

Fast, catalyst-free room temperature production of isocyanate-free polyurethane foams using aromatic thiols

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1. High temperature thiol induced-foaming

1.1. Comparison of the aliphatic and aromatic thiol

Table S1. Properties of PHU foams prepared by the thiol-induced foaming presented in Figure 1 of the main manuscript. T_g , $T_{g \text{ dried}}$, $T_{g \text{ 80\%}}$ are respectively the glass transition temperature measured after equilibration of the foam at room temperature, after drying and after equilibration at 80% of relative humidity at 25°C for 48h, respectively. Water uptake is the water content after incubation of the foam for 48h at 80% of relative humidity at 25°C

Entry	Thiol	NH ₂ (eq vs 5CC)	cat	Time	D (kg.m ⁻³)	GC (%)	T _g /T _{g dried} (°C)	Water uptake (%)	T _{g 80%} (°C)
1	T1	XDA (0.75)	DBU	3h	355 ± 84	92 ± 3	8.4/28.2	7.6 ± 0.2	-6
2	T1	XDA (0.75)	DBU	30'	372 ± 17	86 ± 4	4.2/24.6		
3	T1	XDA (0.75)	-	30'	1100	NA	NA		
4	T2	XDA (0.75)	DBU	3h	203 ± 72	90 ± 2.5	30.1/49.7	9.3 ± 0.6	-8
5	T2	XDA (0.75)	DBU	30'	185 ± 34	91 ± 2	37.4/48		
6	T2	XDA (0.75)	-	30'	141 ± 23	91 ± 3.4	30.3/50.3		
7	T3	XDA (0.75)	DBU	3h	309 ± 8	86 ± 6	41/53	8.8 ± 0.5	19
8	T3	XDA (0.75)	DBU	30'	166 ± 6	93 ± 2	35/47		
9	T3	XDA (0.75)	-	30'	163 ± 13	86 ± 6	48.7/51.6		

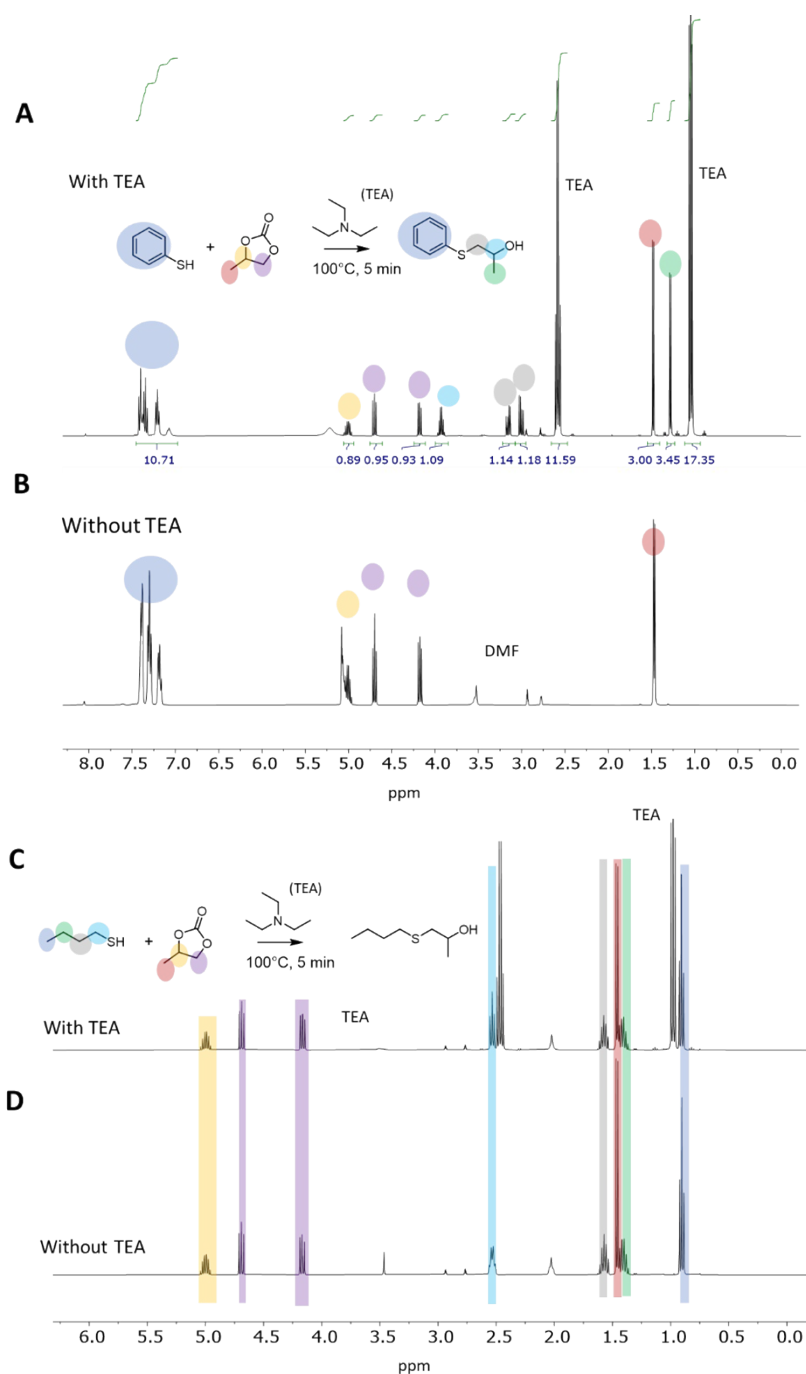


Figure S1. $^1\text{H-NMR}$ spectra of the model reactions between thiol and propylene carbonate in the presence or not of triethylamine. A) Thiophenol with triethylamine (TEA), B) Thiophenol without TEA. C) 1-Butanethiol with triethylamine. D) 1-Butanethiol without triethylamine. Condition: propylene carbonate (5 mmol), thiol (5 mmol), TEA (5 mmol), preheating of the components at 100°C before mixing them, followed by reaction at 100°C for 5 min in a closed vial. Results are discussed in Figure 2 of the main manuscript

1.2. Optimization of the aromatic thiol induced foaming

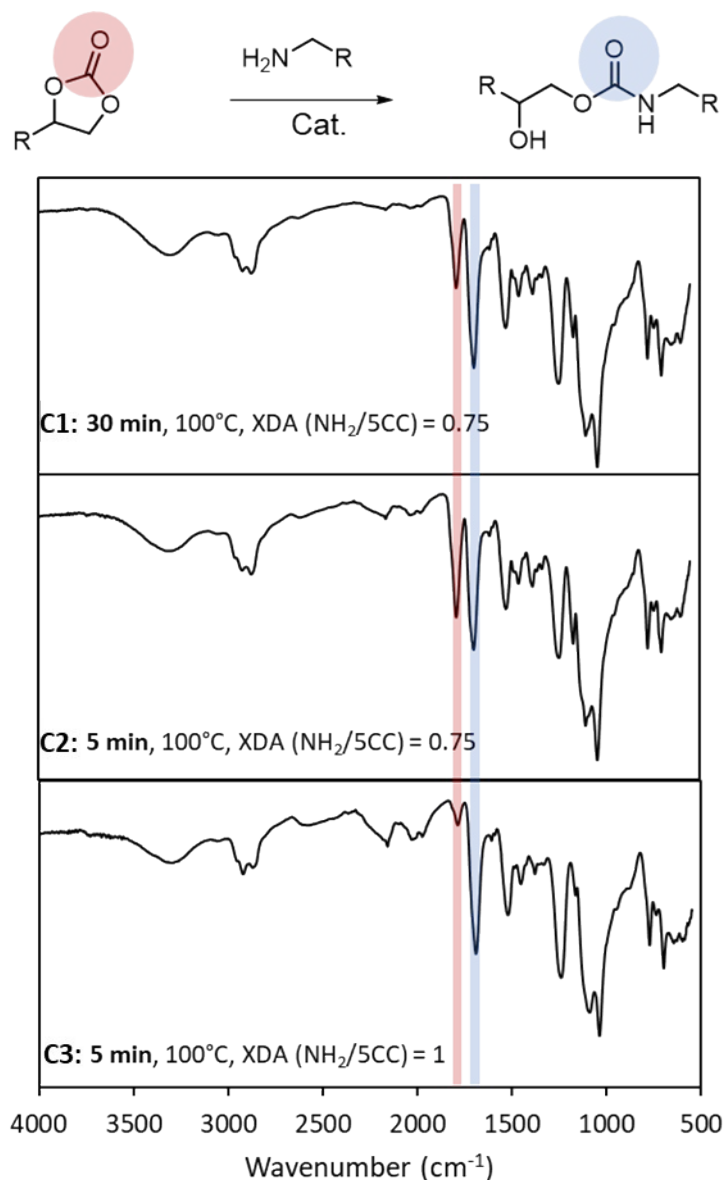


Figure S2. Infrared spectra of the thiol-induced foams showing that in presence of 1 eq of amine (**C3**), the 5CC conversion is higher in 5 min than in 30 min for the same experiment carried out with 0.75 eq of amine (**C1**). Condition: TMPTC, (5CC = 1 eq), XDA (NH₂ = 0.75 eq for **C1** and **C2** or 1 eq for **C3**), **T2** (SH = 0.25 eq), Condition: fast foaming process (preheating all component separately at 100 °C before mixing them, then curing at 100 °C. Results are discussed in Figure 3 of the main manuscript.

Table S2. Properties of PHU foams prepared by the thiol-induced process in 5 min. T_g , $T_{g \text{ dried}}$, $T_{g 80\%}$ are respectively the glass transition temperature measured after equilibration of the foam at room temperature, after drying and after equilibration at 80% of relative humidity at 25 °C for 48h. Water uptake is the water content after incubation of the foam for 48h at 80% of relative humidity at 25 °C.

Entry	Thiol	NH ₂ (eq vs 5CC)	additives	T(°C) (min)	D (kg.m ⁻³)	GC (%)	T _g /T _{g dried} (°C)	Water uptake (%)	T _{g 80%} (°C)
1 (F1)	T2	XDA (1)	-	100	155 ± 21	93 ± 5	33.6/54	9.8± 0.6	7.5
2 (F4)	T2	XDA (1)	HTC	100	144 ± 3	89 ± 3.1	41/52		
3 (F5)	T2	XDA (1)	POR	100	173 ± 19	96.8 ± 5.8	42/52		
4 (F2)	T2	EDR (1)	-	100	156 ± 15	93 ± 5	7.9/27.3		
5	T2	EDR (1)	HTC	100	192 ± 4	73 ± 5	9/28.6		
6 (F3)	T3	XDA (1)	-	100	124 ± 18	93 ± 5.2	42.8/47.7	8.5± 0.3	8.6
7	T3	XDA (1)	-	80	190	97 ± 3	42.6/51		

Table S3. Mechanical properties of PHU foams prepared by the thiol-induced process.

Entry	Thiol	NH ₂ (eq vs 5CC)	additives	Compr modulus (MPa)	Modulus /d (kPa.m ³ /kg)
1 (F1)	T2	XDA (1)		8.3 ± 0.22	54
2	T2	XDA (1)	HTC	6.6 ± 0.28	46
3 (F2)	T2	EDR (1)		0.011 ± 0.004	0.071
4	T2	EDR (1)	HTC	0.013 ± 0.003	0.068
5 (F3)	T3	XDA (1)		2.97 ± 1.7	24

*Normalized modulus

1.3. DSC of thiol induced foam synthesized at 100°C.

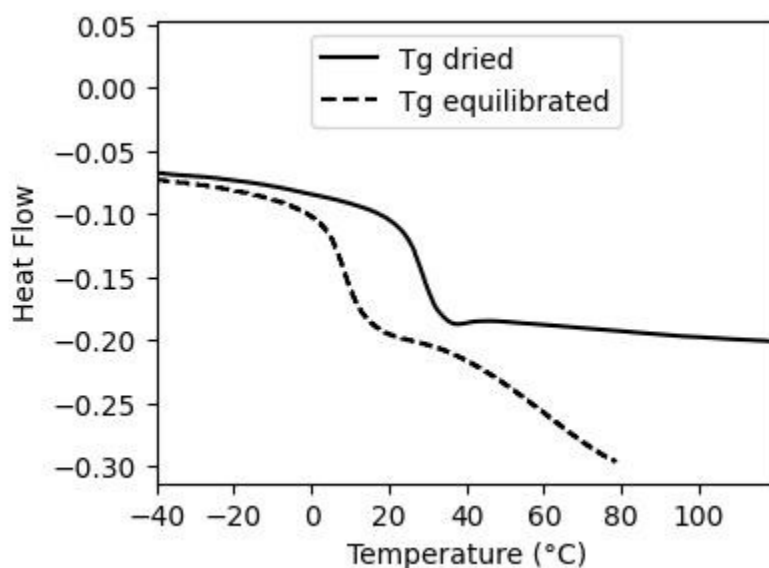


Figure S3. DSC thermogram of flexible foam obtained from aliphatic thiol **T1**, XDA and TMPTC by the classic foaming process (entry 1, Table S1). Condition: [TMPTC]:[XDA]:[**T1**]:[DBU] = 1:0.75:0.25:0.05, foaming 3 h at 100°C

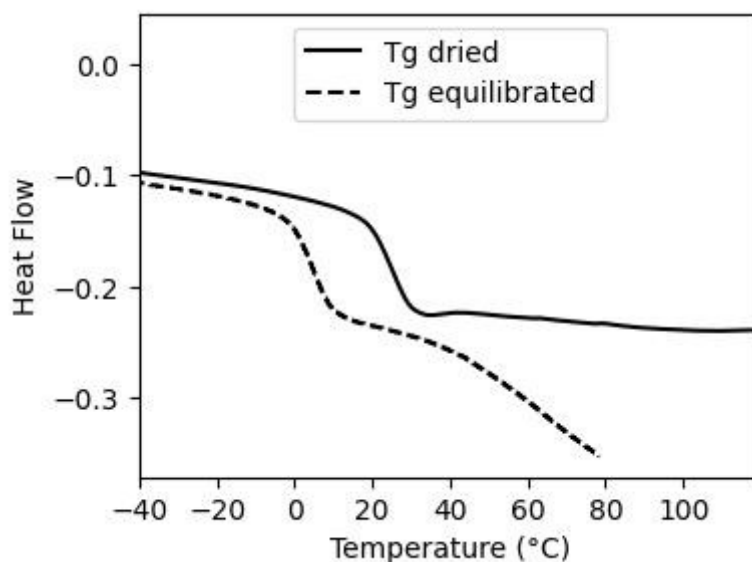


Figure S4. DSC thermogram of flexible foam obtained from aliphatic thiol **T1**, XDA and TMPTC by the fast foaming process (entry 2, Table S1). Conditions: [TMPTC]:[XDA]:[**T1**]:[DBU] = 1:0.75:0.25:0.05 foaming 30 min at 100 °C after preheating the component separately at 100 °C.

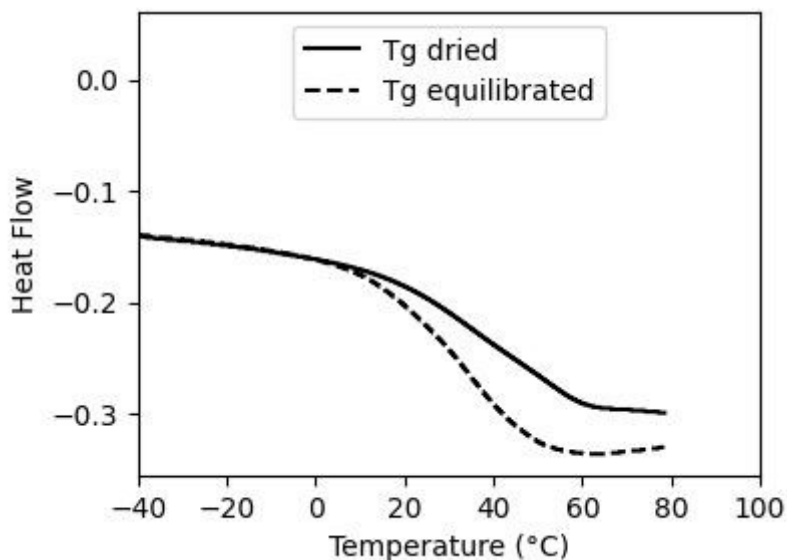


Figure S5. DSC thermogram of foam **F1** (entry 1, Table S2) discussed in Figure 4 of the main manuscript. Conditions: $[TMPTC]:[XDA]:[T2]$ (catalyst free) = 1:1:0.25, foaming 5 min at 100 °C after preheating the component separately at 100 °C.

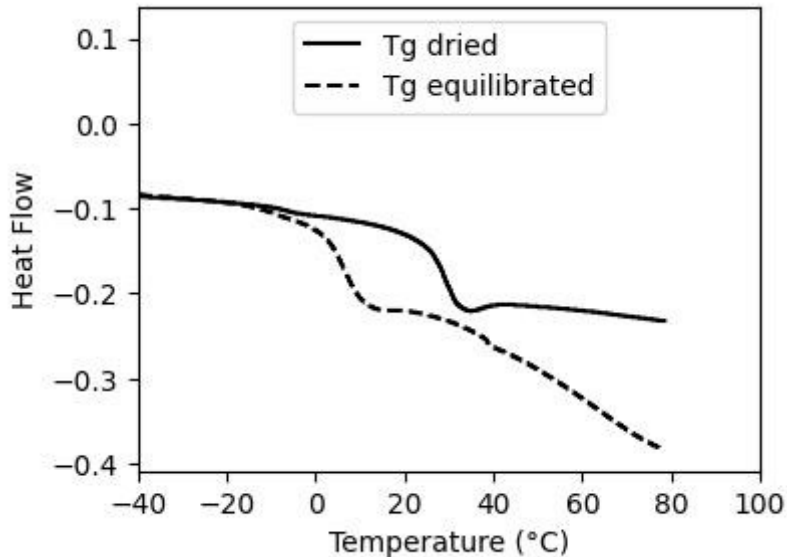


Figure S6. DSC thermogram of flexible foam **F2** presented in entry 4 of Table S2 and discussed in Figure 4 of the main manuscript. Conditions: $[TMPTC]:[EDR148]:[T2]$ (catalyst free) = 1:1:0.25, foaming 5 min at 100 °C after preheating the component separately at 100 °C.

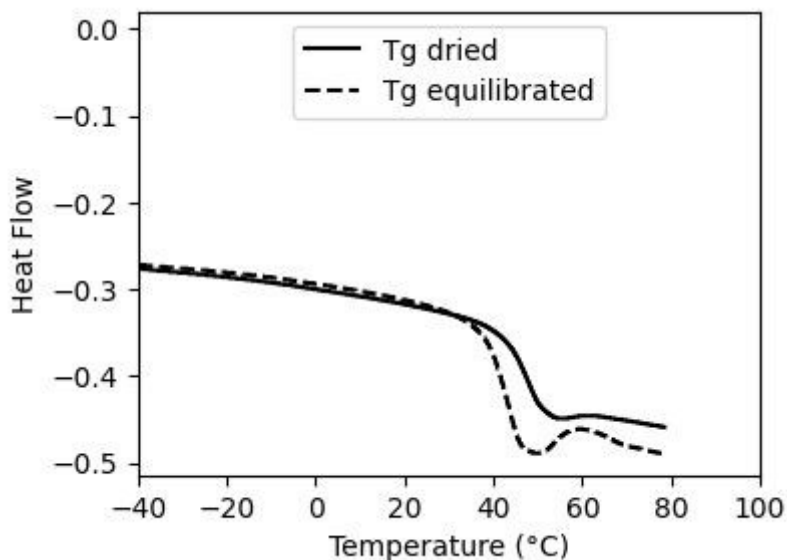


Figure S7. DSC thermogram of foam **F3** (entry 6, Table S2) discussed in Figure 4 of the main manuscript. Conditions: [TMPTC]:[XDA]:[T3] (catalyst free) = 1:1:0.25, foaming 5 min at 100 °C after preheating the component separately till 100 °C.

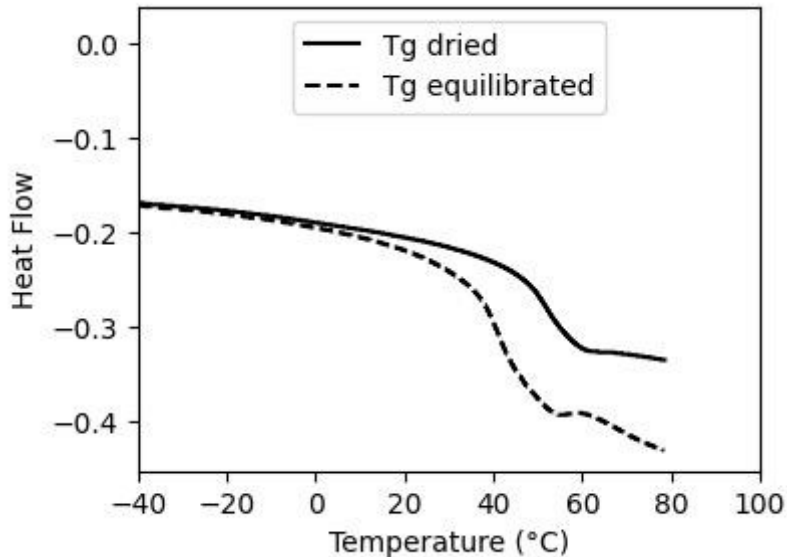


Figure S8. DSC thermogram of foam **F4** (entry 2, Table S2) discussed in Figure 4 of the main manuscript. Conditions: [TMPTC]:[XDA]:[T2] (catalyst free) = 1:1:0.25, with hydrotalcite as filler (12 wt% of TMPTC), foaming 5 min at 100 °C after preheating the component separately at 100 °C.

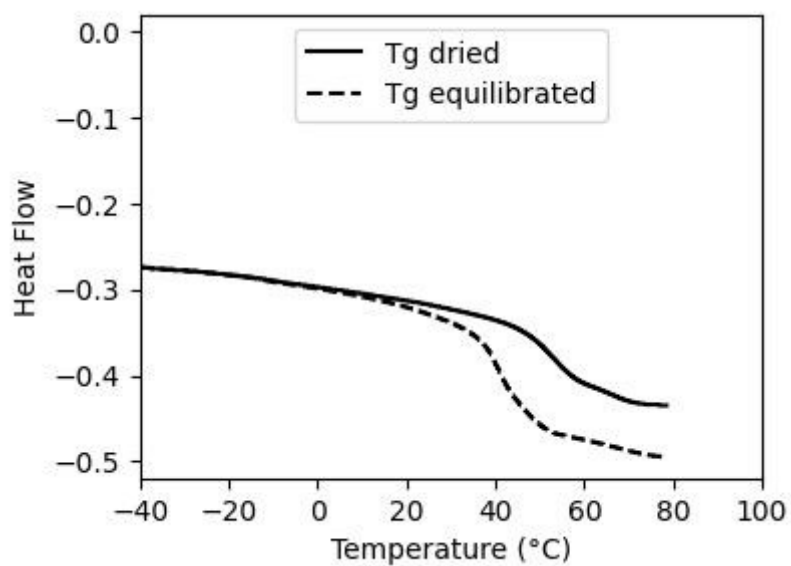


Figure S9. DSC thermogram of foam **F5** (entry 3, Table S2) discussed in Figure 4 of the main manuscript. Conditions: $[TMPTC]:[XDA]:[T2]$ (catalyst free) = 1:1:0.25, with *Portaflame*TM as filler (12 wt% of TMPTC), foaming 5 min at 100 °C after preheating the component separately at 100 °C.

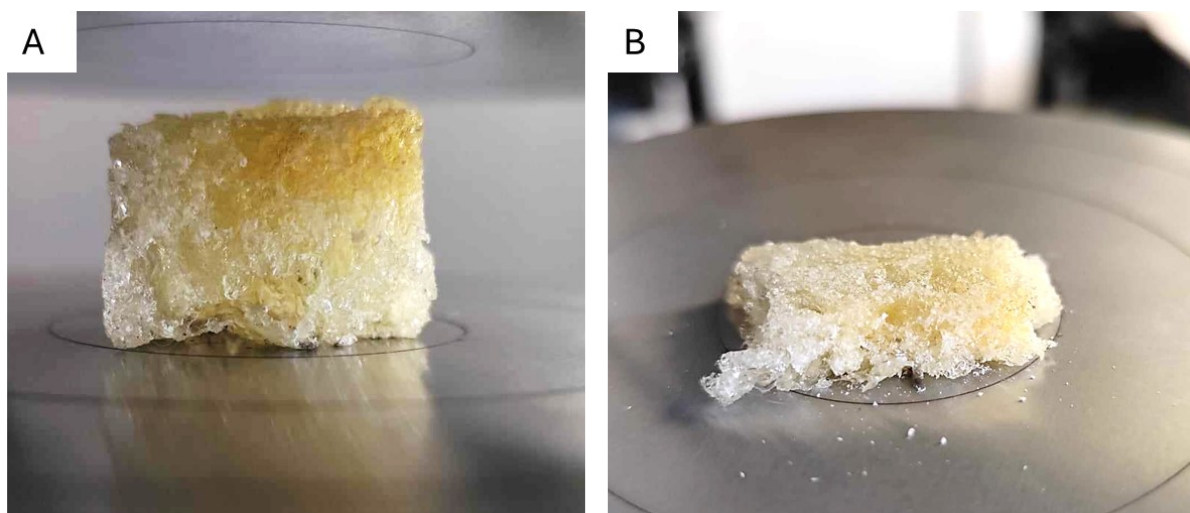


Figure S10. Picture of foam **F3** before and after compression test.

2. Room temperature foaming

2.1. Infrared analyses of the foams synthesized at room temperature

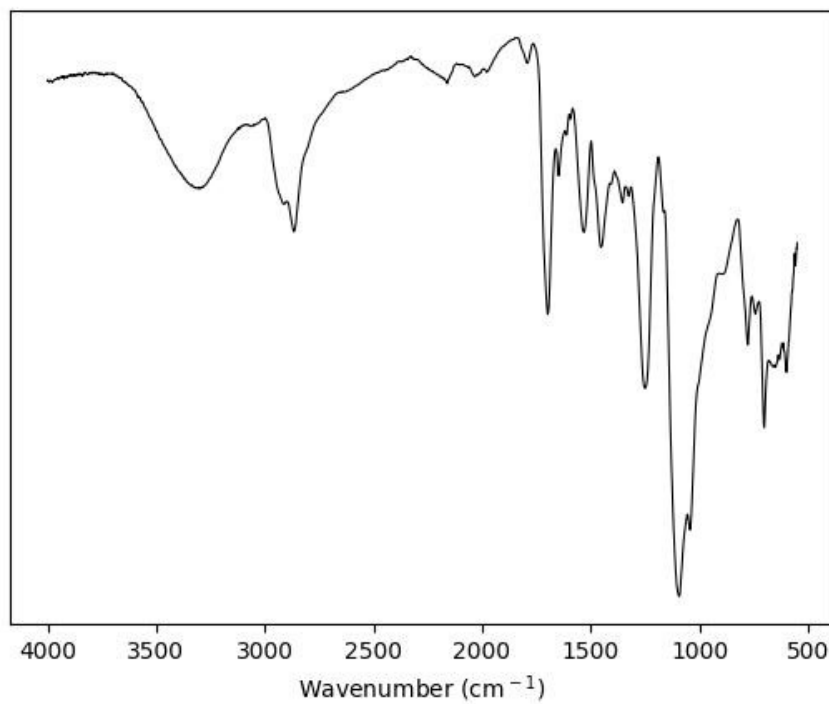


Figure S11. Infrared spectra of foam **F6_(DBU)** (TMPTC, BDGE, **T1**, XDA, DBU) at room temperature.

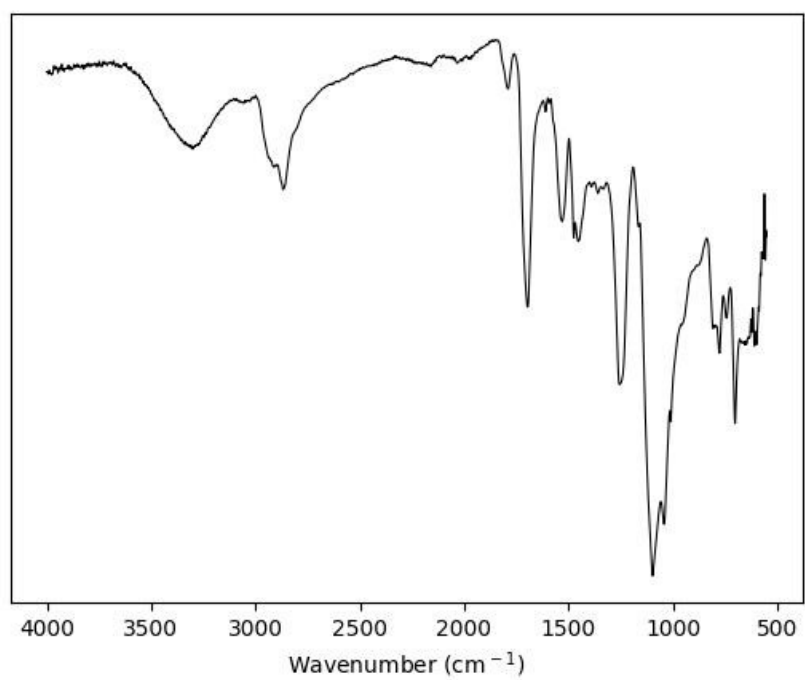


Figure S12. Infrared spectrum of foam **F7** (TMPTC, BDGE, **T3**, XDA)

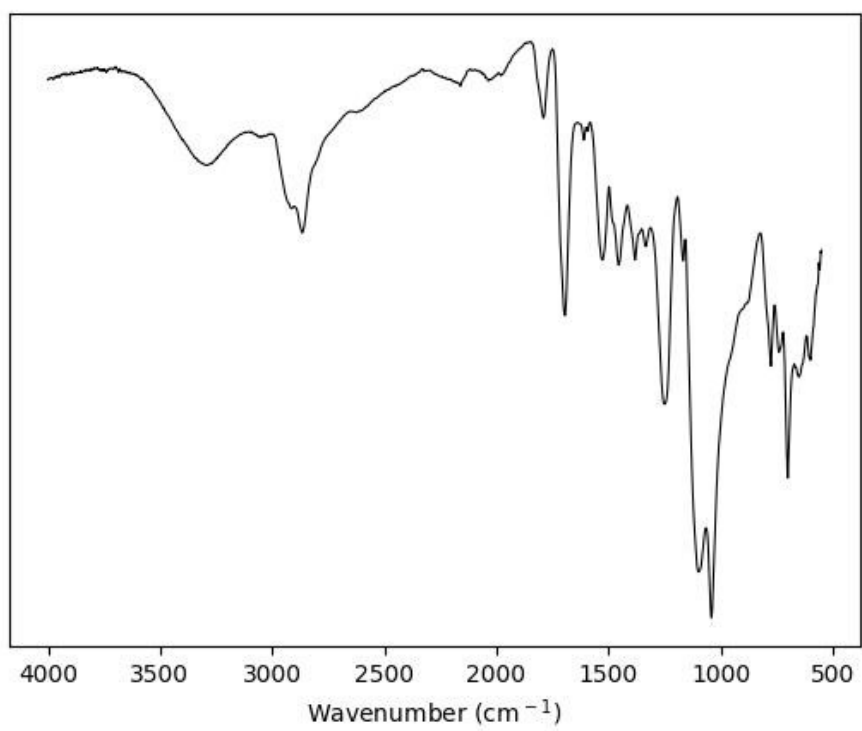


Figure S13. Infrared spectra of foam **F8** (TMPTC, BDGE, **T2**, XDA)

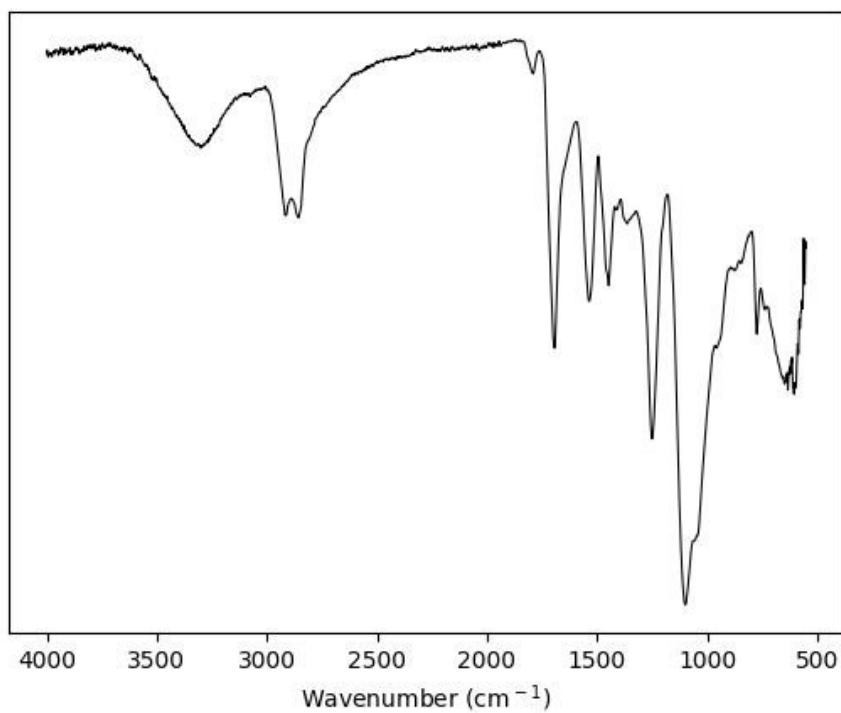


Figure S14. Infrared spectrum of foam **F9** (TMPTC, BDGE, **T2**, 1,3-BAC)

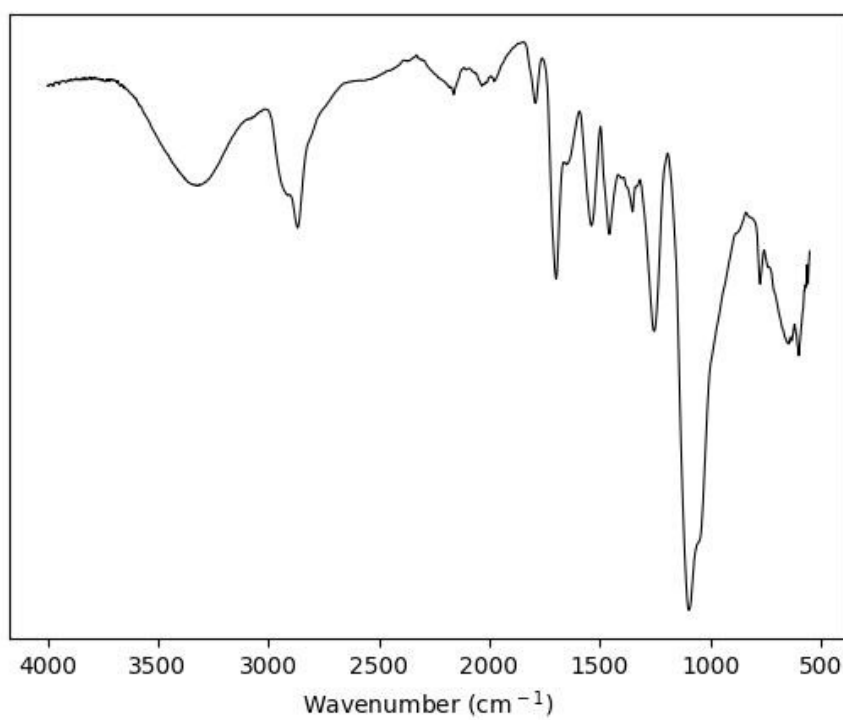


Figure S15. Infrared spectrum of foam **F10** (TMPTC, BDGE, **T2**, EDR148)

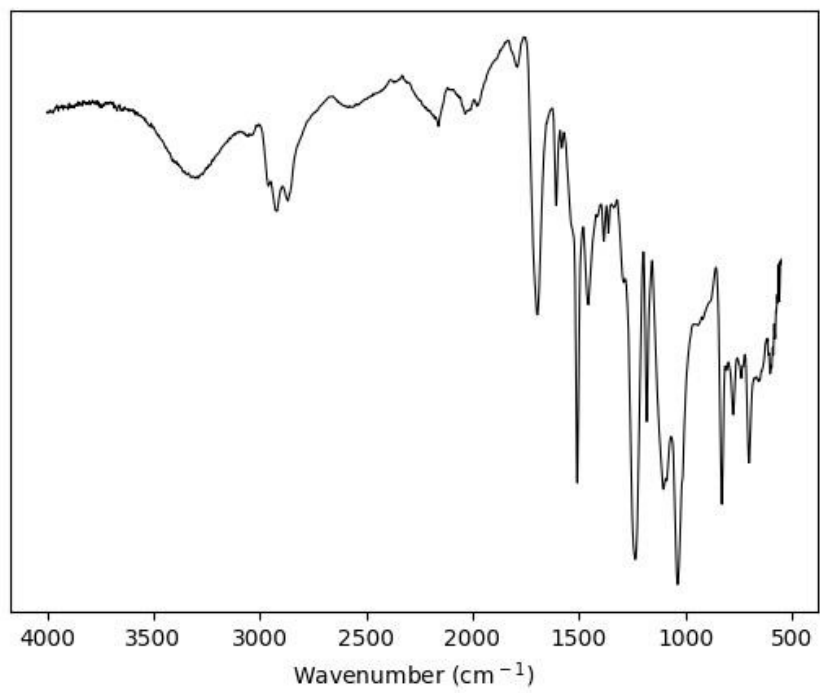


Figure S16. Infrared spectrum of foam **F11**(TMPTC, DER332, **T2**, XDA)

2.2. Thermogram of the different foams synthesized at room temperature

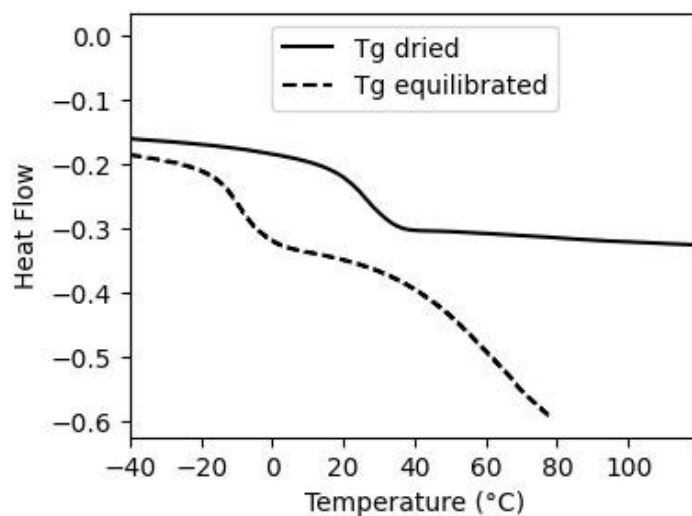


Figure S17. DSC thermogram of foam F6_(DBU) (TMPTC, BDGE, T1, XDA). T_g equilibrated states for glass transition temperature measured on foam equilibrated under ambient condition, T_g dried states for glass transition temperature for dried foam.

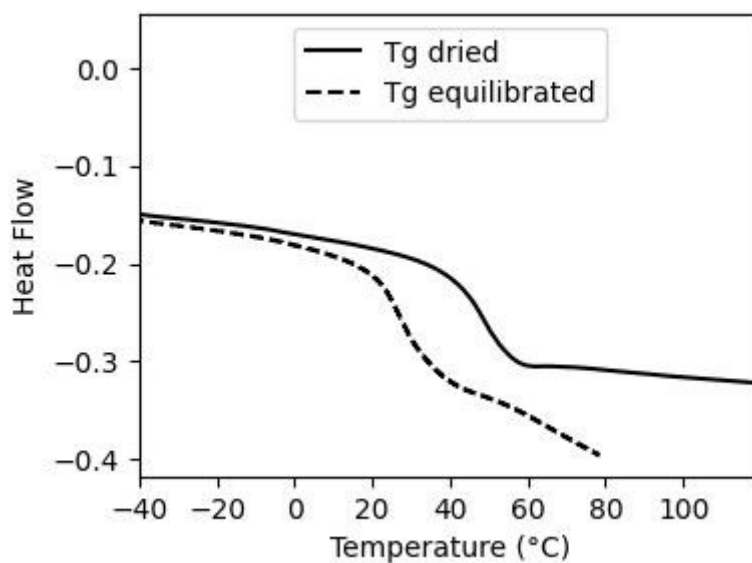


Figure S18. DSC thermogram of foam F7 (TMPTC, BDGE, T3, XDA). T_g equilibrated states for glass transition temperature measured on foam equilibrated under ambient condition, T_g dried states for glass transition temperature for dried foam.

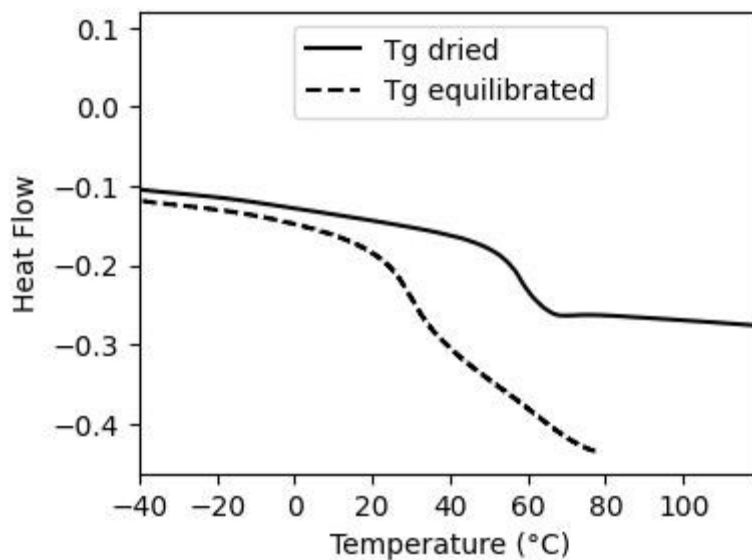


Figure S19. DSC thermogram of foam **F8** (TMPTC, BDGE, **T2**, XDA). T_g equilibrated states for glass transition temperature measured on foam equilibrated under ambient condition, T_g dried states for glass transition temperature for dried foam.

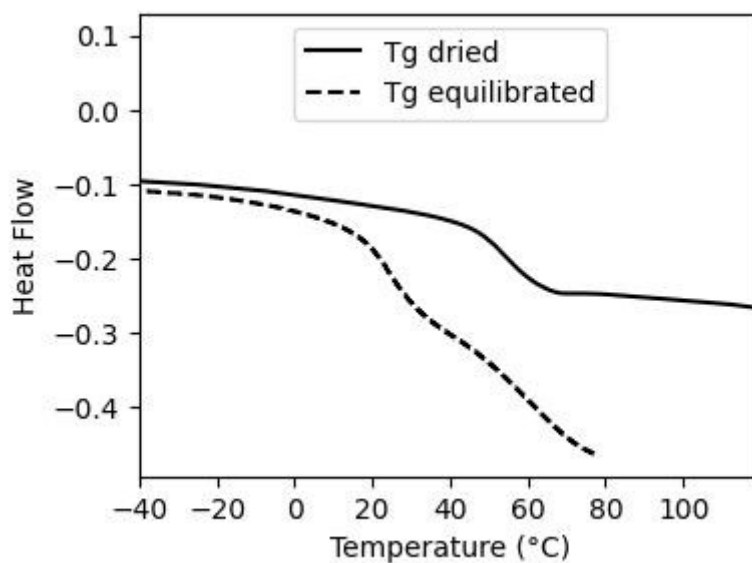


Figure S20. DSC thermogram of foam **F9** (TMPTC, BDGE, **T2**, 1,3-BAC). T_g equilibrated states for glass transition temperature measured on foam equilibrated under ambient condition, T_g dried states for glass transition temperature for dried foam.

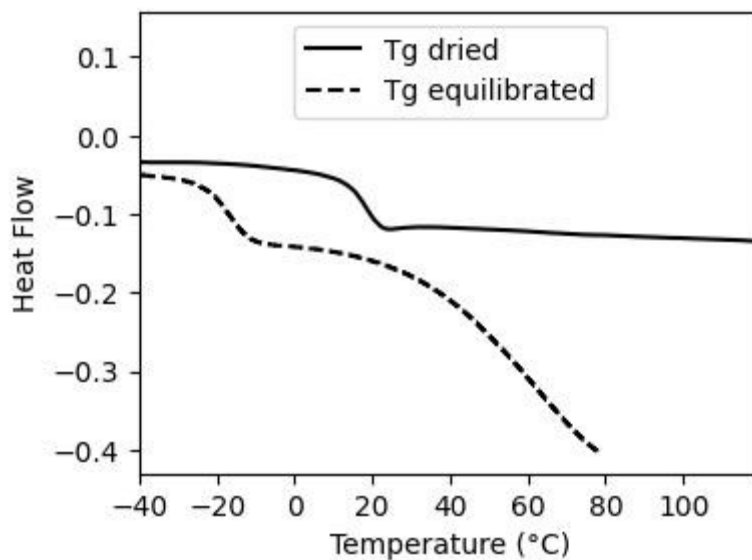


Figure S21. DSC thermogram of foam **F10** (TMPTC, BDGE, **T2**, EDR148). T_g equilibrated states for glass transition temperature measured on foam equilibrated under ambient condition, T_g dried states for glass transition temperature for dried foam.

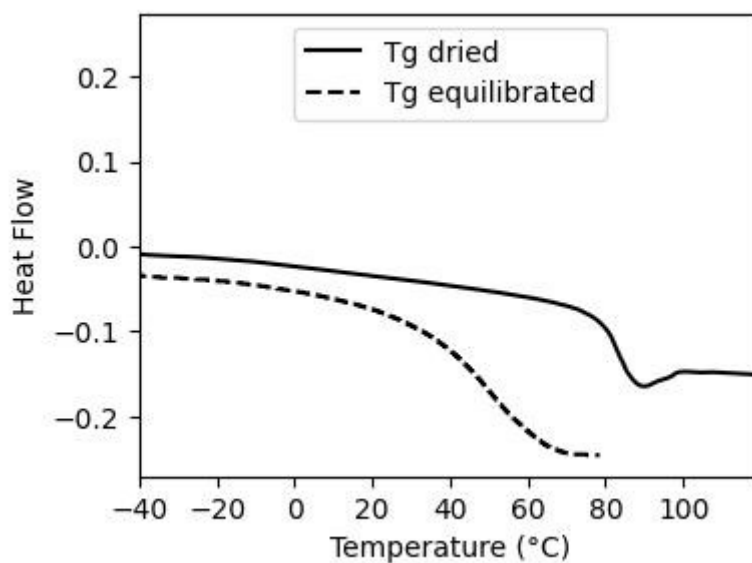


Figure S22. DSC thermogram of foam **F11** (TMPTC, DER332, **T2**, XDA). T_g equilibrated states for glass transition temperature measured on foam equilibrated under ambient condition, T_g dried states for glass transition temperature for dried foam.

2.3. ^1H NMR of model reaction between thiol and epoxide

The conversion of epoxide reacting with the different thiols was calculated as follows:

For each spectra intensity of peak **a** ($-\text{CH}_3$ terminal of 1,2-epoxydodecane) was normalized at 3. The conversion for each reaction was calculated dividing the intensity of peak **b** ($I_{b(\text{react})}$) ($-\text{CH}$ of epoxide) by intensity of peak at zero conversion given by the intensity peak $I_{b(\text{ref})}$ from reference spectra (1,2-epoxydodecane without addition of thiol, Figure S23), according the

$$\text{formula : conversion (\%)} = \left(1 - \frac{I_{b(\text{react})}}{I_{b(\text{ref})}} \right) \times 100$$

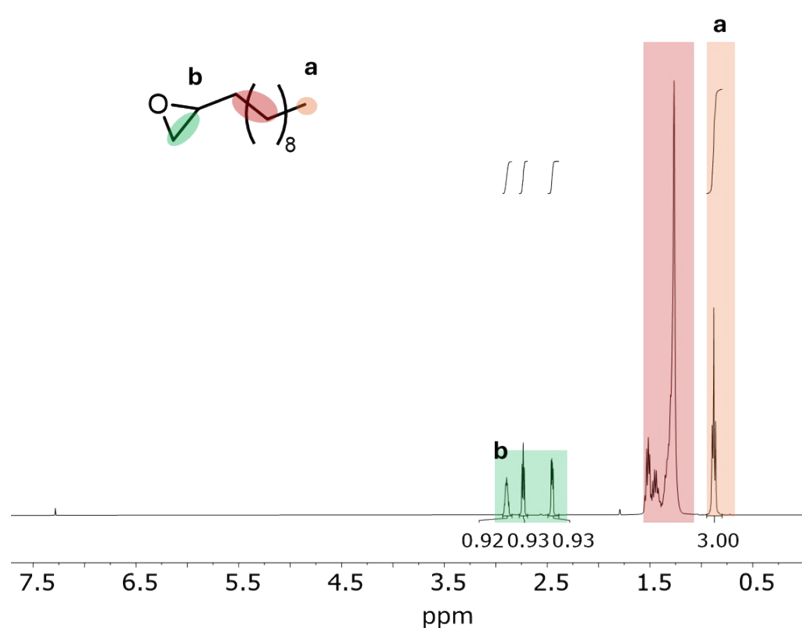


Figure S23. ^1H NMR spectra in CDCl_3 of the 1,2-epoxydodecane used as model epoxide

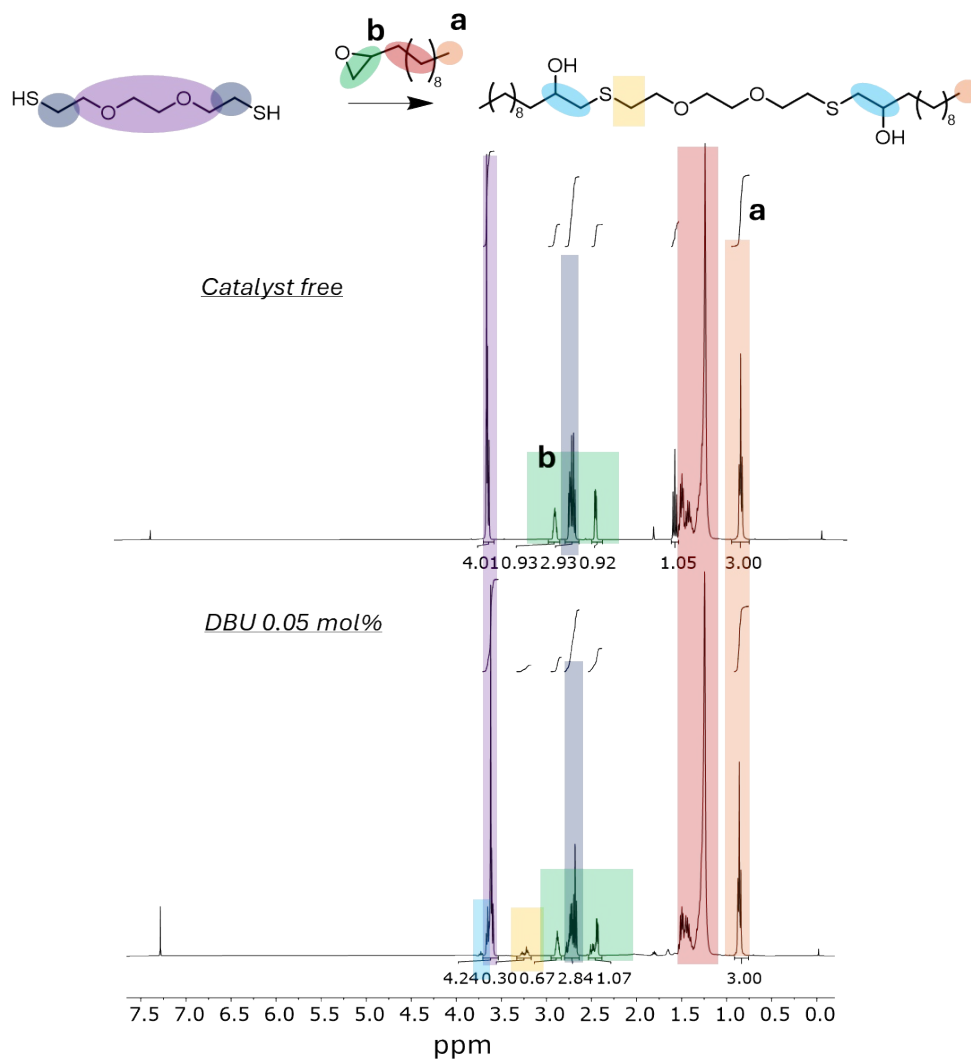


Figure S24. ¹H NMR spectra in CDCl₃ of the catalyst free reaction between **T1** and 1,2-epoxydodecane under catalyst-free and DBU catalyzed condition.

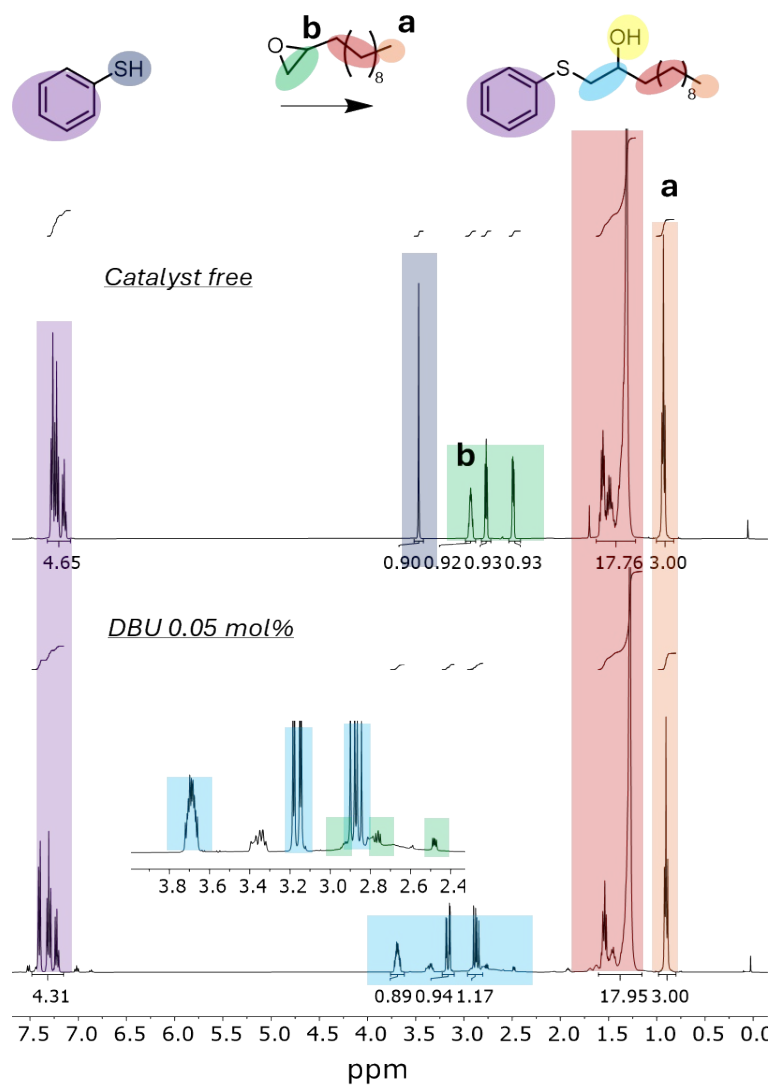


Figure S25. ¹H NMR spectra in CDCl₃ of the catalyst free reaction between thiophenol (T4) and 1,2-epoxydodecane under catalyst-free and DBU catalyzed condition.

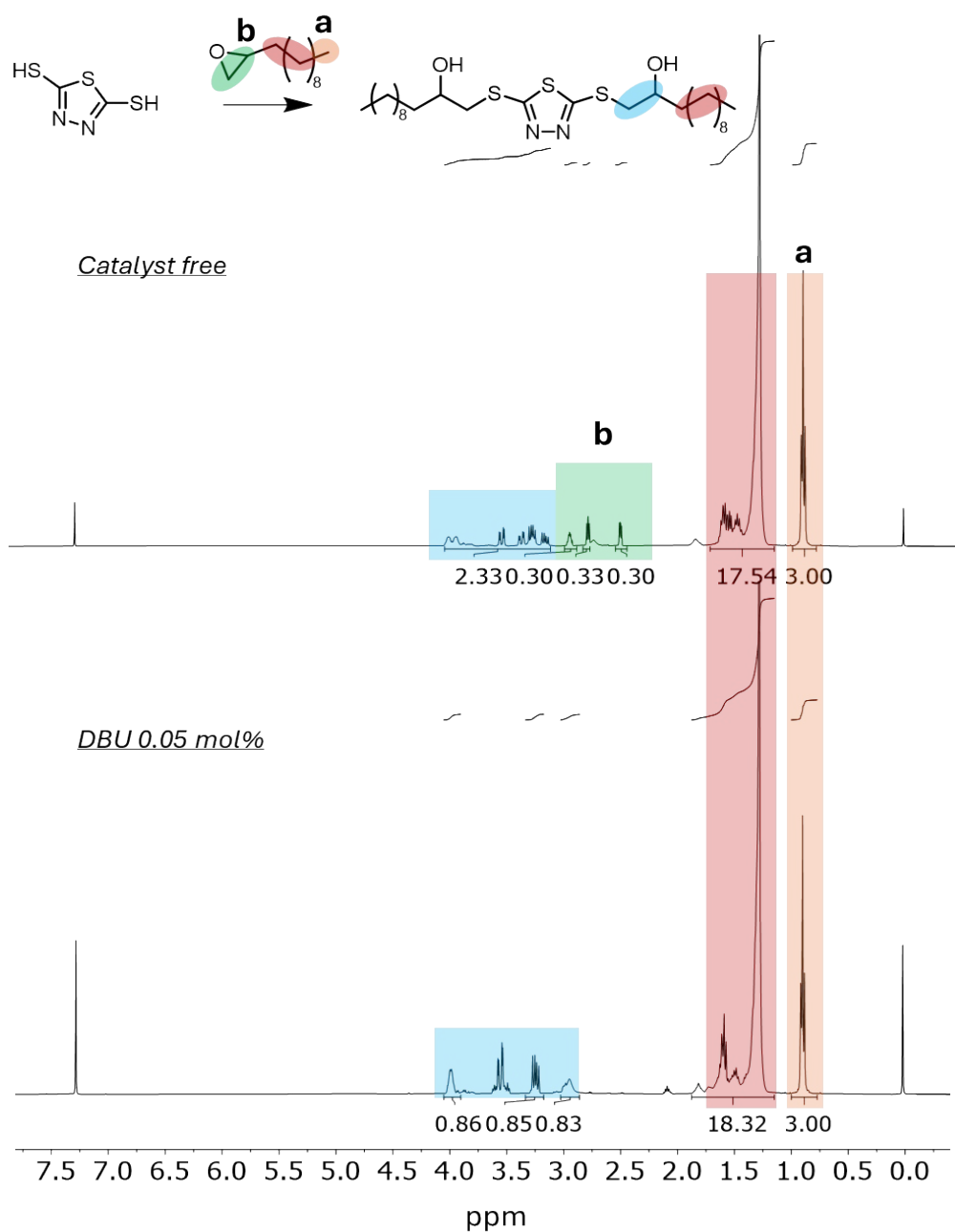


Figure S26. ¹H NMR spectra in CDCl₃ of the catalyst free reaction between **T2** and 1,2-epoxydodecane under catalyst-free and DBU catalyzed condition.

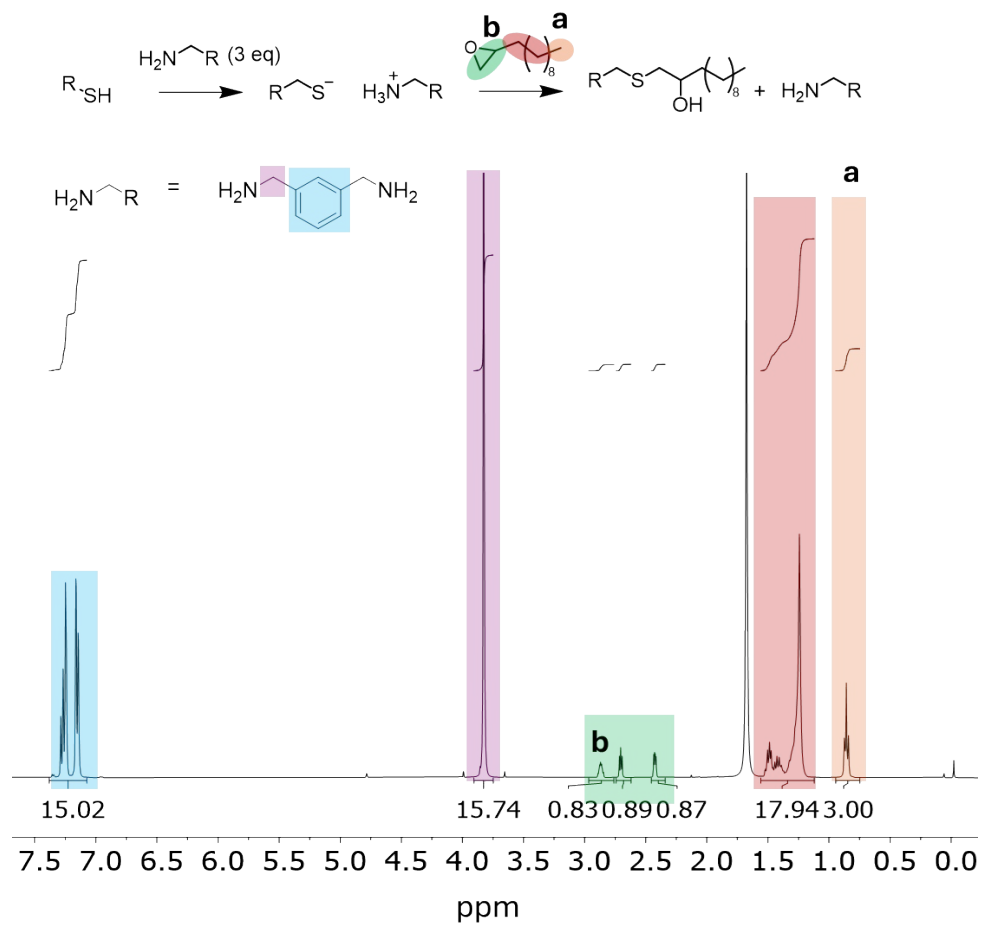


Figure S27. 1H NMR spectra in $CDCl_3$ of the catalyst free reaction between **T2-XDA** preformed salt and 1,2-epoxydodecane.

2.4. *Reaction of thiophenol with model epoxide in the presence or not of amine at different temperatures*

In this section, we have evaluated the possibility of the thiols to form disulfide bonds during foaming. For that purpose, we have performed model reactions with monofunctional molecules in the absence or presence of the base catalyst (the amine) at different temperatures in order to monitor the possible formation of disulfides by $^1\text{H-NMR}$ spectroscopy. The model reactions involved 1,2-epoxydodecane and benzenethiol (T4) as a representative aromatic thiol. In the absence of base catalyst, we observed no modification of the integrals of the exchangeable SH proton and the aromatic ones, which indicated that no reaction occurred with no formation of disulfide bonds (Figure S28). Indeed, Figure S28 shows that the epoxide function remained unchanged, showing that no reaction occurred in the absence of the amine) Moreover, the resonance at 3.4 ppm (R-SH) did not decrease in comparison to those of the aromatic protons between 7 and 7.5 ppm, evidencing that no disulfide bonds were formed.

When this experiment was conducted in the presence of 1 eq of amine to mimic the foaming conditions (see Figure S29 below), the exchangeable proton cannot be detected anymore at 25 °C due to the acid-base reaction of the thiol with the amine. No other reaction was however identified. When the same experiment was carried out at 60 and 100 °C, the epoxide was almost completely converted into the thioether after 15 min of reaction. No disulfide was here detected again, within the accuracy of NMR analysis, corroborating the fact that if some disulfide bonds were produced, they are in negligible amounts.

Experimental protocols: 1,2-epoxydodecane (1.2 g, epoxide = 6.5 mmol), thiophenol (715 mg, SH = 6.5 mmol) for Figure S28 and with benzylamine for Figure S29 (665 mg, 6.5 mmol) were added in this order and then mixed briefly at room temperature before thermostated for 15 min at 25, 60 or 100 °C. Then, a sample was picked out and directly solubilized in CDCl_3 and maintained at -20 °C to avoid any further reaction. The sample was then analyzed by $^1\text{H NMR}$ spectroscopy.

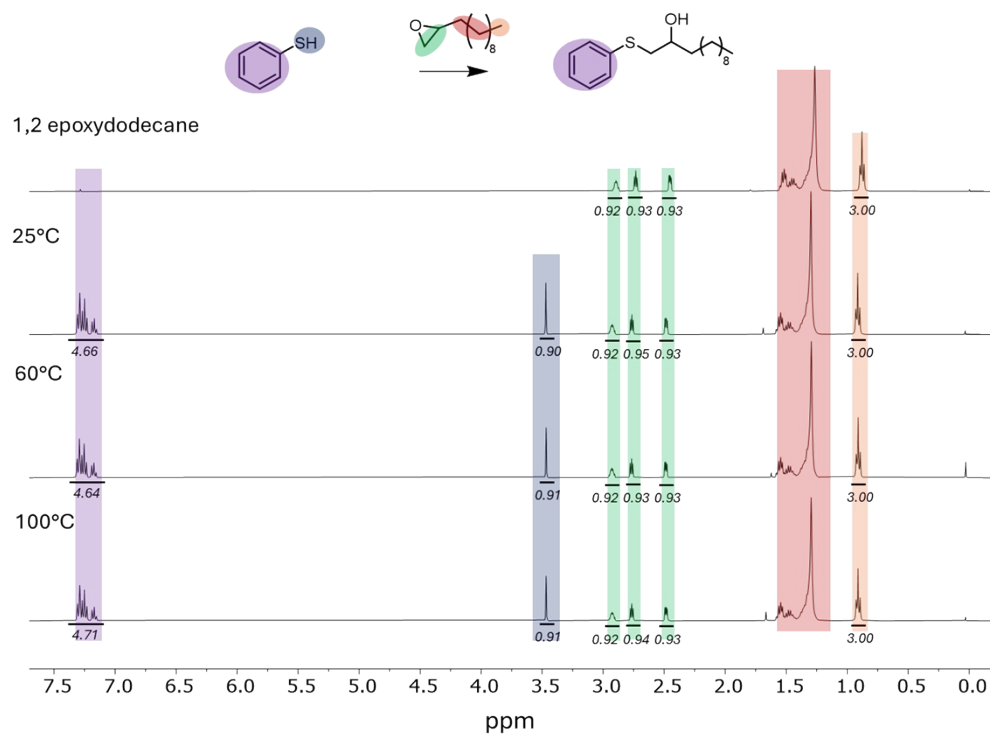


Figure S28. ^1H NMR spectra in CDCl_3 of the reaction between **T4** and 1,2-epoxydodecane under catalyst-free conditions at different temperatures.

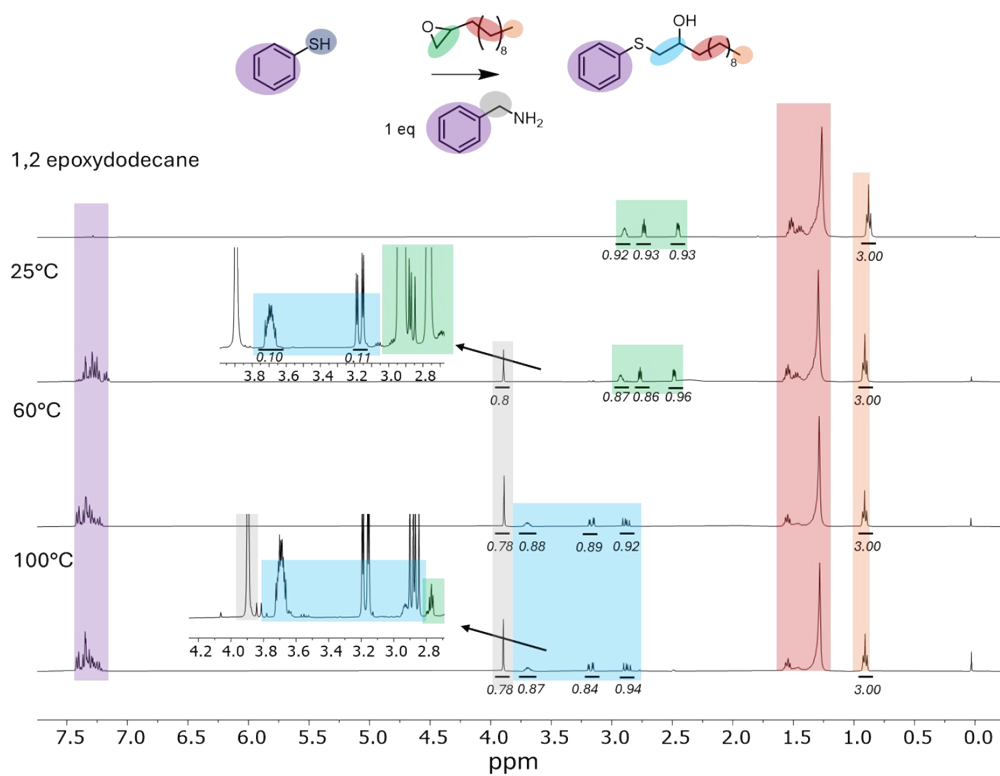


Figure S29. ^1H NMR spectra in CDCl_3 of the reaction between **T4** and 1,2-epoxydodecane in the presence of benzylamine at different temperatures.

2.5. Room temperature foaming of foam with T1 catalyzed by DBU

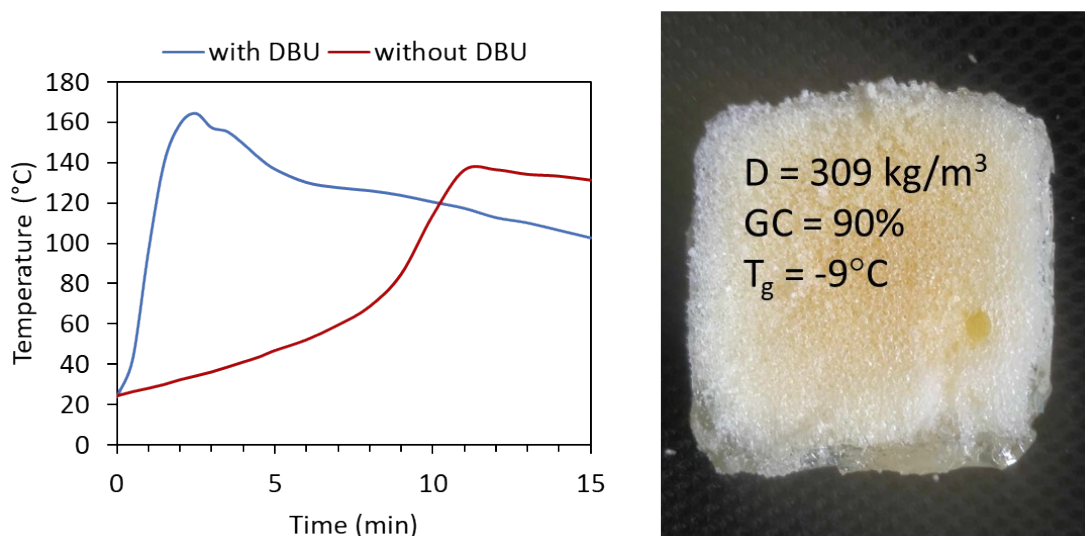


Figure S30. Exotherm of the foaming and properties of foam **F6**_(DBU) obtained at room temperature with DBU as catalyst. Condition: TMPTC, BDGE, XDA, T1, DBU, [5CC]:[epoxide]:[NH_{2 total}]:[SH]:[DBU] = 1:1:1.5:0.5:0.05, foaming RT.

2.6. Evaluation of the reactivity between aromatic thiol and internal epoxide

1.560 g of ESBO (EEW = 195 g/eq, epoxide = 8 mmol) is mixed with 0.6g bismuthiol (SH = 8 mmol) and left to react for 15 min at RT in a silicon vial with a temperature probe to measure the exotherm (Figure S31B). Then a sample is picked out and solubilized in CDCl₃ and directly analyzed by ¹H NMR (Figure S31A). After normalization of the NMR spectra on proton **a**. The following formula is used to calculate the conversion of the epoxide into thioether bond:

$$\text{conv (\%)} = \left(1 - \frac{I_{c,d \text{ esbo} + \text{bismuthiol}}}{I_{c,d \text{ esbo}}} \right) \times 100 = 17 \%$$

In a plastic (PE) bottle of 8 cm height and 6 cm diameter, TMPTC (17.9 g, 5CC = 124 mmol) and ESBO (24.18 g, epoxide function = 124 mmol) were mixed together until the obtention of a homogeneous mixture. XDA (NH₂ = 186 mmol) was then added and mixed for 30 seconds till homogenization. Finally, Bismuthiol (SH = 62 mmol) was added and briefly mixed for 15 sec. The exotherm was measured with a Martindale DT173 temperature probe along reaction

time. The probe was introduced at the center of the formulation and exotherm was reported in Figure S31C. No foam was obtained in these conditions.

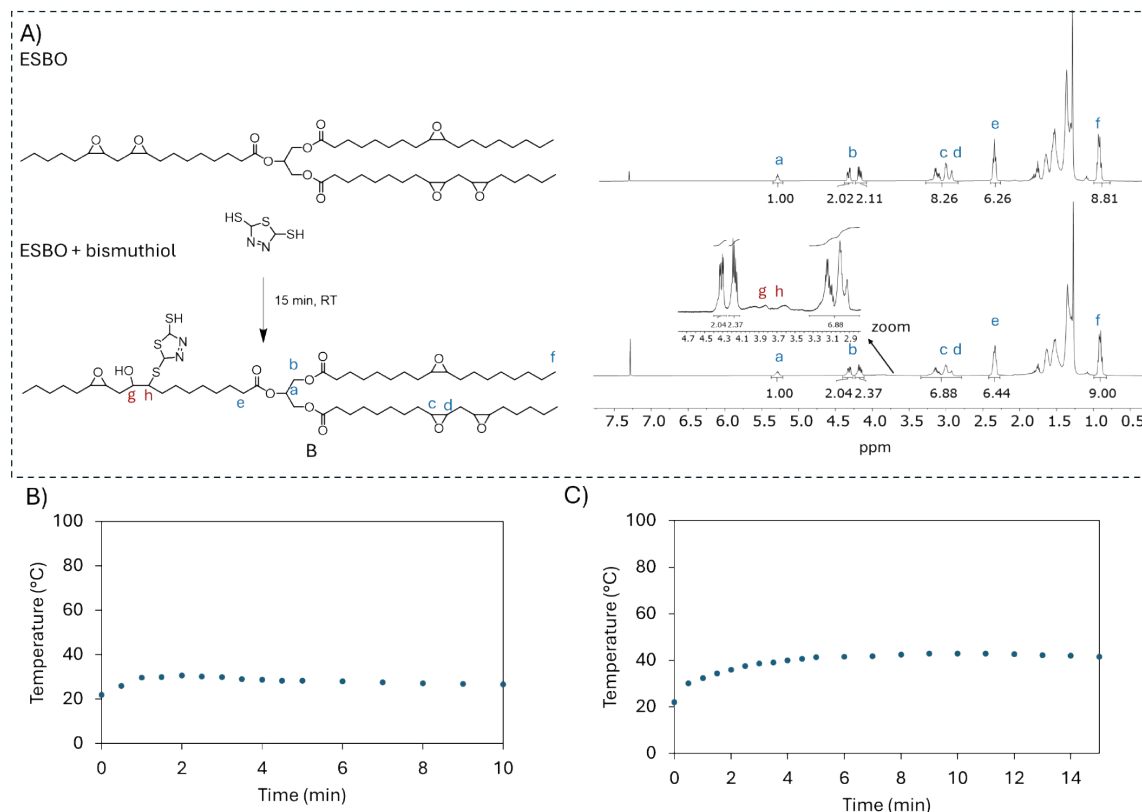


Figure S31. Reactivity between internal epoxide and aromatic thiol. A) ^1H NMR spectra in CDCl_3 of the catalyst free reaction between **T2** and ESBO. B) Exotherm of this model reaction. C) Exotherm measured for the foaming formulation (TMPTC, ESBO, XDA, Bismuthiol).

Table S4. Mechanical properties of hybrid PHU foams prepared by the thiol-induced process at room temperature

	d(kg/m³)	Modulus (MPa)	Modulus/d (kPa.m³/kg)
F7	196	19.4	99
F8	142	5.1	36
F9	156	23.5	151
F10	275	0.096	0.3
F11	208	81	389

*normalized modulus.

3. Synthesis of trimethylolpropane triglycidyl carbonate (TMPTC) in kilogram scale.

In a typical experiment, trimethylolpropane triglycidyl ether (TMPTE, 1 L, 1.157 kg) was transferred into a 2 L high pressure reactor. Then, 35.29 g of tetrabutylammonium iodide (TBAI, 2.5 mol% vs TMPTE) were added prior closing the cell. The cell was then equilibrated at 110 °C for 24 h, keeping the CO₂ pressure constant to 90 bar and the stirring rate to 200 rpm. After reaction, the stirring was stopped, the cell was slowly depressurized at 110 °C and the viscous product was collected and analyzed by ¹H-NMR in CDCl₃. TMPTC was produced with a yield of > 98% (collected crude product > 1,400 kg). Before use, product was degassed by thermal treatment at 80 °C for 16 h and then by vacuum treatment at 60 °C for 16 h.

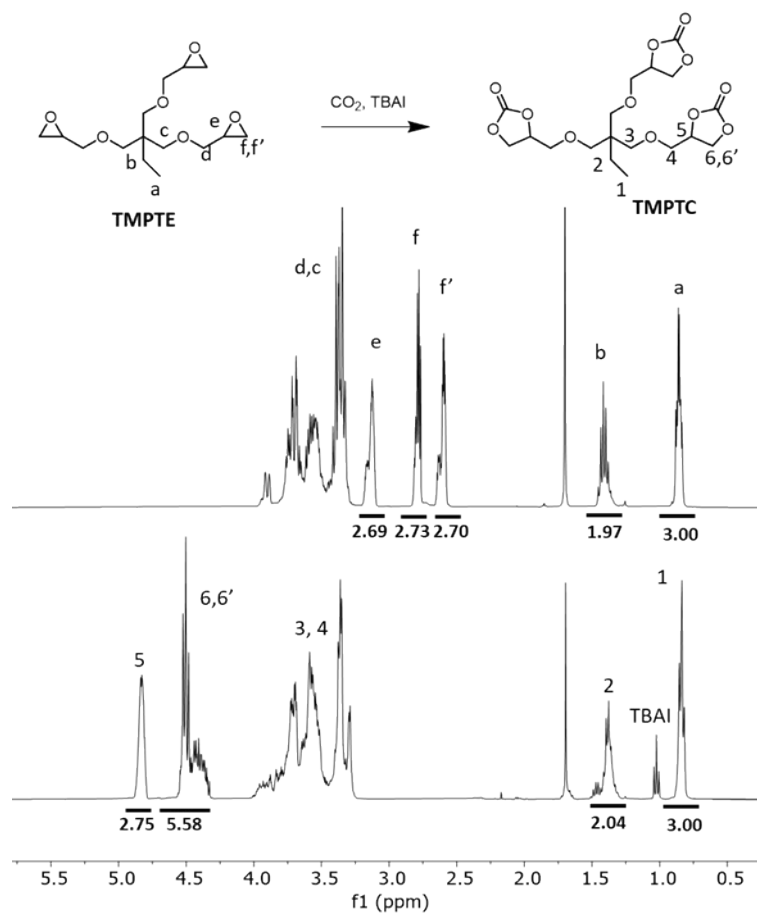


Figure S32. ¹H-NMR spectra of crude trimethylolpropane triglycidyl carbonate (TMPTC) and its precursor (TMPTE) in CDCl₃.