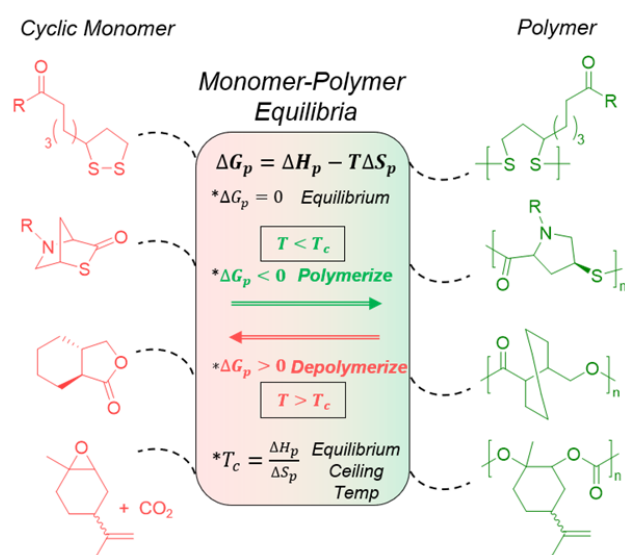


Figure 5. Exemplary novel linear polymers formed from ROP.

described repeated transition metal-catalyzed¹⁷⁸ or organocatalytic¹⁷⁹ chemical recycling of a fused-ring γ -butyrolactone monomer (Figure 5). In a major innovative step, this same monomer was copolymerized with another cyclic lactone to create chemically recyclable materials with barrier and mechanical properties comparable to commodity plastics such as PE or PET.¹⁸⁰ Aromatic polymers such as PET, are renowned for good thermomechanical properties, but most sustainable biopolyesters contain aliphatic backbones. Shaver and coworkers have reported a novel aromatic polyester with full chemical recyclability to monomer.¹⁸¹⁻¹⁸² Such polymers still remain rare, but this study is an important advancement to tougher chemically recyclable plastics.

Chemically recyclable thermoplastics should gain traction as new polymers existing near thermodynamic equilibrium (polymerization/depolymerization reaction) are continually developed.¹⁸³ Significant advancements in the field trend toward the use of cyclic monomers capable of ring-opening polymerization (ROP) where the thermodynamic parameters¹⁸⁴ or reaction conditions¹⁸⁵ can be judi-

ciously adjusted to control monomer/polymer equilibrium (Figure 5). In fact, there are fresh, intriguing monomers that have been used for dynamic ROP. A naturally occurring cyclic disulfide monomer that reversibly forms poly(disulfides) was used for switchable architectural control (cyclic *versus* linear), including reversible supramolecular network formation (Figure 5).¹⁸⁶⁻¹⁸⁷ Sustainably sourced thiolactones synthesized from collagen derived 4-hydroxyproline¹⁸⁸ (Figure 5) or the naturally occurring amino acid penicillamine¹⁸⁹, exhibited high polymerizability and the resultant polythioesters could be catalytically depolymerized back to thiolactones for subsequent polymerization. A recent exciting example employs a scalable bridged bicyclic thiolactone monomer to afford stereocontrolled polythioesters with robust thermomechanical properties and maintenance of intrinsic chemical recyclability.¹⁹⁰ These innovative examples offer the prospect of robust chemically recyclable plastics and lead the field ahead, beyond the first-generation bio-polyesters formed from cyclic lactones such as lactide or ϵ -caprolactone.¹⁹¹

OUTLOOK

Despite the pervasive issues associated with plastics usage, it would be naïve to speculate a transition to a “plastic-free” society since they are so critical to current (and future) infrastructures. Plastics have revolutionized modern society and we cannot do without them, nor should we try. Nevertheless, it remains acutely imperative to address the poor sustainability. Ultimately, new materials will be essential to advancing the sustainable materials economy by delivering polymers that are actually designed for recyclability, reducing our reliance on fossil sources, and increasing their overall biodegradability. Ensuring that these plastics will eventually biodegrade should be a priority for all newly designed formulations since any closed-loop, circular economy process is bound to suffer from material leakage and the products will eventually reach end-of-life regardless of salvage efforts. Infinitely recyclable renewable bio-polyesters¹⁹² could satisfy most of these requirements, but more work is warranted to address their inferior thermomechanical properties before wider implementation and adoption.

The development of more efficient, selective, and low energy chemical recycling processes will be required to lessen the complicating impact this could introduce into recycling systems, as well as to deal with our legacy PCW plastic from petroleum sources. Many catalytic chemical recycling technologies are immature when compared to thermal pyrolytic methods and physical recycling. While commercial scale catalytic chemical recycling processes are being pioneered for materials such as PET¹⁹³, it will be prudent to apply these lessons to other materials, both present and future. We propose several desirable targets for depolymerization conditions that serve as a research

directive and target for groups in the field to identify and encourage industrially viable processes:

- 1) High reaction efficiency under mild conditions (temperature < 100 °C, time ≤ 1 h)
- 2) Reaction selectivity (reaction products ≥ 95 % purity, < 5 per plastic)
- 3) Catalyst tolerance (minimal interaction and/or deactivation by contaminants, especially additional plastics, additives or food waste)
- 4) Catalyst recyclability (suitable for repeated batch reactions or flow chemistry processes)

Even though the challenges to recycling are not identical among different cities, regions, or countries in the world, there remains a ubiquitous lack of infrastructure for collecting, sorting and storing PCW plastic streams and/or their depolymerized resins. Nevertheless, innovations regarding catalyst development are accelerating and chemo-selective technologies to handle mixed-waste streams containing different classes of polymers would be a watershed moment for the field. In spite of these challenges, chemical recycling technologies hold considerable potential to modernize the plastics industry.

Recent public engagement on our relationship with plastics is reassuring. However, we must be careful about impulsive policy reactions in response to this civic sentiment, which has been overwhelmingly negative. Much of the reason for this backlash can be attributed to the emotive consequences of seeing plastic within and negatively

affecting our environment. Positive perceptions toward plastics have been lost, but plastics are not inherently the problem. Instead, how we choose to use them, and more importantly dispose of them, determines their impact. Better communication and advocacy of the importance of plastics combined with highlighting the problems and emerging solutions associated with their use will allow for a more constructive dialogue moving forward. This will be especially important when engaging with policy makers on future matters.

Long-lasting resolutions to the plastics problem will likely be found in eventually replacing many of our current materials with sustainable alternatives, however their adoption will almost certainly require sizeable subsidies, along with tax and policy changes, to make them economically competitive. And, it will certainly require time. Our existing plastics technological infrastructure will not be replaced with swiftness. An increase in polyester-based materials, for example, could complicate existing sorting and recycling efforts but considering chemical recycling at the heart of a purpose-designed recycling industry will leverage opportunities to chemically sort materials into single products. Even if (or when) these approaches are adopted, we will still be left with millions up millions of tonnes of legacy plastics. As dire as that may sound, there is a great opportunity for chemical recycling technologies to repurpose our PCW plastic by creating chemicals of intrinsic value in a fresher, greener economical approach.

REFERENCES

- (1) Jambeck, J. R.; Geyer, R.; Wilcox, C.; Siegler, T. R.; Perryman, M.; Andrady, A.; Narayan, R.; Law, K. L., Plastic Waste Inputs from Land into the Ocean. *Science* **2015**, *347* (6223), 768.
- (2) Geyer, R.; Jambeck, J. R.; Law, K. L., Production, Use, and Fate of All Plastics Ever Made. *Science Adv.* **2017**, *3* (7), e1700782.
- (3) Rieger, B.; Künkel, A.; Coates, G. W.; Reichardt, R.; Dinjus, E.; Zevaco, T. A., *Synthetic Biodegradable Polymers*. Springer-Verlag: Berlin, Heidelberg, 2012.
- (4) Bioplastics Market Data 2019, European Bioplastics. <https://www.european-bioplastics.org/market/>.
- (5) Mathers, R. T., How Well Can Renewable Resources Mimic Commodity Monomers and Polymers? *J. Polym. Sci. A. Polym. Chem.* **2012**, *50* (1), 1-15.
- (6) Haider, T. P.; Völker, C.; Kramm, J.; Landfester, K.; Wurm, F. R., Plastics of the Future? The Impact of Biodegradable Polymers on the Environment and on Society. *Angew. Chem. Int. Ed.* **2019**, *58* (1), 50-62.
- (7) Napper, I. E.; Thompson, R. C., Environmental Deterioration of Biodegradable, Oxo-Biodegradable, Compostable, and Conventional Plastic Carrier Bags in the Sea, Soil, and Open-Air over a 3-Year Period. *Environ. Sci. Technol.* **2019**, *53* (9), 4775-4783.
- (8) Hottle, T. A.; Bilec, M. M.; Landis, A. E., Sustainability Assessments of Bio-Based Polymers. *Polym. Degrad. Stab.* **2013**, *98* (9), 1898-1907.
- (9) Singh, N.; Hui, D.; Singh, R.; Ahuja, I. P. S.; Feo, L.; Fraternali, F., Recycling of Plastic Solid Waste: A State of Art Review and Future Applications. *Compos. B. Eng.* **2017**, *115*, 409-422.
- (10) *Oecd (2020), Environment at a Glance 2020*; Paris, <https://doi.org/10.1787/4ea7d35f-en>.
- (11) Hahladakis, J. N.; Velis, C. A.; Weber, R.; Iacovidou, E.; Purnell, P., An Overview of Chemical Additives Present in Plastics: Migration, Release, Fate and Environmental Impact During Their Use, Disposal and Recycling. *J. Hazard. Mater.* **2018**, *344*, 179-199.
- (12) *The New Plastics Economy - Rethinking the Future of Plastics*; World Economic Forum, Ellen MacArthur Foundation, McKinsey & Company: 2016;
- (13) *Handbook of Plastics Recycling*. Smithers Rapra: Shrewsbury, UK, 2002.
- (14) Ragaert, K.; Delva, L.; Van Geem, K., Mechanical and Chemical Recycling of Solid Plastic Waste. *Waste Manag. Res.* **2017**, *69*, 24-58.
- (15) Saito, K.; Jehanno, C.; Meabe, L.; Olmedo-Martínez, J. L.; Mecerreyes, D.; Fukushima, K.; Sardon, H., From Plastic Waste to Polymer Electrolytes for Batteries through Chemical Upcycling of Polycarbonate. *J. Mater. Chem. A* **2020**, *8* (28), 13921-13926.

- (16) Kalmykova, Y.; Sadagopan, M.; Rosado, L., Circular Economy – from Review of Theories and Practices to Development of Implementation Tools. *Resour. Conserv. Recycl.* **2018**, *135*, 190-201.
- (17) Bucknall, D. G., Plastics as a Materials System in a Circular Economy. *Philos. Trans. R. Soc. London, A* **2020**, *378* (2176), 20190268.
- (18) Burange, A. S.; Gawande, M. B.; Lam, F. L. Y.; Jayaram, R. V.; Luque, R., Heterogeneously Catalyzed Strategies for the Deconstruction of High Density Polyethylene: Plastic Waste Valorisation to Fuels. *Green Chem.* **2015**, *17* (1), 146-156.
- (19) Chandrasekaran, S. R.; Kunwar, B.; Moser, B. R.; Rajagopalan, N.; Sharma, B. K., Catalytic Thermal Cracking of Postconsumer Waste Plastics to Fuels. 1. Kinetics and Optimization. *Energy Fuels* **2015**, *29* (9), 6068-6077.
- (20) Hong, M.; Chen, E. Y. X., Chemically Recyclable Polymers: A Circular Economy Approach to Sustainability. *Green Chem.* **2017**, *19* (16), 3692-3706.
- (21) Jehanno, C.; Pérez-Madrigal, M. M.; Demartean, J.; Sardon, H.; Dove, A. P., Organocatalysis for Depolymerisation. *Polym. Chem.* **2019**, *10* (2), 172-186.
- (22) García, J. M., Catalyst: Design Challenges for the Future of Plastics Recycling. *Chem* **2016**, *1* (6), 813-815.
- (23) Rahimi, A.; García, J. M., Chemical Recycling of Waste Plastics for New Materials Production. *Nat. Rev. Chem.* **2017**, *1*, 0046.
- (24) Schneiderman, D. K.; Hillmyer, M. A., 50th Anniversary Perspective: There Is a Great Future in Sustainable Polymers. *Macromolecules* **2017**, *50* (10), 3733-3749.
- (25) Coates, G. W.; Getzler, Y. D. Y. L., Chemical Recycling to Monomer for an Ideal, Circular Polymer Economy. *Nat. Rev. Mater.* **2020**.
- (26) Kaminsky, W., *Polyolefins: 50 Years after Ziegler and Natta*. Springer-Verlag: Berlin Heidelberg, 2013.
- (27) Kuczynski, B.; Geyer, R., Material Flow Analysis of Polyethylene Terephthalate in the Us, 1996-2007. *Resour. Conserv. Recycl.* **2010**, *54* (12), 1161-1169.
- (28) Ghosh, S.; Makeev, M. A.; Qi, Z.; Wang, H.; Rajput, N. N.; Martha, S. K.; Pol, V. G., Rapid Upcycling of Waste Polyethylene Terephthalate to Energy Storing Disodium Terephthalate Flowers with Dft Calculations. *ACS Sustainable Chem. Eng.* **2020**, *8* (16), 6252-6262.
- (29) Tang, H.; Li, N.; Li, G.; Wang, A.; Cong, Y.; Xu, G.; Wang, X.; Zhang, T., Synthesis of Gasoline and Jet Fuel Range Cycloalkanes and Aromatics from Poly(Ethylene Terephthalate) Waste. *Green Chem.* **2019**, *21* (10), 2709-2719.
- (30) Fuentes, J. A.; Smith, S. M.; Scharbert, M. T.; Carpenter, I.; Cordes, D. B.; Slawin, A. M. Z.; Clarke, M. L., On the Functional Group Tolerance of Ester Hydrogenation and Polyester Depolymerisation Catalysed by Ruthenium Complexes of Tridentate Aminophosphine Ligands. *Chem.-Eur. J.* **2015**, *21* (30), 10851-10860.
- (31) Krall, E. M.; Klein, T. W.; Andersen, R. J.; Nett, A. J.; Glasgow, R. W.; Reader, D. S.; Dauphinais, B. C.; Mc Ilrath, S. P.; Fischer, A. A.; Carney, M. J.; Hudson, D. J.; Robertson, N. J., Controlled Hydrogenative Depolymerization of Polyesters and Polycarbonates Catalyzed by Ruthenium(II) Pincer Complexes. *Chem. Commun.* **2014**, *50* (38), 4884-4887.
- (32) Kratish, Y.; Li, J.; Liu, S.; Gao, Y.; Marks, T. J., Polyethylene Terephthalate Deconstruction Catalyzed by a Carbon-Supported Single-Site Molybdenum-Dioxo Complex. *Angew. Chem. Int. Ed.* **2020**, *n/a* (n/a).
- (33) Westhues, S.; Idel, J.; Klankermayer, J., Molecular Catalyst Systems as Key Enablers for Tailored Polyesters and Polycarbonate Recycling Concepts. *Science Adv.* **2018**, *4* (8), 10.1126/sciadv.aat9669.
- (34) Geyer, B.; Lorenz, G.; Kandelbauer, A., Recycling of Poly(Ethylene Terephthalate) – a Review Focusing on Chemical Methods. *Express Polym. Lett.* **2016**, *10*, 559-586.
- (35) Adams, C. J.; Earle, M. J.; Seddon, K. R., Catalytic Cracking Reactions of Polyethylene to Light Alkanes in Ionic Liquids. *Green Chem.* **2000**, *2* (1), 21-24.
- (36) Wang, H.; Li, Z.; Liu, Y.; Zhang, X.; Zhang, S., Degradation of Poly(Ethylene Terephthalate) Using Ionic Liquids. *Green Chem.* **2009**, *11* (10), 1568-1575.
- (37) Nunes, C. S.; Vieira da Silva, M. J.; Cristina da Silva, D.; Freitas, A. d. R.; Rosa, F. A.; Rubira, A. F.; Muniz, E. C., Pet Depolymerisation in Supercritical Ethanol Catalysed by [Bmim][Bf4]. *RSC Adv.* **2014**, *4* (39), 20308-20316.
- (38) Wang, Q.; Yao, X.; Tang, S.; Lu, X.; Zhang, X.; Zhang, S., Urea as an Efficient and Reusable Catalyst for the Glycolysis of Poly(Ethylene Terephthalate) Wastes and the Role of Hydrogen Bond in This Process. *Green Chem.* **2012**, *14* (9), 2559-2566.
- (39) Sun, J.; Liu, D.; Young, R. P.; Cruz, A. G.; Isern, N. G.; Schuerg, T.; Cort, J. R.; Simmons, B. A.; Singh, S., Solubilization and Upgrading of High Polyethylene Terephthalate Loadings in a Low-Costing Bifunctional Ionic Liquid. *ChemSusChem* **2018**, *11* (4), 781-792.
- (40) Zhou, L.; Lu, X.; Ju, Z.; Liu, B.; Yao, H.; Xu, J.; Zhou, Q.; Hu, Y.; Zhang, S., Alcoholysis of Polyethylene Terephthalate to Produce Diethyl Terephthalate Using Choline Chloride-Based Deep Eutectic Solvents as Efficient Catalysts. *Green Chem.* **2019**, *21* (4), 897-906.
- (41) Fukushima, K.; Coulembier, O.; Lecuyer, J. M.; Almegren, H. A.; Alabdulrahman, A. M.; Alsewaleem, F. D.; McNeil, M. A.; Dubois, P.; Waymouth, R. M.; Horn, H. W.; Rice, J. E.; Hedrick, J. L., Organocatalytic Depolymerization of Poly(Ethylene Terephthalate). *J. Polym. Sci. A. Polym. Chem.* **2011**, *49* (5), 1273-1281.
- (42) Horn, H. W.; Jones, G. O.; Wei, D. S.; Fukushima, K.; Lecuyer, J. M.; Coady, D. J.; Hedrick, J. L.; Rice, J. E., Mechanisms of Organocatalytic Amidation and Trans-Esterification of Aromatic Esters as a Model for the Depolymerization of Poly(Ethylene) Terephthalate. *J. Phys. Chem. A* **2012**, *116* (51), 12389-12398.
- (43) Gardea, F.; Garcia, J. M.; Boday, D. J.; Bajjuri, K. M.; Naraghi, M.; Hedrick, J. L., Hybrid Poly(Aryl Ether Sulfone Amide)S for Advanced Thermoplastic Composites. *Macromol. Chem. Phys.* **2014**, *215* (22), 2260-2267.
- (44) Fukushima, K.; Coady, D. J.; Jones, G. O.; Almegren, H. A.; Alabdulrahman, A. M.; Alsewaleem, F. D.; Horn, H. W.; Rice, J. E.; Hedrick, J. L., Unexpected Efficiency of Cyclic Amidine Catalysts in Depolymerizing Poly(Ethylene Terephthalate). *J. Polym. Sci. A. Polym. Chem.* **2013**, *51* (7), 1606-1611.
- (45) Jehanno, C.; Flores, I.; Dove, A. P.; Müller, A. J.; Ruipérez, F.; Sardon, H., Organocatalysed Depolymerisation of Pet in a

Fully Sustainable Cycle Using Thermally Stable Protic Ionic Salt. *Green Chem.* **2018**, *20* (6), 1205-1212.

(46) Basterretxea, A.; Jehanno, C.; Mecerreyes, D.; Sardon, H., Dual Organocatalysts Based on Ionic Mixtures of Acids and Bases: A Step toward High Temperature Polymerizations. *ACS Macro Lett.* **2019**, *8* (8), 1055-1062.

(47) <https://plasticsrecycling.org/pet-design-guide> (accessed September 24 2020).

(48) Liu, F.; Li, Z.; Yu, S.; Cui, X.; Ge, X., Environmentally Benign Methanolysis of Polycarbonate to Recover Bisphenol a and Dimethyl Carbonate in Ionic Liquids. *J. Hazard. Mater.* **2010**, *174* (1), 872-875.

(49) Liu, M.; Guo, J.; Gu, Y.; Gao, J.; Liu, F., Degradation of Waste Polycarbonate Via Hydrolytic Strategy to Recover Monomer (Bisphenol a) Catalyzed by Dbu-Based Ionic Liquids under Metal- and Solvent-Free Conditions. *Polym. Degrad. Stab.* **2018**, *157*, 9-14.

(50) Liu, M.; Guo, J.; Gu, Y.; Gao, J.; Liu, F.; Yu, S., Pushing the Limits in Alcoholysis of Waste Polycarbonate with Dbu-Based Ionic Liquids under Metal- and Solvent-Free Conditions. *ACS Sustainable Chem. Eng.* **2018**, *6* (10), 13114-13121.

(51) Guo, J.; Liu, M.; Gu, Y.; Wang, Y.; Gao, J.; Liu, F., Efficient Alcoholysis of Polycarbonate Catalyzed by Recyclable Lewis Acidic Ionic Liquids. *Ind. Eng. Chem. Res.* **2018**, *57* (32), 10915-10921.

(52) Quaranta, E.; Sgherza, D.; Tartaro, G., Depolymerization of Poly(Bisphenol a Carbonate) under Mild Conditions by Solvent-Free Alcoholysis Catalyzed by 1,8-Diazabicyclo[5.4.0]Undec-7-Ene as a Recyclable Organocatalyst: A Route to Chemical Recycling of Waste Polycarbonate. *Green Chem.* **2017**, *19* (22), 5422-5434.

(53) Do, T.; Baral, E. R.; Kim, J. G., Chemical Recycling of Poly(Bisphenol a Carbonate): 1,5,7-Triazabicyclo[4.4.0]-Dec-5-Ene Catalyzed Alcoholysis for Highly Efficient Bisphenol a and Organic Carbonate Recovery. *Polymer* **2018**, *143*, 106-114.

(54) Quaranta, E.; Minischetti, C. C.; Tartaro, G., Chemical Recycling of Poly(Bisphenol a Carbonate) by Glycolysis under 1,8-Diazabicyclo[5.4.0]Undec-7-Ene Catalysis. *ACS Omega* **2018**, *3* (7), 7261-7268.

(55) Singh, R.; Shahi, S.; Geetanjali, Chemical Degradation of Poly(Bisphenol a Carbonate) Waste Materials: A Review. *ChemistrySelect* **2018**, *3* (42), 11957-11962.

(56) Jones, G. O.; Yuen, A.; Wojtecki, R. J.; Hedrick, J. L.; Garcia, J. M., Computational and Experimental Investigations of One-Step Conversion of Poly(Carbonate)S into Value-Added Poly(Aryl Ether Sulfone)S. *Proc. Natl. Acad. Sci. U.S.A.* **2016**, *113* (28), 7722.

(57) Jehanno, C.; Demartean, J.; Mantione, D.; Arno, M. C.; Ruipérez, F.; Hedrick, J. L.; Dove, A. P.; Sardon, H., Synthesis of Functionalized Cyclic Carbonates through Commodity Polymer Upcycling. *ACS Macro Lett.* **2020**, *9* (4), 443-447.

(58) Simón, D.; Borreguero, A. M.; de Lucas, A.; Rodríguez, J. F., Recycling of Polyurethanes from Laboratory to Industry, a Journey Towards the Sustainability. *Waste Manag. Res.* **2018**, *76*, 147-171.

(59) Wang, X.; Chen, H.; Chen, C.; Li, H., Chemical Degradation of Thermoplastic Polyurethane for Recycling Polyether Polyol. *Fibers and Polymers* **2011**, *12* (7), 857.

(60) Borda, J.; Pásztor, G.; Zsuga, M., Glycolysis of Polyurethane Foams and Elastomers. *Polym. Degrad. Stab.* **2000**, *68* (3), 419-422.

(61) Kopczyńska, P.; Calvo-Correas, T.; Eceiza, A.; Datta, J., Synthesis and Characterisation of Polyurethane Elastomers with Semi-Products Obtained from Polyurethane Recycling. *Eur. Polym. J.* **2016**, *85*, 26-37.

(62) Simón, D.; Borreguero, A. M.; de Lucas, A.; Rodríguez, J. F., Glycolysis of Viscoelastic Flexible Polyurethane Foam Wastes. *Polym. Degrad. Stab.* **2015**, *116*, 23-35.

(63) Zhu, P.; Cao, Z. B.; Chen, Y.; Zhang, X. J.; Qian, G. R.; Chu, Y. L.; Zhou, M., Glycolysis Recycling of Rigid Waste Polyurethane Foam from Refrigerators. *Environ. Technol.* **2014**, *35* (21), 2676-2684.

(64) Simón, D.; de Lucas, A.; Rodríguez, J. F.; Borreguero, A. M., Flexible Polyurethane Foams Synthesized Employing Recovered Polyols from Glycolysis: Physical and Structural Properties. *J. Appl. Polym. Sci.* **2017**, *134* (32), 45087.

(65) Simón, D.; de Lucas, A.; Rodríguez, J. F.; Borreguero, A. M., Glycolysis of High Resilience Flexible Polyurethane Foams Containing Polyurethane Dispersion Polyol. *Polym. Degrad. Stab.* **2016**, *133*, 119-130.

(66) Wang, Y.; Song, H.; Ge, H.; Wang, J.; Wang, Y.; Jia, S.; Deng, T.; Hou, X., Controllable Degradation of Polyurethane Elastomer Via Selective Cleavage of Co and Cn Bonds. *Journal of Cleaner Production* **2018**, *176*, 873-879.

(67) Kathalewar, M. S.; Joshi, P. B.; Sabnis, A. S.; Malshe, V. C., Non-Isocyanate Polyurethanes: From Chemistry to Applications. *RSC Adv.* **2013**, *3* (13), 4110-4129.

(68) Shukla, S. R.; Harad, A. M.; Mahato, D., Depolymerization of Nylon 6 Waste Fibers. *J. Appl. Polym. Sci.* **2006**, *100* (1), 186-190.

(69) Klun, U.; Kržan, A., Rapid Microwave Induced Depolymerization of Polyamide-6. *Polymer* **2000**, *41* (11), 4361-4365.

(70) Kaiso, K.; Sugimoto, T.; Kashiwagi, K.; Kamimura, A., Effective Depolymerization of Nylon-6 in Wet Supercritical Hydrocarbons. *Chem. Lett.* **2011**, *40* (4), 370-371.

(71) Kamimura, A.; Oishi, Y.; Kaiso, K.; Sugimoto, T.; Kashiwagi, K., Supercritical Secondary Alcohols as Useful Media to Convert Polyamide into Monomeric Lactams. *ChemSusChem* **2008**, *1* (1-2), 82-84.

(72) Kamimura, A.; Shiramatsu, Y.; Kawamoto, T., Depolymerization of Polyamide 6 in Hydrophilic Ionic Liquids. *Green Energy Environ.* **2019**, *4* (2), 166-170.

(73) Yamamoto, S.; Kamimura, A., Preparation of Novel Functionalized Ammonium Salts That Effectively Catalyze Depolymerization of Nylon-6 in Ionic Liquids. *Chem. Lett.* **2009**, *38* (11), 1016-1017.

(74) Kamimura, A.; Yamamoto, S., A Novel Depolymerization of Nylons in Ionic Liquids. *Polym. Adv. Technol.* **2008**, *19* (10), 1391-1395.

(75) Kamimura, A.; Yamamoto, S., An Efficient Method to Depolymerize Polyamide Plastics: A New Use of Ionic Liquids. *Org. Lett.* **2007**, *9* (13), 2533-2535.

(76) Kamimura, A.; Ikeda, K.; Suzuki, S.; Kato, K.; Akinari, Y.; Sugimoto, T.; Kashiwagi, K.; Kaiso, K.; Matsumoto, H.;

- Yoshimoto, M., Efficient Conversion of Polyamides to Ω -Hydroxyalkanoic Acids: A New Method for Chemical Recycling of Waste Plastics. *ChemSusChem* **2014**, *7* (9), 2473-2477.
- (77) Kamimura, A.; Kaiso, K.; Suzuki, S.; Oishi, Y.; Ohara, Y.; Sugimoto, T.; Kashiwagi, K.; Yoshimoto, M., Direct Conversion of Polyamides to Ω -Hydroxyalkanoic Acid Derivatives by Using Supercritical Meoh. *Green Chem.* **2011**, *13* (8), 2055-2061.
- (78) Matsumoto, H.; Akinari, Y.; Kaiso, K.; Kamimura, A., Efficient Depolymerization and Chemical Conversion of Polyamide 66 to 1,6-Hexanediol. *Journal of Material Cycles and Waste Management* **2017**, *19* (1), 326-331.
- (79) Kárpáti, L.; Fogarassy, F.; Kovácsik, D.; Vargha, V., One-Pot Depolymerization and Polycondensation of Pet Based Random Oligo- and Polyesters. *J. Polym. Environ.* **2019**, *27* (10), 2167-2181.
- (80) Rogge, S. M. J.; Bavykina, A.; Hajek, J.; Garcia, H.; Olivos-Suarez, A. I.; Sepúlveda-Escribano, A.; Vimont, A.; Clet, G.; Bazin, P.; Kapteijn, F.; Daturi, M.; Ramos-Fernandez, E. V.; Llabrés i Xamena, F. X.; Van Speybroeck, V.; Gascon, J., Metal-Organic and Covalent Organic Frameworks as Single-Site Catalysts. *Chem. Soc. Rev.* **2017**, *46* (11), 3134-3184.
- (81) Goetjen, T. A.; Liu, J.; Wu, Y.; Sui, J.; Zhang, X.; Hupp, J. T.; Farha, O. K., Metal-Organic Framework (Mof) Materials as Polymerization Catalysts: A Review and Recent Advances. *Chem. Commun.* **2020**, *56* (72), 10409-10418.
- (82) Schmidt, B. V. K. J., Metal-Organic Frameworks in Polymer Science: Polymerization Catalysis, Polymerization Environment, and Hybrid Materials. *Macromol. Rapid Commun.* **2019**, *n/a* (n/a), 1900333.
- (83) Mochizuki, S.; Kitao, T.; Uemura, T., Controlled Polymerizations Using Metal-Organic Frameworks. *Chem. Commun.* **2018**, *54* (84), 11843-11856.
- (84) Henckens, M. L. C. M.; Driessen, P. P. J.; Worrell, E., Metal Scarcity and Sustainability, Analyzing the Necessity to Reduce the Extraction of Scarce Metals. *Resour. Conserv. Recycl.* **2014**, *93*, 1-8.
- (85) Dubey, R. J. C.; Comito, R. J.; Wu, Z.; Zhang, G.; Rieth, A. J.; Hendon, C. H.; Miller, J. T.; Dincă, M., Highly Stereoselective Heterogeneous Diene Polymerization by Co-Mfu-4l: A Single-Site Catalyst Prepared by Cation Exchange. *J. Am. Chem. Soc.* **2017**, *139* (36), 12664-12669.
- (86) Manna, K.; Ji, P.; Lin, Z.; Greene, F. X.; Urban, A.; Thacker, N. C.; Lin, W., Chemoselective Single-Site Earth-Abundant Metal Catalysts at Metal-Organic Framework Nodes. *Nature Commun.* **2016**, *7* (1), 12610.
- (87) Comito, R. J.; Fritzsche, K. J.; Sundell, B. J.; Schmidt-Rohr, K.; Dincă, M., Single-Site Heterogeneous Catalysts for Olefin Polymerization Enabled by Cation Exchange in a Metal-Organic Framework. *J. Am. Chem. Soc.* **2016**, *138* (32), 10232-10237.
- (88) Chuck, C. J.; Davidson, M. G.; Jones, M. D.; Kociok-Köhn, G.; Lunn, M. D.; Wu, S., Air-Stable Titanium Alkoxide Based Metal-Organic Framework as an Initiator for Ring-Opening Polymerization of Cyclic Esters. *Inorg. Chem.* **2006**, *45* (17), 6595-6597.
- (89) Wong, S.; Ngadi, N.; Tuan Abdullah, T. A.; Inuwa, I. M., Catalytic Cracking of Ldpe Dissolved in Benzene Using Nickel-Impregnated Zeolites. *Ind. Eng. Chem. Res.* **2016**, *55* (9), 2543-2555.
- (90) Karisathan Sundararajan, N.; Ramachandran Bhagavathi, A., Experimental Investigation on Thermocatalytic Pyrolysis of Hdpe Plastic Waste and the Effects of Its Liquid Yield over the Performance, Emission, and Combustion Characteristics of Ci Engine. *Energy Fuels* **2016**, *30* (7), 5379-5390.
- (91) Achilias, D. S. e. a., Chapter 1: Recent Advances in the Chemical Recycling of Polymers. In *Material Recycling: Trends and Perspectives*, Achilias, D. S., Ed. InTech: Rijeka, Croatia, 2012.
- (92) Mastral, J. F.; Berrueco, C.; Gea, M.; Ceamanos, J., Catalytic Degradation of High Density Polyethylene over Nanocrystalline Hzsm-5 Zeolite. *Polym. Degrad. Stab.* **2006**, *91* (12), 3330-3338.
- (93) Aguado, R.; Olazar, M.; San José, M. J.; Gaisán, B.; Bilbao, J., Wax Formation in the Pyrolysis of Polyolefins in a Conical Spouted Bed Reactor. *Energy Fuels* **2002**, *16* (6), 1429-1437.
- (94) Jia, X.; Qin, C.; Friedberger, T.; Guan, Z.; Huang, Z., Efficient and Selective Degradation of Polyethylenes into Liquid Fuels and Waxes under Mild Conditions. *Science Adv.* **2016**, *2* (6), e1501591.
- (95) Yao, D.; Yang, H.; Chen, H.; Williams, P. T., Investigation of Nickel-Impregnated Zeolite Catalysts for Hydrogen/Syngas Production from the Catalytic Reforming of Waste Polyethylene. *Appl. Catal., B* **2018**, *227*, 477-487.
- (96) Singh, P.; Déparrois, N.; Burra, K. G.; Bhattacharya, S.; Gupta, A. K., Energy Recovery from Cross-Linked Polyethylene Wastes Using Pyrolysis and Co₂ Assisted Gasification. *Appl. Energy* **2019**, *254*, 113722.
- (97) Diaz-Silvarrey, L. S.; Zhang, K.; Phan, A. N., Monomer Recovery through Advanced Pyrolysis of Waste High Density Polyethylene (Hdpe). *Green Chem.* **2018**, *20* (8), 1813-1823.
- (98) Choi, D.; Jang, D.; Joh, H.-I.; Reichmanis, E.; Lee, S., High Performance Graphitic Carbon from Waste Polyethylene: Thermal Oxidation as a Stabilization Pathway Revisited. *Chem. Mater.* **2017**, *29* (21), 9518-9527.
- (99) Bäckström, E.; Odelius, K.; Hakkarainen, M., Trash to Treasure: Microwave-Assisted Conversion of Polyethylene to Functional Chemicals. *Ind. Eng. Chem. Res.* **2017**, *56* (50), 14814-14821.
- (100) Shin, J.; Chang, A. Y.; Brownell, L. V.; Racoma, I. O.; Ozawa, C. H.; Chung, H.-Y.; Peng, S.; Bae, C., Hydrophilic Graft Modification of a Commercial Crystalline Polyolefin. *J. Polym. Sci. A Polym. Chem.* **2008**, *46* (11), 3533-3545.
- (101) Bae, C.; Hartwig, J. F.; Boen Harris, N. K.; Long, R. O.; Anderson, K. S.; Hillmyer, M. A., Catalytic Hydroxylation of Polypropylenes. *J. Am. Chem. Soc.* **2005**, *127* (2), 767-776.
- (102) Bae, C.; Hartwig, J. F.; Chung, H.; Harris, N. K.; Switek, K. A.; Hillmyer, M. A., Regiospecific Side-Chain Functionalization of Linear Low-Density Polyethylene with Polar Groups. *Angew. Chem. Int. Ed.* **2005**, *44* (39), 6410-6413.
- (103) Bunesco, A.; Lee, S.; Li, Q.; Hartwig, J. F., Catalytic Hydroxylation of Polyethylenes. *ACS Cent. Sci.* **2017**, *3* (8), 895-903.
- (104) Jiao, X.; Zheng, K.; Chen, Q.; Li, X.; Li, Y.; Shao, W.; Xu, J.; Zhu, J.; Pan, Y.; Sun, Y.; Xie, Y., Photocatalytic Conversion of Waste Plastics into C₂ Fuels under Simulated Natural Environment Conditions. *Angew. Chem. Int. Ed.* **2020**, *n/a* (n/a).
- (105) Gazi, S.; Đokić, M.; Chin, K. F.; Ng, P. R.; Soo, H. S., Visible Light-Driven Cascade Carbon-Carbon Bond Scission for Organic

- Transformations and Plastics Recycling. *Adv. Science* **2019**, *6* (24), 1902020.
- (106) Williamson, J. B.; Czaplinski, W. L.; Alexanian, E. J.; Leibfarth, F. A., Regioselective C–H Xanthylation as a Platform for Polyolefin Functionalization. *Angew. Chem. Int. Ed.* **2018**, *57* (21), 6261–6265.
- (107) Williamson, J. B.; Na, C. G.; Johnson, R. R.; Daniel, W. F. M.; Alexanian, E. J.; Leibfarth, F. A., Chemo- and Regioselective Functionalization of Isotactic Polypropylene: A Mechanistic and Structure–Property Study. *J. Am. Chem. Soc.* **2019**, *141* (32), 12815–12823.
- (108) Celik, G.; Kennedy, R. M.; Hackler, R. A.; Ferrandon, M.; Tennakoon, A.; Patnaik, S.; LaPointe, A. M.; Ammal, S. C.; Heyden, A.; Perras, F. A.; Pruski, M.; Scott, S. L.; Poepelmeier, K. R.; Sadow, A. D.; Delferro, M., Upcycling Single-Use Polyethylene into High-Quality Liquid Products. *ACS Cent. Sci.* **2019**.
- (109) Chen, W.-T.; Jin, K.; Linda Wang, N.-H., Use of Supercritical Water for the Liquefaction of Polypropylene into Oil. *ACS Sustainable Chem. Eng.* **2019**, *7* (4), 3749–3758.
- (110) Gorgas, N.; Kirchner, K., Isoelectronic Manganese and Iron Hydrogenation/Dehydrogenation Catalysts: Similarities and Divergences. *Acc. Chem. Res.* **2018**, *51* (6), 1558–1569.
- (111) Ramli Sulong, N. H.; Mustapa, S. A. S.; Abdul Rashid, M. K., Application of Expanded Polystyrene (Eps) in Buildings and Constructions: A Review. *J. Appl. Polym. Sci.* **2019**, *136* (20), 47529.
- (112) Maharana, T.; Negi, Y. S.; Mohanty, B., Review Article: Recycling of Polystyrene. *Polym.-Plast. Technol. Eng.* **2007**, *46* (7), 729–736.
- (113) Williamson, J. B.; Lewis, S. E.; Johnson Iii, R. R.; Manning, I. M.; Leibfarth, F. A., C–H Functionalization of Commodity Polymers. *Angew. Chem. Int. Ed.* **2019**, *58* (26), 8654–8668.
- (114) Lewis, S. E.; Wilhelmy, B. E.; Leibfarth, F. A., Upcycling Aromatic Polymers through C–H Fluoroalkylation. *Chem. Sci.* **2019**, *10* (25), 6270–6277.
- (115) Lewis, S. E.; Wilhelmy, B. E.; Leibfarth, F. A., Organocatalytic C–H Fluoroalkylation of Commodity Polymers. *Polym. Chem.* **2020**.
- (116) Lee, S.-Y.; Yoon, J.-H.; Kim, J.-R.; Park, D.-W., Degradation of Polystyrene Using Clinoptilolite Catalysts. *J. Anal. Appl. Pyrolysis* **2002**, *64* (1), 71–83.
- (117) Ukei, H.; Hirose, T.; Horikawa, S.; Takai, Y.; Taka, M.; Azuma, N.; Ueno, A., Catalytic Degradation of Polystyrene into Styrene and a Design of Recyclable Polystyrene with Dispersed Catalysts. *Catal. Today* **2000**, *62* (1), 67–75.
- (118) Zhang, Z.; Hirose, T.; Nishio, S.; Morioka, Y.; Azuma, N.; Ueno, A.; Ohkita, H.; Okada, M., Chemical Recycling of Waste Polystyrene into Styrene over Solid Acids and Bases. *Ind. Eng. Chem. Res.* **1995**, *34* (12), 4514–4519.
- (119) Kim, J.-S.; Lee, W.-Y.; Lee, S.-B.; Kim, S.-B.; Choi, M.-J., Degradation of Polystyrene Waste over Base Promoted Fe Catalysts. *Catal. Today* **2003**, *87* (1), 59–68.
- (120) Woo, O. S.; Ayala, N.; Broadbelt, L. J., Mechanistic Interpretation of Base-Catalyzed Depolymerization of Polystyrene. *Catal. Today* **2000**, *55* (1), 161–171.
- (121) Bajdur, W.; Pajęczkowska, J.; Makarucha, B.; Sułkowska, A.; Sułkowski, W. W., Effective Polyelectrolytes Synthesised from Expanded Polystyrene Wastes. *Eur. Polym. J.* **2002**, *38* (2), 299–304.
- (122) Hearon, K.; Nash, L. D.; Rodriguez, J. N.; Lonneck, A. T.; Raymond, J. E.; Wilson, T. S.; Wooley, K. L.; Maitland, D. J., A High-Performance Recycling Solution for Polystyrene Achieved by the Synthesis of Renewable Poly(Thioether) Networks Derived from D-Limonene. *Adv. Mater.* **2014**, *26* (10), 1552–1558.
- (123) Yu, J.; Sun, L.; Ma, C.; Qiao, Y.; Yao, H., Thermal Degradation of Pvc: A Review. *Waste Manag. Res.* **2016**, *48*, 300–314.
- (124) Mio, H.; Saeki, S.; Kano, J.; Saito, F., Estimation of Mechanochemical Dechlorination Rate of Poly(Vinyl Chloride). *Environ. Sci. Technol.* **2002**, *36* (6), 1344–1348.
- (125) Lopez-Urionabarrenechea, A.; de Marco, I.; Caballero, B. M.; Laresgoiti, M. F.; Adrados, A., Catalytic Stepwise Pyrolysis of Packaging Plastic Waste. *J. Anal. Appl. Pyrolysis* **2012**, *96*, 54–62.
- (126) Dutcher, B.; Fan, M.; Russell, A. G., Amine-Based CO₂ Capture Technology Development from the Beginning of 2013—a Review. *ACS Appl. Mater. Interfaces* **2015**, *7* (4), 2137–2148.
- (127) Podgórski, M.; Fairbanks, B. D.; Kirkpatrick, B. E.; McBride, M.; Martinez, A.; Dobson, A.; Bongiardina, N. J.; Bowman, C. N., Toward Stimuli-Responsive Dynamic Thermosets through Continuous Development and Improvements in Covalent Adaptable Networks (Cans). *Adv. Mater.* **2020**, *32* (20), 1906876.
- (128) Rowan, S. J.; Cantrill, S. J.; Cousins, G. R. L.; Sanders, J. K. M.; Stoddart, J. F., Dynamic Covalent Chemistry. *Angew. Chem. Int. Ed.* **2002**, *41* (6), 898–952.
- (129) Chakma, P.; Konkolewicz, D., Dynamic Covalent Bonds in Polymeric Materials. *Angew. Chem. Int. Ed.* **2019**, *58* (29), 9682–9695.
- (130) Scheutz, G. M.; Lessard, J. J.; Sims, M. B.; Sumerlin, B. S., Adaptable Crosslinks in Polymeric Materials: Resolving the Intersection of Thermoplastics and Thermosets. *J. Am. Chem. Soc.* **2019**, *141* (41), 16181–16196.
- (131) Roy, N.; Bruchmann, B.; Lehn, J.-M., Dynamers: Dynamic Polymers as Self-Healing Materials. *Chem. Soc. Rev.* **2015**, *44* (11), 3786–3807.
- (132) Zhang, Z. P.; Rong, M. Z.; Zhang, M. Q., Polymer Engineering Based on Reversible Covalent Chemistry: A Promising Innovative Pathway Towards New Materials and New Functionalities. *Prog. Polym. Sci.* **2018**, *80*, 39–93.
- (133) Fortman, D. J.; Brutman, J. P.; De Hoe, G. X.; Snyder, R. L.; Dichtel, W. R.; Hillmyer, M. A., Approaches to Sustainable and Continually Recyclable Cross-Linked Polymers. *ACS Sustainable Chem. Eng.* **2018**, *6* (9), 11145–11159.
- (134) Snyder, R. L.; Fortman, D. J.; De Hoe, G. X.; Hillmyer, M. A.; Dichtel, W. R., Reprocessable Acid-Degradable Polycarbonate Vitrimers. *Macromolecules* **2018**, *51* (2), 389–397.
- (135) Taynton, P.; Ni, H.; Zhu, C.; Yu, K.; Loob, S.; Jin, Y.; Qi, H. J.; Zhang, W., Repairable Woven Carbon Fiber Composites with Full Recyclability Enabled by Malleable Polyimine Networks. *Adv. Mater.* **2016**, *28* (15), 2904–2909.
- (136) Zou, Z.; Zhu, C.; Li, Y.; Lei, X.; Zhang, W.; Xiao, J., Rehealable, Fully Recyclable, and Malleable Electronic Skin

Enabled by Dynamic Covalent Thermoset Nanocomposite. *Science Adv.* **2018**, *4* (2), eaaq0508.

(137) Lei, X.; Jin, Y.; Sun, H.; Zhang, W., Rehealable Imide–Imine Hybrid Polymers with Full Recyclability. *J. Mater. Chem. A* **2017**, *5* (40), 21140–21145.

(138) Yuan, Y.; Sun, Y.; Yan, S.; Zhao, J.; Liu, S.; Zhang, M.; Zheng, X.; Jia, L., Multiply Fully Recyclable Carbon Fibre Reinforced Heat-Resistant Covalent Thermosetting Advanced Composites. *Nature Commun.* **2017**, *8* (1), 14657.

(139) Zhang, Y.; Ying, H.; Hart, K. R.; Wu, Y.; Hsu, A. J.; Coppola, A. M.; Kim, T. A.; Yang, K.; Sottos, N. R.; White, S. R.; Cheng, J., Malleable and Recyclable Poly(Urea-Urethane) Thermosets Bearing Hindered Urea Bonds. *Adv. Mater.* **2016**, *28* (35), 7646–7651.

(140) Yu, K.; Shi, Q.; Dunn, M. L.; Wang, T.; Qi, H. J., Carbon Fiber Reinforced Thermoset Composite with near 100% Recyclability. *Adv. Funct. Mater.* **2016**, *26* (33), 6098–6106.

(141) Wang, C.; Mavila, S.; Worrell, B. T.; Xi, W.; Goldman, T. M.; Bowman, C. N., Productive Exchange of Thiols and Thioesters to Form Dynamic Polythioester-Based Polymers. *ACS Macro Lett.* **2018**, *7* (11), 1312–1316.

(142) Worrell, B. T.; McBride, M. K.; Lyon, G. B.; Cox, L. M.; Wang, C.; Mavila, S.; Lim, C.-H.; Coley, H. M.; Musgrave, C. B.; Ding, Y.; Bowman, C. N., Bistable and Photoswitchable States of Matter. *Nature Commun.* **2018**, *9* (1), 2804.

(143) Li, Q.; Ma, S.; Wang, S.; Yuan, W.; Xu, X.; Wang, B.; Huang, K.; Zhu, J., Facile Catalyst-Free Synthesis, Exchanging, and Hydrolysis of an Acetal Motif for Dynamic Covalent Networks. *J. Mater. Chem. A* **2019**, *7* (30), 18039–18049.

(144) García, J. M.; Jones, G. O.; Virwani, K.; McCloskey, B. D.; Boday, D. J.; ter Huurne, G. M.; Horn, H. W.; Coady, D. J.; Bintaleb, A. M.; Alabdulrahman, A. M. S.; Alsewailem, F.; Almegren, H. A. A.; Hedrick, J. L., Recyclable, Strong Thermosets and Organogels Via Paraformaldehyde Condensation with Diamines. *Science* **2014**, *344* (6185), 732.

(145) Li, Z.; Qiu, J.; Pei, C., Recyclable and Transparent Bacterial Cellulose/Hemiaminal Dynamic Covalent Network Polymer Nanocomposite Films. *Cellulose* **2016**, *23* (4), 2449–2455.

(146) Fox, C. H.; ter Huurne, G. M.; Wojtecki, R. J.; Jones, G. O.; Horn, H. W.; Meijer, E. W.; Frank, C. W.; Hedrick, J. L.; García, J. M., Supramolecular Motifs in Dynamic Covalent Peg-Hemiaminal Organogels. *Nature Commun.* **2015**, *6* (1), 7417.

(147) Ogden, W. A.; Guan, Z., Recyclable, Strong, and Highly Malleable Thermosets Based on Boroxine Networks. *J. Am. Chem. Soc.* **2018**, *140* (20), 6217–6220.

(148) Liu, H.; Nelson, A. Z.; Ren, Y.; Yang, K.; Ewoldt, R. H.; Moore, J. S., Dynamic Remodeling of Covalent Networks Via Ring-Opening Metathesis Polymerization. *ACS Macro Lett.* **2018**, *7* (8), 933–937.

(149) Christensen, P. R.; Scheuermann, A. M.; Loeffler, K. E.; Helms, B. A., Closed-Loop Recycling of Plastics Enabled by Dynamic Covalent Diketoenamine Bonds. *Nature Chem.* **2019**, *11* (5), 442–448.

(150) Song, F.; Li, Z.; Jia, P.; Zhang, M.; Bo, C.; Feng, G.; Hu, L.; Zhou, Y., Tunable “Soft and Stiff”, Self-Healing, Recyclable, Thermadaptable Shape Memory Biomass Polymers Based on Multiple Hydrogen Bonds and Dynamic Imine Bonds. *J. Mater. Chem. A* **2019**, *7* (21), 13400–13410.

(151) Fukuda, K.; Shimoda, M.; Sukegawa, M.; Nobori, T.; Lehn, J.-M., Doubly Degradable Dynamers: Dynamic Covalent Polymers Based on Reversible Imine Connections and Biodegradable Polyester Units. *Green Chem.* **2012**, *14* (10), 2907–2911.

(152) Park, S.-A.; Jeon, H.; Kim, H.; Shin, S.-H.; Choy, S.; Hwang, D. S.; Koo, J. M.; Jegal, J.; Hwang, S. Y.; Park, J.; Oh, D. X., Sustainable and Recyclable Super Engineering Thermoplastic from Biorenewable Monomer. *Nature Commun.* **2019**, *10* (1), 2601.

(153) Tuba, R.; Balogh, J.; Hlil, A.; Barló, M.; Al-Hashimi, M.; Bazzi, H. S., Synthesis of Recyclable Tire Additives Via Equilibrium Ring-Opening Metathesis Polymerization. *ACS Sustainable Chem. Eng.* **2016**, *4* (11), 6090–6094.

(154) Trovatti, E.; Lacerda, T. M.; Carvalho, A. J. F.; Gandini, A., Recycling Tires? Reversible Crosslinking of Poly(Butadiene). *Adv. Mater.* **2015**, *27* (13), 2242–2245.

(155) Polgar, L. M.; van Duin, M.; Broekhuis, A. A.; Picchioni, F., Use of Diels–Alder Chemistry for Thermoreversible Cross-Linking of Rubbers: The Next Step toward Recycling of Rubber Products? *Macromolecules* **2015**, *48* (19), 7096–7105.

(156) Bockstal, L.; Berchem, T.; Schmetz, Q.; Richel, A., Devulcanisation and Reclaiming of Tires and Rubber by Physical and Chemical Processes: A Review. *Journal of Cleaner Production* **2019**, *236*, 117574.

(157) Tonkin, S. J.; Gibson, C. T.; Campbell, J. A.; Lewis, D. A.; Karton, A.; Hasell, T.; Chalker, J. M., Chemically Induced Repair, Adhesion, and Recycling of Polymers Made by Inverse Vulcanization. *Chem. Sci.* **2020**, *11* (21), 5537–5546.

(158) Lee, J. M.; Noh, G. Y.; Kim, B. G.; Yoo, Y.; Choi, W. J.; Kim, D.-G.; Yoon, H. G.; Kim, Y. S., Synthesis of Poly(Phenylene Polysulfide) Networks from Elemental Sulfur and P-Diiodobenzene for Stretchable, Healable, and Reprocessable Infrared Optical Applications. *ACS Macro Lett.* **2019**, *8* (8), 912–916.

(159) Karunarathna, M. S.; Lauer, M. K.; Thiounn, T.; Smith, R. C.; Tennyson, A. G., Valorisation of Waste to Yield Recyclable Composites of Elemental Sulfur and Lignin. *J. Mater. Chem. A* **2019**, *7* (26), 15683–15690.

(160) Arslan, M.; Kiskan, B.; Yagci, Y., Recycling and Self-Healing of Polybenzoxazines with Dynamic Sulfide Linkages. *Sci. Rep.* **2017**, *7* (1), 5207.

(161) Griebel, J. J.; Nguyen, N. A.; Namnabat, S.; Anderson, L. E.; Glass, R. S.; Norwood, R. A.; Mackay, M. E.; Char, K.; Pyun, J., Dynamic Covalent Polymers Via Inverse Vulcanization of Elemental Sulfur for Healable Infrared Optical Materials. *ACS Macro Lett.* **2015**, *4* (9), 862–866.

(162) Chung, W. J.; Griebel, J. J.; Kim, E. T.; Yoon, H.; Simmonds, A. G.; Ji, H. J.; Dirlam, P. T.; Glass, R. S.; Wie, J. J.; Nguyen, N. A.; Guralnick, B. W.; Park, J.; Somogyi, Á.; Theato, P.; Mackay, M. E.; Sung, Y.-E.; Char, K.; Pyun, J., The Use of Elemental Sulfur as an Alternative Feedstock for Polymeric Materials. *Nature Chem.* **2013**, *5* (6), 518–524.

(163) Griebel, J. J.; Li, G.; Glass, R. S.; Char, K.; Pyun, J., Kilogram Scale Inverse Vulcanization of Elemental Sulfur to Prepare High Capacity Polymer Electrodes for Li-S Batteries. *J. Polym. Sci. A. Polym. Chem.* **2015**, *53* (2), 173–177.

(164) Sheppard, D. T.; Jin, K.; Hamachi, L. S.; Dean, W.; Fortman, D. J.; Ellison, C. J.; Dichtel, W. R., Reprocessing

- Postconsumer Polyurethane Foam Using Carbamate Exchange Catalysis and Twin-Screw Extrusion. *ACS Cent. Sci.* **2020**, *6* (6), 921-927.
- (165) Yardley, R. E.; Kenaree, A. R.; Gillies, E. R., Triggering Depolymerization: Progress and Opportunities for Self-Immolative Polymers. *Macromolecules* **2019**, *52* (17), 6342-6360.
- (166) Baker, M. S.; Kim, H.; Olah, M. G.; Lewis, G. G.; Phillips, S. T., Depolymerizable Poly(Benzyl Ether)-Based Materials for Selective Room Temperature Recycling. *Green Chem.* **2015**, *17* (9), 4541-4545.
- (167) Fan, B.; Trant, J. F.; Wong, A. D.; Gillies, E. R., Polyglyoxylates: A Versatile Class of Triggerable Self-Immolative Polymers from Readily Accessible Monomers. *J. Am. Chem. Soc.* **2014**, *136* (28), 10116-10123.
- (168) Sirianni, Q. E. A.; Rabiee Kenaree, A.; Gillies, E. R., Polyglyoxylamides: Tuning Structure and Properties of Self-Immolative Polymers. *Macromolecules* **2019**, *52* (1), 262-270.
- (169) Kaitz, J. A.; Diesendruck, C. E.; Moore, J. S., End Group Characterization of Poly(Phthalaldehyde): Surprising Discovery of a Reversible, Cationic Macrocyclization Mechanism. *J. Am. Chem. Soc.* **2013**, *135* (34), 12755-12761.
- (170) Lutz, J. P.; Davydovich, O.; Hannigan, M. D.; Moore, J. S.; Zimmerman, P. M.; McNeil, A. J., Functionalized and Degradable Polyphthalaldehyde Derivatives. *J. Am. Chem. Soc.* **2019**, *141* (37), 14544-14548.
- (171) Lloyd, E. M.; Lopez Hernandez, H.; Feinberg, A. M.; Yourdkhani, M.; Zen, E. K.; Mejia, E. B.; Sottos, N. R.; Moore, J. S.; White, S. R., Fully Recyclable Metastable Polymers and Composites. *Chem. Mater.* **2019**, *31* (2), 398-406.
- (172) Miller, K. A.; Morado, E. G.; Samanta, S. R.; Walker, B. A.; Nelson, A. Z.; Sen, S.; Tran, D. T.; Whitaker, D. J.; Ewoldt, R. H.; Braun, P. V.; Zimmerman, S. C., Acid-Triggered, Acid-Generating, and Self-Amplifying Degradable Polymers. *J. Am. Chem. Soc.* **2019**, *141* (7), 2838-2842.
- (173) Diesendruck, C. E.; Peterson, G. I.; Kulik, H. J.; Kaitz, J. A.; Mar, B. D.; May, P. A.; White, S. R.; Martinez, T. J.; Boydston, A. J.; Moore, J. S., Mechanically Triggered Heterolytic Unzipping of a Low-Ceiling-Temperature Polymer. *Nature Chem.* **2014**, *6*, 623.
- (174) Hu, X.; Zeng, T.; Husic, C. C.; Robb, M. J., Mechanically Triggered Small Molecule Release from a Masked Furfuryl Carbonate. *J. Am. Chem. Soc.* **2019**, *141* (38), 15018-15023.
- (175) Poland, S. J.; Darensbourg, D. J., A Quest for Polycarbonates Provided Via Sustainable Epoxide/CO₂ Copolymerization Processes. *Green Chem.* **2017**, *19* (21), 4990-5011.
- (176) Darensbourg, D. J., Comments on the Depolymerization of Polycarbonates Derived from Epoxides and Carbon Dioxide: A Mini Review. *Polym. Degrad. Stab.* **2018**, *149*, 45-51.
- (177) Li, C.; Sablong, R. J.; van Benthem, R. A. T. M.; Koning, C. E., Unique Base-Initiated Depolymerization of Limonene-Derived Polycarbonates. *ACS Macro Lett.* **2017**, *6* (7), 684-688.
- (178) Zhu, J.-B.; Watson, E. M.; Tang, J.; Chen, E. Y. X., A Synthetic Polymer System with Repeatable Chemical Recyclability. *Science* **2018**, *360* (6387), 398.
- (179) Cywar, R. M.; Zhu, J.-B.; Chen, E. Y. X., Selective or Living Organopolymerization of a Six-Five Bicyclic Lactone to Produce Fully Recyclable Polyesters. *Polym. Chem.* **2019**, *10* (23), 3097-3106.
- (180) Sangroniz, A.; Zhu, J.-B.; Tang, X.; Etxeberria, A.; Chen, E. Y. X.; Sardon, H., Packaging Materials with Desired Mechanical and Barrier Properties and Full Chemical Recyclability. *Nature Commun.* **2019**, *10* (1), 3559.
- (181) Lizundia, E.; Makwana, V. A.; Larrañaga, A.; Vilas, J. L.; Shaver, M. P., Thermal, Structural and Degradation Properties of an Aromatic-Aliphatic Polyester Built through Ring-Opening Polymerisation. *Polym. Chem.* **2017**, *8* (22), 3530-3538.
- (182) MacDonald, J. P.; Shaver, M. P., An Aromatic/Aliphatic Polyester Prepared Via Ring-Opening Polymerisation and Its Remarkably Selective and Cyclable Depolymerisation to Monomer. *Polym. Chem.* **2016**, *7* (3), 553-559.
- (183) Greer, S. C., Physical Chemistry of Equilibrium Polymerization. *J. Phys. Chem. B* **1998**, *102* (28), 5413-5422.
- (184) Olsén, P.; Odelius, K.; Albertsson, A.-C., Thermodynamic Presynthetic Considerations for Ring-Opening Polymerization. *Biomacromolecules* **2016**, *17* (3), 699-709.
- (185) Olsén, P.; Undin, J.; Odelius, K.; Keul, H.; Albertsson, A.-C., Switching from Controlled Ring-Opening Polymerization (Crop) to Controlled Ring-Closing Depolymerization (Crcdp) by Adjusting the Reaction Parameters That Determine the Ceiling Temperature. *Biomacromolecules* **2016**, *17* (12), 3995-4002.
- (186) Zhang, Q.; Deng, Y.-X.; Luo, H.-X.; Shi, C.-Y.; Geise, G. M.; Feringa, B. L.; Tian, H.; Qu, D.-H., Assembling a Natural Small Molecule into a Supramolecular Network with High Structural Order and Dynamic Functions. *J. Am. Chem. Soc.* **2019**, *141* (32), 12804-12814.
- (187) Liu, Y.; Jia, Y.; Wu, Q.; Moore, J. S., Architecture-Controlled Ring-Opening Polymerization for Dynamic Covalent Poly(Disulfide)s. *J. Am. Chem. Soc.* **2019**, *141* (43), 17075-17080.
- (188) Yuan, J.; Xiong, W.; Zhou, X.; Zhang, Y.; Shi, D.; Li, Z.; Lu, H., 4-Hydroxyproline-Derived Sustainable Polythioesters: Controlled Ring-Opening Polymerization, Complete Recyclability, and Facile Functionalization. *J. Am. Chem. Soc.* **2019**, *141* (12), 4928-4935.
- (189) Xiong, W.; Chang, W.; Shi, D.; Yang, L.; Tian, Z.; Wang, H.; Zhang, Z.; Zhou, X.; Chen, E.-Q.; Lu, H., Geminal Dimethyl Substitution Enables Controlled Polymerization of Penicillamine-Derived B-Thiolactones and Reversed Depolymerization. *Chem* **2020**, *6* (7), 1831-1843.
- (190) Shi, C.; McGraw, M. L.; Li, Z.-C.; Cavallo, L.; Falivene, L.; Chen, E. Y. X., High-Performance Pan-Tactic Polythioesters with Intrinsic Crystallinity and Chemical Recyclability. *Science Adv.* **2020**, *6* (34), eabc0495.
- (191) Albertsson, A.-C.; Varma, I. K., Recent Developments in Ring Opening Polymerization of Lactones for Biomedical Applications. *Biomacromolecules* **2003**, *4* (6), 1466-1486.
- (192) Tang, X.; Chen, E. Y. X., Toward Infinitely Recyclable Plastics Derived from Renewable Cyclic Esters. *Chem* **2019**, *5* (2), 284-312.
- (193) Tullo, A. H., Firms Back Chemical Recycling of Plastics. *Chem. Eng. News* **2019**, *97* (10).

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