Chemical Upcycling of Polymers Factual Status Document

The artwork on the cover depicts chemical upcycling of poly(ethylene terephthalate) (PET) (top) to bis(2-hydroxyethyl) terephthalate (middle) and repolymerization back to PET (bottom) to illustrate the vision of chemical circularity. The background image consists of polymer pellets.
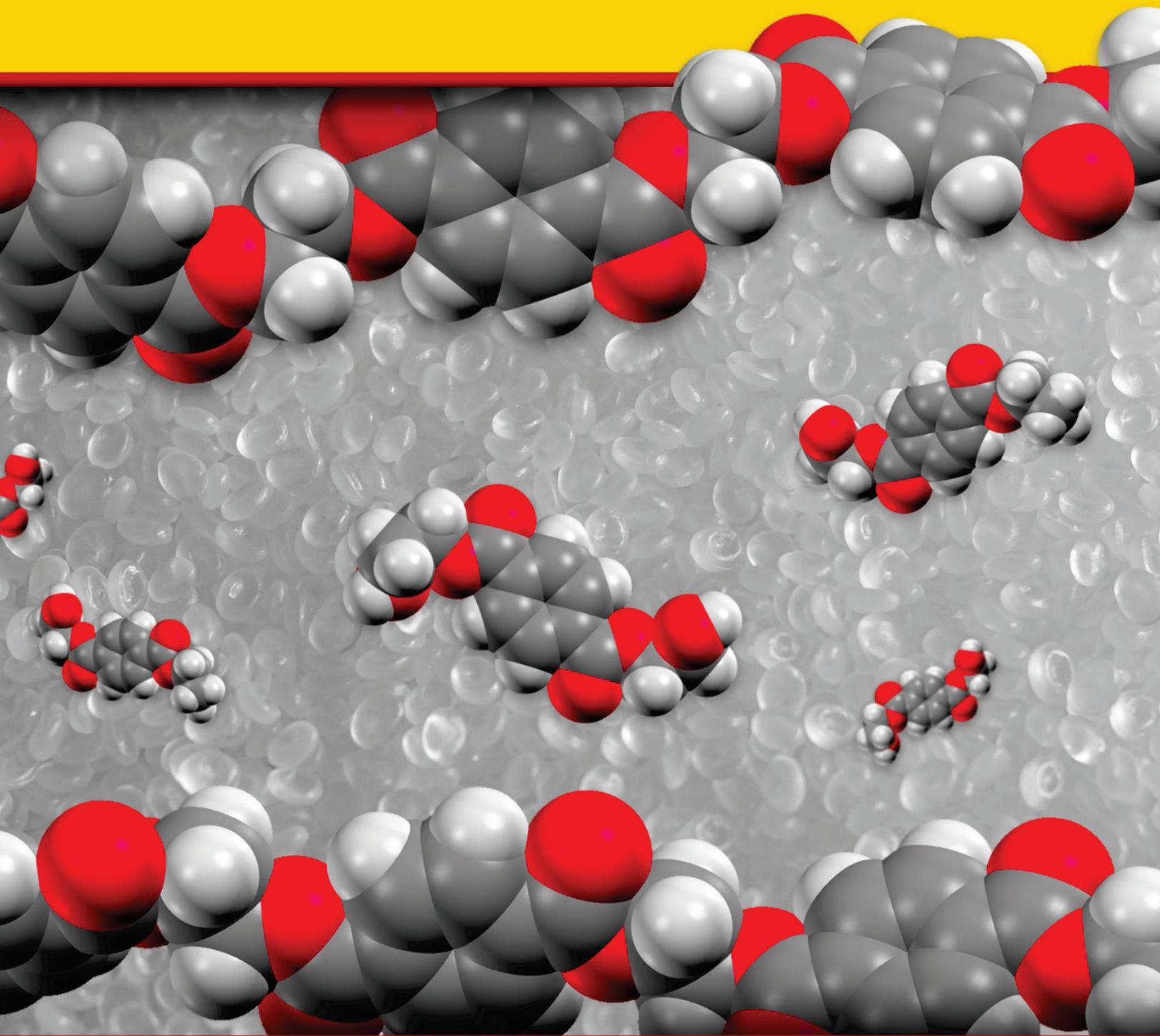
Factual Document for the Office of Basic Energy Sciences Roundtable on Chemical Upcycling of Polymers

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April 2019

Table of Contents

List of Figures

List of Abbreviations, Acronyms, and Initialisms

3D	three-dimensional
4*p*SA	4-propylsyringyl acrylate
ABS	acrylonitrile-butadiene-styrene
BDO	butanediol
BES	Basic Energy Sciences
BHET	bis(2-hydroxyethyl) terephthalate
BHETA	bis (2-hydroxyethyl) terephthalamide
Bmim	1-butyl-3-methylimidazolium
BPA	bisphenol A
CF	carbon fiber
DEG	diethylene glycol
DES	deep eutectic solvent
DGEBA	diglycidyl ether of bisphenol A
GBL	γ-butyrolactone
H$_2$pdca	2,6-pyridinedicarboxamide
HDPE	high-density polyethylene
HPW	phosphotungstic acid
LDPE	low-density polyethylene
MAC	5-methyl-5-allyloxy-carbony-1,3-dioxan-2-one
MEA	monoethanolamine
MHET	mono-(2-hydroxyethyl)terephthalic acid
MMA	methyl methacrylate
MSA	methanesulfonic acid
*n*BA	*n*-butyl acrylate
NVP	*N*-vinyl-2-pyrrolidone
P(T6HP)	poly(trans-hexahydrophthalide)
P3HB	poly(3-hydroxybutyrate)
PBAT	poly(butylene adipate-*co*-terephthalate)
PBSA	poly(butylene succinate-*co*-adipate)
PCL	polycaprolactone
PDMS	polydimethylsiloxane
PE	polyethylene
PEG	polyethylene glycol
PET	polyethylene terephthalate
PGBL	poly(γ-butyrolactone)
PHA	polyhydroxyalkanoate
PHU	polyhydroxyurethane
PLA	polylactic acid
PMMA	poly(methyl methacrylate)
PP	polypropylene
PS	polystyrene
*p*TSA	*p*-toluenesulfonic acid
PVC	polyvinyl chloride
ran	random copolymer
ROP	ring-opening polymerization
P*n*BA	poly(*n*-butyl acrylate)
RT	room temperature
T6HP	trans-hexahydrophthalide

TBD	triazabicyclodecene
TBT	titanium(IV) n-butoxide
T_c	ceiling temperature
T_g	glass transition temperature
T_m	melting temperature
T_v	topology freezing transition temperature
THETA	tetrakis (2-hydroxyethyl) terephthalamide
TPA	terephthalic acid
TPE	thermoplastic elastomer
UV	ultraviolet

1   Introduction

This factual document was developed for the US Department of Energy Office of Science, Basic Energy Sciences (BES) Roundtable on Chemical Upcycling of Polymers, which was held April 30–May 1, 2019, in Rockville, Maryland. This document provides the workshop participants with a high-level assessment of the current status of chemical upcycling of polymers. In this document, *upcycling of polymers* is meant to describe the use of discarded plastics to produce new chemicals, fuels, and materials of higher value than the original materials. Upcycling can create a circular life cycle for plastics. This document focuses on the synthetic methods, catalysts, and chemical mechanisms needed to deconstruct polymers into targeted intermediates, monomers, or fuels; processing methods for deconstruction and reconstruction to targeted products; and synthesis of next-generation polymeric materials made for upcycling. For each of these areas, this document concisely summarizes the advances in science and technology that have been made over the past decade, the current state of the art for the technology, the technological challenges, and the barriers to polymer upcycling concepts. This document defines the state of the field but does not provide guidance on future research directions. Although the document is not meant to be an exhaustive review, key references in the field are provided.

2   Polymer Upcycling Background and Overview

2.1   Current Situation

Plastics are an integral part of everyday life and are used in a wide variety of applications, including packaging, building/construction, transportation, consumer products, textiles, health care, and electronics. They are strong, lightweight, durable, chemically resistant, moldable, and low in cost. These favorable qualities have led to a significant growth in plastic production, which is predicted to continue into the future. One of the biggest uses of plastic is in packaging, which is commonly designed for single use and immediate disposal. In 2015, plastic materials contributed 13% (34.5 million tons) to municipal solid wastes in the United States with less than 10% recycled and approximately16% combusted for energy recovery.[1] Increased plastic recycling is an important pathway to reduce discarded plastic and has clear economic, energy, and environmental impacts. Recycling discarded plastic to make similar products rather than producing items from virgin feedstocks (e.g., petroleum) can save energy. Recycling one ton of plastics saves about 130 million kJ of energy;[2] therefore, recycling one-third of the discarded plastic annually could reduce the total US energy consumption by about 1%. Additionally, the value of plastic materials lost to the environment each year from single-use plastic items is approximately $80–120 billion.[3] If plastic production continues at its current growth rate, then the plastics industry could account for 20% of the world's total oil consumption by 2050; and by then, the ocean could contain more plastic than fish, by weight.[3]

The main technology used in industrial-scale processing of discarded plastics—mechanical recycling involving sorting, shredding, washing, heating, and remolding of plastic material—is applied only to limited plastic types (thermoplastics) to create new products. Polymer upcycling could significantly expand the types of plastics recycled, including plastic mixtures. Advances in polymer upcycling will require new catalysts and chemical processes to deconstruct polymeric materials into targeted molecular intermediates and reassemble them into desired products.[4] Here, *deconstruction* means breaking down the polymeric material into smaller molecular intermediates (which could include oligomers) but does not necessarily mean a complete depolymerization to its monomeric form. Industrial-scale implementation of these processes will require going beyond current chemical recycling approaches (e.g., pyrolysis and catalytic pyrolysis upgrading) that can treat a range of plastic types but operate at high temperatures, which requires large energy input and results in a mixture of products.[2] As a short term goal, these

methods (i.e., mechanical recycling or chemical deconstruction and reconstruction methods) can extend the lifetime of a plastic before it is considered waste. For the long-term goal of a circular economy, new polymers must be made with properties that are similar or superior to those of today that can be efficiently upcycled.

2.2 Types of Discarded Polymers

In 1988, the Society of the Plastics Industry (now the Plastics Industry Association) established identification codes for different plastics. The codes assist in sorting materials and address the need for different recycling paths to preserve the plastics' value. The chart in Figure 1 shows six codes that cover 87% of the plastics and a seventh code that covers all other plastics.[5] Complexities in the plastics' chemistries and composition (including additives, stabilizers, and fillers) make reuse strategies different for different materials.

# Plastic Resin Identification Codes

PETE	HDPE	PVC	LDPE	PP	PS	OTHER
Polyethylene Terephthalate	**High-Density Polyethylene**	**Polyvinyl Chloride**	**Low-Density Polyethylene**	**Polypropylene**	**Polystyrene**	**Other**
Common products: to-go containers, cups, jars, trays, soda & water bottles	**Common products:** grocery bags, milk jugs, flower pots, detergent & shampoo bottles	**Common products:** pipe, pool liners, siding, automotive product bottles, sheeting	**Common products:** bread bags, paper towel overwrap, squeeze bottles, trash bags	**Common products:** yogurt tubs, cups, twine, straws, hangers, shipping bags, non-woven bags	**Common products:** to-go containers, razor handles, flatware, CD cases, hot & cold cups, foam packing, trays, egg cartons	**Common types & products:** polycarbonate, nylon, ABS, acrylic, PLA; multi-layer packaging, bottles, safety glasses, CDs, lenses, pouches
Recycled products: clothing, carpet, clamshells, soda & water bottles	**Recycled products:** detergent bottles, flower pots, crates, pipe, decking	**Recycled products:** pipe, siding, binders, carpet backing, flooring	**Recycled products:** trash bags, decking, furniture, shipping envelopes, compost bins	**Recycled products:** paint cans, speed bumps, auto parts, hangers, plant pots, toothbrush handles	**Recycled products:** picture frames, crown molding, rulers, flower pots, hangers, toys, tape dispensers	**Recycled products:** electronic housings, auto parts
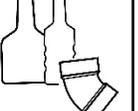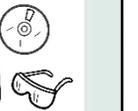
Moore Recycling Associates Inc. (available for download from the Association of Plastic Recyclers at http://www.plasticsrecycling.org/membership/apr-meetings/147-recycling-beyond-bottles/residential-bulky-rigids)

Figure 1. Different plastic identification codes. *Source: Moore Recycling Associates. Available for download from the Association of Plastic Recyclers at http://www.plasticsrecycling.org/membership/apr-meetings/147-recycling-beyond-bottles/residential-bulky-rigids.*

2.3 Challenges and Potential Opportunities

Recycling discarded plastics imposes many challenges due to the inherent incompatibilities of different polymers and the economic inefficiencies and difficulties in presorting polymers into a pure stream. Additionally, even presorted polymers often contain different types of additives—including fillers, plasticizers, flame retardants, antioxidants, and colorants—and contaminants, such as food or product residue and dirt. The materials isolated from discarded plastics are typically mixed or heterogeneous in nature and frequently require rigorous preprocessing steps. Although polymer upcycling requires energy input and chemicals for processing, it can still reduce petrochemical use, save energy, minimize the need for landfills, and protect the environment. These benefits lead to new and challenging questions: How can

one enhance the performance and functionality of repurposed materials from end-of-life plastics? Can one design energy-efficient processes for recovery of chemicals or materials from discarded plastics? Can research into chemical upcycling offer new opportunities to efficiently and economically use discarded plastics as a feedstock to produce new products? Can new polymers be designed with upcycling in mind?

Three major challenges must be addressed to answer those questions and enable polymer upcycling. The first challenge is to design and control chemical transformations to deconstruct polymers and create targeted molecular intermediates that provide building blocks for new products. Molecules or materials that increase the rate of chemical reactions without being changed or consumed (i.e., catalysts) can enable selected bonds to be cleaved to deconstruct polymers. Although progress has been made on the deconstruction of some types of polymers, such as plant biomass (i.e., polymeric material making up plant cell walls, such as cellulose, hemicellulose, and lignin) and polyethylene terephthalate (PET), low-temperature catalytic processes for selective deconstruction of most plastics do not currently exist. Additionally, each starting polymer will require the design of new catalysts and catalytic processes in addition to separations methods to produce the targeted molecular products selectively and efficiently. The wide range of polymer compositions, structures (including some that are particularly hard to deconstruct such as thermosetting polymers), additives, and impurities (such as degradation products) increases the difficulty.

The second challenge is to design integrated processes that target the creation of desired end-products (e.g., fuels, chemicals, and materials) rather than targeting intermediate molecular building blocks for producing new polymers. The scientific community has dedicated significant efforts to understanding the chemical mechanisms of polymerization and has more recently focused on depolymerization. The needed innovation is to integrate deconstruction with reconstruction rather than independently investigate the two processes, so that they can work together to efficiently form new products. Catalysts can enable selective bond breaking as well as bond formation and will be essential in deconstruction and assembling molecular species into more complex products. Selective chemical methods to identify, separate, and purify polymeric materials or molecular fragments from complex mixtures will also be critical.

The third challenge is to design new polymeric materials that are easily separated, easily recycled, and have properties that make them essential products in today's economy. Advances are being made in the development of next-generation recyclable polymers, such as biodegradable plastics and recyclable cross-linked polymers, which will allow for a circular life cycle in which a large fraction of the future plastics produced are continually reused. However, the difficulty here builds on the previous two challenges: integrating the design of materials by providing specified properties with the design of deconstruction/reconstruction processes.

2.4   Why the Department of Energy and Why Basic Energy Sciences?

Advancing the fundamental sciences required to enable the chemical upcycling of polymers falls directly within BES's mission—which includes the support of fundamental research to understand chemical transformations that impact energy generation, storage, and use—and to provide the knowledge base for discovering and designing new materials with novel structures, functions, and properties. BES research includes novel catalyst design and quantum- and molecular-level control of chemical transformations; understanding reaction mechanisms, enabling precise identification and manipulation of catalytic active sites, their environments, and reaction conditions for optimized efficiency and selectivity; studies of enzymes that provide a basis for highly selective and efficient bio-inspired catalysts; and design and synthesis of novel materials with an emphasis on the chemistry and chemical control of structure and collective properties. This strong foundation of scientific research positions BES to rapidly advance a research agenda in chemical upcycling of polymers.

BES research has contributed significantly to the scientific foundations required to advance a fundamental research agenda in polymer deconstruction and reconstruction. For example, BES research in chemical and biological transformations and catalysis provides the foundation for advancing science for the polymer upcycling challenge. This research has provided fundamental insights into the catalytic and enzymatic conversion of plant biomass and has advanced the ability to convert it into fuels and chemicals. Although the chemical composition and structural complexity of plant cell wall polymers are different from those of most synthetic plastics and, therefore, will require new catalysts and chemistries, successfully deconstructing biomass demonstrates the ability to make progress on the selective conversion of complex, heterogenous, and recalcitrant polymers. The new computational and analytical tools, including high-performance computing and x-ray and neutron scattering, developed in the BES program can be used to address the challenges of chemical upcycling of polymers.

There is also extensive experience in BES programs in understanding the detailed mechanisms of polymerization reactions, which provides the foundation for producing a wide range of synthetic polymers with diverse properties from a group of building blocks. Efforts to tailor new functional products from molecular building blocks can also build on studies of polymer synthesis in natural organisms that are supported by BES bioscience programs. This research is developing a mechanistic understanding of how plants selectively synthesize complex molecular species.

Using synthetic polymers and polymer composites as functional materials is highly advantageous given the wide range of bulk properties (e.g., mechanical, thermal, rheological, chemical, optical) that are possible by varying the molecular-scale building blocks, processing conditions, polymer chain lengths, and porosity. BES-supported research has made a sustained contribution to the scientific understanding that links atomic and molecular-scale details to the observed properties of the bulk polymeric material; this understanding provides a strong foundation for addressing the polymer upcycling challenge. These scientific insights have enabled new polymeric materials with a combination of desired properties, such as high ionic conductivity and mechanical strength, and are critical to designing synthetic polymers that are functional and capable of efficient and controlled deconstruction into valuable products at end-of-life.

3   Objectives of this Roundtable and the Factual Document

The report from the roundtable addresses fundamental challenges to enable the transformation of discarded plastics into fuels, chemicals, and new materials. It also identifies fundamental chemical and materials science research opportunities to provide foundational knowledge that will lead to efficient, selective, low-temperature conversions of polymers to high-value products. The main scientific challenges addressed are:

- Devising chemical mechanisms to deconstruct polymers and create targeted molecular intermediates that provide building blocks for new products
- Creating integrated processes for depolymerization and/or reassembly that target desired end products (i.e., fuels, chemicals, new materials) from starting polymers
- Designing next-generation polymeric materials that enable efficient depolymerization and reassembly

Crosscutting opportunities for advancing experimental, computational, and data science approaches to address these scientific challenges will also be examined. This document concisely summarizes the advances in science and technology that have been made over the past decade, the current state of the art for the technology, the technological challenges, and the barriers to polymer upcycling.

4 Deconstruction of Polymers to Building Blocks

4.1 Deconstruction of Synthetic Polymers

Polymers have become ubiquitous in everyday life due to their desirable mechanical properties and chemical resistance. The deconstruction of synthetic polymers embraces an underlying paradox: the most widely used polymers are the most mechanically and chemically stable, yet during the recycling process, they must be susceptible to mechanical and chemical breakdown.

Approximately 90% of all synthetic plastics are thermoplastics and fall into six categories (see Figure 1): polyethylene terephthalate (PET), high-density polyethylene (HDPE), polyvinyl chloride (PVC), low-density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS).[2] From those polymers, PET, HDPE, PP, and PS are the most recycled.[6] The only large-scale recycling method that is widely used is mechanical recycling. Mechanical recycling refers to shredding, melting, and remolding of washed used plastics, which often requires blending with virgin polymer to reach appropriate manufacturing properties.[4] However, mechanical plastics recycling only delays their disposal because the quality of the material quickly degrades through recycling, and its properties are no longer suitable for the use intended for the original polymer. Other complications during the recycling process arise upon exposure to oxygen; for instance, polyethylene (PE) exposure to air at high temperature (>280 °C) during the extrusion process induces degradation into several different products, including aldehydes and organic acids.[7] Despite the complications, transition from mechanical recycling to chemical recycling is not widespread because chemical recycling is, in many cases, not economically viable relative to mechanical recycling.[8,9] Nonetheless, for thermosets, which are cross-linked polymers that are unrecyclable through mechanical methods, chemical recycling is the only option.

Broadly speaking, current depolymerization strategies can be divided into four categories: thermal processing, solvolysis, catalysis, and biocatalysis. Catalytic pyrolysis is an approach that overlaps thermal decomposition and catalysis, whereas catalytic solvolysis is the overlap between catalysis and solvolysis. The range of catalysts explored include solid catalysts, organic catalysts, ionic liquids, and deep eutectic solvents; the range of solvents explored include a variety of organic compounds and fluids at sub- and supercritical conditions. In many cases, the solvents have a catalytic role in the reaction mechanism, and thermal and catalytic decomposition are concurrent; therefore, it is often difficult to draw hard lines between different deconstruction approaches. Although there are reports on the photodegradation of polymers derived from bio-sources in the literature,[10–12] there are no recent developments in the photodegradation of synthetic polymers. In the following paragraphs, recent discoveries that represent the state of art of synthetic polymer deconstruction are highlighted.

Thermal decomposition. This section covers pyrolysis, catalytic pyrolysis, and polymer hydrothermal treatment. Pyrolysis, also called *non-oxidative thermochemical cracking*, consists of degrading polymers in the absence of oxygen through heat and pressure. This process has been primarily considered for fuel production[13–15] since the harsh pressure and heat conditions make controlling product selectivity challenging. In a few cases, pyrolysis can lead to monomer recovery at high yield (>95%) as in the pyrolysis of poly(methyl methacrylate) (PMMA) to methyl methacrylate (MMA).[16] Additionally, mass and heat transfer limitations are typically present during pyrolysis.[17] For instance, PP pyrolysis (500–900 °C) gives a mixture of products (C_1–C_9 alkanes and alkenes), but it imposes a high energy requirement to crack the relatively stable polymer.[2,18] The term *catalytic pyrolysis* is used when the decomposition occurs partly as a result of thermal bond breaking and partly as a result of catalyst-assisted cleavage/formation of the bonds at high temperatures (typically above 250 °C). Catalytic pyrolysis usually enhances the selectivity and lowers the temperature of the reaction. For instance, PET can thermally degrade above approximately 300 °C and at lower temperatures with an acid catalyst into fragments terminated with carboxylic acid and vinyl groups.[19] Pyrolysis of PE, PP, and PS have been studied at 400–800 °C in the

presence of a fluid cracking catalyst (e.g., HZSM-5) or under catalyst-free conditions.[17,20,21] The catalytic pyrolysis of poly(hydroxyalkanoates) at 200 °C over $Mg(OH)_2$ selectively yields alkenoates.[22,23] Supported metal catalysts have also been tested for catalytic pyrolysis,[24] and the acid-base properties of metal oxide supports have been related to selectivity trends during thermal and catalytic transformation of PS.[25] The presence of a catalyst not only allowed the pyrolysis to be conducted at lower temperature than without a catalyst but also suppressed the formation of oligomeric species, providing a more efficient and selective degradation path of polymers.[9]

Pyrolysis of discarded plastics can lead to by-products that are not polymerizable, which impact the re-polymerization of monomers. Additionally, corrosive chemicals can be generated during the process.[26] This issue is exemplified in the pyrolysis of PMMA in which the by-products (methyl isobutyrate, methyl pyruvate and 2,3-butanedione) were found to be nonpolymerizable, their presence disrupted the polymerization reaction, and they reduced the quality of re-polymerized PMMA.[27] Moreover, the net yield of monomers can be hampered by random cleavage of C-C bonds during thermal depolymerization, which leads to the recombination of radical fragments and radical addition reactions.[2] Recently, cold plasma–assisted pyrolysis of HDPE was studied (without and with catalyst, SO_4^{2-}-ZrO_2 and HZSM-5), and although it showed better performance than traditional pyrolysis, only 22–25 wt % ethylene was recovered.[28]

The oxidative depolymerization of PS to styrene occurs at high temperatures (600–900 °C); high selectivity for styrene (>85%) was achieved in the presence of Rh-ceria or Pt-ceria on α-alumina in an autothermal reactor (Figure 2).[29] Repolymerization to PS affords material with the desired properties, but production of the recycled material relies on the quality of the original material; and the cost of depolymerization makes recycled PS more expensive.

Figure 2. Oxidative pyrolysis of polystyrene into styrene monomers in an autothermal fixed-bed catalytic reactor. *Photo courtesy of Lu Han, Oak Ridge National Laboratory.*

Solvolysis and catalytic solvolysis. Efforts to depolymerize synthetic polymers, such as condensation polymers, can rely exclusively on solvolysis (i.e., deconstruction by a solvent) in which the nature of the solvent determines the type of products produced since the solvent caps the monomer/oligomers after the breakdown of the polymer backbone. Using excess solvent is a strategy for controlling selectivity by avoiding reconstruction of fragments.[30] In many cases, including a catalyst has been shown to increase deconstruction rates, as will be discussed later in this document. Using a catalyst creates some additional challenges. Homogenous catalysts favor the contact between the polymer and the catalytic active site, but they can be difficult to recover. In contrast, heterogeneous catalysts are easier to recover but mass and heat transfer limitations are more significant. In either case, contamination of the final product with components leached from the catalyst must be considered. In this section, the advances in solvolysis and catalytic solvolysis are reviewed and specific subsections are devoted to ionic liquids, deep eutectic solvents, and the catalytic deconstruction of thermosets in which supercritical fluids have been found useful.

Zhao et al.[31] reported the hydrothermal treatment of plastics used in electronics (i.e., high-impact PS, polycarbonate, acrylonitrile butadiene styrene [ABS], and polyamide 6) at 250–350 °C. This approach is based on the successful hydrolysis of natural polymers, such as lignocellulosic material, at moderate temperatures (150–250 °C). According to Zhao et al., one key advantage of this hydrothermal process is that sorting the various plastics types might not be necessary and organic contaminants are not an
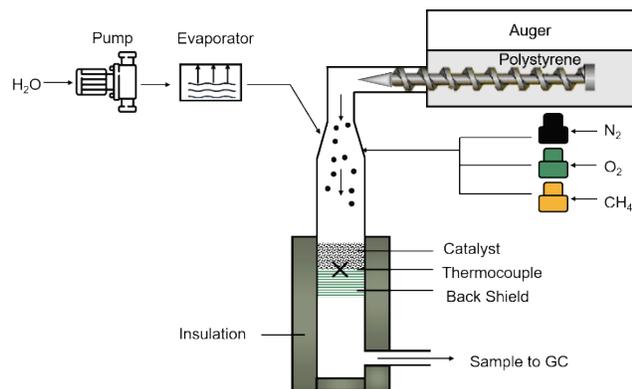
obstacle.[31] The temperature of the treatment greatly impacts the distribution of products formed, which include styrene, styrene derivatives, bisphenol A (BPA), caprolactam, and other valuable commodity chemicals. Hydrothermal treatments have the advantage of running at lower temperatures (350 °C)[31] than pyrolytic approaches and of producing high yields of products (up to 98%).

Surface-grafted organometallic catalysts can be used for deconstruction of hydrocarbon polymers, which are hard to selectively deconstruct by other methods. These catalysts provide mechanisms for carbon-carbon bond cleavage, and the molecular weights of the products are primarily controlled by the degree of conversion. In a seminal example, hydrogenolysis of PE, PP, and PS is catalyzed by an aluminum-doped silica-supported zirconium hydride at ~150 °C under a hydrogen atmosphere.[32,33] This reaction is proposed to involve metalation of the polymer chain, β-alkyl elimination, and then hydrogenolysis. The presence of aluminum in close proximity to zirconium is proposed to be important for the catalysis, although direct evidence of the locations of zirconium and aluminum is unknown. Additionally, the supported zirconium hydride catalyzes the progressive cleavage of all the C-C bonds over time (62 h), giving rise to a mixture of light hydrocarbons (C_1–C_5).

In a recent report by Jia et al., the prospect of polymer upcycling of alkanes has been revitalized with new discoveries in depolymerization metathesis.[30] The work reported the deconstruction of PE (HDPE, LDPE, and linear LDPE), including common discarded plastic, into liquid fuels and waxes. PE degradation in the presence of a light alkane was achieved using a tandem catalytic approach in which a pincer Ir-catalyst dehydrogenated PE and the light alkane, creating double bonds on both structures. Later, a second catalyst, Re_2O_7/γ-Al_2O_3, scrambled those double bonds to create lower molecular weight species containing a fraction of the initial polymer and a fraction of the initial alkane (Figure 3).[30] PE was diluted in an excess of light alkanes to prevent redundant metathesis between two PE chains and improve mass and heat transfer. This depolymerization strategy also successfully used a low-cost and readily available metathesis reagent, petroleum ether.[30] A dehydrogenation catalyst that forms internal olefins is the key for better performance because that process increases the depolymerization rate. Additionally, the product distribution could be ideally controlled by a catalyst that turns inactive after the hydrocarbon structure reaches a desired length. Also, heterogeneous catalytic systems have been shown to have longer lifetimes and activity compared with their homogeneous counterparts for alkane metathesis.[34]
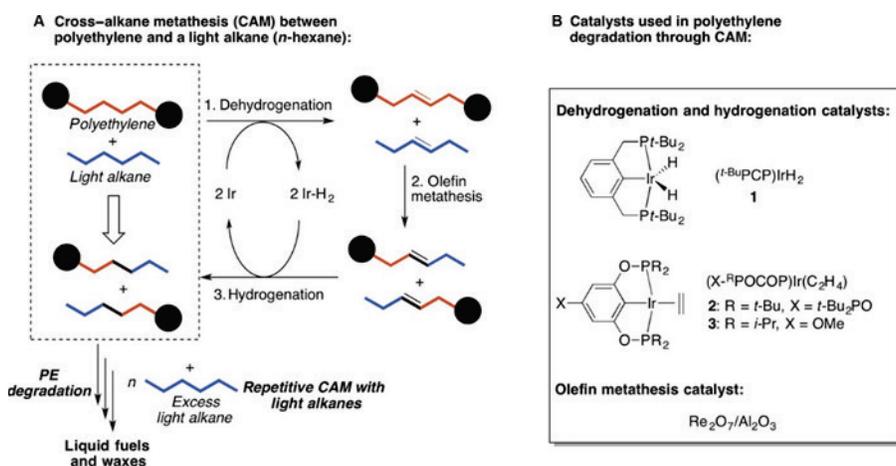
Figure 3. Alkane cross-metathesis for PE degradation via Re₂O₇/Al₂O₃ catalyzed alkene metathesis and iridium-catalyzed hydrogen transfer. *Reprinted by permission from Creative Commons Attribution Noncommercial license. Reprinted from X. Jia et al., "Efficient and Selective Degradation of Polyethylenes into Liquid Fuels and Waxes under Mild Conditions," Sci. Adv. 2016, 2 (6), e1501591; https://creativecommons.org/licenses/by-nc/4.0/.*

In a similar example, polybutadiene rubber and alkynes reacted via ene-yne metathesis to give 2-functionalized 1,3-cyclohexadienes[35] or by cross alkene metathesis with acrylates to give ester-terminated oligo-dienes.[36] Polybutadiene was converted predominantly to *trans, trans, trans*-cyclododecatriene via ring closing alkene metathesis (Figure 4).[37] The lack of saturation present in polybutadiene rubber was central to its upcycling to value-added small molecules.
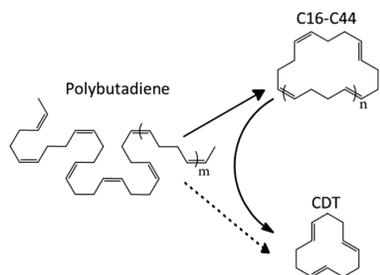
Figure 4. Schematic representation of the formation of macrocycles and cyclopentene/cyclohexene derivatives from vinyl-containing 1,4-polybutadiene. *Republished with permission of Royal Society of Chemistry, from A. Dewaele et al., "Depolymerization of 1,4-polybutadiene by Metathesis: High Yield of Large Macrocyclic Oligo(butadiene)s by Ligand Selectivity Control," Catal. Sci. Technol. 2016, 6 (21), 7,708–7,717; permission conveyed through Copyright Clearance Center Inc.*

Catalytic depolymerization of discarded polyesters and polycarbonates have also been recently reported.[38,39,40,41] Ru-based homogeneous hydrogenolysis catalytic systems have been shown to be capable of polyester deconstruction under mild conditions to the diols in the case of polyesters and diols and methanol in the case of polycarbonates (Figure 5).[39,42,43] The diols can be reused in the synthesis of new polyesters, resulting in novel possibilities for efficient polymer recycling within a circular economy approach. Additionally, an iron pincer complex can depolymerize polyesters via transfer-hydrogenation catalysis using ethanol as a source of hydrogen.[38] For example, the adipic acid/1,6-hexanediol copolymer can be deconstructed at 100 °C in 24 h to 1,6-hexanediol in 87% yield, employing 5 mol % iron catalyst.
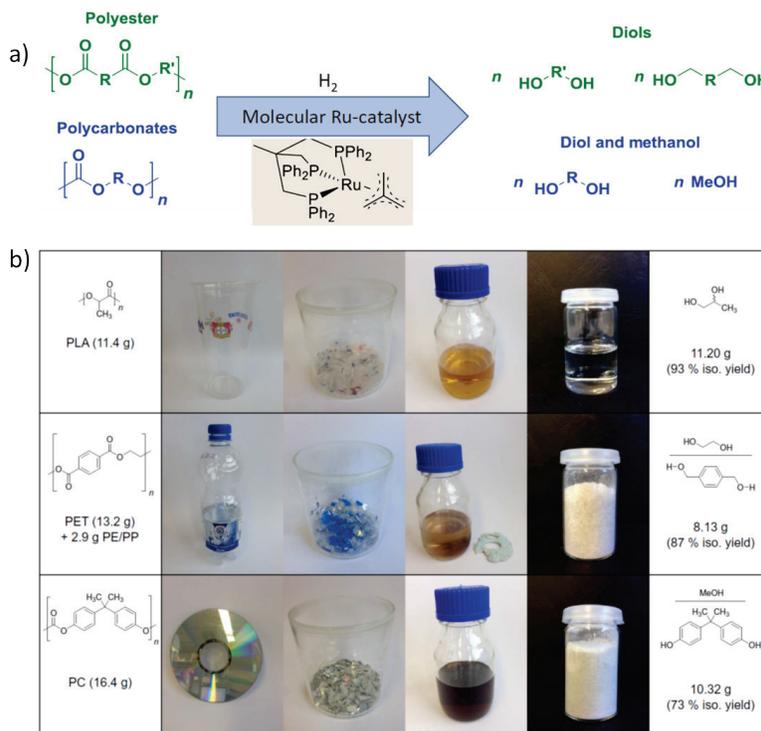
Figure 5. (a) Reductive depolymerization of discarded polymers with a molecular ruthenium catalyst and (b) hydrogenolysis up-scaling for selected polyesters and polycarbonate consumer products. *Reprinted by permission from Creative Commons Attribution Noncommercial License 4.0. Revised from S. Westhues et al., "Molecular Catalyst Systems as Key Enablers for Tailored Polyesters and Polycarbonate Recycling Concepts," Sci. Adv. 2018, 4 (8), eaat9669; https://creativecommons.org/licenses/by-nc/4.0/.*

The depolymerization of PET has been widely studied.[44,45] Current research efforts focus on increasing the yield of monomer, performing the reaction at mild conditions (atmospheric pressure and below ~200 °C) and reducing the reaction time required to reach maximum yield (under 1 h for the best catalytic systems).[46] PET has been depolymerized via glycolysis (using ethylene glycol) to bis(2-hydroxyethyl) terephthalate (BHET) by using a catalyst called *protic ionic salt*, which is a mixture of triazabicyclodecene (TBD) (a common organic base) and methanesulfonic acid (MSA) (a common organic acid).[47] This versatile catalyst can be used to depolymerize PET to BHET (180 °C) and repolymerize BHET back to PET (250–270 °C), depending on the operating temperature. BHET yields up to ~90% were obtained under an inert atmosphere and good yields were obtained under air. The properties of the repolymerized PET were similar to those of the virgin PET. Additionally, the protic ionic salt showed much better thermal stability—which is key for repolymerization—than TBD and MSA separately. The TBD:MSA (1:1) mixture also showed stable depolymerization performance during at least six recycling processes.

Imran et al.[48] studied catalytic glycolysis of PET into BHET at 300 °C using Mn_3O_4 or ZnO supported on silica nanoparticles or microparticles with the Mn_3O_4 metal oxide on silica nanoparticles providing the highest monomer yield (>90%). The performance of Mn_3O_4/silica nanoparticles was attributed to the material having the highest surface area and largest pore volume. Glycolysis in the absence of a catalyst also occurred under the studied conditions but gave much lower yields.[48] Lima et al. reported that PET depolymerization is possible using sodium titanate nanotubes or zinc titanate nanotubes to form BHET.[49] Nanostructuring the titanates led to higher yields under milder conditions than in previous studies.

Ionic liquids and deep eutectic solvents. Ionic liquids can be used as environmentally friendly solvents and catalysts for the depolymerization of polymers. Ionic liquids are tunable, have unique solubility properties, are nonvolatile while also achieving high thermal stability, and have large liquidus and electrochemical windows. Thus, unique chemistries and processing technologies are possible. For instance, the strongly basic ionic liquid 1-butyl-3-methylimidazolium ([Bmim]) hydroxide showed the best catalytic performance for the depolymerization of PET into BHET in the presence of ethylene glycol when compared with [Bmim] bicarbonate, [Bmim] chloride, and [Bmim] bromide. At optimum conditions of 190 °C, a BHET yield of 71% was obtained.[50] Glycolysis has also been conducted in the presence of a Lewis base ionic liquid, [Bmim] acetate, with a yield of 58.2% at 190 °C.[51] 1,3-Dialkylimidazolium ionic liquids are reported to deprotonate to *N*-heterocyclic carbenes to catalyze the depolymerization of PET (in the presence of ethylene glycol) to BHET.[8,52,53]

Deep eutectic solvents (DESs), a special type of ionic solvent formed from a eutectic mixture of Lewis or Brønsted acids and bases, are active catalysts for solvolysis of PET. Wang et al. synthesized DESs using urea/metal salt mixtures.[54] The best catalyst ($4[urea]/1[ZnCl_2]$), under optimized glycolysis conditions at 170 °C, gave conversion and selectivity to BHET of 100% and 83%, respectively. This combined catalyst (DES) outperforms the separate components, urea and $ZnCl_2$. Aminolysis of PET in DESs choline chloride.$xZnCl_2$ and choline chloride.2urea have also been investigated. Yields in excess of 80% were attainable for different products: N_1,N_1,N_4,N_4-tetrakis (2-hydroxyethyl) terephthalamide (THETA), terephthalic acid (TPA), and bis (2-hydroxyethyl) terephthalamide (BHETA). THETA and TPA are produced when using diethanolamine, and BHETA is produced when using ethanolamine as solvents.[55]

Catalytic degradation of thermosets. Thermosets have applications in many industries, including electronics, automotive, and aerospace. Epoxy is commonly used as a matrix resin for carbon fibers (CFs) because of its chemical resistance and mechanical properties.[2] Many chemical recycling efforts have been devoted to recover the CFs, and the chemical recycling of the epoxy matrix is secondary.[56,57] Traditional chemical recycling uses strong acids, which are corrosive to equipment and prone to damage the recovered fibers; the separation-purification of the recovered polymers is time-consuming and costly.[58,59] El Gersifi et al.[60] studied the depolymerization of a diglycidyl ether of BPA epoxy (DGEBA)/hexahydrophthalic anhydride network by refluxing in diethylene glycol/titanium(IV) *n*-

butoxide (DEG/TBT) at 245 °C and in monoethanolamine (MEA, without catalyst). The solvent/catalyst system could "liquefy" the amine-cured epoxy via the cleavage of the ether linkage.[61] The authors[62] further compared the catalytic effects of four different catalysts—TBT, CH$_3$ONa, LiClO$_4$, and *p*-toluenesulfonic acid (*p*TSA)—on the bond cleavages of a model compound for the amine-cured epoxy in butanediol (BDO), and the result indicated that CH$_3$ONa (strong base, 30 wt %) and *p*TSA (strong acid, 3 wt %) were most efficient. Yang et al.[63] used a poly(ethylene glycol)/NaOH catalytic system to depolymerize a DGEBA/anhydride network at 180 °C for 50 min and claimed complete dissolution compared with only 26.4% dissolution with MEA; DEG/TBT and BDO/*p*TSA were not effective. However, the high boiling point solvents are not easily recyclable, and the residual solvent in the degraded product is a toxicity concern.

To find the most valuable use of the deconstructed polymer in new resins, the degradation of epoxy matrix composites must be performed in a more controllable manner (i.e., selective cleavage of the C-N and C-O bonds and leaving the C-C bonds intact). Deng et al. evaluated the catalytic decomposition of DGEBA/3,3-dimethyl-4,4-diaminodicyclohexylmethane in H$_2$O with different Lewis acids.[64] The authors found that ZnCl$_2$ was the most effective in cleaving the C-N bonds of the epoxy network structure. However, effective epoxy depolymerization was achieved with a concentrated ZnCl$_2$ solution (50 wt % or higher) at 210 °C or higher temperatures. In another study, degradation of the same epoxy was studied in an acetic acid medium at 180 °C, and AlCl$_3$ (15 wt %) was found to be the most effective among all the metal salts evaluated.[65] However, the resulting decomposed polymer contained as much as 13% chlorine based on the elemental analysis.

In recent years, two efficient ways to recycle epoxy composites and reuse of the recyclates have been reported.[66] It is well understood that epoxy-amine and epoxy-anhydride are the most common epoxy curing systems. For decomposition of amine-cured epoxies, a solution of ethanol/zinc acetate was used as the catalyst. The CF-reinforced composite was decomposed at a mild temperature (190 °C) with a modest catalyst concentration (<20 wt %). The recovered CF exhibited an average tensile strength of ~7.5 GPa, which is very close to that of the virgin fibers. For the anhydride-cured epoxies, phosphotungstic acid (HPW) was introduced as a highly efficient catalyst in aqueous solution. HPW is an eco-friendly strong acidic catalyst that has been widely used to replace the highly corrosive protonic acids in reactions. At a mild reaction temperature (190 °C) and a low catalyst concentration (1 wt %), the HPW/water catalyst system effectively cleaved the ester bonds and left other chemical bonds intact. In both cases, the decomposed polymers were found in the oligomer form and contained multifunctional reactive groups as a result of the mild reaction conditions; thus, they could be used as reactive ingredients for preparing new thermosetting materials.

Solvolysis of polymer composites in subcritical or critical fluids has also received significant attention. Solvents with relatively low boiling points—including acetone, short chain alcohols such as methanol, ethanol and 1-propanol, and water—were used in this method. Current research under sub- or supercritical conditions is focused on recovering the more valuable fibers with little attention on the use of the decomposed polymer. Additionally, the high temperature and possible oxidation involved tend to yield a decomposed polymer of more complex composition.[57,67–69]

Biocatalysis. Plastics are generally quite resistant to microbial degradation, which is why they have long lifetimes in the environment. Low surface area and hydrophobicity are among the strong drivers for resisting environmental degradation. Although many studies have looked at the biodegradation pathways of plastics using microorganisms and enzymes, few have addressed the use of degradation products from these pathways for recycling or upcycling purposes. Wei and Zimmerman published a status report in 2017 on the use of microbial enzymes for recycling.[70] Koshti et al. reviewed PET recycling via biocatalytic pathways.[71] PET, in particular, shows promise for enzymatic routes for recycling. PET degradation via enzymatic hydrolysis has been shown to produce useful products, including ethylene glycol and terephthalic acid using polyester hydrolase TfCut2.[72] However, other reaction products formed

using this enzyme, particularly mono-(2-hydroxyethyl)terephthalic (MHET) acid, can inhibit the enzyme. Thus, mechanisms to continuously remove deleterious products, be it through separations or the addition of other enzymes, have been or could be used to keep the desired degradation pathway open.[72,73] Cutinases as well as lipases have been investigated with a goal of enabling simultaneous glycolysis and hydrolysis.[74] Alternatively, new bacterial species could provide new approaches, such as Ideonella sakaiensis, which degrades PET with higher activity than polyester hydrolase TfCut2 as it rapidly metabolizes MHET.[73] Notably lacking in studies to date are enzymatic pathways for PE degradation that would enable it to be upcycled biocatalytically. Enzymes can show low efficiency for degradation; thus, there are discussions as to whether catalysis using whole cells could be a better approach, including for recalcitrant PE.[75]

4.2 Deconstruction of Natural Polymers

Biomass. Fundamental research into the depolymerization of biomass, a naturally occurring polymer, into value-added products has been of significant interest over the last three decades.[76–78] Lessons can be learned from these studies and applied to the deconstruction of synthetic polymers. Biomass includes a wide range of organic materials, which are generally composed of cellulose, hemicellulose, lignin, lipids, proteins, simple sugars, and starches. Among these, cellulose, hemicellulose, and lignin are the main components and are often referred to as "lignocellulose." These carbohydrate polymers contain different sugar monomers (six and five carbon sugars), and they are tightly bound to lignin. Lignocellulosic biomass can be deconstructed to release useful chemical intermediates, including sugars, phenols, and oxygenated benzene derivatives. In general, unlike grain polysaccharides (e.g., starch and sugar cane) connected by flexible α-1,4-glycosidic bonds, lignocellulose is connected with inflexible β-1,4-glycosidic bonds, which is more complex in structure, making it highly resistant to chemicals and enzymatic processes. Hydrogen bonding within cellulose is both intra- and intermolecular, giving rise to its highly crystalline structure. Consequently, hydrolysis of cellulose by any chemical or biological means is challenging.

Two primary routes are used to deconstruct cell walls to produce chemicals and fuels that are under development: thermochemical and biochemical conversion.[76–78] Thermochemical conversion processes mainly include pyrolysis, gasification, and liquefaction. The stored energy within biomass can be released directly as heat via combustion/co-firing or could be transformed into solid (e.g., charcoal), liquid (e.g., bio oils), or gaseous (e.g., syngas) products via pyrolysis, liquefaction, or gasification for various uses. Fast pyrolysis[79] of biomass has attracted a lot of attention since it is, to date, the only industrially realized technology for the high-yield production of bio oils. However, the bio oils are very complex, corrosive, and reactive. Lignin is particularly difficult to deconstruct because of its very stable polyphenolic structure.[80] Fast pyrolysis[81,82] and catalytic fractionation[83] of lignin can produce valuable phenolic monomers/dimers, which are key intermediates used in phenol-formaldehyde polymers. Plasma gasification is mainly applied to hazardous waste treatment because of the high destruction and reduction efficiencies. However, it also has great potential to produce syngas because of its high yields of H_2 and CO and its extremely low yield of tar. Supercritical water gasification is a promising approach for hydrogen generation from biomass feedstocks, particularly those with high moisture contents, such as sewage sludge. Since water can be considered an effective and "green" solvent, direct liquefaction can also process wet biomass feedstocks directly. Ionic liquids have also been investigated as green solvents for lignocellulose deconstruction due to their ability to dissolve the cellulose portion of lignocellulosic biomass and simultaneously disrupt the lignin and hemicellulose network.[84]

Epps et al. recently reported a new and robust strategy toward using the chemicals directly obtained from raw biomass deconstruction.[85] Poplar deconstruction followed by minimal purification steps (filtration and extraction) produced two aromatic compounds, 4-propylsyringol and 4-propylguaiacol, in high yield and high purity. A noteworthy and translatable aspect of this effort was the use of a monomer obtained

from the deconstruction of real biomass rather than a model compound or lignin-mimic to generate well-defined, nanostructured polymers.

Biochemical conversion[86,87] of biomass to chemicals and fuels offers the potential for high selectivity, high yields, moderate temperatures, and low cost. Enzymatic hydrolysis of biomass into fermentable sugars is the most important and complex step in the process. One difficulty associated with gaining access to these cell wall polymers for conversion to reactive intermediates is termed biomass recalcitrance. To overcome this recalcitrance, low-severity thermochemical treatment (pretreatment) at temperatures between 100 and 200 °C are used to partially break down the cell wall and improve enzymatic accessibility. Then, enzymes or microbial catalysts can convert the carbohydrates to soluble sugars, which are then converted to fuels. Many challenges still remain, including understanding the fundamental mechanisms of how enzymes deconstruct the cell wall to discover and design new, more efficient catalysts and enzymes; how to optimize pretreatment, enzymatic hydrolysis, and fermentation; and how to reduce oxygen functional groups in fuel molecules. Because the plant cell wall is a solid composite material, enzymes must work directly at the solid-liquid interface and engage in the surface depolymerization of individual cellulose chains to hydrolyze carbohydrate polymers.

Coal. Coal is a heterogenous polymer composed of over 50 wt % carbon with hydrogen, oxygen, nitrogen, sulfur, and inorganic mineral matters. Coal has been processed for centuries into higher value products such as aromatic chemicals, pitch, and carbon. Lessons learned from coal processing can be applied to the conversion of synthetic polymers to higher value products. The extractable organic components in coal often have a network structure in which single and multiple aromatic rings are cross-linked or associated and thus show structural similarities to polymers. Coal conversion often involves the thermochemical breakdown of the heterogenous polymeric structures, which is also referred to as *depolymerization* or *destructive distillation*. The chemistry of coal depolymerization is complex due to the heterogeneity of the starting materials from the molecular level (different chemical composition, structure, and connectivity) to the macroscopic level (organic and inorganic matters, different macerals within the coal structure). There are many different ranks of coals from various regions in the United States and the world. These coals are classified in the order of increasing carbon content (and decreasing heteroatom content) and increasing heating value (i.e., lignite, subbituminous, bituminous, and anthracite).

The organic matter in coal can be converted to gaseous, liquid, and solid carbonaceous products by gasification, liquefaction, and carbonization, respectively.[88] There are reviews in the literature on the chemistry of coal liquefaction[89] and coal pyrolysis.[79] The depolymerization of coal organic matter begins when coal is heated above 280–320 °C. The cleavage of weak C-O bonds is generally accepted to begin at relatively lower temperatures, whereas C-C bonds cleave at higher temperatures. When these bonds breaks, two radicals are formed that can initiate radical chain reactions involving hydrogen abstraction, β-scission, and radical addition reactions in the gas or liquid phase. However, there are mass transfer limitations in coal and discarded plastics. If the radicals from bond breaking are not stabilized effectively, then they can recombine in a different fashion that causes the resulting bond to be stronger than the initial bond. Using hydrogen donor solvents, such as tetralin and/or gaseous hydrogen, can stabilize the radicals from the thermal depolymerization of coal structures, which typically leads to higher yields of liquid products. The effects of tetralin on the pyrolysis of long-chain paraffins have been studied.[90] Tetralin addition can effectively inhibit paraffin decomposition and change the product distribution. Several other compounds can also be used as hydrogen donors, such as tetrahydroquinoline.[91]

Catalysts including alkaline earth and alkali metals, activated char, Lewis acids, and supported metals have been used in coal pyrolysis and can influence the quality and composition of the final products.[79,82] The arrangement of the catalysts and coal material can significantly affect the product yield, highlighting the importance of mass transfer in such solid-solid reactions. Mass transfer is also expected to be an issue in catalytic depolymerization of polymers.

In addition to the traditional pyrolysis, hydropyrolysis,[92–94] oxidative hydrothermal dissolution[95,96] of coal permits alternative pathways to specialty chemicals and carbon-rich products.

5   Deconstruction Followed by Upgrade or Reconstruction

Despite the robust plastic sorting technologies developed decades ago, the reuse of discarded plastic remains immature. Currently, the technology is primarily focused on the mechanical recycling of aged plastics, resulting in downgraded products.[97,98] The depolymerization of these discarded polymers to monomeric building blocks is thermodynamically energy intensive. The complete deconstruction of the plastics to monomers requires stabilization during thermochemical or catalytic depolymerization to prevent unwanted side reactions. Additionally, depolymerized monomers must be separated, purified, and stored for future reconstruction to products. Despite these challenges, recent success with biomass deconstruction and the complete depolymerization of cellulose to sugar followed by enzymatic conversion to biofuel provide encouragement and inspiration for the chemical upcycling of plastics.

This section summarizes the current state of the art for chemical upcycling of polymers involving the direct use of end-of-life plastics via deconstruction followed by the synthesis of new, higher value polymers without going through extensive building block separation. In some cases, partial deconstruction (due to thermal degradation) is avoided via additive-aided stabilization of the feedstock during processing, and material performance is enhanced by using cross-linkers (i.e., small molecules that form covalent bonds between two polymer chains) or compatibilizers (i.e., molecules that migrates to the interface of an immiscible polymer blend to improve stability). In other cases, specific deconstructed intermediates are reacted with additional monomers and polymers to produce new polymeric materials of controlled architecture, performance, and recyclability. In some cases, the deconstruction to small molecular products such as fuels are preferred for high-volume applications. Other repurposing methods include the conversion of discarded plastic to carbon and the performance-advantaged hybrid polymeric products. Therefore, this section covers solutions based on combinations of mechanical and chemical processes since a single unit-operation or chemistry does not provide a viable solution.

5.1   Direct Processing of Discarded Feedstock

Primary recycling of plastics, which involves shredding, melting, and remolding polymeric materials, works well only with pre-consumer discarded thermoplastics or process scraps in combination with pristine polymers. Otherwise, in most cases, primary recycling causes deleterious effects in performance. Such effects in primary recycling are due to the process-induced degradation in post-consumer plastics molecular architecture. This section analyzes the current methods to avoid such downcycling.

Compatibilization of discarded plastics. One challenge to recycling and upcycling discarded polymers is that it is difficult to obtain a clean (i.e., single polymer) stream. Many thermoplastics—such as PE and PP, which are used in packaging—are relatively easy to reprocess because of their higher thermal stability compared with other polymers. However, they are difficult to separate, and they are not compatible even though they are very chemically similar. Simple blending of these polymers during melt extrusion results in a brittle product that has poor mechanical performance due to the poor mixing and chemical compatibility of PE and PP, which results in a weak interface. Conventional blends of PE and PP need high loading (~10 wt %) of a compatibilizer—such as ethylene-octene or ethylene-propylene rubber, which are essentially random copolymers—to provide good mixing and mechanical properties.[99] Ethylene-octene and styrene-ethylene-butylene-styrene block copolymers are well-known amorphous compatibilizers that enhance interfacial bonding at high loading (Figure 6). Eagan et al. recently devised a tetra-block copolymer of isotactic PP-PE-isotactic PP-PE sequence with ultrahigh molecular weight (300 kg/mol) that can be loaded at 1–5 wt % in PP and PE blends to make repurposed products with exceptional toughness.[100] The performance of the blends significantly exceeds that obtained for diblock

copolymers of PP and PE as compatibilizers, even with very high block molecular weights. The tetra-block copolymer additives with high block molecular weights essentially form nanoscale layers of semicrystalline phases. Even at low loading (~1 wt %), these additives stitch the layers at the interface of a binary mixture of PE/PP through the formation of trapped entangled loops that are difficult to pull out during mechanical deformation. Using the tetra-block compatibilizer leads to a homogeneous microstructure (no visible phase contrast under scanning electron microscopy at <1 μm scale) unlike an incompatible blend of PP/PE (2–4 μm domains of PP in PE matrix) (Figure 6).[100]
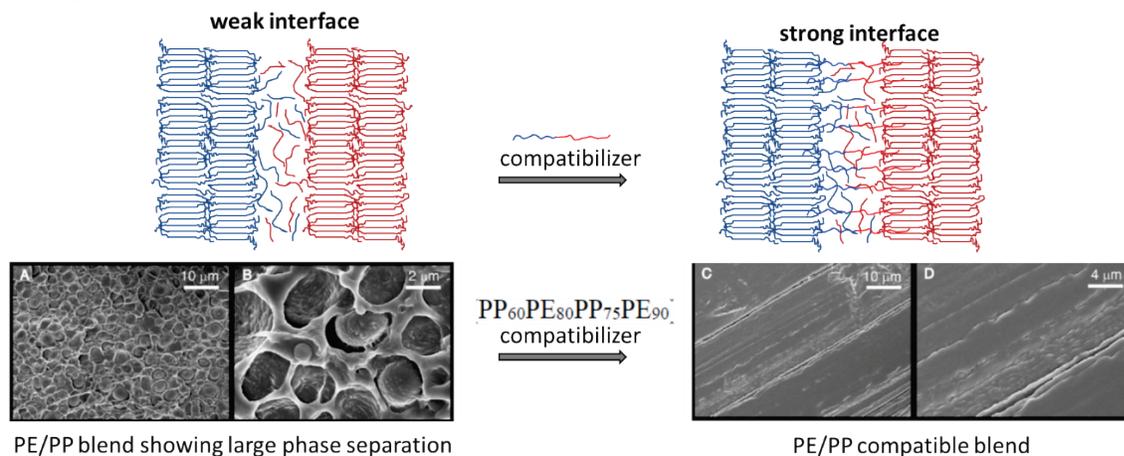

Figure 6. Compatibilizers enhance interfacial bonding and form a homogeneous system. For example, PE/PP incompatible blends compatibilized with isotactic PP_{60k}-PE_{80k}- isotactic PP_{75k}-PE_{90k} tetra-block copolymer show significantly improved performance and homogeneous morphology in contrast to the incompatible blend. *Upper images used courtesy of Xi Chen, Oak Ridge National Laboratory. Lower images from J. M. Eagan et al., "Combining Polyethylene and Polypropylene: Enhanced Performance with PE/iPP Multiblock Polymers," Science 2017, 355 (6327), 814–816. Reprinted with permission from AAAS.*

Mixtures of PS, PVC, and HDPE that are inherently immiscible were successfully converted to a compatible system by using ethylene-vinyl acetate copolymer and styrene-ethylene-butylene-styrene copolymer as compatibilizers to produce extraordinarily ductile and tough polymer blends. The performance was further enhanced by gamma irradiation, which resulted in interfacial cross-linking.[101] Compatibilization of polycarbonate and PET was accomplished during melt extrusion of the blend via transesterification.[102] However, these compatibility enhancements are not expected to deliver endless recyclability—even for low-density polyolefins known for excellent thermal stability even in the molten state—because of degradation in the reprocessing.[2]

Stabilization of structures, rheological properties, and performance enhancement in mechanically recycled plastics. Structural degradation of polymers during primary recycling is common under certain processing conditions. For example, PP is a thermally reusable material until it reaches an optimal thermal history beyond which it exhibits thermo-oxidative degradation. Tertiary carbon centers in PP form stable free radicals that can subsequently react with oxygen, leading to chain scission.[2,98] Therefore, after several cycles of processing, PP degrades and its performance deteriorates faster than that of PE. To avoid a decrease in molecular weight, PP is usually compounded with free-radical-scavenging stabilizers, such as hindered phenols. Often, a combination of these hindered phenols with phosphite or thioethers offers synergistic stabilization to avoid the abrupt reduction of viscosity and polymer downcycling. These stabilized polymers are excellent feedstocks for additively manufacturing (i.e., 3D printing) complex-shaped parts by an extrusion-based deposition of layers.[103] A similar approach recently demonstrated success with thermoplastic-grade lignin, a renewable hindered phenol, that can stabilize a nylon 12 thermoplastic melt to develop a 3D printable composition with appropriate melt-rheology and mechanical performance.[104]

Using amorphous acrylic and styrenic plastics (e.g., PMMA or PS) to make melt-processable fibers or melt-blown nonwovens is limited due to a lack of melt-rheological properties for fiber generation and thermal instability that further affects the viscosity profile. Conventional cross-linking can enhance extensibility under an applied elongational flow field; however, continuous melt extrusion of such networked products is not feasible. Ellison and colleagues devised an anthracene-based reversible cross-linking methodology via UV irradiation and thermal dissociation of networks for the fabrication of 4–10 μm diameter filaments functionalized with pendant anthracene rings.[105] The team also devised another approach with functionalization of these inherently non–fiber-forming polymers, such as acrylates, silicones with furan, and bismaleimide for thermo-reversible Diels-Alder reaction.[106] Those reactants are decoupled during thermal processing but bond during cooling (Figure 7). Functionalization is accomplished by free radical copolymerization with functionalizable monomers or grafting reversibly cross-linkable functional moieties.

One-pot synthesis of new polymers using depolymerized building blocks. During mechanical treatment, polymers that have been reprocessed in a mold-and-remold cycle exhibit diminished thermal and mechanical properties compared with virgin materials. For example, the measured ductility of PET is diminished from ~310 to ~218% after one cycle, and by the third cycle, it plummets to 2.9%.[107] As a result, very little PET is recycled for bottle production; most (50–77%) recycled PET is used for fibers in applications such as carpets, which can no longer be recycled. Alternatively, PET can be depolymerized by solvolysis (e.g., hydrolysis, methanolysis, and glycolysis). Depolymerized intermediates are subsequently polymerized to make unsaturated polyester resin, which is widely used to make composite products.[108] The depolymerized mixture is repolymerized or fed with other PET flakes for subsequent condensation reaction, along with devolatilization of impurity, at high temperatures with an applied vacuum. Aminolysis of PET by aniline or aminophenols can lead to the formation of an ester-amide reconstructed intermediate that reacts with bisphenol and difluorodiphenylsulfone via nucleophilic aromatic substitution polymerizations to yield poly(aryl ether sulfone amide)s containing 10–30 wt % amide functionality.[109] The amide group offers facile melt extrusion characteristics, and the rigid sulfone offers stiffness in the polymers for its engineering applications. Other co-monomers can be substituted in the current method to form other engineering thermoplastics, such as polyimides.

Fukushima et al. have shown that aminolysis can be performed using organic bases to upcycle PET, forming a range of value-added crystalline terephthalamide compounds.[110] Likewise, triazabicyclodecene has been found to be a good catalyst for the methanolysis of BPA-based polycarbonates.[47] The benefit here is that the BPA and dimethyl carbonate can be recovered. Ethylene glycol combined with diethanolamine resulted in the decomposition of polyurethane foams, which resulted in a two-phase mixture, one of which is the polyol.[111] Thus, this process can be used to produce adhesives from polyurethane.

Instead of breaking covalent bonds, another approach is to disrupt the hydrogen bonding network to generate polymers with improved properties. For example, a single-pot approach was used to partially deconstruct biomass to an intermediate by boiling with a mixture of NaOH and Na_2SO_3, which increased its deformability, and then converting it into a high-performance product by eliminating structural defects and pores.[112] In another approach, wood pieces were first soaked in an ionic liquid solvent that loosened the hydrogen bonded networks between cellulose and lignin. This materials was then consolidated, and the networked structure (from the native cross-linked structure and reformed hydrogen bonding) was restored with improvements in the mechanical properties.[113] As discussed in Section 6.1, a similar approach can be use for processing and recycling thermoset polymers containing dynamic colavent networks.
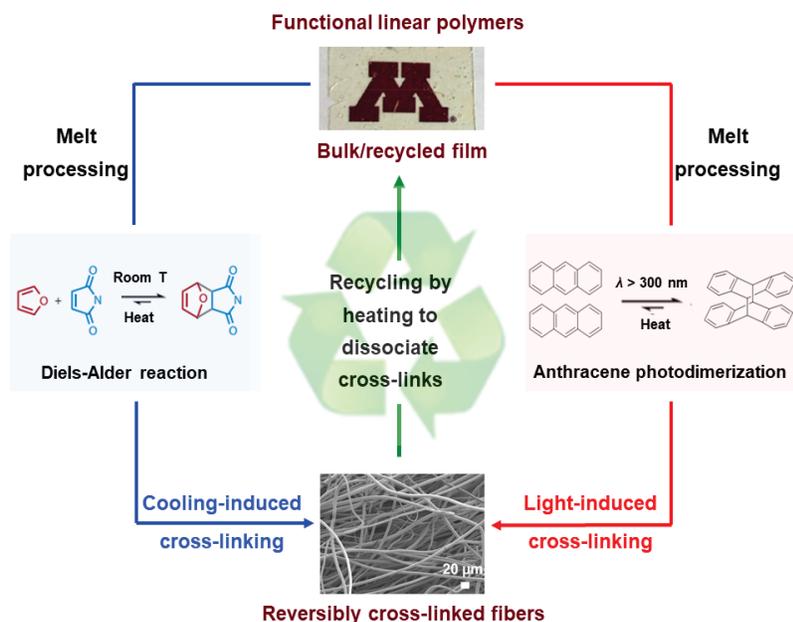
15

Figure 7. Route to cross-linked fibers suitable for high-performance applications from commodity polymers (i.e., acrylic, styrenic, and siloxane backbones). Linear commodity polymers containing reactive functional groups were melt-blown into fibers and subsequently cross-linked via a Diels-Alder reaction or a light-induced anthracene photodimerization. The reversibly cross-linked fibers can be recycled into bulk films or secondary fibers via heating because of their dynamic nature at elevated temperatures. *Adapted with permission from K. Jin et al., "Mechanically Robust and Recyclable Cross-Linked Fibers from Melt Blown Anthracene-Functionalized Commodity Polymers," ACS Appl. Mater. Interfaces 2019, 11 (13), 12,863–12,870; and K. Jin et al., "Melt-Blown Cross-Linked Fibers from Thermally Reversible Diels–Alder Polymer Networks," ACS Macro Lett. 2018, 7 (11), 1,339–1,345. Copyright 2019 American Chemical Society. Image courtesy of Chris Ellison and Kailong Jin, University of Minnesota.*

5.2 Synthesis of Materials from Deconstructed Intermediates Aided by Additional Components

Polymeric materials can be depolymerized into intermediate building blocks for reconstruction to a material form without going through extensive separation or isolation of chemical intermediates. Synthesis of materials from depolymerized monomers often requires removal of impurities, additional feedstock, and catalysts to make a designed product.

Endless reversibility of deconstruction and reconstruction. Polymers with a low ceiling temperature (T_c) are readily depolymerizable back to their monomers under mild conditions, but they typically do not possess robust physical and mechanical properties that are useful for common applications; repolymerization must be performed under low-temperature and high-concentration conditions. For example, poly(γ-butyrolactone) (PGBL) synthesized via catalyzed ring-opening polymerization (ROP) of bio-derived GBL can be selectively and quantitatively depolymerized back to GBL via thermolysis at 260 °C or by chemolysis at room temperature (RT) with a catalyst. However, repolymerization of GBL requires energy-intensive, low-temperature conditions (−40 °C), and PGBL exhibits limited thermostability and crystallinity with a low melting temperature (T_m) of 60 °C.[114] The chemoselective ROP of biomass-derived α-methylene-γ-butyrolactone also led to a completely recyclable polymer, but again, low temperatures (−60 °C) are required for polymerization and repolymerization.[115]

To address these challenges, a trans-fusion strategy was developed to increase the ring-strain of GBL and thus T_c, which enables polymerization and repolymerization at RT, and to enhance the properties of the resulting polymer while preserving the complete chemical recyclability. Thus, trans-fusing a cyclohexyl ring to GBL at the α,β-positions gives trans-hexahydrophthalide (T6HP) (Figure 8) a monomer derived

16

from bio-sourced fumaric acid. Indeed, T6HP can be effectively polymerized into high-molecular-weight polymers under RT and neat (i.e., solvent-free) conditions.[116] In the presence of a metal-based catalyst (50 ppm), A linear P(T6HP) with high $M_n = 1.11 \times 10^6$ g/mol ($Đ = 1.09$) was produced. A cyclic polymer can also be produced at RT with a different catalyst and no initiator. The resulting polymers exhibited a high decomposition temperature of T_d = ~340 °C, and a crystalline stereocomplexed material with a high T_m = ~190 °C was generated by physical blending of enantiomeric polymers. Moreover, the polymer exhibited the robust thermal and mechanical properties of common commercial plastics. Most importantly, P(T6HP) can be depolymerized back to a monomer in quantitative yields via thermolysis at temperatures ≥300 °C or via chemolysis at lower temperature (120 °C) using a catalytic amount (2 mol %) of a metal salt (e.g., $ZnCl_2$). The monomer was quantitatively recovered in a pure state from the depolymerization and was directly repolymerized neat at RT without a decrease in the subsequent monomer conversion and polymer quality. Such consecutive polymerization-depolymerization-repolymerization circular cycles have also been realized on a multigram scale. In principle, this process can be repeated infinitely, establishing a circular life cycle of such chemically recyclable polymers.
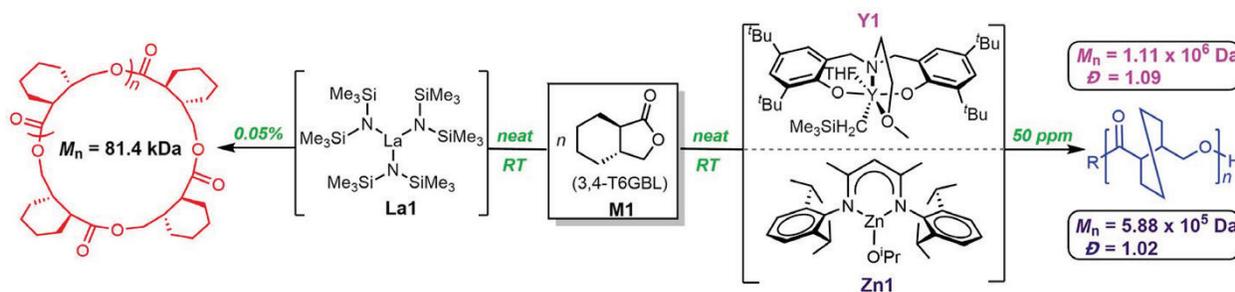

Figure 8. A synthetic polymer system based on T6HP with endless reversibility of depolymerization and repolymerization. The catalyzed ROP of T6HP under RT and neat conditions produced high-molecular-weight polymers with linear or cyclic topology and robust properties of common plastics. The catalytic depolymerization of P(T6HP) recovered the monomer in quantitative yield and high purity. The monomer can be directly and repeatedly repolymerized into the same polymer. *From Figure 1A in J.-B. Zhu et al., "A Synthetic Polymer System with Repeatable Chemical Recyclability," Science 2018, 360 (6387), 398–403.*

Upcycled performance-advantaged products from the deconstruction of oligomer feedstock. Discarded polymers are often converted to oligomeric feedstocks that are combined with other feedstocks to make polymeric products that do not necessarily replace petrochemical derivatives but are of higher value. This group of materials is considered as performance-advantaged products. For example, phenol monomers and oligomers derived from deconstruction of lignin can be used as renewable feedstocks for the construction of alternatives to PS and PMMA. The aromatic structure of lignin monomers can deliver strength in plastics, just as innate lignin does for trees.[117] The approach involves modifying the phenols via transesterification or epoxidation reactions to create reactive functional groups for their direct polymerization.[118-120] In another example, guaiacyl alcohol-based lignin oligomers were reactively processed with unsaturated rubbers containing a high-acrylonitrile content to deliver a partially renewable thermoplastic elastomer.[121] The superior material properties were due to the enhanced interaction between the rubber and the highly dispersed (6–60 nm) lignin rigid phase.[121]

Finally, fractionating lignin into a multifunctional polyphenol oligomer—which contains carboxylic acid, alcohol, and phenol groups—provides a highly reactive matrix with inherent stiffness, which makes it an ideal building block for tough functional polymers.[122] Extending this method to polymer deconstruction and biodegradable polymers[123] increases the upcycling efficiency (no need to depolymerize to monomer) and provides a new platform for copolymer formation, which is difficult to obtain by traditional polymerization methods. For example, when these functional oligomers react with epoxy-terminated PEG, the reaction yields a self-healing elastomer and thermoplastic elastomer (Figure 9).[122]
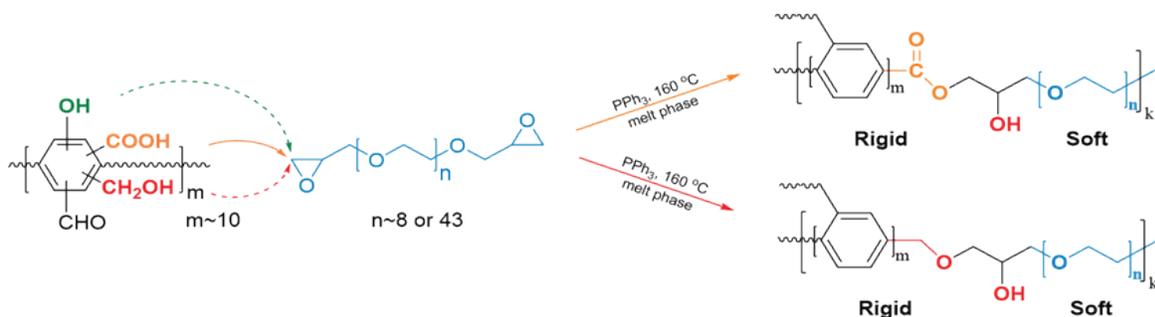
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Figure 9. Reactions between functional lignin and diglycidyl ether PEG at melt-phase yield a covalently networked and hydrogen bonded elastomeric material that exhibits self-healing behavior. *Adapted with permission from M. Cui, et al., "Rigid Oligomer from Lignin in Designing of Tough, Self-Healing Elastomers," ACS Macro Lett. 2018, 7 (11), 1,328–1,332. Copyright 2019 American Chemical Society.*

A recent report highlighted success in upcycling bottle-grade polyester via diol-based deconstruction to a glycolyzed polyester oligomer followed by condensation with a biobased diacid, such as succinic acid or muconic acid, to produce high-performance copolyesters. A life cycle analysis suggests that these products enable reductions in energy input and greenhouse gas emissions compared with standard manufacturing practices.[124]

5.3 Thermochemical Conversion of Polymers for Synthesis of New Products

Instead of complete depolymerization, fast catalytic thermochemical pyrolysis is often used to convert petrochemical-derived plastics into transportation fuel. This section briefly summarizes current state-of-the-art pyrolysis methods for fuel production from discarded plastics and the successful efforts for pyrolytic conversion of discarded plastics to high-performance, high-temperature-resistant solids with unique functionalities. These groups of products are not necessarily polymeric end products but are carbonaceous in nature.

Polymers to fuel and chemicals. Pyrolysis of discarded polyolefins yields hydrocarbon fuels. Catalysis helps promote a specific reaction and enhances process efficiency by creating a desired product combination at reduced temperature. Usually, pyrolysis of PE increases alkane content, whereas PS yields higher aromatic content in the pyrolyzed liquid. The presence of PP favors alkene formation. Therefore, the desired end product with a specific octane number can be obtained by adequately blending discarded plastics.[125] A recent report highlights a novel catalytic conversion of PE to liquid fuels and wax. This method showed excellent selectivity for linear short alkane formation.[30]

Progress has been made on understanding the fundamental processes for the total upcycling of lignocellulosic biomass via catalytic deconstruction to chemical intermediates and fuels.[126] A detailed understanding of how catalytic hydropyrolysis and in situ hydrodeoxygenation can lead to drop-in hydrocarbon fuels was established. Isotopic labeling experiments closely coupled with theory have revealed fundamental reaction mechanisms during fast pyrolysis of carbohydrates.[127,128] Fast pyrolysis of lignin resulted in monomeric and dimeric products via concerted Maccoll and retro-ene elimination mechanisms that cleave β-O-4 linkages.[129] Methods of catalytic deconstruction[130] of lignin or biomass into low-molecular-weight aromatic chemicals were further modified to yield saturated or unsaturated branched products that are well-known polymer building blocks. For example, cellulosic residue can produce furfurals and levulinic acid, and lignin can yield muconic acid.[131] To transform cellulose, a novel catalysis with ruthenium and ammonium meta-tungstate was developed, which produced ethylene glycol, propylene glycol, and 1,2-butane diol in a 90% yield. New research shows catalytic recovery of these building blocks for a circular economy.[39] Lignin-deconstructed chemicals, such as 2-methoxy-4-propylphenol, were modified to yield biobased epoxy networks with variable cross-linking densities that

exhibited improved performance characteristics compared with fossil fuel–derived thermoset materials.[132, 133] Successful biomass deconstruction and conversion of the feedstock to tunable polymeric products[134] also teach general approaches to chemical upcycling of discarded plastics.

Discarded polymers to carbon. Thermochemical conversion of discarded plastics to high-value carbon materials have revealed new opportunities with plastic upcycling. For example, high-pressure (~1,000 psi) and high-temperature (~700 °C) treatments of PE in the absence of any solvent or chemicals produced carbon microspheres that were applicable for energy storage applications.[135] When pyrolyzed after an acid treatment, discarded tire rubber produced mesoporous carbon that exhibited excellent anodic capacity for lithium or sodium ion batteries.[136] Studies have shown that biomass-derived porous carbons exhibit excellent properties for supercapacitors.[137] Some studies show potential for manufacturing structural carbon fibers from PE.[138,139] Catalytic pyrolysis of PE and PVC delivered hydrogen along with the growth of carbon nanotubes on the catalysts.[140] A recent study showed the successful conversion of textile-grade PAN fibers to structural carbon fibers.[141] Similarly, the new sulfonation chemistry of PE fibers showed successful conversion to structural carbon fibers.[139] These examples demonstrate the upcycling potential of various discarded textiles to structural carbon fibers for high-performance applications.

6 Next-Generation Upcycling of Polymers

Although the upcycling of discarded plastics has made progress, significant challenges still exist. A need exists to develop the next generation of polymers with the desired physical, chemical, and mechanical properties that can be efficiently upcycled for a circular economy. Further advancement is also needed for biodegradable polymers. Although polylactide is the most successful example of biodegradable polymers, the range of material properties is rather limited, and the properties do not meet the needs of many applications. Developing next-generation polymeric materials that have equivalent or even superior properties compared with currently used polymers and that can be repeatedly reprocessed will change the landscape of plastics in many applications.

6.1 Reversible Synthetic Polymers

Since 1972, with the opening of the first plastic recycling mill in Conshohocken, Pennsylvania, innovation has driven the ability to recycle commercial thermoplastics. In contrast, thermosets—polymers that are chemically cross-linked during the curing process—have historically been viewed as impossible to recycle because their interconnected structures prevent thermal recycling. The strength and stability imbued by their cross-links make thermosets ideal for use as adhesives, foams, and composites. Although thermosets make up around 15–20% of all the polymers produced in the United States, they are not currently recyclable; and extending these materials' life cycles through reprocessing while also preserving their properties remains an alluring challenge.[142] Over the past few decades, significant attention has been devoted to incorporating dynamic bonds into polymer networks for reprocessability.[143] Unlike covalent bonds, dynamic interactions—including hydrogen bonds, electrostatic interactions, and dynamic covalent bonds—allow bonds to be exchanged upon the application of a stimulus to improve processability. The primary chemistry that enables recyclable or reprocessable cross-linked polymers uses reversible functional groups, including dynamic exchangeable groups (i.e., vitrimers) or dynamic reversible groups (Figure 10).[142] Depending on the postulated mechanism of the cross-link exchange, these materials can also be referred to as *covalent adaptable networks*[144]—which encompass associative and dissociative exchange reactions—or as *vitrimers*—which refer to networks whose cross-links exchange specifically through associative processes. A recent paper summarizes the current state of the art and provides a perspective on continually recyclable cross-linked polymers.[142] This section highlights key studies of reversible polymers.

Vitrimers. Leibler's group first developed a new class of processable thermosets, referred to as *vitrimers*.[145] Vitrimers are polymers with thermally exchangeable chemical cross-links that behave as insoluble thermosets and flowable thermoplastics upon the application of heat and pressure. The term *vitrimer* refers to the materials' temperature-dependent viscosities reminiscent of vitreous silica. The cross-link network can change the topology via associative exchange reactions that can be thermally triggered, resulting in malleability (Figure 10 [b]).[142,146] A transition from viscoelastic solid to viscoelastic liquid occurs at the topology freezing transition temperature, T_v, which is conventionally defined at the temperature with a viscosity of 10^{12} Pa·s.[145,146] Whereas a traditional thermoplastic displays an abrupt viscosity drop when heated above its T_g, a vitrimer behaves more like a glass once heated above its T_g and its T_v.[146] This property is attributed to the presence of associative

Figure 10. Illustration of reprocessable cross-linked polymers. Covalent adaptive networks are divided into two groups based on the exchange reaction. (a) One mechanism uses dissociative dynamic exchange reactions and has a temporary loss of cross-link density. (b) Another mechanism uses associative dynamic exchange reactions, which retain the cross-link density (i.e., vitrimers). *Used by permission from Creative Commons Attribution 3.0 Unported License from Figure 1 in W. Denissen et al., "Vitimers: Permanent Organic Networks with Glass-Like Fluidity," Chem Sci. 2016, 7, 30–38. Published by the Royal Society of Chemistry.*

exchange reactions so that the polymer network maintains the same cross-link density as it is being reshaped (Figure 10 [b]). By modulating the polymer identity and linker chemistry, designing vitrimers with useful thermal and mechanical properties at service temperatures is possible, along with malleability at elevated temperatures for reprocessing. Thus, thermally reprocessable vitrimers are excellent candidates for the post-industrial recycling of plastics used in subtractive manufacturing, which involves cutting material away from a solid block to form the desired shape.

The first vitrimer reported by Leibler's group used a carboxylic acid-epoxy transesterification reaction with the presence of a catalyst, such as zinc acetylacetonate (e.g., 5 or 10 mol %) (Figure 11).[145] The dynamic polyester networks showed Arrhenius-like gradual viscosity variations, which are similar to vitreous silica. They demonstrated the weldability of the polyester vitrimer to make complex objects by local heating without the use of molds. Although the pioneering work by Leibler's group opened up a new field, the system used large amounts of catalyst. Using a catalyst can produce rapid and modifiable rates of exchange, but the catalyst might be unstable or prone to leaching from the network, which could undermine the material's recyclability.[147]
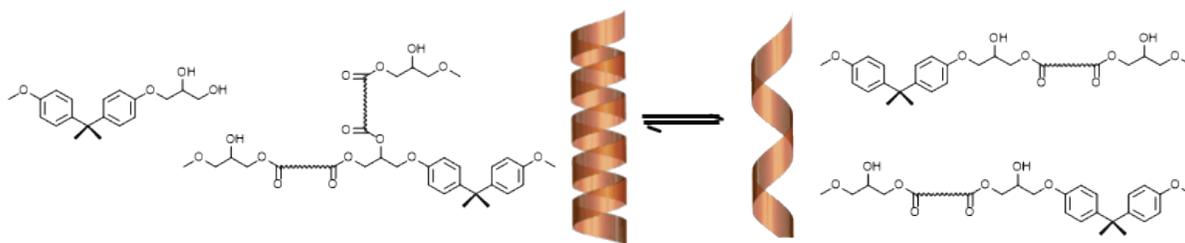

Figure 11. Vitrimer based on carboxylic acid-epoxy transesterification. *Modified from D. Montarnal et al., "Silica-Like Malleable Materials from Permanent Organic Networks," Science 2011, 334 (6058), 965–968. Reprinted with permission from AAAS.*
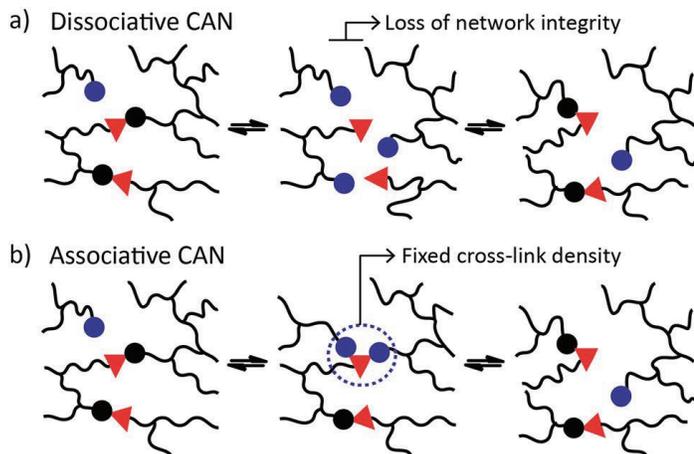
More recently, an instructive example comes from Dichtel et al. on the synthesis of catalyst-free polyhydroxyurethane (PHU) vitrimers.[148] Bis(cyclic carbonate) and tris(2-aminoethyl)amine were copolymerized to form cross-linked urethane-containing polymers with free primary alcohols (Figure 12).[148] The as-synthesized samples showed properties similar to those of other thermosets, with average Young's moduli of 2.2 ± 0.4 GPa, strain-at-break of 6.9 ± 3.8%, and thermal stability up to 250 °C by thermogravimetric analysis. However, unlike most thermosets, these materials demonstrated stress relaxation at temperatures above T_v (111 °C). The transcarbamoylation reaction proceeded via an associative mechanism without needing an exogenous catalyst, which was required in other vitrimers. In addition to allowing for stress relaxation, the presence of dynamic bonds in these vitrimers allowed for thermal reprocessing. After grinding of the pristine polymer, the samples were repaired by compression molding at 160 °C for 8 h. The reprocessed materials showed good mechanical property retention with a 76% recovery of Young's modulus and 69% recovery of strain at break. Other vitrimers exhibited similar reprocessability. Polycarbonate networks were synthesized with bis(cyclic carbonate) and 1,4-butanediol with 1–4 mol % titanium isopropoxide as a transcarboxylation catalyst. Ground samples of polycarbonate could be reformed at 140 °C to provide fully fused polymer networks with 80% recovery of the tensile strength of the as-synthesized material.[149] Other researchers have developed materials with negligible loss of mechanical properties upon recycling, such as the catalyst-free polyimine networks reported by Taynton et al. that demonstrated no loss in mechanical strength and increased tensile strength after three reprocessing cycles.[150]
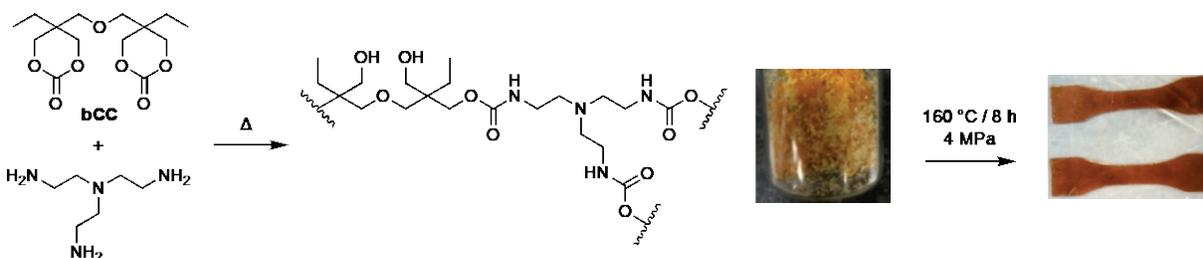

Figure 12. The synthesis and reprocessing of PHU vitrimers. *Image courtesy of Ben Elling and William Dichtel. Adapted with permission from D. J. Fortman et al., "Mechanically Activated, Catalyst-Free Polyhydroxyurethane Vitrimers," J. Am. Chem. Soc. 2015, 137 (44), 14,019–14,022. Copyright 2019 American Chemical Society.*

Another example of catalyst-free vitrimers was developed by Sumerlin's group.[147] The researchers used commercially available and inexpensive reagents to prepare vitrimers from vinyl monomer-derived prepolymers that contain cross-linkable β-ketoester functional groups. Random copolymers of poly(methyl methacrylate)-co-(2-acetoacetoxyethyl methacrylate) afforded linear prepolymers that were converted into vitrimers in one step by a trifunctional amine treatment. The network polymer showed retention of urethane cross-links and reprocessability over as many as six cycles. Additionally, a secondary form of recycling was implemented by uncross-linking the network with mono-functional amine to yield a modified prepolymer, which could be readily repurposed or recross-linked.[147]

Drockenmuller's group reported vitrimers based on a trans-alkylation reaction of 1,2,3-triazole and pendant alkyl halides (Figure 13).[151] Tunable networks were synthesized by the solvent- and catalyst-free polyaddition of an α-azide-ω-alkyne monomer and simultaneous alkylation of the resulting poly(1,2,3-triazole)s with a series of difunctional cross-linking agents. The polymerized ionic liquid network exhibited vitrimer behavior, and counter–ion exchange provided altered stress relaxation kinetics. Bromide-, iodide-, and mesylate-containing networks exhibited characteristic relaxation time (τ^*) values of 347 s, 1,030 s, and 180,000 s, respectively, when the characteristic relaxation time was correlated to their malleability.

Reversible polymers via supramolecular interactions. Supramolecular polymers possess versatile capabilities—including processability, recyclability, and self-healing—due to their reversible interactions.[152] For example, multivalent hydrogen bonding,[153] metal-ligand interactions,[154] and π–π stacking[155] have been explored for the design of recyclable and self-healing polymers. By using a non-covalent linkage such as hydrogen bonding, an oligomeric building block can form a supramolecular structure, which behaves similarly to high–molecular-weight polymers. Also, the hydrogen bonding readily dissociates at elevated temperatures to provide good processability (Figure 10 [a]). These dynamic linkages also allow intrinsic self-healing without any stimuli, which could be considered as recycling on the spot. A good, general summary of supramolecular polymers can be found elsewhere;[152] the recent progress in supramolecular polymers exhibiting intrinsic self-healing properties is summarized in this section because of their potential for extended longevity and unlimited recyclability.
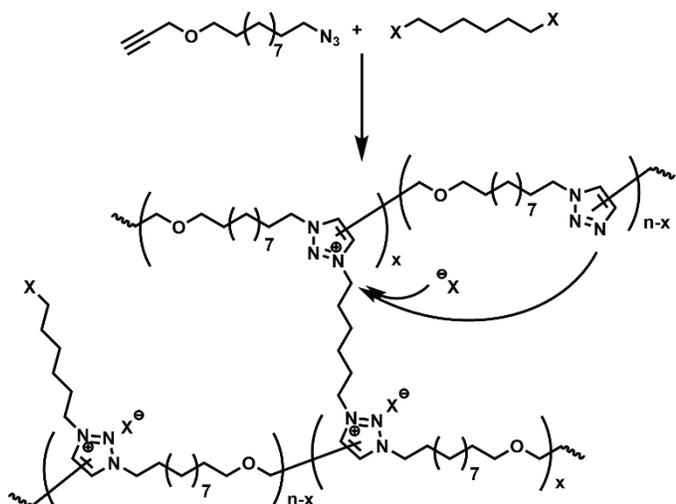

Figure 13. Vitrimer based on the exchange between 1,2,3-triazoles and 1,2,3-triazoliums. *Adapted with permission from M. M. Obadia et al., "Reprocessing and Recycling of Highly Cross-Linked Ion-Conducting Networks through Transalkylation Exchanges of C-N Bonds," J. Am. Chem. Soc. 2015, 137 (18), 6,078–6,083. Copyright 2019 American Chemical Society.*

Leibler's group reported that oligomers with complementary hydrogen bonding exhibited self-mending properties at RT.[153] A mixture of fatty diacid and triacid was reacted with diethylene triamine followed by urea, resulting in oligomers with multiple hydrogen bonds (Figure 14).[153] The supramolecular assembly with complementary hydrogen bonding in these oligomers allowed for self-healing. The neat material exhibited ~600% elongation with 3–3.5 MPa tensile strength with self-healibility; full recovery of the mechanical properties by self-healing was not reported. Bao et al. used similar chemistry for a polymer binder in a silicon anode.[156] Using a soft, rubbery, and self-healable polymer binder prevented the typically severe capacity fade found in silicon-based electrodes, which stemmed from the inherent volume expansion during alloying (up to 280% for $Li_{15}Si_4$), pulverization of the silicon anode, disconnection of active materials with the conducting network or current collector, and instability of the solid electrolyte interface layer. Bao et al. expanded the self-healing chemistry to ionic-based coordination in rubbery polymers, in which a telechelic low-molecular-weight polydimethylsiloxane (PDMS) (5,000–7,000 g/mol) containing a 2,6-pyridinedicarboxamide (H_2pdca) ligand was cross-linked with Fe(III) (Figure 15).[157] The H_2pdca ligands coordinated with Fe(III) through two different interactions: a strong pyridyl–iron and two weaker carboxamido–iron bonds with the nitrogen and oxygen atoms of the carboxamide groups. The $[Fe(Hpdca)_2]^+$ readily dissociated to $[Fe(Hpdca)]^{2+}$, in which the iron centers remained attached to the ligands through the stronger interaction with the pyridyl ring. The Fe(III) coordination can break and reform, which allows reversible unfolding and refolding of the chains. The reversible iron-coordination in a very soft PDMS matrix allows the polymer to possess an exceptionally high stretchability and self-healibility. The tensile data indicated that Fe-Hpdca-PDMS could be stretched by 10,000% if the sample had a lower amount of Fe-Hpdca (H_2 pdca:PDMS = 1:6). Healing at RT for 48 h resulted in equivalent elongation and stress to that of the original polymer. Similarly, Saito et al. recently developed self-healing elastomers with capabilities for extreme stretching, excellent energy damping, and intrinsic self-healing.[158] A polymeric elastomer was synthesized by urea functionalization of PDMS. The polymer showed high elongation at the breaking point (984–5,600%), and adjusting the

chain length of the PDMS segments provided polymeric elastomers with the desired mechanical strength, elasticity, and extensibility. After cutting, the polymer's mechanical strength and gas separation performance recovered completely within 2 h at ambient temperature or within 20 min at 40 °C. These polymers also exhibited excellent acoustic and vibration-damping properties from −50 to 120 °C.
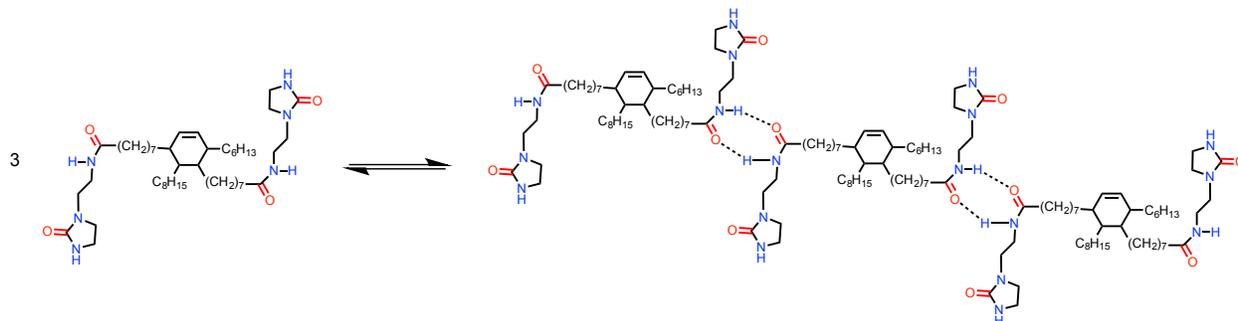

Figure 14. Oligomers equipped with complementary hydrogen bonding, synthesized by condensation of a mixture of fatty diacid and triacid with diethylene triamine and subsequent reaction with urea. *Image courtesy of Tomonori Saito, Oak Ridge National Laboratory.*
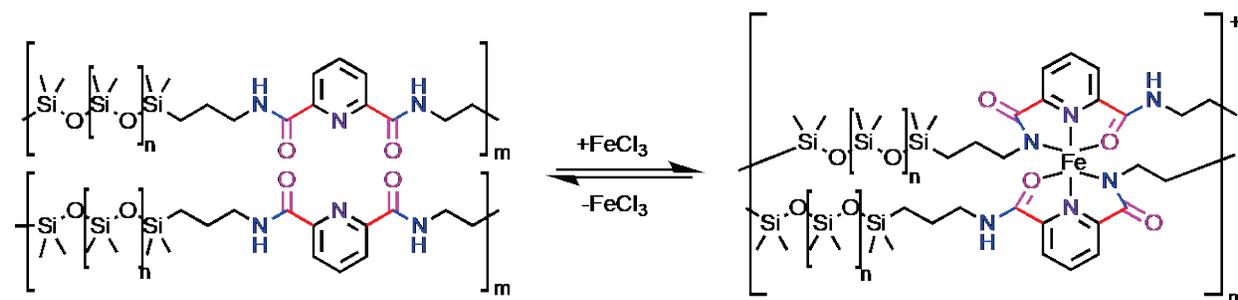

Figure 15. The self-healing polymer of PDMS with H₂pdca ligand. *Image courtesy of Tomonori Saito, Oak Ridge National Laboratory.*

Urban et al. recently demonstrated that self-healing can occur even with Van der Waals interactions.[159] The authors studied random copolymers of PMMA-*ran*-poly(*n*-butyl acrylate) (PMMA-*r*-P*n*BA) and determined that statistical copolymers with an alternating tendency can provide autonomous healing.[160] A narrow window of the copolymer composition from MMA/*n*BA = 45/55 to 50/50 exhibited self-healing behavior. PMMA-*r*-P*n*BA with MMA/*n*BA = 45/55 to 50/50 exhibited 90–100% tensile property recovery after 14 h of healing at RT. The interesting finding was that samples with a lower T_g than ambient temperature, such as MMA/*n*BA = 40/60, did not self-heal even after many days. The study suggested that the polymer conformation and the resulting cohesive energy were the keys to self-healing via Van der Waals interactions. Molecular dynamics simulations determined that a statistical copolymer with an alternating tendency (MMA/*n*BA = 45/55 to 50/50) tended to form a helix-like chain conformation and provide the highest cohesive energy densities among all possible compositions of PMMA-*r*-P*n*BA.

Although most of the reported intrinsic self-healable polymers have soft and rubbery components,[152,157,158,161] several reports exist of more mechanically robust self-healing polymers.[162,163] Weitz et al. produced tough self-healing elastomers by combining covalent and reversible hydrogen-bonding networks.[162] The elastomer exhibited a high fracture energy of 13,500 J/m² and high tensile strength as an elastomer, 10–20 MPa. After 12 h of healing at RT, the elastomer exhibited a tensile strength of ~4 MPa, which was ~30% of its original value. Aida et al. also reported that low–molecular-weight polymers with dense thiourea groups exhibited mechanical robustness with ready repairability.[163] The tensile strength was as high as 40 MPa and the Young's modulus was 1.0–1.9 GPa. Although these

polymers did not exhibit autonomous self-healing, the compression allowed the fractured surfaces to be repaired. The thiourea polymers exhibited a mostly recovered tensile strength and Young's modulus with 1 h compression, especially at temperatures slightly above RT. Forming a zigzag hydrogen-bonded array in the presence of a thiourea group in each repeat unit activated the exchange of hydrogen-bonded pairs and enabled healing by compression on the fracture.

Guan's group also successfully demonstrated a multiphase design concept to combine stiffness, toughness, and high reversibility, such as an autonomous self-healing capability (Figure 16).[164] In the group's multiphase material design, the dynamic soft matrix enabled autonomous self-healing, whereas the hard phase provided stiffness and strength to the material. The key design concept was to program dynamic supramolecular interactions into the soft phase, merging the unique properties of nanocomposites (stiffness and toughness) with those of supramolecular assemblies (dynamic and autonomic healing). By applying this multiphase concept, Guan et al. obtained materials that were mechanically robust and truly self-healing without needing any additives, healing agents, or external stimuli. They further demonstrated this concept in several multiphase systems, including brush copolymers,[164–166] block copolymers,[167,168] and core-shell nano-particles.[169] In addition to using hydrogen bonding as the healing motif, they also demonstrated the use of dynamic metal-ligand interactions for malleable and self-healing polymer designs.[166,170]
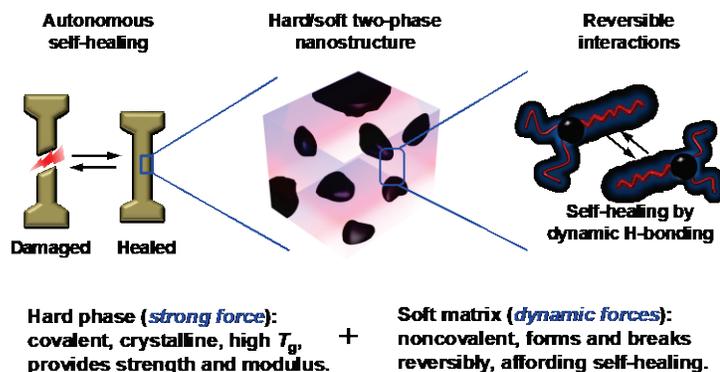

Figure 16. Design concept for the multiphase self-healing polymer system. *Image courtesy of Zhibin Guan, University of California–Irvine.*

Reprocessable thermosets. This section summarizes recent advances in upcycling thermosets, which mainly use the mechanism of depolymerization and repolymerization or dynamic dissociation and association (Figure 10 [b]). A notable example of reprocessable thermosets was developed by Garcia et al. at IBM Research, in which recyclable strong thermosets were formed by condensing paraformaldehyde with diamines (Figure 17).[4,171] The thermosets were readily digested at a low pH (<2) to recover bisaniline monomers, and the reaction mechanism for depolymerization was elucidated.[172] Incorporating hydrolyzable hexahydrotriazine rings as cross-links for thermosetting resins allowed for controlled and efficient depolymerization to monomers under acidic conditions. The pH-dependent reversibility of this thermoset demonstrated stimuli-responsive chemical recycling, allowing the original starting monomers to be recovered in sufficient purity to produce a new product.[173] This work is the first example of a cross-linked thermosetting polymer that can be selectively and completely reverted back to a monomer based on response to a stimulus (pH). This new material will likely have applications in transportation, microelectronics, and anticorrosive coatings.
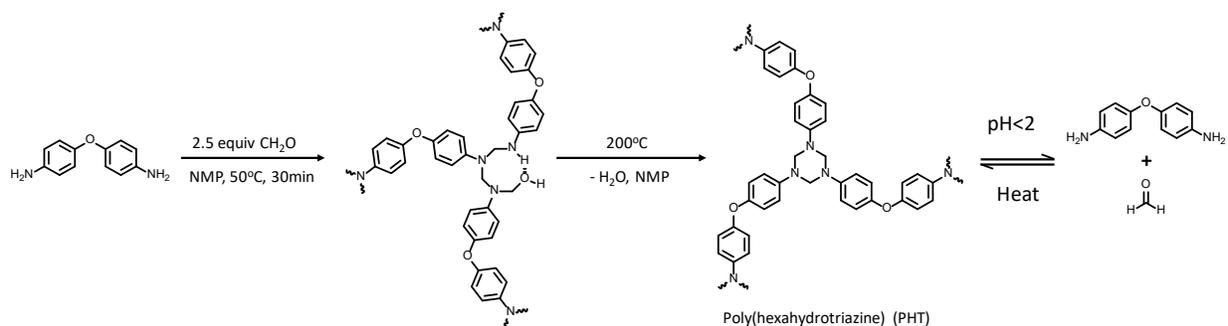
Figure 17. Reprocessable thermosets via paraformaldehyde condensation with diamines. *Modified from J. M. Garcia et al., "Recyclable, Strong Thermosets and Organogels via Paraformaldehyde Condensation with Diamines," Science 2014, 344 (6185), 732–735. Reprinted with permission from AAAS.*

The IBM Research group subsequently found that PEG-based poly(hemiaminal) organogels containing dynamic covalent interactions and secondary hydrogen bonding interactions imparted self-healing properties.[174] These organogels, which contain >90% liquid, could be used in additive manufacturing, as cargo carriers, or in reversible adhesive applications. Poly(hemiaminal) organogels formulated with a polymerizable solvent (*N*-vinyl-2-pyrrolidone, NVP) could be melt-processed and cured by UV-induced free radical polymerization to form poly(NVP) irreversibly.[175] During the course of this work, insights gleaned from model studies on hexahydrotriazines and hemiaminals inspired the synthesis of sulfur-based poly(hemiaminal) analogs as a new class of dynamic covalent networks (Figure 18).[176] The dynamic character of the resulting poly(hemiaminal) and its relatively slow hydrolysis kinetics enabled the incorporation of therapeutics (peptides, proteins, and genes), and the linkages served as pH-dependent moieties for cargo release.[176]
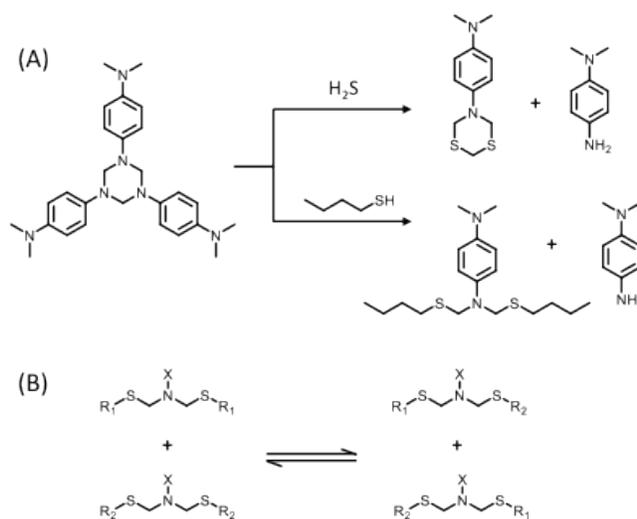

Figure 18. (a) Reaction of hexahydrotriazine with hydrogen sulfide and butane thiol; (b) exchange reaction between thioaminals. *Adapted with permission from R. J. Wojtecki et al., "Developments in Dynamic Covalent Chemistries from the Reaction of Thiols with Hexahydrotriazines," J. Am. Chem. Soc. 2015, 137 (45), 14,248–14,251. Copyright 2019 American Chemical Society.*
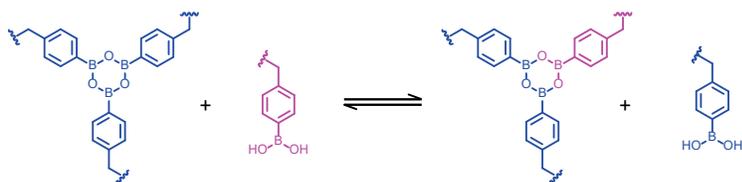

Figure 19. Boroxine-based malleable and recyclable thermosets. *Image courtesy of Tomonori Saito, Oak Ridge National Laboratory.*

Guan's group has developed several malleable thermosets by using robust dynamic covalent chemistry. In one design, the researchers achieved a malleable cross-linked rubber system by using olefin cross-metathesis of thermodynamically strong and stable carbon-carbon double bonds.[177,178] In another design, the first example of boronic ester–based malleable thermosets were reported using strong B–O dynamic bonds.[179] Subsequently, they have reported simple boroxine-based covalent networks that were fully reprocessable and recyclable (Figure 19).[180] Additionally, the polymer could be converted to its starting monomer, a

diboronic acid, via heating in boiling water. More recently, Guan's group has demonstrated silyl ether as a superior dynamic covalent motif for malleable thermoset design because of its high chemical and thermal stability, easy accessibility, and general applicability (Figure 20).[181] First, the Si–O linkage showed excellent stability under heat and oxidation. Second, silyl ether motifs were easily introduced to polymers by silylation of free hydroxyl groups, copolymerization, or radical grafting, making it generally applicable to a wide range of polymers. Finally, the scope of materials containing a Si–O motif is vast, ranging from soft rubbers, such as PDMS, to strong and hard materials, such as inorganic glass. This range provides a wide range for dynamic polymer designs.

Although the associative exchange reactions in vitrimers have allowed for the reprocessing of cross-linked networks, dissociative exchange reactions can also be employed in recyclable materials (Figure 10 [a]). Unlike with vitrimers, networks that contain dissociative dynamic bonds lose cross-linking density upon application of a stimulus, resulting in materials that flow like conventional thermoplastics. The most common applications of this type of chemistry are networks containing Diels–Alder adducts of furan and maleimide derivatives.[182] At elevated temperatures, these adducts will undergo the retro-Diels–Alder reaction, thereby decreasing the material's cross-linking density. Other dissociative exchange reactions have also been employed. For example, disulfide bonds may be incorporated into PHU networks to yield networks with fast stress relaxation that could be reprocessed at milder conditions.[183]
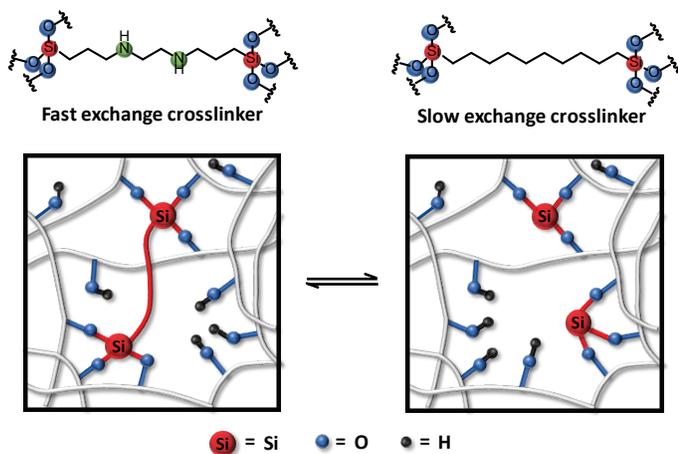

Figure 20. Silyl ether-based malleable thermosets. *Adapted with permission from Y. Nishimura et al., "Silyl Ether as a Robust and Thermally Stable Dynamic Covalent Motif for Malleable Polymer Design," J. Am. Chem. Soc. 2017, 139 (42), 14,881–14,884. Copyright 2019 American Chemical Society.*

Recyclable polycarbonate using CO₂ from meso-epoxy intermediates. Polymerization methods that deliver stereoselective products with excellent mechanical performances are of interest to the scientific community. Conversion of CO_2 to high-performance polymers requires a catalyst to induce reactivity in the thermodynamically stable CO_2 feedstock. Coates et al. developed a new catalyst system for the stereoselective copolymerization of CO_2 and alicyclic meso-epoxides (Figure 21).[184] C1-Symmetric β-diiminate zinc catalysts yielded highly isotactic poly(cyclohexene carbonate) and poly(cyclopentene carbonate) with units of up to 94% ee under mild conditions. The isotacticity of the diblock copolymer of CO₂/cyclohexene oxide and CO₂/cyclopentene oxide polymer affected its melting temperature and
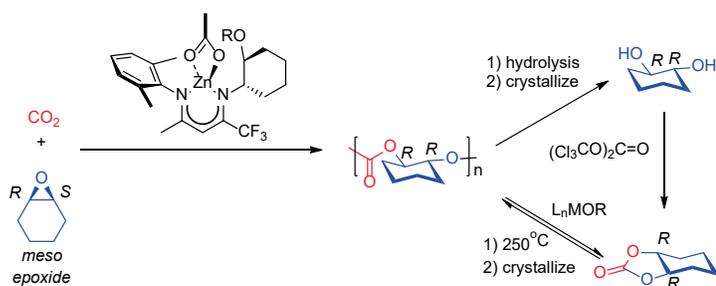

Figure 21. Copolymerization of CO₂ and meso-epoxides. *Republished with permission of Royal Society of Chemistry, from W. C. Ellis et al., "Copolymerization of CO₂ and Meso Epoxides Using Enantioselective Beta-Diiminate Catalysts: A Route to Highly Isotactic Polycarbonates," Chem. Sci. 2014, 5(10), 4,004–4,011; permission conveyed through Copyright Clearance Center Inc.*

semicrystalline morphology.[184] Although this example (shown in Figure 21) is not a cross-linked polymer, the recyclable polycarbonate can be depolymerized and repolymerized, similar to the reprocessable thermosets (Figure 10 [b]). Polycarbonates can also be synthesized under metal-free conditions by anionic copolymerization of an epoxide and CO_2.[185] In this approach, well-defined alternating copolymers of CO_2 and propylene oxide or cyclohexene oxide were formed by activating the epoxide with a Lewis acid, such as triethylborane, and activating the CO_2 with a cation. The initiator can be an onium salt, such as tetrabutylammonium chloride; an alkoxide, such as potassium *t*-butoxide; or a carbonate, such as tetrabutylammonium carbonate.[186] Strong organic bases can also be used to catalyze the depolymerization of polycarbonates to yield an epoxide and CO_2, a cyclic carbonate product, or both.[187] Selective catalysts are being developed that would allow these polycarbonates to be fully recycled back to an epoxy monomer and CO_2, making them truly sustainable.[188]

6.2 Recent Progress in the Design of Polymers Made for Deconstruction and Their Upcycling

PLA, a successful biodegradable polymer, had an estimated global demand of 360,000 metric tons in 2013.[142] Although PLA has many applications,[189] the properties of PLA and other types of biodegradable polymers, such as PHA,[190] must be improved for wider application.[97] Designing new biodegradable polymers with full chemical recyclability built into their properties and performance is highly desirable and represents a possible direction for sustainable polymers with closed-loop life cycles.[191–193] Ideally, such polymers should be completely depolymerizable into their monomers on demand with high selectivity, yield, and purity. The recovered monomers should be directly repolymerizable into virgin-quality polymers under cost-effective conditions. To realize such polymers for chemical circularity, three challenges must be met: energy input, polymerization and depolymerization selectivity, and depolymerizability/performance trade-offs (Figure 22). This section highlights some recent notable examples of biodegradable polymers.

Figure 22. Designing new chemically recyclable polymers. *Image courtesy of Jing Tang and Eugene Chen, Colorado State University.*
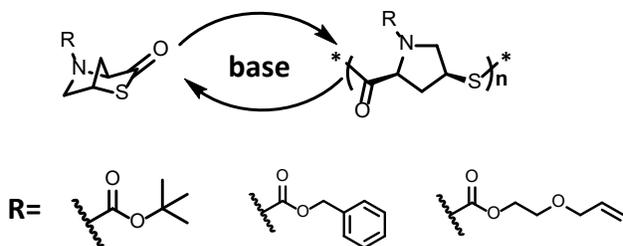

Figure 23. Biosourced polythioesters. *Adapted with permission from J. Yuan et al., "4-Hydroxyproline-Derived Sustainable Polythioesters: Controlled Ring-Opening Polymerization, Complete Recyclability, and Facile Functionalization," J. Am. Chem. Soc. 2019, 141 (12), 4,928–4,935. Copyright 2019 American Chemical Society.*

In this context, new chemically recyclable polythioesters based on bio-sourced 4-hydroxyproline were successfully designed and recently realized (Figure 23).[194] The bio-sourced *N*-substituted *cis*-4-thia-L-proline thiolactone monomer possessed a five-member (thiolactone) ring fused with another five-member ring, which enabled the polymerizability of the monomer at RT to high–molecular weight polymers. Selective and complete depolymerization of the polymer in dilute solution and mild temperature reformed the monomer cleanly.

27

PHAs are naturally occurring biodegradable polyesters produced by an extensive variety of microorganisms. The most promising PHAs, polyhydroxybutyrate and polyhydroxyvalerate, have similar physical properties to polyolefins—such as PP and PE—but offer the advantage of degradability in ambient environments, including the ocean. However, PHAs still have limitations that must be overcome, including poor mechanical properties, high production cost, incompatibility with conventional thermal processing techniques, and susceptibility to thermal degradation.[190] Since more than 150 different PHA monomers have been identified, there is an opportunity to create a wide variety of biodegradable polymers and copolymers with tunable properties. For example, bacterial poly[(R)-3-hydroxybutyrate] (P3HB) is a stereoregular, isotactic crystalline thermoplastic material that is an attractive biodegradable alternative to petroleum-based plastics, especially isotactic PP. But its high costs and low volumes of production are impractical for commodity applications. Recently, a new route for the synthesis of P3HB was developed by the ring opening polymerization of racemic cyclic diolide derived from bio-sourced succinate.[195] Importantly, this new synthetic route provided rapid, scalable access via chemical catalysis to biodegradable P3HB and potentially many of its derivatives, which could allow them to be used as biorenewable and biodegradable commodity plastics. It also offers the potential for the chemical recycling of P3HB and other new biodegradable polymer derivatives through the polymerization of cyclic diolides and depolymerization to 3-hydroxybutyric acid and then diolides, which can be repolymerized via chemical and catalytic means.[196] The microbial synthesis of P3HB and other PHA copolymers from organic waste streams[23] and the selective catalytic pyrolysis of these materials to alkenoates[22,197] provide closed-loop strategies for polymer synthesis and reuse.

Recent research demonstrated that high performance polyester elastomers could be derived from lactone monomers obtained from biomass, indicating a promise for biodegradability and renewability.[198] The elastomers were synthesized using a bis(β-lactone) cross-linker and star-shaped, hydroxyl terminated poly(γ-methyl-ε-caprolactone) (Figure 24).[198] The bis(β-lactone) cross-linker could undergo acyl bond cleavage to afford β-hydroxyesters at the junctions. The elastomers demonstrated high thermal stability and a low T_g (−50 °C) and exhibited rubber–band-like mechanical properties. The cross-linked polyester networks were readily hydrolyzed at a neutral pH and

Figure 24. Sustainable polyester elastomers from lactones.
Adapted with permission from G. De Hoe et al., "Sustainable Polyester Elastomers from Lactones: Synthesis, Properties, and Enzymatic Hydrolyzability," J. Am. Chem. Soc. 2018, 140 (3), 963–973. Copyright 2019 American Chemical Society.

environmentally relevant temperatures (2−40 °C). This work was another example of high-performance, sustainable alternatives to conventional elastomers.
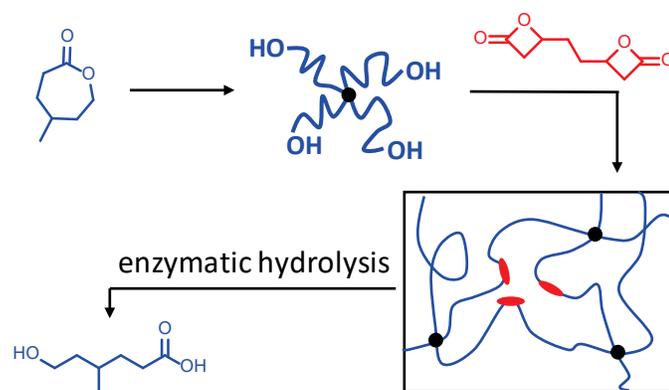
Other types of new biodegradable polymers include polymers from macrolactones.[199] Recent advances of macrolactones ROP allow the synthesis of novel degradable polymeric materials with long aliphatic chains. Furthermore, additive manufacturing of new biodegradable cross-linked polymers has been reported. Unlike conventionally fused deposition modeling of PLA, Dove's group synthesized 3D printable biodegradable polymers.[200] The ROP of the cyclic carbonate monomer—5-methyl-5-allyloxy-carbony-1,3-dioxan-2-one (MAC)—resulted in poly(MAC). Using thiol-ene click chemistry, photo-cross-linking of poly(MAC) was achieved with a four-arm thiol, pentaerythritol tetrakis(3-mercaptopropionate) (Figure 25).[200]
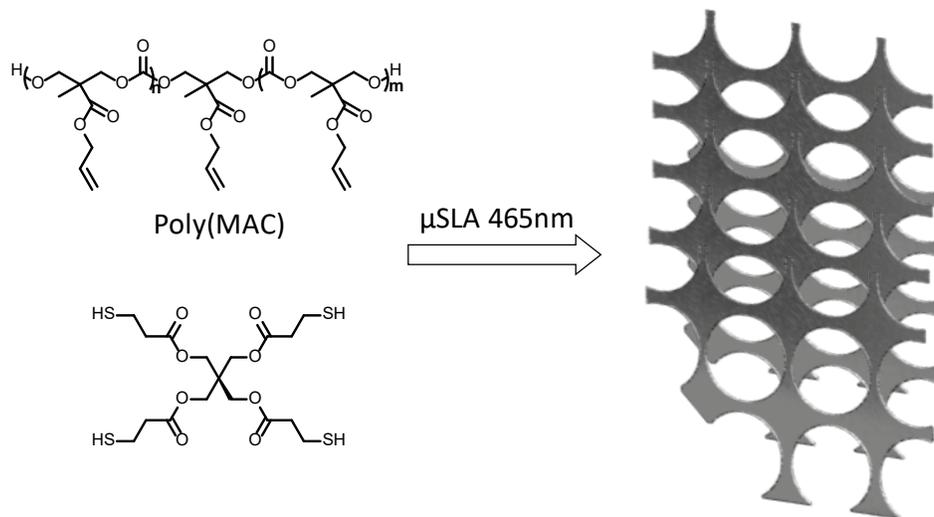
Figure 25. Micro-stereolighography-based on thiol-ene chemistry. *Adapted by permission from Creative Commons Attribution 3.0 Unported License. Reprinted from I. A. Barker et al., "A Microstereolithography Resin based on Thiol-ene Chemistry: Towards Biocompatible 3D Extracellular Constructs for Tissue Engineering." Biomater. Sci. 2014, 2 (4), 472–475; https://creativecommons.org/licenses/by/3.0/.*

Microstereolighography of poly(MAC) and the four-arm thiol in the presence of a photo-initiator allowed preparation of a new type of biodegradable scaffold. As the fabrication of anatomically relevant scaffolds by additive manufacturing approaches gains interest, newly designed biodegradable polymers for additive manufacturing will be needed in these applications.

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