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Isocyanate-free routes to polyurethanes and poly(hydroxy urethane)s

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Abstract

Greener routes to polyurethanes are required and arouse a growing interest in the academic and industrial communities. To this purpose, the depletion of fossil resources exacerbates the need of renewable materials. This review details two main routes to phosgene-free and isocyanate-free pathways to polyurethanes: the transurethanization and the cyclic carbonate/amine routes. A focus is also made on bio-based synthons toward non-phosgene and non-isocyanate PUs.

Keywords: thermoplastic polyurethanes (TPUs), poly(hydroxyurethane)s (PHU), bio-based, vegetable oils, fatty acid, isocyanate free, phosgene-free, transurethanization, carbamate, (bis) cyclic carbonate, catalysis.

Introduction

In the current context of sustainable chemistry development and new regulations, research groups and industries have to replace hazardous chemicals and harsh reaction conditions by greener intermediates and processes. In the past few years, plastic market has seen growing its interest for polyurethane materials. According to *PlasticsEurope*, the worldwide production reached 21 million tons in 2012[1]. These specialty performance polymers combine numerous properties required in aeronautic, medical applications, adhesives or even textile industry. Classically, polyurethanes (PUs) result from the polyaddition of a diol (or polyol) onto a diisocyanate (or poly-isocyanate). The latter is directly produced from the corresponding amine and phosgene which is highly toxic. Sentence removed

Therefore, alternative pathways for PU synthesis become more and more attractive for industry and academic research. Meier and coll. reviewed modern and more sustainable routes to PUs precursors[2] and particularly focused on the synthesis of bio-based isocyanates for greener polymerizations. Figure 1 presents an overview of the main synthetic routes to polyurethanes according to their dependence in phosgene and isocyanate. Among those methods, the copolymerization of aziridines with carbon dioxide is one of the less dependent in terms of phosgene and isocyanate content. But a green access to aziridines and their toxicity remain an issue.[3] The rearrangement of acyl azide followed by its polycondensation with alcohol functions represents another route to access polyurethane, through an in situ isocyanate formation during polymerization.[4-5] These pathways cannot replace the isocyanate route as some precursors or reagents used are not safe to handle. In this concern, the most studied and promising routes to PUs and PHUs are the transurethanization polycondensation between a bis-carbamate and a diol [6-10] and the polyaddition between cyclic carbonates and amines.[11-12]

The first part of this review will be devoted to the transurethanization process, reviewing the synthesis of phosgene- and isocyanate-free carbamates, their polymerizations with alcohols and the bio-based polymers obtained from this route.

Afterward, a detailed description will be made on thermoplastic poly(hydroxyurethane)s (PHUs), regarding the synthesis of cyclic carbonates and amines, the corresponding model reactions, mechanisms, catalysts and polymerizations. The synthesis of bio-based PHUs will be finally presented.

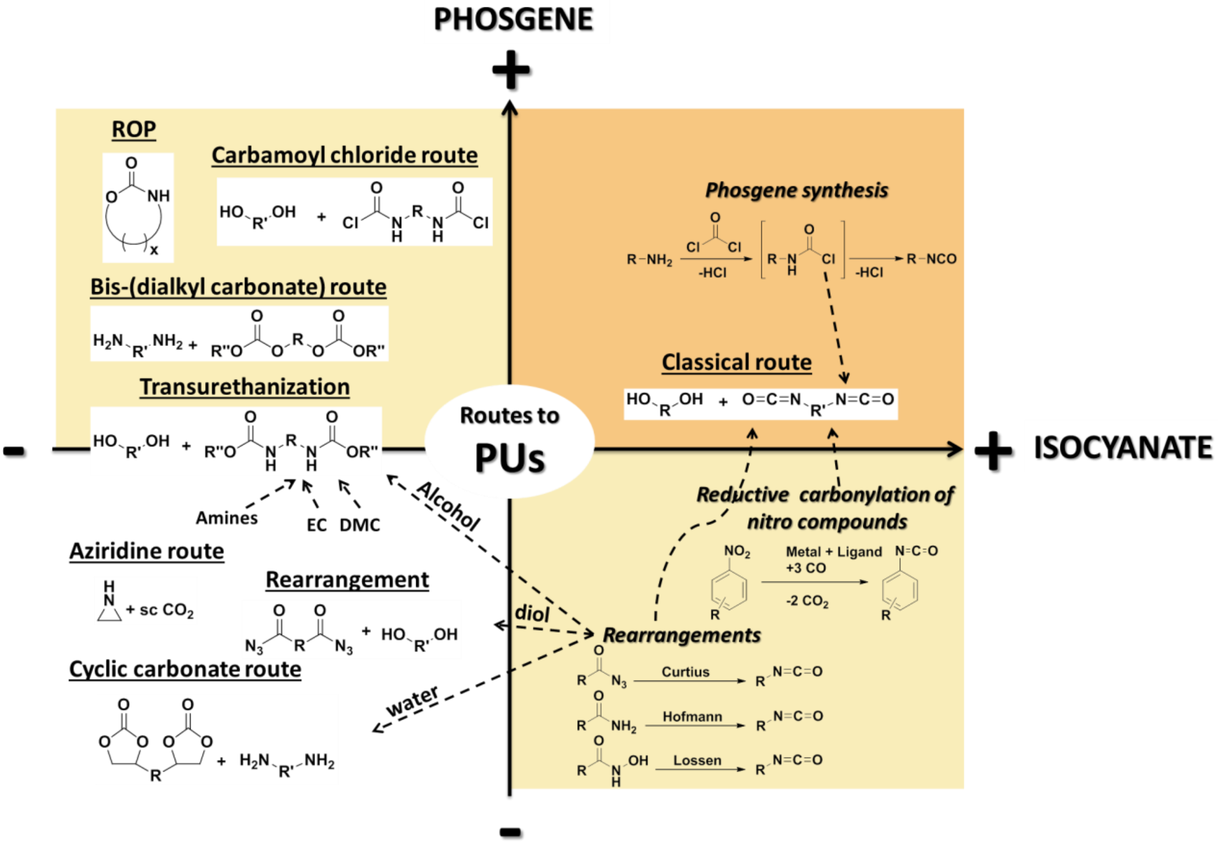
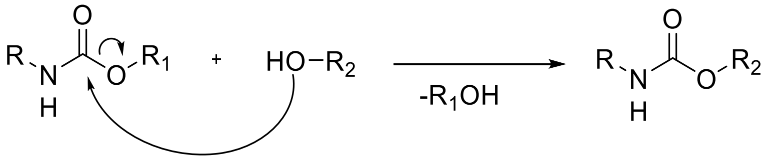


Figure 1- Overview of synthetic routes to polyurethanes.

1- Transurethanization: towards phosgene-free polyurethanes

The condensation of an alcohol on a carbamate can lead to urethanes; this reaction is a transurethane reaction, also called transurethanization or transcarbamoylation (Scheme 1). When plurifunctional monomers are used, polyurethanes are produced. The side product generated is an alcohol, usually with a low molar mass.



Scheme 1- Mechanism of transurethanization

These PUs obtained by polycondensation have similar structures as those produced by the polyaddition of polyisocyanates and polyols. It is thus a way to make non-isocyanate PUs (NIPUs) that have similar characteristics with industrial PUs. For this purpose, phosgene-free carbamate monomers have been synthesized, their condensation with alcohols studied as well as their polymerization with polyols.

1.1 Phosgene-free and isocyanate-free carbamate synthesis

Carbamates can be synthesized by many routes.[2,7] Here, we will discuss only the phosgene-free routes that have been used for further transurethanization reactions. Three types of carbamate synthons can be distinguished: bis-alkylcarbamates, bis-hydroxyalkylcarbamates and AB-type synthons (***Figure 2***).

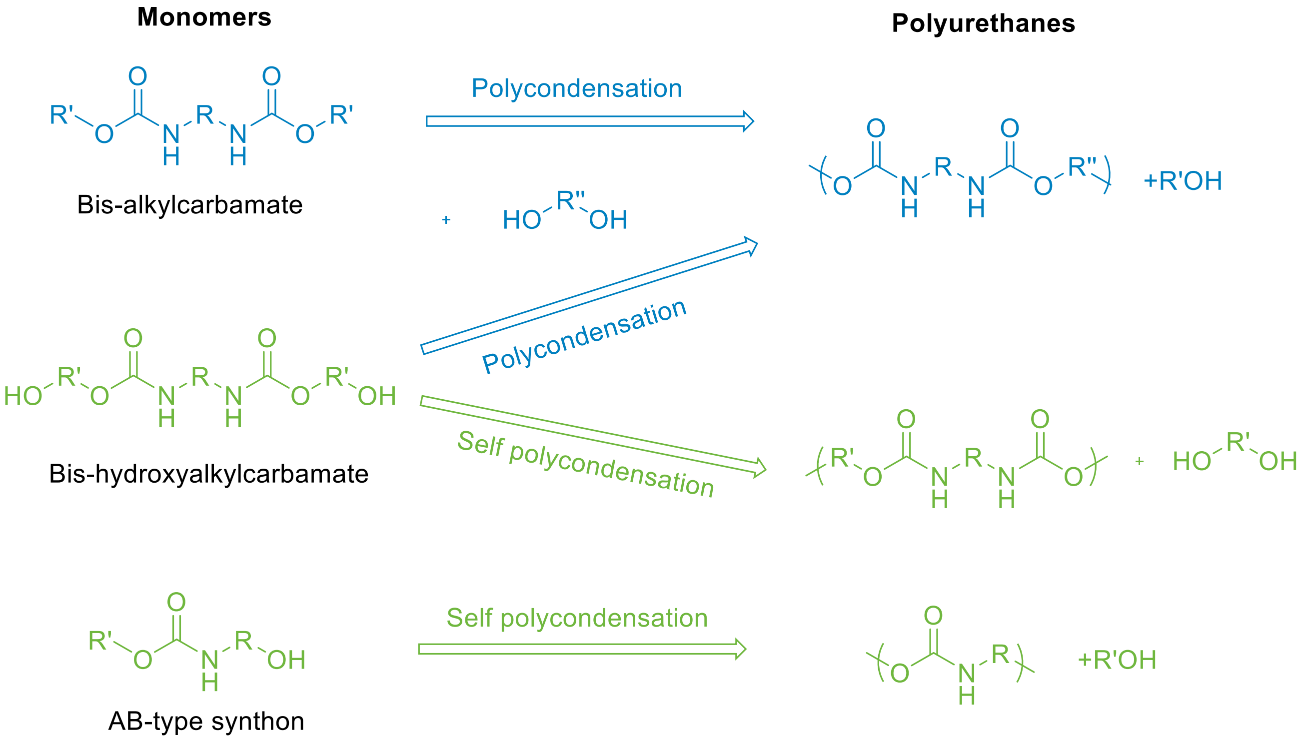
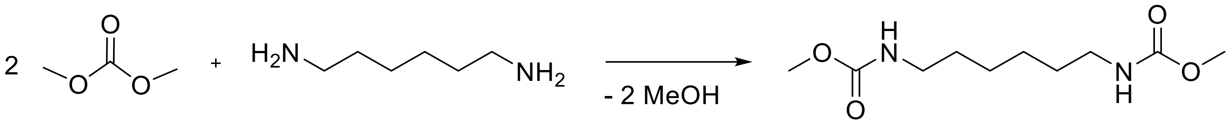


Figure 2- Three main routes to PU via a transurethane polymerization

1.1.1 Synthesis of bis-alkylcarbamates

Bis-alkylcarbamates can be easily synthesized by reacting diisocyanates with alcohols such as methanol or phenol.[13] In order to avoid the use of isocyanates, dialkylcarbonates can be reacted with diamines to prepare bis-alkylcarbamates. The most used dialkylcarbonate is dimethylcarbonate (DMC); it was originally formed industrially by phosgenation of methanol. Nowadays, a phosgene-free route is available using carbon monoxide, methanol and dioxygen.[14] It can also be synthesized from carbon dioxide and methanol.[15-16] Other bis-alkylcarbonates are obtained from dimethylcarbonate by transcarbonation with alcohols.[17]



Scheme 2- Methoxycarbonylation of hexamethylene diamine with dimethylcarbonate

Bis-methylcarbamates are easily obtained by methoxycarbonylation of diamines with dimethylcarbonate (Scheme 2). Dimethylcarbonate (or other dialkylcarbonates) is usually used in excess to solubilize the diamines. Various catalysts are used in the literature for alkoxycarbonylations; the latter are summarized in Figure 3. Metallic catalysts were originally used,[18-21] but they can be replaced by organic ones. Deepa and coll. used an excess of dimethylcarbonate in the presence of sodium methoxide with hexamethylene diamine or isophorone diamine, the authors obtained the desired bis-methylcarbamates after 6h under reflux.[22-24] Other research groups used organic catalyst 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) in similar conditions.[25-27] A supported catalyst, based on mesoporous silica (Na-MCM-41) was also efficient to form a bis-methylcarbamate from hexamethylene diamine under reflux. Other catalysts enable the reaction; Quaranta *et. al.* obtained various monomers using aliphatic and aromatic diamines in 36h to 48h with Sc(OTf)$_3$.[28] Jain and coll. obtained methylcarbamates from linear, cyclic and aromatic mono-amines using L-proline and TBAB after 3h at room temperature.[29] Another route is the use of ionic liquids as catalysts; Deng and coll. studied different ionic liquids and were able to get the methoxycarbonylation of hexamethylene diamine in a few hours at 60-100°C with $[MIm(CH_2)_4SO_3H]TfO$.[30]

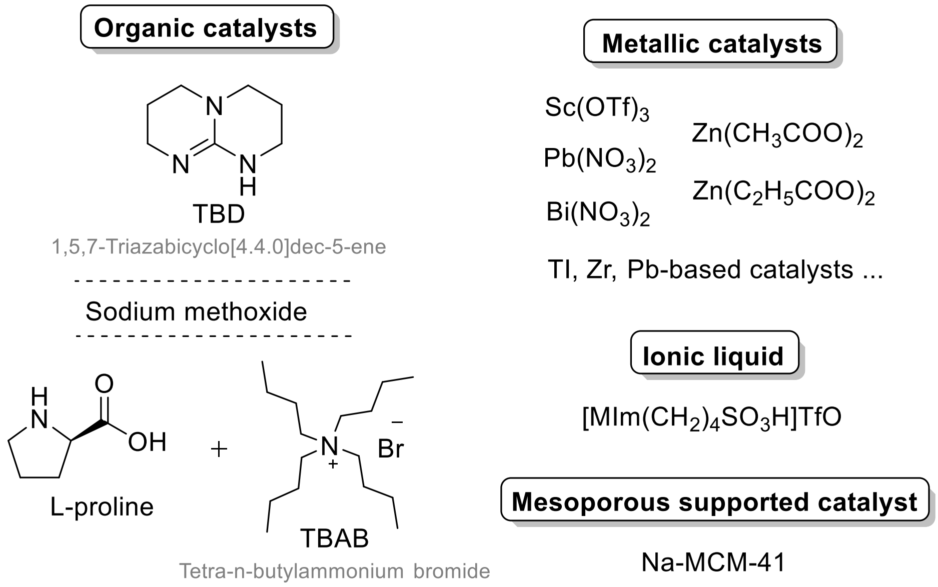


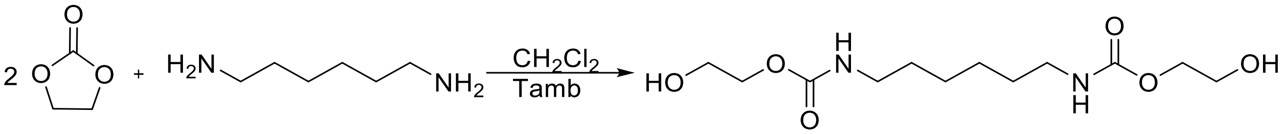
Figure 3- Catalysts for the synthesis of bis-alkylcarbamates

It is worth noting that most of these syntheses are solvent-free and thus can be considered as green syntheses. Moreover, two different research groups found a way to make the methoxycarbonylation of mono-amines without any catalyst using supercritical carbon dioxide.[31-32]

Other alkylcarbamates have been synthesized, such as ethylcarbamates and phenylcarbamates using respectively diethylcarbonate and diphenylcarbonate, with similar reaction conditions as dimethylcarbonate.[33-35] Noteworthy, there are other routes for the synthesis of methylcarbamates and bis-methylcarbamate monomers in the literature using bio-based derivatives. They will be discussed in the bio-based polymers section (§1.3).

1.1.2 Synthesis of bis-hydroxyalkylcarbamates

Bis-hydroxyalkylcarbamates are easily formed by the addition of a diamine on cyclic carbonates such as ethylene carbonate and propylene carbonate (***Scheme 3***).[36-38] Ethylene carbonate is an attractive precursor as it can be obtained from ethylene oxide and carbon dioxide. The reaction is exothermic and catalyst free. Primary or secondary amines can be used.



***Scheme 3- Synthesis of a bis-hydroxyalkylcarbamate from ethylene carbonate and 1,6-hexanediamin*e** [39]

Rokicki and coll. performed this reaction with 1,4-butanediamine and 1,6-hexanediamine with ethylene carbonate in methylene chloride at room temperature.[39] Later, Yang and coll. did the reaction in bulk and increased the temperature to 120°C.[40-41]

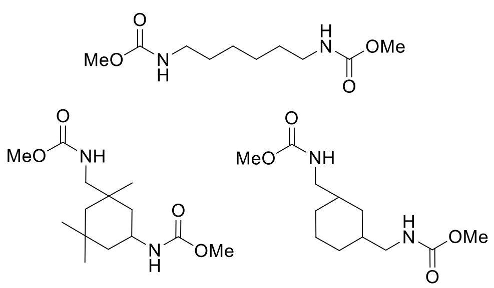
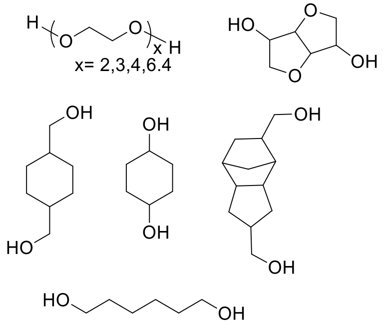
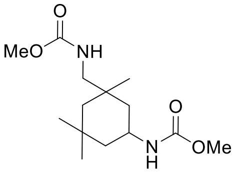
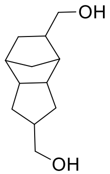
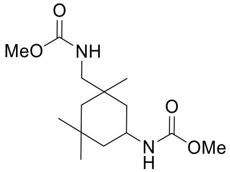
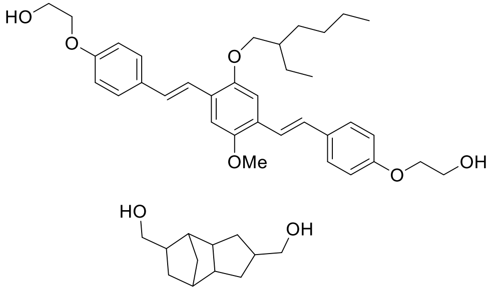
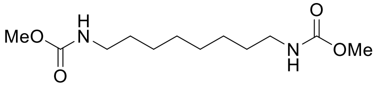
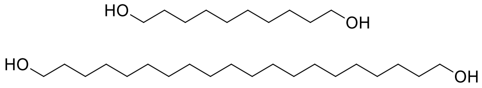
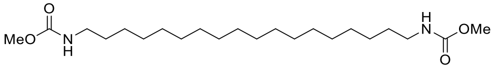
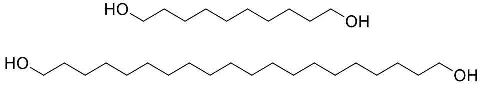
1.1.3 Synthesis of AB-type synthons

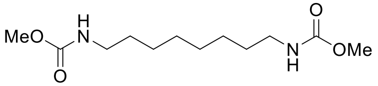
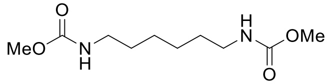
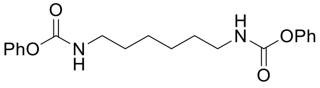
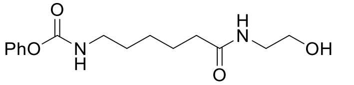
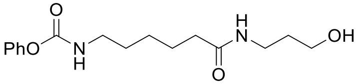
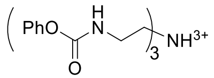
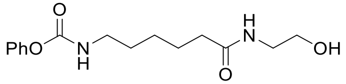
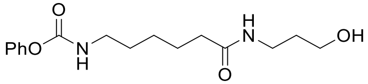
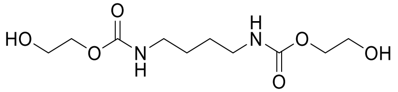
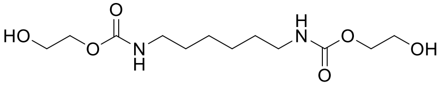
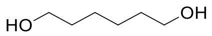
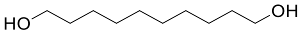
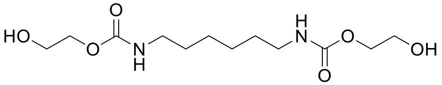
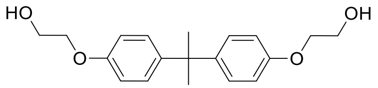
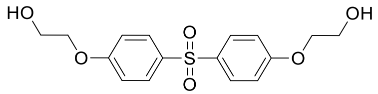
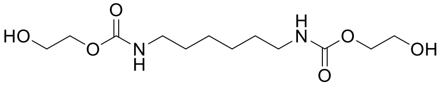
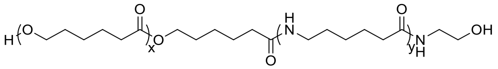
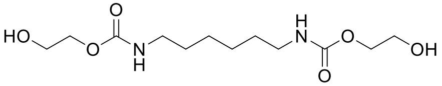
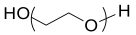
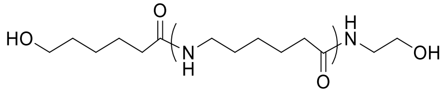
Difunctional monomers are necessary to perform the polymerization. An interesting route to get polyurethane is the synthesis of AB-type monomers that bear two different functionalities: a carbamate and an alcohol. The advantage of such monomers is that the stoichiometry between both functionalities is always achieved, and thus the polymerization is not limited by the stoichiometry. There are few examples in the literature of such monomers; Sharma *et al.* used amino alcohols and ε-caprolactone with diphenylcarbonate or ethylene carbonate to obtain AB-type monomers.[34-35,42]

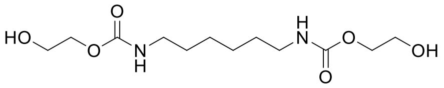
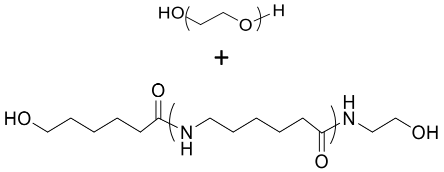
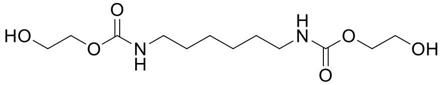
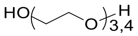
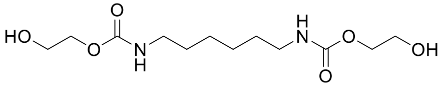
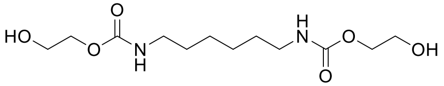
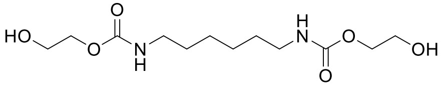
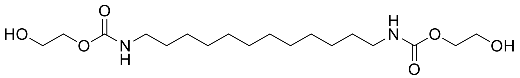
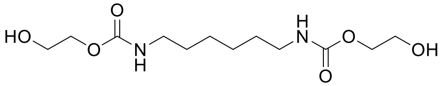
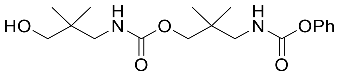
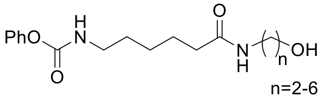
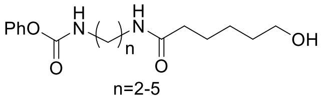
1.2 From carbamates to polyurethanes

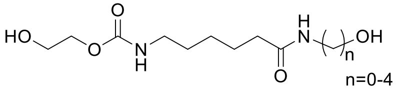
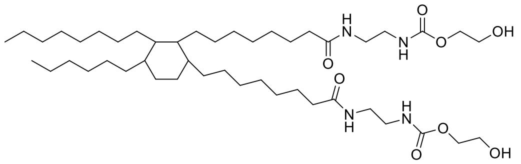
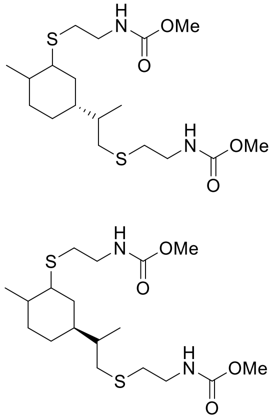
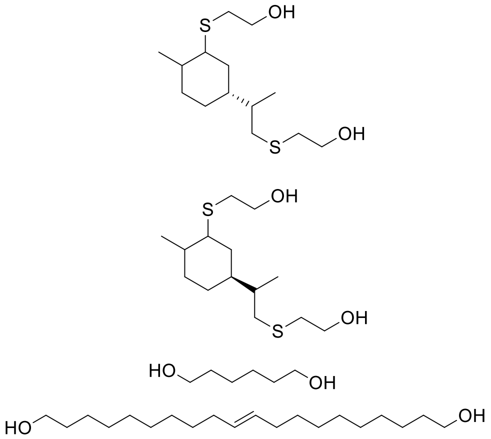
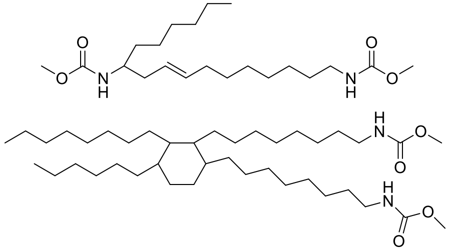
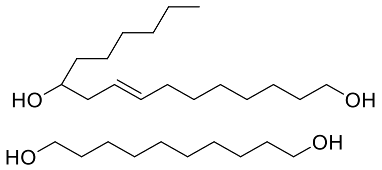
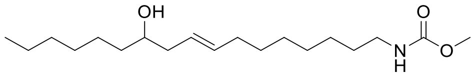
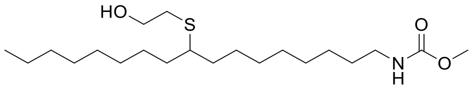
In the literature, the polymerizations usually occur at high temperature above 150°C using a catalyst. Two-step procedures are used; the first step consists in the oligomerization under air or nitrogen. Then, reduced pressure is applied in order to remove the alcohol generated by the reaction so as to shift the reaction toward the polymerization.

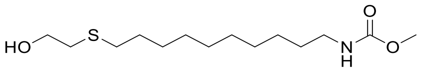
Table 1 summarizes the main examples of polymerization by transurethanization in the literature.

Biscarbamates	Polyols	Reaction conditions	$\bar{M}_n$ (g.mol^{-1}) and [Dispersity]	Thermal properties(°C)	Ref
		1. Ti(OBu)$_4$, 3.3mol%, 150°C, 4h, N$_2$ 2. 150°C, 2h, reduced pressure	3200-20000 ^{b} [1.25-3.11]	T$_g$=-31-118 ^{f}	22-23
		1. Ti(OBu)$_4$, 3.3mol%, 150°C, 4h, N$_2$ 2. 150°C, 2h, reduced pressure	32500 ^{b} [2.4]	T$_g$=118 ^{f}	24
		1. Ti(OBu)$_4$, 150°C, 4h, N$_2$ 2. 150°C, 2h, reduced pressure	4300-6800 ^{b} [1.5-3.6]	T$_g$=103-120 ^{f}	24
		1. TBD, 0.1-0.3eq, 120°C, 2h, reduced pressure 2. 140°C, 2h, reduced pressure 3. 160°C, 12h, reduced pressure	7100-24600 ^{e} [1.88-2.14]	T$_m$=135-145 ^{f,g}	43
		1. TBD, 0.1-0.3eq, 120°C, 2h, reduced pressure 2. 140°C, 2h, reduced pressure 3. 160°C, 12h, reduced pressure	10600-15400 ^{e} [1.24-1.54]	T$_m$=121-123 ^{f,g}	43

 	Poly(carbonate macrodiol)	1. Bu_2SnO, 100°C, 1h 2. 160-185°C, 2.5-4h, reduced pressure	35000-51000 [b] [1.27-1.63]	-	44
	 	1. $Bu_2Sn(OCH_3)_2$, 5wt%, 90°C, 2h, N_2 2. 90°C, 3h, reduced pressure	5000-10800 [d] [1.3-1.8]	-	35
	 	1. $Bu_2Sn(OCH_3)_2$, 5wt%, 90°C, 2h, N_2 2. 90°C, 3h, reduced pressure	7100-7300 [d] [1.7-1.8]	-	35
 	 	Xylene, Bu_2SnO, 5mol%, 145-150°C, 5-6h	1600-3500 [e] [1.8-1.9]	T_g=18.5 [g] T_m=141.5	39
	 	BaO, zinc borate, 3.3-6.8wt%, up to 220°C, reduced pressure	-	-	45
		1. $SnCl_2$, 0.2wt%, 170-190°C, 4h, N_2 2. 180-190°C, 5-6.5h, 3mmHg	30000-45000 [a] [1.2-1.5]	T_g=12.9-29.6 [f] T_c=48.7-91.7	41
	 + 	1. $SnCl_2$, 0.1-0.2wt%, 170-190°C, 5h, N_2 2. 170-190°C, 9.5-12.8h, 3mmHg	11600-13500 [a] [1.11-1.19]	T_g=11-15 [f] T_c=50-56 T_m=154-178	46

		1. $SnCl_2$, 0.2wt%, 170-190°C, 5h, N_2 2. 170-190°C, 6h, 3mmHg. 3. Addition of diurethane, 180-200°C, 1.5-10h, 3mmHg.	7400-18400 [a] [1.03-2.66]	T_g=-4-11 [f] T_c=39-48 T_m=145-177	46
		1. $SnCl_2$, 0.19-0.25 mol%/both monomers, 170°C, 2h, N_2 2. 170°C, 4h, 30mmHg, 3. 170°C, 8-16h, 1-3mmHg	32000-50900 [c] [1.29-2.06]	T_g=11.2-28.2 [f] T_c=63.4-85.3 (X_c=36.5-78.3%)	40
	-	1. $SnCl_2$, 0.26mol%, 170°C, 2h, N_2 2. 170°C, 4h, 30mmHg, 3. 170°C, 10h, 2mmHg	30900 [c] [2.03]	T_g=25.6 [f] T_c=81.8 (X_c=83.6%)	40
	-	1. $SnCl_2$, 0.2wt%, 170°C, 4h, N_2 2. 180°C, 5h, 3mmHg	29000 [a] [1.36]	T_g=29.6 [f] T_c=82.8	41
	-	Xylene, Bu_2SnO , 10mol%, 145-150°C, 6-24h, Air or N_2	2200 [a] [1.33] (air) 3200-5300 [1.39-1.97] (N2)	T_g=26 [f] T_m=166	47
	-	Xylene, Bu_2SnO , 10mol%, 145-150°C, 24h, N_2	4100 [a] [1.23]	-	47
	-	BaO, 3.3-6.8wt%, 150°C, reduced pressure	-	-	45
	-	$Bu_2Sn(OCH_3)_2$ or $Bu_2Sn(OOC\text{-}(CH_2)_{10}\text{-}CH_3)_2$, 0.84mol%, 120°C, 10h, 0.1mbar or 1bar	48000-60000 [b]	-	48
	-	1. $Bu_2Sn(OCH_3)_2$, 5wt%, 90 or 120°C, 1h, N_2 2. 90 or 120°C, 2-3h, reduced pressure	3300-11500 [d] [1.16-1.64]	T_m=151-190 [f]	35,42
	-	1. $Bu_2Sn(OCH_3)_2$, 5wt%, 120°C, 1h, N_2 2. 120°C, 4h, reduced pressure	5700-7900 [d] [1.26-1.38]	T_m=148-188 [f]	34

	-	1. $Bu_2Sn(OCH_3)_2$, 5wt%, 150°C, 1h, N_2 2. 150°C, 4h, reduced pressure	7500-10900 ^{d} [1.52-1.78]	T_m=138-175 ^{f}	42
	-	150°C, 9h, reduced pressure	7700 ^{b} [2.2]	T_g=-10 ^{f} T_m=73	49
		TBD, 0.05eq/carbamate group, 120°C, 16h, reduced pressure	7900 to 12600 ^{e} [1.79-2.15]	T_g=14.6-18.5 ^{f} T_m= 6 for C11 diol	50
		1. TBD, 0.1eq, 120°C, 3h, N_2 2. 140°C, 3h 3. 160°C, 16h or 1. K_2CO_3, 0.05eq, 120°C, 3h, N_2 2. 140°C, 3h 3. 200°C, 16h	3500-13900 ^{e} [1.3-2.7]	T_g=(-38)-44 ^{f} T_m=61-188	25
	-	1. $Ti(OBu)_4$, 3.3mol%, 130°C, 4h, N_2 2. 130-150°C, 2h, reduced pressure	5000-6900 ^{b} [1.4-2]	T_g=-44 ^{f}	51
	-	1. $Ti(OBu)_4$, 130°C, 4h, N_2 2. 130°C, 2h, reduced pressure	2800 ^{b} [1.14]	T_{g1}=-39.4 ^{f} T_{g2}=25.3	5

	-	1. $Ti(OBu)_4$, 130°C, 4h, N_2 2. 130°C, 2h, reduced pressure	2100 [b] [1]	T_{g1}=-17.8 [f] T_{g2}=32.1	5

SEC conditions = a : (DMF/LiBr, PS St) b: (THF, PS St); c (DMF, PS St); d: (DMAC, LiCl, PS St), e : other methods
DSC conditions = f : 10°C/min; g : 20°C/min

Table 1- Summarized literature about non-isocyanate polyurethanes from transurethanization process

1.2.1 Polycondensation of bis-alkylcarbamates and polyols

The polycondensation of bis-alkylcarbamates and polyols has been mainly studied with bis-methylcarbamate and bis-phenylcarbamate monomers. Indeed, phenol is a good leaving group and methanol is easily removed from the reaction mixture by evaporation.

The polymerization of bis-methylcarbamates BMCs (Figure 4) has been studied by Jayakannan and coll.[22-24] Various diols were investigated, such as aliphatic, cyclic or polymeric diols. The polymerization process consisted in heating the monomers in bulk at 150°C for 4h under a nitrogen flux in the presence of $Ti(OBu)_4$ in catalytic amounts. Then the reaction went on for 2h under reduced pressure. Logically, the PUs characteristics depended on the monomers used; the T_g could be modulated from 31°C to 120°C and $\overline{M}_w$ values from 3.9 to 47.7 kg.mol^{-1}. Primary alcohols showed higher reactivity in those conditions than secondary ones; thus leading to higher polymer molar masses. On the other hand, there was no difference in reactivity between BMCs when polymerized with the same diol.

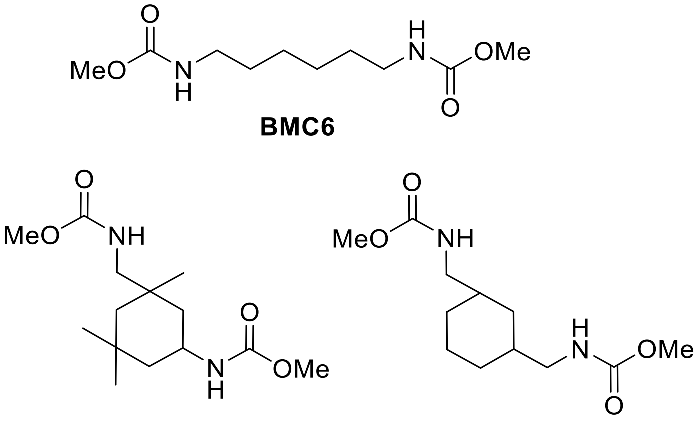


Figure 4- Bis-methylcarbamates BMCs

More recently, Hengshui and coll. performed the polymerization of BMC6 with a polycarbonate macrodiol in similar conditions.[44] The catalyst used is Bu_2SnO, the first step consisted in heating at 100°C for 1h and then the temperature is increased up to 185°C for a few hours under reduced pressure. An optimization of the process was necessary to avoid degradation and side-reaction that occurred at high catalyst loading and long reaction time, as confirmed by FTIR. A decrease in intrinsic viscosity and a yellowing of the product was then observed. The polymers obtained were poly(carbonate urethane)s, their $\overline{M}_{\mathrm{w}}$ values ranged from 57 to 79 kg.mol^{-1} with dispersities between 1.3 and 1.6. XRD analysis demonstrated the semi-crystalline features of the polymers depending on the hard and soft segment lengths and, in some cases, a microphase separation was observed.

In all the examples given in the literature, it is worth noting that no polymerization occurs when no catalyst is used. Moreover, no urea formation has been reported with alkylcarbamates as precursors.

1.2.2 Polycondensation of bis-hydroxyalkylcarbamates

Bis-hydroxyalkylcarbamates can be self-polymerized as they bear both the bis-alcohol and the bis-carbamate functionalities. The self-polymerization has been studied on the bis-hydroxycarbamates BHC6 and BHC12 described in Figure 5. The ethylene glycol formed can be removed *in vacuo* or by azeotropic distillation with xylene.

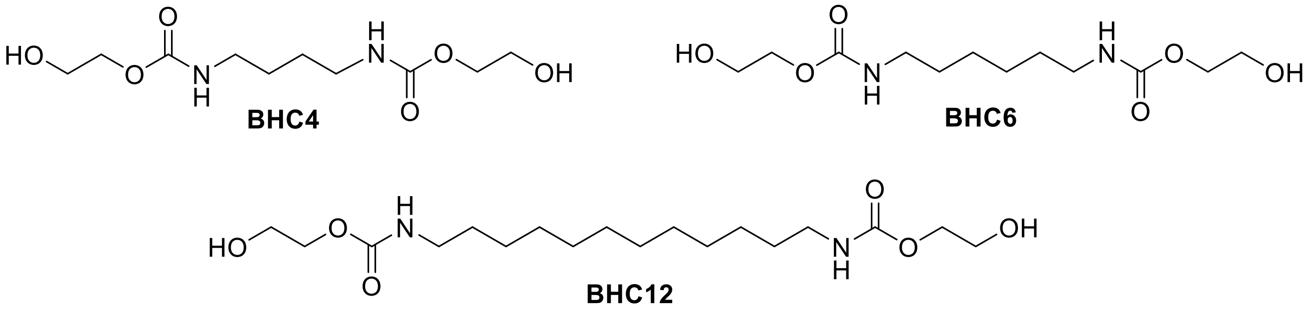
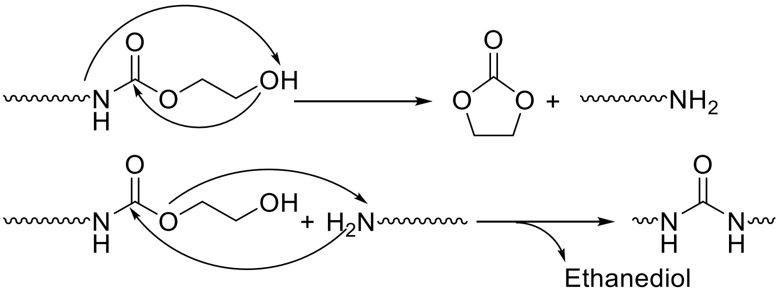


Figure 5- Bis-hydroxycarbamates

In 1957, Scott and coll. published the polymerization of BHC6 in bulk using barium oxide in catalytic proportions at 150°C under reduced pressure.[45] Later, Yang and coll. used a two-step procedure; the polymerization of BHC6 was performed in bulk at 170°C in presence of tin(II) chloride under N_2 during the first hours and then a reduced pressure was applied for several hours in order to remove the ethylene glycol formed and to pursue the reaction.[40-41] High molar masses up to $\overline{M}_{\mathrm{w}}$=62.7 kg.mol^{-1} with a dispersity of 2 were obtained. The polymers were crystalline with a T_g around 25-30°C and a T_m of 153°C. Urea units in the backbone were observed. It can be explained by the generation of ethylene carbonate through back-biting reactions of the hydroxyl function on the carbamate, as shown in Scheme 4. The amine formed can then react with another hydroxyalkylcarbamate to form urea units. This could be suppressed by decreasing the reaction temperature below 180°C.[41] Utsuno and coll. studied the influence of the reaction conditions (catalyst, atmosphere) on the polymerization of such bis-hydroxyalkylcarbamate using a tin catalyst at 145-150°C in xylene under air or nitrogen.[47] Better results were obtained with nitrogen and Bu_2SnO; the molar mass was higher and the product obtained was colorless compared to samples obtained under air. Still, the molar masses were low, with a $\overline{M}_{\mathrm{n}}$ up to 5.3 kg.mol^{-1} and a dispersity of 2. The T_g of the polymer obtained from BHC6 was 26°C.



Scheme 4- Back-biting side reaction followed by urea formation

In order to tune the properties of the PU obtained with these bis-hydroxyalkylcarbamates, the latter can be polymerized with various diols to bring hard or soft segments, and thus tune the T_g and the crystallinity depending on the needs.

Scott and coll. performed the polymerization of BHC6 with two different diols; the 2,2-bis(4-β-hydroxyethoxyphenyl)-propane and the 4,4’-bis-(-2-hydroxyethoxy)-phenylsulfone.[45] The polymerization was performed in bulk with barium oxide and/or zinc borate under reduced pressure at high temperature (up to 220°C). Later, Piotrowska and coll. performed the polymerization of BHC4 and BHC6 with aliphatic diols in xylene with Bu_2SnO.[39] Low molar masses semi-crystalline polymers ($\overline{M}_\mathrm{n}$=3.5 kg.mol^{-1} with a dispersity of 1.8-1.9) were obtained. The polymers obtained from BHC6 and 1,6-hexanediol had a T_g of 18.5°C and a melting temperature of 141.5°C. Presence of urea in the backbone was proved by NMR.

Recently, Yang and coll. performed the polymerization of BHC6 with various diols such as PEG, polyamide and poly(ester-amide) with hydroxyl end groups.[40-41,46,52] The catalyst used was $SnCl_2$, and the reaction temperature was between 170 and 200°C depending on the diol used. The reaction was performed in several steps, starting with the polymerization with an N_2 atmosphere and then under reduced pressure. The thermomechanical properties and the crystallinity of these polymers are extensively described. The molar mass of the polymers obtained depended on the conditions; for example the polymerization with PEG enabled the formation of polymers with $\overline{M}_\mathrm{n}$=32-51 kg.mol^{-1} and $\overline{M}_\mathrm{w}$=54-94 kg.mol^{-1}.

1.2.3 Self-polymerization of AB-type monomers

Various AB-type monomers have been synthesized for polymerization as shown in Figure 6.

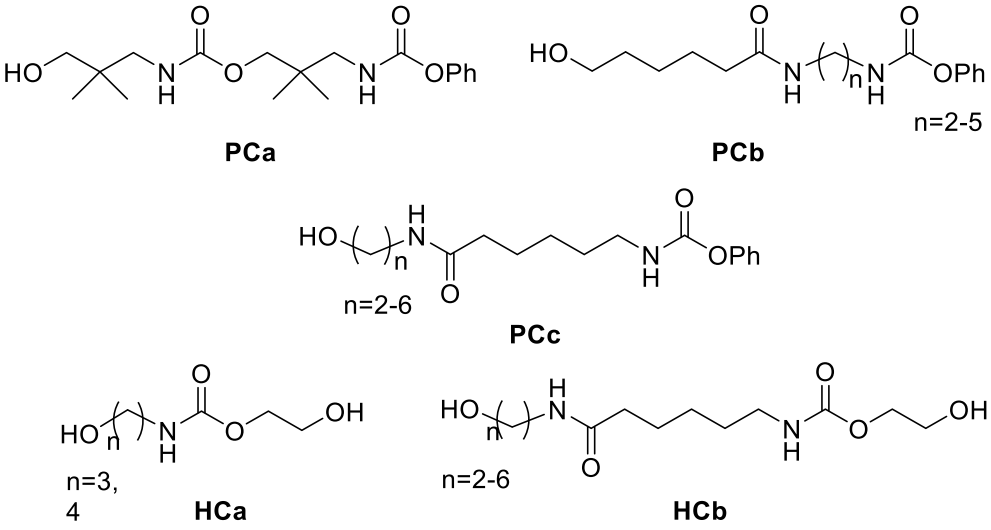


Figure 6- AB-type monomers: phenylcarbamates and hydroxycarbamates

Keul and coll. studied the polymerization of PCb and PCc in bulk at 90 or 120°C with $Bu_2Sn(OCH_3)_2$ as catalyst.[34-35] The phenol generated was removed *in vacuo*. The polymers obtained were semi-crystalline. For PCc, the molar masses were up to $\overline{M}_{\mathrm{n}}$=11.3 kg.mol^{-1} with dispersities ranging from 1.1 to 1.6. For PCb, they were up to $\overline{M}_{\mathrm{n}}$=7.9 kg.mol^{-1} with dispersities around 1.3. A side reaction was identified by the presence of urea linkage in the backbone. In another study, Keul and coll. investigated the influence of the leaving group on the formation of urea with the self-polycondensation of PCc and HCb.[42] For PCc polymerization, the side product is phenol while it is ethylene glycol for HCb. The amount of urea linkage in the backbone was higher for HCb polymers as ethylene carbonate is generated and evaporated at high temperature. The amine formed then reacted with another carbamate to form urea. For example, for PCc with n=4 (Figure 6), the ratio of urethane to urea was 94:6 when it was 81:19 for the corresponding HCb.

Höcker and coll. studied the polymerization of PCa in bulk with tin catalysts at 120°C under reduced pressure.[48] The authors were able to obtain molar masses up to $\overline{M}_{\mathrm{w}}$ =52 kg.mol^{-1}.

This polymerization is presented as an alternative to the polymerization by ring-opening of 2,2-dimethyltrimethylene urethane which is thermodynamically disfavoured.

1.3 Bio-based polymers

There are few examples in the literature of bio-based polyurethanes obtained by transurethanization polycondensation. The monomers, bis-alkylcarbamates and bis-hydroxyalkylcarbamates, can be obtained from dimethylcarbonate or ethylene carbonate. Fatty acids can also be modified by other means to get methylcarbamate functionalities. It is important to note that the side reaction leading to the formation of urea moieties is not mentioned in the following articles.

1.3.1 Bis-Carbamates based on dimethylcarbonate or ethylene carbonate

Narayan and coll. synthesized a bis-hydroxycarbamate using a dimerized fatty acid by transamidation of ethylene diamine on the carboxylic acid functions and further reaction with ethylene carbonate (Figure 7).[49] The polymerization strategy is a self-polymerization of the bis-hydroxycarbamate. The polymers obtained after 9h at 150°C under reduced pressure exhibited a $\overline{M}_\mathrm{n}$ of 7.7 kg.mol^{-1} and $\overline{M}_\mathrm{w}$ of 14 kg.mol^{-1}, a glass transition temperature of -10°C, and a melting temperature of 73°C.

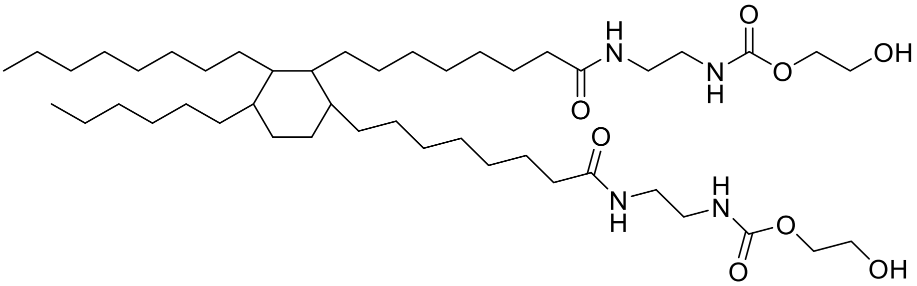
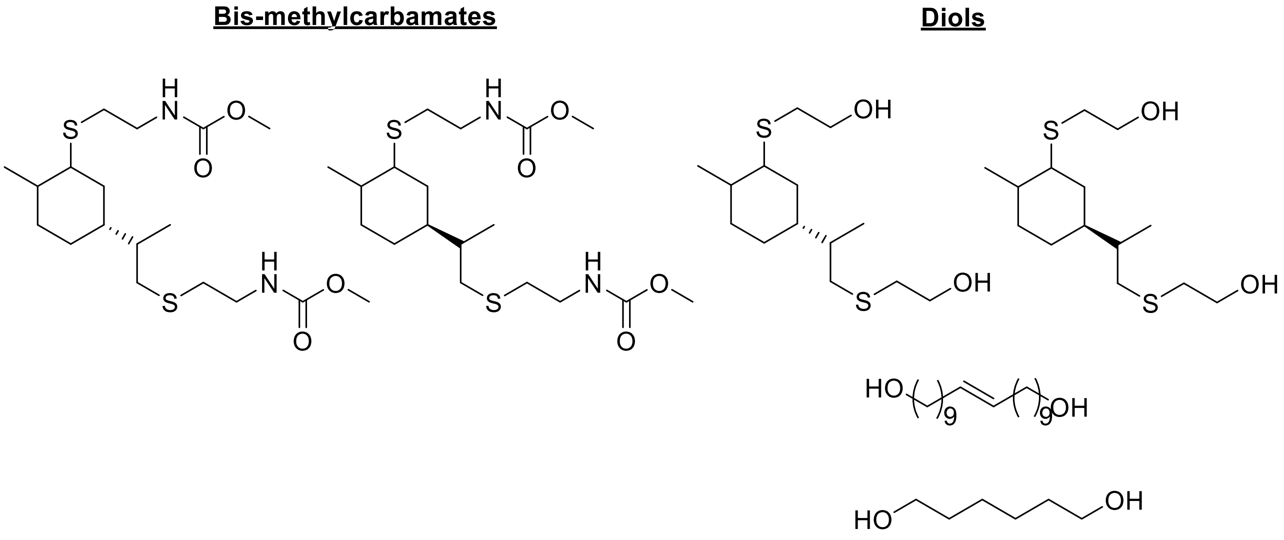


Figure 7- Fatty acid based bis-hydroxycarbamate [49]

Meier and coll. used limonene as bio-based raw material for the synthesis of bis-methylcarbamates and diols.[50] The authors took advantage of the insaturations to bring amine functionalities by thiol-ene reaction with cysteamine hydrochloride. The diamines formed were then reacted with dimethylcarbonate to form bis-methylcarbamates; the latter being polymerized with limonene-derived diols and other bio-based diols (Figure 8). The polymerization was performed under reduced pressure at 120°C for 16h with 0.05eq of TBD per carbamate function. The polymer molar masses were ranging from $\overline{M}_n$=7.9 to 12.6 kg.mol^{-1}, with dispersities from 1.8 to 2.1. The glass transition temperatures were ranging from 14.6 to 18.5°C. A melting point was observed for the polymerization with the C20 diol at 62°C.


Bis-methylcarbamates

Diols

Figure 8- Limonene and vegetable based monomers for fully bio-based PU synthesis [50]

Recently, Burel and coll. synthesized various bio-based PUs from bio-based diols and bis-methylcarbamates.[25] The bis-methylcarbamates were synthesized from bio-based diamines and DMC in the presence of TBD. The bis-methylcarbamates produced are presented Figure 9; the latter are derived from a fatty acid dimer and ricinoleic acid. The PUs were then synthesized by polycondensation with diols with TBD or K_2CO_3 as catalyst, following several steps: 3h at 120°C, 3h at 140°C and then 16h at 160°C for TBD and 200°C for K_2CO_3. A nitrogen flux allows the removal of methanol.

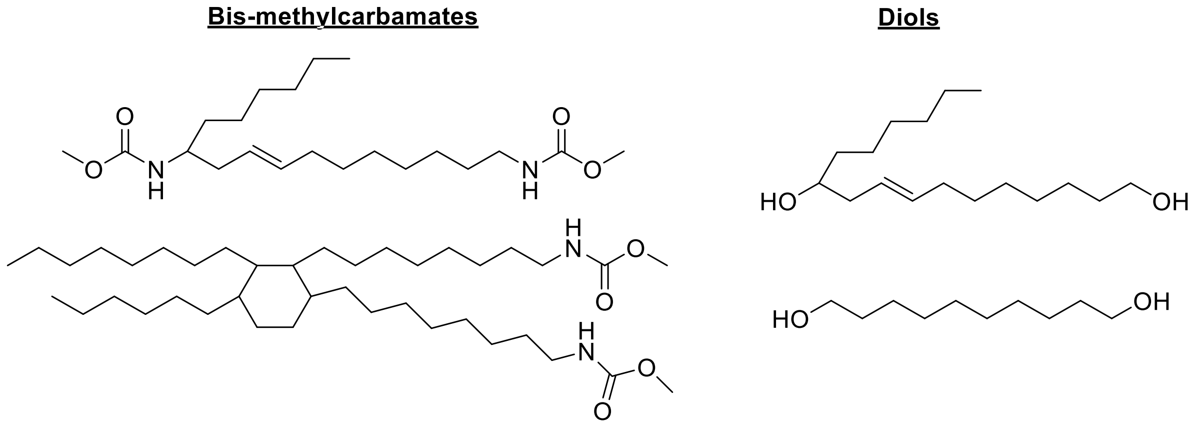
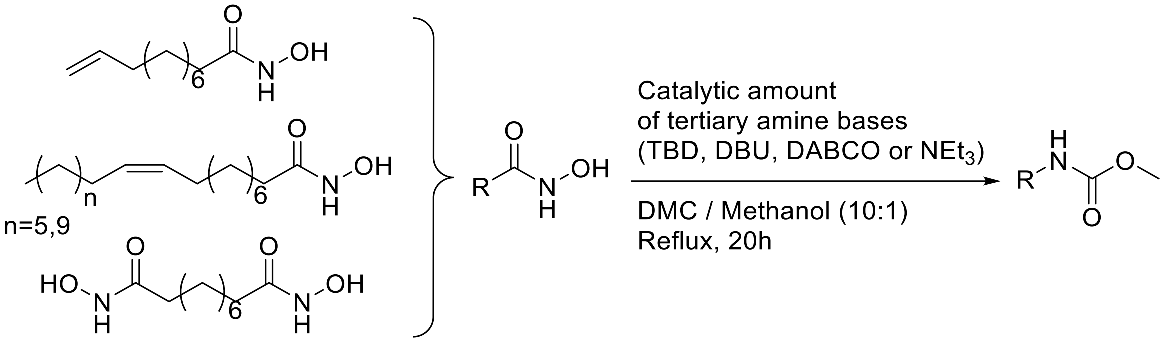


Figure 9- Monomers derived from fatty acids for the synthesis of PUs[25]

The PUs catalyzed by TBD have $\overline{M}_\mathrm{n}$ from 3.5 to 9.9 kg.mol^{-1} with dispersities between 1.3 and 2.7 while the ones catalyzed by K_2CO_3 have a $\overline{M}_\mathrm{n}$ of 13.9 kg.mol^{-1} and a dispersity of 1.9. This study demonstrates that K_2CO_3 is an interesting transurethanization catalyst; however, the polymerization temperatures are different impeding a real comparison between those catalysts. The glass transition temperatures of the PUs so-formed are ranging from -38 to -19°C. Most PUs are amorphous due to the presence of dangling chains brought by the fatty acid derivatives, but some present a fusion temperature around 61-64°C.

1.3.2 Fatty acid-based carbamates

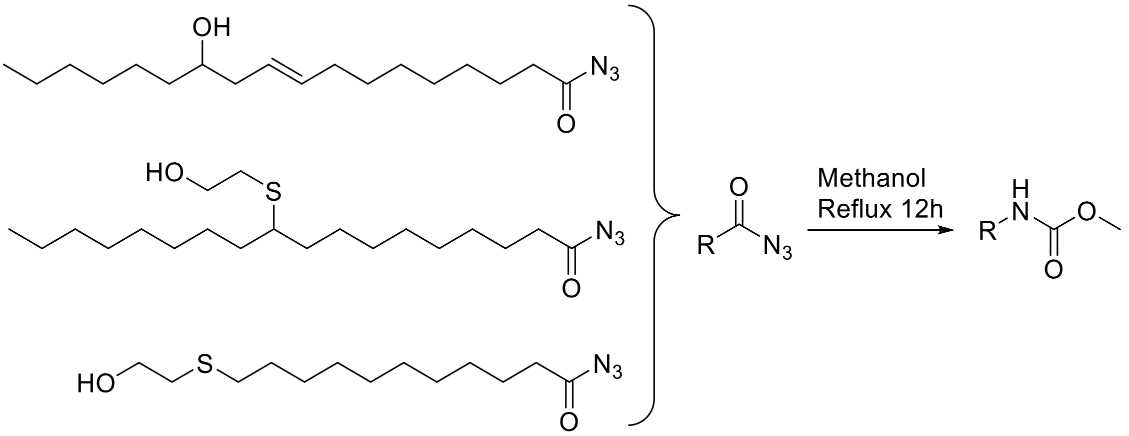
The Lossen rearrangement is usually used to transform hydroxamic acids into isocyanates. Meier and coll. introduced a modified method to get the corresponding carbamates with a catalytic amount of an organic base such as TBD in the presence of methanol. [43,53] Fatty acid methyl esters were easily turned into hydroxamic acids using hydroxylamine hydrochloride and potassium hydroxide. Bis-methylcarbamates and fatty carbamates were synthesized using this method (Scheme 5).



Scheme 5- Catalytic Lossen rearrangement towards fatty carbamates[43,53]

The polymerization of such bis-methylcarbamate with bio-based aliphatic diols was performed in bulk with catalytic amount of TBD under reduced pressure by increasing the temperature from 120°C to 160°C. The polymers obtained were crystalline with melting temperatures ranging from 120 to 145°C. The molar masses were comprised between $\overline{M}_{\mathrm{n}}$=7.1 and 24.6 kg.mol^{-1} with dispersities of 1.2 to 2.1.

Thanks to the plural functionality of fatty acids, AB-type synthons were synthesized by Cramail and coll. (Scheme 6). The hydroxyl function is naturally occurring in the alkyl chain of ricinoleic acid or it was brought by thiol-ene addition on the double bond of oleic acid and derivatives. The methylcarbamate functionality was brought by transforming the carboxylic acid into acyl azide by reaction with sodium azide. The acyl azide was then reacted with methanol to form the methylcarbamate.[5,51] Self-polymerizations were performed in the presence of $Ti(OBu)_4$ as catalyst at 130°C under N_2 atmosphere for 4h and then under reduced pressure for 2h. Polyurethanes obtained had low molar masses; with $\overline{M}_{\mathrm{n}}$ from 2.1 to 6.9 kg.mol^{-1} and dispersities from 1 to 2. Glass transition temperatures were ranging from -44 to -18°C. A second glass transition temperature was visible at around 25 to 32°C for PUs synthesized from thiol-ene modified synthons, which indicated a phase-separated morphology.



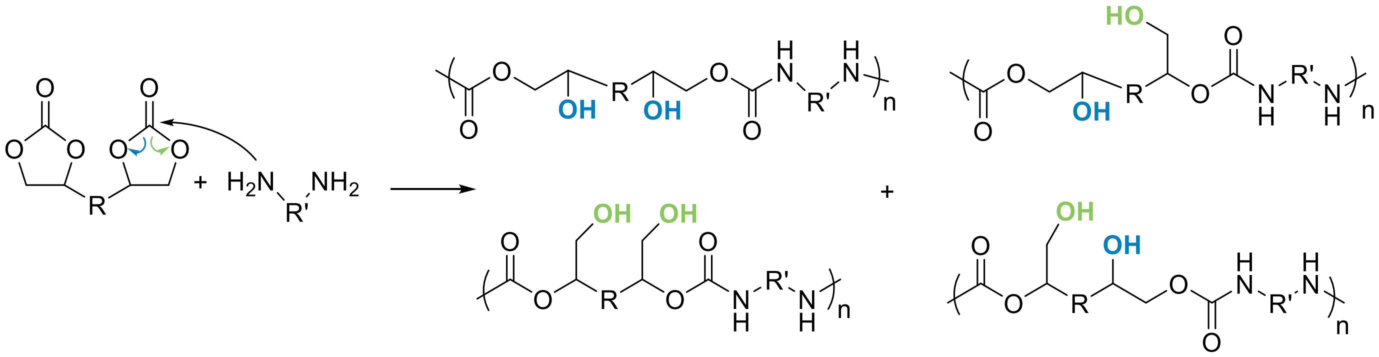
Scheme 6- Fatty acids-based AB-type synthons [5,51]

The transurethanization route can be applied to a wide variety of monomers, from petroleum-based diols and diamines to renewable ones. The monomer synthesis using dimethylcarbonate or ethylene carbonate is simple, green and can be easily done on an industrial scale. The polymerization process implies a removal of alcohol, usually methanol, which might be an issue for the scale up of the process. Moreover, the polymerization temperatures are pretty high, usually between 100 and 200°C and catalysts are necessary. Nevertheless, the PUs obtained by this route are equivalent to the PU obtained from diisocyanates and diols.

In the second part of this review, another NIPU route is discussed: the synthesis of poly(hydroxyurethane)s.

2- Thermoplastic poly(hydroxyurethane)s (PHUs)

Among non-isocyanate and non-phosgene routes to PUs, the approach involving the reaction of cyclic carbonate and amine functions is one of the most studied. The main route is a polyaddition of bis-5-membered cyclic carbonates and diamines leading to the formation of linear PHUs with primary or secondary alcohols, as illustrated in Scheme 7. One of the pioneers in this field are Groszos *et al.* [54]; the authors patented in 1957 the preparation of oligo hydroxyl-urethanes by the reaction between cyclic carbonate, amine compound and urea. Studies on cyclic carbonates [55-57] and PHUs [6,8-12,58-59] have been reviewed by several research groups.



Scheme 7 - Synthesis of polyhydroxyurethanes from bis 5-membered cyclic carbonates and diamines.

The PHUs obtained by this route exhibit various advantages such as the bypass of isocyanate and phosgene making the process safer, and the capture of CO_2 in some cases. The non-moisture sensitivity is also an advantage of this pathway. Indeed, no particular caution during the storage processes is required and no formation of irreversible side products (urea and CO_2) like in the classical isocyanate/alcohol route is observed. [9] Besides, the possibility to prepare materials with no release of volatile organic compounds promotes the use of this route for coating applications. [7] The presence of the hydroxyl groups in the structure gives specific properties to the polymer. The hydroxyl groups formed at the β-carbon atom of the urethane moiety can participate into intramolecular and intermolecular hydrogen bonds. Those hydrogen bonds combined with non-porous materials and the absence of thermally labile biuret and allophanate groups enable improved thermal stability and chemical resistance to non-polar solvents.[9,60] The authors disagree on the water absorption effect of PHUs compared to classical PUs. Some claimed lower water absorption thanks to the hydrogen bonds [11], but others presented higher water absorption due to the hydrophilicity of the polymer formed. [61] Moreover, the reactive pendant hydroxyl groups enable further post-functionalizations of the PHUs with chemical and biological functionalities. [6]

Figure H-bonding : deleted

2.1- Precursors for poly(hydroxyurethane)s

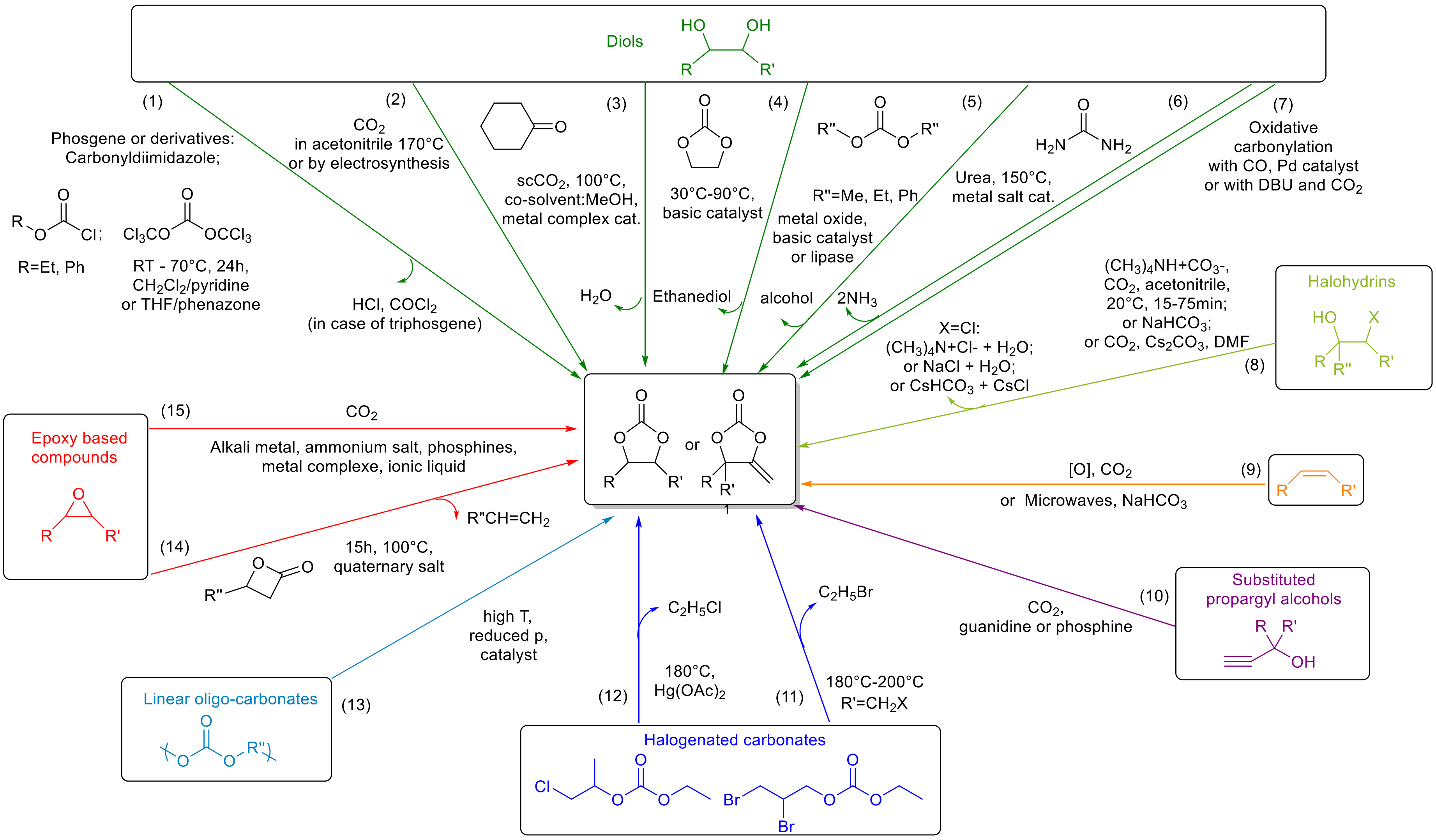
2.1.1- Synthesis of 5-membered cyclic carbonates (5CC)

The synthesis of 5-membered cyclic carbonates (or 1,3-dioxolan-2-one)-based compounds has been extensively studied along the years, through various methods. It is noteworthy that ethylene carbonate and propylene carbonate have been commercially available since over 45 years. Recently, the commercially available glycerol carbonate generated global interest in the community. [62-64] Generally speaking, the 5-membered cyclic carbonates can be achieved from linear oligo-carbonates, diols, halohydrins, olefins, substituted propargyl alcohols, halogenated carbonates and, in a larger proportion, from epoxy compounds and CO_2. [56,65-67] The main approaches are summarized in the Scheme 8.

The group of Carothers [68-71] was the first to report the synthesis of various size cyclic carbonates in the early 1930s. Cyclic carbonates were obtained by depolymerization of the respective linear oligo-carbonates using high temperatures and reduced pressure as well as various catalysts such as Sn(II), Mn(II), Fe(II), and Mg(II) chlorides, carbonates or oxides (Scheme 8-(13)).

Diols and polyols are ones of the main precursors, with epoxy compounds, for the synthesis of 5-membered cyclic carbonates. The first route from diols is the phosgenation approach using phosgene or its derivatives such as the triphosgene (Scheme 8-(1)). For the first time in 1883, Nemirovsky synthesized ethylene carbonate directly by using phosgene and ethylene glycol. [72] As another example, Burk and Roof [73] synthesized 5-membered cyclic carbonates from 1,2-diols and triphosgene using pyridine in CH_2Cl_2 at 50°C with yields in the range 87% to

99%. Endo and coll. [61,74] also used triphosgene for the synthesis of cyclic carbonates. The high toxicity and hazards of phosgene make this way not suitable even if high yields of cyclic carbonates could be reached.



Scheme 8- Main routes for the synthesis of 5-membered cyclic carbonates. [7-9,75]

Other methods are the reactions of 1,2-diols with carbon dioxide using metallic acetates in acetonitrile [76] or by electrosynthesis [77-78] (Scheme 8-(2)), and the oxidative carbonylation with carbon monoxide using for instance palladium-based catalysts (Scheme 8-(7)). [79-80] The approach involving the formation of a ketal from ethylene glycol and cyclohexanone, which then reacts in the presence of supercritical CO_2 is also a route to cyclic carbonates (Scheme 8-(3)). [81] In another way, the carbonate interchange reaction between 1,2-diols and ethylene carbonate (Scheme 8-(4)) [82] or dialkyl carbonates (dimethyl carbonate, diethyl carbonate or diphenyl carbonate) (Scheme 8-(5)), leads to cyclic carbonates with good yields (40-80%) in the presence of catalysts such as for instance organic bases, metal oxide (MgO, CaO, La_2O_3) catalysts, hydrotalcite or enzymes. [10,65,83-86] The reaction with urea in the presence of catalysts is another possibility for the synthesis of cyclic carbonates from 1,2-diol (Scheme 8-(6)). [87-88] Recently, Lim *et al.* [89] achieved the synthesis of cyclic and linear carbonates from diols and alcohols by using a transition metal free synthesis. The cyclization process was carried out with DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) in dibromomethane under 5 to 10 bars of CO_2, and lead to good yields (47-86%).

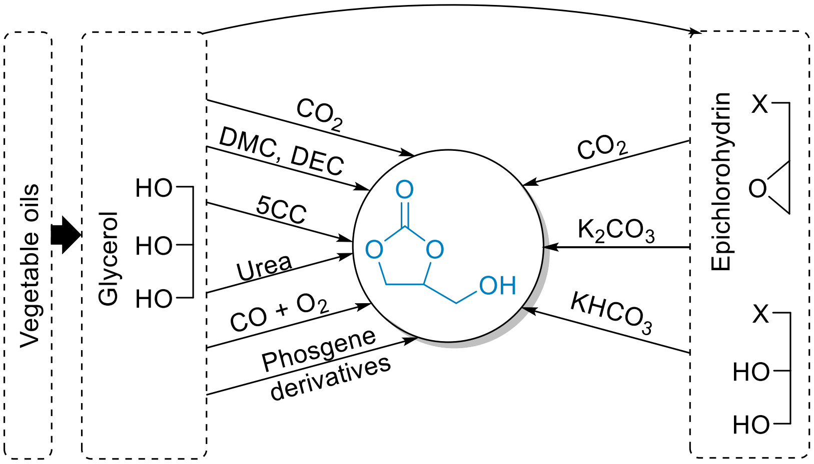
Cyclic carbonates can also be prepared from halohydrins using sodium bicarbonate (Scheme 8-(8)) [90] or cesium carbonate in DMF [91] under mild conditions, or directly from olefins by oxidative carboxylation (Scheme 8-(9)). [92-93] Furthermore, the reaction of substituted propargyl alcohols with CO_2 (Scheme 8-(10)) in the presence of guanidine catalyst can produce cyclic carbonates with yields up to 82%. [94] The phosphine-catalyzed transformation of propargyl alcohol (Scheme 8-(10)) gives also access to cyclic carbonates. [95] Taking another example, halogenated carbonates can be converted into cyclic carbonates at a temperature between 180°C and 200°C (Scheme 8-(11)-(12)). [96-97]

In addition, epoxy compounds can be converted into cyclic carbonates by the reaction with β-butyrolactone (Scheme 8-(14)) [98] or in a much more common approach by the chemical insertion of CO_2 (Scheme 8-(15)). The latter strategy has been extensively studied throughout different reaction conditions and catalysts optimizations. This method presents various advantages compared to the previous presented routes. Indeed, first the recapture of the CO_2 is a benefit regarding both the economical and environmental points of view.[99] Second, even if this reaction is usually performed at high pressure, in presence of a suitable catalyst, very high yields can be reached and it is a 100% atom economical reaction. The carbon dioxide both acts as an aprotic solvent and as a reagent. [100] A plethora of catalysts has been investigated including homogeneous or heterogeneous ionic liquids, ammonium or phosphonium salts, amines, metal oxide, metal halide and metal complexes. The most commonly used catalysts are the tetraalkylammonium halide. [67,101-102, 103]

Starting from olefin moieties, Yang *et al.* [104] showed a possible one-pot microwave assisted synthesis of cyclic carbonates, passing by an epoxide intermediate, using $NaHCO_3$ as co-reactant.

A particular case of 5-membered cyclic carbonate, which is already commercially available and bio-based, is the glycerol carbonate. [62-64] The latter can be synthesized either from glycerol (obtained from vegetable oils by saponification or methanolysis) following the methods developed above, or from activated glycerol (3-chloro-1,2-propanediol) or epichlorydrin using

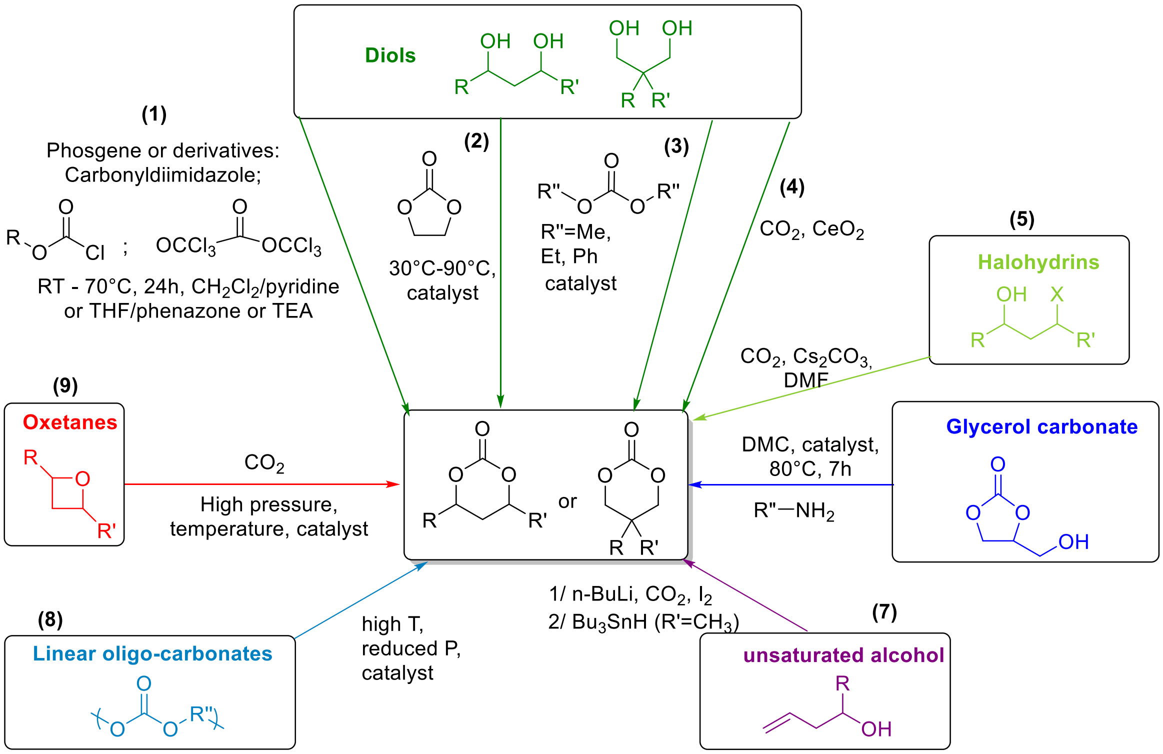
CO_2 or alkaline carbonate as sketched in Scheme 9. From glycerol, one of the most interesting routes would be the use of CO_2 to reach glycerol carbonate; however this route suffers from low conversions and yields. The more suitable processes are the use of ethylene carbonate or dialkyl carbonates, indeed. [64]



Scheme 9- Synthesis of glycerol carbonate. (DMC=dimethyl carbonate, DEC=diethyl carbonate, 5CC=ethylene carbonate).

2.1.2- Synthesis of 6- and 7-membered cyclic carbonates (6CC and 7CC)

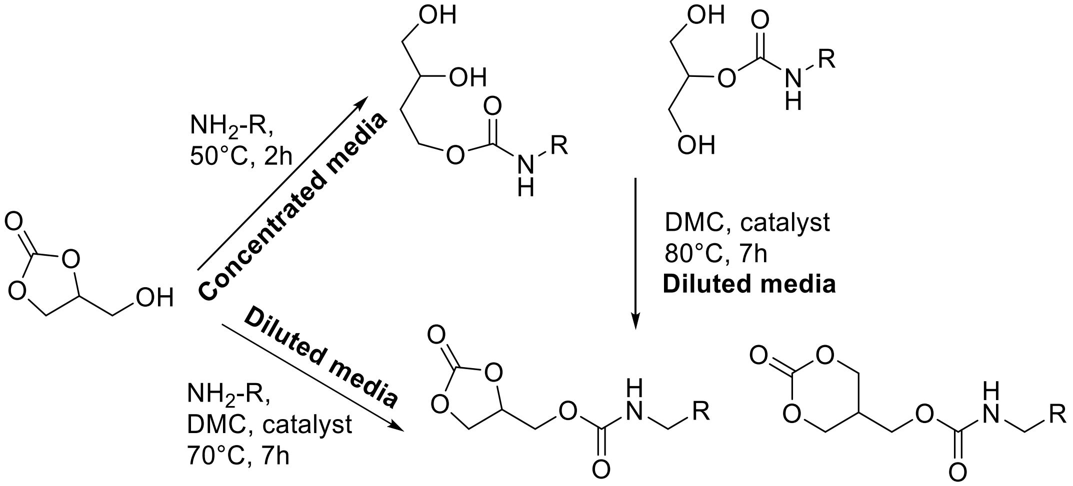
The 6-membered cyclic carbonates can be prepared by similar methods as the ones used for the synthesis of 5-membered cyclic carbonates. [9] They can be achieved in a large proportion from 1,3-diols (also indirectly from glycerol carbonate), and, in a lower extent from 3,4-unsaturated alcohols, oxetanes using CO_2, or halohydrins. The main approaches are summarized in the Scheme 10.



Scheme 10- Main synthetic methods for the synthesis of 6-membered cyclic carbonates.

The depolymerization process of linear oligo-carbonate presented in the previous part is still applied in the synthesis of 6- and 7-membered and of larger size aliphatic cyclic carbonates (Scheme 10-(8)). In another method, the 1,3-diols or 1,4-diols can be transformed into 6- and 7-membered cyclic carbonates respectively using phosgene derivatives such as triphosgene (Scheme 10-(1)) [74,105] or ethyl chloroformate. [62, 63] A closed method to afford 6-membered cyclic carbonates from 1,3-diols is the use of dialkyl carbonates (Scheme 10-(3)). The presence of a catalyst is essential for this carbonate interchange.[66] Possible catalysts are alkaline metals, [106-107] amines, basic ion-exchange resins, [11] oxide, alkoxide, or carboxylate salt of zinc, titanium, or tin, [108-110] enzymatic catalyst, [111]… Pyo *et al.* [111-112] reported that six-membered cyclic carbonates with functional groups could be synthesized in the presence of lipase (Novozym 435), in a solvent-free medium.

The possibility of synthesizing 5- and 6-membered cyclic carbonates with α-urethane group from glycerol carbonate and dimethyl carbonate (DMC) (Scheme 10-(6); Scheme 11) has been investigated in the presence of various catalysts, without solvents. [113] .



Scheme 11- Synthesis of 5- and 6-membered cyclic carbonates with an α-urethane group. [113]

A recent study exhibited the synthesis of 6-membered cyclic carbonates from various diols with CO_2 (130-160°C, 5MPa) and CeO_2 as catalyst (Scheme 10-(4)). [114] The yields were particularly high (>99%).

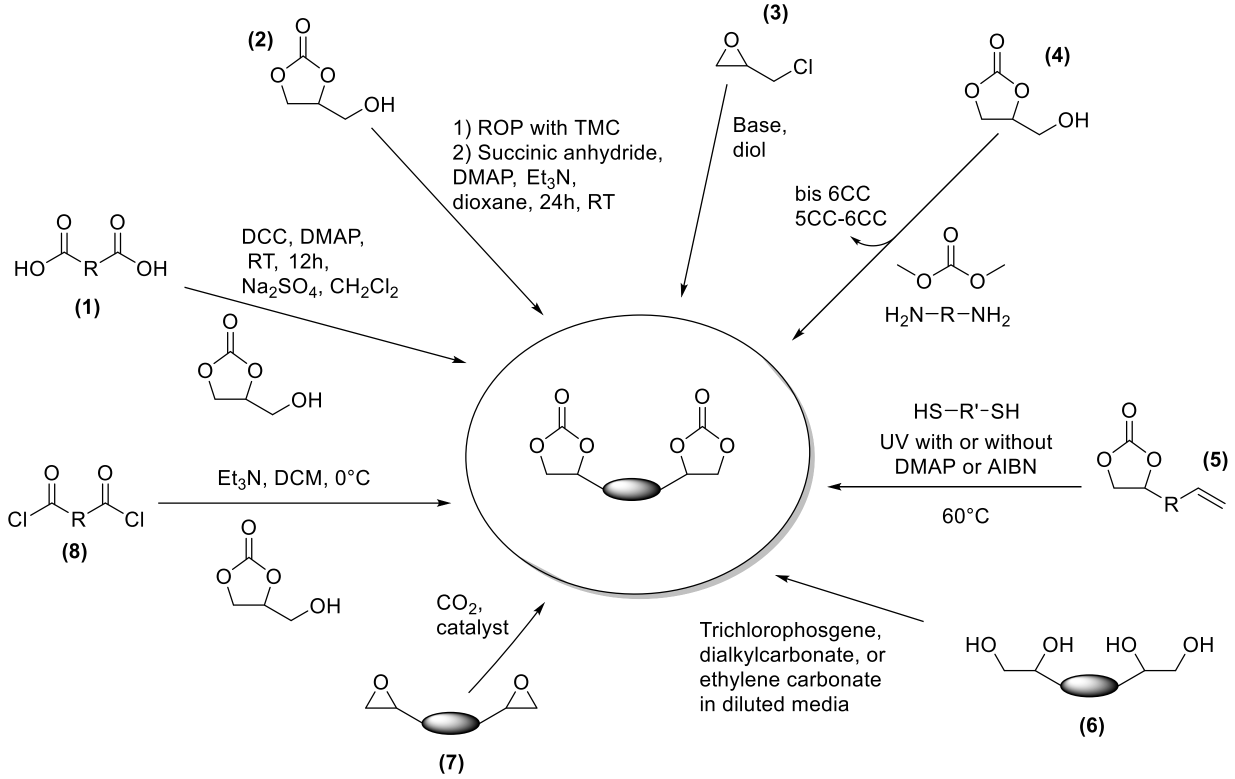
The reaction of oxetane with CO_2 (Scheme 10-(9)) can also be used to prepare 6-membered cyclic carbonates. The addition of CO_2 is less efficient in the case of oxetane than for epoxides. Moreover, the efficiency of this reaction dramatically decreases with the number and the size of the substituents. [115-116] The 6-membered cyclic carbonates have also been synthesized from halohydrins with CO_2 using cesium carbonate in DMF (Scheme 10-(5)). [91]

In case of 7-membered cyclic carbonates, they can be prepared by the same carbonation reaction pathways as those leading to 5- and 6-membered cyclic carbonates, or by the reaction of an appropriate diol with phosgene (or its derivatives) in the presence of phenazone. Moreover, according to the depolymerization method, the corresponding cyclic dimers are formed almost exclusively when the expected monomer cycle size is from 7 to 12.[56]

2.1.3- Synthesis of bis-cyclic carbonates (bCC)

In order to obtain poly(hydroxyurethane)s by polyaddition, various techniques have been developed to synthesize bis cyclic carbonates. For the first presented methods, the bis 5-membered cyclic carbonates are derived from already formed 5-membered cyclic carbonates which present another reactive group such as in glycerol (hydroxyl) or in unsaturated-based cyclic carbonate (double bond). In order to keep the cyclic carbonate functions, mild reaction conditions are required for the coupling.

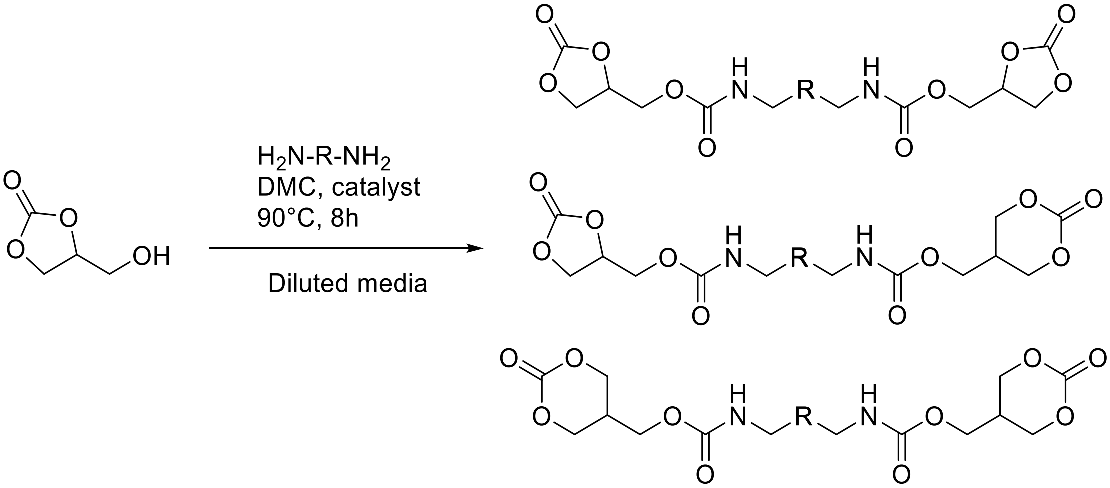
Scheme 12 illustrates the various routes to synthesize bis 5-membered cyclic carbonates. Similar methods have been employed for the coupling to obtain bis 6-membered cyclic carbonates. [61,117]



Scheme 12- Synthesis of 5-membered bis-cyclic carbonates.

From glycerol carbonate, a transesterification with a diacid using dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) (Scheme 12-(1)) at room temperature enables the formation of a bis cyclic carbonate. [7,118] Recently, Carré *et al.*[119] synthesized a bis-cyclic carbonate from sebacoyl chloride and glycerol carbonate (Scheme 12-(8)), using triethylamine in dry DCM to perform the reaction. Ring-opening polymerization has also been carried out using the hydroxyl of the glycerol carbonate as initiator. The biscyclic carbonate was then obtained using the same mild condition coupling (Scheme 12-(2)). [120] Another option is the thiol-ene reaction on unsaturated cyclic carbonates by photochemical initiation (Scheme 12-(5)) [121-122] or *via* thermal means using azobisisobutyronitrile.[61,117,121]

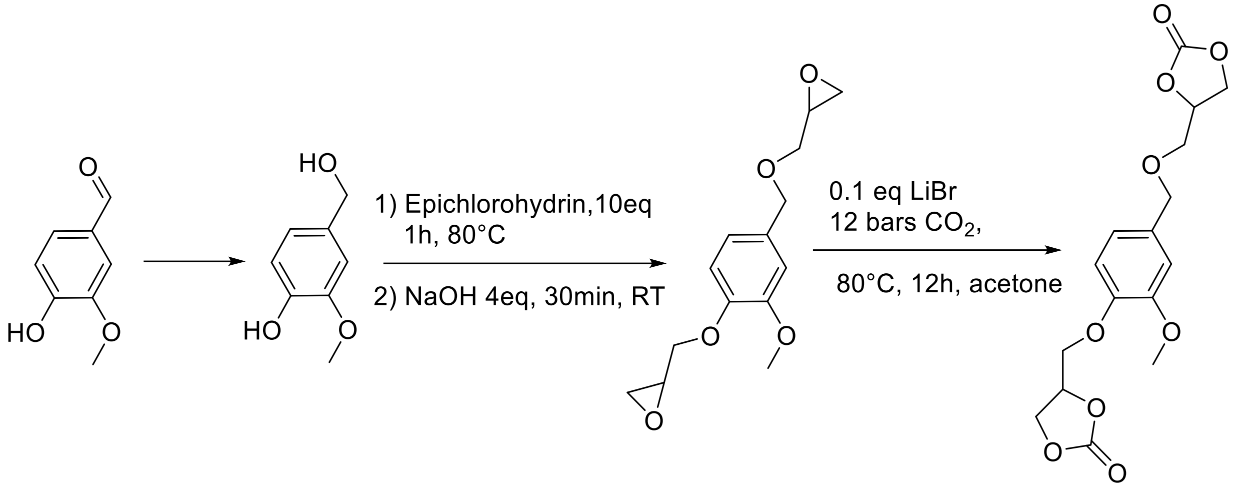
Mouloungui and coll. [113] prepared a mixture of 5- and 6-membered cyclic carbonates directly from glycerol carbonate, dimethyl carbonate and diamine (Scheme 12-(4), Scheme 13). The authors optimized the conditions by playing on the solubility properties of dimethyl carbonate and methanol and by using a strong basic liquid catalyst.



Scheme 13- Synthesis of 5- and 6-membered bis cyclic carbonates from glycerol carbonate, dimethyl carbonate and diamine.[113]

Following another strategy, other bis or poly(5-membered cyclic carbonate)s were synthesized either from bisepoxy [123-125] or polyepoxides [126] by insertion of CO_2 (Scheme 12-(7)), or from tetraols or polyols using phosgene derivatives [127], diethyl carbonate [128-129], imidazole carboxylic esters or ethylene carbonate [82] (Scheme 12-(6)) in particular conditions.

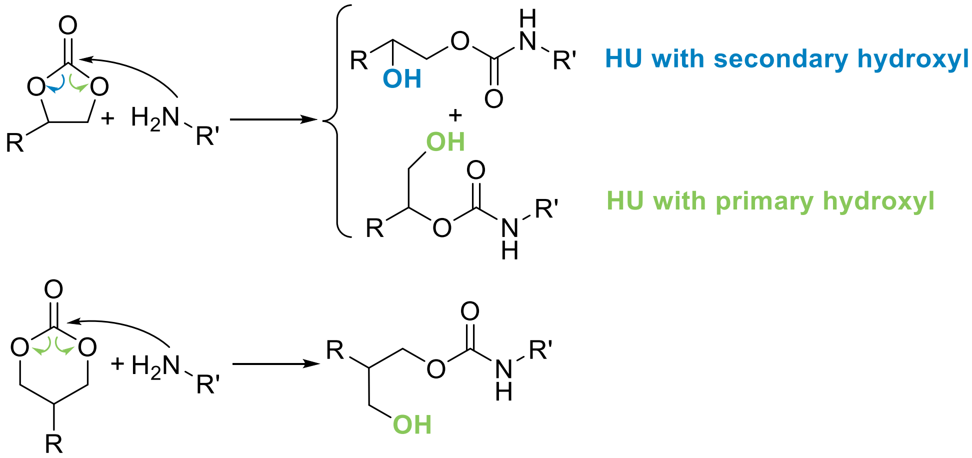
Recently, Caillol and coll.[130] synthesized several monomers based on vanillin as polymer starting material. The corresponding bis-carbonate was synthesized by reduction of vanillin, followed by the reaction with epichlorohydrin. The resulting bis-epoxide was carbonated under CO_2 pressure at 80°C (Scheme 12-(3), Scheme 14).



Scheme 14- Synthesis of bis cyclic carbonate from vanillin moiety. [130]

2.2- Studies on the model cyclic carbonate / amine reaction

Before performing the synthesis of PHUs, authors have studied the reactivity of cyclic carbonates with amines on model reactions to have a better understanding of the nucleophilic addition reaction between cyclic carbonates and amines, as illustrated in the Scheme 15.



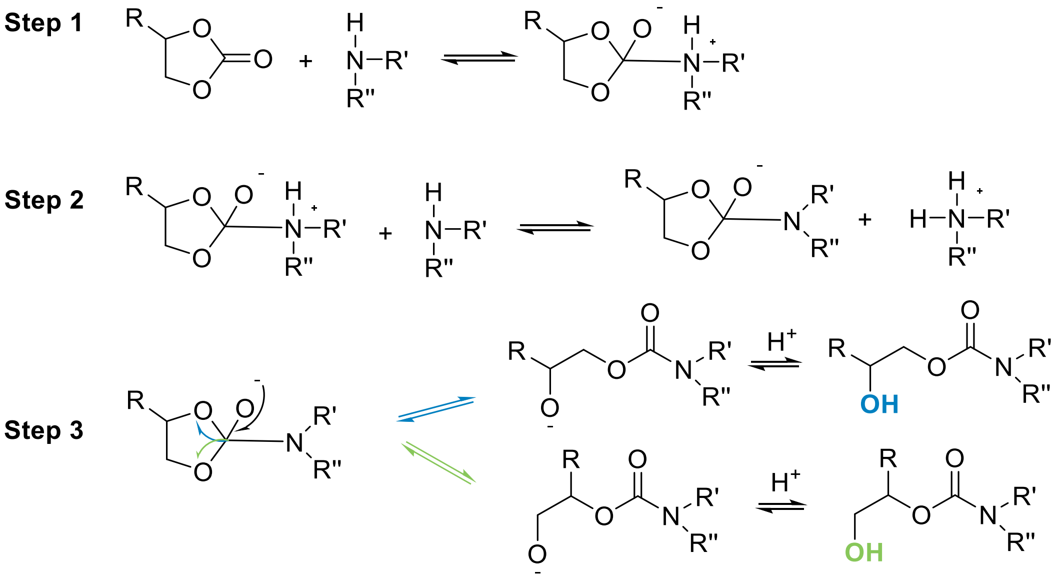
Scheme 15- Model reaction on 5- and 6-membered cyclic carbonates leading to hydroxyurethanes.

2.2.1- Mechanism of cyclic carbonate aminolysis

Two reaction mechanisms have been proposed. First, Tomita *et al.* [131] suggested a mechanism through an amphoteric tetrahedral intermediate (Scheme 16). Garipov *and coworkers* [132-133] proposed a similar mechanism proceeding in three steps and involving also a tetrahedral intermediate.

Zabalov *et al.*[134] established with DFT calculations that hydroxyurethane formation may progress notably throughout a six centers ring intermediate based on the 5-membered cyclic carbonate and two amine molecules, one playing a catalytic role.

Finally, the authors agree that the participation of a second amine molecule is necessary and substantially accelerates the process.



Scheme 16- Mechanism through the formation of a tetrahedral intermediate for the reaction between 5-membered cyclic carbonates and amines.

2.2.2- Kinetic and reaction conditions

The kinetic of the reaction has been studied by different research groups. Moreover, various reaction conditions have been tested in the literature for the addition of amines on cyclic carbonates. Some authors pointed out the effect of the temperature, the initial concentration of the reactants and the solvent.

The increase of the reaction temperature leads to higher reaction rate. However, Burgel *et al.* [135-136] proved that using a temperature higher than 100°C resulted in the formation of side products. Besides, depending on the selected solvent, the reaction rates are variable. Most of the reactions are performed in DMSO or DMF. Tomita *et al.* [131,137] demonstrated a slight increase of conversion and yields for reaction in toluene compared to DMSO.

Concerning the effect on the reaction of the presence of solvent and the initial concentration of the reactants, it has been shown in various studies that the reaction of cyclic carbonates and amines occurs faster in bulk than in solvent. [138] A decrease of the initial concentration of the reactants also affects the reaction rate as it has been shown by Tabushi *et al.* (review by Webster *et al.*) [55], Nemirovsky *et al.* [139] and Burgel *et al.* [140].

The majority of the authors who studied the kinetic of the reaction of cyclic carbonates with amines in aprotic solvents agree on a kinetic of an overall second order. [74,131,138-139,141-144] However, few reports relate higher kinetic order with respect to the amine,[132] as well as the auto-catalytic effect of the hydroxyurethane formed.[55]

The polyaddition of amines onto cyclic carbonates is governed by several parameters such as solubility, type of solvents, concentration and temperature. Besides, the chemical structure of both amines and cyclic carbonates has a significant impact on the polymerization rate.

2.2.3. Selectivity of the reaction

Two isomers can be formed while reacting 5-membered cyclic carbonates with amines: one with primary hydroxyl groups and one with secondary ones. In the case of the reaction between 6-membered cyclic carbonates, only primary hydroxyl groups are obtained if the carbonate is substituted in β of the oxygen (Scheme 15). In a general trend, it was found that substituted 5-membered cyclic carbonates react with amines to give preferentially secondary hydroxyl groups. Steblyanko *et al.* [124] reacted glycerine carbonate benzoate with benzyl amine at room temperature. The secondary hydroxyl group product was predominant in a ratio of OH I:OH II of 18/82%. They carried out theoretical calculations and confirmed that the secondary hydroxyl product was enthalpically more stable than the primary hydroxyl group product by about 1.67 kcal.mol^{-1} : $_{\Delta Hf(OH\ I)}$=-8.10 Kcal.mol^{-1} and $_{\Delta Hf(OH\ II)}$=-9.77 Kcal.mol^{-1} (Figure 10).

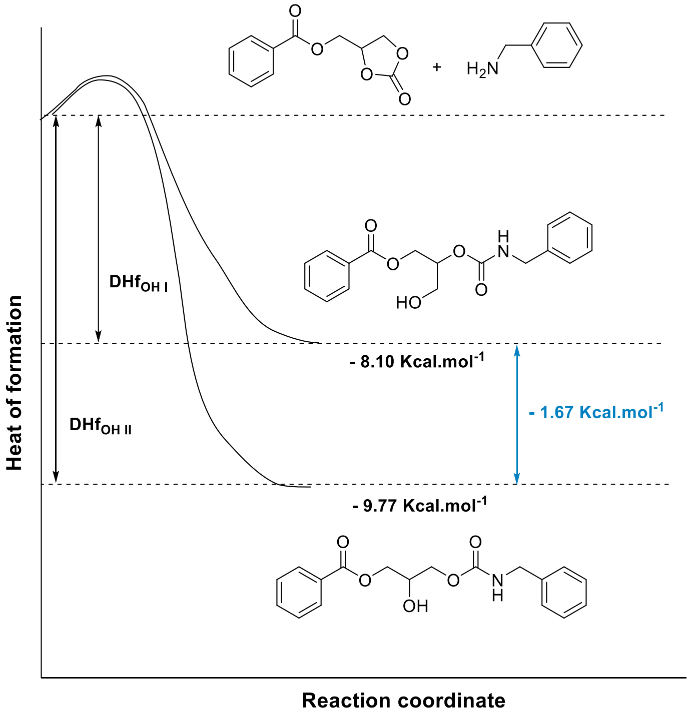


Figure 10- Energy profile of ring-opening addition of 5-membered cyclic carbonate with benzylamine. [124]

Accordingly the bond orders in substituted 5-membered cyclic carbonate calculated by the ab initio method, indicate that there should be more of the hydroxyurethane containing secondary hydroxyl moiety than hydroxyurethane containing primary hydroxyl group (Figure 11). [131,137]

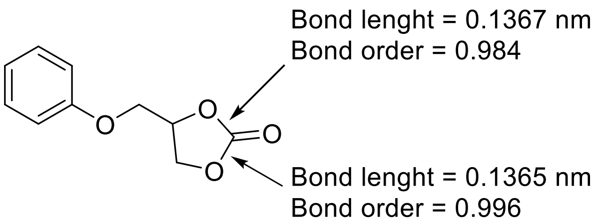


Figure 11- Bond lengths and order calculated by the ab initio method using the STO-3G basis set. [137]

Authors found an influence of the solvent and the chemical structure of amines and cyclic carbonates on the isomers ratio, although the selectivity of hydroxyurethane seems independent of the reaction temperature. Tomita [137] conducted a study of the effect of reaction conditions on the structure of the urethane formed. Their analysis indicated an isomer ratio slightly dependent on the solvent polarity and the amine structure. For instance the isomer with secondary hydroxyl is less formed in DMSO than in toluene.[131,137] The influence of the amine chemical structure was reported by different research groups [162, 163] One of them showed that a lower amount of hydroxyurethanes containing secondary hydroxyl was obtained when benzylamine was preferentially used to hexylamine.[137] Another research group concluded that as the alkyl chain of the amine increases, the yield increases and the ratio OH I:OH II increases.[145] With secondary amines, they even found an equivalent proportion of OH I and OH II.

In addition, the effect of the cyclic carbonate substituents was clearly demonstrated and explained by the mechanism (Scheme 16).[131-132,138] The selectivity of the reaction favored the secondary hydroxyl-based hydroxyurethane as the electron withdrawing character of the substituent increased. [131] Indeed, the inductive effect increases the acidity of the negatively charged oxygen and stabilizes the transition state. The reaction thus favors the formation of structures with secondary hydroxyl groups. Iwasaki *et al.* [146] also observed this trend with phenyl substituents having para-groups of different electron withdrawing effect. As an extreme result, Ochiai [147] obtained only secondary hydroxyl group performing the reaction between diethyltriamine and carbonated epichlorohydrin.

2.2.4- Effect of the chemical structure of the amine

The chemical structure of the amine influences the reaction rate as proved by numerous studies. All authors agree that secondary amines are less reactive, even non-reactive, toward cyclic carbonate compared to primary ones. The nucleophilicity of the amine seems to govern its reactivity. [55,74,132,136,140,148]

Lately, Camara *et al.* [149] also studied the lower reactivity of secondary amines towards cyclic carbonates. Nevertheless, basing their observation on a model reaction, the authors pointed out the possibility for polyhydroxyurethanes bearing secondary amine functions in their backbone to crosslink with the remaining cyclic carbonates from a certain temperature.

Besides, Diakoumakos *et al.* demonstrated that amines with strong electron withdrawing groups in the α or β position with respect to the reactive amino group are more reactive. Besides, their research indicates that the molar mass of amines has a certain influence on their reactivity.

Higher molar mass amines were less reactive than shorter ones. The scale of reactivity of the tested amines was illustrated (See Figure 12). Demonstrating a same trend, Nohra *et al.* [145] found that as the alkyl chain of the amine increases, the carbonate yield slightly decreases.

The authors concluded that the reaction rate depends on the nucleophilicity, the chemical structure and the steric hindrance of the amine. [74,150]

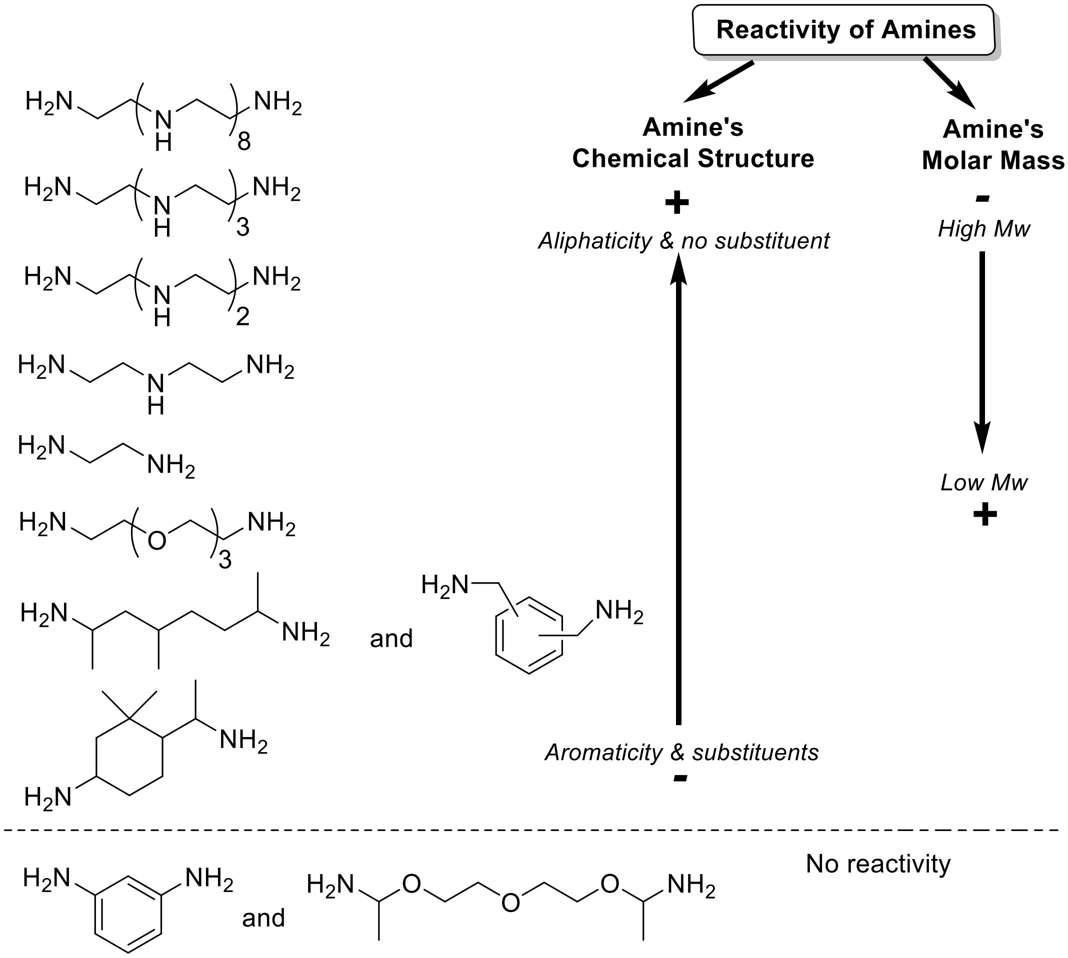


Figure 12- Scale of reactivity of various amines toward a model cyclic carbonate (according to Diakoumakos et al) . [151]

2.2.5- Effect of the substituents and size of the cyclic carbonate

Several studies relate the effect of the cyclic carbonate substituent on the reaction rate and the final isomer product. First papers reported either that electron withdrawing groups on the cyclic carbonate retarded the reaction rate (Mikheev *et al.* reviewed by Webster *et al.* [55]), or that the cyclic carbonate substituent has a limited influence on the reaction rate (Couvret *et al.* [138]). Those conclusions are not in accordance with more recently published literature.

Tomita et al. [131] studied a large series of mono-substituted 5-membered cyclic carbonates and found that the reaction rate with amine increased as the electron withdrawing character of the substituent increased. Garipov et al. [132] proved that the presence of an electron releasing substituent (+I) in the cyclic carbonates results in a decrease of the partial positive charge on the carbonyl carbon. This results in a reactivity decrease of the cyclic carbonate towards amine. On the contrary, electron-withdrawing substituents (-I) increase the electrophilicity of the carbonyl carbon and thus favor higher reaction rate with amines. (See Figure 13)

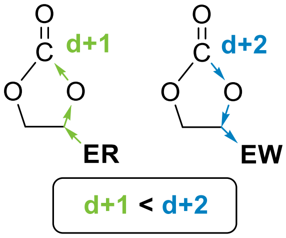


Figure 13- Effect of the electron releasing (ER) and electron withdrawing (EW) substituents.

He *et al.* [142] examined the reactivity of various 5-membered cyclic carbonates bearing either urethane with the oxygen atom near the cyclic carbonate in α or in β. The authors concluded that the more distant the electron-withdrawing group is from the cyclic carbonate, the less reactive it is.

In another study, Ochiai *et al.* [141] found out that a 6-membered cyclic carbonate was more reactive than a 5-membered one, and supposed that the difference in reactivity comes from the different ring-strain. In 2001, two chemically similar bis cyclic carbonates were synthesized by another research group [61], one with two 5-membered rings (b5CC) and the second one with 6-membered rings (b6CC). The bis 6-membered cyclic carbonate was converted quantitatively after 48 hours although the conversion of the bis 5-membered cyclic carbonate was only 67% during this time period. Moreover, the bis 6-membered cyclic carbonate enabled forming PHUs with a molar mass of 26 000 g.mol^{-1} after 48h, whereas the molar mass obtained in the case of bis 5-membered cyclic carbonate was only of 15 000 g.mol^{-1} after 14 days ($\overline{M}_{\mathrm{n}}$, DMF, LiBr, PS standards). The calculated reaction rate constant enabled quantifying the higher reactivity of the 6-membered cyclic carbonate toward the 5-membered one: $k_{b6CC\text{-}30°C}$= 0.70 L.mol^{-1}.h^{-1}; $k_{b6CC\text{-}50°C}$= 0.89 L.mol^{-1}.h^{-1}; $k_{b6CC\text{-}70°C}$= 1.07 L.mol^{-1}.h^{-1} and $k_{b5CC\text{-}30°C}$= 0.03 L.mol^{-1}.h^{-1}; $k_{b5CC\text{-}50°C}$= 0.06 L.mol^{-1}.h^{-1}; $k_{b5CC\text{-}70°C}$= 0.10 L.mol^{-1}.h^{-1}. The reaction rate for the bis 6-membered cyclic carbonate was lower than the one calculated for the 6-membered cyclic carbonate, probably because of the lower mobility of the reactive sites of the bifunctional monomer and polymer ends. In contrast, they were almost equal in the case of bifunctional and monofunctional 5-membered cyclic carbonates, certainly because of their low reactivity. Besse *et al.* [117] in 2013 also observed higher molar mass for the PHU from bis 6-membered cyclic carbonate compared to the ones from bis 5-membered cyclic carbonate. He *et al.* [152] confirmed the difference in reactivity of the two different size rings, studying monomers bearing a 5- and a 6-membered cyclic carbonates.

Additionally, Tomita *et al.* [74] found that 6-membered cyclic carbonates were more reactive than the 5-membered homologues, with reaction rate constants 29 to 62 times higher. Maisonneuve *et al.* [144] confirmed their greater reactivity with a factor 30 between both reaction rate constants. Going even further, the group of Endo [105] prepared bis 7-membered cyclic carbonates and observed higher reactivity and molar mass than bis 5- and 6-membered cyclic carbonates. Molar masses up to 35 700 g.mol^{-1} ($\overline{M}_{\mathrm{n}}$, Đ=2.8, DMF, LiBr, PS standards) were obtained after only 6 hours of reaction. Regarding 6- and 7-membered cyclic carbonates, the authors did not mentioned any side reaction generated by the attack of the primary hydroxyl group formed onto the carbonyl of the cyclic carbonate. However, due to the high reactivity of the 7-membered cyclic carbonates, its reaction rate constant in DMSO at 50°C was not calculated.

2.2.6- Additives and catalysts for the cyclic carbonate/amine reaction

Theoretically, the ring-opening reaction of cyclic carbonates by amines may be accelerated through activation of the monomers. To this purpose, either weakly Lewis acidic and oxophilic additives may be added to increase the electrophilicity of the cyclic carbonate group, or basic additives can be used to increase the nucleophilicity of the amines and even to deprotonate the amines. Another possibility is to use a Lewis base to attack the carbon of the cyclic carbonate carbonyl. The Lewis base will be then a potential good leaving group that will favor the attack of the amine molecule.

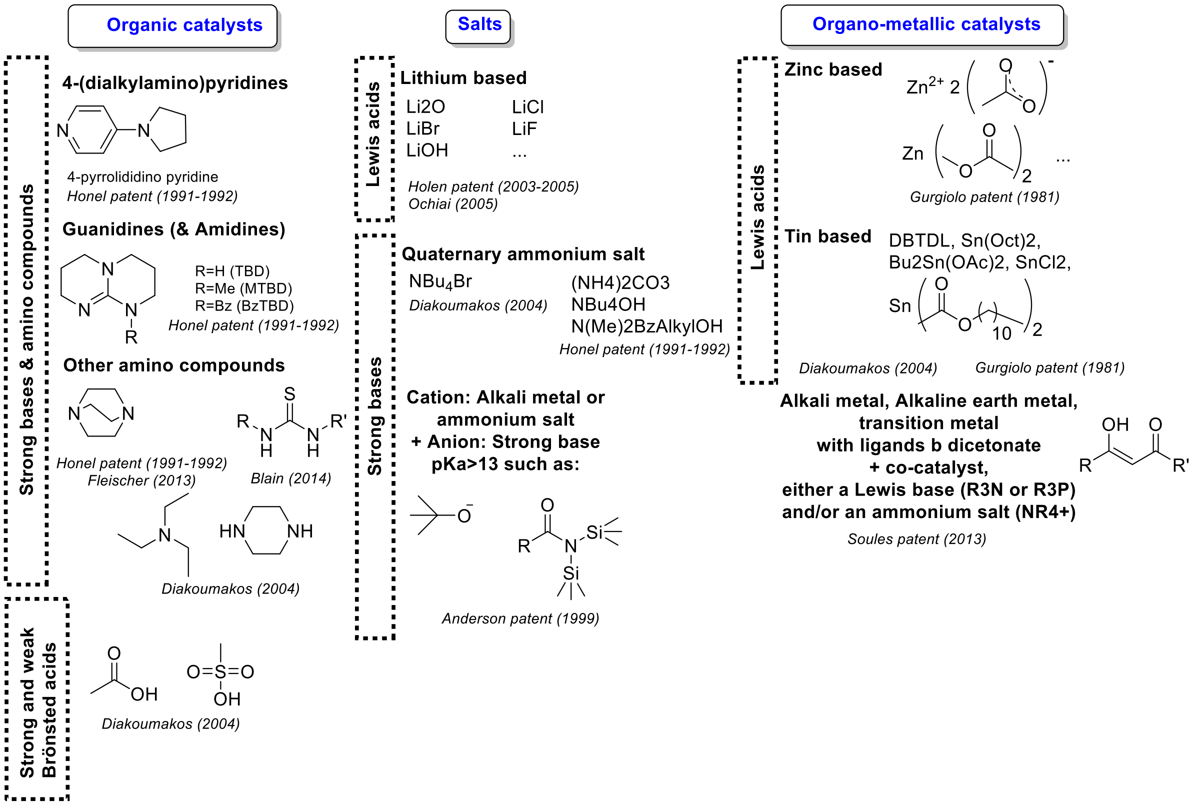


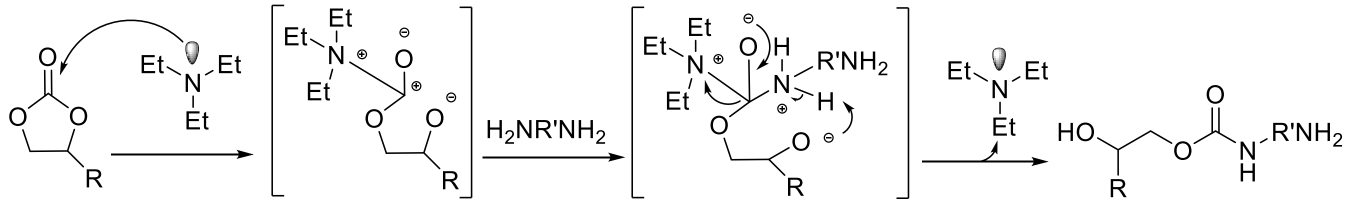
Figure 14- Various tested catalysts for the cyclic carbonate / amine reaction.

Concerning the catalysis of this reaction, almost exclusively patents have been reported. There are only few papers that deal with this specific point. They are discussed in priority after a general overview. Most of the tested catalysts and additives used are summarized in Figure 14. Different classes of catalysts have been tested, among them organic catalysts, organometallic catalysts and salts.

Amongst organic catalysts, either strong bases (such as 4-pyrrolididino pyridine, guanidines (TBD, MTBD), 1,4-diazabicyclo[2.2.2]octane (DABCO), piperazine and triethylamine) [151,153-156], or strong or weak Brönsted acids (glacial acid acetic, methanesulfonic acid)[151] have been used for the catalysis of the cyclic carbonate / amine reaction. Salts combining an alkali metal or ammonium salt cation, with an anion such as OH^-, CO_3^{2-}, Br^-, Cl^-,… or a strong base have also been tested.

[151,153-154,157] In this category lithium based salts such as Li_2O, LiBr, LiCl, LiOH, LiF,… were investigated. [155,158-160] For organometallic catalysts, zinc, tin and chrome-based compounds have been found to have some activity to catalyze the cyclic carbonate / amine reaction. [151,160-162] Nanoclays have also been patented for a beneficial effect on the rate of gelling and cure time. [163] Alkali metal-based Lewis acid such as LiCl, LiBr or LiF can be employed to increase the reaction rate. [122,164] They activate the carbonyl group without the deactivation of the amine. Ochiai *et al.* [160] observed that the higher molar masses were obtained with LiCl, LiF and Bu_4Sn, which give molar masses of 36 700 $g.mol^{-1}$ ($\overline{M}_n$, Đ=1.84), 31 600 $g.mol^{-1}$ ($\overline{M}_n$, Đ=1.71) and 32 700 $g.mol^{-1}$ ($\overline{M}_n$, Đ=1.70) respectively, compared to 19 300 $g.mol^{-1}$ ($\overline{M}_n$, Đ=1.88) without catalysis in the same conditions (DMF, phosphoric acid, LiBr, PS standards).

The reaction can also be effectively catalyzed by the use of triethylamine which reduces the activation energy of the reaction by up to 17.5% compared to that of the non-catalyzed system.[151] The authors proposed a mechanism for the catalysis with triethylamine as depicted in Scheme 17. In the same study, various other catalysts, including acid (glacial acetic acid, methanesulfonic acid), base (piperazine, TBABr, or tin-based catalysts (tin (II) octanoate, DBTDL), etc. were also used effectively.



Scheme 17- Proposed mechanism of the activation of cyclic carbonates with triethylamine. [151]

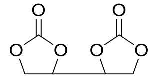
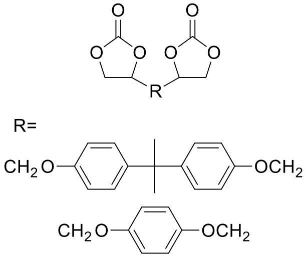
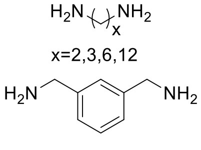
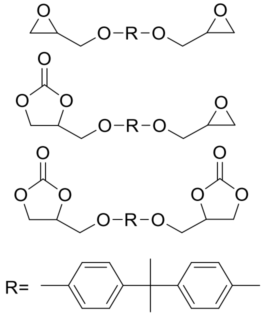
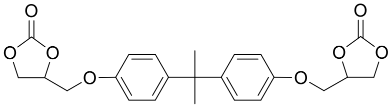
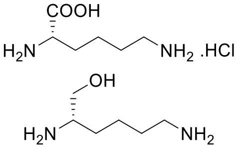
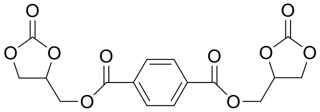
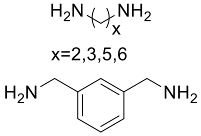
Fleischer *et a*l. [155] performed the polyaddition between a bis 5-membered cyclic carbonate and hexane-1,6-diamine in mold. The authors observed that 1 wt% of DABCO could increase the conversion from 60% to 90% at room temperature in 2 minutes.

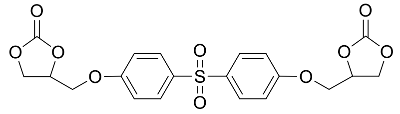
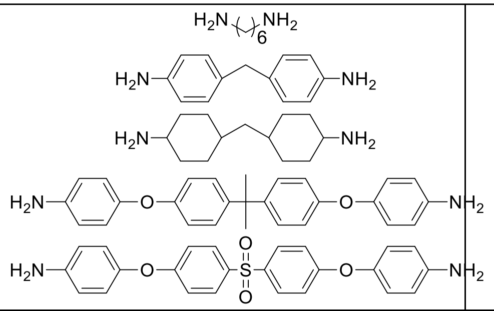
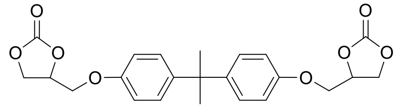
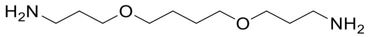
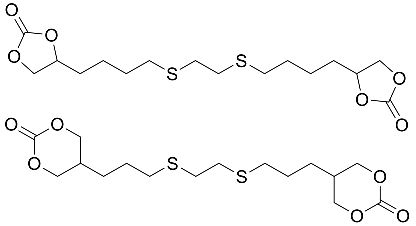
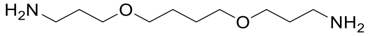
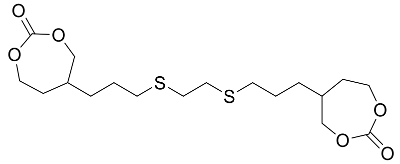
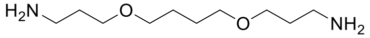
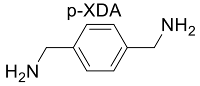
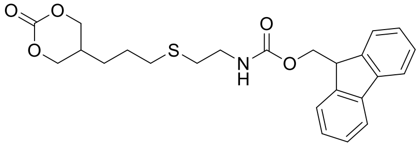
Recently, Andrioletti and coll.[143] carried out a complete screening of catalytic systems for the ring opening of cyclic carbonates by amines in solvent model reactions. Organocatalysts displayed a higher efficiency than inorganic lewis acids. TBD and cyclohexylphenyl thiourea appeared as promising catalysts for production of poly(hydroxyurethane)s. On the other hand, Maisonneuve *et al.* [165] performed a catalytic study in bulk using a model reaction between the propylene carbonate and the hexylamine. Schreiner catalyst, LiCl, DBU, ZnAc, MTBD or DMP were loaded at 5% mol. Catalysts were effective at the beginning of the reaction. However, after 1h, similar conversion to uncatalyzed system was observed. This could be explained by the high H-bonds density progressively formed with the conversion, due to the generated hydroxyl groups.

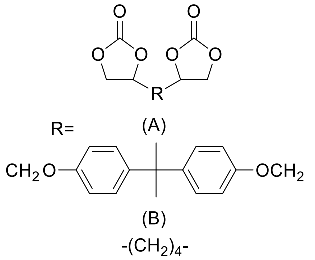
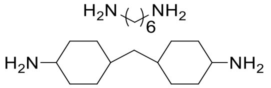
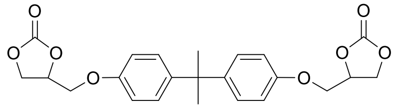
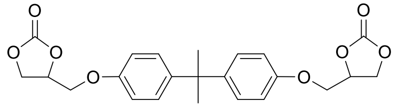
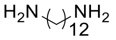
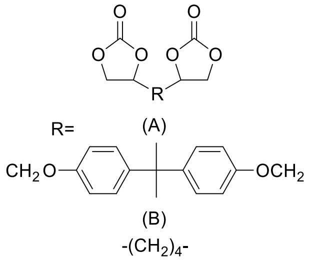
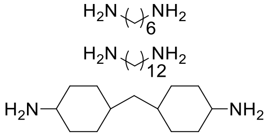
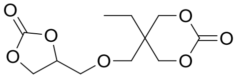
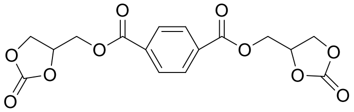
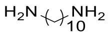
More recently, a cooperative catalysis has been developed by Scheidt and coworkers[166] using TBD and LiOTf as co-catalyst for the ring-opening of cyclic carbonates by amines at room temperature. This new Lewis acid / Lewis base combination substantially decreased reaction times for tested model reactions and polymerizations.

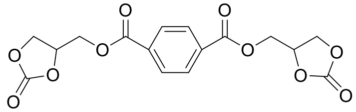
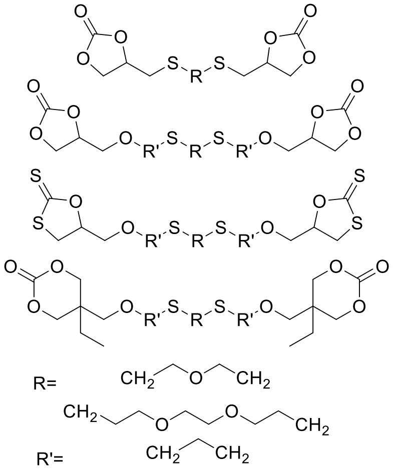
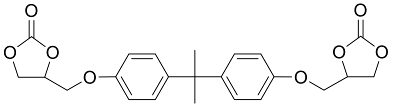
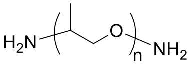
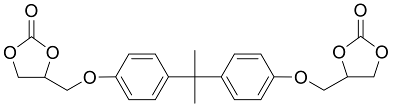
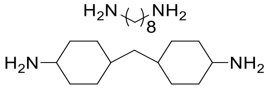
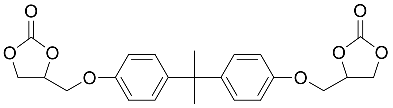
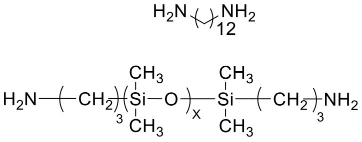
2.3- Thermoplastic PHUs

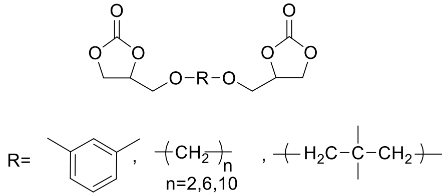
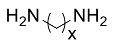
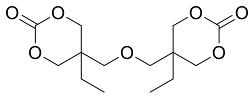
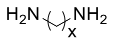
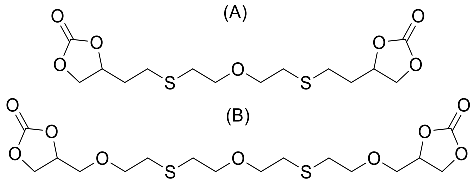
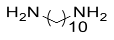
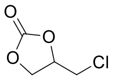
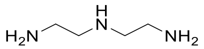
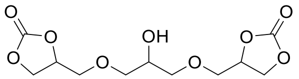
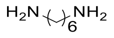
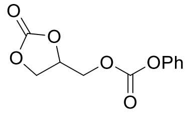
The reaction of cyclic carbonates and amines lead to hydroxyurethanes. Many authors reported the preparation of PUs with pendant hydroxyl groups from bis- or poly-cyclic carbonates and di- or poly-amines or from AB or AB_x monomers with a cyclic carbonate and an amino group. Due to the scope of this manuscript, only thermoplastic poly(hydroxyurethane)s will be discussed in this part. The Table 2 gives an overview of the poly(hydroxyurethane)s described in the literature.

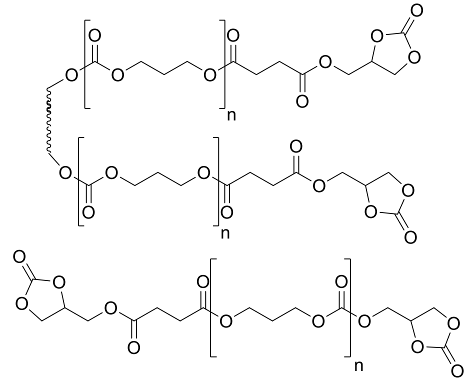
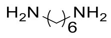
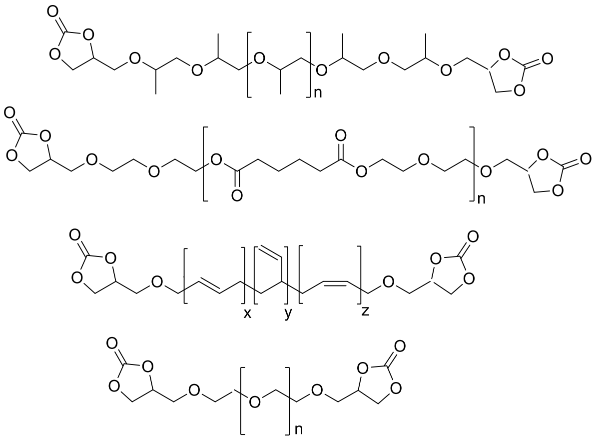
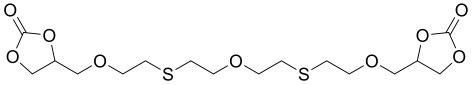
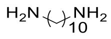
Bis-Cyclic carbonates	**Diamines**	**Reaction conditions**	**$\overline{M}_n$ (g.mol^{-1}) and [Dispersity]**	**Thermal properties(°C)**	**Ref.**
Petroleum-based cyclic carbonates					
	Primary aliphatic unhindered diamine C_2-C_{20}	EtOAc, DMSO, DMF, benzene, 0-140°C	Higher $\overline{M}_n$ in solvent	-	90
 CH2O-(CH2)4-OCH2 CH2OCO-(CH2)4-COOCH2		DMSO, 24h, 70°C or 100°C (no reaction at RT)	13000-28000 [1.39-2.16] [a]	T_g= 34 [f] T_d= 310	123
	1,6-diaminohexane, xylylene diamine, 1,8-diamino-3,6-dioxaoctane and piperazine Many secondary diamines (N,N'-dibenzyl ethylene diamine)	DMSO, 75°C	3170-7700 [1.6-2.35] [b]	-	167
		DMAC, DBU(1eq) or TEA(2eq), 24h	13000-24000 [1.3-1.58] [a]	-	168
		DMF,10 mol.L^{-1}, RT, 72 h	6300-7700 [1.52-1.80] [a]	T_g= 3-29 [f] $T_{d10\%}$= 177-277	124

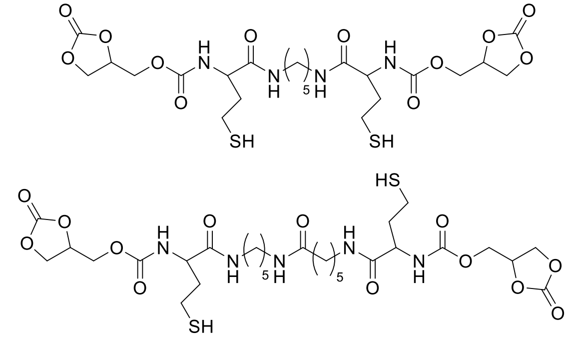
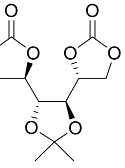
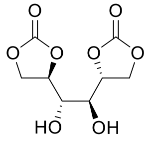
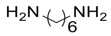
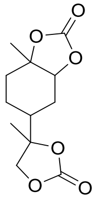
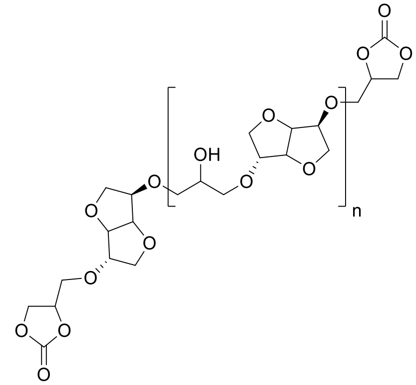
		DMSO, 1 mol.L^{-1}, 100°C, 24h	4300-12900 [1.18-1.99] [e]	T_g= 50-102 T_d= 339-388	125
		DMSO, 0.5 mol.L^{-1}, 70°C, 30d	-	-	137
		- DMAC, 1 mol.L^{-1}, 50°C, 24h - B6CC 100% conv. and 67% for B5CC in 48h - B5CC conv. did not reach 100% even after 14d	B6CC: 26000 (48h) [a] B5CC: 15000 (14d)	-	61
	DODDA  p-XDA 	DMSO, 0;5 mol.L^{-1}, 30-50-70°C, 6h	10900-35700 [1.3-2.8] [a]	-	105
 fluorenylmethoxycarbonyl (Fmoc)-protected amino groups		DMSO, 1 mol.L^{-1}, 30-50 or 70°C, 14d	3200-11000 [1.1-1.2] [a]	-	169

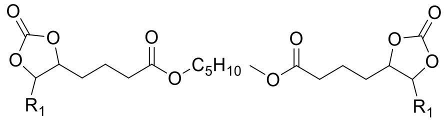
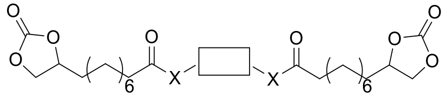
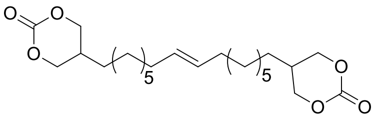
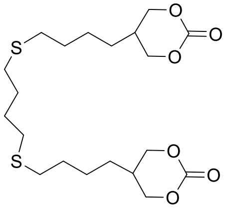
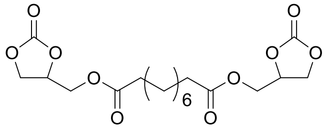
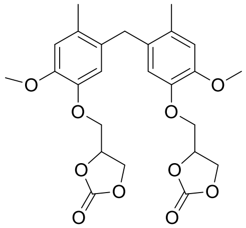
		Water, 0.5 mol.L^{-1}, organic solvent and surfactant free, 50-100°C, 24h/48h	500-4400 [1.03-2.16] [a]	-	170
		DMSO, 1.7 mol.L^{-1}, 70°C, 6h + 5mol% Additives such as lithium salts, NaCl, Bu_4NCl, $CaCl_2$, Bu_4Sn, $Bu_2Sn(OAc)_2$, K_2CO_3, CaH_2	- without additive: 19300 [1.88] [a,*] - with additive: 14600-36700 [1.73-1.84][a,*]	-	160
		DMSO, 1 mol.L^{-1}, LiCl, 70°C, 24h, Y=93%	26200 [1.71] [a,*]	T_g= 46 [f]	171
		1/ Ionic liquid, 0.2-1mol.L^{-1}, 70°C, 24h Y:88-92% 2/ water : N-n-butylimidazolium hexafluorophosphate (0.5:1), different T°C, 24h, Y:51-94%	1/ 4200-20800 [1.7-2.11] [a] 2/ 600-5100 [1.57-7.54] [a]	-	172
	1,6-diaminohexane, 4,9-dioxadodecane-1,12-diamine, triethylenetetramine and combination	Solvent, RT or T°C (60-90°C), in one or two step, 3d (°C) or 60d (RT), Y:85-96%	1340-8800 [1.45-2.11] [a]	-	152
		DMF, 1.3 mol.L^{-1}, 75-120°C, 48h	8000-20000 [1.9-2.5] [c]	T_g= 41-48 depend on the polymerization T°C	173

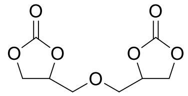
	Various diamines	DMF, 75°C, 48h	3800-18000 [≈2] ^{c}	T_g= 4-78	*118*
	Isophorone diamine, diethylenetriamine	(A) DMF, RT or 60°C, 90h (B) THF, 16h, hydroxyethylacrylate (C) DMF, RT or 60°C, 24h, 2mol% diisopropylethyl-amine	1800-20400 [1.4-3.1] ^{c}	T_g= -29-19 ^{f} $T_{d20\%}$= 252-296	*117*
	 (Jeffamine D-2000)	Solvent, microwave reactor (10-50 min, 50-250 W), 5% catalyst (LiBR or TBAC)	8600-13000 [1.05-1.24] ^{e}	T_d= 150-268	*174*
		DMSO, TBD, 20h + 4h quenching, RT-80°C	5430-53400 [1.17-1.39] ^{a}	-	*175*
	 X= 1.1 or 11	PGMAC (propylene glycol monomethyl ether acetate) , 80-100°C, 24h	12000-15500 [1.76-3.67] ^{e}	T_g= 1-40 $T_{d5\%}$= 300	*176*

	 x=2,3,6	Bulk, 60°C 20 min, 80°C 2h No catalyst	25400-30200 [1.18-1.22] [a]	T_g= -2-9 $T_{d5\%}$= 206-266	177
	 x=3,6,12	DMF, 0.5 mol.L^{-1}, 70°C, 24h	3800-6300 [2.11-2.61] [a]	-	178
Semi bio-based cyclic carbonates					
		DMF, 75°C, 24h	(A) 7000 [1.5] [c] (B) 9000 [3.2] [c]	(A) T_g= -14 ; $T_{d5\%}$=227 (B) T_g= -31 ; $T_{d5\%}$=227 [g]	121
	 0.5eq.	Polyaddition proceeded through nucleophilic addition of the primary amino group to the cyclic carbonate structure (THF, RT) and quarternization of the secondary amino group with the chloromethyl (in molten salts)	940-3120 [1.18-1.81] [e]	-	147
		25-50-70-100°C, 8h, in a mold T<70°C	-	T_g= 20 [f]	155
 AA* monomer	 x=2,3,4,5,6	DMAC, 2 mol.L^{-1}, RT, 20h	6400-8700 [1.46-1.57] [d]	T_g= 22.6-52.8 [f] T_d=225	179

	 5eq.	DCM, 43 mmol.L^{-1} 70°C, 5d	68100 [1.2] ^{a}	-	*120,180*
	JEFFAMINEs (230-2000 g.mol^{-1})	Bulk, 25-80°C, catalysts (LiBr, ^{t}BuOK, ZnCl$_2$, LiOTf, …), 16 h	1100-68000 [1.8- 2.6] ^{a,b}	-	*181*
		DMF, 80°C, 6 days	10 300 [2.2] ^{c}	-	182
Fully bio-based cyclic carbonates					

 Thiolactone couplers	Various diamines	DMF or THF, 0.35 mol.L^{-1}, 70°C, 13-43h	3100-6400 [1.99-3.33] [c]	-	183
 (A)  (B)	 $H_2N(CH_2)_6NH_2$	DMAC, diglyme, dioxane, THF, 0.1-0.2 mol.L^{-1}, 25-80°C, 12-24h	$\overline{M}_w$:20000-87000 [1.4-1.6] [d]	(A) T_g= 50-70 [f] (B) T_g= 64-79; T_m=160-190 T_d=180-224	184
	1,4-diaminobutane, 1,6-diaminohexane, isophorone diamine, 1,8-diaminooctane	Bulk, 60°C then gradually until 120°C	960-1840 [1.2-1.5] [b]	T_g= 33-70 Amorphous or T_m=80-100	185
 $\overline{M}_n$:392 and 524g.mol^{-1}	Jeffamine D-400, 1,10-diaminodecane, diethylenetriamine and isophorone diamine	DMF, catalyst, RT, 12h	7500 and 8600 [2.6-6.3] [c]	T_g= -8-59 [g] $T_{d5\%}$= 234-255	186

 R_1= C_8H_{17} or H	Ethane-1,2-diamine Isophorone diamine	Bulk, no catalyst, 70-110°C, 9-12h	$\overline{M}_w$:4300 and 13500 [1.1- 1.5] ^{b}	T_g= -25 - -13 ^{f}	*187*
 X= O, NH or N	1,4-diaminobutane Isophorone diamine Priamine 1075 Jeffamine 400	Bulk, 70-140 °C, 1-13 days	11000-31100 [1.2- 2.9] ^{a}	T_g= -29-55 ^{f}	*165*
 		DMF, 1mol.L^{-1}, RT-50°C, 1 day	9000-23000 [1.4- 1.7] ^{a}	-	*144*
	Jeffamine 2 grades (f_{NH2}=2.0 or 2.2)	1) Bulk, 75°C, 2h, inert atm 2) In a mold, oven at 75°C, 94h, vaccum	6000-9000 [2.4- 3.1] ^{b}	T_g= -23- -14 ^{f} T_d= from 200	*119*
	Hydrated hydrazine, 1,6-diaminohexane, isophorone diamine	DMSO, 1mol.L^{-1}, TBD (0-10%), RT-110°C, 24h	46000-1100 [9.4-1.1] ^{b}	T_g= 44-90 ^{f} $T_{d, 5\%}$ = 244-308	188

	 x=1,5,9 Isoidide diamine Priamine	Bulk, RT to 110°C, 5h	4900-13500 [1.8-3.2] ^{d}	T_g= -7.2-65.5 ^{f} $T_{d,\ 10\%}$ = 229-259	189

bCC=bis-cyclic carbonate; nCC=n-membered cyclic carbonate; Y=Yield; conv=conversion; T=temperature; RT=room temperature;
SEC conditions = ^{a} *: (DMF/LiBr, PS St)* * *phosphoric acid;* ^{b}*: (THF, PS St);* ^{c} *(DMF, PMMA St);* ^{d}*: (DMAC, LiCl, PS St),* ^{e} *: other SEC conditions*
DSC conditions = ^{f} *: 10°C/min;* ^{g} *: 20°C/min*

Table 2- Summarized literature about poly(hydroxyurethane) superscripts in italic in the table

2.3.1- Reaction conditions, yield and kinetics

The polyaddition of bis 5-membered cyclic carbonates and diamines are mostly carried out in a solvent medium of high polarity such as DMSO, DMAC and DMF at a reactant concentration from 0.5 to 1 mol.L^{-1} and from room temperature (reaction times in days) to 100 °C. Proempers *et al.* [184] screened different solvents and demonstrated that higher yields can be obtained with less polar solvents such as dioxane and THF compared to DMAC and diglyme. Ochiai *et al.* [170] tried to use water and ionic liquids as solvents. In water, the authors tested the polymerization of two bis 5-membered cyclic carbonates with hexane-1,6-diamine or 4,4'-diamino-dicyclohexylmethane. The polymerization was found to be feasible in case of quite hydrophobic bis 5-membered cyclic carbonate and hexane-1,6-diamine. The formed dispersion was somewhat slightly protecting the bis-cyclic carbonate from hydrolysis. However, hydrolysis was observed for both bis 5-membered cyclic carbonates, which can explain the low molar masses obtained even in the best case ($\overline{M}_{\mathrm{n}}$=4 200 g .mol^{-1} and Đ=1.86 -in DMF/LiBr, PS standards-).[170] The same group studied this polymerization in ionic liquid and in a mixture of water and ionic liquid. [172] In the case of purely ionic liquids, comparable results with the ones obtained in DMSO are achieved. However, while using a proportion of water, hydrolysis of the cyclic carbonate is observed and lower molar masses ($\overline{M}_{\mathrm{n}}$) are obtained compared to the ones in DMSO.

Polar aprotic solvents were especially used to bypass the solubility issues of the PHUs. This critical parameter was reported by various studies. It depends on the chemical structures of the monomers used but there were found to be less soluble in organic solvents than the corresponding model PUs. [123] Presumably due to the hydrophilicity given by the hydroxyl groups along the polymer backbone, the PHUs were in majority only soluble in aprotic solvents with high polarity such as DMSO, DMF and DMAC. [124-125] Moreover, Steblyanko *et al.* [184] observed that using less soluble monomers lead to lower yields. [124] Besides, as for the model reaction, it has been shown that an increase of the reactants concentration leads to an increase in yields.

Although most of the polymerizations are carried out in solvent, some research teams try to prepare PHUs in bulk, in order to obtain higher molar masses. Recently, Sheng *et al.*[177] synthesized PHUs with different bisCC and diamines in bulk at 80°C. Molar masses up to 30 200 g.mol-1 ($\overline{M}_{\mathrm{n}}$, DMF/LiBr, PS Standards) could be reached. Few other works reported bulk polymerizations such as Maisonneuve *et al.*[165] that could end up with PHUs of 31 100 g.mol^{-1} (DMF/LiBr, PS Standards) performing their polymerizations in bulk (70-140°C, 1-13 days).

The temperature of the reaction has also a certain influence on the polyaddition of bis 5-membered cyclic carbonates (b5CC) and diamines. This expected behavior has been observed and quantified by the group of Endo. [61,168] The authors observed that the yield increased with the temperature [168] and calculated the effect of the temperature on the reaction rate constant (from 0.03 L.mol^{-1}.h^{-1} at 30°C to 0.10 L.mol^{-1}.h^{-1} at 70°C). (Ea) could be also evaluated as 9.2 and 24.9 kJ.mol^{-1} for bis 6-membered and bis 5-membered cyclic carbonates respectively. [61] The higher reaction rates at higher temperature were explained by the decrease of the viscosity of the mixture with temperature. Moreover, the viscosity increase with the formation of the polymer is an important parameter, [155] taking into account that PHU can undergoes hydrogen bonds. In order to optimize the reaction temperature, Benyahya *et al.* [173] performed a complete rheological study on the polyaddition of a bis 5-membered cyclic carbonate and decane-1,10-diamine in DMF. A temperature beyond 120°C was shown to be excessive for the polymerization, due to side reactions (See 2.3.3).

2.3.2- PHUs molar masses

While comparing the different molar masses and dispersities obtained, one must be sure to compare SEC analyses performed with the same solvent and the same standards for the calibration. Besides, one can notice that no indications about the quenching of the reaction mixture are usually given. Most of the authors used DMF with LiBr and PS standards. In those conditions, the molar masses obtained for the polyaddition of 5-membered cyclic carbonates and diamines mainly ranged 6 300 g.mol^{-1} to 28 000 g.mol^{-1} ($\overline{M}_\mathrm{n}$), with dispersities comprised between 1.39 and 2.16. In other SEC solvents, the molar masses were in the range 3 800-9 000 g.mol^{-1} ($\overline{M}_\mathrm{n}$, Đ:1.5-3.2, DMF, PMMA standards), 5 000-76 250 g.mol^{-1} ($\overline{M}_\mathrm{n}$, Đ:1.4-1.6, DMAC, LiCl, PS standards), 4 300-12 900 g.mol^{-1} ($\overline{M}_\mathrm{n}$Đ:1.18-1.99, chloroform) and 960-7 700 g.mol^{-1} ($\overline{M}_\mathrm{n}$, Đ:1.6-2.35, THF, PS standards). However, using optimized reaction conditions determined by rheology (in DMF at 90°C), Benyahya *et al.* [173] managed to reach relatively high molar masses up to 20 000 with dispersities up to 2.5 ($\overline{M}_\mathrm{n}$, DMF, PMMA standards). More recently, Guillaume and coll. [181] synthetized poly(hydroxyurethane)s with molar masses up to 68 000 g.mol-1 ($\overline{M}_\mathrm{n}$, DMF, 80°C, PS standards), obtained by processing the reaction between Jeffamine and polyols which were prior functionalized by glycerol carbonate at the chain end.

Various polymerization parameters can influence the molar masses notably the temperature,[123,184] the concentration of the monomers in the solvent,[184] the chemical structure of the monomers and the solvent.

Furthermore, the chemical structure of the monomers influences the molar masses. Less soluble diamines lead to lower molar masses. [124] The use of aromatic diamines also causes a decrease in molar masses due to a lowering of the structural flexibility. [125]

The chemical structure of the 5-membered cyclic carbonate also influences the molar masses. The inductive effect of the substituent of the 5-membered cyclic carbonate plays a role on its reactivity. Most of the polymerizations reported in the literature were performed with cyclic carbonates bearing an electron-withdrawing substituent on the α, β or γ position. In the latter study, Tomita *et al.* [61] polymerized an inactivated 5-membered cyclic carbonate with 4,9-dioxadodecane-1,12-diamine. The authors managed to reach only a conversion of 95% and a molar mass of 15 000 g.mol^{-1} after 14 days ($\overline{M}_{\mathrm{n}}$, DMF, LiBr, PS standards). In the same trend, Maisonneuve *et al.*[165] performed polymerizations with various diamines and different bisCC bearing aliphatic backbone next to the cyclic carbonate moiety. Molar masses in the range 11 000 - 31 110 g.mol^{-1} ($\overline{M}_{\mathrm{n}}$, DMF/LiBr, PS Standards) were achieved.

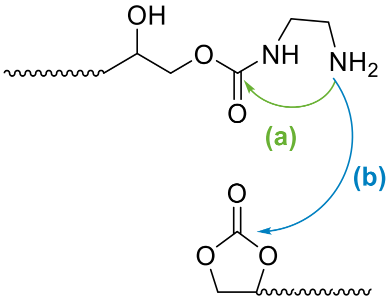
As discussed above, the use of water as solvent or co-solvent leads to the hydrolysis of the cyclic carbonates and thus to lower molar masses ($\overline{M}_{\mathrm{n}}$). [170] Proempers *et al.* [184] also demonstrated an influence of the solvent. Higher molar masses ($\overline{M}_{\mathrm{w}}$) were obtained in aprotic less polar solvents (dioxane, THF), than in high polar aprotic ones (DMAC, diglyme), which is in agreement with the corresponding difference in yield.[184]

Lastly, the presence of a catalyst in the system can greatly influence the molar mass of the final poly(hydroxyurethane). Ochiai *et al.*[160] compared the polymerization between a bisCC and the 1,12-diaminodecane with and without catalyst. PHUs molar mass could be doubled -from 19 300 to 36 700 g.mol^{-1} ($\overline{M}_{\mathrm{n}}$, DMF/LiBr, PS Standards)- using LiCl as catalyst. As it is mentioned above, Annunziatta *et al.*[181] also reached high molar masses ($\overline{M}_n$ up to 68 000 g.mol^{-1}) using LiBr as catalyst.

2.3.3- Selectivity and side reactions

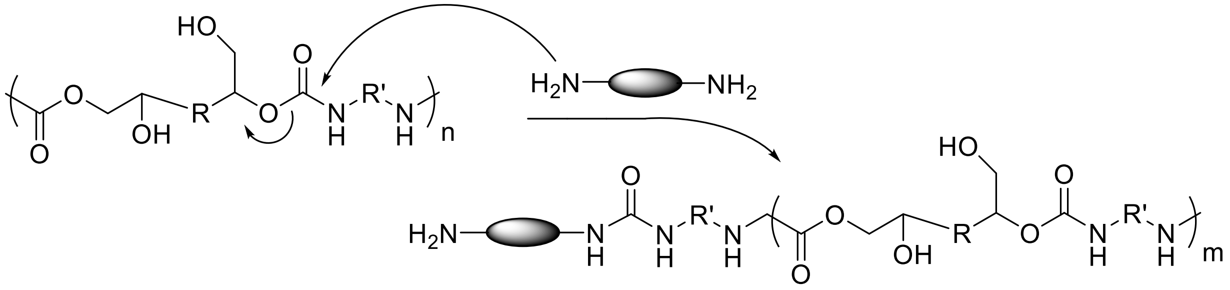
The polyaddition of bis 5-membered cyclic carbonates and diamines lead to the formation of primary and secondary alcohols along the polymer chain. The different authors found that more secondary alcohols were generated during the poly(hydroxyurethane) formation. Ratios between primary and secondary alcohols ranged from 38:62 to 6:94. [143,172,184]

Concerning side reactions, only few studies reported the presence or the analysis of potential side products. Kihara *et al.* [123] found lower molar masses while using ethylene and propylene diamines. Their hypothesis was that side reaction occurs with these diamines by cyclization with the neighboring urethane to afford cyclic urea (Scheme 18). However, the authors were not able to confirm this hypothesis maybe due to the really low quantity of the formed rings. Urea formation was also reported by Bürgel *et al.* [167] when performing the polyaddition in bulk at high temperature.



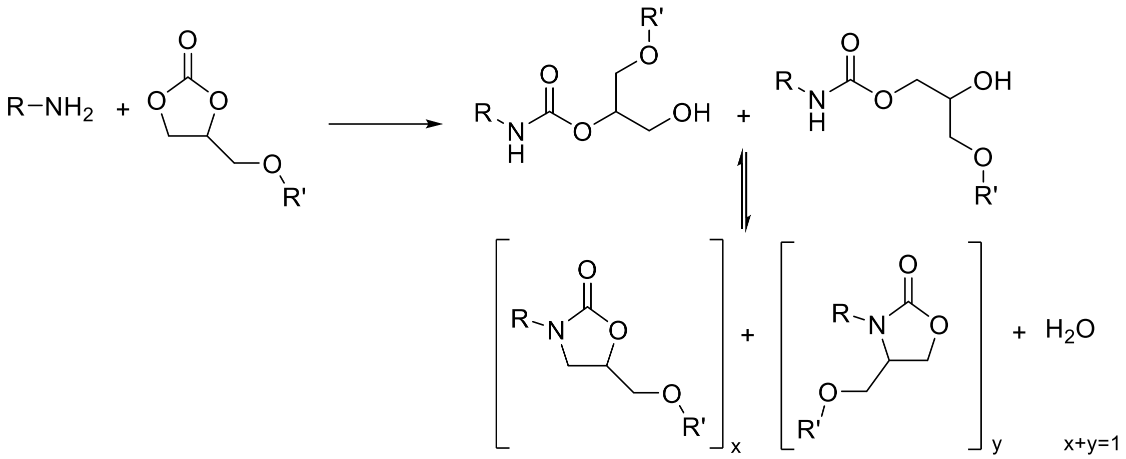
Scheme 18- Reactions involved during poly(hydroxyurethane)s synthesis – (a) cyclization process and (b) addition process. [123]

In theory, the use of cyclic carbonates bearing ester functions could lead to amidation reaction while performing the reaction with amines, if the amine reacts with the ester function instead of the carbonyl of the cyclic carbonate (Scheme 19). Boyer *et al.*[187] found that the formation of amide linkages was affected by the type of diamine used. Indeed, while no amide groups were detected in the case of the secondary diamine IPDA, one could observe that some of the ester groups were converted into amide functions when EDA was used as the co-monomer. However, Endo and coll. demonstrated that no amidation of the ester function occurs during the polymer formation both by IR analyses [124] and, by obtaining totally comparable molar masses ($\overline{M}_{\mathrm{n}}$) and dispersities than those of bis 5-membered cyclic carbonates bearing no ester groups.[123] Additionally, the use of water as solvent or co-solvent for the preparation of PHUs was accompanied with the hydrolysis of the cyclic carbonates as discussed above. [170]



Scheme 19- Amidation side reaction leading to urea formation in the PHU backbone.

Very recently, Besse *et al.* [182] published a complete study showing formation of ureas, oxazolidinones (Scheme 20) and dehydration products during the reaction between cyclic carbonates and amines. The numerous by-products identified by HRMS and ^{13}C DEPT NMR analysis explained the incapacity of PHUs to reach high molar masses.

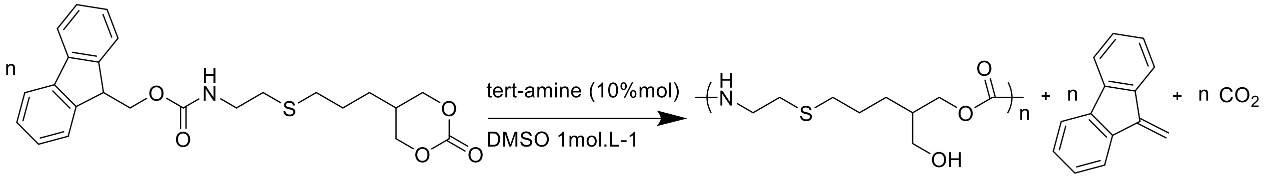


Scheme 20- Dehydration reaction leading to oxazolidinone formation. [182]

2.3.4- Different reactivity for specific monomers

PHUs from other monomers such as protected amines or ammonium salts, bis 6- and 7-membered cyclic carbonates, bis-1,3-oxathiolane-2-thiones, AA* monomers with 5-membered cyclic carbonates and either an open carbonate, a thio-lactone, or a 6-membered cyclic carbonate have also been prepared. The specificity of those monomers as well as the difference in reactivity depending on the monomer chemical structure is developed in this part.

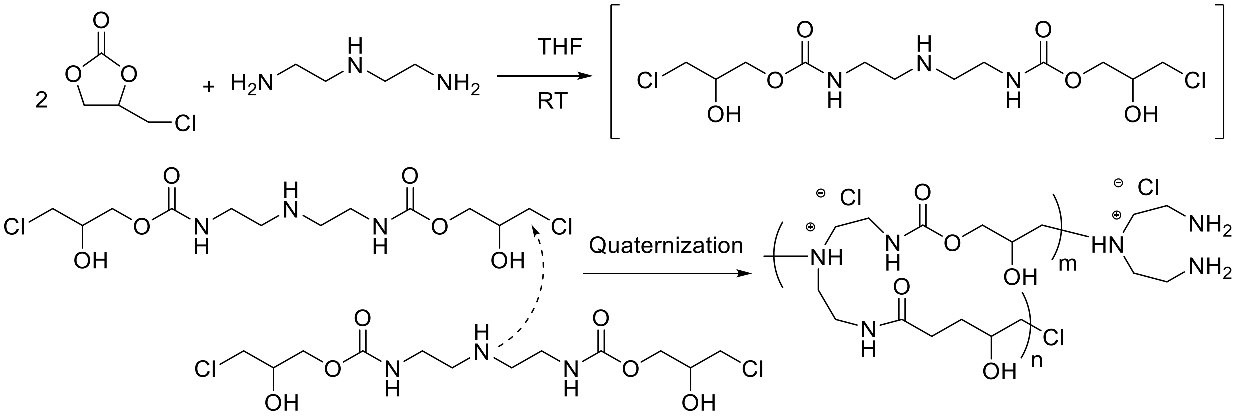
One example of AB monomer has been reported in the literature by Tomita *et al.* [169] in 2001. The authors synthesized a precursor bearing a protected amine group and at the same time a 6-membered cyclic carbonate (Scheme 21). The polymerizations were performed at different temperature (30°C, 50°C and 70°C) in DMSO at 1 mol.L^{-1} during 14 days. The use of 10 mol% of tertiary amines such as N,N-diisopropylethylamine, 4-(dimethylamino)pyridine or triethylamine was necessary for the *in-situ* deprotection of the amino group. The molar masses were in the range 3 200-11 000 g.mol^{-1} with dispersities of 1.1-1.2, ($\overline{M}_{\mathrm{n}}$, DMF, LiBr, PS standards).



Scheme 21- Polyaddition of the protected AB type monomer synthesized by Tomita et al. [169]

Using another strategy, Kihara *et al.* [168] synthesized optically active PHUs from a 5-membered cyclic carbonate and L-lysine hydrochloride. 2 equivalents of triethylamine or 1 equivalent of DBU were used. The higher molar mass obtained was 24 000 g.mol^{-1} with a dispersity of 1.58 ($\overline{M}_{\mathrm{n}}$, DMF, LiBr, PS standards).

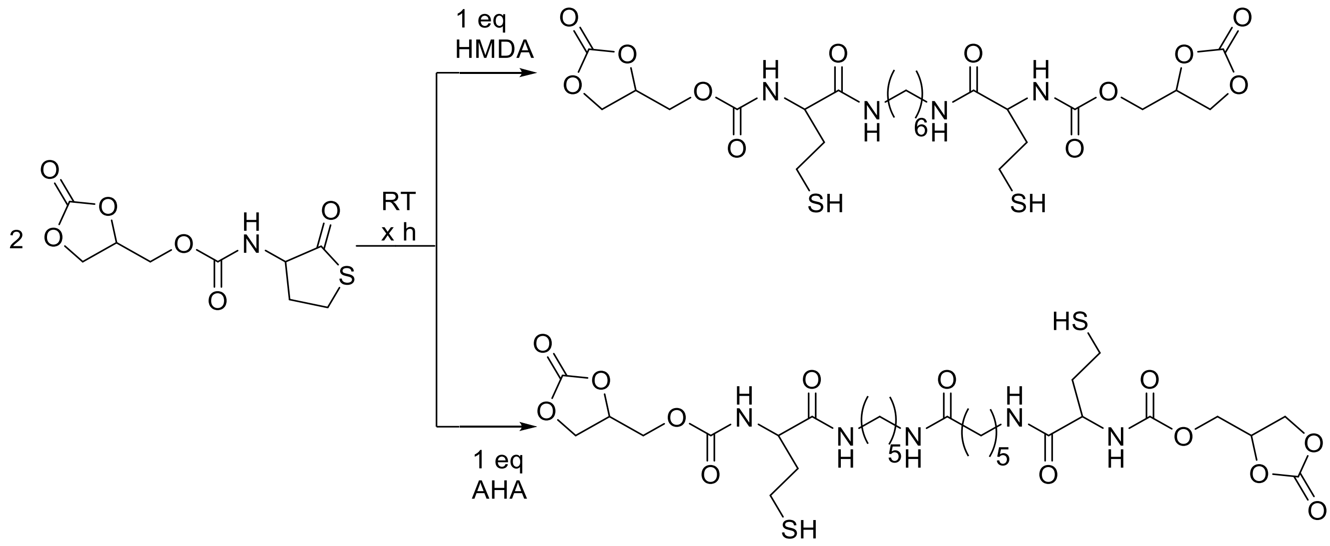
In this part, a particular close case concerning the branched cationic PHUs prepared by Ochiai *et al.* [147] in 2012 can be mentioned (Scheme 22). The polyaddition proceeded through the nucleophilic addition of the primary amino group of diethylenetriamine (DETA) onto the carboxyl group of carbonated epichlorohydrin (Cl5CC), followed by the quarternization of the secondary amino group with the chloromethyl group in molten salts, resulting in hyperbranched polymers.



Scheme 22- Synthesis of branched cationic polyhydroxyurethane via polyaddition of Cl5CC with DETA. [147]

Various AA* monomers with at least one 5-membered cyclic carbonate have been synthesized along the literature. The first example of AA* monomers was reported by Ubaghs *et al.* [179] The authors synthesized a precursor having both a 5-membered cyclic carbonate and an open carbonate with phenol as leaving group. The polymerizations were carried out in DMAC at 2 mol.L^{-1} at room temperature for 20 hours using various aliphatic diamines. Molar masses in the range 6 400-8 700 g.mol^{-1} were obtained with dispersities from 1.46 to 1.57, ($\overline{M}_{\mathrm{n}}$, DMAC, LiCl, PS standards). This polymerization involved the removal of phenol as by-product. Other leaving groups were also tested by the preparation of different bifunctional carbonate coupling agents from glycerol. [190]

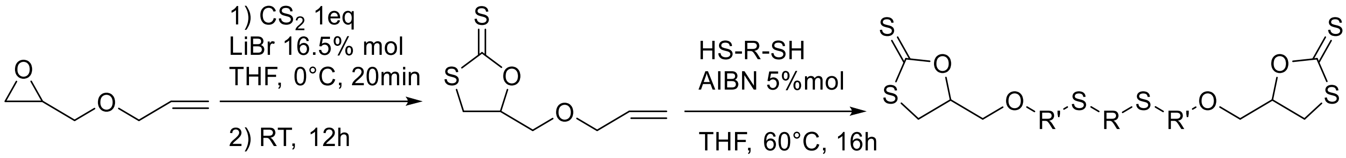
Recently, another AA* monomer bearing a 5-membered cyclic carbonate and a 5-membered thio-lactone has been prepared by Keul *et al.* (Scheme 23). [183] This AA* was reacted with a purely aliphatic amine (HMDA) or ones having urethane or ether linkages (AHA) in DMF or THF at 0.35 mol.L^{-1} and 70°C to give poly(hydroxyurethaneamide)s. In order to prevent cross-linking of the thiol groups of the resulting polymer, 1 to 5 mol% of D,L-dithiothreitol was added. Molar masses in the range 3 100-6 400 g.mol^{-1} ($\overline{M}_{\mathrm{n}}$) were reached with dispersities from 1.99-3.33. The dispersities above 2 have been explained by the presence of few disulfide bonds formed. Based on the higher reactivity of the thio-lactone group, the authors were able to prepare dimers having two 5-membered cyclic carbonates. [183]



Scheme 23- Reaction of thio-lactone coupler with HMDA (hexamethylene diamine) and AHA (6-amino-N-(5-aminopentyl)hexanamide) . [183]

Following a similar strategy, He *et al.* [152] synthesized AA* monomers with one 5- and one 6-membered cyclic carbonate. The aim of this AA*, as bifunctional coupling agent, is to prepare multifunctional polymers either (i) by reacting polyamines with bifunctional coupling agents already reacted with monofunctional amines, or (ii) by reacting polyamines already functionalized with bifunctional coupling agents with monofunctional amines. This is possible by the difference in reactivity of 5- and 6-membered cyclic carbonates. By reacting the dimer with diamines, molar masses from 1 340 g.mol^{-1} to 8 800 g.mol^{-1} were obtained ($\overline{M}_{\mathrm{n}}$, Đ:1.45-2.11 ; DMF, LiBr, PS standards).

In 2013, Besse *et al.* [117] studied the compared reactivity of various bis-1,3-oxathiolane-2-thiones (Scheme 24). Slightly lower molar mass ($\overline{M}_{\mathrm{n}}$=7 000 g.mol^{-1} and Đ=1.9) was obtained for the poly(thiourethane) prepared with diethylenetriamine, compared to the one prepared with the bis 5-membered cyclic carbonates ($\overline{M}_{\mathrm{n}}$:10 300-13 000 g.mol^{-1} and Đ=2.1-2.2) (DMF, PMMA standards). Moriguchi *et al.* [191] also studied the polyaddition of bis-1,3-oxathiolane-2-thiones with diamines and obtained molar masses from 5 000 g.mol^{-1} to 12 000 g.mol^{-1} ($\overline{M}_{\mathrm{n}}$, Đ=1.38-1.62, THF, PS standards).



Scheme 24- Synthesis of bis-1,3-oxathiolane-2-thione [117]

2.3.5- Thermo-mechanical properties and thermal stability

Numerous studies have been reported on the thermo-mechanical properties as well as the thermal stability of the synthesized PHUs. The results clearly showed the expected influence of the chemical structure of the monomers onto the glass transition temperature, the presence or not of a melting point and the degradation temperature as exposed below.

The glass transition temperatures range between −30°C [121] and 100°C [125], depending on the chemical structure of reactants. Semi-crystalline PHUs were also achieved with melting points in the range 80°C [185] to 190°C [184]. With aliphatic diamines, different studies demonstrated that the glass transition temperature decreases with longer aliphatic diamines due to lower urethane linkage density along the polymer backbone. [118,124,179] In the case of aromatic diamines, Kim *et al.* [125] demonstrated higher glass transition temperatures than with aliphatic ones. Moreover, Besse *et al.* [117] observed similar glass transition temperatures with bis 5- and 6-membered cyclic carbonates.

Concerning the degradation temperatures, only general trends can be given due to the disparity of the analyses. The analysis are generally performed at 5°C.min^{-1} [117,186], 10°C.min^{-1} [123,125,179,184] or 20°C.min^{-1} [121] in order to study either the initial decomposition temperature or temperatures after 5%, 10% or 20 wt% loss. The highest thermal degradation was reported by Kim *et al.* to be up to 388°C (10°C.min^{-1}), for PHUs with a large part of aromatic structures. [125] In contrary, Proempers *et al.* [184] reported a starting thermal decomposition as low as 180°C (10°C.min^{-1}). The thermal study of Kihara *et al.* [123] can be reported here. The authors proved with one example that similar initial decomposition temperatures (around 310°C) are obtained with PHUs in comparison with the corresponding conventional PU without pendant hydroxyl groups.

Moreover, Fleischer *et al.* [155] were the first to study some mechanical properties for linear PHUs. Young modulus of 7±1 MPa, tensile strength of 9±2 MPa and elongation at break of 280±50% were obtained for a PHU from a 5-membered cyclic carbonate and hexane-1,6-diamine.

The carbonate/amine route appears as a promising route since resulting polyhydroxyurethanes are synthesized via a polyaddition without any by-products. Additionally, the large availability and variability of cyclic carbonates and amines could enable the industrial production of a wide range of polymers. Indeed, cyclic carbonates can be synthesized from various precursors (Scheme 8 and Scheme 10) and especially from a simple epoxidation-carbonation of olefins. However, the most efficient epoxidation of terminal double bonds involves MCPBA that can not be processable at the industrial scale; it is therefore necessary to find another valuable synthesis of terminal epoxides able to be scaled-up. Besides, this polymerization process confers new properties to polyurethane materials since hydroxyl groups are generated. However, their presence along the polyurethane backbone can dramatically change material properties and subsequent applications. Along these lines, crosslinking or further post-functionalizations can be considered to tune properties such as hydrophobicity or thermo-mechanical behaviors.[164,171,184]

Nonetheless, side reactions during the polyaddition have been observed by formation of urea or oxazolidinones for instance. This route needs further investigations to avoid side reactions in order to improve the polymer molar masses, usually below 30 kg.mol^{-1}. But the main issue of the cyclic carbonate/amine route remains its non-competitive reactivity compared to the classical isocyanate/alcohol one. Academic research has developed 6- and 7-membered cyclic carbonates for the purpose of increasing the ring opening kinetic of cyclic carbonates by amines, but the pot life of these monomers is too short (due to hydrolysis of the cyclic carbonate) and their syntheses too tedious for industrial applications. Hence, catalysis of 5 membered cyclic carbonate ring-opening appears as key-challenge for increasing their reactivity toward amines.

2.4- Towards bio-based poly(hydroxyurethane)s

As presented previously in the review, numerous studies have been developed to prepare 5-membered cyclic carbonates for PHUs synthesis. However, due to the depletion of fossil resources, chemistry knows today a growing interest for bio-based precursors. Indeed, Biomass including vegetable oils, lignin or polysaccharides represents an attractive platform for producing polymers. From this perspective, different research groups worked on the synthesis of bio-based (or semi-bio-based) cyclic carbonates in order to replace petroleum-based PHUs, using fatty acids and glycerol from transesterification of vegetable oils or other interesting natural molecules such as limonene or D-mannitol.

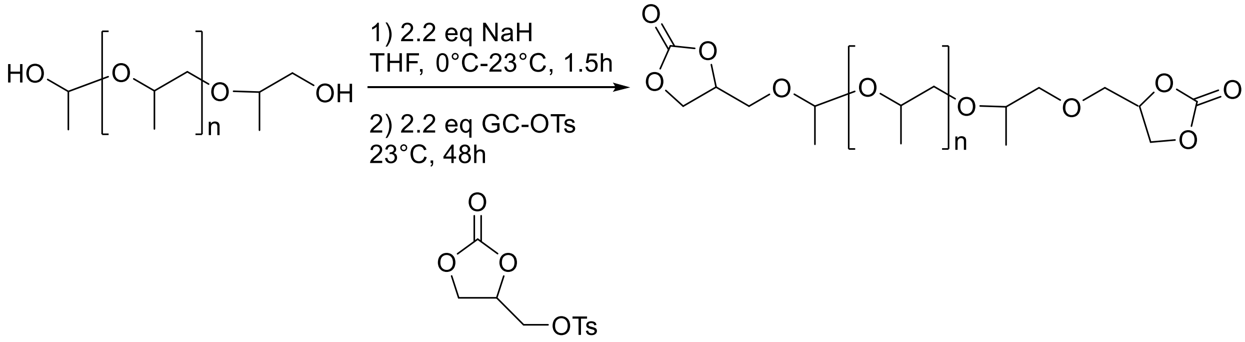
2.4.1- Vegetable oil-based cyclic carbonates to PHUs

As far as vegetable oils are concerned, the 5-membered cyclic carbonate monomers have been mainly synthesized from glycerol carbonate or by epoxidation followed by carbonation of the fatty acid chain unsaturations.

For instance, Carpentier and coll.[181] used prepolymers such as poly(propylene glycol), poly(ethylene glycol) and polybutadiene bearing terminal hydroxyl groups (Scheme ***25***). A nucleophilic substitution was performed with tosylated-glycerol carbonate in alkaline condition to obtain bis-cyclic carbonate prepolymers. The authors achieved one of the highest molar masses ever reported in the literature ($\overline{M}_{\mathrm{n}}$: 68 000 g.mol^{-1}, DMF/LiBr, PS Std) while polymerizing the prepolymers with various Jeffamines.

The glycerol platform was also used by Ochiai *et al.*[147] in 2012. The authors first synthesized cyclic (chloromethyl)ethylene carbonate from the carbonation of epichlorohydrin, that can be easily obtained by chlorination of glycerol [192] instead of using allyl chloride as starting material. An atypical polymerization was then performed in two steps, comprising the polyaddition of a diamine on the bis-cyclic carbonate, followed by the quaternization of the secondary amino groups (Scheme 22).

Using another strategy, Fleischer *et al.*[155] carbonated glycidyl ether of glycerol to end up with an activated bisCC with a pendant hydroxyl group. The PHU molar mass was not reported but a complete conversion in 4h at 70°C was mentioned.



Scheme 25- Synthesis of the glycerol carbonate-functionalized prepolymers. [181]

Vegetable oils can be used as raw material for the production of carbonated oils. However, the uncontrolled functionality of the triglycerides (Figure 15) restrains the control of PHUs structure and properties. The use of such poly(cyclic carbonate)s leads to thermosets that are not described in this review.

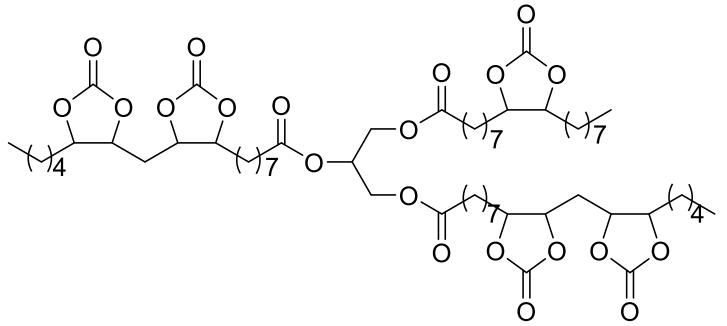
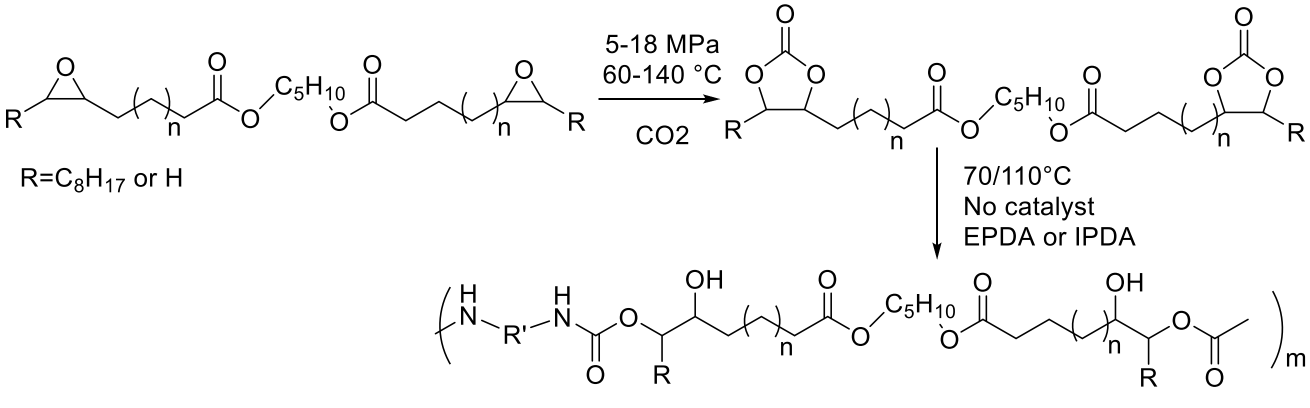


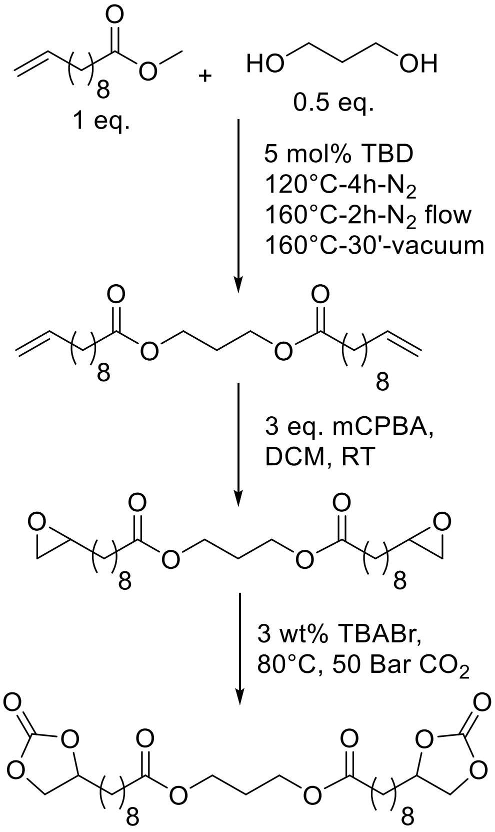
Figure 15- Structure of carbonated soybean oil.

The first example relating the synthesis of thermoplastic PHUs from fatty acid derivatives was reported by Boyer *et al.*[187] in 2010. The fatty acid-based bis 5-membered cyclic carbonates were synthesized by a three-step process composed of (1) a transesterification of fatty acid methyl esters, (2) an epoxidation of the double bonds and (3) a carbonation of the resulting epoxides. The solubility of the fatty acid or triglyceride-based mono-, bis- and poly-epoxides in supercritical CO_2 has been studied. [193] Two bis 5-membered cyclic carbonates, internal carbonated fatty acid diester (ICFAD) and terminal carbonated fatty acid diester (TCFAD), prepared from methyl oleate and methyl undecenoate respectively, were polymerized with ethane-1,2-diamine (EDA) and isophorone diamine (IPDA) to form PHUs containing hydroxyl moieties (Scheme 26). [187,194] The PHUs exhibited molar masses up to 13 500 g.mol^{-1} ($\overline{M}_{\mathrm{w}}$) and relatively low glass transition temperatures ranging from -25°C to -13°C. Nevertheless, an amidation side reaction occurred between EDA and the ester linkages of the diester bis cyclic carbonates, giving amide groups which can partly explain the low molar masses. [187,194]



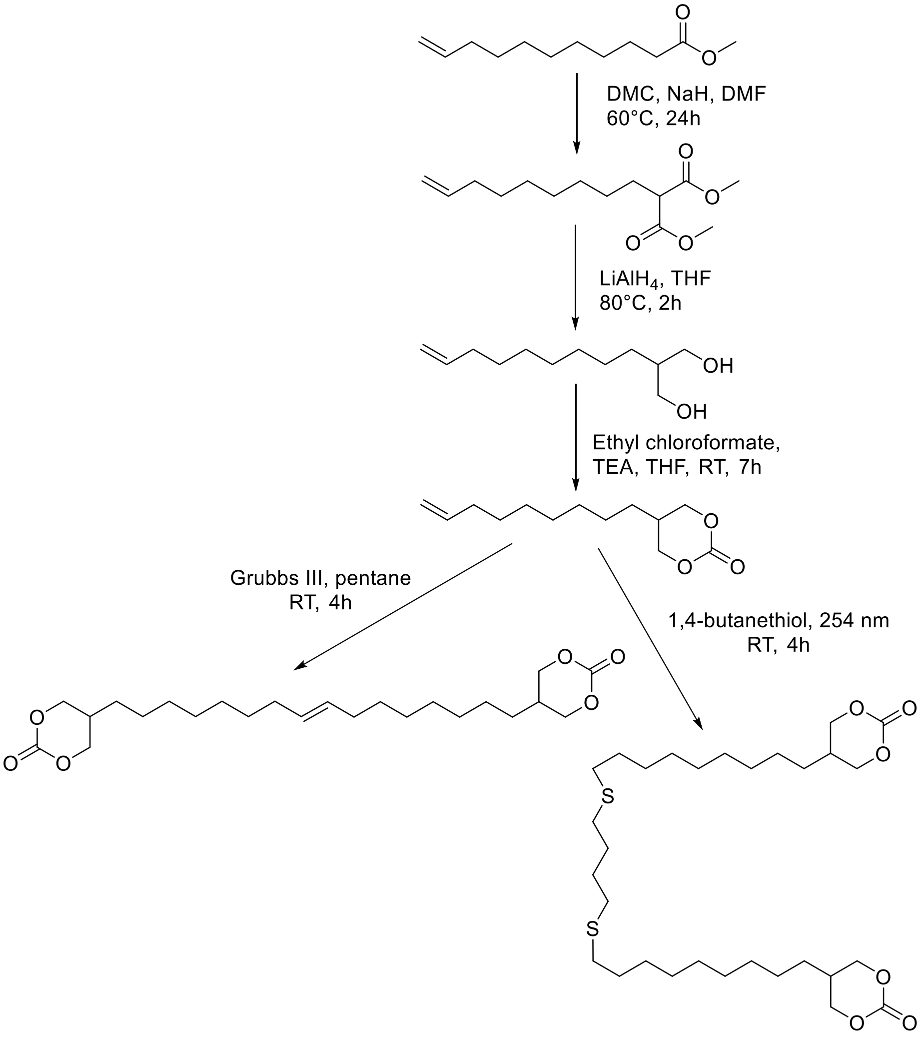
Scheme 26- Bis cyclic carbonates and poly(hydroxyurethane)s from fatty acid or fatty acid methyl ester. [187]

More recently, our group [165] reported the synthesis of several fatty acid based bisCC using the epoxidation/carbonation strategy. Two fatty acid chains were first dimerized by amidation or transesterification reactions with butane-1,4-diamine, piperazine, N,N'-dimethylpropane-1,3-diamine, N,N’-dihexyldecane-1,10-diamine and 1,3-propanediol. The produced aliphatic bis-unsaturated was epoxidized and carbonated following the procedure indicated in Scheme 27. The polymerization of these dimers presenting different central blocks with various diamines (such as Jeffamine, isophorone diamine or –diaminobutane) led to a broad range of T_g from -29°C to 55°C.



Scheme 27- Strategy for the synthesis of 5-membered bis-cyclic carbonates from fatty acid derivatives. [165]

A recent study carried out by Maisonneuve *et al.* [144] exhibited the synthesis of more reactive bis 6-membered cyclic carbonates from methyl undecenoate by malonization, reduction and carbonation of the resulting diol. The mono-cyclic carbonate obtained was dimerized either by thiol-ene or metathesis reaction (Scheme 28). The synthesized bifunctional 6-membered cyclic carbonates were effectively used as building blocks for thermoplastic isocyanate-free PHUs in combination with dodecane-1,12-diamine as comonomer. Molar masses up to 23 000 g.mol^{-1} ($\overline{M}_n$, Đ=1.7) were obtained after only one day in DMF (1mol.L^{-1}) at 50°C. At higher conversion, a chemical gel was obtained, probably due to cyclic carbonate ring opening by the formed hydroxyl function. However, the formation of such a gel was not completely elucidated.



Scheme 28- General procedure for bis 6-membered cyclic carbonate synthesis from methyl undecenoate. [144]

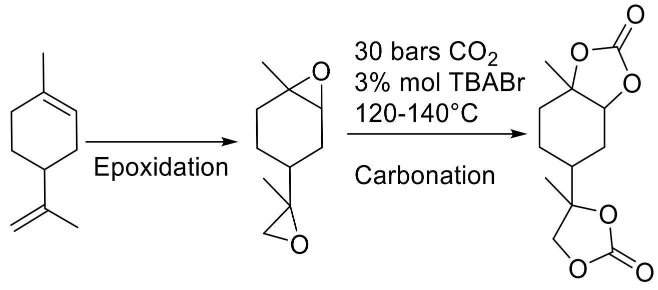
Hence, fatty acid derivatives represent a platform of bio-based building blocks for poly(hydroxyurethane) synthesis. Caillol and coll. [195] highlighted the large possibilities offered by this platform for both linear and crosslinked polymers. In a recent study, diglycerol dicarbonate was synthesized from diglycerol and dimethyl carbonate. The short dimer was subsequently reacted with several diamines to obtain PHUs with molar masses ranged from 4100 to 9400 g.mol^{-1} ($\overline{M}_{\mathrm{n}}$). The abundance of reactive hydroxyl functionalities present along the PHU backbone could enable further curing process and post-functionalization.[189]

Nohra *et al*.[11] mentioned in their critical review the alternative use of vegetable oils as starting material. However, other bio-based molecules can be chemically modified to meet the needs of PHUs production.

2.4.2- Other bio-based cyclic carbonates to PHUs

Few years ago, Proempers *et al*.[184] modified the D-mannitol by carbonation to obtain the bis(ethylene carbonate) monomers 3,4-*O*-isopropylidene-D-mannitol-1,2:5,6-dicarbonate and the D-mannitol-1,2:5,6-dicarbonate. Polyurethane molar masses with pendant hydroxyl groups were in the range of 20 000 to 87 000 g.mol^{-1} with dispersity of 1.6 ($\overline{M}_{\mathrm{w}}$, SEC, dimethylacetamide/LiCl, PS Standards).

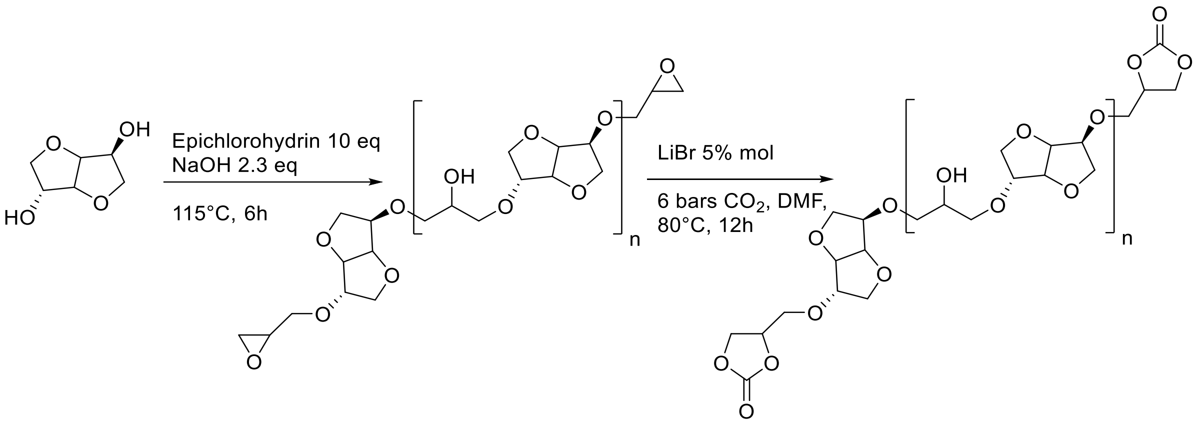
Another research team [185] converted the limonene in a bis-cyclic carbonate by the epoxidation/carbonation strategy (Scheme 29). In contrast to conventional plant-oil-based cyclic carbonates, such terpene-based cyclic carbonates afford much higher CO_2 fixation and do not contain ester groups. Novel linear PHUs and prepolymers were obtained with diamines such as 1,4-butane diamine, 1,6-hexamethylene diamine, 1,12-dodecane diamine and isophorone diamine. The highest T_g (70°C) was observed when the two polymerized monomers were cycloaliphatic.



Scheme 29-Limonene-based bis cyclic carbonate synthesis. [185]

More recently, Besse *et al.* [186] synthesized isosorbide diglycidyl ether oligomers by reaction of epichlorohydrin on the hydroxyl functions of the bio-based diol. The carbonation of the resulting molecule was performed to obtain an isosorbide based bis-cyclic carbonate (

Scheme 30) that was then polymerized with four commercial diamines. The polymerizations were completed within 12h and showed PHUs with T_g values in the range from -8°C to 59°C.



Scheme 30- Isosorbide-based bis cyclic carbonate synthesis. [186]

Lately, new bis-cyclic carbonates were designed from lignin derived bisphenols, by glycidylation and subsequent carbonation. [188] Rigid PHUs with T_g from 44 to 90°C and molar masses up to

$\overline{M}_{\mathrm{w}}$=46000 g.mol^{-1} were obtained after polymerization between the produced dimers and various diamines.

Despite the ongoing interest for biopolymers, the cyclic carbonate/amine route suffers from a lack of bio-based amines and more specifically vegetable oil-based amines, restraining the access to fully bio-based PHUs. Vegetable oil-based amines have been prepared either (i) by bringing the amine moiety via thiol-ene reaction [196], ring opening of triglycerides epoxy intermediates with an excess of diamines [197] or metathesis reaction with acrylonitrile [198], or (ii) by the direct synthesis of the amine function into the triglyceride derivatives via the synthesis of nitrile [199], amide, [200] acyl azide [201] or bromo intermediates.[202] Concerning industrial amine-based compounds from fatty acid derivatives; the most prominent example is the AB-type fatty amino acid precursor of PA-11, which is produce from castor oil for nearly fifty years from ricinoleic acid by Arkema under the trade name Rilsan®. [203, 204] The double bond of undecenoic acid is converted by HBr into the subsequent bromo-based derivative, which is then transformed in ω-aminoundecanoic acid by reaction with ammonia. [205] Another chemical company, Evonik, produces fully bio-based PA from bio-based decane-1,10-diamine (VESTAMID® Terra, fully bio-based PA-10,10 and PA-10,12).

Conclusion

The two pathways discussed in this review differ in terms of chemistry and polymer properties. From a chemical point of view, the transurethanization route benefits from many diols and bio-based diols and the synthesis of bis-carbamates from dimethyl carbonate and diamines is scalable. For the PHU route, the synthesis of bis-carbonates is more complex with usually several steps, especially for 6 and 7-membered cyclic carbonates. Concerning the polymerization step, the transurethanization route is a polycondensation, thus the alcohol generated has to be removed, which can be an issue for the industrialization. Besides, the transurethanization conditions are harsh with temperatures between 100-200°C and a catalyst while the PHUs are synthesized by polyaddition in milder conditions.

Polymer properties of NIPUs obtained by transurethanization route are equivalent to the ones obtained by the isocyanate route, enabling the replacement of the existing PUs. On the other hand, carbonate-amine route leads to PHUs which will possess different properties than PUs due to the hydroxyl functions along the backbone; they can be an advantage for post-functionalization or for some applications where hydrogen bonds tackle the needs. As such, PHUs are not the perfect candidates to replace all PUs, still the potential of this new class of polymer cannot be underestimated.

Both of these routes to NIPUs have been studied using monomers from renewable resources, especially vegetable oils derivatives. Many bio-based diols have been industrially developed for isocyanate-based PUs, they can also be used for NIPUs by the transurethanization pathway. In the case of PHUs, more and more raw materials such as lignin, fatty acid derivatives or glycerol are used to produce green monomers, bringing different properties to the final polymers depending on their structure. It is also necessary to notice that few industries offer bio-based diamines that are essential precursors for both routes.

Although non-isocyanate polyurethanes have been extensively studied by academic research, the two different processes encounter difficulties to be industrialized due to their respective drawbacks. However, the cyclic carbonate/amine route knows a growing interest in the industrial community since regulations on the chemical compound toxicity have become stricter. A recent patent described the synthesis of hybrid adhesive formulations based on bio-sourced poly(hydroxyurethane)s and polyepoxides, in order to enhance cork properties.[206] Fire resistant hybrid coatings made of inorganic material and PHUs have also been described in a latter patent that claims better properties, such as fire and chemical resistance or processability.[207] Additionally, Hybrid Coating Technologies has developed cross-linked hybrid non-isocyanate polyurethanes for coatings, from a reaction between mixture of mono/polycyclic carbonate and epoxy oligomers and aliphatic or cycloaliphatic polyamines with primary amino groups. This material was rewarded by the 2015 Presidential Green Chemistry Challenge.[208] As another example, ECOAT patented and industrialized a cross-linking process via NIPU technology.[209] The general industrial trend suggests that PHUs will be used as thermosets and more especially in hybrid cross-linked materials.

Note

The authors declare no competing financial interest.

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Biographies

Prof. Henri Cramail received his engineering degree from Polytechnic Institute of Bordeaux in 1987 and obtained his PhD from the University of Bordeaux 1 in 1990. After a postdoctoral stay at the University of Durham, U.K., he became an Assistant Professor of Polymer Chemistry at the University of Bordeaux 1. In 1999, he was appointed Professor at the same University. Prof. Cramail is currently the director of the Laboratory of Chemistry of Organic Polymers (LCPO) and he is leading the "Biopolymers and Biobased Polymers" team within LCPO. His research concerns the development of green pathways to biobased polymers from renewable resources. Indeed, he has been working in the development of sustainable polymerization processes for the synthesis of polyurethanes, including the synthesis of polyurethanes using isocyanate-free routes, water-based polymerization processes, or the use of metal-free catalyst methods.

Etienne Grau obtained his Masters degree in chemistry from the Ecole Normale Supérieure of Cachan (ENS Cachan). He moved to the University of Lyon, where he received in 2010 his PhD degree studying ethylene polymerization under the guidance of V. Monteil, C. Boisson and R. Spitz. After a post-doc on Ziegler–Natta catalysis in the groups of P. Sautet, C. Copéret and V. Monteil, he joined the group of S. Mecking at the University of Konstanz. Since January 2013, he has been an Assistant Professor at the University of Bordeaux, in the team of Prof. H. Cramail, working on catalysis for bio-based polymers.

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