



Fully Renewable Non-Isocyanate Polyurethanes via the Lossen Rearrangement

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In this work, a straightforward and efficient synthesis approach to renewable non-isocyanate polyurethanes (NIPUs) is described. For this purpose, suitable and renewable carbamate monomers, possessing two double bonds, are synthesized from hydroxamic fatty acid derivatives via the Lossen rearrangement in a one-step synthesis, and sustainable dithiols are synthesized from dialkenes derived from renewable feedstock (i.e., limonene and 1,4-cyclohexadiene). Subsequently, the comonomers are polymerized with the highly efficient thiol–ene reaction to produce NIPUs with M_n values up to 26 kg mol⁻¹ bearing thioether linkages. The main side product of the Lossen rearrangement, a symmetric urea, can also be polymerized in the same fashion. Important in the view of sustainability, the monomer mixture can also be used directly, without separation. The obtained polymers are characterized by NMR, attenuated total reflection-infrared spectroscopy, differential scanning calorimetry, and size exclusion chromatography.

Polyurethanes (PUs) are polymers composed of carbamate linkages, typically synthesized by the polyaddition of polyisocyanates with polyols. This polyaddition reaction was discovered by Otto Bayer in 1937 at IG Farben, and published in 1947.^[1] The new class of materials showed various interesting properties, offering many advantages compared to the already known plastics at the time, like increased flexibility and coating efficiency, and thus its importance rose further especially after commercialization of polyisocyanates. Due to these reasons, nowadays, PUs are used for various applications, for example

as construction materials,^[2–5] high-performance adhesives,^[6,7] furniture coatings,^[8–10] and hard plastic parts,^[11,12] with an annual demand of 16 million tons worldwide.^[13] Despite these manifold application possibilities and the non-toxicity of the final PUs, isocyanates are known to be hazardous to the human body via respiratory^[14] as well as dermal^[15] exposure. Additionally, the industrial preparation of isocyanates requires the use of phosgene, a highly toxic gaseous substance. Exposure through inhalation can lead to pulmonary edema, heart failure, chronic bronchitis, and emphysema. Moreover, no antidote exists so far.^[16] Thus, it is obvious that the development of milder and more sustainable synthetic routes toward PUs has become of great interest by many research groups.^[17–25]

Alternative synthetic routes toward isocyanates have been known for more than 150 years, for instance, the well-established rearrangement reactions developed by Curtius,^[26] Hoffmann,^[27] and Lossen,^[28] forming isocyanates *in situ* without the use of phosgene. The first two examples often result in higher yields, but show major drawbacks since explosive acid azides (Curtius) or toxic bromine (Hoffmann) are required. In comparison to that, the Lossen rearrangement, which was discovered in 1872, is known for the stability and lower toxicity of the used starting materials and milder reaction conditions. Hydroxamic acids are prepared from their respective methyl esters, are typically harmless, and are commonly employed in the medical field as siderophores against iron poisoning.^[29] Additionally, such compounds are currently being developed as anticancer agents^[30–32] and as cure against HIV^[33] and neurodegenerative diseases.^[34] Very recently, different polymers bearing hydroxamate groups have been synthesized, possessing desirable chelating properties and biocompatibility for medical purposes, surface coatings, and material science.^[35] For the Lossen rearrangement, it was assumed that an activating group such as O-acylating,^[36] O-silylating,^[37,38] or O-phosphorylating^[39] agent was necessary for the rearrangement to occur. In 1974, it was commonly known that a hydroxamic acid could rearrange in strongly alkaline solution.^[40] Still, Honda and co-workers^[41] recently confirmed a self-propagative mechanism for the Lossen rearrangement, whereby the activating agents are reduced to catalytic amounts of a base. A more sustainable approach of the Lossen rearrangement has previously been reported by our group, using alkyl and aryl carbonates in the

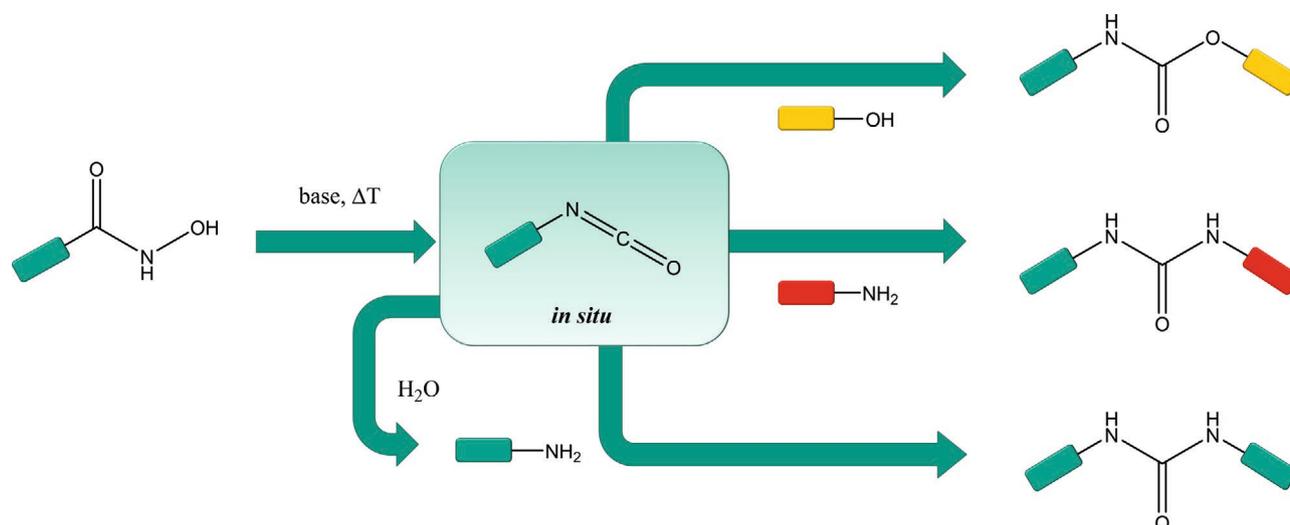
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Scheme 1. Schematic representation of the Lossen rearrangement and thereof derived products.

presence of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as catalyst. This catalytic system was applied for the herein reported monomer synthesis.^[42] Generally, by using suitable reagents, carbamates, amines as well as unsymmetric and symmetric ureas can be synthesized via the Lossen rearrangement (**Scheme 1**).

The rearrangement toward the three possible products has already been described for the synthesis of NIPUs, typically using difunctional molecules as monomers.^[43–46] Further synthesis approaches to obtain NIPUs are based on polycondensations,^[19,47,48] ring opening polymerizations,^[49] and polyadditions.^[50] Most commonly discussed are dimeric cyclic carbonates, which are reacted with diamines, yielding polyhydroxyurethanes. In this work, a novel alternative is presented, in which the carbamate function is prepared before polymerization by TBD-catalyzed Lossen rearrangement, resulting in a renewable monomer bearing two double bonds. Such compounds can subsequently be polymerized using a suitable polymerization technique. The advantage lies not only in the facile synthetic method but also in the possibility to use of the main by-product, the urea, for the same polymerization purpose, increasing the sustainability of the overall process even further.

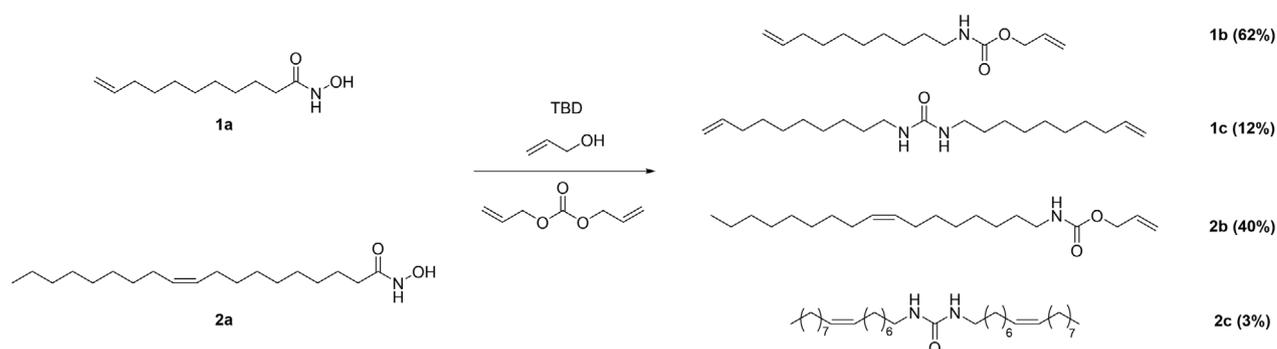
In this work, two renewable diene monomers bearing a carbamate or a urea moiety were polymerized with renewable as well as commercially available dithiol monomers via thiol–ene step-growth polymerization. Here, NIPUs are thus not obtained via the typically used transcarbamoylation or ring opening of cyclic carbonates, but by first synthesizing the urea or carbamate moiety and its subsequent incorporation into a polymeric backbone via the highly efficient thiol–ene chemistry. This polymerization method was chosen because of the high selectivity, mild conditions, and short reaction times, which are important aspects with regard to sustainability. Starting materials were chosen for their renewability and availability. Undecenoic acid can be obtained from castor oil,^[51] and oleic acid is the most commonly occurring fatty acid in nature. Additionally,^[52] diallyl carbonate can be synthesized from dimethyl carbonate, often described as a “green” reagent, and allyl alcohol is produced by heating glycerol in the presence of formic acid.^[53] To prepare

the required monomers, hydroxamic acid **1a** was reacted with 2 eq. diallyl alcohol and catalytic amounts of TBD as base in diallyl carbonate and heated at 110 °C overnight according to a report on catalytic Lossen rearrangements (**Scheme 2**).^[42] The precipitated urea by-product was isolated by simple filtration, while the carbamate was purified via flash column chromatography. The desired monomer **1b** and the urea side-product **1c** were isolated in 62% and 12% yield, respectively, and characterized by NMR, IR, and electrospray ionization-mass spectrometry (ESI-MS) (see the Supporting Information). The carbamate and urea carbonyl stretch signals in the IR spectrum are clearly visible at ≈ 1700 and 1610 cm^{-1} , respectively (Figures S15 and S16, Supporting Information). Moreover, NMR analysis (^1H and ^{13}C) confirmed the structures with new signals arising at 4.74 ppm for the carbamate and 4.37 for the urea amide protons (Figures S3 and S4, Supporting Information) and the shift of the adjacent methylene groups from 2.28 to 3.15 ppm. The optimized reaction conditions were also applied for the synthesis of monomer **2b** derived from oleic acid.

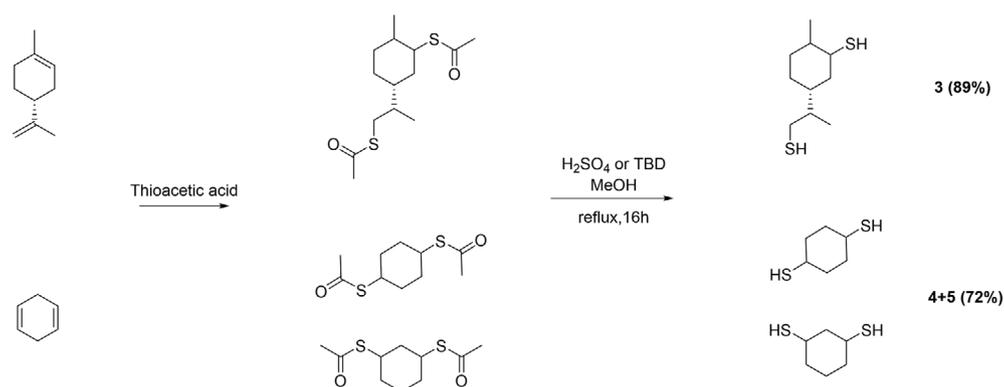
Two sustainable dithiols were prepared according to our previous report, while considering renewability. The first starting material is (R)-(+)-limonene, a terpene extracted from citrus peel oil, and the second 1,4-cyclohexadiene, which can be obtained by metathesis of plant oils with high linolenic acid content.^[55] According to our previous report,^[54] the diene was reacted with two equivalents thioacetic acid and then acidified or saponified to yield the respective dithiol. The presence of the thioester intermediates was confirmed by gas chromatography-mass spectrometry (GC-MS) (Figure S18, Supporting Information), while the dithiols were characterized via high-resolution mass spectrometry (HRMS), IR, and NMR. Worthwhile noting, the synthesis starting from cyclohexadiene resulted in a monomer mixture (i.e., **4** and **5**), as expected, which was used as such for further experiments. The same procedure was attempted with γ -terpinene, but yielded only the monosubstituted product, supposedly because of the steric hindrance of the terpene structure.

In the next steps, monomer **1b** was polymerized with both renewable and commercially available dithiols via thiol–ene

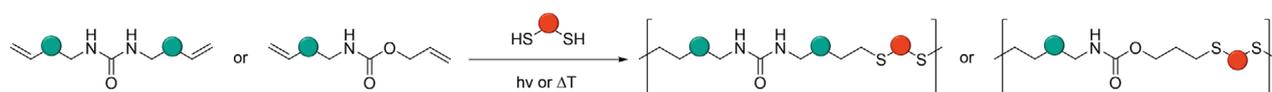
Base catalyzed Lossen rearrangement in diallyl carbonate



Dithiol synthesis



Thiol-ene polymerization



Scheme 2. Catalytic Lossen rearrangement of renewable hydroxamic acids in diallyl carbonate to yield diene monomers (top), synthesis of the renewable dithiols (middle),^[54] and their polymerization via thiol-ene chemistry (bottom).

chemistry (compare Scheme 2). The diene and dithiol were mixed in a 1:1 ratio in the solvent of choice and a suitable radical initiator. Then, the mixture was irradiated with UV light or heated for the desired time. The crude mixtures were analyzed via hexafluoroisopropanol-size exclusive chromatography (HFIP-SEC) to determine dispersity and molecular weight, as well as to confirm the presence of unreacted monomer or oligomers in the crude mixture. NMR and IR samples were measured after purification by precipitation from concentrated tetrahydrofuran (THF) solution in cold methanol or through washing with CHCl_3 . Worth mentioning is the fact that oleic acid derived monomers were unreactive, forming only oligomers. Polymerizations of compounds **2b** and **2c** were therefore not further investigated.

For the radical thiol-ene polymerization, two options for initiation are known, i.e., thermal or photochemical initiation (the latter with or without added initiator). First investigations were performed with 1,4-butanedithiol as a model substrate in a 5 M solution in THF for 3 h at room temperature. Worthwhile noting, in principle also 1,4-butanedithiol could

be prepared in a renewable fashion, but here a commercially available compound was used. SEC results clearly showed that polymerizations involving thermal initiation with AIBN at 60 °C resulted in low molecular weight oligomers below 2 kg mol^{-1} (Table S1, Supporting Information). For experiments involving UV irradiation, reactions were performed at room temperature in glass vials and 2,2-dimethoxy-2-phenylacetophenone (DMPA) was used as photoinitiator, revealing that a wavelength of 365 nm led to the formation of a polymer with molecular weights above 26 kg mol^{-1} , while at 254 nm only oligomers could be identified from the SEC chromatogram. Thus, further experiments at 254 nm were performed only in quartz glass flasks (Table S1, Supporting Information, entry 1), while all other polymerizations were carried out in normal glass vials.

The effect of concentration was further investigated. Therefore, 1,4-butanedithiol was used as comonomer (Table 1, entry P1) and THF as solvent (Table S2, Supporting Information), revealing that higher concentrations (from 0.1 to 5 mol L^{-1}) led to higher molecular weights (up to 26 kg mol^{-1}). The approximately halved value of 13 kg mol^{-1} for the bulk reaction can be

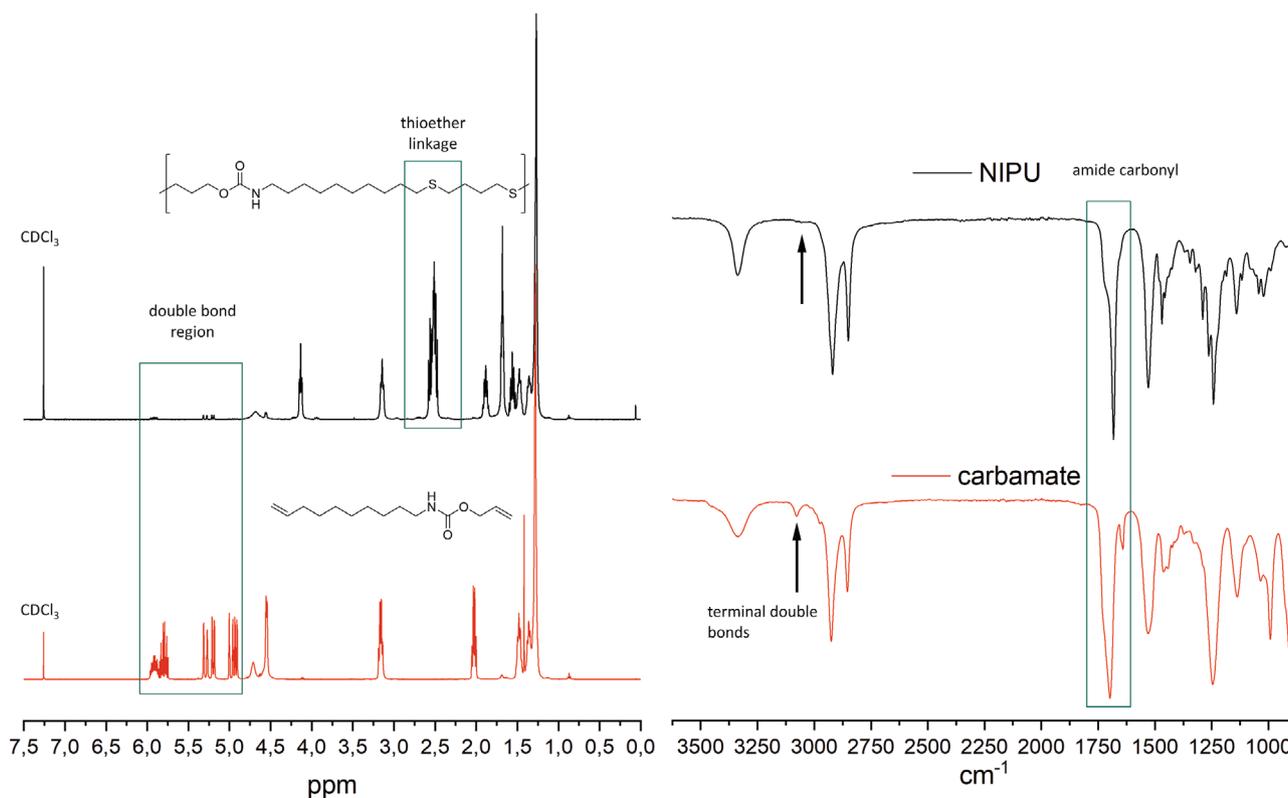


Figure 1. Left: ^1H NMR spectrum of P1 (top) compared to 1b (bottom,); right: IR spectrum of P1 (top) compared to 1b (bottom).

explained by the strongly increasing viscosity and formation of solid polymer in the early stages of polymerization. The addition of a small amount of solvent thus appears to provide better results compared to bulk conditions.

Furthermore, various solvents were tested for the synthesis of the renewable NIPUs. The obtained results of molecular weight (M_n) and dispersity are summarized in Table S3 (Supporting Information). During these experiments, commercially available solvents as well as more sustainable solvent alternatives, according to solvent selection guides, were applied.^[56,57] Solvents belonging to the first category, i.e., CHCl_3 and THF, led to higher molecular weights over 20 kg mol^{-1} . While these two examples are problematic in terms of sustainability,

“greener” alternatives such as Me-THF and PolarClean also gave satisfying results, reaching M_n values of 13 and 11 kg mol^{-1} , respectively. The other tested solvents, i.e., gamma-valerolactone (GVL), gamma-butyrolactone (GBL), dimethyl carbonate, and Cyrene gave similar outcomes in the range of 3 to 7 kg mol^{-1} . In every trial, early formation of a solid was observed, and the reaction mixture could not be stirred further. The obtained SEC results and the presence of oligomers in the crude mixture suggested incomplete conversions. Even if the last four candidates are known to be more sustainable, their poor ability in solubilizing even oligomers is a main drawback for this synthesis. Thus, further investigations were carried out with THF, CHCl_3 , and Me-THF.

Table 1. Thermal properties of the synthesized polymers.

Polymer	Diene monomer	Dithiol monomer	M_n^a [g mol^{-1}]	\bar{D}^a	T_m [$^{\circ}\text{C}$]	T_g [$^{\circ}\text{C}$]
P1	1b	Butane	26 600	1.9	67.7	
P2	1c	Butane	5750	2.2	137.4	
P3	1b	3	21 150	2.1		-12.1
P4	1c	3	7400	2.1	67.5	
P5	1b+1c ^b	Butane	21 250	1.9	68.3	
P6	1b+1c ^b	3	7900	2.7		-13.0
P7	1b	4+5	6150	2.0		-14.6
P8	1c	4+5	1800	4.2	122.1	

^a)HFIP-SEC calibrated with PMMA standards; ^b)Mixture of 0.9 eq. **1b** and 0.1 eq. **1c**.

After these initial investigations, commercially available as well as the above described renewable dithiols were polymerized with carbamate **1b** (Table 1, entry P1, P3, and P7). As shown in Table S4 (Supporting Information), by increasing the spacer length between the thiol functionalities, the molecular weight of the resulting polymer decreases. Especially for 1,10-decanedithiol, the reaction mixture was not completely homogeneous after the addition. Also the dithiol monomers derived from limonene and cyclohexene were poorly soluble in THF. However, if the polymerization was carried out in bulk, molecular weights of 21 and 6 kg mol⁻¹ could be obtained, respectively (Table S4, Supporting Information). Additionally, while NIPUs from aliphatic dithiols form white polymer powders, the NIPUs prepared using the renewable monomers resulted in transparent, viscous, and sticky substances, clearly demonstrating the reduced crystallization due to the introduced bulky moieties. Differential scanning calorimetry (DSC) measurements of the renewable NIPUs confirmed these observations, showing glass transitions (T_g) between -12 and -15 °C, instead of a melting point (T_m) if aliphatic dithiols are used.

As already mentioned in the introduction, the synthesis method presented in this work offers the advantage to employ both products (main and by-product) of the Lossen rearrangement for further polymerization. The symmetric urea by-product **1c** can be easily obtained through precipitation at room temperature, followed by filtration and a simple washing process. Possessing two-terminal double bonds like carbamate **1b** makes this compound another perfect candidate for the thiol-ene reaction.

At room temperature, urea **1c** is soluble only in CHCl₃. Therefore, first tests with different comonomers were performed in the same solvent. The trend in molecular weight does not resemble the effect observed with carbamate **1b**, with molecular weights ranging from 5 to 7 kg mol⁻¹, independent of the dithiol monomer (Table S5, Supporting Information). In order to improve the M_n values, other approaches were attempted, for instance, the addition of cosolvents, change of solvent, different initiation methods, or increased reaction times. However, an increase in molecular weight could not be observed. Thus, the focus of this work was shifted toward renewable aspects (see next), as well as thermal and structural characterization of the synthesized polymers.

In order to improve the synthesis process in view of sustainability, further purification steps should be avoided. Therefore, carbamate **1b** and urea **1c** were used as obtained in a mixture and copolymerized with a dithiol (see Table 1, entry P5 and P6). The most promising results to solubilize the urea component were achieved with CHCl₃, thus further optimizations were performed in this solvent. In the first optimization step, a mixture of 0.1 eq. **1c** and 0.9 eq. **1b** was investigated at a concentration of 3.33 mol L⁻¹ (Table S6, Supporting Information), resulting in low molecular weights (<5 kg mol⁻¹). The dilution of the reaction mixture (1.67 mol L⁻¹) led to increased M_n values of up to 21 kg mol⁻¹, but rapidly declining at even lower concentrations. ¹H-NMR measurements of the crude mixture of the Lossen rearrangement after removing the solvent by vacuum, consisting of ≈70% **1b** and 30% **1c**, resulted in a rather low molecular weight of ≈6.0 kg mol⁻¹. However, the procedure clearly demonstrates that using the mixture

is a sustainable way to obtain suitable monomers, avoiding excessive purification steps and thus prevent high amounts of waste.

Thermal properties were determined by DSC (Figure S19, Supporting Information). As shown in Table 1, NIPUs containing bulky structures, which are highly viscous and transparent, possess T_g values between -12 and -15 °C (Table 1, entry P3 and P7), while the colorless, solid NIPU synthesized from aliphatic butanedithiol (Table 1, entry P1) shows a melting point of ≈70 °C. Copolymers of **1b** and **1c** (Table 1, entry P5 and P6), depending on the chosen dithiol, show slightly higher T_m and lower T_g with respect to their pure NIPU counterparts (Table 1, entry P1 and P3). Polyurea melting points are also greatly affected by the thiol moiety, confirmed by the difference of 70 °C between the T_m values of P2 and P4. The presence of stronger hydrogen bonding of ureas compared to carbamates is also observed by an increase of T_m of about 70 °C from P1 to P2.

In this work, the synthesis of renewable carbamate, urea, and dithiol monomers and their subsequent thiol-ene copolymerization toward non-isocyanate polyurethanes, including the optimization of reaction conditions, is described. The obtained NIPUs show high M_n values with a maximum molecular weight of 26 kg mol⁻¹. Additionally, it was demonstrated that dithiols from renewable feedstock such as limonene have a major impact on thermal properties of the polyurethane, resulting in glass transitions instead of melting points, caused by the increased steric hindrance of the bulkier terpene structure compared to aliphatic chains. The broad scope of this procedure also enabled the synthesis of interesting macromolecules such as polyureas and copolymers by employing by-products of the Lossen rearrangement as monomers, improving the overall sustainability of this method.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

fatty acids, Lossen rearrangement, non-isocyanate polyurethane, renewable polymers, terpene

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