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FAST AND FACILE ONE-POT ONE-STEP PREPARATION OF NONISOCYANATE POLYURETHANE HYDROGELS IN WATER AT ROOM TEMPERATURE

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Abstract

Since the discovery of polyurethanes (PU) by Otto Bayer in 1937, PU hydrogels are still commonly produced by the polyaddition of nasty and toxic polyisocyanates with polyols in organic solvents or in bulk, followed by their swelling in water. Their direct one-pot one-step synthesis in water is not possible because of the fast hydrolysis of isocyanates. The attractive greener variant for PU that consists of the polyaddition of poly(5-membered cyclic carbonate)s with polyamines is also suffering from a similar drawback (the hydrolysis of the cyclic carbonates), but also from the low reactivity of the reagents at room temperature. Herein, we report the first synthesis of PU hydrogels by a nonisocyanate route in water at room temperature from easily accessible CO_2-sourced five-membered cyclic carbonates (5CCs) and a commercially available polyamine. We demonstrate that PU hydrogels are now formed with impressive short gel times (15−20 min) provided that the pH is adjusted in the 10.5−11.5 range to limit 5CCs hydrolysis. Hydrogels of good mechanical properties and high swelling ability are prepared in a facile one-pot process. The robustness of the process is also illustrated by dispersing clays (natural or synthetic) or a natural hydrosoluble polymer (gelatin) in the formulation. These additives do not perturb the polymerization and enable modulation of the mechanical properties of the hydrogel. This work opens up enormous perspectives in the design of elusive PU-based materials in water from largely accessible five-membered cyclic carbonates.

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INTRODUCTION

The polyaddition of polyisocyanates with polyols remains the main production route to polyurethanes (PUs),[1] a world-leading polymer that finds numerous applications in various sectors (transportation, health, construction, etc.).[2] Although highly reactive and versatile, the isocyanate chemistry presents substantial drawbacks. First, isocyanates are toxic and their use is now associated with strict regulations.[3] Second, they are easily hydrolyzed, which renders difficult the PU synthesis in water. Driven by environmental considerations, strategies to prepare PUs in an aqueous medium are extensively searched for. Aqueous dispersions techniques were implemented and mainly consisted of the presynthesis of reactive PUs oligomers in bulk or in organic solvent, followed by their dispersion in water in the presence of an appropriate stabilizer[4−9] and chain extender. These waterborne PU dispersions are particularly adaptable to applications like sustainable inks[10] or low VOC emitting coatings.[11] However, when hydrosoluble PUs or PU hydrogels are concerned, their direct one-pot one-step preparation in water cannot be performed because of the fast hydrolysis of the isocyanates.[12−15] The polymerizations are therefore conducted in bulk or in organic solvents, which are followed by swelling of the cross-linked PU in water (when PU hydrogels are envisioned).[16] One of the main applications of PU hydrogels is in the biomedical sector (drug delivery devices, enzyme immobilization, etc.), which requires the incorporation of bioactive components.[17] As some drugs or enzymes are characterized by low thermal stabilities, are denaturated by the solvent, or react with isocyanates, their incorporation in the hydrogel can be performed only by impregnation of the preformed PU gel in a drug/enzyme solution.[18] Therefore, engineering a robust green and solvent-free procedure to access in water in single-step PU hydrogels with the possible incorporation of sensitive molecules still remains an elusive endeavor. The extension of these aqueous-based strategies to the incorporation of natural hydrosoluble polymers should also open the door to the preparation of hybrid hydrogels with tunable properties.

The polyaddition of a di- or poly(cyclic carbonate) with a di- or polyamine represents one of the most promising sustainable alternative routes for the isocyanate-free synthesis of PUs, providing the so-called poly(hydroxyurethane)s (PHUs).[19−23]

The five-membered cyclic carbonates (5CCs) are the most popular cyclic carbonates used for that purpose and are easily accessible by quantitative catalyzed [3 + 2] coupling of CO_2 to epoxides[24−27] (that can be partially or fully biosourced[28−32]). As the result of the slow aminolysis rate of the cyclic carbonates, polyadditions are thermally activated (range of 60−140 °C) in organic solvents[33−37] or in bulk,[29,32,38−40] but are also facilitated by the use of (organo)catalysts.[38,41−45] Its implementation to water as the sole polymerization medium is an attractive greener alternative to the solvent-based processes but examples are rare, mainly limited to the preparation of hydrophobic PHU in aqueous dispersions in the presence of (internal) stabilizers/surfactants.[46−50] To the best of our knowledge, only one report describes the preparation of PHU oligomers by the polymerization of a hydrophobic bis(5CC) with hexamethylenediamine in water at 50−70 °C in the absence of stabilizers.[51] The hydrophobic nature of bis(5CC) was essential to prevent its hydrolysis by excluding water from the carbonate groups. When hydrophilic bis(5CC) was used, complete hydrolysis of the cyclic carbonate was noted at 70 °C, with no

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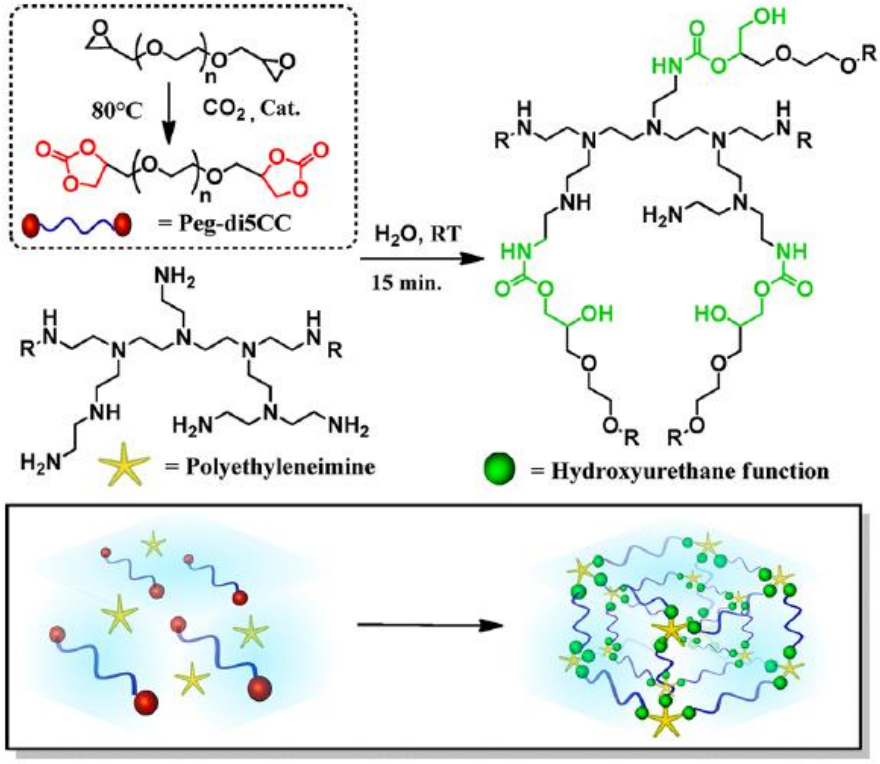
PHU formation. Because extensive hydrolysis of the cyclic carbonates avoided the preparation of PHU in water, the only example of PHU hydrogels was obtained in a two-step strategy by the polyaddition of a hydrophilic bis(5CC) with a mixture of hydrophilic di- and triamines in the bulk at 60 °C, followed by immersing the so-formed PHU in water.[52] The direct preparation of polyurethane (isocyanate-based or not) hydrogels in water still remains a challenge.

Herein, we report the first one-pot one-step preparation of PHU hydrogels in water at room temperature (rt), starting from water-soluble precursors, poly(ethylene glycol) dicyclic carbonate (PEG-di5CC), and a polyamine (polyethylene imine, PEI) (**Scheme 1**). The influence of the experimental conditions, more particularly, the adjustment of the basicity of the solution, on the PHU hydrogel formation is discussed, and the mechanical properties of the gels are evaluated. Moreover, the robustness of the process is further demonstrated by designing composite (by dispersing natural or synthetic clays) or hybrid (by solubilizing a hydrosoluble natural polymer (gelatin) in the formulations) hydrogels displaying promising mechanical performances.



Scheme 1. Reaction for PHU Hydrogel Formation

RESULTS AND DISCUSSION

Aminolysis of Hydrophilic Five-Membered Cyclic Carbonates in Water. We first studied the formation of the hydroxyurethane (HU) linkages and the possible hydrolysis of 5CC via a model reaction between water-soluble PEG-di5CC with 2,2′-(ethylenedioxy) bis(ethylamine) by ^{1}H NMR spectroscopy in D_2O at

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room temperature (**Figure 1**A). PEG-di5CC was selected as it is accessible at the multikilogram scale in our laboratory by solvent-free quantitative organocatalyzed coupling of CO_2 to PEG-diepoxide.[52,53] To highlight the key role of the basicity of the reaction medium in the efficiency of the reaction, experiments were realized under equimolar conditions in reactive groups ([5CC]/[NH_2] = 1) while adjusting the initial pH at 12.5, 10.5, and 9 through the addition of 2 M DCl.

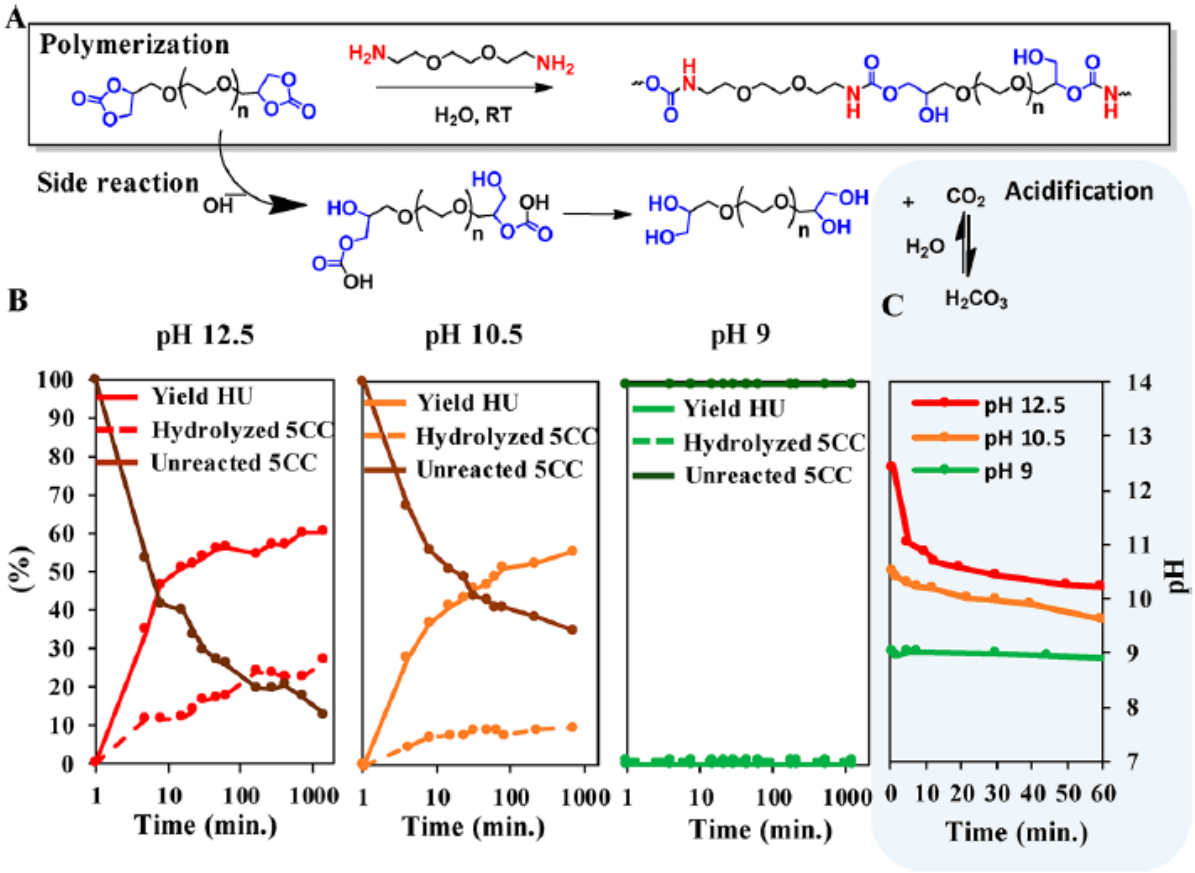

Figure 1. Model reaction study between PEG-di5CC and 2,2'-ethylenedioxy bis(ethylamine) at different pH. (A) Scheme of the reaction. (B) Kinetic of HU formation, unreacted and hydrolyzed 5CC at different pH. (C) Evolution of the pH during the reaction. (HU states for hydroxyurethane and 5CC for cyclic carbonate.)

Figure 2 shows the time evolution of the ^{1}H NMR spectra of the reaction medium at an initial pH of 12.5. Under these conditions, PEG-di5CC and 2,2'-ethylenedioxy bis(ethylamine) rapidly formed the corresponding hydroxyurethane adduct, as shown by the appearance of the characteristic peaks of protons g at 4.8 ppm, i and h at 3.9–4.15 ppm, and k and j at 3.3 ppm. The intensity of the peaks associated with the cyclic carbonate moieties a, b, and c and to the amine f decreased, as the result of their consumption during the reaction. Carbonation of the amine was also detected as attested by the appearance of the characteristic peak at 3.18 ppm (protons n), in agreement with the chemical shifts observed for the carbonatation of various amines.[54] It has to be noted that protons f were progressively located downfield with time as the result of the pH decrease during the reaction, thus to the protonation of the amine (see later). The integral ratio of peaks h and g shows that hydroxyurethanes with 30% of primary alcohol and 70% of secondary alcohol were formed, in line with data in the scientific literature.[51]

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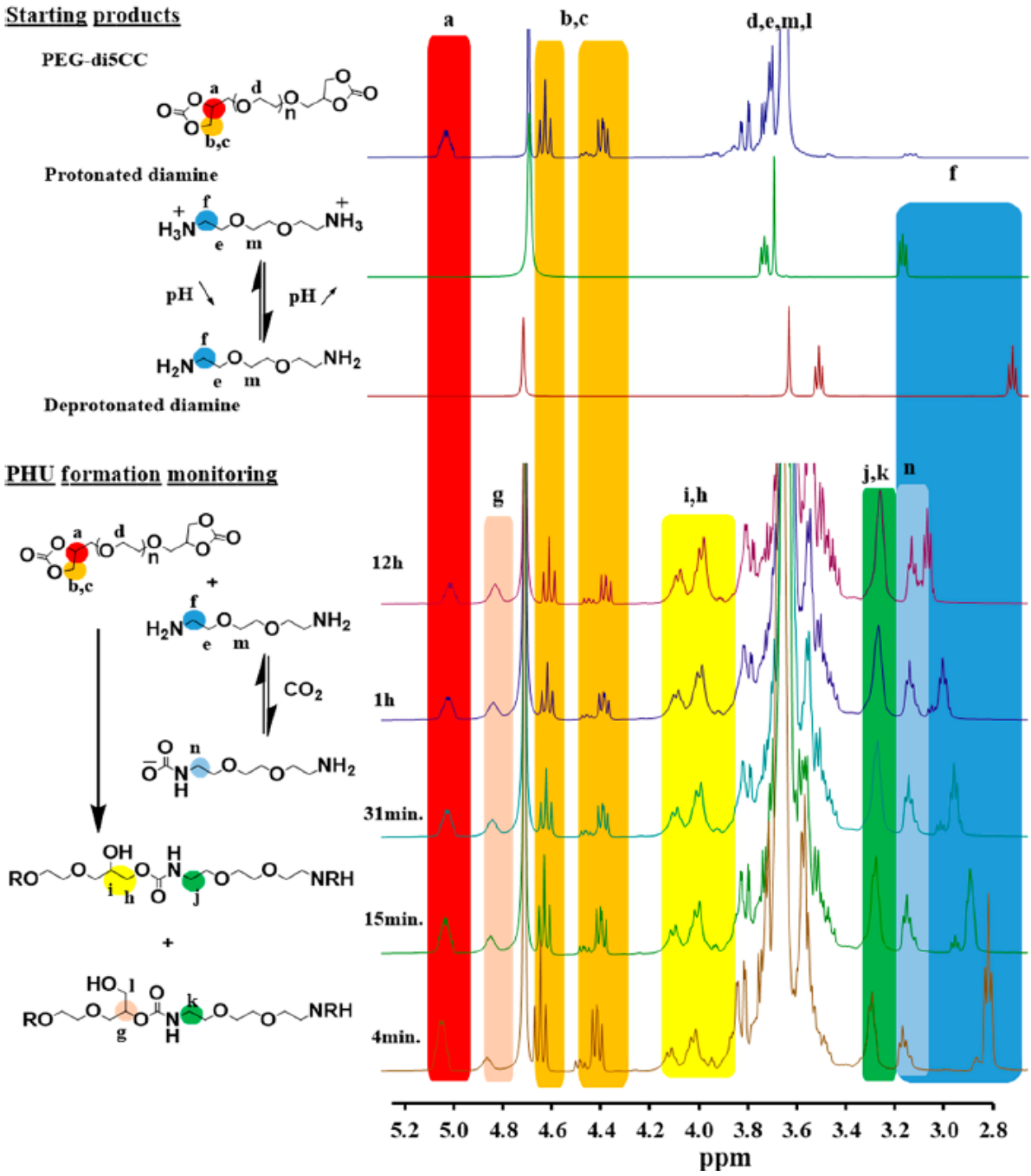

Figure 2. ^{1}H NMR spectra of PEG-di5CC, 2,2'-ethylenedioxy bis(ethylamine) (protonated or not), and the evolution of the ^{1}H NMR spectra during the model reaction at pH 12.5 and rt in D_2O.

The difference between the 5CC conversion and the HU formation was attributed to the 5CC hydrolysis.[55] The results, collected in **Figure 1**B, clearly show that the initial pH had a strong influence on the advent of the reaction. At pH 12.5, about 90% of 5CCs were consumed after 16 h with the formation of only 60 mol % HU linkages and a substantial amount of hydrolyzed byproduct (~30 mol %). By lowering the pH to 10.5, the hydrolysis rate was strongly decreased and the content of hydrolyzed product was maintained very low (~9 mol % after 16 h, **Figure 1**B) (**Figure S3** for ^{1}H NMR study). This is in sharp contrast to the total hydrolysis of hydrosoluble 5CCs that was observed when

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the reaction was carried out with *n*-butyl amine in water at 70 °C.[51] At a pH of 9, we did not note any reaction at rt as the result of the amine protonation (pK_a = 9.7) that prevented the ring opening of the 5CCs (**Figure 1**B, and **Figure S4** for kinetics by ^{1}H NMR spectroscopy). At pH 10.5, size exclusion chromatography (SEC) analysis of the crude product collected after 24 h of reaction shows the remaining starting products (5CCs and diamine) at the low molar mass side of the SEC chromatogram, and the formed linear PHU at the higher molar mass side (**Figure S5**). However, the PHU molar mass remains quite low because the conversion in 5CC is only 60% after this period of time.

By monitoring the pH during the reactions (**Figure 1**C), we observed an important and fast decrease of the initial pH, from 12.5 to 10.2 (for an initial pH of 12.5). This pH decrease with time was the result of the decarboxylation of 5CCs during hydrolysis that acidified the reaction medium due to the formation of H_2CO_3.[56] This acidification was also confirmed by ^{1}H NMR spectroscopy with the shift of the proton f in α position of the amino group, indicating a change in protonation state of the amine, from 2.82 ppm (neutral form) at the early stage of the reaction to 3.05 ppm (protonated state) upon amine protonation (**Figure 2**). This acidification was also noted at pH 10.5, but was less pronounced as the hydrolysis was very limited under these conditions. The comparison of the ^{13}C NMR spectrum of the reaction medium obtained by aminolysis of PEGdiCC with the diamine at pH 12.5 for 24 h attests for the presence of the 1,2-diol formed by hydrolysis of the 5CC ring with the presence of the characteristic peaks of CHOH and CH_2OH at 72 and 63 ppm, respectively (proton j and k, **Figure S6**). This analysis further confirms that decarboxylation occurs at high pH.

When the model reaction (PEG-di5CC + diamine) was performed at lower pH (4.5 and 0.5), no reaction was observed, confirming again that the amine should be deprotonated to react with 5CC (**Figure S7**). Also, this experiment shows that 5CC is stable, even at a pH of 0.5, no hydrolysis being observed at rt after 24 h (Figure S8), in contrast to the experiments carried out at higher pH (12.5 and 10.5; **Figure 1**).

Synthesis PHU Hydrogel in Water at Room Temperature. We then investigated the preparation of PHU hydrogels at a pH of 10.5 to minimize the 5CCs hydrolysis. PEI was first selected as the polyamine as it is water-soluble over a broad pH range and is commercially available. It has to be noted that PEI contains both primary and secondary amines. Although a previous report showed that secondary amines may react with cyclic carbonates,[57] our operating conditions did not promote this reaction, as attested by the absence of any ring-opened product when adding a model secondary amine, diethanolamine, to PEG-di5CC at a pH of 10.5 (see **Supporting Information** for detailed discussion, **Figure S9**). Therefore, only the primary amines of PEI were considered for the reaction with PEG-di5CC. Various [NH_2]/[5CC] ratios were screened to identify the best conditions for the fast formation of hydrogels. After solubilization of PEI in water and fixing of the pH by the addition of HCl, the solution was added to PEG-di5CC. The solid content was fixed to 30 wt % for all experiments. The gel formation was monitored by rheology at rt, and the gel point (evaluated as the crossover point between G′ and G″, **Figure S10**) for the different formulations is depicted in **Figure 3**A. The cross-linking rate increased when the [NH_2]/[5CC] ratio increased, within the investigated range from 0.55 to 1.5. Impressively, the gel point was reached after only 15 min for a [NH_2]/[5CC] ratio of 0.8. The G′ value plateau (reached at the end of the experiment, thus when the PHU gel was formed and did not evolve further) showed a maximum value for [NH_2]/[5CC] ratios of 0.65 and 0.8, and decreased for the other ratios (**Figure 3**A and **Figure S11**), indicating that higher cross-linking degrees are reached in these conditions.

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Compression tests were then carried out on the samples obtained after 24 h of reaction. As all hydrogels were directly synthesized in water at the same concentration, their mechanical properties could be compared (**Figure 3**B,C). Both the strain and stress at break were strongly affected by the initial $[NH_2]/[5CC]$ ratio. Harder hydrogels were obtained for ratios of 0.65 and 0.8 and softer ones for the other ratios, in line with the G′ values noted by rheological measurement (**Figure 3**A). For a $[NH_2]/[5CC]$ ratio of 1.5, thus with a large excess of amine, a viscous liquid was formed and no compression test could therefore be performed.

The equilibrium water absorption (EWA) and gel content (GC) of all hydrogels were then measured after their immersion in water for 48 h (**Table 1**). The highest GC (85%) was obtained for the initial $[NH_2]/[5CC]$ ratio of 0.8, with a EWA value of 1175%. The lower EWA values were in line with the higher GC. Higher EWA values were noted for the other formulations, with the highest value observed for the $[NH_2]/[5CC]$ ratio of 0.55 (EWA = 2403%) and GC of 78%. These results confirm that higher cross-linking degrees were obtained for $[NH_2]/[5CC]$ ratios between 0.65 and 0.8. For a similar GC of about 85%, hydrogels formed by this process presented an impressive 500% EWA increase compared to previously reported PHU hydrogels that were prepared in the bulk and then swollen in water.[52] We can explain this difference as follows: When the cross-linking occurred in water, the polymer was in a swollen state, and the chain segments between cross-linked points were in a nonstretched state in a higher volume compared to that of the synthesis in bulk. PHU prepared in water could therefore accommodate more water upon swelling and stretching of the chains. The compression tests were then performed on the swollen hydrogels (**Table 1**). The highest Young's modulus was again observed for $[NH_2]/[5CC]$ ratios between 0.65 and 0.8 with values between 100 and 140 kPa. Interestingly, these values obtained with EWA higher than 1000% are similar to the values measured for hydrogels prepared in bulk and that were characterized with much lower EWA (125 kPa, EWA = 214%).[52] At similar EWA, our hydrogels presented a 300% increase in Young's modulus compared to those prepared in bulk and then swollen in water (EWA = 967%, 37 kPa).

Table 1. Mechanical and Gel Properties of PHU Hydrogel after 48 h of Swelling in H_2O for Different $[NH_2]/[5CC]$ Ratops at pH 10.5

$[NH_2]/[5CC]$	EWA (%)	gel content (%)	Young's modulus (kPa)	stress at break (kPa)	strain at break (%)
0.55	2403 ± 110	78 ± 0.8	74 ± 1	48 ± 10	38 ± 2
0.65	1263 ± 19	80 ± 2.9	139 ± 6	78 ± 20	35 ± 4
0.8	1175 ± 37	85 ± 1.8	108 ± 3	61 ± 22	37 ± 5
0.95	1262 ± 58	78 ± 3.1	38 ± 2	22 ± 3	37 ± 4
1.1	1494 ± 41	75 ± 3.3	22 ± 3	10 ± 4	31 ± 5
1.5					

As the pH of the medium strongly influenced the rate and selectivity of the reaction for the model reaction (**Figure 1**B), we studied its impact on the PHU hydrogel formation and on its final properties. The same experimental procedure as above was implemented by using the $[NH_2]/[5CC]$ ratio of 0.8. This ratio was selected as it provided the hydrogel with the highest GC, Young's modulus, and stress at break (**Figure 3**C). **Figure 3**D summarizes the gel points, determined by rheology, for the reactions carried out at pH 9.5, 10.5, 11.5, and 12.5. No gelation was noted at pH 9, even after 24 h, in agreement with the model reaction that did not occur at this pH because of the presence of protonated amines (**Figure 1**B). A PHU gel was formed by increasing the pH to 9.5; however, the reaction was slow with a

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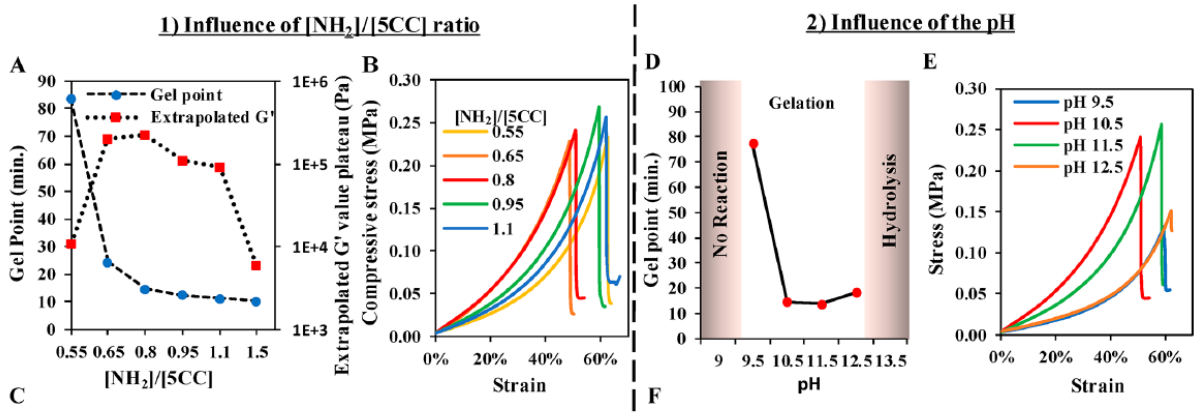
gel time of 78 min. It was strongly accelerated by raising the pH to 10.5, with a gel point that was reached after only 14 min. Similar high cross-linking rates were noted at pH 11.5 and 12.5. For higher pH of 13.5, no gel was collected, presumably because of the fast hydrolysis of 5CCs (**Figure S12**). As evidenced by attenuated total reflection (ATR) spectroscopy of the dried PHU hydrogels prepared at different pH for 24 h, the band characteristic of the carbonate groups of PEG-di5CC at 1795 cm^{-1} is observed no more, attesting for the full consumption of the cyclic carbonate (**Figure S13**).

Compression tests were then carried out on the PHU hydrogels prepared after 24 h at rt (**Figure 3**E,F). Hydrogels prepared at pH of 9.5 and 12.5 presented poor mechanical resistance with a low Young's modulus (~70 kPa). For those prepared at pH of 10.5 and 11.5, Young's modulus strongly increased by more than 300% and 200%, respectively. Although the increase was more modest, a similar trend was noted for stress at break, whereas strain at break was slightly decreased by about 10%. Adjusting the initial pH of the formulation at 10.5 was therefore required to synthesize PHU hydrogels with the best mechanical performances, thanks to a higher cross-linking degree obtained at this pH as demonstrated by the higher gel content and storage modulus values (**Figure 3**F).



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[NH_2]/[5CC]	Young modulus (kPa)	Stress at break (kPa)	Strain at break (%)
0.55	101 ± 14	240 ± 17	62 ± 2
0.65	233 ± 11	176 ± 5	46 ± 5
0.8	233 ± 6	221 ± 16	51 ± 1
0.95	173 ± 16	275 ± 32	58 ± 3
1.1	136 ± 5	228 ± 42	61 ± 3
1.5	-	-	-

F

pH	Young modulus (kPa)	Stress at break (kPa)	Strain at break (%)
9.5	68 ± 6	139 ± 24	60 ± 2
10.5	233 ± 6	222 ± 16	51 ± 1
11.5	149 ± 11	233 ± 47	57 ± 2
12.5	73 ± 3	170 ± 20	62 ± 2

Figure 3. Influences of [NH_2]/[5CC] ratio and pH on the PHU hydrogel formation, and on its mechanical properties at a concentration of 30 wt %. (1) Influence of [NH_2]/[5CC]. (A) Gel time and G' values. (B) Compressive curve at the wet state (30 wt % solid content). (C) Mechanical properties at the wet state (30 wt % solid content). (2) Influence of the pH. (D) Gel time. (E) Compressive curve at the wet state (30 wt % solid content). (F) Mechanical properties at the wet state (30 wt % solid content).

Preparation and Characterization of PHU/Layered Silicates Hydrogels. We then investigated the improvement of the mechanical properties of PHU (prepared from PEGdi5CC and PEI) by adding nanoclays to the formulations, prior to polymerization. Indeed, clays are often used to reinforce polymers,[58] including hydrogels,[52,59−62] provided that the filler is homogeneously dispersed in the matrix. A natural clay, Cloisite Na, and a synthetic one, Laponite S182, that differ by their aspect ratio and dispersion in water, were tested in this work. For the sake of comparison with the previous

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experiments, the solid content (PHU + clay) was maintained constant at 30 wt %, the [NH_2]/[5CC] ratio was fixed to 0.8, and the pH was at 10.5. Both clays were homogeneously dispersed in the formulation, at least up to 2.5 wt %.

Prior to synthesis of the PHU/clay nanocomposites, we performed control rheological measurements to probe possible interactions between clay and one of the components used for preparing PHU, thus, PEG-di5CC or PEI. Results are summarized in **Figure S14**. These experiments demonstrate some interactions between PEI and Cloisite with a solid behavior that is observed with G' values that are higher than G'' ones (**Figure S14**a). Only limited interactions were noted between PEG-di5CC and Cloisite (**Figure S14**a). This behavior was however not observed with Laponite (**Figure S14**b), probably as the result of the lower aspect ratio of this clay (nanodiscs of 25 nm diameter compared to nanosheets of ~150 nm for Cloisite). Interestingly, these interactions did not inhibit the formation of the PHU network. In comparison to that of PHU hydrogels without clay, gel time was slightly longer for Laponite (18 vs 15 min), and the increase of G' due to PHU network formation occurred after 20 min for Cloisite. Final G' values were very similar to or without clay (**Figure 4**A,B). Transparent hydrogels were formed for all formulations, attesting for the good and homogeneous clay dispersion within the material (**Figure 5**A). The addition of clay significantly increased the Young's modulus (up to 170−180%) and stress at break (up to 330% with Cloisite and 170% with Laponite) of the hydrogel under compressive tests (**Figure 5**B,D), without affecting significantly the gel content that remained around 85% (**Table S1**). No decrease of the strain at break was noticed in the presence of clay, indicating that the nanofiller improved the cohesion of the PHU hydrogel. It has to be noted that the nature of the clay had almost no influence on the Young's modulus but rather on the stress at break that was much higher for Cloisite. Importantly, ATR spectroscopy of the dried PHU hydrogels loaded by the clays and formed after 24 h of reaction at rt demonstrated the absence of unreacted cyclic carbonate, confirming the completeness of the reaction (**Figure S15**).

After drying at rt for 5 days, all PHUs contained about 10% of residual water. They were characterized by a high resistance to elongation with strain at break as high as 450% or 380% with Cloisite or Laponite, respectively, compared to 200% for unfilled PHU (**Figure 5**C,D). Young's modulus and stress at break were also strongly increased in the presence of clay. These improvements were more pronounced with Cloisite (155% for Young's modulus and 180% for stress at break).

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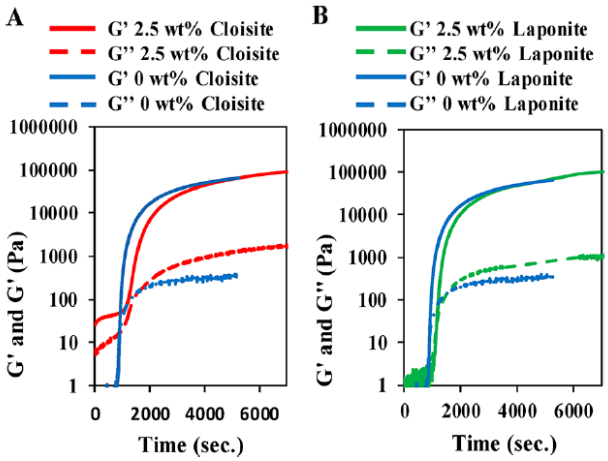
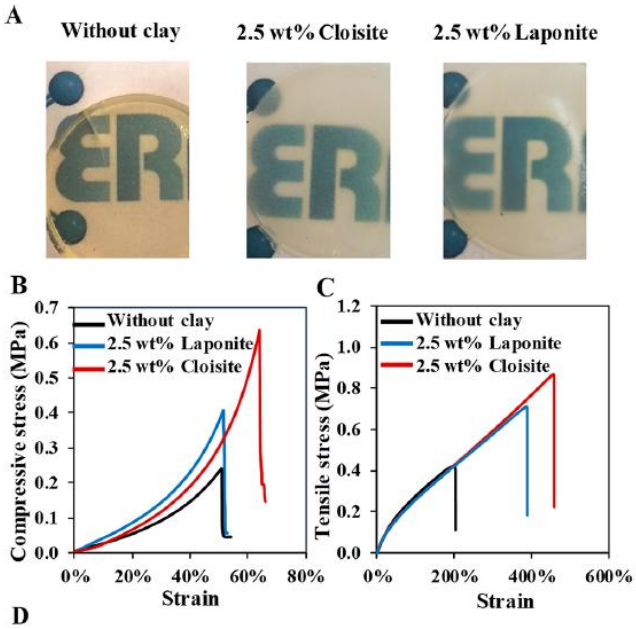


Figure 4. Rheology measurement during the formation of PHU with and without clay (conditions: pH 10.5, $[NH_2]/[5CC]$ = 0.8, 2.5 wt % of clay, 30 wt % solid content). (A) Comparison between PHU and PHU reinforced by Cloisite Na. (B) Comparison between PHU and PHU reinforced by Laponite S482.



D

Additives	Water content (%)	Modulus (kPa)	Stress at break (kPa)	Strain at break (%)
Without clay	69.8	223 ± 16 [a]	221 ± 16 [a]	51 ± 1 [a]
	10.3	540 ± 70 [b]	490 ± 98 [b]	210 ± 10 [b]
2.5 wt% Laponite	68.8	398 ± 11 [a]	368 ± 59 [a]	52 ± 3 [a]
	10.7	615 ± 63 [b]	768 ± 77 [b]	386 ± 6 [b]
2.5 wt% Cloisite	69	373 ± 25 [a]	733 ± 208 [a]	64 ± 6 [a]
	10.2	843 ± 130 [b]	895 ± 52 [b]	490 ± 15 [b]

Figure 5. (A) Images of PHU hydrogels with and without clay. Group Logo designed by Michaël Alexandre. Image taken by Maxime Bourguignon. (B) Compressive curve at the wet state (solid content: 30 wt %). (C) Tensile curve at the wet state (solid content: 90 wt %; hydrogel dehydrated for 5 days at room temperature under ambient atmosphere). (D) Summary of the Young's moduli, stresses, and strains at break values measured for the hydrogels with solid contents of 30 or 90 wt %.

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[a]Hydrogels at 30 wt % solid content. [b]Hydrogels at 90 wt % solid content obtained by dehydration of hydrogels at 30 wt % for 5 days at room temperature under ambient atmosphere.

Preparation and Characterization of PHU/Gelatin Double Network Hydrogels. Finally, we investigated the formation of double network (DN) PHU-based hydrogels by using a natural water-soluble polymer, gelatin, able to form a physical network (Figure 6). DN hydrogels formed by two independent networks composed by both a covalent and a physical one can support higher stresses compared to simple covalently cross-linked hydrogels.[63−67] This performance improvement is the result of the dissipation mechanism via the disruption−reconstruction behavior of the physical network.[67] Gelatin, which is extracted from collagen by acidic or basic treatment, is known to rapidly and reversibly form triple helix at a temperature below 35−40 °C, leading to a physically cross-linked hydrogel that liquefies upon heating.

To prepare our DN hydrogel, we first solubilized gelatin at 50 °C in water, before the addition of the PHU precursors (PEG-di5CC and PEI, $[NH_2]/[5CC]$ = 0.8, pH 10.5). Two proportions of PHU/gelatin were studied (10/2 and 10/6, in weight ratio) while maintaining constant the solid content of the gel (30 wt %). The homogeneous solutions were then cooled down to rt while monitoring the reaction by rheology. **Figure 6**B shows that G' value increased drastically and rapidly, with a crossover point with G'' (and thus a gel point) appearing directly (in less than 1 min) for PHU/gelatin 10/2 and 10/6, indicating the fast formation of a first network. A similar behavior was observed when PEG-di5CC was replaced by PEG terminated by hydroxyl groups (PEG-diOH), thus not able to form PHU by reaction with PEI. This control experiment demonstrates that the first network was formed by the gelatin triple helix network. When the reaction was allowed to pursue, a second jump in G' value was observed in the presence of PEG-di5CC, whereas it was absent with PEG-diOH. This second increase in G' value was promoted by the reaction between PEG-di5CC and PEI, forming the PHU network. The second gel point (evaluated by the appearance of a second bend in the G' curve) was observed after about 14 min (PHU/gelatin = 10/2) or 20 min (PHU/gelatin = 10/6), and was thus in the same range as the gel points measured for PHU without gelatin (15 min). The final G' value reached for the two DN networks hydrogels was close to the obtained value for the PHU network (≈10^5 Pa), while the hydrogel with PEG-diOH is significantly lower (10^4 Pa) as a result of the absence of PHU network in the latter case.

We then evaluated the impact of the addition of gelatin on the compressive properties of the hydrogels, containing all the same water content (**Figure 6**C). For the lowest PHU/gelatin ratio (PHU/gelatin = 10/2), Young's modulus and strain at break were similar to those of the PHU hydrogel without gelatin, with however a stress at break that was twice increased. In contrast, for the highest PHU/gelatin ratio (PHU/gelatin = 10/6), the gelatin network imparted a huge improvement in stress and strain at break of the DN hydrogel. Indeed, the strain at break was much higher (90% vs 50%) and stress at break was impressively increased by 5100% (11.4 vs 0.22 MPa) (**Figure 6**D). When the gelatin hydrogel was considered in the presence of PEG-diOH and PEI (thus without PHU covalent network), the stress and strain at break were higher than those for classical PHU, with however a Young's modulus far away from the DN hydrogel (0.047 vs 0.23 MPa).

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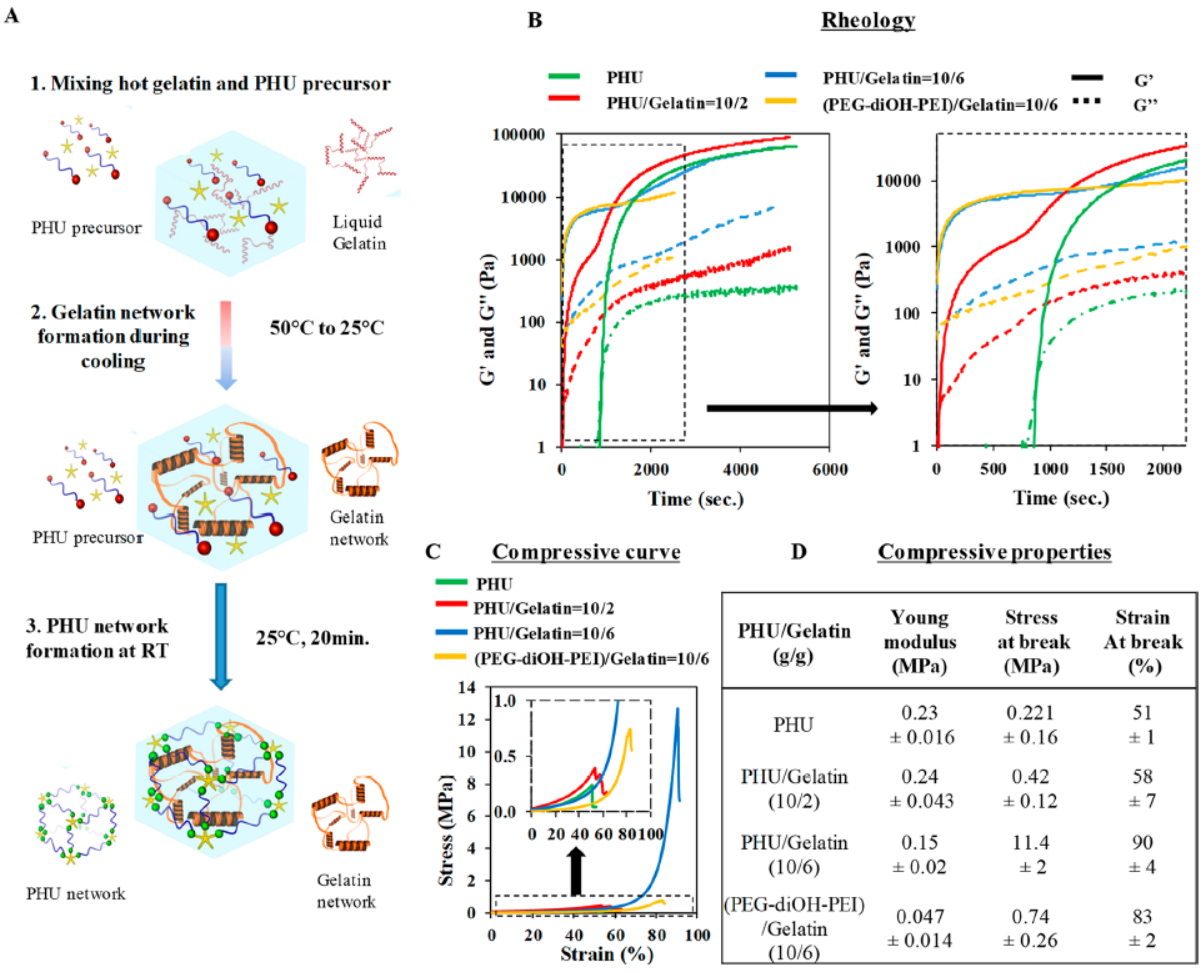

PHU/Gelatin (g/g)	Young modulus (MPa)	Stress at break (MPa)	Strain At break (%)
PHU	0.23 ± 0.016	0.221 ± 0.16	51 ± 1
PHU/Gelatin (10/2)	0.24 ± 0.043	0.42 ± 0.12	58 ± 7
PHU/Gelatin (10/6)	0.15 ± 0.02	11.4 ± 2	90 ± 4
(PEG-diOH-PEI) /Gelatin (10/6)	0.047 ± 0.014	0.74 ± 0.26	83 ± 2

Figure 6. (A) Scheme of the DN hydrogel formation with the formation of gelatin network first and then PHU. (B) Rheology of PHU hydrogel, DN hydrogel with different gelatin contents, and gelatin containing PEI and PEG-diOH (conditions: pH 10.5, $[NH_2]/[5CC]$ ratio = 0.8, 30 wt % solid content). (C) Stress−strain experiments of the various hydrogels at the wet state (30 wt % solid content). (D) Compressive properties of hydrogel at the wet state (30 wt % solid content).

CONCLUSIONS

This work demonstrates that nonisocyanate polyurethane hydrogels can be prepared by the facile polyaddition of hydrosoluble bis(5-membered cyclic carbonate)s with a polyamine in water in a one-pot one-step procedure. By adjusting the pH of the solution in the 10.5−11.5 range, short gel times are noted (15−20 min) at room temperature. Clays or a natural hydrosoluble polymer (gelatin) can also be added to the formulation to improve the mechanical properties of the hydrogels. Despite five-membered cyclic carbonates (prepared by the quantitative organocatalyzed coupling of CO_2 to the parent epoxides) being prone to hydrolysis and being poorly reactive toward amines at rt, we have shown that the synthesis of PHU hydrogels is feasible in water in a facile one-pot process. This robust process is a greener alternative to conventional polyurethane hydrogels that are commonly produced by toxic isocyanate chemistry with multiple-steps procedures.

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EXPERIMENTAL SECTION

Materials. Tetrabutylammonium iodide, polyethylene glycol diglycidylether (Mn = 500 g/mol), 2,2'-ethylenedioxy bis(ethylamine), diethanolamine, polyethylenimine (PEI, Mn = 800 g/mol), polyethylene glycol (Mn 600 g/mol), and Gelatin type A 300g Bloom were provided by Sigma-Aldrich. Perfluoro-*tert*-butanol was provided by Fluorochem. Cloisite Na and Laponite S482 were provided by Southern Clay and Rockwood, respectively. All other products were used as received.

Characterizations. *Nuclear Magnetic Resonance (NMR) Spectroscopy.* ^{1}H NMR analyses were performed on Bruker Avance 250 or 400 MHz spectrometers in D_2O, at 25 °C in the Fourier transform mode. ^{13}C NMR analyses were performed on Bruker Avance 400 MHz spectrometers in D_2O, at 25 °C.

Gel Content (GC) Measurements. After 24 h of gelification, the hydrogels were freeze-dried for 16 h. After weighing (w_1), they were immersed separately in 10 mL of deionized water at room temperature for 48 h. Then the gels were removed from water and freeze-dried for 16 h. Gel was finally weighed (w_2). The gel content was estimated by **eq 1**.

$$\mathrm{GC}(\%) = 100 \times \frac{w_2}{w_1} \qquad (1)$$

Swelling Behavior of PHU Gels. After 24 h of gelification in water, the gel (0.5 cm × 0.5 cm) was immersed for 48 h in 10 mL of water at room temperature. Excess of nonabsorbed water was removed by drying with cellulosic paper. The gel was weighed (w_s), and then freeze-dried and weighed (w_d). Equilibrium water absorption (EWA) was measured by **eq 2**.

$$\mathrm{EWA} = 100 \times \frac{(w_s - w_d)}{w_d} \qquad (2)$$

Rheology. The gel point, the storage modulus (G'), and the loss modulus (G'') were determined by rheology measurements carried out on ARES from Rheometric Scientific TA Instruments using time sweep measurements at constant frequency (1 Hz) and strain deformation (1%).

Mechanical Properties. Compressive and tensile properties measurements were performed with an Instron 5586 machine linked to the BlueHill software. Compression tests on hydrogels were carried out at room temperature for three quadratic samples (5 mm length × 5 mm thickness × 5 mm width) at a compression rate of 1 mm/min. Compression modulus was determined by measuring the slope between 1 and 10% compression strain which corresponds to the linear (elastic) region of the stress−strain curve. Traction tests on dried hydrogels (2 mm × 0.8 mm × 0.4 mm) were measured at room temperature at a rate of 10 mm/min. Modulus was determined by measuring the slope at the beginning of the curve.

ATR Spectra. ATR spectra were measured by using a Nicolet IS5 spectrometer (Thermo Fisher Scientific) equipped with transmission or diamond attenuated transmission reflectance (ATR) device. Spectra were obtained in transmission or ATR mode as a result of 32 spectra in the range of 4000−500 cm^{-1} with a nominal resolution of 4 cm^{-1}. Spectra were analyzed with an ONIUMTM (Thermo Fisher Scientific) software.

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Reactions. *Model Reaction Study.* All model reactions were carried out according to the following procedure. 2,2-Ethylenedioxy bis(ethylamine) (132 mg, 8.9×10^{-4} mol) was solubilized in D_2O (2 mL) and DCl was added to fix the pH at 12.5, 10.5, or 9. PEG-di5CC (560 mg, 8.9×10^{-4} mol) was added to the solution under vigorous stirring. An aliquot of the solution (700 μL) was transferred into a NMR tube and directly analyzed by ^{1}H NMR spectroscopy at 25 °C with acquisition at different periods of time. In the same time, pH was measured on the remaining solution that was not analyzed by NMR.

PHU Hydrogel Synthesis. In a typical experiment, PEI was added to 2 mL of deionized water and pH was adjusted with 12 M HCl. This solution was added to PEG-di5CC and was mixed thoroughly for 30 s. The solution was then deposited in a circular plastic mold 2.5 cm in diameter. The solution was covered to avoid evaporation and left to polymerize for 24 h at rt.

Procedure for the Formation of PHU/Gelatin (10/6) DN. Gelatin (300 mg) was solubilized in 2 mL of water at 50 °C for 10 min. This solution was then added to the PEI (150 mg) and the pH was adjusted at 10.5 by concentrated HCl (12 M). The resulting solution was then added to PEG-di5CC (350 mg). Gel was then directly deposited in a circular plastic mold 2.5 cm in diameter and 5 mm depth at room temperature. The solution was covered to avoid evaporation and left to polymerize at rt. The total solid content of the gel was maintained at 400 mg for 1 mL of water, and $[NH_2]/[5CC]$ molar ratio was kept at 0.8.

ADDITIONAL CONTENT (SUPPORTING INFORMATION)

1. SYNTHESIS OF DICYCLOCARBONATED PEG

The synthesis of dicyclocarbonated poly(ethylene glycol) (PEG-di5CC) was carried out by organocatalytic coupling of CO_2 to poly(ethylene glycol) diglycidylether according to a procedure described in a previous work[1]. Briefly, PEG diglycidylether (30g, 60mmol), tetrabutylammonium iodide (0.92g, 2.5mmol), perfluoro-*tert*-butanol (346µL, 2.5mmol) were added to a 80 mL high pressure reactor. The cell was then equilibrated at 80°C and 100 bar of CO_2. Reaction occurred for 16h under stirring. The product was then recovered. Residual CO_2 and perfluoro-*tert*-butanol were removed under vacuum for 16h at 60°C. Conversion of the epoxide groups into cyclic carbonates was calculated by ^{1}H-NMR in $CDCl_3$ with the disappearance of the peaks in the zone between 2.5 and 3.5 ppm (peak **1, 2** in **Figure S1** A) and appearance of peaks **b, c** at 4.5 and **a** 4.9 ppm (**Figure S1** B).

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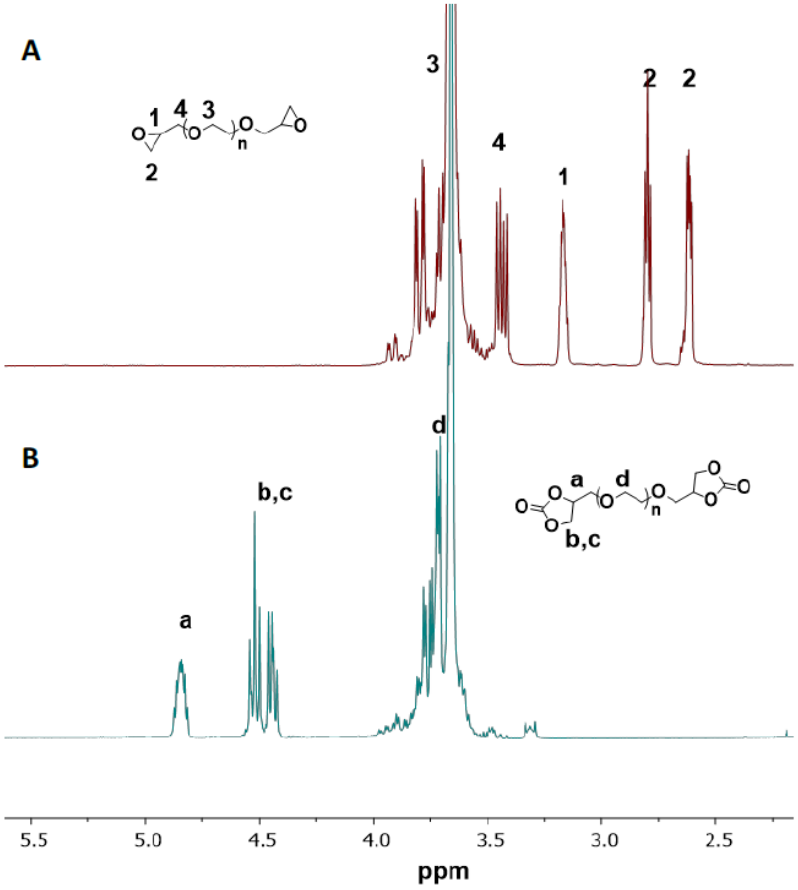

Figure S1. ^{1}H NMR of PEG-diglycidyl ether (A) and PEG-di5CC (B) in $CDCl_3$.

2. MONITORING OF THE REACTION BETWEEN PEG-DI5CC AND 2,2'-ETHYLENEDIOXY BIS(ETHYLAMINE) AT DIFFERENT PH

Kinetic curves presented in **figure 1**B are calculated following the next method. Since the diamine was precisely weighted, proton in alpha of the amine was used to normalized all the spectra, hence, sum of intensity of peaks **f, j, k** and **n** were normalized at an intensity = 4 (as 4 protons are in alpha position of amino group whenever the urethane, carbamic acid or amine form). As equimolar amount of cyclic carbonate was added compared to amine, signals of protons **a, b** and **c** have an intensity of two at t=0.

So remaining amount of cyclic carbonate (**unreacted 5CC**) can be directly calculated by equation 3:

$$\textbf{Unreacted 5CC} = \left(\frac{I_a}{2}\right) * 100 \text{ (eq. 3) with } I_a \text{ = integral of } \textbf{a}.$$

Formation of Urethane (**HU yield**) was calculated by equation 4:

$$\textbf{HU yield} = \left(\frac{I_{j,k}}{4}\right) * 100 \text{ (eq. 4) with } I_{j,k} \text{ = integral of } \textbf{j,k}$$

Hydrolysis of cyclic carbonate (**hydrolyzed 5CC**) was calculated by equation 5:

$$\textbf{hydrolyzed 5CC} = 100 - (\text{Unreacted 5CC}) - (\text{HU yield}) \text{ (eq.5)}$$

2.1. KINETIC AT PH 12.5

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Discussion and partial results of kinetic at pH 12.5 are presented in the main text and in the **figure 2**.

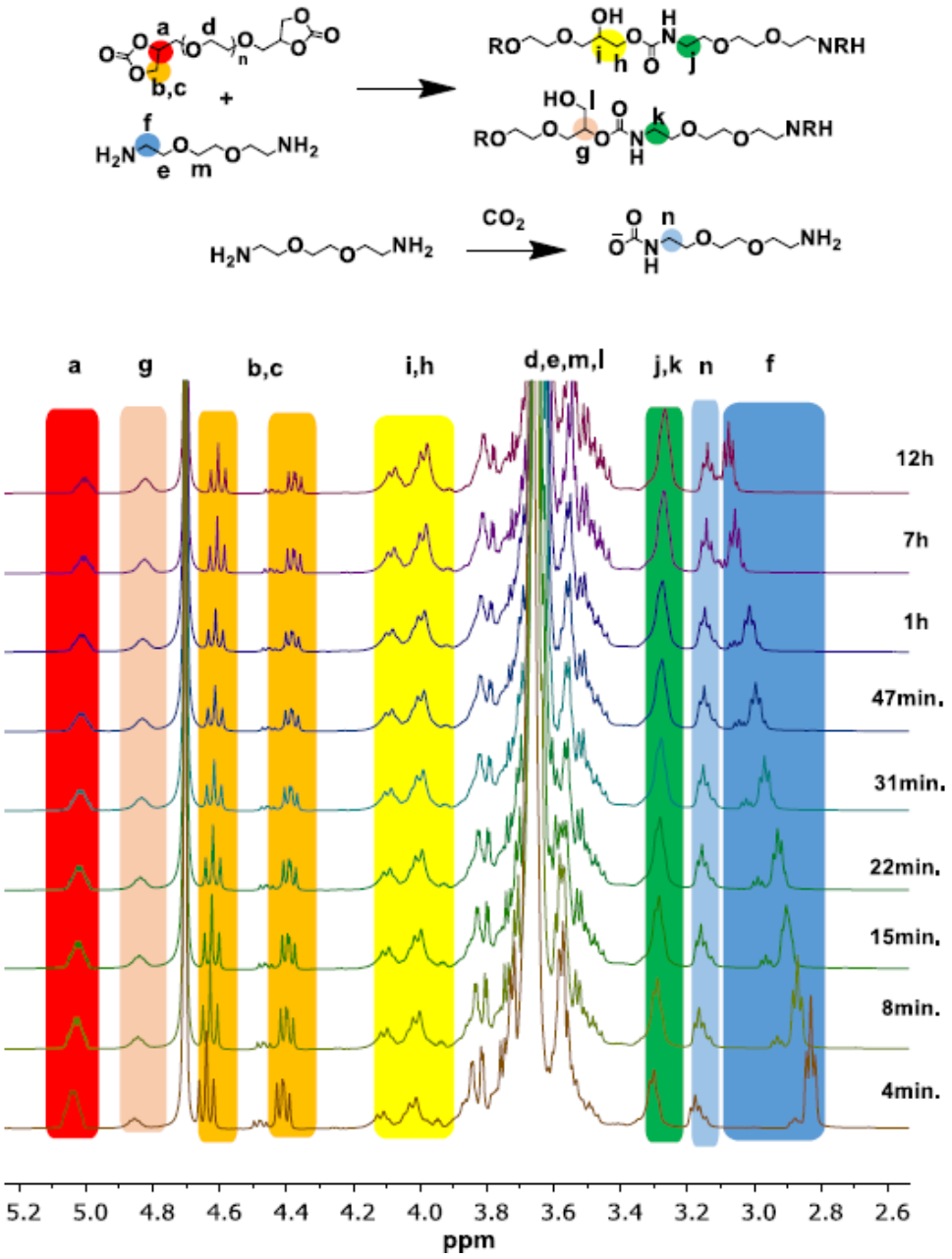

Figure S2. Evolution of the ^{1}H-NMR spectra during the reaction of PEG-di5CC with 2,2'-ethylenedioxy bis(ethylamine) at pH 12.5 in D_2O. Yield in hydroxyurethane (HU), content in residual cyclic carbonate (5CC) and hydrolyzed 5CC are summarized in **Figure 1**B.

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2.2. KINETIC AT PH 10.5

PEG-di5CC and 2,2'-ethylenedioxy bis(ethylamine) were rapidly reacting with the formation of the corresponding adduct, as shown by the appearance of the characteristic peaks of protons **g** at 4.8 ppm, **i** and **h** at 3.9 to 4.15 ppm, **k** and **j** at 3.3ppm. Carbonated amine was also formed as attested by the appearance of the characteristic peak at 3.18 ppm (protons **n**). It has to be noted that protons **f** (-**CH_2NH_2**) were progressively located downfield with time as the result of the pH decrease during the reaction. As illustrated in **Figure 1**c and discussed in the main manuscript, this pH decrease during the reaction was due to partial hydrolysis of the cyclic carbonates.

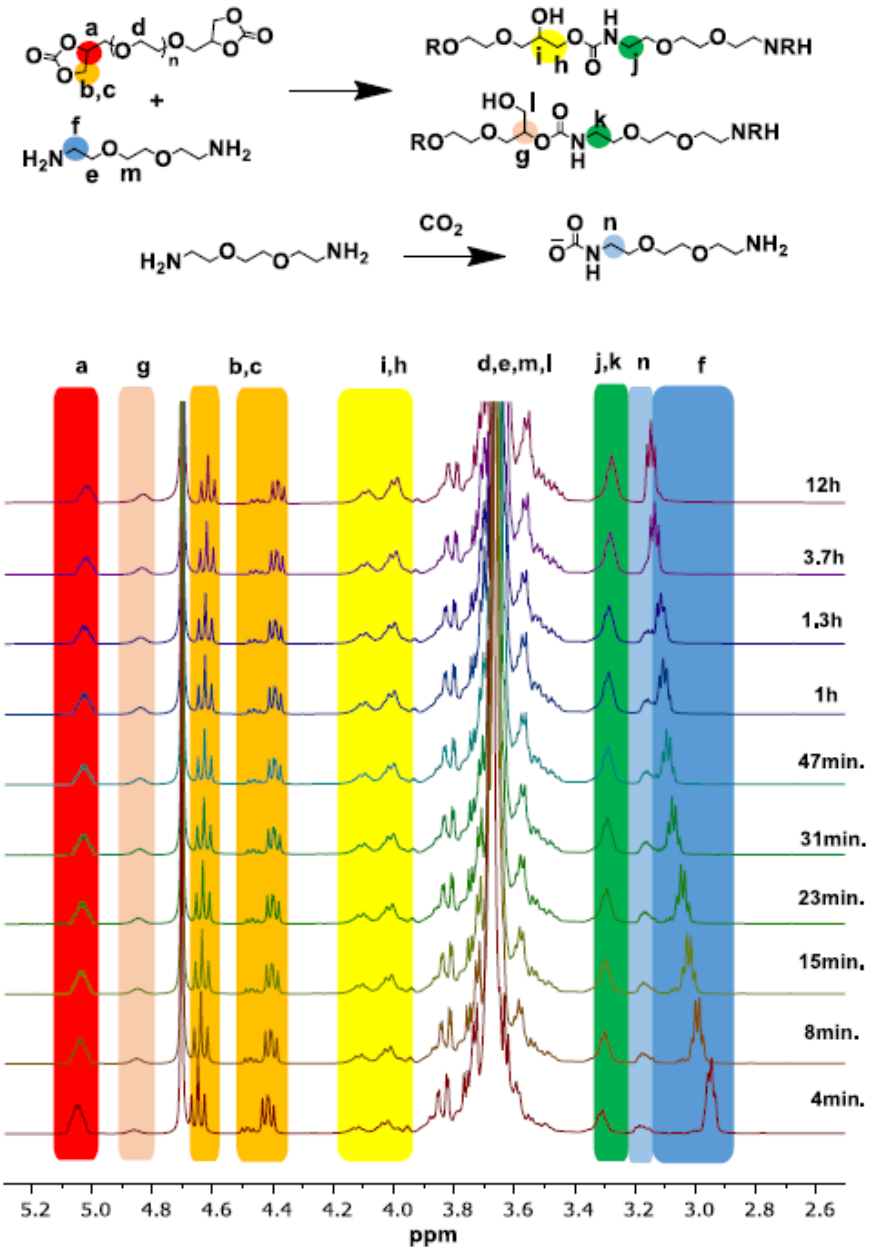

Figure S3. Evolution of the ^{1}H-NMR spectra during the reaction of PEG-di5CC with 2,2'-ethylenedioxy bis(ethylamine) at pH 10.5 in D_2O. Yield in hydroxyurethane (HU), content in residual cyclic carbonate (5CC) and hydrolyzed 5CC are summarized in **Figure 1**B.

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2.3. KINETIC AT PH 9

As illustrated in **Figure S4**, the characteristic peaks of 2,2'-ethylenedioxy bis(ethylamine) and PEG-di5CC did not evolve with time, and no additional signal was observed, attesting for the absence of formation of the corresponding adduct, even after 21 h of reaction.

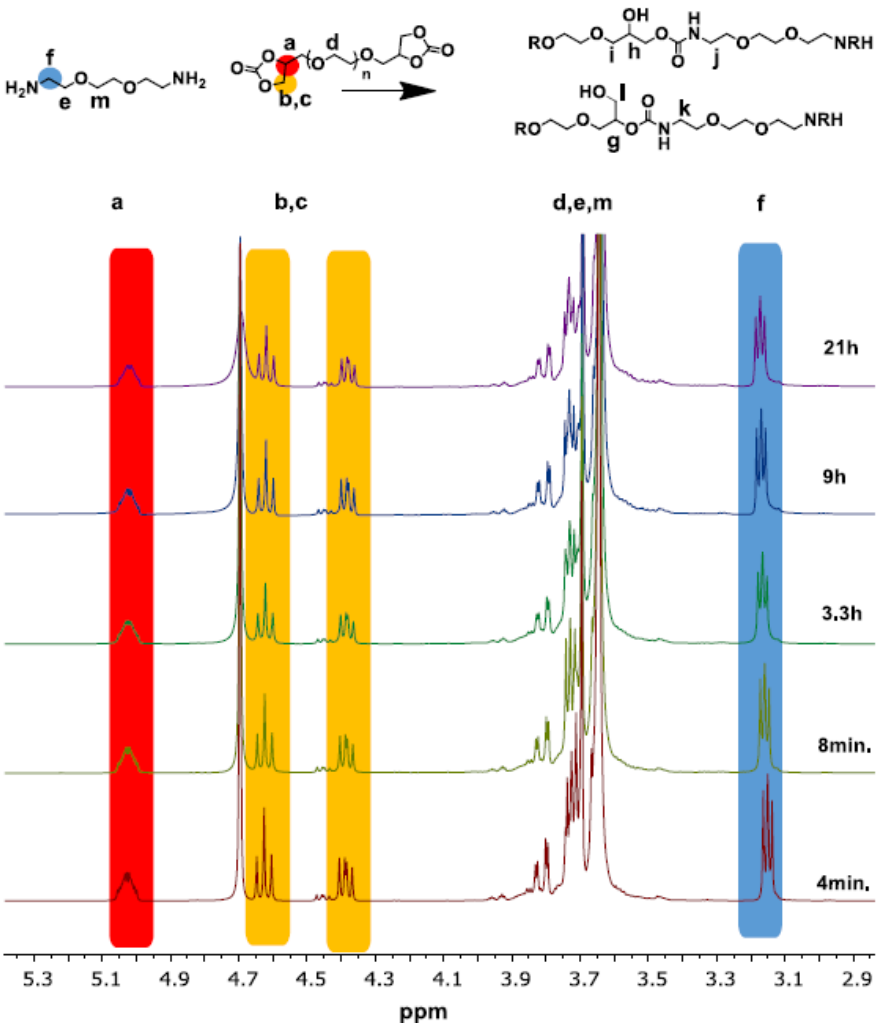

Figure S4. Evolution of the ^{1}H-NMR spectra during the reaction of PEG-di5CC with 2,2'-ethylenedioxy bis(ethylamine) at pH 9 in D_2O. No reaction is noted after 21h. Yield in hydroxyurethane (HU), content in residual cyclic carbonate (5CC) and hydrolyzed 5CC are summarized in **Figure 1**B.

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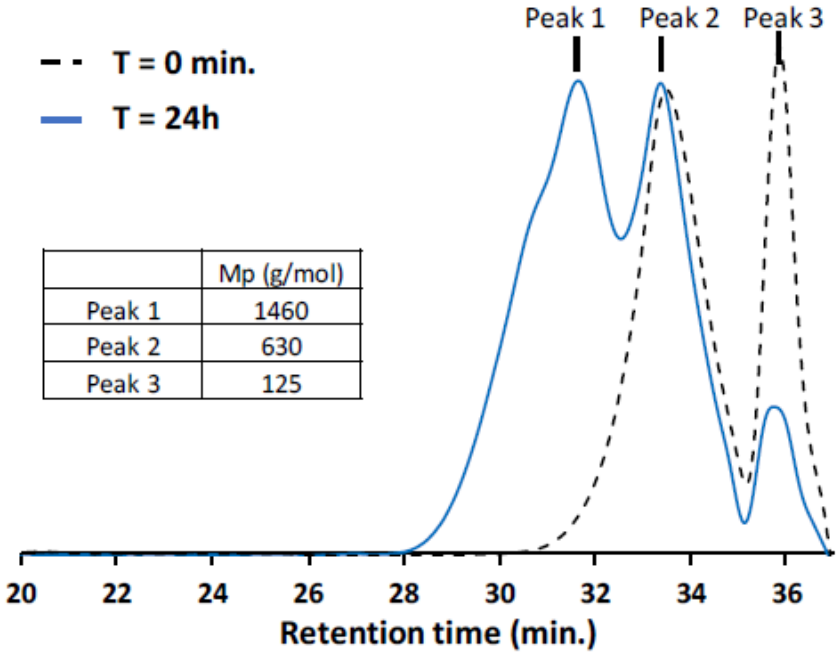
2.4. SIZE EXCLUSION CHROMATOGRAPHY OF PHU FORMED BY REACTION OF PEG-DI5CC WITH 2,2'-ETHYLENEDIOXY BIS(ETHYLAMINE) AT ROOM TEMPERATURE AT PH 10.5 AFTER 24H.



	Mp (g/mol)
Peak 1	1460
Peak 2	630
Peak 3	125

Figure S5. SEC chromatograms of the reaction between PEG-di5CC and 2,2'-ethylenedioxy bis(ethylamine) at pH 10.5 in D_2O at 25°C for 0 min and 24h. Peak 1: PHU; peak 2: PEG-di5CC; peak 3: 2,2'-ethylenedioxy bis(ethylamine).

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3. INVESTIGATION OF THE HYDROLYSIS (AND THUS DECARBOXYLATION) OF PEG-DI5CC DURING PHU FORMATION BY ^{13}C-NMR ANALYSIS.

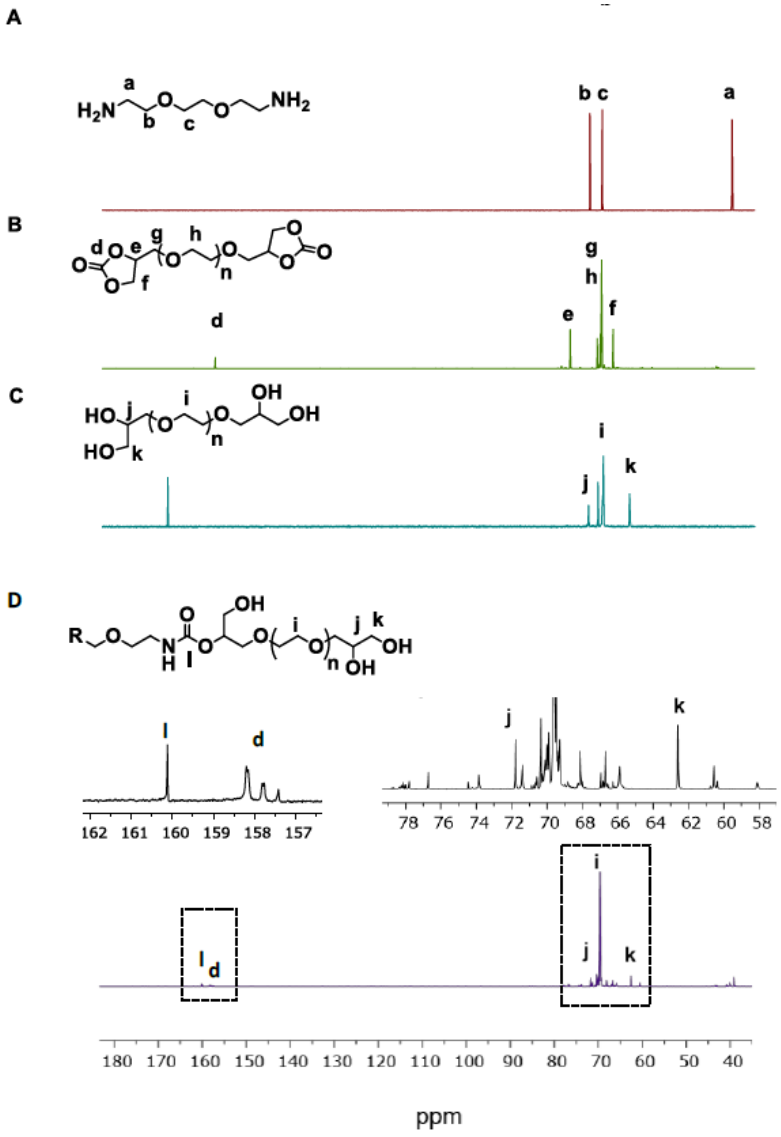

Figure S6. ^{13}C NMR analysis of (A) 2,2'-ethylenedioxy bis(ethylamine), (B) PEG-di5CC, (C) hydrolyzed PEG-di5CC (obtained by hydrolysis at pH 14 for 24h) and (D) PHU formed by reaction of 2,2'-ethylenedioxy bis(ethylamine) with PEG-di5CC at pH 12.5 in D_2O for 24h.

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4. MODEL REACTION BETWEEN PEG-DI5CC AND 2,2'-ETHYLENEDIOXY BIS(ETHYLAMINE) AT ROOM TEMPERATURE, AND AT PH 4.5 AND 0.5

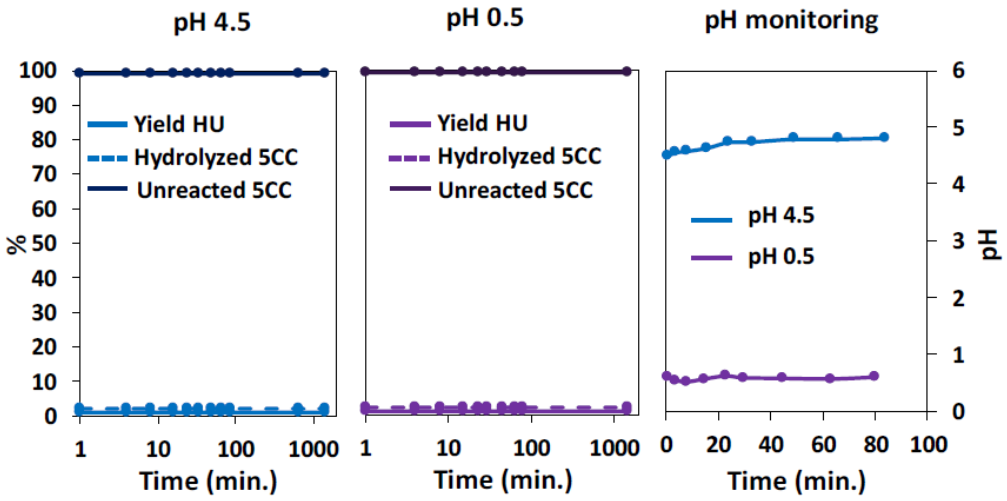

Figure S7. Model reaction study between PEG-di5CC and 2,2'-ethylenedioxy bis(ethylamine) at pH of 4.5 and 0.5. A, Kinetic of HU formation, unreacted and hydrolyzed 5CC at different pH. B, Evolution of the pH during the reaction. (HU states for hydroxyurethane and 5CC for cyclic carbonate).

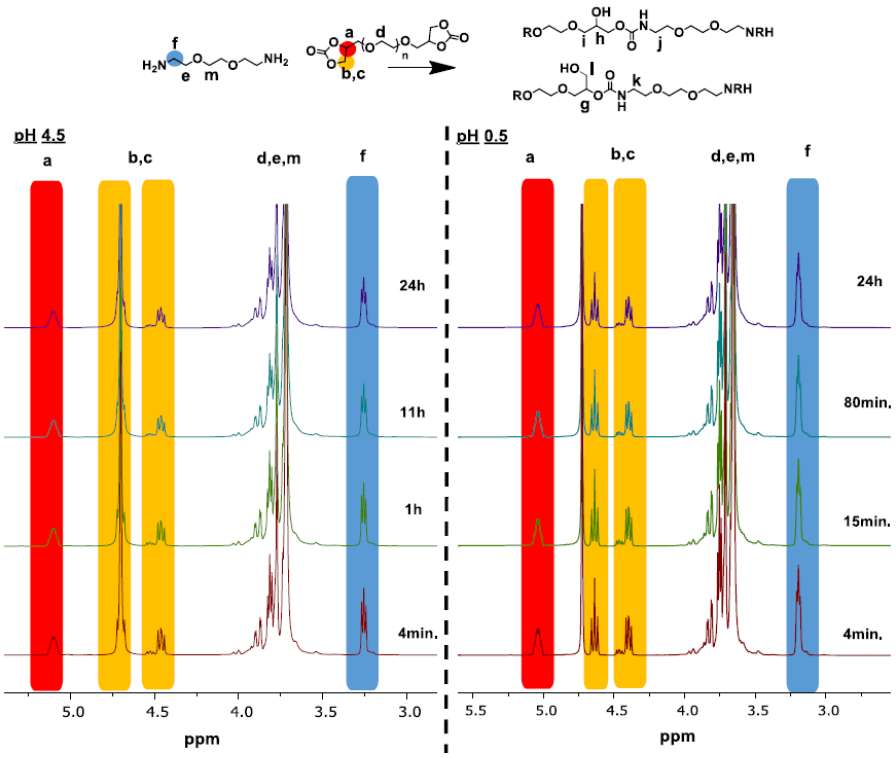

Figure S8. Evolution of the ^{1}H-NMR spectra during the reaction of PEG-di5CC with diethanolamine at pH of 4.5 or 0.5 in D_2O.

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5. MONITORING OF THE REACTION BETWEEN PEG-DI5CC AND DIETHANOLAMINE

Diethanolamine (184mg, 1.76 10^{-3} mol) was solubilized in D_2O (2mL) and DCl was added to fix the pH at 10.5. PEG-di5CC (560mg, 8.9 10^{-4} mol) was added to the solution under vigorous stirring. An aliquot of the solution (700µL) was transferred into a NMR tube and directly analyzed by ^{1}H-NMR spectroscopy at 25°C with acquisition at different time (**Fig. S9**). No formation of HU function was observed after 1h of reaction, attesting that the secondary amine did not react with the cyclic carbonate, in contrast to the primary amine (**Fig. S3**). Some carbonation of the secondary amine was observed with the appearance of the characteristic **n** protons at 3.35 ppm (**Fig. S9**).

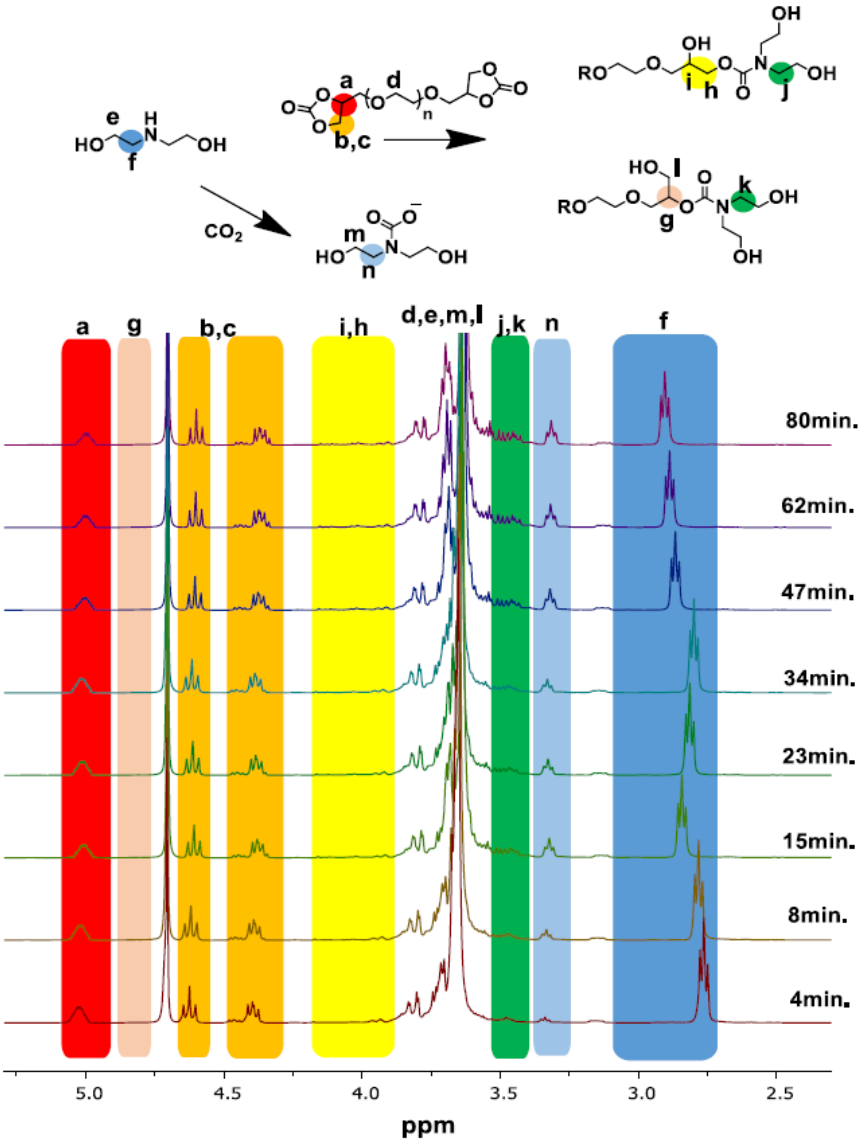

Figure S9. Evolution of the ^{1}H-NMR spectra during the reaction of PEG-di5CC with diethanolamine at pH 10.5 in D_2O.

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6. SYNTHESIS AND CHARACTERIZATION OF PHU HYDROGELS

6.1. EVALUATION OF THE [PRIMARY AMINE]/[CYCLIC CARBONATE] RATIO ([NH_2]/[5CC] ON THE PHU HYDROGEL FORMATION AND PROPERTIES

The primary amine content in PEI was calculated by the following equation: $n_{1°amine} = 0.25\frac{m}{MM}$ where MM is the molar mass of a monomer unit in PEI (43g/mol) and 0.25 is the estimated ratio of primary amine on total amine in PEI. The [NH_2]/[5CC] ratio was varied from 0.55 to 1.5 while pH was fixed at 10.5. The solid content (PEG-di5CC + diamine) was kept constant (30 wt% in water).

6.1.1. Kinetics of crosslinking by rheology.

PEI was added to 2 ml deionized water and pH was adjusted to 10.5 by HCl 12M. This solution was then added to PEG-di5CC, and was mixed thoroughly for 30 s. The solution was then deposited on the parallel plate of the rheometer (**Figure S10**).

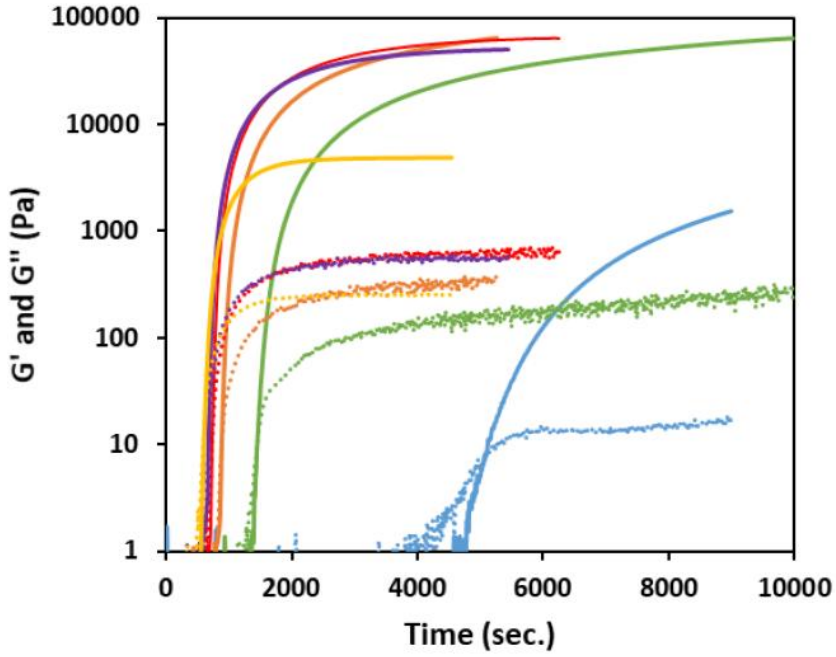

Figure S10. Curing kinetics and time sweep measurements of PEG-di5CC/PEI at rt for different [NH_2]/[5CC] ratios in water at a fixed pH of 10.5 (30 wt% solid content). G' are presented in solid line, G'' are presented in dotted line. Blue: [NH_2]/[5CC] =0.55; Green: [NH_2]/[5CC] =0.65; Orange: [NH_2]/[5CC] =0.8; Red: [NH_2]/[5CC] =0.95; Purple: [NH_2]/[5CC] =1.1; Yellow: [NH_2]/[5CC] =1.5. Gel points are summarized in **Figure 3**a.

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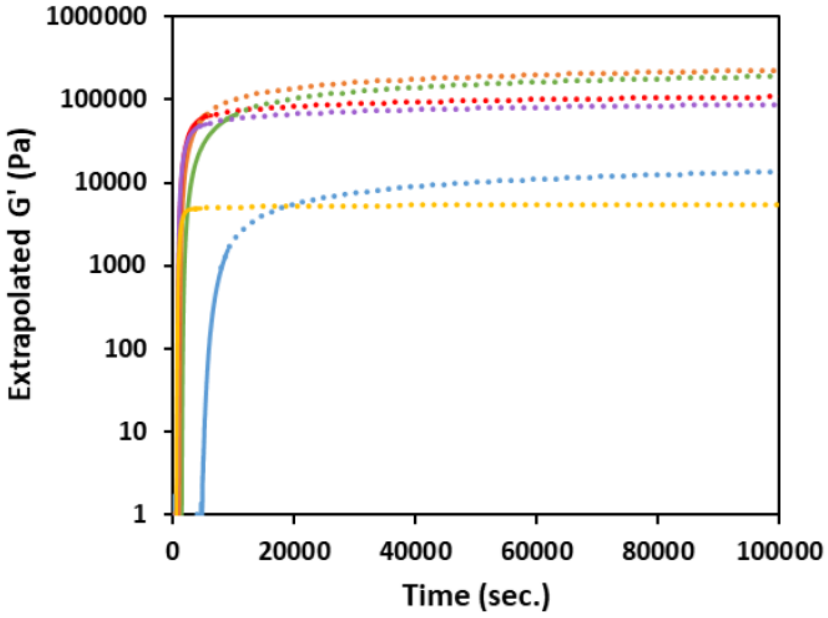

Figure S11. Rheology of the hydrogel formation at different monomer ratio. Experimental data are represented in solid line. Blue: $[NH_2]/[5CC]$ =0.55; Green: $[NH_2]/[5CC]$ =0.65; Orange: $[NH_2]/[5CC]$ =0.8; Red: $[NH_2]/[5CC]$ =0.95; Purple: $[NH_2]/[5CC]$ =1.1; Yellow: $[NH_2]/[5CC]$ =1.5. Dotted line is G' estimation by extrapolation until plateau (summarized in **Figure 3**a)

6.1.2. Compressive measurements

In a typical experiment, PEI was added to 2 ml desionized water and pH was adjusted to 10.5 by HCl 12M. This solution was added to PEG-di5CC and was mixed thoroughly for 30s. The solution was then deposited in a circular plastic mold of 2.5 cm of diameter. The solution was covered to avoid evaporation and left to polymerize for 24 hours at rt. Compressive properties were realized on samples of similar water content. This content was verified by weighting the hydrogels before and after drying, and was equal to 30±2 wt%. Compressive curves for these PHU hydrogels are shown in **Figure 3**b, and Young's modulus, stress at break and strain at break are summarized in **Figure 3**c.

For compressive properties at maximum water content, the PHU hydrogels obtained above at 30 wt% were then swollen in water for 48h. Equilibrium water absorption (EWA), gel content (GC), Young's modulus, stress and strain at break values are summarized in **Table 1**.

6.2. INFLUENCE OF THE PH ON PHU HYDROGEL FORMATION

6.2.1. Mechanical properties of PHU hydrogel

In a typical experiment, PEI (240 mg) were mixed to 2 ml desionized water. pH was adjusted at the desired value by addition of HCl 12M. This solution was then added to PEG-di5CC (560mg), and mixed thoroughly for 30s. The solution was then deposited in a circular plastic mold (2.5 cm of diameter). The casted hydrogel was covered to avoid evaporation and was left to polymerize at rt for 24 hours before demolding. Compressive curves for these PHU hydrogels are shown in **Figure 3**e, and Young's modulus, stress at break and strain at break are summarized in **Figure 3**f.

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6.2.2. Kinetics of crosslinking by rheology.

PEI (240 mg) was mixed to 2 ml of desionized water and pH was adjusted at the desired value by adding HCl 12M. This solution was added to PEG-di5CC (560mg) and was mixed thoroughly for 30s. The solution was then deposited on the parallel plate of the rheometer. Gel formation was not observed for hydrogel at pH 9 and 13.5. (**Figure S12**)

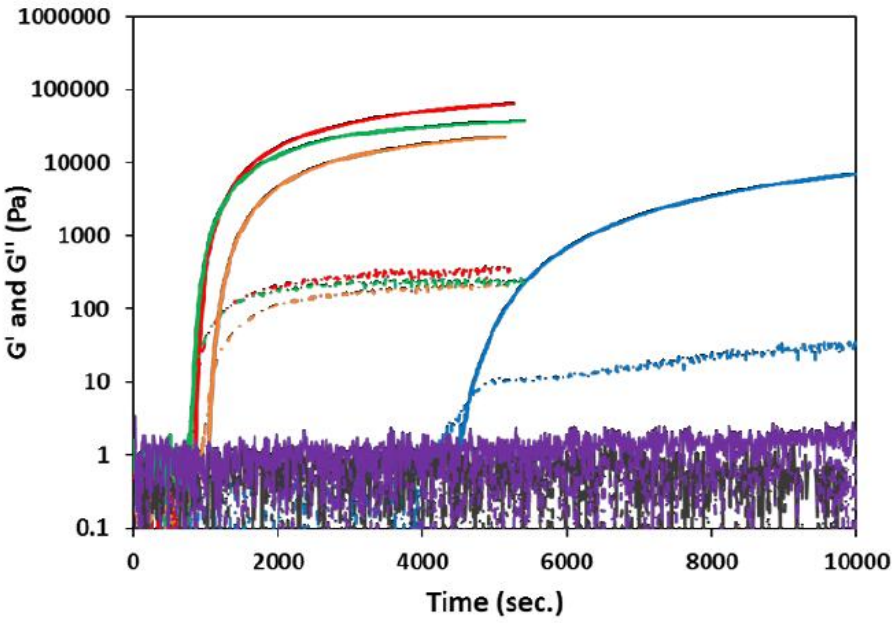

Figure S12. Curing kinetics and time sweep measurements of PEG-di5CC/PEI at different pH for a fixed [NH_2]/[5CC] ratio of 0.8 in water at rt (30 wt% solid content). G' are presented in solid line, G'' are presented in dotted line. Black: at pH 9 ; Blue: at pH 9.5 ; Red: at pH 10.5; Green: at pH 11.5; Orange: at pH 12.5; Purple: at pH 13.5. Gel points values is summarized in **Figure 3**d.

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6.2.3. ATR spectra of PEG-di5CC and PHU hydrogels prepared at various pH at rt for 24h (PHU were freeze-dried for 24 h before ATR analysis).

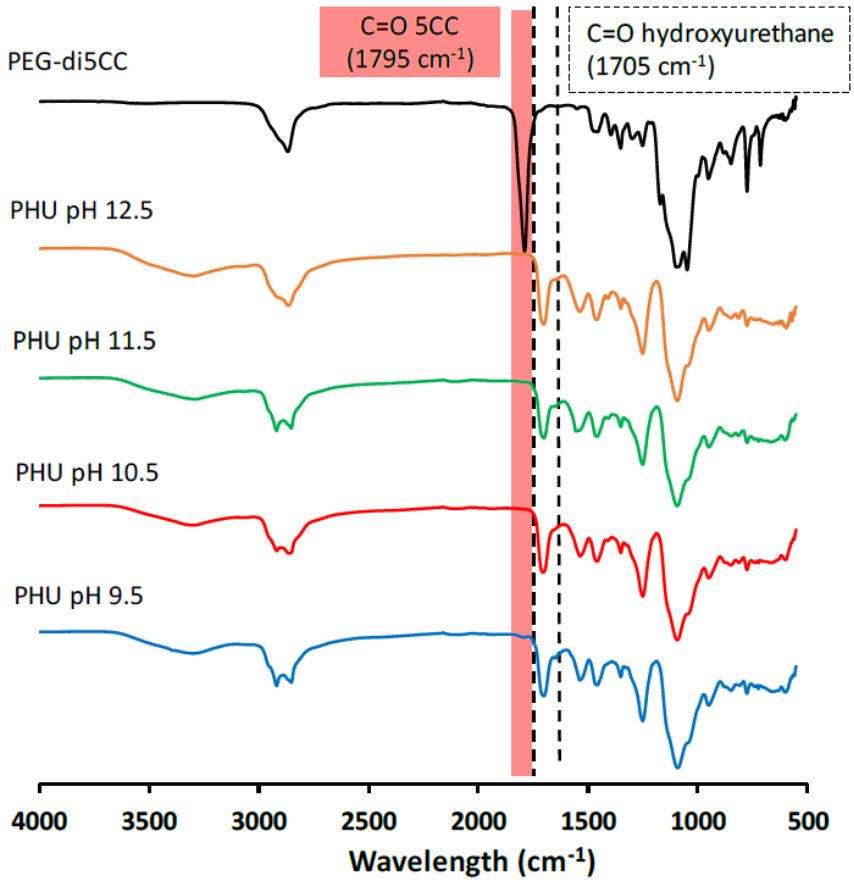

Figure S13. ATR spectra of PEG-di5CC and PHU hydrogels after 24h of reaction in H_2O at different pH. The total disappearance of the band at 1795 cm^{-1} corresponding to C=O of the carbonate group indicates the full conversion of 5CC of PEG-di5CC after 24h of reaction.

7. PHU HYDROGELS REINFORCED BY CLAYS

7.1. HYDROGEL PREPARATION

PEI (240 mg) was solubilized in 1ml of deionized water and pH was fixed to 10.5 by the addition of HCl 12M. Nanoclay (20mg) was dispersed in 1mL of deionized water. The PEI solution and clay dispersion were then mixed together, and the mixture was added to PEG-di5CC (560 mg). This solution was then deposited into a mold of 2.5cm of diameter and covered to avoid evaporation. The curing occurred at rt for 24h.

7.2. MECHANICAL PROPERTIES OF PHU HYDROGEL

Compressive curves for these PHU nanocomposite hydrogels are shown in **Figure 5**b, and Young's modulus, stress and strain at break are summarized in **Table 5**d.

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For tensile properties measurements of PHU hydrogels with or without clay, the hydrogels were dried in air at room temperature for 5 days. The residual water content was determined by weighting after freeze drying and was around 10 wt% for all samples. Elongation curves are presented in **Figure 5**c. Modulus, stress and strain at break under elongation of the samples are summarized in **Table 5**d.

EWA and GC after 48h of immersion of the hydrogel in water are presented in **table S1**.

Table S1. EWA and GC for PHU hydrogels with or without clays

Additives	EWA (%)	GC (%)
PHU without clay	1175 ± 37	85 ± 1.8
PHU + Laponite 2.5 wt%	943 ± 68	82 ± 3
PHU + Cloisite 2.5 wt%	1052 ± 49	84 ± 0.9

7.3. KINETICS OF CROSSLINKING BY RHEOLOGY.

For rheology measurements, the solution containing PEG-di5CC, PEI and clay as prepared above was directly placed between parallel plates of rheometer after mixing. Results are presented in **Figure 5**a and **5**b. Interaction between both clays and PEI or PEG-di5CC are also evaluated by rheology after mixing 10mg of clays in 1ml of H_2O with 280mg of PEG-di5CC or 120mg of PEI , followed by fixing the pH at 10.5. Results are presented in **Figure S14**.

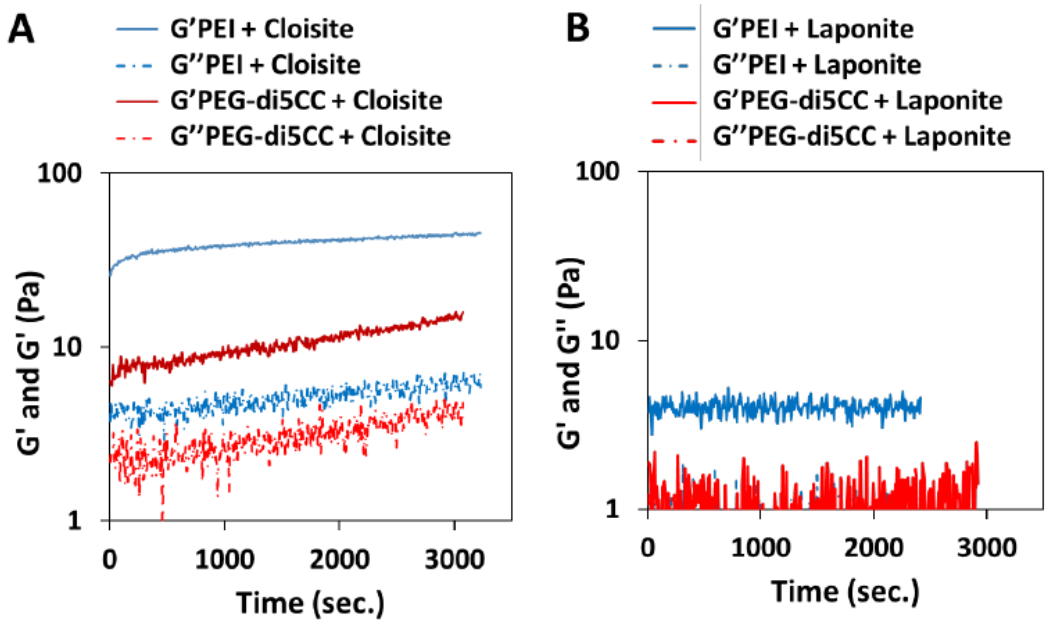

Figure S14. Interaction between clays and PEI or PEG-di5CC studied by rheology. A, Interaction with Cloisite in water and B, interaction with Laponite in water. In blue, interaction of clays with PEI. In red, interaction of clays with PEG-di5CC. In solid line G' and in dotted line G''.

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7.4. ATR SPECTRA OF PEG-DI5CC AND PHU HYDROGELS LOADED OR NOT WITH CLAY AND PREPARED AT PH 105 AT RT FOR 24H (PHU WERE FREEZE-DRIED FOR 24 H BEFORE ATR ANALYSIS).

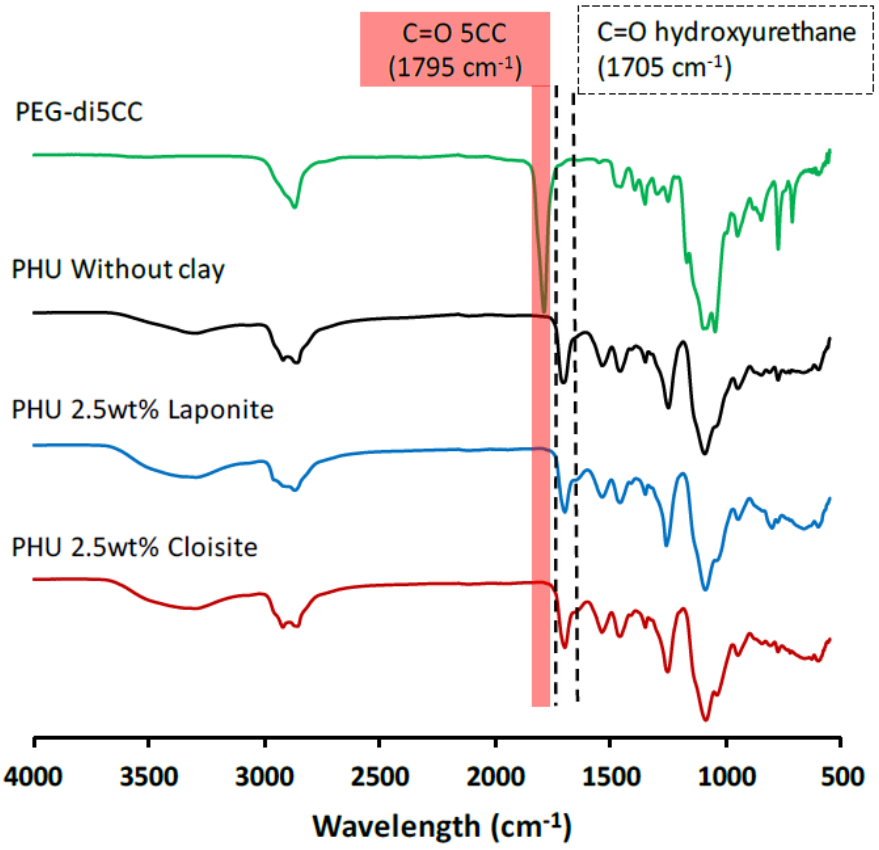

Figure S15. ATR analysis of PEG-di5CC, PHU hydrogel loaded or not with clay after 24h of reaction in H_2O at rt and pH = 10.5. The total disappearance of the band at 1795 cm^{-1} corresponding to C=O of the carbonate group indicates the full conversion of 5CC of PEG-di5CC after 24h of reaction.

8. SYNTHESIS OF PHU BASED DOUBLE NETWORK HYDROGEL.

8.1. PROCEDURE FOR THE FORMATION OF PHU/GELATIN (10/2) DN.

Gelatin (133 mg) was solubilized in 2ml of water at 50°C for 10min. This solution was then added to the PEI (200 mg) and the pH was adjusted at 10.5 by concentrated HCl (12M). After stirring, the resulting solution was then added to PEG-di5CC (467 mg) and stirred again. The solution was then directly deposited in a circular plastic mold of 2.5 cm of diameter and 5mm depth at room temperature. The solution was covered to avoid evaporation and left to polymerize at RT. The total solid concentration of the gel was maintained at 400mg for 1ml of water, and NH2/5CCs molar ratio was kept at 0.8.

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8.2. PROCEDURE FOR THE FORMATION OF (PEG-DIOH-PEI)/GEL (10/6) HYDROGEL

Gelatin (300 mg) was solubilized in 2ml of water at 50°C for 10min. This solution was then added to the PEI (150 mg) and the pH was adjusted at 10.5 by concentrated HCl (12M). The resulting solution was then added to 350mg PEG-diOH (Mn 600g/mol) and was stirred vigorously. Gel was then directly deposited in a circular plastic mold of 2.5 cm of diameter and 5mm depth at room temperature. The solution was covered to avoid evaporation and left at RT. The total solid concentration of the gel was maintained at 400mg for 1ml of water, and NH2/5CCs molar ratio was kept at 0.8.

8.3. REHOLOGICAL MEASUREMENT

Rheology measurements are carried out at 25°C. Directly after mixing the different component to the gelatin solution at 50°C and strong stirring for 30 sec, the solution was placed between parallel plates of the rheometer.

Result concerning Rheological measurement and mechanical properties of DN hydrogel are featured in **figure 6**.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

NOTES

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ABBREVIATIONS USED

5CC, 5-membered cyclic carbonate; PEI, polyethylenimine; PU, polyurethane; PHU, polyhydroxyurethane; PEG-diOH, hydroxyl-terminated polyethylene glycol; PEG-di5CC, 5CC terminated polyethylene glycol; rt, room temperature

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