Sustainable Synthesis of Non-Isocyanate Polyurethanes Based on Renewable 2,3-Butanediol

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In this work, three different cyclic carbonates are obtained from renewable diols and transformed into carbamates by reacting them with renewable 11-amino undecanoic acid methyl ester to synthesize non-isocyanate poly(ester urethane)s in a sustainable manner. A procedure using 2,3-butanediol (2,3-BDO) as a renewable starting material to synthesize a cyclic carbonate with dimethyl carbonate (DMC) is introduced, catalyzed by 1,5,7-triazabicylco[4.4.0]dec-5-ene (TBD). Three purification strategies, i.e., column chromatography, extraction, and distillation, are compared regarding their E-Factors. Propylene glycol (PG) and ethylene glycol (EG) are used as alternative starting materials to broaden the substrate scope and compare material properties, their cyclic carbonates likewise react to carbamates with 11-amino undecanoic acid methyl ester. All carbamates are then polymerized in a bulk polycondensation reaction, yielding non-isocyanate polyurethanes (NIPUs), specifically poly (ester urethane)s, with molecular weights (M_n) up to 10 kDa. Complete characterization is reported using differential scanning calorimetric (DSC), size exclusion chromatographic measurements (SEC), ^{1}H-NMR as well as IR spectroscopy. The rheological properties of the poly(ester urethane)s are investigated in the framework of small amplitude oscillatory shear (SAOS) and uniaxial elongation.

1. Introduction

Polyurethanes (PUs) demonstrate one of the most important classes of polymers with a world production exceeding 10 Mill. t/year. PUs offer manifold application possibilities in various fields of automobiles, building industry, medical applications, textile industry, furniture, or electronics.[1,2] This relates to their versatile and tunable properties, both on a molecular and macroscopic level. For instance, their superior hardness, mechanical strength, and elongation properties.[3] In 1937, the first PUs were discovered by Otto Bayer in the laboratories of I.G. Farben in Germany, using aliphatic diisocyanate and glycol. This step-growth polymerization to PUs was then published in 1947.[4] The new materials offered advantages in terms of increased flexibility and coating efficiency compared to other plastics known at the time. After commercializing polyisocyanates, the importance of PUs rose even further. However, industrially, PUs are manufactured using isocyanates, which are not only toxic themselves but require hazardous and toxic phosgene for their synthesis.[5,6]

With the field of sustainable chemistry increasing in importance within the last decades, the aim is to find novel ways to replace hazardous chemicals and processes by "greener" starting materials and alternatives. Furthermore, the production of chemicals must be shifted from fossil-fuels to a production based on renewable resources, not only because petroleum resources are dwindling. A common concept towards sustainable chemical production is based on the 12 Principles of Green Chemistry, especially with the widespread interest to combine environmental and economic goals by using new chemical innovations.[7,8] Therefore, developing alternative syntheses routes for PUs become increasingly attractive.[1] Thus, non-isocyanate polyurethanes (NIPUs) gained great attention in the scientific community.[9] In general, the synthesis of NIPUs can be split into different methods, i.e., step-growth polymerizations or ring-opening polymerization.[3]

Synthesizing NIPUs or NIPU-foams from cyclic carbonates, by reaction with amines, becomes more and more established.[10] In 1957, the preparation of NIPUs using ethylene carbonate was reported by Dyer and Scott.[11] Nowadays, many different

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synthetic routes are already well-known, often focusing on using cyclic carbonates and amines obtained from biobased resources.[12] Cyclic carbonates show a lower toxicity (i.e., ethylene carbonate: LD_{50}, oral, rat, >10 g kg^{-1}) compared to industrially used isocyanates (i.e., hexamethylene diisocyanate: LD_{50}, oral, rat, <960 mg kg^{-1} methyl isocyanate).[6,13] However, lower reactivity in comparison to isocyanates often requires the use of catalysts.[14]

The primary reactant for the synthesis of NIPUs, i.e., cyclic carbonates, can be prepared by various methods, differentiating between 5- to 7-membered rings. The reaction of CO_2 and epoxides is well-known, whereas the reaction of CO_2 with diols is more challenging.[15] Instead of using CO_2 to synthesize cyclic carbonates, strategies are published using dimethyl carbonate (DMC), acting simultaneously as reagent and solvent.[16] Our group reported a direct condensation of diols to cyclic carbonates using DMC and 1,5,7-triazabicylco[4.4.0]dec-5-ene (TBD) as organocatalyst.[17] Ethylene glycol (EG) and propylene glycol (PG), which are biodegradable, renewable and show a low toxicity, are known to be simply transferred in such reactions.[18–20]

Suitable key intermediates for the direct conversion to NIPUs are carbamates, which can be polymerized via a transurethanization reaction. For the synthesis of such carbamates, cyclic carbonates are promising substrates.[21] It is possible to use a wide range of amines to ring-open cyclic carbonates, leading to highly diversified carbamates.[14] Such carbamates are structurally related to industrially synthesized urethanes obtained by reacting an alcohol with an isocyanate.[22]

For the ring-opening of cyclic carbonates to carbamates, different strategies were reported. A three-step mechanism of the reaction of amines with cyclic carbonates was proposed in 2003 by Garipov et al.[23] Despite using amines for the ring-opening, the use of amino acid methyl esters is also known.[14] Moreover, methyl 10-undecenoate was investigated as starting material for the polymer synthesis based on AA- and AB-monomers.[24]

In this study, carbamates were synthesized based on 2,3-butanediol (2,3-BDO), a renewable but not often used diol for polymer synthesis, being structurally related to EG and PG.[25] Various strategies are published on producing 2,3-BDO in an efficient and economical way through fermentation of biomass.[26] The interest in 2,3-BDO was started by Harden and Walpole in 1906 using *Klebsiella pneumoniae*.[27] The first industrial production followed in 1933, proposed by Fulmer.[28] Using 2,3-BDO for polymer chemistry recently gained great attention in developing a low carbon economy and a more sustainable future.[29] More common applications of 2,3-BDO include dehydration to form methyl ethyl ketone, which is used as liquid fuel additive.[30] Furthermore, the diol is used in structural analogy to glycerol or glycol as antifreeze agent due to its low freezing point, while its derivatives find application as a plasticizer and in the solvent production. Conversion to 1,3-butanediene leads to the possible application in the rubber production, whereas dehydrogenation of 2,3-BDO to diacetyl serves a valued flavouring agents in food products.[31] In the polymer research area, 2,3-BDO is furthermore used to synthesize renewable polyesters.[32]

In this project, the direct condensation of 2,3-BDO to its cyclic carbonate was performed under similar reaction conditions as described recently by us.[17] The other two diols, EG and PG, were transformed in the same manner. 11-Amino undecanoic

Table 1. GC-FID-screening of the condensation reaction of **1** with DMC and different organocatalysts at different catalyst loadings. Biphenyl was used as an internal standard. (n.a.: not available, as no measurement was performed).

Diol 1 [equiv.]	DMC [equiv.]	Base/[mol%]	Conversion/[%]				
			TBD	DBU	DBN	Pyridine	TMG
1.00	1.20	0.1	<1	n.a.	n.a.	n.a.	<1
1.00	1.20	1.0	26	15	4	<1	2
1.00	1.20	3.0	47	42	28	<1	16
1.00	1.20	5.0	61	53	37	12	23
1.00	1.20	10.0	78	67	n.a.	n.a.	n.a.

Conditions: 80 °C, atmospheric pressure, 3 h reaction time.

acid methyl ester was then reacted via ring-opening of the respective cyclic carbonate to form carbamate monomers, which could be polymerized to obtain NIPUs, more precisely poly(ester urethane)s. A comparison between the different diols used demonstrated a change in different material properties of these polymers.

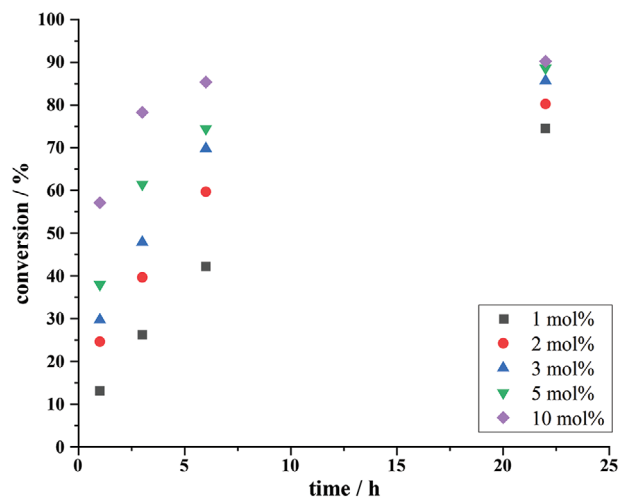## 2. Results and Discussion

2.1. Monomer Synthesis

The synthesis of symmetric and unsymmetric organic carbonates was already investigated by our group, using DMC and TBD as organocatalyst.[17] DMC covers fundamental aspects in terms of Green Chemistry, as it is biodegradable and shows relatively low toxicity (LD_{50}, oral, rat >5 g kg^{-1}), whereas TBD can be synthesized using inexpensive and nontoxic chemicals.[17,33] Here, a direct condensation of the renewable diol 2,3-BDO **1** was first investigated at atmospheric pressure and 80 °C using DMC as solvent and reactant.

First, reaction conditions were optimized. Thus, the direct condensation of **1** was studied using TBD as organocatalyst in different concentrations (0.10 to 10 mol%) using GC-FID to follow the reaction progress (see **Table 1**).

In further approaches, 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU), 1,5-diazabicyclo(4.3.0)non-5-ene (DBN), pyridine, and 1,1,3,3-tetramethylguanidine (TMG) were tested as alternative organocatalysts at otherwise identical reaction conditions.

The results showed that 10 mol% TBD led to a conversion of 78% and 10 mol% DBU to 67%. Thus, TBD and DBU seemed to be the most suitable organocatalysts for the transformation of **1** into its cyclic carbonate **2**. DBN, pyridine, and TMG also produced **2**, but with significantly lower conversions. With increased catalyst loadings, higher conversions were observed. However, as DBU led to a brownish solution and the reaction with TBD remained colourless, the latter was used for further optimizations regarding the reaction time. **Figure 1** shows the conversions obtained via GC-FID, measured at different reaction times and TBD concentrations.

As shown in Figure 1, the conversion of **1** continuously increases with higher reaction times and catalyst loading. The highest conversion of ≈90% was achieved after 22 h using 10 mol%

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Figure 1. Conversion of **1** to **2** after different reaction times, using TBD in different concentrations, analyzed via GC-FID-screening.

Table 2. Purification strategies for **2**, the related E-Factors; sEF (excluding solvents) and cEF (including solvents) and resulting yields. (n.a.: not applicable, as no additional solvents had to be used).

Purification strategies	sEF	cEF	Yield/[%]
Vacuum Distillation	3.44	n.a.	38
Column Chromatography	2.82	520	45
Extraction	2.99	223	43

TBD. Nevertheless, with a rising TBD concentration, by-products were detected via GC-FID. Furthermore, lower catalyst loadings are of interest in Green Chemistry. Since after 22 h reaction time, the conversion was similar for different catalyst concentrations, 1 mol% TBD was chosen as optimum, leading to ≈75% conversion and no side-product formation. Increasing the reaction time to 66 h did not enhance the conversion of the reaction further.

Three purification strategies were evaluated for the purification of the cyclic carbonate **2**, namely vacuum distillation, column chromatography, and extraction. The different methods were compared regarding their efficiency and E-Factor (see **Table 2**). The E-Factor is generally accepted as a useful measure to compare the environmental acceptability of chemical processes. The calculation includes the actual amount of waste produced in the process and therefore considers solvent losses, chemical yield, and includes all reagents in principle. Thus, the ideal E-Factor is zero.[34] Here, the E-Factor of each purification strategy was calculated as simple E-Factor (sEF, meaning the exclusion of solvents in the calculation) and the complete E-Factor (cEF, including solvents used during the purification).[35]

The reaction mixture of the condensation reaction, including unreacted **1**, DMC, TBD, and the product **2**, was always prepurified using a rotary evaporator to remove remaining solvents under reduced pressure. The first purification strategy was then tested using vacuum distillation. Temperatures of 130 °C were needed, combined with vacuum of at least 24 mbar to distil **2**, yielding 38% as yellowish liquid. TBD remained in the flask, as
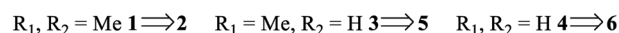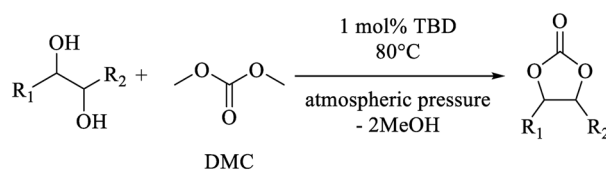
Scheme 1. Condensation reaction of diols. Using diol **1** to form **2**, 20 h reaction time was used. Using diol **3** and **4** to form its cyclic carbonates **5** and **6**, 30 h reaction time was used.

analyzed by ^{1}H-NMR spectroscopy. The E-Factor for the distillation was 3.44 (sEF as well as cEF).

As second purification strategy, column chromatography was tested. Ethyl acetate and cyclohexane in a 1:1 v/v ratio proved to be a suitable solvent mixture, leading to an R_F-value of **2** of 0.47 on TLC. For the column, 2.70 L of solvent mixture was needed, yielding the cyclic carbonate in 45% as colorless liquid. Thus, this purification led to an E-Factor of 2.82 (sEF) and 520 (cEF), respectively.

Extraction of the reaction mixture was tested as third purification strategy. First, the reaction mixture was dissolved in 20 mL of ethyl acetate, followed by washing three times with ≈30 mL of water. The organic phase was dried over sodium sulphate and ethyl acetate was removed under reduced pressure, yielding 43% **2** as a colorless liquid. The E-Factor of the extraction was 2.99 (sEF). Including the used solvents, the E-Factor increased to 223 (cEF).
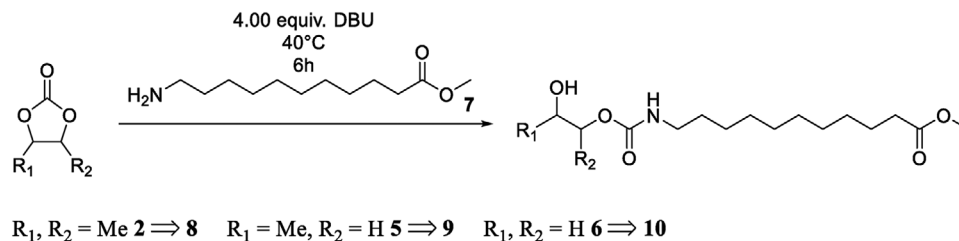
Table 2 shows an overview of the tested purification strategies for **2** and their resulting yields, as well as calculated E-Factors.

Regarding the calculated sEF of the purification strategies, column chromatography shows the lowest with 2.82, followed by an sEF of 2.99 for extraction. However, concerning the cEF with 520, the chromatographic purification strategy shows the highest E-Factor, followed by extraction with 223 (cEF). No recovery of the solvents was tested but should be feasible.

Concerning time issues, extraction was the fastest purification strategy of the three listed. For vacuum distillation, energy was necessarily caused by heating and vacuum. Regarding the resulting yields, all purification strategies were quite similar. However, column chromatography showed the highest yield with 45% followed by a yield of 43% after extraction.

The obtained cyclic carbonate **2** was further analyzed via ^{1}H-NMR spectroscopy to confirm its purity. After purification via column chromatography and extraction, **2** appeared to be pure according to ^{1}H-NMR analysis. The ^{1}H-NMR spectrum of **2** obtained after vacuum distillation still showed impurities (see Figure S3 in the Supporting Information). Thus, extraction seemed to be the "greenest," fastest, and least energy consuming way to purify **2**.

To broaden the substrate scope, PG **3** and EG **4** were tested in the condensation reaction to form the respective cyclic carbonates under the same reaction conditions as for **2** formation (see **Scheme 1**). The conversion and the effect of 1 mol% TBD as catalyst was screened via GC-FID. As already mentioned in the introduction, PG and EG can be obtained from renewables. Therefore, similar to 2,3-BDO, the two diols were included in this study.

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Scheme 2. Ring-opening reaction of cyclic carbonates **2**, **5**, and **6**, using **7**, yielding the carbamate **8**–**10** to be used as step growth monomers.

Using diol **3**, a conversion of 82% after 24 h reaction time was observed, further increasing to 92% conversion after 30 h. For reactions using diol **4**, GC-FID-screenings were not possible, as the signal of **3** overlapped with the solvent signal. Scheme 1 shows both condensation reactions under used reaction conditions.

For the diols **3** and **4**, the reaction time was extended to 30 h to increase the conversion. As a reminder, longer reaction times did not increase the yield in case of **1**. As both resulting cyclic carbonates, i.e., **5** and **6**, were soluble in water, purification using the extraction strategy described for **2** was not possible. Purification via vacuum distillation of **5** and **6** was pursued, since it was identified as unsuitable purification strategy for **2**, also because of its energy consumption. Thus, column chromatography was performed with a solvent mixture 1:1 v/v cyclohexane and ethyl acetate, yielding 86% **5** as colorless liquid and 65% **6** as colorless solid. For the cyclic carbonate **5**, the E-Factor was 1.10 (sEF) and, according to its purification, 387 (cEF). The sEF for the cyclic carbonate **6** was 4.71, whereas cEF was 1671 caused using 2.50 L solvent during column chromatography.

One approach to ring-open cyclic carbonates using unprotected amino acids was already investigated by Olsén et al.[14] Here, biobased 11-amino undecanoic acid, industrially derived from castor oil, was first transformed into its methyl ester **7**.[36] Subsequently, **7** was used to ring-open the above described cyclic carbonates (see **Scheme 2**).

The ring-opening of **2** was performed with DBU instead of using 2.00 equiv. of TEA, the latter resulting in 91–96% yield as described by Olsén et al.[14] However, here 4.00 equiv. of DBU were used in combination with 14.0 equiv. DMSO as solvent to ring-open 1.00 equiv. of cyclic carbonate. Instead of running the reaction at room temperature, 40 °C was used for 6 h, leading to full conversion as observed via GC-FID. Decreasing the amount of DBU to 2.00 equiv. led to a conversion of 85% towards carbamate **8** after 6 h reaction time. Thus, only when using 4.00 equiv. DBU full conversion was obtained. For the ring-opening of **5** and **6** identical reaction conditions were used. All carbamates could be successfully isolated by column chromatography, yielding 81% **8**, 88% **9**, and 91% **10**. A respective reaction scheme is depicted in Scheme 2.

2.2. Step-Growth Polymerization to Poly(ester urethane)s

The TBD catalyzed polycondensation reaction of fatty acid derived dimethyl biscarbamates and diols was previously investigated by us.[2] The reactions were performed under neat conditions in open reaction tubes, using 0.10 equiv. of catalyst. Since TBD is considered to degrade at elevated temperatures, the cata-

Table 3. Results of SEC and DSC measurements of the synthesized poly(ester urethane)s **11**–**13**.

Polymer	Reaction time/[h]	M_n/[Da]	Đ	T_g/[°C]	T_c/[°C]	T_m/[°C]	ΔH_m/[J g^{-1}]
11	20	11 200	2.17	−16	59	77 and 89	29
12	20	9 960	1.94	−48	43 and 67	58 and 85	33
13	8	5 100	2.13	−9	73	86 and 102	45

Conditions: 12.0 mmol carbamate, 0.20 equiv. TBD, full vacuum, 120–160 °C, precipitation in MeOH.

lyst was added in three portions at increasing temperatures under continuous vacuum.[2]

This optimized approach was used to polymerize the carbamate monomers synthesized in this project. TBD was used as catalyst with a loading of 0.20 equiv. added in three portions at an increasing temperature from 120 to 160 °C. The polymerization of monomers **8** and **9** to synthesize the poly(ester urethane)s **11** and **12** was performed for 20 h. For the polymerization of monomer **10** to synthesize the poly(ester urethane) **13**, a reaction time of 8 h was chosen, as longer reaction time led to a completely insoluble reaction mixture. All polymers could be precipitated in a suitable solvent (cold ethanol for **11**, cold methanol for **12** and **13**), yielding colourless to yellowish solids (see **Figure 2**).

NMR spectroscopy of all poly(ester urethane)s could only be performed using a solvent mixture of hexaflourisopropanol (HFIP) and CDCl$_3$. Despite the significant HFIP solvent peak, overlapping with some polymer signals, the structure of poly(ester urethane)s **11**–**13** could be confirmed (see Supporting Information). Further, IR spectroscopy showed typical signals for poly(ester urethane)s, spectra are depicted in Figures S10–S12 in the Supporting Information. To gain information about the molecular weight (M_n) and dispersity (Đ) of the polymers, SEC measurements were performed using HFIP as solvent; the only solvent able to dissolve these polymers, a typical observation for a range of polyurethanes and polyamides. The resulting chromatograms are depicted in **Figure 3**.

Furthermore, DSC measurements were performed to analyse the glass transition temperature (T_g), the crystallization temperature (T_c), the melting point (T_m), and the melting enthalpy (ΔH_m) of each polymer (see Figures S13 and S14 in the Supporting Information). The corresponding DSC data and the reactions times and molecular weights of the polymers are summarized in **Table 3**.

In the case of **13**, the necessary decrease of the reaction time from 20 to 8 h resulted in a lower molecular weight polymer (≈5 kDa), corresponding to oligomers. Higher molecular weights
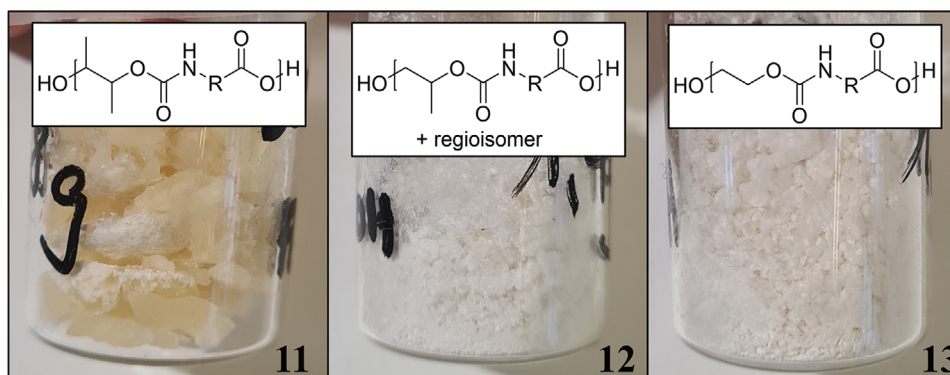
Figure 2. Poly(ester urethane) **11** after precipitation in ethanol and poly(ester urethane)s **12** and **13** after precipitation in methanol. R = -(CH$_2$)$_{10}$-
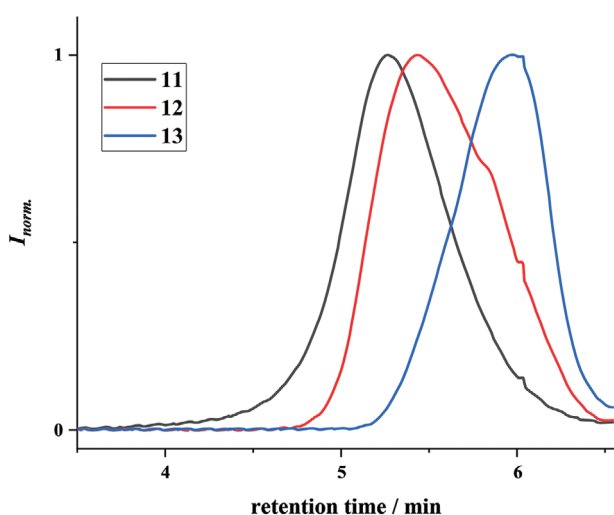

Figure 3. SEC measurements of synthesized poly(ester urethane)s **11**–**13**.

were no longer soluble in HFIP. For **11** and **12**, which were synthesized within 20 h, higher molecular weights of $M_n \approx 9$–11 kDa were reached. The T_g of the poly(ester urethane)s ranged between −48 and −9 °C, and the crystallization temperature increased with decreasing methyl group content from 59 °C (**11**) to 73 °C (**13**). **12** showed a second crystallization peak at 43 °C. Furthermore, each sample showed two melting peaks or at least a shoulder. Both minima of **11** and **13** differ about ≈15 °C, while the difference of **12** is ≈27 °C. It should be noted that **13** has a lower molecular weight due to the decreased reaction time. The melting enthalpy increases with decreased methyl group content from 29 to 45 J g^{-1}, providing information on the crystalline fraction of the polymer. This also relates to a loss in transparency, as can be seen in **Figure 4**, which shows pressed specimens for mechanical and rheological characterization. Sample **11** appears more transparent than **12**, most likely a result of the additional methyl branching, as **12** also seems more transparent than **13**.

Next, the mechanical properties of the synthesized poly(ester urethane)s were investigated to compare the influence of methyl groups within the polymer structure. Therefore, the poly(ester urethane)s were press moulded into suitable forms via a hotpress under vacuum (see Figure 4).
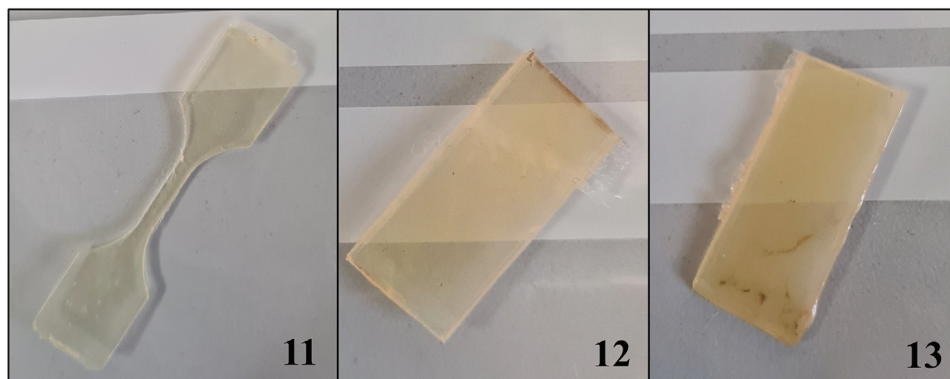
Tensile tests of the pressed polymers were tried using different grips for the measurements. Manual vise grips, wedge grips, and pneumatic grips were tested, resulting in the break of square and bone forms in the grip. Thus, tensile elongation of all three polymers could not be measured as the polymers were simply too brittle for the used grips. However, **13** seemed to be the most brittle polymer, followed by **12**. Sample **11** showed the lowest brittleness of the three poly(ester urethane)s, which is a further indication of the influence of the methyl groups.

Furthermore, poly(ester urethane) **12** and **13** were also too brittle to produce specimens for small-amplitude oscillatory shear (SAOS) and uniaxial elongational measurements with a thickness between 0.5 and 1 mm, as they break already during sample preparation. Thus, rheological measurements were performed using **11**. In **Figure 5**, the storage (G') and loss modulus (G'') as well as the magnitude of the complex viscosity ($|\eta^*|$) of **11** are analyzed at 130 and 150 °C.

Both measurements show neither flow behavior nor crossover even at the lowest measured angular frequency of $\omega = 0.01$ rad s^{-1}. According to DSC measurements, the sample should be melted, and we would expect flow behavior at 130 and 150 °C. This indicates that the sample's chemistry is changing, for instance, some branching or crosslinks are formed at high temperatures, e.g., during polymer pressing and/or SAOS measurements. To analyze the change of the sample at higher temperatures over time, we performed a time sweep at 130 °C, which corresponds to the temperature used for press-molding. The time sweep at a frequency of $\omega = 1$ Hz is shown in **Figure 6**.

The time sweep of **11** further confirms that the sample's chemistry is likely changing over time at a temperature of 130 °C, as discussed above. A further indication is, that the sample is not soluble in HFIP after the pressing anymore.

Incorporating long-chain branched or crosslinks into a polymer chain improves the stretchability of a material.[37,38] Therefore, we measured uniaxial elongation rheology at different Hencky strain rates, ranging from $\dot{\varepsilon} = 1$–0.01 s^{-1}. In **Figure 7**, the elongational viscosity of **11** is shown at 130 and 150 °C. The material shows strain hardening behavior for all investigated strain rates and both temperatures. The strain hardening describes the rise of viscosity above the predicted values from the linear viscoelastic behavior (LVE). The strain hardening factor (SHF) is the ratio of the maximum measured tensile stress growth coefficient η_E^+ over the predicted value of the LVE $\eta_{E,LVE}^+$, as shown in Figure 7.

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Figure 4. Bone shape form (1.45 mm thickness, 3.30 mm width, 45.0 mm length) of **11** pressed at 130 °C under vacuum and square forms (1.33 mm thickness, 7.75 mm width, 34.0 mm length) of **12** pressed at 150 °C and of **13** pressed at 130 °C.
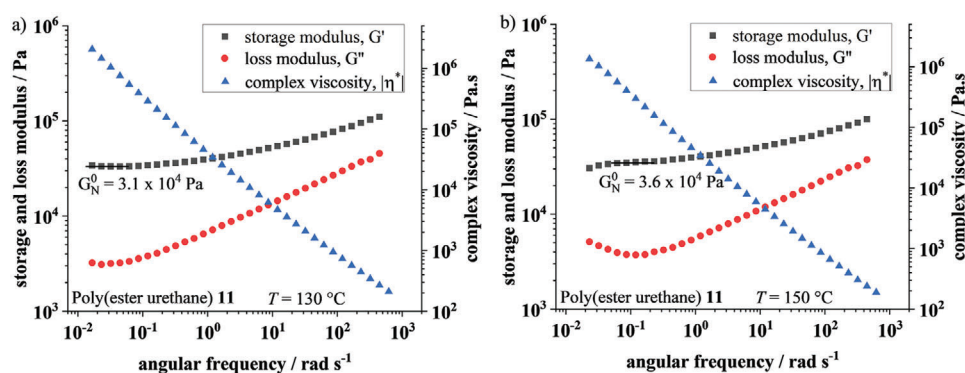
Figure 5. Small-amplitude oscillatory shear measurements of poly(ester urethane) **11** at a) 130 °C and b) 150 °C, each measurement performed with a new pressed specimen.
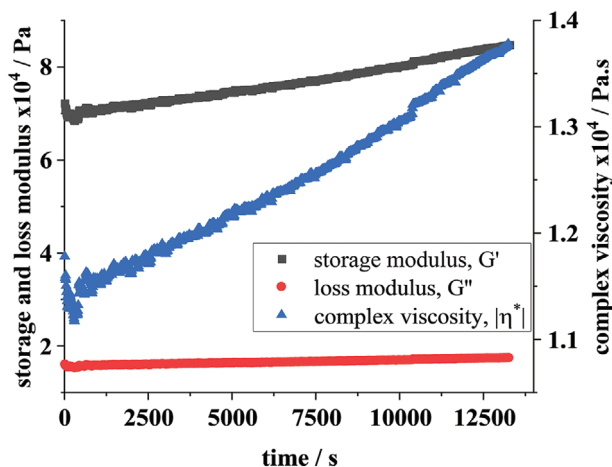
Figure 6. Time sweep of poly(ester urethane) **11** at 130 °C at a frequency of $\omega = 1$ Hz, indicating the chemical change of the material.

The SHF decreases with decreasing Hencky strain rate, which leads to SHF = 19–8 and SHF = 23–5 for 130 and 150 °C, respectively. The higher temperature has only a minor impact on the SHF, and in both cases, the steady state value is not reached. Since strain hardening is hardly seen in linear polymers, this behaviour indicates that the molecular structure of

poly(ester urethane) **11** contains some amount of long chain branching or crosslinks.[38] Therefore, **11** is a good candidate for some polymer processing operations, in which strain hardening behaviour in uniaxial deformation is necessary, e.g., in foaming processes.[39,40]

Thus, we performed proof-of-principle investigations in order to confirm a possible foaming of poly(ester urethane) **11**. One method to foam polymers is the one-step physical foaming process.[41] Within this process, polymers are saturated with a foaming agent, typically supercritical carbon dioxide ($scCO_2$). The saturation occurs at a specific temperature and pressure until the sample is completely saturated, and the nucleation of the cells is triggered by a sudden pressure drop. The cells can expand until the pressure within the cells is no longer sufficient to deform the surrounding polymer.[42] The cell stability during expansion can be enhanced by using a polymer that shows strain hardening, since the polymer melt becomes more stretchable and thus, prevents the cells from rupture and coalescence compared to a polymer without any strain hardening behavior.[43]

Indeed, the observed strain hardening of **11** enabled the foaming of this material. Whereas PU foam is typically produced by chemical foaming, the physical foaming behaviour of the synthesized sample **11** with $scCO_2$ as the foaming agent was observed. The sample was allowed to saturate for 8 h at 120 °C at 500 bar and was foamed during a depressurization rate of ≈200 bar s^{-1}. The resulting foam structure was analyzed using scanning electron

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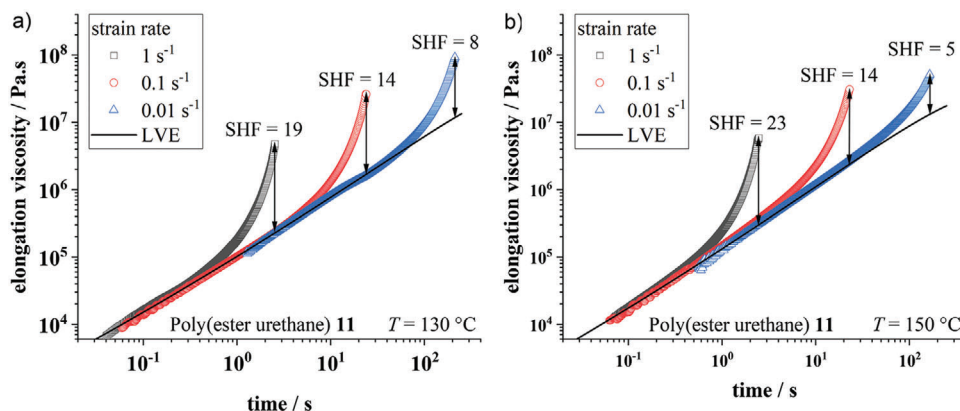
Figure 7. Elongational viscosity versus time for poly(ester urethane) **11** at Hencky strain rates ranging from 1 to 0.01 s⁻¹ at a) 130 °C and b) 150 °C measured with and extensional viscosity fixture (EVF).
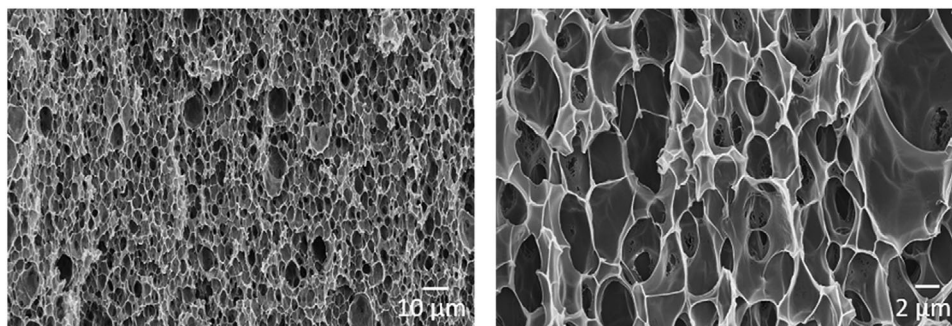
Figure 8. SEM images at different magnifications of **11** foamed with scCO₂ at 120 °C, and 500 bar with a depressurization rate of ≈200 bar s⁻¹.

microscopy (SEM), as shown in **Figure 8**. The structural details like foam density, volume expansion ratio, cell size, and density were analyzed (see the Supporting Information).

The PU-foam showed a predominantly closed-cell structure. However, in the magnification, it is noticeable that some cells are ruptured. The foam had a density of 0.16 g cm⁻³ and a volume expansion ratio of 7.2. The cell sizes are rather inhomogeneous, showing some isolated cells with a mean diameter of around 6 µm, whereas most cells range from 1.25 to 3.53 µm. The mean cell density was about 1.77×10^{12} cells cm⁻³. It should be noted that for semicrystalline polymers, not only the SHF is a relevant parameter, but also the crystallization behaviour.[44–46] Therefore, further to this proof-of-concept, it would be interesting to study the foaming behaviour of this material more in detail to find correlations between the structure-property relationship.

3. Conclusion

A sustainable synthesis of poly(ester urethane)s was investigated using renewable diols as starting materials. First, 2,3-butanediol, propylene glycol, and ethylene glycol were transformed into respective cyclic carbonates, being subsequently ring-opened using the methyl ester of 11-amino undecanoic acid. The obtained carbamate monomers were then polymerized to poly(ester urethane)s with M_n up to 10 kDa, characterized by ^{1}H NMR, IR spectroscopy, SEC and DSC analysis. SAOS and elongational viscosity were measured with the poly(ester urethane) derived from

2,3-BDO. Especially this poly(ester urethane) showed interesting properties, offering a reasonably high melting point of 89 °C in combination with transparency. Small-amplitude oscillatory shear, time sweep, and uniaxial elongation measurements indicate that the sample starts branching and forms crosslinks, as the sample shows no flow behavior in shear, an increasing viscosity over time, and strain hardening in elongation with an SHF of up to 23 at 150 °C and a Hencky strain rate of 1 s⁻¹. A foamed sample showed a density of 0.16 g cm⁻³ and a mean cell size ranging from 1.25 to 3.53 µm.

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.

Keywords

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