Closing the Carbon Loop in the Circular Plastics Economy

Carl G. Schirmeister and Rolf Mülhaupt*

Today, plastics are ubiquitous in everyday life, problem solvers of modern technologies, and crucial for sustainable development. Yet the surge in global demand for plastics of the growing world population has triggered a tidal wave of plastic debris in the environment. Moving from a linear to a zero-waste and carbon-neutral circular plastic economy is vital for the future of the planet. Taming the plastic waste flood requires closing the carbon loop through plastic reuse, mechanical and molecular recycling, carbon capture, and use of the greenhouse gas carbon dioxide. In the quest for eco-friendly products, plastics do not need to be reinvented but tuned for reuse and recycling. Their full potential must be exploited regarding energy, resource, and eco-efficiency, waste prevention, circular economy, climate change mitigation, and lowering environmental pollution. Biodegradation holds promise for composting and bio-feedstock recovery, but it is neither the Holy Grail of circular plastics economy nor a panacea for plastic littering. As an alternative to mechanical downcycling, molecular recycling enables both closed-loop recovery of virgin plastics and open-loop valorization, producing hydrogen, fuels, refinery feeds, lubricants, chemicals, and carbonaceous materials. Closing the carbon loop does not create a Perpetuum Mobile and requires renewable energy to achieve sustainability.

1. Introduction

Epochs in history are not named after emperors or politicians but after materials that brought change to society. Following the stone, bronze, and iron ages, we are now living in the plastic age.[1,2] Plastics are ubiquitous and have reshaped everyday life. In geology, the emergence of plastics serves as an indicator of the beginning of the Anthropocene.[3] On a polymer time scale, we are entering the second-century A.S. (after Staudinger). One hundred years ago, the Nobel laureate Hermann Staudinger recognized that both natural and man-made polymers, which he named macromolecules (giant molecules), are built according to the same blueprint by covalently linking together thousands of small monomer molecules like pearls in a pearl necklace.[4,5] At that time, even scientists firmly believed that humans would never be able to prepare natural polymers in the lab, and most of them even doubted that polymers could exist. Against extremely heavy opposition from his colleagues, Staudinger pushed his new concept of macromolecules and brought about a paradigm change in polymer research and development. Going well beyond traditional trial-and-error material optimization, his molecular design of polymeric materials paved the way for innovations in the plastics industry and biotechnology.[6,7]

In nature and in industry, the composition, molar mass, molar mass distribution, comonomer sequence, and shape of polymers govern plastics' property profiles. Regardless of their synthetic or natural origins, polymers are converted into plastics by polymer processing such as injection molding, extrusion, blow molding, spinning, and casting. Teaming molecular design with processing plays a key role in (bio)plastic development. To facilitate plastics' processing, to modify their properties, and to assure their prolonged service life, a great variety of additives are used in the production of commercial plastics. Typical polymer additives include antioxidants, UV-stabilizers, processing aids, plasticizers, toughening agents, colorants, fire retardants, curing agents, cure accelerators, biocides, blend compatibilizers, fillers, and fibers as matrix reinforcement, just to name a few.[8,9,10] Unlike high-molecular-weight polymers, many low-molecular-weight additives readily migrate and can leak into the environment.[10–12] Most thin polymer films in food packaging contain barrier layers and are difficult to recycle, as they must meet the stringent requirements typical of food applications.[13,14] Formulated products such as rubbers, composites, thermosets, blends, adhesives, and coatings represent complex multicomponent and frequently multiphase systems; recovering their pure components is tedious. While Americans and the British call processable polymers "plastic" and the French "plastique", in 1911, the Germans introduced the name 'Kunststoff' meaning *artificial material,* but also in a more appropriate, second sense, meaning *designable art*

C. G. Schirmeister, R. Mülhaupt
Freiburg Materials Research Center and Institute for Macromolecular Chemistry
University of Freiburg
Stefan-Meier-Str. 31, D-79104 Freiburg, Germany
E-mail: rolfmuelhaupt@web.de
R. Mülhaupt
Sustainability Center
University of Freiburg
Ecker-Str. 4, D-79104 Freiburg, Germany

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/marc.202200247

Figure 1. Plastics progressing from mediocre imitations of natural materials, such as ivory, silk, and natural rubber, to advanced and sustainable materials and systems tuned according to Hermann Staudinger's molecular design concept of macromolecules. (Staudinger image was reprinted with permission from the Archives of the University of Freiburg,[24] other images are licensed from Adobe Stock).

materials, which stimulate the creativity of scientists, engineers, and designers alike. Following World War II, the Germans also included the name 'Plastik' in their vocabulary.

At the beginning of the 20th century, polymer development was aimed exclusively at replacing natural materials that were in short supply, including ivory, silk, and especially natural rubber, that was strategically important during World War I and II. Most early plastics were rather mediocre imitations of natural materials and not at all competitive with modern plastics. During the first century B.S. (before Staudinger), all plastics were bio-based and derived from biopolymers. A prominent example is cellulose nitrate, which was plasticized with camphor to render it moldable. It was marketed in the second half of the 19th century as the first thermoplastic under the trade names of *Parkesine* and *Celluloid*.[15] Plasticized nitrocellulose replaced ivory in applications such as billiard balls, saving the lives of thousands of elephants. Employed as a flexible carrier for photographic films, the *Celluloid* innovation was the pacemaker for the emerging movie industry. On the dark side, the high flammability and explosive character of nitrocellulose, also known as smokeless gun powder, caused many fires and posed severe safety and health hazards in cinemas during the early 20th century. By 1950, bio-based nitrocellulose films were replaced by synthetic polyester films derived from fossil resources. Shortly after the discovery of nitrocellulose, it was solution-processed by spinning to produce the first synthetic truly silk-like fibers, but unmodified nitrocellulose textiles were extremely hazardous even for non-smokers.[16]

The above is a good example of how plastics, regardless of whether they are created using non-renewable or renewable feedstocks, run through multiple ongoing learning cycles and are continuously reinvented to remain competitive with other materials. Modern plastics have little in common with the early generations of plastics. Even between members of the plastic families, there is fierce competition, driven by lowering costs while improving performance and sustainability. In this context, most naturally occurring polymers apart from natural rubber have failed to compete with highly versatile, easily processable synthetic polymers, which represent around 98% of the world's plastic consumption today.

The first synthetic plastic became commercially available in 1907, when Leo Hendrik Baekeland cured phenol with formaldehyde to industrially produce highly crosslinked thermosets marketed as *Bakelite*. This development of plastics as electrical insulators revolutionized electrical engineering and enabled electrification and new communication technologies such as telephones, radio broadcasting, and television. Therefore, Baekeland's milestone innovation marks the beginning of the Plastic Age.[17–21] Today, plastics are highly beneficial to human health, quality of life, and technological progress.[1] As illustrated in **Figure 1**, Staudinger's concept of molecular polymer design has stimulated the discovery of a great variety of plastics that satisfy the elementary human needs for shelter, clothing, protection, communication, mobility, health, and secure distribution of energy, water, food, and drugs. While small molecules such as drugs and food ingredients prolong our life, plastics make life better and safer, improving the quality of life for billions of people across the globe. Anyone who enjoys good health and loves leisure activities such as sports, traveling, and computer games makes extensive use of plastics and would not seriously consider abandoning them. Plastics are shaping the world and present sustainable

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solutions to our fast-changing human needs and emerging technological challenges but they also pose environmental and health hazards when plastic wastes are not recycled and accumulate in landfills and natural habitats.[22,23]

During World War II, predominantly military uses were found for most plastics. Starting in the 1950s, numerous plastics were produced on a large scale and entered manifold civil applications. Soon plastics turned into advanced materials and systems unparalleled in nature. Their unprecedented versatility in terms of properties, design, broad choice of raw materials, processing, and applications is unmatched by other materials. Depending on their molecular design and processing, they can be steel-like or rubbery, electrically and thermally conducting or insulating, permeable or impermeable, transparent or opaque, water-soluble or insoluble, adhering or non-adhering, light emitting or light absorbing, solid or liquid, water repellent or water-absorbing, durable or degradable. Hence, plastics enable new technologies and are in high demand as problem solvers. Today, plastics are essential for virtually any kind of consumer product. Their low weight enables the lightweight construction of fuel-efficient cars, air- and spacecraft, energy-efficient buildings, and durable windmill rotor blades. As cables, pipes, and packaging, they safeguard the reliable transport of energy, water, food, drugs, and a great variety of goods. Polymer membranes enable to desalinate water, to purify blood, and are essential in electrolysis and fuel cells. Polymer coatings protect metal against corrosion and shield plastics against UV radiation. In medicine, plastics are employed in diverse applications ranging from dental fillings and contact lenses to wound dressings, sterile packaging, orthoses and prostheses, drug-release systems, disposable syringes, artificial hips, artificial kidneys, implants, sensors, tissue engineering, and protection against attacks of bacteria, fungi, and viruses. Agricultural plastics in applications such as greenhouses, mulch, silage stretch films, drip irrigation pipes, and nonwovens safeguard and significantly enhance the food output per hectare accompanied by a reduced pesticide demand. Due to their low carbon footprint compared to metals and various other materials, as well as their high oil-like energy content, exceptional energy and resource efficiency, facile processing, recycling capabilities, lightweight construction, and thermal insulation plastics help to save energy and play an important role in sustainable development.

Although these plastic prospects are widely recognized, they are far from being fully exploited in sustainable development and circular economy. As **Table 1** indicates, plastics face several challenges, especially with respect to their waste mismanagement, marine littering, micro- and nanoplastic emission to the environment, and global warming. The Ellen MacArthur Foundation[25–27] and the Heinrich Boell Foundation[28,29] have presented comprehensive overviews on the downsides and challenges of today's linear plastic economy. In their survey, "deep dive into plastic monomers, additives, and processing aids" Wiesinger, Wang, and Hellweg identified more than 10 000 relevant substances, among them 2400 substances pose potential risks of persistence, bioaccumulation, and toxicity.[30] Considering the low recycling quota, plastic littering, and the potential risks associated with micro- and nanoplastic emissions, it was proposed either to classify plastic wastes as hazardous and reinvent safer plastics or to establish closed loop systems in which all plastics are reused and recycled.[31]

Most of plastic's shortcomings are not the ultimate limitations of plastics but reflect problems of humans who exclusively care for their own well-being, ignore the needs of future generations, throw away waste, recklessly deplete natural resources, and pollute the environment. In the case of plastics, curse and blessing come close together. Low price and facile processing render plastics affordable for everybody but also enable the development of single-use throwaway products such as fast-food packaging. High durability is beneficial for most plastic applications but accounts for an extremely long lifetime of plastic wastes in the environment especially when using long-lived plastics in short-lived products such as packaging and depositing plastic wastes in landfills. While the high oil-like energy content of most plastics is advantageous with respect to energy recovery and energy storage for future generations, it requires the addition of large amounts of flame retardants, among them halogen and phosphorous compounds, in special applications such as printed circuit boards, textiles, and construction. Biodegradable plastics enable composting, drug release, and bio-feedstock recovery but can serve as breeding grounds for spores and bacteria that are treacherous to human health. Low-density plastics in packaging save energy in transportation but contribute to the floating of plastic waste on the surfaces of oceans, lakes, and rivers.

Since the 1950s, the rapid growth of plastic production has been driven by the emerging petrochemistry, capable of supplying inexpensive feedstocks on a large scale. In the second half of the 20th century, coal and biomass were rapidly replaced by oil, gas, and feedstocks gained by fracking. Soon, extensive oil and gas exploration turned into a burden for the environment. Since the early days, plastics and petrochemical industries have been close partners. Today, almost all plastics are based on fossil resources, whereas bio-based thermoplastics account for less than 2% of the world's plastics production. As is apparent in **Figure 2** which is based on a survey in *Plastics the Facts 2020*,[32] published and annually updated by PlasticsEurope, around 40% of plastics in Europe are used in packaging with an average product lifetime of only a few days, whereas around 20% serve the needs of construction and building applications with long product lifetimes of decades. Packaging waste mismanagement is the major source of plastic waste emission into the environment. Other European key plastic market segments include the automotive industry (9.6%), electrical appliances and electronics (6.2%), household, leisure and sports (4.1%), and agricultural films (3.4%). Clear leaders of the world's plastic consumption are hydrocarbon thermoplastics such as polyethylene (PE, 29.8%) and polypropylene (PP, 19.4%) amounting to more than half of the world's plastic production followed by polyvinylchloride (PVC, 10%), polyethylene terephthalate (PET, 7.9%), as well as polystyrene and expanded polystyrene (PS and EPS, 6.2%). As sodium hydroxide is produced by electrolysis of sodium chloride with chlorine byproduct formation, PVC is an important non-toxic chlorine sink in the chemical industry and serves the needs for long-lived materials in buildings. However, the processing of PVC requires special additives. Unlike other mostly plasticizer-free thermoplastics, plasticizer addition improves PVC's processability and renders hard PVC soft, flexible, and even elastomeric. In view of emissions, health risks, and recycling, the European PVC industry eliminated cadmium-based PVC stabilizers, is phasing out lead-based PVC stabilizers, and is replacing plasticizers such as

Table 1. Plastic prospects and challenges.

Prospects	Challenges
• Plastics combine high versatility in terms of properties and applications with facile processing and an attractive price/performance ratio. They render advanced polymeric materials and systems affordable with high benefits to humanity.	• Inexpensive and easy-to-process plastics have fostered the unprecedented development of single-use, throwaway products. Moving away from a linear "produce-use-throwaway" economy to a circular "produce-use-reuse" economy is vital for the future of the planet. At end-of-life, plastic waste must be either revived by mechanical recycling or valorized by molecular recycling.
• Plastics are resource-efficient and readily tuned to meet the demands of the growing world population and modern technologies.	• Multilayer packaging and formulated products such as composites, thermosets, rubbers, blends, adhesives, and coatings represent complex multicomponent multiphase systems. Their recycling and valorization are a challenge.
• Plastics such as pipes, cables, and packaging safeguard the distribution of water, food, energy, goods, and drugs. Agricultural plastics such as mulch and stretch films or drip irrigation water pipes significantly enhance the food output per hectare.	• Around forty percent of long-lived plastics are used in short-lived packaging contributing to massive plastic waste emissions. Waste and single-use prevention, design for recycling, efficient collecting, and sorting are needed.
• Most plastics have high oil-like energy content.	• Flammable plastics require the addition of flame retardants in certain applications that pose challenges for closing the carbon loop.
• Plastics have low weight and save energy in transportation and thermal insulation. They enable to design and manufacture of sophisticated parts that are difficult to realize with other material classes	• Low-density plastics used in packaging float on the water surface when they end up in oceans and can harm marine life. It is vital to recycle wastes and to stop carbon leakage.
• Plastics are energy efficient, meaning that they save more energy in use with respect to the energy needed to produce them.	• The use of non-renewable energy and fossil resources in plastic manufacturing contributes to greenhouse gas emissions and global warming. Carbon neutral circular economy is a key challenge.
• Plastics store resources and energy for future generations.	• Today, most plastics end up in landfills and incinerators. Recycling is energy-intensive and currently driven by non-renewable energy. Mechanical and molecular plastic recycling can feasibly exploit plastic waste as a renewable carbon resource.
• Plastics can be derived from any kind of carbon resource, spanning fossil oil and gas as well as renewable carbon resources like biomass, plastic waste, and carbon dioxide.	• Today around 98% of plastics are based on non-renewable fossil resources. Carbon capture and use of CO_2 complement the development of bio-based polymers and hold promise for molecular recycling.
• Most plastics are durable even in harsh environments. Corrosion-resistant polymers protect metals and shield surfaces against environmental attack.	• Abrasion of tires and textiles, slow plastic degradation, and use of micron-sized plastics as additives cause micro- and nanoparticle emissions. Health hazards and micro- and nanoparticle pollution remedies need to be addressed. Recycling strategies for coatings, adhesives, and thermosets are needed.
• Most high-molecular-weight plastics are non-toxic. Plastics qualify for medical and food-contact applications.	• Low-molecular-weight resins, reactive intermediates, monomers, and additives can cause emissions and health hazards and require special safety and handling procedures. Green polymer technologies need to be explored.
• Biodegradable plastics enable composting, biogas formation as a renewable energy source, bio-feedstock recovery, and drug release.	• Biodegradation depends on temperature, moisture, air, and microorganisms and causes carbon dioxide emission. Many plastics that are compostable by industrial composting fail to degrade in seawater. Biodegradation can emit microplastics, serving as a breeding ground for spores and pathogens. More research is needed to better understand biodegradation in the open environment, especially in oceans.
• In rapid response to Covid-19 pandemic challenges plastics industry supplied materials for urgently needed personal protective equipment like face masks, gowns, and shields across the globe	• Most anti-Covid-19 plastics ended up in landfills, incineration, and oceans. In hospitals, the disposal of infectious material is logistically complex, expensive, and associated with risks for staff. It is challenging to establish an on-site waste treatment/valorization in conjunction with the reuse of recyclable material.
• High resource, energy, eco, and cost efficiency, and the low weight and low carbon footprint of plastics enable sustainable developments.	• The potential of existing plastics in sustainable development and circular economy is far from being fully exploited and prompts R&D challenges.

di-2-ethylhexyl phthalate (DEHP), which is believed to cause endocrine disruption in males.[33–35] Halden reviewed the potential health risks of plastics, Bisphenol A, and plasticizers like DEHP.[23] In addition to commodity plastics, polyurethanes (PU) and engineering thermoplastics such as polyamide (PA), acrylonitrile/butadiene/styrene polymers (ABS), and polycarbonate (PC) are produced at around a one-million-ton scale. Roughly 75% of plastics are linear or slightly branched thermoplastics, whereas highly crosslinked thermoset resins serve specialized markets ranging from adhesives, coatings, and electrical insulation to creep-resistant matrix resins for composites and printed circuit boards. While thermoplastic waste is melt-processable, thermosets are infusible and cannot be recycled by remolding.

Compared to other materials such as wood, ceramics, and metals, which have been in use for many centuries, plastics are very young materials, growing at a significantly higher rate since the
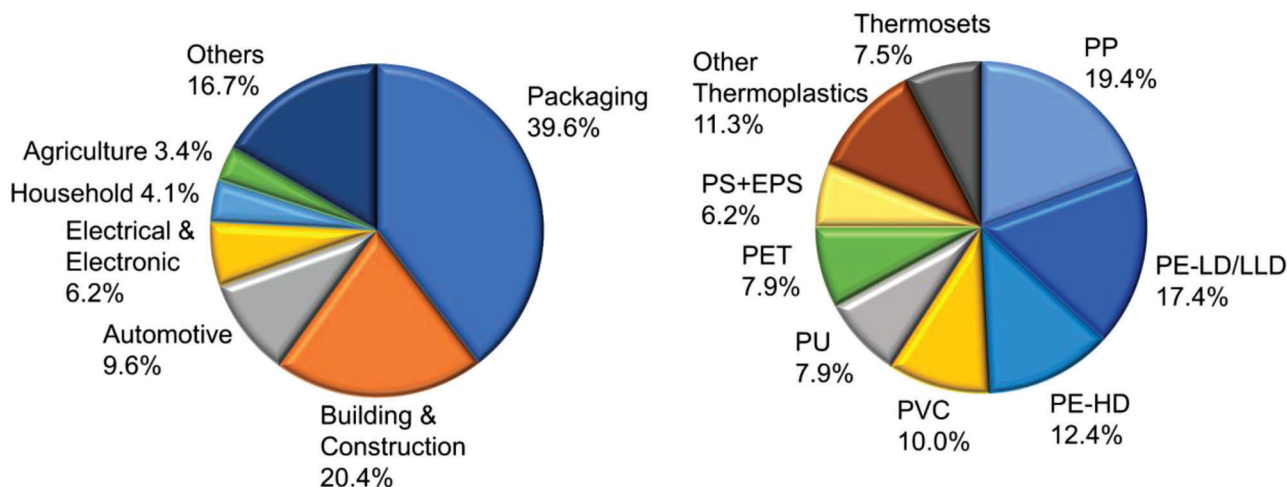
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Figure 2. European Plastics demand 2019 by segment (left) and by resin type (right); data from Plastics the Facts 2020[32] published and annually updated by PlasticsEurope.

second half of the 20th century. In fact, most plastics have entered large commercial scale in the period of the booming postwar economy and never encountered shortages typical of wartime economies. In 1972, the early warning, issued by the Club of Rome concerning the limits of growth, rapid depletion of fossil resources, sustainability, and climate change were ignored in politics, economy, and science alike.[36] The green political spirit appeared in the early 1980s. In 1953, the annual world plastic production was around 3 million tons; production increased to 78 million tons in 1985 and to 367 million tons in 2020.[32] In 2019, the clear leader in plastics production was Asia (51%), followed by the member countries of the North America Free Trade Agreement NAFTA (19%), and Western Europe (16%). With its 31% share, China is now the clear number-one country in plastic manufacturing. From 1950 to 1985, the production of one billion tons of plastics took 35 years, whereas the same amount was produced within 3 years from 2018 to 2020. Plastic growth closely parallels the growth of the world population, rising from 2500 million in 1950 to 5300 million in 1990, and 7800 million in 2020, and is projected to reach around 9700 million in 2050.[37] To satisfy human needs across the globe, plastic consumption will continue to surge as all humans living in high- and low-income countries strive for a better life. Assuming a continuing annual growth rate of around 4% the annual world plastic production displayed in **Figure 3** could exceed 1800 million tons by 2050.

In a linear economy, fossil carbon resources are converted into carbon-based plastics and deposited in landfills or incinerated after completing their product lives. The failure to close the carbon loop accounts for the continued depletion of non-renewable resources accompanied by a massive environmental carbon leakage into the soil, water, and air, thus ultimately destroying the human habitat and biodiversity. Today, plastic waste mismanagement has reached epidemic proportions worldwide. In a business-as-usual scenario, the current global system is expected to collapse halfway through the 21st century.[36] Rethinking plastics and closing the carbon loop while meeting human needs for a better life and sustainability without compromising climate prompts challenges for scientists, engineers, and politicians alike. Herein, approaches toward closing the carbon loop in the circular plastics economy are highlighted and illustrated by selected examples emphasizing polymer research and development challenges.

2. Taming the Plastic Waste Flood

Considering manufacturing, use, and end-of-life scenarios of polymer resins, synthetic fibers, and additives derived from fossil resources, a study by Geyer, Jambeck, and Law on the fate of all mass-produced plastics estimates that around 79% of the 8300 million tons of all plastics produced till 2015 ended in landfill, 12% were incinerated and only around 9% were recycled. In a continued linear economy, the 6300 million tons of plastic waste deposited in landfills would increase to roughly 12 000 million tons by 2050![38] More than half of this plastic waste tidal wave contains packaging wastes and especially wastes of single-use items. In 2018, Europe (28 countries plus Norway and Switzerland) collected 29.1 million tons of post-consumer plastic waste that was incinerated (42.6%), recycled (32.5%), and deposited in landfills (24.9%).[32] Although the amount of recycled plastic is markedly increasing in Europe and circularity is praised everywhere, in 2018, close to half of the plastic waste intended for recycling was exported to other countries across the globe, especially to China. A considerable portion of exported plastic wastes went missing and re-appeared in Asian landfills and in the sea. In 2018, China's ban on plastic waste imports deeply impacted the global waste trade, but plastic waste exports from high-income to low-income countries continue and urgently demand better international regulations.[39–42]

From landfill macro- and microscopic plastic, debris enters rivers, reaches the sea, and meets floating plastic waste dumped by coastal cities, fisheries, and shipping. Plastic pollution endangers marine life, biodiversity, and human health.[43,44] According to a study by the EarthWatch Institute, macroscopic marine plastic litter primarily consists of plastic bottles (14%) and food packaging (12%) together with cigarette butts (9%). It is accompanied by takeaway-food packaging, cotton swabs, and single-use cups.[45] They conclude that the best way to solve the plastic lit-
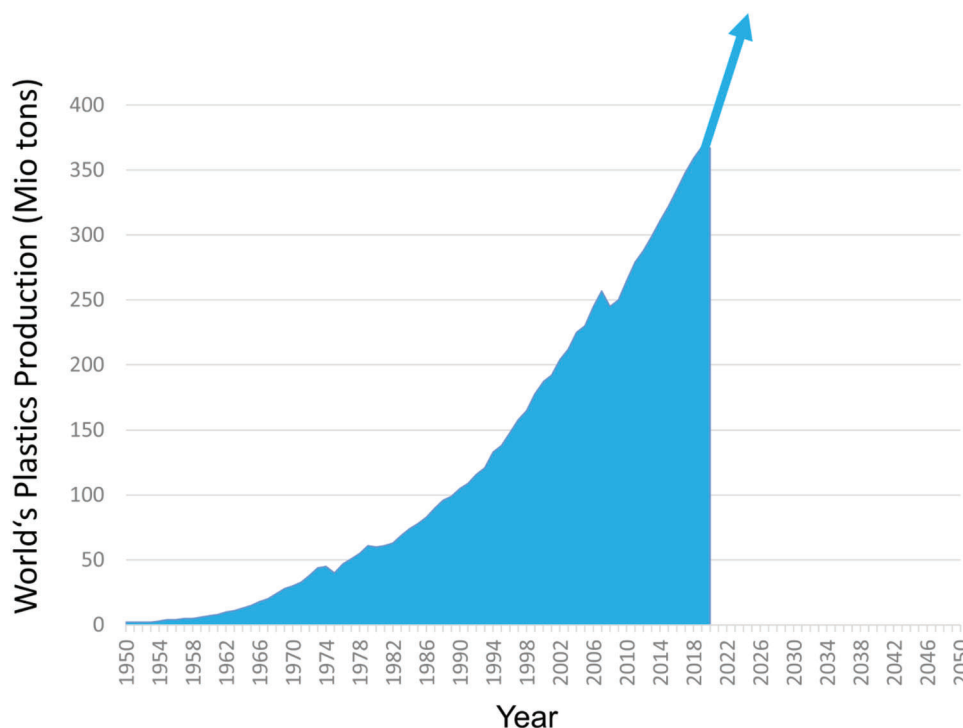
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Figure 3. Growth of the world's plastic production (data obtained from PlasticsEurope).

ter problem is not to render all packaging biodegradable but to reuse cups and bottles or to enforce their correct disposal. Low-density plastics used in packaging, such as PE, dominate plastic wastes floating on the sea surface, whereas plastics with higher densities, such as PVC, PA, polyesters, and composites, are enriched in deep-sea locations.[46] Driven by converging maritime and wind currents, 45 to 129 thousand tons of persistent macroscopic plastic waste containing around 46% fishing net waste and 8% micron-sized plastic debris (microplastics) are floating inside an area of 1.6 million km^2, known as the Northern Pacific Trash Vortex and Pacific Garbage Patch.[47] In 2010, it was estimated that 275 million tons of plastic waste were generated in 192 coastal countries and 4.8 to 12.7 million tons entered the oceans.[48] According to a recent study by Meijer, 1000 rivers, most of them in Asia, account for 80% of the riverine plastic waste emission in the oceans.[49] Countries with high precipitation rates, such as the Philippines, which have a relatively small land surface area compared to the length of their coastline, are the leaders in marine plastic waste emission. Mostly invisible to the human eye, micron- and nanometer-sized plastic particles originating mainly from abrasion of tires and textiles accompanied by microplastics formed by plastic weathering, the release of production wastes, and cosmetic additives rapidly accumulate in the sea,[50,51] freshwater,[52–55] soil,[56] and air.[57] Also landfills of municipal plastic wastes are considered a source of microplastic emission due to slow degradation accompanied by embrittlement and fragmentation of plastic waste.[58] Due to their high porosity resulting from surface and bulk erosion, spongy microparticles can adsorb and concentrate low molecular weight toxic wastes such as pesticides and other chemicals diluted in seawater.[59] In particular, sub-micron plastic particles are likely

to enter the food chain and pose a threat to animal and human health when they are loaded with chemicals.[60] At present, nanoparticles evade most microplastic analytics. As micro- and nanoplastics are continuously transformed and undergo complex interactions depending on their sizes, surfaces, and environmental exposure, more research is required to better understand their impact on the biosphere. Filtration, absorption, biological, and chemical treatments are being explored to remove microplastics.[61]

Fighting environmental plastic pollution and the quest for environmentally benign products is attracting considerable attention from the public and is addressed by numerous organizations, among them the United Nations (UN),[62] the European Union (EU),[63] the Institute for European Environmental Policy (IEEP),[64] the World Economic Forum (WEF),[65] the Ellen MacArthur Foundation,[25–27] and the Alliance to End Plastic Waste (AEPW).[66] At the Sustainability Summit on September 25, 2015, the United Nations adopted 17 sustainable development goals to render global developments sustainable by 2030.[67–69] Plastics are expected to play an important role in achieving these goals.[70] A comprehensive survey on the challenges related to using plastics as a material system in the circular economy and emphasizing the role of technological innovations, legislation, and business practice was presented by Bucknall.[71] Halden pointed out that in the "5 Rs" concept, "reduce, reuse, recycle, rethink, restrain," plastic waste represents the key to steering human society towards sustainable plastic development and circularity.[23] The EU Commission is striving to achieve 100% recycling of packaging wastes by 2030 and presented a plastics strategy in early 2018 that focuses on recycling, waste prevention, and reducing carbon dioxide emissions resulting from plastic production and
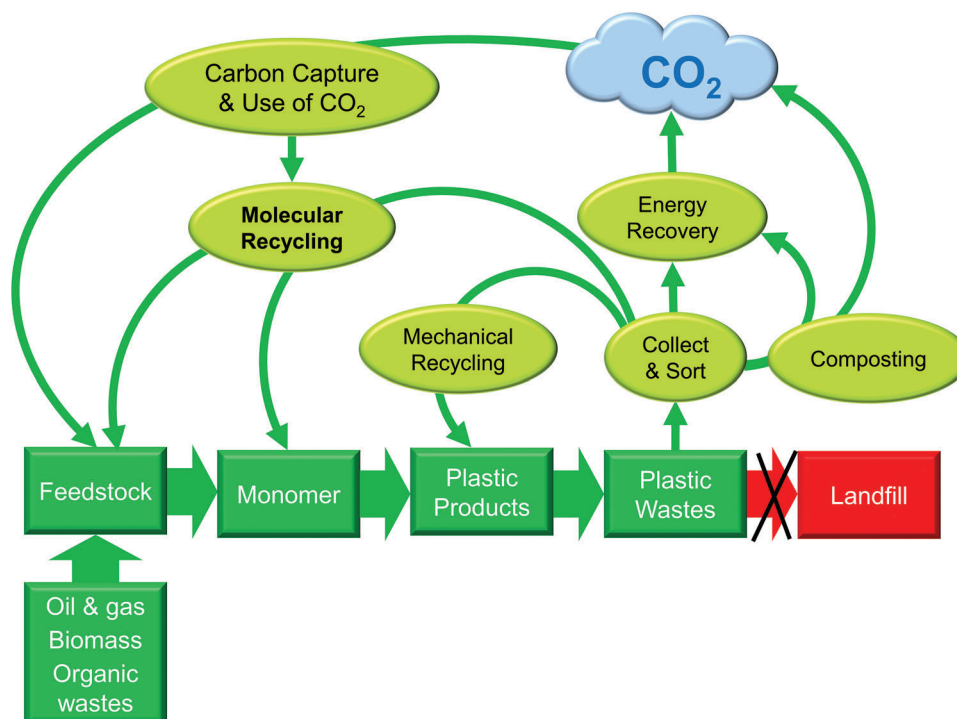
Figure 4. Closing the carbon loop in the circular plastics economy by reuse, mechanical and molecular recycling, energy recovery, and carbon capture and use of CO_2. In an open-loop valorization, plastic waste as a renewable carbon resource produces hydrogen, chemicals, and carbonaceous materials.

disposal.[63] In 2021, the EU Commission banned certain disposable items such as plastic drinking straws and to-go cups made from expanded polystyrene, restricted the use of microplastic additives, and set plans to introduce requirements regarding the proportion of recycled plastic for certain products, regulations on the recyclability of products, and a levy on non-recycled plastic waste.

The political ambition of a stringent circular economy requires a paradigm shift in the plastic economy. Greenwashing products by attaching bio labels is not the right approach. Instead of banning plastics, the tremendous potential of plastics and renewable carbon sources needs to be exploited for the circular economy. Because all biopolymers and industrial plastics are carbon-based, the total decarbonization of the plastics industry remains an illusion and is not expedient in terms of sustainability. However, carbon emissions into the environment are significantly reduced, and carbon neutrality is achieved by closing the carbon loop and by using renewable energy to drive the carbon cycle. As Vander Beke states in his review on recycling of plastics, plastic waste recycling is far from being fully developed and holds enormous potential.[72]

As is illustrated in **Figure 4**, four different carbon-loop strategies toward preventing carbon leakage into the environment exist. The best strategy is to prevent waste, curb single-use packaging, and reuse plastic waste. In the first carbon-loop scenario, reuse by mechanical recycling of non-polluted plastic wastes with known histories, such as post-production/pre-consumer wastes, yields recycled products with identical structures and property profiles as the corresponding virgin plastics. By improving waste collecting and sorting and by redesigning plastics for recycling,

more plastic waste qualifies for reuse by mechanical recycling. In mechanical downcycling using inferior-purity waste streams for mechanical recycling, the resulting lower-value recyclates cannot replace virgin plastics, especially in the original application such as food-contact materials and medical packaging. Reuse on the one hand, as well as mechanical recycling and downcycling on the other hand, are also designated as primary and secondary recycling.[72,73] In the second carbon-loop scenario, molecular recycling, also termed chemical recycling or tertiary recycling,[72,73] plastic wastes unfit for mechanical recycling are broken down into small molecules and upcycled, serving as renewable carbon resources and feedstock for value-added chemicals and virgin plastics. In the third carbon-loop scenario, named quaternary recycling,[72] as an end-of-life option, low-grade wastes of plastics and biomass constitute a high-grade energy source via incineration that generates electricity and steam. In this last-resort scenario, the stored energy and the polymer structure are lost, accompanied by emissions of greenhouse gas (GHG) and harmful combustion byproducts that must be removed by off-gas purification. Also, biological recycling by aerobic and anaerobic industrial composting destroys the polymer structure by generating fertile soil (compost) together with energy and carbon dioxide. In the fourth carbon-loop scenario, carbon capture and use (CCU) by chemical and biological carbon dioxide fixation yields feedstocks, monomers, and polymers. This CCU technology is essential for carbon-neutral recycling and contributes to both climate change mitigation and resource efficiency. While the solar-energy-driven biological carbon dioxide fixation and the use of biomass benefit from the progress made in bioeconomy and biorefining, the chemical carbon dioxide utilization exploits
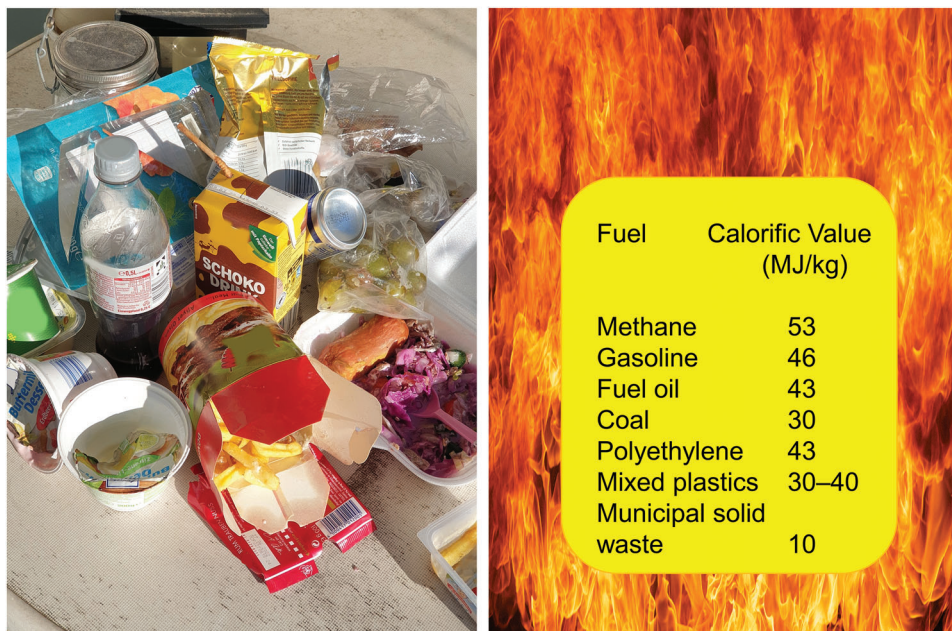
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Figure 5. Mixed waste plastics illustrated by packaging wastes deposited on a table at a campsite close to a fast-food restaurant in the Freiburg region (Germany). Complementing mechanical recycling and downcycling energy recovery exploits the high calorific values of plastics. Incineration is an end-of-life option for polluted mixed wastes which are tedious to separate and yield recyclates with inferior properties, due to chain scission caused by mechanical and oxidative stresses encountered during mechanical recycling. The calorific data were taken from the literature.[100] (Right image licensed from Adobe Stock and modified).

green hydrogen technology based on water splitting by electrolysis using renewable energy. Some researchers hold optimistic views about the feasibility of a rapid move from a fossil-based linear plastic economy toward a circular plastic economy which does not compromise climate change mitigation, due to the increased energy demand for recycling. According to Meys and Bardow, net-zero GHG emission plastics appear to be economically feasible in a circular economy by combining a high recycling rate of roughly 70% with efficient biomass and carbon dioxide utilization. The low-cost supply of carbon dioxide and biomass, in combination with large-scale recycling and lower investment barriers for exploiting renewable carbon technologies are the prime requirements for carbon capture and storage (CCS) to be cost-competitive with the linear plastic economy.[74] In the Nova Institute's Renewable Carbon Initiative scenario, renewable carbon sources could completely replace fossil resources by 2050. Their estimated 1200 million tons of total world's plastic consumption by 2050 could be mainly covered by recycling (750 million tons) together with carbon dioxide-based (315 million tons) and bio-based plastics (135 million tons).[75,76]

Despite growing economic and political incentives for plastic waste recycling, a critical view on the future of recycling by Garcia and Robertson sees the end-of-life options as being quite limited, with obvious constraints on current processes.[77] As stated in a review by Reuter, design for recycling and sustainability are limited by the second law of thermodynamics. In other words, the rise of entropy due to the increasing complexities of recyclates and technologies limits their recovery within the stringent boundaries of consumer behavior, product design, technology, legislation, and economics.[78] In addition, most recycling processes are energy intensive, and recycling frequently yields low-quality materials down the value chain. Plastics do not need to be reinvented but require better recycling processes and plastic waste valorization by utilizing renewable carbon feedstocks while simultaneously lowering their carbon footprint and changing consumer and retailer behavior.

3. Mechanical Recycling and Energy Recovery

The economic success of both mechanical and molecular recycling strongly depends on efficient processes for harvesting valuable, high-quality raw materials from mixed plastic waste streams. In mechanical recycling, thermoplastics are recovered and re-processed by extrusion. Material reclaimers shred, wash, melt, and repalletize plastic wastes and sell them to molders. Unlike clean and easily recyclable thermoplastic post-industrial production wastes, post-consumer plastic wastes account for just a small percentage of municipal waste and are collected together with a great variety of other materials and contaminants. **Figure 5** displays wastes dumped on a table at a campsite near a fast-food restaurant. In essence, only high-quality thermoplastics enable recycling, whereas lower-quality recycled plastics in downcycling serve markets downwards in the value chain. As an alternative to downcycling and energy recovery, upcycling entails breaking lower-quality recycled plastics down into valuable chemical feedstocks via molecular recycling.[79] For highly contaminated plastics and multilayer packaging, the recovery of energy by incineration is a viable end-of-life scenario. Weckhuysen,[80] Van der Beke,[72] Ragaert,[81] Al-Salem,[73,82] and Vogt.[83] have given overviews on recycling, and valorization strategies for plastic solid waste.

Mechanical recycling depends on product design, material compositions, and cost-efficiency of processes. Examples of successful mechanical recycling include plastics such as large carrier bags, bottles, and window frames all of which are large, easy to sort out, melt-processable, and devoid of multimaterial systems. Weckhuysen reviewed the sorting and mechanical recycling processes, key industrial players, and life cycle assessment (LCA).[80] Typically, in mechanical recycling, plastic wastes are collected and removed from other wastes such as metals, glass, and paper before separating them by plastic type. After shredding, the smaller plastic waste particles are washed to remove dirt and dust and sorted again to separate thermoplastics for pelletizing extrusion. At this point, PET pellets may be good enough to qualify for reuse as textiles such as carpets or fleece jackets. Recycled PET is also used as a component of rubber-modified asphalt, thus transforming a durable polymer from short-lived packaging into long-lived construction applications.[84] However, more treatments such as vacuum stripping of volatile pollutants during melt extrusion are required to meet the stringent demands of applications such as food-contact materials. In addition, solid phasing by heating PET pellets above glass temperature builds up molar mass by a chain-extension reaction to achieve better mechanical properties. It remains a challenge to guarantee the high purity of recycled plastics in medical applications to prevent liability suits. In automated sorting processes, near-infrared (NIR) spectroscopy is used in the online monitoring of waste streams.[85–87] However, most NIR devices are not suited for black plastics, which are very common in, for example, electronic wastes or agricultural foils. To overcome this obstacle, mid-wavelength infrared (MIR) technology can be used instead of NIR.[88] Markers can help to spectroscopically specify waste types and trace plastic product's origins.[89] Artificial intelligence systems and robotics are expected to speed up and improve automated sorting. Frequently before re-extrusion, virgin plastics are added to meet manufacturing specifications. Schyns and Shaver reviewed the prospects and challenges of PET, PE, PP, PVC, and PS packaging recycling and pointed out imminent process limitations relating to costs, inconsistent recyclate quality, and the deterioration of mechanical properties by degradation.[90]

In contrast to the successful mechanical recycling of relatively pure PET and PE bottle wastes, profitable value chains for mixed plastic wastes represent a challenge. Multilayer oxygen-barrier films consisting of co-extruded multilayers or metalated films are not recyclable via re-extrusion and are difficult to fully replace by mono-material systems. Due to its complex compositional heterogeneity, recycling multilayer plastic packaging is challenging. A promising route for increasing recycling rates for these materials is delamination, which allows polymers to be recycled separately. For example, in addition to separation by dissolution/precipitation of constituent polymer layers or selectively degrading an individual layer, acids such as formic acid were added to PET multilayer packaging to achieve delamination via debonding.[91] Aging during use as well as thermo-oxidative and mechanical stresses resulting from high shear forces encountered during mechanical recycling deplete polymer stabilizers and trigger oxidative degradation. In the absence of stabilizers, polymer chain scission renders plastics brittle and can account for emissions of both microparticles and low molecular weight degradation products.

Recyclers in Europe experience challenges relating to registration, evaluation, authorization and restriction of chemicals (REACH) requirements, and getting approval for using recyclates as food contact materials.[92] U.S. companies that meet the guidelines on recycled plastics for food packaging receive a letter of no objection from the Food and Drug Administration (FDA).[93] With few exceptions, polymers are highly immiscible, and extrusion of thermoplastic blends, even in the presence of compatibilizers, can drastically reduce toughness and lower recyclate value. Specialized additive packages designed for recycling include antioxidants, impact modifiers, blend compatibilizers, and do much more.[94–96] With decreasing stabilizer content in multiple extrusion of polyolefins, high-performance liquid chromatography and thermo-desorption gas chromatography reveal the formation of lower molar mass odd-numbered linear alkane chains for PE and of oxidized branched alkanes for PP.[97]

In LCA, mechanical recycling can be economically and ecologically advantageous with respect to the production of virgin plastics and composites.[96] In 2018, 1 million tons of European plastic recyclate were exported, and 4 million tons entered markets like building and construction (46%), packaging (24%), and agricultural plastics (13%).[32] According to a survey by Tullo published in Chemical & Engineering News in 2021, US consumer companies such as Coca-Cola, which produces 112 billion plastic bottles a year, Unilever, Procter & Gamble, PepsiCo, Nestlé, Keurig DrPepper, Colgate-Palmolive, and Blue Triton Brands have started rolling out 100% recycled bottles, and most of them claim to strive for 25% content of recycled plastics in all packaging by 2025.[93] However, only 28% of recycled bottles become beverage and food containers again while contaminated waste is phased out in downcycling and energy recovery. Compared to PET, the use of recycled polyolefins in food-contact applications is even more challenging, as they serve more diverse packaging applications and encounter more contaminants in use. Processes such as dissolution/precipitation separation by extraction of polystyrene with p-cymene followed by precipitation in heptane or extraction of polypropylene using supercritical butane, respectively, are considered alternative routes in mechanical recycling that enable efficient removal of low molar mass contaminants.[93] Moreover, solvent extraction enables the removal and recovery of polymer additives, including colorants.[98] Solvent extraction by dissolution/reprecipitation methods and supercritical fluid extraction can produce high-quality plastic recyclates comparable to virgin plastics, such as polyolefins, PET, PS, PC, ABS, and PVC.[99] It is a challenge to phase out hazardous solvents and reduce the emission of volatile organic compounds.

Despite recent progress, closing the carbon cycle through infinite 100% mechanical recycling remains an illusion. As in the case of paper recycling, each cycle deteriorates polymer properties, and degraded recyclates, together with highly contaminated plastic waste, must exit and either enter lower value applications in downcycling or serve as an energy storage material. From the calorific values listed in Figure 5, it is apparent that mixed plastic wastes (30–40 MJ kg^{-1}) and polyethylene (43 MJ kg^{-1}) have high energy content similar to that of fuel oil (43 MJ kg^{-1}), which is far superior to the low energy content of municipal solid waste (10 MJ kg^{-1}).[100] The energy demand of a recycling process should not drastically exceed the sum of the energy recovered by incineration and the energy needed for producing virgin plastics. The

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replacement of oil and gas used in municipal waste incinerators represents an appropriate end-of-life option when recycling is not economically or ecologically feasible. At present, the complete removal of plastics with high energy content from municipal waste requires the use of fossil oil and gas as energy sources for municipal waste incineration.

Mechanical recycling by re-extrusion is restricted to thermoplastics, whereas most crosslinked polymers such as rubber, thermoset resins, fiber-reinforced composites, and high-temperature resistant polymers, such as fluoropolymers, are incinerated or end up in a landfill. Attempts have been made to de-vulcanize rubber, thus rendering rubber wastes flowable and enabling their mechanical recycling.[101–103] In addition, waste tire scrap is used to modify concrete.[104] As tires consist of butadiene/styrene copolymers together with carbon black fillers and mineral oil as a plasticizer, they have a high carbon content and represent attractive energy storage materials for the energy-intensive cement industry that does not require the tedious separation of steel cord or many different formulation components. Aside from incineration, thermosets and their composites are mechanically recycled by milling to produce smaller particles that are useful as fillers.[105] Leibler introduced another approach toward recyclable-by-design thermoset resins and composites in 2011.[106–112] His vitrimers represent covalent networks that are reversibly rendered flowable by thermoactivated bond exchange reactions and behave like viscoelastic liquids, thus enabling the reprocessing of networks. Wang employed high-performance epoxy-based vitrimers derived from renewable resources as the matrix of nondestructive recyclable carbon fiber composites.[110] Their recycling represents a major challenge with respect to the surging demand for carbon-fiber composite in lightweight construction, automotive, and aerospace industries.[105,113] Based on fossil resources, PU makes up close to one-third of the commercial crosslinked polymer market, with applications ranging from foams and coatings to elastomers. Typically, PU waste is disposed of mostly by landfill and incineration, whereas blending and recovering polyol feedstocks enables downcycling.[114] By dynamic urethane exchange reaction during twin-screw extrusion, blends of rigid polyester PU and PU soft polyether PU networks yield materials with tunable mechanical properties that can vary from soft to elastomeric to rigid as a function of the feed composition.[115] Whether dynamic networks with the thermoresponsive bond exchange are, like static covalent networks, creep resistant and enable re-processing of mixed waste streams, including formulated multicomponent thermosets, needs to be demonstrated.

In contrast to fiber-reinforced composites with tedious fiber recovery, self-reinforced plastics are free of alien components and represent single-component composites in which the matrix and reinforcing phase are made of the same polymer, free of alien materials.[116–119] In commercial two-step processes, stretched tapes or woven fibers, both of which consist of oriented polymers, are bonded together with the same polymer, which has a lower crystallinity. An attractive all-polymer composite with respect to facile mechanical recycling is evoked by flow-induced crystallization during melt processing. For example, mechanically recyclable self-reinforced all-hydrocarbon composites are obtained by injection molding of polyethylene reactor blends having tuned ultrabroad bi- and trimodal molar mass distribution and containing un-entangled nanophase-separated ultrahigh molecular weight PE (UHMWPE).[120] During injection molding, flow-induced crystallization yields nanofiber-like extended-chain UHMWPE, which is not achievable from spinning processes. By multiple extrusion and injection molding below 250 °C, this 1D nanostructure and the resulting mechanical properties are fully restored in mechanical recycling. Moreover, in extrusion-based 3D printing, the 1D nanostructure orientation is digitally tuned by the moving pattern of the printhead, which is guided by computer design.[121]

In the future, stimuli-responsive polymers are expected to play an important role in mechanical recycling. It would be highly desirable to design advanced materials that enable debond-, dismantle-, decoat-, and degrade-on-demand triggered by external stimuli. At present, coatings cause problems in mechanical recycling when they are not removed or uniformly dispersed within the recycled plastic matrix during its re-processing by extrusion. Today, adhesives are widely employed in lightweight construction to bond different materials and enable efficient stress transfer, sealing, as well as corrosion resistance. Structural adhesives form durable joints that are difficult to disassemble without destroying the substrate. Bond- and debond-on-command adhesives hold great promise in a circular economy by facilitating repair and reuse of plastics. Moreover, bond- and debond-on-command are also attractive for recycling multilayer- and multicomponent systems of packaging and composites that are currently unsuited for mechanical recycling. First attempts towards bond- and debond-on-command systems exploit thermally expandable particles, thermo-reversible Diels–Alder, and vitrimer chemistry, as well as electrically induced de-bonding.[122–125] Another challenge in design-for-recycling is creating "glueless" bonded structured either by mechanical interlocking or by implementing bond-/debond-on-command function into polymers.

4. Bio-Based Polymers and Biomass Utilization

4.1. Bio-Based Polymers and Biopolymers

In the dream of a green and sustainable circular plastic bioeconomy illustrated in **Figure 6** left, solar power drives the carbon cycle in which photosynthesis converts water and the GHG carbon dioxide into biomass as a source of bioenergy, biofuels, and green bioplastics. In this end-of-life scenario, biodegradation and oxidation convert plastic waste, including marine litter, back into water and carbon dioxide to close the carbon loop. In reality, this inspiring circularity dream faces several challenges, displayed in Figure 6 right and outlined in **Table 2**.[126] First, harvesting and biomass utilization in plastic manufacturing is energy-intensive and can accelerate global warming, given that it is currently driven by non-renewable energy. Second, depending on temperatures and the presence of water and oxygen, biodegradation can be slow, emitting the potent GHG methane by anaerobic digestion, while erosion can form inhalable and migratable micro- and nanoparticles that are nutrients and breeding grounds for spores and microorganisms. Third, stepping up farming on a billion-ton scale with increasing demand for farmland could endanger the food supply of the growing world population and pose a threat to biodiversity due to monocultures with irrigation and massive use of fertilizers, pesticides, and transgenic plants. Fourth, most natural polymers
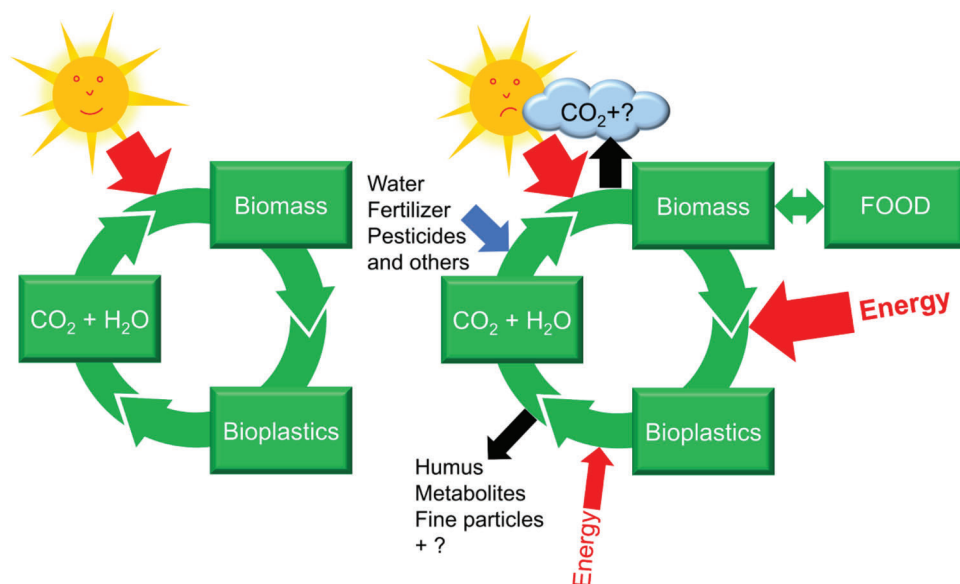
Figure 6. Dream (left) and reality (right) of a closed carbon loop in bioplastic economy. Reproduced and adapted with permission.[126] 2013, Wiley.

Table 2. Prospects and challenges of bio-based plastics.

Prospects	Challenges
• Utilization of biomass as a renewable carbon resource for feedstocks and energy replaces non-renewable fossil resources, reduces oil imports, and lowers carbon footprint by serving as a carbon sink	• Utilization of forestry and agricultural wastes and algae avoids competition with food supply without imposing the negative impact of enhanced farming and land use on biodiversity. However, a significant biomass portion must remain on farmland and in forests to secure soil quality and natural habitats for animals.
• Biopolymers such as cellulose and chitin are abundant.	• Cellulose and chitin are infusible. State-of-the-art processing requires chemical modifications most of which are energy-intensive and fail to meet the criteria of green chemistry. Green chemistry is needed to enable chemical modification of biopolymers.
• Genetic engineering of microorganisms and transgenic plants enables the use of cells as chemical reactors for producing bio-based plastics and monomers, thus exploiting progress made in biotechnology and the bioeconomy.	• Biotechnology processes have a high water footprint. Solvent extraction is used to separate bio-based polyesters from cells. Processes, processing, and tuning polymer properties, such as crystallization rate and toughness of Polylactic acid (PLA) and Polyhydroxyalkanoates (PHAs), require improvements while lowering costs.
• Biodegradation enables composting and anaerobic digestion produces the biogas methane as a renewable energy source.	• Both biodegradation and incineration of bioplastics emit CO_2 but biodegradation can be slow, as it strongly depends on temperature and the presence of water and oxygen. Most compostable plastics do not degrade in seawater. Anaerobic methane emissions in mismanaged landfills contribute to global warming. Designing biodegradable throwaway products is counterproductive to the targeted plastic reuse and recycling.
• Biopolymers are non-toxic.	• Biopolymer processing requires the use of various migratable additives, including special bio stabilizers and processing aids. Bioerosion can release inhalable micro- and nano particles which serve as nutrients and breeding grounds for spores and microorganisms.

in their native form and many biopolymers supplied by biotechnology are not processable and require chemical modifications and migratable additives to qualify for plastic applications. As regards the sustainability of a green carbon loop, a major challenge in a circular plastic economy is avoiding conflict with the food supply by utilizing agricultural, forestry, paper, and vegetable oil wastes, preferably without including non-sustainable natural products, such as palm oil. New opportunities for bio-based

plastic development arise from advances made in biorefining, life sciences, biotechnology, and process engineering.

In the early days of polymer technology, a clear distinction existed between biodegradable bio-based polymers derived from renewable natural resources and non-biodegradable, synthetic plastics derived from fossil resources. The public's use of the term 'bioplastic' is confusing, as it refers to both biodegradation and the bio-based origin of plastics. These two different aspects
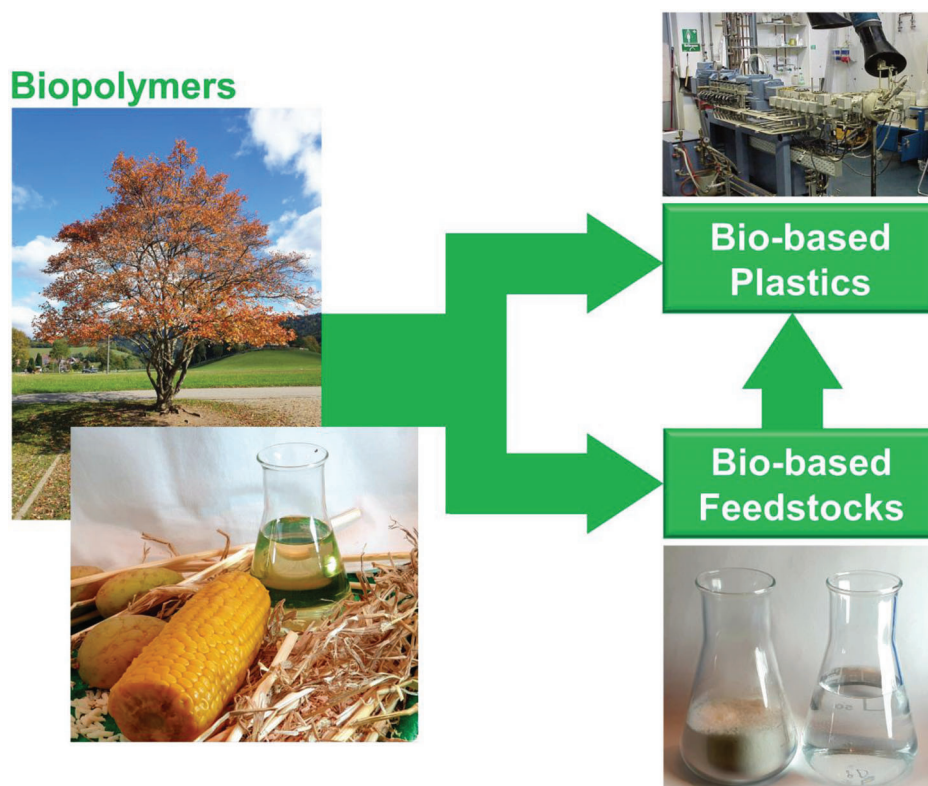
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Figure 7. From renewable carbon resources such as biomass, plastic waste, food waste, used cooking oil, and carbon dioxide to renewable carbon feedstocks and renewable plastics, processable biopolymers are bio-based plastics that are either extracted from natural sources or produced by polymerizing bio-based monomers. The replacement of fossil-based monomers for identical bio-based monomers affords bio-based plastics identical to fossil-based plastics.

of plastic are not at all synonymous. Both synthetic plastics and bio-based polymers can be derived from renewable resources and rendered either durable or biodegradable. Hence, the term 'bioplastics' should not be used. A clear distinction between bio-based and biodegradable plastics must be made. Moreover, the label 'bio' is not synonymous with fully biodegradable, green, environmentally benign, and sustainable. At present, this misconception serves as a marketing tool in greenwashing products by re-labeling them as 'bio'. According to the DIN EN 16575 (2014) definition, 'bio-based' means that a product is made entirely or partly from biomass.[127] Renewable raw materials are naturally replenished on a human timescale. As is illustrated in **Figure 7**, two pathways toward producing bio-based plastics exist. First, in the traditional pathway, natural biopolymers are harvested and modified to enable their processing, which frequently fails to meet the high standards and low cost typical of fossil-based plastics. Second, biorefineries utilize biomass to produce bio-based monomers and bio-based plastics, including biopolymers. Thus, most synthetic plastics can be converted into bio-based versions without affecting their processing and property profiles by using biomass as renewable raw materials. Plant cells synthesize an exceptionally broad range of biopolymers such as carbohydrates and proteins, most of which are not processable and do not qualify for plastic manufacturing.

Since the pioneering days, a key challenge has been improving the processing and properties of biopolymers in plastic man-

ufacturing. The outstanding precision of biosynthesis producing polymers with narrow molar mass distribution is a key prerequisite of protein engineering but represents a disadvantage in melt processing that requires tuning of broad molar mass distributions in order to achieve shear thinning. In contrast to the solvent-free polymerization processes used to fabricate commodity plastics, biosynthesis has a high water demand and requires the complete separation of biopolymers from cells, to qualify as food contact packaging material. Compared to high molecular weight biopolymers, bio-based monomers are much easier to recover and use to produce biopolymers in highly efficient drop-in technologies, such as the solvent-free polymerization processes established for fossil-based plastics. The prospects and challenges of bio-based polymers are summarized in Table 2. Aspects of bio-based plastics for the circular economy and sustainable development have been reviewed by Rosenboom,[128] Iwata,[129] Babu,[130] Wool,[131] Sudesh,[129] van den Oever,[132] and Landis.[133] Brief and concise overviews on bio-based plastics are available from European Bioplastics[134] and the Nova-Institute.[135]

4.2. Bio-Based Plastics Extracted from Nature

The development of plastics derived from renewable natural carbon sources and biopolymers such as carbohydrates, lignin, proteins, and natural rubber has a long tradition but

Figure 8. Opposite to paper (left) and regenerated cellulose (*Cellophane*) (center), LLDPE films (right) are much thinner and highly stretchable.

prompts challenges for sustainable development and the circular economy.[136–145] Today, around 40% of the world's rubber consumption is bio-based and supplied by rubber plantations. Both synthetic and natural rubbers used in tire formulations are highly resistant to bio- and photodegradation. The dumping of waste tires, along with microrubber emission resulting from tire abrasion, pose a severe threat, to the natural environment.[146–149] Due to their high hydrocarbon content, waste tires constitute an energy source for energy-intensive industries as well as feedstock for fuels, chemicals, and plastics based on renewable carbon.[150,151] Plant fibers, wood flour, cellulose, chitin, and numerous other biopolymers are utilized as components of wood plastic compounds, biocomposites, and fiber-reinforced composites that have lower weights and higher calorific values than plastics containing mineral fillers and glass fibers.[152–154] Lignin, a major byproduct of pulping and the second-most abundant biopolymer next to cellulose, mainly serves as a renewable energy source in the energy-intensive paper industry and holds promise as an intermediate for thermosets and thermoplastics.[139,143,144,155] Starch consists of linear helical amylose (20–25%) and highly branched amylopectin (75–80%). It is readily recovered from various plants, such as potatoes, rice, and peas, by extraction with hot water.[156–158] While most starch is used in food applications, the addition of plasticizers such as glycerol and sorbitol lowers melting temperatures below decomposition temperatures and renders starch, preferably with high amylose content, melt processable.[159] To improve its water resistance, starch is melt-compounded with biodegradable and non-biodegradable polymers. A variety of blends and composites are based on starch and other biopolymers.[160] Unlike starch, cellulose is infusible and insoluble in most common solvents. It is rendered solution- and melt-processable by energy-intensive chemical modifications, including acetylation, alkylation, and ethoxylation, most of which currently fail to meet all the criteria for green chemistry. **Figure 8** compares a linear low-density polyethylene (LLDPE) film with paper and a regenerated cellulose (*Cellophane*) film. By utilizing both fossil and renewable carbon sources, highly stretchable and tough, thin LLDPE films are produced in solvent-free ethylene gas phase polymerization processes followed by blow molding, whereas cellulose is not melt-processable. In sulfate and sulfite pulping followed by bleaching, cellulose is separated from lignin to make paper that is also available from de-inked wastepaper slurries. A transparent cellulose foil (*Cellophane*) is obtained by treating cellulose with alkali and toxic carbon disulfide, followed by film extrusion of the resulting cellulose xanthogenate solution (viscose) into a bath of diluted sulfuric acid, in order to split off carbon disulfide and regenerate cellulose, which requires extensive washing to remove sulfur and salt impurities.[161] Other solvents such as ionic liquids enable cellulose solution processing without chemical modifications,[162,163] and progress in biotechnology has improved pulping.[164] However, blow molding cellulose to produce thin stretchable films with a much lower weight similar to polyethylene remains a dream. In recent years, progress has been made by Meier, who introduced a more sustainable process for esterification of cellulose in a switchable 1,8-diazabicyclo[5.4.0]undec-7-en (DBU)/CO_2 solvent system that holds promise for the development and processing of advanced cellulose-based plastics.[165–173] Tough and transparent cellulose nanopaper with high porosity was derived from aqueous dispersions of cellulose nanofibrils.[174–179] Advances in nanofibrillated cellulose production and its potential applications, ranging from nanopaper to nanocomposites, coatings, and food packaging, have been addressed by several reviews.[179–187] Although cellulose, chitin, alginate, and wood pulp serve as renewable raw materials for producing non-toxic biodegradable nanocellulose, mechanical defibrillation of cellulose is an energy-intensive process and chemical treatments are required to enable nanocellulose dispersion in aqueous and non-aqueous media.[179,180,187]

In the "battle of the bag" banning plastic bags was celebrated as a major victory, despite its marginal positive environmental impact. Single-use plastic bags are being replaced by single-use paper bags that are compostable and have a higher recycling quota but have higher weight, exhibit inferior water-sensitive mechanical strength, require high amounts of water in production, and emit significantly more GHGs and pollutants, due to energy-intensive pulping, bleaching, and de-inking. Moreover, with increasing recycling rates, more low-quality paper waste enters paper recycling. This may cause an un-intended spread of chemicals and mineral oils that are residues from printing inks and can migrate into food.[188] Among grocery shopping bags made of paper, nonwoven PP, or woven cotton bags, the cradle-to-gate LCA clearly indicates that reusable shopping bags ("bag-for-life") represent a much better option compared to single-use shopping bags regardless of their fossil or bio origin.[189] In this LCA, reusable nonwoven PP shopping bags, far ahead of woven cotton bags, create significantly lower environmental impacts than single-use plastic and paper bags. Depending on the local energy

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mix and recycling capabilities, several other studies state clear advantages of PE bags compared to paper.[190–193] However, most LCA studies on the environmental impact of carrier bags do not consider the contributions of littering. More research is needed to refine the LCA, by including additional variables, and to sharpen the LCA tool used in decision-making processes.[133,194]

In transportation, cardboard is extensively used as a packaging material. In food applications, however, the high water uptake and adsorption capability of paper require barrier layers to shield paper against water permeation, absorption of food ingredients, and UV irradiation, which destroys vitamins. As one of the most extensively used multilayer food packaging of beverages in the world, *Tetra Pak*, consists of a paperboard layer (70%) sandwiched between PE layers (25%) consisting of functionalized PE adhesive layers together with a non-functionalized, low-density PE layer as a water barrier and a thin aluminum layer (5%) as an oxygen and UV barrier. While mechanical recycling enables the recovery of high-quality pulp, PE and aluminum recyclates fail to qualify for reuse as food contact materials, and are either downcycled, used as energy storage material, or deposited in a landfill.[195]

In the packaging and paper industries, biodegradable coatings are in development for the sake of rendering paper hydrophobic without adversely affecting its reuse in pulping. Examples of biodegradable paper coatings include aliphatic as well as polyesters and their blends, such as *Ecovio* from BASF,[196] chitin/chitosan barrier films,[197–199] and coatings with canola protein,[200] essential oils,[201] Carnauba wax,[202] and zein[203] protein, which is found in maize and forms tough, hydrophobic, and even antimicrobial films. To completely avoid packaging, edible food coatings derived from natural biopolymers are claimed to keep seafood fresh by improving its moisture retention, reducing microbial growth, preventing oxidation, and even delivering food ingredients and stabilizers.[204–206] Instead of energy-intensive recycling of packaging, edible coatings either serve as food ingredient themselves or are collected and composted together with food waste.

4.3. Bio-Based Plastics and Monomers Supplied by Biorefineries

Biorefining converts agricultural, forest, and marine biomass as well as vegetable oils and fats into biofuels, biopower, and a great variety of bio-based products ranging from food and animal feed to chemicals and bio-based materials.[207] In a billion-ton scale, the production of biofuel, biopower, and bio-based plastics would consume considerable natural resources, such as starch and sugar crops, thus endangering the food supplies of the growing world population. Therefore, the focus of biomass utilization is shifting toward exploiting non-food and non-feed (so-called second-generation) bioresources, such as lignocellulose and organic waste. In particular, biological and chemical catalysis and progress made in genetics, biotechnology, and process engineering enable the valorization of agricultural, urban, and industrial biomass waste to platform chemicals.[207–210] Typically, polysaccharide chains are cleaved to form glucose either by acid treatment or by enzymatic degradation, which is expected to improve this process and render it environmentally benign.[211] Moreover, the commercial production of bioethanol

from lignocellulose creates opportunities for transforming the lignin by-product into value-added products.[212–214] As in the case of petrochemistry, the production of biofuels and bio-based plastics are closely linked. Bioethanol as biofuel serves as feedstock for bio-based monomers, such as ethylene and its derivatives used to convert a variety of plastics based on fossil resources into bio-based versions without changing their processing and property profiles.[215] **Table 3** summarizes biorefining processes and biomass sources and lists selected examples of bio-based plastics and bio-based monomers supplied by biorefineries. Biorefining is not new. Triglycerides, as the primary components of vegetable and animal oils and fats, represent a traditional renewable carbon feedstock in the chemical industry with applications spanning biodiesel, surfactants, bio-based plasticizers for PVC, bio-based thermoset resins, and bio-polyols, for example, produced from castor oil, for PUs.[142,216–222] Castor oil is also used as a raw material for producing 11-aminoundecanoic acid and PA 11 (*Rilsan*) together with other polymers and chemicals.[223] The production of biodiesel, formed by transesterification of triglyceride with methanol, generates glycerol as a large byproduct stream and prompts challenges for the valorization of low-priced glycerol. For instance, catalytic and biological processes convert glycerol into bio-based products, including 1,3-propanediol, acrolein, acrylic acid, and biofuels.[224,225] In Solvay's *Epicerol* process, glycerol is converted into bio-based epichlorohydrin, which is an intermediate of bio-based epoxy resins.[226,227] Several bio-based thermoset resins were derived from renewable natural carbon sources such as plant oils, polyphenols, rosin, sugars, terpenes, and lignin.[228–238] In addition to traditional agricultural and forestry renewable carbon sources, microalgae cultivation holds prospects for producing bio-based plastics.[239] In hydrothermal carbonization (HTC), crude plants and organic solid wastes like sewage sludge, food wastes, and plastics are converted into carbonaceous materials (hydrochar) at temperatures in the range of 180–250 °C, which is lower than pyrolysis. Produced via dehydration followed by polymerization and carbonization, value-added carbon materials are available for envisioned uses as solid fuels, renewable carbon feedstock for chemicals, active carbon for sorbents, and energy storage materials, such as supercapacitors.[240–249]

Bacterial synthesis affords starch, cellulose, and linear aliphatic polyesters containing hydroxyalkanoate building blocks, such as polylactic acid (PLA),[250–257] and other polyhydroxyalkanoates (PHAs),[258–271] namely poly(3-hydroxybutyrate) (PHB or better P3HB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (P3HB3V), and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH). By varying the type of carbon sources, including sugars, polysaccharides, vegetable oils, fatty acids, alcohols, and glycerol, microorganisms produce an exceptionally wide range of PHAs with highly variable molecular architectures. Copolymers are formed in a single-step fermentation process without requiring the feed of prefabricated 3-hydroxyalkanoate comonomers in a second step, as in copolymer formation by conventional polycondensation processes. Typically, PLA and other PHAs are formed in the cells of microorganisms and separated from cells by extraction. In the 1980s Imperial Chemical Industries (ICI) commercialized P3HB3V as *Biopol* which was distributed in the United States by Monsanto and later by Metabolix.[272] In 2019, Kaneka introduced the biodegradable thermoplastic PHBH un-

Table 3. Bio-based plastics derived from biomass.

Bio Resources and Processes	Examples
Biomass as renewable carbon source	Starch-, sugar-, and oil-based crops, grasses, straw, algae, vegetable oil, fat, lignocellulose, agricultural, forest, and other organic waste.
Bio-based monomers by microbial processes	Ethylene glycol, propylene glycol, 1,4-butanediol, 2,5-furandicarboxylic acid, isosorbide, itaconic acid, 5-hydroxymethyl furfural, lactic acid, 1,5-pentametylenediamine, 1,3-propanediol, sebacic acid, adipic acid, succinic acid, p-xylene as an intermediate for terephthalic acid, …
Bio-based monomers from vegetable oils	Castor oil-based polyols, dimer- and trimer fatty acid, 1-amino-11-undecanoic acid derived from castor oil, conversion of glycerol as a biodiesel byproduct into 1,3-propanediol, acrolein, acrylic acid, and epichlorohydrin used as an intermediate for bio-based epoxy resins, …
Bio-based monomers from bioethanol	Ethylene, propylene, 1-butene, 1-hexene, 1-octene, butadiene, vinyl acetate, vinyl chloride, acrylic acid, cyclooctene, …
Bio-based plastics by microbial processes	Polylactic acid (PLA), polyglycolic acid (PGA), bacterial cellulose, polyhydroxyalkanoates (PHAs) such as poly(3-hydroxybutyrate) (P3HB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (P3HB3V), poly(3-hydroxybutyrate-co-3-hydroxyherxanoate (PHBH), poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P3HB4HB) poly(3HB-co-lactic acid), …
Bio-based plastics from bio-based monomers	bioPET, bioPE, bioPP, bioPS, bioPVC, bioPA, bioPVA, bio-based polyacrylic acid, PLA and via lactide ring-opening polymerization, polyethylene furanoate (PEF), polybutylene succinate (PBS), bioPU from castor oil and lysine-based isocyanate, …
Biomass utilization processes	• Composting by aerobic digestion • Anaerobic digestion generates methane (biogas) as a renewable energy source. • Gasification yields carbon monoxide and hydrogen as synthesis gas (syngas) for the chemical industry. • Biomass-to-liquid (BtL) and (hydro)pyrolysis yield hydrocarbons as sustainable fuels and chemical feedstocks. • Hydrothermal carbonization and (hydro)pyrolysis form biochar as an intermediate for the chemical industry. • Physical transformation (pressing, milling, distillation) recovers vegetable oils and yields additives for plastics. • Chemical transformation (transesterification, hydrolysis, oxidation, hydrogenation, pulping, …) afford bio-based monomers and polymers. • Biochemical processes using microorganisms and enzymes for chemical feedstocks and biopolymers • Lignocellulose utilization in biotechnology and lignin valorization

der the trade name Green Planet for cutlery, straws, shopping bags, and food packaging. The product was claimed to be degradable in saltwater.[270] For many years, owing to high cost, strong competition by fossil-based polymers, and processing problems related to its thermal decomposition near its melting temperature, the commercial success of PLA was restricted to the medical field, for example, resorbable surgical sutures. Instead of extracting PLA from bacteria using chlorinated solvents, in the commercial PLA (*Ingeo*) process of NatureWorks, fermentation yields lactic acid that is converted into the cyclic dimer (L,L)-lactide, purified by distillation, and polymerized by ring-opening polymerization in the presence of tin (II) octoate. Aspects of lactide purification, polymerization processes, the role of stereoisomers, additives such as stereocomplexes in processing, nucleation of crystallization, biodegradation, and tailoring of PLA and PLA compounds were highlighted by Drumright.[250] PLA and PHAs face several challenges ranging from solvent-free polyester recovery to widening the narrow processing window and lowering costs while improving crystallization rate and toughness. In particular, chain scission by thermal degradation and hydrolysis are accompanied by massive embrittlement. Although halogenated solvents were replaced by ketones, such as acetone and cyclohexanone, the use of solvents is problematic with respect to FDA approval as a food contact material. Selective bacterial cell lysis can separate pure PHA granules from proteins. As most P3HAs start to decompose by chain scission above 150 °C, comonomers such as lactic acid or 4HB, 4HV, and other moieties are incorporated to lower melting temperature. Moreover, the development of nucleating agents is required to improve crystallization rates and to enable injection molding. PHA blends are developed to improve impact strength. Like other thermoplastics, both PLA and PHAs are immiscible with most other polymers, and new strategies for designing compatibilizers are needed.[273] The introduction of new bio-based plastics could disturb the current recycling of plastics and endanger the closing of the carbon loop in mechanical recycling.[274]

Progress made in metabolic engineering has enabled the production of a wide range of bio-based monomers and polymers.[275] When monomers derived from fossil resources are replaced by the same bio-based monomers from biorefineries, plastics are rendered bio-based in drop-in technologies without affecting their facile processing or their property profiles, including a potential use for food and medical applications. Various bio-based polyester and PAs are derived from bio-based diamines, such as 1,4-diaminobutane (putrescine), 1,5-diamino pentane (cadaverine), and 1,6-diaminohexane, bio-based dicarboxylic acids, such as succinic, glutaric, adipic, and sebacic acids, as well as bio-based ω-aminoacids, such as 4-aminobutyric, 5-aminovaleric, and 6-aminocaproic acid, hydroxycarboxylic acids such as lactic acid, and 3-hyxdroxy- or 4-hydroxybutyric acid together with diols such as ethylene glycol, 1,3-propanediol, and 1,4-butanediol. Made from bio-based 1,3-propanediol, polytrimethylene terephthalate (PTT) combines properties of PET and polybutylene terephthalate (PBT) in applications such as apparel and carpeting.[276–280] Compared to PET, polyethylene furanoate (PEF), which is prepared by polycondensation of bio-
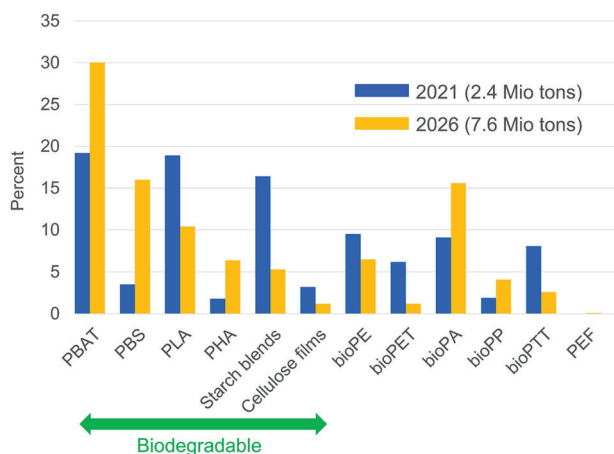
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Figure 9. Percentage of degradable (PBAT, PBS, PLA, PHA, starch blends, cellulose films) and non-biodegradable (bioPE, bioPET, bioPA, bioPP, bioPTT, PEF) bio-based plastics amounting to 2.4 Mio tons in 2021 (blue bars) and estimated to be 7.59 Mio tons in 2026 (yellow bars). Data were taken from European Bioplastics.[296]

based 2,5-furandicarboxylic acid (FDCA) with monoethylene glycol or by ring-opening polymerization of cyclic oligomers, exhibits higher glass temperatures, better tensile strength, and improved gas barrier resistance.[208,281–286] However, several challenges relating to PEF process engineering, processing, and cost-efficient FDCA supply exist. In a cradle-to-grave LCA of fructose-derived PEF, non-renewable energy use was reduced by approximately 40–50%, while GHG emissions were lowered by approximately 45–55%, compared to PET.[287] As a bio-based platform, chemical succinic acid has proven to be cost-competitive with its fossil-based counterpart.[288] High purity bio-based succinic acid is employed in polycondensation with bio-based diols, such as 1,4-butanediol, in order to prepare a variety of bio-based and biodegradable polyesters, among them polybutylene succinate (PBS), which melts at 115 °C and is processible by extrusion, injection molding, blow molding, and compounding.[288–295] Unlike many biopolymers, PBS is fully competitive with many fossil-based plastics, in terms of processability and tuning property profiles. Both easy-to-process PBS and PBAT claim the highest share in emerging bio-based plastics' development (see **Figure 9**).

A review published by Siracusa and Blanco covers the development of bio-based polyethylene terephthalate (bioPET), bio-based polyethylene (bioPE), and bio-based polypropylene (bioPP) in packaging and engineering applications.[297] As the bio-based counterpart of PET with identical properties, bioPET is produced by polycondensation of bio-based monoethylene glycol and terephthalic acid obtained by oxidation of bio-based p-xylene.[298] According to a critical comparison of the LCA of fossil- and bio-based PET bottles, wood-based PET performs better than its corn stover counterpart, but biomass processing is often more emission-intensive than fossil refinery processes.[299] In Braskem's *Green Polyethylene* process, sugarcane-based bioethanol is dehydrated to yield bio-based ethylene, which is polymerized via highly efficient catalytic ethylene polymerization processes established for fossil-based ethylene, in order to produce a wide range of high- and low-density PEs.[300–302] Converting bio-based ethylene into bio-based propy-

lene allows the same strategy to be applied to the production of bioPP. Although the properties of bio- and fossil-based polyolefins are identical, the percentage of "green" carbon can be determined according to ASTM D6866, developed by the American Society of Testing and Materials (ASTM), from the content of the C^{14} isotope, which is essentially zero for fossil-based carbon.[303]

Several LCA studies compared PLA and starch with PE.[133,190,192,194,304–318] As stated by Walker and Rothman in their critical survey on the significance of comparative LCAs of fossil- and bio-based plastics, the use of different methods and the absence of uniform standards account for significant variations between different studies even of the same polymer; no plastic type is conclusively declared as having the lowest environmental impact.[311] Hottle, Bilec, and Landis reviewed published LCAs and commonly used LCA databases quantifying environmental impacts for PLA, PHA, thermoplastic starch, and five common petroleum-derived polymers from their raw materials extraction (cradle) to their end of life (grave).[133] Their literature survey shows that biopolymers exhibit environmental impacts similar to those of petroleum-based plastics. Sufficient LCA data relating to disposal and end-of-life scenario are seen to be critical for future sustainability assessments of biopolymers. The LCA of Benavides compared GHG emissions and fossil energy consumption (FEC) of biodegradable and non-degradable PLA, bioPE, fossil-based high-density PE (HDPE), and low-density PE (LDPE).[313] They chose bioPE and PLA, given their potential to replace fossil-based plastics in single-use applications. The lowest GHG emission was found for bioPE (–1.0 kg CO_2 / kg) and PLA (1.7 kg CO_2/ kg), with no biodegradation compared to HDPE (2.6 kg CO_2 / kg) and LDPE (2.9 kg CO_2 / kg). Moreover, the FEC of bioPE (29 MJ kg^{-1}) was markedly lower than that of PLA (46 MJ kg^{-1}), HDPE (73 MJ kg^{-1}), and LDPE (79 MJ kg^{-1}). Despite biogenic carbon's uptake and carbon credits, composting increased the life cycle GHG emission of PLA (from 1.7 to 3.7 kg CO_2/kg) depending on degradation conditions. The significantly lower GHG emission of bioPE compared to fossil-based PE was attributed to both biomass carbon uptake and the lower energy demands of catalytic bioethanol dehydration with respect to steam cracking of oil. In addition, the FECs of both PLA and bioPE feedstocks were lower than the energy-intensive oil and gas feedstocks of fossil-PE. However, the PLA conversion by bacterial fermentation and subsequent lactide polymerization required more energy than the efficient catalytic polymerization of ethylene produced by steam cracking and by catalytic ethanol dehydration. In contrast to PLA manufactured in a dedicated process, bio-based ethylene replaces fossil-based ethylene in traditional catalytic ethylene polymerization processes.

5. Oxo-, Photo-, and Biodegradable Plastics

5.1. Oxo- and Photodegradation

The natural carbon cycle combines abiotic processes, such as hydrolysis, peroxidation, and photodegradation, with biotic processes, such as bacterial digestion and bio assimilation. Both their molecular architectures and stabilizer addition prevent most industrial plastics from entering this natural carbon loop. In Scott's vision, oxo-biodegradation of durable synthetic plastics, such as polyolefins, is seen as a promising strategy for creat-

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ing plastics with programmed end-of-life options, enabling their biodegradation in a controlled way.[319,320] In essence, durable plastics are rendered fully or at least partially degradable by adding (photo)oxidation catalysts, by varying their molecular architectures, or by blending them with biodegradable polymers, such as starch. However, oxo degradation is not synonymous with oxo biodegradation and can produce non-degradable fragments. Overviews of the use of prodegradants as additives of (bio)degradable polyolefins have been offered by Ammala[321] and Chiellini.[322] Typically, prodegradant additives include redox-active compounds of transition metals, such as cobalt, manganese, and iron, which deplete the antioxidants by oxidation and catalyze polymer autoxidation by catalytically decomposing peroxides. A comparative study, including a literature survey, confirmed that prooxidant/prodegradant additives accelerate the degradation to form small fragments.[323] However, incomplete bio-oxodegradation can cause undesirable microplastic emissions, and small, non-biodegradable fragments may enter the food chain. In 2019, the EU Commission banned single-use plastics made from oxo-degradable plastics.[324] In the presence of a prodegradant, the oxidative degradation of LDPE films is paralleled by a massive loss of molar mass and oxidation, but the fate of the resulting debris remains unclear.[325–327] Both degradable and non-degradable plastics were colonized by microorganisms in seawater.[328] No negative effect on germination or development of the vegetal species was detected in an ecotoxicity assessment.[329] The common edible oyster fungus Pleurotus ostreatus degrades oxo-biodegradable plastics and produces mushrooms using this plastic as substrate.[330] Like biodegradation, oxo degradation depends on temperature, sunlight, and the presence of oxygen, water, and microorganisms.

Most thermoplastics contain UV-stabilizers to protect them against weathering induced by sunlight.[331] Plastics are rendered photodegradable either by incorporating light-absorbing functional groups with heteroatoms as chromophores into their backbones or by using photocatalysts, such as titanium dioxide, preferably its anatase modification, as additives. Daglen and Tyler have highlighted the end-of-life design principles of photodegradable plastics.[332] In photodegradation, the controlled lifetime of plastics depends on UV light absorption, which in turn is affected by the type of chromophores, the presence of antioxidants, polymer crystallinity, and oxygen permeability. In bioremediation, photocatalytic degradation holds great promise as an end-of-life option for plastic fragments, pollutants such as bisphenol As and leaked additives, such as phthalate plasticizers, nonylphenol antioxidants, and brominated flame retardants.[333] For instance, titanium dioxide as a photocatalyst enables photocatalytic degradation of both macro- and microplastics.[334] Commercial polyolefins such as PE and PP do not contain chromophores, because highly active catalysts used in commercial catalytic olefin polymerization are severely poisoned by even minute amounts of polar comonomers, such as acrylics and carbon monoxide. Catalytic ethylene copolymerization with carbon monoxide on palladium catalysts yields strictly alternating polyketone copolymers, which exhibit property profiles that are vastly different from commodity polyolefins.[335] In recent advances, nickel and palladium catalysts were successfully tailored to enable random incorporation of small amounts of carbon monoxide into PE chains.[336,337] High-molar-mass PE containing few isolated in-chain ketone groups is rendered photodegradable without adversely affecting PE-like processing or property profiles. More research is needed to clarify the fate of the resulting photodegraded PE fragments in the environment.

5.2. Biodegradable Plastics

According to terminology introduced by IUPAC, 'biodegradation' means *degradation of a polymer item due to cell-mediated phenomena*.[338] In aerobic biodegradation, plastics are enzymatically decomposed by microorganisms, such as bacteria, fungi, and algae, to yield carbon dioxide, water, and new biomass, whereas anaerobic biodegradation generates methane (biogas) instead of carbon dioxide. The biological conversion of waste bio-based plastics into carbon dioxide, water, renewable energy, and fertile soil (compost) by entering the natural carbon cycle is referred to as biological recycling ("biorecycling"). Accompanied by abiotic degradation, such as hydrolysis and oxidation, biodegradation involves several stages: biodeterioration, biofragmentation, bioassimilation, and mineralization.[339] In the first stage, abiotic and biotic processes, such as weathering, sunlight irradiation, mechanical stresses, hydrolysis, and microbial attack, break up plastics into small pieces. In the second step, chain scission reduces molar mass, and the resulting water-soluble oligomers and monomers are taken up by cells and used as their carbon source. In the third stage, termed "bioassimilation and mineralization", cells increase their cell biomass and produce carbon dioxide and water. Several reviews have addressed the biodegradation mechanisms of natural biopolymers as well as bio- and fossil-based plastics.[339–369] Goel, Luthra, Kapur, and Ramakumar have published a comprehensive review of commercially available biodegradable plastics, key players in the bioplastics industry, and the status of biodegradation test standards clearly state myths and realities of biodegradable/bio-plastics.[369] In the public, it is widely believed that replacing fossil-based plastics with biodegradable bioplastics massively reduces plastics' environmental impact and solves the littering problem. There is considerable confusion concerning the meaning of the technical terms 'biodegradable' and 'compostable'. They are interchangeably misused in the "greenwashing" of product marketing, asserting the superior environmental benefits of "bio"-products without proof to attract consumers who strive for eco-friendly products. However, the label 'compostable' strictly indicates biodegradation in industrial composting and does not mean biodegradation in the open environment, for example, oceans. Moreover, polymer biodegradation is not the exclusive privilege of natural biopolymers such as starch and polyesters, which serve as energy storage and nutrients for cells. For instance, fossil-based polybutylene adipate-co-terephthalate (PBAT) and blends commercialized by BASF (*Ecoflex* and *Ecovio*) are fully biodegradable in agricultural soil.[196,370] Independent of the carbon source, polymer biodegradation mainly depends on molecular architectures, the presence of oxygen and water, types of microorganisms, exposure to sunlight, nutrient availability, concentration, pH, test conditions, polymer properties, such as molar mass, surface wetting, crystallinity, glass transition temperature, oxygen permeability, sample geometry, particle size and shape, film thickness, surface topology, porosity, and particularly on the interactions of

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polymers with specific microorganism populations that vary in different environmental surroundings, such as like soil, industrial, and home compost, marine and freshwater.[371] In the literature, general statements on biodegradation in composting without specifying a standardized test type, such as DIN EN 13432 in the EU, ASTM 6400 in the USA, or AS 4736 in Australia are not considered to be trustworthy. In the past, many agricultural plastics that were claimed to be biodegradable turned out to be merely bioerodable, photodegradable, or only partially biodegradable, respectively.[372–374] Several overviews cover standardized tests and certifications of biodegradable plastics.[345,347,355,369,375–380] According to the European standard EN 13432 for composting, 90% of the organic material must be converted to carbon dioxide within six months. Less than 10% of the product's mass must remain on a sieve with a mesh size of 2 mm after 12 weeks of aerobic composting. Numerous natural biopolymers fail to pass this test. In addition to biological degradability, eco-toxicity and chemical safety related to the presence of pollutants, such as heavy metals and fluorine-containing compounds, represent major concerns as plastics have different compositions and contain various additives. Under certain conditions, biodegradation can form water-soluble toxic metabolites as well as micro- and nanoparticles colonized with hazardous spores. Only when biodegradable plastics clearly meet all defined test criteria in terms of compostability, low eco-toxicity, and low levels of specified heavy metals and fluorine are they admitted as compostable. Yet even products labeled as 100% compostable and industrially composted at elevated temperature may not break down completely in home compost, soil, landfill, or oceans. As stated by Wurm and coworkers in their review, many biodegradable plastics are not as biodegradable as they are claimed to be, and a "one-fits-all" solution, that is, the development of a plastic that readily biodegrades in every kind of ecosystem, appears highly unlikely.[353]

Although in 2021, bio-based plastics still represent less than one percent of the global plastic production, the market for bioplastics grows continuously. A market overview (Figure 9) of biodegradable and non-biodegradable bio-based plastics is available from European Bioplastics.[296] According to data presented by European Bioplastics in cooperation with the Nova-Institute, annual global bioplastic production capacity is expected to pass the 2% line and increase from around 2.42 million tons in 2021 to around 7.59 million tons in 2026. The main drivers on the biodegradable bio-based plastic side are PBAT, PBS, bio-based PA, and PLA, and, on the non-degradable bio-based plastic side, bioPE and bioPP. While bioPET production declines, growth is expected for bio-based PEF, which is planned to enter the market in 2023. Packaging is the largest market segment for bio-based plastics, with 48% (1.15 million tons) in 2021. The land use of bio-based plastics is estimated to be 0.7 million hectares in 2021, equivalent to 0.01% of the global agricultural area of 5 billion hectares. The significant expected growth of global bioplastics is paralleled by increased land use that could rival food production.

While biopolymers currently account for less than 1% of the plastics market, they are a major component of organic solid waste, amounting to approximately 40% of municipal waste compared to its much lower synthetic plastic waste content (<10 wt.%). Yet many composters who are certified for organic farming are reluctant to consider accepting food wastes and compostable plastics, as doing so requires additional capital invest-

ment and poses considerable risks of producing low-quality compost due to contamination. As industrial aerobic composting plants operate at temperatures above 50 °C, there is little or no maturation time. They biologically dry and only partially degrade organic waste, thus failing to produce high-quality compost which can generate odor on rewetting. Anaerobic and aerobic digestion are cascaded to recover resources such as methane (biogas), fertile soil (compost), nutrients, and chemicals, from organic solid wastes and organic liquid waste streams, such as manure.[381,382] In biogas production by anaerobic digestion, upstream strategies such as microbial and enzymatic pretreatments as well as genetic and metabolic engineering are being pursued.[383] In food waste management, biological processes such as composting, anaerobic digestion, feed, and bioethanol fermentation are attracting increasing interest with respect to resource and renewable recovery as viable alternatives to landfills and incineration.[384–386] Because anaerobic digestion consumes a part of biodegradable plastics to produce methane (biogas), the subsequent aerobic biodegradation of residues in composting emits less carbon dioxide.[385–387] Although the use of compost is interesting for sustainable agriculture with reduced fertilizer demand, the prospects of anaerobic digestate as fertilizer are still under debate, and concerns are raised that they may pose a higher risk of harm to the environment and human health than undigested manure.[388] Similar debates are ongoing with respect to the utilization of municipal wastewater sewage sludge.[389–393] As sewage sludge contains an incalculable number of pollutants that are hazardous to the environment and human health, the direct agricultural use of sewage sludge is phased out in the EU, while the recovery of essential phosphorus is envisioned.

Both incineration and composting generate emissions of GHGs such as carbon dioxide, methane, and nitrous oxide, all of which are of special relevance to global warming.[316,394–402] In LCA studies on food waste recycling, bioconversion through insects and incineration show higher environmental benefits with respect to landfill, composting, and anaerobic digestion.[398] In an LCA study, food waste composting has a lower environmental impact than peat mining and transport, but its emissions of carbon dioxide, methane, and ammonia contribute to global warming, acidification, and eutrophication.[399] Without a doubt, composting is relevant to the circular economy and is considered to be a clean, green technology for organic waste utilization. However, in view of negative environmental impacts relating to emissions of low volatility organic compounds and GHGs, composting requires the development of climate change mitigation technologies.[401]

Biodegradable plastics do not replace conventional plastics but complement them with new property profiles.[403] Biodegradation is attractive for applications ranging from agricultural mulch films and compostable food packaging to organic waste bags, drug release systems, tissue engineering, and other medical applications. Furthermore, bioengineering of biological systems, such as bacteria, fungi, and even insects, holds promise for bioremediation, which is the biodegradation of persistent waste plastics and other organic environmental pollutants by exploiting them as a carbon source for environmentally friendly carbon compounds.[343,404–409] It appears feasible to use metabolic pathways for the degradation of PE once the PE chain length decreases to an acceptable range for enzyme action.[321,408,409]
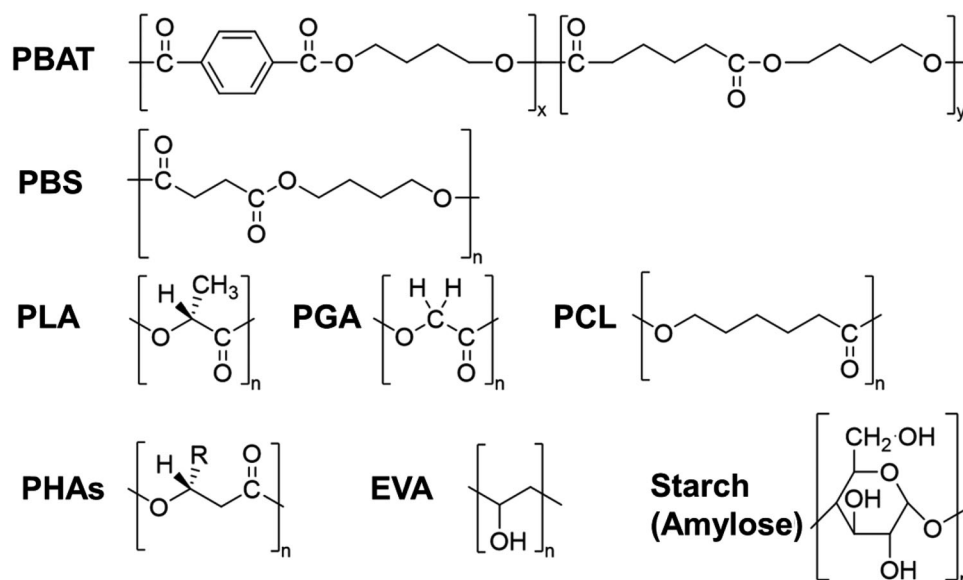
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Figure 10. Biodegradable bio- and fossil-based plastics.

Several reviews have addressed the aspects of design, properties, applications, and biodegradation mechanisms of biodegradable plastics.[321,339,343,351–354,357,359,360,362,363,367,369,409–414] Prominent commercial members of the biodegradable plastics family (**Figure 10**) include bio-based polymers, such as thermoplastic starch (e.g., *Mater-Bi* from Novamont), PLA (e.g., *Ingeo* from NatureWorks), PHBH (e.g. *Green Planet* from Kaneka), PBS (e.g., bioPBS from Mitsubishi Chemical), and fossil-based biodegradable plastics such as polybutylene adipate-terephthalate (PBAT) and their blends with PLA (e.g., *Ecoflex* and *Ecovio* from BASF SE), polycaprolactone (PCL), and polyvinylalcohol (PVA) some of which are also feasible as bio-based versions when using bio-based monomers.[369] Debate is ongoing about the role that biodegradable plastics could play in a circular plastics economy. On one side, proponents of biodegradable plastics euphorically foresee their development as becoming an important cornerstone of the transformation from linear fossil-based economy to a circular bioeconomy. They envision biodegradable plastics as the ultimate solution to the marine littering problem, because biodegradable plastic wastes are derived from natural sources, serve as nutrients for cells, and are expected to enter the natural carbon cycle without causing massive negative environmental impacts.[129,415,416] On the other side, critics see biodegradable plastics as part of the global plastic waste problem. With their expected rapid growth, biodegradable plastics could become an environmental burden by provoking the business-as-usual scenario of throwaway plastic products, given that consumers assume that it is safe to dump them into the environment.[353,369,417] An "all-natural" carbon cycle is a fiction. The entry of million tons of biodegradable plastic wastes into the natural carbon cycle is far from being carbon neutral, as processing and transport are driven by non-renewable energy and intensified farming deeply impacts nature. Their use is perceived to work against recycling by provoking throwaway and impairing reuse strategies as degradation of plastic wastes may deteriorate the quality of recycling streams vital for mechanical recycling without

downcycling.[353,369] Although bio-based plastics are commonly considered to be promising for the circular economy, a survey of LCA studies on bio-based and biodegradable plastics fails to reveal if and how their use can lead to real environmental benefits without a radical shift in the consumption model.[380] In addition to developing environmentally friendly plastics, changing the attitudes and habits of both consumers and the industry is vital.

As Albertsson states, for many decades, it has been a dream to design environmentally benign degradable plastics that perform reliably and fade away and degrade soon after completing their product life, without leaving behind any harmful residues.[418] In practice, most plastics are required to be durable and degradation-on-demand is difficult to realize, as polymer degradation strongly depends on the type of plastic, additives, and environmental surroundings. For many decades, the development of biodegradable plastics has been very successful in medical applications, because the human body is a controlled and well-defined environment that enables the development of degrade-on-command polymer systems for drug delivery and tissue engineering.[419] Although well-controlled environments are also feasible for polymer degradation in industrial composting and pyrolysis plants, polymer biodegradation encounters far more complex and variable environments in nature, with large variations in microorganism populations, temperature, exposure to sunlight, water, and oxygen in tropical, arctic, and deepwater regions. For example, wood composed of lignocellulose is attacked and degraded by fungi and bacteria in a wet soil environment.[420–424] In fact, termites teamed up with fungi are the masters of biorecycling, as they completely degrade and utilize lignocellulose.[425] However, in the absence of fungi, wooden shipwrecks in deep ocean sediments can last hundreds and even thousands of years.[426]

Comparing the biodegradation mechanisms and biodegradation rates of thermoplastic starch, cellulose acetate, and lignin-based thermoplastics with those of corresponding unmodified

starch, cellulose, and lignin used as raw materials reveals that minute chemical modifications of the biopolymer structure, such as esterification of cellulose with acetic acid, strongly affect biodegradation.[362] The influence of the cellulose acetate substitution pattern on biodegradation in the natural environment was reviewed by Yadav and Hakkarainen.[427] The general public is unaware that cigarette butts made of bio-based cellulose acetate represent the most abundant and most harmful plastic pollutant present in soil and oceans.[428] In contrast to non-degradable fossil-based high-molecular-weight plastics and their bio-based versions, all of which are non-toxic when they enter the environment, cigarette butts are hazardous organic wastes loaded with an estimated 4000 toxic chemicals in addition to unsmoked tobacco. They start poisoning water immediately on contact and endanger the health of humans, wildlife, and marine and freshwater organisms.[429,430] In addition, cigarette butts contain cigarette filters, each of which can release approximately 100 small microfibers (<0.2 mm) loaded with toxins per day, amounting to an estimated total of 0.3 million tons per year, that slowly degrade and pose an additional eco-toxicity threat to the marine environment.[431]

Today, macro-, micro-, and nanometer-scaled plastic debris in soil, air, and marine environments are widely recognized as an enormous environmental problem that is not at all restricted to fossil-based plastics and their bio-based counterparts. In contrast to common expectations in the public, Agarwal, Greiner, Laforsch, and Bagheri provided experimental evidence that commercial biodegradable plastics might not solve the marine littering problem because of the conditions encountered in seawater are far from ideal with respect to their rapid biodegradation.[432] They immersed films made of biodegradable polymers, such as poly(lactic-co-glycolic acid) (PLGA), PCL, PLA, P3HB, and PBAT, as well as non-biodegradable fossil-based PET in artificial seawater and freshwater under controlled conditions for one year. Only amorphous PLGA showed 100% biodegradation as verified by weight loss, change in molar mass with time, high-performance liquid chromatography, NMR spectroscopy, and electron microscopy. The far more popular homopolymer PLA is derived from renewable carbon sources, such as corn sugar, potato, or sugar cane, and helps to reduce the demand for fossil resources.[160,251–253] Known to degrade in industrial composting at temperatures above 50 °C and in vivo in biomedical applications, PLA degrades much slower in soil, in comparison, and is not home compostable.[433] When PLA waste ends up in seawater, it does not seem to biodegrade at all.[353,432,434,435] In 2021, the European Parliament endorsed replacing single-use plastics items, including cutlery, straws, plastic plates, and cotton swabs, with biodegradable plastics, in order to fight marine littering. A comparative study of cotton swabs made from the substituted bio-based materials, such as PLA, PBAT, PBS, PHBV, and starch-based plastics (, and *Mater-Bi*), using cellulose and non-biodegradable PP as reference samples, revealed a massive decay of bacterial activity for PP, PLA, and PBS, all of which failed to serve as nutrients and did not biodegrade within a 40-days period of immersion in seawater followed by 94 days of "strict diet conditions with the different plastics as sole carbon source".[434] In contrast, the positive responses of PBAT, *Mater-Bi*, *Bioplast*, and PHBV were similar to that of cellulose. For plastics such as PHB, PBS, and polybutylene sebacate-

terephthalate (PBSeT), biodegradation strongly differs for each plastic type by orders of magnitude, depending on climate zones and local marine habitats.[436] Biodegradation lab tests at 20 °C and mesocosm tests at 20 °C using natural sand and seawater were complemented by field tests in the Mediterranean Sea (12–30 °C) and tropical seas (29 °C) in Southeast Asia. While LDPE did not degrade, the half-life time required for the disintegration of a PHB film varied from 54 days in a southeast Asian ocean to 1247 days in mesocosm pelagic tests. Biodegradation is likely to slow down significantly in arctic oceans and cold deep seas. As a result, and contrary to public expectations, most compostable plastics are long-lived in the oceans. Like fossil-based plastics, they could serve as carriers for pathogens, chemicals, and alien species that endanger the stability of the marine ecosystem and can enter the food chain. As pointed out by EarthWatch, the best option for fighting riverine and marine littering is to reuse and recycle plastic wastes on land and stop them from entering landfills and oceans.[45] Status, key factors affecting biodegradation in the oceans, as well as prospects and challenges of seawater-degradable polymers were reviewed by Wang, Ji, and Wurm, who pointed out the urgent need for uniform test standards to re-examine biodegradation in a marine environment.[435] An important prerequisite for biodegradation in seawater is the presence of certain microorganisms and the facile abiotic and biotic hydrolysis of polymers, which is the rate-determining step in biodegradation. Both high hydrophobicity and high crystallinity of polymers impair their wetting and drastically slow the water permeation and hydrolysis rate, which decreases with the increasing molar mass of the polymer. In contrast to industrial composting, which operates at temperatures above 50 °C, the average temperature in oceans is around 17 °C and around 0–4 °C below 2000 m and in arctic oceans. Current strategies for improving the biodegradation of compostable plastics aim at improving hydrolysis rates by varying their molecular architectures, blending them with hydrophilic biodegradable polymers such as starch, and compounding them with various pro-biodegradant additives, including plasticizers which lower glass transition temperature and thus enhance water permeability. For example, to fight the increased environmental contamination of PLA-based products due to the long PLA lifetime in soil and seawater, PLA was melt-blended with hydrophilic biodegradable polymers like starch, cellulose, chitosan, or polyvinyl alcohol (PVA), respectively. The dispersion of hydrophilic fillers by melt-blending substantially improves water uptake and thus enhances PLA degradation via hydrolysis, as the PLA blends are rendered porous due to their blend morphology, swelling, and dissolution of hydrophilic dispersed phases that serve as nutrients for microorganisms.[435,437–439] In an alternative strategy, the incorporation of acetal groups into the PLA backbone was achieved by ring-opening copolymerization of L-lactide with 1,3-dioxolan-4-one and rendered the resulting polyesteracetals rapidly and fully biodegradable in both distilled water and seawater.[440] On the one hand, enhanced hydrolysis of PLA is highly beneficial to PLA degradation in soil and water. On the other hand, it deteriorates the mechanical properties of recycled PLA and thus compromises mechanical recycling.[441] Compared to PLA, the hydrolysis of PHAs such as PHB and PHBH is markedly faster, nevertheless, degradation in seawater requires improvements achievable by re-designing the molecular architectures, compounding,

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and tuning additive packages containing prodegradants, for example, readily-degrading, water-soluble fillers such as starch and PVA.[414,435,442–449] The development of seawater-degradable plastics is a challenge and requires careful balancing of rapid hydrolysis in saltwater with slow hydrolysis when exposed to humidity during service life and mechanical recycling. In the future, a better understanding of interactions between polymers and microorganisms could realize the dream of degradation-by-design and biodegradation-on-demand via biologically triggered molecular switches built into polymers or their additives. Polymer science and catalysis hold great promise for designing polymers for the circular economy. Mecking elegantly demonstrated that it is possible to merge the distant galaxies of non-degradable polyolefins and biodegradable bio-based polyesters. Derived from renewable carbon sources, such as seed oil or microalgae oil lipids, long-chain difunctional monomers were used in polycondensation to create non-persistent, polyethylene-like bio-based polyesters in which potential degrade-on-command molecular switches were built into a polyethylene-like polyester backbone without sacrificing typical polyethylene processing and properties.[450]

6. Molecular Recycling

6.1. Valorization by Plastic Degradation

Complementary to mechanical recycling, molecular recycling, also termed chemical and tertiary recycling, breaks down plastic wastes into renewable carbon feedstocks that serve as intermediates for virgin plastics, value-added chemicals, and sustainable fuels. Instead of mechanical downcycling that lowers the value of recycled plastics, molecular recycling uses renewable carbon feedstock recovery to upgrade wastes and produce virgin plastics with high quality identical to that of the corresponding fossil-based plastics. Waste plastics represent an extremely valuable and abundant source of renewable carbon. In the circular economy, efficient recovery of renewable carbon sources from organic wastes, biomass, and CO_2 counterbalances the currently surging depletion of fossil resources and is essential for achieving a sustainable zero-landfill and zero-waste future. Valorization of plastic, food, agricultural, and forestry wastes generates economic growth and wealth by creating value-added products, new jobs, and new businesses. Plastic waste management currently relies on landfill, incineration, and mechanical (down)recycling, while molecular recycling as a plastic-to-liquid platform with delocalized pyrolysis, solvolysis, and depolymerization followed by centralized upgrading remains a vision. Yet, molecular recycling is essential for waste-to-wealth transformation in a circular plastics economy. In closed-carbon loop molecular recycling, waste plastics are transformed back into virgin plastics, whereas in a complementary open-loop scenario, waste creates value-added products that exit the plastic carbon loop. In addition to plastic scrap sorted in mechanical recycling, molecular recycling is envisioned to valorize plastic wastes that are unfit for extrusion, such as thermosets, composites, tires, multilayer packaging, formulated mixed plastic products, PUs, and highly contaminated wastes that pose toxicity and safety threats to recyclates. Hence, molecular recycling by (hydro)pyrolysis, gasification, catalytic cracking, chemolysis, solvolysis, and depolymerization is expected to play a key role in the circular economy.[80,451–453]

An overview published by Ragaert compares the prospects and challenges of (thermo)mechanical and chemical recycling.[81] As Weckhuysen states in his review on chemical recycling, going beyond mechanical recycling means "giving new life to plastics wastes".[80] Several reviews have addressed recent advances and challenges of plastics' chemical recycling.[80,82,83,451,454–467] The review of Pérez-Ramirez sees "catalytic processing of plastic waste on the rise" and concludes that organocatalysis gives waste a new life as fuels, chemicals, and virgin plastics under the motto "catalysis generates plastics and should handle their fate".[468] Catalytic molecular recycling is a particularly suitable way to control pyrolysis product compositions and to lower energy demand and carbon footprint.[469] With taxation of carbon dioxide emissions on the rise as part of the climate change mitigation actions, decarbonization of refinery operations using renewable energy and exploiting biomass, plastic waste, CO_2, and hydrogen as non-fossil feedstocks for sustainable fuels, chemicals, and virgin plastics is becoming increasingly attractive for the oil industry. The green transition of the oil industry is in progress. As most plastics have oil-like compositions, molecular recycling and the use of plastic waste as a renewable carbon resource present options for the oil industry. Even though the base technologies, for example, (hydro)pyrolysis and gasification exist, their adaption to the molecular recycling of plastic waste and large-scale operation requires up-scaling and industrial-scale plastic recycling that is still in a very early stage.

6.2. Gasification, Liquefaction, and (Hydro)Pyrolysis

In gasification, plastic wastes are partially oxidized by reacting them with gasification agents such as oxygen, steam, and air at temperatures in the range of 500–1300 °C to generate synthesis gas (syngas) consisting mainly of carbon monoxide and hydrogen.[470–475] Produced from any kind of carbon sources spanning biomass, natural gas, coal, and plastic waste, syngas serves as a raw material for sustainable fuels and chemicals, including methanol as well as synthetic hydrocarbon lubricants and olefin monomers, both of which are formed in a Fischer–Tropsch process stage after gasification. In particular, co-gasification of plastics with coal and biomass as well as pyrolysis coupled with inline reforming are considered to be promising valorization routes.[470] In contrast to mechanical recycling, plastic-to-gas conversion enables the valorization of mixed plastic wastes, such as wastes generated by contaminated disposable coronavirus face masks, which consist of polypropylene, polyethylene, and nylon.[476] In a nitrogen atmosphere, catalytic pyrolysis over Ni/SiO_2 yields mainly methane and hydrogen, while the presence of CO_2 additionally produces CO to generate syngas. In the absence of oxygen, liquefaction and pyrolysis by thermal and catalytic cracking thermally degrade long-chain polymers into short-chain hydrocarbons, methane, and hydrogen. Typically, polymers are broken down into small hydrocarbon fragments equivalent to oil and gas by cleaving C–C bonds in the polymer backbones. When heated at temperatures around 400–450 °C, most commodity and engineering thermoplastics are degraded and can yield up to 80–90% liquid together with gas and char as by-products in liquefaction.[472,477,478] Depending on the thermochemical conversion process, plastic waste and biomass

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afford crude oil, syngas, hydrogen, and aromatic char.[479] The thermolysis of PE in supercritical water produces oil, wax, and gas.[480] As most plastics have an oil-like composition and high oil-like calorific values, the waste-to-energy conversion by liquefaction and pyrolysis yields refinery feeds together with fuels, such as diesel and gasoline.[479,481] As the main components of post-consumer waste, PE and PP were dissolved in a light cycle oil of commercial fluid catalytic crackers to transform polyolefins into C5–C10 alkanes.[482] Aiming at improving energy efficiency, economy, and fuel performance, catalyst development meets the challenge of lowering high thermolysis temperature.[483]

Hydrocracking of waste and virgin plastics by pyrolysis under hydrogen pressure (200 bar) and milder temperatures up to 480 °C improves the yield of liquid hydrocarbons with respect to gases and simultaneously removes sulfur- and other heteroatom-containing groups via hydrogenation.[484] Furthermore, hydrocracking yields saturated alkanes rather than alkenes. Alkanes qualify for use as feeds of steam crackers that produce ethylene and propylene monomers. In principle, direct back-to-monomer molecular recycling appears to be feasible by hydropyrolysis in the presence of bifunctional platinum-doped zeolites under mild conditions (330 °C, 20 bar hydrogen pressure, and 30 min residence time).[485] Thus, hydropyrolysis transforms single and mixed streams of virgin and post-consumer plastics such as HDPE, LDPE, and PP into liquid hydrocarbons that can serve as a renewable carbon source for polyolefins, whereas PS is hydrocracked to yield benzene and ethylbenzene, which are useful as raw materials for virgin PS production.[485] Hydropyrolysis occurs in the presence of hydrogen or water, for example, Shell's IH^2 process, extracts value from non-edible biomass, aquatic plants, and (ligno)cellulosic fractions of municipal wastes, by converting them into sustainable fuels and chemicals.[486] In BtL conversion, (hydro)pyrolysis, gasification, liquefaction, and Fischer–Tropsch processes gain fuels from biomass.[207,487,488] Different processes such as thermal and catalytic pyrolysis, fluid catalytic cracking, microwave-assisted pyrolysis, and co-pyrolysis with biomass replace fossil-based oil in fuel production and render fuel production more sustainable.[489] Compared to mechanical recycling, (hydro)pyrolysis tolerates a much wider variety of mixed organic wastes.

Pyrolysis reactors are commonly classified by the types of heat transfer and solid transport caused by mechanical forces, fluid flow, moving bed, and mechanochemistry. With reference to residence times of hours, minutes, or seconds, pyrolysis processes are termed slow, fast, and ultra-fast. Several reviews have addressed plastic waste pyrolysis and pyrolysis processes for fuel production.[100,454,455,474,486,489–495,72,73,80] A review by Sharuddin et al. addresses the influences of reactor type, pressure, hold-up time, fluidizing gas, and flow rates on oil, gas, and char formation aimed at optimizing oil yield for different types of plastics.[495] In the fluidized bed pyrolysis pioneered by Sinn and Kaminsky at the University of Hamburg,[494] pyrolysis oil and gas yields strongly depend on the polymer type. As is apparent from **Table 4**, both plastics and biopolymers represent attractive carbon sources for the circular plastics economy. While pyrolysis of polyolefins such as polyethylene and polypropylene yields oil and gas in high yields (>98%), polymethylmethacrylate (PMMA) is thermally depolymerized to recover methyl methacrylate (MMA) monomer (>97%). In contrast, heteroatom-containing polymers

Table 4. Fluidized-bed pyrolysis of plastics and biopolymers.

Polymer[a]	Temperature [°C]	Gas [wt.%]	Oil [wt.%]	Residue [wt.%]	Others [wt.%]
PE	760	55.8	42.4	1.8 C	-
PP	740	49.6	48.8	1.6 C	-
PS	580	9.9	24.6	0.6	64.9 Styrene
Polyester	768	50.8	40.0	7.1	2.1 H$_2$O
ABS[b]	740	6.9	90.8	1.1	1.2 HCN
PC	710	26.5	46.4	24.6	2.5 H$_2$O
PMMA	450	1.25	1.4	0.15	97.2 MMA[c]
PVC	740	6.8	28.1	8.8	56.3 HCl
Phenol/Formaldehyde	780	14.4	28.1	49.5	8.0 H$_2$O
SBR[d]	740	25.1	31.9	42.8	0.2 H$_2$S
Lignin	500	3.4	29.9	49.3	17.4 H$_2$O
Cellulose (from bark)	700	47.1	23.0	18.6 C	11.3 H$_2$O

[a] Data from W. Kaminsky, University of Hamburg (W. Kaminsky, H. Sinn in G. Menges, W. Michaeli, M. Bittner, eds., *Recycling von Kunststoffen*, Carl Hanser Publishers, Munich 1992, p. 248) [b] ABS: poly(acrylonitrile-co-styrene-co-butadiene) [c] MMA: methyl methacrylate monomer [d] SBR: poly(styrene-co-butadiene) rubber; reproduced with permission.[120] 2019, Wiley.

such as polyesters, PVC, and cellulose produce oil and gas together with by-products such as CO, H$_2$O, CO$_2$, HCl, HF, HCN, NO$_x$, H$_2$S, and others that are removed and recycled whenever possible. For example, thermolysis of PVC splits off HCl that can be used in oxychlorination to produce vinyl chloride monomers from ethylene.[496,497]

The compositions of oil and gas depend on pyrolysis reaction engineering and vary as a function of process parameters and added catalyst that lowers energy demand.[491,80] In particular, pyrolysis and dehalogenation of plastics are attractive with respect to molecular recycling of waste electrical and electronic equipment (WEEE).[453,464,493,498–501] In addition to valuable metals such as gold, silver, and copper, WEEE contains around 30 wt.% of high-quality polymers, such as ABS, high impact polystyrene (HIPS), PC, PA, and PP as well as epoxy resins contaminated with brominated flame retardants that can emit hydrogen bromide or polybrominated diphenyl ethers/furans in thermolysis. Das reviewed WEEE recycling using thermochemical processes, including high-temperature extraction, incineration, hydrolysis, as well as catalytic and non-catalytic pyrolysis.[502] Molecular recycling of thermosetting composites used in automotive, windmill, and aerospace applications combined with fiber recovery is an end-of-life option and a viable alternative to the current practice of landfill and incineration.[453,503–505] In their review, Gopalraj and Karki addressed the recovery of high-quality glass and carbon fibers, research challenges, as well as the economic and environmental impacts of mechanical, thermal, and chemical composite recycling.[453] Significant progress has been made with respect to lowering pyrolysis temperatures and improving catalytic cracking. Nevertheless, the challenges of plastic pyrolysis relate to up-scaling, achieving stable operation, and dealing with the inconsistent quality and unavailability of plastic waste due to a lack of waste management infrastructure, inefficient sorting, use of mixed organic waste streams, the impact of additives such as flame retardants and catalyst poisons, the low quality of
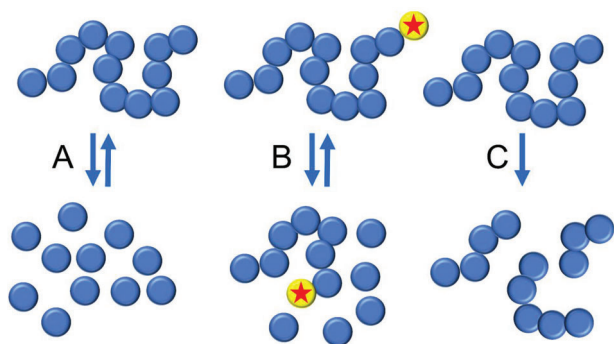
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Figure 11. A) Molecular recycling by depolymerization, B) unzipping a polymer chain from active sites at the chain end, and C) thermal and catalytic fragmentation that requires a second step to recover monomer for repolymerization.

pyrolysis oil, toxicity issues, qualification, standardization, and unclear regulations and registration requirements.[451] Pyrolysis liquids should be classified and admitted as products instead of wastes.[451] The use of renewable energy in photocatalytic, electrolytic, and microwave-assisted molecular recycling is still at an early bench-scale stage.[506,507]

Weckhuysen and coworkers evaluated the available mechanical and molecular recycling processes with respect to their technological and commercial status, end-of-life options for a variety of plastics, and LCA.[80] In terms of CO_2 emission as measured by the CO_2-equivalent emission index, they arrived at the following ranking: incineration >> landfill, pyrolysis, mechanical recycling > solvolysis, dissolution/precipitation. In accordance with this ranking, comparing the life cycle environmental impacts of mixed plastic waste pyrolysis (*ChemCycling* of BASF SE), mechanical recycling, and energy recovery suggest that pyrolysis has a 50%-lower climate change impact and life cycle energy use with respect to energy recovery.[508] Both climate change impact and energy use of pyrolysis and mechanical recycling are similar and depend on recyclate quality, energy mix, geographical region, and carbon conversion in pyrolysis. In particular, a combination of mechanical recycling and pyrolysis outperforms the singular processing of waste streams in terms of ecological and economic criteria.[509]

6.3. Back-To-Monomer Molecular Recycling

In a two-step, back-to-monomer molecular recycling, pyrolysis and gasification convert mixed plastic waste into oil and gas that replaces fossil resources to produce monomers for repolymerization in a third step. Alternatively, thermal and (bio)catalytic depolymerization of a single-type plastic waste yields a high-purity monomer regained in just one step without requiring pyrolysis oil as an intermediate for repolymerization in the second step. **Figure 11** displays three feasible pathways for molecular monomer recycling. In pathway A, all bonds between the monomeric units are broken up by depolymerization to recover monomers and reformed during their repolymerization. In pathway B, all chains have active sites at their chain ends and by catalytic depolymerization or by heating them above their ceiling temperature (T_C), at which the polymerization rate is equal

to depolymerization rate, monomers are recovered. Above T_C, the polymerization/depolymerization equilibrium is shifted toward the monomer and repolymerization occurs well below T_C which is calculated from the ratio of polymerization enthalpy and polymerization entropy.[510] In pathway C, the carbon-carbon bonds in the main chain are broken, but the resulting reactive end groups readily abstract atoms such as hydrogen from other polymer chains that then fragment to form oligomers that can serve as sources for monomer recovery in an additional step. Efficient sorting of wastes is an important prerequisite for achieving the high monomer purity that is vital for repolymerization. For instance, in polycondensation and polyaddition, minute amounts of monofunctional by-products readily terminate growing polymer chains and drastically lower polymer mass, thus causing severe embrittlement of the resulting virgin plastics. Several reviews have addressed back-to-monomer molecular recycling by thermal, chemical, and (bio)catalytic unzipping of polymer chains.[457,459,464,491,511–527,72,79,80,82] Similarly to polymerization catalysis in industrial polymer manufacturing processes, depolymerization catalysis plays a key role in back-to-monomer molecular recycling.[80,468,491,515,526,528]

In contrast to polymers such as polyolefins, acrylics, and vinyl polymers, all of which have hydrolytically stable C–C linkages in their backbones, polycondensation- and polyaddition-based polymers contain ester, amide, urethane, and carbonate groups that enable monomer recovery by hydrolysis and solvolysis.[527] PET bottle waste is industrially available on a large scale, and only high-purity PET recyclate qualifies for reuse as food-contact material via back-to-monomer molecular recycling of PET by hydrolysis. As a result, methanolysis, glycolysis, and aminolysis have made significant progress as alternatives to mechanical downcycling.[511–516,519,529–533,80,81] PET solvolysis requires less energy than PET pyrolysis.[80] For example, as is illustrated in **Figure 12**A, solvolysis (methanolysis, glycolysis) by transesterification of PET with excess methanol or ethylene glycol at elevated temperatures converts PET into dimethyl terephthalate (MT) or bis(2-hydroxyethyl) terephthalate (BHET), respectively. Both output products enable repolymerization by splitting off alcohol, which is recycled during depolymerization. Several detailed overviews address the roles of reaction engineering, the addition of transesterification catalysts such as metal salts, hydrotalcites, organocatalysts, ionic liquids, and enzymes, as well as potential microwave assistance by volumetric heating.[468,530,532,534,80] Glycolysis is also relevant for molecular recycling of PU to recover polyols. While direct isocyanate recovery and separation from polyols remains a challenge, recycled polyols contain polyols such as oligomeric bishydroxyurethanes (BHEU; Figure 12B) derived from the isocyanate component. BHEU/polyol blend formation makes repolymerization of the same PU difficult and can serve as a formulation component of other PUs. Instead of depolymerization by glycolysis, hydrogen-free reductive degradation of PET by depolymerization combined with catalytic hydrodeoxygenation of PET waste affords arenes, including p-xylene, which needs to be separated and oxidized into a terephthalic acid monomer.[535,536] Unlike aliphatic polyesters that readily hydrolyze under mild conditions, polyesters based on aromatic dicarboxylic acids such as PET are hydrolytically much more stable and require harsh reaction conditions, such as heating at temperatures well above 100 °C in corrosive acidic or alkaline aqueous media. Combina-
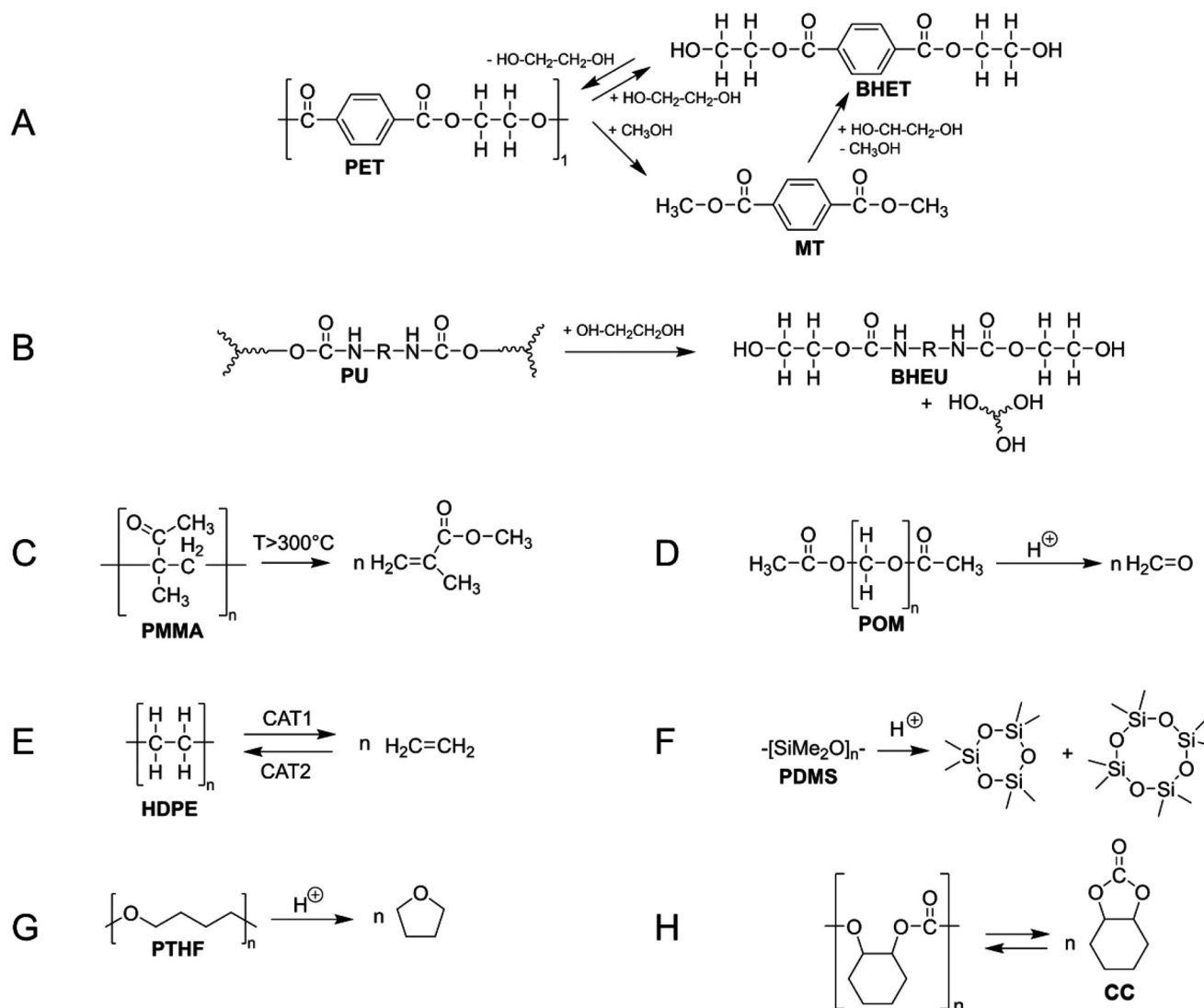
Figure 12. Examples of molecular recycling by depolymerization/repolymerization.

tions such as glycolysis-hydrolysis, glycolysis-methanolysis, and methanolysis-hydrolysis have been considered as strategic options for molecular PET recycling.[537] In essence, enzymatic PET hydrolysis by polyester hydrolases is attractive with respect to molecular recycling, waste stream management, biorecycling, and bioremediation by biodegradation.[526,538–542] While the activities of most PET hydrolases were rather low in the past, an engineered hydrolase depolymerized 90% PET into monomers within 10 h using an enzyme concentration of 3 mg per gram of PET.[526] With increasing production of bio-based polyesters such as PLA, PHB, and PEF, molecular PET recycling is expected to encounter mixed polyester wastes that, by hydrolysis, methanolysis, and glycolysis, yield monomer mixtures that are tedious to separate economically with respect to repolymerization of PET as a food-contact packaging material.[533] Microbial and enzymatic degradation of waste petro-plastics is seen as a promising strategy for depolymerization but faces problems, as enzyme-catalyzed degradation is sensitive to molecular architec-

tures, molar mass, crystallinity, and surface topology.[543] The combination of fermentation and enzymic polymerization processes with enzymatic depolymerization is seen as a closed carbon loop scenario for cellulosic textiles, which are considered indefinitely recyclable.[544]

In nature and industry, following pathways A and B displayed in Figure 11, polysaccharides such as starch and (ligno)cellulose are depolymerized to form glucose, which serves as a source of energy, nutrients, and feedstock for microbial and enzyme-catalyzed processes producing a variety of chemicals, fuels such as bioethanol, bio-based monomers, and polymers in biorefineries.[546–550] At thermolysis temperatures well above the T_C of 220 °C, chain scission of PMMA forms free radical end groups that initiate depolymerization by unzipping. At 450 °C, MMA is recovered at 97% yield (Table 4 and Figure 12C), accompanied by traces of byproducts such as methyl isobutyrate, methyl pyruvate, and the 2,3-butanedione that accounts for the unpleasant stenchy odor of PMMA obtained by repolymerization.[551]

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Polymers such as polymethyl acrylate, PP, PE, and PVC, after thermolysis of C–C bonds in their backbones, readily abstract hydrogen from other polymer chains that fragment to produce liquid and gaseous hydrocarbons instead of monomers. The resulting hydrocarbon fragments replace fossil oil in steam cracking and are transformed in a second step into ethylene and propylene monomers. While end-capped polyoxymethylene (POM) is thermally stable well above its T_C of 125 °C, it rapidly and quantitatively depolymerizes to formaldehyde above T_C (see Figure 12D) in the presence of strong acids, which act as catalysts that cleave acetal bonds to form active cationic end groups.[552]

Perfluorinated plastics such as poly(tetrafluoroethylene) (PTFE) exhibit outstanding chemical and thermal resistance, excellent (di)electrical properties, low adhesion, and low friction.[553] They are the material of choice for lubrication, bearings, coatings, insulation, thermal sealing, and medical applications. Yet fluoropolymer recycling is challenging, as fluoroplastics have an exceptionally long lifetime in the open environment and emit highly corrosive gases, for example, flourine (F_2) and hydrogen flouride (HF), when incinerated. In mechanical recycling. waste consisting of pure PTFE is mechanically broken down into particles that are used as fillers to reduce the friction coefficient of plastics and as additives for paints, greases, and oils.[554] Dyed and electrically conductive fluoropolymers are disposed of in landfills. Molecular monomer recycling by thermolysis enables the recovery of tetrafluoroethylene and hexafluoropropylene.[555] Continuous depolymerization was demonstrated for filled PTFE.[556,557] As polyolefins are inert, their back-to-monomer recycling is challenging. State-of-the-art thermal cracking of polyolefins produces complex mixtures of low-molecular-weight alkanes and alkenes together with aromatics that require separate refining, to convert pyrolysis oil into olefin monomers. Passing LDPE pyrolysis vapors at 500 °C over hierarchical micro- and mesoporous HZSM-5 zeolites with variable Si/Al ratios and modification with boron narrows the product distribution and significantly increases the yield of C2–C4 olefins (Figure 12E) with a minimal carbon footprint.[558]

Another strategy of molecular monomer recycling exploits controlled ring-closure depolymerization combined with repolymerization by controlled ring-opening polymerization. For example, poly(tetramethylene oxide) alias poly(tetrahydrofuran) (PTHF) is produced by the cationic ring-opening polymerization of tetrahydrofuran (THF) that is fully recovered by ring-closure depolymerization (Figure 12G) catalyzed by strong acids at temperatures above its T_C of 85 °C.[559] Furthermore, ring-closure depolymerization (Figure 12F) is the method of choice for regaining cyclic siloxane monomers from polydimethylsiloxane (PDMS), known as versatile silicone rubber.[560] As cyclic siloxane synthesis is capital-, energy-, and resource-intensive, its molecular recycling via depolymerization of PDMS offers economic advantages. According to Albertsson switching back and forth between controlled ring-opening polymerization (cROP) and controlled ring-closing depolymerization (cRCDP) of cyclic carbonates enables reversible transition between monomeric and polymeric states by adjusting reaction parameters that determine T_C.[561]

Coates sees Chemical Recycling to Monomer (CRM), in which plastics are efficiently transformed back into high purity monomers for repolymerization, as an ideal way to create a circular plastics economy.[515] Recycled plastics produced by CRM are fully equivalent to virgin plastics and thus evade the stringent downcycling spiral and do not face open end-of-life questions that are raised for many other recycling processes. Coates's review addresses CRM scope and limitations, CRM mechanisms, as well as CRM prospects of both commercial plastics and his own "new-to-the-world polymers" based on controlled ring-opening-polymerization/ring-closure depolymerization of cyclic carbonates (CC in Figure 12H) derived from epoxides and CO_2.

6.4. Open-Loop Valorization

In a closed-carbon-loop scenario, molecular carbon recycling efficiently transforms plastic wastes back into virgin plastics with structures, properties, and values identical to their fossil-based counterparts. Herein, back-to-monomer recycling avoids the value losses typical of mechanical downcycling. In an open-loop scenario, waste valorization, called upcycling, generates value-added products that exit the plastic carbon loop. It transforms renewable carbon from waste plastics into oil, gas, fuel, hydrogen, monomers, and various carbonaceous materials, together with highly diversified chemicals and organic materials, most of which have significantly higher values and functionalities. Whether these materials enter another external carbon cycle is not always clear. It should be noted that the terms 'recycling', 'upcycling', and 'downcycling' lack clear definitions. Several comprehensive reviews have addressed recent progress in the upcycling and waste-to-wealth transformation of waste plastics.[458,520,562–567] The wide spectrum of upgraded materials derived from plastic wastes spans specialty chemicals, clean fuels, lubricants, waxes, surfactants, proton exchange membranes, energy storage materials, filters, asphalt modifiers, coating and adhesive intermediates, carbon fillers, graphene, and carbon nanotubes. Organic wastes, among them plastics and biomass, are recognized as attractive sources of hydrogen and value-added carbonaceous materials. While incineration of plastic wastes and syngas generates energy together with massive CO emissions contributing to climate change, the recovery of hydrogen from organic waste holds promises for climate change mitigation and emerging hydrogen-based technologies. Among various plastic waste gasification technologies, pyrolysis coupled with in-line reforming generates high-hydrogen-content syngas essentially free of tar residues.[470] The byproduct CO can be removed from hydrogen by gas separation. Williams reviewed in detail the influences of reactor design, process parameters, catalyst addition, and plastic types on hydrogen production using pyrolysis coupled with catalytic steam reforming.[568] As a rule, the hydrogen yield improves with an increased hydrogen content of polymers and is highest for hydrocarbon materials such as polyethylene and polypropylene. Hydrothermal gasification of biomass and plastic wastes in the presence of sub- or supercritical water, respectively, utilizes water to effectively disintegrate organic wastes, producing hydrogen-rich syngas.[471] Reviews have addressed some prospects and challenges of converting plastic wastes into hydrogen for generating decarbonized energy and better sustainability.[569,570]

Instead of generating char as a low value or even undesirable byproduct, catalytic pyrolysis, hydrothermal treatments, and pyrolysis coupled with steam reforming transform plastic wastes

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into high-value-added functional carbonaceous (nano)materials such as carbon black, carbon nanotubes, graphene tuned for applications spanning energy storage materials, electrodes, carbon (nano)fillers, and absorbents for water purification.[571,572] In contrast to fast pyrolysis, the yield of carbonaceous char is higher for slow pyrolysis of PP.[573] Pyrolysis of waste tires yields oil and colloidal pyrolytic carbon, which are useful as rubber reinforcing agents.[574] Heat treatment temperature determines the chemical composition, pore size, and microstructure of pyrolytic carbon derived from plastic waste and biomass.[575] However, the role of precursor structures needs further clarification. Thermolysis at 1450 °C transforms phenolic thermoset resins such as *Bakelite* into graphitic carbon, which is applied as an alternative carbonaceous resource and reducing agent in iron-making processes.[576] At lower temperatures of 210–250 °C, microwave-assisted hydrothermal treatment converts PP into carbonaceous materials.[577] At room temperature, PVC was dehalogenated in the presence of aqueous KOH to produce carbonaceous materials which were essentially free of halogen and useful as high-performance supercapacitors.[578] Both few-layer and multi-layer graphenes were prepared by four different strategies: First, thermolysis of the plastics directly over a metal substrate; second, pyrolysis coupled with chemical vapor deposition (CVD) to generate hydrocarbon feed for CVD; third, thermolysis and subsequent ball milling followed by microwave sintering; fourth, flash Joule heating.[579]

Pyrolysis coupled with CVD is common practice in bench-scale plastic waste upcycling to carbon nanomaterials such as nanoparticles, multi-walled carbon nanotubes, graphene, carbon nano nanofilaments, nanowires, and nanoplatelets.[580–582] Waste plastics, tires, biomass, and the glycerol that is a by-product of biodiesel production are considered to be promising renewable carbon feedstocks for CNT fabrication.[583] In plastic waste, pyrolysis cascaded with steam reforming, the carbonaceous nanomaterial formation is coupled with hydrogen production and depends on reactor design, process parameters, catalyst addition, and the choice of plastic waste type.[568] In an elegant one-step process, microwave-assisted thermolysis of PE, PP, and PS powders, none of which absorb microwave irradiation, are heated in the presence of a microwave-absorbing iron catalyst to yield hydrogen (97% of the theoretical mass) together with predominantly multi-walled carbon nanotubes. This intriguing proof-of-concept advance confirms that waste plastics hold promise as a valuable feedstock for the production of hydrogen together with high-value-added carbonaceous materials that are in high demand in various industries.[584]

7. Sustainable Hydrocarbon Materials

As high molecular weight hydrocarbon materials, polyolefins such as PE and PP, which account for around half of the global plastics production, are equivalent to solid melt-processable versions of low molecular weight hydrocarbon oil. Among plastics, they have the highest hydrogen and oil-like energy content as evidenced by their high calorific values (see Figure 5). They enable a circular plastic economy in an ideal way. They are readily transformed back into oil and gas by thermal and catalytic cracking or into hydrogen and value-added carbon materials by open-loop valorization. Hence, they store energy and valu-

able resources for future generations and should not end up in the open environment to slowly disintegrate and cause micro- and nanoparticle emissions. Due to their high durability, polyolefins hold the promise of creating a closed carbon loop contained exclusively within the technosphere. In this scenario, mechanical recycling is complemented by molecular recycling, in which wastes unfit for re-extrusion are transformed back into monomers and virgin plastics or phased out to an open-loop valorization. Highly efficient polymerization catalysts, solvent-free polymerization processes, facile processing, and recovery of oil and gas or monomers at the end-of-product lifetime, respectively, are the key elements of this renewable carbon scenario, which is schematically displayed in **Figure 13**. On-going progress and breakthroughs in polymerization catalysis, reaction engineering, polymer science, and engineering have greatly simplified polyolefin production. Environmentally benign catalytic olefin polymerization meets the criteria for green chemistry, that is, exceptionally high atom efficiency, absence of organic solvents, waste prevention, high safety standards, energy and resource efficiency, and even use of renewable resources.

In an intriguing way, discoveries in basic science and engineering have, way within a very short time, been translated into successful industrial large-scale manufacturing of advanced hydrocarbon materials.[582–589] Polyolefins are prime examples of how plastics are constantly reinvented and reengineered to meet the highest performance, recycling, and sustainability requirements. Tailoring polyolefins via advanced polymerization catalysis is essential for the emerging circular plastics economy and better sustainability.[590,591] Pioneered by the Nobel laureates Karl Ziegler and Giulio Natta during the 1950s, the discoveries of olefin polymerization catalysts and new materials such as polypropylene have paved the road to success for the polyolefin industry. Modern highly active and selective catalyst systems and low-pressure catalytic olefin polymerization are resource- and energy-efficient, especially compared to free-radical ethylene polymerization, which requires high pressures exceeding 1000 bar and high temperatures well above 150 °C. Advanced supported catalysts enable solvent-free polymerization in the gas phase and liquid monomer without requiring any post-polymerization purification steps such as removal of catalyst residues, solvents, or byproducts such as oligomers or atactic polypropylene, which are typical of first-generation processes. In terms of catalyst activities, some modern industrial polymerization catalysts clearly outperform enzymes that fail to function in the gas phase or with bulk monomers. In polyolefin reactor granule technology, particle growth is controlled by designed supported catalysts to produce both pellet-like granules without requiring pelletizing extrusion and reactor blend spheres containing rubber phases dispersed within PP matrices.[589] Molecular architectures of single-site catalysts such as metallocenes and post-metallocenes give excellent control on molar mass, stereochemistry, long- and short-chain branching, end groups, and comonomer incorporation all of which can be varied over a wide range.[595–600] The family of polyolefin materials spans thermoplastics, thermoplastic elastomers, and rubbers, thus serving highly diversified markets ranging from packaging to textiles, carpets, bumpers, containers, and pipes. Ethylene polymerization in reactor cascades and multizone reactors as well as on multi-site catalysts allows for independently tuning molar mass
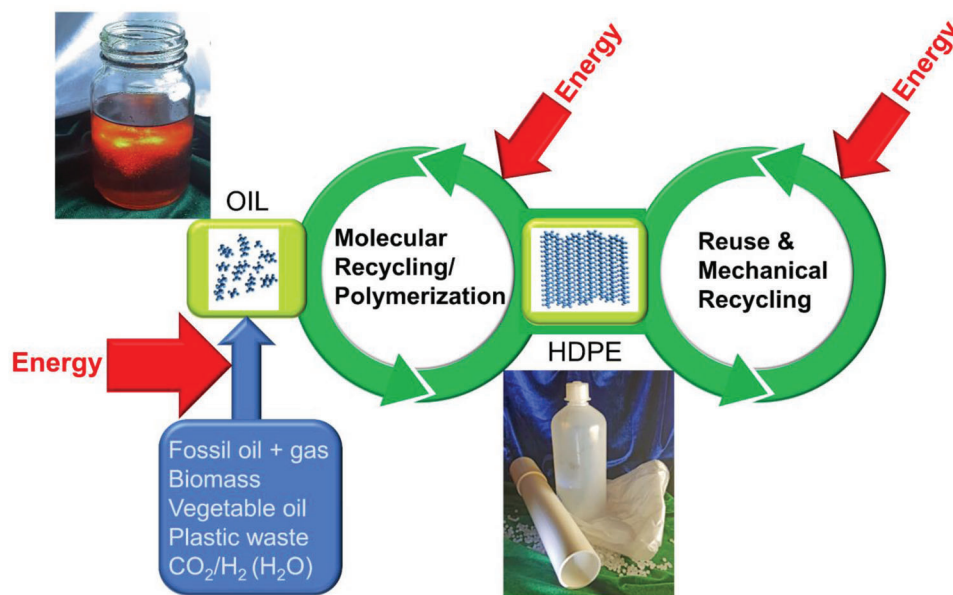
Figure 13. Molecular and mechanical closed-loop recycling of polyolefins complemented by open-cycle valorization to hydrogen, fuel, lubricants, and refinery feeds.

Figure 14. Multizone Gas phase polymerization reactor (*Hyperzone* PE plant, LyondellBasell) (left) and *MoReTec* molecular recycling facility (Lyondell-Basell) (right). (Reproduced with permission from LyondellBasell, 2022).

and branching distributions, both of which are essential for improving the fatigue resistance and lifetime of HDPE pipes by three orders of magnitude.[591,601] The multizone gasphase plant of LyondellBasell is displayed in **Figure 14**. Designed for recycling, ethylene polymerization on supported multi-site catalysts yields PE containing dispersed nanophase-separated, unentangled ultrahigh molecular weight PE (UHMWPE) that creates nanofiber-like UHMWPE during injection molding, extrusion,

and mechanical recycling and thus reinforces HDPE. Such self-reinforced HDPE does not require the addition of alien fibers and their tedious recovery, as the UHMWPE nanostructures are self-assembled during mechanical recycling.[590] In the future, going beyond the scope of current polymerization catalysis, catalyst systems and polyolefin materials designed for recycling, catalytic pyrolysis, and depolymerization catalysis are expected to play prominent roles in both closed-loop molecular recycling

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of polyolefins and open-loop polyolefin valorization.[468,521,602] As presented in Section 6, catalytic cracking makes polyolefin pyrolysis more efficient by lowering its carbon footprint and narrowing pyrolysis product distributions in a controlled fashion. It even enables recovering C2–C4 olefin monomers from mixed LDPE post-consumer waste streams that serve as renewable carbon sources.[558] As PEs and PP have similar densities in the range of 0.93–0.97 g cm^{-3} compared to PET, with 1.43–1.45 g cm^{-3}, they are recovered by sink-float separation and NIR-assisted sorting. Strategic approaches toward open-loop valorization of PP and PE by converting their wastes into value-added products, such as refinery feeds, syngas, fuels, lubricants, waxes, surfactants, ion-exchange resins, value-added carbonaceous materials, energy storage materials, and others, were reviewed by Roy, Garnier, Allais, and Saito.[563] From an economic perspective, open-loop pyrolysis producing high-value wax outperforms closed-loop molecular recycling via feedstock recovery.[603] Due to their high hydrogen content, waste polyolefin gasification coupled with steam reforming holds promise for generating hydrogen together with value-added carbon materials, such as carbon nanotubes (see Section 6).[568,604] The global Covid-19 pandemic triggered the surging demand for personal protective equipment, including face masks, shoe covers, gowns, gloves, and face shields, most of which are made of PP, paralleled by a flood of infectious waste. As a viable alternative to landfills, incineration, and mechanical recycling, molecular recycling by PP pyrolysis is seen as the best option to transform any kind of infectious waste into feedstocks, virgin plastics, and value-added carbon materials.[573] Slow pyrolysis at 300–600 °C, heating rate of 5 °C min^{-1}, and a prolonged residence time of 1–5 h maximized the yield of solid products comprising carbonaceous char and coke for potential applications as water-treatment adsorbents, nanofillers, and catalyst supports.

While polyolefin formation via catalytic olefin polymerization is highly energy-efficient and generates energy due to the exothermic polymerization reaction, oil exploration and refining, and mechanical and molecular recycling are energy-intensive processes. Driven by the taxation/penalty of CO_2 and climate change mitigation, the polyolefin industry strives to achieve a net-zero CO_2 emission by 2050. One strategy is to move away from fossil resources to renewable carbon sources such as sugarcane, used cooking oil, forestry, and agricultural wastes or plastic wastes. In a comparative LCA study, bio-based PE outperformed fossil-based PE and PLA.[313] For example, Braskem commercialized bio-based PE (*I'm Green*) derived from bioethanol using sugarcane as a renewable carbon source.[605] As drop-in technology, bio-based polyolefins do not require any investment in new polymerization and processing technologies. Typically driven by fossil energy, these processes have a reduced carbon footprint but are not carbon neutral. Another strategy toward 100% net-zero CO_2 emission is transforming existing petrochemical plants into thermomechanical recycling plants with closed carbon loops.[606,607] Fossil feedstocks are replaced by pyrolysis oil and gas gained from plastic waste. In addition, steam crackers are electrified while oxycombustion coupled with CCS prevents CO_2 emission. Dow CEO Jim Fitterling was quoted by Chemical & Engineering News as saying that Dow is "turning the corner into a low-carbon, sustainable world" and plans to allocate $1 billion in annual capital spending to decarbonize its manufacturing sites one by one. Cracker off-gases such as methane are transformed into hydro-

gen, which replaces fossil fuels, while the byproduct CO_2 is captured and used in tertiary oil recovery and ultimately enters sequestration. Sabic's *Trucircle* portfolio and services for circular solutions span design for recycling, bio-based hydrocarbon materials, mechanical and molecular recycling, including certified renewables.[608] LyondellBasell has launched its *Circulen* product family to support its goal to manufacture and market two million metric tons of recycled and renewable-based plastics annually by 2030.[609,610] The *Circulen* family members comprise *Circulen*Recover, manufactured by mechanical recycling of pre- and post-consumer plastic waste, *Circulen*Revive, which is made from advanced molecularly recycled plastic waste, for example from its proprietary molecular recycling technology *MoReTec* (see Figure 14), that converts plastic waste unfit for mechanical recycling into hydrocarbon feedstock as drop-in technology to produce virgin and new plastics tuned for a wide range of applications, and *Circulen*Renew, which is derived from renewable carbon feedstocks that are unfit for food use, such as used cooking oil, thus enabling hydrocarbon materials that serve as a carbon sink. Borealis commercialized *Borcycle* recycling technology, which that transforms post-consumer polyolefin waste into value-added recyclates and offers solutions for healthcare.[611]

8. Carbon Capture and Use of Carbon Dioxide

Both plastics manufacturing and recycling are energy-intensive processes. Typically driven by non-renewable energy, they contribute to climate change as their global consumption sharply rises. One of the key challenges in closing the carbon loop is to render the circular plastics economy carbon neutral. Three different strategies exist: First, to fully decarbonize the energy required to drive the carbon cycle by switching from fossil to renewable energy such as electricity and green hydrogen; second, to capture CO_2 by carbon capture and storage (CCS) technology; third, to close the carbon loop by using captured CO_2 as a renewable carbon source to enter the carbon cycle via biological and chemical CO_2 fixation.[612] In Europe, the transition to carbon neutrality is progressing in the energy-intensive steel, pulp and paper, plastics, and meat and dairy industries.[613] While value chains and pathways to carbon neutrality differ markedly across these sectors, the global decarbonization thrust is expected to force sector-coupling and overcome the traditional, currently strict impermeable sector boundaries.

Rissman reviewed technologies and policies to decarbonize global industry and identified mitigation drivers through 2070.[614] The EU with its European Green Deal Initiative is claiming a leading role in this unprecedented and comprehensive economic transformation to reduce GHGs and achieve climate neutrality. In a scenario of a totally fossil-free and electricity-based European plastics industry by 2050, exploiting renewable carbon sources from both biomass and CCU together with green hydrogen for producing all hydrocarbons, the annual demand is estimated to be 180 Mton CO_2 and 1600 TWh electricity, at the expense of two to three times higher hydrocarbon costs than today.[615] Electrification is seen as an important prerequisite for transforming petrochemical plants into carbon-neutral thermomechanical recycling plants with 100% plastic recovery.[606] In CCS named sequestration, the GHG CO_2 is captured before it enters the atmosphere and sent to underground geological
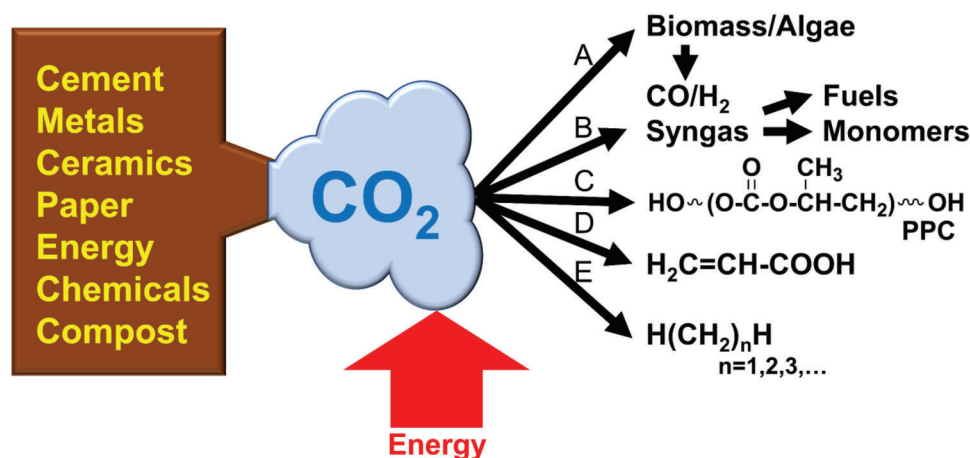
Figure 15. CCU strategies for utilizing CO_2 from air and from the decarbonization of energy-intensive industries via A) biomass such as algae, B) syngas, C) cyclic carbonates and polypropylene carbonate, D) acrylic acid, and E) direct catalytic route to hydrocarbons.

storage for millennia.[616–618] From both economic and environmental perspectives, CCU coupled with the decarbonization of energy-intensive industries or CCU coupled with CO_2 sequestration (CCUS), respectively, are better options than CCS. Today, CCU and CCUS technologies span an extraordinarily wide range comprising enhanced tertiary oil recovery, biomass, underground mineralization to cement feedstock, food and beverages, chemicals, pharmaceuticals, fuels, plastics, and energy storage. Generated by oxidation, CO_2 has a high energy demand for its chemical transformation and valorization. Nevertheless, by using renewable energy and green hydrogen to transform CO_2 into sustainable chemicals, CCU can decouple chemical production from fossil resources, thus reducing the annual GHG emissions by up to 3.5 Gt CO_2 equivalents by 2030.[619] Going well beyond decarbonization of industries, as stated by Leitner et al., "CO_2-based chemistry is stimulated by the significance of the relative improvement in carbon balance and other critical factors defining the environmental impact of chemical production in all relevant sectors in accord with the principles of green chemistry."[620] As a cornerstone of sustainable energy systems, CO_2 valorization and sector coupling via power-to-X technologies, for example, power-to-chemicals, power-to-fuels, power-to-gas, power-to-hydrogen, power-to-food, and power-to-syngas, connect renewable wind and solar energy production with other sectors to chemically store and utilize surplus renewable energy, thus reducing FEC.[621] Net-zero emissions combined with high energy and resource efficiency are considered feasible by coupling the energy, chemical, and recycling sectors to produce olefin monomers from German domestic feedstocks, including plastic waste.[622]

The catalytic transformation of CO_2 as a renewable carbon source into PC, polyester, (non-isocyanate) PU, and polyurea is expected to play a role as an enabler for closing the carbon loop, leading to more sustainable plastics which are non-fossil-based. A comprehensive review of the chemistry of CO_2-based polymers has been given by Detrembleur and coworkers.[636] As schematically displayed in Figure 14 CO_2 is captured from air, energy-intensive industries producing cement, steel, ceramics, or powerplants which incinerate fossil oil and gas, biogas,

biomass, coal, or plastic waste. After CO_2 capture and purification, different strategies are being pursued toward using CO_2 in the plastics industry. Going beyond traditional biomass utilization and avoiding land-use conflict with the food industry, algae produced by biological photosynthesis serve as a source of biopolymers and renewable carbon.[624] Furthermore, algae liquefaction, pyrolysis, and gasification yield syngas (pathway A in **Figure 15**) as an intermediate for sustainable fuels, chemicals, and monomers. In addition, syngas (pathway B in Figure 15) is generated by CO_2 reforming and by CO_2 reduction with green hydrogen supplied by electrolytic, thermolytic, and photolytic water splitting using renewable or nuclear energy.[625] The transformation of CO_2 is expected to become a cornerstone of the methanol economy.[626] In a recent advance, Steinfeld, Furler, and coworkers at ETH Zürich produced carbon-neutral, sustainable fuels such as kerosene and methanol from sunlight, air, and water (pathway B in Figure 15).[627] In their mini solar refinery at ETH Zurich, the first stage comprises air separation to extract CO_2 and water directly from air. In the second stage, the solar catalytic ceria-redox unit is driven by concentrated solar energy transformation of CO_2 and water at 900–1500 °C into syngas which, in the third stage (gas-to-liquid unit), is transformed into liquid hydrocarbons or methanol, respectively. In another strategy (pathway C, Figure 15), low-energy CO_2 reacts with high-energy epoxides to form either cyclic carbonates or via strictly alternating copolymerization of flexible and rigid aliphatic PCs.[628–630] Catalytic ring-opening polymerization and ring-closure depolymerization of cyclic carbonates hold promise for back-to-monomer molecular recycling (see Section 6.3 and Figure 12).[515] The reaction of propylene oxide with CO_2, displayed in Figure 15 (pathway C), yields propylene carbonate as an organic solvent and polypropylene ethercarbonate polyols, which are commercialized by Covestro (*Cardyon*) as an intermediate of PU with a reduced carbon footprint.[631] A variety of epoxy resins are transformed by reactions with CO_2 into polyfunctional cyclic carbonates that are cured with polyfunctional aliphatic amines to produce polyhydroxyurethanes, termed non-isocyanate polyurethanes (NIPU) without using moisture-sensitive and hazardous isocyanate monomers.[632–637] Progress

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in catalysis has enabled another dream reaction to become a reality (Figure 15, pathway D). In a facile one-pot, single-stage process, catalytic CO_2 transformation converts ethylene into acrylic acid and acrylate monomers.[638–641] In the natural carbon cycle, it takes millions of years and high pressure to convert biomass into oil which can be recovered and refined in highly energy-intensive and environmentally harmful processes to produce hydrocarbon fuel. Cargnello and his colleagues at Stanford University succeeded in transforming CO_2 by low-pressure hydrogenation into butane, ethane, and propane in a matter of hours at 250 °C and 6 bar pressure.[642] The selectivity of butane formation versus methane formation increased 1000-fold when the Ru/TiO_2 catalysts were embedded in a shell of a porous, thermally, and chemically stable imine-based plastic. This recent discovery unveiled the enormous potential of catalysis to turn captured CO_2 into valuable industrial chemicals such as monomers, methanol, and ethanol. Energy- and resource-efficient catalytic processes enable closing the carbon loops in the circular plastics and fuel economies without returning massive amounts of CO_2 to the skies.

9. Conclusion

Today, plastics are ubiquitous in everyday life, omnipresent in virtually any consumer product, enablers of modern technologies, and inevitable in sustainable development. Tiny molecules such as drugs and food ingredients prolong life while giant molecules (macromolecules, polymers) like plastics make long life better and safer. One hundred years ago, Nobel laureate Hermann Staudinger recognized that biopolymers in nature and synthetic polymers share the same blueprint. Thousands of small molecular building blocks are covalently linked to build organic materials and tune their property profiles by varying their molecular architecture, self-assembly, shape, and function. Unlike the abundant natural biopolymers, plastics are easy to process and highly versatile in terms of property profiles tuned for diverse applications. On the bright side, inexpensive, versatile, and easy-to-process plastics contribute to meeting humans' needs for clothing, shelter, protection, good health, potable water, clean air, the supply and safe distribution of food, drugs, and energy, communication, mobility, and leisure activities. Plastics preserve food in packaging applications and save energy by lightweight construction of vehicles and building insulation. On the dark side, plastics as problem solvers turned themselves into a global problem and became a victim of their success and the lifestyle that they helped to create. Inexpensive, versatile plastics render products available to anybody and encourage throwaways. The rapid growth of the world population striving for a better life and progressing urbanization have triggered skyrocketing global plastics consumption, which is expected to reach a billion-ton scale by 2050. As only 20% of plastics are recycled, this growth is paralleled by a tidal wave of plastic debris flooding soil, air, rivers, and oceans. In particular, short-lived plastic packaging amounts to around 40% of globally produced plastic and claims a major share of plastic-related carbon emissions.

In the first century A.S. (after Staudinger), the plastics economy has been strictly linear; fossil carbon resources of oil and gas are extracted, refined, and converted into plastics that end up in landfills, oceans, and incinerators. As a result, carbon

is constantly emitted from the geosphere into the atmosphere, water, and soil. Although most high-molecular-weight plastics are inert and durable, their abrasion and slow disintegration release micro- and nanoplastics as well as small molecule additives that pose a potent threat to health, human habitats, and the food chain. One might reasonably ask why recycling and plastic reuse challenges were never seriously addressed in the past. While Staudinger introduced the molecular design concept of plastics in 1920, large-scale global plastics production commenced at the end of 1950s shortly after the discovery of catalytic low-pressure olefin polymerization. Compared to metals, glass, and paper, plastics are much younger materials that never went through war-time shortages, which might have forced their reuse and recycling. In the post-war economic boom, the limits of growth, environmental pollution, and sustainability issues were vastly ignored in society, politics, economy, industry, and science alike. At the beginning of the second century A.S., moving away from a linear "produce-use-throwaway" economy to a zero-waste and carbon-neutral ("produce-use-reuse") circular plastics economy is vital for the future of the planet. Given their versatility and vastly untapped potential for reuse and recycling, plastics enable sustainability, climate change mitigation, and a zero-waste carbon-neutral circular plastics economy. Rethinking plastics means thinking of plastic waste as a valuable renewable carbon resource and opportunity rather than worthless garbage, a nuisance, and an environmental burden. The sustainable circular plastics economy aims to replace fossil fuels with renewable carbon resources and stop carbon waste and carbon reentry into the geosphere by closing the carbon loop. In addition to biomass, both plastic waste and CO_2 are renewable carbon resources.

In essence, there exist three different strategies for closing the carbon loop and replacing fossils with renewable carbon resources: First, reuse and mechanical recycling; second, back-to-monomer molecular recycling; third, capture and use of CO_2. In addition, renewable carbon exits the carbon circle in open-loop valorization and is upgraded to chemicals, waxes, lubricants, hydrogen, and carbonaceous (nano)materials that in turn are part of a wider carbon loop. Plastics do not need to be reinvented but do need to be tuned to enable carbon circularity without compromising their benefits, such as facile processing, versatility, and low cost. A key prerequisite for a circular plastic economy is building a global industrial infrastructure for efficient plastic waste collection, and automated sorting. Closing the carbon loop by reuse and mechanical recycling is mainly restricted to pre-consumer and non-polluted post-consumer thermoplastic wastes. Successful PET recycling in some countries proves that collecting almost 100% PET waste is possible. However, less than one-third of the recycled PET qualifies for reuse as food-contact material. Lower quality recyclate is downcycled to lower-value, non-food applications. Plastics do not have eternal life. As with paper recycling, each cycle deteriorates polymer properties due to chain scission by oxidative and mechanical stresses encountered during sorting and extrusion. As recycling quotas rise, recyclate quality goes down. One end-of-life option for completely downgraded recyclates and complex multicomponent systems is incineration with energy recovery, exploiting the high energy content of most plastics, or gasification to regain valuable chemical building blocks. Both incineration and anaerobic composting destroy valuable carbon resources for the sake of energy re-

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covery. Approaches towards design for mechanical recycling aim at replacing multilayer with monomaterial packaging, developing debond-on-command and dismantle-on-command systems, glueless bonding by mechanical interlocking, remoldable thermosets (vitrimers), and developing recycling strategies for coated thermoplastics.

Instead of sudden death by incineration, molecular recycling as the core of the circular plastics economy gives plastics that are unfit for mechanical (down)recycling a second and perhaps even eternal life. Through thermal, chemical, biological, and catalytic degradation or depolymerization, respectively, feedstocks or monomers are recovered to regain high-quality virgin plastics by (re)polymerization. This is a viable alternative to mechanical downcycling, as plastics produced by one- or two-stage back-to-monomer molecular recycling are fully equivalent to the corresponding virgin fossil-based plastics. Yet molecularly recycled plastics have a lower carbon footprint than identical fossil-based plastics. In addition, molecular recycling holds the promise of recycling thermosets and PUs, and recovering both feedstocks and fibers of composites. As a complement to molecular recycling, CCU of CO_2 transforms CO_2 into biomass or directly via CO_2 reforming and hydrogenation with green hydrogen into methanol, ethanol, hydrocarbons, and monomers, all of which are useful as intermediates for plastics and can enter molecular recycling processes. Progress in catalysis has made dream reactions become a reality, such as solar-powered catalytic refining of CO_2 to produce hydrocarbons and catalytic carboxylation of ethylene to produce acrylate monomers. CCU holds promise for decarbonizing energy-intensive industries that produce cement, steel, or power by capturing CO_2 before it enters the atmosphere and then transforming it into monomers. Hence, a closed plastic carbon loop can help to decarbonize cement production and simultaneously fuel the plastics carbon cycle. Catalysis is essential for molecular recycling and the entire circular plastics economy to make polymerization and degradation processes as well as CO_2 utilization more efficient and lower their carbon footprint.

As part of the natural carbon cycle, biodegradation holds promises for industrial composting, feedstock recovery, and special applications such as compostable food packaging, agricultural mulch films, and organic waste bags. In organic waste composting, biodegradable (bio)plastic packaging enters the natural carbon cycle, in which CO_2 is photochemically transformed back into biomass. The use of biomass as renewable carbon feedstock lowers the carbon footprint of both degradable and durable bio-based plastics. Despite advances made in microbial polymerization, the development of water-insoluble bio-based plastics, that are easy to process, cost-competitive, mechanically recyclable, and biodegradable in all ecosystems, including seawater, remains a challenge. Biodegradation is neither the Holy Grail of the circular plastics economy nor a panacea for fighting plastic littering. In the aftermath of the victorious battle of the bag and the ban of disposable single-use plastic items, most disposable single-use bioplastic substitutes are not as biodegradable as they are claimed to be. It is incorrect to interchangeably use 'compostable' and 'biodegradable'. Biodegradation strongly depends on climate, temperature, sunlight, moisture, oxygen, and microorganism types, all of which differ significantly across ecosystems. Most compostable (bio)plastics fail to biodegrade in seawater, are durable forever in the absence of water and oxygen, and

emit the potent GHG methane in the presence of water when oxygen is absent, such as in mismanaged landfills and swamps. Biodegradation by design is a reality in biomedicine and industrial composting but is challenging in the much more complex open ecosystems, for example, seawater. More insight is needed to better understand biodegradation and the fate of biodegradable (micro)plastics and their metabolites. The anticipated rapid growth of biodegradable plastics could turn into an environmental burden by provoking the business-as-usual scenario of throwaway, if consumers continue to assume that it is safe to dump them into the environment. Their design for throwaway instead of recycling could deeply impact reuse strategies, as degradation of plastic waste pollutes recycling streams in mechanical recycling.

Instead of designing materials for throwaway, a sustainable solution for marine littering is to establish a carbon loop embedded in the technosphere and to stop carbon emissions into landfills, water, and air. For mechanical recycling, durable plastics are clearly advantageous and emit no methane in mis-managed landfills. Complementary mechanical and back-to-monomer molecular recycling enables establishing an economic carbon cycle. Hydrocarbon materials meet the demands of the circular plastics economy in an ideal way. As high-molecular-weight version of hydrocarbon oil, equivalent to half of the world's plastic production, hydrocarbon materials such as polyolefins have the highest energy and hydrogen content among plastics. Their wastes represent renewable carbon resources that, by thermal and catalytic chain scission, are readily and almost quantitatively transformed back into hydrocarbon oil feedstock and monomers for repolymerization in highly efficient, solvent-free catalytic polymerization processes. Alternatively, they serve as a source of hydrogen and value-added carbonaceous materials that are in demand in energy technology. Hence, they store energy and resources for future generations. Instead of renewable hydrocarbon oil from plastic recycling, biomass, even used cooking oil or water with CO_2, can be used as renewable carbon resources to lower carbon footprint. Emerging solar catalytic CO_2 transformation into hydrocarbons and olefin monomers as well as electrification of circular carbon processes is expected to add a new dimension to closed-loop hydrocarbon economy based on renewable carbon. Whereas oil refineries emit massive amounts of CO_2, the sector-coupling of renewable energy with CO_2 transformation holds prospects for decarbonizing energy-intensive industries that supply CO_2 as an abundant source of renewable carbon to the plastics industry. Closing the carbon loop does not create a Perpetuum Mobile; it requires renewable energy in order to achieve sustainability and carbon neutrality.

Acknowledgements

Notes

Circulen, Hyperzone, and MoReTec are trademarks owned and/or used by the LyondellBasell family of companies and are registered in the U.S. Patent and Trademark Office.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

circular economy, plastics, polymers, recycling, sustainability

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Carl G. Schirmeister, born in 1991, studied chemistry at the University of Freiburg, Germany and—as a Fulbright Fellow—at the University of Massachusetts Amherst, USA (2011–2018). He received his Ph.D. at the University of Freiburg, supervised by Prof. Dr. Rolf Mülhaupt, (2018–2021) and joined the company LyondellBasell focusing on sustainable solutions for polymers and polymer compounds. He is the author and co-author of several publications in refereed journals and patents in various areas of application. His expertise includes sustainable polymer solutions, molecular recycling, self-reinforcing polymers, nanocomposites, and 3D printing.

Rolf Mülhaupt, born in 1954, studied chemistry at the University of Freiburg, Germany (1973–1978) and got his Ph.D. at the ETH Zürich (1978–1981). After conducting industrial research at Du Pont Central Research in Wilmington/Delaware, USA (1981–1985), and at Plastics and Additives Division of Ciba in Marly, Switzerland (1985–1989), he was a professor of macromolecular chemistry and director of the Institute of Macromolecular Chemistry at the University of Freiburg (1989–2021). He published 488 papers in refereed journals and filed 112 patent applications. His research spans sustainable polymers, polymerization catalysis, nanocomposites, processing, 3D printing, and specialty polymers.