

Nitrogen-Containing Polymers Derived from Terpenes: Possibilities and Limitations

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Nitrogen-containing polymers are widely applied materials, including polyamides, polyurethanes, and polyureas as well as epoxy thermosets. Their indispensability and the urgent need to replace fossil-based polymers considering more sustainable alternatives lead to significant efforts in exploring renewable feedstock as potential new building blocks. Being obtained from non-edible plant parts and often occurring as waste products, terpenes represent a promising group of renewable compounds that are of possible interest in the synthesis of nitrogen-containing polymers. The structural diversity of terpenes in combination with the mechanical properties that nitrogen-containing moieties bring into polymers can give rise to novel biobased materials that outstand mechanical and thermal properties of conventional fossil-based counterparts. In this review, an overview of the use of terpene compounds in the synthesis of nitrogen-containing polymers is given, covering different approaches to make use of terpenes as a valuable pool of renewable monomers.


1. Introduction

Without a doubt, polyurethanes (PUs) and polyamides (PAs) are essential polymeric materials for many technologies we rely upon

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daily. According to recent estimations, the polyamides market volume will exceed 10 000 kilotons by 2025.^[1] An even higher volume is estimated for PU production, with an amount of 29 million tons by 2029.^[2]

Polyamides are mostly known for applications as synthetic fibers, of which poly(hexamethylene adipamide) (PA-6,6) and poly(caprolactam) (PA-6) are outstanding examples. They further represent the two pathways that can be used for polyamide synthesis, as PA-6,6 is produced by a polycondensation reaction between adipic acid and 1,6-hexanediamine, while PA-6 is obtained by the ring-opening polymerization (ROP) of ϵ -caprolactam.^[3] Polyamide properties differ and can be adjusted depending on the nature of the monomers employed for their synthesis.

Moreover, common remarkable features can be defined due to the common amide linkage of the repeating unit. Indeed, the hydrogen bonding of the amide functionality drives the properties of these polymers. The regularity of the repeating unit gives rise to crystallinity, while hydrogen bond interactions between chains typically increase melting points and mechanical properties. Additionally, if aromatic moieties are present, structural rigidity and temperature resistance provide outstanding properties in aramid fibers. All these observations result in notably high melting temperatures, structural strength, and stiffness as well as good chemical resistance to alcohols, oils, or aromatic hydrocarbons.^[4]

PUs were already introduced at the early stage of polymer research. The first PUs were developed by Otto Bayer et al. in 1937 through a polyaddition reaction between diisocyanates and polyols, offering new materials with versatile properties.^[5] Nowadays, the tunability of PUs is widely acknowledged, leading to highly valuable polymers with large application possibilities.^[6] Combining the durability of metals and the flexibility of rubber, PUs can compensate for the weaknesses of each material class. The final polymer and its properties are adjustable by the choice of monomers, the presence of additives and reaction conditions, thus leading to a wide range of applications and structures. A classification of PUs can be made according to the structure-properties relationship: foams, elastomers, coatings, adhesives, and thermoplastics. Among them, the high production volume of PUs (global market volume of 24.7 Mt in 2021)^[2] is related to foam production. More precisely, rigid PU foams make up 50% of the total PU production worldwide.^[7] The reason behind this is related to their widespread use as insulation material

in the construction sector.^[8] Nowadays, a more sustainable trend concerns the replacement of environmentally and health-hazardous isocyanate monomers, thus avoiding the use of toxic phosgene for their synthesis, by introducing so-called non-isocyanate polyurethanes (NIPUs).^[9]

Similar to PUs, polyureas (PURs) are made from isocyanate and amine oligomers forming urea linkages. This results in properties like durability and high chemical, atmospheric, and biological resistance. High hydrogen bonding density results in excellent mechanical properties.^[10]

Epoxy-resins (ERs) are easily processable thermosetting materials that are valuable due to their high chemical and mechanical resistance, adhesion properties, and toughness, among others. These resins are formed by epoxide compounds and binders through a curing process. The choice of binders has a high influence on the final material concerning their amount and nature (amines, anhydrides, alkali, and catalytic curing agents). Furthermore, the curing process can be differentiated according to the working conditions (room temperature, light, or heat inducted). The applications of these materials include different fields from common adhesives to the aerospace industry. Additionally, to tune their properties, ER composites can be made. Indeed, structural reinforcement can be achieved by including nanomaterials or thermoplastic components.^[11]

The evident increasing need for these materials,^[1,2] combined with the climate crisis and the depletion of fossil resources, describe the urge to develop alternative solutions to petroleum-derived monomers. In addition, increasing focus toward the sustainability of the production processes and end-of-life considerations are omnipresent.^[12]

Examples of bio-based polyamides have been investigated and reported.^[13] A commercial example is PA-11, a product of the polycondensation of 11-amino undecanoic acid derived from natural castor oil.^[14] Alongside, bio-based routes to PUs are also being developed, especially concerning polyol synthesis from natural resources. These monomers can be derived from vegetable oils or lignocellulosic biomass.^[15] Making bio-based precursors for isocyanate monomers is still a challenge, but some examples can be found in the literature.^[16,17] At present, the main drawback of bio-derived polymers remains their higher price compared to petroleum-based ones.

As one of the potential groups of renewable building blocks, terpenes can be considered valuable natural monomer precursors for the development of useful materials, replacing and implementing the fossil-based polymers currently present on the market.

Terpenes are naturally occurring secondary metabolites of diverse plants, fungi, and algae species. The name “terpene” was assigned by Kekulé and derives from “turpentine”, the so-called oil distilled from pine resin.^[18] These compounds often show a characteristic pleasant and balsamic smell, giving the reason for their old name in ancient Rome as *Balsamum terebinthinae*.^[19] In accordance with the “isoprene rule” established by Wallach in 1887, the biosynthesis involves two C5 building blocks: dimethylallyl pyrophosphate and isopentenyl pyrophosphate, which react in a head-to-tail condensation leading to structures with carbon atoms as multiples of five (**Figure 1**). The above-mentioned rule was implemented in the 1950s by Ruzicka as the “biogenic iso-

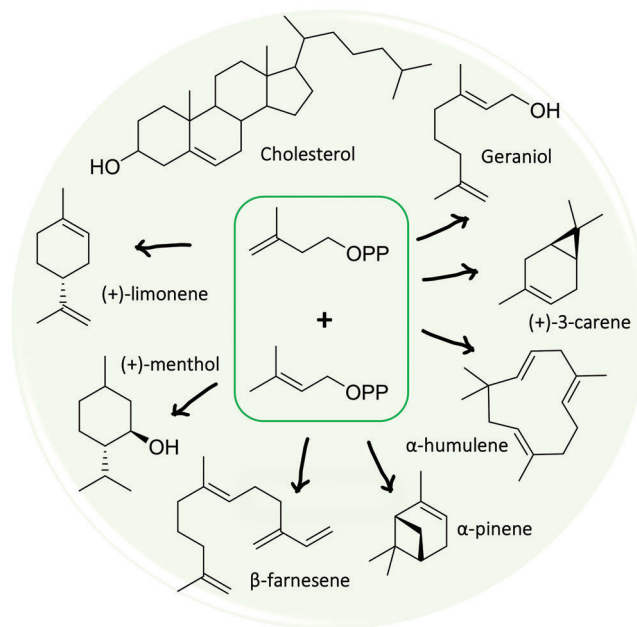


Figure 1. Biosynthetic precursors of different terpene structures.

prene rule”, which asserts the common synthetic pathway, subsequent cyclization, and rearrangements, resulting in many different structural identities.^[16] Therefore, the structure of terpenes can be differentiated into linear and cyclic and into saturated and unsaturated compounds. Next to olefinic groups, alcohol, aldehyde, ketone, and ester moieties occur in terpenoid structures. Regio- and stereo-chemical differences give additional diversity to the different natural activities that terpenes cover.

The purposes of terpenes in nature are manifold, ranging from defense functions to signaling compounds. The protection of plants from their antagonists gives reason to their recognized antibacterial, antifungal, and repellent activity.^[20] Despite the harmful role that terpenes can show against insects, some compounds work in the opposite direction. Indeed, some terpenes have also protective functions in the animal kingdom. Moreover, in addition to the repel activity, terpenes are also messaging deliverers from the flora to bugs to attract pollinators.^[21] The structural diversity, natural availability, and biological activity of terpenes make them attractive substrates for applications in diverse fields such as drug development.^[22] Currently, the highest use of terpenes concerns the fragrance, food, and drink sector because of their pleasant smell.^[23] Relevant additional applications are also exploited, including the use of pyrethrins as insecticides due to their limited persistence in the environment and toxicity,^[18] the potential activity of linalool against neurodegenerative diseases,^[24] and of taxol and geraniol derivatives for cancer treatment.^[25,26] Recently, the potential use as complementary therapeutic agents against the severe acute respiratory syndrome coronavirus type 2 has also been investigated.^[27]

Cyclic terpenes and thereof accessible derivatives can further show high viscosity, high energy density, and high volumetric net heats of combustion, which are appealing characteristics for developing terpene-derived biofuels.^[28]

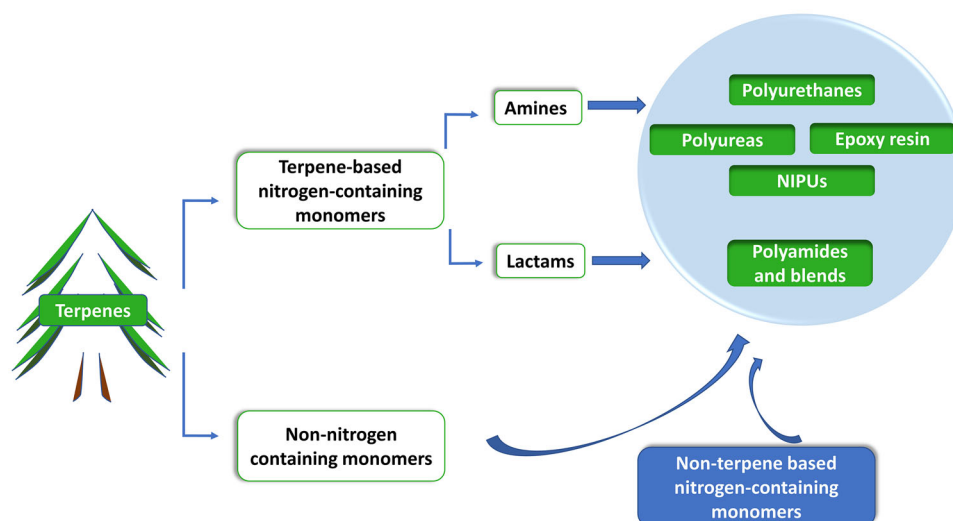


Figure 2. From terpenes to nitrogen-containing polymers.

Occurring in non-edible plant parts, terpenes can be gained from industrial waste and thus are a potentially valuable source to produce useful materials. For instance, α - and β -pinene are derived from the pulp industry from turpentine oil and limonene can be obtained from citrus peel oil from the alimentary factories. Additionally, the development of methods to obtain terpenes from algae and marine fungi shows an alternative to the supply of new terpenes from marine lands and gives the opportunity of increasing the production volume.^[29] Moreover, β -farnesene is produced industrially via fermentation of sugars.^[30] Recently, different works have been published showing the employability of different bacteria and also exploring recombineering for the production of this terpene.^[31]

Presently, terpenes find increasing application in the synthesis of chemicals,^[32] replacing the current fossil-based ones also in polymer synthesis.^[33] Concerning the polymer field, the most common natural terpene-based polymers are polyisoprenes. These polymers are natural rubbers that are commonly subjected to the curing vulcanization process in order to improve their properties. Taking advantage of the wide structural differences that nature supplies, the manifold possibilities of terpene functionalization can offer the opportunity to tune the properties of the final polymer, prospecting a broad range of applications.

Manifold research has been developed on the use of terpenes for sustainable polymer synthesis, as was recently reviewed by Winnacker.^[34] One promising substrate that has been subject to various research approaches is represented by limonene-1,2-epoxide, which is accessible from naturally occurring limonene feedstock either by bromination and subsequent hydrolysis with NaOH^[35] or, as shown by newer research, by selective oxidation using enzyme catalysis.^[36] The epoxide was shown to be a promising monomer for the synthesis of polycarbonates by ring-opening co-polymerization (ROCOP) with CO₂^[37] or polyesters by ROCOP with cyclic anhydrides.^[38,39] Also, other terpene-based epoxide derivatives could be used for similar ROCOP approaches.^[26]

While the synthesis of polycarbonates and polyesters from terpene and terpenoid feedstock contributed to major progress in

terpene-based materials, less focus has been laid on the implementation of the terpene moieties in nitrogen-containing polymers. In this review, we summarize the research and development of nitrogen-containing polymers from terpenes starting from different possible terpenes monomer syntheses and further examples of their polymerizations. Polyamides, polyurethanes (and their non-isocyanate counterparts), polyureas, and epoxy resins will be illustrated. A distinction between the introduction of nitrogen in the polymer chain via the terpene unit or through the complementary monomer will be presented (Figure 2).

2. Terpene-Based Amines and Lactams and Their Use in Polymer Synthesis

Currently, the most common commercial nitrogen-containing compounds for polymer synthesis are caprolactam^[40] and hexamethylene diamine.^[41] With the variety of terpenes covering cyclic and acyclic structures, possibilities arise to replace and complement these platform chemicals that are so far mostly of fossil origin.^[42]

To introduce the desired amino groups into terpene structures, an advantage can be taken by the naturally present double bond functionalities, a versatile functional group presented by nature. As typical reactions for this aim, mostly oxidation and addition reactions are used.

The generation of monoamines from terpenes as well as of secondary and tertiary amines can lead to products with manifold applications in the production of fragrance compounds and pharmaceuticals^[43] as well as for crop protection^[44] or growth regulators.^[45] The group of Wintzer reviewed and summarized different pathways for the generation and possible applications of terpene-based amines in 2014.^[46] For the generation of primary amines, the reductive hydrogenation with ammonia proved a successful and selective method for terpene derivatives containing carbonyl groups.^[47] For the synthesis of primary amines from terpene-based alcohols, also the use of ammonia was described.^[48]

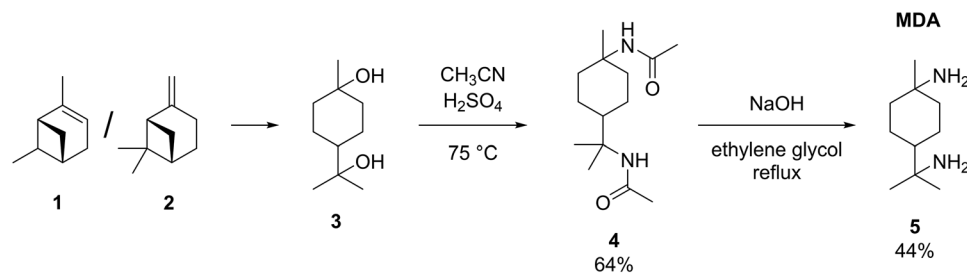


Figure 3. Synthesis of 1,8-menthane diamine from pinene feedstock.^[50,51]

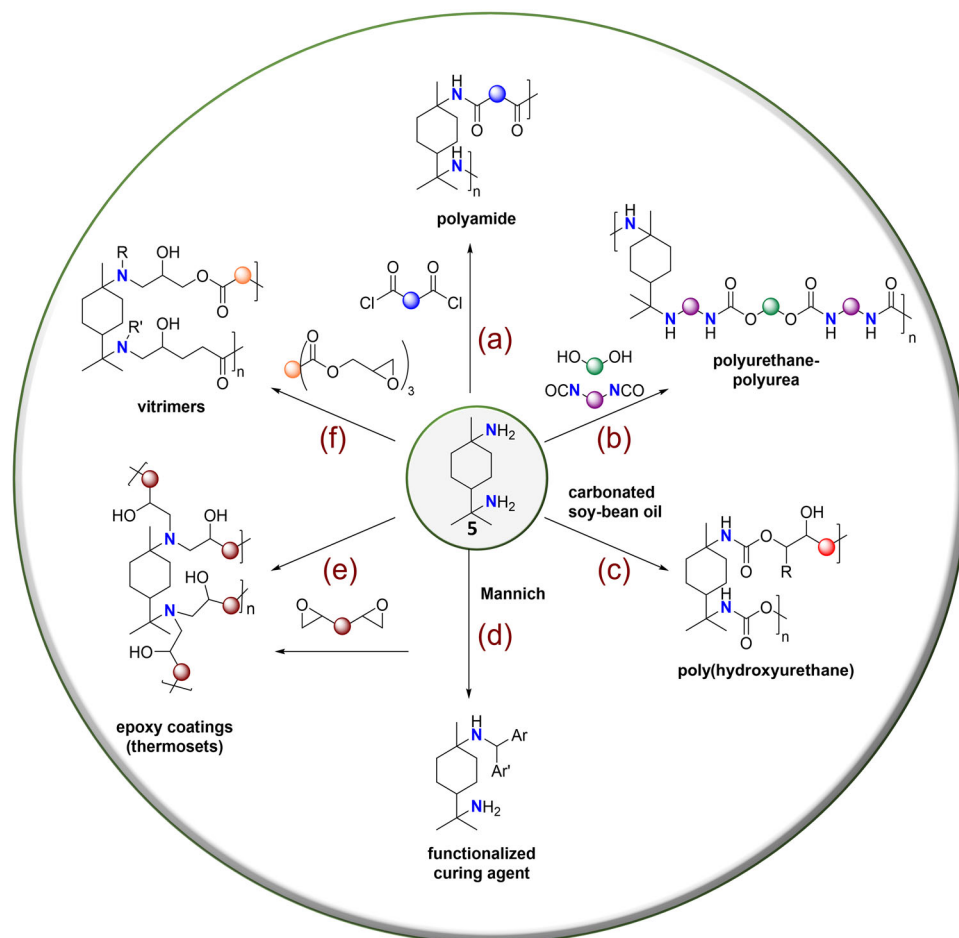


Figure 4. Use of 1,8-menthane diamine 5 in the synthesis of different nitrogen-containing polymers.^[52–57]

2.1. Turpentine-Derived 1,8-Menthane Diamine

One of the earliest examples of a diamine derived from terpenes is 1,8-menthane diamine (MDA) 5. The first published synthesis protocol used hydrogen cyanide and sulfuric acid to gain 5 from different terpenes.^[49] To avoid side product formation and the use of toxic hydrogen cyanide, different synthesis approaches were explored. One strategy is to use acetylated MDA which can be obtained from turpentine-based terpin hydrate by reacting it with acetonitrile.^[50] Although this indirect synthesis protocol shows a lower atom economy, the use of less toxic reagents possibly outweighs this with regard to sustainability. Zhao et al. showed that

hydrolysis of *N,N'*-diacetyl-*p*-menthane-1,8-diamines with NaOH yielded 5 selectively.^[51] Considering both separate reaction steps, an overall yield of 28% was obtained. The full pathway is shown in Figure 3.

An overview of how 5 was used in the synthesis of nitrogen-containing polymers is given in Figure 4. Already in 1988, Trumbo used MDA for the synthesis of polyamides via a polycondensation reaction with different acid chlorides (Figure 4a).^[52] Yet, apart from the use of acid chlorides limiting the sustainability of this approach, only low molar masses were achieved, which was attributed to the low reactivity of the amine groups attached to quaternary carbon centers.

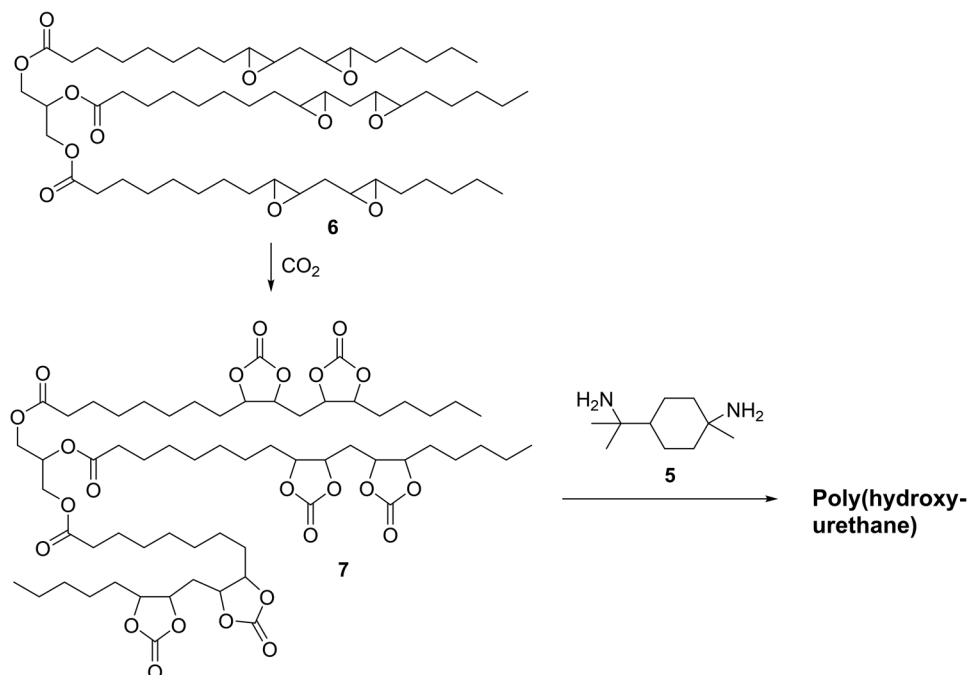


Figure 5. Isocyanate-free synthesis of poly(hydroxyl-urethane) using carbonated soybean oil **7** and 1,8-manthanediamine **5**.^[54]

In 2022, Xu, Wang, and Liu et al. used **5** as chain extender in the synthesis of PUs made from hexamethylene diisocyanate and polytetramethylene ether glycol (Figure 4b).^[53] Additionally, bis(2-hydroxyethyl)disulfide was added as second chain extender, opening the possibility to obtain self-healing materials due to the introduced disulfide bonds. As the diamine **5** also added to the isocyanate groups, urea groups were formed within the polymer. The resulting hydrogen bonds contributed to stronger intramolecular interactions and thus to an improved mechanical performance of the polymer, in combination with the rigid structure of **5**. The urea groups enabling hydrogen bonding further enhanced the self-healing properties of the polymer.

Although the introduction of **5** increases the content of renewable carbon and thus contributes to improved sustainability, still hazardous diisocyanates were used in this approach. Isocyanates are industrially synthesized from highly toxic phosgene and further bring health hazard themselves. In the process of developing more sustainable processes for polymer synthesis, isocyanates thus need to be avoided,^[58] using other concepts for urethane formation, such as transurethanization or the opening of cyclic carbonates by amines.^[59] Yet, the results by Xu, Wang, and Liu showed the benefit of introducing nitrogen-containing linkages in combination with terpene structures into polymers.

Following an isocyanate-free approach, the same group used MDA from turpentine for the curing of cyclic-carbonated soybean oil **7**, yielding a fully bio-based poly(hydroxyl-urethane) (Figure 4c).^[54] The detailed synthesis strategy is shown in Figure 5. The use of CO_2 for the synthesis of **7** by catalytic carboxylation of epoxidized soybean oil **6** and the possibility of performing the polymer synthesis without the need for solvents or catalysts contribute to the overall sustainability of the process. Different ratios of **5** and **7** were compared, and self-healing properties and recyclability of the obtained polymers were confirmed.

This approach is a good example of a synthesis that takes into account not only one aspect of sustainability, that is, the renewability of the terpene derivative, but instead focuses on a holistic approach, using only bio-based starting materials, avoiding hazardous substances, developing a procedure without a high consumption of solvents, and further utilizing CO_2 as feedstock.

Besides the discussed incorporations of **5** into polyamides and PUs, it is mainly used as curing agent in epoxy resins (Figure 4e). As epoxy thermosetting polymers are of great use, for example for coatings, there is an urgent necessity to find bio-based materials for the production of epoxy resins and hardeners.^[60] The first examples of epoxy resins cured with **5** were already published in the 1980s.^[61] Over the years, several studies used **5** for the synthesis of epoxy-amine curings, obtaining materials with interesting properties^[62] and comparing **5** also with other diamine curing agents.^[63]

More recently, Chen et al. used **5** as one of two different curing agents for fully bio-based epoxy coatings for possible anti-icing and anticorrosion applications.^[55] The epoxy building block is derived from cardanol as alternative to commercial petroleum-based diglycidyl ether of bisphenol A. Cardanol can be extracted from cashew nut shell liquid.^[64] No solvent was used for the preparation of the epoxy resins (Figure 6), contributing further to an improved sustainability. In addition, polydimethylsiloxane **8** was added to increase hydrophobicity, instead of a fluorinated substrate. The use of **5** in combination with the epoxy NC514 yielded a promising bio-based coating with low ice-adhesion strength and good anticorrosion performance due to a high cross-linking density and inherent hydrophobicity.

In 2021, the synthesis of another bio-based epoxy thermoset was published by Zhang and Chen et al. (Figure 4f).^[56] They used **5** as curing agent for a tung oil-based triglycidyl ester. The tertiary amine moieties within the material catalyzed the

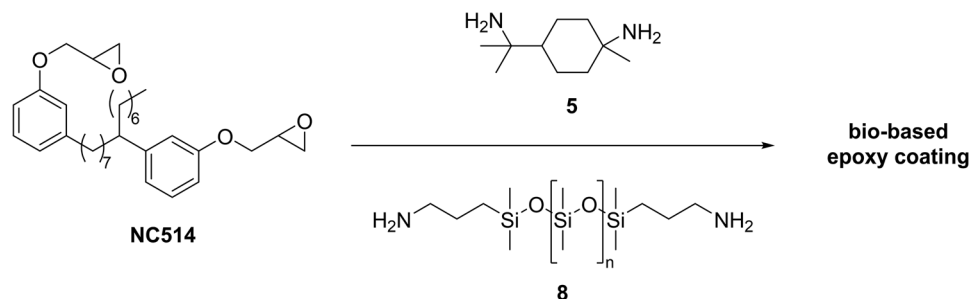


Figure 6. Generation of a bio-based epoxy coating using 1,8-menthane diamine **5** as curing agent.^[55]

transesterification of the ester groups, thus making it a catalyst-free vitrimer matrix applied in carbon fiber-reinforced composites. This shows the advantage of implementing nitrogen-containing moieties into the polymer in order to generate internal catalytic functionalities.^[65] The implementation of **5** was shown to increase the T_g and the stability of the polymer with higher content of **5** due to its rigid structure. Dynamic transesterification reactions of the β -hydroxy esters formed through curing could be confirmed by stress relaxation experiments. Hence, the vitrimers showed good self-healing performance and shape memory behavior and could be physically recycled. By adding woven carbon fibers into the resin matrix, improved mechanical properties could be obtained. The dynamic transesterification facilitates reprocessing, self-adhesion, and chemical degradation of the composites.

In a similar approach from the same group, an epoxidized form of **5** was cured with adipic acid to obtain a vitrimer network also able to undergo dynamic transesterification reactions.^[66] Similar to the example above, the tertiary amine could act as internal catalyst, resulting in vitrimers with good self-healing and the possibility for reprocessing. Further, shape memory behavior was observed. The vitrimers could analogously be used as matrix for fiber-reinforced resins with reprocessing, shape memory, and self-adhesive properties.

Apart from this, also other examples show the possibility of a previous derivatization of **5** instead of it being directly implemented into polymers. In 1981, Scola and Stevens synthesized bisnadimides from **5**.^[67] In yet another approach, the amine groups of **5** were converted into isocyanides.^[68] The resulting diisocyanide served as ligand in a variety of organometallic polymers prepared in the group of Harvey.^[69]

In a work by Lu et al. in 2022, **5** was derivatized with furfural and cardanol in a Mannich reaction to obtain a novel bio-based curing agent (Figure 4d).^[57] For the synthesis of thermosets, functionalized epoxidized soybean oil was used, and a dual curing with the renewable curing agent was performed to obtain thermosets. While the C_{15} chain of cardanol increased the toughness of the obtained thermoset, the three ring structures of the curing agent increased the mechanical strength of the polymer. In a following work of the group, the same curing agent was used for the synthesis of a thermoset with thermal and light-triggered shape memory properties.^[70]

As emphasized in this section, MDA is an example of the numerous possibilities of using terpene-based amines to access novel materials with desirable properties. As an AA monomer for step-growth polymer synthesis, **5** can be applied in a variety of ap-

proaches for the generation of partly or fully bio-based polymers with interesting properties. In many cases, the rigid backbone of **5** in combination with the formed nitrogen-containing functional groups able to undergo hydrogen bonding or nucleophilic attacks improved the mechanical properties of the obtained materials. This shows the potential of transferring these properties to amines from other terpene feedstock that might be future focus of research.

2.2. Limonene-Based Amines

Apart from pinenes, limonene represents one of the most abundant terpenes. It can be industrially gained as a waste product from citrus fruit peel.^[71] Due to its availability, it found application as greener solvent, replacing fossil alternatives,^[72] but it can be also used for polymer synthesis,^[33,73] for example for the production of poly(limonene carbonate).^[74] The two double bonds have been subject to many derivatizations,^[75] also including the introduction of amine units.^[76,77] Additional to monoamines, also diamines were synthesized, thus yielding monomers for PU or PA synthesis.

Different diamines that can be gained via oxidation and subsequent amination of limonene **9** are summarized in Figure 7. In a patent published in 2019, Kobilka et al. introduced the synthesis of four different diamines from limonene (Figure 7a–d).^[78] Depending on the reaction conditions, limonene was oxidized to four different oxygenized species. In two cases (Figure 7a,b), limonene was oxidized to the α,β -unsaturated ketones **10** and **13**, the position of the ketone group depending on the type of reactant. Addition of cyanide to the unsaturated ketones yielded the respective nitriles **11** and **14**, still bearing a ketone group. Via reductive amination of the ketone and reduction of the nitrile, the two diamines **12** and **15** can thus be accessed. In a different approach, two different diols **17** and **20** were synthesized. In route **d** (Figure 7), hydroboration-oxidation yields the diol **20** directly, while in route **c**, one of the methyl groups is first oxidized to the primary alcohol **16** using *Rhodococcus* bacteria. After hydroboration-oxidation of the less hindered double bond, another diol **17** is formed. Both diols can be converted into the diamines **18** and **22** by reaction with ammonia in the presence of a catalyst.

These diamines mimic isophorone diamine, which can be used to produce epoxy resins and PUs.^[79] The authors also developed the further synthesis of diisocyanates from the different diamines. In general, the bifunctionality of the obtained product gives rise to their use in polymer synthesis.

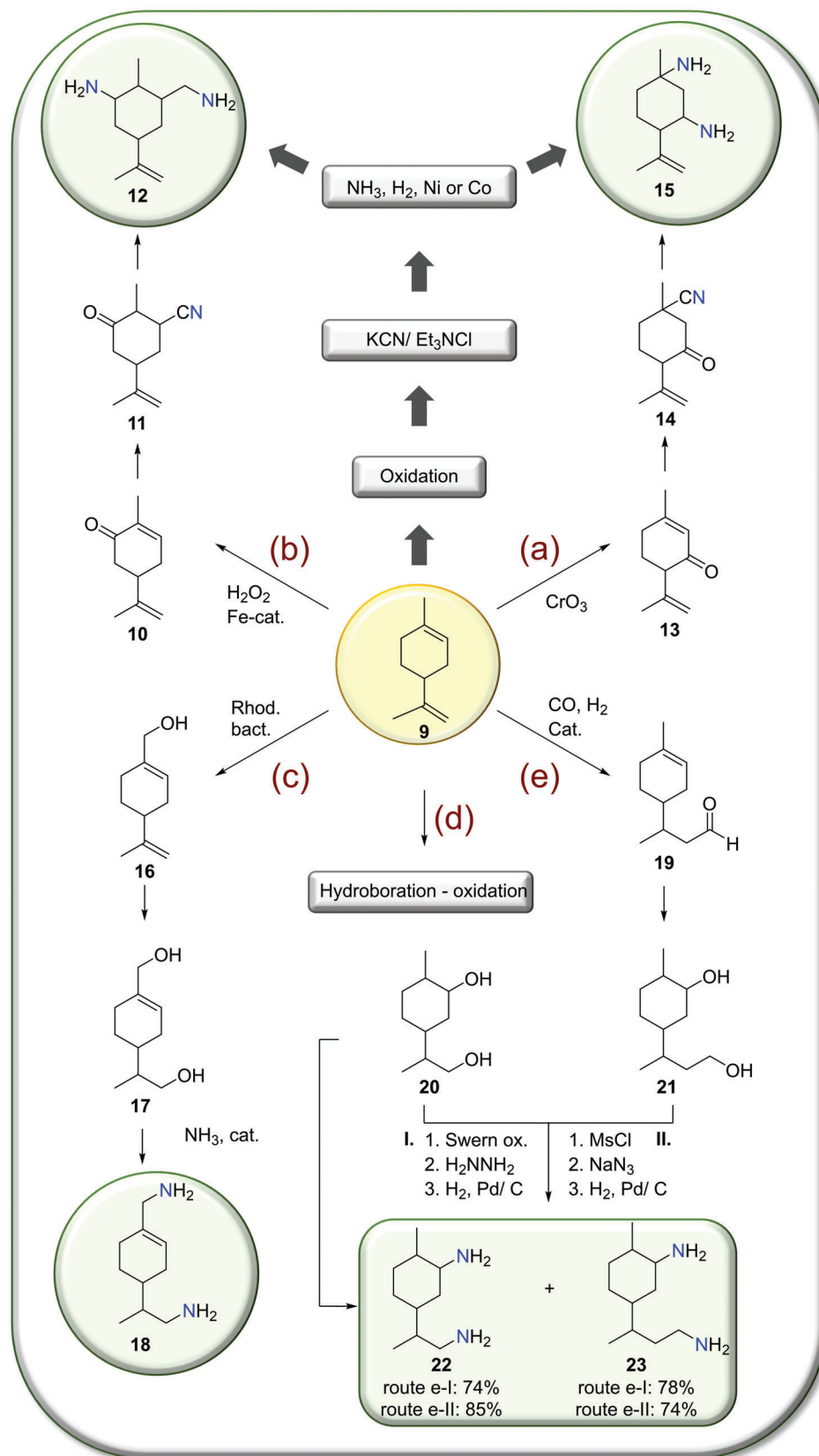


Figure 7. Synthesis of different diamines from limonene via oxidation and subsequent amination.^[78,79] Yields are given as overall yields depending on the synthesis route.

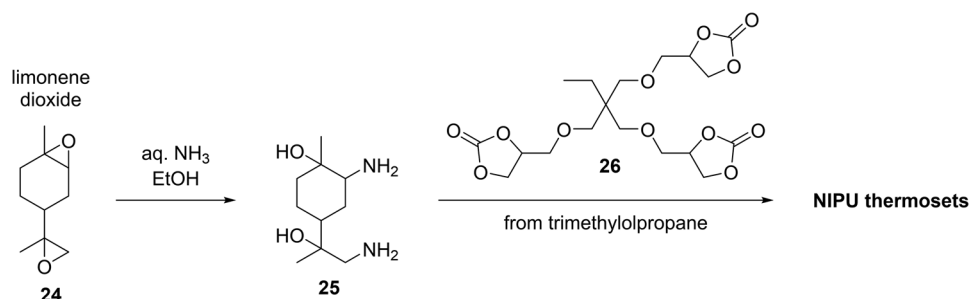


Figure 8. Synthesis of limonene-derived bifunctional β -amino alcohol and use for NIPU thermosets.^[84]

Many synthesis protocols are not optimized according to the principles of green chemistry, with hazardous reactants such as cyanide being necessary, solvents such as CCl₄ being used during synthesis and work-up and the application of multiple column chromatography steps. Yet, it was shown how the two double bonds of limonene can be used to obtain a variety of amine functions at different positions.

Rieger et al. developed a protocol similar to route **d** in 2020, using limonene-based diols **20** and **21** for the synthesis of the corresponding diamines (Figure 7d,e).^[80] Two different diols were obtained via hydroboration-oxidation of limonene and of hydroformylated limonene **19**. As the direct reaction with ammonia was not successful in their case, two alternative routes were developed and compared for the synthesis of the diamines. The first one started with the oxidation of the diols to the ketoaldehydes. These were converted into the hydrazones using hydrazine monohydrate. Reduction of the dihydrazones with hydrogen and a Pd/C catalyst yielded the diamines **22** and **23**. In the second route that was established, the alcohols were converted into mesylate groups, which were subsequently used for an S_N2 reaction with sodium azide. The resulting diazide could then be reduced to the diamine either by using hydrogen and a Pd/C catalyst or by adding PPh₃, with the former being the more sustainable alternative.

Although to our knowledge the two different diamines **22** and **23** that are accessible by this approach have not yet been used in polymer synthesis, they were developed as attractive possible building blocks for the use in nitrogen-containing polymers such as PUs.

All synthesis steps were scaled up in order to obtain several grams of the diamines. High yields and low side product formation were obtained in all steps after optimization of the reaction conditions and a low amount of solvent and purification steps were used. Nevertheless, several derivatization steps were necessary to obtain the amines **22** and **23**, in combination with the use of hazardous substances such as hydrazine or, in the case of the second route, the application of partially high reaction temperatures and long reaction times.

Hydroformylation of limonene is also part of a diamine synthesis based on limonene that was included in a patent in 1986 on the synthesis of polyisocyanates, with following conversion of compound **19** to the primary amine via reductive amination.^[81] Behr and Wintzer published a one-step procedure toward the same primary amine based on metal-catalyzed hydroaminomethylation with ammonia.^[82] Although low yields of maximum 25% were obtained, one synthesis step less and the

high atom economy of the reaction are important steps toward more sustainable routes to nitrogen-containing monomers based on terpenes.

Another often used possibility to oxidize the limonene double bonds is by epoxidation.^[83] The group of Mülhaupt opened limonene dioxide **24** with ammonia to obtain the bifunctional β -amino alcohol **25** (Figure 8).^[84] In this straightforward synthesis protocol, the use of solvent and work-up steps is reduced, requiring an excess of ammonia to avoid the formation of secondary amines. Together with three other renewable trifunctional β -amino alcohols, the product was blended with hexamethylene diamine and used as curing agent for the synthesis of NIPU thermosets with compound **26** among other renewable multifunctional cyclic carbonates. In comparison with using only hexamethylene diamine as curing agent, the NIPUs were formed less readily due to higher viscosity of the β -amino alcohols. Especially the limonene-based monomer required a significantly longer gelation time due to the lower accessibility of the amine groups. At the same time, the stiffness was higher than that of the benchmark material, represented by a significantly higher Young's modulus of 3400 MPa in comparison to 1600 MPa when using 50 wt% β -amino alcohol and a decreased elongation at break.

The introduction of the amine function directly into limonene dioxide using more benign reactants makes this procedure an attractive possibility to access terpene-based amines. Limonene dioxide **24** can be produced effectively by oxidation of limonene; various processes have been published concerning this topic. Furthermore, the obtained diamine can be used for the production of fully biobased NIPUs, thus addressing several principles of green chemistry and contributing to establish more sustainable polymer synthesis routes.

A possibility to introduce amine groups directly into limonene without the need for prior oxidation is by using the double bonds for a thiol-ene reaction. The group of Meier established the reaction of limonene and cysteamine hydrochloride to form diamine **27** in 2013 (Figure 9).^[85] The obtained diamine was used for the direct synthesis of polyamides by a polycondensation reaction with diesters that were previously prepared via thiol-ene reaction from limonene in the same manner.^[86] Besides, different renewable amines and esters were co-polymerized with the limonene-based monomers. Using 1,5,7-triazabicyclododecene (TBD) as catalyst, polyamides with molar masses of up to 12 kDa were obtained. The thermal properties depended strongly on the amount of incorporated terpene. Furthermore, by adding dimethyl carbonate (DMC) in presence of TBD, monomer **28** with two

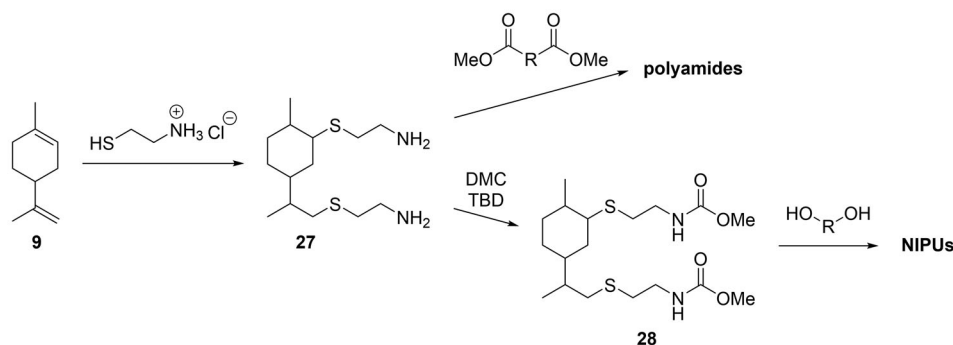


Figure 9. Thiol-ene reaction for the generation of a terpene-based diamine and further use for polyamide and polyurethane synthesis.^[85]

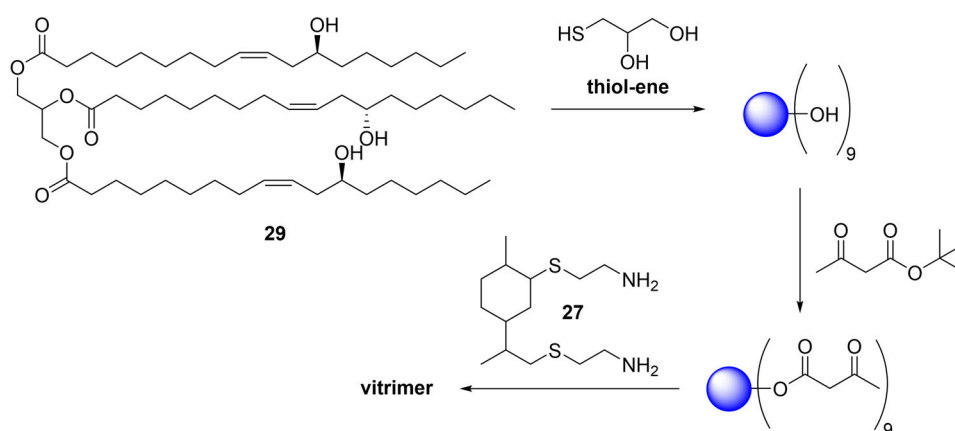


Figure 10. Synthesis of castor oil-based multifunctional acetoacetate and vitrimer synthesis using aminated limonene.^[87]

urethane groups was obtained without the need for isocyanate compounds. Transurethanization of **28** with renewable diols yielded amorphous to semicrystalline NIPUs with molar masses of up to 13 kDa.

In a work by Zhu et al., this limonene-derived diamine was used for the synthesis of vitrimers (**Figure 10**).^[87] Thus, castor oil **29** was equipped with additional hydroxy moieties by thiol-ene addition and subsequently transesterified, resulting in functionalized castor oil bearing approximately nine acetoacetate groups.^[88] Cross-linking of these acetoacetate residues by polycondensation with diamine **27** led to the formation of vinylogous urethane units. Transamination of the vinylogous urethanes allows the polymer networks to exchange during reprocessing, thus representing the properties of a vitrimer.

The aminated limonene **27** can not only be used in PU and PA synthesis, but also as hardener in epoxy-amine resins. In a work by Anda and Langlois et al., it was used as one of three renewable diamines for cross-linking with renewable resorcinol diglycidyl ether, obtaining fully biobased thermosets (**Figure 11**).^[89] Incorporation of the cyclic terpene structure led to comparable flexural strength and modulus to those of similar petroleum-based thermosets. Furthermore, a higher fracture toughness than in the case of the other applied amines was observed. Thus, these results confirm the suitability of aminated limonene as hardener for epoxy resins. In a following study, the same system was com-

pared to thermosets based on a diglycidyl ether derived from bisphenol A regarding their aging performance.^[90] For the bio-based epoxy-amine resins, better fatigue crack resistance properties were measured than for the petrosourced benchmark material. Furthermore, the resins could be reinforced with recycled carbon fibers.^[91] The mechanical properties of the obtained composites were analyzed thoroughly and were superior to analyzed benchmark materials.

Acosta Ortiz et al. functionalized this limonene-derived diamine further by introducing additional allyl groups via nucleophilic substitution using allyl bromide.^[92] Thus, a monomer containing four terminal double bond units in addition to two tertiary amines was synthesized and used as curing agent in an epoxy/thiol-ene photopolymerization with a commercial bio-based epoxy resin and a tetrafunctional thiol, yielding a cross-linked polyether-polythioether co-network. Varying percentages of the curing agent and the thiol were used and resulted in different toughness parameters.

The examples described in this section show the high potential of the two limonene double bonds for various functionalizations, leading to nitrogen-containing monomers. The different routes to polyamine compounds and the versatile possibilities of implementing the obtained monomers into polymers show the need of further research to exploit the advantages that limonene-based amines bring in sustainable polymer synthesis.

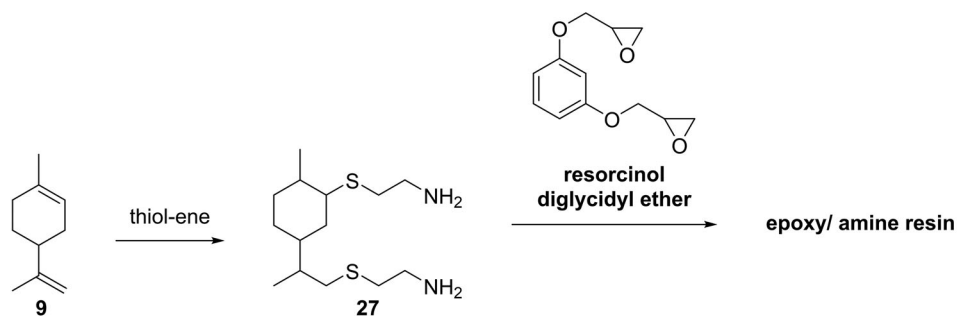


Figure 11. Use of aminated limonene **27** as curing agent for fully biobased epoxy thermosets.^[89]

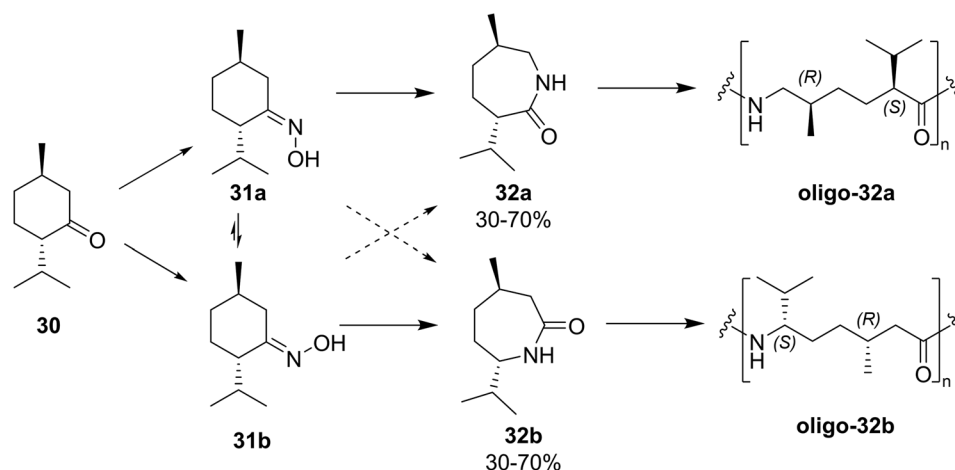


Figure 12. Synthetic pathway from menthone to polyamides.^[97] Overall yields are reported for the monomers. The lactam yields vary depending on which oxime isomers (or mixtures thereof) were used as the starting material.

2.3. Terpene-Based Lactams and Their Use in Polymer Synthesis

PA-6 is the most well-known and widely produced polyamide on the market and is made from caprolactam. Due to the necessity to replace fossil-based polymers, diverse examples of terpene-based lactams and corresponding polyamides have been developed in the last years.

An example of the synthesis of a terpene-based lactam was reported in 1961 by Kono et al., starting from (–)-menthol.^[93] The designed route comprises a first oxidation step by chromic acid, leading to (–)-menthone ketone, followed by oxime formation and subsequent Beckmann rearrangement. A solvent-free polymerization was performed in presence of elemental potassium and a cocatalyst, leading to an optically active polymer with a melting point between 160 and 170 °C. Lactams were also prepared from camphor and α -pinene for pharmaceutical purposes and studied by the group of Thorén in 1970 in order to obtain the final secondary amines by reducing the lactams.^[94] In 2012, Kumar et al. synthesized and investigated the antitussive activity of the (–)-menthone and camphor corresponding lactams.^[95] Nowadays, menthone **30** is achievable in an easier and greener fashion, as reported by Njoo et al. in 2020, using calcium hypochlorite as the oxidizing agent in a polar solvent.^[96]

In 2014, Rieger et al. revived the challenge to polymerize such compounds.^[97] The group studied the model synthetic

pathway reported by Kumar to get a deeper understanding of the formation of lactam isomers. The process is a two-step reaction involving the synthesis of two oxime isomers **31a** and **31b** and a subsequent Beckmann rearrangement (Figure 12). The nitrogen is introduced with a condensation reaction of the oxidized terpene derivative, for example menthone **30**, with hydroxylamine hydrochloride. Later, the reaction in presence of polyphosphoric acid or cyanuric chloride allows the nitrogen atom to rearrange in the ring chain, yielding two corresponding lactam regioisomers **32a** and **32b**. These two monomers lead to two polyamides with different structures and stereochemistry, showing interesting properties. Because of this, separation and isomerization protocols were explored to obtain the *cis*- and *trans*-oximes and the subsequent lactams as pure isomers. The successive oligomerization was performed via anionic and acid-catalyzed ROP. The former proved to be the most effective one with the employment of elemental potassium and additional benzoyl chloride as cocatalyst, leading to the oligomerization of both the lactam isomers, while the acid-catalyzed protocol led to decomposition and byproducts. It was shown that the lactam **32a** was the easier monomer to polymerize due to less steric hindrance caused by the isopropyl substituent. Oligomers **oligo-32a** and **oligo-32b** with different molar masses, with a maximum of 14 monomer units, were detected using MALDI, ESI-MS, and SEC techniques.

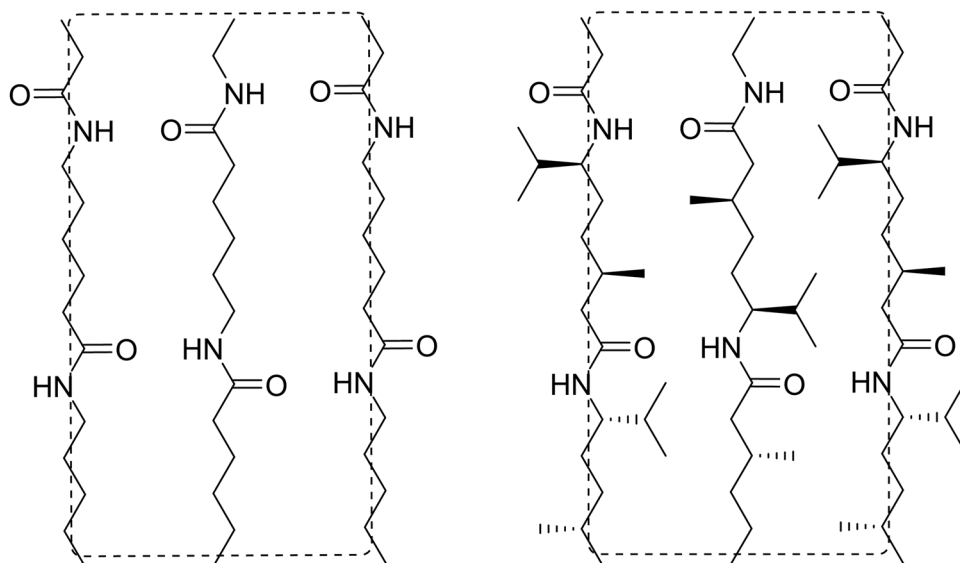


Figure 13. PA-6 and menthone-based polyamide: hydrogen bonding 2D organization.

It is relevant to consider that the ability of the terpene-based lactams to polymerize is influenced by different thermodynamic and kinetic factors. Importantly, substituents on the ring can greatly affect the reactivity of the monomer, depending on their position, steric demand, and polarity.^[98]

Two years later, the same group reported an improved one-step synthesis protocol to obtain menthone-based lactam monomers without isolation of an oxime intermediate, using hydroxylamine-O-sulfonic acid. Moreover, an optimized procedure for the polymerization process was developed. Potassium was substituted with sodium hydride or potassium *tert*-butoxide as the initiator in presence of a benzoyl lactam co-initiator, allowing for a solvent-free reaction besides an easier and potentially scalable approach. Thermal analysis of the obtained polyamides showed a decomposition temperature of nearly 400 °C by TGA, a T_g comparable to commercial PA-6 and a T_m that was 80 °C higher (300 °C). The higher melting point can be explained by the presence of the bulky side groups and stereocenters. Additionally, a significant degree of crystallinity was detected by WAXS analysis. Some of the obtained q -values are shown to be larger than the q -values of PA-6, referable to the hindrance of the isopropyl substituents along the chains (Figure 13).^[99] Overall, this developed method had the advantage to have good control of stereochemistry and of the polymer properties as consequence.

Similar to the synthesis of lactams from menthone, carbonyl derivatives of other terpene compounds can be used for lactam synthesis and subsequent polyamide formation. With β -pinene **2** representing an abundant terpene feedstock, a β -pinene-derived cyclic ketone was obtained by acid-catalyzed oxidation with KMnO_4 and further converted into the lactam by Winnacker and Sag (Figure 14). In this case, the Beckmann rearrangement was discovered to be stereoselective to **2a**, which was polymerized to the corresponding polyamide.^[100] Differently from the first study,^[93] an acid-induced cationic polymerization was found to be the most effective strategy. It was noticed that the final molar mass was greatly affected by reaction time, temperature, and acid molarity. Similar to the polyamides obtained from

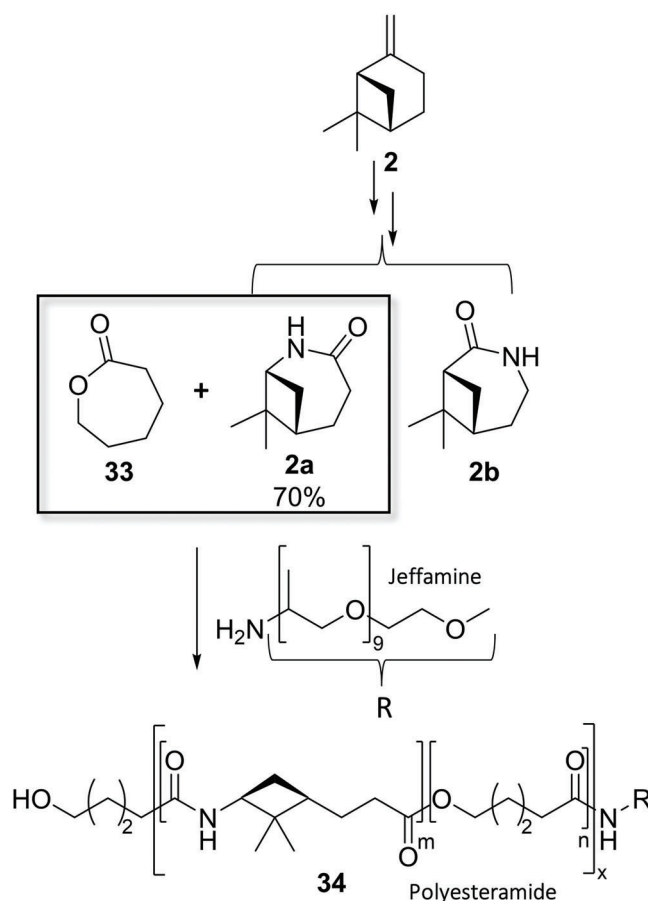


Figure 14. Polyesteramide synthesis from β -pinene **2**. Overall yields are reported for the monomer, referring to the best described results via a three-step synthesis. The product mixture contained 97–100% of isomer **2a**.

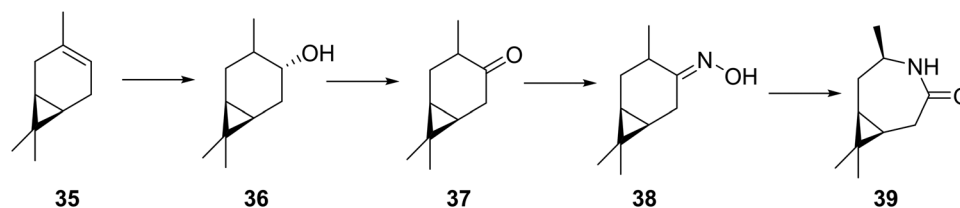


Figure 15. Four-step synthesis from (+)-3-carene to the lactam.^[101] The overall yield is reported for the monomer 39.

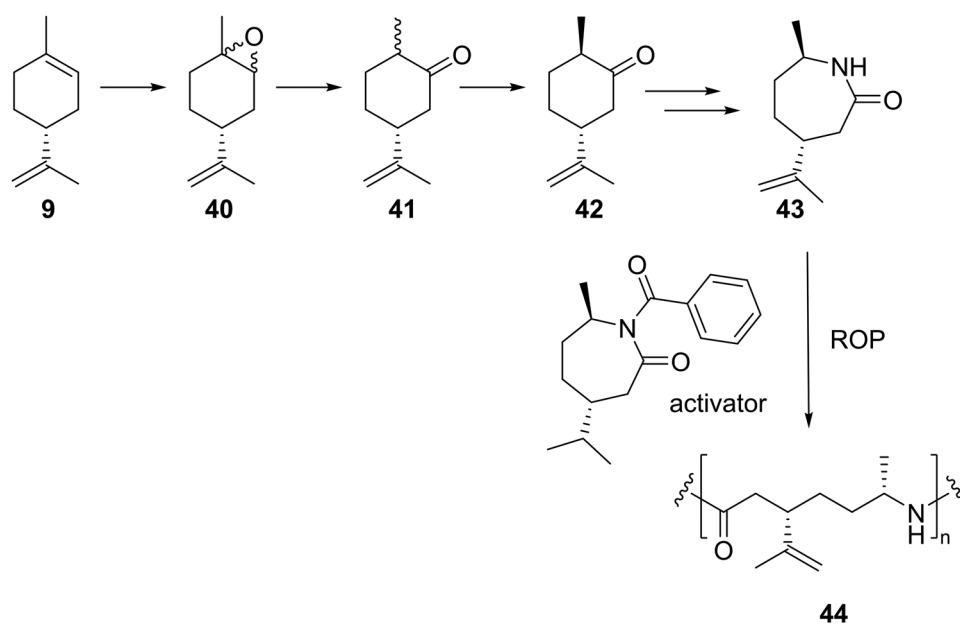


Figure 16. Synthetic pathway to (+)-limonene-based polyamides through activated ring-opening polymerization.^[103] The overall yield is reported for monomer 43.

menthone, the TGA of polymer samples of **poly-2a** showed high decomposition temperatures (400 °C), which are also comparable to those of PA-6. The DSC analysis of **poly-2a** showed a melting temperature (T_m) above 300 °C, which is higher than that of PA-6 and comparable to the ones measured from the (–)-menthone polyamides.

Further research proceeded with the study of the copolymerization of **2a** with ϵ -caprolactone **33** in bulk by ROCOP (Figure 14) and its blend with the biocompatible polyethylene glycol to produce a co-polymer with potential medical applications.

Another terpene investigated by Winnacker's group for potential use in polyamide synthesis is (+)-3-carene **35** (Figure 15).^[101] For this molecule, a different synthetic pathway was proposed, resulting in a more sustainable process. The developed oxidation route was metal-free catalyzed through the formation of the ketone from the respective epoxy compound. The epoxide was synthesized via enzyme catalysis under mild conditions. Studies on the regio- and stereo-selectivity during the formation of the ketone via Meinwald rearrangement with a $\text{Fe}(\text{ClO}_4)_2$ catalyst under mild conditions were carried out. Related to this, Meier et al. showed that such catalytic rearrangements are generalizable and that bismuth triflate was a suitable catalyst at low loading in the more sustainable solvent 2-methyl tetrahydrofuran.^[102] Through

the newly established pathway, Winnacker et al. were able to synthesize the 3S-caranlactam and 3R-caranlactam diastereoisomers each in a four-step process.

Additionally, the synthesis of 3S-caranlactam **39** was also successfully carried out in a one-vessel reaction in 4 L scale reactor, indicating the potential scalability of this approach. The monomers were polymerized to the corresponding homopolyamides, obtaining different properties. The three-membered ring in the polymer backbone explains the high T_g s (105–120 °C). By DSC and XRD analysis, the poly-3S-caranamide showed to be semi-crystalline, on the contrary to poly-3R-caranamide, which exhibited an amorphous morphology. This was the first amorphous terpene-based polyamide documented. Furthermore, co-polymerization of 3S-caranlactam with ϵ -caprolactam **33** and lauro lactam was also performed, giving transparent co-polymer films.

Recently, Winnacker et al. extended this study by exploring the possible synthesis of lactams and, as a result, polyamides from limonene **9** (Figure 16).^[103] The lactam **43** was successfully synthesized through a three-step process. For the first oxidation step, $\text{Fe}(\text{ClO}_4)_2$ was recognized as the most sustainable catalyst to use under mild conditions. The two following reactions to yield the oxime and the lactam **43** were stereospecific, a tendency

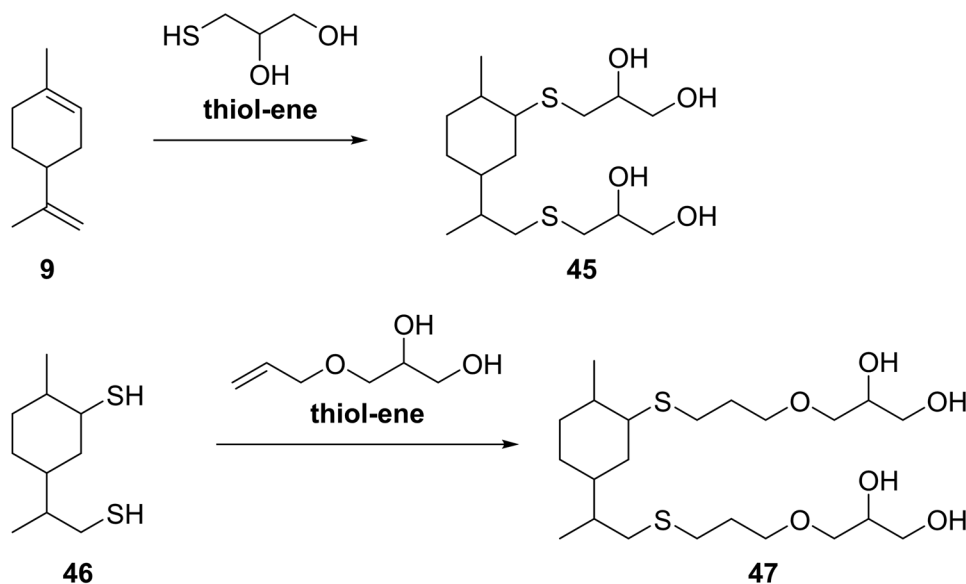


Figure 17. Polyols **45** and **47** from limonene using thiol-ene reaction.^[104]

emphasized by the presence of the steric hindrance of the isopropylene group attached to the ring. For the same reason, during the polymerization process, high molar masses were difficult to reach. The medium molar mass polyamides showed low T_g values, a decomposition temperature of about 423 °C and no detectable T_m . The advantages of using limonene are multiple as it is abundant and the cheapest terpene available. Furthermore, the double bond of the iso-propylene group that is still present within the repeating unit is available for further functionalization. Therefore, this gives rise to a wide range of possibilities to tune the properties of the final macromolecules.

These works demonstrate how nitrogen-containing terpene derivatives can be suitable starting materials for ROP, offering possibilities for versatile polymer repeating units and resulting in the same or sometimes even better final properties than their fossil-based counterparts.

3. Other Nitrogen-Containing Polymers Using Terpene Units

Apart from terpene-based amines and lactams that were discussed above, terpenes can also be incorporated in nitrogen-containing polymers without the terpene-based monomers bearing nitrogen atoms (see Figure 2). This is for instance the case for step-growth polymerization approaches with amines or isocyanates as reaction partners. Some basic concepts will be highlighted in this section, without the claim to be exhaustive.

3.1. Terpene-Based Alcohol and Polyol Monomers

Considering PUs as one of the important nitrogen-containing polymers, one straightforward alternative for implementing terpene moieties without the need for terpene-based amines is the reaction of terpene-based polyols with diisocyanates.

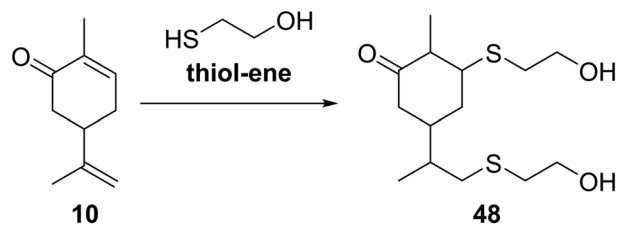


Figure 18. Diol synthesis from carvone using thiol-ene reaction.^[108]

Starting from limonene, Gupta et al. used thiol-ene reaction to introduce hydroxy groups into the molecule (Figure 17).^[104] When directly using limonene **9**, 1-thioglycerol was used as reaction partner. An alternative synthesis used a limonene-based dithiol **46** for a reaction with glycerol-1-allylether. Thus, in both cases, up to four hydroxy groups were implemented in the product molecules **45** and **47**. Determination of the hydroxyl number confirmed the successful reaction and the polyols were used for the production of rigid PU foams by blending with commercial polyols and reacting with mostly methylene diphenyl diisocyanate. Foams with regular shape cells, uniform cell size distribution, and high T_g s were obtained.

The drawback of this approach is the need for hazardous and non-biobased isocyanates. Nevertheless, the presented thiol-ene approach proves to be a mild method to introduce valuable functional groups into the molecule. Both polyols were further used for the synthesis of flame-retardant PU foams.^[105] Further, aromatic units could be introduced into the polyols, for example by implementing eugenol.^[106] In another example, a Mannich polyol based on the reaction of a limonene derivative containing phenol groups with 1,3-*N*-hydroxyethyl oxazolidine could also be synthesized and used for rigid PU foams.^[107]

The example of limonene was transferred to carvone **10** as a substrate (Figure 18).^[108] By the reaction with 2-mercaptoethanol, the diol **48** could be synthesized from carvone. Similar to the

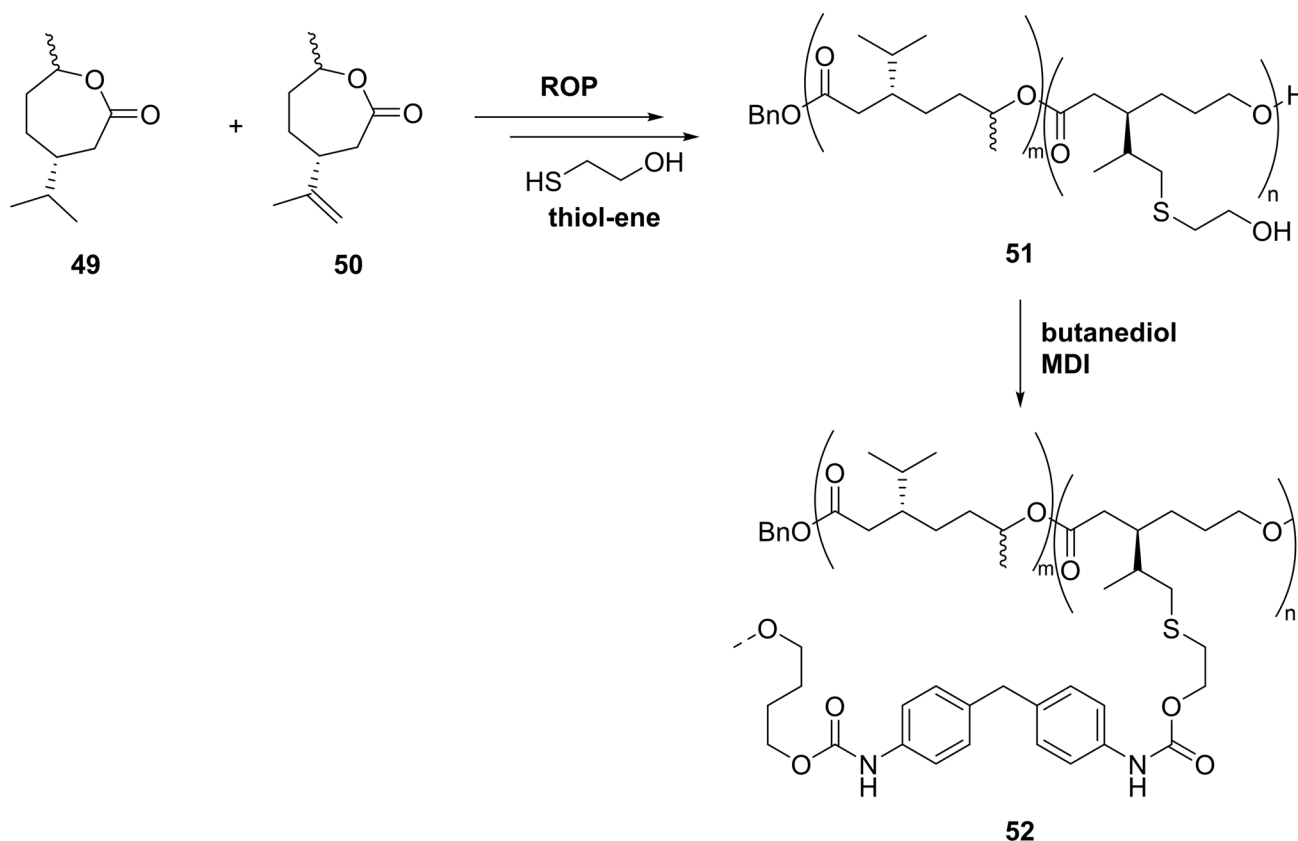


Figure 19. Polyol synthesis from carvomenthide 49 and dihydrocarvide 50 for cross-linked polyurethanes.^[110]

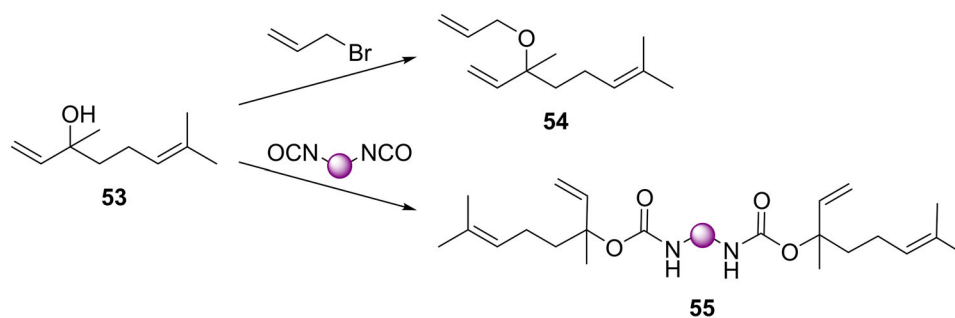


Figure 20. Reaction of linalool 53 with diisocyanates to form urethane monomers 55 for thermoset synthesis using thiol-ene chemistry.^[111]

examples using limonene, rigid PU foams with increased biobased content could be obtained by polyaddition to polyisocyanates. Carvone-based PUs could be used as coatings for automobile industry.^[109]

Alternatively, polyols 51 could be gained from carvone via ROP of carvomenthide 49 and dihydrocarvide 49 and subsequent thiol-ene modification of the side chain double bonds.^[110] With molar masses of around 3 kDa, these polyols could be used for the formation of PUs (Figure 19). Polyols with the most (4–5) hydroxy groups per macromolecule exhibited the highest cross-linking and thus the most favorable mechanical properties.

As a naturally occurring mono-alcohol, Weems et al. used linalool 53 in an approach to produce urethane-containing

multifunctional monomers 55 for 4D printing resins (Figure 20).^[111] By addition of linalool to different diisocyanates, tetra-functional monomers were obtained that could be cross-linked via thiol-ene click reactions with commercial dithiols. By comparing the obtained thermosets with original linalool thermosets, the polymers containing urethane bonds showed an increase in T_g , elastic modulus, and toughness and furthermore an observable shape memory behavior. Thus, the approach shows the benefit of incorporating urethane moieties into the polymer backbone and the potential to include bio-based feedstock for specific applications, yet the percentage of bio-based material is still limited, and hazardous isocyanates were used.

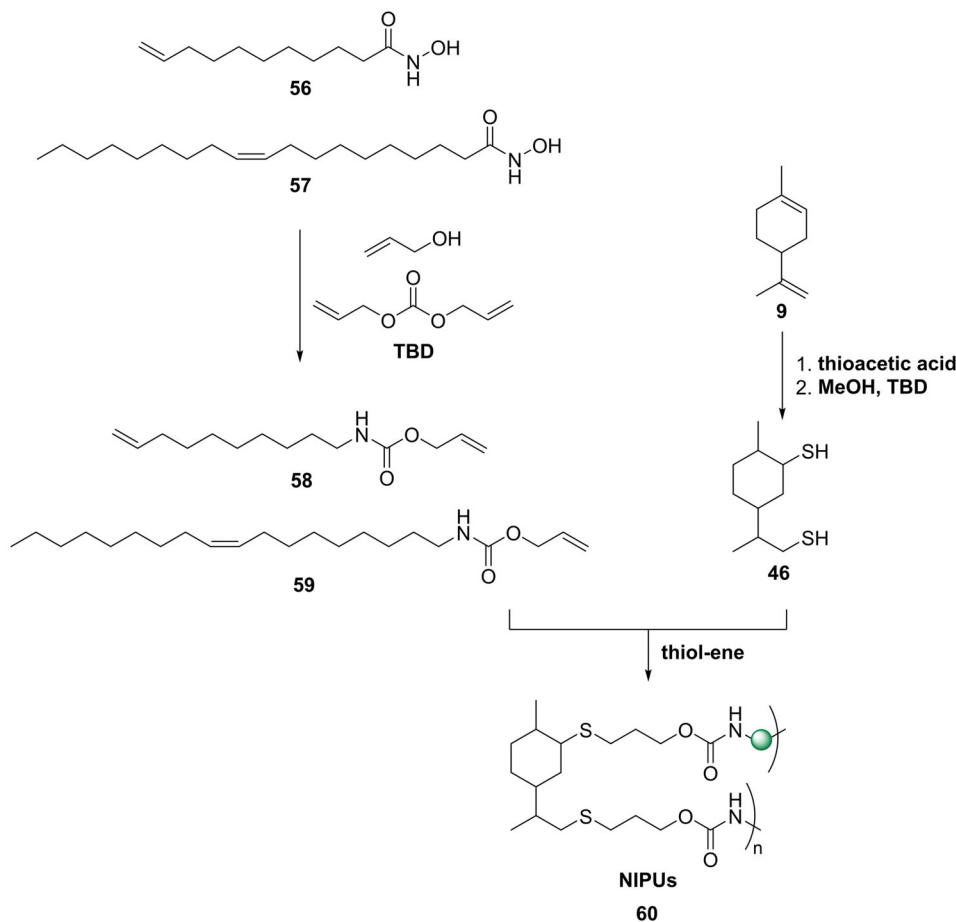


Figure 21. Synthesis of fatty acid-based urethane monomers via Lossen rearrangement and further NIPU synthesis using thiol-ene-addition.^[113]

Although exploring different useful applications from terpenes as sustainable feedstock, all these approaches still do not follow a holistic approach of greener polymer synthesis, as for instance hazardous diisocyanates or allyl bromide and fossil-based feedstock were used. Therefore, the synthesis of PUs from terpenes via isocyanate-free routes will be discussed in the next section.

3.2. Terpene-Based Monomers for NIPUs

Following the previous approach of reacting urethane monomers containing multiple double bonds with dithiols, a possibility to access terpene-based NIPUs is by using a dithiol derived from a terpene. Based on the finding that carbamate structures were accessible from renewable feedstock via catalytic Lossen rearrangement,^[112] the group of Meier developed a synthesis protocol for fatty acid-based monomers **58** and **59** containing a urethane group by Lossen rearrangement of hydroxamic fatty acid derivatives (Figure 21).^[113] In a step-growth polymerization using thiol-ene chemistry, NIPUs **60** with molar masses of above 20 kDa were obtained when using limonene dithiol **48** as comonomer. The Lossen rearrangement proceeds via the in situ formation of isocyanates, which instead of reacting with the alcohols can also react with water present in the reaction mixture,

forming urea bonds. Considering this, the synthesis of PURs as well as mixtures of both was possible. Compared to other dithiols used, the incorporation of the terpene ring structures resulted in detectable glass transition temperatures between -12 and -15 °C.

This approach enables a synthesis of PUs without the necessity of isocyanate isolation from renewable resources including a terpene motif.

Besides the Lossen rearrangement and subsequent transurethanization, a common way to access NIPUs is by the reaction of amines with cyclic carbonates. The two double bonds of limonene can be transferred to epoxides and subsequently to a bifunctional cyclic carbonate, which can be opened by diamines generating PU prepolymers, as was established by the group of Müllhaupt.^[114]

Recently, Della Monica and Kleij et al. developed a synthesis of a bis(cyclic carbonate) **62** derived from β -elemene **61** by epoxidation and subsequent CO₂ insertion.^[115] Polyaddition with different diamines led to the formation of non-isocyanate oligourethanes **63** with molar masses between 1.3 and 6.3 kDa (Figure 22), with a petroleum-based commercial diamine yielding the oligomer with the highest molar mass and lowest viscosity. The latter was used to perform further cross-linking experiments based on the additional double bond in the β -elemene structure and introduction of further double bonds by

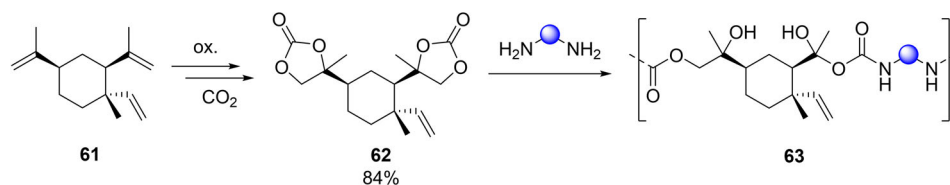


Figure 22. Bifunctional cyclic carbonate and NIPU synthesis with diamines.^[39,115] The reported monomer yield refers to the overall yield after two steps.

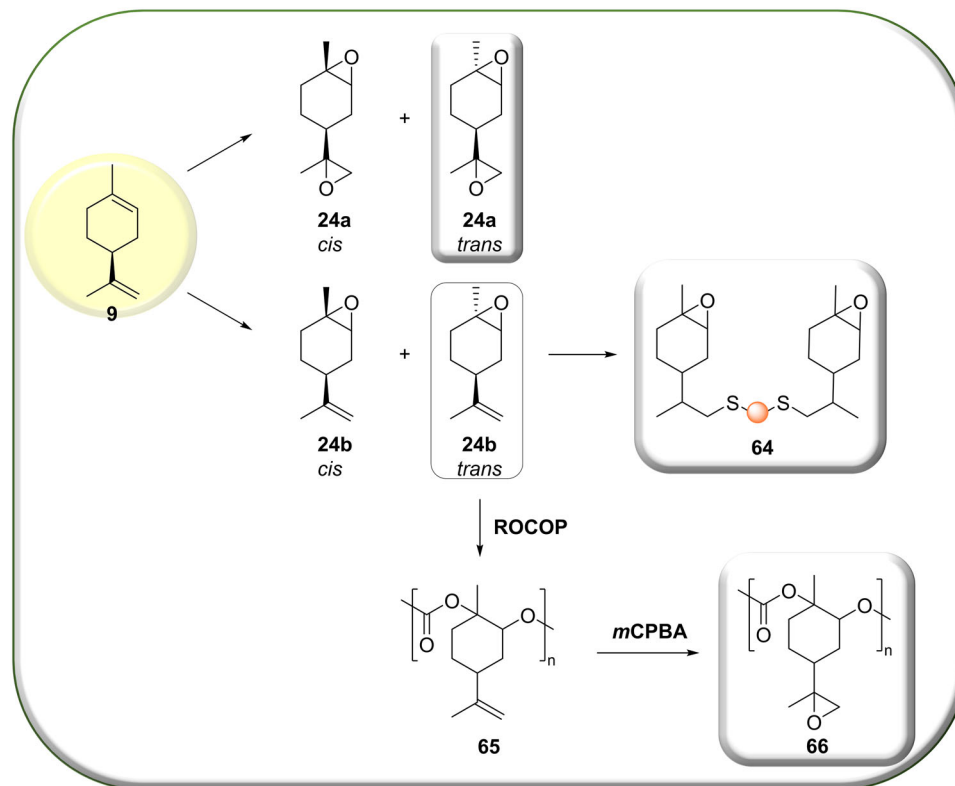


Figure 23. Use of *trans*-limonene oxides for the production of biobased epoxy-amine thermosets.

co-addition of a polyacrylate containing isocyanate units. Thereupon, the synthesized oligo(hydroxyurethane)s were shown to be attractive compounds for applications as prepolymers and for the investigation of further cross-linking possibilities.

Polyamines can also react with terpene-based acetoacetates to form vinylogous urethanes that are possible linkages in covalent adaptable networks. Du Prez et al. recently presented the formation of a vinylogous urethane dynamic network with a vanillin-based β -hydroxyamine that can be derived from lignocellulosic biomass and a bis-acetoacetate from 1,4-bis(hydroxymethyl)cyclohexane accessible from terpene biomass.^[116] The obtained vitrimers showed high stability at room temperature and recyclability when heated.

3.3. Terpene-Based Monomers for Epoxy Resins

Following the previous sections, another important class of nitrogen-containing polymers is represented by epoxy-amine resins. The use of terpene feedstock opens manifold possibilities

to create epoxy groups for possible amine curing, having been reviewed in the focus of renewable epoxy resins.^[60] The double bonds of limonene can be turned into the respective mono- or bisepoxide **24a** and **24b** selectively,^[35] with the *trans*-isomer being more reactive in both cases.^[77,117,118] The different possibilities of using limonene oxides as precursors for epoxy-amine resins are summarized in Figure 23. Recent research shows that molecular oxygen can be used for the oxidation, thus resulting in an access to valuable monomers with high atom economy.^[119] The monoepoxide **24b** can further be linked using thiol-ene chemistry,^[120] yielding monomers **64** for curing with polyamines,^[121] and also the bisepoxide **24a** can be used for epoxy-amine curing.^[122] In an example, cross-linked epoxy resins that were obtained using *trans*-limonene dioxide showed similar properties to resins based on fossil-based bisphenol A diglycidyl ether in the production of thermosets.^[118]

Post-synthetic epoxidation of the double bond in the backbone of poly(limonene carbonate) **65** enabled a curing with different commercial diamines to yield epoxy thermosets for coatings.^[123]

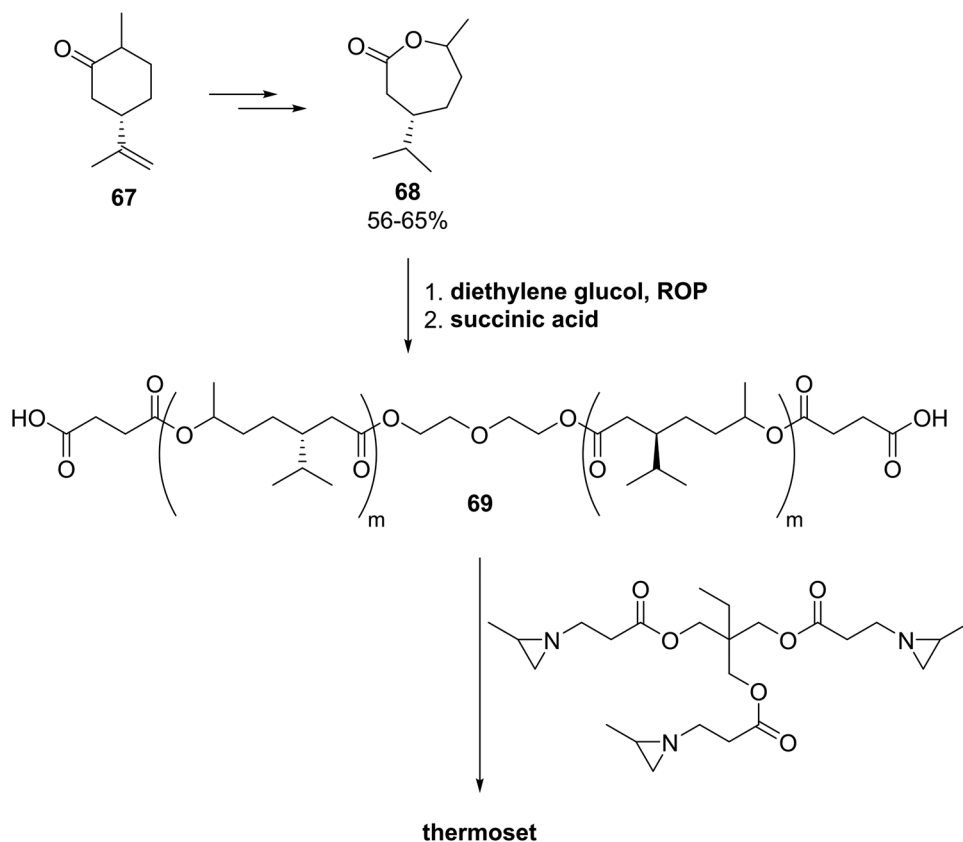


Figure 24. Synthesis of prepolymers by ROP of carvomenthide and end-group functionalization with succinic acid, with subsequent cross-linking using a polyaziridine.^[126] The yield of carvomenthide **68** refers to the overall yield over two steps and varies depending on the oxidant used.

These were compared with epoxy resins derived from non-biobased diglycidyl ethers that are commercially used and showed comparable to superior mechanical properties. When combining limonene oxide **24b** with vinyl cyclohexene oxide in a predetermined ratio during the polymerization and subsequently oxidizing the two sterically different double bond moieties, a partially bio-based oxidized polycarbonate was obtained.^[124] After curing with a diamine, it showed improved adhesion properties in comparison to petroleum-based thermosets.

A curing method that is similar to epoxy-amine resins is the opening of polyaziridines by nucleophilic groups within a polymer chain.^[125] As such, dihydrocarvone-based prepolymers can be reacted with aziridine moieties forming thermoset elastomers, as shown in a work by Kim and Shin et al. in 2015 (**Figure 24**).^[126] By ROP of carvomenthide **68** with diethylene glycol, polyesters of tunable chain length bearing two alcohol end groups were obtained. Esterification with succinic acid yielded prepolymers **70** with acid end groups and molar masses of 3, 6, and 12 kDa, which were then cross-linked with triaziridines. Due to the side chains within the polymer, no crystallinity was observed in contrast to similar polymers from petroleum-based feedstock. The polymers exhibited high thermal resistance with 5% mass loss temperatures of 298–321 °C, high elongation at break of up to 625% and tensile strengths of up to 1.24 MPa.

A similar approach was developed by the same group in 2019 to access triblock co-polymers from carvomenthide and lactide and cross-linking with a polyaziridine.^[127] Like this, thermoset elas-

tomers with a high bio-based content and good mechanical properties were accessible. Further, the introduction of poly(lactide) segments enabled the hydrolytic degradation of the polymers.

4. Conclusion

As it was shown in this review, terpenes are valuable compounds that can lead to different polymeric materials with desirable properties. These molecules have the potential to be sustainable building blocks for the development of bio-based polymers to promote a more sustainable circular economy. Particularly, nitrogen-containing polymers, such as important commercial polyamides, polyurethanes, polyureas, and epoxy resins, can be potentially replaced with terpene-derived analogous materials.

However, for the development of more sustainable polymer synthesis routes, it is important to consider different aspects of green chemistry besides renewability. Especially in cases where it takes several synthesis steps to introduce nitrogen into the monomers, all influences have to be considered and compared to evaluate the overall sustainability of the process. Like this, more sustainable solutions for polymers used in specialty applications may be developed. Realistically, however, it is clear that terpenes, due to their lower availability and less straightforward modification, will play a less important role for industrial applications than nitrogen-containing fatty acid-based polymers.^[128] Probably, they will find further ways for specialty applications, where for

instance the rigid structure of cyclic terpenes offers application advantages.

This work shows various approaches to include terpene moieties in the synthesis of promising nitrogen-containing polymer materials and thus hopes to contribute to further focused research in this area.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

amines, biobased polymers, epoxy-amine resins, polyamides, polyurethanes, sustainability, terpenes

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