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# Design of Plurifunctional Cyclocarbonates and Their Use as Precursors of Poly(hydroxyurethane) Thermosets: A Review

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**Keywords :** Poly(hydroxyurethane) ; poly(cyclic carbonate) ; networks ; curing conditions ; gelation ; room temperature

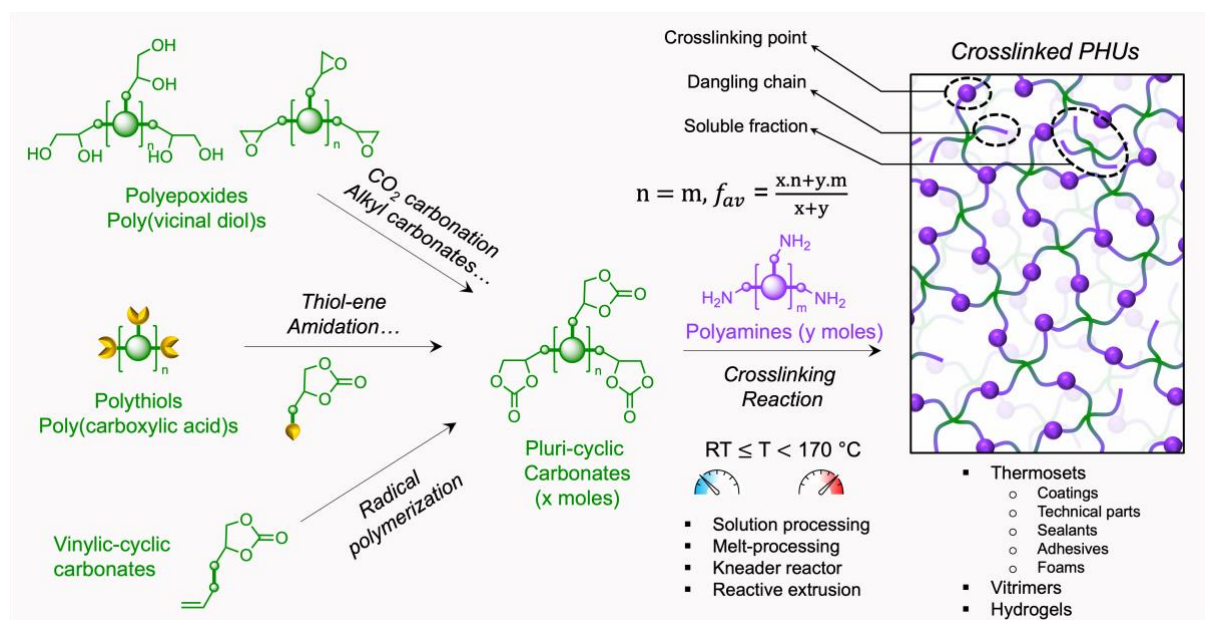
## **Abstract :**

Polyhydroxyurethanes (PHUs) are promising polymers to replace polyurethanes (PUs), classically obtained by the isocyanate-alcohol route. Various application fields of PUs, *e.g.* foams or coatings, require the use of thermosetting polymers. Hence, a great deal of effort has been devoted to the development of PHU thermosets in the recent literature. This review highlights the different strategies developed through the years to synthesize plurifunctional cyclic carbonates, also called poly(cyclic carbonate)s, and whose functionality  $\geq 3$  is a prerequisite for the synthesis of thermosetting PHUs. A special emphasize is accorded to the safe and eco-friendly synthetic approaches (*e.g.* phosgene-free, use of renewable reactants). In addition, the curing strategies implemented to overcome the low reactivity of the monomers and the limitations related to the transitions of the growing networks (*i.e.* viscosification, gelation, vitrification) are described. In the end, the curing of PHUs under mild thermal conditions, down to room temperature, is described. Such curing conditions are uncommon for PHU thermosets and are paving the way to much anticipated applications such as coatings, adhesives or 3D-printing.

## **1. Introduction**

The industrial synthesis of polyurethanes (PUs) is based on the polyaddition between polyisocyanates and polyols, a method developed in 1930 by Otto Bayer. Although this synthesis is rapid, quantitative and involves available and inexpensive reagents, the toxicity of isocyanates is a real threat to health and to the environment.<sup>1</sup> Indeed, most isocyanates used in the industry are both petro-sourced and registered as harmful chemicals by the REACH regulation. In addition, a recent amendment to this regulation, published by the European Commission, will limit the use of the registered isocyanates by the end of August 2023, if the safety measures necessary for their handling are not implemented in factories producing PUs.<sup>2</sup> Therefore, the development and optimization of alternative syntheses for isocyanate-free polyurethanes, also called NIPU for non-isocyanate polyurethane, has been the object of intense research over the past decades.

Among the different synthesis pathways of NIPU, the aminolysis of cyclic carbonates leading to polyhydroxyurethanes (PHUs) is a promising strategy to replace the isocyanate-alcohol route. Indeed, the multitude of synthesis routes to cyclic carbonates of various sizes (X-membered cyclic carbonate, noted XCC, with X varying from 5 to 8) enables the design of PHUs with various thermo-mechanical properties. Nevertheless, the synthesis of thermoplastic PHUs with molar masses adapted to the targeted applications remains an unsolved challenge, even with reactive cyclic carbonates such as 6CC or 8CC. Despite tremendous improvements over the past decade, notably thanks to the use of reactive extrusion,<sup>3</sup> the molar masses of thermoplastic PHUs are usually too small to be competitive with isocyanate-based PUs. When it comes to the synthesis of thermosets, these materials are no longer characterized by their molar masses. Indeed, they are obtained by reacting monomers mixtures whose average functionality,  $f_{av}$ , is strictly larger than 2,  $f_{av} > 2$  (Figure 1). After their gelling point, the resulting crosslinked networks can be seen as an infusible and insoluble giant macromolecule. Providing that the reaction is efficient enough, the soluble fraction (*i.e.* the monomers and polymeric chains that are not incorporated to the network) and the number of dangling chains will remain small, and the thermo-mechanical properties of the resulting network will qualify for the numerous applications of thermosetting materials.



**Figure 1** : From the design of plurifunctional cyclocarbonates to the synthesis of poly(hydroxyurethane) thermosets. Overview of the scope of the review.

Isocyanate-based thermosetting PUs represent a large part of the world production, particularly for applications such as foams or coatings. It is therefore necessary to design alternatives to these polymers, *i.e.* thermosetting PHUs. The first examples of thermosetting PHUs were reported in 2000 by Figovsky *et al.*, with the synthesis of hybrid PHU networks from cyclic carbonate, epoxide and amine oligomers of functionality  $\geq 3$ ,<sup>4</sup> and in 2003 by Wilkes *et al.* with the use of carbonated soybean oil as a cyclic carbonate precursor.<sup>5</sup> Since then, many authors have been interested in the study of PHU networks obtained from multifunctional 5CCs. Many biosourced substrates, in addition to vegetable oils, have also been implemented in the synthesis of thermosetting PHUs.<sup>6,7</sup> In 2015, Fortman *et al.* reported the first synthesis of PHU networks with vitrimeric properties, paving the way to new application perspectives for PHUs.<sup>8</sup> In all these works, the resulting thermosetting PHUs exhibit low soluble fraction (typically  $< 5\text{wt}\%$ ), and their thermomechanical properties are competitive with those

of isocyanate-based PUs, proving that the aminolysis of cyclic carbonate has a bright future in the field of thermosetting chemistry. In many respects, the recent developments of the carbonate-amine chemistry suggest that it behaves similarly to the epoxy-amine chemistry, which also fails in providing high molar masses thermoplastic polymers, and which is essentially used in the field of thermosetting materials.

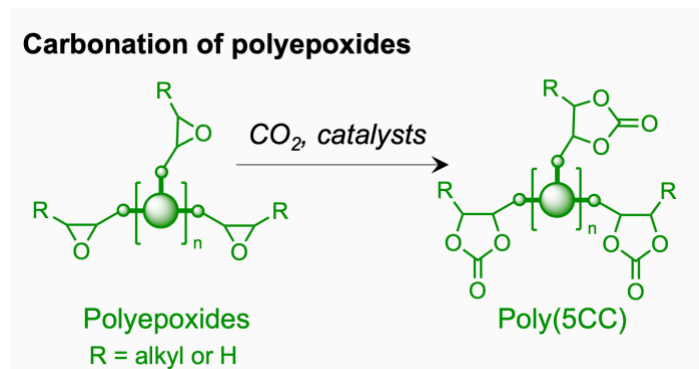
For all these reasons, there is a growing demand for poly(cyclic carbonate)s and/or polyamine precursors with functionality  $\geq 3$  within the PHU community. This is a prerequisite to obtain carbonate-amine mixture with  $f_{av} > 2$ . If different triamines are commercially available, plurifunctional cyclocarbonates with  $f \geq 3$  are more uncommon. Over the past 20 years, numerous strategies have been reported for the synthesis of plurifunctional cyclocarbonates (Figure 1). Recently, there have been an increasing number of references reporting the synthesis of precursors with  $f \geq 3$  that are directly implemented in the synthesis of thermosetting PHUs. To the best of our knowledge, this paper provides the first overview of the synthesis strategies of plurifunctional cyclocarbonates with a functionality higher than or equal to 2, necessary for the synthesis of cross-linked PHUs. A special emphasize is accorded to the safe and eco-friendly synthetic approaches. In particular, a notable attention is devoted to the use of  $\text{CO}_2$  and to the carbonating agents that are not derived from phosgene. Subsequently, the synthesis of thermosetting PHUs under different temperature conditions as well as their potential industrial applications are described. A special emphasize is accorded to the synthesis of thermosetting PHUs at low temperature, down to room temperature. Indeed, it has long been assumed that PHUs thermosets can only be formed at high temperature (typically  $T > 70\text{ }^\circ\text{C}$ ). However, recent examples are proving the contrary, opening new avenues in the field of PHU-based coatings, adhesives, or sealants. Overall, this review provides new guidelines for both academic and industrial researchers interested in the field of PHUs thermosets.

## **2. Synthesis of multifunctional monomers**

The synthesis of thermosetting PHUs requires the use of at least one trifunctional monomer, or of higher functionality, in order to obtain a monomer mixture with  $f_{av} > 2$ , and then a three-dimensional network. While many diamines and triamines are commercially available, most commercial cyclic carbonate precursors are monofunctional and do not, as such, allow the synthesis of PHU networks. The synthesis of original multifunctional cyclic carbonates has therefore been studied and different synthetic strategies have been reported.

### **2.1. Carbonation of polyepoxides and poly(diols)**

#### **2.1.1. Carbonation of polyepoxides**

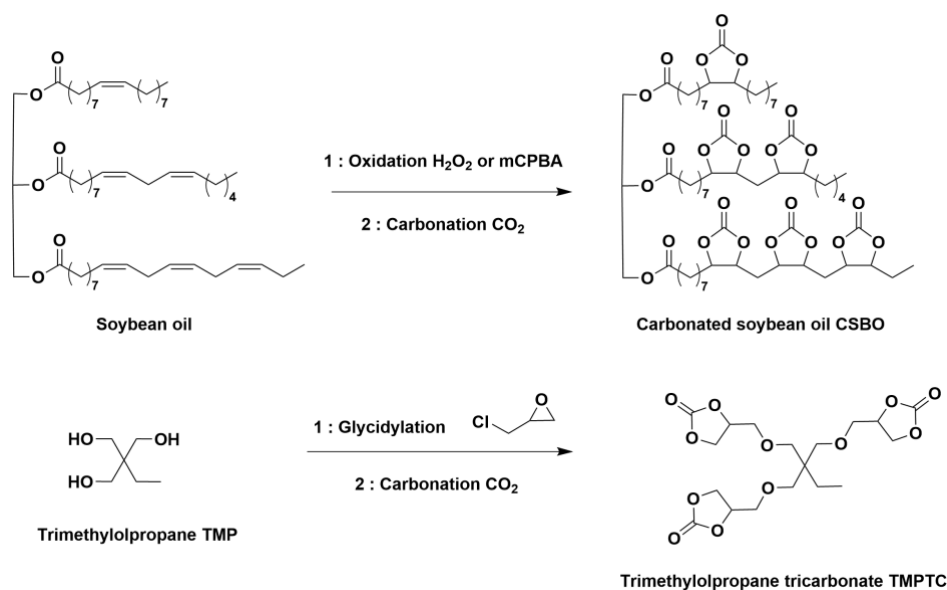


**Figure 2** : General scheme for the synthesis of poly(5CC) from polyepoxides

The carbonation of polyepoxides is one of the most used methods for the synthesis of multifunctional cyclic carbonate monomers containing 5CCs (Figure 2). Indeed, polyepoxy substrates can be easily obtained by oxidation of polyunsaturated compounds or by glycidylation of polyols with epichlorohydrin.

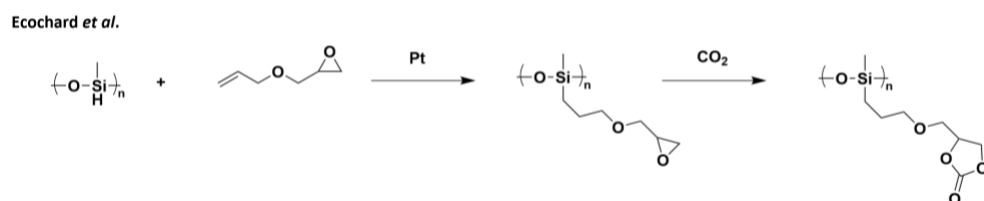
In the first case, carbonated vegetable oils obtained from their epoxidized version are reported as precursors of choice for the synthesis of thermosetting PHUs and, in particular, carbonated soybean oil.<sup>9–16</sup> The latter is obtained by carbonation of epoxidized soybean oil through CO<sub>2</sub> addition in the presence of catalytic amounts of an onium salt such as tetrabutylammonium bromide or iodide (Figure 3). The reactions are generally carried out at high temperature, 110 °C ≤ T ≤ 140 °C, under high CO<sub>2</sub> pressure, 10 bar ≤ P ≤ 100 bar and the complete conversion of epoxides into carbonates is obtained after 1 to 3 days of reaction.<sup>9,10,13</sup> Other carbonated oils with different functionalities, such as sunflower,<sup>17</sup> linseed,<sup>13</sup> jojoba or castor oil<sup>18</sup> are also used as carbonated precursors. Terpenes, such as limonene, can also be oxidized and then carbonated by absorption of CO<sub>2</sub>, as described by Bähr *et al.*,<sup>19</sup> Schimpf *et al.*<sup>20</sup> or Maltby *et al.*<sup>21</sup> The conversion of epoxidized limonene into limonene dicarbonate is also complete in less than 50 h at 140 °C under 30 bar of CO<sub>2</sub> and in the presence of 3 mol% of TBAB.<sup>19</sup>

Many polyepoxide substrates are derived from the glycidylation of polyols and, in particular, the trimethylolpropane triglycidyl ether (TMPTE). It is obtained from trimethylolpropane and its carbonated form is widely used for the synthesis of PHUs.<sup>22–30</sup> As with carbonated oils, the tricarbonates (TMPTC) is obtained *via* the carbonation of TMPTE by CO<sub>2</sub> fixation in the presence of an onium salt type catalyst (Figure 3). Syntheses are performed at high temperature, 80 ≤ T ≤ 140 °C and high CO<sub>2</sub> pressure, 10 ≤ P ≤ 80 bar, leading to quantitative conversion of epoxides into carbonates in approximately 1 day.<sup>26–28,31</sup> Other polyols are also used as precursors such as poly(propylene glycol),<sup>24,25,32,33</sup> tri(4-hydroxyphenyl)methane<sup>34,35</sup> or ethoxylated trimethylolpropane.<sup>31</sup> Biosourced polyols, such as sorbitol,<sup>14,36,37</sup> glycerol, pentaerythritol,<sup>38</sup> or derivatives of ferulic acid<sup>39</sup> can also be glycidylized and then carbonated.



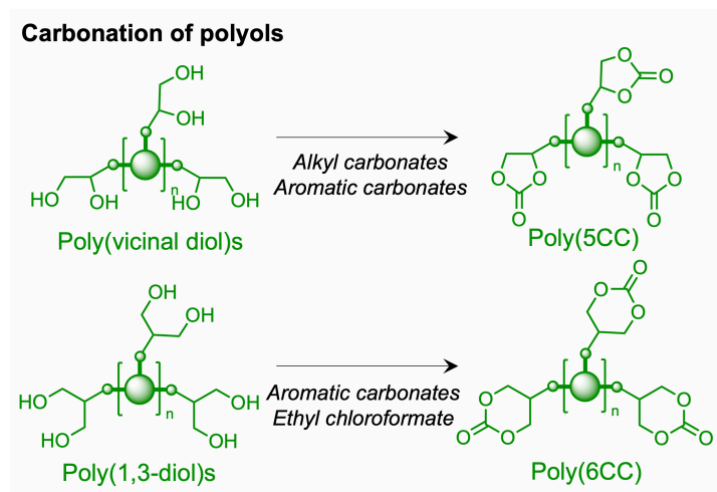
**Figure 3** : General synthesis pathways of CSBO and TMPTC

In a similar fashion, Ecochard *et al.* explored another synthetic route towards polyepoxides based on the hydrosilylation of polysiloxanes with allyl glycidyl ether (Figure 4).<sup>40</sup> The resulting polyepoxides were carbonated under CO<sub>2</sub> pressure to provide polysiloxanes with pendent cyclic carbonate functions which were used for the synthesis of hybrid thermosetting PHUs. By using polysiloxanes of variable functionality ( $3 < f < 6$ ), the authors were able to modulate the thermo-mechanical properties of the PHU networks.



**Figure 4** : Synthesis of polysiloxane based plurifunctional cyclic carbonate proposed by Ecochar *et al.*<sup>40</sup>

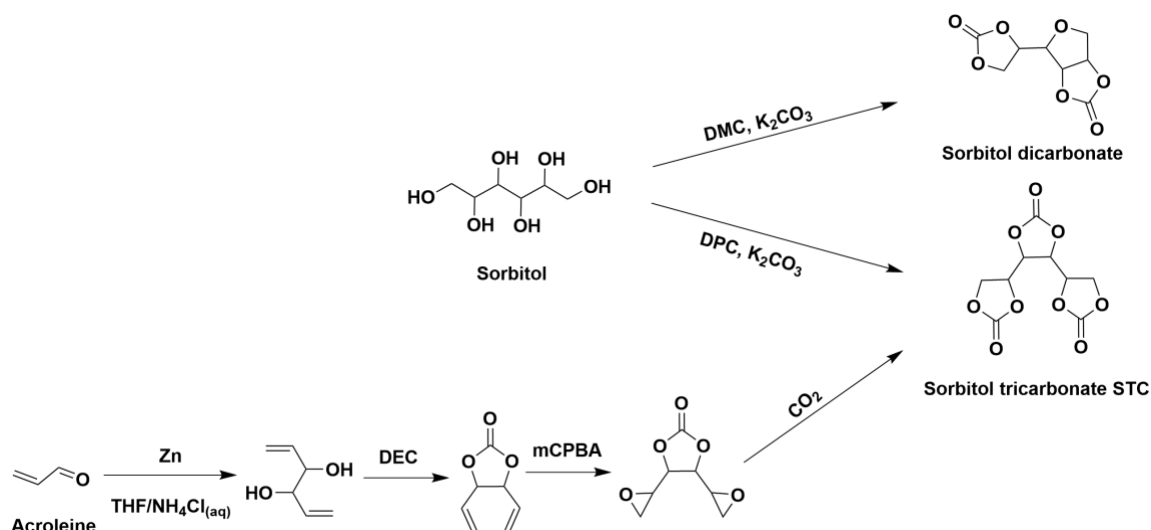
### 2.1.2. Carbonation of polyols



**Figure 5 :** General scheme for the synthesis of poly(5CC)s and poly(6CC)s from pol(vicinal diol)s and poly(1,3-diol)s respectively

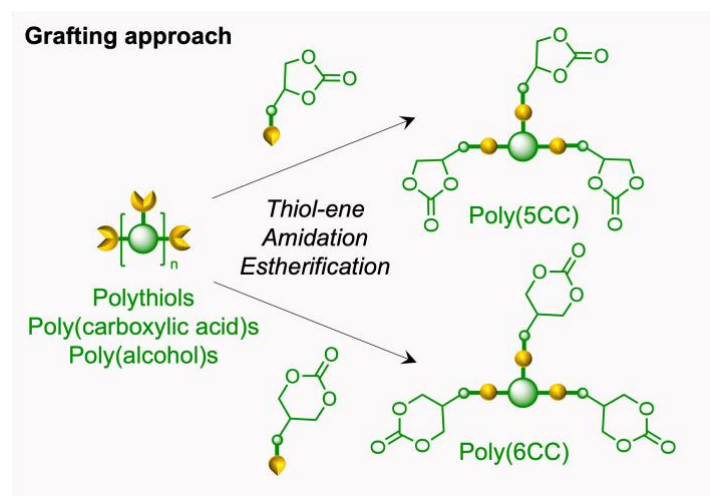
While all polyols can be glycidylized and then carbonated by CO<sub>2</sub> absorption, poly(1,2-diols) (also called poly(vicinal diol)s) and poly(1,3-diols) can be directly carbonated with carbonating agents such as dialkyl/diaryl carbonates, to yield plurifunctional cyclocarbonates, containing 5CCs and 6CCs respectively (Figure 5).

Several examples of sorbitol and mannitol carbonation have been described to obtain di- and tricarbonates.<sup>36,41–43</sup> The direct carbonation of sorbitol and mannitol using dimethyl carbonate (CDM) and K<sub>2</sub>CO<sub>3</sub> yields only dicarbonates with relatively low yields, ~ 40 %, because of the unfavourable stereochemistry of the diols for the formation of 5CC (Figure 6).<sup>41,43</sup> Schmidt *et al.* successfully synthesized a tricarbate from sorbitol by two different synthetic routes. A first technique consists in the carbonation of sorbitol by diphenyl carbonate (CDP) catalyzed by K<sub>2</sub>CO<sub>3</sub> in DMSO at 120 °C.<sup>36</sup> After 19 hours of reaction and recrystallization, the tricarbate is obtained with a yield of 77 %. Another way to obtain this tricarbate is to dimerize acrolein, carbonate the resulting vicinal diol, then oxidize the double bonds and carbonate the epoxides (Figure 6). If the pure tricarbate is obtained, this synthesis is tedious, with many successive synthesis and purification steps and the overall yield is strongly affected, reaching only 31 %.<sup>42</sup> Tetraols containing two couples of vicinal diols can also be carbonated for the synthesis of cyclic dicarbonates such as diglycerol,<sup>44–47</sup> erythritol<sup>48–50</sup> and threitol<sup>49</sup> (5CC). Interestingly, polyols containing 1,3 diols can be carbonated to obtain plurifunctional cyclocarbonate, containing 6CCs. They include ditrimethylolpropane<sup>43,51,52</sup> and pentaerythritol.<sup>53</sup> However, in those cases, the carbonating agent is always diphenyl carbonate or ethyl chloroformate which are both derived from phosgene in their commercial versions.



**Figure 6** : Synthesis pathways to obtain sorbitol di- and tricarbonate according to Mazurek-Budzynska *et al.*,<sup>43</sup> Furtwengler *et al.*<sup>41</sup> and Schmidt *et al.*<sup>36,42</sup>

## 2.2. Grafting of monofunctional cyclic carbonates on plurifunctional backbones



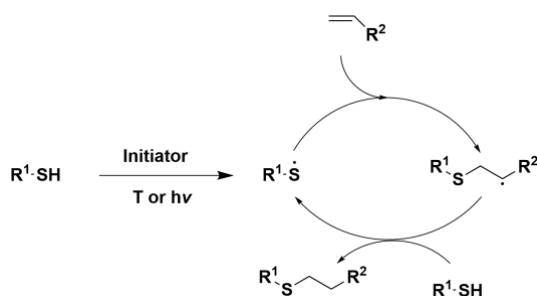
**Figure 7** : General scheme for the synthesis of poly(5CC)s and poly(6CC)s by grafting of monofunctional cyclic carbonates on plurifunctional backbones

Conveniently, several monofunctional 5CCs and 6CCs are commercially available. However, as such, they cannot be used for the synthesis of thermosetting PHUs. In many instances, these monofunctional CCs contain another reactive function, whose reactivity is orthogonal to those of the CC, and which can be used in a coupling reaction with a polyfunctional backbone (Figure 7). The resulting poly(cyclic carbonate)s can then be implemented in the synthesis of PHUs thermosets. The different grafting (or coupling) strategies developed in the literature are presented hereafter with a special emphasize on the mild synthetic approaches such as click-chemistry.



### 2.2.1. Precursor synthesis via thiol-ene reaction

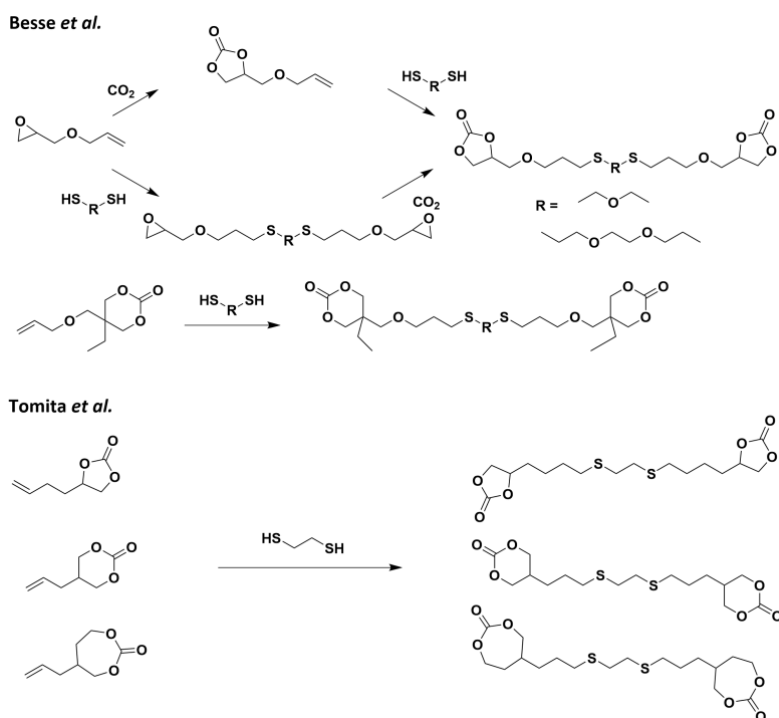
The thiol-ene reaction, which mechanism is represented in Figure 8, is one of the methods to synthesize multifunctional monomers. It usually consists in reacting monocarbonates containing terminal unsaturation with multifunctional thiols *via* a free-radical mechanism. This technique is particularly interesting since the thiol-ene reaction is a so-called “click” chemistry reaction, leading to almost total conversions under mild reaction conditions and generating no by-products.<sup>54</sup> Various authors have thus taken advantage of this reaction to synthesize bis-cyclic carbonates by grafting cyclic carbonates on polythiols backbones of different structures.<sup>18,55–63</sup>



**Figure 8** : Mechanism of the thiol-ene reaction

#### Thermal initiation

Besse *et al.* introduced the synthesis of 5CC and 6CC dicarbonates based on the thiol-ene reaction between allyl cyclic carbonate and dithiols (Figure 9).<sup>62</sup> In the first case, the allyl glycidyl ether (AGE) was first carbonated with CO<sub>2</sub> and the resulting allyl 5CC was grafted on dithiols. In the second case, trimethylolpropane allyl ether (TMPAE) was carbonated with ethyl chloroformate and the resulting allyl 6CC was grafted on the same dithiols. The corresponding 5CC and 6CC dicarbonates were obtained with 90 % and 77 % yields respectively. Alternatively, Besse *et al.* obtained the 5CC dicarbonates by first grafting AGE on the dithiols and then performing the CO<sub>2</sub>-carbonation but this strategy falls into the scope of paragraph 2.1.1. (*i.e.* polyepoxyde carbonation). More recently, Coste *et al.* synthesized a 6CC tetrafunctional monomer by reacting TMPAE with a tetrathiol, the pentaerythritol tetrakis(3-mercaptopropionate), using similar conditions and achieving 87 % yield.<sup>63</sup>

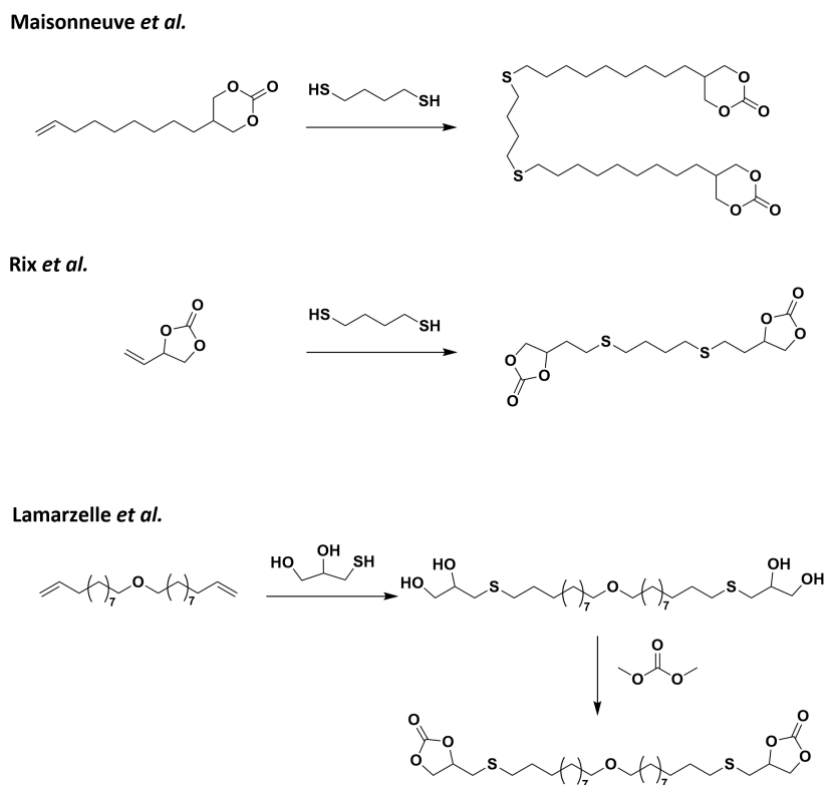


**Figure 9** : Synthesis strategies of plurifunctional monomers through thiol-ene reaction described by Besse *et al.*<sup>62</sup> and Tomita *et al.*<sup>55,56</sup>

Tomita *et al.* also used the thermo-activated thiol-ene reaction for the synthesis of 5-, 6-, and 7-membered cyclic dicarbonates. The corresponding alkene-terminated cyclic monocarbonates were reacted with ethanedithiol at  $T = 60\text{ }^{\circ}\text{C}$  (Figure 9).<sup>55,56</sup> In their case, the synthesis yields are much lower, between 50 and 60 % in the case of 5CC and 6CC and only 31 % in the case of 7CC dicarbonate. This is likely due to the lower reactivity of regular alkene as compared to allyl during the thiol-ene reaction.

#### Photochemical initiation

The thiol-ene reaction triggered by photochemical activation has also been exploited for the synthesis of cyclic dicarbonates. Maisonneuve *et al.* reacted an alkene-terminated 6CC with butanedithiol under UV-irradiation for 4h ( $\lambda = 254\text{ nm}$ ) at room temperature without any photoinitiator (Figure 10).<sup>58</sup> They obtained the corresponding 6CC dicarbonate with a yield of 37 %. According to the authors, the low yield is due to secondary reactions, in particular their experimental data are consistent with the ring opening of the cyclic carbonate. Recent work by Monie *et al.* teach us that thiols can react with cyclic carbonates by decarboxylative S-alkylation.<sup>64</sup> Thus, during the thiol-ene grafting two reactions are in competition: (i) the reaction of the thiol with the alkene, (ii) the reaction of the thiol with the carbonate. The latter is undesirable. In the case of Maisonneuve *et al.* study, the low yield of the synthesis is likely due to the combination of a highly reactive carbonate (6CC) and the absence of a free-radical photoinitiator thus limiting the efficiency of the thiol-ene reaction. In the end, the S-alkylation of the carbonates is more favored than the hydrothiolation of the alkenes.



**Figure 10** : Synthesis strategies of plurifunctional monomers through thiol-ene reaction described by Maisonneuve *et al.*<sup>58</sup>, Rix *et al.*<sup>59</sup> and Lamarzelle *et al.*<sup>60</sup>

Rix *et al.* also synthesized a bis-5 membered cyclic carbonate by thiol-ene reaction *via* a photochemical activation (Figure 10).<sup>59</sup> The mixtures of carbonate, dithiol and DMPA, used here as a photo-initiator, were irradiated at a wavelength  $\lambda = 365$  nm at room temperature. The dicarbonate is obtained with a yield of 100 % after 6 h of irradiation. In this case, the quantitative yield indicates that there are no secondary reactions. Indeed, the decarboxylative S-alkylation of the 5CC is very unlikely in the absence of a base. Moreover, the use of DMPA as a photoinitiator results in a dramatic increase of the thiol-ene kinetics. Overall, in this case, the hydrothiolation of the alkenes is much more favored than the decarboxylation of the cyclic carbonates.

Alternatively, the synthesis of a difunctional vicinal diol from thioglycerol and a fatty acid-derived diene in the presence of DMPA has been described by Lamarzelle *et al.* (Figure 10).<sup>60</sup> Complete conversion of the double bond is achieved after 1 hour of reaction at room temperature ( $\lambda = 365$  nm). The corresponding cyclic dicarbonate is then synthesized using dimethyl carbonate. In this example, the thiol-ene reaction appears as a tool for synthesizing a vicinal polyol which is further used in a synthetic strategy that falls in the scope of the paragraph 2.1.2 (*i.e.* carbonation of poly(vicinal diol)).

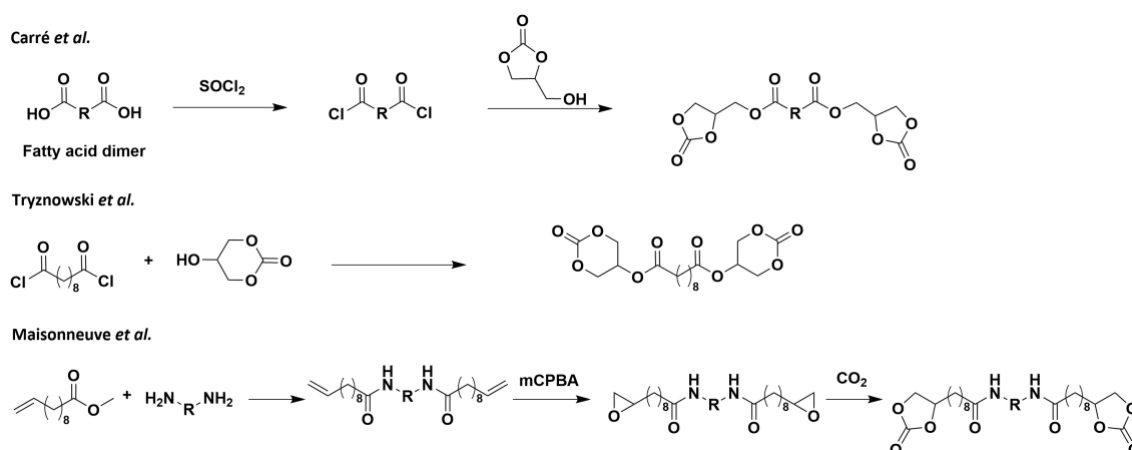
In the end, the thiol-ene reaction appears as a versatile tool for the synthesis of plurifunctional cyclocarbonates in mild conditions. This is well illustrated by its recurrent occurrence in the patent literature related to PHU synthesis.<sup>65-67</sup> Plurifunctional cyclocarbonates with functionality up to  $f=4$  were synthesized which can be easily implemented in the synthesis of PHU thermosets.

### 2.2.2. Precursors synthesis via esterification and amidation

Thanks to esterification and amidation, it is possible to couple mono- and multi-functional carboxylic acids to alcohols and amines respectively. These reactions are therefore particularly used for the synthesis of dicarbonates from biosourced fatty acids and their derivatives. For example, Carré *et al.* described the synthesis of cyclic dicarbonates by esterification of sebacic acid or fatty acid dimers with glycerol carbonate (Figure 11).<sup>68</sup> They used thionyl chloride to activate the carboxylic functions in the form of acyl chlorides. Yields above 99 % demonstrate the efficiency of this approach. Similarly, Rix *et al.* synthesized cyclic dicarbonates from glycerol carbonate and Pripol 1009 or one of its derivatives.<sup>59</sup> The synthesis yields are very high,  $\geq 90\%$ , highlighting once again the good performances of this synthetic pathway.

Tryznowski *et al.* also applied this technique to synthesize a 6-membered cyclic dicarbonate from sebacyl chloride and a 6CC bearing a hydroxyl group (Figure 11).<sup>69</sup> The 6CC dicarbonate was isolated with a 48 % yield. In this case, the efficiency of the reaction is limited by the isomerization of 6CC into 5CC *via* an intramolecular transcarbonation reaction. More generally speaking, the basic conditions necessary for the neutralization of the acid chloride released during the coupling reaction, can be problematic in the presence of 6-membered cyclic carbonates, less stable than their 5-membered counterparts. Therefore, this synthetic pathway seems less suitable for the synthesis of pluri-6CC.

Maisonneuve *et al.* presented the synthesis of a difunctional diene thanks to the reaction of 1,4-butanedi-amine with methyl undecylenate (Figure 11).<sup>70</sup> This new difunctional molecule is epoxidized and then carbonated, leading to a cyclic dicarbonate. This example demonstrates that an amidation reaction can be a useful tool to synthesize a polyepoxide and return to a more conventional strategy based on CO<sub>2</sub>-carbonation such as that mentioned in paragraph 2.1.1. Different diamines are also used by the authors in order to modify the structure of the monomer. The syntheses were made on several grams with yields  $\geq 44\%$  after the three synthetic steps.



**Figure 11** : Synthesis strategies of plurifunctional monomers through esterification and amidation described by Carré *et al.*<sup>68</sup>, Tryznowski *et al.*<sup>69</sup> and Maisonneuve *et al.*<sup>70</sup>

Mokhtari *et al.* also took advantage of this strategy to synthesize a precursor from jojoba and castor oils with a functionality  $f \geq 2$ .<sup>18</sup> First, thioglycolic acid is grafted onto the unsaturations of the triglycerides *via* thiol-ene reaction. Then, the resulting poly(carboxylic acid)s are transformed into plurifunctional cyclocarbonates through an esterification reaction with glycerol carbonate. Thanks to this two-step synthesis, it is possible to obtain vegetable oils containing terminal cyclic carbonate,

which are much more reactive than the pluri-5CC obtained through the CO<sub>2</sub>-carbonation of epoxidized vegetable oils (*c.f.* paragraph 2.1.1).

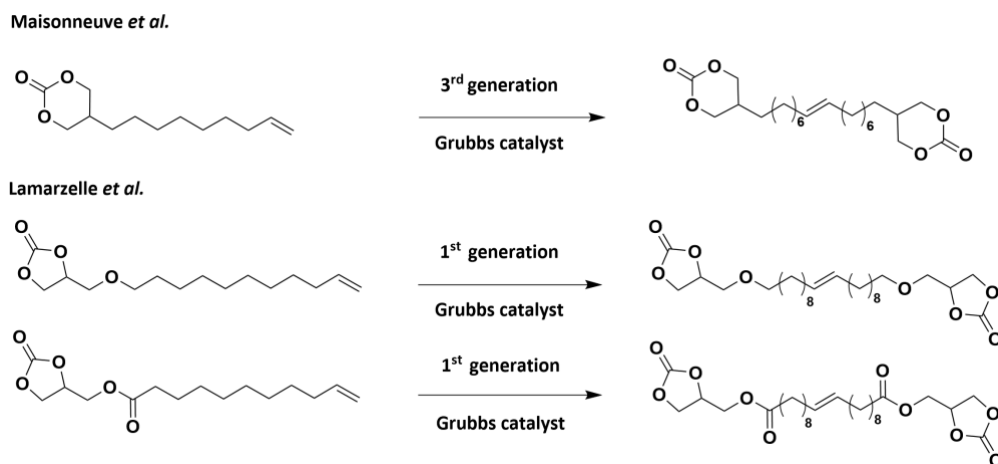
In addition to being an efficient synthetic route to obtain multifunctional monomers, the electron-withdrawing effect of the ester and amide functions on cyclic carbonates contributes to a significant increase of their reactivity, as it has been demonstrated during model reactions by Cornille *et al.*<sup>71</sup> and Lamarzelle *et al.*<sup>72</sup> The degradability of the polymers can also be improved by the presence of the hydrolysable ester functions.

To conclude, esterification and amidation are very efficient strategies for the synthesis of pluricyclic carbonates. They have been implemented for the synthesis of precursors of high functionality (> 3), essentially in the case of 5CC. Unfortunately, the syntheses usually rely on the use of harmful, and potentially explosive, chemicals such as acyl chloride and SOCl<sub>2</sub>. The future studies using these synthetic approaches will have to investigate milder coupling conditions to make it more suitable with the latest safety and environmental regulations.

### 2.2.3. Precursor synthesis via metathesis

The metathesis reaction between two carbonates containing a terminal double bond can be used to synthesize dicarbonates. Maisonneuve *et al.* described the synthesis of a 6CC biscarbonate by metathesis reaction of undecene-6CC (Figure 12).<sup>58</sup> The reaction is carried out at room temperature in anhydrous pentane with a third generation Grubbs catalyst. After 4 h of reaction and purification by column chromatography, the reaction yield reaches 50 %. Lamarzelle *et al.* also reported the synthesis of 5CC biscarbonates, activated by ether and ester groups (Figure 12).<sup>72</sup> In this case, the reactions carried out at room temperature with a Grubbs I type catalyst lead to complete conversions of double bonds, and a yield of 53 % after purification.

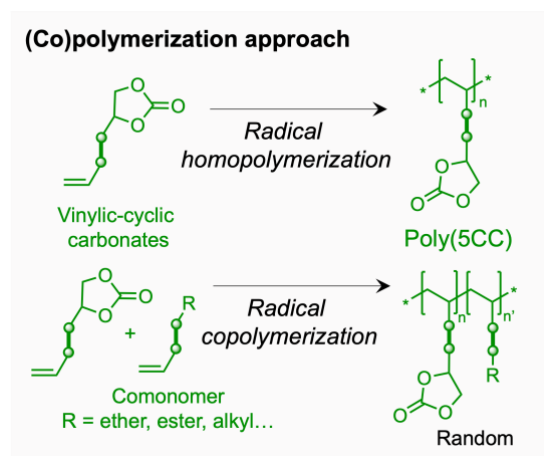
If this reaction may lead to quantitative conversion of monocarbonates into dicarbonates, the limited yields (~ 50 %) indicate that the purification steps necessary to eliminate the Grubbs catalysts result in a substantial loss of product. In addition, the inert synthesis conditions and the high cost of the catalysts can be an obstacle to the use of this technique in an industrial context. Finally, it should be noted that this method essentially leads to symmetrical dicarbonates. It is not possible to consider the synthesis of poly(cyclic carbonate) with a functionality  $\geq 3$ , *i.e.* the precursors that are the most adapted to the synthesis of thermosetting PHUs.



**Figure 12** : Synthesis strategies of plurifunctional monomers through metathesis described by Maisonneuve *et al.*<sup>58</sup> and Lamarzelle *et al.*<sup>72</sup>

### 2.3. (Co)polymerisation of monocyclic carbonate

Mono-cyclic carbonate containing another function of orthogonal reactivity (*e.g.* alcohol, CC double bond) are classically used for the synthesis of pluri-cyclic carbonate *via* a grafting approach, as demonstrated in the previous section. However, they were essentially coupled to difunctional backbones, thus providing pluri-cyclic carbonate with a functionality of  $f = 2$ . When the function of orthogonal reactivity can be engaged in a (co)polymerization reaction, it is possible to synthesize oligomers and polymers with dangling carbonate functions along their chains (Figure 13). This is especially the case with mono-cyclic carbonates containing radically polymerizable functions such as (meth)acrylate or allyl. The resulting oligomers and polymers are pluri-cyclic carbonates with  $f \gg 3$ , that can be straightforwardly implemented in the synthesis of thermosetting PHUs.<sup>40,73–79</sup>

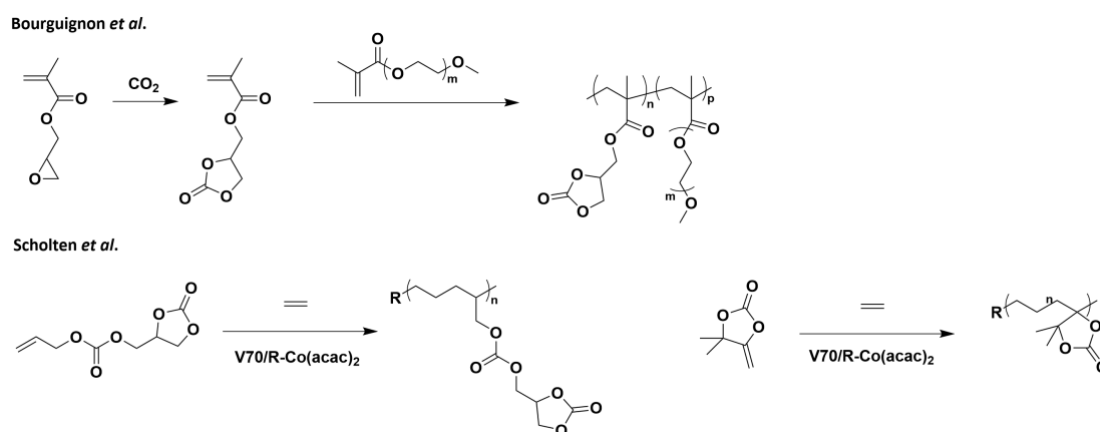


**Figure 13** : Synthesis strategies of plurifunctional monomers through the radical homopolymerization or copolymerization of alkene-containing carbonates

For instance, Bourguignon *et al.* synthesized water-soluble polymers carrying cyclic carbonate functions through radical copolymerization of glycerol carbonated methacrylate with various comonomers (Figure 14).<sup>78</sup> These highly functional monomers have been used to synthesize networks in water at

room temperature, with gel times between 1 and 35 min depending on the pH. These results are particularly interesting considering that PHU syntheses usually take place at high temperature ( $T \geq 70^\circ\text{C}$ ) for several hours.

Scholten *et al.* have copolymerized two cyclic carbonates having an allylic and  $\alpha$ -alkylidene double bond, respectively, with ethylene (Figure 14).<sup>73</sup> Depending on the reaction parameters of the radical copolymerization (*e.g.* type of initiator, ethylene pressure), polymers with variable molar masses have been synthesized. The resulting pluri-5CC present different functionalities,  $> 3$ , and can be used to obtain PHU networks after reaction with plurifunctional amines.



**Figure 14** : Synthesis of plurifunctional monomers through monocyclic carbonates co(polymerization) described by Bourguignon *et al.*<sup>78</sup> and Scholten *et al.*<sup>73</sup>

## 2.4. Summary and outlooks

It is possible to consider numerous substrates, in particular biosourced, for the synthesis of thermosetting PHUs thanks to the different strategies yielding multifunctional cyclic carbonate. If the carbonation of polyepoxides and polyols is the most common technique, the other synthetic methods, *i.e.* grafting and (co)polymerization of cyclic monocarbonates, are particularly interesting for the synthesis of multifunctional monomers with terminal cyclic carbonate functions, which are more reactive than the internal ones.

In addition, all these synthetic strategies can be exploited to create highly reactive monomers, *i.e.* 6 (or more)-membered and/or chemically activated cyclic carbonates. The diversity of monomer structures obtained through these methods can also improve the compatibilization with certain diamines, thus favoring the reactions according to mass processes, and possibly at moderate temperature.

Eventually, it is noteworthy that epoxides and polyols are the elementary bricks behind all the pluri-cyclic carbonates, independently of the synthetic strategy. Advantageously, epoxides are very easily converted into 5CC under  $\text{CO}_2$  pressure, the latter being a renewable resource. However, in many cases, they are derivatives of epichlorohydrin, which is known for being a highly toxic reagent.

Polyols precursors are safer surrogates. Conveniently, the vicinal diols and the 1,3-diols, necessary to synthesize 5CC and 6CC respectively, can be bio-sourced. Glycerol, erythritol or serinol are a few

representative examples. However, they have long been carbonated with toxic phosgene derivatives including diphenyl carbonate or ethyl chloroformate. Dialkyl carbonate (*e.g.* dimethyl carbonate) are innocuous alternatives which are increasingly used in the literature.<sup>48,49</sup> Despite several reports regarding the CO<sub>2</sub> carbonation of vicinal<sup>80–82</sup> and 1,3 diols,<sup>83–88</sup> very few works have been using these strategies to synthesize PHUs precursors so far.<sup>89,90</sup> In this context, the next generation of greener PHUs thermosets will rely on the latest progress regarding the CO<sub>2</sub> carbonation of biosourced polyols.

### 3. Synthesis of thermosetting PHUs : high- versus low-temperature curable systems

#### 3.1. Preamble

Historically, most thermosetting networks are obtained at high temperature for several reasons.<sup>91</sup> First of all, to obtain a 3D network, it is necessary to succeed in mixing the precursors homogeneously and, in the case of solid and/or viscous and/or incompatible precursors, this generally requires an input of thermal energy. Moreover, from a thermodynamic point of view, if the activation energy  $E_a$  of the elementary reaction is too high, then thermal energy is mandatory to accelerate its kinetics. Finally, working at high temperature is necessary to overcome the limits induced by the physico-chemical transformations of the growing network. For example, vitrification results in a drastic reduction of the molecular mobility and, in most cases, in the interruption of the reaction. It is then necessary to increase the reaction temperature above the  $T_g$  of the growing network to pursue the polymerization. The relationships between temperature and the physico-chemical transformations of the growing network over time (*e.g.* gelation, vitrification) is fundamental in thermosetting technology and it is often rationalized using TTT diagrams, for Time - Temperature -Transformation. This type of dynamic phase diagram, introduced by Gillham *et al.*, is a useful tool to distinguish the limits of the different phases of the growing thermosetting network – viscous or vitreous liquid and rubbery or vitreous gel – as a function of time and temperature.<sup>92</sup> Yet, for highly exothermic crosslinking reactions, the final  $T_g$  of the network can be higher than the setpoint temperature of the crosslinking reaction as, in this case, the actual temperature of the system can rise well above the setpoint temperature.

Considering these basic knowledges about thermosetting networks, the ideal room temperature curable system would be composed of liquid precursors, compatible in any proportion and reacting according to a low activation energy reaction. Moreover, the  $T_g$  of the final network would be lower than room temperature. If all these criteria cannot be met, there are methods to bypass the various abovementioned obstacles:

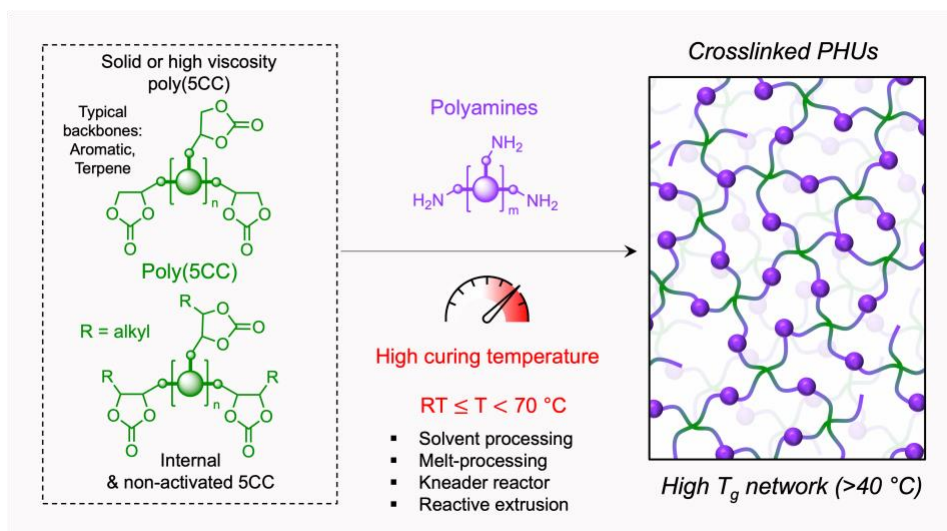
- The use of a solvent to mix solid and/or incompatible precursors. The solvent can also plasticize the growing network during the crosslinking reaction and therefore facilitate species mobility, or even prevent the vitrification of the network. However, a drying step at the end of the crosslinking will be necessary to get rid of the solvent, potentially at high temperature.
- The use of a catalyst to lower the activation energy  $E_a$  of the elementary crosslinking reaction.
- The use of an exothermic system to ensure that the temperature of the system is always higher than its theoretical glass transition temperature, even if the setpoint temperature is not.

With the first examples described in the early 2000s, the literature concerning thermosetting PHUs is still scarce compared to that of epoxy-amine or isocyanate-alcohol systems. Interestingly, the 5CC-amine reaction has often been described as being too slow and inefficient to synthesize PHUs in bulk at room temperature.<sup>55,71,72,93–95</sup> Thus, syntheses of thermosetting PHUs are generally carried out at



high temperature, *i.e.*  $T \geq 70^\circ\text{C}$ , in order to promote the homogenization of the monomers and the carbonate-amine reaction.<sup>9–17,20,23,25–29,31,32,36,38,39,45,68,96–103</sup> However, the following part of this literature review shows that an increasing number of references are reporting the synthesis of PHU networks at low temperatures, using several of the levers previously mentioned. Arbitrarily, the limit to discriminate the high- from the low-temperature curable systems was set at  $70^\circ\text{C}$ .

### 3.2. Synthesis of thermosetting PHUs at high temperature, $T \geq 70^\circ\text{C}$



**Figure 15** : Typical monomers and curing conditions used in the literature for the synthesis of crosslinked PHUs at high temperatures,  $70^\circ\text{C} \leq T$ .

Historically, the first PHUs thermosets were crosslinked at high temperatures. This is for two main reasons: (i) authors were using highly viscous or solid pluricyclic carbonates and (ii) the carbonates were not reactive enough in mild thermal conditions (Figure 15). Very quickly, it was realized that these curing conditions can be detrimental due to the initiation of many undesired side reactions that provoke changes in the polymer structure, e.g. by favoring the formation of urea linkages. However, high curing temperatures are also essential when high  $T_g$  networks are targeted (or at least super-ambient  $T_g$ ). The next section introduces the examples of the literature where crosslinked PHUs are obtained at high temperature. A special emphasize is dedicated to the reasons why a large input of thermal energy is needed, and to the strategies to limit the undesirable impacts of side reactions that come along.

#### 3.2.1. Solid and/or highly viscous precursors

In many cases, the synthesis of PHUs thermosets involves one or several solid precursors. A thermal energy input is then necessary to ensure their homogeneous mixing. Moreover, the resulting materials are usually high  $T_g$  networks, and elevated crosslinking temperatures are also required to avoid the vitrification during the crosslinking reaction. Thus, the crosslinking scheme of these materials usually relies on two steps: (i) one step at moderately elevated temperature ( $T \sim 70\text{--}80^\circ\text{C}$ ) to ensure the mixing of the precursors, (ii) a second step at higher temperature ( $T > 100^\circ\text{C}$ ) to ensure the completion of the

crosslinking reaction.<sup>9-13,17,20,25,28,32,36,39,40,99</sup> Different strategies are implemented to guarantee the efficient mixing of the precursors during the first step. Here, they are classified in three different sections:

#### Conventional mechanical stirring in bulk

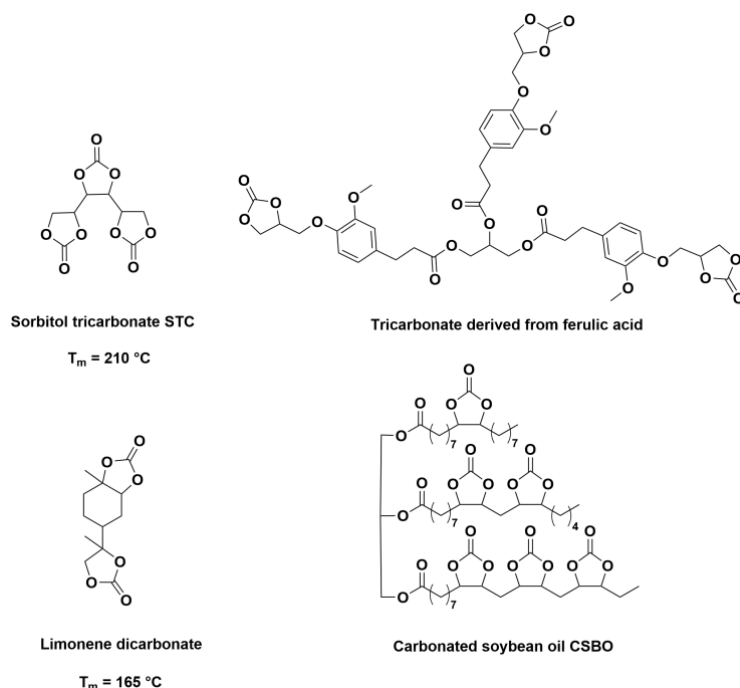
In many instances, the simplest strategy to ensure the efficient mixing of a solid pluri-cyclic carbonate with a polyamine at high temperature is conventional mechanical stirring.

A representative example is sorbitol tricarboxylate (STC, Figure 16). Indeed, it is a crystalline compound with a very high melting temperature ( $T_m \sim 210\text{ °C}$ ). In order to valorize STC, Schmidt *et al.* mixed it with a diamine according to two different procedures. In a first case, they grind STC at room temperature with the chosen diamine, for example Priamine 1074 or IPDA (both liquid), in order to obtain a liquid prepolymer. The latter is then degassed at 60 °C and the crosslinking reaction is completed at 80 °C for 16 h.<sup>42</sup> During a second study, a mixture of STC and sorbitol ether carbonate (a liquid pluri-cyclic carbonate) is heated beforehand to 100 °C in order to obtain a liquid mixture and thus facilitate the homogenization with the diamine. The material is crosslinked at 80 °C for 16 h and then at 100 °C for 4 h.<sup>36</sup>

Another biosourced carbonate that requires working at high temperature is limonene dicarbonate, (Figure 16). For example, Schimpf *et al.* dissolved the grinded dicarbonate in pentaerythritol tetracarboxylate (a liquid pluri-cyclic carbonate) at 130 °C.<sup>20</sup> Pentanediamine (5DA) is then added to the mixture of carbonates at 100 °C using a mechanical stirrer and the whole is crosslinked at 80 °C for 16 h then at 100 °C for 4 h.

Ménard *et al.* described the synthesis of thermosetting PHU from carbonated derivatives of ferulic acid (Figure 16) which are viscous liquids.<sup>39</sup> The preheating of the cyclic carbonates between 60 and 70 °C is required to lower their viscosity in order to homogeneously mix them with the chosen diamine. The authors indicate that the temperature of the system must be sustained until the beginning of the crosslinking procedure to avoid both vitrification and phase separation. The system is crosslinked in two stages, 5 h at 80 °C and 10 h at 100 °C, these two temperatures being respectively lower and higher than the temperature of the maximum of the exothermicity of the crosslinking reaction measured through DSC analysis.

Carbonated vegetable oils are also highly viscous and they usually need to be preheated to ensure their homogeneous mixing with diamines. For example, Tamami *et al.* reported that carbonated soybean oil (CSBO), whose structure is shown in Figure 16, must be preheated at 60 °C to be mixed with ethylenediamine (2DA) or hexanediamine (6DA).<sup>9</sup> The authors specify that, without this preheating step, homogenization with the diamines is not possible, even if the latter are liquid. Panchireddy *et al.* also reported the need to degas the carbonated soybean oil at 60 °C and then to mix it with the diamine at 50 °C for 3 min at 500 rpm to obtain a homogeneous reaction mixture.<sup>11</sup>



**Figure 16** : Structure of solid or viscous liquid pluricarbonates used for the synthesis of crosslinked PHUs<sup>9,10,19,20,36,39,42</sup>

### Use of solvents as diluent and plasticizer

The dissolution of the reactants in a minimum of solvent can also be a solution to ensure their homogeneous mixing, the solvent then being evaporated during the polymerization. This technique was implemented by Chen *et al.* who pre-dissolved all of the PHU thermoset precursors at room temperature, *i.e.* cyclic carbonates such as tri(4-hydroxyphenyl)methane tricarbonate (a solid carbonate), amines such as mxDA and the catalyst DMAP, in THF or DMF.<sup>35</sup> In these examples, the solvent represents 50 wt% to 80 wt% of the total mixture. The mixture is then heated at 80 °C for 12 h under a flow of argon in order to partially remove the solvent while synthesizing the polymer. The gel obtained at the end of this step is then placed under vacuum at 80 °C for 48 h to evaporate the last traces of solvent. This technique facilitates the mixing of the reagents at room temperature, thus limiting the loss of diamine, which is generally volatile at high temperature. Hu *et al.* have also applied this technique for the synthesis of PHU networks from sorbitol ether carbonate.<sup>14</sup> DMF is added to the tricarbonate-diamine mixture in order to reduce its viscosity and to ensure its homogeneity. In this example, the solvent represents approximately 60 wt% of the total mixture. After 24 h of crosslinking at 80 °C, the resulting gel is placed under vacuum for 24 h at 80 °C in order to evaporate the remaining DMF. Recently, Liu *et al.* reported the synthesis of crosslinked PHUs from TMPTC and 2DA *via* a solvothermal route.<sup>26</sup> The crosslinking takes place in an autoclave at 230 °C in ethanol for 12 h and the latter is then distilled under vacuum.

Despite its effectiveness, this technique is not relevant from an industrial point of view, because it relies on the use of potentially flammable and/or toxic solvents. Moreover, the additional drying step results in a more complicated curing process.

### Kneader reactor or twin-screw extruder

In some cases, the homogeneous mixing of the PHU precursors can remain complicated due to the viscosity of the precursors, even at high temperature, or the insolubility of the monomers in usual organic solvents. Kneader reactors or twin-screw extruders can be alternative solutions to facilitate the melt processability of the mixtures.

Poussard *et al.* as well as Grignard *et al.* used a kneader reactor to mix a viscous carbonated soybean oil with a solid amino end-terminated oligoamide (melting point  $\sim 65$  °C).<sup>15,16</sup> The later was first introduced in the kneader. When molten, the carbonated soybean oil was added, and the reaction was conducted for 3 h at 120 °C (rotating speed 30 rpm). This process facilitates the homogenization of the systems, which is initially extremely difficult, and therefore offer to use new formulations for the synthesis of PHU.

More recently, Magliozzi *et al.* described the synthesis of high molar mass linear PHUs by reactive extrusion of diglycerol dicarbonate (DGDC), a solid dicarbonate derived from diglycerol, with different diamines.<sup>3</sup> The same approach was used for the synthesis of thermoset PHUs.<sup>45</sup> To do so, the extruder is preheated at 90 °C and the DGDC is introduced first in order to melt it. Next, tris(2-aminoethyl)amine, a trifunctional amine, is introduced in a stoichiometric amount. The polymerization in the extruder is stopped after 5 min because the machine is no longer able to mix the reaction medium due to gelation. The crosslinked polymer is then removed from the circulating channel of the extruder and post-cured at 90 °C for 3 h to reach the complete conversion of the carbonate functions. The resulting polymer is a densely crosslinked network with a swelling ratio in THF of 15 % and a gel fraction of 94 %. Thanks to this extrusion process, the implementation of mass polymerization was greatly facilitated and it was possible to synthesize a highly crosslinked and homogeneous network in a short period of time at a rather low temperature (90 °C). The extent of side reactions was greatly limited in these conditions.

It is important to note that, in these examples, it is necessary to finely tune the kinetics of the reaction if one wants to inject the growing network in a mold before the gelling point, and thus obtain well defined final shapes.

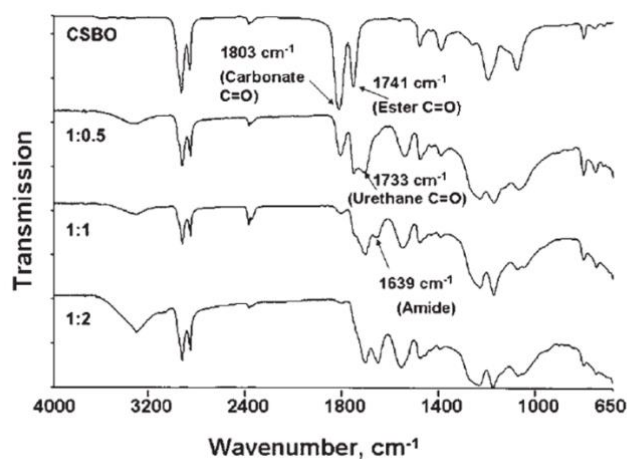
#### 3.2.2. Low-reactivity precursors

Many thermosetting PHUs syntheses must be carried out at high temperature because the carbonated precursors are not reactive enough at  $T < 70$  °C. This is especially the case with carbonated vegetable oils.<sup>9,10,12–17,99,101</sup> Although these oils are widely used for the synthesis of PHUs, they are poorly reactive because of the internal position of the cyclic carbonates.

For example, carbonated soybean oil (CSBO) has been extensively used for the synthesis of cross-linked biobased PHUs. In the first publication reporting the synthesis of thermosetting PHUs, Tamami *et al.* synthesized CSBO by CO<sub>2</sub>-carbonation of epoxidized soybean oil (ESBO) and obtain crosslinked PHUs by reacting CSBO with diamines (*e.g.* ethylenediamine or hexamethylenediamine).<sup>9</sup> After preheating CSBO at 60 °C to lower its viscosity and adding the diamine, the mixture is cured in two stages: 10 h at 70 °C and 3 h at 100 °C. These two high-temperature crosslinking steps are necessary to ensure the complete conversion of cyclic carbonates and to obtain highly crosslinked networks, with gel fractions varying between 89 and 94 %.

Since then, CSBO has been used in a lot of studies for the synthesis of crosslinked PHUs. They all involve crosslinking schemes of several hours in two stages at  $T \geq 70\text{ }^{\circ}\text{C}$ <sup>11,13</sup> or in a single stage at higher temperature,  $T = 120\text{ }^{\circ}\text{C}$ , in a kneader reactor.<sup>15,16</sup> In the latter case, the kinetics of reaction remain long,  $\sim 3\text{ h}$ , when compared to precursors containing terminal carbonates. For instance, in the case of trimethylolpropane triglycidyl carbonate (TMPTC), the carbonates are fully converted after 10 min at  $70\text{ }^{\circ}\text{C}$ .<sup>38</sup> Thus, it seems difficult to work with vegetable oils at low temperature for both processing and reactivity issues.

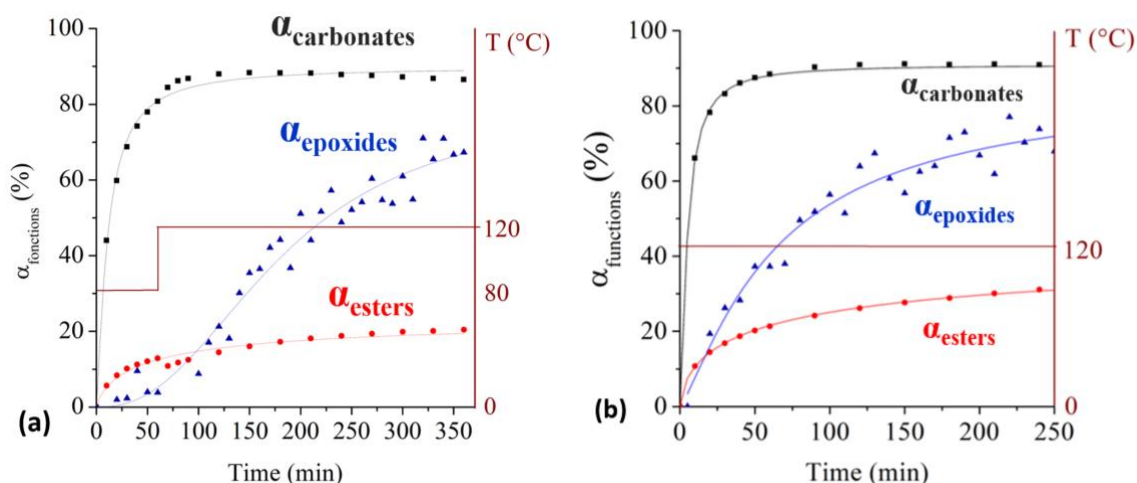
However, at too high temperatures, side reactions can take place, limiting the extent of the crosslinking reaction. Javni *et al.* investigated the impact of these side reactions.<sup>12</sup> The authors worked on the synthesis of crosslinked PHUs from CSBO and aliphatic diamines following the same crosslinking protocol as Tamami *et al.*<sup>9</sup> They observed that the networks are well crosslinked, with soluble fractions between 6 and 11 %. However, the analysis of the latter reveals the presence of amide and glycerol functions, resulting from the aminolysis of the esters. This secondary reaction was clearly highlighted by infrared spectroscopic monitoring of the crosslinking reaction (Figure 17) but also by model reactions with unmodified soybean oil. The results indicate that, even at  $T \leq 100\text{ }^{\circ}\text{C}$ , the esters of vegetable oils are sensitive to aminolysis. Thus, in the case of PHU synthesis from carbonated vegetable oil, the selectivity of the crosslinking reaction is limited due to the initiation of the amidation side reaction at temperatures as low as  $70\text{ }^{\circ}\text{C}$ . A compromise in terms of temperature must then be found in order to ensure both the homogenization of the reagents and the aminolysis of the carbonates while limiting that of the esters.



**Figure 17** : Infrared spectra from the monitoring of the crosslinking reaction between CSBO and 4DA at different CSBO : diamine ratio according to Javni *et al.*<sup>12</sup>

Recently, Helbling *et al.* further investigated the relative reactivity of carbonates and esters, but also of epoxides, by studying the crosslinking reaction of a partially carbonated ESBO with different diamines.<sup>104</sup> A dual-spectroscopic monitoring (infrared and Raman) indicates that cyclic carbonates are more reactive than epoxides, the latter being more reactive than esters. Based on this comprehensive knowledge of the functions reactivity, the authors demonstrate that the extent of ester aminolysis can

be minimized by using a two-stage curing schedule with a first step at 80 °C for 1 h and a second step at 120 °C for 5 h. Figure 18a represents the conversion of the different moieties as a function of time for the two-stage curing schedule while Figure 18b represents the same conversion profiles for a one-step curing schedule at 120 °C for 6 hours. Clearly, the final ester conversion is of about 20 % in the first case against 30 % in the latter case. Furthermore, the gel content of the resulting thermosets decreases from 85 % for the two-stage curing schedule to 80 % for the single stage approach. This curing methodology appeared as a good technique to limit the side reactions by favoring first the reaction of cyclic carbonates with amines at 80 °C, and then the reaction of epoxides at 120 °C.

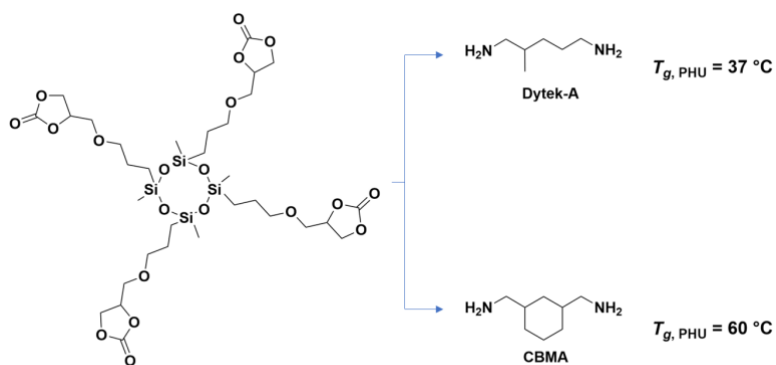


**Figure 18** : Conversion curves of cyclic carbonates, epoxides and esters as a function of time in the case of the reaction between partially carbonated epoxidized soybean oil and octanediamine a) following a two-step curing schedule; b) at 120 °C by Helbling *et al.*<sup>104</sup>

### 3.2.3. Super-ambient and high $T_g$ networks

Networks which  $T_g$  is higher than the reaction temperature can be tough to synthesize due to the vitrification of the reaction medium, limiting the molecular mobility. When targeting high  $T_g$  networks (or at least super-ambient  $T_g$ ), it is thus essential to work at high temperature to promote the growth of the network.

For example, Ecochard *et al.* obtained networks with  $T_g > 35^\circ\text{C}$  by reaction of siloxane D4 monomers bearing four 5CC functions with an aliphatic diamine, 2-methylpentane-1,5-diamine (Dytek-A) and a cycloaliphatic diamine, 1,3-Cyclohexanebis(methylamine) (CBMA) (Figure 19).<sup>40</sup> The networks were cured 4 h at 80 °C then 1 h at 100 °C. With the diamine Dytek-A, the  $T_g$  of the polymer is 37 °C while with CBMA it is increased to 60 °C. Although the crosslinking temperatures are higher than the  $T_g$  of the final networks, the conversion of carbonate is limited to 86 % in the case of Dytek-A. According to the authors, this conversion limit is due to the high viscosity of the reaction medium resulting from strong hydrogen bonding. The authors stress that it is mandatory to use high crosslinking temperatures to increase the molecular mobility of the growing network. But this is accompanied by a larger extent of side reactions that might explain the limited 5CC conversion as well.



**Figure 19** : Tetrafunctional cyclic carbonate D4 C5 developed by Ecochard *et al.* and used for the synthesis of thermoset PHU with two different diamines, Dytek-A and CBMA<sup>40</sup>

Numerous authors used a very similar crosslinking schedule (*i.e.* first step at 80 °C then second step at 100 °C) for the synthesis of networks with super-ambient  $T_g$  (typically  $40\text{ °C} \leq T_g \leq 70\text{ °C}$ ). For instance, Schimpf *et al.* developed partially biobased thermosetting PHU based on limonene dicarbonate.<sup>20</sup> The latter was reacted with increasing amount of pentaerythritol tetracarboxylate (from 10 wt% to 50 wt%) and with stoichiometric amount of pentamethylene diamine (5DA). The  $T_g$ s of the resulting networks are comprised between 45 and 62 °C. The mixtures were all cured according to a two-step scheme, *i.e.* 16 h at 80 °C then 4 h at 100 °C, in order to ensure the completion of the crosslinking reaction of the rigid and brittle networks. Similarly, Ménard *et al.* developed high  $T_g$  networks by reacting an aromatic pluricyclic carbonate obtained from ferulic acid with a series of diamines, including IPDA, 1,10-decanediamine (10DA) and EDR-148.<sup>39</sup> The networks were cured at 80 °C for 5 h then at 100 °C for 10 h, and their  $T_g$ s vary from 38 to 72 °C depending on the amine. The authors stress that they have intentionally slowed down the reaction kinetics by initially working at 80 °C in order to avoid a too fast vitrification of the reaction medium, which would have limited the aminolysis of the carbonates.

In another representative example, Schmidt *et al.* synthesized very high  $T_g$  PHU networks by reacting mixtures of sorbitol tricarboxylate (STC, solid) and sorbitol ether tricarboxylate (STEC, liquid) (Figure 16) with isophorone diamine (IPDA).<sup>36</sup> The  $T_g$ s of the networks increase from 140 °C to 180 °C by increasing the amount of STC, the stiffest precursor, from 0 wt% to 20 wt%. For 0 wt% of STC, the network was cured at 80 °C for 16 h and then at 100 °C for 4 h. The first curing step is necessary to avoid the instantaneous gelation of the network that would limit the aminolysis of the carbonates. This step also facilitates the shaping of the polymer since at 100 °C, the gel point is reached in less than one minute. Remarkably, in this case, the  $T_g$  of the final network (140 °C) is larger than the highest curing temperature, suggesting that the reaction is exothermic enough to be self-sustained. When STC is added to the carbonate mixtures, the  $T_g$ s are larger than 160 °C and a third crosslinking step at 170 °C for 1 h is necessary to complete the crosslinking reaction. For 20 wt% of STC, the  $T_g$  reach the top value of 180 °C, suggesting once again that the reaction is completed thanks to the in-situ input of thermal energy due to its exothermicity.

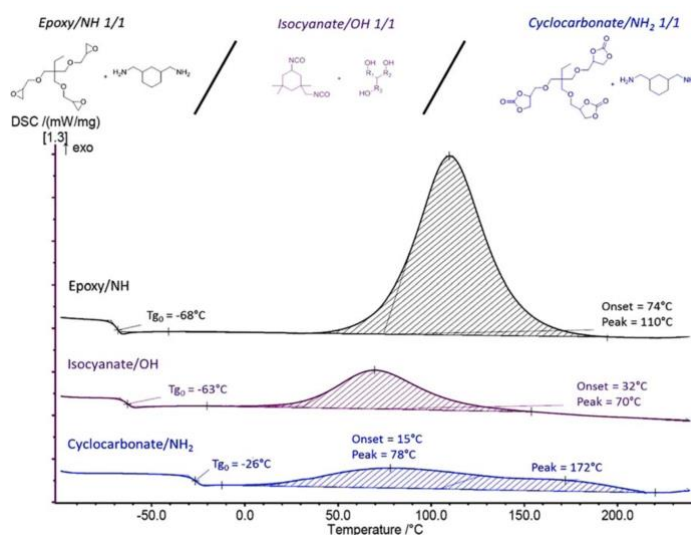
Remarkably, in all the above-mentioned examples, a curing step at high temperature is necessary to complete the crosslinking reaction, however it must be preceded by a first curing step at a moderate

temperature to avoid the instantaneous gelation of the network. Just like vitrification, premature gelation can be detrimental to the formation of homogeneous and densely crosslinked networks.

### 3.2.4 Summary and outlook

To conclude, the synthesis of thermosetting PHUs has long been conducted at high temperatures for several reasons. First, the carbonate precursors are often viscous liquids or solids that must be melt-processed at high temperature. Furthermore, the carbonate-amine reaction is often considered as a slow reaction that requires high temperature to reach full completion over descent periods of times. On top of that, high curing temperatures are mandatory when high  $T_g$  PHU thermosets are targeted.

In their comprehensive study of the curing reaction of thermosetting PHUs, Blain *et al.* compared the carbonate-amine reaction to other conventional chemistries used in thermosetting technologies such as the epoxy-amine and the isocyanate-alcohol reactions.<sup>105</sup> Figure 20 represents the DSC thermograms for three curing systems using precursors of similar structures and based respectively on the epoxy-amine, the isocyanate-alcohol and the carbonate amine chemistry. Clearly, the exotherm of the carbonate-amine system is more diffused than the two other systems. More importantly, it is bimodal with a first peak at rather low temperatures (78 °C) and a second peak at high temperature (172 °C). The authors demonstrated that both peaks can be attributed to the reaction of carbonate with amine. The reaction proceeds in two steps with a second peak at high temperature because an extra input of thermal energy is necessary to compete with the inter-chain hydrogen bonds formed during the first stage of the curing reaction. Unfortunately, Blain *et al.* also observed that side reactions, such as urea formation, are initiated during the second step at high temperature.



**Figure 20** : Study of the enthalpy of reaction of several reactive systems monitored by DSC: epoxy/amine, isocyanate/alcohol, cyclocarbonate/amine according to Blain *et al.*<sup>105</sup>

It is thus critical to finely tune the curing temperatures of PHUs thermosets to obtain a good balance between the kinetics of the carbonate-amine reaction and those of the undesirable side reactions. Interestingly, in the same study, Blain *et al.* stress that the aminolysis of activated carbonate can be initiated at room temperature as emphasized in Figure 20. Indeed, the onset of the exotherm of the

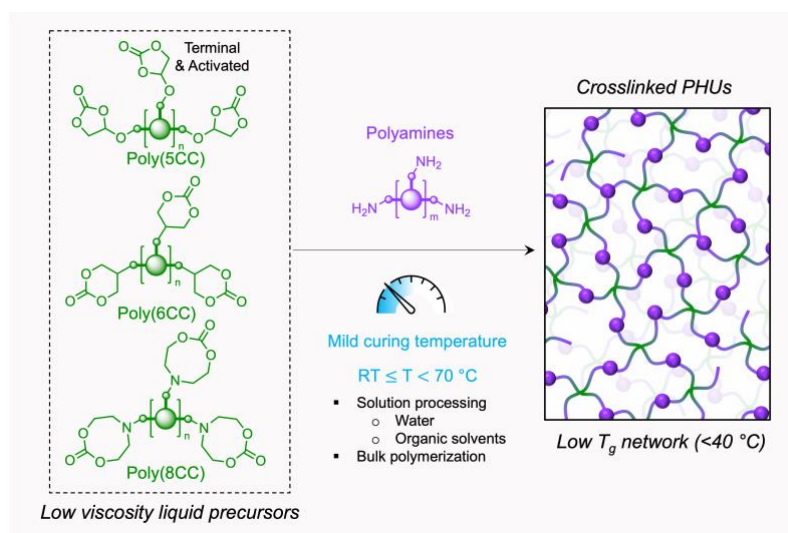


carbonate-amine reaction is observed for  $T_{\text{onset}} = 15\text{ }^{\circ}\text{C}$  (against  $T_{\text{onset}} = 32\text{ }^{\circ}\text{C}$  for the isocyanate-alcohol system and  $T_{\text{onset}} = 74\text{ }^{\circ}\text{C}$  for the epoxy-amine system). This result indicates that, providing a solution is found to circumvent the decrease of the reaction kinetics due to hydrogen bonding, it is in theory possible to form a PHU network at room temperature. This is highly desirable for two reasons. First, low curing temperatures guarantee a lesser extent of side reactions. Second, room temperature curable systems are highly desirable in a myriad of applications such as adhesives, sealing, coating, 3D-printing, etc.

Recently, several authors have introduced carbonate-amine systems that can be fully crosslinked at low temperature ( $T < 70\text{ }^{\circ}\text{C}$ ), including room temperature. They are presented hereafter with a special emphasize on the technical approaches as well as the chemical features of the precursors allowing low temperature curability.

### 3.3. Synthesis of thermosetting PHUs at low temperature, $\text{RT} \leq T < 70\text{ }^{\circ}\text{C}$

The synthesis of PHU thermosets at moderate temperature, such that  $\text{RT} \leq T < 70\text{ }^{\circ}\text{C}$ , reduce the extent of side reactions but is also interesting from an energy point of view. In addition, room temperature curable PHU thermosets could be used by non-professional users for outdoor and “do it yourself” applications (*e.g.* painting, coating, sealing). The idea that the low reactivity of cyclic carbonates is the main obstacle to their use at moderate temperature has long been maintained. However, some chemically activated monomers appear to be reactive enough in mild temperature conditions. Examples of syntheses of thermosetting PHUs at moderate temperature from 5CC<sup>78,106–109</sup> but also from 6CC<sup>8,52,63,106,110–112</sup> and 8CC<sup>113</sup> precursors, are described in the literature and are presented hereafter (Figure 21).



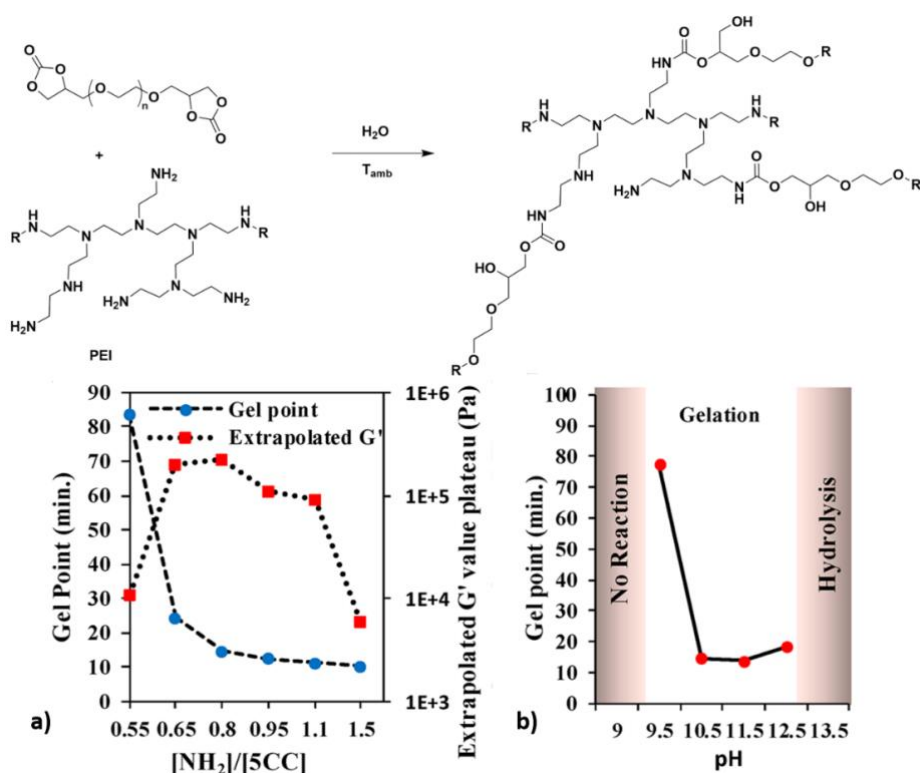
**Figure 21** : Typical monomers and curing conditions used in the literature for the synthesis of crosslinked PHUs at mild temperatures,  $\text{RT} \leq T < 70\text{ }^{\circ}\text{C}$ .

#### 3.3.1. Polymerization in solution

Blain *et al.* demonstrated that the reaction of activated cyclic carbonates with amines can be initiated at room temperature (RT) but that an increase of the curing temperature well above RT is mandatory to compete with inter-chains hydrogen bonding and fully complete the crosslinking reaction.<sup>105</sup> One possible alternative to the temperature increase is to use a solvent that breaks the hydrogen bonds, thus providing sufficient molecular mobility to the growing network to sustain the reactivity until the completion of the crosslinking reaction.

### Hydrogels

Bourguignon *et al.* obtained crosslinked PHUs at RT in water with the aim of synthesizing hydrogels.<sup>78,108</sup> They first developed a one-step synthesis of PHU hydrogels at RT by reacting a dicarbonate derived from polyethylene glycol with polyethyleneimine (PEI) in water as shown in Figure 22.<sup>108</sup>



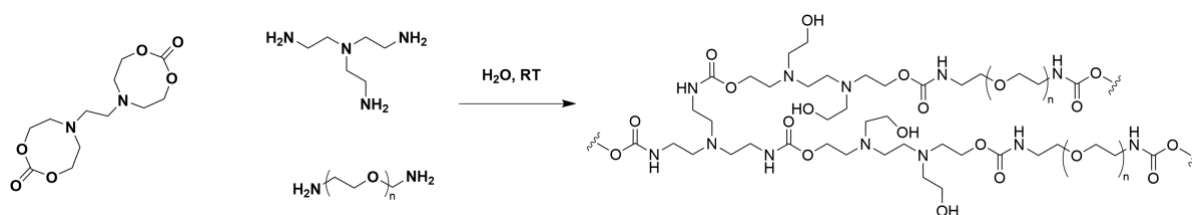
**Figure 22** : Evolution of gel points measured during PHU hydrogels syntheses at room temperature as a function of a) the ratio  $[NH_2] : [5CC]$  at pH = 10.5 b) the pH at a ratio  $[NH_2] : [5CC] = 0.8$  according to Bourguignon *et al.*<sup>108</sup>

For this, an aqueous solution of PEI at a pH between 9 and 12.5 is added to the cyclic dicarbonate and the mixture is left for 24 hours at room temperature until crosslinking. The optimum pH was determined thanks to model reactions with the diamine 2,2'-ethylenedioxy bis(ethylamine). Thus, a high pH,  $\sim 12.5$ , leads to the hydrolysis of 5CCs and limits the formation of hydroxyurethanes, which only corresponds to 60 % of the conversion of carbonates after 16 h of reaction. At a lower pH,  $\leq 9$ , the aminolysis of the carbonate is no longer operative due to the protonation of the amine, whose  $pK_a$  is 9.7. Finally, the intermediate pH of 10.5 leads to the aminolysis of carbonates while limiting the hydrolysis of 5CC to only 9 mol% after 16 h of reaction. The investigation of the curing reaction at pH = 10.5 indicates that the gel point is reached in only 15 minutes for an optimum functional ratio of  $[NH_2] : [5CC] = 0.8$  (Figure 22). Furthermore, analysis of the dried sample by infrared spectroscopy

indicates that the conversion of cyclic carbonates is complete in that case. The resulting hydrogel is rigid and exhibits the highest gel fraction of the series of hydrogels synthesized in this study, *i.e.* 85 % (measured after 48 h of immersion in water).

In another study Bourguignon *et al.* describes the synthesis of a new series of hydro-soluble poly(5CC)s by copolymerization of glycerol carbonated methacrylate with different hydrophilic co-monomers (both neutral and ionic).<sup>78</sup> The poly(5CC)s were then reacted with commercial diamines at RT in water. After pH optimization for each diamine, gel times shorter than 5 min were measured in rheology and the full conversion of cyclic carbonates was confirmed by infrared spectroscopy. Interestingly, the poly(5CC)s obtained from the copolymerization of glycerol carbonated methacrylate with polyethylene glycol methyl ether methacrylate leads to the synthesis of thermoresponsive gels with lower critical solution temperatures in water.

Fanjul-Mosteirin *et al.* took advantage of the high reactivity of N-substituted 8-membered cyclic biscalconates to synthesize semi-crystalline hydrogels with the triamine TAEA and poly(ethylene glycol) diamine at RT (Figure 23).<sup>113</sup> The reagents, mixed in water, react overnight at room temperature to give hydrogels. The complete conversion of the 8CC was confirmed by infrared spectroscopy. Moreover, the curing reaction is monitored by rheology in order to investigate the impact of the reactant concentrations and ratios on gel times. The greater the amount of water in the formulation, the slower the gelation, with a gel point reached in 5.8 h for 50 wt% of water against 12.5 h for 70 wt%. Furthermore, an increase in the quantity of triamine TAEA from 20 mol% to 60 mol% (as compared to the diamine) results in a sharp decrease of the gel time from ~30 h to 3.3 h (70 wt% water). Interestingly, the hydrogels containing less than 35 wt% of water are thermoresponsive. An increase in temperature from RT to 60 °C leads to a significant decrease of their storage modulus  $G'$ , from 1 MPa to ~ 2 kPa with a transition between 35 °C and 45 °C, while a decrease in temperature results in a sharp increase of  $G'$  back to its initial value for  $T = 27$  °C. The correlation between the melting-crystallization transition of the poly(ethylene glycol) skeleton of the diamine and the reversible changing of the mechanical response was confirmed by DSC analysis. This thermoresponsivity is then exploited to 3D-print the hydrogel *via* an extrusion process. Finally, the cytocompatibility of these 3D-printed structures was investigated to confirm their potential use in biomedical applications.

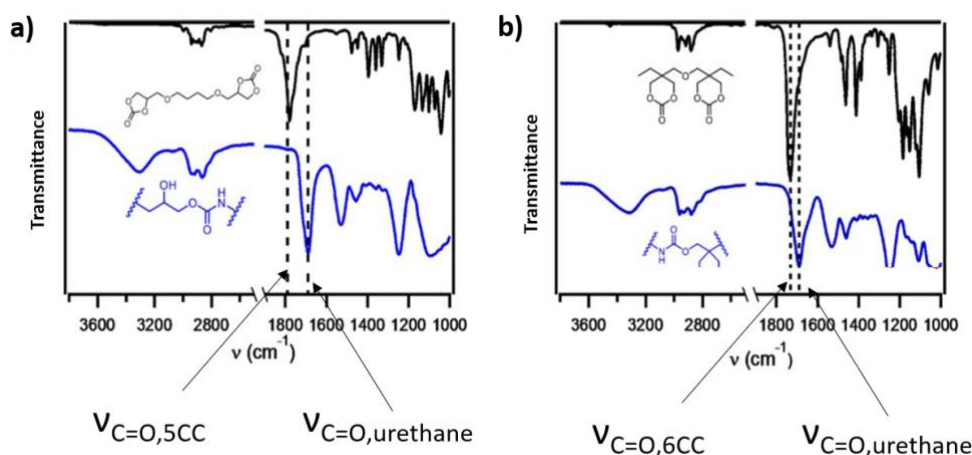


**Figure 23** : Synthesis of crystalline PHU hydrogels at room temperature according to Fanjul-Mosteirin *et al.*<sup>113</sup>

### Curing in organic solvents

PHUs thermosets have been synthesized at moderate temperature in volatile organic solvents.<sup>8,52,106,111,114</sup> In these examples, the role of the solvent is to homogenize the initial reaction medium, but it also acts as a plasticizer that will mitigate the impact of hydrogen bonding, and the potential vitrification of the growing network.

For example, Fortman *et al.* synthesized two PHU thermosets by reacting butanediol glycidyl carbonate, (a bis(5CC)) and di(trimethylolpropane) carbonate (a bis(6CC)), respectively, (Figure 24) with a mixture of hexamethylenediamine and the triamine tris(2-aminoethyl)amine. The reactants were initially dissolved in dichloromethane (typically 75wt% of solvent).<sup>106</sup> The mixture is left at room temperature for 24 h, resulting in a gel after only 1 h of reaction. The latter is then placed under reduced pressure at 90 °C for 2 days to fully evaporate the solvent. The infrared analysis of the gels obtained after 24 h at room temperature reveals the total conversion of the carbonates, for both the 5CC and the 6CC precursors (Figure 24). The final networks are highly crosslinked, with a gel fraction  $\geq 94$  %. They are thermally stable up to 270 °C, with super-ambient  $T_g$  comprised between 35 and 55 °C and elastic modulus between 1.2 and 4.5 MPa at 100 °C. Interestingly, the PHUs based on the 6CC precursor are vitrimers. They can be reprocessed at high temperature (160 °C) *via* compression molding thanks to the transcarbamoylation reaction between the primary hydroxyl and the urethane moieties contained in the network. On the contrary, the reprocessed PHUs based on the 5CC precursor exhibit lower mechanical properties and coloration, likely due to irreversible degradation of the network *via* initial reversion of the PHU linkage and subsequent side reactions of the liberated amine and cyclic carbonate.



**Figure 24** : IR spectra of bis-carbonates a) 5CC and b) 6CC but also of the PHU networks synthesized by the reaction of 5CC or 6CC with TAEA in 24 h at room temperature according to Fortman *et al.*<sup>106</sup>

In a similar fashion, Feng *et al.* synthesized PHUs vitrimers by reacting the same bis(6CC) precursors with tris(2-aminoethyl)amine *via* a solvent-mediated process.<sup>111</sup> The bis(6CC) and the triamine were dissolved separately in dichloromethane (a total amount of approximately 80 wt% of solvent) and the two solutions were combined to provide a crosslinked system after 12 h at room temperature. The carbonate conversion and the gel content were not investigated but the resulting polymer is a transparent, self-standing material, with a stress and a strain at break of 1.5 MPa and 40 % respectively, as measured by tensile testing. After a 18 h post-curing step at 90 °C, the stress and the strain at break become 37 MPa and 4.4 %, respectively. This was attributed to further elimination of residual traces of solvent and to the completion of the crosslinking reaction, but again it was not confirmed by infrared or swelling test investigation. Interestingly, the authors demonstrated that these materials exhibit intrinsic luminescence under UV irradiation ( $\lambda = 365$  nm). This is unusual for nonconjugated polymers, and it is attributed to electron cloud overlapping in clusters of carbamate moieties. The luminescence

of these PHUs was exploited to prepare a composite with paper that could be of interest for anti-counterfeiting applications.

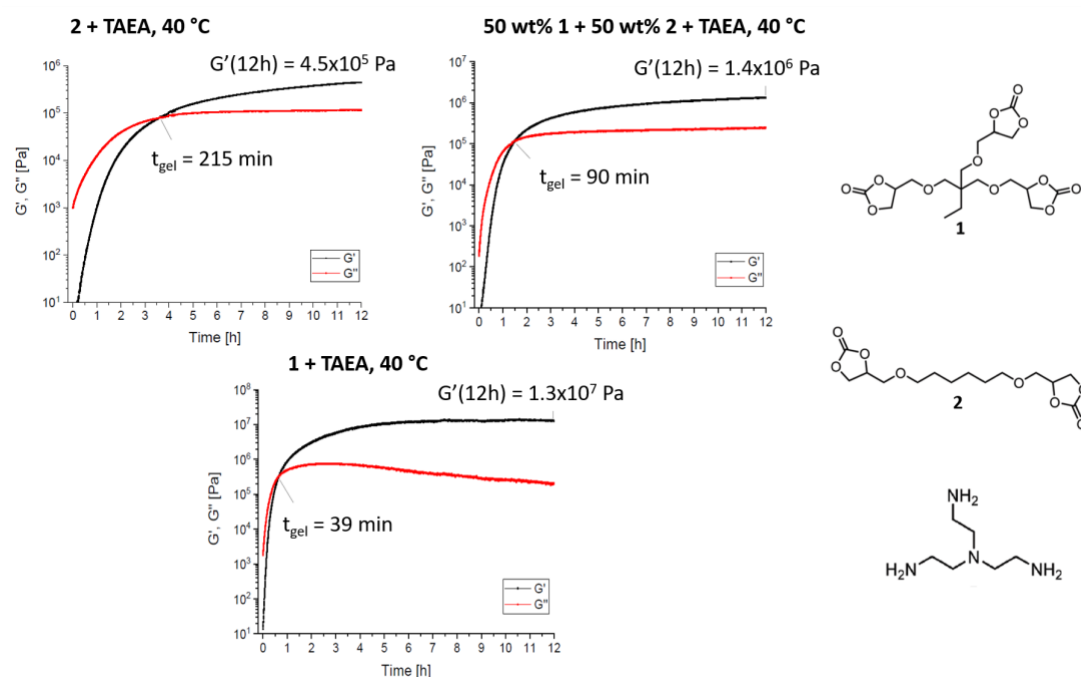
To conclude, solvent processing is a very effective approach to observe the crosslinking reaction of PHU thermosets at room temperature. However, it relies on the use of large quantities of volatile solvents that can be dangerous for human health and the environment. Moreover, this approach is not viable for most industrial applications.

### 3.3.2. Bulk polymerization

Mass polymerization is preferred to solvent mediated processes in an industrial context, notably for adhesive and coating applications.<sup>115</sup> In principle, this is a simple approach, but it can be constrained by several phenomena including an insufficient homogenization of the reactants or the interruption of the crosslinking reaction due to excessive viscosity or vitrification. Each of these constraints can be circumvented by a temperature increase. However, in some cases, it is possible to obtain fully crosslinked PHUs using mild curing temperatures (< 70 °C). To do so, the authors used highly reactive (activated) and easily processable liquid carbonates.<sup>63,116</sup> In some cases, the carbonate-amine reaction was further promoted by using a suitable catalyst.<sup>107,117</sup> Another approach consists in using hybrid systems, *i.e.* functional (oligo)hydroxyurethanes that can be crosslinked according to another chemistry (thiol-ene, Michael addition, etc.).<sup>109,110,112</sup>

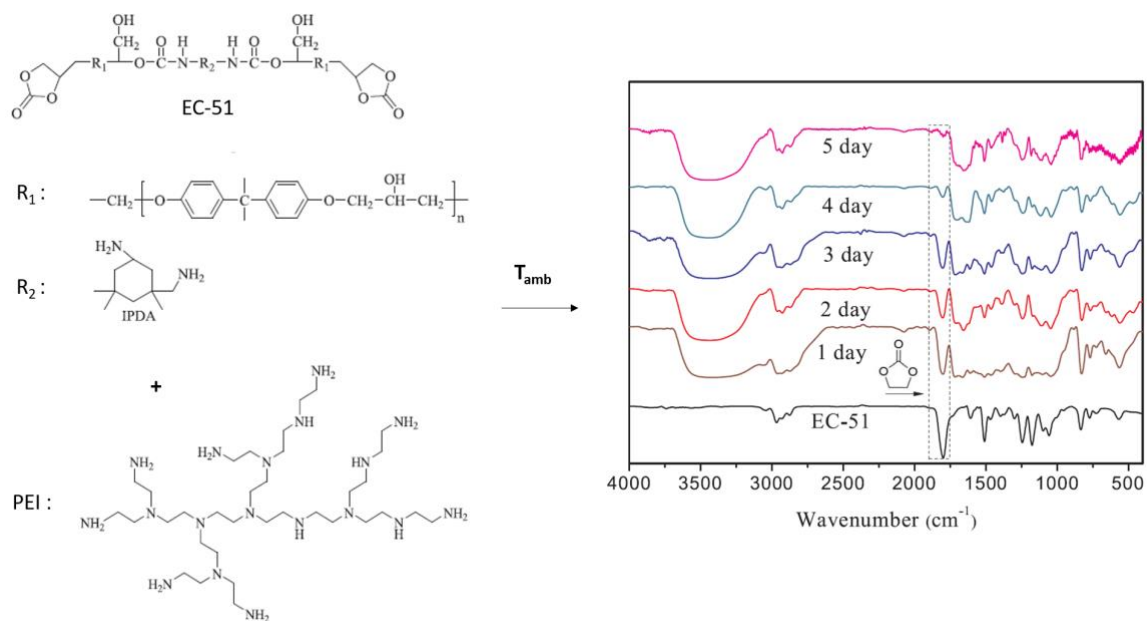
#### Liquid precursors bearing activated cyclic carbonates and catalysis of the carbonate-amine reaction

Capar *et al.* worked on the development of low-viscosity two-pack formulations with potential application in the field of coatings and dental fillings. They carried out the CO<sub>2</sub> carbonation of various di- and trifunctional glycidyl ethers, thus obtaining polyfunctional 5CC in which the carbonate is activated by the electron withdrawing effect of the ether moieties.<sup>116</sup> In particular, they worked with trimethylpropane triglycidyl carbonate (TMPTC) and hexanediol glycidyl carbonate (HGC), respectively noted compound 1 and 2 in Figure 25. The two poly(5CC) are liquids with viscosity of 300 Pa s and 1 Pa s respectively, at 25 °C. They were mixed with the liquid triamine TAEA and the crosslinking reactions were monitored by rheology for 12 h at 40 °C, *i.e.* a temperature close to body temperature. In both cases, the gelation is observed over a short period of time: 39 min in the case of carbonate 1 and 215 min for carbonate 2 (Figure 25). Moreover, it was confirmed by infrared spectroscopy and DSC that the carbonate conversion is total after 12 hours of reaction at 40 °C. The  $T_g$  of the resulting network is 50 °C in the case of carbonate 1, which is slightly higher than the curing temperature. It goes down to 9 °C for carbonate 2. By combining carbonates 1 and 2 (50/50 wt%), it is possible to obtain formulations with intermediate gel times (90 min, Figure 25). The authors used other polyamine including the hydrophilic polyethyleneimine and the hydrophobic Priamine obtained from di- and trimerized fatty acid. Interestingly, this study demonstrates that it is possible to form fully cured PHUs over decent period of time (~ 12 h) but also that the shape of the object, *i.e.* gelation, can be set very quickly (gel time ~ hour). It indicates that the crosslinking of pluri-5CC at moderate temperature without catalyst is possible and relevant for practical applications, when using chemically activated carbonates with low viscosity and good miscibility with the amines.



**Figure 25** : Rheological monitoring of the crosslinking reaction at 40 °C of bis-carbonate 2, tricarbonate 1 and the equimolar mixture of both carbonate with TAEA, respectively, according to Capar *et al.*<sup>116</sup>

Wu *et al.* developed a room temperature curable formulation containing bisphenol A diglycidyl carbonate, a dicarbonate which is known for being a solid.<sup>109</sup> To that purpose, they first reacted the dicarbonate with isophorone diamine (IPDA) in DMF at 150 °C for 3 h to obtain a series of liquid telechelic prepolymers bearing cyclic carbonate (Figure 26). By varying the dicarbonate to diamine ratio, they were able to obtain telechelic prepolymers with molar masses comprised between 470 and 2280 g mol<sup>-1</sup> (Dispersity ~ 1.5) and increasing viscosity. These tailor-made liquid dicarbonates were then reacted with polyethyleneimine at room temperature for 5 days. The conversion of the cyclic carbonates is complete after this period of time according to infrared spectroscopy (Figure 26). Furthermore, the reactions were monitored by rheology, indicating that the gel time,  $t_{gel}$ , is an increasing function of the molar mass of the prepolymer, with  $t_{gel} = 3$  h for  $M_n = 470$  g mol<sup>-1</sup> and  $t_{gel} = 14$  h for  $M_n = 2280$  g mol<sup>-1</sup>. In all cases, the films are tack free in less than 40 min. The  $T_g$  of the film increases from 35 °C to 51 °C by increasing value of the molar mass of the dicarbonate prepolymer. It suggests that the exothermicity of the curing reaction is sufficient to obtain super-ambient  $T_g$  materials, but this point is not discussed by the authors. Interestingly, crosslinking trials with other conventional liquid amines (*e.g.* polyether amine) were unsuccessful at room-temperature. For this reason, the authors hypothesized that the room-temperature curability of the formulation based on polyethyleneimine relies on the numerous secondary and tertiary amines of the polyamine, which catalyze the carbonate-amine reaction. Moreover, it is worth noting that the carbonates are chemically activated by the ether function contained in the starting bisphenol A glycidyl carbonate.

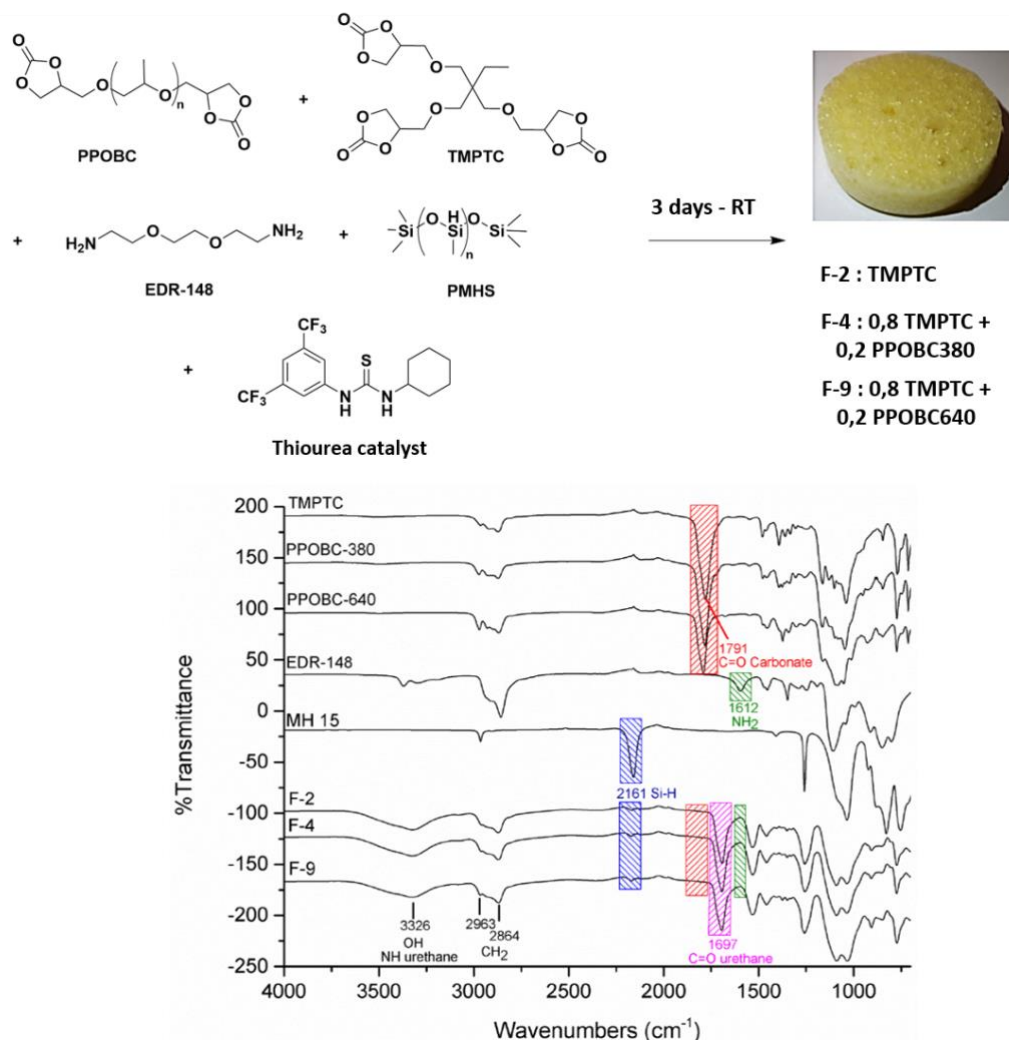


**Figure 26** : PHU prepolymer and PEI structures used for the synthesis of crosslinked PHU and stacking of the infrared spectra recorded during the crosslinking reaction at RT according to Wu *et al.*<sup>109</sup>

In a similar fashion, Kotanen *et al.* reported the synthesis of liquid telechelic PU prepolymers bearing cyclic carbonate functions.<sup>118,119</sup> However, in this case, the synthesis is based on the reaction of glycerol carbonate with commercially available isocyanate-based PU prepolymers terminated with isocyanate functions. The resulting liquid precursors exhibit viscosities comprised between 400 and 560 Pa.s at 25 °C. Just like Wu *et al.*, the authors demonstrate that these dicarbonate prepolymers can be crosslinked with polyethylenimine at room temperature without any catalyst. In most cases, carbonate conversions are > 95 % after 7 days at RT. Moreover, gel contents are > 94 %. The performances of the materials are comparable with those of current industrial polyurethane adhesives. However, they are mostly isocyanate-based materials which is not consistent with the eco-friendly conception of the other examples presented in this review.

In a study describing the synthesis of thermosetting PHU foams, Cornille *et al.* developed room temperature curable formulations based on the use of ether-activated carbonates in combination with a catalyst.<sup>107</sup> Mixtures of TMPTC and poly(propylene oxide) diglycidyl biscarbonate (PPOBC,  $M_n = 380 \text{ g mol}^{-1}$  or  $640 \text{ g mol}^{-1}$ ) were reacted with a polyether amine (EDR-148) in the presence of a thiourea as a catalyst (1 mol% relative to carbonate) and a polymethyl(hydrogensiloxane) as a foaming agent (PMHS, 5 mol% relative to amine) (Figure 27). All the compounds are liquids except for the catalyst. It is first homogenized with the cyclic carbonates and the other reagents are then added to the first mixture. The thiourea catalyst was chosen over TBD, another conventional catalyst of the carbonate-amine reaction, because of its solubility into the carbonates.<sup>25</sup> Crosslinking takes place in a beaker without stirring at room temperature. According to infrared spectroscopy, the conversion of cyclic carbonates is complete after 3 days of reaction (Figure 27). The authors demonstrated that both the catalyst and the foaming agents are necessary to observe the full conversion of carbonates. Catalyst-free mixtures are highly viscous liquid after 3 days of reaction and, in the absence of foaming agent, the materials remain sticky. It is hypothesized that the foaming agent helps in homogenising the

reactants mixture thanks to the local stirring induced around the growing gaseous bubbles. Very interestingly, the authors investigated the exothermicity of the reaction and measured a 10 °C increase of the system temperature. This temperature increase also plays a crucial role in the completion of the curing reaction. In the end, stable foams with  $T_g$  varying from 0 °C to 11 °C and gel fraction > 90 % were synthesized according to this protocol.

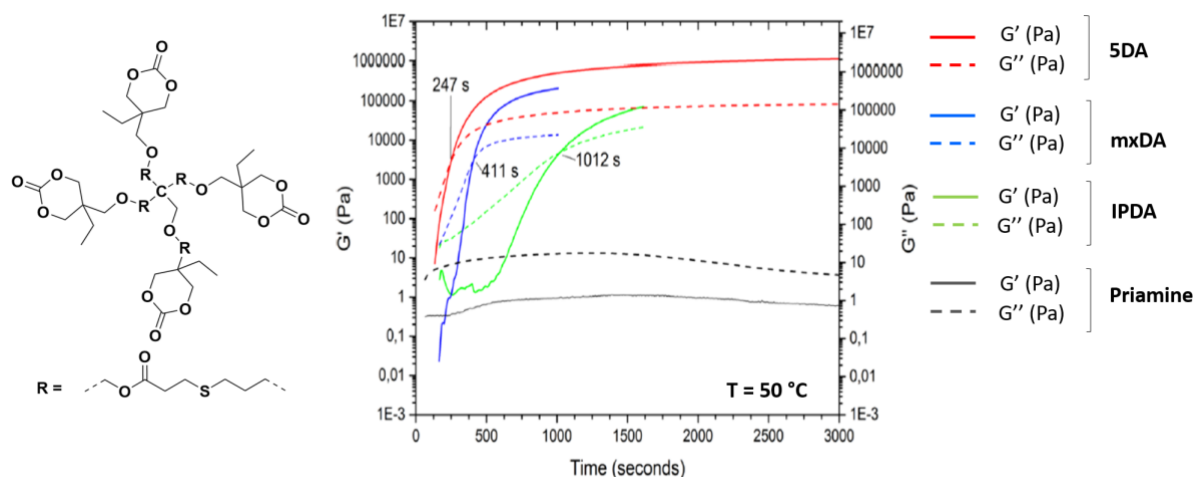


**Figure 27** : Reactants used for the synthesis of PHU foams at RT in bulk and comparison of the IR spectra of the reactants with those of the PHU foams (F2, F4 and F9) obtained after 3 days of crosslinking reaction at room temperature (Cornille *et al.*)<sup>107</sup>

Coste *et al.* synthesized catalyst-free PHU foams in mild temperature conditions, by using a liquid 6CC tetrafunctional monomer, which is known for being more reactive than 5CC monomers (Figure 28).<sup>63</sup> The tetracarboxate, synthesized by thiol-ene reaction beforehand, is manually mixed with PMHS, the same foaming agent than the one used by Cornille *et al.*<sup>107</sup> The amine is then added to the mixture before injection in a silicone mould. Particular attention was paid to the selection of liquid diamines, in particular isophorone diamine (IPDA), m-xylylenediamine (mxDA) and hexamethylene diamine (5DA), in order to ensure the homogeneity of the medium. The final shape of the foams is obtained after only 4 hours at 50 °C, indicating that the crosslinking reaction is well operative in this mild conditions. The foams are further maintained at 50 °C for an additional period of 8 h and a post-curing step is carried



out at 120 °C for 2 h. Indeed, after curing at 50 °C, DSC analysis indicates that the curing reaction is not fully completed. After high-temperature treatment, the 6CC carbonyl absorption band is no longer observed in infrared, proving the full conversion of cyclic carbonates. The good reactivity of these systems in mild conditions was confirmed by the rheological investigation of the crosslinking reaction for formulations free of foaming agent. Very short gel times were recorded for all the amines with  $t_{gel} = 247$  s, 411 s, 1012 s for 5DA, mxDA and IPDA respectively (Figure 28). In the end, stable foams with  $T_g$  varying from 7 °C to 27 °C and gel fraction > 80 % were synthesized according to this protocol.



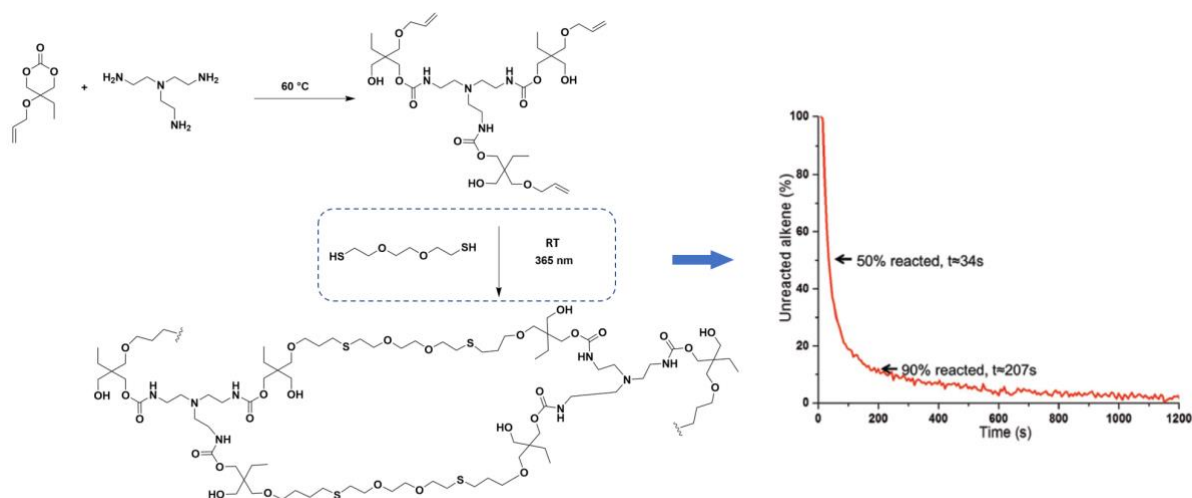
**Figure 28** : Structure of tetra-6CC and evolution of  $G'$  and  $G''$  moduli as a function of the crosslinking time of tetra-6CC with various diamines according to Coste *et al.*<sup>63</sup>

### Liquid (oligo)hydroxyurethanes crosslinkers bearing new functional groups: hybrid systems

A different strategy to obtain PHU networks at room temperature is to design liquid crosslinkers containing hydroxyurethane moieties and bearing functional groups that can be involved in a crosslinking reaction operative at room temperature. In this approach, the hydroxyurethane moieties are formed during the synthesis of the liquid crosslinkers, *i.e.* prior to the crosslinking reaction. The latter is no longer the carbonate-amine reaction. It is another classical reaction of thermosetting technology, such as the epoxy-amine reaction or the free radical polymerization of alkene. For this reason, the resulting materials are often considered as “hybrid” thermosets.<sup>120</sup> For instance, liquid (oligo)hydroxyurethane crosslinkers can be diacrylates that will be crosslinked *via* photoinitiated free radical polymerization or diamines that will be used to crosslink epoxy resins.

Two main strategies can be distinguished in the literature for the synthesis of these liquid (oligo)hydroxyurethanes crosslinkers. The first one consists in reacting a di- or tri-amine with a monocyclic carbonate containing a polymerizable function, usually an alkene. The resulting compound is a di- or tri-hydroxyurethane bearing two or three alkene functions that can be involved in a crosslinking reaction. For example, Hua *et al.* synthesized an allylated tri-hydroxyurethane by reacting the 6CC obtained from carbonation of trimethylolpropane allyl ether with the triamine TAEA (structures represented in Figure 29).<sup>112</sup> The mixture of 6CC and TAEA is heated at 60 °C for 6 h to provide the trihydroxyurethane crosslinker with a quantitative yield. The latter is then mixed with a dithiol and a photoinitiator (benzophenone) in a small amount of diethyl ether. The solvent is evaporated under reduced pressure and the mixture is crosslinked at room temperature *via* thiol-ene reaction under

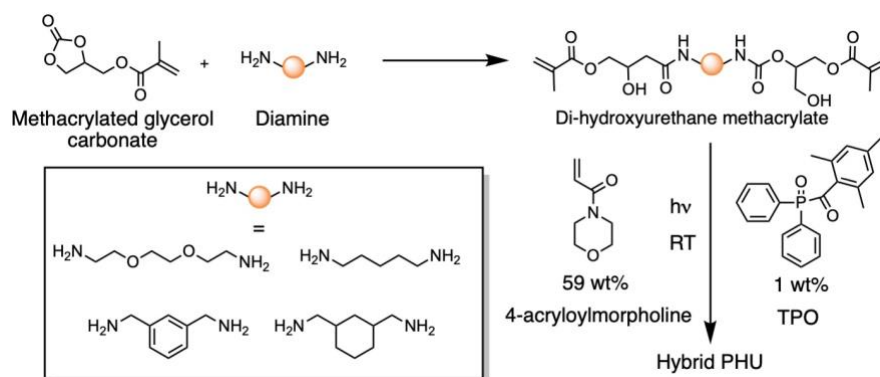
irradiation at 365 nm (Figure 29). 95 % of the double bonds are converted after 20 min of irradiation. The gel fraction of the resulting material is around 90 %, in agreement with the formation of a well crosslinked thermoset.



**Figure 29** : Synthesis of an allylated tri-hydroxyurethane and its photocrosslinking reaction with a dithiol to yield a thermosetting PHU. The plot represents the evolution of the double bond C=C conversion as a function of crosslinking time according to Hua *et al.*<sup>112</sup>

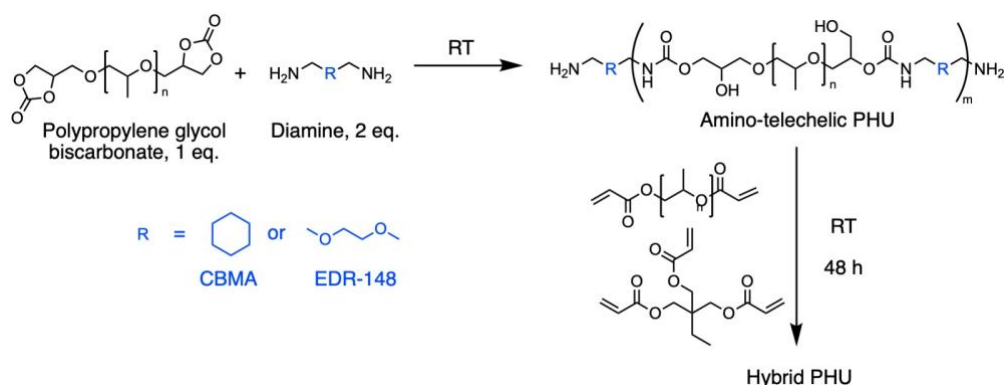
In a similar fashion, Warner *et al.* synthesized an allylated di-hydroxyurethane by reacting the same 6CC with pentamethylenediamine.<sup>110</sup> The resulting di-hydroxyurethane crosslinker is then mixed with tri and tetra-thiols as well as a photoinitiator (Darocure 1173). The mixture is irradiated at a wavelength of  $\lambda = 365$  nm for 5 min, at RT. Infrared measurements indicate the complete conversion of the precursors and the gel fractions measured in chloroform are  $\geq 90$  % confirming the formation of highly crosslinked networks. Their thermo-mechanical properties are dependent on the thiol used, with the highest elastic moduli  $E' = 12$  MPa and  $T_g = 2.3$  °C measured for the polymer derived from tetrathiol.

In another work, Schimpf *et al.* synthesized low viscosity di-hydroxyurethane methacrylates by reacting methacrylated glycerol carbonate with a series of diamines (Figure 30).<sup>121</sup> The resulting compounds exhibit viscosities comprised between 7 Pa.s and 200 Pa.s. They were used as crosslinkers in photocurable formulations composed of the di-hydroxyurethane methacrylates (39 wt%), 4-Acryloylmorpholine (59 wt%) and a radical photoinitiator (diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide, TPO, 1 wt%). Materials were obtained after curing under UV irradiation for 20 min at RT. Interestingly, the authors demonstrate that these formulations can be used in commercial 3D-printers based on stereolithography technologies.



**Figure 30** : Synthesis of di-hydroxyurethane methacrylates and their subsequent photocrosslinking with 4-acryloylmorpholine at room temperature, as proposed by Schimpf *et al.*<sup>121</sup>

A second strategy to obtain liquid (oligo)hydroxyurethane crosslinkers is based on the synthesis of amino-terminated PHU prepolymers. The latter are obtained by reacting dicarbonates with an excess of diamine. The resulting (oligo)hydroxyurethane diamines can then be used as crosslinkers for epoxy or acrylic resins to afford hybrid PHUs, usually at room temperature.<sup>24,122,123</sup> For instance, Cornille *et al.* developed a series of liquid amino-telechelic PHU oligomers by reacting a polypropylene glycol bis carbonate ( $M_n = 640 \text{ g mol}^{-1}$ ) with an excess of diamine, either 1,3-cyclohexanebis(methylamine) (CBMA) or 2,2'-(ethylenedioxy)diethylamine (EDR-148) (Figure 31).<sup>123</sup> The catalyst-free reactions were conducted in bulk at room temperature overnight and the resulting prepolymers were used without any purification. They exhibit viscosities comprised between 0.2 and 500 Pa.s depending on both the amine used for the synthesis and the carbonate/amine ratio. Eventually, the amino-telechelic PHUs were used to crosslink mixtures of a commercially available triacrylates and various polypropylene glycol diacrylates. The curing reaction is based on the Michael addition of the amine onto the acrylate functions and is conducted at room temperature for 48 h. Infrared measurement indicates that the acrylates are fully converted after this period of time. Moreover, the hybrid PHU thermosets exhibit high gel fraction (92-94%) and  $T_g$  varying from  $-59 \text{ }^\circ\text{C}$  and  $-17 \text{ }^\circ\text{C}$ .



**Figure 31** : Synthesis of amino-telechelic PHUs and their subsequent use as crosslinkers of acrylic resin via Michael addition at room temperature, as proposed by Cornille *et al.*<sup>123</sup>

In another example, Asemiani *et al.* used a similar approach to synthesize amino-telechelic PHUs that were further used to crosslink polyepoxides at ambient temperature during 7 days.<sup>24</sup> The resulting

hybrid PHU thermosets are tack-free after periods of time varying from 4 to 16 h and they exhibit gel content of about 80 %.

### 3.3.3. Summary and outlook

All these examples of low-temperature curing of PHU thermosets demonstrate that the carbonate-amine chemistry can be suitable for many ambient applications including coating, sealing or 3D-printing. The growing number of references dedicated to these curing conditions can be used to determine the typical characteristics of the ideal carbonate-amine systems for ambient curing in solvent-free conditions. First, pluricyclic carbonates with viscosity lower than 500 Pa s at 25 °C seems to be the most adapted for an implementation at room temperature (*i.e.* mixing with the amine and further processing such as coating, foaming or injection). Another important point is the reactivity of the carbonate. 5CCs activated by the electron withdrawing effect of an ether function seems to be the best compromise in terms of reactivity *versus* availability of the precursors. Further activation of the carbonate-amine reaction by a catalyst seems to be essential in most cases. Interestingly, the catalyst can be a tertiary amine moiety present in the backbone of the polyamine precursors, thus avoiding the incorporation of a “free” catalyst that could leak out of the crosslinked network afterwards.

Even if the profile of the ideal ambient curable system is getting clearer, many questions are still unaddressed. In particular, the exothermicity of the carbonate-amine reaction has been scarcely investigated. When compared to the abundant literature regarding the detailed thermodynamic analysis of the epoxy-amine reaction, the data related to the carbonate-amine reaction are very poor. Thus, it is extremely difficult to predict the exothermicity of typical carbonate-amine combinations in ambient conditions. To our knowledge, there are no existing TTT diagram (Time-Temperature-Transformation) for a typical crosslinkable carbonate-amine system. This is another indication of the lack of knowledge regarding the thermodynamics of this reaction.

Last but not least, hydrogen bonding has been well identified as one of the main obstacles to low-temperature curing. However, the correlation between the chemical structure of the carbonate and the amine precursors and the extent of hydrogen bonding during the growth of the PHU network has never been investigated. This would be a critical information to determine the ideal precursors for room temperature curability. Torkelson *et al.* investigated the relationship between hydrogen bonding and the chemical structure of the precursors in fully polymerized PHUs.<sup>124,125</sup> These informations should be used as a source of inspiration for future investigations.

## 4. Conclusion

The synthesis of thermosetting PHU is widely documented and different strategies can be applied to obtain these polymers. Various synthesis methods of plurifunctional cyclic carbonates have been described and extensively used in the literature. Most of the poly(cyclic carbonates) have been synthesized through a grafting method *via* the thiol-ene reaction or by co-polymerization in the case of highly functionalized monomers. It is interesting to note that most of the thermosetting PHUs syntheses involve classical curing conditions, *i.e.* high temperature for long reaction times, in order to avoid any physical limitation from the growing network but also to foster the carbonate-amine reaction. If the resulting networks meet the expected thermomechanical properties, those reaction conditions

are not adapted to all the targeted applications, e.g. coatings and adhesives, that are mostly synthesized at room temperature. Even though 5-membered cyclic carbonates are considered as barely reactive at room temperature, catalysis or even chemical activation have been highlighted as solutions to use them in such temperature conditions. Highly reactive X-membered cyclic carbonates, with  $X \geq 6$ , have also been used in the case of syntheses at mild or even room temperature. Finally, various authors have shown that, in water or in bulk, it was possible to use 'classical' 5-membered cyclic carbonates to synthesize thermosetting PHUs at moderate temperature,  $\leq 50$  °C, or even at room temperature, paving the way to new applications for such polymers.

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