

## Room temperature synthesis of non-isocyanate polyurethanes (NIPUs) using highly reactive *N*-substituted 8-membered cyclic carbonates

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There is a growing interest to develop green synthetic pathways towards industrially relevant polymers such as polyurethanes without the use of toxic and dangerous isocyanate monomers. The most promising route towards non-isocyanate polyurethanes (NIPUs) is the aminolysis of dicyclic carbonates derived from renewable resources. Although, cyclic carbonates of 5- and 6-members have been successfully proposed, aminolysis of these compounds require the use of high temperatures to obtain high conversions and subsequent high molecular weight NIPUs. Indeed, these cyclic carbonates do not allow the achievement of high molecular weight NIPUs using low reactive diamines analogous to the two of the most industrially relevant aliphatic diisocyanates. Herein, we report a (bis) *N*-substituted 8-membered cyclic carbonate, that could be prepared from naturally abundant epoxides, diamines and dimethyl carbonate using sustainable chemical routes. This *N*-substituted 8 membered cyclic carbonates appeared to be much more reactive than the smaller 5- and 6-membered cyclic carbonates. Due to this increased reactivity, we obtained high molecular weight NIPUs using a variety of diamines, including industrially relevant hindered aliphatic diamines, such as 5-amino-1,3,3-trimethylcyclohexanemethylamine (IPDA) and 4,4'-methylenebis(cyclohexylamine). The synthesis of NIPUs was demonstrated at room temperature without the need of any additional catalyst. Altogether, this paper shows that (bis) *N*-substituted 8-membered cyclic carbonates are ideal starting materials for the synthesis of sustainable non-isocyanate polyurethanes (NIPUs)

### Introduction

Polyurethanes (PUs) are considered highly versatile and one of the most important classes of polymeric materials. The demand for PUs is rising on average of 4.5% per year, and their production is expected to surpass 18 kilotons annually by 2016.<sup>1</sup> Unfortunately, conventional polyurethane synthesis necessitates the use of isocyanate monomers, which are known to be toxic<sup>2,3</sup> and sensitive to moisture<sup>4</sup>. With an impending European ban of the use of isocyanates, there is an emerging interest to find environmentally friendlier approach towards non-isocyanate polyurethanes (NIPUs).<sup>5,6</sup> Synthetic research work on NIPUs has been reported with the use of polyols<sup>7,8</sup>, CO<sub>2</sub><sup>7,9,10</sup>, and diamines<sup>11</sup>.

One of the more popular approaches to synthesize NIPUs is by the aminolysis of dicyclic carbonates with aliphatic

diamines, which result in poly-hydroxyurethanes. To date, NIPUs from 5-membered dicyclic carbonates prepared from CO<sub>2</sub> and epoxides systems have been extensively studied.<sup>4,8,12–21</sup> These monomers are typically very stable and can be stored over long periods of time without degradation. However, their high chemical and thermal stability properties become a disadvantage during polymerizations. To achieve high molecular weight polymers, the polymerization conditions need the use of high temperatures and catalysts and bulk conditions.

Few authors have reported the synthesis of NIPUs using cyclic carbonates with more than 5-members. For example, Cramail *et al.* synthesized 6-membered dicyclic carbonates from renewable sources and found that they were three times more reactive than the 5-membered dicyclic carbonates.<sup>22–24</sup> However, they were unable to control the polymerizations and gels were obtained at high conversions. In another work, Endo *et al.* reported on the synthesis of 7-membered dicyclic carbonates and NIPUs derived from these dicyclic carbonates.<sup>23,25</sup> The authors observed higher reactivity in the 7-membered carbonate over the smaller 5- and 6-membered dicyclic carbonates. It is believed that high reactivity could be attributed to the increased ring strain of the 7-membered cyclic carbonate ring versus the smaller cyclic carbonates.

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One of the main limitations of the synthesis of NIPUs by the step grow polymerization of dicyclic carbonates and diamines comes when we want to expand the breadth to low reactivity diamines or to carry out the reactions at room temperature. For instance, to use diamines such as 5-amino-1,3,3-trimethylcyclohexanemethylamine (IPDA) and 4,4'-methylenebis(cyclohexylamine) as monomers which are chemical analogous to the industrially relevant isophorone diisocyanate (IPDI) and 4,4'-methylenebis(cyclohexyl isocyanate) (H<sub>12</sub>MDI). To the best of our knowledge, in these two cases, 5 and 6-membered dicyclic carbonates have been unable to achieve high molecular weight NIPUs.

Recently, some of us reported the synthesis of an *N*-substituted 8-membered cyclic carbonates with tertiary amines in their structures.<sup>26,27</sup> One of the main aspects which made the *N*-substituted 8-membered cyclic carbonates attractive was its simple synthesis from diethanolamines, which are inexpensive and readily available starting materials derived from naturally abundant epoxides and aliphatic diamines.

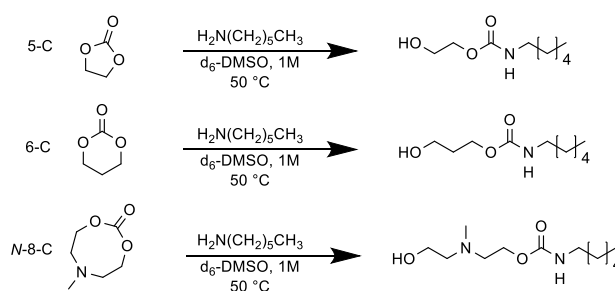
In this work, *N*-substituted 8-membered cyclic carbonates were explored as potential reagents for the synthesis of NIPUs. A kinetic study on ring opening of *N*-substituted 8-membered carbonates with *n*-hexylamine has been performed to demonstrate their high reactivity in comparison to 5- and 6-membered cyclic carbonates. A comprehensive computational study was conducted to gain a deeper insight into the higher reactivity between different sized cyclic carbonate substrates. Finally, different NIPU polymerizations were carried out at room temperature using different diamines, including low reactive industrially relevant diamines.

## Results and discussion

### Comparative study of different cyclic carbonates reactivity towards *n*-hexylamine

To understand the reactivity of the *N*-substituted 8-membered cyclic carbonate (*N*-8-C), aminolysis reactions of different cyclic carbonates with *n*-hexylamine at 50 °C were first carried out. The cyclic carbonates investigated included: ethylene carbonate (5-C, 5-membered cyclic carbonate), trimethylene carbonate (6-C, 6-membered cyclic carbonate), and 6-methyl-1,3,6-dioxocan-2-one (*N*-8-C, *N*-substituted 8-membered cyclic carbonate). Reaction kinetics were investigated by <sup>1</sup>H NMR by carrying out the reaction of cyclic carbonate and *n*-hexylamine in d<sub>6</sub>-DMSO at 50 °C (Scheme 1).

As the cyclic carbonates reacted with the *n*-hexylamine, characteristic <sup>1</sup>H NMR signals of the methylene protons in the cyclic carbonates (CH<sub>2</sub>-OCOO-) disappeared. The appearance of three new signals attributed to the formation of urethane was observed at 4.13 ppm (CH<sub>2</sub>-OCONH), 3.57 ppm (CH<sub>2</sub>-OH) and 3.12 ppm (CH<sub>2</sub>-NHCOO); the conversion was determined by using relative peak integration values.



Scheme 1. Aminolysis of cyclic carbonates with *n*-hexylamine.

Overall, the reactions proceeded by second-order kinetics  $-d[M]/dt = k[M]^2$ , (where  $[M] = [\text{cyclic carbonate}] = [n\text{-hexylamine}]$ ), which was confirmed by the linear relationship between  $t$  and  $1/(1-p)$ , where  $t$  is time and  $p$  is the fraction of monomer converted to urethane. Rate constants,  $k$ , were calculated for each of the cyclic carbonates (Figure 1). We found that the reaction kinetics were highly dependent on the size of the carbonate ring. Our findings were also congruent with the literature about 6-C being three times more reactive than the 5-C.<sup>28</sup> More importantly, we observed that *N*-8-C was five times more reactive than 6-C. Even after 30 min of reaction, we were able to obtain 71% conversion for the case of *N*-8-C.

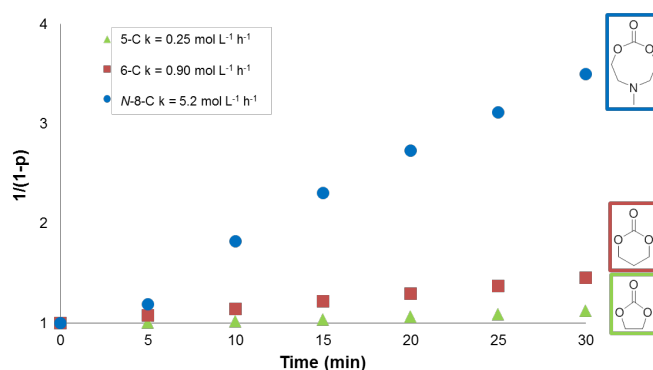


Figure 1. Kinetics plot from the aminolysis of various cyclic carbonates with *n*-hexylamine.

The kinetics of aminolysis of 8-C with *n*-hexylamine was further evaluated at higher temperatures (65 and 80 °C). As expected, we found the reaction rate constant to increase with higher temperatures. For an initial concentration of 1 mol L<sup>-1</sup>, the reaction rate constants at 50, 65, and 80 °C were 5.0, 10.1, and 17.6 L mol<sup>-1</sup> h<sup>-1</sup> respectively. Using these values, the activation energy ( $E_a$ ) for 8-C was estimated at 40 kJ mol<sup>-1</sup> from the Arrhenius plot (see SI). This value was twice the value obtained by Cramail et al. for their 6-membered dicyclic carbonates.<sup>28</sup> Furthermore, even at 80 °C, no side reactions were observed in any of these experiments. This demonstrated the potential of using the *N*-substituted 8-membered cyclic carbonate system for the synthesis of NIPUs.

### Comparative study with low reactivity amines

We expanded our investigation of the reactivity of different sized cyclic carbonates to different amines of varying nucleophilicities, which included: *n*-hexylamine, cyclohexylamine, *N*-methylbutylamine, aniline, and monofunctional poly(ethylene glycol) amine ( $M_w$  1000). Conversions were calculated from relative integral values from  $^1\text{H}$  NMR spectroscopy; results are summarized in Figure 2.

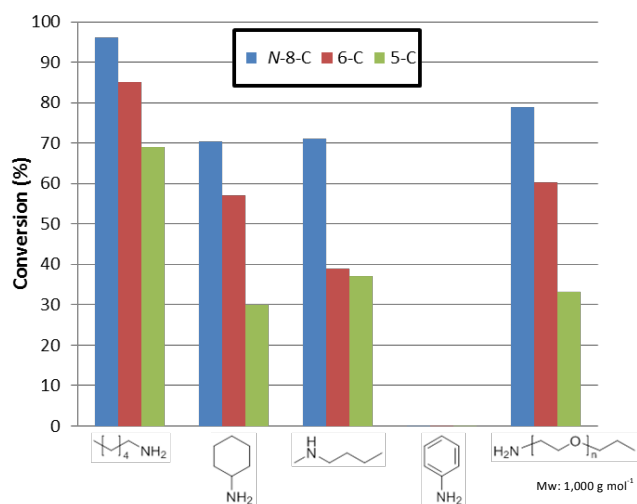


Figure 2. Conversions from reactions with *N*-8-C, 6-C, and 5-C with less reactive amines. Reactions were carried out at 50 °C for 6 h.

In all the studied systems, the reaction conversions were much higher when *N*-8-C was used. The exception was for the case of aniline, where no reaction took place. Amines such as cyclohexylamine and poly(ethylene glycol) amine were able to obtain higher conversions when the size of the cyclic carbonate increased. Besides the reactions with these two amines, we were also able to observe the aminolysis of the cyclic carbonates with *N*-methylbutylamine, a secondary amine. This enhanced reactivity of the *N*-8-C with low reactive amines further is congruent to the trends observed in the kinetics and computation studies, it also demonstrated its potential for the synthesis of NIPUs with various amines of different nucleophilicities.

### Computational modeling

In the literature, two reaction mechanisms have been proposed for the aminolysis of 5- and 6-membered cyclic carbonates. The first mechanism, proposed by Tomita *et al.*, suggested a mechanism through an amphoteric tetrahedral intermediate<sup>29</sup>. On the other hand, Zabalov *et al.* proposed that the formation of the hydroxyurethane from a 5-membered cyclic carbonate with two amines present and proceeds through a six centered ring intermediate. One of the amines behaves as a catalyst, and the other performs the nucleophilic attack.<sup>30</sup>

Here, we present a comprehensive computational study to gain a deeper insight into the aminolysis of 5-C, 6-C, and *N*-8-C. Taking the compound of *N*-8-C as the computational model (in

Figure 3), we first examined the concerted amphoteric tetrahedral mechanism (TS3). We then compared this with a more classical alternative, consisting in a stepwise amine nucleophilic addition (TS1) and a subsequent ring opening process (TS2).

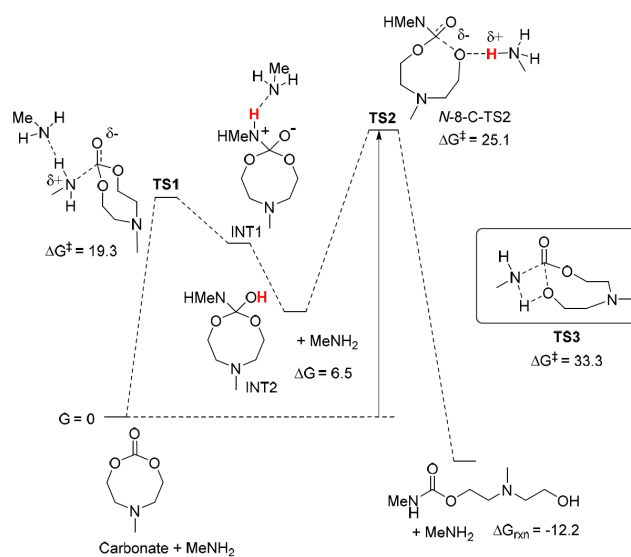


Figure 3. Reaction energy profile for *N*-8-C and its Gibbs Free energies computed at m062x/6-31+G(d,p) (pcm, solvent = DMSO) level.

As expected, the mechanism in TS3 presented a large activation energy of 33.3 kcal mol<sup>-1</sup>, as it contained a 4-membered cyclic transition state that was too strained to be plausible.<sup>31</sup> On the other hand, the computed energies for the stepwise approach were much lower; hence it was a more feasible pathway. Upon closer inspection, the initial amine addition transition state (TS1, Figure 3) presented an activation Gibbs Free energy of 19.3 kcal mol<sup>-1</sup>. The following transition state (TS2) became the rate determining step with a barrier of 25.1 kcal mol<sup>-1</sup>, an affordable amount of energy at the experimental temperatures. It is important to note that a second methylamine molecule was included in these calculations; it helped to stabilize the computed structures and reduce the energy values. In fact, the non-stabilized transition states led to convergence problems and/or broke apart into the reactant structures during optimization (See SI). The stabilization and activation of the reaction by a second methylamine makes perfect sense chemically.<sup>32</sup> In the experimental conditions, this stabilization could also be achieved by using a polar solvent, or by some small amount of water. After the TS1, a high-in-energy zwitterionic intermediate (INT1, ca. 17 kcal mol<sup>-1</sup>) was formed, which then easily rearranges itself to a more stable uncharged INT2 (6.5 kcal mol<sup>-1</sup>) via a simple proton shift. In fact, INT1 and INT2 represent two intermediates of a group of structures in equilibrium, where the H can be shared by the different nitrogen and oxygen atoms (highlighted in red in Figure 3). At the end of the process, an energy difference of -12.2 kcal mol<sup>-1</sup> between the final products and initial reagents was calculated, which indicated an exergonic reaction.<sup>33</sup>

Interestingly, the energy barrier at TS2 for each of the different carbonate substrates (*N*-8-C, 6-C and 5-C), indicated a positive correlation between the size of the cyclic carbonates and their reactivity (Figure 4). This data was in agreement with the experimental observations from our kinetic studies. The computed energy values for the TS2 increased as the ring size decreased, from 25.1 kcal mol<sup>-1</sup> in *N*-8-C-TS2 to 32.0 kcal mol<sup>-1</sup> in 5-C-TS2. In these structures, a second amine molecule is protonated, which then stabilizes the leaving O atom by a strong H-bond (1.3 Å), and then finally facilitates the rupture of the C-O bond (dashed lines in Figure 4).

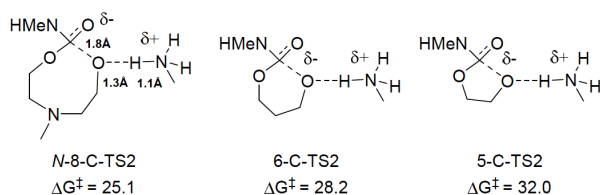
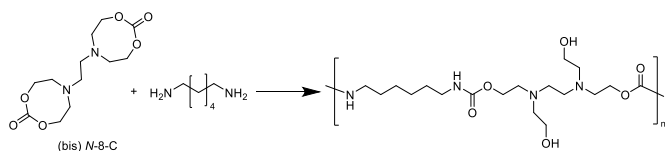


Figure 4. Comparison of the Free Gibbs activation energies for the ring opening process computed at m062x/6-31+G(d,p) (pcm, solvent = DMSO) level.

### Synthesis of NIPUs based on (bis) *N*-8-C and diamines

After obtaining a better understanding of the urethane formation with the *N*-8-C, we decided to investigate their use for polymerization of NIPUs. To do this, we first synthesized the (bis) *N*-substituted 8-membered cyclic carbonates ((bis) *N*-8-C). An additional kinetic experiment with *n*-hexylamine was performed with the (bis) *N*-8-C. A *k* value of 5.0 mol L<sup>-1</sup> h<sup>-1</sup> was obtained, and found to be similar to that of *N*-8-C (5.2 mol L<sup>-1</sup> h<sup>-1</sup>).



Scheme 2. Synthesis of NIPUs with the (bis) *N*-8-C with 1,6-hexamethylenediamine.

After confirming the similar reactivity profiles of (bis) *N*-8-C and *N*-8-C, we investigated the ability of these dicyclic carbonates to synthesize NIPUs using the commercially available 1,6-hexamethylene diamine (Scheme 2). An initial polymerization was carried out using d<sub>6</sub>-DMSO at 1 mol L<sup>-1</sup> and room temperature conditions (NIPU1). The formation of NIPUs was confirmed by <sup>1</sup>H NMR spectroscopy, as shown in Figure 5. We observed the characteristic methylene proton signals of (bis) *N*-8-C at 4.08 and 2.76 ppm gradually disappeared as new signals from the formation of hydroxyl-polyurethanes gradually appeared at 7.01, 3.95, 3.41, 2.93, 2.65, and 2.53 ppm. The polymerization showed a conversion >95% after 24 h, which was more than twice the

conversion value of Cramail's (bis) 6-membered cyclic carbonate with a similar diamine after 24 h at 30 °C.<sup>28</sup>

To further verify the formation of NIPUs, FTIR spectroscopy was performed to the (bis) *N*-8-C monomer and the polyurethane polymer (See Figure 27S, SI). As the reaction proceeded, the complete disappearance of the cyclic carbonate (C=O) stretching band at 1725 cm<sup>-1</sup> was observed. Two new bands which corresponded to the urethane linkage vibrations (amide I at 1688 cm<sup>-1</sup> and amide II at 1529 cm<sup>-1</sup>) appeared after the polymerization. In addition, a broad band centered around 3321 cm<sup>-1</sup> was observed. This band was identified as the N-H and O-H stretching vibrations. The collected data from <sup>1</sup>H NMR and FTIR are congruent with the reports in the literature regarding the formation of NIPUs via aminolysis of cyclic carbonates.<sup>8,28</sup> To confirm the presence of high molecular weight NIPUs, GPC analysis was carried out (SI and Table 1). As observed, a molecular weight of 47,000 g mol<sup>-1</sup> was obtained, which further demonstrated the high reactivity of (bis) *N*-8-C.

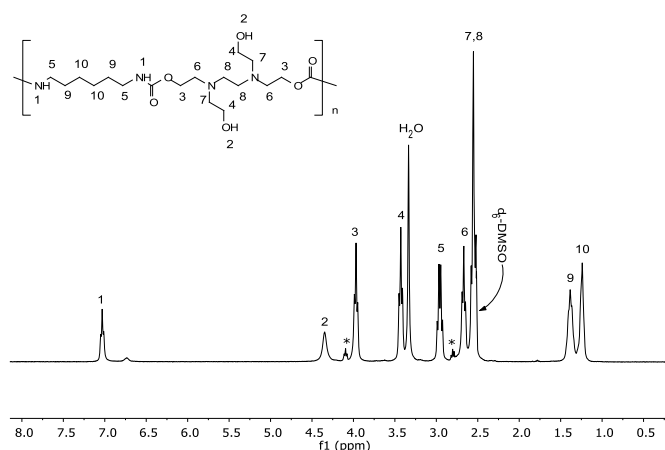
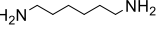
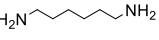
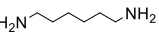
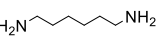

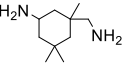
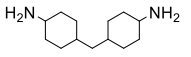


Figure 5. <sup>1</sup>H NMR of NIPU1 after 24 h at 25 °C. Proton signals attributed to the starting material (bis) *N*-8-C have been labeled with \*.

To expand on our preliminary investigations, higher reaction temperatures and other solvent conditions were examined (entries 1, 4 of Table 1). For instance when the reaction was carried out at 50 or 80 °C gelation was observed during the polymerization process. In our opinion the higher temperature could induce some side reactions between the pendant hydroxyl group and the cyclic carbonate as observed by Cramail et al.<sup>28</sup> When water was used as solvent for the reaction, a gel was obtained and we were unable to be characterized it by NMR spectroscopy or GPC. Nevertheless, the synthesized material was analyzed by FTIR spectroscopy (Figure 28, SI) and a clear signals of urethane formation were observed such as the amide I at 1688 cm<sup>-1</sup> and amide II at 1529 cm<sup>-1</sup> and a broad band centered around 3321 cm<sup>-1</sup>. Interestingly this demonstrates the possibility to perform this polymerization in aqueous media, because water not only could act as reaction media but also to stabilize the transition state and facilitate the polymerization as observed computationally.

Because of the high reactivity of (bis) *N*-8-C, we wanted to expand the breadth of our NIPU synthesis to other diamines less reactive than aliphatic primary amines (Table 2). In fact, one of the main limitations of isocyanate free approaches of using cyclic carbonates arises when the nucleophilicity of the amine is reduced. First we considered using a secondary amine to make NIPUs. Many studies have demonstrated that secondary amines are less reactive than their primary amine counterparts, and thus they are typically overlooked for the use of forming NIPUs.<sup>34</sup> In addition to secondary amines, we also put into consideration of using hindered primary diamines analogous to the two of the most industrially relevant aliphatic diisocyanates, which are isophorone diisocyanate and 4,4'-methylenebis(cyclohexyl isocyanate).<sup>8</sup> Thus, we carried out a polymerization reaction at room temperature with the secondary diamine *N,N'*-dimethyl-1,3-propanediamine. Entry 5 in Table 2 shows a 85% conversion by <sup>1</sup>H NMR after 24 h. However, we were unable to obtain a high molecular weight value for this product. On the other hand, two diamines analogous to industrially relevant isocyanates for PUs were screened in entries 6 and 7. The polymerizations were characterized by <sup>1</sup>H NMR spectroscopy and GPC (Table 1). In both cases, we were able to get high conversion and high molecular weights of around 20,000 g mol<sup>-1</sup>. Together, these results confirmed that even with hindered amines, we were able to achieve high molecular weight NIPUs at room temperature.

Table 2. Synthesis of NIPUs from (bis) *N*-8-C and diamines after 24h.

NIPU	T (°C)	Co-monomer	Solvent	Conv. (%) <sup>a</sup>	M <sub>n</sub> (g mol <sup>-1</sup> ) <sup>b</sup>	Đ
1	25		DMSO	95	47,000	1.60
2	50		DMSO	89 <sup>c</sup>	38,200 <sup>c</sup>	1.66 <sup>c</sup>
3	80		DMSO	93 <sup>c</sup>	27,700 <sup>c</sup>	1.46 <sup>c</sup>
4	25		D <sub>2</sub> O	.. <sup>c,d</sup>	.. <sup>c,d</sup>	.. <sup>c,d</sup>
5	25		DMSO	85	.. <sup>e</sup>	.. <sup>e</sup>
6	25		DMSO	88	19,500	1.22
7	25		DMSO	95	22,700	1.26

Summary of NIPUs synthesized in this paper. These NIPUs were synthesized in d<sub>6</sub>-DMSO at room temperature (25 °C). <sup>a</sup> Conversions were calculated by <sup>1</sup>H NMR. <sup>b</sup> M<sub>n</sub> values were obtained by GPC in DMF. <sup>c</sup> Gelation was observed in these cases. <sup>d</sup> Conversion and M<sub>n</sub> values were unobtainable due to insolubility in organic solvents. <sup>e</sup> M<sub>n</sub> values were below the detection limit of the GPC.

## Conclusions

In conclusion, we demonstrated that the (bis) *N*-8-C is a good candidate for the synthesis of non-isocyanate poly(urethanes). Kinetic studies of the aminolysis of both *N*-8-C and (bis) *N*-8-C by *n*-hexylamine confirmed their extraordinary

reactivity over the smaller 5- and 6-membered cyclic carbonates. This set of experimental data was in agreement with our computational study, which revealed that the ring opening of the *N*-8-C by an amine system is kinetically and theoretically more favorable than the smaller cyclic carbonate substrates. Finally, high molecular weights NIPUs were formed by the polyaddition of (bis) *N*-8-C and 1,6-hexamethylenediamine. Furthermore, we were also able to obtain NIPUs with hindered aliphatic diamines and diamines that were analogous to industrially relevant isocyanates. All these results make these (bis) *N*-substituted 8-membered cyclic carbonates ideal candidates for the sustainable synthesis of industrially relevant non-isocyanate polyurethanes.

## Experimental

### General information

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with Bruker Avance DPX 300, Bruker Avance 400, or Bruker Avance 500 spectrometers. The NMR chemical shifts were reported as δ in parts per million (ppm) relative to the traces of non-deuterated solvent (eg. δ = 2.50 ppm for d<sub>6</sub>-DMSO or δ = 7.26 for CDCl<sub>3</sub>). Data were reported as: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constants (J) given in Hertz (Hz), and integration. Fourier transform infrared - attenuated total reflection (FTIR-ATR) spectroscopy was performed with a Bruker Alpha. Gel permeation chromatography (GPC) was performed using a Agilent Technologies PL-GPC 50 Integrated GPC system, with a Shodex KD-806M column. For the GPC, *N,N*-Dimethylformamide with a 10mM concentration of LiBr at 50 °C was used as the solvent and toluene as a marker. Polystyrene of different molecular weights, ranging from 2,100 g mol<sup>-1</sup> to 1,920,000 g mol<sup>-1</sup>, were used for the calibration of the GPC.

### Materials

1,3-Propanediol (98%), triethylamine (≥99%), *N*-methyl-diethanolamine (≥99%), triphosgene (98%), *N,N,N',N'*-tetrakis(2-hydroxyethyl)ethylenediamine (technical grade), *n*-hexylamine (99%), ethylene carbonate (98%), cyclohexylamine (≥99%), aniline (99%), *N*-butylmethylamine (96%), bis(pentafluorophenyl) carbonate (97%), 5-amino-1,3,3-trimethylcyclohexanemethylamine (≥99%), 4,4'-methylenebis(cyclohexylamine) (97%), 1,6-hexamethylenediamine (96%), lithium bromide (≥99%), DCM (≥99.9%), and diethyl ether (≥99.8%), were purchased and used as-is from Sigma Aldrich. Ethyl chloroformate (99%) and THF (≥99%) were purchased and used as is from Acros. Acetone (≥99.5%) and DMF (GPC grade) were purchased and used from Fisher. Methoxypolyethylene glycol amine (M<sub>w</sub> 1,000) was purchased and used from Alfa Aesar. Deuterated solvents such as CDCl<sub>3</sub>, d<sub>6</sub>-DMSO, and D<sub>2</sub>O were purchased from Euro-top and used as is.

### Synthesis of 1,3-dioxan-2-one (6-C)

Synthesis of 6-C was carried out in an adapted version of Toshiro *et al.*<sup>35</sup> A 1 L single neck round bottom flask was charged with 1,3-propanediol (10 g, 0.131 mol, 1 equiv.), ethyl chloroformate (28.6 g, 0.264 mol, 2 equiv.), and 650 mL of anhydrous THF. The round bottom flask was kept in an ice bath and magnetically stirred. Triethylamine (28.1 g, 0.278 mol, 2.1 equiv.) added drip-wise into the reaction over 15 min with an additional funnel. After the addition of triethylamine, the reaction was taken out of the ice bath and stirred for an additional two hours at room temperature. The precipitated triethylamine hydrochloride salt was filtered away and discarded. The THF in the filtrate was evaporated and the remaining residue was recrystallized in diethyl ether. The final product consisted of white crystals (5.6 g, 42% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 4.42 (t, J = 5.7 Hz, 4H), 2.12 (p, J = 5.7 Hz, 2H). <sup>13</sup>C NMR (101 MHz, DMSO) δ 21.17, 39.52, 68.06, 148.13.

#### Synthesis of 6-methyl-1,3,5-dioxazocan-2-one (N-8-C)

Synthesis of N-8-C was carried out in an adapted version of Pascual *et al.*<sup>26</sup> A 1L single neck round bottom flask was charged with a stir bar, 5 g of N-methyldiethanolamine (42 mmol), 9.2 g of triethylamine (90.9 mmol), and 650 mL of anhydrous THF. An additional funnel was affixed to the round bottom flask and charged with 4.6 g of triphosgene (15.5 mmol) and 50 mL of anhydrous THF. The setup was then placed in a liquid nitrogen and acetone mixture. The triphosgene-THF mixture was dripped into round bottom flask and the triethylamine hydrochloride salt could be seen precipitating out of the reaction. After the addition of triphosgene, the reaction was stirred for an additional three hours. The precipitated triethylamine hydrochloride salt was filtered away and discarded. The filtrate was concentrated under reduced pressure and then treated with cold diethyl ether. The remaining triethylamine hydrochloride salt was then removed. The remaining filtrate, free of triethylamine hydrochloride salt, was then concentrated under reduced pressure to give a pink colored liquid as the final product (4.47g, 73% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 4.13 (t, J = 5.4 Hz, 4H), 2.71 (t, J = 5.3 Hz, 4H), 2.43 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 156.11, 68.74, 56.14, 44.44. <sup>1</sup>H NMR (500 MHz, DMSO) δ 4.13 (t, J = 5.3 Hz, 4H), 2.73 (t, J = 5.3 Hz, 8H), 2.41 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO) δ 155.36, 68.71, 55.64, 44.39, 39.52.

#### Synthesis of 6,6'-(ethane-1,2-diyl)bis(1,3,6-dioxazocan-2-one) ((bis) N-8-C)

Synthesis of (bis) N-8-C was mainly carried out in an adapted version of Pascual *et al.*<sup>26</sup> A 1 L single neck round bottom flask was charged with a stir bar, 5 g of N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine (21.16 mmol), 2.247 g of 1,8-bis(dimethylamino)naphthalene (10.48 mmol), and 400 mL of anhydrous THF. An additional funnel was affixed to the round bottom flask and charged with 18.4 g of bis(pentafluorophenyl) carbonate (46.69 mmol) and 50 mL of anhydrous THF. The bis(pentafluorophenyl) carbonate and THF mixture was then dripped into round bottom flask and stirred

at room temperature for two hours. The reaction mixture was then concentrated under reduced pressure and then treated with excess ether. This mixture was then placed in the refrigerator overnight. The precipitated material was then collected and dried to give the 8-DC product (4.3 g, 71% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 4.18 (t, J = 5.3 Hz, 8H), 2.82 (t, J = 5.3 Hz, 8H), 2.77 (s, 4H). <sup>1</sup>H NMR (300 MHz, DMSO) δ 4.08 (t, J = 5.3 Hz, 8H), 2.76 (t, J = 5.3 Hz, 8H), 2.62 (s, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 156.42, 69.27, 55.40, 54.95. <sup>13</sup>C NMR (75 MHz, DMSO) δ 53.50, 53.54, 68.89, 155.26.

We were also able to synthesize (bis) N-8-C by using the ring closing method with dimethyl carbonate, as reported by Meuldijk *et al.*<sup>36</sup> However, the yield was much lower than the ring closing method with bis(pentafluorophenyl) carbonate.

#### General procedure for the kinetic study

In a typical procedure, carbonate (1 equiv.) was directly added into a NMR tube and dissolved in d<sub>6</sub>-DMSO to give a 1 M concentration. An amine (1 equiv.) was then added into the tube and then quickly inserted into the NMR. A spectrum was recorded every 5 min over a 30 min period.

#### General procedure for the comparative study of low reactivity amines

In a typical procedure, carbonate (1 equiv.) was added into a vial and dissolved in d<sub>6</sub>-DMSO to give a 1 M concentration. An amine (1 equiv.) was then added into the vial. The reaction was then stirred for 6 h at 50 °C.

#### General procedure for polymerization

In a typical procedure, a vial was charged with (bis) N-8-C (100 mg, 347 μmol, 1 equiv.), a diamine (1 equiv.), 347 μL of d<sub>6</sub>-DMSO, and a stir bar. The reaction was stirred at room temperature for 1 d. The reaction was then characterized with <sup>1</sup>H NMR, FTIR-ATR, and GPC.

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