

Cyclic carbonates as building blocks for non-isocyanate polyurethanes

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Abstract

Three different cyclic carbonates (ethylene, propylene and butylene carbonate) that can be derived from CO₂ were successfully polymerized with hexamethylenediamine to form non-isocyanate polyurethanes (NIPUs) via self-polycondensation route without the use of harmful di-isocyanates. Three different catalysts were compared for their performance in self-polycondensation. Increasing the side chain length in cyclic carbonate increased the amount of urea side reaction and decreased the solubility of the final product. The increased amount of urea lead to a more thermoset behavior as the melting and decomposition took place simultaneously. Furthermore, the extent of urea side reaction and melting behavior were adjustable with the selection of the catalyst or polymerization parameters. With ethylene and propylene carbonate based precursors, it was possible to obtain promising melting temperatures and lap shear strength for the NIPUs when optimized polymerization parameters and catalyst were used.

1. Introduction

Non-isocyanate polyurethanes (NIPUs) are widely investigated in academia in order to replace conventional polyurethanes (PU) synthesized from polyols and harmful di-isocyanates. This need originates from the restriction set by European Chemical Agency (ECHA) to di-isocyanates due to their tendency to cause respiratory sensitization that could lead to occupational asthma ¹. Finding industrially viable NIPUs would have a significant impact on the human safety as PUs have several different industrial applications. For example, PU forms one fifth of the resin markets covering coatings, adhesives and sealants ².

NIPUs can be synthesized by several approaches, of which the step-growth polymerization or the polycondensation are recognized as the most viable ones ^{3,4}. In the step-growth polymerization, polyhydroxyurethanes (PHUs) are formed by reactions between di- or polyamines and mono- or polycyclic carbonates ³. PHUs differ from the conventional PU by their pendant OH groups ⁴.

These pendant OH groups are considered to increase adhesion, yet making PHU more prone to water absorption that might affect the long-term durability in industrial applications ^{4,5}. This could limit its use in demanding industrial applications. The polycondensation route on the other hand forms similar structures as the conventional PU and a diol condensates as side product during the reaction ³. Polycondensation can be performed as self-polycondensation when bis-alkyl or bis-hydroxyl carbamates are used as they have both carbamate and hydroxyl functionalities ^{6,7}. One example of such bis-hydroxyl carbamate is dihydroxyurethane (DHU) synthesized from monocyclic carbonate and diamine similarly as in the step-growth polymerization ³. In the literature, starting materials for the DHU synthesis are often based on ethylene carbonate (EC) and different amines such as hexamethylenediamine (HMDA) ⁶⁻⁹, diamines with secondary functionalities ¹⁰, diaminododecane ⁶ or diamines derived from vegetable oils ^{3,11}. Aside from self-polycondensation, the polycondensation reaction can be performed also between a carbamate and a diol ^{7,12-14} or a diacid ^{10,11}.

Even though there are well recognized alternative routes for the PU synthesis, there are certain technical limitations. In the polycondensation reaction, the molecular weights remain low ^{7,15} and

long reaction times are needed ¹⁵. To overcome this limitation, Rokicki et al. increased the molecular weight with the use of a catalyst and methylene chloride as the solvent ⁷. Moreover, by increasing the reaction temperature, higher molecular weights were achieved, although there was an increased risk of unwanted side reactions such as urea formation. Critical temperature for urea formation in ethylene carbonate and HMDA polycondensation was estimated by Ochiai et al. to be 150 °C ⁶. Higher yields were obtained by using a reduced pressure to shift the equilibrium towards the polycondensation reaction ⁶. With such optimized process parameters, high molecular weights from 12 000 to 21 000 g/mol were achieved. Similarly, Li et al. ⁹ achieved high molecular weights and tensile strength after performing the polycondensation reaction in bulk in the presence of a catalyst at elevated temperature and reduced pressure. Another approach to obtain higher molecular weights with improved mechanical properties is to introduce chain extenders or crosslinkers to the NIPU skeleton ¹⁰. These attempts have shown promising results and with careful selection of starting materials and their molar fractions, materials from very soft to hard and brittle can be tailored similar to conventional PUs ^{9,11,12,14}.

In addition to finding more user-friendly chemicals, there is a constant need to discover non-fossil based raw materials for polymer synthesis. One interesting pathway is to utilize CO₂, one of the greenhouse gases that can be captured from the air, as a starting material for chemical synthesis ¹⁶. Cyclic carbonates, such as ethylene carbonate (EC), propylene carbonate (PC) and butylene carbonate (BC), can be synthesized from CO₂ and diols ¹⁶ or epoxides ¹⁷ when a right catalyst is used ¹⁸. Furthermore, it is possible to achieve fully bio- or CO₂ based cyclic carbonates if the epoxide is manufactured from bio-ethanol, bio-naphtha ¹⁹ or epoxidized light olefin produced from CO₂ ²⁰. Light olefins can be synthesized directly from CO₂ and hydrogen with a novel reverse water gas shift (RWGS) reaction followed by a Fischer-Tropsch (FT) reaction²¹. Therefore, these monocyclic carbonates enable an attractive way of making more environmentally benign NIPU with the polycondensation method. With the right selection of diamine used in the DHU reaction, it is possible to produce fully biobased NIPUs. Biobased amines can be derived from natural polymers such as chitin, from corresponding amino acids, from vegetable oils or from biobased acids and

polyols²². HMDA can be synthesized from biobased sources such as high fructose syrup, starch or from 5-(hydroxymethyl)furfural²³ or from adipic acid²².

Successful NIPU self- or polycondensation has been conducted with EC and some diamines⁷, yet very little or no information exists on the reactivity and behavior of other monocyclic carbonates such as PC or BC that could also be derived from CO₂. In this study, all these environmentally benign monocyclic carbonates (EC, PC and BC) were compared in DHU synthesis with HMDA and subjected to self-polycondensation in reduced pressure and at elevated temperature with three different catalysts previously used in transesterification reactions^{24–26}. The ring-opening reaction with asymmetric cyclic carbonates (PC and BC) can yield either primary or secondary hydroxyl end-groups in DHU⁴ and the influence of different hydroxyl groups and pendant hydrocarbon chains of DHU in self-polycondensation was investigated for the first time. Basic characterization was performed with Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR). In addition, performance of the synthesized NIPUs were evaluated based on their molecular weight in size exclusion chromatography (SEC) and thermal properties were evaluated with differential scanning calorimetry (DSC) and with thermogravimetric analysis (TGA). Finally, NIPUs were evaluated for their industrial viability as hotmelt adhesives. The achieved novel results on the usability of monocyclic carbonates that can be derived directly from CO₂ gas, open new opportunities of using such environmentally friendly chemicals in industrial syntheses in the future.

2. Materials and Methods

2.1 Materials

Commercially available raw materials were used as received. Ethylene carbonate (EC, 99.5 %) and propylene carbonate (PC, 99.7%) were obtained from Huntsman and butylene carbonate (BC, 99 %), hexamethylene di-amine (HMDA, 98%), zinc acetate, titanium tetraisopropoxide and stannous octoate from Merck. Commercial raw materials were used for availability purposes in this

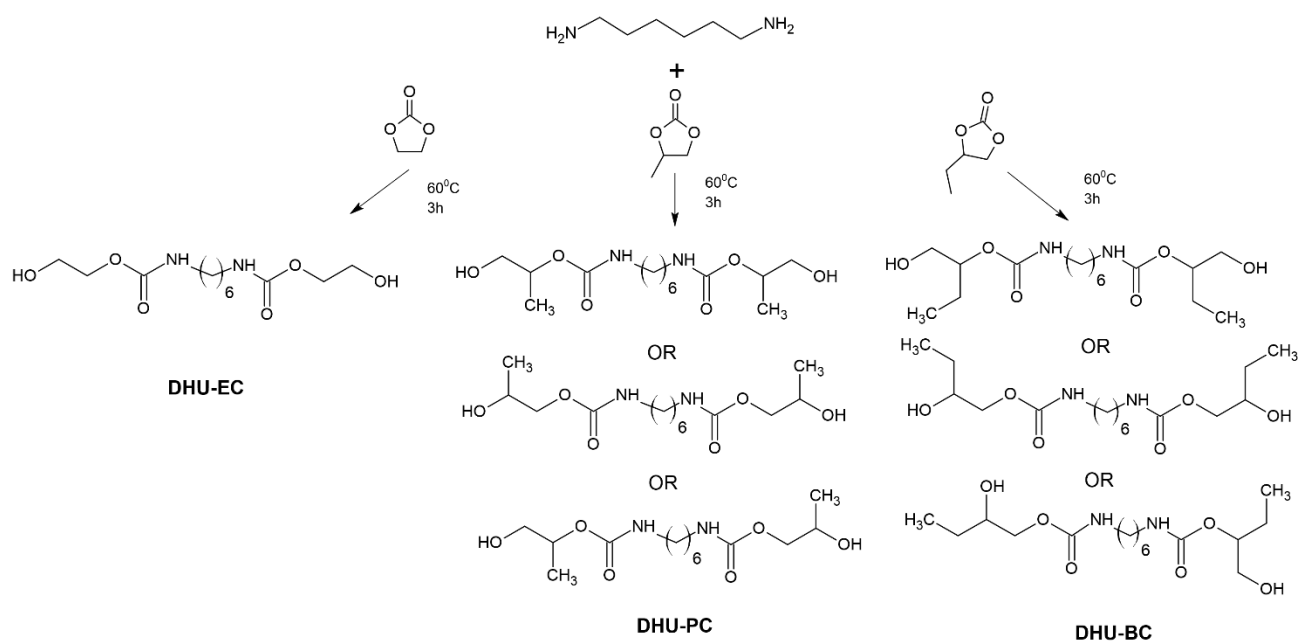
research, yet all the studied cyclic carbonates and HMDA could also be derived from CO₂²⁷ or bio based sources^{22,23}. The reagents DMSO-d₆ as well as 5 mM sodium trifluoroacetate (98%) were purchased from Sigma-Aldrich and 1,1,1,3,3,3-hexafluoro-2-propanol (99.9%) from Fluorochem.

2.2 Synthesis procedures

2.2.1 Dihydroxyurethane synthesis

Initially DHUs were prepared from EC, PC or BC with HMDA. The selected cyclic carbonate was weighed into a glass reactor of 50 ml equipped with mixing system, nitrogen inlet, temperature control with oil bath and a vacuum pump. After that a stoichiometric amount of amine was added and the reactions were conducted for 3 hours at 60 °C. The reaction schemes of DHU syntheses are shown in Scheme 1. Two types of hydroxyl end groups are possible to be formed with PC and BC, as the hydroxyl group is either in the primary or secondary position depending on the regioselectivity of the ring-opening⁴. Synthesized DHU samples, ethylene dihydroxyurethane (DHU-EC), propylene dihydroxyurethane (DHU-PC) and butylene dihydroxyurethane (DHU-BC) were used without further purification and analyzed with DSC, FTIR and NMR. Typical amounts of synthesized DHU varied from 5-7 g.

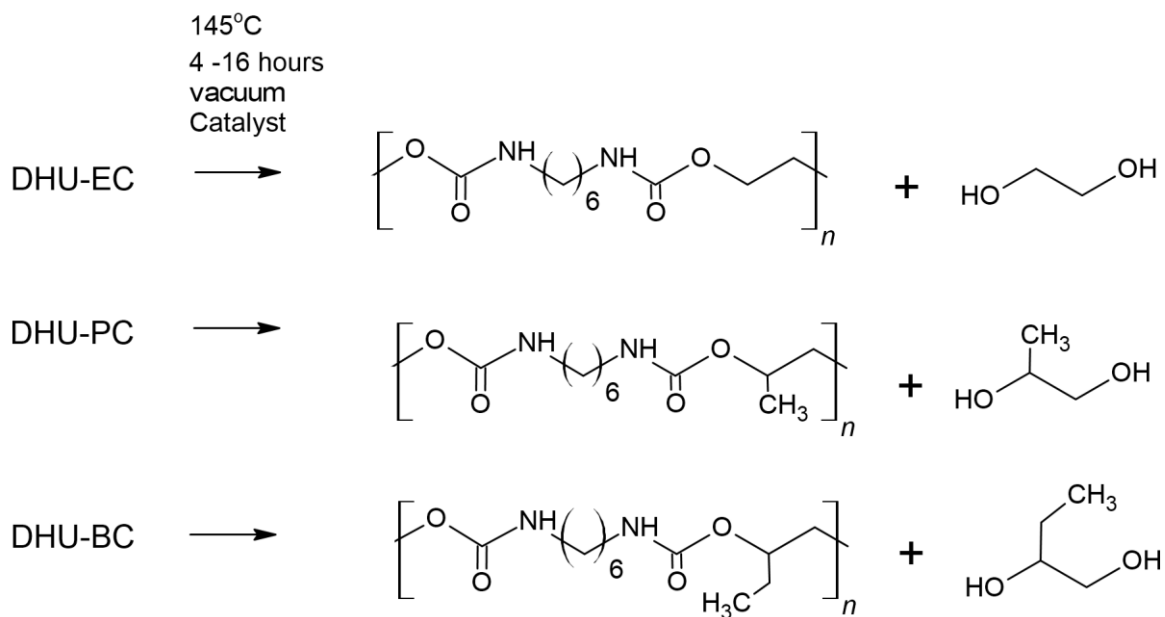
Scheme 1. Possible DHU structures with different carbonates. In DHU-PC and DHU-BC the DHU can also contain both primary and secondary end groups.



2.2.2 Self-polycondensation reaction

Self-polycondensation was performed at 145 °C in reduced pressure less than 2 mbar. **Typical amount in the self-polycondensation was 5 g of DHU precursor in a 50 ml glass vessel.** Initially the selected DHU and 5 mol% of catalyst were added to the reaction vessel while mixing with a magnetic stirring. A similar synthesis protocol has been used previously²⁸. Samples were taken over the time period (4-16 hours) to evaluate the influence of the polymerization time on the molecular weight. After the reaction time of 16 hours was completed, the material was left to cool down to room temperature and used as such for further analysis (SEC, NMR, DSC and FTIR). Three different catalyst types were evaluated: zinc acetate (Zn), titanium tetraisopropoxide (Ti) and stannous octoate (Sn). Samples were named NIPU-EC, NIPU-PC and NIPU-BC. The reaction scheme of the self-polycondensation reaction is shown in Scheme 2.

Scheme 2. Self-polycondensation of EC, PC and BC with possible structures



2.3 Characterization of materials

2.3.1 FTIR

FTIR measurements were performed with a Perkin Elmer Frontier FT-IR spectrometer equipped with a Specac attenuated total reflectance (ATR) diamond module. Spectra were collected over a range of 4000 - 550 cm^{-1} with a resolution of 0.4 cm^{-1} and with 8 scans per run. The spectra were analyzed with the PerkinElmer Spectrum (version 10.4.2.279). A press was used to ensure a close contact with the ATR diamond.

2.3.2 Molecular weight analysis

Molecular weights and molecular weight distributions of prepared polymers and their precursors were determined by SEC at 40 °C. The system was equipped with Waters Styragel columns and Waters 2410 refractive index detector. The eluent used was 1,1,1,3,3,3-hexafluoro-2-propanol (99.9%, Fluorochem) with 5 mM sodium trifluoroacetate (98%, Sigma-Aldrich) and was delivered at a rate of 0.5 mL/min. The results were calibrated against poly(methyl methacrylate) standards (Agilent Technologies).

2.3.3 Thermal analysis

DSC analysis was used to determine the melting temperature (T_m) and glass transition temperature (T_g) of the NIPU samples. The differential scanning calorimeter (DSC2, Mettler Toledo) was equipped with intra-cooler (TC 100MT, Huber) and run under nitrogen atmosphere. Samples of 3-6 mg were weighed into 40 μ L aluminum crucibles, lids were perforated, and crucibles were closed with cold-pressing. Samples were heated twice with the heating rate of 10 $^{\circ}$ C/min. In the first scan, the samples were cooled down to -50 $^{\circ}$ C and heated to 100 $^{\circ}$ C. In the second scan, samples were cooled down to -50 $^{\circ}$ C and heated to 320 $^{\circ}$ C. The results were obtained with the Mettler Toledo STARe software (version 13.0). The data were collected from the second heating scan.

TGA was carried out with the Netzsch STA 44F1 equipment to evaluate the thermal stability of the samples. Samples of 9-11 mg were weighed into 85 μ L open aluminum crucibles. Samples were heated at a heating rate of 20.0 $^{\circ}$ C/min over a temperature range of 40 – 900 $^{\circ}$ C under nitrogen atmosphere. The analysis was carried out with the Netzsch Proteus software. The weight loss of 5 %, $T_{5\%}$, was used to analyze the thermal stability.

2.3.4 NMR

Liquid phase NMR spectra were recorded using a Bruker Avance III 500 NMR spectrometer with a magnetic flux density of 11.7 T. The spectra were acquired with a 5 mm BB(F)O double resonance probehead and DMSO- d_6 was used as a solvent. The spectra were referenced either to residual (1 H, 2.52 ppm) or deuterated signal (13 C{ 1 H}, 39.52 ppm) and the relaxation delay between the successive scans was 20 s.

In propylene DHUs and NIPUs, the ratio between urea (5.71 ppm, 2H), urethane (1.13 ppm, 3H), primary-OH (1.09 ppm, 3H) and secondary-OH (1.04 ppm, 3H) end-groups was calculated from the baseline corrected integrals. In the case of ethylene DHUs and NIPUs, the ratio between the urea (5.71 ppm, 2H), urethane (4.07 ppm, 4H), and end-groups (3.93 + 3.52 ppm, 4H) were calculated similarly. The characterization and assignation of both ethylene and propylene DHU as

well as ethylene NIPU has been reported previously^{7,29}. Conversely, the differentiation of butylene DHU and NIPU spin-systems were determined using double-quantum filtered COSY, HSQC, and H2BC 2D NMR. In this case, urea (5.71 ppm, 2H), urethane (3.97 ppm, 2H), primary-OH (4.49, 1H), and secondary-OH (3.48, 1H) end groups were differentiated.

The ¹³C cross-polarization (CP) magic angle spinning (MAS) NMR measurements were performed using an Agilent DD2 600 NMR spectrometer with a magnetic flux density of 14.1 T, equipped with a 3.2 mm T3 MAS NMR probe operating in a double resonance mode. Samples were packed in ZrO₂ rotors, and the MAS rate in experiments was set to 10 kHz. Contact time of 3 ms and relaxation delay from 5 to 7 s between the scans were used. Protons were decoupled during acquisition using SPINAL-64 proton decoupling. The chemical shifts were externally referenced via hexamethylbenzene by setting the high field signal to 38.3 ppm.

2.3.5 Microscopic evaluation

Microscopic evaluation was conducted with Zeiss Zxio Scope A1 with heatable Linkam stage THMS 350V. Tested temperature range was 25 to 290 °C with a heating rate of 3 °C/min. The analysis was done with Zeiss Zen 32 software.

2.3.6 Lap shear strength tests

Lap shear strength testing was performed according to the EN 1465 standard using Instron 3366 machine with a load cell of 10 kN. The analysis was performed with Bluehill software. The material was melted at 130 °C, applied on beech surface and pressed until the sample was cooled. Three parallel test specimens were tested with a speed of 10 mm/min. The length of specimen overlap was 12.5 ± 0.25 mm, and the exact surface area was measured prior the test.

3. Results and discussion

3.1 Synthesis of DHU

Synthesized DHU-EC and DHU-PC were white solids and DHU-BC was a clear viscous liquid. The DHU-EC ^1H NMR, ^{13}C NMR and FTIR spectral data (Figure ESI 1, 2, 3) were in close agreement with the published resonances ^{7,29}. The ^1H NMR spectra of DHU-PC matched well with the previously published reference (Figure ESI 4) ²⁹. Furthermore, as expected, both primary and secondary hydroxyl groups were detected in the ^1H NMR spectra due to the regiochemistry of the ring-opening reaction of PC ⁴. Based on NMR spectra, the obtained DHU-PC contained primary and secondary hydroxyl at fractions of 60% and 40%, respectively. This is in accordance to the previous research on the ring-opening reaction with PC ^{29,30}. As in case of DHU-EC, these findings were supported by ^{13}C NMR in which two carbonyl signals were detected (Figure ESI 5) and the FTIR spectrum showed the absorption bands typical for polyurethane (Figure ESI 6).

DHU-BC was a novel compound and previous spectral data was not available. Based on FTIR (Figure ESI 7) and ^1H and ^{13}C NMR analysis (Figure ESI 8, 9) the signals matched well the expected DHU structure. The structure was confirmed with 2D NMR (COSY, HMBC, H2BC) (Figure ESI 10,11 and 12). Similarly to DHU-PC, the mixture of regioisomers was 60% primary and 40% secondary hydroxyl groups.

In the second heating scan with DSC of DHU-EC (Table 1, Figure ESI 13), two melting points, T_m , at 44 °C and 92 °C were detected accompanied with cold crystallization in between. No glass transition point, T_g , was observed in DHU-EC, which suggests a very rigid structure due to both short linear hard segments as well as multiple hydrogen bonding sites from urethane groups. DHU-PC and DHU-BC had T_g at -19 °C and -29 °C, respectively, implying that the hydrocarbon side group in DHU-PC and DHU-BC increased the mobility and amorphous nature of the DHU. DHU-PC had a melting point at 63 °C. DHU-BC was a viscous liquid and the melting point of crystalline part was not detected.

As a conclusion it was possible to synthesize DHU compounds from selected cyclic carbonates, EC, PC or BC. The ring opening reaction was fully completed within 3 hours. The side group originating from the cyclic carbonate structure in case of PC and BC decreased the rigidity and increased the amorphous nature of DHU structures.

3.2 Self-polycondensation

All synthesized DHU samples were used as precursors in self-polycondensation reaction at elevated temperature and reduced pressure with either zinc acetate (Zn), titanium tetraisopropoxide (Ti) or stannous octoate (Sn) catalyst. Analyses of NIPUs after 16 hours of self-polycondensation are collected in Table 1, while more detailed molecular weight results are presented in the supplementary material (Table ESI 1). In the next sections, the NIPU production using different precursors (EC, PC or BC), are discussed separately in more detail.

Table 1. Analysis results of NIPU materials after 16 hours of self-polycondensation

Sample	Catalyst*	Molecular weight			DSC			TGA	FTIR		
		Mn [g/mol]	Mw [g/mol]	PDI [-]	Tg [°C]	Tm [°C]	H [J/g]	T5% [°C]	NH [cm-1]	C=O [cm-1]	Amide [cm-1]
DHU-EC	-				-	44 / 92	43/174		3325	1682	1526
NIPU-EC	Zn	2591	10919	4.2	29	170	81	230	3309	1681	1531
NIPU-EC	Ti	863	14131	16.4	36	170	79	245	3312	1681	1531
NIPU-EC	Sn	1141	6559	5.7	35	257/270	56/3	265	3318	1615	1567
DHU-PC	-				-19	63	103		3323	1681	1524
NIPU-PC	Zn	3135	32869	10.5	42	250/281	54/21	220	3318	1692/1621	1531
NIPU-PC	Ti	2624	15213**	5.8	-	243/281	26/60	250	3320	1620	1563
NIPU-PC	Sn	2162	16059	7.4	55	252/281	26/63	240	3322	1699/1615	wide 1567
DHU-BC	-				-29	271	254		3322	1683	1533
NIPU-BC	Zn	3633	39260**	10.8	31	252/284	49/59	225	3322	1694/1618	wide 1557
NIPU-BC	Ti	2495	17590**	7.1	43	248/272	19/78	265	3320	1615	1567
NIPU-BC	Sn	2649	19292**	7.3	-	284	128	275	3319	1614	1567

* Zn (zinc acetate), Ti (titanium tetraisopropoxide), Sn (stannous octoate)

** Partially soluble

3.2.1 NIPU-EC

Self-polycondensation of DHU-EC has been demonstrated in other publications^{6,7,28}. The self-polycondensation of DHU-EC was followed over time and the final analysis was carried out after 16

hours reaction time. It was noticed that after 16 hours NIPU-EC molecular weights remained relatively low and the polydispersity index (PDI) was high, particularly with the Ti catalyst (Table 1). Such high values indicates insufficient solubility of the sample, and the results were not considered as reliable. The NMR analysis was conducted for NIPU-EC-Zn (Figure 1) and NIPU-EC-Ti (Figure ESI 14) samples, but NIPU-EC-Sn was not soluble enough for the analysis. Clearly, the catalyst selection impacted the solubility and thus the self-polycondensation reaction. The only recognized side reaction in the literature for self-polycondensation of DHU is the back-biting reaction of the hydroxyl end group, forming an amine and a cyclic carbonate, leading to urea (Scheme 3)^{6,7}. Polyurea is known to have a poor solubility in common solvents making the analyses difficult³¹, which was the plausible reason for the NIPU-EC-Sn solubility issues. This was further supported with solid state ¹³C CP-MAS spectra where only polyurea signal was detected (Figure ESI 15).

The detailed ¹H NMR analysis from NIPU-EC-Zn (Figure 1) showed a successful synthesis of NIPU. The spectra matched well the resonances reported by Ochiai et al.⁶. In addition to similar peak assignments as in DHU-EC, relative signals of DHU end groups have reduced, the signals for polyurethane and urea signal have appeared. The amount of urea and urethane groups were calculated from the ¹H NMR spectra and the amount of urea was 11% both in NIPU-EC-Zn and NIPU-EC-Ti. This is in accordance with the research by Ochiai et al.⁶. Furthermore, the amount of DHU end groups were evaluated from the ¹H NMR spectra. The Ti catalyst was slightly more effective in the reaction progression (12% of end groups left) than Zn (22% end groups left). The FTIR analysis supported the findings (Figure 2). With NIPU-EC-Zn and NIPU-EC-Ti almost identical spectra were obtained with absorption bands typical for urethane at 3309 cm⁻¹, 1681 cm⁻¹, 1531 cm⁻¹ and 1250 cm⁻¹. The urethane carbonyl absorption band at 1681 cm⁻¹ was wider than the one in DHU-EC indicating that polyurea absorption band (at around 1620 cm⁻¹³¹) was overlapping with the polyurethane carbonyl absorption band. The wavelengths were relatively low compared to typical urethane values indicating strong hydrogen bonding³². In the FTIR spectra of NIPU-EC-Sn sample, the main carbonyl absorption band had shifted from 1681 cm⁻¹ to 1615 cm⁻¹ indicating that the carbonyl absorption band originates from urea groups instead of urethane^{31,33}. However, a

small shoulder was observed at around 1680 cm^{-1} that could originate from the urethane carbonyl group. Furthermore, the N-H bending was shifted from 1531 to 1567 cm^{-1} .

Scheme 3. Urea side reaction ^{6,7}

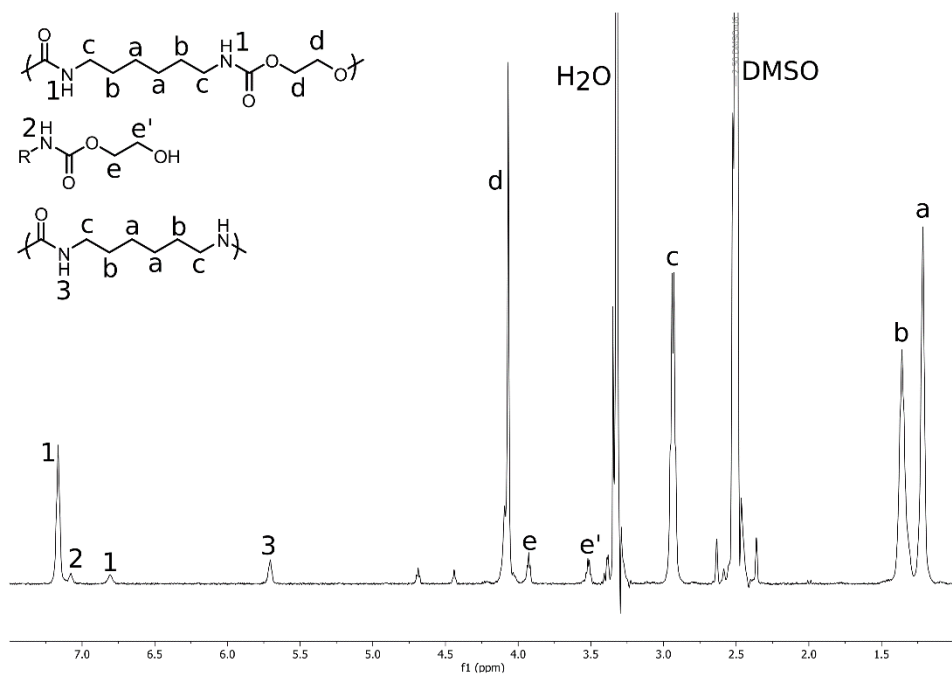
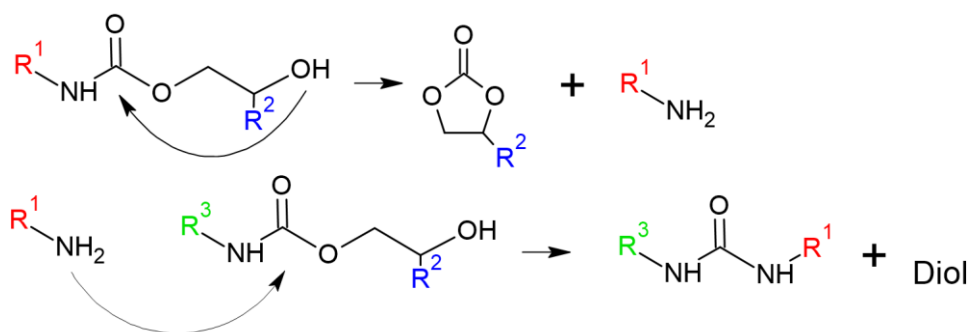


Figure 1. ^1H NMR ($\text{d}_6\text{-DMSO}$) for NIPU-EC-Zn with selected assignments

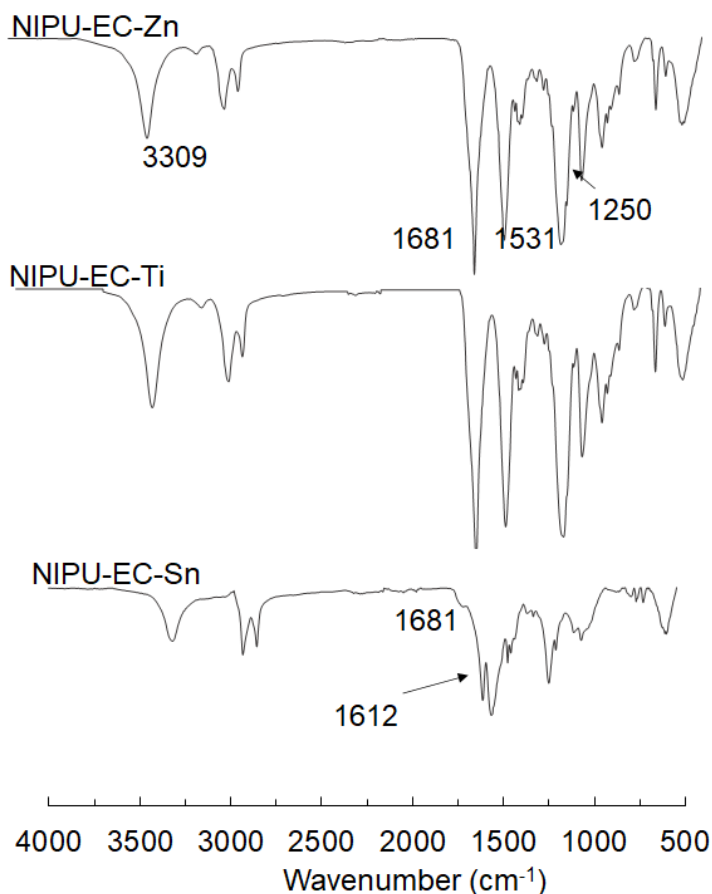


Figure 2. FTIR spectra of NIPU-EC synthesized in presence of three different catalysts

Thermal analyses were performed for NIPU-EC samples (Table 1, Figure ESI 16, 17). Thermal stabilities were at the similar level as previously reported for NIPUs^{6,14} and the stability decreased in the order of Sn-Ti-Zn. In the second heating scan with DSC, differences were detected between each catalyst confirming the NMR and FTIR observations. Ti- and Zn-catalyzed NIPU-ECs had a melting point of 170 °C, whereas Sn-catalyzed NIPU-EC only melted simultaneously to its decomposition process. All NIPU-ECs had relatively high T_g of 29-36 °C indicating rigid polymer structure originating from short linear repeating units consisting of hard segments and from strong hydrogen bonding. The higher melting point of Sn-catalyzed NIPU-EC can be explained by urea formation, as urea has a high melting point (269 °C³¹) due to strong hydrogen bonding interactions. In order to evaluate the melting behavior of NIPU-EC-Sn further, heating under a microscope was performed and the reactions were monitored visually. During the heating to 290 °C no clear melting behavior was detected, and the material did not flow at elevated temperatures

(Figure ESI 18) indicating that the polymer did not fully melt, and melting was accompanied with polymer degradation as seen from TGA and DSC results.

Based on these analyses, NIPU-EC could reach an industrially interesting melting point of 170 °C with low urea formation when using the Ti or Zn catalyst. If the Sn catalyst was used, the synthesis was directed more towards polyurea formation. Polyurea increased the melting temperature of NIPU-EC-Sn close to its decomposition temperature making the material difficult to be used as such in thermoplastic applications.

3.2.2 NIPU-PC

The self-polycondensation on DHU-PC has not been reported elsewhere. Synthesized NIPU-PC materials had similar solubility issues as NIPU-EC-Sn in SEC and in NMR measurement. The NMR analysis was carried out for Zn- and Sn-catalyzed NIPUs after 16 hours (Figure 3, Figure ESI 19), but Ti-catalyzed NIPU-PC analyses was conducted only after 6 hours due to the solubility issues (Figure ESI 20).

In ^1H NMR spectra of NIPU-PC-Zn (Figure 3), urea and urethane signals were detected in addition to the same signals as in DHU-PC. FTIR analyses support the findings (Figure 4) where the absorption bands consist of typical polyurethane absorption bands (3318 cm^{-1} , 1692 cm^{-1} , 1531 cm^{-1}) as well as typical polyurea bands (1621 cm^{-1} and 1560 cm^{-1}). These findings are further supported with the comparison of the solid-state ^{13}C CP-MAS spectra of DHU-PC and NIPU-PC-Zn that indicated the presence of both urethane and urea groups in the solid sample, dispelling doubts that the liquid state ^1H NMR obtained from the poorly soluble sample misrepresents the overall bulk material (Figure ESI 21).

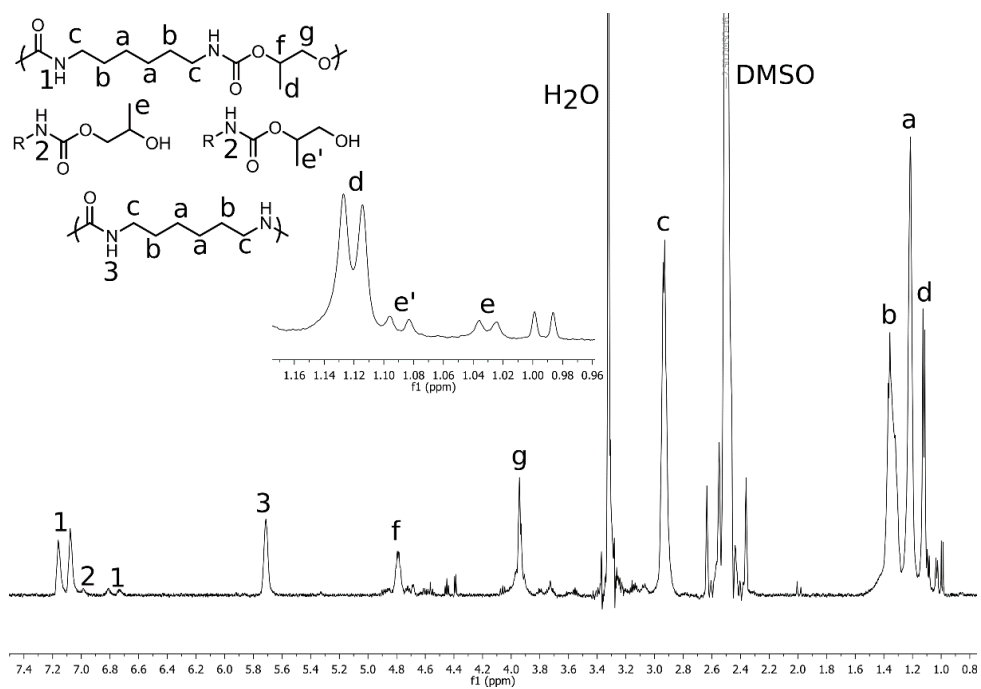


Figure 3. ^1H NMR ($\text{d}_6\text{-DMSO}$) spectra for NIPU-PC-Zn with selected assignments

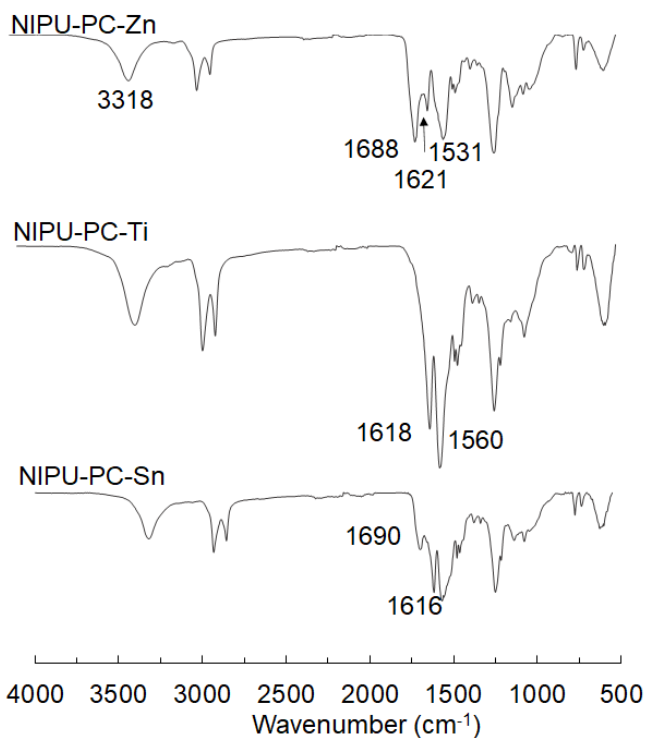


Figure 4. FTIR spectra of NIPU-PC samples prepared with three different catalysts

From NMR and FTIR analyses it is evident that the amount of urea groups was increased compared to NIPU-EC and the amount of urea groups calculated from NMR spectra varied from 37% (Zn) to 52% (Sn). The increased amount of urea groups compared to NIPU-EC could be due

to the different hydrogen bonding capability of DHU-PC with side chain that reduce the number of hydrogen bonds between chains compared to linear DHU-EC^{34,35}. Another possible reason could be the reactivity differences for cyclic carbonate, where the amine originating from back biting reaction more readily attacks the NIPU polymer instead of the cyclic carbonate to reform DHU. This is supported by the fact that in DHU synthesis PC has been found less reactive²⁹. Significant reactivity differences between the secondary and primary OH groups were not identified with Zn or Ti catalysts, but with Sn catalyst the relative amount of primary groups was decreased over secondary groups. The calculated amount of unreacted DHU and NIPU hydroxyl end groups in NMR were 15% (Zn), 25% (Sn), and 18% (Ti, 6 hours). When evaluating molecular weights of NIPU-PC in SEC after 16 hours, the sample prepared with Zn catalyst had the highest molecular weight, yet the PDI was high, which was expected due to the poor solubility. Further some undissolved matter was detected with Ti catalyst. Thus the molecular weight results cannot be considered accurate.

Thermal stability of NIPU-PC was on the same level as with NIPU-EC, although Ti catalyst had the best stability (Figure ESI 22). In the second DSC heating scan (Figure ESI 23) NIPU-PC had similar melting behavior regardless of the catalyst with two T_m s at 250 °C and 280 °C. All NIPU-PC samples had a higher amount of polyurea compared to NIPU-EC-Zn and NIPU-EC-Ti and therefore the melting of crystals seemed to happen at the same time with degradation as in case of NIPU-EC-Sn sample. In addition, T_g s were slightly increased from those of NIPU-EC: NIPU-PC-Sn had T_g at 42 °C and NIPU-PC-Zn at 55 °C. With the Ti catalyst no T_g was observed. Some surface changes were observed in microscopic analysis during heating of NIPU-PC sample (Figure ESI 24). However, the material became dark brown suggesting that decomposition took place simultaneously.

NIPU synthesis was successful with the DHU-PC precursor. The amount of urea side reactions increased compared to NIPU-EC. Furthermore, NIPU-PC had high T_m parallel to its decomposition temperature making the NIPU-PC unsuitable to be used in an industrial application as such. Thus,

further formulating of NIPU-PC offers intriguing possibilities for further research in order to improve the melt behavior.

3.2.3 NIPU-BC

BC is a less abundant material commercially and it has not been studied previously in NIPU reactions. Yet, in case that cyclic carbonates would be manufactured from CO₂ with RWGS and FT method, the cyclic carbonates synthesized from epoxidized mixed olefins would yield a mixture of EC, PC and BC. Therefore, the reactivity and usability of BC in self-polycondensation is of interest.

Similar to NIPU-PC, NIPU-BC samples had solubility issues for performing SEC and NMR measurements. The NMR analysis (Figure 5, Figure ESI 25-27) was carried out only from Zn-catalyzed NIPU-BC (NIPU-BC-Zn), yet some solubility challenges made the analysis less certain with NIPU-BC-Zn as well. However, based on solid state ¹³C CP-MAS spectra, both urea and urethane signals were detected supporting the liquid state ¹H NMR results (Figure ESI 28). The liquid state ¹H NMR analysis revealed presence of urea signal in addition to the signals identified in DHU-BC. The amount of urea groups was estimated to be 40% and the amount of end groups was 12% after 16 hours of reaction. In the FTIR spectra (Figure 6) NIPU-BC-Zn had both urethane and urea carbonyl absorption bands (1694 and 1618 cm⁻¹). Same is shown in wide amide absorption band at 1533-1557 cm⁻¹ where urea and urethane amide absorption bands overlap. With Sn- and Ti-catalyzed NIPU-BC only absorption band from polyurea carbonyl was visible at 1616 cm⁻¹ indicating that polyurea was the main component in the polymer.

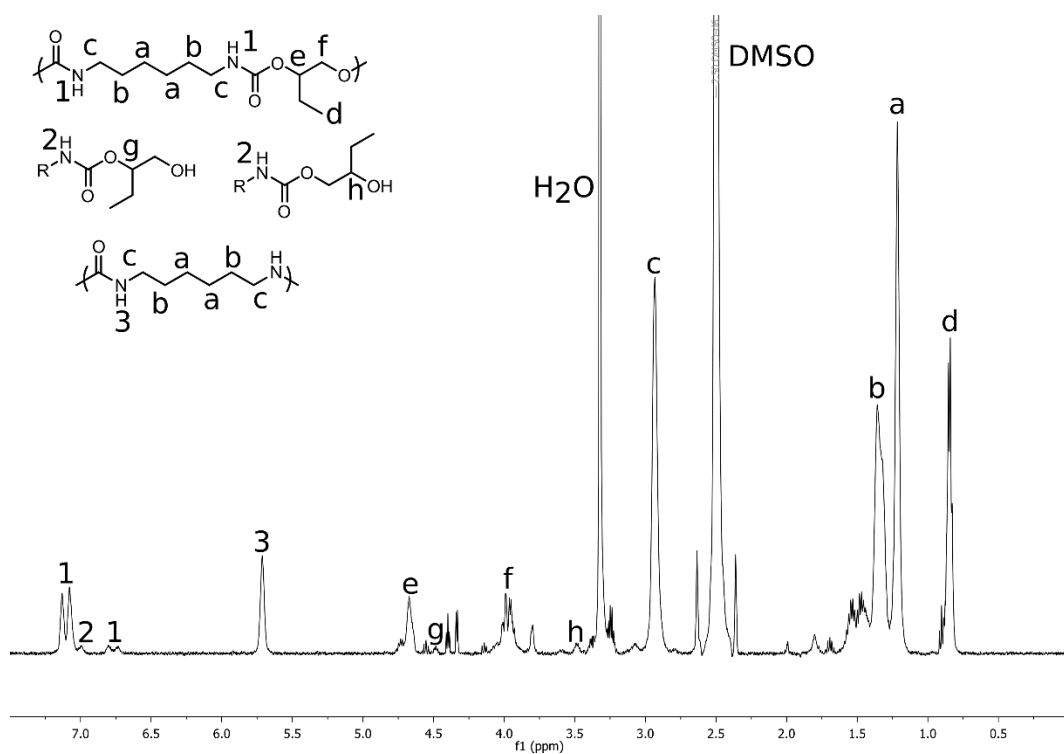


Figure 5. ^1H NMR ($\text{d}_6\text{-DMSO}$) spectra for NIPU-BC-Zn with selected assignments

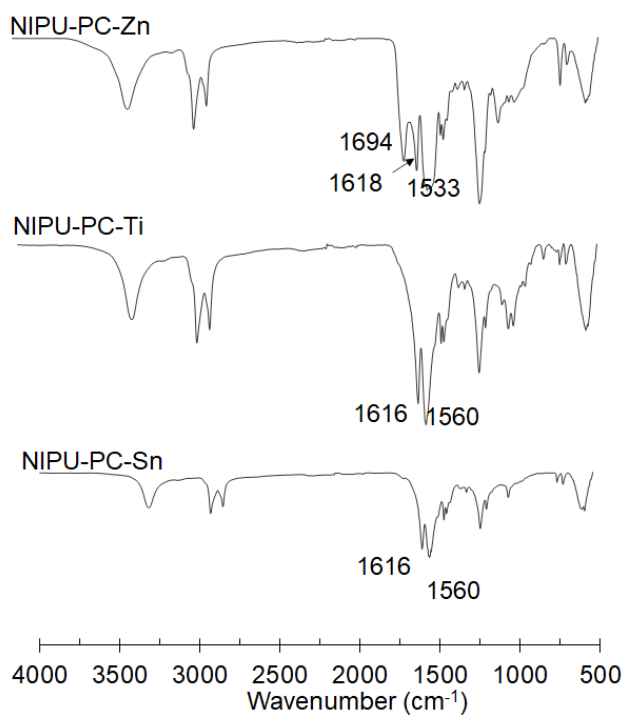


Figure 6. FTIR spectra of NIPU-BC samples prepared with three different catalysts

Based on the thermal data (Figure ESI 29, 30) two melting points were detected with Zn- and Ti-catalyzed systems at 250 °C and 280 °C, which were parallel to the degradation temperature

according to TGA data. Sn-catalyzed samples had a higher melting temperature and the second melting point was not clearly detected due to polymer degradation. Clear melting behavior of NIPU-BC was not detected in microscopic evaluations further verifying the overlapping melting and decomposition processes (Figure ESI 31). The observed T_g s varied from 34 °C to 43 °C with Zn and Ti catalyst. No T_g was observed with Sn catalyst. This could be due to the higher amount of urea and its stronger tendency for hydrogen bonding. Thermal stability decreased in order of the Sn>Ti>Zn catalyst and was on a similar level as with NIPU-EC and NIPU-PC.

To summarize, the self-polycondensation reaction with DHU-BC was demonstrated. However due to the bulky side groups, urea formation was favored. This caused the melting temperature to overlap with the decomposition temperature making the polymer unusable in thermoplastic applications.

3.3 Industrial feasibility of synthesized NIPUs as adhesives

In order to evaluate the industrial feasibility as hotmelt adhesives, an additional study was carried out to evaluate the adhesive properties of NIPU samples. The laboratory scale up was performed with EC and PC due to their better commercial availability and Sn catalyst was selected as it is a liquid and easy to use in industrial processes. The samples were named NIPU-EC-IND and NIPU-PC-IND.

Firstly, the minimum level of catalyst was determined with NIPU-PC as it was less reactive than in case of NIPU-EC. It was noticed from the SEC results that the high amount of catalyst (5 mol%) could also have an adverse effect on polymerization and side reactions (Table ESI 2). Based on the screening on NIPU-PC samples, decreasing the catalyst amount to 0.05 mol% was possible and the reaction advanced well based on the SEC data. Therefore, it was decided to use 0.05 mol% of catalyst dosage in the laboratory scale up tests.

The larger scale equipment was equipped with a 2000ml glass reactor in an oil bath with mixing rate of 100 rpm. Typical amount for the scale up was 250 g of precursor DHU. The equipment had

less effective vacuum (10 mbar) compared to the initial self-polycondensations. Based on initial screening it was decided to use higher temperature of 175 °C and shorter reaction time of 4 hours (Table ESI 4). Still, molecular weights remained rather low with high PDI with both NIPU-EC-IND and NIPU-PC-IND (Table 2). The measured molecular weights correlated to the amount of end groups calculated from NMR. The amount of unreacted end groups calculated from NMR was high with NIPU-EC-IND (40%) (Figure ESI 32) and the molecular weight was low. Interestingly, the amount of end groups was clearly lower in NIPU-PC-IND (16%) (Figure ESI 33) and the molecular weight was higher than in NIPU-EC-IND. The urea amount based on ¹H NMR of NIPU-EC-IND was slightly higher than the urea amount of Ti- or Zn-catalyzed NIPUs in the initial tests (14% vs 11%). With NIPU-PC-IND, the urea amount was relatively small (27%) considering the low amount of end groups (16%) compared to the initial self-polycondensation with 5 mol% of catalyst (urea amount 52% with 25% end groups). The amount of primary and secondary hydroxyl groups matched with initial polymerizations. FTIR analyses supported the lower amount of urea as the absorption band for polyurethane carbonyl was clearly present at 1685 cm⁻¹ both in NIPU-EC-IND and NIPU-PC-IND (Figure ESI 34). The lower amount of urea was expected due to the combination of smaller amount of catalyst and weaker vacuum.

In DSC analyses (Figure ESI 35), NIPU-EC-IND had two melting temperatures at 110 °C and 140 °C while NIPU-PC-IND had a melting temperature at 130 °C. The lower melting temperature of NIPU-EC-IND compared to previous analyses on NIPU-EC could be due to lower molecular weight and therefore the higher amount of unreacted end groups seen in NMR analysis. Yet, the thermal stability was on the same level as in previous initial polymerizations (Figure ESI 36). Typical melting range for hotmelt adhesives lay at 90-140 °C which lead to proper wetting on surface³⁶

Lap shear strength specimen on beech was used for evaluating the adhesive properties. The samples were manufactured at 130 °C and both showed promising lap shear strength results on beech ranging from 2.1 to 2.6 N/mm² for NIPU-EC-IND and NIPU-PC-IND respectively. This is on a similar level to previous hotmelt adhesion results on NIPUs in wood bonding, where dry strength varied from 2.76 to 3.25 N/mm² ³⁷.

Table 2. Results for scale up of NIPU-EC-IND and NIPU-PC-IND

Sample*	Molecular weight			T _g [°C]	DSC**		TGA		FTIR			LSS*** [N/mm ²]
	M _n [g/mol]	M _w [g/mol]	PDI [-]		T _m [°C]	H [J/g]	T5% [°C]	NH [cm ⁻¹]	C=O [cm ⁻¹]	Amide [cm ⁻¹]		
NIPU-EC-IND	330	6476	19.6	0	110 / 140	9 / 45	230	3318	1682/1615	1531	2.1	
NIPU-PC-IND	1895	8873	4.7	28	130	10	245	3316	1685/1625	1530	2.6	

*Sn catalyst, 0,05 mol%, 175C, 10 mbar, 4 hours,** Second heating scan, *** Lap shear strength on beech

Based on the larger scale self-polycondensation reaction, urea content can be reduced with less vacuum and catalyst. However, there were challenges with high PDI and the molecular weight remained low. The reduction of urea content leads to lower melting temperatures, which enables suitability for hotmelt adhesives in industrial applications. Furthermore, the promising adhesive properties evaluated as lap shear strength on beech paves the way towards industrial applications.

4. Conclusions

It has been shown that different monocyclic carbonates (EC, PC and BC) that can be produced from CO₂ can be utilized in DHU synthesis together with HMDA. For all these monocyclic carbonates, synthesis of NIPUs by self-polycondensation reactions of DHU precursors was demonstrated. All synthesized NIPUs had similar thermal stability as those reported in the literature. Based on the analysis of this study, the solubility decreased and the amount of urea side groups increased when asymmetric cyclic carbonate with a hydrocarbon side group was used. The decrease in solubility could be due to poor solubility of polyurea segments as well as the strong hydrogen bonding capability of short chained polymers. In addition to the starting cyclic carbonate, it was discovered that the amount of urea could be controlled with selecting the right processing parameters (catalyst, polymerization time and vacuum). When PC or BC was used in the reaction, both primary and secondary hydroxyl end groups were introduced to DHU in a ratio of 60% primary hydroxyl and 40% secondary hydroxyl groups. Some differences of the reactivity of primary or secondary hydroxyl groups in self-polycondensation were detected depending on the selected

catalyst, and in some cases the primary hydroxyl groups were observed to be more reactive than secondary hydroxyl groups. The available end groups for self-polycondensation seemed to decrease faster with the increasing length of cyclic carbonate side group, which might partly be due to urea side reactions. When the polymer contained both polyurethane and a significant amount of polyurea, the melting point was increased to the same level as the decomposition temperature. When the amount of urea was smaller, the thermal behavior was more suitable for industrial purposes and promising lap shear strengths on beech were obtained in larger test batch with lower vacuum.

All the synthesized NIPUs consisted solely of hard segments. However, looking at the promising adhesive strength results and high thermal stability of the hard segments, industrially viable polymers could be synthesized with the introduction of soft segments to the polymer. More effort should be placed on finding suitable soft segments and faster and more reliable polycondensation parameters in order to enable effective industrial processes.

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Appendix A. Supplementary material

Supplementary data is available.

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