Natural Product Reports

REVIEW

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Monomer design strategies to create natural product-based polymer materials

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In an effort towards enhancing function and sustainability, natural products have become of interest in the field of polymer chemistry. This review details the blending of chemistries developed through synthetic organic chemistry and polymer chemistry. Through synthetic organic chemical transformations, such as functional group interconversion, a protection/deprotection series, or installation of a functional group, various designs towards novel, synthetic, bio-based polymer systems are described. This review covers several classifications of natural products – oils and fatty acids, terpenes, lignin, and sugar derivatives – focusing on exploring monomers prepared by one or more synthetic steps.

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1. Introduction – the power of synthetic organic chemistry to transform materials science

In what has been coined as the age of scalability in organic chemistry,[1] the development of scalable transformations for natural products and their derivatives is more important than ever in materials science. The practicality of using functionalized natural products for polymerization is more of a reality as syntheses and isolation techniques become more concise. The ever expanding chemical toolbox of novel reactions is also powerful for monomer synthesis. Whether it is the synthesis of a natural product with inherent polymerizable groups from readily-available starting materials or the functionalization of an isolated compound, scalability is the key to creating sustainable society-enhancing polymeric materials. While this

review focuses on the functionalization of naturally-derived compounds, introducing sustainability in the syntheses of polymeric materials encompasses a vast scope of topics including greener solvents[2] or catalyst design.[3,4]

Implementing the use of natural products for the replacement of petrochemical-based monomers has the potential to decrease the dependence on fossil fuels and increase the number of material applications of more renewable resources. One way of expanding the content of natural products in polymeric materials is through the incorporation of bio-based materials and their derivatives as the monomer units. Bio-based materials are defined by the ASTM: "a material is an organic material in which carbon is derived from a renewable resource *via* biological processes. Bio-based materials include all plant and animal mass derived from CO_2 recently fixed *via* photosynthesis, per definition of a renewable resource".[5] Specifically, the introduction of bio-based materials leads to the potential to remove some petrochemical-based components and take advantage of the renewability of natural products. There are several examples of naturally-sourced monomers currently on the market, such as Coca-Cola natural sourcing part of the poly(ethylene terephthalate) in plastic bottle production.[6] In another example, the naturally-derived compound, isosorbide, is being utilized by Mitsubishi Chemical[7] in polycarbonate materials. Both academic and industrial research have made great strides in the area of bio-based materials, however, the myriad natural products generate boundless directions for the synthesis of polymeric materials.

Beyond the replacement of petrochemical-based materials, the synthesis of novel materials from natural products has the potential to yield novel reactions/methodologies, and ultimately

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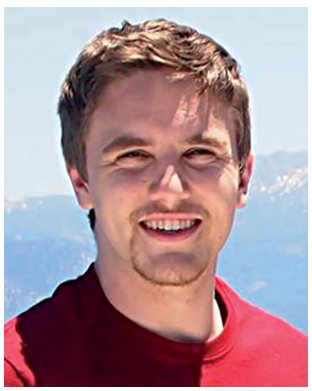

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lead to materials with emergent, unforeseen properties. The sheer chemical, structural, and stereochemical diversity of natural products compared to petrochemicals from which polymers are synthesized greatly lends itself toward the development of these potentially new processes and materials from bio-based sources. Designing bio-based monomers requires innovation to maintain high percentages of biomass in the materials, which can be introduced through developing new chemistry. For example, Hoye and co-workers explored the Diels–Alder (DA) reaction of itaconic anhydride with various furans through a study of the kinetic and thermodynamic properties of the reaction.[8] The compounds developed through this novel chemistry can later be utilized in the polymerizations of several different polymer classes.

Regardless of the rationalization for the use of natural products in materials science applications, each natural product is initially limited in its potential final application, as it only possesses the functionalities that are inherent to the compound. However, through synthetic organic chemistry, additional functionalities can be installed to afford a compound with vastly different structural and chemical functionalities for polymerization. Numerous reviews have recently discussed the incorporation of renewable resources in polymer science.[9–14] In a slightly different approach, this review will focus on the synthetic design applied to the monomer units towards polymerization. Herein, this review details the use of synthetic chemistry to transform molecules derived from four distinct sources: oils and fatty acids, terpenes, lignin, and sugars. These four sources of biomass occur on multi-ton scales, each allowing for convenient access to economically-relevant starting materials. Each category of monomer is of varying structural complexity, utilizing diverse chemistry types. This review has also been focused solely on natural products from oils, terpenes, lignin, and sugar derivatives, given that all types of natural product classes currently under investigation could not adequately be covered in one review. Several examples of other natural product classes that have not been discussed here include α-amino acids,[15,16] and cashew nut shell liquid.[17,18] While brevity is important to incorporate these natural products into polymer systems, the focus of this review is the explored chemistries that rely on one or more synthetic steps to the monomer of interest.

2. Oils and fatty acids

2.1 Introduction – oils and fatty acids

Approximately 120 billion tons of carbon in biomass, equivalent to 80 billion tons of crude oil, are generated annually by photosynthesis, of which only about 5% are used by humans. The annual global production of the major vegetable oils amounted to 176 million metric tons in 2014/2015, increasing to 178 million metric tons in 2015/2016, and projected to increase to 180 million metric tons in 2016/2017.[19] Oils have become important renewable raw materials of the chemical industry, due to their application possibilities,[20] such as in surfactants, lubricants, and coatings. Compared to industrial processing of oils, a key advantage of organic synthesis is the introduction of new functionalities, therefore, synthetic routes from natural oils to synthetic monomers can lead to new properties of the corresponding polymeric materials, to allow them to be utilized in demanding applications.

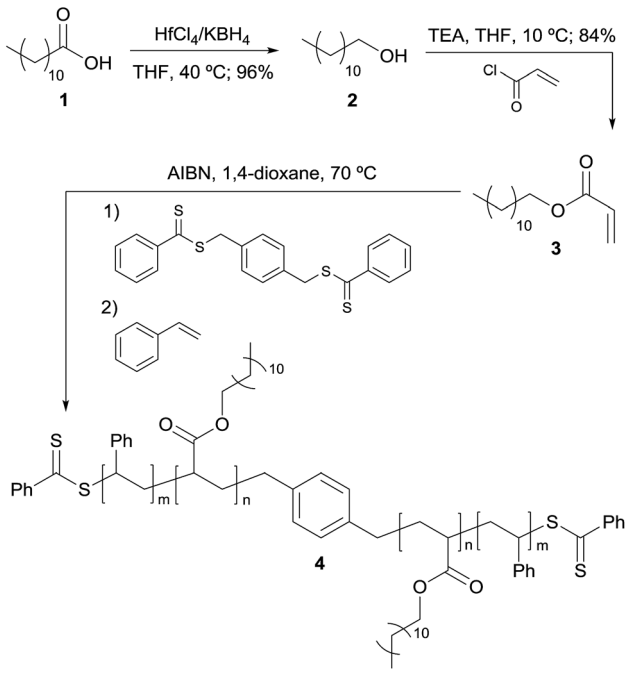
The main structural component of oils is triglyceride, which consists of glycerol and fatty acids,[21–24] and further functional groups in addition to the carboxylic and alkene groups of the fatty acids are desirable, for the aim of developing new monomers and decreasing the reliance on petrochemical sources. Hence, examples of chemical modification based on the carboxylic group and/or double bond of fatty acids that enables the synthesis of a variety of monomers for the development of polymers[25] will be discussed. Fatty acid composition depends on the source of oils (Table 1),[26] and they can be classified as saturated, monounsaturated, and polyunsaturated fatty acids. In this section, fatty acids from common natural resources such as soybean oil, linseed oil, ricin oil, and sunflower oil, will be given as examples for monomer design strategies. These naturally-existing fatty acids are introduced in an order from saturated fatty acids to monounsaturated fatty acids, and are further classified into functionalities for polymerization. Polyunsaturated acids for monomers and polymers then follow. In addition, a different strategy to undergo functional group transformation is included, which uses algae oil, a unique resource of "unusual" classes of fatty acids differing from high animals and plant organisms.

2.2 Saturated fatty acids

Saturated fatty acids are carboxylic acids with a long saturated aliphatic chain. Due to the lack of reactive functional groups on the saturated chain, chemical modification from saturated fatty acids to monomers has only been reported on carboxylic acid functional groups. An important class of thermoplastic elastomers, which is composed of linear ABA triblock copolymers such as poly(styrene-*b*-butadiene-*b*-styrene) and poly(styrene-*b*-isoprene-*b*-styrene), has been found to have limited oxidative stability because of the olefin bond in the midblock. Robertson and co-workers[27,28] explored fatty acid-derived long chain poly(*n*-alkyl acrylate)s as the midblock to overcome this deficiency.

Table 1 Fatty acid composition of different oils

Kind of oil	Saturated	Mono-unsaturated	Poly-unsaturated
Safflower oil	9	13	78
Sunflower oil	11	20	69
Corn oil	13	25	62
Olive oil	14	77	9
Soybean oil	15	24	61
Peanut oil	18	48	34
Sockeye salmon oil	20	55	25
Cottonseed oil	27	19	54
Lard	41	47	12
Palm oil	51	39	10
Beef tallow	52	44	4
Butterfat	66	30	4
Palm kernel oil	86	12	2
Coconut oil	92	6	2



Scheme 1 Synthesis of biorenewable thermoplastic elastomeric triblock copolymers from **1**.

Lauryl acrylate (**3**), which was synthesized from lauric acid (**1**) through reduction[29] and acylation (Scheme 1),[30] has been used for the development of biorenewable thermoplastic elastomeric triblock copolymer **4**.

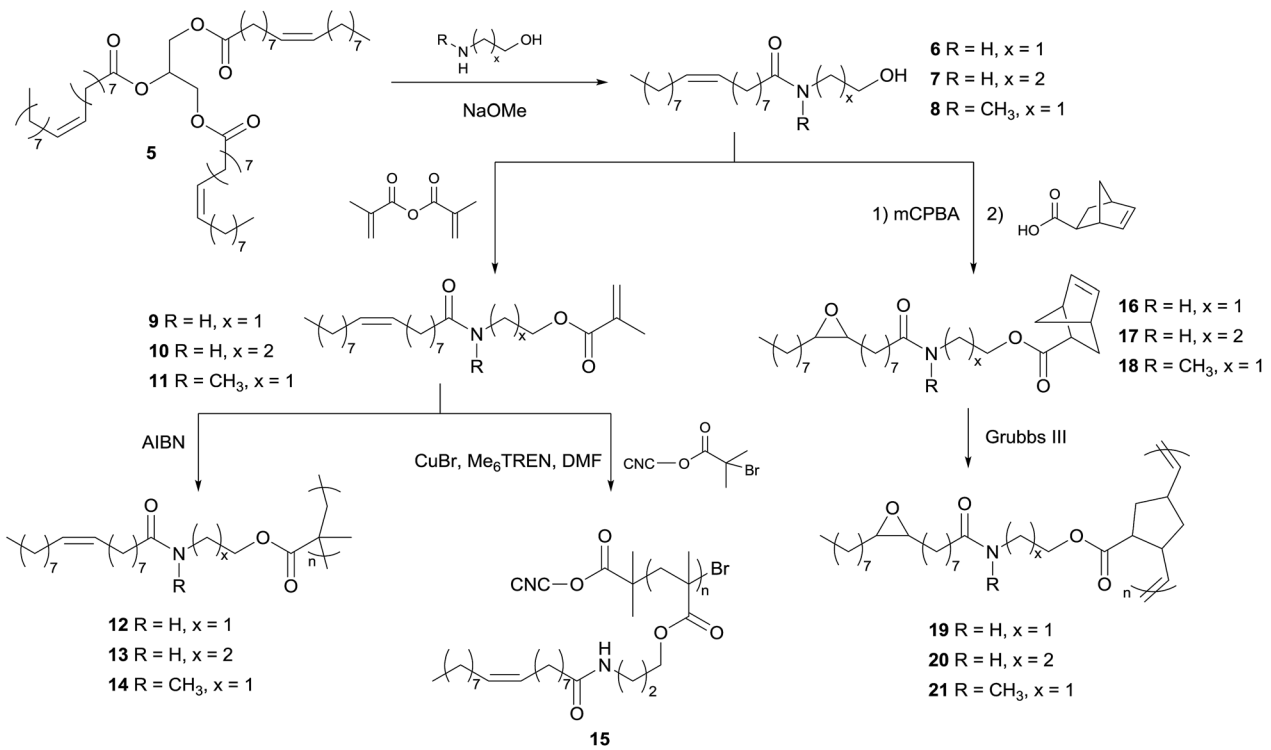
2.3 Monounsaturated fatty acids: polymerization through carboxylic acid-derived functional groups

Unlike saturated fatty acids, unsaturated fatty acids have one or more alkene moieties that undergo hydrogenation,[31] oxidation,[32] epoxidation,[33] polymerization,[34] and metathesis reactions.[35] Hence, selectivity of reactions for different functional groups should be taken into consideration in the monomer design strategies.

Amidation with amino alcohols[36] *via O–N* intramolecular acyl migration[37–39] is commonly explored for esters on triglycerides. Tang and co-workers[40,41] reported the use of several amino alcohols **6–8** as intermediates in converting oleic acid-derived triglyceride **5** into various polymers, **12–15** and **19–21**, with yields higher than 95% (Scheme 2). Polymerizations of methacrylates **9–11** were performed through free radical polymerization and atom-transfer radical-polymerization (ATRP), to prepare shape-memory polymers with cellulose nanocrystals (CNCs), without the aliphatic chain alkenes interfering, due to the formation of a stable radical on the methacrylate. In contrast, alkenes were protected for norbornene-based monomers **16–18** for ring-opening metathesis polymerization (ROMP) because metathesis can also take place on the aliphatic chain alkenes.

2.4 Monounsaturated fatty acids: polymerization through alkene-derived functional groups

Polyurethanes are typically made from polyaddition reactions between diols and diisocyanates.[42] Most investigations of fatty acids for polyurethanes involve the synthesis of polyols,[43] beginning with oxidation of the alkene on monounsaturated



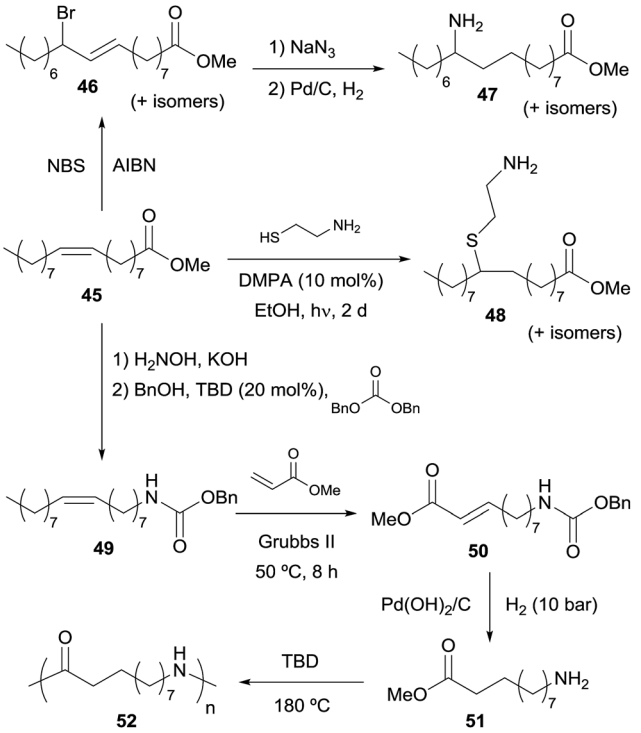
Scheme 2 Free radical polymerization, ATRP and ROMP of monomers derived from triglyceride **5**.

fatty acids. Cramail's group has investigated the synthetic pathway that transformed fatty esters **22–23** into diol monomers[44,45] **34–38**, **39–41**, and **43–44**, by utilizing an epoxidation reaction followed by ring-opening, or by thiol–ene click chemistry (Scheme 3).[46,47]

2.5 Monounsaturated fatty acids: polymerization through both acid- and alkene-derived functional groups

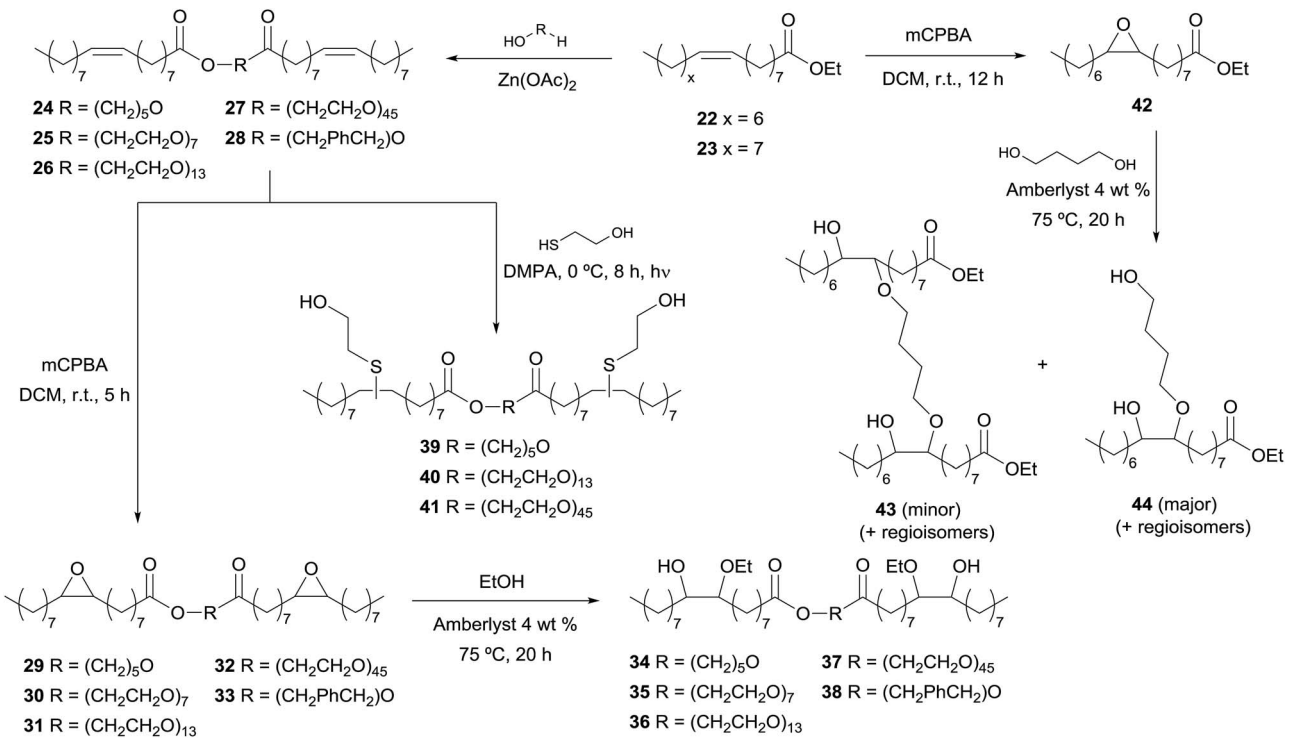
Exploiting both carboxylic acid and alkene moieties in monomer design diversifies the number and type of possible polymer structures that can be produced. Compared to polymerization on acid- or alkene-derivatives only, there are more examples taking advantage of both functional groups, and they will be introduced in an order of polymer types (*i.e.*, polycarbonate, polyurethane, *etc.*).

Introducing amide bonds in the synthesis of polyamides from fatty esters was achieved by modifying the unsaturated aliphatic chain into an amine, followed by the condensation of the amine with an ester. Meier's group[48] has demonstrated the use of thiol–ene reaction between aminoethanethiol hydrochloride and various monounsaturated fatty esters, such as methyl oleate (**45**) to afford eight different polyamides including **48**, with a number average molecular weight (M_n) up to 19.2 kDa (Scheme 4). Another amination route by a Wohl–Ziegler bromination, followed by reductive amination was also reported to give **47**.[49] Besides alkene chemical modification, the ability to install a carbamate functionality on the esters yielded **49**, which was reduced to amine **51** by a Lossen rearrangement, and produced polyamides (**52**)[50] in a polycondensation reaction with M_n up to 22.6 kDa.

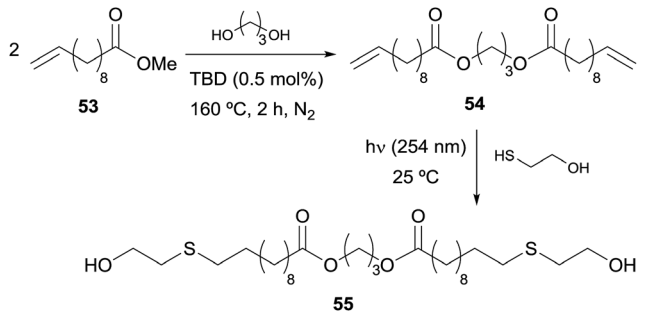


Scheme 4 Selected examples of amination from **45** to polyamide **52**.

Cramail and co-workers have reported the synthesis of bio-based diols and diisocyanates from fatty esters. For example, diol **55** from methyl 10-undecenoate (**53**) was achieved through dimerization with 1,3-propanediol followed by thiol–



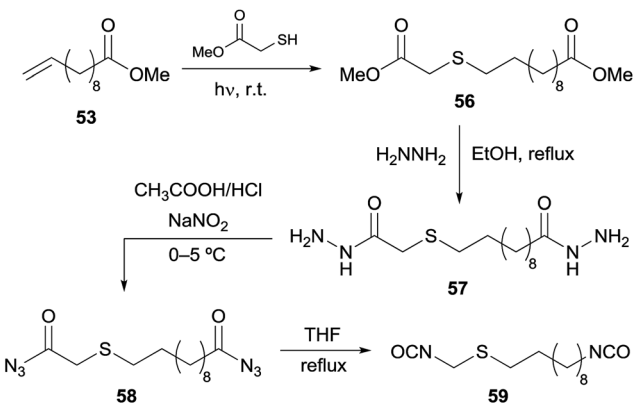
Scheme 3 Synthetic routes to various diols for the synthesis of polyurethanes from monounsaturated fatty esters.



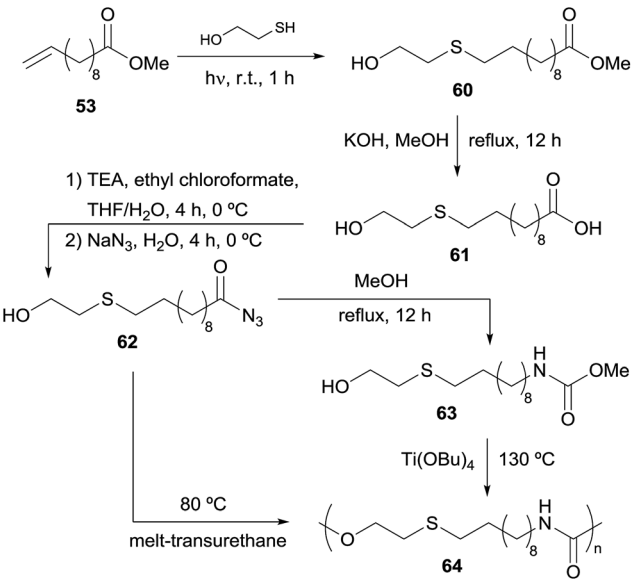
Scheme 5 Synthetic pathway to diol-containing ester from **53** and 1,3-propanediol.

ene click chemistry (Scheme 5),[51] while a diisocyanate from **53** was made through Curtius rearrangement of dicarboxylic azide (Scheme 6).[52] Synthesis of AB type monomers containing alcohol and isocyanate functionalities that self-condense into polyurethanes **64** from **53** was performed *in situ* through a melt-transurethane method, and stepwise from carboxylic azide **62** (Scheme 7).[53] However, isocyanates, which are often directly produced from the corresponding amine and phosgene, are considered to exhibit high reactivity and toxicity, thus demanding safety precautions.[54] The Long (Scheme 8) and Cramail groups (Scheme 9) worked on the scalable production of polyurethanes from the reaction of diamines and cyclic carbonates, **67**, **74–76**, and **78–79**,[55,56] which utilized carbon dioxide as a feedstock and eliminated the use of isocyanates.

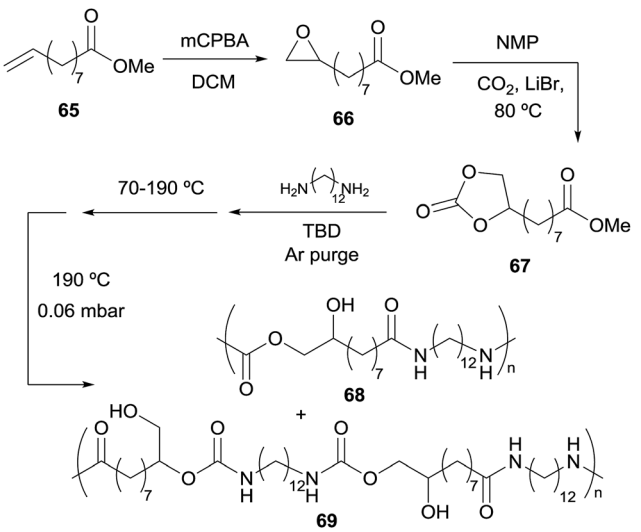
After more than 90 years, since the first isonitrile-based multicomponent reaction to obtain 1-(alkyl carbamoyl)alkyl alkanoates in 1921,[57] the Passerini three-component reaction and the Ugi four-component reaction still play important roles in combinatorial chemistry for natural product synthesis.[58] Recent examples were reported in synthesizing polyolefins through acyclic diene metathesis (ADMET) from **83–85** and **86–88** by Meier and co-workers (Scheme 10). Synthesis of acyclic dienes was also achieved from aldol condensation,[59] and such reactions yielded flame-retarding



Scheme 6 Synthetic pathway to diisocyanate-containing ester from **53** *via* Curtius rearrangement.



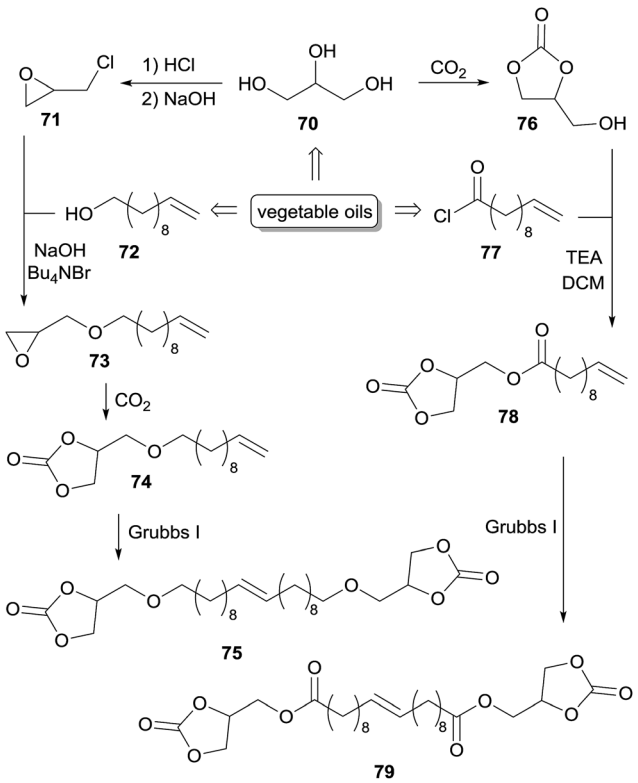
Scheme 7 Synthetic pathway to AB type monomers for polyurethane syntheses from **53**.



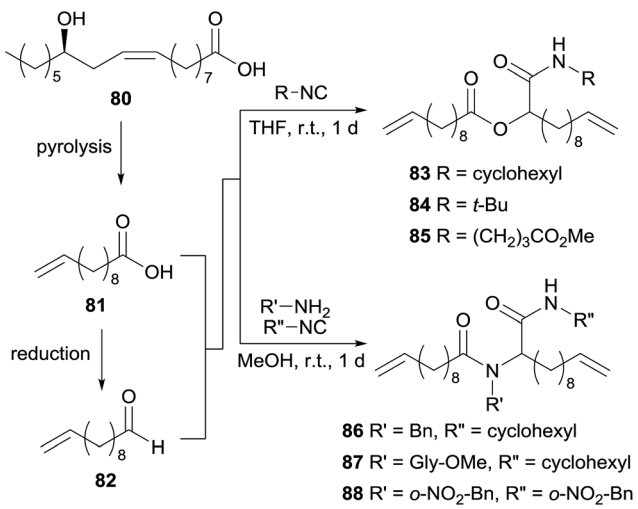
Scheme 8 Isocyanate-free syntheses of polyurethanes from **65**.

materials by a collaboration between the Meier and Ronda groups.[60]

The thioether functionality in polythioethers allows for the synthesis of polymers with similar structures to existing bulk and engineering plastics. Oxidation by hydrogen peroxide into sulfone linkages results in polysulfones. Du Prez and co-workers demonstrated a series of reactions to transform 10-undecenoic acid (**81**) into thiol **92** (Scheme 11), which was self-polymerized into polythioethers *via* thiol–ene chemistry.[61] Instead of using a protection/deprotection route, the Du Prez group developed a strategy based on thiolactone precursors **94**, which underwent polyaddition to give **95–102** in a one-pot preparation (Scheme 12).[62]



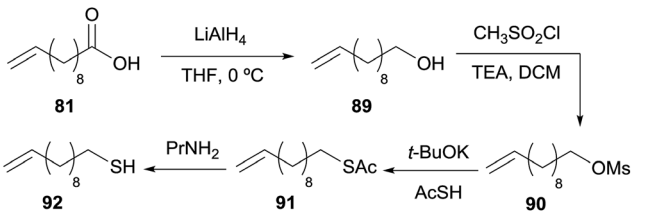
Scheme 9 Isocyanate-free synthesis of polyurethane monomers from the use of both glycerol and fatty acid derivatives.



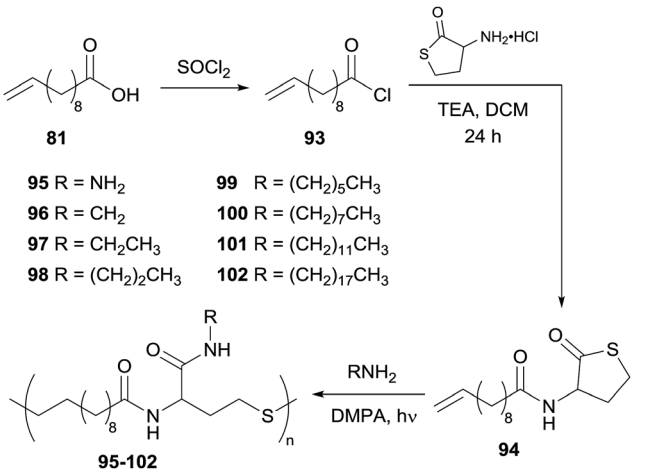
Scheme 10 Selected examples on preparation of monomers for utilization in multicomponent Passerini and Ugi reactions for ADMET polymerization.

2.6 Polyunsaturated fatty acids

Polyunsaturated fatty acids are fatty acids with more than one alkene on the aliphatic chain. Olefin metathesis that reacts multiple olefin bonds can serve as a unique way to functionalize polyunsaturated fatty acids. For example, 1,4-cyclohexadiene (**104**) was derived from the self-metathesis of linoleic acid (**103**),



Scheme 11 Transformation of **81** into thiol **92** for the synthesis of polythioethers.



Scheme 12 One-pot stepwise photopolymerization from **81** using thiolactone as precursor of thiol.

and it was further synthesized into 1-cyclohex-2-enone (**106**) for polyamides **119–121** *via* Beckmann rearrangement,[63] and cyclohexene oxide (**122**), as well as 1,4-cyclohexadiene oxide (**122**) for polycarbonates **124–125** *via* selective biphasic reduction (Scheme 13).[64,65]

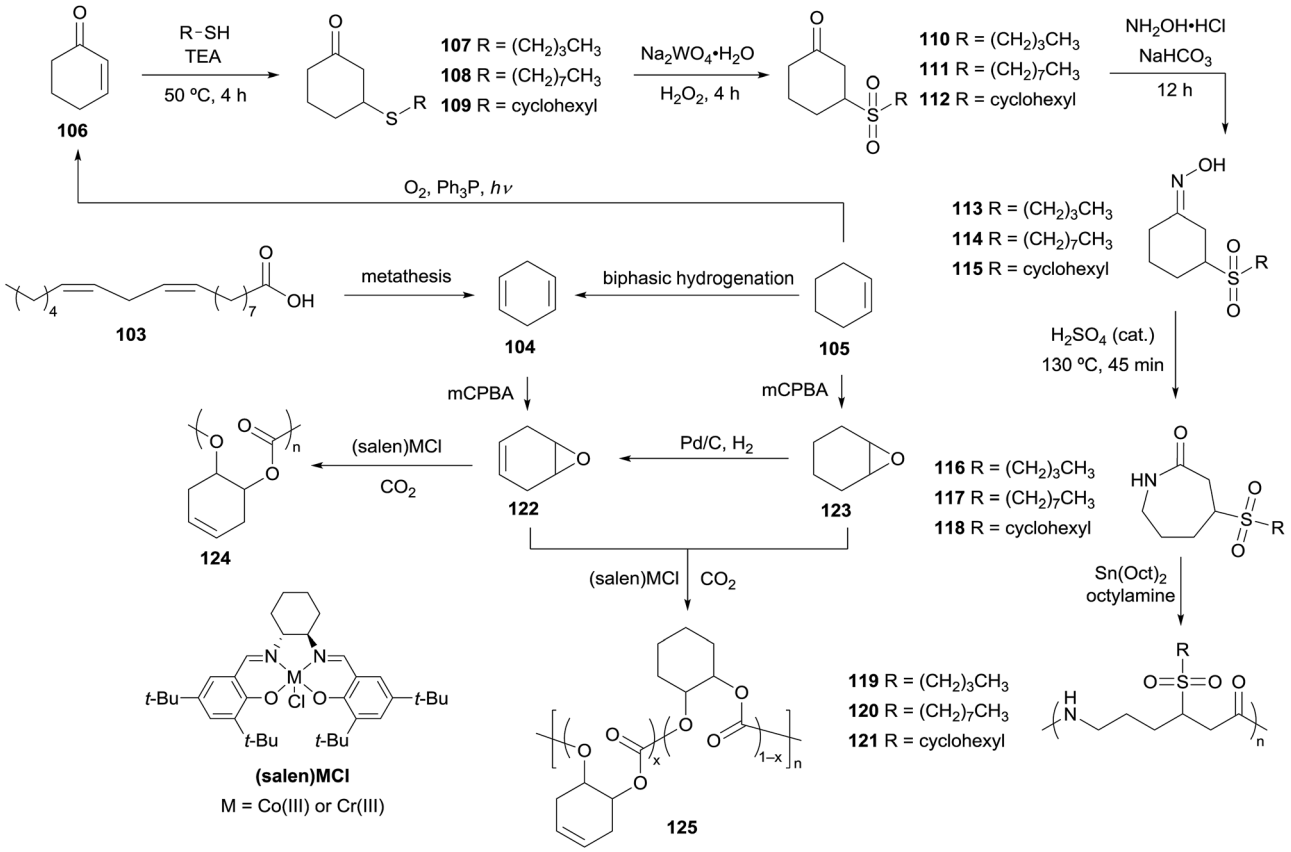
2.7 Algae oil

In contrast to plant oils, algae oils do not contain fatty acids primarily in the form of triacylglycerides, but rather as diacylglycerides **126** substituted with polar substituents such as phosphate groups on the third hydroxyl moiety of glycerol. Efforts of using algae oils industrially comprise deoxygenation, pyrolysis, and gasification, to produce hydrocarbons. In order to make algae oils into useful monomers, the Mecking and Kroth groups have demonstrated the use of a Pd catalyst[66] in alkoxycarbonylation isomerization in the presence of carbon dioxide and methanol, to eliminate the polar substituents and yield the corresponding diesters **127–128** and diols **128–130** (Scheme 14),[67] which were polymerized into polyesters **131–132** *via* polycondensation.

3. Terpenes

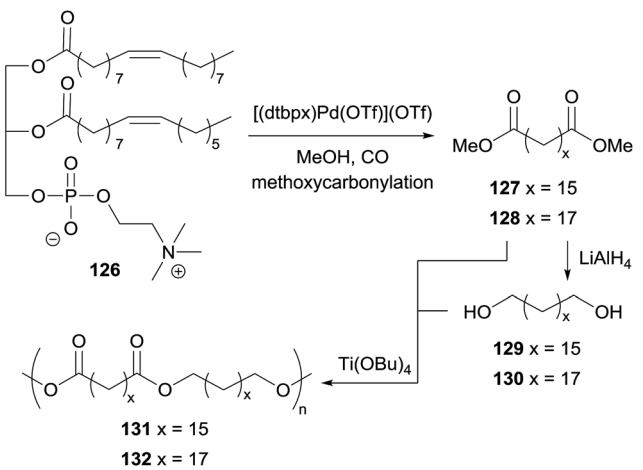
3.1 Introduction – terpenes

Terpenes, terpenoids, and rosin are hydrocarbon-based molecules with one or more isoprene (2-methyl-1,3-butadiene) units



Scheme 13 Polyamides and polycarbonates from **104**, a metathesis product of **103**.

that comprise the largest single group of natural products.[68] Biosynthesis (typically from mevalonic acid) can lead to structurally-diverse materials with few isoprene units (*e.g.* monoterpene) to many (*e.g.* polyterpene), as well as those with various oxygen-containing moieties, sometimes referred to as terpenoids. Terpenes have been industrially important for years, particularly in the fine chemical and fragrance industries. As such, several common methods are known for obtaining terpenes. The most common terpenes are isolated either directly from natural sources, such as in the extraction of turpentine from conifer resin – which yields α- and β-pinene and rosin – or indirectly as by-products from industrial processes, as in the citrus fruit industry (limonene), or through more cost-effective catalytic industrial synthetic processes (α-terpineol, camphor).[69] The terpenes mentioned above are only a fraction of the important terpene building blocks produced for use in pharmaceutical, fragrance, solvent, and chiral catalysis applications. Recent research efforts have focused on developing synthetic methodology for the functionalization and chemical diversification of terpenes, among other natural products.[70–73] As most of the industrial processes and applications for terpenes in their current form are thoroughly developed, introducing terpenes into new markets could be highly advantageous – common market entry barriers for natural products, such as reaching economies of scale, high research and development costs, or set up costs for obtaining the raw material, in this case, terpenes, have been significantly reduced.



Scheme 14 Approach from algae oils to diesters and diols for polycondensation to polyesters (dtbpx = 1,2-bis((di-*t*-butylphosphino) methyl)benzene).

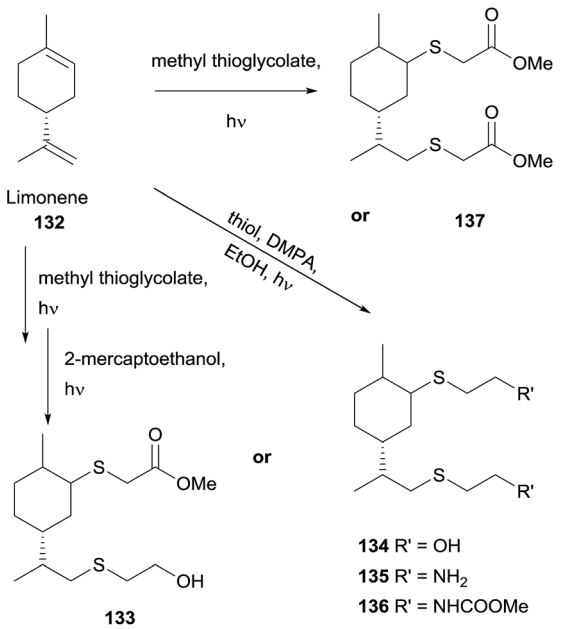
Besides the use of terpenes for small molecule applications, there is interest in terpenes for polymeric materials. Currently, several industrially-relevant polymerization processes are known, which take advantage of widely abundant terpenes, *e.g.* the cationic polymerization of α-pinene for adhesives, coatings, and inks.[74] Because these structurally diverse and renewable small molecules can be obtained on large scales, there have

been increasing numbers of reports in recent years that have focused on the design and chemical transformation of terpenes into new, renewable monomers. Several examples that illustrate the chemical versatility of monomers derived from limonene, pinene and other common terpenes are elaborated here; interested readers may be directed to the synthesis of terpene-based polymers, including thermosets and highly crosslinkable materials discussed in other recent reviews.[75,76] The terpenes in this review, have been chosen largely based on the scale on which they are currently produced (but typically not used in polymer applications), or based on new developments with interesting chemistries.

3.2 Limonene

While terpenes naturally contain alkene moieties that can polymerize by cationic or free radical methods, these direct methods have proven difficult and lack control. Typically, direct polymerizations have relied on commercially non-viable methods and did not yield well-defined, high molecular weight polymers, on account of differing reactivity and steric hindrance of the endocyclic *vs.* exocyclic double bonds.[11] However, a recent report has shown β-pinene, with an exocyclic double bond can yield high molecular polymers *via* living cationic polymerization with $EtAlCl_2$.[77] To overcome the difficulties associated with direct polymerization of terpenes, a recent strategy has relied on functionalization of the alkene moieties so as to produce chemically- and structurally-diverse monomers, which are more amenable to polymerization. In the case of limonene, the presence of both an endocyclic and exocyclic alkene has led to development of regioselective chemical functionalizations to obtain monomers, particularly through thiol–ene reactions. In 2011, Firdaus *et al.* reported sequential addition of methyl ester- and alcohol-appended thiols to limonene (**133**), taking advantage of the difference in reactivity between the internal and terminal olefins.[78] These heterobifunctional monomers were produced without need for solvent or radical initiator and were subsequently reacted with organocatalyst, TBD, under reduced pressure and heat to afford limonene-based polyesters with M_n up to 10.5 kDa and $T_g \approx 10$ °C (Scheme 15). This work was expanded for the generation of renewable polyamides and polyurethanes from monomer produced through the same thiol–ene functionalization approach, **135–138**.[79] In addition, the polyurethanes were prepared successfully while avoiding use of isocyanates and polymer properties were readily tuned through judicious choice of a comonomer. One strength of this chemistry is that any thiol small molecule may be appended to limonene to create a bifunctional monomer in few steps and generally high yields, owing to the nature of thiol–ene click chemistry.

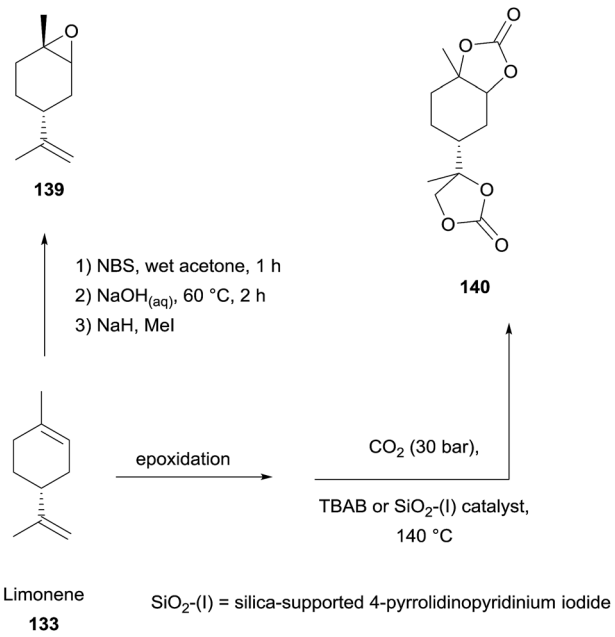
In addition to thioether-functionalized limonene, there has been much interest in the epoxidation of limonene, followed by conversion into poly(limonene carbonate) and other limonene oxide-derived polymers as sustainable replacements for current petroleum-derived polycarbonates or polyurethanes, due to interesting thermomechanical and physical properties, *e.g.* $T_g =$ 110 °C.[80–83] In regards to poly(limonene carbonate), however,



Scheme 15 Limonene thioether-based monomers produced with thiol–ene chemistry for polyester, polyamide, and polyurethane materials.

direct polymerization from commercial sources is limiting, as limonene oxide contains impurities that may inhibit formation of high molecular weight polymers and both diastereomers, *cis*- and *trans*-limonene oxide, are present. The latter fact is problematic given typical catalyst preference for incorporation of *trans*-limonene oxide.[80] One major step forward in producing a regio- and stereoselective *trans*-limonene oxide (**139**) with few impurities came from Hauenstein *et al.*[84] Starting from limonene, limonene oxide was produced on a kilogram scale through electrophilic bromination, bromohydrin formation, and subsequent ring closure to generate the epoxide in a batch reactor in an overall yield of 72% (Scheme 16). Although the synthesized monomer contained fewer impurities than commercial sources, it was further purified through an *O*-alkylation and concomitantly dried. This procedure allowed for large-scale synthesis of low polydispersity poly(limonene carbonate) with the highest molecular weights reported to date (M_n = 109 kDa). In a similar fashion, the cyclic limonene dicarbonate (**140**) has been produced using both hetero- and homogeneous catalysts from commercially-available limonene dioxide to afford non-isocyanate polyurethanes from the reaction with multifunctional amines.[85]

As mentioned, terpenes do not easily homopolymerize by free radical or cationic methods. Previous work has focused on synthetic methods toward limonene derivatives that may prove more amenable to free radical polymerization.[86,87] Recently, the Howdle and Stockman groups developed a new approach by installation of acrylate moieties, which have well-known chemistry.[88] The general method allows for functionalization of several monocyclic terpene monomers from limonene, carvone, and α- and β-pinene. In the case of limonene, the two step hydroboration/oxidation and esterification synthesis to the

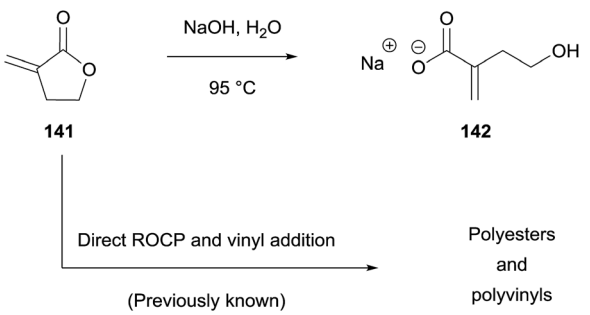


Scheme 16 Synthetic pathways to limonene carbonate monomers and their polymers.

monomer produced a 1 : 1 mixture of diastereomers. The (*R*)-(+)-limonene acrylate polymer, while thermally stable (≈400 °C), had a substantially lower T_g to the terpene counterparts studied (−5 °C *vs.* ≥70 °C or higher).

3.3 Tulipalin A

Tulipalin A, or α-methylene-γ-butyrolactone (**141**), is a well-known renewable monomer in research settings that is used in direct polymerizations by radical, anionic, and metal complexation methods through its exocyclic double bond,[89–91] as well as through ring-opening copolymerization (ROCP) of the five-membered lactone.[92] Recently, Kollár *et al.* reported the radical polymerization of the ring-opened salt of tulipalin A, sodium 4-hydroxy-2-methylenebutanoate (**142**).[93] While post-polymerization saponification of a copolymer containing tulipalin A has been reported for the generation of superabsorbent materials,[94] the ring-opening first approach (Scheme 17) followed by copolymerization with acrylamide and amine cross-linker allowed for superior polymer swelling and handling properties.



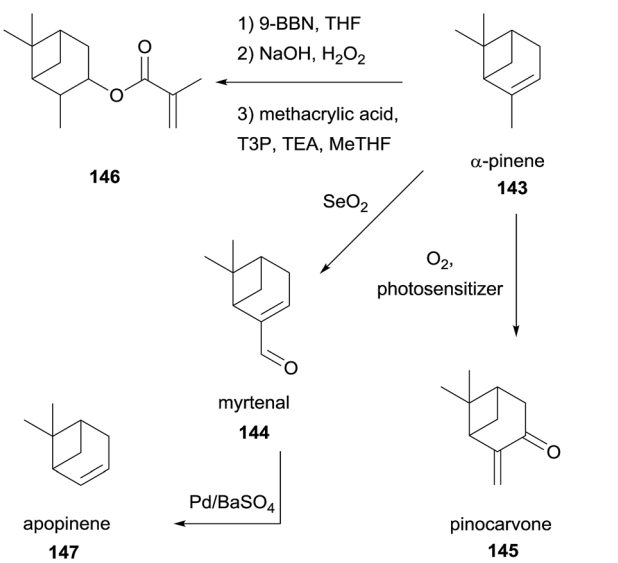
Scheme 17 Synthesis of a tulipalin A-based monomer.

3.4 Pinene

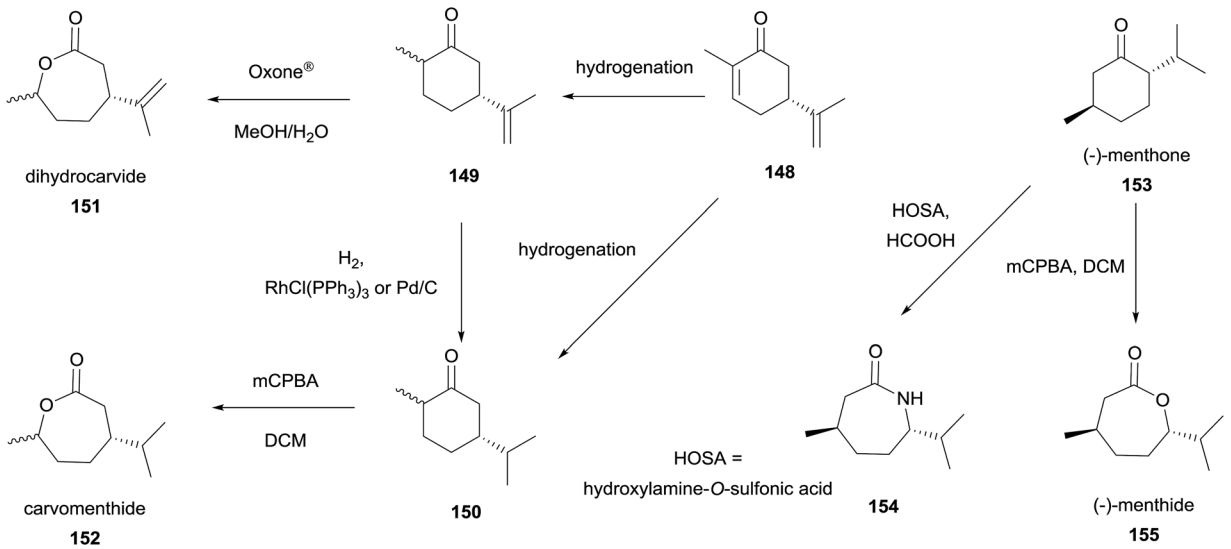
As pinenes are the most abundant monoterpenes in Nature, the simple chemical transformation of these terpenes into readily polymerizable monomers is quite desirable. Acrylate moieties may be installed, **146**, using stoichiometric or catalytic reagents and, subsequently, polymers with large ranges of glass transition temperatures and other properties are possible, *e.g.* α-pinene acrylate/methacrylate, 12 < T_g < 142 °C.[88] Using free radical polymerization methods, Miyaji *et al.* reported the synthesis of high molecular weight polyketones from the α-pinene-derived pinocarvone (**145**) obtained *via* visible-light photooxidation with singlet oxygen.[95] In a different approach, ROMP-amenable monomer, apopinene (**147**), was synthesized from α-pinene through an allylic oxidation and decarbonylation sequence (Scheme 18).[96] Although α-pinene cannot engage in ROMP, the synthesis of an apopinene-based polymer by ROMP was possible, due to reduced steric hindrance and higher strain enthalpy of the apopinene monomer.

3.5 Carvone and menthone

Carvone (**148**) is found in several oils and produced on scales of 10^4 metric tons per year.[97] Reduction of carvone yields several natural products, such as dihydrocarvone (**149**) and carvomenthone (**150**), which have been studied as starting materials for the production of polyesters and polyamides (Scheme 19). Seminal work by Lowe *et al.* provided mild procedures to the lactone, dihydrocarvide (**151**), as well as carvomenthide (**152**) using either Oxone® or mCPBA.[98] Polyesters were produced in bulk at elevated temperatures and post-polymerization functionalization was possible in the case of poly(dihydrocarvide) by epoxidation or radical crosslinking. Since this report, well known Baeyer–Villiger oxidations have been used to synthesize

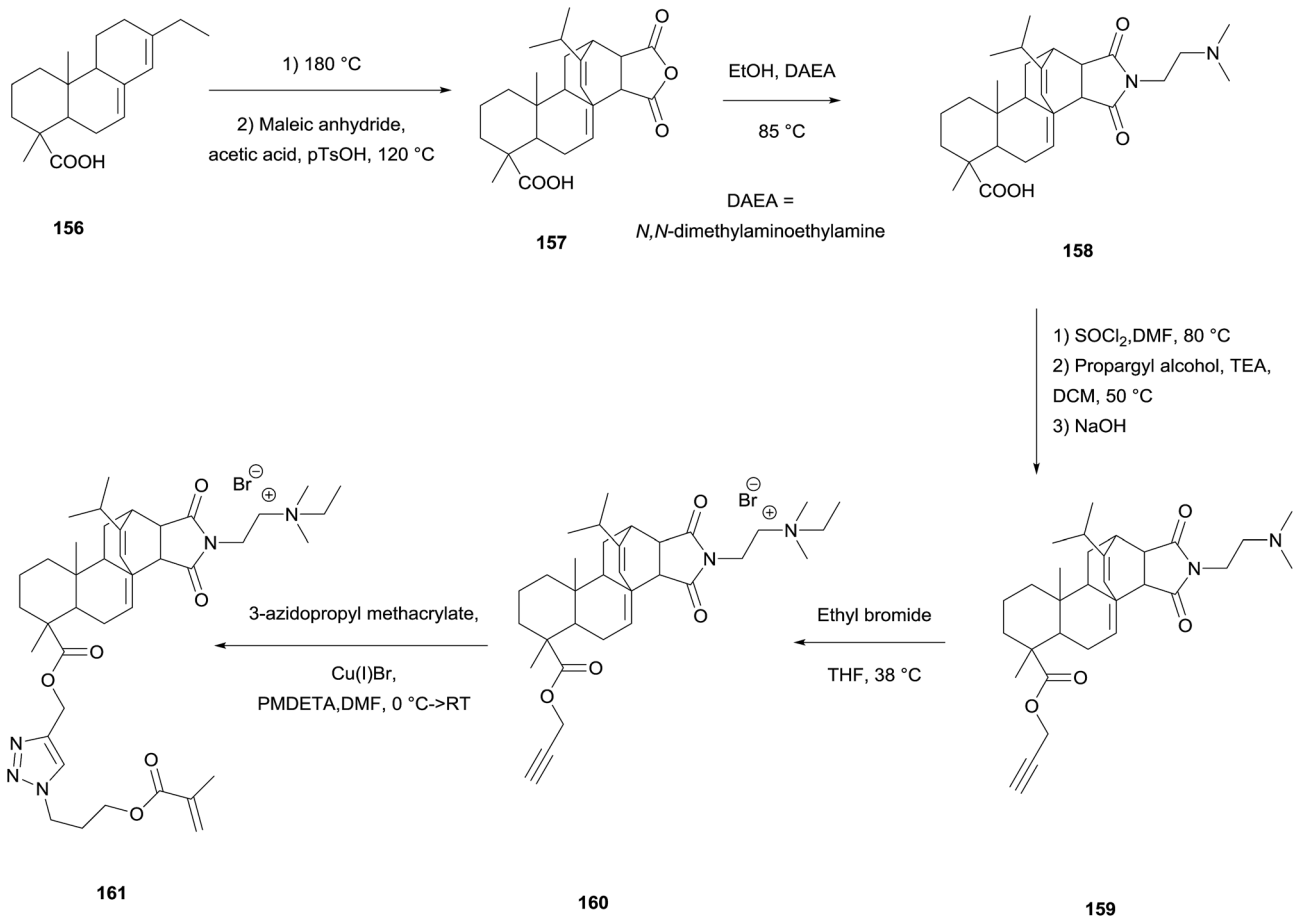


Scheme 18 Monomers produced from α-pinene.



Scheme 19 Synthesis of monomers from carvone and menthone through reductions, oxidations and rearrangements.

carvomenthide (**152**) and its regioisomer, menthide (**155**), which are suitable monomers for thermoplastic or thermoset elastomers, as well as for use as pressure sensitive adhesive materials.[89,99,100] As opposed to polyesters, the Rieger group has extensively investigated the synthesis of lactams from menthone (**153**) to produce polyamides *via* anionic and cationic ROP



Scheme 20 Synthesis of a methacrylate functionalized resin acid monomer for use in an ATRP polymerization.

methods. Original synthetic procedures required two steps to produce regioisomeric lactams from menthone *via* oxime formation and Beckmann rearrangement.[101] Subsequent work has improved in the use of a regioselective one-step synthesis of the lactam, **154**, using hydroxylamine-*O*-sulfonic acid.[102,103] Although there are several attractive features of the resulting polyamides, such as green synthetic procedures, high melting temperatures, and chirality, currently only low molecular weight oligomers have been synthesized.

3.6 Resin acids

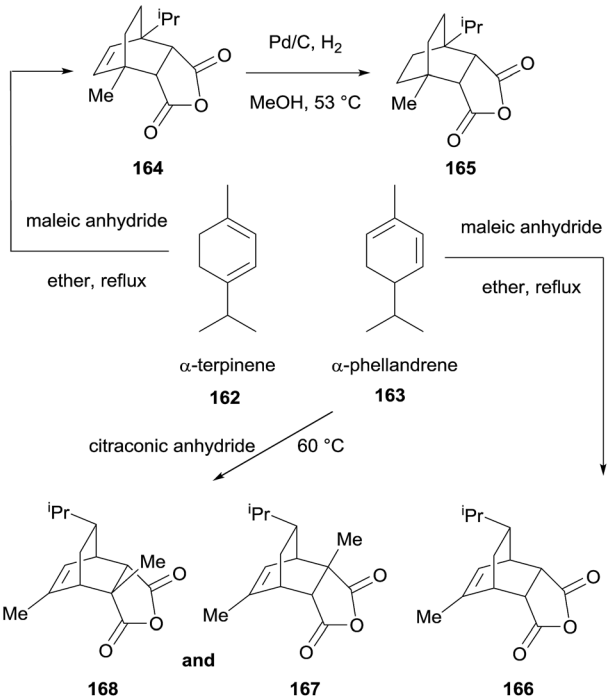
Crude rosin and gum rosin are produced on scales greater than 1 million tons annually and are good sources of resin acids, such as abietic acid and dehydroabietic acid. These low-cost natural products have been used in antifouling, adhesive, and ink applications.[104] Recently, several groups have further developed new rosins through various functionalization approaches towards polymers for antimicrobial and antifouling applications, as well as for use in xerographic toner and shape memory applications.

In particular, the Tang group has reported several monomers based on dihydroabietic acid, a gum rosin material, which has been functionalized with acrylates through esterification of the natural product.[105,106] Quaternary ammonium salts based on poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMAEMA) and a pendant dihydroabietic ester moiety have been realized in decent yields and gram scales for the generation of cationic, rosin-based antimicrobial materials *via* ATRP. More recently, abietic acid-based quaternary ammonium-modified monomer precursor (**160**) was synthesized on a 100 g scale in four steps with no column chromatography purification required and in 47% total yield.[107,108] The alkyne-functionalized resin acid was then coupled to 3-azidopropyl methacrylate in good yields (Scheme 20) on multigram scales to generate a methacrylate monomer (**161**) that was subsequently polymerized by ATRP. Other alkyne-functionalized acids have similarly been used in grafting-to approaches for antimicrobial polymers.[109]

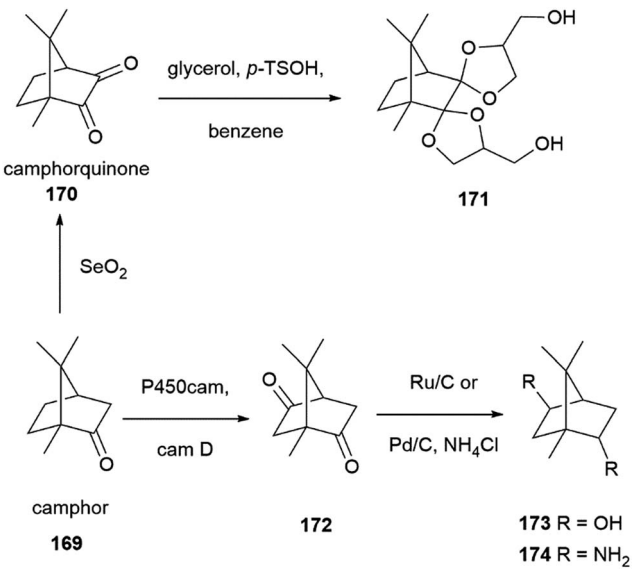
In other reports, a diol rosin monomer was synthesized from rosin maleic anhydride in three steps after a rosin imidodicarboxylic acid chloride was coupled with ethylene glycol. The diol was then incorporated as a hard segment in shape memory polyurethanes.[110] Sacripante and co-workers demonstrated a simple, economical method for functionalizing dehydroabietic acid to a diol rosin for the generation of polyester resins. Reaction conditions were screened leading to a solventless, one-pot, two-step reaction to produce the desired rosin monomer.[111]

3.7 Terpinene and phellandrene

The DA reaction of conjugated terpenes has been used previously in a number of applications, both synthetic- and polymer-related.[112–116] The Coates group has developed several DA-adducts from the reaction of α-phellandrene and α-terpinene with maleic anhydride (Scheme 21) for use in copolymerization of tricyclic anhydrides and propylene oxide with metal salen catalysts.[117,118] Terpene-based monomer structure and catalyst electronics had effects on undesirable transesterification side reactions and thermal properties of resulting polymers. Recent work has further



Scheme 21 Tricyclic anhydride monomers, derived from terpenes *via* DA approaches, used in polyester copolymers.

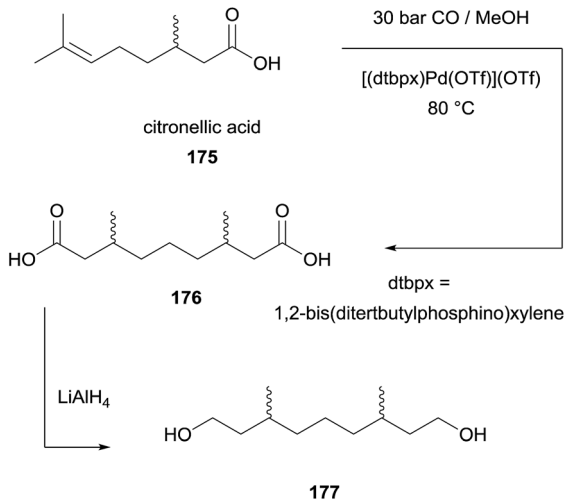


Scheme 22 AA monomers from chemical and biological transformations from camphor.

developed 100% renewable monomers from the DA reaction of α-phellandrene and citraconic anhydride (**167** and **168**) in addition to incorporation of cyclohexene oxide as a comonomer.[119]

3.8 Camphor

Camphor, like most terpenes, is a readily available terpene but does not contain much chemical functionality that allows for the direct synthesis of renewable polymers. One derivative,



Scheme 23 Citronellic acid derived diol for the synthesis of linear polymers.

camphorquinone (**170**), may be obtained from natural sources or, more readily, through SeO_2 oxidation of camphor.[120] A diol monomer may then be used in polycarbonate synthesis after cyclic ketal formation with glycerol in the presence of an acid catalyst (Scheme 22).[121] Notably, the monomer (**171**) is fully bio-based and polymerized without the need of solvent to yield polycarbonates with $T_g = 128$ °C. Biocatalytic methods are also known to yield a diketobornane regioisomer (**172**) of camphorquinone that is reduced to either a diol or diamine, **173** or **174**, with carbon-supported metal catalysts.[122] These monomers may be promising for the chemically divergent syntheses of polyesters, polycarbonates, and polyamides.

3.9 Linear terpenes

Other reports on the chemical modification of terpenes that do not fit into the above categories exist. Citronellic acid (**175**), a product obtained *via* direct oxidation of citronellol, has been shown to dimerize through an isomerizing methoxycarbonylation reaction (Scheme 23).[123] The diester (**176**) may be reduced to the diol (**177**) with lithium aluminum hydride for the polymerization of the bifunctional monomers.

Hillmyer and co-workers developed a conjugated monomer, 3-methylenecyclopentene, from myrcene *via* ring-closing metathesis that produced a 1,4-regiocontrolled polymer *via* cationic polymerization with zinc chloride.[124] The diene monomer also avoids DA reactions with electron poor maleimides and has subsequently been copolymerized with *N*-substituted maleimides in controlled radical polymerizations.[125]

4. Lignin

4.1 Introduction – lignin

Lignocellulose is one of the largest biomass sources in the world and is characterized by three main components: hemicellulose, cellulose, and lignin. Of these components, lignin is a polymer consisting of aromatic rings and aliphatic side chains.[126] To produce high-value compounds including monomers, numerous lignin valorization processes have been well-studied,[127–130] although a process for large-scale applications is still being sought for many of these monomers. Depending on the source of the lignin, the structure varies,[131] therefore, different compounds can be isolated with diverse functionalities. Post-isolation, compounds and their derivatives, have the potential to be polymerized. Small molecule aromatic compounds are important in polymer chemistry and those of interest in this review are vanillin, ferulic acid, eugenol, creosol, and sinapyl alcohol derivatives. The particular chemistries discussed are highly dependent upon the structure of the monomer, therefore, the rationale is discussed at the beginning of each section for lignin-based monomers.

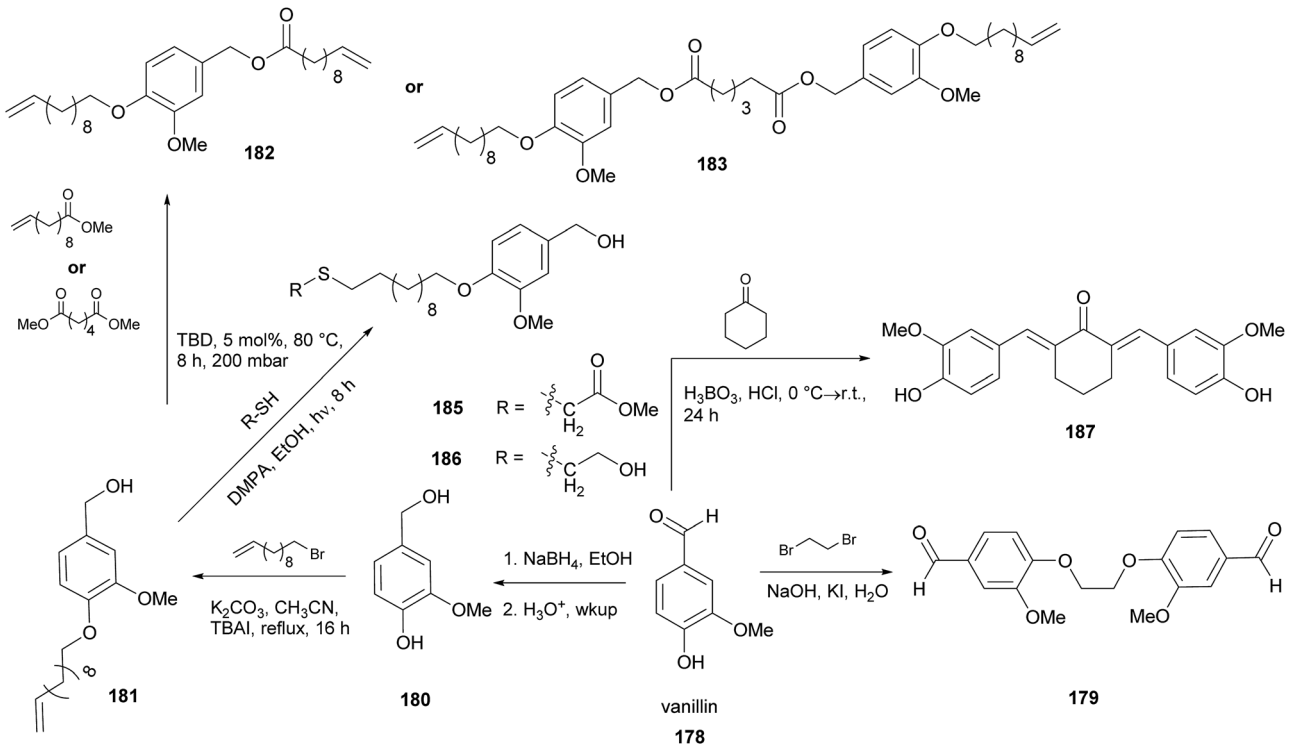
4.2 Vanillin

Vanillin (**178**) is a phenolic compound that is produced from a variety of sources, including lignin. It is produced on a multi-ton scale per year for many markets, including fragrance and flavoring.[132] Common methods for the synthesis of vanillin-based monomers are *via* dimerization or transformation of the inherent functional groups to polymerizable moieties.

4.3 Vanillin dimers

Miller *et al.* synthesized a dimer of vanillin, as well as other lignin-based natural products, through the phenol groups under basic conditions by reacting the natural product with 1,2-dibromoethane to afford **179** (Scheme 24).[133] The remaining aldehydes were then copolymerized with tetraols, pentaerythritol or di-trimethylolpropane, under acid-catalyzed conditions through a condensation polymerization to synthesize polyacetal ethers. The resulting polymers had M_n values of 10.6–22.2 kDa and a measurable T_g range of 80–152 °C. When subjected to acidic aqueous conditions, facile degradation was detected as early as 24–48 h, as measured by the decrease in particle size using dynamic light scattering.

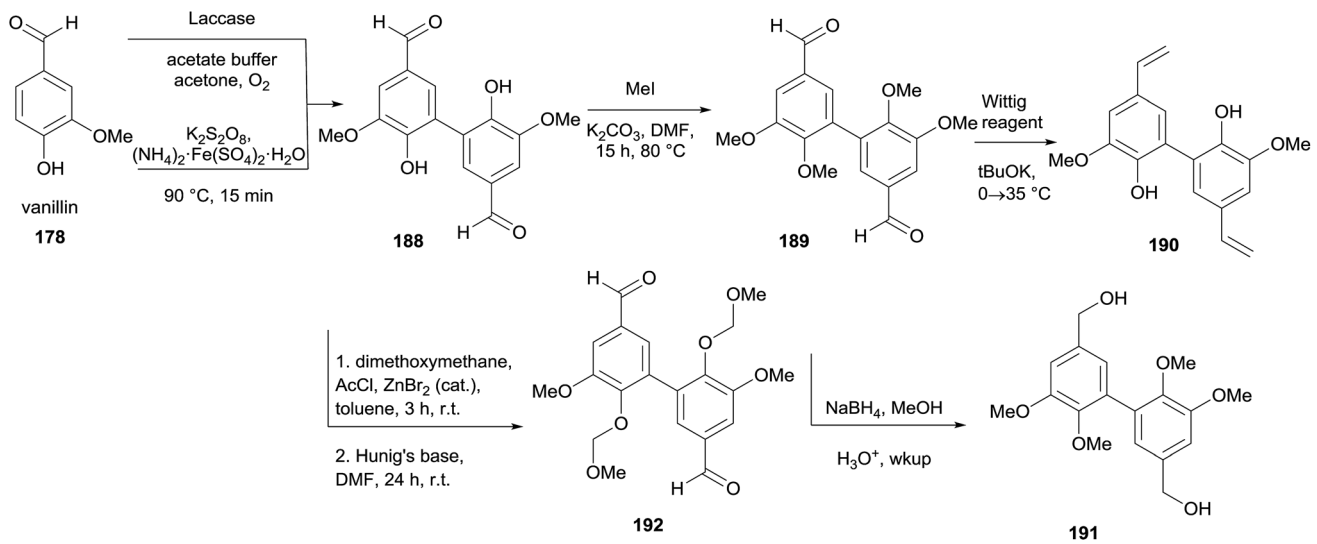
Dimerization can also occur through functionalization of the aldehyde of vanillin.[134] An initial reduction of the aldehyde to an alcohol **180** afforded a key functionality to be exploited later in the synthetic route. Next, **180** was allowed to react with 11-bromo-1-undecene to afford **181**, followed by transesterification with dimethyl adipate to generate monomer **183**. The alkene functionalization allows for polymerization through either ADMET or thiol–ene chemistry. Rather than dimerization of **181**, a second alkene moiety was installed through a reaction with methyl undec-10-enoate to afford monomer **182**. The reaction of **181** with a thiol containing compound was also performed to afford **185** or **186** with either an ester or alcohol, respectively. Functionalization with an ester or alcohol provided a route to polyesters through self-condensation (when functionalized with the ester) or copolymerization with di-esterified castor oil derivatives. Also, through the aldehyde functionality, in another route, the reaction of two equivalents of vanillin with one equivalent of cyclohexanone in an aldol condensation produced **187**, which was subsequently copolymerized with a spirobifluorene containing monomer to afford a poly(ester-



Scheme 24 Synthetic routes towards dimers of vanillin.

imide). This polymerization provided a route to new n-type electroluminescent materials emitting blue-greenish light (maxima 400–600 nm).[135]

Vanillin dimerizes either through enzymatic or chemical oxidative processes (Scheme 25). Using the laccase from *Trametes versicolor* in a green process, a biphenyl of vanillin, **188**, was synthesized. In an example by Cramail and co-workers, the methylated divanillyl diol **188** underwent further reaction with methyl iodide to afford **189**. The Wittig reagent methyltriphosphonium iodide was generated *in situ* and allowed to react with **189** to afford **190**.[136] This α,ω-diene premonomer was polymerized *via* ADMET using Grubbs' 2nd generation catalyst. The polymer had a high T_g of 160 °C and an onset of thermal degradation at 380 °C. In a follow-up study, the same route to synthesize **189** was taken, however, the aldehydes were then reduced to primary alcohols allowing for polymerization through condensation with dimethylsebacate or sebacic acid. Following the optimization of conditions for the copolymerization, six other co-monomers were polymerized to compare thermal and mechanical properties, giving a new family of



Scheme 25 Synthetic routes towards various vanillin-based monomers.

polyesters.[137] Utilizing a Biginelli multicomponent polymerization strategy with **188**, Meier *et al.*, copolymerized renewable diacetonates and urea to afford high T_g 3,4-dihydropyrimidin-2(1*H*)-one polymers.[138]

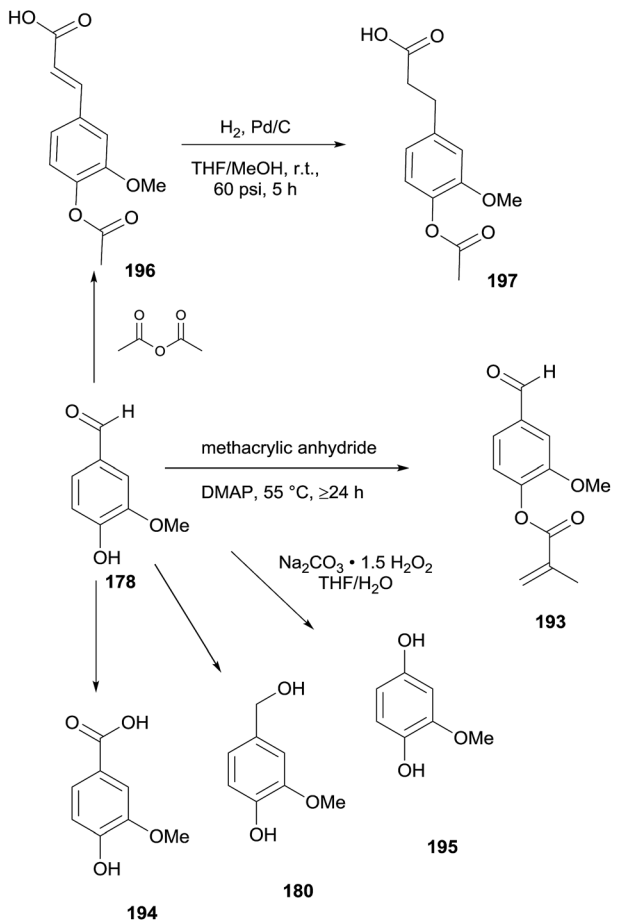
Alternatively, one electron oxidation with $K_2S_2O_8$ and $(NH_4)_2 \cdot Fe(SO_4)_2 \cdot H_2O$ generates **188**. *O*-Alkylation of the dimer using an *in situ* generated MOMCl affords **192**. This monomer was used in the synthesis of advanced models of lignin to incorporate 5-5 linkages which are present in softwood.[139]

4.4 Vanillin monomers

The concise functionalization of aromatic natural products with a methacrylate group has been thoroughly investigated by the Epps group.[140–142] In one example,[143] vanillin was reacted with methacrylic anhydride in the presence of DMAP to produce **193**. Reversible addition–fragmentation chain transfer (RAFT) polymerization was employed to synthesize homopolymers and block copolymers to give a range of thermal and mechanical properties.

To demonstrate a breadth of chemical reactions undergone by vanillin, the Caillol group used it to access three different platform chemicals (Scheme 26). Vanillic acid (**194**) and vanillyl alcohol (**179**) are commercially available but **195** was synthesized through a Dakin reaction to yield a substituted benzenediol. The platform chemicals were then functionalized with similar moieties to give twenty-two different potential monomers.[144] No polymers were synthesized, however, routes were proposed towards polymers, including polyhydroxyurethanes, polycarbonates, polymers from radical polymerization, polyesters, polyimides, polyureas, polyamides, and polyacrylates.

The synthesis of a α,β-unsaturated aromatic acid from acetic anhydride and vanillin, *via* a Perkin reaction, afforded a ferulic acid derivative **196**, which was then hydrogenated to furnish **197**.[145] Homopolymerization through the acetate and carboxylic acid groups using a zinc catalyst produced poly(dihydroferulic acid).



Scheme 26 One-step synthesis of various vanillin-based monomers.

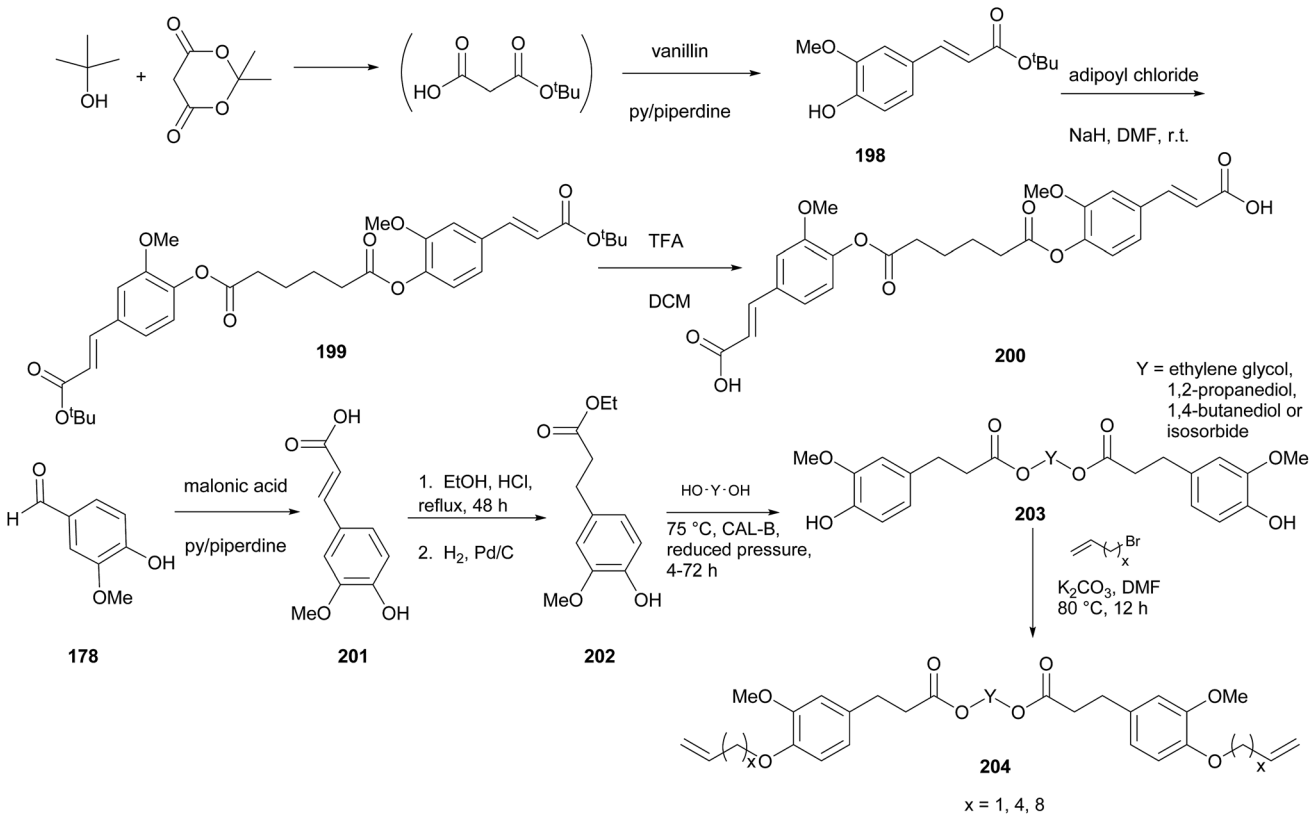
4.5 Ferulic acid

Ferulic acid can be found in lignin, as well as readily accessed from vanillin. The alcohol and carboxylic acid functionalities allow for diverse functionalizations to either afford two separate functional groups for polymerization or perform dimerization through one functional group to generate a new monomer that can be polymerized through the remaining functional groups. The two different functionalization methods allow for diversity in polymer structures.

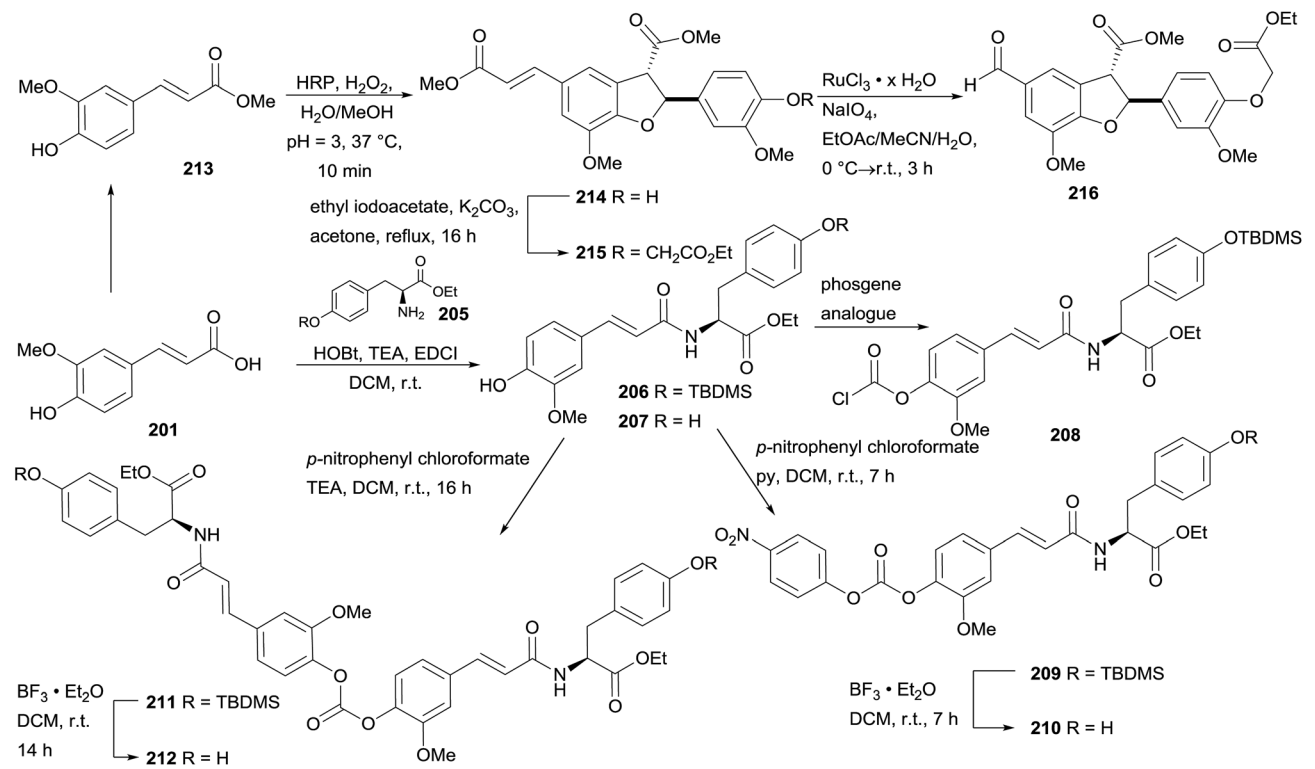
A ferulic acid derivative was synthesized in one step from vanillin by reacting Meldrum's acid with tertiary butanol to generate mono-*tert*-butyl malonate *in situ* followed by the addition of vanillin to produce **198**. The ferulic acid derivative was then allowed to react with adipoyl chloride under basic conditions to afford the pre-monomer **199**, and finally deprotection with trifluoroacetic acid to yield carboxylic acids (**200**).[146] Polymerization using triphosgene then afforded poly(anhydride-esters)s. The resulting polymers were hydrolytically degradable with products that were shown to exhibit antioxidant and antibacterial activity.

Allais and co-workers employed chemo-enzymatic reactions to access a core monomer for further functionalization towards two different polymer types.[147] Ferulic acid (**196**) was transformed into ethyl dihydroferulate (**202**) following a Knoevenagel condensation with malonic acid and vanillin in a piperidine/pyridine mixture. The natural product was converted to intermediate **202** through a one-pot two-step reaction involving a Fischer esterification and catalytic hydrogenation (Scheme 27). Various monomers were synthesized through an environmentally-friendly lipase-catalyzed transesterification with different natural diols. This green process requires no phenol protection, no/green solvent, and is atom economical. The monomer was utilized in the synthesis of poly(ester-urethane)s from commercially-available isocyanates.[148] Further functionalization of **203** though *O*-alkylation with allyl bromide or acryloyl chloride afforded monomers **204** for ADMET-based polymerization reactions.[149]

Through phenolic protection/deprotection of ferulic acid, our own work has involved the design of ferulic acid–tyrosine monomers, with control over the backbone regiochemistry as either regioregular or regiorandom polymers (Scheme 28).[150]



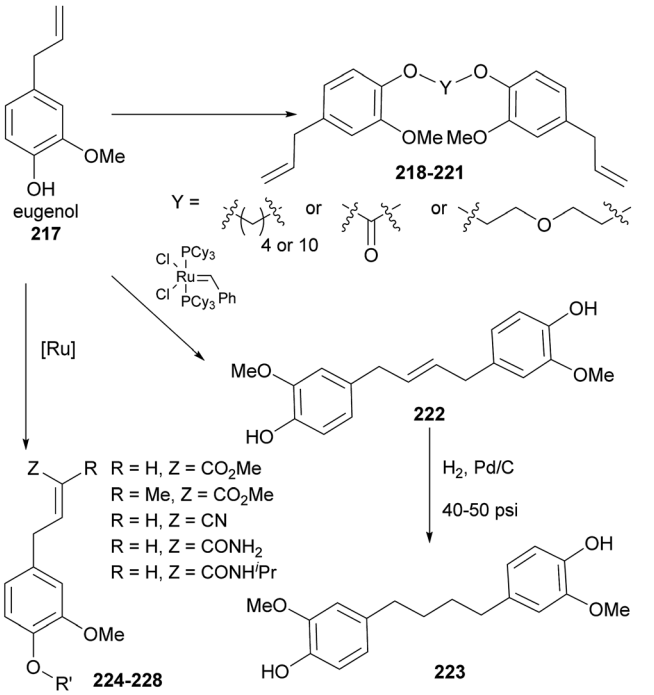
Scheme 27 Synthesis of various ferulic acid-based monomers.



Scheme 28 Synthesis of ferulic acid derived monomers having different regiochemistries (206–212) and a lignin monomer model (216).

Silyl protected tyrosine, **205**, allowed peptide coupling with ferulic acid to yield **206**. Monomers with AA′A′A and AA′AA′ regiochemistries were accessed by either chloroformate functionalization **208**, nitrophenyl carbonate functionalization **210** or dimerization with *p*-nitrophenyl chloroformate **212**, respectively. Alternatively, a monomer for regiorandom condensation polymerization was synthesized through the peptide coupling of ferulic acid and L-tyrosine ethyl ester hydrochloride (**207**). Interestingly, different regiochemistries afforded different polymer properties, in particular, the regiorandom polymer exhibited higher fluorescence emission intensity and at longer wavelength than did two regioregular analogs, head-to-tail and head-to-tail-to-tail-to-head.

Ferulic acid was also utilized in the development of a softwood lignin model monomer.[139] The route began with esterification (**213**), followed by the horseradish peroxidase (HRP)-mediated oxidative dimerization to obtain **214**. The latter was further subjected to basic condition for alkylation using ethyl iodoacetate to afford the pre-monomer **215**. Finally, **215** was oxidatively cleaved with catalytic $RuCl_3$ in the presence of $NaIO_4$ to afford monomer **216**. This monomer was copolymerized with other comonomers found in lignin to generate lignin models.



Scheme 29 Synthesis of eugenol-based monomers.

4.6 Eugenol

Eugenol-based monomers often take advantage of the terminal alkene, which is a different functionalization route than other lignin-based monomers. This inherent functional group allowed for cross-metathesis reactions. Alternatively, similar to other lignin-based monomers, functionality was installed utilizing the phenol.

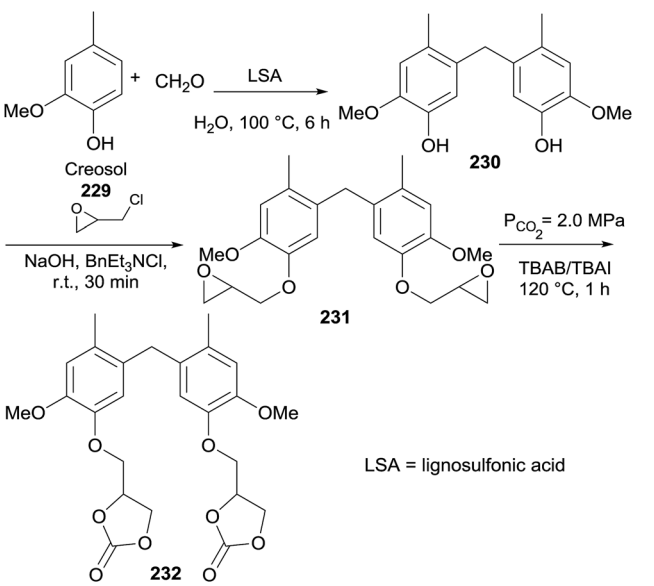
A succinct method of synthesizing a eugenol-derived monomer began with dimerization through the phenol moieties with either an alkyl chain, carbonate or diethylene glycol to afford monomers with two naturally-occurring terminal alkenes **218–221** (Scheme 29).[151] These dimers were polymerized *via* ADMET using Grubbs' 2nd generation catalyst to afford amorphous and transparent polymers.

Rather than dimerizing through the phenol or using enzymatic processes, cross metathesis through the alkene group afforded **222**, followed by catalytic hydrogenation of the olefin to yield **223**.[152] The monomer was copolymerized with triphosgene to afford a polycarbonate that was rigid and flexible with a modest T_g (51–71 °C).

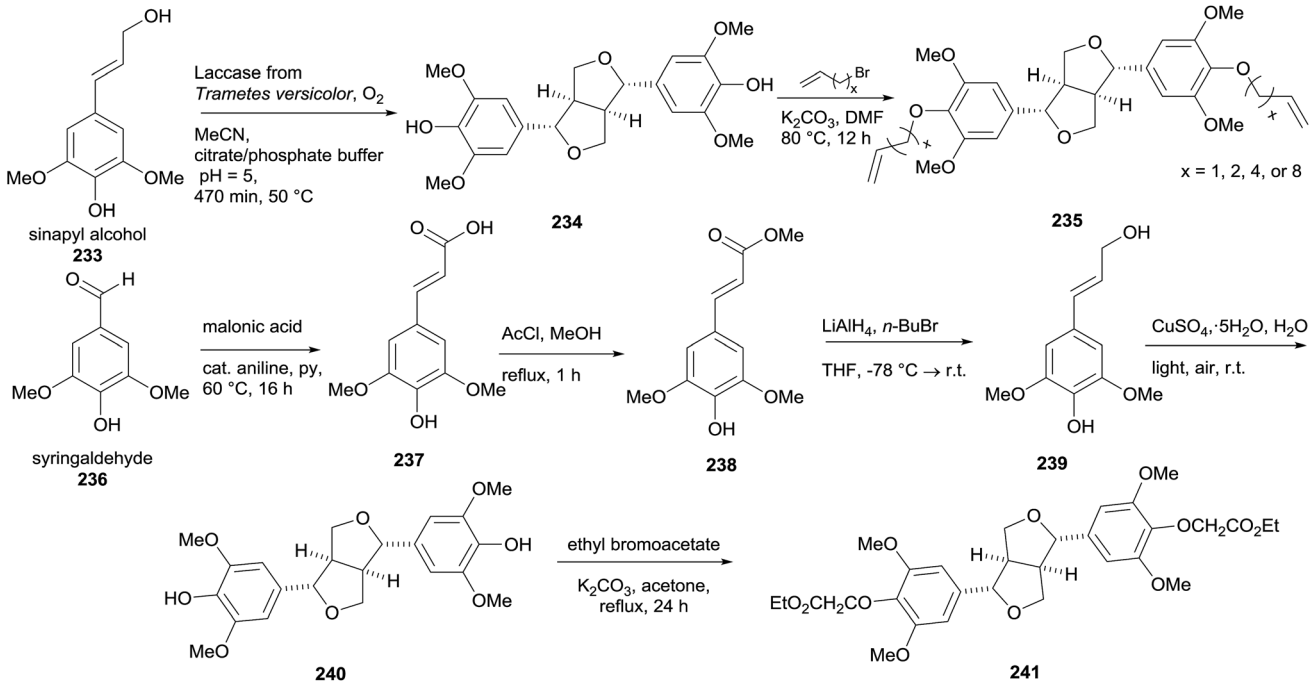
The Fischmeister and Bruneau groups investigated eugenol-derived monomers through ruthenium-catalyzed cross-metathesis in the presence of 1,4-benzoquinone, an isomerization inhibitor, to afford **224–228**.[153] These compounds may be applied to a variety of polymeric systems.

4.7 Creosol

Although the phenol of creosol is the only functional group of the molecule that can be reacted by similar methods to other lignin-based monomers, an interesting condensation reaction of the natural product and formaldehyde affords a bisphenol for further functionalization to produce various monomers. In a joint effort, the Xie, Zhao, and Bao groups collaborated to explore the synthesis of bisphenols from creosol utilizing green catalysts.[154] Lignosulfonic acid, a biomacromolecule-derived catalyst was used to promote the reaction of creosol and formaldehyde to generate **230**. A combination of the electron donating methoxy and methyl groups of creosol directed the major regiochemistry of dimer formation. The diphenolic product was subjected to condensation polymerization with triphosgene to afford a polycarbonate. In another



Scheme 30 Creosol-based monomers for the synthesis of polycarbonates or polyurethanes.



Scheme 31 Various sinapyl alcohol derivatives and their synthetic routes towards monomers.

example by the Xie, Zhao, and Bao groups, **230** was allowed to react with epichlorohydrin for conversion to the di-reacted product **231**, followed by cycloaddition with CO_2 in the presence of catalytic amounts of TBAB/TBAI under reduced pressure to generate the cyclic carbonate monomer **232**.[155] The cyclic carbonate provided a reaction site for hydrazine hydrate to afford high T_g polyurethanes by an isocyanate-free process (Scheme 30).

4.8 Sinapyl alcohol derivatives

Although sinapyl alcohol derivatives have had limited use in polymeric materials, the inherent functional groups serves a two-fold purpose: allowing for installation of multiple functional handles and enabling a diverse array of chemistry applicable for the present functional groups.

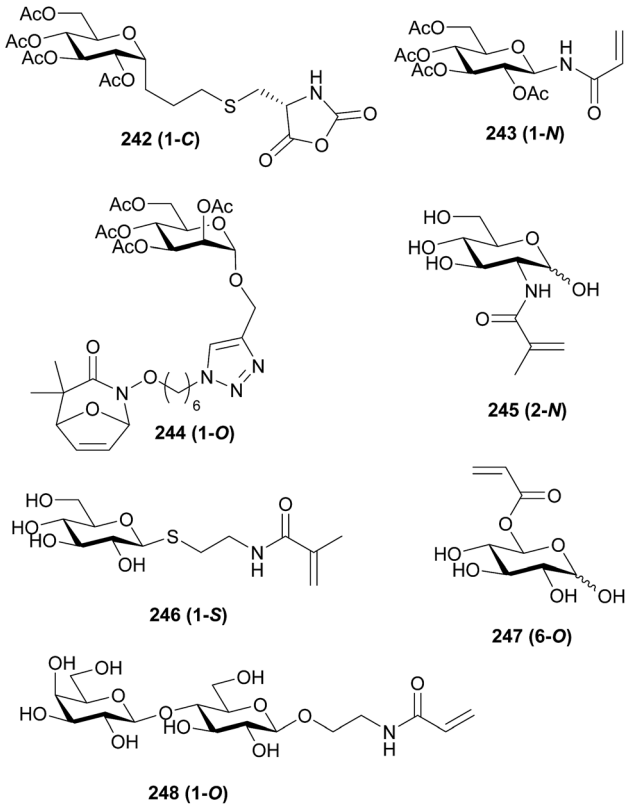
In work from Allais and co-workers, a pre-monomer, (±)-syringaresinol (**234**) was accessed through the reaction of sinapyl alcohol (**233**) with laccase of *Trametes versicolor* in buffer in the presence of O_2.[156] The *O*-alkylation of the remaining phenols with various alkyl chains afforded monomers (**235**) with terminal alkenes (Scheme 31). Polymers were accessed using ADMET.

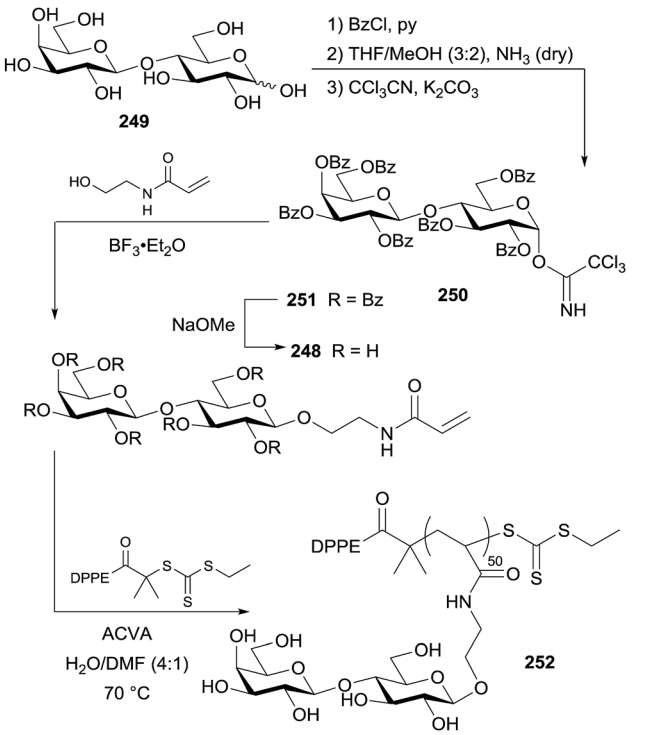
En route to **241**, several natural product derivatives were synthesized by the Westwood group.[139] A Knoevenagel condensation of syringaldehyde with malonic acid gave sinapic acid (**237**) which was esterified, enabling access to **238**, followed by reduction of the ester to generate a sinapyl alcohol derivative **239**. Reaction of **239** *via* a biomimetic oxidative dimerization afforded the pre-monomer **240**, which was then condensed with ethyl bromoacetate to produce the esterified monomer (Scheme 31).

5. Sugar derivatives

5.1 Introduction – sugar derivatives

Carbohydrates are particularly convenient raw materials, as they are inexpensive, abundant in Nature (more than 150 billion tonnes of polysaccharides are produced naturally per year), and present considerable structural and stereochemical diversity, of which, polysaccharides, *e.g.*, cellulose, starch, and glycogen, play essential roles in energy storage and many biological processes.[157] Using chemical or enzymatic processes, polysaccharides can be converted into monosaccharides, unsaturated carboxylic acids, polyols, and furan derivatives, which could be manipulated to afford versatile monomers for subsequent polymerization.[11] These synthetic polymers are able to mimic the structure and function of natural polymers with improved physical and chemical properties. Considering the recent reviews of polymers from polyols[158] and furan derivatives,[12,159] this review focuses on synthetic polymers with monosaccharides and disaccharides as the basic building blocks. Based on structural differences, recently developed sugar based monomers and corresponding polymers are divided into two groups: (1) mono-substituted monomers (except the protecting groups) to afford poly(vinylsaccharide)s and other conventional functionalized polymers having sugars pendant from the main chain of the polymer, mainly utilized for biomedical applications; and (2) di-substituted monomers (except the protecting groups) to access polymers with sugar units incorporated into the backbone either in the ring-closed or open configuration *via* glycosidic or other linkages, used for their mechanical properties given the high T_gs. Also, some work combines both structural stiffness and bio-functionality.[160]





Scheme 32 Synthesis and RAFT polymerization of **248**.

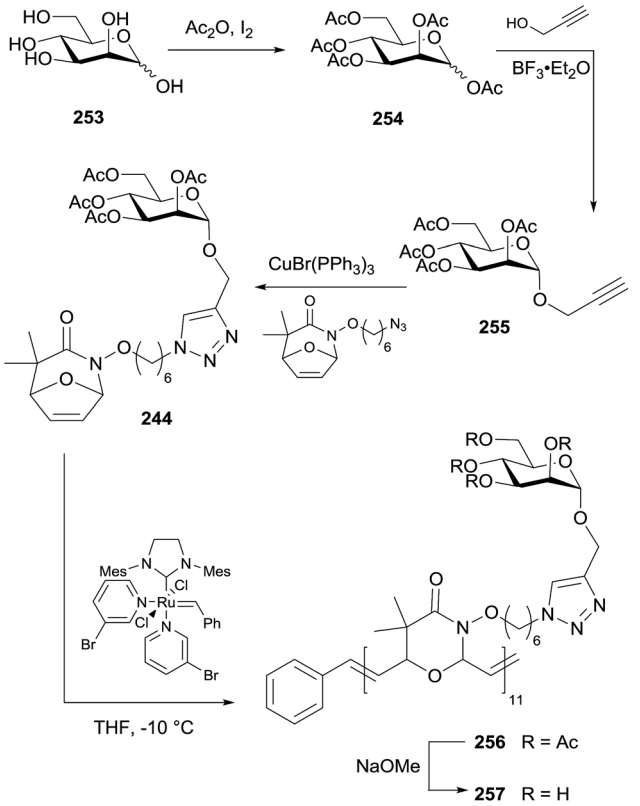
5.2 Mono-substituted monomers and corresponding glycopolymers

Given the inherent sugar multifunctionalities, glyco vinyl monomers,[161–164] norbornene based glyco monomers[165] and glyco *N*-carboxyanhydrides (NCAs)[166] have been designed and synthesized with *O*-(**244**, **247**, **248**), *N*-(**243**, **245**), *C*-(**242**), and *S*-(**246**) linkages *via* C-1, C-2 and C-6 glycosidic bonds. These monomers have been polymerized through free radical polymerization, ATRP, RAFT, ROMP, and ROP, *etc.*, to afford glycopolymers with variable lengths, architectures, and functionalities, mostly used for biomedical applications. Considering the syntheses of sugar monomers are typically multi-step, effective leaving groups, and highly efficient, orthogonal reactions are discussed in this review.

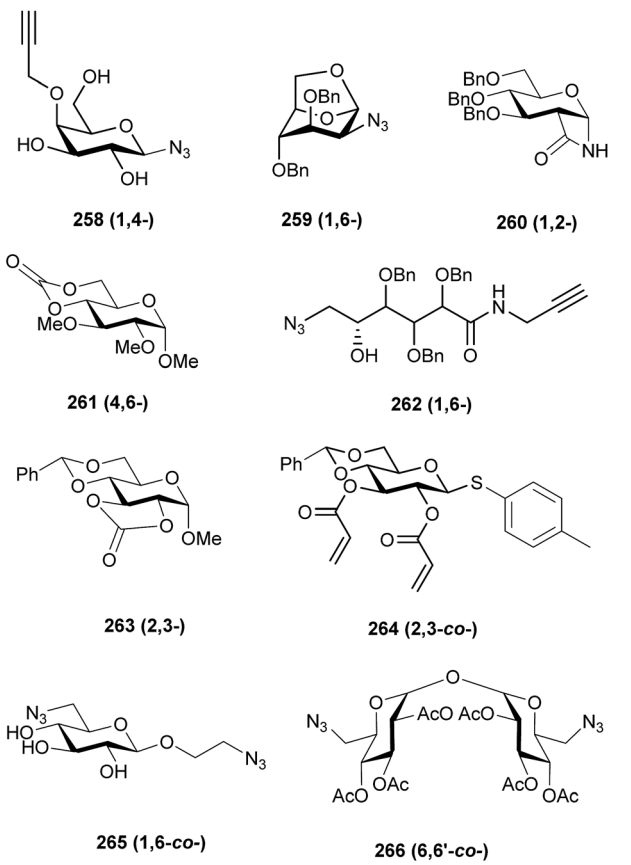
Coupling between a glycosyl donor sugar and a polymerizable functional acceptor is the most frequently used strategy to generate glycomonomers. Glycomonomers **243**, **245**, **246**, **247**, and **248** were all achieved by glycosylation coupling reactions. The Kiessling group has synthesized a series of norbornene-based glycomonomers *via* glycosylation coupling reactions between D-mannose or D-glucose intermediates and norbornene-based acceptors, which underwent ROMP – the resulting glycopolymers were used as powerful tools to reveal the molecular mechanisms that underlie carbohydrate-mediated signal transduction.[165] The Bertozzi group[167] reported the synthesis of (2-*N*-acryloyl-aminoethoxy (β-D-galactopyranosyl)-(1,4)-β-D-glucopyranoside) (**248**) using a participatory glycosyl donor sugar **250** and *N*-(2-hydroxyethyl)acrylamide to create the desired β-anomeric stereochemistry (Scheme 32). The benzoyl protecting groups in the resulting sugar precursor **251** were removed with sodium methoxide to afford glycomonomer **248**. RAFT was employed to access well-defined glycopolymer **252** with $Đ$ of 1.2. Further labeling of **252** with different fluorescent dyes was done to investigate galectin–glycan interactions on live cell membranes through Förster resonance energy transfer (FRET).

Besides glycosylation coupling reactions, highly effective reactions, *e.g.*, click reactions, have been used to achieve more variable glycomonomers. The Deming group[168] explored the synthesis of NCA **242** using thiol–ene click chemistry with an alkene-terminated saccharide. The Haddleton group[169] and Kiessling group[170] have reported the use of azide–alkyne cycloaddition click chemistry to furnish glycomonomers with a triazo linkage. Recently Kiessling *et al.* developed a bicyclic oxazinone-based glycomonomer.[170] As shown in Scheme 33, Lewis acid-catalyzed glycosylation was carried out with per-acetylated-D-mannopyranoside (**254**) and propargyl alcohol to afford 1-propargyl-α-D-mannose-2,3,4,6-tetraacetate (**255**), which was further utilized for azide–alkyne cycloaddition with *N*-(6-azidohexyloxy)-8-oxo-2-azabicyclo[3.2.1]oct-6-en-3-one in the presence of tris(triphenylphosphine) copper(I) bromide to generate monomer **244**. ROMP was performed to generate well-defined glycopolymer **256**, which was deprotected with sodium methoxide to afford **257**. This polymer could be broken down to simple building blocks in acid or base solutions, making it a novel biomaterial in drug delivery and regenerative medicine.

Post-polymerization modification is another alternative strategy for facile and precise glycopolymer preparation. The monomers with reactive functional groups were polymerized and subsequently modified by further chemical reactions with the sugar moiety. The Bertozzi group[171] prepared a number of



Scheme 33 Synthesis and ROMP of **244** derived from D-mannopyranose.



glycopolymers *via* the addition reaction between poly(vinyl ketone)s and aminooxy-terminated saccharides. The Haddleton group[172] and the Lecommandoux group[173] utilized azide–alkyne cycloaddition reaction to generate glycopolymers with alkyne-terminated saccharides. The Davis group[174] employed the thiol–epoxy reaction to afford glycopolymers.

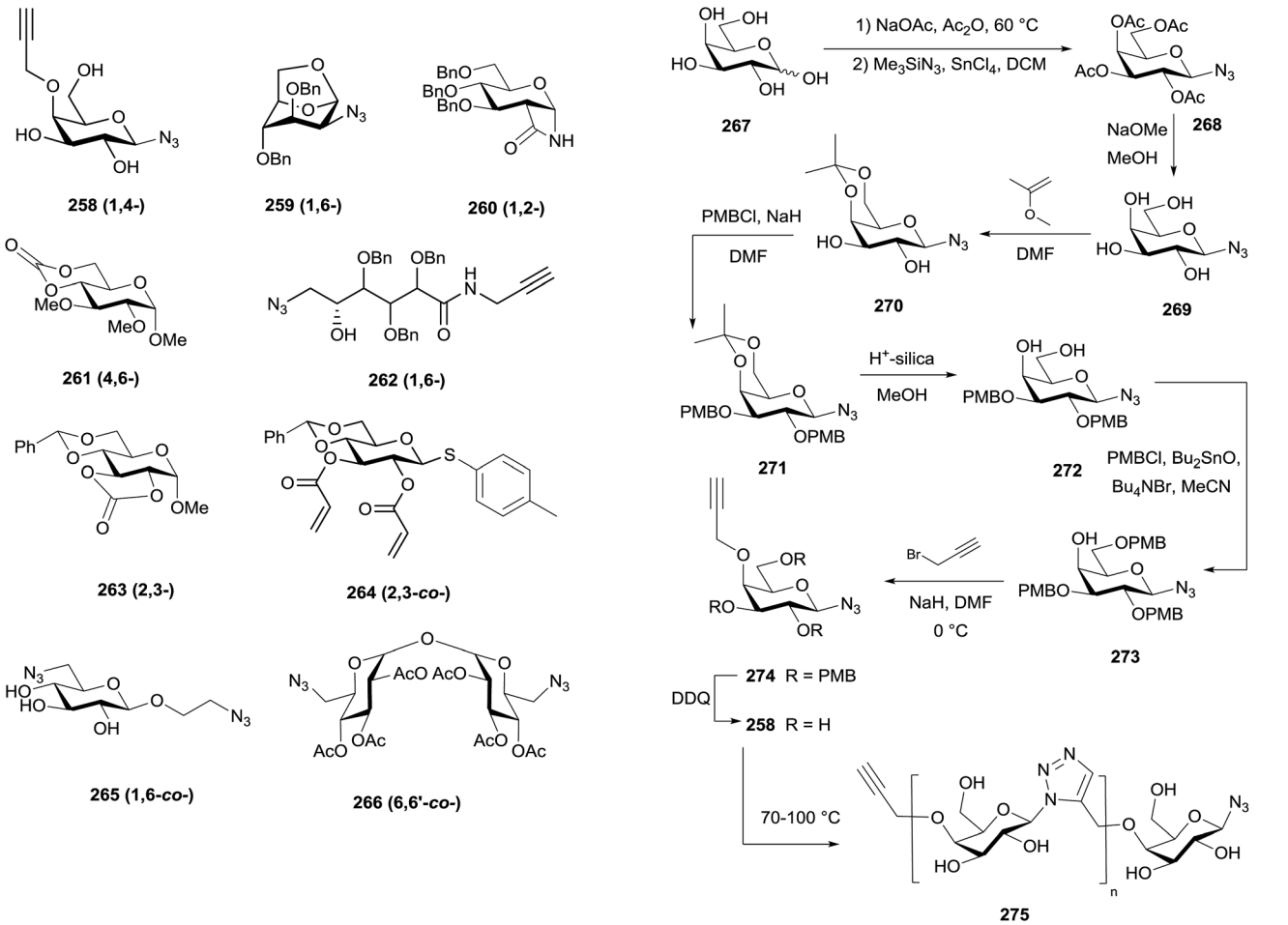
5.3 Di-substituted monomers and corresponding polymers

Synthetic polysaccharides with sugar units incorporated into the backbone either in the ring-closed or open configuration are interesting polymers, as they are rigid, chiral, non-toxic and renewable. These di-substituted monomers are of interest for both basic and applied studies. To date, however, there have been fewer reports on the synthesis of such polymers. Reports have shown ether,[175] ester,[176] amide,[160,177] carbonate,[178,179] and triazolyl[180,181] linkages utilized between 1,4-(**258**), 1,6-(**259**, **262**, **265**), 1,2-(**260**), 2,3-(**263**, **264**), 4,6-(**261**) positions in monosaccharides or 6,6′-(**266**) position in disaccharides. These monomers with di-substituted functional groups have been polymerized or co-polymerized *via* ROP, click reactions, and Michael addition reactions to afford polyesters, polycarbonates, polyamides *etc.* which are biocompatible and biodegradable.

Natural glycosidic linkages are mainly 1,4- and 1,6-linked, as in cellulose, starch, and chitin, to form either linear or branched structures. To mimic 1,4-linkages, Sureshan *et al.*[180,182] have synthesized β-1-azido-4-*O*-propargyl-D-galactose (**258**) in nine steps starting from D-galactopyranose. Due to sugar multifunctionalities, selective protection–deprotection manipulation was frequently used in the preparation of **258** (Scheme 34). D-Galactopyranose was acetylated with acetic anhydride, followed by selective azidation at the anomeric carbon to generate 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl azide (**268**). After removal of the acetate groups from **257** by reaction with sodium methoxide, coupling with 2-methoxypropene, and then benzylation with 4-methoxybenzyl chloride gave the PMB ether **271**. Removal of the isopropylidene group and subsequent selective benzylation generated **273**, having a free hydroxyl group in the C-4 position, which was then coupled with propargyl bromide to give the benzylated monomer **274**. After acid hydrolysis, the crystal of monomer **258** underwent a crystal-to-crystal topochemical azide–alkyne dipolar cycloaddition reaction to afford a stereoregular polysaccharide, poly(1,4-triazolyl β-galactose) (**275**). Notably, the polymerization was conducted without using a solvent or a catalyst, and the degree of polymerization could be easily tuned by reaction time and temperature.

The 1,6-glycosidic bond is used for the formation of branch points in glycogen and starch. Hattori *et al.*[175] realized 1,6-linkages *via* ROP of the 1,6-anhydro-2-(*N*,*N*-dibenzylamino)-mannose derivative of **259**. The Bueno-Martínez group[177] also achieved 1,6-glycosidic bond *via* click reaction between azides and alkynes in the similar ring-opened glucose derivative **262**.

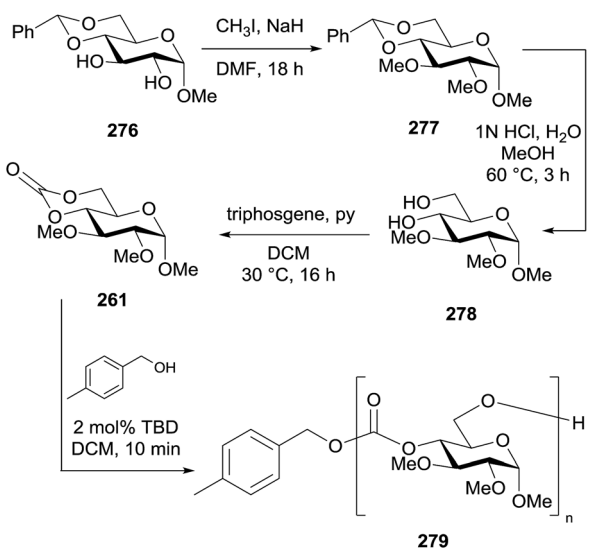
Linkages other than glycosidic bonds are not common in Nature, but can be synthesized. For instance, our group has designed and synthesized a series of glucose-based polycarbonates. The bicyclic carbonate 1,2,3-*O*-methyl-4,6-*O*-



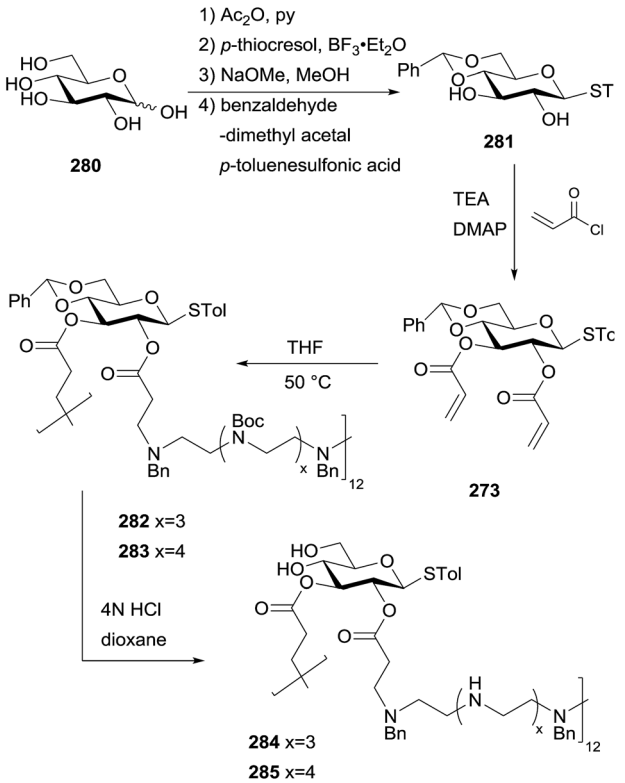
Scheme 34 Synthesis of **258** deriving from D-galactopyranose and the topochemical azide–alkyne dipolar cycloaddition reaction.

carbonyl-α-D-glucopyranoside (**261**), containing a 4,6-cyclic carbonate linkage, is readily synthesized since these two positions easily form six-membered cyclic structures that are ideal for ROP. This monomer underwent organocatalytic ROP through the 4,6-carbonate linkage to yield either homopolymer poly(D-glucose carbonate)s (**279**)[178] or diblock copolymers with **279** connected to a biocompatible polyphosphoester segment.[183] To achieve the bicyclic carbonate, commercially-available methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**276**) was methylated by reaction with methyl iodide in high yield (95%). Subsequent removal of the benzylidene group *via* acid-catalyzed hydrolysis and formation of the bicyclic monomer with triphosgene gave carbonate monomer in 25% yield after recrystallization in hexanes/ethyl acetate (Scheme 35). ROP was carried out with 4-methylbenzyl alcohol as initiator and TBD as catalyst to access **279** with narrow $Đ$ of 1.1. It is noteworthy that in comparison with typical aliphatic polycarbonates, **279** exhibited a high T_g that arose from the cyclic sugar ring. Using a similar strategy, a 2,3-linked monomer **263** was developed by the Endo group and polymerized by anionic ROP.[179]

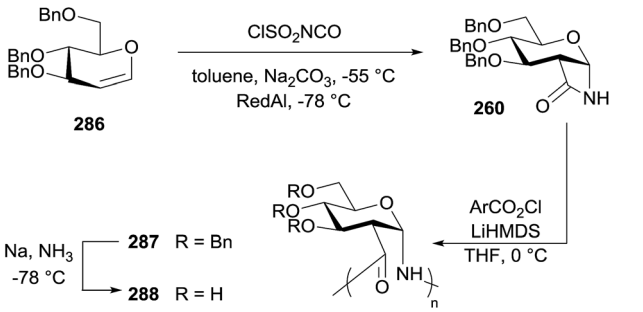
Recently, the Reineke group developed a diacrylate–glucose monomer *p*-methylphenyl-4,6-*O*-benzylidene-2,3-*O*-acrylic acid methyl ester-1-thio-β-D-glucopyranoside (**264**), starting from D-glucopyranose in five steps with an overall yield of 36% (Scheme 36).[176] D-Glucopyranose was first protected by acetylation and reaction with *p*-thiocresol afforded *p*-methylphenyl-2,3,4,6-acetyl-1-thio-β-D-glucopyranoside.[179] Subsequently, the acetate groups were hydrolyzed and 4,6-*O*-benzylation was conducted to



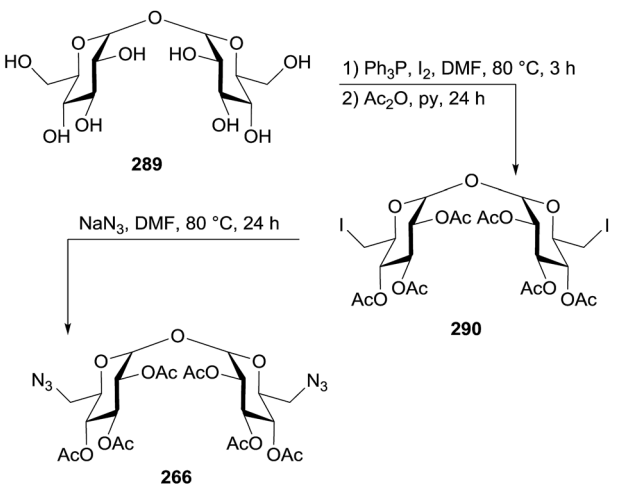
Scheme 35 Synthesis and ROP of **261** derived from D-glucopyranose.



Scheme 36 Synthesis and Michael addition of **273** derived from D-glucopyranose.



Scheme 37 Synthesis and ROP of **260**.



Scheme 38 Synthesis of **266** derived from trehalose.

afford **281**, which was further reacted with acryloyl chloride in the presence of trimethylamine and 4-dimethylaminopyridine, yielding the diacrylate–glucose monomer **264**. Step-growth polymerization *via* Michael addition proceeded at the C-2, C-3-functionalized positions with oligoethylene-amine monomers containing terminal secondary amines and three or four internal Boc-protected secondary amines. After Boc removal, the ester bonds of the resulting polymers between the sugar and the ethyleneamine moieties (**284** and **285**) facilitated rapid polymer hydrolysis and nucleic acid release.

The 1,2-linkage was realized by Grinstaff and co-workers recently.[160] They synthesized a β-lactam sugar monomer, obtained *via* the stereoselective cycloaddition of tri-*O*-benzyl-D-glucal (**286**) and chlorosulfonyl isocyanate, followed by *in situ* reduction to remove the sulfonyl group. As depicted in Scheme 37, α-*N*-1,2-D-glucose poly-amido-saccharides (**288**) were synthesized *via* anionic ROP, with controlled molecular weight and narrow dispersity ($Đ = 1.1$). After debenzylation with sodium metal in ammonia, the β-polypeptides linked through the 1,2-α-amide linkage became hydrophilic and retained their initial stereochemistry. The resulting **288** exhibited similarities with natural polysaccharides and β-polypeptides, making them promising biomimetic materials.

In comparison with di-substituted monosaccharides, disaccharide analogues allow for more variable linkages. The Reineke group reported the synthesis of the diazido trehalose monomer **266** in two steps starting from trehalose (**289**). Trehalose was selectively iodized at the primary hydroxyl groups and then the residual hydroxyl groups were acetylated to afford **290**, which could be easily transformed into diazido monomer **266** by reaction with sodium azide at elevated temperature (80 °C). A series of trehalose–oligoethyleneamine linear copolymers were generated with dialkyne amines (Scheme 38).

6. Conclusions and future directions

There has been exciting work in the design of natural products to ready them for the development of polymer materials. Given that the transformation of small molecules into polymers leads to enhancements in the physical and mechanical properties to allow them to be utilized in demanding applications from plastic tubing and packaging to rubber tires and asphalt additives to polymer electronic materials, and beyond, polymer materials are of critical importance to society. While there is no single formula for the ideal natural product to be utilized in polymeric materials because the desired properties will dictate the structural features required, one common motif is that it must be functional. Whether the desired functional groups for polymerization are inherent to the natural product or are designed into the material through functional group interconversion or other reactions, the starting material requires functional handles for these organic transformations.

The rich structural and stereochemical diversity of natural products, combined with the vastness of synthetic chemical transformations that are possible for their conversion into monomers that allow for the preparation of well-defined polymers with tunable properties have been driving the development of new monomers. In addition, a desire to decrease the reliance on petrochemical sources is motivating a revolution in the polymer chemistry community, to shift to sustainable, bio-based feedstocks. This review has attempted to highlight those classes of natural products that have seen the most development and that are exceptionally promising in terms of realizing monomers and polymers in a scalable fashion, considering the sourcing and availability of each natural product, as well as the scalability and diversity of the chemical transformations and the emerging properties of resulting polymers. However, we must also recall historical perspectives, which in the early-to-mid 1900's fueled the transition from scarce naturally-sourced polymer materials to abundant synthetics, *e.g.* polyisoprene as a replacement for limited sources of rubber during World War II. As the world's population continues to grow, selection of natural products from which to produce functional polymer materials will need to be balanced by production capabilities and avoidance of competition with food supplies. Following this approach, natural product-based polymers would appear to be ideal to replace petrochemically-based polymers and to supplant currently marketed materials, as well as for use in new applications, considering that natural product-based polymers may have exceptional properties for which there is no petrochemical equivalent. Although there has been much recent work, not only in the polymer chemistry community, to realize the aims mentioned, there are numerous hurdles that plague the introduction of these monomers and polymers on industrial scale use. For example, as a byproduct, lignin is used as a fuel source in biorefineries and current technological processes are leading to much more available lignin that could potentially be used in value-added small molecule or polymer applications. However, a major hurdle and ongoing research efforts focus on the valorization of lignin – that is, to generate well-defined, pure small molecule products for downstream applications in high yields.[127] Much fundamental and applied work is still needed to delineate the origins of heterogeneity in lignin depolymerization in order to supply vanillin, ferulic acid, eugenol, *etc.* In the case of sugars, the DOE's highlighted top twelve chemicals from Biomass have generated incentives for corporations to focus on production of twelve sugar-derived building blocks. This attention has resulted in companies such as BASF, BioAmber, Myriant, and Reverdia to focus on bio-production of succinic acid. Along with other diacids, such as furan dicarboxylic, fumaric, glucaric, itaconic, and malic acid, the bio-based transformation of sugars into these small molecules feeds directly into, often, already established technologies *e.g.* petroleum-based succinic acid is currently used in food and polymer industries. The sugar-derived monomers of this review, often require multiple synthetic steps and high purities that would be expected to demand greater costs in production than the DOE highlighted sugar-based molecules. In light of these hurdles, currently, the greatest potential for any class of natural products in larger scale polymer applications through synthetic transformations resides in those that are readily available and of lower cost production *via* established technologies and current use in industry, namely, oils and terpenes. In reality, to break into sustained, commercial use, however, the natural product-based materials discussed in this review would certainly need to enter, initially, into smaller-volume, higher-margin, emerging markets.

Long term goals in this field, would include the continued development and eventual use of advanced synthetic organic chemistry techniques to realize complex polymers by simple methods from these natural products and their derivatives on industrial scales towards society-enhancing materials. Additionally, applying innovative chemical transformations with underutilized natural products such as flavonoids, tannins, and lignans is expected to add to the diversification of bio-based materials.

Considering the sheer diversity of natural products, we anticipate expansion of both the natural product types and monomers produced for this field. In addition, a continued focus employing green chemistry principles and new synthetic chemistries in the transformations and processes for producing natural product-based polymers on a large scale will be highly important. As the toolbox of synthetic chemical transformations and catalysts continues to grow, so will the opportunities for synthesizing new monomers and polymers. Finally, controlled degradation of the polymers where desired should be considered as this may help in reducing landfill or aquatic waste and potentially recycling by-products. Meticulous attention to the design of bio-based materials to include the linkages (*i.e.* carbonates, esters, *etc.*) between natural product-based repeat units allows for degradation into the monomer and other benign by-products that decreases waste by producing environmentally-friendly small molecules rather than filling landfills with plastics. Focused cross-collaborative research between synthetic organic and organometallic chemists, polymer chemists, engineers, and others, will be crucial to furthering the aims of this field.

7. Acknowledgements

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