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A divergent aminolysis approach for constructing recyclable self-blown non-isocyanate polyurethane foams

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ABSTRACT

We report an approach to fabricate self-blown non-isocyanate polyurethane (NIPU) foams by capitalizing on the divergent chemistries of amines with cyclic carbonates - creating the polymer network - and thiolactone - delivering *in-situ* a thiol that generates the blowing agent (CO₂) by reaction with a cyclic carbonate. Multiple linkages (hydroxyurethanes, thioethers, amides) are created within the polymer network by this domino process. This one-pot methodology furnishes flexible to rigid foams with open cell morphology at moderate temperature. The foams are easily repurposed into films or structural composites by thermal treatment, showing the first example of recyclable NIPU foams. Remarkably, both the formation and the recycling of the thermoset foams do not necessarily require the use of a catalyst. This facile and robust process is opening new avenues for designing more sustainable PU foams and offers new end-of-life options by facile material repurposing.

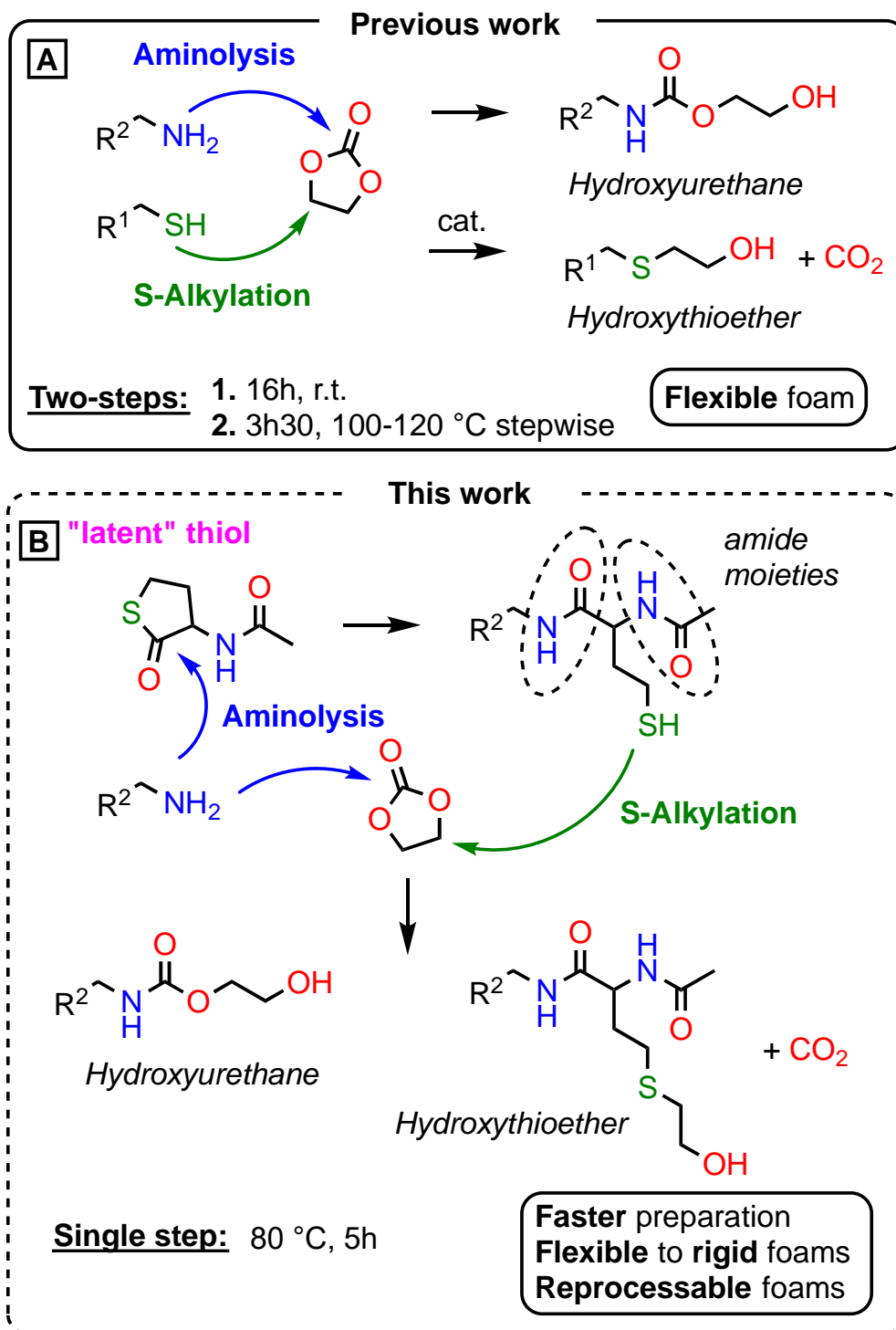
Polyurethane foams (PUF) are leading the market with a growth projected from 42.8 billion\$ in 2021 to 61.5 billion\$ by 2026.¹ These materials find multiple applications in thermal and sound insulation, comfort (mattresses, seats, etc.) or filtration systems, to cite only a few.^{2,3} Most of commercial PUF are produced from water-induced CO₂ self-blowing polyols/polyisocyanates formulations.^{4,5} Although extremely versatile and facile, this isocyanate-based chemistry is rising severe environmental and regulatory concerns,⁶ causing their restriction of use⁷ and justifying the urgent quest for greener and safer alternatives. Non-isocyanate polyurethanes, particularly poly(hydroxyurethane)s (PHUs) made by the polyaddition of poly(5-membered cyclic carbonate)s with polyamines, are ideal alternatives.⁸⁻¹¹ However, unlike the conventional PU foaming, the cyclic carbonates are less prone to decarboxylation by hydrolysis, making the *in-situ* formation of CO₂ as the blowing agent very challenging. PHUs foams were mainly prepared by using physical (supercritical CO₂, solkane)^{12,13} or external chemical blowing agents (siloxanes, citric acids, bicarbonate)¹⁴⁻¹⁷. Developing a facile and versatile self-blown PHU foaming process that mimics the conventional PU foaming method is highly desirable.¹⁸ Recently, we conceptualized the first CO₂ self-blown PHU foams prepared by adding thiols to a

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formulation composed of poly(cyclic carbonate)s and polyamines. The S-alkylation by the cyclic carbonates generated CO₂ and the thiol participated to the construction of the PHU matrix, provided that a superbase catalyst was added (Scheme 1A).^{19,20} Although this process is promising for designing the future generation of polyurethane foams, it still suffers from the multistep procedure needed to adjust the initial formulation viscosity prior foaming, the use of thiol additives with unpleasant smell, and the unknown end-of-life scenario of the foams (a critical issue at present time).

Herein, we discovered that thiols masked under a latent form, i.e. a thiolactone, strongly alleviate these issues and facilitate the construction of soft and rigid PHU foams, while offering end-of-life options. The new process (Scheme 1B) involves divergent and regioselective domino reactions, i.e. (1) a fast aminolysis of the thiolactone to create a reactive thiol intermediate, (2) the aminolysis of the cyclic carbonate into hydroxyurethane and (3) the formation of CO₂ upon decarboxylative S-alkylation by the cyclic carbonate. Remarkably, the so-produced thermoset foams display an easy open-loop upcycling ability with possible repurposing into films or structural composites, in line with the sustainability goals of our modern society.

N-acetylhomocysteine thiolactone (NAHcT), a commercially available cyclic thioester made from renewable amino acid homocysteine, has been largely exploited in polymer chemistry to quantitatively release a latent thiol by aminolysis.^{21,22} This thiol group has been involved in multiple reactions to build, functionalize or crosslink polymers.^{23,24} We postulated that the addition of this commercial thiolactone in a PHU formulation should generate by aminolysis an amide - expected to increase the formulation viscosity by hydrogen bonding - and a thiol - that will generate CO₂ by methylene attack to the cyclic carbonate. This is proven in concept by surveying and benchmarking the aminolyses of NAHcT and ethylene carbonate (EC) by butylamine (BuA), followed by monitoring the one-pot NAHcT/EC/BuA tricomponent reaction that mimics the foaming process.



Scheme 1: General strategies for self-blowing PHUs

The model reactions were realized under equimolar conditions at 25 °C in DMSO with or without DBU (5 mol%) as catalyst. DBU was added as it was reported to be necessary to promote the CO₂ formation upon decarboxylative S-alkylation.²⁰ Figure 1A shows that the NAHcT ring-

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opening is significantly faster than the EC aminolysis, with a conversion reaching 88% in 2h. No significant influence of DBU was noted, whereas it accelerates the urethane formation, providing a EC conversion of 86% in 4h (70% without catalyst). The two reactions are highly selective with the formation of the hydroxyurethane **1**, 2-hydroxyethyl butylcarbamate, for the EC aminolysis and the thiol amide compound **2**, 2-acetamido-N-butyl-4-mercaptobutanamide, for that of NAHcT (see Figures S1-S10 for characterizations).

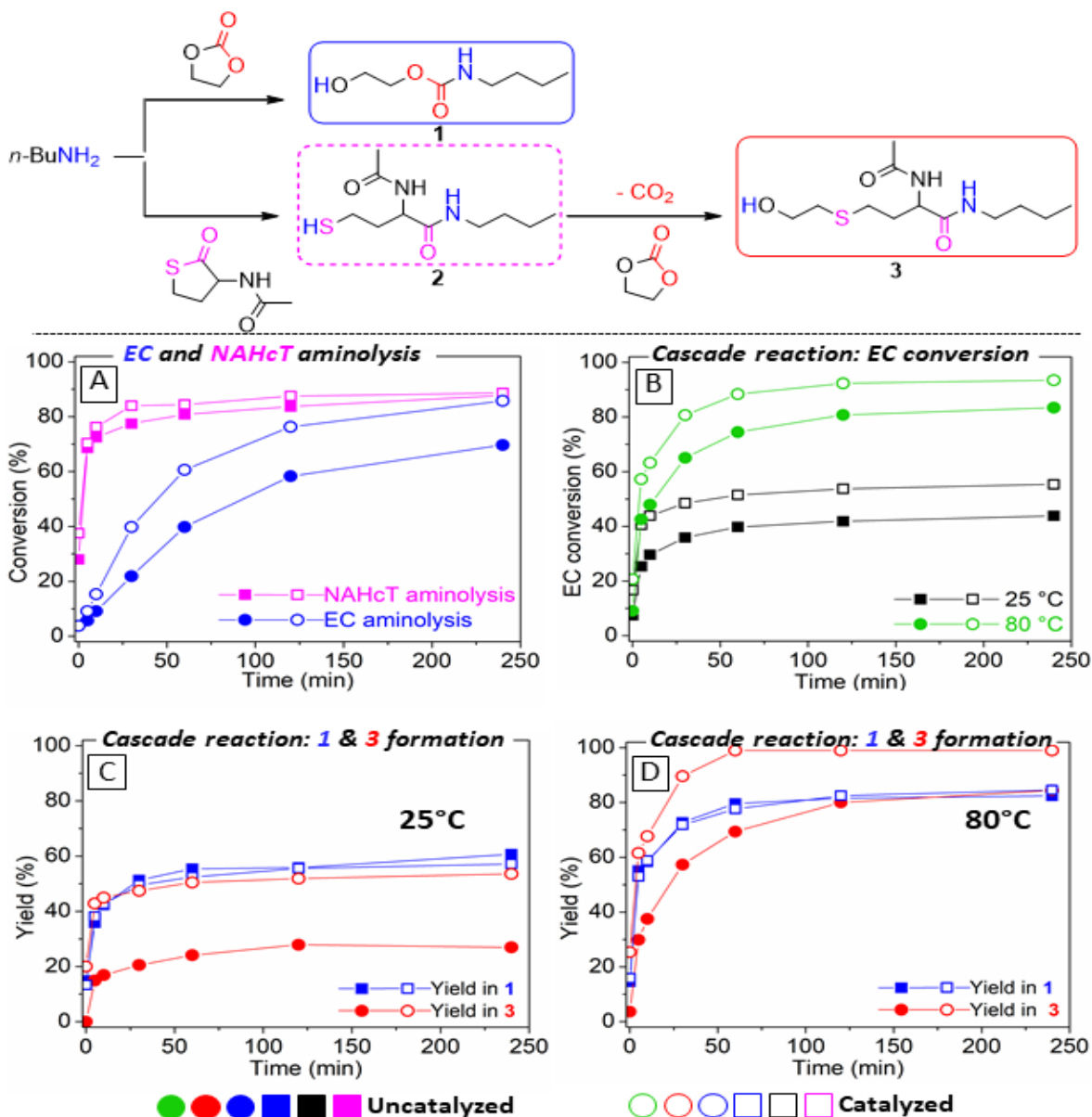
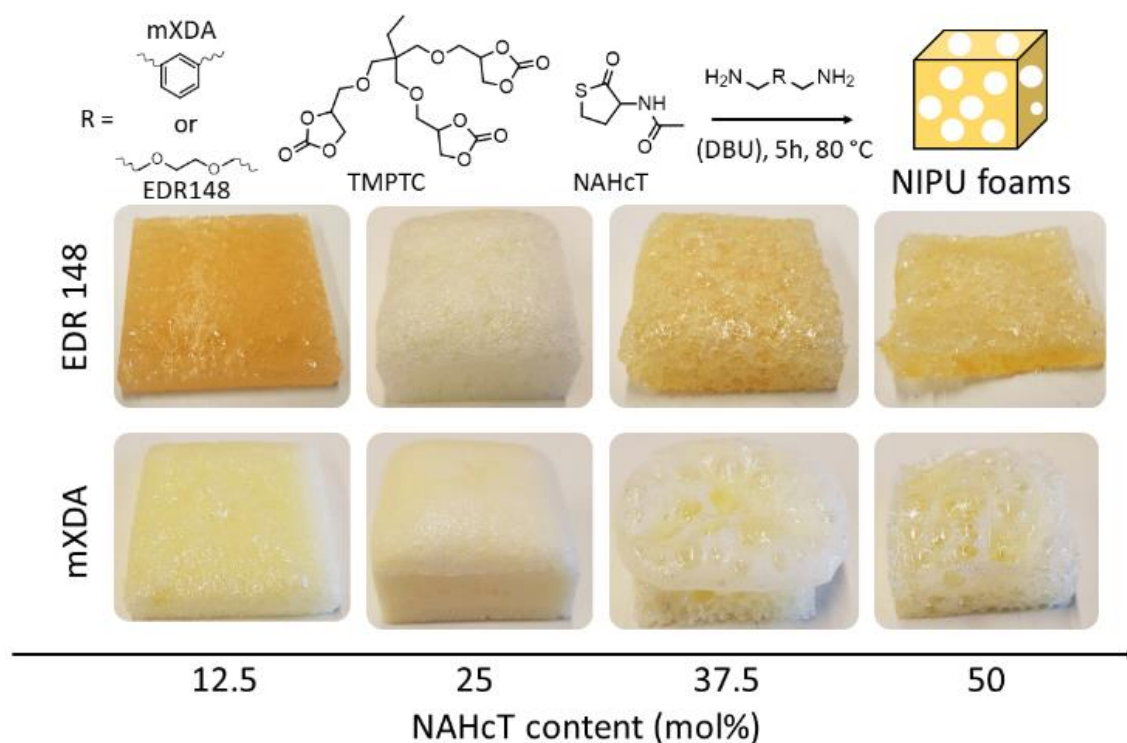


Figure 1: EC and NAHcT aminolyses with BuA (A); total EC conversion in cascade aminolysis of NAHcT with BuA and S-alkylation with EC (B); time evolution of **1** and **3** yields at 25°C (C) and 80°C (D). Conditions: (A) [NAHcT]/[BuA], [EC]/[BuA] = 1, 25°C; (B,C,D) [NAHcT]/[EC]/[BuA] = 1/2/2, 25°C. When used: 5 mol% DBU vs EC. Reactions in dry DMSO.

In the NAHcT/EC/BuA three-component scenario (Figure 1B-D, Figure S11-15), the urethane formation directly competes with the domino S-alkylation via the *in-situ* created 2-acetamido-N-butyl-4-mercaptobutanamide intermediate **2**. For [NAHcT]/[EC]/[BuA] = 1/2/2 with DBU (5 mol%), 55% and 93% of EC were consumed in 4h at 25°C and 80°C (Figure 1B), respectively. The S-alkylated product **3**, i.e. 2-acetamido-N-butyl-4-((2-hydroxyethyl)thio)butanamide, was formed with NMR yields of 54% (at 25°C) and >95% (at 80°C) (Figures 1C and 1D). In contrast to the hydroxyurethane **1**, the formation of the thioether **3** was strongly accelerated in the presence of DBU. Importantly and in contrast to previous work,²⁰ the S-alkylation also proceeded under catalyst-free conditions, however slower (Figure 1C-D), suggesting that the PHU foaming will not necessarily require a catalyst.

Then, we prepared self-blown PHU foams by using a mixture of a trifunctional cyclic carbonate (trimethylpropane triscarbonate, TMPTC), NAHcT thiolactone and either the aliphatic 1,2-bis(2-aminoethoxy)ethane (EDR148) (for flexible foams) or the aromatic m-xylylene (mXDA) diamine (for rigid foams). The foaming was realized at 80°C for 5h with DBU (5 mol%) in open molds with an equimolar content of cyclic carbonate (5cc) and amine (NH₂) groups, and various contents of NAHcT (from 12.5 to 50 mol% vs 5cc) (Table 1).

Table 1. Influence of the NAHcT content on the PHU formulation foaming and foam densities



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Sample	Hardener	NAHcT content (mol%) ^{a)}	Catalyst content (mol %) ^{a)}	Density (Kg m ⁻³)
PHUF1	EDR148	12.5	5	1150 ^{b)}
PHUF2	EDR148	25	5	167+- 3
PHUF3	EDR148	37.5	5	469 ^{b)}
PHUF4	EDR148	50	5	810 ^{b)}
PHUF5	EDR148	25	0	442+- 10
PHUF6	mXDA	12.5	5	424+- 25
PHUF7	mXDA	25	5	185+- 23
PHUF8	mXDA	37.5	5	273+- 40
PHUF9	mXDA	50	5	439 ^{b)}
PHUF10	mXDA	25	0	310+- 18

^{a)}vs 5cc moieties; ^{b)}Approximative densities

Conditions: [5cc]/[NH₂]=1, DBU (5 mol% vs 5cc moieties), 80 °C, 5h.

The optimal foaming window was identified at 25 mol% NAHcT (thus, [5cc]/[NH₂]/[NAHcT] = 1/1/0.25) (Figure 2, Table 1), yielding PHU foams with the lowest densities of 167 kg/m³ (with EDR148) and 185 kg/m³ (with mXDA) (Table 1, entries 2 and 7). Other NAHcT contents afforded microcellular materials of higher densities and poorer quality, preventing any accurate measure of the foams density in many cases. In line with the model experiments, foams of higher densities (310-442 kg/m³) were also fabricated under catalyst-free conditions after 5h at 80°C (Table 1, PHUF5 and PHUF10). In contrast to foams prepared in the presence of catalyst, DBU-free foams were slightly sticky. Extension of the reaction time to 24h at 80°C was therefore needed to suppress their sticky touch (i.e. for total curing), with no observable changes in the morpho-structural properties of the foams. IR analysis of all foams attests for the almost total consumption of the cyclic carbonate with the disappearance of the carbonyl stretching band at around 1800 cm⁻¹ (Figure S16). The C=O elongation bands at 1695 cm⁻¹ and 1650 cm⁻¹ attest for the formation of urethane and amide linkages, respectively

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The morphology of the foams was then investigated by scanning electron microscopy (SEM, Figure 2 and S17). PHUF2 displayed a broad cells size distribution between 0.5 and 5mm while cells with smaller diameters and narrower distribution centered around 0.6mm were noted for PHUF7. Both foams displayed an open cell porosity with holes-on-cell area ratio A_h/A_c (inspired by Fitzgerald's work²⁵) of 7.3% (for PHUF2) and 10% (for PHUF7). The foams obtained under DBU-free conditions (PHUF5, PHUF10) also provided microcellular foams with an open cell porosity and a mean cells size around 500 μm (Table 2, Figure S17). Holes-on-cell area ratio A_h/A_c were in the same range with 9.3% and 10.3% for PHUF5 and PHUF10, respectively.

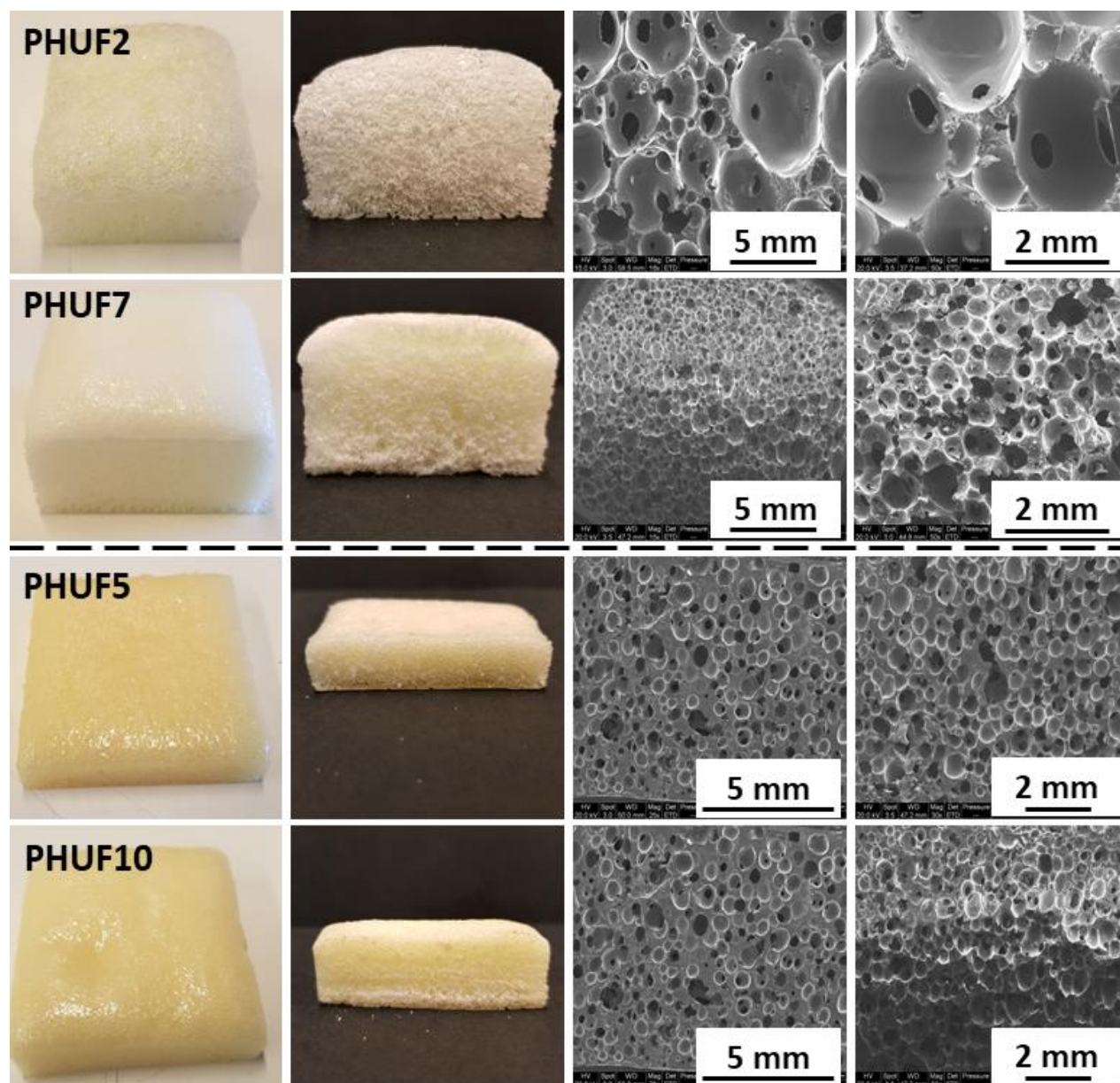


Figure 2: Morpho-structural characterization PHU foams, top: with DBU, down : uncatalyzed

Table 2: Main characteristics of the self-blown PHU foams

Properties	PHUF2 ^a	PHUF7 ^a	PHUF5 ^b	PHUF10 ^b
T _g (°C) of moistened sample ^d	-25	+15	-1	+43
T _g (°C) of dried sample ^e	+27	+56	+30	+55
A _H /A _C (%)	7.3	10	9.3	10.3
T _{d5%} (°C)	237	237	231	233
Young modulus (kPa) ^d	1.33 +/- 0.058	211 +/- 35	n.d. ^c	n.d. ^c
Swelling index (% in THF)	156 +/- 19	245 +/- 35	n.d	n.d
Gel content (% in THF)	95 +/- 0.18	95 +/- 0.25	94 +/- 0.61	97 +/- 0.26

Processing conditions : premixing 2 min, rt, then foaming at 80°C for 5h ^a using 5 mol% of DBU vs 5CC; ^b no catalyst; ^c not determined because of the slightly sticky touch of the materials; ^d sample equilibrated under ambient atmosphere for at least 48h; ^e sample dried at 50°C under vacuum for 24h.

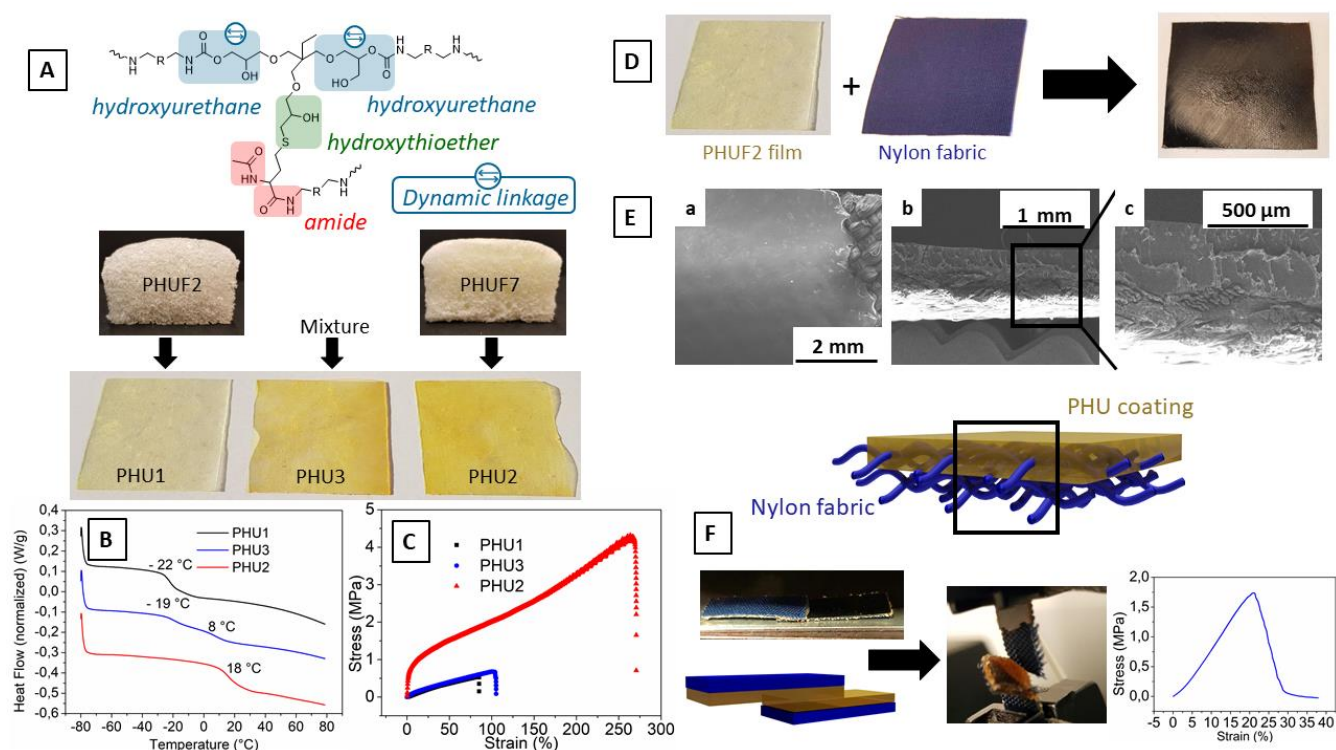


Figure 3: (A) Chemical structure of the PHU foams and images of the foams and reprocessed films, (B) DSC and (C) tensile test of PHU1-3 films of reprocessed foams after equilibration at ambient atmosphere for 48h, (D) Fabrication of the nylon/PHU1 coating composite; (E)(a) SEM top view of the PHU1 layer on the fabric; (b,c) SEM transversal views; (F) tensile test of the welded fabric.

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The thermal properties of the equilibrated foams (i.e. stored at least 48h under ambient atmosphere) were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA). The aromatic mXDA furnishes PHUF7 foam with the highest T_g value of +15°C vs -25°C for PHUF2 made from the aliphatic EDR148 (Table 2, Figure S18a). For PHUF5 and PHUF10 foams, the T_g s were measured to -1°C and +43°C, respectively (Table 2, Figure S19a). All foams presented a comparable thermal decomposition behavior with a degradation temperature $T_{d5\%}$ around 231-237 °C (Figures S18b and S19b), in the same range of $T_{d5\%}$ measured for similar PHUs.^{14,26} Importantly, the low weight loss between 50 and 200°C (about 2-3 wt% depending on the sample, see ESI for details) corresponded to the loss of absorbed water in PHU. As low amounts of absorbed water were recently demonstrated to strongly plasticize PHU-based coatings,²⁷ the dried foamed samples (50°C, vacuum, 24h) were also analyzed by DSC and data are collected in Table 2. Figure S20 compares the thermograms for the moistened and dried samples. An impressive increase of T_g was noted for the dried samples, i.e. of 52°C for PHUF2, 41°C for PHUF7 and 31°C for PHUF5 (Table 2, Figures S20a-c). Only sample PHUF10 presented a less impressive increase of T_g of 12°C upon drying. Importantly, the dried foams prepared from the same formulation presented similar T_g values, whatever the foaming was catalyzed or not. This suggests that the chemical structure of the foams is similar, perfectly in line with the model reactions that showed that the catalyst only affected the reaction rate and not the structure of the formed products (Figure 1D). The discrepancy between T_g values for the moistened samples is assumed to be the result of a slight difference of water content between the samples (see discussion in Figure S20 for details).

The mechanical resistance and shape recovery of the PHU foams (equilibrated under ambient atmosphere to fit their real life application) was evaluated by compression tests (Table 2). The flexible nature of PHUF2 was highlighted by the full recovery of its initial shape within 35 min after a deformation of 80%. While this foam exhibits a low Young's modulus of 1.33 +/- 0.058 kPa, the most rigid PHUF7 presents a two orders higher value of 211 +/- 35 kPa with a low strain at break of ~10% (Figure S21). The two foams are crosslinked as evidenced by the high gel content (95%) and swelling index values in THF (Table 2). Both foams produced under catalyst-free condition also displayed high gel content values of 94% and 97% for PHUF5 and PHUF10, respectively, confirming the crosslinked nature of the materials.

The urgent environmental concerns regarding plastics pollution are now forcing researchers to design materials that are easily recyclable. Conventional PU foams are composed by a crosslinked matrix that imposes their chemical recycling as their main end-of-life scenario. Thermosetting polymers can however be mechanically recycled when dynamic chemical bonds able to rearrangements are adequately introduced in the network.²⁸⁻³⁰ Although now largely investigated for many thermosets, this concept was only recently applied for PU foams by promoting transurethanization reactions during extrusion when the foam was loaded by a tin based catalyst.^{31,32} Unfoamed PHU networks with recycling ability were also reported when transcarbamylation reactions,³³ eventually combined to other reversible reactions (e.g.

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transesterifications),^{34,35} were induced in the presence of an appropriate catalyst during thermal treatment.³³⁻³⁵ In PHU thermosets, the pending hydroxyl groups were responsible for the transcarbamylation reactions and thus, for the thermoset reprocessability.³³⁻³⁷ Despite the importance of self-blown PHU foams, there is no report regarding their recyclability. Herein, we evaluate the ability of our foams to be reprocessed and repurposed. As they are also of the PHU-type and contain many pendant hydroxyl groups, transcarbamylation reactions are expected to allow reprocessing the foams into second life materials.

PHUF2 and PHUF7 foams were first repurposed into free-standing films by compression at 160°C for 2h maintaining a constant pressure of 10 MPa (ESI for details). Both recycled foams furnished cracks- and holes-free films (Figure 3A), and their thermo-mechanical properties were addressed via DSC and DMA (Table S1, Figures 3B-C, S23). The plateau value of the storage modulus above the T_g transition as well as the high gel content (> 95%) of the reprocessed materials confirmed the preservation of their crosslinked nature after reprocessing. The thermo-mechanical properties of the films are reported in Table S1 (ESI), where PHU1 and PHU2 state for the reprocessed films made from PHUF2 and PHUF7, respectively. T_g values of moistened samples of -22 and +18°C, young's moduli of 8.48 +/- 0.76 kPa and 373 +/- 191 kPa, and deformation at break of 87% and 258% were determined for PHU1 and PHU2, respectively. Importantly, the reprocessing of a 50/50 PHUF2/PHUF7 blend furnished a homogeneous and defects-free film (PHU3) characterized by 2 T_g , located in between the ones of reprocessed PHU1 and PHU2 (Table S1, Figure 3B). PHU3 displayed mechanical performances intermediate to PHU1 and PHU2, highlighting that blending two foams of different compositions is a straightforward route to prepare reprocessed materials with adjustable properties (see ESI for further discussion). Importantly, PHUF5 and PHUF10 foams prepared without DBU were also successfully reshaped under similar conditions into films (PHU4 and PHU5, respectively) of similar visual aspect, indicating that the reprocessing did not require any catalyst (Figure S24). IR spectra of the films (prepared with or without DBU) are similar to the one of the original foams, suggesting no degradation of the polymer during reprocessing (Figure S25). Similarly to the foams, the films absorbed moisture which induced a strong hydroplasticization. This is illustrated by an impressive decrease of T_g of about 45-50 °C for moistened PHU1, PHU2 and PHU3 films compared to the dried samples (Table S1, Figure S26). A similar effect was observed for films prepared by reprocessing DBU-free foams (Figure S27). T_g values of dried foams (Table 2) and the corresponding reprocessed films (Table S1) present similar values, confirming that the reprocessing does not modify the chemical structure of the polymer (in line with IR data, Figure S25).

For the proof of concept, we also evaluated the potential of the foams to be repurposed into other materials, such as structural composites (Figure 3D). As conventional PUs are largely used as fabric coatings (for technical textiles, tarpaulin trucks, etc.), we assessed the potential of the PHU1 film for this application. By hot-pressing the film on a nylon fabric (160°C, 20 MPa, 2h), a crack-free homogeneous and adherent PHU coating (Figure 3D-E) was obtained. SEM

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analysis showed that the coating well soaked the textile, suggesting favorable interactions and wettability of PHU onto the nylon mat (Figure 3E). Remarkably, two pieces of the coated textile were also welded by pressing them together at 160°C and moderate pressure (below the apparatus sensitivity, Figure 3F). After 10 min, tensile test was realized, giving a stress at break of 2 +/- 0.4 MPa and an elongation at break of 20.5 +/- 4.1 %. Although the adhesion performance might be optimized, these experiments show that PHU foams are easily repurposed as textile coatings and hot-melt adhesives.

In summary, a divergent aminolysis approach has been established to prepare recyclable self-blown PHU foams by using a combination of thiolactone, tris-cyclic carbonate and diamine. This provides multiple linkages within the PHU network (hydroxyurethane, amide, thioether), and the blowing agent is generated following a domino process that leads to the decarboxylation of cyclic carbonates. This one-pot process is operative at rather low temperature (80°C), even under catalyst-free conditions. As the thiol is generated by the thiolactone aminolysis, and thus mainly grafted to the polymer matrix, odorless foams are obtained (no free volatile low molar mass thiols of bad smelling). The crosslinked foams are also repurposed into films or structural coatings by thermal treatment without necessarily requiring a catalyst. Similarly to a recent report on PHU coatings,²⁷ our PHU materials (foams and reprocessed films) absorb a low content of air moisture that induces a strong hydroplasticization of the polymer. Although the mechanism behind the repurposing of the foams has to be further studied, this new process offers enormous perspectives for producing the next generation of greener and recyclable polyurethane foams. Also, a multitude of PHU-based materials are now accessible by reprocessing blends of PHU foams of different nature/composition.

Supporting Information

Experimental procedures for model reactions and characterization of the products; experimental procedures to design foams, their morphostructural and thermo-mechanical characterizations; characterization technics and procedures; foams recycling. "This material is available free of charge via the Internet at [10.1021/acsmacrolett.1c00793](https://doi.org/10.1021/acsmacrolett.1c00793).

Author Contributions

The manuscript was written through equal contributions of all authors.

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ABBREVIATIONS

PU, polyurethane; NIPU, nonisocyanate polyurethane; PHU, polyhydroxyurethane; EC, ethylene carbonate; NHAcT, *N*-acetylhomocysteine thiolactone; , BuA, butylamine; DBU, 1,8-Diazabicyclo[5.4.0]undec-7-ene; mXDA, meta-xylylene diamine; THF, tetrahydrofuran; DMSO, dimethylsulfoxide; NMR, nuclear magnetic resonance; SEM, scanning electron microscopy; DSC, differential scanning calorimetry; TGA, thermogravimetric analysis; DMA, dynamic mechanical analysis; T_g , glass transition temperature; T_d , degradation temperature; T_α , onset temperature.

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