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Fully biobased vitrimers: future direction towards sustainable cross-linked polymers

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Abstract

Improving the sustainability of polymer networks is a crucial challenge in polymer science, due to their important role in industry. Their traditional syntheses conflict with several principles of Green Chemistry as the employed monomers are petroleum-based, their production involves the use of toxic reagents and their permanently cross-linked structures impede their chemical recycling and reshaping. The development of vitrimers represents a unique solution to address the issue of polymer network end-of-life by enabling reprocessability while maintaining good thermomechanical properties and solvent resistance. Although over the last decades biomass has proved to be an excellent feedstock for the production of permanently cross-linked polymers, the field of biobased vitrimers is still at its infancy. In this review, we present a comprehensive overview of vitrimers synthesized from biobased monomers. The emphasis is set on the compatibility of the biomass structure with the nature of the dynamic covalent chemistry, as well as the sustainability of the synthetic approaches. Implementing renewable feedstocks and recyclability in the production of polymer networks paves the way for the development of the next-generation of sustainable materials.

1. Introduction

Nowadays, polymer networks find widespread applications in diverse areas due to their outstanding mechanical properties and resistance.^[1, 2] Even if the production of these polymers represents ~20% of the overall polymer production, their sustainability is questionable due to their lack of degradability and other environmental concerns. Indeed, the permanently cross-linked topology obtained after their syntheses impedes their chemical recycling and narrows their end-of-life to incineration or mechanical recycling.^[3, 4] Recently, to tackle this issue, different concepts, such as covalent adaptable networks, structurally tailored and engineered macromolecular networks, living additive manufacturing, macromolecular metamorphosis and covalent adaptable networks have emerged.^[5-9] All these strategies are based on the presence of reversible interactions in the polymer backbone or between the polymer chains. Such polymers exhibit a dynamic behavior that enables them to reversibly assemble and disassemble under specific conditions while remaining mechanically robust under utilization conditions (**Figure 1**).^[10]

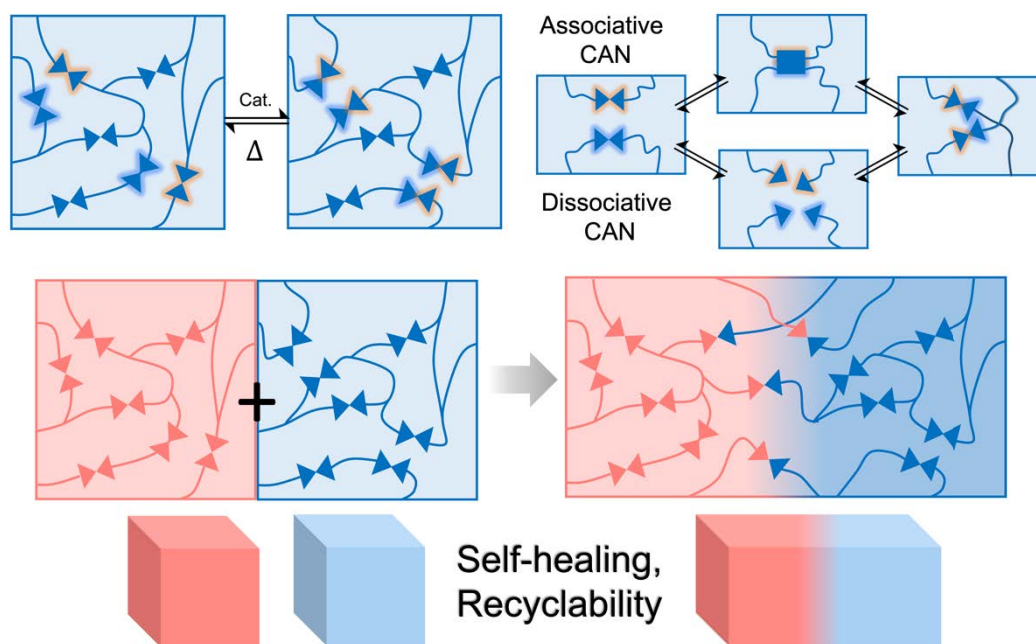


Figure 1. Structure of covalent adaptable networks (CAN) exhibiting associative or dissociative mechanisms and schematization of the self-healing or reprocessability of polymer networks

Covalent adaptable networks (CANs) are traditionally classified into two categories: dissociative and associative CANs. Associative CANs imply reversible exchange reactions, in

which bond formation precedes bond dissociation, thus resulting in materials with a constant cross-linking density.^[11-15] In 2011, Leibler's group named the associative CANs vitrimers, as their viscosity-temperature relationship resembles that of vitreous silica by following an Arrhenius-like dependence.^[16] However, the classification of CANs depending on the dynamic covalent chemistry mechanism is not trivial as the viscosity-temperature dependence of some dissociative CANs still follow Arrhenius' law, and competitions between associative and dissociative mechanisms exist. When the association constant of the reversible addition reaction is largely higher than the dissociation constant, macroscopic properties similar to vitrimers are observed. Some authors referred to these polymers by vitrimer-like materials.^[17-19] In 10 years, the development of vitrimers became an intensive research area of polymer science.^[20-26]

Even if it is crucial to consider the end-of-life of a product, its sustainability evaluation starts from the analysis of the employed feedstock and its extraction.^[27] In search for alternatives to the finite fossil feedstocks, which are depleting and cause environmental issues, the renewability and structural diversity of biomass makes it an excellent candidate. A large number of publications describe the synthesis of monomers and polymers from biomass, including for the preparation of thermosetting polymers.^[28-37] Aliphatic, cycloaliphatic or aromatic structures are available in nature, enabling the synthesis of biobased polymers with a broad range of thermomechanical properties (**Figure 2**). Vegetable oils constitute a platform of aliphatic hydrocarbons, particularly studied as polymer precursors due to their good availability, low price, inherent biodegradability and potential for chemical modifications as they can feature double bonds and hydroxyl groups. Triglycerides were directly used in the synthesis of polymer networks, generally with low glass transition temperatures.^[38-41] Well-defined fatty acids can be recovered after hydrolysis of triglycerides and further separation and purification.^[42] Notably, after further modifications, ricinoleic acid can be transformed into an aliphatic diacid, sebacic acid, and linoleic acid can be dimerized into a mixture of diacids and triacids named Pripol.^[43, 44] The corresponding mixture of diamines and triamines is named Priamine.^[45] Among the naturally occurring feedstocks, carbohydrates, including cellulose, starch, hemicellulose, alginate, chitin, etc. are composed of different monosaccharides (cycloaliphatic molecules). They constitute the most abundant part of plant biomass and possess a high diversity and accessibility. While cellulose, starch, and hemicellulose have only hydroxy functional groups, chitin offers amide groups and alginate has free carboxylic acid moieties. Cellulose and hemicellulose can be deconstructed into sugar compounds, which are precursors of a broad range of platform chemicals, including bicyclic derivatives, such as isosorbide, isomannide and isoidide, aromatic furan-based monomers, such as 2,5-furandicarboxylic, or short aliphatic

molecules such as itaconic acid, levulinic acid, succinic acid...^[46-48] All these molecules were used as monomers for biobased polymer synthesis.^[49-59] Terpenes, terpenoids and rosin, synthesized by plants and fungi, constitute another class of cycloaliphatic chemical feedstock accessible in large scale from various essential oils or as byproducts from diverse industrial processes. Their remarkable structural diversity offers versatile functionalization possibilities due to the presence of double bonds and hydroxyl, carbonyl or carboxylic acid groups in some cases. These molecules were directly used, or derivatized first, for biobased polymer production.^[60-64] The main source of phenolic, and so aromatic compounds is lignin. Isolated from wood or annual plant, this biopolymer constitutes the second most abundant renewable polymer after cellulose, and can also be recovered as a byproduct of the pulp industry. Its molecular structure contains methoxylated phenylpropanoid units, naturally built up from coumaryl alcohol, syringyl alcohol, and coniferyl alcohol to a heterogeneous, complex, macromolecular structure. Lignin can be directly used as a monomer, chemically modified, or depolymerized to recover aromatic monomers such as vanillin, syringaldehyde, or hydroxybenzoic acid.^[65-71]

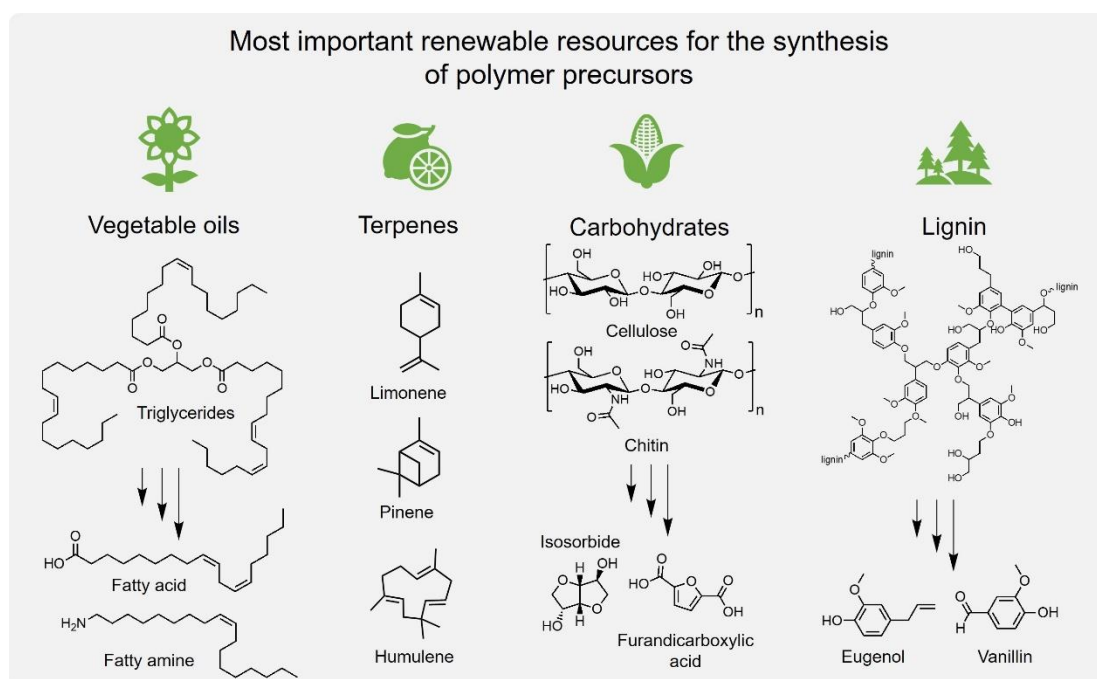


Figure 2. Most abundant biomass and structures of common biobased building blocks in polymer science

Using renewable feedstocks for the synthesis of vitrimers addresses two of the twelve principles of green chemistry, i.e. use of renewable resources and design for degradation, introduced by

Anastas and Warner.^[72,73] However, the development of sustainable chemical modification and polymerization methods, including nontoxic and environmentally benign reagents, catalytic procedures performed under mild conditions, and a decrease of energy consumption should also be considered to decrease the environmental impact of vitrimers.^[74]

Integrating the concepts of renewability, recyclability and green chemical procedures into the preparation of cross-linked polymers sets up the framework for the design of sustainable polymer networks. However, in the expanding subfield of dynamic cross-linked polymers, only few studies report the use of bioresources. This review gathers recently published works describing the implementation of renewable resources for the synthesis of materials featuring vitrimer properties. Based on these studies, the compatibility of bioresources with the different dynamic covalent chemistries generally employed for vitrimer synthesis is addressed. The sustainability of the synthetic approaches for the preparation of the polymer precursors is discussed qualitatively based on the chemical modifications required to produce the monomers and the use of hazardous and toxic materials. All copolymers with one petroleum-based comonomer are therefore not presented in details.

2. Transesterification reactions

2.1. Reactions between epoxides and carboxylic acids

The first example of vitrimer described by Leibler and coworkers in 2011 involved transesterification reactions (**Figure 3**) in partially biobased polymer networks.^[16] The networks were synthesized by reaction of the petroleum-based diglycidyl ether of bisphenol A with a mixture of fatty dicarboxylic and tricarboxylic acids. In the presence of zinc catalysts, at high temperature, these cross-linked polymers exhibited viscoelastic properties such as stress relaxation and malleability. Although monomers featuring acid and epoxide moieties can be easily synthesized from most of the bioresources, only few examples of fully biobased vitrimers were synthesized employing this chemistry. The structures of the poly(acids) and poly(epoxides), as well as the chemical pathways followed for their preparations are displayed in **Figure 4** and **Figure 5**.

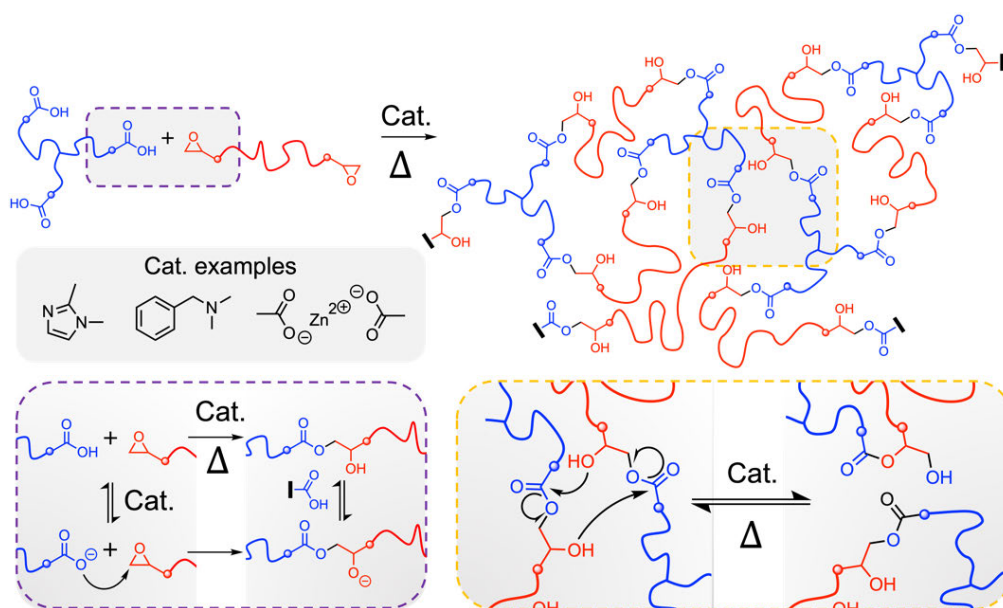


Figure 3. General scheme of polymer network formation from poly(carboxylic acids) and poly(epoxides) and mechanism of the exchange reaction (transesterification)

Liu and coworkers reported a vitrimer synthesis by reaction between epoxidized soybean oil (E1, Figure 4) and a rosin derivative, fumaropimaric acid (A4, Figure 5). Fumaropimaric acid is a triacid synthesized by Diels Alder reaction of rosin and fumaric acid, which can be produced via biotechnological processes starting from glucose.^[75] With their cycloaliphatic structure, such monomers are widely used to improve mechanical properties of vegetable oil-based polymers. A 1:1 mixing ratio of the two monomers provided, in the presence of zinc acetylacetonate catalyst, a polymer network with a glass transition temperature (T_g) of 65 °C. The relaxation times (time to reach $G/G_0 = 1/e$) of the network measured at different temperatures (1349 s at 200 °C) fitted the Arrhenius equation and an activation energy (E_a) of 87.9 kJ.mol⁻¹ was calculated. These materials exhibited a triple-shape memory using the molecular motion reached above the T_g , and the topological rearrangements occurring above the topology freezing transition temperature (T_v). Self-healing of cracked samples was observed at 180 °C. The vitrimers were degraded in the presence of ethanol at 140 °C without the addition of external catalyst. The physical recycling of the vitrimers was also achieved by compression molding at 160 °C.^[76]

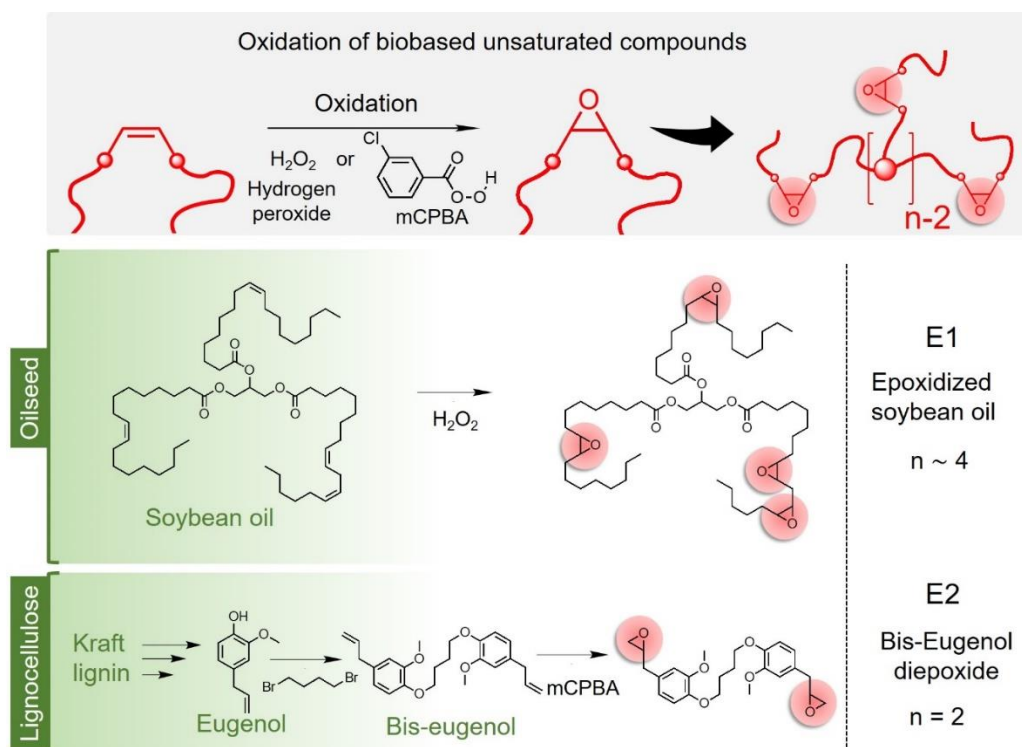


Figure 4. Synthesis of biobased poly(epoxides) by epoxidation of double bonds

Li and coworkers reported the synthesis of a fully biobased vitrimer from epoxidized soybean oil (**E1**, **Figure 4**) and glycyrrhizic acid (**A2**, **Figure 5**), which is a natural triterpene saponin, mainly found in licorice roots.^[77] Glycyrrhizic acid exhibits three acid groups and multiple hydroxyl groups that are crucial to induce transesterification reactions in the vitrimer. In the presence of an organocatalyst, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), the network formed with a carboxylic acid:epoxy ratio of 0.5 displayed a relaxation time of 425 s at 200 °C and an E_a of 112 kJ.mol⁻¹. The T_g of the vitrimers ranged from 39 to 64 °C depending on the molar ratios between the two monomers. Welding without pressure and crack-healing were observed at 200 °C. Shape memory, as well as adhesive properties on aluminium sheets were evidenced. The vitrimers were degraded in 14 h at 180 °C in the presence of ethylene glycol. The biocompatibility of the vitrimer was shown by cell culture experiments of fibroblasts NIH-3T3.

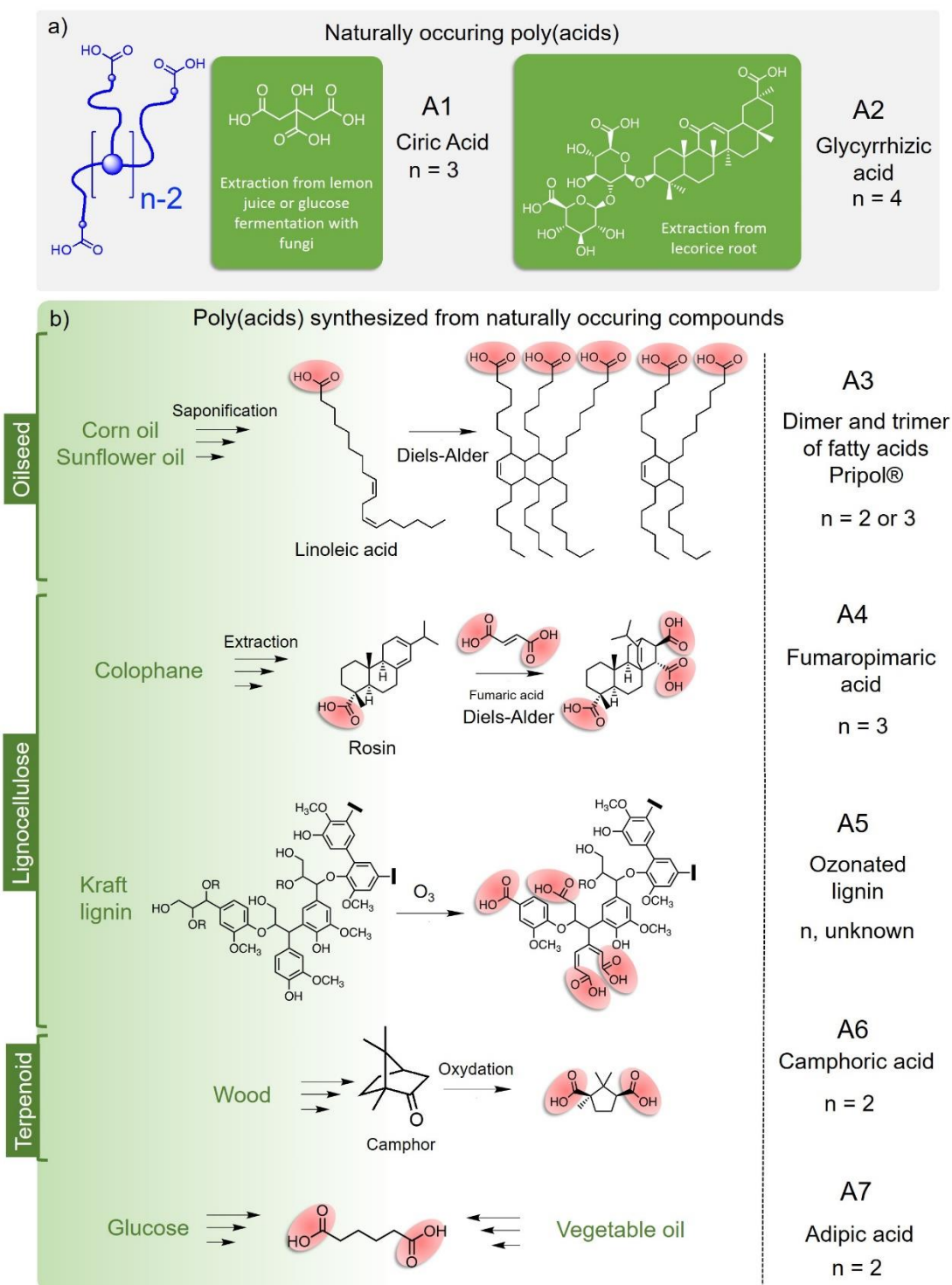


Figure 5. a) Structures of naturally occurring poly(acids), b) synthesis of biobased poly(acids)

Zhang and coworkers described the synthesis of a fully biobased vitrimer from ozonated Kraft lignin (**A5**, **Figure 5**) and a sebacic acid derived diepoxide (**E3**, **Figure 6**).^[78] The ozone oxidation of lignin is responsible for the reduction of lignin molar mass and the introduction of carboxylic acid moieties. The ozonated lignin displayed an acid content of 2.30 mmol.g^{-1} and an OH content of 0.96 mmol.g^{-1} . A diepoxide was prepared from castor oil-derived sebacic acid

by reaction with epichlorohydrin. During the curing of ozonated lignin with the sebacic acid derived diepoxide, in the presence of zinc catalyst, epoxy-carboxylic acid reactions and the epoxy-phenol reactions were observed respectively between 100-160 °C and 160-200 °C. Due to the aromatic structure of lignin, the networks exhibited relatively high T_g , ranging from 95 °C to 133 °C, depending on the monomer composition. The polymers showed stress relaxation at 160 °C and 200 °C but the activation energy was not determined. The relaxation times at 200 °C decreased from 1290 s, 223 s to 81 s when increasing the epoxy:(phenolic OH+carboxylic acid) ratio from 1:0.75, 1:1 to 1:1.5. Self-healing of a surface scratch and physical recycling by hot press occurred at 190 °C. The shape memory behavior and potential use of these lignin-based vitrimers as thermally recoverable adhesives were also demonstrated in this work. The level of adhesion on aluminium sheet was comparable to some traditional epoxy-based adhesives with the additional ability to rebound two substrates after a cohesive failure upon a thermal treatment. The sustainability of this approach has to be balanced as ozone is toxic and potentially carcinogenic. Moreover, even if epichlorohydrin can be synthesized from glycerol, a biobased building block (**Figure 6b**), it remains toxic as well as carcinogenic, mutagenic and reprotoxic (CMR).

Smaller building blocks obtained from lignin depolymerization were also used for the synthesis of transesterification-based vitrimers. For instance, Abu-Omar and coworkers synthesized an epoxy monomer starting from vanillyl alcohol and 4-methylcatechol, two compounds derived from lignin.^[79] Their condensation product featured a phenol and a catechol moiety that were glycidilated with epichlorohydrin to provide a triepoxide (**E4, Figure 6**). E4 was obtained in mixture with a monoepoxide exhibiting an a benzoxadioxane moiety (monoE, not represented here, obtained as a side-product). The ratio of the two products and then, the functionality of the mixture, could be tuned by adjusting the reaction conditions. Polymers were obtained by reaction with a mixture of fatty acid dimers and trimers (**A3, Figure 5**), in the presence of zinc catalyst. By decreasing the monoE:E4 ratio, the cross-linking density of the polymer network, and thus, the T_g increased from 11 °C to 23 °C. The monoE:E4 ratio of 86:14 was not sufficient to obtain a cross-linked structure. Increasing the E4 content to 60:40 and 36:64 led to the formation of dynamic polymer networks exhibiting a stress relaxation typical of vitrimers. With a relaxation time of 456 s at 120 °C the vitrimer with a composition of 60:40 relaxed faster than its homologue with a composition of 36:64 (relaxation time of 10 693 s at 130 °C) due to its lower cross-linking density. E_a of 59.5 kJ.mol⁻¹ and 24.3 kJ.mol⁻¹ were calculated for the compositions of 60:40 and 36:64, respectively. All the vitrimers exhibited elastomeric

properties. After breaking, welding of the polymers at 120 °C in 4 h and self-healing by simply contacting two pieces at 100 °C for 10 s were achieved.

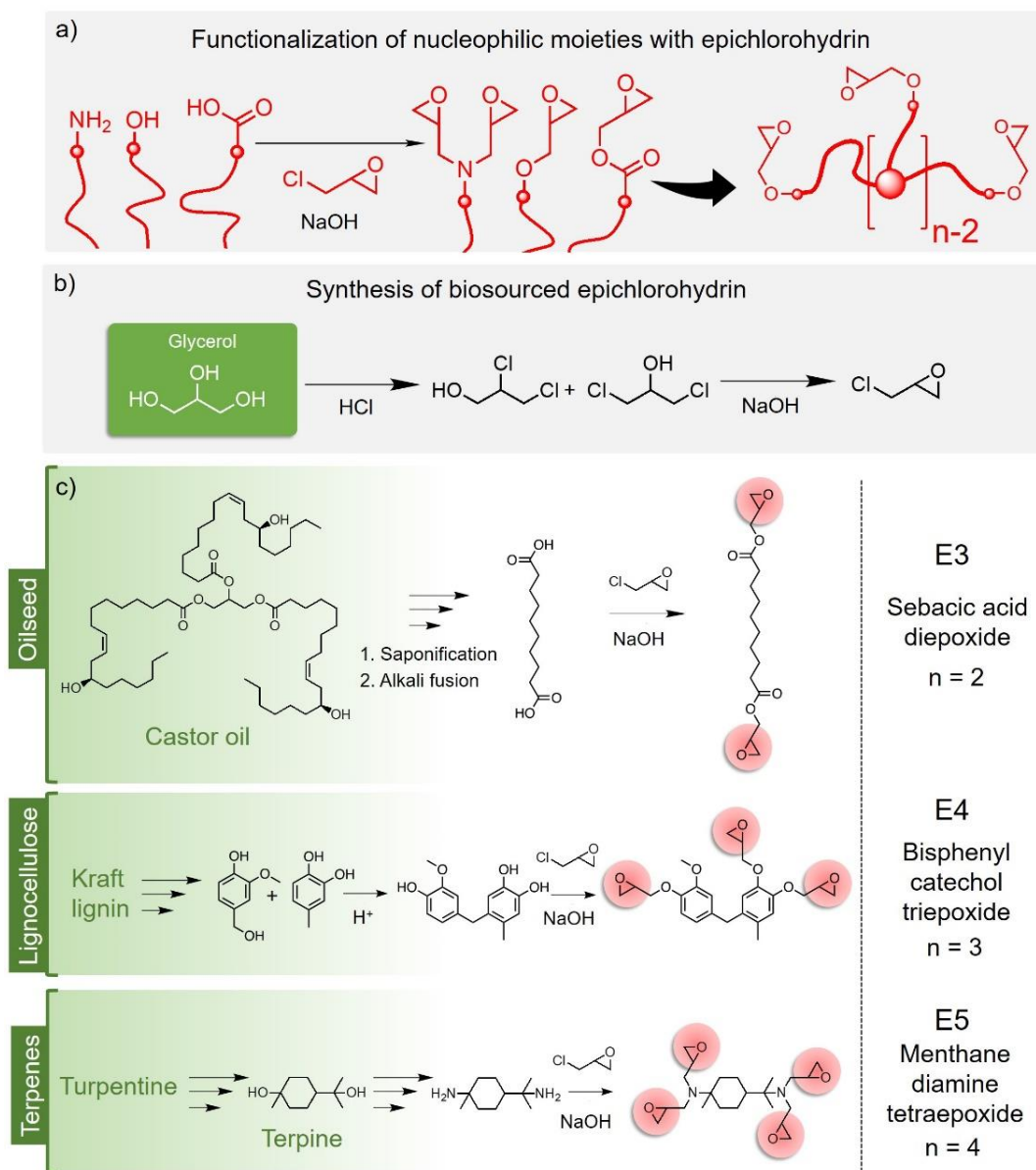


Figure 6. a) Functionalization of nucleophilic moieties with epichlorohydrin, b) synthesis of biobased epichlorohydrin, c) synthesis of biobased poly(epoxides) employing epichlorohydrin

All the above cited examples rely on catalysts to accelerate the exchange reaction. This strategy implies risk of leaching out of the material and limits the recyclability. To overcome this issue, internal catalysis or neighboring group participation were envisaged.^[80] Williams and coworkers reported one example of fully biobased vitrimer that did not require the use of additional catalyst.^[81] The authors cross-linked epoxidized soybean oil (**E1**, **Figure 4**) with an aqueous solution of citric acid (**A1**, **Figure 5**). The reaction was internally catalyzed by protons

produced by the dissociation of citric acid in water. After a certain time, the solution was drop-casted and post-cured at elevated temperature to form the desired network. The presence of β -hydroxyesters and vicinal diols induced transesterification reactions at elevated temperature in the absence of extrinsic catalyst. The relaxation times of the network measured at different temperatures (around 9000 s at 160 °C) fitted the Arrhenius equation and an E_a of 106 kJ.mol⁻¹ was calculated. This value is slightly higher than the value reported by Leibler and coll. (88 kJ.mol⁻¹) for the first epoxy-acid vitrimer catalyzed by Zn²⁺. The ability of the material to self-heal and its recyclability at 160 °C was also shown. T_g evaluated by DMA ranged from 0 to 40 °C depending on the comonomer composition and post-curing time.

Biobased epoxy vitrimers involving transesterification reactions have been used as matrices in carbon fiber reinforced composites. Chen and coworkers synthesized vitrimers by reaction of adipic acid (**A7, Figure 5**), a diacid derived from vegetable oils, with epoxidized menthane diamine (**E5, Figure 6**), obtained by glycidylation of menthane diamine with epichlorohydrin.^[82] 1,8-p-Menthane-diamine can be synthesized from turpentine, a natural product from pine tree.^[83] The tertiary amines internally present in the system catalyzed the transesterification reactions without the need of additional catalysts. For an acid:epoxy ratio of 1:1, a vitrimer with a T_g of 72 °C, a relaxation time at 160 °C of 2642 s and an E_a of 105.8 kJ.mol⁻¹ was obtained. A composite, with 60% mass fraction of carbon fibers (CFs) was prepared by dipping CFs layer by layer in the mixture of monomers heated at 100 °C. The coated carbon fibers were cured at temperatures up to 150 °C under pressure of 150 MPa. The composite showed improved mechanical properties compared to the native matrix. It exhibited reprocessability at 180 °C and shape memory properties that could be programmed at 100 °C. Self-adhesion was achieved by bonding together 2 pieces under a hot press at 180 °C, thus avoiding the use of external adhesives. Chemical recycling was shown by adding ethanol amine to degrade the vitrimer matrix and recover CFs. The chemical analyses and SEM images of the recycled CFs, which surfaces were clean and smooth, similarly to the native CFs, indicated a good removal of the polymer matrix. With the same objectives, Hu and coworkers proposed the use of fully biobased dynamic cross-linked matrices from camphoric acid (**A6, Figure 5**) and epoxidized soybean oil (**E1, Figure 4**).^[84] Camphoric acid is the oxidation product of the bicyclic terpene camphor, which is widely distributed in the camphor laurel tree.^[85] In the presence of 5 mol% TBD catalyst, for an acid:epoxy content ratio of 1:1, a vitrimer with a T_g of around 45 °C, a relaxation time of 7245 s at 200 °C and an E_a of 84 kJ.mol⁻¹ was obtained. A composite, with 60% mass fraction of CFs was prepared by dipping CFs layer by layer in the mixture of monomers and TBD, heated at 100 °C. The coated carbon fibers were cured at

temperatures up to 200 °C under pressure of 10 tons. Samples could be reprocessed or combined by self-adhesion at 200 °C. Shape memory properties were observed at 100 °C. The scratch width of a damaged sample could be decreased from 100 μm to 50 μm simply by heating the composite at 200 °C. It was completely repaired by adding a drop of ethylene glycol onto the remaining scratch. The polymer matrix was degraded in 20 h in the presence of ethylene glycol at 190 °C.

Finally, Zhou and coworkers took advantages of transesterification reactions to develop “super green” smart coatings by integrating renewable resources, microwave-assisted synthesis, and dynamic covalent chemistry into UV-curable coatings (**Figure 7**).^[86] A first intermediate was produced from tung oils by Diels–Alder reaction of the double bonds with maleic anhydride. This synthesis was performed in a microwave reactor, which advantageously reduces reaction times (here 10 min) and improves product yield. The opening of the anhydride functions resulted in the formation of a poly(acid). The latter was further modified by reaction of the pendent acid functions with the epoxide moieties of glycidyl methacrylate. This reaction was performed under microwave (15 min) to yield oligomers (**TMG, Figure 7**) decorated with ester moieties, free hydroxyl groups and vinyl functions that can be photopolymerized. In parallel, a reactive diluent (**MM, Figure 7**) was prepared by Steglich esterification of malic acid, a diacid present in fruits, with methallyl alcohol. The coatings were prepared by mixing TMG, MM, Zn(acac)₂ and a UV initiator (Darocur 1173). The degassed mixture was casted into a polytetrafluoroethylene mold or coated on polished tinplate sheets using a film maker and cured using a 400 W UV light-curing microprocessor. A vitrimer with a T_g of 70 °C and an E_a of 117.6 kJ.mol⁻¹ was obtained for a 9:1 TMG:MM weight ratio. The relaxation time value was 2500 s at 180 °C and decreased to 200 s at 220 °C. Crack reparation at 180 °C for 1 h and removability of the coating after immersion in glycol for 6 h at 180 °C were observed. The films exhibited dual shape memory properties (100 °C and 180 °C). The vitrimer was grinded into powder and successfully reprocessed as a film in a hot press at 100 °C and 10 MPa. In this work, the global synthetic pathway involves a methacrylic acid derivative and methallyl alcohol that are currently mainly produced from fossil feedstocks using toxic reagents. However, several greener alternatives based on direct biotechnological processes from sugars, or chemical reactions of molecules that can be biobased are currently under development.^[87-89] Additionally, even though catalytic processes were implemented to synthesize maleic anhydride from bioresources, this molecule remains toxic.^[90]

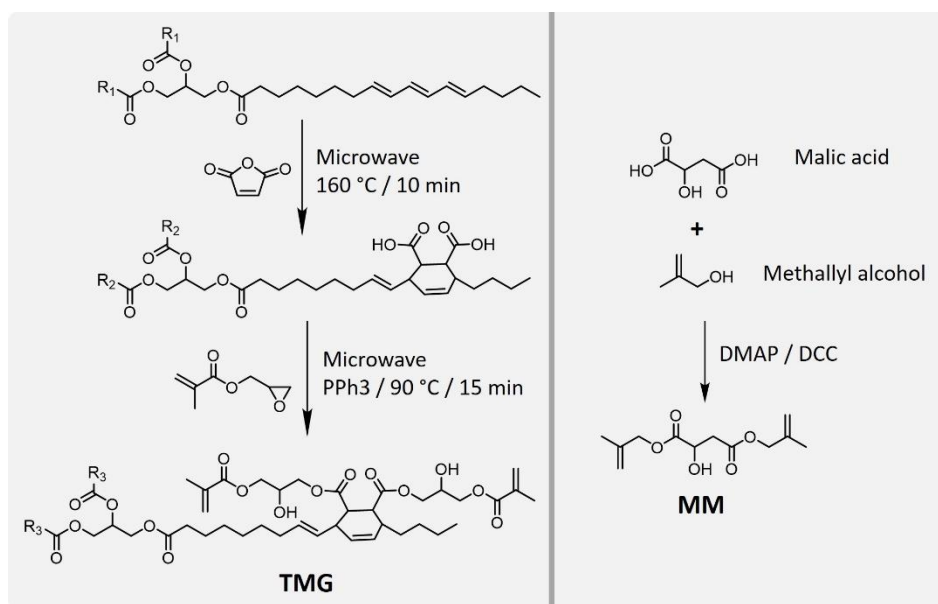


Figure 7. Synthetic routes to methacrylated tung oil (TMG) and a malic acid-based monomer (MM)

2.2. Reactions between epoxides and anhydrides

Epoxy thermosets can also be synthesized using anhydrides as hardener. The reaction mechanism consists of an alternating ring opening polymerization of anhydride and oxirane rings initiated by a base (**Figure 8**). The polymerization mechanism results in the formation of hydroxyl groups (or their corresponding alcoholate) only when the last monomer added at the end of the growing chains is an epoxide, *i.e.* when the epoxide monomers are used in excess as compared to the anhydride. Thus, an excess of epoxide is mandatory to observe transesterification reactions in such cross-linked polymers.^[91] In practice, the epoxy-anhydride thermosets behave as vitrimers for epoxy/anhydride ratio as low as 1:0.5.^[92,93] It is worth noting that water and/or alcohols present in the monomer or the initiator enable the introduction of further hydroxyl groups inside the polymer network, through the initiation of additional growing chains or through transfer reactions with existing growing chains (**Figure 8**).

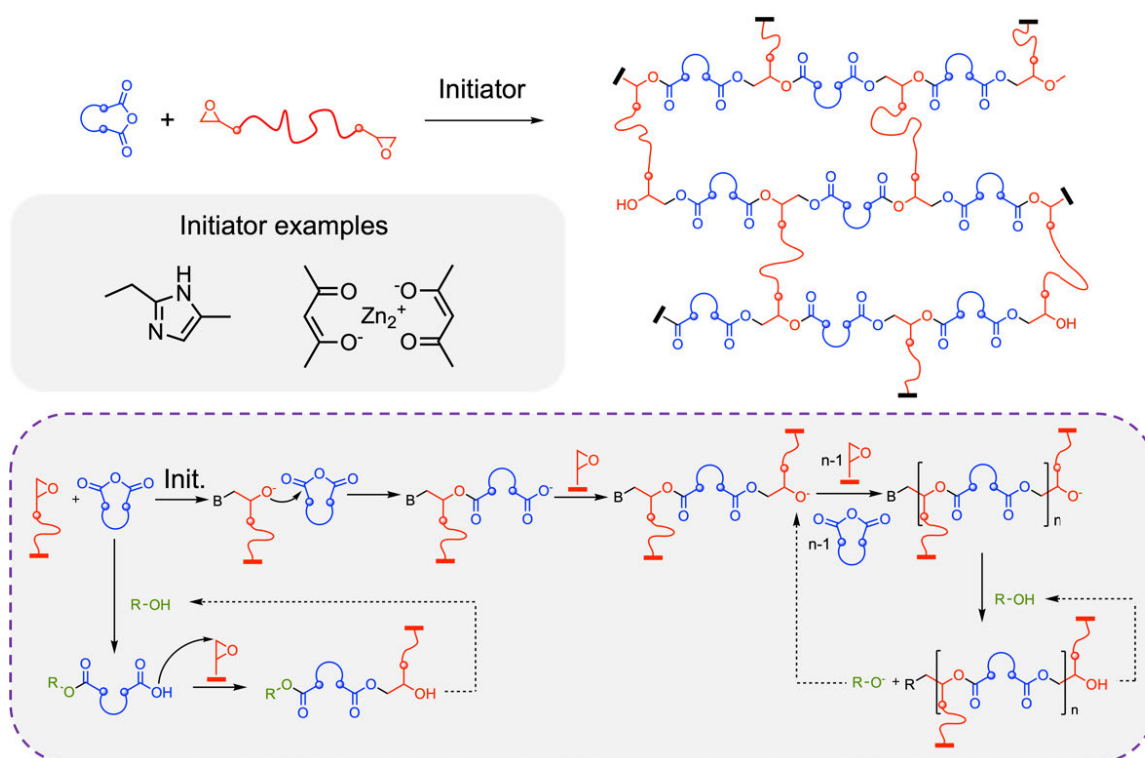


Figure 8. Mechanism of polymer network formation from anhydrides and poly(epoxides). Transesterification reactions occurring in the presence of a sufficient amount of OH groups in the system (R-OH = residual water (R=H), alcohols coming from the catalyst or the monomers)

A number of partially biobased epoxy/anhydride vitrimers are reported in the literature. The authors used only one biobased precursor (e.g. lignin, vanillin and guaiacol, or cellulose nanocrystals) in combination with the fossil-based hexahydro-4-methylphthalic anhydride (MHHPA).^[94-96] As renewable alternatives, succinic anhydride is a simple biobased building block that was implemented in vitrimer synthesis (**Figure 9**).

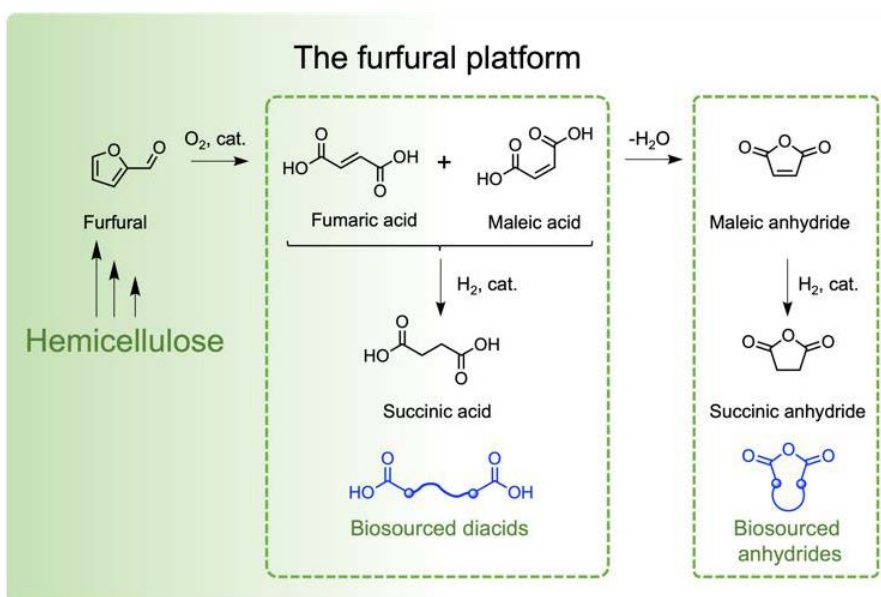


Figure 9. Synthesis of succinic anhydride from hemicellulose

Zhang and coworkers described the preparation of vitrimers from a diepoxide derived from eugenol (**E2, Figure 4**) and succinic anhydride (**Figure 9**).^[97] First, a symmetrical eugenol diepoxide was synthesized in a two-step procedure by a Williamson ether synthesis between the phenolic group and 1,4-dibromobutane followed by epoxidation of the double bonds with *m*-chloroperoxybenzoic acid. Three polymer networks were synthesized by reaction of the eugenol-based diepoxide with succinic anhydride in different ratio 1:0.5, 1:0.75, 1:1 in the presence of zinc acetate catalysts. All materials exhibited T_g at around 50 °C, crack-healing at 190 °C and shape memory. Chemical recycling by degradation was performed in the presence of ethanol in a pressure reactor at 160 °C for 5 h without adding external catalysts. However, only the polymer network with a epoxy:anhydride ratio of 1:0.5 could be successfully reprocessed by hot pressing at 200 °C after fragmentation. This sample features the highest number of free hydroxyl groups, resulting in the lowest relaxation times, which at 200, 160, and 120 °C were 128, 1000, and 1300 s, respectively. No activation energy was calculated for this system. As Williamson syntheses require a large excess of strong bases and the use of toxic alkylhalides, greener alternatives, such as reactions with organic carbonates, cross-coupling reactions or acid mediated bimolecular dehydration of alcohols are developed and should be implemented for the synthesis of greener vitrimers.^[98-101]

2.3. Discussion

Biobased vitrimers involving transesterification reactions appear as a promising route to develop sustainable and environmentally benign cross-linked polymers. One major advantage of the transesterification chemistry is that it relies on chemical functions that are naturally occurring in a large number of biobased building blocks (e.g. carboxylic acid, esters, alcohols). The introduction of epoxide groups can be achieved by glycidylation or by direct epoxidation of double bonds, naturally present in some biomass. In terms of sustainability, the second route should be preferred as it has a better atom economy and avoid the use of toxic epichlorohydrin. However, in the works described in this section, the epoxidation procedures of the double bonds are incompatible with several principles of green chemistry, especially in terms of safety, atom economy and waste management. Indeed, they rely on the use of large amounts of peracids and strong acids that require neutralization and removal from the final products. Recent advances in catalysis could help circumventing these issues and render epoxide syntheses greener.^[102-106] Alternatively, transesterification-based vitrimers could be synthesized via epoxide-free route. For instance, ester and hydroxyl containing biosourced monomers could be cross-linked by free radical polymerization of C=C unsaturation, another common chemical function in biobased precursors.

Beyond the use of the epoxide chemistry, another limitation of transesterification-based vitrimers is that they cannot be reprocessed fast enough to meet the requirements of industrial manufacturing by extrusion or injection molding, despite the use of catalysts.^[21]

The chemistry of carbonates is often compared to the ester chemistry. Thus, polycarbonate vitrimers undergoing transcarbonation exchange reactions with free hydroxyl groups and carbonate interexchange were developed. Only examples of partially biobased carbonate vitrimers have been found in literature.^[107-109] With the substitution of highly toxic phosgene by organic carbonates, the use of CO₂ for carbonatation reactions, and naturally occurring hydroxyl functionalized raw materials, biobased polycarbonate vitrimers are good candidates for the development of sustainable cross-linked materials.^[100, 110]

3. Transcarbamylation reactions

3.1. Polyurethanes

Although polyurethanes (PU) are one of the most commonly used polymeric materials, with applications as rigid and flexible foams, coatings, elastomers and adhesives, the recyclability of polyurethane networks has been relatively poorly addressed.^[111] The Xie and Urban groups

pioneered the investigation of the carbamate bond reversibility for the preparation of PU vitrimers. In the presence of free hydroxyl groups in conventional isocyanate-alcohol PU, transcarbamoylation reactions were observed (**Figure 10**).^[112, 113] Due to the “sluggish” behavior of these reactions together with the competition between an associative and dissociative mechanism, the synthesis of vitrimers *via* the isocyanate-alcohol route has been hardly developed.^[114, 115]

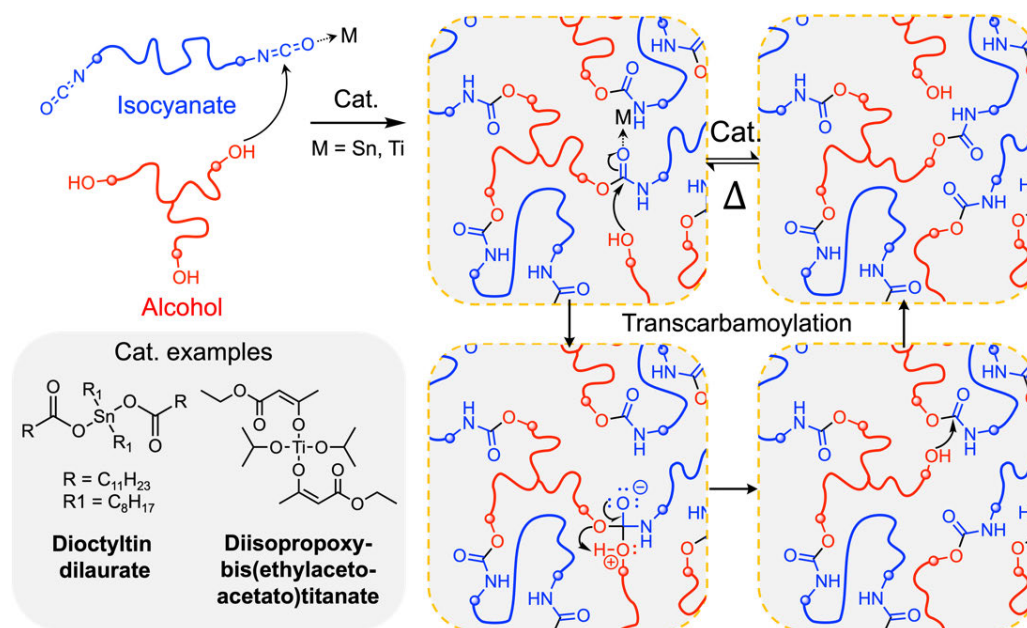


Figure 10. General scheme of polyurethane network formation and mechanism of the exchange reaction (transcarbamoylation)

A few works report the synthesis and characterization of partially biobased polyurethane vitrimers in the presence of a catalyst. Even if lignin, vegetable oils and sugar derivatives were used as polyols, the diisocyanate was in all cases petroleum-based.^[116-118] For this reason, and the classification of isocyanates as CMR substances, these studies are not described in this review.

3.2. Polyhydroxyurethanes

Today, poly(hydroxyurethane)s (PHU)s, synthesized by polyaddition of cyclic carbonates and amines, are considered as greener alternatives to conventional polyurethanes (**Figure 11**).^[119-122] PHUs bear additional primary or secondary hydroxyl groups, in comparison to classic polyurethanes, that faster bond exchanges and enable the preparation of vitrimers.^[123]

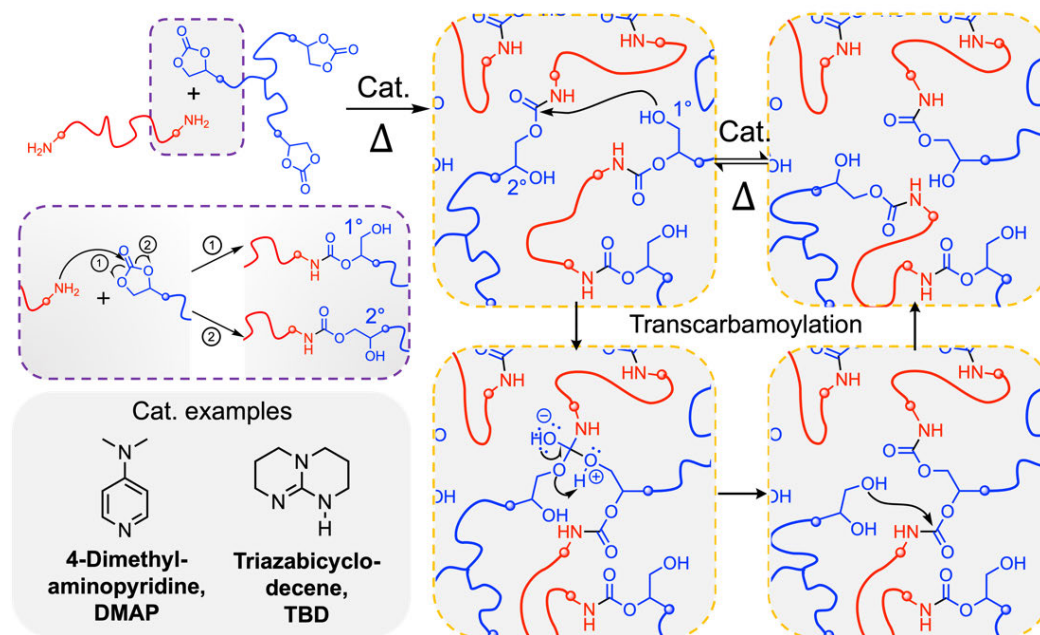


Figure 11. General scheme of poly(hydroxyurethane) network formation and mechanism of the exchange reaction (transcarbamylation: associative mechanism)

Besides being more reactive in the polymerization, 6-member ring cyclic carbonates (6CC) are also more suitable than 5-membered cyclic carbonates (5CC) for vitrimer preparation.^[124] Indeed, 6CC-derived PHUs exhibit primary hydroxyl groups that can undergo transcarbamylation reactions at elevated temperature without catalyst. 5CC-derived PHUs display a lower thermal stability and feature mainly secondary hydroxyl groups that are less nucleophilic and thus, less reactive for exchange reactions.^[125] However, in 2017, Torkelson and coworkers showed that 5CC-derived PHU networks could exhibit both transcarbamylation exchange chemistry (associative mechanism) and reversible cyclic carbonate aminolysis chemistry (dissociative mechanism) (**Figure 12**) in the presence of 4-(dimethylamino)pyridine (DMAP) catalyst.^[126]

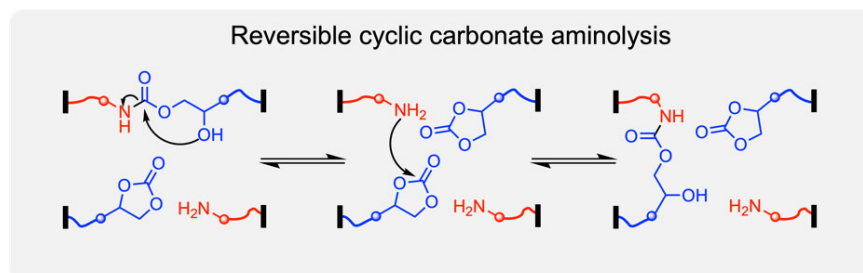


Figure 12. Mechanism of the reversible cyclic carbonate aminolysis chemistry (dissociative mechanism)

5CC can be easily synthesized from several bioresources, mainly either by epoxidation of double bonds or by reaction with epichlorohydrin, followed by carbonatation with CO₂ (**Figure 13a**).^[127] CO₂-carbonatation presents several advantages in terms of green chemistry as it is 100% atom economic and uses the highly available greenhouse gas CO₂ to produce valuable chemicals.^[128]

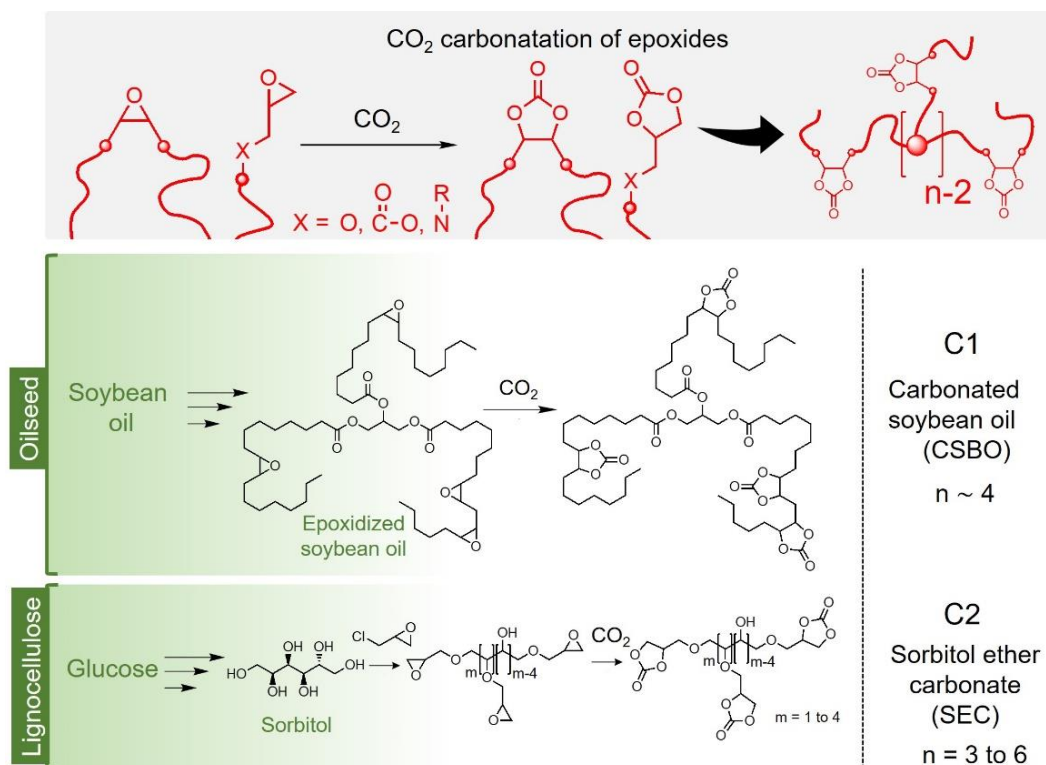


Figure 13. General scheme of carbonation reaction of poly(epoxides) and synthesis of biobased poly(carbonates)

On the other hand, even if only few naturally occurring amines are available (*e.g.* chitosan and poly(lysine)), existing protocols enable to transform most of molecules derived from biomass into polyfunctional amines (**Figure 14**).^[129-131] Sustainable procedures respecting the principles of Green Chemistry should be favored for such syntheses.^[132-134]

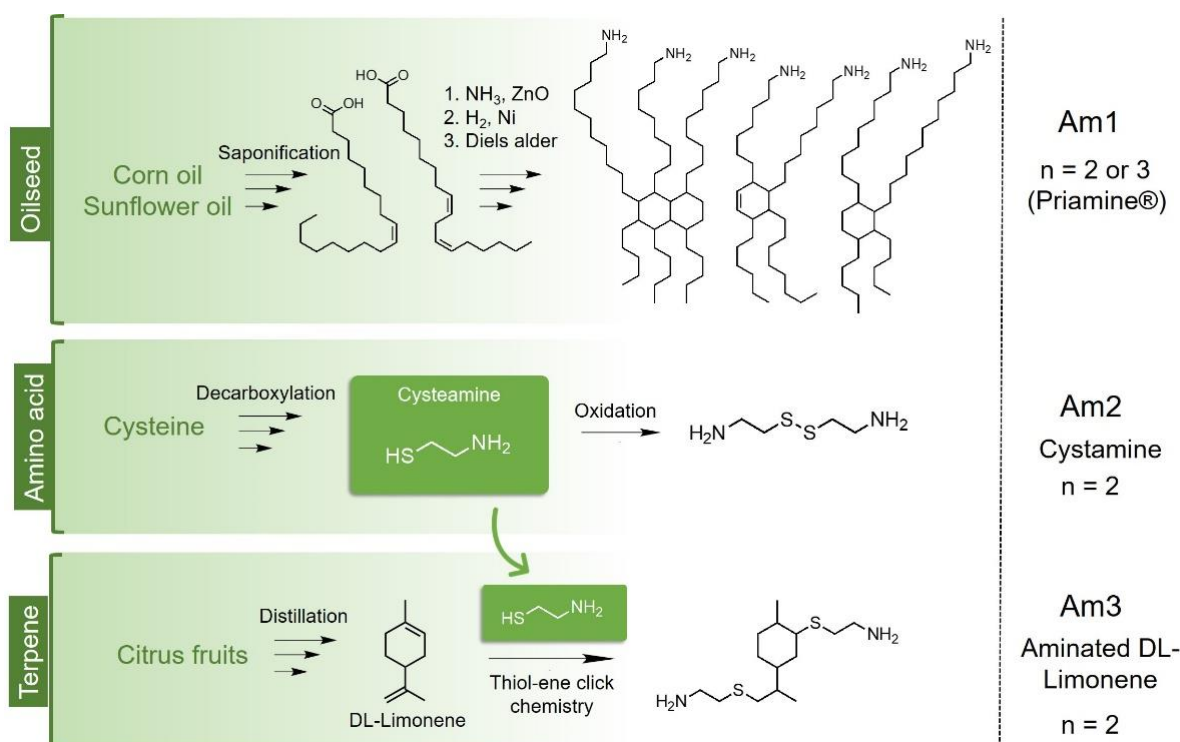


Figure 14. Synthesis of biobased poly(amines) from different biomass

Torkelson and coworkers prepared fully biobased PHU vitrimers from poly(amines) derived from oleic and/or linoleic acid, Priamines (**Am1**, **Figure 14**), and 2 types of 5CC cyclic carbonates, carbonated soybean oil (CSBO) (**C1**, **Figure 13**), and sorbitol ether carbonate (SEC) (**C2**, **Figure 13**) using DMAP catalyst.^[135] As the authors have previously shown that material processability can be limited if volatile components are generated by the reversible cyclic carbonate aminolysis reaction, the diamine was selected for its low volatility.^[126] SEC was synthesized by reaction between sorbitol and epichlorohydrin, followed by CO₂ fixation (**C2**, **Figure 13**).^[136] As SEC is particularly reactive for PHU synthesis, due to the short chain length between the carbonate and adjacent functional groups, a short gelation time was observed. However, the conversion did not reach completion during the network synthesis, possibly due to steric hindrance. Additionally, these networks exhibited poor reprocessability, even with increased catalyst load and reprocessing time and temperature. CSBO was used as an alternative to SEC. CSBO was synthesized by CO₂ fixation on epoxidized soybean oil. During the polymerization with Priamine, performed under solvent free conditions, full conversion of the cyclic carbonate group was achieved. The obtained polymer network exhibited a T_g of -14 °C and an elastomeric behavior. Samples were cut into pieces and reprocessed by compression at 110 °C. After reprocessing, the PHU network displayed complete mechanical property recovery and constant cross-linking density. The authors showed

that three different chemistries were involved in the reprocessing step: (i) transcarbamoylation reactions, (ii) reversible cyclic carbonate aminolysis, and (iii) transesterification reactions between pendent hydroxyl groups and the ester groups present in CSBO. The activation energy of this system was not determined. Recently, Shen and coworkers also prepared dynamic covalent networks from CSBO, but in combination with the fossil-based 4,4-diaminodiphenyl methane (DDM). Under catalyst free conditions, they reported an E_a of $89.2 \text{ kJ}\cdot\text{mol}^{-1}$.^[137] Liu and coworkers replaced the DDM by another fossil-based diamine featuring a disulfide moiety, *i.e.* 4,4'-diaminodiphenyldisulfide (DDS) to adjust the temperature and energy required for the bond exchange reaction.^[138] Such dual dynamic networks benefited from a synergetic effect between the two dynamic covalent chemistries, as the relaxation times at a specific temperature and E_a were lower than the ones of single disulfide and PHU-networks. This combination imparted the network with novel properties such as self-healing and reprocessing under milder conditions. Achieving self-healing under mild conditions decreases the energy consumption, and thus, the environmental impact of the process. The use of cystamine that derives from naturally occurring cysteine, as sustainable alternative to DDS, proved to be efficient to obtain PHU networks with self-healing efficiency (**Am2, Figure 14**).^[139] Using this amine, vitrimers with biobased contents ranging from 79 to 87% were prepared due to the presence of isophorone diamine to increase the mechanical properties.

3.3 Discussion

A small number of fully biosbased vitrimers involving transcarbamoylation exchange reactions have been described so far. Contrarily to vitrimers based on transesterification reactions, this strategy involves chemical functions that are uncommon in naturally occurring substances, *e.g.*, carbamates, cyclic carbonates, amines. In particular, in all the fully biobased examples mentioned above, the cyclic carbonates were obtained by carbonatation of epoxide intermediates, raising again the issue of the toxicity of the epoxide precursors such as epichlorohydrin and peroxides. As alternatives, several methods to circumvent the use of epoxides have been developed for the green synthesis of cyclic carbonates, for instance by carbonatation of 1,2 and 1,3 diols.^[127] They are usually based on the use of CO_2 ^[140, 141] or dimethyl carbonate,^[142] a green alternative to phosgene-based carbonates such as diphenyl carbonate. Instead of epoxides, these strategies rely on the use of diol precursors that are abundant in naturally occurring substances. Moreover, the carbonatation of 1,3 diols provides 6CC cyclic carbonates, which proved to be more suitable for vitrimer preparation. In

conclusion, there is still room for improvements both for the sustainability of the precursors syntheses and for the performances of the biobased PHUs. The limited availability of biobased amines also represents an obstacle to the development of fully biobased PHU vitrimers.

4. Vinylogous urethanes

Vinylogous urethane vitrimers are known to possess fast stress relaxation making them suitable for extrusion processing.^[143] The presence of a vinylic bond between the electron donating nitrogen and the electron withdrawing acyl moiety confers Michael-type reactivity. In the presence of a free amine group, transamination reactions occur through conjugate addition followed by elimination (**Figure 15**).^[144] The synthesis of vinylogous urethane vitrimers involves the reaction of amines with β -keto esters. β -keto esters have been easily synthesized from bioresources such as castor oil and cardanol. Two studies report their reaction with fossil-based diamines such as xylene diamine or 4,4-diaminocyclohexylmethane, which led to the synthesis of partially biobased vinylogous urethane vitrimers.^[145, 146]

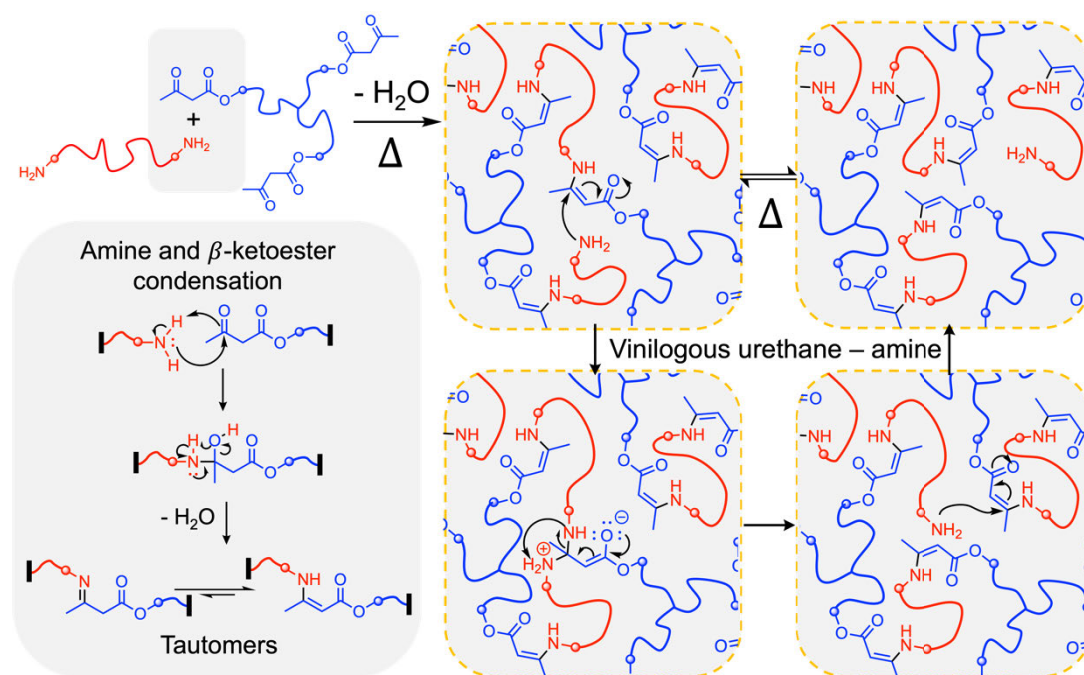


Figure 15. General scheme of polymer network formation from poly(acetoacetates) and poly(amines) and mechanism of the exchange reaction (transamination reactions)

Lin and coworkers described the synthesis of a fully biobased vinylogous urethane vitrimer.^[147] They modified castor oil to bear nine acetoacetate groups by thiol-ene reaction of the double

bonds with 1-thioglycerol followed by esterification of the OH groups with *t*-butylacetoacetate (**Act1**, **Figure 16**). They synthesized a diamine by thiol-ene reaction between DL-limonene and 2-aminoethanethiol hydrochloride (**Am3**, **Figure 14**). A ratio of acetoacetylated castor oil:aminated limonene of 1:1.02 was used to prepare a vitrimer film at room temperature without catalyst. The film exhibited a gel content of 95% and a T_g of around 40 °C. The film was able to retain the mechanical properties even after 3 reprocessing cycles under thermocompression (6 MPa at 130 °C for 30 min). Relaxation times decreasing from 595 s to 179 s when temperature raised from 70 °C to 130 °C were measured and an E_a of 26 kJ.mol⁻¹ was calculated. Excellent shape memory behavior was obtained at 70 °C. Depolymerization in the presence of benzyl amine was shown.

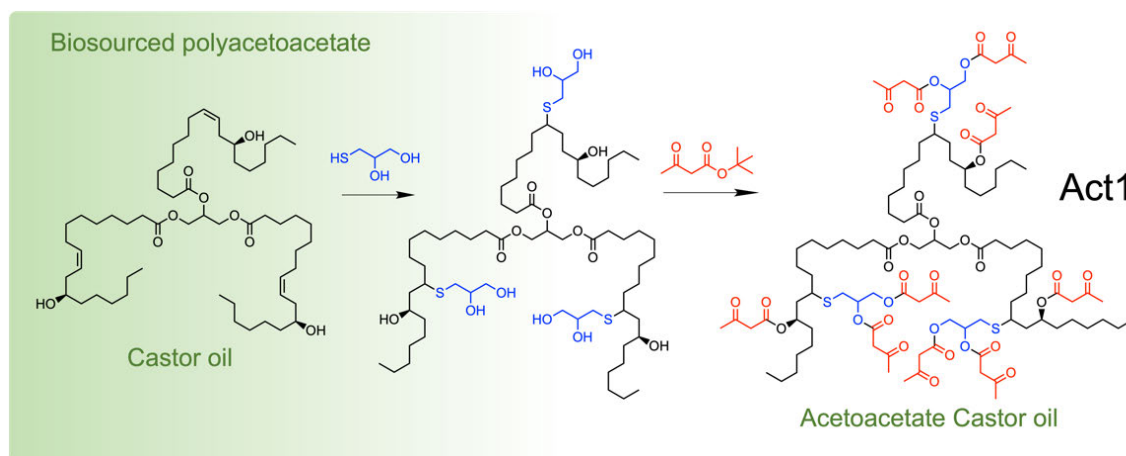


Figure 16. Synthesis of acetoacetylated castor oil by thiol-ene reaction of castor oil followed by esterification with *t*-butylacetoacetate

To the best of our knowledge, the system of Liu *et al.* is the only fully biobased vinylogous urethane vitrimer reported to date. However, given the simplicity of the synthesis of the poly(β -ketoester) and the excellent performances of the resulting vitrimers, this route is one of the most promising for future developments of sustainable cross-linked polymers. Indeed, the esterification of OH groups with *t*-butylacetoacetate is a straightforward synthetic approach with a moderate environmental impact. *t*-butylacetoacetate is a low molecular weight, cheap and innocuous fossil-based precursor and the side product of the esterification reaction with OH groups is non-toxic (tert-butanol). Thus, this strategy can be implemented with the wide variety of available biobased polyols to conceive new fully biobased vinylogous urethane vitrimers.

5. Imine bond exchange reactions

Imines, also called “Schiff’s bases”, are the condensation products of a carbonyl group and a primary amine.^[148] The dynamic covalent behavior of imines has been widely exploited for vitrimer synthesis. Imines have three main reactivities: (i) a dissociative hydrolysis followed by reaction with another amine, (ii) transamination, which consists in an associative exchange between imine and a free amine and (iii) a direct associative imine-imine exchange called imine metathesis (**Figure 17**).^[149]

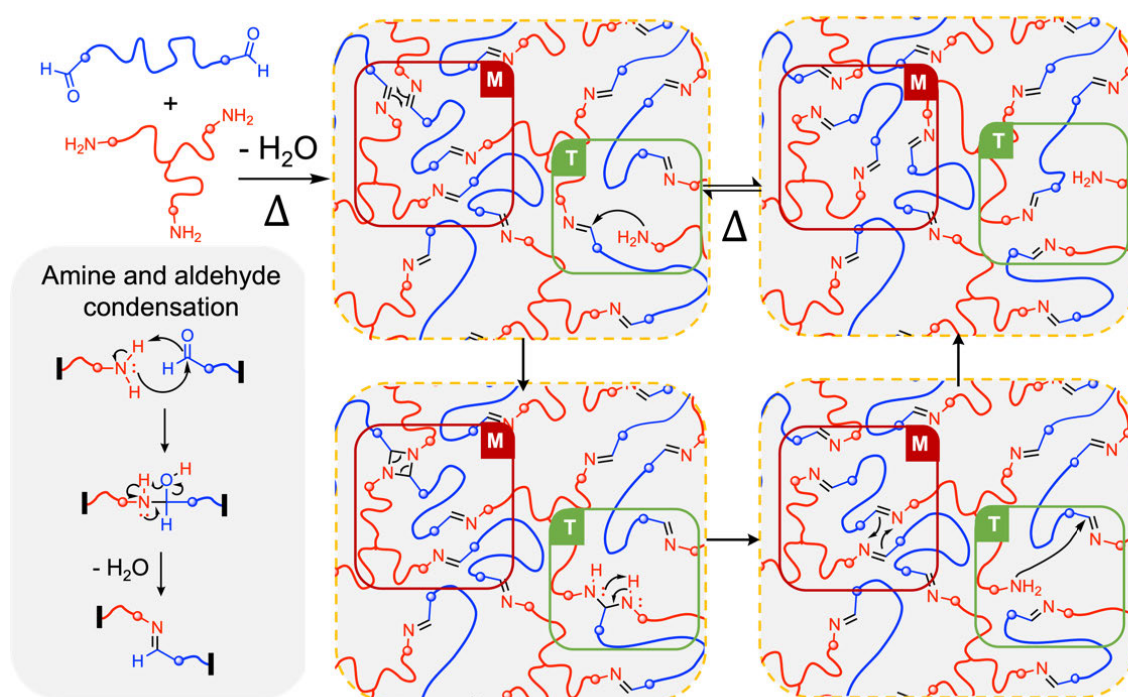


Figure 17. General scheme of polyimine network formation by condensation of poly(aldehydes) and poly(amines) and mechanism of the exchange reaction (T = transamination, M = imine metathesis)

Featuring an aldehyde in its structure, vanillin is a biobased key substrate for the synthesis of imine vitrimers. Vanillin, which is historically extracted from vanilla beans, can also be industrially produced from liginosulfonates, a by-products of the sulfite pulping industry. Different synthetic approaches for the preparation of vitrimers from vanillin have been developed. Polyimine networks were directly synthesized by condensation reaction of di- or tri-amines with di- or tri-aldehydes obtained by vanillin coupling on its phenolic moiety (**route A**, **Figure 18**).^[150, 151] In another approach, polyamines were reacted with a vanillin derivative

containing an epoxy function (**route B, Figure 18**).^[152, 153] The latter was obtained by glycidylation of the phenolic function of vanillin with epichlorohydrin. Thus, the cross-linking reaction with polyamine was based on a dual mechanism: the addition onto the epoxide on the one hand, and the condensation with the aldehyde on the other hand. Another strategy to obtain vanillin-based imine vitrimers relied on the synthesis of polyphenol precursors by condensation of the aldehyde function of vanillin with poly(amines) (**route C, Figure 18**).^[154-156] The resulting polyphenols were then used to cross-link the poly(epoxide) precursors, thus providing an imine-containing cross-linked polymer. Finally, another approach reported in the literature was based on the photopolymerization of a polyfunctional methacrylate monomer derived from vanillin (**route D, Figure 18**).^[157] The latter was obtained by methacrylation of the phenolic moiety of vanillin with methacrylic anhydride followed by the imination of the aldehyde function with a polyamine. The resulting polyfunctional methacrylate monomer was then photocrosslinked *via* free radical polymerization to provide a cross-linked material containing imine linkages. However, all the cited works employed fossil-based diamines.

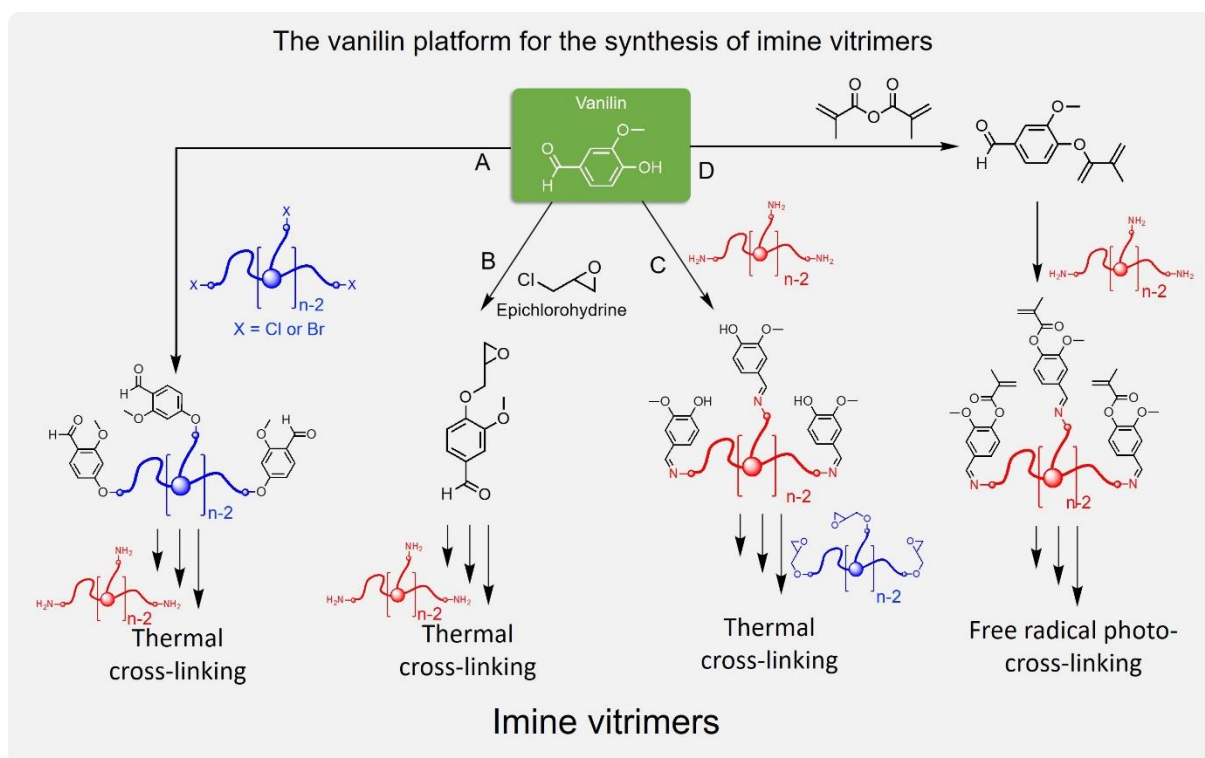


Figure 18. Different routes for the synthesis of imine vitrimers from vanillin

The only example combining vanillin derivatives with a biobased amine, i.e. Priamine, was described by Liu and coworkers.^[158] Vanillin-derived poly(aldehydes) were synthesized by reaction of 2 equivalents of vanillin with 1,3-dibromopropane (**Ad1, Figure 19**) and 3

equivalents of vanillin with phosphorous oxychloride (**Ad2, Figure 19**). Polyimine networks were produced under catalyst free conditions by reaction with Priamines of different grades (**Am1, Figure 14**) with a 1 to 1 amine:aldehyde ratio. Polymer networks with T_g between 13 and 32 °C and high elongation at break (similar to elastomers) were obtained depending on the monomer combination. Short relaxation times, ~30-40 s at 80 °C, and low E_a of 15 kJ.mol⁻¹ were determined. The vitrimers were reprocessed by hot-pressing at 120 °C and under 10 MPa for 6 min several times. The mechanical properties slightly decreased after each cycle. Due to the presence of the phosphorus-containing organic biobased monomer, the vitrimer displaying the highest cross-linking degree showed excellent adhesion to an iron plate. After the adhesive failure, the iron plates could be rebonded 30 min at 120 °C for and the rebuilding strength of 5.76 N/mm² was in the same range as the native one (6.75 N/mm²). The vitrimers degraded in a 0.1 M HCl solution and the aldehyde monomer could be precipitated and reused to realize a close-loop cycle. Although both monomers used in this study are biobased, the toxicity of the coupling agents has to be underlined.

Avérous and coworkers also used a mixture of difunctional and trifunctional Priamine (**Am1, Figure 14**) in combination with 2,5-furandicarboxaldehyde (**Ad3, Figure 19**) for the synthesis of imine vitrimers with 100% renewable carbon content.^[159] The green synthesis of 2,5-furandicarboxaldehyde from fructose can be achieved in one pot using recyclable catalysts.^[160] Polyimine networks were produced under catalyst free conditions with an amine:aldehyde ratio of 1.2:1. A dark red opaque elastomeric film with a T_g of -10 °C was obtained. Full stress relaxation was achieved in 40 s at 80 °C and 1300 s at 40 °C. The relaxation times of the network measured at different temperatures fitted the Arrhenius equation and an E_a of 64 kJ.mol⁻¹ was calculated. The vitrimer mechanical properties assessed by uniaxial tensile tests after three reprocessing cycles achieved by compression molding for 10 minutes at 120 °C were unchanged. The vitrimers showed good hydrolytic stability at room temperature in neutral, acidic (1 M HCl) and basic water (1 M NaOH), probably due to the hydrophobic nature of the diamine. The polymer networks could be depolymerized by stirring with an excess of butylamine in THF overnight.

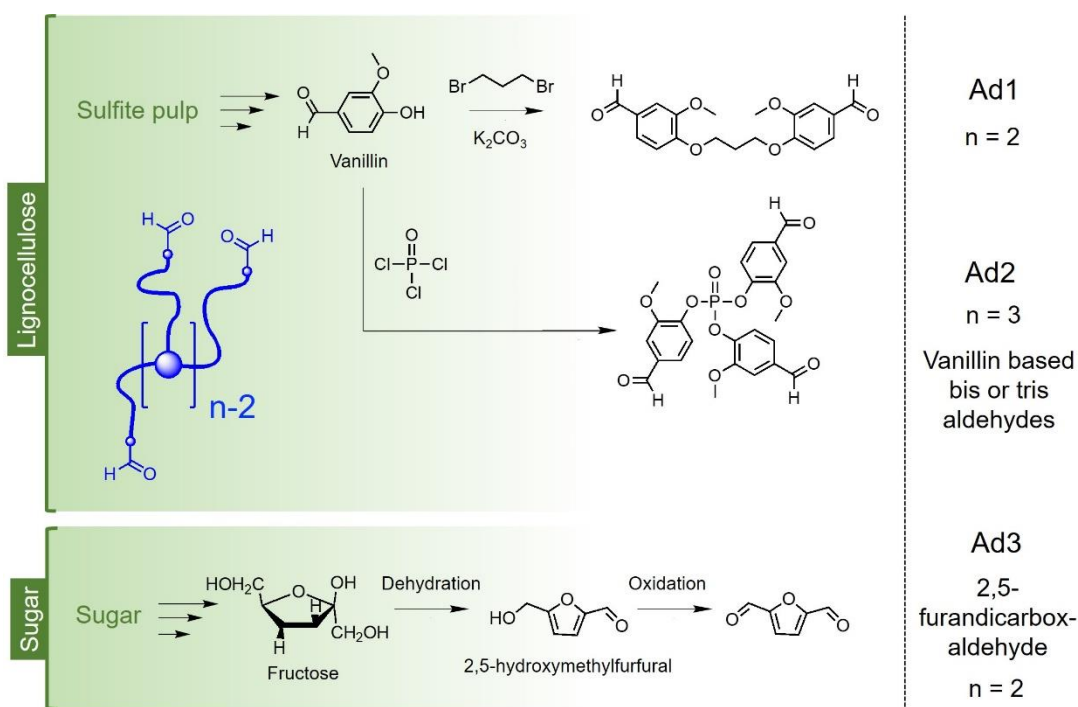


Figure 19. Synthesis of biobased poly(aldehydes) from different biomass

To conclude on this part, the implementation of imine dynamic covalent bonds in biobased cross-linked polymers appears as a promising strategy to upgrade the sustainability of thermosetting or elastomeric materials. Indeed, a large number of polyaldehydes with high contents of renewable carbon can be synthesized from biobased aldehydes derived from lignocellulose and sugars. They can be used in combination with the biobased poly(amines). Moreover, the resulting vitrimers feature very fast stress relaxation compared to most vitrimers (~ 1 min) under the mildest conditions ($< 100^\circ\text{C}$). Thus, they exhibit a high potential in terms of (re)processability and recyclability. However, the very fast dynamics of this material comes with an increased sensitivity to hydrolysis and further investigations should focus on understanding the long-term stability of these networks, in environmental conditions, and the combination with other permanent or dynamic networks.^[161]

5. Other dynamic covalent chemistries

Few other dynamic covalent chemistries that have been implemented for the synthesis of partially biobased vitrimers will be mentioned in this section. These examples are not discussed into details because one of the monomer is petroleum-based.

Acetal bond exchange, which can proceed through transacetalization with an alcohol or through acetal metathesis, has been adopted for the synthesis of covalent adaptable materials with

vitramer behaviors.^[162, 163] Especially, acetal metathesis has been proven to occur in cross-linked spiro acetal polymers under catalyst free conditions.^[164] Ma and coworkers implemented this strategy to prepare partially biobased degradable epoxy resins based on vanillin derived diacetal structures.^[165] In this study, bisphenol monomers, exhibiting spiroacetal linkages, were synthesized by reaction of 2 equivalents of vanillin with pentaerythritol or with erythritol. After glycidylation with epichlorohydrin, the diepoxides were cured with fossil-based diamines. Only the degradation under acid conditions and recovery of the starting material was demonstrated, the reprocessability induced by acetal exchange reactions was not addressed. Acyclic acetals can also be formed by reaction of hydroxyl groups with vinyl ethers. Following this approach, the same authors prepared partially biobased covalent adaptable networks from biobased epigallocatechin gallate and fossil-based tri(ethylene glycol) divinyl ethers via one-step “click” cross-linking without using catalysts or releasing small-molecule byproducts.^[166] They showed that the presence of phenolic hydroxyl neighboring groups accelerated the exchange reaction, thus enabling fast reprocessing, including continuous extrusion method. Although the relaxation times followed an Arrhenius law, these materials cannot be classified as vitrimers due to the presence of a dissociative bond-exchange mechanism but are covalent adaptable networks exhibiting a vitramer behavior. With the availability of naturally occurring aldehydes or polyols, fully biobased polyacetal networks would be good candidates as sustainable cross-linked materials.

As dioxaborolane metathesis is a rapid and robust reaction that takes place without catalyst at temperature as low as 60 °C, it became a key reaction for vitramer preparation.^[167] Up to date, two studies report the preparation of partially biobased vitrimers from fossil-based 2,2'-(1,4-phenylene)-bis[4-mercaptan-1,3,2-dioxaborolane and a rosin-based diepoxide or epoxidized soybean oil acrylate.^[168, 169] To the best of our knowledge, no study with higher renewable content was published.

6. Conclusion and Prospects

Even if biobased vitrimers appear as a sustainable alternative to polymer networks, this subfield is far from its maturity. Taking advantage from the rich and varied biomass, fully biobased vitrimers involving transesterifications, transcarbamoylations, transamination and Michael additions have been synthesized but the number of examples is limited (**Table 1**).

Table 1 Overview of the fully biobased vitrimers including their glass transition temperatures and activation energies

| <i>Dynamic Covalent Chemistry</i> | <i>Ref</i> | <i>Biobased monomer 1</i> | <i>Biobased monomer 2</i> | <i>Catalyst</i> | <i>T_g (°C)</i> | <i>E_a^{c)} (kJ.mol⁻¹)</i> |
|------------------------------------|---|---------------------------|---------------------------|-----------------------------|---------------------------|---|
| | <i>Liu and coll.</i> ^[75] | E1 | A4 | <i>Zn(acac)₂</i> | 25 - 50 ^{a)} | 88 |
| | <i>Li and coll.</i> ^[77] | E1 | A2 | <i>TBD</i> | 39 - 64 ^{a)} | 112 |
| | <i>Zhang and coll.</i> ^[78] | E3 | A5 | <i>Zn(acac)₂</i> | 95 - 133 ^{a)} | N.D. |
| | <i>Abu-Omar and coll.</i> ^[79] | E4 | A3 | <i>Zn(acac)₂</i> | 11 - 23 ^{b)} | 24 - 60 |
| Trans-esterifications | <i>Williams and coll.</i> ^[81] | E1 | A1 | <i>Catalyst-free</i> | 0 - 40 ^{a)} | 106 |
| | <i>Chen and coll.</i> ^[82] | E5 | A7 | <i>Catalyst-free</i> | 72 - 86 ^{a)} | 108 |
| | <i>Hu and coll.</i> ^[84] | A6 | E1 | <i>TBD</i> | 40 - 48 ^{a)} | 84 |
| | <i>Zhou and coll.</i> ^[86] | TMG | MM | <i>Zn(acac)₂</i> | 70 - 78 ^{a)} | 118 |
| | <i>Zhang and coll.</i> ^[97] | Succinic anhydride | E2 | <i>Zn(acac)₂</i> | 53 - 57 ^{a)} | N.D. |
| Trans-carbamoylations (PHU) | <i>Torkelson and coll.</i> ^[126] | C1 | Am1 | <i>DMAP</i> | -14 ^{a)} | 89 |
| Vinylogous urethanes | <i>Lin and coll.</i> ^[147] | Act1 | Am3 | <i>Catalyst-free</i> | 48 ^{a)} | |
| | <i>Liu and coll.</i> ^[158] | Ad1 | Am1 | <i>Catalyst-free</i> | 8 - 13 ^{a)} | N.D. |
| Polyimines | <i>Liu and coll.</i> ^[158] | Ad2 | Am1 | <i>Catalyst-free</i> | 30 - 32 ^{a)} | 12 - 16 |
| | <i>Avérous and coll.</i> ^[159] | Ad3 | Am1 | <i>Catalyst-free</i> | -10 | 64 |

^{a)}Determined by DMA from tanδ curve, ^{b)}Determined by DSC, ^{c)}Determined from relaxation stress experiments

Similarly, to their petroleum-based analogues, examples of vitrimers displaying a high thermal stability are rare. Indeed, in most of the studies, the glass transition temperatures are relatively low because at least one vegetable oil derivative is involved (e.g. triglyceride or fatty acid dimer/trimer). Using biomass featuring an aromatic structure, mainly lignin or lignin derivatives, is a strategy to reach T_g above 100 °C, which is classic for thermosets but comes with processability issues. The thermal stability of biobased vitrimers would also require that no side reaction occur while the exchange reaction is performed at high temperature. Additionally, the number of fully biobased vitrimers is limited by the availability of biobased diamines and especially aromatic diamines. The two main naturally occurring polyamines are: poly(ϵ -L-lysine) produced by *Streptomyces* microorganism and chitosan, issued from deacetylation of crustacean or insect chitin. Several pathways are investigated to prepare polyamines from functional groups naturally present in bioresources, such as aldehydes and hydroxyl groups, either by chemical or biotechnological processes.^[130] Intensive efforts were devoted to this issue over the last decades, mainly with the objective to synthesize fully biobased epoxy resin, which could be beneficial for the field of biobased vitrimers.

As emphasized all along this review, the route of biobased vitrimers only considering the renewability of the feedstock is not a sustainable solution if the environmental impact of the precursors syntheses is not taken into account. On the one hand, some functional building blocks are directly available in nature, such as diacids or polyols, which is valuable compared to fossil-based equivalents demanding multiple-step syntheses. On the other hand, many biobased synthons are still obtained according to multistep syntheses involving toxic and/or fossil-based reagents and large waste generation. However, the real impact of these strategies must be quantitatively evaluated using different evaluation tools such as E factor, EQ factor, atom economy, EATOS (Environmental Assessment Tool for Organic Synthesis). Ideally, the complete assessment of the sustainability of a chemical or a product should be based on a full life cycle assessment (LCA).

The research field of classic (mainly petroleum-based) vitrimers has triggered an enthusiasm in the polymer community. In terms of chemistry, the room for innovations can pursued different directions. It includes the development of new dynamic exchange reactions, the control of the activation energy of existing systems, the synthesis of multiple networks... All these advances could be directly implemented to biobased vitrimers.

Finally, this review highlighted the use of biobased vitrimers for applications as recoverable adhesives, self-healing materials, matrices for composites, and UV curable coating. The range of applications of vitrimer materials is broader and includes 3D printing, stimuli responsive

materials, smart activator, for instance. With these perspectives, vitrimers are considered as one of the major pillars of next generation of polymer materials. As such, the implementation of renewable resources for their synthesis is a key aspect to this transition. To conclude, biobased vitrimers possess the ability to meet the requirements of today's society and their development represent another step towards circular economy and an opportunity to reduce the carbon footprint of the plastic industry.

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The development of vitrimers addresses the recyclability issue of polymer networks. Combining vitrimers with the use of renewable resources represents another step towards circular economy. This review gathers recently published works describing the preparation of vitrimers from biobased monomers, and discusses the sustainability of the synthetic approaches.

Thomas Vidil, Audrey Llevot**

Fully biobased vitrimers: future direction towards sustainable cross-linked polymers

