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High Molar Mass Non-Isocyanate Polyurethanes by Transurethanization of Diols with Isophorone-Based Bismethylcarbamate

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The synthesis of thermoplastic polyurethanes (TPU) has been associated with sustainability issues, prompting the development of alternative synthesis routes avoiding the use of isocyanates. One approach deals with non-isocyanate polyurethanes (NIPUs), which are obtained by transurethanization of bismethylcarbamates and diols. However, this reaction exhibits reactivity penalties in comparison to the polyaddition of isocyanates with diols, and the optimization of the reaction conditions is required to achieve high molar mass polyurethanes. In this report, a series of NIPUs is synthesized via transurethanization using methyl((5-((methoxycarbonyl) amino)-1,3,3-trimethylcyclohexyl) methyl)carbamate and various diols. The reaction is first optimized using 1,12-dodecanediol and different catalysts are investigated. High molar mass polyurethanes (M_n up to 30 kDa) are achieved using potassium carbonate (K_2CO_3) as a catalyst, confirming that the polytransurethanization route is a good alternative to the isocyanate route. The optimized conditions are then applied to different diols. The thermal properties of the resulting polymers are analyzed by differential scanning calorimetry (DSC), in which all investigated NIPUs exhibited an amorphous character with a glass transition temperature (T_g) varying from −68 to 128 °C.

1. Introduction

Polyurethanes (PUs) are versatile polymers with a wide range of mechanical and thermal properties due to the variety of potential monomers, especially polyols, available for their synthesis. PUs are thus relevant for a plethora of applications, including foams, coatings, adhesives, or thermoplastic elastomers.[1–3] Commercially available PUs are produced by the polyaddition reaction between diisocyanates and polyols (**Scheme 1a**).[1–3] However, diisocyanates are synthesized by reacting diamines with phosgene, a hazardous and toxic chemical.[4] Furthermore, isocyanates are also toxic compounds, and their use was recently restricted by the REACH regulation.[5] In this perspective, PUs obtained from more sustainable synthesis approaches, that do not use isocyanates, have been intensively investigated.[1–3] They are termed non-isocyanate polyurethanes (NIPUs).

Currently, there are several synthesis routes to produce NIPUs. Among them, two are highlighted: (i) the polyaddition between cyclic carbonates and amines leading to polyhydroxyurethanes (PHUs) and (ii) the polycondensation of carbamates with diols by transurethanization, yielding PUs (Scheme 1b).[1–3] PHUs are often applied as coatings, adhesives, or foams.[6–8] However, due to the presence of hydroxyl groups (primary or secondary) in the polymer backbone, their properties are not always comparable with those of PUs produced from isocyanates. In particular, to date, thermoplastic PHUs cannot compete with thermoplastic polyurethanes (TPUs).[2] For this reason, NIPUs obtained by transurethanization are promising substitutes for isocyanate chemistry because they exhibit the same chemical structure and, consequently, similar properties as classical PUs.[1,2,9]

The transurethanization reaction requires the use of biscarbamates as monomers. Generally, biscarbamates are synthesized by the carbonylation of diamines with a carbonate source, such as ethylene carbonate[10–12] or dimethyl carbonate,[13–15] to yield bis(hydroxyethyl) carbamate or bismethylcarbamate, respectively, with the latter being the most investigated. However, in practice, the use of bismethylcarbamate is still limited as it leads to lower polymerization rates and molar masses compared to diisocyanate-based polyurethane syntheses.[3,10,13,16]

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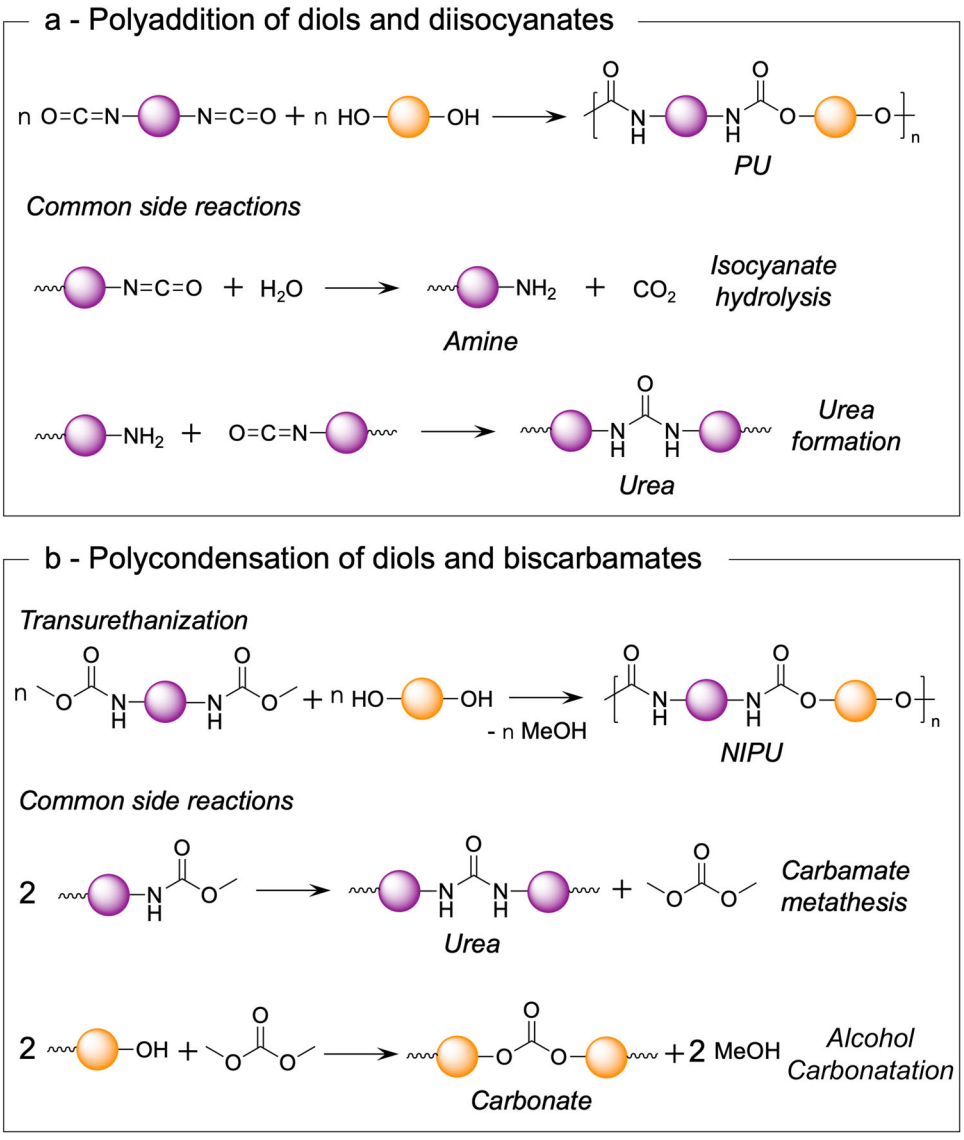
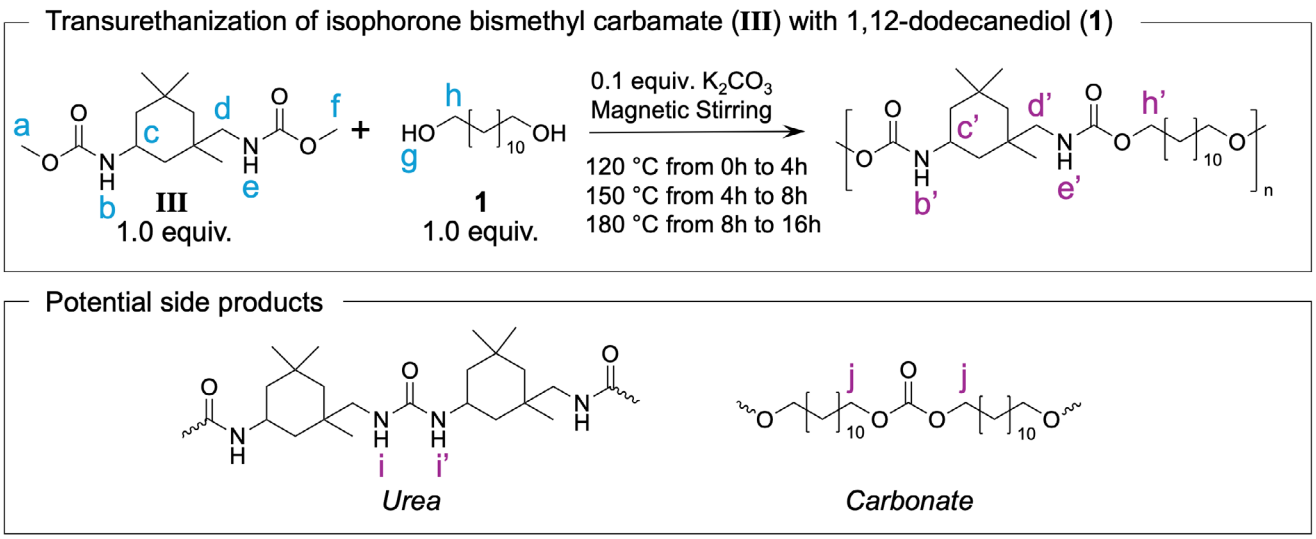


Scheme 1. The synthesis of polyurethanes via: (a) the polyaddition of diols and diisocyanates, (b) the polycondensation of diols and biscarbamates, i.e., the transurethanization. The most common side reactions associated to both polymerizations are represented.

To improve the effectiveness of bismethylcarbamates toward transurethanization, the reaction is usually performed in the presence of a catalyst, at high temperatures (ranging between 160 to 200 °C) under reduced pressure.[12,15] Despite these conditions, M_n values remained limited to values to 30 kg mol^{-1}.[3,14,15] Indeed, during polymerization, high temperatures promote a series of side reactions (Scheme 1b). It includes the metathesis of bismethylcarbamate, which generates ureas along with dimethylcarbonate (DMC).[17] The subsequent reaction of alcohols with DMC can lead to the formation of oligocarbonates.[9,18] These reactions affect the chain length and the polymer properties. To increase their molar masses, NIPUs were prepared from telechelic oligoethers,[16,19] oligoesters,[20,21] or oligocarbonates,[18,22] which resulted in relatively high M_n values, up to 93 kg mol^{-1}.[23] Hence, there is significant potential to optimize the transurethanization reaction.

To date, only one study focused on optimizing the transurethanization reaction, in which the polycondensation of hexamethylene dicarbamate and telechelic oligocarbonate diols was monitored by measuring intrinsic viscosity.[24] However, the authors did not investigate the PU molar masses through size exclusion chromatography or the occurrence of side reactions through spectroscopic approaches. In addition, dibutyltin oxide, considered as toxic, was used as a catalyst.[25]

In this work, the transurethanization of methyl((5-((methoxycarbonyl) amino)-1,3,3-trimethylcyclohexyl) methyl)carbamate (**III**) and 1,12-dodecanediol (**1**) was optimized considering reaction temperature, catalyst, and comonomer ratios. The reactions were monitored by ^{1}H NMR spectroscopy and size exclusion chromatography (SEC) measurements. As a proof of concept that the transurethanization route could be a good substitution to the isocyanate pathway, a reference polyurethane



Scheme 2. The synthesis of **NIPU 1** via the transurethanization of bismethylcarbamate **III** and 1,12-dodecanediol **1**. Representation of the potential urea and carbonate side products.

obtained from isophorone diisocyanate was compared with its analogous NIPU, in terms of chemical structure and thermal properties.

2. Results and Discussion

2.1. Optimization of the Transurethanization of Isophorone-Based Bismethyl Carbamate (III) with 1,12-Dodecanediol (1)

Bismethylcarbamate (**III**), synthesized by the methoxycarbonylation of isophorone diamine (**I**) with dimethyl carbonate (**II**) (see Scheme 5), was reacted with 1,12-dodecanediol (**1**) by transurethanization. The transurethanization reaction was performed in bulk, under magnetic stirring, using potassium carbonate as a catalyst (0.1 equiv. as compared to the carbamate), to afford **NIPU 1a** (**Scheme 2**). An equimolar amount of **III** and **1** was used, meaning that the alcohol to carbamate ratio, [OH]/[Carb.], was 1. The temperature program of the reaction was adjusted as follows: *i*) 120 °C for 4 h, *ii*) 150 °C for 4 h, and eventually *iii*) 180 °C for 8 h. It is inspired from previous reports in the literature showing that a step-wise temperature increase is beneficial to reach completion of the polymerization while avoiding monomer degradation and evaporation at the early stages of the polymerization.[3] The polymerization reaction was monitored by ^{1}H NMR and the evolution of the spectra with time is represented in **Figure 1**. Due to the unsymmetrical structure of **III**, two different methyl (**a** and **f**) and amino protons (**b** and **e**) were observed, which were accurately assigned by COSY and HMBC measurements (the detailed attribution of the signals is available in Figures S1–S4, Supporting Information).

During the transurethanization, the signals corresponding to the NH protons, **b**, and **e**, experienced a broadening and were shifted to 6.9 ppm (**b'**) and to 7.1 ppm (**e'**), respectively. As these signals are broad and overlap, this spectral region was unsuitable for the conversion calculation. Similarly, the signal of the α-methylene protons of the alcohol (**h**) decreased over time, and a new signal associated with the α-methylene protons from the polymer carbamate appeared at 3.91 ppm (**h'**).[13,14] However, **h** overlapped with the H_2O signal from DMSO-d_6.

To monitor the reaction, the signals **a+f** and **g**, assigned to the CH_3 protons of the carbamates and the OH proton, respectively, are the most suitable due to their disappearance during the transurethanization. Conveniently, they can be used to calculate the alcohol conversion and the carbamate conversion, respectively. As the methyl proton signals **a** and **f** overlap, the latter were properly identified by deconvolution using the software Fityk, as shown in Figure S5 (Supporting Information). Based on this deconvolution, it was observed that the primary carbamates (**a**) react more rapidly at lower temperatures (T < 180 °C), with a conversion of 95% after 8 h of reaction, in contrast to 63% for the secondary carbamates (**f**). The conversion plots are represented in Figure S6 (Supporting Information). When the temperature is further increased to 180 °C, the conversions of both types of carbamates align ≈95% for t = 12 h (i.e., after 4 h into the 180 °C segment), before reaching a nearly quantitative conversion (> 99%) for t = 16 h.

However, the diol conversion was slightly lower, ≈96.3% (**Table 1**, Entry 1, Conversion plot in Figure S6, Supporting Information). The discrepancy between both monomers is due to the previously reported carbamate metathesis side reaction,[10,17,19] which generates dimethyl carbonate and urea (Scheme 1). That reaction is particularly prevalent under harsh conditions, such as under vacuum and high temperatures in the presence of base catalysts, i.e., the conditions used in this work.

The signals **i** and **i'** (between 5.40 ppm and 6.00 ppm), typical of protons of urea moieties, confirm the occurrence of the metathesis reaction during the transurethanization of **NIPU 1a**. The metathesis reaction also results in the production of dimethylcarbonate that can react with the unreacted diols to form carbonate linkages (Scheme 1). The presence of the α-methylene signals **j**, associated with carbonate groups was also observed on the ^{1}H NMR spectra ≈4.2 ppm. After 16 h, the relative urea and carbonate contents of **NIPU 1a** are ≈2.2 mol% and 0.25 mol%, re-

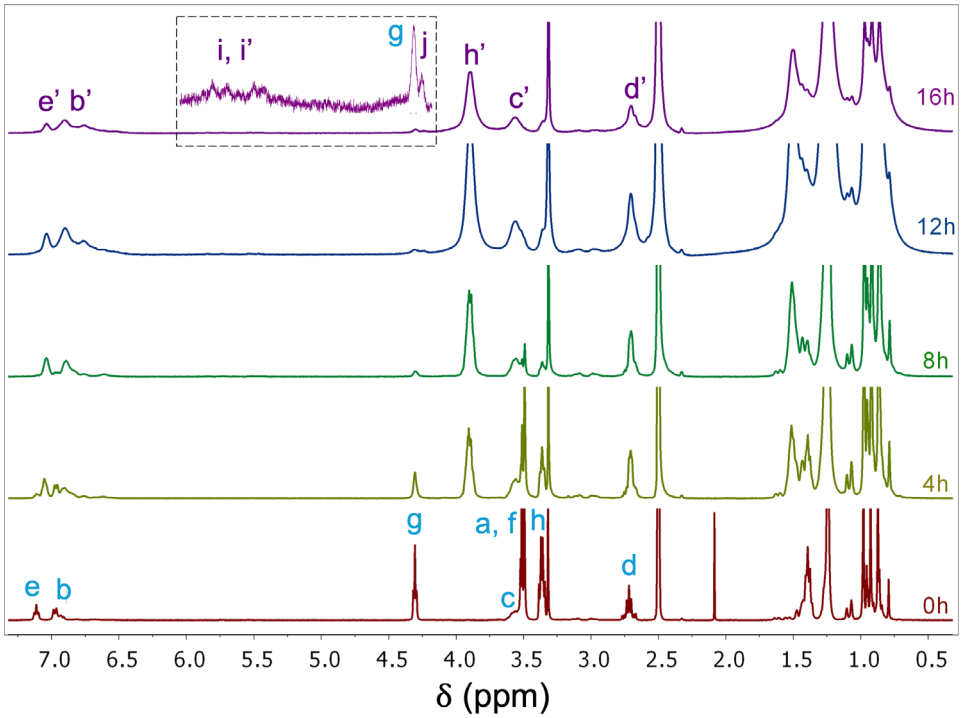


Figure 1. ^{1}H NMR monitoring for the transurethanization of bismethylcarbamate **III** and 1,12-dodecanediol **1**, during the synthesis of **NIPU 1a** (bulk, [OH]/[Carb.] = 1.0, 0.1 equiv. K_2CO_3). Aliquots are collected from the crude product and analyzed in DMSO-d_6.

Table 1. Molecular characteristics for all the synthesized NIPUs.

Entry	NIPU	Catalyst [0.1equiv.]	[OH]/[Carb.]	M_n[a] [kg mol^{-1}]	Đ[a]	OH conversion[b] [%]	Carbamate conversion[b] [%]	Urea content [mol%]	Carbonate content[b] [mol%]
1	**1a**	K_2CO_3	1.00	33.0	4.0	96.3	≥99.9	2.2[b]/9.0[c]	0.25[b]/1.3[c]
2	**1b**[d]	K_2CO_3	1.00	16.6	2.2	94.4	96.7	1.3[b]	0.4 [b]
3	**1c**	K_2CO_3	1.10	15.3	3.0	96.8	≥99.9	1.0[b]/9.1[c]	1.0[b]/1.5[c]
4	**1d**	KOMe	1.10	16.0	3.5	96.5	≥99.9	2.2[b]	1.2[b]
5	**1e**	KOH	1.10	13.3	4.3	96.6	≥99.9	2.6[b]	0.6[b]
6	**1f**	$CaCl_2$	1.10	11.8	5.5	95.7	≥99.9	8.8[b]	0.1[b]
7	**1g**	$Bi(Oc)_2$	1.10	10.0	2.4	94.8	≥99.9	4.2[b]	0.6[b]
8	**1h**	$Zn(Ac)_2.2H_2O$	1.10	7.5	3.4	≥99.9	93.7	0.3[b]	0.0[b]
9	**1i**	$Ti(BuO)_4$	1.10	5.5	2.3	86.8	≥99.9	7.1[b]	1.8[b]
10	**1j**	TBD	1.10	5.7	2.3	93.1	95.0	2.3[b]	0.5[b]
11	**1k**	K_2CO_3	1.02	29.1	3.5	95.0	≥99.9	1.3[b]/9.0[c]	2.2[b]/1.3[c]
12	**1l**	K_2CO_3	1.05	26.0	2.7	96.5	≥99.9	1.0[b]/8.4[c]	1.1[b]/1.3[c]
13	**1m**	K_2CO_3	0.90	–[e]	–[e]	–[e]	–[e]	–[e]/18.8[c]	–[e]/2.1[c]
14	**1n**	K_2CO_3	0.95	–[e]	–[e]	–[e]	–[e]	–[e]/15.1[c]	–[e]/1.6[c]
15	**1o**	K_2CO_3	0.98	–[e]	–[e]	–[e]	–[e]	–[e]/13.2[c]	–[e]/3.0[c]
16	**2**	K_2CO_3	1.00	6.8	4.5	94.6	97.7	28.5[b]	1.6[b]
17	**3**	K_2CO_3	1.00	2.2	2.2	71.0	90.3	3.5[b]	3.3[b]
18	**4**	K_2CO_3	1.00	–[e]	–[e]	–[e]	–[e]	–[e]	–[e]
19	**5**	K_2CO_3	1.00	35.8	1.6	87.3	86.7	0.5[b]	0.2 [b]
20	**PU1**	–	1.00	7.8	2.0	–	–	0.9[b]/4.1[c]	–

[a] Obtained by SEC analysis in DMF using polystyrene as a standard; [b] Estimated from ^{1}H NMR; [c] Estimated by FTIR; [d] Sample prepared at 150 °C last isothermal; [e] Non-applicable due to sample insolubility; [f] Obtained by SEC analysis in HFIP using PMMA as a standard.

spectively, where the relative contents are defined as molar ratios as compared to the total amount of carbamate, urea, and carbonate bonds (see *Materials and Methods* section).

In an attempt to minimize the side reactions without compromising the final NIPU molar mass, the transurethanization of **III** and **1** was investigated by varying the reaction temperature and the nature of the catalyst.

As previously mentioned, the extent of the metathesis side reaction increases with temperature.[10,17,19,24] For this reason, the synthesis of **NIPU 1** was thus performed at a lower temperature, with a two-step temperature program proceeding as follows: (i) 120 °C for 4 h, (ii) 150 °C for 12h. The resulting polymer is noted as **NIPU 1b**. Similar to **NIPU 1a**, the reaction was monitored by ^{1}H NMR to measure the alcohol and carbamate conversions, as well as its relative content of urea and carbonate moieties. The final molar mass of the polymer was investigated by SEC. All results are collected in Table 1 (Entry 2).

Clearly, the carbamate and alcohol conversion plateau at lower values in the case of **NIPU 1b**, i.e., at 96.7 and 94.4% respectively, against 100 and 96.3% in the case of **NIPU 1a**. This can be attributed to the enhanced catalytic effect of K_2CO_3 at high temperatures (> 160 °C), which was correlated to its improved miscibility in the reactive medium, particularly under bulk conditions.[15,26] Similarly, the relative content in urea (Table 1) decreased in the case of **NIPU 1b** (1.3 mol% against 2.2 mol% for **NIPU 1a**), suggesting that a decrease of the reaction temperature reduces the extent of the metathesis side reaction. In both cases, the carbonate content stays relatively low (< 0.5 mol%).

As expected, the reduction in the monomer conversions resulted in a much lower molar mass for **NIPU 1b** (M_n = 16 kg mol^{-1}) as compared to **NIPU 1a** (M_n = 33.0 kg mol^{-1}) (SEC chromatograms are available in Figure S7, Supporting Information). Inversely, the significant increase of the extent of the side reaction in the case of **NIPU 1a** is probably responsible for the high dispersity, Đ = 4.0, against Đ = 2.2 for **NIPU 1b** (Table 1). In summary, we concluded to maintain a 3-step temperature program ((i) 120 °C for 4 h, (ii) 150 °C for 4 h, and eventually (iii) 180 °C for 8 h) in order to maximize the monomer conversions.

The impact of the catalyst was then investigated. KOMe, KOH, $CaCl_2$, $Bi(Oc)_2$, $Zn(Ac)_2{\times}2H_2O$, $Ti(BuO)_4$ and TBD were all tested for the polycondensation of bismethylcarbamate (**III**) and 1,12-dodecanediol (**1**) using the same conditions as for **NIPU 1a**, except an excess of diol was used, [OH]/[Carb.] = 1.10, in order to limit the extent of carbamate metathesis that usually comes with solubility issues. The resulting polymers are noted **NIPU 1d** to **1j**. For comparison purposes, K_2CO_3 was also tested using the same conditions ([OH]/[Carb.] = 1.10), and the resulting polymer is noted **NIPU 1c**. For all these polymers, the results of ^{1}H NMR and SEC analyses are collected in Table 1 (Entry 3 to 10, Figure S8, Supporting Information). **Figure 2**a represents the value of the molar mass as measured by SEC. It suggests that the potassium-based salts and bases, such as K_2CO_3 (**NIPU 1c**), KOMe (**NIPU 1d**), and KOH (**NIPU 1e**), provide the polymer with the highest molar masses. The highest M_n value was obtained for **NIPU 1d** (M_n = 16 kg mol^{-1}). These observations align with previous studies highlighting potassium salts as particularly effective catalysts for the transurethanization of other diols and dicarbamates.[27] Furthermore, the superior efficiency of

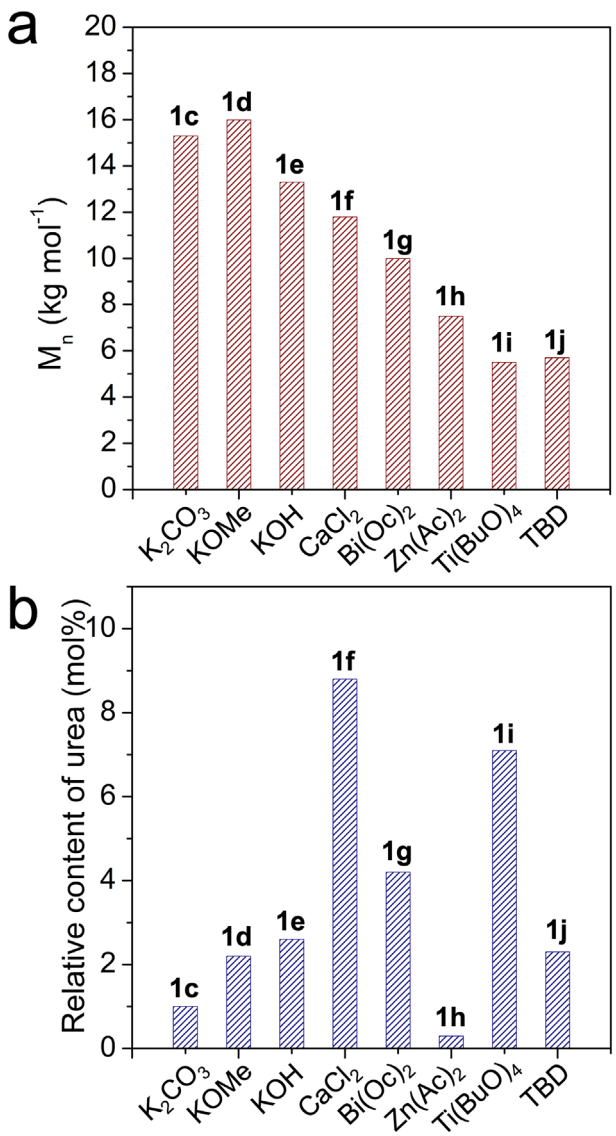


Figure 2. (a) Variation of the molecular weight, M_n, as a function of the catalyst used for the synthesis of **NIPU 1** (bulk, [OH]/[Carb.] = 1.10, 0.1 equiv. catalyst). M_n is measured by SEC in DMF. (b) Corresponding evolution of the relative urea content as measured by ^{1}H NMR.

KOMe is typically attributed to its higher basicity, with a pKa of 15.5 compared to 13.5 for KOH and 10.2 for K_2CO_3.

Considering the relative content in urea (Figure 2b), **NIPU 1f** (8.8 mol%) and **NIPU 1i** (7.1 mol%) exhibit particularly high values, thus suggesting that $CaCl_2$ and $Ti(BuO)_4$ are strong promoters of the metathesis reaction at high temperature. In comparison, the content measured for **NIPU 1h** (0.3 mol%) or the benchmark **NIPU 1c** (1.0 mol%) indicates that $Zn(OAc)_2{\times}2H_2O$ and K_2CO_3 are the most selective catalysts. In all cases, the carbonate content remained relatively low, indicating that the carbonation of alcohol with dimethyl carbonate is not influenced by the nature of the catalyst. For all the catalysts, the carbamate conversion (Table 1) was >99.9%, except for TBD (95%). In this latter case, it is likely that the very high temperature of the polymerization

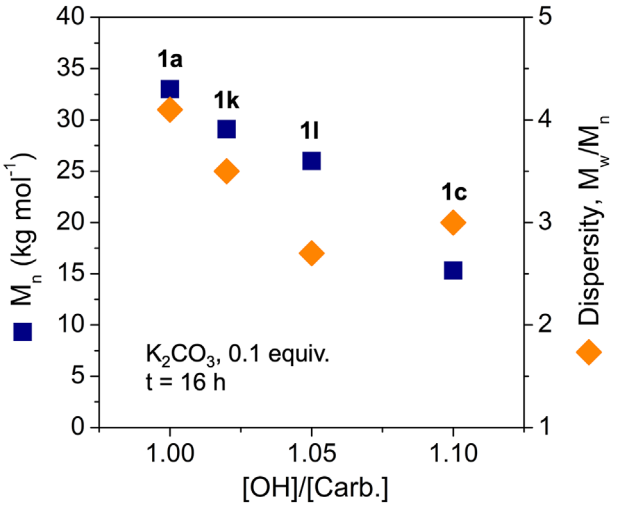


Figure 3. Variation of the molecular weight, M_n, and the dispersity, Đ, as a function of the hydroxyl to carbamate ratio, [OH]/[Carb.], for the synthesis of **NIPU 1** (bulk, 0.1 equiv. K_2CO_3). M_n and Đ are measured by SEC in DMF.

reaction resulted in the degradation of the organo-base.[3] This most probably explains the low value of the molar mass measured in SEC as well (M_n = 5.5 kg mol^{-1}). As for the alcohol conversion, there are no significant variations for most of the considered catalysts, with an average conversion of ≈ 95%. It is worth mentioning that, considering the alcohol-to-carbamate ratio ([OH]/[Carb.] = 1.10), the maximum OH conversion was expected to be 90%. The observation of a higher value is likely due to the partial evaporation of the alcohol, especially in the reaction conditions employed in this work, i.e., under relatively high temperatures (T ≥ 120 °C) and vacuum.

In the end, K_2CO_3 provided the best compromise in terms of molar mass and selectivity, and it was selected for the rest of this study. It is however interesting to note that the nature of the catalyst can be varied to tune the urea content, a valuable tool for the control of the thermo-mechanical properties of the resulting NIPUs. By analogy, in conventional PUs, the urea content is used to tailor the material properties, classically through the partial hydrolysis of the isocyanates with catalytic amounts of water (Scheme 1).[28]

The impact of the alcohol to carbamate ratio, [OH]/[Carb.], was investigated next. Formulations with a [OH]/[Carb.] ratio ranging from 1.1:1 to 0.9:1 were investigated, aligning with the ranges commonly used in previous studies on the transurethanization of other diols and dicarbamates.[24,27] The reaction was first conducted with an excess of alcohol. The polymer obtained for [OH]/[Carb.] = 1.02 and 1.05 are noted **NIPU 1k** and **NIPU 1l** (Entries 11 and 12, Table 1), while the polymer obtained for [OH]/[Carb.] = 1.00 and 1.10 corresponds to **NIPU 1a** and **NIPU 1c** (Entries 1 and 3, Table 1), as described above. **Figure 3** represents the evolution of M_n and Đ as a function of [OH]/[Carb.] (SEC chromatograms are available in Figure S9, Supporting Information). Clearly, M_n is maximal for [OH]/[Carb.] = 1.00 (33 kg mol^{-1}). As the diol content increased, the M_n value decreased, reaching a minimum of 15.3 kDa for **NIPU 1c**, consistent with the Carothers equation and previous findings.[13] Notably, the dispersity (Đ) decreased as the diol content increased from 4.05 for **NIPU 1a** ([OH]/[Carb.] = 1.00) to 3.00 for **NIPU 1c** ([OH]/[Carb.] = 1.10). The excess of diol may have prevented the occurrence of side reactions. This is consistent with the lower urea content of **NIPU 1c** (1.0 mol%) as compared to **NIPU 1a** (2.1 mol%), as indicated in Table 1. These results reflect that, with a diol excess, the carbamate preferentially reacts with the alcohol rather than undergoing metathesis. They correlate well with previous reports of the literature, where urea-free hydroxy-terminated NIPUs were synthesized using a significant excess of diol ([OH]/[Carb.] = 2.00).[23]

The reaction was then performed with an excess of carbamate. The polymer obtained for [OH]/[Carb.] = 0.90, 0.95, and 0.98, **NIPU 1m**, **NIPU 1n** and **NIPU 1o** (Entries 13, 14, and 15, Table 1), are all partially insoluble in conventional organic solvents (DMSO, DMF, THF, HFIP, $CHCl_3$, and DCM), and could not be properly analyzed via ^{1}H NMR and SEC analyses. This is likely due to the formation of a crosslinked network, either chemical or physical. A chemical network could result from the reaction between carbamates and ureas, leading to the formation of allophanates or biurets as covalent crosslinking points, as reported by others.[13,23] Alternatively, a physical network may arise from strong non-covalent interactions between polymer chains, driven by hydrogen bonding of the urea moieties.

FTIR spectroscopy was used as an alternative to investigate the influence of the monomer ratios on the structure of the polymer, as well as the origin of their insolubility. **Figure 4a** depicts the FTIR spectra of **NIPU 1a** ([OH]/[Carb.] = 1.00) and **NIPU 1 m** ([OH]/[Carb.] = 0.90). The polyurethane structure is well confirmed by the presence of the NH stretching vibrational bond at 3325 cm^{-1} and the bending of the NH bond (1523 cm^{-1}), typical of carbamate bonds.[13,14]

Due to the presence of distinct C = O bonds that overlap in the carbonyl region, the signals of the urethane, the urea, and the carbonate groups were deconvoluted for quantification (the detailed procedure is provided in the ESI, Figure S10, Supporting Information).[9,29–31] Figure 4b displays the deconvolution for **NIPU 1m**. Five different carbonyl bands can be distinguished and associated with carbonate (≈1740 cm^{-1}), free urethane (≈1724 cm^{-1}), hydrogen-bonded urethane (≈1692 cm^{-1}), free urea (≈1650 cm^{-1}), and hydrogen-bonded ureas (≈1624 cm^{-1}).[9] The areas of these distinctive bands were used to estimate the relative contents in urea and carbonate, as defined previously (see *Materials and Methods* section). The results obtained for all the tested [OH]/[Carb.] ratios are reported in Table 1. When compared to the results obtained by ^{1}H NMR, the values measured via FTIR are systematically higher. This discrepancy is not unexpected, given the significantly different experimental conditions of the two techniques. This observation highlights the importance of interpreting these values not as absolute measurements but as relative indicators for comparative purposes. In this context, FTIR was specifically employed to compare the series of NIPUs obtained for different [OH]/[Carb.] ratios.

The relative urea content as a function of [OH]/[Carb.] is plotted in **Figure 5c**. For [OH]/[Carb.] ≥ 1.02, a minimal urea content of ≈ 9 mol% is reached. At equimolar conditions, the urea content is ≈10.5% (**NIPU 1a**) and it increases significantly as [Carb.] increases, to reach a maximum value of 18.4% for [OH]/[Carb.] = 0.90 (**NIPU 1m**). These findings confirm that an excess of

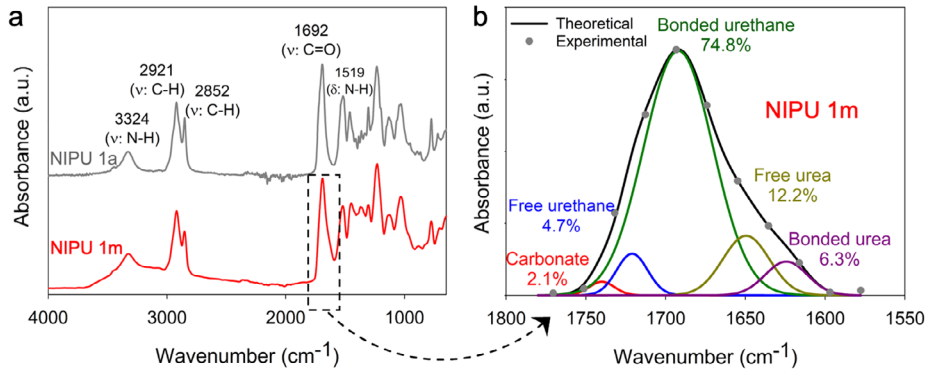


Figure 4. (a) FTIR spectra of **NIPU 1a** (bulk, [OH]/[Carb.] = 1.00, 0.1 equiv. K_2CO_3) and **NIPU 1 m** (bulk, [OH]/[Carb.] = 0.90, 0.1 equiv. K_2CO_3). (b) Deconvolution of the band corresponding to the vibration of the carbonyl bonds, C = O, for **NIPU 1m**.

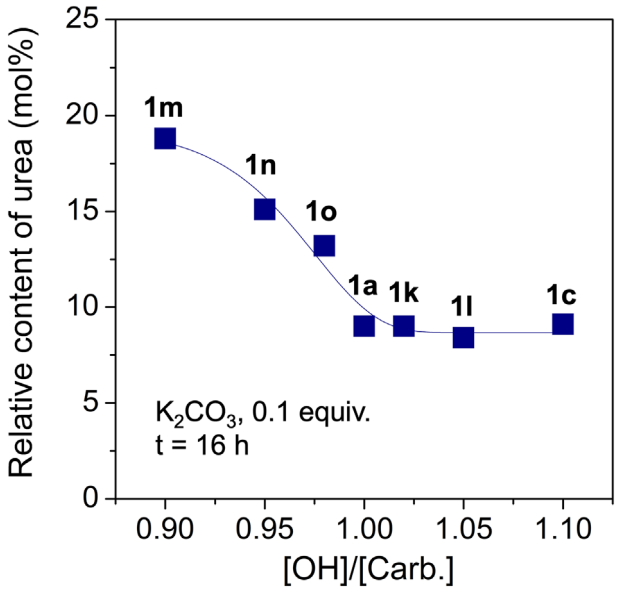


Figure 5. Relative urea content (mol%) as a function of the hydroxyl to carbamate ratio, [OH]/[Carb.], for the synthesis of **NIPU 1** (bulk, 0.1 equiv. K_2CO_3). Values are measured by FTIR analysis.

carbamate promotes more side reactions. They also indicate that for all insoluble NIPUs (i.e., [OH]/[Carb.] < 1), the urea content is high (>10 mol%), supporting the hypothesis of a physically crosslinked network driven by inter-chain hydrogen bonding. Conversely, the formation of a covalent network is not supported by FTIR analysis, as no allophanates or biurets were detected in the spectra. However, it is important to note that even very small amounts – potentially below the detection limit of FTIR – could contribute to the insolubility of the synthesized NIPUs.

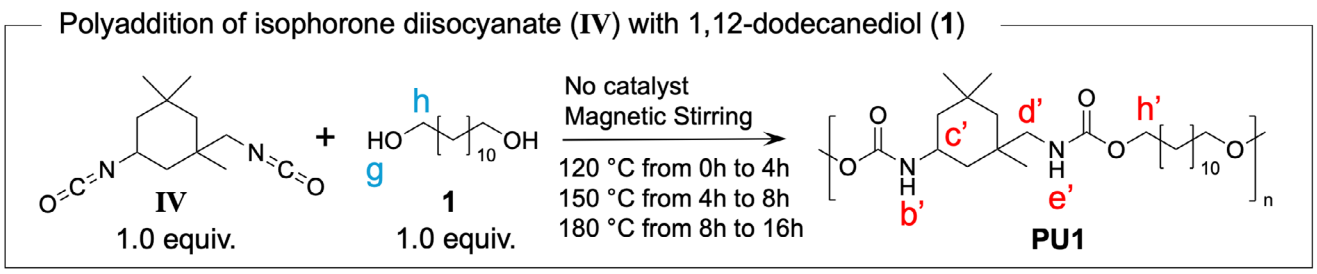
In the end, the screening of the alcohol-to-carbamate ratio suggests that a conventional equimolar ratio provides the best compromise in terms of molar mass, side reactions extent, and solvent processability of the NIPUs.

2.2. Comparison of NIPU 1 with Conventional PU

As previously stated, NIPUs obtained by transurethanization represent a promising alternative to conventional PUs synthesized from isocyanates and diols. For comparison purposes, a PU was synthesized via the conventional polyaddition of isophorone diisocyanate (**IV**) with 1,12-dodecanediol (**1**) (**Scheme 3**). The polyaddition was conducted using the same conditions as for the polycondensation reaction leading to **NIPU 1a**, i.e., 4 h at 120 °C, 4 h at 150 °C, and 8 h at 180 °C, under vacuum. The resulting polymer is noted **PU1** and it was analyzed by FTIR and ^{1}H NMR spectroscopy, as well as by SEC. The FTIR spectra of **NIPU 1a** and **PU1** (**Figure 6a**) are superimposable, thus confirming that both polymers are structurally similar.

Their ^{1}H NMR spectra, as shown in Figure 6b, are also indicative of their structural similarities. However, the magnification of the region corresponding to the urea protons (**i** and **i'**), as well as the CH_2 protons in α position of the carbonate functions (**j**), reveals their differences (4.0 ppm $\leq \delta \leq$ 6.0 ppm). As illustrated earlier, **NIPU 1a** contains both ureas and carbonates, while **PU1** contains only ureas. In this case, they are likely formed through the partial hydrolysis of the isocyanates due to the residual water present in the starting materials (*cf.* Scheme 1). The integration of the signals indicates that the relative urea content is of 0.9 mol%, against 2.2 mol% in the case of **NIPU 1a**. Thus, the transurethanization resulted in a larger content of urea, due to the metathesis side reaction. As expected, **PU1** does not contain carbonate moieties because dimethylcarbonate is not released during the polyaddition route (Scheme 1).

According to SEC analysis (**Figure 7**), the molar mass and dispersity of **PU1** are M_n = 7.8 kg.mol^{-1} and Đ = 2.0. These values are much lower than those measured for **NIPU 1a** (M_n = 33 kg.mol^{-1} and Đ = 4.0, respectively). The chromatograms of both polymers are depicted in Figure 7a. It must be stressed that the partial hydrolysis of isocyanates, in the case of **PU1**, comes with a stoichiometric imbalance that is not compensated by any other reaction. On the contrary, the metathesis of carbamate comes with the release of dimethylcarbonate that can further react with alcohols (see Scheme 1). This additional side reaction can contribute to the growing of the polymer chains, while increasing their dispersity, and may partially explain the differences observed between **NIPU 1a** and **PU1**. It might be hypothesized that the low molar mass of **PU1** was also due to inappropriate polymerization conditions, as isocyanate-based PU is classically synthesized at a temperature < 100 °C. However, a previous report of the literature indicates that the polyaddition of isophorone diisocyanate (**IV**) with diol **1** using milder conditions



Scheme 3. Synthesis of polyurethane **PU1** by polyaddition of **IV** with **4**.

(bulk, 60 °C), provides a PU with even lower molecular weight (M_n = 3.4 kg.mol^{-1}, Đ = 2.2).[32] This difference demonstrates that the high temperatures used for **PU1** synthesis are not detrimental. On the contrary, they likely provide a beneficial effect by reducing the viscosity of the growing polymer, enhancing the efficiency of magnetic stirring, and thereby improving the extent of the polyaddition reaction. Furthermore, the SEC chromatogram of **PU1** (Figure 7) shows no peaks at long elution times, indicating the absence of low-molar-mass degradation products.

In conclusion, the polycondensation of bismethyl carbamate **III** with diol **1**, catalyzed by K_2CO_3, provides a polyurethane with a much higher molar mass and dispersity than the isocyanate route, and larger contents of side products (e.g., urea and carbonate). Depending on the intended applications, these characteristics might be either beneficial or undesirable. In any case, as stated earlier, the properties of **NIPU 1** are strongly influenced by the choice of the catalyst and the [OH]/[Carb.] ratio. These levers can be used to tailor the properties of the NIPU, including molar mass and urea/carbonate content, allowing

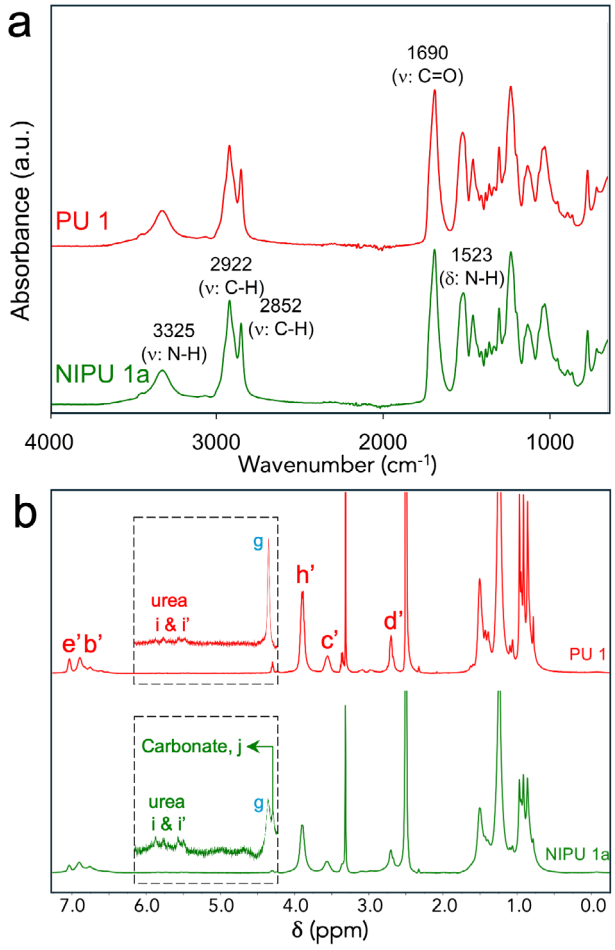


Figure 6. (a) FTIR spectra of **PU1** (bulk, [OH]/[Isocyanate] = 1.00, no catalyst) and **NIPU 1a** (bulk, [OH]/[Carb.] = 1.00, 0.1 equiv. K_2CO_3). (b) ^{1}H NMR spectra of and **PU1** and **NIPU 1a**.

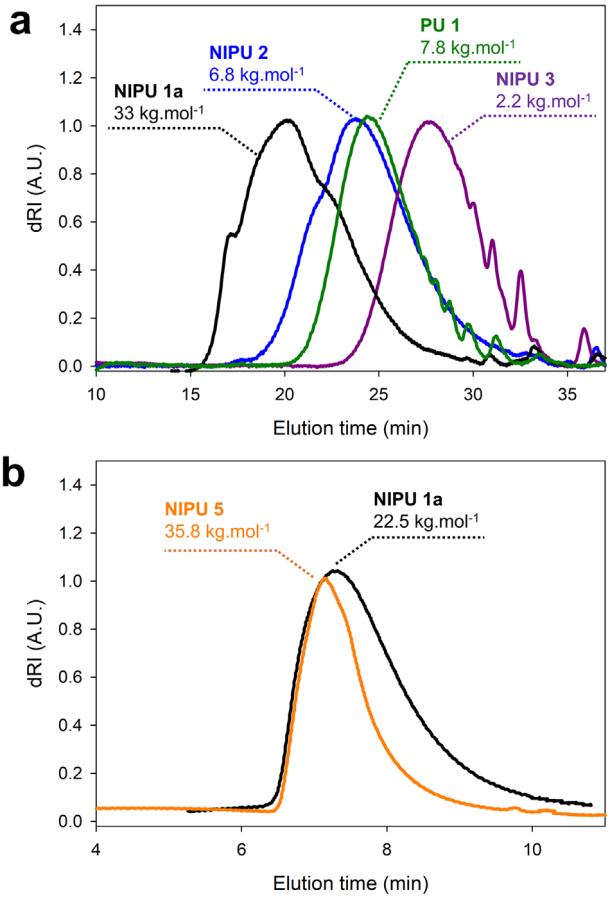
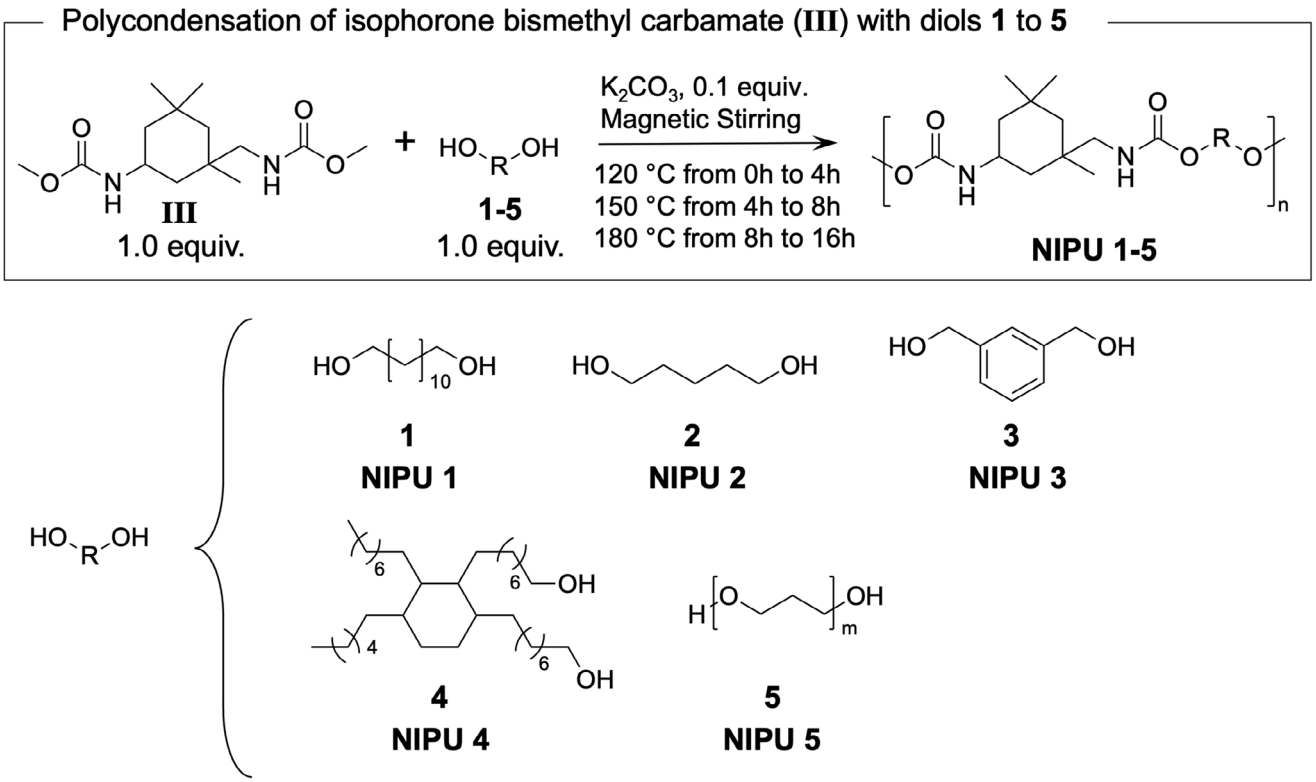


Figure 7. (a) SEC chromatograms in DMF (polystyrene standard) for **PU1**, **NIPU 1a**, **NIPU 2,** and **NIPU 3**. (b) SEC chromatograms in HFIP (poly(methyl methacrylate) standard) for **NIPU 1a** and **NIPU 5**.



Scheme 4. The synthesis of **NIPU 1–5** via the transurethanization of bismethylcarbamate **III** with diols **1–5** and molecular structures of diols **1–5**.

for customization to meet specific requirements. For instance, **NIPU 1 h** (Catalyst: $Zn(Ac)_2{\times}2H_2O$, [OH]/[Carb.] = 0.90, Table 1, entry 8) exhibits properties closely resembling those of **PU1** (Table 1, entry 20). In the end, the polycondensation reaction is highlighted as a versatile approach for synthesizing NIPUs with diverse macromolecular characteristics, that can compete effectively with the isocyanate-based route, provided that the use of stringent catalytic conditions is acceptable.

2.3. Molar Mass and Thermal Properties of NIPUs Synthesized from Different Diols

To further illustrate the versatility of the polycondensation reaction developed in this study, a series of NIPUs was synthesized by the transurethanization reaction of **III** with different diols (**Scheme 4**), including one shorter alkane diol (pentanediol, **2**), the 1,3-benzenedimethanol (**3**), a dimer of fatty alcohol (*Pripol*, **4**) and a biobased polypropanediol polyethylene glycol (**5**, M_n = 2000 g mol^{-1}). The resulting NIPU are labeled **NIPU 2** to **5**. They were synthesized using the same conditions as for **NIPU 1a**, as displayed in Scheme 3. Their characteristics as measured by ^{1}H NMR (Figures S11–S16, Supporting Information) and SEC are collected in Table 1, entries 16 to 19. The chromatograms obtained in SEC are depicted in Figure 7.

Noteworthily, **NIPU 4**, produced using *Pripol* **4**, was entirely insoluble in common organic solvents, rendering it impossible to characterize this polymer. This is most certainly due to the crosslinking of the polymer resulting from traces amount of triol in **4** (2 wt.% according to the supplier). **NIPUs 2** and **3** exhibited low molar masses of 6.8 kg mol^{-1} and 2.2 kg mol^{-1}, respectively. This can likely be attributed to the relatively low boiling points of 1,5-pentanediol (**2**) and 1,3-benzenedimethanol (**3**), which may have been partially evaporated under vacuum, leading to a stoichiometric imbalance. This is further confirmed by the ^{1}H NMR analysis of **NIPU 2** (Figures S11 and S12, Supporting Information). Indeed, the integration of the signals revealed a particularly high content in urea groups, 28.5 mol%. At the same time, the alcohol conversion is elevated (≈ 95%), a tendency consistent with the evaporation of the alcohol.

NIPU 5, derived from the biosourced polyether **5**, is not soluble in DMF and was characterized by SEC chromatography in HFIP (Figure 7b). It exhibits a high molar mass, M_n = 35.8 kg mol^{-1}, in accordance with the increase of the size of the diol as compared to the previous examples. It is worth noting that the dispersity is quite low, Đ = 1.6, which, according to the Carothers equation, suggests that the polymerization reaction is incomplete. This is consistent with the alcohol and the carbamate conversions measured in NMR, that level off ≈87%. For comparison purposes, the molecular weight, M_n = 22.5 kg mol^{-1}, and the dispersity, Đ = 2.1, of **NIPU 1a** were also measured in HFIP SEC (chromatogram in Figure 7b). If compared to the results obtained for **NIPU 5**, they are consistent with the relative sizes of diols **1** and **5**.

Eventually, DSC analyses were performed to assess the influence of the diols on the NIPU's thermal properties. For all the polymers, the second heating ramp of the DSC thermograms is depicted in **Figure 8** (cooling ramps are available in Figure S17, Supporting Information). They all show a single glass transition

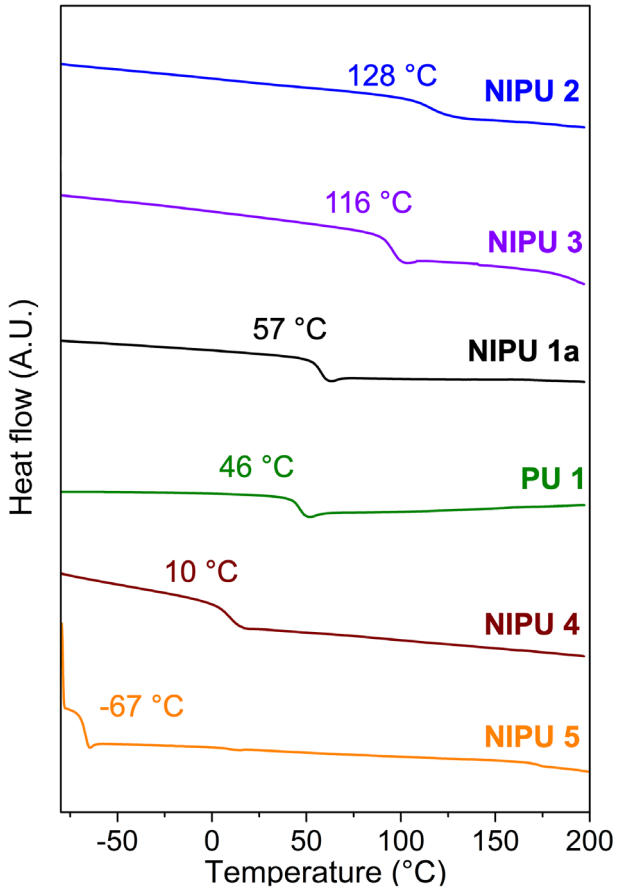


Figure 8. DSC traces of **NIPU 1** to **5** and **PU 1** (10 °C min^{-1}, 2nd heating ramp).

(T_g), characteristic of an amorphous morphology as expected for isophorone-based polyurethane.[33,34] Indeed, the different isomeric forms and the cycloaliphatic nature of the isophorone backbone hinder the crystallization of the polymer chains.[34] The T_g of the different polyurethanes varies between -67 °C and 128 °C, in accordance with the length and the rigidity of the diols used.[14,33] Additionally, with the same chemical structure, **NIPU 1a** showed a higher T_g (57 °C) than **PU 1** (46 °C). This can be attributed to the higher M_n value for **NIPU 1a**, as well as its higher urea content. For the same reasons, it is anticipated that adjusting the nature of the catalyst used in the synthesis can effectively tune the thermal properties of the NIPUs. Furthermore, the wide range of T_g values explored in this study is another evidence of the versatility of the transurethanization approach and underscores its potential as a viable alternative to the isocyanate route.

3. Conclusion

Non-isocyanate polyurethanes (NIPUs) were synthesized via the polycondensation of an isophorone-based biscarbamate with various diols. A systematic investigation was conducted to evaluate the effects of the temperature, the reaction time, and the catalyst employed during synthesis, as well as the [OH]/[Carb.] ratio, on the molecular structure of the resulting NIPUs. The molar mass and dispersity of the polymers were analyzed using size exclusion chromatography, while the urea and carbonate contents – two classical side products of transurethanization polymerization – were carefully quantified using ^{1}H NMR and FTIR spectroscopy.

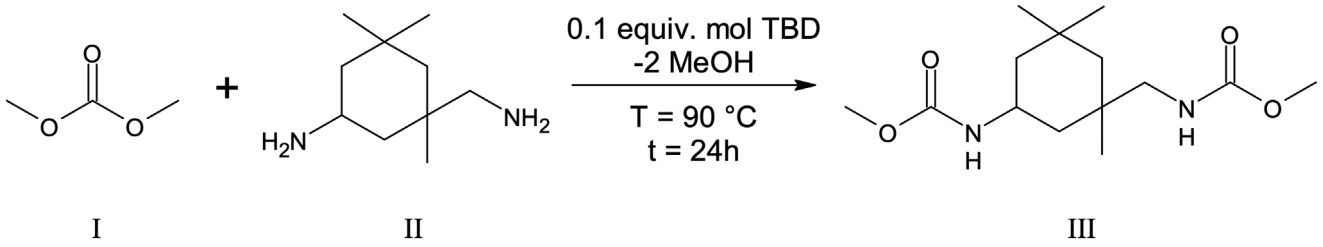
The results demonstrated that a stepwise temperature increase was beneficial for achieving high molar masses while minimizing diol volatilization and the formation of side products. In this regard, the optimal balance was achieved using incremental temperature steps from 120 to 180 °C, over 16 h, in combination with potassium-based catalysts (K_2CO_3) and an equimolar reactant ratio ([OH]/[Carb.] = 1.0). This approach yielded a Mn = 33.0 kg mol^{-1} with a moderate urea content of 2.2 mol%. Interestingly, both the nature of the catalyst and the [OH]/[Carb.] ratio emerged as effective levers for controlling the urea, offering a means to tune the properties of the resulting NIPUs.

The NIPU synthesized using 1,12-dodecanediol was compared to a reference polyurethane (PU) with a similar chemical structure. Under the experimental conditions employed in this study, the NIPU exhibited significantly higher molecular weight and dispersity compared to the conventional PU (M_n = 7.8 kg.mol^{-1}), accompanied by a higher urea content. These differences can be largely attributed to the additional side reactions inherent to the transurethanization process. Notably, the glass transition temperature of the NIPU (T_g = 57 °C) was found to be 10 °C higher than that of the PU (T_g = 46 °C), likely as a result of the increased urea content and molecular weight. Interestingly, these findings suggest that the side reactions occurring during transurethanization can be leveraged as an advantage in applications where dispersity is less critical.

Finally, a series of NIPUs was synthesized using various diols. As expected, the protocol was less effective with low-boiling-point diols, resulting in polymers with lower conversion (Carbamate conversions < 98%) and reduced molar mass (M_n < 7 kg mol^{-1}). In such cases, optimizing the temperature program could help mitigate evaporation and enhance the final molar mass. Despite the lower transurethanization efficiency with low-boiling-point diols, the thermal properties remained tunable, with T_g's ranging from −67 to 128 °C. Additionally, high-molar-mass bio-based diols, such as polypropene diol, produced NIPUs with high molar mass (M_n = 35.8 kg mol^{-1}), further highlighting the potential of this approach for the sustainable synthesis of next-generation, environmentally friendly polyurethanes.

4. Experimental Section

Materials: Dimethyl carbonate (**I**, 99%, 90.08 g mol^{-1}) and isophorone diamine (**II**, 99%, 170 g mol^{-1}) were purchased from Across Organics. Calcium chloride ($CaCl_2$, 99%), titanium butoxide ($Ti(BuO)_4$, 99%), potassium methoxide (KOMe, 95%), 1,12-Dodecanediol (**1**, 99%, 202.33 g mol^{-1}) and isophorone diisocyanate (**IV**, 98%, 222.28 g mol^{-1}) were purchased from Sigma–Aldrich. 1,5-Pentanediol (**2**, 97%, 104.15 g mol^{-1}) was acquired from Fluka. 1,3-Benzene dimethanol (**3**, 99%, 138.16 g mol^{-1}), and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%, 139.20 g mol^{-1}) were purchased from TCI. The diol dimer with the commercial name *Pripol* 2033 (**4**) was supplied by Croda. The polypropanediol (M_n = 2000 g mol^{-1}) (**5**) was obtained from Sigma-Aldrich. Potassium carbonate (K_2CO_3, 99%, 138.21 g mol^{-1}) was purchased from Acros Organics. Sodium methoxide (NaOMe, 98%, 54.03 g mol^{-1}) and bismuth octoate ($Bi(Oct)_3$) were acquired by Alfa



Scheme 5. Methoxycarbonylation of **II** in the presence of DMC (**I**) and TBD as a catalyst.

Aesar. Potassium hydroxide (KOH, 85%) was obtained from ABCR. Dimethyl formamide (DMF, 99.8%) was obtained from VWR and deuterated dimethyl sulfoxide (DMSO-d_6, 99.5%) was obtained from Eurisotop. The diols were dried in a vacuum oven at 50 °C overnight. All the other reactants were used without any further purification.

Methods—Synthesis—Methoxycarbonylation of Isophorone Diamine: The methoxycarbonylation of isophorone diamine (**II**) to obtain methyl((5-((methoxycarbonyl)amino)-1,3,3-trimethylcyclohexyl) methyl)carbamate (**III**) was performed adding **I** (1 equiv. mol, 8.605 mmol, 1 g) to a 250 ml Schlenk flask with an excess of **II** (10 equiv. mol, 86.051 mmol, 7.75 g) without or with the presence of TBD as a catalyst (0.1 equiv. mol, 0.1197 g). The reaction was performed with a magnetic stirring under a static nitrogen atmosphere at 90 °C for 24 h. Then, the excess of dimethyl carbonate and methanol generated during the methoxycarbonylation of diamine were removed under a vacuum at 65 °C.

The product was solubilized in dichloromethane (DCM) and washed with 5 wt. % HCl solution, followed by washing with brine to remove the catalyst and remaining non-reacted diamine. The organic phase was dried with sodium sulfate. Finally, DCM was removed under vacuum at 45 °C for 12 h. **III** is a transparent solid product at 25 °C. The synthesis of **III** by methoxycarbonylation is depicted in **Scheme 5**.

*Methods—Synthesis—Optimization of the Transurethanization of **III** with **1***: The transurethanization of **III** with **1** was optimized in terms of temperature, catalyst and molar ratio between **III** and **1**. The conditions for the temperature optimization were as follows: **III** (1 equiv. mol, 3.4918 mmol, 1 g), **1** (1 equiv. mol, 3.8410 mmol, 0.7771 g) and K_2CO_3 as a catalyst (0.1 equiv. mol. 0.3492 mmol, 3.9 mg) were mixed under vacuum and stirred using magnetic stirring. Regarding the temperature optimization, two isothermal protocols were performed: in the first one, two isothermal regimes, at 120 °C for 4 h and at 150 °C for 12 h were performed; in the second, three isothermal regimes were considered, a first at 120 °C for 4 h, a second at 150 °C for 4 h and a third at 180 °C for 8h. This latter temperature protocol was the best and was kept further for the transurethanisation optimization.

Then, the catalyst screening was performed by adding **III** (1 equiv. mol, 3.4918 mmol, 1 g) with a slight excess of **1** (1.1 equiv. mol, 3.8410 mmol, 0.7771 g) and using 0.1 equiv. mol of the catalyst.

A similar protocol was followed to investigate the influence of the molar ratio **1:III** on the transurethanization reaction, where K_2CO_3 0.1 equiv. mol was used as a catalyst; the **1:III** ratio was varied from 0.9 to 1.1.

Methods—Synthesis—Synthesis of Amorphous Non-Isocyanate Polyurethanes: The transurethanization was carried out in a 10 ml Schlenk-flask equipped with a magnetic stirring under vacuum. **III** and several diols (1,12-dodecanediol (**1**), 1,5-pentanediol (**2**), 1,4-benzenedimethanol (**3**), Pripol (**4**), polypropane diol (**5**)) were added to the flask at stoichiometric ratio (1:1) in the presence of potassium carbonate (K_2CO_3) as a catalyst (0.1 equiv. mol). First, the mixture was heated to 120 °C and maintained for 4 h to promote the pre-polymerization. The pre-polymer was then heated to 150 °C and held for 4 h. Finally, the sample was heated to 180 °C for 8 h to guarantee the maximum conversion. The NIPUs were analyzed without any further purification.

Methods—Synthesis—Synthesis of a Reference Polyurethane: The polyaddition of isophorone diisocyanate (**IV**, 1 equiv. mol) was performed with **1** (1 equiv. mol) in a 10 ml Schlenk flask equipped with magnetic stirring and under vacuum. The reaction was performed with three different isotherms: first, the mixture was heated to 120 °C and maintained for 4 h to promote the pre-polymerization. Then, the pre-polymer was heated to 150 °C and held at this temperature for 4 h. Finally, the sample was heated to 180 °C for 8 h, corresponding to a total reaction of 16h.

Characterization: The ^{1}H NMR, ^{13}C NMR, COSY, HSQC, and HMC were recorded by a Bruker Avance 400 spectrometer (400 MHz). The samples were solubilized in hot DMSO-d_6 to assist the sample solubilization, and the analyses were performed at room temperature (≈25 °C). From ^{1}H NMR, the conversion of **1** OH protons, carbamate NH protons, and the urea and carbonate percentages were calculated.

The urea and carbonate contents are calculated as follows:

$$ureamol\% = \frac{\frac{\int (i+i')}{2}}{\int (e'+b') + \frac{\int (i+i')}{2} + \frac{\int j}{4}} \quad (1)$$

$$carbonatemol\% = \frac{\frac{\int j}{4}}{\int (e'+b') + \frac{\int (i+i')}{2} + \frac{\int j}{4}} \quad (2)$$

where $\int (i+i')$, $\int (e'+b')$ and $\int j$ are the integrals of the signals of the protons $i+i'$, $e'+b'$, and j, respectively, as defined in Figure 1.

Size exclusion chromatography (SEC) was used to estimate the polymer number-average molar mass ($\overline{M_n}$), weight average molecular weight ($\overline{M_w}$), and dispersity ($D = \overline{M_w}/\overline{M_n}$). Due to different samples solubility, the analysis was performed either with dimethylformamide (DMF) and lithium bromide (1g L^{-1}) as eluent or HFIP containing 0.10 wt.% potassium trifluoroacetate. For the SEC measurements using DMF as eluent, the measurements were performed in an Ultimate 3000 system from Thermoscientific equipped with a diode array detector (DAD), multiangle light scattering detector (MALLS), and a differential refractive index detector (dRI) from Wyatt Technology. The polymers were separated in a set of two columns GF310+510 Asahipak containing polyvinyl alcohol as stationary phase (7.5×300, exclusion limit: 300 000) and a controlled temperature of 50 °C. The samples were analyzed using a calibration with a polystyrene standard. SEC in HFIP was performed at 30 °C with a TOSOH ECOSEC HLC-8320 SEC system, at a solvent flow of 0.40 mL min^{-1} and a sample concentration of 1 mg mL^{-1}. The analysis was performed on a three-column system: PSS PFG Micro precolumn (3.0 × 0.46 cm, 10 000 Å), PSS PFG Micro (25.0 × 0.46 cm, 1000 Å), and PSS PFG Micro (25.0 × 0.46 cm, 100 Å). The system was calibrated with linear poly(methyl methacrylate) standard (Polymer Standard Service, Mp: from 800 Da to 1.6 MDa).

The NIPUs were analyzed by Fourier-transform infrared spectroscopy (FTIR) on a Bruker VERTEX 70 instrument on attenuated total reflectance (ATR) equipped with a DLaTGS MIR detector. The analysis was performed with a resolution of 4 cm^{-1} and 32 scans.

The urea and carbonate contents are calculated as follows:

$$ureamol\% = \frac{\mathcal{A}_{free-urea} + \mathcal{A}_{H-urea}}{\mathcal{A}_{tot}} \quad (3)$$

$$carbonatemol\% = \frac{\mathcal{A}_{carbonate}}{\mathcal{A}_{tot}} \quad (4)$$

where $\mathcal{A}_{tot} = \mathcal{A}_{free-urethane} + \mathcal{A}_{H-urethane} + \mathcal{A}_{free-urea} + \mathcal{A}_{H-urea} + \mathcal{A}_{carbonate}$ and $\mathcal{A}_{free-urethane}$, $\mathcal{A}_{H-urethane}$, $\mathcal{A}_{free-urea}$, $\mathcal{A}_{H-urea}$ and $\mathcal{A}_{carbonate}$ are the areas of the bands corresponding to the vibration of the free-urethanes, the H-bonded urethanes, the free ureas, the H-bonded ureas, and the carbonates, respectively, as obtained by deconvolution of the carbonyl peak (C = O) of the NIPUs (Figure 4).

The polymer thermal transitions were identified by differential scanning calorimetry (DSC) using a DSC Q200 from TA samples. The samples (≈6 mg) were analyzed using a standard aluminum crucible with three temperature ramps at a heating rate of 10 °C min^{-1}: the first from −100 to 150 °C, the second from 150 to −100 °C and the last from −100 to 200 °C.

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

carbamate, NIPU, polycondensation, transurethanization

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