

Sustainable polymers from renewable resources

Yunqing Zhu¹; Charles Romain²; Charlotte K. Williams^{1*}

1. Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Oxford OX1 3TA, UK.

2. Department of Chemistry, Imperial College London, London SW7 2AZ, UK.

charlotte.williams@chem.ox.ac.uk

Preface

Renewable resources are used increasingly in the production of polymers. In particular, monomers such as carbon dioxide, terpenes, vegetable oils and carbohydrates can be used as feedstocks for the manufacture of a variety of sustainable materials and products, including elastomers, plastics, hydrogels, flexible electronics, resins, engineering polymers and composites. Efficient catalysis is required to produce monomers, to facilitate selective polymerizations and to enable recycling or upcycling of waste materials. There are opportunities to use such sustainable polymers in both high-value areas and in basic applications such as packaging. Life-cycle assessment can be used to quantify the environmental benefits of sustainable polymers.

Modern life relies on polymers, from the materials that are used to make clothing, houses, cars and aeroplanes to those with sophisticated applications in medicine, diagnostics and electronics. The vast majority of these polymers are derived from petrochemicals. Many polymers contribute considerably to an improved quality of life and a cleaner environment, for example, as materials that enable the purification of water or as polymer composites with improved fuel economy for aerospace applications. Only about 6% of the oil produced worldwide is used in the manufacture of polymers, yet there are environmental concerns associated with both the raw materials used to make them¹ and their end-of-life options². Although there is no panacea for these complex environmental problems, one option is to

develop more-‘sustainable’ polymers. Research has focused mainly on replacing fossil raw materials with renewable alternatives and on developing end-of-life options that generate materials that are suitable for recycling or biodegradation. Where biomass from plants is used as the renewable raw material, the polymers are often referred to as bioderived. In terms of biodegradation, it is important to recognize that some petrochemical polymers are biodegradable, and that not all bioderived polymers will biodegrade. The potential for sustainable polymers is stimulated by policy, legislation and international agreements, including some negotiated at the 2015 United Nations Climate Change Conference (COP21) (ref. 3) in Paris on reducing CO₂ emissions. Although the commercial application of bioderived polymers can benefit from improvements in environmental performance (as well as from supportive policy or legislation), it will also require favourable economics and material properties that are better than seen in conventional materials, including thermal resistance, mechanical strength, processability and compatibility. Taken together, these are tough criteria that could explain, in part, why there are few commercially successful sustainable polymers at present. In 2014, for example, only 1.7 megatonnes of more than 300 megatonnes of polymers produced globally were bioderived, of which the three main products, by volume, were polyethylene terephthalate (PET), polyethylene and polylactide⁴. There are two general approaches to preparing sustainable polymers: lessening the environmental impact of conventional production, for example by using biomass to make known monomers or polymers such as PET and polyethylene; and the preparation of new, ‘sustainable’ structures, such as polylactide, from renewable raw materials.

This Review highlights some of the opportunities for creating sustainable polymers from four renewable raw materials: carbon dioxide, terpenes, vegetable oils and carbohydrates (Fig. 1). These feedstocks enable the production of polymers and materials with a wide range of properties and applications. (The use of modified natural polymers such as cotton, silk, thermoplastic starch, cellulose derivatives and natural peptides is not discussed, although the potential for producing polymers from lignin is mentioned briefly.) The examples highlighted have been selected because they address some of the overarching challenges of sustainable polymer production.

The first challenge is that transformation of renewable resources and the production of polymers must be highly efficient to reduce costs. Production can be made more efficient by using mixtures of raw materials, producing monomers of lower purity or through the ‘upcycling’ of waste materials from agriculture or industry. Second, sustainable polymers must show complementary or improved properties compared with the polymers available at present. Applications with high-value markets, such as thermoplastic elastomers, rigid plastics and polyols, might present more favourable economics than applications such as packaging. Third, life-cycle assessment should be used to quantify the impact of sustainable polymers and to compare them with existing petrochemical benchmarks; this technique is usually used to assess environmental impacts and outputs that are associated with polymer production. Although the need for such comparisons might seem obvious, there are complexities associated with selecting appropriate benchmarks, boundaries and data⁵. At present, materials in the early stages of development, particularly in academic labs, are not routinely examined by life-cycle assessment. Here we highlight examples of life-cycle assessment that demonstrate the improved sustainability of the polymers, and where the findings are relevant to the design and development of future materials.

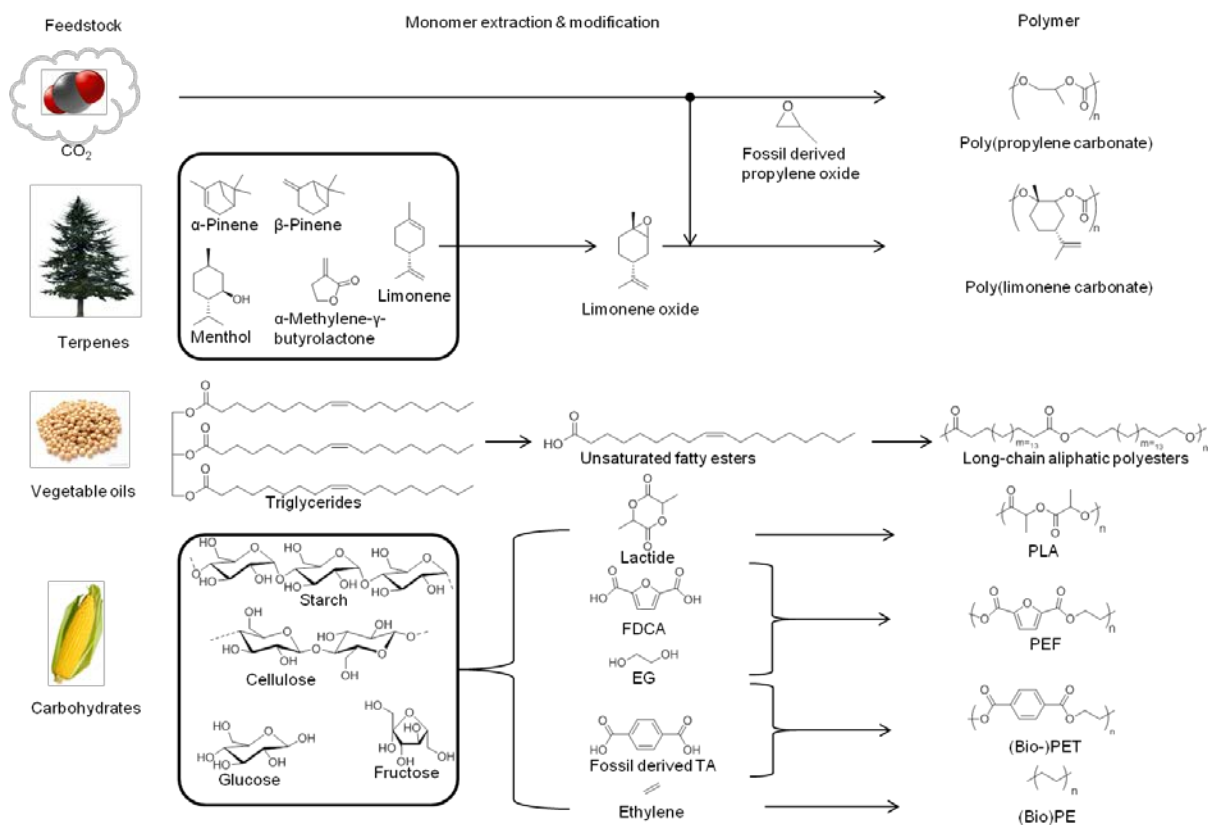


Figure 1: Options for replacing petrochemicals as raw materials in the manufacture of polymers. Carbon dioxide is copolymerized with propylene oxide to generate propylene carbonate polyols. Terpenes, such as limonene, are chemically transformed to limonene oxide and copolymerized with carbon dioxide to generate poly(limonene carbonate). Triglycerides, from vegetable oils, are transformed into long-chain aliphatic polyesters. Natural carbohydrate polymers, such as starch, are broken down to glucose, which is subsequently transformed to polymers such as poly(ethylene furanoate) (PEF), polylactide (PLA), bioderived poly(ethylene terephthalate) ((bio)PET) or bioderived polythene ((bio)PE).

Upcycling carbon dioxide into polymers

Using waste greenhouse gases such as carbon dioxide to prepare useful and valuable polymers has long been of interest to researchers, and this chemical process is now on the cusp of commercialization. It is a rare example of a process that consumes carbon dioxide as a reagent. It enables 30–50% of a polymer's mass to be derived from carbon dioxide, with the remainder derived from petrochemicals, and it delivers both economic and environmental benefits⁶⁻¹² (Fig. 2).

Sustainable polymers can be produced through alternating copolymerization of epoxides, commonly propylene oxide, and carbon dioxide. The efficiency of the process is highly dependent on the catalyst that is applied, and efforts worldwide have focused on improving and understanding the underlying catalysis^{6,13-19}. Generally, homogeneous catalysts deliver a much greater uptake of carbon dioxide into the polymer, which results in balanced epoxide–carbon dioxide enchainment and produces aliphatic polycarbonates. By contrast, heterogeneous catalysts require considerably higher pressures and result in lower levels of carbon dioxide incorporation, thereby producing polyether carbonates in which the ether linkages result from sequential epoxide enchainment. It is also feasible to selectively combine the alternating copolymerization of epoxides and carbon dioxide with the polymerization of other bioderived monomers to produce block copolymers that are composed of ester, ether and carbonate blocks²⁰⁻²³. Although these methods are at an early stage of development, they highlight the need for more-selective chemistry that uses monomer mixtures and the potential to use block copolymers to control the macroscopic properties; both are important areas for future development.

The commercialization of polymers made with carbon dioxide addresses two distinct molecular-weight regimes and areas of application. Low-molecular-weight hydroxyl end-capped polycarbonates or polyether carbonates are applied as polyols in the manufacture of polyurethane^{6,11}. Polyols with low viscosities and low glass transition temperatures could be substitutes for some common petrochemical-based polyols that are used to make furniture foams, adhesives, clothing and resistant coatings¹⁵. Alternatively, high-molecular-weight polycarbonates are already in use as binders and sacrificial materials, which are used to ‘pattern’ a substrate before being burnt away during the fabrication process. Improvements to their properties might widen their applications to include rigid plastics and blends with petrochemical-based polymers^{12,24}.

An important benefit of upcycling carbon dioxide — although not shared by many bioderived monomers — is that polymers can be produced easily using present infrastructure for petrochemical-based polymer manufacturing. In particular, polymerizations can proceed using existing reactors and methods for processing and purification. There is also no dependence on agriculture for raw materials or on complex pretreatments and transformations of monomers.

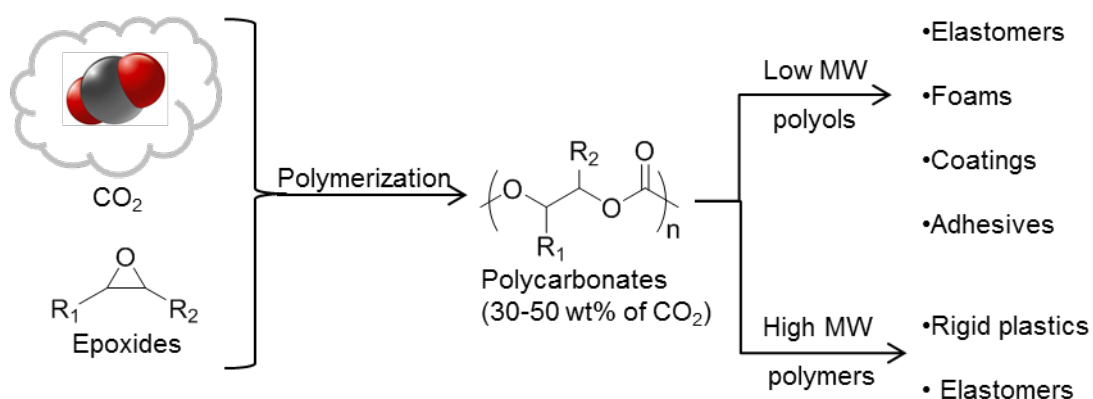


Figure 2: Upcycling of carbon dioxide into sustainable polymers of high value. Carbon dioxide and epoxides can be copolymerized to deliver aliphatic polycarbonates. Polycarbonate polyols of low molecular weight may be suitable to prepare foams, coatings and adhesives, whereas high-molecular-weight polycarbonates may be used as rigid plastics or elastomers.

With a view to sustainability, an obvious question to ask is whether the manufacturing process is truly compatible with the recycling of waste carbon dioxide. The first signs are

encouraging, with successful polymerization being achieved using carbon dioxide emissions that were captured from a coal-fired power station in the United Kingdom¹¹. The catalytic performance of the reaction and the quality of the product were almost equivalent to those achieved with ultrapure carbon dioxide. The entire process was surprisingly tolerant of contaminants such as water, nitrogen and oxygen, as well as any small-molecule amines and thiols that are present owing to the capture process.

Life-cycle assessment has been used to compare polyols made by the copolymerization of propylene oxide and carbon dioxide with those prepared only by propylene oxide polymerization²⁵. Even when propylene oxide was only partially substituted with carbon dioxide, the net reductions in the emission of greenhouse gases and the depletion of fossil resources were about 11–20%. It is important to emphasize that these environmental benefits arise from the replacement of the epoxide by carbon dioxide and not just from the recycling of carbon dioxide. Epoxides that are derived from limonene and vegetable oil have the potential to yield fully renewable polycarbonates^{26,27}. Polylimonene carbonate is qualified for use in various applications, including as a resistant and hard dry-powder coating produced by crosslinking the pendant alkene functional group that is introduced on the limonene unit^{12,26,28}. By selecting the catalyst carefully, it is also possible to prepare highly crystalline stereocomplexed polylimonene carbonate — a co-crystallite formed from polymer chains of opposite chirality — which has better thermal properties, including a higher degradation temperature (265 °C), than do analogues of lower crystallinity²⁹. These findings highlight the potential of bioderived materials to deliver products of high impact and value by taking advantage of naturally ‘rigid’ chemical functionalities and by providing cost efficiency through the use of waste as a raw material. However, there are insufficient physical, rheological and processing data to fully understand this potential.

From plants to plastics

The field of polymer science originates from studies of biopolymers such as cellulose³⁰. Many commercial sustainable polymers are sourced from plants that are rich in sugar or starch, including sugar cane (*Saccharum officinarum*), wheat (*Triticum* spp.) or sugar beet (*Beta*

vulgaris). In bio-PET, for example, there is a partial substitution of a petrochemical-derived raw material: up to 30 % by weight (wt%) of the ethylene glycol monomer is produced from starch. This process is complex and involves starch degradation, glucose fermentation, ethanol dehydration, ethene oxidization and hydrolysis of the product. A number of research programmes, including some already at the pilot stage, are actively investigating PET that is fully derived from biomass, in which the co-monomer terephthalic acid is also produced from biomass³¹. Life-cycle assessment of the present generation of bio-PET shows reductions of 20–50% in the emission of greenhouse gases in comparison to petrochemical-derived PET. Like PET, polyethylene can also be produced from sugar cane, with the ethylene monomer obtained through the dehydration of ethanol. This method of polymer production is controversial and requires a well-developed sugar-cane industry; it is being explored mainly in Brazil³². After ethylene has been produced, the process of polymerization and the properties of the resulting polymer are identical to those for petrochemical-derived polyethylene. Regardless of the method of production, polyethylene usually persists in and pollutes the environment, and it is unlikely to become economically viable to recycle the material.

An advantage of developing bioderived monomers as direct substitutes — such as those used in the production of PET and polyethylene — is that the processing and applications of the resulting polymers are identical, thereby simplifying their adoption and accelerating their uptake. This is particularly important for PET, one of the few polymers for which large-scale recycling infrastructures exist, and life-cycle assessment indicates positive contributions to its sustainability if it is recycled³³. Highly efficient catalytic methods have been pioneered that enable the chemical recycling of PET and show the potential for subsequent ‘upcycling’ of PET into other polymers³⁴. Such methods could be a promising alternative to well-established mechanical recycling. Generally, technologies that use renewable resources to prepare polymers are front-runners in the commercialization of sustainable polymers.

It is important to consider whether using edible feedstocks to prepare polymers will have a societal impact. At first, this seems analogous to the controversy that surrounds some biofuels. However, it is apparent that polymer production is dwarfed in magnitude by that of

biofuels, and bioderived materials are still a niche market in the polymer sector. A detailed study of bioderived-polymer production in the European Union substantiates the possible land-use requirements³⁵. It envisages a market share of 1–4% for bioderived polymers by the year 2020, with the exact value dependent on various economic and growth models. In a scenario in which wheat is the only source of starch, just 1–5% of the land used presently to grow wheat would be needed³⁵.

From terpenes to elastics and coatings

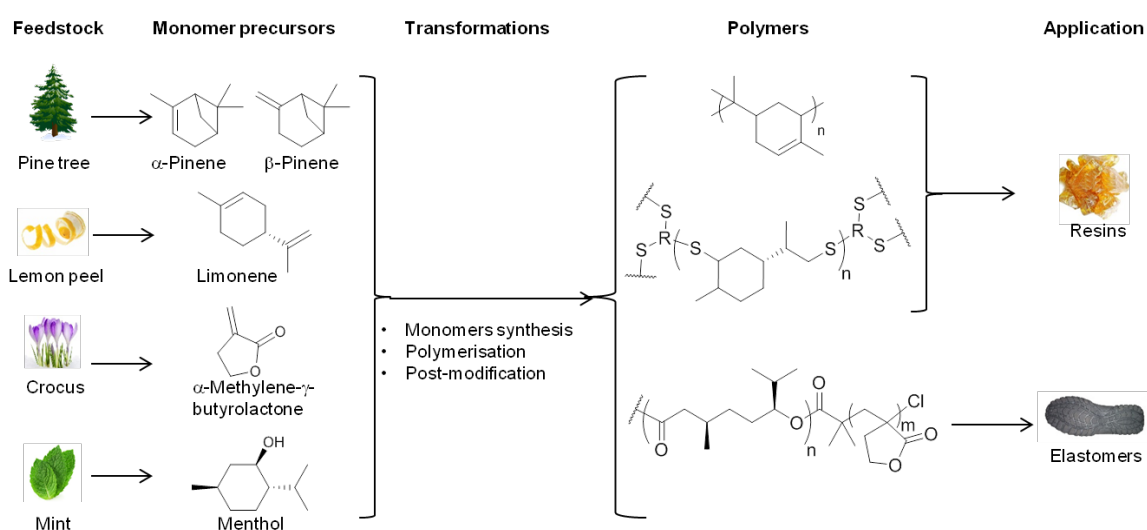


Figure 3. Sustainable polymers produced from terpenes and terpenoids. Terpenes such as pinene and menthol are extracted from plants such as pine or mint. They can then be transformed into polymer resins or elastomers before being used.

Terpenes and terpenoids are components of essential oils that are derived from plants and have a common isoprene unit in their chemical structures³⁶. The best-known example of a polyterpene is probably natural rubber. More than 10 megatonnes are produced per year, and the main constituent is polyisoprene. Other terpenes are being investigated as monomers for polymer production, although on a much smaller scale. These include turpentine, which is extracted from pine trees (*Pinus* spp.) and is composed mainly of α -pinene (45–97%) and β -pinene (0.5–28%), and limonene, which is extracted from the peel of citrus fruits³⁷ (Fig. 3). Worldwide production of these monomers is modest: in 2013, about 0.3 kilotonnes of turpentine³⁸ and about 0.7 kilotonnes of limonene³⁹ were produced. Commercially available polymer resins from these terpenes already exist^{36,37,39,40}.

A drawback of terpenes is the low molecular weights of their polymers, which limits their mechanical performance. It might be possible to achieve considerably higher molecular weights through a cationic polymerization of β -pinene followed by hydrogenation⁴⁰. The resulting polymer exhibits some thermal and mechanical properties that are akin to those of polymethyl methacrylate, and the material also shows high optical transmittance. Another option is to copolymerize terpenes with common petrochemical-derived vinyl monomers, such as methacrylates, by means of radical polymerization, which enables the production of materials with partial bio-based content^{41,42}. The recycling of polymers is an important aspect of sustainability. Limonene, for example, can be used both as a reagent and as a solvent for recycling⁴³. One example involves dissolving a polystyrene drinking cup in limonene; the subsequent crosslinking reaction forms an elastomer that can be moulded into a mobile-phone cover⁴³.

A further limitation in the commercialization of terpenes is their relatively high cost, which can be ameliorated through the fabrication of products of higher value such as thermoplastic elastomers (Fig. 3). Current thermoplastic elastomers are derived mostly from petrochemicals and are produced in quantities greater than 3.5 megatonnes per year for applications as diverse as car suspension systems, window seals, coatings of household goods or electronics, shoe soles or medical devices⁴⁴. The use of terpene monomers derived from wild mint (*Mentha arvensis*) and a tulip (*Tulipa gesneriana*), together with methods of controlled polymerization, has led to the production of block copolymer thermoplastic elastomers^{45,46} (Fig. 3). The bioderived polymer with the best mechanical performance has a Young's modulus of more than 6.0 megapascals, which is within the range that is observed for commercial polystyrene-butadiene-styrene (SBS). In contrast to SBS, however, the bioderived elastomer has a very high glass transition temperature (T_g) of 170–190 °C, which enables it to retain elasticity at elevated temperatures — a feature that might be desirable for applications in harsh environments. Most bio-based elastomers show elongation-at-break values of less than 1,000%. The mechanical properties remain inferior to those of petrochemical-derived polymers.

Value-added vegetable oils

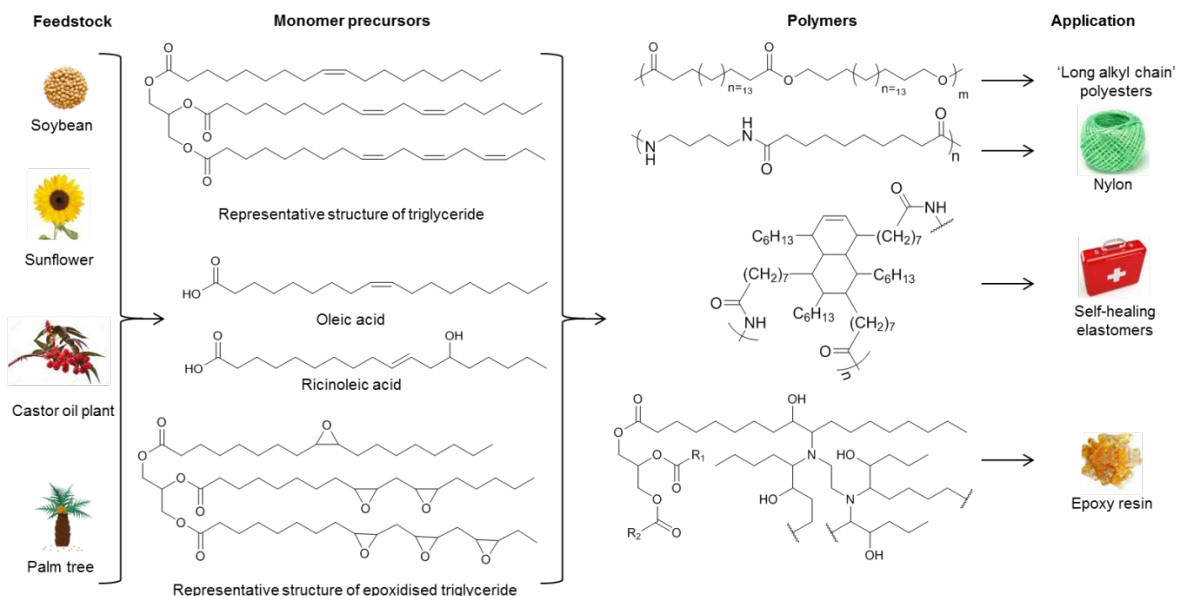


Figure 4. Sustainable polymers produced from vegetable oils. Plants such as soybean, sunflower, castor oil or palm tree are good sources of triglycerides. The triglycerides are transformed to polymers such as polyesters or nylons and are subsequently applied as elastomers or resins.

Triglycerides are harvested from the seeds of certain plants, the top four of which, by volume, are soybean (*Glycine max*), oil palm (*Elaeis*), oilseed rape (*Brassica napus*) and sunflower (*Helianthus*). They are produced on a very large scale (156 megatonnes in 2012): the majority are used as food, about 30 megatonnes are used as biofuels, and about 20 megatonnes are used as chemical feedstocks⁴⁷. They also represent an important and long-standing raw material for polymer production (Fig. 4). Indeed, there is a strong track record of using linoleum (produced from linseed oil) and epoxidized oils as resins, coatings and in paints. The commercial production of polyamides from castor oil, which is extracted from the seeds of the castor oil plant (*Ricinus communis*), yields nylon 11, nylon 6,10 and nylon 4,10. Some of these bioderived nylons have beneficial properties, including low water absorption, high chemical resistance, high temperature stability and a lack of long-term ageing⁴⁷. They have been used as toothbrush fibres, in pneumatic air-brake tubing and in flexible oil and gas pipes. An important limitation on the production of such nylons is the reliance on castor oil, which contains a secondary hydroxyl group in the fatty-acid chain that facilitates its efficient transformation to monomers and subsequent polymerizations. Notably, castor oil costs almost twice as much as more common oils such as palm oil or rapeseed oil.

Although triglycerides are found in almost all plants, the quantity that is available varies, and even common crops such as soybeans are estimated to yield only 20 wt% of triglycerides. Another challenge is that the chemical compositions of triglycerides vary both between and within a particular crop. Triglycerides are composed of three, often distinct, fatty-acid groups that are linked together through ester bonds to a glycerol unit. They are commonly processed by transesterification reactions to produce fatty esters and glycerol. In terms of polymer production, glycerol can be used as a crosslinking agent in resin production, or as a raw material for the production of monomers such as epichlorohydrin and lactic acid^{48,49}. However, the main opportunity probably comes from the fatty esters, which feature long alkyl chains (C12–C22) and include a considerable number of internal alkene functional groups⁵⁰. On polymerization, they can have properties that are intermediate between those of polyalkenes, such as polyethylene, and more-polar short-chain polyesters. A common set of polymerization methods makes use of the alkene groups found in unsaturated fatty esters (Fig. 4). Indeed, a considerable proportion (about 20–60 wt%) of the plant oils produced in the largest volumes worldwide is composed of such unsaturated fatty acids. More recently, crop engineering has produced a strain of soybean that yields more than 75% mono-unsaturated oleic acid — a particularly useful monomer⁵¹. Many methods exist for transforming the alkene groups to polymers, including the thiol-ene reaction, acyclic diene metathesis, epoxidation and radical or thermal crosslinking reactions^{50,52} (Fig. 4). An area that has considerable potential is reacting the alkene to produce α,ω -diesters or α,ω -diols. These monomers undergo conventional condensation polymerizations to yield bioderived polyesters, and if α,ω -diamides are used as the monomer, nylons can be produced. One limitation is that α,ω -difunctionalized monomers are usually produced in reactions such as olefin metathesis, ozonolysis or oxidative cleavage of the carbon–carbon double bond, and in all cases, only about half of the fatty acids are used and several by-products are produced⁵³. An elegant solution involves the use of selective chemical catalysis to isomerize the internal alkene group to the chain end. Following an alkoxy-carbonylation process, this enables near-quantitative production of the desired α,ω -difunctionalized monomers⁵³⁻⁵⁵. The diesters are produced with more than 95% selectivity, at high conversion rates and without significant by-products⁵³⁻⁵⁵. Polyesters can be prepared through conventional polycondensations and

the resulting materials have thermal properties, solid-state crystalline structures and tensile properties similar to those of polyethylene⁵⁶. Enzyme catalysts that enable similar polycondensations have also been developed that show efficient activity over a range of temperatures, solvents and substrates⁵⁷. Despite the ability to process the long-chain polyester products using existing industrial methods such as injection moulding or film extrusion⁵⁴, these bioderived polyesters have so far been unable to compete with the cost of petrochemical-derived polyethylene. However, the high crystallinity, thermal and chemical resistance and degradability of bioderived polyesters are still valuable properties, and the application of these materials as compatibilizers in blends of petrochemicals or as macromonomers is feasible.

Polycondensation requires monomers of very high purity and balanced stoichiometry to successfully produce polymers. An alternative method applies to macrolactones, which are derived from fatty acids and can undergo ring-opening polymerization to produce similar long-alkyl-chain polyesters. It enables the production of high-molecular-weight polymers and is compatible with block copolymerization. Bioderived macrolactones that consist of up to 23 atoms have been polymerized⁵⁸, and some macrolactones, such as pentadecalactone or ambrettolide, are naturally occurring biochemicals. The resulting polyesters have thermal and rheological properties akin to those of linear low-density polyethylene⁵⁹. In a biocatalytic approach, mixtures of glucose and oleic acid were fermented to efficiently produce more than 200 grams per litre of the macrolactone lactonic sophorolipid, which features both disaccharide and alkene functional groups. The ring-opening metathesis polymerization of this macrolactone leads to the production of carbohydrate functionalized polyesters⁶⁰.

Concerns regarding land use can arise because many triglycerides are also used as foods. One solution might be to engineer algae to biosynthesize unsaturated fatty acids. Algae can be grown on non-arable land and might even flourish in brackish water. They also require only sunlight and carbon dioxide as sources of energy. Algal biosynthesis of triglycerides has enabled dry-weight yields of 20–50%, which is higher than the yields of many crops⁶¹.

Triglycerides have also been used to prepare thermoplastic elastomers, including a

self-healing and thermoreversible elastomer⁶². The Young's modulus of this material is comparable to that of the petrochemical-derived polymer SBS, and its maximum strain exceeds 500%. The use of reversible supramolecular hydrogen-bonding interactions for crosslinking facilitates its processing, and the elastomer might even be recyclable — which is not usually possible for conventional elastomers. Although mechanical creep and other rheological properties have not yet been reported, the diversity of available fatty acids and the novelty of the methods for tuning the physical properties are attractive. Fatty acids can also form vitrimers, which are polymers that show reversible temperature-induced thermoset to thermoplastic transitions, for example through thermally controllable transesterification reactions^{63,64}.

Sugars as sustainable materials

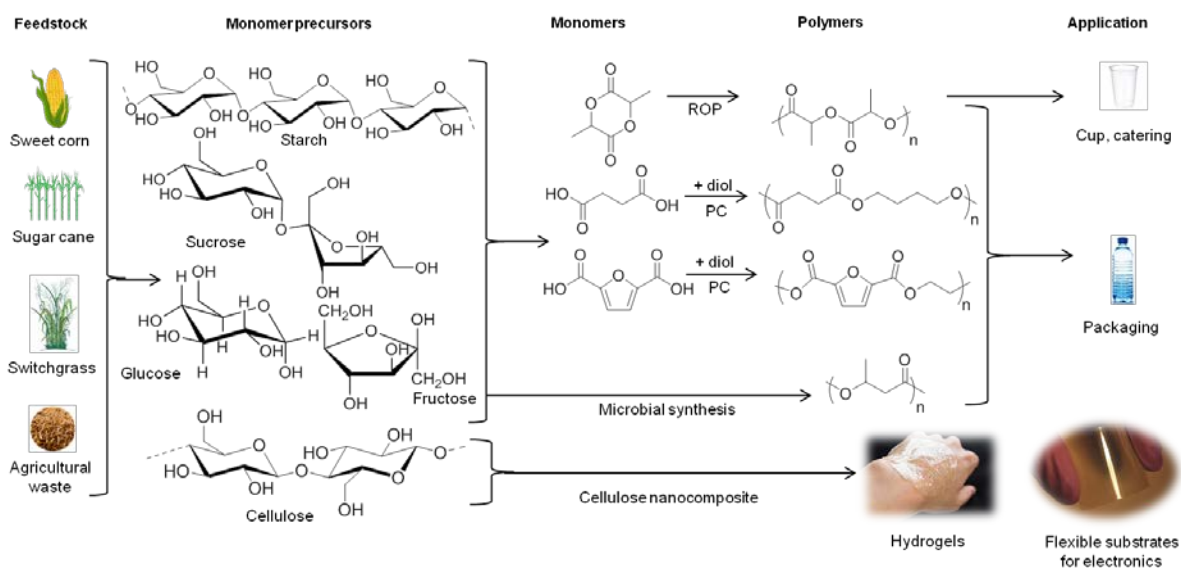


Figure 5. Sustainable polymers produced from polysaccharides. Plants such as sugar cane and maize are good sources of sucrose or starch, which can be transformed to monomers, including lactide, succinic acid and 2,5-furandicarboxylic acid (FDCA). The monomers are polymerized to produce polylactide (PLA), poly(butylene succinate) or poly(ethylene furanoate) (PEF), respectively. Poly(hydroxyalkanoate) (PHA) may be produced directly from glucose by biosynthesis. Cellulose fibres can be used to reinforce composites for use as hydrogels or flexible substrates for electronics.

Each year, more than 150 billion tonnes of polysaccharides are produced naturally, with humans consuming only about 1% of this volume. To make synthetic polymers, these biopolymers must be separated and depolymerized to obtain monosaccharides known as

pentoses and hexoses. The most abundant is glucose: at present, glucose is obtained through the saccharification of starch or sucrose hydrolysis, but in the future it could come from lignocellulosic sources. Glucose is transformed into building-block chemicals such as lactic acid or succinic acid, which are polymerized directly or are reacted further through chemical or enzymatic routes to produce monomers^{65,66} (Fig. 5). In 2004, the US Department of Energy published a landmark report that highlighted the top value-added chemicals from biomass, which were selected on the basis of their availability and the ability to transform them into useful products⁶⁷. These molecules include lactic acid, succinic acid and 2,5-furandicarboxylic acid (FDCA), which have already delivered useful polymers (Fig. 5). In some cases, it is necessary to use new polymerization methods and processes because the monomers involved are more polar and highly functionalized (that is, oxygenated) than are those derived from fossil raw materials.

One important example is commercially available polylactide (PLA), which is made from starch-rich crops such as maize (corn; *Zea mays*) (Fig. 5). PLA is produced through the fermentation of starch to lactic acid, followed by the preparation of lactide and its subsequent polymerization. It has properties that enable it to replace petrochemical-derived plastics in some types of packaging and fibres^{68,69}. The fabrication process requires the efficient production of lactic acid and lactide, the former of which is achieved through microbial fermentation^{70,71}. Advances, including the use of cheaper fermentation substrates such as glycerol, agricultural waste and even algae-produced carbohydrates⁷⁰, may improve efficiency and profitability. Chemical catalysis might also be of interest as a means to produce racemic mixtures of lactide from sugars⁷². The selective polymerization of such mixtures might increase the thermal resistance and range of applications of PLA⁷³. In terms of its end-of-life fate, PLA can be recycled and degraded. It is even compostable at high temperatures, degrading to lactic acid, which can be metabolized naturally. Life-cycle assessment has shown reductions of up to 40% in greenhouse-gas emissions and up to 25% in non-renewable-energy use for PLA compared with petrochemical-derived polymers such as polyethylene or PET^{74,75}. However, the production of PLA might have other environmental impacts, including the use of water and fertilizer, which are more difficult to compare with the

impacts of fossil-fuel extraction, purification and storage. Another substantial hurdle is to replace virgin crops (such as maize or sugar cane) with lignocellulosic or waste biomass⁷⁶.

Another group of renewably sourced polyesters are the polyhydroxyalkanoates (PHAs), which are obtained through the fermentation of sugar⁷⁷ (Fig. 5). They occur naturally and can be harvested in excellent yields from microorganisms directly, without the need for intermediate monomer isolation. Biosynthesis is achieved by culturing bacteria under growth-limiting conditions and results in the accumulation of considerable quantities of the polymer in the cytoplasm. The most promising PHAs have similar physical properties to polyalkenes such as polypropylene, but also offer the advantage of degradability. Production in bacteria is not cost-effective for commodity applications at present, although small-scale production is being explored and might be suitable for higher-value medical applications⁶⁵.

Polyethylene furanoate (PEF) is an attractive example of a fully bioderived material with properties that make it suitable as a substitute for PET in some applications. Although it has not yet been commercialized, pilot-scale production of PEF seems to be under way. It is produced by the transformation of fructose or glucose to hydroxymethyl furfural (HMF) through acidification and dehydration reactions⁷⁸. HMF is unstable, which limits the efficiency of the process and results in side products such as levulinic acid. An improved route to HMF ethers, which are more stable and can be oxidized to FDCA, has been reported⁷⁹ (Fig. 5). FDCA is then copolymerized by polycondensation with bioderived ethylene glycol to yield fully bioderived PEF. Importantly, both the polymerization and oxidation reactions are compatible with PET manufacturing, and this potential to use existing infrastructure might accelerate the translation and uptake of bioderived PEF⁷⁹. PEF has a higher T_g and improved barrier properties, especially with respect to oxygen permeability, than does PET⁷⁹, and it is less likely to undergo cold crystallization. A life-cycle assessment that benchmarked bioderived PEF against petrochemical-derived PET showed a reduction in greenhouse-gas emissions of up to 55% (refs 78, and 80). It is difficult to compare the costs of the two materials because of the disparity in scales of production; however, larger-scale production of PEF will probably reduce its cost⁷⁸.

Succinic acid is an important monomer that is derived from the highly efficient fermentation of glucose and is produced in quantities of 170 kilotonnes per year⁸¹. It can be reacted through polycondensation with bioderived 1,4-butanediol to produce PBS, which is produced commercially in quantities of about 40 kilotonnes per year. Polybutylene succinate is a semicrystalline polymer with a high melting temperature (T_m) of 115 °C, and it can be processed using some conventional techniques, although it presents rheological limitations to the production of blown films⁸¹. It has been used as a barrier in packaging and also in blends. An alternative method for producing related polyesters with repeated succinic acid units is to copolymerize epoxides with succinic anhydride⁸². The method is attractive because it can be controlled; it might obviate the need for precise control of reagent stoichiometry and it yields materials with predictable molecular weights. Stereocomplexes of polypropylene succinate have been created that are crystalline and thermally resistant materials with T_m values of around 120 °C (ref. 83). Succinic acid can also be dehydrated at elevated temperatures to produce γ -butyrolactone. Historically, it was considered to be impossible to polymerize this five-membered ring lactone owing to its low ring-strain. However, optimized low-temperature processes involving *in situ* polymer precipitation have enabled the production of some polymer⁸⁴. Despite issues that impede the commercial deployment of polymerized γ -butyrolactone, including the method of production, the stability of the polymer and that the monomer is a controlled substance⁸⁵, this example demonstrates the potential for selective catalysis and the recycling of bioderived monomers and polymers.

Carbohydrates could provide a more cost-effective route to thermoplastic elastomers than terpenes. In particular, they show potential as block copolyester elastomers. Engineered *Escherichia coli* bacteria have been used to prepare a functionalized lactone at high efficiency (88 grams per litre in semi-batch mode), with the cost of the monomer estimated at US\$2 per kilogram, which is within the acceptable range for some commodity applications⁸⁶. The lactone is polymerized using controlled ring-opening polymerization to produce an elastomer with a T_g of -50 °C, and its copolymerization with polylactide yields a thermoplastic elastomer that can be stretched to 18 times its original length without breaking.

It has been known for more than a century that cellulose can be used to produce commercial

polymers such as cellophane or cellulose acetate. Cellulose fibres are also used as reinforcements in natural-fibre–polymer composites, which makes them attractive as engineering materials⁸⁷⁻⁸⁹. Semi-renewable hydrogels have been prepared by polymerization from the hydroxyl groups of hemicellulose that is harvested from the Norway spruce (*Picea abies*)⁹⁰. The method is straightforward, tolerant of the reaction conditions, and allows control of the crosslinking density, which enables tailoring of the polymer's ultimate mechanical properties. In an alternative approach, cellulose nanofibrils derived from wood have been used to replace PET as the flexible substrate in electronics manufacture. The cellulose fibrils show a high electrical breakdown tolerance (up to 1,100 volts), and the paper product undergoes fungal biodegradation without adverse environmental effects⁹¹.

Outlook and future prospects

Sustainable polymers from renewable resources are already gaining importance, and in the future, society will both want and need materials that have a smaller ecological footprint. Early successes in creating sustainable polymers have led to commercial products that are mostly used in packaging and as fibres. An important challenge is to identify platform chemicals or building blocks that can be easily prepared from abundant feedstocks and that do not compete for resources with food crops or alter the ecosystem.

Improvements to agricultural methods for crop production and harvesting, for example to optimize yields, are likely both to enhance the economic impact and to ease the environmental impact of bioderived polymers. Research should include ways to make better use of waste from agriculture and industry as monomers, including corn stover, fruit pulp, forestry waste and carbon dioxide emissions. Another important opportunity arises from the ready availability worldwide of lignocellulosic biomass: however, improved biopolymer separation, degradation and transformation chemistry and biochemistry will be required to optimize both the yield and cost of the monomers. Carbohydrates are the most abundant and easily processed sources of sustainable monomers, and a number of interesting carbohydrate-based processes and polymers are already being developed. To prepare high-value products, research needs to exploit the high degree of natural functionality of

carbohydrates, which includes taking advantage of rigid carbohydrate ring structures, as well as the extensive opportunities for non-covalent interactions and stereoregularity that carbohydrates offer^{92,93}. In tandem, the transformation of lignins to polymers has been underdeveloped owing to the highly complex and changeable structures of the lignins⁹⁴. Further methods to selectively transform lignin into monomers are needed: studies have highlighted the potential for catalysis to deliver these monomers, although so far they have focused on model compounds rather than native lignin^{95,96}. Another interesting option is to apply ferulic acid, which can be derived from either lignin or agricultural waste, to yield interesting polyesters and resins that are suitable as substitutes for petrochemical-derived polymers^{97,98}. A crucial, and sometimes underestimated, design criterion is the need to prioritize routes to monomers and polymers that are compatible with existing industrial infrastructure. The low cost and efficient purification of raw materials and products also requires much greater optimization for the highly oxygenated bio-based materials. The ability to retrofit existing manufacturing infrastructure to enable sustainable polymer production will continue to be an important driver in reducing costs and accelerating implementation.

The continued use of sustainable polymers in disposable applications such as packaging will result in the end-of-life fate exerting a considerable influence on sustainability. Innovative recycling, degradation or disposal options are likely to become even more important for preventing new materials from contributing to existing plastic waste issues, and there might also be an opportunity for supporting policy and legislation to shape the outcome. Although the direct quantification and comparison of sustainable polymers with petrochemical-derived equivalents is at an early stage, there have been sufficient studies to demonstrate that in many cases, the impacts of production are reduced, particularly on greenhouse-gas emissions and the depletion of fossil resources. Studies should also consider the life of the product beyond manufacture and the impacts associated with disposal. So far, few polymers have been designed to be both fully bioderived and degradable, although aliphatic polyesters such as polylactide are notable successes.

Packaging is an important opportunity at present for the application of bio-based polymers; however, it is challenging for such materials to compete economically with

petrochemical-derived polymers. Instead, bio-based polymers should seek to compete in the higher-value and higher-performance application areas, including thermoplastic elastomers, engineering plastics or composite materials. To facilitate success, it will be important to tailor and improve the properties of such polymers. For example, the preparation of polymers with higher thermal resistance would enable them to compete with existing semi-aromatic polyesters and nylons. And elastomers that show greater elongation-at-break values would be able to compete with petrochemical-derived polymers. Understanding and engineering the degradation profiles of bio-based polymers, for example by combining long-term durability with triggered degradation, represents a further challenge for research.

The task of widening the scope and range for sustainable polymers is considerable; to solve these complex problems, researchers will need to work together across the conventional disciplines of agriculture, biology, biochemistry, catalysis, polymer chemistry, materials science, engineering, environmental impact assessment, economics and policy. In the future, society will need more materials that have been made efficiently from natural waste and that are suitable for recycling or biodegradation.

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YZ and CR contributed equally to the review, CKW is the corresponding author.

Authors Information

Reprints and permissions information is available at www.nature.com/reprints. The authors declare competing financial interests: see go.nature.com/2flghz8. Readers are welcome to comment on the online version of this paper at <http://go.nature.com/2flghz8>. Correspondence should be addressed to C.K.W. (charlotte.williams@chem.ox.ac.uk).

Reviewer information

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