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WATER-BORNE ISOCYANATE-FREE POLYURETHANE HYDROGELS WITH ADAPTABLE FUNCTIONALITY AND BEHAVIOR

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Polyurethane hydrogels are attractive materials finding multiple applications in various sectors of prime importance; however, they are still prepared by the toxic isocyanate chemistry. Herein the facile and direct preparation in water at room temperature of a large palette of anionic, cationic, or neutral polyurethane hydrogels by a non-isocyanate route from readily available diamines and new hydrosoluble polymers bearing cyclic carbonates is reported. The latter are synthesized by free radical polymerization of glycerin carbonated methacrylate with water-soluble comonomers. The hydrogel formation is studied at different pH and its influence on the gel time and storage modulus is investigated. Reinforced hydrogels are also constructed by adding $CaCl_2$ to the formulation that in-situ generates $CaCO_3$ particles. Thermoresponsive hydrogels are also prepared from new thermoresponsive cyclic carbonate bearing polymers. This work demonstrates that a multitude of non-isocyanate polyurethane hydrogels are easily accessible under mild conditions without any catalyst, opening new perspectives in the field.

KEYWORDS : CYCLIC CARBONATES, NON-ISOCYANATE POLYURETHANES, POLYHYDROXYURETHANES, HYDROGELS

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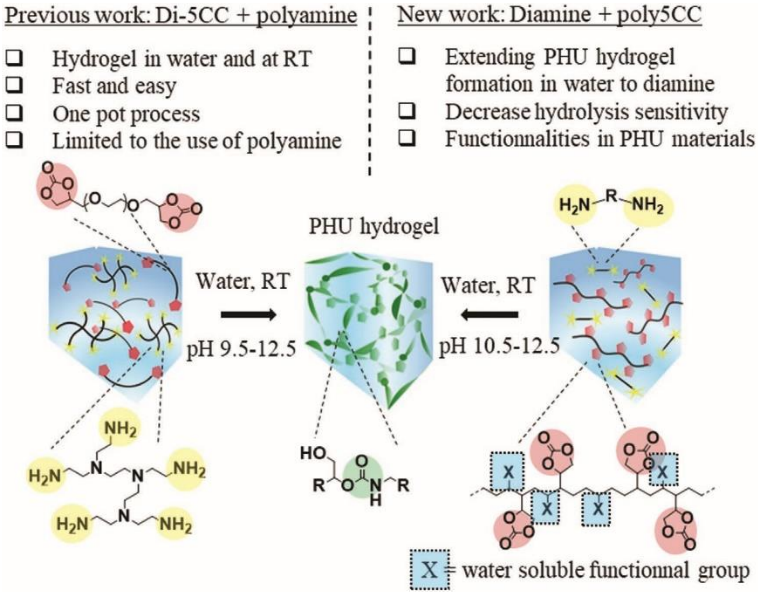
1. Introduction

Polyurethane is a world-leading polymer generally synthesized by the polyaddition between a polyol and a polyisocyanate.[1] The high reactivity of isocyanates and high diversity of the available monomers make PU materials very useful in coatings, foams, glues, ink manufacture.[2] However, isocyanates are toxic and lead to harmful health effect.[3] Therefore, their use is controversial and the trend is to replace them by less toxic and greener substitutes.[4,5] With this in mind, the aminolysis of 5-membered cyclic carbonates (5CCs) leading to the formation of hydroxyurethane functions has attracted some attention. 5CCs can be easily synthesized by the quantitative catalyzed [3+2] coupling of CO_2 to epoxides[6–9] in a green and safe approach using cheap and inexhaustible CO_2. For these reasons, several studies involved the formation of poly(hydroxyurethane) s (PHU) by the polyaddition of a di- or poly(5-membered cyclic carbonate) to di- or polyamine.[5,10–15] This chemistry has demonstrated a high potential for the formation of PHU materials like elastomers,[16–18] thermosets,[19–22] foams,[23–26] using whether petrochemical[27] or biobased 5CC precursors.[20–22,28,29] Although several works were carried out to improve the efficiency of 5CC aminolysis by the addition of catalysts[25,30–34] or the substitution of 5CC,[35,36] their reactivity is still lower than isocyanates for PU synthesis.For this reason, the preparation of PHUs is carried out under thermal treatment in bulk[16,20,21,25,37] or in organic solvent[38–42] to reach high monomer conversion in a reasonable period of time.

PU hydrogels are attractive materials that find multiple applications in the biomedical sector,[43,44] like for tissue engineering,[45,46] drug delivery,[47–50] antibiofouling,[51,52] or for robust and smart hydrophilic materials.[53,54] Although there are many reports on PU hydrogels, examples of analogue material made of PHU are rare. The first PHU hydrogels was based on a two-steps process involving first the preparation of PHU in the bulk by polyaddition of an hydrophilic poly(ethylene glycol) dicyclic carbonate (PEG-diCC) to a diamine and a crosslinker (triamine), followed by their swelling in water.[55] The sole example of PHU hydrogels prepared in water consisted in the aminolysis of PEG-diCC with polyethyleneimine at room temperature (**Scheme 1**).[56] This synthesis in water was possible by a careful adjustment of the pH of the solution to facilitate the aminolysis (the amine had to be deprotonated, thus at pH > p*K*a of the amine) and to disfavor the hydrolysis of the cyclic carbonate moieties. While promising, this technique still suffered from limitations. First, the cyclic carbonate hydrolysis could not be completely prevented at basic pH, providing some unbounded or pending monofunctional chains which were not entailed in the network. Second, the scope of available watersoluble polyamines was limited and some of them are expensive and/or poorly soluble in basic media (e.g., polyallylamine or chitosan). The possible variations of the hydrogel structure and therefore properties were therefore very limited.

Scheme 1. *Scheme of the strategies leading to the formation of PHU hydrogels in water. In previous work, a hydrosoluble dicyclic carbonate was crosslinked by a polyamine. In the present work, a diamine was crosslinked with a water-soluble poly-5CC*



In order to enlarge the scope of water-borne PHU hydrogels and provide them adaptable functionality and behavior, we explore in this work the use of water-soluble novel polymeric polycyclic 5CCs (poly-5CCs) in combination with commercially available primary amines that are water soluble in a large pH range. Some poly-5CCs are commercially available or are described in the literature and derived from carbonated epoxy resin hardeners, renewable vegetal oils or polyols.[19,21,28,29] Free radical polymerization of glycidyl methacrylate or its carbonated form has also been used to produce polyfunctional polymers bearing cyclic carbonates.[57–62] However, to the best of our knowledge, there is no hydrosoluble poly-5CC (with more than 2 CC units) reported in literature that were used for the preparation of PHU hydrogels.

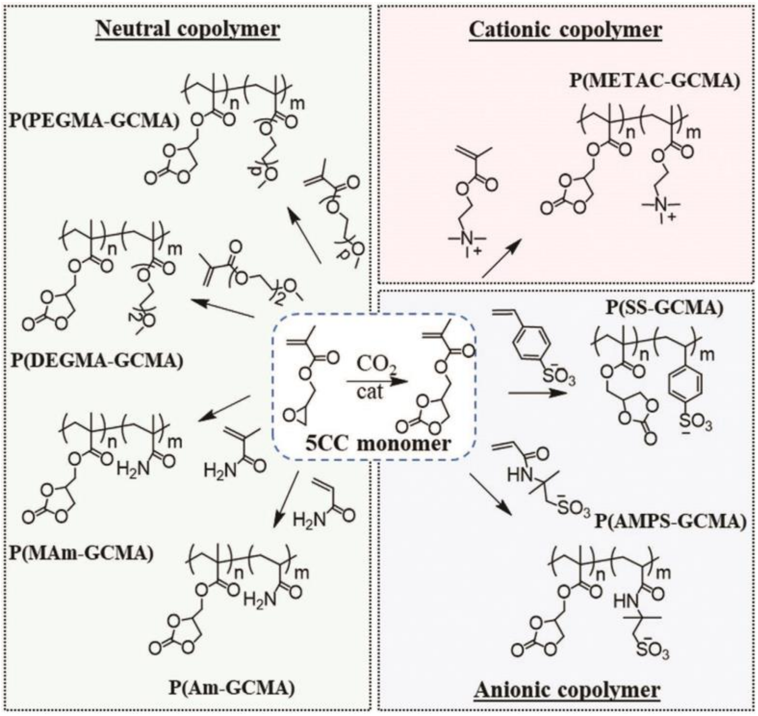
Herein we describe the synthesis of new water-soluble poly5CC and their exploitation for the fabrication of PHU hydrogels in water under mild conditions (Scheme 1). Free radical copolymerization (FRP) of glycerin carbonated methacrylate (GCMA) with different hydrosoluble monomers was first considered in order to design poly-5CCs of different microstructures. Their ability to react with diamines was then studied by rheology and infrared spectroscopy, showing the influence of the amine structure and p*K*a on the cross-linking process in water at room temperature. Advantageously, the presented method allows the incorporation of specific functions like negatively charged styrene sulfonate, quaternary ammonium, or thermosensitive polyethylene glycol methacrylate groups inside the poly-5CC precursors and so enhances the versatility of the resulting hydrogels, potentially enlarging the application range of these products. Notably, we will illustrate the preparation of thermoresponsive PHU hydrogels.

2. Results and Discussion

2.1. SYNTHESIS AND CHARACTERIZATION OF POLYMERS-BEARING PENDANT CYCLIC CARBONATE GROUPS (POLY-5CCS)

The synthesis of polymers with 5-membered cyclic carbonates functionality was already described by (co)polymerization of GCMA in previous works.[60,61] However, due to the hydrophobic nature of GCMA and the comonomers used, the polymers were not water-soluble and were thus not appropriate for our study. In order to prepare water-soluble poly-5CCs, we copolymerized GCMA with hydrosoluble comonomers using AIBN as free radical initiator. All the syntheses were conducted in DMSO (a common solvent for all monomers and polymers) at 65 °C for 24 h. We also benefitted from the large diversity of available hydrosoluble monomers to synthesize poly-5CCs with customizable anionic, cationic, or neutral behavior to enlarge the potential application spectrum of PHU hydrogels (**Scheme 2**). The comonomers that were evaluated are illustrated in Scheme 2, and consist in poly(ethyleneglycol) methyl ether methacrylate (PEGMA with M_n = 500 g mol^{-1}), di(ethyleneglycol) methyl ether methacrylate (DEGMA), methacrylamide (MAm) and acrylamide (Am) for neutral monomers, [2-(methacryloyloxy)ethyl]trimethylammonium chloride (METAC) for a cationic representative, and sodium styrene sulfonate (SS) and sodium 2-acrylamido 2-propane sulfonate (AMPS) for anionic ones. A molar ratio of 50 mol% in GCMA was targeted to produce multifunctional 5CC cross-linkers even for low molar mass polymer chains.

Scheme 2. *Molecular structure of the different poly-5CCs produced by FRP.*



The ^{1}H NMR spectra of the different copolymers prepared at high monomer conversion after 16 h of reaction in DMSO and purified from the residual monomers (see Experimental Section for details), show the presence of signals typical of the cyclic carbonate moieties (5 between 4.8 and 5.5 ppm, and 3,4,6,7 between 3.8 and 4.7 ppm) confirming the incorporation of GCMA within the chains (Figure S2, Supporting Information). The composition of the copolymer was reported in Table 1 and the GCMA content fits with the initial comonomer feed for all polymers (the calculation of the copolymer composition and the ^{1}H NMR detailed spectra used for calculation are described in Section 2 and Figures S3–S9,Supporting Information). The relative molar masses were measured for polymers that were soluble in the solvent used for SEC analysis (i.e., DMF/LiBr) and are presented in the Table 1 (Figures S10–S14, Supporting Information, for chromatograms, ESI). Except for P(AMPS-GCMA) and P(METAC-GCMA) which cannot be analyzed due to their insolubility in the solvent used for SEC analysis, relative number average molar masses (M_n) of 20–124 kg mol^{-1} were measured.

Table 1. *FRP of GCMA with water-soluble comonomers. Conditions: $[GCMA]_0$:$[Comonomer]_0$:$[AIBN]_0$ = 50/50/1, [GCMA] = 0.25 m, DMSO, 65 ℃.*

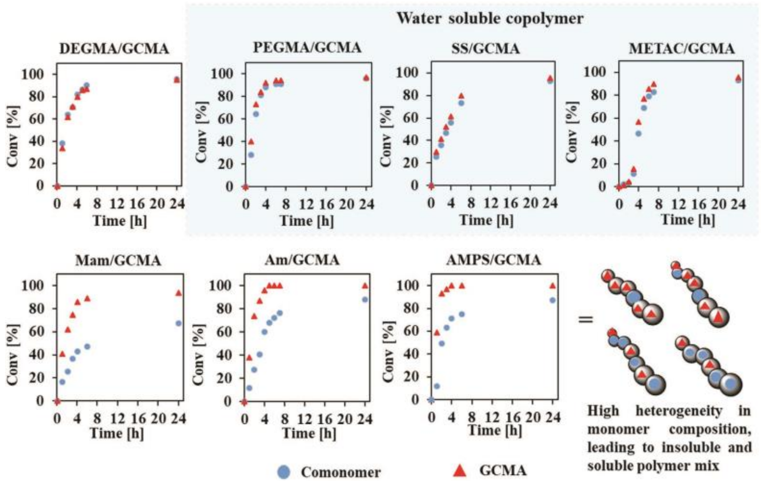
Polymer	GCMA [mol%][a)]	Yield [%][b)]	M_n [g mol^{-1}][c)]	D[c)]	Soluble part [wt%]	GCMA content in soluble fraction [mol%][d)]	GCMA content in insoluble fraction [mol%][e)]
P(PEGMA-GCMA)	50	91	107000	5.6	100	50	–
P(DEGMA-GCMA)	50	94	59000	9.0	< 5	–	50
P(MAm-GCMA)	53	84	51000	6.0	10	30	65
P(Am-GCMA)	48	88	124000	3.2	27	23	72
P(METAC-GCMA)	50	74	–	–	100	52	–
P(AMPS-GCMA)	54	93	–	–	62	40	80
P(SS-GCMA)	54	85	20000	1.8	100	50	–

[a)] GCMA content in the copolymer determined by 1H-NMR of the purified product; [b)]determined by the weight percentage between final product and reactants; [c)]determined by SEC analysis in DMF/LiBr by using a polystyrene calibration; [d)]GCMA composition in the soluble fraction of the copolymer; [e)]GCMA composition in the insoluble fraction of the copolymer.

The solubility of all copolymers in water was then evaluated. Only P(PEGMA-GCMA), P(SS-GCMA) and P(METAC-GCMA) were fully soluble in water at a concentration of at least 200 mg mL^{-1}. The other copolymers displayed partial solubility and their soluble/insoluble fractions were isolated, quantified and the content of GCMA in each fraction was determined by ^{1}H-NMR analysis. Results are collected in Table 1. P(DEGMAGCMA) was almost completely insoluble (>95 wt%) and only the composition of the insoluble part was calculated (50 mol% of GCMA). P(MAm-GCMA) and P(Am-GCMA) were mainly insoluble (90 and 73 wt% of insoluble fraction, respectively). The soluble fractions contained around 30 and 23 mol% of GCMA while the insoluble fractions were composed by 65 and 72 mol% of GCMA. P(AMPS-GCMA) presented a higher solubility, thanks to the presence of the ionic nature of AMPS, with 62 wt% of soluble fraction that contained 40 mol% of GCMA. The insoluble part was still richer in GCMA (i.e., 80 mol%). Therefore, the use of Am, MAm and AMPS as comonomer lead to mixtures of water insoluble GCMA rich chains and soluble GCMA poor chains.

The difference of solubility between the various copolymers can be rationalized by the difference of reactivity between GCMA and the different comonomers during the radical polymerization. **Figure 1** summarizes the comonomers conversion with the reaction time calculated for each comonomer couple (See Figures S15–S21, Supporting Information, for ^{1}HNMR spectra). When the copolymerizations were carried out with DEGMA, PEGMA, SS, or METAC, the two comonomers were polymerized at similar rates. In that case, each polymer chain contained enough water soluble monomer to guarantee the solubility of the whole chain, excepted for P(DEGMAGCMA) for which the DEGMA monomer is not hydrophilic enough to ensure water solubility of the copolymer. In contrast to the above mentioned monomers, MAm, Am, and AMPS were converted much slowlier than GCMA as illustrated in Figure 1. This suggests the formation of mixtures of copolymers rich in GCMA at the early stages of the polymerization and chains poor in GCMA at the later one (Figure 1).

Figure 1. *Consumption of the comonomers during the copolymerization of GCMA with various comonomers and impact on the copolymer structure. Conditions: [GCMA]$_0$:[Comonomer]$_0$:[AIBN]$_0$ = 50/50/1, [GCMA]$_0$ = 0.25 m, DMSO, 65 °C.*

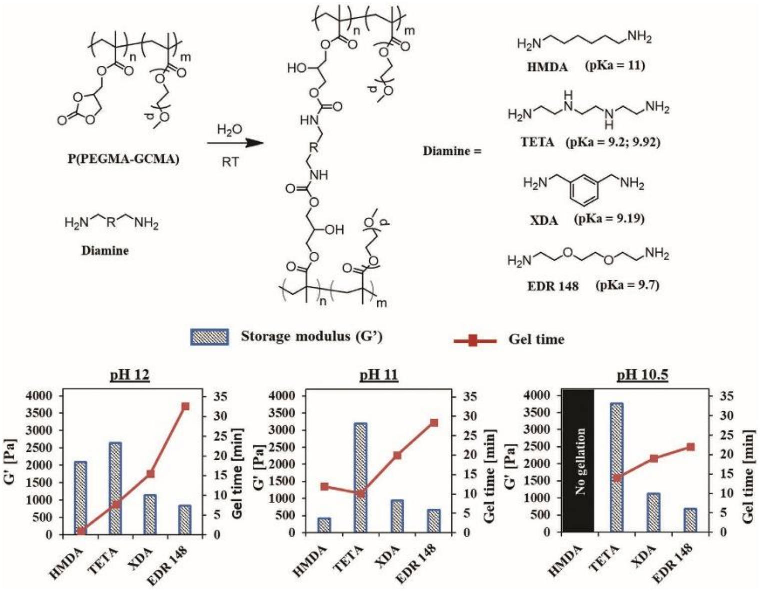


Finally, to further confirm the distribution of GCMA into the polymer chains for the three water-soluble copolymers presented above, the reactivity ratios were calculated for the three copolymerizations (PEGMA/GCMA, Table S1 and Figure S22, Supporting Information; SS/GCMA, Table S2 and Figure S23, Supporting Information; METAC/GCMA, Table S3 and Figure S24, Supporting Information). They were carried out by using different feed ratios and stopped at low monomer conversion to avoid composition drift. The reactivity ratios for the PEGMA/ GCMA copolymerization (r_{GCMA} = 1.72 and r_{PEGMA} = 0.67) were closed to those calculated in the literature for polymerizations of GCMA with other methacrylic monomers[61] and indicated that both PEGMA and GCMA prefer to add to GCMA. Reactivity ratio observed for GCMA/SS (rGCMA = 1.06 and rSS 0.74), indicating that radical shows few preferences to add both monomers. In the copolymerization of GCMA and METAC, GCMA growing chains have a slight tendency to react with another GCMA rather than METAC whereas METAC can react with both monomers without preference (rGCMA = 1.50 and rMETAC = 1.06).

2.2. PREPARATION OF NEUTRAL PHU HYDROGELS AND IMPORTANCE OF THE DIAMINE

We studied the ability of various commercially available primary diamines of different p*K*a values (i.e., hexamethylenediamine (HMDA, p*K*a = 11), m-xylylenediamine (XDA, p*K*a = 9.19), 2,2′–ethylenedioxy bis(ethylamine) (EDR 148, p*K*a = 9.7; **Figure 2**) to react with the neutral hydrosoluble poly-5CCs (P(PEGMA-GCMA)) and to form hydrogels in water at different pH. We also tested triethylenetetramine (TETA, p*K*a = 9.2 and 9.92) characterized by two primary amines and two secondary ones. As previously demonstrated, the secondary amines are not able to compete with the aminolysis of 5CC promoted by primary amines in these conditions.[56]

Figure 2. *Storage modulus evaluated after 2 h of reaction and gel time for PHU hydrogels prepared by reacting P(PEGMA-GCMA) with various diamines at different pH. Conditions: 330 mg mL* $^{-1}$ *P(PEGMA-GCMA), [5CCs] = 0.5 m, [5CCs]/[NH*$_2$*] = 1, 25 ℃, water at pH 10.5, 11, and 12. Gel time was determined by the time to reach cross-over between G′ and G″.*



The reactions were carried out at a P(PEGMA-GCMA) concentration of 330 mg mL^{-1} (0.5 m in 5CC) in water at room temperature under equimolar conditions between the reactive groups ([NH$_2$]/[5CC] = 1). The gel times, corresponding to the crossover point between *G*′ and *G*″, were evaluated by rheology measurements by following the evolution of *G*′ and *G*″ with the reaction time (Figure S25, Supporting Information). Gel times and *G*′ values for all systems at the different pH are compared in Figure 2.

At pH of 12, thus above the p*K*a of all amines, gels were formed in all cases with HMDA that presented the highest reactivity with an impressive gel time of less than 1 min. The sharp increase in *G*′ value indicated a rapid increase in the cross-linking density. Based on the comparison of the gel times, the reactivity of the amines were HMDA > TETA > XDA > EDR 148 at pH 12. A quasi-plateau of *G*′ was observed for HMDA after 2 h of reaction (Figure S25, Supporting Information), indicating that the reaction was close to completion. In contrast, *G*′ was still increasing after this period of time for all other amines (EDR 148, XDA, TETA), suggesting that the crosslinking reactions were not finished. Indeed, our previous work has demonstrated that some hydrolysis of 5CCs was occurring under alkaline conditions with the concomitant acidification of the reaction medium and thus the decrease of the pH of the reaction medium.[56] In order to demonstrate that the 5CCs of P(PEGMA-GCMA) were also hydrolyzing in these conditions, this polymer was solubilized in water at pH of 12 (at 330 mg mL^{-1}) without the primary amine and the evolution of the hydrolysis was followed by ^1H NMR spectroscopy. Figure S26, Supporting Information, evidenced a complete hydrolysis within 16 h as attested by the complete disappearance of the proton signals of the 5CCs ring of P(PEGMA-GCMA) at 5.2, 4.7 and 4.5 ppm and the appearance of new signals corresponding to protons characteristics of generated primary ($CH_2{-}OH$ at 3.7 ppm) and secondary alcohol ($CH{-}OH$ at 3.9 ppm). A kinetics of reaction performed at pH of 12 (under buffered conditions with triethylamine, TEA) demonstrated that the hydrolysis is fast in the absence of primary amine, with 40% of the 5CC that were hydrolyzed in less than 1 h (Figure S27, Supporting Information). We thus monitored the pH evolution in a solution of P(PEGMA-GCMA) ([5CC] = 0.5 m) containing TEA (0.5 m), an amine that cannot react with 5CC but mimics the presence of an amine in the medium (Figure S28, Supporting Information). Under these conditions, we observed that the pH rapidly decreased from 12 to 11 (so near p*K*a of HMDA) within 15 minutes, resulting from the decarboxylative hydrolysis of 5CC rings.

When pH is close to p*K*a, HMDA is (partly) protonated and less prone to react with 5CC,[56] while lower p*K*a diamines like TETA are still under deprotonated state and able to ring-open 5CCs. Storage modulus (*G*′) measured after 2 h of reaction were in the same range for HMDA and TETA (2091 Pa and 2635 Pa, respectively), and lower for XDA and EDR 148 (1142 Pa and 830 Pa, respectively).

When the pH was lowered to 11, the HMDA performance in the cross-linking reaction was drastically decreased with a gel time that was increased to 12 min (instead of 1 min at pH 12) and *G*' reached rapidly a plateau at a lower value in line with a lower cross-linking density (Figure 2). At this pH which is similar to the amine p*K*a, about 50% of the amines were protonated and were not able to react with 5CC. In contrast to HMDA, the other amines presented similar reactivity (gel time, *G*' values) as at pH 12 as they are all characterized by a p*K*a that is lower than pH of the reaction medium.

When pH was further decreased to 10.5, thus at a value lower than p*K*a of the HMDA (p*K*a = 11), no cross-linking reaction was observed with this amine. The other amines were however still active for the crosslinking reaction, in line with their p*K*a that was lower than pH.

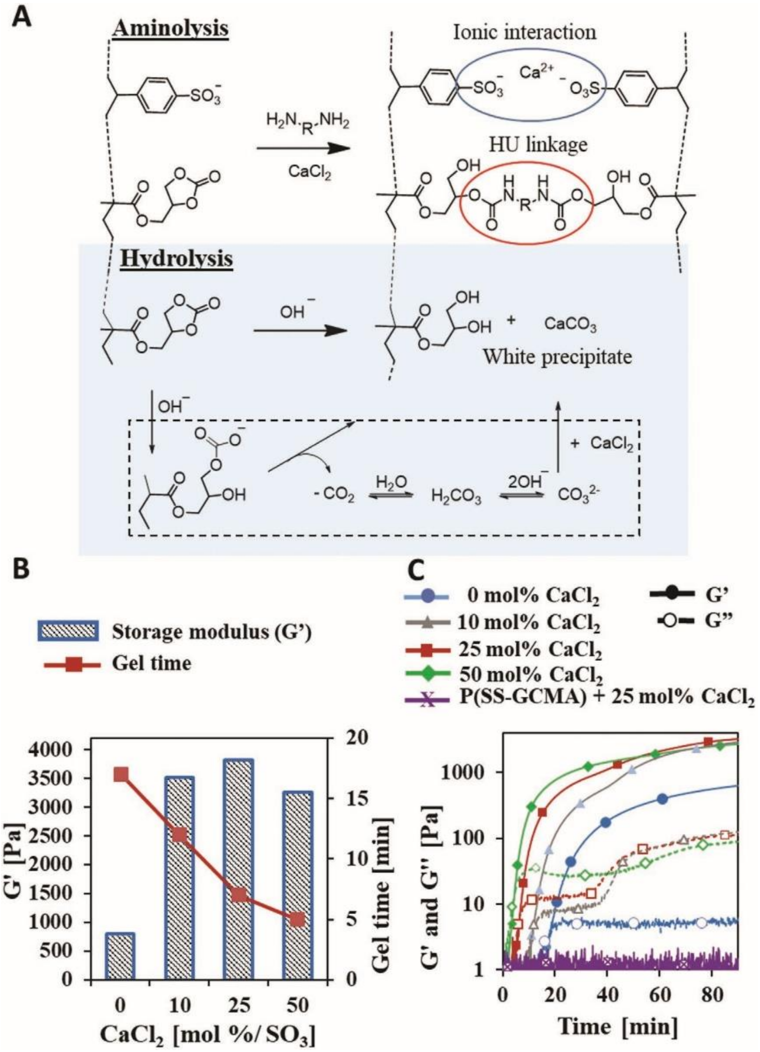
The product formed at the three different pH by the reaction of HMDA with P(PEGMA-GCMA) after 7 days of polymerization were analyzed by infrared spectroscopy after lyophilization (Figure S31A, Supporting Information). At pH 12 and 11, we observed the complete disappearance of the carbonyl elongation of the cyclic carbonate at 1800 cm^{-1} due to the full consumption of 5CC during the reaction. The carbonyl band of the hydroxyurethane function (1705 cm^{-1}) was not clearly observed as the result of the broadening and the shift of carbonyl ester group of both GCMA and PEGMA toward lower wavelength (from 1735 to 1720 cm^{-1}). Urethane formation was confirmed by the appearance of $N{-}H$ bending of urethane function at 1540 cm^{-1}.[63] On the other hand, attenuated transmission reflectance (ATR) spectra of the product formed at pH 10.5 did not present the above characteristics confirming that PHU was not formed. We only noticed the slight decrease of the intensity of the band at 1800 cm^{-1} probably as the result of some 5CC hydrolysis.

The products formed at the three pH (12, 11, and 10.5) when using TETA, XDA, or EDR 148 instead of HMDA presented all the IR bands characteristics of PHUs, confirming that PHUs were formed in these conditions, in line with the conclusions drawn from the rheology measurements (Figures S31B, S32, and S33, Supporting Information).

2.3. CATIONIC OR ANIONIC PHU HYDROGELS

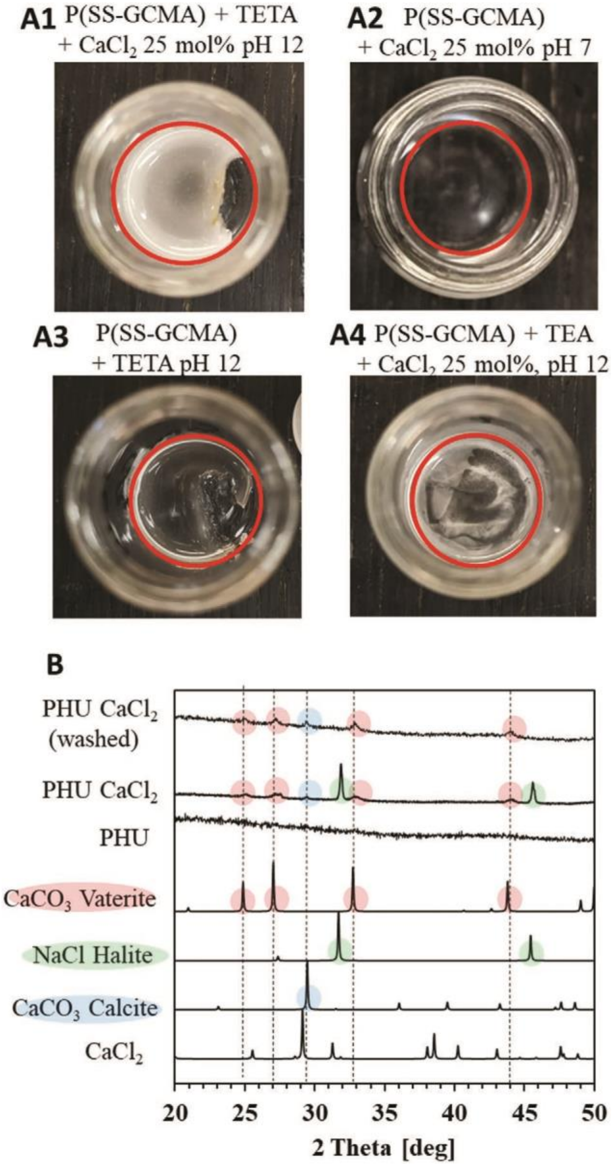
The amine (TETA) that presented the best activity for the three investigated pH for the formation of the neutral PHU was evaluated for the formation of the negatively charged PHU by reaction with P(SS-GCMA) (**Figure 3**). A gel time of 17 min was noted at pH 12 with a G' value of 800 Pa after 120 min (Figure 3B). Interestingly, we found that the addition of $CaCl_2$ to P(SS-GCMA) prior to the amine addition had a beneficial effect on the gel formation. Figure 3B shows that the gel time strongly decreased by increasing the $CaCl_2$ concentration, from 17 min without $CaCl_2$ to 5 min with 50 mol% of $CaCl_2$ (vs sulfonate groups), and the storage modulus was also significantly increased (807 Pa without $CaCl_2$ and 3260 Pa with 50 mol% $CaCl_2$ vs sulfonates). It is important to note that G' and G'' evolutions with the reaction time presented a two steps behavior in the presence of $CaCl_2$ with a second sharp increase in G'/G'' values after 35–40 min of gelation. The addition of 25 mol% of $CaCl_2$ provided the highest storage modulus (3800 Pa) and so the highest crosslinking density after 2 h of reaction, corresponding to a 470% increase in comparison to the hydrogel without $CaCl_2$. We noted that P(SS-GCMA) was more difficult to solubilize when the content of $CaCl_2$ was increased, presumably due to ionic interactions between Ca^{2+} and the sulfonate groups. However, no cross-linking was observed in the presence of 25 mol% of $CaCl_2$ without TETA (Figure 3C). Therefore, $CaCl_2$ did not contribute to the polymer crosslinking in that case.

Figure 3. *Cross-linking reaction between P(SS-GCMA) (200 mg mL−1, [5CC] = 0.5 m) and TETA at pH 12 with or without CaCl2. A) Scheme of the crosslinking reaction and formation of CaCO3 particles. B) Gel time and storage modulus after 2 h measured by rheology. C) Time evolution of G′ and G″ values by rheology. Synthesis conditions: P(SS-GCMA) 200 mg mL−1, [5CCs] = 0.5 m, [5CCs]/[NH2] = 1, 25 °C, water. The magenta curve corresponds to the addition of CaCl2 to P(SS-GCMA) that does not contain TETA.*



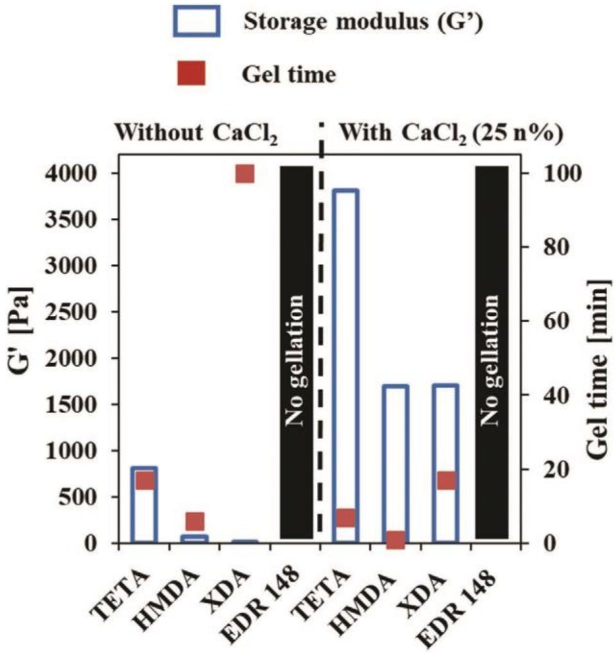
The gelation in presence of $CaCl_2$ and TETA was accompanied by a visual change of the hydrogel, from a clear transparent material to a white and cloudy one (**Figure 4**A1). This transformation was not observed when $CaCl_2$ or TETA were mixed to the polymer (Figure 4A2,A3). This PHU bleaching was assigned to the formation of white $CaCO_3$ crystals, as supported by XRD analysis (Figure 4B). Indeed, the reflections at 2θ = 24.9, 27.0, 32.7, and 43.8 degrees correspond to the vaterite polymorph of $CaCO_3$, while the reflection detected at 2θ = 29.5 degrees corresponds to the position of the main reflection of the calcite polymorph of $CaCO_3$. Two strong reflections at 2θ = 31.8 and 45.5 degrees are related to the formation of NaCl due to the crystallization during drying for XRD analysis. Washing hydrogel for 24 h in water suppressed the NaCl signal and showed only vaterite and calcite in the XRD pattern. $CaCO_3$ was formed as the result of the partial hydrolysis of the cyclic carbonate at this pH. During this hydrolysis, the released carbon dioxide solubilized in water to form carbonate anions that provided insoluble $CaCO_3$ in the presence of $CaCl_2$ (Figure 3A). In order to give some clues to this hypothesis, P(SS-GMA) was mixed by $CaCl_2$ at pH of 7, no $CaCO_3$ was formed because the cyclic carbonate did not hydrolyse at this pH (Figure 4A2). On the contrary, by adding TEA to the same reaction medium to buffer the medium at a pH of 12, no gel was formed since no cross-linker was present. However, a white precipitate was observed due to the hydrolysis of the cyclic carbonate and the precipitation of $CaCO_3$ (Figure 4A4). Therefore, the cyclic carbonate hydrolysis can be exploited for the in situ generation of $CaCO_3$ particles that reinforced the PHU hydrogel, as attested by a much higher *G*' value measured by rheology (Figure 3B).

Figure 4. *A) Pictures of different formulations: A1: P(SS-GCMA) + TETA + CaCl2 (25 mol%) at pH 12; A2: P(SS-GCMA) with CaCl2 (25 mol%) at pH 7; A3: P(SS-GCMA) + TETA without CaCl2 at pH 12; A4: P(SSGCMA) + TEA + CaCl2 (25 mol%) at pH 12. B) Experimental XRD patterns of lyophilized PHU (PHU), PHU obtained in the presence of CaCl2 (PHU CaCl2), PHU obtained in the presence of CaCl2 and washed with water after synthesis (PHU CaCl2 (washed)), and reference XRD patterns of CaCO3 vaterite, NaCl halite, CaCO3 calcite and CaCl2. PHU synthesis condition: P(SS-GCMA) 200 mg mL−1, [5CCs] = 0.5 m, [5CCs]/[NH2] = 1, 25 °C, water, 24 h.*



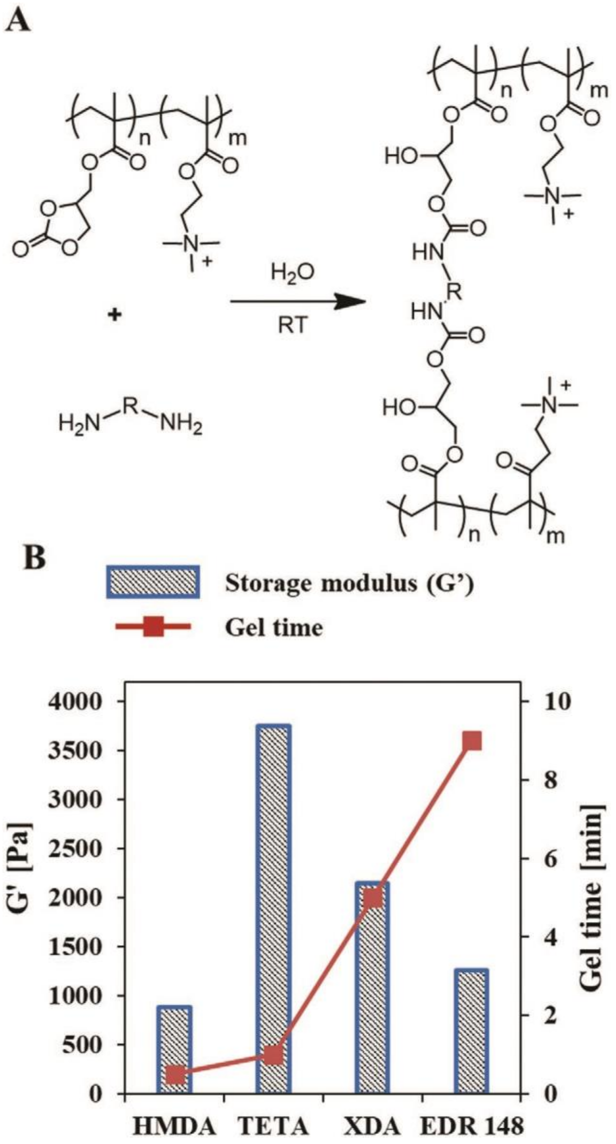
The addition of $CaCl_2$ (25 mol% vs sulfonate groups) was then evaluated for the same reaction carried out in the presence of HMDA and XDA. Similarly to the reaction performed with TETA, the gelation process was also significantly faster (**Figure 5** and Figure S35, Supporting Information) and lead to higher storage modulus in the presence of $CaCl_2$ (Figure 5). Surprisingly no cross-linking occurred with EDR 148 with or without the presence of $CaCl_2$. We cannot explain this curious but reproducible observation. The highest storage modulus was again noted for the reaction with TETA.

Figure 5. *Storage moduli after 2 h and gel times measured by rheology during crosslinking reaction between P(SS-GCMA) and different diamines with or without CaCl2 (25 mol%/SO3−). Conditions: 200 mg mL−1 P(SSGCMA), [5CCs] = 0.5 m, [5CCs]/[NH2] = 1, 25 °C, pH = 12, water.*



The positively charged PHU hydrogels were prepared by reacting the cationic poly-5CCs (P(METAC-GCMA)) with the different diamines at a pH of 12 (**Figure 6**A). Based on rheological measurements (Figure 6B), we found exactly the same conclusions than for the two others poly-5CCs. Gel times were in the order HMDA (30 s) < TETA (1 min) < XDA (5 min) < EDR 148 (9 min), and the highest *G*' values were higher with TETA.

Figure 6. *Formation of positively charged PHU hydrogels by reaction of P(METAC-GCMA) with various diamines in water. A) Scheme of the reaction. B) Storage modulus after 2 h and gel times. Conditions: 200 mg mL−1 P(METAC-GCMA), [5CCs] = 0.5 m, [5CCs]/[NH2] = 1, 25 °C, pH = 12, water.*

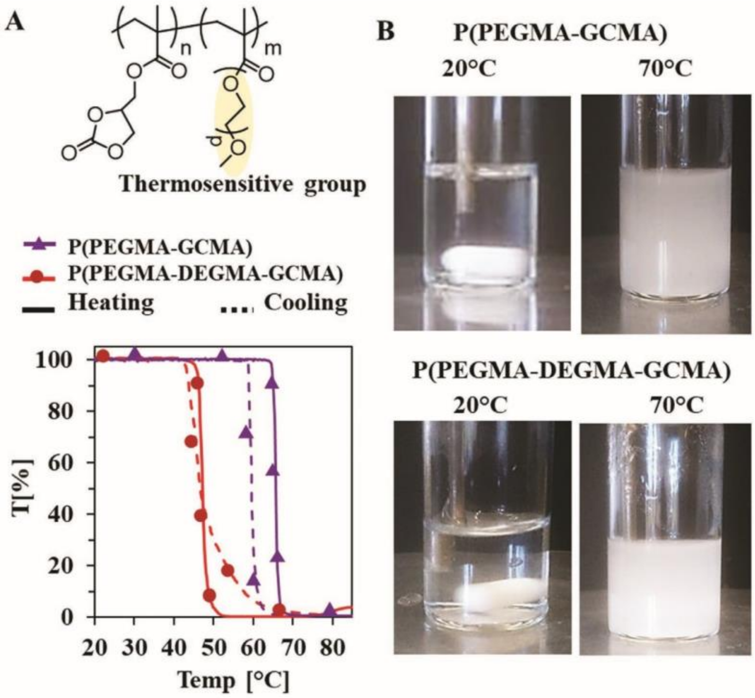


2.4. THERMORESPONSIVE PHU HYDROGELS

Finally, we benefited from oligo(ethylene glycol) methacrylate side chain of P(PEGMA-GCMA) to synthesize PHU hydrogel presenting a thermosensitive swelling behavior and transparency. Indeed, poly-oligo(ethylene glycol) methacrylate (P(PEGMA)) presents a LCST behavior,[64–66] and is thus water soluble at a temperature up to the transition temperature thanks to hydrogen bonding between water and their hydrophilic side chains. Above this temperature, polymers aggregate due to hydrogen bonding breaking and the increase of hydrophobic interactions. The LCST temperature was related to the length of oligo(ethylene glycol) side chain, the longer, the higher the hydrophilicity and the higher the cloud point.[66]

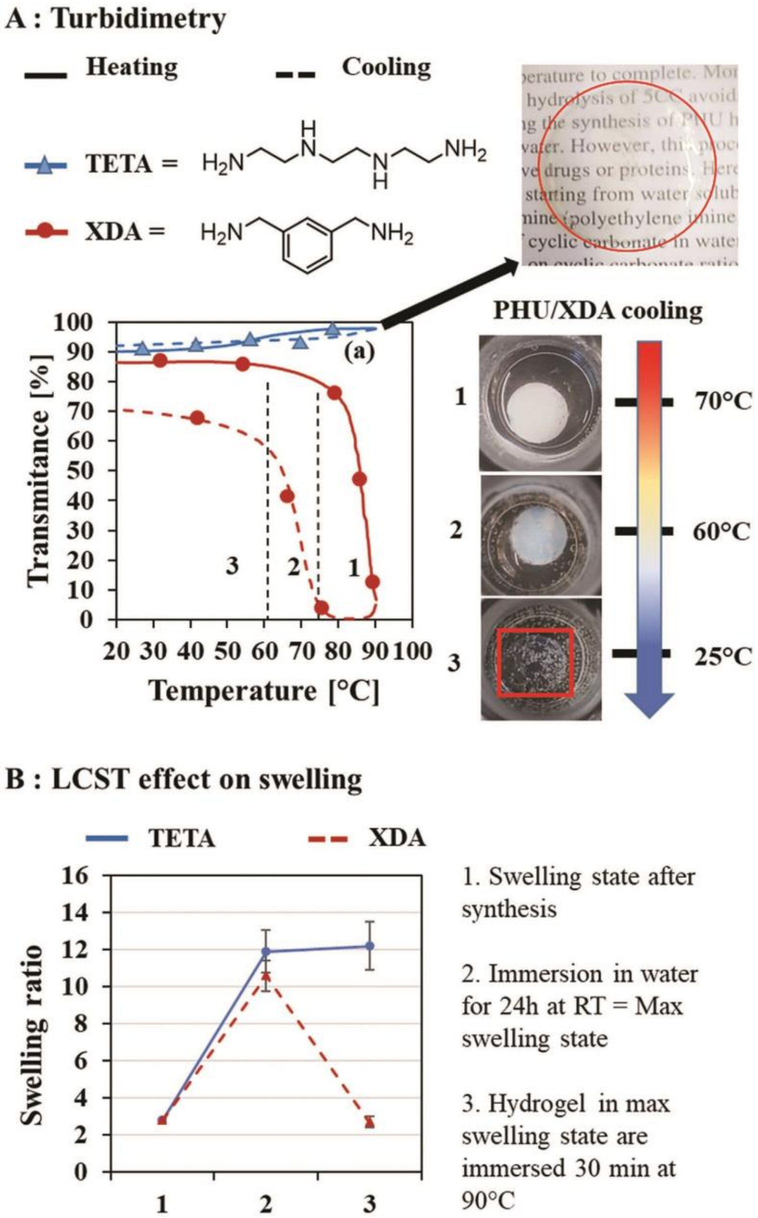
Turbidimetry experiments were first carried out on an aqueous solution of our P(PEGMA-GCMA) copolymer (10 mg mL^{-1}) in order to evidence a possible thermoresponsive character of this novel polymer bearing pendant cyclic carbonate groups. **Figure 7** evidences a transition temperature at around 66 °C (Figure 7a). The loss of transmittance was supported by a change from a transparent and clear solution at 20 °C to a cloudy solution at 70 °C (Figure 7b). This transition was also reversible, and decreasing the temperature leads to a transparent solution with a high transmittance. A slight hysteresis phenomenon was observed, shifting the LCST value to a lower temperature when cooling (LCST = 61 °C). It is often interesting to be capable to tune LCST of a polymer to perfectly fit the need of the application. It has been shown that LCST in poly-oligoethyleneglycol methacrylate can be easily modulated by changing the length of the oligo(ethylene glycol) side chain.[64] However, in our case this modification had to be taken carefully since copolymer with short oligoethylene oxide chain like P(DEGMA-GCMA) was not water soluble due to the hydrophobicity of cyclic carbonate side chain. Therefore, DEGMA and PEGMA were copolymerized with GCMA in order to set the LCST of the copolymer at a lower temperature value.[67,68] The feeding ratio of GCMA:DEGMA:PEGMA = 0.5:0.25:0.25 was chosen and ^{1}HNMR of the copolymer confirmed that the molar ratio of the copolymer was 50 mol% in GCMA. Although it was impossible to determine the molar ratio of the two other monomers in this polymer due to structural similarities and signal overlapping, it was expected that this ratio was close to the feeding ratio since the reactivity of the two monomers with GCMA was very similar (Figure 1) and the monomer conversions were close to completion after 24h of reaction. Unlike P(DEGMA-GCMA), this terpolymer was water soluble at room temperature thanks to the incorporation of hydrophilic PEGMA monomer units. At 10 mg mL^{-1}, a sharp decrease in the transmittance was observed at 47 °C (Figure 7A). The incorporation of DEGMA enabled to decrease the copolymer LCST by 20 °C. During cooling, the transition of the polymer from insoluble to soluble was slower and occurred over a broader temperature range (between 65 and 45 °C) compared to P(PEGMA-GCMA).

Figure 7. *LCST behavior of (P(PEGMA-GCMA) and P(PEGMA-DEGMA-GCMA) in water. A) Turbidimetry of the thermoresponsive polymers at 10 mg mL−1. B) Images of the copolymer solutions at 20 °C and 70 °C.*



The thermoresponsive P(PEGMA-GCMA) copolymer was then evaluated for preparing thermoresponsive PHU hydrogels by crosslinking with diamines (TETA or XDA, [5CC]/[NH_2] = 1) at a pH of 10.5. After 24 h of reaction, a temperature ramp was applied between 20 and 90 °C and the transmittance against water was measured. No LCST transition was observed in the range of tested temperature with TETA, probably due to the high hydrophilicity of the amine with two secondary amines. On the other hand, when a more hydrophobic diamine was used such as XDA, a sharp transition was observed at around 87 °C. Upon cooling, a transition from an opaque white hydrogel to a blue turbid one was observed at 67 °C, and the hydrogel became transparent below 50 °C (**Figure 8**A). A loss in transmittance was observed after cooling to 20 °C due to the presence of bubbles trapped in the hydrogel during the first heating step. Despite the loss of measured transmittance, photography of the resulting hydrogel showed a high remaining transparency (Figure S37, Supporting Information). The thermal behavior of the PHU hydrogel had also an impact on its swelling ability (Figure 8B). Hydrogels formed by reaction between P(PEGMAGCMA) and XDA or TETA were immersed in water after 24 h of cross-linking. Swelling at room temperature was measured after 24 h and the swelling ratio of PHU hydrogel with XDA or TETA was largely increased (from 2.8 to 10.6 or 11.8, respectively). Then water and gel were heated at 90 °C for 30 min, which promoted a recovery of the initial swelling ratio for gel cross-linked by XDA (swelling ratio of 2.6) and no decrease for gel cross-linked by TETA (swelling ratio of 12.2).

Figure 8. *Thermosensitivity of the PHU hydrogels prepared by reaction of P(PEGMA-GCMA) with TETA or XDA. A) Transmittance analysis, B) Swelling analysis.*



3. Conclusions

In this work, we have investigated the FRP of GCMA with various water soluble monomers with the objective to prepare water-soluble polymers bearing cyclic carbonate pendants. The final goal was to engage them in crosslinking reactions with various diamines to furnish isocyanate-free polyurethanes, polyhydroxyurethane (PHU), and hydrogels in water. Amongst the different water soluble monomers that were tested, styrene sulfonate (SS), poly(ethyleneglycol) methyl ether methacrylate (PEGMA) and 2-methacryloyl aminoethyl trimethylammonium chloride (METAC) polymerized in a similar rate than GCMA and provided the desired water-soluble copolymers with a content of 50 mol% GCMA. Neutral, anionic, or cationic PHU hydrogels were then successfully prepared by reaction with various amines (HMDA, TETA, XDA, and EDR 148) in water at room temperature. By following the reactions by rheology, the gel time and storage modulus of all systems were evaluated at three different pH (12, 11, and 10.5). HMDA presented the highest activity with gel times as short as 1 min at pH of 12, however became inactive at pH of 10.5 as the result of the protonation of the amines. With a lower p*K*a, TETA provided the hydrogels with the highest storage modulus over the entire investigated pH range. We also observed that the addition of $CaCl_2$ to the anionically charged polymer (P(SS-GCMA)) prior to the addition of the diamine decreased the gel time and strongly improved the storage modulus of the hydrogel. These improved performances were the result of the in-situ formation of $CaCO_3$ crystals that originated from the partial hydrolysis of 5CCs units of the polymer at pH 12. This hydrolysis released CO_2 that, upon dissolution in water, yielded carbonate anions that formed insoluble $CaCO_3$ that reinforced the PHU hydrogel. Finally, the hydrosoluble Poly-5CC bearing pendant polyethylene glycol chains were exploited for the preparation of thermoresponsive PHU hydrogels. This work has shown that a large palette of PHU hydrogels (neutral, anionic, or cationic) can be easily prepared in water at room temperature from readily available water-soluble amines, opening new perspectives in the field of isocyanate-free polyurethanes.

4. Experimental Section

MATERIALS

Tetrabutylammonium iodide (TBAI, 98%), Glycidyl methacrylate (GMA, 97%), Hexamethylenediamine (HMDA, 98%), 2,2′–ethylenedioxy bis(ethylamine) (EDR 148, >98%), m-xylylenediamine (XDA, 99%), 4-styrene sulfonic acid sodium salt (SS), Poly(ethyleneglycol) methyl ether methacrylate (M_n = 500, 100 ppm MEHQ, and 200 ppm BHT as inhibitor) (PEGMA), Di(ethyleneglycol) methyl ether methacrylate (DEGMA, 95%), Methacrylamide (Mam, Acrylamide (Am, 98.5%), Triethylamine (TEA, 99%) were supplied 98%), METAC, 75% in water, Azobisisobutyronitrile (AIBN, 98%), by Acros and triethylene tetramine (TETA, tech. grade) by Janssen. and Calcium Chloride (CaCl2, 97%), were provided by Sigma Aldrich. Perfluoro-tert-butanol was provided by Fluorochem. All products were used as received. 2-Acrylamido-2-methylpropane sulfonic acid (AMPS, 99%) was provided by Sigma Aldrich and was neutralized until pH 7 by NaOH 2 m and lyophilized before use.

CHARACTERIZATIONS

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

^{1}H NMR analyses were carried out on Bruker Avance 400 MHz spectrometers at 25 °C in the Fourier transform mode.

RHEOLOGY EXPERIMENTS

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

INFRARED CHARACTERIZATIONS

Infrared spectra were measured by using a Nicolet IS5 spectrometer (Thermo Fisher Scientific) equipped with a transmission or with a diamond 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.

SIZE EXCLUSION CHROMATOGRAPHY

The macromolecular parameters were determined in DMF LiBr (0.025 m) with a polystyrene calibration at 55 °C (flow rate 1 mL min^{-1}) with a chromatograph Waters 600 on PSS gram analytical 30A and 1000A columns and with a 410 refraction index detector.

TURBIDIMETRY MEASUREMENTS

Turbidimetry measurements were performed on Jasco V630 UV spectrometer at 700 nm. Turbidimetry on thermoresponsive polymer was measured at a 10 mg mL^{-1} in water in a 1 cm quartz cell equipped with a magnetic stirrer in a temperature controller (ETCS-761). Temperature was incremented from 1 °C min^{-1}. Turbidimetry of the PHU hydrogel was carried out in plastic cell. Data were analyzed with the spectra manager program from Jasco.

X-RAY DIFFRACTION MEASUREMENTS

X-ray diffractograms of the *samples* placed on a zero-background plate were collected using a Bruker D8 TWIN-TWIN diffractometer in Bragg-Brentano configuration (Cu Kalpha radiation, 0.02° step size, 0.5 s/step/strip with a 192-strip Lynxeye XET detector).

REACTIONS-PROCEDURE FOR COPOLYMER SYNTHESIS

In a typical experiment, GCMA (1.4 g 7.5 mmol, 1 eq.), comonomers (7.5 mmol, 1 eq.), and AIBN (25 mg, 0.15 mmol, 0.02 eq.) were added in a reaction tube with DMSO (30 mL). The solution was degassed in a sealed tube for 10 min with argon. Polymerization was carried out at 65 °C for 24h under inert atmosphere. The resulting polymer was purified by dialysis against water for 20 h with a dialysis membrane of 1000 MWCO and was finally freeze dried. Yield of the reaction was calculated by the weight ratio between recovered purified polymer and reactant (i.e., GCMA, comonomer, and AIBN) according to the formula: Yield (%) = $(m_{\text{polymer}} \ / \ m_{\text{reactant}}) \times$ 100. Comonomer content calculations are presented in Figures S3–S9, Supporting Information.

SOLUBILITY MEASUREMENTS

200 mg of the copolymer (P(DEGMAGCMA), P(AM-GCMA), P(MAm-GCMA), P(AMPS-GCMA) were added to 1 mL of water under stirring at 25 °C. After 30 min, the soluble and insoluble fractions were separated by centrifugation at 4000 rpm for 10 min. The two fractions were then freeze dried before ^{1}H NMR analysis and weighing.

PROCEDURE FOR THE MEASUREMENT OF COMONOMER CONSUMPTION DURING POLYMERIZATION

In a typical experiment, GCMA (140 mg 0.75 mmol, 1 eq.), comonomers (0.75 mmol, 1 eq.), and AIBN (2.5 mg, 0.015 mmol., 0.02 eq.) were added in a reaction tube with deuterated DMSO (3 mL). The solution was degassed in a sealed tube for 10 min with argon. Polymerization was carried out at 65 °C under inert atmosphere. Samples was picked out after different time, were then added by an equivalent volume of deuterated DMSO and were immediately stored at −20 °C. The samples were analyzed by 1H NMR spectroscopy to determine the conversions as described in ESI (Figures S15–S21, Supporting Information).

PROCEDURE FOR THE DETERMINATION OF THE REACTIVITY RATIOS

In a typical experiment, different feed ratios in both monomers (GCMA and comonomer, C_{total} = 1.5 mmol) and AIBN (2.5 mg, 0.015 mmol) were added in a reaction tube containing deuterated DMSO (3 mL). 0.5 mL of sample was picked out and conserved at −20 °C as starting point of polymerization. The remaining solution was degassed in a sealed tube for 10 min with argon. Polymerization was carried out at 65 °C under inert atmosphere. Polymerization was stopped after 20 min by mixing 1 mL of the polymerization medium with an equivalent volume of deuterated DMSO and was immediately stored at −20 °C. Consumption of both monomers was calculated by ^{1}H NMR, according to formula presented in ESI in Figures S15–S21, Supporting Information.

PROCEDURE FOR THE SYNTHESIS OF PHU HYDROGELS

In a typical experiment, a solution of poly-5CC in water (0.75 mL; concentration in 5CC groups = 0.67 m) was added with a solution of the diamine (0.25 mL; C = 1 m) at the appropriate pH. The pH of the diamine solution was adjusted at 12, 11, or 10.5 by the addition of HCl (37%) prior to adding the diamine to the poly-5CC solution. Vigorous stirring was maintained for 30 s before adding to a vial. Polymerization occurred in a closed vial to avoid water evaporation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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