β-Pinene-Derived Polyesteramides and Their Blends: Advances in Their Upscaling, Processing, and Characterization

*Magdalena Maria Kleybolte and Malte Winnacker**

Terpene-based polyesteramides (PEAs) are sustainable and have a variety of favorable properties, making them suitable for a wide range of applications and for contribution to a much more sustainable polymer industry. This work focuses on the synthesis of the lactam from β-pinene and its copolymerization with ε-caprolactone. An important step in synthesizing β-pinene lactam is the oxidation of β-pinene to nopinone. To make the established oxidative cleavage more sustainable and efficient, the required amounts of Al_2O_3 and $KMnO_4$ are significantly reduced by using H_2SO_4 as a catalyst. For the Beckmann rearrangement various catalysts and co-reagents are screened. Among these, the reaction with tosyl chloride is found the most favorable. Subsequently, the chain lengths of the β-pinene-based PEAs are remarkably increased from 6000 g mol^{-1} to more than 25 100 g mol^{-1} by fine-tuning reaction time, temperature, and decreasing catalyst and initiator concentrations. Also, different catalysts for polymerization are tested. The resulting material shows melting temperatures of ≈55 °C and decomposition temperatures of 354 °C or higher. Processing via melt pressing or casting turned out to be quite difficult due to the polymer's brittleness. Furthermore, regarding biomedical applications, blends of PEA with polyethylene glycol were successfully prepared, yielding a more hydrophilic material.

1. Introduction

Due to their diverse properties and cost-efficient mass production, plastics are almost irreplaceable in daily life and find a wide variety of applications. However, due to their durability and resistance to physiological influences, conventional polymers for mass plastics are often not able to degrade, resulting in many environmental challenges. Also, many of these polymers are processed in a costly, wasteful manner. The majority of polymers are still based on fossil resources, but depletion of the oil reserves due to the increasing energy demand is challenging us to find other monomer feedstocks.[1,2]

Biopolymers have the high potential of replacing conventional plastics by more sustainable materials.[3–5] In addition to natural functional polymers,[6] biopolymers are defined as such if they are either produced from biobased raw materials and/or if they are biodegradable.[7–11] Biobased materials are produced from renewable biogenic sources, for example, biomass. Biodegradability by itself describes the ideally complete degradation of a material by natural microorganisms to carbon dioxide, water, ammonia, or other metabolic products.[12,13]

The advantage of biobased materials is that—in addition to their sustainability, where their production etc. also have to be considered—new or complex molecules can be obtained relatively easily from nature, which cannot be obtained so easily via fossil-based synthetic pathways. Typically, it is challenging to synthesize molecules with special structural properties such as chirality. By using natural molecules, molecules that are difficult to synthesize can be sourced even in high quantities and in stereospecific forms. A differentiation can be made between a polymer approach, where natural polymers (e.g., polysaccharides) are utilized, and a monomer approach, where small molecules (e.g., carboxylic acids, terpenes, …) are used for polymerization, either directly or upon further modification, is possible.[14–17]

For the synthesis of sustainable polymers, abundant natural materials, especially from non-edible plant parts, are preferable. Since terpenes obtained from many plants, like turpentine oil which is extracted from wood production in large quantity, they are particularly well suited as starting materials. The family of terpenes has a diverse range of structural properties with favorable, difficult-to-synthesize properties such as chirality or side groups.[18–20] For this reason, terpene-based polymers are a main

M. M. Kleybolte, Dr. M. Winnacker
WACKER-Chair of Macromolecular Chemistry
Technische Universität München
Lichtenbergstraße 4, Garching bei München 85747, Germany
E-mail: malte.winnacker@tum.de

M. M. Kleybolte, Dr. M. Winnacker
Catalysis Research Center
Technische Universität München
Ernst-Otto-Fischer-Straße 1 Garching bei München 85748, Germany

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/marc.202100065
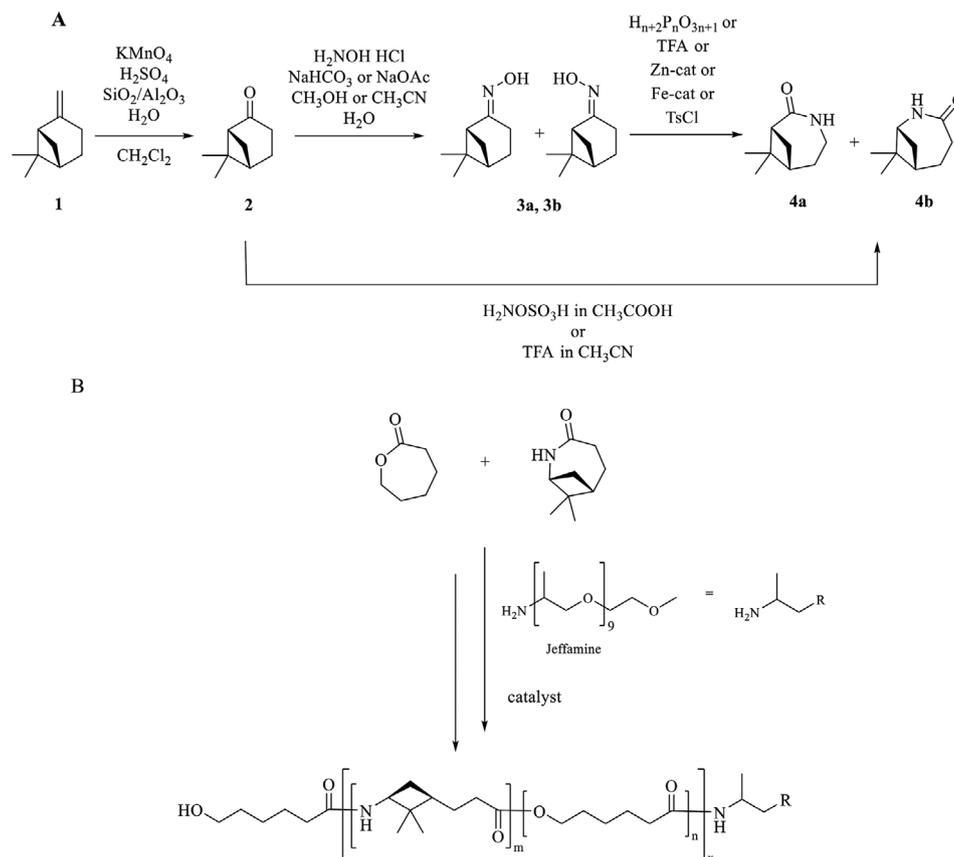
Figure 1. A) Overview of different synthesis routes of the lactams **4a**, **4b** and B) its polymerization.

aim in modern polymer chemistry, since they are not only non-food-based, sustainable, environmentally friendly but also have a wide range of structures and property profiles.[21–28]

Polyesteramides (PEAs) are very important polymers which can also combine the stiffness and excellent thermal and mechanical properties of polyamides with the biocompatibility and biodegradability of polyesters.[29–31] Moreover, because they are copolymers, it is possible to tune these properties in a variety of ways. Thus, terpene-based PEAs are prominent examples for biobased and biodegradable polymers and have been investigated in this study.

Pinenes are the main constituents of turpentine oil and have chiral centers, making them a particularly promising starting material. Although β-pinene occurs less frequently than α-pinenes, their exocyclic double bond is located more favorably for further synthesis. This work is therefore focused on β-pinene-based polyesteramides. To obtain such polyesteramides or polyamides, cyclic terpenoid ketones are converted to their corresponding lactams, which are then polymerized.[32]

β-Pinene-lactam-based polyesteramides have the potential to cover many important applications, and they could contribute to a more sustainable and "greener" polymer economy. Cost-effective, reliable procedures of their production are essential for this purpose. This study aims to investigate and significantly improve the synthesis of β-pinene-based polyesteramides and their terpene monomer. Further optimizing and analyzing the synthesis of β-pinene lactam as well as its copolymerization with

ε-caprolactone represents an important progress toward a better understanding of the synthesis methods of these sustainable polymers.

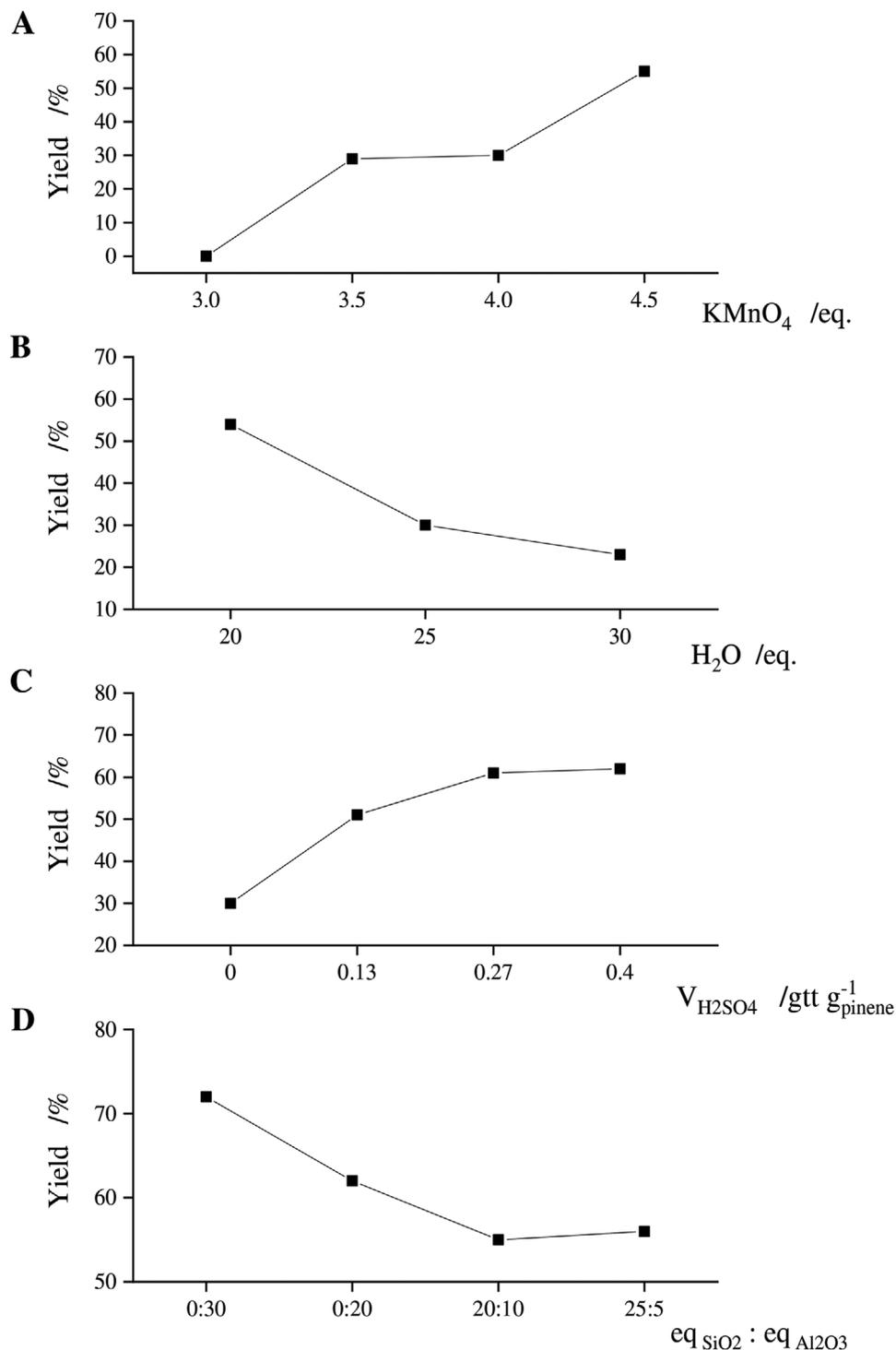## 2. Results and Discussion

2.1. Monomer Synthesis

The first step of synthesizing β-pinene lactam is the oxidation of β-pinene (**1**) to nopinone (**2**). For the further reaction to the lactams (**4a**, **4b**), two reaction routes are possible: the two-step reaction in which two regioisomeric oximes (**3a**, **3b**) are formed as intermediate products, and the one-step reaction with trifluoroacetic acid (TFA) or hydroxylamine-O-sulfonic acid (HOSA).[33–35] The corresponding overall reactions are depicted in **Figure 1**A. The lactam is then polymerized with ε-caprolactone by means of Sn-, Zn- or P-catalyst to the pinene-based polyesteramide (Figure 1B).

2.1.1. Nopinone Synthesis

The oxidation of β-pinene to nopinone (**2**) is a decisive step for this procedure that has fundamental significance also for further upscaling and possible industrial applications. In this study, this reaction is based on an experimental procedure described by Lee

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Figure 2. Trends and dependencies of the nopinone (oxidized β-pinene) synthesis. A) The higher the amount of $KMnO_4$ the higher the yield. B) With increasing $V(H_2O)$ yield decreases. C) With increasing H_2SO_4 amount yield increases, where a limit occurs and D) with higher Al_2O_3 amounts higher yields were observed.

et al. using $KMnO_4$ as oxidant.[31] This initially cumbersome reaction requires large amounts of solvent, support (Al_2O_3), oxidant, and purification via column chromatography. Herein, the oxidation reaction was remarkably optimized with respect to reaction time, reaction equivalents, and purification method. For

these further improvements, sulfuric acid was added as a catalyst, with the amount of H_2SO_4 having the greatest influence on the obtained yield (see **Figure 2**C). The yield increases with increasing acid amount, although no major improvement is apparent at a volume content higher than 0.27 gtt per 1 g β-pinene.

Table 1. Reaction conditions and results of selected tested catalysts.

Entry	m_{Oxime} [g]	Catalyst	Eq$_{catalyst}$	Solvent	$V_{solvent}$ [mL]	t [h]	T [°C]	Yield [%]
1	6	PPA	a)	–	–	6.5	125	55
2	7	PPA	b)	–	–	7	125	63
3	2	TFA	2.6	MeCN	26	5	80	traces[d], oligomers
4	2	Zn(ClO$_4$)$_2$ 6H$_2$O	0.01	MeCN	26	6	80	traces[d]
5	2	Zn(OTf)$_2$	0.01	MeCN	26	6	80	traces[d]
6	2	Zn(OTf)$_2$	0.01	MeCN	26	4	85	traces[d]
7	2	Fe(OTf)$_2$	0.01	MeCN	26	4	85	–
8	2	Fe(ClO$_4$)$_2$ H$_2$O	0.01	MeCN	26	4.5	85	traces[d], oligomers
9	7.8	TsCl	1.05	MeCN/ 2 м NaOH	40/72	25	<20	31
10	5	TsCl	1.05	MeCN/ 2 м NaOH	20/46	24	<20	44
11	5	TsCl	1.05	MeCN/ 2 м NaOH	20/46	26	<20	59
12	1	citric acid	3	hexane	20	7	80	–
13	1	citric acid	0.3	–c)	–	1.5	160	–

Temperature, (T); time, (t); volume, (V); acetonitrile, (MeCN); a) 288 mL; b) 144 mL; c) inert atmosphere; d) analyzed with ¹H-NMR.

In addition, adsorbent Al$_2$O$_3$ could partly be replaced by SiO$_2$ and the initially 30 eq. of Al$_2$O$_3$ were reduced to 10 eq. of each SiO$_2$ and Al$_2$O$_3$. Also, 4.9 eq. of KMnO$_4$ were reduced to 4 eq. An acid catalyzed upscale to 15 g was successfully established with yields of up to 62% and to 20 g with yields up to 30%. Furthermore, the complex purification step by column chromatography was replaced by convenient vacuum distillation ($T_{overhead}$: 52 °C, $T_{oil\,bath}$: 60 °C, p: 0.02 mbar). Although these oxidation reagents by themselves are not really green, their strong quantity reduction compared to previous procedures[21,36] make this synthesis much more easy and environmentally friendly. General trends and dependencies are shown in Figure 2 and resulted by a combination in the optimized nopinone synthesis. More detailed data can be found in the Supporting Information in Table S1, Supporting Information.

2.1.2. Lactam Synthesis

Two-Step Approach: The desired oxime (**3a**, **3b**) was first synthesized via the classical approach by converting nopinone (**2**) with hydroxylamine hydrochloride and sodium hydrogen carbonate for 6–7 h at 65–70 °C in MeOH/H$_2$O.[37] The yields increased at longer reaction time and increasing solvent-oxime ratio up to 90%. An upscale was also successful: 25 g could be converted to **3a** and **3b** with yields as high as 92%. Alternatively, **2** was converted overnight at room temperature with NH$_2$OH·HCl and sodium acetate in MeCN/H$_2$O or MeOH/H$_2$O with yields up to 97% (see Table S2, Supporting Information). Following the paper by P. Stockmann et al. this mild synthesis route *o.n.* is more suitable for an industrial application.[23] Both isomers of the oxime were used in an unpurified state to synthesize the lactams **4a**, **4b** by Beckmann rearrangement, although the oxime was obtained nearly regioselective (¹H-NMR and IR-spectra is shown in the Supporting Information).

For the Beckmann rearrangement several catalysts and co-reagents were tested. **Table 1** shows the different catalysts/chemicals and their corresponding yields.[38] Although

polyphosphoric acid (PPA) achieves higher yields, the alternative with tosyl chloride (TsCl) in 2 м NaOH (aq.) is preferable, since it is not only well suited for upscaling but also for industrial applicability as demonstrated by Stockmann et al. In addition, PPA is difficult to handle and due to the additional step of quenching also not very convenient.[23]

Generally, the selectivity of lactam as compared to side products was rather low, yields up to 63% were achieved. However, a selective synthesis between the lactams **4a** and **4b** was observed since lactam **4a** was obtained >98–100% in all cases. Regarding entries **5** and **6**, not only the selectivity but also the conversion was low, since more than 50% of the oxime remained unreacted. In case of entries **3** and **8**, not only **4a** was detected but also oligomers, which points to the high potential of these catalysts. For citric acid (entries **12**, **13**), surprisingly a complete conversion back to nopinone (**2**) was observed. Conventionally, the lactam is purified by column chromatography. Herein, this procedure could be replaced by recrystallization in hexane and subsequent sublimation (T: 70 °C, p: 0.03 mbar), rendering it much more suitable for industrial applications.

TFA-/HOSA-Route: HOSA and TFA[39] were explored as a potentially more efficient and less cumbersome single-step alternative to the two-step method. However, the HOSA route was more complicated and had a lower yield than the two-step method, while the TFA route only yielded traces of lactam **4a** and oxime **3a**, **3b** (see Table S4, Supporting Information).

In the case of the HOSA route, **2** is completely converted, indicating that the poor yield is due to the multiple favored side reactions. The already low selectivity, which was observed for the previous route, is therefore aggravated by condensing its two steps into one. In addition, if product was present (confirmed by ¹H-NMR) it could not be properly isolated even though the purification method was adjusted several times. This calls to question simple reaction screenings by NMR or GC-MS, which do not subsequently attempt to isolate the product. All in all, the two-step lactam synthesis via oxime and subsequent Beckmann rearrangement with TsCl has worked best here and has the highest potential for industrial applications.

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2.2. Polymerization of the Monomers to β-Pinene-Based Polyesteramides

β-pinene-based polyesteramides were synthesized using catalytic ring-opening copolymerization (ROCOP) in bulk. Different tin, zinc, and phosphorus catalysts were used for the copolymerization: tin(II)-2-ethylhexanoate (Sn(Oct)$_2$), dibutyltin(II) dilaurate (Sn(Lau)$_2$), -which are known from neat lactone polymerizations-diethylzinc (ZnEt$_2$) and diphenyl phosphate (DPP). In addition to different reaction times and temperatures, different concentrations and catalyst-initiator ratios were tested. In order to obtain the PEAs, the two monomers β-pinene lactam and ε-caprolactone were copolymerized by adding the catalyst and initiator under inert conditions at given temperatures and times. The polymerizations with both ZnEt$_2$ and DPP resulted in polyesters with less than 1% polyamide content. They therefore indicate that they are well suited for ring-opening polymerization (ROP) for lactones, but not suitable for lactams.

The ROCOPs with Sn(Oct)$_2$ and Sn(Lau)$_2$ were initially carried out under certain conditions which were previously used in a study about PEAs that can form bioactive surfaces.[40] In the course of further improvements, reducing the catalyst concentration from 0.25 mol% to 0.05 mmol% and increasing the concentration ratio of monomer Jeffamine-M600 from 20 to 700, led to substantially higher molar masses (entries **6–9** and **2–5**) and higher yields (entry **b0-2**). Further increase in the concentration ratio of Jeffamine did not achieve additional improvements and the yield decreased again for ratios higher than 700 (entries **2–5**, **20–26**).

In general, it is important to mention that chain length and polymer yield was significantly increased with respect to the previously described procedure.[36] It should be noted that the standard crimp vial caps were replaced with temperature-stable ones with a PFTE/silicon insert. The best temperatures for the polymerization were determined to be between 200–205 °C. Temperatures of 105 °C and below failed to yield a polymer and temperatures of 250 °C led to short polymer chains and low yields.

After the polymerization parameters were optimized, an upscaling from 0.05 to 1.5 g was performed (entry **20–30**). As expected, chain length and yields decreased with increasing monomer concentration, leading to increase polydispersity indices (PDI). This is probably due to the differences in mixing and heat transfer. Selected polymerizations and their parameters are shown in **Table 2**. A more extensive table can be found in the Supporting Information (Table S5, Supporting Information).

Generally, the interpretations and assignments as previously reported were primarily used as a guide.[36] It is known that it is often challenging to characterize polymers by NMR, since dynamic processes coexist on very different time scales and both structural disorder and dynamic heterogeneity are present.[41] This challenge can also be observed regarding our polymers. In some cases, the assignments of the peaks to the polymers turned out to be quite difficult—due to the increased chain lengths compared to the previous study.[36] As a result, not all polyamide groups are clearly visible, since peaks have merged or are overlapping with the prominent polycaprolactone peaks, since they lie in the similar ppm ranges. Nevertheless, the char-

acteristic polyamide and polyester peaks could be detected in all tested polymers with ^{1}H-NMR and/or IR spectroscopy (see **Figure 3**). In IR, the characteristic amide adsorption bands at wavelengths of 3280 and 1635 cm^{-1} and in ^{1}H-NMR the characteristic methyl groups at 0.88 and 1.14 ppm confirm the presence of polyamide. All detectable integrals of the polyamide were used for comparison with those of the polyester to calculate the incorporated monomer ratios. The highest amide–ester-ratio detected was 29:71.

In addition to chain lengths and monomer incorporations, the thermal and mechanical properties of the polymers were further investigated. First, the thermal properties were measured using TGA and DSC. The decomposition temperature of the measured polymers ranged from 275–557 °C. On average, the materials had decomposition temperatures above 354 °C, which shows their high stability. Melting temperatures were with up to 54 °C close to those of conventional polycaprolactones, and recrystallization temperatures were between 25–37 °C. However, these measurements do additionally show the presence of polyamide, due to wide melting temperature ranges or two different melting temperatures. The melting point tends to increase with increasing molecular weights as expected (**Table 3** and Table S5, Supporting Information).

To assess the material's mechanical properties, the PEAs were processed via melt pressing and casting. Due to the low proportion of polyamides, the material was expected to be elastic and easy to process. However, as soon as the material cooled down and hardened, spherulite structures appeared, demonstrating the PEAs' brittle character (Figure S12, Supporting Information).

2.3. Polyesteramides-Polyethylene Glycol Blends

PEA polymers have the potential to cover many important applications like bioactive materials in regenerative biomedicine. Since the polymers alone can be too hydrophobic for many biomedical purposes, that is, cell adhesion and cell growth,[42] blends with the hydrophilic biocompatible polyethylene glycol (PEG) M6000 were prepared with equal mass fractions.

Contact angle measurements (CAM) were performed for further surface analysis. CAM is an analytical method for determining the hydrophilicity within polymers. With increasing hydrophilicity, the contact angle (Θ_{av}) decreases. Therefore, the water droplet on the polymer surface becomes flatter. According to this analysis, the PEG blends have—as expected—a significantly lower contact angle and thus a higher hydrophilicity than the pure polyester amides (see **Table 4** and Figure S11, Supporting Information). It was also not possible to measure the Young's modulus since the blends were still too brittle despite their high PEG content. It was expected that the PEG content would result in an improvement of the mechanical properties.

2.4. Additional Analysis

Additional analyses such as scanning electron microscope (SEM) and biodegradability studies were performed. Both the fracture sites and the polymer surface of PEA-21 display a lamellar structure, making it a characteristic feature. A layered, flaky structure

Table 2. Reaction conditions and results of selected polymerizations and the resulting polymers. The molar ratio of lactam and lactone in feed was 1:1, except a) with 2:1 and b) 4:1.

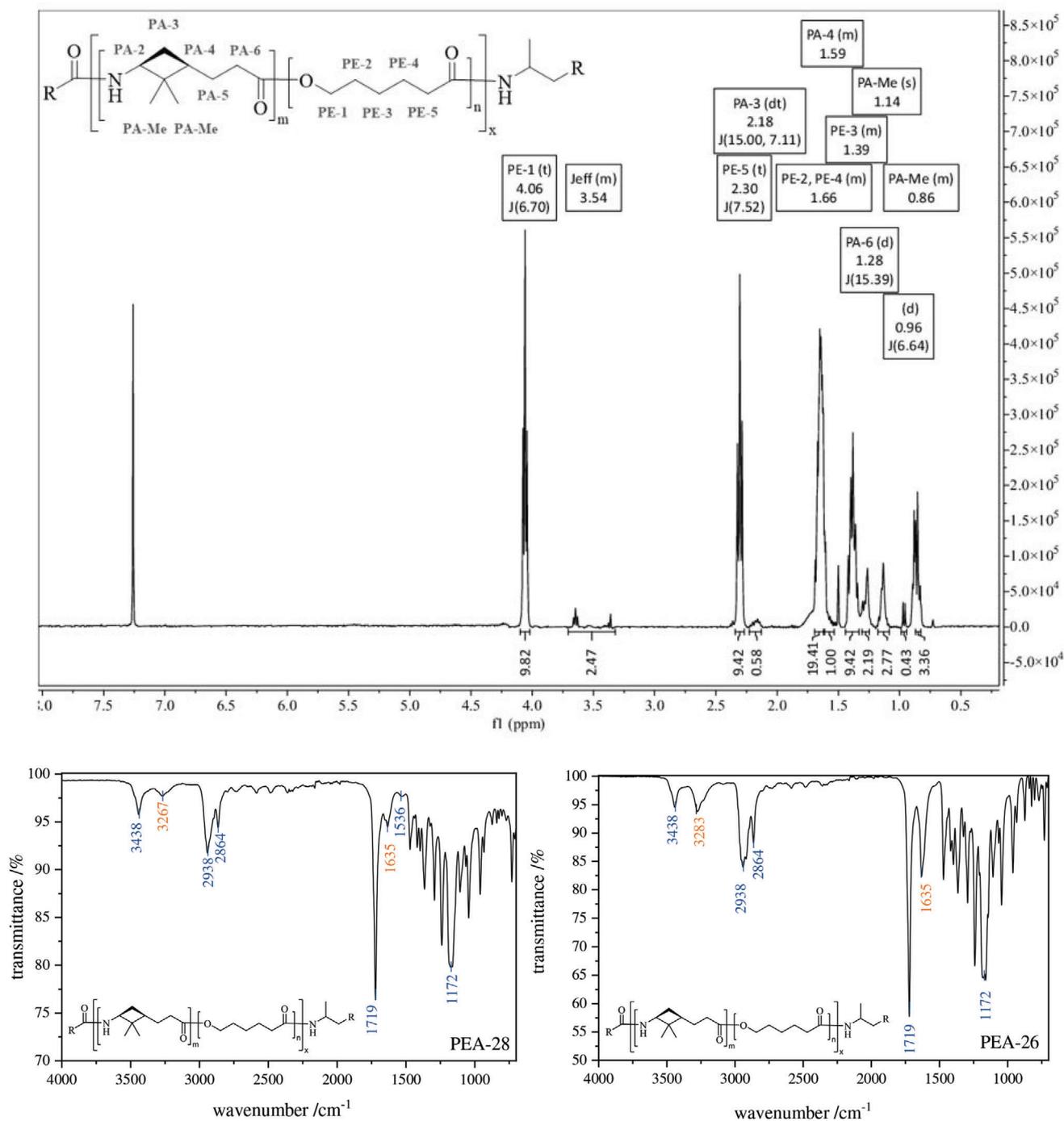| Entry	$m_{\beta\text{-PLa}}$ [g]	catalyst	Catalyst [mol%]	[M]/[Jeff] ratio	t [h]	T [°C]	M_w[a] [g mol^{-1}]	M_n[a] [g mol^{-1}]	PDI	Yield [%]	PA:PE[b]
b0	0.05	–	–	50	7	205	5300	2300	2.3	2	2:98
1	0.05	Sn(Oct)$_2$	0.2	50	7	205	1500	900	1.7	8	–
2	0.05	Sn(Oct)$_2$	0.02	50	7	205	7700	4700	1.6	13	13:87
3	0.05	Sn(Oct)$_2$	0.02	500	7	205	7200	4400	1.7	21	7:93
4	0.05	Sn(Oct)$_2$	0.02	600	7	205	8700	5100	1.7	25	6:94
5	0.05	Sn(Oct)$_2$	0.02	700	7	205	9000	5500	1.6	21	3:97
6	0.05	Sn(Oct)$_2$	0.2	900	7	205	1900	1200	1.7	20	–
7	0.05	Sn(Oct)$_2$	0.02	700	7	205	6100	3800	1.6	24	3 : 97
8	0.05	Sn(Oct)$_2$	0.02	700	7	205	8100	4800	1.7	28	–
9	0.05	Sn(Oct)$_2$	0.002	700	7	205	12100	6100	2	31	2:98
10	0.05	Sn(Oct)$_2$	0.002	700	7	205	15700	7100	2.2	23	2:98
11	0.05	Sn(Lau)$_2$	0.2	700	7	205	6400	3600	1.8	22	–
12	0.05	Sn(Lau)$_2$	0.02	700	7	205	16900	7300	2.3	30	6:94
13	0.05	Sn(Lau)$_2$	0.02	900	7	205	14100	6800	2.1	21	4:96
15[a]	0.05	Sn(Oct)$_2$	0.2	700	7	205	700	500	1.6	8	–[c]
16[b]	0.05	Sn(Oct)$_2$	0.2	700	7	205	1400	600	2.2	8	–[c]
			[mmol%]								
17	0.075	Sn(Oct)$_2$	0.2	500	8	205	28300	14300	2	88	–
18	0.075	Sn(Lau)$_2$	0.6	500	8	205	25500	12500	1.8	86	–
19	0.08	Sn(Lau)$_2$	0.03	600	7.5	205	13000	7100	1.8	79	–
20	0.08	Sn(Oct)$_2$	0.06	600	7.5	205	38800	18400	2.1	80	–
21	0.5	Sn(Oct)$_2$	0.1	700	8	205	25100	13600	1.9	13	20:80
22	0.5	Sn(Lau)$_2$	0.05	700	8	205	20300	11100	1.8	25	23:77
23	0.5	Sn(Oct)$_2$	0.1	700	7.5	205	6600	4500	1.5	14	17:83
24	0.5	Sn(Lau)$_2$	0.05	700	7.5	205	7300	4700	1.6	30	20:80
25	1	Sn(Oct)$_2$	0.1	900	7.5	205	10300	6100	1.7	48	29:71
26	1	Sn(Lau)$_2$	0.05	900	7.5	205	20400	9500	2.2	31	4:96
27	1	Sn(Oct)$_2$	0.1	900	7.5	205	10300	8300	2	13	–
28	1	Sn(Lau)$_2$	0.05	900	7.5	205	17800	10200	1.8	16	18:82
29	1.5	Sn(Oct)$_2$	0.2	700	7.5	205	7200	4700	1.5	9	6:94
30	1.5	Sn(Oct)$_2$	0.2	700	7.5	205	34600	11700	2.9	32	4:96

Temperature, (T); time, (t); molecular weight, (M); polydispersity index, (PDI); monomer concentration, [M]; (b0 = blind experiment; [a] Determined by Gel permeation chromatography/ Size exclusion chromatography (GPC/SEC) and rounded up; [b] Calculation as accurate as possible. Difficulties due to peak overlap and it has to be considered that there can be different homogeneities in the sample; [c] not measurable due to high PA content thus solubility difficulties.

can be observed for the PEA-PEG-blend. As expected, its surface is similar to PEA-21, but it seems to be more structured (**Figure 4** and Figure S9, Supporting Information). This indicates a successfully prepared, relatively homogenous blend. Generally, structured surfaces can be observed in both cases. Especially regarding the PEA-PEG blend, these surfaces could be well suited for cell adhesion or similar bio-applications. In terms of biodegradability, the polymers show resistance and a high stability in soil over several weeks/month (Figure S10, Supporting Information); therefore, also experiments for longer times and within other environments are ongoing. In addition, exemplary images of the contact angle measurements (Figure S11, Supporting Information) and images of the test specimen (Figure S12, Supporting Information) are available in the Supporting Information.

3. Conclusion

β-Pinene-based polymers show great potential for different applications, and as a bio-based replacement for conventional plastics, or as HPPs. This work has focused on polyesteramides (PEAs) and their preparation using Sn-, Zn-, and P-based catalyst systems.

The synthesis route starts with the oxidation of β-pinene and proceeds with the formation of its lactam. β-pinene lactam is then copolymerized with ε-caprolactone forming PEAs. By searching over possible educt quantities and concentration as well as alternative down-streaming processes, the monomer synthesis reaction was significantly optimized. Compared to the current state of the art, this optimized reaction is much more efficient while requiring a much smaller amount of educts,

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Figure 3. ^{1}H-NMR and IR-spectroscopy measurements (determined PA:PE ratios, left: 18:82, right: 4:96) of exemplaric β-PLa-*co*-CLo copolymers.

compared to previous procedures. These findings render this production both less costly and much more sustainable. Other, more "green" oxidation procedures are currently under investigation. Also, different reaction pathways for the lactam formation were investigated. The oxime reaction could be optimized in terms of milder reaction conditions. Regarding the Beckmann rearrangement the normally used strong acids like polyphosphoric acid or sulfuric acid could be replaced with tosyl chloride

in aq. NaOH. This not only enables an easier purification, but also renders upscaling more feasible, thus moving the reaction one step closer to a potential industrial application. Sn(Oct)$_2$ and Sn(Lau)$_2$ turned out to be the most promising ROCOP catalysts, since the other catalysts favored the ROP of ϵ-caprolactone. Therefore the polymerization of monomers to PEAs using tin catalyst systems was further improved. Besides optimizing temperature as well as catalyst and initiator concentration, replacing
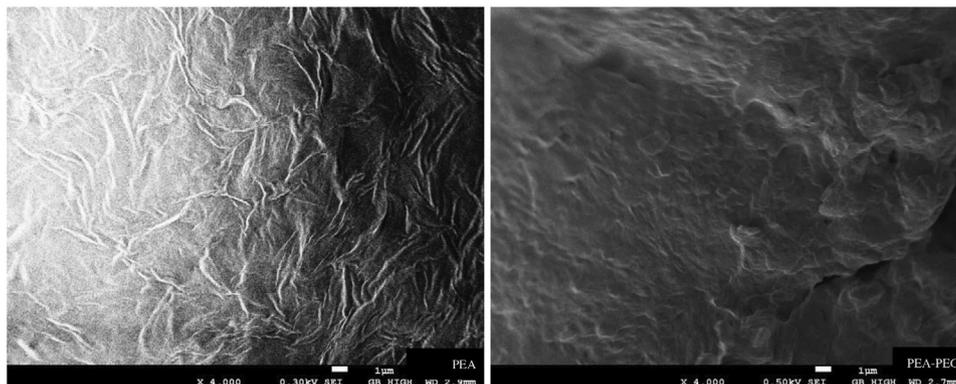
Figure 4. SEM imaging of PEA-21 PEA-PEG-blend.

Table 3. Thermal analytics of selected examples.

Entry	PE:PA	T_m [°C]	T_c [°C]	T_d [°C]
2	13:87	45.9[a]	24.3	–
3	7:93	47	23.6	–
4	6:94	49.6	28.8	–
5	3 97	49.9	29.5	–
11	–	49.7[a]	30.2	–
12	6:94	53.9[a]	36.6	–
13	4:96	53.6[a]	34.8	–
21	20:80	51.5[a]	34.3	–
22	23:77	–	–	368.1
23	17:83	42.6	29.1	353.7
24	20:80	43.2	29.5	351.8;557.2
25	29:71	45.9[a]	31.1	334;525.9
26	4:96	45.3[a]	33.8	418.2
27	n.p.	44.4[a]	27.2	177.7;404.6
28	18 :82	38.8[a]	25.3	167.7;362.7

[a] broad peak, indicating PA content; [b] two peaks indicating a high PA content.

Table 4. Contact angle (Θ) measurements of two selected PEA-PEG blends and their PEA.

Polymer	Θ_1	Θ_2	Θ_3	$\Theta_{average}$
PEA-21	91.5	86.5	95	91
PEA-21-PEG	79	72.5	78	76.5
PEA-c21	99.5	91	92	94.2
PEA-c21-PEG	62	62	63	62.3

the standard crimp vial caps with ones with a PTFE/silicone seal led to polymer chain lengths with more than M: 25 000 g mol^{-1}. This work shows that the investigated tin catalyst systems are very promising candidates for producing polyesteramides with high molar masses. However, to make the reaction more sustainable, "greener" catalyst systems than tin-based ones will be investigated in the future. High decomposition temperatures demonstrate the stability of these polymers, and melting points close to that of polycaprolactone confirm a relatively high proportion of polyester within these PEA copolymers.

Both thermal and mechanical properties can be further improved with increased chain lengths. They will also further be optimized by changing the ratio between polyamides and polyesters. The materials may be interesting for the biomedical field, and—depending on its properties—they could also find use as a replacement for conventional plastics or an HPP. As the polymer alone is too hydrophobic for most biomedical purposes, for example, cell adhesion and cell growth, blends with PEG were produced, which have an increased hydrophilicity. As a first step in this direction, the mechanical properties of the blends—as compared to the polymer alone—are presumingly improved, since the processing of the polymer-blends to test specimen were possible (Figure S11, Supporting Information). Additional catalysts as well as the synthesis of block copolymers are now under further investigation. Additionally, improving not only the PEA alone, but also PEA blends would likely improve these properties and should therefore a focus of future research. Also, other biobased polymers for blend production, such as polysaccharides, other terpene-based PEA, polyesters, and polyamides, as well as polyhydroxyalkanoates are possible candidates for further optimizations. In the future, the reactions should further be optimized in order to render the polymers suitable for large-scale applications. The family of β-pinene-based polymers should be further explored, with regards to polyesteramides, polyamides, or polymer blends.

This work has thus made further steps in this direction by making the production of β-pinene lactam, a structurally significant terpene resource, much more efficient and by improving the subsequent copolymerizations with a lactone, and it has thus further illustrated the great potential of these resulting materials.

4. Experimental Section

All experimental details are explained in the Supporting Information.

Supporting Information

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

Acknowledgements

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[1] Plastic Atlas: Facts and figures about the world of synthetic polymers, Heinrich-Böll-Stiftung, Berlin **2019**.

[2] K. Schüler, Aufkommen und Verwertung von Verpackungsabfällen in Deutschland im Jahr 2016, https://www.umweltbundesamt.de/sites/default/files/medien/2546/publikationen/aufkommen_und_verwertung_von_verpackungsabfaellen_in_deutschland_im_jahr_2016_final.pdf. (accessed: January **2021**).

[3] R. Mülhaupt, *Macromol. Chem. Phys.* **2013**, *214*, 159.

[4] A. Gandini, T. M. Lacerda, A. J. F. Carvalho, E. Trovatti, *Chem. Rev.* **2016**, *116*, 1637.

[5] M. Eissen, J. O. Metzger, E. Schmidt, U. Schneidewind, *Angew. Chem., Int. Ed.* **2002**, *41*, 414.

[6] P. H. Seeberger, T. Carell, *Curr. Opin. Chem. Biol.* **2003**, *7*, 715.

[7] R. T. Mathers, *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 1.

[8] S. Mecking, *Angew. Chem., Int. Ed.* **2004**, *43*, 1078.

[9] M. A. Hillmyer, W. B. Tolman, *Acc. Chem. Res.* **2014**, *47*, 2390.

[10] R. A. Sheldon, *Green Chem.* **2014**, *16*, 950.

[11] S. A. Miller, *ACS Macro Lett.* **2013**, *2*, 550.

[12] M. Vert, Y. Doi, K.-H. Hellwich, M. Hess, P. Hodge, P. Kubisa, M. Rinaudo, F. Schué, *Pure Appl. Chem.* **2012**, *84*, 377.

[13] T. Iwata, *Angew. Chem., Int. Ed.* **2015**, *54*, 3210.

[14] P. S. Löser, P. Rauthe, M. A. R. Meier, A. Llevot, *Philos. Trans. R. Soc., A* **2020**, *378*, 20190267.

[15] A. Llevot, P.-K. Dannecker, M. Von Czapiewski, L. C. Over, Z. Söyler, M. A. R. Meier, *Chem. - Eur. J.* **2016**, *22*, 11510.

[16] K. Yao, C. Tang, *Macromolecules* **2013**, *46*, 1689.

[17] P. T. Anastas, N. Eghbali, *Chem. Soc. Rev.* **2010**, *39*, 301.

[18] M. Golets, S. Ajaikumar, J. -P. Mikkola, *Chem. Rev.* **2015**, *115*, 3141.

[19] a) M. R. Thomsett, T. E. Storr, O. R. Monaghan, R. A. Stockman, S. M. Howdle, *Green Materials* **2016**, *4*, 115; b) M. Winnacker, B. Rieger, *ChemSusChem* **2015**, *8*, 2455.

[20] J. Zhao, H. Schlaad, *Adv. Polym. Sci.* **2013**, *253*, 151.

[21] M. Winnacker, J. Sag, *Chem. Commun.* **2018**, *54*, 841.

[22] M. Winnacker, J. Sag, A. Tischner, B. Rieger, *Macromol. Rapid Commun.* **2017**, *38*, 1600787.

[23] P. N. Stockmann, D. Van Opdenbosch, A. Poethig, D. L. Pastoetter, M. Hoehenberger, S. Lessig, J. Raab, M. Woelbing, C. Falcke, M. Winnacker, C. Zollfrank, H. Strittmatter, V. Sieber, *Nat. Commun.* **2020**, *11*, 509.

[24] D. H. Lamparelli, V. Paradiso, F. Della Monica, A. Proto, S. Guerra, L. Giannini, C. Capacchione, *Macromolecules* **2020**, *53*, 1665.

[25] M. Winnacker, A. J. G. Beringer, T. F. Gronauer, H. H. Güngör, L. Reinschlüssel, B. Rieger, S. A. Sieber, *Macromol. Rapid Commun.* **2019**, *40*, 1900091.

[26] F. Auriemma, C. De Rosa, M. R. Di Caprio, R. Di Girolamo, W. C. Ellis, G. W. Coates, *Angew. Chem., Int. Ed.* **2015**, *54*, 1215.

[27] O. Hauenstein, S. Agarwal, A. Greiner, *Nature Commun.* **2016**, *7*, 11862.

[28] F. Della Monica, A. W. Kleij, *Polym. Chem.* **2020**, *11*, 5109.

[29] M. Winnacker, B. Rieger, *Polym. Chem.* **2016**, *7*, 7039.

[30] G. Deshayes, C. Delcourt, I. Verbruggen, L. Trouillet-Fonti, F. Touraud, E. Fleury, P. Degée, M. Destarac, R. Willem, P. Dubois, *Macromol. Chem. Phys.* **2009**, *210*, 1033.

[31] A. C. Fonseca, M. H. Gil, P. N. Simões, *Prog. Polym. Sci.* **2014**, *39*, 1291.

[32] S. Naumann, M. Winnacker, *Nachr. Chem.* **2020**, *68*, 67.

[33] J. M. Blanco, O. Caamaño, F. Fernández, G. Gómez, I. Nieto, *Synthesis* **1996**, *27*, 281.

[34] D. G. Lee, T. Chen, Z. Wang, *J. Org. Chem.* **1993**, *58*, 2918.

[35] H. K. Hall, Jr., *J. Org. Chem.* **1963**, *28*, 3213.

[36] M. Winnacker, D. H. Lamparelli, C. Capacchione, H. H. Güngör, L. Stieglitz, K. S. Rodewald, M. Schmidt, T. F. Gronauer, *Macromol. Chem. Phys.* **2020**, *221*, 2000110.

[37] J. Clayden, N. Greeves, S. G. Warren, *Organic Chemistry*, Oxford University Press, Oxford **2012**.

[38] S. R. Thopate, S. R. Kote, S. V. Rohokale, N. M. Thorat, *J. Chem. Res.* **2011**, *35*, 124.

[39] F. Aricò, G. Quartarone, E. Rancan, L. Ronchin, P. Tundo, A. Vavasori, *Catal. Commun.* **2014**, *49*, 47.

[40] a) M. Winnacker, D. H. Lamparelli, C. Capacchione, H. H. Güngör, L. Stieglitz, K. S. Rodewald, M. Schmidt, T. F. Gronauer, *Macromol. Chem. Phys.* **2020**, *221*, 2000110; b) M. Winnacker, DECHEMA e.V.-Report, Max-Buchner-Forschungsstipendium (MBFSt-Kennziffer 3676), **2019**.

[41] K. Saalwächter, in *NMR Methods for Characterization of Synthetic and Natural Polymers* (Eds: R. Zhang, T. Miyoshi, P. Sun), The Royal Society of Chemistry, London **2019**.

[42] W. L. Murphy, T. C. McDevitt, A. J. Engler, *Nat. Mater.* **2014**, *13*, 547.