Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Polyhydroxyurethane Covalent Adaptable Networks: Looking for Suitable Catalysts

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Supplementary analysis

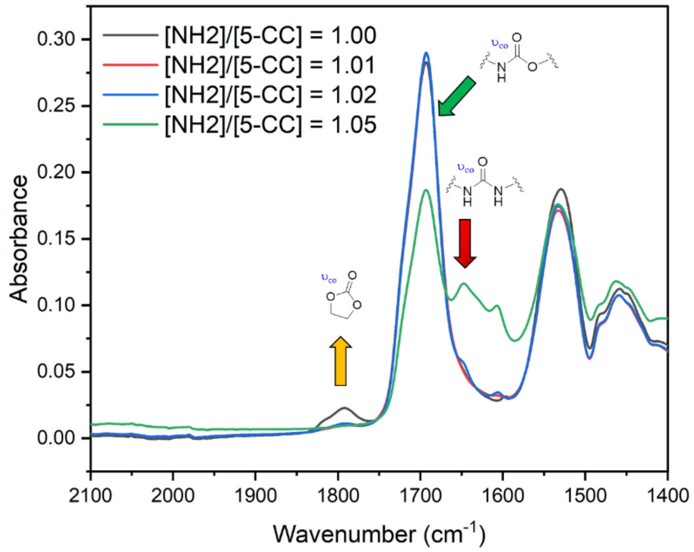
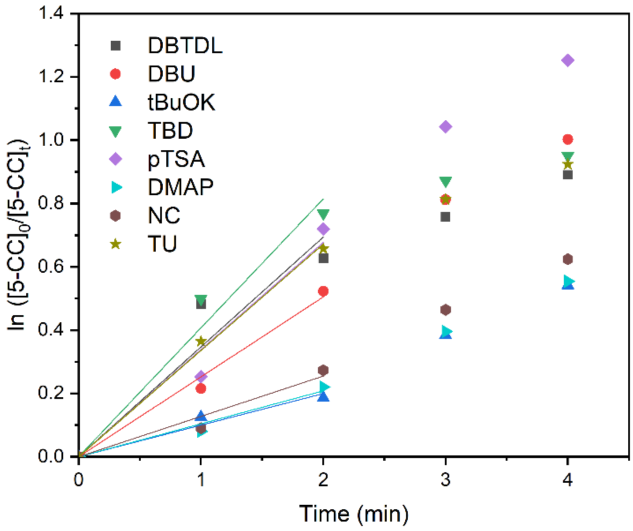


Figure S1. ATR-IR spectra (zoom on 2100-1400 cm^{-1}) of non-catalysed formulation with different excess of primary amine (0, 1, 2 and 5 mol% NH_2 excess as compare to 5-CC functions).



Equation	y = a + b*x							
Plot	DBTDL	DBU	*t*-BuOK	TBD	p-TSA	DMAP	NC	TU
Intercept	0 ± --	0 ± --	0 ± --	0 ± --	0 ± --	0 ± --	0 ± --	0 ± --
Slope	0.34693 ± 0.04775	0.25233 ± 0.01293	0.09977 ± 0.00911	0.40724 ± 0.03239	0.33844 ± 0.03014	0.1041 ± 0.00849	0.12748 ± 0.01318	0.33574 ± 0.01019

R²	0.94525	0.99216	0.97542	0.98126	0.97658	0.9803	0.96862	0.99724

Figure S2. ln([5-CC]$_0$/[5CC]$_t$) *vs.* time plot used to calculate (k_{cat}/k_{NC}) presented in Table 1 (bulk, 80°C for 24h, [NH2]$_0$/([5-CC]$_0$ = 1.01). The linear fit was performed between 0 and 2 min of polymerisation as a clear deviation is observed when conversion reach 50%.

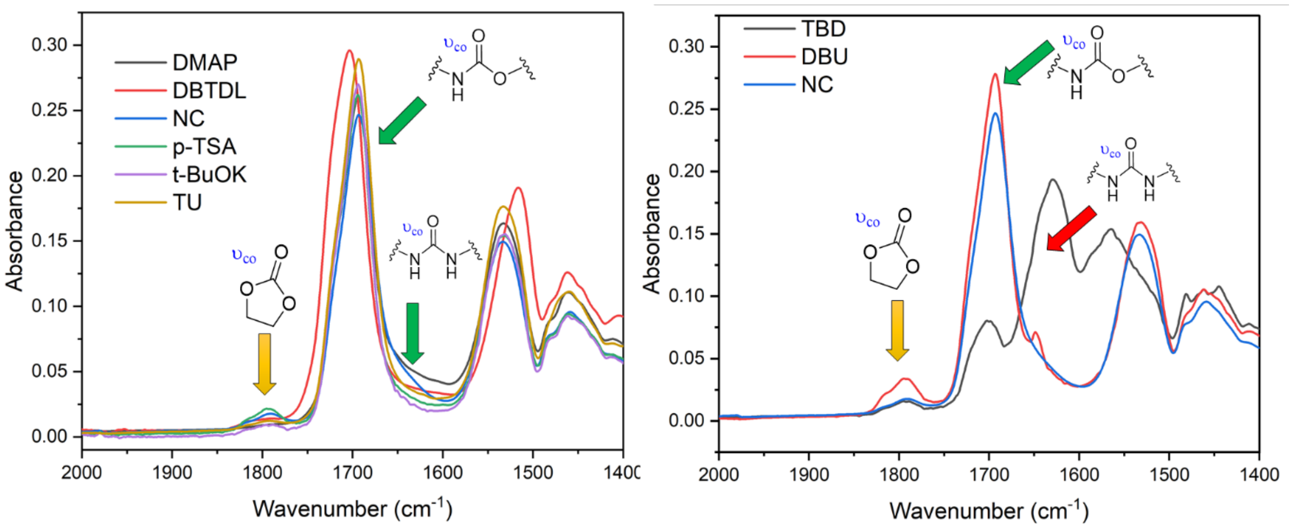


Figure S3. ATR-IR spectra of PHU networks after 24h at 80°C.

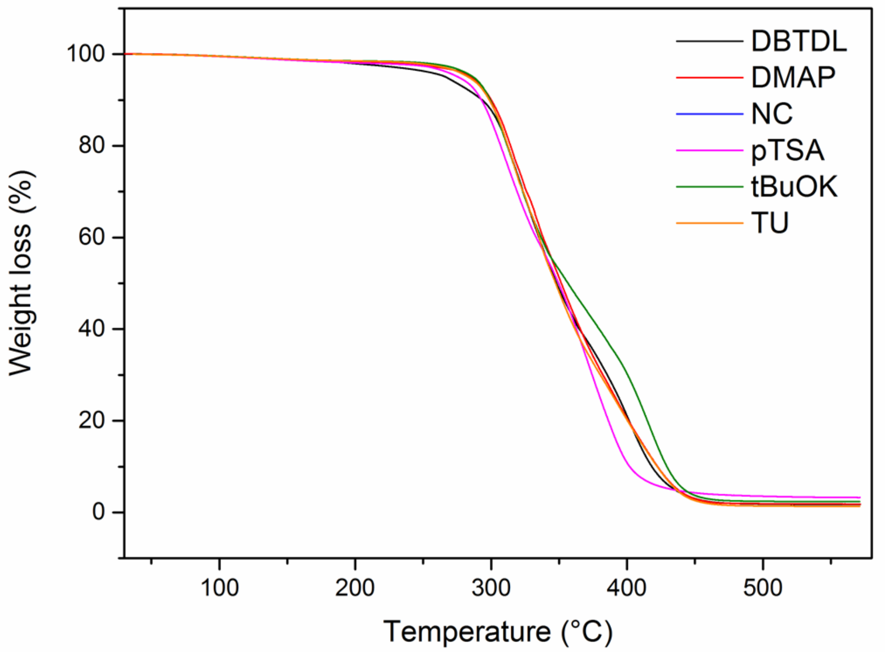


Figure S4. TGA analysis of PHU network after 24 h at 80 °C.

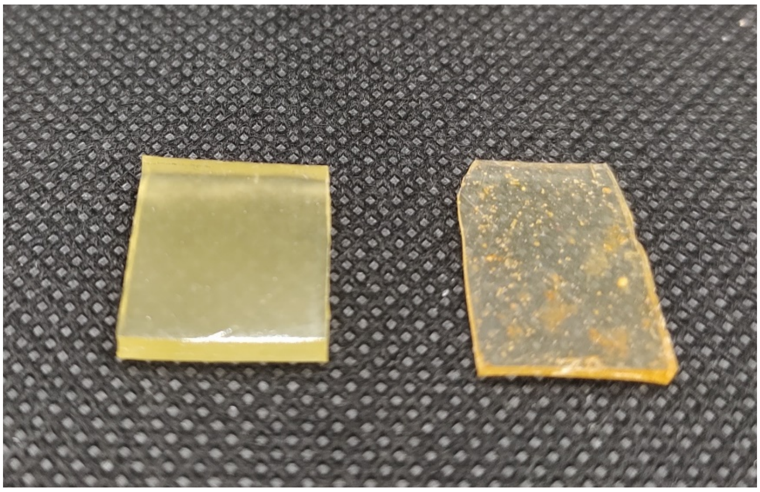


Figure S5. Picture PHU-NC (non-catalyzed formulation, on the left) and PHU containing 5 mol% of *t*-BuOK after curing at 80°C for 24h.

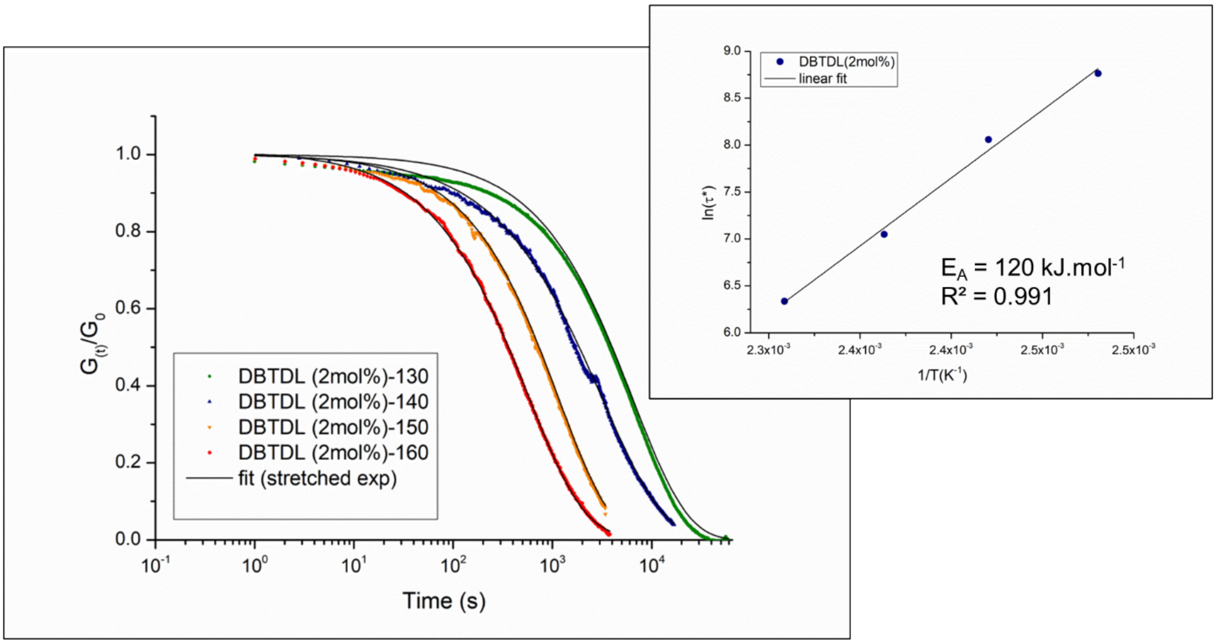


Figure S6. Normalised stress relaxation curves and Arrhenius plot for DBTDL-PHU system (SR curves were fitted using stretched exponential fitting function to determine the characteristic relaxation time).

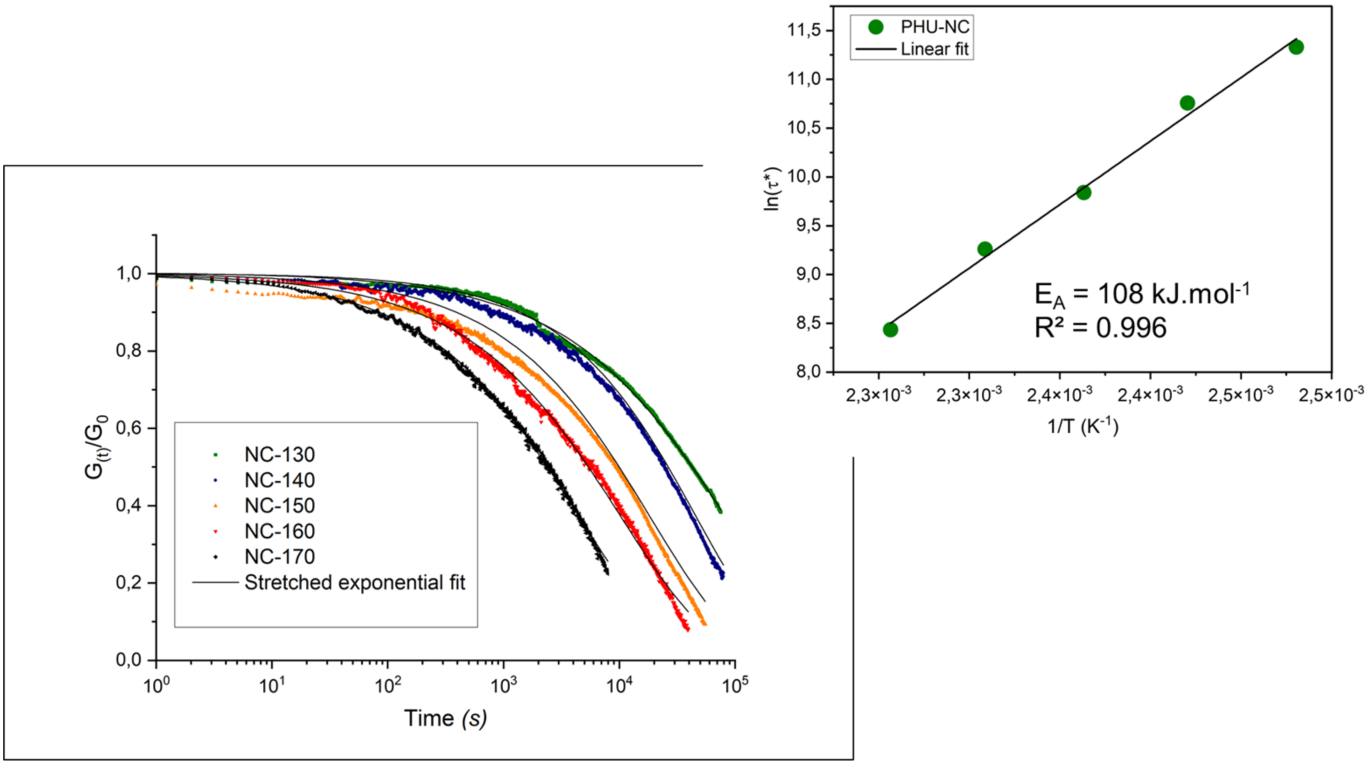


Figure S7. Normalised stress relaxation curves and Arrhenius plot for NC-PHU system (SR curves were fitted using stretched exponential fitting function to determine the characteristic relaxation time).

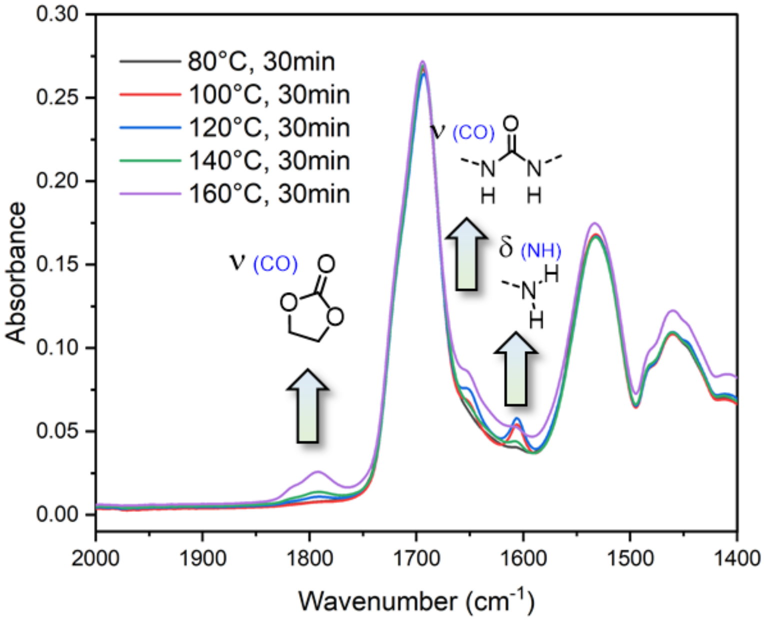


Figure S8. ATR-IR spectra of PHU-DMAP networks after sweep experiments after 30 min at 80 °C, 100 °C, 120 °C, 140 °C and 160 °C.

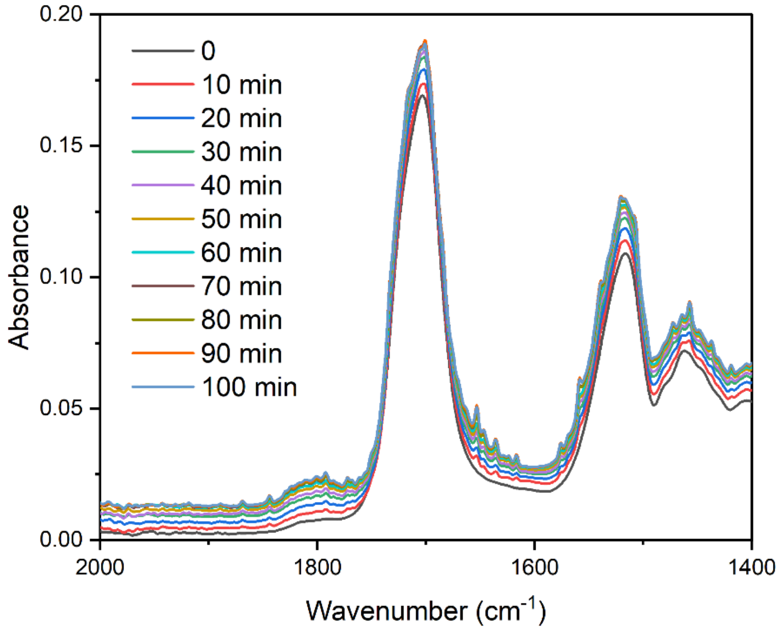


Figure S9. ATR-IR spectra (in absorbance) at 140°C of PHU-DBTDL material as a function of time. The spectra showed no significant evolution of ATR characteristic bands.

Table S1. Swelling indices and gel contents of PHU networks carried out in 1,4 butanediol at 140°C for one week.

Catalyst	Swelling index (%)	Gel content (%)
No catalyst	340 ± 10	82 ± 1
t-BuOK	200 ± 20	87 ± 2.5
Thiourea	300 ± 5	82 ± 3
DBTDL	Soluble	Soluble
DBTDL (after 3 reprocessing cycles)	Soluble	Soluble
DMAP	260 ± 20	83 ± 2
p-TSA	310 ± 50	72 ± 8

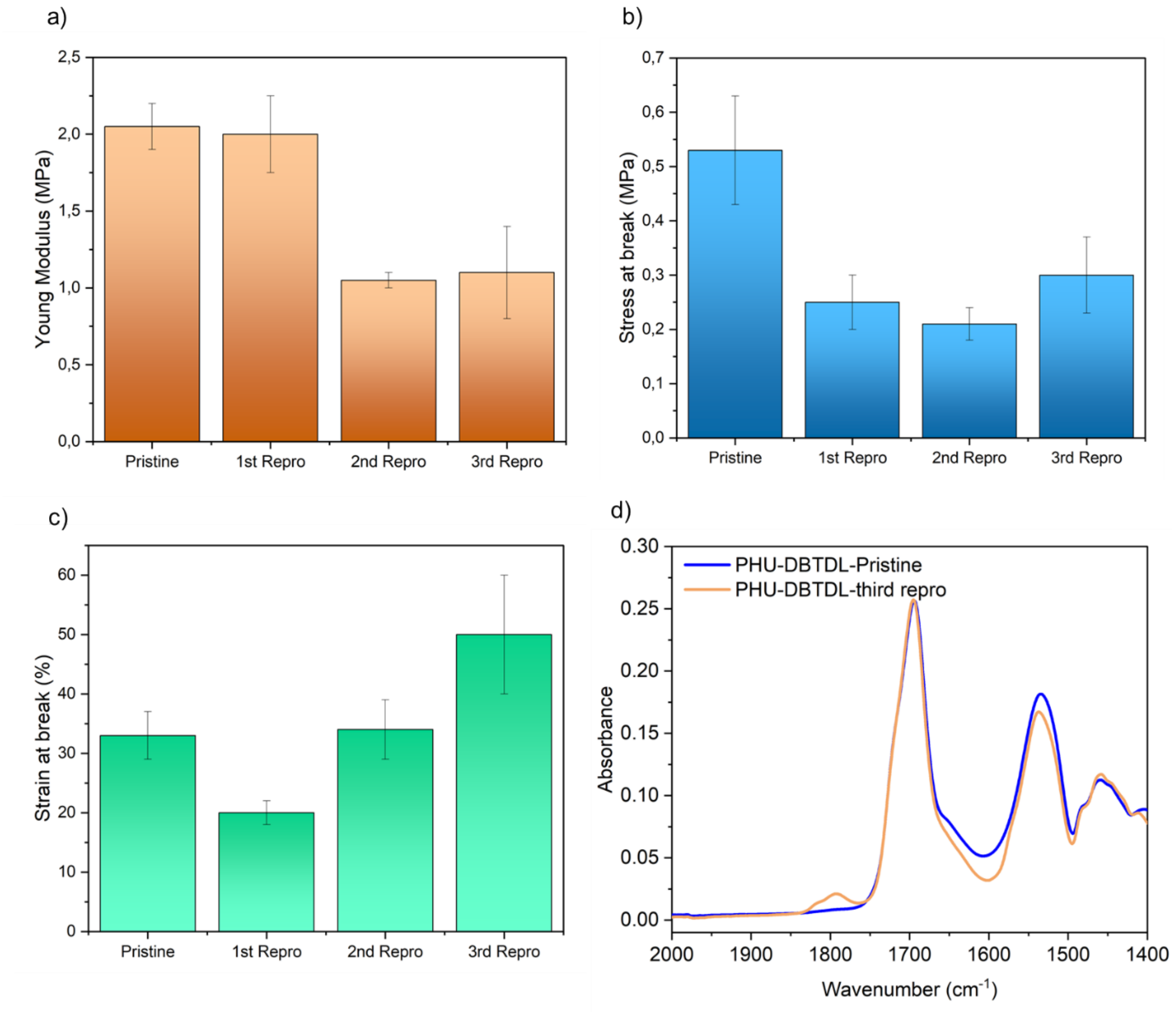


Figure S10. Reprocessing ability of PHU-DBTDL network measured by tensile test after each reprocessing cycle (8h, 120°C, 3 tons) a) young modulus, b) stress at break and c) strain at break. d) ATR-IR spectra before (blue) and after (orange) three reprocessing cycles.

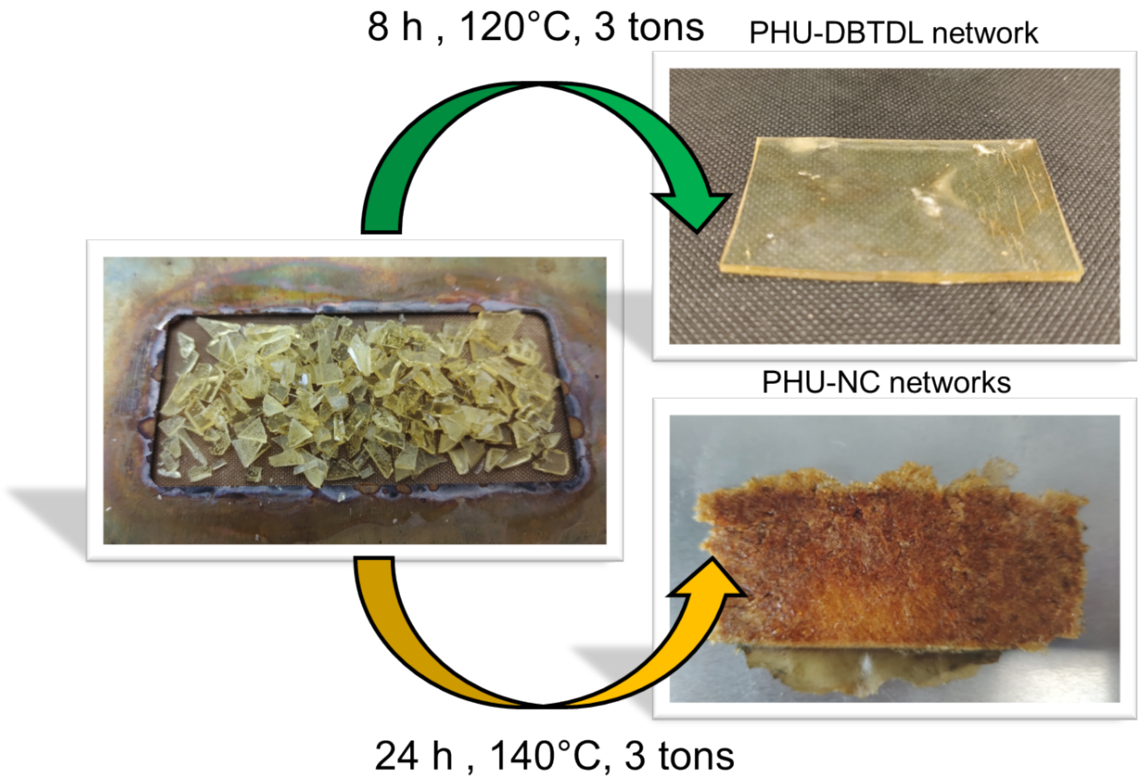


Figure S11. Picture of reprocessed samples (top) PHU-DBTDL at 120°C, 8h, hot press, 3 tons and (bottom) PHU-NC at 140°C, 2h, hot press, 3 tons.

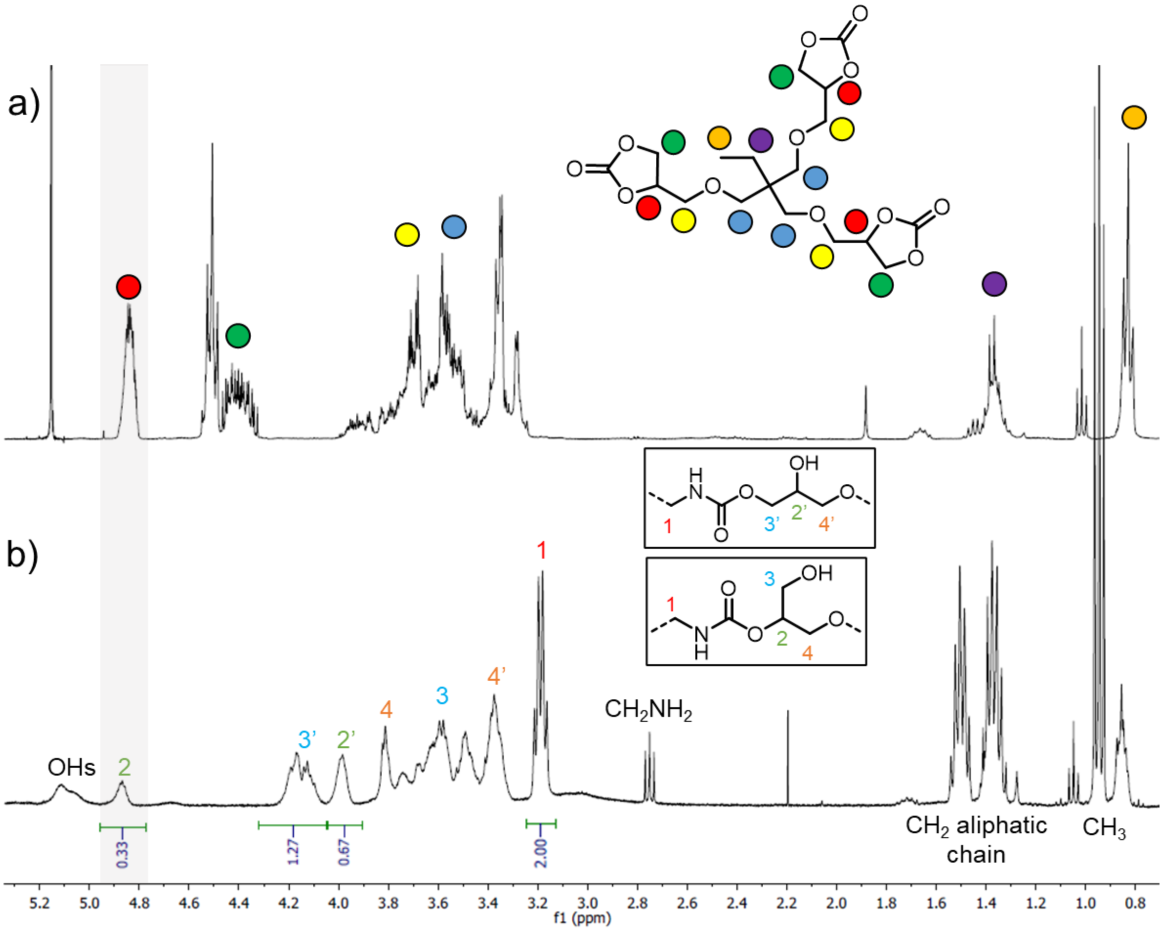


Figure S12. a) ^1H NMR spectrum (in $CDCl_3$) of trimethylolpropane tricarbonate and b) ^1H NMR spectrum (in $CDCl_3$) of the model reaction of trimethylolpropane tricarbonate with 3 equivalents of *n*-butyl amine (at 80°C for 24h without catalyst).

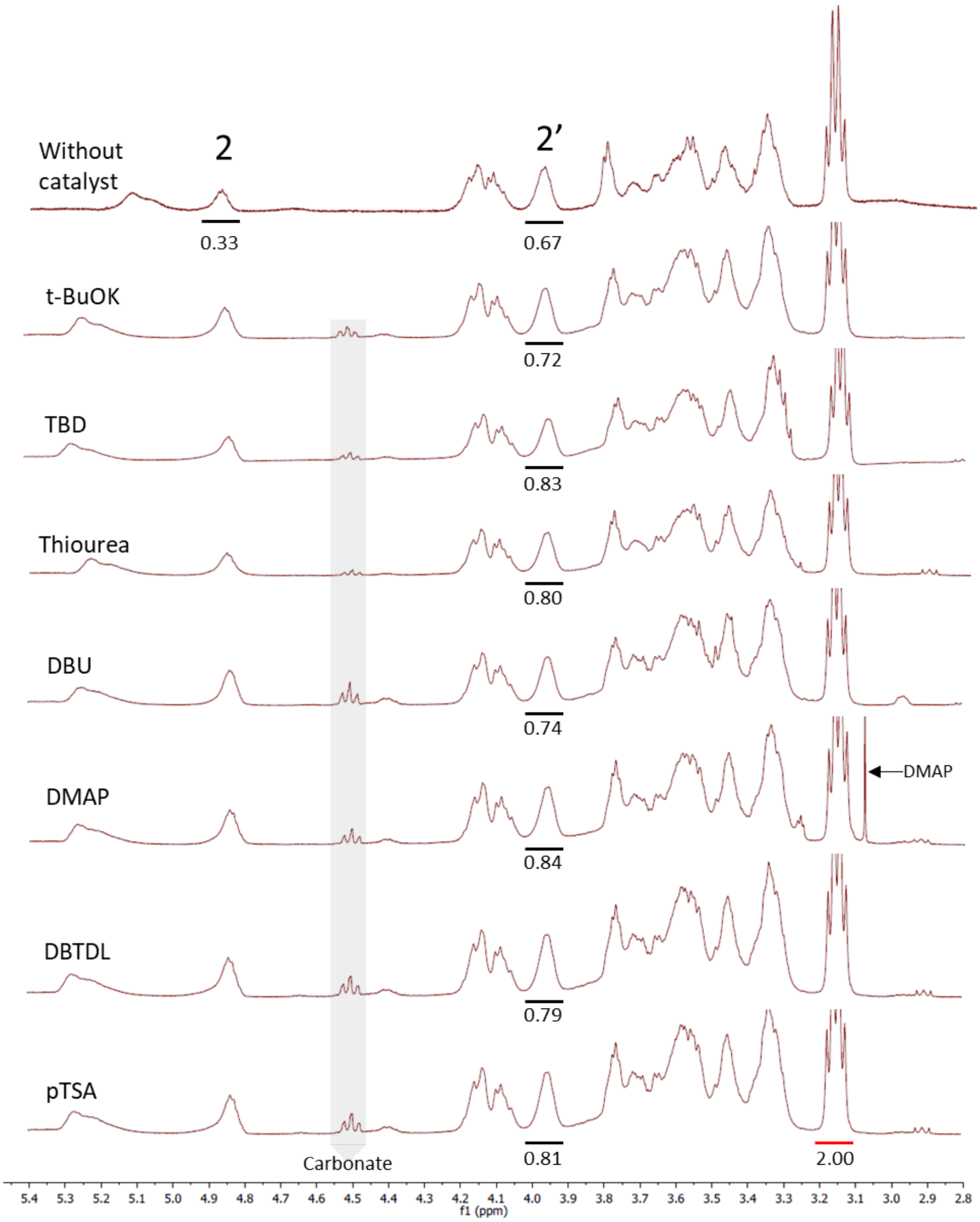


Figure S13. ^{1}H NMR spectra (in $CDCl_3$) of model reaction of trimethylolpropane tricarbonate with 3 equivalents of *n*-butyl amine (at 80°C for 24h with different catalysts).

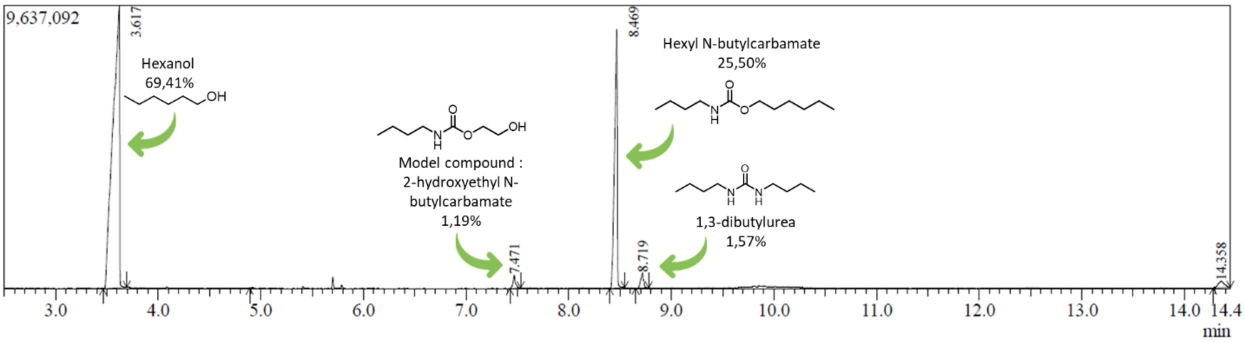


Figure S14. GC-MS chromatogram of the crude resulting from the reaction of 2-hydroxyethyl butylcarbamate and hexanol (5 equivalents) with *t*-BuOK (5 mol%) in bulk at 140°C for 72h.

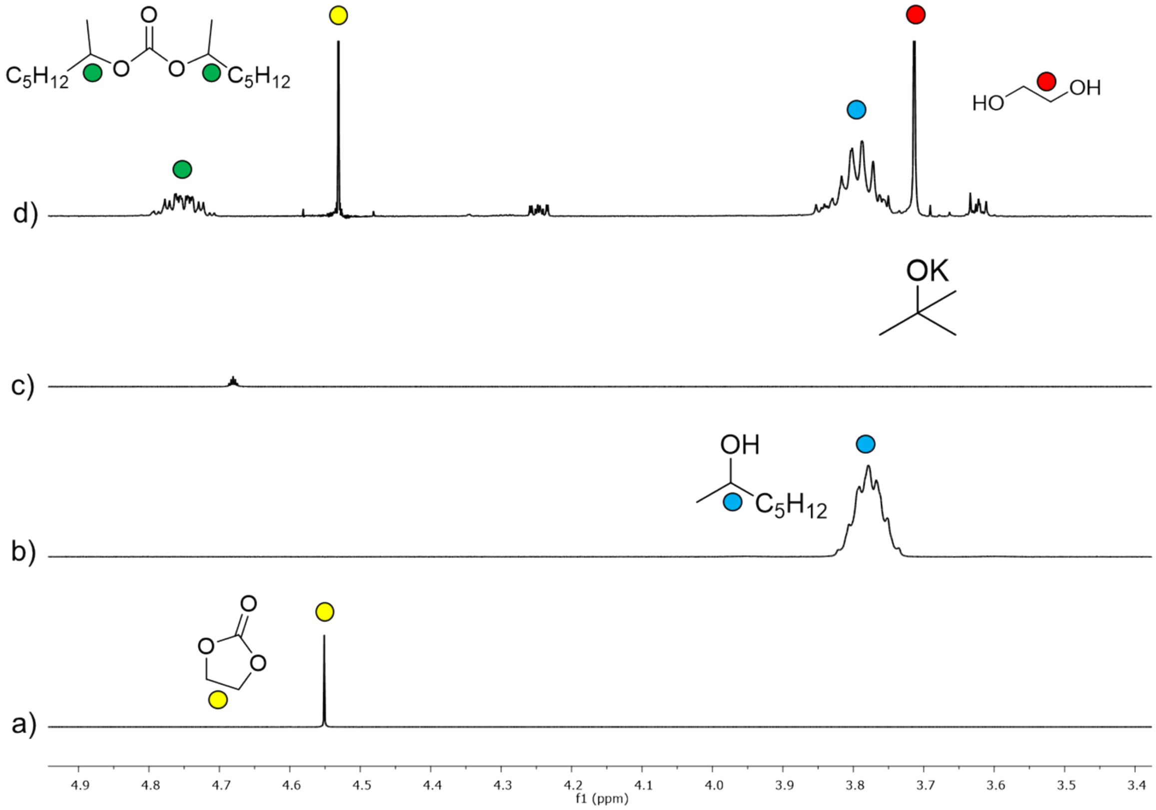


Figure S15. ^{1}H NMR spectra (in $CDCl_3$) of a) ethylene carbonate, b) 2-heptanol, c) *t*-BuOK and d) model reaction of ethylene carbonate with 5 equivalents of 2-heptanol (at 140°C for 48h), the dicarbonate structure (green dots) is suggested to explain the formation of ethylene glycol during the reaction.

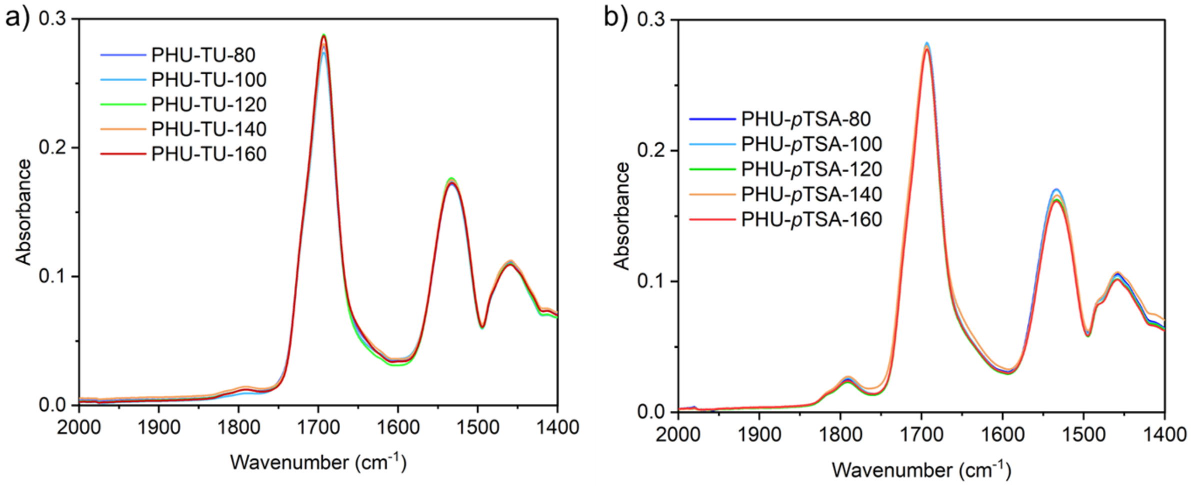


Figure S16. ATR-IR spectra (in absorbance) after frequency sweep experiments at 80°C, 100°C, 120°C, 140°C and 160°C of a) PHU-TU material and b) PHU-*p*TSA material. The spectra showed no significant evolution of ATR characteristic bands.