

# SUPPORTING INFORMATION

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

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### Materials

Ethylene carbonate (98%, EC), DL-*N*-Acetylhomocysteine thiolactone (98%, NAHcT), n-butylamine (99.5%, BuA), m-xylylenediamine (99%, mXDA) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (98%, DBU) were purchased from Aldrich. Jeffamine EDR-148 was supplied by TCI. All reagents were used without any purification. Trimethylolpropane triglycidyl carbonate (TMPTC) was synthesized from CO<sub>2</sub> and trimethylolpropane triglycidyl ether as reported elsewhere by our group.<sup>1</sup> TMPTC was synthesized by pouring trimethylpropane triglycidyl ether (TMPTE) precursor in a stainless-steel reactor with 2.5 mol% tetrabutylammonium iodide as the catalyst. The reactor was then closed and the reaction was performed at 80 °C under 100 bar of CO<sub>2</sub> for 24h to give TMPTC. Complete conversion was confirmed by <sup>1</sup>H-NMR. TMPTC was used as it is after degassing for 30 minutes at 50 °C under reduced pressure.

### Characterizations

<sup>1</sup>H, <sup>13</sup>C and 2D NMR analyses were performed on a Bruker Avance 400 MHz spectrometers in the Fourier transform mode in DMSO-*d*<sub>6</sub>.

*Infrared* (IR) measurements were carried out on a Nicolet ISS spectrometer (Thermo Fisher Scientific) equipped with a diamond attenuated total reflectance (ATR) device. 32 scans were recorded for each sample over the range of 500 – 4000 cm<sup>-1</sup> with a normal resolution of 4 cm<sup>-1</sup>.

*Differential scanning calorimetry* (DSC) was performed on a TA DSC250 apparatus. About 4 mg of samples (PHU foam or reprocessed as PHU film) were sealed in a Al pan for analysis. The T<sub>g</sub> was then determined between -80 °C and 80 °C with a heating ramp of 10 °C/min under N<sub>2</sub> flow. For the analysis of the moistened samples (i.e. equilibrated under ambient atmosphere for at least 48h), the T<sub>g</sub> value was obtained on the first cycle in order to avoid water evaporation. For the analysis of the dried samples (i.e. dried at 50°C under vacuum for 24h), a first cycle was performed until 80 °C, then the temperature was maintained for 30 minutes in order to erase thermal history. Two heating cycles that superimposed were then performed between – 80 °C and 80 °C to determine the T<sub>g</sub> value.

*Thermogravimetric analysis* (TGA) in the polymers were performed on a TGA2 instrument from Mettler Toledo. Around 5 mg of sample was heated between 30 and 600 °C at a rate of 20 °C/min under N<sub>2</sub> flow.

*Foams density measurement*: The average density of the foams is evaluated by weighting three foamed cubic samples with dimension of 10 x 10 x 10 mm.

Scanning electron microscopy (SEM) was realized with a QUANTA 600 apparatus microscope from FEI. The *cells size and morphology* of the PHU foams was determined on equilibrated foams. The cells size distributions were determined by averaging the diameter measurements of 100 cells of 6 SEM images (100 measures for each sample). Cell-faces area ( $A_c$ ) and cell-face holes area ( $A_h$ ) were estimated using ImageJ software. For each sample, the areas of 30 cells and their cells holes areas (if any) were measured thanks to the elliptical selection tool. The holes on cells area ratio were then computed for each cell and averaged for each sample to get the final value of  $\frac{A_h}{A_c}$ . We only took into account holes that exhibited clear dark pixels.

*Dynamic mechanical analyses (DMA)* were realized with a TA Q800 DMA on rectangular sample (25 x 6 mm with a thickness of 0.5 mm) with a preload force of 0.01N and an oscillating amplitude of 5  $\mu\text{m}$  between -80 and 160  $^{\circ}\text{C}$  at an heating rate of 3  $^{\circ}\text{C}/\text{min}$ .

*Tensile and lap-shear tests* were performed at 298K using an Instron 5594 tensile machine. Tensile tests were realized at a speed of 2 mm/min with a 10 000 N load cell. E-modulus, tensile strength and elongation at break were estimated by the average values of at least 3 reprocessed PHU films.

Lap shear test of structural coatings were conducted with a 10,000 N load cell and a displacement rate of 2 mm  $\text{min}^{-1}$ .

*Compression tests* were performed on an INSTRON device in compression mode with a 10 kN setup. Compression was performed at a rate of 2 mm/min on cubic foam samples of about 1 $\text{cm}^3$ .

*Swelling index* was obtained by weighting 4 samples of +- 100 mg each before ( $m_0$ ) and after ( $m_1$ ) being immersed for 24h in THF. SI is obtained from the following equation:

$$SI = \frac{m_1 - m_0}{m_0} \times 100$$

Samples are then dried at 50  $^{\circ}\text{C}$  for 24h in order to remove the solvent and weighted again ( $m_2$ ). The Gel Content (GC) is obtained from the following equation:

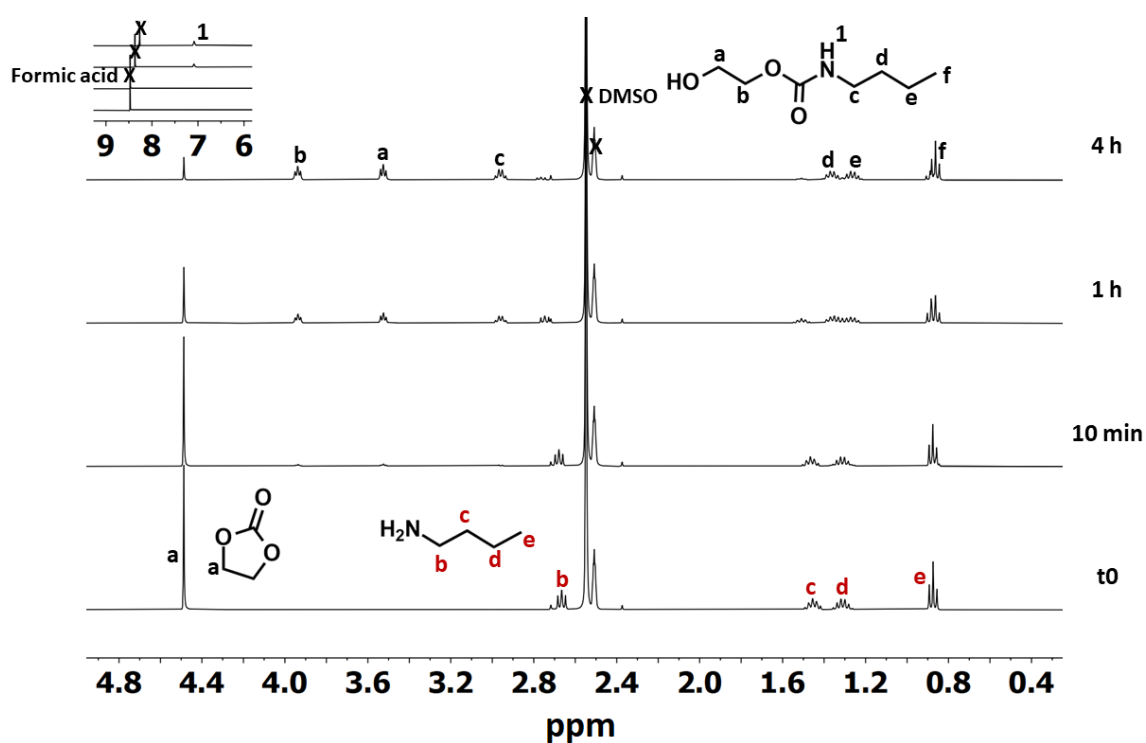
$$GC = \frac{m_2}{m_0} \times 100$$

## Model reactions and characterizations

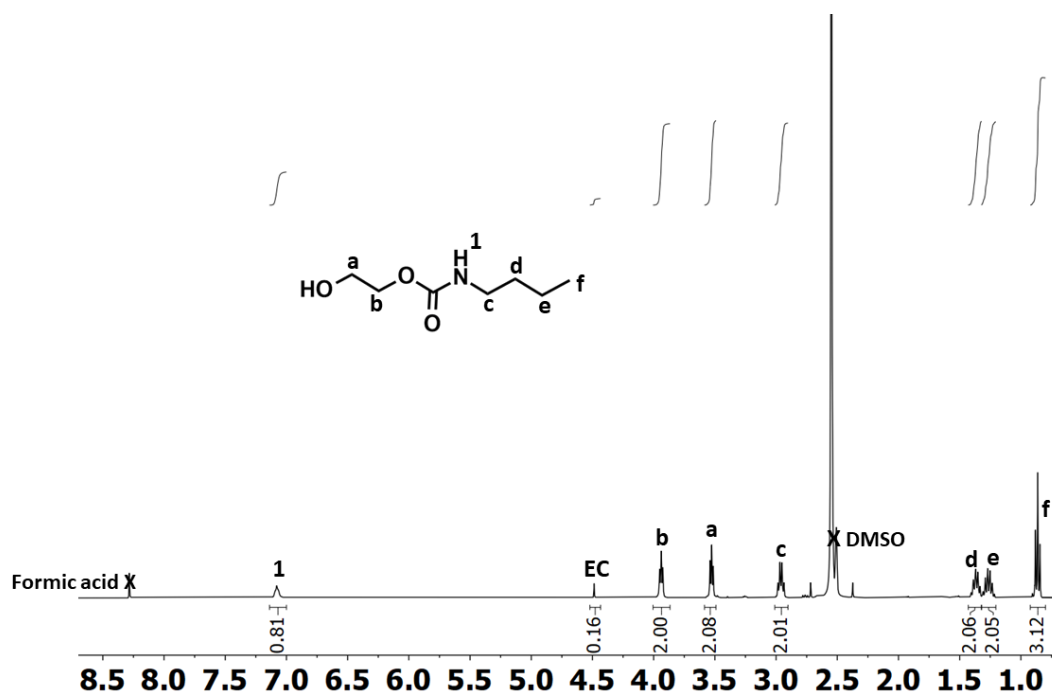
### - Aminolysis of EC by BuA

*Typical procedure.* EC (0.2765 g, 3.14 mmol) was dissolved in 1 mL of dry DMSO. The reaction was started by adding equimolar amount of butylamine (0.310 mL, 3.14 mmol) and optionally the DBU catalyst (0.024 mL, 0.157 mmol, 5 mol% vs EC). The vial was thermostated in an oil bath at 25°C. At regular intervals of time, a sample was picked out the reaction medium, quenched with diluted formic acid and characterized by NMR in DMSO-*d*<sub>6</sub>. EC conversion was determined by using the integration of EC residual signal and an isolated one of the product **1** (Figure S2, signals **EC** and **a** respectively) as followed:

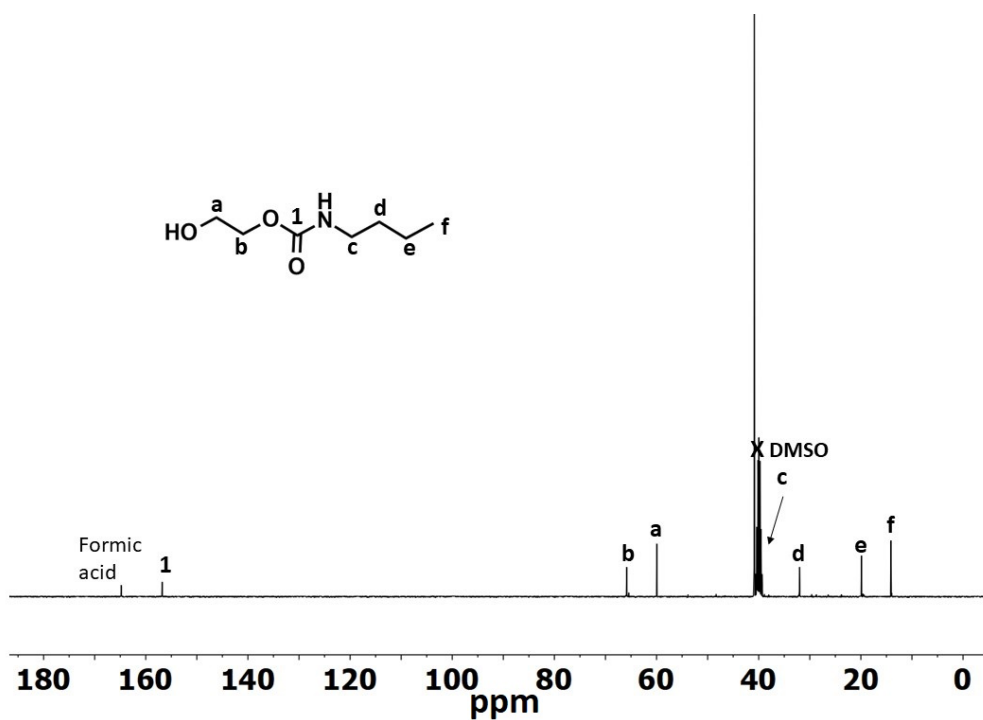
$$EC\ conv\% = \frac{\left(\frac{\int H_a}{2}\right)}{\left(\frac{\int H_{EC}}{4} + \frac{\int H_a}{2}\right)} \times 100$$



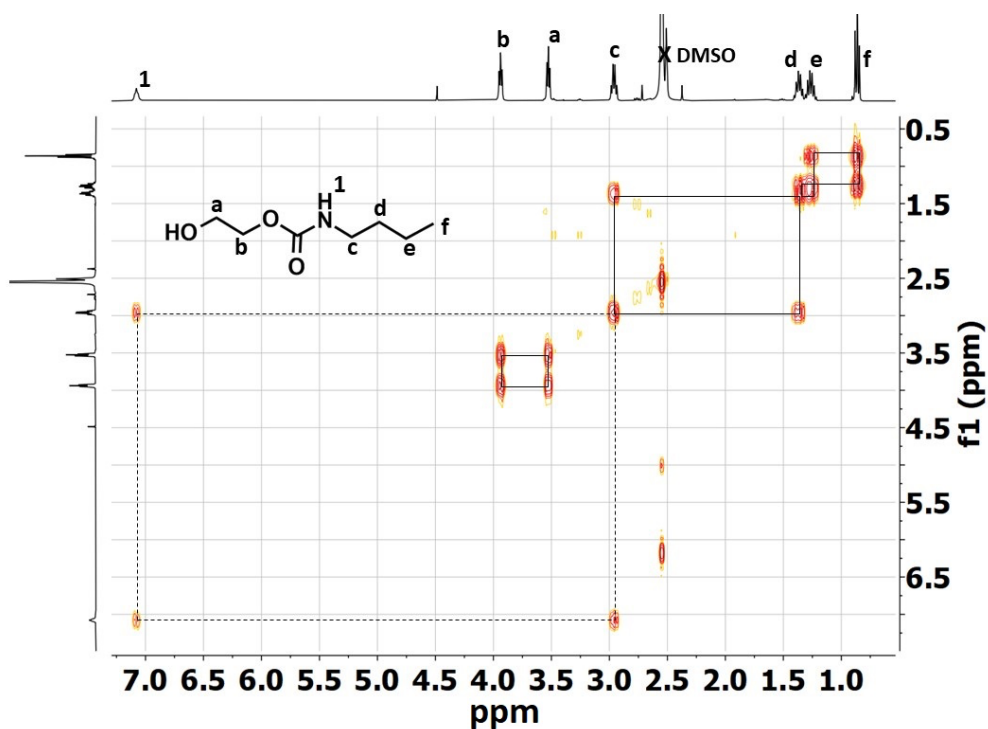
**Figure S1:** <sup>1</sup>H NMR monitoring of the EC aminolysis in dry DMSO-*d*<sub>6</sub> at 25 °C.



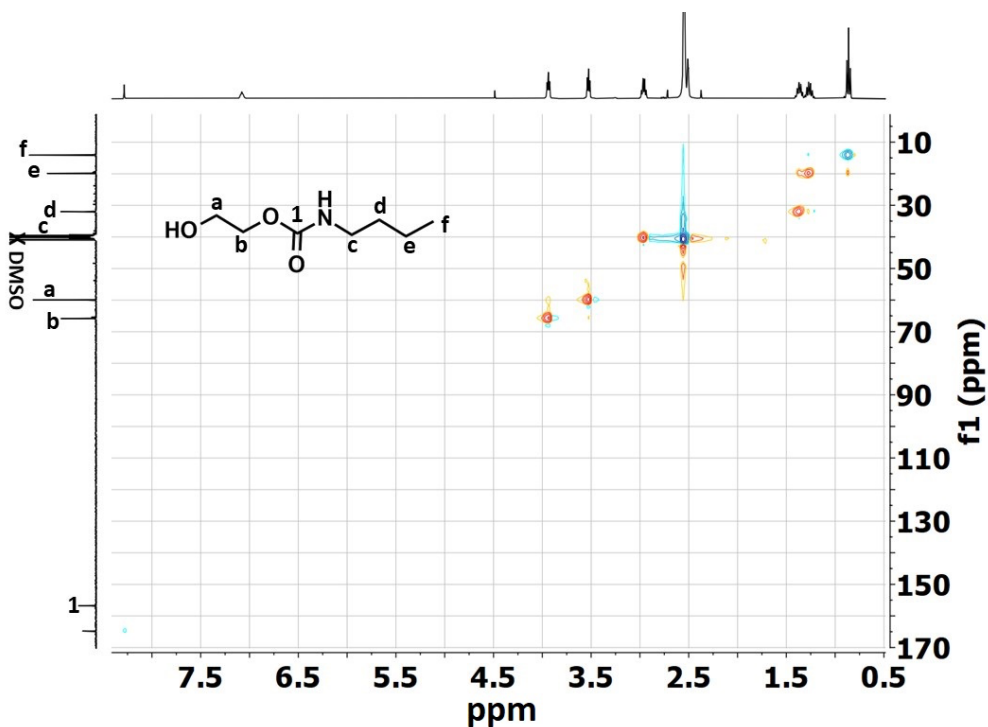
**Figure S2:** <sup>1</sup>H-NMR spectrum of the crude 2-hydroxyethyl butylcarbamate (product 1) formed by aminolysis of EC by butylamine at 25 °C in the presence of 5 mol% DBU (vs EC) after 24h.



**Figure S3:** <sup>13</sup>C-NMR spectrum of the crude 2-hydroxyethyl butylcarbamate (product 1) formed by aminolysis of EC by butylamine at 25 °C in the presence of 5 mol% DBU (vs EC) after 24h.



**Figure S4:**  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of the crude 2-hydroxyethyl butylcarbamate (product 1) formed by aminolysis of EC by butylamine at 25 °C in the presence of 5 mol% DBU (vs EC) after 24h.



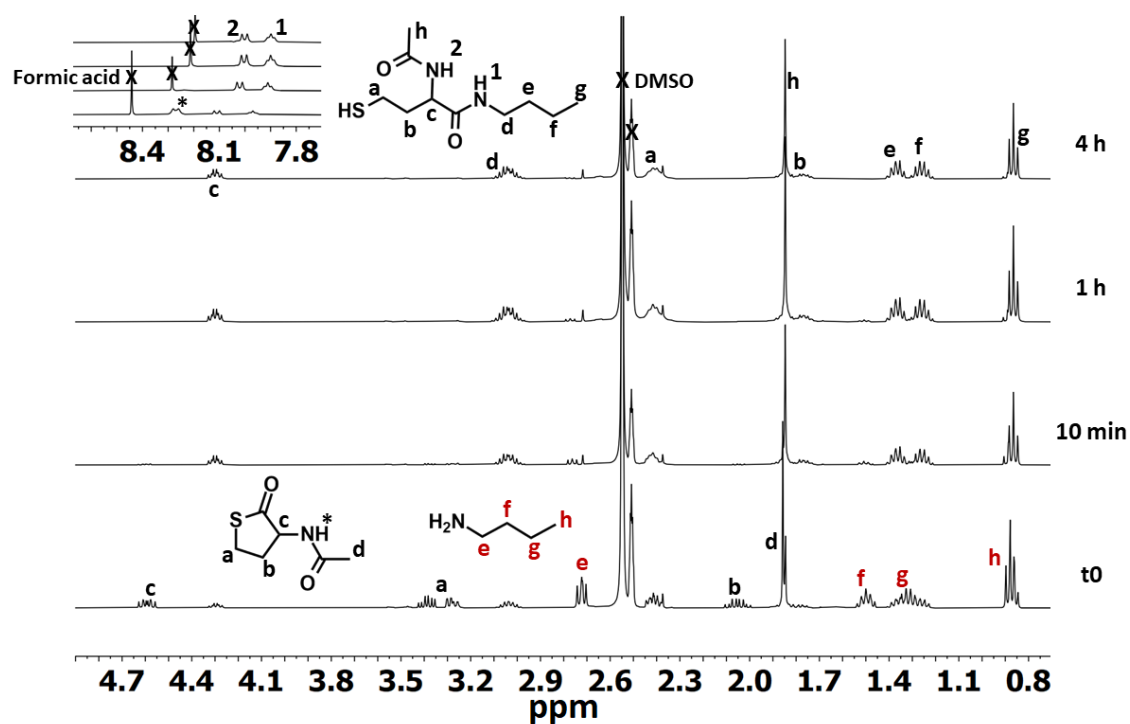
**Figure S5:** HSQC NMR spectrum of the crude 2-hydroxyethyl butylcarbamate (product 1) formed by aminolysis of EC by butylamine at 25 °C in the presence of 5 mol% DBU (vs EC) after 24h.

#### **- Aminolysis of NAHcT by BuA**

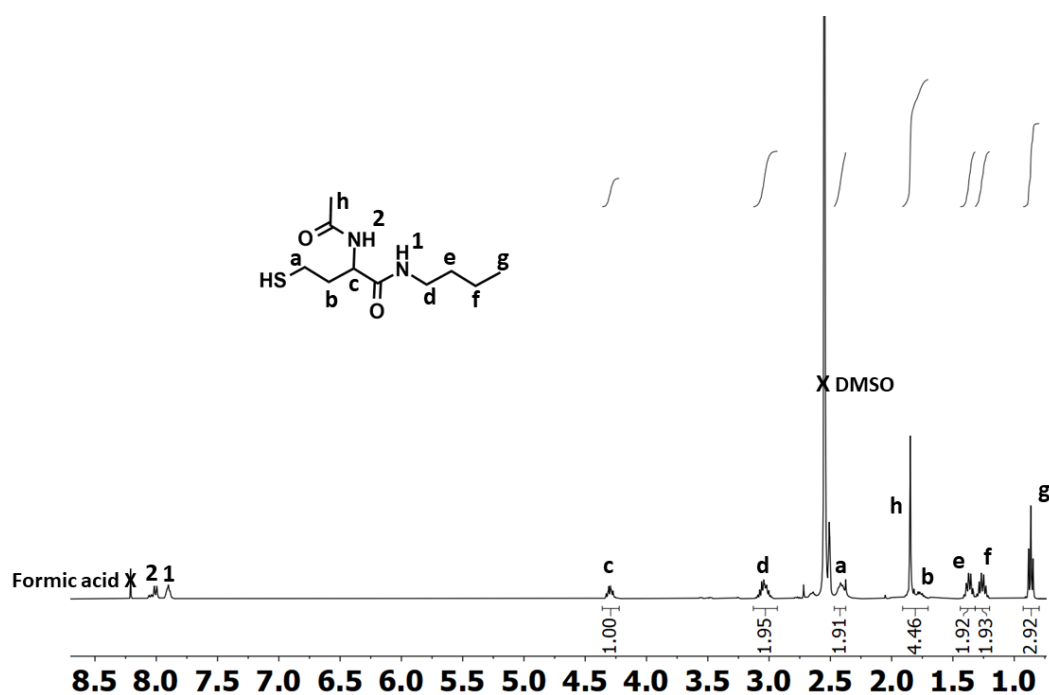
*Typical procedure.* NAHcT (0.5 g, 3.14 mmol) was dissolved in 1 mL of dry DMSO. The reaction was started by adding equimolar amount of butylamine (0.310 mL, 3.14 mmol) and optionally the DBU catalyst (0.024 mL, 0.157 mmol, 5 mol%

vs EC). The vial was thermostated in an oil bath at 25°C. At regular intervals of time, a sample was picked out the reaction medium, quenched with diluted formic acid and characterized by NMR in DMSO-*d*<sub>6</sub>. Conversion was determined by using the integration of thiolactone residual signal and an isolated one of product **2** (Figure S6, signals **c** at t<sub>0</sub> and **c** at 4h respectively) as follow:

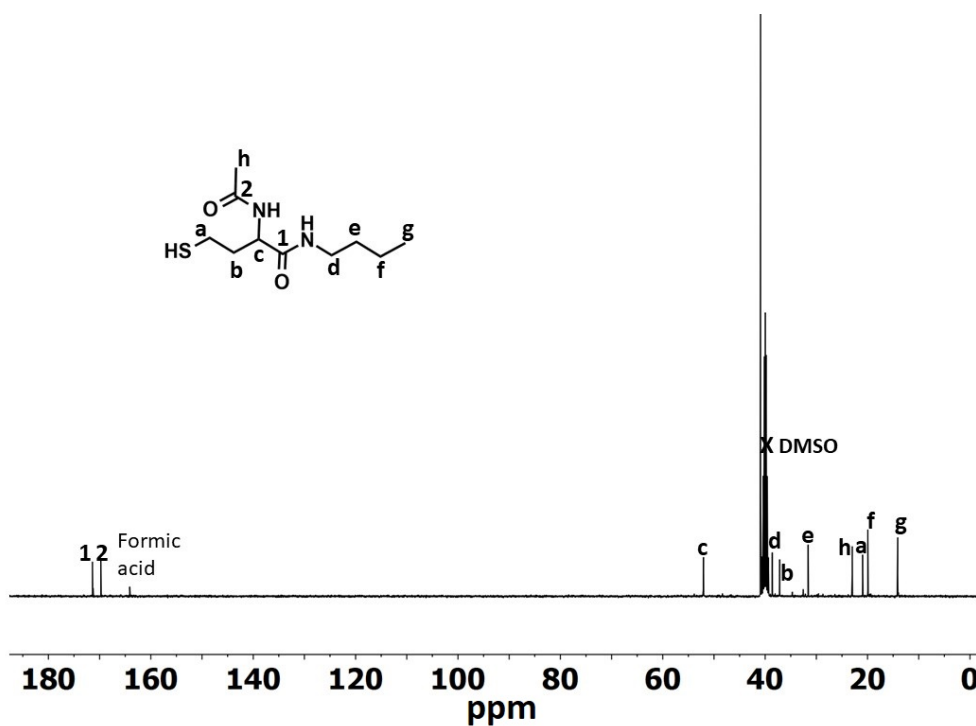
$$EC\ conv\% = \frac{\int H_c(\text{product } 2)}{\int H_c(\text{product } 2) + \int H_c(\text{NAHcT})} \times 100$$



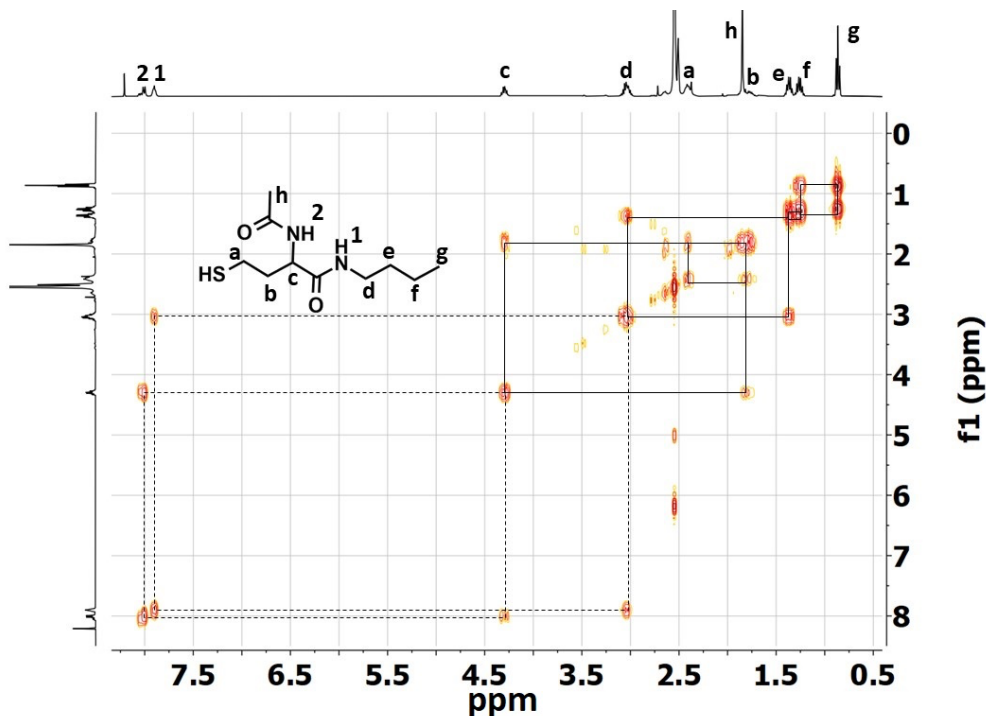
**Figure S6:** <sup>1</sup>H-NMR monitoring of the NAHcT aminolysis in dry DMSO at 25 °C.



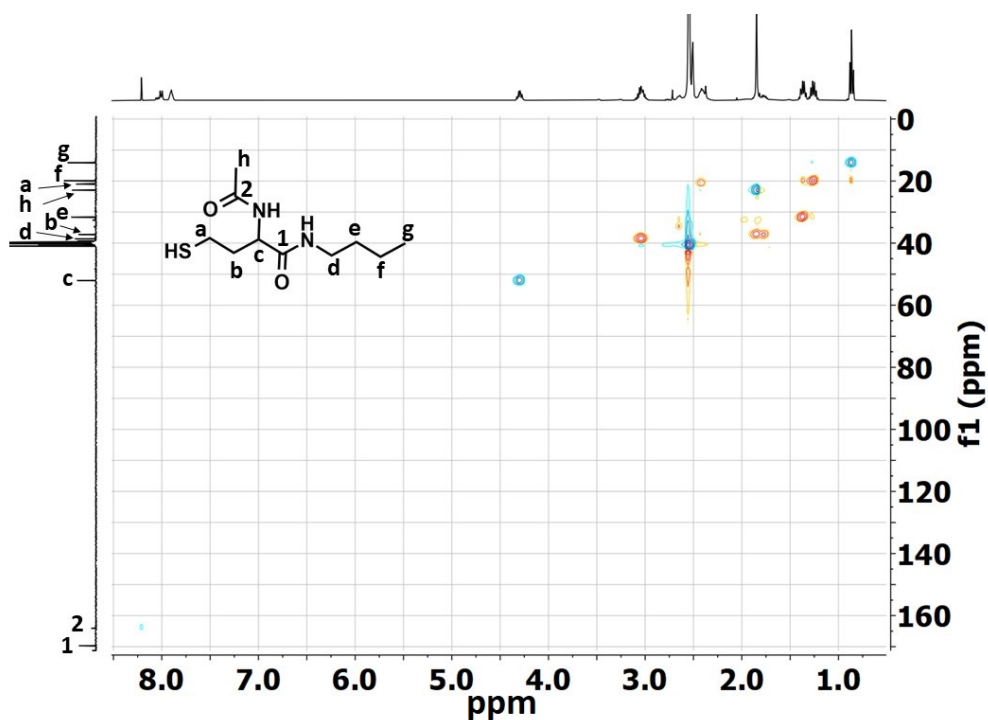
**Figure S7:**  $^1\text{H}$ -NMR spectrum of the crude 2-acetamido-N-butyl-4-mercaptobutanamide (product 2) formed by the aminolysis of NAHcT by butylamine at 25 °C with 5 mol% DBU (*vs* NAHcT) after 24h.



**Figure S8:**  $^{13}\text{C}$ -NMR spectrum of the crude 2-acetamido-N-butyl-4-mercaptobutanamide (product 2) formed by the aminolysis of NAHcT by butylamine at 25 °C with 5 mol% DBU (*vs* NAHcT) after 24h.



**Figure S9:**  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of the crude 2-acetamido-N-butyl-4-mercaptobutanamide (product 2) formed by the aminolysis of NAHcT by butylamine at 25 °C with 5 mol% DBU (*vs* NAHcT) after 24h.

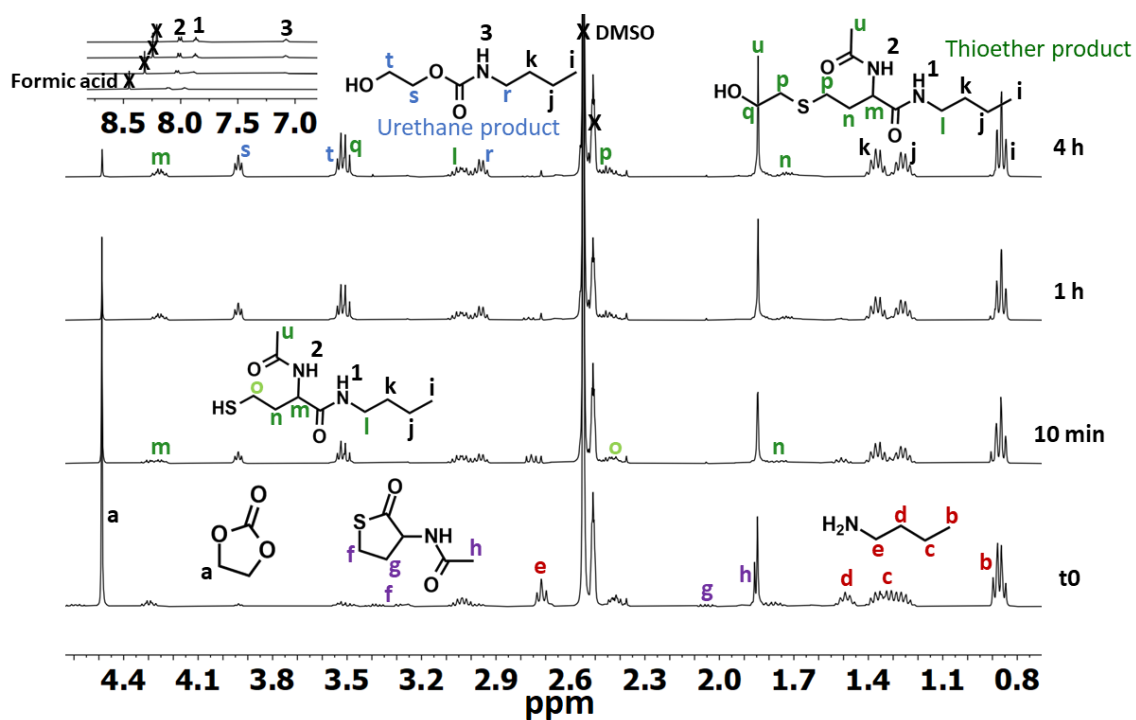


**Figure S10:** HSQC NMR spectrum of the crude 2-acetamido-N-butyl-4-mercaptobutanamide (product **2**) formed by the aminolysis of NAHcT by butylamine at 25 °C with 5 mol% DBU (*vs* NAHcT) after 24h.

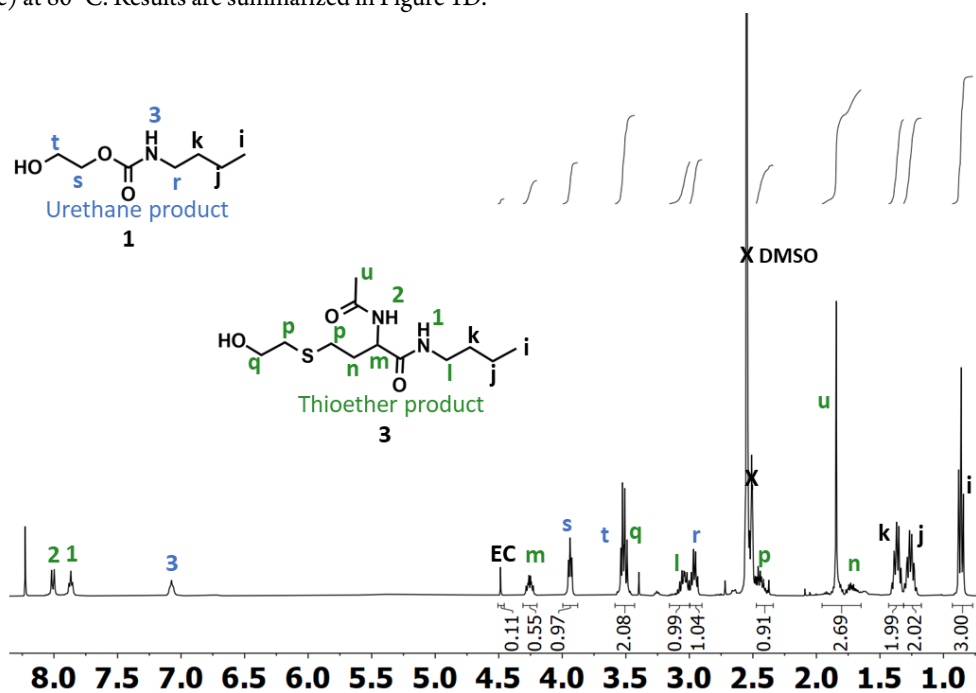
**- Tricomponent EC/NAHcT/BuA reaction**

*Typical procedure.* NAHcT (0.5 g, 3.14 mmol, 1 eq.) and of EC (0.553 g, 6.28 mmol, 2eq.) were dissolved in 1 mL dry DMSO. Reaction was started by adding successively DBU (0.024 mL, 0.157 mmol, 5 mol% *vs* EC) and butylamine (0.621 mL, 6.28 mmol, 2 eq.). The reaction medium was then thermostated at 25 or 80 °C. At regular intervals of time, samples were picked out to monitor the reaction, quenched with diluted formic acid and characterized by NMR in DMSO-*d*<sub>6</sub>.





**Figure S11:** <sup>1</sup>H-NMR monitoring of the one pot tricomponent reaction of EC, BuA and NAHcT, catalyzed by DBU (5 mol% vs Ec) at 80 °C. Results are summarized in Figure 1D.



**Figure S12:** <sup>1</sup>H-NMR spectrum of the crude mixture of products **obtained** by the one pot reaction of EC, BuA and NAHcT catalyzed by 5 mol% DBU (vs Ec) at 80 °C for 24h.

After 24 h of reaction, only product **1** and **3** are obtained with a yield of 85 % and >95 %, respectively. All EC was consumed and product **2** was no more observed as it was totally converted into **3** after this reaction time.  $\int H_x$  being defined as the integral of the signal corresponding to proton x, we describe the global EC conversion as follow:

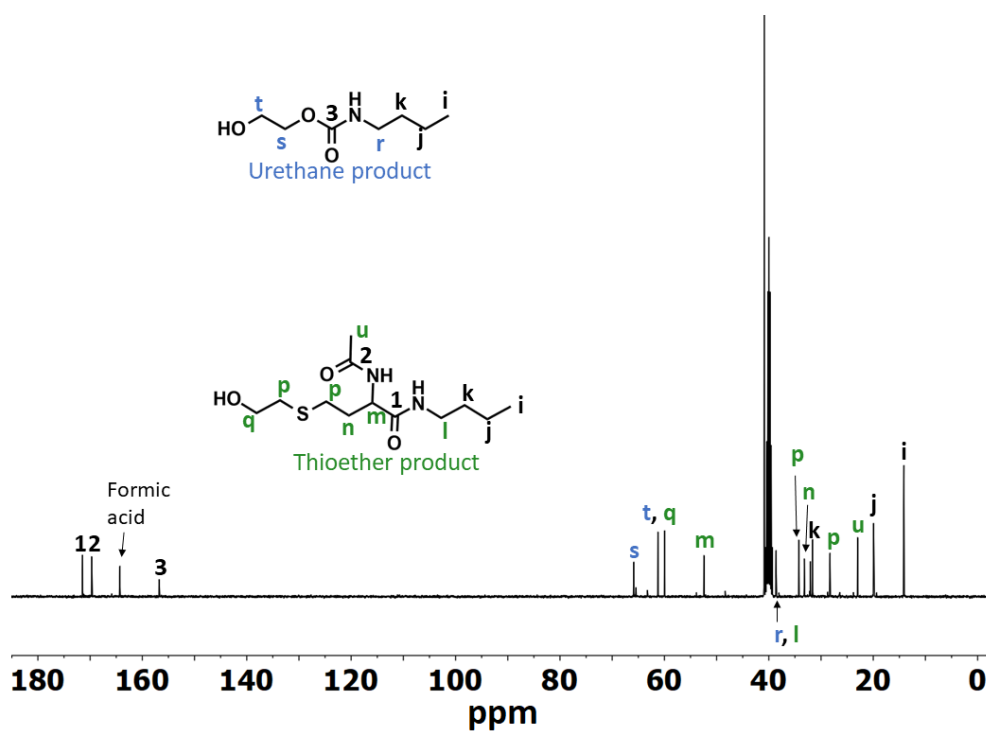
$$EC\ conv\% = \frac{\left(\frac{\int H_{t+q}}{2}\right)}{\left(\frac{\int H_{EC}}{4} + \frac{\int H_{t+q}}{2}\right)} \times 100$$

Where  $\int H_{t+q}$  is the integral of superimposing signals **t** and **q** belonging to products **1** and **3** (Figure S12), respectively, both accounting for 2 protons. Similarly, we define the yield in products **1** as:

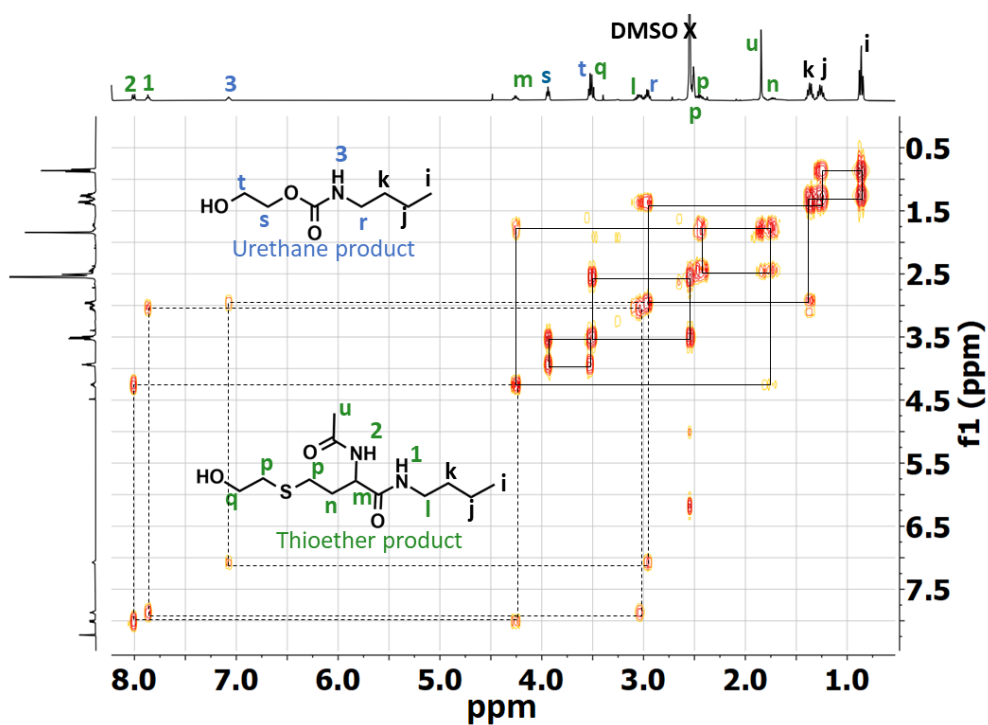
$$Product\ 1\ Yield\% = 2 \times \frac{\left(\frac{\int H_s}{2}\right)}{\left(\frac{\int H_{EC}}{4} + \frac{\int H_{t+q}}{2}\right)} \times 100$$

where  $\frac{\int H_s}{2}$  is the isolated signal **s** of product **1** (Figure S12). We could then obtain the Yield in product **3** as:

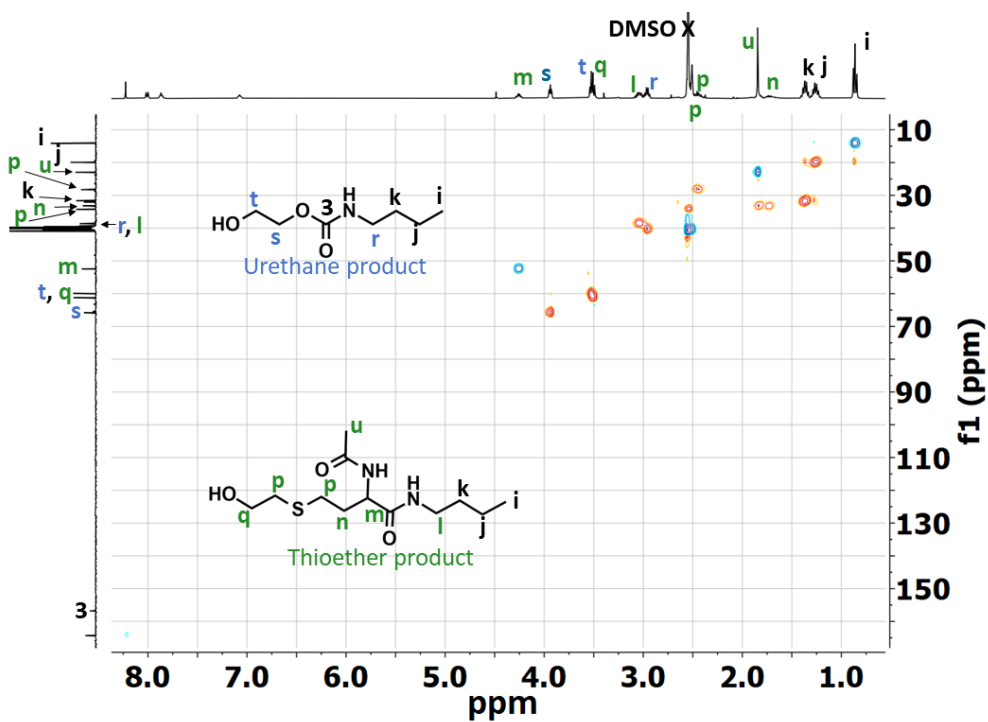
$$Product\ 3\ Yield\% = 2 \times \frac{\left(\frac{\int H_{t+q}}{2} - \frac{\int H_s}{2}\right)}{\left(\frac{\int H_{EC}}{4} + \frac{\int H_{t+q}}{2}\right)} \times 100$$



**Figure S13:** <sup>13</sup>C-NMR spectrum of the crude mixture obtained by the one pot reaction of EC, BuA and NAHcT catalyzed by 5 mol% DBU (vs EC) at 80 ° C for 24h.



**Figure S14:**  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of the crude mixture obtained by the one pot reaction of EC, BuA and NAHcT catalyzed by 5 mol% DBU (*vs* EC) at 80 °C for 24h.

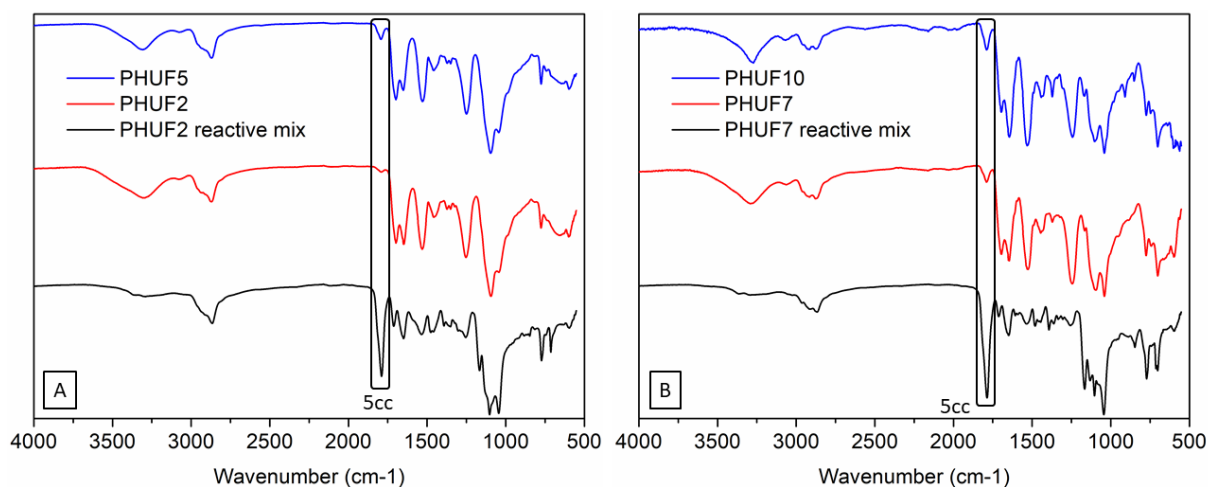


**Figure S15:** HSQC NMR spectrum of the crude mixture obtained by the one pot reaction of EC, BuA and NAHcT catalyzed by 5 mol% DBU (*vs* EC) at 80 °C for 24h.

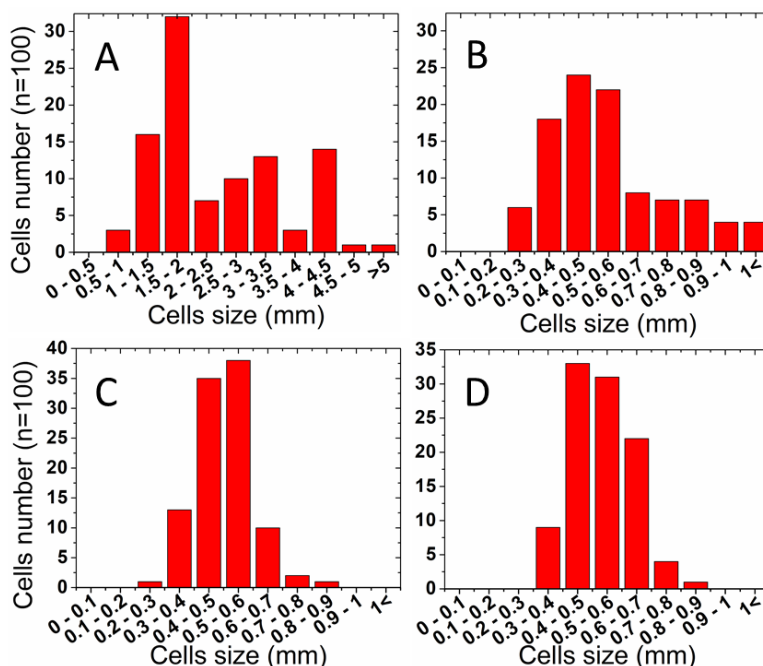
## Self-blown PHU foams preparation and reprocessing into films and structural composites

### Foams preparation and characterizations

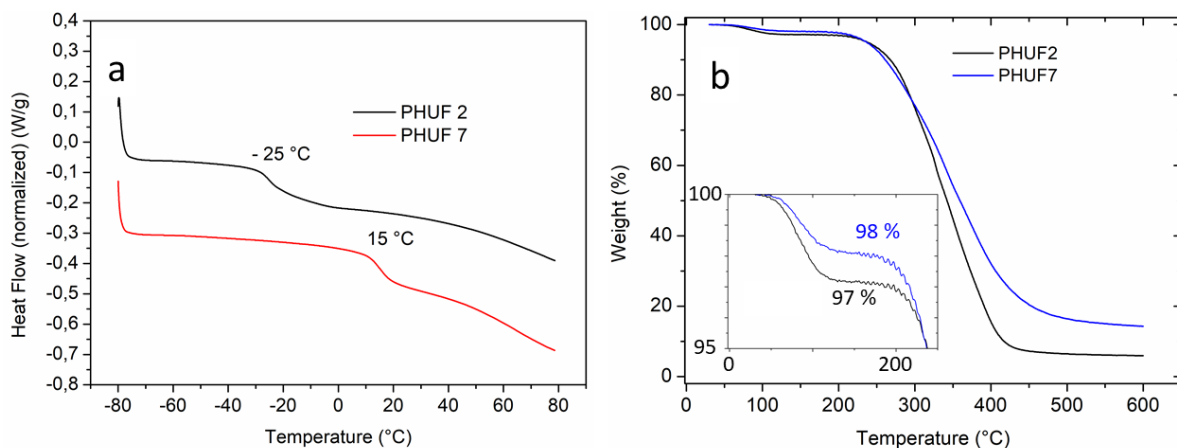
*Representative procedure described for PHUF2 and PHUF7.* TMPTC (5 g, 11.5 mmol), NAHcT (1.37 g, 8.6 mmol), Jeffamine EDR148 (2.56 g, 17.25 mmol) ( $[5cc]/[NH_2]/[NAHcT] = 1/1/0.25$ ) and DBU (0.26 g, 1.7 mmol) were introduced in a beaker and mechanically stirred at room temperature for 2 minutes to obtain a homogeneous viscous paste. The formulation is then poured in a silicon mold and placed in an oven at 80 °C. After 5 minutes at 80 °C, an additional manual mixing of the formulation is realized to guarantee the perfect homogenization of the mixture. The sample was then left for foaming at 80 °C for 5h and the so-produced foam was demolded after cooling to room temperature. The foam characterizations were only performed after an equilibration of at least 24h under ambient atmosphere and room temperature. PHUF7 was obtained by substituting EDR148 by mXDA (2.35 g, 17.25 mmol) while applying an identical processing method. PHUF5 and PHUF10 were produced by applying the same protocol but without DBU.



**Figure S16:** IR spectra of the reactive formulation before foaming and of the resulting foams (PHUF2, 5, 7 and 10).

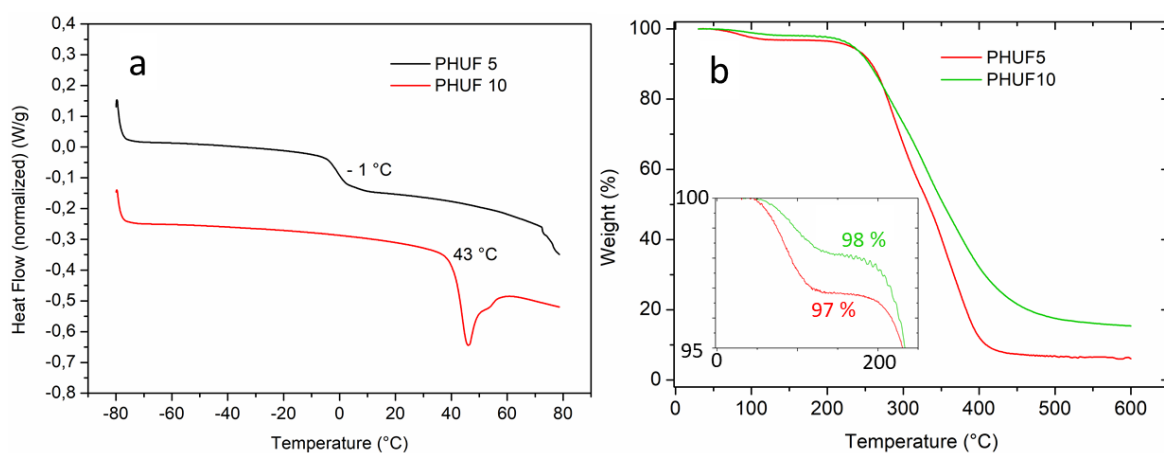


**Figure S17:** Cells size distribution of selected PHU foams PHUF2 (A), PHUF7 (B), PHUF5 (C) and PHUF10 (D)



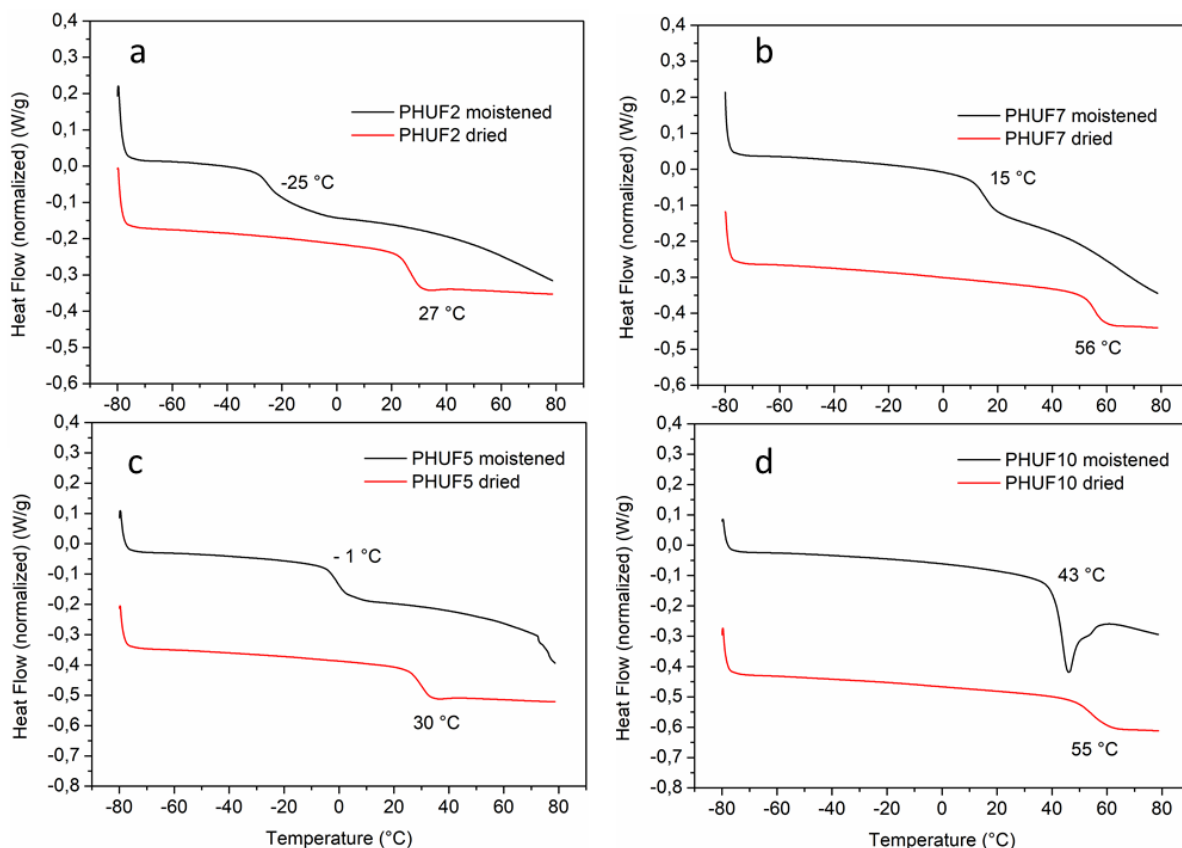
**Figure S18:** Thermal analyses of PHUF2 and PHUF7 foams equilibrated at ambient atmosphere for 48h: (a) DSC (first scan) and (b) TGA (inset = zoom of the 0-200°C region)

The weight loss between 50 and 200°C corresponds to the loss of water absorbed by the foams. (Figure S18B). As expected, the most hydrophobic foam prepared from the aromatic amine (mXDA) contains less absorbed water (2 wt%; sample PHUF7).



**Figure S19:** Thermal analyses of PHUF5 and PHUF10 foams equilibrated at ambient atmosphere for 48h: (a) DSC (first scan) and (b) TGA (inset = zoom of the 0-200°C region)

The weight loss between 50 and 200°C corresponds to the loss of water absorbed by the foams. (Figure S19B). As expected, the most hydrophobic foam prepared from the aromatic amine (mXDA) contains less absorbed water (2 wt%; sample PHUF10).

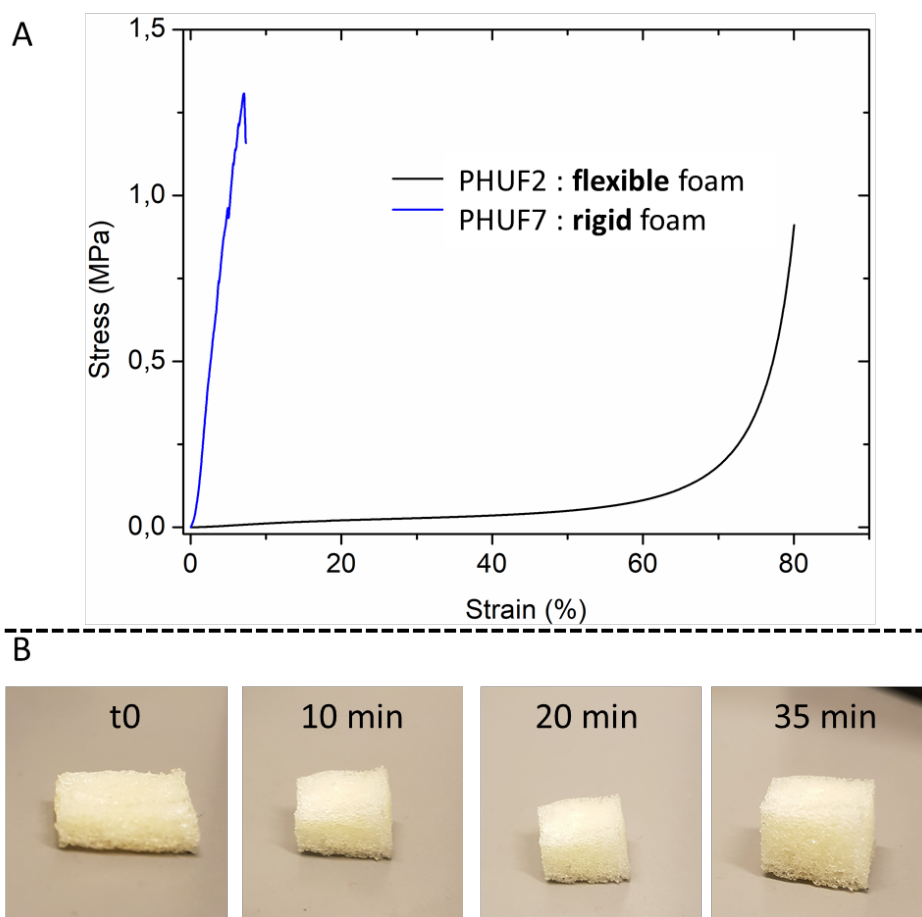


**Figure S20:** Evaluation of hydro-plasticization of the foams by comparison of DSC thermograms of moistened and dried foams: (a) PHUF2, (b) PHUF7, (c) PHUF5 and (c) PHUF10.

It has to be noted that the endotherm after 40-50°C for the moistened samples is in line with the water evaporation observed in TGA (Figure S18-S19). It is not observed for the dried samples, confirming that they are perfectly dried.

The dried foams prepared from the same formulation presented similar  $T_g$  values, whatever the foaming was catalyzed or not. Indeed PHUF2 (catalyzed) and PHUF5 (uncatalyzed) prepared from EDR148 present a  $T_g$  of +27 and +30°C, respectively. PHUF7 (catalyzed) and PHUF10 (uncatalyzed) prepared from mXDA present a  $T_g$  of +56 and +55°C, respectively. This suggests that the chemical structure of the foams is similar and not affected by the catalyst, in line with the model reactions (Figure 1D).

The discrepancy between  $T_g$  values for the moistened samples prepared from the same formulation in the presence or not of the catalyst is assumed to be the result of a slight difference of water content in the samples. Although similar water contents were measured for samples prepared from the same composition (i.e. about 3 wt % for PHUF2 and PHUF5, and 2 wt% for PHUF7 and PHUF10; Figure S18B and S19B), TGA analysis is not accurate enough for precisely quantifying such low contents. As demonstrated in the manuscript in Table 2, a very low content of absorbed water has an impressive effect on the  $T_g$  values (from 30 to more than 50°C, depending on the samples for approximative water contents of 2-3wt%). We thus assume that slight differences in water content in the samples - that cannot be accurately quantify by TGA analysis - accounts for the  $T_g$  value discrepancy observed for the moistened samples. When  $T_g$  of samples have to be compared, the dried samples have to be studied in order to get rid from hydroplasticization.

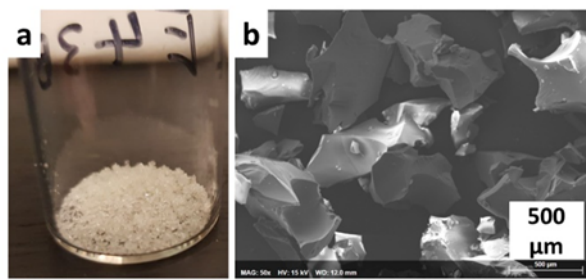


**Figure S21:** (A) Compression tests of PHUF2 and PHUF7; (B) Shape recovery of the flexible PHUF2 foam after an initial deformation of 80%

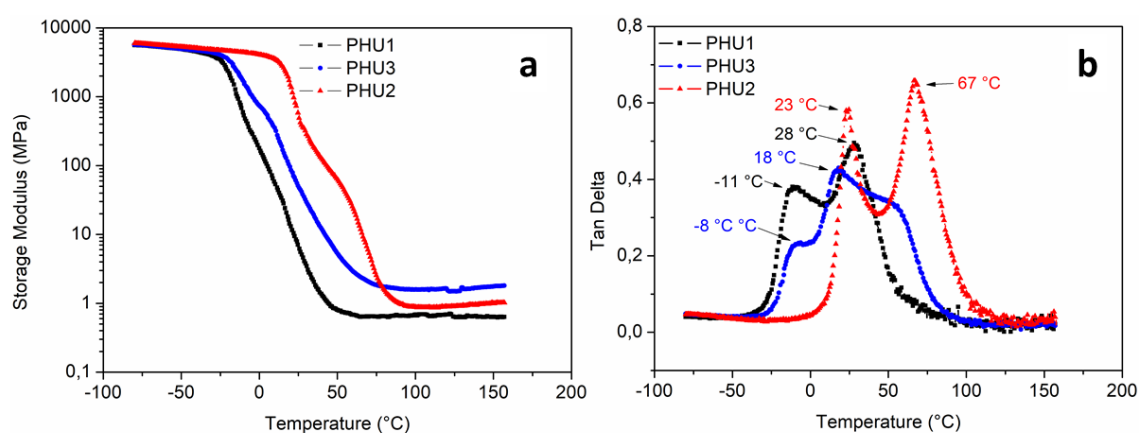
### PHU foams recycling

*Reprocessing method.* In a typical experiment, a 0.5 cm thick slice of PHU foam (PHUF2 or PHUF7) was sandwiched between two Teflon sheets and pressed for 2h at 160 °C under a 1 ton force (about 10 MPa). During the first 10 minutes, 3 cycles of apply-release pressure were realized to allow the formation of regular PHU films. A similar protocol was applied for repurposing PHUF5 and PHUF10 into films. Thermo-mechanical properties of the films are summarized in Table S1.

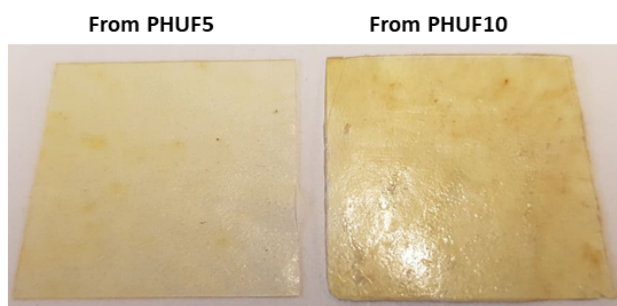
For preparing PHU film from blends of PHU, 1 g of the PHUF2 foam was grinded manually in a mortar with 1 g of PHUF7 and liquid nitrogen during 3 minutes to form a homogeneous fine powder (Figure S22). This powder was then dried at 50 °C for 20 minutes and then sandwiched between two Teflon sheets and reprocessed as previously described. Thermo-mechanical properties of the films are summarized in Table S1. It has to be observed that the reprocessed film of 50/50 PHUF2/PHUF7 blend showed a significantly lower Young modulus despite 50% of rigid PHUF7 was used. As the dynamic exchange reactions are occurring during reprocessing, a mixture of different PHU materials was expected to be formed. Indeed, the mixture of grinded foams are processed at 160°C under a given pressure for reprocessing. Chain mobility is thus very limited as there is no shear. Bonds are thus expected to be exchanged in-between a PHU “grain” of same composition (yielding a similar PHU at the end of the reprocessing) but also at the interface of two PHU “grains” of different chemical nature (furnishing a new PHU). This might explain why the mechanical properties are different to a simple combination of the properties of a blend of two separate PHU. As the product is a thermoset, it is however impossible to isolate and characterize the microstructure of the product by conventional techniques (NMR for instance).



**Figure S22:** (A) macroscopic aspect of grinded PHUF2/PHUF7 blend and (B) SEM characterization of the shape and size of the so-produced PHU particles

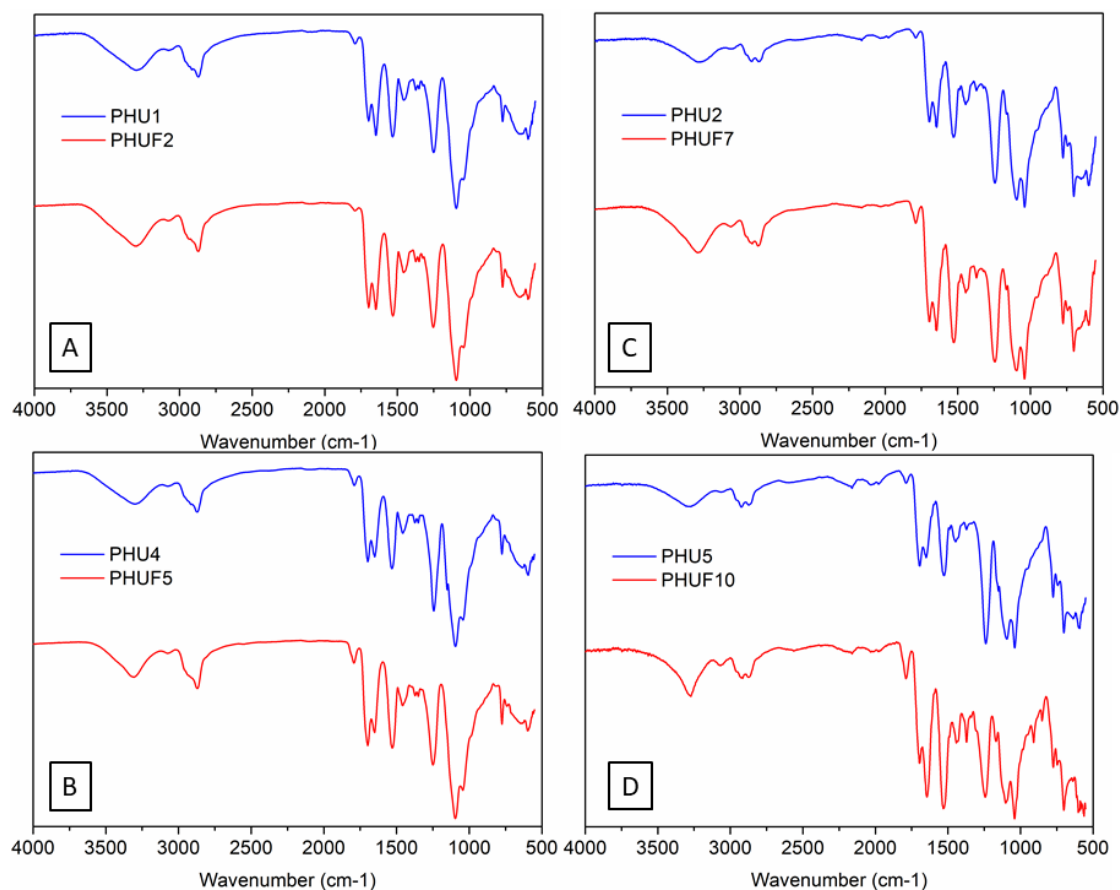


**Figure S23:** DMA analysis of PHU1-3 reprocessed foam samples that were equilibrated under ambient atmosphere for 48h. (a) storage modulus and (b) tan delta at the  $T_g$  transition between -80 °C and 160 °C.



**Figure S24:** PHU films obtained by reprocessing of the foams that were produced in the absence of DBU. Left: PHU4 obtained by reprocessing the foam PHUF5; right: PHU5 obtained by reprocessing the foam PHUF 10.



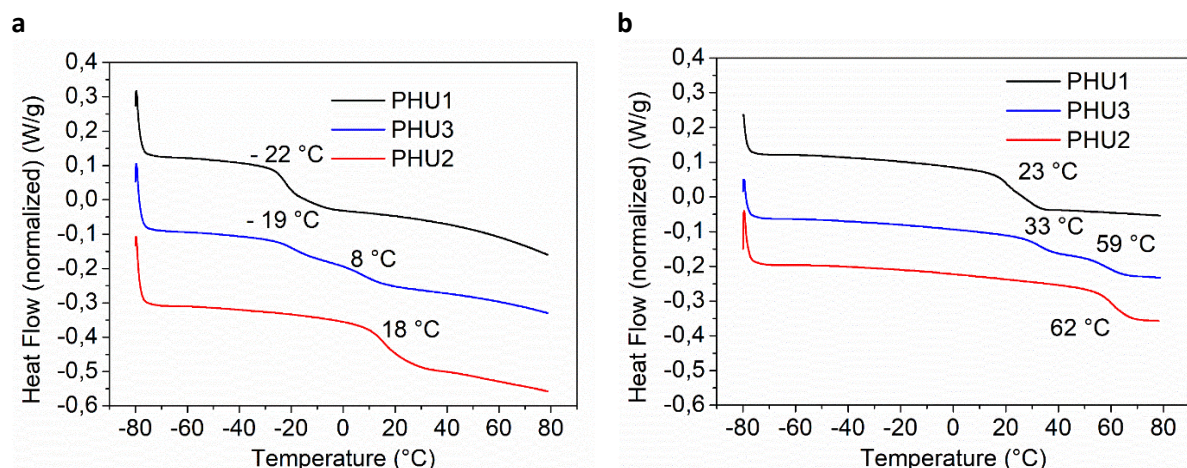


**Figure S25:** IR spectra of (A) EDR148 based foams prepared in the presence of catalyst (PHUF2) and corresponding reprocessed film (PHU1), (B) same foams produced without catalyst (PHUF5) and corresponding reprocessed film (PHU4). IR spectra of (C) mXDA based foams prepared in the presence of catalyst (PHUF7) and corresponding reprocessed film (PHU2), (D) same foams prepared without catalyst (PHUF10) and corresponding reprocessed film (PHU5).

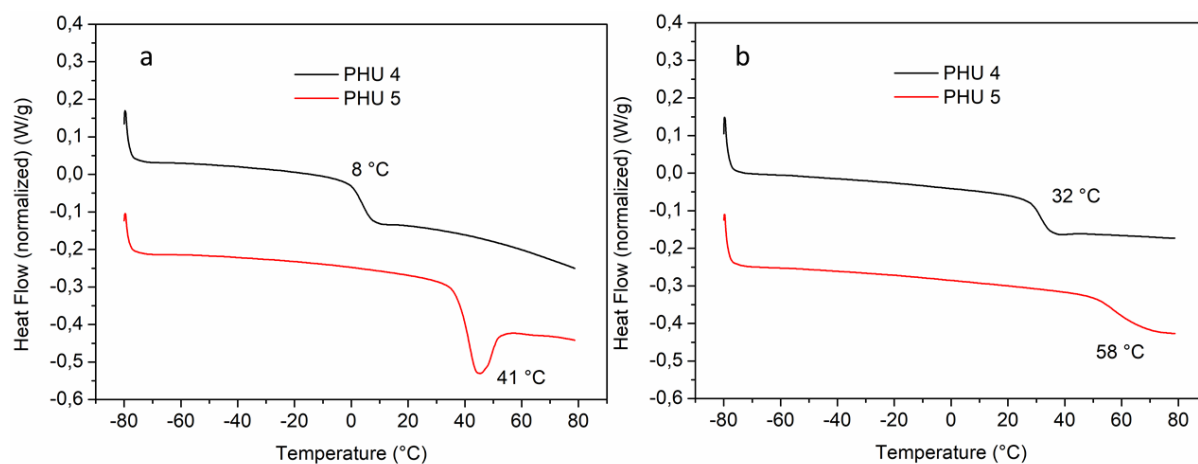
**Table S1.** Thermo-mechanical properties of reprocessed foams into films.

Properties	PHU1	PHU2	PHU3	PHU4	PHU5
$T_g$ (°C) <sup>a</sup>	-22	+18	-19/+8	+8	+41
$T_g$ (°C) <sup>b</sup>	+23	+62	+33/+59	+32	+58
$T_\alpha$ (°C) <sup>a</sup>	-11	+23	-8/+18	n.d.	n.d.
Young modulus (kPa) <sup>a</sup>	8.48 +/- 0.76	373 +/- 191	11.1 +/- 0.82	n.d.	n.d.
Deformation at break (%) <sup>a</sup>	87 +/- 10	258 +/- 35	100 +/- 6	n.d.	n.d.

<sup>a</sup> equilibrated samples under ambient atmosphere for 48 h. <sup>b</sup> dried samples. N.d. not determined.



**Figure S26:** Evaluation of hydro-plasticization of the reprocessed films by comparison of their DSC thermograms for moistened and dried samples (PHU1, PHU2, PHU3). (a) moistened and (b) dried samples.



**Figure S27:** Evaluation of hydro-plasticization of the reprocessed films (obtained from DBU-free foams) by comparison of DSC thermograms of moistened and dried samples (PHU4 and PHU5). (a) moistened and (b) dried samples.

### PHU-nylon fabric composites preparation

In a typical experiment, a PHU1 film was placed on a cordura® nylon fabric with a linear density of 185g/m<sup>2</sup> and pressed for 2h at 160 °C under a 4 tonnes force (about 20 MPa). Lap-shear samples were prepared by cutting 0.5 x 3cm pieces of composites, placing them with PHU film faces in contact and pressing with a minimum force (below device sensibility) to ensure good contact between pieces for 10 minutes at 160 °C.

### Reference.

<sup>1</sup>Panchireddy, S.; Thomassin, J.-M.; Grignard, B.; Damblon, C.; Tatton, A.; Jerome, C.; Detrembleur, C. Reinforced poly(hydroxyurethane) thermosets as high performance adhesives for aluminum substrates. *Polymer Chemistry* **2017**, *8*, 5897-5909.