Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

NON-ISOCYANATE POLYURETHANES AT ROOM TEMPERATURE
A DREAM BECOMING REALITY

Thomas Habets[a,1],Bruno Grignard [a,b], Christophe Detrembleur [a,c,*]

[a] *Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, University of Liege, Sart-Tilman B6a, Liege 4000, Belgium*
[b] *FRITCO2T Platform, University of Liege, Sart-Tilman B6a, Liege 4000, Belgium*
[c] *WEL Research Institute, Wavre 1300, Belgium*

Keywords:

Polyurethane
Non-isocyanate polyurethane
Room temperature
Cyclic carbonate
Polymerization
Catalysis
Monomer design

Abstract

Polyurethanes (PUs) are one of the most widely utilized classes of polymers worldwide. However, their conventional production relies on toxic and hazardous isocyanate compounds whose usage is being limited by recent regulations. This has driven the development of new chemical strategies to access nonisocyanate PUs, or NIPUs. While the traditional PU synthesis typically occurs at room temperature (r.T) due to the high reactivity of isocyanates, NIPU synthesis generally requires elevated temperatures to surpass the low reactivity of the precursors. Considering societal needs and regulatory changes, achieving NIPU synthesis at r.T could reduce the energy footprint of the process, facilitate transition to NIPUs within existing PU manufacturing facilities and in consumer-grade applications –a more seamless switch from PUs to NIPUs. Additionally, r.T reactions are desirable for minimizing side reactions and enabling a wider functional group tolerance. This review critically gathers unbridged data and recent strategies aimed at achieving NIPU synthesis at r.T. This includes advances in monomer design, catalysis, and the use of r.T- efficient hybrid chemistries. Various polymerization techniques from a wide diversity of precursors are discussed, along with the advantages and limitations of each approach.

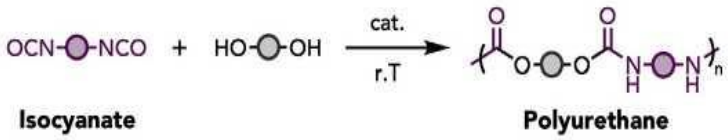
Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

1. Introduction

Polyurethanes (PUs) are among the most widely utilized polymers globally, with an annual production of about 30 million metric tons in 2022 [1] –a testament to their critical role in numerous industries. Their applications span high-performance thermoplastics elastomers [2], foams for comfort and insulation [3,4], as well as adhesives and coatings [5]. This widespread usage stems from the ability to finely tune their unique properties by simple monomer variations to target specific applications, distinguishing them from other polymer classes [6–8].

Conventional PUs are synthesized by the step-growth polymerization of polyisocyanates with polyols (Scheme 1). This reaction is often conducted at room temperature using catalysts such as dibutyltin dilaurate (DBTDL) or an organobase like 1,4- Diazabicyclo[2.2.2]octane (DABCO). However, isocyanates are toxic and hazardous compounds, posing significant health and environmental issues. In response to this hazard, European REACH regulations have imposed drastic restrictions of use on isocyanates. This intensified research for safer non-isocyanate alternatives, referred to as non-isocyanate polyurethanes (NIPUs).

Scheme 1. *Conventional PU synthesis from isocyanates.*



The 12 principles of Green Chemistry [9] emphasize minimizing energy requirements, thus encouraging near-ambient or room temperature processes [10,11]. This not only reduces the energy footprint of a process, but also enhances selectivity and minimizes side reactions – commonly observed at elevated temperatures [12]. This approach also enables greater functional group tolerance, crucial in polymer chemistry where functional groups on the polymer backbone significantly influence the final material properties. Additionally, the capacity to formulate and cure these materials at ambient temperature makes polyurethanes more accessible for consumer applications without the need for specialized equipment, but also to fit in existing PU industrial facilities.

While offering significant economic and environmental benefits, the room temperature synthesis of NIPUs presents enormous challenges, primarily due to the low reactivity of the monomers compared to isocyanates. Moreover, this low reactivity complicates the formation of materials endowed with complex architectures, such as PU foams. In traditional PU foam synthesis, water is introduced in the formulation and reacts with isocyanates, generating CO2 as chemical blowing agent to create the foam cellular structure. Achieving similar results without isocyanates at r.T thus requires innovative approaches to replicate isocyanate-based expanded materials.

This literature review will explore the chemical strategies developed to enable room-temperature polymerizations toward NIPUs. It will critically examine the routes that have proven successful to synthesize NIPUs at r.T and highlight the strategies that have made this possible. This includes reaction optimization through molecular engineering of the monomers, the usage of specific catalysts, or solvation effects in specific reaction routes. This is generally achieved by examination of small model molecules reactivity studies, and/or directly during polymerization.

2. NIPUs by aminolysis of 5-membered cyclic carbonates

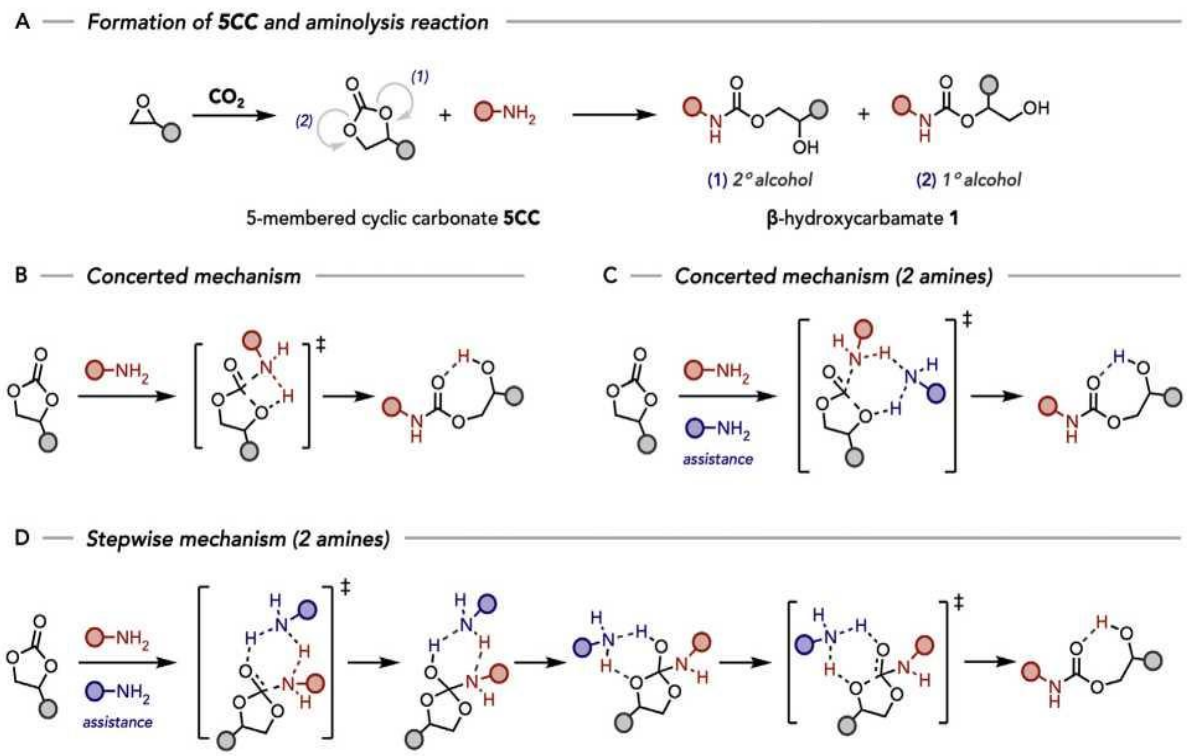
One of the most promising strategies toward NIPUs is the step-growth polyaddition between polyfunctional 5-membered cyclic carbonates (5CC) and polyamines to produce poly(hydroxyurethane)s (PHUs). (Poly)5CC can be synthesized by the well-established coupling of CO2 onto epoxides (Scheme 2a), with an ever-expanding library of molecules. This approach is not only relatively inexpensive but has also been scaled up to the kilogram level [13]. The

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

reaction between 5CC and amines occurs via nucleophilic attack of the amine onto the electrophilic carbonyl function of the carbonate, followed by ring-opening to yield a hydroxyurethane product 1 (Scheme 2a). The bond scission can occur on both sides, yielding a mixture of two isomers: (i) an isomer containing a secondary alcohol, which is formed in larger amounts, and (ii) an isomer containing a primary alcohol.

However, these 5CC scaffolds display low reactivity toward amines at room temperature, and polymerizations are typically achieved at temperatures above 80°C. Additionally, side reactions are reported for this reaction at temperatures above r.T. This leads to an undesired decrease of molecular weight in thermoplastic or cross-link density in thermosets, as well as irregularities in the (macro)molecular structure. There exist only few reports of polymerizations at r.T. In this section, we will discuss (i) the mechanism of reaction and side reactions, (ii) strategies employed to achieve reaction at lower temperature, (iii) the current limitations of this chemistry, (iv) the reported polymers synthesized at r.T, and (v) a perspective to better understand and, consequently, overcome these roadblocks.

Scheme 2. *(A) CO_2 fixation on epoxide toward* ***5CC****, followed by its aminolysis into* ***1****. Several mechanisms were computationally unraveled, such as (B) a simple concerted mechanism, (C) the same concerted mechanism with the assistance of an extra amine, and (D) a stepwise mechanism with the assistance of an extra amine.*



2.1 MECHANISM OF REACTION AND REPORTED SIDE REACTIONS

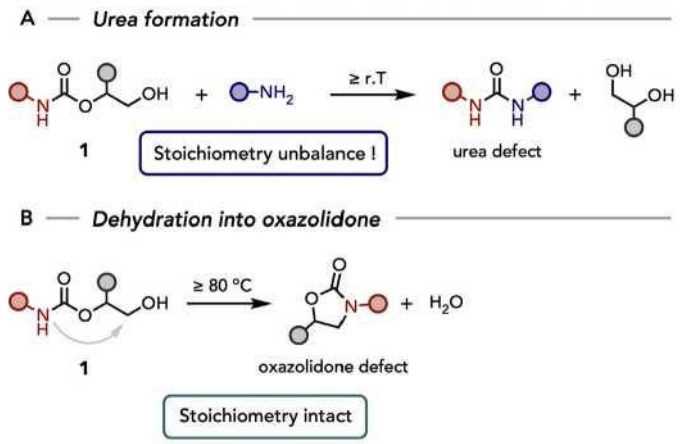
Kinetic experiments demonstrated that the overall reaction rate is governed by two contributing noncatalytic and autocatalytic pathways. This means the aminolysis of cyclic carbonates can happen either with one amine reacting with 5CC, or through a process involving two amines, where one serves as a catalyst [14–18]. These mechanisms were supported by computational insights on model compounds. Zabalov suggested in 2011 that the amine attacks the cyclic carbonate following a one-step addition and ringopening process involving either one or two amines. The presence of a second amine in the autocatalytic route significantly lowers the energy barrier of the reaction [19,20]. When a second amine is involved, it serves as a proton relay, forming a more stable 6membered ring within the

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

transition state (TS). It replaces the strained 4-membered ring formed when only one amine is involved, as illustrated in Scheme 2b and 2c. Alternatively, an even more favorable multi-step process featuring a tetrahedral inter-mediate was also demonstrated when two amines are involved (Scheme 2d).

Model reactions evidenced that side reactions occur with this chemistry. The most frequently reported is the formation of unreactive urea and diol, occurring through the reaction of a free amine with a hydroxyurethane **1** [21] (Scheme 3a). Although most studies evidence its formation in small amounts at 80°C [22], up to 6% of these products were observed at temperatures as low as 50°C or even r.T [23–25]. At higher temperature (generally starting from 80°C), a five-membered oxazolidone can be formed through dehydrative ring-closure (Scheme 3b). The formation of urea is problematic as it leads to a stoichiometry deviation in the system, consequently leading to low molecular weight polymers. The formation of oxazolidones does not hamper step-growth polymerization but is responsible for the release of water molecules, which can be troublesome if water-sensitive functionalities are present.

Scheme 3. *Main side reactions in PHU chemistry: (A) urea formation, and (B) oxa- zolidone formation.*



2.2 STRATEGIES FOR INCREASING REACTIVITY

Different strategies were adopted to increase the rate of 5CC aminolysis at low temperature either by playing on the chemical structure of **5CCs** and amines, by catalyzing the reaction, or by utilizing solvents. Each of them will be discussed point-by-point below. As most of the works dealing with PHUs concern the preparation of thermosets for coating, adhesive or foam applications, monitoring the reactivity of the monomers is not straightforward due to the crosslinked nature, and thus insolubility, of the product. Model reactions and theoretical works on small molecules were thus carried out by many research groups in the last years to better understand the influence of each parameter on the reaction as well as to facilitate the characterization of the (by)products.

2.2.1 INCREASED REACTIVITY BY MOLECULAR ENGINEERING OF 5CC

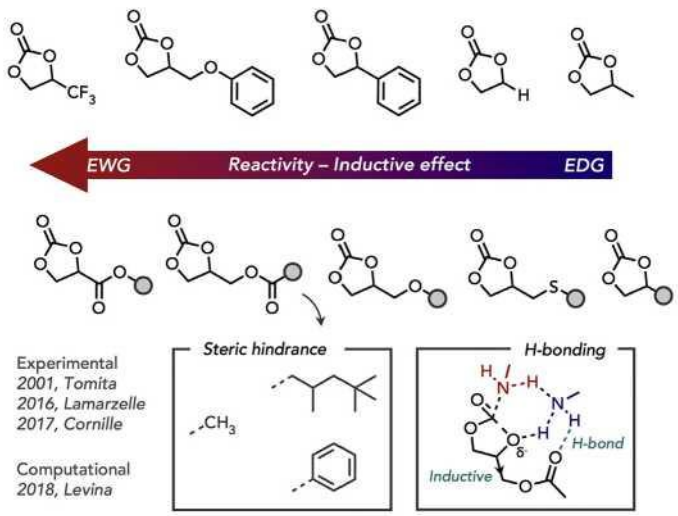
The most straightforward strategy to accelerate the reaction rate is to increase the reactivity of the reactants. The structure of **5CC** can be easily modulated thanks to the broad diversity of available (poly)epoxides and synthesis pathways thereof. Cornille identified three key parameters affecting the reaction rate: (i) the presence and position of electron-withdrawing groups (EWGs), (ii) the steric hindrance around the functional group, and (iii) the ability of the group to form hydrogen bonds with free amines [18]. It was found that EWGs in the vicinity of the carbonate function significantly accelerated the reaction by pulling electrons away from the carbonate through negative inductive effect (I^-), thus rendering the carbonate function more electrophilic [16,18,23,24,26]. These groups also help to stabilize transition states where partial negative charges appear when the amine adds to the ring. A ranked list of **5CCs** with varying substituents is provided in Scheme 4 by order of reactivity. Furthermore, the proximity between the carbonate and the EWG has shown crucial for increasing the reaction rate [27].

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

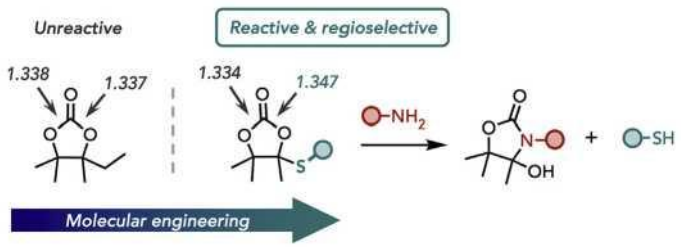
A computational study further supported the reactivity order of the cyclic carbonates and the contribution of an EWG in stabilizing transition states [28]. It revealed that the inductive effect of an ester group contributed to stabilizing the transition state (TS) by 2 kcal·mol^{-1}, while hydrogen-bonding provided a more moderate stabilization of 1 kcal·mol^{-1}. Both contribute to the overall decrease in energy barrier, thereby accelerating the reaction rate.

Less explored is the impact of the ring substitution degree on the reactivity of **5CCs** with amines. However, sterically congested di- and tri-substituted **5CCs** react slowly with amines and only at high temperatures [29–33]. Endo showed that di-substituted **5CCs** fused with aliphatic cyclohexyl or cyclopentyl rings are less reactive than ethylene carbonate, probably due to an increased substitution and a positive inductive effect stemming from the aliphatic nature of the rings. However, a **5CC** bearing the six-membered fused ring exhibited greater reactivity than the five-membered analog, matching the induced ring strain [34].

Scheme 4. 5CCs with varying functional groups ranked by order of reactivity.



Scheme 5. *Molecular design of tetra-substituted* ***5CC*** *to render them reactive toward aminolysis.*



As a general trend, tetra-substituted ethylene carbonates are inert to primary amines in the absence of catalysts, even at temperatures as high as 100°C [35]. In the presence of a nitrogen base (e.g.TBD), only low degree on conversions were obtained and side reactions were observed [31,36]. This difficulty has been recently surpassed by smart design of tetra-substituted cyclic carbonates embedding *O,S*-acetal linkages (Scheme 5) [35]. The attachment of the sulfur-containing group to the ring significantly activates the carbonate due to a destabilization of the C-O bond in the vicinity of the sulfur atom, likely attributed to stabilizing interactions between the oxygen atom and the introduced thioether group. The selective destabilization of the C-O bond not only promoted efficient ring-opening, but also ensured complete regioselectivity during aminolysis, yielding a single densely substituted cyclic carbamate (oxazolidone) along with the released thiol. This molecular engineering strategy offers potential for designing reactive densely substituted cyclic carbonates toward novel carbamate (macro)molecules.

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

2.2.2 INCREASED REACTIVITY BY THE CHOICE OF THE AMINE

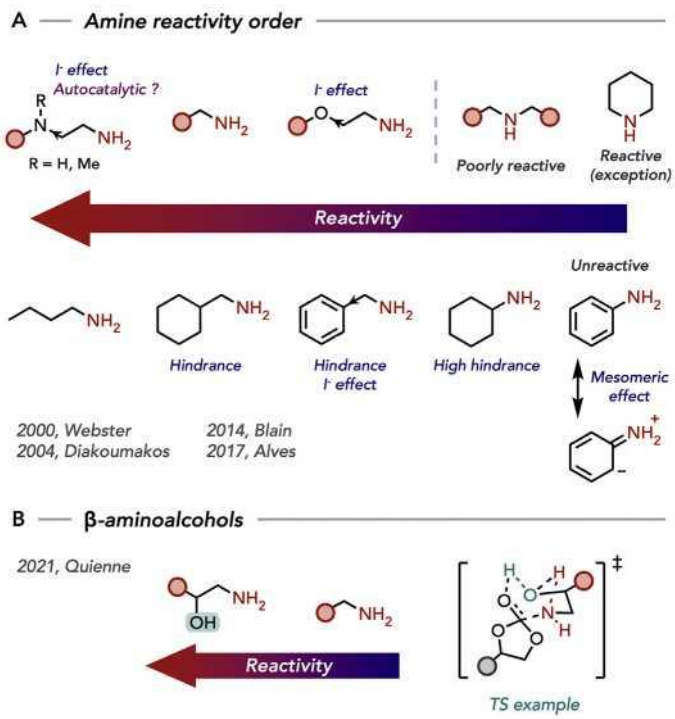
The reactivity of amines toward **5CC** is highly dependent on several factors identified through comparative kinetic studies: (i) the amine order, (ii) steric hindrance, (iii) electronic effects, and (iv) the molecular weight of the (poly)amine [37]. Among these, the amine order is critical – secondary amines generally show low reactivity with **5CC** at r.T, except for piperidine derivatives [38–40]. Consequently, primary amines are the obvious choice for synthesizing PHUs. Steric hindrance significantly impacts the reaction rate by reducing the spatial accessibility of the amine group. For example, cyclohexyl- and *α*-alkylated- amines (such as *n*- Methylbutylamine) typically exhibit low reaction rates. In contrast, less hindered aliphatic amines (such as *n*-Butylamine) demonstrate higher reaction rates [39,41–43].

Electronic effects nearby the amine group also markedly influence reactivity. EWGs such as benzyl or ethoxy groups diminish reactivity due to their negative inductive effect I^- compared to aliphatic amines. Interestingly, despite their negative inductive effect, the presence of a secondary or tertiary amine in the *β* position of the primary amine group significantly increases the reaction rate [38,39]. Although this has not been rationalized, this effect might potentially arise from an internal autocatalytic effect brought by the basic nature of amines [44]. Aromatic amines generally exhibit no reactivity in the absence of a catalyst, as the mesomeric effect makes the amine poorly nucleophilic [39,41,42]. A ranking of amines ordered by reactivity is presented in Scheme 6a.

Interestingly, *β* -aminoalcohols have shown greater reactivity toward **5CC** than aliphatic amines despite the inductive I^- effect of the hydroxyl group [16,38,45]. A computational study rationalized this difference through the stabilization of transition states by intramolecular hydrogen-bonding and proton relay effects (Scheme 6b) [45].

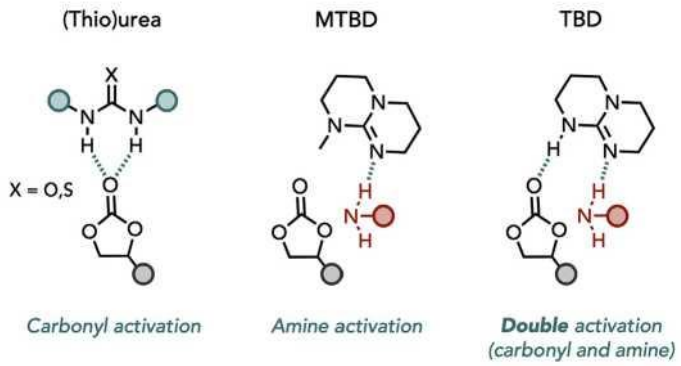
Finally, it was demonstrated that decreasing the molecular weight of diamines increased their reactivity [39,40]. Although this was not commented, this effect might arise from higher mobility and accessibility of the amine groups in small molecules rather than in oligomeric ones.

Scheme 6. *(A) Amines ranked by order of reactivity toward* ***5CC****. (B) Enhanced reactivity of β-aminoalcohols and example of a transition state for the amine addition onto* ***5CC****.*



Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

Scheme 7. *Typical catalysts and activation modes of* ***5CC*** *and amine.*



2.2.3 INCREASED REACTIVITY THROUGH CATALYSIS

A common strategy to lower energy barriers and consequently increase reaction rate at low temperature involves catalysis. Many catalysts were evaluated, such as inorganic salts (e.g. $MgBr_2$, $FeCl_3$, LiCl) [41,46,47], organobases (e.g. TEA, DBU, TBD, MTBD, DMAP, DABCO, phosphazenes) [41,46,48], phosphines [41], and (thio)urea derivatives [41,46,48,49]. Among these, TBD and (thio)urea-derived catalysts have demonstrated superior performance in terms of reaction rates, though they differ in their substrate activation mechanism.

(Thio)ureas enhance the carbonate electrophilicity of **5CC** through strong hydrogen bonding interactions with the carbonyl group. In contrast, MTBD acts as a strong base, interacting with the amine protons to enhance the amine nucleophilicity. TBD shows superior substrate activation compared to other organobases of similar pKa value. This is due to the dual activation mechanism that involves both amine nucleophilicity enhancement and carbonate activation via hydrogen bonding. The proton of TBD indeed lowers the energy of the tetrahedral intermediate by stabilization of the partial negative charge following amine addition on the ring. Furthermore, TBD serves as a proton transfer agent, simultaneously donating and accepting protons in concerted steps. Computational studies support this dual behavior, revealing that the bifunctional nature of TBD is crucial, particularly when compared to MTBD, for significantly lowering the energy barrier of the manifold (Scheme 7) [42,50].

It must be noted that the efficiency of TBD was further applied to the aminolysis of challenging substrates, including densely substituted cyclic carbonates [36,51] and to the use of aromatic amines to produce arylcarbamates [52]. Lombardo studied more complex binary systems comprising TBD and LiOTf, which has demonstrated a 3-fold decrease in reaction time compared to TBD alone [53].

2.2.4 INCREASED REACTIVITY BY THE CHOICE OF THE SOLVENT

Solvents have a significant impact on the reaction between **5CC** and amines. It was observed that aprotic polar solvents, such as DMSO or DMF, enhance the reaction rate more effectively than solvents with lower dielectric constants, such as dioxane, toluene, or THF [16,18,21,28]. This enhancement is attributed to the proton acceptor capabilities of polar aprotic solvents (Scheme 8a). Computational studies align with these experimental findings through the addition of numerous explicit solvent molecules in the model (Scheme 8b). In the case of DMSO, they demonstrate that weak hydrogen bonds involving two solvent molecules contribute to stabilizing the TSs and, consequently to lower energy barriers. These bonds aid in solvating the reactants and shielding the electronic density around electronegative oxygen atoms [54,55]. Studies with dioxane revealed only slight stabilization, the energy barrier being unaffected whether one or more solvent molecules are included [56,57].

Interestingly, chloroform demonstrated to be a good solvent for the reaction, reaching the rate observed in DMF [18,21]. It is hypothesized that chloroform may act as a weak proton donor, assisting the reaction process (Scheme 8c) [45].

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

Protic solvents have proven to be particularly effective and significantly increased the reaction rate [16–18,21,28]. It was proposed that such solvents, such as methanol (MeOH), might create hydrogen bonds with the oxygen atoms of the cyclic carbonate, thereby increasing **5CC** electrophilicity (Scheme 8c). Subsequent computational studies reported the solvation of transition states by explicit solvent molecules, forming stable cycles resulting in a twofold decrease in energy barrier compared to reactions conducted in the gas phase or including implicit solvation models (Scheme 8b) [54,57]. Methanol thus plays a crucial dual role: (i) it stabilizes the

TSs through less strained rings formation while shielding partial negative charges created on oxygen atoms, and (ii) it acts as a proton transfer agent, which is not possible with aprotic solvents such as DMSO.

Scheme 8. *(A) Solvents ranked by order of reaction rate enhancement. (B) Transition states including explicit solvents molecules. (C) Effect of methanol and chloroform on the substrate activation.*

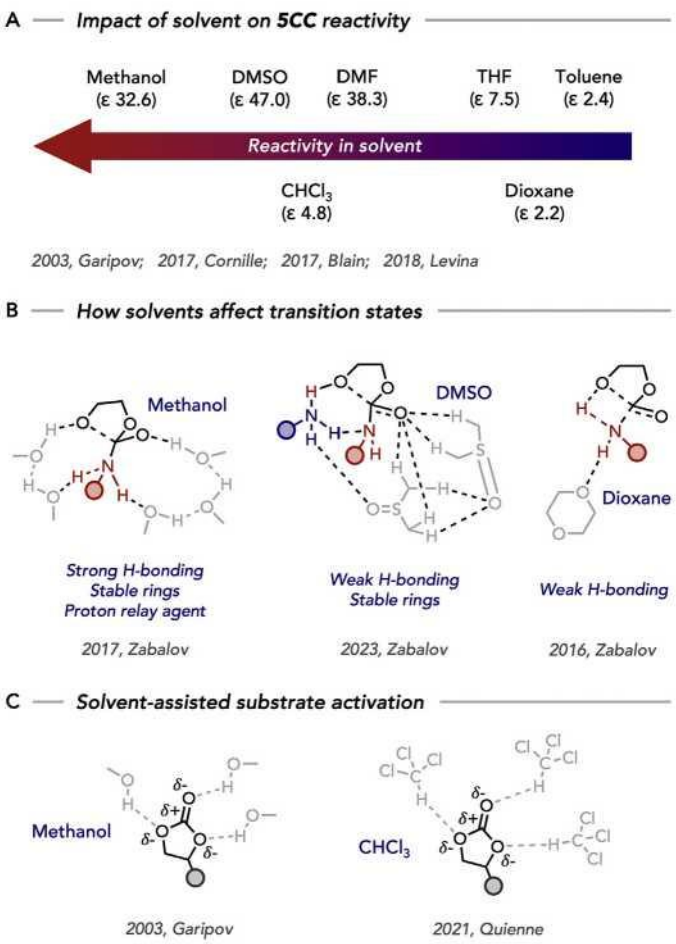
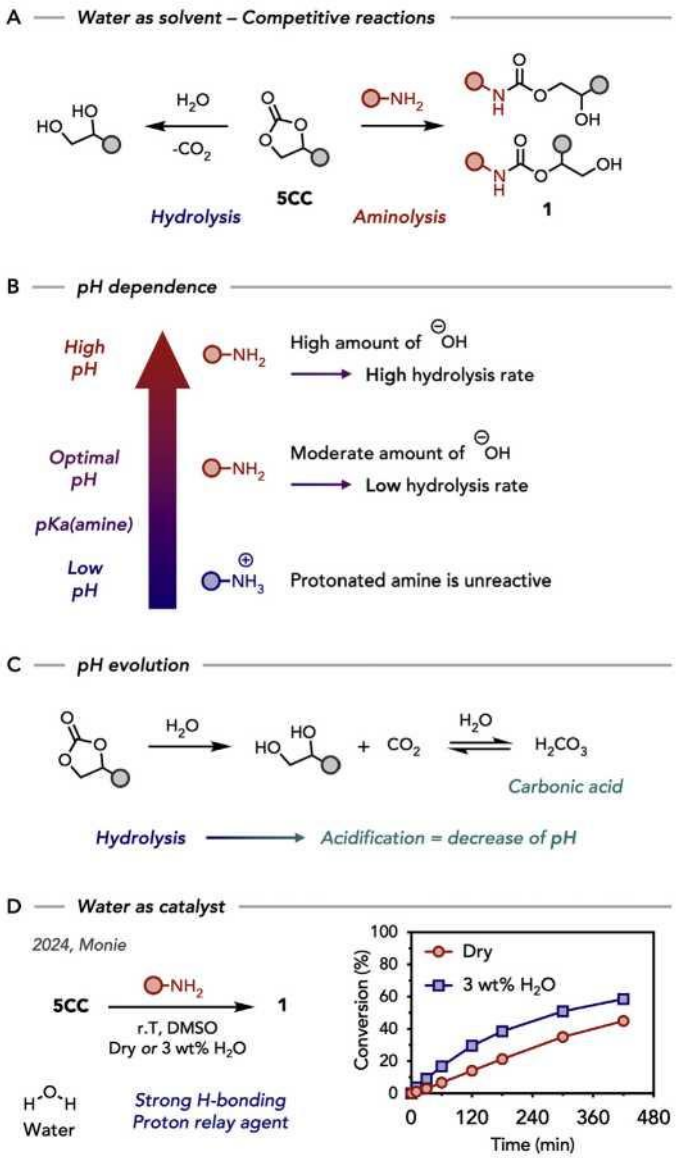


Fig. 1. *(A) Competitive aminolysis and hydrolysis reactions with* ***5CC****. (B) pH dependence of the reactivity of* ***5CC*** *for both reactions. (C) The hydrolysis reaction releases* CO_2 *, responsible for solution acidification through carbonic acid formation. (D) Aminolysis reaction at r.T in DMSO in the presence or not of 3 wt% of water.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



2.2.5 WATER AS SOLVENT

The use of protic solvents like methanol has been associated with excellent aminolysis rates. It might be expected that water would function similarly, acting as both a hydrogen bonding agent to stabilize transition states and as proton transfer agent. Nohra demonstrated the feasibility of this approach by the aminolysis of **5CC** in water at 50°C, achieving 90% of conversion in approximately 15 minutes [40]. However, the reaction proceeded at the cost of competitive hydrolysis of **5CC** , releasing CO_2 and a diol, providing the carbamate product along with around 15% of the by-products (Fig. 1a). Olsén later reported the reaction between **5CC** and unprotected amino acids in water [58], noting that the presence of a carboxylic acid group might interfere with the reaction by neutralizing the amine function and altering the reaction mechanism. It was shown that the reaction rate was dependent on the pH of the solution. If the pH is too low, the amine becomes protonated and unreactive (Fig. 1b). The balance between aminolysis and hydrolysis is highly sensitive to the amount of base used to regulate the medium basicity, requiring careful adjustments to favor aminolysis over hydrolysis. Bourguignon further studied this tradeoff, emphasizing the importance of adjusting the pH relative to the amine pKa. Importantly, he noted that pH can fluctuate as CO_2 released from **5CC** hydrolysis leads to water acidification (Fig. 1c). This topic will be thoroughly discussed in the polymerization

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

section. Additionally, Bourguignon also reported no hydrolysis of **5CC** even at 100°C in the absence of a base catalyst [59]. The hydrolysis reaction was observed in the presence of primary amines and, to a larger extent, in the presence of strong organobases such as DBU. Using water in large excess for PHU synthesis is therefore expected to yield only low molecular weight oligomers due to the competitive hydrolysis leading to a stoichiometric deviation between the two monomers.

Very recently, Monie demonstrated that a small amount of water (3 wt%; 62 mol%) in a diluted medium (DMSO) exhibited catalytic activity in the model reaction between **5CC** and amine at r.T (Fig. 1d) [60]. Methanol (62 mol%) had a similar effect. Water- catalyzed model reactions conducted in bulk showed that this approach significantly increased the reaction rate with only limited hydrolysis (around 3%).

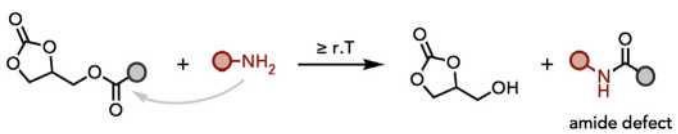
2.3 LIMITATIONS OF THE CHEMISTRY

Careful examination of kinetic experiments on model molecules reactions indicates that the synthesis of NIPUs from this **5CC** aminolysis chemistry suffers from different drawbacks: (i) inherent side reactions, (ii) slow reaction kinetics at r.T, and (iii) incomplete **5CC** conversions in most processes.

First, irreversible side reactions pose significant issues. Although less prevalent at low temperature (r.T), even slight deviation from stoichiometry prevents to reach high molecular weight through step-growth polymerization. Although ester groups are effective activating groups, they also cause potential side amidation by free amines with concomitant release of an alcohol (Scheme 9). This side reaction was reported to occur at temperatures as low as 50°C or even r.T [18,23,61]. Due to the absence of extra side reactions and their easier synthesis, ether-derived **5CCs** are now preferred [62]. If the ester-containing monomers have to be used, it is underlined that maintaining r.T is critical to minimize the importance of the side reactions and achieve defect-free high molar mass polymers.

Secondly, the reactivity of **5CC** is inherently low. Molecular engineering of the precursors and catalysis have proven useful to improve reactivity, but the reaction remains sluggish at r.T, particularly with industrially relevant diamines that show low reactivity such as ethoxy-containing or hindered diamines - e.g. 2,2′ - (Ethylenedioxy)bis(ethylamine) (EDR-148), Jeffamine, isophorone diamine (IPDA), 4,4′ -Diaminodicyclohexylmethane (PACM). Consequently, most reported PHUs have been synthesized at temperatures of 80 °C or higher, increasing energy consumption and the occurrence of side reactions.

Scheme 9. *Amidation side reaction with ester-containing **5CC**.*



Finally, many studies noted that aminolysis of **5CC** generally plateaus and fails to reach complete conversion, even after extended reaction time (Fig. 2a) [18,21,23,26,45,46,48,49]. The team of Caillol suggested in numerous works that this may be ascribed to the formation of a dense H-bonded network of hydroxyurethanes **1** [18,21,45,62]. However, the incomplete reaction was also observed in diluted media and with small model molecules, where diffusion is faster than in macromolecular architectures. This feature has been overlooked by researchers and would deserve more attention to overcome this roadblock to the synthesis of high molar mass polymers. Besides, Fortman evidenced in 2017 that the aminolysis of **5CC** is reversible, with cyclic carbonate and amine back-formation at high temperature from hydroxyurethane **1** [63]. Similar observations have been made by other groups [64,65]. The conversion plateau may thus originate from an equilibrium state between the reactants and products, preventing decent chain growth. Following Carothers equation, non-quantitative monomers consumption indeed inherently leads to polymers with low molar masses.

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

In the context of this review, we aimed to gather hints hidden in data from previous research, giving new directions for further studies that might rationalize the incomplete **5CC** conversion. First, reaction kinetics in the pseudo-first order regime showed that the reaction rate is governed by the combined contributions of two terms: one involving the reaction of one amine with **5CC**, and a second term involving a second amine in an autocatalytic process (Fig. 2a) [14,17]. The second term is largely predominant, meaning the rate is mainly governed by the reaction involving two amine molecules. This is in line with mechanistic studies showing the important decrease in energy of activation when several amines are involved in the process [19,20]. It can be hypothesized that this autocatalytic effect allows for fast reaction kinetics at the start of the reaction, and becomes negligible as the amine gets consumed, therefore reaching a plateau as depicted in Fig. 2b. To support this hypothesis, it was shown that if the temperature is raised, the plateau is still observed, albeit at higher conversion [18]. Moreover, introducing additional amine molecules in the system at r.T increases the conversion. In conclusion, we hypothesized that the reaction might become unfavorable as the amine gets consumed, with the need of higher temperatures to overcome the high energy barriers where only one amine molecule is involved.

However, it is noteworthy that two exceptions exist in the literature: (i) when the reaction is catalyzed by TBD [46] (Fig. 2a), and (ii) when the reaction is carried out in methanol [18].

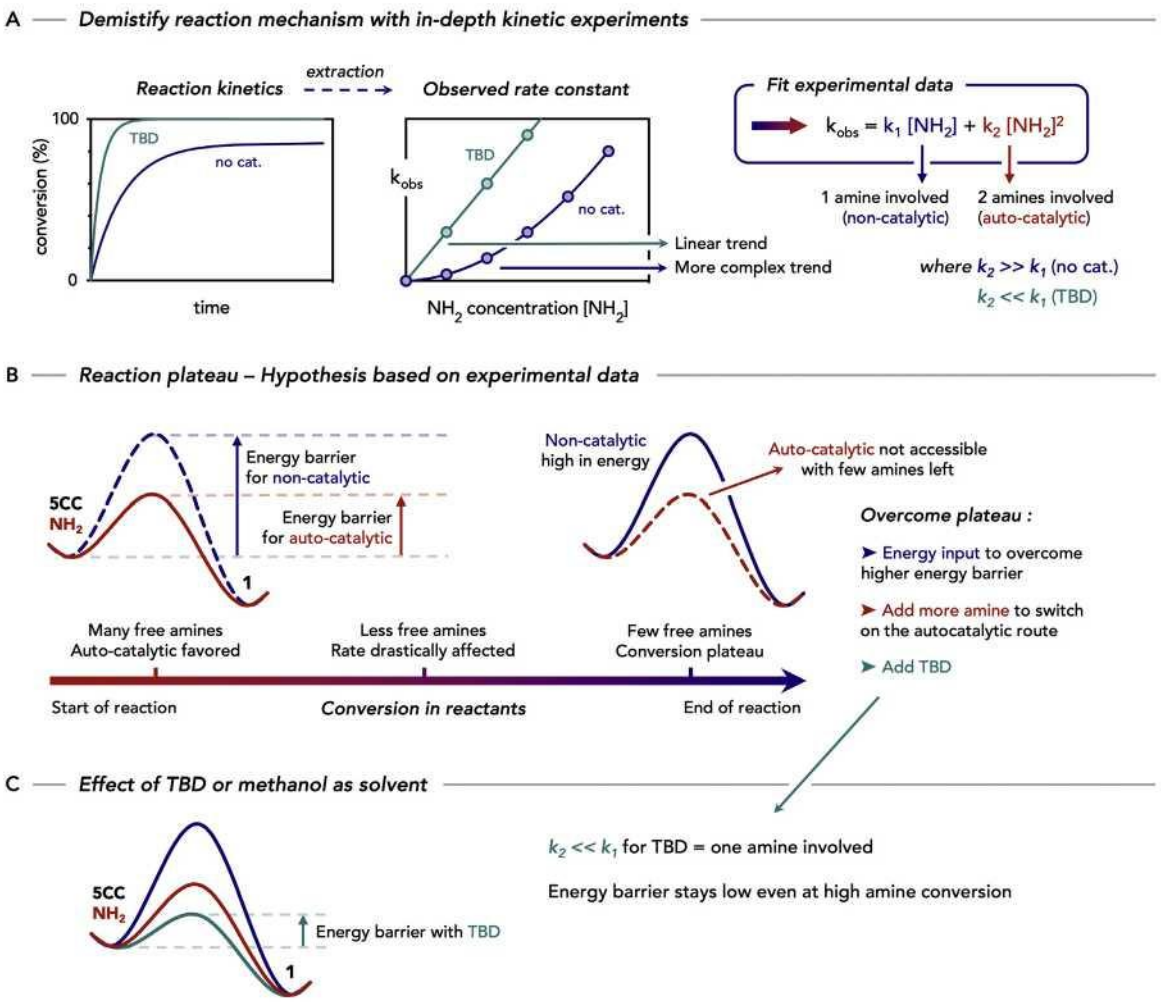
Zabalov demonstrated that the use of TBD as catalyst accelerated the reaction but also modified the importance of the two contributions to the overall reaction rate, the noncatalytic term becoming greater than the autocatalytic one (Fig. 2c) [50]. This might be rationalized by the ability of TBD to both activate the substrates and play the role of efficient proton transfer agent [66], explaining why this catalyst enables to reach complete conversion while others fail at this task.

Without catalyst, it has also been observed that performing the reaction in chloroform reached a plateau after 24 h and did not evolve 7 days later. The same reaction in methanol as solvent allowed to reach quantitative conversion after 24 h [18]. As already discussed, the acceleration of the reaction in methanol was effective thanks to the stabilization of TSs through solvation and proton relay effect [57]. Reaction kinetics proved that the non-catalytic and the autocatalytic routes might be in close competition [17], while only the autocatalytic route is prominent in other aprotic solvents. The use of methanol as solvent could therefore have the same impact as TBD on the reaction, favoring the non-catalytic term in the reaction rate to get quantitative conversion even at high amine consumption.

This discussion shows that there is still room for fundamental research around this reaction to better understand the origin of the non-quantitative conversion in diverse conditions, and to the design of catalysts or other additives that might favor quantitative conversions.

Fig. 2. *(A) Schematic representation of kinetics experiments for the reaction of* ***5CC*** *and amines. From these kinetics are extracted observed reaction rates* k_{obs}*. This allows to rationalize the contribution of two mechanisms in the overall reaction rate. (B) Hypothesis of mechanism switch between the start and the end of the reaction as a consequence of amine consumption. (C) Hypothesis on the effect of TBD or methanol to reach quantitative conversions.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



2.4 REPORTED POLYMERIZATIONS AT R.T

2.4.1 LINEAR POLYMERS

Only few works reported the polymerization of poly(**5CC**)s and polyamines at room temperature. In 2000, Steblyanko reported the synthesis of PHUs by the reaction of an ester-activated bis**5CC M1** and several diamines in DMF at r.T for 3 days [67]. Polymers **P1** with M_n ranging from 6,300 to 13,200 *g* ·mol^{-1} were obtained and they were characterized by T_gs ranging from 0 to 30°C (Fig. 3a).

In 2014, Annunziata reported the synthesis of PHUs from oligomeric poly(propylene glycol) PPG-derived bis**5CC M2** and poorly reactive diamines (Jeffamine, high steric hindrance and EWG in *β* position) [68] (Fig. 3b). Only a low conversion of 31% has been obtained at 25°C after 48 h. This study highlighted the challenging polymerization of non-ideal precursors (Jeffamine – ethoxy-containing diamine with hindrance), even at higher temperature.

In 2015, another group polymerized a lignin-based bis **5CC M3** with two different diamines in DMSO at room temperature for 24 h [69] (Fig. 3c). The aliphatic diamine led to a PHU with a high M_n of 23,000 *g* ·mol^{-1}, which could be increased to 30,000 *g* ·mol^{-1} using 5 mol% of TBD catalyst. This monomer therefore seems to show increased reactivity compared to most scaffolds, but this feature was not discussed by the authors. Using a more hindered diamine resulted in slow polymerization and low molecular weight (M_n = 3,300 *g* ·mol^{-1}, improved to 6,300 *g* ·mol^{-1} with TBD). The polymers **P3** had high T_gs of 60 and 90°C.

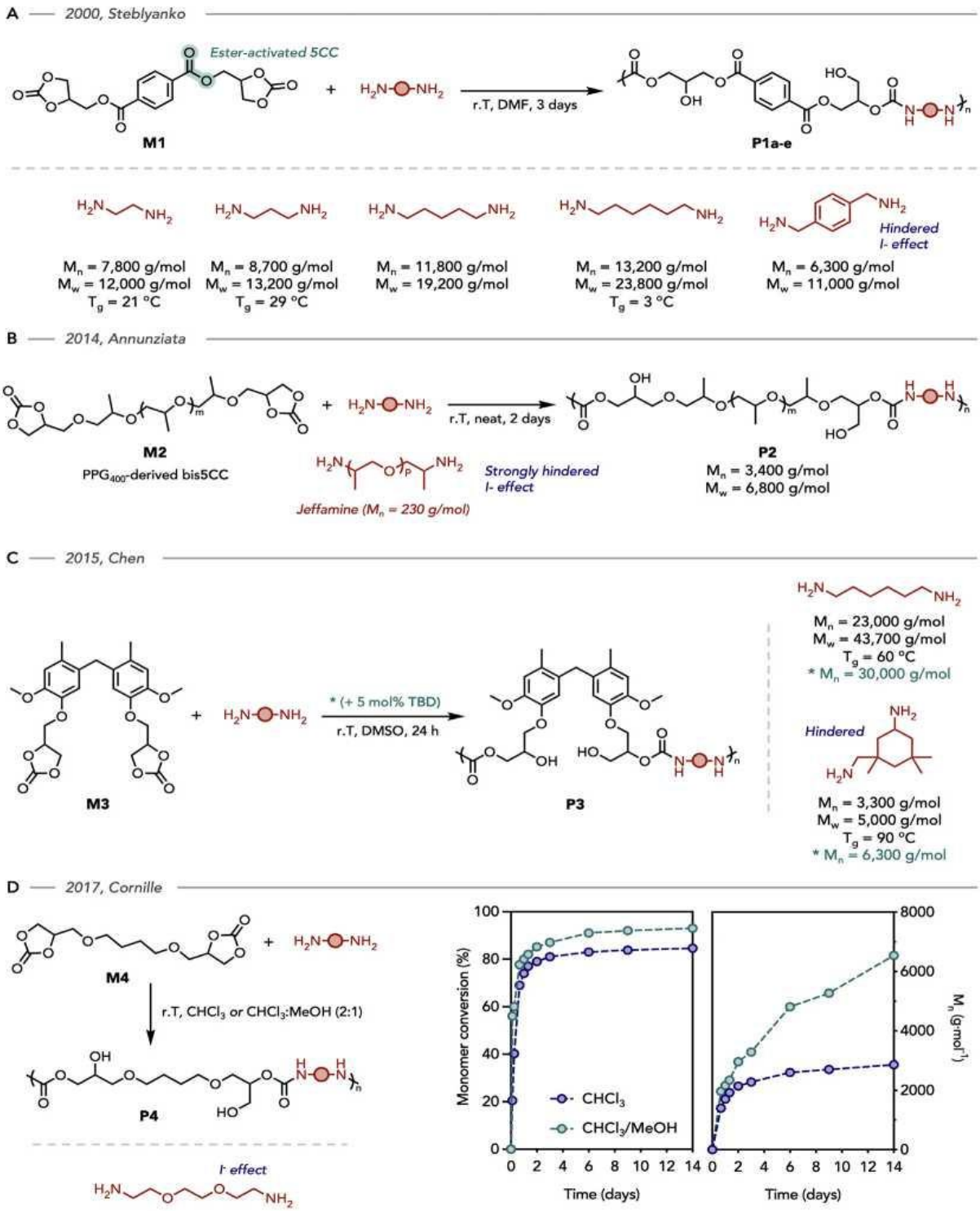
Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

In 2017, Cornille compared a polymerization from **M4** at r.T in chloroform or in a 2:1 mixture of chloroform and methanol as solvents [18] (Fig. 3d). The polymerization was rather slow and low conversions of 74 and 80% were respectively obtained after 24 h together with M_n values of 1,700 and 2,200 $g \cdot mol^{-1}$. After 14 days, the conversion in chloroform remained limited at a plateau value of 85% with a M_n of 2,800 $g \cdot mol^{-1}$ but the reaction mixture containing methanol as co-solvent provided 93% of conversion together with a higher M_n of 6,600 $g \cdot mol^{-1}$. In both cases, the reaction is slow, certainly due to the mild reaction conditions (r.T), the absence of catalyst, and the usage of the challenging EDR148 as diamine embedding electron-withdrawing ether groups. It is however noted that higher conversions and, therefore, higher molar masses, are obtained in the presence of methanol as co-solvent.

Synthesizing linear PHUs with high molar masses at r.T represents a significant challenge, showcased by the limited number of examples described in the literature where long reaction times and the use of organic solvents –preventing vitrification –are generally needed. However, the synthesis of thermosets is comparatively less elusive as it does not require high monomer conversion to form a gel, and minor side reactions typically do not compromise too much the final material properties. Despite these advantages, the inherently low reactivity of **5CC** monomers still poses a challenge in achieving thermoset materials in short times as illustrated below.

Fig. 3. *Synthesis of PHUs at r.T from (A) ester-activated bis**5CC**, (B) PPG-derived bis**5CC**, and (C) lignin-derived bis**5CC**. (D) Solvent effect ($CHCl_3$ vs $CHCl_3$/MeOH 2/1) on PHU synthesis. Both monomer conversion and Mn were followed along time.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



2.4.2 THERMOSETS

Diakoumakos demonstrated that bulk polymerization of a trifunctional **5CC M5** with DETA was very slow, requiring 8 days to reach completion [39] (Fig. 4a). The reaction time was halved by adding triethylamine as a base catalyst, with a gel time of 6.5 h.

Fleischer later polymerized trifunctional **M6** and a short diamine, reaching a conversion plateau of 60 %, which could

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

be increased to 90% by adding DABCO (1 wt%) as a base catalyst [70] (Fig. 4b). This plateau was the result of the polymer T_g higher than r.T (47 °C), in contrast to the previous work of Diakoumakos for which the T_g was determined to -14°C. This stresses the importance of targeted polymer Tg in the curing process at r.T: if the Tg of the resulting material is too high, vitrification quickly hampers further cross-linking (Fig. 4c).

Most PUs formulations incorporate solvents to achieve a lower viscosity state, facilitating efficient mixing and enabling higher conversion of reactants. This is particularly useful for applications like coatings or adhesives, where reduced viscosity enhances the ease of application of the formulations onto substrates. However, regulatory measures aim to restrict the amount of volatile organic compounds (VOCs), which pose health and environmental risks.

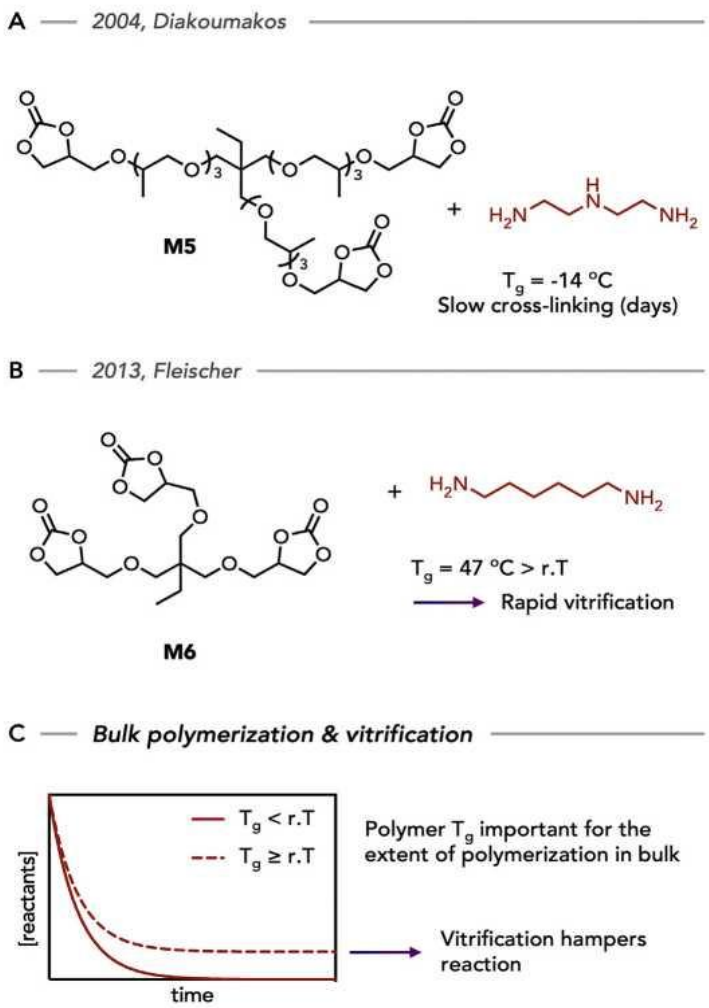
Wu evaluated ambient-curable coating through the polymerization of pre-polymers. They first reacted an excess of bis**5CC** and a diamine at high temperature (150°C) in DMF as solvent to yield **5CC**-terminated PHU prepolymers **M7**. These prepolymers were subsequently reacted with PEI at r.T and applied as coatings [71] (Scheme 10). The gel time varied between 3 and 14 h depending on the pre-polymer and PEI molecular weight, and Tgs values ranged from 35 to 50°C. Although not highlighted by the authors, the polymers contained 50 wt% DMF, likely serving as a plasticizer to mitigate viscosity and prevent early vitrification.

Fortman has shown that polymerization of a bis**5CC** with Tris(2- aminoethyl)amine (TREN) occurred in 1 h at r.T in DCM as solvent [63]. After 24 h, the gel was subjected to reduced pressure and elevated temperature (90°C) to eliminate the solvent. However, the actual gel time and the extent of **5CC** consumption in the gel state were not determined, and high temperatures during gel drying might post-cure the material.

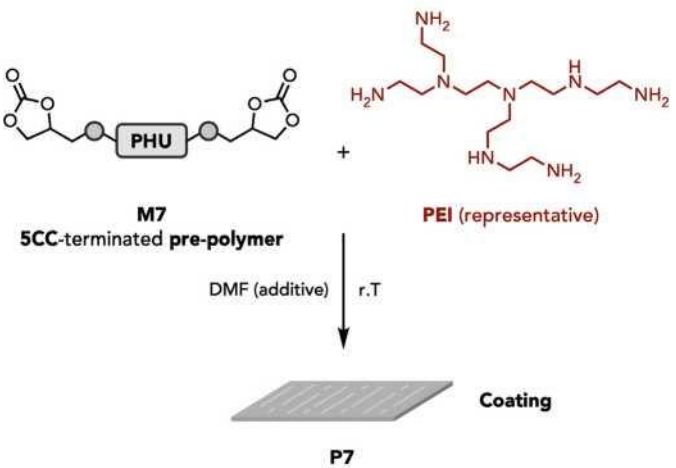
To align with the regulations on VOCs, waterborne conventional PUs (made from isocyanates) were largely adopted, offering significant environmental and safety advantages. Translating the process to NIPUs is therefore of high interest.

Fig. 4. *Bulk polymerization of trifunctional **5CC** with diamines yielding either a (A) low Tg polymer **P5** or a (B) high Tg polymer **P6**. (C) Schematic representation of the reactants conversion in the two situations.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



Scheme 10. *Polymerization of* ***5CC*** *-terminated PHUs with PEI (representative structure) at r.T for coating applications.*



Although the use of water as solvent is detrimental for making linear PHUs due to the competitive hydrolysis reaction, Bourguignon successfully synthesized hydrogels in short reaction times by designing water-soluble monomers. In a

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

first work, water-soluble PEG-derived bis **5CC M8** was reacted with polyethyleneimine (PEI) in water [72] (Fig. 5a). It was demonstrated that the pH of the solution has a drastic impact on the polymerization reaction – protonation of the amine at low pH (pH = 9) prevents polymerization, while a high pH (pH = 12.5) accelerates hydrolysis (30% hydrolysis; 60% of hydroxyurethane formation) (Fig. 5b). The solution acidification during the reaction due to released CO_2 from hydrolysis (see Fig. 1c) further complexifies the system. By properly selecting the solution pH (optimal conditions at pH 10.5 in this case), the hydrolysis was limited to 9% while enhancing the aminolysis, although **5CC** consumption remained limited (60%). A small excess of **5CC** was found beneficial for the reaction (0.8 eq. of amine for 1 eq. of **5CC**) (Fig. 5b). This ratio is rationalized by a consumption of all amines with the presence of additional sacrificial **5CC** functions that inevitably undergo hydrolysis. In optimal conditions of pH and monomers ratio, a gel point was rapidly obtained within 15 minutes at r.T, with complete **5CC** consumption. A high gel content of 85% confirmed the crosslinked nature of the hydrogel.

For comparison, the bulk polymerization of various bifunctional ether-activated **5CC** with a reactive triamine (TREN) at 40°C resulted in gel times between 2.5 and 16 h [73]. Impressively short gel times were thus achieved when performing the crosslinking reactions in water at r.T compared to neat conditions.

The authors also investigated how additives could enhance the mechanical properties of hydrogels. Notably, by adding a small amount (2.5 wt%) of nanoclays as fillers, a 180% increase in Young's modulus and a 330% increase in stress at break were achieved. A second strategy involved the creation of a double network – (i) the synthesized covalent PHU network and (ii) a physical network made of gelatin relying on non-covalent interactions. For a 10/6 weight ratio of PHU to gelatin, an outstanding 5100% increase in stress at break was obtained, likely due to the rearrangement of the physical cross-link nodes within gelatin upon stress application. This proof-of-concept not only demonstrated the robustness of the waterborne PHU hydrogels synthesis, but also showed the significant potential for hydrogels properties enhancement through the use of numerous additives.

In a second work, the scope of hydrogels was extended by developing water-soluble poly(**5CC**) that react with a broad array of diamines, of varied molecular structure and pKa [74]. A methacrylate derivative of **5CC** was synthesized and co-polymerized with hydrophilic monomers, resulting in water-soluble polymers embedding reactive **5CC** groups and hydrophilic functional groups: neutral PEG (**M9a**), anionic sulfonate (**M9b**), and cationic ammonium groups (**M9c**) (Fig. 6a). At pH 12, HMDA reacted with **M9a**, achieving gelation in only 1 min. The storage modulus (G') plateaued after 2 h of reaction, indicating complete conversion. The gel time of other diamines varied: a few minutes for reactive TETA, and significantly longer for less reactive XDA and EDR148 (Fig. 6b). This aligns with the previously reported reactivity trend of primary amines (see Scheme 6). Interestingly, the gel time for HMDA increased to 12 min at pH 11, with only minor changes for other diamines. At pH 10.5, HMDA was unreactive, unlike other monomers. This highlights the strong relationship between the amine pKa and the pH of the solution: amines with a higher pKa require a sufficiently high pH to prevent excessive protonation inhibiting the reaction. For amines of lower pKa, a lower pH may be chosen to minimize competitive hydrolysis (Fig. 6b). As a general trend, a fast crosslinking with limited **5CC** hydrolysis requires a solution pH of one unit higher than the pKa value of the involved amine.

Using anionic **M9b**, gels with TETA formed within 17 min at pH 12. The authors took advantage of the anionic sulfonate functional groups to decrease gel time (5 min) and increase the crosslink density (475% increase) of the scaffold through the addition of $CaCl_2$ (25 mol% vs sulfonate groups), creating non-covalent ionic bonds (Fig. 6c). The network also became opaque due to the formation of $CaCO_3$ within the hydrogel following hydrolysis-driven decarboxylation and formation of carbonate anions (Fig. 1c). The authors hypothesized these $CaCO_3$ particles to participate in the network reinforcement.

Cationic **M9c** provided gels in <1 to 9 min from different diamines, and the resulting polymers exhibited thermoresponsive properties.

In another work, poly(vinyl amine) was used with PEG-derived bis**5CC M8** at pH 10 to produce PHU coatings **P10** for

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

indoor air purification (Fig. 7a), particularly for formaldehyde (FA, an emblematic toxic indoor air pollutant) capture [25]. For that purpose, the coating had to contain excess amine groups that irreversibly capture FA by the formation of a six-membered ring as illustrated in Fig. 7b. An optimal ratio of [NH_2]/[**5CC**] of 4 was therefore selected to target a high cross-link density value for a hydrogel decorated by NH_2 groups needed for FA capture. This resulted in a short gel time of 2.5 min at r.T and an end of reaction after 2 h. The gel time was also adjusted by the pH, extended from 2.5 min at pH 10 to 20 min at pH 8.5. It is important to note that poly(vinyl amine) tends to promote the formation of some urea through the formation of six-membered rings facilitated by the proximity of the neighboring amine functions (48% of the polymer functionalization at pH 8.5; 31% at pH 10; the rest of the functionalization being carbamate linkages) (Fig. 7a). When the coating was evaluated for gaseous **FA** capture, up to 97% of **FA** was effectively trapped within the PHU after 1 day. Reloading the test chamber several times proved that the polymer was capable of continuously trapping more **FA**. As the pollutant is covalently trapped, no release was observed from the PHU after capture.

These developments not only represent a significant advance in the synthesis of PHU thermosets at r.T, but also emphasize the role of water in readily increasing reaction rates to reach short gel times. An explanation for this exceptional activity is detailed in the solvent effect section (see Sections 2.2.4-5), where both a catalytic activity of water and a specific solvation power characteristic to protic solvents were discussed. Additionally, recent extensive rheological studies by Monie further evidenced the role of water in facilitating PHU network formation [60]. The reaction between dry reagents (bis **5CC M5, EDR148**) led to a gel time of 15.5 h at r.T, while adding 5wt% of water to the formulation reduced the gel time to 4 h, a 4-fold decrease. This significant reduction is attributed to the catalytic effect of water (Fig. 1d) and to hydroplasticization of the polymer matrix that lowers the polymer Tg and delays vitrification. This enhanced chain mobility is due to the high affinity of water for hydroxyl-containing PHUs as determined by rheological analyses. Water effectively disrupts intra- and interchain hydrogen bonds, thus enhancing molecular mobility and accelerating the growth of polymer chains (Scheme 11). This study underlines the dual role of water as a catalyst and plasticizer in facilitating fast network formation. It is worth mentioning that numerous studies in PHU chemistry do not report whether reagents and catalysts were dried or used as stored. As a minimal amount of water can significantly impact reaction rates and gel times, the comparability between studies may be biased depending on the reagents grades and purities, as well as environmental humidity conditions.

Fig. 5. *(A) Waterborne PHU synthesis at r.T from water-soluble PEG-derived bis**5CC M8** and PEI to yield a hydrogel **P8**. (B) Importance of the amine to **5CC** functions ratio (left) and the pH (right) on the gel time and the Young's modulus of the material final properties.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

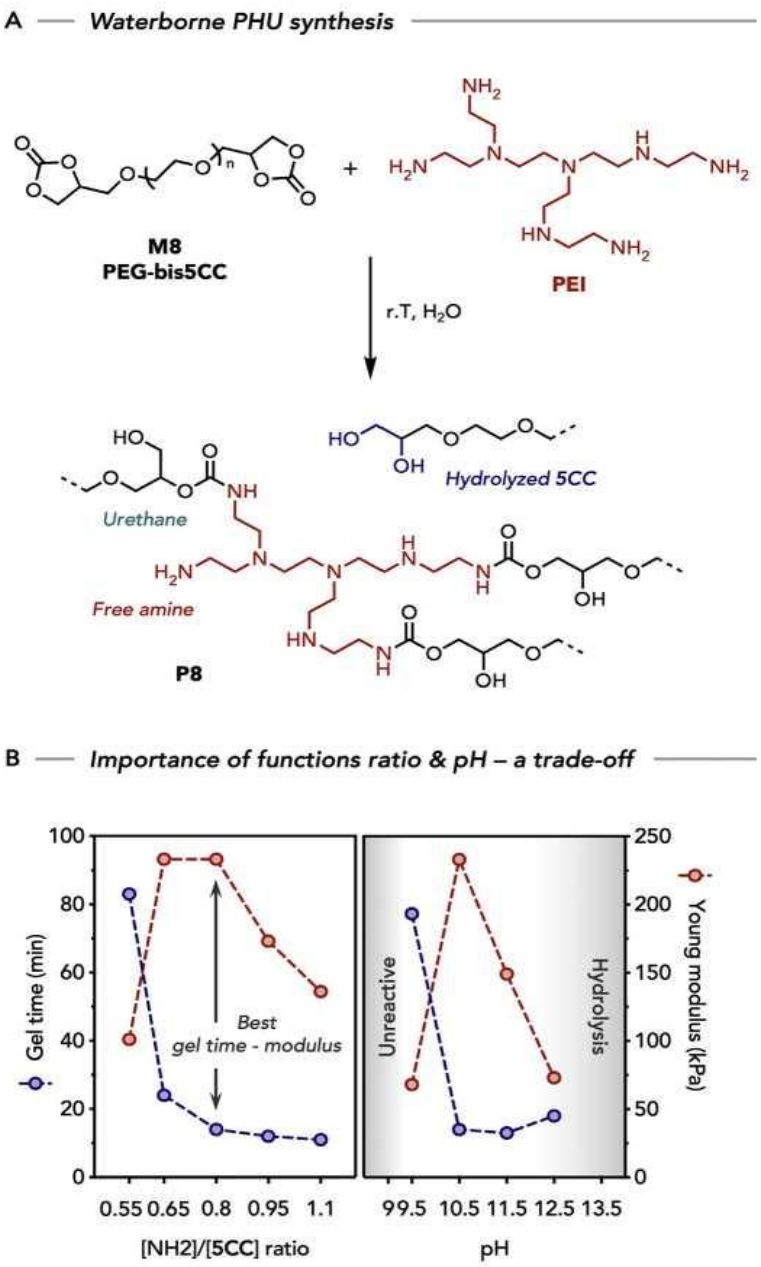


Fig. 6. *(A) Synthesis of water-soluble polyfunctional* ***5CC*** *monomers* ***M9****. (B) pH-dependence on the amines respective reactivities using* ***M9a****. (C) Improvement of gel time and cross-link density in hydrogel from anionic* ***M9b*** *and TETA with the addition of* $CaCl_2$ *as additive, creating additional non-covalent crosslinking nodes.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

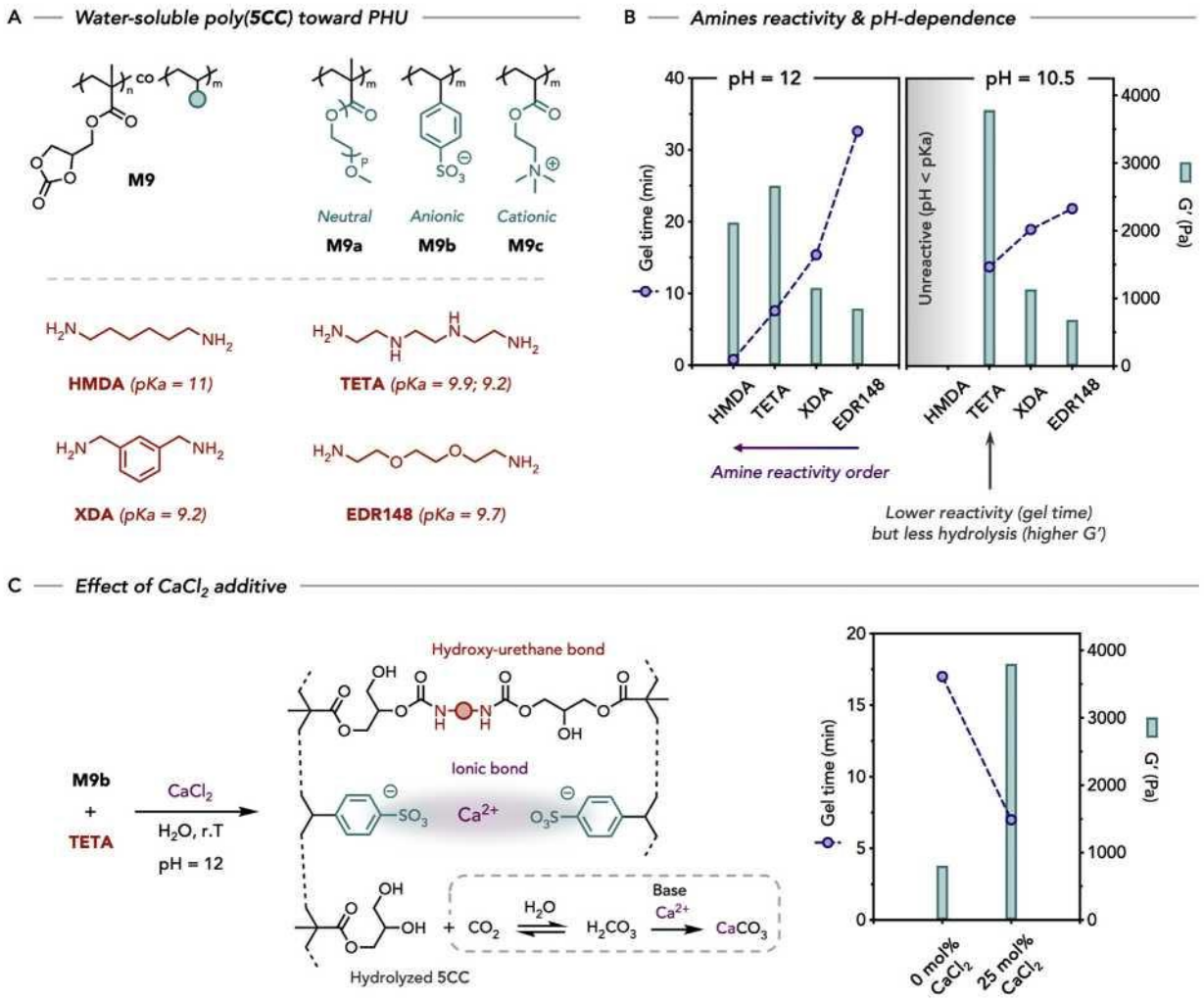
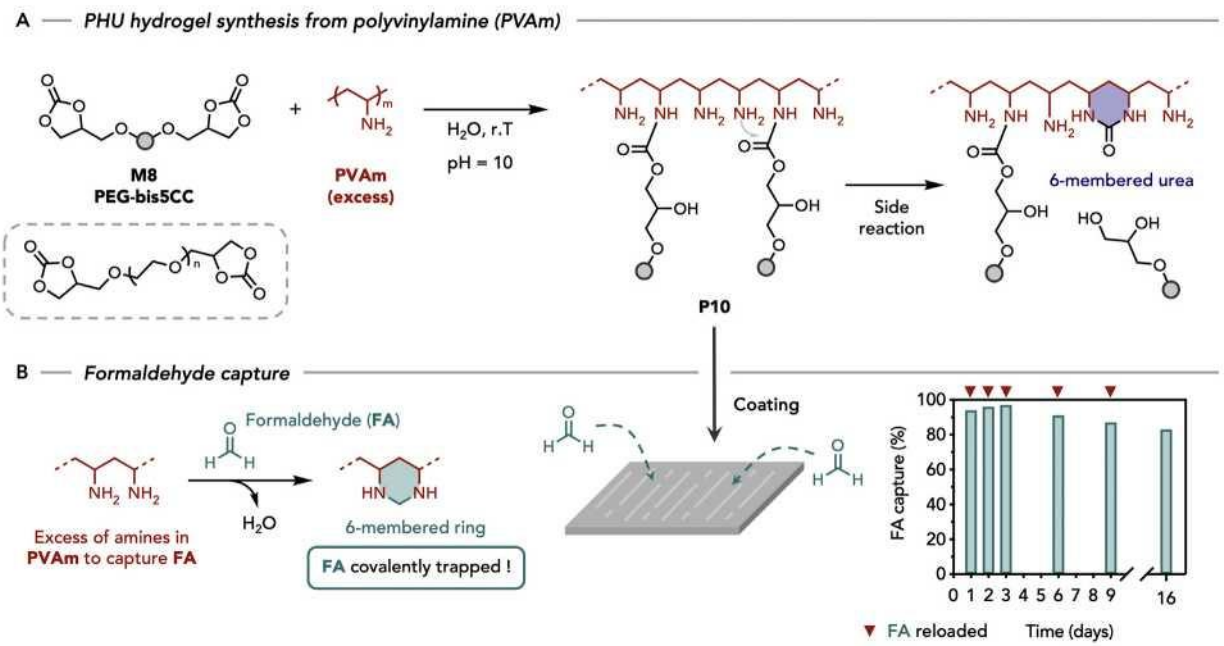


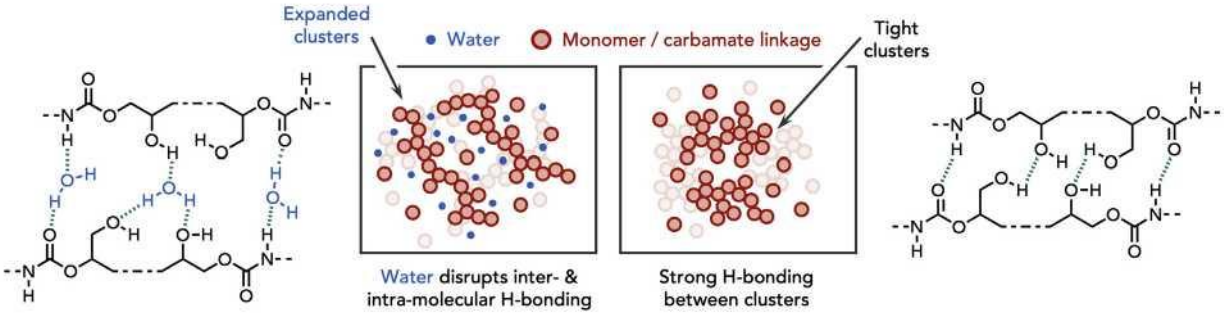
Fig. 7. *(A) Amine-rich NIPU hydrogel* ***P10*** *synthesis from* ***M8*** *and an excess of polyvinylamine (****PVAm*** *). Urea formation at r.T is facilitated by the formation of stable sixmembered rings. (B) Polymer* ***P10*** *can be applied as coating to trap formaldehyde (* ***FA****) pollutant through chemical capture into six-membered rings and water release. The coating can consecutively capture a large quantity of* ***FA*** *as demonstrated by the day-per-day renewal of* ***FA*** *atmosphere around the material.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

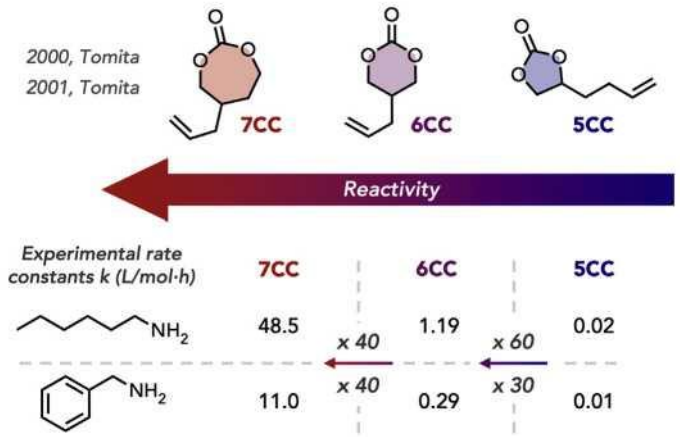


Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

Scheme 11. *During PHU network formation, water can act as hydrogen bond donor and acceptor, thus disrupting hydrogen-bonding within and between the PHU clusters in formation. The clusters are more expanded and benefit from higher mobility. In the absence of water, the clusters are in strong interactions and are tightly grouped, restraining their diffusion power.*

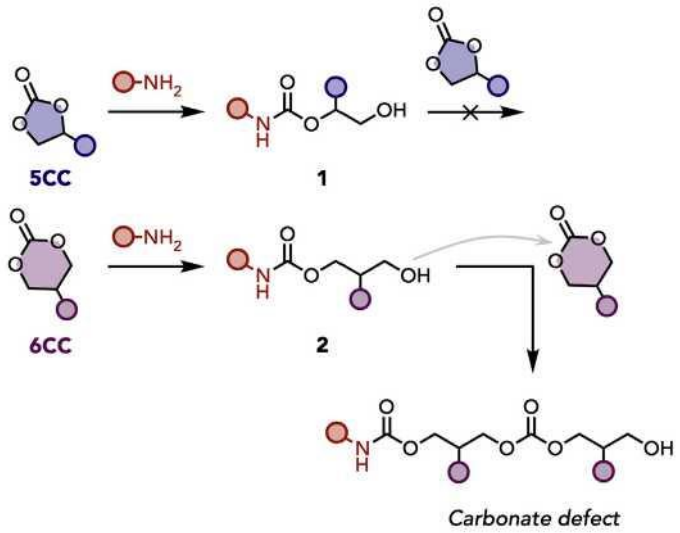


Scheme 12. *Experimental rate constants for the aminolysis reaction of* ***5CC*** *as compared to* ***6CC*** *and* ***7CC*** *in similar reaction conditions.*



Scheme 13. *Ring-opening of* ***6CC*** *by pending alcohols on* ***2*** *to furnish carbonate defects.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



3. NIPUs by aminolysis of 6- to 8-membered cyclic carbonates

3.1 REACTIVITY, SIDE REACTIONS, AND REPORTED POLYMERIZATIONS AT R.T

Increasing the cyclic carbonate ring size is an effective strategy to enhance the cyclic carbonate reactivity as compared to more stable five-membered cyclic carbonates **5CC**. Tomita demonstrated through model reactions that the reactivity of 6-membered cyclic carbonates (**6CC**) was over 30 times greater than that of a comparable **5CC** [75] (Scheme 12). Maisonneuve confirmed this finding and showed through kinetic experiments that although the reaction starts quickly, complete **6CC** conversion can take up to 4 days. Raising the temperature to 50°C reduces the reaction time to approximately 24 h [76]. Similar to **5CC**, variation of the ring substituents through inductive effect can further increase the reaction rate [18,23,24]. A simplistic computational study demonstrated that the difference in heat of formation between the carbamate products and the cyclic carbonates (**5CC** to **7CC**) with an amine was larger with increased ring size [77]. Tomita suggested this trend to be ascribed to the ring-strain difference between the different cyclic carbonates. However, a low level of theory (semi- empirical model) was used in the study and modern DFT methods might provide more accurate values. Moreover, these values must be confirmed by experimental data to validate the methodology.

Tomita compared the reactivity of two representative bis**5CC** and bis**6CC** with a diamine at 50°C using DMAc as solvent [78]. A full monomer conversion was attained with bis**6CC** after 48 h of reaction, reaching a Mn of 26,000 $g{\cdot}mol^{-1}$. In contrast, the conversion in bis**5CC** remained incomplete after 14 days, with a Mn of 15,000 $g\ {\cdot}mol^{-1}$. Maisonneuve performed similar polymerizations at various temperatures, emphasizing the significance of increasing the temperature from r.T to 50°C to go from M_n of 14,000 to 22,000 $g\ {\cdot}mol^{-1}$ [76]. However, prolonged reaction at 50°C resulted in an insoluble gel. This was ascribed to undesirable reaction of pendant alcohol functionalities of the **6CC**-derived hydroxyurethane product **2** with **6CC** functions to produce a carbonate linkage (Scheme 13). It is important to note that this side reaction was not observed with **5CC** as they are less reactive than **6CC**.

Lambeth realized an in-depth study of the effect of catalysts on the course of the reaction and associated side reactions. He concluded that gelation occurs even without any catalyst at r.T due to the alcohol initiated ring-opening of **6CC** [79]. Through activation of the carbonyl function by a thiourea organocatalyst, the Mn was increased from

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

10,000 $g \cdot mol^{-1}$ (without catalyst) to 22,000 $g \cdot mol^{-1}$ at r.T and up to 90,000 $g \cdot mol^{-1}$ at 50°C. Using TBD as organocatalyst proved detrimental to PHU formation due to the strong activation of **6CC** toward ring-opening polymerization (ROP).

Tomita reported the synthesis and aminolysis of sevenmembered cyclic carbonates (**7CC**), hypothesizing that their reactivity might surpass that of **6CC**. Model reactions demonstrated a 40-fold increase in reactivity for **7CC** over **6CC** at r.T, with complete reactant consumption in 1 h, even with the less reactive benzylamine [77] (Scheme 12). The synthesis of PHUs from bifunctional monomers was successfully carried out at r.T in DMSO (Scheme 14), yielding polymers with a Mn of 33,000 $g \cdot mol^{-1}$ using a reactive aliphatic diamine after 6 h, and with a lower Mn of 11,000 $g \cdot mol^{-1}$ with a benzylic diamine after 24 h. This study highlighted a significant enhancement in molecular weight at r.T compared to smaller rings **6CC** and **5CC**.

Based on the same assumption, Yuen reported the synthesis of 8-membered cyclic carbonates (**8CC**) as PHU precursors [80]. Comparative model reactions showed **8CC** to be significantly more reactive than **5CC** and **6CC**. Polymerizations from bis**8CC M13** and HMDA at r.T for 24 h in DMSO yielded polymers of high molecular weight with M_n of 47,000 $g \cdot mol^{-1}$. The scope was extended to challenging sterically hindered diamines, such as IPDA and PACM, resulting in polymers **P14** of decent molecular weight (M_n = 20,000 and 23,000 $g.mol^{-1}$, respectively) (Scheme 15). A secondary diamine was included in the scope but exhibited too low reactivity to form polymers.

Following excellent results obtained for **5CC** hydrogels, **8CC** precursors were evaluated for the waterborne PHU synthesis [81]. By reaction of the bis**8CC** with PEG-diamine and TREN as cross-linker (0.4 eq.), it was found that lower water content reduced gel times (50 wt% water content leaded to a gel time of 350 min; 70 wt% to a gel time of 750 min), indicating an important concentration effect. With excessive water, not only the gel was not formed after 24 h, but it also favored **8CC** hydrolysis over aminolysis. Expectedly, an increase in triamine over diamine resulted in significant gel time decrease, from 30 h with 0.2 eq. of cross-linker to seconds with 1 eq. of cross-linker.

3.2 LIMITATIONS OF HIGHER RINGS AND PERSPECTIVES

Although cyclic carbonate rings of increased size are promising precursors for the synthesis of high molar mass NIPUs, their use faces several limitations. One major issue is the side reaction of ring-opening by primary alcohols, which are prevalent in the hydroxyurethane product **2** . While this typically occurs at 50°C or higher [76,80], Lambeth's work demonstrated that gelation can occur at r.T [79]. An in-depth investigation on the influence of various factors such as substituent or solvent effect might be needed to understand the extent of the undesired side reaction over the aminolysis. Moreover, the reported rather high molecular weights for the polymers prepared from bis**6CC** to **8CC** might possibly account for branched species if ring-opening by pendant alcohols occurs even at low extent.

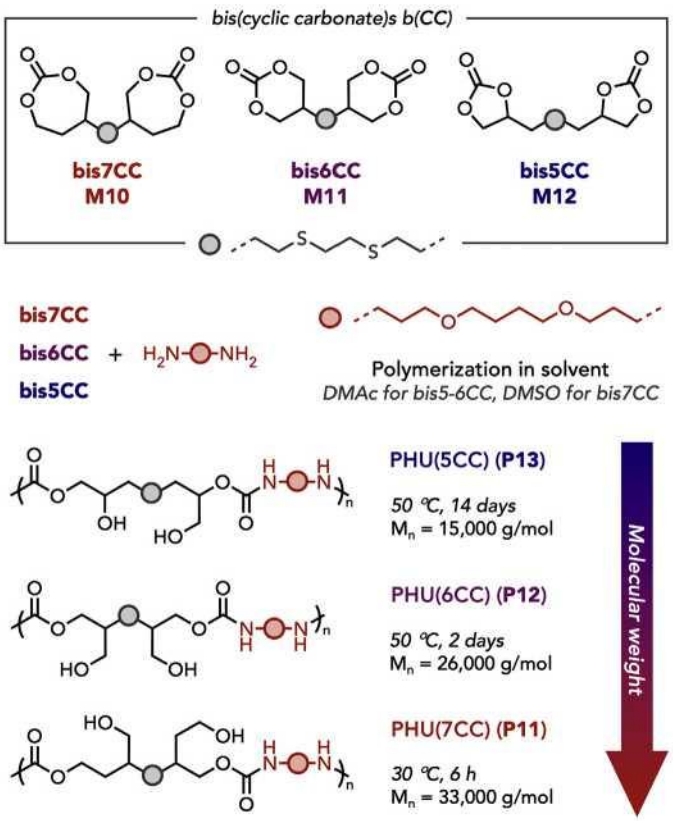
The use of a catalyst might be essential in some scenarios, especially in the case of bis**6CC** and challenging amines. Besse reported the use of DIPEA (2 mol%) for the polymerization of bis**6CC** at r.T without observable gelation after 24 h [82]. Lambeth later studied the influence of TU and TBD catalysts as they have proven to have high catalytic activity for the aminolysis of **5CC**. While TU was beneficial for reaching high molecular weights, gelation was obtained extremely rapidly with TBD, certainly because it is an excellent activator for 6-membered [83–85] and 8-membered [86,87] cyclic carbonates ROP. There remains a need for a systematic search for catalysts that selectively promote aminolysis of cyclic carbonates over ROP by alcohols.

Finally, a limitation of these precursors is their difficult synthesis. While **5CC** is easily produced from CO_2-epoxide coupling, larger rings are more challenging to obtain due to their facile ringopening by diverse substrates compared to less reactive **5CC**. These are most easily and commonly prepared from nasty reagents including phosgene or derivatives [88,89]. More sustainable alternatives are currently searched, notably using CO_2 as feedstock [83,90–94],

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

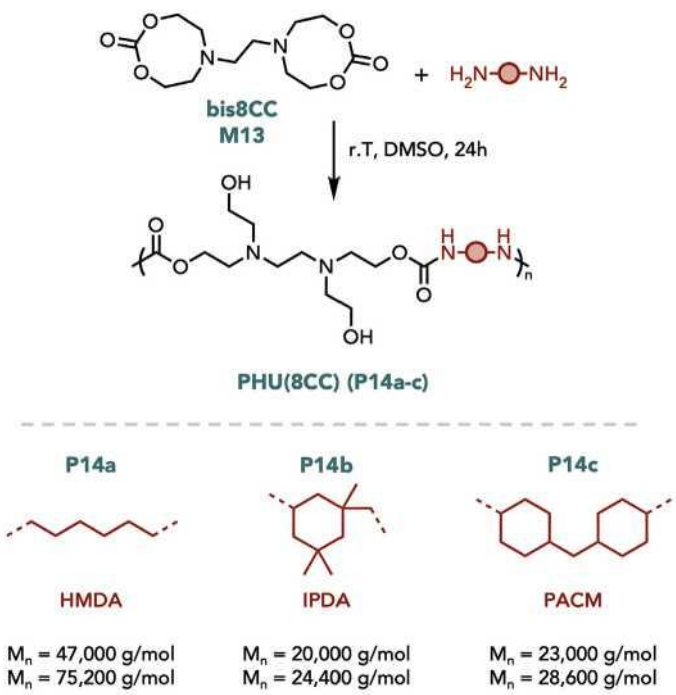
but there remains much work for the scaled production of bifunctional monomers.

Scheme 14. *Comparative polymerization of bis**5CC M12**, bis**6CC M11**, and bis**7CC M10** analogs with the same diamine.*



Scheme 15. *Polymerization of bis **8CC** (**M13**) with diamines at r.T into PHU **P14a-c** .*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



4. NIPUs by aminolysis of α;-alkylidene cyclic carbonates

α-alkylidene cyclic carbonates (***α*CC**) are five-membered cyclic carbonate derivatives featuring an exo- or endo-vinylene group. Exovinylene cyclic carbonates are commonly produced from the well-studied catalyzed CO_2 fixation onto propargyl alcohols [95– 98] (Scheme 16a). In contrast, endo-ones are typically obtained by reaction of *α*-hydroxy ketones with phosgene derivatives [99,100] (Scheme 16b). Recent works have however demonstrated their availability from diphenyl carbonate [101], and from the rearrangement of exo-vinylene ones [102].

Exovinylene ***α*CC** undergo smooth aminolysis with both primary amines and secondary amines to provide (a)cyclic carbamates in good to high yields at r.T [103–108] (Fig. 8a), sometimes in an one- pot approach starting from a mixture of the propargyl alcohol, the amine, and CO_2 [109–112]. The aminolysis of ***α*CC** occurs through regioselective ring-opening of the carbonate via the side of the exovinylene group, creating an enol that tautomerizes into a ketone to form an *oxo*-urethane **3**. If the amine is primary, the -NH- group of the urethane further undergoes an intramolecular ring-closure with the adjacent ketone to provide a hydroxy-oxazolidone **4**. The exceptional reactivity of ***α*CC** at r.T is attributed to increased ring strain provided by the exovinylene function (Fig. 8b). Once ring- opened, the tautomerization towards the *oxo*- adduct drives the equilibrium toward product formation. Although the regioselective opening has not been rationalized yet, crystallographic structures of ***α*CC** derivatives indicate an increased bond length at the side of bond scission, suggesting a weaker bond strength certainly induced by the neighboring exovinylene group (Fig. 8c).

Scheme 16. *(A) Synthesis of exo-vinylene **αCC** from CO2 and propargyl alcohol. (B) Synthesis of endo-vinylene **αCC** from α-hydroxyketone and phosgene or diphenyl carbonate. The endo- can also be obtained from an exo-analog by rearrangement if one ring substituent is an H atom.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

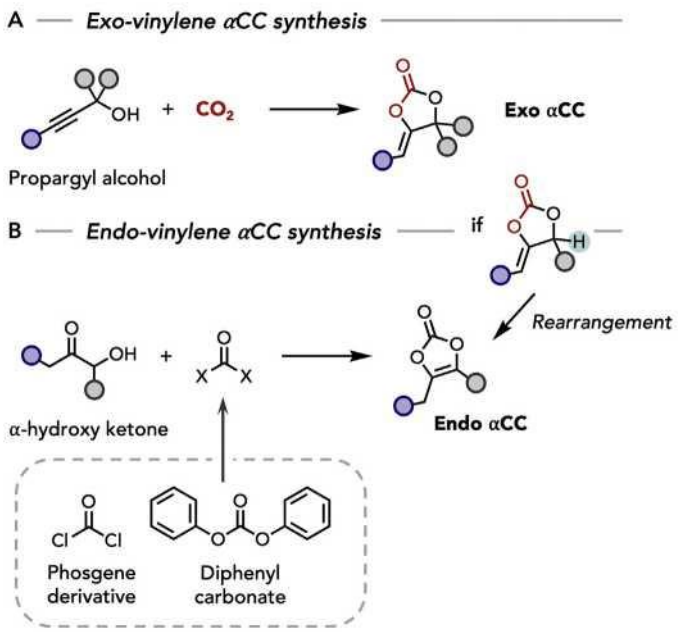
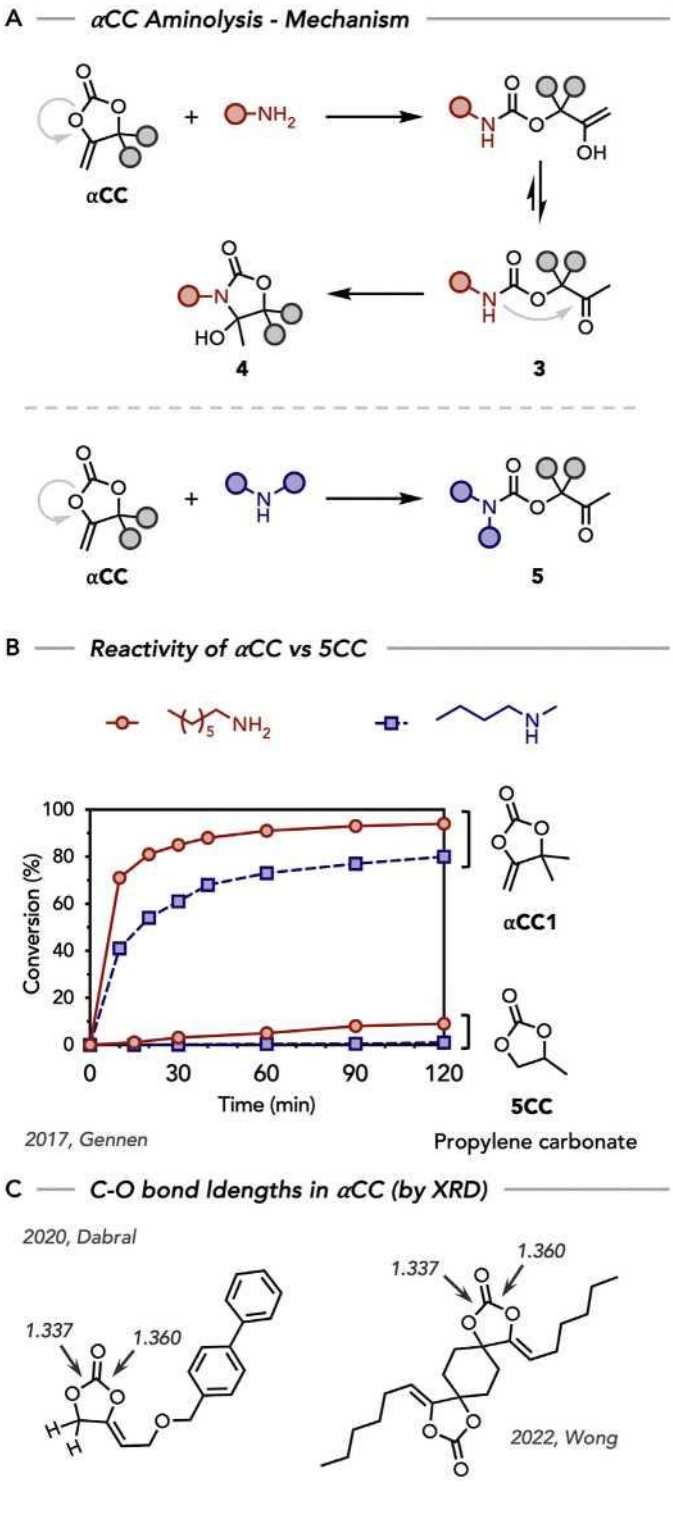


Fig. 8. *(A)* ***αCC*** *aminolysis mechanism in the presence of primary and secondary amines. (B) Comparative reactivity of a substituted exovinylene* ***αCC*** *(* ***αCC1*** *) and* ***5CC*** *(propylene carbonate) toward primary and secondary amines at r.T without catalyst. Plot adapted with permission from [107]. (C) Molecular structure of two* ***αCC*** *compounds as determined by XRD.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

4.1 REACTIVITY AND MODEL REACTION STUDIES

4.1.1 EFFECT OF THE A CC STRUCTURE

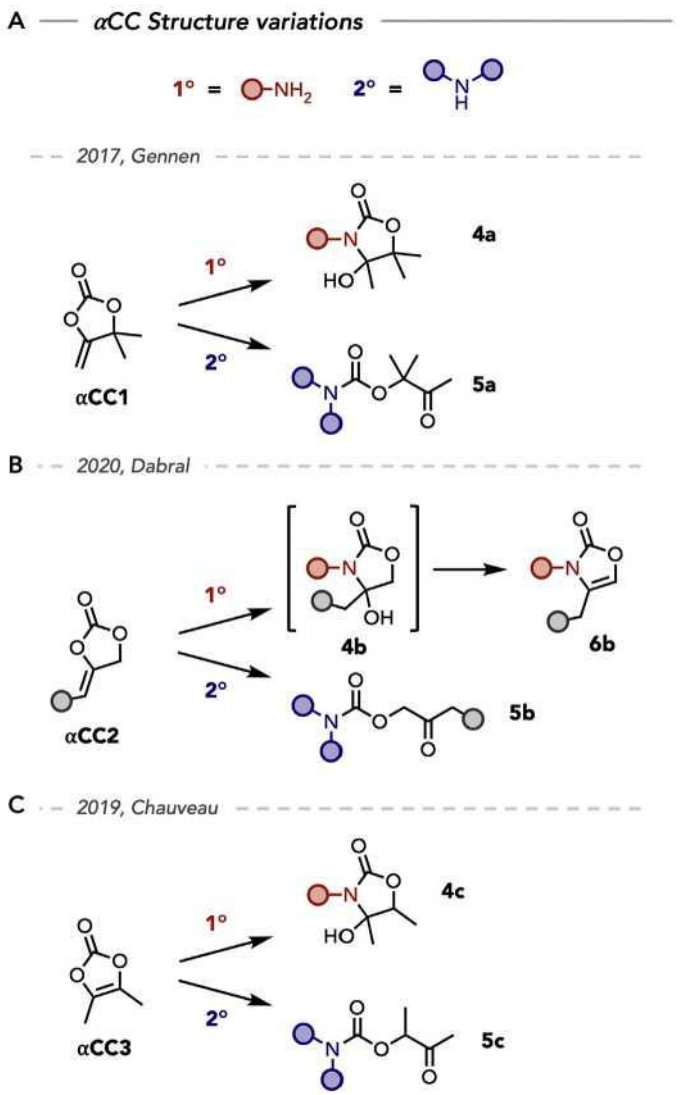
Kinetic experiments attest the substantial increase in reactivity of **αCC1** compared to **5CC** (propylene carbonate) toward primary and secondary amines at r.T (Fig. 8b). The formation of **4a** by reaction of **αCC** with primary amines is fast and quantitative within few hours, while the reaction with secondary amines, though slower, keeps complete in 24 h to produce *oxo*- urethane **5** (Scheme 17a) [107]. It was also observed that adding a catalytic amount of DBU speeds up these reactions.

Following this seminal work, subsequent studies explored the reactivity of structurally divergent substrates. Dabral synthesized elusive unsubstituted exovinylene cyclic carbonates **αCC2** from primary propargyl alcohols [113]. The reaction with primary amine is fast at r.T, providing a hydroxy-oxazolidone **4b** which spontaneously dehydrates into an endo-vinylene oxazolidone **6b** [97] (Scheme 17b). The reaction with a secondary amine (pyrrolidone) is slower but still provides quantitative reaction at r.T in 6 h.

Chauveau assessed the reactivity of commercial disubstituted endo-vinylene cyclic carbonate **αCC3** [114]. With primary amines, the reaction is smooth at r.T and provides a hydroxy-oxazolidone **4c**. When a secondary amine is used with a catalytic amount of DBU (1 mol%), the reaction quickly produced the *oxo*-urethane **5c** in 3 h (Scheme 17c). However, translation of the **αCC3** aminolysis to polymer chemistry failed with low monomer conversion and side reactions.

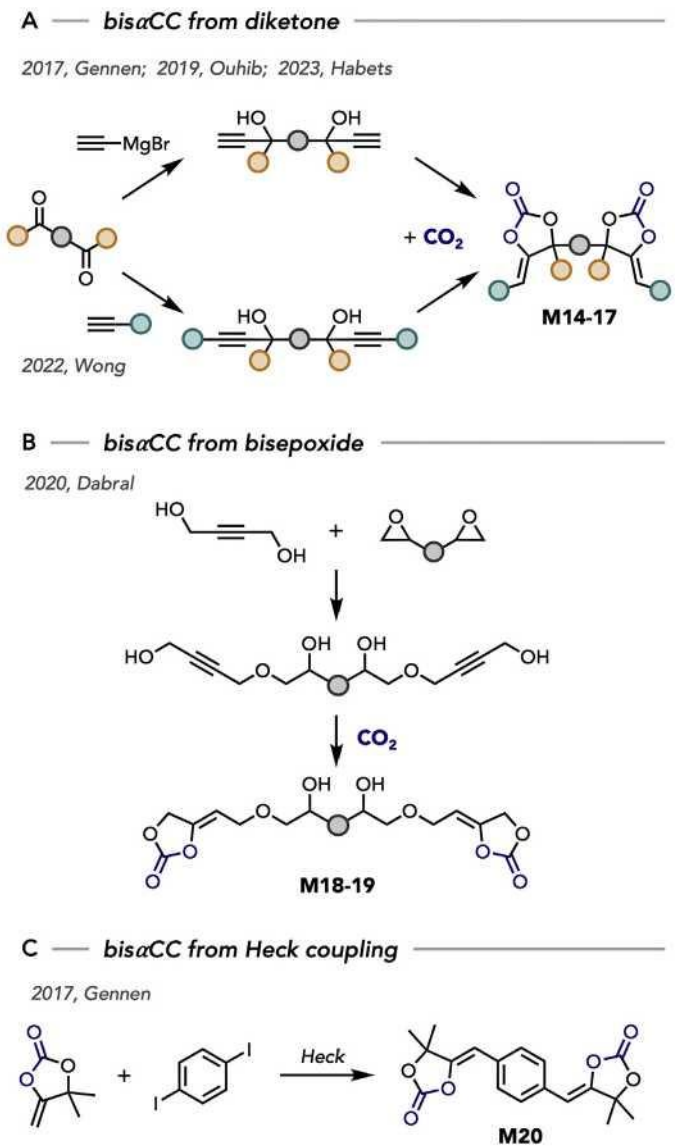
Scheme 17. *Reactions of **αCC** variants with primary and secondary amines. (A) Substituted exovinylene cyclic carbonate; (B) Unsubstituted exovinylene cyclic carbonate; (C) Disubstituted endovinylene cyclic carbonate.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



Scheme 18. *Synthesis of bis**αCC** from (A) diketones, (B) bisepoxides, and (C) using Heck coupling reaction.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



4.1.2 EFFECT OF THE AMINE

The reaction of **αCC1** and amines is slower with increased steric hindrance around the amine function [108]. Kinetic experiments established the order of reactivity for three representative amines as follows: heptylamine > benzylamine > cyclohexylamine. Despite variations in reaction rate, the reactions reached quantitative conversion after 24 h. The *oxo*-urethane **3** is observed during the reaction for all amines and gets consumed as the reaction proceeds, therefore driving the equilibrium toward products. The ring-closure into hydroxy-oxazolidone **4** occurs quickly for the aliphatic amine but is considerably slower for sterically hindered cycloaliphatic amine, such as cyclohexylamine (24% of remaining **3** after 24 h). Interestingly, for hindered benzylamine, the ringclosure is exceptionally rapid, with the intermediate **3** barely detectable during the reaction and leading to full selectivity toward **4**. The high reactivity of benzylamine toward ring-closure suggests that other factors than steric hindrance might influence this step.

The addition of DBU as catalyst (5 mol%) significantly accelerates both amine addition and ring-closure steps,

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

rendering the reaction with cyclohexylamine selective toward **4** after 24 h.

4.2 POLYMERIZATIONS

The high efficiency of this chemistry to quantitatively provide carbamates at r.T and within 24 h was translated to the fabrication of linear polymers via step-growth polymerization. Bifunctional **αCC** monomers were synthesized following different strategies, mostly based on the synthesis of bis(propargyl alcohol)s obtained from diketones [107,115] (toward substituted bis **αCC M14**- **M17**, Scheme 18a) or from bisepoxides [97] (toward unsubstituted bis **αCC M18**-**M19**, Scheme 18b). Another approach relies on the Heck coupling of monofunctional **αCC** toward **M20** (Scheme 18c) [107].

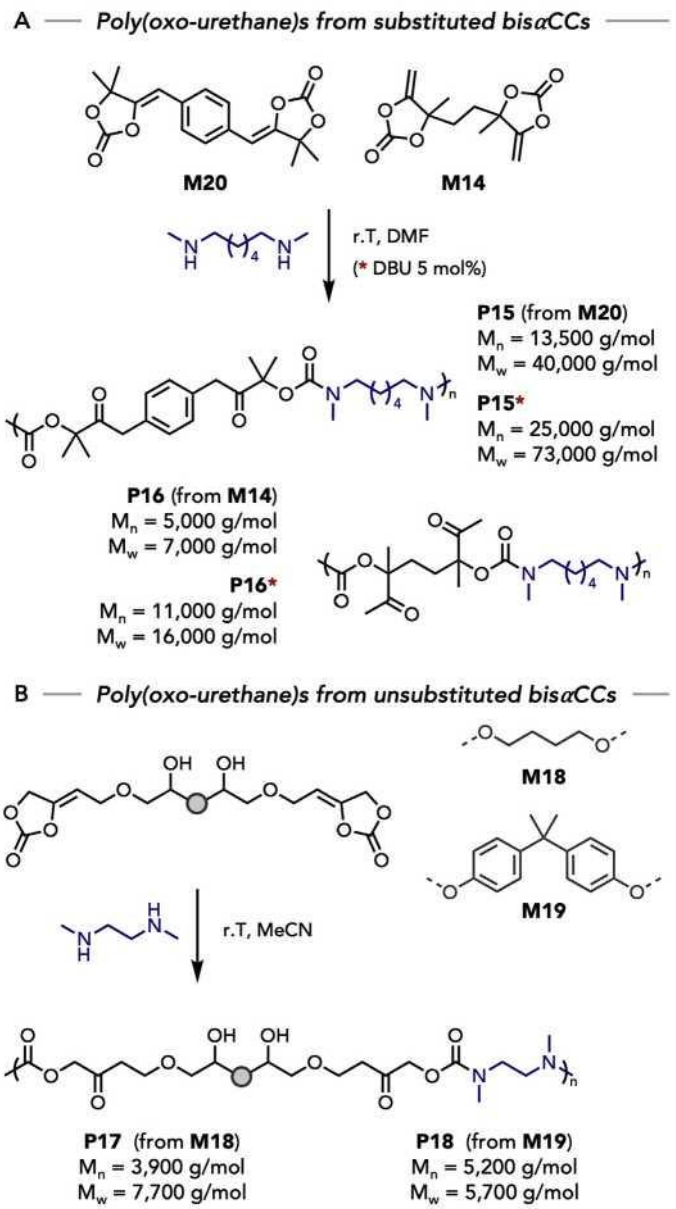
4.2.1 POLY(OXO- URETHANE)S

Gennen demonstrated the polymerization of **M14** and **M20** with secondary diamines at r.T, using $CHCl_3$ or DMF as solvents [107]. DMF was superior as demonstrated by a 2- to 3-fold increase in molar mass of the polymers compared to $CHCl_3$. The monomer structure was varied for the polymerization in DMF, affording Mn of 13,500 $g \cdot mol^{-1}$ for **M20** and 5,000 $g \cdot mol^{-1}$ for **M14** after 24 h of polymerization (Scheme 19a). This suggests that **M20** might have increased reactivity compared to **M14**. However, it is important to note that the molar mass determined by *SEC* is relative and heavily influenced by the molecular structure. The addition of a catalytic amount of DBU increased the molar mass to M_n 25,000 $g \cdot mol^{-1}$ for **M20** and M_n 11,000 $g \cdot mol^{-1}$ for **M14**.

Unsubstituted bis αCCs **M18** and **M19** were co-polymerized with a secondary diamine at r.T in acetonitrile, affording polymers with moderate molar mass up to M_n 5,200 $g \cdot mol^{-1}$, with a full conversion of the monomers after 24 h (Scheme 19b) [97]. However, the solvent was not varied nor the addition of a catalyst to optimize the reaction conditions.

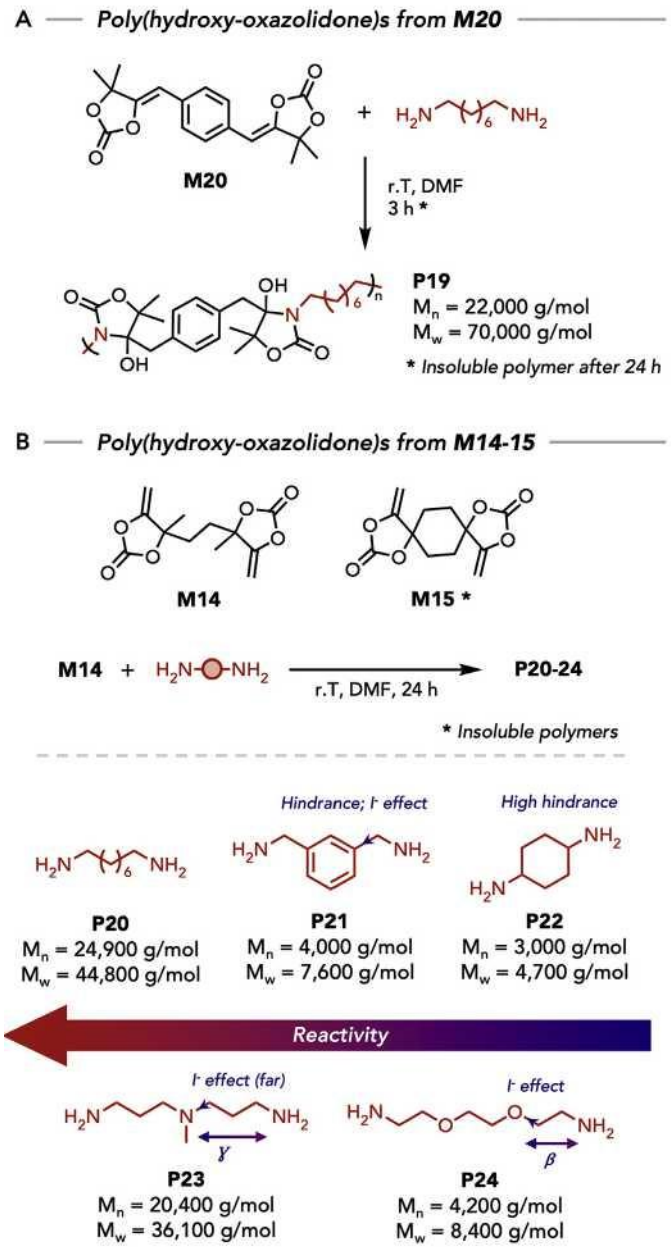
Scheme 19. Poly(*oxo*-urethane) synthesis from (A) substituted bis αCCs and (B) unsubstituted bis αCCs.

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



Scheme 20. *Poly(hydroxy-oxazolidone) synthesis from (A)* ***M20*** *and 1,8- octanediamine and (B)* ***M14–15*** *and several diamines.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



4.2.2 POLY(HYDROXY-OXAZOLIDONE)S

Gennen synthesized poly(hydroxy-oxazolidone)s by reacting **M20** with primary diamines at r.T in DMF, providing polymers of high molar mass after only 3 h (up to M_n = 22,000; M_w = 77,000 $g \cdot mol^{-1}$) (Scheme 20a). These polymers became insoluble after 24 h of reaction, likely due to increased molecular weight. Polymerization using **M14** provided soluble polymers after 24 h, characterized by a M_n of 21,500 $g \cdot mol^{-1}$.

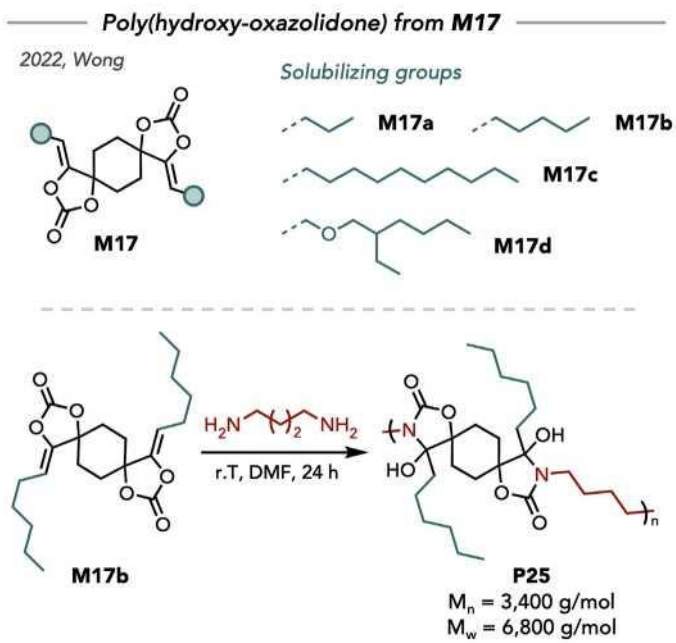
Habets expanded the scope of polymers using a spirocyclic monomer **M15**, along **M14** , to polymerize with a broad range of primary diamines at r.T in DMF for 24 h (Scheme 20b). Using **M14** as monomer, moderately high molecular weight poly(hydroxyoxazolidone)s were obtained using unhindered diamine monomers (M_n 20,000 - 25,000 $g \cdot mol^{-1}$; M_w 36,000 - 45,000 $g \cdot mol^{-1}$) with a full selectivity toward the hydroxy- oxazolidone **4** linkage. However, using more

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

hindered benzylic MXDA resulted in lower molecular weight (M_n = 4,000 *g*· mol^{-1}; M_w = 7,600 *g* ^mol^{-1}), with a complete selectivity toward the hydroxy-oxazolidone **4** linkage, in line with the model experiments (*vide infra*). Highly hindered and rigid cyclohexyldiamine was even less efficient, resulting in low molar mass polymers (Mn 3,000 *g* · mol-1; M_w 4,700 *g* · mol^{-1}) and in a partial selectivity toward the hydroxy-oxazolidone linkage (32% of *oxo*-urethane **3** linkage persisted after 24 h). EDR148 also produced low molecular weight polymers (M_n = 4,200 *g* -mol^{-1}; M_w = 8,400 *g* ·mol^{-1}) despite its unhindered structure, certainly affected by the negative inductive effect of *β* -ethoxy bonds. The addition of 5 mol% of DBU was evaluated for the challenging amines. For EDR148, the molecular weight significantly increased to M_n of 15,500 *g* -mol^{-1} (M_w = 25,500 *g* -mol^{-1}), demonstrating the beneficial effect of a catalyst for challenging substrates. However, the DBU-catalyzed addition of more hindered cyclohexyl- and benzylic diamines yielded insoluble polymers, possibly due to molecular weight exceeding solubility thresholds. All the poly(hydroxy-oxazolidone)s derived from the spirocyclic monomer **M15** were insoluble in all organic solvents.

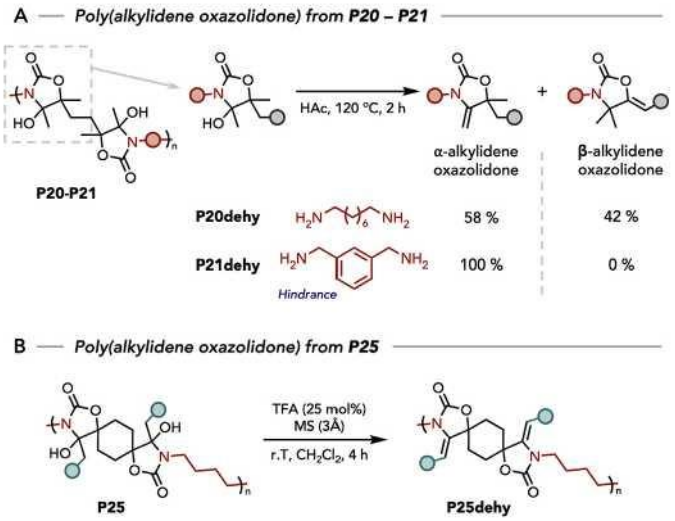
This non-isocyanate chemistry has shown great promise for producing elusive poly(oxazolidone)s with moderate molecular weight at r.T, while this class of PU is generally synthesized in harsh conditions (> 150°C, catalysts) from epoxides and isocyanates. A major limitation is the low solubility of the synthesized polymers, likely due to the combined effects of structural rigidity and the dense hydrogen bonding network formed by the pending hydroxyl functions of the polymer backbone. To address this issue, Wong very recently incorporated solubilizing groups on the double bond of the challenging monomer **M17** to enhance the solubility of the polymer in solvents, yielding monomers **M17a-d** [116] (Scheme 21). High temperatures (80°C) were mostly used in the work, but one example was achieved at r.T from **M17b** and 1,4-butanediamine in the presence of DBU (25 mol%). The polymer contained exclusively hydroxy-oxazolidone **4** linkages but was characterized by a low molecular weight (Mn = 3,400 *g* -mol^{-1}; M_w = 6,800 *g* -mol^{-1}). The introduction of solubilizing groups resulted in improved solubility of the polymers in various solvents, particularly when the groups included the more flexible ether- containing chain in **M17d**.

Scheme 21. *Poly(hydroxy-oxazolidone)* ***P25*** *synthesis from* ***M17***.



Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

Scheme 22. (A) Dehydration of poly(hydroxyoxazolidone)s **P20** and **P21** to yield poly(alkylidene oxazolidone)s embedding one or two different linkages depending on the amine steric hindrance. (B) Dehydration of poly(hydroxy-oxazolidone) **P25**.



The tertiary alcohol in the hydroxyoxazolidone **4** has shown to provide opportunities for further functionalization through a dehydration reaction to yield poly(alkylidene oxazolidone)s. This was first demonstrated by Habets with the dehydration of, for instance, **P20** and **P21**, by reflux in acetic acid (120°C) for 2 h, furnishing **P20dehy** and **P21dehy** respectively [108] (Scheme 22**a**). Similarly, Wong performed this reaction on **P25** , but at r.T in the presence of trifluoroacetic acid (TFA, 25 mol%) and molecular sieves (3A) [116]. While **P21dehy** exhibited only the expected *α*-alkylidene oxazoli- done linkage, **P20dehy** contained 58% of the *α*-alkylidene oxazoli- done linkage and 42% of the *β*-analog. It was rationalized that a Wagner-Meerwein rearrangement led to the formation of the more stable trisubstituted alkene in the *β* -linkage. The feasibility of this rearrangement seemed ruled by the hindrance of the amine group. In the case of **P25dehy**, no rearrangement occurred in the absence of a neighboring labile methyl group (Scheme 22b). The thermal stability of the dehydrated polymers generally improved compared to poly(hydroxy-oxazolidone)s, enabling their characterization by DSC. Polymers **P20dehy** and **P21dehy** were characterized by Tgs values of 89 and 130°C respectively, while the polymer **P25dehy** was semi-crystalline with a T_g of 85°C and a T_m of 207°C.

In recent works from Detrembleur's team, more soluble poly(hydroxyoxazolidone) polymers were synthesized by incorporating flexible segments within the polymer backbone. This was accomplished through the copolymerization of the bis *α*CC monomer **M14** with polyamines and polythiols, resulting in poly(hydroxyoxazolidone- *co*-thiocarbonate) polymers [117]. These modifications enabled their thorough purification and characterization. Thermal degradation studies revealed a spontaneous dehydration of the polymers at temperatures ranging from 110 to 160°C in bulk and in the absence of catalysts, yielding quantitatively and selectively polymers with *α*-alkylidene oxazolidone linkages. This feature is of particular interest for achieving polymer transformation without the need of purification, with heat alone as the dehydration trigger. Another peculiar observation was the presence of two Tgs, although the origin of the second Tg is not fully understood. These unique characteristics have been constantly observed across various works involving soluble poly(hydroxyoxazolidone) polymers derived from **M14–16** monomers [118,119].

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

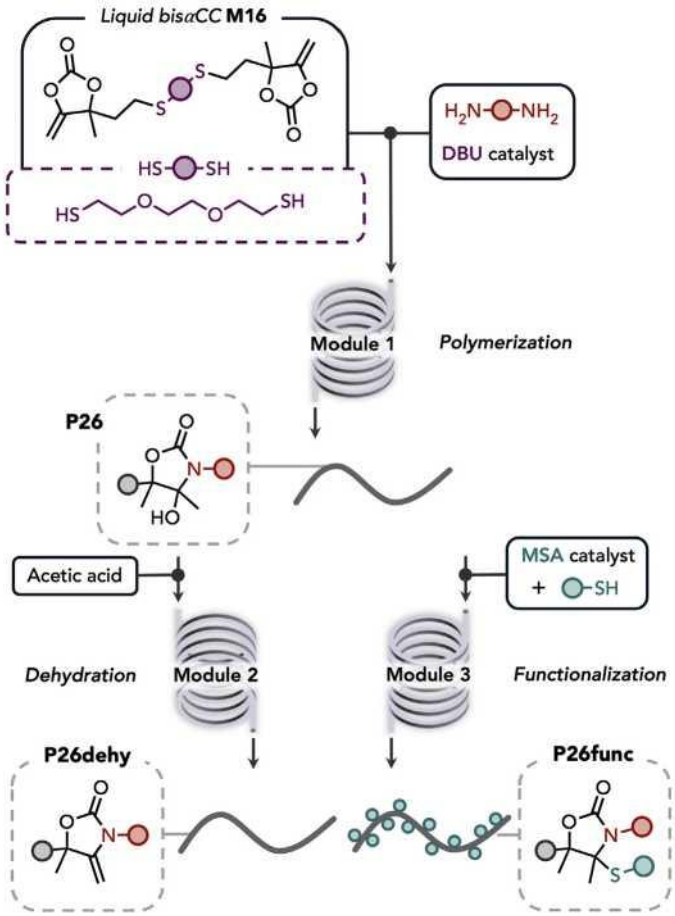
Recently, a liquid bis *α***CC** monomer **M16** was developed [120] and employed in flow reactors to produce poly(hydroxyoxazolidone)s **P26** at r.T in a low residence time of 23.5 min (Scheme 23) [118]. Although the reaction conditions were optimized at higher temperatures, a polymer with a molecular weight of M_n = 3,000 *g*-mol^{-1} (M_w = 6,800 *g* -mol^{-1}) was obtained at r.T, using DBU as organocatalyst. The polymer exhibited high solubility in various solvents and was characterized by a relatively low T_g of 13°C - this is attributed to the introduction of flexible segments in **M16**. The production of polymeric urethanes by step-growth polymerization in flow was so far limited to one example relying on the isocyanate chemistry [121], as very efficient reactions are required to form the polymer within such short residence time in the reactor. By fine-tuning the microfluidic setup, plug and play modules can be added to either dehydrate the polymer into the corresponding poly(alkylidene oxazolidone) **P26dehy**, or dehydrate and functionalize the polymer into **P26func** in a one-step process by a cationic thiol-ene reaction, taking advantage of the so-formed pendant unsaturations.

4.3 LIMITATIONS AND PERSPECTIVES

The *α*-alkylidene cyclic carbonate chemistry is an emerging toolbox for the synthesis of regioregular and well-defined NIPUs in mild conditions. By the selection of the amine nature (primary or secondary), both acyclic and cyclic polyurethanes can be produced. However, many aspects of this chemistry remain unexplored, such as the effect of the cyclic carbonate structure on the reaction rate, the identification of optimal catalysts, solvent effects, and the development of materials with practical applications that leverage the unique properties of this chemistry. Moreover, bifunctional precursors remain challenging to access with multi-step syntheses and column chromatography work-ups. There is therefore space for further studies on both the synthesis of propargyl alcohol derivatives and the aminolysis reaction, but also for identifying and developing applications for the so-produced polymers.

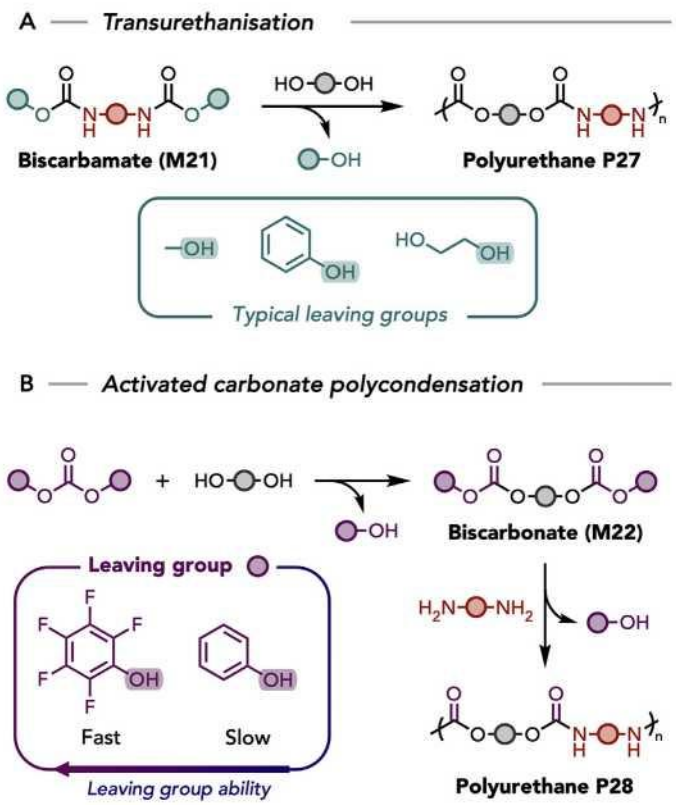
Scheme 23. *The liquid bis αCC monomer **M16** was developed and used for producing poly(hydroxyoxazolidone)s in flow reactors. The first module is used to combine the monomer **M16** with the diamine and the organobase catalyst (DBU) to provide the polymer **P26**. A second in-line module can be added to the first to either obtain the dehydrated polymer **P26dehy** or a functionalized polymer **P26func**.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



Scheme 24. *NIPUs by polycondensation through (A) transurethanisation, and (B) activated carbonates.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



5. NIPUs by polycondensation approaches

5.1 TRANSURETHANISATION

NIPUs can be synthesized using polycondensation methods, typically through the well-established transurethanisation of biscarbamates **M21** with diols. The monomeric diols replace a leaving alcohol condensate to form a new carbamate bond (Scheme 24a). To shift the equilibrium toward high conversion and therefore, high molecular weight, the condensate must be removed from the reaction medium. Consequently, this reaction requires high temperatures and reduced pressure in the presence of suitable catalysts. This approach is highly attractive as the resulting polymers possess the same molecular structure as isocyanate-based PUs. However, performing transurethanisation at r.T is illusory due to the need to remove the alcohol condensates.

5.2 POLYCONDENSATION FROM ACTIVATED CARBONATES AND DIAMINES

Polycondensation into polymers with identical chemical structures can be achieved by engineering carbonates into so-called ' *activated carbonates*' [122–124]. The strategy relies on the synthesis of a biscarbonate **M22** terminated with good leaving groups (fluorinated phenols). By reaction of this monomer with a diamine in mild conditions, the carbonate is selectively cleaved to release the desired leaving group, yielding carbamate linkages (Scheme 24b). Biscarbonates can be synthesized from chosen diols to tune the polymer properties, also altered by the choice of the diamine during polymerization. For instance, Sardon designed biscarbonates using both rigid (1,6-hexanediol) and

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

flexible (PEG) linkers, which were used in different ratios to tailor the final polymer properties. The polymerization was conducted in water, with an equimolar ratio between the biscarbonate and the amine, along with triethylamine in equimolar ratio *vs* reactive functions. Polymers **P28** with M_n of around 16,000 $g \cdot mol^{-1}$ were obtained after only 1 h of reaction at r.T without needing reduced pressure, though it must be kept in mind that polymers were obtained from oligomeric biscarbonates (PEG-derived) and diamines. The polymers exhibited crystallinity due to the PEG domains and a low T_g of around -55 °C. A significant drawback from this approach is the release of toxic and hazardous pentafluorophenol during polymerization. Additionally, the biscarbonate was synthesized from bis(pentafluorophenyl)carbonate, which originates from phosgene. Substituting this effective leaving group with more environmentally friendly phenol significantly slowed down the reaction. Although it was not discussed by the authors, the presence of triethylamine might benefit to the reaction by quenching the acidic released phenolic species, hence shifting the reaction equilibrium.

5.3 POLYCONDENSATION FROM CO2 -DERIVED CARBAMATES ADDUCTS AND DIHALIDES

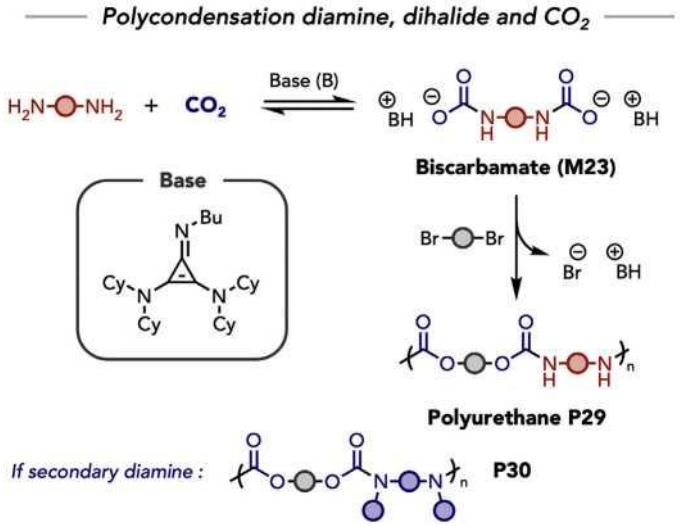
Wu recently described a polycondensation strategy combining diamines and dihalides in the presence of CO_2 to synthesize polyurethanes [125] (Scheme 25). This terpolymerization method relies on the formation of dicarbamate adducts from diamines and CO_2 in mild conditions and in the presence of a base (1 eq. *vs* reactive functions). The resulting dicarbamate adducts undergo stepgrowth polymerization with a dihalide (bromide here), producing a polyurethane and an acid-base condensate. Previous reports required higher temperatures, resulting in defects within the polymer backbone and stoichiometric unbalance [126]. The authors found that a cyclopropeneimine base enabled chemoselectivity at r.T and yielded soluble carbamate adducts, unlike other commercial superbases such as DBU or TBD. Their methodology involved adding the base in equimolar amount to the amine with CO_2, thereby forming the carbamate adduct. After the addition of the dihalide in a second step, the polymers **P29** were obtained after 24 h at r.T under 1 atm of CO_2, and were characterized by a moderate to high molecular weight (M_n = 4,000 to 420,000 $g \cdot mol^{-1}$) depending on the diamine. Aromatic, hindered, and deactivated through inductive effect amines were less efficient than aliphatic diamines. Interestingly, secondary diamines were effective monomers to provide NIPUs bearing *N*-substituted carbamate linkages **P30**. The Tg of the polymers was greatly influenced by the monomers structure, ranging from -20 to 140°C. Although the authors mentioned to reach molecular weight up to 420,000 $g \cdot mol^{-1}$, this was achieved using one specific monomer and exhibiting unusual low dispersity (near 1) for polymers produced by a step-growth process (typical dispersity of 2). Although the base is used in equimolar ratio and is not commercially available, the authors claimed that it can be quantitatively recovered without chromatographic separation.

5.4 LIMITATIONS

Polycondensation reactions are appealing for producing NIPUs of the same chemical structure as conventional PUs, therefore matching their potential applications. However, applying condensation processes at r.T are limited by the challenging elimination of condensates, which has only been made possible by the use of undesired fluorinated molecules or salts adducts as excellent leaving groups. The atom efficiency of these reactions is inherently low and is therefore much less attractive than polyaddition strategies.

Scheme 25. *Polycondensation of diamines, dihalides and CO_2 into NIPUs **P29** and **P30** with an in-situ generated intermediate (biscarbamate adducts **M23**).*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



6. NIPUs by ROP of cyclic carbamate

Ring-opening polymerization (ROP) offers several advantages over step-growth polymerization strategies commonly used for NI- PUs synthesis: the ability to reach high molecular weight even at incomplete conversion, a control over the molecular weight, the possibility to reach low dispersities, and a control over the polymer architecture (e.g. blocks, star-shaped polymers). However, due to the stability of the cyclic carbamates, their ROP is challenging, rendering this polymerization approach much less developed. Examples remain scarce and the polymerizations are generally carried out at elevated temperatures (70°C or higher) [127,128].

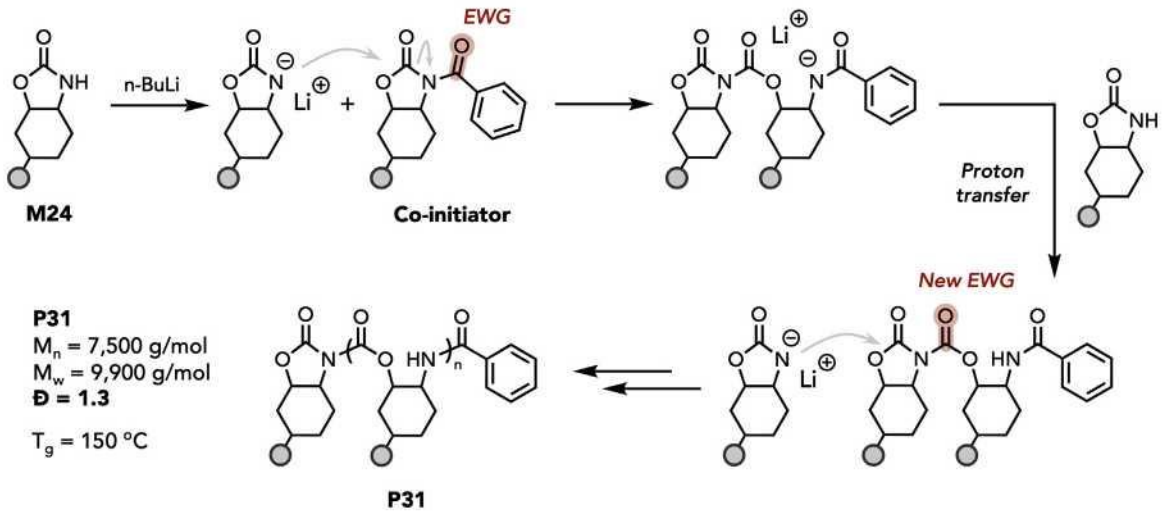
In 2019, two authors proposed the anionic ROP of fivemembered cyclic carbamates at low temperature (0°C to r.T). Zhang reported that ROP was only feasible on bicyclic oxazolidone fused to a six-membered ring **M24**, certainly due to the higher ring strain provided to the five-membered carbamate [129] (Scheme 26). The challenging ring-opening of the stable cyclic carbamate monomer **M24** was addressed by the introduction of a more electrophilic coinitiator bearing an electron-withdrawing acyl group on the carbamate. Activated by a strong base, e.g. BuLi, the nucleophilic nitrogen in the carbamate of **M24** can thereby attack the co-initiator. Following proton transfer, a new acyclic carbamate bond is created. The growing chain is therefore constituted of carbamate linkages with a cyclic carbamate chain-end, whose electrophilicity is activated by the acylurethane group, acting as new growing centers. Only low molar mass NIPUs **P31** were obtained (M_n = 7500 *g* ·mol^{-1}) with a rather low dispersity (1.3) after polymerization in THF at 0 °C for 24 h. The effect of temperature remained unexplored by the authors. The resulting polyurethane was characterized by a high Tg of 150°C.

Haba proposed the polymerization of a similar monomer derived from sugar containing a fused 6-membered ring [130]. The monomer was polymerized in DMF at 0 °C in the presence of t- BuOK, conditions in which a M_n of 7,800 *g*· mol^{-1} was reached. Performing the reaction at r.T has led to a decrease in molecular weight (M_n = 3,400 *g* ·mol^{-1}) though this deviation was not rationalized.

Despite the many advantages of ROP to provide polymers of controlled architecture, reports at r.T remain scarce due to the inherent stability of five-membered cyclic carbamates. Enhancing the reactivity of these rings through molecular engineering – such as using strained rings structures or introducing substituents to trigger reactivity – could offer a potential solution.

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

Scheme 26. *Synthesis of NIPU* ***P31*** *by ROP of cyclic carbamate monomer* ***M24****.*



7. Harnessing established chemistries to build NIPUs at r.T

The difficulty to elaborate efficient ambient polymerization or curing systems prompted researchers to build NIPUs by taking advantage of other well-established chemistries [131,132]. This is generally achieved by synthesizing NIPUs pre-polymers which can further undergo polymerization or curing at r.T, incorporating chemical functions beyond urethanes in the backbone of the resulting polymers. In more rare examples, all functionalities are incorporated in a one-step strategy thanks to the compatibility between both chemistries.

7.1 UV-CURABLE (METH)ACRYLATE RESINS

PUs (meth)acrylate resins combine the desirable features of PUs and the advantages of (meth)acrylate-derived resins. Of high interest, the rapid free radical polymerization under UV allows for fast curing at r.T, rendering this technique environmentally friendly and energy efficient. They are therefore typically used in medical devices and dental health, coatings, adhesives, and 3D printing. A typical formulation contains monomers and/or oligomers, reactive diluents to reduce resin viscosity, a photoinitiator, and additives.

Given these advantages, research has focused on developing NIPU acrylate resins by the synthesis of acrylate precursors from existing urethane or oligo-urethanes.

Schimpf and Buchheit capitalized on the aminolysis of glycerol carbonate methacrylate (GCMA) to design vinyl-type monomers embedding hydroxyurethane linkages (**HUMA, M25**) [133,134]. By optimization of the experimental procedure to suppress the undesired aza-Michael reaction, a library of monomer is easily accessible from the large choice of commercial polyamines (Scheme 27a). These UV-curable vinyl-type monomers have been further exploited (optionally in combination with 4-acryloylmorpholine ACMO as reactive diluent - ratio ACMO:precusor of 60:40) to fabricate thermosets. This was exemplified with the fabrication of various polymers **P32** obtained after UV curing for 2 × 10 min or via photo3D printing (Scheme 27b). The material properties were governed by the **HUMA** structure. Those made from the more flexible diamines provided polymers with T_g as low as 78°C, and the value was increased

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

to 120°C with **HUMA** made from more rigid diamines. As the **5CC** aminolysis provides hydroxyurethane **1**, the pendant hydroxyl groups were exploited for further functionalization, i.e. for introducing additional methacrylate moieties (**UMA, M26**). This allows for a more than 2-fold decrease in viscosity compared to **M25** by suppressing strong H-bonds. By the addition of more methacrylate units, a polymer with a T_g as high as 218°C was produced.

Meyer's team proposed the synthesis of **UMA** from widely available simple **5CC** (ethylene carbonate or propylene carbonate) [135–137]. By the reaction of **5CC** with a diamine, a bis(hydroxyurethane) **HU** was obtained. The two hydroxyl groups were then methacrylated into **UMA M27** (Scheme 28a). Interestingly, they also reported the synthesis of a mono-functional **UMA** (**mUMA**), which has shown very low viscosity and was therefore used in the formulation as reactive diluent (Scheme 28b). By using different ratios of **M27** and **mUMA**, and through the use of different diamine spacers, the polymer properties were tuned, with Tgs ranging from -11 to 100°C for **P33** (Scheme 28c). The high reactivity of these species made them ideal candidates for 3D printing. It was noticed that the structure of **5CC** and the diamine were important for the successful photo-crosslinking reaction. For instance, when a simple aliphatic diamine such as 1,6-hexanediamine was used with ethylene carbonate as precursors, strong packing of the chains by H-bonding hindered diffusion and led to fast vitrification before the end of the reaction. This was solved by introducing branching using propylene carbonate as **5CC** or branched aliphatic diamines, or by the use of more flexible ether-containing diamines, providing full double bond conversion in 30 seconds. Carmenini recently proposed a similar strategy by using an itaconic acid-derived methacrylate for reaching high biobased content (up to 90 wt%) in the resin [138].

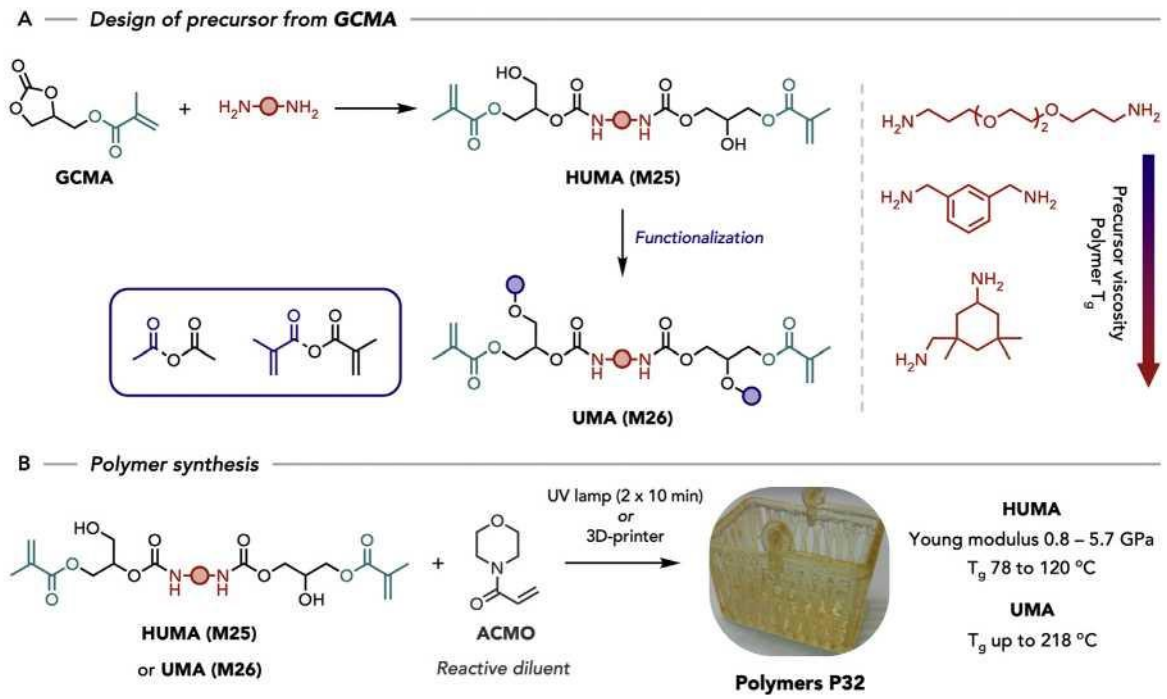
Ultimately, Zareanshahraki reported the synthesis of methacrylamide-terminated PHU by amidation of amine-terminated oligo-PHUs [139,140] (**PHUMA, M28**, Scheme 29a). Bi- and tri-functional acrylate co-monomers were added to **M28** yielding resins for UV-curable coating applications (Scheme 29b).

7.2 THIOL-ENE REACTION

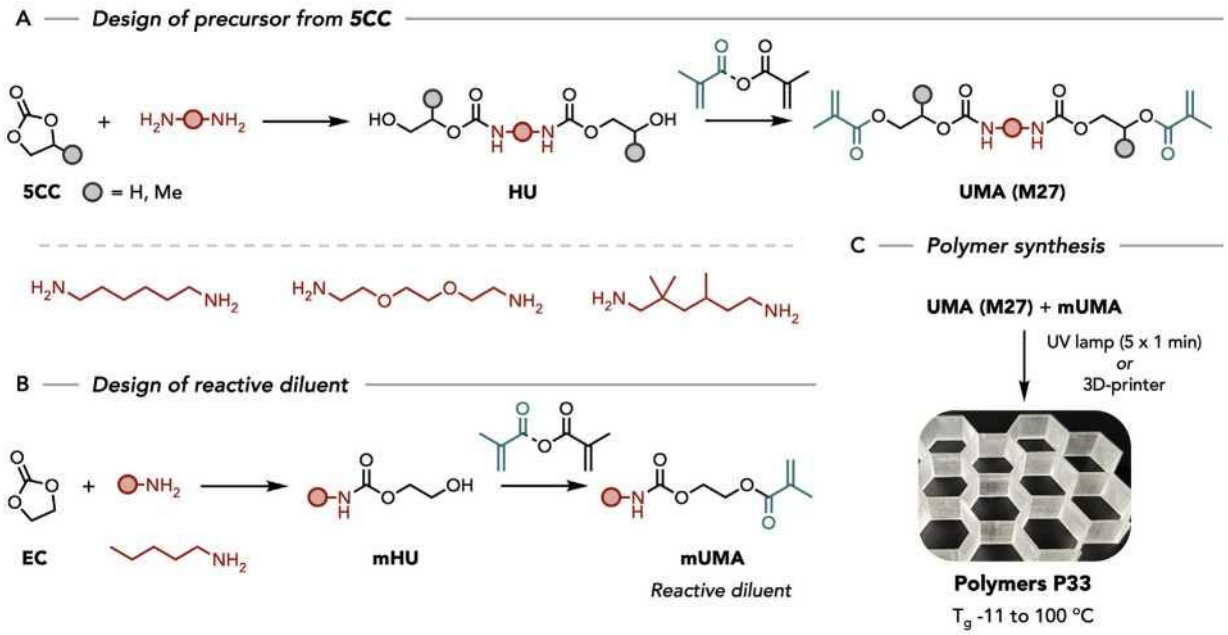
The thiol-ene reaction relies on the anti-Markovnikov addition of thiols onto alkenes to yield thioethers products. It is part of the "click" reactions family, meaning the reaction is generally fast and efficient, is not sensitive to water nor oxygen, and works in mild conditions to give the desired product in high yield [141]. An advantage of this chemistry is the ability of photo-initiation of the reaction, giving a spatio-temporal control on the reactivity, notably to make polymeric materials. The material often presents high uniformity, and is well-defined, in contrast to materials made from acrylate-derived curing. The thiol-ene therefore represents a method of choice for making NIPU materials at r.T.

Scheme 27. (A) Design of methacrylated precursors **M25–26** . (B) Polymerization of **M25–26** by UV curing in the presence of a reactive diluent into **P32** .

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



Scheme 28. *(A) Design of methacrylated precursors* ***M27****. (B) Design of a reactive diluent* ***mUMA****. (C) Polymerization of* ***M27*** *by UV curing in the presence of a reactive diluent (****mUMA*** *) into polymers* ***P33****.*



7.2.1. LINEAR POLYMERS BY THIOL-ENE

In 2014, Calle aimed at the synthesis of a AB-type monomer **M29** embedding a carbamate function (Scheme 30a)

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

[142]. This monomer, able to self-polymerize and deliver linear chains, was synthesized by the reaction of cysteamine with allyl chloroformate to a scale up to > 60 g with a high yield (> 80%). **M29** was polymerized in bulk under UV in the presence of a photoinitiator at r.T. After few minutes, the liquid monomer vitrified and turned into a solid, with 98% of alkene being consumed in only 5 minutes. The polymer **P35** was characterized by a Mn of 14,300 $g{\cdot}mol^{-1}$, a Tg of -4°C, and a Tm of 105°C.

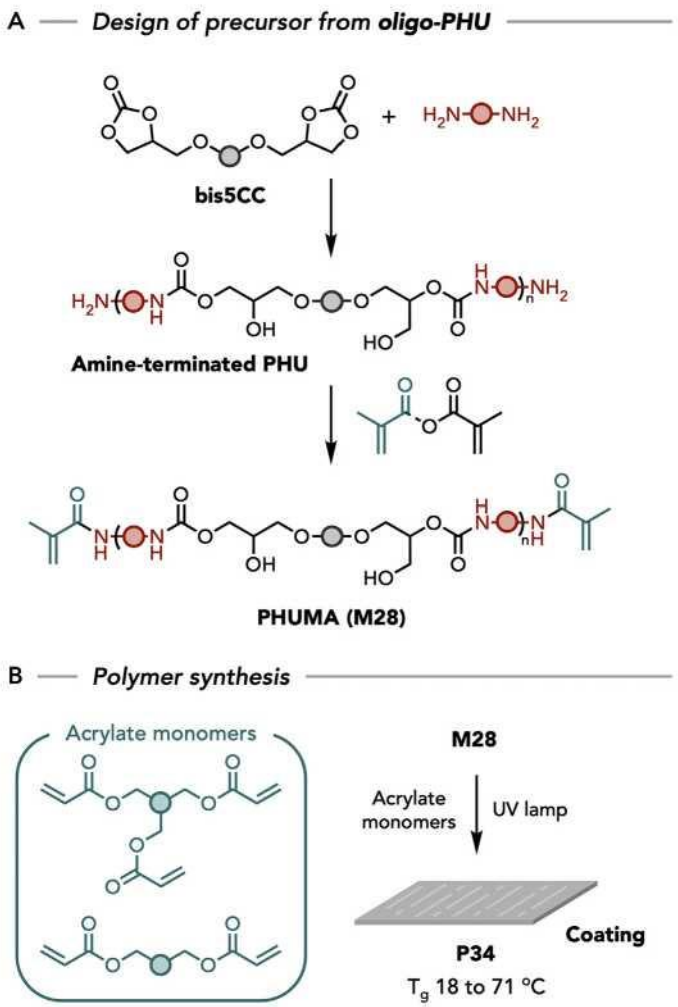
Recently, Xie leveraged the reversible capture of CO_2 by diamines in the presence of an organic base (TMG) to form carbamate adducts [143] in a similar manner than of Wu (see Scheme 25, *vide infra*). These species reacted in one-pot with bromo-alkene derivatives to yield dienes monomers **M30** containing two urethane moieties in moderate yields (∼ 50%) (Scheme 30b). **M30** was combined with dithiols to carry out UV-mediated thiol-ene reaction, furnishing poly(urethane- *co*-thioether)s **P36** of Mn up to 10,800 $g\ {\cdot}mol^{-1}$ (Mw 25,000 $g{\cdot}mol^{-1}$) after 4-24 h in THF [143]. The properties of the polymers were varied through the choice of the diamine, the length of the bromoalkene, and the length of the aliphatic dithiol. Most of the polymers were semi-crystalline with a Tg varying between -30 and 0°C, and a T_m between 100 and 130°C.

Other dienes were synthesized by Scheelje from limonenebased terpenes and carvone (Scheme 31) [144]. To introduce the urethane function within the monomers, the compounds were first epoxidized, then carbonated by CO_2 fixation and finally, reacted with allylamine derivatives to target ene-terminated monomers **M31**. Dienes monomers were copolymerized with different dithiols at r.T in 2-Me-THF for 24 h, providing a library of 9 polymers **P37** with molar masses up to Mn 31,200 $g{\cdot}mol^{-1}$. The Tg for these materials was ranging from 0 to 30°C.

In a similar fashion, Razavi-Esfali synthesized ene-terminated bis(hydroxyoxazolidone)s by aminolysis of bis **αCC M14** (Scheme 32). The so-formed diene monomer **M32** was subsequently reacted with a series of dithiols by UV-initiated thiol-ene to produce poly(hydroxyoxazolidone- *co*-thioether)s **P38** of high molar masses (up to Mn 27,000 $g{\cdot}mol^{-1}$ and Mw 116,000 $g{\cdot}mol^{-1}$) after 24 h of irradiation in DMF [119]. Five polymers were produced with T_gs values ranging from 7 et 40°C. Tensile tests performed on a high molecular weight hydroxyoxazolidone-based polymer showed that the material exhibited elastic and ductile mechanical behavior. However, after dehydration, the polymer behaved as a viscous liquid and exhibited flowing. This highlights the crucial role of hydroxyl groups in forming hydrogen bonds significantly enhancing the mechanical properties of the polymer.

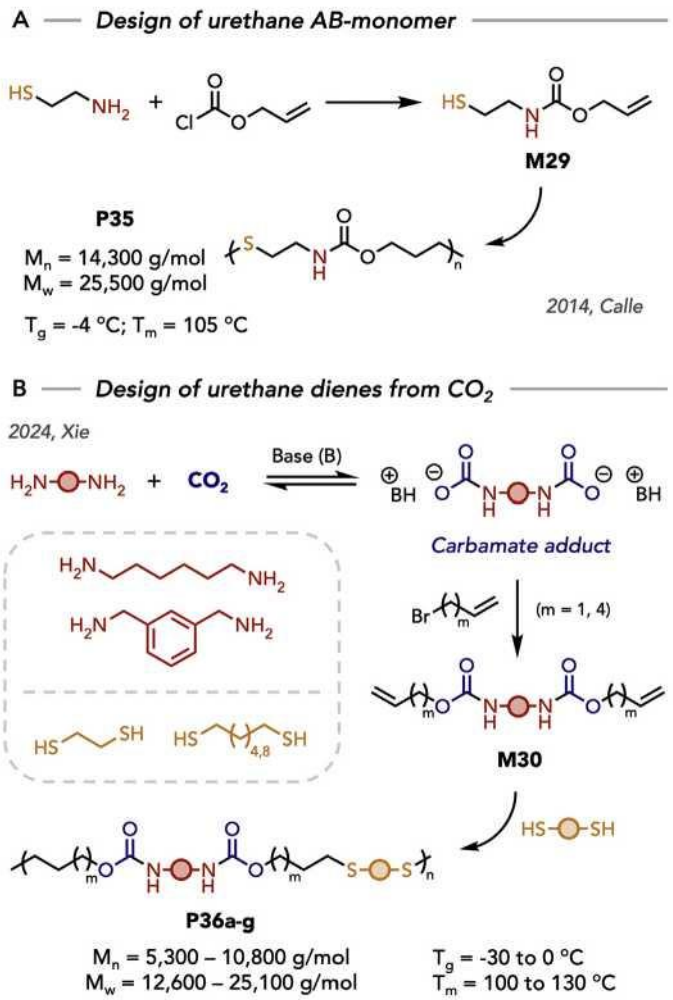
Scheme 29. *(A) Design of methacrylamide end-functionalized PHU precursors* ***M28*** *. (B) Polymerization of* ***M28*** *by UV curing in the presence of polyfunctional acrylate monomers into polymers* ***P34****.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



Scheme 30. *(A) Design of AB-monomer* ***M29*** *for NIPU thiol-ene polymerization into* ***P35****. (B) Design of dienes* ***M30*** *from the condensation of carbamate adducts with allyl halides. The thiol-ene polymerization with different dithiols provides polymers* ***P36****.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



7.2.2. CROSS-LINKED POLYMERS BY THIOL-ENE

The UV-initiated thiol-ene has also served to crosslink NIPUs. A **6CC** precursor containing a reactive allyl group (**6CC-allyl**) has served to the fabrication of ene-urethane adducts by reaction with di- [145] or tri- [146] amines **(**products **M33**, Scheme 33**a**). The trifunctional monomer was mixed with a dithiol and subjected to UV light to yield the network. The double bond conversion attained 90% after few minutes, and was increased after longer irradiation (95% after 20 min). The polymer networks embedding tertiary amines and thioether bonds were further functionalized by quaternization of the amine and methylation of the thioether to impart antibacterial activity to the material. In a second contribution by Warner, a difunctional ene-urethane monomer **M33** was crosslinked with mixtures of di-, tri-, and tetra-thiols to provide thermosets [145] (Scheme 33b). FTIR indicated complete alkene consumption after 5 min of irradiation. All polymers were characterized by similar T_gs around 0°C. However, the thiol functionality imparted the networks with very different mechanical properties, notably the Young's modulus which varied from 500 to 2,500 MPa. As a proof-of-concept, a spatially patterned material was 3D-printed through control of the polythiol composition in the resin. Additionally, the material displayed biocompatibility.

Pierrard reported the synthesis of NIPU networks by thiol-ene starting from bis**5CC** synthons following two distinct approaches [147,148]. In the first one, oligomeric PPG-derived **5CC** was reacted with allylamine in the presence of

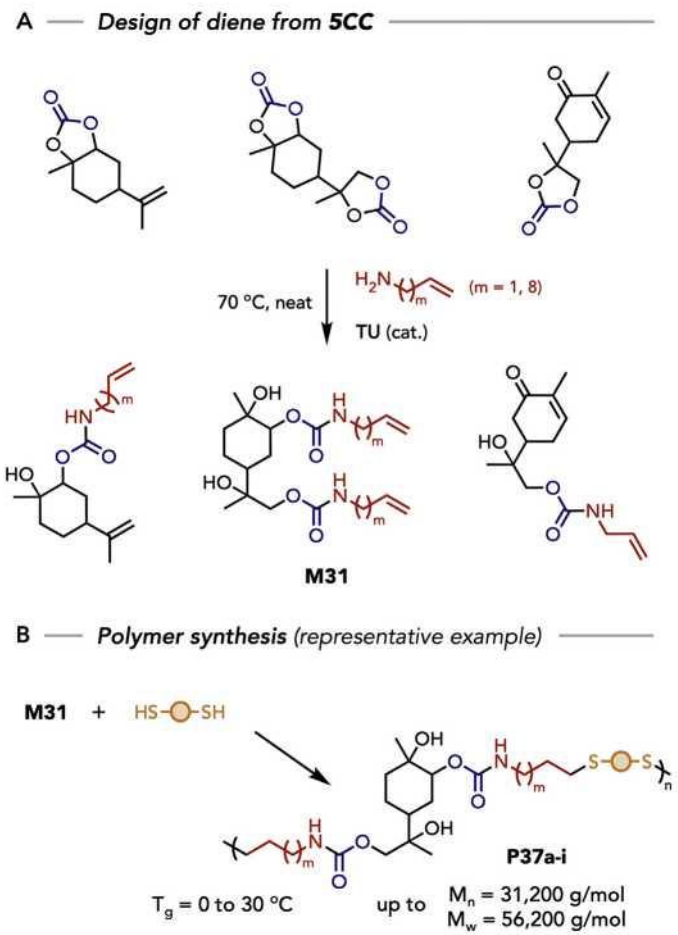
Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

DBU at 40°C for 4 days [147] (Scheme 34a). The resin was formulated by adding a trithiol and a photoinitiator to the diene monomer **M34**. Networks **P40** were produced upon UV irradiation at r.T for 15 min (Scheme 34b). A gel time of 4 min was determined by rheology and the Tg varied between -23 to -5°C depending on the length of PPG spacer within the monomer. The fast reaction and the low viscosity of the formulation allowed for 3D-printing of the polymer.

In a second work, the same PPG-derived bis **5CC** was used to make a PHU polymer by reaction with a rigid diamine (MBCHA) at 70°C for 4 days in bulk. The polymer was characterized by a moderate molar mass (M_n = 7200 *g* -mol^{-1}; M_w = 16,100 *g* ·mol^{-1}). Allyl groups were introduced by the addition of a CO_2 -derived allyl- containing **αCC** synthon, reactive to alcohols moieties in the presence of an organocatalyst [148]. The dissolved polymer in DMF was mixed with allyl- **αCC** (equimolar ratio *vs* hydroxyl groups) and DBU (10 mol%) at r.T for 24 h. The PHU was entirely functionalized with pendant carbonate functions terminated by a reactive alkene (Scheme 35a). This polyfunctional ene **M35** was then mixed with a photoinitiator and a poly(thiol) (di-, tri-, or tetra-functional), and irradiated under UV for 15 min to yield **P41** at r.T (Scheme 35b). Very short gel times of 6 to 8 seconds were determined by rheology whatever the thiol functionality. The network Tg was influenced by the thiol functionality, with values of 8, 25 and 42 ° C with the di-, tri-, and tetra-thiol, respectively. The mechanical properties were also drastically impacted by the thiol functionality, with the Young's modulus ranging from 2.4 to 16.0 MPa. The elongation at break was also decreased with increased cross-linking density. By adjusting the viscosity with a high boiling point solvent (NMP), 3D printing was successfully achieved. The purified materials proved to be bio- and hemo-compatible, therefore being promising candidates for specialized medical devices.

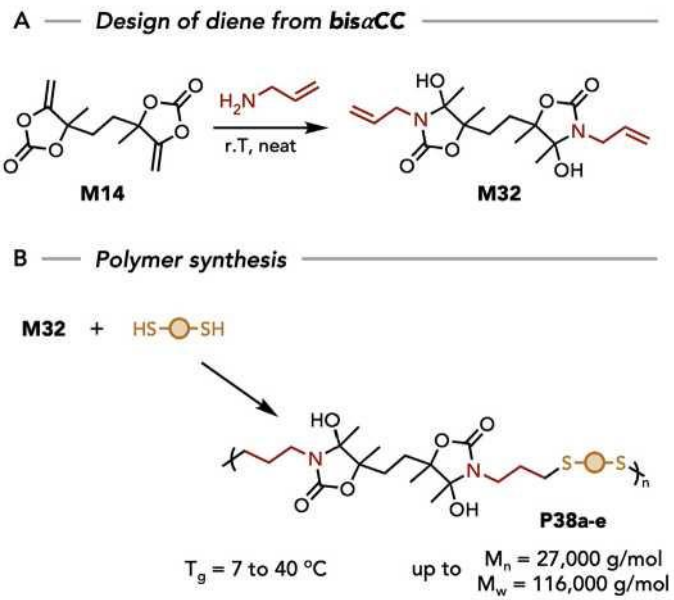
Scheme 31. *(A) Design of dienes **M31** by ring-opening aminolysis of **5CC**. (B) Polymerization with dithiols to yield **P37***
.

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

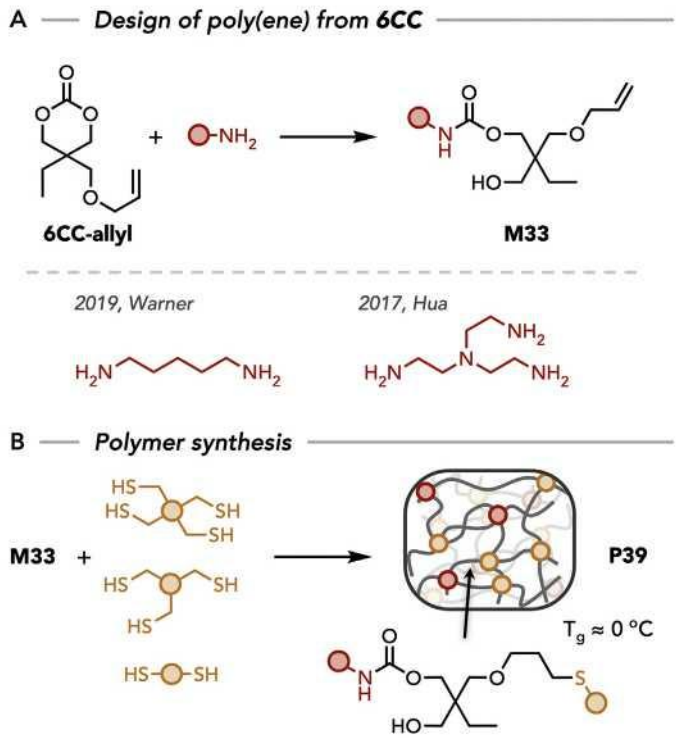


Scheme 32. *(A) Design of dienes* ***M32*** *by ring-opening aminolysis of bis α****CC M14****. (B) Polymerization with dithiols to yield* ***P38****.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



Scheme 33. *(A) Di- or tri-ene* ***M33*** *synthesis from* ***6CC-allyl*** *and di- or tri-amines respectively. (B) Polymer* ***P39*** *synthesis by thiol-ene of* ***M33*** *with di, tri-, and tetrathiols.*



7.2.3. DYNAMIC NETWORKS BY CATIONIC THIOL-ENE REACTION

In contrast to radical-initiated or base-catalyzed thiol-ene reactions, the uncommon cationic thiol-ene reaction

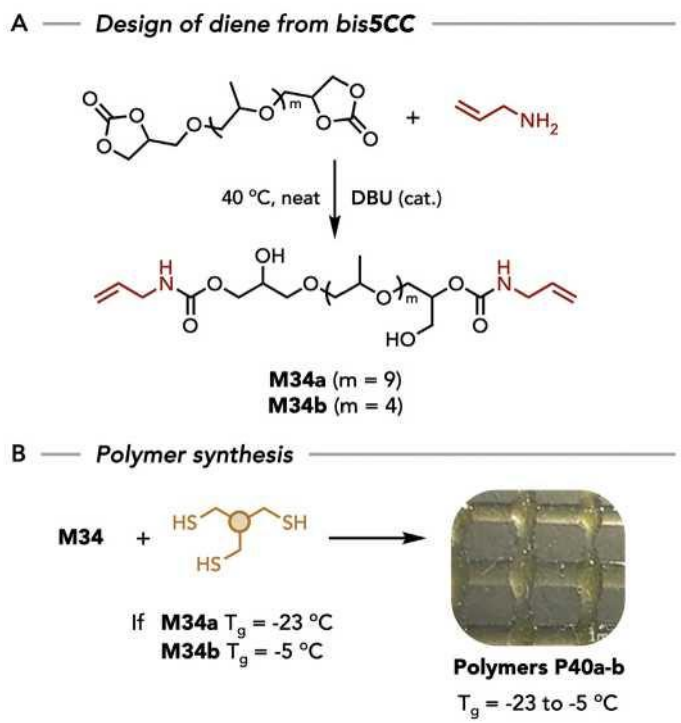
Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

produces a Markovnikov addition product. The reaction requires alkenes with electron-donating groups and is initiated in the presence of an acid catalyst (Scheme 36a) [149]. Recently, this reaction was applied to the synthesis of NIPU thermosets by Habets using alkylidene oxazolidone scaffolds, which possess electron-rich alkenes thanks to the presence of the carbamate nitrogen atom in α-position of the unsaturation. The reaction has shown to proceed smoothly and rapidly at r.T –it was therefore applied to the synthesis of polymers [150].

The design of bifunctional monomers **M36** can be achieved from **αCC1** through a one-pot diamine addition and dehydration step (Scheme 36b). By varying the diamine, monomers with flexible or rigid segments can be synthesized. Model studies demonstrated that the cationic thiol-ene reaction of alkylidene oxazoli- dones forming *N,S*-acetals linkages is equilibrated and highly dynamic, preventing its use for the step-growth polymerization into linear polymers. However, this feature has been advantageously exploited to create innovative covalent adaptable networks, i.e. a class of recyclable thermoset [150–154]. By reaction with a tetrathiol, an array of polymers **P42** were produced with Tgs ranging from 8 to 62°C. Depending on the choice of the monomer **M36**, the mechanical properties are drastically affected and can range from soft elastomers to glassy materials. The polymers were recycled both mechanically and chemically by leveraging the dynamic nature of the bonds.

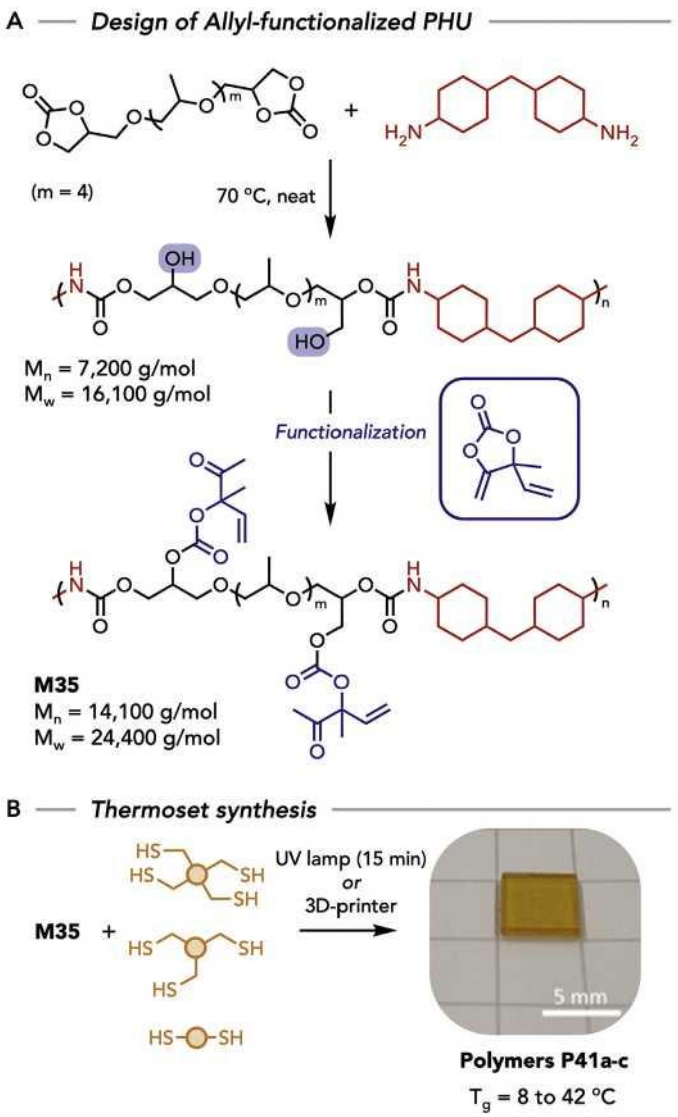
Another approach for the design of recyclable thermosets relies on using poly(alkylidene oxazolidone)s (Scheme 36c) [35]. These linear polymers contain pendant alkylidene groups on their backbone which can be chemically reacted with a dithiol. The so-formed polymer **P43**, with a T_g of 72°C, displayed promising mechanical properties and ease of recyclability.

Scheme 34. *(A) Synthesis of dienes **M34** from aminolysis of PPG-derived bis**5CC** (of different lengths) by allylamine. (B) Polymers **P40** synthesis by thiol-ene with a trithiol.*



Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

Scheme 35. *(A) Synthesis of a PHU polymer and functionalization using allyl- α**CC** into **M35**. (B) Resin photo-curing using **M35** and polyfunctional thiols into **P41**.*



7.3. EPOXIDE – AMINE REACTION

The reaction between epoxides and amines is a well-known process occurring at r.T, leading to the formation of amino-alcohols **7** (Scheme 37). Formulations of polyfunctional reactants have led to the development of epoxy resins, largely used in industrial and consumer contexts for their excellent properties: robust mechanical properties, excellent substrate adhesion, and chemical resistance [155]. They find applications in coatings and paints, adhesives, composite materials, or electronics. This chemistry is therefore of high interest and compatible with the NIPU chemistry, yet furnishing hybrid NIPU thermoset materials. By using epoxy additives, the curing process is accelerated, and the crosslinking density can be increased due to the double reactivity of the amine with epoxies as

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

illustrated in Scheme 37. Two approaches were reported to produce hydrid NIPU materials. In the first one, amine-terminated pre-polymers containing urethane linkages are reacted with epoxides to build the network as a mimic of the polyamine hardener used in epoxy resin formulations. In the second, the curing is performed directly from all precursors in one pot by mixing the poly**5CC**, the polyamine, and the polyepoxide.

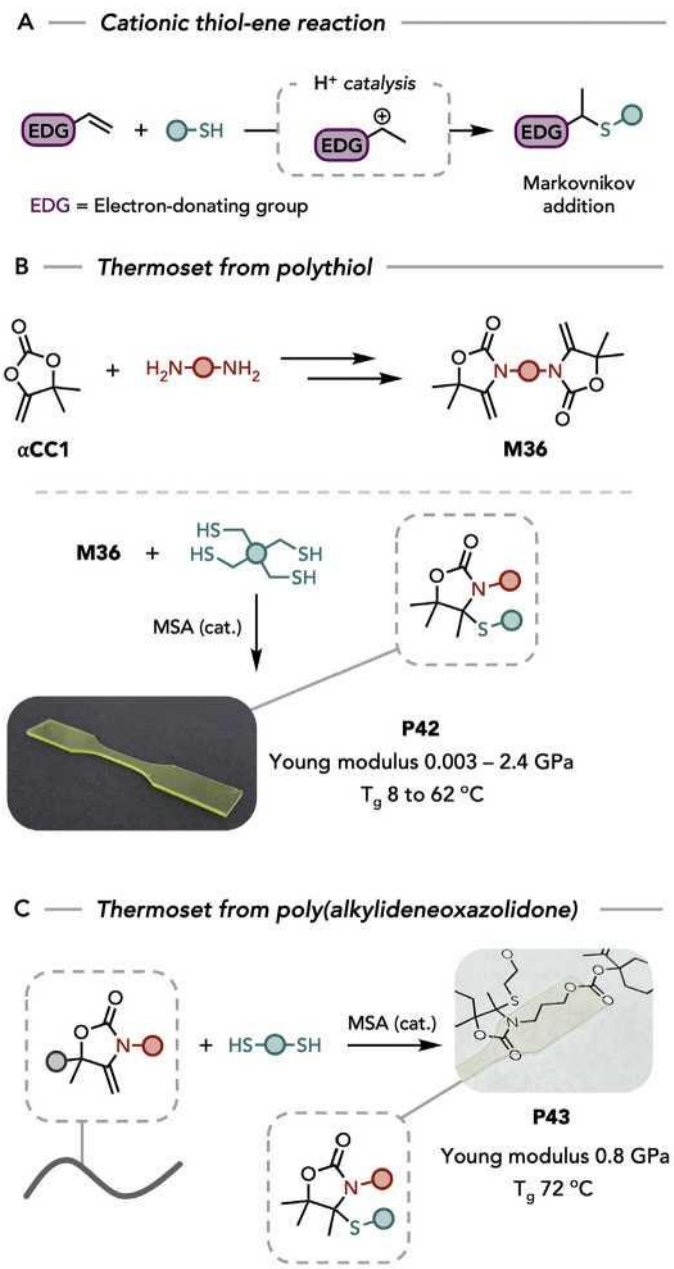
7.3.1. PRE-POLYMER APPROACH

Asemani synthesized amine-terminated PHU prepolymers **M37** by the reaction of an excess of diamine with a bis**5CC**. Both the structure of bis**5CC** and diamine were varied. The pre-polymers were then mixed with the polyepoxide, a nitrogen organobase and other additives typically used in coatings (surface additive, defoamer, solvent for adjusting viscosity) (Scheme 38) [156]. The coatings were cured for 7 days at r.T, but experienced tack-free between 4 and 12 h depending on the formulation. These materials showed adhesion performances similar to references commercialized isocyanate-based PUs products, and the properties were overall largely varied upon selection of the prepolymer structure and epoxy curing agent.

In a second work, Centeno-Pedrazo synthesized aminoterminated PHUs prepolymers from carbonated soybean oil. The prepared polyamines were then reacted with bisepoxides in the presence of MEK as solvent to adjust the formulation viscosity [157]. The resin was cured at r.T and characterized after 28 days, time at which the hardness value of the coating reached a plateau. The coatings were however tack-free in less than 24 h. The authors evidenced that coating properties readily improve with this hybrid chemistry compared to pure PHUs formulations, with a considerable increased hardness.

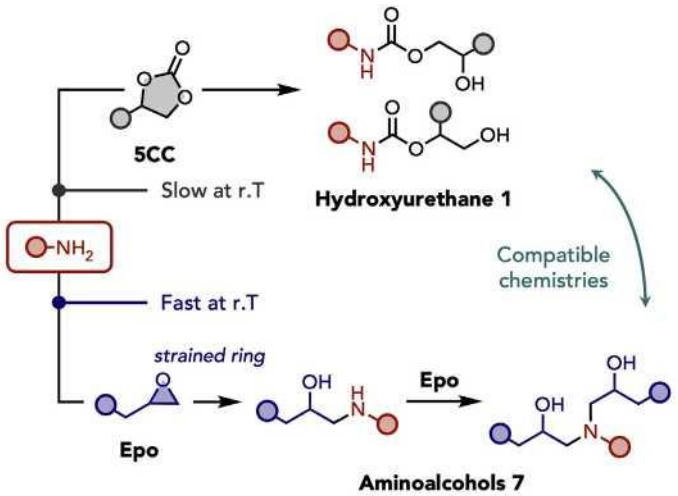
Scheme 36. *(A) Cationic thiol-ene reaction from an electron-enriched alkene. (B) Design of bifunctional alkylidene oxazolidone monomers* ***M36*** *and polymerization with a tetrathiol in the presence of MSA (methanesulfonic acid) as acid catalyst to yield polymers* ***P42****. (C) Design of a linear poly(alkylidene oxazolidone) crosslinked using a dithiol to form* ***P43****.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



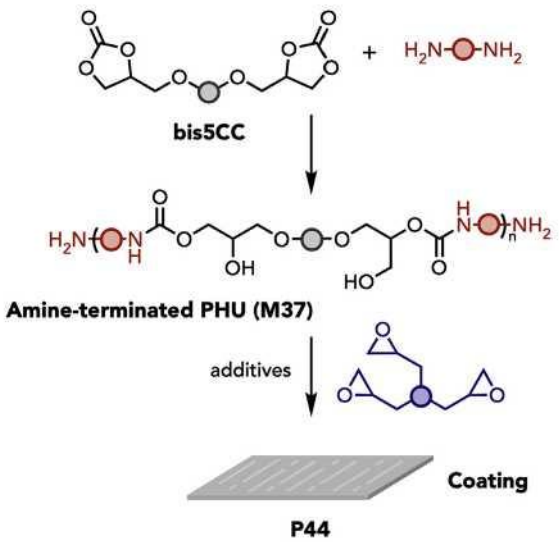
Scheme 38. *Synthesis of amine-terminated PHU (**M37**) and polymerization with polyepoxides into polymeric coatings **P44**.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



Scheme 37. Slow aminolysis of **5CC** to yield hydroxyurethane **1**, and fast aminolysis of epoxide to yield amino-alcohols derivatives **7**. Both chemistries are compatible and can be carried out simultaneously.

*Hybrid PHU-epoxy networks from **oligo-PHU***



7.3.2. ONE-STEP APPROACH

Figovsky valorized partially carbonated polyepoxides to access materials at r.T [158]. Used as an additive in commercial bisepoxides and diamine hardeners formulations, he obtained cured materials in 7 days. Even if the hydroxyurethane content within the final epoxy-like resin was as low as 5 to 10%, he demonstrated that the presence of these linkages improved the adhesion performances and provided higher strength of the polymer.

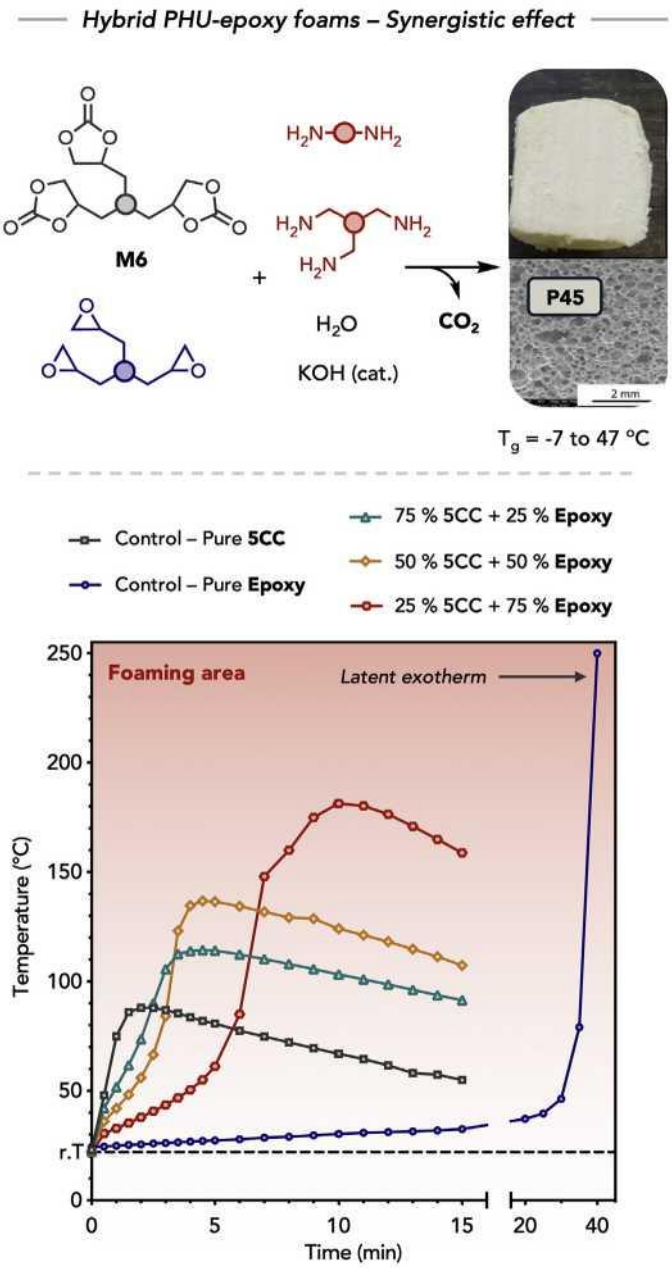
Bourguignon recently reported a methodology for producing CO_2 self-blown hybrid PHU foams in a matter of minutes from formulations at r.T [13] Previous works reported foaming in around 30 minutes at 100°C from formulations composed of a trifunctional **5CC** (**M6**), a polyamine, water as a chemical foaming agent, KOH as catalyst, and a filler for foam homogeneity [59]. The addition of a trifunctional epoxide in the formulation promoted an exotherm needed to reach the foaming temperature ~ 100°C (Fig. 9). Through control experiments, it was observed that the aminolysis

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

and hydrolysis of **5CC** were exothermic processes, though at a too low extent to impulse the foaming. The epoxy-amine was however highly exothermic when the reaction medium reached about 50°C. Cascade exotherms, initiated by the **5CC** aminolysis and hydrolysis, impulse the epoxy amine reaction, rapidly increasing the formulation temperature well beyond the foaming area. Using this strategy, the maximum foam expansion was reached in less than 1 minute after foaming initiation. The introduction of low amount of epoxide had only small effects on the final material properties. However, at higher content, both Tgs and thermal degradation temperature were increased. The compression modulus was drastically affected and readily increased with epoxide content, as expected from the more densely cross-linked structure. Modulation of the nature and functionality of both the epoxide and amine enabled to tune the mechanical properties of the foams. Foams of high bio-based content (90 wt%) were also accessible by properly selecting bio-based monomers. However, typical applications in the PU market such as adhesive and coatings couldn't benefit from this approach as they rely on application of thin films of formulation on substrates, allowing for high energy dissipation. In the context of NIPUs foams, other exothermic reactions that are compatible with the PHU chemistry might be great candidates for producing new hybrid PHU foams of diverse properties.

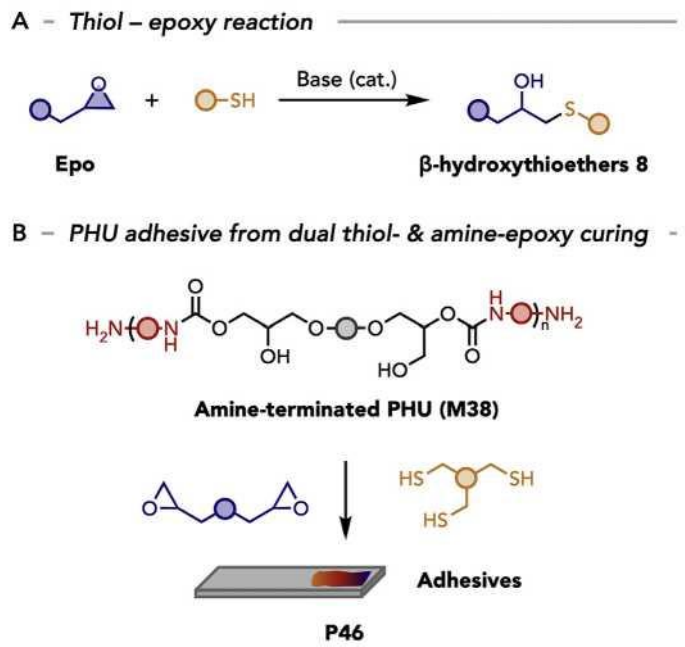
Fig. 9. *Preparation of hybrid NIPU foams* ***P45*** *through the synergistic reaction of trifunctional* ***5CC*** *(****M6****) and a trifunctional epoxide with polyamines to provide exotherms. The hydrolysis of* ***5CC*** *by water releases* CO_2 *as blowing agent*.

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



Scheme 39. *(A) Base-catalyzed reaction of thiol with epoxides (Epo) to yield β- hydroxythioethers* ***8****. (B) PHU adhesive* ***P46*** *from an amine-terminated PHU (****M38****) reacting with a bisepoxide and a trithiol.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



7.4. EPOXIDE – THIOL REACTION

The epoxy-thiol reaction, analog to the epoxy-amine reaction, is recognized as part of the "click reactions", typically high- yielding and fast in mild conditions leading to the formation of *β* -hydroxythioethers **8** (Scheme 39a). It is generally catalyzed by a base that deprotonates the thiol into a nucleophilic thiolate. This reaction has so far been applied to many applications, in the biological and pharmaceutical fields to the development of adhesives, coatings and composites [141].

This reaction was recently applied by Gomez-Lopez for the production of ambient-curable PHU adhesives [159]. Following a process similar to the epoxy-amine curing of PHU (Scheme 38), an amine-terminated PHU pre-polymer **M38** was first synthesized and was combined to a commercial bisepoxide and a trithiol (Scheme 39b). While the gel time exceeded 2 h in all cases and was not precisely determined by the authors, it was demonstrated that the addition of trithiol to the formulation readily accelerated the increase in shear modulus. Interestingly, the curing occurred in the absence of an organobase catalyst, certainly because the amine monomers play this role. FT-IR analysis confirmed complete reaction in 24 h. The adhesive performances have shown to significantly improve from a pure amine-epoxy system to the dual amine-thiol-epoxy cure (leap-shear strength increasing from 7.6 to 12.8 MPa).

7.5 CHEMISTRY OF SILANES AND ALKOXY SILANES

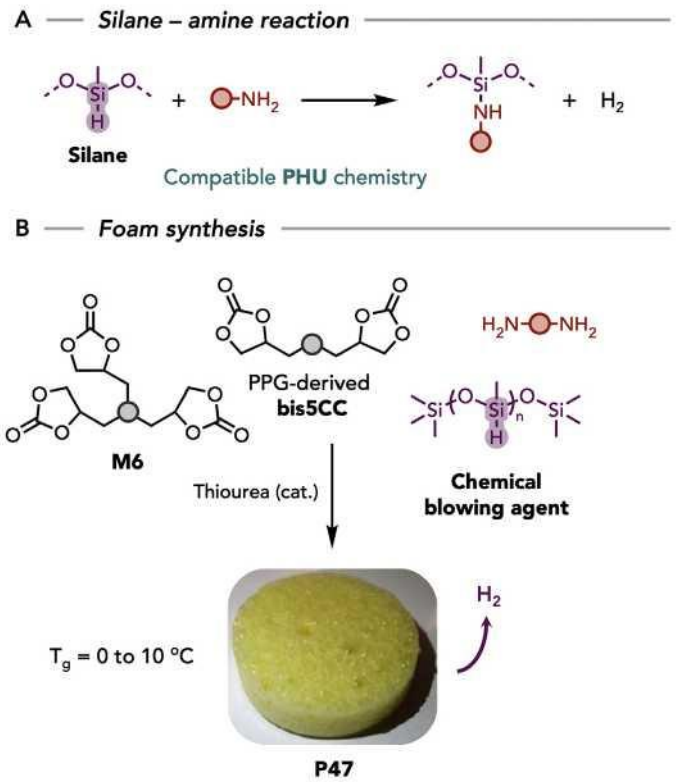
7.5.1 SILANE-AMINE REACTION

Cornille reported the preparation of NIPU foams at r.T by leveraging the chemistry of silanes toward amines (Scheme 40a) [160]. The formulations were based on a mixture of di- and tri-functional **5CC**, a diamine, and a polysiloxane chain containing reactive silane groups (Scheme 40b). The presence of a thiourea catalyst was required for efficient cross-linking of the PHU matrix at r.T. In the meantime, the amines reacted with the silane groups – participating in the cross-linking of the material –and concomitantly releasing dihydrogen (H_2) that created pores within the network, thus forming PHU foams. The Tg of the foams ranged between 0 and 10°C, and IR analyses showed consumption of

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

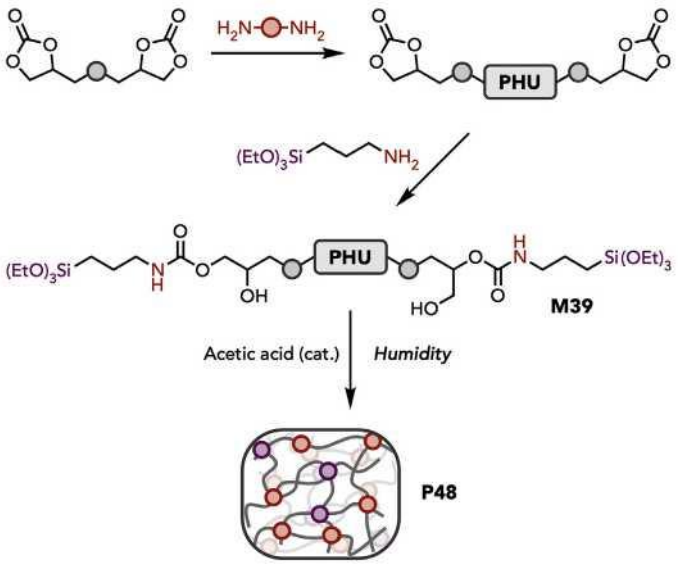
the **5CC** and silane bonds after three days. This example demonstrates how using compatible chemistries allow to access complex architectures, such as porous materials, through concomitant curing and foaming agent release. However, the long curing time at r.T and the release of a flammable gas render this approach inherently less attractive than the synergistic **5CC**-epoxide aminolysis proposed by Bourguignon (see Fig. 9, *vide infra*).

Scheme 40. *(A) Silane-amine chemistry releasing hydrogen gas. (B) Synthesis of foams* ***P47*** *using silanes as chemical blowing agent, releasing dihydrogen (H_2) gas in the polymer matrix.*



Scheme 41. *Synthesis of triethoxysilane-functionalized PHUs (****M39****) and their polymerization driven by humidity in the presence of acetic acid as catalyst.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



7.5.2. HUMIDITY-INDUCED ALKOXYSILANE CROSS-LINKING

Alkoxysilanes are well-established cross-linkers, forming strong siloxane bonds after sol-gel condensation of silanol-containing species, themselves produced by hydrolysis of alkoxysilane. Chemical bonds can also be formed with the surface of various substrates, which makes these cross-linkers excellent candidates for coating and adhesive applications.

Gomez-Lopez reported the formation of **5CC**-terminated PHU pre-polymers by reaction of an excess of bis**5CC** with a diamine. The prepolymer was then functionalized with an amine bearing a triethoxysilane functional group (Scheme 41). Upon addition of a catalyst (acetic acid), the material cured at r.T and provided adhesives **P48**, with a gel time of 5 h [161]. The process yielded better results at 100°C, though the authors demonstrated that curing was possible at r.T.

Asemani recently reported a dual cure system based on the reaction of amine-terminated PHU prepolymers with both polyepoxides and epoxides bearing a triethoxysilane functional group [162]. This provided a dual curing system promoted by the epoxy-amine reaction and the moisture-driven polysiloxane formation. Curing was achieved at r.T for 7 days and the authors demonstrated that the dual cure process was faster than a simpler curing from polyepoxides only.

7.6. MICHAEL ADDITION

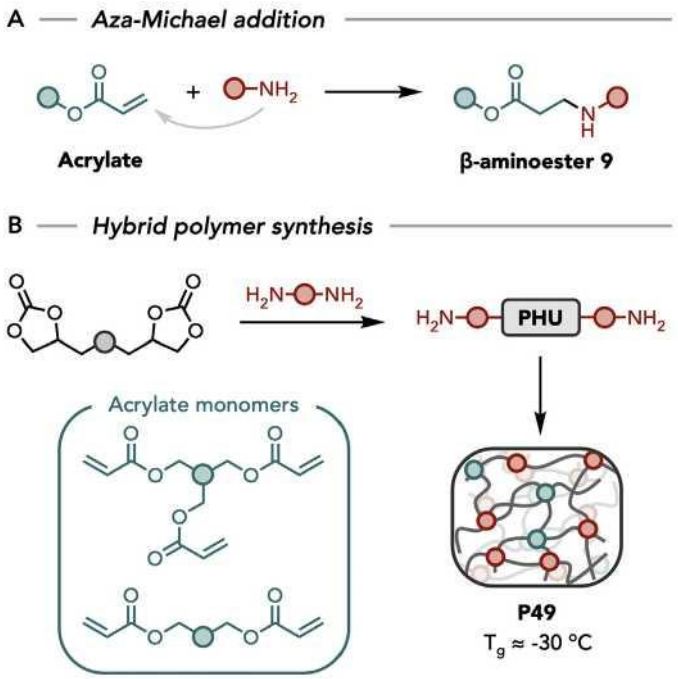
The Michael addition is a well-known robust reaction used in many contexts in organic synthesis (bioactive drugs, *β*-amino acids) [163] and polymer chemistry [164,165]. It consists in the reaction between a Michael acceptor, most often *α*, *β*-unsaturated carbonyl-containing groups (ester, ketone, amide, etc.) and a Michael donor such as amines. The reaction generally proceeds smoothly and quantitatively at r.T, rendering this reaction a good candidate to produce polymers in mild conditions.

Cornille reported PHU formulations containing commercial polyacrylates, which can be attacked by amines through a azaMichael addition (Scheme 42a) [166]. Amine-terminated prepolymers were first synthesized by reaction of excess amine with a PPG-derived bis**5CC**. The telechelic polymers were then reacted with di- and tri-acrylates without

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

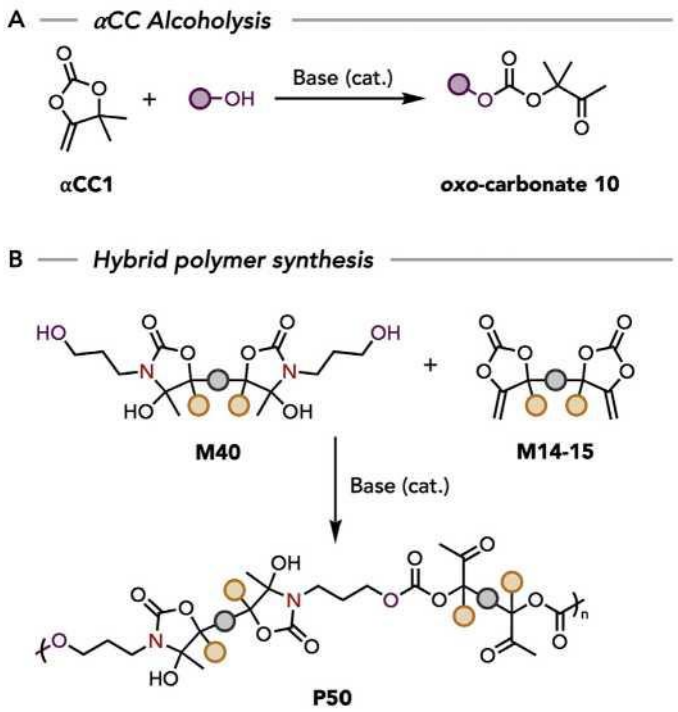
catalyst nor solvent, providing full acrylate conversion after 48 h (Scheme 42b). The materials **P49** presented low T_g values of around -30°C, certainly due to the very flexible nature of the PPG-derived precursors and of the created *β* - amino ester linkages. The cross-linking efficiency was validated by gel contents higher than 90 %.

Scheme 42. *(A) The aza-Michael addition of amine onto acrylate moieties to form β-aminoesters* ***9****. (B) Synthesis of amine-terminated PHUs and their reaction with di- and tri-acrylate to provide hybrid polymers* ***P49****.*



Scheme 43. *(A) The base-mediated reaction of* ***αCC*** *with alcohols to provide oxocarbonates* ***10****. (B) Design of hydroxyl-terminated bis(hydroxyoxazolidone)s* ***M40*** *and their reaction with bis* ***αCC*** *monomers* ***M14–15*** *toward polymers* ***P50****.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



7.7 A-ALKYLIDENE CYCLIC CARBONATES – ALCOHOL REACTION

α-alkylidene cyclic carbonates were earlier discussed in this review for their efficient reaction with amines to provide NIPUs at r.T. However, these reactive cyclic carbonates variants have shown to ring-open in the presence of other nucleophiles, such as alcohols, in the presence of an organobase such as DBU [95,107,167]. The reaction is efficient at r.T and provides *oxo*-carbonate **10** linkages (Scheme 43a).

As such, similar primary alcohol-terminated bis(hydroxy ox- azolidone)s were produced in two separate studies and these hydroxyl-terminated carbamates were reacted with bis(*α***CC**)s **M14** or **M15** at r.T and in the presence of DBU as catalyst to provide alternate poly(hydroxyoxazolidone- *co*-oxocarbonate)s **P50** (Scheme 43b) [35,168].

7.8 LIMITATIONS AND PERSPECTIVES

The integration of well-established r.T-efficient chemistries in the development of NIPUs offers a compelling solution to the inherent room-temperature reactivity challenges encountered in promising technologies, particularly with the nowadays well- studied PHU chemistry from five-membered cyclic carbonate aminolysis. Efficient and well-established chemistries can be utilized, either on pre-synthesized urethane-containing synthons or along their formation to reach moderate to high molecular weight and efficient curing within desirable timeframes. However, the synthesis of urethane-containing polyfunctional molecules or prepolymer precursors is most often required as the non-isocyanate introduction of urethanes in the polymer backbone commonly relies on the aminolysis of five-membered cyclic carbonates, generally achieved at high temperatures. Exploring synergistic reactions has demonstrated to be particularly valuable to expand the reactivity and applicability capabilities beyond simple combination of divergent chemical bonds. Moreover, incorporating additional functionalities can impart NIPUs with unique properties, such as chemical resistance, improved adhesion, or the ability for rapid photocuring in 3D-printed resins. There is still room for exploring and optimizing new processes to furnish hybrid NIPUs at r.T without relying

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

on hazardous but yet efficient isocyanates for their production.

8. Non-isocyanate polythiourethanes (NIPTUs)

The growing interest in sulfur-derived polymers has driven the emergence of thiourethanes as a complementary synthetic tool for producing new polymers with unique properties and expanding the range of applications. This is largely due to the distinct reactivity and inedite properties that sulfur imparts to the polymers, different from their oxygenated analogs.

In 1995, Endo's team pioneered the synthesis of non-isocyanate polythiourethanes (NIPTUs) through the reaction of cyclic dithiocarbonates with primary amines (Scheme 44) [169]. Analogous to cyclic carbonate aminolysis, the amine attacks the (thio)carbonyl group, leading to ring opening. In the case of cyclic dithiocarbonates, the reaction exhibits complete regioselectivity, with selective C–S bond cleavage, yielding thiourethane **11** linkages with pendant thiol groups [170]. The synthesis of the polymers was achieved at r.T in 24 h. However, oxidation of the pendant thiol groups resulted in cross-linked networks via disulfide bonds. This crosslinking step could be prevented by a post-reaction thiol protection using acetic anhydride and triethylamine, yielding acetylated derivatives with Mw ranging from 7,700 to 20,000 $g{\cdot}mol^{-1}$ [170]. More recently, Vanbiervliet harnessed the high reactivity of **5CDTC** to build NIPTUs networks from the reaction between bifunctional dithiocarbonates and polyfunctional amines [171]. Although crosslinking was observed through oxidation of the pendant thiols in air, MnO_2 was added to the mixture as an oxidizing agent to quantitatively oxidize the remaining unreacted thiols, reducing the gel time from more than 2 h to few minutes.

Cornille later demonstrated with model reactions that the aminolysis reaction rate constant presented a 20-fold increase when shifting from oxygenated cyclic carbonates to the dithiocarbonate analogs of similar structure (Scheme 44) [18]. The difference in reactivity was attributed to the weaker thio-carbonyl bond compared to conventional carbonyl groups. However, computational studies are lacking to fully elucidate the reaction mechanism and explain the differences in reactivity. There is therefore space for DFT studies in direct comparison to the well-studied oxygenated cyclic carbonates.

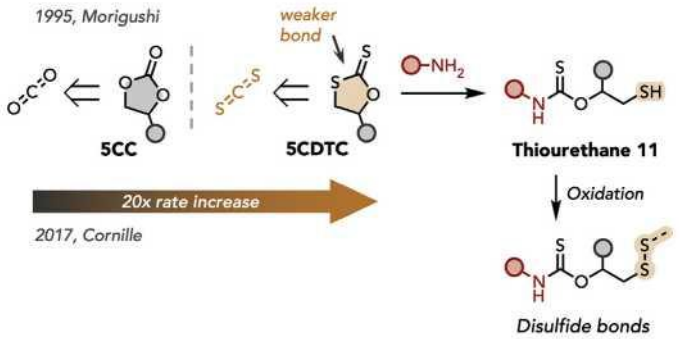
The five-membered cyclic dithiocarbonate carbonates **5CDTC** were synthesized by the fixation of carbon disulfide (CS_2) onto epoxides, analogous to the CO_2-epoxide route for oxygenated cyclic carbonates [172]. However, CS_2 is a hazardous, volatile, and highly flammable and explosive compound [173], introducing additional safety concerns compared to the safer, inert, and abundant CO_2 used in the synthesis of **5CC**.

In 2001, Tomita from Endo's team reported the aminolysis of cyclic monothiocarbonates **5CTC**, featuring a thiocarbonyl group replacing the carbonyl in conventional cyclic carbonates **5CC** (Scheme 45a) [174]. The reaction proceeds similarly to the **5CC** aminolysis, yielding two hydroxythiourethane **12** isomers, the isomer containing the secondary alcohol being predominantly formed (around 90% selectivity). However, no rationale was proposed to compare this key selectivity difference with the aminolysis of **5CC**. Importantly, the reaction rate was readily accelerated by shifting from **5CC** to **5CTC**, as demonstrated in model reactions. Under diluted conditions, **5CTC** was quantitatively converted to **12** in about 1 h at r.T, whereas **5CC** only reached 58 % of conversion after 10 days. Rate constants measured at 30°C showed a 10,000 to 20,000fold increase for **5CTC** over **5CC** (Scheme 45a). The reaction of bifunctional adducts at r.T in DMSO for 6 h yielded polymers with a Mw up to 150,000 $g{\cdot}mol^{-1}$ (Scheme 45b). In contrast, **5CC**-based polymers were characterized by a Mw up to 25,000 $g{\cdot}mol^{-1}$ after 4 days of reaction. No thermal properties were reported for these polymers. Unlike **5CDTC**, **5CTC**-derived polymers lack pendant thiol groups, hence no undesired branching / cross-linking takes place during the formation of the linear macromolecules.

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

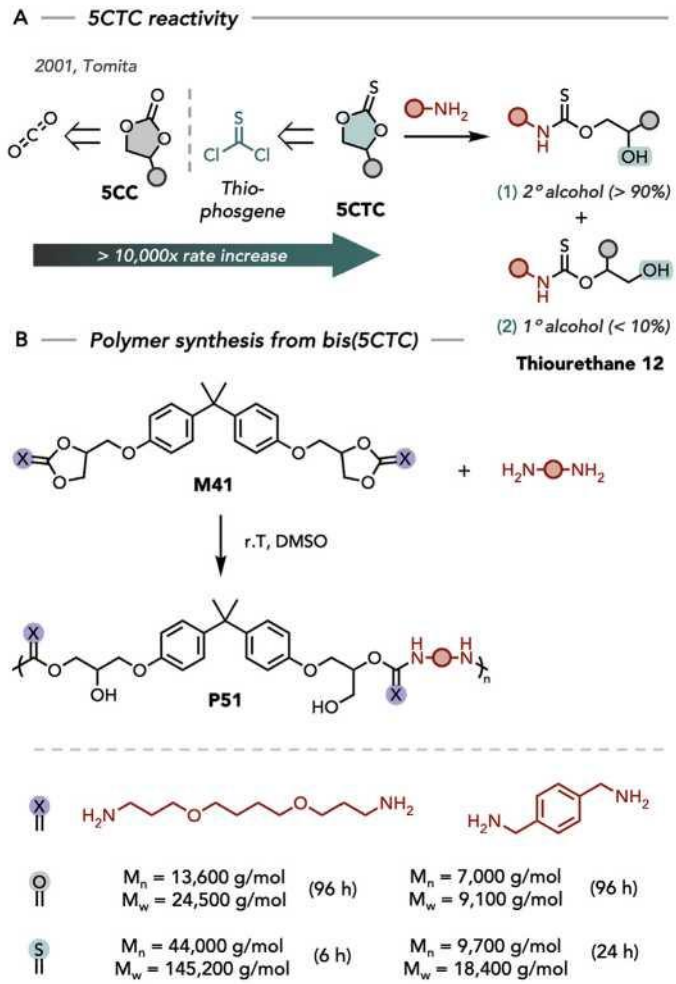
Although this approach seems very promising, the **5CTC** adducts are typically synthesized from the respective constituting diols and thiophosgene derivatives –a class of very hazardous and toxic compounds. To the best of our knowledge, no safer synthetic routes have been reported, likely explaining the stagnation of this approach over the past two decades. Developing less hazardous synthetic methods could unlock the potential of this underexplored chemistry.

Scheme 44. *Synthesis of cyclic dithiocarbonate* ***5CDTC*** *from CS2 as compared to the synthesis of cyclic carbonates* ***5CC*** *from CO_2. The aminolysis proceeds regio- selectively to yield a thiourethane* ***11*** *with oxydable pendant thiol groups.*



Scheme 45. *(A) Synthesis of cyclic monothiocarbonate* ***5CTC*** *from thiophosgene as compared to the synthesis of cyclic carbonates* ***5CC*** *from CO_2 . The aminolysis yields two hydroxythiourethane* ***12*** *isomers. (B) Polymerizations from oxygenated or sulfur-derived monomers* ***M41*** *and diamines yield the corresponding NIP(T)Us* ***P51****.*

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



The second non-isocyanate route toward NIPTUs at r.T involves the copolymerization of aziridine with carbonyl sulfide (COS). Although the reaction of aziridine **M42a** with supercritical CO_2 has been reported for the formation of NIPUs, the reaction was only performed in harsh conditions, i.e. at high temperature and pressure (typically 100°C and 220 bars of CO_2), and the polymers **P52** presented amine defects due to aziridine homopolymerization (Scheme 46a) [175,176]. By using COS, perfectly alternating polymers **P53** were obtained at r.T and without any defects (Scheme 46b). This difference between COS and CO_2 was attributed to the higher acidity of the aziridine-CO_2 adduct, promoting the formation of ammonium species prone to ring-opening by another aziridine, thus leading to the formation of amine linkages defects [175,177]. With COS, a zwitterionic intermediate is supposedly formed selectively without the formation of ammonium species. The negatively charged sulfur atom of the intermediate initiates nucleophilic attack onto another intermediate, driving chain propagation (Scheme 46b) [177,178]. The copolymerization was achieved in 5 minutes to 2 h at r.T, with Mw up to 19,000 $g{\cdot}mol^{-1}$. Macrocyclic structures were mainly obtained through intramolecular back-biting reaction, leading to chain termination. C- substituted aziridines **M42a** could be used to obtain polyurethanes with a N-H bond on the urethane, and N-derived aziridines **M42b- c** to yield N-substituted urethanes (Scheme 46b). The N-H polymer has shown to be amorphous with a T_g of 90°C. N-alkyl substituted polymers exhibited low solubility and high crystallinity, with Tm of 137 and 170°C for n-butyl (**M42c**) and n-ethyl (**M42b**) substituents respectively. Although very promising in term of reaction time and polymer properties,

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

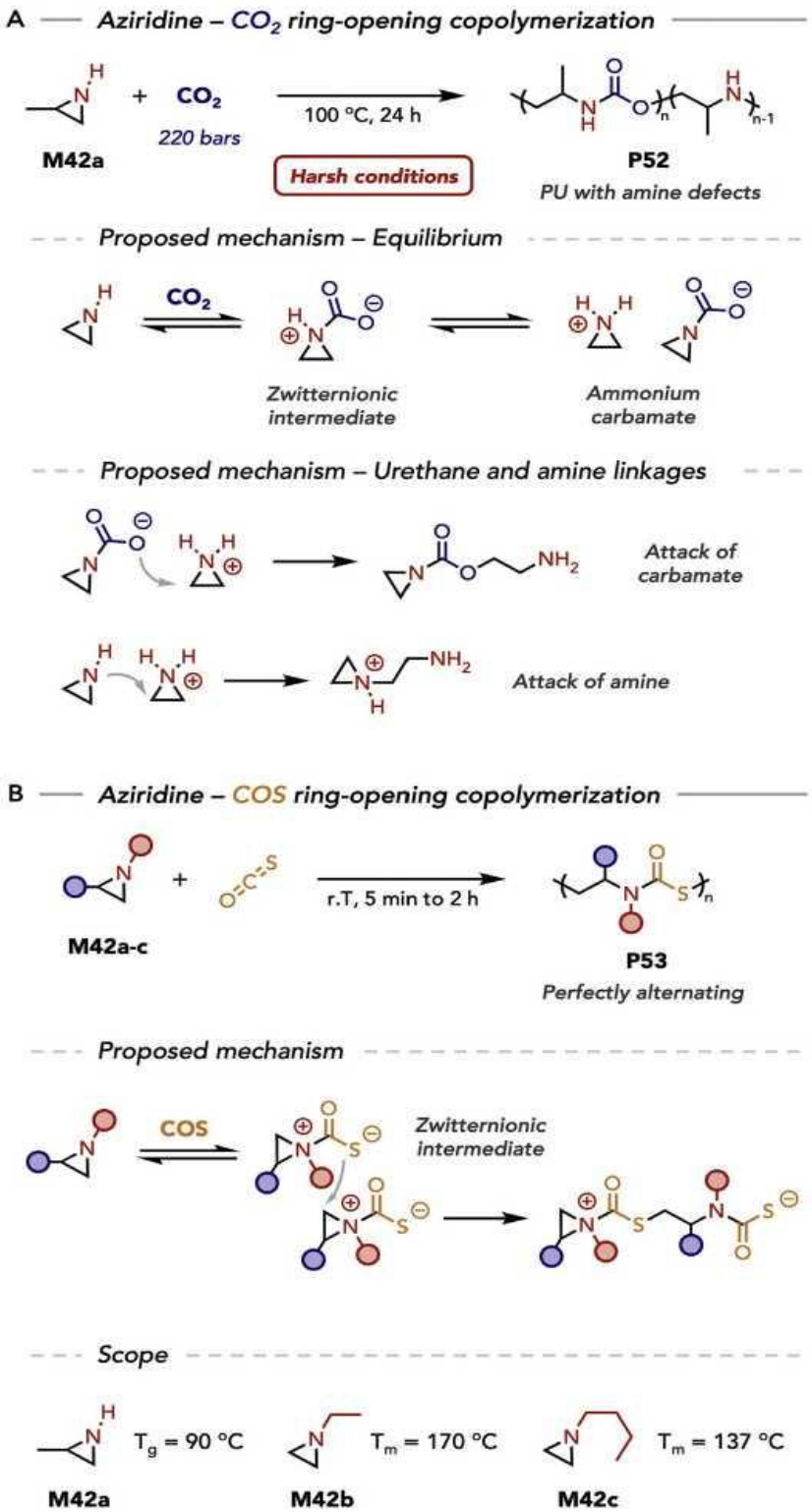
this route is limited by the availability of commercial aziridines and their extreme toxicity, often directly converted into non-toxic intermediates after their production [179].

The ring-opening polymerization (ROP) of cyclic thiourethanes derived from an amino acid was investigated by Endo's team.

In contrast to five-membered cyclic carbamates, thiocarbamate analogs undergo polymerization at r.T using methyl trifluoromethanesulfonate (MeOTf) as initiator (Scheme 47a) [180]. The reactive intermediate, isolated and identified as a stable salt between the cyclic thiourethane and the alkyl sulfonate, proved air- and moisture-stable, and could serve as initiator for further polymerization [181]. The polymerizations were achieved in 22 to 35 h at r.T, and have shown a good control with low dispersity (typically < 1.1) over the whole range of studied molecular weight (Mn between 2,000 and 25,000 $g \cdot mol^{-1}$) (Scheme 47B). The polymers **P54**, derived from a chiral amino acid **M43**, exhibited optical activity due to the presumed secondary structures stabilized by hydrogen bonding [182,183]. The strength of these interactions was reflected in a higher Tm for polymers derived enantiopure monomers (140°C) compared to those from racemic mixtures (100°C).

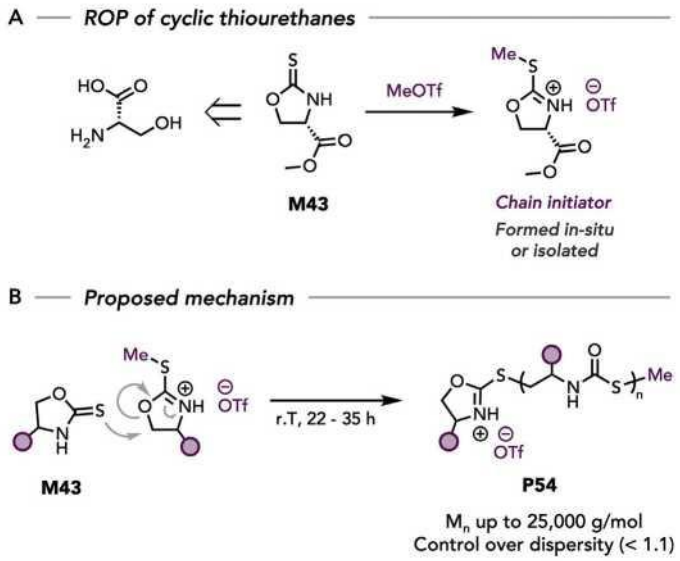
Scheme 46. (A) Ring-opening copolymerization (ROCOP) of aziridines with CO2 . Upon introduction of CO_2, a zwitterionic intermediate is formed, which can give its proton to another aziridine to yield an ammonium and a carbamate. The proposed mechanism involves chain propagation through the carbamate, yielding urethane linkages, or through the aziridine, yielding amine linkages. (B) Perfectly alternating polymers are obtained by the ROCOP of aziridines with COS in mild conditions. The propagation is proposed to only proceed from zwitterionic intermediates, yielding exclusively thiourethane linkages.

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)



Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

Scheme 47. (A) Cyclic thiourethanes **M43** can be obtained from amino acids (here, L-serine). Upon addition of MeOTf, a stable salt is formed, able to initiate polymerization by in-situ formation or isolated prior polymerization. (B) Proposed mechanism for the polymerization of **M43** into **P54**.



9. Conclusion and outlook

This comprehensive review highlighted the technological advances enabling the synthesis of non-isocyanate polyurethanes (NI- PUs) at room temperature (r.T). These developments align closely with industrial and environmental goals to reduce the use of hazardous reagents and minimize energy consumption. Additionally, the ability to manufacture these polymers at r.T offers economic advantages, facilitating their integration into existing polyurethane production infrastructures and opening opportunities for large- scale consumer applications.

The aminolysis of five-membered cyclic carbonates (**5CC**) remains the most explored and promising approach for NIPU synthesis. This route has gathered significant research attention, leading to a considerable number of publications and patents on both the fundamental chemistry and the applications of the produced polymers. However, several limitations hinder a match with the performance of isocyanate-based materials. These include side reactions, limited reaction conversion, and the low reactivity of cyclic carbonate precursors compared to the highly reactive but toxic isocyanates. Performing the reaction at r.T mitigates side reactions but typically results in slow kinetics and reduced molecular weight, which ultimately affects the mechanical properties of the materials. Monomer design, catalysis, and solvent optimization have been explored to address these issues, but they have not yet closed the performance gap with isocyanate-based polyurethanes.

Hybrid chemistries have emerged as an effective alternative, leveraging highly efficient room-temperature chemistries such as the thiol-ene or the epoxy-amine reactions to synthesize both linear and cross-linked NIPUs with tailored properties. A notable success is the synthesis of NIPU foams at r.T through an in-situ generated exotherm approach, with foaming rates that are competitive to isocyanate-based processes. The technology is sufficiently mature to be assessed for NIPU foam production, meeting current industry specifications through formulation adjustments. However, this strategy is scale-dependent and is not applicable to thin-layer applications such as coatings and adhesives when fast curing are needed.

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

Despite the recent progress, the industrialization of this approach remains hindered by the limited availability of cyclic carbonate **5CC** precursors, primarily produced via CO_2-epoxide cycloaddition –a process that is highly efficient but not yet industrially implemented for the large scale production of polycyclic carbonates. Furthermore, the lack of clear added value of the new NIPU materials compared to conventional isocyanate-based systems reduces the incentive for industrial transition. Demonstrating the versatility and potential of this new chemistry to industrial stakeholders is crucial for driving adoption. Techno-economic analyses (TEAs) and life cycle assessments (LCAs) can support this effort by identifying cost-reduction opportunities and quantifying the carbon footprint of the processes. To date, only Liang and Jadidi have assessed the economic viability of polyhydroxyurethane (PHU) technology, suggesting competitive pricing with conventional polyurethanes [184]. However, their conclusions relied on non-industrial processes and approximations, emphasizing the need for future TEAs and LCAs based on optimized protocols, real materials (in complex formulations), and market-driven product development for specific applications.

From an academic point of view, there remains significant space for understanding the fundamental chemistry and addressing its limitations. An important remaining issue is to fully assess the impact of hydroplasticization of the NIPU matrix on its properties, and to adopt facile measures to reduce it if required for the application. Although some technologies are mature enough to be tested for real applications, e.g., self-blowing NIPUs, the claimed technology advantages of high bio-based contents (> 90%) and fast r.T. operation under industrially relevant procedures are still not enough to convince the industry to adopt it. Researchers have now to demonstrate that these products present competitive performance compared to commercial PUs and are cost-effective. The cyclic carbonates have also to present low toxicity and should be available at very large scale to meet the market needs. A multidisciplinary approach is necessary, involving the design of more reactive cyclic carbonate monomers, the development of cost-effective synthetic processes, and the formulation of high-performance materials tailored to specific applications. Closing the performance gap with isocyanate-based polyurethanes will require progress across all mentioned areas.

Emerging chemistries involving larger cyclic carbonates (six- to eight-membered) and α-alkylidene cyclic carbonates show promise for reaching high molecular weights or faster curing rates under mild conditions. However, these routes are still in their infancy, with limited understanding of their reactivity, polymer properties, and differences compared to existing NIPUs and conventional polyurethanes. Furthermore, their synthesis is currently costly and not readily scalable. Further development of these technologies is required to reach maturity, when their commercial potential can be reevaluated.

Ring-opening polymerization (ROP) represents another promising yet challenging strategy for NIPUs. Unlike step-growth processes, ROP offers the potential to achieve controlled architectures, narrow molecular weight distributions, and complex polymer structures (e.g., block copolymers, star polymers, and brushes). However, the strategy is limited by the high stability of cyclic carbamate precursors, necessitating innovative monomer design and catalytic systems. While controlled polymerizations at r.T remain a distant dream, unlocking this route could open doors to new applications.

Ultimately, the future of NIPUs lies not only in their potential to replace isocyanate-based systems but also in their ability to enable novel polymer architectures and functionalities beyond the reach of conventional polyurethane chemistry. Bridging the performance gap through tailored formulations, supported by interdisciplinary research and process optimization, will be key to realizing this vision. Sustained efforts in fundamental research, economic assessment, and application-driven development will facilitate the transition toward safer, more sustainable polyurethane materials.

In summary, while some NIPU technologies are mature enough for real-world applications, their adoption for more sustainable commercial products depends on the industry's willingness to shift its business model. However, major

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

PU players remain reluctant to move away from their highly profitable isocyanate-based business unless compelled to do so, despite the existence of promising, albeit still evolving, potentially more sustainable alternatives. We anticipate that these technologies will first be adopted in niche applications, where cost is less of a concern and stakeholders are more open to innovation.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

C.D. and B.G. are named as co-inventors in the patent Self-blowing isocyanate-free polyurethane foams, WO patent 2023104362A1.

CRediT authorship contribution statement

Thomas Habets: Writing – original draft, Methodology, Formal analysis, Conceptualization. **Bruno Grignard:** Writing – review & editing, Supervision, Conceptualization. **Christophe Detrembleur:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Data availability

No data was used for the research described in the article.

Acknowledgments

The authors thank FNRS for financial support in the frame of the CO_2Switch project under grant T.0075.20. C.D. thanks the Region Wallonne for funding the Win2Wal project "ECOFOAM" (convention 2010130) and the FRFS-WEL-T Advanced Grant "Chemistry" (convention WEL-T-CR-2023 A).

References

[1] AgileIntel Research (ChemIntel360). Market volume of polyurethane worldwide from 2015 to 2022, with a forecast for 2023 to 2030; 2023. https:// www.statista.com/statistics/720341/global- polyurethane- market- size- forecast/

[2] Holden G. Thermoplastic Elastomers. In: Applied Plastics Engineering Handbook. Elsevier; 2024. p. 97–113. doi:10.1016/B978-0-323-88667-3.00020-5.

[3] Peyrton J, Avérous L. Structure-properties relationships of cellular materials from biobased polyurethane foams. Mater Sci Eng: R: Rep 2021;145:100608. doi:10.1016/j.mser.2021.100608.

[4] Monie F, Vidil T, Grignard B, Cramail H, Detrembleur C. Self-foaming polymers: Opportunities for the next generation of personal protective equipment. Mater Sci Eng: R: Rep 2021;145:100628. doi:10.1016/j.mser.2021. 100628.

[5] Sonnenschein MF. Polyurethanes: Science, Technology, Markets, and Trends. 1st ed. Wiley; 2014. doi:10.1002/9781118901274.

[6] Engels H, Pirkl H, Albers R, Albach RW, Krause J, Hoffmann A, Casselmann H, Dormish J. Polyurethanes: versatile materials and sustainable problem solvers for today's challenges. Angew Chem Int Ed 2013;52:9422–41. doi:10.1002/ anie.201302766.

[7] Eling B, Tomovic´ Ž, Schädler V. Current and future trends in polyurethanes: an industrial perspective. Macro Chem Phys 2020;221:2000114. doi:10.1002/ macp.202000114.

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

[8] Das A, Mahanwar P. A brief discussion on advances in polyurethane applications. Adv Indust Eng Polymer Res 2020;3:93–101. doi:10.1016/j.aiepr.2020. 07.002.

[9] Anastas P, Eghbali N. Green chemistry: principles and practice. Chem Soc Rev 2010;39:301–12. doi:10.1039/B918763B.

[10] Vidal F, Van Der Marel ER, Kerr RWF, McElroy C, Schroeder N, Mitchell C, Rosetto G, Chen TTD, Bailey RM, Hepburn C, Redgwell C, Williams CK. Designing a circular carbon and plastics economy for a sustainable future. Nature 2024;626:45–57. doi:10.1038/s41586-023-06939-z.

[11] Brahmachari G. Design of organic transformations at ambient conditions: our sincere efforts to the cause of green chemistry practice. Chem Record 2016;16:98–123. doi:10.1002/tcr.201500229.

[12] Karpf M. Organic synthesis at high temperatures. gas-phase flow thermolysis [new synthetic methods (57)]. Angew Chem Int Ed Engl 1986;25:414–30. doi:10.1002/anie.198604141.

[13] Bourguignon M, Grignard B, Detrembleur C. Cascade exotherms for rapidly producing hybrid nonisocyanate polyurethane foams from room temperature formulations. J Am Chem Soc 2024;146:988–1000. doi:10.1021/jacs. 3c11637.

[14] Bürgel T, Fedtke M. Reactions of cyclic carbonates with amines: Model studies for curing process. Polymer Bull 1991;27:171–7. doi:10.1007/BF00296027.

[15] Bürgel T, Fedtke M. Epoxy resins with cyclic carbonate structures: Model studies for amine curing. Polymer Bull 1993;30:61–8. doi:10.1007/ BF00296235.

[16] Garipov RM, Sysoev VA, Mikheev VV, Zagidullin AI, Deberdeev RYa, Irzhak VI, Berlin AlAl. Reactivity of cyclocarbonate groups in modified epoxy–amine compositions. Doklady Phys Chem 2003;393:289–92. doi:10.1023/B:DOPC. 0000003463.07883.c9.

[17] Levina MA, Krasheninnikov VG, Zabalov MV. Tiger RP. Nonisocyanate polyurethanes from amines and cyclic carbonates: kinetics and mechanism of a model reaction. Polym Sci Ser B 2014;56:139–47. doi:10.1134/ S1560090414020092.

[18] Cornille A, Blain M, Auvergne R, Andrioletti B, Boutevin B, Caillol S. A study of cyclic carbonate aminolysis at room temperature: effect of cyclic carbonate structures and solvents on polyhydroxyurethane synthesis. Polym Chem 2017;8:592–604. doi:10.1039/C6PY01854H.

[19] Zabalov MV, Tiger RP, Berlin AA. Reaction of cyclocarbonates with amines as an alternative route to polyurethanes: a quantum-chemical study of reaction mechanism. Dokl Chem 2011;441:355–60. doi:10.1134/S0012500811120032.

[20] Zabalov MV, Tiger RP, Berlin AA. Mechanism of urethane formation from cyclocarbonates and amines: a quantum chemical study. Russ Chem Bull 2012;61:518–27. doi:10.1007/s11172-012-0076-8.

[21] Blain M, Cornille A, Boutevin B, Auvergne R, Benazet D, Andrioletti B, Caillol S. Hydrogen bonds prevent obtaining high molar mass PHU s. J Appl Polymer Sci 2017;134:44958. doi:10.1002/app.44958.

[22] Besse V, Camara F, Méchin F, Fleury E, Caillol S, Pascault JP, Boutevin B. How to explain low molar masses in Polyhydroxyurethanes (PHUs). Eur Polymer J 2015;71:1–11. doi:10.1016/j.eurpolymj.2015.07.020.

[23] Lamarzelle O, Durand PL, Wirotius AL, Chollet G, Grau E, Cramail H. Activated lipidic cyclic carbonates for non-isocyanate polyurethane synthesis. Polym Chem 2016;7:1439–51. doi:10.1039/C5PY01964H.

[24] Lamarzelle O, Hibert G, Lecommandoux S, Grau E, Cramail H. A thioglycerol route to bio-based bis-cyclic carbonates: poly(hydroxyurethane) preparation and post-functionalization. Polym Chem 2017;8:3438–47. doi:10.1039/ C7PY00556C.

[25] Bourguignon M, Grignard B, Detrembleur C. Introducing polyhydroxyurethane hydrogels and coatings for formaldehyde capture. ACS Appl Mater Interfaces 2021;13:54396–408. doi:10.1021/acsami.1c16917.

[26] Tomita H, Sanda F, Endo T. Model reaction for the synthesis of polyhydroxyurethanes from cyclic carbonates with amines: Substituent effect on the reactivity and selectivity of ring-opening direction in the reaction of five-membered cyclic carbonates with amine. J Polym Sci A Polym Chem 2001;39:3678–85. doi:10.1002/pola.10009.

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

[27] He Y, Goel V, Keul H, Möller M. Synthesis, characterization, and selectivity of bifunctional couplers. Macro Chem Phys 2010;211:2366–81. doi:10.1002/ macp.201000340.

[28] Levina MA, Zabalov MV, Krasheninnikov VG, Tiger RP. Comparative reactivity of cyclocarbonate groups of oligomeric triglycerides based on soybean oil and model compounds in the reactions of nonisocyanate urethane formation. Polym Sci Ser B 2018;60:563–70. doi:10.1134/S1560090418050081.

[29] Bähr M, Bitto A, Mülhaupt R. Cyclic limonene dicarbonate as a new monomer for non-isocyanate oligo- and polyurethanes (NIPU) based upon terpenes. Green Chem 2012;14:1447. doi:10.1039/c2gc35099h.

[30] Schimpf V, Ritter BS, Weis P, Parison K, Mülhaupt R. High purity limonene dicarbonate as versatile building block for sustainable nonisocyanate polyhydroxyurethane thermosets and thermoplastics. Macromolecules 2017;50:944–55. doi:10.1021/acs.macromol.6b02460.

[31] Scholten PBV, Demarteau J, Gennen S, De Winter J, Grignard B, De- buigne A, Meier MAR, Detrembleur C. Merging CO_2 -based building blocks with cobalt-mediated radical polymerization for the synthesis of functional poly(vinyl alcohol)s. Macromolecules 2018;51:3379–93. doi:10.1021/ acs.macromol.8b00492.

[32] Maltby KA, Hutchby M, Plucinski P, Davidson MG, Hintermair U. Selective catalytic synthesis of 1,2- and 8,9-cyclic limonene carbonates as versatile building blocks for novel hydroxyurethanes. Chem A Eur J 2020;26:7405–15. doi:10.1002/chem.201905561.

[33] Maquilón C, Brandolese A, Alter C, Hövelmann CH, Della Monica F, Kleij AW. Renewable beta-elemene based cyclic carbonates for the preparation of oligo(hydroxyurethane)s. ChemSusChem 2022;15:e202201123. doi:10.1002/ cssc.202201123.

[34] Ochiai B, Matsuki M, Miyagawa T, Nagai D, Endo T. Kinetic and computational studies on aminolysis of bicyclic carbonates bearing alicyclic structure giving alicyclic hydroxyurethanes. Tetrahedron 2005;61:1835–8. doi:10.1016/ j.tet.2004.12.014.

[35] Habets T, Méreau R, Siragusa F, Grignard B, Detrembleur C. Fast, regioselective aminolysis of tetrasubstituted cyclic carbonates and application to recyclable thermoplastics and thermosets. ACS Macro Lett 2024;13:1425–32. doi:10.1021/acsmacrolett.4c00570.

[36] Sopeña S, Laserna V, Guo W, Martin E, Escudero-Adán EC, Kleij AW. Regioselective organocatalytic formation of carbamates from substituted cyclic carbonates. Adv Synth Catal 2016;358:2172–8. doi:10.1002/adsc.201600290.

[37] Maisonneuve L, Lamarzelle O, Rix E, Grau E, Cramail H. Isocyanate-free routes to polyurethanes and poly(hydroxy urethane)s. Chem Rev 2015;115:12407– 39. doi:10.1021/acs.chemrev.5b00355.

[38] Webster DC, Crain AL. Synthesis and applications of cyclic carbonate functional polymers in thermosetting coatings. Prog Org Coat 2000;40:275–82. doi:10.1016/S0300-9440(00)00114-4.

[39] Diakoumakos CD, Kotzev DL. Non-isocyanate-based polyurethanes derived upon the reaction of amines with cyclocarbonate resins. Macromolecular Symposia 2004;216:37–46. doi:10.1002/masy.200451205.

[40] Nohra B, Candy L, Blanco J, Raoul Y, Mouloungui Z. Aminolysis reaction of glycerol carbonate in organic and hydroorganic medium. J Americ Oil Chem Soc 2012;89:1125–33. doi:10.1007/s11746-011-1995-5.

[41] Blain M, Jean-Gérard L, Auvergne R, Benazet D, Caillol S, Andrioletti B. Rational investigations in the ring opening of cyclic carbonates by amines. Green Chem 2014;16:4286–91. doi:10.1039/C4GC01032A.

[42] Alves M, Méreau R, Grignard B, Detrembleur C, Jérôme C, Tassaing T. DFT investigation of the reaction mechanism for the guanidine catalysed ring-opening of cyclic carbonates by aromatic and alkyl-amines. RSC Adv 2017;7:18993–9001. doi:10.1039/C7RA00220C.

[43] Guzmán Agudelo AF, Pérez-Sena WY, Kebir N, Salmi T, Ríos LA, Leveneur S. Influence of steric effects on the kinetics of cyclic-carbonate vegetable oils aminolysis. Chem Eng Sci 2020;228:115954. doi:10.1016/j.ces.2020.115954.

[44] Hernández A, Houck HA, Elizalde F, Guerre M, Sardon H, Du Prez FE. Internal catalysis on the opposite side of the fence

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

in non-isocyanate polyurethane covalent adaptable networks. Eur Polymer J 2022;168:111100. doi:10.1016/j. eurpolymj.2022.111100.

[45] Quienne B, Poli R, Pinaud J, Caillol S. Enhanced aminolysis of cyclic carbonates by *β*-hydroxylamines for the production of fully biobased polyhydroxyurethanes. Green Chem 2021;23:1678–90. doi:10.1039/D0GC04120C.

[46] Lambeth RH, Henderson TJ. Organocatalytic synthesis of (poly)- hydroxyurethanes from cyclic carbonates and amines. Polymer 2013;54:5568–73. doi:10.1016/j.polymer.2013.08.053.

[47] Ochiai B, Inoue S, Endo T. Salt effect on polyaddition of bifunctional cyclic carbonate and diamine. J Polym Sci A Polym Chem 2005;43:6282–6. doi:10. 1002/pola.21081.

[48] Maisonneuve L, More AS, Foltran S, Alfos C, Robert F, Landais Y, Tas- saing T, Grau E, Cramail H. Novel green fatty acid-based bis-cyclic carbonates for the synthesis of isocyanate-free poly(hydroxyurethane amide)s. RSC Adv 2014;4:25795–803. doi:10.1039/C4RA03675A.

[49] Blain M, Yau H, Jean-Gérard L, Auvergne R, Benazet D, Schreiner PR, Caillol S, Andrioletti B. Urea- and thiourea-catalyzed aminolysis of carbonates. Chem- SusChem 2016;9:2269–72. doi:10.1002/cssc.201600778.

[50] Levina MA, Zabalov MV, Krasheninnikov VG, Tiger RP. Green chemistry of polyurethanes: The catalytic n-butylaminolysis of ethylene carbonate as a model chain-growth reaction in the formation of nonisocyanate polyurethanes. Polym Sci Ser B 2017;59:497–505. doi:10.1134/ S1560090417050074.

[51] De La Cruz-Martínez F, Francés-Poveda E, North M, Castro-Osma JA, Lara- Sánchez A. Base-catalyzed highly regioselective synthesis of bio-based hydroxyurethanes. Eur J Org Chem 2024:e202400275. doi:10.1002/ejoc. 202400275.

[52] Guo W, Gónzalez-Fabra J, Bandeira NAG, Bo C, Kleij AW. A metal-free synthesis of N-aryl carbamates under ambient conditions. Angew Chem Int Ed 2015;54:11686–90. doi:10.1002/anie.201504956.

[53] Lombardo VM, Dhulst EA, Leitsch EK, Wilmot N, Heath WH, Gies AP, Miller MD, Torkelson JM, Scheidt KA. Cooperative catalysis of cyclic carbonate ring opening: application towards non-isocyanate polyurethane materials. Eur J Org Chem 2015;2015:2791–5. doi:10.1002/ejoc.201500313.

[54] Zabalov MV, Levina MA, Tiger RP. Molecular organization of reagents in the kinetics and catalysis of liquid-phase reactions: XIII. cyclic transition states involving solvent molecules in the mechanism of aminolysis of cyclocarbonates in an alcohol medium. Kinet Catal 2020;61:721–9. doi:10.1134/ S0023158420050134.

[55] Zabalov MV, Levina MA, Krasheninnikov VG, Tiger RP. Reactivity of new monomers of the polyurethanes green chemistry, the reaction mechanism, and the medium effect. Polym Sci Ser B 2023;65:467–74. doi:10.1134/ S1560090423701063.

[56] Zabalov MV, Tiger RP. The supermolecule method, as applied to studies of liquid-phase reaction mechanisms taking cyclocarbonate aminolysis in dioxane as an example: specific features. Russ Chem Bull 2016;65:631–9. doi:10. 1007/s11172-016-1347-6.

[57] Zabalov MV, Tiger RP. Specificities of application of the supermolecule method to the calculation of reaction mechanisms in a protonodonor medium. Ethylene carbonate aminolysis in methanol. Theor Chem Acc 2017;136:95. doi:10.1007/s00214-017-2124-9.

[58] Olsén P, Oschmann M, Johnston EV, Akermark B. Synthesis of highly functional carbamates through ring-opening of cyclic carbonates with unprotected *α*-amino acids in water. Green Chem 2018;20:469–75. doi:10.1039/ C7GC02862H.

[59] Bourguignon M, Grignard B, Detrembleur C. Water-induced self-blown nonisocyanate polyurethane foams. Angew Chem Int Ed 2022;61:e202213422. doi:10.1002/anie.202213422.

[60] Monie F, Vidil T, Grau E, Grignard B, Detrembleur C, Cramail H. The multifaceted role of water as an accelerator for the preparation of isocyanate-free polyurethane thermosets. Macromolecules 2024;57:8877–88. doi:10.1021/acs. macromol.4c01672.

[61] Ruiz L, Aghmiz A, Masdeu-Bultó AM, Lligadas G, Ronda JC, Galià M, Cádiz V. Upgrading castor oil: from heptanal to non-

isocyanate poly(amide- hydroxyurethane)s. Polymer 2017;124:226–34. doi:10.1016/j.polymer.2017.07. 070.

[62] Cornille A, Auvergne R, Figovsky O, Boutevin B, Caillol S. A perspective approach to sustainable routes for non-isocyanate polyurethanes. Eur Polymer J 2017;87:535–52. doi:10.1016/j.eurpolymj.2016.11.027.

[63] Fortman DJ, Brutman JP, Hillmyer MA, Dichtel WR. Structural effects on the reprocessability and stress relaxation of crosslinked polyhydroxyurethanes. J Appl Polymer Sci 2017;134:44984. doi:10.1002/app.44984.

[64] Chen X, Li L, Jin K, Torkelson JM. Reprocessable polyhydroxyurethane networks exhibiting full property recovery and concurrent associative and dissociative dynamic chemistry via transcarbamoylation and reversible cyclic carbonate aminolysis. Polym Chem 2017;8:6349–55. doi:10.1039/C7PY01160A.

[65] Bakkali-Hassani C, Berne D, Bron P, Irusta L, Sardon H, Ladmiral V, Caillol S. Polyhydroxyurethane covalent adaptable networks: looking for suitable catalysts. Polym Chem 2023;14:3610–20. doi:10.1039/D3PY00579H.

[66] Levina MA, Zabalov MV, Krasheninnikov VG, Tiger RP. Kinetics and quantum chemical aspects of the mechanism of the guanidine (TBD) catalyzed aminolysis of cyclocarbonate containing soybean oil triglycerides as the model process of green chemistry of polyurethanes. Reac Kinet Mech Cat 2020;129:65– 83. doi:10.1007/s11144-019-01683-w.

[67] Steblyanko A, Choi W, Sanda F, Endo T. Addition of five-membered cyclic carbonate with amine and its application to polymer synthesis. J Polym Sci A Polym Chem 2000;38:2375–80. doi:10.1002/1099-0518(20000701)38: 13 (2375::AID-POLA100)3.0.CO;2-U.

[68] Annunziata L, Diallo AK, Fouquay S, Michaud G, Simon F, Brusson JM, Carpentier JF, Guillaume SM. *α*, *ω*-Di(glycerol carbonate) telechelic polyesters and polyolefins as precursors to polyhydroxyurethanes: an isocyanate-free approach. Green Chem 2014;16:1947–56. doi:10.1039/C3GC41821A.

[69] Chen Q, Gao K, Peng C, Xie H, Zhao ZK, Bao M. Preparation of lignin/glycerol- based bis(cyclic carbonate) for the synthesis of polyurethanes. Green Chem 2015;17:4546–51. doi:10.1039/C5GC01340B.

[70] Fleischer M, Blattmann H, Mülhaupt R. Glycerol-, pentaerythritol- and trimethylolpropane-based polyurethanes and their cellulose carbonate composites prepared via the non-isocyanate route with catalytic carbon dioxide fixation. Green Chem 2013;15:934. doi:10.1039/c3gc00078h.

[71] Wu Z, Cai W, Chen R, Qu J. Synthesis and properties of ambient-curable non-isocyanate polyurethanes. Prog Org Coat 2018;119:116–22. doi:10.1016/j. porgcoat.2018.02.006.

[72] Bourguignon M, Thomassin JM, Grignard B, Jerome C, Detrembleur C. Fast and facile one-pot one-step preparation of nonisocyanate polyurethane hydrogels in water at room temperature. ACS Sustain Chem Eng 2019;7:12601– 10. doi:10.1021/acssuschemeng.9b02624.

[73] Capar Ö, Tabatabai M, Klee JE, Worm M, Hartmann L, Ritter H. Fast curing of polyhydroxyurethanes *via* ring opening polyaddition of low viscosity cyclic carbonates and amines. Polym Chem 2020;11:6964–70. doi:10.1039/ D0PY01172J.

[74] Bourguignon M, Thomassin J, Grignard B, Vertruyen B, Detrembleur C. Waterborne isocyanate-free polyurethane hydrogels with adaptable functionality and behavior. Macromol Rapid Commun 2021;42:2000482. doi:10.1002/ marc.202000482.

[75] Tomita H, Sanda F, Endo T. Reactivity comparison of five- and sixmembered cyclic carbonates with amines: Basic evaluation for synthesis of poly(hydroxyurethane). J Polym Sci A Polym Chem 2001;39:162–8. doi:10. 1002/1099-0518(20010101)39:1 (162::AID-POLA180)3.0.CO;2-O.

[76] Maisonneuve L, Wirotius AL, Alfos C, Grau E, Cramail H. Fatty acidbased (bis) 6-membered cyclic carbonates as efficient isocyanate free

poly(hydroxyurethane) precursors. Polym Chem 2014;5:6142–7. doi:10.1039/ C4PY00922C.

[77] Tomita H, Sanda F, Endo T. Polyaddition of bis(seven-membered cyclic carbonate) with diamines: a novel and efficient synthetic method for polyhydroxyurethanes. J Polym Sci A Polym Chem 2001;39:4091–100. doi:10.1002/ pola.10058.

[78] Tomita H, Sanda F, Endo T. Polyaddition behavior of bis(five- and sixmembered cyclic carbonate)s with diamine. J Polym

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

Sci A Polym Chem 2001;39:860-7. doi:10.1002/1099-0518(20010315)39:6(860::AID-POLA1059) 3.0.CO;2-2.

[79] Lambeth RH, Mathew SM, Baranoski MH, Housman KJ, Tran B, Oyler JM. Nonisocyanate polyurethanes from six-membered cyclic carbonates: catalysis and side reactions. J Appl Polymer Sci 2017;134:44941. doi:10.1002/app. 44941.

[80] Yuen A, Bossion A, Gómez-Bengoa E, Ruipérez F, Isik M, Hedrick JL, Mecer- reyes D, Yang YY, Sardon H. Room temperature synthesis of non-isocyanate polyurethanes (NIPUs) using highly reactive N-substituted 8-membered cyclic carbonates. Polym Chem 2016;7:2105–11. doi:10.1039/C6PY00264A.

[81] Fanjul-Mosteirín N, Aguirresarobe R, Sadaba N, Larrañaga A, Marin E, Martin J, Ramos-Gomez N, Arno MC, Sardon H, Dove AP. Crystallization-induced gelling as a method to 4d print low-water-content non-isocyanate polyurethane hydrogels. Chem Mater 2021;33:7194–202. doi:10.1021/acs.chemmater. 1c00913.

[82] Besse V, Foyer G, Auvergne R, Caillol S, Boutevin B. Access to nonisocyanate poly(thio)urethanes: a comparative study. J Polym Sci Part A: Polym Chem 2013;51:3284–96. doi:10.1002/pola.26722.

[83] Gregory GL, Jenisch LM, Charles B, Kociok-Köhn G, Buchard A. Polymers from sugars and CO_2 : synthesis and polymerization of a d -mannosebased cyclic carbonate. Macromolecules 2016;49:7165–9. doi:10.1021/acs. macromol.6b01492.

[84] Nederberg F, Lohmeijer BGG, Leibfarth F, Pratt RC, Choi J, Dove AP, Waymouth RM, Hedrick JL. Organocatalytic ring opening polymerization of trimethylene carbonate. Biomacromolecules 2007;8:153–60. doi:10.1021/ bm060795n.

[85] Hedrick JL, Piunova V, Park NH, Erdmann T, Arrechea PL. Simple and efficient synthesis of functionalized cyclic carbonate monomers using carbon dioxide. ACS Macro Lett 2022;11:368–75. doi:10.1021/acsmacrolett.2c00060.

[86] Yuen AY, Bossion A, Veloso A, Mecerreyes D, Hedrick JL, Dove AP, Sar- don H. Efficient polymerization and post-modification of *N* -substituted eight-membered cyclic carbonates containing allyl groups. Polym Chem 2018;9:2458–67. doi:10.1039/C8PY00231B.

[87] Venkataraman S, Ng VWL, Coady DJ, Horn HW, Jones GO, Fung TS, Sar- don H, Waymouth RM, Hedrick JL, Yang YY. A simple and facile approach to aliphatic *N* -substituted functional eight-membered cyclic carbonates and their organocatalytic polymerization. J Am Chem Soc 2015;137:13851–60. doi:10.1021/jacs.5b06355.

[88] Tempelaar S, Mespouille L, Coulembier O, Dubois P, Dove AP. Synthesis and post-polymerisation modifications of aliphatic poly(carbonate)s prepared by ring-opening polymerisation. Chem Soc Rev 2013;42:1312–36. doi:10.1039/ C2CS35268K.

[89] Yu W, Maynard E, Chiaradia V, Arno MC, Dove AP. Aliphatic polycarbonates from cyclic carbonate monomers and their application as biomaterials. Chem Rev 2021;121:10865–907. doi:10.1021/acs.chemrev.0c00883.

[90] McGuire TM, López-Vidal EM, Gregory GL, Buchard A. Synthesis of 5- to 8membered cyclic carbonates from diols and CO2: a one-step, atmospheric pressure and ambient temperature procedure. J CO2 Util 2018;27:283–8. doi:10.1016/j.jcou.2018.08.009.

[91] Vara BA, Struble TJ, Wang W, Dobish MC, Johnston JN. Enantioselective small molecule synthesis by carbon dioxide fixation using a dual brønsted acid/base organocatalyst. J Am Chem Soc 2015;137:7302–5. doi:10.1021/jacs.5b04425.

[92] Whiteoak CJ, Kielland N, Laserna V, Escudero-Adán EC, Martin E, Kleij AW. A powerful aluminum catalyst for the synthesis of highly functional organic carbonates. J Am Chem Soc 2013;135:1228–31. doi:10.1021/ja311053h.

[93] Brege A, Méreau R, McGehee K, Grignard B, Detrembleur C, Jerome C, Tas- saing T. The coupling of CO2 with diols promoted by organic dual systems: towards products divergence via benchmarking of the performance metrics. J CO2 Util 2020;38:88–98. doi:10.1016/j.jcou.2020.01.003.

[94] Bhat GA, Luo M, Darensbourg DJ. Catalysis of carbon dioxide and oxetanes to produce aliphatic polycarbonates. Green Chem 2020;22:7707–24. doi:10. 1039/D0GC03219K.

[95] Ngassam Tounzoua C, Grignard B, Detrembleur C. Exovinylene cyclic carbonates: multifaceted CO_2-based building blocks for modern chemistry and polymer science. Angew Chem Int Ed 2022;61:e202116066. doi:10.1002/anie. 202116066.

[96] Johnson C, Dabral S, Rudolf P, Licht U, Hashmi ASK, Schaub T. Liquid-liquidphase synthesis of *exo* -vinylene carbonates

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

from primary propargylic alcohols: catalyst design and recycling. ChemCatChem 2021;13:353–61. doi:10. 1002/cctc.202001551.

[97] Dabral S, Licht U, Rudolf P, Bollmann G, Hashmi ASK, Schaub T. Synthesis and polymerisation of α-alkylidene cyclic carbonates from carbon dioxide, epoxides and the primary propargylic alcohol 1,4-butynediol. Green Chem 2020;22:1553–8. doi:10.1039/C9GC04320A.

[98] Ouyang L, Tang X, He H, Qi C, Xiong W, Ren Y, Jiang H. Copper-promoted coupling of carbon dioxide and propargylic alcohols: expansion of substrate scope and trapping of vinyl copper intermediate. Adv Synth Catal 2015;357:2556–65. doi:10.1002/adsc.201500088.

[99] Fischler HM, Heine HG, Hartmann W. Darstellung einiger dialkylsubstitu- ierter vinylencarbonate und ihre photosensibilisierte cycloaddition an äthylen. Tetrahedron Lett 1972;13:1701–4. doi:10.1016/S0040-4039(01)84725-0.

[100] Svahn CM, Merenyi F, Karlson L. Tranexamic acid derivatives with enhanced absorption. J Med Chem 1986;29:448–53. doi:10.1021/jm00154a004.

[101] Onida K, Haddleton AJ, Norsic S, Boisson C, D'Agosto F, Duguet N. Organocatalytic synthesis of substituted vinylene carbonates. Adv Synth Catal 2021;363:5129–37. doi:10.1002/adsc.202100870.

[102] Qiao C, Engel PD, Ziegenhagen LA, Rominger F, Schäfer A, Deglmann P, Rudolf P, Comba P, Hashmi ASK, Schaub T. An organocatalytic route to *endo* - vinylene carbonates from carbon dioxide-based *exo* -vinylene carbonates. Adv Synth Catal 2024;366:291–8. doi:10.1002/adsc.202301374.

[103] Bruneau C, Dixneuf PH. Catalytic incorporation of CO2 into organic substrates: synthesis of unsaturated carbamates, carbonates and ureas. J Molecular Catal 1992;74:97–107. doi:10.1016/0304-5102(92)80227-8.

[104] Titov IYu, Chernysheva NB, Chudinov YuB, Bogolyubov AA, Semenov VV. 4- Methylenedioxolan-2-ones as convenient synthons for the preparation of natural products of the berbine and calycotomine series. Russian Chem Bull 2006;55:569–75. doi:10.1007/s11172-006-0293-0.

[105] Shi M, Shen Y, Chen YJ. Reactions of 5,5dimethyl4-methylene-1,3-dioxolan-2- one with amines in the presence of palladium catalyst. Heterocycles 2002;57. doi:10.3987/COM- 01- 9379.

[106] Gennen S, Grignard B, Jérôme C, Detrembleur C. CO2-sourced nonisocyanate poly(urethane)s with pH-sensitive imine linkages. Adv Synth Catal 2019;361:355–65. doi:10.1002/adsc.201801230.

[107] Gennen S, Grignard B, Tassaing T, Jérôme C, Detrembleur C. CO_2-sourced α-alkylidene cyclic carbonates: a step forward in the quest for functional regioregular poly(urethane)s and poly(carbonate)s. Angew Chem Int Ed 2017;56:10394–8. doi:10.1002/anie.201704467.

[108] Habets T, Siragusa F, Grignard B, Detrembleur C. Advancing the synthesis of isocyanate-free poly(oxazolidones)s: scope and limitations. Macromolecules 2020;53:6396–408. doi:10.1021/acs.macromol.0c01231.

[109] Qiu J, Zhao Y, Zhao Y, Wang H, Li Z, Wang J, Jiao T. Cu(I)/ionic liquids promote the conversion of carbon dioxide into oxazolidinones at room temperature. Molecules 2019;24:1241. doi:10.3390/molecules24071241.

[110] Song QW, Liu P, Han LH, Zhang K, He L-N. Upgrading CO2 by incorporation into urethanes through silver-catalyzed one-pot stepwise amidation reaction. Chin J Chem 2018;36:147–52. doi:10.1002/cjoc.201700572.

[111] Song QW, Chen WQ, Ma R, Yu A, Li QY, Chang Y, He L-N. Bifunctional sil- ver(i) complex-catalyzed CO_2 conversion at ambient conditions: synthesis of α-methylene cyclic carbonates and derivatives. ChemSusChem 2015;8:821–7. doi:10.1002/cssc.201402921.

[112] Kikuchi S, Yoshida S, Sugawara Y, Yamada W, Cheng HM, Fukui K, Sekine K, Iwakura I, Ikeno T, Yamada T. Silver-catalyzed carbon dioxide incorporation and rearrangement on propargylic derivatives. Bull Chem Soc Japan 2011;84:698–717. doi:10.1246/bcsj.20110078.

[113] Dabral S, Bayarmagnai B, Hermsen M, Schießl J, Mormul V, Hashmi ASK, Schaub T. Silver-catalyzed carboxylative cyclization of primary propargyl alcohols with CO2. Org Lett 2019;21:1422–5. doi:10.1021/acs.orglett.9b00156.

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

[114] Chauveau C, Fouquay S, Michaud G, Simon F, Carpentier JF, Guillaume SM. α, ω-Di(vinylene carbonate) telechelic polyolefins: synthesis by metathesis reactions and studies as potential precursors toward hydroxy-oxazolidonebased polyolefin NIPUs. Eur Polymer J 2019;116:144–57. doi:10.1016/j. eurpolymj.2019.03.052.

[115] Ouhib F, Grignard B, Van Den Broeck E, Luxen A, Robeyns K, Van Spey- broeck V, Jerome C, Detrembleur C. A switchable domino process for the construction of novel CO_2-sourced sulfur-containing building blocks and polymers. Angew Chem Int Ed 2019;58:11768–73. doi:10.1002/anie.201905969.

[116] Wong AR, Barrera M, Pal A, Lamb JR. Improved characterization of poly- oxazolidinones by incorporating solubilizing side chains. Macromolecules 2022;55:11006–12. doi:10.1021/acs.macromol.2c02104.

[117] Habets T, Siragusa F, Müller AJ, Grossman Q, Ruffoni D, Grignard B, Detrem- bleur C. Facile construction of functional poly(monothiocarbonate) copolymers under mild operating conditions. Polym Chem 2022;13:3076–90. doi:10.1039/D2PY00307D.

[118] Siragusa F, Crane L, Stiernet P, Habets T, Grignard B, Monbaliu JCM, Detrembleur C. Continuous flow synthesis of functional isocyanate- free poly(oxazolidone)s by step-growth polymerization. ACS Macro Lett 2024;13:644–50. doi:10.1021/acsmacrolett.4c00203.

[119] Razavi-Esfali M, Habets T, Siragusa F, Grignard B, Sardon H, Detrembleur C. Design of functional isocyanate-free poly(oxazolidone)s under mild conditions. Polym Chem 2024;15:1962–74. doi:10.1039/D4PY00101J.

[120] Habets T, Olmedo-Martínez JL, Del Olmo R, Grignard B, Mecerreyes D, De- trembleur C. Facile access to CO_2-sourced polythiocarbonate dynamic networks and their potential as solid-state electrolytes for lithium metal batteries. ChemSusChem 2023;16:e202300225. doi:10.1002/cssc.202300225.

[121] Lopez De Pariza X, Erdmann T, Arrechea PL, Perez L, Dausse C, Park NH, Hedrick JL, Sardon H. Synthesis of tailored segmented polyurethanes utilizing continuous-flow reactors and real-time process monitoring. Chem Mater 2021;33:7986–93. doi:10.1021/acs.chemmater.1c01919.

[122] Sardon H, Engler AC, Chan JMW, Coady DJ, O'Brien JM, Mecerreyes D, Yang YY, Hedrick JL. Homogeneous isocyanate- and catalyst-free synthesis of polyurethanes in aqueous media. Green Chem 2013;15:1121. doi:10.1039/ c3gc40319j.

[123] Bossion A, Jones GO, Taton D, Mecerreyes D, Hedrick JL, Ong ZY, Yang YY, Sardon H. Non-isocyanate polyurethane soft nanoparticles obtained by

surfactant-assisted interfacial polymerization. Langmuir 2017;33:1959–68. doi:10.1021/acs.langmuir.6b04242.

[124] Hosokawa S, Nagao A, Hashimoto Y, Matsune A, Okazoe T, Suzuki C, Wada H, Kakiuchi T, Tsuda A. Non-isocyanate polyurethane synthesis by polycondensation of alkylene and arylene bis(fluoroalkyl) bis(carbonate)s with diamines. Bull Chem Soc Japan 2023;96:663–70. doi:10.1246/bcsj.20230066.

[125] Wu D, Martin RT, Piña J, Kwon J, Crockett MP, Thomas AA, Gutierrez O, Park NH, Hedrick JL, Campos LM. Cyclopropenimine-mediated CO2 activation for the synthesis of polyurethanes and small-molecule carbonates and carbamates. Angew Chem Int Ed 2024;63:e202401281. doi:10.1002/anie. 202401281.

[126] Chen Z, Hadjichristidis N, Feng X, Gnanou Y. Poly(urethane–carbonate)s from carbon dioxide. Macromolecules 2017;50:2320–8. doi:10.1021/acs.macromol. 7b00142.

[127] Rokicki G, Parzuchowski PG, Mazurek M. Non-isocyanate polyurethanes: synthesis, properties, and applications. Polymers Adv Techs 2015;26:707–61. doi:10.1002/pat.3522.

[128] Grignard B, Gennen S, Jérôme C, Kleij AW, Detrembleur C. Advances in the use of CO_2 as a renewable feedstock for the synthesis of polymers. Chem Soc Rev 2019;48:4466–514. doi:10.1039/C9CS00047J.

[129] Zhang D, Zhang Y, Fan Y, Rager MN, Guérineau V, Bouteiller L, Li MH, Thomas CM. Polymerization of cyclic carbamates: a practical route to aliphatic polyurethanes. Macromolecules 2019;52:2719–24. doi:10.1021/acs. macromol.9b00436.

[130] Haba O, Akashika Y. Anionic ring-opening polymerization of a five-membered cyclic urethane derived from d-

glucosamine. J Polym Sci Part A: Polym Chem 2019;57:2491–7. doi:10.1002/pola.29511.

[131] Bizet B, Grau E, Asua JM, Cramail H. Hybrid nonisocyanate polyurethanes (H- NIPUs): a pathway towards a broad range of novel materials. Macro Chem Phys 2022;223:2100437. doi:10.1002/macp.202100437.

[132] Ecochard Y, Caillol S. Hybrid polyhydroxyurethanes: how to overcome limitations and reach cutting edge properties? European Polymer Journal 2020;137:109915. doi:10.1016/j.eurpolymj.2020.109915.

[133] Buchheit H, Bruchmann B, Stoll K, Mülhaupt R. Functionalized acrylic polyhydroxy urethanes as molecular tool box for photocurable thermosets and 3D printing. J Polymer Sci 2021;59:882–92. doi:10.1002/pol.20210115.

[134] Schimpf V, Asmacher A, Fuchs A, Bruchmann B, Mülhaupt R. Polyfunctional acrylic non-isocyanate hydroxyurethanes as photocurable thermosets for 3D printing. Macromolecules 2019;52:3288–97. doi:10.1021/acs.macromol. 9b00330.

[135] Singh N, Bakhshi H, Meyer W. Developing non-isocyanate urethanemethacrylate photo-monomers for 3D printing application. RSC Adv 2020;10:44103–10. doi:10.1039/D0RA06388F.

[136] Bakhshi H, Kuang G, Wieland F, Meyer W. Photo-curing kinetics of 3Dprinting photo-inks based on urethane-acrylates. Polymers 2022;14:2974. doi:10.3390/polym14152974.

[137] Kuang G, Bakhshi H, Meyer W. Urethane-acrylate-based photo-inks for digital light processing of flexible materials. J Polym Res 2023;30:141. doi:10.1007/ s10965- 023- 03519- 7.

[138] Carmenini R, Spanu C, Locatelli E, Sambri L, Comes Franchini M, Ma- turi M. Isocyanate-free urethanediol itaconates as biobased liquid monomers in photopolymerization-based 3D printing. Prog Addit Manuf 2024. doi:10. 1007/s40964-024-00598-w.

[139] Zareanshahraki F, Mannari V. Formulation and optimization of radiation- curable nonisocyanate polyurethane wood coatings by mixture experimental design. J Coat Technol Res 2021;18:695–715. doi:10.1007/ s11998-020-00453-x.

[140] Zareanshahraki F, Asemani HR, Skuza J, Mannari V. Synthesis of nonisocyanate polyurethanes and their application in radiation-curable aerospace coatings. Prog Org Coat 2020;138:105394. doi:10.1016/j.porgcoat.2019. 105394.

[141] Hoyle CE, Bowman CN. Thiol–ene click chemistry. Angew Chem Int Ed 2010;49:1540–73. doi:10.1002/anie.200903924.

[142] Calle M, Lligadas G, Ronda JC, Galià M, Cádiz V. An efficient nonisocyanate route to polyurethanes via thiol-ene self-addition. J Polym Sci Part A: Polym Chem 2014;52:3017–25. doi:10.1002/pola.27347.

[143] Xie S, Li Y, Chai Y, Chen Q, North M, Xie H. Introducing the reversible reaction of CO_2 with diamines into nonisocyanate polyurethane synthesis. ACS Macro Lett 2024;13:14–20. doi:10.1021/acsmacrolett.3c00621.

[144] Scheelje FCM, Meier MAR. Non-isocyanate polyurethanes synthesized from terpenes using thiourea organocatalysis and thiol-ene-chemistry. Commun Chem 2023;6:239. doi:10.1038/s42004-023-01041-x.

[145] Warner JJ, Wang P, Mellor WM, Hwang HH, Park JH, Pyo SH, Chen S. 3D printable non-isocyanate polyurethanes with tunable material properties. Polym Chem 2019;10:4665–74. doi:10.1039/C9PY00999J.

[146] Hua G, Odelius K. Isocyanate-free, UV-crosslinked poly(hydroxyurethane) networks: a sustainable approach toward highly functional antibacterial gels. Macromolecular Bioscience 2017;17:1700190. doi:10.1002/mabi.201700190.

[147] Pierrard A, Aqil A, Detrembleur C, Jérôme C. Thermal and UV curable formulations of poly(propylene glycol)–poly(hydroxyurethane) elastomers toward nozzle-based 3D photoprinting. Biomacromolecules 2023;24:4375–84. doi:10.1021/acs.biomac.2c00860.

[148] Pierrard A, Melo SF, Thijssen Q, Van Vlierberghe S, Lancellotti P, Oury C, Detrembleur C, Jérôme C. Design of 3D-photoprintable, bio-, and hemocompatible nonisocyanate polyurethane elastomers for biomedical implants. Biomacromolecules 2024;25:1810–24. doi:10.1021/acs.biomac.3c01261.

[149] Sutherland BP, Kabra M, Kloxin CJ. Expanding the thiol–X toolbox: photoinitiation and materials application of the acid-catalyzed thiol–ene (ACT) reaction. Polym Chem 2021;12:1562–70. doi:10.1039/D0PY01593H.

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

[150] Habets T, Seychal G, Caliari M, Raquez JM, Sardon H, Grignard B, Detrem- bleur C. Covalent adaptable networks through dynamic *N,S*-acetal chemistry: toward recyclable CO_2 -based thermosets. J Am Chem Soc 2023;145:25450– 62. doi:10.1021/jacs.3c10080.

[151] Zheng N, Xu Y, Zhao Q, Xie T. Dynamic covalent polymer networks: a molecular platform for designing functions beyond chemical recycling and selfhealing. Chem Rev 2021;121:1716–45. doi:10.1021/acs.chemrev.0c00938.

[152] Zhang V, Kang B, Accardo JV, Kalow JA. Structure–reactivity–property relationships in covalent adaptable networks. J Am Chem Soc 2022;144:22358– 77. doi:10.1021/jacs.2c08104.

[153] Elling BR, Dichtel WR. Reprocessable cross-linked polymer networks: are associative exchange mechanisms desirable? ACS Cent Sci 2020;6:1488–96. doi:10.1021/acscentsci.0c00567.

[154] Kloxin CJ, Bowman CN. Covalent adaptable networks: smart, reconfigurable and responsive network systems. Chem Soc Rev 2013;42:7161–73. doi:10. 1039/C3CS60046G.

[155] Dodiuk H, editor. Handbook of Thermoset Plastics. Fourth edition. Oxford Cambridge, MA: William Andrew; 2022.

[156] Asemani H, Zareanshahraki F, Mannari V. Design of hybrid nonisocyanate polyurethane coatings for advanced ambient temperature curing applications. J of Applied Polymer Sci 2019;136:47266. doi:10.1002/app.47266.

[157] Centeno-Pedrazo A, Freixa Z, Feola R, Lunzer F, Garcia-Suarez EJ, Ortiz P. Bringing non-isocyanate polyurethanes closer to industrial implementation using carbonated soybean oil-based amino hardeners. Prog Org Coat 2023;185:107925. doi:10.1016/j.porgcoat.2023.107925.

[158] Figovsky O, Shapovalov L, Birukova O, Leykin A. Modification of epoxy adhesives by hydroxyurethane components on the basis of renewable raw materials. Polym Sci Ser D 2013;6:271–4. doi:10.1134/S1995421213040047.

[159] Gomez-Lopez A, Grignard B, Calvo I, Detrembleur C, Sardon H. Accelerating the curing of hybrid poly(hydroxy urethane)-epoxy adhesives by the thiol-epoxy chemistry. ACS Appl Polym Mater 2022;4:8786–94. doi:10.1021/ acsapm.2c01195.

[160] Cornille A, Guillet C, Benyahya S, Negrell C, Boutevin B, Caillol S. Room temperature flexible isocyanate-free polyurethane foams. European Polymer Journal 2016;84:873–88. doi:10.1016/j.eurpolymj.2016.05.032.

[161] Gomez-Lopez A, Grignard B, Calvo I, Detrembleur C, Sardon H. Monocomponent non-isocyanate polyurethane adhesives based on a Sol–gel process. ACS Appl Polym Mater 2020;2:1839–47. doi:10.1021/acsapm.0c00062.

[162] Asemani HR, Mannari V. Dual-curable coatings obtained from multifunctional non-isocyanate polyurethane oligomers. J Coat Technol Res 2022;19:1393–407. doi:10.1007/s11998-022-00614-0.

[163] Yu Rulev A. Aza-michael reaction: a decade later –is the research over? Eur J Org Chem 2023;26:e202300451. doi:10.1002/ejoc.202300451.

[164] Desmet GB, D'hooge DR, Omurtag PS, Espeel P, Marin GB, Du Prez FE, Reyniers MF. Quantitative first-principles kinetic modeling of the aza-michael addition to acrylates in polar aprotic solvents. J Org Chem 2016;81:12291– 302. doi:10.1021/acs.joc.6b02218.

[165] Taplan C, Guerre M, Du Prez FE. Covalent adaptable networks using *β*- amino esters as thermally reversible building blocks. J Am Chem Soc 2021;143:9140–50. doi:10.1021/jacs.1c03316.

[166] Cornille A, Ecochard Y, Blain M, Boutevin B, Caillol S. Synthesis of hybrid polyhydroxyurethanes by Michael addition. European Polymer Journal 2017;96:370–82. doi:10.1016/j.eurpolymj.2017.09.028.

[167] Siragusa F, Van Den Broeck E, Ocando C, Müller AJ, De Smet G, Maes BUW, De Winter J, Van Speybroeck V, Grignard B, Detrembleur C. Access to biore- newable and CO_2-based polycarbonates from exovinylene cyclic carbonates. ACS Sustain Chem Eng 2021;9:1714–28. doi:10.1021/acssuschemeng.0c07683.

[168] Siragusa F, Habets T, Méreau R, Evano G, Grignard B, Detrembleur C. Catalyst- free approach for the degradation of bio- and CO_2-sourced polycarbonates: a step toward a circular plastic economy. ACS Sustain Chem Eng 2022;10:8863–75. doi:10.1021/acssuschemeng.2c01891.

Published in : Progress in Polymer Science, 165, 101968.
doi:10.1016/j.progpolymsci.2025.101968
Status : Postprint (Author's version)

[169] Kihara N, Tochigi H, Endo T. Synthesis and reaction of polymers bearing 5-membered cyclic dithiocarbonate group. J Polym Sci A Polym Chem 1995;33:1005–10. doi:10.1002/pola.1995.080330701.

[170] Moriguchi T, Endo T. Polyaddition of bifunctional dithiocarbonates derived from epoxides and carbon disulfide. synthesis of novel poly(thiourethanes). Macromolecules 1995;28:5386–7. doi:10.1021/ma00119a035.

[171] Vanbiervliet E, Fouquay S, Michaud G, Simon F, Carpentier JF, Guillaume SM. Non-isocyanate polythiourethanes (NIPTUs) from cyclodithiocarbonate telechelic polyethers. Macromolecules 2019;52:5838–49. doi:10.1021/ acs.macromol.9b00695.

[172] Kihara N, Nakawaki Y, Endo T. Preparation of 1,3-oxathiolane-2-thiones by the reaction of oxirane and carbon disulfide. J Org Chem 1995;60:473–5. doi:10. 1021/jo00107a034.

[173] National Research Council (U.S.) . Acute Exposure Guideline Levels for Selected Airborne Chemicals, 7. Washington, D.C: National Academies Press; 2009.

[174] Tomita H, Sanda F, Endo T. Polyaddition of bis(cyclic thiocarbonate) with diamines. novel efficient synthetic method of polyhydroxythiourethanes. Macromolecules 2001;34:727–33. doi:10.1021/ma001353l.

[175] Ihata O, Kayaki Y, Ikariya T. Aliphatic poly(urethane-amine)s synthesized by copolymerization of aziridines and supercritical carbon dioxide. Macromolecules 2005;38:6429–34. doi:10.1021/ma050549o.

[176] Ihata O, Kayaki Y, Ikariya T. Synthesis of thermoresponsive polyurethane from 2-methylaziridine and supercritical carbon dioxide. Angew Chem Int Ed 2004;43:717–19. doi:10.1002/anie.200352215.

[177] Tan D, Hu X, Cao Z, Luo M, Darensbourg DJ. Zwitterionic alternating polymerization to generate semicrystalline and recyclable cyclic polythiourethanes. ACS Macro Lett 2020;9:866–71. doi:10.1021/acsmacrolett.0c00302.

[178] Wu S, Luo M, Darensbourg DJ, Zeng D, Yao Y, Zuo X, Hu X, Tan D. Nonisocyanate and catalyst-free synthesis of a recyclable polythiourethane with cyclic structure. ACS Sustainable Chem Eng 2020;8:5693–703. doi:10.1021/ acssuschemeng.0c00435.

[179] Gleede T, Reisman L, Rieger E, Mbarushimana PC, Rupar PA, Wurm FR. Aziridines and azetidines: building blocks for polyamines by anionic and cationic ring-opening polymerization. Polym Chem 2019;10:3257–83. doi:10. 1039/C9PY00278B.

[180] Nagai A, Miyagawa T, Kudo H, Endo T. Controlled cationic ring-opening polymerization of 1,3-oxazolidine-2-thione derived from l L-serine. Macromolecules 2003;36:9335–9. doi:10.1021/ma030320d.

[181] Nagai A, Ochiai B, Endo T. Living cationic ring-opening polymerization by water-stable initiator: synthesis of a well-defined optically active polythiourethane. Chem Commun 2003:3018. doi:10.1039/b310735c.

[182] Nagai A, Ochiai B, Endo T. Observation of optical activity in polythiourethane obtained by the controlled cationic ring-opening polymerization of chiral cyclic thiourethane derived from serine. J Polym Sci A Polym Chem 2005;43:1554–61. doi:10.1002/pola.20624.

[183] Nagai A, Ochiai B, Endo T. Cationic ring-opening polymerization of optically active N-substituted cyclic thiourethanes. Macromolecules 2004;37:7538–42. doi:10.1021/ma049114b.

[184] Liang C, Jadidi Y, Chen Y, Gracida-Alvarez U, Torkelson JM, Hawkins TR, Dunn JB. Techno-economic analysis and life cycle assessment of biomass- derived polyhydroxyurethane and nonisocyanate polythiourethane production and reprocessing. ACS Sustain Chem Eng 2024;12:12161–70. doi:10.1021/ acssuschemeng.4c04046.