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From Forest to Future: Synthesis of Sustainable High Molecular Weight Polyamides Using and Investigating the AROP of β-Pinene Lactam

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Polyamides (PA) are among the most essential and versatile polymers due to their outstanding characteristics, for example, high chemical resistance and temperature stability. Furthermore, nature-derived monomers can introduce hard-to-synthesize structures into the PAs for unique polymer properties. Pinene, as one of the most abundant terpenes in nature and its presumable stability-giving bicyclic structure, is therefore highly promising. This work presents simple anionic ring-opening polymerizations of β-pinene lactam (AROP) in-bulk and in solution. PAs with high molecular weights, suitable for further processing, are produced. Their good mechanical, thermal (T_ds up to 440 °C), and transparent appearance render them promising high-performance biomaterials. In the following, the suitability of different initiators is discussed. Thereby, it is found that NaH is the most successful for in-bulk polymerization, with a degree of polymerization (DP) of about 322. For solution-AROP, *i*PrMgCl·LiCl is successfully used for the first time, achieving DPs up to about 163. The obtained PAs are also hot-pressed, and the dynamic mechanical properties are analyzed.

1. Introduction

Synthetic polymers are nowadays indispensable. They are not only replacing expensive natural materials such as silk and metal, but also have superior properties regarding thermal and mechanical stability, weight, and production costs. In 1935, the first polyamide (PA) Nylon was synthesized by Carothers and Hill.[1] Since then, PAs have been particularly in the spotlight by playing an essential role in various fields of application. Their diverse set of properties, for example, temperature stability, solvent resistance, and superior mechanical properties, allow them to replace heavy or high-resistance materials and also to be used, for example, for multipurpose fibers. Especially the success of existing high-performance PAs has fueled the demand for new materials in fields such as lightweight construction, the automotive industry, and electronics.[2]

Biopolymers as well as bio-PAs, can meet many of these demands and open the doors to novel fields of application, such as biomedicine. This is because their bio-based monomers often have structural properties that are otherwise difficult to synthesize, for example, functionalizable olefin moieties and chirality.[3–8] Furthermore, using bio-based monomers not only paves the way for a sustainable polymer future but also renders their production independent from non-renewable raw materials.[9–13]

In this context, terpenes and terpenoids are important as they not only pose an abundant and renewable monomer feedstock but also show unique structural properties.[14–19] To preserve these functionalities, for example, double bonds, cyclic terpenes can be modified to their lactams as suitable monomers for anionic ring-opening polymerization (AROP).[3,20,21] This procedure is analogous to the established Nylon-6 (Perlon) synthesis from cyclohexanone via ϵ-caprolactam[3,20,22]

The most common terpenes in nature are pinenes, which can be relatively easily isolated from non-edible plant parts, for example, wood processing (turpentine oil). Among all pinene isomers, β-pinene is the easiest to modify to its lactam, as it exhibits an exocyclic double bond. This double bond can be oxidized efficiently to the ketone (nopinone), which is converted to its oxime and lactam, respectively. β-Pinene is therefore an attractive monomer for sustainable PAs.[23,24] Additionally, it is assumed that the bicyclic structure introduces high mechanical and thermal stability into the PA. In 2017, our group successfully "polymerized" β-pinene lactam for the first time, yielding rather oligomers than polymers.[3] In the following years, the monomer synthesis was further optimized in our laboratories, and the co-polymerization of β-pinene lactam with ϵ-caprolactone to polyesteramides was studied.[23,25,26] However, we were particularly interested in

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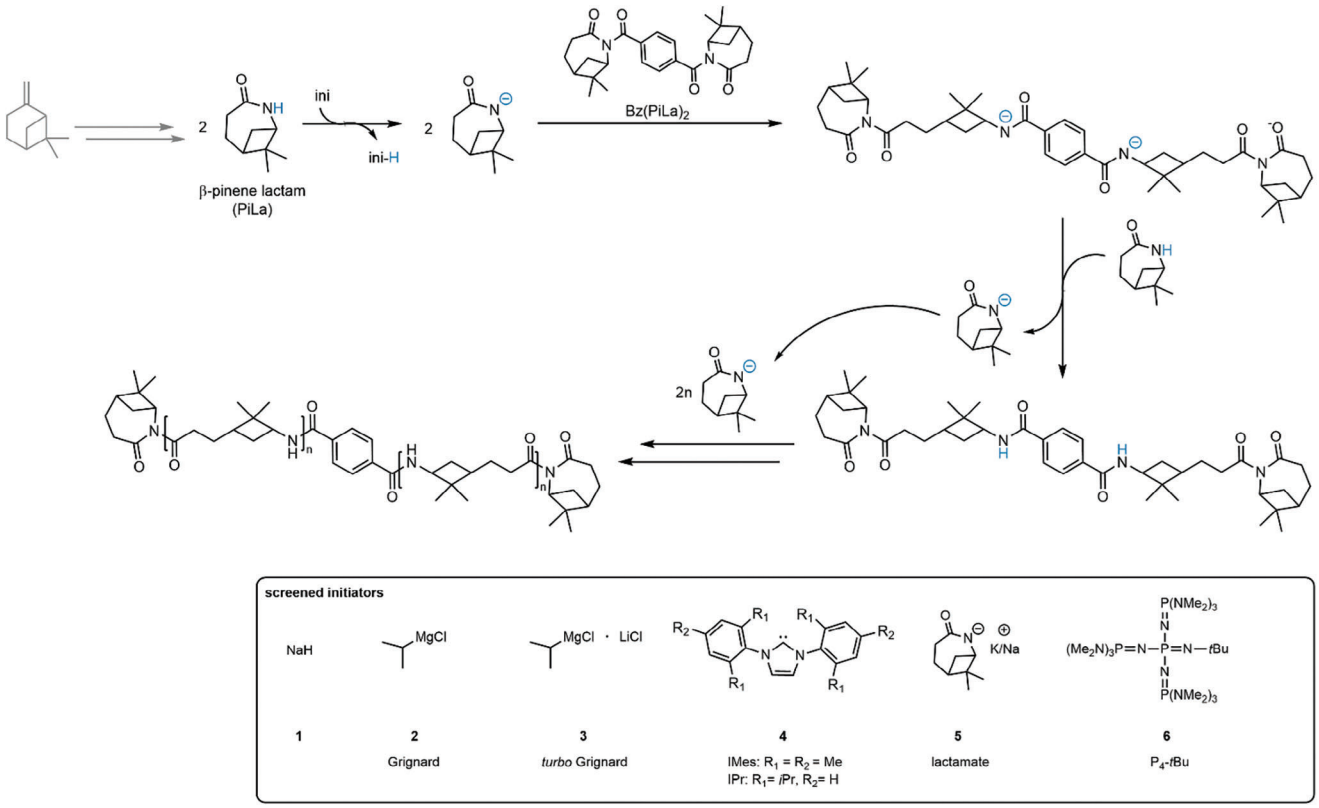

Scheme 1. General mechanism of the anionic ring-opening polymerization of β-pinene lactam (derived from β-pinene) with *N,N′*-terephthaloylbis(pinene lactam) as the activator. Showing six different initiators: NaH (1), Grignard *i*PrMgCl (2), turbo-Grignard *i*PrMgCl·LiCl (3), the carbenes IMes and IPr (4), pinene lactamate (5), the sterically hindered super-base P_4-*t*Bu (6).

bio-polymers, which are able to enter the high-performance field of application. Accordingly, it became obvious that we would need to increase the molar mass of the β-pinene oligomers significantly. Therefore, we want to shine light onto the preparation of high molecular weight β-pinene-PAs. Further, this work aims to prove that β-pinene-based PAs are materials with high mechanical and thermal stability caused by the bicycle.

In this work, we compare and evaluate different initiators for the anionic ring-opening polymerization of β-pinene lactam (PiLa) regarding their efficiency and suitability for high molecular weight PAs. We were also able to establish a solution-polymerization as an alternative to the commonly used in-bulk polymerization. Especially polymerization kinetics will be discussed in this context. Since we aim for processable PAs, we upscaled the polymerization and processed the resulting PA via hot-pressing. Furthermore, the synthesized PA specimens were analyzed regarding their dynamic mechanical properties.

2. Results and Discussion

AROP is the most commonly used method for polymerizing lactams.[27] As an initiator, AROP requires a strong but less nucleophilic base.[3] In our case, particular emphasis is placed on entirely removable or at least non cell-toxic initiators for a possible biomedical application of the obtained biopolymers. Therefore, the hydride NaH (1), *i*PrMgCl (2), the turbo-Grignard *i*PrMgCl·LiCl (3), the carbenes IMes (4) and IPr (5), and the isolated lactamate salt (6) were chosen as initiators.

The sole use of strong bases as initiators is only possible to a limited extent since this would result in high polymerization temperatures and relatively slow reaction rates; side reactions would therefore be unavoidable. Moreover, only the more reactive lactams, such as ϵ-caprolactam, readily polymerize in non-activated reaction conditions. The less reactive lactams are much harder to polymerize because the formation of the imide dimer is less favored. These limitations can be circumvented if the imide is generated beforehand by the reaction of the lactam with an acylating agent and used as an activator, often referred to as a co-initiator.

As illustrated in **Scheme 1**, the propagation step in the AROP of lactams is composed of the nucleophilic attack of the lactamate anion to the acyl lactam-type activator ($Bz(PiLa)_2$) and the following proton transfer from another lactam monomer molecule to the resulting amidate anion. Therefore, it can be concluded that the AROP depends on the activator's ring-opening ability and the lactamate's nucleophilicity.[28,29] Here, the bifunctional *N,N′*-terephthaloylbis(pinene lactam) ($Bz(PiLa)_2$) with two possible chain starts was chosen as the standard activator. Bz-PiLa, Jeffamine M600, and benzyl alcohol were also briefly tested as commonly used activators, especially in preparing related polyesters and polyesteramides.

We chose conventional in-bulk polymerization for the initial testing and evaluation of the various initiators listed in Scheme 1. This way, we tried to circumvent the solvent's influence, thus

Table 1. 1 mol% NaH and/or 1 mol% lactamate initiated ROP of 0.2 g PiLa at 170 °C for 4.5 h in-bulk with $Bz(PiLa)_2$ as the activator. In all cases we achieved full conversion and quantitative yields.

Entry	ini	5	n(act)/[mol%]	M_n/[kg mol^{-1}]	M_{theo}/[kg mol^{-1}]	PDI
1	1	–	0.3	15.6	51.1	2.5
2	1	K+	0.3	27	51.1	8.6
3	1	Na+	0.3	28.9	51.1	9.9
4	—	K+	0.25	22	61.3	7.8
5	—	Na+	0.3	18.3	51.1	7

solubility of the monomer, and a temperature limitation. Also, in-bulk is often industrially favored and, therefore, of great interest.[30] The temperatures were screened between 120–200 °C. 200 °C was chosen as the upper limit as we observed an uncontrolled auto-ring–opening above this temperature. In reverse, we observed no or nearly no conversion with temperatures below 120 °C. In previous studies, we have already found that 150–170 °C is a good temperature range for in-bulk homo-polymerization of limonene-, menthone-, and carene-derived lactams, proofing the observed temperature range for β-pinene lactam.[20,21,31]

However, besides the mentioned advantages of in-bulk polymerization, disadvantages like bad heat-transfer and diffusion limitations render the AROP uncontrolled. In contrast, solution polymerization is able to introduce new processing methods, workups, and control over the polymerization and gives access to other initiators.

2.1. In-Bulk AROP

Since NaH is a commonly used initiator in the AROP of lactams, we first analyzed the system NaH with $Bz(PiLa)_2$ as activator. In all in-bulk polymerizations we were able to prepare transparent PA with high yields and full conversion. However, in the first tests, we observed relatively broad polydispersity indices (PDI) (up to 10) especially with a longer polymerization time (>7 h). In this context, high PDIs are one of the major drawbacks and especially problematic regarding control, processing, and mechanical properties.

According to Hashimoto et al.[28], high PDIs can also be explained by the relationship between initiation (k_i) and propagation (k_p) rate constant k_i/k_p. Generally, a low PDI of PAs can be caused by the high value of k_i/k_p, whereas one reason for a high PDI can be a low value of k_i/k_p.[28] Since β-pinene lactam is more sterically hindered than in the case of, for example, ϵ-caprolactam, and its bicyclic structure favors a ring-opening due to ring strain, we already expected comparatively high PDIs. However, the values depicted in **Table 1** exceed this expectation by far higher PDIs. Kaalber et al.[32] state that viscosity and, thus, diffusion of the reaction mixture play a vital role in the nature of the polymerization kinetics. In our case, we noticed a significant viscosity increase up to the solidification of the sample during the in-bulk polymerization, which very likely causes a diffusion limitation. Additionally, heat transfer is significantly hindered due to the increase in viscosity, causing a temperature increase, which can lead to an "overshooting" of the polymerization. These assumptions were all validated by the results depicted in Table 1 and Figure S2, Supporting Information.

Based on these results we wanted a better insight into the polymerization behavior of β-pinene lactam. Instead of an in situ lactamate generation with NaH or KO*t*Bu via proton abstraction, we isolated this lactamate (5) and used it in comparison. Since k_i for 5 is greater than for NaH, we expected a PDI reduction. When the performance of NaH and 5 are compared, however, we observed higher molecular weights but also broader PDIs (see Table 1) for the lactamate. Apparently, the polymerization rates and thus viscosity increase so fast that their negative impact on the PDI overrules the positive aspect of the increasing k_i/k_p ratios.

Kinetic measurements for in-bulk polymerizations are especially challenging since it is difficult to draw aliquots due to possible quenching reactions and high viscosity. Nevertheless, for a first approximation of the kinetics, we prepared samples with NaH as initiator that were as identical as possible and extracted them from the heating block (170 °C) at different times (see section 3.1.1 in the Supporting Information). In general, the AROP of lactams is considered a quasi-living polymerization.[29,33] Because of the disadvantageous properties of in-bulk polymerization, the living character could not be observed here. Nevertheless, we were able to observe a controllable polymerization when activator and initiator concentrations were varied (see section 3.1.2. in the Supporting Information). As expected, the molar mass increases with initiator concentration and decreases with activator concentration due to the increasing number of chain starts. We found that long polymerization times either have no or even a disadvantageous effect on the chain length and PDI caused by the gel-effect/ diffusion limitation common for in-bulk polymerizations (see Figure S3, Supporting Information).

To overcome the broad PDIs, we choose Grignard and turbo-Grignard reagents as alternative initiators. This assumption was based on the fact that $k_{i,\,Grignard}$ is larger compared to $k_{i,\,NaH}$ and that probably fewer side reactions take place.[34]

In 2006, Knochel and co-workers succeeded in developing the mixed lithium and magnesium amide bases $R_1R_2NMgCl{\cdot}LiCl$ by reacting *i*PrMgCl·LiCl with the corresponding secondary amines.[35] Here we assume that an in situ Mg/Li-amide ($R_1R_2NMgCl{\cdot}LiCl$) base is formed via metalation of β-pinene lactam. Subsequently, this amide base initiates the AROP, as shown in Scheme 1.[34]

In this work, turbo-Grignard was—to the best of our knowledge—used for the first time as an AROP initiator of lactams. Even though we observed significant lower molar masses for turbo-Grignard–initiated AROPs (degree of polymerization up to 80) than those of NaH-initiated PAs (DP up to 322), it is evident that this initiator is advantageous regarding the PDIs (see **Table 2**). We will find this advantage again later in the solution polymerization. In addition, the decomposition and by-products of the initiator do not appear to have any known cytotoxic effects and, thus, do not appear to interfere with a potential biomedical application.

Finally, carbenes were screened as a promising initiator group. Although carbenes such as IMes and IPr are currently considered suitable for AROP, they were less effective than the other initiators in our case (see Table S3, Supporting Information).[36] They exhibited low yields and low molecular weights (degree of

Table 2. turbo-Grignard (*i*PrMgCl·LiCl) 1.3 M in THF initiated AROP of 0.2 g PiLa at 170 °C in-bulk with $Bz(PiLa)_2$ as activator.

Entry	*n*(ini)/ [mol%]	*n*(act)/ [mol%]	*t*/ [h]	M_n/ [kg mol^{-1}]	M_{theo}/ [kg mol^{-1}]	*Y*/ [%]	PDI
1	0.5	0.1	4.5	3.4	153.2	52	1.8
2	0.5	0.3	4.5	12	51.1	73	1.7
3	2	0.3	4.5	8.3	51.1	83	1.5
4	5	1	4	11.3	15.3	93	2.6
5[1)]	5	1	6	12.3	15.3	n.d.	3.9
6	11	1	4.5	14.5	15.3	98	1.8

[1)] Stirred for 4 h at 170 °C, 1 h at 180 °C, and 1 h at 190 °C

polymerization up to 25), and a brittle and black appearance of the polymers. However, as they are reported to be good initiators for ROPs and can tolerate oxygen and moisture when paired with Li- or Mg-salt, they will be investigated more in the future.

Even though in-bulk AROPs have, in general, several advantages, such as being a straightforward method for producing transparent PAs in quantitative yields that can easily be upscaled, we also observe several challenges and difficulties mentioned above.

2.2. Solution AROP

To suppress possible side reactions and broad PDIs, mild and controlled conditions are favorable. Solution polymerization usually prevents an abrupt increase in viscosity, guarantees a homogeneous mixed solution and thus allows a stable heat transfer and a more controlled polymerization reaction. Since the AROP of lactams requires somewhat high reaction temperatures, frequently used solvents, such as toluene and tetrahydrofuran, are not suitable. Additionally, lactams and their PAs have polar amide bonds with strong hydrogen bonding, so that their polymerization rate is strongly affected by (the changes in) the permittivity of the reaction mixture during the polymerization.[28]

Suitable solvents for AROP of pinene lactam are either DMSO (bp. 189 °C) or NMP (bp. 202 °C). The latter was used preferably in previous ROP studies for PAs, for example, by Cywar et al.[37] When we look at NMP and DMSO, both solvents perform similarly, although NMP seems to be slightly better. Differences are also not apparent costly wise and regarding the handling. However, DMSO stands out from NMP due to its safety profile. DMSO is non-toxic by all exposure routes, biodegradable and safe. Therefore, DMSO should be considered the more suitable solvent. Especially since we are aiming in the long run for biomedical applications.

Starting with initiator screening we adopted the polymerization conditions, that is, 0.4 mL solvent, from Cywar et al. (see **Table 3**).[37] Generally, we obtained—as expected—lower yields and molecular weights with similar reaction times also used for in-bulk polymerization. This can be explained by the lower concentration, and thus a lower chance to "meet," thus reacting with each other. Since a quasi-living AROP can take place when using a solvent, the yield and molecular weight are directly proportional to the polymerization time.[22]

Table 3. Solution AROP of 0.2 g PiLa with different initiators (NaH (1), Grignard (*i*PrMgCl) 2 M in THF (2), turbo-Grignard (*i*PrMgCl·LiCl) 1.3 M in THF (3), lactamate (5), P_4tBu (6)) in 0.4 mL NMP (entry 1–5) or 0.4 mL DMSO (entry 6–8) and $Bz(PiLa)_2$ as activator.

Entry	ini	*n*(ini)/ [mol%]	*n*(act)/ [mol%]	*t*/ [h]	*T*/ [°C]	*Y*/ [%]	M_n/ [kg mol^{-1}]	PDI
1	1	2	0.5	5	120	38	18	3.3
2	1	2	0.3	4	120	17	8.2	1.9
3	5	2	0.3	4	120	13	5.7	1.6
4	6	2	0.3	4	120	23	9.7	2.4
5	3	3	1	5	150	62	9.4	2.4
6	1	2	0.5	4	170	30	5.8	2.6
7	2	2	0.3	7	120	93	8.8	1.4
8	3	2	0.3	7	120	51	6.5	1.3

However, another advantage is the controlled polymerization termination with formic acid addition, which leads to a gel-like reaction mixture and easy purification by single precipitation in acetone. This purification method is very promising for fiber spinning, which renders processing facile and effective. But not only the processing and the work-up are significant advantages of solvent polymerization, but also the already mentioned more controlled reaction since we observed an increase in yield with increasing activator and initiator concentration. In Table 3, selected results are presented. If we compare the efficiency of the different initiators, it becomes apparent that 2 and 3 are the most efficient ones. However, also P_4tBu seems to be a very promising candidate.[38]

In contrast to in-bulk polymerizations, the kinetics measurement of solution polymerizations is much easier to conduct. In this work, we polymerized in a small scale using high-temperature NMR (HT-NMR) to analyze the reaction kinetics. For this purpose, the polymerization in deuterated DMSO is heated in a J. Young NMR tube to 140 °C—the upper-temperature limit of the instrument—and a ^{1}H-NMR is measured every 30 min to 1 h.

The conversion of the polymer is calculated by comparing the integrals of the polymer and lactam signals (see Supporting Information section 3.1.3.). This method for kinetic measurements is a rather convenient one, however, it is important to keep in mind that no stirring, that is, homogeneous mixing and heat transfer, can be guaranteed. **Figure 1** shows the conversion versus time of the best initiators for the in-solution AROP of β-pinene: Grignard reagent 2 and turbo-Grignard reagent 3. 3 was able to achieve an almost complete conversion after ≈9 h while 2 shows not only a lower polymerization rate (see Figure S4, Supporting Information) but also a conversion limitation of around 60%.

It has been reported that AROP can be supported by simple Li-salts addition.[39] It can therefore assumed that the usage of turbo-Grignard reagents is also beneficial for AROP.[34,35] Hermann et al. give recent insights into the enhanced reactivity of turbo-Grignard reagents via their different transition states. They postulate a barrier lowering effect of the incorporated lithium chloride influencing reactivity and, thus conversion.[40] We assume that a turbo-Hauser base formation can take place when *i*PrMgCl·LiCl is used.[35]

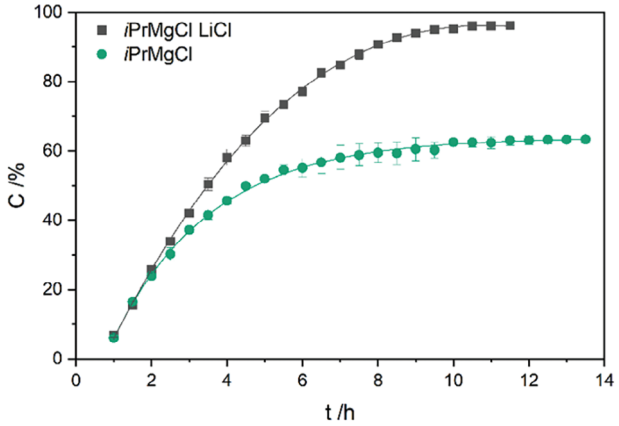

Figure 1. Kinetics of the HT-NMR measurements of the AROP with Grignard 2 and turbo-Grignard 3 as initiators at 140 °C in DMSO-d6. Every data point was measured at least three times to ensure reproducibility.

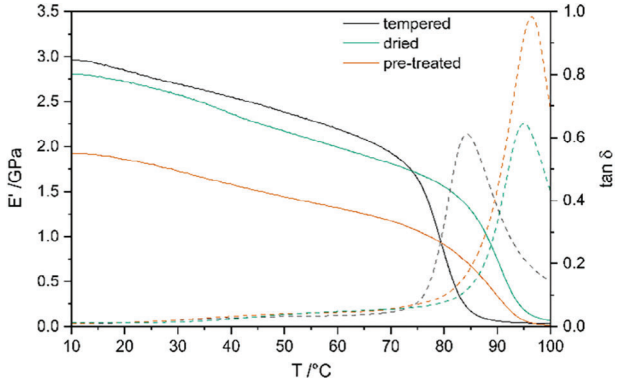

Figure 2. Influence of tempering and moisture for β-pinene PA analyzed via DMA measurements.

Summarized we introduced a successful in-solution polymerization of β-pinene lactam, which renders various processing and purification steps more straightforward. In addition, we were able to get a better analytical insight into the β-pinene-based PAs and were able to conduct in situ kinetic measurements of the AROP. HT-NMRs for the kinetic calculations can be found in the Supporting Information (see Figure S5, Supporting Information).

Comparing the kinetics of in-bulk polymerization and solvent polymerization, we should note that the methods of determining the kinetics are fundamentally different. Apart from this aspect, we can see that in-bulk polymerization is much faster but also much more uncontrolled. We need higher temperatures and harsh purification methods for the in-bulk polymerization whereas for solution polymerization higher reaction times, solvents and initiator concentration is required. All in all, both polymerization methods feature their own advantages and disadvantages and should be selected according to the following processing methods and applications.

2.3. Thermal Properties of β-Pinene Polyamide

Regarding the thermal properties (measured with TGA and DSC), we found very high T_gs up to 195 °C, T_ds up to 440 °C, and no detectable T_m. Especially the T_ds indicate a very temperature-stable PA. For a detailed insight, sections 4.3 and 4.4 in the Supporting Information can be consulted.

The lack of a T_m could be due to problems of forming dense parallel arrangements of the chains when larger and/or more complex side groups are present. In general, the larger the side groups, the worse the polymer can crystallize. Terpene-based amorphous PAs were also observed in carene PA: Amorphousness, micro-crystallinity, or a significantly longer crystallization time were reported by Stockmann et al.[33] and are consistent with our observations. Surprisingly, no formation of a T_m, and thus crystallization, was generated even after various processing methods such as milling, hot-pressing, solvent casting, or repeated heating and subsequent slow cooling.

2.4. Dynamic Mechanical Properties of β-Pinene Polyamide by Means of Hot-Pressed Specimen

The usual processing of polymers and plastics, including nylons, is melting and subsequent processing of the polymers by various techniques such as extrusion, molding, fiber spinning, and pressing. In our case we yielded amorphous PAs without a T_m which is usually necessary for the standard processing method melt pressing. Therefore, only hot-pressing at elevated temperatures was possible. For this reason, we used the determined thermal properties of β-pinene PA and prepared test specimens by hot-pressing and analyzed their dynamic mechanical properties via DMA. Through milling, washing, drying, and hot-pressing our PA, we obtained various transparent specimens (for more detailed information and pictures, see Supporting Information section 1.3 and Figure S1, Supporting Information).

If we compare both DSC and DMA analyses, we directly notice that the T_gs differ significantly and are considerably lower in the case of the DMA values. In general, we can attribute the reduction of the T_g to three main reasons. First, hot-pressing of the polymer granulate leads to increasing PDIs since the needed temperature is with 200 °C relatively high. To validate this hypothesis, we measured GPC for the milled and washed polyamide followed by GPC measurement of the hot-pressed specimen. We observed a decrease in chain length (from 8.9 to 7.69 kg mol^{-1}) and an increased PDI (from 4.3 to 5.8). Not only can the high temperature simply degrade the polymer, but also the terminal lactams can open and react at higher temperatures (see **Figure 2**). Self-polymerization and transamidation was already observed in former studies at 200 °C.[23] The second reason for the T_g differences in DSC and DMA measurements could be rooted in DMA-sample preparation after hot-pressing. Generally speaking, the hydrogen bonds between the polymer chains cause the high T_g. At the same time, however, the ability to form hydrogen bonds and the high polarity also cause the high moisture absorption of the PAs. Depending on the moisture uptake during sample preparation, different T_gs are therefore observed (see Figure 2). In addition, we produced the specimens by fusion molding and did not mill the specimen out of a polymer block obtained by cast molding. Uneven edges and surface defects like air inclusion can also contribute to lower T_gs and is very likely.

Last but not least large differences are often found in T_gs values determined by different methods due to the temperature range of the transition area and due to the fact that they reflect various aspects (mechanical or purely thermal) of the same process.[41]

In Figure 2, we can see, as mentioned above, the influence of temperature treatment and moisture content on the dynamic mechanical properties of pinene PA. Although the $T_{g,DMA}$ differs greatly from the $T_{g,DSC}$ intrinsic tendencies can be observed. First, the polymer specimen was stored under air for 2 days before the DMA measurements (pre-treated, orange). After measurement, we dried the sample overnight in a vacuum (dried, green) or tempered the specimen at 200 °C (tempered, black) for subsequent analysis. Based on this experiment, we can conclude that moisture has a negative effect on the dynamic-mechanical properties of the PA , as the storage modulus (E') deteriorates by almost one third. Tempering, on the other hand, improves the stiffness of the polymer up to 3 GPa (E') but lowers the T_g significantly.

We can conclude that the thermal and mechanical properties can be improved by modifying the preparation method, that is, milling out of a polymer block and tempering. The obtained results, however, already indicate a highly stable PA with possible applications for specialty and high-performance materials.

3. Conclusion and Outlook

In this study, we have developed and optimized simple AROP techniques for the bio-based β-pinene–lactam. By using AROP, we can prepare transparent bio-PAs with high molecular weights and conversion, which are suitable for further processing and applications. Both in-bulk and solution AROP can be controlled regarding PDI and molecular weight. Solution AROP, however, could also combine purification and processing, which would render this polymerization route favorable. The resulting PAs were characterized by their thermal and dynamic mechanical properties. Their excellent characteristics make them a promising bio-PA for high-performance or specialty materials for, for example, biomedicine.

We were able to extend previous work conducted in the field of terpene-based homo.PA in various aspects. First, when comparing the efficiency of other initiators in PA preparation with emphasis on subsequent biomedical applications, we concluded that NaH and the turbo-Grignard *i*PrMgCl·LiCl are the most suitable initiators. The solvent polymerization enabled the investigation of its kinetics up to a quantitative conversion. We were additionally able to study our otherwise hard-to analyze homo-PAs. Turbo-Grignard reagents, used for the first time for AROPs, seem to be promising alternatives, especially for reducing the PDIs for in-bulk polymerization and in terms of solution polymerization. Although their role still needs to be further investigated, we can already see the advantages over conventional used initiators, for example the ability to fully convert β-pinene lactam to its PA with nearly no side reactions. Second, to evaluate whether the proposed polymerization can be applied in industry, we analyzed the mechanical and thermal properties of the resulting PAs. In all polymerization approaches we were able to produce transparent polymer films. Both the thermal and mechanical properties were very good with T_ds up to 440 °C. Also, hot-pressing was possible, and fiber spinning seems very promising when polymerizing in solution.

In the end, this paper should give an overview of the possible application fields of this biomaterial and underline the promising features of the high molecular weight β-pinene-based PAs.

Polymeric biomaterials are widely used in biomedicine. They are not only easy to manufacture, flexible, and biocompatible but also possess a wide—often tunable—range of mechanical, chemical, and thermal properties.[42] β-Pinene-based PA could introduce a high level of stability and durability into a biomaterial. However, β-pinene-based PAs have some challenges regarding processability and biocompatibility, for example, bad solubility, hydrophobic properties, or high processing temperatures. In the future, we will move beyond the homo-PA by studying copolymerization with other bio-based lactams, particularly limonene lactam. We hope this will allow us to overcome the already mentioned problems and introduce functionalizability into the PA.

4. Experimental Section

For the polymerization, the reagents were always added under an argon atmosphere in crimp vials and sealed with the corresponding air-tight high-temperature crimp lids. Syringes, needles, and spatulas were prior heated to 130 °C overnight before being transferred into the glovebox.

In-bulk Polymerization: β-Pinene lactam, activator, and initiator(s) were weighted in a glovebox in a crimp vial equipped with a stirring bar. The vial was closed with a flaring tool in the glove box, "sealed" with parafilm and placed in a pre-heated aluminum heating block outside the glovebox. After the reaction time, the samples were abruptly cooled to room temperature and immediately exposed to air. Since the polymer was insoluble in conventional solvents, they were cut into little pieces, sonicated in ethyl acetate over 4 h, and soaked in ethyl acetate overnight. After drying the samples in vacuo, they were analyzed via GPC, DSC, TGA, and IR.

Solvent Polymerization: β-Pinene lactam, activator, and initiator(s) were weighted in a glovebox in a crimp vial equipped with a stirring bar. The solvent was added via syringe into the crimp vial, which was subsequently closed with a flaring tool in the glove box and "sealed" with parafilm. The samples were placed in a pre-heated aluminum heating block outside the glovebox. After the reaction time, the vials were abruptly cooled to room temperature and immediately exposed to air, and 1 mL TFAA was added. After the polymer solvent mixture was completely dissolved, the polymer mixture was slowly participated in acetone by using a syringe. The resulting white polymer fibers were washed three times with acetone, dried, and analyzed via GPC, TGA, DSC, and IR.

Hot-Pressing of DMA Specimen: The purified polymer was milled and again washed with EtOAc and dried. The mold for hot-pressing was filled with the obtained white polymer powder and placed in the preheated hot press (200–210 °C). After the sample was heated for 3 min, 150 bar was applied and heated for another 5 min. The cooled sample was then removed from the mold and polished. The transparent specimen was then analyzed to determine its mechanical properties.

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.

Data Availability Statement

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

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