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(+)-Limonene-Lactam: Synthesis of a Sustainable Monomer for Ring-Opening Polymerization to Novel, Biobased Polyamides

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In this work, the synthesis of limonene lactam starting from limonene epoxide and its subsequent ring-opening polymerization (ROP) to novel polyamides is presented. Sustainable, biobased materials are gaining interest as replacements of conventional, petroleum-based materials, and even more important, as high-performance materials for new applications. Terpenes—structurally advanced biobased compounds—are therefore of great interest. In this research, limonene lactam, a novel biobased monomer for preparing sustainable polyamides via ROP, can be synthesized. Limonene lactam possesses an isopropylene and a methyl side group, thus stereocenters posing special challenges and requirements for synthesis, analysis and polymerization. However, these difficult-to-synthesize structural elements can generate novel polymers with unique properties, e.g., functionalizability. In this work, a sustainable monomer synthesis is established, and simplified to industrial needs. For the sterically demanding in-bulk ROP to limonene polyamides, various initiators and conditions are tested. Polyamides with more than 100 monomer units are successfully synthesized and confirmed via nuclear magnetic resonance (NMR) spectroscopy and gel permeations chromatography (GPC). Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) are used to analyze its thermal properties. In summary, a sustainable monomer synthesis is established, and promising polyamides with intact double bond and interesting thermal properties are achieved.

1. Introduction and Theory

Green Chemistry aims to reduce or eliminate the use or generation of hazardous substances in the development, production and application of chemical products.[1,2] Therefore, one of the most important criteria of green chemistry is the utilization of renewable starting materials.[3] This objective poses major challenges since renewable biobased compounds can suffer from high production costs and different performance that we are not used from conventional petroleum-based materials. To fully exploit the potential of natural compounds, it is therefore important to make them superior to fossil-based resources.[4,5,6,7] Polymer chemistry can achieve this goal by using biobased monomers with unique, hard-to-synthesize chemical structures, suitable for subsequent polymerization.[8] This so-called "monomer approach" distinguishes from the "polymer approach," where natural polymers (e.g., cellulose, natural rubber) are directly accessed. Even if the polymer approach appears to be more straightforward, the monomer approach offers more possibilities to tune the polymers

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as needed, since the monomers themselves or the polymerization can be modified. Also, with successful incorporation of the biobased monomers, the already mentioned hard-to-synthesize properties are also incorporated into the polymers. This use of biobased monomers will not only establish a future-oriented and sustainable polymer industry, but they also give access to special thermal, mechanical and chemical properties, rendering them suitable for further functionalization or modification. This clearly differentiates them from conventional petrochemical polymers.[9]

In this context, terpenes are very important building blocks for the synthesis of biobased polymers.[10,11] Most of them are abundant and derived from non-edible parts of plants, therefore generally considered as "green" and "sustainable." There are over 80 000 terpenoid structures, of which many have the desired stereocenters or functional groups, making this class of natural compounds to be a "gold mine" for polymer and materials chemistry.[12,13,14] A classification can be made into acyclic, monocyclic, bicyclic and polycyclic terpenes, as well as into the number of isoprene (C5) structural units.[15] Accordingly, many different terpene-based polymers have already been described, e.g., different polyolefin/hydrocarbon polymers[16] and polyesters.[17] Modification of the terpenes expand the pool of available compounds.[18]

Limonene—one of the most common cyclic terpenes—is extracted from, e.g., citrus peels with over 70 000 t/a.[19] Although this already shows a high availability, the amount is expected to rise with an increasing utilization, thus increasing demand for limonene, which can be promoted by a variety of functionalization strategies.[20] Limonene is present in the stereoisomers (R)-(+) and (S)-(−) and has both, an intracyclic and an exocyclic double bond, suitable for further modifications. The utilization and functionalization of limonene is therefore a highly researched topic, and remarkable progress regarding limonene-based polymers like polycarbonates,[21,22,23] polyurethanes and polyamides,[24] and polyesters[25] have already been made.[26,27]

Especially polyamides (PAs) are a very important polymer class with a wide range of applications from consumer goods to high-performance polymers in the technical or biomedical field.[28] PAs are characterized by a good property range: They show favorable mechanical properties even at high temperatures and good chemical resistance. On top of that they show a low gas permeability, high toughness, tensile strength, and impact resistances. These properties render polyamides indispensable for everyday and also high-performance applications. Some biobased polyamides (i.e., PA 410, PA 610) are already produced in remarkable quantities for high-performance engineering thermoplastics and for fibers.[29]

Accordingly, terpene-based PAs are very promising "green" alternatives to petroleum-based polyamides. In addition, the formation of novel polyamides that address new or unsolved needs/problems is possible. In the cases of cyclic terpenes, PAs are produced by modifying the cyclic molecules to lactams and subsequent ring-opening polymerization (ROP).[30] Examples for already modified terpenes to lactams for PA-synthesis are (−)-Menthone[31,32,33], β-Pinene[34,35,36], Camphor and *3*-Carene.[37,38] Also, co-polymers such as polyesteramides have been synthesized from these building blocks.[39]

In this work, we have developed a simple monomer synthesis route to limonene lactam for subsequent ring-opening polymerization to produce PA as a potential high-performance biopolymer. For this purpose, starting from commercially available (+)-limonene epoxide (*cis/trans*-diastereomeric mixture) **1**—which can be easily obtained from limonene by oxidation—the corresponding ketone **2** was formed using different Lewis-acids in a Meinwald rearrangement. Oximation of **2** yielded limonene oxime **3** which was transformed in limonene lactam **4** via Beckmann rearrangement. The resulting ϵ-lactam of limonene was subsequently polymerized by ring-opening polymerization (ROP) to Limonene-Polyamide (**LiPA**) (**Scheme 1**). Regarding the ROP to **LiPA** various initiators/catalysts were investigated. With this work, we aim to introduce an optimized, facile, and "green"[d] monomer synthesis route starting from limonene and to demonstrate the potential of these building blocks with respect to the formation of biobased polyamides.

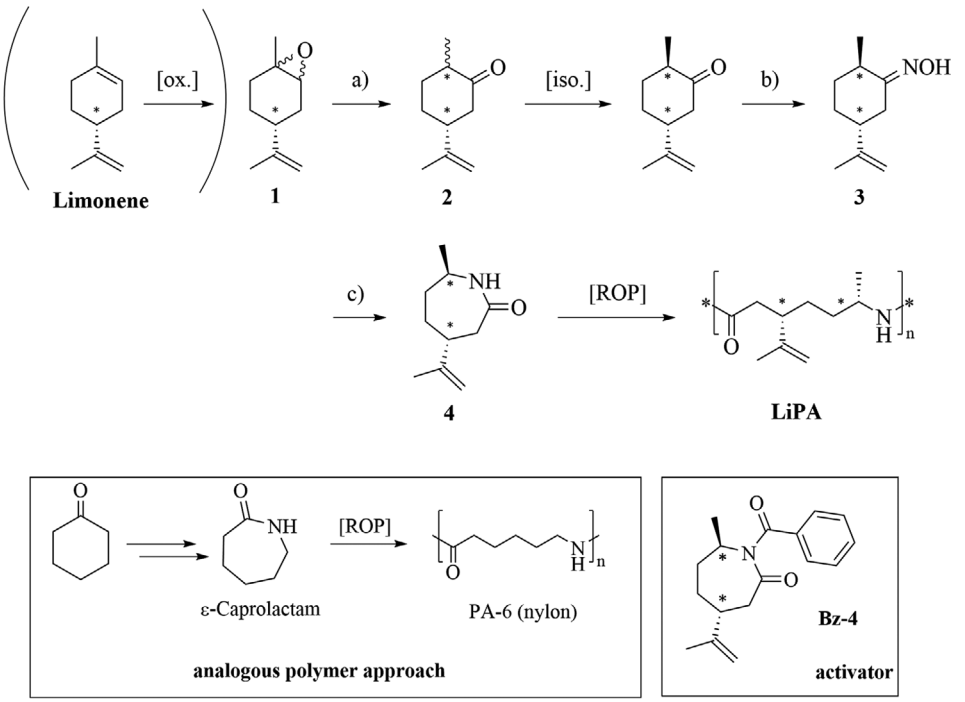
2. Results and Discussion

2.1. Synthesis of the Monomer Limonene Lactam

To obtain limonene ketone **2**, a Meinwald rearrangement of the commercially available *cis-trans* mixture (+)-limonene oxide **1** is necessary. In general, several catalysts can be considered for a Meinwald rearrangement.[40] We tested four different candidates: $ZnBr_2$, $Fe(ClO_4)_2$, $Zn(OTf)_2$, and $Zn(ClO_4)_2$.

$Zn(OTf)_2$ and $Zn(ClO_4)_2$ are not suitable, since $Zn(ClO_4)_2$, shows low conversion and yield for the Meinwald reaction despite relative high amounts of catalyst, while $Zn(OTf)_2$ shows high conversions and passable yields in a short period of time but also many side reactions. The remaining catalysts $ZnBr_2$ and $Fe(ClO_4)_2$ show hardly any difference in terms of conversion (>99%) and yield (>90%), but differ significantly in reaction time (19 and 4 h) and catalyst amounts (50 and 0.5 mol%). Regarding a more sustainable, "greener" and convenient synthesis, the method with $Fe(ClO_4)_2$ is therefore preferable due to catalytic amounts (0.5 mol %) of catalyst and short reaction time of 4 h at 60 °C or 6 h at 40 °C. In addition, the down-stream of the reaction catalyzed by $Fe(ClO_4)_2$ is much easier since distillation directly from the reaction mixture is possible (0.025 mbar, oil bath temperature: 60 °C, thermometer temperature: 33 °C). Particularly important is the complete dissolution of the catalyst in the reaction mixture, which means in this case that $Fe(ClO_4)_2$ has to be pre-solved in EtOAc, since the catalysis is homogeneous. We were also able to upscale the reaction to 40 g yielding over 96%. The dependencies of catalyst concentration, time and temperature are shown in Table S1 (Supporting Information). With these reaction conditions, the process design is simplified for future industrial use but also renders the reaction cheaper and "greener" compared to other possibilities mentioned for Meinwald rearrangements.

Although we found that an high isomer ratio (as close as possible to isomeric purity) is important for subsequent reaction, isomerization of **2** is not necessary due to the enhanced stereoselectivity of the reaction with $Fe(ClO_4)_2$ in cyclohexane (analyzed via GC) and adjusted oximation reaction. Oxime **3** is formed by the addition of hydroxylamine hydrochloride and sodium acetate in ethanol and water. Stirring the mixture over night at room



Scheme 1. Synthesis of limonene lactam **4** and its polyamide LiPA from limonene oxide **1** via ketone **2** and oxime **3**. a) $ZnBr_2$, EtOAc or $Fe(ClO_4)_2$, cy-Hex; b) NH_2OH*HCl, NaOAc, EtOH:H_2O; c) NaOH, TsCl in MeCN or TFA, $AlCl_3$; d) ROP with NaH, NHCs, DPP, H_3PO_4, P_4-tBu or HCl. Box: Established synthesis of Nylon from ϵ-caprolactam, and benzoylated LiLa (**Bz-4**) functioning as activator.

Table 1. Catalyst screening for the formation of limonene lactam **4** starting from **3**. Yields were determined either via ^{1}H-NMR or GC-MS (*). *T* = temperature, *t* = time, o.n. = overnight, M = molar, PPA = Polyphosphoric acid.

Entry	m_{Oxim}[g]	Catalyst	Eq_{cat}	Solvent	t [h]	*T* [°C]	Yield [%]
1	1	–	–	PPA	4	120	–
2	1	–	–	H_2SO_4	3	85	–
3		$AlCl_3$	0.1	MeCN	4	75	traces*
4	1	TFA	1	MeCN	4	75	traces*
5	1	$Fe(ClO_4)_2$	0.1	MeCN	2	85	–
6	1	TsCl	1.05	MeCN/ 2M NaOH	*o.n.*	0-r.t.	94
7	5.5	TsCl	1.05	MeCN/ 2M NaOH	*o.n.*	5-r.t.	>90*
8	10.5	TsCl	1.05	MeCN/ 2M NaOH	*o.n.*	0-r.t.	>99*
9	40	TsCl	1.05	MeCN/ 2M NaOH	*o.n.*	0-r.t.	81

temperature yielded over 90% of **3**, as white crystals. In addition to solvent reduction (8 mL g^{-1} of each solvent 1:1), we were able to lower the reaction time to 6 h once temperatures of 60 °C were applied and to introduce environmentally friendly solvents.

The last step of the monomer synthesis is the Beckmann rearrangement of **3** to lactam **4**. For this reaction, we tested different reagents and conditions, obtaining the best results with TsCl in basic medium (**Table 1**). Although Lewis-acid-catalyzed rearrangements are also possible, they show difficulties in purification as well as significantly poorer yields and an increased number of side reactions. Additionally, for the rearrangement with tosyl chloride an upscale up to 40 g was possible with yields above 80%. For a simple isolation of the product 100% conversion of the oxime is necessary. If a total conversion is not achieved, the reaction mixture can "re-react" with TsCl without damaging the already formed product. We could purify the resulting monomer up to 99.99% (confirmed by GC analysis) via crystallization in n-hexane and subsequent sublimation. GC-MS, IR spectroscopy, NMR and X-ray crystallographic measurements confirmed the intact lactam monomers with an double bond and allow a precise structure elucidation (see **Figures 1–3**).

In principle, there are two stereoisomers respectively for the ketone, the oxime, and the lactam. In the case of **2** we can observe two isomers via GC-MS and ^{1}H-NMR (see Figure S1, Supporting Information). However, the conversion of the ketone **2** to limonene oxime (**3**) and LiLa (**4**) is stereospecific (see Figure 2, see Figures S5–S8, Supporting Information). From literature it is well known that the Beckmann rearrangement for ketoximes is stereospecific. Exceptions can sometimes be created by choosing specific solvents and reaction conditions. However, we expect that the bulky side groups of **4** enhance stereoselectivity, since the migrating group aligns anti-periplanar to the leaving group at the nitrogen.[41] For the stereo-information of **4**, we performed a NOESY experiment (see Figure S8, Supporting Information) and recorded its crystal structure via X-ray shown in Figure 2. ^{1}H-/^{13}C-NMR, COSY, and NOESY indicate that only one stereo-configuration for **4**—either a *SS*- or *RR*-configuration—occurs. The crystal structure not only verifies this finding but also specifies the stereo-information to a *RR*-configuration. Via crystal structure we could also observe a boat-chair conformation as most stable conformation like already suspected in NOESY.[42] Following this finding the methyl and *iso*-propyl group are

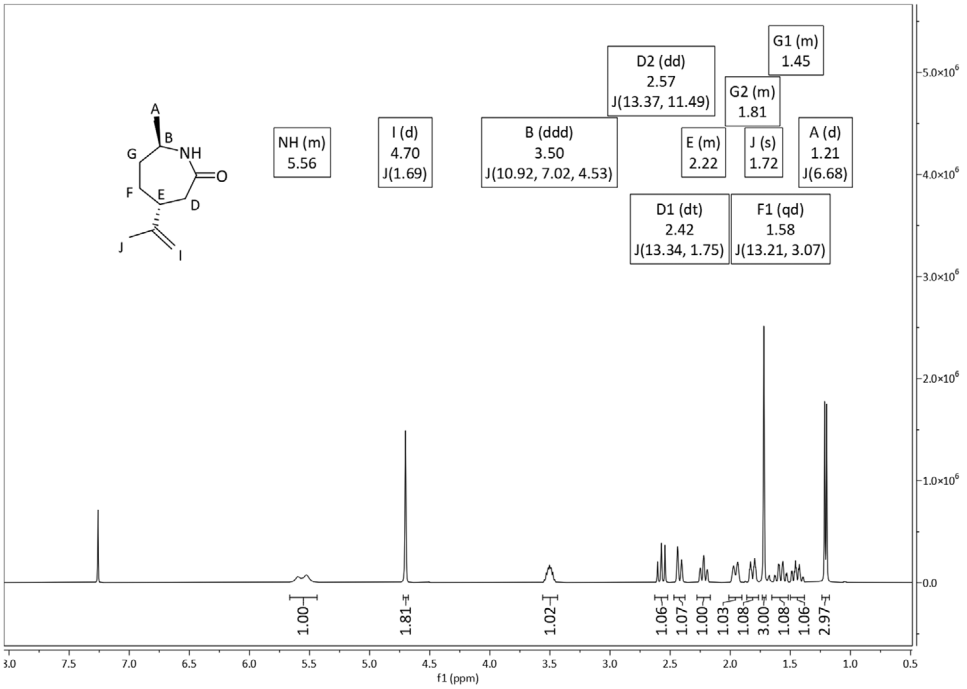


Figure 1. ^{1}H-NMR spectrum of limonene ϵ-lactam 4. Signal of the double bond (H_I) is found at 4.7 ppm while H_B at 3.5 ppm indicates the proton next to NHCO.

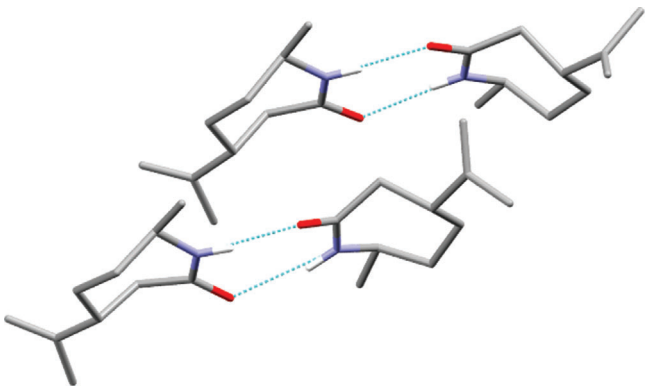


Figure 2. Crystal structure of **4**. Methyl and iso-propyl group show equatorial arrangement.

arranged equatorial. These structural properties are likely to hinder the attack of acids, bases, carben, or other initiators. Additionally, ring-opening itself is more difficult, since the to-be-opened C–N bonds arrange themselves facing each other due to hydrogen bonding (see Figure 2: blue lines).

2.2. Polymerization of Limonene Lactam to LiPA

Formation of the new limonene polyamide LiPA is achieved by ring-opening polymerization through different mechanisms. For this purpose, we tested different catalysts. Typical acids such as HCl and H_2PO_3, diphenyl phosphate (DPP) as acidic organocatalyst or Lewis acids like $AlCl_3$ can initiate cationic ROP via positively charged reaction sites. When aqueous acids such as aq. HCl are used, hydrolytic polymerization occurs in addition to the cationic mechanism. We also investigated anionic ROPs by testing bases, like triazabicyclodecene (TBD), NaH and P_4-tBu, as well as carbenes, i.e., IMes and iPr. As an activator for the anionic ROP, **4** was benzoylated (**Bz-4**). Such activators can facilitate the nucleophilic attack of deprotonated lactams at the amide bonds, thus promoting anionic chain propagation. Since **4** is a novel ROP monomer, we performed polymerizations at common temperatures for in bulk ROPs: 150, 200, 250 °C. In the following, the most successful catalysts are reported for the respective temperatures see **Table 2**. More detailed data can be found in Table S4 (Supporting Information).

Table 2. Catalyst/initiator screening for the polymerization of 0.2 g limonene lactam 4 at different temperatures for 24 h in bulk.

Entry	Initiator	$n_{activator}$ [mol%]	T [°C]	M_n [g mol^{-1}]	M_w [g mol^{-1}]	PDI
1	NaH	10	200	4400	6100	1.4
2	IMes	–	200	9100	9700	1.1
3	P_4-tBu	10	200	4700	5800	1.2
4	NaH	10	150	4800	5900	1.2
5	IMes	–	150	7300	8000	1.1
6	P_4-tBu	10	150	3900	4700	1.2
7	HCl	–	250	8400	22 000	2.6

The polymers were purified by solving or suspending them in chloroform and subsequent precipitation in n-hexane, followed by a washing step with hot n-hexane, EtOAc and filtration. According to the more detailed Tables S4 and S5 (Supporting Information), it becomes apparent that 200 °C is the preferred

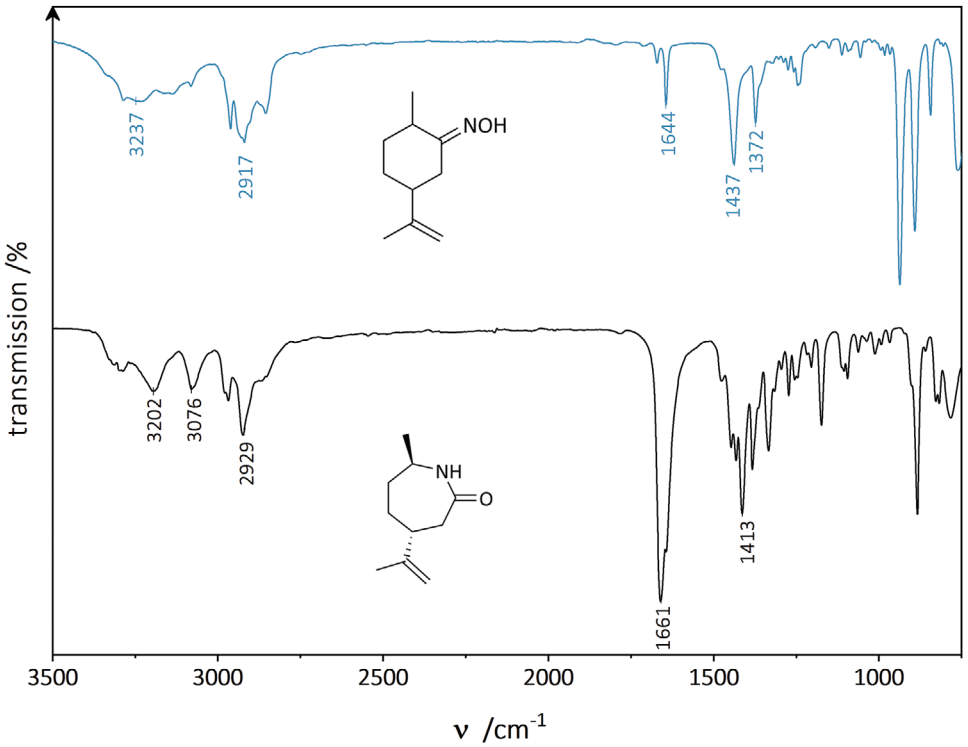


Figure 3. IR-spectrum of limonene oxime **3** and ϵ-lactam **4** in comparison. C=C vibrations at 1644 cm^{-1} (In the case of lactam this vibration overlaps with the CO vibration).

temperature for ROP of **4**. In particular IMes, P_4-tBu and NaH achieve at this temperature good results with molecular weights up to 9700 g mol^{-1} (58 monomer units). Polymerizations with the commonly used HCl or H_3PO_2 at 150 or 200 °C did not give sufficient results.[43,44] However, in the case of 250 °C HCl yielded LiPA with M_w = 22000 g mol^{-1} (131 monomer units) but with a high PDI. This will be investigated to a greater extent in the future, but we can already anticipate that this is most likely due to uncontrolled polymerization when using aqueous acids. It is important to note that with the use of acids, heat, and water, amino acid formation is likely to occur, rendering a termination of the polymerization possible, but also polycondensation. In general, we observed that a monomer purity below 99.9% achieve uncontrolled ring openings with very high PDIs. Since IMes, P_4-tBu and NaH achieved the best results at 200 °C, NaH was further investigated due to its easy handling, cheapness and commonness as living anionic ROP-initiator. We were able to observe a deterioration of the molar masses in relation to increasing time which raises the question of whether our polymer is experiencing depolymerization or chain multiplication (see **Table 3**). As an additional explanatory approach, we examined the anionic ROP at different times (see Figure S14, Supporting Information). Since decreasing molecular weight but increasing yield after 3 h can be observed, a chain multiplication is likely. This effect occurs when the sterically demanding lactam opens to a linear, sterically less demanding, polymer. This is followed by the attack of activated monomer on amide functionalities, resulting in a chain split. Chain multiplication lowers the molecular weight and increases the number of polymeric chains.[45] This question and ROP using different initiator systems and/or organocatalysts will be further investigated and constitutes the main focus of our research on terpene-based polyamides in the future.

Table 3. Time screening for the anionic polymerization of limonene lactam **4** (0.2 g) with NaH at 200 °C with different initiator amounts.

Entry	$n_{catalyst}$ [mol%]	$n_{activator}$ [mol%]	t [h]	M_n [g mol^{-1}]	M_w [g mol^{-1}]	PDI
1	10	10	12	5700	7400	1.3
2	5	5	12	5200	6900	1.3
3	5	0.5	12	3000	5600	1.8
4	10	10	24	4400	6100	1.4
5	5	5	60	1600	3800	2.4

Regarding the thermal properties (measured by TGA and DSC), we found relatively high T_gs up to 100 °C, T_ds up to 423 °C, and no detectable T_m. In general, PA chains form hydrogen bonds among each other, causing high decomposition and melting temperature, even though the polymer chains are not very long. Hexafluoroisopropanol (HFIP) has the ability to prevent this bonding, making it possible to analyze the single polymer molecules via GPC.[46] For a detailed insight, the section "2.4 Thermal Analysis" in the Supporting Information can be consulted.

The lack of a T_m could be caused by problems with a dense parallel arrangement of the chains when larger side groups, i.e., high steric demand, are present. Generally, the larger the side groups, the poorer can be the crystallization of the polymer. To the best of our knowledge, terpene-based amorphous polyamides were first observed in carene polyamide. Amorphousness,

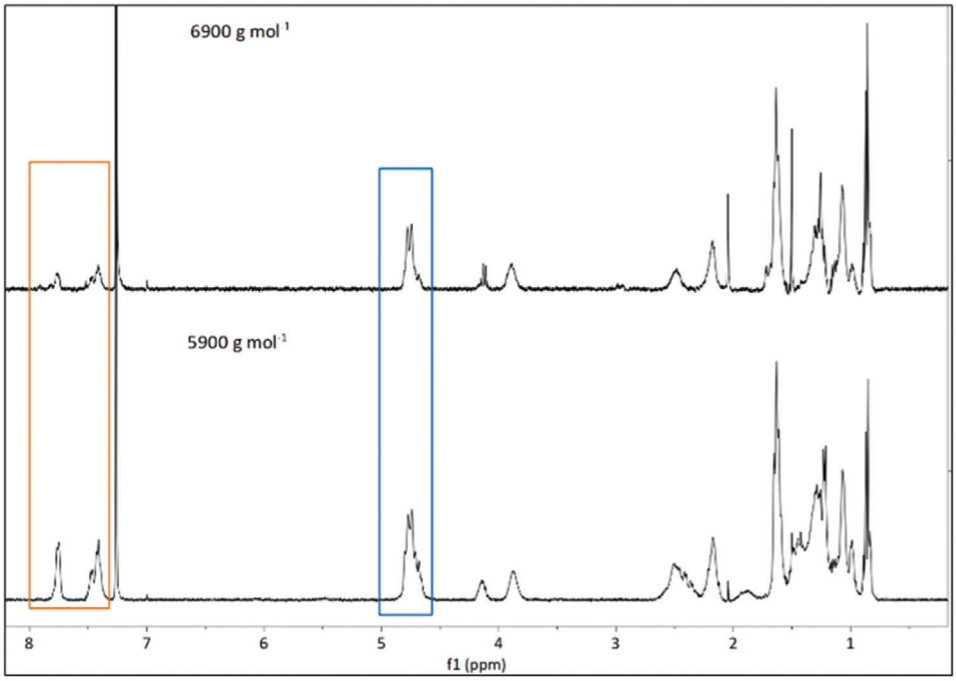


Figure 4. ^{1}H-NMR spectrum of LiPA with different molecular masses (5900, 6900 g mol^{-1}) polymerized via anionic ring-opening polymerization. Signal of the double bond is found at 4.7 ppm (blue) while the aromatic signals from activator **Bz-4** are found at 7.3–7.75 ppm (orange).

microcrystallinity, or a significantly longer crystallization time were reported by Stockmann et al. [37] and is consistent with our observations. This finding will be further investigated.

The polymer was not only analyzed in respect of its thermal properties, but also by means of NMR (see **Figure 4**) and IR (see Figure S10, Supporting Information). This allowed us to determine whether the polymer has an intact double bond, which was the case (blue box). A more accurate peak assignment without the observed overlap, especially regarding the polymer backbone, for example –CH_2–, can be made when longer LiPAs with small PDIs are produced.

3. Conclusions

In this study we could clearly demonstrate the potential of limonene as a biobased monomer for the ring-opening polymerization to sustainable polyamides. We have successfully synthesized the monomer limonene ϵ-lactam **4** possessing two chiral centers and a functionalizable iso-propylene group. We were also able to simplify the reaction significantly, especially regarding purification, rendering the synthesis route more attractive for industry and future applications.

By evaluating monomer synthesis according to the principles of green chemistry (*PRODUCTIVELY*) by Tang et al.,[47] we can consider the reaction route to limonene lactam as an important step toward green monomer synthesis since it meets most of the following criteria/principles:

By optimizing ketone and oxime formation, we not only reduce waste (*P*) but also improve the E-factor (*E*), establish the use of low toxic substances (*L*), like ethanol instead of methanol and in the case of ketone formation $FeClO_4$ instead of $ZnBr_2$ which also ticks the box for using catalytic reagents (*C*). All reaction steps are relatively simple (*Y*) to perform and down-stream (*U*) without additional derivation steps (*O*) and high temperatures and pressures (*T*). This signifies not only that our reaction meets the definition of green chemistry by Tang et al.[47] but also show the possibility of an easy upscale and therefore industrially application.

For the ring-opening polymerization, we have investigated different conditions and catalysts with NaH, IMes, and P_4-tBu as most promising catalysts/initiators for subsequent studies. The polymerization of **4** to oligomers and medium chain polymers over 80 chain units were successfully proven by GPC and NMR. However, we found the polymerization of limonene lactam restricted by its sterically hindered structure and possible cyclic polymer formation. For the future, especially anionic ROP with different activator systems should be investigated. We will also focus on the potential of organocatalysts like carbenes to obtain the desired biobased polymers and materials with good mechanical and physical properties. For this purpose, we will also consider lactam polymerizations in solution which seems to be promising after first attempts in THF. Copolymerizations with other lactams to, e.g., PA-co-PAs, and with lactones[48] to PEAs are under further investigation also with regards to kinetics and the different monomer reactivities. Incorporated double bonds of **4** enable functionalization of the resulting PA, leading to its tunability. Since terpene-based Polyamides seem to be very promising regarding biocompatibility[35] further work will also address the investigation of the biocompatibility of limonene-based (co-)polymers and blends/ composites, and their effects on living cells with regards to different (bio-)medical applications.

4. Experimental Section

Materials: All chemicals were purchased at *Sigma Aldrich* and used as received except HFIP, which was purchased from *Carbolution* Chemicals GmbH.

If not stated otherwise, the reactions were carried out on air at atm.

(5R)-2-Methyl-5-(prop-1-en-2-yl)Cyclohexan-1-One (2): Cis and trans mixture of (+)-limonene oxide (**1**) (1.0 eq.) was dissolved in cyclohexane (3 mL $g^{-1}{}_1$). A solution of $Fe(ClO_4)_2 \bullet H_2O$ (358 mg, 1.31 mmol, 0.5 mol%) in EtOAc (4 mL) was added. The reaction mixture was stirred for 4 h, cooled to room temperature and organic solvent removed under reduced pressure. The yielded brown oil contained 96% of **2** (analyzed via NMR) which was directly distilled from the crude mixture.

(5R)-2-Methyl-5-(prop-1-en-2-yl)Cyclohexan-1-One Oxime (3): **2** (60 g, 394.12 mmol, 1 eq.) was dissolved in a mixture of water (8 mL g^{-1}) and EtOH (8 mL g^{-1}) before NaOAc (48.50 g, 591.18 mmol, 1.5 eq.) and $NH_2OH \bullet HCl$ (30.13 g, 433.53 mmol, 1.1 eq.) were added. The reaction mixture was stirred at room temperature overnight. Subsequently 150 mL water were added, and the mixture extracted with cyclohexane (4 × 200 mL). The combined organic layers were washed with sat. aq. $NaHCO_3$ solution (1 × 200 mL), sat. aq. NaCl solution (1 × 200 mL) and dried over Na_2SO_4. Organic solvents were removed under reduced pressure to yield crude **3** as white crystals, which was purified by crystallization in n-hexane to yield colorless crystals (55.37 g, 331.06 mmol, 84%).

(4R)-7-Methyl-4-(prop-1-en-2-yl)Azepan-2-One (4): In a round bottom flask **3** (10 g, 59.8 mmol, 1.0 eq.) was dissolved in MeCN (80 mL) and cooled to 0 °C, followed by dropwise addition over 30 min of 2 M NaOH solution (92 mL, 3.1 eq.). The reaction mixture was stirred at 0 °C for 1.5 h. Subsequently, TsCl (11.9 g, 62.8 mmol, 1.05 eq.) was slowly added over 30 min. Afterward, the reaction mixture was stirred for 3 h at 0 °C and then allowed to warm up to room temperature overnight. The phases were extracted with EtOAc (3 × 150 mL). The combined organic layers were washed with sat. aq. $NaHCO_3$ solution (1 × 100 mL), sat. aq. NaCl solution (1 × 100 mL) and dried over Na_2SO_4. The organic solvent was removed under reduced pressure and the crude product was crystallized from n-hexane and sublimated (70 °C at 0.04 mbar) to yield **4** (9.37 g, 56.0 mmol, 94%) as colorless crystals.

(4R)-1-Benzoyl-7-Methyl-4-(prop-1-en-2-yl)Azepan-2-One (Bz-LiLa): 25 mL 2-Methyl-THF (21.25 g, 8.2 eq) were cooled in an ice bath and NaH (540 mg, 15.5 mmol, 2.60 eq.) was added under inert conditions. After 10 min **4** (1.00 g, 6.0 mmol, 1.00 eq) was added portion-wise within 5 min. After stirring for 2 h, benzoyl chloride (1.00 mL, 7.80 mmol, 1.30 eq.) was slowly given to the mixture. The mixture was allowed to reach room temperature and was stirred for 12 h before 20 g ice was slowly added. After extraction with cyclohexane (3 × 100 mL), the combined organic phases were washed with NaOH (2.0 M, 2 × 100 mL), with sat. aq. $NaHCO_3$ solution (1 × 100 mL) and sat. aq. NaCl solution (1 × 100 mL) and dried using Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (4:1 cyclohexane: EtOAc, Rf: 0.3) to yield **Bz-LiLa** (0.85 g, 3.30 mmol, 75%) as white crystals.

Polymerization: Specific quantities of 4, Bz-LiLa and catalyst/initiator were added to a crimp neck vial under argon atmosphere. The vial was sealed and placed in a heating block for 12, 24, or 60 h time at a given temperature. Subsequently, the vial was cooled to room temperature and opened. The obtained product was dissolved/suspended in chloroform (1 mL) and precipitated in n-hexane (20 mL). After centrifugation (4300 rpm, room temperature, 4 min) the product was washed with hot n-hexane (5 mL) and EtOAc (1 mL), filtered and dried in vacuo. The obtained LiPAs were analyzed via GPC, NMR, DSC and TGA.

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.

Author Contributions

M.M.K., P.N.S., and M.W. conceived the work and designed the project. M.M.K. and L.Z. performed the synthetic experiments and M.M.K. performed the characterizations. X-ray experiments and structure determination via X-ray and related manuscript/supplementary sections were conducted by J.Y.L. M.M.K. and M.W. wrote the manuscript and the supplementary information.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

limonene, polyamides, ring-opening polymerizations (ROP), sustainable polymers, terpenes

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