

THE MULTIFACETED ROLE OF WATER AS AN ACCELERATOR FOR THE PREPARATION OF ISOCYANATE-FREE POLYURETHANE THERMOSETS

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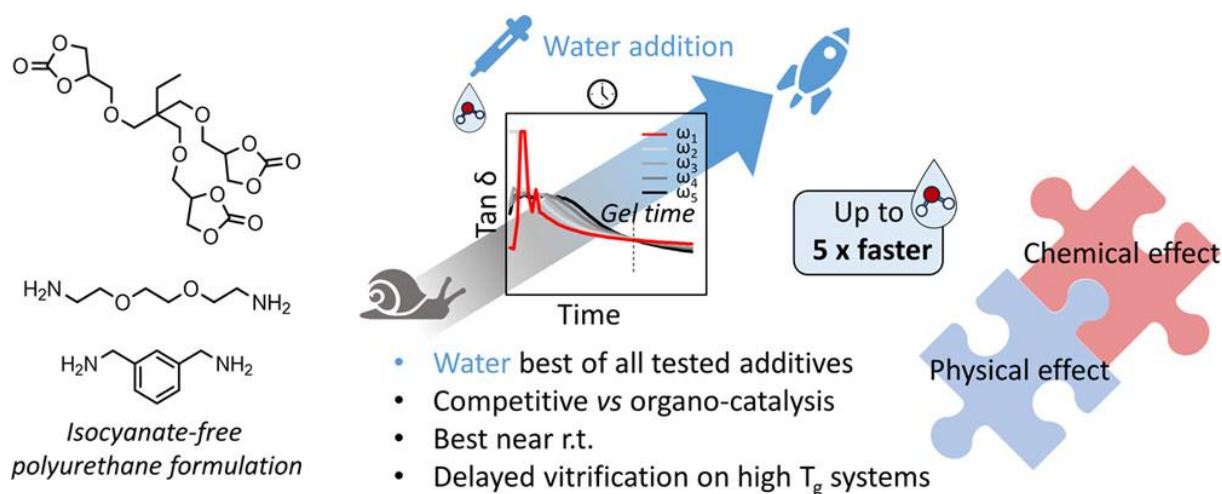
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ABSTRACT

Polyhydroxyurethane (PHU) thermosets are the most promising isocyanate-free substitutes to polyurethane ones when targeting the main applications of the PU business (coatings, adhesives, and foams). However, the curing of their solvent-free formulations at near-room temperature is slow and requires the utilization of organocatalysts, limiting the large-scale deployment of the technology. Herein, we study the impact of water, introduced as an additive (2 to 10 wt %), on the cross-linking rate of common solvent-free thermosetting PHU formulations composed of a polycyclic carbonate and a diamine. Rheology measurements, using a multifrequency approach, indicate that even small amounts of water (<5 wt %) impressively shorten gel times by up to 5-fold at 40 °C. The multifrequency methodology highlights for the first time the strong interactions of water with the growing PHU network during the cross-linking reaction. It suggests that water breaks down the multiple intra/intermolecular H-bond interactions within the PHU clusters, consequently enhancing the molecular mobility and delaying the vitrification (hydroplasticization), both phenomena that contribute to accelerating the cross-linking rate. On top of that, through a combination of model reactions and computational calculations, we demonstrate that water is an actual catalyst of cyclic carbonate aminolysis. Eventually, thanks to its multifaceted role, water can efficiently substitute the organocatalysts (e.g., TBD, DBU) usually required to cure PHU formulations at near-ambient temperature. This work demonstrates that the use of additive amounts of water in solvent-free formulations is a cost-effective, nontoxic, and robust solution to accelerate the production of PHU materials, free of any organocatalyst. It offers promising prospects for the deployment of PHU-based materials requiring mild processing conditions.



Introduction

Polyhydroxyurethanes (PHUs) obtained by the aminolysis of CO_2 -sourced 5-membered cyclic carbonates (5CCs) are one of the most promising isocyanate-free alternatives to conventional polyurethanes (PUs). (1) They are extensively investigated as PU substitutes for coating, (2,3) adhesive, (4,5) and foam applications, (6–10) to name a few. However, one of their persisting limitations is their seemingly slower polymerization kinetics when compared to isocyanate-based PUs, especially at (near-)room temperature (RT). (11) One of the main reasons is the progressive formation of a H-bonded network during PHU polymerization, due to their multiple pendant hydroxyl groups. (12,13) The intra- and interchain hydrogen bonds refrain the chains mobility and the diffusion of the monomers. Then, it is usually necessary to increase the polymerization temperature ($\geq 80^\circ\text{C}$) to observe the full conversion of the monomers over a reasonable period of time. (11) Unfortunately, this comes at the expense of side reactions. (14,15) Another alternative consists of the addition of a protic solvent to disrupt the H-bonded network and restore the chain mobility at low temperature. Alcohols, mostly methanol (MeOH), were described as excellent solvents for the synthesis of thermoplastic PHUs. (12,13)

When it comes to the synthesis of thermosets, the use of large amounts of solvent is poorly appropriate. Nevertheless, small additions of unreactive molecules, sometimes called plasticizers, are classically incorporated in thermosetting formulations to impart molecular mobility and improve the diffusion of the monomers, especially when approaching the vitrification of the polymeric network. (12,16,17) In that case, an imperative prerequisite is to use innocuous compounds, as they might leak out of the network and contribute to the emission of undesirable volatile organic compounds.

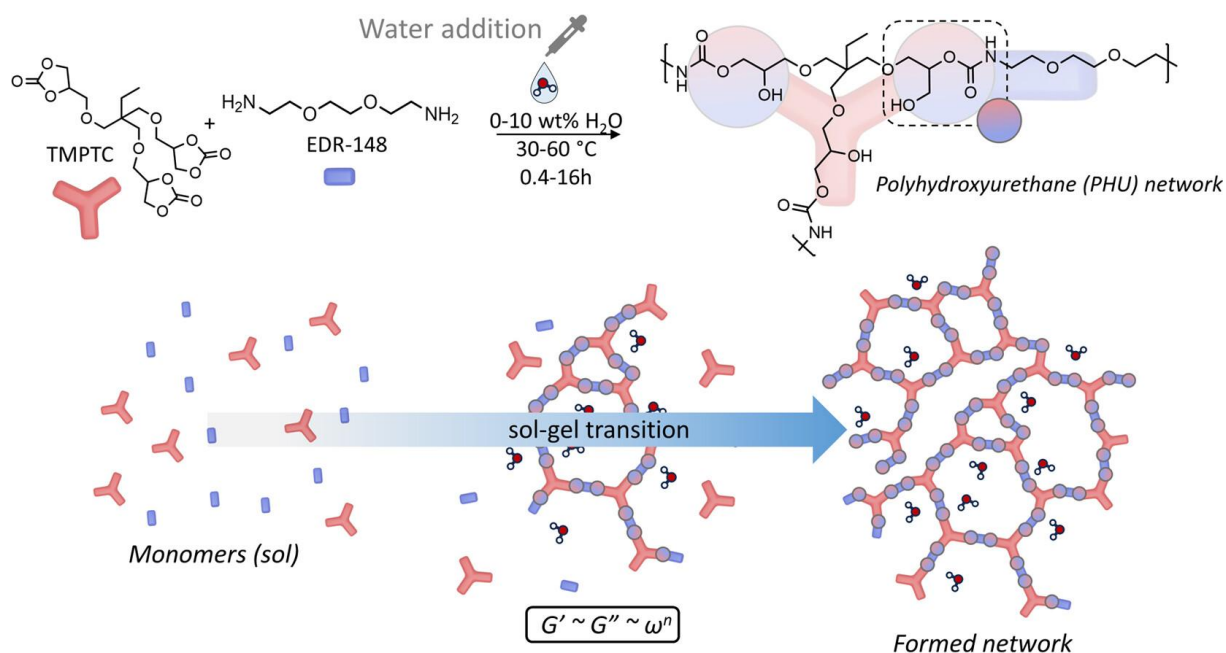
Interestingly, water (H_2O) is well-known for its ability to accelerate the cross-linking reaction of epoxy-amine formulations. (18,19) Choi et al. demonstrated that small amounts of H_2O (1 to 3 wt

%) are sufficient to significantly accelerate the curing reaction of conventional epoxy resins based on diglycidyl ether of bisphenol A. (18) In that case, a catalytic effect based on a hydrogen-bonded termolecular complex of epoxide-amine-water is suspected to be responsible for the acceleration of the reaction. This phenomenon is now of industrial importance and is used, for instance, to reduce the curing time of infusion epoxy-amine resins when repairing wind turbine blades. (20)

Surprisingly, even if the hydroplasticization of PHU thermosets by atmospheric moisture is a well-known phenomenon, (3,21–25) the impact of H₂O during the cross-linking reaction of 5CC-amine formulation has never been closely considered. It is likely that the risk to promote the undesired hydrolysis of 5CC has refrained this research axis. (26) However, recent studies demonstrated that, except at high temperatures (>100 °C) or in the presence of specific catalysts, (7) 5CCs are quite stable in aqueous media. For instance, using hydrophilic monomers, Bourguignon et al. recently reported the synthesis of PHU hydrogels at RT. (27–29) In contrast with PHU thermosets synthesized in bulk, the cross-linking time of these hydrogels are extremely fast (gel time, $t_{\text{gel}} < 10$ min), thus suggesting that water helps in accelerating the polymerization reaction. During their investigations of site- and chemo-selective synthesis of hydroxyurethanes at ambient temperature, Kleij et al. observed unexpected reactivities in catalyst-free conditions. (30) Considering that their reactions were not performed under anhydrous conditions, they hypothesized that water might contribute to the activation of the aminolysis reaction. The authors used computational calculations to propose a mechanism based on the involvement of two molecules of water acting as so-called “proton-relay” in between the N–H protons of the amine and the oxygens of the carbonate ring. However, the authors did not push further their experimental investigations to confirm this hypothesis. In particular, they did not conduct a systematic investigation by using controlled amounts of water in previously dried formulations. More recently, Salanti et al. observed that the aminolysis of a lignin-based poly-5CC was faster in water than in other conventional organic solvents for reactions conducted at 80 °C. (31) The authors concluded on a catalytic effect of water without quantifying the magnitude of this phenomenon or explaining its origin.

Herein, we study the impact of water, introduced as an additive (2 to 10 wt % with respect to the overall mass of reagents), on the cross-linking rate of common solvent-free thermosetting 5CC-amine formulations. An in-depth rheological investigation of the cross-linking reaction, using a multiwave methodology, reveals for the first time that water strongly interacts with the growing polymer network. By disrupting the H-bond interactions within the growing network and restoring molecular mobility, water contributes to a tremendous decrease in the gel times. Model reactions combined with computational calculations also demonstrate that water is an actual catalyst of the aminolysis of 5CC. In line with the current knowledge of the 5CC aminolysis mechanism, we proposed a catalytic pathway based on six-center ring transition state involving a single molecule of water. In our model, the latter acts as a proton shuttle during the ring opening of the 5CC, thus offering transition states with barrier energies lower than those of previously reported mechanisms. Eventually, we show that, thanks to its multifaceted action, water can be as effective as common organocatalysts (e.g., DBU) in accelerating the cross-linking reaction of PHU under

mild conditions. These results offer unprecedented prospects for the production of safer and cost-effective PHU-based materials under solvent- and organocatalyst-free conditions.



Scheme 1. Molecular Formulae of the Reactants Used in This Study, TMPTC and EDR148, and Schematic Representation of the Sol–Gel Transition

Results and Discussion

The experiments were performed on a formulation comprising trimethylolpropane triglycidyl carbonate (TMPTC) as a trifunctional cyclic carbonate and 1,2-bis(2-aminoethoxy)ethane, i.e., Jeffamine EDR148, as a diamine. The structures of these two very common liquid precursors of thermosetting PHU can be seen in Scheme 1. Both reactants were carefully dried before use (see the Materials section in the Supporting Information (SI)). They were first mixed in stoichiometric proportions (i.e., 5CC:NH₂ = 1:1), without any additives, before they were introduced in the rheometer (parallel plates, Ø 25 mm), preheated at 40 °C. Their cross-linking reaction was investigated through small amplitude oscillatory shear (SAOS) experiments, (32,33) using Fourier transform mechanical spectroscopy (FTMS) (34) to record the storage ($G'(\omega)$) and loss ($G''(\omega)$) moduli at different frequencies, ω , simultaneously (i.e., multiwave mode of the rheometer). In order to precisely identify the sol–gel transition, the gel time, t_{gel} , was determined using the Winter–Chambon criterion (detailed procedure in SI section 1.2). (15,35–39) According to this criterion, the relaxation modulus of the network at the gel point, also called the critical gel, follows a power law: $G(t) \sim t^{-n}$, where t is the time and n is called the critical exponent. Thus, $G'(\omega)$ and $G''(\omega)$ are expected to depend on frequency in an identical manner: $G'(\omega) \sim G''(\omega) \sim \omega^n$. This means that, at t_{gel} , the loss factor $\tan \delta(\omega) = G''(\omega)/G'(\omega)$ is independent of ω . In practice, $G'(\omega)$ and $G''(\omega)$ are monitored at different frequencies, ω , and $\tan \delta$ is plotted for all of them as a function of time. Then, t_{gel} corresponds to the intersection point of the different $\tan \delta(t)$ plots.

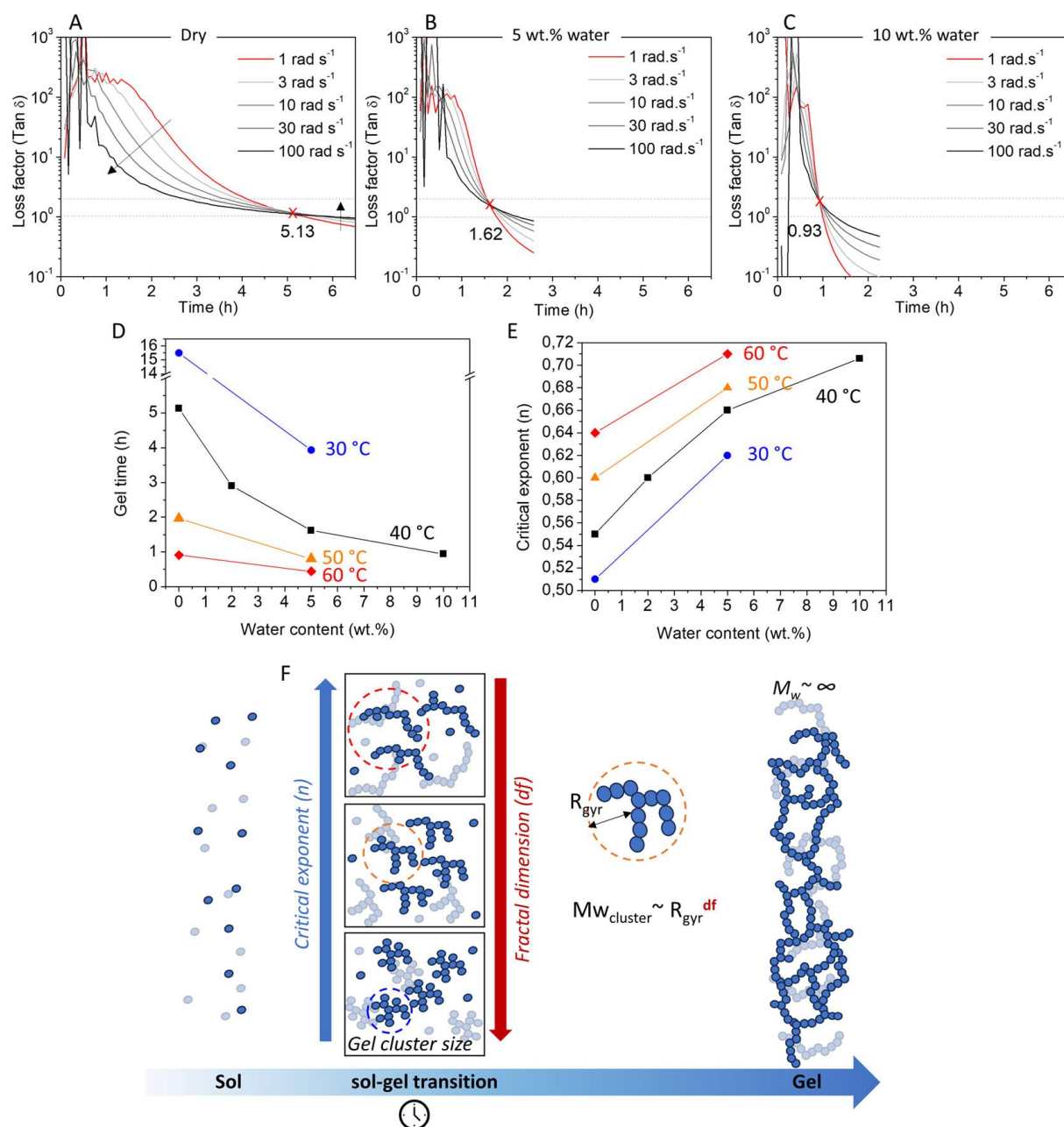


Figure 1. Variation of the loss factor ($\tan(\delta)$) as a function of time for the cross-linking reaction of TMPTC and EDR148 at 40 °C in the presence of (A) 0 wt %, (B) 5 wt %, and (C) 10 wt % of added water (multiwave mode, 1.97% global strain amplitude, $\omega = 1, 3, 10, 30, 100 \text{ rad s}^{-1}$, horizontal dotted lines correspond to loss factor values of 1 and 2). (D) Variation of the gel time, t_{gel} , and (E) the critical exponent, n , as a function of the water content (wt %) for different curing temperatures. (F) Schematic representation of the relationship between the critical exponent, n , and the dimensions (M_w and R_{gyr}) of the pre-gel clusters during the sol-gel transition.

This is represented well for the dry sample in Figure 1A. The storage and loss moduli were recorded at 5 different frequencies, $\omega = 1, 3, 10, 30$, and 100 rad s^{-1} , and the plots of $\tan \delta(t)$ intersect at $t_{\text{gel}} = 5.1$ h. This experiment was repeated for the same system with the addition of 5 wt % (Figure 1B) and 10 wt % (Figure 1C) of water, revealing the significant impact of the additive on the sol-gel transition. t_{gel} dropped from 5.1 h for the dry system to 1.6 and 0.9 h for the systems containing 5 and 10 wt % of water, respectively. This is illustrated well by plotting t_{gel} as a function of the water

content in Figure 1D (black plot). It is worth mentioning that the addition of 2 wt % of water is already sufficient to observe a significant decrease of the gel time to $t_{\text{gel}} = 2.9$ h (Table S1). For this system, the limit of water solubility was between 10 and 15 wt %, beyond which the presence of two heterogeneous phases persists even after 2 min of mixing (at RT). Thus, 10 wt % was the maximum water content considered in this study. For each experiment (curing at 40 °C with 0, 5, and 10 wt % of added water), triplicate measurements confirm their excellent reproducibility. The variation of t_{gel} was always within less than 4% of deviation.

Similarly, the effect of water was investigated at three other temperatures: 30, 50, and 60 °C (Figure S4, Table S1). The variation of t_{gel} as a function of the water content is represented in Figure 1D for all of the temperatures. The addition of 5 wt % of water in a dry formulation leads to an impressive 4-fold decrease of t_{gel} from 15.5 to 3.93 h at 30 °C, against a 2-fold decrease from 0.91 to 0.44 h at 60 °C. This temperature dependence was used to estimate the apparent activation energy of gelation, $E_{a,g}$, via a classical Arrhenius plot (Figure S5, more details in SI section 2.2). (40) A decrease of $E_{a,g}$ from around 80 kJ mol⁻¹ for the dry formulation to 61 kJ mol⁻¹ for the formulation containing 5 wt % water further illustrates the ability of water in accelerating the PHU cross-linking process, especially in a temperature window close to ambient. This was further confirmed by monitoring the reaction through IR spectroscopy (SI section 2.3). The decrease (resp. the increase) of the intensity of the band at 1790 cm⁻¹ (resp. at 1700 cm⁻¹) corresponding to the vibration of the C=O bond of the 5CC (resp. the urethanes) is much faster in the formulations containing water. Unfortunately, quantitative values of the 5CC conversion cannot be extracted from these measurements due to the impossibility of measuring the intensities of the bands at $t = 0$, i.e., before the beginning of the aminolysis reaction. However, the plots of the intensity of the band corresponding to the vibration of the C=O bond of the 5CC normalized by the intensity of the band corresponding to the vibration of the C–H bonds (at 2860 cm⁻¹) is provided in Figure S6E–G. For all the systems (i.e., dry, 5 wt % water, and 10 wt % water), the value of the normalized intensity at t_{gel} is approximately the same, thus suggesting that the conversion at the gel point, x_{gel} , is not significantly impacted by the addition of water.

We first hypothesized that one of the underlying mechanisms of the accelerating role of water is the well-known hydroplasticization of PHU resulting from the formation of hydrogen bonds between water and the pendant hydroxyl groups of the polymer. (3,21,23,24) The specific interaction of water with the growing PHU network is expected to increase the polymer chains' mobility and the diffusion of the monomers, thus contributing to an acceleration of the cross-linking reaction and a decrease of t_{gel} . Conveniently, the multiwave methodology used during the rheological monitoring provides an unprecedented illustration of this phenomenon. Indeed, in addition to the accurate determination of t_{gel} , the frequency dependence of the moduli in the vicinity of the sol–gel transition, $G'(\omega) \sim G''(\omega) \sim \omega^n$, gives access to the critical exponent, n (see SI section 1.2 for details). In the frame of the percolation theory, which 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 Figure 1F and Scheme S1. Right before gelation, it is demonstrated that the critical exponent, n , is related to the fractal dimension of the clusters, d_f . This exponent relates the mass of the objects,

$M_{w,cluster}$, to their spatial size, R_{gyr} , i.e., their gyration radius: $R_{gyr}^{d_f} \sim M_{w,cluster}$. (41) Further elaborations of the percolation theory indicate that the critical exponent varies as the inverse of the fractal dimension (SI section 1.2). With these considerations in hand, 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 . (42–44) Inversely, tightly cross-linked clusters will exhibit a large d_f and a small exponent n (Figure 1F).

Using the preceding rheological measurements, the value of n was measured for the cross-linking reactions of TMPTC with EDR148 in the presence of various amounts of water and at different temperatures (see SI section 2.2 for the detailed procedure, Figure S4). Clearly, n is an increasing function of the water content for all temperatures (Figure 1E). For instance, at 40 °C, n increases from 0.55 for the dry system to 0.71 for the system containing 10 wt % water. Considering the scaling laws of the percolation theory, it can be concluded that water results in an expansion of the clusters before the gel point, which is consistent with its expected affinity for the hydroxyl functions of PHU and the hydroplasticization effect. Let us note that n variations of similar magnitude were reported for the cross-linking of PDMS gels with the addition of small amounts of good solvents of the polymer. (43) For a given water content, for instance, 5 wt %, n increases from 0.61 at 30 °C to 0.71 at 60 °C. The temperature dependence of the critical exponent is classically explained due to variations of molecular mobility. (45,46) In the end, the multiwave investigation of the cross-linking reaction of the PHU confirms the strong interaction of water with the growing clusters of the polymer. As expected, this will disrupt the intra/interchain hydrogen bonds of the clusters, improve their molecular mobility, and in turn accelerate their growing rate (Scheme S1).

To further test the validity of our experimental approach, water was compared to other solvents (Figure 2A). We selected two alcohols (protic solvents): methanol (MeOH), described as a good solvent for the synthesis of PHU due to its ability to decrease inter- and intramolecular hydrogen bonding, and *tert*-butanol (*t*-BuOH), a bulkier alcohol. Three nonprotic polar solvents were also tested including dimethyl sulfoxide (DMSO) and two ethers: tetrahydrofuran (THF) and glyme. They are all good solvents of the precursors. They were first compared for a constant loading of 5 wt %. Rheology data are provided in SI section 2.4 (Figures S7 and S8, Table S3). The gel times are reported in Figure 2B (points located on the same vertical dashed line). All the nonprotic solvents have a very similar impact on the cross-linking reaction with $t_{gel} \sim 4$ h, i.e., a moderate acceleration as compared to the additive-free system ($t_{gel} \sim 5$ h), without common measure with water ($t_{gel} \sim 1.6$ h). For MeOH, $t_{gel} \sim 2.6$ h. This is the shortest gel time of all of the tested solvents after water. Surprisingly, *t*-BuOH exhibits the longest gel time ($t_{gel} \sim 4.4$ h) of the series. Similarly, the critical exponent results are reported in Figure 2C (points located on the same dashed line). The use of all the solvents results in an increase of n as compared to the additive-free system but of smaller magnitude than water. Again, MeOH ($n = 0.64$) is responsible for the biggest increase after water ($n = 0.66$). Back to the percolation theory, this observation indicates that MeOH induces a substantial expansion of the pre-gel clusters, just like water and in good accordance with its ability to reduce t_{gel} . Once again, the protic character of the two substances and their hydrogen bonding capability with the growing PHU seem to contribute to their ability to accelerate the cross-linking reaction. The contradictory performance of the other protic solvent, *t*-BuOH ($n = 0.59$), is likely due to its

lower affinity with the PHU clusters, as compared to MeOH and water. This is confirmed well by the swelling experiments performed later in this study (Table 1).

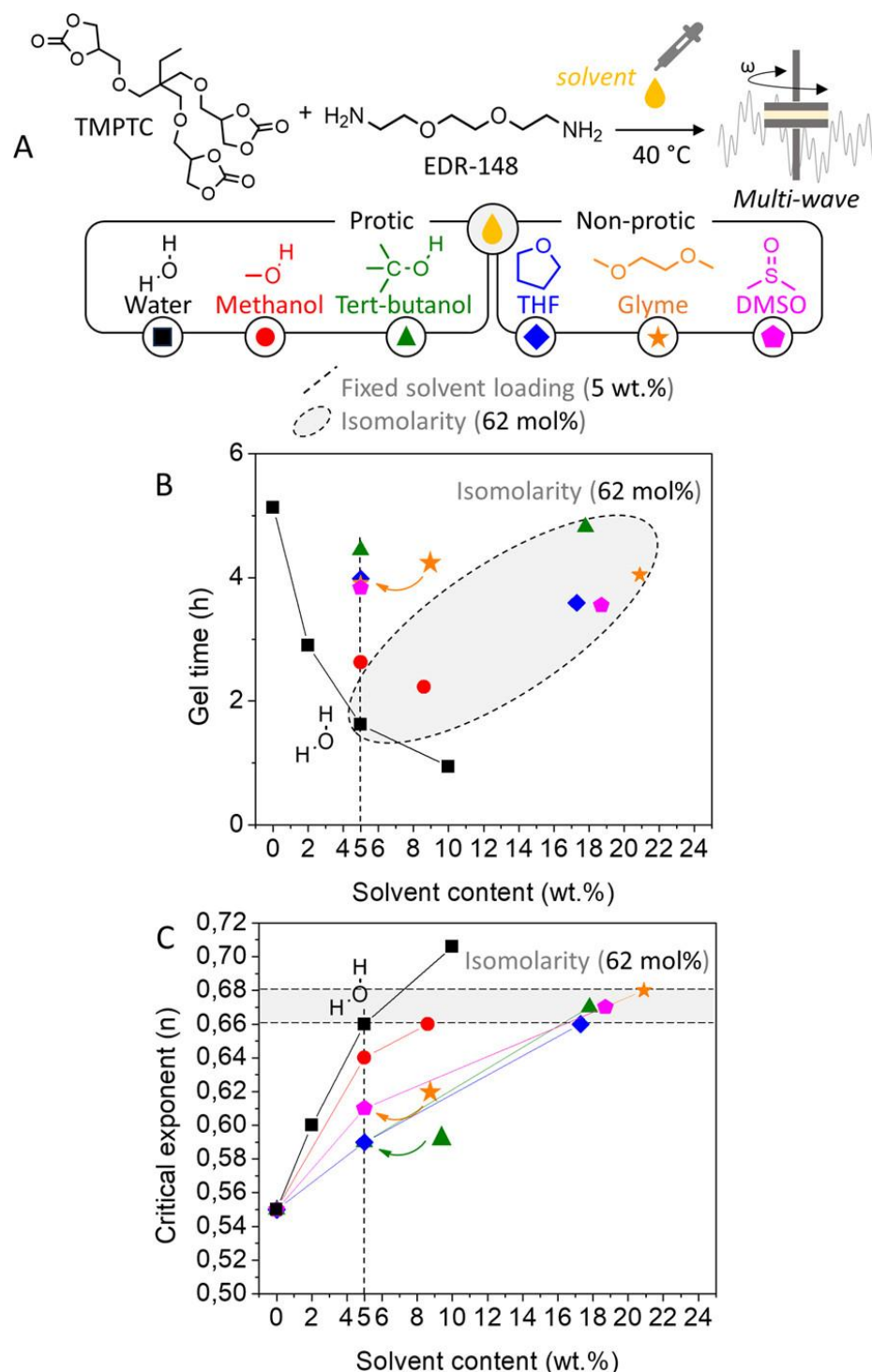


Figure 2. (A) Solvents tested as additives for the cross-linking reaction of TMPTC and EDR148 at 40 °C. (B) Variation of the gel time, t_{gel} , and (C) the critical exponent, n , as a function of the solvent content (wt %) for the different tested solvents. The solvents were compared at both a fixed mass loading (5 wt %) and a fixed molar content (62 mol % with respect to 5CC).

Table 1. Swelling Behavior and Gel Content in Different Solvents for the PHU Thermosets Cured under Dry Conditions or in the Presence of 5 wt % Added Water

sample	swelling solvent	Swelling index (SI, %) ^d	linear swelling ratio (λ) ^e	gel content (GC, %) ^d
no additive, dry^{a,c}	H ₂ O	47	1.15	91
	THF	66	1.21	98
	MeOH	92	1.31	90
	<i>t</i> -BuOH	11	1.03	>99
H₂O, 5 wt %^{b,c}	H ₂ O	52	1.13	91
	THF	68	1.19	99
	MeOH	103	1.34	88
	<i>t</i> -BuOH	11	1.04	>99

^a Materials prepared from the cross-linking reaction of TMPTC with EDR148 (5CC:NH₂ = 1:1) after 8 h of curing at 50 °C. ^b Same as *a* with 5 wt % of added water. ^c Before immersion in the swelling solvents, the samples were dried 16 h at 50 °C under vacuum. ^d Typical error bar is $\pm 1\%$. ^e Typical error bar is ± 0.03 .

It is worth noting that by using a constant mass loading for all the solvents, their molar percentage as compared to the monomers is much smaller than that of water, the additive with the smallest molar mass. Thus, all of the solvents were further compared by using the same molecular content. They were used at ~ 62 mol % (or 0.62 equiv) with respect to 5CC moieties (this corresponds to the molar ratio of water when it is used at 5 wt %). The gel times, t_{gel} , and the critical exponents, n , are reported in panels B and C of Figure 2, respectively (points located in the same elliptic or horizontal gray area). Interestingly, at this molar ratio, all the solvents induce a similar, or even longer, gel time than previously reported at 5 wt % loading. The increase of the molar ratio does not improve their ability to accelerate the cross-linking reaction. However, for all of them, the critical exponent is now close to $n \sim 0.67$, i.e., the value reported for water. In reality, for these mass loadings (~ 18 –20 wt %), it is likely that the excessive dilution of the monomers cancels the potential benefits of the increase of the molecular mobility of the clusters. For instance, Palmese et al. reported a decrease of the cross-linking kinetics of epoxy-amine formulations containing ≥ 20 wt % THF. (47) When considering MeOH, the increase of its molar ratio results in a further decrease of t_{gel} (~ 2.2 h), just like water. Contrarily to the other solvents, the corresponding increase of its mass loading is moderate (62 mol % = 8.6 wt %), thus limiting the risk of a dilution effect.

In order to evaluate the affinity of the tested solvents with the PHU network, fully cured samples of PHU (TMPTC + EDR148, 5CC:NH₂ = 1:1, 50 °C, 8 h) were prepared for swelling experiments. Vacuum-dried samples (16 h, 50 °C) were swollen in water, MeOH, and *t*-BuOH as protic solvents as well as in THF. Their swelling index (SI) as well as their linear swelling ratio (λ) were measured over a period of 48 h (SI section 2.5, Figure S9). The stabilized values of SI and λ are reported in Table 1, along with the estimation of the gel content (GC). Clearly, water, MeOH, and THF are good swelling

solvents of the PHU network with an SI and λ comprised between 47% and 1.15 for water and 92% and 1.31 for MeOH, respectively. These results indicate that water is not the best swelling solvent. However, they reveal that its affinity with the PHU network is much bigger than its affinity with the starting monomers. Indeed, ~47 wt % water can swell the PHU network, while no more than ~10–15 wt % of water can be added to the initial mixture of TMPTC + EDR148. It indicates that, during the cross-linking reaction, water will have much more affinity for the growing PHU clusters than for the mixture of monomers. Water will greatly contribute to the expansion of the clusters, which is in accordance with the large increase in the critical exponent n . Inversely, *t*-BuOH affinity for the PHU network is significantly lower than the rest of the tested solvents, with SI ~ 11% and λ ~ 1.03. In comparison, we were able to add ~20 wt % of *t*-BuOH to the initial mixture of TMPTC + EDR148 (Figure 2C), thus suggesting that it has a better affinity for the monomers. Again, this observation correlates well with the rheology results and the very limited increase of the critical exponent n observed with *t*-BuOH.

Evidently, these series of rheological experiments combined with swelling tests demonstrate that small protic molecules are excellent accelerating agents of the cross-linking reactions of PHU. They also suggest that the underlying acceleration mechanism is the specific interaction of these protic solvents with the PHU clusters of the critical gel via hydrogen bonding, even at a very small mass loading (~5 wt %). Clearly, under all of the tested conditions and within the limit of its solubility with the monomers, water always provides the shortest t_{gel} .

It led us to think that water might also play the role of a catalyst of the aminolysis reaction, just like it does for the addition of amine onto epoxides. (18,48) To test this hypothesis, a simple model reaction was performed by mixing propylene carbonate (PC) with our diamine (EDR148) in dilute medium (DMSO, [PC] ~ 5 mol L⁻¹), both in dry conditions and in the presence of a controlled amount of water (Figure 3A). Dried precursors were first mixed together in a closed vial to prevent moisture uptake, and the reaction was performed at 40 °C under continuous stirring. The same reaction was then performed in the presence of 0.62 equiv of water as compared to PC, i.e., the H₂O:5CC ratio used in the thermosetting formulation containing 5 wt % water. Both experiments were also performed at 25 and 60 °C. Figure 3B displays the NMR spectra of the model reactions containing water, after 420 min, for the different temperatures (detailed NMR results in SI section 2.6, Figures S10–S21). The consumption of PC is attested by the disappearance of the doublet **a** at 1.37 ppm, while the concomitant formation of the two regioisomers of hydroxyurethane is confirmed by the appearance of the doublets **b** and **c** at 1.05 and 1.15 ppm, respectively. The PC conversion as a function of time is plotted for the different model reactions in Figure 3C (the corresponding values of the integrals of the peaks are shown in Figure S20). Clearly, for all temperatures, the kinetics are faster in the presence of water. For instance, at 40 °C, the time needed to reach 50% PC conversion is reduced from ~280 min for the dry systems to ~150 min for the system containing 0.62 equiv of water, i.e., a decrease by a factor of ~2. Triplicates of the reactions performed at 40 °C (Table S4) confirm the excellent repeatability and support the significance of these results. Because these experiments are performed in diluted conditions, where the role of water as an enhancer of molecular mobility through hydrogen bond disruption is completely overlapped by the solvent (i.e., DMSO, an excellent hydrogen bond disruptor), it can be

concluded that water is a true catalyst of 5CC aminolysis. Figure 3C clearly suggests that at higher temperature (e.g., 60 °C), the difference between the reaction rate of the noncatalyzed (dry) and catalyzed (5 wt % water) systems decreases. This is consistent with the increase in the probability to overcome the energy barriers at higher temperatures for both systems.

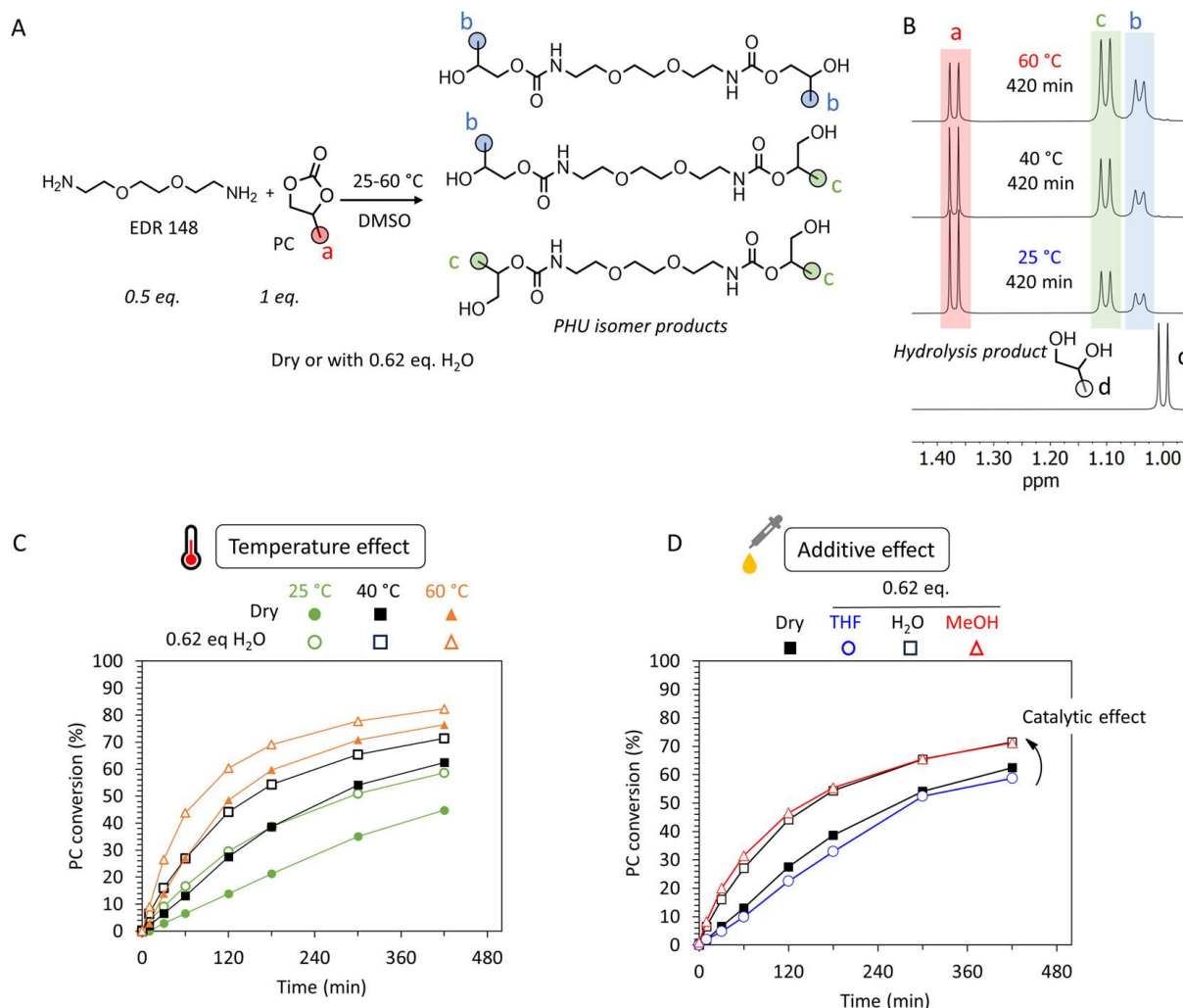


Figure 3. (A) Model reaction between propylene carbonate (PC) and EDR148, performed in dry DMSO at various temperatures, both in dry conditions and with added water (0.62 equiv as compared to 5CC). (B) NMR spectra of the model reactions in the presence of water after 420 min at various temperatures. The comparison with the NMR spectrum of propylene glycol (bottom spectrum) indicates that the hydrolysis of PC is negligible under these conditions (full NMR analyses are provided in Figures S10–S21). (C) PC conversion as a function of time at various temperatures in dry conditions and with added water. (D) PC conversion as a function of time in the presence of different additives (H₂O, MeOH, and THF, 0.62 equiv as compared to 5CC) at 40 °C.

Importantly, the comparison of the NMR spectra of the model reactions to that of propylene glycol (PG), the hydrolysis product of PC (Figure 3B), confirms that PG is not formed in a quantifiable amount during these experiments. To validate that this is also the case during the cross-linking reactions, i.e., in bulk, the same model reactions were conducted in solvent-free conditions (Figure S22, Table S5). The results indicate that only 2 to 3 mol % of the 5CC is converted in the hydrolysis product under these conditions and confirms that the extent of this side reaction is very limited for

the cross-linking reactions as well. It is worth noting that, in bulk, the model reactions are nearly quantitative with PC conversions >90% after 7 h (Table S5).

Water was then substituted with MeOH and THF under the same diluted conditions (DMSO, [PC] ~ 5 mol L⁻¹). Figure 3D indicates that MeOH displays catalytic activity comparable to that of water, while THF has no impact on the kinetics (i.e., same conversion profile as the additive-free system). These results are in accordance with the trend observed in the rheology results.

Given the work of Kleij et al., a mechanism based on a hydrogen-bonded tetramolecular complex involving two molecules of water could be considered (concerted “proton-relay” catalysis). (30) However, the free energy barriers reported by the authors are high (~24 kcal mol⁻¹) and do not seem to reflect the magnitude of the catalytic effect of water observed in our study. Moreover, the molecularity of this mechanism, i.e., two molecules of water for one molecule of 5CC, is unlikely in our case given the substoichiometric amount of water used as a reference (i.e., 62 mol % or 0.62 equiv vs 5CC). For all of these reasons, it appeared reasonable to consider another possible mechanism. In particular, it seemed more appropriate that the catalytic activity of protic compounds such as H₂O and MeOH could be rationalized through a mechanism that was already described for amine R-NH₂. Indeed, it is well accepted that amines accelerate their own addition on carbonates (cyclic or linear) through a two-step mechanism (Figure 4, X = NH). (49–53) The catalytic amine acts as a proton shuttle, forming a six-center ring transition state, TS1, leading to an intermediary state, IS, corresponding to a cyclic amino alkoxide anion interacting with a NH₃⁺ ammonium. When H₂O or MeOH are considered, they may play a similar role with an IS made of the same anion in interaction with a hydronium cation (H₃O⁺, X = O, R = H) or a methoxonium cation (MeOH₂⁺, X = O, R = Me), respectively. To test these hypotheses, DFT calculations were conducted to compare the catalytic activity of R-NH₂, MeOH, and H₂O (SI section 2.7, Figures S23 and S24). The Gibbs free energy of TS1 is reported in Figure 4 for the formation of primary hydroxyurethane. Clearly, for the rate-determining step, TS1 is approximately 3 kcal mol⁻¹ smaller in the case of MeOH and H₂O compared to R-NH₂, thus suggesting that they are performing better as proton shuttles and therefore exhibit better catalytic activity. The same trend is confirmed for the formation of secondary hydroxyurethane (Figure S23B). Importantly, the free energy barriers calculated in these scenarios (~10–15 kcal mol⁻¹) are much smaller than those reported by Kleij et al., thus supporting that the proton shuttling mechanism seems to be more appropriate than the “proton-relay” hypothesis they proposed. To reinforce the accuracy of the computational method, energy minimization was performed through the nudged elastic band (NEB) method. (54) Three initial spatial dispositions of the molecules were envisioned: (i) H₂O in closer proximity of 5CC, (ii) H₂O in closer proximity of NH₂, and (iii) H₂O equidistant from 5CC and NH₂. The corresponding NEB paths with up to 24 intermediate images are provided in Videos S1, S2, and S3, respectively. In all cases, the minimum energy path leads to a single transition state geometry corresponding to TS1, thus supporting our initial hypothesis. In the end, these calculations are in line with the results of both the rheological measurements and the model reactions. Interestingly, it can be hypothesized that the hydroxyl groups formed in the course of the polymerization might be involved in the catalysis of the reaction as well. This was already suggested by other authors. (55) The careful consideration of the conversion plots obtained for the dry systems (Figure 4C) reveals a slightly

sigmoidal evolution that could be consistent with autocatalytic behavior. However, an in-depth investigation of the reaction kinetics using hydroxyurethanes as a catalyst will be necessary to fully corroborate this hypothesis. In practice, in a thermosetting network, the hydroxyl groups will play two antagonistic roles: (i) their well accepted role as hydrogen bond promoters, resulting in the formation of a physical network that impairs molecular mobility and the progress of the reaction, and (ii) their potential role as proton shuttles for the catalysis of the aminolysis reaction. At this stage, our experiments do not permit us to predict if the predominance of one role over the other evolves as the cross-linking reaction proceeds. The same interrogation applies for the different roles played by water, i.e., plasticizer vs catalyst. Advanced calculations such as reactive molecular dynamics (56) could provide a deeper understanding of the system in future investigations.

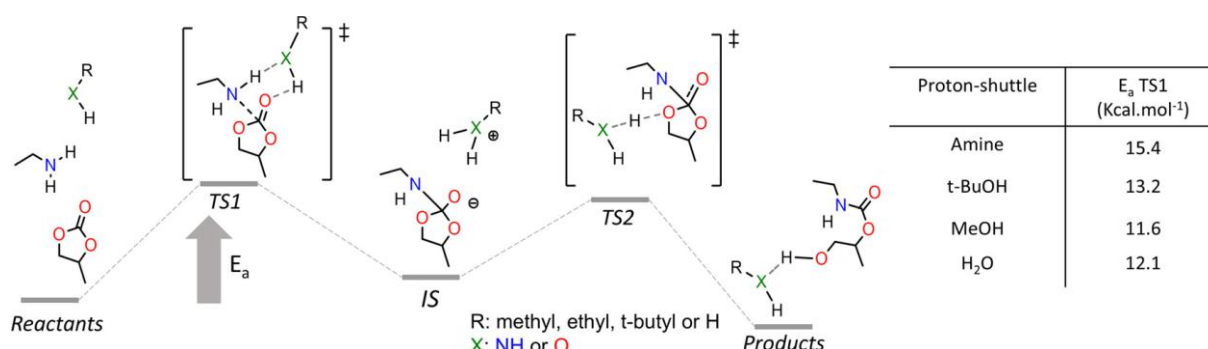


Figure 4. General representation of the energy levels of the transition states (TS) and intermediate states (IS) for the mechanistic pathway corresponding to the reaction of ethylamine with propylene carbonate in the presence of a proton shuttle catalyst (R-XH). The Gibbs free energies of TS1 obtained via DFT calculations are provided in the table for the different proton shuttles considered in this study. The full DFT calculations are available in SI sections 2.7 and 2.11.

These very promising results encouraged us to compare water to conventional organocatalysts of the 5CC-amine reaction. Indeed, when prepared in mild conditions ($RT \leq T \leq 50$ °C), PHUs are classically obtained with the help of catalysts such as bicyclic amidines (e.g., DBU) or guanidines (e.g., TBD). (14,57,58) They are known to favor faster kinetics and higher yields. However, due to their very strong pK_a , they can also activate a number of undesirable side reactions including 5CC hydrolysis, when water is present, (7,26,27) or amide formation, when the precursors contain ester functions. (15) Moreover, amidine and guanidine are expensive chemicals and can pose safety issues when leaking out of the polymer network.

Here, we decided to compare the gel time and the critical exponent, n , when curing the TMPTC/EDR148 formulation in the presence of water vs DBU or TBD. For all the additives, we used a conventional catalyst loading, e.g., 3 wt %, and the curing reaction was performed at 40 °C. The full rheological investigations are provided in the SI (section 2.8, Figure S25, Table S6). The variations of t_{gel} and n are represented in Figure 5. Clearly, water provides the shortest gel time, $t_{gel} = 2.2$ h vs $t_{gel} = 2.5$ and 4.6 h for DBU and TBD, respectively. Impressively, water can compete with a well-established liquid organocatalyst such as DBU. When the variation of the critical exponent is considered, n is larger in the case of water (0.63), thus confirming that one of the underlying accelerating mechanisms relies on the interactions of water with the PHU clusters. The smaller value of n in the case of DBU (0.58) indicates that this catalyst has a milder impact on the dynamics

of the clusters in the vicinity of the gel point, which is mostly due to its smaller molar content compared to that of water (5 mol % for DBU against 42 mol % for water). From this viewpoint, the very small molar mass of H₂O can be seen as a strong advantage over conventional organocatalysts, as it enables improvement of the molecular mobility of the growing network even at very low mass loading. Concerning TBD, a solid compound, it is of low activity here due to its lack of solubility in the solvent-free formulation. Its efficient use would require an organic solvent to guarantee its homogeneous addition to the PHU precursors. From the perspective of the principles of green chemistry, using water instead is a much more sustainable alternative.

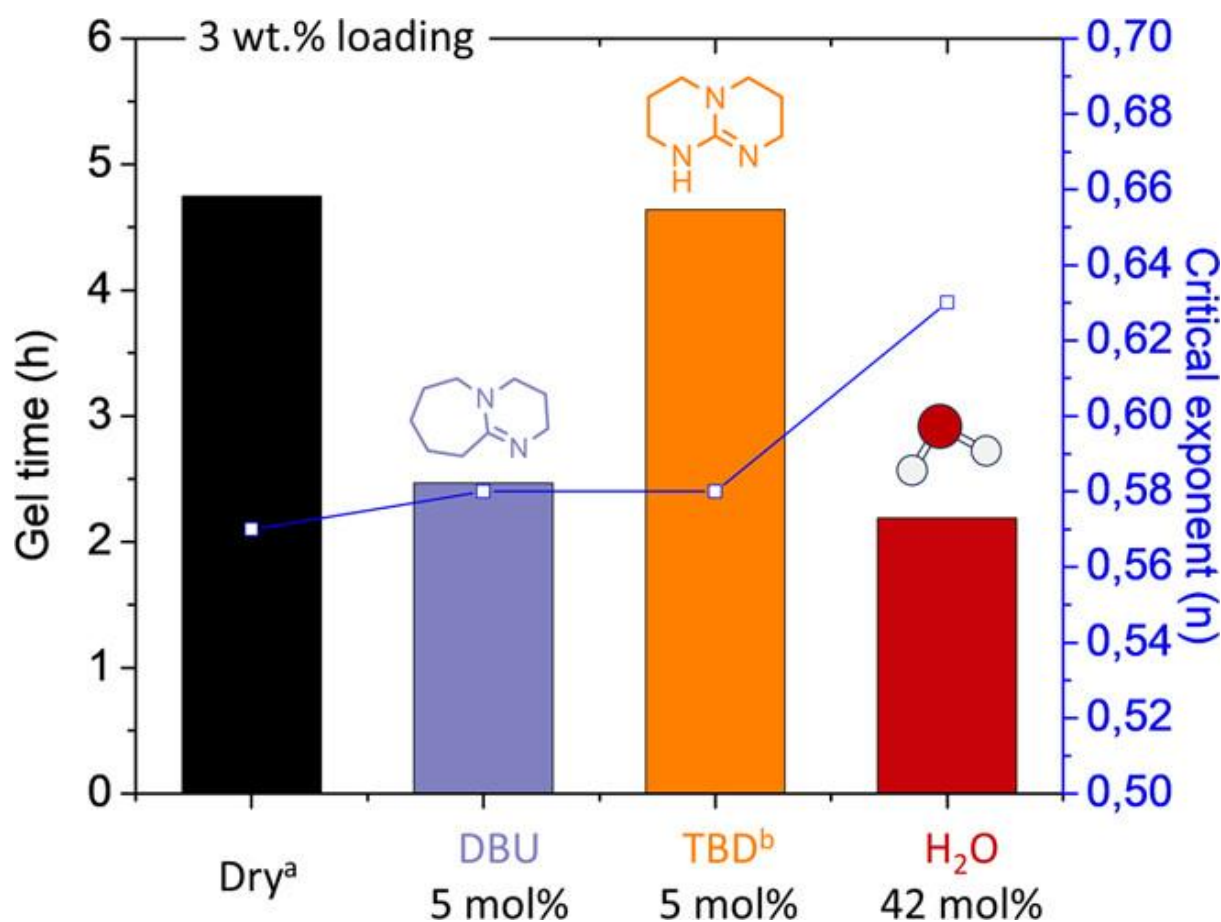


Figure 5. Gel time, t_{gel} , and critical exponent, n , for the cross-linking reaction of TMPTC and EDR148 at 40 °C in dry conditions and in the presence of 3 wt % DBU, TBD, or water. Note a: the dry experiments were performed with a different model of the rheometer. This explains the slight difference of t_{gel} compared to the results presented in Figure 1; see the SI for details. Note b: TBD was not miscible in the formulation.

To confirm the practical relevance of water, the thermomechanical properties of the different networks were compared. Knowing that these properties are strongly impacted by atmospheric moisture, (24,25,59) the samples were subjected to accelerated conditioning in an atmospheric chamber to ensure a consistent comparison. 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 via differential scanning calorimetry (DSC), and the mechanical properties of the conditioned samples were investigated via tensile testing. The DSC thermograms as well as

the tensile profiles are available in SI section 2.9 (Figures S26–S28). The T_g values, tensile moduli, E , stress at break, σ_b , and strain at break, ϵ_b , are detailed in Table 2.

Table 2. Thermal and Mechanical Characterizations of the PHU Thermosets Cured under Dry Conditions or in the Presence of 5 wt % Added Water and 3 wt % Added DBU

	as cured	dried	equilibrated at 50% RH			
sample	$T_g, 1$ (°C) ^d	$T_g, 2$ (°C) ^e	$T_g, 3$ (°C) ^f	E (kPa) ^g	σ_b (kPa) ^h	ϵ_b (%) ⁱ
dry (catalyst-free)^a	0	13	–6	7.9 ± 0.27	1.09 ± 0.18	197 ± 41
water (5 wt %)^b	–7	10	–6	5.6 ± 0.18	0.98 ± 0.12	258 ± 39
DBU (3 wt %)^c	10	12	–10	7.4 ± 0.15	0.83 ± 0.11	155 ± 28

^a Materials prepared from the cross-linking reaction of TMPTC with EDR148 (5CC:NH₂ = 1:1) after 8 h of curing at 50 °C. ^b Same as a with 5 wt % water. ^c Same as a with 3 wt % DBU, corresponding to around 5 mol % catalyst with respect to 5CC, a common catalyst loading in the literature. ^d Glass transition temperature of the “as cured” sample on the 1st DSC cycle. ^e Glass transition temperature of the cured material after drying at 50 °C under vacuum for 16 h on the 3rd DSC cycle. ^f Glass transition temperature of the priorly dried materials after conditioning in a climatic chamber for 24 h at 25 °C and 50% RH on the 1st DSC cycle. ^g Young Modulus. ^h Stress at break. ⁱ Strain at break of the priorly dried materials (50 °C under vacuum for 16 h) conditioned for 24 h at 25 °C and 50% RH, average on 5 replicates per sample.

Directly after curing, the water-cured sample exhibits the smallest T_g , –7 °C, which was expected given the strong plasticization ability of water (Figure S26). After the drying step, all samples exhibit similar T_g values, comprised between 10 and 13 °C, thus suggesting that, in these conditions, the samples are essentially the same (Figure S27). This is further confirmed by comparing their IR spectra (Figures S29 and S30), which are superimposable. The same observation is valid after conditioning at 50% relative humidity, with T_g values comprised between –10 and –6 °C. Remarkably, the tensile testing indicates that all the conditioned samples behave as rubbery elastomers with very similar behavior at break (Figure S28), although both the water-cured and DBU-cured samples exhibit discrepancies compared to the neat sample. A decrease of the tensile modulus is observed in the case of the water-cured sample, while a decrease of the stress and the strain at break is noticed in the case of the DBU-cured network. These differences are very certainly due to a small extent of side reactions. They potentially include some 5CC hydrolysis during the cross-linking reaction for the water-cured samples (see the model reactions in Figure S22) or main chain degradation catalyzed by DBU during the conditioning step for the DBU-cured sample, as previously reported by other authors. (60) In any case, the magnitude of these differences is classical for thermosets cured with different catalytic systems. They are well accepted when compared to the benefit in terms of curing time, especially for applications such as coatings or adhesives.

Finally, to further exemplify the general potential of water as an accelerating agent of the cross-linking reaction of PHU, it was tested for the reaction of TMPTC with another common and more hydrophobic diamine, *m*-xylylenediamine (MXDA, Figure 6A). The cross-linking reaction was monitored through multiwave rheological measurements at 70 °C for the dry system and the

system containing 5 wt % water. The evolution of the $\tan(\delta)$ curves as a function of time is represented in Figure 6B,C. A significant decrease of t_{gel} from 1.7 to 0.5 h is observed, thus confirming that water accelerates the cross-linking reaction of this more hydrophobic system as well. It is worth noting that, for this system, the T_g of the dried, fully cured network is $\sim 45^\circ\text{C}$ (SI section 2.10, Figure S33A,B). Thus, when monitoring the reaction in rheology for the dry system at temperatures lower than 70°C , vitrification interferes with gelation (SI section 2.10, Figure S31A,C,E). Such behavior is in agreement with other works on high T_g thermosets. (61) Conveniently, the addition of 5 wt % of water lowers the T_g of the growing network (hydroplasticization), which enables the system to cross-link even at 40°C while limiting the impact of vitrification (Figure S31B,D,F). Noteworthy, the critical exponent was also affected by this vitrification interference (Table S7 and related discussion).

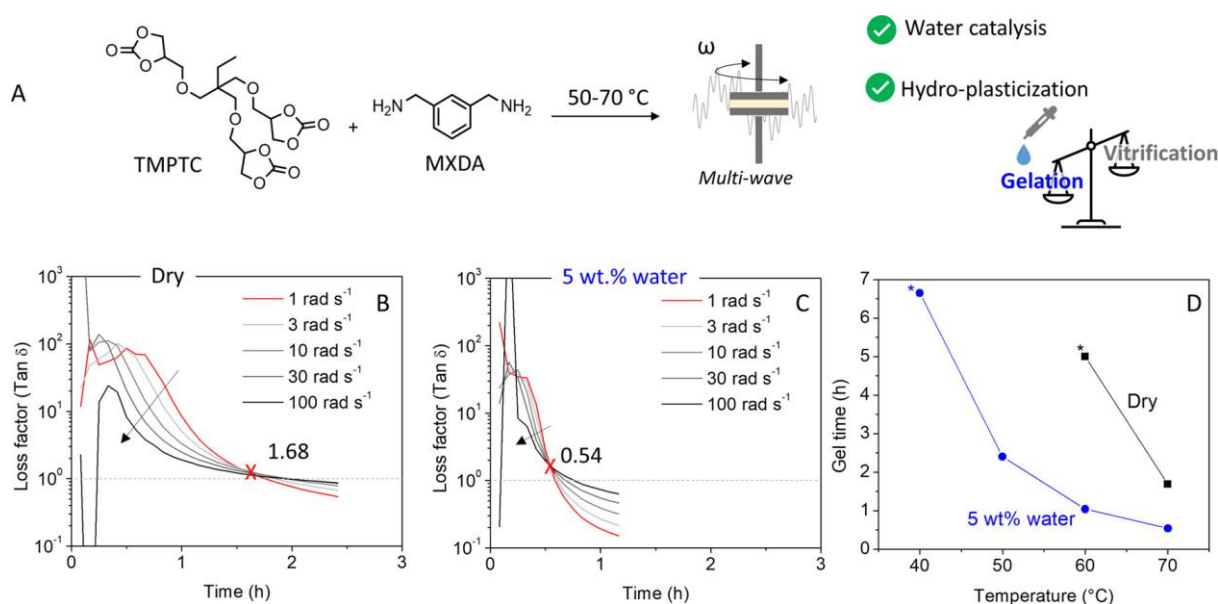


Figure 6. (A) Investigation of the cross-linking reaction of TMPTC with MXDA both in dry conditions and with 5 wt % of added water at various temperatures (multiwave mode, 1.97% global strain amplitude, $\omega = 1, 3, 10, 30, 100 \text{ rad s}^{-1}$). Variation of the loss factor ($\tan(\delta)$) as a function of time for the cross-linking reaction of TMPTC and MXDA at 70°C in the presence of (B) 0 and (C) 5 wt % of added water (horizontal dotted lines correspond to a loss factor value of 1). (D) Variation of the gel time, t_{gel} , as a function of temperature for both the dry system and the system containing 5 wt % of added water. Data points with asterisks (*) correspond to temperatures for which vitrification interferes with gelation.

Conclusion

To conclude, this work provides the first in-depth investigation of the role of water during the cross-linking reaction of PHU thermosets and its huge consequences on materials design. Rheology measurements, using a multifrequency approach, indicate that even very small amounts of water (<5 wt %) impressively shorten gel times (2- to 5-fold decrease). The multifrequency methodology provides an unprecedented illustration of the interaction of water with the PHU thermoset under construction. Water breaks down the multiple intra- and intermolecular H-

bonding interactions within PHU. The main consequences are the enhancement of the molecular mobility within PHU clusters and their delayed vitrification (hydroplasticization), all contributing to accelerate the PHU growing rate. Moreover, we demonstrate that water catalyzes the aminolysis of 5CC as evidenced by a combination of model reactions and DFT calculations. Overall, this study not only clarifies how water influences the PHU cross-linking rate but also provides guidelines for applying PHU technology in industrially relevant applications, such as coatings and adhesives, that require rapid curing at near-ambient temperatures. It suggests that, in some instances, water can substitute the common organocatalysts that are required to reach such curing performance, thus avoiding their drawbacks (e.g., cost, toxicity, and activation of side reactions). Adding a small amount of water to solvent-free PHU formulations is a cost-effective, simple, and robust manner to facilitate the production of more sustainable PHU materials. Overall, this work opens great perspectives for the development of PHU-based materials requiring mild processing conditions.

Associated Content

SUPPORTING INFORMATION

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.4c01672>.

- Materials and methods, additional rheological data, FTIR monitoring of the cross-linking reactions, DSC thermograms and tensile testing of the materials, NMR monitoring of all model reactions, DFT calculations, and atoms coordinates for all catalyzed aminolysis reactions (PDF)
- Video S1: nudged elastic band path for the aminolysis of 5CC_H₂O close to 5CC (MP4)
- Video S2: nudged elastic band path for the aminolysis of 5CC_H₂O close to NH₂ (MP4)
- Video S3: nudged elastic band path for the aminolysis of 5CC_H₂O equidistant (MP4)

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Abbreviations

5CC, 5-membered cyclic carbonate; TMPTC, trimethylolpropane triglycidyl carbonate; EDR148, 1,2-bis(2-aminoethoxy)-ethane; THF, tetrahydrofuran; MeOH, methanol; DMSO, dimethyl sulfoxide; SAOS, small amplitude oscillatory shear; FTMS, Fourier transform mechanical spectroscopy; PC, propylene carbonate; MXDA, meta-xylylenediamine; Tg, glass transition temperature; SI, swelling index; GC, gel content; DSC, differential scanning calorimetry

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