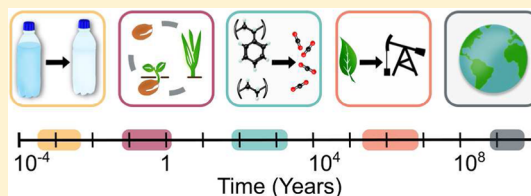


50th Anniversary Perspective: There Is a Great Future in Sustainable Polymers

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ABSTRACT: It is likely that a half-century ago even enthusiastic and optimistic proponents of the synthetic polymer industry (Mr. McGuire included) could not have predicted the massive scale on which synthetic polymers would be manufactured and used today. Ultimately, the future success of this industry will rely on the development of sustainable polymers—materials derived from renewable feedstocks that are safe in both production and use and that can be recycled or disposed of in ways that are environmentally innocuous. Meeting these criteria in an economical manner cannot be achieved without transformative basic research that is the hallmark of this journal. In this Perspective we highlight five research topics—the synthesis of renewable monomers and of degradable polymers, the development of chemical recycling strategies, new classes of reprocessable thermosets, and the design of advanced catalysts—that we believe will play a vital role in the development of sustainable polymers. We also offer our outlook on several outstanding challenges facing the polymer community in the broad area of sustainable polymers.



I. INTRODUCTION

To highlight the magnitude of an important challenge now facing polymer science, we begin this Perspective on sustainable polymers with a broad look at a seemingly unrelated topic, earth science. There is currently a rift in the field of geology. At the heart of the controversy is nomenclature, specifically whether or not the *Holocene*—the epoch which began almost 12 000 years ago at the end of the last glacial period and which encompasses all written human history—has now ended.^{1,2} Although a host of climatic, atmospheric, biological, and geochemical data support the idea that we are now living in a new geological epoch, the *Anthropocene*,^{3,4} some earth scientists contend that there is not enough evidence in the rock record to make this designation.⁵ In 2016, a process to formalize the *Anthropocene* was launched within the International Commission of Stratigraphy (ICS). This process begins with identifying a primary signal to serve as a marker of this new epoch in the rock record. Among those currently favored are plutonium fallout and radiocarbon spikes from atomic bomb tests, increases in carbon dioxide concentration from burning fossil fuels, and, most relevant to our discussion, plastic.^{6,a} The history of the synthetic polymer industry, from the localized introduction of Bakelite and Rayon in urban centers during the early 20th century to the global proliferation of commodity plastics following the Second World War, will be recorded in the sediment for centuries regardless of the specific marker chosen by the ICS.

Over the past 50 years, the uses for and production of synthetic polymers have increased exponentially. This is in large part due to the undeniable fact that these materials provide many societal benefits including those strongly and positively connected to sustainability (e.g., lightweight transportation to reduce fuel consumption, membranes for efficient water

purification, and food packaging to prevent spoilage). However, polymer prices often do not reflect the true costs associated with their manufacture and disposal.⁷ One major issue many synthetic polymers share is that they are derived from nonrenewable resources. Today a small but non-negligible percentage of the total oil produced annually (~8%) is consumed for the manufacture of polymers, with the amount being used *directly* as the carbon source for the synthesis of monomers roughly equal to the quantity consumed *indirectly* for production processes.⁸ This number is increasing monotonically; some argue that by 2050 the plastics industry alone will account for almost 20% of the total oil consumed annually.⁸ The large scale on which synthetic polymers are produced can be concerning from an energy security and from an economic standpoint for the simple reason that petroleum consumed in their production (and their embedded energy content) is generally not recovered. As a specific example, currently over 40% of the ~80 million tons of plastic packaging used every year is discarded in landfills with an astonishing 32% escaping the collection system or being dumped illegally.⁹

Aside from the considerable economic losses that result from the disposal of polymeric materials after a single use (estimated at ~100 billion dollars annually for packaging materials alone), there are also the direct costs of disposal and the indirect, and often difficult to quantify, environmental costs of polymer pollution.^{7,9} Synthetic polymers make up ~11% of the total municipal solid waste (MSW) stream by mass; however, they take up a disproportionate volume in landfills due to their low density.¹⁰ Unlike many other forms of trash, most synthetic

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polymers are not biodegradable (and also do not degrade quickly via abiotic processes); once in landfills they can remain there indefinitely. Although the costs of disposal vary widely by region, MSW collection can cost hundreds of dollars per metric ton.¹¹ For synthetic polymers that escape collection, cleanup efforts also can be very costly. In the United States removal of litter, largely plastic pollution, from the west coast alone costs taxpayers over half a billion dollars every year.¹²

Because of typically outstanding durability and low density (two attributes that are, in fact, beneficial for many applications), terrestrial plastic pollution often infiltrates marine and freshwater ecosystems over time (Figure 1). In fact, while

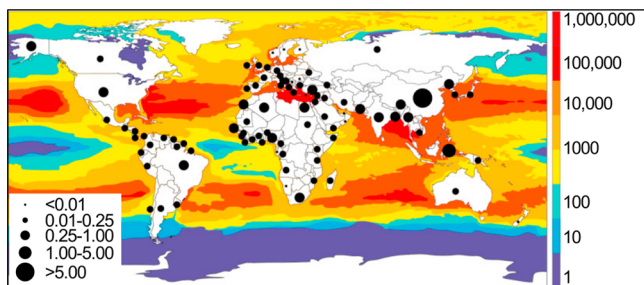


Figure 1. A contour map showing distribution of pelagic microplastics (defined as pieces that are >1 mm and ≤ 4.75 mm, and measured in pieces per meter squared) and plastic waste available to enter oceans in 2010 in millions of metric tons (mMT) generated within 50 km of the coast (indicated by ● markers). Adapted with permission from Zalasiewicz et al.⁶

plastics make up only a small portion of MSW, over 80% of waste that accumulates on shorelines is plastic.¹³ In 2016, the MacArthur Foundation published a startling statistic: if current trends continue, the mass of plastics in the ocean will equal the mass of fish by 2050.^{9,14–16} Larger pieces of debris can harm aquatic animals via entanglement; so-called *ghost fishing* caused by derelict gear can result in significant economic losses for fisheries.¹⁷ Plastic fragments of all sizes can also pose ingestion hazards, both acute (e.g., internal bleeding, abrasion and ulcers, blockage of the digestive tract) and chronic (e.g., weight loss due to reduced appetite) in nature. While most polymers are chemically inert, many contain residual monomers, flame-retardants, and plasticizers that can leach into the environment over time. Moreover, plastics can increase in toxicity by concentrating persistent organic pollutants (including polychlorinated biphenyls, polycyclic aromatic hydrocarbons, and organo-chlorine pesticides) present in water.¹⁸ Although the effects of plastic pollution on the food cycle are not yet fully understood, laboratory studies indicate small molecule additives present in plastic particles can be transferred to the blood and tissue of animals via ingestion.¹²

Disturbingly, exposure to plastic pollution seems to affect behavioral ecology in a complex manner. In terrestrial and estuarine ecosystems, it has been shown that some turtles and birds consume plastics both intentionally (many harbor nutritious bacteria and fungi) and by accident (plastic artifacts may resemble native food sources, in both appearance and smell).^{19,20} It is conceivable that microplastic particles can even pass directly between trophic levels, as they have been found in the gastrointestinal tracts of small invertebrates (themselves prey for larger creatures), and such a transfer has previously been observed in a laboratory environment.^{21,22} The extent to which humans are exposed to organic pollutants via

consumption of seafood and wildfowl is currently unclear; however, the implications of exposure on public health should not be overlooked. For example, small-molecule additives in plastics, including 2,2-bis(hydroxyphenyl)propane (bisphenol A, or BPA) and polybrominated diphenyl esters, are known endocrine disruptors in humans.²³

The most often quoted definition of sustainability comes from the United Nations World Commission on Environment and Development, where sustainable development is described as “meeting the needs of the present without compromising the ability of future generations to meet their own needs”.²⁴ This definition seems straightforward, yet sustainability can be very difficult to quantify. Life cycle analysis (LCA) seeks to consider the environmental impacts of a product from cradle to grave and is a valuable tool in environmental policy. However, LCAs often rely on rough and unverifiable estimates of energy fluxes and on system boundaries that can be arbitrarily defined.^{25,26} Moreover, while environmental considerations are undoubtedly an important component of sustainability, social and economic factors must also be considered, as exemplified by triple bottom line (environment, social, and financial) accounting and sustainability reporting frameworks.^{27,28}

The development of polymers that are sustainable from combined environmental, societal, human health, and economic perspectives is a major challenge facing the field of polymer science. Academic scientists often have the latitude to work on basic research problems that deepen our understanding and *could* have long-term practical repercussions but to some seem to have limited immediate relevance to contemporary problems. Looking back at the early issues of *Macromolecules*, it is obvious how fundamental research published in this journal shaped the development of polyolefins, which today dominate the synthetic polymer industry. We are confident that these tremendous successes in fundamental research will now be duplicated in the development of polymers that are safe in production and use and have sensible end of life options. It is our view that confronting this problem is not a luxury for polymer scientists but a responsibility. Fortunately, the associated challenges simultaneously offer both intellectually and commercially rewarding opportunities. We are optimistic that human ingenuity will prevail in the service of society.

In this Perspective we discuss five areas of contemporary polymer research (renewable feedstocks, degradable materials, chemical recycling, reprocessable thermosets, and advanced catalysis) that we believe will play an integral role in shaping future development of a sustainable polymer industry. We focus on representative publications from *Macromolecules*, the flagship journal for polymer science over the past half-century, and describe both historical advances and recent work. To begin, we first explore a mainstay for sustainable polymer research: the development of renewable feedstocks for polymers that reduce our reliance on petrochemical feedstocks.

II. RENEWABLE RESOURCES

The current petrochemical industry is both highly integrated and centralized. Whereas the cracking of naphtha yields olefins (specifically ethylene, propylene, and mixtures of C_4 and C_5 molecules), catalytic reforming is used to produce aromatics (namely benzene, toluene, xylene, and naphthalene). These platform chemicals are not only valuable precursors for the synthesis of nearly all common chemical products but also frequently useful monomers in their own right. For example, ethylene is polymerized directly to produce polyethylene and is

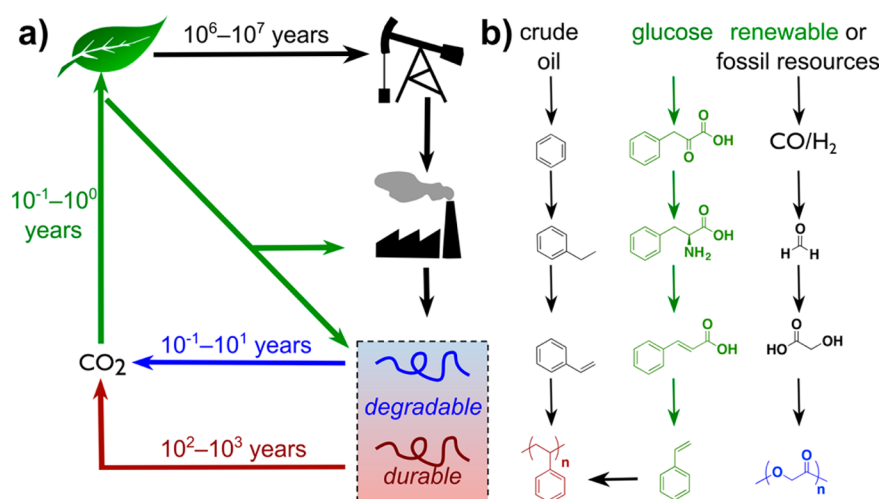


Figure 2. (a) Diagram showing the relative time scales of cycles for production of synthetic polymers from fossil fuels and directly from biomass. (b) Example syntheses of polystyrene (a representative durable plastic) using two different methods from two different feedstocks. Whereas the industrial method uses benzene from crude oil to make styrene in two steps, the biosynthetic path using an engineered Shikimate pathway to overproduce the key intermediate phenylalanine from glucose, as described by McKenna and Nielsen.³¹ Also shown is a method for the production of poly(glycolic acid) (a representative degradable polymer) using synthesis gas.

used as a precursor for the synthesis of other monomers including ethylene oxide, dichloroethylene, tetrafluorethylene, ethylene glycol, and vinyl acetate. As summarized in Figure 2, this paradigm is viewed as problematic by some, as the time scale on which petroleum forms from biomass is much slower than the rate at which the polymers products are made, used, and discarded.⁶ Replacing well-known and widely utilized petroleum-derived monomers with renewable alternatives is appealing and has attracted a great deal of research in both academia and industry.^{29–33} The utilization of bio-derived polymers is supported by recent government incentives, e.g., the USDA BioPreferred Program.³⁴ This program, and others like it, has helped to increase consumer awareness of and demand for bio-based products.

One approach that has attracted considerable research effort is the synthesis of traditional monomers and platform chemicals from renewable resources (illustrated in Figure 2b).³⁵ (In a recent editorial Miller arranges a number of synthetic polymers into a sustainability matrix arranged by feedstock renewability and polymer degradability, another useful representation.³⁶) It seems reasonable, given recent history, to assume that nearly any petrochemical monomer can be made from a renewable resource on a lab scale given sufficient chemurgic skill. Indeed, routes for the synthesis of commodity petrochemicals, including ethylene,³⁷ ethylene glycol,³⁸ terephthalic acid,³⁹ *p*-xylene,^{40,41} benzene,⁴² toluene,⁴³ xylene,⁴⁴ succinic acid,⁴⁵ isoprene,⁴⁶ and 1,4-butanediol⁴⁷ from renewable resources have already been described. Whether or not any of these examples are feasible on an industrial scale and are more sustainable than the status quo is another matter altogether.⁴⁸ An obvious advantage of using bio-derived monomers as drop-in replacements is that they are compatible with the current infrastructure, provided similar purity levels can be achieved. Moreover, the markets for polymers derived from these monomers are already well established. However, a significant challenge is that these bio-derived monomers must compete with their petrochemical counterparts from a cost perspective. As long as oil prices remain low and the utilization of petrochemical feedstocks is not discouraged, it will be difficult for renewable production methods to compete with steam

cracking. In the long term we expect increases in the cost of fossil resources combined with governmental policies that incentivize a low carbon economy will foster the growth of the renewable/bio-based industry.

While it may be tempting to assume a bio-sourced polymer will be more sustainable than a nonrenewable competitor, this is often incorrect. Such an evaluation relies heavily on one's operational definition of sustainability and on assumptions about product disposal, which may not be known. For example, while more total energy may be required to produce low-density polyethylene (LDPE) from sugar cane than from petroleum, if the LDPE is landfilled after use, the global warming potential of the bio-derived plastic can be considerably lower.^{49,c} Contriving efficient ways to make traditional commodity polymers such as polyethylene,⁵⁰ polypropylene,³⁰ poly(ethylene terephthalate),³⁹ and polystyrene^{33,32,31,51} from renewable resources has been and continues to be an important area of research. In *Macromolecules*, however, the design, synthesis, and development of new, bio-based polymers with improved sustainability have been given much more emphasis.^{52–58}

Designing entirely new renewable polymers that can compete with existing petrochemical polymers requires integrated knowledge of polymer structure–property relationships and selection of abundant, low-cost, starting materials that can be produced on an industrial scale. While polymer scientists and engineers tend to focus on the former, the latter is also important as it dictates to a large degree which polymer structures can be practically accessed. Two major strategies that have been successfully exploited are *biorefining*, isolating abundant biochemicals (e.g., sugars, oils, fats, and amino acids) or biopolymers (e.g., lignin, cellulose, starch, chitin) from natural sources, and *bioengineering*, using genetically modified microbes to produce natural and non-natural metabolites. In the bioengineering category, lactic acid, propanediol, and succinic acid stand out. A number of excellent reviews discuss the merits of these approaches.^{59–65}

Foundational studies have focused on renewable biopolymers derived from natural sources directly and then modified chemically to adjust the property profile. An example of this

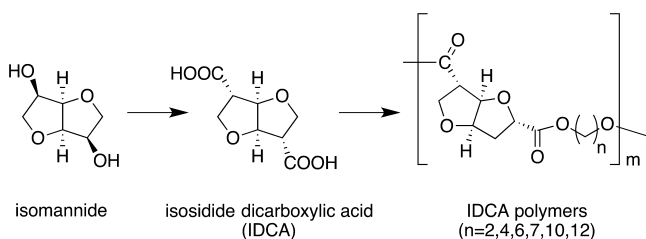
approach is the study of the structure and physical properties of polyhydroxyalkanoates (PHAs), copolymers that are produced naturally by bacteria as a form of energy storage.^{66–69} These thermoplastics were commercialized by the Imperial Chemical Industries as early as 1980 and remain prominent in the bioplastics market today. The synthesis, chemical modification, and study of PHAs continue to be active areas of research.^{70,71}

Regarding metabolic engineering, intermediates that are only a few biochemical steps removed from major metabolic pathways (e.g., glycolysis or the citric acid cycle) are attractive biosynthetic targets as they can often be produced in high yield, productivity, and titer and as a general rule are nontoxic. However, a major challenge is that they are, by definition, consumed in a number of many catabolic and anabolic pathways, which limit the overall productivity and yield of the desired product. While it may be desirable to eliminate these reactions, doing so may affect cell growth, plasmid retention, and survival; effective design therefore necessitates a systemwide understanding of the whole cell.⁷²

Organic acids have long been an attractive platform biochemical for a renewable polymer industry. In particular, organic acids with keto or hydroxyl groups are attractive building blocks for the direct synthesis of polyesters; further chemical modification can yield diols or diamine monomers for polyurethanes. Examples of organic acids that are both accessible via biotransformation or fermentation and are of commercial interest include glycolic (C2), 3-hydroxypropionic (C3), lactic (C3), succinic (C4), itaconic (C5), muconic (C6), and adipic (C6) acids. Of these, lactic acid is already produced on a scale of approximately 400 000 tons annually, led by the companies Galactec, Natureworks, and Purac. Bio-derived 3-hydroxypropionic acid, itaconic acid, and succinic acid have also been explored commercially, albeit on much smaller scales.⁷³ A couple recent examples concerning abundant renewable starting materials for advanced polymers are highlighted below.

One often-used example is the family of monomers that can be accessed from sugars. Of the numerous sugar derivatives available, isohexides from the dehydration of six-carbon sugar alcohols have received a great deal of attention. Isosorbide is the prototypical example of a rigid diol that has been incorporated into numerous polymers given that it is susceptible to several condensation polymerization protocols. However, the secondary alcohols on these derivatives are usually of low reactivity. Thus, strategies that allow for the incorporation of this rigid moiety into polymers in a more facile manner are of interest. Along these lines, the groups of Noordover, van Es, and Koning have developed a synthesis of isoidide dicarboxylic acid (IIDCA)⁷⁴ and used it for the preparation of various polyesters using a range of diol monomers (Scheme 1).⁷⁵ The authors were able to generate relatively high molar mass polymers with IIDCA using

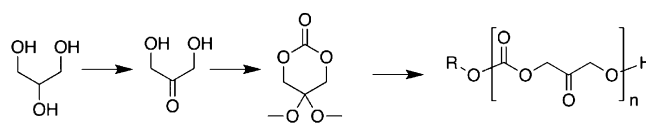
Scheme 1. Structure of Isosorbide and IIDCA Polymers⁷⁵



dibutyltin oxide as the catalyst. The IIDCA polyesters were semicrystalline with relatively low glass transition temperatures. This group of researchers went on to develop isoidide dimethanol (IIDM) from the hydrogenation of IIDCA and used that diol and other rigid diols in the preparation of polyesters with IIDCA to give all isohexide-based polyesters.⁷⁶

Combining bio-based molecules in clever ways can facilitate the synthesis of new materials with useful and unprecedented property profiles. In 2012, Simon et al. demonstrated an interesting approach by combining dihydroxyacetone, a product of microbial fermentation, with glycerol (the abundant byproduct from biodiesel production).⁷⁷ In fact, they showed that dihydroxyacetone could be prepared from glycerol through a selective catalytic oxidation process (Scheme 2).

Scheme 2. Synthesis of MeO₂DHAC Monomer and Resulting Polycarbonate⁷⁷



Conversion of this molecule to the corresponding dimethyl acetal (MeO₂DHAC) allowed for the catalytic oxidative carbonylation to the corresponding cyclic carbonate in good yield. From methanol, carbon monoxide, oxygen, and glycerol—all renewable compounds—the authors prepared the cyclic monomer MeO₂DHAC that was susceptible to ring-opening polymerization. The organocatalyzed polymerization of this monomer in the melt proceeded to near quantitative conversion with little residual monomer; similar copolymerizations with ϵ -caprolactone were also carried out successfully. Conversion of the acetal to the corresponding ketone was accomplished to give a series of materials with high melting points and thermal degradation temperatures. Although the biodegradation of the product polymers was not explored, given the known reactivity of aliphatic polyesters and polycarbonates, it is likely that they are susceptible to hydrolysis. Such degradation is the focus of the next section.

III. DEGRADABLE MATERIALS

Although the creation of bio-derived durable plastics will help address consumer interest in renewable products, these materials suffer from the same end of life issues as traditional petroleum-derived plastics. Bio-derived and compostable plastics have the potential to solve the disposal issues but come with unique challenges. Although a few bio-based compostable polyesters have been commercialized, the development of this industry has been lethargic due to a lack of composting infrastructure. Other technical challenges include removal of these new polymers from existing recycling streams (where they are often viewed as contaminants) and tuning their property profiles to match existing petroleum-derived polymers. One complicating factor is that many consumer products (e.g., those shown Figure 3) are manufactured using combinations of different polymers that degrade at different rates and by different mechanisms. The optimal solution would involve a chemical switch that would render a durable product susceptible to rapid degradation at the end of its life—a challenge because, excluding extreme examples (e.g., polar or desert climates), environmental temperature and humidity are

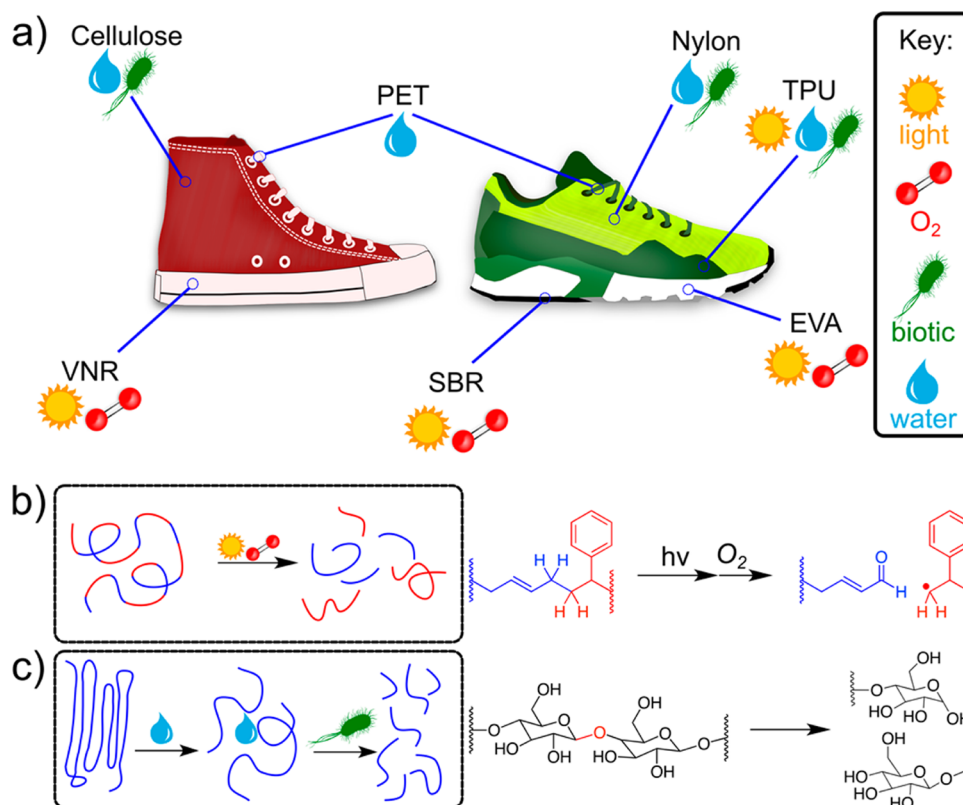


Figure 3. (a) Given the ubiquity and specialized nature of athletic shoes, they serve as a good example of consumer products made from a combination of different polymers. The sneaker on the left is comprised of a renewable cellulose canvas and renewable vulcanized natural rubber (VNR). While the former degrades relatively quickly (~ 10 years) above ground, the latter degrades much more slowly (50–100 years in the same location) via a photo-oxidative mechanism. These degradation estimates are given in Minneapolis, MN, a location with a continental climate (Köppen type Dfa). The running shoe on the right is composed of a nylon mesh vamp, a polyurethane (TPU) quarter, a poly(ethylene-co-vinyl acetate) (EVA) midsole, and a styrene–butadiene rubber (SBR) outsole. Whereas nylon and TPU are susceptible to hydrolysis and, in some cases, biodegradation, EVA and SBR degrade via photo-oxidative mechanisms. Both shoes contain poly(ethylene terephthalate) (PET) laces which degrade extremely slowly due to their high hydrophobicity but are susceptible to hydrolysis. (b) Cartoon representation and chemical reaction showing the photo-oxidative cleavage of polymer chains in SBR.⁷⁸ (c) Cartoon representation of degradation through hydrolysis, which may or may not be assisted by the action of microbes. This degradation rate is controlled both by the crystallinity and hydrophobicity of the polymer, as well as the type of bond broken.

not typically much different than range that most polymers are subjected to during normal use.

Degradable polymers hold tremendous promise. However, there are several practical aspects of degradable polymers that limit their utility. One dilemma is that the rate of degradation is highly dependent on the eventual fate of the polymer. A polymeric material could end up in a landfill, in a compost facility, or released in the environment as pollution. Unfortunately, only a small subset of commercial polymers is compostable, and only a small fraction of those actually end up in a composting facility. In landfills, even polymers that are designed to be compostable (e.g., poly(lactide)) may not degrade because of the limited water and available oxygen.⁷⁹ It has been argued that renewable polymers, including PLA, may serve as a carbon sink if landfilled based on LCAs. We note such an assumption is probably an oversimplification.⁷⁹ In the environment the degradation rate varies widely and is dependent on temperature, humidity, and oxygen available.

The design of polymers that are robust in use yet readily degrade if discarded indiscriminately in the environment is a huge challenge. There have been a number of recent efforts to selectively trigger degradation using light, temperature, or other stimuli. This may not be a practical approach to preventing the accumulation of polymer pollution in the environment; oceans

are dark, cold, and, excluding a small surface layer, largely anoxic—conditions that do not facilitate degradation of most polymers. However, these efforts are notable from a waste management perspective as such a strategy could be used to expedite chemical recycling (as discussed in the next section) or to improve compostability.

Nearly a decade ago, Kitamura and Matsumoto explored the synthesis of polyperoxide poly(($-$)lactide) (PLLA) branched polymers and gels.⁸⁰ These materials were synthesized using an interesting approach; dienyfunctional telechelic PLLA was first prepared via polymerization of LLA monomer from a sorbic alcohol initiator (or ethanol initiator with a sorbic acid terminator), and then graft polymers were synthesized by radical copolymerization of these macromonomers with oxygen. Bisdiényfunctional PLLA macromonomers were also synthesized and copolymerized with oxygen to create gels. Both the branched and gel materials degraded on heating to produce a linear polyperoxide and PLLA. Intriguingly, peroxy linkages, such as those utilized in this work, are also pH sensitive, susceptible to UV degradation, and vulnerable to peroxidase enzymes. These degradable peroxy junctions are therefore also attractive for controlling the lifetime of products generated using not only PLLA but also other thermoplastics.

More recent work in this area has focused on enhancing the degradation rate of polymers that are already biodegradable. Almutairi et al., for example, prepared poly(lactic acid-co-glycolic acid) (PLGA) derivatives with stimuli-responsive pendant protected nucleophiles.⁸¹ Deprotection of the nucleophiles, affected by irradiation with UV light, resulted in degradation via an intramolecular cyclization reaction to form a substituted five-membered ring lactone. Although the motivation of this work was in fact triggered degradation *in vivo* for drug delivery applications, it is conceivable that a similar system could be exploited for other applications (e.g., disposable packaging), provided the polymers can be produced economically on a large scale.

Hydrolytically sensitive polyacetals can be designed to degrade in aqueous environments.⁸² Samanta et al. recently described a set of simple polyacetals from the acid-catalyzed step growth polymerization of diols with divinyl ethers.⁸³ The molar masses of the polymers produced were rather low, but they showed tunable solution behavior in water. The cloud points could be readily tuned through the hydrophilic/hydrophobic balance in the monomers. The polyacetals were relatively stable at neutral pH but readily degraded under acidic conditions. High molar mass versions of these polyacetals may hold promise for water-degradable polymers for applications in, for example, personal care products.

Hedir et al. recently reported an attractive method for the preparation of functionalized degradable aliphatic polyesters by the controlled radical ring-opening copolymerization of 2-methylene-1,3-dioxepane with various monomers including vinyl acetate.⁸⁴ In this report a RAFT/MADIX polymerization protocol was followed to give a range of copolymers with controlled molar mass. The resultant poly(ϵ -caprolactones) were degradable under aqueous base conditions, as expected. This method will help expand the range of degradable polymers available by exploiting radical methods as opposed to typical cyclic ester ring-opening reactions.

An inescapable challenge is to design materials in such a way that the byproducts of the degradation are nontoxic. While polymer scientists often neglect this area of research in initial phases of the development of new materials for consumer applications, it is much more thoroughly investigated in the arena of biomaterials. It is worth noting that medical applications (including drug delivery or degradable implants) may serve as a gateway for the introduction of degradable polymers into other commercial markets. In the early 2000s, PLA was limited to a medical suture market, sold by DuPont for ~\$1000 per kilogram.⁸⁵ Scientific and technological breakthroughs eventually facilitated production at a volume and cost (~\$2/kg) that today allow PLA to also be used in packaging applications. The products of polymer degradation can also have value, and as such chemical recycling is an attractive strategy to recovery value from plastics at their end of life.

IV. CHEMICAL RECYCLING

Physical recycling methods are largely designed to preserve molar mass and physical properties in the recycled material. Unfortunately, many mechanical processes used to recycle plastics lead to some property deterioration, e.g., discoloration or loss of strength caused by decreases in molar mass or contamination with food residue or other types of polymer. Only rarely are postconsumer recycled plastic resins used to make the original product. The terms *downcycling* and *cascade*

recycling have thus been used to describe such traditional mechanical recycling. Poly(ethylene terephthalate) (PET) stands out as one of the most recycled polymers. About 30% of PET is recycled on first use compared to 14% for all thermoplastics.⁸⁶ However, as summarized in Figure 4, even

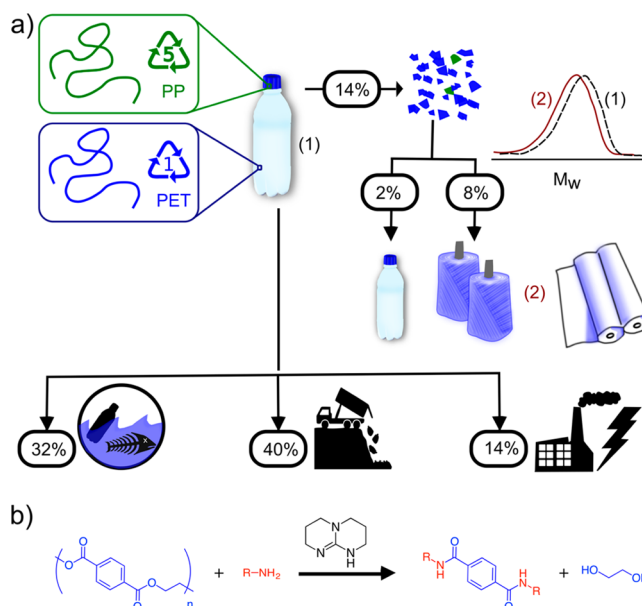


Figure 4. (a) Diagram showing the possible fates for thermoplastics after first use: collected for mechanical recycling (14%), landfilled (40%), leaked into the environment (32%), or incinerated for energy (14%). Of the 14% collected for recycling, 14% (2% of total) is lost, 57% (8% of total) is used to make lower quality resin for different applications, and 28% (2% of total) is used to make similar quality resin for products of similar applications. The inevitable loss of value upon multiple recycling cycles is due to property deterioration, for example, the loss in molar mass going from (1) virgin resin to (2) recycled material. The data for this figure were taken from ref 9. (b) Example reaction for the chemical recycling of PET. The specific chemistry is reported in detail in ref 88.

PET is not immune to downcycling; while over 85% of recycled PET comes from food and beverage containers, the majority of postconsumer recycled PET is used to make fiber for carpet or clothing, which is generally not recycled after use.⁸⁶

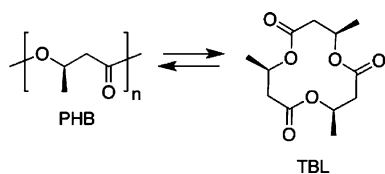
One strategy that has been gaining serious attention is depolymerization of polymers to allow the reclamation of high value small molecules from discarded polymers. This *chemical recycling* generally aims to retrieve the monomers in pure enough form to allow the recovered monomers to be polymerized into materials with the same quality and functionality as the original. The key for this type of strategy is to use the polymer as a starting reagent and generate high purity monomer using simple and efficient transformations that do not compromise the economics of the overall approach. Chemical recycling may also be used to generate other high-value products, rather than the starting monomer. As an example, PET can be cleaved by a variety of reagents including water, alcohols, acids, glycols, and amines. These processes give a variety of small-molecule products depending on the reactant used.⁸⁷ As a specific example, Hedrick and co-workers have investigated the organocatalyzed aminolysis of PET to produce a variety of terephthalamide monomers.⁸⁸

Although PET is a thermoplastic and as such can be melt reprocessed, similar strategies have also been used for the

chemical recycling of thermoset materials, which, due to a chemically cross-linked structure, are difficult to reprocess via conventional methods. Our lab has reported the synthesis of chemically recyclable polyurethane foams⁸⁹ and, more recently, thermoset elastomers⁹⁰ that in the presence of a transesterification catalyst depolymerize to a lactone monomer, β -methyl- δ -valerolactone, in high purity and yield. The chemical recyclability of these materials relies on the relatively low ceiling temperature: at room temperature in the bulk the polymerization reaches a maximum of $\sim 90\%$ conversion, while the bulk monomer is predicted to not polymerize above $\sim 225^\circ\text{C}$.⁹¹ The concept of thermodynamic recycling of polymers is an active and important area of research, with recent advances by Chen and co-workers being especially relevant.⁹²

There are also a number of earlier examples of thermodynamic recycling where the polymer is degraded to make other small molecules (e.g., cyclic oligomers) rather than the original monomer. A noteworthy publication by Melchior et al. explored the depolymerization of poly[(*R*)-3-hydroxy butyrate] (PHB), a degradable biopolymer, to the corresponding cyclic trimer (TBL).⁹³ Through heat capacity and bomb calorimetry experiments, the authors showed the thermodynamic feasibility of depolymerization of PHB to give TBL (Scheme 3).

Scheme 3. Degradation of Polyhydroxybutyrate To Yield TBL⁹³



They were able to carry out this transformation at high temperature either in the melt state or in solution. In some cases, the authors achieved up to 80% cyclic oligomers. A key aspect of any thermodynamic recycling strategy is the subsequent polymerization of the recovered cyclics (usually at lower temperature). In fact, Melchior et al. were able to convert TBL back to PHB, even though their thermodynamic analysis suggested that this would not be feasible. They discuss the factors that lead to this apparently contradictory result (e.g., monomer–polymer interactions and polymer crystallinity) and highlight the limitations associated with their calorimetric analyses.

Because large cyclic oligomers are potential products from the chemical recycling of polyesters and polycarbonates, the polymerization of these species is of particular importance. One early example by Brunelle and Shannon outlines the formation and subsequent polymerization of cyclic oligomers derived from bisphenol A.⁹⁴ In that work, they showed how to convert these cyclic oligomers into high molar mass polymers in an entropically driven polymerization. This groundbreaking publication influenced subsequent studies on the macrocyclic oligomer polymerizations, including the ring-opening polymerization of cyclic oligomers from 3-hydroxypropionic acid.⁹⁵

In some cases, thermal degradation of a polymer can be controlled through choice of catalyst to recover monomer or another valuable small molecule that can be subsequently polymerized. In a recent study by Nishida et al. the cyclic diester, tetramethyl glycolide, was prepared from biomass-derived lactic acid or pyruvic acid derivatives.⁹⁶ Not only could

tetramethyl glycolide be polymerized using traditional anionic polymerization initiators to obtain high molar mass polymers in good yields, the glass and melting transition temperatures of the resultant polymer were higher than those of poly(lactide) (an encouraging breakthrough because the modest T_g of PLA, 55°C , limits its use at higher temperatures). Moreover, in the presence of a tin catalyst, the polymers could also be catalytically degraded to recover tetramethyl glycolide in greater than 80% yield. In contrast, in the presence of a different catalyst, magnesium oxide, the polymer degraded to give similarly high yields of methacrylic acid, another polymerizable molecule. This example highlights the utility and versatility of catalysis for the chemical recycling of biomass-derived polymers.

Simple thermal degradation of polymers can also be achieved in condensation polymerizations by assembling polymers through the formation of weak covalent bonds. By controlling the nature of the condensation structures, it is possible to create polymers that can be thermally depolymerized back to their corresponding monomers. Otsuka et al. reported a particularly nice example of this in the synthesis of a new class of main chain poly(hemiacetal esters) through the condensation of ethylene glycol divinyl ethers and common diacids.⁹⁷ The corresponding poly(hemiacetal esters) were thermally stable up to about $150\text{--}200^\circ\text{C}$ in most cases but rapidly lost mass at higher temperatures. Presumably this degradation was caused by reversion of the polymer back to the starting monomers. Poly(hemiacetal esters) can also be prepared by ring-opening polymerization and have been shown to be hydrolytically degradable.^{98,99} This class of polymers highlights the contemporary importance of developing polymers with designed degradation pathways.

Polymers containing hydrolytically cleavable groups along the backbone such as esters, acetals, amides, or ethers are often described as degradable. However, all polymers are degradable, provided one is willing to wait long enough or heat to a high enough temperature. The two largest volume polymers, polyethylene and polypropylene, are hydrocarbons consisting of stable C–C and C–H bonds; under normal environmental conditions, these break down slowly via a photo-oxidation pathway. These polyolefins can be broken down more quickly using high-temperature pyrolysis ($>400^\circ\text{C}$). Analogous to steam cracking, this process is energy intensive and produces carbonaceous byproducts.¹⁰⁰ Given their abundance, selectively and efficiently degrading polyolefins to yield useful products would be a significant advance in chemical recycling. If such processes could be rendered efficient enough to be cost-effective, there would be value in waste polyethylene as a feedstock for, as an example, diesel fuel.

Jia et al. recently investigated the iridium-catalyzed alkane cross-metathesis of polyethylene and low molar mass (light) alkane additives under relatively mild conditions.^{101,102} Using this process, high molar mass polyethylene can be degraded down to compounds that can be used as liquid fuels and waxes, provided enough of the light alkane is added. Under the preferred catalytic conditions, only alkanes were produced. In a particularly compelling example, a commercial grade high-density polyethylene containing antioxidants and other stabilizers was degraded into liquid and wax materials. Multiple grades of PE, including ultra-high molecular-weight, linear low density, low density polyethylenes, and postconsumer polyethylene waste, were efficiently broken down. Interestingly, the distribution of alkanes in the final products could be controlled

by the choice of the catalyst system. This example helps to highlight the critical role that catalysis will play in sustainable polymer research in general and controlled polymer degradation in particular.

V. REPROCESSABLE THERMOSETS

Replacing plastics employed in single use packaging applications with renewable and degradable alternatives is particularly attractive from an environmental perspective. However, a major challenge is to develop new polymers that can compete with established commodity thermoplastics in cost. Because of low production cost and price of commodity plastics, it may be easier to invent cost competitive renewable polymers for higher value engineering and specialty applications. However, it is difficult to design materials that are both degradable and high performance. Indeed, as described by Mark in an early review, traditionally resistance against chemical deterioration is one characteristic that helps to define a high-performance polymer.¹⁰³ In many applications, the terms *degradable* and *high performance* are considered to be mutually exclusive. We argue that triggered degradation after use could also be viewed as a desirable performance characteristic in the future.

The commercial success of new renewable and degradable polymers will therefore hinge on the invention of low-cost, mechanically tunable materials. Optimally, the degradation rate of these materials should be matched to their desired applications. As mentioned in a previous section, an appealing strategy is to design so-called smart polymers that contain chemical responsive switches that can be tripped at end of life to trigger degradation or enable either reprocessing or chemical recycling. In theory, such strategies could be used for thermosets as well as thermoplastics.¹⁰⁴ A knock-on effect will be that thermoset products made from these dynamic materials will be capable of repair or self-healing when damaged (Figure 5a). We outline a few examples below to highlight the versatility and potential of this strategy, focusing first on a class of materials, thermosets, which have traditionally been difficult to reprocess or recycle.

In particular, a number of recent efforts have focused on the reversible cross-linking of rubber (a paradigmatic example of a thermoset). Currently, postconsumer rubber products are typically landfilled, burned for energy recovery, or downcycled for use in a variety of products (e.g., artificial turf).¹⁰⁵ Modifying the structure of thermosets in general and rubber in particular to design for recyclability is appealing from a sustainability perspective, and a number of different strategies have been explored. One early work in this area by Chino and Ashiura involved the synthesis of polyisoprene substituted with reversible hydrogen bonding moieties (Figure 5b).¹⁰⁶ These materials were prepared using an efficient two-step process. Specifically, reactive maleated polyisoprene was first synthesized via addition of maleic anhydride, and then hydrogen bonding moieties were introduced through the reaction of 3-amino-1,2,4-triazole with the maleic anhydride substituents. Similar to vulcanized natural rubber, physically cross-linked samples were found to have low creep and improved mechanical properties relative to uncured polyisoprene. Like thermoplastic elastomers, however, the hydrogen bonded materials could be reformed multiple times without loss of performance.

Others have explored the use of reversible covalent bonds for cross-linking rubber. While thermoset rubbers that are only lightly chemically cross-linked can display some inherent

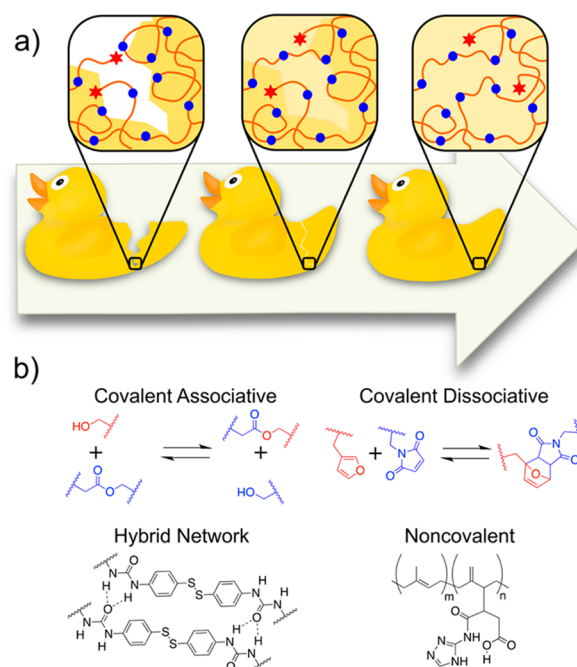


Figure 5. (a) Diagrammatic representation of repair of a damaged thermoset product (a rubber duck made of a covalently cross-linked polymer network). The cartoon representation of the healing process is typical of a covalent associative network. (b) Representative examples of different classes of reprocessable materials discussed above. The specific noncovalent (hydrogen bonding) network shown is described in ref 106, while the hybrid network (which combines hydrogen bonding interactions with a dynamic disulfide bonds) is described in ref 113.

adhesion and healing properties due to the reptation of dangling chains, this generally comes at the expense of mechanical performance. However, it has been demonstrated that addition of dynamic covalent cross-links greatly increases healing.¹⁰⁷ The key potential advantages of this strategy over a supramolecular cross-linking approach are improved solvent resistance, decreased creep, and higher thermal stability. In short, materials cross-linked with reversible covalent bonds have the potential to be remolded or chemically recycled without sacrificing the advantages of a chemically cross-linked material.

As a recent example, Picchioni and co-workers explored the use of Diels–Alder (DA) chemistry to prepare thermoreversibly cross-linked elastomers from maleated rubber modified with furfurylamine groups.¹⁰⁸ These pendant groups act as DA dienes; addition of bismaleimide small molecules resulted in insoluble cross-linked materials that could be reprocessed by heating. A slightly earlier publication by Yin and co-workers described the use of thiol–ene click reactions to prepare furan-substituted polybutadienes. These materials were also cross-linked using reversible DA reactions with a bismaleimide.¹⁰⁹ Both of these studies are interesting examples; however, since one key advantage of vulcanized rubber over thermoplastic elastomers is increased mechanical stability at high temperatures, the use of temperature as an external trigger for healing is not ideal.

Dynamic cross-linking reactions viable under lower temperature conditions have also been explored. In one interesting example, Endo and co-workers prepared styrene derivatives with pendant tricarbonyl moieties. Owing to the high reactivity

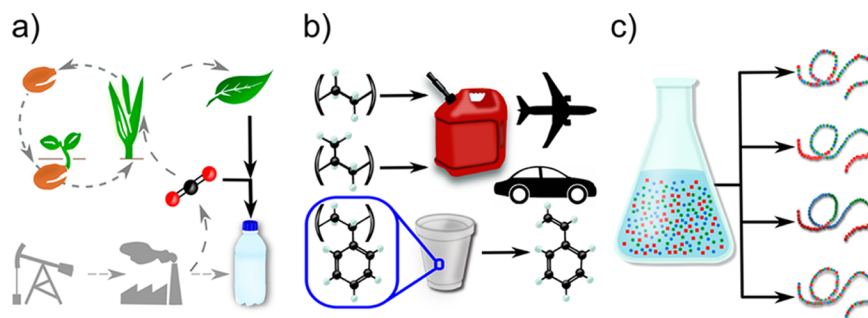


Figure 6. (a) The development of new catalysts will play a critical role in transforming low value, low energy waste products (e.g., CO_2) and nonfood agricultural products (e.g., cellulose and lignin) into more sustainable polymers. (b) As discussed in previous sections, the chemical recycling of polyolefins and styrenic polymers is possible; however, breakthroughs in catalysis will be required to make these processes economical. (c) A longstanding challenge in catalysis is sequence control, defined as the ability to polymerize a mixture of monomer selectively to obtain statistical, blocky, or alternating architectures. The ability to do this with robust catalysts on mixtures of renewable monomers would enable the facile creation of high value sustainable polymers.

of the electrophilic central carbonyl group, the resulting polymers were found to undergo water–alcohol exchange reactions at room temperature.¹¹⁰ Whereas in water the polymer existed as a linear gem-diol hydrate, in an acetone solution with 1,6-hexanediol a cross-linked gel formed. Conversely, boronic ester networks, investigated in recent examples by the Sumerlin and Guan research groups, undergo exchange reaction under ambient conditions but are stable in water and humid environments.^{111,112}

By exploiting multiple distinct dynamic cross-linking strategies in tandem, it may be possible to design cross-linked materials with relatively low processing temperatures for robust recycle applications. However, we note a significant side effect of this healing ability is the tendency of the materials to creep over time, which may preclude their use in many applications. To avoid this problem, some researchers have investigated materials containing reversible supramolecular interactions in addition to covalent cross-links.¹¹³ A recent interesting example by Michaud and co-workers explored rubbers including a combination of reversible hydrogen bonding interactions and chemical cross-links.¹¹⁴ These particular materials were synthesized via condensation of polyacids functionalized with hydrogen bonding reactive groups using di- and tetrafunctional peroxides. These cross-linked systems retained the ability to heal at room temperature and exhibited much higher creep resistance relative to a physically cross-linked control.

Cross-linked polymers that can rearrange through associative (isodesmic) reactions have also been explored. Seminal work by the Leibler group in this area demonstrated that these *vitrimers* are strong glass formers that behave as thermosets below a freezing transition but can flow like viscoelastic liquids at higher temperatures.^{115,116} These materials are thus reprocessable but maintain a constant number of covalent bonds. The first examples of these network compounds were polyester epoxy resins impregnated with a zinc catalyst;¹¹⁷ however, subsequent publications have explored renewable or partially renewable alternatives, including urethane-cross-linked-poly(lactide),¹¹⁸ fatty acid silica-reinforced nanocomposites,¹¹⁹ and citric acid cross-linked with epoxidized soybean oil.¹²⁰ Although pioneering publications in this area focused on dynamic metal-catalyzed transesterification reactions, typically occurring at high temperatures, more recently polyhydroxyurethanes have demonstrated exchange reactions in the absence of catalyst due to mechanically activated transcarbamoylation reactions.¹²¹ An alternative synthetic route, which avoids the use of potentially

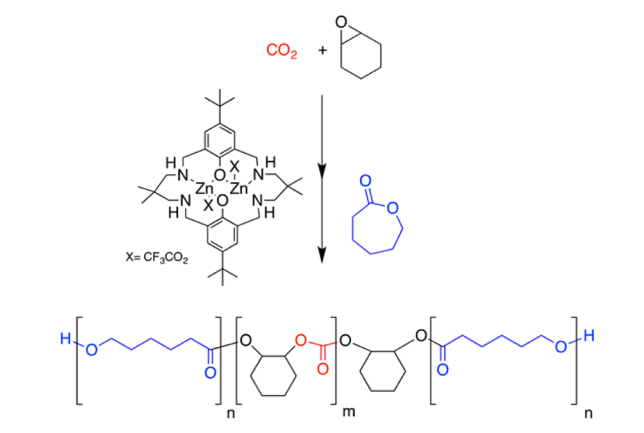
toxic isocyanates, involves copolymerization of six-membered cyclic carbonates and amines. Other types of associative reactions used to form vitrimer-like materials have recently been summarized in a review by Du Prez and co-workers.¹²² In several of the above examples, catalysts play a key role in facilitating reprocessing. Undoubtedly, catalysis will continue to play a critical role in the future of sustainable polymers in a broader sense.

VI. ADVANCED CATALYSIS

Advances in catalysis have revolutionized the polymer industry, as exemplified by the evolution of Ziegler–Natta catalysts for the conversion of simple olefins into the largest volume commercial plastics. Catalysis has played a very important role in the development of sustainable polymers. Indeed, the chemistry discussed in the previous sections relies on the use of efficient catalysts. This is especially true in the design of polymers from low value waste products (e.g., CO_2 or lignin and cellulose from agricultural byproducts) and the chemical recycling of polyolefins (Figures 6a and 6b, respectively). Another area in which catalyst development has been instrumental is in the synthesis of degradable polymers, specifically aliphatic polyesters and polycarbonates. Sequence specific polymers (Figure 6c) are another area in which developments in catalysis will be essential to future progress in the field. While the majority of polymerization catalysts to date have been organometallic complexes, metal-free organocatalysts have also made tremendous impact. The precision and efficient conversion of renewable, abundant monomers to high molar mass polymers with control over sequence, tacticity, and architecture is of paramount importance to enhance the utility and practicality of sustainable polymers.

Many important contributions to this area have been reported in *Macromolecules*. A recent relevant example by Paul et al. highlights the importance of catalysis for the synthesis of sustainable polymers.¹²³ The authors prepared an interesting set of block polymers using a mixture of ϵ -caprolactone, cyclohexene oxide, and carbon dioxide. First, they prepared a polycarbonate via the controlled alternating copolymerization of cyclohexene oxide and carbon dioxide and then used chain extension with ϵ -caprolactone to prepare a triblock polymer *in situ*. Interestingly, in the presence of all three monomers, the polycarbonate is produced exclusively, and poly(ϵ -caprolactone) is then generated upon removal of the carbon dioxide.

Scheme 4. One-Pot Synthesis of Degradable A-(B-*alt*-C)-A Triblock Polymers¹²³



Mechanistic studies are crucial for the development of new highly active, highly selective catalysts for the preparation of sustainable polymers. Building on seminal advances by the Coates group,¹²⁴ a more recent example by the Darensbourg group described the catalytic preparation of telechelic polycarbonates from carbon dioxide and epoxides.¹²⁵ In that work, the authors showed that water acts indirectly as a chain transfer agent in the cobalt-catalyzed copolymerization of propylene oxide and carbon dioxide via the initial rapid hydrolysis of propylene oxide to generate 1,2-propanediol as the active chain transfer agent. This careful mechanistic study has shed light on the induction period commonly observed in the copolymerization of epoxides with CO₂ and has helped to solve a mechanistic dilemma in the field.

In 2014, Ding et al. published a noteworthy paper which helped to elucidate the mechanistic details associated with the ring-opening polymerization of ϵ -caprolactone using discrete metal catalysts.¹²⁶ Most metal alkoxide-catalyzed polymerizations of cyclic esters reported in the literature fall under the mechanistic umbrella of coordination–insertion polymerizations. The relative importance of the coordination and the insertion steps had not previously been decoupled; hence, the relative importance of these two putative steps was not well understood. By exploring the polymerization of ϵ -caprolactone at high initial concentrations of monomer, Ding and co-workers were able to apply a saturation kinetics scheme that enabled separation of the initial coordination step and the subsequent alkoxide insertion step. This approach, combined with insights from theory, has facilitated other studies that have carefully teased apart these mechanistic details and are useful in the design of new catalysts using rational design principles.¹²⁷

As mentioned previously, polymers developed for niche applications in which degradation into innocuous small molecules is essential (e.g., degradable medical implants) can eventually penetrate higher volume commercial markets like packaging where degradation is environmentally beneficial but not required. To make this transition, industrial expertise is required to overcome the technological barriers that initially prevent efficient and low-cost production on a large scale. If correctly conducted, collaborations among industry and academia can create a positive feedback loop for innovation. A good example of this is the application of organocatalysts to polymer synthesis. Ingenious work by Waymouth and Hedrick has established a variety of new organocatalysts for anionic, group transfer, ring-opening, and condensation polymerization

techniques.¹²⁸ While this work was originally motivated by the desire to make metal-free polymers for electronics applications, it has had far reaching implications for research in sustainable polymers.

VII. OUTLOOK

In this section we offer our perspective on a subset of outstanding challenges for the polymer community in the broad area of sustainable polymers. We firmly believe that these will only be addressed through continued basic research in the area and that future publications in *Macromolecules* will ultimately lead to exceptional polymers that have both environmental and economic sustainability. Moreover, collaboration between the chemists, chemical engineers, and materials scientists is of paramount importance as advances in polymer science and engineering that integrate diverse sets of expertise will be critical to move the field forward. We frame these challenges with the following questions:

1. To What Degree Should Polymer Scientists and Engineers Rely on Sustainability Metrics To Guide Basic Research? We are often asked to quantify the sustainability of products and processes we develop on an academic lab scale. The short and honest answer is that a good deal of intuition goes into the evaluation, as it is simply not practical to perform full LCA on every material and every process that we explore *prior to embarking* on an attractive and chemically stimulating research project. This intuitive approach may be frustrating and unsatisfying, particularly to those accustomed to using the scientific method—the very individuals posing the original question. However, we argue that not only is attempting a full life cycle analysis not all that useful, that strategy can also stifle creativity and thwart innovation.

We recently investigated a polyester that could, in principle, be derived from low-cost and abundant lignin. However, the catalytic breakdown of lignin to give the target monomer precursor uses toxic, expensive, and rare-metal catalysts. To make matters even worse, at current selectivity levels, the overall process would be energy intensive. Finally, there are currently a multitude of practical considerations that preclude the use of lignin as a monomer feedstock. Any reasonable LCA would suggest this project would be impractical and the resulting polymer unsustainable using the *technologies and infrastructure that currently exist*. Our optimistic outlook is that as technologies continue to improve, the case for any particular sustainable polymer will continue to become more convincing. The development of low-cost catalysts capable of selectively producing small molecule precursors from lignin in a low-energy process is certainly a feasible and attractive target. Efficient conversion of these small molecules to monomers suitable for polymerization could be game changing if the product polymer has an attractive property profile, which is what we focus on in the basic research arena.

We argue that efforts to design and synthesize new polymers are also valuable as they help to establish what is chemically possible. Such investigations are also critical for understanding structure–property relationships and should not be preemptively abandoned—at least by researchers in academia—on the basis of LCA conducted using assumptions based on the status quo. Naturally, once a polymer product leaves the lab and begins the journey to commercialization, LCA analyses are very important to help identify areas that may compromise the overall sustainability metrics. A beautiful example of this is the collection of peer-reviewed LCA analyses that have been done

on poly(lactide).^{129–131} To this end, cooperation between the polymer industry and academic researchers is essential.

2. How Should the Cost of a Particular Material or Strategy Be Emphasized When Carrying out Basic Research in the Area of Sustainable Polymers? Given the current structure of the polymer industry, only low-cost solutions will be viable to make a substantive impact in sustainability. Does this mean that polymer researchers should limit their investigations to projects that utilize low-cost monomers, abundant catalysts, and simple, low-energy processes? Our answer is of course not. Again, judgment must be applied. Clearly, a polymer made from a monomer that can only be manufactured in a seven-step, low-yielding synthetic procedure from an expensive, low-abundance, natural product would be an impractical replacement for polyethylene. However, even monomers derived from relatively high-cost natural products can be converted into polymers that can be studied to learn what particular property profiles are accessible. This research can be used to inform the design of new materials with similar property profiles from more abundant starting materials. Again, this type of work can motivate chemists in other fields to work on new strategies to develop more efficient chemical transformations.

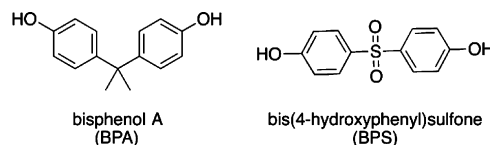
Anecdotally, we, together with the Tolman research group, explored the use of poly(menthene), a renewable aliphatic polyester with a low glass transition temperature, as a midblock for the synthesis of degradable thermoplastic elastomers. As described in a recent *Account*, we were successful in preparing the target materials and their performance as elastomers was outstanding.¹³² However, the cost of menthol, the starting material for poly(menthene), was prohibitively expensive (the price of menthol is about \$20 per kilogram) to hope for serious interest in the large volume elastomer market. Yet, this foundational work set the stage for subsequent investigations using a more cost-effective monomer that could be produced efficiently from sugar using *E. coli*.⁹¹

3. What Changes Can We Implement in the Immediate Future To Improve the Sustainability of the Current Suite of Synthetic Polymers? A topic of major importance that we have not discussed here, and one area in which we believe the sustainability of existing plastics can be drastically improved, is human health. However, to do so effectively will require cooperation between polymer scientists and medical health professionals. The current problem is not with the plastics themselves but in the additives used to increase the longevity or otherwise improve the performance of polymer products. These low molar mass species can leach out of the polymer matrix over time. Not only does this cause the product to weather, and in some cases fragment to form microplastics, the additives themselves can be toxic to humans or animals.

End of life issues notwithstanding, in use, the obvious benefit of increased product lifetime must be weighed against potential for human health risks. For example, concerns over the adverse health effects of lead resulted in a voluntary phase out of the use of lead stabilizers in water piping in 2005.¹³³ Similarly, the discovery that bisphenol, a monomer, plasticizer, stabilizer, and known endocrine disruptor, can be found at low levels in the blood of most humans has led to the introduction of BPA-free alternatives.¹³⁴ However, caution must be exercised when replacing small molecule additives of *known* toxicity with those of *unknown* toxicity—and regrettably often such caution is not exercised. As a specific example, a growing number of studies

now suggest that 4-hydroxyphenyl sulfone (Scheme 5), currently used in many BPA-free products, has nearly identical

Scheme 5. Structural Comparison of BPA and BPS



hormone mimicking effects as BPA.^{135,136} More communication between biologists, medical researchers, and polymer scientists and engineers will be beneficial when designing new materials.

One strategy that has been investigated to minimize potential toxicity is to develop polymeric stabilizers. As an example, Ellison and co-workers have made significant advances in using biomacromolecules, specifically natural melanin and synthetic melanin mimics, to increase the thermal stability of commercial thermoplastics with well-studied degradation behavior (e.g., PMMA, PP, and PS).^{137,138} Encouragingly, synthetic melanin was shown to increase the thermo-oxidative stability of PP and PMMA (by ~50 and ~90 °C, respectively) even at low levels of incorporation. More recently, work from the same group has explored the use of polydopamine nanocoatings as flame-retardant flexible polyurethane foams.¹³⁹ These renewable stabilizers are noteworthy for two reasons. First, as macromolecules they are less likely to leach from the polymer matrix than small molecule additives. Second, they are known to occur naturally *in vivo* and have very low toxicity.

4. What Lessons Can We Learn from Natural Biopolymers and What Unique Advantages Do Bio-derived Monomers Offer over Petrochemical Monomers? The highest volume and lowest cost synthetic polymer is polyethylene, manufactured globally on a combined scale of nearly 100 million tons per year. While impressive, this pales in comparison to 180 billion tons of cellulose annually produced by plants.¹⁴⁰ Semisynthetic materials manufactured from cellulose were the forerunners to today's modern plastics, yet as recently as a century ago only the elemental composition of cellulose [C₆H₁₀O₅] was known.¹⁴¹ Studies on the X-ray crystal structure of cellulose are of great historical importance to the field of polymer science;¹⁴² undoubtedly, there are *still* lessons that can be drawn from the way nature uses biopolymers in the sustainable design of synthetic polymers.

Cellulose comprises glucose molecules that are bound together with β -1,4 linkages (Figure 3b). However, a description of the primary structure of the polymer belies the hierarchical complexity and versatility of this material. Individual high molar mass, linear poly(β -glucose) chains assemble in small (4 nm diameter) *protofibrils* held together by hydrogen bonds. To minimize surface free energy, these coalesce into larger *microfibrils* composed of both amorphous and highly crystalline regions. Cellulose microfibrils may be collected into *macrofibrils* which may themselves assemble to form fibers (e.g., as we know them as cotton).¹⁴³ Within cell walls, microfibrils are often organized into perpendicular layers forming a cross-hatched network bound together by pectin or hemicellulose. This is but one example of a recurring motif in biology; relatively simple primary structures give rise to complex higher-order structures with corresponding emergent properties.

The elegance of this approach is it greatly simplifies the number of unique enzymes that must be dedicated to manufacture monomers; Nature is parsimonious out of necessity. The same glucose monomer used to make cellulose for structural applications is also used for short-term energy storage. The code of life is written using only four nucleotide bases, and the millions of distinct enzymes and proteins use the same 22 proteinogenic amino acids. Nature only achieves this feat through precise control over the sequence, stereochemistry, and architecture of polymeric structure. By studying the structure–property relationships of biological polymers, polymer chemists, materials scientists, and chemical engineers extract important design principles for the generation of sophisticated materials from simple starting materials. As discussed above, achieving such a level of sophistication will require an in-depth understanding of polymer phase behavior and the invention of advanced polymerization catalysts.

The majority of commodity plastics are hydrocarbons devoid of inherent stereochemical features (isotactic polypropylene is a conspicuous exception) and of heteroatoms in the polymer backbone. While chain packing and crystallization greatly influence the properties these polymers exhibit (the drastic difference in mechanical performance of the different grades of polyethylene is a good example), most commercial polymers do not even approach the structural complexity of oligomeric polypeptides. From biorenewable feedstocks, an enticing array of new monomers can be envisioned. Reflective of the elemental composition of biochemicals, one might envision that renewable monomers will contain heteroatoms (i.e., nitrogen and oxygen) and will also contain (often multiple) stereocenters. Embedding these chemical features in polymeric structures will allow polymer chemists to simultaneously tune the physical properties and degradation rates of yet-undiscovered sustainable polymers.

VIII. SUMMARY

Three big challenges that face society are the continual supply of potable water, clean energy, and safe food. Encompassing all of these is the idea of sustainable development—that is, how do we feed, clothe, and shelter a growing population while ensuring future generations will still have the resources necessary to meet their own needs. Scientists, particularly chemists, chemical engineers, and materials scientists, can and should be working on research to solve the many technical problems associated with sustainable development. In many cases, technological solutions will rely on the development of advanced materials to access property profiles that simply do not exist at present. Polymer scientists and engineers have the expertise necessary to identify and design novel materials to meet these needs. Success in this endeavor hinges on productive collaboration (both intra- and interdisciplinary) at the academic level and cooperation between academic and industry researchers, nongovernment entities, and legislative bodies.

Ultimately, the long-term sustainability of the polymer industry will hinge on the successful introduction of new polymers that are derived from annually renewable resources. These materials must have sensible end of life options (e.g., they should be capable of being recycled by physical or chemical means, biodegraded to innocuous compounds, or cleanly incinerated to recover the energy content). In order for these new materials to compete with the fossil fuel based, largely nondegradable polymers that currently dominate the

industry, they must be competitive from both performance and cost perspectives. We will not achieve this instantaneously, and bridging technologies will be required during the transition. In a recently published perspective in this journal, Bates and Bates state “block polymers will play a key role in the development of sustainable polymers derived from natural sources such as sugar and cellulose.”¹⁴⁴ We agree with this statement and wish to expand on that sentiment here.

Yes, block polymer architectures will indubitably be instrumental in the creation of useful renewable and degradable materials. Yes, the adoption of these materials for high volume applications like packaging will help to address the very real problem of plastic pollution. But, it is also true that the synthesis of materials with complex architectures *from polymers that are not renewable or degradable* will also likely play a big role in sustainable development. In the future, the world will need efficient and selective membranes both for water purification and for chemical separations, robust conducting materials for energy storage, and improved excipients for oral drug delivery. While it is likely that *some* of the polymers used for these applications will be both renewable and degradable, in some cases it will be important to design materials that are robust, with properties that are currently best achieved by using hydrocarbon polymers from monomers that are most efficiently produced from petrochemical sources. As previously discussed, “unsustainable polymers” can play key roles in advancing sustainability. This was recently highlighted in an article in *Chemical and Engineering News* focused on food packing with complex multilayered polymer films.¹⁴⁵

The challenges facing our society today can sometimes seem overwhelming. Even narrow topics such as sustainable polymers can be formidable in scope. In the [Introduction](#) we mentioned an ongoing debate in earth science, specifically the question of whether or not we are living in a new geologic epoch. We believe the *Anthropocene* debate speaks to the cumulative power of mankind. That humans have managed to change our environment on a geologic scale in such a short period of time is both terrifying and awe-inspiring. No matter how firmly established the current polymer industry seems, it is worth remembering that all synthetic polymers that comprise the panoply of commodity plastics were invented in the past century.^d The polymer industry in its current state does not exist because it was thoughtfully designed. The majority of plastics are durable not because they need to be but because the monomers used to make them are practically free. Indeed, postconsumer polymers are not allowed to escape collection and enter the environment because they are worthless but because the oceans are common resources and are not as valued as one would hope.¹⁴⁶ In light of this, we should not accept the status quo because designing a better alternative is daunting. We conclude with what we believe is an apt aphorism, and one that is likely familiar to any student of rheology, *πάντα ρεῖ* (everything flows). Change is more than possible—it is inevitable.

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The authors declare the following competing financial interest(s): Marc A. Hillmyer has equity and royalty interests in, and serves as secretary and on the Board of Directors of Valerian Materials, a company involved in the commercialization of β -methyl- δ -valerolactone. The University of Minnesota also has equity and royalty interests in Valerian Materials. These interests have been reviewed and managed by the University of Minnesota in accordance with its Conflict of Interest policies. DKS is a consultant for Valerian Materials. The authors declare no other competing financial interests.

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Marc A. Hillmyer grew up in Florida and earned a B.S. degree in chemistry at the University of Florida in Gainesville. He earned his Ph.D. in chemistry from the California Institute of Technology in Pasadena and was a postdoctoral research associate in the Department of Chemical Engineering and Materials Science at the University of Minnesota in Minneapolis. He is currently the McKnight Presidential Endowed Chair in the Department of Chemistry at the Twin Cities of the University of Minnesota.

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ADDITIONAL NOTES

^aIn this context, Giulio Natta's introduction to Herman Mark's 1966 book *Giant Molecules* "If our age were to be named for the materials that characterize it—as were the Stone and Bronze Ages of the past—this might be known as the age of plastics." seems a bit prophetic!

^bThe time scale of oil and coal formation is more easily related to geological eras than the chemical reactions typically encountered in polymer synthesis. The majority of petroleum deposits date to the Mesozoic era (65–225 million years ago). Many coal beds date to the Paleozoic era, specifically the Carboniferous period (359–298 million years ago).

^cIt could thus be fairly stated that whether or not Braskem's *I'm Green Polyethylene* fulfills the promise of its name depends largely on where the product containing the polymer is used and how the consumer chooses to dispose of it, rather than the resin itself.

^dThere are, in fact, a small but significant number (>100) of people alive today who were born before the invention of Bakelite (in 1906).

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