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# Chemo- and regio-selective additions of nucleophiles to cyclic carbonates for the preparation of self-blowing non-isocyanate polyurethane foams

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**Abstract:** Polyurethane (PU) foams are indisputably daily essential materials found in many applications, notably for comfort (e.g. mattresses) or energy saving (e.g. thermal insulation). Today, greener routes for their production are intensively searched for avoiding the use of toxic isocyanates. We now describe an easily scalable process for the simple construction of self-blown isocyanate-free PU foams by exploiting the organocatalyzed chemo- and regio-selective additions of amines and thiols to easily accessible cyclic carbonates. These reactions are first validated on model compounds and rationalized by DFT calculations. Various foams are then prepared and characterized in terms of morphology and mechanical properties, and the scope of the process is illustrated by modulating the composition of the reactive formulation. This work illustrates how chemo- and regio-selective additions can be exploited for the easy construction of more sustainable PU foams.

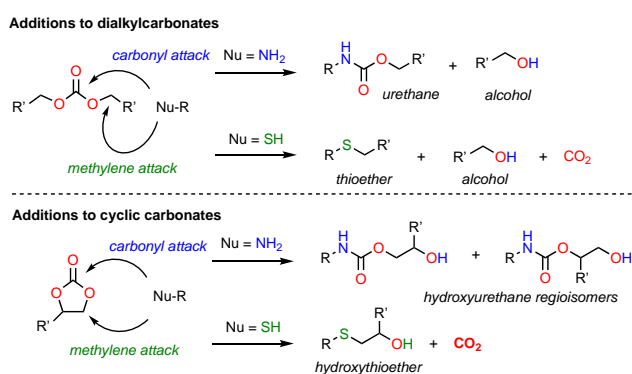
## Introduction

Polyurethanes (PUs) foams, with a world-wide production expected to reach 12.7 million tons by 2024,<sup>1</sup> are key materials of our modern life with a broad range of applications for comfort and wellness (furniture, mattresses, seats...), shock absorption, thermal/acoustic insulation or as sealants. Industrially, PUs are made by polyaddition of di- or polyisocyanates and di- or polyols.<sup>2</sup> Their foaming is generally induced by hydrolysis of the isocyanates with concomitant formation of CO<sub>2</sub>. The *in-situ* release of this gas expands the polymer during its formation, leading to foams with properties that depend on the composition of the reactive formulation.<sup>2</sup> Due to the large diversity of polyols that can be used, rigid to soft foams can be easily produced by this simple process. However, the health concerns and regulation changes associated to the use of toxic isocyanates are motivating the industries and the scientists to explore novel routes to design isocyanate-free PU foams. The recent advances in the chemical transformations of CO<sub>2</sub> opened new opportunities to solve this challenge and multiple pathways are now accessible to fabricate PUs by directly using CO<sub>2</sub> as a comonomer or by copolymerizing CO<sub>2</sub>-based building blocks.<sup>3</sup> Amongst them, the step-growth copolymerization of di- or polyamines with 5-membered polycyclic carbonates, easily synthesized by the [3+2] coupling of CO<sub>2</sub> with epoxides,<sup>4</sup> is growing rapidly and gives access to poly(hydroxyurethane)s (PHUs).<sup>5</sup> Unlike isocyanates, cyclic carbonates however do

not decompose spontaneously by simple addition of water to release CO<sub>2</sub> as the blowing agent, rendering impossible the formation of self-blowing PHU foams. To date, foaming procedures for PHUs are rare and very limited in scope. The first strategy was reported by Caillol by thermal decomposition of Momentive MH15, i.e. poly(methylhydrogenosiloxane), into dihydrogen (a highly flammable gas) that expanded the PHU matrix during its formation.<sup>6</sup> Another approach reported by Mulhaupt consisted in adding Solkane, i.e. a fluorocarbon physical blowing agent, that foamed the PHU matrix by evaporation during the polymerization.<sup>7</sup> Self-blown rigid PHU foams with open cells porosity were designed by using sodium bicarbonate as chemical blowing agent at high temperature (>200°C)<sup>8</sup>, or by the addition of maleic acid and glutaraldehyde to a PHU formulation (the foaming mechanism is however not clear in this case).<sup>9</sup> Only two relevant works have described the use of CO<sub>2</sub> as blowing agent for the production of PHU foams without requiring the addition of external reagents. The first one reported the fabrication of microcellular PHU foams with promising heat insulating properties by the supercritical CO<sub>2</sub>-assisted batch foaming technology.<sup>10</sup> In that case, pre-synthesized PHUs thermoplastics were impregnated by CO<sub>2</sub> at the supercritical state and, upon release of the pressure, CO<sub>2</sub> was expanding the polymer matrix. The foam morphology, the density and the pore size were adjusted by a fine control of the CO<sub>2</sub> pressure, the impregnation and foaming conditions. In 2018, the first CO<sub>2</sub> self-blowing PHU foam was reported by North by exploiting a specific bis(cyclic carbonate) monomer, i.e. sorbitan bis-carbonate, that underwent an intramolecular side-reaction provoking the partial decarboxylation of the monomer during thermally driven aminolysis.<sup>11</sup> The CO<sub>2</sub> release was however observed at a low level and this strategy was limited to sorbitan bis-carbonate, therefore strongly limiting the scope of the process. The quest for a universal strategy to producing self-blowing PHUs that is versatile, simple, compatible to industrial processes (reactive extrusion foaming, reactive molding, foaming in place, etc.) and that mimics the conventional PUs foaming methodology (by the *in-situ* generation of CO<sub>2</sub>) is highly desirable for the next generation of greener PU foams.

To tackle this challenge, we took inspiration from the dialkylcarbonates chemistry responding to the Pearson's Hard-Soft Acid-Base (HSBA) theory. Dialkylcarbonates display two electrophilic sites, the carbonyl and methylene carbons, with a reactivity that can be discriminated by the

Hard-Soft character of the nucleophile.<sup>12</sup> Hard nucleophiles (e.g. amines) are undergoing carbonyl attack whereas methylene attack occurs with soft nucleophiles (e.g. thiols) (Scheme 1). The same situation is also noted for 5-membered cyclic carbonates (5CCs) but under harsher reaction conditions. We therefore postulated that combining two types of nucleophiles with distinct hard and soft characters within a single PHU formulation should lead to two competitive and selective 5CC ring-opening pathways, i.e. the acylation of the amine to form  $\beta$ -hydroxyurethane linkages (via carbonyl attack, Scheme 1) and the alkylation of the soft nucleophile with concomitant *in-situ* release of CO<sub>2</sub> (via methylene attack, Scheme 1). Although the S-alkylation of thiols was sparsely reported with dialkylcarbonates,<sup>12c</sup> we identified thiols as ideal soft nucleophiles to combine with amines (hard nucleophiles) for fabricating PHU foams from reactive formulations.



**Scheme 1.** (Regio)selective addition of amines or thiols to dialkylcarbonates or 5-membered cyclic carbonates

In this work, we explore the formation of self-blown PHU foams by directing the concomitant selective aminolysis of the cyclic carbonate and the decarboxylative S-alkylation of a thiol from reactive formulations containing amines, thiols and cyclic carbonates. First, we investigate the organocatalyzed regio-selective addition of model thiols to five-membered cyclic carbonates that leads to the decarboxylative formation of hydroxythioethers or poly(hydroxythioether)s, and we approach the reaction mechanism by combining kinetics studies and DFT modeling. We then report how to exploit this reaction for the preparation of microcellular PHU foams and we illustrate the scope of this process. We also show that, beside the generation of the blowing agent during the PHU formation, the thiol/cyclic carbonate reaction provides hydroxythioether linkages that contribute to the polymer matrix construction and improve the thermal properties of the final material.

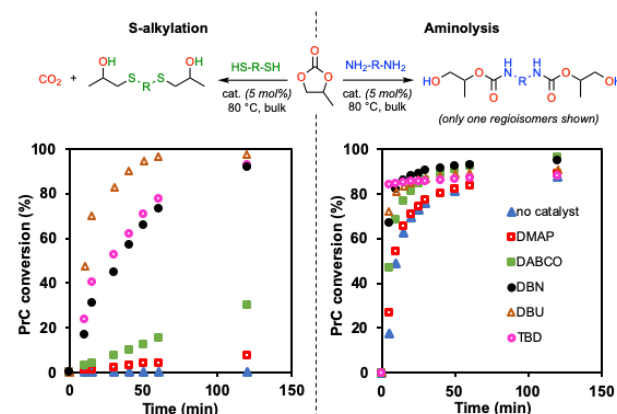
## Results and Discussion

### Model reactions

The self-blowing PHU foaming method lies on two competitive reactions, i.e. the aminolysis of 5CC to form the urethane linkages and to construct PHU, and the S-alkylation of thiols to generate the blowing agent (CO<sub>2</sub>) while creating thioether linkages. The rates and selectivity of the reactions

have to be adjusted for controlling both the PHUs synthesis and foaming. Ideally, both reactions have to take place in a range of temperature between 80 °C and 120 °C, which are common operative conditions to synthesize PHUs.<sup>5</sup> The main challenge in self-blowing processes is to form polymer chains with a sufficient viscosity and a crosslinking degree prior to the release of the blowing agent (CO<sub>2</sub>) in order to avoid the collapse of the foam. In our case, this means that the 5CC ring-opening by the amine should be faster than the decarboxylation promoted by the thiol. The S-alkylation of thiols with dialkylcarbonates has been reported but was slow and generally realized under demanding conditions (T = 100–180 °C, K<sub>2</sub>CO<sub>3</sub> as catalyst).<sup>12c</sup> These operative conditions are not compatible with the PHU chemistry as they will favor the occurrence of side-reactions such as the urea formation and provoke a deviation of the stoichiometry which is detrimental for the step-growth polymerization.<sup>5i, 13</sup>

Identifying a single catalyst that is able to catalyze both the S-alkylation and the aminolysis is then a prerequisite for the formation of self-blowing PHU. Organobases such as DBU, DBN, TBD, DMAP, DABCO are potential candidates and some of them are known to catalyze the aminolysis of 5CC.<sup>14</sup> We therefore investigated and compared the organobase catalyzed additions of a diamine (2,2'-(Ethylenedioxy)bis-ethylamine) and a dithiol (2,2'-(ethylenedioxy)diethanethiol) as a model 5CC (Figure 1). These reactions were carried out under equimolar conditions between the reactive groups without any solvent and under ambient atmosphere at 80 °C in order to approach reactions conditions that will be implemented for the foaming. The reactions were monitored by <sup>1</sup>H-NMR spectroscopy as described in Supporting Information (Figure S1 and S2).



**Figure 1.** Conversion of propylene carbonate (PrC) with the reaction time for (a) the S-alkylation of thiol and (b) the aminolysis catalyzed by organobases (DMAP, DABCO, TBD, DBN or DBU). Conditions:  $[SH]$  or  $[NH_2]/[PrC] = 1$ , organobase = 5 mol% compared to PrC, 80 °C, bulk.

Under catalyst-free conditions, the thiol did not react with PrC, which is in sharp contrast to the amine that provided the expected two hydroxy-urethane regioisomers (80 % PrC conversion in 1h).<sup>14</sup> By adding weak bases such as DMAP or DABCO (5 mol% compared to PrC), the S-alkylation of the thiol by decarboxylative addition onto PrC was observed, however was slow with respectively 10 or 30 % conversion in 2 h. Importantly, this reaction was accelerated by using superbases with conversions as high as 90 % in 2 h with DBN

or 96 % with DBU in 1 h, with the selective formation of the S-alkylated regioisomer that originates from the thiol attack at the electrophilic methylene site of PrC. Although DMAP did not affect the PrC aminolysis, the addition of DABCO, DBU and DBN significantly accelerated the reaction with the production in all cases of the two hydroxyurethane regioisomers. The comparison of the kinetics profiles for the two considered reactions, i.e. the S-alkylation of thiol and the aminolysis of PrC, gave clear insights into the feasibility of the PHU foaming methodology. First, whatever the catalyst, the aminolysis of PrC was always faster than the S-alkylation of the thiol which is a prerequisite to tailor PHU chains before the *in-situ* formation of the blowing agent ( $\text{CO}_2$ ). Second, by the choice of the catalyst, the rates of these two competitive reactions can be adjusted, which constitutes an additional lever for tuning the viscosity of the reaction medium prior PHU expansion. From the comparative kinetic studies, DBU was selected in the next studies as it catalyzed both reactions under reasonable period of time (Figure S3). It is also operative over a broad range of temperature (25-100 °C) for the S-alkylation of the thiol (Figure S4).

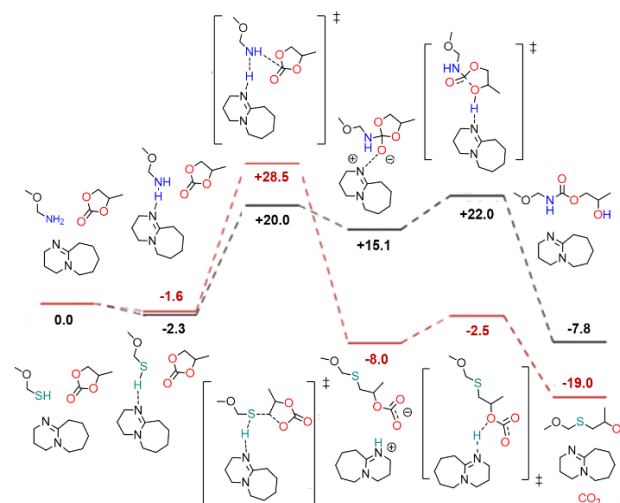
### DFT calculations

Model reactions carried out in the presence of DBU were confronted to mechanistic DFT calculations at the M062X/6-311G(d,p) level of theory (see ESI5 for details). Figure 2 depicts the two competitive pathways (i.e. aminolysis and S-alkylation) catalyzed by DBU using simplified model amine and thiol of similar structure ( $\text{CH}_3\text{-O-CH}_2\text{-NH}_2$  and  $\text{CH}_3\text{-O-CH}_2\text{-SH}$ ).

In the case of the aminolysis, the overall reaction proceeds in 2 steps. From the van der Waals complex ( $-2.3 \text{ kcal.mol}^{-1}$ ), the initial step corresponds to the nucleophilic attack of the amine onto the carbonate group of 5CC accompanied by a proton transfer from the amine towards the  $\text{sp}^2$  N atom of DBU. This step is the rate determining step with a barrier height of  $22.3 \text{ kcal.mol}^{-1}$ . The resulting cyclic amino alkoxide anion (interacting with  $\text{DBUH}^+$  by H-bond) is then encountering a ring opening by C-O bond cleavage and a simultaneous proton transfer between  $\text{DBUH}^+$  and the adjacent O atom of the carbonate to product the target hydroxyurethane and the regeneration of DBU with a barrier height of  $6.9 \text{ kcal.mol}^{-1}$ .

The S-alkylation reaction is also proceeding in two elementary steps. The first one consists in the initial van der Waals complex ( $-1.6 \text{ kcal.mol}^{-1}$ ) that reacts by a methylene attack of the thiol onto the non-substituted carbon atom of the 5CC while the thiol proton is transferred to the  $\text{sp}^2$  N atom of DBU. This step exhibits a barrier height of  $30.1 \text{ kcal.mol}^{-1}$ , making it the rate determining step of the S-alkylation reaction. In a second step, a decarboxylation of the resulting linear carbonate anion occurs together with the formation of the hydroxythioether by proton transfer from  $\text{DBUH}^+$  and then the regeneration of DBU with a barrier height of  $5.5 \text{ kcal.mol}^{-1}$ .

Therefore, the barrier heights of the rate determining step of the aminolysis ( $22.3 \text{ kcal.mol}^{-1}$ ) and the S-alkylation ( $30.1 \text{ kcal.mol}^{-1}$ ) reactions obtained from DFT calculations are in good agreement with the kinetic trends observed, i.e. the 5CC ring-opening by the amine is easier and faster than the decarboxylation promoted by the thiol.

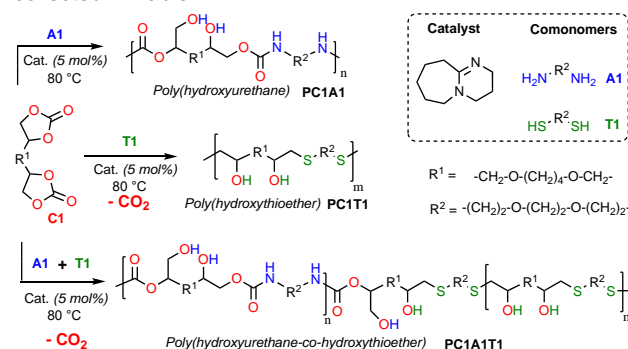


**Figure 2.** Mechanistic insight of the DBU-catalyzed aminolysis (black) and S-alkylation (red) of propylene carbonate at the M062X/6-311G(d,p) level. The Gibbs free energies are expressed in  $\text{kcal.mol}^{-1}$

### Copolymerization of bis(cyclic carbonate) with dithiols and/or diamines

We then investigated the influence of adding a dithiol to a formulation producing PHU, thus containing a mixture of a bis(cyclic carbonate) and a diamine. Indeed, although the step-growth copolymerization of a diamine with a bis(cyclic carbonate) is largely described in the literature for the synthesis of PHU, the terpolymerization with dithiols or even the direct copolymerization of dithiols with bis(cyclic carbonate)s was never reported. Series of DBU-catalyzed polymerizations were performed under solvent-free conditions at 80 °C under ambient atmosphere for 24 h (5 mol% DBU vs the bis(cyclic carbonate)). Note that ambient atmosphere was used here to fit the conditions that are conventionally used for foaming PUs.

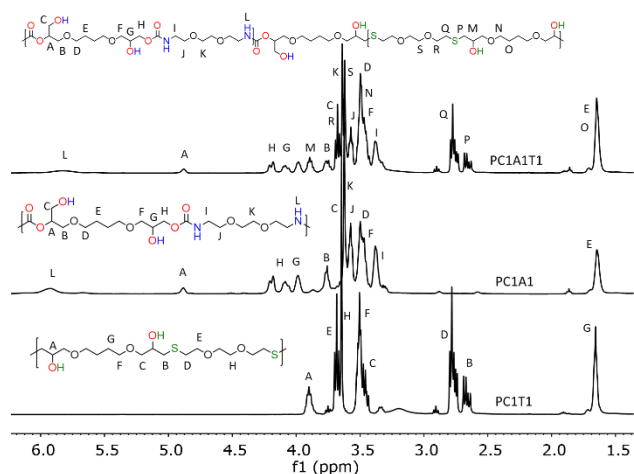
Scheme 2 illustrates the structure of the monomers used for this study, i.e. the bis(cyclic carbonate) **C1** (4,4'-[1,4-Butanediylbis(oxyethylene)]bis(1,3-dioxolan-2-one)), the diamine **A1** (1,2-bis(2-aminoethoxy)ethane) and the dithiol **T1** (2,2'-(ethylenedioxy)diethanethiol). Various comonomer molar ratios  $[\text{C1}]/[\text{A1}]/[\text{T1}]$  were tested from 1/1/0 (to produce PHU) to 1/0/1 (to yield poly(hydroxythioether)), with intermediate compositions in order to tentatively synthesize unprecedented poly(hydroxyurethane-co-hydroxythioether)s. The results are collected in Table 1.



**Scheme 2.** Synthesis of poly(hydroxyurethane), poly(hydroxythioether) and poly(hydroxyurethane-co-hydroxythioether) by DBU-catalyzed step-growth copolymerization.

The macromolecular characteristics of the polymers were determined by size exclusion chromatography (SEC) on

the crude product in order to avoid any polymer fractionation during purification (Figure S5). As expected the poly(hydroxyurethane) **PC1A1** was formed by copolymerizing **C1** with **A1**, however the relative number average molar mass was rather low ( $M_n = 4,200$  g/mol) as the result of the uncomplete **C1** conversion (Table 1, entry 1). By adding dithiol **T1** to the **C1/A1** formulation, almost full **C1** conversion was noted under identical conditions, with the formation of polymers of higher molar masses for all compositions ( $M_n = 8,400$ - $8,800$  g/mol; Table 1, entries 2-4). Importantly, the copolymerization of the dithiol **T1** with the bis(cyclic carbonate) **C1** was also efficient with the formation of a polymer characterized by a  $M_n$  of 9,200 g/mol (Table 1, entry 5). No **C1/T1** copolymerization was observed in the absence of DBU, highlighting the importance of the organobase for the thiol/cyclic carbonate reaction in agreement with the previous model reactions.



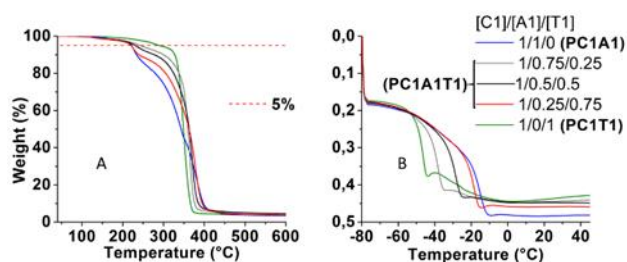
**Figure 3.**  $^1\text{H}$ -NMR spectrum of poly(hydroxyurethane) **PC1A1**, poly(hydroxythioether) **PC1T1** and a representative poly(hydroxyurethane-co-hydroxythioether) **PC1A1T1** with  $[\text{A1}]/[\text{T1}] = 1$ .

The microstructure of the poly(hydroxyurethane) **PC1A1**, poly(hydroxythioether) **PC1T1** and a representative poly(hydroxyurethane-co-hydroxythioether) **PC1A1T1** were elucidated by  $^1\text{H}$ - (Figure 3) and  $^{13}\text{C}$ -NMR (Figure S6) spectroscopy. **PC1A1** displayed the typical resonances of the two methylene groups  $-\text{CH}_2-\text{N}(\text{C}(\text{O})\text{O})-$  and  $-\text{CH}_2-\text{O}(\text{C}(\text{O})\text{N})$ -adjacent to the urethane moiety at  $\delta = 4.10$ - $4.17$  ppm and  $3.37$  ppm, as well as the methylene and the methyne groups close to the alcohol function at  $3.65$  and  $4.88$  ppm, respectively. The microstructure of **PC1A1** was further confirmed by the presence of the carbonyl signal of the urethane at  $157$  ppm in the  $^{13}\text{C}$ -NMR spectrum (Figure S6). The  $^1\text{H}$ -NMR spectrum of **PC1T1** highlighted the formation of thioether moieties with the two signals at  $2.67$  and  $2.78$  ppm corresponding to the methylenes linked to the sulfur atom as well a methyne resonance ( $-\text{CH}-\text{OH}$ ) at  $3.9$  ppm. The S-alkylation of **T1** via decarboxylative addition onto **C1** was further confirmed by the absence in the  $^{13}\text{C}$ -NMR spectrum of a resonance typical of a carbonyl group that could have been produced via the formation of a thiocarbonate linkage. This

characterization confirmed the selective addition of the thiol onto the methylene site of the cyclic carbonate ring. The organocatalyzed S-alkylation of dithiols with bis(cyclic carbonate) is therefore highly attractive to construct regio-regular poly(hydroxythioether)s that are currently only accessible by the exothermic LiOH driven thiol-epoxy click reaction.<sup>15</sup> **PC1A1T1** displayed the typical signals of the methylene or methyne groups of both the hydroxyurethane and hydroxythioethers units at similar chemical shifts as the one observed in **PC1A1** and **PC1T1**. This observation confirms that both **A1** and **T1** were inserted in the growing chains when the terpolymerization of **C1**, **A1** and **T1** was considered.

### Thermal analysis of the copolymers

The thermal stability and glass transition temperature of the polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively (Figure 4). Interestingly, the introduction of thioether units within the chains strongly improved the thermal stability of the polymers. The thermal degradation temperature ( $T_{d5\%}$ ) increased progressively with the thioether linkages content and evolves from  $222$  °C for the pure PHU **PC1A1** to  $289$  °C for the pure poly(hydroxythioether) **PC1T1** (Table 1, Figure 4A). This observation is consistent with a recent study reporting the higher thermal stability of sulfur-containing polyurethanes prepared by the isocyanate chemistry.<sup>16</sup> DSC curves (Figure 4B) showed clear endothermic transitions corresponding to the  $T_g$  of the different polymers. The  $T_g$  values were dependent on the **A1/T1** molar content of the reactive formulation and evolved from  $-15$  °C for the pure PHU (**PC1A1**) to  $-46$  °C for the poly(hydroxythioether) (**PC1T1**) (Table 1). This observation is linked to the interchain hydrogen-bonding interactions favored at high content of urethane linkage which reduced the chain mobility. The presence of only one  $T_g$  for each polymer, whatever its **A1/T1** composition, suggests that the urethane and thioether linkages were relatively randomly distributed in the polymer chains.



**Figure 4.** (A) Thermogravimetric (TGA) and (B) dynamic scanning calorimetry (DSC) analyses of poly(hydroxyurethane) **PC1A1**, poly(hydroxythioether) **PC1T1** and poly(hydroxyurethane-co-hydroxythioether) **PC1A1T1** with various  $[\text{A1}]/[\text{T1}]$  compositions.



**Table 1.** Poly(hydroxyurethane) **PC1A1**, poly(hydroxyurethane-co-hydroxythioether) **PC1A1T1** and poly(hydroxythioether) **PC1T1** prepared at 80 °C in the presence of DBU: reaction conditions, macromolecular characteristics and thermal properties.

| Entry | [C1]/[A1]/[T1] | Conv. <sup>a</sup><br>(%) | Mn <sup>b</sup><br>(g/mol) | Mw <sup>b</sup><br>(g/mol) | Đ    | Td <sub>5%</sub><br>(°C) | Tg<br>(°C) |
|-------|----------------|---------------------------|----------------------------|----------------------------|------|--------------------------|------------|
| 1     | 1/1/0          | 95                        | 4,200                      | 6,000                      | 1.44 | 222                      | -15        |
| 2     | 1/0.75/0.25    | 99                        | 8,400                      | 14,000                     | 1.69 | 220                      | -18        |
| 3     | 1/0.5/0.5      | 99                        | 8,600                      | 14,700                     | 1.70 | 230                      | -28        |
| 4     | 1/0.25/0.75    | 99                        | 8,800                      | 15,400                     | 1.74 | 242                      | -38        |
| 5     | 1/0/1          | 99                        | 9,200                      | 17,400                     | 1.89 | 289                      | -46        |

Conditions: 80 °C, 24 h, catalyst loading = 5 mol% compared to the carbonate moiety, bulk.

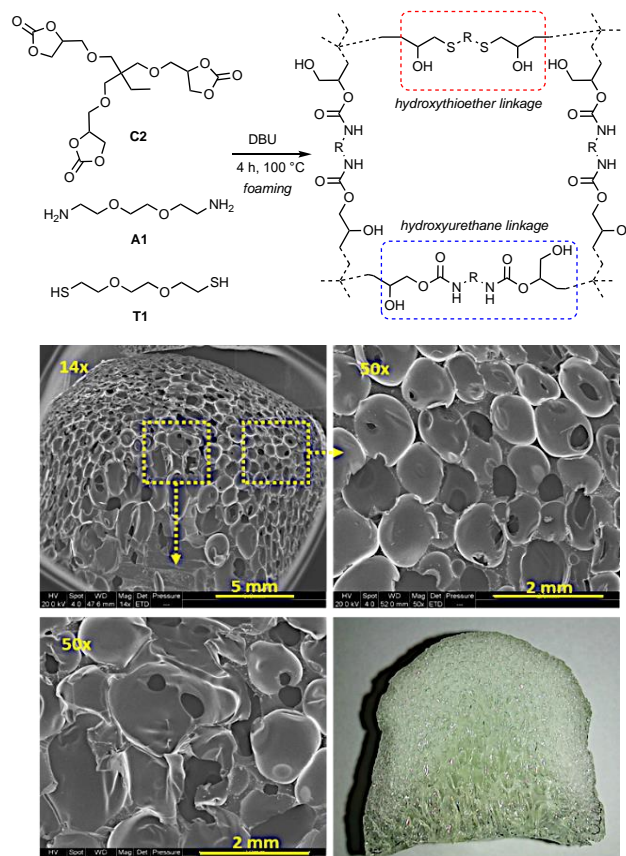
<sup>a</sup> Cyclic carbonate conversion determined by <sup>1</sup>H-NMR spectroscopy on the crude samples

<sup>b</sup> Determined by SEC using a polystyrene standard calibration and DMF with LiBr as eluant.

## Preparation and characterizations of PHU foams

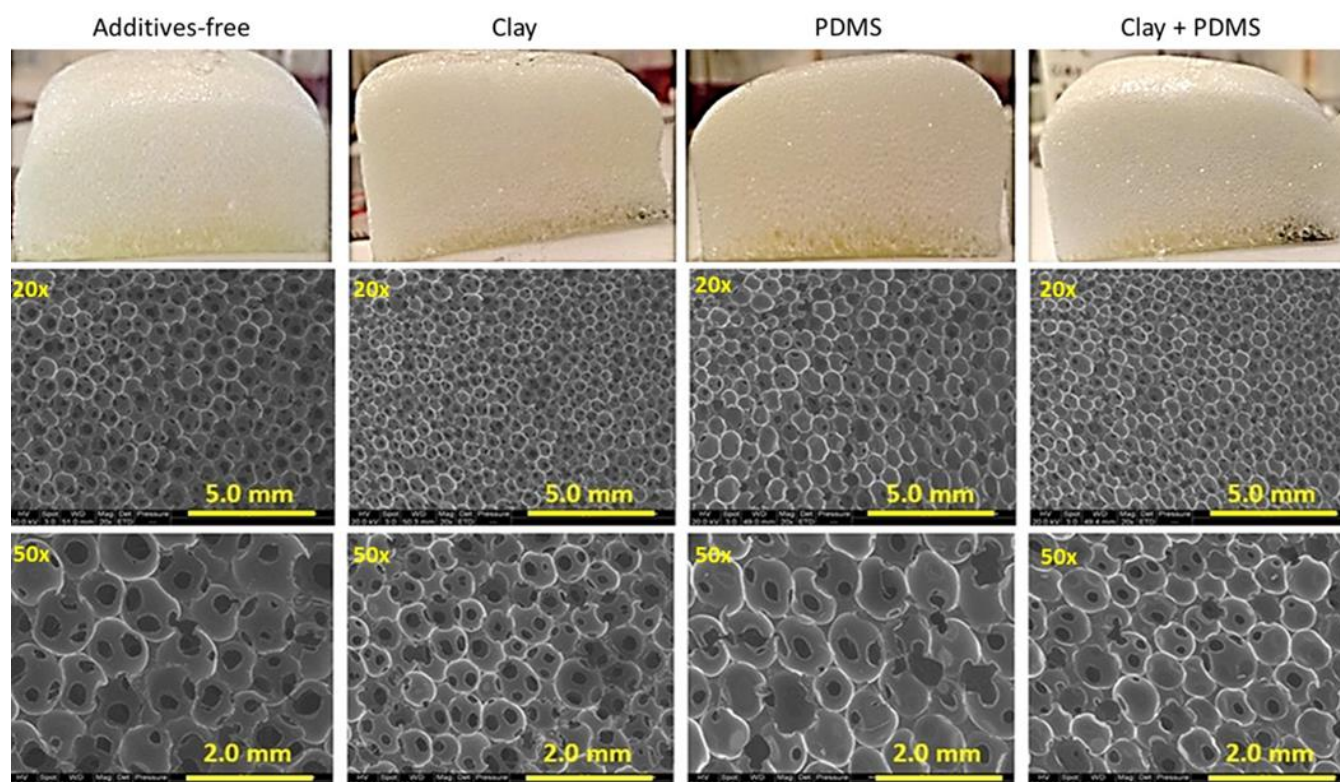
In order to prepare CO<sub>2</sub> self-blowing PHU foams with dimensional stability, crosslinking of the polymer chains has to occur during the expansion of the foam. We therefore added a tris(cyclic carbonate) **C2** (trimethylolpropane triscarbonate) to the PHU formulation containing the diamine **A1** and the dithiol **T1**. We worked under stoichiometric conditions in the complementary reactive groups ([**C2**]/[**A1**]/[**T1**] = 1/1.125/0.375; thus [5CC]/[NH<sub>2</sub>]/[SH] = 1). After homogenization of the mixture under solvent-free conditions with DBU (5 mol% compared to **C2**) at room temperature for 2 min, the formulation was poured in a silicone mold. By heating this formulation at 100 °C, a tacky-free foam was collected after 6 h. The foam was however heterogeneous with a large distribution of pores (from 800 μm to 2.7 mm) (Figure 5), which was assigned to a too low initial viscosity of the reactive formulation. Analysis of the PHU foam by Raman spectroscopy evidenced the disappearance of the S-H stretching band around 2550 cm<sup>-1</sup> of the thiol **T1** and carbonate band at 1800 cm<sup>-1</sup> of the cyclic carbonate **C2** present in the initial formulation (Figure S7). This analysis also demonstrated the presence of two specific linkages in the foam, thioether and urethane, with the new bands at 500 cm<sup>-1</sup> for the C-S-C thioether bending and at 1715 cm<sup>-1</sup> for the C=O urethane one.

To improve the foaming, the formulation was pre-reacted at 25 °C for a longer time in order to pre-polymerize PHU and increase the viscosity prior to the decarboxylation promoted by the thiol. Figure S8 shows that the viscosity indeed increased progressively up to 715 Pa.s in 16 h due to the slow aminolysis of **C2** with the formation of oligohydroxyurethanes. The absence of a gel point (corresponding to the crossover point in the time evolution of G' and G'' values) after 16 h suggested that the polymer was not crosslinked under these conditions. The foaming was then thermally induced by a curing for 2 h at 100 °C followed by a temperature increase to 120 °C in 30 min and an additional 1 h post-curing treatment at 120 °C (this optimal procedure has been identified and selected after screening different conditions). This foaming methodology enabled us to design self-blown PHU foams in a reproducible manner (Figure 6). Although some shrinkage was observed at the end of the foaming process as soon as the foam was removed from the oven, the material recovered its expended shape either spontaneously after 1 to 2 h at 25 °C or by heating the sample at 80 °C for 1 min. At this stage, we do not understand this phenomena but the process is perfectly reproducible and systematically furnished homogeneous PHU foams.



**Figure 5.** PHU formulation and SEM characterizations of self-blown foams made from **C2**, **A1** and **T1**. Conditions: [**C2**]/[**A1**]/[**T1**] = 1/1.125/0.375, DBU (5 mol% compared to 5CCs), mixing for 2 min at rt, curing at 100 °C for 4 h.

To demonstrate the robustness of the process but also to tune the characteristics and properties of the foams, some additives were added to the formulation, such as a synthetic clay (Laponite S482) or an epoxy-functionalized PDMS oligomer (TEGOMER E-Si 2330). Laponite is a hydrophilic nanosheet clay that was chosen to reinforce the polymer matrix and to act as a nucleating agent that is expected to favor the formation of homogeneous foams with small cells size. The PDMS oligomers was selected as a surface acting agent for the stabilization of the cells during their growth. All formulations added by clay (1.5 wt%), PDMS (0.01 eq compared to **C2**) or by the two additives (clay + PDMS) provided foams after curing



**Figure 6.** SEM characterization of self-blown PHU foams a) additives-free PHU foam, b) PHU foam loaded with 1.5 wt% clay, c) PHU foam loaded with 0.1 eq compared to **C2** of Tegomer Si-C 2230 and d) PHU foam loaded with both PDMS and clay.

**Table 2.** Composition and characteristics of the self-blown PHU foams.

| Entry | PHU Foam formulation        |             | PHU Foam characteristics     |                |                                |  | Thermo-mechanical properties of PHU foams |                     |                           |                                |
|-------|-----------------------------|-------------|------------------------------|----------------|--------------------------------|--|---|---------------------|---------------------------|--------------------------------|
|       | [C2]/[A1]/[T1] <sup>a</sup> | Additives   | Density (g/cm <sup>3</sup> ) | Pore size (mm) | A <sub>f</sub> /A <sub>c</sub> | Cell density (Ncell) (cells/cm <sup>3</sup> ) <sup>b</sup> | T <sub>d5%</sub> (°C)                     | T <sub>g</sub> (°C) | Stress <sup>c</sup> (kPa) | Recovery Time <sup>d</sup> (s) |
| 1     | 1/1.125/0.375               | None        | 0.166 +/- 0.007              | 0.98 +/- 0.35  | 17.2                           | 1,620 +/- 110  | 248                                       | 3.6                 | 8.2 +/- 0.2               | 30 +/- 2                       |
| 2     | 1/1.125/0.375               | Clay        | 0.207 +/- 0.011              | 0.62 +/- 0.23  | 23.7                           | 4,570 +/- 50   | 246                                       | 7.9                 | 11.4 +/- 0.7              | 17 +/- 0.5                     |
| 3     | 1/1.1325/0.3775             | PDMS        | 0.196 +/- 0.005              | 0.87 +/- 0.23  | 9.7                            | 2,280 +/- 310  | 247                                       | 3                   | 11.2 +/- 0.9              | 10 +/- 0.2                     |
| 4     | 1/1.1325/0.3775             | Clay + PDMS | 0.180 +/- 0.005              | 0.60 +/- 0.21  | 11.5                           | 5,070 +/- 240  | 244                                       | 2.4                 | 8.7 +/- 0.5               | 8.4 +/- 0.1                    |

<sup>a</sup> molar ratio adjusted to take into account the epoxy groups of Tegomer in entries 3 and 4

<sup>b</sup> Ncell = (nM/A)3/2ps/pp with n = the number of cells in the SEM image (average value on 6 SEM images), M the magnification, A the surface area of the image (mm<sup>2</sup>) and ps and pp the solid and the foamed sample densities. The solid density was estimated to 0.98 +/- 0.02 g/cm<sup>3</sup> on non-foamed samples

<sup>c</sup> at 50 % of strain

<sup>d</sup> for a 99 % shape recovery

following the procedure described above. The foams morphology, the cells size and distribution, as well as the open-to-close cell ratio were determined by scanning electron microscopy (SEM) characterizations. Figure 6 illustrates the morphologies of the self-blown PHU foams and their characteristics are summarized in Table 2. In all cases, homogeneous microcellular foams with an open cell morphology were formed with a density ranging from 0.166 to 0.207 g/cm<sup>3</sup>. In the absence of additives, foams with a homogeneous cells size distribution and a large average cell diameter of  $0.98 \pm 0.35$  mm were obtained. The addition of PDMS reduced the pore size to  $0.87 \pm 0.23$  mm and their distribution. As expected, loading the formulation with clay further decreased the cell size to  $0.62 \pm 0.23$ . PHU foams loaded with both clay and PDMS were also highly homogeneous with a pore size of  $0.60 \pm 0.21$  mm (Figure S9). The PHU foam with the lowest density of 0.166 g/cm<sup>3</sup> was obtained with the additive-free formulation. The other foams were characterized with slightly higher densities ranging from 0.207 g/cm<sup>3</sup> (with clay) to 0.180 g/cm<sup>3</sup> (with clay + PDMS).

The open-to-close cells ratio was then evaluated by SEM images treatment following the methodology reported by Fitzgerald.<sup>17</sup> Cell-faces area  $A_c$  and cell-face holes area  $A_h$  were measured, and the  $A_h/A_c$  ratio was calculated<sup>[31]</sup> and is reported in Table 2. The  $A_h/A_c$  ratio values show that PDMS reduced the open porosity of the foams from 17.2 for an additive-free PHU foam to 9.7 in the presence of PDMS. At the opposite, clay increased the content of open pores to 23.7. For PHU foams containing both additives, the  $A_h/A_c$  ratio was estimated to 11.2 showing that the increase of open porosity induced by clay was counter-balanced by PDMS.

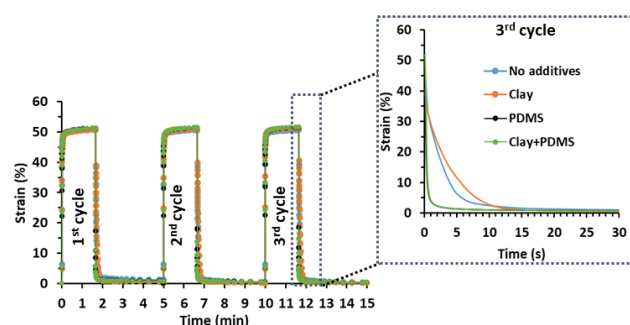
The thermal degradation of the foams was evaluated by TGA. All samples depicted a similar degradation profile (Figure S10) with a degradation temperature ( $T_{d5\%}$ ) at around 245 °C (Table 2). There was therefore no significant influence of the additive on the degradation temperature of the foam, at least within the additive loading range that was considered in this work. DSC analysis showed an endothermic transition for all samples, with  $T_g$  values between 2.4 and 7.9 °C. The rather similar values are not surprising as the  $T_g$  is mainly guided by the choice and content of the comonomers that are almost identical in all formulations. Preliminary mechanical properties were realized by dynamic mechanical analysis (DMA). Figure S11 illustrates the compression stress-strain

compression. For each sample, three compression-release cycles at a fixed strain of 50 % were applied and the time for the foams to recover their initial shape was evaluated (Figure 7). After the third compression, all samples recovered over 99 % of their initial shape in less than 30 s, qualifying these materials as flexible (Table 2). The PHU foams containing the PDMS additive displayed the fastest shape recovery rate in only 8.4 to 10 seconds, in line with the high flexibility of silicones, even

Finally, other commercially available diamines, i.e. 1,6-hexamethylene diamine (HMDA, **A2**) and m-xylylenediamine (MXDA, **A3**) were tested in combination with **C2** and **T1** in order to illustrate the robustness of the new methodology and the possible variations of the PHU structures. As the intrinsic reactivity of the amine with the cyclic carbonate is dependent on their respective structural features, the foaming protocols (curing steps) were adjusted to identify the most appropriate foaming window of the reactive PHU formulations (these procedures are detailed in Supporting information, ESI 13). Under optimized foaming conditions, the reactive mixture  $[C2]/[A2]/[T1] = 1/1.125/0.375$  added by 5 mol% of DBU (compared to the carbonate moieties) provided a PHU foam that did not collapse after preparation. The PHU material displayed an open cell microcellular morphology with a cell size average of  $0.26 \pm 0.085$  mm (Figure 8A, Table S1, entry 1) and a foam density of  $0.320 \pm 0.012$  g/cm<sup>3</sup>. For a similar formulation with **A3** in replacement of **A2** ( $[C2]/[A3]/[T1] = 1/1.125/0.375$ ), a foam with an open cells size gradient from 0.3 mm to 3.5 mm was collected with a density of  $0.210 \pm 0.041$  g/cm<sup>3</sup> (Figure 8B, Table S1, entry 2). Blending **A3** with **A2** (with a  $[A3]/[A2]$  molar ratio of 80/20) enabled to preparing homogeneous foams that displayed open cells of  $0.62 \pm 0.11$  mm and a density of  $0.250 \pm 0.02$  g/cm<sup>3</sup> (Figure 8C, Table S1, entry 3). All PHU foams made from **A2**, **A3** or a blend of **A2** and **A3** showed similar thermal behavior with  $T_g$  and  $T_{d5\%}$  values of 20.5-24.6 °C and 232-238 °C, respectively (Table S1). Note that the  $T_g$  values close to the room temperature prevented us to determine the mechanical properties of the foams with sufficient accuracy.

## Conclusion

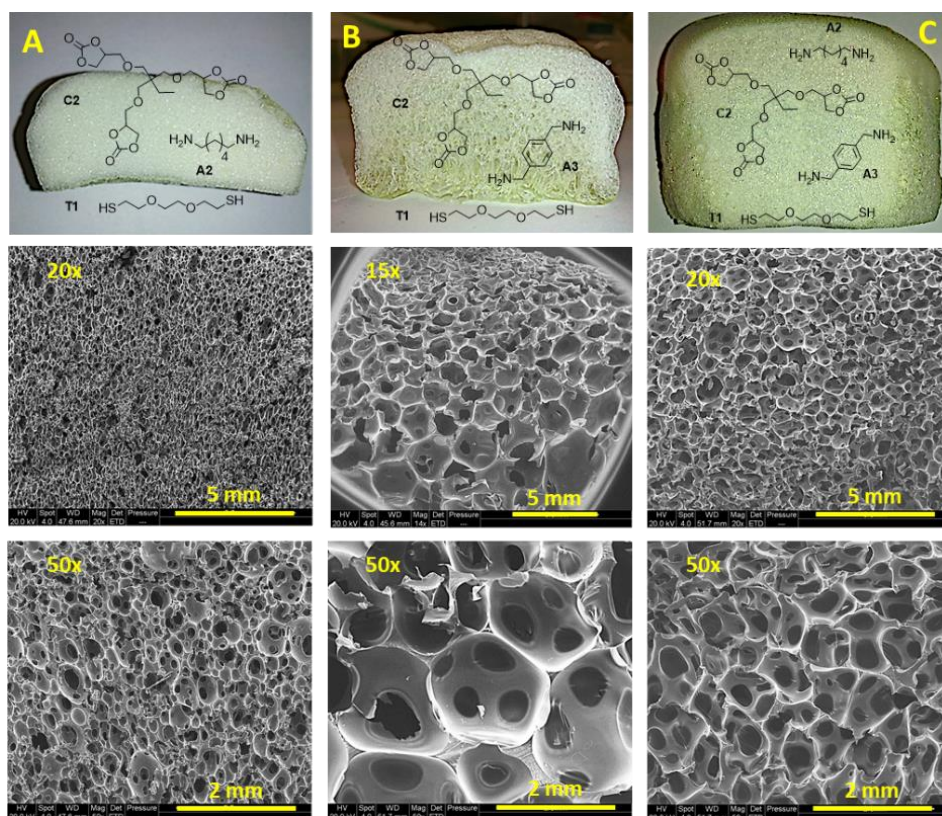
This work describes a general strategy to prepare microcellular self-blown isocyanate-free polyurethane foams by exploiting chemo- and regio-selective additions of amines and thiols to 5-membered cyclic carbonates (5CCs), resulting in an attractive alternative to conventional PU foams. The main challenge of this work was to demonstrate that poly(cyclic carbonate)s used in the preparation of poly(hydroxyurethane)s (PHU) by copolymerization with diamines could also be involved in the matrix foaming by generation of the blowing agent (CO<sub>2</sub>) by decarboxylation. We first investigated on model compounds the reaction conditions that promoted the formation of urethane linkages by aminolysis of 5CC and the release of CO<sub>2</sub> by the attack of the thiol to the methylene site of 5CC with the formation of thioether



**Figure 7.** Shape recovery rate of the PHU foams after a 50% deformation as determined by dynamic mechanical analysis (DMA).

Creep experiments were then realized to evaluate the ability of the foams to recover their initial shape after





**Figure 8.** SEM characterizations of self-blown PHU foams. A) PHU foam made from  $[C2]/[A2]/[T1] = 1/1.125/0.375$ , B) PHU foam made from  $[C2]/[A3]/[T1] = 1/1.125/0.375$ , C) PHU foam made from  $[C2]/[Ax]/[T1] = 1/1.125/0.375$  with  $[Ax]$  being a blend of  $A3$  and  $A2$  with a molar ratio  $[A3]/[A2] = 80/20$ .

linkages. While the aminolysis was possible at 80°C without any catalyst, the decarboxylation promoted by the thiol required the use of an organobase (e.g. DBU) to occur. When this organocatalyst was added at 5 mol%, the two chemoselective additions were possible, with a faster aminolysis. DFT calculations of the mechanism of the two competitive reactions enabled to rationalize the difference of reactivity between the amine and the thiol for the addition to 5CC. Applied to di(cyclic carbonate)s, these reactions give access to new polymers containing both urethane and thioether linkages by DBU-catalyzed copolymerization with diamines and dithiols.

The PHU foaming was then considered from reactive formulations containing a tri(cyclic carbonate), a diamine and a dithiol for the proof of concept. In the presence of DBU and an appropriate mild thermal curing, the aminolysis of 5CC provided the PHU matrix that expanded by the decarboxylation of 5CC promoted by the thiol. The formation of thioether bonds during the formation of the blowing agent participated in the polymer network construction and fixed the thiol to the polymer matrix. Homogeneous microcellular PHU foams with open cell morphology were easily prepared under ambient atmosphere. Highly flexible foams were prepared as a proof of concept, and we demonstrate that the process is compatible to the addition of additives such as clay and/or PDMS. The main components of the formulation (the amines and the thiols) are accessible at large scale and low cost, and the cyclic carbonates are easily prepared by coupling  $CO_2$  to the corresponding epoxides in a cost effective fashion. Due to the impressive diversity and accessibility of these components and all possible additives that can be employed in the reactive formulation, this new solvent-free process is offering new avenues for constructing more sustainable PU

foams with various properties that could fit a broad range of applications.

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