



Feature Article

Vanillin, a key-intermediate of biobased polymers



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ABSTRACT

The use of vanillin for the preparation of renewable polymers is reviewed in this work. The synthesis of polymers from renewable resources is a burning issue that is actively investigated. Vanillin is currently one of the only biobased and aromatic compounds that are industrially available. For this reason, vanillin recently gained much attention from the polymer community. The first part of this work aims at giving an overview of the different existing sources of vanillin, and of their relevance in the context of a potential use in polymer science. The second part of this work sums up the efforts of the scientific community to prepare a wide range of vanillin-based polymers, e.g. phenolic, epoxy and benzoxazine resins, polyesters, acrylate and methacrylate polymers. The interest in the use of vanillin to prepare renewable polymers is recent but the number of contributions on this subject is growing fast.

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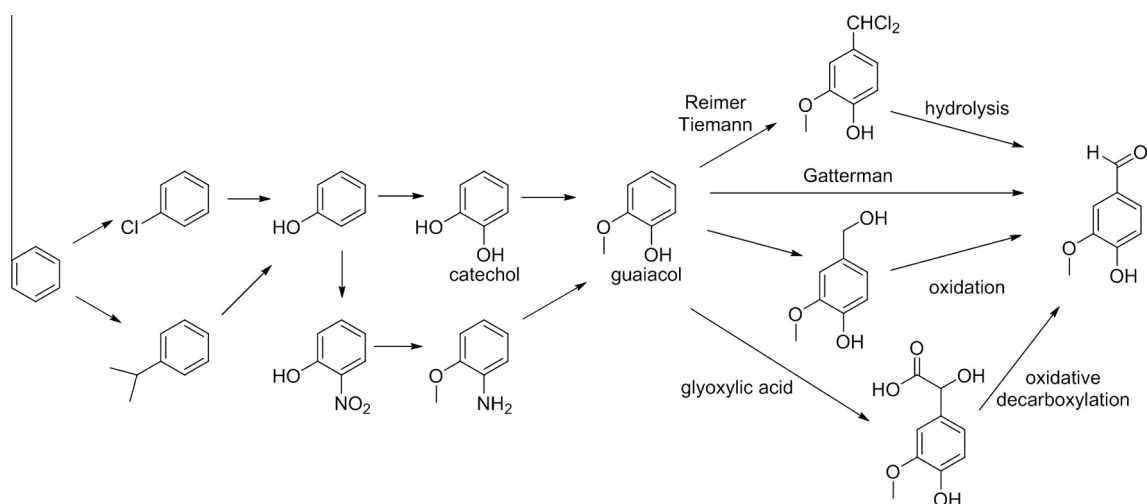
1. Introduction

Vanillin (4-hydroxy-3-methoxybenzaldehyde), a plant metabolite, is the main component of natural vanilla

extract and is responsible for its flavoring properties. Natural vanilla is originally extracted from vanilla orchid pods. The composition of natural vanilla extract is complex and contains many more compounds than only vanillin. Also, vanilla orchid growing and harvesting is a costly process. For these reasons, vanillin from natural extract accounts for less than 1% of the total vanillin production

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Scheme 1. Outlines of petrochemical synthesis of vanillin adapted from [2].

worldwide [1]. This sourcing is not adapted to an industrial use of vanillin.

As a flavoring and fragrance ingredient, the current global demand for vanillin is estimated to be roughly 20,000 tons per year [1]. To satisfy constantly increasing markets, new chemical routes for the synthesis of vanillin were developed. Today, 85% of the vanillin is produced from the petroleum-based raw material guaiacol [2] (Scheme 1). Solvay-Rhodia dominates the vanillin market using the catechol–guaiacol process.

However, vanillin produced through this process cannot be labeled as “natural vanilla flavor”. According to EU regulations, vanillin can be sold as “natural vanilla aroma” only if the base material and the process are natural. This led to the development of other ways of producing vanillin using biotechnology, improving the scientific knowledge and financial investment in this field along the way.

Numerous strategies have been envisaged to produce vanillin by biotechnology processes. Literature reports can be classified in plant-based and microorganism-based approaches. Plant-based strategies [3] consist in growing plant tissues or cells to make use of their biosynthetic pathways for the conversion of various substrates to vanillin. This approach consistently suffers from low and inconsistent yields. Microorganism-based approaches have been extensively reviewed [4–6] and consist in using biotransformation reactions from native or genetically-modified fungi [7,8], yeast [9] or bacteria [10] to produce vanillin (or a derivative in a different oxidation state) from a structurally close substrate. The most available and promising substrates include, ferulic acid extracted from sugar beet pulp [7] or waste of rice bran oil processing [8], glucose [11,12], and even lignin fragments [5]. Separation technologies are maturing [13] and play a key role for the industrial-scale production of vanillin from biotechnologies. Recently, Solvay-Rhodia and Evolva entered a pre-production phase from yeast fermentation of rice bran oil processing waste and glucose respectively [1]. These processes are still emerging technologies producing high-cost vanillin, which is suitable for the aroma and fragrances

field for marketing reasons, but not for potential use in renewable resources-based polymers.

One last production method might however suit this purpose. The production of vanillin from wood actually accounts for about 15% of the total vanillin production and Borregaard, the second largest vanillin producer worldwide, produces vanillin from lignin [14]. Indeed, chemical depolymerization of liguosulfonate by-products from the paper industry was historically the first industrial synthetic process for vanillin production [15]. However, vanillin-from-lignin plants raised environmental concerns [2]. Recently, this process regained attention thanks to the understanding of lignin depolymerization mechanism [16–18], better yields through process improvement and catalysis [18–22], and better separation and purification techniques [14,23–25].

These advances promoted the lignin-to-vanillin process to one of the most promising in terms of sustainability and economical relevance. Indeed, lignin is the second most available renewable raw material with around 50 million tons per year produced [26]. Vanillin is currently one of the only aromatics industrially available from lignin. The production of other biobased aromatics from lignin depolymerization, although under intense investigation, is not a mature technology yet [27]. The production of vanillin from lignin is not in the scope of this review and more details are available elsewhere [28]. However, the fact that processes to produce vanillin from wood exist, at an industrial scale, and with high sustainability, leads us to consider vanillin as a top-priority renewable building block. Its use for the synthesis of biobased polymers is reviewed in this work.

2. Polymers based on vanillin and derivatives

2.1. Context

The investigation of vanillin as a biobased building block has been very dependent on its sourcing. Indeed,

the early production of vanillin was from biomass – between the 1930s and the 1980s – and works from this period actually deal with the chemistry of vanillin, such as the series of papers from Pearl for example [29]. With the advent of petroleum-based chemistry, the wood-based chemistry fell almost into oblivion. Vanillin production, as a by-product of the paper industry, was one of the only industrial remains in this field. Vanillin requires quite a few reaction steps to be produced from petro-based resources (Scheme 1) and was thus confined to high value-added applications like aroma or pharmaceuticals. Recently, however, the awareness about the predicted scarcity of oil and the necessity of using renewable resources has risen. Lignin chemistry started to be re-investigated with modern analytical tools and processes [26,27]. New opportunities for the future are identified [30], especially the use of lignins in polymer science [31–33]. However, lignins suffer from drawbacks such as complex and variable structures, high molecular weights, and limited processability. Vanillin from lignin, one of the only molecular aromatics largely available from biomass, was thus recently used to prepare renewable polymers and this is the scope of this review.

Using chemicals from biomass is not the only aspect of the development of a “green”, sustainable chemistry. Energy efficiency, waste reduction, atom economy, safety toward human health and environment, are also important green chemistry requirements. Using a chemical as a new building-block, as exemplified in this review with vanillin, leads to the development of new reactions, new materials and new processes. This fresh start is an excellent opportunity not to repeat past mistakes by taking into account from the start the green chemistry principles. Numerous efforts have been made by the scientific community to integrate this approach to the preparation of vanillin-based polymers.

Strategies to prepare vanillin-based polymers can be classified in three groups. The first one is a direct mono- or difunctionalization of a vanillin derivative, giving a monoaromatic monomer. The second one is the coupling of two vanillin derivatives prior to functionalization, giving a difunctional and diaromatic monomer with the same group on both ends. The third one is the grafting of a vanillin derivative onto a pre-existing polymer. These strategies were employed to prepare a wide range of polymers, either by step-growth or chain-growth polymerization.

2.2. Epoxy polymers

Epoxy polymers are widely employed thermosets, especially in applications with demanding thermo-mechanical conditions such as in the aeronautic or electronic industry.

Indeed, epoxy monomers usually have an aromatic structure, which brings stability to the network. Thus, vanillin and its derivatives are excellent candidates for the biosourcing of epoxy polymers. A few teams worked on this topic and used various strategies.

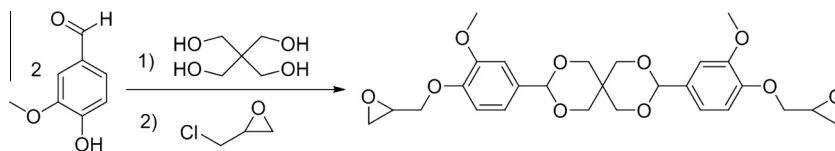
In a review article [34], Koike described an interesting diepoxy monomer based on a coupling strategy as depicted in Scheme 2.

The first step is performed by the acetalization of two vanillin molecules with pentaerythritol. The second step is the glycidylation of the two phenolic hydroxyl groups to obtain a difunctional epoxy monomer. This compound is interesting as the reactants involved in its synthesis are biobased and widely available, and the reactions are well-known and easy to implement. The major drawback of this monomer, however, is the fragility of the acetal group. Indeed acetals are usually employed as protecting groups of carbonyl compounds, as the deprotection is conducted at room temperature in aqueous acidic medium. Nevertheless, Koike reports an epoxide equivalent weight of 270 g/eq, a crosslinking reaction with diaminodiphenylmethane, as well as good impact strength, tensile strength, and elongation of the final material.

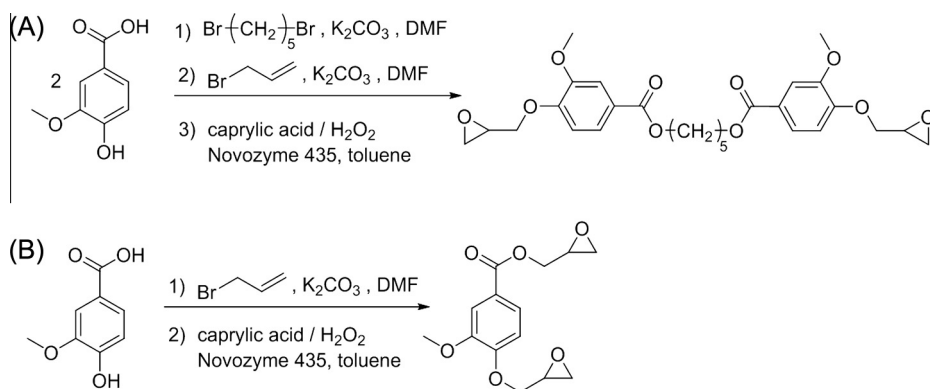
Aouf et al. also used a coupling strategy to prepare a diepoxy monomer from vanillic acid [35] as shown in Scheme 3A.

This diepoxy monomer is based on vanillic acid, which is easily obtained from vanillin and also an available synthon from lignin depolymerization. Ultimately, the epoxidation step is a chemo-enzymatic process (Scheme 3A), a very interesting reaction in terms of sustainability due to the use of a catalytic system (enzyme) and mild conditions (40 °C). It led to a mixture of diepoxidized product (66%) and monoepoxidized product. However, the use of DMF as solvent (category 1B reproductive toxicity) in the allylation step is less ideal in terms of safety, and an alternative solvent could be a possible improvement for this reaction. Also, the presence of ester linkages might limit the thermo-stability of the final material. The same team also used another strategy by directly functionalizing vanillic acid in a two-step procedure (Scheme 3B) to prepare another diepoxy monomer. Once again the diepoxidation was only partial (70%) and the same concerns about the use of allyl bromide and DMF can be raised, even if this enzymatically catalyzed epoxidation reaction is an interesting alternative to the use of epichlorohydrin. These compounds were envisaged as epoxy monomers but polymers were not prepared.

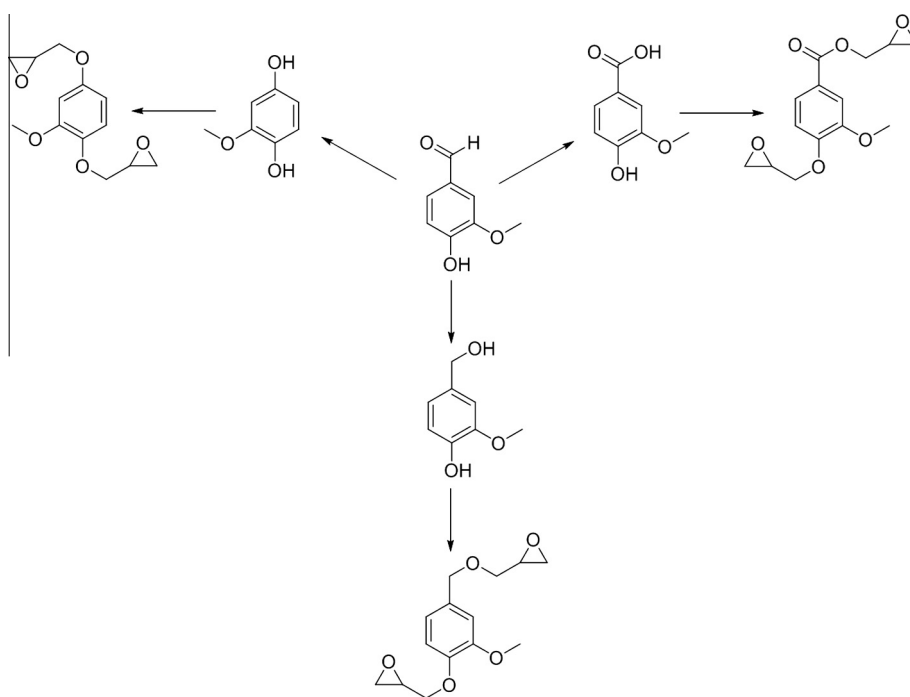
Our team also prepared diepoxy monomers from vanillin derivatives [36]. Scheme 4 shows the three diepoxy monomers prepared from the same direct functionalization strategy.



Scheme 2. Synthesis of diaromatic epoxy monomer from vanillin, pentaerythritol, and epichlorohydrin.



Scheme 3. Chemo-enzymatic synthesis of a epoxy monomers from vanillic acid.



Scheme 4. Diepoxy monomers prepared by direct functionalization of vanillin derivatives.

The three vanillin derivatives chosen were in different oxidation states, either oxidized or reduced. It is worthy to note that methoxyhydroquinone was prepared through a green vanillin oxidation process leading to the loss of one carbon atom. Briefly, vanillin was subjected to a Dakin oxidation with sodium percarbonate as an environmentally-friendly oxidant in a THF/water mixture at room temperature. Sodium percarbonate is a large-scale available chemical commonly used in laundry detergents. It is a good alternative to hydrogen peroxide, which storage and transportation is not desirable for safety reasons. On the contrary, sodium percarbonate is an environmentally-friendly solid compound composed of sodium carbonate and hydrogen peroxide. It is a powerful oxidant, while being cheap, non-toxic, stable upon storing, and easily handled.

Vanillic acid and vanillyl alcohol were purchased as their syntheses (the former by oxidation and the latter by reduction) are conventional reactions, well-described in the literature. Epichlorohydrin was used to perform a one-step glycidylation of these compounds and obtain the three diepoxy monomers shown. It is worthy to note that acid- and amine-functionalized vanillin derivatives were also prepared in the same work. They could potentially be employed as hardeners in epoxy thermosets.

These diepoxy monomers were used to prepare bio-based epoxy thermosets [37]. The polymers, all hardened with the same diamine, displayed excellent thermo-mechanical properties (Fig. 1), matching the ones from the current industrial reference, the DiGlycidyl Ether of Bisphenol A (DGEBA). For instance, a T_g of 152 °C was

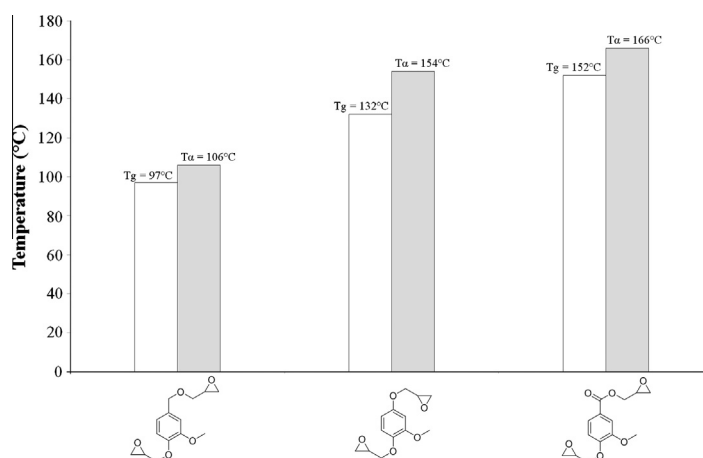
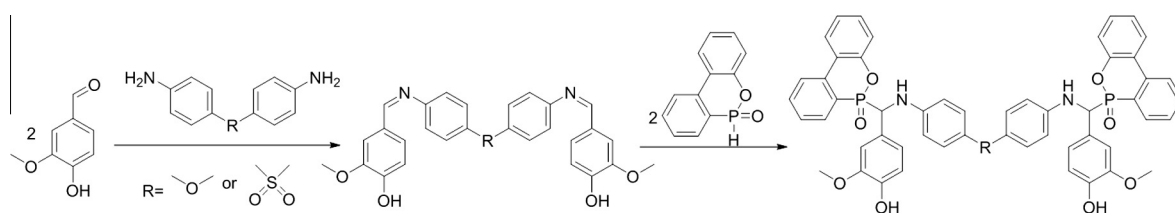


Fig. 1. T_g and T_a from vanillin-based epoxy materials.



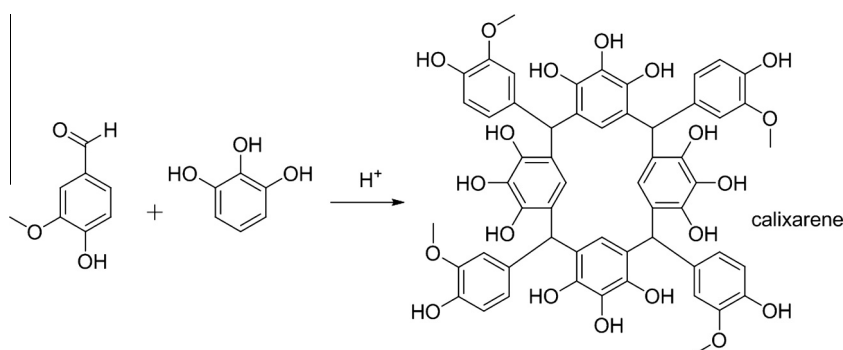
Scheme 5. Synthesis of a vanillin-based, phosphorus-containing, flame-retardant epoxy hardener.

found for the thermoset prepared from the diglycidyl ether of vanillic acid. Moreover, properties could be tuned depending on the starting monomer. They are candidates to the substitution of Bisphenol A in epoxy polymers. Work is underway to prepare oligomers from these diepoxy monomers, using the strategy currently used for the preparation of industrial epoxy resins.

Vanillin can not only be used to prepare epoxy monomers, but also to prepare hardeners for epoxy curing. The study of Gu et al. employed this strategy as they prepared two vanillin derivatives by a coupling strategy to be used as co-curing agents [38]. Additionally, the authors designed these co-curing agents as halogen-free, flame retardants by introducing a common phosphorylated flame-retardant moiety onto them: the 9,10-Dihydro-9-

oxa-10-phosphaphenanthrene 10-oxide (DOPO). Their synthetic strategy is shown in Scheme 5.

Briefly, the first step consisted in reacting two vanillin molecules with a diamine to form a bis-aldimine with pendant phenols. The DOPO was then grafted on the aldimine liaisons by a Pudovik-like reaction, i.e. the addition of the P-H liaisons on the C=N double bonds. The reaction is straightforward and was conducted as a one-pot procedure. The product is a phosphorus-containing diphenol which was used as a co-hardener during the polymerization of a DGEBA prepolymer with a commercial diamine. The thermal and flame-retardation properties of the thermosets prepared were investigated. The char yield and morphology were improved by the introduction of this vanillin-based co-hardener. The preparation of efficient



Scheme 6. Preparation of a calixarene from vanillin and pyrogallol.

and safe flame-retardant epoxy thermosets is a hot industrial topic in which vanillin could prove useful.

In another study, epoxy polymers were prepared using vanillin in an unexpected way. Indeed, Shimasaki et al. [39] first prepared a calixarene by condensing pyrogallol (also biobased) and vanillin as shown in Scheme 6.

The next step of their work was to prepare a composite with a sorbitol-based epoxy matrix hardened with the calixarene they synthesized from vanillin. They obtained a polymer with a T_g of 148 °C, which is high for biobased epoxy polymers. The next step of their work was to use wood flour as a filler in this epoxy matrix, leading to a fully biobased epoxy composite. One of the major highlight of this work is the preparation of the calixarene used as hardener. This compound was formed by the condensation reaction used to prepare phenolic resins, but in their case, the oligomer formed has a well-defined, polyphenolic cyclic structure. The performance of this compound in other fields might be worth investigating; in catalysis or supramolecular chemistry for its potential host–guest interactions for instance.

2.3. Phenolic resins

Thermosetting phenolic resins were developed as early as the 1900's with the Bakelite resin formed by the condensation of phenol and formaldehyde. Since then, their low price combined with very good thermo-mechanical properties maintained them as an important class of polymers, irreplaceable in some applications. With the current urge to switch from petrobased to renewable resources, there is surprisingly very few studies dealing with the bio-sourcing of this kind of polymer. Yet, vanillin is a good starting point as it is aromatic, biobased and bears both a phenol and an aldehyde moiety.

Chauhan prepared a terpolymer using the condensation reaction of vanillin and acetophenone with furfural, also a biobased compound [40]. He proposed the following structure (Fig. 2).

Even though the structure of the polymer obtained is likely to be more complex, ^1H NMR showed the presence of all three monomers in the final material. Interestingly, the author depicted the vanillin aldehyde moiety as unreacted; although the residual signal of the aldehyde proton in the ^1H NMR of the final material is very weak. Further characterization of this polymer revealed a microporous structure and a high thermal stability that could lead to an application in catalysis for example.

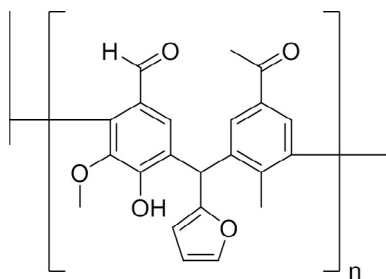


Fig. 2. Proposed structure of a vanillin–furfural–acetophenone terpolymer.

The same author prepared another terpolymer based on the condensation reaction of vanillin oxime and acetophenone with formaldehyde [41]. The oxime group is widely employed for its antimicrobial properties. The preparation of vanillin oxime from vanillin and hydroxylamine is a simple and easy-to-implement reaction with a high yield. The polymer displayed moderate to good antimicrobial activity, depending on the bacteria or fungus tested. The author envisaged the use of this polymer for medical device coating. A drawback of this method is however the use of formaldehyde, a category 1B carcinogenic compound that would advantageously be replaced by a less dangerous, biobased aldehyde.

2.4. (Meth)acrylic polymers

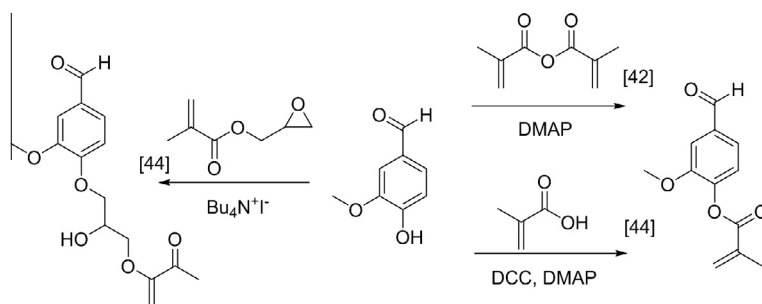
Functionalization with acrylic groups, e.g. acrylate, methacrylate, or acrylamide, is among the most common strategies employed when it comes to the use of chain-growth polymerization. Their polymerization is easily induced by UV or heat in the presence of an appropriate initiator.

A handful of papers report the functionalization of vanillin with methacrylate groups. They are summed up in Scheme 7.

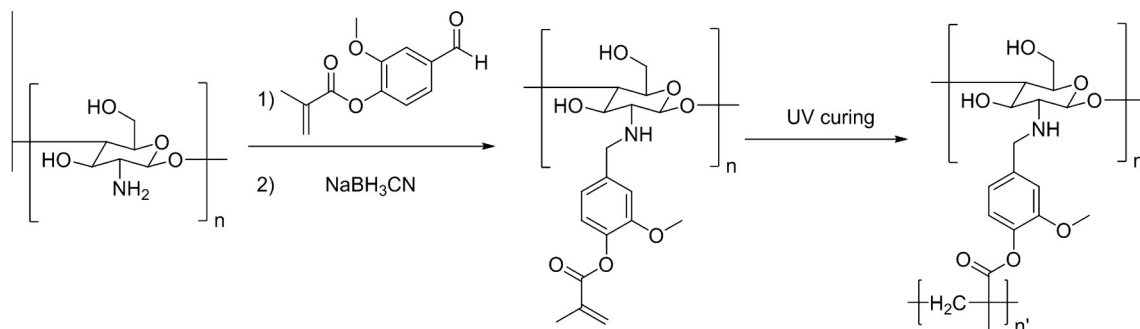
In their work, Stanzone III et al. prepared vanillin methacrylate and polymerized it to obtain a biobased thermoset with glycerol methacrylate as a crosslinker [42]. The reaction was carried out without solvent, which is relevant from a sustainability point of view. Indeed, solvents can be volatile, flammable, and/or harmful substances. Avoiding them is thus beneficial in terms of safety. Also, less waste is generated in the case of solvent-less reactions. The polymer synthesized exhibited a T_g of 155 °C at the $\tan \delta$ maximum, T_g being the temperature of the α transition, related to the glass transition but under mechanical stress (and thus frequency-dependent). This temperature was taken, as it is common in the literature, as the glass transition temperature (T_g) of the polymer. It is worthy to note that only few biobased polymers are able to reach the thermo-mechanical properties displayed in this work, properties that the authors compared to commercial vinyl ester resins. They envisaged an application as matrix for composites.

Holmberg et al., from the same team, also synthesized by RAFT polymerization [43] homopolymers from vanillin methacrylate with a controlled molecular weight, which exhibited T_g values between 110 °C and 120 °C. They also prepared block copolymers of vanillin methacrylate and lauryl methacrylate and showed that this copolymer self-assembled into nanospheres.

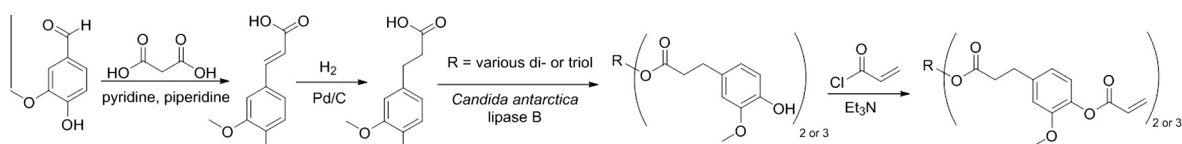
Renbutsu et al. [44] also prepared vanillin methacrylate using a different method: they performed a Steglich esterification (Scheme 7) of the phenolic hydroxyl of vanillin with methacrylic acid. The next step of their work was to functionalize the free amine groups of chitosan by a reductive amination reaction with the aldehyde moiety of vanillin methacrylate. Finally, they crosslinked the system by UV-induced radical polymerization of the methacrylate moieties as shown in Scheme 8.



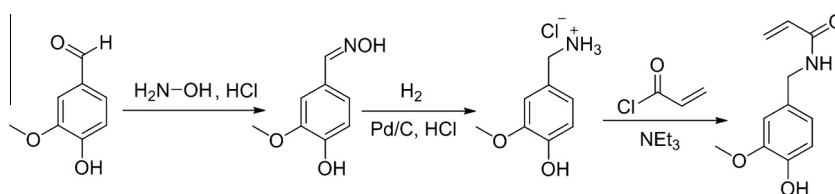
Scheme 7. Vanillin functionalization with acrylate and methacrylate groups.



Scheme 8. Chitosan functionalization with vanillin methacrylate and crosslinking of the system.



Scheme 9. Multi-step procedure to obtain di- or triacrylates from vanillin and various potentially biobased alcohols.



Scheme 10. Synthesis of an acrylamide monomer from vanillin.

The same authors also prepared another methacrylate derivative of vanillin by reacting the phenolic hydroxyl of vanillin with glycidyl methacrylate as shown in [Scheme 7](#). This compound was also used to functionalize chitosan and prepare a crosslinked material, using the strategy depicted in [Scheme 8](#). These crosslinked chitosan derivatives were tested for palladium adsorption and electroless plating with good results in both cases.

Pion et al. used vanillin to prepare acrylates in a multi-step procedure [\[45\]](#) shown in [Scheme 9](#).

The first part of their work is the preparation of ferulic acid from vanillin by a Knoevenagel condensation with

malonic acid. Ferulic acid could also be directly obtained from lignin but its production is not industrially developed compared to vanillin. This compound was reduced into dihydroferulic acid, which was then enzymatically esterified with various di- or triols to obtain biobased bis- and trisphenols. These phenols were further functionalized to acrylates to be used as crosslinking agents. Even though the whole procedure might not be industrially viable because of the many steps involved, the intermediates accessed during the synthesis are interesting for the bio-sourcing of a variety of polymers such as epoxy thermosets or polyesters.

Liu et al. [46] designed an acrylamide monomer from vanillin (Scheme 10). This monomer possesses great potential as it can lead, by radical polymerization, to a vanillin-based polyacrylamide bearing pendant phenolic moieties.

The procedure was performed at room temperature, which is interesting from the energy economy aspect. This monomer was then polymerized to give a polyacrylamide having pendant, covalently bound phenols along the chains acting as antibacterial moieties. The conventional radical polymerization of this monomer proved tricky. Whatever the conditions used (reaction time, initiator concentration and temperature) average molar masses were relatively low ($\leq 11,000$ g/mol). Authors attributed this phenomenon to the well-known polymerization inhibition effect of phenolic moieties. Branching was also observed, which was attributed to transfer reactions of macroradicals to phenols. The mechanistic aspects of the reaction were investigated by MALDI-TOF. In spite of their low molar masses, one can imagine many applications for this type of innovative polymer. The team focused their work on surface coatings. The authors demonstrated that this polymer with pending phenols exhibited an anti-biofilm activity against *Bacillus subtilis*. As the antibacterial moieties – phenols – are covalently bound to the surface, authors proposed an inhibition of bacterial growth by contact with the surface. Coatings of medical devices could be a potential application.

2.5. Polyesters

The third most-produced polymer worldwide (18%) is Poly(Ethylene Terephthalate) (PET). This fact alone could justify the need of biosourcing polyesters, even if there are many other well-known types of polyester used in a myriad of applications. Numerous strategies exist to obtain biobased polyesters with properties similar to PET, including the direct replacement with bio-PET, which is already an industrial reality, or the use of furan dicarboxylic acid as a substitute to terephthalic acid. Vanillin, being one of the very few biobased aromatic synthon available, has also been used to prepare polyesters.

Mialon et al. used a strategy very similar to the one described above for acrylates in their effort to prepare polyesters from vanillin [47]. More precisely, they used a Perkin reaction to prepare acetylferulic acid, which was then reduced to acetyl dihydroferulic acid. This AB type monomer was then polymerized by a condensation reaction to lead to a vanillin-based renewable polyester as shown in Scheme 11.

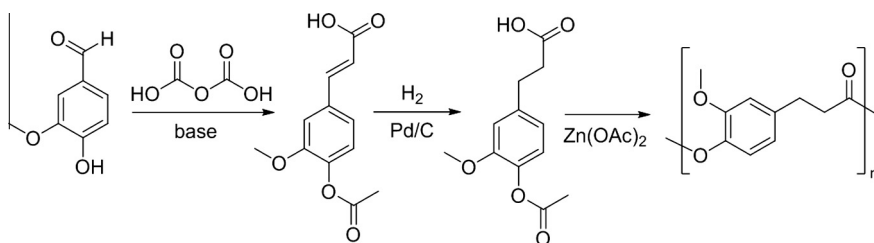
This polymer displayed interesting thermal properties: Its melting temperature is 30 °C lower than PET while both have a T_g around 70 °C. Such properties are critical when it comes to processing and this biobased polymer could thus be envisaged as a PET substitute. This strategy of mimicking PET properties with a polyester derived from renewable resources was also patented [48].

The same team also prepared polyesters from vanillic acid among other hydroxybenzoic acids obtained from wood [49]. They demonstrated that the polymerizations of vanillic acid either by direct esterification or from a transesterification reaction with an AB type monomer – methyl vanillate or O-acetyl vanillic acid – were unsuccessful or only yielded oligomers at best. This might be due to the presence of phenolic hydroxyls, which are less reactive than aliphatic ones. Also, the absence of aliphatic moieties might dramatically increase the viscosity of the mixture during the reaction, limiting the conversion. The authors prepared AB type monomers bearing aliphatic hydroxyls, best suited for direct esterification reaction, and were successful in preparing a series of polyesters (see Scheme 12). They observed a decrease in the T_g with an increasing number of carbons in the alkylene segment. The monomers were prepared by reaction of the phenol group either with chloroalkyls or with oxirane ring-containing compounds like ethylene oxide.

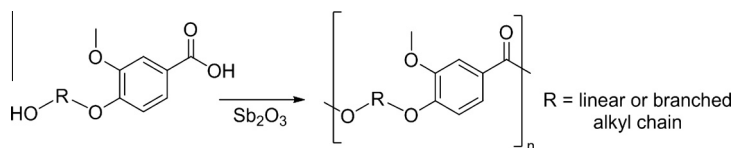
This last reaction had already been discussed in a previous paper by Lange et al. to prepare the AB type monomer from vanillic acid and ethylene oxide, leading to poly(ethylene vanillate) [50]. In the same paper, the authors also mentioned the synthesis of a dibenzoic acid from vanillic acid using a coupling strategy with dibromoethane and the subsequent polymerization of the monomer prepared. They reported a reaction of the phenolic hydroxyls on dibromoethane.

Pang et al. used a similar coupling strategy to prepare the two monomers shown in Fig. 3(A and C) from vanillic acid. Dibromobutane reacted with phenolic hydroxyls of methyl vanillate [51] or vanillic acid [52] to lead to these monomers. Various polyesters were prepared from these two monomers. In the case of the vanillic acid derivative, esterifications with various common alkyl diols [52] were performed. In the case of the methyl vanillate derivative, polymerizations were performed via transesterifications with aliphatic diols prepared via thiol-ene chemistry [51].

The same team also prepared the two asymmetric monomers shown in Fig. 3(B and D) from the same reactants but with another synthetic strategy, i.e. by reacting them with methyl chloroacetate. These monomers were



Scheme 11. Synthesis of an aromatic polyester from vanillin.



Scheme 12. Vanillic acid-based polyesters by esterification of AB type monomers.

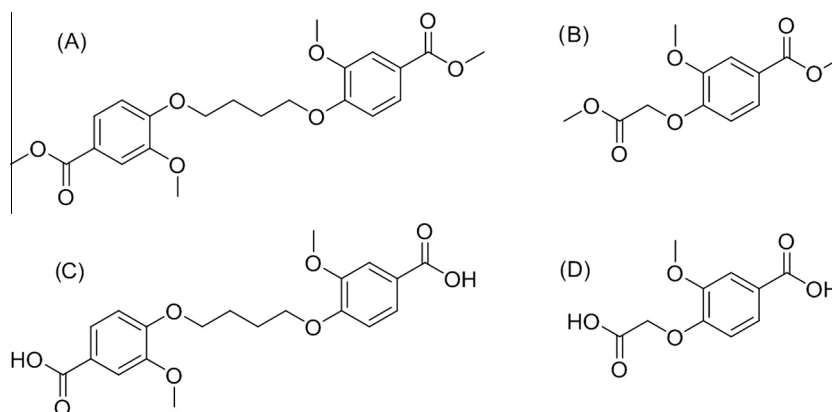
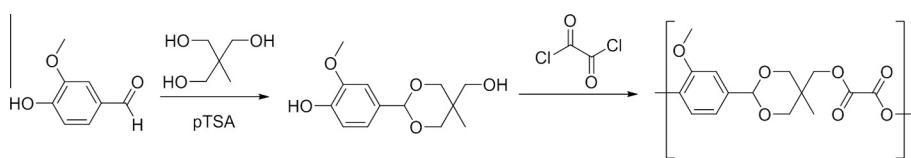


Fig. 3. Di(methyl vanillate) monomers polymerizable by transesterification.



Scheme 13. Synthesis of an acid- and oxidant-sensitive polyester from vanillin.

reacted with the same diols as previously mentioned. In summary, the authors obtained two series of polyesters, either from the asymmetric monomers or from the ones prepared by a coupling strategy. All these polymers were characterized and authors investigated their crystallinity, molecular weight, transition temperatures, mechanical properties, improving the overall knowledge on biobased polyesters.

Original polyester microparticles based on vanillin were synthesized by Kwon et al. [53]. Their approach is shown in Scheme 13. In a first step, vanillin was acetalized with trimethylolethane to form a dihydroxyl intermediate that was polymerized in a second step with oxalyl chloride to form a polyester.

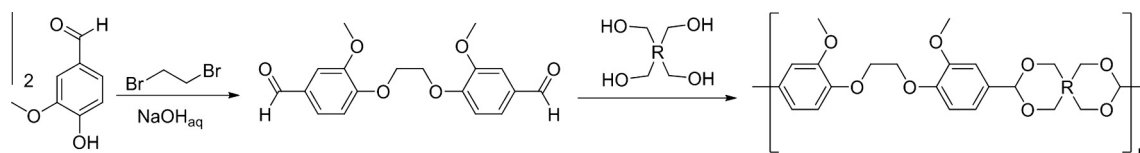
The authors designed this polyester to contain vanillin molecules in its backbone that were released in acidic or oxidative conditions by chain cleavage, along with

trimethylolethane and CO₂. The free vanillin molecules released had an excellent anti-oxidative and anti-inflammatory activity. These stimulus-responsive polyester microparticles could be used for the controlled release of therapeutics (vanillin here) to treat oxidative stress-associated inflammatory diseases.

2.6. Polyacetal

The contribution of Pemba et al. to the development of polymers from renewable resources also involved the acetalization of vanillin. More precisely, the authors synthesized a polyacetal from dialdehyde and tetraol monomers [54] as displayed in Scheme 14.

The first step of this synthesis involved the preparation of a difunctional monomer from vanillin by a coupling strategy. Two molecules of vanillin reacted on dibromoethane to



Scheme 14. Synthesis of a polyacetal from vanillin.

lead to a dialdehyde monomer. In a second step, this monomer was reacted with a tetrafunctional alcohol – also potentially biobased – to form a polyacetal. Authors investigated the properties of the polymers prepared and reported relatively high T_g for biobased thermoplastic polymers, ranging from 68 °C to 152 °C depending on the structure and molecular weight. The presence of aromatic rings along the backbone might explain this result. The authors also mentioned the rapid hydrolysis of acetal bonds in aqueous acidic media, which can be either a drawback or an advantage depending on the property desired (stability or degradability). When it comes to lowering the carbon footprint of polymers, (bio)degradable and/or easily recyclable polymers are a very promising option.

2.7. Polyaldimines (Schiff base from aldehyde)

The reaction between an aldehyde and an amine leading to a secondary aldimine, better known as a Schiff base, is a well-described reaction. Schiff bases are widely used compounds in many fields such as biochemistry, catalysis as ligands, organic synthesis and polymers. The aldehyde group of the vanillin molecule can undergo such a reaction with an amine. The literature reports many studies where free amines on chitosan chains were functionalized with pendant vanillin molecules as shown in Scheme 15. Amines and aldimines pictured in this scheme might be protonated, depending on the pH conditions used in the studies. This vanillin-modified chitosan has numerous applications.

For instance, Jagadish et al. used this reaction to prepare a vanillin-modified chitosan with a degree of substitution of 63% relative to the amino group. In a second step, they reduced the aldimine bonds with sodium cyanoborohydride. Thus, the authors prepared a N-vanillylamine chitosan polymer [55] and evidenced improved tensile strength, transparency, and water vapor transmission properties compared to native chitosan. Antifungal properties against *Aspergillus flavus* were also assessed. A moderate decrease in biomass proliferation was detected, and also, interestingly, a marked reduction of the aflatoxin produced by the fungus. From these findings, authors proposed the use of this polymer in food packaging applications.

Peng et al. also used the reaction shown in Scheme 15 to synthesize a vanillylimine chitosan polymer. They prepared resveratrol-loaded microspheres [56] from it and assessed the potential of the system for drug delivery applications. The authors mentioned that the formation of these microspheres took place through a chemical crosslinking reaction between chitosan and vanillin. However, as it can be seen in Scheme 15, the Schiff base

formation cannot account for a covalent crosslinking as the pendant phenolic hydroxyls groups do not form covalent bonds with the chitosan backbone.

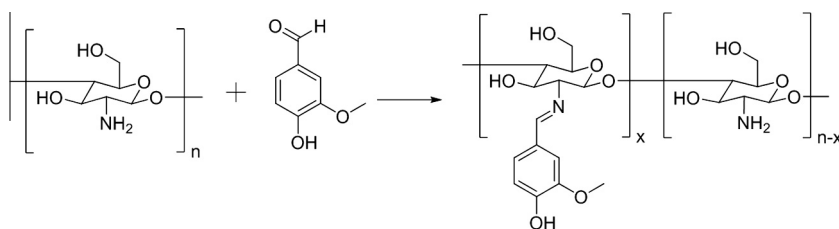
Marin et al. investigated the reaction in more details [57]. They reported the formation of strong gels and attributed this to strong H-bonding instead of covalent crosslinking. Chitosan is only soluble in acidic aqueous medium but the authors obtained very low degrees of substitution in these conditions. This result might be explained by the fact that imine groups are not stable in such conditions: they can be protonated to iminium groups which undergo hydrolysis to give back the starting aldehyde (Stephen reaction). In this case, aldimine bonds are thus reversible and the authors demonstrated that pendant group exchanges took place and called the materials prepared biodynamers. Finally, the authors demonstrated that the solution-to-solid state change process is highly beneficial for imine bond formation and that conversion dramatically increased in a hydrophobic environment.

The same team confirmed by XRD that this crosslinking of vanillin-modified chitosan happened through strong H bonding formation [58], especially at high degree of substitution. They also showed that through this H bonding, vanillin-modified chitosan presented a self-organized lamellar phase in the solid state as displayed in Fig. 4. The antifungal properties of these films on *Candida albicans* strain were investigated and found to be outstanding.

Vanillin-modified chitosan also found applications in water treatment, as a metal ion sorbent. Indeed, imine groups are known for their chelation properties. Cestari et al. studied the thermodynamics of the adsorption of Cu(II) on membranes of vanillin-modified chitosan and were able to fit a Langmuir model to the phenomenon. They concluded that the mechanism followed a monolayer adsorption and that this material was effective to remove low concentrations of Cu(II) from aqueous solutions [59].

Amarasekara et al. also investigated interactions of aldimine groups from vanillin with metal ions, but instead of preparing physically crosslinked materials through H bonding, they prepared covalently crosslinked polymers [60]. They synthesized bisvanillin by an enzyme-catalyzed oxidative coupling of two vanillin molecule (Scheme 16). Then, they used this product as a difunctional aldehyde monomer and polymerized it with various diamines.

The authors used the basic form of the polymer to chelate Fe(II), Cu(II), and Co(II) ions and obtained insoluble materials. Authors confirmed that the metal ions were bound to the imine and phenolic sites. These polymers could be used in water treatment.



Scheme 15. Chitosan functionalization with vanillin by an aldimine bond formation.

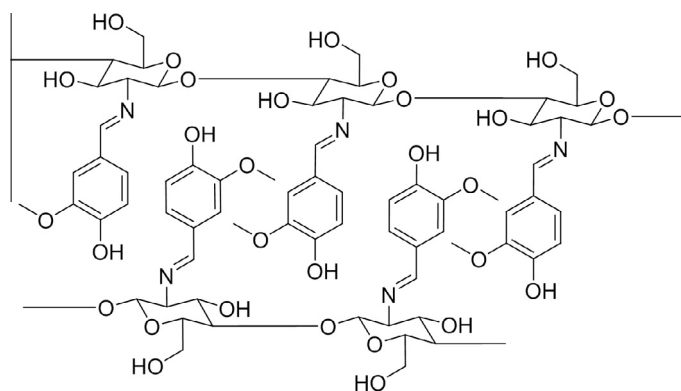
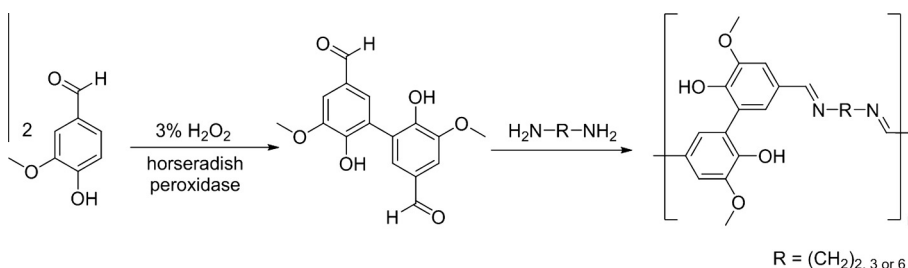
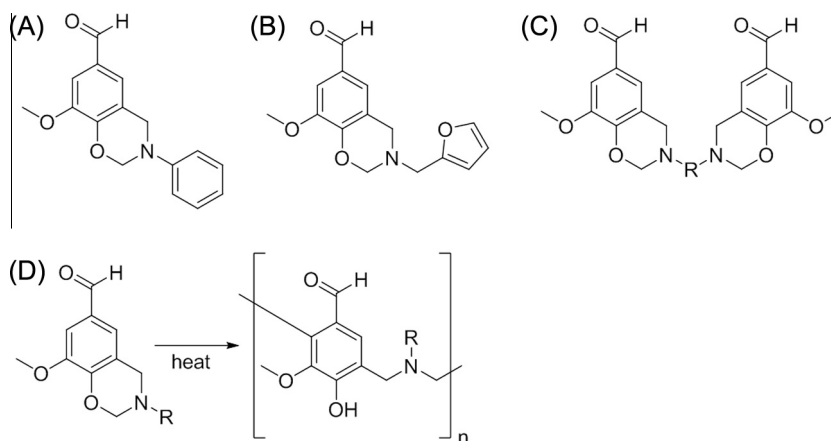


Fig. 4. Lamellar self-organized phase of vanillin-modified chitosan.



Scheme 16. Bisvanillin synthesis and polymerization with diamines to poly(aldimines).



Scheme 17. Benzoxazine monomers based on vanillin and their polymerization.

2.8. Polybenzoxazines

Polybenzoxazines are a relatively new class of high performance thermosetting polymers. They exhibit excellent thermo-mechanical properties and chemical resistance. As for many high performance thermosets, benzoxazine monomers have an aromatic structure. Recently, many contributions reported the synthesis of biobased benzoxazine monomers and polymers. The benzoxazine ring is formed by reacting a phenol, a primary amine and formaldehyde. In some of these works, the phenol used was vanillin.

Van et al., for instance, prepared the monomer displayed in Scheme 17A by reacting vanillin, aniline and paraformaldehyde. The monomer was heated to prepare a thermosetting polymer [61] by ring opening polymerization of the benzoxazine ring as shown in Scheme 17D.

The authors also further functionalized this compound to prepare a surfactant by grafting a Jeffamine hydrophilic tail onto the benzoxazine monomer. The grafting reaction took place between the primary amine of the Jeffamine and the free aldehyde of the benzoxazine to form an aldimine. This surfactant was successfully used in the

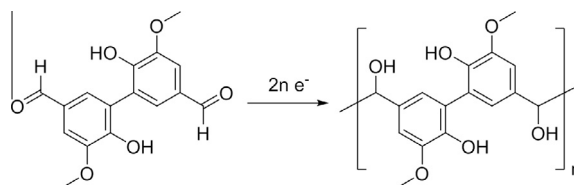
emulsion polymerization of styrene as the hydrophobic benzoxazine part had a strong affinity for (poly)styrene.

The team of Sini et al. also reported the synthesis and polymerization of a benzoxazine monomer based on vanillin. They used the biobased furfurylamine [62] to prepare the monomer depicted in Scheme 17B and increase the content of renewable carbon in their polymer. The same authors also reported the synthesis of bisbenzoxazine monomers from vanillin and various diamines [63] as shown in Scheme 17C. The T_g reported for the polymers based on bisbenzoxazines were above 200 °C and very broad, which might be explained by a very high cross-linking density. In all of these works, the polymers prepared displayed outstanding thermal stability, which supports this hypothesis. However, high polymerization temperatures (around 200 °C) are needed, which is usual for polybenzoxazines but can be a drawback when it comes to their application.

2.9. Polymers from alkenes

The carbon–carbon double bond has always been a valuable tool for polymer chemists, traditionally useful for chain-growth polymerization reactions. Recently however, reactions involving alkenes and leading to polymers by a step-growth mechanism instead of chain-growth were developed. These reactions are Acyclic Diene MEtaThesis (ADMET) and thiol-ene reactions. Both display good control, useful to prepare well-defined architectures, high efficiency, and high functional group tolerance. These characteristics gained importance in the context of green chemistry. ADMET is a transition metal-catalyzed reaction that takes place between two terminal alkenes and that is driven by the release of ethylene (Scheme 18A). Thiol-ene reaction is a well-known example of click chemistry and can be either UV- or heat-induced (Scheme 18B). In their contribution, Firdaus and Meier prepared vanillin-based monomers bearing terminal C=C double bonds suitable for these reactions [64] as shown in Scheme 18C.

These C–C double bonds are introduced either by transesterification with an unsaturated fatty ester or by Williamson etherification with an alkene bromide. The first option might be better from a sustainable chemistry point of view.



Scheme 19. Bisvanillin polymerization by reductive coupling.

2.10. Polymers from reductive coupling of aldehydes

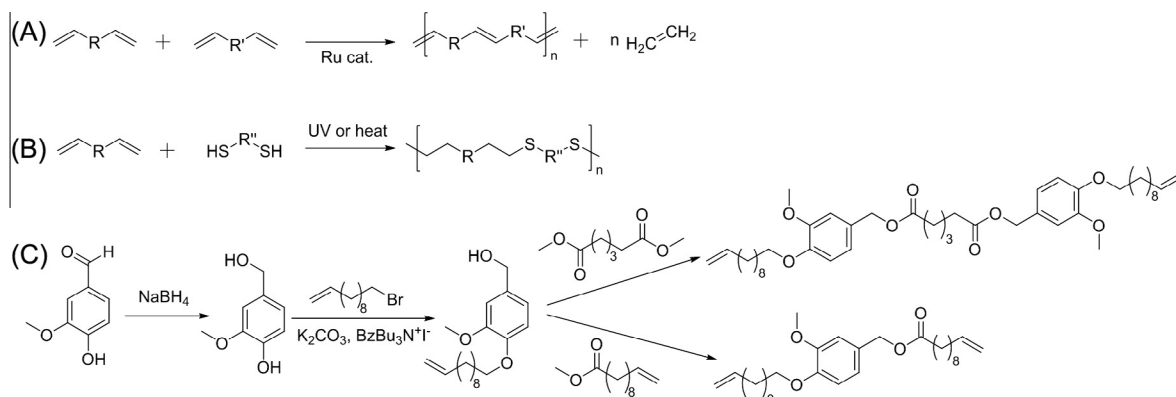
The use of renewable resources is only one aspect among many others that have to be considered to improve chemistry in general. Energy efficiency, atom economy, safety, etc. are examples of green chemistry requirements. To achieve this, new, greener processes are under development. The work of Amarasekara et al. is an example of this research trend.

As mentioned before, they prepared bisvanillin by an enzyme-catalyzed oxidative coupling of two vanillin molecule (Scheme 16). They used an original approach for the step-growth polymerization of this compound: bisvanillin was homopolymerized [65]. Authors used the reductive pinacol coupling of aldehydes to vicinal diols to prepare a polymer entirely based on vanillin as shown in Scheme 19.

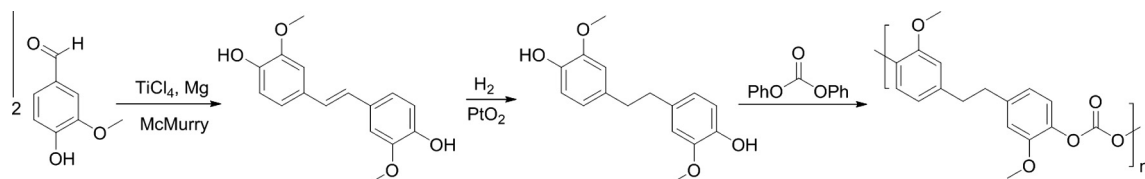
This elegant reaction was performed in an electrochemical cell; the scaling-up to an industrial process will thus require further development. Harvey et al. also used this reductive pinacol coupling of vanillin on a 40 g-scale to prepare hydrovanilloin in a 69% yield [66], which might be a first hint that this process can be used on a larger scale.

Their efforts were directed toward the synthesis of diphenolic monomers. This team also used a harsher reductive coupling reaction, i.e. the McMurry reaction [66], to attain their goal. Instead of obtaining a vicinal diol, the product of this reaction was a diphenolic stilbene, as shown in Scheme 20.

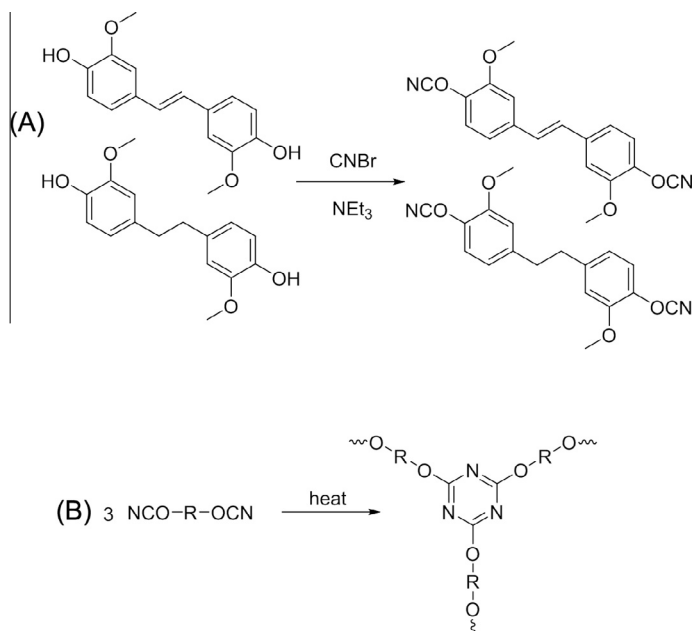
This compound was further reduced by catalytic hydrogenation to the alkyl derivative, which was used as a monomer to prepare a polycarbonate by a transcarbonation reaction with diphenyl carbonate. The authors investigated the thermal stability of this vanillin-based polycarbonate



Scheme 18. ADMET and thiol-ene polymerization of difunctional terminal alkenes monomers and their synthesis from vanillin.



Scheme 20. Synthesis of two diphenols from a McMurry reductive coupling of vanillin.



Scheme 21. Vanillin-based cyanate esters and their polymerization.

and evidenced an interesting feature of the degradation: the formation of benzodioxolones as a result of the methoxy group ortho to the carbonate.

Both of the diphenol monomers prepared were then modified to cyanate esters (Scheme 21A). Cyanate esters polymerize via a cyclotrimerization reaction (Scheme 21B) to form crosslinked cyanurate thermosets that possess a high thermal stability.

In this study, a high T_g of 202 °C was detected and a high temperature of 335 °C was reached for a 5% weight loss of the polymer. Once again, this work demonstrates the potential of vanillin as a key building block for polymers, here in the case of high performance materials.

3. Conclusion

The use of renewable resources is a burning issue to design a more sustainable chemistry. In polymer science, the use of oils and polysaccharides is already an industrial reality. However, a large number of polymers are based on aromatic monomers. The biosourcing of aromatics is more problematic because the widely available aromatic feedstocks, like lignin, are polymers with complex and variable structures, high molecular weights, and limited processability. Very few molecular aromatic compounds from renewable resources are readily available. Vanillin is one

of them. It is also harmless and offers many functionalization possibilities. Considering these advantages, studies on the use of vanillin for renewable polymers are surprisingly recent and rare, although their number is growing fast.

Vanillin can potentially be used to prepare many types of polymers, especially in high-performance thermosets such as epoxy polymers or polybenzoxazines, for which the first results seem very promising. Vanillin also shows potential uses for thermoplastics requiring aromatic monomers such as polyesters. As a consequence of this diversity, vanillin-based polymers, as reported in this review, could be used in a broad range of applications, such as composites, drug delivery, water treatment, flame retardation and antibacterial coatings. It is worthy to note that many research papers were published using vanillin in other contexts than the use of renewable resources, for instance liquid crystalline polymers, even if it was not in the scope of this study.

With the predicted shortcoming of petroleum-based resources and the resurgence of wood-based chemistry, vanillin has the potential to become one of the key building blocks of tomorrow's polymer chemistry. This review underlines the efforts of the scientific community to develop these new, more sustainable polymers from vanillin and shows that the number of contributions on this subject is growing fast.

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