The quest for high glass transition temperature bioplastics

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Complete List of Authors:	Nguyen, Ha; University of Florida, Chemistry Qi, Pengxu; University of Florida, Chemistry Rostagno, Mayra; University of Florida, Chemistry Feteha, Amr; University of Florida, Chemistry Miller, Stephen; University of Florida, Department of Chemistry

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REVIEW ARTICLE

The quest for high glass transition temperature bioplastics

Ha Thi Hoang Nguyen, Pengxu Qi, Mayra Rostagno, Amr Feteha and Stephen A. Miller*

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The field of biorenewable polymers is ever-expanding, aided by the interest of the general public to adopt more sustainable practices for natural resource utilization as well as waste generation. This review summarizes recent efforts to synthesize biobased thermoplastics with glass transition temperature (T_g) values exceeding that of polylactic acid (PLA), near 55 °C. A high T_g is essential for materials that aspire to replace any incumbent commodity plastics employed in the amorphous state. The first section focuses on commercial bioplastics and describes: approaches toward biorenewable polyethylene terephthalate (PET); efforts to improve the T_g of PLA; and advances toward polyethylene furanoate (PEF). The remaining sections catalogue a wide variety of novel, high T_g bioplastics categorized as: aromatic biopolymers, carbocyclic and heterocyclic biopolymers, and vinyl-type biopolymers synthesized via radical polymerization.

1. Introduction

In the early 19th century, the world's first synthetic plastic, Bakelite, was commercialized.[1] Since then, plastic consumption has grown exponentially as these manufactured materials have become increasingly indispensable. Six types of commodity plastics dominate the current market: (1) polyethylene terephthalate (PET); (2) high-density polyethylene (HDPE); (3) polyvinyl chloride (PVC); (4) low density polyethylene (LDPE) and linear low density polyethylene (LLDPE); (5) polypropylene (PP); and (6) polystyrene (PS). Each has a recycling number introduced by the Society of the Plastics Industry (SPI) in 1988 (Figure 1),[2] but this number certainly does not guarantee an easy route to recycling. Regulations and procedures are highly dependent on the city, state, and country. For example, foamed polystyrene (Styrofoam™) articles are recycled in Los Angeles,[3] but not in San Francisco.[4]

Worldwide plastic production was 322 billion kg in 2015,[5] strikingly equivalent to the mass of 5 billion people. The aforementioned commodity plastics constitute the majority of this output (269 billion kg, Figure 1)[6] and these are produced from petroleum and natural gas, consuming about 5% of all harvested fossil fuel resources.[7] Considering the dramatic rise in plastic consumption and the inevitable depletion of fossil fuel reserves,[8] we must seek and find alternative, renewable resources[9] to build our indispensible plastics.[10] An equally important consideration is the final destination of these materials. What happens to the 300+ billion kg of plastics synthesized each year? In the United States, less than 10% of plastics are recycled,[11] about 60% accumulates in landfills, and the remaining 30% is unaccounted for, contributing to the *trash crisis*[12] as it escapes to the terrestrial and aquatic environment.

Fig. 1 Global demand of commodity plastics in 2015.[6]

Modest estimates suggest that 10 tons of floating plastics (PE, PP, foamed PS) are discarded into the ocean every minute.[13] Ominous forecasts suggest that by the year 2050, these accumulated plastics will outweigh the fish in the ocean.[14] Unfortunately, environmental plastics have not reached a steady-state equilibrium, and accumulation will assuredly increase. That is, the rate of addition vastly outpaces the rate of degradation, which could be 500 to 1000 years for the polyolefins PE, PP, or PS.[15] Indeed, the list of

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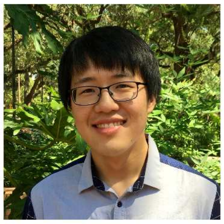
The George and Josephine Butler Laboratory for Polymer Research, Department of Chemistry, University of Florida Gainesville, Florida 32611-7200, USA. Fax: +1-352-392-9741; Tel: +1-352-392-7773; E-mail: miller@chem.ufl.edu

In 2016, Ha Nguyen completed her Ph.D. studies in the Department of Chemistry, University of Florida, under the supervision of Professor Stephen A. Miller. Previously, she received her Engineering Diploma in Organic Chemistry from Ecole Nationale Supérieure de Chimie de Clermont-Ferrand (ENSCCF) and a double Master degree in Bioorganic and Environmental Chemistry from ENSCCF and Université Blaise Pascal. Her research interests include the synthesis and characterization of biorenewable polymers and polyolefins.

Mayra Rostagno was born in Buenos Aires, Argentina where she spent her formative years, and received her B.Sc. in Chemistry from the Universidad de Buenos Aires. In 2012, she moved to Gainesville, Florida to pursue a Ph.D. in Polymer Chemistry at the University of Florida under the supervision of Professor Stephen A. Miller. Her research focused on the synthesis of renewable polyacetals with the aim of mimicking commodity plastics. Mayra received her Ph.D. in May 2017.



Pengxu Qi graduated from Beijing Institute of Technology with a B.S. degree in 2011. He then joined the Ph.D program in the Chemistry Department of the University of Florida. In 2016, he received his Ph.D. degree under the supervision of Professor Stephen A. Miller, focusing on the design and synthesis of biorenewable and degradable polymers with properties comparable to those of incumbent packaging materials.

Amr Feteha was born in Cairo, the capital of Egypt. He received his bachelor's degree in Chemistry from Benha University, Egypt in 2000. Thereafter, he worked at Benha University as a teaching assistant in organic chemistry courses and received his master's degree as well. He began his Ph.D studies in the Chemistry Department at the University of Florida in 2010. There, he investigated the synthesis of sustainable polymers utilizing RAFT/radical polymerization under the supervision of Professor Stephen A. Miller. Amr received his Ph.D. in May 2017.

In 1994 Stephen A. Miller received coterminal B.S. and M.S. degrees in Chemistry from Stanford University, where Robert M. Waymouth served as his undergraduate and M.S. Thesis advisor. He then earned a Ph.D. in Chemistry at the California Institute of Technology in 1999 with John E. Bercaw before conducting postdoctoral research with Richard R. Schrock at the Massachusetts Institute of Technology during 2000–2001. He held the position of Assistant Professor of Chemistry at Texas A&M University from 2001 until 2007, when he accepted his current positions of Associate Professor of Chemistry and Member of the Butler Polymer Research Laboratory at the University of Florida. His primary research efforts target the synthesis of biorenewable and degradable polymers that mimic petroleum-based plastics. A particular emphasis is placed on amorphous, high glass transition temperature materials because of the historical challenge to generate these polymeric properties from biobased feedstocks.

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drawbacks for fossil fuel-based plastics is long and compels the search for novel materials that derive from biorenewable feedstocks, degrade readily in the environment, yet offer material properties that match or excel those they aim to replace.

According to IUPAC terminology, "A *bioplastic* is a biobased polymer derived from biomass or issued from monomers derived from the biomass and which, at some stage in its processing into finished products, can be shaped by flow."[16] In other words, a bioplastic is a biobased thermoplastic.

Many bioplastics have been commercialized since the 1800s such as cellulose-based polymers (celluloid,[17] cellulose acetate,[18] and rayon[19]), starch-based plastics (Plastarch Material[20] and CornZein[21]), polylactic acid (PLA), bio polyethylene terephthalate (bioPET, PlantBottle®), bio polytrimethylene terephthalate (bioPTT, Sorona®), bio polyamides (bioPA) (bioPA11, bioPA610, bioPA6, bioPA66, and bioPA69), bio polyhydroxyalkanoates (bioPHAs), biopolyethylene (bioPE), bio polyvinyl chloride (bioPVC), and bio polyurethane (bioPUR).[22,23] Among these, bioPET and bioPTT are only 30% biobased, since the terephthalate component comes from conventional sources. Very recent efforts by Avantium in the Netherlands have targeted the commercialization of polyethylene furanoate (PEF).[24]

It is important to clarify the difference between bioplastics and biodegradable or otherwise environmentally degradable plastics. Bioplastics are not necessarily degradable. This term defines the source atoms for the polymer, but in no way guarantees a facile remediation in the environment. For example bioPE or bioPET have the same material properties as their fossil fuel-based cognates, including catatonic degradation behaviors.

Shen, Worrell, and Patel have estimated that the technical substitution potential of bioplastics for replacing petroleum-based plastics is 90%.[22] However, there remain two major issues limiting their prompt adoption: 1) high production costs and 2) lingering mechanical and thermal properties that are unsatisfactory compared to petroleum-based counterparts.[25] Concerning the first issue, iterative optimization and financial investments tend to decrease production costs. Economies of scale will be achieved only with increased demand and production. For example, twenty years ago PLA was priced about 15–20 times greater than PET, but today the surcharge is merely 1.15 to 1.25 times.[13] The second issue of poor polymer properties has confounded polymer scientists, but is also an area of extreme opportunity as structure/property relationships become clearer in the context of available biobased feedstocks. At the moment, corn-based PLA is arguably the most successful bioplastic.[26] Despite several positive hallmarks, PLA suffers from a low glass transition temperature (T_g) of 55 °C,[27] brittleness,[28] poor barrier properties,[29] and slow degradation under typical environmental conditions.[15,30]

The low T_g of PLA has especially limited its market expansion to replace higher T_g materials such as PET and PS.[31] For amorphous plastics, the T_g is the most important thermal parameter defining the range of applications. For semi-crystalline plastics, the melting temperature (T_m) assumes this defining role. While melting temperatures offer a greater thermal window than glass transition temperatures, for many applications amorphous polymers are preferred because the lack of crystallites generally permits superior optical transparency. PET is the epitome of this difference when comparing water bottles (amorphous) and clothing (semi-crystalline).

The lack of commercially available, high glass transition temperature bioplastics has created an opportunity in academia and industry to fill this market void. This review will focus on recent efforts to surpass the glass transition temperature of PLA (55 °C) with synthetic polymers having greater than 50% biobased content. The scope will be narrowed by avoiding the following: polymers with non-linear morphologies such as dendrimers[32] or stars;[33] composites;[34] natural polymers like lignin or starch that have been further functionalized; crosslinked/thermoset systems;[35,36,37,38] and bionylons since most of these are unavoidably semi-crystalline and a high glass transition temperature is not a targeted property. To begin, the current commercial landscape will be set by describing bioPET, PLA, and upstart PEF.

2. Commercial bioplastics

2.1. Bio polyethylene terephthalate (bioPET)

Polyethylene terephthalate (PET) is one of the most important synthetic polymers and is used in many applications, predominantly synthetic fibers[39] (about two thirds) and food/liquid packaging (about one third). Worldwide production of PET was estimated to exceed 24 billion kg in 2015.[40] PET is generally produced via polycondensation of terephthalic acid (TPA) or bis-(2-hydroxyethyl)terephthalate (BHET), and ethylene glycol. The resulting thermoplastic polyester possesses a T_g of 76 °C and T_m of 247 °C.[41] Answering an increasing demand for green polymers, Coca-Cola introduced PET containing 30% of plant-based starting material.[42] This partial biobased PET, known as PET *PlantBottle*, was made from bioethanol-based ethylene glycol and petroleum-based TPA, synthesized conventionally via oxidation of *p*-xylene. Therefore, the synthesis of biobased TPA has become an attractive area of research as a necessary step for producing 100% biobased PET.

Figure 2 summarizes the reported biorenewable starting materials for synthesizing bio-TPA. Diels-Alder (DA) cycloaddition is a key pathway for creating the six-membered ring from a dienophile and various renewable dienes, including: muconic acid/ester,[42] isoprene,[43] sorbic acid/ester,[44,45] or coumalic acid/ester.[46] In general, DA cycloaddition yields a six-membered aliphatic ring, which is subjected to dehydrogenative aromatization. Recently, Tachibana *et al.* utilized the DA reaction between biorenewable furan and maleic anhydride to afford TPA with 98.7% biobased carbon content.[47] Another useful diene that derives from fructose is 2,5-dimethyl furan, which combines with ethylene prior to aromatization to afford *p*-xylene.[48,49,50,51] An alternative approach was developed by Colonna *et al.* based on naturally occurring limonene.[52] The dehydration of bio-limonene produced *p*-cymene, followed by oxidation to yield bio-TPA. Its dimethyl ester was reacted with ethylene glycol to afford bioPET with 79 % biobased content and a T_g values of 82 °C.

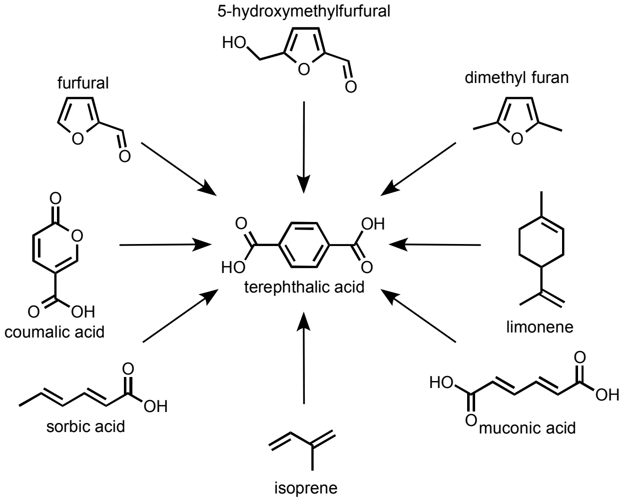


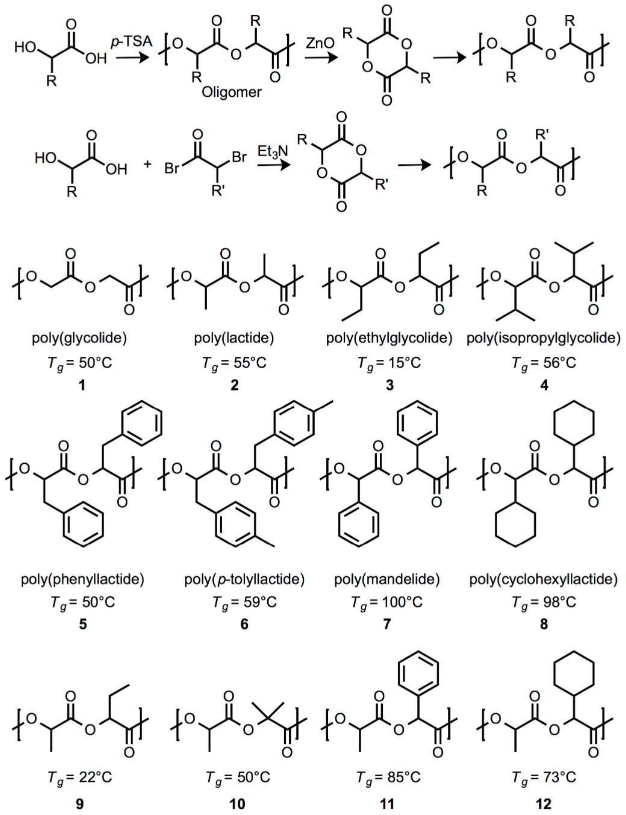
Fig. 2 Precursors for the synthesis of bio-terephthalic acid (bio-TPA) from renewable feedstocks[42–52]

2.2. Polylactic acid (PLA)

As one of the most successful and fully biorenewable polyesters, PLA, still suffers from limited applicability, partially because of its low glass transition temperature (T_g ~ 55°C).[53] To improve the T_g, different approaches have been applied either by optimization of PLA characteristics (*i.e.*, molecular weight, tacticity, and crystallinity) or chemical modification of its molecular structure.[27]

Research regarding the first category has been pursued for decades and two recently developed strategies have provided the most promising results. First, a 1:1 stereocomplex of enantiopure poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) has been reported to effectively improve the T_m (220–230°C) and T_g (65–72°C).[54,55] This technique optimizes chain-chain interactions by the supramolecular interaction of two helical polymers. However, it could be problematic with high molecular weight PLA (>100,000 Da) when the mixture is likely to undergo homochiral crystallization, shortchanging the system of its stereocomplexed fraction. Commercially, it is important to note that D-lactide is more challenging to produce via fermentation strategies, but has been accomplished on a large scale in Spain and Thailand.[56] An alternative approach for achieving similar thermal property improvement is a stepwise chain-extension technique, which condensed PLLA and PDLA oligomers to yield high molecular weight, stereoblock PLA copolymers.[57]

Because of practical limitations for controlling PLA stereochemistry and/or stereoblocks, more attention has been given to chemical modification of the PLA main-chain. Generally, a significant increase of T_g can be achieved by introducing conformational restriction around single bonds, either by rigid and/or sterically demanding or moieties. Thus, lactides with groups larger than methyl have been a focus of several recent studies.[58] Thermal behaviors of several poly(alkyl glycolide)s and poly(aryl glycolide)s were investigated by the Baker Group and the results are summarized in Scheme 1.[59,60] Lactide monomers were synthesized via two synthetic pathways: 1) oligomerization of substituted glycolic acids, followed by distillation with ZnO, or 2) cyclization of α-bromoacyl bromide with substituted glycolic acids. The former route allowed for PLA-type polymers with various R groups instead of methyl. The latter route allowed for PLA-type polymers of alternating R and R′ groups. These substituents contributed differently to the T_g of the corresponding polymer. In general, alkyl groups barely increased and usually decreased the T_g, whereas cyclic aliphatic or aryl groups increased the T_g. Two opposing effects of adding substituents should be considered: conformational restriction and increased free volume.



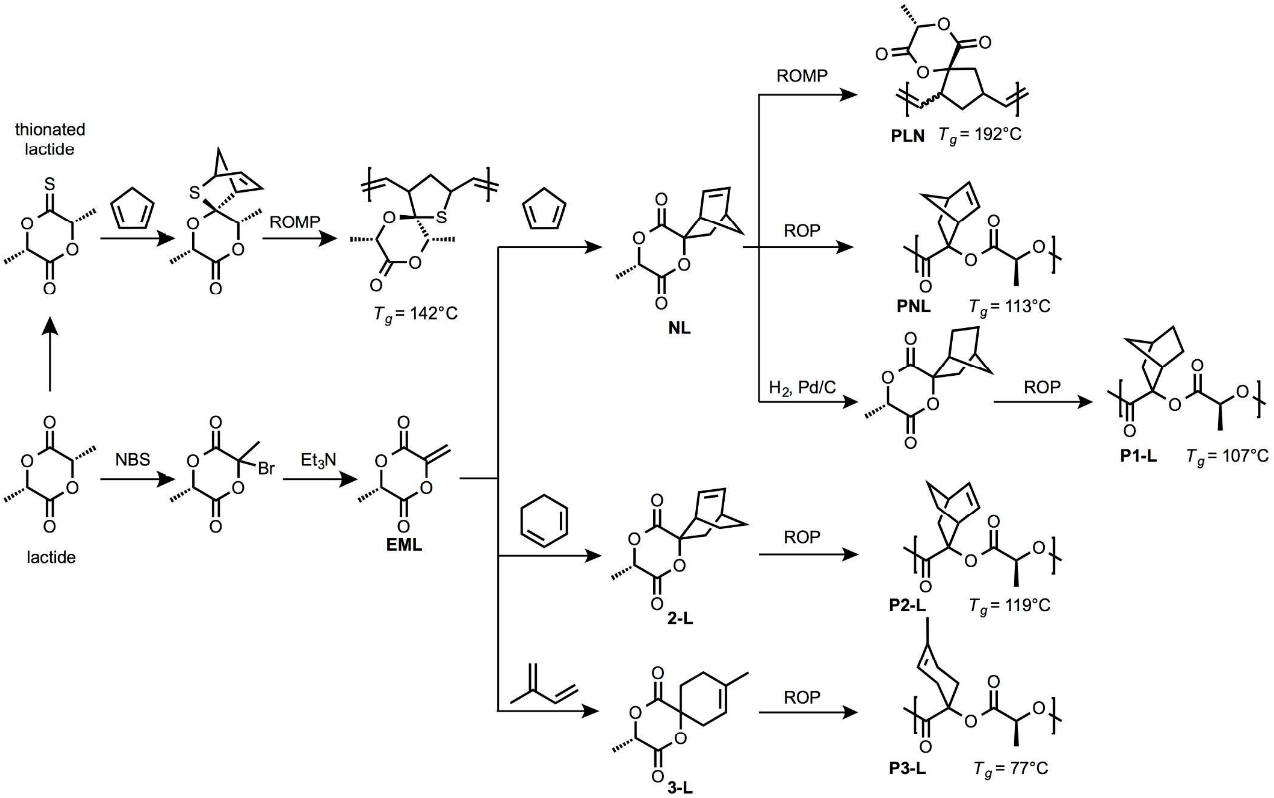
Scheme 1 Two approaches for synthesizing substituted glycolides and a series of substituted polyglycolides thereby obtained.[59,60]

Enlarging the H substituent of poly(glycolide) (**1**) to the methyl of PLA (**2**) increased conformational barriers, but did not introduce much free volume; hence the T_g increased modestly. The change from methyl (**2**) to ethyl (**3**) did not increase conformational barriers, but did introduce added free volume, resulting in a substantial drop in T_g. The isopropyl group of **4** or benzyl group of **5** contribute offsetting effects of conformational restriction and added free volume and thus poly(isopropylglycolide) and poly(phenyllactide) have T_g values comparable to that of PLA. In contrast, the attachment of large, conformationally restricted groups such as phenyl (**7**) or cyclohexyl (**8**) did not introduce substantial free volume; hence, the conformational effect prevailed to considerably increase the observed T_g values. The methyl/R′ alternating polymers **9**–**12**, showed similar T_g trends, but note that the R′ group can dominate the methyl group to give a low (R′ = ethyl) or high (R′ = phenyl) T_g value. The variously substituted PLA analogues of Scheme 1 are generally not biogenic, but are useful for understanding the structure/T_g relationships possible for this class of polyester.

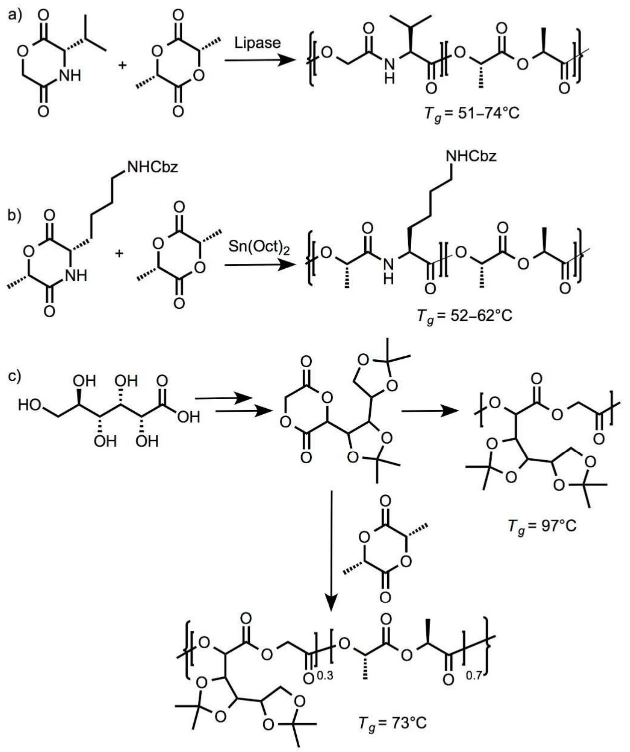
To expand the previous study of substituted lactide-type monomers, the Hillmyer Group exploited a versatile lactide vinylidene derivative made via bromination of its tertiary carbon followed by elimination.[61] Modification of this exomethylenelactide (**EML**) with different dienes via the Diels-

Alder reaction was then possible, as described in Scheme 2,[62,63] yielding a series of unsaturated, spirocyclic lactides. These derivatives possessed two polymerizable rings: the lactide and the bicyclic cyclohexene. The authors exemplified this dual capability with norbornene substituted lactide (**NL**), from which **PLN** and **PNL** were synthesized through ring-opening metathesis polymerization (ROMP), and ring-opening polymerization (ROP), respectively. High T_g values (192°C and 113°C) were detected with these sterically-conjested polymers. Substituent effects were readily studied. For example, a modest change of the T_g was detected by hydrogenating **NL** and then polymerizing to **P1-L** (107°C) or by expanding the bicyclic structure by one carbon atom (**P2-L**, 119°C). In contrast, the pendant monocyclic structure of **P3-L**, made by a Diels-Alder reaction of **EML** with isoprene, resulted in a considerably lower T_g (77°C). Related spirolactides have been reported by Pietrangelo, *et al.*[64] In this case, lactide was first converted to thionated lactide before Diels-Alder reaction of the C=S double bond with cyclopentadiene. The norbornene-type monomer was subjected to ROMP, yielding a polymer reminiscent of polymer **PLN**, but with a lower T_g value of 142 °C (Scheme 2).

Partial amide analogues of PLA have been prepared from naturally abundant amino acids, which were converted to functionalized morpholine-2,5-diones via different approaches, as outlined in Scheme 3.[65,66] Ring-opening copolymerization of these monomers with lactide yielded poly(ester amides) (PEA) with a variable degree of amide functionality. Amino acids with multiple methylene groups generally conferred low T_g values because of their plasticizing effect. Scheme 3 depicts two polymers with T_g values as high as 74 °C for valine or 62 °C for lysine (carboxybenzyl-protected).[67,68] In both cases, the T_g value was maximized by using zero lactide comonomer. Scheme 3 also illustrates PLA-type polymers bearing bulky, cyclic ketal pendent groups derived from biobased D-gluconic acid.[69,70] Apparently, this polymer substituent substantially impedes conformational mobility and thereby increases the T_g to 97°C. The copolymer containing 70% lactide shows a lower T_g of 73°C.



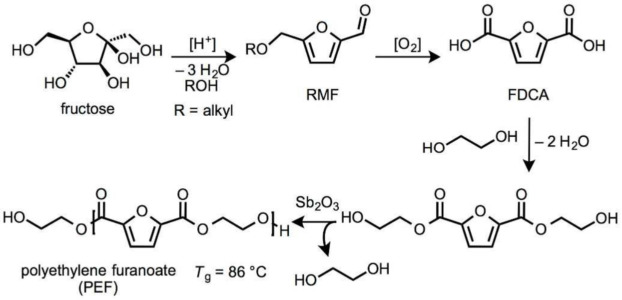
Scheme 2 Synthesis of various spirolactides via the Diels-Alder reaction of exomethylenelactide (**EML**), and polymers therefrom.[62,63] Thionated lactide has also been converted to a spirolactide and subsequently polymerized.[64]



Scheme 3 a) Synthesis of a valine-based poly(ester amide).[67] b) Synthesis of carboxybenzyl-protected lysine-based poly(ester amide).[68] c) Synthesis of PLA-type polymers with bulky, cyclic ketal pendent groups derived from D-gluconic acid.[69,70]

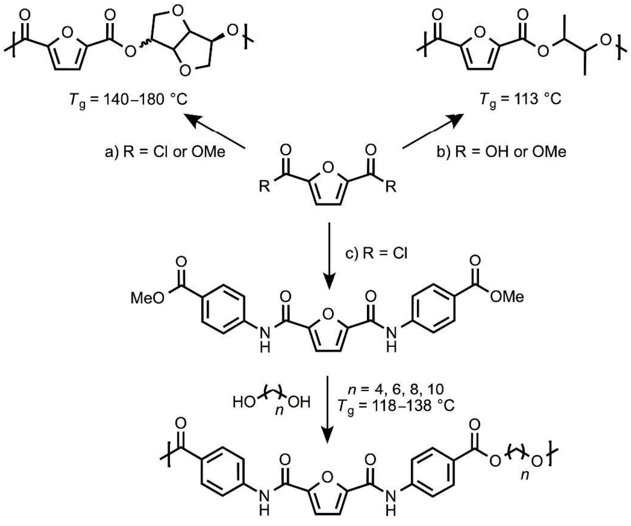
2.3. Polyethylene furanoate (PEF)

Considerable attention has recently been focused on polyethylene furanoate (PEF), a polyester derived from biobased hydroxymethylfurfural (HMF). In 2010, Avantium began commercialization efforts to apply PEF to various applications including films, fibers, and packaging bottles.[71] In 2015, Avantium opened an operational pilot plant for PEF production with capacity up to 50 kilotons/year and aims to have a full-scale industrial plant in 2017-2018 with 300-500 kilotons/year in Geleen, The Netherlands.[72] PEF is advertised to possess better thermal properties and outstanding barrier properties compared to those of PET. The T_g of PEF is higher by over 10 °C (86 °C *vs.* 74 °C) and its lower T_m (235 °C *vs.* 265 °C) results in more facile processability. Its barrier to oxygen, carbon dioxide, and water excelled that of PET by ten times, four times, and two times, respectively.[24] PEF is commercially produced in 3 steps from industrial sugars: 1) catalytic dehydration of fructose in alcohol solvent to form alkoxy-methylfurfural (RMF); 2) catalytic oxidation in acetic acid to generate furandicarboxylic acid (FDCA); and 3) catalytic polymerization in the presence of ethylene glycol (EG) to form, initially, bis(hydroxyethyl)-2,5-furandicarboxylate, followed by transesterification polymerization to obtain PEF (Scheme 4).[73] Avantium also showed that PEF can be recycled by blending with PET because it did not substantially affect the mechanical or physical properties of PET.[24] Because of the commercial prospects of PEF, several reviews are available detailing the history of PEF, how FDCA is obtained, and related, low-T_g furan-based polymers.[36,71] Herein, we only highlight furan-based polymers with T_g values surpassing 100 °C.



Scheme 4 Synthetic route of polyethylene furanoate (PEF).[73]

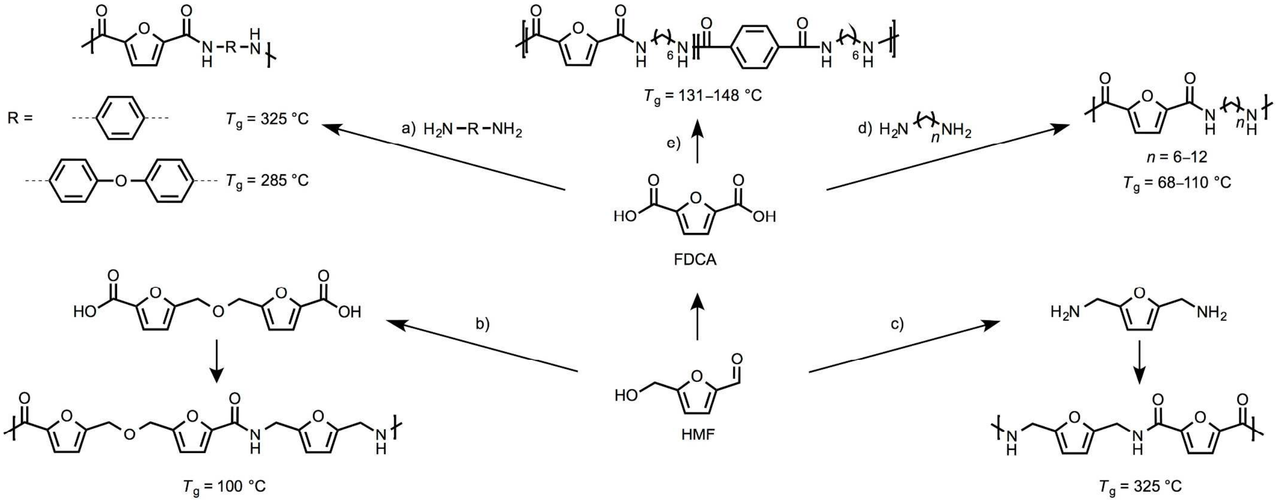
In 2009, Gandini *et al.*[74] claimed to produce a thermally stable polymer from D-isosorbide and furandicarbonyl dichloride which displayed a very high T_g of 180 °C. Polymerization procedures, molecular weight analyses, and NMR data were reported later in 2011.[75] The authors also made the analogous polyester with isoidide, a stereoisomer of isosorbide, which gave a relatively high T_g of 140 °C (Scheme 5a). Jasinska-Walc *et al.*[76] optimized the melt polycondensation of 2,5-furandicarboxylic acid or dimethylfurandicarboxylate and 2,3-butanediol using various catalysts (Scheme 5b). The best catalyst, Sn(Oct)$_2$, was loaded twice during the reaction. The best conditions generated a fully amorphous polymer with a T_g of 113 °C and a molecular weight of 13,000 Da.



Scheme 5 Polyesters based on furan with high T_g values.[74-77]

Rastogi and coworkers[77] studied the influence of the 2,5-furandicarboxamide moiety on hydrogen bonding in aliphatic/aromatic poly(ester amide)s. The polymer was synthesized from 2,5-furandicarboxamide dimethyl ester and linear diols. The dimethyl ester monomer was obtained from FDCA dichloride and methyl 4-aminobenzoate. In comparison with poly(ester amide)s containing other aromatic ring systems such as terephthalic, thiophene, and isophthalic moieties, polymers with the furan moiety gave the highest T_g values (118–138 °C) and molecular weights, but the lowest melting temperatures (Scheme 5c).

Linear aliphatic polyamides from HMF derivatives, such as furandicarboxylic acid, have been studied since 1961.[78,79] Many authors have since investigated similar materials,[71] notably Mitiakoudis and Gandini. In 1985, they combined FDCA with several aromatic diamines to obtain polymers with high T_g values ranging from 285 to 325 °C (Scheme 6a).[80] In 1991, they reported additional analysis of those polymers, as well as fully furanic polymers prepared from FDCA or its dimer and a diamine derived from HMF. The resulting semi-crystalline polymers exhibited a T_g value of 100 °C for the poly(ether amide) (Scheme 6b) and 325 °C for the pure polyamide (Scheme 6c).[81] Recently Fehrenbacher, *et al.*[82] utilized linear diamines with 6 to 12 methylene carbons and obtained T_g values ranging from 68 to 110 °C, but low M_n values approaching 7,000 Da (Scheme 6d). Finally, Avantium and Solvay filed patents in 2014 reporting optimized protocols for synthesizing these polyamides, along with related copolymers.[83,84] The patent from Avantium focused on the polymer having a T_g of 136 °C from FDCA and hexamethylenediamine (HMDA) obtained through a prepolymerization technique.[83] In Solvay's patent, copolymers were synthesized using HMDA, FDCA diester, and varying amounts of terephthalic or isophthalic diesters, and were obtained with high T_g values ranging from 131 to 148 °C, some of which were semi-crystalline (Scheme 6e).[84] Many other polyamides have been prepared from FDCA, and Sousa, *et al.* have reviewed these recently.[71]



Scheme 6 Polyamides based on furan.[80-84]

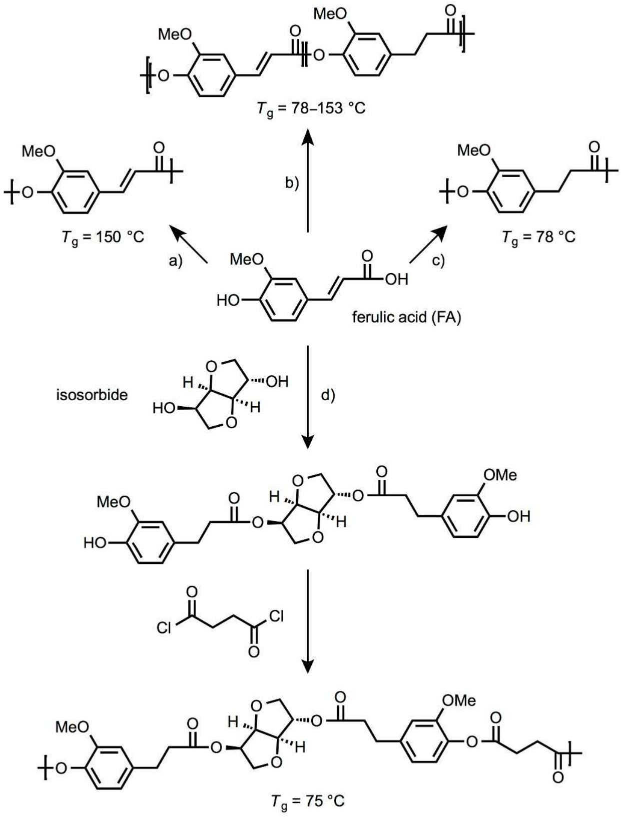
3. Aromatic biopolymers

One general strategy for creating high glass transition temperature polymers is to incorporate a considerable fraction of "hard" segments into the polymer backbone. Such hard segments can have high conformational barriers and/or strong intra- or interchain interactions through polar (*e.g.*, dipolar, quadrupolar) associations. Compared to aliphatic segments, aromatics usually impose high conformational barriers and strong polar associations (*e.g.*, pi-pi stacking). Thus, the pursuit of high glass transition temperature bioplastics has often exploited lignin, the richest resource of biorenewable aromatics and the second most abundant organic polymer on earth after cellulose.[85] Several hydroxyacids, including vanillic acid, syringic acid, and 4-hydroxybenzoic acid, can be produced directly or indirectly from lignin.[86] The respective hydroxyaldehydes (vanillin, syringaldehyde, and 4-hydroxybenzaldehyde) can also be obtained. Other miscellaneous molecules, including sinapic alcohol and creosol, can also be harvested via the chemical treatment of lignin. Meanwhile, extraction of lignocellulose generates ferulic acid, coumaric acid, and caffeic acid.[87,88] Another source of bioaromatic compounds is amino acids, particularly tyrosine.[89,90] Finally, an underutilized strategy for obtaining bioaromatics is biochemical synthesis. Two examples are 4-hydroxyphenyllactic acid and 4-aminocinnamic acid, obtained from genetically engineered *Corynebacterium Glutamicum*[91] and *Escherichia Coli*,[92] respectively. Polymers which either have a relatively low T_g or low biochemical constitution will not be covered in this review, but have been aptly described elsewhere.[35,36,38,71,93]

3.1. Polyesters

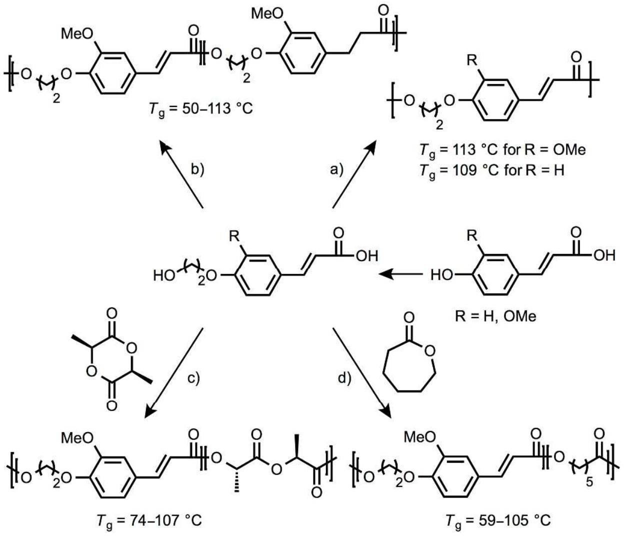
a) Ferulic acid and coumaric acid based polymers

Ferulic acid (FA) and coumaric acid (CA) are the two most abundant compounds within the hydroxycinnamic acid family.[87,88] Many polymer scientists have worked with these compounds. In 1980, a patent reported polyferulic acid (PFA) as an intractable polymer with a very high T_g of 150 °C and a T_m of 325 °C (Scheme 7a).[94] After reducing two sp^2 hybridized carbons of ferulic acid, our group produced a new polymer, poly(dihydroferulic acid) (PHFA), which exhibited better solubility and a T_g (73 °C) that slightly excelled that of PET (67 °C) (Scheme 7c).[95] Nonetheless, PHFA showed a substantially lower T_m (234 °C) than PET (265 °C). By copolymerizing acetyl ferulic acid with its hydrogenated analogue, rational control of the T_g was possible (Scheme 7b).[96] As the feed percentage of the unsaturated monomer increased by decades, the T_g increased steadily from 78 to 153 °C. Copolymers were obtained in good yields (73 to 87%) and with acceptable molecular weights, with half of the M_n values exceeding 15,000 Da. Allais *et al.*[97] synthesized bis-*O*-dihydroferuloyl isosorbide from ethyl dihydroferulate, enzymatically catalysed by *Lacasse*. The polymer obtained from this bisphenol and succinyl chloride showed a high T_g of 75 °C, comparable to that of PET but with a moderate M_n of 7,500 Da (Scheme 7d). The best molecular weight results were obtained in bulk monomer or when the monomer concentration remained high in solvent polymerization.



Scheme 7 Copolymers based on ferulic acid.[94-97]

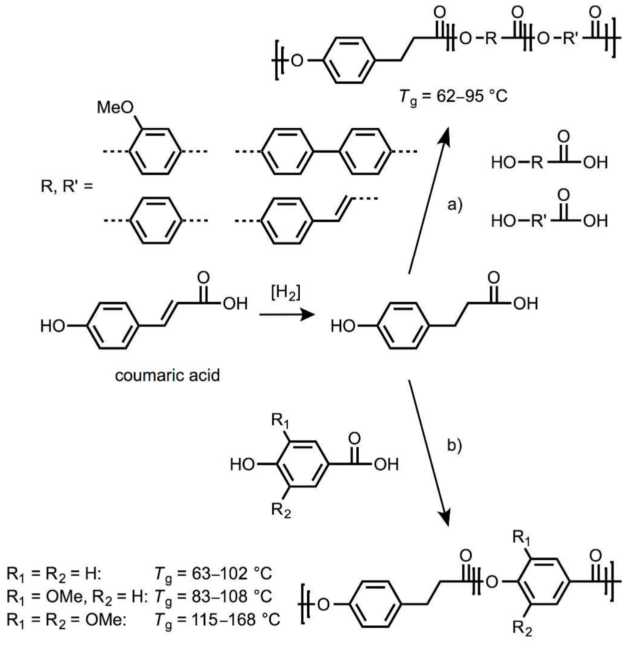
Reducing the double bond of ferulic acid by hydrogenation proved a viable strategy for improving polymer tractability and solubility. A related approach was conducted by installing a flexible aliphatic segment outside of the ferulic acid or coumaric acid unit. Thus, α,ω-chloroalcohols were appended to the alcohol end of FA or CA. With chloroethanol (2 methylene spacers), polyethylene ferulate (R = OMe) and polyethylene coumarate (R = H) were synthesized and exhibited high T_g values of 113 °C and 109 °C, respectively (Scheme 8a).[98] Longer chloroalcohols resulted in lower T_g values. The copolymer series from hydroxyethylferulic acid and hydroxyethyldihydroferulic acid yielded a well-behaved glass transition temperature trend from 32 to 113 °C as the double bond content of the polymer increased (Scheme 8b).



Scheme 8 Polymers based on hydroxyethyl ferulic acid (R = OMe) and hydroxyethyl coumaric acid (R = H).[98,99]

Separately, our group sought to increase the T_g of PLA and polycaprolactone (PCL) by copolymerizing L-lactide or ε-caprolactone with hydroxyacid bioaromatics such as hydroxyethylferulic acid, hydroxyethylcoumaric acid, hydroxyethylvanillic acid, and hydroxyethylsyringic acid. A generalized and efficient one-pot ring opening polymerization (ROP)/polycondensation methodology in the melt between L-lactide or ε-caprolactone and hydroxyacid bioaromatics was demonstrated (Scheme 8c and 8d, respectively).[99] Although ROP is initially faster than polycondensation, NMR confirmed that random copolymers were ultimately obtained, likely via transesterification reactions. The incorporation of aromatics significantly improved the thermal stability of PLA from 207 to 323 °C and T_g values were increased from 50 °C up to 107 °C, albeit at high levels of aromatic incorporation. In addition to improving the T_g of polycaprolactone (PCL) drastically from –60 °C up to 105 °C, this method boosted the biobased content since caprolactone is a petroleum-based monomer. These thermal properties suggest that PLA and PCL polymers with substantial bioaromatic content are well-suited for higher temperature applications. Furthermore, the successful synthesis of random copolymers of caprolactone or lactide with hydroxy-acid bioaromatics indicates the reaction scope could extend to other ROP/polycondensation systems.

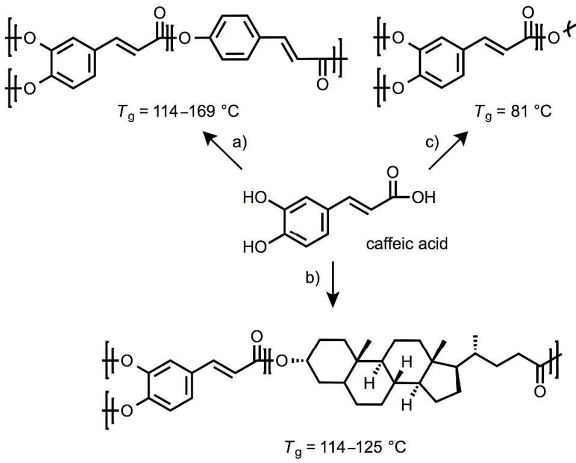
In 1997, Kricheldorf and Stukenbrock[100] described copolymers and terpolymers prepared by polycondensation of trimethylsilylester/acetylated dihydrocoumaric acid with trimethylsilylester/acetylated 4-hydroxybenzoic acid, vanillic acid, or 4'-hydroxybiphenyl-4-carboxylic acid (Scheme 9a). High glass transition temperatures from 62 to 95 °C were found, but molecular weights were not reported. Most of the polymers are thermotropic liquid crystals. Then in 2000, Nagata[101] resynthesized the copolyesters containing dihydrocoumaric acid, hydroxybenzoic acid, and vanillic acid by a direct polycondensation method in pyridine using diphenyl chlorophosphate and lithium bromide as condensation agents. These polymers exhibited T_g values comparable to those of Kricheldorf. Additionally, these copolymers were generated in various monomer ratios and a new copolymer series from syringic acid ($R_1 = R_2 = OMe$) was synthesized (Scheme 9b). The syringic acid comonomer expanded the T_g range considerably upward: 63 to 168 °C. Measured molecular weights were moderate with broad dispersity (*Đ*) values up to 4.0.



Scheme 9 Copolymers based on dihydrocoumaric acid.[100,101]

b) Caffeic acid based polymers

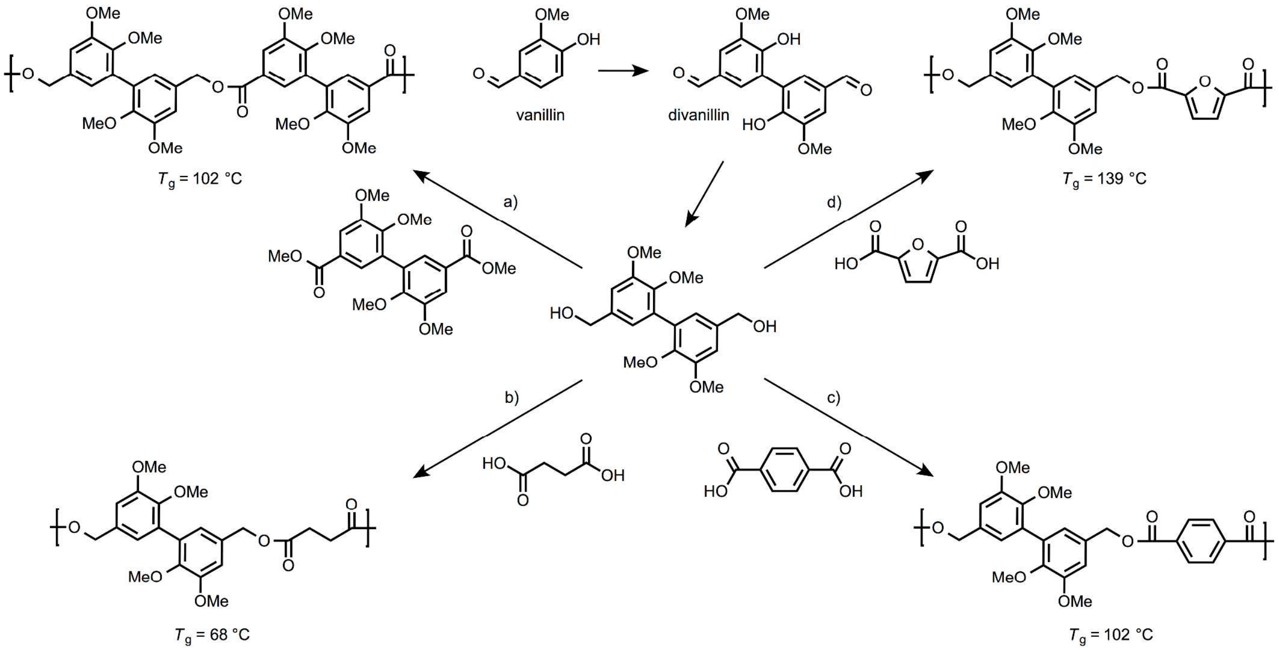
In 2006, the Kaneko Group reported a copolymer series made from caffeic acid and coumaric acid with various monomer feed ratios (Scheme 10a). Polymerization was conducted in the presence of acetic anhydride and sodium acetate with mechanical stirring at 200 °C.[102] The whole polymer series exhibited higher molecular weights and better mechanical performance values compared to those of PHB, PCL, PLA, and PC. Higher glass transition temperatures were also found, ranging from 114 to 169 °C. After photochemical crosslinking with UV irradiation, the mechanical properties improved significantly and the degradation rates accelerated up to 4 times faster depending on the copolymer ratio. More recently, Chen, Gijsman, and coworkers described the copolymerization between caffeic acid and lithocholic acid (a bile acid)[103] or 10-hydroxydecanoic acid derived from castor oil[104] in different molar ratios using the same procedure as Kaneko described. The incorporation of lithocholic acid diminished the T_g range (114 to 125 °C), but it enhanced the solubility and thermal stability of the copolymers and allowed for higher fluorescence emission intensity, but slowed the degradation rate (Scheme 10b). For the 10-hydroxydecanoic acid copolymer series, only the copolymer with 25 mol% of this monomer exhibited a relatively high T_g (81 °C), but this material suffered from a high degree of brittleness (Scheme 10c).



Scheme 10 Copolymers based on caffeic acid.[102-104]

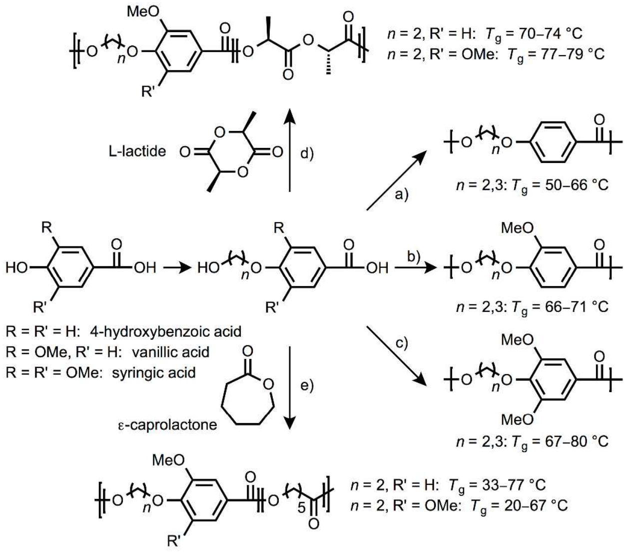
c) Vanillic acid, syringic acid, and 4-hydroxybenzoic acid based polymers

Cramail *et al.*[105] have utilized laccase from *Trametes versicolor* to oxidatively dimerize vanillin to a compound termed divanillin. In turn, this dialdehyde can be modified to other polymerizable monomers. For example, a diol variant was copolymerized with a variety of diacids, with 0.5 mol% $Ti(OBu)_4$ as catalyst (Scheme 11).[106] These polymers possessed a low storage modulus (1.3 to 2.0 GPa) and their intractability generally precluded molecular weight determination. Nonetheless, copolymers with terephthalic acid, furandicarboxylic acid, or an oxidized divanillin diacid exhibited high T_g values in the range of 102 to 139 °C. The copolymer with succinic acid showed a lower T_g value of 68 °C.



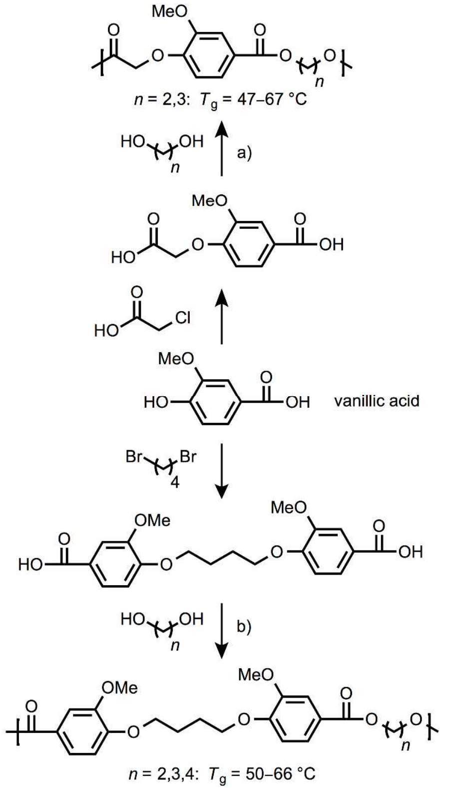
Scheme 11 Copolymers based on divanillin, an oxidized dimer of vanillin.[106]

In 2011, our group reported that monomers for polyalkylene 4-hydroxybenzoates (Scheme 12a), polyalkylene vanillates (Scheme 12b), and polyalkylene syringates (Scheme 12c) could be prepared from 4-hydroxybenzoic acid, vanillic acid, and syringic acid, respectively, via alkylation with α,ω-chloroalcohols of varying lengths.[107] A clear structure/property relationship impacted the glass transition temperature: more methylene groups in the original α,ω-chloroalcohols translated into lower T_g values. Understandably, as the aromatic component was diluted with low conformational barrier polyethylene segments, the measured T_g decreased. Most polymers in this class exhibited T_g values from 50 to 80 °C and aromatic methoxy groups generally increased T_g, likely because of greater conformational barriers. Hydroxyethylvanillic acid and hydroxyethylsyringic acid were also copolymerized with lactide (Scheme 12d) and caprolactone (Scheme 12e) through the aforementioned ROP/polycondensation route (see Scheme 8c and 8d).[99] The inherent T_g of PLA (~55 °C) and of polycaprolactone (–60 °C) could be improved to ranges of 70—79 °C and 33—77 °C, respectively, albeit with considerable (50–90 mol%) bioaromatic content required.



Scheme 12 Polymers derived from 4-hydroxybenzoic acid, vanillic acid, and syringic acid.[99,107]

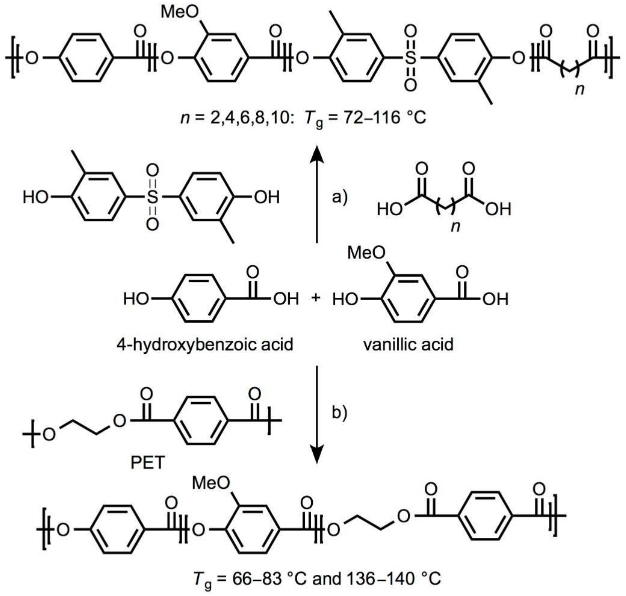
Wu, Ma, and coworkers[108] synthesized two series of poly(ether-ester)s from diols and an unsymmetrical or symmetrical diacid made from vanillic acid. As expected, short diol comonomers resulted in the highest glass transition temperatures. The polymer from the unsymmetrical diacid (Scheme 13a) showed a T_g of 47—67 °C when ethylene glycol or 1,3-propandiol were used. The polymer from the symmetrical diacid (Scheme 13b) showed a T_g of 50—66 °C when ethylene glycol, 1,3-propandiol, or 1,4-butanediol were used. These poly(ether-ester)s showed excellent mechanical properties.



Scheme 13 Copolymers derived from vanillic acid and diols.[108]

Vanillic acid and hydroxybenzoic acid have been used as essential components of liquid crystalline copolymers. Montes de Oca *et al.*[109] showed that thermotropic terpolymers can be obtained from hydroxybenzoic acid, vanillic acid, 4,4'-sulfonyl bis(2-methylphenol), and various aliphatic acids via solution polycondensation (Scheme 14a). These polymers exhibited high T_g values ranging from 72 to 116 °C and good mechanical properties. Furthermore, their degradation rate was less temperature sensitive than lactide/glycolide copolyesters and their biological response was similar to that of PGA. On the same aromatic-aliphatic liquid crystalline polymers series (Scheme 14a), Ries, Montes de Oca, and coworkers performed deeper studies on the phase behaviour, morphology, molecular relaxation behaviour, and modelling of mechanical properties.[110,111] The results concluded that these polymers could potentially be employed in future medical devices.

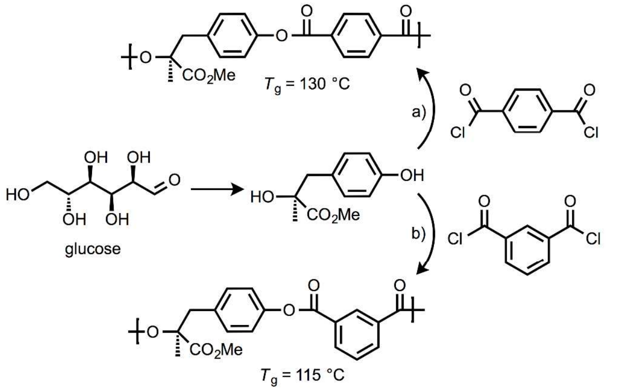
Li *et al.*[112] were successful in terpolymerizing acetylvanillic acid, 4-acetoxybenzoic acid, and polyethylene terephthalate (PET) in the melt at various feed ratios (Scheme 14b). The glass transition temperature of these copolymers was interrogated by three experimental techniques: differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermomechanical analyses (TMA). These results were compared to values predicted by theoretical equations, including the Uematsu, the Johnston, and the Couchman equations. The polymers exhibited two distinct glass transitions; the lower T_g near 66–83 °C, was attributed to the polyethylene terephthalate rich phase; and the higher T_g near 136–140 °C, was assigned to the 4-acetoxybenzoic acid rich phase. This study showed that both Uematsu and Johnston equations were able to predict the T_g values of these terpolymers precisely.



Scheme 14 Terpolymers from 4-hydroxybenzoic acid and vanillic acid.[109-112]

d) Building blocks from glucose

In addition to lignin and lignocellulose, biorenewable monomers expected yield a high polymeric T_g can be obtained from carbohydrates. For example, 4-hydroxyphenyllactic acid was synthesized through a microbial fermentation process of glucose by Kaneko and coworkers.[91] The methyl ester was subjected to polymerization with terephthaloyl chloride (Scheme 15a) or isophthaloyl chloride (Scheme 15b) under reflux in a solution of THF and DMAc. The resulting polymers exhibited high optical transparency and high T_g values of 130 and 115 °C, respectively. The fibers of the terephthaloyl polymer showed the higher Young's modulus of 14.46 MPa, but the degradation rate of this polymer was slower than that of PLA. For comparison, copolymerization of the methyl ester with aliphatic diacid chlorides $Cl(CO)(CH_2)_n(CO)Cl$ afforded polymers of low T_g (0–45 °C for n = 8–2).



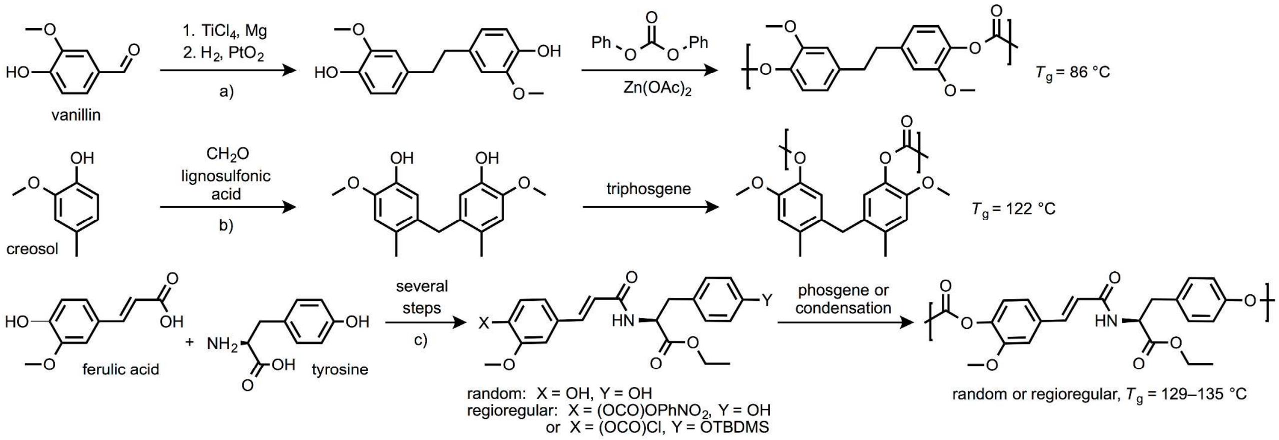
Scheme 15 Polymers with aromatic content derived from glucose.[91]

3.2. Polycarbonates

Biobased polycarbonates are often synthesized from bisphenol molecules with the objective of replacing harmful bisphenol A along with phosgene,[113,114] the usual monomers for the preparation of commodity polycarbonate (PC), which has a T_g of 147°C.[115] Harvey *et al.* utilized vanillin to synthesize a stilbene type bisphenol via a McMurry coupling (using $TiCl_4$/Mg).[116] The substituted stilbene was hydrogenated and then polymerized via transesterification with diphenyl carbonate (Scheme 16a). The obtained polymer had a relatively low M_n of 3,600 and $Đ$ of 1.9 by GPC, but an encouraging T_g value of 86 °C and T_{95} of 290 °C.

Xie and coworkers condensed the less exploited but renewable creosol (Scheme 16b) with formaldehyde, catalyzed by lignosulfonic acid, a byproduct of the paper production industry.[117] This reaction yielded bisphenols, the regiodistribution of which the authors studied by NMR to conclude that the illustrated *para-para'* regioisomer was the major product. This bisphenol was reacted with triphosgene to yield a crystalline polycarbonate with a T_g value of 122 °C, a high T_m of 314 °C, and a molecular weight of 46,800 Da determined by viscometry.

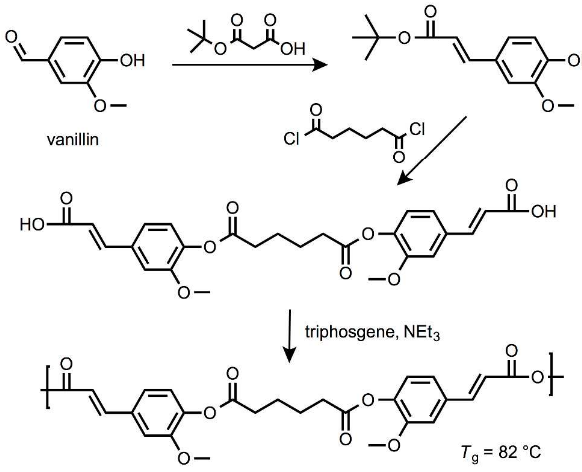
Wooley and co-workers designed a poly(carbonate-amide) system by synthesizing different monomers from ferulic acid and tyrosine.[89] These monomers were essentially asymmetric bisphenols, which were then converted to polycarbonates. The authors prepared four different monomers, yielding head-to-head, tail-to-tail, and head-to-tail regioregular polymers, along with a regiorandom polymer (Scheme 16c). Thermal properties of the polymers were not considerably perturbed by the regioregularity. High T_g values ranged from 129 to 135 °C, high thermal degradation temperatures ranged from 337 to 350 °C, and M_n molecular weights ranged from 5,800 to 18,600 Da. Further studies on the hydrolytic degradation of the regiorandom polymer showed that the carbonate links degraded moderately within a month under harsh conditions of 70 °C and pH 12.[118]



Scheme 16 Polycarbonates obtained from a) vanillin via McMurry coupling, hydrogenation, and transesterification with phenyl carbonate;[116] b) creosol, following condensation with formaldehyde and polymerization with triphosgene;[117] and c) ferulic acid and tyrosine after coupling by amidation to yield regiorandom or regioregular polymers.[89]

3.3. Polyanhydrides

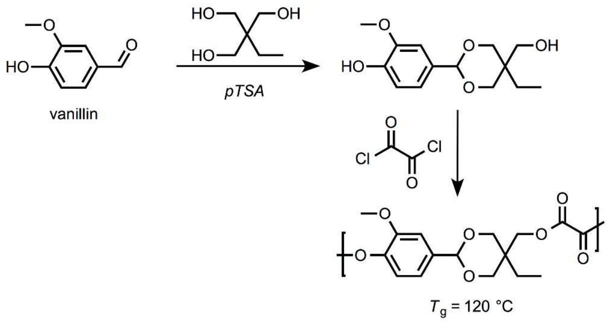
Polyanhydrides are attractive systems because of their facile hydrolytic degradation, which requires water but no extreme pH concentration. As described in Scheme 17, vanillin was used to synthesize a polyesteranhydride.[119] A Knoevenagel reaction was applied to vanillin, yielding *tert*-butylferulate, which was subsequently transformed into a diacid by reaction with adipoyl chloride. A polyesteranhydride was synthesized by condensing the obtained diacid with triphosgene. The polymer showed good properties, including a T_g of 82 °C, thermal degradation at 332 °C, a molecular weight (M_n) of 21,700, and a $Đ$ of 1.7. The polyanhydride was found to partially degrade hydrolytically within 30 days in phosphate-buffer saline (neutral pH conditions), releasing free ferulic acid.



Scheme 17 Vanillin is transformed into *tert*-butylferulate and esterified with adipoyl chloride. Further condensation with triphosgene yields a polyesteranhydride.[119]

3.4. Polyoxalates

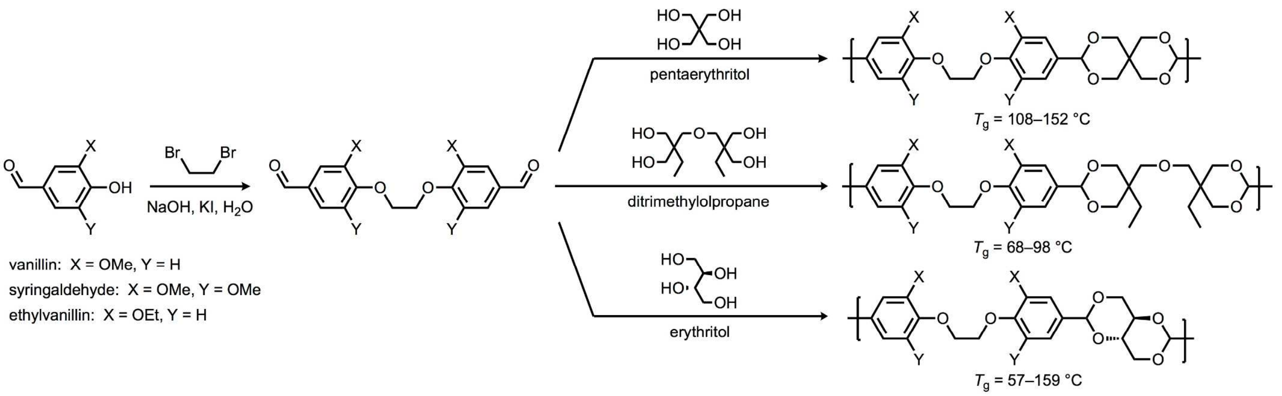
Polyoxalates are a special type of polyester with two directly adjoined ester functional groups. The proximity of one carbonyl group enhances the electrophilicity of the other, allowing for facile hydrolysis, even with humid air.[120] Kwon *et al.* reacted vanillin with trimethylolpropane (TMP) to yield an acetal diol, which was then polymerized with oxalyl chloride (Scheme 18).[121] The obtained polyoxalate showed a high T_g value of 120 °C, a good M_n of 13,800 Da, and a $Đ$ of 1.6. The polymer was found to hydrolyze easily under acidic (pH 5.5) or neutral conditions, releasing vanillin within 36 hours.



Scheme 18 An acetal diol from vanillin is copolymerized with oxalyl chloride to yield a regiorandom polyoxalate that is rather susceptible to hydrolytic degradation.[121]

3.5. Polyacetals

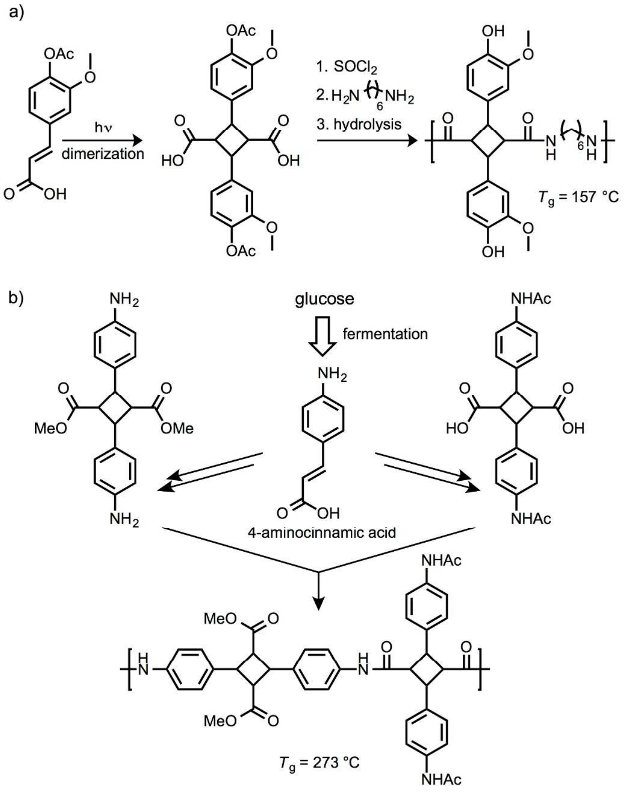
Polyacetals have been explored in our group for a variety of reasons, including the relative dearth of the acetal functional group among commercial polymers, the facile hydrolysis generally enjoyed by acetal groups, and the abundance of this functional group in biology. It is Nature's favorite polymer linking group since it is responsible for connecting the glucose units of Nature's most abundant polymer, cellulose. In recent work, dialdehyde monomers were synthesized from bioaromatics (vanillin, syringaldehyde) or a synthetic aromatic (ethyl vanillin) by a double Williamson ether synthesis with dibromoethane.[122] These monomers were copolymerized with tetraols (pentaerythritol and ditrimethylolpropane) utilizing a drying agent to capture the water formed in the condensation reaction (Scheme 19). The obtained polymers possessed cyclic or spirocyclic structures which, along with the aromatic rings, conferred adequate thermal properties to the polymers. The resulting amorphous materials showed T_g values ranging from 68 to 152 °C; the maximum value was observed with the syringaldehyde monomer combined with pentaerythritol. Number average molecular weight (M_n) values ranged from 10,600 to 22,200 Da and T_{95} was found above 300 °C in all cases, indicating good thermal stability. The polymers were also shown to hydrolyze easily in acidic dimethyl sulfoxide over the course of 48 hours. Two of the dialdehydes (from vanillin and syringaldehyde) were reacted under similar conditions with erythritol, a biogenic molecule derived from glucose, to afford two new polyacetal ethers.[123] Because of its lower reactivity, erythritol was copolymerized with the aforementioned (and more reactive) pentaerythritol and ditrimethylolpropane to provide four new series of polyacetals with tunable thermal properties. According to the choice of monomers and feed ratios, T_g values in the range of 57 to 159 °C can be selected. Molecular weight M_n values ranged from 1,400 to 21,700 Da. Short term and long term heterogeneous degradation studies showed the susceptibility of the acetal linkages to hydrolysis in acidic media.



Scheme 19 Polyacetals from the polyacetalization of lignin-derived aromatic aldehydes (vanillin, syringaldehyde, or synthetic ethylvanilin) and tetraols (pentaerythritol, ditrimethylolpropane, and erythritol).[122,123]

3.6. Polyamides

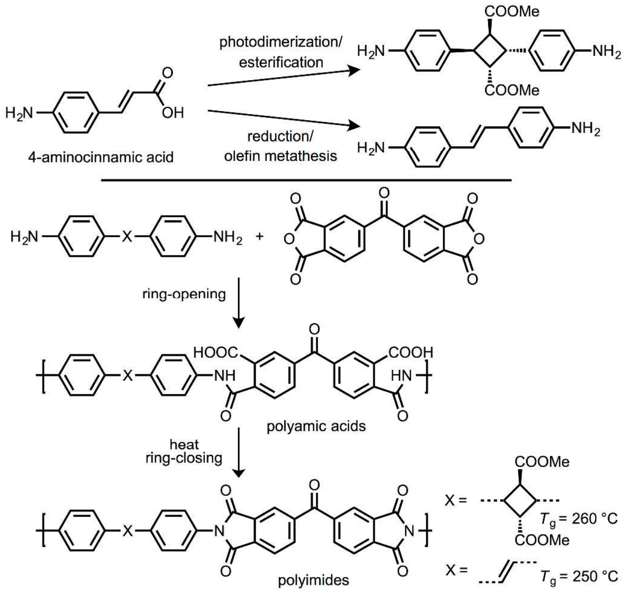
Hasegawa *et al.* acetylated ferulic acid and then conducted a [2+2] photo-dimerization with UV irradiation to procure a diacid monomer containing a cyclobutane ring.[124] Two different methods were used to generate a polyamide with hexamethylene diamine comonomer. The first method yielded a crosslinked polyester structure with the ferulic acid dimer by elimination of acetic acid, followed by amidation of the remaining carboxylic acid groups with hexamethylene diamine. The second method transformed the diacid dimer into the diacid chloride and then reacted that with hexamethylene diamine in a classic interfacial, linear polymerization (Scheme 20a). Both polymers exhibited high T_g values. The T_g for the crosslinked polyester amide was 151 °C and that for the linear polyamide was 157 °C. A related polymeric structure was later achieved by Takaya, Kaneko, *et al.*,[125] who developed a method to harvest the exotic 4-aminocinnamic acid (4ACA) from recombinant *E. coli* by fermentation of glucose. Divergent synthesis from 4ACA yielded the diamine and truxillic acid derivatives depicted in Scheme 20b. Polymerization of these yielded a conformationally rigid polyamide with M_n of 10,000, M_w of 21,000, and a T_g of 273 °C. This high T_g value could be attenuated by copolymerization with various flexible, linear diacids.



Scheme 20 a) Photo-dimerization of acetylferulic acid afforded a diacid that was polymerized with hexamethylene diamine to afford a polyamide.[124] b) Photo-dimerization of glucose-derived 4-aminocinnamic acid gave diamine or diacid monomers, which also could be polymerized to polyamides.[125]

3.7. Polyimides

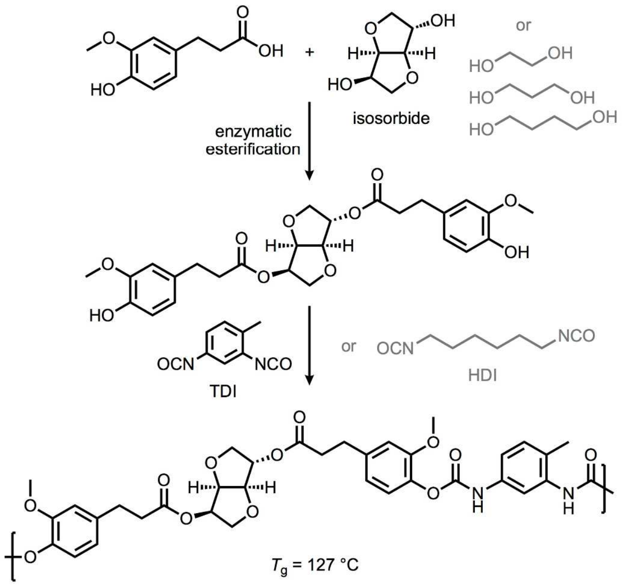
The field of sustainable, high-T_g polyimides has been explored by Kaneko and coworkers. Their group has exploited the aforementioned 4-aminocinnamic acid (4ACA), fermented from glucose. In 2014, 4ACA was photo-dimerized and then esterified to yield a diamine containing a cyclobutane ring.[92] Then, in 2016, another diamine was prepared by reducing the acid group on 4ACA to yield an allyl alcohol, followed by olefin metathesis with Grubbs' catalyst, generating a 4,4'-disubstituted stilbene.[126] Both monomers were combined with a series of cyclic dianhydrides, initially forming polyamic acids (PAAs) by ring-opening and then polyimides (PIs) after ring-closing, effected by heating (Scheme 21). With the photodimer system, the authors reported that all the PAAs had very high number average molecular weights above 100,000 Da. The insolubility of the eventual polyimides precluded their molecular weight analysis, but they exhibited excellent thermal properties with T_{95} above 350 °C in all cases, and T_g values ranging from 240–275 °C, where detectable. Some T_g values were suspected to be above the decomposition temperature, and therefore not measureable. The diaminostilbene monomer could be used directly or after alkene hydrogenation. The formed PAAs also showed very high M_n values—in all cases above 100,000 Da. The subsequently formed polyimides were very heat-resistant, with T_{95} values above 400 °C in all cases. Only two samples showed detectable glass transitions, both with the stilbene diamine: 250 °C for the stilbene polyimide shown in Scheme 21 and 330 °C for the stilbene polyimide from pyromellitic dianhydride. Similar to the polyimides reported in 2014, many of these polymers apparently degraded before their glass transition. Finally, all samples exhibited excellent mechanical properties.[126]



Scheme 21 4-aminocinnamic acid (4ACA) can be converted to diamine monomers by photochemical dimerization/esterification,[92] or by reduction/olefin metathesis.[126] These yield polyimides upon copolymerization with dianhydrides.

3.8. Polyurethanes

Allais and coworkers employed ferulic acid to prepare polyurethanes.[127] The unsaturated aromatic acid was hydrogenated and then condensed with diols (*e.g.*, ethylene glycol, 1,3-propanediol, 1,4-butanediol, and isosorbide) via enzymatic methods (*C. antarctica* lipase B) to yield bisphenol esters. These bisphenols were polymerized with commercially available hexamethylene diisocyanate (HDI) and toluene diisocyanate (TDI) in bulk or in methyl ethyl ketone (MEK) (Scheme 22). Polymers prepared in MEK as solvent had better properties, giving greater molecular weights (M_n up to 11,700 Da) and higher T_g and T_{95} values in comparison to bulk polymerizations. T_g values were invariably higher for TDI (62–127 °C) than for HDI (28–68 °C). For the diol impact on T_g, isosorbide clearly bested the linear diols: isosorbide/HDI ranged from 67—68 °C while linear diols/HDI ranged from 28—40 °C); and isosorbide/TDI ranged from 106—127 °C while linear diols/TDI ranged from 62—96 °C.

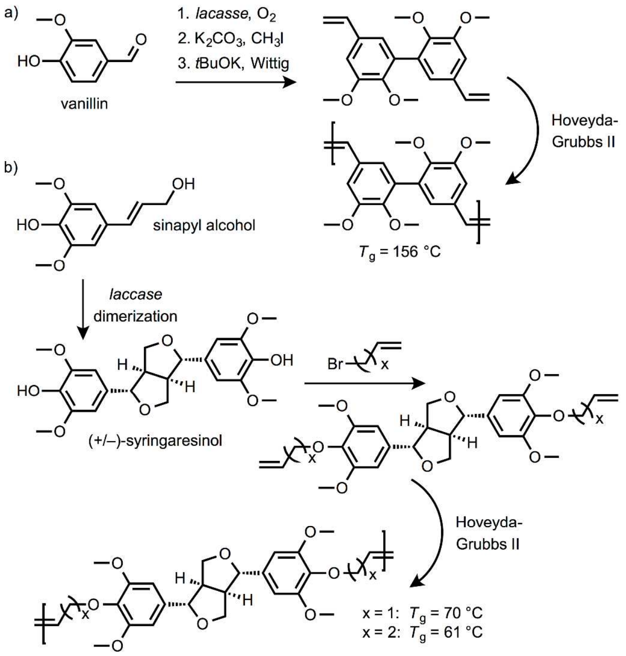


Scheme 22 Hydrogenated ferulic acid was enzymatically linked to diols (*e.g.*, isosorbide) yielding a bisphenol, which was then reacted with commercial diisocyanates (TDI or HDI) to generate polyurethanes.[127]

3.9. Polymers from ADMET methodology

The Acyclic Diene METathesis (ADMET) methodology is useful for preparing polymers from renewables that are first converted to dienes. For example, Cramail *et al.* prepared a biphenyl monomer by enzymatic oxidative coupling of vanillin with *lacasse*, followed by phenolic methylation, and finally a Wittig reaction, yielding an α,ω-diene.[128] Application of ADMET using several olefin metathesis catalysts was successful and the highest M_n of 40,000 Da ($Đ$ = 1.7) was found with a Hoveyda-Grubbs 2nd generation catalyst (Scheme 23a). The polymer exhibited excellent thermal properties with a T_g value of 156 °C and a T_{95} value of 380 °C. The authors rationalized the high T_g by the conjugated backbone of the polymer, as well as its all-trans configuration, confirmed by NMR analysis. ADMET polymers were also synthesized with the coupled biphenyl monomer from eugenol, but its T_g value of 54 °C did not excel that of PLA.

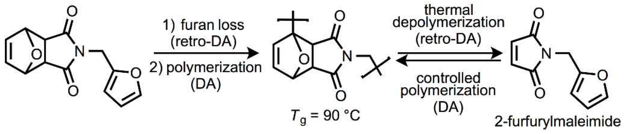
Separately, Allais *et al.* employed the relatively unexplored sinapyl alcohol.[129] The unsaturated molecule was dimerized with *laccase* from *Trametes versicolor* to give (+/–)-syringaresinol. The bisphenol was extended with bromoalkenes $Br(CH_2)_xCH=CH_2$ (x = 1, 2, 4, or 8) to yield an α,ω-diene. ADMET polymerization was carried out either in bulk or in dichloromethane (Scheme 23b). The obtained polymers had moderate molecular weights with M_n up to 14,100 Da. The highest T_g found was 70 °C for x = 1 (from allybromide). The T_g values invariably decreased with increasing x.



Scheme 23 a) A biphenyl diene, from enzymatic coupling of vanillin, is subjected to ADMET olefin polymerization.[128] b) Enzymatic dimerization of sinapyl alcohol results in racemic syringaresinol, which is then converted into dienes and polymerized via ADMET.[129]

3.10. Polymers from Diels-Alder methodology

Gandini *et al.* devised an elegant and simple polymer from 2-furfurylmaleimide.[130] Furfurylamine and the classical furan/maleic anhydride DA adduct were combined to yield the starting monomer of Scheme 24. Loss of furan (retro-Diels-Alder) followed by Diels-Alder polymerization yielded a prepolymer, which formed the monomer 2-furfurylmaleimide cleanly upon retro-Diels-Alder depolymerization. Controlled repolymerization via Diels-Alder chemistry afforded the desired polymer, which exhibited a T_g of 90 °C. NMR analysis showed a low M_n near 1800 Da and the polymer depolymerized readily near 110 °C, just above its T_g transition.



Scheme 24 Controlled Diels-Alder polymerization of 2-furfurylmaleimide and its facile retro-Diels-Alder depolymerization at higher temperature.[130]

4. Carbocyclic and heterocyclic biopolymers

4.1. Sugar-based polymers

The synthesis of polymers from sugars—one of the most abundant natural resources—has been of great importance in the biorenewable polymer field. A variety of building blocks originating from carbohydrates has been developed in the last few decades, significantly contributing to the library of biobased monomers, such as sugar alcohols and their derivatives, as well as other multifunctional products.[131] Since carbohydrate related polymers have been comprehensively reviewed,[131,132,133] we focus here specifically on biopolymers with high glass transition temperatures. High T_g values are more readily achieved when cyclic motifs are present within the polymer main-chain; such motifs limit conformational freedom.

a) Isohexides

Isohexides have been extensively investigated by polymer chemists because of their availability, structural rigidity, and non-toxicity. Polymers containing the conformationally rigid, bicyclic structure of isohexides are expected to possess practical thermal properties such as high glass transition temperature. The production of isohexides from sugars was first reported in the 1950s.[134,135,136] The general synthetic procedure started with the extraction and enzymatic processing of starch. The obtained hexose sugars were reduced and dehydrated to yield isohexides.[131,137,138] 1,4:3,6-dianhydro-D-glucitol (isosorbide), 1,4:3,6-dianhydro-D-mannitol (isomannide), and 1,4:3,6-dianhydro-L-iditol (isoidide) are the most common diastereomers in the isohexide family derived from D-sorbitol, D-mannitol, and L-iditol, respectively, and depicted in Figure 3.[139] These isohexides all present sterically hindered secondary alcohols and thus are less reactive than primary alcohols. Moreover, intramolecular hydrogen bonding further contributes to poor reactivity and thus, these isohexides generally show decreasing reactivity in the order of isoidide, isosorbide, and isomannide (least reactive).[139,140,141]

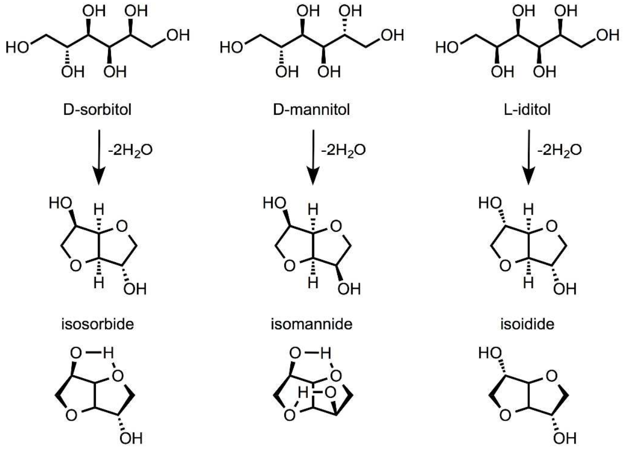
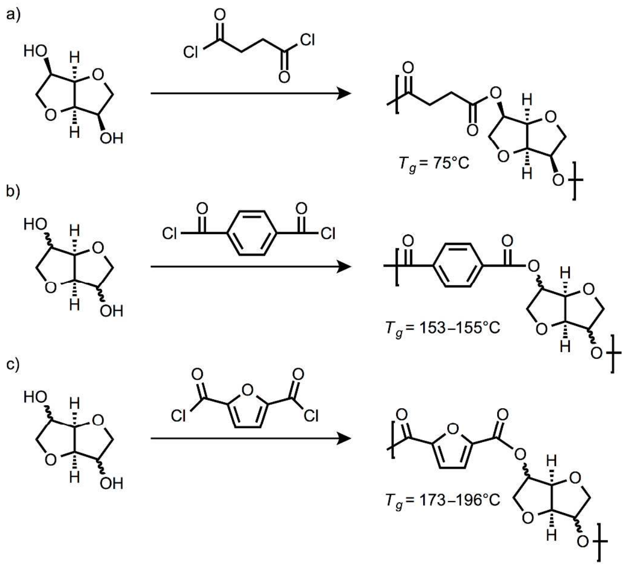


Fig. 3 Source and structure of isosorbide, isomannide, and isoidide.[139]

Nonetheless, aliphatic polyesters containing these three stereoisomers have been synthesized via polycondensation with highly reactive dicarboxylic acid chlorides. Okada *et al.* first studied the polycondensation reactions between isohexides and linear, aliphatic diacyl chlorides having 2, 3, 4, or 8 methylene spacers (MSP).[142] Polymerizations were generally performed in bulk at 140–160°C without any catalysts and polymers were obtained with relatively high molecular weights ranging from 8,000 to 34,000 Da and narrow *Đ* values between 1.2 and 1.8. Among them, only the polymer from isomannide and succinyl chloride (MSP = 2) possessed a high T_g, measured at 75°C (Scheme 25a); it was also the only variant to show crystallinity, with a T_m of 175°C. This polymer has structural and thermal similarities with PET (T_g = 76°C)[41] and therefore isomannide is justifiably compared to terephthalic acid.

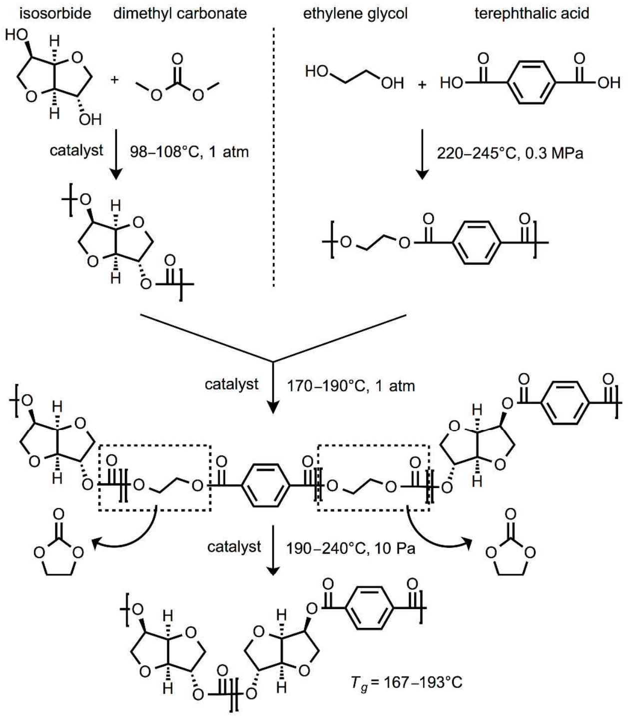


Scheme 25 (a) Synthesis of poly(isomannide succinate), (b) poly(isohexide terephthalate), and (c) poly(isohexide furandicarboxylate).[143,144,145]

Exchanging aliphatic diacid chlorides for aromatic diacid chlorides was an obvious approach for increasing the T_g of isohexide polyesters. Considering the industrial success of terephthalic acid, Thiem and Lüders reported the first work of polymerizing terephthaloyl chloride with isohexides (Scheme 25b).[143] Polymers were synthesized similarly to their aliphatic counterparts without solvent at elevated temperature (180°C). The molecular weights, determined by vapor pressure osmometry, were rather low (3,000 and 3,800 Da), as might be expected from the copolymerization of two conformationally rigid monomers. As predicted, high T_g values were observed: 155°C for poly(isosorbide terephthalate) (PIST) and 153°C for poly(isoidide terephthalate) (PIIT). The authors suggested that the lability of isomannide prevented its coherent polymerization because largely insoluble, possibly crosslinked polymers were obtained via ring rupture under the polymerization conditions.[143] Ballauff *et al.* tried to optimize the reaction conditions by performing the polymerization in solution.[144] Toluene and pyridine functioned as solvent and acid scavenger, respectively. After 2 days of reflux, PIST and PIIT were precipitated quantitatively from methanol with higher molecular weights of 14,500 and 25,600 Da, respectively. The glass transition temperatures, a molecular weight dependent parameter, were increased to over 200°C. Although the highest molecular weights were achieved by this method, the complications of using acid chlorides and toxic pyridine have precluded this approach for commercial polyester manufacture.

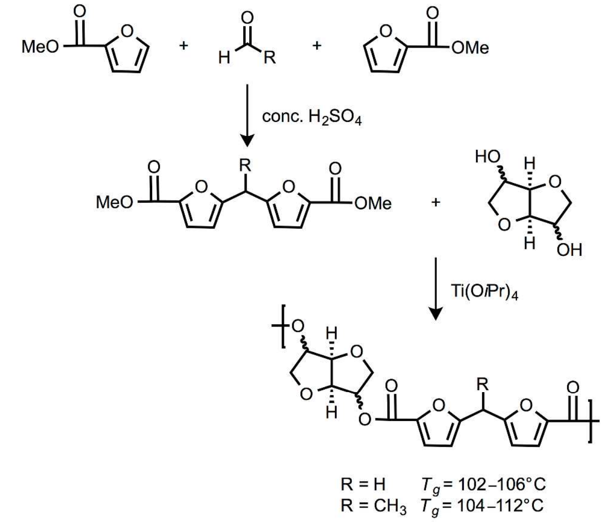
After terephthalic acid and its derivatives were investigated, furanic aromatic systems were considered. Storbeck and Ballauff first demonstrated fully biorenewable polyesters from 2,5-furandicarboxylic acid chloride and isohexides (Scheme 25c).[145] The polymerization was performed in 1,1,2,2-tetrachloroethane for four days. Polymers with high T_g values (173–196°C) were obtained with molecular weights ranging from 9,000 to 25,000 Da, as determined by membrane osmometry.

Zheng *et al.* successfully developed a methodology to overcome the low reactivity of isosorbide.[146] As shown in Scheme 26, isosorbide is first activated by reaction with dimethyl carbonate, forming a polycarbonate pre-polymer. This is subjected to transesterification with polyethylene terephthalate to yield a polyester carbonate with all four monomers present. Further heating under transesterification conditions evolves volatile cyclic ethylene carbonate via back-biting, yielding poly(isosorbide carbonate-*co*-terephthalate) with high molecular weights (above 20,000 Da). The polymers showed T_g values in the range of 167–193°C.



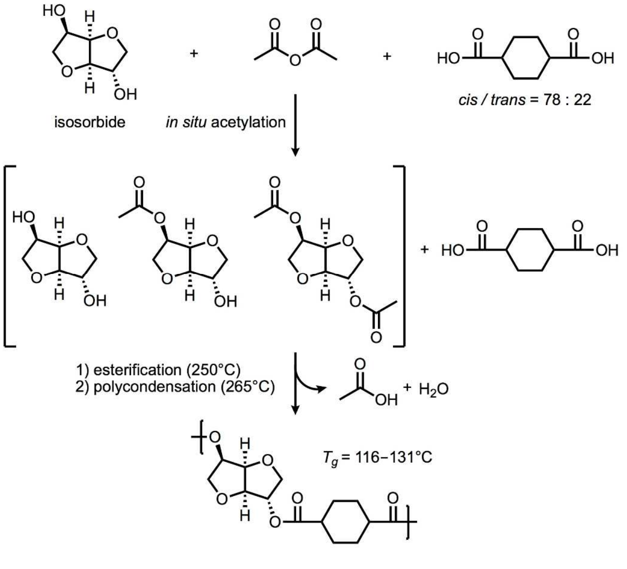
Scheme 26 Synthesis of poly(isosorbide carbonate-co-terephthalate) *via* two-step melt polycondensation of isosorbide, dimethyl carbonate, terephthalic acid, and ethylene glycol.[146]

Okada *et al.* expanded their study of the aforementioned aliphatic polyesters to furan-containing polyesters from bis(5-(methoxycarbonyl)-2-furyl)methane and 1,1-bis(5-(methoxycarbonyl)-2-furyl)ethane.[147,148] These two diesters are built from two units of biorenewable furfural and potentially biorenewable formaldehyde or acetaldehyde (Scheme 27). Transesterification with isosorbide or isomannide was conducted in the melt at 220°C, catalyzed by titanium tetrakis(isopropoxide). Generally, low molecular weights (4,800–9,300 Da) but high T_g values (102°C–112°C) were found for these polyesters. The nature of the R group introduced by formaldehyde (R=H) or acetaldehyde (R=Me) had little effect on the T_g.



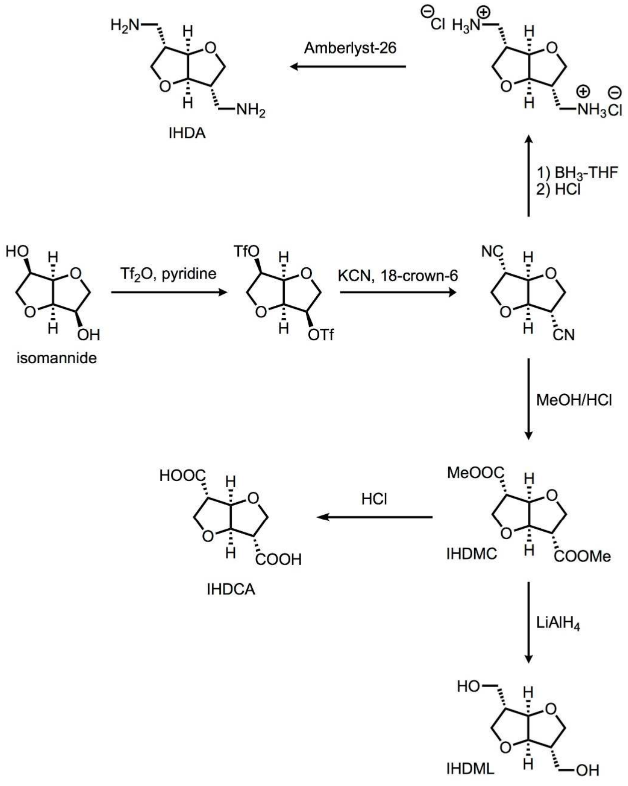
Scheme 27 Synthesis of furanic diesters and their polymers with isosorbide or isomannide.[147,148]

Aromatic polymers can undergo degradation and/or yellowing upon prolonged exposure to ultraviolet (UV) light, especially in the presence of oxygen or air pollutants;[149,150] hence, alicylic polymers have attracted attention because of their excellent durability and weatherability.[151,152] 1,4-Cyclohexane dicarboxylic acid (CHDA), the hydrogenated product of terephthalic acid, was utilized by Kricheldorf *et al.* to polymerize with isohexides.[153] Three different methods were tested but, as expected, activated CHDA dichlorides were necessary for facile polycondensation. With dichloromethane as solvent and an excess of pyridine, a fair molecular weight (11,000 Da) and a high T_g value (145 °C) were obtained. The same polymer (Scheme 28) was prepared by Im and coworkers by activating isosorbide via *in situ* acetylation during polymerization.[154] Even though higher molecular weights (11,600–18,300 Da) were obtained, the broad *Đ* (2.3–5.9) and lower T_g (116–131°C) compared to that reported by Kricheldorf[153] suggested the occurrence of side reactions under such harsh conditions. This report provided NMR evidence of isosorbide ring-opening, which would certainly account for the lower T_g values.

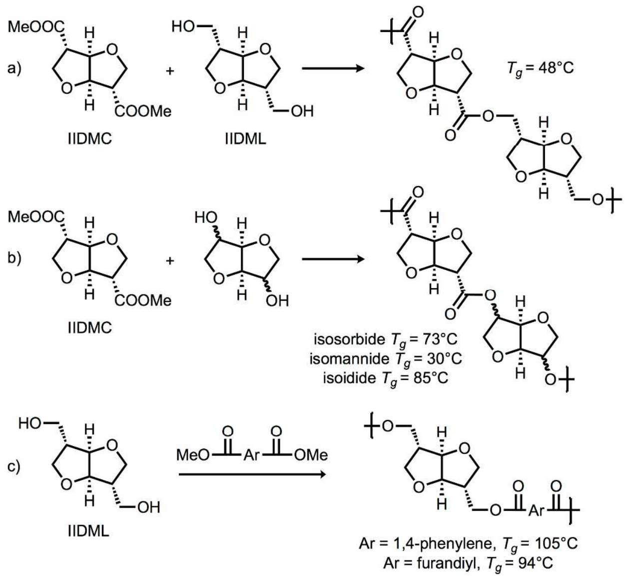


Scheme 28 Polymerization of isosorbide and 1,4-cyclohexane dicarboxylic acid (CHDA) via *in situ* acetylation.[154]

Another effective method of modifying passive secondary alcohols is to chemically convert them into active functional groups such as carboxylic acids or primary alcohols. van Es *et al.* designed synthetic routes to convert isohexides to isohexide dicarboxylic acid (IHDCA), isohexide dimethyl carboxylate (IHDMC), isohexide dimethanol (IHDML) and isohexide diamine (IHDA), as versatile building blocks for polymer synthesis (Scheme 29).[155] It should be noted that in the second step, attack by cyanide is an S_N2 process that effects inversion of the stereocenters. Thus, isomannide is converted to isoidide dimethyl carboxylate (IIDMC) and isoidide dimethanol (IIDML), which can be copolymerized by melt condensation to give the polymer in Scheme 30a.[156] Despite the relative steric accessibility of the primary alcohols of IIDML, the molecular weight of the IIDMC/IIDML polymer was still quite low (5,400 Da). The added methylene groups of IIDML lowered the T_g to 48 °C from the isoidide analogue, which has a T_g of 85 °C (Scheme 30b). The polyester from IIDMC and isosorbide showed a comparably high T_g of 73 °C, but that from isomannide was fairly low at 30 °C, probably because of an anomalously low molecular weight (1,200 Da). IIDML was further investigated by copolymerizing it with dimethyl esters of terephthalic acid (TPA) or 2,5-furandicarboxylic acid (FDCA) to give poly(isoidide-2,5-bismethylene terephthalate) and poly(isoidide-2,5-bismethylene furan-2,5-dicarboxylate) (Scheme 30c).[157] Prepolymers were synthesized in the melt, followed by solid-state post-condensation (SSPC) in order to achieve higher molecular weights (7,700 and 30,300 Da) with narrow *Đ* values near 2. High glass transition temperatures were also achieved for both polymers (105°C and 94°C).



Scheme 29 Synthetic pathway for converting isohexides into more active monomers.[155]



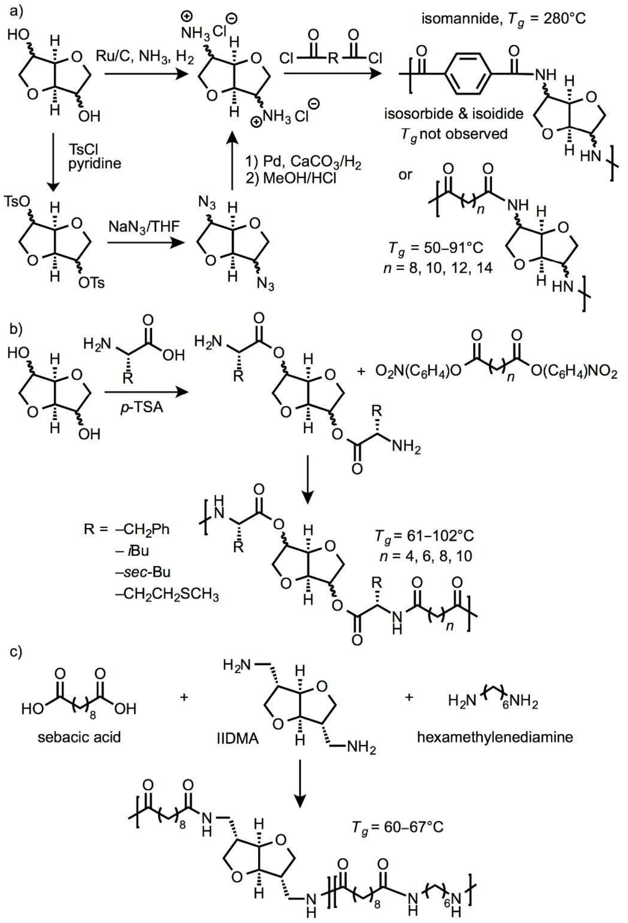
Scheme 30 a) Polycondensation between IIDMC and IIDML versus the analogous polycondensation with the original isohexides (b).[156] c) Semi-aromatic polyesters derived from IIDML and dimethyl esters of TPA or FDCA.[157]

Polyamides cannot be directly synthesized from the isohexides. However, access to these tough and usually crystalline materials can be accomplished via conversion of isohexides to diamines or dicarboxylic acids[155,158,159] or by introduction of an amine or aniline via nucleophilic substitution.[160,161,162] Most of the literature in this area focuses on crystalline melting temperature and overlooks the glass transition temperature. Because of this and the fact that many examples have low biobased content, only a few examples will be discussed here.

Thiem and Bachmann first reported the synthesis of isohexide-derived polyamides through the polycondensation of isohexide diammonium salts and different acyl chlorides.[158] Three stereoisomeric isohexides, as well as linear aliphatic (MSP from 8 to 14) and aromatic (terephthalic and isophthalic) acyl chlorides were investigated. The emulsion polymerization was performed in water with K_2CO_3 as the base and lauryl hydrogen sulfate as the emulsifier (Scheme 31a). Moderate to good molecular weights were obtained (5,200–24,600 Da) and glass transition temperatures of the aliphatic polyamides ranged from 50 to 91 °C. For the three aromatic polyamides, a glass transition was only detected for the isomannide variant, at 280°C.

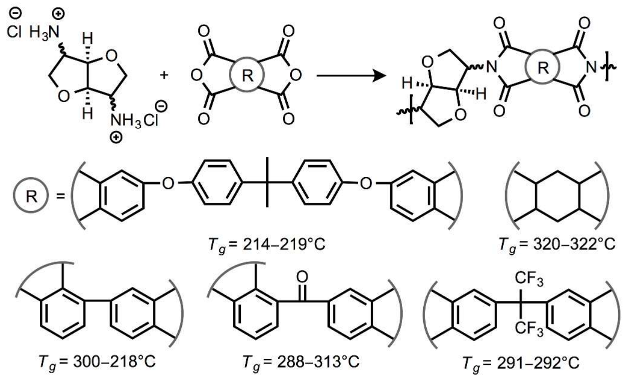
Kricheldorf and coworkers employed amino acids as the biorenewable linker to create polyesteramides (PEAs).[163] The condensation of two amino acids (phenylalanine, leucine, isoleucine, or methionine) onto isosorbide or isomannide (catalyzed by *p*-toluenesulfonic acid, *p*-TSA) yielded a series of diamines. These were polymerized with linear aliphatic diesters (MSP = 4, 6, 8, 10) based on *p*-nitrophenol (Scheme 31b). Solution polymerization yielded PEAs with decent T_g values ranging from 61°C to 102°C, depending on the amino acid and the length of the aliphatic comonomer.

After publishing the synthesis of several difunctionalized isohexide derivatives,[155] Wu *et al.* employed these to prepare polyamides from isoidide-2,5-dimethyleneamine (IIDMA), 1,6-hexamethylenediamine, and sebacic acid (Scheme 31c).[164] Even with long, flexible hexamethylene and octamethylene segments, the detectable glass transition temperatures ranged from 60 to 67 °C. Meuldijk *et al.* expanded this polyamide study by switching to pimelic acid (MSP = 5) as the diacid monomer and 1,4-diaminobutane as the comonomer.[165] A rather high T_g of 102 °C was observed, although this could be diminished predictably by incorporating dimerized fatty acids into the main chain.



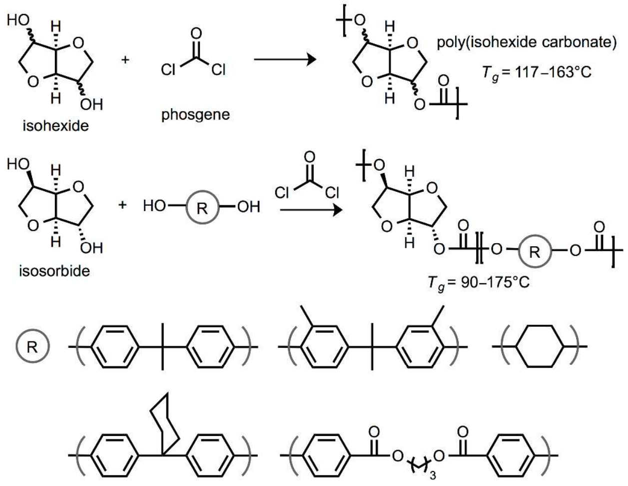
Scheme 31 a) Polyamide synthesis from isohexide diamines.[158] b) Polyesteramides from amino acids and isohexides.[163] c) Copolyamides from sebacic acid, IIDMA, and 1,6-hexamethylenediamine.[164]

Ultra-high glass transition temperatures can often be achieved with polyimides (PI) which, as engineering plastics, generally exhibit excellent thermal stability and mechanical performance.[166] Chen, *et al.*[167] and Wang *et al.*[168] introduced biorenewability into the PI field via isohexide-derived diamines. Different diamine building blocks were prepared by strategies similar to the two mentioned previously. Prepolymerizations of diamines and dianhydrides (Scheme 32) were conducted in solution, followed by cyclization of the polyamic acids to polyimides at high temperatures with applied high vacuum. All of the obtained polymers possessed T_g values over 200 °C and decomposition temperatures over 400°C.



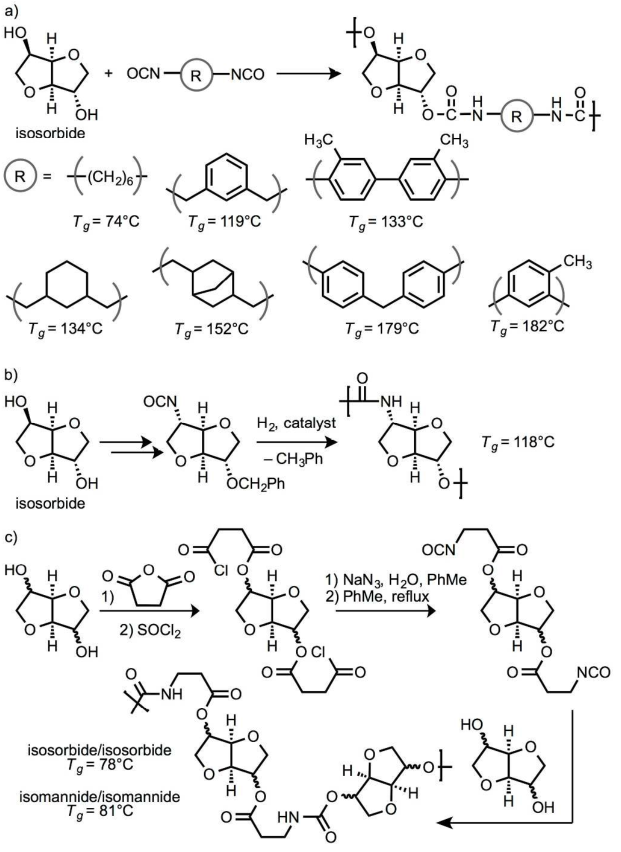
Scheme 32 Polyimide synthesis from isohexide-derived diamines and different dianhydrides.[167,168]

As one of the most widely used and functionally reliable engineering plastics, polycarbonate is predominately produced from likely endocrine disruptor bisphenol-A (BPA) and phosgene. Isohexides have been proposed as surrogate diols to mimic BPA, but with biorenewability and non-toxicity. However, various challenges have impeded the production of poly(isohexide carbonate) (PIC) having high molecular weight. Tremendous research effort has focused on PIC polymerization optimization. So far, three main strategies have been reported: 1) activation of isohexides prior to polycondensation;[169,170,171,172] 2) solution polymerization of isohexides with diphosgene or triphosgene;[173,174,175] and 3) polycondensation of isohexides with diphenol carbonate (DPC) or dialkyl carbonate in bulk.[176,177,178,179] A high molecular weight (up to 50,000 Da), linear poly(isosorbide carbonate) with high T_g (117 – 163°C) can be obtained via all three methods (Scheme 33). Copolymerization of isosorbide and isomannide invariably resulted in low molecular weight materials, in accordance with the unreactive nature of isomannide.[173] Random and alternating copolycarbonates of isosorbide with various bisphenols (bisphenol-A, 3,3'-dimethyl bisphenol-A, bisphenol-C, 1,3-bis(4-hydroxybenzoyloxy) propane, and 1,4-cyclohexane diol) were prepared and the T_g values of these copolymers mostly dropped (90°C – 143°C) in comparison with the homopolymer (163°C), except for biphenol C (175°C, built from cyclohexanone), indicating the variable rigidity of bisphenols.[174]



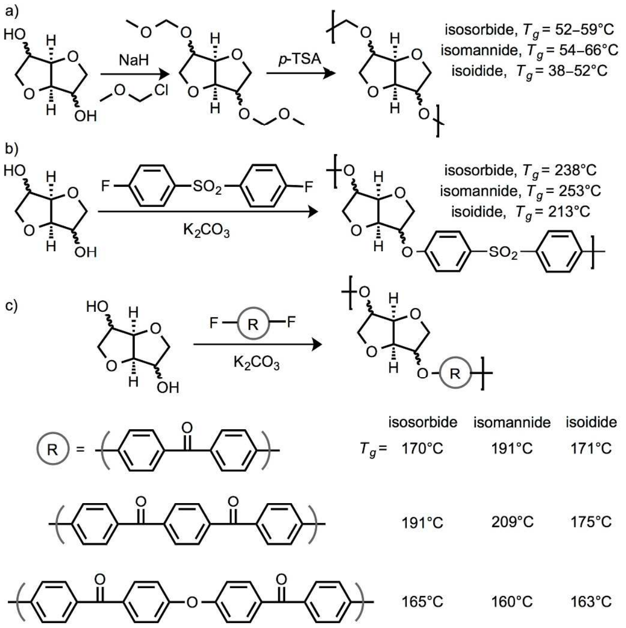
Scheme 33 Homopolycarbonates from isohexides along with copolycarbonates of isosorbide with common diols.[173,174]

The activation of isohexide for polymerization is almost always required; an exception is the production of polyurethanes because of the high reactivity of isocyanate. After initial reports of incorporating isohexides into polyurethanes,[180,181] subsequent strategies gradually forked into two pathways: 1) polycondensation of isohexide with commercially available aromatic or aliphatic diisocyanates or 2) with proprietary isocyanates or diisocyanates made from isohexide itself. For the former pathway, libraries of polyurethanes from different diisocyanates were elaborated by three different groups.[182,183,184] The approach by Muñoz-Guerra[182] effected higher molecular weights than that of Lee and Kato;[183] Delolme[184] did not report molecular weights. However, the reported difference in glass transition temperature for the isosorbide/MDI polyurethane was negligible (179°C *vs.* 183°C, Scheme 34a). For the latter pathway, Thiem and coworkers devised a 5-step synthetic strategy that converts isosorbide into a protected hydroxy/isocyanate monomer (Scheme 34b).[185] Hydrogenation conditions released toluene and formed the hydroxy/isocyanate AB-type monomer *in situ*, which underwent polyaddition. The obtained polyurethane was rigid with a number average molecular weight of 12,000 Da and a T_g of 118°C. Kessler *et al.* synthesized a diisocyanate monomer from isosorbide or isomannide beginning with double esterification using succinic anhydride.[186] The formed diacid was converted to the diacyl chloride, followed by a two-step Curtius rearrangement with NaN_3 to afford the product (overall yield of 52%). AA-BB-type polyadditions were then performed between the isohexide-based diisocyanates and the parent isohexides. Two polymers with acceptable molecular weights (14,300 and 15,300 Da) and good T_g values (78°C and 81°C) were collected in high yields (Scheme 34c).



Scheme 34 Polyurethanes from isohexides a) copolymerized with conventional diisocyanates;[182,183,184] b) via an *in situ* hydroxy/isocyanate monomer;[185] and c) copolymerized with isohexide-derived diisocyanates.[186]

Besides the major categories of isohexide-derived polymers chronicled above, a few other miscellaneous polymers with interesting thermal properties were also explored. Chikkali and his team reported the first sustainable polyacetal from isohexide.[187] Isohexides were deprotonated with sodium hydride and acetalated with chloromethyl methyl ether (Scheme 35a). The subsequent polycondensation was conducted by Acetal Metathesis Polymerization (AMP).[188] Low molecular weight polymers were generated (1,500–4,400 Da) with fair T_g values over 50°C for all three polymers (52–66°C). Poly(ether sulfone)s from isohexides were described by Kricheldorf *et al.*[189] In this case, isohexides served as the nucleophiles in nucleophilic aromatic substitution (NAS) on a commercially available sulfone monomer, 4,4-difluorodiphenyl sulfone (DFDPS) (Scheme 35b). A 2 mol% excess of DFDPS guaranteed high molecular weight, reported only via viscometry. T_g values were observed at 238°C, 253°C, and 213°C for poly(ether sulfone)s from isosorbide, isomannide, and isoidide, respectively. Finally, Kricheldorf *et al*. extended their isohexide/NAS methodology to poly(ether ketone)s (Scheme 35c).[190] In this case, 4,4′-difluorodiphenylketone, 1,4-di(*p*-fluorobenzoyl)benzene, and 4,4′-bis(4-fluorobenzoyl) diphenyl ether were polymerized with three isomeric isohexides in solution for 48h. The obtained polymers displayed high T_g values ranging from 160 to 209°C).



Scheme 35 Synthesis of a) isohexide-derived polyacetals;[187] b) isohexide-derived poly(ether sulfone)s;[189] and c) isohexide-derived poly(ether ketone)s.[190]

b) Sugar alcohols

Sugar alcohols represent the group of sugar-based organic compounds bearing multiple alcohol functional groups. Generally, sugar alcohols possess sequential, internal, secondary alcohols flanked by two terminal, primary alcohols. Among them, the hexitols D-mannitol, D-glucitol (sorbitol), and D-galactitol (Fig 4.), as well as their corresponding diacids, were comprehensively studied by the Muñoz-Guerra Group. The number of exposed alcohols of a hexitol can be decreased by acetalization, which consumes two alcohols per acetal formed. This modification not only prevents undesired crosslinking during polymerization, but also increases chain stiffness of the target polymers.

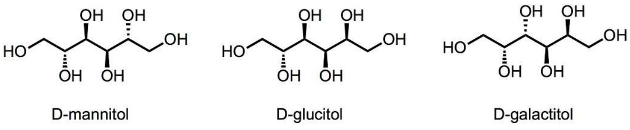
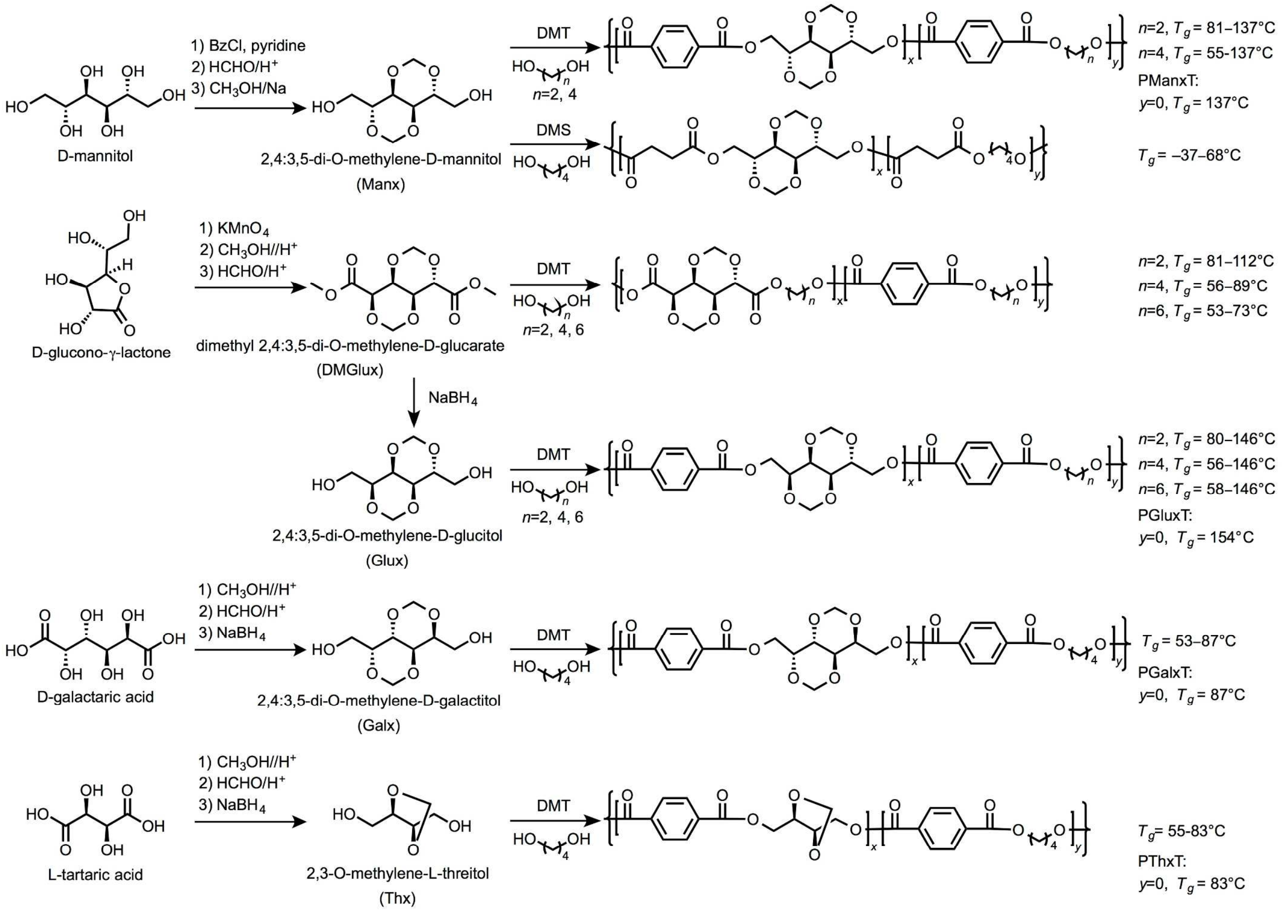


Fig. 4 Structures of the hexitols D-mannitol, D-glucitol, and D-galactitol.[131]

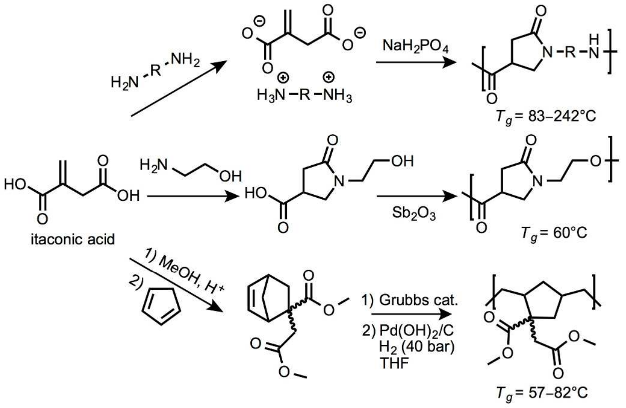
Several aromatic and aliphatic polyesters and copolyesters were synthesized and are described in Scheme 36. Monomer synthesis was carried out either from a sugar alcohol, its diacid variant, or a lactone with relatively low overall yields. For example, 2,4:3,5-di-O-methylene-D-mannitol (Manx) was prepared from D-mannitol by selective protection of the primary alcohols, acetalization with formaldehyde, and then deprotection.[191] Dimethyl 2,4:3,5-di-O-methylene-D-glucarate (DMGlux) was made by oxidation, esterification, and acetalization of D-glucono-γ–lactone.[192] Reduction of this product gave 2,4:3,5-di-O-methylene-D-glucitol (Glux). Dimethyl 2,4:3,5-di-O-methylene-D-galacarate (DMGalx) and its reduced sibling 2,4:3,5-di-O-methylene-D-galactitol (Galx) were similarly synthesized from D-galactaric acid.[193] Polymerizations were performed under similar conditions using dibutyl tin oxide (DBTO, 0.6 mol%) as the catalyst. In general, the polymers were obtained with a high M_n and narrow *Đ*, except for the homopolymers containing bicyclic monomers. Random copolymerization was confirmed by ^{1}H NMR. The thermal properties varied predictably according to the bicyclic monomer content. Glass transition temperatures of the three homopolymers (PGluxT, PManxT, and PGalxT) using only dimethylterephthalate (DMT) as the diacid were 154°C,[194] 137°C,[195] and 87°C,[196] respectively, indicating the similar rigidity of Glux and Manx, but a notably lower T_g was observed for PGalxT. This trend was further illustrated by homopolymers of poly(butylene Glux) (T_g = 89°C) and poly(butylene Galx) (T_g = 18°C).[196] Generally for the copolymers, increasing the bicyclic composition at the expense of the terephthalate composition increased T_g, although this augmentation was minimal for DMGalx. However, an increased bicyclic composition lowered crystallinity and slowed the crystallization rate. Furthermore, bicyclic composition accelerated hydrolytic degradation and biodegradation compared to the terephthalate-rich polymers. Interestingly, despite the fact that the acetal functional group is typically vulnerable to hydrolysis, degradation mainly occurred at the main chain ester group, leaving the bicyclic structure intact.[197] The low ring strain of the 6-membered rings probably contributed to the differential stability. Tartaric acid, a 4-carbon diacid with two secondary OH groups, was similarly acetalized and subjected to polymerization (Scheme 36, bottom). A series of random copolymers with dimethylterephthalate and 1,4-butanediol was prepared with good molecular weights, except for the homopolymer PThxT made without any flexible 1,4-butanediol (Mn = 3,800 Da). The T_g of PThxT was measured at 83°C—lower than the aforementioned bicyclic polymers, but still higher than that of polybutylene terephthalate itself (PBT, T_g = 45°C).[198]



Scheme 36 Polyesters made from diacids (such as DMT, dimethylterephthalate) and diols based on acetalized mannitol, glucitol, galactitol, or tartaric acid. [191,192,193,194,195,196,197]

c) Itaconic acid

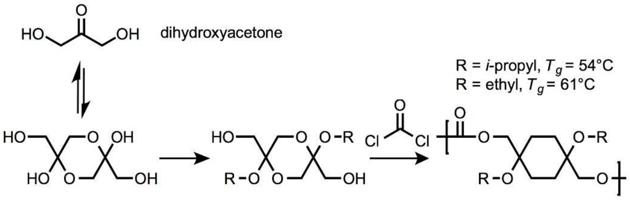
Itaconic acid (IA) is mass-produced via glucose fermentation with *Aspergillus terreus* and has attracted considerable attention because of its availability and nontoxicity.[199] The electrophilic α,β-unsaturated carbonyl group allows chemical modification and facile heterocycle formation. Even though numerous heterocyclic systems have been reviewed,[200] only a few have been applied to polymer chemistry.[201,202,203] A 2-pyrrolidinone ring, a five-membered lactam heterocycle, is synthesized from IA and a primary amine via aza-Michael Addition followed by cyclization. The Kaneko Group elaborated the one-pot synthesis of polyamides by melt polymerization of premade organic salts from IA with aliphatic or aromatic diamines (Scheme 37).[202,203] These salt precursors ensured the correct stoichiometry of the diacid and diamine, a similar approach utilized in nylon production. The aliphatic diamines ranged from ethylene diamine to hexamethylene diamine and the aromatic diamines employed were *p*-phenylenediamine, *p*-xylylenediamine, *m*-xylylenediamine, and oxydianiline. Polymerizations were promoted by NaH_2PO_4 and the obtained polymers showed high molecular weights (M_n = 27,500–67,200 Da) and high T_g values (83–242°C). The authors performed several degradation experiments and confirmed a hydrolytic ring-opening degradation mechanism under strong photochemical conditions (UV irradiation with 250–450 nm light for 6h). The reluctance toward degradation was proposed to originate with stable hydrogen bonding within the polyamide. Miller, Qi, and coworkers focused on the synthesis of pyrrolidinone-based polyesters.[203] Monomer synthesis employed IA and ethanolamine to form a hydroxy-acid (Scheme 37), or two equivalents of IA and ethylenediamine to form a diacid. Polycondensation was accomplished with Sb_2O_3 as the catalyst. A series of polyesters was synthesized with high molecular weight (M_n = 19,500–24,900 Da). Without amide hydrogen bonding, T_g values were lower (24–62°C), but nearly complete hydrolytic degradation was observed under environmentally relevant conditions (neutral water, one year). The Meier Group used the electron-deficient dimethyl itaconate (DMI) as a dienophile to generate norbornene derivatives with cyclopentadiene, through the Diels-Alder (DA) cycloaddition reaction (Scheme 37).[204] The norbornene monomer underwent ring-opening metathesis polymerization (ROMP), followed by hydrogenation, to give carbocyclic polymers with T_g values up to 82°C.



Scheme 37 Cyclic polymers from itaconic acid (IA) and various comonomers.[202,203,204]

d) Dihydroxyacetone

Dihydroxyacetone (DHA) is an intermediate of glucose metabolism. Its biorenewability and multifunctionality make it an attractive building block for biomaterials.[205] DHA suffers from an equilibrium with its hemiacetal dimer in solution, which usually complicates its polymerization. However, Zelikin and Putnam successfully locked the DHA dimer by conversion to the bis-acetal by reaction with ethanol or isopropanol. (Scheme 38).[206] Polycarbonates with high molecular weights (M_n up to 25,700) were obtained with moderate T_g values (up to 61°C for R = ethyl) by polycondensation with phosgene.

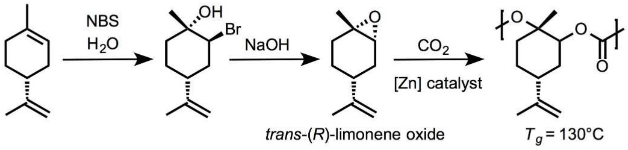


Scheme 38 Synthesis of polycarbonates from phosgene and cyclic acetal dimers of dihydroxyacetone.[206]

4.2. Terpene based polymers

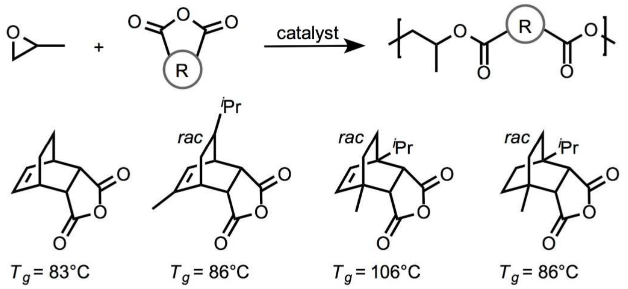
Terpenes are a class of naturally occurring isoprene oligomers mainly extracted from trees—especially pine trees and other conifers.[207] The tree extract is refined and assorted products are collected. As most of the terpenes contain cycloaliphatic units, the derived polymers could possess highly rigid structures with valuable thermal and mechanical properties. Radical polymerization of terpenes attracts the majority of the attention among polymer scientists and will be reviewed later in the radical section. Presently, we concentrate on step-growth polymerization of terpene-derived monomers.

Carbon dioxide, an abundant and renewable greenhouse gas, has been extensively studied for the synthesis of partially or fully renewable polycarbonates. Since the carbon of CO_2 is in the highest oxidation state, its incorporation into polymers presents various challenges.[208] Fully renewable polycarbonate originating from the alternating copolymerization of limonene oxide (LO) and CO_2 was first published by the Coates Group using β-diiminate zinc acetate catalysts under mild conditions.[209] Although (*R*)-limonene oxide is commercially available as a mixture of *cis* and *trans* diastereomers, the employed catalysts only showed reactivity for the *trans*-LO, yielding a regioregular and stereoregular polycarbonate with decent molecular weight (M_n up to 9,300 Da) and a T_g value of 111°C. Greiner *et al.* addressed the low molecular weight issue by devising a scalable, stereoselective, and high-yielding synthesis of *trans*-LO (Scheme 39).[210] The high *trans* content (>85%) and low hydroxyl impurity level of this monomer was critical for molecular weight improvement, which exceeded 100,000 Da and increased the T_g value to 130°C.



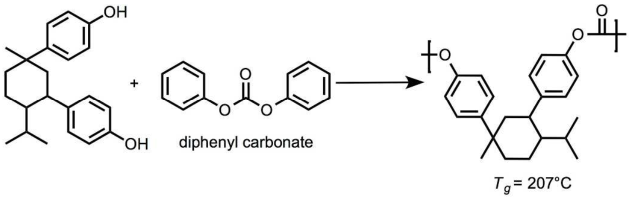
Scheme 39 Synthesis of *trans* limonene oxide and its polycarbonate obtained by alternating copolymerization with CO_2.[210]

The ring-opening copolymerization of epoxides and cyclic anhydrides offers an efficient pathway to polyesters. Phthalic anhydride was initially investigated as a comonomer because of its high rigidity and potential biorenewability, as reported later from biobased furan and maleic anhydride.[211,212] A relatively active chromium salophen catalyst was selected to produce decent molecular weight polyesters (M_n up to 9,700 Da) assisted by bis(triphenylphosphoranylidene)ammonium chloride (PPN^+Cl^-). A significant fluctuation of measured T_g values (38–82°C) was detected for this polyester, possibly resulting from low molecular weight samples and/or residual monomers. Inspired by the green synthesis of phthalic anhydride, the Coates Group devised the synthesis of terpene-based anhydrides and conducted their copolymerization with propylene oxide (PO) (Scheme 40).[213] α-Phellandrene and α-terpinene were converted to biobased, rigid, cyclic anhydride monomers. 1,3-cyclohexadiene (1,3-CHD) was also used for comparison. Structural subtleties of these terpene-based cyclic anhydrides impacted the glass transition temperature of the corresponding polymers. For example, placement of the bulky isopropyl group on a bridgehead position yielded the highest T_g of 106°C, whereas locating it elsewhere or excluding it (via 1,3-CHD) yielded lower T_g values in the range of 83–86°C.



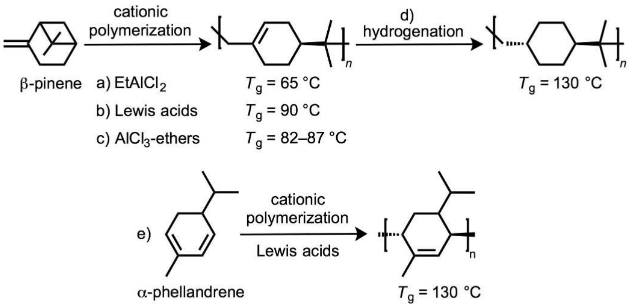
Scheme 40 Synthesis of polyesters from terpene-based cyclic anhydrides and propylene oxide.[213]

The terpene-derived bisphenol of Scheme 41 is commercially available (Yasuhara Chemical Co.) and made from limonene and phenol. This diol has been copolymerized with diphenyl carbonate in the melt with no catalyst to produce a partially biobased polycarbonate having a somewhat low molecular weight (M_n = 7,700 and M_w = 18,400), but a high T_g value of 207°C.[214] Note that bisphenol A (BPA) can substitute for this biobased bisphenol, but BPA lowers the T_g value for all levels of incorporation. For example, the 50:50 feed ratio affords a polycarbonate with a 47:53 composition and a T_g value of 177°C.



Scheme 41 Synthesis of polycarbonate from a limonene-based bisphenol and diphenyl carbonate.[214]

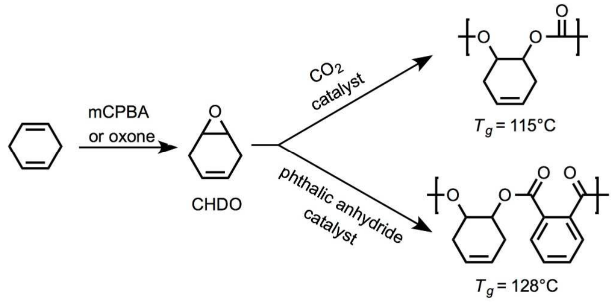
Keszler and Kennedy first reported the cationic polymerization of β-pinene in 1992.[215] They utilized a conventional catalyst, $EtAlCl_2$ (likely with adventitious H_2O as the proton source), which resulted in a polymer having a T_g of 65 °C and a high M_n up to 40,000 Da (Scheme 42a). Their results were followed by Satoh and coworkers in 2006, who also polymerized β-pinene, as well as α-phellandrene, catalyzed by a collection of Lewis acids.[216] For β-pinene, a higher T_g up to 90 °C was reported, along with an M_n of 25,100 Da (Scheme 42b). The authors also hydrogenated poly(β-pinene) and observed that T_g increased to 130 °C (Scheme 42d), a result that likely reflects assumption of a rigid equatorial/equatorial chair conformer (1,4 *trans*). Poly(α-phellandrene) excelled poly(β-pinene) with a T_g value around 130 °C but with lower M_n values approaching 6,000 Da (Scheme 42e). Kostjuk *et al.* further explored the cationic polymerization of β-pinene. The authors surveyed several catalyst systems made from $AlCl_3$-ether complexes (Scheme 42c), with only a one minute reaction time.[217] The polymer T_g values (T_g = 82–87 °C) were somewhat lower than those reported by Satoh *et al.* perhaps because M_n values were somewhat lower at 9,000 to 14,000 Da ($Đ$ around 2.0).



Scheme 42 Cationic polymerization of cyclic terpenes:[215,216,217] a–c) polymerization of β-pinene with three different catalytic systems; d) hydrogenation of poly(β-pinene) increases T_g; e) polymerization of α-phellandrene catalyzed by Lewis acids.

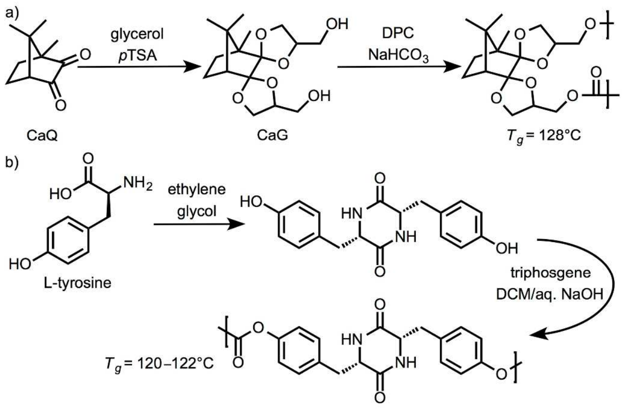
4.3. Other non-aromatic cyclic containing polymers

1,4-cyclohexadiene was recently identified as a readily accessible byproduct of polyunsaturated fatty acid olefin metathesis.[218] With this potential bioavailability, 1,4-cyclohexadiene (1,4-CHD) has been thoroughly studied for its conversion to epoxide and subsequent use as a building block for biorenewable materials.[219] 1,4-CHD was oxidized by either *meta*-chloroperbenzoic acid (*m*CPBA) or oxone to afford cyclohexadiene oxide (CHDO) (Scheme 43). Unsaturated polymers were collected via ROP of CHDO with CO_2 or ROP of CHDO with phthalic anhydride. High T_g values of 115°C and 128°C were measured for the polycarbonate and polyester, respectively. These polymers not only exhibit great thermal properties, but are amenable to post-polymerization modifications via the double bond.



Scheme 43 Synthesis of unsaturated cyclic polymers from cyclohexadiene oxide (CHDO) and CO_2 or from CHDO and phthalic anhydride.[219]

Camphorquinone diketal glycerol (CaG) was synthesized via double acetalization of camphorquinone (CaQ) with glycerol (Scheme 44a).[220] Polymerization of CaG with diphenyl carbonate (DPC) was performed, yielding a polycarbonate with decent molecular weight (M_n = 8,300 Da) and a high T_g value of 128°C. Separately, Xia and coworkers exploited the phenolic functional group of tyrosine by first conducting cyclodimerization and then interfacial polymerization with triphosgene, yielding a rigid polycarbonate with a T_g of 120–122°C (Scheme 44b).[90]

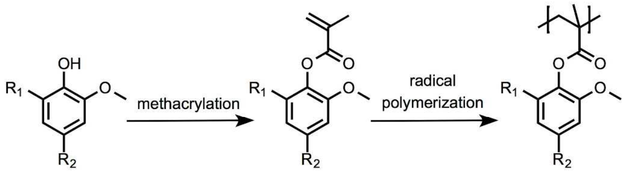


Scheme 44 a) Synthesis of CaG (from camphor-derived CaQ) and its polycarbonate;[220] b) Cyclodimerization of tyrosine and the polycarbonate made via polymerization with triphosgene.[90]

5. Radical Polymerization

5.1. Lignin-based polymers

Lignin derived aromatics are widely employed in the free radical polymerization field. Those bioavailable aromatics bearing a reactive hydroxyl functionality are easily converted to acrylate or methacrylate monomers, usually polymerizable via standard radical methods. Scheme 45 shows a variety of bioaromatics subjected to methacrylation and then radical polymerization.



	R$_1$	R$_2$			T_g (°C)
guaiacol	H	H	GM	PGM	92–120
vanillin	H	CHO	VM	PVM	120–139
creosol	H	Me	CM	PCM	132
4-ethylguaiacol	H	Et	EM	PEM	116
syringol	OMe	H	SM	PSM	185–205

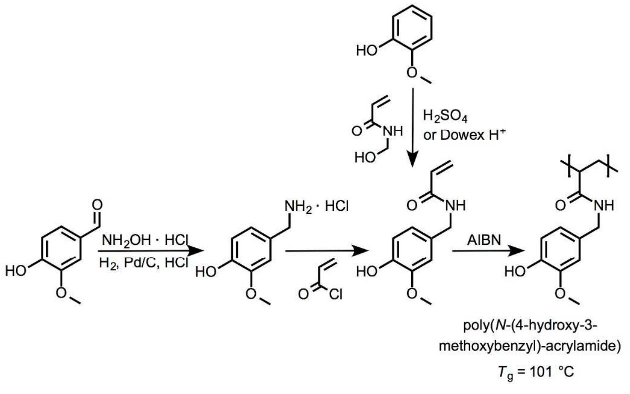
Scheme 45 Lignin-based monomers formed via methacrylation and their radical polymerization.[221–227]

Wool, Epps, *et al.*[221] prepared vanillin methacrylate (VM) by reacting vanillin with methacrylic anhydride, followed by reversible addition-fragmentation chain transfer (RAFT) polymerization to afford a series of PVM polymers. The obtained PVM showed a T_g of 120 °C with no evidence of crosslinking via the *p*-formyl group (at

R_2). An unexpected reaction occurred with methanol during the methanol wash of the workup procedure; 20% of the pendent aldehyde groups were converted to dimethyl acetal groups. This caused a slight decrease down to 111 °C for the T_g value of PVM. Finally, chain extension of PVM with lauryl methacrylate (LM) generated PVM-*b*-PLM as a sustainable alternative for hard-soft styrenic block copolymers.

As expected, the T_g value was influenced by various factors such as side-chain substituents[222] and polymer molecular weight.[223] Wool, Epps, *et al.* also reported the T_g values for three other guaiacolic lignin-based polymers: poly(4-ethylguaiacol methacrylate) (PEM), poly(creosol methacrylate) (PCM), and poly(guaiacol methacrylate) (PGM), each formed via RAFT polymerization.[224] PVM possessed the highest T_g value of 139 °C for the series. Replacement of the formyl group by either H or an alkyl group (Me or Et) adversely impacted the T_g value. PEM (R_2 = Et) showed the lowest T_g of 116 °C. PCM (R_2 = Me) and PGM (R_2 = H) exhibited intermediate T_g values of 132 and 120 °C, respectively. Previously, the T_g value of PGM was given as 92 °C, but no molecular weight data was revealed in this initial report.[225] Furthermore, terpolymerizations employing EM, GM, CM, and VM—as a strategy to minimize separation of bioproducts[226]—resulted in random terpolymers with T_g values ranging from 111 to 119 °C.[224] In addition to guaiacolic lignin-based polymers, Wool, Epps, and coworkers successfully polymerized syringyl methacrylate (SM)—prepared via acrylation of syringol, a bioaromatic from hardwood lignin—via RAFT polymerization. Compared to PGM with its T_g of 120 °C, the two *ortho*-methoxy groups of PSM vastly increased the T_g value up to 205 °C.[227]

Roger *et al.* employed the two approaches of Scheme 46 to synthesize an acrylamide monomer from either guaiacol or vanillin.[228] The first approach employs the Friedel-Crafts alkylation of guaiacol with *N*-(hydroxymethyl)acrylamide. The second approach reacted vanillin with hydroxylamine, followed by reduction, then acrylation using acryloyl chloride, yielding *N*-(4-hydroxy-3-methoxybenzyl)-acrylamide. Conventional radical polymerization (with AIBN) of the resulting acrylamide monomer resulted in a polyacrylamide decorated with guaiacol side groups having a T_g of 101°C and M_n values up to 11,000 Da.



Scheme 46 Synthesis and polymerization of a guaiacol-acrylamide monomer.[228]

Eugenol is an aromatic biomass feedstock readily extracted from cloves (Figure 5a). Despite its allyl group, it shows limited reactivity toward radical polymerization, likely because of its radical-scavenging activity.[229] To remedy this problem, eugenol was methacrylated, which masked the phenolic functionality and introduced an alkene substantially more polymerizable. The polymerization of eugenol methacrylate was investigated in solution[230] and with bulk monomer[225] to produce polymers with relatively high T_g values in the range of 95–103 °C (Figure 5b). Only polymers with low-conversion (~10%) were soluble in common organic solvents, suggesting that some degree of cross-linking occurred via the allylic double bond during polymerization at high conversion.[230] These results comport with recent work by Deng *et al.* regarding self-cross-linked poly(eugenol methacrylate).[231] Copolymerization of ethyl methacrylate (EMA)[230] or 2-hydroxyethyl methacrylate (HEMA)[232] with eugenol methacrylate showed no significant impact on the T_g of the copolymers (90–95 °C) since the reported T_g values of PEMA and PHEMA are 70 and 89 °C respectively. Separately, the phenylpropanoid coumaric acid (Figure 5c) was subjected to methacrylation and polymerized by Ree, Kim, and coworkers.[233] First, coumaric acid was esterified in methanol to generate methyl coumarate. Then the resulting coumarate was acrylated using methacrylic acid in the presence of coupling agent 1,3-dicyclohexylcarbodiimide (DCC). Conventional radical polymerization in THF yielded a polymer having an M_w of 37,000 Da and a relatively high T_g of 128 °C (Figure 5d).

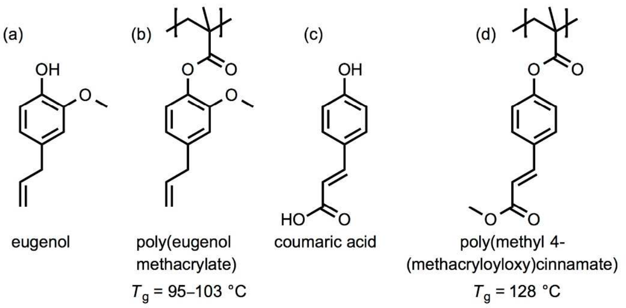
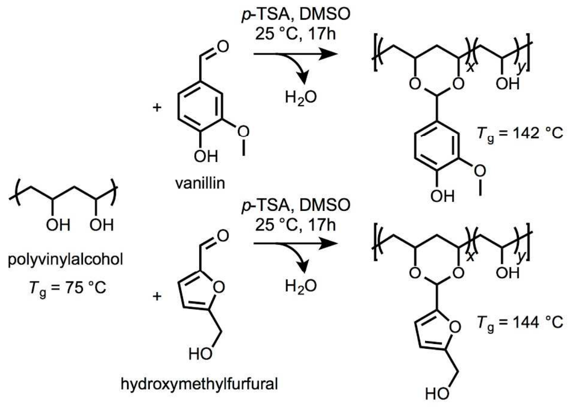


Fig. 5 High T_g methacrylate polymers based on eugenol (a)[225,230,231] and coumaric acid (c).[233]

Poly-polymerization attachment of pendent bioaromatics has been applied to commercial polyvinyl alcohol (PVA, T_g = 75 °C), which is made via radical polymerization of vinyl acetate, followed by hydrolysis. Scheme 47 shows two of the thirteen aromatic aldehydes that were successfully attached to PVA via acetalization, yielding a family of polyacetals with 54 to 75% of the –OH groups reacted.[234] A wide T_g range of 114 to 157 °C was observed and correlated to the bioaromatic structure, in terms of conformational flexibility, substituent free volume, and hydrogen bonding. Importantly, hydrolytic degradation under aqueous acidic conditions yielded benign aromatics and water-soluble, biodegradable PVA.



Scheme 47 The T_g of polyvinylalcohol (75 °C) is vastly boosted by appending bioaromatic aldehydes via acetalization.[234]

5.2. *Exo*-methylene lactone and lactide-based polymers

Cyclic monomers containing *exo*-cyclic double bonds adjacent to a carbonyl group generally yield sterically congested polymers upon their radical polymerization. For example, α-methylene-γ-butyrolactone (α-MBL), also known as Tulipalin A, is a naturally occurring cyclic lactone which can be found in Tulips. α-MBL resembles a cyclic version of methyl methacrylate (MMA, Figure 6), but this structural difference provides α-MBL greater reactivity for radical polymerization. This augmented reactivity derives from a rigid *s*-cis conformation of α-MBL, which stabilizes the propagating radical via enforced conjugation with the carbonyl group during chain propagation.[235]

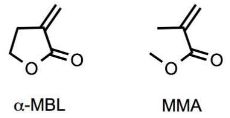
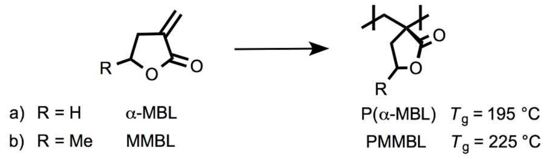


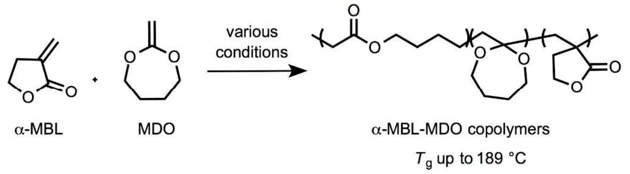
Fig. 6 Molecular structures of α-methylene-γ-butyrolactone (α-MBL, Tulipalin A) and methyl methacryate (MMA).[235]

The free radical and anionic polymerization of α-MBL were reported by Akkapeddi.[236] Poly(α-MBL), synthesized radically, was amorphous with a high T_g of 195 °C and showed thermal stability up to 320 °C (Scheme 48a). The high T_g of poly(α-MBL) compared to that of PMMA (105 °C) was explained by the rigidity of the lactone ring, which greatly restrains the conformational mobility of the polymer backbone. With this high T_g, poly(α-MBL) was also exploited for novel thermoplastic elastomer synthesis. Chain extension of pre-made bifunctional, biorenewable poly(menthide) *via* ATRP polymerization of α-MBL yielded hard/soft/hard triblock copolymers with two glass transitions of 170–190 °C and -21 °C.[237]



Scheme 48 Synthesis of poly(α-MBL) and poly(MMBL).[236,240]

Separately, copolymerization of α-MBL with 2-methylene-1,3-dioxepane (MDO) was investigated by Agarwal and Kumar in order to generate degradable polymers with high molecular weight (Scheme 49).[238] The authors described both random and block copolymers and claimed that the polymerization process involved concurrent ring-opening and ring-retaining enchainment mechanisms of MDO. It was noted that changing the monomer feed ratio, temperature, and initiators could alter the copolymer thermal properties. Although increasing ring-opened MDO content enhanced copolymer degradability, it decreased the T_g. Elevation of the reaction temperature from 70 to 120 °C promoted the MDO ring-opening mechanism from 47% to 72% which consequently dropped the T_g from 145 °C and 189 °C (two T_g values were observed for two blocks in one polymer segment) down to 118 °C. On the other hand, the T_g of α-MBL-MDO copolymers increased in parallel with an increasing α-MBL composition from 50 to 150 °C.

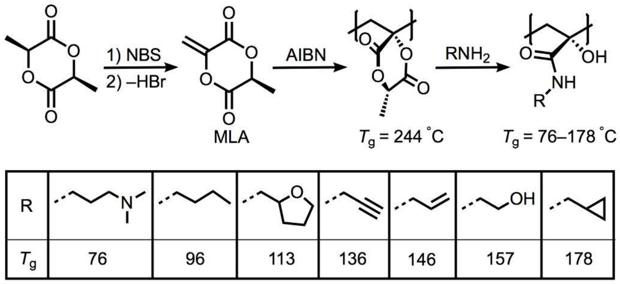


Scheme 49 Synthesis of α-MBL / MDO copolymers.[238]

γ-Methyl-α-methylene-γ-butyrolactone (MMBL) is another relevant methylene lactone monomer which can be produced from a biobased feedstock, levulinic acid.[239] Stille *et al.*[240] have reported the synthesis and polymerization of racemic MMBL and (*R*)-MMBL under different conditions (Scheme 48b). The stereoregularity of the polymers did not impact the observed T_g values, which were consistently found around 215 °C. A slightly higher T_g of poly(MMBL) at 225°C was reported later by Chen *et al.*[241] Additionally, the thermal properties of MMBL / styrene (St) copolymers were reported by Luo and co-workers.[242] Copolymer T_g values were increased by increasing the MMBL content. For example, poly(MMBL-*co*-St) with 55 and 72 weight% MMBL incorporation exhibited T_g values of 154 and 179 °C, respectively.

(*S*)-Methylenelactide (MLA) can be synthesized from L-lactide in two steps: 1) bromination of L-lactide using *N*-bromosuccinimide followed by 2) dehydrobromination (Scheme 50). This biobased methylene lactone has been polymerized via a radical mechanism.[243,244] Polymerization of MLA was described by Britner and Ritter.[243] ^1H and ^{13}C NMR indicated an isotactic structure and the polymer exhibited a higher T_g (244 °C) than that of poly(MMBL). Aminolysis of poly(MLA) with various primary amines afforded poly(α-hydroxyacrylamide)s, which displayed a wide variation of T_g

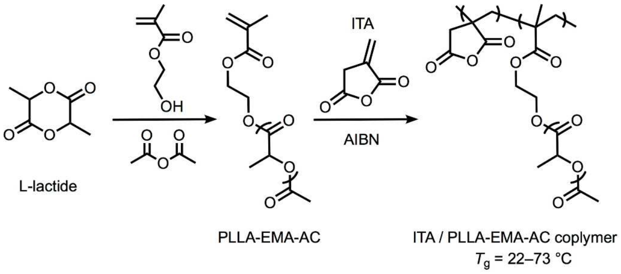
from 76 to 178 °C (Scheme 50). Also in 2015, Chen *et al.*[244] reported a broad T_g range for poly(MLA) from 229 up to 254 °C; this breadth of T_g derives from the assortment of molecular weights. To further investigate polymeric thermal properties, a radical copolymerization of MLA with MMBL was accomplished. A random copolymer with a 50:50 molar incorporation ratio and a high M_w of 670,000 Da showed a high T_g of 242 °C. A somewhat lower T_g of 224 °C was found for the copolymer with only 11 mol% MLA and a lower M_w of 187,000 Da.



Scheme 50 Synthesis of poly(MLA) and post-polymerization aminolysis to yield poly(α-hydroxyacrylamide)s.[243,244]

5.3. Polymers based on itaconic anhydride and its derivatives

Because of the relatively high T_g of poly(itaconic anhydride) (129 °C),[246] itaconic anhydride (ITA) has been further pursued as a key ingredient for copolymers with improved thermal properties. Scheme 51 depicts the copolymerization of ITA with a methacrylate terminated, PLA-based macromonomer (PLLA-EMA-AC). Wallach and Huang showed that 2-hydroxyethyl methacrylate initiated the ROP of L-lactide and the 800 Da oligomer could be terminally acetylated with acetic anhydride.[245] A series of ITA / PLLA-EMA-AC copolymers was prepared with 15–85% macromonomer incorporation using AIBN as an initiator. The T_g values of these copolymers increased from 22 °C (T_g of the PLLA-EMA-AC homopolymer) up to 73 °C by increasing the ITA content.



Scheme 51 Synthesis and polymerization of PLLA-EMA-AC with ITA.[245]

Weiss *et al.*[246] monitored the solution copolymerization of ITA with stearyl methacrylate (SM, $CH_2CMe(CO)O(CH_2)_{16})CH_3)$ using various molar ratios and produced a series of comb-like random copolymers. With a high incorporation fraction of SM (over 95 mol%), side-chain crystallinity of the long stearyl groups supressed observation of the T_g. However, increasing ITA content within the copolymer chain helped separate the stearyl side-chains and decreased the crystallinity. As a result, the T_g of the copolymers was observable and ranged from 44 °C (15 mol% ITA) to 110 °C (85 mol% ITA). Subsequently, the authors reported post-polymerization ring-opening of the ITA moieties via hydrolysis and partial neutralization, yielding ionomers with T_g values 20–25 °C higher than the parent copolymers.[247] Mormann and Ferbitz copolymerized ITA with *tert*-butyl methacrylate (*t*BM) in butanone using AIBN.[248] The ITA-*t*BM copolymers exhibited M_n values in the range of 5,800–54,100 Da and T_g values between 116 and 137 °C, but with no report on copolymer compositions.

A few studies described the synthesis and polymerization of *N*-aryl itaconimides (itaconic acid imides), which can be prepared from ITA and primary amines via a net dehydration process.[249,250,251,252] In general, the itaconimide-based polymers exhibited significantly higher T_g values (220—238 °C) versus ITA polymers. Figure 7 summarizes structures and reported T_g values for various poly(*N*-aryl itaconimide)s, including poly(*N*-phenylitaconimide) (PPhI), poly(*N*-*p*-tolyl itaconimide) (PTII), poly(*N*-(*m*-chlorophenyl itaconimide), and poly(*N*-(*p*-chlorophenyl itaconimide).

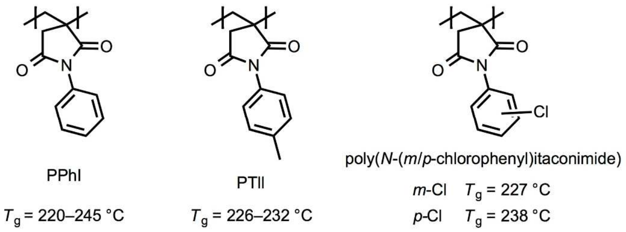
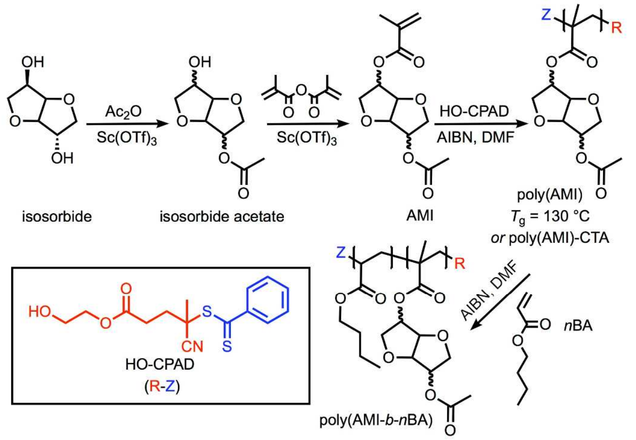


Fig. 7 Thermal properties of poly(*N*-aryl itaconimide)s.[249,250,251,252]

Moreover, copolymerization of *N*-aryl itaconimides with styrene[249] and MMA[250,251] showed significant enhancement of the PS or PMMA T_g as the *N*-substituted itaconimide incorporation increased. Finally, ABA triblock copolymers containing PPhI or PTII (hard terminal blocks) were synthesized by chain extension of pre-made, bifunctional poly(itaconic acid esters) (soft midblock) to provide thermoplastic elastomers; these showed two distinct T_g transitions (204–219 °C and -8–17 °C) attributable to micro-phase separation.[252]

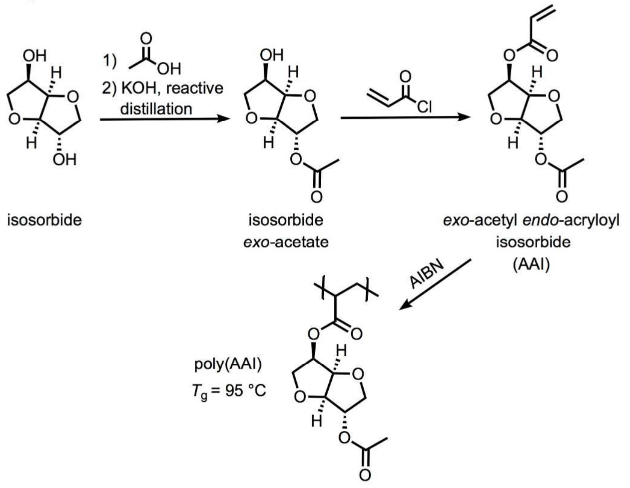
5.4. Isosorbide-based polymers

In a manner similar to lignin-based acrylate monomers (Scheme 45), isosorbide has been modified into radically polymerizable species by attaching appropriate functional groups. Reineke *et al.*[253] reported the synthesis and radical polymerization of acetylated methacrylic isosorbide (AMI) (Scheme 52). Isosorbide was mono-acetylated with acetic anhydride and a $Sc(OTf)_3$ catalyst; this occurred with partial stereoselectivity, yielding the *endo*-acetate stereoisomer over the *exo*-acetate in a 4.2:1 ratio. Therefore, subsequent methacrylation afforded two diastereomeric monomers, *endo*-AMI and *exo*-AMI. Conventional radical polymerization of these AMI stereoisomers afforded poly(AMI) with a high T_g of 130 °C, T_{d95} of 251 °C, and M_n of 88,900 Da ($Đ$ = 1.88). In order to study the effect of monomer stereochemistry on polymeric thermal properties, isomerically pure poly(*endo*-AMI) was prepared; differences were negligible between this and poly(*endo*-AMI / *exo*-AMI). Furthermore, the authors applied RAFT polymerization to AMI, thereby producing the macro chain transfer agent poly(AMI)-CTA (Scheme 52, R and Z end groups derived from HO-CPAD) with controlled M_n (14,000–31,000 Da) and T_g values in the range of 94–108 °C, proportional to the molecular weight. Exposure of poly(AMI)-CTA to *n*-butylacrylate (*n*BA) yielded diblock copolymers, which exhibited well separated T_g values corresponding to the poly(AMI) block (*ca.* 120 °C) and the poly(*n*BA) block (*ca.* -45 °C), indicating microphase separation.



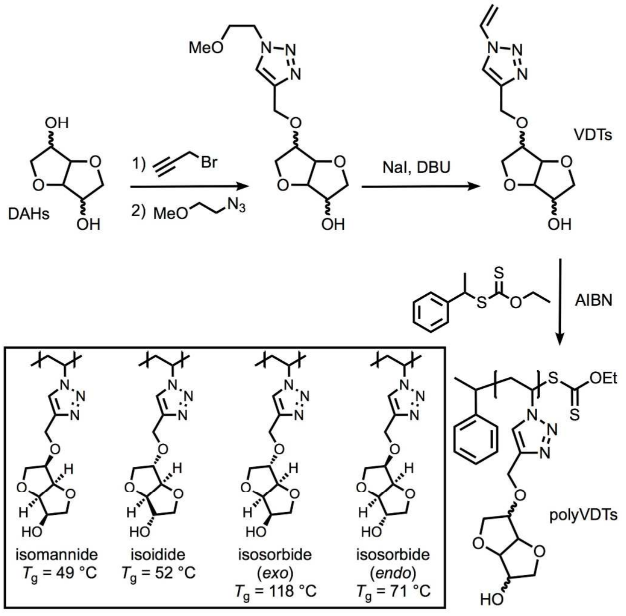
Scheme 52 Synthesis of poly(AMI) and poly(AMI-*b*-*n*BA).[253]

More recently, Reineke and coworkers synthesized and polymerized an acetylated acrylic isosorbide (AAI) monomer using conventional radical polymerization (Scheme 53).[254] Isosorbide was reacted with acetic acid to provide isosorbide *exo*-acetate, followed by acrylation to yield a single AAI stereoisomer, *exo*-acetyl *endo*-acryloyl isosorbide. Solution polymerization of AAI was conducted using AIBN to afford poly(AAI) with a high M_n of 120,000 Da ($Đ$ = 4), a T_g of 95 °C, and a T_{d95} of 331 °C.



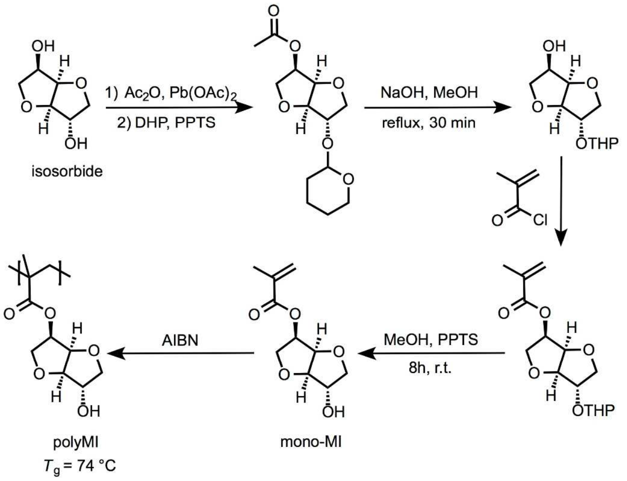
Scheme 53 Synthesis of poly(AAI) from isosorbide.[254]

Drockenmuller and coworkers described a route to synthesize vinyl triazole monomers of 1,4:3,6-dianhydrohexitols (DAHs), including isomannide, isoidide, and isosorbide based on click reactions (Scheme 54).[255] The four prepared 1-vinyl-4-dianhydrohexitol-1,2,3-triazole stereoisomers (VDTs) were polymerized via RAFT to provide a series of polyVDTs. Isomannide- and isoidide-based polymers showed similar T_g values in the range of 49–52 °C. In the case of polymers derived from *exo*- or *endo*-substituted isosorbide, interesting thermal results were observed. A drastically higher T_g (118 °C) was recorded for the *exo* stereoisomer versus the *endo* stereoisomer (71 °C). This difference is not readily explained since the *exo*-isosorbide stereoisomer presents a similar alcohol as the isomannide stereoisomer, rendering the nominal assumption of similar hydrogen bonding for these two polymers. Nonetheless, all four polyVDTs showed similar thermal stability with T_{d90} values in the range of 310–318 °C.



Scheme 54 Synthesis of polyVDT polymers derived from isomannide, isoidide, or isosorbide.[255]

Synthesis of mono methacrylated isosorbide (mono-MI) and its conventional free radical polymerization was reported by Mansoori *et al.*[256] Scheme 55 describes the reaction of isosorbide *endo* acetate with 3,4-dihydro-2H-pyran (DHP) in the presence of pyridinium *p*-toluenesufonate (PPTS) allowing the preparation of *exo* methacrylated isosorbide. Polymerization of mono-MI with AIBN yielded polyMI with a T_g of 74 °C and a T_{90} up to 168 °C.



Scheme 55 Synthesis of polyMI from isosorbide.[256]

5.5. Terpenes, terpenoids, and rosin acids

Terpenes, terpenoids, and rosin acids (Figure 8) are naturally occurring, hydrocarbon-rich molecules that can be extracted from various plants and trees.[257] Even though terpenes and terpenoids naturally possess unsaturation, relatively few reports about their direct radical polymerization have been made. Because of the usual substitution of their double bonds, such compounds prefer polymerization though a cationic mechanism.

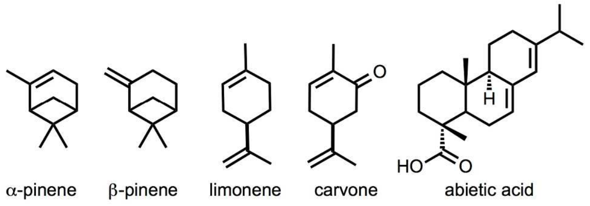
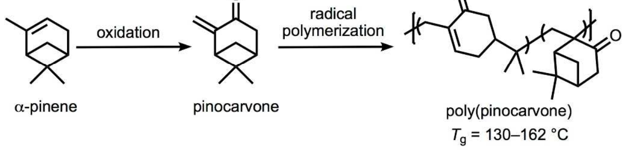


Fig. 8 Chemical structures of abundant terpenes, terpenoids, and a rosin acid.[257]

Singh and Kamal claimed that conventional solution polymerization of limonene gave a polymer with a T_g value of 116 °C.[258] However, no molecular weight data of the obtained polymer was provided. Satoh, Kamigaito, *et al.*[259] investigated the copolymerization of limonene with *N*-phenyl and *N*-cyclohexylmaleimide under conventional and controlled polymerization conditions. The 1:2 alternating copolymers displayed T_g values in the range of 220–250 °C with moderate molecular weights. More recently, Satoh, Kamigaito, *et al.* exploited a green conversion of (-)-α-pinene to a polymerizable monomer, (+)-pinocarvone, which owns an active external double bond.[260] Polymerization of pinocarvone was impacted by solvents, providing a series of polymers with various ring-opening : ring-retaining ratios (Scheme 56). In most cases, radical polymerization favored the ring-opening pathway over the ring-retaining pathway, which consequently increased the T_g of poly(pinocarvone), up to 162 °C. Exploiting the α,β-unsaturated ketone functionality of poly(pinocarvone), a post-polymerization thiol-ene reaction with *para*-toluenethiol was applied (with about 30% conversion) to vault the T_g up to 208 °C.



Scheme 56 Synthesis and radical polymerization of pinocarvone, occurring via both ring-opening and ring-retaining pathways.[260]

Methacrylate derivatives of terpenes are more obviously polymerized via free radical vinyl polymerization pathways. Recently, four novel methacrylated terpenes and terpenoids were synthesized as renewable monomers by Stockman, Howdle, *et al.*[261] Alcohol derivatives of α-pinene, β-pinene, and limonene were synthesized using a hydroboration/oxidation process, while carvone was reduced by $LiAlH_4$. After acrylation, the resulting monomers were subjected to radical polymerization using dodecanemercaptan (DDM) as a chain transfer agent in order to control the molecular weight of the polymers (Figure 9). Poly(α-pinene acrylate) exhibited a T_g up to 71 °C depending on its molecular weight. However, higher T_g values were observed for poly(α-pinene methacrylate)s in a range of 85–142 °C because of increased polymer backbone stiffening (greater conformational barriers) versus polyacrylate analogues. Poly(β-pinene methacrylate) showed a lower T_g value of 115 °C compared to poly(α-pinene methacrylate) with similar molecular weights—presumably because of the added flexibility (and increased free-volume) imposed by the methylene spacer. Finally, poly(carvone methacrylate) was found to have a T_g value of 117 °C.

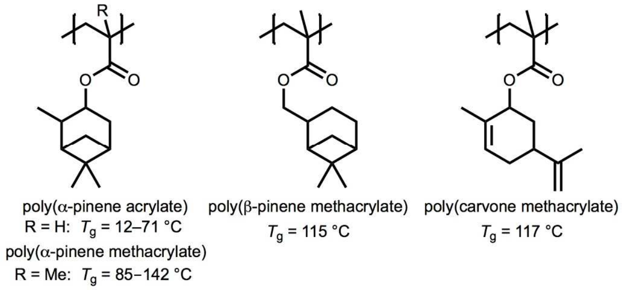
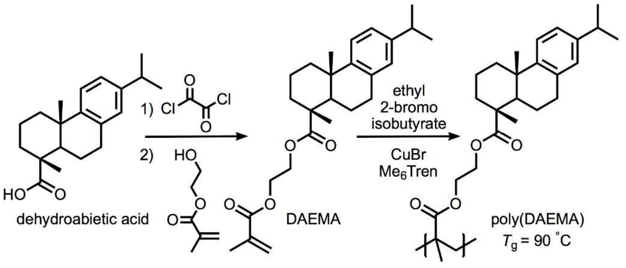


Fig. 9 Polyacrylate and polymethacrylates derived from α-pinene, β-pinene, and carvone.[261]

Tang *et al.*[262] have focused on a commercially available resin acid, dehydroabietic acid, which is obtained from crude and gum rosins (Scheme 57). The authors reported a synthesis of dehydroabietic ethyl methacrylate (DAEMA) from dehydroabietic acid in a high yield. DAEMA then was successfully polymerized using atom transfer radical polymerization (ATRP). The resulting polymer exhibited a relatively high M_n around 32,000 Da and a T_g of 90 °C.



Scheme 57 Synthesis of poly(DAEMA) from the gum rosin dehydroabietic acid.[262]

6. Conclusions and Outlook

The transition of polymer feedstocks from petrochemical to renewable resources is imperative considering the dwindling availability of these geological reserves, as well as growing concerns about environmental impacts associated with their use.[263] Fortunately, an increasing amount of research has been directed toward sustainable polymer synthesis during the last few decades. A library of natural, biorenewable resources[9,10] has been well constructed to provide not only diverse organic synthetic pathways and unique property discovery, but also development and application of bio-derived polymeric materials.

Amorphous polymers with high glass transition temperatures (T_g) attract special attention because of their wide-ranging applications—both short-term and long-term. T_g is the thermal transition from a hard and relatively brittle glassy state to a soft and rubbery state. Hence, polymers in these two states exhibit drastically different physical properties and the location of this thermal transition is critical to many applications. Based on all the efforts summarized in this review, four interrelated approaches were applied to fulfill the goal of achieving high polymeric T_g. First, incorporation of conformationally rigid components into the backbone, such as aliphatic or aromatic rings, is a rather effective and popular approach. Second, the structure of various side chain groups can be chosen to impart low chain mobility. Third, an increase in T_g usually results from introduction of high conformational barriers along the polymer backbone—for example, by introducing extra substituents or sp^2 hybridized carbons in the main chain. Fourth, augmentation of chain-chain interactions, which increases T_g, can result from the interaction of polar groups or hydrogen bonding groups.

Despite the great triumph in designing and synthesizing numerous polymeric materials with high biorenewability, only a small fraction of these have found commercial application. Various impediments exist to a more extensive adoption of bioplastics in the industrial realm. The main obstacle is cost and it will take more time for the biorefinery approach to catch up with the well-established petroleum industry that has developed highly optimized and scalable polymerization strategies over the course of about eight decades. Commodity polymers have been selected because of their low cost, but many believe that their "true" cost is heavily underestimated because of long-term, negative environmental impacts (*e.g.*, remediation costs).[264] Beyond cost factors, the true sustainability of bioplastics has been questioned and evaluated. Almost unavoidably, production processes have environmental impacts such as: extensive land usage; pollution from crop pesticides; high levels of energy and water consumption; and use of hazardous chemicals or additives.[265] Other challenges, including comparative performance of biobased polymers versus their petrochemical counterparts,[22] or competition of bioplastic feedstocks with our food supply, remain mostly unsolved.[266]

Still, the nascent field of bioplastics has made tangible progress including, for example, the production of partially/fully renewable commodity plastics (*e.g.*, plant bottle, or bio-HDPE), biorenewable polymers homologous with extant materials (*e.g.*, PEF as a replacement for PET), or biobased polymers with no true predecessors (*e.g.*, PLA). As time passes and technology accelerates, the quest for replacing incumbent commodity plastics with sustainable polymers from renewable resources will continue to flourish, aided by the dilemma of steeply rising demand for plastics and the imminent depletion of fossil fuels.

Conflicts of interest

There are no conflicts of interest to declare.

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Table of content text and graphic:

This review describes recent strategies for synthesizing polymers that are mostly or fully biobased and exhibit a high glass transition temperature.