From Petrochemical Polyurethanes to Biobased Polyhydroxyurethanes

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ABSTRACT: From a green and sustainable chemistry standpoint, the current challenge in the polyurethane's industry is to switch from petrobased polyurethanes (PUs) to biobased polyhydroxyurethanes (PHUs). This review describes the main alternative strategies being developed with a focus on PHUs from vegetable oils and derivatives. The substitution of petrobased polyols by natural oil based polyols was the first route to biobased PUs to be developed. The second strategy involves synthesis without the need of harmful isocyanate by the nucleophilic polyaddition of polyamines to polycyclic carbonates. The technological barrier to the synthesis of biobased cyclic carbonates could be overcome by the chemical transformation of epoxidized vegetable oils or by the use of glycerine carbonate-based intermediates. New families of biobased PHUs with a lower environmental footprint could be generated.
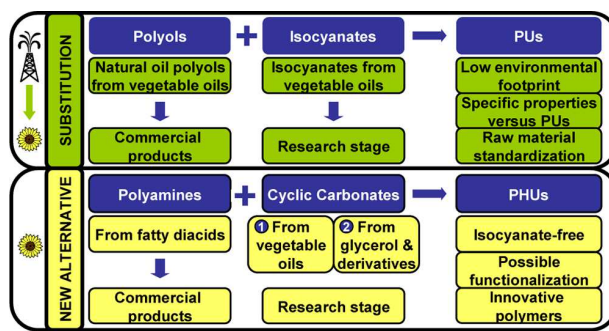
1. INTRODUCTION

Polyurethane (PU) development began in the 1940s, with the work of Otto Bayer and colleagues. They reacted a polyol and a diisocyanate to obtain the first PUs, which had excellent adhesive properties. PUs are plastic polymers widely used in modern life, due to their physical state and versatile properties.[1] They are used in many applications[2] such as foams, coatings, and adhesives (paints/varnishes, glue, binders), isolation and upholstery (cushioning and mattresses).

The PU market currently accounts for about 5% of the global polymer market.[2] PUs are the sixth most widespread group of polymers.[3] According to *Research and Markets*, the global market for PUs was estimated at 14 Mt in 2010, and is expected to reach 18 Mt by 2016.

The chemical reaction underlying PU synthesis is a polyaddition reaction between the hydroxyl group (−OH) of the polyol and the isocyanate group (−NCO) (Figure 1). The molecular weight of PUs depends on the OH/NCO ratio and
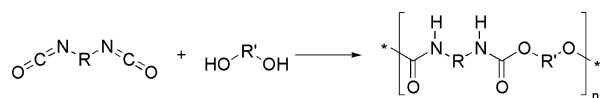
reaction promotion. The reaction between two difunctional molecules does not necessarily give a linear melt and soluble PUs, because isocyanate functional groups can also react with water (present in some reactants) and with the condensation products obtained.[4,5] R and R′ are mostly derived from aromatic toluene diisocyanate (TDI) and methylenediphenyl diisocyanate (MDI).

The latest advances in PU research have focused on the replacement of petro-based polyols and isocyanates with biobased molecules, as a response to concerns about the depletion of petrochemical resources. Current trends are for the use of chemical platforms based on vegetable oils and involving the valorization of natural oil polyols or NOPs.[6,7]

However, although several very promising molecules have been developed, substitution with biobased products cannot solve the problems arising from the use of isocyanates: high toxicity and volatility of di- and polyisocyanates and production through the phosgenation of diamines. The "isocyanate route" has been shown to constitute a threat both to the environment and to the health of operators. The replacement of these hazardous substances has become an academic and industrial
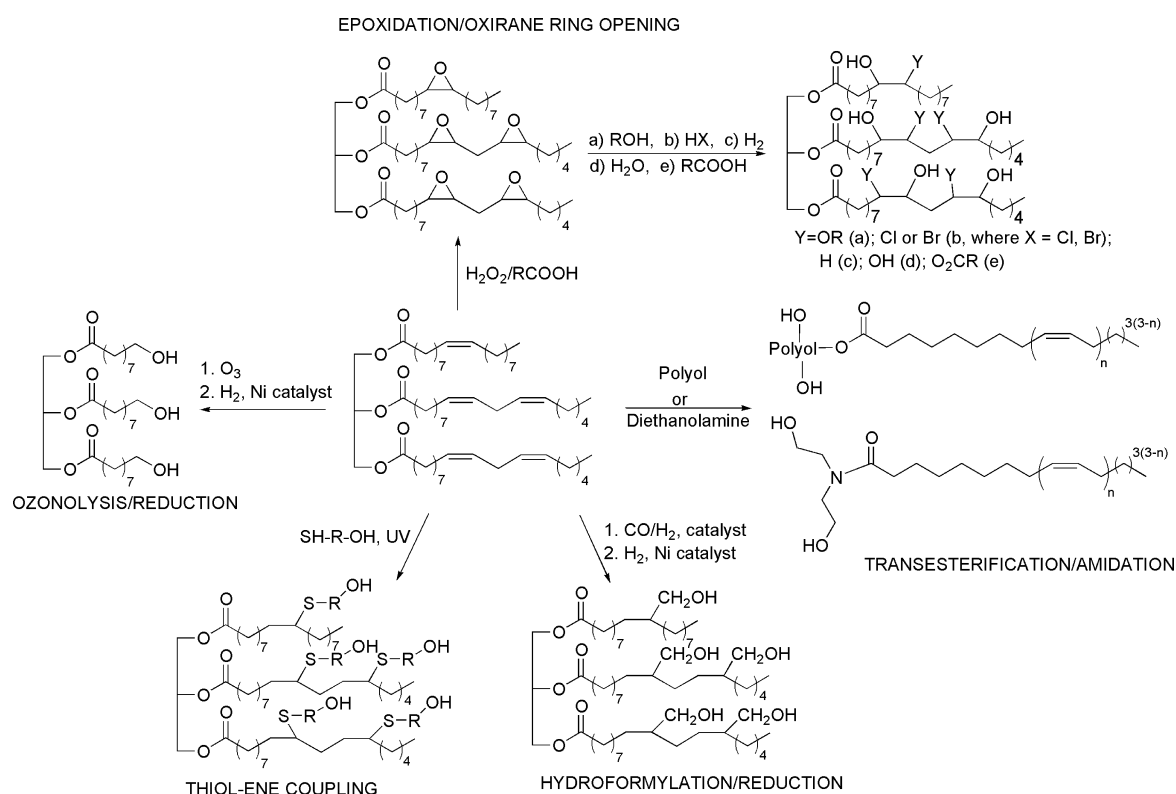

Figure 1. Synthesis of polyurethanes by the polyaddition reaction between a polyol and a polyisocyanate.

Figure 2. The most common routes to vegetable oil-based polyols (adapted from ref12).

concern, given the constraints now imposed by European regulations. According to appendix XVII of the REACH regulation, when sold as a constituent of mixtures, MDI should constitute no more than 0.1% of the mixture, by weight.[8]

Faced with this health and safety problem, the scientific community has been working for many years toward the development of innovative synthetic routes for replacing isocyanates in the manufacture of PUs. In 1957, Groszos et al.[9] patented the preparation of hydroxycarbamates by a reaction between a cyclic carbonate and a "urea polyamine". This major reactive strategy has since been studied extensively, and is more far-reaching than a simple replacement of isocyanates. Instead of generating PUs by adding isocyanates to polyols, PHUs are generated by the nucleophilic addition of diamines to cyclic carbonates.

In PHUs production, the first reactant is a primary, secondary, aliphatic, or aromatic amine, and the second reactant is an organic cyclic carbonate. Thus, to overcome the need for isocyanates, it is important to review the reactants, including cyclic carbonates in particular, and to work on new polymer products of technically feasible alternative synthesis methods. In this context, PHUs are the future of PUs.

In this review, we will first provide a brief overview of PUs from plant resources, including vegetable oils in particular, and we will then focus on the isocyanate-free preparation of PHUs from mono and polycyclic carbonates. We will describe the various methods for synthesizing five- and six-membered cyclic carbonates, before looking at their aminolysis by monoamines or polyamines. After outlining the various applications of PHUs, we will study the synthesis of PHUs from biobased cyclic carbonates.

2. POLYURETHANES FROM VEGETABLE OILS

Isocyanates and polyols are currently synthesized from petrochemical resources. Most efforts to develop alternatives have focused on their replacement with natural oil-based polyols and isocyanates.

2.1. Natural Oil Polyols (NOPs). Most (75%) of the polyols used for PU synthesis are polyether polyols, obtained from the reaction between a "starter" polyol and an alkylene oxide, both petrobased. The 25% remaining are polyester polyols synthesized by the polycondensation reaction between a dicarboxylic acid and a polyol.[10] Initial efforts to increase the renewable content of PUs involved the use of a saccharide "starter", such as sorbitol or sucrose, for polyether polyol synthesis, or of 1,3-propanediol from glycerol as a "starter" for reaction with adipic or succinic biobased acids for the synthesis of polyester polyols. All these synthons are low-molecular weight molecules. Recent attempts to overcome this problem and to valorize low-cost renewable resources have focused on the use of vegetable oils and their derivatives. This approach to generating polyester polyols has been widely studied and reviewed.[7,11−18]

For use in flexible foams, the polyol should have a functionality of 3 and a molecular weight of 3000−6000 g/mol, corresponding to a hydroxyl number of 56−28 mg KOH/g. For use in rigid foams, a higher functionality (3 to 6), a lower molecular weight (<1000 g/mol) and a higher hydroxyl number (>200 mg KOH/g) are required. Hydroxylated vegetable oils are suitable for PU synthesis if they contain more than 2.5 OH groups/molecule. The only vegetable oil that can be used directly for this purpose is the non edible castor oil ((2.7 OH/triglyceride). The resulting PUs present a uniform cross-linked structure and, consequently, good

Table 1. General Characteristics of the Main Synthesis and Chemical Properties of NOPs

|	synthesis characteristics		chemical properties of the polyol				
NOP route	number of steps from natural oil	commercial or research stage	primary or secondary OH	dangling chains	functionality	OH number (mg KOH/g)	MW (g/mol)
epoxidation	2	commercial	secondary	yes	3–4	150–200	900–1100
transesterification	1	commercial	primary	yes	2–2.5	250–300	350–450
hydroformylation	2	research	primary	yes	>4	>200	900–1100
ozonolysis	2	research	primary	no	maximum 3	200–300	500–700
castor oil	0	commercial	secondary	yes	2.7	150–170	930–950
thiol-ene coupling	1	research	primary	yes	>2	200–250	1070–1440
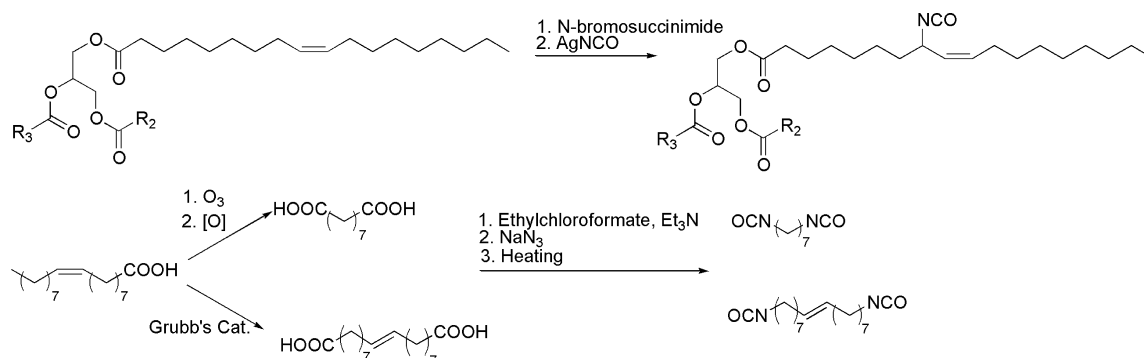
Figure 3. Synthesis of VOIs: (a) bromination route and (b) Curtius rearrangement route.[12]

mechanical properties. Functionality and hydroxyl content can be increased by transesterifying castor oil with various polyols (glycerol, sorbitol, pentaerythritol), generating more rigid PUs. Other studies have investigated ways of introducing several hydroxyl groups into a natural renewable resource that initially had no such groups. The reactive chemical sites on vegetable oils used to reach polyols are the ester and its α position and/or the double bonds and their allylic positions (Figure 2).

Epoxidation Route. Vegetable oils are epoxidized, and the epoxide is opened by adding various proton donors. The use of alcohols, such as methanol in particular, is preferred, as this results in liquid polyols with large numbers of functional groups. Only secondary hydroxyl groups are generated, resulting in a lack of reactivity with isocyanates. Moreover, the hydroxyl groups are present in the middle of the aliphatic chains, which are not included in the polymeric network after the reaction with isocyanates, resulting in less rigid PUs.

Hydroformylation/Reduction Route. The introduction of a primary hydroxymethylated group into the ethylene functional group is achieved by a two-step reaction with expensive catalysts: treating the vegetable oil with syngas (CO/H_2) to obtain an aldehyde further reduced by H_2. The resulting PUs are always amorphous or glassy materials, because of the dangling chains.[15]

Ozonolysis/Reduction Route. The C−C double bond is cleaved in three steps to obtain terminal primary hydroxyl groups: the vegetable oil is treated with ozone to obtain an ozonide, which is further reduced first to aldehyde and then to alcohol. As no dangling chains remain, the resulting polyols have a higher T_g and better mechanical properties. This route can also be applied to oleic acid, to generate pelargonic acid (saturated C_9) and azelaic acid ($\alpha-\omega$ diacid), which is reduced to a saturated diol with lithium aluminum hydride. An unsaturated C_{18} $\alpha-\omega$ diol can also be formed by the self-metathesis of oleic acid in the presence of Grubbs catalyst, followed by a reduction step.

Transesterification Route. Like castor oil, all vegetable oils can be transesterified in the presence of bases or enzymes as catalysts, with polyols, preferentially polyols with no β-hydrogen (pentaerythritol and trimethylolpropane), which have higher chemical and thermal stabilities.[19] Diethanolamides can also be obtained by the amidation of vegetable oils with ethanolamine. In both cases, the fatty acid chains can act as plasticizers, tending to weaken the mechanical properties of the resulting PUs.

Thiol-ene Coupling Route. Methyl-10-undecenoate from ricin oil,[20] oleic acid, and rapeseed oil[21] and diols from ricin or sunflower oils[22] have been successfully reacted with mercaptoethanol and other thiols under UV irradiation, to yield NOPs. This simple, one-step reaction scheme makes it possible to introduce a new heteroatom into the triglyceride structure. However, it has the drawback of being accompanied by secondary reactions (disulfide formation, esterification) generating byproducts, many of which are hydroxylated.

Metathesis Route. Long-fatty acid chain diols can be obtained in two steps by a metathesis reaction[11,23] followed by reduction, with ruthenium as the catalyst.[11,18]

A general evaluation of the synthesis and chemical properties of NOPs is provided in Table 1. None of the syntheses involved any more than two steps. Knowledge of the chemical characteristics of each class of NOP can guide their selection for use as raw materials for PU synthesis.

2.2. Fully Vegetable Oil-Based PUs. The second step is the production of completely vegetable oil-based PUs, by one of two different strategies: the addition of vegetable oil-based isocyanates (VOIs) to the NOPs or vegetable-oil based AB monomer polymerization. Whichever strategy is adopted, most petrobased isocyanates are aromatic and much more reactive than the aliphatic isocyanates than can be obtained from vegetable oils, which are usually reserved exclusively for coating applications.

Table 2. General Characteristics of the Synthesis and Chemical Properties of VOIs

|	synthesis characteristics		chemical properties of the biobased isocyanate			
route	steps from natural oil	commercial or research	aliphatic or aromatic	NCO position	functionality	MW (g/mol)
allylic bromination	2	research	aliphatic	α double bond	3–4	1000–1100
Curtius rearrangement	5	research	aliphatic	terminal	2	107 (from oleic)
Curtius rearrangement	4	research	aliphatic	terminal	2	280–320
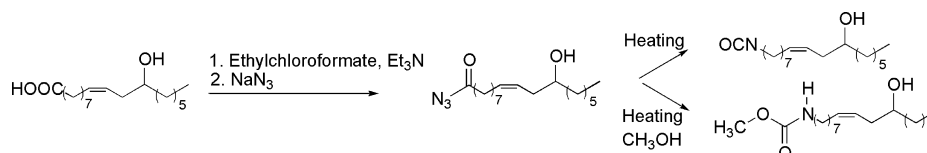
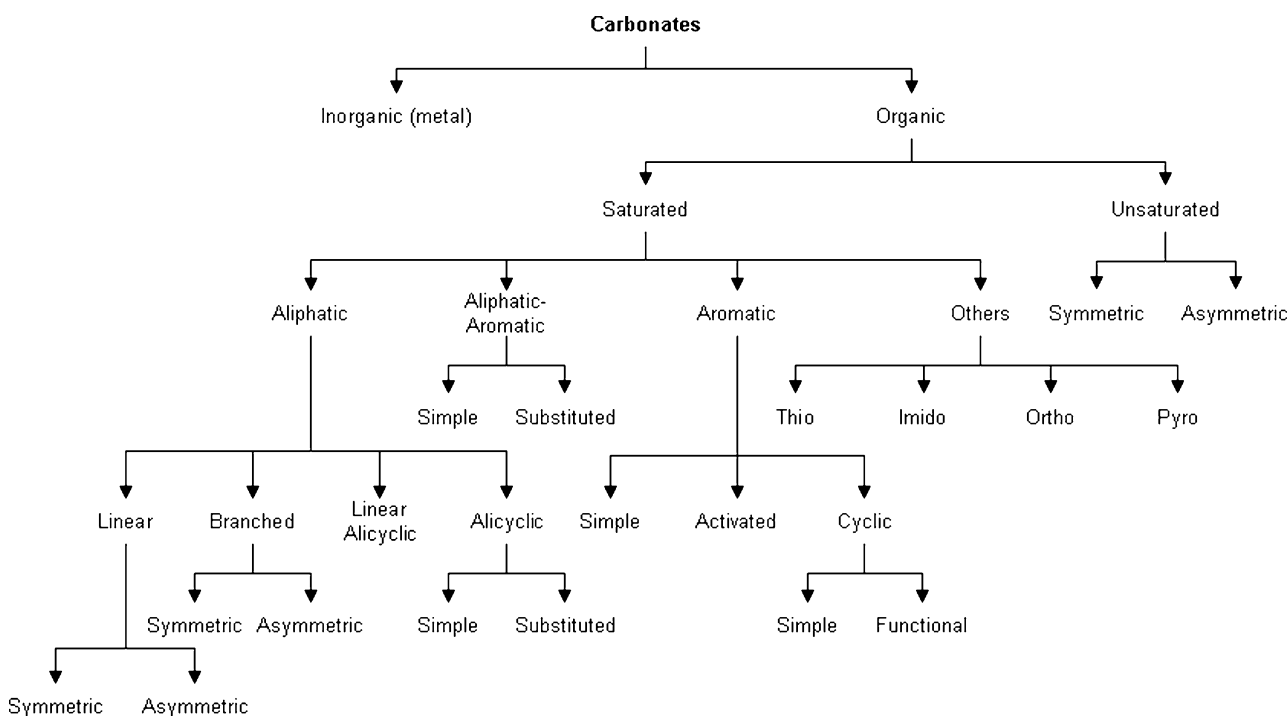**Figure 4.** Preparation of fatty acid-based AB-type monomers[27].

Figure 5. Classification of organic carbonates.[30]

For the first strategy, two routes for the production of VOIs have been studied (Figure 3, Table 2). They differ in terms of both the number of steps involved and the chemical properties of the resulting isocyanates. For example, PUs can be synthesized by a condensation reaction between castor oil and soybean oil-based allylic isocyanates.[24] These materials have potential applications as flexible foams. The diisocyanates synthesized by the Curtius rearrangement have been reacted with polyols obtained by the ozonolysis/reduction of canola oil.[25,26] The two diols synthesized from oleic acid have been reacted with the 1,7-heptamethylene diisocyanate. The resulting PUs have properties similar to those of the petrobased 1,6-hexamethylene diisocyanate.

The other strategy is based on the vegetable oil-based AB-type self-condensation reaction.[27] Monomers are obtained from ricinoleic acid or from oleic acid, by epoxidation/oxirane ring-opening with methanol. The acyl azide is initially prepared by reacting sodium azide with the terminal carboxylic acid group. Upon heating, it decomposes to an isocyanate that reacts with

the secondary hydroxyl groups. The acyl azide is then reacted with methanol to form a methyl carbamate (Figure 4). A transurethanization reaction with a titanium catalyst is then carried out to yield PUs. Molecular weights of 2000 to 9000 g/mol and a low T_g (−53 to +26 °C) have been recorded for these compounds.

AB-type monomer is obtained in a four-step reaction from castor oil, and a six-step reaction from high oleic vegetable oils.

2.3. Advantages and Drawbacks of Vegetable Oil Based PUs. The polycondensation reaction between iso-cyanates and polyols requires little energy. The reaction of biobased reactants therefore allows the direct use of existing industrial technologies and installations. Nevertheless, before reacting biobased isocyanates and NOPs, multistep reactions must be performed. Unless castor oil is used directly, NOPs are obtained by a two-step procedure, whereas the production of VOIs requires two to five steps. This first strategy is thus slowed by its overall complexity and is both highly time-consuming and costly in terms of energy. This is also the case

for vegetable oil based AB-type monomers, synthesized in at least four steps before the autocondensation reaction.

Industrial groups, such as BASF, Cargill, Oleon, and Huntsman, have developed their own biobased polyester polyols from vegetable oils, more than 20 different types of which are currently available commercially.[18] The use of these molecules makes it possible to obtain PUs with a biobased content of 60–70%, by weight. This lowers the environmental footprint of PUs synthesis considerably. The production of 100% biobased PUs can be foreseen, provided economic and technical improvements are achieved in the use of vegetable AB-type monomers and isocyanates.

The physicochemical properties of NOPs depend on two main parameters: the chosen vegetable oil and the synthesis route. Each vegetable oil has its own fatty acid profile, which may also vary with geographic origin and year of harvest. The standardization of raw materials by crop engineering will be required to obtain a standard range of NOPs. Moreover, from a homogeneous batch of a single vegetable oil, each chemical route provides NOPs with different chemical structures (type, number and position of hydroxyl groups, dangling chains and molecular weight), physical properties (e.g., viscosity, solubility) and, consequently, reactivity. A broad range of NOPs is therefore generated and requires accurate characterization before use as reactants. Similar observations apply to VOIs and vegetable AB-type monomers.

Inherent chemical structure of NOPs classifies them as reactants of the polyester polyol type. This can be seen as a drawback, because they cannot replace petrochemical polyols in all PUs derivatives. Even as polyester polyols, their uses are limited by their original structures, preventing their use in some of the applications of petrochemical polyester polyols. If the requirements for substitution are replication of the exact same properties as for petrochemical derivatives, then the original nature of NOPs is clearly a drawback. However, if the objective is to develop a new range of PUs with innovative properties, then working with new reactants will be an advantage. The major drawback of the substitution strategy for PUs synthesis remains the use of molecules bearing the highly reactive but toxic isocyanate functional group. The non-isocyanate route of synthesis from polycyclic carbonates and polyamines, generating PHUs, may be considered more promising in this context.[28]

3. SYNTHESIS OF FIVE- AND SIX-MEMBERED CYCLIC CARBONATES

3.1. Classification of Organic Carbonates.
Carbonates can be classified into two groups: organic and inorganic. In 1979, Hegarty,[29] described organic carbonates as carbon dioxide derivatives, generated via carbonic acid (H_2CO_3). The synthesis of carbonates by the esterification of carbonic acid earned them the name "esters of carbonic acid" or, more simply, "carbonic esters". Depending on their precise structure, organic carbonates can be further subdivided as shown in Figure 5. This reference work was produced in 1996 by Shaikh and Sivaram.[30] Five- and six-membered cyclic carbonates are classified as organic saturated aliphatic alicyclic substituted carbonates.

3.2. Methods for the Synthesis of Five- and Six-Membered Cyclic Carbonates.
Various types of cyclic carbonates are available commercially. However, very precise conditions are usually needed for cyclic carbonate synthesis, which is thus relatively costly.[31] Moreover, these cyclic carbonates do not seem to be able to satisfy all the requirements for PHU preparation. However, there is nevertheless a considerable demand for the synthesis of five- and six-membered cyclic carbonates for use in the synthesis of PHUs without isocyanate.[28,32,33]

Phosgene was the first reactant used to transform a diol into a cyclic carbonate. In 1883, Nemirovsky[34] described for the first time the preparation of ethylene carbonate from ethylene glycol and phosgene. In this method, hydroxyl compounds (aliphatic, aromatic) are dissolved in a single inert, anhydrous solvent or a mixture of such solvents (dichloromethane, chloroform, benzene and toluene) with excess pyridine and phosgenated at or below room temperature. Pyridine acts as an acid acceptor and reacts with phosgene, forming an ionic adduct. Pyridine is only one of the many acid acceptors that may be used. This reaction can, therefore be carried out continuously, without difficulty, with high carbonate yields. The reaction mixture is washed with dilute HCl (to neutralize excess pyridine) and then with water (to remove salt). Pure organic carbonate is obtained either by distillation or recrystallization from suitable solvent or solvent mixtures. High yields of five- or six-membered cyclic carbonates of 1,2- and 1,3-dihydroxy compounds can be obtained in this manner and have proved useful monomers for the preparation of high-molecular weight polymers.

The main drawbacks of this reaction are: the need for toxic and hazardous chemicals, such as pyridine and phosgene, the need to neutralize the excess pyridine and to eliminate the salt byproduct.[35] This involves additional purification steps. For these reasons, this method has been replaced by other methods.

Burk and Roof[36] replaced phosgene by triphosgene (Figure 6). In CH_2Cl_2 and pyridine, 1,2-diols react with triphosgene to
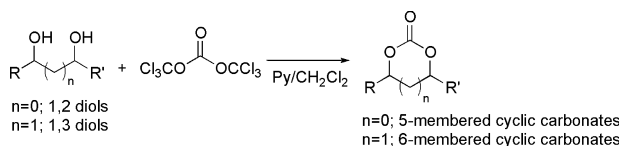
Figure 6. Synthesis of cyclic carbonates by phosgenation.

yield 87–99% five-membered cyclic carbonates at 50 °C. Following the same protocol, 1,3-diols are transformed at 70 °C in THF to form six-membered cyclic carbonates.

The second method commonly used for the synthesis of cyclic carbonates is the chemical insertion of carbon dioxide into an epoxide. Much attention has focused on carbon dioxide chemistry in recent years. The production of useful chemicals from CO_2 is not only economically beneficial, it also has a positive impact on the global environment.[37] Reactions of oxiranes with CO_2 generating high yields of five-membered cyclic carbonates are very attractive both economically and environmentally.[38] This reaction is usually carried out at high pressure, in the presence of a catalyst. Various types of catalysts have been investigated, including amines, phosphanes, alkaline metal salts, transition metal complexes, organotin halides, magnesium oxides, calcinated hydrotalcites, and phthalocyaninatoaluminum.[39,40] This type of synthesis was first described in 1943, when Vierling applied this strategy to the production of ethylene carbonate.[41]

The reaction of carbon dioxide with oxetane can also be used to generate six-membered cyclic carbonates. In the case of oxiranes, the addition is selective and yields are high, but the use of cyclic ethers with larger ring sizes (oxetane, pyranes)

results in less efficient CO_2 addition. In this reaction, the process used to produce oxetane is enhanced by the substituent having a good leaving group. This reaction has been studied, with the use of Sb as a catalyst, at very high pressure (50 kg/cm^2).[42]

Darensbourg et al.[43] demonstrated that catalysts based on aluminum and chromium and some salts of n-Bu$_4$NX (X = Cl or N$_3$), are selective for the coupling of CO_2 to oxetane (trimethylene oxide) to form the correspondent polycarbonate with traces of ether bonds. It has been shown that active catalysts of CO_2 coupling, such as complexes based on salts (MX) in the presence of a cocatalyst, can be efficient for this kind of coupling. The substituent effect feature of the reaction mechanism has recently been used to fine-tune the reaction pathway for poly(trimethylene carbonate) formation from oxetane and CO_2 via trimethylene carbonate through ring-opening polymerization.[44,45] This was accomplished through the use of a less electrophilic cobalt(II) Schiff base complex, preventing polymer chain propagation, or the use of CrCl in the presence of n-Bu$_4$NBr and a lowering of reaction temperature, to favor six-membered cyclic carbonate production over polymer chain growth.[44] In 2010, Darensbourg et al.[46] described a simple catalytic reaction for synthesizing trimethylene carbonate from trimethylene oxide and carbon dioxide. They used VO(acac)$_2$ in the presence of an ammonium salt. The process was found to be highly selective and quantitative for the production of six-membered cyclic carbonates under mild reaction conditions: 60 °C and 1.7 MPa. Other approaches have also been developed for the use of CO_2 to synthesize cyclic carbonates.[47−49]

Bruneau et al.[50] described a new method for synthesizing a six-membered cyclic carbonate containing an unsaturated bond (4H-[1,3]dioxan-2-one). It was easily prepared from propargylic alcohols and carbon dioxide (Figure 7). The activation
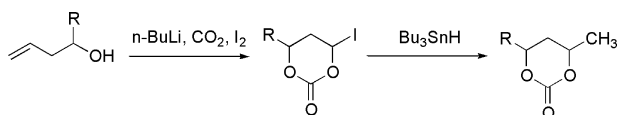

Figure 7. Synthesis of six-membered cyclic carbonates from propargylic alcohols and carbon dioxide.

of these precursors with suitable palladium catalyst precursors yields reactive zwitterionic allenyl palladium species and straightforward routes of synthesis for functional α-allenol derivatives upon hydrogenolysis, by coupling with terminal alkynes and monocarbonylation. However, this process is still fraught with side reactions and severe reaction conditions, including relative high pressure and temperature.

The methods currently used for the synthesis of cyclic carbonates are transesterification and transcarbonation, which lead to the formation of n-membered cyclic carbonates from diols (Figure 8). The carbonates obtained are ethylene carbonate from ethylene glycol and trimethylene carbonate from 1,3-trimethylene glycol. Dialkyl carbonates, such as dimethyl carbonate (bp = 90 °C), diethyl carbonate (bp = 126−128 °C) and diphenyl carbonate (bp = 306 °C) are used for this type of reaction as alkylation agents and aprotic polar solvents.

The presence of a basic catalyst is essential for this reaction.[51] The catalysts used are alkaline metals, amines, such as
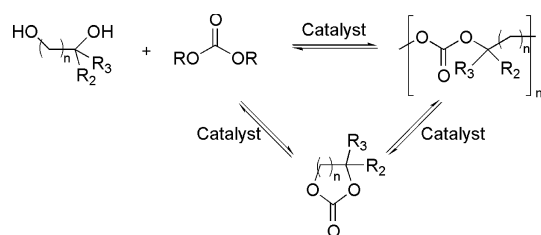

Figure 8. Synthesis reaction for n-membered cyclic carbonate and polycarbonate through a reaction between diols and dialkyl carbonate.

imidazole, ethylamine, and 1,8-diazabicyclo[5.4.0]undecene (DBU) and basic ion-exchange resins.

The synthesis of six-membered cyclic carbonates by the transesterification of propane-1,3-diol with diethyl carbonate, catalyzed by sodium ethanolate, as described by Carothers et al.,[52] gives a yield of 40%. Sarel and Pohoryles[53] reported the synthesis of various six-membered cyclic carbonates from propane-1,3-diols with different substituents. By contrast, single six-membered cyclic carbonates were produced exclusively when 2,2-diethyl-2-phenylpropane-1,3-diol, 2-ethyl-2-phenyl-propane-1,3-diol, pentane-2,4-diol, 2-methylpentane-2,4-diol,[39] and butane-1,3-diol were subjected to the transesterification reaction. A similar method was reported by Albertson et al.,[54] in which equimolar amounts of propane-1,3-diol and diethyl carbonate were used, with stannous 2-ethylhexanoate as the transesterification catalyst, giving a yield of 53%. In this method the reactants were refluxed for 8 h before the removal of ethanol. It has been suggested that stannous 2-ethylhexanoate can act both as an agent of both polymerization (at lower temperature) and depolymerization (at higher temperature).[48]

Hu et al.[47] reported that this method afforded 70% yields of trimethylene carbonate (TMC). For the transesterification reaction, two catalysts (sodium ethanolate and dibutyltin dilaurate) were used and the reaction temperature was controlled, xylene refluxing. By contrast to previous methods, prepolymer depolymerization was carried out with tin powder as the catalyst, after neutralization of the basic catalyst with p-toluenesulfonic acid.

Huntsman[55] proposed two six-membered cyclic carbonates: XHC-27 and XHC-30. XHC-27 is a pale solid with a melting point of 104 °C, whereas XFC-30 is a slightly viscous liquid. Both were prepared from 1,3-diols with two or several methyl or alkyl groups, in the presence of numerous basic substances known to catalyze the reaction between dialkyl carbonate and 1,3-diols. These authors found that compounds based on zinc and titanium, or tin and zirconium, were useful as catalysts for this reaction.

The transesterification reaction has also been described with different chemical[48,53] and enzymatic catalysts.[56,57] Pyo et al.[56] recently reported that six-membered cyclic carbonates with functional groups could be synthesized in the presence of lipase, in a solvent-free medium.

Nohra et al.[58] investigated the possibility of synthesizing five- and six-membered cyclic glyceryl carbonates (5CGC and 6CGC) with exocyclic urethane groups from glycerol carbonate and dimethyl carbonate, in the presence of various catalysts, without the use of toxic solvents (Figure 9). The two-step route involved two consecutive reactions: total aminolysis of glycerol carbonate in a concentrated medium without an added catalyst and transesterification with various catalysts, such as phosphazene, sodium carbonate, zinc acetylacetonate and
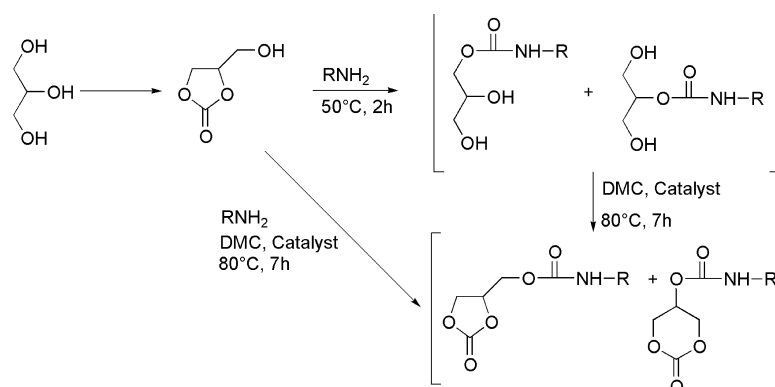
Figure 9. "Two-step" and "single-reaction" routes for the synthesis of (2-oxo-1,3-dioxolan-4-yl)methyl alkylcarbamate and 2-oxo-1,3-dioxan-5-yl alkylcarbamate.[58]

potassium tertbutoxide. Phosphazene was the most soluble catalyst. It therefore had the highest catalytic activity and promoted a homogeneous transesterification process. The use of DMC as both reactant and solvent increased system compatibility. The reaction was also affected by increasing the length of the alkyl chain, with higher conversion rates for the shorter alkyl chains of the HU. For the single-reaction synthesis, competition between the products was observed during the course of the reaction. This route favored side reactions, such as the aminolysis of 6CGC and the formation of dialkyl urea. The "two-step" synthesis gave the highest yields of 5CGC/6CGC, but the single-reaction synthesis yielded higher conversion rates for the β isomer and higher selectivity for 6CGC. The controlled and combined effects of catalyst and DMC present in excess and acting as both solvent and reactant make it possible to control the aminolysis and trans-esterification reactions selectively.

In the cyclic carbonate transcarbonation reaction, ethylene carbonates and propylene carbonates are the principal sources used (Figure 10). Reactions involving ethylene carbonates have
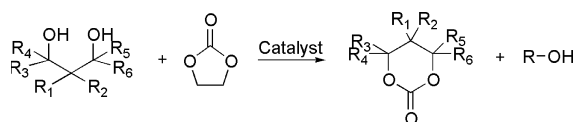

Figure 10. Reaction between ethylene carbonate and diols.

the double advantage of being rapid and occurring in mild conditions. The transcarbonation reaction has also been achieved with mannitol derivatives. Cyclic derivatives have been obtained after 15 and 40 min, with a yield of 65—90%. This conversion leads to the formation of five- and six-membered cyclic carbonates.[59] These carbonate interchange reactions are particularly interesting, as they lead to the production of alcohols that are economically recoverable. This is the case for ethylene glycol and propylene glycol, which are released when ethylene carbonate and propylene carbonate, respectively, are used as carbonate sources. Transesterification and transcarbonation are preferable to certain other methods because their reactants and byproducts are not noxious.

3.3. Application to the Synthesis of Five- and Six-Membered Bicyclic Carbonates. As for monocyclic carbonates, various methods have been used to synthesize bicyclic carbonates[60−63] (Figure 11). Some of these methods are laborious and make use of toxic and dangerous reactants,

such as glycidol or phosgene, and most are based on epoxides or diols.

In method 1, glycidol is acylated by benzoyl dichloride to give glycidyl dibenzoate. A CO_2 insertion and an extension of the three-membered carbonates to give five-membered cyclic carbonates result in the production of glycerol carbonate dibenzoate, with a yield of 65%. Method 2 is the conventional method based on the carbonation of tetraol blocked by phenyl chloroformate, generating the corresponding five-membered bicyclic carbonates. In method 3, carbodiimidazole is used as a basic catalyst for the carbonation of vicinal diols to five-membered bicyclic carbonates. In method 4, triphosgene is used to perform for the carbonation of vicinal diols at room temperature, to give five-membered bicyclic carbonates with a double substitution of phenyl groups in the fourth position. Finally, in method 5, five- and six-membered bicyclic carbonate thioethers are generated by the radical addition of ethane-1,2-dithiol to 4-(3-butenyl)-1,3-dioxolan-2-one or by a reaction between 4-ethenyl-1,3-dioxolan-2-one (AC) and several thiols.

Nohra et al.[58] have recently synthesized five- and six-membered bicyclic carbonates from glycerol carbonate. The experimental conditions used for the synthesis of monocyclic carbonates were transposed for the synthesis of bicyclic carbonates (Figure 12). Engineering of the medium, making use of the solubilizing properties of DMC and methanol, combined with the use of a strong basic liquid catalyst, can also provide optimal conditions for the synthesis of bicyclic carbonates.

4. SYNTHESIS OF POLYHYDROXYURETHANES BY THE AMINOLYSIS OF FIVE- AND SIX-MEMBERED CYCLIC CARBONATES

4.1. Investigations on the Model Reaction. Our principal objective here is to provide readers with a full understanding of the nucleophilic addition reaction between amine and cyclic carbonate (Table 3). Such an understanding is necessary for comprehension of the polyaddition reaction between bicyclic carbonates and polyamines to generate PHUs.

Mechanism of the Reaction of Cyclic Carbonates with Amines. Hydroxyurethanes are obtained by the aminolysis of cyclic carbonates. This nucleophilic addition of amine to cyclic carbonates leads to the formation of two isomers from five-membered cyclic carbonates and to a single hydroxyurethane product from six-membered cyclic carbonates (Figure 13). For five-membered cyclic carbonates, the two isomers can be
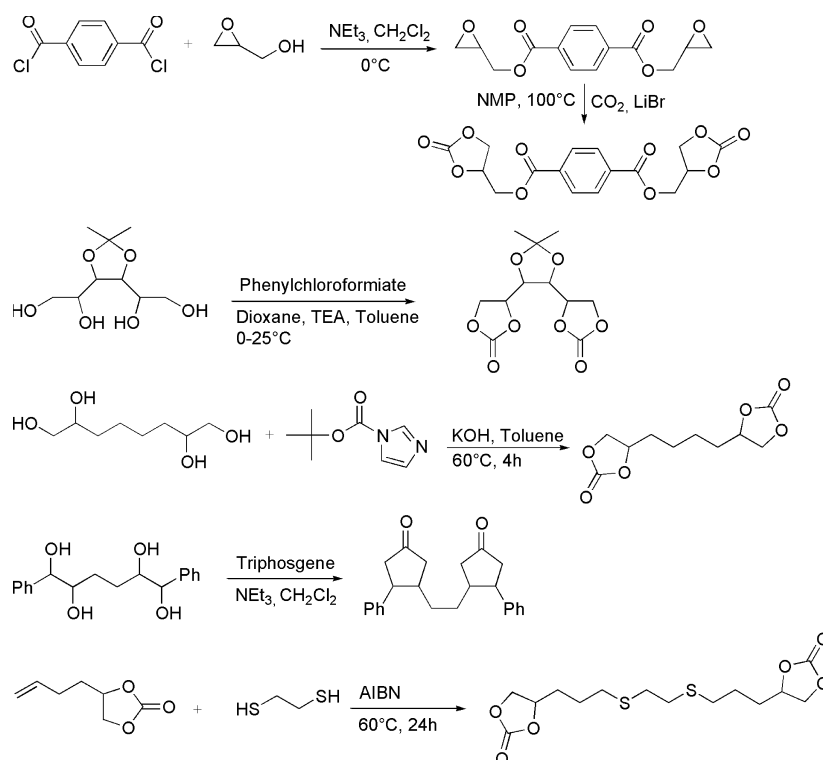
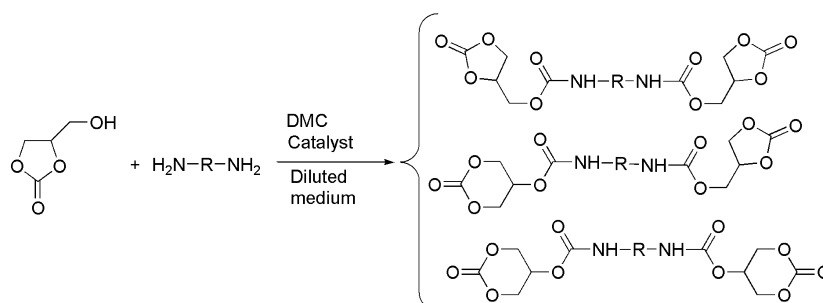**Figure 11.** Different methods for the synthesis of five-membered bicyclic carbonates.

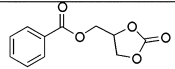**Figure 12.** "Single-reaction" scheme for the synthesis of five- and six-membered bicyclic glycerilic carbonates.[58]
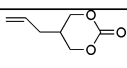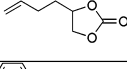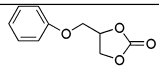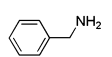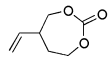
distinguished on the basis of the presence of primary and secondary hydroxyl groups. In most cases, the preferred isomer is the compound with the secondary hydroxyl group. Only primary hydroxyl group is obtained from reactions with six-membered carbonates.

The mechanism of the cyclic carbonate-amine reaction underlying hydroxyurethane production can be interpreted in two ways. First, this reaction may be under ionic control, via an amphoteric tetrahedral intermediate, as proposed by Tomita et al.[63] (Figure 14). Nucleophilic attack of the amine in the carboxylic group of the alkylene carbonate results in the formation of a tetrahedral intermediate. The breaking of the carbon–oxygen bond is favored by the high electron density at the nitrogen atom, and the nascent alkoxide ion is rapidly transformed into a reaction product. According to the bond orders and length of the five-membered cyclic carbonate calculated by the *ab initio* method on the basis of STO-3G, there should be more of the hydroxyurethane containing the secondary alcohol moiety than of that containing the primary alcohol moiety.[64]

Alternatively, the mechanisms of hydroxyurethane formation may be considered to involve a single reaction or a multiple-stage reaction pathway including the formation of a series of solvated intermediates and their transformation into products.[65] Zabalov et al. carried out a quantum chemical study of urethane formation from ethylene or propylene carbonates and methyl-amine. They demonstrated that addition may proceed via the formation of several intermediates of different stabilities. Single-stage and multistage mechanisms have been proposed. A mechanism involving two amine molecules has an energy of activation only one-third that of a one-stage bimolecular reaction (Figure 15). This suggests that the second amine molecule acts as a catalytic assistant.

This reaction is controlled by the addition of one reactant to another and may be catalyzed by alkaline compounds. Intramolecular hydrogen bonds are formed between the hydroxyl and carbonyl groups of the urethane chain. Steric hindrance due to the oxygen of the carbonyl group greatly decreases the susceptibility of the urethane group to hydrolysis. This resistance is enhanced by the presence of hydrogen bonds.

Table 3. Kinetics and Thermodynamic Studies of the Aminolysis Reaction of Five- and Six-Membered Cyclic Carbonates

Authors	Year	A= Cyclic carbonate	B=Amine	Results
Rokicki [74]	1989	R= OC$_4$H$_9$, CH$_2$-CH=CH$_2$, Ph.	Triethylene tetramine	• The presence of polar groups permits the formation of inter- and intra-molecular hydrogen bonds. The mobility of the molecules decreases and viscosity increases. • Hydrogen bonds are weakened at higher temperatures.
Couvret [66]	1990	R= CH$_2$OH, CH$_3$, CH$_2$COOCH$_3$	Butylamine	• Reaction with or without solvent: faster without • Little influence of R on the reaction rate but influence on the ratio of isomers with primary and secondary OH groups • Kinetics: 2nd order with respect to the amine
Bürgel [75]	1991	R=OPh (PMD)	Butylamine, Benzylamine	• The reaction depends on the initial concentration of amine or carbonate. • Kinetics : 2nd order with respect to the amine • $k_{butylamine}$ = 0.11 l/mol. min^{-1} >> $k_{benzylamine}$ = 0.035 l/mol. min^{-1} • At T> 100°C, urethane reacts with butylamine to form urea and a diol.
Steblyanko [76]	2000		benzylamine NH$_2$	• Ratio primary OH / secondary OH: 18/82 • ΔH_f determination by molecular modeling: $\Delta H_{f\ Iary\ OH}$ = -8.1 kcal/mol > $\Delta H_{f\ IIary\ OH}$ = -9.8 kcal/mol.
Webster [70]	2000		Sec-butylamine, 2-Ethylhexylamine, Butylamine, 3-aminopropanol	• The conversion rate of the reaction is greater in polar solvent than in apolar solvent. • Model reaction for the development of adhesive coatings • Sec-butylamine is less reactive than butylamine • Different reaction rates for the amines depend on the nucleophilicity of the amine and steric hindrance.
Tomita [63]	2001	R = CF$_3$, PhOCH$_2$, Ph, H, Me	Hexylamine	• The greater the inductive effect of R, the faster the reaction • Kinetics: 2nd order with respect to cyclic carbonate
Tomita [67]	2001		Hexylamine or benzylamine NH$_2$	• Benzylamine less reactive than hexylamine • Kinetics: 2nd order in relation to amine and carbonate • Activation energies: 10.1 kJ/mol (C6-hexylamine) and 24.6 kJ/mol (C5-hexylamine)
Tomita [64]	2001			• Yield = 88-98% • Ratio primary OH / secondary OH: 15/85
Tomita [77]	2001			• The rate constant of the ring-opening of the 7-membered cyclic carbonate (C$_7$) is greater than those for the 6-membered (C$_6$) and 5-membered (C$_5$) carbonates. • $\Delta H_f C_7$ = -8.56 kcal/mol > $\Delta H_f C_6$ = -5.58 kcal/mol > $\Delta H_f C_5$ = -2.74 kcal/mol (molecular modeling).
Ochiai [78]	2005		Hexylamine	• Yield : 54% and 82%, respectively • Cyclic carbonate bearing cyclohexane is more reactive than cyclic carbonate bearing cyclopentane.
He [71]	2011	NH-C$_{12}$H$_{25}$; NH-O-C$_{12}$H$_{25}$; (CH$_2$)$_4$-O-NH-C$_{12}$H$_{25}$; O-C$_{12}$H$_{25}$	Hexylamine	• Reactivity differs as a function of the distance between the cyclic carbonate and the urethane • Cyclic carbonate 2 is the most reactive and cyclic carbonate 3 is the least reactive • Rate constants: k2 > k4> k1 > k3. • Cyclic carbonates at the α position more reactive than those at the δ position.
Nohra [73]	2012	OH	C$_n$H$_{2n+1}$-NH$_2$ with n= 4, 6, 8, 12, 16, C$_n$H$_{2n+1}$-NH-C$_m$H$_{2m+1}$ (n,m) = (1,2) or (1,4)	• The conversion of carbonate was dependent on the reaction temperature and the amine ratio. • Ratio α HU > β HU: primary amine and Ratio α HU ≈ β HU: secondary amine • Selectivity of α vs. β independent of reaction temperature but dependent on the solvent and amine. • Water as a solvent affects the formation of β isomer and increases the formation of glycerol.

Kinetic Study of the Aminolysis Reaction. A kinetic study of aminolysis reaction was carried out to describe the reaction and the effects of the various parameters. Aminolysis reactions are second order reactions with respect to organic carbonate and amine.[63,66,67] Tabushi and Ogata[68] studied the kinetics of the reaction of ethylene carbonate with various amines. They showed that reaction rate depended on amine concentration. The number of hydrogens in the α position is correlated with the reaction rate of the amine. Thus, an amine on a primary carbon reacts faster than an amine on a secondary carbon.
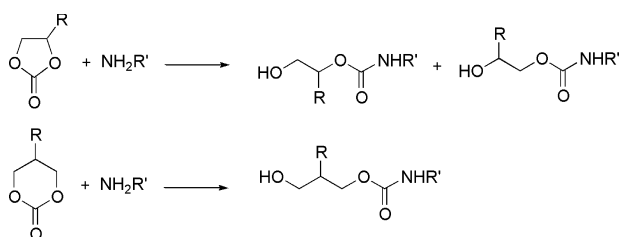
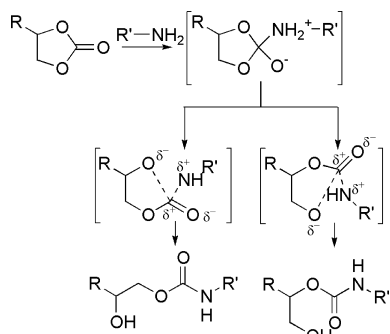Figure 13. Aminolysis reaction of five- and six-membered cyclic carbonates.

Figure 14. Mechanism for the opening of the ring of cyclic carbonates with primary amines.[63].

Garipov et al.[69] studied the kinetic interaction between a cyclic carbonate group and a primary amine group. They proposed a three-step mechanism. In the first step, nucleophilic attack of the amine of the carboxyl group in cyclic carbonates results in the formation of a tetrahedral intermediate. In the second step, a sequenced attack, by another amine, on the tetrahedral intermediate results in the removal of hydrogen ions. Finally, the carbon—oxygen bond is broken, due to the strong electron-withdrawing effect of nitrogen atoms, leading to the formation of hydroxyurethane isomers. These authors also studied the effect of the cyclic carbonate and amine structures and that of the solvent on the reaction rate. The presence of electrons in a cyclic carbonate was found to slow the reaction
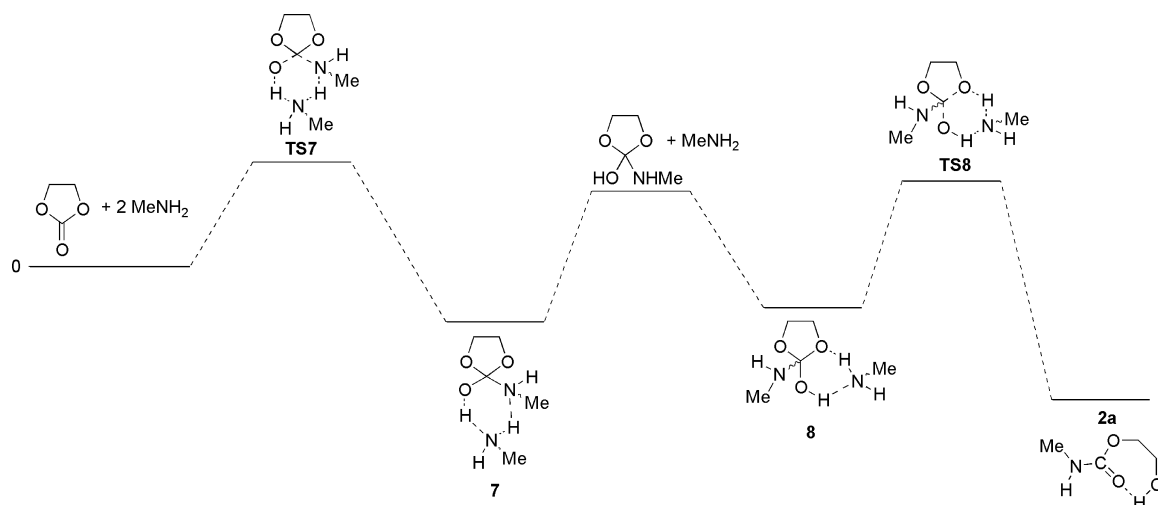
rate, which was significantly higher in protic polar solvents than in apolar solvents.

The rate of reaction between propylene carbonate and various amines with one or several functional groups was estimated by Webster et al.,[70] by near-infrared spectroscopy. They showed that the reaction rate was faster with polar solvent and that secondary amines were less reactive than primary amines. Amines differ in reactivity due to the nucleophilicity of the amine and the steric effect.

Couvret et al.[66] performed kinetic studies on the reaction of amines with cyclic carbonates branching from functional polymers. They demonstrated that the rate of reaction of cyclic carbonates with butylamine was independent of the substituent in the ring. Thus, the rate of the aminolysis for polymers functionalized by cyclic carbonates is similar to that of model cyclic carbonates. The reaction was also found to be slower in a medium containing solvent than in a solvent-free medium. For example, the kinetic constants of the reaction between butylamine and glycerol carbonate are equivalent in dichloromethane at 60 °C and without a solvent at 25 °C.

Effect of the Substituent R of the Cyclic Carbonate. The effect of the substituent R of the cyclic carbonate has been studied in the case of aminolysis with hexylamine.[63] It was concluded that speed of the reaction increased with the inductive effect of R. 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.

Reactivity of Five-Membered and Six-Membered Cyclic Carbonates. According to the work of Tomita et al.,[67] six-membered cyclic carbonates, such as 5-(2-propenyl)-1,3-dioxan-2-one, may react quantitatively with hexylamine at 30 °C over a period of 24 h in the presence of N-dimethylacetamide, whereas five-membered cyclic carbonates, such as 4-(3-butenyl)-1,3-dioxolan-2-one, are converted at much lower rates (e.g., 34%). These authors also demonstrated differences in the tension energies of the rings by molecular modeling. This study confirmed the greater reactivity of the six-membered cyclic carbonates, which react 28—60 times faster than five-membered cyclic carbonates. Similarly, He et al.[71] studied the reaction of the bicyclic carbonate coupler BC56

Figure 15. Mechanism of the reaction of ethylene carbonate with methylamine involving two methylamine molecules.[65]

Table 4. Process Conditions and Conclusions for the Synthesis of Linear Polyhydroxyurethanes with Average Molecular Weights

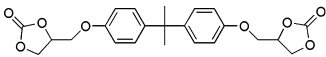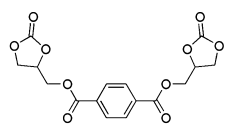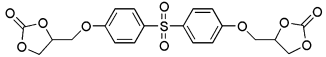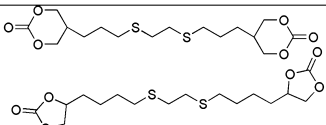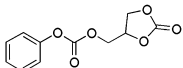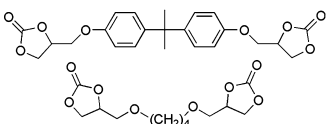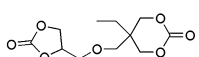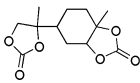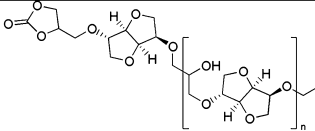| Authors	Year	A= Bicyclic carbonate	B=Amine	Results
Kihara[88]	1993		NH_2-R-NH_2 R=$(CH_2)_n$; n = 2, 3, 6, 12.	• M_n = 13000-28000 g.mol^{-1} • T increases, MW increases • Preferentially secondary OH groups • For short-chain diamines, partial intramolecular cyclization between the terminal amine and urethane group.
Tomita[64]	2001		R=Jeffamine[®]	• Yield = 100% • Ratio primary OH /secondary OH: 24/76
Ochiai[83]	2005		NH_2-R-NH_2 R = $(CH_2)_{12}$	• Catalysts tested: LiCl, LiF, LiBr, LiI, NaCl, Et_4NCl, $CaCl_2$ • Carbonate consumption is higher in the presence of a catalyst based on Li halides (Lewis acid), allowing the activation of the carbonyl group.
Steblyanko[76]	2000		NH_2-R-NH_2 R=$(CH_2)_n$; n = 2,3,5,6 R= CH_2-Ph-CH_2.	• Yield = 43% (cyclic) to 98% (CH2)5 • Mn = 6300-13200 g.mol-1.; Tg : 3°C to 29°C ; Td : 177°C to 277°C • Transparent colorless substance that is highly hydrophilic, readily forming a film • Ratio primary OH / secondary OH: 15/85 (model confirmation) • PHU soluble in DMF, DMA, DMSO.
Kim[60]	2000		NH_2-R-NH_2 R=$(CH_2)_6$; Ph-CH_2Ph ; (cyclohexane)$_2$-CH_2	• M_n = 4900-12900 g.mol^{-1} ; Td: 375-388°C • MW depends on the diamine/bicyclic carbonate ratio. It decreases with increasing diamine ratio; due to steric hindrance of the amine.
Tomita[86]	2001		R= Jeffamine[®]	• B6CC: quantitative reaction in 48 h, Mn=26000 g.mol-1 • B5CC : 85% conversion of carbonate in 48h, Mn= 15000 g.mol-1 • Kinetic constant evaluation : kB6CC= 15 kB5CC • Activation energy evaluation : EaB5CC = 2,7 EaB6CC
Ubaghs[89]	2004		NH_2-R-NH_2 R=$(CH_2)_n$; n = 2-6	• Amorphous product or colorless powder • M_n = 6400-8700 g.mol^{-1}; M_w= 9300-13700 g.mol^{-1}. • Tg ↘ when n↗. Values of 23°C to 53°C • Stable until 225°C, thermal stability increasing with n • Attack on the cyclic carbonate and on the O-phenyl with phenol elimination • Ratio primary OH / secondary OH: 20/80
			NH_2-R-NH_2 R=$(CH_2)_6$ + catalyst	• Ratio primary OH / secondary OH: 25/75 • The use of a catalyst, such as Bu_2Sn(OMe)$_2$, does not increase the molecular weight but modifies the regional selectivity of t ring-opening in favor of the primary OH group
Ochiai[85]	2005		Hexadiamine	• The higher the temperature, the greater the rate of carbonate conversion • Molecular weight increases with reaction time. • The primary OH / secondary OH ratios are identical to those obtained in solvent medium • Study of competition between the aminolysis reaction of carbonates in water and hydrolysis. Carbonate 1: less hydrolysis/ carbonate 2: quantitative hydrolysis
			$(NH_2(CH_2)_2)_2$NH	• Resulting PHUs with NH groups in their structure can react by cross-linking in a 2nd step
He[87]	2011		NH_2-R-NH_2 R=$(CH_2)_6$, $(CH_2)_{12}$ R= $C_6H_{18}N_4$	• Mn = 2000-3000 g.mol^{-1} • In DMAC, M_n=4500-6100 g.mol^{-1}. In a polar solvent (THF, CHCl$_3$), M_n= 10000 g.mol^{-1}. • The reaction of BC56 couplers with 1 eq. amine leads to the consumption of six-membered cyclic carbonate only.

Table 4. continued

Authors	Year	A= Bicyclic carbonate	B=Amine	Results
Bahr[90]	2012		NH$_2$-R-NH$_2$ R=(CH$_2$)$_4$, (CH$_2$)$_{12}$ Isophoronediamine	• Catalytic carbonation of epoxidized limonene with CO$_2$ in the presence of tetrabutylammonium bromide or silica-supported 4-pyrrolidinopyridinium iodide. • Absence of ester groups prevents side reaction during amine cure. • Mn: 1840 g.mol^{-1}.
Besse[91]	2013		Isophoronediamine NH$_2$-R-NH$_2$ R=(CH$_2$)$_{10}$ Jeffamine D-400 Diethylenetriamine	• Isosorbide-based PHU: conversion of isosorbide into carbonated oligoisosorbide • Catalytic addition of amines at room temperature in DMF • Absence of ester groups prevents side reaction during amine cure • Presence of aromatic structures provides rigidity • Mn = 7800-8600 g/mol ; Tg = -8°C to 59°C ; Td = 234-255°C.
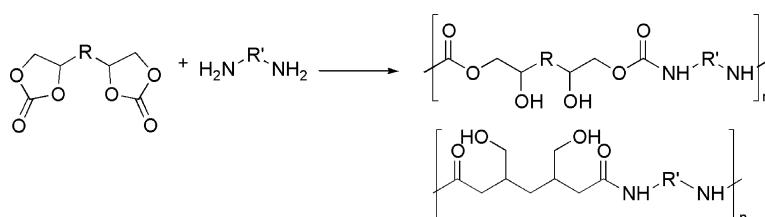
Figure 16. Preparation of linear polyhydroxyurethanes from bicyclic carbonates and diamines.
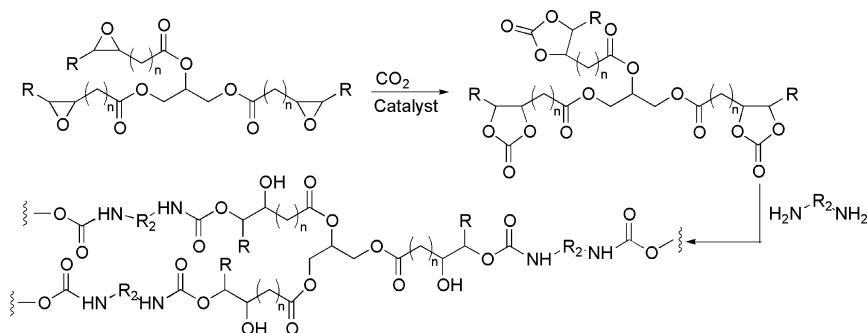
Figure 17. Strategy for non-isocyanate polyurethanes (PHUs).[109]

Table 5. Worldwide Production of Glycerol with Oleochemical Activities from 1992–2010 (in Millions of Tonnes)

	production (10^6 tonnes)					
	1992	1999	2005	2006	2008	2010
soap	208	198	160	150	130	90
fatty acids	268	322	410	450	490	535
biodiesel	6	57	368	550	1060	1600
fatty alcohols	78	108	130	160	200	240
synthetic	78	75	20	–	–	–
others		44	35	30	40	40
total	638	804	1123	1340	1920	2505
annual increase		4.4%		19.3%	20%	14%

Figure 18. Radical homopolymerization of glycerol carbonate acrylate and glycerol carbonate methacrylate.[121]

structure and molecular weight of the amine influenced this reactivity.

Nohra et al.,[73] studied the reaction of glycerol carbonate with aliphatic amines of various alkyl chain lengths. The aminolysis reaction gives rise to two N-alkylhydroxyurethane isomers, differing in terms of the position of the urethane group at either the α or β position on the glycerylic skeleton. They found that the length of the alkyl chain of the amine affected the regional selectivity of ring-opening.

Influence of the Reaction Conditions on the Regional Selectivity of Ring-Opening. Tomita et al.[67] conducted a study

with 1 equiv of a primary amine at low temperature. They observed the exclusive conversion of the six-membered ring.

Influence of the Amine. Diakoumakos et al.[72] studied the reactivity of Laprolate-803 (L-803, an aliphatic tricyclic carbonate) with various amines. They demonstrated that the
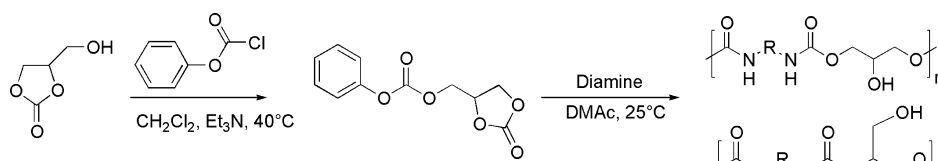
Figure 19. Synthesis of PHU from phenoxycarbonyloxymethyl ethylene carbonate synthesized from glycerol carbonate.[89]
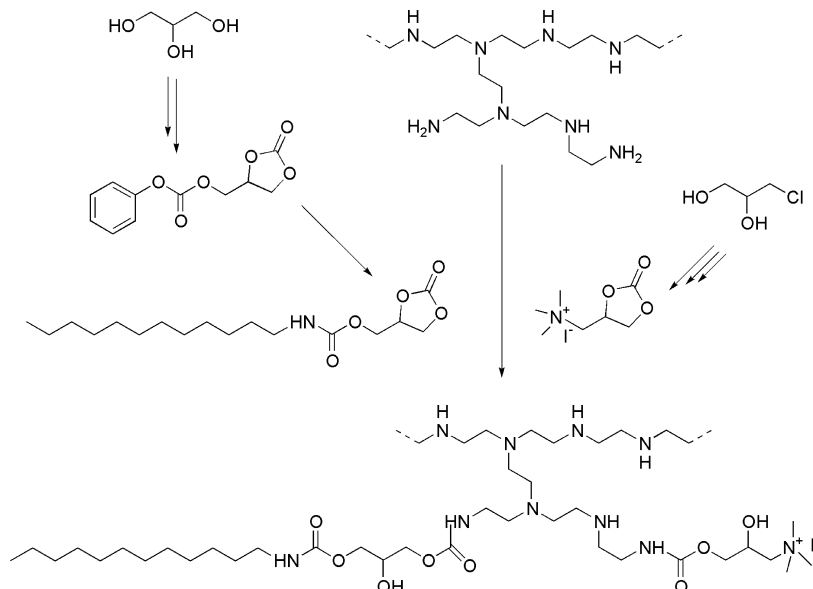
Figure 20. Synthesis of PHUs from glycerol carbonate and polyethylene imine (PEI).[124]
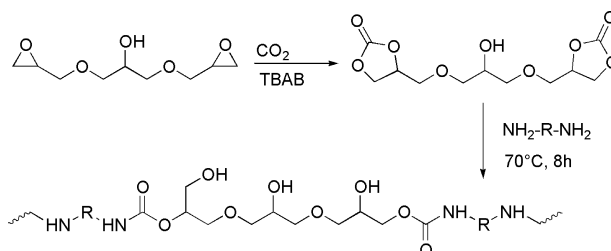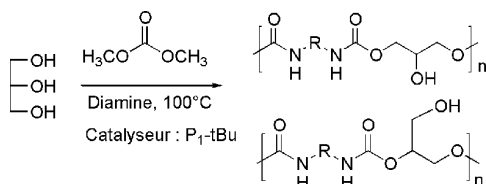
Figure 21. Synthesis of PHUs from glycerol.[125]
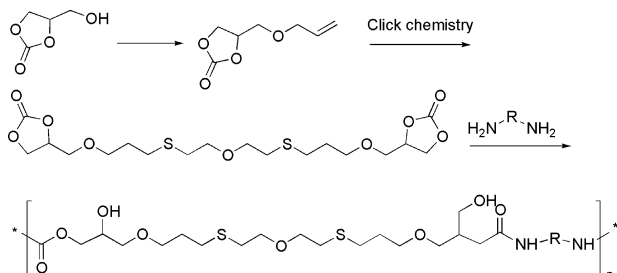
Figure 22. Synthesis of PHUs from 4-[(prop-2-en-1-yloxy)methyl]-1,3-dioxolan-2-one (AGC).[126]

Figure 23. Synthesis of PHUs from glycerol glycidyl ether.[127]
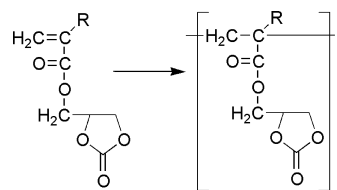
Influence of Water in the Aminolysis Reaction. When using water as a solvent, side reactions must be considered, such as the decomposition of glycerol carbonate into glycerol, decreasing product yield.[73] The nucleophilic addition of the amine to the cyclic carbonate competes with the chemical instability of the reactant in the presence of aqueous amines. For short-chain amines, the competition between aminolysis and the decomposition of glycerol carbonate favors this decomposition, because water can easily reach the cyclic carbonate, which is not the case for longer hydrophobic amines.

4.2. Synthesis and Applications of Polyhydroxyurethanes from Bicyclic Carbonates and Polyamines.

Synthesis. The polyaddition of bicyclic carbonates to polyamines leads to the generation of PHUs (Table 4). PHUs may be classified as linear PHUs or hybrid PHU networks. Linear PHUs are obtained by the reaction of bicyclic carbonates with diamines[74,79] (Figure 16). For example, erythritol dicarbonate and unhindered primary aliphatic diamines can react in

on the effect of the reaction conditions on the structure of the carbamate formed. Their analysis revealed the preferential formation of compounds with secondary hydroxyl groups. The ratio of primary hydroxyl/secondary hydroxyl compounds appears to be insensitive to reaction temperature and slightly affected by solvent polarity and amine structure.
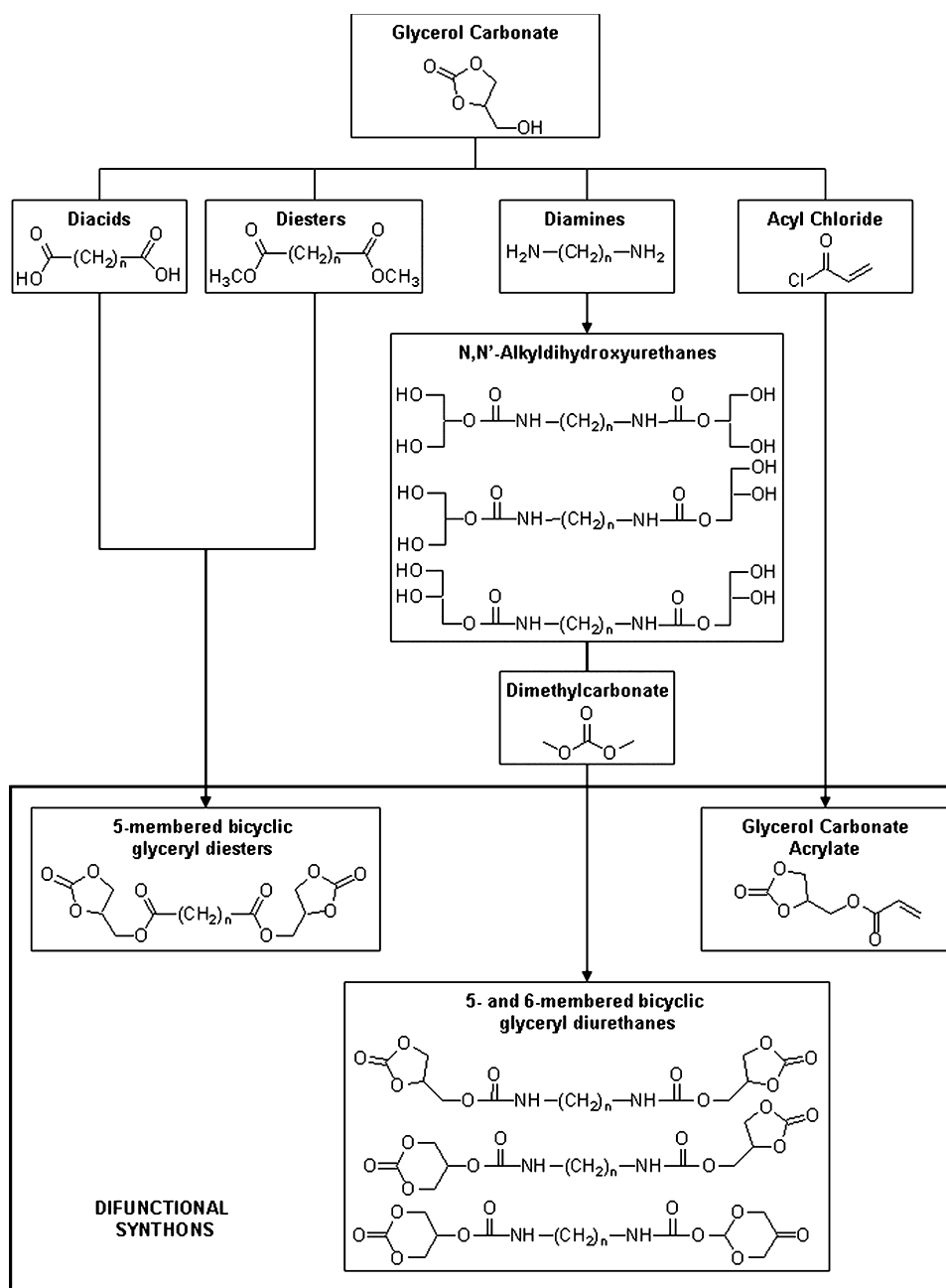
Figure 24. Difunctional synthons developed from glycerol carbonate for use in the synthesis of PHUs.[58,128,129]

dimethylformamide at room temperature, generating linear PHUs.[80] This product is almost colorless and brittle at low molecular weight. Mikheev et al.[81] and Rockiki et al.[82] reported similar PHU syntheses.

For five-membered bicyclic carbonates, most of the PHUs obtained have secondary hydroxyl groups. Molecular weight can be increased by increasing reaction time.[83] The use of a catalyst to activate the carbonyl group leads to greater carbonate consumption and the production of polymers with a higher molecular weight.[83] The rheology of the reaction system affects the kinetics and thermodynamics of the reaction, but it also has an impact on the physicochemical characteristics of the PHUs synthesized.[84] Moreover, of the use of higher

temperatures is associated with higher carbonate conversion rates.[85]

These stoichiometric reactions are mostly carried out in a solvent medium (DMSO, DMAc, and DMF) at 50 to 100 °C, for about 24 h. The reactant concentrations are from 0.5 to 1 mol/liter in the synthesis solvent. Purification is achieved by precipitating the polymer in ethylic ether, washing it with water and then drying it under vacuum.[67,76] The synthesis of PHUs in water was described by Ochiai et al.[85] The nucleophilic addition of a butylamine residue to hydrophobic bicyclic carbonates results in the effective production of hydroxyurethanes, accompanied by the hydrolysis of bicyclic carbonates to generate diols. A hydroxyurethane/diol ratio of 84/16 was
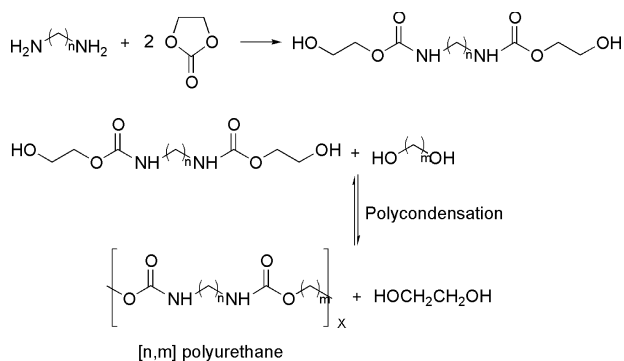
Figure 25. Two-step preparation of linear PUs without isocyanate[74].

reported. The use of less hydrophobic bicyclic carbonates leads to the total hydrolysis of carbonate rings to diols.

As for monocyclic carbonates, five-membered bicyclic carbonates are less reactive than six-membered bicyclic carbonates.[86] Molecular weights range from 10000 to 30000 g·mol^{-1} and depend on the initial composition of the cyclic carbonate:[67,77] Mn C_5 < Mn C_6 < MnC_7, although synthesis from five- and six-membered bicyclic carbonate couplers does not increase the molecular weight of PHUs.[87]

These PHUs are characterized by high degradation temperatures, of 177[71] to 388 °C,[57] depending on the amine and the monomer.[60] They trigger hydrophilic behavior, because they are characterized by a high density of hydroxyl groups and urethanes. They are also characterized by chemical stability to hydrolysis. The formation of strong hydrogen bonds between hydroxyl units and urethane bonds decreases susceptibility to water absorption and increases the stability of PHUs.[85]

Examples of Applications. Applications for non-isocyanate PUs have recently been reviewed.[28,33,92] PHUs have better porosity, water absorption, thermal and chemical resistance than PUs, which have been subject to long-term academic and applied studies.[93]

PHUs prepared from copolymers of 3-(2-vinyloxyethoxy)-1,2-propylene carbonate, and *N*-phenylmaleimide have low volatile organic compound levels.[94] Coatings based on such structures display a good combination of durability and hardness.[95] Moreover, the chemical resistance and permeability of PHUs without isocyanate coatings are 1.5 to 2.5 times better than those of conventional PU coatings. Birukov et al.[96] have

synthesized a liquid hydroxylamine oligomer. The weight gain as achieved may be as little as 1—3% after seven days in water, at room temperature.

Unlike conventional UV-curable coatings, the formulations developed by Figovski et al.[97] provide greater elasticity, while maintaining the basic strength characteristics. The use of these compounds improves the adhesion of the cured composition to concrete, making it possible to decrease the number of coating layers to two, with the application of a layer up to 0.8 mm at a rate of polymerization allowing the use of standard curing technology and standard equipment.

The basic composition and a technique for mixing and foaming for insulating foam applied by spraying were developed by Birukov et al.,[98] based on the use of synthetic raw materials. This led to approval for a standardized procedure for obtaining polyurethane foams.

PHUs may also find new applications in the preparation of high-performance sealants. An example is provided by the use of acrylic-modified PHUs in indoor or outdoor sealing applications. The sealant can be cured by ultraviolet radiation.[99]

Finally, PHUs have applications in electrical equipment.[100]

4.3. Focus on Polyhydroxyurethanes from Vegetable Oils.
The use of vegetable oils and their derivatives as chemical platforms for the synthesis of polymers presents multiple advantages, including inherent biodegradability, low (or no) toxicity and low cost. The emergence of polymers from renewable resources has led naturally to the synthesis of PHUs.

Synthesis of PHUs from Triglyceride Derivatives. In the past few years, modern synthetic methods have been applied extensively to fatty compounds for selective functionalization of the alkyl chain, yielding a large number of novel molecules with potentially interesting properties.[101,102] One of the most interesting derivatives of unsaturated fatty compounds is epoxidized triglyceride oils (ETO), including epoxidized soybean oil (ESBO) in particular. ESBO has been used principally as a plasticizer for polyvinyl chloride, chlorinated rubber and polyvinyl emulsions, to improve their stability and flexibility.[103] The products of reactions between ETO and carbon dioxide are of particular interest, because they can be used for the synthesis of PHUs without isocyanate.

Reaction of ESBO with carbon dioxide, at atmospheric pressure, with the use of tetrabutylammonium bromide as a catalyst, resulted in conversion rates of 94% for carbonated soybean oil (CSBO) after 70 h.[104] The use of a combination of
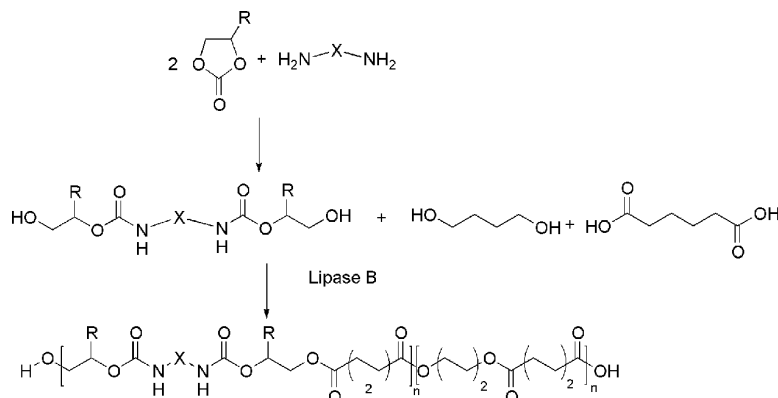

Figure 26. Enzymatic synthesis of polyesterurethane (PEU) in the presence of lipase, by urethane diol polyesterification with various diacid/diester couplers.[130]
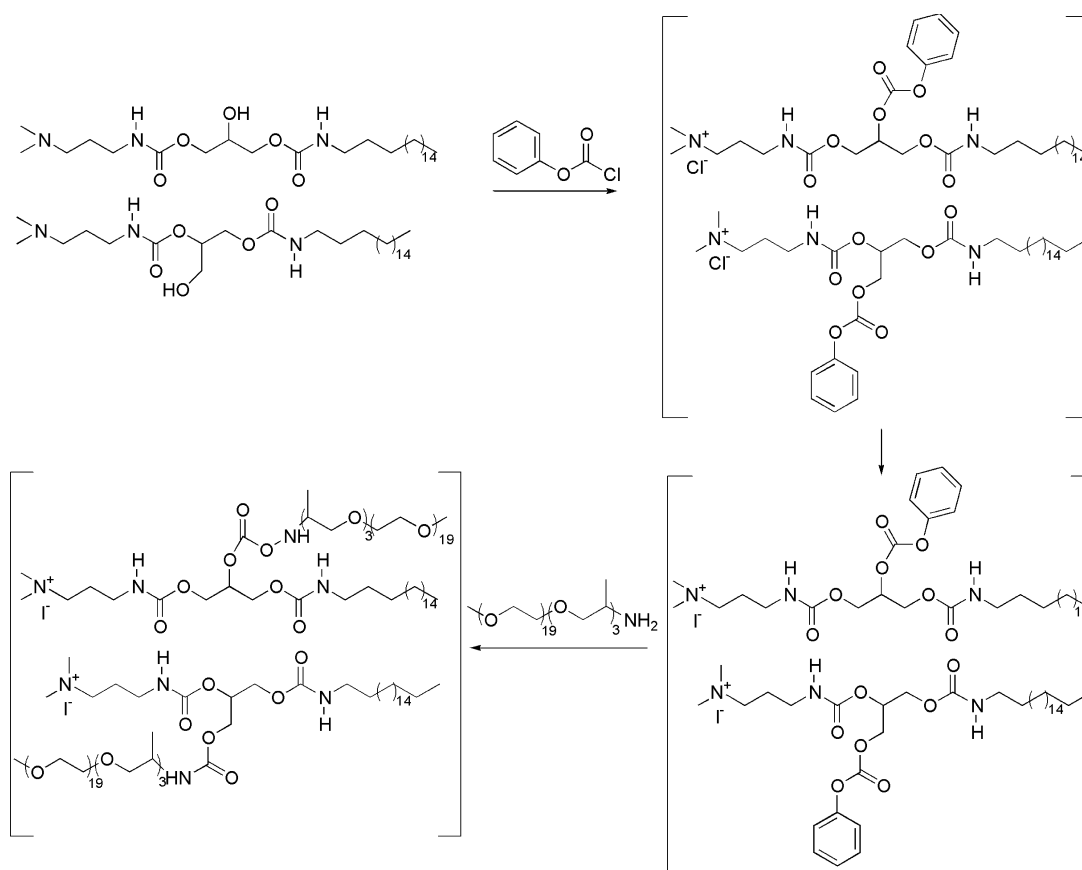
Figure 27. Preparation of linear PHUs without isocyanate, with amphiphilic heads, C₃A18-QI-J1000 via C₃A18-QI-Ph.[87]
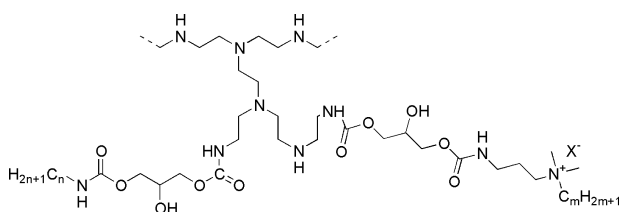

Figure 28. Hydrophobic polycations synthesized from functionalized ethylene carbonate and PEI[124]

potassium iodide/crown ether as a catalyst, at 130 °C and 6 MPa pressure, has been reported to lead to 100% conversion.[105] Doll et al.[106] reduced the reaction time by one-third, using supercritical carbon dioxide, leading to 100% conversion of ESBO into CSBO after 40 h. Li et al.[107] prepared CSBO with a novel composite catalyst consisting of SnCl₄·5H₂O and tetrabutylammonium bromide (TBABr). They investigated the effects of catalyst formulation and various reaction conditions on the reaction. The activity of these catalysts could be ranked in the following order: SnCl₄·5H₂O/TBABr (2:1) < SnCl₄·5H₂O/TBABr (1.5:1.5) < SnCl₄·5H₂O/TBABr (1:5) < SnCl₄·5H₂O/TBABr (1:2) < SnCl₄·5H₂O/TBABr (1:4) < SnCl₄·5H₂O/TBABr (1:3). In particular, ESBO conversion rates of 89.2% were achieved at a ratio of 1:3. ESBO conversion rates were found to be better with this composite catalyst under mild conditions.

PHUs have been prepared by a non-isocyanate route by reacting CSBO with various diamines.[108] The effect of amine structure and carbonate-to-amine ratio on polyurethane structure and mechanical, physical and swelling properties has been studied. The reactants 1,2-ethylenediamine, 1,4-butylene-diamine, and 1,6-hexamethylenediamine were used with carbonate-to-amine ratios of 1:0.5, 1:1, and 1:2. In addition to generating urethane, the amine group reacted with ester groups to form amides. All amines produced elastomeric PUs with glass transition temperatures between 0 and 40 °C and hardness values of between 40 and 90 Shore A.

Bahr et al.[109] recently investigated soy and linseed oil based PHUs prepared by curing carbonated soybean (CSBO) and linseed (CLSO) oils with various diamines. The reaction was catalyzed with tetrabutylammonium bromide (TBAB) and silica-supported 4-pyrrolidinopyridinium iodide. The seed oil carbonates had various carbonate contents (20.2 to 26.8 wt %) and were cured with 1,2-ethane diamine (EDA), 1,4-butane diamine (BDA) and isophorone diamine (IPDA), for investigations of the thermal and mechanical properties of the resulting non-isocyanate PUs (NIPU) (Figure 17). Use of the cycloaliphatic curing agent IPDA for the curing of CLSO increased the glass transition temperature from 20 to 60 °C and improved stiffness. Most conventional CSBO-based systems are rather soft and flexible, but this approach indicates that NIPUs can be developed to meet the demands of engineering applications requiring higher dimensional stability and stiffness.

Foltran et al.[110] studied supercritical carbon dioxide/vegetable-based epoxidized oil mixtures and the fixation of CO₂ catalyzed by ionic liquids. The cyclic carbonates obtained were considered to be polyhydroxyurethane precursors.
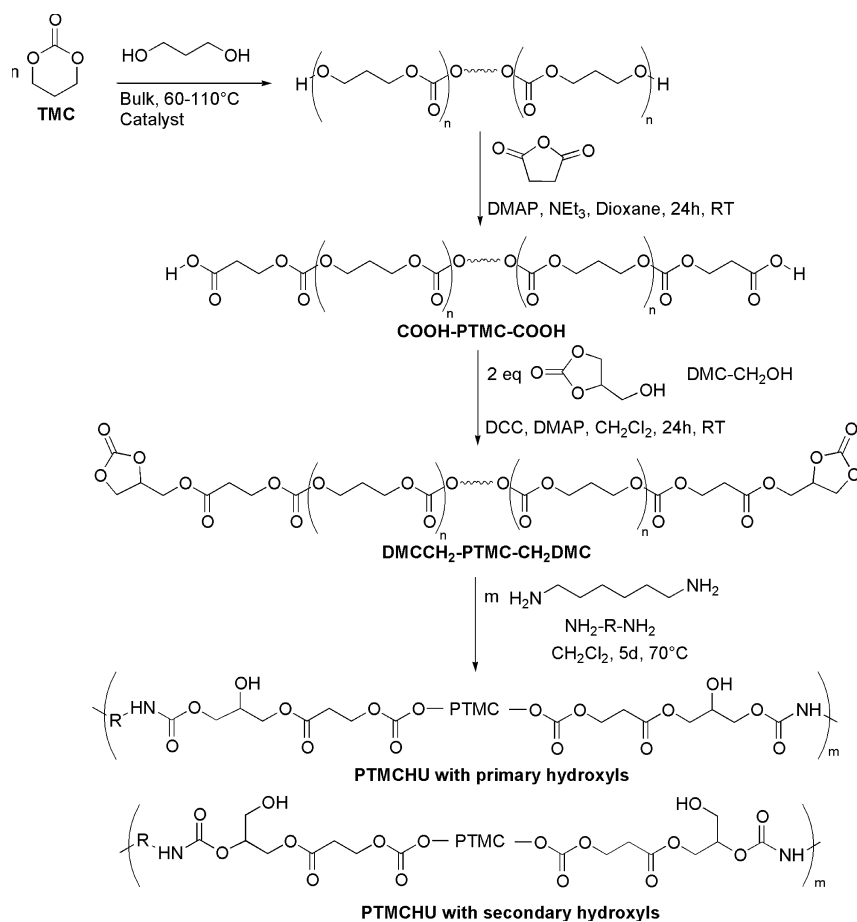
Figure 29. Functionalization of a diacid by glycerol carbonate to form poly(ester–urethane) or poly(ester–carbonate).[133]
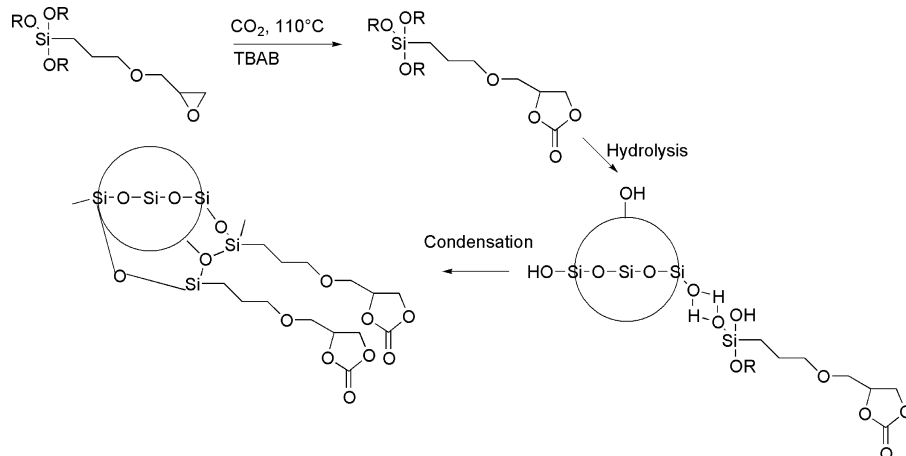
Figure 30. Synthesis of carbonated functional silica particles.[134]

Mahendran et al.[111] obtained a new biobased non-isocyanate urethane by reacting a cyclic carbonate synthesized from a modified linseed oil and an alkylated phenolic polyamine (phenalkamine) from cashew nut shell liquid.

Birukov et al.[112] proposed a new method for producing a hybrid polyhydroxyurethane network: (a) Reaction of epoxidized unsaturated fatty acid triglycerides with carbon dioxide in the presence of a catalyst to obtain carbonated-epoxidized

unsaturated fatty acid triglycerides, with the conversion of oxirane groups to 2-oxo-1,3-dioxolane groups (cyclic carbonate groups) for these carbonated epoxidized unsaturated fatty acid triglycerides at rates of 35% to 85%; (b) mixing and reaction of the carbonated-epoxidized unsaturated fatty acid triglycerides with a compound with an amine group including at least one primary amine, at or close to a balanced stoichiometry; (c) mixing and reaction of the product of part b with a compound

having an amino group including at least two primary amines, carried out in the presence of an excess of a compound with amine groups; (d) mixing of the product of part c with a compound having amino-reactive groups and selected from the group comprising: (i) a compound with epoxy groups and (ii) a mixture of the compound with epoxy groups and carbonated-epoxidized unsaturated fatty acid triglycerides, with the ratio of the sum of amino-reactive groups to the sum of amine groups stoichiometric or within the normal range of composition at ambient temperature.

In 2013, Javni et al.[113] prepared PUs via a non-isocyanate route, by reacting carbonated soybean oil (CSBO) with aromatic and cycloaliphatic diamines. Non-isocyanate PUs prepared from CSBO and aliphatic diamines have relatively low tensile strength and one possible ways to increase their strength and rigidity is to use diamines with rigid aromatic or cyclic structures. All amines produce elastomeric PUs with glass transitions between −6 and +26 °C. T_g is controlled principally by the amine-to-cyclic carbonate ratio, and, to a lesser extent, by amine structure. Tensile strength and hardness are greater than those of aliphatic diamine-based PUs.

Synthesis of PHUs from Glycerol Derivatives. The use of renewable feedstocks is essential for the sustainable development of society. Much attention has been devoted to the use of green catalytic processes for converting biorenewable feedstock into commodity chemicals and clean fuels. Glycerol (propan-1,2,3-triol) is widely available and is traditionally obtained as a byproduct of vegetable oils in different processes: soap manufacture, fatty acid production, fatty ester production. Glycerol can be obtained from biomass (including rapeseed and sunflower oil) via hydrolysis or the methanolysis of triglycerides. The reactions mediating the direct transformation of vegetable oils and animal fats into methyl esters and glycerol have been known for over a century. However, it is only recently, after more than 10 years of research and development, that the transesterification of triglycerides from rapeseed, soybean and sunflower oils has risen to significance in the manufacture of high-quality biodiesel fuel. As a result, several chemical[114] and enzymatic[115] processes for producing fatty acid methyl esters from vegetable oil are now carried out commercially. Glycerol is normally generated at the rate of one mole of glycerol for every three moles of methyl esters synthesized, corresponding to about 10% of the total product by weight.[114]

Biodiesel has proved valuable as a fuel for diesel engines,[115,116] being both renewable and clean[115,116] although its net energy balance remains a matter of debate.[117] The HBI office in Kuala-Lampur, Malaysia, has reported the impact of oleochemical activities on the production of biodiesel from 1992 to 2010 (Table 5).

The availability of glycerol opens up opportunities for new applications in the chemical industry and new possibilities for several derivatives, such as epichloryhdrin, propylene glycol and glycerol carbonate.[118,119] In response to Department of Energy incitement in the US, glycerol and glycerol carbonate are now considered among the top 30 chemicals for the chemical industry, in terms of the added value they provide.[120]

As a raw material, glycerol carbonate may be considered as a monomer for the synthesis of new polymers, such as innovative PHUs.

In 1990, Brosse et al.[121] studied the synthesis of PHUs from glycerol carbonate acrylate and methacrylate. The cyclic carbonate reactant is an oligomer or a mixture of oligomers

comprising several terminal cyclic carbonate groups. Cyclic carbonate oligomers can be obtained by polymerizing unsaturated cyclic carbonate monomers, by heating-induced radical copolymerization with methoxylates, alkyl acrylate or styrene, or by the UV photopolymerization of cyclic carbonate monomers (Figure 18). When subjected to radical polymerization, vinylene carbonate forms a colorless solid polymer, which yields a water-soluble product containing −[CH-(OH)]$_n$− repeating units on hydrolysis. The copolymerization of vinylene carbonate with styrene[122] yields poly(styrene-*co*-vinylene glycol) after hydrolysis, which can be cleaved with periodic acid to yield polystyrene terminating in aldehyde groups.[122,123] These cyclic carbonates can then be reacted with diamines to form PHU networks.

In 2004, Ubaghs et al.[89] reported the synthesis of PHUs from phenoxycarbonyloxymethyl ethylene carbonate (Figure 19). Phenoxycarbonyloxymethyl ethylene carbonate was synthesized from glycerol carbonate and phenyl chloroformate. PHUs with dangling hydroxyl groups were obtained from polycondensation reactions of this AA* monomer with diamines. These polymers contained both primary and secondary hydroxyl groups. The polymers obtained were amorphous, with glass transition temperatures decreasing with increasing numbers of methylene groups between the urethane groups. The molecules obtained had molecular weights of 6400 to 8700 g·mol^{-1}.

In 2008, Pasquier et al.[124] synthesized hyperbranched PHU networks from glycerol carbonate (Figure 20). They synthesized cyclic carbonates from phenyl chloroformiate and glycerol carbonate and reacted them with polyethylene imine (PEI) with primary amine groups.

In 2010, Rhodia[125] patented the synthesis of PHUs from glycerol (Figure 21), dimethyl carbonate and isophorone diamine, in the presence of a catalyst, such as phosphazene. The reaction was carried out overnight, at 100 °C. The molecular weight of the PHUs was not specified and they were used for coating applications. This patent describes the production of isocyanate-free PHUs as organic, aqueous or hydro-organic formulations.

In 2011, Benyahya et al.[126] reported the synthesis of PHUs from 4-[(prop-2-en-1-yloxy)methyl]-1,3-dioxolan-2-one (AGC), a glycerol carbonate derivative (Figure 22). The synthesis of 4-[(prop-2-en-1-yloxy)methyl]-1,3-dioxolan-2-one (AGC) was performed by Williamson ether synthesis, from glycerol carbonate. Bicyclic carbonates were synthesized by the UV thiol-ene coupling of allyl-cyclic carbonate with a 2,20-oxidiethanethiol. This photochemical thiolene reaction was carried out under air, with neither solvent nor photoinitiator. The bicyclic carbonates synthesized were used, without purification, for the synthesis of PHUs by stepwise polyaddition with 1,10-diaminodecane. These polymers had glass transition temperatures of 14 to 31 °C, molecular weights of 7000 g mol^{-1} to 9000 g mol^{-1} and degradation temperatures for 5% weight loss (T_d 5%) between 227 and 250 °C.

In 2013, Fleischer et al.[127] studied catalytic carbon dioxide fixation by the carbonation of glycerol glycidyl ether and the curing of the resulting glycerol-based cyclic carbonate (GGC) with hexamethylenediamine and citric acid amino amides (Figure 23). The addition of 1,4-diazabicyclo[2.2.2]octan as a catalyst makes it possible to synthesize the polymer at room temperature. The resulting non-isocyanate PUs are flexible but have poor mechanical resistance. The blending of GGC with cyclic carbonates of higher functionality (carbonated pentaerythritol and trimethylolpropane glycidyl ethers) results in

positive synergism with greater dimensional stability and stiffness.

Difunctional glycerol carbonate can be transformed into new difunctional cyclic carbonate synthons.[128,129] These sequences of chemical transformations generate three families of cyclic carbonate building blocks (Figure 24), with new double functionalities rendering them suitable for PHU synthesis by polyamine addition. The five-membered bicyclic glyceryl carbonate diesters are second-generation chemicals produced from glycerol by esterification or transesterification processes involving the addition of fatty diacids or diesters. As both reactants can be obtained from plant resources, the chemical footprint of such processes is low. The PHUs synthesized by polycondensation with diamines have both ester and hydroxyurethane functional groups. The final PHUs consist principally of secondary hydroxyl groups (primary/secondary ratio of 30/70). The five- and/or six-membered bicyclic glyceryl carbonate diurethanes are synthesized by adding diamines and dimethylcarbonate to glycerol carbonate.[58] Higher-molecular weight PHUs with added structural urethane units are thus obtained. The primary/secondary ratio is displaced toward secondary hydroxyl groups (60/40 ratio). Such PHUs would be more reactive for further modifications. Finally, glycerol carbonate acrylate (GCA), characterized by a five-membered glyceryl cyclic carbonate and an acrylate functional group has been studied. The electrophilic character of the cyclic carbonate, coupled with electron delocalization on the acrylate carbon atoms, leads to the production of innovative aminoester PHUs.

The reaction schemes for the synthesis of polycyclic carbonates follow strategies based on the transformation of raw materials into multifunctional couplers. A coupler can be defined as a molecule with two or more functional groups that can react selectively, such that different functional groups are combined within a single molecule.[87]

As raw materials, glycerol and glycerol carbonate are thus ideal biobased candidates, as most of the desired five- and six-membered cyclic carbonates mimic the glycerilic skeleton.

4.4. Functional Hydroxyurethanes and Polyhydroxyurethanes.

The presence of hydroxyl groups in the PHU structure transforms hydroxyurethanes and polyhydroxyurethanes into synthons or reactive polymers. The functionalization or chemical modification of hydroxyl groups has been studied as a means of improving the properties of PHUs and/or increasing their molecular weights.

Synthesis of Polyurethanes from Dihydroxyurethanes. Rokicki et al.[74,82] synthesized PUs by the polycondensation of dihydroxyurethanes with polyols. The first step in this process consisted of the diaminolysis of ethylene carbonate to generate a dihydroxyurethane that reacts with polyol by polycondensation at 150 °C and in the presence of a tin catalyst ($Bu_2Sn(OCH_3)_2$ or Bu_2SnO) to form a linear polyurethane with a mean molecular weight of 5500 g·mol^{-1} (Figure 25).

Similarly, Matsumara et al.[130] used an enzymatic process to synthesize linear polyester urethanes in the presence of lipase B (Figure 26). These new polymers have potential applications as biomaterials and bioplastics, thanks to their mechanical properties, which resemble those of conventional PUs. They can be recycled with ease and are degradable by microorganisms. Molecular weights of 6800 g·mol^{-1} and 31000 g·mol^{-1} have been obtained.

Functionalization of PHU Hydroxyl Groups. Ochiai et al.[131] modified PHUs by the acetylation, benzoylation or silylation of dangling hydroxyl groups. The introduction of ester or silyl groups decreases the hydrophilicity of the polymers displayed in Figure 16. These authors tried to increase the molecular weight of PHUs by adding polyisocyanates. Like procedures for producing PU, this approach has the drawback of requiring the use of isocyanate or the addition of initiators of radical polymerization. With the use of initiators, PHUs with high molecular weights were obtained by long-term or expensive synthesis.

He et al.[71,87,132] studied functionalization of the primary or secondary hydroxyl groups of PHUs with phenyl chloroformiate (Figure 27). This method uses a reactant with a good leaving group. It is therefore possible to displace the phenyl group and replace it with polyfunctional amine groups by transamidation. By increasing the density of urethane units on PHUs, the molecular weight can be increased to 20 000 g·mol^{-1} and the physicochemical properties of these polymers can be improved. He et al. also used the reactivity of hydroxyl groups to achieve a ring-opening step-polymerization by reacting hydroxyurethanes with ε-caprolactone at 130 °C in the presence of tin catalyst. The polycaprolactone obtained had an amphiphilic head. These authors also prepared a radical polymerization initiator by reacting the hydroxyl groups of dihydroxyurethane with 2-bromo-2-methylpropionyl bromide. This initiator can be used for copolymerization with methyl methacrylate.

Some Examples of Functional Di- and Polyhydroxyurethanes. Pasquier et al.[124] synthesized hyperbranched PHU networks from glycerol carbonate (Figure 28). They synthesized cyclic carbonates from phenyl chloroformiate and glycerol carbonate and reacted them with polyethylene imine (PEI) with primary amine groups. These hyperbranched networks have properties rendering them potentially interesting as antimicrobial agents.

In 2011, Guillaume et al.[133] synthesized a poly(carbonate−urethane) and a poly(ester−urethane) from glycerol carbonate (Figure 29). They carried out a transesterification reaction with polytrimethylene carbonate diacid (HOOC−PTMC−COOH) to generate bicyclic carbonates (DMCCH$_2$−PTMC−CH$_2$DMC). The polyaddition reaction with bicyclic carbonates (DMCCH$_2$−PTMC−CH$_2$DMC) and hexamethylene diamine carried out at 70 °C for five days led to the formation of poly(ester-urethane) or poly(carbonate-urethane) with a molecular weight of 68 100 g·mol^{-1}. This strategy improves the physical properties of linear PHUs, but also increases their molecular weight.

A final example of PHUs functionalization is provided by silane-modified PHUs. It is possible to use aminosilanes and cyclic carbonates for the preparation of thermostable compounds. Multiaminosilane oligomers can be prepared by the hydrolysis of aminopropyltriethoxysilane (Figure 30). The amino groups of the oligomer can react with cyclic carbonate to form silylated PHUs. Yokota et al.[134] reported the synthesis of poly(arylenesiloxane) by reacting bisphenol A oligocyclocarbonate and polycarbonate with cyclosiloxanes. The −Si(OR)$_n$ groups can react further with the hydroxyl groups of many kinds of matrices, resulting in good adhesion and better mechanical properties.

Coury et al.[135] described a method for preparing PHUs with polydimethylsiloxane incorporated in the chain. This method involved reacting polydimethylsiloxane with terminal amine

groups with cyclic carbonates to produce urethane diols. These urethane diols react with one or more diisocyanates or polyisocyanates to form PUs.

Urethane diols containing silica atoms have also been synthesized, by Webster et al.,[70] by a reaction between siloxane oligomers containing amine functional groups with poly(ε-caprolactone).

Cyclic carbonate oligomers modified by both acrylic molecules and siloxane have been reported for the development of a high-level ultraviolet-stable coating that is curable, at room temperature, within 24 h.[93]

5. THE FUTURE OF BIOBASED POLYHYDROXYURETHANES

Since the 1940s and 1950s, the use of PUs for diverse applications has greatly increased. These molecules are easily obtained for use as foams, elastomers and adhesives, by the reaction between polyols and isocyanates. With the depletion of petrochemical resources, the replacement of classical petro-chemical reactants with biobased molecules is of increasing importance. For polyester polyols, the substitution strategy, based on several chemical routes, has led to the production of NOPs. Epoxidation followed by the opening of the oxirane ring is used to generate NOPs, even commercially. With a biobased material content of 60−70%, these PUs could replace petrobased polyester polyols in the most common PU applications. Efforts to achieve a 100% biobased content currently involve research into the development of biobased isocyanates and vegetable oil-based AB-type monomers, for the production of lines of PUs with specific properties.

The substitution strategy does not overcome the need to use toxic isocyanates. The synthesis of PHUs by the stepwise polyaddition of bicyclic carbonates to polyamines constitutes a new reaction scheme that could ensure the future of these polymers. The carbonation of epoxidized vegetable oils provides secondary hydroxylated PHUs. There are several advantages to the development of a range of new cyclic carbonates from glycerol and glycerol carbonate. No toxic or hazardous reactants are involved and this approach uses glycerol as the feedstock. As a first-generation derivative, glycerol carbonate is a highly valuable reactant that can not only store CO_2 but also uses CO_2 as a starting material for the polymerization process. A new network of five- and six-membered cyclic glycerylic carbonates can now be synthesized from glycerol carbonate. These molecules further react with polyamines to produce PHUs with a high hydroxyl content. The presence of both secondary and primary hydroxyls favors additional functionalization. Depending on the glyceryl cyclic carbonate used, the variability of the chemical structure of the PHUs can be controlled. A densification of urethane, ester, or aminoester units could also be incorporated into the PHUs. This variability could potentially broaden the range of applications.

Economic factors are always a major large hurdle when trying to market biobased materials. PHUs could therefore be considered as much more than mere substitutes for traditional PUs. They represent a new family of polymers that will find increasing numbers of applications in various industries, provided that their performance, in terms of properties, is demonstrated. We can promote the major benefits of synthesizing PHUs from vegetable oils and glycerol, by focusing on the non-isocyanate reaction strategy, which makes use of innocuous substrates and products, and green, safe chemical reaction schemes, and creates innovative and possibly fully biobased PHUs.

Academic and industrial efforts should be to develop the synthesis of low-cost, biobased polyamines. For natural amines or polyamines, it might be possible to use proteins, peptides or amino acids (lysine) to generate bacteriostatic and optically active PHUs. The use of fatty diamines and polyamines that are already commercially available could also be considered, as could the use of chitosan as a polysaccharide material. However, the idea of developing a tailor-made synthesis system for polyamines seems remains promising, as shown by its development for research on polycyclic carbonates.

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Notes
The authors declare no competing financial interest.

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