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Hybrid Polyhydroxyurethanes: how to overcome limitations and reach cutting edge properties?

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† In memory of Prof Jean-Pierre Pascault

Abbreviations

AFM: Atomic Force Microscopy

AIBN: Azobisisobutyronitrile

BADGE: Bisphenol-A Diglycidyl Ether

CC: Cyclic Carbonate

CSBO: Carbonated Soybean Oil

DBTDL: Dibutyltin Dilaurate

DETA: Diethylenetriamine

DMA: Dynamic Mechanical Analysis

DMF: Dimethylformamide

DSC: Differential Scanning Calorimetry

DYTEKA: 2-methylpentane-1,5-diamine

EDA: Ethylenediamine

FTIR: Fourier Transform Infrared Spectroscopy

GCMA: Glycidylmethacrylate

HMDA: 1,6-hexamethylenediamine

H-NIPU: Hybrid Non-Isocyanate Polyurethane

HUM: Hydroxyurethane Modifier

IPDA: Isophoronediamine

IPDI: Isophorone Diisocyanate

MDI: Methylene Diphenyl Diisocyanate

MIBK: Methylisobutylcetone

MWCNT: Multi-walled Carbon Nanotube

NIPU: Non-Isocyanate Polyurethane

PDMS: Polydimethylsiloxane
PHU: Polyhydroxyurethane
POSS: Polyhedral Oligomeric Silsesquioxanes
PPG: Polypropylene Glycol
PS: Polystyrene
PU: Polyurethane
SEM: Scanning Electron Microscopy
TBD: Triazabicyclodecene
TDI: Toluene Diisocyanate
TEDA: Triethylenediamine
TEPA: Triethylenepentamine
TETA: Triethylenetetramine
TGA: Thermogravimetric Analysis
THF: Tetrahydrofuran

Abstract

The restrictions on isocyanate substances have encouraged researchers to find alternative methods for the synthesis of Polyurethanes (PUs). New pathways have been designed with focus on non-hazardous and eco-friendly substances. The reaction of cyclic carbonates and amines has appeared as the most promising substitute for the synthesis of Non-Isocyanate Polyurethanes (NIPUs). The obtained Polyhydroxyurethanes (PHUs) have been deeply studied these last decades to offer the best solutions in the substitution of isocyanates in PUs synthesis. Strong efforts have been paid to understand key parameters for the synthesis of PHUs and to design new architectures. However, some limitations in terms of kinetics, conversion and molar masses still remain and impede PHUs expansion. Therefore, this review aims to detail the recent progress that has been made on a new strategy, the hybrid PHUs. The characteristics of additional reactants such as a high reactivity, a low viscosity or the ability to reach higher conversions can be combined with the properties of PHUs in hybrid networks. Other functional groups such as acrylates, methacrylates, epoxies, alkenes or siloxanes give access to new designs and materials with higher performances. Hence, the different strategies to perform hybrid PHUs are discussed and detailed. The main strategies employed are the co-

polymerization in one-step, the synthesis of prepolymers with various architectures and the synthesis of organic/inorganic and composite PHUs. Furthermore, a short overview of reprocessable PHUs is given as another outlook for PHU development.

Keywords

Polyhydroxyurethane; Hybrid Polyhydroxyurethane; Cyclic carbonate; Acrylate; Epoxy; Siloxane; Prepolymer

I. Introduction

Since the development of PolyUrethanes (PUs) by Otto Bayer in 1937,[1] the interest for this class of polymer has grown continually. In 2016, they have reached the rank 6th in the worldwide polymer production with an average production of 16.9 million tons and a forecasted global demand of more than 21 million tons by 2021.[2,3] PUs are indeed very versatile polymers found in a broad range of applications such as foams, clothes, adhesives, paintings, packaging, elastomers or high performance materials.[4–9] The global polyurethane market is shared in volumes between flexible foams (31%), rigid foams (25%), molded foams (11%), adhesives and sealants (6%) and elastomers (6%). Nevertheless, the use of polyurethanes has raised several health and environment concerns in the three stages of their life cycle.[10,11] First, phosgene, a very toxic gas, is required for the synthesis of isocyanates. Second, the toxicity of isocyanates is increasingly suspected and several isocyanates are now seriously limited by regulations and authorities. Moreover, Methylene Diphenyl Diisocyanate (MDI) and Toluene Diisocyanate (TDI) are also classified as CMR (Carcinogenic, Mutagenic and Reprotoxic) by European Reach Regulation and Global Harmonized System.[12,13] Finally, the decomposition of PUs may induce the release of toxic substances such as HCN or aromatic amines. Therefore, new alternatives have emerged to avoid isocyanates in the synthesis of PUs which are called Non-Isocyanate Polyurethanes (NIPUs). Three pathways are described in the literature to obtain NIPUs: the AB-type azide condensation, the transurethane reaction and the aminolysis. The formation of alcohol by condensation, the high reaction temperatures required and the use of more toxic reagents for the AB-type azide condensation and the transurethane reaction have led to focus interest on the third route, the aminolysis. Hence, the most developed access routes to NIPUs involve the reaction of cyclic carbonates and amines to yield PolyHydroxyUrethanes (PHUs). The chemical name of cyclic carbonates is 1,3-dioxoran-2-one and they are generally noted CC. In addition to the use of less toxic substances, PHUs are also promising candidates to develop greener processes and renewable materials. Indeed, these researches tend to comply more and more with the requirements of Green Chemistry and the new routes to synthesize polymers should meet these new specifications. Hence, PHUs have been subject of numerous publications and gained increasing interest since the current and upcoming regulations on isocyanates. To summarize all these scientific advances, numerous reviews on PHUs and their state of the art were published. Several research groups published reviews on cyclic carbonates synthesis, aminolysis parameters and perspectives of PHUs development.[14–20] Other teams chose to focus on sustainable development with presentation

of biobased cyclic carbonates and amines as well as “green” routes for the PHUs synthesis.[21–23] Furthermore, the valorization of CO₂ has appeared as a promising way avoid release of CO₂ in atmosphere. Therefore, the conversion of CO₂ into valuable products is a major concern of sustainable development. As a renewable feedstock for polymer synthesis, several reviews presented CO₂ as a top value product in cyclic carbonate and PHUs synthesis.[24–28] To optimize the reaction conditions and to access to the desired properties, many researches have focused on the understanding of the key parameters of the aminolysis of cyclic carbonates. For example, the group of Endo deeply investigated the kinetic parameters of this reaction.[29–32] Thus, they compared the reactivity of cyclic carbonates with different ring size and studied the role of the cyclic carbonate substituents. Many studies also focused on the influence of the amine substituents.[33–35] With a new design, new properties have also emerged. The aminolysis of cyclic carbonates with amines affords urethane functions with an additional hydroxyl group, either primary or secondary. The high density of hydrogen bonds in PHUs makes them suitable for adhesive applications and tend to strongly improve their mechanical properties.[36–38] Despite the growing interest on PHUs development, several limitations slow however their expansion on an industrial scale. First, the kinetics of the aminolysis is quite low and PHUs are difficult to obtain in mild conditions.[39] Several studies nevertheless succeed to obtain PHUs in mild conditions but with specific approaches. Furthermore, the high density of hydrogen bonds and the presence of side-reactions limit the advancement of polymerization. Therefore, scientists struggled to obtain linear PHUs with high molar masses.[40,41] In order to circumvent these limitations other polymers are generally used in addition to PHUs. This strategy precisely consists in the synthesis of Hybrid Non-Isocyanate Polyurethanes (H-NIPUs) or hybrid PHUs. Hybrid PHUs aim to overcome PHUs limitations and to confer new properties coming from both systems. We propose to define the term hybrid in H-NIPUs as the polymerization, in one step or more, of two or more polymer systems. For hybrid PHUs, one polymer system is of polyhydroxyurethane type. This hybridation involves other polymerization mechanisms than the aminolysis, with the formation of covalent bonds. Therefore, three categories of hybrid PHUs may be defined. First, the co-polymerization in one-step of cyclic carbonates, amines and other amine-reactive monomers. Second, the synthesis of prepolymers with reactive groups; these reactive groups being either telechelic, dangling or in the main chain. The prepolymers are then polymerized in a last step. Finally, organic/inorganic hybrid PHUs and composites hybrid PHUs will be considered on the condition that fillers are fixed to the polymer network with covalent bonds. Three different approaches of polymerization are found among these strategies depending on the functional groups: either

cyclic carbonates, amines or other groups such as epoxies, acrylates or alkenes, Figure 1. Therefore, this present review aims to give an overview of the works carried out on hybrid PHUs which could answer to the search for improved PHUs, in terms of either polymerization conditions or new cutting edge properties. First, a short introduction to PHUs will be presented to highlight the main limitations in PHUs synthesis. In a second part, the scientific advances in hybrid PHUs synthesis will be described as solutions to overcome PHUs limitations. Finally, some perspectives and outlooks will be given with new designs and utilizations of PHUs.

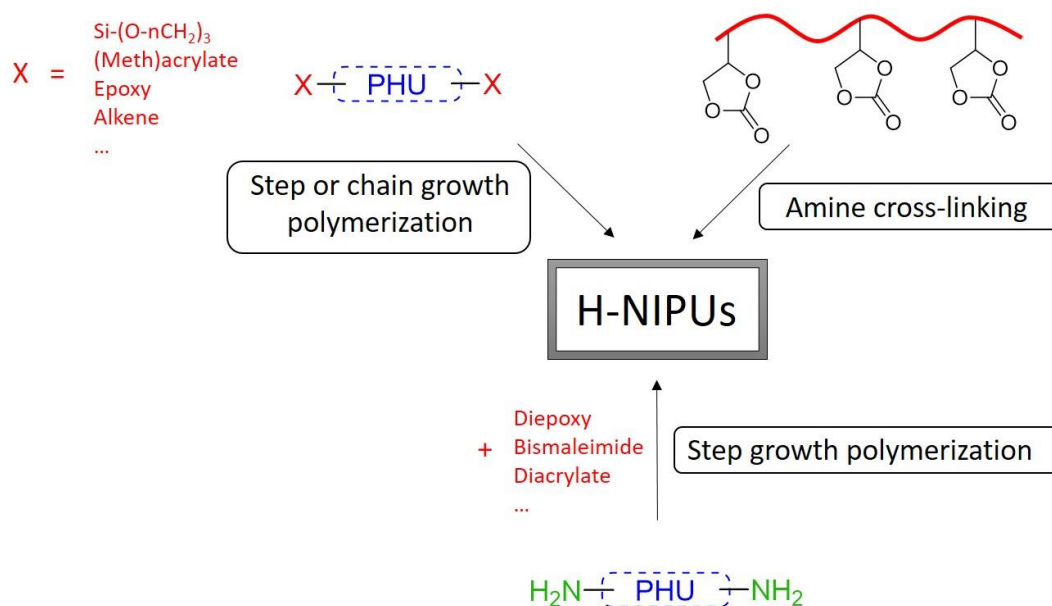


Figure 1. Different routes to hybrid non-isocyanate polyurethanes depending on the functional groups involved

II. Generalities about PHUs

In order to avoid the use of isocyanates in the synthesis of PUs, NIPUs have been developed. Few different synthetic routes of NIPUs have been described in the literature such as azide condensation, transurethanization and aminolysis. Among them, the aminolysis presents the most advantages and has been extensively described in recent decades. This reaction between Cyclic Carbonates (CC) and amines leads to the formation of urethane groups with an additional hydroxyl group, giving the name polyhydroxyurethanes.

1. Development of PHUs

The recent development of PHUs has been enhanced due to better understanding in the key points of this chemistry. First, the synthesis of cyclic carbonates from different reactants gives access to new compounds and industrial development of common cyclic carbonates. Numerous

reviews on PHUs dealt specially with the synthesis of new cyclic carbonate monomers.[14,15,22,23,25,26] Furthermore, the parameters affecting the ring opening of cyclic carbonates with amines have been fully described and analyzed in order to reach targeted properties. A large number of properties has thus been met, making PHUs promising candidates for the substitution of PUs. New properties and perspectives have also emerged.

The historical pathway for the synthesis of cyclic carbonates involves the reaction between diols and phosgene.[42,43] Despite the high reactivity and yields of this reaction, less toxic new alternatives have been progressively developed. The majority of these reactions involves diols and carbon dioxide and the most common route is the carbonation of epoxides with CO₂. The main routes to obtain cyclic carbonate monomers from diols, epoxies and alkenes are presented Figure 2.

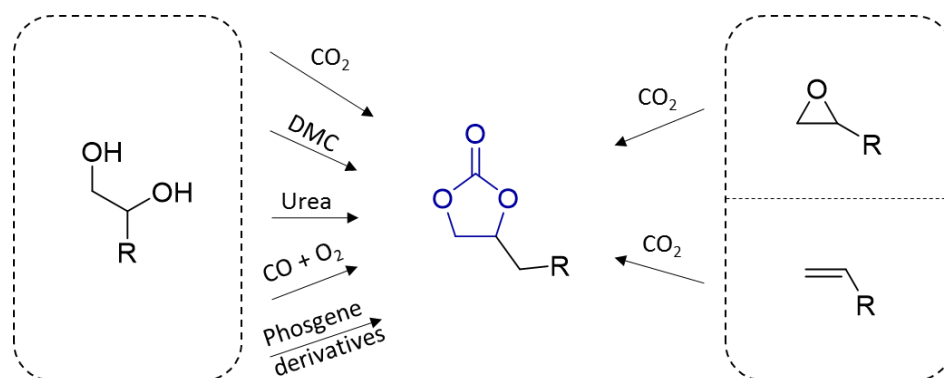


Figure 2. Main routes for the synthesis of cyclic carbonate monomers

The ring opening of cyclic carbonates with amines was fully described by Garipov *et al.* who proposed a three-step reaction mechanism.[44] Studies of activation energy in the aminolysis reaction and selectivity towards primary or secondary alcohols was performed by Steblyanko *et al.* in 2000.[45] The reaction of aminolysis between an amine and a cyclic carbonate is presented Figure 3. Since then, many scientists have studied and analyzed the main parameters affecting the aminolysis. The group of Endo particularly developed these studies.[29–32] The main parameters affecting the aminolysis reaction are summarized Figure 4.

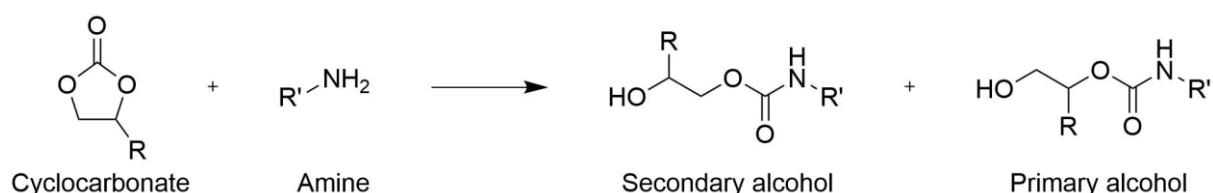


Figure 3. Aminolysis of cyclic carbonate

First, the structure of amines and cyclic carbonates compounds as well as their substituents play a key role in the kinetic and the advancement of this reaction. Cyclic carbonates with different

ring sizes have been synthesized from 5 to 8-members, and their reactivity was compared.[31,46–51] Through these studies a reactivity scale was established: 5CC < 6CC < 7CC < 8CC. Despite their lower reactivity, 5CC remain the most studied cyclic carbonates due to easier, less toxic and greener routes of synthesis.

The substituents close to the carbonate ring have also a great influence on its reactivity. Cornille *et al.* detailed a reactivity scale of different cyclic carbonates regarding to an amine (EDR-148) in order to propose the following scale: ethyl ester > acetate > trimethylhexanoate > benzoate ethyl ether > phenyl ether > butane.[39] Besides an influence on the reactivity, the substituents also affect the selectivity of the reaction.[32,52]

Novel syntheses of cyclic carbonates were largely reported in the literature. Nevertheless, to play on final properties of PHU materials, the structure of the amine remains crucial. Therefore, many studies described and compared the reactivity of different amines toward cyclic carbonate moieties since the substituted group close to the amine function is a key parameter for this reactivity.[33,35] Diakoumakos and Kotzev ranked different amines owing to their reactivity towards a cyclic carbonate by varying their nucleophilicity and their size.[34]. Primary amines were generally studied for this reaction but Camara *et al.* also demonstrated the reactivity of secondary amines.[53]

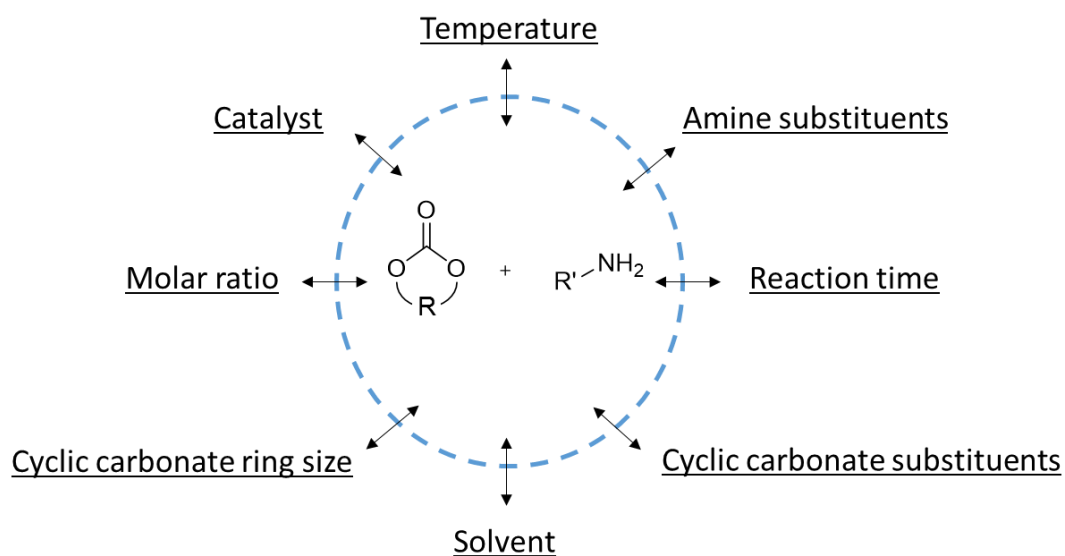


Figure 4. The main reaction parameters affecting the aminolysis

Different types of catalysts can be used to improve the reactivity of the aminolysis reaction. Three mechanisms are generally encountered: the increase of the electrophilicity of the cyclic carbonate (acid derivatives), the increase of the nucleophilicity of the amine (basic derivatives) or a direct attack on the cyclic carbonate to further react as a leaving group (Lewis bases). As

organic catalysts, pyridines, guanidines or other amino-compounds such as thioureas have demonstrated their efficiency.[34,54] The catalytic performances of acidic or basic salts, strong bases or organo-metallic catalysts were also demonstrated.[34,55,56] Most of the studies showed that TBD and thiourea eventually present the higher catalytic efficiency, Figure 5.[57] Despite strong improvements in terms of reactivity with the use of catalytic systems, conversion of cyclic carbonates remains low due to the hydrogen bond density in PHUs which tends to block the mobility of reactive species during polymerization.

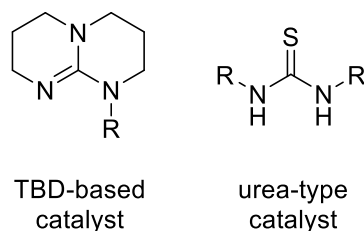


Figure 5. Main catalysts for the synthesis of PHUs

The use of solvents has also a great impact on reactivity and conversion of the aminolysis reaction. Proempers *et al.* compared the influence of different polar solvents (DMAc, diglyme) and obtained higher yields with less polar solvents (dioxane, THF).[58] Garipov *et al.* conducted a study on the aminolysis reaction in various solvents and determined that the use of protic solvents modifies the limiting step of the reaction from the nucleophilic attack to the deprotonation.[44] Cornille *et al.* completed this study with comparisons of kinetics and conversions in protic and aprotic solvents.[39] Hence, they demonstrated that protic solvents tend to strongly improve reactivity and conversion by increasing the positive charge on the carbonyl and also by limiting intramolecular hydrogen bonds between PHU chains.

The temperature is also an important parameter for PHUs curing. The temperature of polymerization improves the reaction rate. Indeed, the group of Endo demonstrated these trends with calculation of the reaction rate at 30 °C and 70 °C and the activation energy for 5CC, 6CC and 7CC.[29,31,50] These results are explained by the decrease of the viscosity with temperature. The hydrogen bonds that strongly limit the reactivity and the conversion are reduced with the temperature. However, side-reactions can occur above 100 °C.[19,20]

The ideal molar ratio between cyclic carbonates and amines was demonstrated to be 1:1 *ie* one carbonate function for one active hydrogen.[53,59–61] Indeed, primary amines have only one active hydrogen for the reaction with cyclic carbonates. Deviations in this stoichiometric ratio tend to increase side-reactions. Therefore, this ratio should be controlled as far as possible, since the molar masses of linear PHUs strongly decrease with side-reactions.

2. Limitations in PHUs synthesis

The parameters affecting PHUs chemistry have been fully studied and described in order to design PHUs as the best substitute for PUs. Nevertheless, despite their promising properties, numerous limitations in terms of kinetics, conversions and molar masses slow down industrial development of PHUs. To better understand these limitations, their origins and their impact on PHUs properties are presented below.

a) Secondary reactions

Different side-reactions have been reported in the literature for the aminolysis reaction: amine carbonation, in-situ CO_2 production, urea synthesis, amidation reaction or oxazolidinone synthesis, Figure 6.

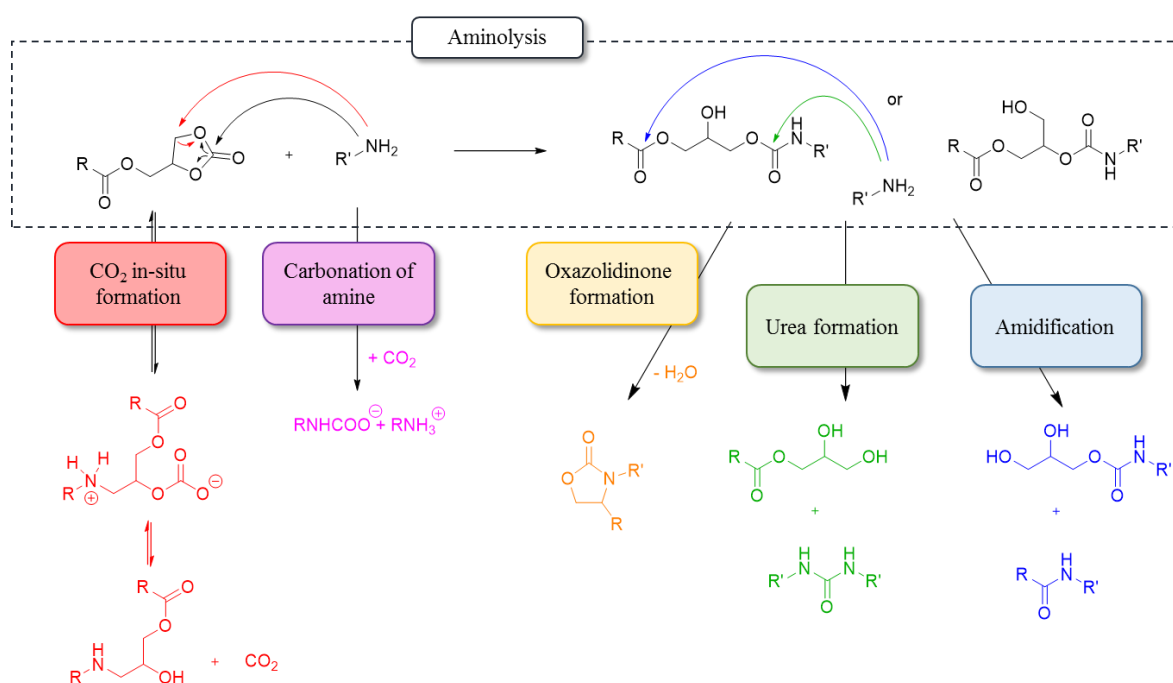


Figure 6. Main side-reactions between cyclic carbonates and amines

These side-reactions could involve additional moieties from external sources, reactants, products or internal reorganization as shown in Figure 6. First, the nucleophilic attack of amine groups may occur onto the α carbon of the carbonyl to form CO_2 in-situ.[62,63] The presence of CO_2 in air or from other reactions may induce amine carbonation and formation of carbonate anions and ammonium salts.[64,65] The formed hydroxyurethane can also produce oxazolidinone by rearrangement and dehydration. This reaction was first reported by Clements[63] and then presented as a side-reaction in PHU synthesis by Besse *et al.*[41] The urea formation by transurethanization and amidation is induced by the nucleophilic attack of

amines on formed carbamates or esters. The group of Sardon showed that the amount of catalyst such as TBD tends to encourage the formation of urea.[66] The transurethanization reaction was also reported in several publications.[41,67,68] Furthermore, the presence of ester groups could lead to the formation of amide groups. Indeed, amines may react on the carbonyl of ester groups instead of the one of carbamates.[41,69] Boyer *et al.* as well as Doley *et al.* showed the influence of the amine used in the formation of amide groups.[70,71]. Finally, the formation of amide groups was strongly encouraged with the use of an excess of amine.[61]

These reactions generally occur above 100 °C and could be promoted with the use of catalysts. All these reactions may cause deviation in the stoichiometric ratio and should be therefore controlled to access desired properties.

b) Hydrogen bonds

In contrast to PUs, PHUs have an additional hydroxyl group close to each carbamate group. This hydroxyl group strongly increases the density of hydrogen bonds by inter- or intramolecular interactions, Figure 7. Despite strong improvements in terms of mechanical and thermal properties, hydrogen bonds are also responsible of limitations during the PHU polymerization.[39,72,73] Leitsch *et al.* highlighted the influence of hydrogen bonds in nano-phase separated PHUs. They succeeded to tune mechanical properties while controlling the nano-phase separation with different soft segments.[74] Blain *et al.* detailed the high importance of hydrogen bonds in PHUs and their negative action towards conversion and hence molar masses.[40] Through DSC analyses supported by NMR studies they revealed the presence of a second enthalpy of reaction caused by hydrogen bonds. These bonds decrease the mobility of species and thus limit the conversion.

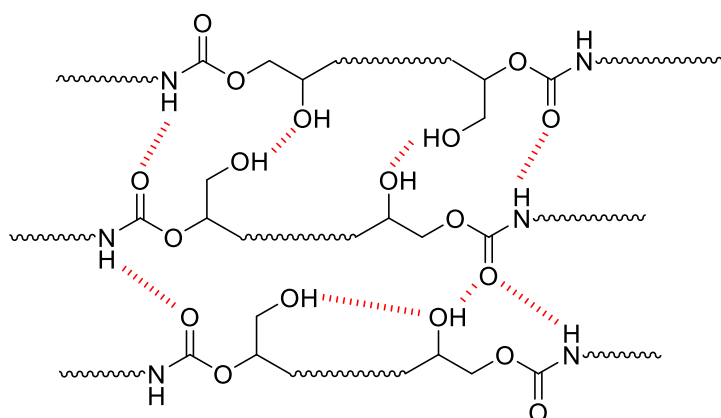


Figure 7. Hydrogen bonds between PHU chains

c) Impact of limitations on PHUs properties

The characteristics and parameters of the aminolysis present some limitations for the optimization of PHUs properties. The low reactivity, the low conversions of the aminolysis as well as the side-reactions and the high density of hydrogen bonds are drawbacks in PHU synthesis. As detailed earlier, the reactivity of the aminolysis is low and PHUs need long-time curing and temperature generally around 100 °C. Blain *et al.* performed DSC studies to compare enthalpies of reaction (Δ_rH) of isocyanate/alcohol, epoxy/amine and cyclic carbonate/amine couples.[40] The peak of Δ_rH for PHU is broad and of low intensity. Two peaks are observed and the second one was attributed to the presence of hydrogen bonds and the formation of urea, both limiting molar masses in PHU synthesis. Indeed, side-reactions limit the conversion by consuming reactants, often amines, and induced a deviation of the stoichiometric ratio. The conversion of species are thus partial and molar masses are strongly limited as detailed in Carother's equation.

Several papers highlighted the low conversions obtained with PHUs through model reaction monitored by NMR and FTIR analyses. Most of the time, in the absence of catalysts or solvents, conversions barely exceed 80%.[31,32,39,75]

Molar masses obtained with PHUs are lower than those of conventional PUs. For instance, PHUs with molar masses up to 13,700 g.mol⁻¹ (\bar{M}_n , DMF) were synthesized by Lamarazelle *et al.* at 70 °C in DMF.[69] Carré *et al.* obtained molar masses up to 22,000 g.mol⁻¹ (\bar{M}_n , THF, PS standards) with sebacic cyclic carbonate and aliphatic diamines.[60] Maisonneuve *et al.* synthesized a series of PHUs with molar masses up to 31,000 g.mol⁻¹ (\bar{M}_n , DMF/LiBr, PS Standards).[76] Annunziata *et al.* performed PHUs with molar masses up to 68,000 g.mol⁻¹ (\bar{M}_n , DMF, 80 °C, PS standards), ones of the highest obtained, *via* the reaction of PPG-carbonates and PPG-diamines (Jeffamine®).[77] The given molar masses come from different papers were the teams used different SEC setups and different calibrations. These molar masses are relative and therefore cannot be compared. They are indicative information.

3. Outlooks for PHUs development

Many studies have therefore contributed to understand all the parameters affecting the aminolysis reaction. The structural parameters such as the carbonate ring size, the substituents of cyclic carbonates and the substituents of amines have been deeply studied, but also the main kinetic parameters of reaction such as the solvents, the time and the temperature, the catalysts and the molar ratio between reagents. Despite the growing understanding of the aminolysis reaction and its key parameters, several limitations remain. Among them the low molar masses, the low reactivity and the low conversion are the most problematic. The development of new

polymers and their industrial scale-up are nevertheless based on specific requirements. New questions have also emerged with the development of green chemistry. Indeed, the traditional chemistry is accompanied with a serious waste of resources, pollution, and toxicity issues for health. In order to eliminate toxicity, pollution, save resources and energy, sustainable developments is a priority.[78] To replace polymers such as polyurethanes, the new emerging polymers should fit with all these new specifications. The industrial processes have to use non-toxic, renewable and green reagents, green or less solvents or catalysts. In term of green chemistry and sustainable developments, PHUs are very promising. Several publications and reviews presented PHUs as a green alternative to polyurethanes. Indeed, numerous green and non-toxic reactants are involved in cyclic carbonates and amines syntheses. Furthermore, PHUs are one of the only sustainable route to obtain urethanes without the use of toxic isocyanates. The final properties of PHUs suffer nevertheless from several limitations in terms of reaction parameters. To overcome PHUs limitations the use of catalysts, solvents, higher temperatures or longer reaction times are generally required. However, these improvements do not correspond all the time to the principles of sustainable development. Several studies and researches focused on this problems with for example the design of catalysts to obtain PHUs in mild conditions. Furthermore, to avoid the use of organic solvents, current trends propose to work in bulk (without solvent),[79] in water [80–83] or under reactive extrusion or blending.[84–87] Besides, new routes have also emerged to avoid side-reactions, low conversions, low molar masses and the need of high temperature. For this purpose but also to obtain better properties, the use of different reactive sites is required. Hence, the synthesis of hybrid PHUs appears as the best way to access to the desired properties and requirements following green chemistry principles. Therefore, the hybrid technology purposes to facilitate PHUs process in a first approach. In addition to be environmental friendly, PHUs present excellent and promising mechanical and adhesion properties. Indeed, many studies highlighted the better adhesion properties of PHU compared to PUs. Thus, another approach of hybrid technologies consists in “doping” polymers with the addition of PHUs. Hybrid polymers are therefore presented in many studies as the best alternative to preserve PHUs properties while overcoming their limitations.

III. Hybrid PHUs: a promising way to overcome PHUs limitations

PHUs are undoubtedly very promising to replace polyurethanes and the use of toxic isocyanates. Many researches have been performed to control the parameters of the aminolysis

reaction, to design new cyclic carbonates and amines and to obtain properties close to original PUs. Despite these encouraging studies, few points are hindrances to industrial development of PHUs. In order to overcome these limitations, a new type of PHUs has emerged, the hybrid non-isocyanate polyurethanes and more specifically the hybrid polyhydroxyurethanes. Through the action of other systems in addition to PHUs, drawbacks can be balanced and properties optimized. Additional new polymers can therefore improve the reactivity, the conversion, the viscosity or the mechanical properties. PHUs properties can reversely improve the properties of existing polymers. Few reviews already mentioned the development of H-NIPUs as an encouraging outlook.[16,18,20,24,88–90] The present review aims to present the major publications dealing with hybrid polyhydroxyurethanes, as a new key for PHUs development. The different hybrid polyhydroxyurethanes will be classified in three categories: hybrid PHUs obtained by co-polymerization in one step, hybrid PHUs obtained through prepolymers synthesis, organic/inorganic hybrid PHUs. Each section will be ordered following the type of polymer used in addition to PHUs.

1. Hybrid PHUs by one-step co-polymerization

The co-polymerization of PHUs with other polymers is one of the different pathways to access to hybrid polyhydroxyurethanes. Mixing cyclic carbonates, amines and amine-reactive moieties in one step leads to blended networks, linked by covalent bonds.

Few papers mentioned the addition of epoxies or acrylates to a mixture of cyclic carbonates and amines, in order to develop H-NIPU polymers and improve their properties. The Figure 8 presents the strategy of the one-step polymerization and an example of the polymer structure obtained. A patent of Birukov *et al.* detailed the synthesis of nanostructured hybrid oligomers comprising an epoxy, a cyclic carbonate and an amine.[91] They also claimed the addition of an acrylate or methacrylate component to the previous mixture. Indeed, epoxies, cyclic carbonates and acrylates reacted with amines to form a complete network. These hybrid materials have showed better abrasion resistance, higher impact resistance and better flexibility compared to epoxy materials without cyclic carbonates.

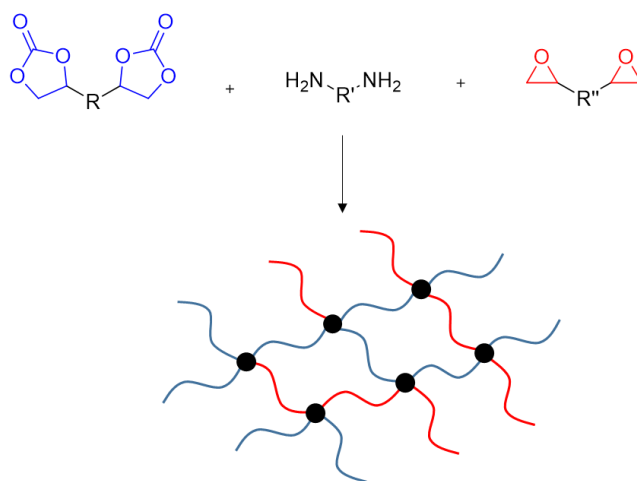


Figure 8. Synthesis of hybrid epoxy-PHU materials via a one-step polymerization

Another particular approach is the partial conversion of epoxy groups into cyclic carbonates.[92–94] This partial conversion leads to a mixture of monomers with epoxy or cyclic carbonate functions on the same molecule. These two functional groups may further cross-link with amines. The presence of both cyclic carbonates and epoxies on the same molecules allows to avoid the issues linked to the difference of reactivity. The Figure 9 presents the structures of the monomers mixture obtained from the partial carbonation of Bisphenol-A DiGlycidyl Ether (BADGE). Since two decades, Figovsky has written several patents about hybrid technology between PHUs and epoxy-amine polymers.[95–98] Among other things, he described the partial conversion of epoxies into cyclic carbonates to access to hybrid oligomers. Nevertheless, the control of the partial conversion of epoxies into cyclic carbonates is difficult and may cause repeatability issues.

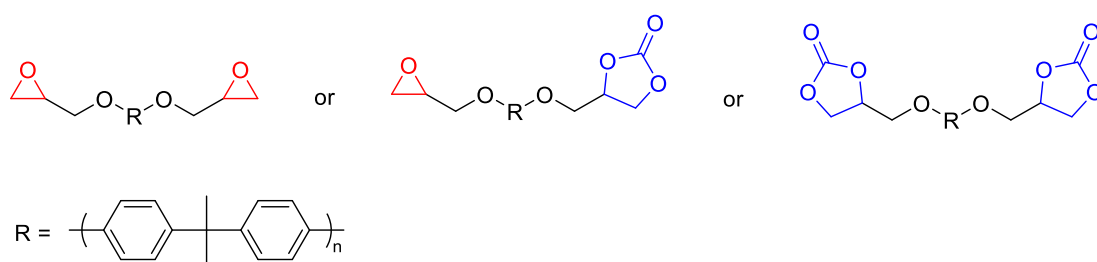


Figure 9. Mixture obtained from the partial carbonation of diglycidyl ether of BPA. Mixture of monomers with either two epoxies or one epoxy and one carbonate or two carbonates (Rokicki et al. and Bürgel et al. [92,93])

He *et al.* synthesized H-NIPU materials by the one-step method between cyclic carbonates from dimer acid, oligomers of ethylene diamine (DETA, TETA, TEPA) and bisphenol-A epoxy resins.[99] These different materials were characterized and compared to NIPUs without epoxy content. The addition of epoxy moieties increased the cross-linking density due to their reactivity towards secondary amines. Indeed, the aminolysis between cyclic carbonates and

secondary amines is very low and required higher temperatures. Thermal and mechanical properties were therefore improved with the addition of epoxy moieties. Nevertheless, the ratio used is not detailed and the mixture may react owing to different routes. Indeed, the reaction rates of cyclic carbonates and epoxies with primary and secondary amines are very different. Reactivity of epoxies towards alcohol was also suggested but not proved.

Lambeth *et al.* mixed epoxies and cyclic carbonates from trimethylol propane with different ratios from 100/0 to 25/75 and cured the mixture with 4,4-diaminodicyclohexylmethane at 80 °C for 48 h.[73] The addition of cyclic carbonates tended to modify the T_g , the Young's modulus, the cross-linking density, the swelling index and the adhesive strength. These values tended to increase slightly with the carbonate content. Several properties are nevertheless negatively impacted by high contents of carbonates. This is mainly explained by the numerous hydrogen bonds formed. Finally, these hybrid polymers revealed promising adhesives properties thanks to the addition of a moderated amount of cyclic carbonates.

Cyclic carbonates were also used as reactive diluents in epoxy formulations.[100] For example, the addition of ethylene glycol cyclic carbonate in epoxy resin (bisphenol-A diglycidyl ether) was performed to decrease the viscosity of the epoxy resin and improve the final mechanical properties.[72] These effective improvements were explained by the addition of urethane linkages, hydrogen bonds, a lower cross-linking density and the presence of unreacted carbonate groups.

Doley *et al.* prepared H-NIPU materials based on sunflower oil-based cyclic carbonates, epoxy resin and isophorone diamine.[101] The mechanical properties increased with the epoxy content and the best properties were obtained with 30%_w of epoxy resin. Nanocomposites were finally prepared with amine-functionalized graphene oxide (GO) and the H-NIPU mixture. The performant covalent interactions between the GO and the mixture resulted in strong improvement of the composite properties.

To improve mechanical properties and chemical resistance of NIPUs, Ke *et al.* added various amount of epoxy (bisphenol-A diglycidyl ether) to their formulations.[59] The final H-NIPU materials with epoxy contents up to 45%, exhibited outstanding chemical resistance, better flexibility and an improved impact resistance.

Parzuchowski *et al.* showed that the addition of cyclic carbonate monomers in epoxy resin allowed to induce phase separation in the final network.[102,103] A higher impact strength was attributed to the presence of a phase segregation.

Dithiocarbonates were also used to promote the adhesion performances of epoxy-amine materials.[104]

PHUs can be used to fix different problems of epoxy-amine polymer properties. Stroganov *et al.* detailed the modification of epoxy-amine networks with cyclic carbonates to solve fragility and hardness problems.[105] Cyclic carbonates as additional fragments affected the molecular mobility and the relaxation properties. The elastic deformation was therefore enhanced.

The addition of NIPUs (10%) in epoxy resin modified with nanoparticules was investigated by Białkowsk *et al.*[106] The hybrid nanocomposites were compared to NIPU-free nanocomposites. FTIR and SEM analyses were used to characterize the network and the surface. The interpenetrated network between the two polymers exhibited higher ductility, crack resistance and fracture toughness.

To conclude, H-NIPU materials managed to mix properties of PHUs and epoxies while balancing their respective lack of properties or drawbacks. For example, epoxy moieties may react with secondary amines much more easily than cyclic carbonates. Higher cross-linking density are therefore obtained. The addition of low viscous monomers in a mixture has also been used to improve processing. Adhesion properties of epoxy materials can also be improved with the help of hydroxyurethanes. Nevertheless, epoxies and cyclic carbonates have different reactivity towards amines. The order of reactivity is neither taken into consideration nor discussed in the papers. However, the lower reactivity of cyclic carbonates may be problematic in terms of homogeneity or polymerization control for instance. Therefore, another way in two steps is generally employed.

2. Hybrid PHUs by prepolymer synthesis

The major pathway to access to hybrid PHUs is a two-step procedure. The synthesis of prepolymers in a first time allows to design oligomers with a controlled position and number of reactive functions. These reactive functions may further react with another cross-linking agent.

a) PU/PHU

Two papers reported the synthesis of hybrid polyurethane/polyhydroxyurethane by preparing cyclic carbonate prepolymers with polyurethane backbones. These oligomers with cyclic carbonate end-groups were able to react with diamines for a complete polymerization, Figure 10. This strategy enabled to avoid the use of isocyanates at the curing step. Indeed, despite the high performances of polyurethanes, the toxicity of isocyanates is a major issue. The contact of final users and customers with toxic substances must be prevented. In this case, isocyanates are handled only in chemical industries where protective equipment is more easily provided.

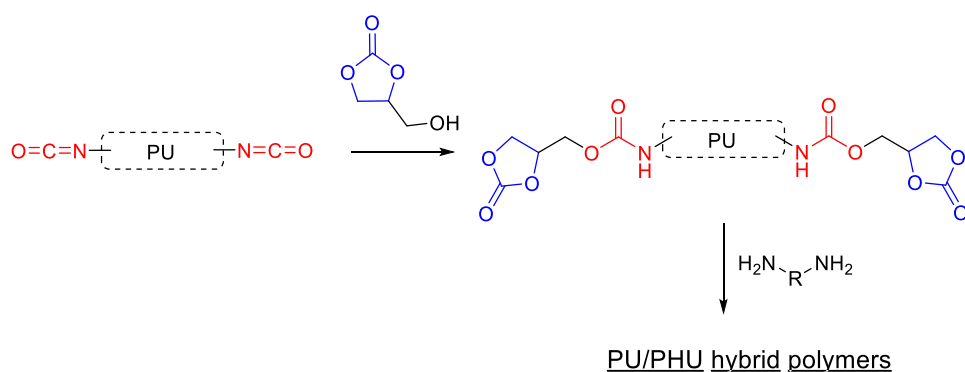


Figure 10. Synthesis of hybrid PU/PHU polymers through the synthesis of cyclic carbonate-terminated PU prepolymers

Leitsch *et al.* prepared in a first time isocyanate-terminated PU oligomers from TDI and polypropylene glycol polyol.[107] These oligomers were further reacted with glycerol carbonate to synthesize cyclic carbonate-terminated PU oligomers. The final polymerization occurred with triethylenetetramine as a chain extender to obtain PU/PHU hybrid materials. The isocyanate/alcohol reactions were performed at 80 °C with DiButylTin DiLaurate (DBTDL) as catalyst and PHUs curing were performed at 60 °C for 1 hour and at ambient temperature for 7 days. The study finally highlighted the improvement of adhesion properties of synthesized materials compared to traditional PUs. The better adhesion properties obtained on polyimide, PVC and aluminum were attributed to the additional hydrogen bonds afforded by PHUs.

Kotanen *et al.* synthesized hybrid PU/PHU materials from a large diversity of isocyanates and amines.[108] Four isocyanate-terminated prepolymers from TDI, HDI and IsoPhorone Diisocyanate (IPDI) were chosen as starting reagents. First, the isocyanates were directly reacted with glycerol carbonate in the presence of bismuth-based catalyst (0.1%) to afford cyclic carbonate-terminated PUs. These prepolymers were then cured with various diamines. The conditions of curing were evaluated based on their physical appearance at room temperature, 70 °C and 90 °C. Twelve amines were chosen for this study with functionality from 2 to 16.8 with aliphatic, aromatic, PPG-based or ethylenediamine-based structures. Despite the initial intention of an ambient curing, highest temperature were required to obtain optimum properties. The good adhesion performances of PHUs through their high density of hydrogen bonds was once again demonstrated.

The tuning of PUs with PHUs aims to increase the adhesion properties of materials and to avoid the use of isocyanates in the final step of polymerization. Nevertheless, PHUs have been developed to fully replace isocyanates, their toxicity being problematic from their synthesis to their handling.

b) Epoxy/PHU

Epoxy/amine is a well-known polymer system, widely used in industry. On the other hand, due to the reactivity of epoxies towards primary and secondary amines as well as the good conversions obtained, epoxy monomers are ideal candidates in the synthesis of hybrid PHUs. Many studies reported the curing of PHU prepolymers with epoxy moieties. Indeed, the reaction of bicyclic carbonates with an excess of diamines led to amine-terminated PHU prepolymers. The strong advantages of the excess of diamines lies in the complete conversion of cyclic carbonates obtained and the higher reactivity of the aminolysis.

Before the expansion of PHUs and the use of epoxies as doping substituents in hybrid PHUs synthesis, cyclic carbonates were used to increase the reactivity and properties of epoxy/amine systems. Rokicki was one of the first scientists to perform hybrid PHUs. He detailed the synthesis of modified amine cross-linking agents with the addition of cyclic carbonates.[109] The obtained β -hydroxyurethane groups were shown to improve the thermal and mechanical properties of epoxy/amine thermosets and also tended to shorten the gel times.

The HydroxyUrethane Modifier (HUM) is also another method developed by Figovsky to prepare hybrid PHU/epoxy-amine.[110,111] HUM are synthesized in a first step and added to epoxy resins in a second step. They are obtained through the reaction of mono-cyclic carbonates and polyamines at temperature up to 120 °C, Figure 11. The products of the reaction of propylene carbonate with Vestamin TMD (2,2,4-trimethyl hexamethylene diamine) and isophorone diamine have been registered in a US patent.[112] The addition of HUM in epoxy resins improved the gelation time, the wear resistance, the flexibility, the mechanical and chemical resistance. HUM and the polymer network are not attached by covalent bonds, there are only physical bonds such as hydrogen bonds.

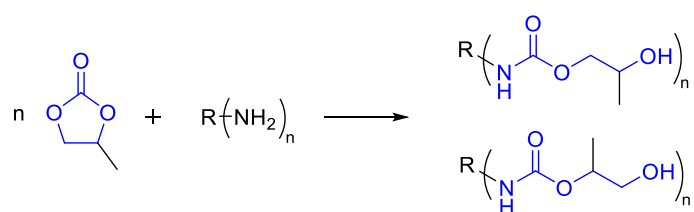


Figure 11. HydroxyUrethane Modifier (HUM) synthesis between propylene carbonate and amines

The limitations in PHU synthesis encouraged researchers to use epoxies in hybrid PHUs syntheses, mainly due to their ability to react with secondary amines and the high reactivity of the epoxy/amine reaction. Ke *et al.* synthesized a series of PHU prepolymers from PPG cyclic carbonate and various diamines with 0 to 3 internal secondary amines (EDA, DETA, TETA, TEPA).[113] The amines were used with slight excess from 1 to 1.64 equivalents compared to the cyclic carbonate. The excess was nevertheless not sufficient to complete the conversion of

cyclic carbonates. The prepolymers were further reacted with bisphenol-A diglycidyl ether as an epoxy cross-linking agent, Figure 12. The obtained materials were characterized through FTIR, swelling, TGA, DMA and tensile strength. They showed good mechanical performances and thermal stability due to the high cross-linking density and aromatic rings brought by BADGE. In another study, the authors deepened their previous works.[114] A kinetic study conducted through FTIR analyses was performed to determine curing conditions of cyclic carbonate monomers with EDA at 25 °C, 35 °C, 60 °C, 70 °C, 90 °C and with TriEthyleneDiAmine (TEDA) as catalyst. Higher amine ratios were used (up to 2.11) and demonstrated better cross-linking. The number of secondary amines was shown to improve the mechanical performances of final materials.

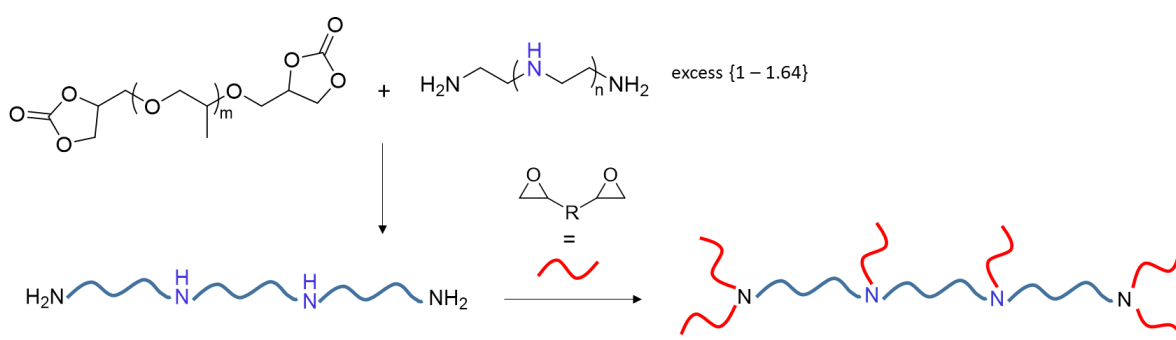


Figure 12. Synthesis of PHU prepolymers with amine end-groups and in the main chain. Cross-linking of these prepolymers with epoxy moieties (Ke *et al.*[113,114])

Another strategy developed by Cornille *et al.* involves the use of volatile amine (EDA) which can be removed after PHU prepolymers synthesis.[115] Various excess of EDA were used to prepare PHU prepolymers: 1.3, 2, 3.3 and 6.5 which reacted with PPG-380 or PPG-640 cyclic carbonates at 60 °C for 12 hours. Three epoxy monomers from bisphenol-A, phloroglucinol and cardanol (NC-514) were used to cross-link these prepolymers at 50 °C for 12 hours. The final materials obtained included a sequence of soft and hard segments as in regular polyurethanes. A large range of properties was therefore obtained depending on the excess of diamines, the length of the cyclic carbonate monomers and the nature of the epoxy cross-linking agent.

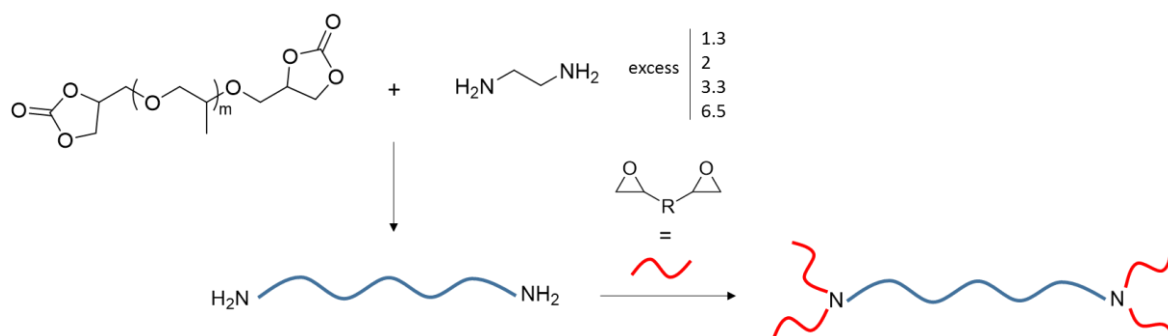


Figure 13. Synthesis of amine-terminated PHU prepolymers and cross-linking with epoxy moieties (Cornille et al.[115])

A recent publication of Asemani *et al.* reported the synthesis of hybrid PHUs for coatings.[116] The PHU prepolymers were synthesized from various cyclic carbonate and amine monomers varying the amine/cyclic carbonate ratio (1.4 or 1.7). The reactions were carried out at 90 °C in toluene and parachlorobenzotrifluoride. A first screening of coating properties led choosing trimethylolpropane triglycidyl ether as the optimum cross-linking agent. A mixture of toluene, MethylIsoButylCetone (MIBK), and parachlorobenzotrifluoride was added to adjust the viscosity of mixtures. Performant coatings were finally obtained and compared to conventional PU coatings. The mechanical, physical, and chemical properties were found to be comparable, however the thermal stability was significantly inferior for hybrid PHUs.

Birukov *et al.* detailed in a patent a method to obtain carbonated-epoxy unsaturated fatty acid triglycerides by the partial conversion of epoxy into cyclic carbonate groups with conversions from 35% to 85%.[117] They proposed to react two different amines in a two-step curing with the previous carbonated-epoxy triglyceride. The obtained prepolymers were finally cured at ambient temperature with amine-reactive groups such as epoxy monomers or a mixture of epoxy monomers and the carbonated-epoxy triglyceride. The final polymers contained between 14.9wt% and 28.1wt% of urethane groups.

Several patents also reported the synthesis of hybrid PHUs obtained by curing of PHU prepolymers with epoxy compounds.[98,118]

Besides, He *et al.* proposed an alternative method for the preparation of PHU prepolymers and their cross-linking with epoxies.[119] Ethylene carbonate was chosen to react with ethylenediamine oligomers (EDA, DETA, TETA and TEPA) to afford hydroxy-terminated urethanes. PHU prepolymers were then obtained through the polycondensation of the hydroxy-terminated urethanes with acid dimers. The formed linear prepolymers were finally cross-linked with epoxies *via* the secondary amines of the chain, Figure 14. These materials were characterized by TGA and DMA and demonstrated good thermal stability. The micro- and nano-phase separation were finally investigated through SEM and AFM.

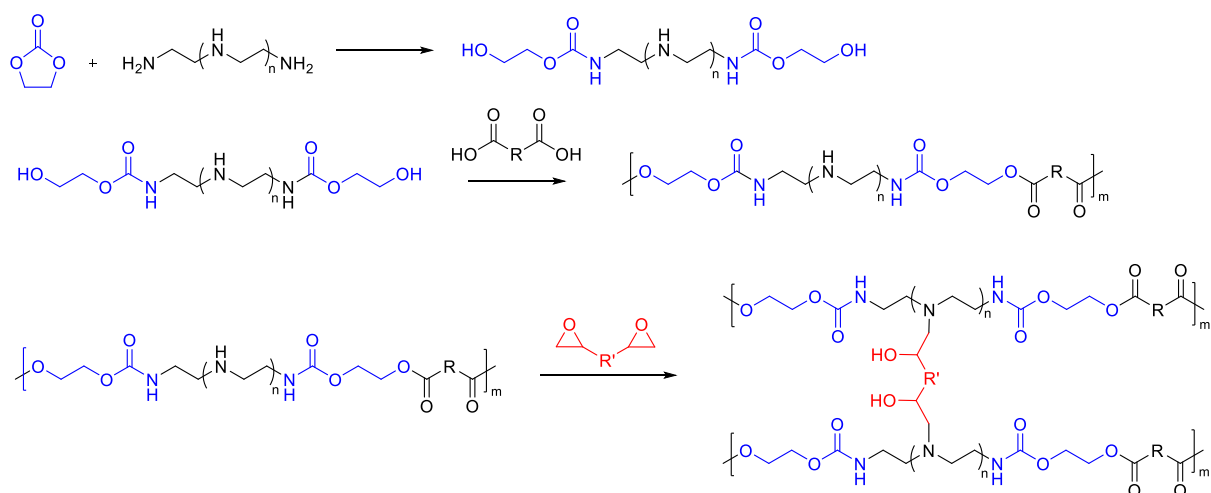


Figure 14. Synthesis of hybrid PHUs through the polycondensation of hydroxy-terminated urethanes and dimer acid and the cross-linking with epoxies (He *et al.*[119])

c) PHU coupled with alkene polymerization

A third kind of polymer usually combined to PHUs to prepare hybrid PHUs is based on polymerization of alkenes (C=C). Several groups are involved in these syntheses, for example acrylates, methacrylates, maleimides or vinyls. Three different approaches were found in the literature. First, the synthesis of amine-terminated PHU prepolymers, which can be further cross-linked with amine-reactive groups. Second, the synthesis of PHU prepolymers with alkene end-groups. Finally, the synthesis of prepolymers with dangling cyclic carbonate functions, obtained from the radical polymerization of monomers including double bonds and cyclic carbonates. They can thus be cross-linked with amines in a final step.

i. Synthesis of PHU prepolymers with NH₂ end-groups

The reaction of cyclic carbonates with an excess of amines leads to amine-terminated prepolymers. As previously described with epoxies, these prepolymers can be cross-linked with amine-reactive monomers. Cornille *et al.* detailed the preparation of amine-terminated PHU prepolymers and their cross-linking with acrylates.[120] The excess of diamine used in the first step has several advantages. The cyclic carbonate conversion is complete, the reaction is performed at room temperature without solvent nor catalyst and the free amines remaining in the mixture act as reactive diluent. The final cross-linking with acrylates through the Michael reaction afforded fully cured hybrid PHU thermosets. This method provided PHU thermosets at room temperature with an improved reactivity and the full conversion of cyclic carbonate

monomers. Furthermore, the material properties can be modulated with several parameters: the excess of amine, the structure and length of monomers and the functionality of acrylate cross-linkers.

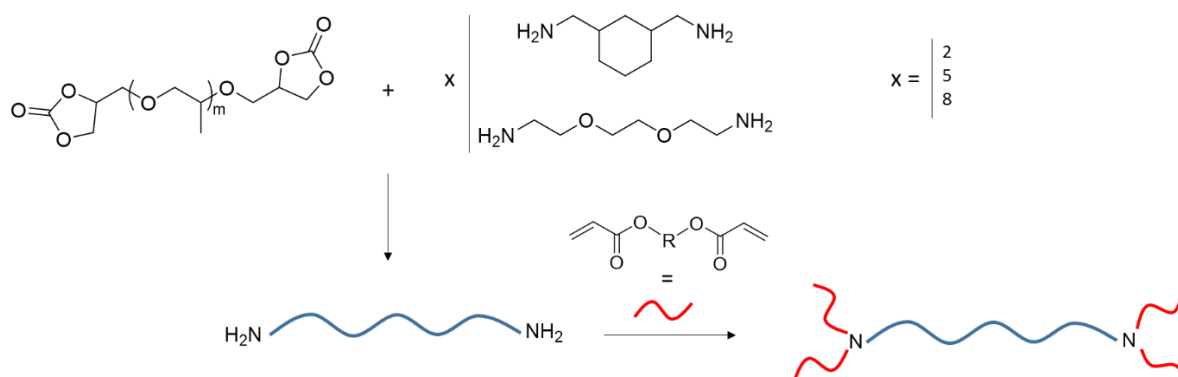


Figure 15. Synthesis of amine-terminated PHU prepolymers and cross-linking with acrylate moieties (Cornille *et al.*[120])

ii. Synthesis of PHU prepolymers with alkene end-groups

PHU prepolymers may also be synthesized with alkene end-groups such as acrylates or methacrylates for cross-linking by radical or metathesis polymerization. Assumption *et al.* synthesized urethane dimethacrylate monomers by ring-opening of ethylene carbonate with diamines or amino-alcohols.[121] The formed urethane diols were reacted with methacrylic anhydride to form mono- and bis-urethane dimethacrylate monomers, Figure 16. They finally investigated the photopolymerization of the methacrylate prepolymers. Wang *et al.* followed the same procedure to prepare urethane dimethacrylate prepolymers as reactive diluent.[122] They compared the performances of these reactive diluents with ethylene glycol dimethacrylate though different characterizations: tensile and thermal properties, pencil hardness, chemical resistance, impact resistance, and gloss. Significant improvements were highlighted in impact resistance and elongation at break and attributed to hydrogen bonds brought by urethane groups.

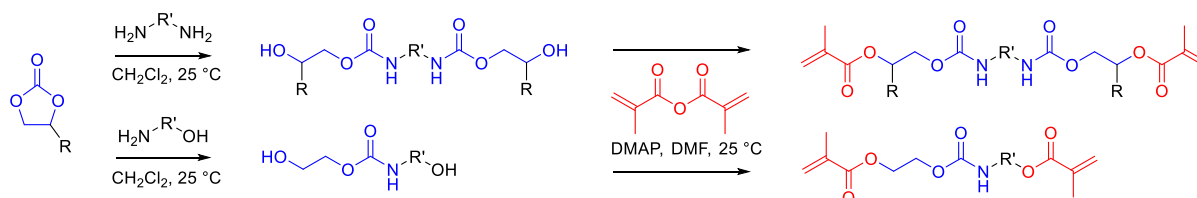


Figure 16. Preparation of methacrylate-terminated PHUs through the reaction of hydroxy-terminated PHUs and methacrylic anhydride (Assumption *et al.*[121])

Ochiai and Utsuno cross-linked by radical polymerization (AIBN, DMF, 60 °C) methacrylate polyurethanes obtained by polycondensation of diurethanes.[123] The diurethanes were obtained from the reaction of diamines with ethylencarbonate. Methacrylates were grafted to

the alcohol-terminated polyurethanes with glycidyl methacrylate. The reaction is presented Figure 17.

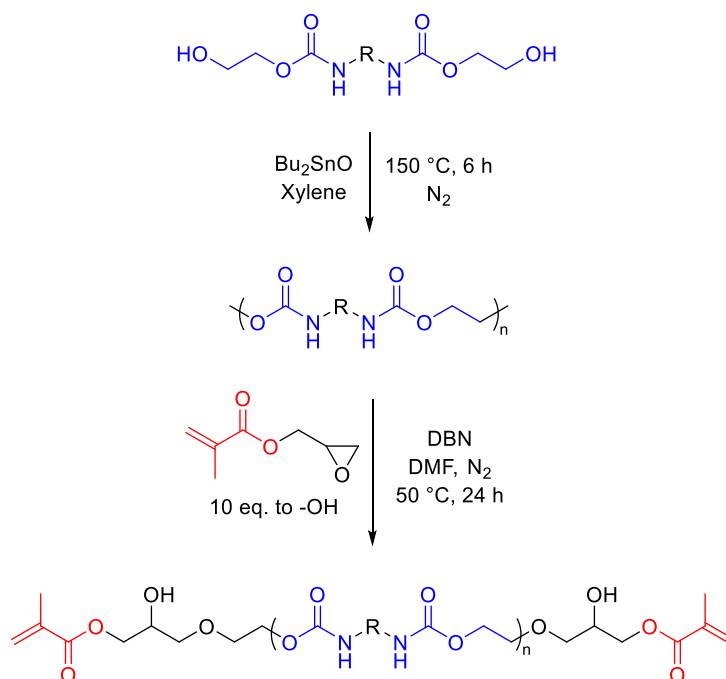


Figure 17. Elaboration of methacrylic-terminated PHU in two steps procedure. First the polycondensation of diurethane. Then, the addition of glycidyl methacrylate (Ochiai and Utsuno [123])

Meng *et al.* prepared functional latexes by emulsion copolymerization of hydroxyurethane methacrylates with methyl and butyl methacrylates.[124,125] Ethylene carbonate and monoamines were reacted together and methacrylates were grafted onto terminal alcohol produced in the previous reaction. As already seen in many hybrid materials, urethane groups increased mechanical properties thanks to the presence of numerous hydrogen bonds.

Decostanzi *et al.* synthesized thermosets by radical polymerization of hydroxyurethane methacrylate prepolymers.[126] Hence, amino-terminated PHU prepolymers were obtained by the reaction of cyclic carbonates with an excess of diamines. Then, those prepolymers reacted with ethylene carbonate to form alcohol-terminated PHU prepolymers. Finally, methacrylic anhydride was used to obtain methacrylic-terminated PHU prepolymers. The different steps are presented Figure 18.

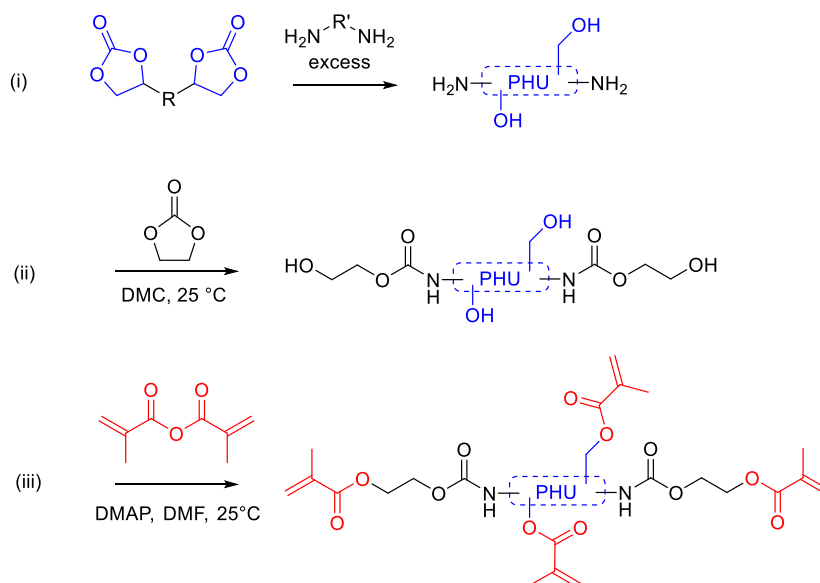


Figure 18. Synthesis of hydroxyurethane methacrylate prepolymers in three steps: (i) synthesis of amine-terminated PHU prepolymers; (ii) addition of ethylene carbonate; (iii) grafting of methacrylic functions from methacrylic anhydride (Decostanzi *et al.*[126])

UV-curable coatings were prepared from tung-oil modified by Diels-Alder-reaction, PHUs and acrylates. Huang *et al.* grafted in a first time anhydride groups on tung-oil by the Diels-Alder reaction between maleic anhydride and double bonds of tung-oil.[127] This monomer was then reacted with PHU prepolymers obtained *via* the reaction of ethylene carbonate with diamines. Finally the UV-curable prepolymers were obtained by grafting methacrylate groups *via* the addition of glycidyl methacrylate. Good properties of adhesion were obtained helped by the presence of PHU moieties.

Besides classic radical polymerization of alkenes, such as acrylates, methacrylates or vinyls, other methods have also been explored. Indeed, hybrid PHUs have been obtained by metathesis of terminal alkene groups. Bigot *et al.* prepared PHU prepolymers through the reaction of undecylenate carbonate with diamines, hexamethylenediamine and isophoronediamine.[128] These alkene-terminated prepolymers were finally polymerized by metathesis with a Hoveyda-Grubbs catalyst 2nd generation, Figure 19.

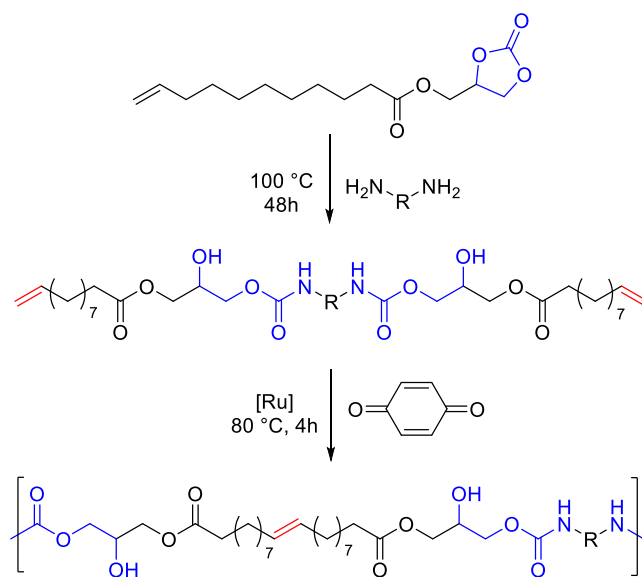


Figure 19. Polymerization by metathesis of alkenyl-terminated PHU prepolymers (Bigot *et al.*[128])

iii. Prepolymers with dangling cyclic carbonate groups obtained by polymerization of alkenes

Among the different end-groups used to prepare prepolymers for hybrid PHU synthesis, several publications mentioned cyclic carbonates. Therefore, the double bond polymerization of monomers bearing both alkenes and cyclic carbonates leads to oligomers with dangling cyclic carbonate functions, Figure 20. The main strategies to polymerize alkenes are either the radical polymerization of acrylates, methacrylates and vinyls, or the metathesis of alkenes. Ochiai *et al.* described the radical polymerization of vinyl substituted cyclic carbonate: the 4-phenyl-5-vinyl-1,3-dioxolan-2-one.[129] Vinyl polymerization was allowed thanks to the stability of the cyclic carbonate ring. This monomer was homopolymerized and copolymerized with vinyl acetate or maleic anhydride. Molar masses below 10,000 g.mol⁻¹ (\bar{M}_n , DMF, PS standards) were nevertheless obtained. Thermosets were finally obtained through the cross-linking with hexamethylenediamine, by reaction with cyclic carbonate or anhydride functions.

Camara *et al.* performed a complete study of the radical polymerization of Glycerin Carbonate MethAcrylate (GCMA).[130] They identified the by-products of the monomer synthesis and the possible transfer reactions during the polymerization. Polyglycerin carbonate methacrylates were obtained in DMSO with molar masses from 62,000 to 102,000 g.mol⁻¹ (\bar{M}_n , DMF, PMMA standards), depending on the GCMA concentration. Polymerizations were performed at 60 °C for 16 hours with AIBN initiator. Furthermore, the GCMA monomer has demonstrated a reactivity 1.7 times higher than methyl methacrylate. Another way was also explored through the post carbonation of glycidyl methacrylate. Lower molar masses were obtained but since

cyclic carbonates may induce cross-linking during homopolymerization, linear and branched chain are not comparable.

Sabatini *et al.* polymerized the 4-vinyl-1,3-dioxolane-2-one *via* free radical polymerization initiated by benzoyl peroxide.[131] The reaction was monitored during 168 hours and molar masses of $82,900 \text{ g}\cdot\text{mol}^{-1}$ were obtained with dispersity of 1.43 (\bar{M}_n , DCM, PS standards). The 4-vinyl-1,3-dioxolane-2-one was then copolymerized with styrene. Polymers with various ratios of monomers were obtained in good yields with molar masses close to $100,000 \text{ g}\cdot\text{mol}^{-1}$.

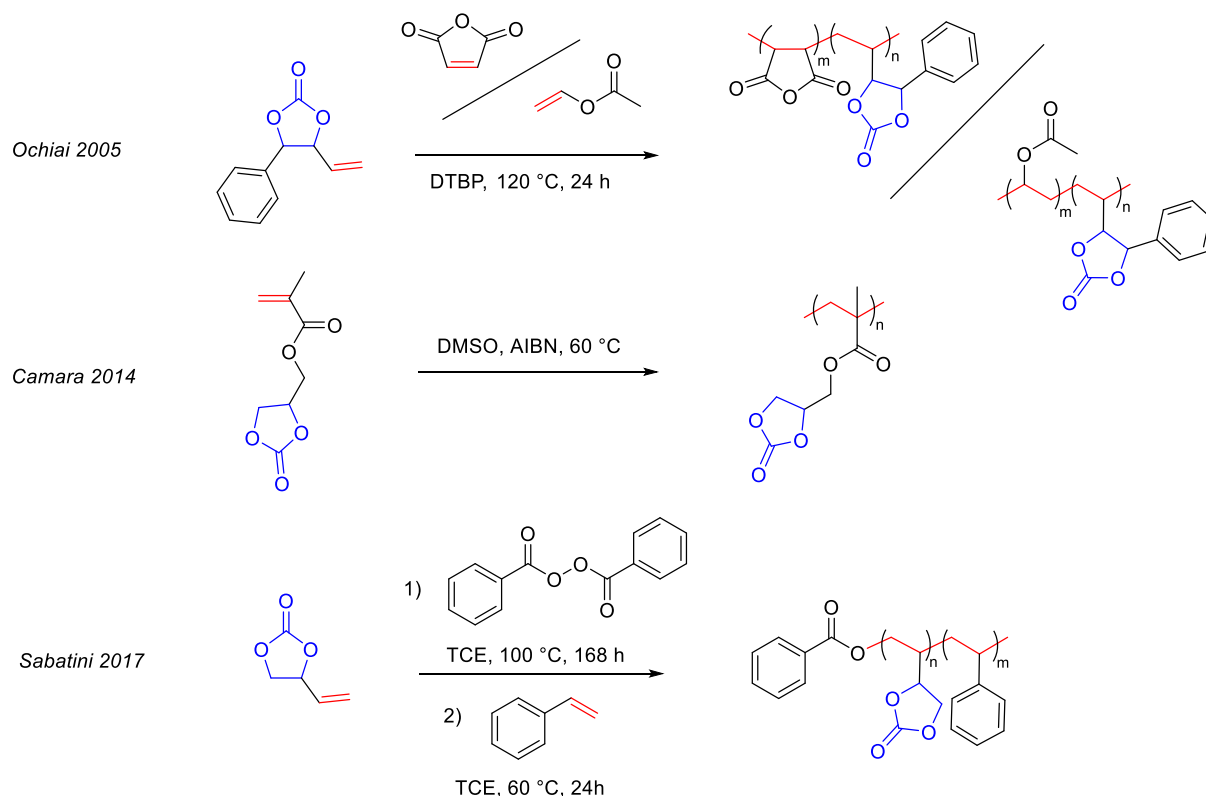


Figure 20. Synthesis of prepolymers with dangling cyclic carbonate groups via radical polymerization[129–131]

The team of Detrembleur also performed the synthesis of several allyl- and vinyl-cyclic carbonate monomers as well as their polymerization either by cobalt-mediated radical polymerization or free and controlled radical polymerizations.[132,133]

NIPUs from the reaction of acrylic cyclic carbonates and amines were also prepared by Figovsky *et al.*. They evaluated the UV-stability of these coatings over time.[111,134,135]

Another approach to obtain terminal cyclic carbonates has been developed by Guillaume *et al.*[136] They proposed the tandem reaction of ring-opening metathesis polymerization of cyclooctene and the cross-metathesis of cyclic carbonate olefins. Three cyclic carbonates have been investigated and compared. The hex-3-ene-1,6-dioate dicyclic carbonate presented the most effective activity. However, the polymerization of this prepolymer with amine (EDR-148) did not succeed due to the numerous side-reactions between cyclic carbonates and amines.

Several cyclic carbonate monomers bearing double bonds can thus be polymerized to prepare linear prepolymers with dangling cyclic carbonate functions. Through direct homopolymerization or copolymerization with other monomers, these obtained cyclic carbonate prepolymers are amine-reactive and are thus promising to synthesize hybrid PHUs. Nevertheless, the cross-linking of cyclic carbonates in a last step cannot avoid the limitations such as the low reactivity and the low conversions of PHUs.

d) Polyester/PHU

Quienne *et al.* developed a new strategy to synthesize biobased polyester/PHUs.[137] The reaction of glycerol carbonate with diamines led to short PHU prepolymers with four terminal hydroxyl groups. These prepolymers were then reacted with sugar-derived dimethyl-2,5-furan dicarboxylate. The control of the molar ratio between hydroxyl and carboxylic acid groups allowed to design star-shape macromolecules with specific size and chain end. They also highlighted the presence of exchange bonds induced by thermal stimuli.

3. Organic/inorganic hybrid PHUs

The third category of hybrid PHUs concern the organic/inorganic PHUs. The aim of the hybrid strategy is to mix properties of both inorganic and organic (PHU) parts. The most common inorganic moieties used with PHUs are based on silicon, generally siloxane or silica. Siloxanes are organosilicon polymers consisting in Si-O-Si bonds, which are widely used in polymer industry particularly due to their properties of hydrophobicity, thermal resistance, flexibility, gas permeation. A very common route to synthesize organic/inorganic materials is the elaboration of composite materials. They are composed of a polymer matrix and a filler. One of the main fillers used as inorganic filler is the silica, a silicon oxide (SiO₂). Few other types of fillers are nevertheless found in addition to PHUs such as zinc oxide or carbon nanotubes. For this review, only the composite materials which involved covalent bonds between the matrix and the filler were considered.

a) Synthesis of hybrid PHU-siloxanes

Polysiloxanes are composed of siloxane units based on Si-O-Si linkages and are generally linear or cyclic macromolecules. Several groups are linked to the silicon atom such as methyl, hydrogen or vinyl which opens the fields to various functionalization. Therefore, the addition of polysiloxanes to PHUs required specific functionalization. The main routes involved the

synthesis of amine-terminated polysiloxanes or the synthesis of polysiloxanes bearing cyclic carbonates units.

The group of Endo prepared such hybrid PHUs by polyaddition of cyclic carbonates (from bisphenol-A) and amine containing siloxane backbones.[138] Polymerization was performed in Propylene Glycol Methyl Ether Acetate (PGMAC) at 80-100 °C for 24 h. Two lengths of siloxane-amine were used and compared to dodecanediamine. The silicone-containing materials exhibited lower T_g than reference one. Indeed, siloxanes provide flexibility to PHUs which extends the properties of PHU materials and their potential applications.

Cyclic carbonates may also be grafted onto polysiloxanes *via* hydrosilylation to afford cyclic carbonate prepolymers. The hydrosilylation is the reaction of alkenes with Si-H bonds, usually catalyzed by platinum, rhodium or ruthenium derivatives.

Zhu *et al.* synthesized linear polysiloxanes bearing cyclic carbonate groups from vinyl-containing cyclic carbonates and PolyHydroMethylSiloxane (PHMS).[139] This reaction was performed in acetonitrile at 60 °C for approximately 10 hours.

Another more largely used method is the addition of allyl glycidyl ether to polysiloxanes with SiH groups and the carbonation of epoxies with CO₂ into cyclic carbonates in a second step, Figure 21.

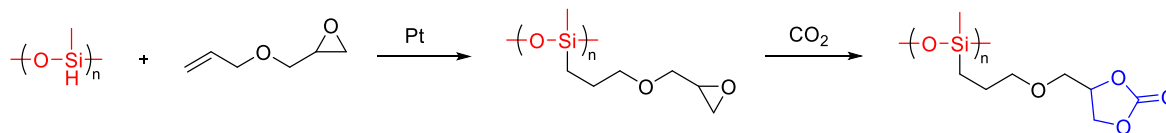


Figure 21. Grafting of cyclic carbonates on polysiloxanes via hydrosilylation of allyl glycidyl ether and CO₂ carbonation

Blattman and Mülhaupt obtained such hybrid PHUs from Polyhedral Oligomeric SilSesquioxanes (POSS), Figure 22.[140] Glycidyl ether-functionalized POSS were firstly converted into cyclic carbonates with CO₂. Finally, POSS cyclic carbonates were directly cured with hexamethylenediamine and isophoronediamine or blended with glycerol carbonate, trimethylolpropane carbonate or pentaerythritol carbonate before curing. Numerous materials were obtained and characterized to determine their mechanical properties and morphologies. Such high functional cyclic carbonates with low viscosity are thus promising to improve properties and processing of PHUs.

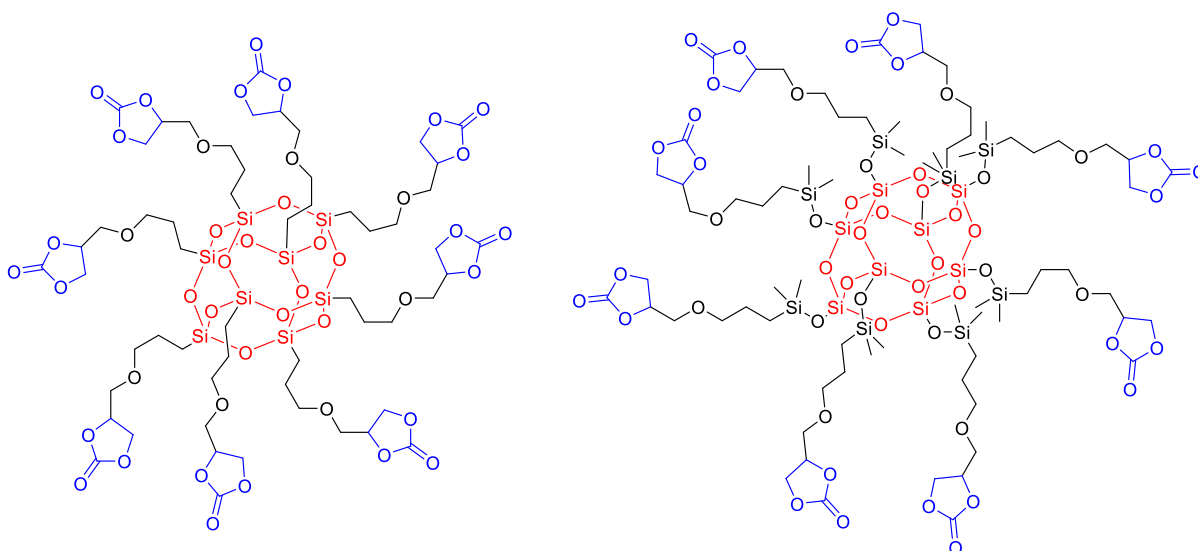


Figure 22. Structures of POSS-cyclic carbonates synthesized by Blattman et Müllhaupt[140]

Liu *et al.* prepared linear siloxane prepolymers with various contents of dangling cyclic carbonate functions.[141] Copolymers of PolyDiMethylSiloxane (PDMS) and PHMS were used to adapt the cyclic carbonate content. Isophorone diamine, 4,4'-diaminodicyclohexylmethane, 1,2-propanediamine and 1,6-hexamethylenediamine (HMDA) were chosen as curing agents to obtain hybrid PHU coatings. Properties of final materials were compared depending on the amine used and the content of cyclic carbonate. First, cycloaliphatic amines have shown better properties than aliphatic ones. Second, higher carbonate content led to higher Young's modulus, T_g and tensile strength but lower thermal stability and water resistance.

Furthermore, Ecochard *et al.* designed four cyclic carbonate structures from linear and cyclic polysiloxanes, Figure 23.[142] High functional and low viscous monomers were therefore obtained *via* two pathways, by reaction of Si-H groups with either allyl glycidyl ether or epoxidized eugenol. Epoxy groups were then converted into cyclic carbonates through CO_2 carbonation. They cured these monomers with 2-methylpentane-1,5-diamine (DYTEKA) and 1,3-cyclohexanedimethanamine (CBMA) to afford hybrid PHUs with various properties. Good yields and conversions were obtained thanks to the low viscosity of siloxanes. The role of the functionality, the length and the shape of siloxane chains, and the presence of aromatic groups were evaluated through thermal and mechanical analyses.

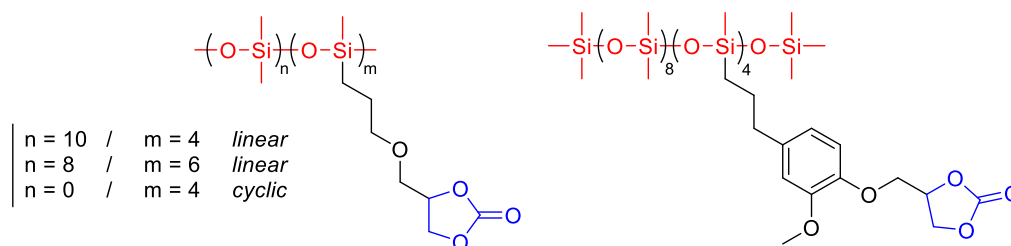


Figure 23. Hybrid polysiloxanes with dangling cyclic carbonate functions (Ecochard *et al.*, [142])

A patent has been filed by Hanada *et al.* which presented the synthesis of polysiloxanes with cyclic carbonate end-groups. [143] This invention claimed the carbonation of epoxy-modified polysiloxane with CO₂ to prepare difunctional monomers. The proposed structures are shown Figure 24.

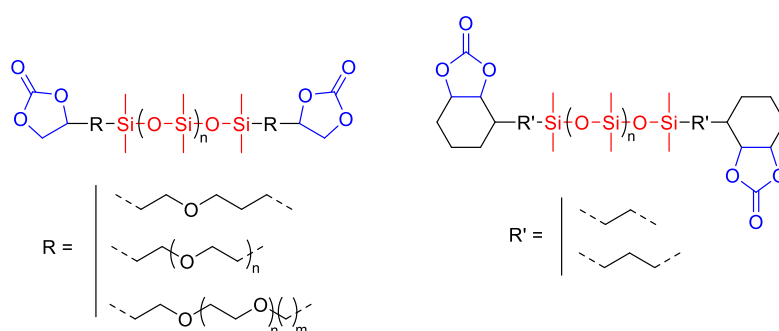


Figure 24. Hybrid polysiloxanes with cyclic carbonate end-groups (Hanada *et al.*, [143])

b) Synthesis of hybrid PHUs *via* sol-gel routes

The addition of silicon in PHU synthesis can also be achieved *via* sol-gel routes. This is one of the most common methods to prepare organic/inorganic materials based on silica mainly due to the mild conditions required. The sol-gel process involves the cross-linking of alkoxy silane groups, such as trimethoxysilane or triethoxysilane, by hydrolysis. Therefore, the addition of such groups onto cyclic carbonate monomers may lead to hybrid organic/inorganic PHU materials.

Birukov claimed in a patent the elaboration of nanostructured hybrid liquid oligomers based on the mixture of amines with epoxy and/or cyclic carbonate and/or methacrylate or acrylate components where at least one of them contained alkoxy silane units. [91] This mixture was curable at low temperature through sol-gel routes. The authors also claimed that the hydroxyl groups formed by the aminolysis reactions between cyclic carbonates and amines activated the alkoxy silane hydrolytic condensation (the process of cross-linking). Such approach is indeed a good example of the synergic effect of hybrid materials.

Hosgor *et al.* prepared polyhydroxyurethane-silica hybrid coatings *via* sol-gel routes.[144] First two difunctional cyclic carbonates were obtained from bis(4-glycidyloxy phenyl)phenyl phosphine oxide and poly(propyleneglycol)diglycidyl ether. A sol-gel formulation was also prepared between tetramethylorthosilicate and cyclic carbonate functional alkoxy silane. This formulation was finally mixed with the cyclic carbonate monomers and cured by sol-gel method and hexamethylene diamine, Figure 25. The Young's modulus and the hardness of coatings were enhanced by the amount of silica phosphine oxide contents. Higher char contents were also obtained with hybrid materials compared to the corresponding organic coatings.

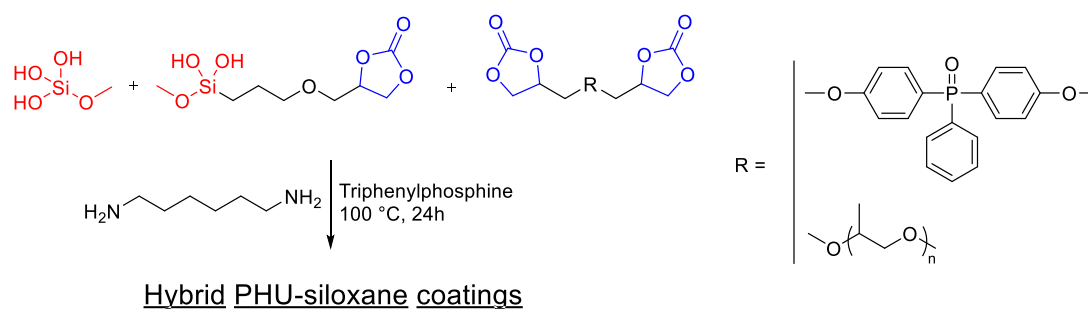


Figure 25. Synthesis of hybrid PHU-siloxane coatings *via* sol-gel process (Hosgor *et al.* [144])

Hybrid PHU-siloxanes were also obtained by sol-gel polycondensation of PHU prepolymers with alkoxy silane end-groups. Kathalewar and Sabnis first synthesized hybrid PHU coatings.[145] Later, Decostanzi *et al.* prepared telechelic PHU oligomers with trimethoxysilane end-groups for thermoset synthesis, Figure 26.[146] These oligomers were obtained owing to two different routes. The first route was the reaction of diamines with a monomer bearing a cyclic carbonate end-group and a trimethoxysilane end-group. The second route was the reaction of a dicyclic carbonates with a monomer bearing an amine group and a trimethoxysilane end-group.

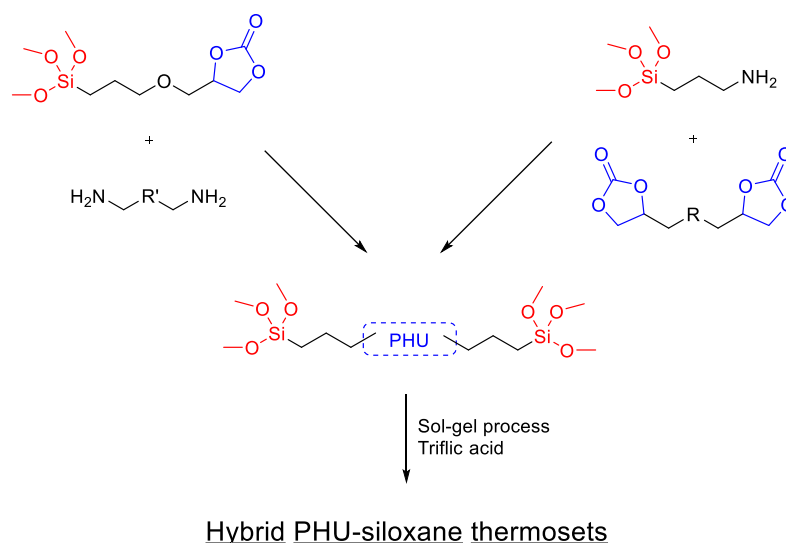


Figure 26. Synthesis of PHU-siloxanes via sol-gel routes from trimethoxysilane-terminated PHUs (Decostanzi *et al.*[146])

Lopez *et al.* also obtained such alkoxy-silane-terminated PHU prepolymers.[147] They prepared hybrid siloxane thermosets by adding (3-aminopropyl)triethoxysilane to a previously prepared PHU prepolymer based on five-membered cyclic carbonates (poly(propylene glycol)dicarbonate) and/or (resorcinol dicarbonate) and Priamine 1074. PHU adhesives were prepared from this monocomponent formulation cured in the presence of acetic acid as catalyst. The group of Endo synthesized a novel cyclic dithiocarbonate bearing a siloxane group $\text{Si}(\text{OMe})_3$. [148–151] They explored several pathways to obtain hybrid cross-linked polymers through the addition of amine with the siloxane moiety, its polycondensation and/or the reaction of the resulting thiols with isocyanates or epoxy groups.

c) Synthesis of composite PHU materials

Composite materials are formed by a polymer matrix filled with fibers, nanoparticles or other solid and non-miscible compounds named fillers. Properties of the matrix and the fillers are significantly different but synergistic when combined. Few papers described the utilization of PHUs as a matrix for the elaboration of composite materials. Although covalent bonds between the fillers and the matrix are not necessarily required in composite materials, only this type of composites will be described in this part.

To prepare PHU/silica hybrid materials, Türünç *et al.* synthesized carbonate functional silica particles, Figure 27.[152] They first prepared silica nanoparticles (≈ 125 nm) *via* sol-gel route and grafted cyclic carbonate functions *via* trimethoxysilane groups. These functional particles were then mixed with carbonated soybean oil (CSBO) and PPG bis-cyclic carbonate and then the mixture was cured with butylenediamine for 24 h at 75 °C. Functionalization of nanoparticles improved the compatibility with the matrix. Compatibility problems were nevertheless observed with CSBO but corrected with the addition of PPG-carbonate segments. Tang *et al.* chose to graft amine groups instead of carbonate groups onto silica nanoparticles.[153] These functional nanoparticles were mixed with bisphenol A-based cyclic carbonate and hexamethylenediamine for curing at 100 °C for 48 h in DMF. They measured a percentage of grafting of 27% and a grafting efficiency of 19%.

Chen *et al.* studied the reprocessability of hybrid PHU composites depending on the surface treatment of silica nanoparticles.[154] Three types of silica nanoparticles were used for this study: standard one with OH groups, amine-terminated silica particles and superhydrophobic silica particles. The reprocessability of PHU network was permitted by exchanges due to two reactions: first, the transcarbamoylation between urethane groups and hydroxy groups; second,

the reversible aminolysis reactions. Hence, they compared in a first time the recovery of E'_{rubbery} values for neat PHUs and PHU composites. After two cycles of processing, hydroxy- and amine-functionalized nanoparticles tended to decrease these values and thus the cross-linking density. In the case of reprocessable PHUs, covalent interactions between the nanoparticles and the polymer matrix were disadvantageous. Indeed, the OH and NH groups at the surface of nanoparticles participated in the dynamic exchange. However, they caused a decrease of the cross-linking density because some links did not “exchange back” and might instead form loops at the surface of particles. On the other hand, the authors observed that the fillers with hydrophobic groups strongly increased the Young’s modulus and the tensile strength compared to neat PHUs. Moreover, this composite exhibited a full recovery of its properties after reprocessing.

Although silica nanoparticles are the most widespread filler in PHU composites, other types of fillers can nevertheless be found. Therefore, Kathalewar *et al.* grafted cyclic carbonates on zinc oxide (ZnO) by addition of carbonate-functional trimethoxysilane, Figure 27.[155] Nanocomposite coatings were prepared by mixing cyclic carbonate based on bisphenol-A, 1-3wt% of particles (with or without grafted cyclic carbonates) and 4,9 dioxadodecane-1,12-diamine as hardener. Curing was performed at 70 °C for 30 min and at 135 °C for an additional hour. The nanocomposite coatings were finally compared to coatings without particles and coatings with non-treated nanoparticles. The hybrid PHU coatings have revealed better properties in scratch hardness and abrasion resistance tests. A very performant anticorrosion protection was also observed for this coating through salt spray exposure, electrochemical potential and Z modulus measurements.

Panchireddy *et al.* synthesized functional SiO_2 or ZnO fillers with cyclocarbonate groups.[156,157] These fillers were added to formulations of cyclic carbonates and amines in order to design reinforced PHU composites. The addition of PHU functional fillers tended to improve thermal and mechanical properties of materials as well as their adhesion performances.

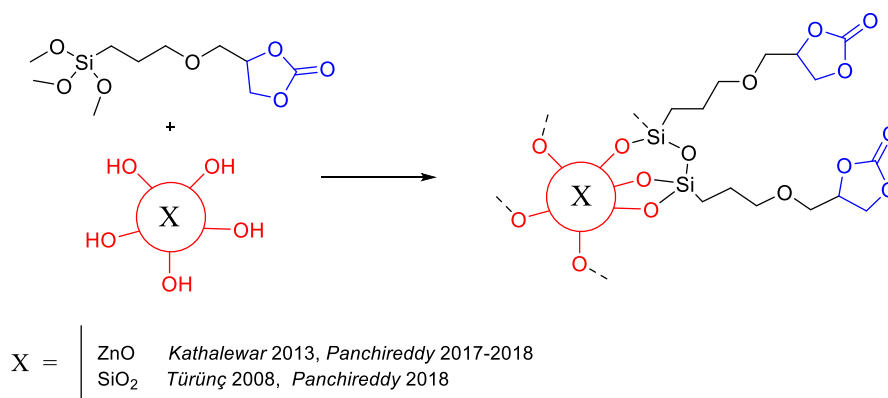


Figure 27. Synthesis of functional nanoparticles through the reaction of alkoxy silane carbonate with ZnO or SiO₂ nanoparticles [152,155–157]

Multi-wall carbon nanotubes (MWCNTs) were also used to prepare hybrid PHU composites.[158] He *et al.* functionalized MWCNTs with COOH, NH₂, Au and Fe₃O₄ groups. The nanotubes were mixed with PHU oligomers containing NH groups in the chain. Diglycidyl ether of bisphenol-A was then added to the mixture to cross-link the composite through the NH groups. Indeed, the amino groups of MWCNT-NH₂ may thus react with the matrix. Higher cross-linking density and Young's modulus were therefore obtained. They also showed that the presence of polar amino groups improved the water absorption.

The addition of inorganic moieties to PHUs has therefore many advantages in order to meet complementary properties. Indeed, the sol-gel process is a new way to cross-link PHUs in mild conditions. On the other hand, urethane functions allow to strongly improve the mechanical properties of siloxanes which are initially quite low. The addition of siloxane units in PHU materials also lead to better thermal stability and higher char content. Different fillers have hence been used in addition with PHUs to prepare hybrid PHU composite materials with promising properties.

4. Conclusion

Many different strategies have been adopted by researchers to synthesize hybrid PHU materials. Few of them have directly mixed cyclic carbonates, amines and amine-reactive monomers in a one-step polymerization. Others chose to first synthesize prepolymers bearing various reactive groups and performed cross-linking in a second step. Finally, organic/inorganic approach has also been adopted through the addition of silicon-based substituents or the elaboration of composite materials. We propose to summarize these different approaches in a global scheme, presented Figure 28 . The general strategies are illustrated in five parts and attributed to the different systems as detailed in the review. These strategies are: (i) the direct mixing and polymerization of the reactants, (ii) the partial conversion of epoxy groups into cyclic carbonates and their co-polymerization with amines, (iii) the synthesis of functional prepolymers and their cross-linking with different reactants, (iv) the synthesis of prepolymers with dangling functional groups and the cross-linking of these prepolymers through the dangling groups, (v) the addition of functionalized fillers to synthesize composite materials.

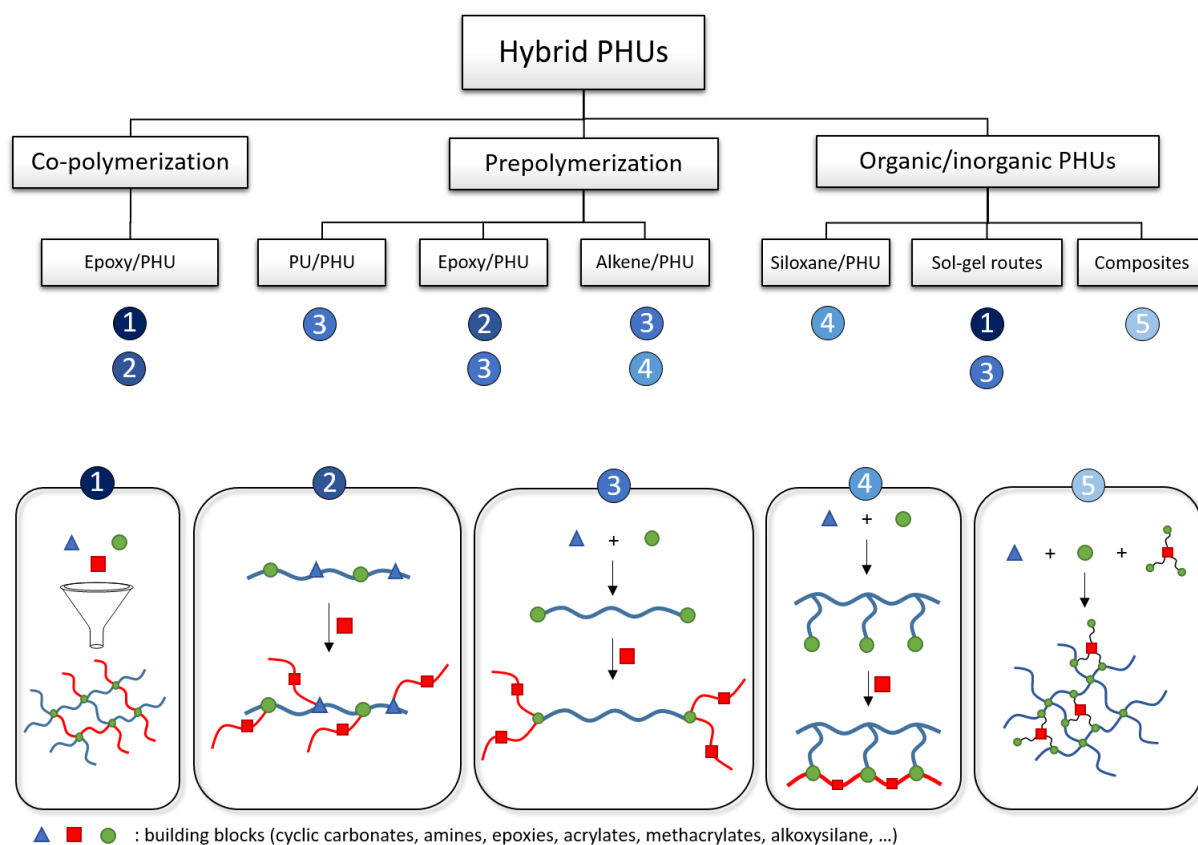


Figure 28. General view of the different strategies to synthesize hybrid PHU materials. These strategies are associated with the different systems, as organized in the review. Five general strategies are presented : (i) the direct mixing of building blocks and their polymerization, (ii) the partial conversion of epoxy groups into cyclic carbonates and their co-polymerization with amines, (iii) the synthesis of functional prepolymers and their cross-linking with different reactants, (iv) the synthesis of prepolymers with dangling functional groups and the cross-linking of these prepolymers through the dangling groups, (v) the addition of functionalized fillers to synthesize composite materials.

IV. Emerging alternatives for PHUs synthesis

In an effort to replace toxic isocyanates in polyurethanes, many studies have struggled to both understand and control the parameters for the synthesis of polyhydroxyurethanes. The key parameters of the aminolysis reaction have been deeply studied and their limitations highlighted. Besides, many cyclic carbonate monomers have been synthesized to increase the reactivity, the conversion or the molar masses of PHUs and to cover a broad range of properties. Special focus have also been put to fulfill the green chemistry requirements such as the use of green reactants, less solvents or catalysts and low temperature of polymerization. Several limitations remained nevertheless strong obstacles to the development of PHUs in an industrial scale. To overcome these limitations hybrid systems have appeared as very promising pioneering routes. Many works on hybrid PHUs were presented, illustrating the different approaches and strategies to co-polymerize PHUs with other systems, allowing to meet

complementary properties. Other emerging solutions have also appeared to provide new horizon to PHUs materials.

The sustainable development in polymer science has recently drawn attention to recycling and reprocessing networks. Therefore, strong attention has been paid to self-healing polymers thanks to their capability to recover their total properties after reprocessing. The incorporation of dynamic bonds into cross-linked materials is now a major challenge. A first approach to this new class of polymers involves dissociative bond exchange mechanism. The covalent bonds can be broken under a stimulus and can be reformed with another. Diels-Alder reaction or disulfide exchange are mainly used for this purpose.

Dolci *et al.* synthesized cyclic carbonate-terminated prepolymers between furfuryl cyclocarbonate ether and bismaleimide oligomers. The polymerization of these prepolymers with amines afforded thermoresponsive PHUs.[159,160] Karami *et al.* compared such cyclic carbonate prepolymers to their epoxy-equivalent prepolymers.[161] Zhang *et al.* obtained a series of NIPU prepolymers with furan groups from transurethanization reaction.[162] These prepolymers were cross-linked with bismaleimides and demonstrated thermo-reversibility properties. Dynamic disulfide bonds have also been used with PHUs to enable reprocessing.[163] Incorporation of disulfide-containing cystamine in PHU synthesis have shown good reprocessing properties with high recovery of cross-linking density and moderate mechanical properties under mild conditions. On the other hand, Matsukizono and Endo used the reversibility of acetal structures to perform reworkable poly(acetal-hydroxyurethane) networks.[164]

The aminolysis is not the only reaction occurring between cyclic carbonates and amines. It has been shown that numerous side-reactions could occur which are often presented as drawbacks for conversion and molar masses of cyclic carbonates. Nevertheless, other approaches interestingly took advantage of these side-reactions to access to novel utilization of PHUs. Indeed, the reversibility of the aminolysis, the transcarbamylation and the transesterification reactions could give access to reprocessable PHUs. Few recent publications intended to synthesize PHU networks with reprocessable properties or PHU vitrimers. Reprocessable PHUs were synthesized from both 5-membered or 6-membered cyclic carbonates.[165–168] Chen *et al.* also successfully obtained reprocessable PHUs composites.[154]

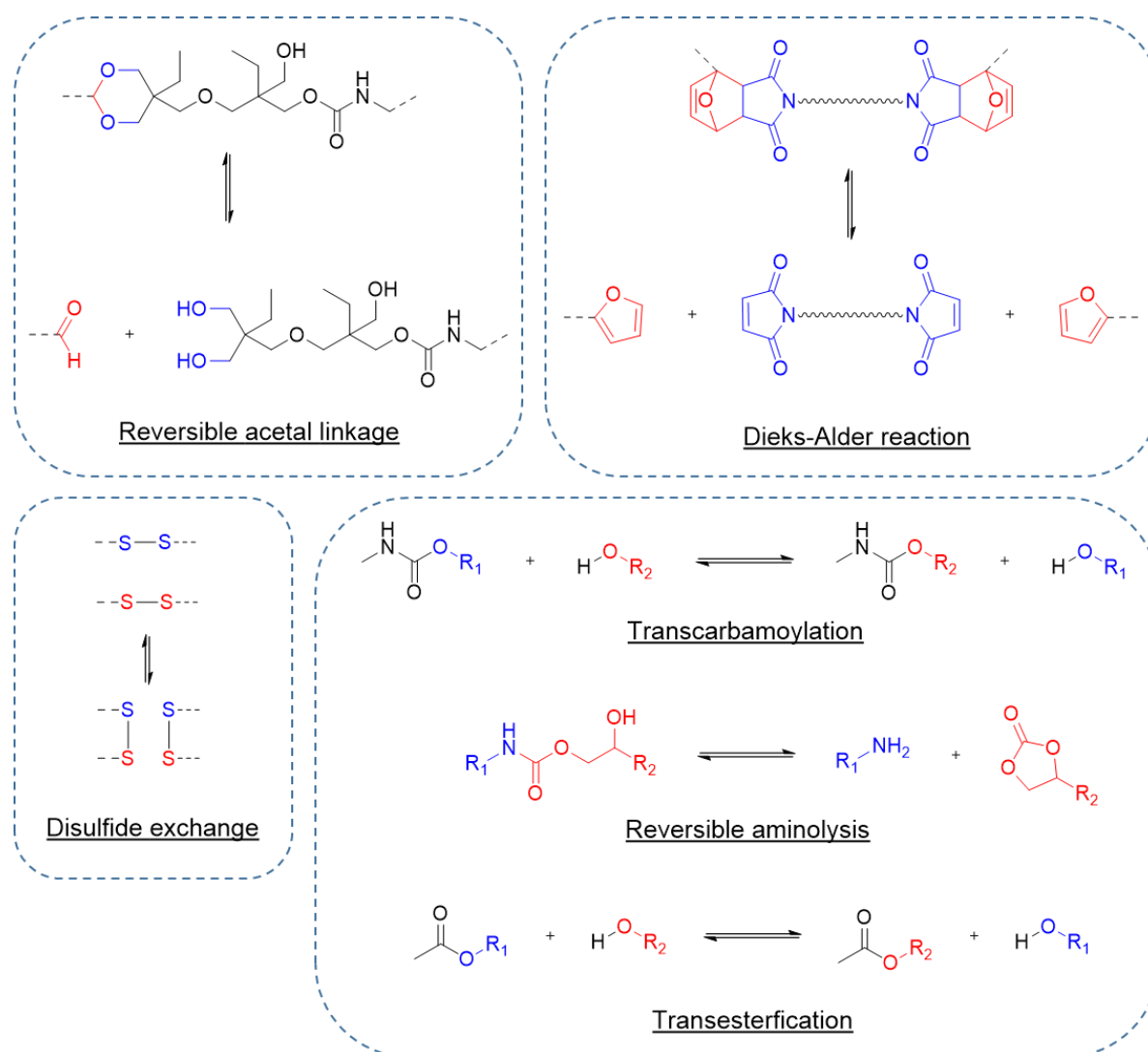


Figure 29. Example of reversible reactions used for the synthesis of reprocessable PHUs

Many studies dealt with polyhydroxyurethanes and their promising properties. Recent outlooks in the field of reprocessable PHUs have led to new developments, new designs and new properties. Some examples of reversible reactions involved in the synthesis of reprocessable PHUs are presented Figure 29. Their limitations have first appeared as strong brakes for their developments but new solutions have been conceived to circumvent them. They have also been used to design new structures and access to polymers with tunable architectures. Therefore, reprocessable PHUs offer new field of exploration for PHUs synthesis.

V. Conclusion

The development of PHUs has been strengthened in recent decades and new opportunities have emerged. The substitution of isocyanates in the PUs synthesis has drawn increasing attention to this new class of polymers. As a green and less toxic design, PHUs are promising candidates to

replace PUs. Numerous routes led to the synthesis of cyclic carbonates and many studies attempted to develop greener routes or to use renewable feedstock. PHUs are indeed in agreement with green chemistry and sustainable development in an effort to avoid toxicity issues, favor renewable content and CO₂ utilization. The high density of hydrogen bonds, partly favored by the additional hydroxyl group close to the urethane function, confers to PHUs excellent adhesion properties and strong thermal and mechanical performances. The main parameters affecting the aminolysis of cyclic carbonates by amines have been deeply studied in terms of structure and kinetics. Many scientists described the influence of amine and cyclic carbonate substituents or the size of carbonate-ring. The roles of temperature, time, solvents, catalysts or molar ratio have also been clearly identified. Despite a growing knowledge on the aminolysis reaction, several drawbacks however hindered the industrial development of PHUs. These limitations are generally the low kinetic of reaction, the low conversion obtained and the low molar masses reached. Several solutions have been nevertheless proposed to design PHUs in milder conditions, including appropriate reaction conditions, catalysts or new processes. Therefore, side-reactions could be disfavored and several drawbacks avoided.

New investigations have also emerged to propose new strategies to overcome these limitations. Among them, the contribution of other polymer systems in the PHUs synthesis has appeared very promising. This growing interest to hybrid PHUs, also called H-NIPUs, offers new alternatives for their development. High thermal, mechanical and adhesion performances of PHUs could be combined with systems of higher reactivity and other designs. Different strategies have been performed to mix PHUs with other polymers. First, the co-polymerization in one blend of cyclic carbonates, amines and amine-reactive moieties. The formed network is a mixture of the different systems. However, the final composition of the polymer cannot be properly defined since the reactivities of the reactants can be very different. Another strategy largely described is the synthesis of hybrid PHUs in several steps *via* the synthesis of prepolymers. This route allows to design oligomers with targeted length, functionality and with the desired reactive functions. This strategy gives access to a broad number of designs with reactive functions at different positions, in the main chain, in telechelic positions or hanging off the main chain. These prepolymers are usually cross-linked in a last-step through their reactive functions. Finally, hybrid PHUs with organic-inorganic structures have been presented. This strategy involves the addition of inorganic moieties such as siloxanes or the addition of fillers for hybrid PHU composites. Different functions are commonly used for the synthesis of hybrid PHUs. Amine-reactive functions are often found such as epoxies, acrylates or maleimides. Isocyanates have also been used in addition to PHUs to prepare PU-PHU hybrid polymers.

Other types of polymerization were also found in literature such as sol-gel routes with alkoxysilanes or polymerization of olefins through radical polymerization or metathesis. However, attention must be paid to the toxicity of additional moieties in hybrid synthesis. The use of systems with toxicity comparable to those of isocyanates should be avoided in order to be consistent with PHUs requirements.

Hence, hybrid PHUs pave the way to an industrial development of PHUs with the access to combined properties and solutions to circumvent their limitations. The higher reactivity of epoxies or acrylates toward amines may lower the reaction time and PHUs may be obtained in milder conditions. The good adhesion properties of PHUs combined to the fast curing of acrylates and methacrylates are also very promising for coatings applications. New properties are also favored with the addition of siloxanes. Their low viscosity may increase the molecular motions and balance the high density of hydrogen bonds. Furthermore, their flexibility and thermal resistance are very interesting additional properties. Therefore, hybrid PHUs appears as new designs for controlled architectures and materials with specific properties. New perspectives have also recently appeared in PHU synthesis. The identification of reversible reaction in PHU systems has opened the field of reprocessable PHUs. The interest for PHUs is still in expansion.

Declaration of Competing interest

The authors declared that there is no conflict of interest.

Acknowledgements

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