Electronic Supplementary Information

The multifaceted role of water as an accelerator for the preparation of isocyanate-free polyurethane thermosets

Florent Monie,[a, b] Thomas Vidil,[a,*] Etienne Grau,[a] Bruno Grignard,[b] Christophe Detrembleur,[b,c,*] Henri Cramail[a,*]

[a] University of Bordeaux, CNRS, Bordeaux INP, LCPO, 16 avenue Pey-Berland 33600 Pessac, France

[b] Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, University of Liege, Sart-Tilman B6a, 4000 Liege, Belgium

[c] WEL Research Institute, Wavre 1300, Belgium

*Corresponding authors: thomas.vidil@enscbp.fr, Christophe.Detrembleur@uliege.be, henri.cramail@enscbp.fr

1 MATERIALS AND METHODS

1.1.Materials

Trimethylolpropanetriglycidylether (TMPTE), metaxylylene diamine (MXDA), propylene carbonate (PC), methanol (99.5%), DMSO, THF, tert-butanol (*t*-BuOH), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), formic acid were provided by Sigma Aldrich. 1,2-bis(2-aminoethoxyethane) (EDR148), 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) were provided by TCI, glyme was provided by Acros. Distilled water was obtained from an Elga Purelab prima water distiller.

Trimethylolpropanetriglycidylcarbonate (TMPTC) was synthesized according to a previously established protocole.[1] 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 CO_2 pressure constant to 90 bar and the stirring rate to 200 rpm. TMPTC was degassed for 30 minutes at 50 °C under reduced pressure to remove adsorbed CO_2. The NMR characterization of TMPTC is provided below in the Supporting Data.

TMPTC was dried at 50-60 °C under vacuum for 24h before use. EDR148, MXDA, PC, THF, DMSO, t-BuOH and DBU were obtained from freshly open bottles and stored on molecular sieves (3 Å) for at least 24 h before use. Methanol was obtained from a freshly open bottle. TBD (solid) was used without further purification.

1.2. Multiwave rheology

1.2.1. Experimental set-up, protocol and sample preparations

The course of the reaction was monitored by Small Amplitude Oscillatory Shear experiment (SAOS) using an Anton Paar MCR302 rheometer equipped with disposable aluminium parallel plates (d = 25 mm) and operating in the multiwave mode using Fourier Transform Mechanical Spectroscopy (FTMS).[2,3] A multiwave signal with a fundamental set at 1 rad s^{-1} and harmonics of 3, 10, 30, and 100 rad s^{-1} was used. A strain signal of 0.5% amplitude was used for all the harmonics, resulting in an absolute peak amplitude of 1.97% for the total signal. G' and G" were collected every 5 minutes for the different frequencies. The disposable plates were preheated at the desired temperature (40 °C) in the oven of the rheometer under N_2 flow before loading the samples. The gap between the plates was fixed at 1 mm.

When indicated, the measurements were performed on another machine: a TA-instrument ARES-G2 rheometer. The same geometry (aluminium parallel plates, d=25 mm) and the same protocol (multiwave signal 1, 3, 10, 32, and 100 rad s^{-1}, strain signal of 0.5%) were used. The only difference are the frequency of the third harmonic, 32 rad s^{-1} instead of the 30 rad s^{-1} with the above machine, and the value of the resulting absolute peak amplitude, 2.08% against 1.97% with the above machine. However, this difference has no impact on the measurement of the gel time or the critical exponent. For a given samples, both machines give gel time and critical exponent values with less than 5% difference.

Samples investigated in rheology were prepared from preliminarily dried precursors (see the Materials section) by mixing stoichiometric proportions (*i.e.* 5CC/NH_2 = 1) of TMPTC with the desired diamines, and, when applicable, a controlled amount of additive (water, or MeOH, THF, *t*-BuOH, glyme, DBU or TBD). The reactants were mixed altogether and stirred for 2 minutes, then 0.5 ml of the resulting formulation was loaded between the rheometer plates with a syringe. The effective measurement started immediately after the sample loading. Overall, the time corresponding to the mixing, the stirring and the loading steps was of about 4-5 min. It was kept constant for all the samples.

Note:

In Fourier Transform Mechanical Spectroscopy, the experimental approach consists in applying a sum of sinusoidal waveform ($\gamma_i \sin(\omega_i t)$) simultaneously on the samples. The resulting compound waveform is: $\sum_i^m \gamma_i \sin(\omega_i t)$.

In our case, m = 5, ω_i = 1, 3, 10, 30 and 100 rad s^{-1} for the Anton Paar machine (or 1, 3, 10, 32, and 100 rad s^{-1} for the TA machine) and γ_i = 0.5% for all the frequencies.

The resulting absolute peak amplitude is provided by the modulus of the compound waveform, *i.e.* $|\sum_i^m \gamma_i \sin(\omega_i t)|$ which is calculated by the software of the rheometer.

For ω_i = 1, 3, 10, 30 and 100 rad s^{-1}, $|\sum_i^m \gamma_i \sin(\omega_i t)|$ = 1.97%

For ω_i = 1, 3, 10, 32 and 100 rad s^{-1}, $|\sum_i^m \gamma_i \sin(\omega_i t)|$ = 2.08%

In both cases, these values are within the linear viscoelastic domain of the gel.

1.2.2. Methodology for the determination of the gel time, t_{gel}, and the critical exponent, n

According to the Winter-Chambon criterium, the relaxation modulus of the network at the gel point, also called the *critical gel*, follows a power law: G(t) ~ t^{-n}, where *t* is the time and *n* is called the *critical exponent*.[4,5,6] Thus, G'(ω), and G''(ω) are expected to depend on frequency in an identical manner: G'(ω) ~ G''(ω) ~ ω^{n}. This means that, at the gel time t_{gel}, the loss factor Tanδ(ω) = G"(ω)/G'(ω) is independent of ω.

Then, as mentioned in the main manuscript, t_{gel} can be estimated by the crossing point of the Tan δ(t) curves corresponding to the various frequencies used in the multiwave protocol. This method is the most straightforward if one wants to read t_{gel} on a graph plotted in real time, in the course of the experiment. In this study, it was used for a first estimation of t_{gel}.

However, t_{gel} can be estimated with greater precision by considering the frequency dependence of the moduli G' and G", in the vicinity of the gel point. Going back to the equation G'(ω) ~ G''(ω) ~ ω^{n}, it is expected that, at t_{gel}, G' and G" vary in an identical manner as a function of the frequency ω. In particular, in a log-log scale, the plots of G'(ω) and G"(ω) are expected to be linear with a slope equal to *n*, the critical exponent. This is well illustrated in Figure S1A for the crosslinking reaction of TMPTC with EDR148 at 40 °C (no additive, dry formulation). G'(ω) and G"(ω) are represented for 5 different times close to t_{gel} (estimated from the crossing point of the Tan δ(t) curves). Using linear regression, it is possible to estimate the slope of both G'(ω) and G"(ω) curves for these 5 different times. Then, the evolution of the slopes as a function of time (*i.e.* the time during the crosslinking reaction) can be plotted for both G'(ω) and G"(ω). This is illustrated in Figure S1B for the crosslinking reaction of TMPTC with EDR148 at 40 °C (no additive, dry formulation). In the frame of the Winter-Chambon criterion, the crossing point of the two plots corresponds to the exact moment of the gel point. Conveniently the abscise of this point provides the gel time, t_{gel}, and the ordered provides the critical exponent, *n*.

For all the systems investigated in this study, t_{gel} and *n* were determined according to this methodology.

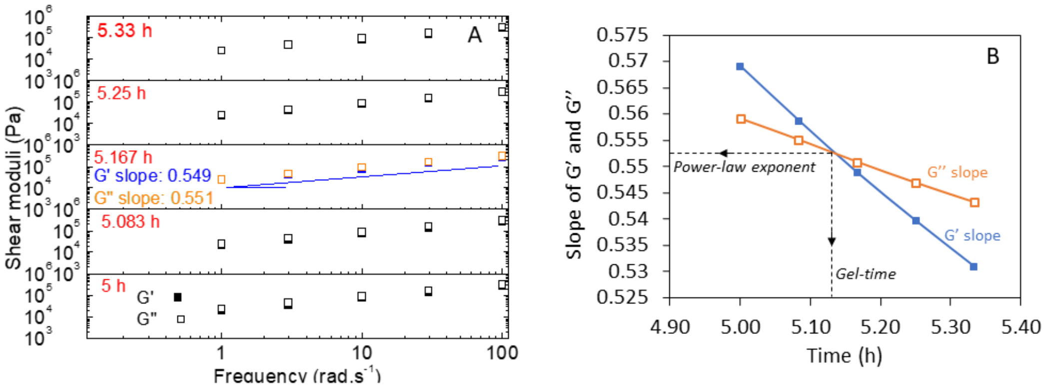


Figure S1: (A) Evolution of the storage modulus, G', and the loss modulus, G'', as a function of the frequency, ω, for 5 different times, and (B) corresponding evolution of the slop of the frequency dependence of G'(ω) and G"(ω) as a function of time, for the crosslinking reaction of TMPTC with EDR148 at 40 °C (no additive, dry formulation).

1.2.3. Methodology for the determination of the fractal dimension, d_f

In the frame of the percolation theory,[7] that is conventionally used to describe the sol-gel transition of a thermoset, the formation of the *critical gel* – *i.e.* the polymer at t_{gel} – results from the interconnection of clusters of polymer that grow separately as represented in Scheme S1.

The value of the critical exponent, *n*, is related to the fractal dimension of the gel-clusters, d_f, at the sol-gel transition (*i.e.* for t = t_{gel}) *via* the following equation introduced by Muthukumar in 1989: [8]

$$n = \frac{d(d + 2 - 2d_f)}{2(d + 2 - d_f)}$$

Where d is the space dimension of the network, *n* is the critical exponent of the relaxation power law obtained from rheology experiments (cf. above section), and *df* the fractal dimension of the gel-clusters.

For a three dimensional network, d = 3, and the equation can be simplified as:

$$n = \frac{15 - 6d_f}{10 - 2d_f} \Leftrightarrow d_f = \frac{10n - 15}{2n - 10}$$

According to these equations, *df* is a decreasing function of *n* for the typical values of *n* explored when considering the crosslinking reaction of thermosetting materials (*i.e.* *n* ∈ $[0.5; 1]$). This is well illustrated by representing the evolution of *df* as a function of *n* (Figure S2).

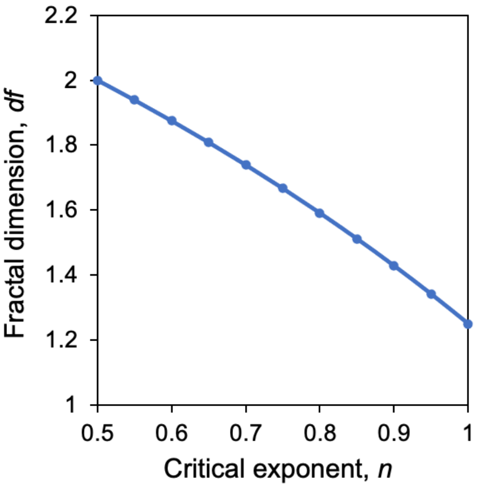
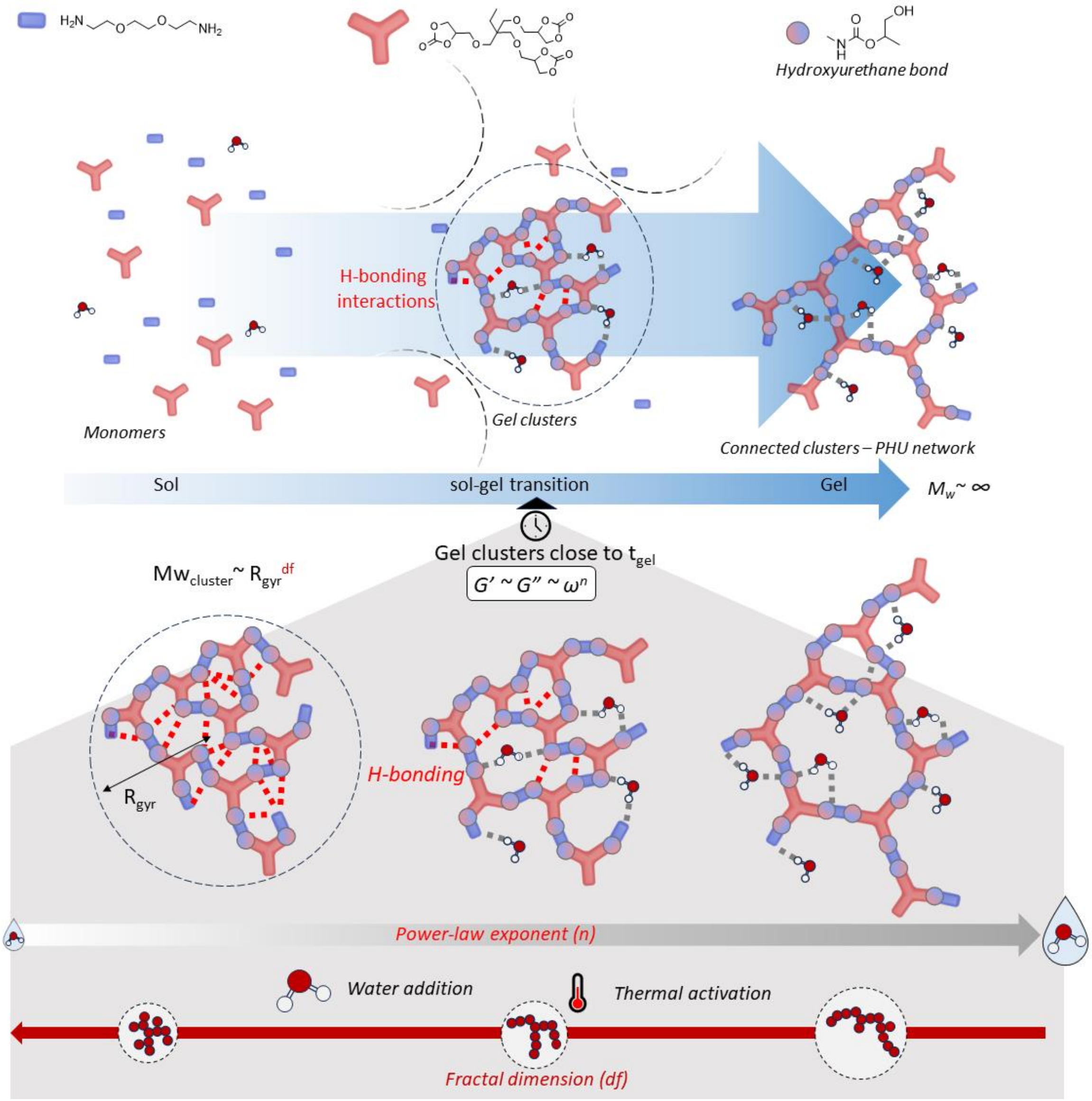


Figure S2. Evolution of d_f as a function of n according to the model of Muthukumar for n ∈[0.5;1]

As mentioned in the manuscript, d_f relates the mass of the objects, $Mw_{cluster}$, to their spatial size, R_{gyr}, *i.e.* their gyration radius: $R_{gyr}^{d_f} \sim Mw_{cluster}$. Given the above equations, it is well accepted that clusters with poorly cross-linked structures and/or expanded by molecules of solvent (or unreacted monomers) will exhibit a small fractal dimension, d_f, and thus a large critical exponent, *n* (clusters schematically represented on the right of the red arrow in Scheme S1). Inversely, tightly crosslinked clusters will exhibit large d_f and small exponent *n* (clusters schematically represented on the left of the red arrow in Scheme S1).



Scheme S1: Schematic representation of the sol-gel transition during the crosslinking reaction of TMPTC with EDR148. The typical evolution of the critical exponent and the fractal dimension of the clusters as a function of temperature or solvent addition is schematically represented. In essence, the addition of a solvent (or an increase of temperature) results in an expansion of the clusters, i.e. a decrease of the fractal dimension, corresponding to an increase of the critical exponent.

1.3. Preparation of fully cured samples for swelling experiments, infrared and thermomechanical analyses

Curing procedure:

Samples were prepared from preliminarily dried precursors (see the Materials section) by mixing stoichiometric proportions (*i.e.* 5CC/NH_2 = 1) of TMPTC with the desired diamines, and, when applicable, a controlled amount of additive (water or DBU). The reactants were mixed altogether and stirred for 2 minutes, then poured in a mold and introduced in an oven at 50 °C for 8 h to provide PHU films with average thickness of ~1.5 mm.

Conditioning procedure:

As cured samples were dried for 16 h under vacuum. The resulting samples were used for swelling experiments, DSC analysis and infrared analysis.

For tensile testing, dried samples were further conditioned for 24h at 50% relative humidity (RH) and 25°C to mimic standard ambient conditions in an environmental chamber.

1.4. Swelling experiments

Circular samples (diameter = 6 mm, thickness = ~1 mm) were immersed for 2 days in either water, methanol, THF or t-BuOH. The variation of the sample diameter and mass were accurately measured by using a caliper and a precision weighting scale respectively.

Swelling index (SI) was obtained thanks to the following formula:

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

In which m_0 is the masse of the dry sample and m_i the mass of the sample after swelling for a given time in the solvent.

The linear swelling ratio (λ) was obtained as follow:

$$\lambda = \frac{D_i}{D_0}$$

With D_0 the diameter of the dry sample and D_i the diameter of the sample after swelling for a given time in the solvent.

Ultimately, the gel content (GC) was measured at the end of the swelling experiment (after 48 h of immersion in the solvent) as follow:

$$GC = \frac{m_1}{m_0} \times 100$$

Where m_1 is the mass of the sample collected after 48 h of swelling in the solvent and dried for 40 h at 50 °C under vacuum.

1.5. Characterizations

1.5.1. NMR analyses

All NMR characterizations have been performed on a Bruker advance 400 MHz spectrometer equipped with a cryoprobe. ^{1}H spectra result from 16 scans acquisitions while ^{13}C spectra were obtained from 1000 scans. All analyses were performed in DMSO-d_6.

The precise functionality of TMPTC was assessed by 1H NMR, setting a relaxation time (d1) of 10 s. Integrating the methyl protons signal (Figure S3, signal c) and methylene protons of 5CC moieties (Figure S3, signals a or a') gave access to the functionality of the monomer (f ~ 2.7).

1.5.2. FTIR analyses

Fourier Transform InfraRed (FTIR) spectra were recorded on a Bruker-VERTEX 70 instrument (400 to 4000 cm^{-1}, 4 cm^{-1} resolution, 32 scans, DLaTGS MIR) equipped with a Pike GladiATR optical design diamond crystal) for attenuated total reflectance (ATR).

1.5.3. DSC analyses

DSC were performed on TA Instruments Q100 and Q250. 3 to 10 mg of samples were sealed in an aluminum pan and analyzed under nitrogen flow. 3 cycles were performed between -40°C and 50 °C (or 70 °C for the MXDA based formulation) under N_2 flow at 10 °C min^{-1}.

1.5.4. Tensile Testing

Measurements were performed using dog bone shaped samples according to type 5 ASTM D638-5 standard. The preparation of the samples proceeds as follow: the mixture of reactants was obtained using the protocol described in the curing procedure above. It was poured in a large square mold and introduced in a vacuum oven at 50 °C. Reduced pressure was briefly applied to remove the air trapped in the liquid formulation during the mixing step. It was then cured for 8h at 50 °C under atmospheric pressure. Samples were then cut out of the resulting films using a dog bone shape punch with the appropriate dimensions. When applicable, they were conditioned (dried or humidified) using the procedure described above. Tests were performed with working length: 25 mm, width: 3.18 mm, thickness: ~1.5 mm dimensions. The strain−stress curves were recorded using an INSTRON 34TM-10 tensile testing machine equipped with a 500N probe, at a constant crosshead speed of 5 mm min^{-1}, with a starting gap of 2.5 cm. For each sample, 5 replicates were performed.

1.6. Model reactions

In a typical model experiment, 0.5 g PC (4.9 mmol) were weighted in a glass tube with 1 ml of dry DMSO-d_6 (preliminarily dried on activated molecular sieves (3Å) for at least 24 h before use) and a magnetic stirrer. When applicable, 0.053 g of distilled water (3.04 mmol) were also added. Then, 0.363 g of EDR 148 (2.45 mmol) were added. The tube was sealed with a rubber septum and immersed in an oil bath at 40 °C. At the given reaction times (t0, 10, 30, 60, 120, 180, 300, 420 min), aliquots (~ 2 drops) of the crude were collected with a syringe and diluted in 450 µl of DMSO-d_6 with 1 drop of dilute formic acid (20% solution in DMSO-d_6) to quench the aminolysis. The resulting samples were analyzed by ^{1}H NMR to monitor the reaction.

The same protocol was used for model reactions in solvent-free conditions in the absence of DMSO-d_6. ^{1}H NMR spectra were recorded at t0 and after 7h of reaction at 25, 40 and 60 °C to evaluate the extent of the hydrolysis of cyclic carbonates, 5CC.

1.7. DFT calculations

The DFT calculations were performed using hardware and software described in a previous work of our group.[9]

ORCA quantum chemistry program: Geometry of the reactant, products, intermediate states and transitions states were optimized by DFT using ORCA with BP86 hybrid functional and a high quality def2-SVP basis set[10,11] together with the Grimme method[12,13] to describe the Van der Walls interactions and the universal solvation model. Calculations were performed usually on 4 cores on a “home- made” setup equipped with 4 Dual Intel Xeon Silver 4214 2.2 GHz, 3.2 GHz Turbo, 12C and 8x32 GB DDR4 2933 MHz RDIMM ECC Memory.

NEB-CI calculations[14] were performed using 24 images from reactants to the product using PM3 set. The images were generated using IDPP.

2 SUPPORTING DATA

2.1. TMPTC functionality

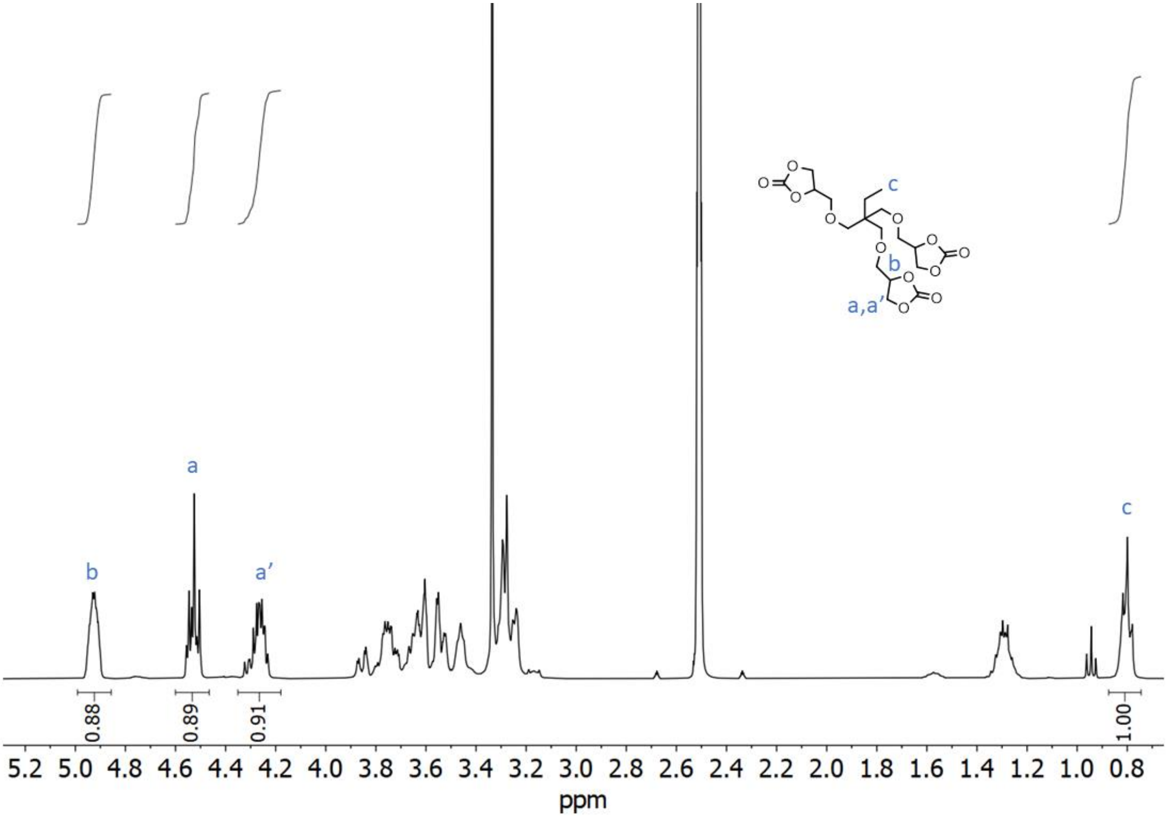


Figure S3: ^{1}H NMR spectrum of TMPTC dried for 24h at 60 °C under vacuum. D1 (relaxation time) was set to 10s. From the integrals above, TMPTC functionality was approximated to 2.7.

2.2. Temperature dependence of t_{gel} and n for the crosslinking reaction of TMPTC with EDR148

The impact of the temperature on t_{gel}, the critical exponent, n, and the fractal dimension d_f, was investigated for the crosslinking reaction of TMPTC with EDR148, with no additives (dry formulation) and in the presence of 5 wt% of water, for T = 30, 40, 50 and 60 °C. For each condition, the plots of Tan δ(t) are represented in Figure S4 They were used to obtain a first estimation of t_{gel}.

The corresponding value of t_{gel}, n, and d_f, determined according to the procedure reported in the material and method section, are reported in Table S1.

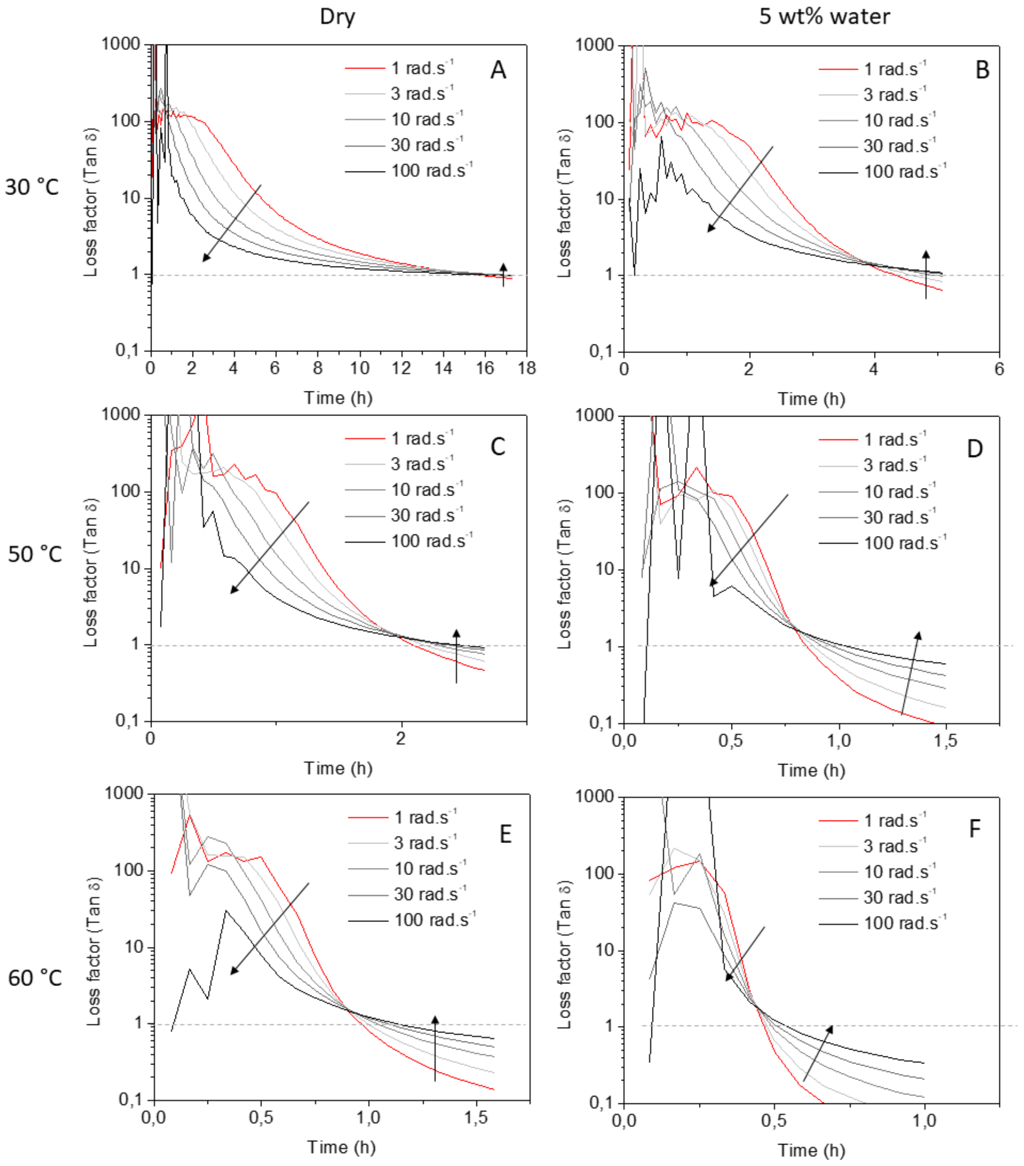


Figure S4: Variation of the loss factor (tan(𝛿)) as a function of time for the crosslinking reaction of TMPTC and EDR148 without additives (dry formulation) at (A) 30 °C, (C) 50 °C and (E) 60 °C, and with 5 wt% of water at (B) 30 °C, (D) 50 °C and (F) 60 °C (multiwave mode, 1.97% global strain amplitude, ω = 1, 3, 10, 30, 100 rad s^{-1}, the horizontal doted line corresponds to tan(𝛿) = 1).

Temperature (°C)	Water content (wt%)	t_{gel} (h)	n	d_f
30	0	15.5	0.51	1.99
	5	3.93	0.62	1.85
40	0	5.205 ±0.196	0.549 ±0.006	1.94
	2	2.9	0.6	1.88
	5	1.643 ±0.019	0.663 ±0.007	1.79
	10	0.943 ±0.014	0.706 ±0.001	1.73
50	0	1.96	0.6	1.88
	5	0.8	0.68	1.77
60	0	0.91	0.64	1.82
	5	0.44	0.71	1.72

Table S1: t_{gel}, critical exponent (n) and fractal dimension (d_f) values for the crosslinking reaction of TMPTC and EDR148 without additives (dry formulation) and with 5 wt% of water, at various temperatures. The values were determined according to the procedure reported in the material and method section.

As usual for the crosslinking reaction of thermosets, the temperature dependence of t_{gel} obeys an Arrhenius law.[15,16] This is well verified by plotting $\ln(t_{gel})$ as a function of $1/T$ (Figure S5: Arrhenius plot of the temperature dependency of the gel time for the crosslinking reaction of TMPTC and EDR148 without additives (dry formulation, grey plot) and with 5 wt% of water (green plot).). For both systems (dry and 5 wt% of water), a linear plot is obtained. According to Equation S1, the slope of the linear plot provides the apparent activation energy of gelation ($E_{gelation}$) and the intercept provides the pre-exponential factor (A). The values of $E_{gelation}$ and A are reported in Table S2

$$\ln(t_{gel}) = \ln(A) + \frac{E_{gelation}}{RT} \qquad S1$$

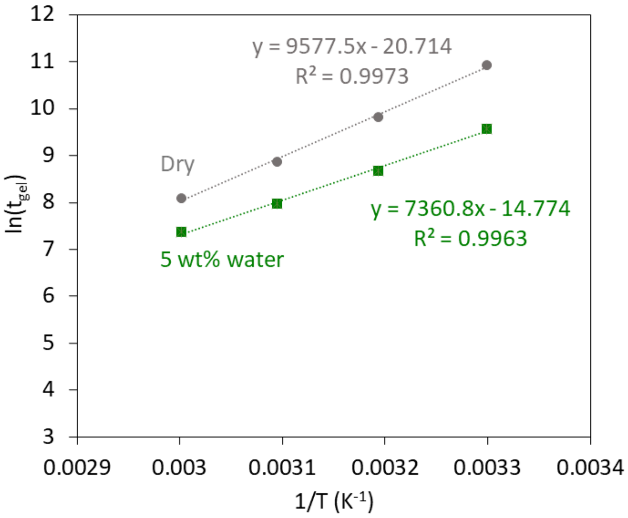


Figure S5: Arrhenius plot of the temperature dependency of the gel time for the crosslinking reaction of TMPTC and EDR148 without additives (dry formulation, grey plot) and with 5 wt% of water (green plot).

Parameters	Dry formulation	5 wt% water
$\ln(A)$	-20.7	-14.8
$E_{gelation}$ (kj/mol)	80	61

Table S2. Apparent activation energy of gelation ($E_{gelation}$) and pre-exponential factor (A) for the crosslinking reaction of TMPTC and EDR148 without additives (dry formulation) and with 5 wt% of water.

2.3. Infrared monitoring of the crosslinking reaction of TMPTC with EDR148

The crosslinking reaction of TMPTC with EDR148 was monitored by infrared spectroscopy at 40 °C (i) without additives (dry system), (ii) with 5 wt% of water and (iii) with 10 wt% of water. Samples were prepared with the protocol used for the rheology investigation (cf. material and method section). Two drops of the resulting formulations were placed on the ATR crystal of the spectrometer pre-heated at 40 °C and equipped with a solvent trap. Then, a spectrum was collected every 5 min.

For all systems, a selection of the spectra collected in-between t0 and t = 3 h are represented in Figure S6. In all cases, a fast decrease of the intensity of the band corresponding to the vibration of the C=O bond of the 5CC carbonate (1790 cm^{-1}) is accompanied by an increase of the corresponding band of the urethanes (1700 cm^{-1}). This is consistent with the aminolysis reaction. More importantly, a magnification of the spectra for the wavenumber comprised in-between 1500 cm^{-1} and 2000 cm^{-1} (Figure S6D), clearly suggests that the aminolysis is faster for the systems containing water, in accordance with the rheological investigation.

As the first spectrum is collected (for t0), a significant amount of 5CC is already consumed (confirmed by the intensity of the band corresponding to the C=O bond of the urethanes). Then, it is not possible to determine the absolute conversion of 5CC. For indicative purpose only, the relative intensity of the band corresponding to the C=O bond of the 5CC and the urethanes were plotted in Figure S6 E, F, G for all the systems. The band corresponding to the C-H bonds (2860 cm^{-1}) was used as a reference for normalization. Quantitative information cannot be extracted from these plots, however they suggest that the aminolysis rate increases as the water content increases.

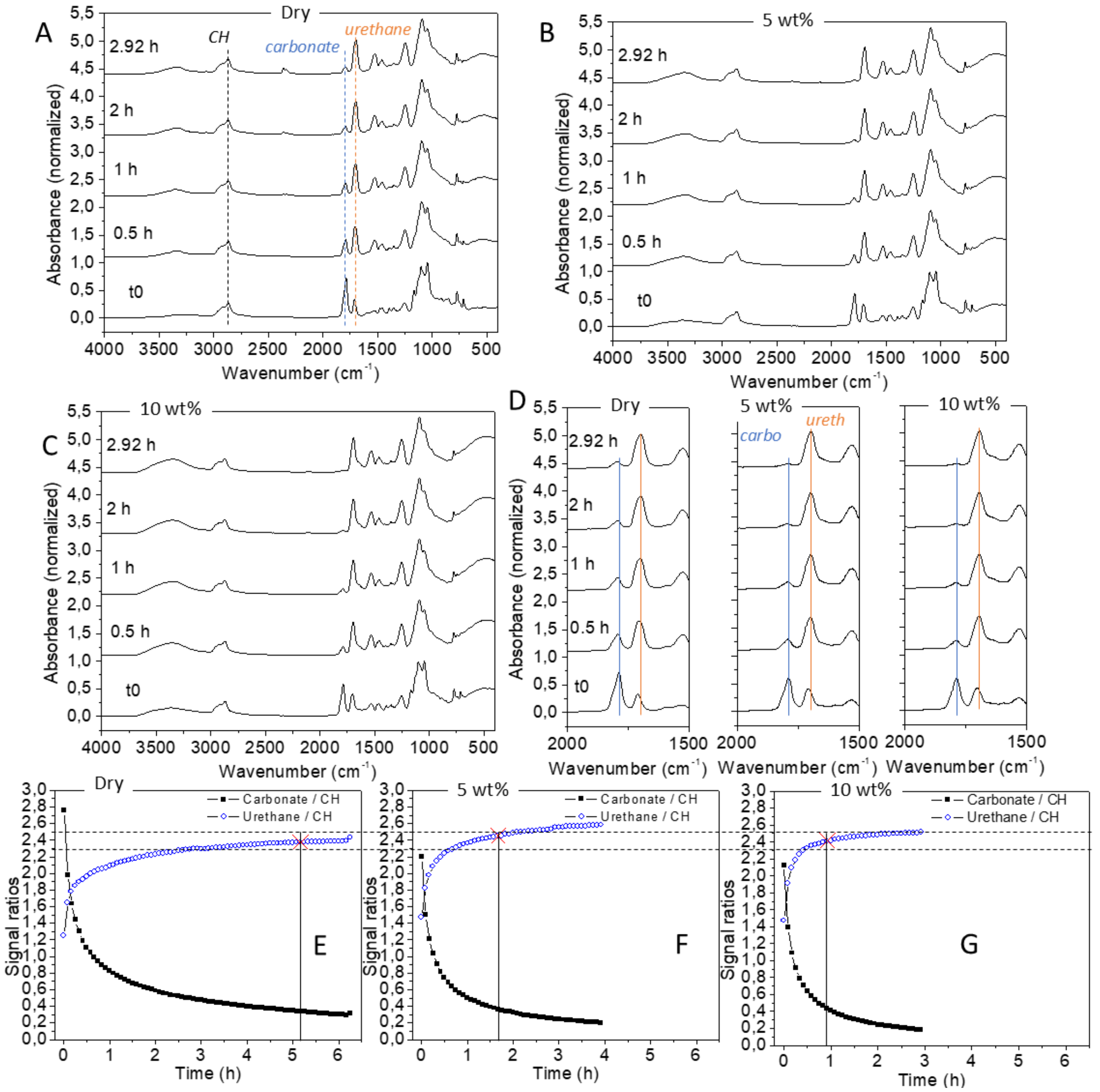


Figure S6: FTIR investigation of the crosslinking reaction of TMPTC and EDR148 at 40 °C: (A) without additives (dry formulation), (B) with 5 wt% of water, (C) with 10 wt% of water. (D) Magnification of the spectra for the wavenumber comprised in-between 1500 cm^{-1} and 2000 cm^{-1}. Evolution of the intensity of the bands corresponding to the C=O bond of the 5CC and the urethanes (normalized by the band corresponding to the C-H bonds) as a function of time for the systems: (E) without additives (dry formulation), (F) with 5 wt% of water, (G) with 10 wt% of water. A red cross and a vertical black line indicates the reaction time corresponding to t_{gel} measured in rheology.

2.4. Comparison of water with other solvents: MeOH, *t*-BuOH, THF, Glyme, DMSO

Water was compared to other solvents for the crosslinking reaction of TMPTC with EDR148, at 40 °C. We selected two alcohols (protic solvents): methanol (MeOH), tert-butanol (*t*-BuOH). Three non-protic polar solvents were also tested including dimethylsulfoxide (DMSO) and two ethers: tetrahydrofuran (THF) and Glyme. They were all tested for a mass loading of 5 wt%, and a molar loading of 62 mol% (*i.e.* 0.62 eq. by respect to 5CC moieties of TMPTC). For water only (the reference additive), 5 wt% = 62 mol%.

For each condition, the plots of Tan δ(t) are represented in Figure S7 and Figure S8. They were used to obtain a first estimation of t_{gel}.

The corresponding values of t_{gel}, n, and d_f, determined according to the procedure reported in the material and method section, are reported in Table S3.

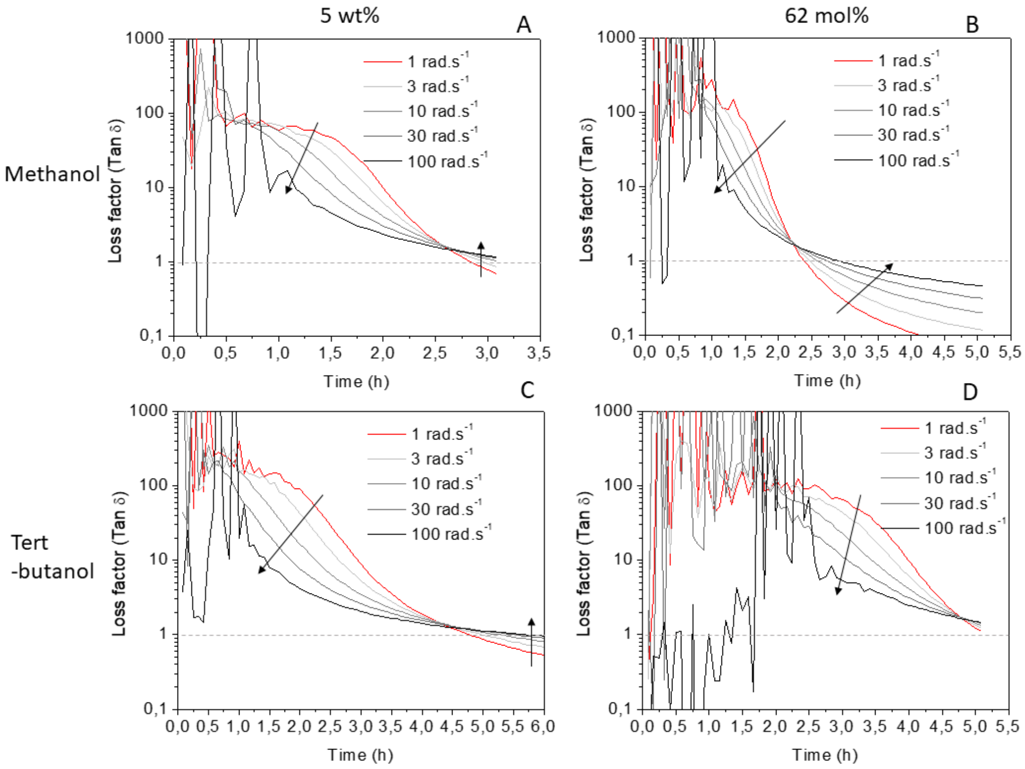


Figure S7: Variation of the loss factor (tan(δ)) as a function of time for the crosslinking reaction of TMPTC and EDR148 at 40 °C with methanol: (A) 5 wt%, (B) 62 mol%, and t-BuOH: (C) 5 wt%, (D) 62 mol% (multiwave mode, 1.97% global strain amplitude, ω = 1, 3, 10, 30, 100 rad s^{-1}*, the horizontal doted line corresponds to tan(δ) = 1).*

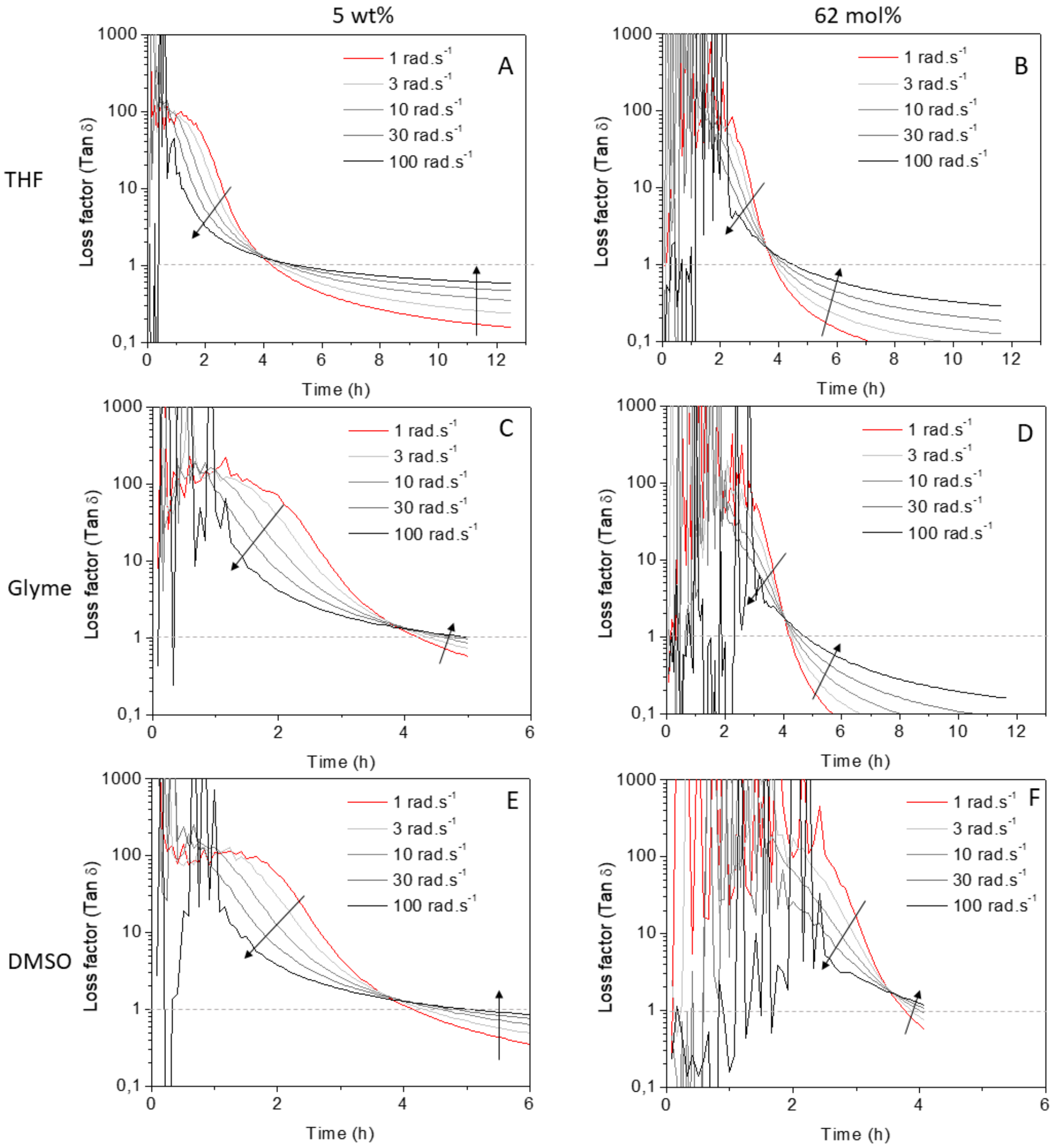


Figure S8: Variation of the loss factor (tan(δ)) as a function of time for the crosslinking reaction of TMPTC and EDR148 at 40 °C with THF: (A) 5 wt%, (B) 62 mol%, Glyme: (C) 5 wt%, (D) 62 mol%, and DMSO: (E) 5 wt%, (F) 62 mol% (multiwave mode, 1.97% global strain amplitude, ω = 1, 3, 10, 30, 100 rad s^{-1}, the horizontal doted line corresponds to tan(δ) = 1).

Solvent	Solvent loading (wt%)	t_{gel} (h)	*n*	d_f
Water	0	5.13	0.55	1.94
	2	2.9	0.6	1.88
	5^a	1.62	0.66	1.79
	10	0.93	0.7	1.74
Methanol	8.6^a	2.23	0.66	1.79
	5	2.63	0.64	1.82
tert-butanol	17.8^a	4.81	0.67	1.78
	5	4.44	0.59	1.89
THF	17.3^a	3.59	0.66	1.79
	5	3.98	0.59	1.89
Glyme	20.9^a	4.04	0.68	1.77
	5	3.91	0.61	1.86
DMSO	18.7^a	3.55	0.67	1.78
	5	3.83	0.61	1.86

Table S3: t_{gel}, critical exponent (n) and fractal dimension (d_f) values for the crosslinking reaction of TMPTC and EDR148 at 40 °C with various solvents used as additives, with a mass loading of 5 wt% and a molar loading of 62 mol% (i.e. *0.62 eq. by respect to 5CC moieties of TMPTC). [a] Mass loading corresponding to the molar loading of 62 mol%. For water only (the reference additive), 5 wt% = 62 mol%. The values were determined according to the procedure reported in the material and method section.*

2.5.Swelling behavior of TMPTC-EDR148 networks in different solvents.

PHU films obtained from the crosslinking reaction of TMPTC with EDR148 were prepared according to the procedure reported in the materials and method section. Two formulations were investigated: (i) no additives (dry), (ii) 5 wt% of water. After curing at 50 °C for 8 h, they were vacuum dried (50 °C, 8 h). Circular samples cut out of the film were then immersed in the different swelling solvents and the evolution of the swelling index and the linear swelling ratio was monitored as a function of time according to the procedure described in the material and method section.

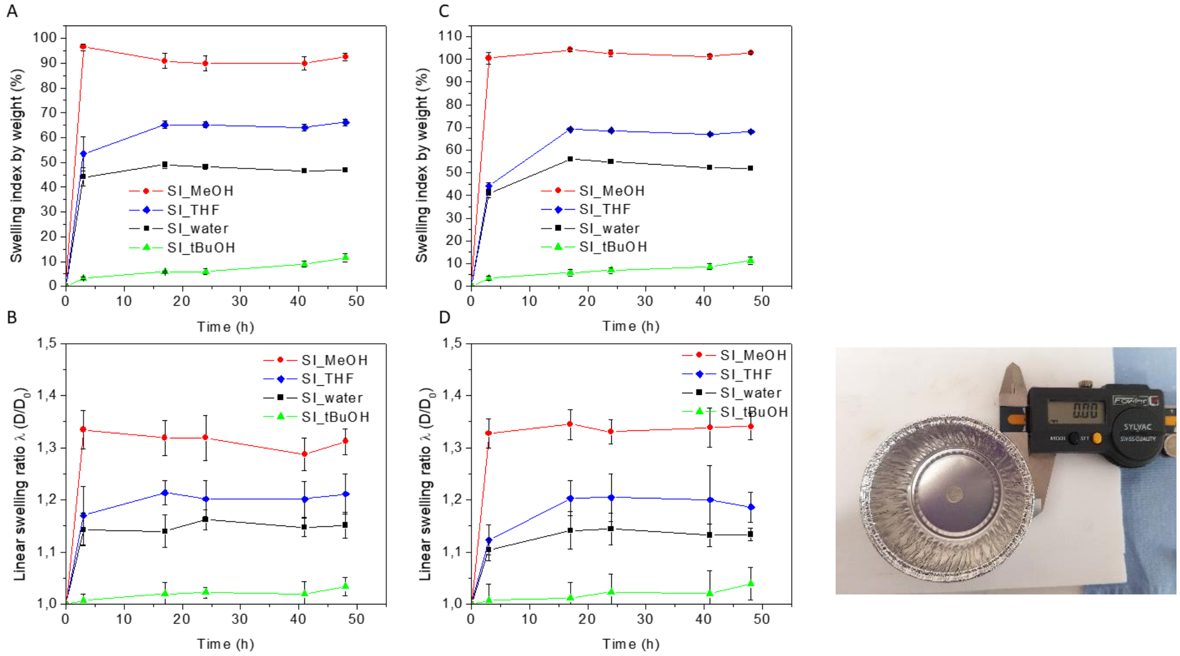


Figure S 9: Variation of the swelling index and the linear swelling ratio as a function of time for PHU networks obtained from TMPTC-EDR148 formulations cured for 8h at 50°C with (A,B) no additives (dry) and (B,C) 5 wt% of water. Samples were first dried for 16h at 50°C under vacuum before swelling. Picture represents the measurement of swollen sample diameter with a caliper.

2.6.Model reactions: PC + EDR148

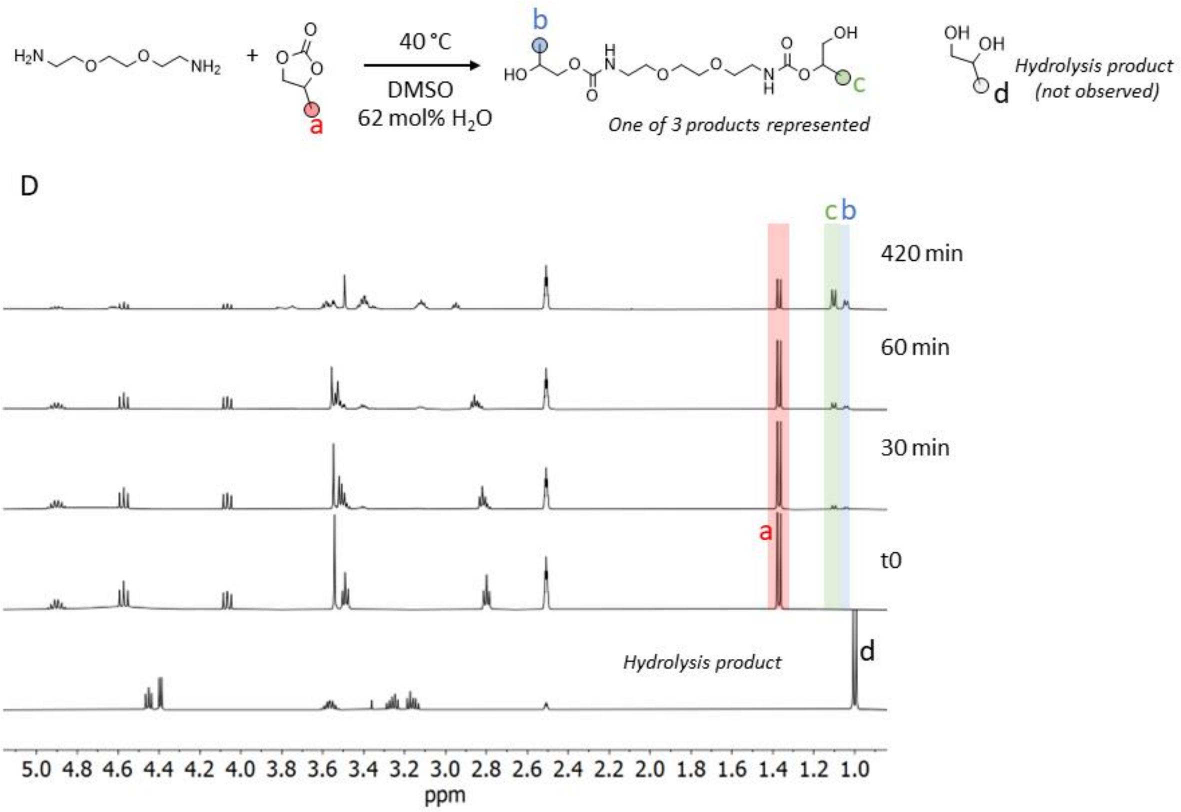


Figure S10: Model reaction has been performed between PC and EDR 148 in dry DMSO at 40 °C both in dry conditions and with 62 mol% of water. NMR monitoring of the reaction when water was added is given with a spectrum of the expected product of PC hydrolysis (bottom spectrum). The integration of the methyl groups signals between 1 and 1.4 ppm allowed to monitor the PC conversion over time in both conditions.

PC conversion was calculated as follow:

$$conv_{PC}(\%) = \left(\frac{\int b + \int c}{\int a + \int b + \int c}\right) \times 100$$

Where a is the signal corresponding to the methyl group of propylene carbonate (Figure S10), b and c are the signals corresponding to the methyl groups of both possible hydroxyurethane products.

Time (min)	**PC conversion (%)**	
	Dry	**62 mol% water**
60	13.3±0.4	26.8±2.4
120	27.7±0.3	43.4±3
180	39.3±0.6	53.6±2.6

Table S4: Reproducibility study for the kinetic monitoring of PC-EDR148 reaction at 40°C in dry DMSO without and with 62 mol% of added water. The conversion was measured after 1 h, 2 h and 3 h for 3 different samples to provide the error bars.

2.6.1. Model reaction performed under dry conditions at 40 °C

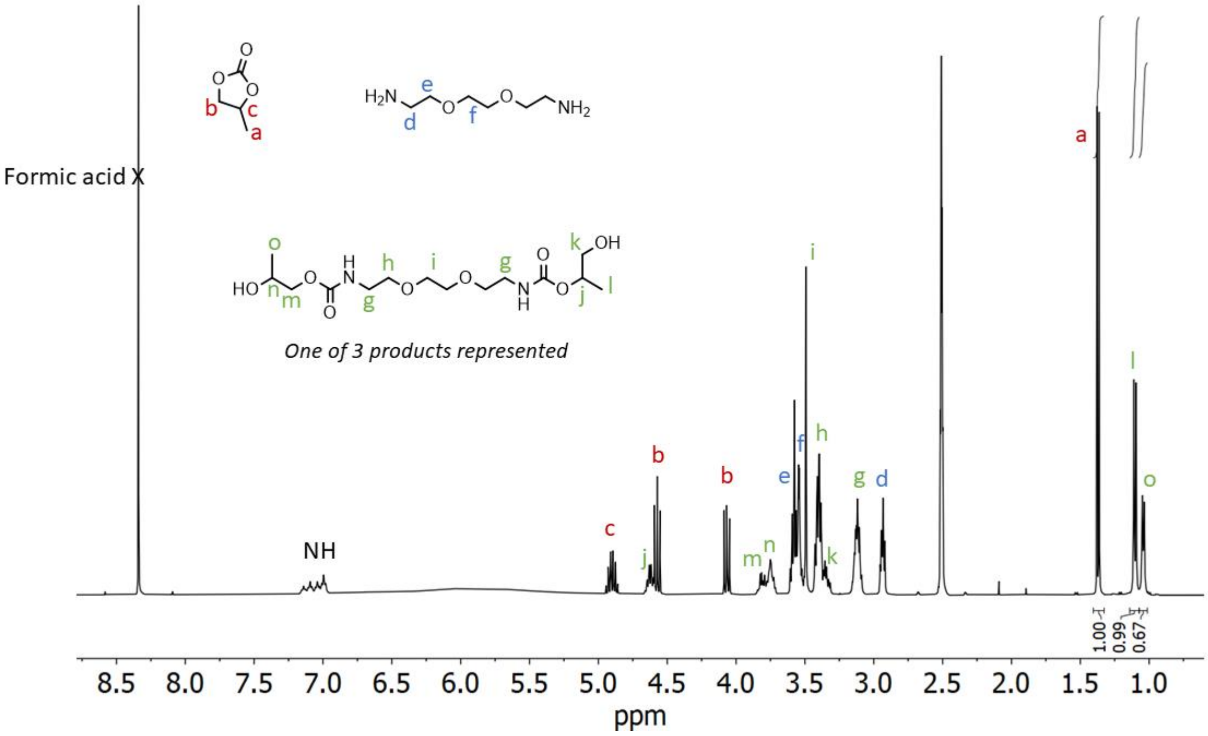


Figure S11: ^{1}H NMR spectrum of PC aminolysis under dry conditions after 7 h at 40 °C in dry DMSO.

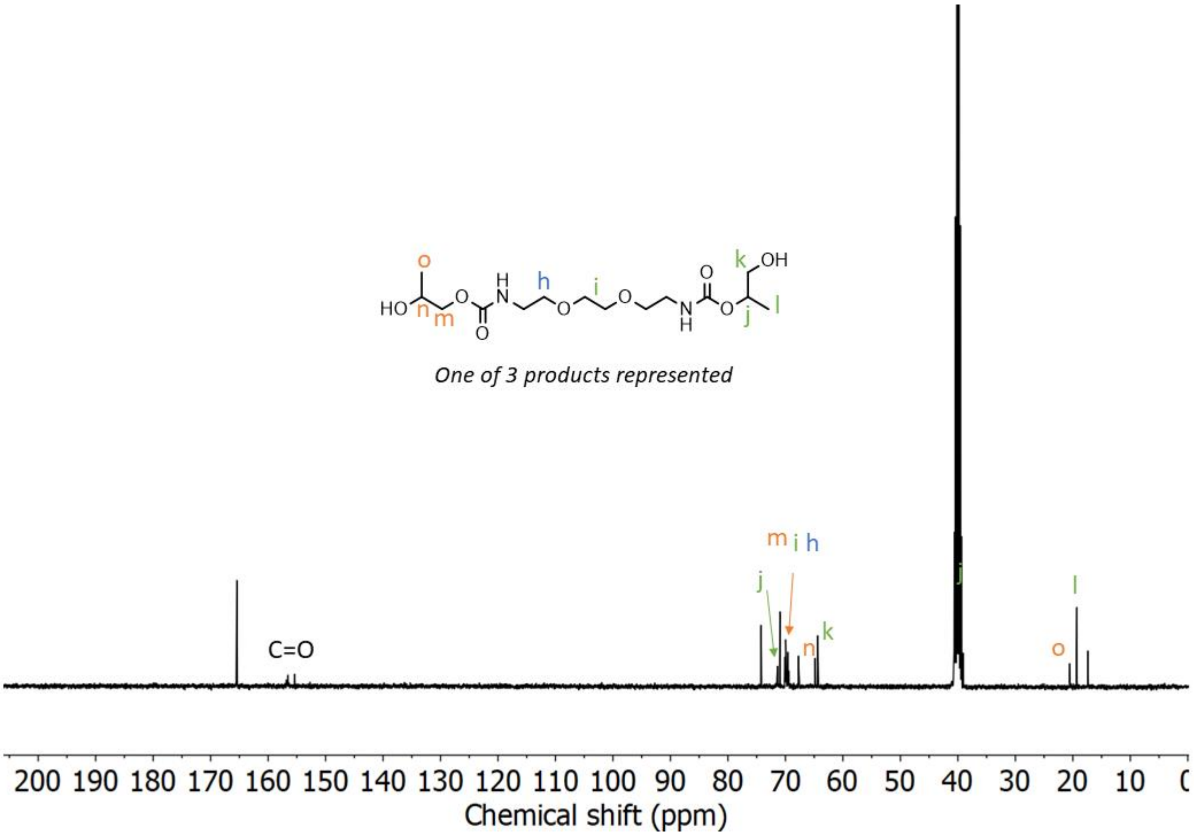


Figure S12: ^{13}C NMR spectrum of PC aminolysis under dry conditions after 7 h at 40 °C in dry DMSO.

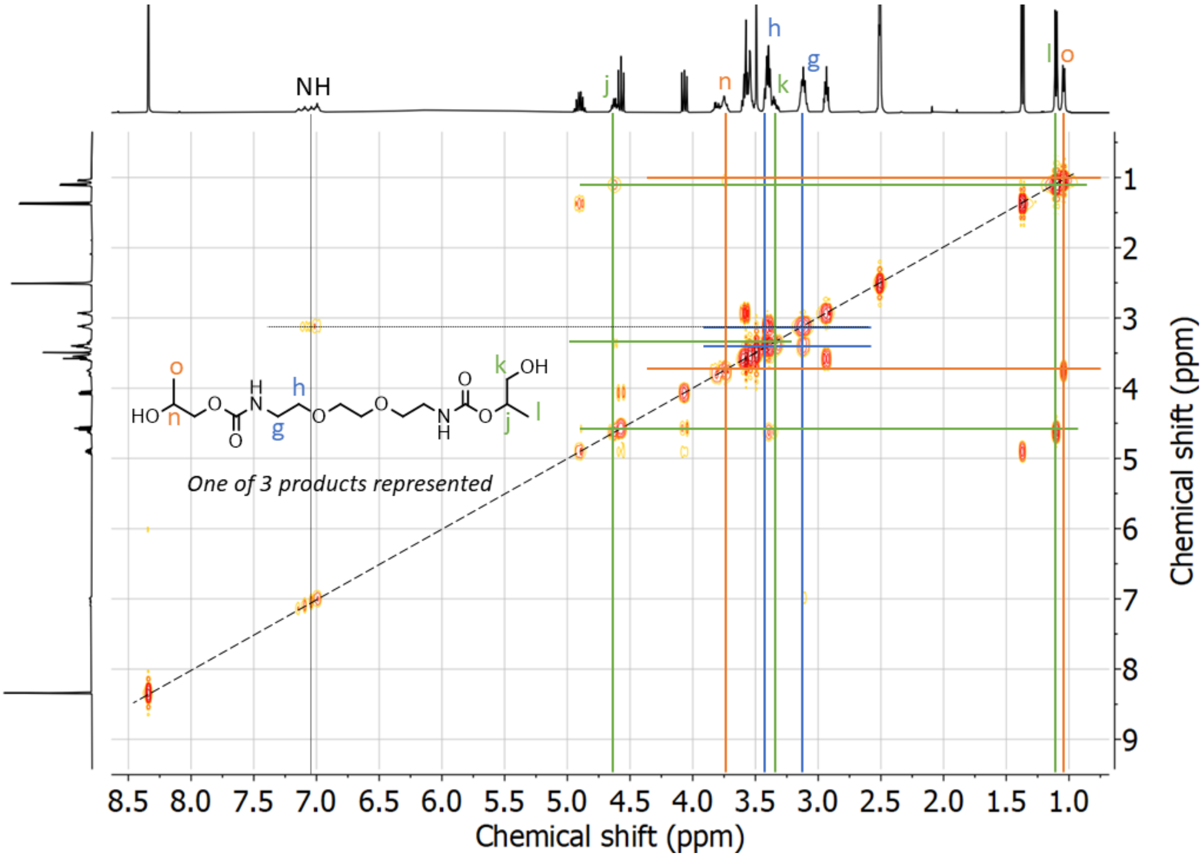


Figure S13: COSY NMR spectrum of PC aminolysis under dry conditions after 7 h at 40 °C in dry DMSO.

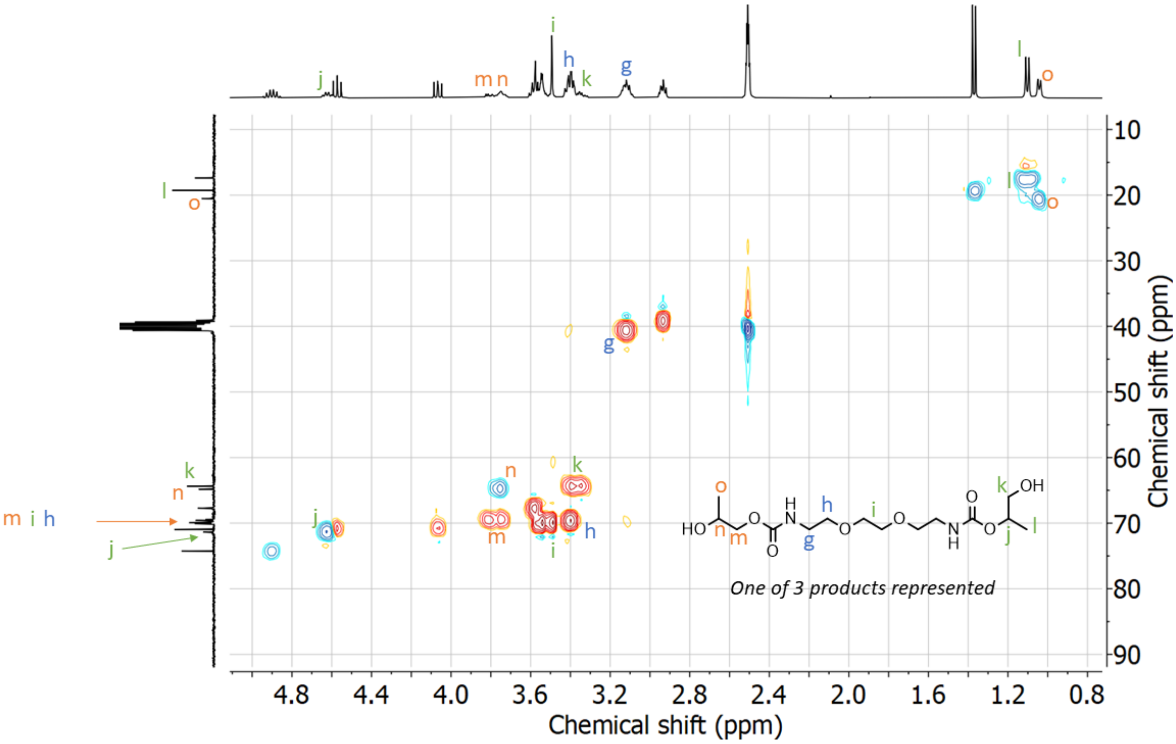


Figure S14: HSQC NMR spectrum of PC aminolysis under dry conditions after 7 h at 40 °C in dry DMSO.

2.6.2. Model reaction performed with 62 mol% of water at 40 °C

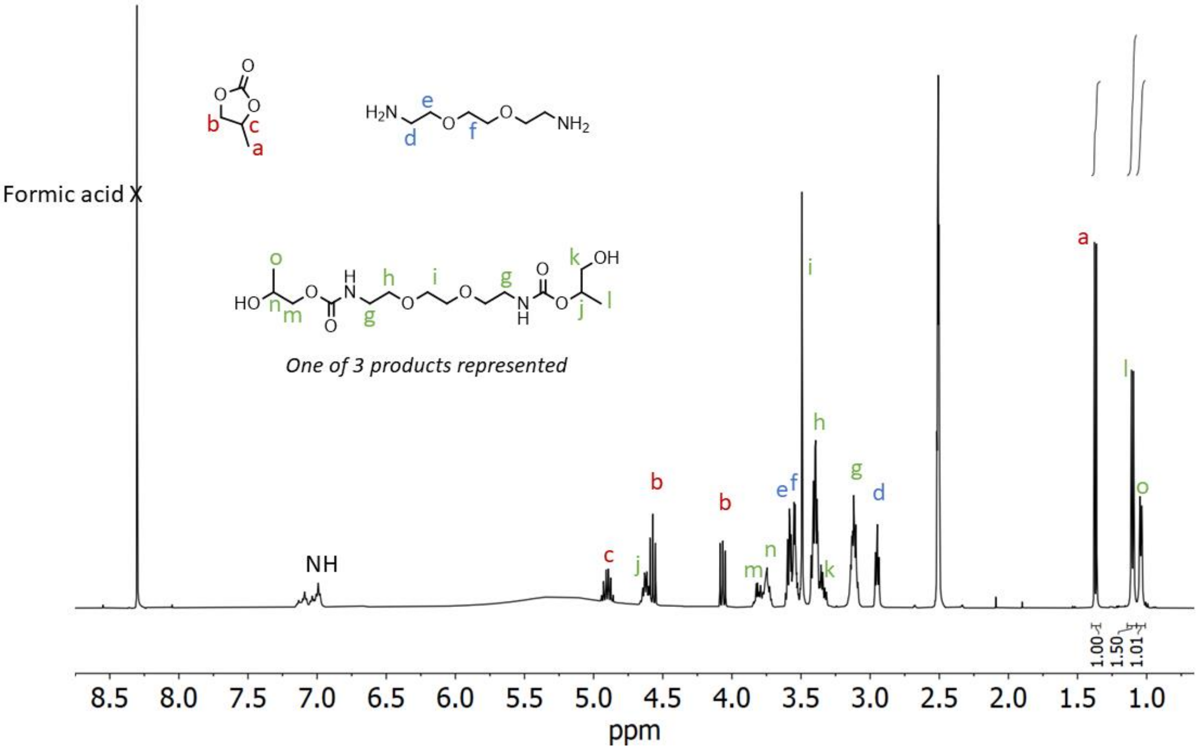


Figure S15: ¹H NMR spectrum of PC aminolysis with 62 mol% water after 7 h at 40 °C in dry DMSO.

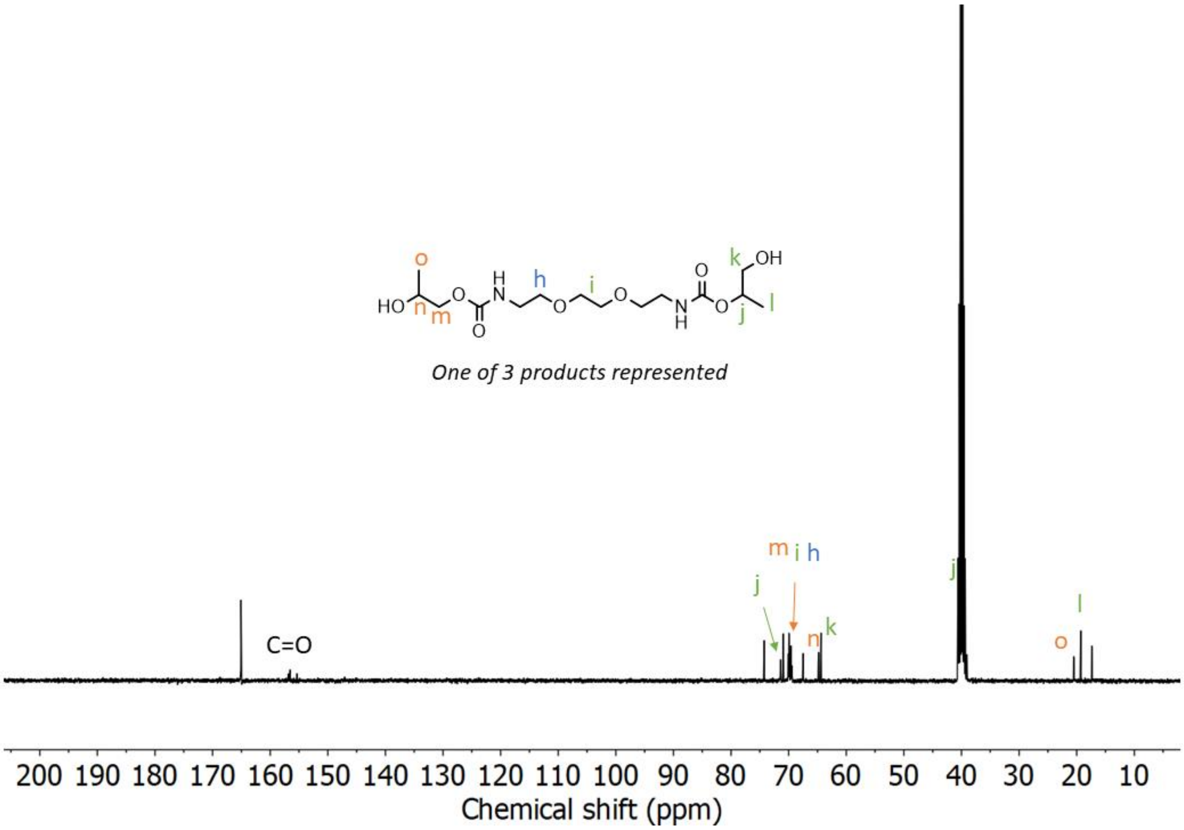


Figure S16: ¹³C NMR spectrum of PC aminolysis with 62 mol% water after 7 h at 40 °C in dry DMSO.

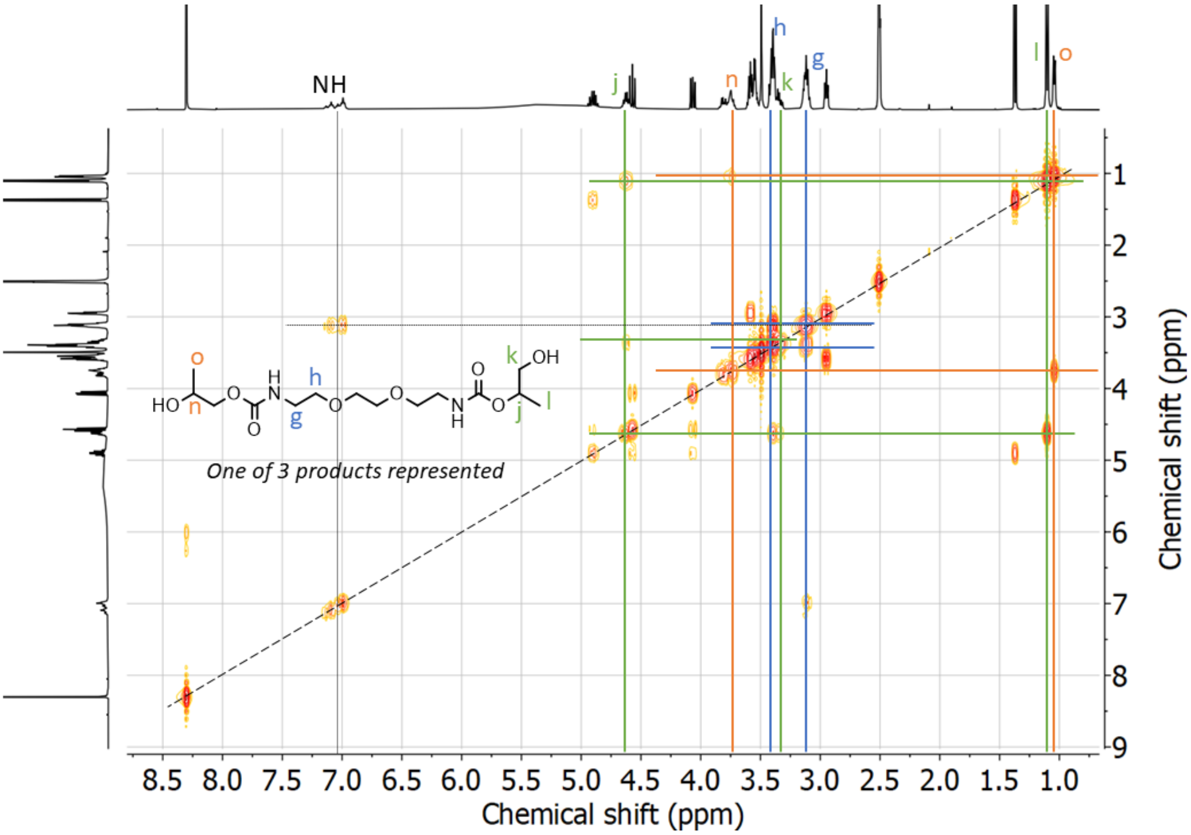


Figure S17: COSY NMR spectrum of PC aminolysis with 62 mol% water after 7 h at 40 °C in dry DMSO.

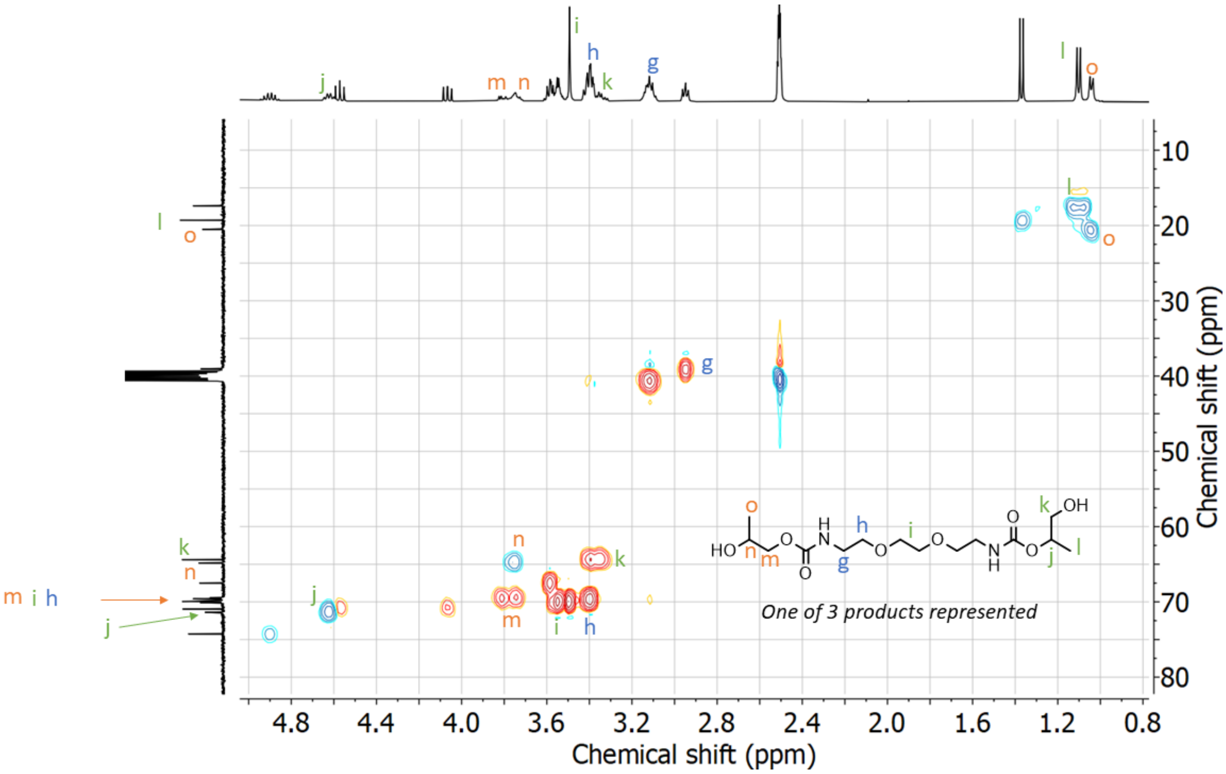


Figure S18: HSQC NMR spectrum of PC aminolysis with 62 mol% water after 7 h at 40 °C in dry DMSO.

2.6.3. Model reactions performed at various temperatures (dry conditions and 62 mol% of water)

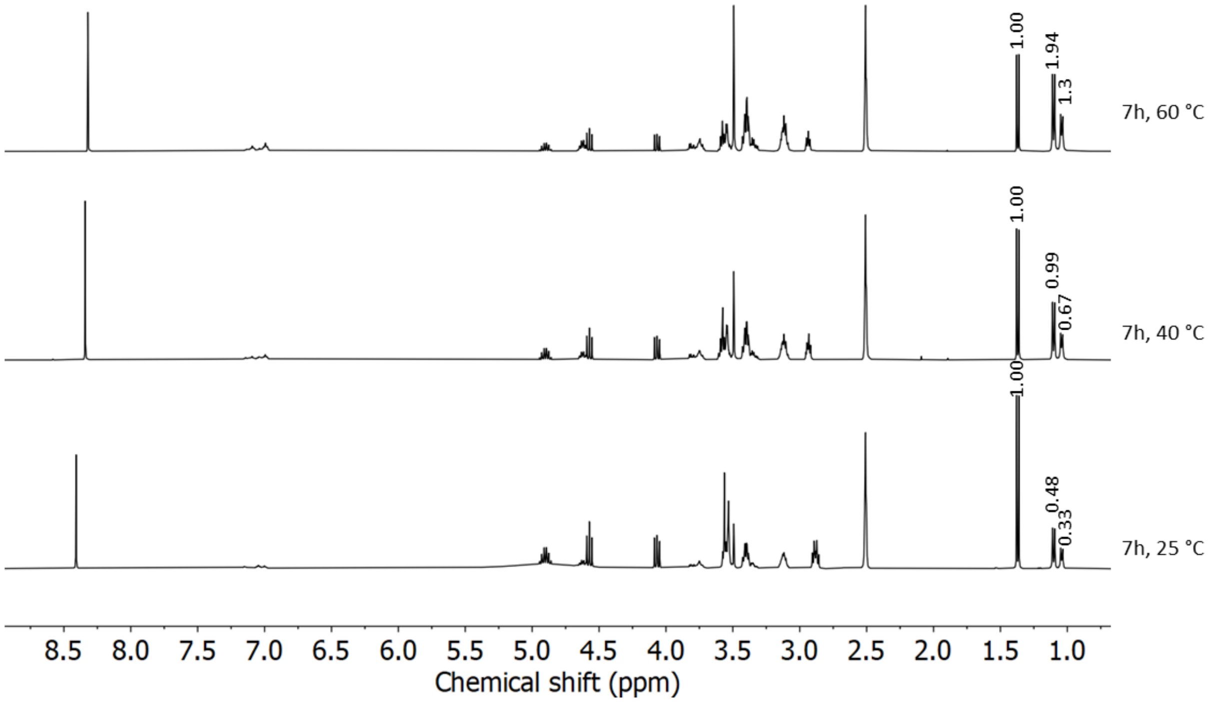


Figure S19: ^{1}H NMR spectra of PC aminolysis under dry conditions at various temperatures after 7 h in dry DMSO.

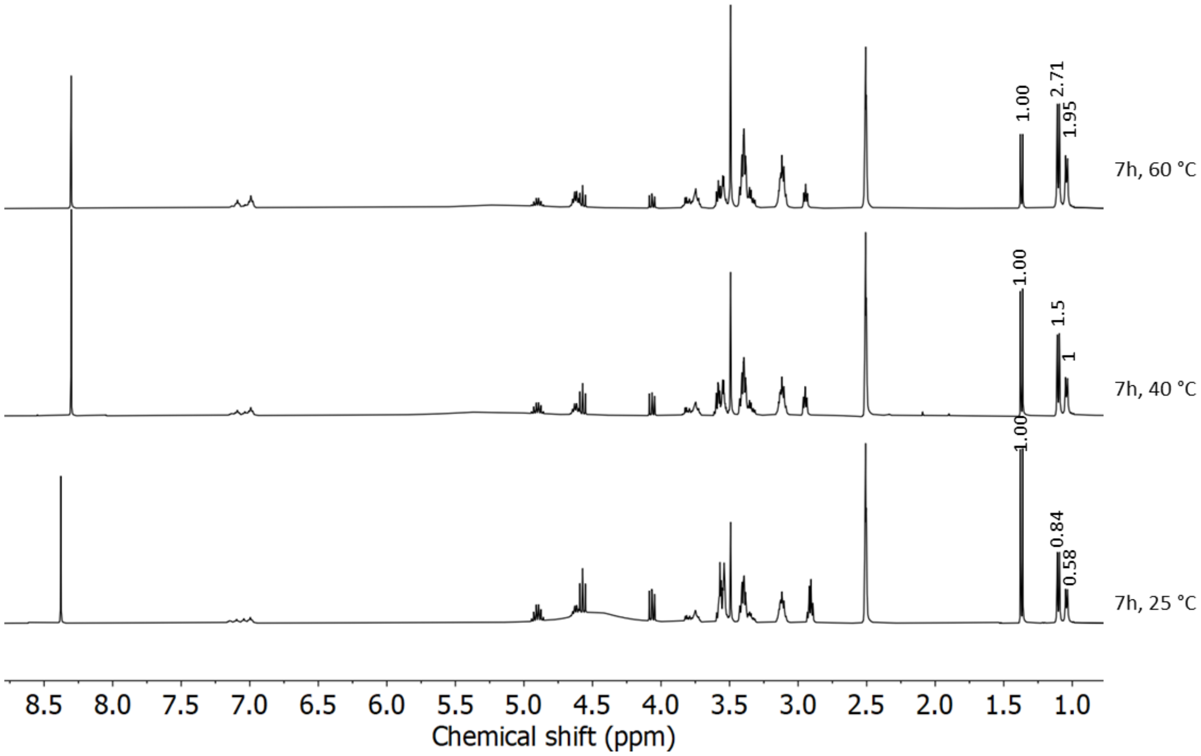


Figure S20: ^{1}H NMR spectra of PC aminolysis with 62 mol% of water at various temperatures after 7 h in dry DMSO.

2.6.4. Model reactions performed at 40 °C with 62 mol% of MeOH and THF

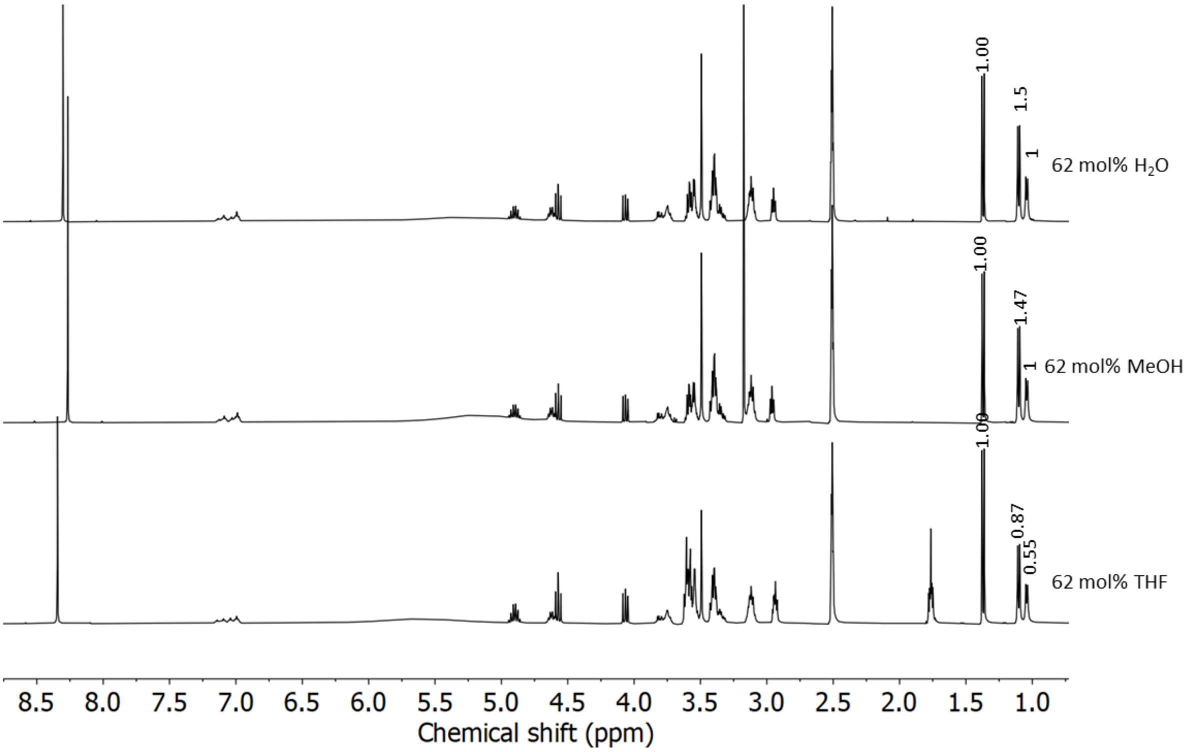


Figure S21: ^1H NMR spectra of PC aminolysis with 62 mol% added solvent at 40 °C after 7 h in dry DMSO.

2.6.5. Model reactions performed in solvent-free conditions (bulk)

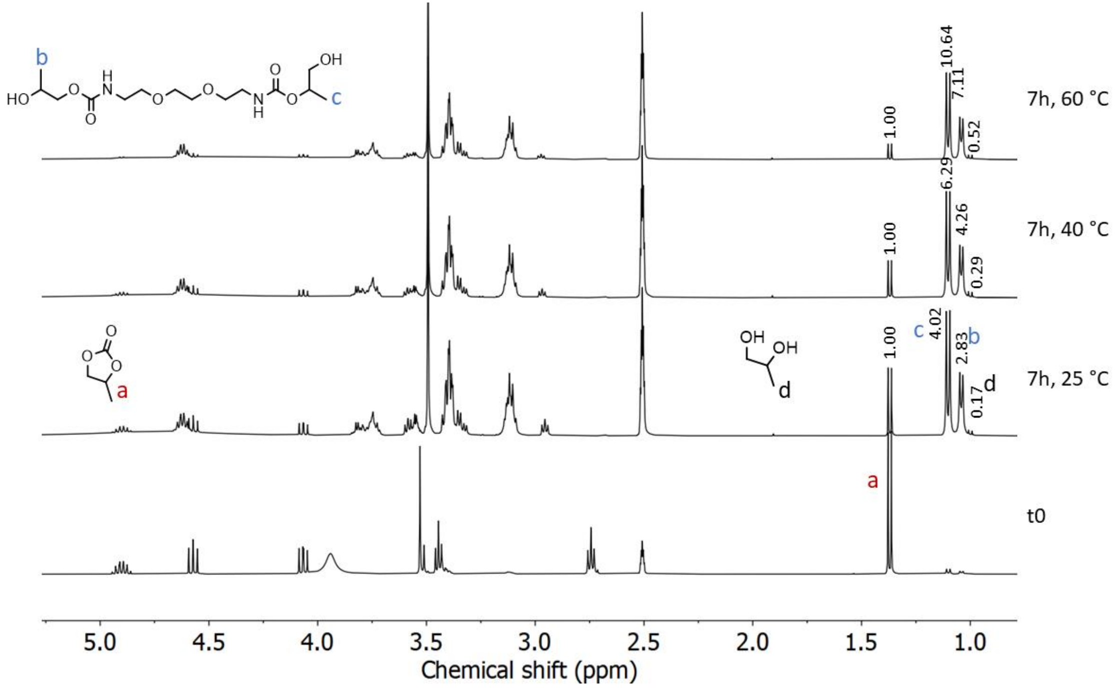


Figure S22: ^1H NMR spectra of PC aminolysis with 62 mol% of water at 25, 40 and 60 °C after 7h under solvent-free conditions.

Temperature (°C)	PC conversion (%)	Hydrolysis yield (%)
25	88	2
40	92	2
60	95	3

Table S5: PC conversion and hydrolysis yield for model reaction performed at 25, 40 and 60 °C under solvent free conditions for 7 h.

PC hydrolysis was estimated as follow:

$$Yield_{hydrolysis}(\%) = \left(\frac{\int d}{\int b + \int c + \int d + \int a}\right) \times 100$$

2.7.DFT calculations

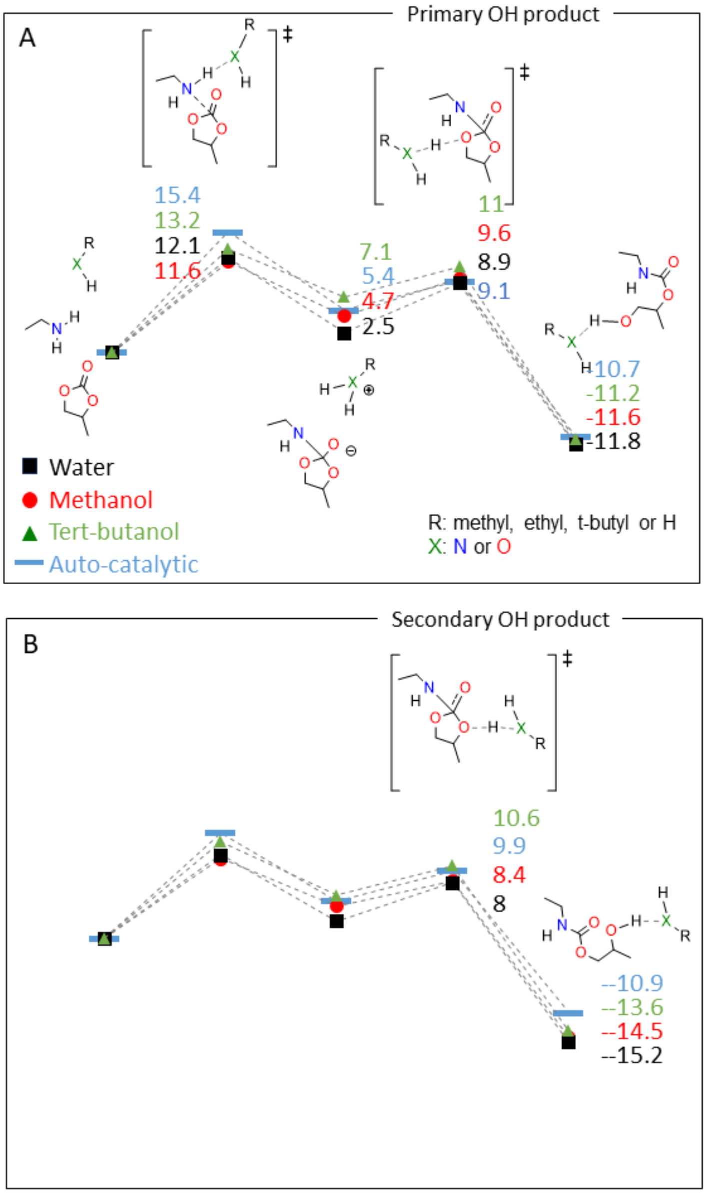


Figure S23: Energy levels of the transition states (TS) and intermediate states (IS) obtained from the DFT calculations for the aminolysis of propylene carbonate (PC) by ethylamine in the presence of different proton-shuttle: (i) water (R=H, X=O, black squares), (ii) Methanol (R=methyl, X=O, red circles), (iii) tert-butanol (R=t-butyl, X=O, green triangle) or (iv) the amine it-self (R=ethyl, X=NH, blue bars). The energy levels are provided for the formation of the two possible regioisomers of the hydroxyurethanes, i.e. the primary (A) or the secondary hydroxyl products (B). Values are the approximate computed Gibbs free energies in kcal mol^{-1}.

For easier representation, Figure S24 bellow shows the aminolysis of PC with water as proton shuttle leading to the formation of either 1° OH or 2° OH hydroxyurethane products.

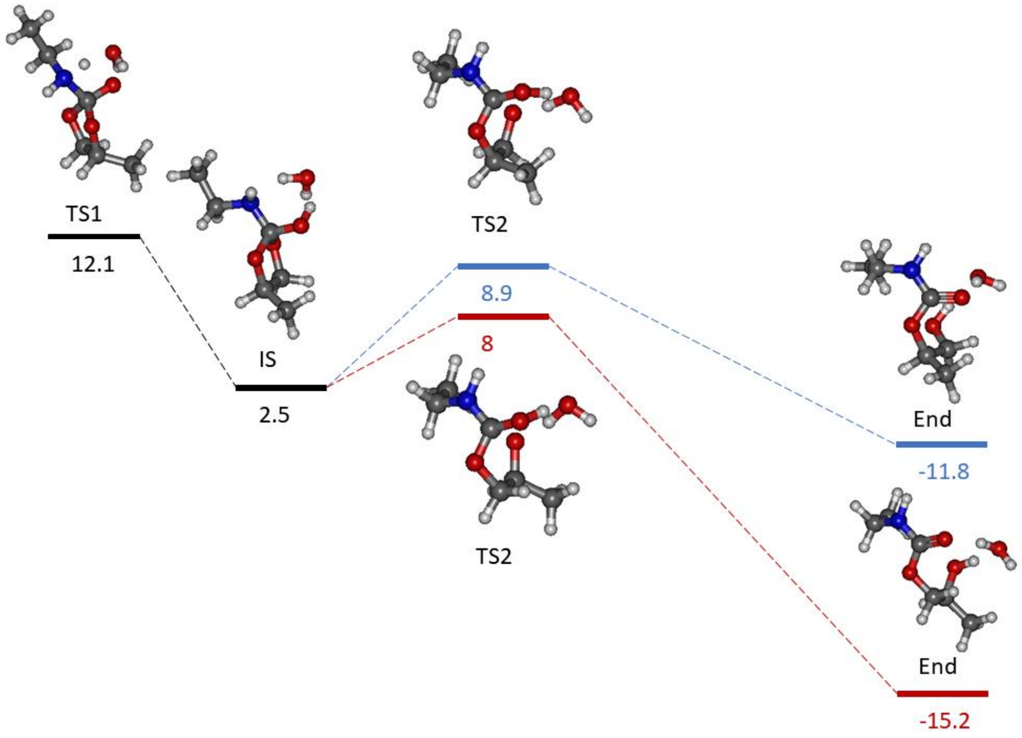


Figure S24. Reaction path for the water-catalyzed aminolysis of propylene carbonate. Gibbs free energy values provided in kcal/mol.

Only TS2 and the final product energy levels are different for the two isomeric products. Molecular structures are only schematic representations of the molecular arrangement for easier reading. Gibbs free energies are expressed in kcal mol^{-1} computed at the BP86/def2-SVP level in DMSO at 25 °C. The raw data of the optimized geometries for the considered reaction paths are provided at the end of this document.

2.8. Comparison of water with organobase catalysts: DBU and TBD

This comparative study was performed on a TA-instrument ARES-G2 rheometer (see the materials and method section).

For the curing of TMPTC/EDR 148 formulations, water was compared to DBU and TBD. Samples were prepared using the procedure reported in the materials and method section, with 3 wt% of either water, DBU or TBD (*i.e.* ~ 42 mol% of water and ~ 5 mol% of organobase by respect to 5CC moieties). In each case, the evolution of the Tanδ curve as a function of time is reported in Figure S25. The corresponding values of t_{gel} and the critical exponent, *n*, are reported in Table S6.

Sample	**t_{gel} (h)**	**n**
Dry	4.75	0.57
3 wt% DBU	2.47	0.58
3 wt% TBD	4.64	0.58
3 wt% H_2O	2.19	0.63

Table S6: t_{gel} and critical exponent (n) values for the crosslinking reaction of TMPTC and EDR148 at 40 °C with 3 wt% of either water, DBU or TBD. The values were determined according to the procedure reported in the material and method section.

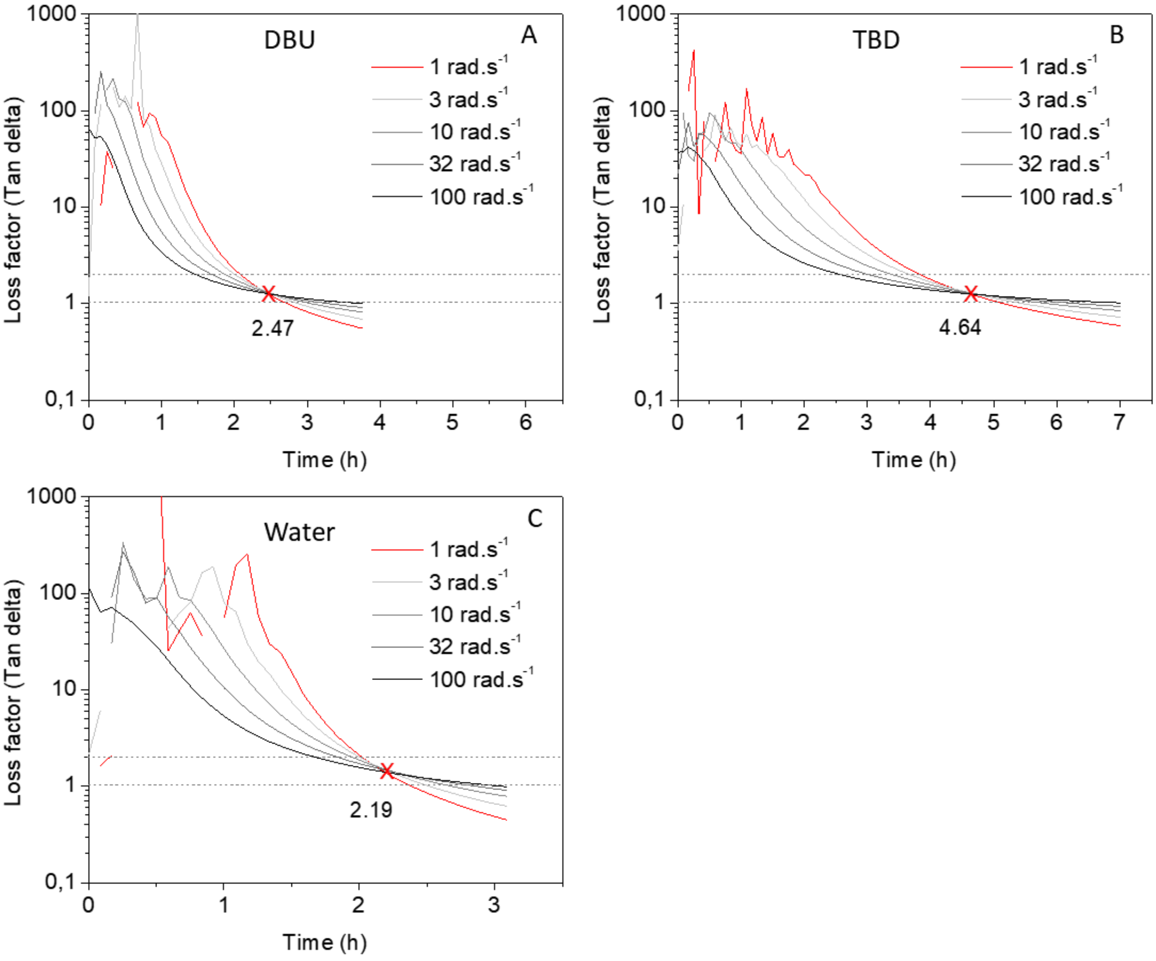


Figure S25: Variation of the loss factor (tan(δ)) as a function of time for the crosslinking reaction of TMPTC and EDR148 at 40 °C in the presence of (A) 3 wt.% of DBU (B) 3 wt.% of TBD (C) and 3 wt.% of water (multiwave mode, 2.08% global strain amplitude, ω = 1, 3, 10, 32, 100 rad s^{-1}, horizontal doted lines correspond to loss factor values of 1 and 2).

2.9. Thermomechanical and FTIR analyses of the fully cured networks

PHU films obtained from the crosslinking reaction of TMPTC with EDR148 were prepared according to the procedure reported in the materials and method section. Three formulations were investigated: (i) no additives (dry), (ii) 5 wt% of water, (iii) 5 mol% DBU (~3 wt%). After curing at 50 °C for 8 h, they were vacuum dried (50 °C, 16 h), before a 24 h conditioning at 50% relative humidity (RH) and 25 °C, *i.e.* conditions mimicking a standard outdoor atmosphere. The glass transition temperature, T_g, was measured at each step of the process. Figure S 26 represents the DSC thermograms of the "*as cured*" samples and the samples obtained after vacuum drying at 50 °C for 16h. Figure S 27 represents the DSC thermograms of the samples after 24 h conditioning at 50% relative humidity (RH) and 25 °C.

The tensile properties of the samples conditioned at 50% relative humidity (RH) were investigated according to the procedure reported in the materials and method section. Figure S 28 represents the stress-strain curves of each sample.

Finally, the as cured and the dried samples were analyzed using FTIR. The FTIR spectra are represented in Figure S 29 and Figure S 30.

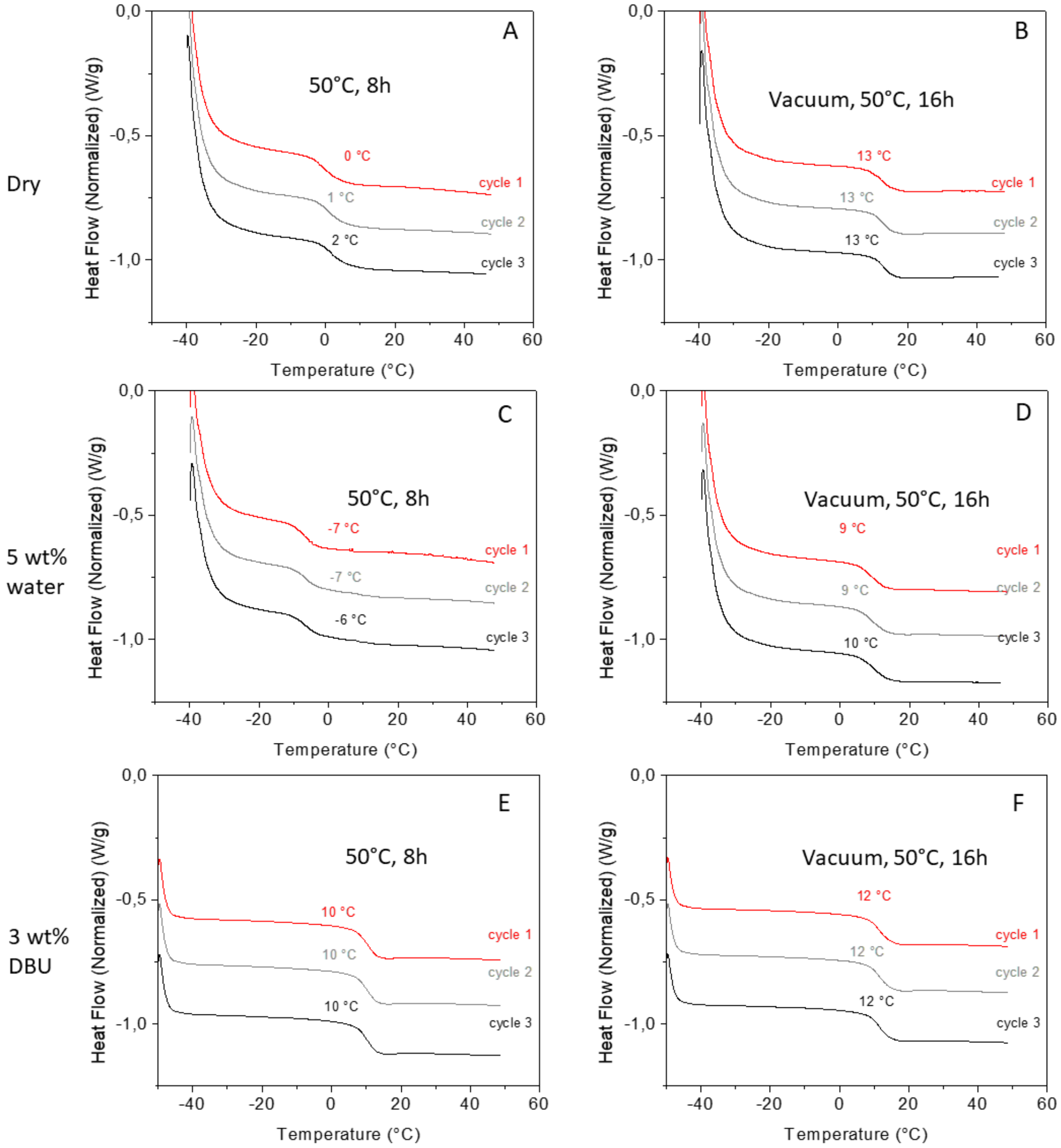


Figure S 26: DSC thermograms of TMPTC-EDR148 formulations after curing for 8h at 50°C with (A) no additives (dry), (C) 5 wt% of water or (E) 3 wt% (= 5 mol%) of DBU. (B), (D), (F) represent the thermograms of the corresponding networks dried for 16h at 50°C under vacuum.

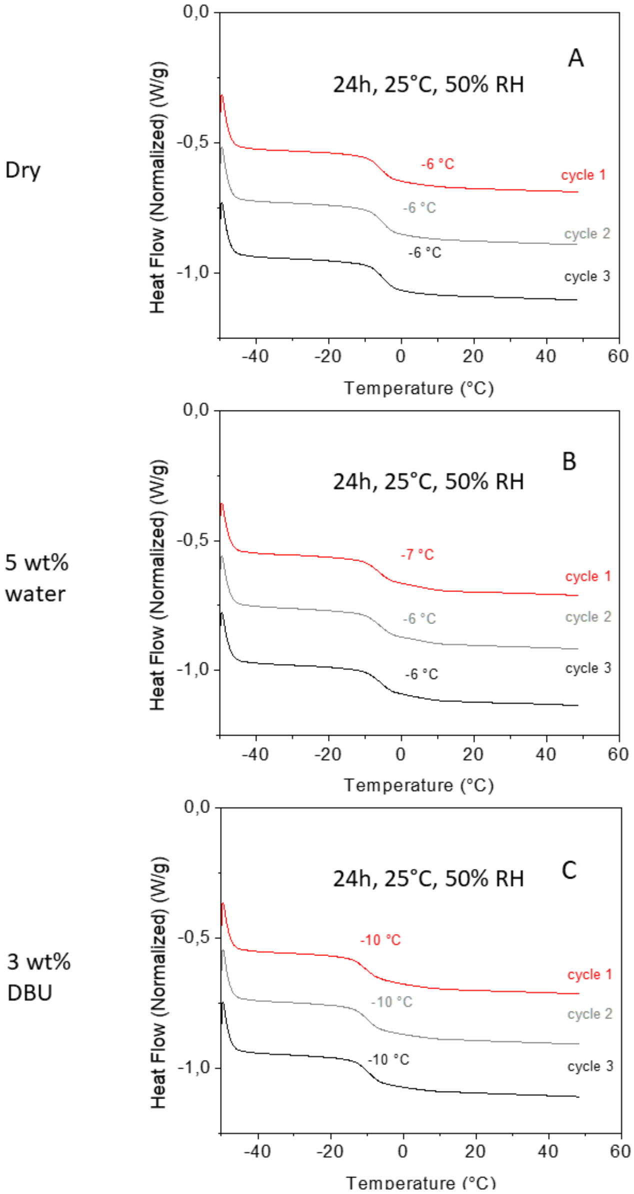


Figure S 27: DSC thermograms of TMPTC-EDR148 formulations cured for 8h at 50°C with (A) no additives (dry), (B) 5 wt% of water or (C) 3 wt% of DBU, and dried for 16h at 50°C under vacuum followed by 24h conditioning at 25°C and 50% relative humidity.

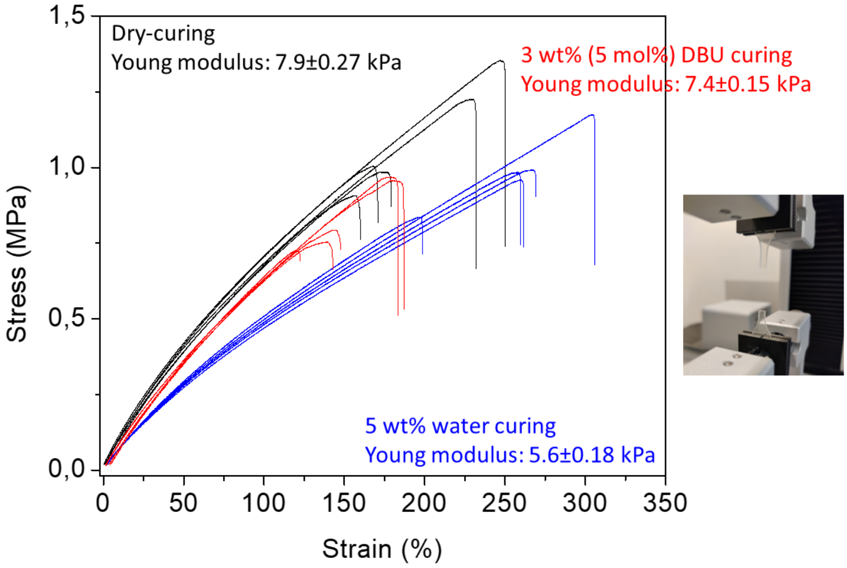


Figure S 28: Strain-stress curves of PHU networks obtained from TMPTC-EDR148 formulations cured for 8h at 50°C with (black curve) no additives (dry), (blue curve) 5 wt% of water and (red curve) 5 mol% of DBU. Samples were dried for 16h at 50°C under vacuum and conditioned at 25°C, 50% RH for 24h before analysis.

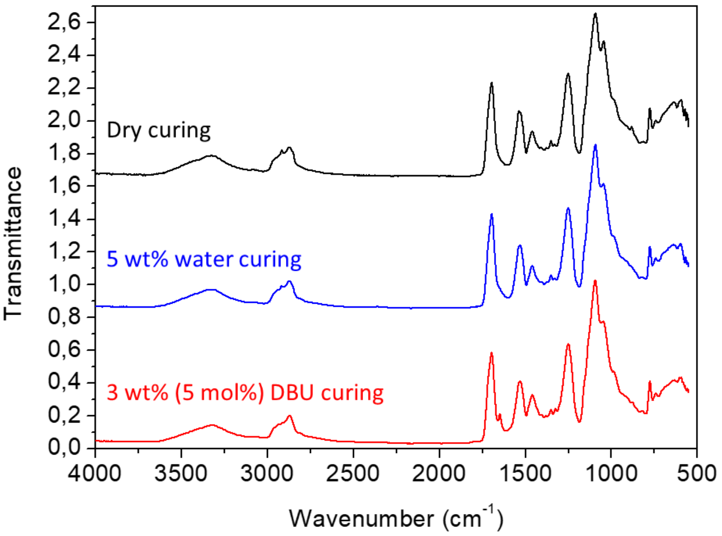


Figure S 29: FTIR spectra of PHU networks obtained from TMPTC-EDR148 formulations cured for 8h at 50°C with (black curve) no additives (dry), (blue curve) 5 wt% of water and (red curve) 5 mol% (= 3wt%) of DBU.

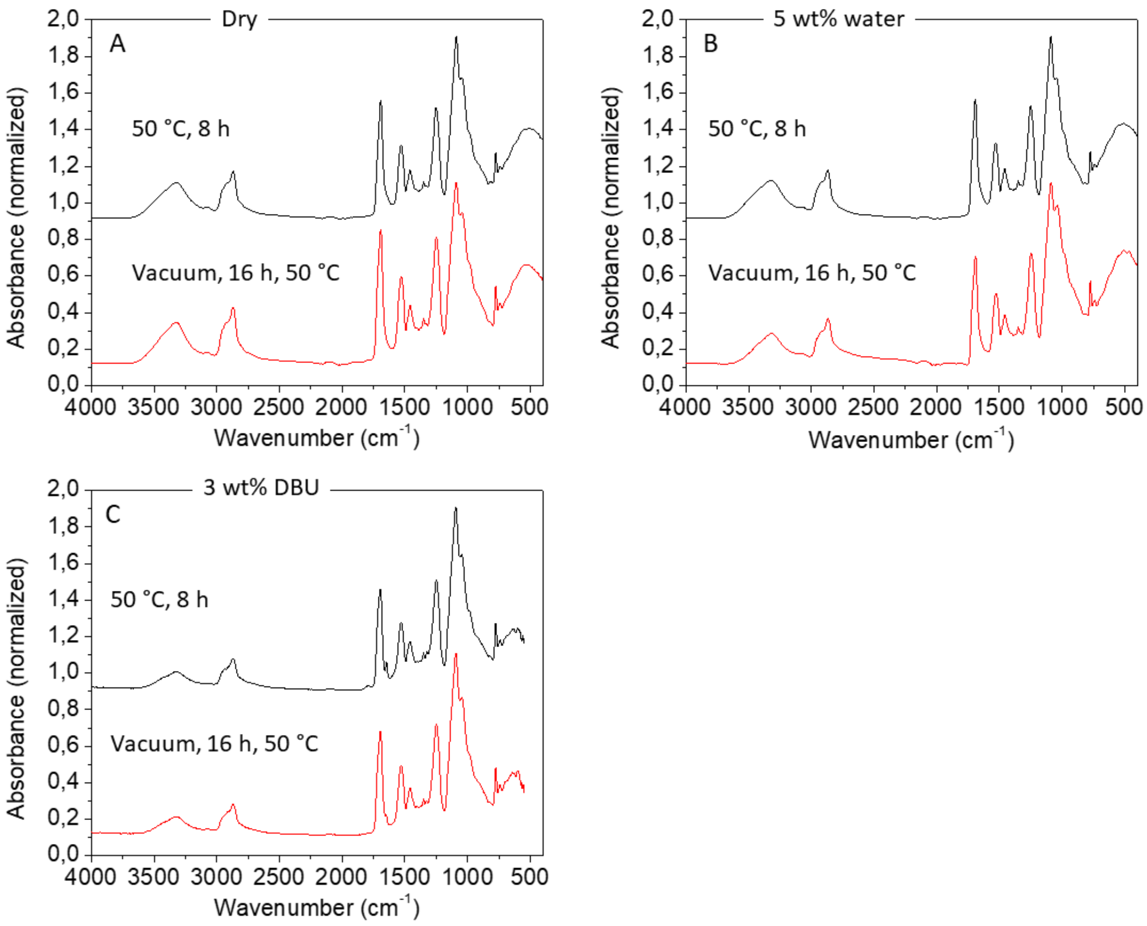


Figure S 30: FTIR spectra of PHU networks obtained from TMPTC-EDR148 formulations cured for 8h at 50°C with (A) no additives (dry), (B) 5 wt% of water and (C) 3 wt% (=5mol%) of DBU. Black curves are the spectra of the as cured samples, while red curves are the spectra of the samples after drying for 16h at 50°C under vacuum.

2.10. Investigation of the crosslinking reaction of TMPTC with m-XDA: effect of water

The crosslinking reaction of TMPTC with m-XDA was investigated by multiwave rheology at different temperatures (T = 40, 50, 60, 70 °C) without additives and in the presence of 5 wt% of water. Samples were prepared according to the procedure reported in the material and method section, and the same protocol was used in rheology (multiwave mode, 1.97% global strain amplitude, ω = 1, 3, 10, 30, 100 rad s^{-1}).

For all the systems, the plots of the variation of the loss factor (tan(δ)) as a function of time are reported in Figure S31 and Figure S32. When considering the curing of the dry system at 50 °C (Figure S31C), it is noteworthy that the tan(δ) curves do not converge in a single point. On the contrary, it looks like they diverge in opposite directions after more than 10 h of reaction. Inflexion and drop of the curves corresponding to the highest frequencies (30 rad s^{-1} and 100 rad s^{-1}) were observed after around 6 h. This can be attributed to the vitrification of the system in the course of the crosslinking reaction. Indeed, while gelation phenomenon is governed by longer relaxation times (probed by lower frequencies), vitrification exhibits an opposite behavior by first impacting the shortest relaxation times (probed by higher frequencies).[17] This result suggests that, at 50 °C, the system vitrifies before its gel point.

To verify this hypothesis, fully cured samples were obtained for both systems by using the protocol described in the material and method section (i.e. curing for 8h), except the curing was performed at 70 °C. The *"as cured"* samples (no conditioning) were analyzed in DSC. The thermograms are represented in Figure S33. They indicate that the T_g of dry system is ~ 45 °C, while the T_g of the system cured with 5 wt% of water is ~ 35 °C.

For the dry system, when the rheology monitoring is performed at 50 °C, the curing temperature is very close to the T_g, and vitrification interferes with gelation, thus precluding the observation of the later. When increasing the curing temperature at 60 °C (Figure S31E), the tan(δ) curves converge in a crossing point for all frequencies, except the one corresponding to the highest frequency (100 rad s^{-1}). It suggests that vitrification is still impacting the sol-gel transition but to a lesser extent. At this temperature, the gel time of the dry systems TMPTC+m-XDA, t_{gel} = 5h, can be compared to that of TMPTC+EDR-148, t_{gel} = 0.9h (see Table S1). Thus, gelation is much faster in the case of TMPTC+EDR-148. This was expected for two reasons: (i) it is known that m-XDA is less reactive than EDR 148, because it is bulkier,[18] (ii) the interference of the vitrification with the gelation, in the case of the system TMPTC+m-XDA, is expected to slow down the crosslinking kinetics due to a drastic reduction of the molecular mobility in the vicinity of the glass transition.

By further increasing the curing temperature to 70 °C (Figure S32A), the tan(δ) curves converge in a crossing point for all frequencies, with no exception, meaning that gelation is no longer impacted by vitrification. Similar observations were reported in the literature for the investigation of epoxy-amine systems.[15] The corresponding values of t_{gel} and n, determined according to the procedure reported in the material and method section, are reported in Table S 7.

When considering the system crosslinked in the presence of 5 wt% of water, the plots of the variation of the loss factor (tan(δ)) as a function of time (Figure S31B, D, F and Figure S32B) indicate that vitrification interferes with gelation only for T = 40 °C. This is consistent with the T_g of the fully cured materials as measured by DSC (Figure S33B, T_g ~ 35 °C). For all the other temperatures, the convergence of the tan(δ) is observed without any indication of potential vitrification interferences. The corresponding values of t_{gel} and n are reported in Table S 7. Importantly, for T = 60 °C and 70 °C, the gel time of the system crosslinked in the presence of 5 wt% of water are substantially shorter than those of the dry system, thus confirming that water is an effective accelerator of the crosslinking process of this system as well. In the end, these experiences reveal that water can also be beneficial by allowing the curing to be performed close to the T_g of the fully cured dry network, thanks to a conventional hydroplasticization phenomenon.

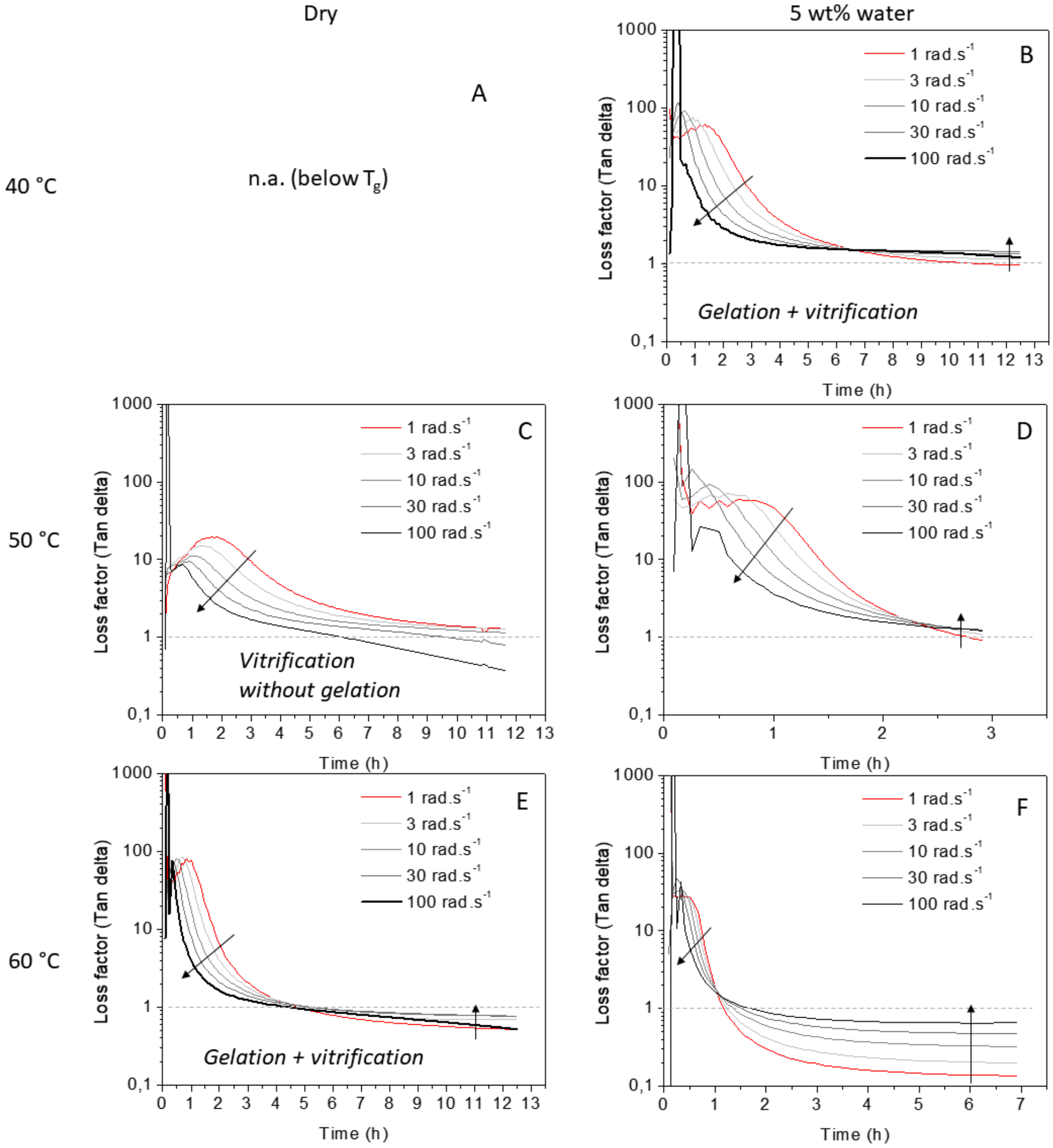


Figure S31: Variation of the loss factor ($\tan(\delta)$) as a function of time for the crosslinking reaction of TMPTC and m-XDA without additives (dry formulation) at (A) 40 °C, (C) 50 °C and (E) 60 °C, and with 5 wt% of water at (B) 40 °C, (D) 50 °C and (F) 60 °C. For the dry system, it was not possible to monitor the reaction at 40 °C (A) due to the very premature vitrification of the system at this temperature (multiwave mode, 1.97% global strain amplitude, ω = 1, 3, 10, 30, 100 rad s^{-1}, the horizontal dotted line corresponds to $\tan(\delta)$ = 1).

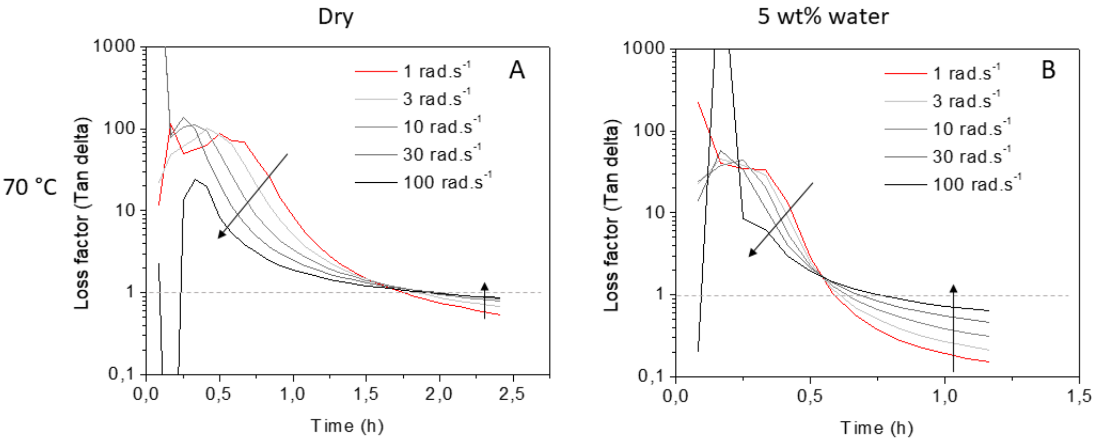


Figure S32: Variation of the loss factor (tan(𝛿)) as a function of time for the crosslinking reaction of TMPTC and m-XDA at 70 °C (A) without additives (dry formulation) and (B) with 5 wt% of water (multiwave mode, 1.97% global strain amplitude, ω = 1, 3, 10, 30, 100 rad s-1, the horizontal dotted line corresponds to tan(𝛿) = 1).

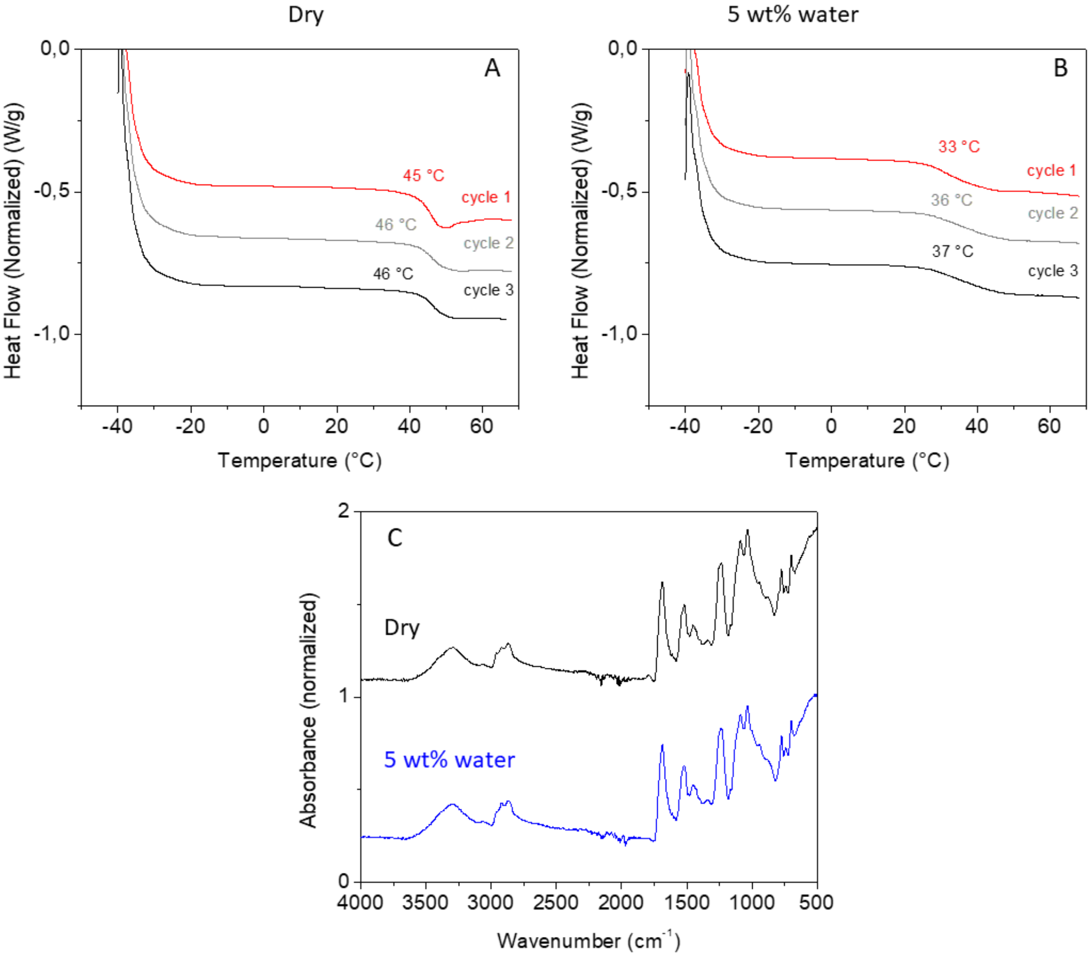


Figure S33: DSC thermograms of TMPTC-m-XDA formulations cured for 8h at 70°C with (A) no additives (dry), (B) 5 wt% of water. Samples were analyzed "as cured" (no conditioning). (C) Infrared spectra of the corresponding samples, indicating the full conversion of the 5CC at the end of the reaction for both formulations(C).

Temperature (°C)	Water content (wt%)	t_{gel} (h)	*n*
40	5	6.65[c]	0.63
50	0	n.a.[a]	n.a.
	5	2.4	0.62
60	0	5[b]	0.51
	5	1.04	0.66
70	0	1.68	0.57
	5	0.54	0.67

Table S 7: t_{gel} and critical exponent (n) values for the crosslinking reaction of TMPTC and m-XDA without additives (dry formulation) and with 5 wt% of water, at various temperatures. The values were determined according to the procedure reported in the material and method section. [a] Not provided due to interference between gelation and vitrification phenomena. [b] All Tanδ curves converge, except the one corresponding to the higher frequency (100 rad s^{-1}) attesting that vitrification interferes with the gelation. [c] All Tanδ curves converge, however the higher frequencies diverge very soon after the transition, attesting that vitrification is occurring. Higher n value is also observed compared to the one at higher temperature, contrasting with the expected trend. Similar observations were reported in previous studies.[15]

2.11. Atoms coordinates for the DFT calculations

Below are provided the xyz data for the optimized geometries of the reaction paths considering addition of an extra amine, water, t-BuOH or methanol.

Reactants, TS1 (1st transition state), IS (intermediate state), TS2_1 (2nd transition state towards 1° hydroxyl product), TS2_2 (2nd transition state towards 2° hydroxyl product), Product_1 (1° hydroxyl hydroxyurethane product), Product_2 (2° hydroxyl hydroxyurethane product).

2.11.1. Reactants

Amine

N	0	5.797554	-12.461406	-1.812203
C	0	6.359665	-13.546086	-2.620869
C	0	6.517920	-13.114485	-4.081274
H	0	5.724378	-12.758402	-0.830400
H	0	4.829425	-12.279270	-2.112840
H	0	5.775149	-14.504776	-2.593501
H	0	7.363352	-13.795916	-2.209284
H	0	7.046848	-13.920763	-4.654890
H	0	7.111250	-12.175020	-4.128533
H	0	5.511374	-12.942082	-4.529710

5CC

O	0	0.920158	1.109640	-0.021790
C	0	-0.503443	1.284021	-0.058794
C	0	-1.038566	-0.069258	0.421724
O	0	0.071910	-0.948397	0.124153
C	0	1.210307	-0.220890	-0.019773
O	0	2.303034	-0.676070	-0.128988
C	0	-2.296644	-0.559147	-0.261012
H	0	-0.768358	2.117798	0.590093
H	0	-0.803577	1.506919	-1.087246
H	0	-1.161339	-0.071008	1.510067

H	0	-2.570832	-1.552122	0.099284
H	0	-3.128550	0.118952	-0.048575
H	0	-2.158088	-0.610280	-1.343491

H_2O

O	0.40556491766611	0.04871484110243	0.00000000000000
H	-0.29327825286407	0.72895657188887	0.00000000000000
H	-0.11228566480204	-0.77767141299131	0.00000000000000

Methanol

O	5.79758957327949	-12.45684132267163	-1.85188699996645
C	6.34553824911277	-13.53268781736028	-2.58752859156927
H	5.71677670430207	-12.74861363946185	-0.92598561390658
H	6.43656493048928	-13.20214580932252	-3.64222768969046
H	5.70552883241641	-14.44961549863801	-2.58390145022239
H	7.36740671039997	-13.83343391254568	-2.24721365464484

Tert-butanol

O	5.80849560831930	-12.48252518132247	-1.90857036737312
C	6.37484524693031	-13.59235692611423	-2.62803215443868
C	6.51027738426807	-13.10320179502922	-4.07442708732178
C	5.42531044351702	-14.80113433265269	-2.54703700636599
C	7.75368743425364	-13.94187707852371	-2.03963151299527
H	5.70977576716127	-12.76977236073557	-0.98128490253399
H	6.94903243175739	-13.88723766410701	-4.72280990147162
H	7.15943116002892	-12.20567216912439	-4.11275380726452
H	5.51669339117338	-12.82392629666170	-4.47811464076056
H	5.80277685080578	-15.66303341093955	-3.13501621630084
H	4.42257077267373	-14.52529266644212	-2.93041773460865
H	5.31000424888436	-15.14068741480688	-1.49509616110047
H	8.24392420985603	-14.76589355283014	-2.59795057665595
H	7.65796897650735	-14.26691666900804	-0.98112506480691
H	8.41707307386342	-13.05434748170223	-2.06652686600162

2.11.2. Amine as shuttle

TS1

O	0	3.067201	1.128610	2.508319
C	0	1.786393	1.755827	2.436939
C	0	0.959058	0.691592	1.684590
O	0	1.895113	0.082078	0.815710
C	0	3.280102	0.435836	1.257153
O	0	3.995383	1.012160	0.371899
N	0	3.851019	-0.957825	1.640711
C	0	5.126833	-0.867429	2.370654
C	0	5.759407	-2.238821	2.606820
C	0	1.852580	3.108545	1.723633
H	0	1.426820	1.884716	3.480548
H	0	0.125408	1.132263	1.095601
H	0	0.523130	-0.049646	2.400706
H	0	3.142965	-1.464569	2.190406
H	0	5.786877	-0.221470	1.754174
H	0	4.972805	-0.330623	3.332138
H	0	6.719950	-2.115646	3.173449

H 0	5.058940	-2.875251	3.195789
H 0	5.969205	-2.725290	1.626873
H 0	0.859242	3.604655	1.720733
H 0	2.199314	2.970018	0.680852
H 0	2.577078	3.770484	2.237866
C 0	3.015364	-1.667837	-1.664801
N 0	4.190105	-1.249163	-0.880904
C 0	2.824776	-3.184747	-1.664322
H 0	2.144705	-1.165109	-1.195875
H 0	3.090300	-1.289593	-2.709151
H 0	4.213382	-0.173012	-0.695833
H 0	5.079861	-1.592602	-1.265177
H 0	1.919729	-3.448703	-2.272682
H 0	3.725170	-3.673216	-2.105296
H 0	2.682964	-3.541197	-0.619052
H 0	4.044850	-1.404892	0.365411

IS

O 0	1.041719	-0.615387	0.757359
C 0	2.055239	0.335219	0.462406
C 0	1.279149	1.611276	0.012272
O 0	-0.079656	1.165405	-0.068304
C 0	-0.082805	-0.253729	-0.085916
O 0	0.084885	-0.692005	-1.379392
N 0	-1.255809	-0.814997	0.502100
C 0	-1.645929	-0.347144	1.829747
C 0	-2.656921	-1.298301	2.473919
C 0	1.768880	2.183433	-1.313419
H 0	2.718860	-0.027178	-0.356581
H 0	2.666129	0.495185	1.373360
H 0	1.312511	2.393133	0.803549
H 0	0.256913	-1.698331	-1.307344
H 0	-2.015915	-0.764622	-0.184135
H 0	-0.721674	-0.312491	2.441881
H 0	-2.050910	0.693837	1.813430
H 0	-2.953808	-0.903135	3.481186
H 0	-3.559448	-1.377485	1.824485
H 0	-2.196305	-2.304182	2.594048
H 0	2.825592	2.516128	-1.232771
H 0	1.155021	3.055556	-1.613659
H 0	1.690242	1.409891	-2.102612
C 0	-0.520518	-4.021066	-0.237872
N 0	0.645160	-3.227732	-0.652164
C 0	-0.267737	-5.010079	0.906257
H 0	-0.914160	-4.558589	-1.128182
H 0	-1.298739	-3.292682	0.071526
H 0	1.045911	-2.738044	0.165784
H 0	1.387630	-3.827460	-1.036051
H 0	-1.217642	-5.557449	1.144902
H 0	0.516211	-5.741263	0.599784
H 0	0.074606	-4.454394	1.809487

TS2_1

O	0	0.414901	-0.822908	0.518554
C	0	1.645736	-0.237764	0.778290
C	0	1.642367	1.170067	0.113997
O	0	0.282724	1.609934	0.255094
C	0	-0.657543	0.655200	-0.073126
O	0	-0.891365	0.387166	-1.331564
N	0	-1.755915	0.726671	0.756864
C	0	-1.651708	0.810737	2.205889
C	0	-1.605771	-0.554923	2.907795
C	0	2.119940	1.194536	-1.337679
H	0	2.504032	-0.834307	0.374405
H	0	1.827835	-0.115548	1.879157
H	0	2.238151	1.891892	0.711188
H	0	-2.566064	0.234341	0.376200
H	0	-0.729986	1.386146	2.423997
H	0	-2.499655	1.420426	2.592112
H	0	-1.494986	-0.403908	4.014052
H	0	-2.549936	-1.112051	2.700680
H	0	-0.739914	-1.138305	2.527768
H	0	3.204277	0.963788	-1.384992
H	0	1.954782	2.195309	-1.784510
H	0	1.563845	0.459978	-1.948409
C	0	0.631104	-2.276954	-2.739994
N	0	-0.332512	-2.008193	-1.662896
C	0	0.018997	-2.097927	-4.130368
H	0	1.071450	-3.296230	-2.642971
H	0	1.471158	-1.562952	-2.607818
H	0	0.125971	-1.869408	-0.703489
H	0	-1.079260	-2.713988	-1.618657
H	0	0.794926	-2.313098	-4.911726
H	0	-0.837331	-2.800472	-4.253101
H	0	-0.339776	-1.051374	-4.246186
H	0	-0.747894	-0.752827	-1.598470

TS2_2

O	0	0.548177	-0.643756	0.519909
C	0	1.721443	0.079569	0.735352
C	0	1.482469	1.457263	0.069151
O	0	0.119058	1.760861	0.346013
C	0	-0.698746	0.717655	-0.025676
O	0	-0.866957	0.488230	-1.303718
N	0	-1.804812	0.613437	0.784882
C	0	-1.728284	0.640710	2.238457
C	0	-1.542241	-0.741650	2.879877
C	0	2.970630	-0.615710	0.186761
H	0	1.877678	0.258997	1.834865
H	0	1.644874	1.389755	-1.031478
H	0	2.097102	2.277911	0.486919
H	0	-2.548461	0.050818	0.367905

H	0	-0.880523	1.304405	2.499867
H	0	-2.645218	1.132197	2.635345
H	0	-1.490806	-0.633060	3.995425
H	0	-2.403385	-1.396836	2.608851
H	0	-0.598877	-1.197661	2.510999
H	0	3.886796	-0.019201	0.384987
H	0	2.885727	-0.766202	-0.910483
H	0	3.099964	-1.609045	0.660324
C	0	0.799263	-1.935767	-2.836674
N	0	-0.133595	-1.849389	-1.707891
C	0	0.077630	-1.938119	-4.185289
H	0	1.458087	-2.832496	-2.756278
H	0	1.466507	-1.049469	-2.773275
H	0	0.348835	-1.684774	-0.769901
H	0	-0.758684	-2.664431	-1.655518
H	0	0.831089	-2.014966	-5.013104
H	0	-0.618630	-2.808327	-4.233532
H	0	-0.499739	-0.993667	-4.299290
H	0	-0.683686	-0.610769	-1.581605

Product_1

O	0	4.292158	3.828473	-0.184867
C	0	3.111741	4.043661	-0.916074
C	0	2.495052	2.741615	-1.468811
O	0	3.496117	1.867868	-2.060007
C	0	4.342731	2.341033	-3.002265
O	0	4.200154	3.384648	-3.645393
N	0	5.396862	1.479960	-3.173174
C	0	5.800845	0.481798	-2.185157
C	0	6.411113	1.096886	-0.917505
C	0	1.331180	2.989188	-2.422788
H	0	5.049984	4.146195	-0.781184
H	0	3.276040	4.745477	-1.764885
H	0	2.330020	4.501729	-0.262861
H	0	2.159048	2.131533	-0.604814
H	0	6.086924	1.814628	-3.846436
H	0	4.908287	-0.118027	-1.916881
H	0	6.515907	-0.210346	-2.678384
H	0	6.676257	0.280241	-0.195236
H	0	7.329340	1.668433	-1.186262
H	0	5.673191	1.781055	-0.444676
H	0	0.537547	3.571314	-1.911040
H	0	0.889027	2.031598	-2.761726
H	0	1.674854	3.556631	-3.308991
C	0	6.055430	6.321827	-1.727348
N	0	6.084783	4.868362	-1.937689
C	0	6.433244	6.679206	-0.287602
H	0	5.017778	6.665720	-1.928263
H	0	6.709707	6.880743	-2.441240
H	0	5.648382	4.593486	-2.833849
H	0	7.048919	4.511845	-1.932253

H 0	6.303588	7.782374	-0.129194
H 0	5.776948	6.123315	0.417283
H 0	7.497270	6.402363	-0.102390

Product_2

O 0	4.684154	3.890616	-0.489813
C 0	3.369019	3.953875	-0.991646
C 0	3.282822	3.472558	-2.452232
O 0	3.841229	2.157272	-2.560319
C 0	5.103476	2.053388	-3.057798
O 0	5.660792	2.909037	-3.748361
N 0	5.655243	0.842693	-2.743106
C 0	5.219802	0.029654	-1.607523
C 0	5.662602	0.603885	-0.254213
C 0	2.743473	5.349947	-0.854625
H 0	5.296556	4.460337	-1.072204
H 0	2.772021	3.239091	-0.378851
H 0	3.826905	4.155923	-3.137361
H 0	2.227146	3.402101	-2.785424
H 0	6.627313	0.763353	-3.046580
H 0	4.115059	-0.039764	-1.646275
H 0	5.611018	-0.999252	-1.756897
H 0	5.243064	-0.025047	0.574833
H 0	6.775514	0.602352	-0.195655
H 0	5.286552	1.646661	-0.152059
H 0	1.672694	5.356914	-1.147666
H 0	3.275329	6.088286	-1.490943
H 0	2.820841	5.689617	0.196581
C 0	6.008725	6.552238	-2.630206
N 0	6.381334	5.211424	-2.171397
C 0	6.018048	7.558009	-1.476911
H 0	4.981627	6.489423	-3.054647
H 0	6.655122	6.930584	-3.460526
H 0	6.319087	4.508595	-2.931068
H 0	7.347997	5.201663	-1.819774
H 0	5.594584	8.535545	-1.829026
H 0	5.401146	7.166749	-0.638016
H 0	7.065180	7.713955	-1.127598

2.11.3. Water as shuttle

TS1

O	3.45267329091085	1.33098490733966	2.62667121295830
C	2.18323980249927	1.99784874707410	2.69989774996642
C	1.24268889920712	0.91443214001361	2.13783003716686
O	2.04840613996199	0.23976447238850	1.18092620877732
C	3.44754084000092	0.52707560636016	1.45496261340432
O	4.11307488515271	0.99588952884698	0.43643205933437
N	4.02775236219435	-0.86022049284829	1.84823829113036
C	5.34091667938233	-0.79218777961937	2.53088841929250
C	5.97075099260119	-2.17507911460845	2.66448867973790
C	2.18486048665685	3.29967094466113	1.89969095377327

H	1.98574001558321	2.19640355333816	3.77430648200002
H	0.34619036865925	1.33287288081696	1.63496405140023
H	0.90302214871377	0.21948273326316	2.94390926396432
H	3.33199387885711	-1.37446793515309	2.40713929529395
H	5.96780223838188	-0.12311743192355	1.90806994687519
H	5.21250777562787	-0.29428931973579	3.51398408824638
H	6.96063618485476	-2.10134086768671	3.15680070191585
H	5.34271345617747	-2.85460947838628	3.27882258669440
H	6.11510952203419	-2.64230520017034	1.66950242715478
H	1.21683509757186	3.83127548004400	2.01210205516461
H	2.36382912359775	3.09020463842706	0.82652273032625
H	2.99561503471386	3.96363039991997	2.25864452022590
O	4.41503547932700	-1.18031626082427	-0.57703434798376
H	3.56577671773009	-1.36368980938710	-1.02334901550801
H	4.31994161883163	-0.02673357012545	-0.28679809696404
H	4.17749496077069	-1.29752777202476	0.69498508565230

IS

O	1.10378876447087	-0.73289139061206	0.68203023505948
C	2.10017212529991	0.23809735012637	0.38347968777025
C	1.29253634636698	1.51655948128568	0.02178303698653
O	-0.04859363326518	1.02448132206871	-0.14958625833157
C	-0.01374835957693	-0.38402810816345	-0.14709404224527
O	0.13572995052881	-0.83409932890166	-1.44379145686044
N	-1.18872084699496	-0.97751490291684	0.45407892458873
C	-1.54271223831954	-0.50429690508058	1.80085190490721
C	-2.75793204844416	-1.25492502844206	2.33671229323973
C	1.79016924418376	2.22507284826417	-1.23049879416879
H	2.72495655181007	-0.08782572035144	-0.47911014948124
H	2.74750396647581	0.36469770740781	1.27311500051916
H	1.26732593995879	2.22311698590161	0.88150393257394
H	0.17166046367055	-1.83755653770380	-1.35511783963543
H	-1.96543772291199	-0.83968123730062	-0.20630582736063
H	-0.65874205066341	-0.68068179779546	2.44565107928401
H	-1.72454566778780	0.59513117963085	1.80226898012259
H	-3.01328677484438	-0.90914614797393	3.35822884347456
H	-3.65142556980824	-1.08892997409845	1.69811529083610
H	-2.56891976245827	-2.34700476780251	2.37631920349468
H	2.82899740894253	2.59015048392615	-1.08720275656037
H	1.14946210017251	3.09657165796122	-1.46892543673630
H	1.76859756261392	1.52746687741362	-2.09114763809053
O	0.06207273915747	-3.31693591083686	-0.43007936699197
H	-0.58445077791981	-2.74983666693385	0.08181983173357
H	0.88171628934270	-3.13983046907259	0.07496232187200

TS2_1

O	0.14347613488680	-0.81845596688024	0.65796520528309
C	1.36700810791205	-0.24783604737718	0.99075186296946
C	1.38951255971822	1.19522037224745	0.41546696934668
O	0.04222705549899	1.66728284478058	0.62430661731254
C	-0.94608249257962	0.82375835527167	0.20842893219654
O	-1.18280479691409	0.65111677421003	-1.07310595016358

N	-2.03218620279657	0.83093018580782	1.02818115893180
C	-1.94599012051173	0.84440517349822	2.48497625380632
C	-1.90790471036227	-0.56160797305334	3.09377564828409
C	1.83141968025635	1.27406098452715	-1.04495617321684
H	2.23767316249451	-0.81825444282312	0.57929484921742
H	1.50318592420957	-0.19904523413619	2.10044161598572
H	2.01448951412606	1.86948841229896	1.03607181944357
H	-2.84482638846364	0.37519019443925	0.60691196053999
H	-1.02976442913787	1.41057256929933	2.74074191108816
H	-2.80356903574033	1.43085195281768	2.88023681929378
H	-1.77485512017780	-0.50864732633808	4.19377033733721
H	-2.85249228272416	-1.11214262415494	2.89536031161470
H	-1.07490236590524	-1.13350653575712	2.63892932864797
H	2.92619424536094	1.10816530875185	-1.11260425563259
H	1.59679909708166	2.26630460636164	-1.47708434736166
H	1.31862644270831	0.50471073212481	-1.64951045765051
O	-0.29246934482234	-1.56929520637642	-1.62446054106846
H	0.50819344091957	-1.54761399865277	-2.18046456756978
H	0.03689448430291	-1.42621720154115	-0.59782653932303
H	-0.83085755934029	-0.30604590934589	-1.45847976931259

TS2_2

O	0.35073219090866	-0.62836727214065	0.81543270732339
C	1.55276147215967	0.06510974726401	0.97038873877591
C	1.28823811719886	1.52264525937676	0.48802748324909
O	-0.07315787019957	1.79817198761186	0.82405859253814
C	-0.89718749645409	0.84995685175433	0.30562809996586
O	-0.94059784933897	0.71001540747450	-1.00260711115803
N	-2.04535728208612	0.66610459507685	1.01166353223630
C	-2.08959898363456	0.60576252989664	2.47072397759724
C	-1.94583192779305	-0.81639805882706	3.02050196820908
C	2.72115010728963	-0.56381486529846	0.20486273092031
H	1.82419371427948	0.11213697277016	2.05713282760703
H	1.42223065903288	1.59941352802541	-0.61366321347086
H	1.90857718625327	2.28455398739841	0.99541798595198
H	-0.76537172157878	-0.31933776943259	-1.28743809950364
H	-2.75216654638801	0.13667217227241	0.49646863442726
H	-1.27080490944231	1.25420195868665	2.83651965726372
H	-3.04065823743613	1.07239670060701	2.80789585499187
H	-1.95485053876309	-0.80783376560126	4.12984976425941
H	-2.78088666046392	-1.46607149983749	2.68188825173362
H	-0.99467517446928	-1.25164539896800	2.65676702694319
H	3.65807767260679	0.01710309416433	0.33834414891861
H	2.49139705844381	-0.59990436427486	-0.88158804687321
H	2.90427172177720	-1.59829237854256	0.55666742780609
O	-0.32944147173077	-1.65634366004974	-1.31450278331490
H	0.42032497283628	-1.73327483526315	-1.93377066174649
H	0.10803179699212	-1.40529292414351	-0.36790449465098

Product_1

O	4.45896847458458	3.69687154171414	-0.22256192978439
C	3.24402926549598	4.00769573631026	-0.85802333390790

C	2.56693518223729	2.77302543638352	-1.49619275914317
O	3.52420658719175	1.87468705938065	-2.12275288354185
C	4.47627878948680	2.37350123608844	-2.93440826062337
O	4.43006806283528	3.48458012219838	-3.48726442918137
N	5.49966597529724	1.48844355481048	-3.10878629052871
C	5.78400920753958	0.37712839220352	-2.19793386751354
C	6.39342925380638	0.83698800304366	-0.86958648143129
C	1.44255935731645	3.14718432910122	-2.45490390259798
H	5.17333092423427	4.16030198412203	-0.74550731438561
H	3.38613785335825	4.78530985842820	-1.63983806024044
H	2.50743663543114	4.41475896617788	-0.12271113710469
H	2.17501278111543	2.13370647622412	-0.67855814533773
H	6.26443247378563	1.86470880223455	-3.67195902467080
H	4.83330041603633	-0.16227412748734	-2.02209349502486
H	6.45767580919262	-0.32437122459852	-2.73268280746820
H	6.55609665158535	-0.02683862574889	-0.19297017874663
H	7.37195659319296	1.33537584223958	-1.03019833528046
H	5.71746272121694	1.56196889370376	-0.37192431171243
H	0.67826179539619	3.75330264343927	-1.92626126314595
H	0.94513701955521	2.24158942053781	-2.85408350700473
H	1.84250366808113	3.73853964464651	-3.30120503376588
O	6.08690912564841	4.94748039204160	-1.98764369366561
H	5.84179001700981	5.89038892110734	-2.02659999621773
H	5.55399235936875	4.53075572169767	-2.72322755797457

Product_2

O	4.72276918232445	3.81434543533999	-0.42862652206965
C	3.42275631709779	3.94856915932752	-0.96375576791925
C	3.38321055157132	3.55373032787827	-2.45224908270385
O	3.94500977552731	2.24502617264031	-2.61721985991368
C	5.26219734947711	2.17822404230101	-2.94178764356401
O	5.89987119551462	3.09008498103479	-3.48283807864444
N	5.78598481622362	0.95068299965564	-2.66928327472213
C	5.21443637787911	0.01236716973408	-1.70144686657039
C	5.54520883501311	0.38321579467754	-0.25150391683024
C	2.84589146988751	5.35524678252399	-0.76334959789519
H	5.31824359453838	4.46483469893435	-0.90425153131283
H	2.79063364172570	3.21574204427629	-0.41243037701695
H	3.95706776058949	4.27740260829545	-3.06657886204519
H	2.34233220314322	3.50227072505023	-2.82954600420948
H	6.79016492648901	0.90171311670988	-2.85273165228100
H	4.11954297998955	0.00021721098045	-1.86015456321061
H	5.58758105059990	-1.00183518273634	-1.95575272124188
H	5.04392274278229	-0.30973722028886	0.45503941993678
H	6.63781577403970	0.32552487828003	-0.06355298444735
H	5.21676641584218	1.42123106144935	-0.03677353393441
H	1.79793952698739	5.43249240252479	-1.12076525682879
H	3.45340684093069	6.10596655288337	-1.31158106759908
H	2.87212342177766	5.61992482520121	0.31146443655301
O	6.31854392882944	5.30290906834417	-2.03249081162232
H	5.92428445101081	6.04653280800281	-2.52397762461089
H	6.28850587020833	4.54478453697951	-2.68165125529609

2.11.4. Methanol as shuttle

TS1

O	3.15348323664296	1.22382300803548	2.37727518521681
C	1.87737702861055	1.87510913993552	2.47279139837540
C	0.94265353506411	0.78491977326894	1.91623505786316
O	1.74180788493329	0.13667704697094	0.93603089059427
C	3.14378556770174	0.41818389779395	1.20607566196037
O	3.80795925576337	0.88511891730833	0.18654485393825
N	3.72351025885161	-0.97120005000278	1.60344672014941
C	5.00747696294206	-0.90302662425258	2.34045654067267
C	5.64377267510436	-2.28275925628474	2.47596403900258
C	1.85417374629363	3.18173583374168	1.68128001477070
H	1.69247083236048	2.06437615064228	3.55118015225429
H	0.03089879008004	1.19371491449253	1.43399966499628
H	0.63010747803402	0.07477051507746	2.72004900265325
H	3.01034143187508	-1.49867454229776	2.12668329267669
H	5.65470898888910	-0.21910957926528	1.75575868842606
H	4.83468332538775	-0.42306932687743	3.32542459271023
H	6.61081079823804	-2.20986144697961	3.01183189635456
H	4.99621893775005	-2.97891015306371	3.05018450160607
H	5.83550664790860	-2.73027633294538	1.47994420180510
H	0.88382955272462	3.70471536179205	1.81310073234878
H	2.01632054291436	2.98087522973583	0.60372654717608
H	2.66518489821522	3.85021563334620	2.03111163297948
C	3.12917299948404	-1.69348972152942	-1.62912119286227
O	4.20642512481377	-1.27996098568704	-0.80040552790932
H	3.09370036606510	-2.80383017874170	-1.68604179101368
H	2.14651443096796	-1.32676430891438	-1.25309498191106
H	3.26642667572767	-1.30944820651704	-2.66394378118699
H	4.06963971910443	-0.13155973286183	-0.52069368020447
H	3.92981230755198	-1.40257197592053	0.45946568655730

IS

O	0.92981899436307	-0.81102330761690	0.67303309407615
C	2.01193534430999	0.07874195274719	0.40381307456721
C	1.32660311907850	1.43838958241184	0.06869027439260
O	-0.07137493029374	1.11604334612053	0.04587424181511
C	-0.21022009249851	-0.28186740051878	-0.07284546702118
O	-0.13817180585520	-0.63681979089878	-1.40694018488730
N	-1.39211352736275	-0.78705506849212	0.53507656624428
C	-1.71374644461523	-0.31268970336094	1.88214131838682
C	-2.89133409715445	-1.08924827839427	2.46567450937179
C	1.79267340431338	2.04535440505339	-1.24940779940137
H	2.61704137528213	-0.28243074616954	-0.45796775702114
H	2.65770104575618	0.12615023741945	1.30273290905144
H	1.46688701953454	2.16578532799875	0.89814897365213
H	0.04429793553202	-1.62616935826055	-1.41169799767596
H	-2.16892368858088	-0.67912993091462	-0.12576421660591
H	-0.80725216573387	-0.46716890592306	2.50232071034400

H	-1.92309838704953	0.78321271953199	1.89839607951107
H	-3.12857036171136	-0.73631833726276	3.48947349446888
H	-3.80675974428435	-0.95697893836377	1.85038208277100
H	-2.66997040413784	-2.17483137325959	2.51175675035636
H	2.87614907214262	2.28528516320064	-1.20867123388108
H	1.24047053398291	2.98125309375184	-1.46455363099875
H	1.60953937428069	1.33050562105273	-2.07542371170669
C	-0.36395420916472	-3.98214286528804	-0.26299516012507
O	0.64418671265407	-3.11092157292451	-0.76944918154317
H	0.05232704543874	-4.71557194973611	0.46496336265007
H	-0.77888199158962	-4.55317569984011	-1.11754114765143
H	-1.18775696516943	-3.41581814789552	0.22578843010914
H	0.93508083853265	-2.52053707416839	-0.02809738324901

TS2_1

O	0.43990600256020	-0.86800862696985	0.44943277526143
C	1.70564409879929	-0.33049477402662	0.65351882914196
C	1.70393408494833	1.14568233956918	0.14468216107476
O	0.35428838465404	1.60248826065360	0.37698358162613
C	-0.61887570324109	0.75673804146454	-0.05329137922454
O	-0.79505480140956	0.56844196156561	-1.34345852917087
N	-1.72988389144993	0.76433862274226	0.73558936733711
C	-1.68306205342921	0.76973726850890	2.19506095566378
C	-1.67368599182969	-0.63673195624125	2.80317792489850
C	2.15630721444431	1.32685478096701	-1.30264582131419
H	2.51045662398632	-0.89354780543107	0.11885507928207
H	1.97062399875253	-0.33547911658686	1.74008687849492
H	2.32116178766906	1.78840327077632	0.80484258703394
H	-2.53543615011273	0.31755776035442	0.29193065086842
H	-0.76926729293249	1.32736529615001	2.47741899827744
H	-2.54568069239530	1.36355769750325	2.56797966114862
H	-1.58584554016633	-0.58401143744123	3.90777125556132
H	-2.61032152376274	-1.18551818031741	2.56578872119107
H	-0.82134083492349	-1.20739958764226	2.38412323369581
H	3.24306996694329	1.11611911360419	-1.37864845348334
H	1.97806223091141	2.36715566108651	-1.63921315424625
H	1.61159699321615	0.65015569361844	-1.98516721788888
C	0.62058070808076	-2.16027254519238	-2.63746500851146
O	-0.33547134018555	-1.81182043657925	-1.65070718981065
H	0.11257819855074	-2.27566731707776	-3.61744453157958
H	1.10531948280222	-3.13112143291866	-2.39216997818583
H	1.42619923016896	-1.39756515453580	-2.75719879016398
H	0.13973195722250	-1.59133953669528	-0.69833849133771
H	-0.69384914787200	-0.48773886090856	-1.61879611563999

TS2_2

O	0.57762302567454	-0.66013484689743	0.44775339077577
C	1.76719383021596	0.03669112268948	0.67869514244738
C	1.53338801652548	1.46893389267544	0.13228759768527
O	0.17600333942968	1.77611237792825	0.46391044877761
C	-0.67069205616102	0.81868422315394	-0.00107302813333
O	-0.78673948057222	0.67263469411937	-1.30639430344163

N	-1.78617200161834	0.65284298846837	0.76232438658561
C	-1.75577343590463	0.59815898929268	2.22169853593288
C	-1.60756079293615	-0.82392015364631	2.77079213634390
C	2.99870533563520	-0.61814395669382	0.04910557910273
H	1.94156633571539	0.12385897370910	1.78349766069070
H	1.66548591439640	1.49259078648012	-0.97245964012177
H	2.16657902540028	2.24379954704852	0.60371993817347
H	-0.65824850371583	-0.35879157341433	-1.58442802516843
H	-2.52471023603466	0.12872944830132	0.28791744461143
H	-0.90948232768680	1.23587867026719	2.54167589087843
H	-2.68024089494861	1.08137834700216	2.60621584385969
H	-1.55421772906721	-0.81023779101432	3.87883003640279
H	-2.47271406639150	-1.45905474875765	2.48354187048119
H	-0.68759165485763	-1.28101258405902	2.35684739965671
H	3.92203072530217	-0.05057047478467	0.29090087898962
H	2.90087046738487	-0.66494703937786	-1.05560145955860
H	3.12261198576489	-1.65093536598337	0.43017136878158
C	0.78186026694753	-1.81795005689156	-2.70206276456404
O	-0.17136261340369	-1.68519879409821	-1.66095148232072
H	0.25189048788960	-2.01076933292707	-3.65723214282660
H	1.46603036638062	-2.67477721172850	-2.51347605746945
H	1.40479778529532	-0.90184315097813	-2.83759461790824
H	0.31638588534036	-1.43293797988371	-0.74752102866395

Product_1

O	4.33827774137645	3.69295792091925	-0.14513678445498
C	3.13940259964937	3.97606760804987	-0.82388465413896
C	2.51199911988290	2.73429835086327	-1.49783715752626
O	3.50746650564164	1.87948197907782	-2.12886434072801
C	4.44882810793851	2.42461755020505	-2.92209027671146
O	4.37331223224974	3.54734439354784	-3.44886878671438
N	5.50303187868467	1.57818205167479	-3.10273179275330
C	5.81244470249404	0.45538124906427	-2.21426534633119
C	6.37345515761265	0.90349260708687	-0.86086473359938
C	1.39024967638359	3.09137885913189	-2.46593357966621
H	5.07490366964680	4.09068814065809	-0.68941266777229
H	3.28059485259041	4.76807711687842	-1.59094108053832
H	2.37283881962805	4.35254938684965	-0.10470351557964
H	2.13040256646541	2.06545477811334	-0.69925784231517
H	6.26183287888524	1.99171915896423	-3.64748272837336
H	4.88158106885464	-0.12732207909489	-2.07338919150434
H	6.52618279775523	-0.20262193375864	-2.75212224301713
H	6.56527821562488	0.02816775451066	-0.20707784292241
H	7.32820646681158	1.45482904102920	-0.98644011425963
H	5.65280931598207	1.57714582186144	-0.35405413085859
H	0.59707235757371	3.65798315050805	-1.93619745127780
H	0.93124516548934	2.17847636864437	-2.89362302293781
H	1.78129010324324	3.71593547218814	-3.29231235210953
C	5.92044046116645	6.32796493630159	-1.85445755470474
O	6.02438310278283	4.91316704389834	-1.87904465174923
H	6.46968157095449	6.69673863215733	-0.96522169876738
H	4.86726758207582	6.68717005906238	-1.77701896636132

H	6.37877469394823	6.79462981221135	-2.75641737911711
H	5.49481558860791	4.55855476939597	-2.64735611321004

Product_2

O	4.68564104794848	3.83378082717811	-0.44250232207259
C	3.37232966271875	3.93103696275387	-0.95318880714013
C	3.31603482451800	3.53424458947033	-2.44011245015421
O	3.90076832619920	2.23499407297807	-2.60996347075108
C	5.21201572366351	2.18828223318283	-2.95559045388764
O	5.82511709544309	3.10717567029911	-3.51505177918668
N	5.76275472595114	0.97332836837713	-2.68185059782999
C	5.22562125146162	0.03355032412440	-1.69567792487933
C	5.57394559659115	0.42500101475137	-0.25535541526530
C	2.75175637996644	5.31640425323253	-0.73638747952768
H	5.26348838701029	4.48852424325706	-0.93466495963505
H	2.77526456325543	3.17706942179216	-0.39140074182352
H	3.85975572204390	4.26647403320416	-3.07191984467741
H	2.26963201769749	3.45768165359770	-2.79715154868943
H	6.76373677465039	0.93974446880850	-2.88513643538334
H	4.12865374192282	-0.00098957057234	-1.83575707158968
H	5.61419645282592	-0.97551539457775	-1.94706524452055
H	5.09455813287681	-0.26800789169762	0.46618024675670
H	6.67011402131216	0.38611977039865	-0.08427502221972
H	5.23267173576786	1.45997976823800	-0.04578547332335
H	1.69156780582426	5.35177004813026	-1.06312981984077
H	3.30993960312857	6.09257062907992	-1.30072247885362
H	2.79622934270157	5.58055922997728	0.33799500186763
C	5.91839637665002	6.46588556549387	-2.72410268842637
O	6.29221718962995	5.27472354640115	-2.05858715688393
H	5.90146083786398	7.28862619588120	-1.98050936439207
H	4.90553737001349	6.41090935101906	-3.19278492853133
H	6.64332150861481	6.74531643390695	-3.52291004804548
H	6.24135878174885	4.51723218131400	-2.70775872109407

2.11.5. Tert-butanol as shuttle

TS1

O	3.39058002717417	0.80983304021390	2.80866679790781
C	2.06980404291182	1.28192598791428	3.11578994675748
C	1.20811720926735	0.11297120127591	2.60301322618302
O	1.93877492872773	-0.36378819108993	1.47962522135474
C	3.32118128075797	0.08701147718533	1.58598434339189
O	3.76510024384284	0.70981431496223	0.52894137303299
N	4.12255987800898	-1.22382606531621	1.78412513628516
C	5.48870931339033	-1.01922430181988	2.32306766286305
C	6.32049181400881	-2.29351875818446	2.21599741448642
C	1.77833157974405	2.61831037911335	2.43589370738576
H	2.01291060790825	1.38042360506849	4.22030189968150
H	0.19562926268039	0.42489981914472	2.27413851768669
H	1.09966395541981	-0.68040132252146	3.38208685376821
H	3.57558058120458	-1.87799789493748	2.36147504883361

H	5.93122393311454	-0.20331514765413	1.71752392675646
H	5.41596009588190	-0.64902492193555	3.36587911995243
H	7.34457900566960	-2.11872054791083	2.60119951627929
H	5.87888272957985	-3.12348724999415	2.80653685872789
H	6.39987940584604	-2.62279338584217	1.16033585216830
H	0.77508341121942	2.99433087333622	2.72532833078062
H	1.82200460431902	2.50587716662909	1.33436146675700
H	2.53546225539705	3.36945277506009	2.73499154589619
C	3.38193472578184	-1.88401166232984	-1.56780871975548
O	4.35341212261891	-1.30000679126259	-0.66713998938364
C	2.53487439454932	-2.91496883705666	-0.79986713042195
C	2.48145153164907	-0.77023234547988	-2.12682173633775
C	4.17442331156314	-2.56427378280610	-2.69256529597940
H	1.80238707285306	-3.40993480640855	-1.47024580932958
H	3.18334337239639	-3.70550189740933	-0.36674495324865
H	1.97357266541391	-2.41979218514426	0.01841490064456
H	1.74543040630218	-1.17915994861648	-2.84939315488349
H	3.09155133007403	-0.00686030946127	-2.65136518778993
H	1.93209965277424	-0.26858406680363	-1.30634456517462
H	3.49878508925486	-3.03665383264864	-3.43524348970741
H	4.84071360741631	-3.34778064832342	-2.27720954910359
H	4.80855439743353	-1.82039768326540	-3.21564757027866
H	4.06209007724320	-0.20860775799269	-0.28498431219812
H	4.21509207660143	-1.55586229768861	0.59317279601119

IS

O	1.22897064912216	-0.80522833009455	0.90026846813457
C	2.38242934100842	-0.05952064947891	0.51126531904391
C	1.84704511563032	1.38230500479784	0.25478062149077
O	0.42600397063571	1.24531550464213	0.39702372686995
C	0.09379246729943	-0.12251736071083	0.28745807714224
O	-0.03001055709293	-0.45758405607778	-1.04853401325266
N	-1.06960023716749	-0.47552804624184	1.02271494375180
C	-1.17933870196908	0.01276450637215	2.39776522657050
C	-2.34071893716682	-0.66250453666284	3.12283997023567
C	2.23321403907029	1.94034940186951	-1.11005370747819
H	2.83421197667988	-0.48681217076551	-0.41194674946232
H	3.12390456230745	-0.11036099782051	1.33263268714152
H	2.17710885267533	2.07409445602209	1.06042030432538
H	0.11956487205768	-1.44965010864093	-1.11391679914289
H	-1.89443822732041	-0.26917525563341	0.44980766302592
H	-0.22116795183709	-0.22885609876087	2.90109066912248
H	-1.28492224022452	1.12275725236802	2.43943453997636
H	-2.42013899616855	-0.29878393740031	4.16719495001173
H	-3.30912593133465	-0.44716342706008	2.62308092866941
H	-2.21029089394836	-1.76350028754776	3.14330702720160
H	3.33625329757574	2.03472272220401	-1.19671688107806
H	1.78853136162280	2.94373703468571	-1.26066444868802
H	1.86247377099987	1.26723611716404	-1.90759268592568
C	-0.01657738839012	-4.09824320743054	-0.28307616588874
O	0.81106459327644	-2.97254719479396	-0.67859599716573
C	0.40692836440215	-4.55115052953368	1.12194613378718

C	0.24578287954979	-5.19374445879957	-1.32246041004611
C	-1.49331055944006	-3.67012644884919	-0.29157959800691
H	1.05538934005874	-2.45342220695768	0.13014059396018
H	-0.18408923701956	-5.42769729602740	1.45556650375127
H	1.48033140784373	-4.83051746059258	1.13481785273787
H	0.24746189805595	-3.73262508000617	1.85474763917625
H	-0.37162372672170	-6.09179180861537	-1.11956558886073
H	1.31466032213545	-5.48647312956709	-1.31459973961318
H	-0.00106259193648	-4.82283836705526	-2.33759364454989
H	-2.15624234310446	-4.50687868040386	0.01033042276403
H	-1.79352904399174	-3.34384819530313	-1.30848718535445
H	-1.64371551717332	-2.81909067329370	0.40298234562292

TS2_1

O	0.09581859852532	-0.20243908398866	0.23413401088882
C	1.27826874623025	0.56846654961695	0.37887582871176
C	0.89310462432699	1.97299975633151	-0.14573054466749
O	-0.52414953708376	1.99945654991298	0.05722129158208
C	-1.06056667744582	0.72490213377352	-0.16323805394192
O	-1.34567391734714	0.50185761481800	-1.49132525346023
N	-2.18916517826403	0.53126528279150	0.64601172478028
C	-2.08125076634378	0.53288501158401	2.09775325326441
C	-1.76796901621387	-0.82920695355135	2.73130085380431
C	1.28620967111295	2.23104890271221	-1.59988084736682
H	2.11220476605156	0.12335756394537	-0.20784996530720
H	1.58218698146919	0.59987949353516	1.44956109381983
H	1.31114541905909	2.76918197067777	0.50471182055480
H	-2.85470653393596	-0.12712960715657	0.23728187775952
H	-1.29991161618525	1.27642451903528	2.35600347515333
H	-3.02953067353688	0.93501595085910	2.51896245693031
H	-1.71869690441584	-0.75047453010765	3.83776086140722
H	-2.55464874360160	-1.57331030816130	2.48279751287143
H	-0.80228393343073	-1.21920144641216	2.35617510003004
H	2.38958993777197	2.30246778675036	-1.69432419119686
H	0.84183791240754	3.18313995260482	-1.94985959358480
H	0.91671309452664	1.42199105543290	-2.25788918851958
C	0.25783874352205	-2.48645978858115	-2.56896852700256
O	-0.65213024981434	-2.06943493420175	-1.51716855919327
C	0.07558017242995	-1.54987399978338	-3.77485624352842
C	-0.13128561228946	-3.92563455067645	-2.93351388326532
C	1.70317067518421	-2.42404968231014	-2.05490352414952
H	-0.13719561755438	-1.63204349243524	-0.78628932556192
H	0.72554237587229	-1.85266265256226	-4.62040031638642
H	-0.97695450814853	-1.56960594048560	-4.12324698103769
H	0.32397453986643	-0.50575405832969	-3.49838608456129
H	0.48462648790833	-4.30942723512462	-3.77188572630729
H	-1.19695203792231	-3.96378046457602	-3.23542083232917
H	0.00135592067601	-4.59353337820320	-2.05885076561049
H	2.41566957376880	-2.77802944186126	-2.82679341026580
H	1.82691310458114	-3.05836952503336	-1.15357353754648
H	1.98069872979532	-1.38230423344740	-1.79271531728618
H	-1.24735455155236	-0.48570278739219	-1.65704848948142

TS2_2

O	0.52454667783239	-0.77646753575388	0.60834632437251
C	1.69268406957331	-0.04697007324462	0.75566494639839
C	1.37456957221217	1.48924102112176	0.60794687907423
O	-0.04702075242666	1.61762826836365	0.82827824798181
C	-0.81228973065548	0.69655148719362	0.20171347857325
O	-0.83420276147599	0.64713578237928	-1.10857784803966
N	-1.94612325220179	0.36532365914879	0.87914698088069
C	-1.99332693913549	0.15766036594360	2.32437915753423
C	-1.77788162066216	-1.30223498312037	2.73329504903338
C	1.82606606679092	2.11302843767342	-0.70907526696967
H	2.47750040509974	-0.31003263686395	-0.00072772542892
H	2.14888089013558	-0.22124094143867	1.76193990810770
H	1.81869145388351	2.05646290561687	1.45088273566650
H	-0.72436442782315	-0.40950582440675	-1.43744714246300
H	-2.61716394976684	-0.15349247075476	0.30832034111269
H	-1.21324432722187	0.81004089424981	2.76069280228129
H	-2.96982544313249	0.53735234648366	2.69622404584042
H	-1.81399439893530	-1.40689089992575	3.83726824989612
H	-2.56451463610898	-1.95947583611290	2.30642059316824
H	-0.79456843111735	-1.64467908835514	2.35721789280363
H	1.47885978627235	3.16269830610796	-0.78362479907261
H	1.42778897604358	1.55200026079884	-1.57291845096510
H	2.93452955170230	2.11051613915251	-0.75750920759905
C	0.48004120228639	-2.17606523787774	-2.53521501357450
O	-0.35493396896734	-1.70639105456952	-1.45520802555924
C	-0.46162596425873	-2.52515705710432	-3.69474995049102
C	1.22646409106343	-3.42370824917696	-2.03862935649423
C	1.47281468391759	-1.07830408287748	-2.95256928231494
H	0.21060939404257	-1.46237065641146	-0.54917880775093
H	0.10299458963015	-2.92802323385854	-4.55966324471343
H	-1.20130014620024	-3.28379205794571	-3.37072899706137
H	-1.01387346284406	-1.62457496710768	-4.03222770874364
H	1.85726475926917	-3.85842504378795	-2.84056374370921
H	0.50264433295665	-4.19245044448000	-1.70292572732972
H	1.88227200714332	-3.16904329842343	-1.18109438356674
H	2.11715155712692	-1.41734222496717	-3.78946213739040
H	2.13338770930217	-0.80505054237540	-2.10492336252138
H	0.93667443664973	-0.16566643329359	-3.28124345096632

Product_1

O	4.07051789737497	3.75432108863433	-0.11698145538390
C	2.84844391276180	3.86988634318900	-0.80315480836129
C	2.38283626163728	2.55104101360586	-1.46226079834968
O	3.47205352001953	1.83249016937042	-2.10889321706621
C	4.30813602559109	2.48705685960761	-2.93737762587983
O	4.07451870449036	3.58607332130704	-3.46584454113792
N	5.46004481443678	1.78344398724815	-3.14288400538395
C	5.95359845956394	0.74414238391375	-2.23582338829873
C	6.47867090694040	1.30754610617316	-0.91156359607721
C	1.20649880471425	2.74969662593124	-2.41118668419536

H	4.77936743790163	4.14950623378042	-0.70028724888003
H	2.88249490165932	4.66612139723360	-1.57785591213857
H	2.04196487980856	4.15066217992721	-0.08512123061976
H	2.10859188799525	1.84176806193326	-0.65443198501107
H	6.14609598640079	2.30122497317213	-3.69531982962467
H	5.12338199477612	0.03417858265701	-2.05427083366298
H	6.74280110969278	0.18389909222470	-2.77916687323140
H	6.84846013061566	0.49126843821417	-0.25776167635501
H	7.31112573840388	2.02005524753241	-1.08403581385029
H	5.67164318149457	1.85176310344102	-0.38053101329776
H	0.35246464068454	3.20442546284472	-1.86851408166932
H	0.86972251647131	1.78121540900700	-2.83036494676001
H	1.49478180866421	3.41891636917364	-3.24475509253790
C	5.99241746424124	6.29287434515261	-1.82372459722992
O	5.80334530574572	4.86092843143404	-1.88061299586390
C	6.48839709491655	6.58474213570236	-0.40328451199521
C	4.65734537174540	7.00438416382211	-2.09749743986965
C	7.04476943696217	6.68456390578155	-2.87432152767190
H	5.25431653649022	4.62610238344842	-2.67799314919873
H	6.66973872351545	7.66851842005334	-0.26026896514157
H	7.43342236851608	6.04003247189426	-0.20663057907089
H	5.73542740257207	6.24751566946473	0.33701274629327
H	4.77947113463559	8.10646093865524	-2.08621917722620
H	3.90620138243460	6.73229723336997	-1.32972398786315
H	4.25646523194545	6.71607135358738	-3.09152148672641
H	7.27084095620259	7.76987325220563	-2.83735619934077
H	6.68344262727915	6.44603138301882	-3.89630968685112
H	7.98405944069848	6.12308546228749	-2.69930678447092

Product_2

O	4.73204669786233	3.77988591629776	0.07349704565668
C	3.36938203098105	3.75411616652599	-0.29739808142449
C	3.18869665129107	3.32926531006834	-1.76632378166263
O	3.85679888832523	2.07763821861125	-1.98785242375473
C	5.10139551110071	2.12807991233103	-2.52393520986377
O	5.54652376528831	3.07842389988489	-3.18151876138618
N	5.78891443502932	0.97154650995762	-2.31002727112846
C	5.48209662717768	0.02295326072263	-1.23738120825292
C	5.98291128608513	0.49503985653025	0.13200416114938
C	2.65931190504588	5.08636174725378	-0.02887031401570
H	5.19980845663262	4.47028247880726	-0.47826242189536
H	2.90284965415927	2.96286931351818	0.33266220499828
H	3.60259174547444	4.09149492411737	-2.45606562100647
H	2.11925005192292	3.16440862911388	-2.00702985953959
H	6.74920692083387	1.01418655189705	-2.65682620555927
H	4.38454250462384	-0.11649246564176	-1.22342011913951
H	5.92751551654426	-0.95457181773549	-1.51751844278356
H	5.67653551130783	-0.21526366959644	0.92722000596270
H	7.09069412292638	0.56576606300861	0.15008614701845
H	5.57206166439486	1.49921271074610	0.36592641579943
H	1.57061006950490	5.02808973935503	-0.23653535959998
H	3.08715011134824	5.89113769233170	-0.66255115574002

H	2.80019256457804	5.37647606170954	1.03039059397996
C	6.09503978544803	6.51060979507684	-2.38353403395371
O	6.10706597627537	5.23991566894828	-1.70786883236201
C	6.07982238731757	7.57111250374939	-1.27730447984604
C	4.84429462972673	6.62319314175701	-3.27386302871210
C	7.37213070619221	6.62294203684237	-3.23490498666853
H	6.02177079952669	4.50758155949972	-2.37858184571844
H	6.09175449809331	8.59333948955043	-1.70494241110188
H	5.17173960636397	7.46442644746421	-0.64997445763736
H	6.96495504102913	7.45150578143837	-0.62114707080673
H	4.82346492645318	7.58708088626055	-3.82241056500160
H	3.92263855066026	6.55856829386445	-2.66098965803402
H	4.82331993554655	5.80145962260617	-4.01863491996002
H	7.43660117749759	7.60549252786486	-3.74601924660761
H	7.38962846300038	5.83053528006149	-4.01154644894508
H	8.26786382443058	6.49795495520103	-2.59459735245704

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