



Bio-based polymers with performance-advantaged properties

Robin M. Cywar^{1,2}, Nicholas A. Rorrer², Caroline B. Hoyt², Gregg T. Beckham²✉ and Eugene Y.-X. Chen¹✉

Abstract | Bio-based compounds with unique chemical functionality can be obtained through selective transformations of plant and other non-fossil, biogenic feedstocks for the development of new polymers to displace those produced from fossil carbon feedstocks. Although substantial efforts have been invested to produce bio-based polymers that are chemically identical to and directly replace those from petroleum, a long-pursued goal is to synthesize new, sustainable, bio-based polymers that either functionally replace or exhibit performance advantages relative to incumbent polymers. Owing to anthropogenic climate change and the environmental consequences of global plastics pollution, the need to realize a bio-based materials economy at scale is critical. To that end, in this Review we describe the concept of performance-advantaged, bio-based polymers (PBPs), highlighting examples wherein superior performance is facilitated by the inherent chemical functionality of bio-based feedstocks. We focus on PBPs with C–O and C–N inter-unit chemical bonds, as these are often readily accessible from bio-based feedstocks, which are heteroatom-rich relative to petroleum-derived feedstocks. Finally, we outline guiding principles and challenges to aid progress in the development of PBPs.

Synthetic polymers are ubiquitous in modern society owing to their relative ease of synthesis from petroleum-derived intermediates, ability to be formulated into diverse materials, extreme durability and low cost¹. Monomers for commodity polymer production are typically either direct products from fossil carbon processing or chemically accessible from the primary olefin and aromatic building blocks. It is widely recognized that fossil-based carbon use is leading to anthropogenic climate change², and polymer production is projected to reach 20% of global fossil fuel consumption by 2050 (REF.³). The detrimental environmental consequences of global plastics pollution are also palpable⁴. Thus, it is imperative to transition from a fossil-based materials (and energy) economy to a materials economy, ideally circular, founded on building blocks sourced sustainably from plants and other non-fossil, biogenic feedstocks (here, referred to as bio-feedstocks for brevity)^{5–24}. This transition presents an opportunity to harness the unique chemistries afforded by heteroatom-rich bio-feedstocks to redesign synthetic polymers.

To facilitate the transition to more sustainable polymers, research efforts have long focused on converting bio-feedstocks into compounds identical to those derived from petroleum^{6,13,25}. Making direct replacement chemicals and polymers is generally considered to be commercially viable, but likely more sustainable in

scenarios in which fossil carbon prices are high, or with taxes on fossil carbon that account for the externalities associated with fossil carbon production, consumption and disposal^{19,26}. However, to manufacture direct replacements from bio-feedstocks, selective chemical processes are required to remove chemical functionality afforded naturally by many bio-feedstocks. Conversely, the production of heteroatom (X)-containing polymers from fossil-based hydrocarbon feedstocks requires the addition of oxygen or nitrogen. The chemical distance measured by H:C and X:C (X=O, N) ratios from fossil-based feedstocks and bio-feedstocks to today's common polymers are exemplified in the van Krevelen diagram shown in FIG. 1.

Although direct replacements can offer straightforward cost and sustainability benchmarks to surpass, the established markets make it challenging for a new bio-feedstock and the associated, capital-intensive manufacturing processes to compete with amortized petrochemical operations solely on a price basis. To compete at scale with fossil-based polymers, we posit that bio-based polymers must exhibit performance-advantaged properties that harness the inherent chemical functionalities of the starting bio-feedstocks. Generalizing to bioproducts (not limited to polymers), Fitzgerald and Bailey defined performance-advantaged bioproducts as bio-based molecules that do not resemble existing

¹Department of Chemistry, Colorado State University, Fort Collins, CO, USA.

²Renewable Resources and Enabling Sciences Center, National Renewable Energy Laboratory, Golden, CO, USA.

✉e-mail: gregg.beckham@nrel.gov; eugene.chen@colostate.edu

<https://doi.org/10.1038/s41578-021-00363-3>

petroleum-derived molecules in structure, and that offer a performance advantage over existing products^{27,28}. For polymers, performance-advantaged attributes include improvements in manufacturability, properties in applications and end-of-life considerations.

In this Review, we highlight progress in leveraging the unique chemical functionalities of bio-feedstocks to synthesize bio-based polymers with performance-advantaged properties. First, we give an overview of bio-feedstocks and describe shortcomings of current synthetic polymers. The majority of the Review highlights recent successes in the development of performance-advantaged, bio-based polymers (PBPs) with C–O or C–N linkages in their backbones. We end by summarizing guiding principles and challenges for the development of such materials.

Sourcing bio-feedstocks

Sustainably sourced feedstocks for the synthesis of PBPs are available across a wide range of forms and volumes, both as natural polymers and as small molecules. We briefly discuss typical feedstocks available on a large scale as polymers or small molecules (FIG. 2) and describe several transformations that can be applied to these bio-derived intermediates, including those relevant to the PBPs highlighted below. Note that the direct use of naturally occurring polymers as polymeric materials is a major research field but is not covered here^{12,29,30}.

Agricultural crops are used to produce starch and soluble sugars at the commodity scale for use as precursors to a few bio-based chemicals. In many cases in which bio-based polymer precursors are derived from carbohydrates, this availability offers a bio-based feedstock for immediate use at scale.

Beyond starch and soluble sugars, the plant cell-wall polysaccharides, cellulose, hemicellulose³¹ and pectin³², and the aromatic polymer lignin³³ have been pursued

as sustainable feedstocks for more than a century, and with renewed vigour since the 2000s. The development of chemical processes to extract, fractionate and deconstruct plant cell-wall polymers into building blocks is intensely researched. Numerous biological, chemical and thermal processes are used to transform plant cell-wall polymers into small-molecule intermediates, such as carbohydrates, lignin-derived aromatic compounds, pyrolysis-derived intermediates and extractives³⁴ (FIG. 2). Other plant polymers include cutin and suberin, which are natural polyesters and a readily accessible source of fatty acids and aromatic carboxylic acids³⁵. Plants also commonly harbour diverse small molecules in the form of phytochemicals, including alkaloids, terpenoids, phenolics and fatty acids, among others, which can often be liberated through mild chemical extraction processes or made as targets of metabolic engineering from more abundant feedstocks. The non-food components of plants, thus, offer a rich source of natural polymers and small molecules for conversion into unique building blocks through selective transformations or direct use (discussed further below).

Besides plants, additional sources of bio-feedstocks include other structural polymers, such as chitin, a polysaccharide found in fungi and arthropod exoskeletons³⁶. Chitin is a homopolymer of β -1,4-*N*-acetylglucosamine (FIG. 2) and, thus, has been a focus of the nitrogen-based chemicals and materials field^{37,38}. Chitin can be converted into useful chemicals by methods mirroring those used in the conversion of plant cell-wall polysaccharides³⁹. Additionally, polysaccharides, proteins and oils common to heterogeneous food-waste streams offer bio-feedstocks that can be fractionated and processed into many of the same building blocks as those from plant cell-wall components.

To convert bio-based feedstocks into building blocks for PBPs often requires additional chemical

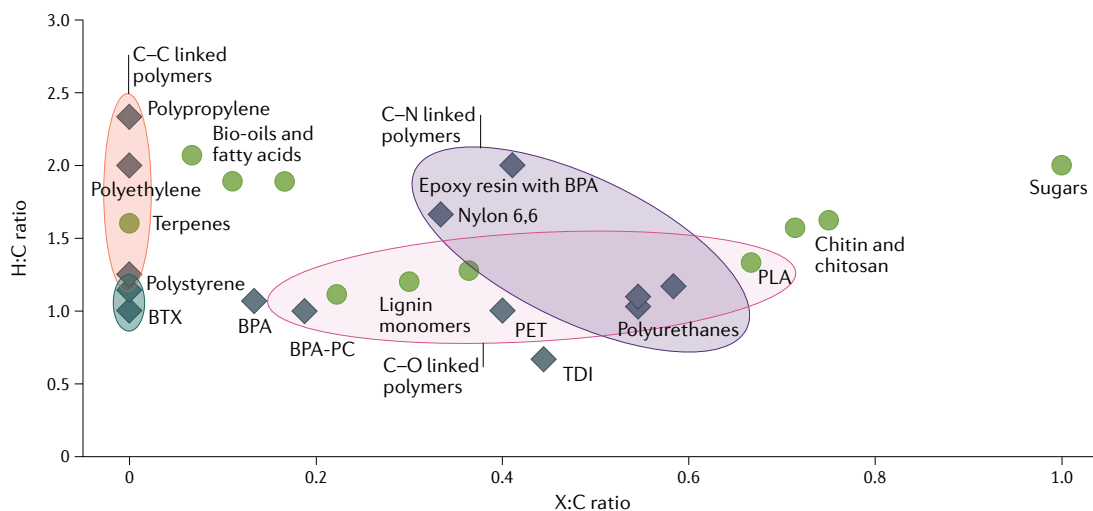


Fig. 1 | Van Krevelen diagram for select polymers. Select fossil-based polymers or feedstocks (black diamonds) and select bio-feedstocks and monomers or polymers (green circles) plotted relative to their heteroatom to carbon ratio (X:C, where X = O, N, among others) and their hydrogen to carbon ratio (H:C). As many C–O and C–N linked polymers and their respective monomers have X:C and H:C ratios similar to those of bio-feedstocks, they are a focus of work in the bio-based polymer field and of this Review. BPA, bisphenol A; BPA-PC, poly(bisphenol A carbonate); BTX, benzene–toluene–xylene; PET, polyethylene terephthalate; PLA, polylactic acid; TDI, toluene diisocyanate. Data available in the Supplementary information.

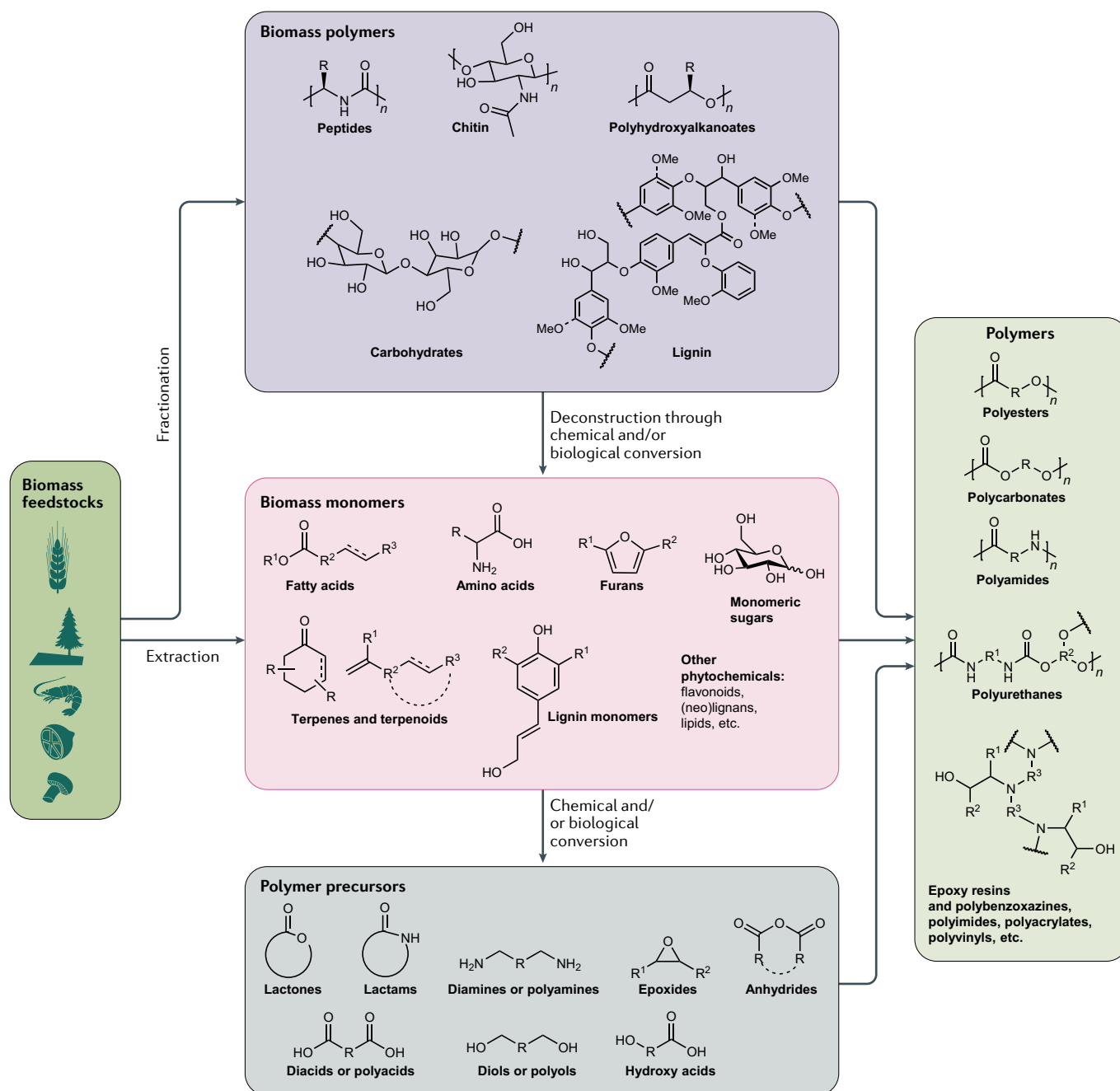


Fig. 2 | Polymers from biomass. A range of biomass feedstocks yield biopolymers, which can be deconstructed into constituent products through chemical and/or biological conversion as well as incorporated directly into polymers. Small molecules can also be extracted directly from the biomass feedstock. These monomeric bio-derived compounds, if not already polymerizable, can be transformed into precursors for polymer synthesis. Structures shown are illustrative and do not fully represent the structural complexity and variety afforded by nature, which can be further compounded through synthetic transformations, and polymer repeating units may vary slightly depending on the particular polymerization strategy.

transformations to obtain the necessary functionality for polymerization. Fortunately, there is a vast research community focused on selective chemical and biological transformations of bio-feedstocks and small-molecule intermediates into building blocks for new bio-based polymers. As highlighted below, these transformations often involve chemical catalysis¹³, biological catalysis⁴⁰ or some combination thereof^{20,41–43} (FIG. 2).

Polymer properties

The unique chemical functionality of bio-derived monomers can endow the resulting polymers with performance-advantaged properties. However, before these materials can be scaled up or petrochemical feedstocks replaced, the polymer properties must be characterized and benchmarked relative to the incumbent materials.

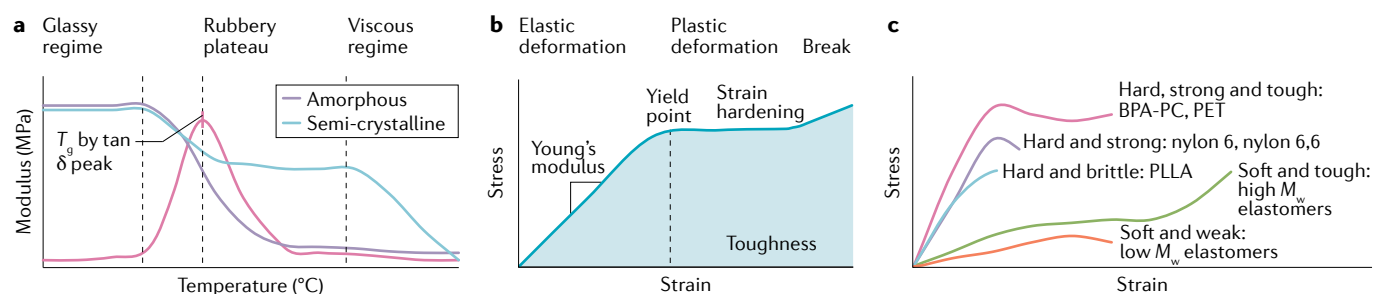


Fig. 3 | Fundamental thermomechanical polymer properties. **a** | Idealized dynamic mechanical analysis plots for amorphous and semi-crystalline polymers with characteristic regions defined. **b** | Idealized stress–strain plot with tensile properties defined. **c** | Idealized stress–strain curves illustrative of common material classes and synthetic polymers. BPA-PC, poly(bisphenol A carbonate); M_w , weight-average molecular weight; PET, polyethylene terephthalate; PLLA, poly-L-lactic acid; T_g , glass transition temperature.

Fundamental polymer properties

The fundamental properties of bio-based polymers (that is, thermomechanical properties) (FIG. 3) must be measured and compared with those of typical polymers (TABLE 1) to determine whether they exhibit performance-advantaged properties. In general, polymers must be above a critical molecular weight to experience chain entanglement (M_e) and show consistent properties. The M_e is polymer dependent and can be determined by rheology, marked by the zero-shear viscosity exhibiting a non-linear scaling with molecular weight. Typically, the number and weight-average molecular weights (M_n and M_w , respectively) and chain-length dispersity index (D , calculated by M_w/M_n) are determined using gel permeation chromatography and expressed in daltons. Thermal properties, which dictate the working temperature window of a polymer, are usually characterized by differential scanning calorimetry, with exothermic and endothermic curves revealing when a material undergoes a glass, melting or crystallizing transition at the temperatures T_g , T_m and T_c , respectively. The thermal decomposition temperature (T_d) is measured by thermogravimetric analysis. Dynamic mechanical analysis reveals thermal transitions as a function of the storage and loss moduli (E' and E'' , respectively) versus temperature (FIG. 3a), illustrating how the glass transition corresponds to softening of a material. For an amorphous, low M_w polymer, the transition to viscous flow occurs immediately, whereas a semi-crystalline polymer has a rubbery plateau between its T_g and T_m and can be used up to the T_m . In terms of mechanical properties, tensile testing (FIG. 3b,c) provides a stress (σ)–strain (ϵ) curve, the shape of which (the initial slope is defined as the Young's modulus, E , and the area underneath as toughness) and the ultimate stress and strain at break (σ_b and ϵ_b , respectively) determine the suitability of a polymer for applications. For example, a material that continues to elongate after reaching maximum stress is considered tough, whereas one that does not is brittle. Although each polymer class (for example, polyesters) or material type (for example, rubbers) has a typical range of thermomechanical properties, the profile can vary depending on functionality, architecture and processing conditions.

Performance-advantaged properties

Performance-advantaged properties include improved manufacturability, properties for specific applications and/or end-of-life considerations (such as recyclability

or degradability). Importantly, the application properties must be at least on par with those of incumbent materials, and are generally evaluated by the thermomechanical profile. As an example of property enhancement, structurally rigid functional motifs (such as alkenes, ketones, aromatics and bicyclics) often lead to a higher T_g and, thus, such materials can be used at higher temperatures, whereas long alkyl chains ($>C_6$) containing heteroatoms, which are more difficult to obtain from petroleum-based feedstocks, can render greater ductility^{44–46}. These properties, among others such as flame-retardant properties, are often achieved with polymer additive formulations. Using bio-based monomers to form polymers that inherently exhibit these properties avoids the use of often toxic additives (for example, phthalate plasticizers or brominated flame retardants). Thus, bio-derived monomers could mitigate the toxicological effects associated with polymer manufacturing, use or degradation. Styrene, for example, can yield polymers with robust thermomechanical performance, but its high volatility and toxicity pose health risks⁴⁷. Similarly, bisphenol A (BPA) imparts favourable properties to polymers owing to its rigidity, but is an endocrine disruptor^{48–50}. In both cases, bio-derived aromatic monomers can serve as advantaged replacements because additional ring substitutions reduce volatility, toxicity and the potential for endocrine disruption^{51–53}. Furthermore, bio-based chemical functionality can facilitate processing, such as faster cure times (that is, the time for crosslinking of individual components to form a network) through amine–ketone condensation compared with typical epoxide–amine chemistries⁵⁴. The bio-based monomer 1,3-propanediol has replaced 1,4-butanediol and ethylene glycol in some terephthalate polyester products, owing not only to an inexpensive and low-energy production route but also to the resultant changes in polymer morphology that improve the crystallization rate, structure and material elasticity, among other advantages in applications, manufacturing and recycling^{55,56}. Indeed, the prevalence of hydroxy acids, lactones, amines, aldehydes and ketones in bio-based monomers offers unlimited potential to redesign plastics to be chemically recyclable or biodegradable.

To fully capitalize on the unique functionality afforded by bio-feedstocks, it is necessary to establish structure–property relationships. Additionally, new catalysts and

synthetic methodologies are needed to accommodate the complex sterics, electronics and functionalities of these monomers. In the following, we further explore how bio-derived functionalities give rise to polymers with performance-advantaged properties, focusing on renewable polymers with oxygen-linked and nitrogen-linked backbones for non-biomedical applications. For these heteroatom-linked polymers, functionality for step-growth polymerization is often more directly accessible from bio-feedstocks. Chain-growth, ring-opening polymerization (ROP), however, offers more control of the polymerization and often superior polymer properties, as small molecules are removed during monomer synthesis rather than during polymerization. For vinyl addition chain-growth monomers, it is common for an acrylic portion to be installed on the biomolecule, although this is also easily bio-based⁵⁷. Although not reviewed here, bio-based polymers with hydrocarbon backbones (that is, vinyl and acrylic)^{44,58–62}




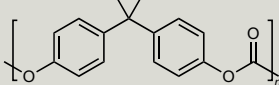
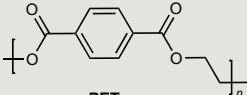
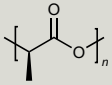
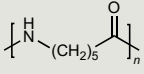
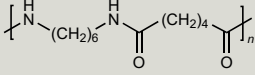
can also be performance-advantaged. For example, the α -methylene- γ -butyrolactone (MBL; also known as Tulipalin A) family yields acrylic bioplastics with increased thermal and solvent resistance as well as depolymerization selectivity for monomer recovery relative to polymethyl methacrylate, due to stabilization of radical intermediates by the natural pendent lactone motif^{58,63}.

C–O linked polymers

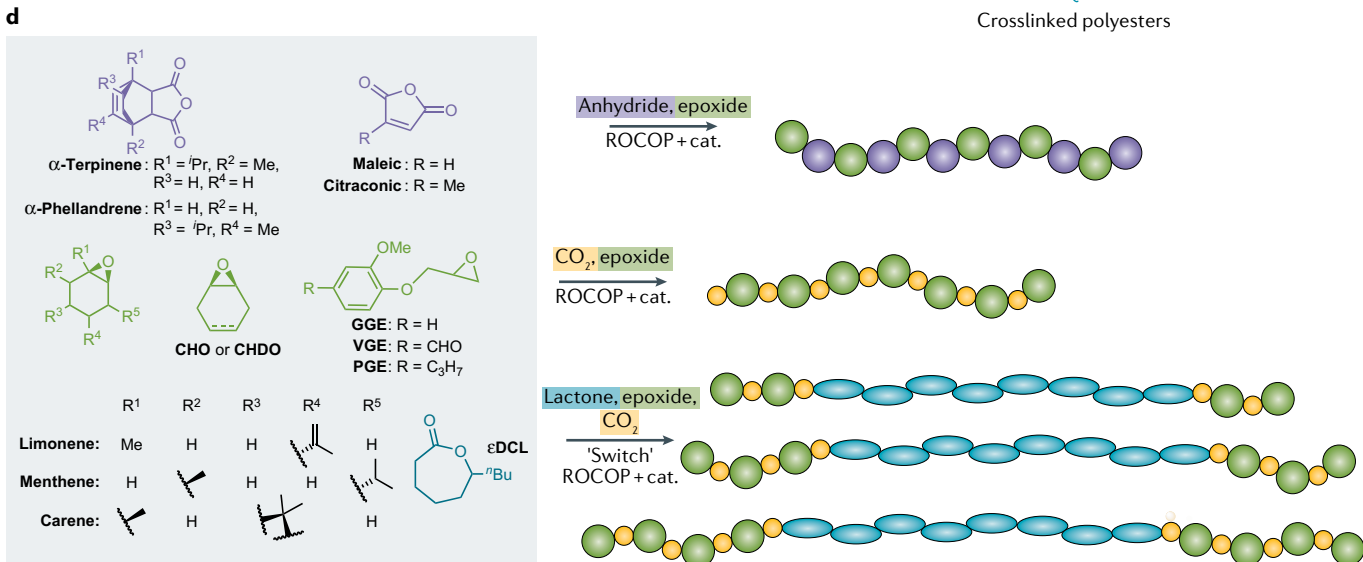
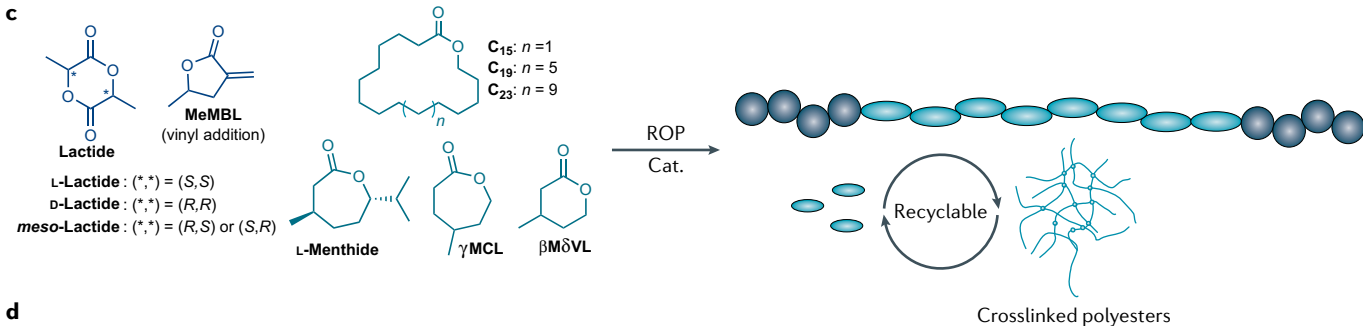
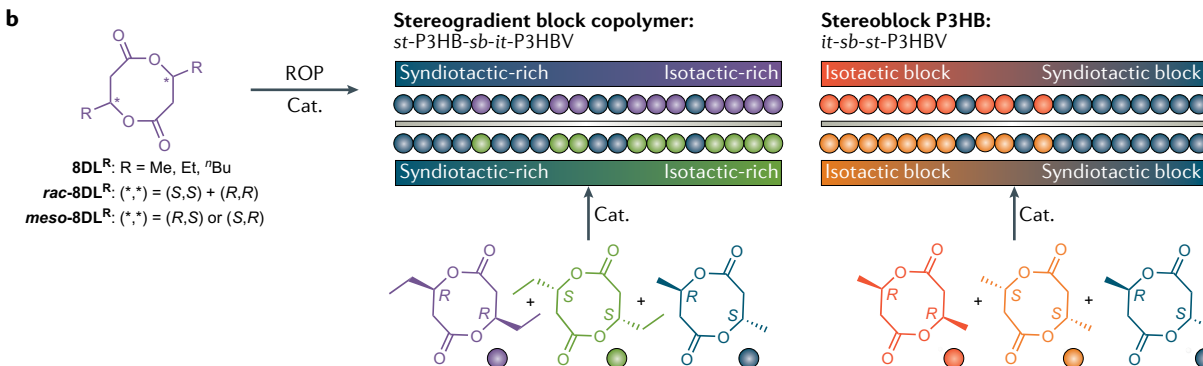
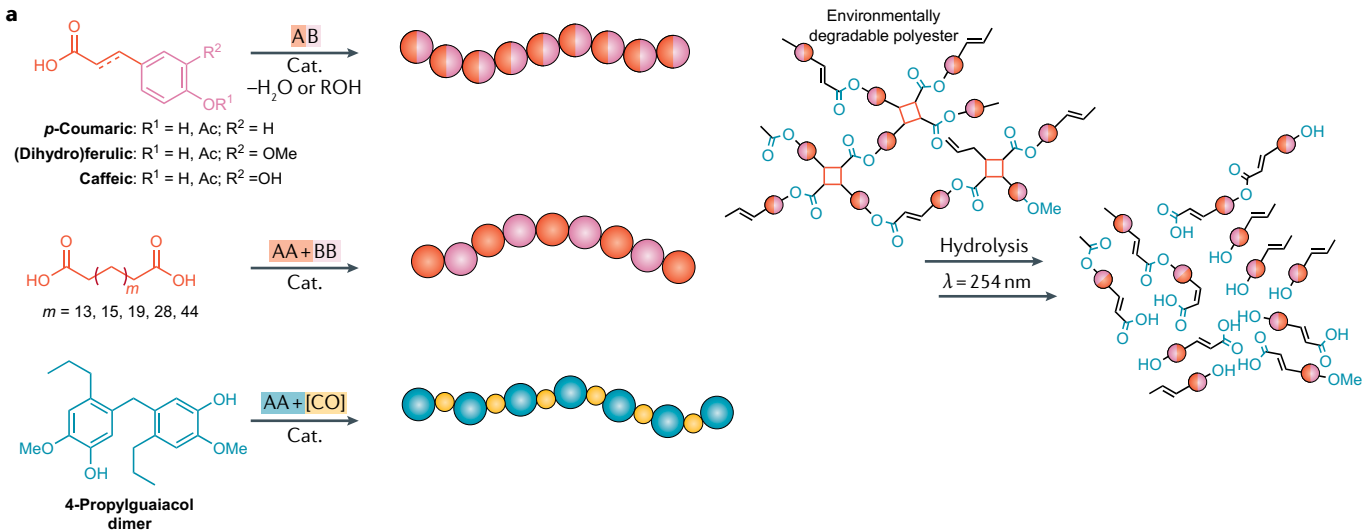
Polyesters

Polyesters are versatile materials traditionally synthesized by condensation of oxygenated AA/BB or AB monomers (FIG. 4), and are ideal targets from bio-derived monomers, garnering considerable attention^{16,17,21,23,44,64–68}. Microorganisms directly synthesize polyesters for carbon and energy storage as polyhydroxyalkanoates (PHAs)^{69,70} (FIG. 2), whereas synthetic polyesters are made through step-growth condensation of carboxylates and diols or hydroxy acids, chain-growth

Table 1 | Thermomechanical properties of common polymers

Polymer	Structure	T_g (°C)	T_m (°C)	σ_B (MPa)	E (MPa)	ϵ_B (%)
HDPE	 Linear HDPE	$-140 \leq T_g \leq -100$	130–137	22–31	1,070–1,090	100–1,200
LDPE	 Branched LDPE	< -40	80–115	8.3–34	100–300	100–800
it-PP	 it-PP	$-20 \leq T_g \leq -10$	160–170	31–41	1,140–1,550	100–700
BPA-PC	 BPA-PC	$145 \leq T_g \leq 150$	–	60–121	2,068–2,410	65–107
PET	 PET	67–75	245–260	48 ^a –172 ^b	2,757 ^a –4,136 ^b	100 ^b –500 ^a
PLLA	 PLLA	55–65	160–186	60	1,720	3–6
Nylon 6	 Nylon 6	40–60 ^c	218–231	50–95	1,500–3,000 ^c	5–300
Nylon 6,6	 Nylon 6,6	50–80 ^c	265–280	35–90 ^c	1,500–3,500 ^c	5–200

Data for all polymers from the [Polymers: A Property Database](#) (mechanical property data obtained with standardized methods from ASTM International and ISO). ϵ_B , strain at break; σ_B , stress at break; BPA-PC, poly(bisphenol A carbonate); E, Young's modulus; HDPE, high-density polyethylene; it-PP, isotactic polypropylene; LDPE, low-density polyethylene; PET, polyethylene terephthalate; PLLA, poly-L-lactic acid; T_g , glass transition temperature; T_m , melting temperature. ^aAmorphous. ^bBiaxially oriented. ^cMeasured from humid to dry conditions.



◀ Fig. 4 | **Variety of available bio-based polymer architectures with C–O inter-monomer linkages.** Examples of bio-derived monomers and polymerization methods for synthesizing C–O linked polymers. **a** | Condensation of AA/BB or AB monomers to form polyesters (red and pink) and polycarbonates (blue and yellow). [CO] refers to a carbonyl-containing co-monomer, such as phosgene or dimethyl carbonate, used to form the carbonate linkage in polycarbonates. Synthesis of the hyperbranched polyester is followed by light-initiated cycloaddition of the α,β -unsaturated moieties to crosslink the polymer shown on the right; accelerated hydrolysis and irradiation at 254 nm results in degradation to small molecules, whereas burying in soil for 10 months leads to gradual biodegradation⁸⁴. **b** | Selective ring-opening polymerization (ROP) of eight-membered cyclic diolides (8DL⁸) to form (stereo)block (right) or (stereo)gradient (centre) polyhydroxyalkanoate (PHA) copolymers. Random copolymers are accessible but not shown. **c** | ROP of lactones (soft monomers shown as teal ovals and hard monomers as navy spheres) to polyesters, including crosslinked homopolymers and tri-block copolymers (tri-BCPs). **d** | Ring-opening copolymerization (ROCOP) of anhydrides (purple) and epoxides (green) to polyesters, and CO₂ (yellow) and epoxides to polycarbonates. Switchable ROCOP of lactones, epoxides and CO₂ to produce polyester–polycarbonate BCPs. Epoxide and some anhydride structures shown are derived from terpene in the associated labels and are not the native structures. β M δ VL, β -methyl- δ -valerolactone; γ MCL, γ -methylcaprolactone; ϵ DCL, ϵ -decalactone; CHDO, cyclohexadiene oxide; CHO, cyclohexene oxide; GGE, guaiacol glycidyl ether; *it*, isotactic; MeMBL, γ -methyl- α -methylene- γ -butyrolactone; P3HB, poly(3-hydroxybutyrate); P3HBV, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate); PGE, propylguaiacol glycidyl ether; *sb*, stereoblock; *st*, syndiotactic; VGE, vanillin glycidyl ether. Panel **b** adapted with permission from REF.¹⁰⁷, AAAS.

ROP of cyclic esters (lactones or lactides) or alternating ring-opening copolymerization (ROCOP) of anhydrides and epoxides^{21,71}. The most widely consumed polyester is polyethylene terephthalate (PET), which is mass produced for textiles and packaging; however, PET persists in the ambient environment for >400 years (REF.⁷²). Bio-based polylactic acid (PLA) is a commercially available and industrially compostable alternative to PET for short-term packaging applications; the inherently chiral monomer leads to a highly isotactic polymer (poly-L-lactic acid (PLLA)) with improved properties relative to atactic PLA. Sugar-derived polyethylene furanoate (PEF) has been proposed to compete with PET, as its thermal properties are similar but it has ~10 \times lower oxygen permeability (0.0107 barrer versus 0.114 barrer for PET), which is advantageous for food preservation⁷³. However, PEF is brittle and does not exhibit strain-hardening, which limits its use in pressurized environments^{74–76}. These examples demonstrate the need for comprehensive benchmarking of bio-based materials. In this section, we discuss examples of performance-advantaged polyesters made by step-growth and ring-opening chemistries.

Step-growth polyesters. Lignin-derived monomers are commonly used to produce semi-aromatic polyesters^{17,30,44,77,78}. Although various PET analogues exhibit T_g values comparable with or higher than that of PET, the mechanical properties are understudied^{79–83}. Thus, there is little evidence to suggest these materials offer advantages over PET in applications. A potential exception is poly(dihydroferulic acid), which is synthesized from an AB monomer and possesses the requisite PET-like thermal properties ($T_g \approx 73^\circ\text{C}$, $T_m \approx 234^\circ\text{C}$ (~30 $^\circ\text{C}$ lower than that of PET), $T_c = 196^\circ\text{C}$), and crystallizes faster, implying processing benefits; however, tensile analysis was not reported⁷⁹.

Another lignin-derived AB monomer, *p*-coumaric acid (FIG. 4a), has an α,β -unsaturated acid motif that

can participate in a post-polymerization, light-initiated cycloaddition (at wavelengths (λ) >280 nm) to increase the mechanical strength of hyperbranched poly(coumaric-*co*-caffeic acid)⁸⁴. The photoreaction increased σ_b from 50 to 104 MPa and E from 16 to 19 GPa, comparable with those of poly(bisphenol A carbonate) (BPA-PC). Moreover, the potential for biodegradation was demonstrated in soil, or with a combination of accelerated hydrolysis and further ultraviolet irradiation ($\lambda = 254\text{ nm}$) producing oligomeric and monomeric units ($M_n < 1,000\text{ Da}$). Polymers of aliphatic camphoric acid, derived from the oxidation of a bicyclic terpene, exhibit T_g values exceeding that of PET owing to the rigid five-membered ring, and hydrolysis over 14 days yielded monomers and oligomers ($M_n < 600\text{ Da}$), even at neutral pH⁸⁵. Although exploratory, these examples demonstrate how bio-derived functionalities can afford useful thermal and mechanical properties paired with built-in degradation mechanisms.

Trans,trans-muconic acid, which can be obtained from carbohydrates or lignin after facile isomerization of biologically produced *cis,cis*-muconic acid^{86–89}, has furnished unsaturated polyesters for performance-advantaged fibre-reinforced plastics^{52,90}. The backbone alkenes in these polyesters allow for reaction with small-molecule crosslinkers, and employing *trans,trans*-muconic acid avoids the use of maleic anhydride to introduce unsaturation and noxious styrene to crosslink. Relative to maleic anhydride-based polyester resins for fibre-reinforced plastics, muconate-containing polyester materials showed improved strength, thermal properties and adhesion to fibres, because the diene functionality increases the rigidity of the initially linear polymer matrix and provides more crosslinking sites. Additionally, the use of bio-based cinnamic acid with methacrylic acid as branching units showed better compatibility with the unsaturated polyester, and therefore reactivity, than did styrene. In a demonstration of upcycling, *trans,trans*-muconate was polymerized with reclaimed PET oligomers, producing composites that transform US\$0.51 lb⁻¹ waste into a useful US\$2.60 lb⁻¹ product⁹¹. These composites have attractive mechanical properties and are predicted to save 57% in supply chain energy and decrease greenhouse gas emissions by 40% relative to the preparation of conventional unsaturated polyesters for fibre-reinforced plastics, demonstrating both manufacturing and in-use advantages.

Fatty acids have been transformed into long-chain (C_{17} , C_{19} , C_{23}) aliphatic polyesters (FIG. 4a) with properties similar to those of low-density polyethylene (LDPE)^{45,92–96}. The transformation involves isomerizing alkoxycarbonylation to give diesters, which subsequently undergo polycondensation with their reduced diol counterparts to form polyesters^{45,92–96}. Even longer-chain C_{32} and C_{48} diesters produce polyesters with a higher T_m (120 $^\circ\text{C}$)⁹⁷. The degradability of long-chain aliphatic polyesters is often claimed as an advantage over their comparative polyolefins and is attributed to their likeness to cutin or suberin. A polyester comprising C_{12} and C_6 monomers showed favourable gas permeability properties, but did not compost at 40 $^\circ\text{C}$ over 140 days; only more hydrophilic copolymers with lower crystallinity

degraded under the composting conditions⁹⁸. Polyesters that are more crystalline and hydrophobic would require modification to biodegrade in soil or compost.

PHAs, however, are well known for biodegradability under ambient conditions^{69,70,99–101}. Poly(3-hydroxybutyrate) (P3HB) has exceptional gas barrier properties and outperforms prevalent packaging plastics, because its perfect isotacticity imparts a high degree of crystallinity¹⁰². However, P3HB is very brittle ($\epsilon_B \approx 3\%$) with a T_m ($\sim 175^\circ\text{C}$) close to the T_d ($\sim 250^\circ\text{C}$), limiting its use¹⁰¹. Properties can be tailored by incorporating more flexible co-monomers, enabling commercial ventures to begin marketing various PHA products⁶⁶, whereas converting municipal and agricultural waste into PHAs is an active research area^{21,99,101,103–105}. Synthetic PHAs offer further scope for property enhancement. After 60 years of research, the chemical synthesis of PHAs was finally accomplished by ROP, with the materials rivalling natural PHAs, and with increased control of \bar{D} and copolymer microstructures^{106–109} (FIG. 4b). However, the chemical circularity of PHAs needs to be addressed, as degradation in the environment is a fail-safe, leading to loss of value¹¹⁰.

ROP polyesters. Although many bio-derived functionalities enable straightforward polycondensation of AA/BB or AB monomers, process efficiency can suffer owing to steric and electronic factors as well as competing functionalities of more complex monomers. Precise control of monomer stoichiometry and high temperature and vacuum for long periods can be necessary to reach entanglement M_e while fighting thermal degradation. Conversely, ROP of lactones offers exquisite control of the polymerization characteristics (M_n , \bar{D} , stereoselectivity, microstructure, chain ends and topology), offers tunable kinetics using organometallic and organic catalysts, and can be conducted under mild conditions. Alternating ROCOP has also enabled polyester synthesis from cyclic anhydride and epoxide monomers^{21,71}. Additionally, although all polyesters are inherently hydrolysable, catalytic depolymerization enables lactone recovery when the thermodynamics are well balanced¹¹¹. ROP further allows for different (co) polymer architectures, such as random, block, graft, star-shaped and cyclic structures, as well as the inclusion of (reversible) crosslinkers⁶⁴. Block copolymers (BCPs) can now be screened in high throughput by exploiting the tunable activity of cyclic oxygenate monomers with organocatalysts; for example, 100 unique polymers were produced in just 9 min using a continuous flow reactor¹¹². Thus, ROP polyesters are often performance-advantaged owing to their modularity and end-of-life options.

The recent success in chemically synthesizing PHAs was inspired by the synthesis of PLA, which proceeds through ROP of a six-membered cyclic monomer comprising two lactic acid units (lactide; monomer shown in FIG. 4c), with ROP leading to a polymer superior to that produced through hydroxy acid polycondensation. For PHAs, an eight-membered cyclic diolide monomer (8DL^R, R = Me, Et or ⁿBu) (FIG. 4b) is ring-opened^{106–108}. In contrast to enantiopure L-lactide ROP, whereby a single stereoisomer is polymerized by a non-selective tin catalyst, racemic (*rac*) mixtures of 8DL^R are polymerized by

stereoselective catalysts. *Rac*-8DL^{Me} produces perfectly isotactic P3HB under ambient conditions in 1 min, and different 8DL^R monomers can be copolymerized to produce various PHAs. The microstructures and resulting material properties are controlled by the catalyst selectivity and co-8DL^R feed ratios, leading to random, (stereo) block or (stereo)gradient copolymers that are ductile and tough while maintaining high crystallinity. Polymerizing 1:1 *rac*:*meso*-8DL^{Me} increased the ϵ_B of P3HB six-fold, owing to the syndiotactic stereoblock ($T_m = 157$, 141°C) (FIG. 4b, right). Elongation of nearly 600% was attained by polymerizing 4:1 *meso*-8DL^{Me}:*rac*-8DL^{Et} to form a syndiotactic P3HB block capped by an isotactic poly(3-hydroxyvalerate) (P3HV) block (FIG. 4b, centre). These microstructures were formed owing to the kinetic preference of the selected catalyst for 8DL^{Me} over 8DL^{Et}, and for the *rac* over the *meso* diastereomer for a given monomer. Compared with P3HB, the P3HB–P3HV copolymer ($T_m = 135^\circ\text{C}$, $\sigma_B = 24\text{ MPa}$, $E = 169\text{ MPa}$) has a wider processing window and application space, but maintains polyolefin-like properties. However, the effects of unnatural tacticities require further characterization¹¹³. The 8DL^R monomers are synthesized in four steps from succinate, but there is opportunity to dimerize hydroxy acids by shape-selective catalysis¹¹⁴; this would enable the circular life cycle of PHAs, which can be hydrolysed to *rac* or enantiopure hydroxy acids¹¹⁵.

ROP of larger lactones is entropy driven and, thus, requires high temperatures. However, enzymatic and coordination catalysis methods have enabled ROP of plant oil-based C₁₅, C₁₉ and C₂₃ lactones^{21,96,116–122}. Reactive extrusion coupled to an enzymatic process was recently demonstrated¹²², and accelerated degradation studies show that the incorporation of smaller (C₆) lactones allows for more rapid hydrolysis by breaking up the hydrophobic backbone¹¹⁹.

Owing to unique sets of bio-derived functionalities, bio-based polyesters show performance advantages in applications such as elastomers and adhesives, wherein non-degradable vinyl polymers dominate^{64,123,124}. ROP of lignocellulose-derived β -methyl- δ -valerolactone (β M δ VL) and γ -methylcaprolactone (γ MCL) (FIG. 4c) with ester-based crosslinkers produces materials with ϵ_B , σ_B and elasticities on par or superior to those of vulcanized natural rubber bands^{125,126}. Recycling of poly(β M δ VL) recovered 90% monomer, whereas poly(γ MCL) yielded its hydroxy acid when subjected to enzymatic degradation¹²⁷. Advantages for adhesives beyond competitive adhesive strength include hydrolysability (non-degradable counterparts cause gumming problems in recycling processes), reduced use or elimination of volatiles and toxics, toughness or flexibility and hydrophobicity^{124,128}. Pressure-sensitive adhesives formed through the condensation of fatty acid and sugar-based monomers with 99%+ bio-based content and tunable properties have been commercialized, with a preliminary life cycle analysis showing lower environmental impact compared with polyacrylic tapes^{123,129}. However, ROP offers more opportunities to tune properties through design of BCPs with specific segment lengths and hardness, by virtue of telechelic end groups and the wide variety of applicable bio-based monomers⁶⁴.

In an ABA tri-BCP approach to pressure-sensitive adhesives, terpene-derived L-menthene (FIG. 4c) was used as a low T_g central block and PLA as short, hard end blocks¹²⁸. The backbone substituents suppress crystallization whereas the hard PLA end caps induce the microphase separation necessary for good viscoelasticity. When mixed with a bio-based rosin-ester tackifier, the tri-BCP displayed adhesive properties superior to or comparable with those of styrene-based tapes (with a peel adhesion strength of 3.2 N cm⁻¹ versus 1.9–4.2 N cm⁻¹ for commercial tapes). With hard poly- γ -methyl- α -methylene- γ -butyrolactone (P(MeMBL), a bio-based polyacrylate) as the end caps, similar competitive properties were realized with the added advantage of a heat-fail temperature of >150 °C due to the high thermal stability of poly(α -methylene- γ -butyrolactone)s, surpassing that of non-crosslinked styrenic BCP adhesives¹³⁰.

The most impressive pressure-sensitive adhesive, which does not require tackifier to outperform commercial tapes, is part of a series of ABA polycarbonate-block-polyester-block-polycarbonate BCPs made by switchable ROCOP catalysis¹³¹. With an optimized coordination catalyst and reaction conditions, a mixture of bio-based ϵ -decalactone and cyclohexene oxide (to which a bio-based route has been established¹³²) was selectively polymerized to poly(ϵ -decalactone) by ROP until CO₂ was introduced, after which the mechanism switched to epoxide/CO₂ ROCOP to produce poly(cyclohexane carbonate) (PCHC) end blocks (FIG. 4d). Tough plastics, elastomers or adhesives are formed depending on only the block lengths. The shortest PCHC block led to an adhesive with a peel strength of 10 N cm⁻¹, which is far higher than those of commercial tapes and other bio-based tri-BCPs. When the polymer is 50 wt% PCHC, a strong and tough plastic is realized (ϵ_B = 20 MPa, σ_B = 900%), whereas 28 wt% produces an elastic material with shape recovery. Similarly, a strong, tough plastic with near-ideal elasticity is produced when a recyclable poly(β M δ VL) mid-block is capped by 32% semi-crystalline PLLA (ϵ_B = 28 MPa, σ_B = 1,720%), and a similar PLLA content with a γ MCL mid-block has an ϵ_B of 35 MPa and σ_B of 895%^{133,134}. The customizability of oxygenated ABA BCPs, enabled by tunable catalysts, is key to producing these PBPs.

Bio-derived functionalities are apt for epoxide/anhydride ROCOP systems (FIG. 4d), leading to polyesters with high and tunable T_g values. Epoxidation and Diels–Alder chemistry enable the conversion of bio-derived functionalities to both monomer types, whereas the one-pot cyclization of diacids to anhydrides and subsequent ROCOP with an epoxide has been demonstrated with tandem catalysis¹³⁵. Epoxides derived from terpenes and 1,4-cyclohexadiene (CHD), a by-product of fatty acid metathesis, undergo ROCOP with phthalic anhydride (FIG. 4d), affording materials with respectable M_n values of up to 25 kDa and T_g values in the range 59–165 °C (REFS^{132,136}). Introducing unsaturation into ROCOP polyesters is reportedly easier with CHD oxide (CHDO) than with maleic anhydride¹³². Sugar and terpene-based dienes have served as precursors to tri-cyclic anhydrides by Diels–Alder reaction with maleic

anhydride. These anhydrides polymerize with propylene oxide or cyclohexene oxide to form polyesters with T_g values of 66–184 °C (REFS^{137,138}). For example, the polyester formed from propylene oxide and the adduct of α -terpinene and maleic anhydride has a T_g of 109 °C (M_n = 55 kDa)¹³⁷. Moreover, CO₂ can be added to introduce random carbonate linkages along the backbone and potentially enhance materials²¹.

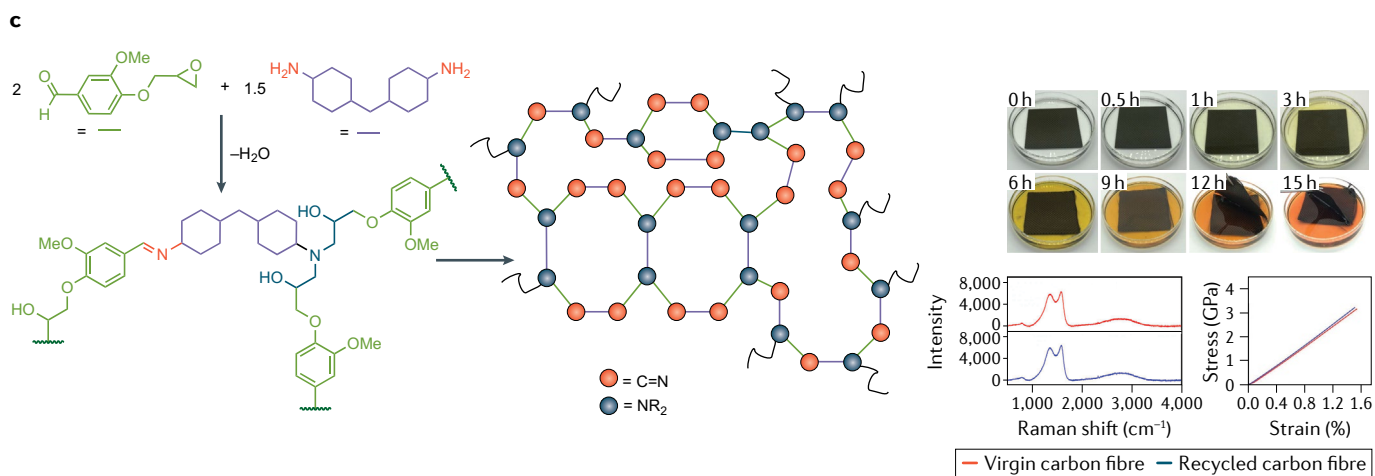
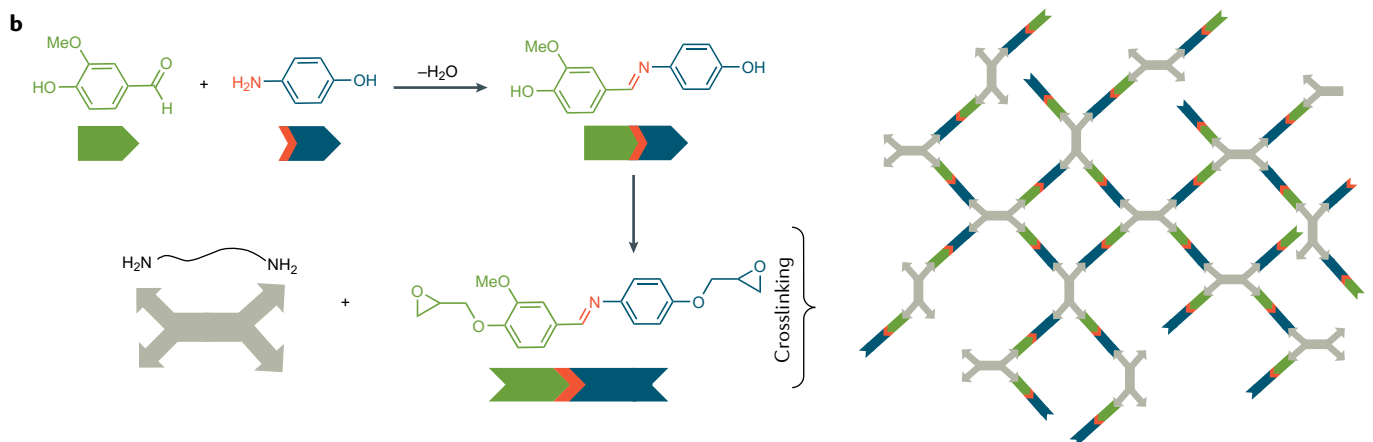
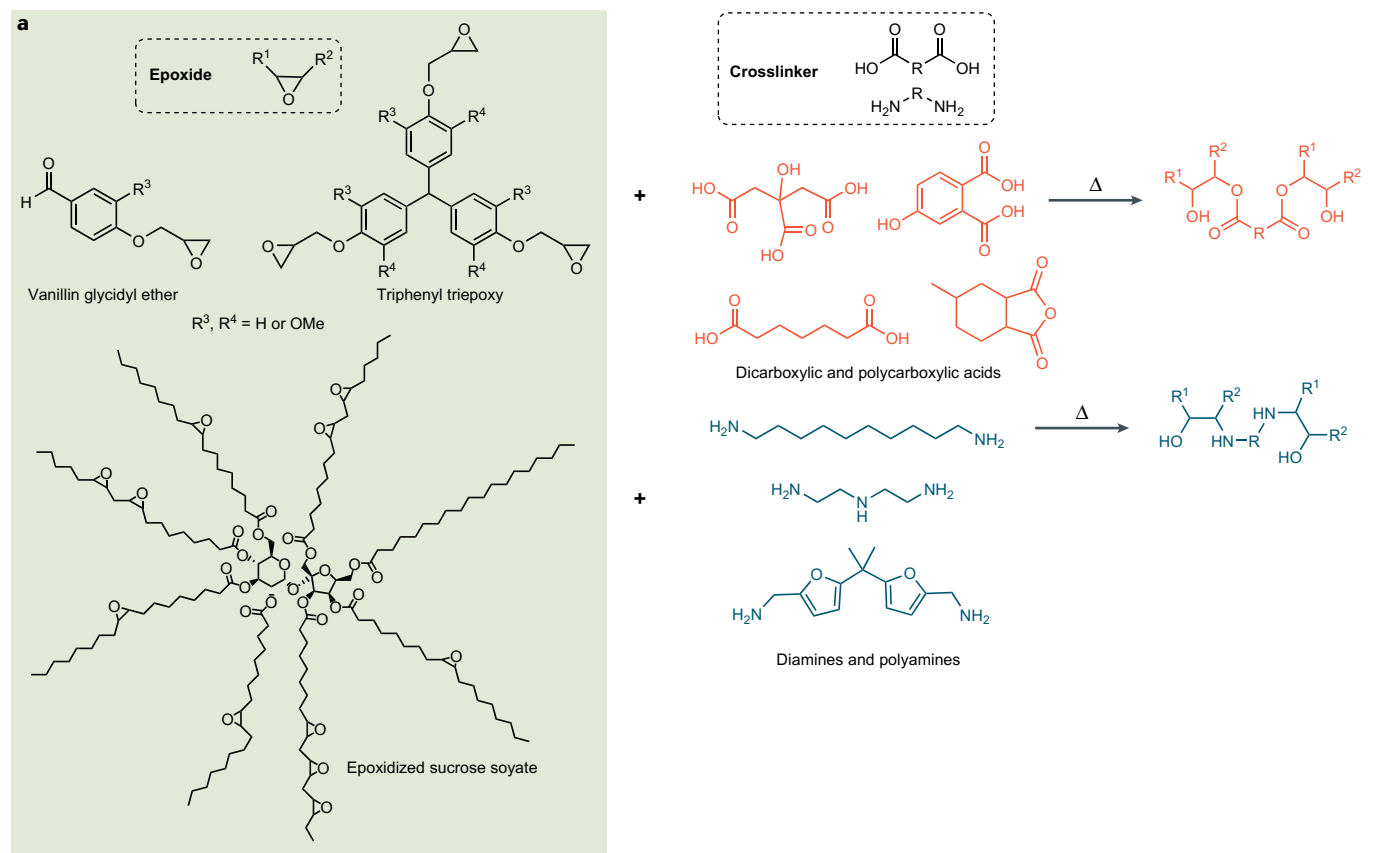
ROCOP studies have focused on understanding relationships between monomer combinations, catalyst performance (activities and selectivities) and thermal properties, but not on mechanical properties. Although T_g values are high, the proximity of ester linkages (two or three carbons apart) could curb the strength and ductility²¹. Thus, research should move towards establishing PBPs using now well-developed ROCOP methods. For example, using ROCOP, polyesters were made from phthalic anhydride, guaiacol glycidyl ether (epoxide) and a small fraction of vanillin glycidyl ether¹³⁹ (FIG. 4d). Both glycidyl ethers participate in ROCOP, whereas the pendent aldehyde groups on vanillin glycidyl ether can react with a diamine to form reversible imine crosslinks. The resulting crosslinked polyesters are hard and strong, reprocessible and recyclable, with T_g values of ~60–70 °C.

Polycarbonates

BPA-PC, the most common polycarbonate, is amorphous, hard and tough (FIG. 3c), with a high T_g (145–150 °C) (TABLE 1), outstanding impact strength and optical clarity, making it a valuable engineering plastic. However, BPA is an endocrine disruptor, and its replacement analogues are also not inert^{48–51}, whereas the co-monomer phosgene is lethal, initiating research into safer alternatives from bio-feedstocks^{51,140}. ROCOP of epoxides/CO₂ and selective ROP of cyclic carbonates are phosgene-free routes to polycarbonates, but monomer scope is more limited²¹. In the former, carbonate linkages are only two or three carbons apart, but properties can be modulated by introducing ester linkages. Aliphatic polycarbonates are easily bio-derived and biodegradable¹⁴¹, but are not engineering plastics. Applications include biomedical materials^{68,139,142–144}, coatings^{145,146}, transparent elastomers^{144,146} or as components of other materials (such as polyethercarbonates and polycarbonate polyols)^{147–149}.

Step-growth polycarbonates. Oestrogen receptor binding is hampered when phenolics have an *ortho*-methoxy substituent, a common lignin-derived functionality⁵¹. In human oestrogen receptor studies, the dimer of 4-*n*-propylguaiacol (FIG. 4a), derived from lignin, shows a pronounced reduction in potency (10–100×) compared with BPA and related analogues. A polycarbonate made from the 4-*n*-propylguaiacol dimers and triphosgene shows a T_g of 99 °C, but optimization of the low M_n (~5 kDa) could further increase the T_g . Owing to the propyl chains, this polycarbonate is more soluble than those made from the other bisphenols, which is advantageous for processing. However, a higher M_n and mechanical characterization are necessary to establish a performance-advantaged bio-polycarbonate.

Properties competitive with those of BPA-PC have been achieved using isosorbide, a rigid bicyclic diol,



◀ Fig. 5 | **Design and synthesis of bio-epoxy resins.** **a** | Formation of epoxy networks from a bio-based epoxide-containing monomer (green box) crosslinked with diacid or polyacid (red), or diamine or polyamine (blue)^{154,155,172,174}. **b** | Synthesis of an epoxy network containing reversible imine bonds, which are installed during monomer synthesis through the reaction of vanillin (green) with aminophenol (blue), among permanent C–O and C–N linkages. Polymerization of the epoxide monomer with a diamine crosslinker (grey) yields the imine-containing network; this strategy avoids H₂O evolution during network formation¹⁷⁸. **c** | Formation of a dynamic epoxy network (left and centre) with reversible imine bonds from a vanillin-derived epoxide (green, with permanent ring-opened epoxide bonds in navy) and a diamine (purple, with reversible imine bonds in red)¹⁸¹. A composite comprising the dynamic epoxy and carbon fibre can be recycled through acid hydrolysis (right). After 15 h, the epoxy network is completely dissolved (top right), allowing the carbon fibre cloths to be recovered with retention of tensile properties (bottom right, stress–strain plot) and chemical structure (bottom left, Raman spectrum). Panel **b** adapted with permission from REF.¹⁷⁸, ACS. Panel **c** adapted with permission from REF.¹⁸¹, RSC.

and diphenyl carbonate, employing highly active amino acid-based ionic liquid catalysts¹⁵⁰. High molecular weights ($M_w > 100$ kDa) and yields were reached in 1 h, and the resulting polycarbonate has a T_g of 174 °C. However, owing to brittleness, isosorbide was copolymerized with 1,4-butanediol and 1,4-cyclohexanedimethanol. With 50% isosorbide, the resulting polycarbonate had a T_g of 98 °C with impressive σ_B , ϵ_B and E values of 57 MPa, 145% and 979 MPa, respectively. These properties show good potential for BPA-PC applications and beyond. An isosorbide-based poly(arylene ether) also outperformed BPA-PC. The bio-based super-engineering plastic is recyclable, transparent and has a high M_n (>100 kDa), exhibiting a high T_g of 212 °C, σ_B of 78 MPa and a low coefficient of thermal expansion¹⁵¹.

ROP polycarbonates. ROCOP of limonene oxide (LO) or CHDO (FIG. 4d) and CO₂ produces polycarbonates with high T_g values (~110–120 °C) that are biodegradable and chemically recyclable^{111,142,143,145,152}. When hydroxyl impurities from the limonene source are masked, poly(limonene carbonate) (LO-PC) reaches a T_g of 130 °C—the highest reported for an aliphatic polycarbonate. Upon scaling the synthesis to >1 kg, LO-PC reached a high M_n of >100 kDa, enabling mechanical characterization¹⁴⁶. This hard and strong polycarbonate has mechanical properties ($\epsilon_B = 15\%$, $\sigma_B = 55$ MPa) between those of polystyrene and BPA-PC with desirable optical properties. This methodology also used an immobilized chelating agent for catalyst removal, decreasing solvent use by tenfold during polymer purification. However, LO-PC can discolour in the melt owing to a low T_d . As an additive, ethyl oleate reduces discolouration, but results in a trade-off between rheological and thermomechanical properties¹⁵³. Both LO-PCs and CHDO-PCs have unsaturated bio-derived functionalities for post-functionalization, which is especially useful for lower M_n polymers. When crosslinked with tri-thiols, the resulting materials have properties important for coatings: high transparency and hardness, solvent and scratch resistance, and good adhesion to metal¹⁴⁵.

Epoxy resins

Epoxy resins (epoxies) are widely used thermosets in construction, energy, food and transportation sectors, with their tunability, high T_g , low density, robust mechanical strength and solvent resistance making

them suitable for use in coatings^{154,155} and adhesives¹⁵⁶, or to reinforce other materials¹⁵⁷. The reliance on BPA and volatile solvents as well as the lack of recyclability have inspired a search for safer, high-performance alternatives with superior end-of-life properties^{48,51,53,78,158–161}. In this regard, bio-based monomers have afforded less toxic epoxies with improved thermomechanical and end-of-life features^{46,54,154,155,162–175}. Epoxy networks comprise an epoxide-containing monomer and a crosslinking monomer (hardener), which provide structural modularity and tunability for specific applications (FIG. 5a). Rigid aromatic epoxide monomers from lignin can provide high T_g values¹⁷², although multiple methoxy substituents progressively lower the T_g (REFS^{172,176}). Conversely, unsaturated fatty acids can be epoxidized to provide a flexible component when cured with various bio-based hardening agents^{154,155}. For example, varying the bio-based polyacid hardener reacted with epoxidized sucrose soyate (FIG. 5a) tunes the thermomechanical properties of the epoxy resin and can promote a H₂O-soluble formulation¹⁵⁵.

Dynamic covalent networks could address the waste issue associated with conventional thermosets, as the exchange of bonds in response to heat allows for reprocessing of the network^{160,161}. In a lignin-based example, vanillin and guaiacol were joined in a triphenyl-triepoxy monomer, which was reacted with an anhydride to yield a network with a T_g of 187 °C, which is 30 °C higher than that of the BPA counterpart¹⁷⁷. The material undergoes dynamic transesterification with an embedded catalyst, self-healing within 10 min, and thus is repairable with a high service temperature. In another example, vanillin was coupled with aminophenol to form an imine-containing monomer before functionalization with epichlorohydrin. Subsequent crosslinking with a diamine produces an imine-containing network¹⁷⁸ (FIG. 5b). This material is reprocessable and recyclable through heat (no catalyst) or acid hydrolysis, respectively, without notable decreases in thermomechanical properties ($T_g = 71$ °C, $\sigma_B = 46$ MPa, $\epsilon_B = 4.4\%$). Another vanillin–imine network with properties comparable with those of a BPA epoxy was recycled three times without a decline in mechanical properties¹⁷⁹. An entirely renewable epoxy adhesive was synthesized using ozone-treated kraft lignin with sebacic acid, demonstrating a T_g range of 95–133 °C, reversible adhesion with a lap-shear strength of 6.3 MPa (equivalent to that of the BPA epoxy) and damage repair at 190 °C (REF.¹⁵⁶).

Recyclability and degradability are also advantageous for reinforced epoxy resins. Composite materials endow typical thermosets with mechanical properties for demanding applications but are destined for landfills. Recycling of both polymer and reinforcement components is particularly beneficial when the reinforcements are expensive, such as carbon fibre. Examples of this practice are scarce; however, one example used vanillin coupled with pentaerythritol to produce a rigid spiro-diacetal structure that has acid-catalysed reversibility, which was exploited to recycle carbon fibre from the composite¹⁸⁰. This material performed as well as the BPA analogue ($T_g = 169$ °C, $\sigma_B = 87$ MPa, $E = 2.8$ GPa), and the recycled carbon fibre showed

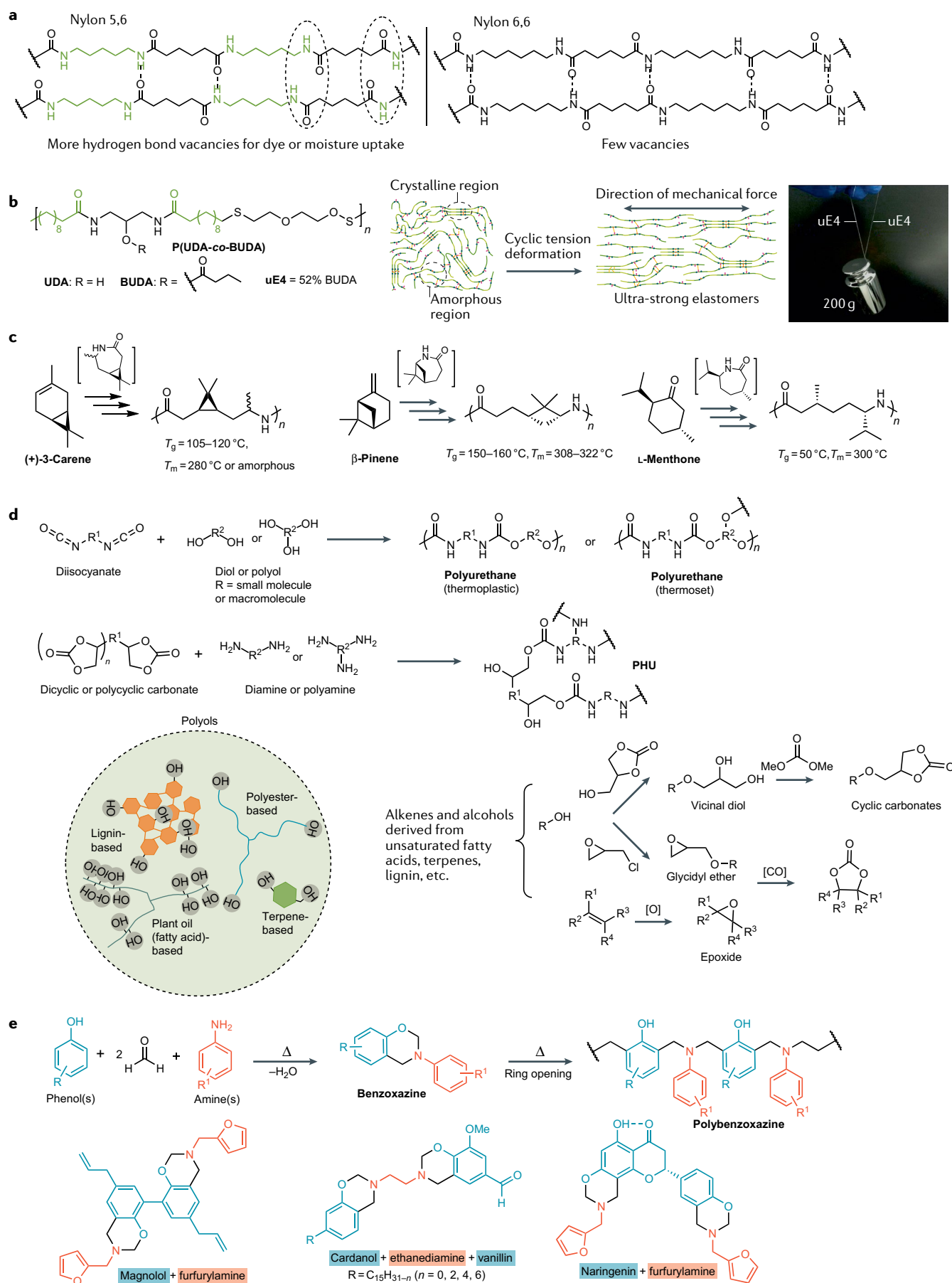


Fig. 6 | Use of bio-derived functionalities in C–N linked polymers. a | Comparison of structures and hydrogen bonding patterns of nylon 5,6 and nylon 6,6, with bio-based content shown in green¹⁸⁶. **b** | Copolymerization of two diene monomers, *N,N'*-(2-hydroxypropane-1,3-diyl)bis(undec-10-enamide) (UDA) and 1,3-di(undec-10-enamido)propan-2-yl butyrate (BUDA), with a dithiol affords the polyimide P(UDA-co-BUDA) (bio-based content shown in green)¹⁹⁶. Cyclic tension deformation applied to P(UDA-co-BUDA) induces rearrangement of the microstructure to produce ultra-strong elastomers (uEs). uE4 is formed from the P(UDA-co-BUDA) with 52% BUDA, and a uE fibre (~135 µm in diameter) is pictured holding a 200-g weight. **c** | Examples of polyamides produced through ring-opening polymerization of terpene-based lactams (substituted caprolactams) and the thermal properties of the polymers. Polymerizability and balance between thermal properties increases from right to left^{197–201}. **d** | Synthesis of polyurethane and polyhydroxyurethane (PHU), and routes to cyclic carbonates for PHU synthesis, with a single starting alcohol shown for simplicity. Examples of polyols for the synthesis of polyurethanes and PHUs are shown in the green circle; polyols derive from the conversion of alkenes present in terpenes and fatty acids from various feedstocks. For PHU synthesis, cyclic carbonate precursors can be prepared directly from alkenes, or through alcohols and polyols. **e** | General synthesis of polybenzoxazine (PBz) (top), and three examples of bio-based benzoxazine monomers (bottom)^{226–228}. *T_g*, glass transition temperature; *T_m*, melting temperature. Panel **b** adapted from REF.¹⁹⁶, CC BY 4.0.

no degradation in performance. In another example, vanillin-based imine chemistry was used to form epoxy and imine crosslinks simultaneously¹⁸¹ (FIG. 5c). The epoxy network can be reformed or repaired through dynamic imine exchange and degraded by acid hydrolysis to recover the carbon fibre, which fully retained its structural integrity. The reprocessed epoxy also behaved identically to the virgin material (*T_g* = 172 °C, σ_b = 81 MPa, *E* = 2.1 GPa) and had a higher ϵ_b (15%) than the BPA epoxy analogue (8.6%).

C–O linked polymer summary

The versatility of bio-based, C–O linked polymers has been well demonstrated, with the most tangible advantages stemming from the use of bio-derived functionalities to enable applications beyond those of commodity thermoplastics and thermosets, or to overcome their specific drawbacks. The role of catalysis in generating performance-advantaged polymers is irrefutable and allows for easy hybridization of polymer types, and entire fields of catalysis have been developed around the polymerization of highly oxygenated bio-based monomers²¹. The coupling of catalysis to bio-derived functionalities not only enables controlled polymerization, but also rapid and precision polymerization, which is advantageous to manufacturing. There remain opportunities to further develop catalysts to accommodate the size and complexity of bio-based monomers to control architectures for tailored performance.

There are also enormous health and process benefits associated with C–O linked, bio-based polymers. Phosgene and BPA can be evaded in the manufacturing of polycarbonates, and for epoxies, opportunities for advancement include lower cure temperatures and enhanced degradation to single components for complete circularity. Although polyesters have hydrolysable backbones, biodegradability claims should not be made based on the polyester identity alone. Collaborative studies for promising materials are needed to address degradability beyond accelerated hydrolysis. The importance of this is exemplified by the recalcitrance of PET, and of PLLA in any environment other than industrial composting, leading to public confusion¹¹⁰. Additionally,

claims made for performance should be backed by data, from comparisons with control materials tested in parallel rather than with cited data¹²⁴.

C–N linked polymers

Polyamides

Polyamides are prevalent in high-performance applications, owing to their strength, toughness, durability, and thermal and chemical resistance, and are typically produced by condensation of AA/BB or AB monomers, or ROP of lactams¹⁸². Aliphatic polyamides, or nylons, are ubiquitous in automotive parts, outdoor gear, industrial fishing equipment and carpet. Drawbacks of conventional nylons are moderate *T_g* values and a trade-off between strength, *T_m* and H₂O absorption. Short-chain (*C₆*) nylons are stronger and higher melting but absorb more H₂O, whereas long-chain ($\geq C_{10}$) counterparts are more hydrophobic but weaker with a lower *T_m*. Moisture absorption is beneficial in textiles, whereas dimensional stability is preferred for other applications. Nylon 11 has been produced from castor oil for >70 years and shows advantages over both petroleum-derived short-chain polyamides and nylon 12. Compared with nylon 12, nylon 11 has a higher hydrogen bond density and, thus, exhibits a higher *T_m*, lower gas permeability (ideal for fuel applications) and improved abrasion and impact resistance. Bio-based sebacic acid (*C₁₀*) provides a balance between H₂O absorption and strength in nylon 6,10. Additionally, nylon 4 is a long sought-after material with cotton-like textile properties, biodegradability and/or chemical recyclability, and straightforward renewability from γ -aminobutyric acid or pyrrolidone; however, low polymerizability and thermal instability hinder its industrial production¹⁸³.

Step-growth polyamides. Cadaverine (1,5-diaminopentane) is one of few linear diamines with bio-fixed nitrogen, as it is derived directly from the essential amino acid lysine after decarboxylation^{40,184}. In the last decade, the first line of odd–even polyamides has been commercialized, namely nylon 5,X and a series of *C_{11–18}* diacids. Compared with traditional nylon 6,6, the hydrogen bonding pattern in nylon 5,6 is shifted, leaving more vacant sites (FIG. 6a). These sites enable improved dyeing while maintaining comparable strength, leading to consistent quality and, ultimately, cost-savings in textile production^{185–188}. Additional in-use advantages of nylon 5,6 fabric over nylon 6,6 include better elastic recovery, antistatic, fire safety and moisture-absorbance properties. When adipic acid is replaced by bio-derived β -keto adipic acid in nylon 6,6, the ketone contributes to an increase in *T_g* (to 130 °C), a reduction in H₂O uptake and a high *T_m* (~400 °C); however, melting occurs close to degradation⁸⁹. Thus, the incorporation of smaller amounts of β -keto adipic acid could enhance conventional nylon 6,6. Bio-based polyamides have largely been based on bio-based amino acid or diacid monomers with petroleum-derived diamines, as linear diamines are a less common bio-derived functionality and are typically installed by amination chemistry^{188–191}. Efficient conversion of other functional groups to amines via catalysis can provide sustainable access to polyamides, such as those derived from plant oils⁹⁶. These polyamides have a low density of amide

groups owing to the long aliphatic chains, balancing crystallinity and hydrophobicity for minimized H_2O uptake and further chemical resistance.

Cysteamine (2-aminoethanethiol) is a bifunctional biomolecule that can be used to introduce primary amines through thiol–ene click chemistry^{189,192,193}. For example, cysteamine hydrochloride was added to limonene to form a bulky diamine monomer that was used to plasticize polyamide 6,6 (nylon 6,6) in copolymers¹⁹². Similarly, AB monomers produced by clicking cysteamine with unsaturated fatty monoesters have been used to realize plasticized copolymers¹⁹³. The bio-derived functionalities used in these examples impart new features to commodity materials, such as built-in plasticization and hydrophobicity, but mechanical and rheological studies are necessary to fully demonstrate their potential.

Furandicarboxylic acid, or its dimethyl ester, is a common AA monomer for polycondensation, and when polymerized with a diamine produces furan-based polyamides, polyaramids or polyphthalamides^{194,195}. However, melt polycondensation of furanics can lead to undesired oxidation and resin formation. Alternative step-growth methods, such as thiol–ene addition and acyclic diene metathesis polymerization, have been applied to avoid condensation, occurring under milder conditions^{45,188,193,196}. In one demonstration, the production of polyamides by thiol–ene addition polymerization combined clever material design with processing techniques to achieve outstanding properties, with the materials reported to be the strongest elastomers of all long-chain aliphatic polycondensates¹⁹⁶. Symmetric castor oil-derived monomers featuring a central alcohol or ester flanked by two amide groups with C_{11} terminal alkene chains, *N,N'*-(2-hydroxypropane-1,3-diyl)bis(undec-10-enamide) (UDA) and 1,3-di(undec-10-enamido)propan-2-yl butyrate (BUDA) (FIG. 6b, left), were copolymerized with a dithiol. It was hypothesized that nanocrystalline domains, formed through highly localized hydrogen bonding, dispersed throughout an amorphous matrix would lead to exceptional strength. The optimal P(UDA-co-BUDA) copolymer, P4, contains 52% UDA and achieves mechanical properties ($E = 150 \text{ MPa}$, $\sigma_B = 18.4 \text{ MPa}$, $\epsilon_B = 576\%$ and a toughness of 65 MJ m^{-3} at 17% crystallinity) comparable with or superior to those of commercial aliphatic polyamides and polyesters; however, T_g (24°C) and T_m (81°C) are comparatively low. Unidirectional stretching induces alignment of the crystalline domains, forming ultra-strong elastomers (uEs) (FIG. 6b, centre and right). Deformation of P4 to form uE4 increases σ_B sevenfold to 115 MPa , and although ϵ_B decreases to 30%, uE4 maintains a high elastic recovery of 95%. Overcoming the usual trade-off of a weaker material with long-chain monomers, these materials exhibit high strength and toughness for ambient-temperature applications. Interestingly, by virtue of the clustered crystalline microstructure, these materials fluoresce, which is remarkable for an aliphatic material without chromophores.

ROP polyamides. ROP of terpene-derived monomers has revealed performance-advantaged polyamides by capitalizing on inherently rigid cyclic structures and

chirality^{188,197,198}. Lactam monomers derived from menthone, α -pinene and β -pinene, and (+)-3-carene have been systematically investigated (FIG. 6c) to determine structure–property relationships, cumulating in the scalable synthesis of high-performance polyamides^{197–201}.

The ketone L-menthone was converted to a lactam through the oxime Beckmann rearrangement (as used industrially in the conversion of cyclohexanone to ϵ -caprolactam for the preparation of nylon 6) and subsequently ring-opened in bulk under typical anionic lactam ROP conditions¹⁹⁹. The resulting polyamide was produced in low yields ($\sim 20\%$) and had low M_n values ($< 2 \text{ kDa}$), but exhibited impressive thermal properties ($T_g = 50^\circ\text{C}$, $T_m = 300^\circ\text{C}$). Polyamides of β -pinene lactam were also synthesized employing the oxime route^{200,201}. The structure and stereochemistry of the substituents are retained in the polymer backbone upon bulk ROP (anionic or cationic), and the resulting polyamides were obtained in good yields, with cationic polymerizations leading to higher M_n , albeit still $< 10 \text{ kDa}$. The T_m ($308\text{--}322^\circ\text{C}$) and thermal stability ($T_d \approx 400^\circ\text{C}$) of poly(β -pinanamide) are comparable with those of the menthone system, but with a much higher T_g of $150\text{--}160^\circ\text{C}$ due to the rigidity and stereoregularity of the backbone cyclobutane ring. However, melt processing is inhibited by the close T_m and T_d values. Polymerization of α -pinene lactam was unsuccessful, as the cyclobutyl ring rearranges, leading to crosslinking side reactions¹⁹⁸.

Polyamides derived from (+)-3-carene, a by-product of the pulping industry, are more promising, reaching much higher M_n values (up to 33 kDa) and yields of up to 77% ¹⁹⁸. The methyl and geminal-dimethyl cyclopropane substituents, on the same face of the lactam, endow rigidity and hydrophobicity, with the polyamide showing a high T_g of 120°C and H_2O uptake of 40% relative to that of nylon 6, but no melting transition was observed before decomposition at 400°C . Monomer stereochemistry was retained, yet the material was amorphous, resulting in transparent films. The effects of (+)-3-carene stereochemistry and its copolymerization with conventional lactams have been investigated to reveal further performance-advantaged polyamides¹⁹⁷. Diastereomers of the lactam derived from (+)-3-carene were obtained selectively, with large-scale, multistep monomer synthesis demonstrated in a single vessel without purification of the intermediates. The *R* diastereomer has substituents on the same face of the ring, and the substituents in the *S* diastereomer have a *trans* orientation (FIG. 6c). The change in orientation of the methyl group has a pronounced effect on polymer crystallinity. The polymer derived from the *S* diastereomer is semi-crystalline, with a T_m of up to 280°C , which is 60°C higher than that of nylon 6, and a T_g of $105\text{--}115^\circ\text{C}$ ($\sim 50^\circ\text{C}$ higher than that of nylon 6). By contrast, the polymer formed from the *R* diastereomer is amorphous, with a T_g of $115\text{--}120^\circ\text{C}$. Regardless of some kinetic differences, conversions of almost 90% were achieved for both diastereomers.

In the copolymerization of *S*-carene lactam with caprolactam or laurolactam, differences in the reaction kinetics of the monomers result in gradient copolymer microstructures, which show increased T_g values

(increasing linearly with the amount of carene lactam incorporated) and disrupted crystallinities relative to nylon 6 and nylon 12. These properties could enhance the conventional application space, with transparent films, increased working temperature range, chirality and other additive effects achieved by changing the polymer composition. As γ -substituents tend to favour ring-closing, this bio-derived functionality might also provide a thermodynamic driving force for reversibility.

Polyurethanes and polyhydroxyurethanes

Polyurethanes are conventionally synthesized from alcohols and isocyanates. Given the propensity for bio-feedstocks to yield hydroxyl groups, polyurethanes are thus obvious candidates for synthesis from bio-based monomers. Polyurethanes can be linear (thermoplastic) or networked (thermoset), and are often used in foams, rigid or flexible, as the reaction of excess isocyanate with H_2O evolves CO_2 . Polyurethane monomers and thermo-mechanical properties vary widely to meet the requirements of diverse applications, from automotive bushings to industrial adhesives. Polyurethanes are often thermosets with long lifetimes, but have limited end-of-life options and use toxic isocyanates^{78,202}. Most polyurethanes are manufactured from flexible diols or polyols and rigid isocyanates (such as toluene diisocyanate). Bio-feedstocks provide access to many aliphatic alcohols, but bio-based phenolics can also be the rigid component (FIG. 6d).

Direct use of lignin in polyurethanes has received much attention owing to the high phenolic content. There are also diverse lignin feedstocks and numerous modifications performed, typically the conversion of phenols to reactive primary alcohols³⁰. Generally, lignin-derived polyurethanes have higher compressive strengths than their petroleum counterparts, and, in some cases, can enable biodegradation at lignin loadings as low as 25 wt%²⁰³. Despite promising features, it is difficult to draw correlations between bio-derived functionalities and material performance because lignin composition varies widely.

Although lignin-based polyurethanes use rigid aromatic polyols, the use of aliphatic polyols is more conventional. Fatty acids can be easily converted to polyols through alkene epoxidation and subsequent hydrolysis^{204–207}. These polyols can then react with aromatic diisocyanates to form polyurethanes that exhibit properties similar to those of polyether-based polyurethanes, for which T_g is in the range 30–50 °C and the mechanical properties are strongly dependent on crosslink density. The benefit of plant oil-based polyurethanes over polyether-based counterparts is a delay in T_d by up to ~75 °C, due to a lower oxygen content. Higher molecular-weight polyols for flexible foams are also produced industrially by hydroformylation and transesterification of polyunsaturated fatty acids²⁰⁸. Hydroxyl-terminated polymers, such as polycarbonates¹⁴⁹ and polyesters, can also be used as polyols, and have gained traction industrially. Use of poly(β M δ VL) as a polyol enables chemical recycling of the polyol component^{127,209}, and algae-derived polyester polyols yield a biodegradable polyurethane foam with properties suitable for footwear applications²¹⁰.

Polyhydroxyurethanes (PHUs) offer isocyanate-free routes (FIG. 6d) to materials that are structurally similar to polyurethanes^{202,211–213}. PHUs form by reaction of amines with cyclic carbonates to give urethane and hydroxyl groups. In general, the urethane group maintains the properties of a polyurethane, whereas the additional hydroxyl can endow better adhesive properties²¹¹. Cyclic carbonates are not inherent bio-derived functionalities but can be introduced by the carbonation of epoxides, through alkene or alcohol functionalization with epichlorohydrin⁷⁸. It is possible to avoid toxic epichlorohydrin by alkylation of an alcohol to a vicinal diol, followed by transesterification with dimethyl carbonate²¹⁴ (FIG. 6d). These alternative routes to cyclic carbonates enable benign manufacturing of PHUs, using green solvents and recoverable catalysts, and have been applied to lignin, but terpenes and fatty acids are also suitable building blocks. Additionally, owing to the hydroxyl groups, PHUs can undergo intermolecular transesterification for material healing²¹⁵.

Some of the earliest bio-based PHUs were synthesized using limonene²¹⁶. Limonene is first converted to a branched dicyclic carbonate, which is subsequently reacted with C_5 – C_6 diamines to form PHUs. The resultant thermosets possess T_g values of 40–70 °C and a favourable E (3–5 GPa), and are strong but brittle with ϵ_B and σ_B of <2.5% and 53 MPa (REF.²¹⁶), respectively. Use of unpurified limonene carbonate results in plasticization (with a 40 °C decrease in T_g and 45% decrease in E'). Thiol–ene click chemistry provides access to more amine monomers for polyurethanes and PHUs, enabling fully bio-based systems¹⁹². Carbonated oils can also be implemented in PHUs; for example, the product of carbonated soybean oil and ethylene diamine results in a favourable ϵ_B (80%), but at low σ_B (≤ 1.6 MPa)²¹⁷. Despite the benefits of PHUs over traditional polyurethanes, most studies do not compare against standard petroleum polyurethanes or provide adequate material characterization.

Polyimides

Polyimides exhibit exceptional thermo-oxidative stability and mechanical properties, solvent and radiation resistance, and low density, making them suitable for aerospace applications^{218,219}. Polyimides are also used in electronics and energy sectors owing to unique dielectric properties. However, the high thermochemical resistance and thermosetting nature of polyimides come with major processing limitations. A pre-polymer formulation must be cured at high temperatures (200–300 °C), which can be complicated by the release of volatiles and incomplete curing. Additionally, polyimides are often coloured. These drawbacks limit their integration into technological applications that require low-temperature processing or colourless transparency²²⁰.

More recently, machine learning and genomic engineering have been leveraged to develop bio-based polyimide films with both processing and in-use advantages for various electronics applications^{57,221,222}. These patented polyimides use traditional di-anhydride monomers with bio-based polyamines to realize solution-processable, colourless and transparent materials with outstanding mechanical properties²²⁰.

The exact formulation is undisclosed, but the bio-based components are reportedly responsible for the advanced properties^{220,223}. For touch sensors, the high mechanical strength ($E = 3.1$ GPa, $\sigma_b = 117$ GPa for a film 25 μm thick) enables use of thinner films and, thus, full-coverage touch sensing in flexible devices, whereas the high thermal stability ($T_g = 195^\circ\text{C}$, $T_d = 460^\circ\text{C}$)²²³ during annealing with inorganic components leads to better function. Similarly, thin films and the thermal stability expedite the manufacturing of optical filters. Moreover, the material is solderable, eliminating the need for epoxy or acrylic adhesives in printed circuit boards, resulting in a thinner and more flexible system that is completely transparent.

Polybenzoxazines

Polybenzoxazine (PBz) resins have emerged as high service temperature thermosets that can replace phenolic or epoxy resins in aerospace, defence and electronics applications²²⁴. Benzoxazine monomers are synthesized from a phenol (often BPA), amine and formaldehyde, and then polymerized at high temperatures (160–220°C) to create tertiary amine connections and regenerate autocatalytic and hydrogen bond-forming phenols across the network (FIG. 6e). Curing does not require a catalyst, and occurs without by-product evolution, void formation, shrinkage or expansion. PBzs show low flammability, high char yield, strength, low H_2O absorption and high stability towards chemicals and ultraviolet radiation. The use of bio-based monomers has begun to address the high cure temperatures and brittleness^{225–228}, and although promising monomers are not the most abundant, their polymers make a compelling case for them as targets of metabolic engineering.

Chavicol, a bio-based phenol with an allyl group, was used to form PBz resins with a high T_g (350°C) through additional allyl crosslinking, but required high cure temperatures (230–300°C)²²⁵. Magnolol — the 2,2'-biphenol dimer of chavicol — has been combined with furfurylamine to form a high-performance PBz²²⁷. The magnolol-furfurylamine benzoxazine monomer (FIG. 6e) was synthesized in a 5-min microwave reaction, followed by simultaneous curing of benzoxazine and allyl functionalities at 160–250°C (with a polymerization temperature (T_p) of 229°C). The resulting PBz showed excellent thermal stability with a T_g of 303°C, which is higher than that of widely used BPA PBzs ($T_g \approx 180^\circ\text{C}$), as well as an onset T_d of 440°C and a high char yield of 62%. The thermal stability is thought to be enhanced by the participation of the furan ring in crosslinking, in addition to allyl and amine crosslinks, leading to high stiffness ($E' = 2.46$ GPa at room temperature). Additionally, the benzoxazine monomer showed excellent rheological properties with low viscosity (<1 Pa s), providing ample time in the melt before gelling, which is essential for resin transfer moulding.

Softness has been induced in PBzs by combining vanillin and cardanol as rigid and flexible components, respectively, within an asymmetric benzoxazine monomer²²⁶ (FIG. 6e). PBzs formed from cardanol alone have low T_g values, whereas those formed from vanillin cannot be processed because curing occurs close to the

monomer T_m . By contrast, the PBz derived from the asymmetric benzoxazine monomer possesses a wide processing window (monomer $T_m = 101^\circ\text{C}$, $T_p = 227^\circ\text{C}$) and a balanced T_g of 129°C. The E' is 700 MPa, suggesting a much softer material than that formed from magnolol and illustrating how PBz properties can be tailored by judicious use of bio-derived functionalities.

A fully bio-based, performance-advantaged PBz was synthesized from furfurylamine and naringenin, a flavonoid²²⁸ (FIG. 6e). An autocatalytic free phenol is in place in this system, as naringenin has three phenol groups, one of which is untouched during network formation. Immobilization of the acidic phenol proton by intramolecular hydrogen bonding at low temperatures yields a stable benzoxazine monomer with a long shelf-life. This latent catalytic proton is released upon heating to effect a low T_p of 166°C; the lowest reported for all pure PBzs. The PBz has a T_g of 286°C, onset T_d of 361°C and 64% char yield. Furthermore, the material is self-extinguishing and non-ignitable with a comparatively low heat release capacity and total heat release compared with BPA-based controls. The addition of 5 mol% naringenin-furfurylamine benzoxazine to a BPA-based PBz modified the properties, decreasing the T_p from 257 to 238°C and increasing the T_g (from 162 to 178°C) and onset T_d (from 324 to 344°C), and also notably improved the flammability metrics.

Polyimines

Imine bonds confer catalyst-free reprocessability to polyesters and epoxies, but dynamic networks can also be based entirely on this motif. Petroleum-based polyimines serve as recyclable composites for carbon fibre and self-healing matrices for solid-state batteries^{229–231}, but precursor aldehydes are a common bio-derived functionality. Recent examples of bio-based polyimine networks have established structure–property relationships and show good potential for thermoset applications^{232,233}.

An elastomeric material formed from furan dialdehyde and a commercially available mixture of fatty polyamines displays a T_g of -10°C and a T_d of up to 300°C, and undergoes rapid stress relaxation at room temperature²³². The material can be reprocessed with heat or selectively depolymerized in an amine solvent yet remains stable in acidic or basic solutions; this desirable hydrolytic stability is attributed to the hydrophobic amines. Furan dialdehyde, in combination with different amines, has also been used to directly study the relationship between crosslink density and physical properties and to establish relationships between fast stress relaxation and creep resistance, illuminating fundamental design principles for future materials²³³.

Vanillin was dimerized to a dialdehyde by linking the phenols, and the dialdehyde networked with simple aliphatic polyamines to form light-yellow polyimine films²³⁴. With an increase in crosslinking, T_g increased from 48 to 64°C, and all networks were stable up to $\sim 300^\circ\text{C}$ with high char yields. The films show reasonable toughness, with σ_b and ϵ_b in the ranges 47–57 MPa and 13–16%, respectively. After hot reprocessing, the networks with a higher crosslink density showed better retention of mechanical properties, although the colour

darkened. The dialdehyde monomers could be recovered by mild heating in strong acid and then used to regenerate light-yellow films. Fire-retardant thermosets have also been achieved by substituting phosphorus oxychloride with three vanillins through their phenols, leaving the aldehydes available for network formation with different amines²³⁵. The materials demonstrated T_g , σ_B and E of up to 178 °C, 69 MPa and 1.9 GPa, respectively, in combination with flame-retardant properties superior to those of BPA-based thermosets. Although the phosphorus and nitrogen are not directly bio-based, the aromatic ring of vanillin contributes to the base mechanical properties and char formation whereas its phenols provide straightforward access to the aldehyde monomer. Reprocessing was rapid, completed in 2–10 min at temperatures close to the T_g without discoloration of the yellow thermosets. Additionally, high-purity monomer was recovered in up to 77% yield by acid-catalysed depolymerization. Although bio-derived functionalities can be leveraged to target distinct thermomechanical profiles for recyclable thermoset applications, better balance of stress relaxation and creep deformation must be addressed for materials to have marketable performance advantages.

C–N linked polymer summary

Bio-derived monomers endow promising material properties and can enhance the property space of

conventional C–N linked polymers. These enhancements include circumventing the use of non-benign monomers or additives, advanced architectures (that can inherently incorporate additive effects), superior thermomechanical properties, greater stability, lower flammability and improved end-of-life options, processing conditions and appearance. Moving forward, it is imperative to test properties directly against petroleum standards and, where possible, use bio-fixed nitrogen monomers, which will hopefully see greater availability in coming years. It is also important to demonstrate performance advantages in the highly specific application environments associated with specialty polymers, which could be further revealed through collaboration with industry.

Outlook

The inherent functionality of bio-derived compounds can enhance the performance of polymers relative to current petroleum-derived materials. True performance advantages can stimulate industry adoption of bio-based materials, yet much work remains to turn this early promise into a viable enterprise. This work includes thorough thermomechanical and rheological characterization of materials, optimization of monomer sourcing and synthesis, demonstration of realistic end-of-life options and production modelling analyses for the most promising systems²⁴. When designing or evaluating a bio-based material with performance advantages, researchers should consider the guiding principles listed in BOX 1.

There are several major challenges in demonstrating PBPs. The first challenge is narrowing down a near infinite combinatorial design space in terms of both monomer combinations and catalyst design. Alongside the hypothesis-driven, combinatorial approach to the selection of co-monomers and design of polymer architectures, computational methods such as machine learning and molecular dynamics are emerging as tools to assist in predicting polymer structures with promising properties^{12,236}. A second challenge lies in identifying molecules with hidden performance advantages, such as the ability of naringenin to act autocatalytically during PBz formation²²⁸. Third, ensuring that all requisite properties are at least maintained, if not exceeded, poses a great challenge. As multiple properties are often correlated, an increase in one property might be at the detriment of another. For example, materials with higher T_g may have a wider working temperature window but may be too brittle in practice. Finally, the coupling of performance advantages, especially the coupling of end-of-life considerations with superior processing or application properties, remains a key challenge. Overcoming these challenges while following the guiding principles will require research at multiple scales and the identification of the optimal products to advance.

This Review has focused on research at the proof-of-concept level, but there are additional considerations when designing commercially viable materials. Challenges associated with bringing a PBP to market include understanding its rheological properties under industrial processing conditions, assessing its

Box 1 | Guiding principles for the development of performance-advantaged bioproducts

Obey the principles of green chemistry and engineering

Monomer and polymer synthesis should be guided by the principles of green chemistry, with emphasis on designing for energy efficiency, implementing safer solvents and auxiliaries, maintaining a high atom economy and favouring catalytic reagents over stoichiometric ones.

Identify performance advantages

New bioproducts should be assessed for advantages across manufacturing, application properties and end-of-life considerations (such as recyclability or degradation).

Correlate performance advantages with inherent bio-derived functionalities

Typically, performance advantages are directly related to bio-derived functionality; thus, it is preferable to use fewer chemical transformations in order to retain these bio-derived functionalities. For example, muconic acid can be converted to adipic acid as a direct replacement chemical, or the unsaturated bonds can be retained for additional performance.

Perform characterizations using standardized tests and compare with incumbent materials

Bioproducts should be characterized across a range of properties (including thermomechanical, rheological, optical, barrier and degradability). To claim that a material can serve as a performance-advantaged replacement, it is necessary to report properties relative to the incumbent material under the same synthesis and test conditions, as commercial polymer products will often use trace amounts of co-monomers and/or additives to facilitate processing and optimize properties (such as isophthalates in polyethylene terephthalate (PET)). If not synthesized, data can also be obtained using purchased standards with known compositions.

Validate performance advantages at multiple scales

Once physical properties are established, the performance at different mass scales should be validated. Moreover, promising systems should be subjected to life cycle analyses, techno-economic analyses and supply chain modelling. It is important to avoid assumptions, such as that all bio-based monomers have lower greenhouse gas emissions than petroleum-derived counterparts. Indeed, some bio-based direct replacement chemicals can result in greater greenhouse gas emissions, often due to extensive separations or the disposal of waste by-products²³⁸.

performance lifetime under specific application conditions, selecting suitable precursor feedstocks and optimizing the production of these precursors. Introducing new products into an established market presents another set of challenges and opportunities. These challenges include the upfront cost for manufacturing a new material; competing with the incumbent industry, which has a tested foundation; and potential regulatory barriers for certain applications, such as regulatory procedures for food packaging. These challenges are not unique to PBPs but should be acknowledged as barriers to entry for transitioning any new products from laboratory to market.

Lessons can be learned from bioproducts that have already penetrated the market. Examples of products with adequate market penetration include epoxidized soybean oil as a plasticizer, PLA and sebacic acid for nylon 6,10, which have gained traction owing to their avoidance of health risks, compostability and lack of thermal expansion, and lower H₂O permeabilities, respectively. In each case, the performance advantages have facilitated their market penetration. PLA is an example of a material that has overcome several of the above challenges. Although initially postulated to be a widely applicable compostable packaging polymer, high

H₂O permeability makes it unsuitable for long-term food and beverage preservation; however, minimal thermal shrinkage makes it ideal as a 3D printing filament. Additionally, to overcome issues associated with the manufacture of lactic acid, acid-tolerant microbes were developed and simulated moving bed chromatography used to reduce salt waste and remove H₂O. At the time of writing, lactic acid has a market size of 75,000 tonnes per year, growing at a rate of ~19% per year²³⁷. Thus, market penetration is possible when a PBP solves a specific problem relative to incumbent materials and manufacturing is optimized to lower cost.

Through further research, the field of performance-advantaged bioproducts has the potential not only to enable the bioeconomy but also to advance numerous scientific and engineering fields. For example, unexplored monomers from biomass offer new structure–property relationships to be studied and invite new catalyst designs and method development. The potential of bio-derived functionalities and their unique combinations within compounds can provide an incentive for the use of biomass feedstocks and, ultimately, bring sustainable polymers to fruition.

Published online 23 September 2021

- Andrady, A. L. & Neal, M. A. Applications and societal benefits of plastics. *Phil. Trans. R. Soc. B* **364**, 1977–1984 (2009).
- Davis, S. J., Caldeira, K. & Matthews, H. D. Future CO₂ emissions and climate change from existing energy infrastructure. *Science* **329**, 1330–1333 (2010).
- World Economic Forum, Ellen MacArthur Foundation & McKinsey. The new plastics economy — rethinking the future of plastics (World Economic Forum, 2016).
- MacArthur, E. Beyond plastic waste. *Science* **358**, 843–843 (2017).
- Hermann, B. G., Blok, K. & Patel, M. K. Producing bio-based bulk chemicals using industrial biotechnology saves energy and combats climate change. *Environ. Sci. Technol.* **41**, 7915–7921 (2007).
- Dodds, D. R. & Gross, R. A. Chemicals from biomass. *Science* **318**, 1250–1251 (2007).
- Bozell, J. J. & Petersen, G. R. Technology development for the production of biobased products from biorefinery carbohydrates — the US Department of Energy's "top 10" revisited. *Green Chem.* **12**, 539–554 (2010).
- Tuck, C. O., Pérez, E., Horváth, I. T., Sheldon, R. A. & Poliakoff, M. Valorization of biomass: deriving more value from waste. *Science* **337**, 695–699 (2012).
- Shen, L., Worrell, E. & Patel, M. K. Comparing life cycle energy and GHG emissions of bio-based PET, recycled PET, PLA, and man-made cellulose. *Biofuel Bioprod. Biorefin.* **6**, 625–639 (2012).
- Weiss, M. et al. A review of the environmental impacts of biobased materials. *J. Ind. Ecol.* **16**, S169–S181 (2012).
- Chen, G.-Q. & Patel, M. K. Plastics derived from biological sources: present and future: a technical and environmental review. *Chem. Rev.* **112**, 2082–2099 (2012).
- Babu, R. P., O'Connor, K. & Seeram, R. Current progress on bio-based polymers and their future trends. *Prog. Biomater.* **2**, 8–23 (2013).
- Sheldon, R. A. Green and sustainable manufacture of chemicals from biomass: state of the art. *Green Chem.* **16**, 950–963 (2014).
- Gandini, A. & Lacerda, T. M. From monomers to polymers from renewable resources: recent advances. *Prog. Polym. Sci.* **48**, 1–39 (2015).
- Isikgor, F. H. & Becer, C. R. Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers. *Polym. Chem.* **6**, 4497–4559 (2015).
- Zhu, Y., Romain, C. & Williams, C. K. Sustainable polymers from renewable resources. *Nature* **540**, 354–362 (2016).
- Delidovich, I. et al. Alternative monomers based on lignocellulose and their use for polymer production. *Chem. Rev.* **116**, 1540–1599 (2016).
- Galbis, J. A., Garcia-Martín, Md. G., de Paz, M. V. & Galbis, E. Synthetic polymers from sugar-based monomers. *Chem. Rev.* **116**, 1600–1636 (2016).
- Hillmyer, M. A. The promise of plastics from plants. *Science* **358**, 868–870 (2017).
- Shanks, B. H. & Keeling, P. L. Bioprivileged molecules: creating value from biomass. *Green Chem.* **19**, 3177–3185 (2017).
- Zhang, X., Fevre, M., Jones, G. O. & Waymouth, R. M. Catalysis as an enabling science for sustainable polymers. *Chem. Rev.* **118**, 839–885 (2018).
- Debuissy, T., Pollet, E. & Averous, L. Biotic and abiotic synthesis of renewable aliphatic polyesters from short building blocks obtained from biotechnology. *ChemSusChem* **11**, 3836–3870 (2018).
- Hong, M. & Chen, E. Y.-X. Future directions for sustainable polymers. *Trends Chem.* **1**, 148–151 (2019).
- Nicholson, S. R., Rorrer, N. A., Carpenter, A. C. & Beckham, G. T. Manufacturing energy and greenhouse gas emissions associated with plastics consumption. *Joule* **5**, 673–686 (2021).
- Nikolaou, B. J., Perera, M. A. D. N., Brachova, L. & Shanks, B. Platform biochemicals for a bio-renewable chemical industry. *Plant J.* **54**, 536–545 (2008).
- Hermann, B. G. & Patel, M. Today's and tomorrow's bio-based bulk chemicals from white biotechnology. *Appl. Biochem. Biotechnol.* **136**, 361–388 (2007).
- Fitzgerald, N. D. Chemistry challenges to enable a sustainable bioeconomy. *Nat. Rev. Chem.* **1**, 0080 (2017).
- Fitzgerald, N. & Bailey, A. *Moving Beyond Drop-in Replacements: Performance-Advantaged Biobased Chemicals* (US Department of Energy Office of Energy Efficiency and Renewable Energy Bioenergy Technologies Office, 2018).
- Klemm, D., Heublein, B., Fink, H. P. & Bohn, A. Cellulose: fascinating biopolymer and sustainable raw material. *Angew. Chem. Int. Ed.* **44**, 3358–3393 (2005).
- Upton, B. M. & Kasko, A. M. Strategies for the conversion of lignin to high-value polymeric materials: review and perspective. *Chem. Rev.* **116**, 2275–2306 (2016).
- Scheller, H. V. & Ulvskov, P. Hemicelluloses. *Annu. Rev. Plant Biol.* **61**, 263–289 (2010).
- Mohnen, D. Pectin structure and biosynthesis. *Curr. Opin. Plant Biol.* **11**, 266–277 (2008).
- Boerjan, W., Ralph, J. & Baucher, M. Lignin biosynthesis. *Annu. Rev. Plant Biol.* **54**, 519–546 (2003).
- Chundawat, S. P., Beckham, G. T., Himmel, M. E. & Dale, B. E. Deconstruction of lignocellulosic biomass to fuels and chemicals. *Annu. Rev. Chem. Biomol. Eng.* **2**, 121–145 (2011).
- Pollard, M., Beisson, F., Li, Y. & Ohlrogge, J. B. Building lipid barriers: biosynthesis of cutin and suberin. *Trends Plant Sci.* **13**, 236–246 (2008).
- Rinaudo, M. Chitin and chitosan: properties and applications. *Prog. Polym. Sci.* **31**, 603–632 (2006).
- Yan, N. & Chen, X. Sustainability: don't waste seafood waste. *Nature* **524**, 155–157 (2015).
- Hülsey, M. J., Yang, H. & Yan, N. Sustainable routes for the synthesis of renewable heteroatom-containing chemicals. *ACS Sus. Chem. Eng.* **6**, 5694–5707 (2018).
- Ma, X. et al. Upcycling chitin-containing waste into organonitrogen chemicals via an integrated process. *Proc. Natl Acad. Sci. USA* **117**, 7719–7728 (2020).
- Lee, S. Y. et al. A comprehensive metabolic map for production of bio-based chemicals. *Nat. Catal.* **2**, 18–33 (2019).
- Wheeldon, I., Christopher, P. & Blanch, H. Integration of heterogeneous and biochemical catalysis for production of fuels and chemicals from biomass. *Curr. Opin. Biotechnol.* **45**, 127–135 (2017).
- Zhou, X. et al. Computational framework for the identification of bioprivileged molecules. *ACS Sus. Chem. Eng.* **7**, 2414–2428 (2019).
- Huo, J. & Shanks, B. H. Bioprivileged molecules: integrating biological and chemical catalysis for biomass conversion. *Annu. Rev. Chem. Biomol. Eng.* **11**, 63–85 (2020).
- Nguyen, H. T. H., Qi, P., Rostagno, M., Feteha, A. & Miller, S. A. The quest for high glass transition temperature bioplastics. *J. Mater. Chem. A* **6**, 9298–9331 (2018).
- Gandini, A. & Lacerda, T. M. *Polymers from Plant Oils* 2nd edn (Scrivener Publishing, 2019).
- Mahajan, J. S., O'Dea, R. M., Norris, J. B., Korley, L. T. J. & Epps, T. H. Aromatics from lignocellulosic biomass: a platform for high-performance thermosets. *ACS Sus. Chem. Eng.* **8**, 15072–15096 (2020).
- Scott, A. Styrene leak in India kills at least 13. *Chemical & Engineering News* <https://cen.acs.org/safety/industrialsafety/Styrene-leak-India-kills-least/98/web/2020/05> (2020).
- Terasaki, M., Kazama, T., Shiraishi, F. & Makino, M. Identification and estrogenic characterization of impurities in commercial bisphenol A diglycidyl ether (BADGE). *Chemosphere* **65**, 873–880 (2006).

49. Shi, M., Sekulovski, N., MacLean, J. A. & Hayashi, K. Effects of bisphenol A analogues on reproductive functions in mice. *Reprod. Toxicol.* **73**, 280–291 (2017).
50. Ramskov Tetzlaff, C. N., Svingen, T., Vinggaard, A. M., Rosenmai, A. K. & Taxvig, C. Bisphenols B, E, F, and S and 4-cumylphenol induce lipid accumulation in mouse adipocytes similarly to bisphenol A. *Environ. Toxicol.* **35**, 543–552 (2020).
51. Koelewijn, S. F. et al. Sustainable bisphenols from renewable softwood lignin feedstock for polycarbonates and cyanate ester resins. *Green Chem.* **19**, 2561–2570 (2017).
52. Rorrer, N. A., Vardon, D. R., Dorgan, J. R., Gjersing, E. J. & Beckham, G. T. Biomass-derived monomers for performance-differentiated fiber reinforced polymer composites. *Green Chem.* **19**, 2812–2825 (2017).
53. Koelewijn, S. F. et al. Promising bulk production of a potentially benign bisphenol A replacement from a hardwood lignin platform. *Green Chem.* **20**, 1050–1058 (2018).
54. Patel, A., Maiorana, A., Yue, L., Gross, R. A. & Manas-Zloczower, I. Curing kinetics of biobased epoxies for tailored applications. *Macromolecules* **49**, 5315–5324 (2016).
55. Kurian, J. V. A new polymer platform for the future — Sorona® from corn derived 1,3-propanediol. *Polym. Env.* **13**, 159–167 (2005).
56. Sarathchandran, C., Chan, C. H., Karim, S. R. B. A. & Thomas, S. in *Physical Chemistry of Macromolecules* Ch. 19 (eds Chan, C. H., Chia, C. H. & Thomas, S.) 573–617 (Apple Academic, 2014).
57. Bomgardner, M. Is clarity coming for biobased chemicals? *C&EN Glob. Enterp.* **98**, 28–33 (2020).
58. Gowda, R. R. & Chen, E. Y.-X. in *Encyclopedia of Polymer Science and Technology* (Wiley, 2013).
59. Satoh, K. Controlled/living polymerization of renewable vinyl monomers into bio-based polymers. *Polym. J.* **47**, 527–536 (2015).
60. Winnacker, M. & Rieger, B. Recent progress in sustainable polymers obtained from cyclic terpenes: synthesis, properties, and application potential. *ChemSusChem* **8**, 2455–2471 (2015).
61. Kristufek, S. L., Wacker, K. T., Tsao, Y.-Y. T., Su, L. & Wooley, K. L. Monomer design strategies to create natural product-based polymer materials. *Nat. Prod. Rep.* **34**, 433–459 (2017).
62. Winnacker, M. Pinenes: abundant and renewable building blocks for a variety of sustainable polymers. *Angew. Chem. Int. Ed.* **57**, 14362–14371 (2018).
63. Gilsdorf, R. A., Nicki, M. A. & Chen, E. Y. X. High chemical recyclability of vinyl lactone acrylic bioplastics. *Polym. Chem.* **11**, 4942–4950 (2020).
64. Hillmyer, M. A. & Tolman, W. B. Aliphatic polyester block polymers: renewable, degradable, and sustainable. *Acc. Chem. Res.* **47**, 2390–2396 (2014).
65. Muñoz-Guerra, S., Lavilla, C., Japu, C. & Martínez de Ilarduya, A. Renewable terephthalate polyesters from carbohydrate-based bicyclic monomers. *Green Chem.* **16**, 1716–1739 (2014).
66. Tullio, A. H. A biopolymer whose time has come. *C&EN Glob. Enterp.* **97**, 20–21 (2019).
67. Martínez de Ilarduya, A. & Muñoz Guerra, S. Ring opening polymerization of macrocyclic oligoesters derived from renewable sources. *Polym. Chem.* **11**, 4850–4860 (2020).
68. Gregory, G. L., López-Vidal, E. M. & Buchard, A. Polymers from sugars: cyclic monomer synthesis, ring-opening polymerisation, material properties and applications. *ChemComm* **53**, 2198–2217 (2017).
69. Muhammadi, Shabina, Afzal, M. & Hameed, S. Bacterial polyhydroxyalkanoates-eco-friendly next generation plastic: production, biocompatibility, biodegradation, physical properties and applications. *Green Chem. Lett. Rev.* **8**, 56–77 (2015).
70. Anjum, A. et al. Microbial production of polyhydroxyalkanoates (PHAs) and its copolymers: a review of recent advancements. *Int. J. Biol. Macromol.* **89**, 161–174 (2016).
71. Longo, J. M., Sanford, M. J. & Coates, G. W. Ring-opening copolymerization of epoxides and cyclic anhydrides with discrete metal complexes: structure–property relationships. *Chem. Rev.* **116**, 15167–15197 (2016).
72. Sang, T., Wallis, C. J., Hill, G. & Britovsek, G. J. P. Polyethylene terephthalate degradation under natural and accelerated weathering conditions. *Eur. Polym. J.* **136**, 109873 (2020).
73. Burgess, S. K., Karvan, O., Johnson, J. R., Krieger, R. M. & Koros, W. J. Oxygen sorption and transport in amorphous poly(ethylene furanoate). *Polymer* **55**, 4748–4756 (2014).
74. Eerhart, A. J. J. E., Faaij, A. P. C. & Patel, M. K. Replacing fossil based PET with biobased PEF: process analysis, energy and GHG balance. *Energy Environ. Sci.* **5**, 6407–6422 (2012).
75. Knoop, R. J. I., Vogelzang, W., van Haveren, J. & van Es, D. S. High molecular weight poly(ethylene-2,5-furanoate): critical aspects in synthesis and mechanical property determination. *J. Polym. Sci. A Polym. Chem.* **51**, 4191–4199 (2013).
76. Burgess, S. K. et al. Chain mobility, thermal, and mechanical properties of poly(ethylene furanoate) compared to poly(ethylene terephthalate). *Macromolecules* **47**, 1383–1391 (2014).
77. Xu, C., Arancon, R. A. D., Labidi, J. & Luque, R. Lignin depolymerisation strategies: towards valuable chemicals and fuels. *Chem. Soc. Rev.* **43**, 7485–7500 (2014).
78. Fache, M. et al. Vanillin, a promising biobased building-block for monomer synthesis. *Green Chem.* **16**, 1987–1998 (2014).
79. Mialon, L., Pemba, A. G. & Miller, S. A. Biorenewable polyethylene terephthalate mimics derived from lignin and acetic acid. *Green Chem.* **12**, 1704–1706 (2010).
80. Mialon, L., Vanderhenst, R., Pemba, A. G. & Miller, S. A. Polyalkylenehydroxybenzoates (PAHBs): biorenewable aromatic/aliphatic polyesters from lignin. *Macromol. Rapid Commun.* **32**, 1386–1392 (2011).
81. Nguyen, H. T. H., Reis, M. H., Qi, P. & Miller, S. A. Polyethylene ferulate (PEF) and congeners: polystyrene mimics derived from biorenewable aromatics. *Green Chem.* **17**, 4512–4517 (2015).
82. Nguyen, H. T. H., Short, G. N., Qi, P. & Miller, S. A. Copolymerization of lactones and bioaromatics via concurrent ring-opening polymerization/polycondensation. *Green Chem.* **19**, 1877–1888 (2017).
83. Schijndel, J. et al. Repeatable molecularly recyclable semi-aromatic polyesters derived from lignin. *J. Polym. Sci.* **58**, 1655–1663 (2020).
84. Kaneko, T., Thi, T. H., Shi, D. J. & Akashi, M. Environmentally degradable, high-performance thermoplastics from phenolic phytomonomers. *Nat. Mater.* **5**, 966–970 (2006).
85. Nsengiyumva, O. & Miller, S. A. Synthesis, characterization, and water-degradation of biorenewable polyesters derived from natural camphoric acid. *Green Chem.* **21**, 973–978 (2019).
86. Beckham, G. T., Johnson, C. W., Karp, E. M., Salvachúa, D. & Vardon, D. R. Opportunities and challenges in biological lignin valorization. *Curr. Opin. Biotechnol.* **42**, 40–53 (2016).
87. Johnson, C. W. et al. Enhancing muconic acid production from glucose and lignin-derived aromatic compounds via increased protocatechuate decarboxylase activity. *Metab. Eng. Commun.* **3**, 111–119 (2016).
88. Settle, A. E. et al. Iodine-catalyzed isomerization of dimethyl muconate. *ChemSusChem* **11**, 1768–1780 (2018).
89. Johnson, C. W. et al. Innovative chemicals and materials from bacterial aromatic catabolic pathways. *Joule* **3**, 1523–1537 (2019).
90. Rorrer, N. A. et al. Renewable unsaturated polyesters from muconic acid. *ACS Sus. Chem. Eng.* **4**, 6867–6876 (2016).
91. Rorrer, N. A. et al. Combining reclaimed PET with bio-based monomers enables plastics upcycling. *Joule* **3**, 1006–1027 (2019).
92. Quinzler, D. & Mecking, S. Linear semicrystalline polyesters from fatty acids by complete feedstock molecule utilization. *Angew. Chem. Int. Ed.* **49**, 4306–4308 (2010).
93. Stempf, F., Quinzler, D., Heckler, I. & Mecking, S. Long-chain linear C₁₅ and C₂₅ monomers and polycondensates from unsaturated fatty acid esters. *Macromolecules* **44**, 4159–4166 (2011).
94. Stempf, F., Ritter, B. S., Mülhaupt, R. & Mecking, S. Long-chain aliphatic polyesters from plant oils for injection molding, film extrusion and electrospinning. *Green Chem.* **16**, 2008–2014 (2014).
95. Roesle, P. et al. Synthetic polyester from algae oil. *Angew. Chem. Int. Ed.* **53**, 6800–6804 (2014).
96. Stempf, F., Ortmann, P. & Mecking, S. Long-chain aliphatic polymers to bridge the gap between semicrystalline polyolefins and traditional polycondensates. *Chem. Rev.* **116**, 4597–4641 (2016).
97. Witt, T., Häußler, M., Kulpa, S. & Mecking, S. Chain multiplication of fatty acids to precise telechelic polyethylene. *Angew. Chem. Int. Ed.* **56**, 7589–7594 (2017).
98. Genovese, L. et al. Biodegradable long chain aliphatic polyesters containing ether-linkages: synthesis, solid-state, and barrier properties. *Ind. Eng. Chem. Res.* **53**, 10965–10973 (2014).
99. Jiang, G. et al. Carbon sources for polyhydroxyalkanoates and an integrated biorefinery. *Int. J. Mol. Sci.* **17**, 1157 (2016).
100. Wang, S. et al. Biodegradation of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) plastic under anaerobic sludge and aerobic seawater conditions: gas evolution and microbial diversity. *Environ. Sci. Technol.* **52**, 5700–5709 (2018).
101. Winnacker, M. Polyhydroxyalkanoates: recent advances in their synthesis and applications. *Eur. J. Lipid Sci. Technol.* **121**, 1900101 (2019).
102. Sangroniz, A. et al. Packaging materials with desired mechanical and barrier properties and full chemical recyclability. *Nat. Comm.* **10**, 3559 (2019).
103. Myung, J., Flanagan, J. C. A., Waymouth, R. M. & Criddle, C. S. Methane or methanol-oxidation dependent synthesis of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) by obligate type II methanotrophs. *Process Biochem.* **51**, 561–567 (2016).
104. Flanagan, J. C. A., Myung, J., Criddle, C. S. & Waymouth, R. M. Poly(hydroxyalkanoate)s from waste biomass: a combined chemical–biological approach. *ChemistrySelect* **1**, 2327–2331 (2016).
105. Myung, J., Flanagan, J. C. A., Waymouth, R. M. & Criddle, C. S. Expanding the range of polyhydroxyalkanoates synthesized by methanotrophic bacteria through the utilization of ω -hydroxyalkanoate co-substrates. *AMB Express* **7**, 118 (2017).
106. Tang, X. & Chen, E. Y.-X. Chemical synthesis of perfectly isotactic and high melting bacterial poly(3-hydroxybutyrate) from bio-sourced racemic cyclic diolide. *Nat. Commun.* **9**, 2345 (2018).
107. Tang, X., Westlie, A. H., Watson, E. M. & Chen, E. Y.-X. Stereosequenced crystalline polyhydroxyalkanoates from diastereomeric monomer mixtures. *Science* **366**, 754–758 (2019).
108. Tang, X. et al. Biodegradable polyhydroxyalkanoates by stereoselective copolymerization of racemic diolides: stereocontrol and polyolefin-like properties. *Angew. Chem. Int. Ed.* **59**, 7881–7890 (2020).
109. Westlie, A. H. & Chen, E. Y.-X. Catalyzed chemical synthesis of unnatural aromatic polyhydroxyalkanoate and aromatic–aliphatic PHAs with record-high glass-transition and decomposition temperatures. *Macromolecules* **53**, 9906–9915 (2020).
110. Haider, T. P., Völker, C., Kramm, J., Landfester, K. & Wurm, F. R. Plastics of the future? The impact of biodegradable polymers on the environment and on society. *Angew. Chem. Int. Ed.* **58**, 50–62 (2019).
111. Coates, G. W. & Getzler, Y. D. Y. L. Chemical recycling to monomer for an ideal, circular polymer economy. *Nat. Rev. Mater.* **5**, 501–516 (2020).
112. Lin, B., Hedrick, J. L., Park, N. H. & Waymouth, R. M. Programmable high-throughput platform for the rapid and scalable synthesis of polyester and polycarbonate libraries. *J. Am. Chem. Soc.* **141**, 8921–8927 (2019).
113. Siracusa, V. Microbial degradation of synthetic biopolymers waste. *Polymers* **11**, 1066 (2019).
114. Dusselier, M., Van Wouwe, P., Dewaele, A., Jacobs, P. A. & Sels, B. F. Shape-selective zeolite catalysis for bioplastics production. *Science* **349**, 78–80 (2015).
115. de Roo, G., Kellerhals, M. B., Ren, Q., Witholt, B. & Kessler, B. Production of chiral R-3-hydroxyalkanoic acids and R-3-hydroxyalkanoic acid methyl esters via hydrolytic degradation of polyhydroxyalkanoate synthesized by pseudomonads. *Biotechnol. Bioeng.* **77**, 717–722 (2002).
116. van der Meulen, I. et al. Catalytic ring-opening polymerization of renewable macrolactones to high molecular weight polyethylene-like polymers. *Macromolecules* **44**, 4301–4305 (2011).
117. Witt, T. & Mecking, S. Large-ring lactones from plant oils. *Green Chem.* **15**, 2361–2364 (2013).
118. Hodge, P. Entropically driven ring-opening polymerization of strainless organic macrocycles. *Chem. Rev.* **114**, 2278–2312 (2014).
119. Wilson, J. A., Hopkins, S. A., Wright, P. M. & Dove, A. P. Synthesis of ω -pentadecalactone copolymers with independently tunable thermal and degradation behavior. *Macromolecules* **48**, 950–958 (2015).
120. Myers, D. et al. Ring opening polymerization of macrolactones: high conversions and activities using an yttrium catalyst. *Polym. Chem.* **8**, 5780–5785 (2017).

121. Witt, T., Häußler, M. & Mecking, S. No strain, no gain? Enzymatic ring-opening polymerization of strainless aliphatic macrolactones. *Macromol. Rapid Commun.* **38**, 1600638 (2017).
122. Li, C. et al. Lipase-catalyzed ring-opening copolymerization of ω -pentadecalactone and δ -valerolactone by reactive extrusion. *Green Chem.* **22**, 662–668 (2020).
123. Vendamme, R., Schüwer, N. & Eevers, W. Recent synthetic approaches and emerging bio-inspired strategies for the development of sustainable pressure-sensitive adhesives derived from renewable building blocks. *J. Appl. Polym. Sci.* **131**, 40669 (2014).
124. Heinrich, L. A. Future opportunities for bio-based adhesives — advantages beyond renewability. *Green Chem.* **21**, 1866–1888 (2019).
125. Brutman, J. P., De Hoe, G. X., Schneiderman, D. K., Le, T. N. & Hillmyer, M. A. Renewable, degradable, and chemically recyclable cross-linked elastomers. *Ind. Eng. Chem. Res.* **55**, 11097–11106 (2016).
126. De Hoe, G. X. et al. Sustainable polyester elastomers from lactones: synthesis, properties, and enzymatic hydrolyzability. *J. Am. Chem. Soc.* **140**, 963–973 (2018).
127. Schneiderman, D. K. et al. Chemically recyclable biobased polyurethanes. *ACS Macro Lett.* **5**, 515–518 (2016).
128. Shin, J. et al. Pressure-sensitive adhesives from renewable triblock copolymers. *Macromolecules* **44**, 87–94 (2011).
129. Vendamme, R. et al. Interplay between viscoelastic and chemical tunings in fatty-acid-based polyester adhesives: engineering biomass toward functionalized step-growth polymers and soft networks. *Biomacromolecules* **13**, 1933–1944 (2012).
130. Shin, J., Lee, Y., Tolman, W. B. & Hillmyer, M. A. Thermoplastic elastomers derived from menthene and tulipalin A. *Biomacromolecules* **13**, 3833–3840 (2012).
131. Sulley, G. S. et al. Switchable catalysis improves the properties of CO₂-derived polymers: poly(cyclohexene carbonate-*b*- ϵ -decalactone-*b*-cyclohexene carbonate) adhesives, elastomers, and toughened plastics. *J. Am. Chem. Soc.* **142**, 4367–4378 (2020).
132. Winkler, M., Romain, C., Meier, M. A. R. & Williams, C. K. Renewable polycarbonates and polyesters from 1,4-cyclohexadiene. *Green Chem.* **17**, 300–306 (2015).
133. Xiong, M., Schneiderman, D. K., Bates, F. S., Hillmyer, M. A. & Zhang, K. Scalable production of mechanically tunable block polymers from sugar. *Proc. Natl Acad. Sci. USA* **111**, 8357–8362 (2014).
134. Watts, A., Kurokawa, N. & Hillmyer, M. A. Strong, resilient, and sustainable aliphatic polyester thermoplastic elastomers. *Biomacromolecules* **18**, 1845–1854 (2017).
135. Robert, C., de Montigny, F. & Thomas, C. M. Tandem synthesis of alternating polyesters from renewable resources. *Nat. Commun.* **2**, 586 (2011).
136. Peña Carrodegua, L., Martín, C. & Kleij, A. W. Semiaromatic polyesters derived from renewable terpene oxides with high glass transitions. *Macromolecules* **50**, 5337–5345 (2017).
137. Van Zee, N. J. & Coates, G. W. Alternating copolymerization of propylene oxide with biorenewable terpene-based cyclic anhydrides: a sustainable route to aliphatic polyesters with high glass transition temperatures. *Angew. Chem. Int. Ed.* **54**, 2665–2668 (2015).
138. Sanford, M. J., Peña Carrodegua, L., Van Zee, N. J., Kleij, A. W. & Coates, G. W. Alternating copolymerization of propylene oxide and cyclohexene oxide with tricyclic anhydrides: access to partially renewable aliphatic polyesters with high glass transition temperatures. *Macromolecules* **49**, 6394–6400 (2016).
139. Snyder, R. L. et al. Mechanically robust and reprocessable imine exchange networks from modular polyester pre-polymers. *Polym. Chem.* **11**, 5346–5355 (2020).
140. Sommerfeld, S. D., Zhang, Z., Costache, M. C., Vega, S. L. & Kohn, J. Enzymatic surface erosion of high tensile strength polycarbonates based on natural phenols. *Biomacromolecules* **15**, 830–836 (2014).
141. Xu, J., Feng, E. & Song, J. Renaissance of aliphatic polycarbonates: new techniques and biomedical applications. *J. Appl. Polym. Sci.* **131**, 39822 (2014).
142. Byrne, C. M., Allen, S. D., Lobkovsky, E. B. & Coates, G. W. Alternating copolymerization of limonene oxide and carbon dioxide. *J. Am. Chem. Soc.* **126**, 11404–11405 (2004).
143. Auriemma, F. et al. Stereocomplexed poly(limonene carbonate): a unique example of the cocrystallization of amorphous enantiomeric polymers. *Angew. Chem. Int. Ed.* **54**, 1215–1218 (2015).
144. Kristufek, T. S. et al. Rapidly-cured isosorbide-based cross-linked polycarbonate elastomers. *Polym. Chem.* **7**, 2639–2644 (2016).
145. Stöfer, T. et al. Bio-derived polymers for coating applications: comparing poly(limonene carbonate) and poly(cyclohexadiene carbonate). *Polym. Chem.* **8**, 6099–6105 (2017).
146. Hauenstein, O., Reiter, M., Agarwal, S., Rieger, B. & Greiner, A. Bio-based polycarbonate from limonene oxide and CO₂ with high molecular weight, excellent thermal resistance, hardness and transparency. *Green Chem.* **18**, 760–770 (2016).
147. von der Assen, N. & Bardow, A. Life cycle assessment of polyols for polyurethane production using CO₂ as feedstock: insights from an industrial case study. *Green Chem.* **16**, 3272–3280 (2014).
148. Langanke, J. et al. Carbon dioxide (CO₂) as sustainable feedstock for polyurethane production. *Green Chem.* **16**, 1865–1870 (2014).
149. Allen, S. D. et al. Polycarbonate polyol compositions and methods. US Patent 8,247,520 B2 (2012).
150. Zhang, Z. et al. A non-phosgene process for biodevised polycarbonate with high molecular weight and advanced property profile synthesized using amino acid ionic liquids as catalysts. *Green Chem.* **22**, 2534–2542 (2020).
151. Park, S.-A. et al. Sustainable and recyclable super engineering thermoplastic from biorenewable monomer. *Nat. Commun.* **10**, 2601 (2019).
152. Li, C., Sablong, R. J., van Benthem, R. A. T. M. & Koning, C. E. Unique base-initiated depolymerization of limonene-derived polycarbonates. *ACS Macro Lett.* **6**, 684–688 (2017).
153. Neumann, S., Leitner, L.-C., Schmalz, H., Agarwal, S. & Greiner, A. Unlocking the processability and recyclability of biobased poly(limonene carbonate). *ACS Sus. Chem. Eng.* **8**, 6442–6448 (2020).
154. Ma, S. & Webster, D. C. Naturally occurring acids as cross-linkers to yield VOC-free, high-performance, fully bio-based, degradable thermosets. *Macromolecules* **48**, 7127–7137 (2015).
155. Hevus, I., Ricapito, N. G., Tymoshenko, S., Raja, S. N. & Webster, D. C. Biobased carboxylic acids as components of sustainable and high-performance coating systems. *ACS Sus. Chem. Eng.* **8**, 5750–5762 (2020).
156. Zhang, S. et al. Preparation of a lignin-based vitrimer material and its potential use for recoverable adhesives. *Green Chem.* **20**, 2995–3000 (2018).
157. Toldy, A., Szolnoki, B. & Marosi, G. Flame retardancy of fibre-reinforced epoxy resin composites for aerospace applications. *Polym. Degrad. Stab.* **96**, 371–376 (2011).
158. Maiorana, A., Spinella, S. & Gross, R. A. Bio-based alternative to the diglycidyl ether of bisphenol A with controlled materials properties. *Biomacromolecules* **16**, 1021–1031 (2015).
159. Zago, E. et al. Synthesis of bio-based epoxy monomers from natural allyl- and vinyl phenols and the estimation of their affinity to the estrogen receptor α by molecular docking. *New J. Chem.* **40**, 7701–7710 (2016).
160. Winne, J. M., Leibler, L. & Du Prez, F. E. Dynamic covalent chemistry in polymer networks: a mechanistic perspective. *Polym. Chem.* **10**, 6091–6108 (2019).
161. Scheut, G. M., Lessard, J. J., Sims, M. B. & Sumerlin, B. S. Adaptable crosslinks in polymeric materials: resolving the intersection of thermoplastics and thermosets. *J. Am. Chem. Soc.* **141**, 16181–16196 (2019).
162. Liu, X. & Zhang, J. High-performance biobased epoxy derived from rosin. *Polym. Int.* **59**, 607–609 (2010).
163. Pan, X., Sengupta, P. & Webster, D. C. High biobased content epoxy-anhydride thermosets from epoxidized sucrose esters of fatty acids. *Biomacromolecules* **12**, 2416–2428 (2011).
164. Chrysanthos, M., Galy, J. & Pascault, J.-P. Preparation and properties of bio-based epoxy networks derived from isosorbide diglycidyl ether. *Polymer* **52**, 3611–3620 (2011).
165. Hong, J., Radojč, D., Ionescu, M., Petrovič, Z. S. & Eastwood, E. Advanced materials from corn: isosorbide-based epoxy resins. *Polym. Chem.* **5**, 5360–5368 (2014).
166. Hu, F., La Scala, J. J., Sadler, J. M. & Palmese, G. R. Synthesis and characterization of thermosetting furan-based epoxy systems. *Macromolecules* **47**, 3332–3342 (2014).
167. Liu, W., Zhou, R., Goh, H. L. S., Huang, S. & Lu, X. From waste to functional additive: toughening epoxy resin with lignin. *ACS Appl. Mater. Interfaces* **6**, 5810–5817 (2014).
168. Qin, J., Liu, H., Zhang, P., Wolcott, M. & Zhang, J. Use of eugenol and rosin as feedstocks for biobased epoxy resins and study of curing and performance properties. *Polym. Int.* **63**, 760–765 (2014).
169. Gandini, A., Lacerda, T. M., Carvalho, A. J. F. & Trovatti, E. Progress of polymers from renewable resources: furans, vegetable oils, and polysaccharides. *Chem. Rev.* **116**, 1637–1669 (2016).
170. Zhang, C., Garrison, T. F., Madbouly, S. A. & Kessler, M. R. Recent advances in vegetable oil-based polymers and their composites. *Prog. Polym. Sci.* **71**, 91–143 (2017).
171. Li, R. et al. Use of hempseed-oil-derived polyacid and rosin-derived anhydride acid as curing agents for epoxy materials. *ACS Sus. Chem. Eng.* **6**, 4016–4025 (2018).
172. Zhao, S., Huang, X., Whelton, A. J. & Abu-Omar, M. M. Renewable epoxy thermosets from fully lignin-derived triphenols. *ACS Sus. Chem. Eng.* **6**, 7600–7608 (2018).
173. Ocampo, C., Ecochard, Y., Decostanzi, M., Caillol, S. & Avérous, L. Dynamic network based on eugenol-derived epoxy as promising sustainable thermoset materials. *Eur. Polym. J.* **135**, 109860 (2020).
174. Hollande, L. et al. Preparation of renewable epoxy-amine resins with tunable thermo-mechanical properties, wettability and degradation abilities from lignocellulose- and plant oils-derived components. *Front. Chem.* **7**, 159 (2019).
175. Gandini, A., Carvalho, A. J. F., Trovatti, E., Kramer, R. K. & Lacerda, T. M. Macromolecular materials based on the application of the Diels-Alder reaction to natural polymers and plant oils. *Eur. J. Lipid Sci. Technol.* **120**, 1700091 (2018).
176. Hernandez, E. D., Bassett, A. W., Sadler, J. M., La Scala, J. J. & Stanzione, J. F. Synthesis and characterization of bio-based epoxy resins derived from vanillyl alcohol. *ACS Sus. Chem. Eng.* **4**, 4328–4339 (2016).
177. Liu, T. et al. A self-healable high glass transition temperature bioepoxy material based on vitrimer chemistry. *Macromolecules* **51**, 5577–5585 (2018).
178. Zhao, S. & Abu-Omar, M. M. Recyclable and malleable epoxy thermoset bearing aromatic imine bonds. *Macromolecules* **51**, 9816–9824 (2018).
179. Yu, Q. et al. Vanillin-based degradable epoxy vitrimers: reprocessability and mechanical properties study. *Eur. Polym. J.* **117**, 55–63 (2019).
180. Ma, S. et al. Readily recyclable, high-performance thermosetting materials based on a lignin-derived spiro diacetal trigger. *J. Mater. Chem. A* **7**, 1233–1243 (2019).
181. Wang, S. et al. Facile in situ preparation of high-performance epoxy vitrimer from renewable resources and its application in nondestructive recyclable carbon fiber composite. *Green Chem.* **21**, 1484–1497 (2019).
182. Marchildon, K. Polyamides — still strong after seventy years. *Macromol. React. Eng.* **5**, 22–54 (2011).
183. Barnes, C. E. Nylon 4 — development and commercialization. *Lenzing. Ber.* **62**, 62–66 (1987).
184. Kim, H. T. et al. Development of metabolically engineered *Corynebacterium glutamicum* for enhanced production of cadaverine and its use for the synthesis of bio-polyamide 510. *ACS Sus. Chem. Eng.* **8**, 129–138 (2020).
185. Lane, J. Terry, L. A next-generation fiber: innovative, cost-competitive, biobased polyamide for textiles. *Biofuels Digest* <http://www.biofuelsdigest.com/bdigest/2014/11/10/terryl-a-next-generation-fiber-innovative-cost-competitive-biobased-polyamide-for-textiles/> (2014).
186. Caswell, P. J. Terry, L. Presented at the Biotechnology Innovation Organization (BIO) World Congress (2014).
187. Yi, Z., Bingbing, Q. & Chi, L. Blended fiber and preparation method thereof and fabric comprising the blended fiber. CN Patent 105,040,156 A (2014).
188. Winnacker, M. & Rieger, B. Biobased polyamides: recent advances in basic and applied research. *Macromol. Rapid Commun.* **37**, 1391–1413 (2016).
189. Froidevaux, V., Negrell, C., Caillol, S., Pascault, J.-P. & Boutevin, B. Biobased amines: from synthesis to polymers; present and future. *Chem. Rev.* **116**, 14181–14224 (2016).

190. Pingen, D. et al. Diamines for polymer materials via direct amination of lipid- and lignocellulose-based alcohols with NH_3 . *ChemCatChem* **10**, 3027–3033 (2018).
191. Citoler, J., Derrington, S. R., Galman, J. L., Bevinakatti, H. & Turner, N. J. A biocatalytic cascade for the conversion of fatty acids to fatty amines. *Green Chem.* **21**, 4932–4935 (2019).
192. Firdaus, M. & Meier, M. A. R. Renewable polyamides and polyurethanes derived from limonene. *Green Chem.* **15**, 370–380 (2013).
193. Türünc, O., Firdaus, M., Klein, G. & Meier, M. A. R. Fatty acid derived renewable polyamides via thiol–ene additions. *Green Chem.* **14**, 2577–2583 (2012).
194. Jiang, Y., Maniar, D., Woortman, A. J. J., Alberda van Ekenstein, G. O. R. & Loos, K. Enzymatic polymerization of furan-2,5-dicarboxylic acid-based furanic–aliphatic polyamides as sustainable alternatives to polyphthalamides. *Biomacromolecules* **16**, 3674–3685 (2015).
195. Mitiakoudis, A. & Gandini, A. Synthesis and characterization of furanic polyamides. *Macromolecules* **24**, 830–835 (1991).
196. Song, L. et al. Ultra-strong long-chain polyamide elastomers with programmable supramolecular interactions and oriented crystalline microstructures. *Nat. Commun.* **10**, 1315 (2019).
197. Stockmann, P. N. et al. Biobased chiral semi-crystalline or amorphous high-performance polyamides and their scalable stereoselective synthesis. *Nat. Commun.* **11**, 509 (2020).
198. Stockmann, P. N. et al. New bio-polyamides from terpenes: α -pinene and (+)-3-carene as valuable resources for lactam production. *Macromol. Rapid Commun.* **40**, 1800903 (2019).
199. Winnacker, M., Neumeier, M., Zhang, X., Papadakis, C. M. & Rieger, B. Sustainable chiral polyamides with high melting temperature via enhanced anionic polymerization of a menthone-derived lactam. *Macromol. Rapid Commun.* **37**, 851–857 (2016).
200. Winnacker, M., Sag, J., Tischner, A. & Rieger, B. Sustainable, stereoregular, and optically active polyamides via cationic polymerization of ϵ -lactams derived from the terpene β -pinene. *Macromol. Rapid Commun.* **38**, 1600787 (2017).
201. Winnacker, M. & Sag, J. Sustainable terpene-based polyamides via anionic polymerization of a pinene-derived lactam. *ChemComm* **54**, 841–844 (2018).
202. Maisonneuve, L., Lamarzelle, O., Rix, E., Grau, E. & Cramail, H. Isocyanate-free routes to polyurethanes and poly(hydroxy urethane)s. *Chem. Rev.* **115**, 12407–12439 (2015).
203. Luo, X., Xiao, Y., Wu, Q. & Zeng, J. Development of high-performance biodegradable rigid polyurethane foams using all bioresource-based polyols: lignin and soy oil-derived polyols. *Int. J. Biol. Macromol.* **115**, 786–791 (2018).
204. Guo, A., Javni, I. & Petrović, Z. Rigid polyurethane foams based on soybean oil. *J. Appl. Polym. Sci.* **77**, 467–473 (2000).
205. Zlatanić, A., Lava, C., Zhang, W. & Petrović, Z. S. Effect of structure on properties of polyols and polyurethanes based on different vegetable oils. *J. Polym. Sci. B Polym. Phys.* **42**, 809–819 (2004).
206. Babb, D. A. in *Synthetic Biodegradable Polymers* (eds Rieger, B. et al.) 315–360 (Springer, 2012).
207. Peyrton, J., Chambaretaud, C., Sarbu, A. & Avérous, L. Biobased polyurethane foams based on new polyol architectures from microalgae oil. *ACS Sus. Chem. Eng.* **8**, 12187–12196 (2020).
208. Lysenko, Z. et al. Vegetable oil based polyols and polyurethanes made therefrom. WO Patent 2,004,096,882 A1 (2004).
209. Gurusamy-Thangavelu, S. A. et al. Polyurethanes based on renewable polyols from bioderived lactones. *Polym. Chem.* **3**, 2941–2948 (2012).
210. Gunawan, N. R. et al. Rapid biodegradation of renewable polyurethane foams with identification of associated microorganisms and decomposition products. *Bioresour. Technol.* **11**, 100513 (2020).
211. Cornille, A. et al. Promising mechanical and adhesive properties of isocyanate-free poly(hydroxyurethane). *Eur. Polym. J.* **84**, 404–420 (2016).
212. Zhang, K. et al. Non-isocyanate poly(amide-hydroxyurethane)s from sustainable resources. *Green Chem.* **18**, 4667–4681 (2016).
213. Carré, C., Ecochard, Y., Caillol, S. & Avérous, L. From the synthesis of biobased cyclic carbonate to polyhydroxyurethanes: a promising route towards renewable non-isocyanate polyurethanes. *ChemSusChem* **12**, 3410–3430 (2019).
214. Kühnel, I., Saake, B. & Lehnen, R. A new environmentally friendly approach to lignin-based cyclic carbonates. *Macromol. Chem. Phys.* **219**, 1700613 (2018).
215. Chen, X., Li, L., Jin, K. & Torkelson, J. M. Reprocessable polyhydroxyurethane networks exhibiting full property recovery and concurrent associative and dissociative dynamic chemistry via transcarbamoylation and reversible cyclic carbonate aminolysis. *Polym. Chem.* **8**, 6349–6355 (2017).
216. Schimpf, V., Ritter, B. S., Weis, P., Parison, K. & Mülhaupt, R. High purity limonene dicarbonate as versatile building block for sustainable non-isocyanate polyhydroxyurethane thermosets and thermoplastics. *Macromolecules* **50**, 944–955 (2017).
217. Tamami, B., Sohn, S. & Wilkes, G. L. Incorporation of carbon dioxide into soybean oil and subsequent preparation and studies of nonisocyanate polyurethane networks. *J. Appl. Polym. Sci.* **92**, 883–891 (2004).
218. Liaw, D.-J. et al. Advanced polyimide materials: syntheses, physical properties and applications. *Prog. Polym. Sci.* **37**, 907–974 (2012).
219. Lau, K. S. Y. in *Handbook of Thermoset Plastics* 3rd edn Ch. 10 (eds Dodiuk, H. & Goodman, S. H.) 297–424 (William Andrew Publishing, 2014).
220. McNamara, J., Harvey, J. D., Graham, M. J., Scherger, C. Optically transparent polyimides. WO Patent 2019/156,717 A2 (2019).
221. Serber, Z., et al. Microbial strain improvement by a HTP genomic engineering platform. WO Patent 2017/100,377 A1 (2018).
222. Zymergen. *Zymergen Reimagines Electronics with Breakthrough Bio-fabricated Materials* (Zymergen, 2020).
223. Lane, J. Super clear, super thin, super durable: Zymergen bends it like Beckham, electronics-wise. *Biofuels Digest* <http://www.biofuelsdigest.com/bdigest/2020/04/06/super-clear-super-thin-super-durable-zymergen-bends-it-like-beckham-electronics-wise/> (2020).
224. Santhosh Kumar, K. S. & Reghunadhan Nair, C. P. in *Handbook of Thermoset Plastics* 3rd edn Ch. 3 (eds Dodiuk, H. & Goodman, S. H.) 45–73 (William Andrew Publishing, 2014).
225. Dumas, L., Bonnaud, L., Olivier, M., Poortman, M. & Dubois, P. Chavicol benzoxazine: ultrahigh T_g biobased thermoset with tunable extended network. *Eur. Polym. J.* **81**, 337–346 (2016).
226. Puchot, L. et al. Breaking the symmetry of dibenzoxazines: a paradigm to tailor the design of bio-based thermosets. *Green Chem.* **18**, 3346–3353 (2016).
227. Teng, N. et al. Making benzoxazine greener and stronger: renewable resource, microwave irradiation, green solvent, and excellent thermal properties. *ACS Sus. Chem. Eng.* **7**, 8715–8723 (2019).
228. Zhang, K., Liu, Y., Han, M. & Froimowicz, P. Smart and sustainable design of latent catalyst-containing benzoxazine-bio-resins and application studies. *Green Chem.* **22**, 1209–1219 (2020).
229. Whiteley, J. M., Taynton, P., Zhang, W. & Lee, S.-H. Ultra-thin solid-state Li-ion electrolyte membrane facilitated by a self-healing polymer matrix. *Adv. Mater.* **27**, 6922–6927 (2015).
230. Taynton, P. et al. Re-healable polyimine thermosets: polymer composition and moisture sensitivity. *Polym. Chem.* **7**, 7052–7056 (2016).
231. Taynton, P. et al. Repairable woven carbon fiber composites with full recyclability enabled by malleable polyimine networks. *Adv. Mater.* **28**, 2904–2909 (2016).
232. Dhers, S., Vantomme, G. & Avérous, L. A fully bio-based polyimine vitrimer derived from fructose. *Green Chem.* **21**, 1596–1601 (2019).
233. Hajj, R., Duval, A., Dhers, S. & Avérous, L. Network design to control polyimine vitrimer properties: physical versus chemical approach. *Macromolecules* **53**, 3796–3805 (2020).
234. Geng, H. et al. Vanillin-based polyschiff vitrimers: reprocessability and chemical recyclability. *ACS Sus. Chem. Eng.* **6**, 15463–15470 (2018).
235. Wang, S. et al. Robust, fire-safe, monomer-recovery, highly malleable thermosets from renewable bioresources. *Macromolecules* **51**, 8001–8012 (2018).
236. Kim, C., Chandrasekaran, A., Huan, T. D., Das, D. & Ramprasad, R. Polymer genome: a data-powered polymer informatics platform for property predictions. *J. Phys. Chem. C* **122**, 17575–17585 (2018).
237. Hackett, M., Zang, L., Viciu, L. & Masuda, T. *Lactic Acid, Its Salts, and Esters* (IHS Markit, 2018).
238. Montazeri, M., Zaimes, G. G., Khanna, V. & Eckelman, M. J. Meta-analysis of life cycle energy and greenhouse gas emissions for priority biobased chemicals. *ACS Sus. Chem. Eng.* **4**, 6443–6454 (2016).

Acknowledgements

This work was authored in part by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the US Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by the US DOE, Office of Energy Efficiency and Renewable Energy Bioenergy Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the US Government. The US Government retains and the publisher, by accepting the article for publication, acknowledges that the US Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for US Government purposes. E.Y.-X.C. acknowledges support from the US National Science Foundation (NSF-1955482).

Author contributions

R.M.C., N.A.R., C.B.H. and G.T.B. wrote the manuscript and designed the figures. G.T.B. and E.Y.-X.C. prepared the initial draft outline. All authors edited the manuscript prior to submission.

Competing interests

The authors declare no competing interests.

Peer review information

Nature Reviews Materials thanks the other anonymous reviewers for their contribution to the peer review of this work.

Publisher's note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Supplementary information

The online version contains supplementary material available at <https://doi.org/10.1038/s41578-021-00363-3>.

RELATED LINKS

Nylon 11: <https://www.extremematerials-arkema.com/en/product-families/rilsan-polyamide-11-family/key-properties/>
Polymers: A Property Database: <https://poly.chemnetbase.com/faces/polymers/PolymerSearch.xhtml>

© Alliance for Sustainable Energy, under exclusive licence to Springer Nature Limited 2021