Hybrid Nonisocyanate Polyurethanes (H-NIPUs): A Pathway towards a Broad Range of Novel Materials

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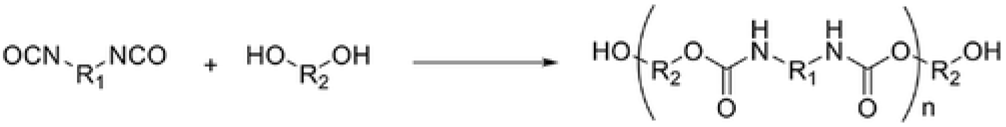
Abstract

The increasing demand for using less toxic and dangerous products has fostered the development of nonisocyanate polyurethanes (NIPUs). Despite several years of progress within the search for these novel materials, they are still facing difficulties to reach the market. This may be due to the low mechanical properties obtained, which can be explained by the difficult access to high molar masses polymers. The combination of NIPUs with other types of polymers, thus forming polymer–polymer hybrid-NIPUs (so called H-NIPUs) can be an interesting alternative for the valorization of NIPUs though. This review describes the latest advancements in the developments of H-NIPUs, with a specific focus on the combination with epoxy, polyacrylic, and silicium-containing polymers. Finally, the emerging field of combining NIPUs with biopolymers is discussed. A specific focus on the synthetic challenges is provided, as well as their resulting influence onto the final material properties, thus showing how the synergistic combination of NIPUs with other polymers can be a promising pathway toward the formation of novel materials.

1 Introduction

Since their discovery in 1937 by Bayer,[1] polyurethanes (PUs) have become of major interest within the polymer community. These materials are produced through the polyaddition reaction between a diol (or polyol) and a diisocyanate—**Scheme 1**.



Scheme 1: Reaction of a diol and a diisocyanate to yield polyurethane.

By varying the monomer functionality and structure, PUs with an extremely broad variety of thermomechanical properties can be produced. These materials find applications in a wide range of fields including foams, coatings, adhesives, and elastomers among others. The PU formation process typically consists of a two-step process. First, a soft polyol is reacted with an excess of diisocyanate in order to form a homotelechelic NCO-terminated PU prepolymer. In a second step, the addition of a shorter diol (yielding PUs) or diamine (yielding polyurethane-urea—PUU) allows for chain extension. PUs are composed of a succession of hard (urethane and urea units) and soft (polyol) segments that tend to organize so that hard nanophases are distributed within the soft phase. This allows for the formation of unique thermoplastic elastomers exhibiting elasticity as well as mechanical strength.

The main drawback of these otherwise high-performing materials is that isocyanates are used in their synthesis. Studies have demonstrated the potential link between prolonged exposure time to isocyanates and health issues such as asthma, dermatitis, and in some cases poisoning.[2, 3] Some isocyanates are even classified as CMR (carcinogenic, mutagenic, reprotoxic).[2, 4, 5] The isocyanates not only exhibit a very high toxicity, but also require the use of phosgene in their synthesis. Phosgene is a very toxic gas itself, which can lead to death in case of inhalation. All of this has raised awareness on the need for alternative pathways towards the synthesis of nonisocyanate polyurethanes (NIPUs).

In spite of about two decades of research in the field of NIPUs, the replacement of the isocyanate-based pathways still appears very challenging. This is certainly because of the fact that NIPUs are still cornered by synthesis limits that have yet not been overcome. Therefore, the scope of NIPU materials is still very narrow. Some examples have been published claiming the formation of NIPU (and especially poly(hydroxy urethane)) elastomers,[6] adhesives,[7, 8] foam,[9, 10] coatings,[11] hydrogels,[12] vitrimers,[13] or latexes,[14, 15] but there are still very few and often limited to the lab scale, notably because of the scarcity of the monomers that are usually not commercially available, and the low molar masses obtained upon synthesis. In this regard, the development of hybrid materials appears as a potential solution for further valorization of NIPUs. Hybrid-NIPUs (or H-NIPUs) consist in the synthesis of materials composed of two polymers (or polymers and oligomers), one of them being a NIPU.

Hence, the objective of this review consists in the detailed description of how H-NIPUs can become a solution for the development of novel materials, exhibiting a broad range of properties. To do so, a fast description of the chemistry of NIPUs will be provided to focus later on the synthesis and properties of the different types of H-NIPUs that can be encountered in the scientific literature.

2 NIPUs

The synthetic routes for the production of NIPUs have been reviewed by several authors.[16-19] Cramail and co-workers suggested a classification of the different existing pathways according to their dependence on phosgene and/or isocyanate (**Figure 1**).[16]

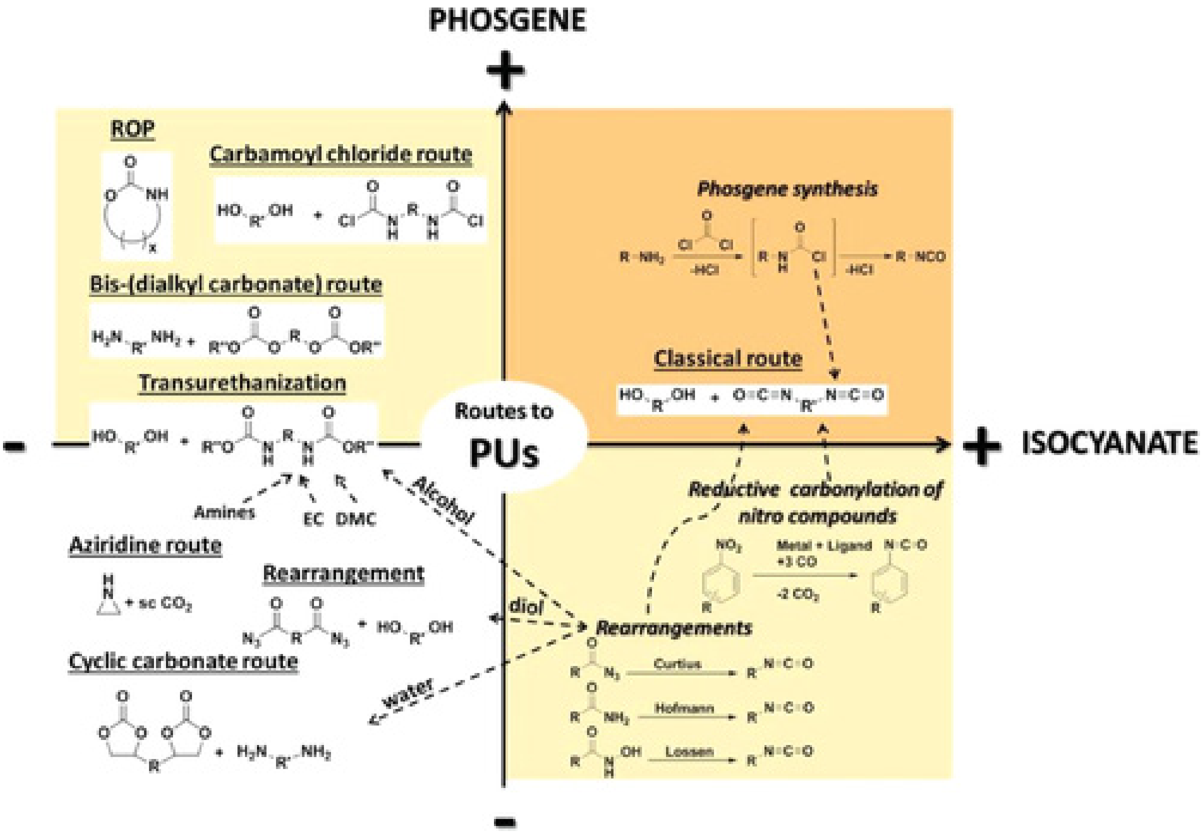


Figure 1: Isocyanate-free and phosgene-free routes towards polyurethanes—from Cramail and co-workers.[16] Reproduced with permission.[16]

Among the less demanding routes in phosgene and/or isocyanate, the copolymerization of CO_2 with aziridines appears as an interesting alternative.[20] This route however still poses challenges in terms of the synthesis of aziridines through green pathways. Their toxicity can also be regarded as an issue. Rearrangement reactions of acyl azide and their subsequent polycondensation reaction with diols—relying on the formation of an in situ isocyanate moiety upon polymerization—is another potential pathway.[21, 22] However, these alternatives are less appealing than the transurethanization process and the aminolysis of cyclic carbonate compounds, which involve the use of less toxic reactants in the synthesis of the monomers.

The transurethanization process and the aminolysis of cyclic-carbonates rely on different monomers, different mechanisms and do not yield the same products (**Figure 2**).

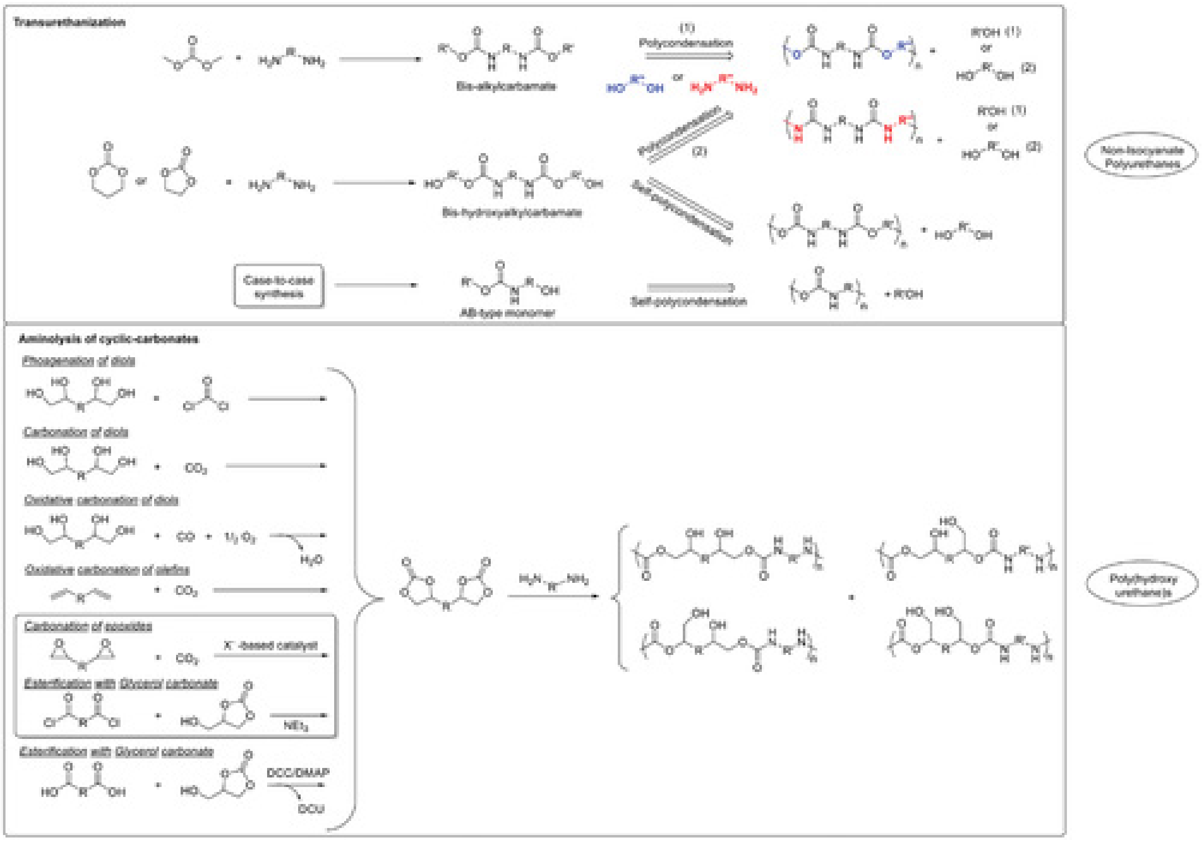
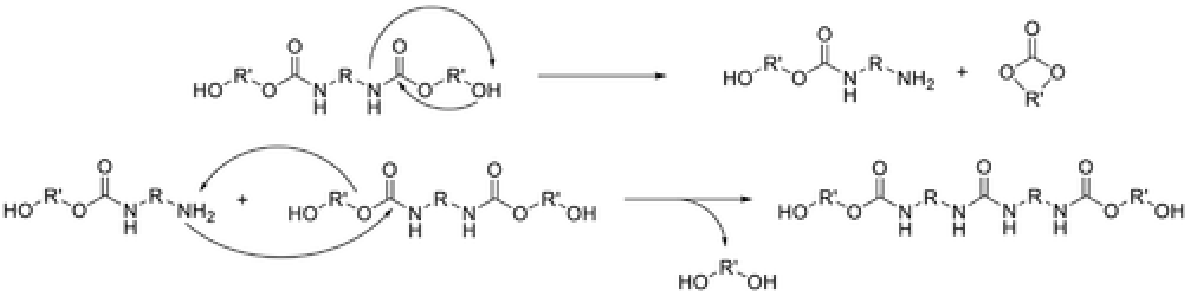


Figure 2 Transurethanization and aminolysis of cyclic-carbonates towards the formation of nonisocyanate polyurethanes.[16, 24]

The transurethanization (also called transurethane reaction or transcarbamoylation) consists in the reaction of an alcohol with a carbamate. The bis-alkyl carbamates, bis-hydroxyalkylcarbamates formed are reacted with diols and/or diamines yielding the polyurethane urea. The reaction is carried under vacuum to shift the equilibrium and achieve high degree of polymerization. The advantage of this route is that such technology is very close to the traditional isocyanate-based process and yields polymers with chemical structures very close to the ones already known.

Whereas the condensation with diols, yielding NIPUs, usually does not suffer from side reactions, the condensation with diamines, yielding NIPUreas, involves N-alkylation side-reactions, hence leading to a deviation from stoichiometry,[23] which affects the degree of polymerization achievable. Moreover, backbiting side-reactions can occur yielding urea by-products—**Scheme** 2. All of this generally leads to the generation of low molar mass polymers that is a hurdle for industrial implementation.



Scheme 2 Backbiting followed by urea formation in the transurethanization reaction of bis-hydroxyalkylcarbamates.[16]

On the other hand, NIPUs can also be formed by aminolysis of cyclic carbonate compounds. The ring opening of the cyclic carbonate yields polyurethanes containing pendent hydroxyl-groups—also called poly(hydroxy urethane)s or PHUs. Depending on the ring-opening mechanism at stake, either primary or secondary hydroxyl groups can be formed. This pathway is interesting since it is a polyaddition. Therefore, no by-product has to be removed for the polymerization to proceed. The formed PHUs can be considered as novel materials since the presence of those OH-moieties provides specific properties to the formed materials, as well as the potential for further functionalization.

An exhaustive description of the synthesis and underlying challenges in NIPU chemistry has already been extensively described in numerous and several reviews[16, 17, 19, 24, 25] and is out of the scope of this review. Therefore, only a brief overview of the remaining limitations of NIPU chemistry will be provided in the next section and the reader is encouraged to refer to the previous reviews should more detailed explanations be needed.

Moreover, excellent reviews on the synthesis of the cyclic carbonates are available.[16, 19, 24] Among the different chemical pathways available, the use of CO_2 as a renewable C1 source for monomers benefits from a growing interest as described in the review from Detrembleur and co-workers.[19]

The aminolysis of cyclic carbonates is a complex reaction that in most cases yields low molar masses that limit the mechanical properties. The strategies aimed at increasing the molar mass of the PHUs are summarized in **Figure 3** and include enhancing the reactivity of bis-cyclic carbonates and amines structure and modifying the reaction conditions. The reader is referred to the existing reviews on the subject.[16, 17, 19, 24]

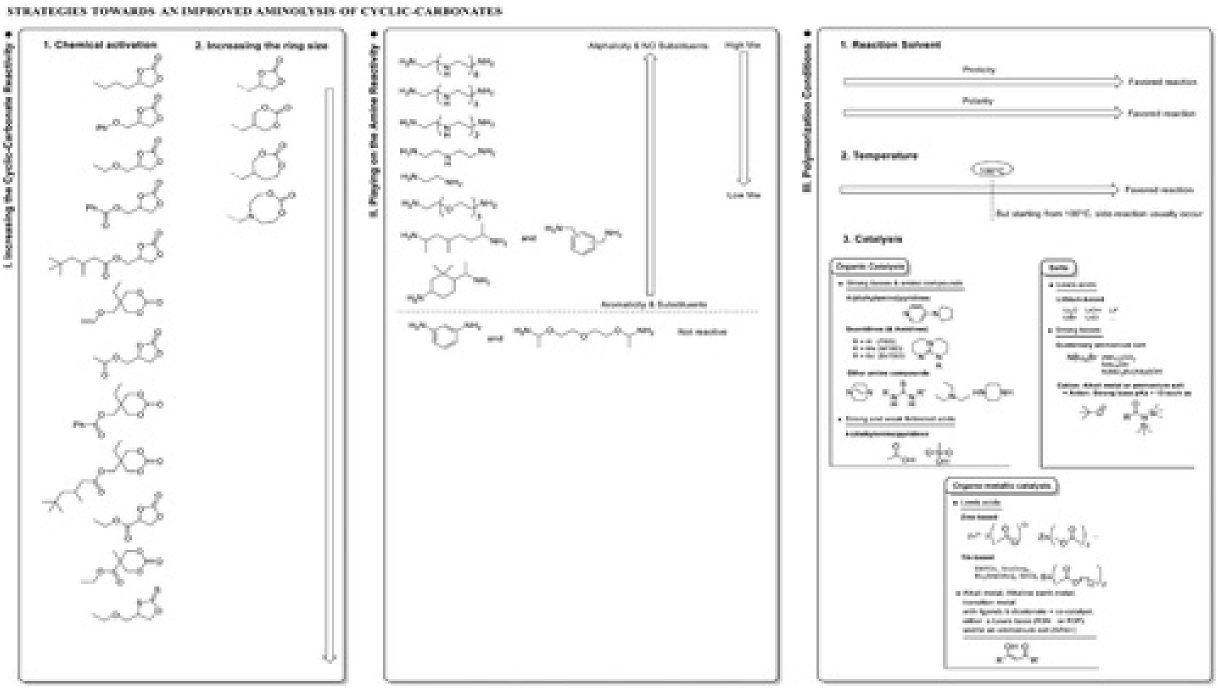


Figure 3 Strategies towards an improved aminolysis of cyclic carbonates.[16, 17, 24]

The growing knowledge of the structure-properties relationship of NIPUs has been summarized in a review from 2016.[26] The potential uses of NIPUs are summarized in **Figure 4**. A review from Sardon and co-workers has also been published in 2021 summarizing the trends in NIPU development, and the different challenges yet to overcome for NIPUs to reach commercialization with respect to the targeted applications.[27] The same group reviewed the use of NIPs for adhesives and coatings.[28]

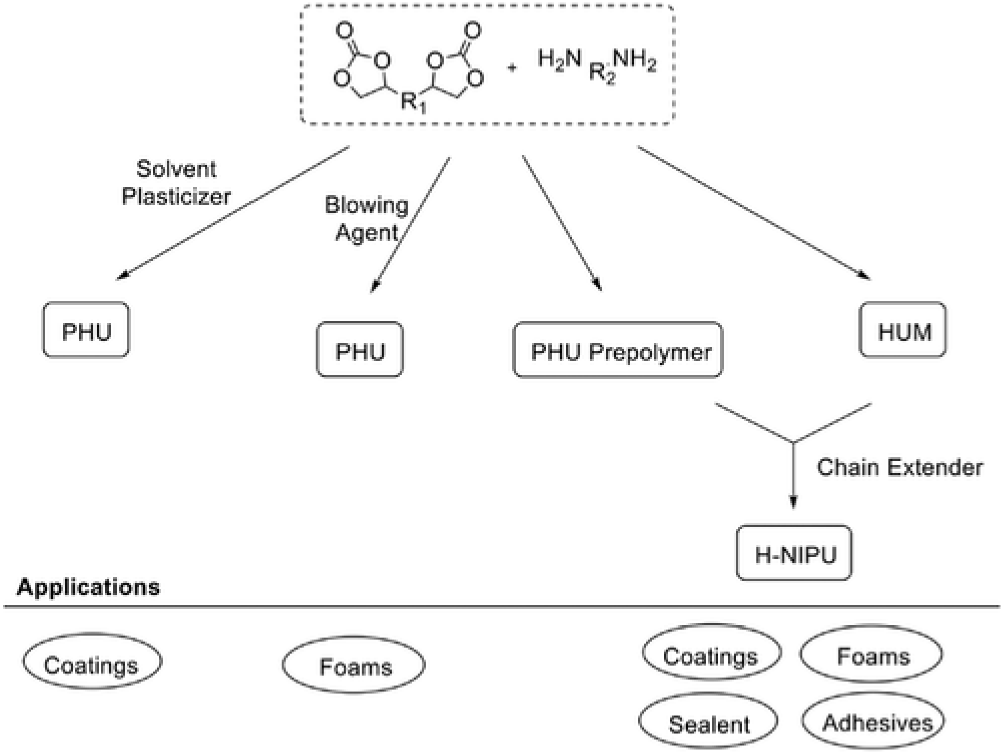


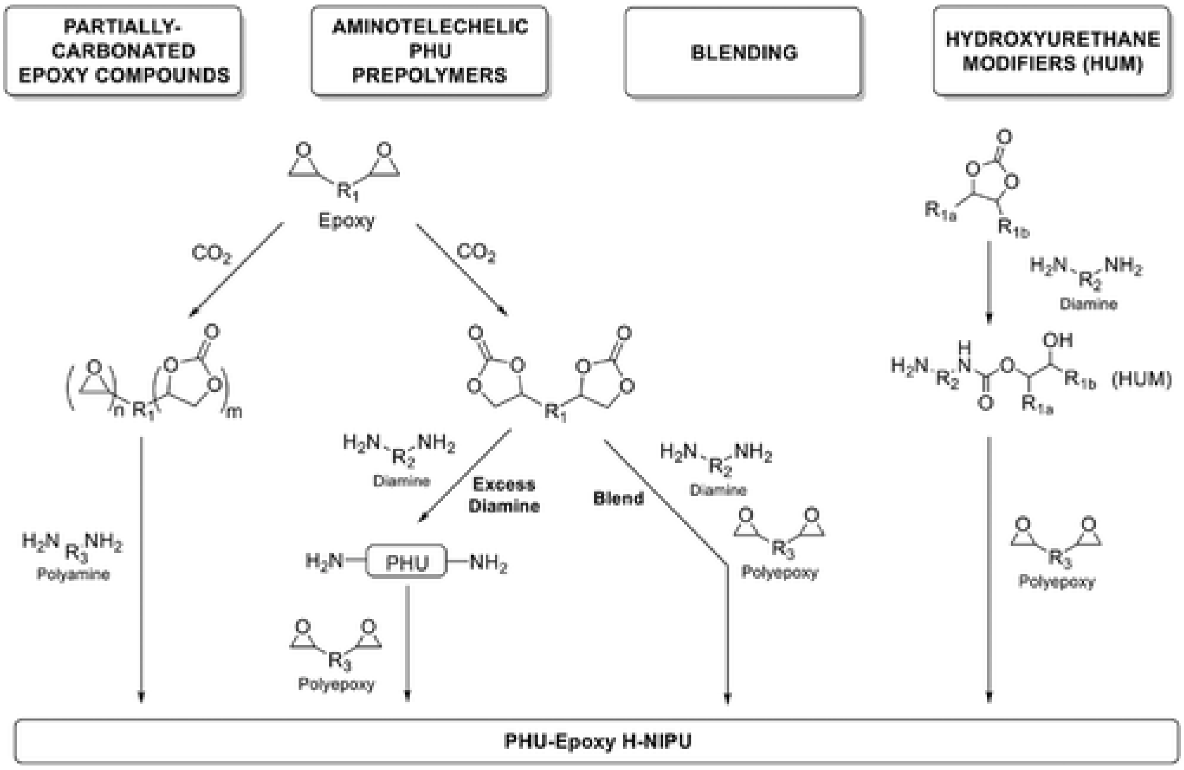
Figure 4 Potential valorization pathways for NIPUs towards their industrial implementation.[17]

3 Hybrid NIPUs: Novel Materials for a Broad Range of Properties

As discussed in the previous section, the low molar masses currently obtained with the NIPUs preclude their commercial use. In this context, polymer–polymer hybrids represent an opportunity for the practical use of NIPUs. Polymer hybrids aim at achieving properties that are a synergistic combination of those of the constituting materials. Polymer–polymer hybrids can be formed by simply mixing two polymers together, but this often leads to phase separation especially when the two polymers have a poor compatibility.[29-32] Phase separation can be avoided by grafting and this represents an opportunity for NIPUs because the high molar mass can be provided by the other polymer. Therefore, one can imagine as many different hybrids for NIPUs as they exist for polyurethanes. What follows is a review of hybrid NIPUs.

NIPU–Epoxy

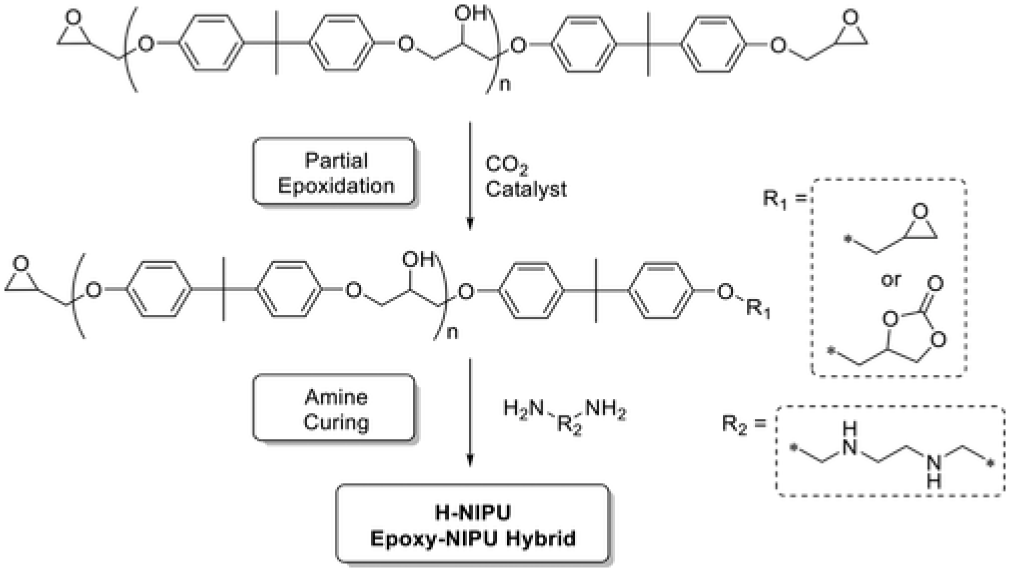
In the first NIPU–epoxy hybrid, NIPUs were used as modifiers in order to improve the flexibility of epoxy resins for lacquers and adhesives.[33] Four different chemical pathways have been used for the synthesis of NIPU–epoxy hybrids (**Scheme 3**).[17] The first route consists in reacting partially carbonated epoxy compounds with a polyamine. Polyamines are able to react with both the epoxy and carbonate moieties to yield NIPU–epoxy hybrids. The second alternative is a two-step process for which an amine homotelechelic NIPU–prepolymer is formed first. Then, the amine-terminated NIPU reacts with a polyepoxy yielding the NIPU–epoxy hybrid. The third possibility consists in blending a carbonated epoxy resin with an epoxy resin and an amine as a curing agent. Finally, the so-called hydroxy urethane modifiers (HUM) are obtained by forming a mono-hydroxy urethane that upon reaction with a polyepoxy yields the final NIPU–epoxy hybrid.



Scheme 3 Different routes towards the formation of polymer–polymer NIPU–epoxy hybrids.[17]

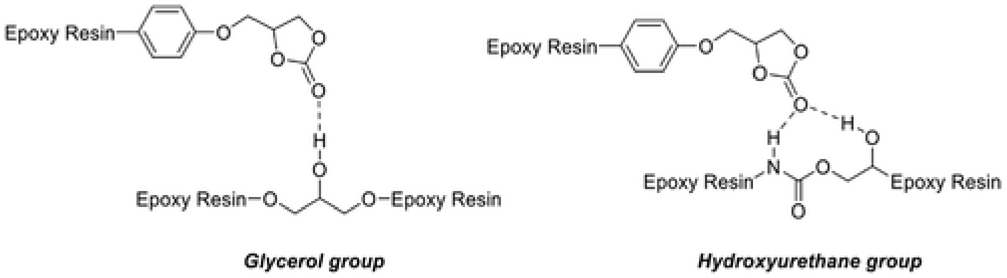
3.1.1 Epoxy–NIPUs through the Reaction of Partially Carbonated Epoxy Compounds

Rokicki et al. pioneered the synthesis of NIPU–epoxy hybrids by partially carbonating a bisphenol-A diglycidyl ether (BADGE)-based epoxy resin with CO_2 and then curing with triethylenetetramine (TETA) to form a 3D network—**Scheme 4**.[33]



Scheme 4 BADGE-based H-NIPU through the amine curing of a partially carbonated epoxy resin.

The authors noticed an increase in viscosity with an increasing degree of carbonation of the modified epoxy resin, that was explained by the presence of a high density of H-bonds between the oxygen of the C═O group of the carbonate and the hydroxyl group of the forming polymer. Later the effect of carbonation on the viscosity was found to be epoxy-resin dependent.[34] The reactivity of the partially carbonated macromonomer with TETA was measured by determining the gelation time. It was found that the gelation time decreased by increasing the carbonate content, hence suggesting that the energetic barrier for the reaction was higher for the epoxy than for the cyclic carbonate. Interestingly, the introduction of five-membered carbonate moieties (both internally less stressed and of lower functionality for curing than the 3-membered epoxy) also allowed to decrease both the intensity of the reaction exotherm as well as the time needed to reach it, making such a process very interesting for production purposes. These findings were confirmed by the work of Bürgel who ran a mechanistic study of this polymerization process.[35] The functionality of the curing amine played a role in the preference of the amine to react either with the cyclic carbonate or with the epoxy moiety. Primary amines would rather react with carbonate moieties whereas secondary amines would react with both carbonate and epoxy moieties.[25,35,36] Increasing the reaction temperature led to higher conversions,[36, 37] shorter gelation times,[33, 34, 37] lower viscosity (explained by weaker H-bonding effects),[33, 37] and promoted reaction with the epoxy moiety to a higher extent.[33, 37] However, side reactions were also noticed starting at 100°C, suggesting that there is room for optimization of the reaction temperature, which can be system-dependent.[35] When considering thermo-mechanical properties of the formed H-NIPUs, superior properties were obtained for the carbonated epoxy resins, especially in terms of impact resistance, hardness, and compressive strength as compared with the unmodified epoxy resin.[34] Good tensile properties could also be obtained, that were attributed to a physical crosslinking resulting from the presence of unreacted cyclic carbonate moieties forming H-bonds with the ▯NH-functions of the hydroxyurethane moieties formed upon polymerization—**Scheme 5**.

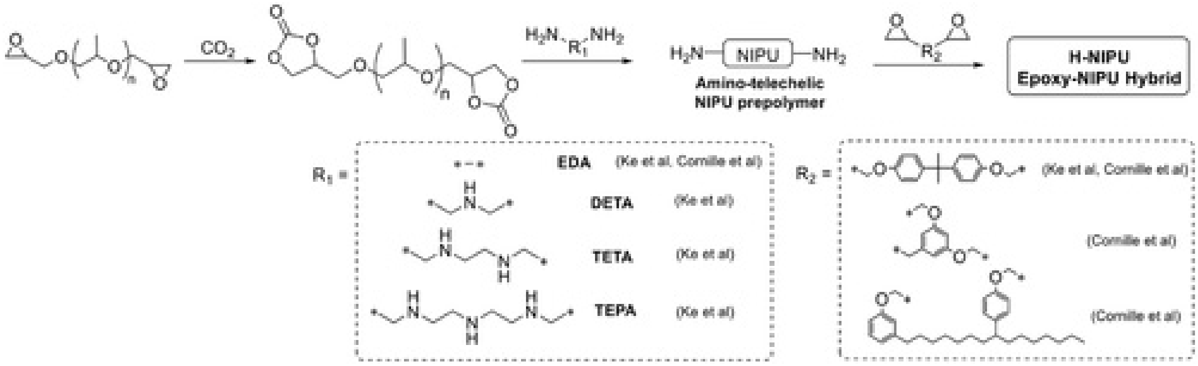


Scheme 5 Physical crosslinking by H-bonding in epoxy–NIPU hybrids.

Figovsky et al. patented a process in which partially epoxidized compounds were cured with an epoxy resin and oligomeric amines for the preparation of H-NIPUs to be used for constructive glues, sealants, coatings, and construction materials.[38]

3.1.2 Epoxy–NIPUs through the Reaction of Aminotelechelic NIPU Prepolymers with Curing Agents

An epoxy resin is completely carbonated with CO_2 and the resulting bis-cyclic carbonate reacted with a diamine. When an excess of diamine is used an amino telechelic NIPU prepolymer is obtained. The amino-telechelic NIPU (and more specifically in this case a PHU) prepolymer is cured with an epoxy compound (**Scheme 6**).[39-41] This technology is particularly appealing for the design of materials with defined sequences of soft (NIPUs) and hard segments (epoxy) within the final 3D-hybrid network.[39, 40]



Scheme 6 NIPU–epoxy H-NIPU formation through the preparation of poly(propylene oxide) bis-cyclic carbonate amino homotelechelic prepolymer prior to further curing with a bis-epoxy compound.[39-41]

Most published occurrences rely on the preparation of poly(propylene oxide) bis-cyclic carbonate-based amino-telechelic prepolymers. The challenge in this reaction is to form prepolymers of sufficiently high chain length while limiting side reactions. The effects of the type of diamine[40, 41] and process parameters such as the reaction time,[39, 41] the reaction temperature,[41] and catalysis[41] were investigated. In general, low molar masses (2000–5700 g mol^{-1}) were obtained due to the excess of diamine used. For an AA + BB step-growth polymerization, this limits the maximum degree of polymerization attainable.

When curing the amino-telechelic prepolymers with bisphenol-A diglycidyl ether (BADGE),[41] the ratio between the amine and epoxy moieties played an important role in the determination of the microstructure of the final hybrid materials. When too low NH_2/epoxy ratios were used, carbonate moieties could still be observed by infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) analyses revealed non-homogeneous microstructures, that were attributed to an incomplete crosslinking of the material. Increasing the NH_2/epoxy ratios led to a better crosslinking of the material as shown by tensile and swelling tests, and SEM analyses (continuous morphologies were observed). Finally, when too high amounts of diamine were incorporated into the formulation, more linear structures of H-NIPUs were obtained and higher elongations at break could be obtained through tensile tests.

Shortening of the gelation times was observed when multiamines containing secondary amines (e.g., diethylene triamine, DETA; triethylene tretramine, TETA; and tetraethylene pentamine, TEPA) were used in the curing process with BADGE. This was attributed to the reaction between the inner secondary amines and BADGE that increased the crosslinking degree of the final materials.[40, 41] As expected the higher the crosslinking the higher the Young's modulus, and the tensile strength, and the lower elongation at break.[41]

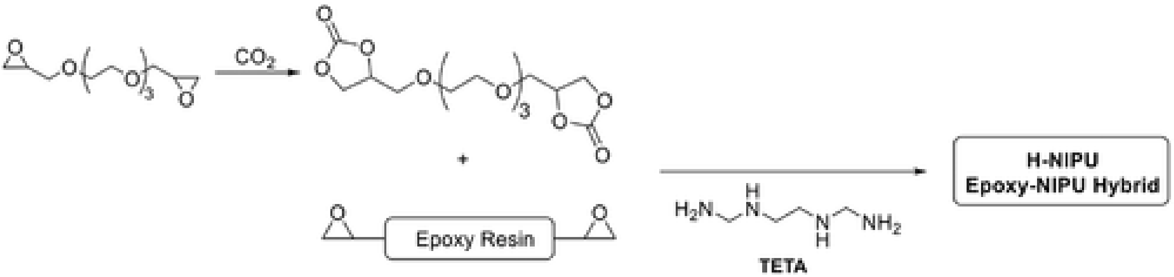
Mannari and co-workers[42] reported the design of room temperature curable coatings based on amino-telechelic NIPUs and trimethylolpropane triglycidyl ether. They synthesized a series of various amino-telechelic NIPUs, by reaction of carbonated-epoxy compounds with different diamines (employing amine/cyclic carbonate ratios of 1.4 or 1.7). Curing was performed at room temperature in a mixture of toluene, methylisobutylketone (MIBK) and Oxsol 100 (Parachlorobenzotrifluoride), added to adjust the viscosity of the mixture. The addition of free amine in the curing formulation was also tested as a way to accelerate the rate of curing. The resulting coatings were tested in terms of flexibility at -54 °C, curing time, and resistance of the samples to various chemical conditions (methylethylketone, lubricating oil, hydraulic fluid among others) in order to obtain epoxy–NIPU coating suitable for aerospace specifications. Isophorone diamine-based coating exhibited in general superior performances with respect to aliphatic amines (including trimethyl hexamethylene diamine), especially when dealing with chemical resistance (enhanced MEK resistance). Isophorone diamine was also found to exhibit faster curing rate when compared to 4,4’-diaminodicyclohexylmethane, probably thanks to a higher reactivity.

Ke et al. studied the influence of using methanol and the mode in which the reactants were charged into the reactor on the amine telechelic NIPU prepolymer.[43] It was found that the molar mass of the prepolymer increased in the presence of methanol that catalyzed the ring-opening reaction. However, urea was formed. Addition of the diamine in semicontinuous reduced the urea content and increased the molar mass of the prepolymer (up to $M_n = 4300$ g mol^{-1}). Prepolymers of different molar masses were cured with BADGE yielding NIPU-epoxy hybrids. It was found that the higher the molar mass of NIPU oligomers, the higher the gel content (>90%) and the higher the Young's modulus and the tensile strength.

Harder materials exhibiting a lower swelling index and a higher degree of crosslinking were obtained when using such a tri-functional epoxy compound as curing agent.[39]

3.1.3 Epoxy–NIPUs through the Reaction of a Mixture of Carbonated Epoxy Resins and Epoxy Resins with Curing Agents

An epoxy resin is completely carbonated with CO_2 and the resulting bis-cyclic carbonate reacted with a diamine. Rokicki and Łaziński tried to prepare H-NIPUs from a mixture of a commercial epoxy resin (Epidian 6), cured with an aliphatic cyclocarbonate resin based on triethylene glycol diglycidyl ether (shortened TGDEC below) and TETA—**Scheme 7**.[34]



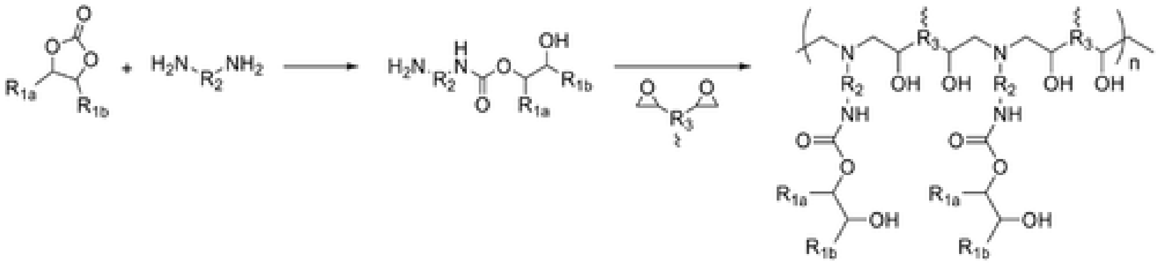
Scheme 7 NIPU–epoxy H-NIPU formation through the preparation of triethylene glycol diglycidyl ether bis-cyclic carbonate (TGDEC) homotelechelic oligomer prior to further curing with a bis-epoxy resin and triethylenetetraamine (TETA).[34]

The viscosity of TGDEC was higher than that of the native triethylene glycol diglycidyl ether (the dynamic viscosity of the carbonated epoxy resin ranged from about 8000 mPa s (at 20 °C) to 2000 mPa s (at 45 °C), while it ranged from 200 mPa s (at 20 °C) to 90 °C (at 45 °C) for the native epoxy resin. However, it was still lower than the viscosity of the Epidian epoxy resin alone (from about 35 000 mPa s (at 20 °C) to 4000 mPa s (at 45 °C)). Therefore, the higher the content of TGDEC, the lower the viscosity of the mixture of epidian and TGDEC. When curing those mixtures with triethylenetetraamine (TETA), the polymerization behaviors and the resulting properties of the epoxy–NIPU hybrids were very similar to the ones described in the case of partially carbonated epoxy resins.[33] The higher the content in TGDEC, the shorter the gelation time and the lower the exotherm measured by DSC. When comparing the Epidian resin cured with TETA alone with the hybrids, no significant change was observed in hardness. However, the higher the TGDEC, the higher the impact resistance. Moreover, hybrids also exhibited higher tensile strengths, yield strength, and also higher elongations at break than the epidian–TETA epoxy resin. These outcomes may look surprising since the degree of crosslinking is lower in the case of hybrids because the functionality of cyclic carbonates is lower than the one of epoxy moieties. The authors attributed the increased mechanical properties to the establishment of H-bonds physical crosslinking.

The ratio between the carbonated telechelic PHU and the epoxy and amine used affect the mechanical properties of the Epoxy-NIPU hybrids.[44] In the case of carbonated ethylene glycol diglycidyl ether (bisCC-EDGE) cured with BADGE and DETA, both tensile strength and elongation at break increased with bisCC content. This simultaneous increase was attributed to the intermolecular H-bonding and to the plasticization caused by the unreacted carbonate moieties. Above 15–20 wt% of bisCC the crosslinking density decreased that much that both tensile strength and elongation at break decreased. Similar trends were obtained with NIPU–epoxy noncrosslinked blends with poly(propylene carbonate), suggesting the importance of the presence of those H-bonds for the properties of the final materials.[45]

3.1.4 Epoxy–NIPUs through the Incorporation of Hydroxyurethane Modifiers

The hydroxyurethane modifiers (HUMs) are synthesized by reacting a monocyclic carbonate with an amine (Scheme 3).[46] It is important to note that this approach was quite different from the other pathways in the sense that noncrosslinked epoxy–NIPU hybrids were obtained. The hybrid has a comb-like microstructure (**Scheme 8**).



Scheme 8 H-NIPU composed of an epoxy polymer chain modified with pendant hydroxyurethane moieties.

These HUMs were shown to accelerate the curing process of the epoxy–amine. Additives such as diluents or pigments can also be incorporated if needed. It was claimed that the modified epoxy-amine hybrids exhibited improved curing characteristics and provided cured products with better wear resistance, flexibility, well-balanced mechanical properties (hardness, tensile strength), and chemical resistance than conventional comparative compositions without any HUM.[46]

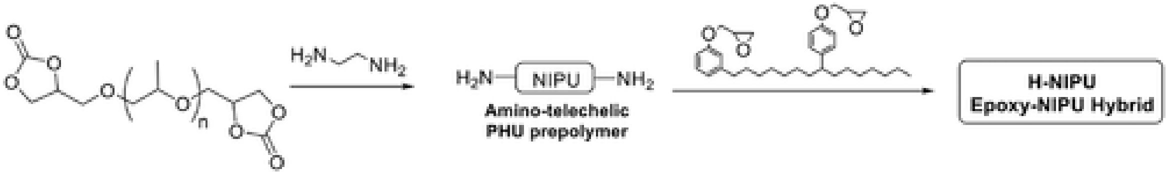
Other examples of HUMs-based epoxy–NIPU hybrids have been reported.[37, 47, 48] This methodology is to some extent an equivalent of the hydroxyurethane methacrylates (or “HUMAs”) that will be described later.

Using the versatility of the synthetic process, it is possible to design 3D networks with a controlled number of nodes through a wise selection of the reagents. Thus, diamines containing inner □NH□ moieties (for instance diethylenetriamine—DETA) can be used in the synthesis of HUMs. Superior and tunable mechanical properties could thus be obtained, with Young moduli in the range 0.9 to 12 MPa and elongations at break in the range of 70 to 275% depending on the diamine used.[47] In 2016, Wazarkar et al. demonstrated the potential of such compounds to be used as corrosion protective coatings, with a good balance between the hardness provided by the epoxy resin and flexibility given by the hydroxyurethane moieties.[48] Those properties were enhanced due to the superior adhesion properties of the H-NIPUs onto the substrates due to the presence of pendant hydroxyl moieties.

3.1.5 Epoxy–NIPUs from Biobased Resources

In a global context of the development of a more sustainable chemistry, some studies used biobased monomers in the synthesis of PHU–Epoxy H-NIPUs.[39, 49, 50] Parzuchowski et al.[50] used partially carbonated soybean oil (CSO) as a modifier for the curing process of a bisphenol-A diglycidyl ether (BADGE)-based resin with different types of amines. A higher reactivity of the amine towards the epoxy moiety than towards the inner cyclic carbonate included in the fatty acid chain of the CSO was observed. This ultimately brings to a phase separation and the formation of spherical domains of CSO-based NIPU trapped in the epoxy-amine resin. In terms of mechanical properties, a similar trend as the one described before was observed when curing with triethylenetetramine (TETA): there is an optimum concentration of carbonate moieties (here about 10%) that allows for enhanced tensile strength with respect to the native epoxy-amine resin. Higher amounts of carbonate did not fully react and plasticized the hybrids, hence increasing the elongation at break. A toughening effect was observed as a result of the introduction of CSO (from 5 to 40 wt%) within epoxy amine formulations.[50] These results agree with those reported for epoxy–NIPU hybrids for adhesive and sealant applications.[49] When adding up to 10 wt% of carbonated soybean oil in the formulation of a diglycidyl ether of bisphenol A-based epoxy resin cured with [2,2,4 (2,4,4)-trimethyl hexamethylene diamine], the tensile strength increased by 20–60%, and the elongation at break by 1.5–2 times. Comparing their results to the ones of Parzuchowski et al.,[50] they observed a microphase separation within the polymer matrix. In addition to the difference in reactivity between epoxy and cyclic carbonate, the authors claimed that an adverse aminolysis reaction of the modified triglycerides occurred upon curing, which had an additional influence on the properties of hybrid compositions. Similar results were obtained when hyperbranched polyglycerol was used instead of CSO.[51]

Cornille et al. synthesized fully biobased epoxy–PHU hybrids.[39] They used amino-telechelic PHU prepolymers that reacted with a cardanol-based bis epoxy compound —**Scheme 9**. For comparison, the resulting materials were compared with H-NIPUs made of the same prepolymers that were reacted with bisphenol A diglycidyl ether and phloroglucinol tris-epoxy. It was necessary to increase the reaction temperature up to a minimum of 50 °C for the curing process in order to form a crosslinked hybrid material. It was noticed that the H-NIPUs made with the cardanol-based bis epoxy compound exhibited the highest swelling indexes of all synthesized materials, due to the long aliphatic chain contained in the monomer. These materials also had gel contents of only 77–86% in THF, which was attributed to the low purity of the cardanol-based bis epoxy compound because of the presence of monoepoxy compounds. Interestingly, the obtained glass transition temperature was quite low (around 5 °C) due to the flexibility of the utilized reagents.



Scheme 9 Biobased Epoxy-PHU H-NIPU as designed by Caillol and co-workers.[39]

Another example is the work of Doley et al. who prepared epoxy–NIPU hybrids made from the carbonation of sunflower oil (CSFO) that was reacted with isophorone diamine and epoxy resin.[52] Using of the same number of amine equivalents than the sum of CSFO and epoxy, they varied the amount of epoxy resin from 10 to 30 wt% (based on CSFO). The tensile strength increased (from 5.7 to 8.4 MPa) together with the scratch hardness (from 4.4 to 5.5 kg) when the epoxy content increased. They further studied the covalent bonding of these hybrids with amine-functionalized graphene oxide (GO) obtaining tougher and harder materials. The GO-modified hybrids also exhibited an increased resistance to temperature and better flame retardancy.

NIPU–Acrylic Hybrids

The complementary properties of polyurethane (toughness, flexibility) and acrylic polymers (weatherability, alkali resistance) have led to a popular family of hybrids that are used in a broad range of applications including adhesives, elastomers, and coatings.[32] Looking for a more sustainable alternative, this naturally led to the development of NIPU–acrylic hybrids.

The different synthetic strategies are summarized in **Figure 5**. A first route involves the (co)polymerization of unsaturated cyclic carbonates leading to polymer chains with pendant cyclic carbonates that are then used to create pendant NIPUs.[53] Another approach involves the synthesis of the so-called hydroxyurethane methacrylates (HUMAs), which can be considered as equivalents of the previously described hydroxyurethane modifiers (HUMs) in PHU–epoxy hybrids. The subsequent acrylic polymerization allows for the formation of the final acrylic–NIPU hybrids.[54, 55] Finally, the synthesis of unsaturated NIPU prepolymers, opening the scope of applications towards segmented NIPU–acrylic networks were published.[56-59] All of them are reviewed below.

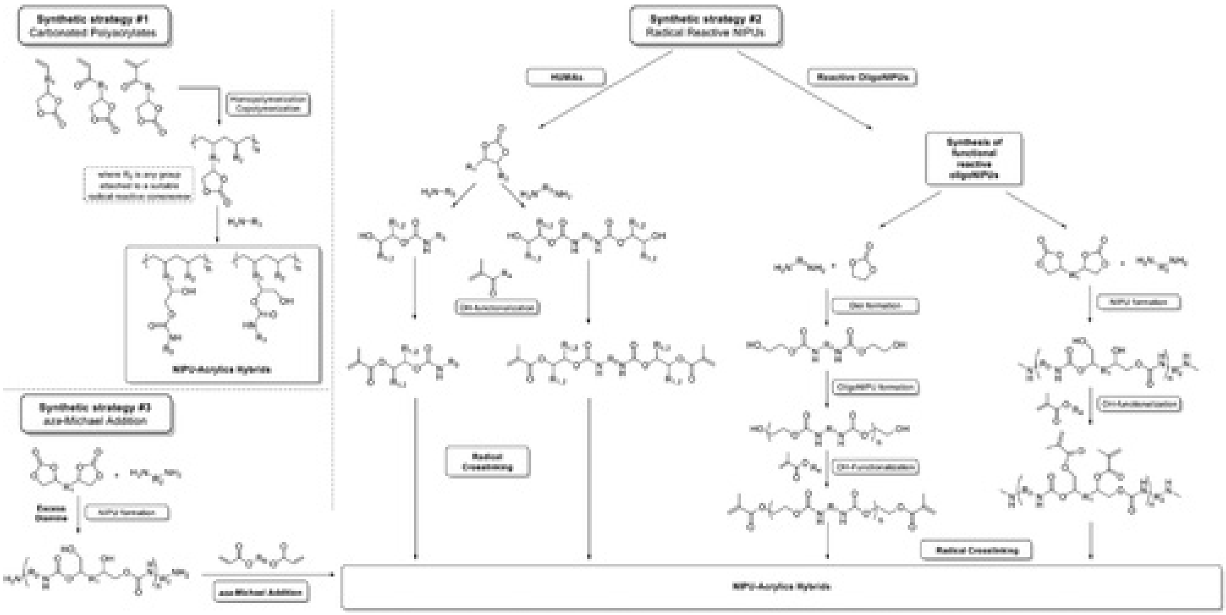


Figure 5 Overview of the different synthetic strategies for the synthesis of NIPU–acrylics hybrid polymers.

3.2.1 Unsaturated Cyclic Carbonates and their Acrylic Polymerization

The synthesis of unsaturated cyclic carbonates capable of orthogonal chemistry is the bottleneck for the synthesis of NIPU–acrylic hybrids. Boutevin and co-workers[53] have extensively reviewed the synthesis of such compounds up to 2013, as well as their polymerization behaviors through reaction of the carbon–carbon double bond. They include, among others, vinyl ether,[60, 61] vinylic,[62] allylic[63-65] and allyl ether,[66] styrenic[67, 68] and (meth)acrylic cyclic carbonates[69-76] (**Figure 6**). Biobased allylic cyclic carbonates have also been synthesized.[77] Most of the polymers were aliphatic backbones with pendant carbonate moieties that are later reacted with amines to give the acrylic–NIPU hybrids.[60-62] Some of those monomers were directly dimerized with the help of thiol–ene chemistry prior to reacting them with diamines to yield poly(hydroxyurethane)s—PHUs and no NIPU–acrylic hybrids were synthesized.[63, 64, 66]

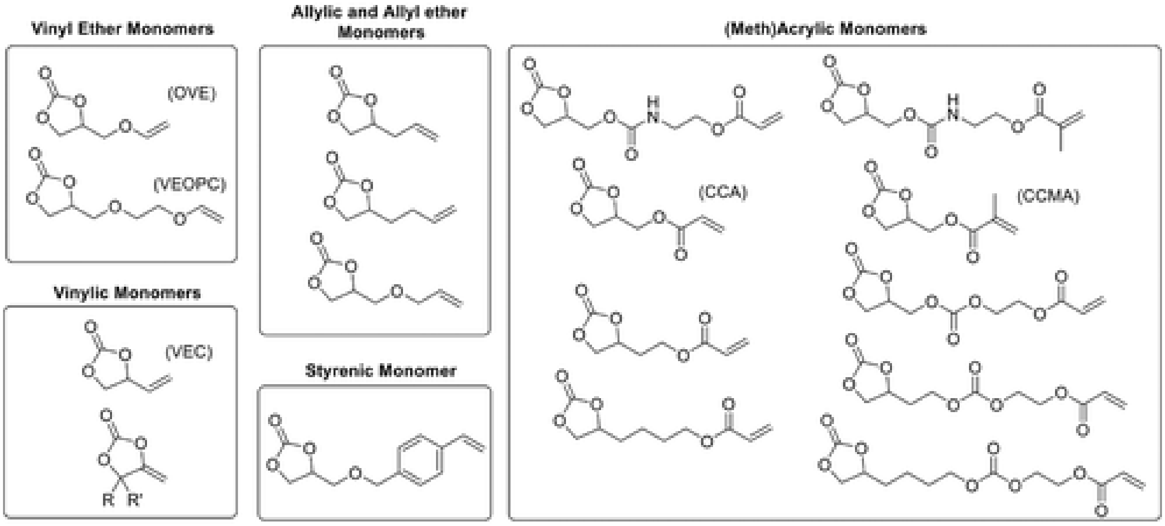
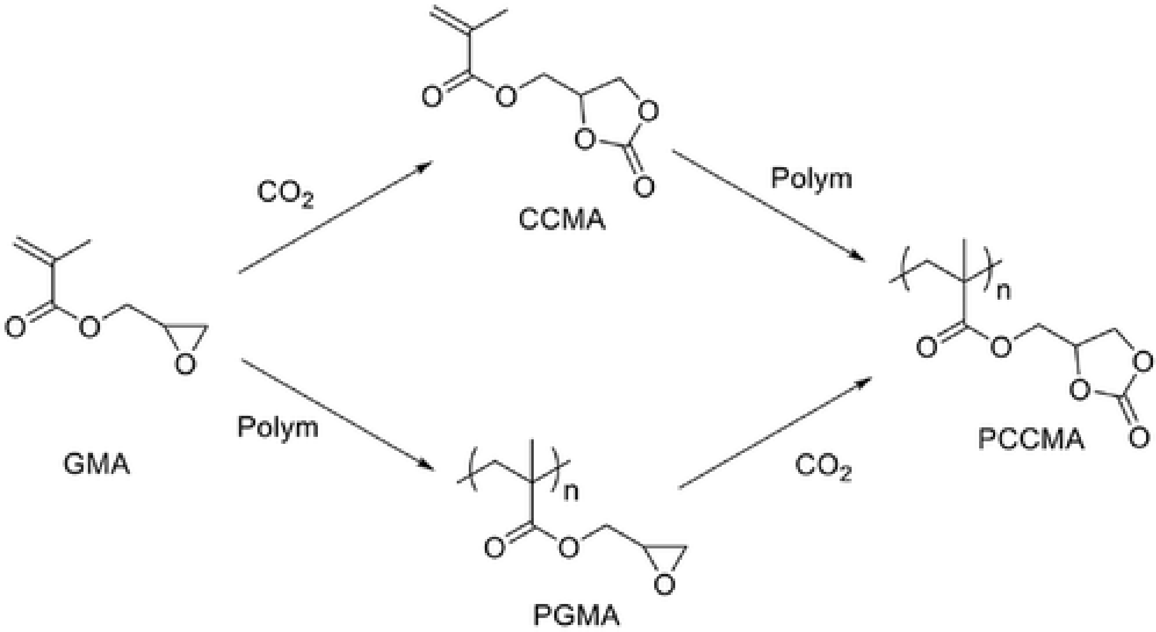


Figure 6 Radical reactive cyclic carbonates.

The radical copolymerization of (2-oxo-1,3-dioxolan-4-yl) methyl vinyl ether (OVE) with acrylonitrile, methyl methacrylate, N-phenylmaleimide and maleic anhydride in acetonitrile gave yields up to 87% depending on the comonomer composition.[60] The authors further reacted the pendant carbonate moieties with butylamine and benzylamine up to 84% and 96% conversion respectively. Kalinina et al. reported the copolymerization of 3-(2-vinyloxyethoxy)-1,2 propylene carbonate (VEOPC) and N-phenyl maleimide (around equimolar composition) in methylethylketone (MEK) using azobisisobutyronitrile (AIBN) as thermal initiator.[61] The copolymers were post-functionalized with ethylene diamine (EDA) and hexamethylenediamine (HMDA) to form H-NIPUs that were used as coatings. They exhibited good solvent resistance and low moisture absorption, but poor adhesion to metal and poor impact strength. Webster and Crain studied the copolymerization of vinyl ethylene carbonate (VEC) with vinyl esters.[62] Further carbonate-amine postfunctionalization studies were performed in propylene glycol monomethyl ether. Primary amines born onto primary carbons were preferred. It was shown that the solvent resistance increased with the amount of amine incorporated up to a certain value (ratio amine/carbonate = 1.0) above which no further improvement was observed. This was correlated with the fact that the crosslinking reaction reaches a maximum conversion, which is a classical result in PHU chemistry. Otherwise, good gloss, pendulum hardness, and impact resistance were observed for the formed coatings.

Cyclic carbonate (meth)acrylate (CC(M)A) polymerization has been reported.[53] Cyclic carbonate methacrylate (CCMA) can be synthesized through many reaction pathways that have been summarized by Webster[73] and Caillol et al.[53] However, the carbonation reaction by catalytic fixation of CO_2 onto glycidyl methacrylate (GMA) remains the main alternative. It is important to mention that pure CCMA alone is unstable, but stable up to 100 °C when unpurified from the utilized catalyst (either triphenylphosphine or DABCO) according to Kihara and Endo.[78] Moreover, the only way to purify the product was found to be by liquid chromatography (distillation was found to induce polymerization). This instability can still be an issue after polymerization. Therefore, there is a general agreement on the fact that the radical polymerization of glycidyl methacrylate—GMA—followed by its carbonation reaction with CO_2 presents advantages with respect to the direct polymerization of CCMA (**Scheme 10**).[79-81]



Scheme 10 Different synthetic pathways towards the formation of poly(CCMA). Adapted with permission.[82]

Attempts to react CCMA-containing oligomers with amine-containing compounds to yield hydroxyurethane have been reported. Kihara and Endo functionalized CCMA-containing oligomers with butylamine, benzylamine, cyclohexylamine, and dibutylamine.[78] Excess of amine was necessary for reaching full conversion of the carbonate. Secondary amines barely reacted due to steric hindrance. Finally, when hexamethylene diamine (HMDA) was introduced with a 1:1 (repeating units : amino group) ratio, gelation occurred after 1.5 h in dimethylsulfoxide (DMSO). The infrared (IR) analysis revealed that the reaction was not complete since traces of cyclic carbonate and amine could be observed, trapped in the polymer network. The obtained film was reported as both hard and flexible. The same team published[79] the post-functionalization of a copolymer of CCMA and GMA (30:70, M_n = 22 000 g mol^{-1}, $Đ$ = 2.5) via an aminolysis reaction with butylamine. In this case, attention to the reactivity of the oxirane and the carbonate moieties should be paid. If an acidic treatment was performed prior to aminolysis, then the oxirane moieties would open and the amine would selectively react with the carbonate moieties. The obtained polymers displayed solubility in water and methanol, which was not the case before functionalization with the amine. When the aminolysis was performed before the acidic treatment, crosslinking through an “epoxy-like” mechanism occurred and made the final polymer insoluble. Jana et al. used atom transfer radical polymerization (ATRP) in order to synthesize homopolymers, triblock copolymers, and terpolymers bearing cyclic carbonate pendant groups.[74] They postfunctionalized the CCMA moieties with 2-phenylethylamine in order to modify the solubility and wettability properties of the obtained polymers. The reaction was carried out in dimethylformamide (DMF) and different degrees of functionalization were achieved. Only 40% of functionalization was enough to make the polymers soluble not only in polar aprotic solvents such as DMF and DMSO but also in more common solvents such as acetonitrile (ACN) and tetrahydrofuran (THF). Higher extents of functionalization (≈90%) allowed solubilizing the polymers in chloroform. Functionalization helped transitioning from a quite brittle to uniform, transparent and continuous films cast onto glass substrates using DMF as solvent. The water contact angle continuously increased with the degree of functionalization in spite of the concomitant appearance of hydroxyl groups. This was attributed to the effect of the hydrophobic side group of the 2-phenylethyl amine used. This suggests that tuning of the hydrophilic/hydrophobic balance of the final polymer could probably be achieved by changing the amine.

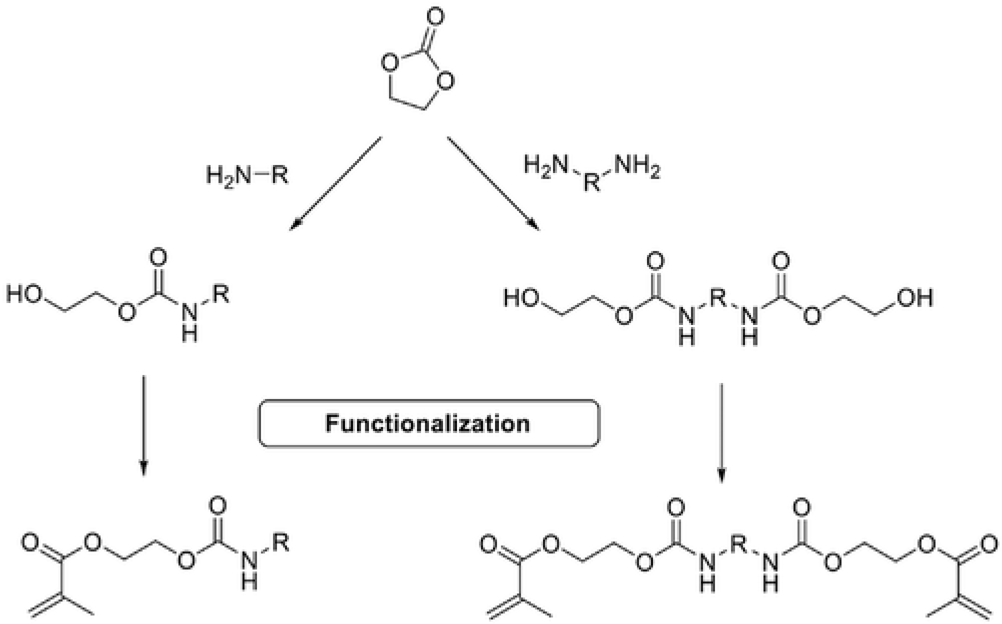
Such technologies were also patented. For example, Iwamura and co-workers patented aminolysis of cyclocarbonate-based oligomer to produce coatings for automotive applications.[83]

CCMA has been incorporated into formulations for emulsion copolymerization. Yang et al.[84] patented an interesting process in which different latexes were prepared. Some bearing CCMA moieties, some bearing amines (by reaction of aziridines with carboxylic moieties contained in the polymeric chains), and a third type bearing both CCMA and amine in the same chain. It was shown that the latex containing both CCMA and amines on the same polymer chain, as well as a 1:1 (weight basis) mixture of both latexes containing either CCMA or amines were able to form nontacky films at room temperature after 24 h drying, followed by 3 d of curing. The films exhibited gel contents around 90% and 60% in acetone respectively. They also exhibited water resistance, a result that was interpreted as a crosslinking that occurred between the CCMA and the amine groups. This result was further enhanced because the latex containing only amine groups could form films of around 60% gel content in acetone, but with a much poorer water resistance, a feature that was explained by the ionic interaction between the carboxylic and the amine groups contained in the polymer.

Cyclic carbonate acrylate (CCA) has also been studied, although to a lesser extent than for CCMA. The synthetic routes towards the formation of CCA are very similar to those to synthesize CCMA.[85-88] Yields of 85% were obtained through the carbonation of glycidyl acrylate with CO_2 at 60 °C in the presence of inhibitors (4-methoxyphenol).[88] The reaction conditions as well as the purification steps are of extreme importance because the acrylates are much more reactive than the methacrylates[89] and can suffer from side reactions or even start polymerizing at temperatures as low as 40 °C. Homopolymerization of CCA in solution usually led to insoluble polymers, which was explained because of the transfer reaction from the carbonate ring with proton removal and radical recombination.[78, 90] The copolymerization with 2-ethylhexyl acrylate was found to be a solution to yield soluble polymers in benzene, dichloromethane and tetrahydrofuran.[90] Photopolymerization was also implemented.[91, 92] The carbonate moieties were also functionalized with butylamine.[90]

3.2.2 (Hydroxy)Urethane Methacrylates—(H)UMAs

(Hydroxy)urethane methacrylates ((H)UMAs) are short oligomers (usually dimers or trimers) synthesized by aminolysis of a cyclic carbonate and subsequent functionalization of the hydroxyl group. **Scheme 11** presents mono and dimethacrylate hydroxyurethanes but more complex structures have also been designed.[25, 54, 55, 93]



Scheme 11 Formation of UMAs via the aminolysis of ethylene carbonate followed by subsequent functionalization.

(H)UMAs were originally designed to be used as reactive diluents. Such compounds can for example be employed in ultraviolet (UV)-curable coatings, that present fast curing and low energy consumption.[94] Figovsky et al. reported UV-curable concrete floor coatings able to cure instantly.[95] A general composition of a UV-curable coating is a mixture of photoinitiator, oligomer and reactive diluent, the latter being used to decrease the viscosity of the global mixture, while polymerizing in the crosslinking reaction to form a 3D network. According to Wang and Soucek, monofunctional reactive diluents usually lead to a lower Young's modulus and higher ductility whereas bi- and/or multi-functional reactive diluents have the opposite effect.[54] It was also reported that the introduction of acrylic moieties into the (H)UMAs overcame the yellowing of the PHU caused by sunlight.[96] Due to their versatile composition, and the diversity of components that can be used for copolymerization purposes, UV-curable formulations can find other applications such as the development of injectable liquids, paste, or gels (dental composite applications being a potential example).[55, 97]

Assumption and Mathias published in 2003 a method for synthesizing isocyanate-free urethane methacrylates UMAs via the ring opening aminolysis of ethylene carbonate with various amines.[55] Hexamethylene diamine (HMDA), 3-amino-1-propanol and 2,2-dimethyl-1,3-propanediamine were used, and methacrylic anhydride was utilized in the functionalization step in order to catalytically react with all the hydroxyl groups—**Figure 7**. The kinetics of the radical photopolymerization of the formed UMAs was measured and extremely fast polymerization rates (plateauing conversion after 100 s reaction time) were obtained. An immediate autoacceleration was noticed and the fastest polymerization rates were reached after 4 to 5 s. The reaction rate was found to strongly depend on the monomer structure of the UMA. In particular, the presence of H-bonding by interaction between ▯$NH_{urethane}\cdots O{=}C_{urethane}$ moieties or ▯$NH_{urethane}\cdots O{=}C_{ester}$, allowing preassociation effects between the monomers enhanced the polymerization rates, which is in accordance with the work of Jansen et al.[69] Wang and Soucek[54] varied the structure of the cyclic carbonate compound introducing an additional methyl moiety. 2-(methacryloyloxy)ethyl 2-

(methacryloyloxy)ethylcarbamate (EOAED), 2-(methacryloyloxy)ethyl 3-(methacryloyloxy)propylcarbamate (POAED), and 1-(methacryloyloxy)propan-2-yl 3-(methacryloyloxy)propylcarbamate (POAPD) were synthesized by functionalization with methacrylic anhydride—Figure 7. The reactive diluents were tested in a formulation containing an acrylated oligoester and were compared to ethylene glycol dimethacrylate (EGDMA, a reactive diluent that does not contain urethane moieties). It was observed a general increase of tensile strength when adding up to 40 wt% of the nonisocyanate-based reactive diluents, while the elongation at break reached a maximum value starting from 20 wt% of reactive diluent (and did not change when increasing up to 40 wt%). Glass transition temperatures (T_gs), α-transition temperatures T_αs and gel contents also increased with the reactive diluent content, due to the higher crosslinking density. One drawback is the water sensitivity that increased with the reactive diluent content. This was attributed to the increase of ester-urethane group concentration, a polar group capable of interacting with water. Finally, the higher the content of reactive diluents, the lower the impact resistance. However, the impact resistance values were higher when incorporating up to 20 wt% of nonisocyanate reactive diluent when compared to the acrylated oligo polyester alone.

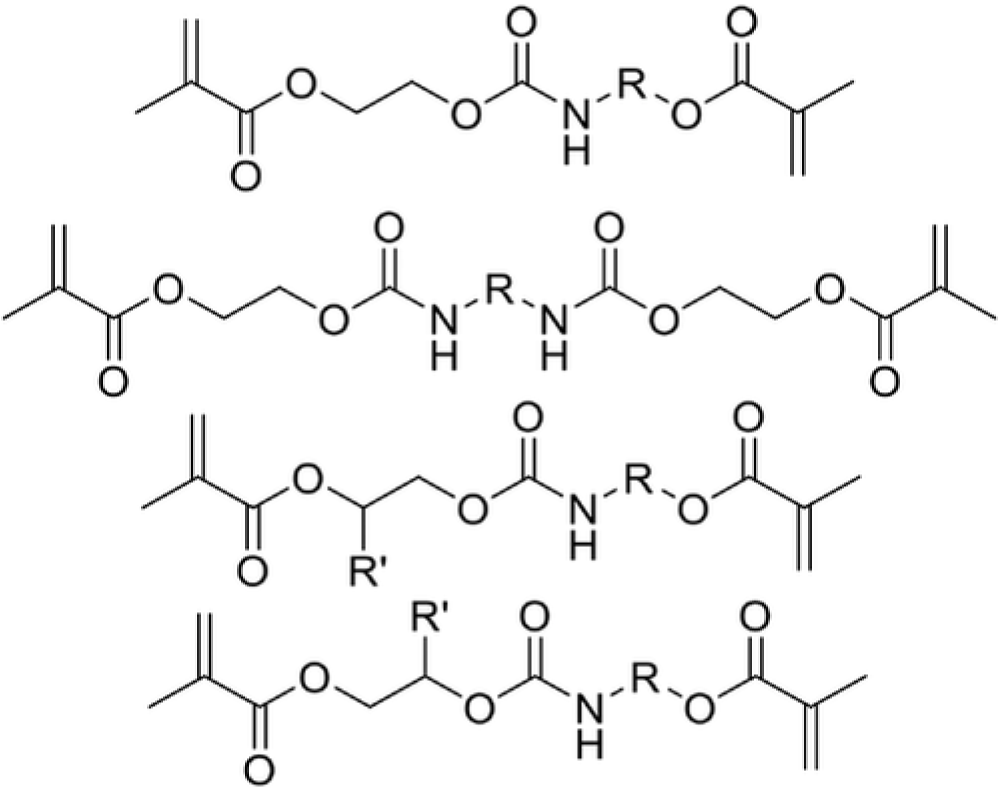
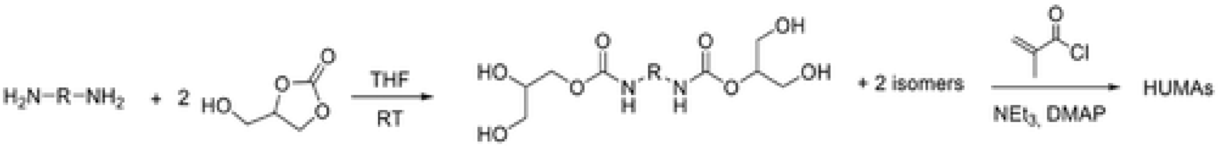


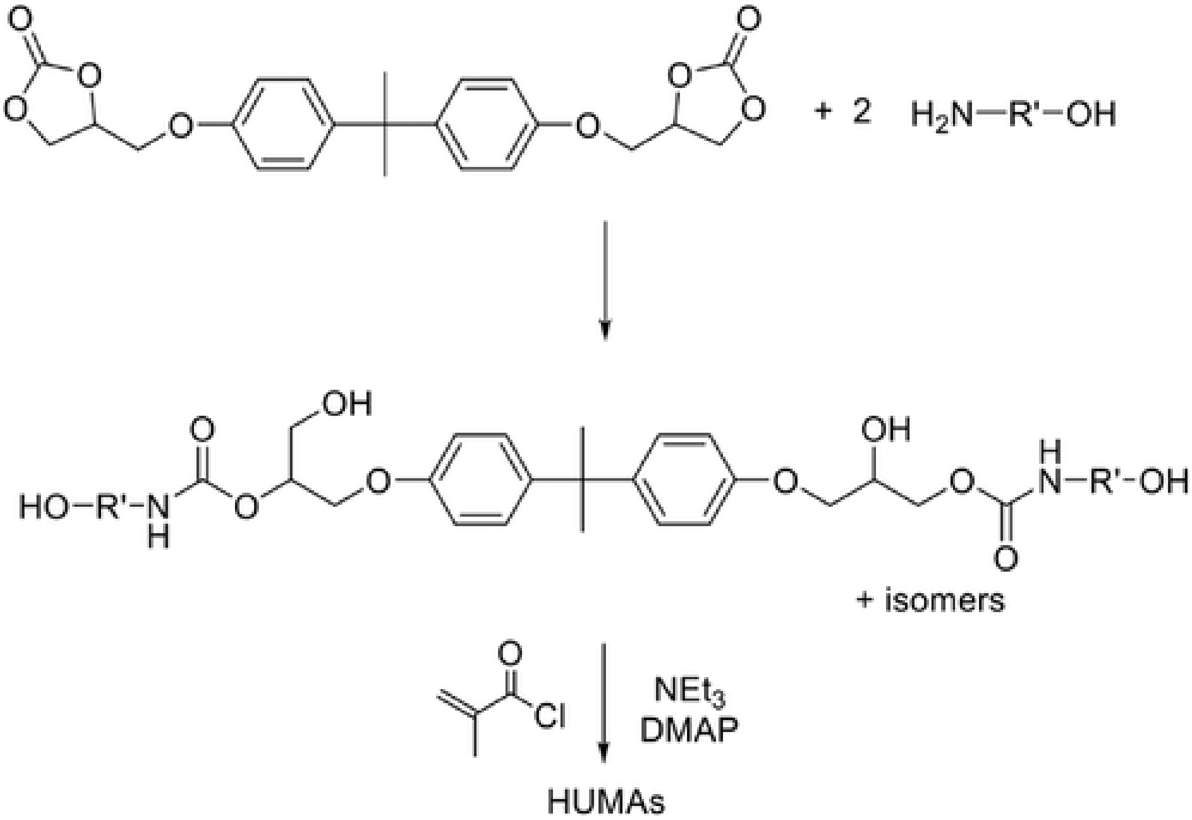
Figure 7 Reactive diluents prepared by Assumption et al.[55] and Wang et al.[54]

Multifunctional hydroxyurethane methacrylates (HUMAs) were prepared by aminolysis of glycerol carbonate with a diamine. The formed hydroxyurethane quadriols (3 isomers can be obtained) were subsequently modified by reacting with methacryloyl chloride or methacrylic anhydride to form the corresponding quadrimethacrylate (**Scheme 12**).[25] Various amines could be used for the synthesis, including 1,3-diaminopropane, 1,2-diaminoethane, and isophorone diamine (IPDA). Amino alcohols were also used and yielded trifunctional urethane methacrylates.



Scheme 12 Multifunctional HUMAs via functionalization of glycerol carbonate-based quadriols by methacryloyl chloride according to Biernat and Rokicki.[25] (Note that DMAP stands for 4-dimethylaminopyridine).

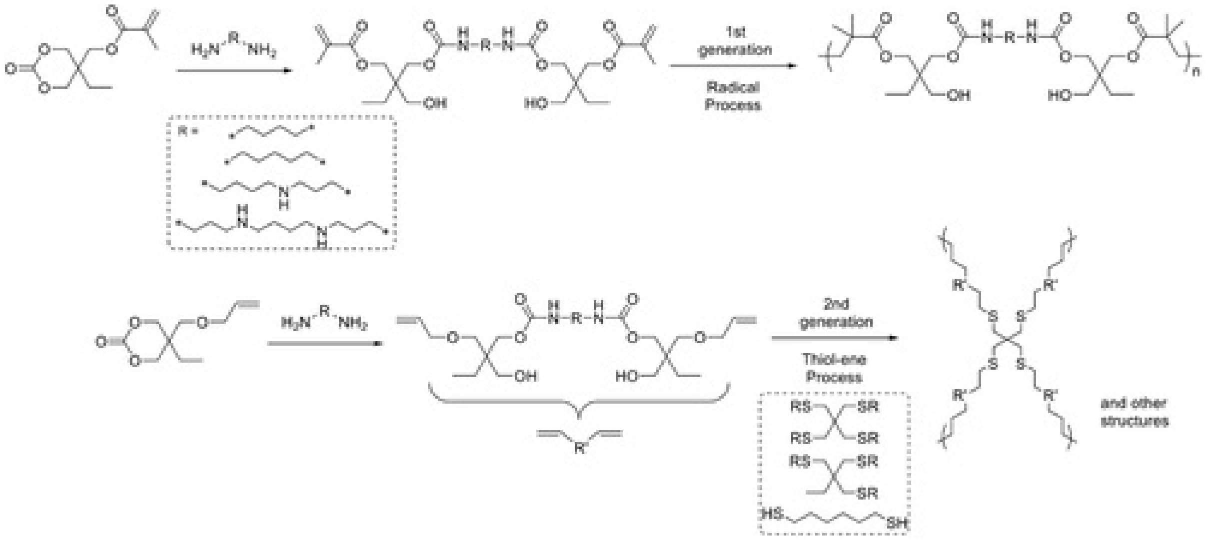
Multifunctional HUMAs have been synthesized using carbonated-bisphenol-A diglycidyl ether (BADGE).[25] The quadri-functionality was brought through the reaction with an amino-alcohol that was further modified with methacryloyl chloride to yield the final products (**Scheme** 13).



Scheme 13 Multifunctional HUMAs via functionalization of carbonated-BADGE-based quadriols by methacryloyl chloride according to Biernat and Rokicki.[25] (Note that DMAP stands for 4-dimethylaminopyridine).

The synthesized resins have low viscosity and exhibit high flexural strength after curing and superior toughness than a reference resin for dental compositions. Due to the high crosslinking density, a high hardness is usually obtained.

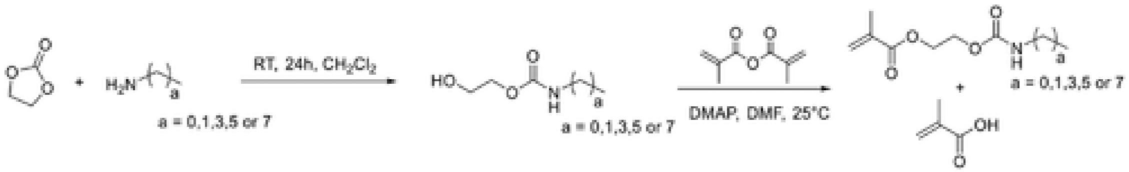
Attention has recently been paid toward the development of new kinds of materials for 3D—printing purposes.[98] The ability of (hydroxy)urethane methacrylates—(H)UMAs—to photopolymerize makes them perfect candidates for such applications. 3D-printable resins have been synthesized based on the formation of a diurethane adduct via the aminolysis of a vinylic- (or methacrylic-) 6-membered cyclic carbonate monomer with a diamine. Two polymerization pathways were proposed: a first one involved a radical photoinduced process whereas a second proceeded through a thiol–ene route (**Scheme** 14).[99, 100]



Scheme 14 3D-printable HUMAs based on a six-membered cyclic carbonate diurethane adducts, further polymerized either by radical photopolymerization (1st generation)[99] or via thiol-ene chemistry (2nd generation).[100]

In the first pathway, the diurethane adduct containing methacrylic moieties was formed first and then crosslinked via an UV-induced radical process to yield the final material. The obtained products were amorphous and stable up to temperatures higher than 200 °C. They were 3D-printed in a continuous optical printing system using a layer-by-layer polymerization methodology. Materials of tunable stiffness with smooth contours could thus be designed. In the second approach, a vinylic cyclic carbonate was copolymerized also in a UV-induced thiol–ene process with bi- to quadrifunctional thiols. The biocompatibility of these materials for potential biomedical applications was evaluated. (Hydroxy)urethane methacrylates—HUMAs—were synthesized through the reaction of a series of diamines with two equivalents of cyclic carbonate methacrylate (CCMA) in a bulk process for 3D-printing purposes.[101] The HUMAs were further copolymerized with 4-methacryloylmorpholine (ACMO) with the help of a photoinitiator. When mixed at a ratio of 59:39 (ACMO:HUMA) weight ratio, cyclic rigid diamines (such as xylylene diamine or IPDA)-based and pentane diamine-based HUMAs gave resins with the highest values of viscosities (630 to 880 mPa s). Etheramine-based HUMAs yielded resins of much lower viscosities (190 to 310 mPa.s) and were closer to the commercial reference (Laromer UA 9089 from BASF) which exhibited a viscosity of 160 mPa s. However, all of them remained within industrially acceptable viscosity ranges (below 1300 mPa s). Short and flexible etheramines were preferable because they offered a compromise between low viscosity and very good mechanical performance (Young modulus of 3600 MPa, and tensile strength of 85 MPa were measured in the case of 1,8-diamino-3,6-dioxaoctane-based HUMAs). Multifunctional HUMAs obtained by functionalization of the pendant OH groups with methacrylate anhydride led to an increase in thermomechanical properties (Young modulus of 4200 MPa instead of 3600 MPa and a T_g of 173 °C instead of 86 °C were obtained).

There are two examples of the use of urethane methacrylates (UMAs) in waterborne systems.[102, 103] The UMAs were prepared via the aminolysis reaction of ethylene carbonate with a series of aliphatic amines prior to the functionalization with methacrylic anhydride (**Scheme 15**).[102] This process allowed to target different hydrophobicity level for the reactive diluents, that were subsequently copolymerized with MMA/BA in a seeded semibatch emulsion polymerization under monomer starved conditions, with a solid content of 30 wt%. It was observed that the T_gs and the MFFTs of the latexes decreased with the increasing aliphatic chain length to reach values close to room temperature for UMAs containing 6 to 8 carbons. BEM (butyl-based UMA, *a* = 3 in Scheme **15**) was also used in seeded emulsion polymerization, namely a seed of MMA/BA (48/52 wt/wt) was synthesized and then reacted with another feed of BEM/MMA/BA.[103] The emulsion polymerization process (batch vs semibatch addition mode of BEM/MMA/BA) as well as the particle morphology (homogeneous vs core–shell) and the location and concentration of BEM within the particle (in the core or in the shell) in terms of film properties were the focus of the study. It was shown that because BA reacts slower than the other methacrylates, the copolymer composition of the latexes originating from the batch mode was broader than in semibatch, which affected the mechanical properties of the cast films: higher Young's modulus and stress at break, as well as smaller elongation at break were obtained in the base of the batch than in semibatch. Remarkably, when increasing the BEM content from 0 to 20 wt%, Young's modulus, stress at break and elongation at break increased (whereas a decrease in elongation at break would have been expected). This effect was much stronger when the BEM was located in the shell of the particles, while when in the core, its impact of the reinforcement of the material was less significant. This reinforcement was interpreted as an effect of H-bonds forming the N⍰H and the O═C groups contained in the polymer matrix.[102, 103] The water-based NIPUs have been recently reviewed.[15]



Scheme 15 Preparation of monofunctional UMAs of different hydrophobicity according to Meng et al.[102]

3.2.3 Unsaturated NIPU–Prepolymers: Oligonipus

An interesting way of preparing NIPU–acrylic hybrids is by copolymerization of (meth)crylate monomers and NIPU prepolymers bearing double bonds. The NIPU prepolymers can be either telechelic (meth)acrylates or PHUs bearing (meth)acrylate groups along the chain that are incorporated by functionalization of the hydroxyl groups.

Radical Reactive Telechelic Polyurethanes: Isocyanate-free urethane methacrylates UMAs (oligoUMA) were designed by Ochiai and Utsuno by functionalizing oligomeric polyurethane diols with glycidyl methacrylate (GMA).[56] The oligomeric polyurethanes (PUs) originate from a transurethanization process. As the ring opening of GMA did not proceed to full conversion, an excess was employed for maximizing the extent of functionalization. The oligoUMAs were further copolymerized with methyl acrylate (MA) (in a 50:50 ratio in reactive moieties) in dimethylformamide (DMF) at 60 °C using AIBN as thermal initiator for 24 h (**Figure 8**). The formed polymer almost instantaneously became a gel, which was insoluble in any organic solvent. The polymer was composed of hard PU segments and soft poly(methyl methacrylate) ones. After thermal treatment in the DSC, the PU and the acrylate phase became miscible and a single T_g of 34 °C was obtained. The T_g was found to be higher than both the native PU and poly(MA), a phenomenon that was attributed to the restricted motion of the polymer chains in the 3D network.

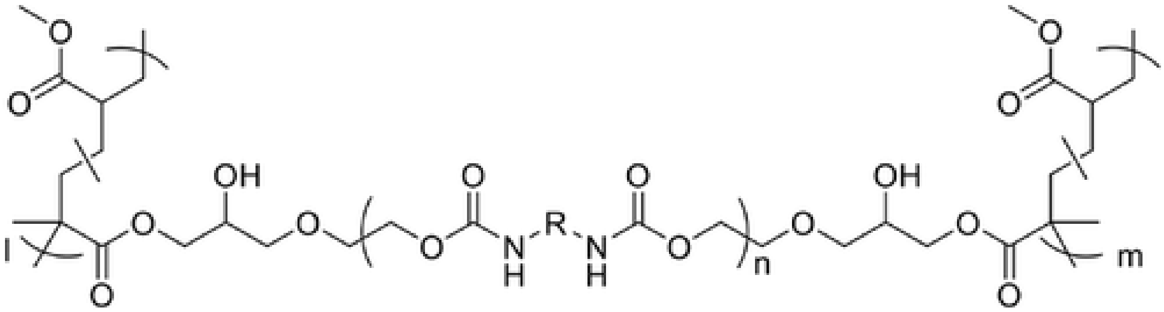
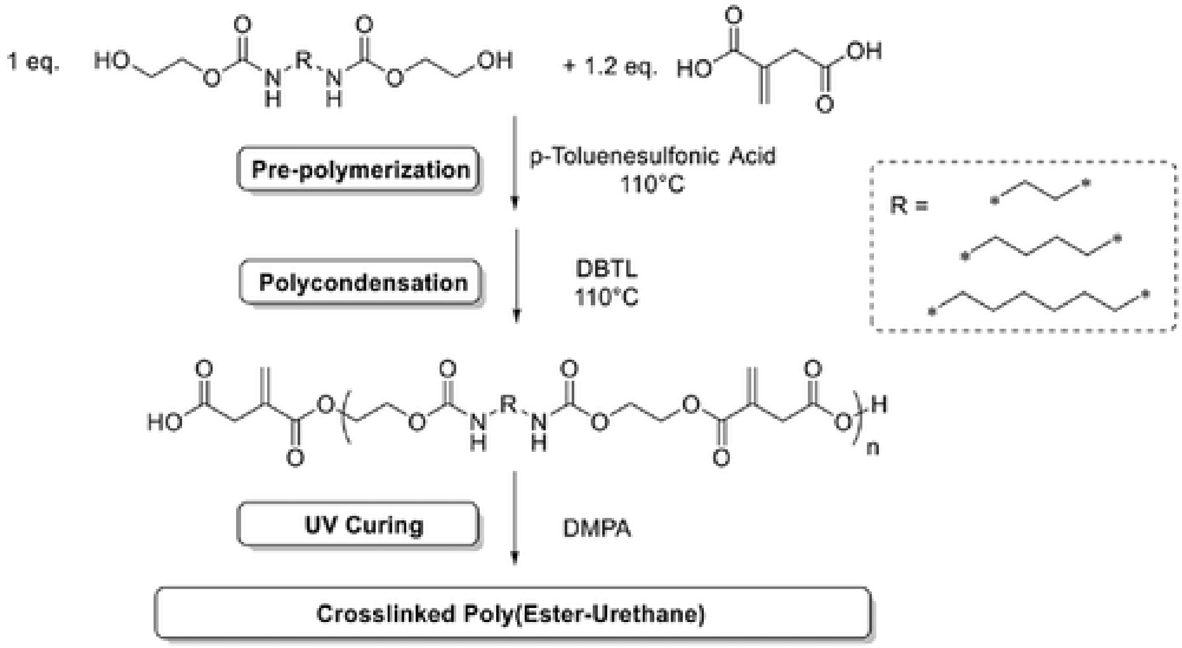


Figure 8 Copolymer from oligoUMA and MA according to Ochiai et al.[56]

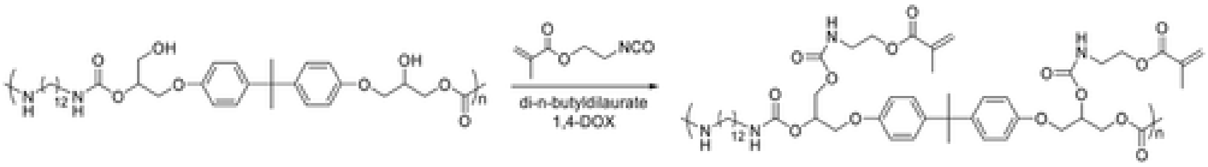
More recently, we demonstrated that the incorporation of radical telechelic fatty acid-based PHUs in (meth)acrylic formulations (in this case butyl methacrylate/stearic acrylate—96%/4%), followed by their subsequent dispersion in water and polymerization of the acrylic phase drove to the formation of latexes of H-NIPUs via a miniemulsion process.[57, 58] The functionalization of the PHU was performed by reacting amino-telechelic preformed PHUs with the carbonate-derivative of GMA. When incorporating 20 wt% of bifunctional PHU, a high molar mass material was obtained ($M_w > 10^8$ g mol^{-1}) with a gel content of 84% as measured by Soxhlet extraction in THF. The formation of VOC-free films at 30 °C was shown. They exhibited a higher toughness than the films originating from non-crosslinked hybrids. This was attributed to a more homogeneous microstructure of the films, in which the PHU was better distributed among the poly(acrylic) phase, thus avoiding the formation of PHU clusters.[57, 58]

Hydroxyl-Group Functionalization of PHUs: Han et al. developed a new kind of poly(ester-urethane)s that were functionalized with the biobased itaconic acid (**Scheme 16**).[59] NIPU prepolymers were synthesized by ring opening of ethylene carbonate with various diamines. The formed diols were then reacted with an excess of itaconic acid and subsequent polycondensation led to radical reactive oligo(Ester-Urethane)s. The latter were further cured by a UV-induced process with dimethylpropionic acid (DMPA). Gel contents in the range 80% to 88% in acetone were obtained. The tensile strength depended on both the chain length of the diamine and the cross-linking density, with the best mechanical properties obtained in the case of putrescine-based oligo(Ester-Urethane) (Young modulus of 52 MPa, a tensile strength of 2.5 MPa and an elongation at break of 33%).



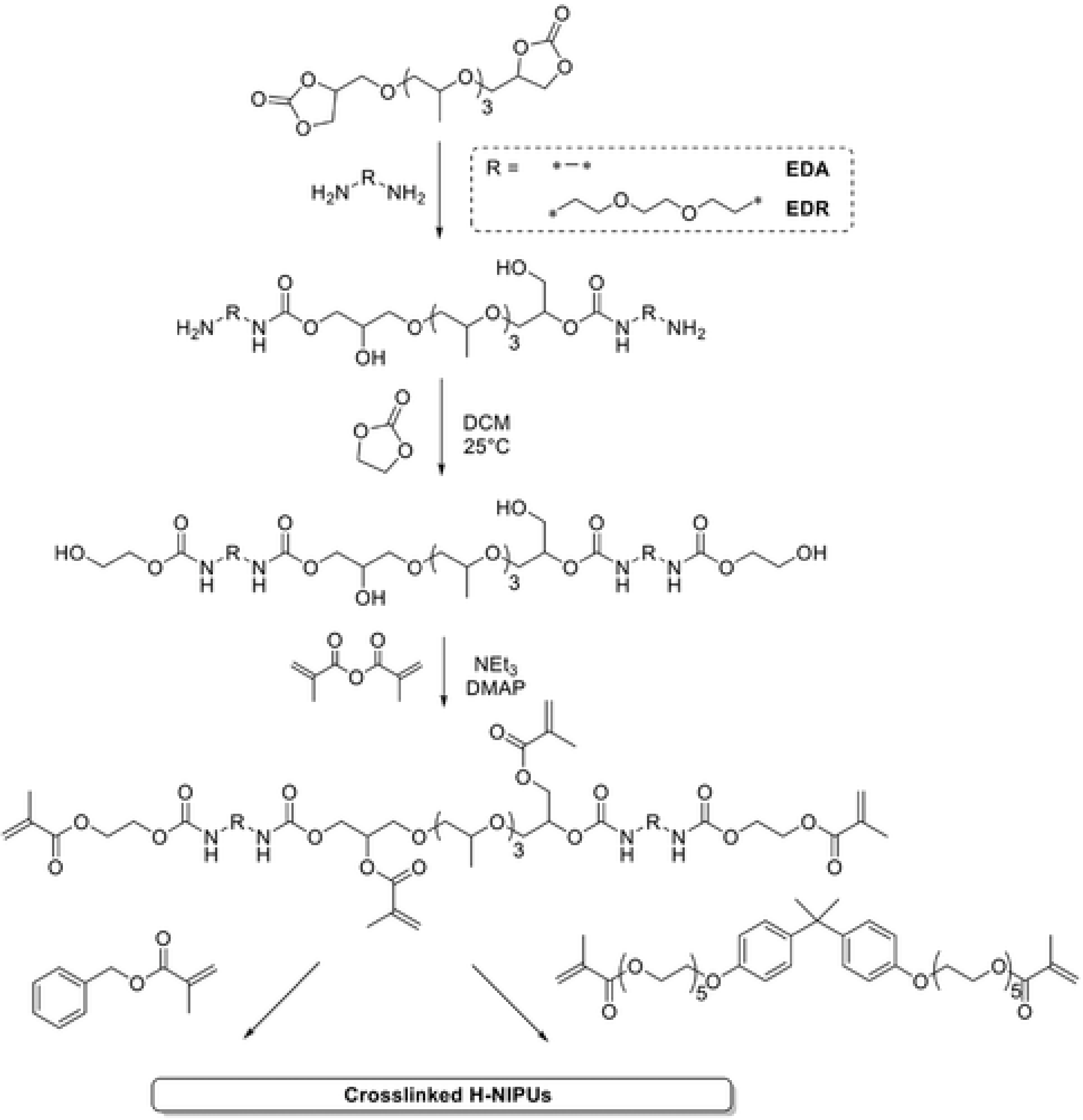
Scheme 16 Fully-biobased HUMAs functionalized by itaconic acid according to Han et al.[59]

The group of endo functionalized the pendant OH groups of a carbonated bisphenol-A diglycidyl ether (BADGE)-based oligoPHU[104] by reacting them with 2-methacryloyloxyethyl isocyanate (**Scheme 17**). The urethanization was carried out at room temperature to avoid polymerization of the methacrylate moieties. The functionalization degree of the hydroxyl groups could be tuned depending on the ratio between the OH groups and the 2-methacryloyloxyethyl isocyanate (with a preferred conversion of the primary OH, more reactive than the secondary ones). A full conversion of the hydroxyl groups to urethane could be obtained when adding 2.2 eq. of isocyanate compared to hydroxyls, while a 1 to 1 (mol:mol) ratio yielded an oligoPHU with 50 mol% of the OH-groups converted to methacryloyl-urethane moieties 50% functionalized BADGE-based oligoPHU was successfully copolymerized with several monomers (hydroxyethylmethacrylate (HEMA), methyl methacrylate (MMA) and *N*-isopropylacrylamide (NIPAM) in dioxane. In all the cases, the viscosity of the polymerization mixture increased during the reaction until the formation of insoluble gels. T_gs lower than or identical to that of the corresponding homopolymers (polyMMA, polyHEMA and polyNIPAM) were measured, suggesting that the distance between crosslinking nodes was sufficiently long to allow mobility of the incorporated PHU chains. It should however be mentioned that this synthetic process, despite being extremely interesting, is unfortunately not fully isocyanate free.



Scheme 17 Functionalization of the pendant OH-groups of carbonated BADGE-based oligoPHUs according to Endo and co-workers.[104]

A very recent example, from Caillol and co-workers, described the synthesis of hydroxyurethane methacrylates (HUMA) capable of crosslinking thermally, without using any initiator.[105] A carbonated poly(propylene oxide) diglycidyl ether (shortened PPOBC) was reacted with ethylene diamine (EDA) or with (ethylenedioxy)diethylamine (EDR) to form a diamino-telechelic compound, which was further functionalized with ethylene carbonate. The diol was then modified with methacrylic anhydride into the corresponding HUMA as described in **Scheme** 18. The HUMAs were further homopolymerized or crosslinked with either benzyl methacrylate or poly(ethylene oxide) bisphenol-A dimethacrylate.



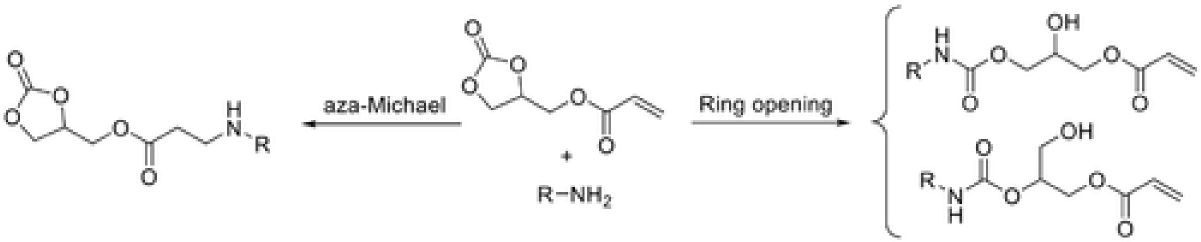
Scheme 18 PPOBC-based HUMAs as prepared by Caillol and co-workers.[105]

In order to thermally initiate the radical polymerization, a specific temperature program incrementing from 80 °C to 150 °C was implemented. The step-by-step increase in temperature was designed so that the formation of bubbles was avoided. High gel contents (>97%) were obtained. Swelling in dichloromethane indicated that the solvent uptake was higher in the case of EDA-based methacrylic-NIPUs than in the case of EDR-based ones, a result that was attributed to the higher chain length of EDA-based methacrylic-NIPUs. (The NH_2/carbonate ratio was lower in the case of EDA than for EDR).

The thermal stability of the materials was not significantly improved when copolymerizing with aromatic ring-containing acrylic monomers according to TGA ($Td_{5\%}$ between 245 °C and 260 °C were obtained for hybrids made with EDA-based HUMAs, $Td_{5\%}$ between 280 °C and 300 °C for hydrids made with EDR-based HUMAs, while the $Td_{5\%}$ for the homopolymer of poly(ethylene oxide) bisphenol-A dimethacrylate was of 353 °C). On the other hand, the char yield increased when benzylmethacrylate was used in the formulation. The T_g of the homopolymer made of EDA-based methacrylic-NIPU (43 °C) was lower than that of the EDR-based one (69 °C). This was attributed to the longer chain length of the EDA-based NIPUs. When copolymerizing with poly(ethylene oxide) bisphenol A dimethacrylate), lower T_gs were obtained, a result that was attributed to the flexibility brought by the poly(ethylene oxide) moieties. No clear trend was obtained with benzyl methacrylate. With EDA-based methacrylic NIPUs, the T_g increased (52 °C) whereas it decreased with EDR-based methacrylic NIPUs (55 °C). The authors attributed this effect due to a balance between *π*-staking interactions, the bulkiness of the aromatic groups (favoring chain mobility) and the NIPU chain lengths. Dynamic mechanical thermal analysis (DMTA) revealed very broad tan *δ* peaks, suggesting that the formed materials were highly heterogeneous.

We recently reported on the synthesis of waterborne acrylic–NIPU hybrids.[57, 58] A fatty-acid-based PHU was multifunctionalized by reacting methacrylic acid onto the hydroxyl moieties (50% functionalization was targeted) prior to being solubilized in a (meth)acrylic phase (composed of butyl methacrylate/stearic acrylate—96%/4%) and miniemulsified in water.[58] The resulting miniemulsion was then polymerized by free radical polymerization, yielding latexes that were used to cast films at 30 °C. The microstructure of the films was investigated by means of TEM analysis and revealed a homogeneous distribution of the PHU within the acrylic phase (core–shell structure of the nanoparticles with PHU in the shell could be identified), that was similar to the one observed with methacrylic-telechelic PHUs.[58] Tensile tests showed that the Young's modulus of the films originating from the multi-functional radical reactive PHUs (86 MPa) was much higher than the ones casted from the radical telechelic and the nonfunctionalized PHUs (46 and 52 MPa respectively).[57, 58]

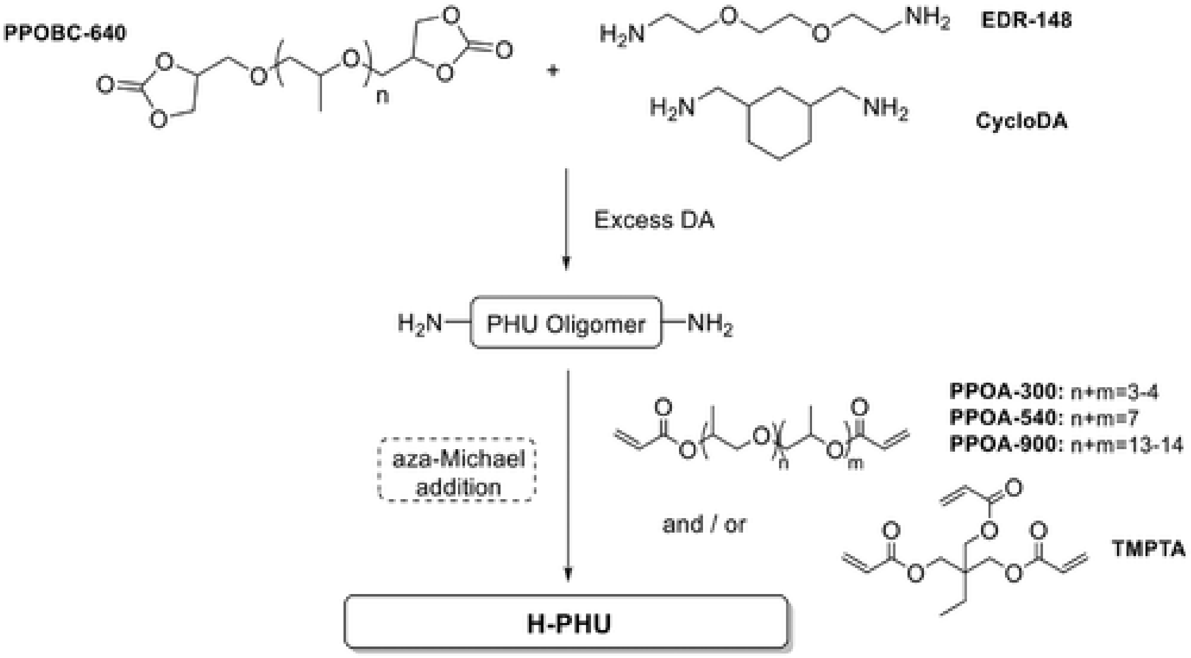
H-NIPUs via aza*-Michael Addition*: It is striking to notice that very few examples of radical reactive hydroxy-urethanes involve acrylic-modified components. The reason is that due to the high reactivity of the acrylic moieties toward amines, the cyclic carbonate acrylates can react with amine by either the ring opening of the cyclic carbonate moiety resulting in the formation of the classical hydroxy–urethane adducts, or with the acrylic moiety through an *aza*-Michael type mechanism (**Scheme 19**).[57] For cyclic carbonate acrylate (CCA), Bassam et al. proved that the *aza*-Michael type addition was favored compared to the ring opening reaction.[76]



Scheme 19 Competition between ring opening of the cyclic carbonate and *aza*-Michael addition onto the acrylic moiety in the reaction between CCA and an amine.

As a matter of comparison, Mülhaupt et al. found that only 2% of methacrylate moieties were converted in an *aza*-Michael addition when the amine was added in excess.[101]

Caillol et al. developed new types of hybrid-NIPUs (H-NIPUs), synthesized via an *aza*-Michael type process[106] by reacting in a bulk process a polypropylene oxide-based bis cyclic carbonate with an excess of diamine to yield homotelechelic oligoPHUs. The latter further reacted with different poly(propylene oxide) bis-acrylate (PPOA) and trimethylolpropane tris-acrylate (TMPTA) to form the hybrid NIPUs (**Scheme 20**).



Scheme 20 H-NIPUs formed via the *aza*-Michael addition of amino homotelechelic oligoPHUs with polyacrylics.[106]

The viscosity of the PHUs depended on the degree of polymerization and the diamine structure. The H-NIPUs were cured at room temperature and 48 h were needed to ensure an almost complete conversion of the acrylic moieties. The T_g was a compromise between the rigidity originating from the amount of the triacrylate and the flexibility provided by the chain length of the bis-cyclic carbonate. However, most of the obtained materials were brittle. When diacrylates were added into the formulation to increase flexibility, the T_gs usually were around -30 °C. Gel contents were higher than 90%. Short amino-telechelic oligomers were found to be detrimental because they provoked demixing, especially when long acrylic chains were used.

3.2.4 Radical Reactive (H)UMAs—Summary of the Synthetic Strategies

The synthetic pathways towards the formation of (hydroxy)urethane methacrylates—(H)UMAs discussed above are summarized in **Figure 9**.

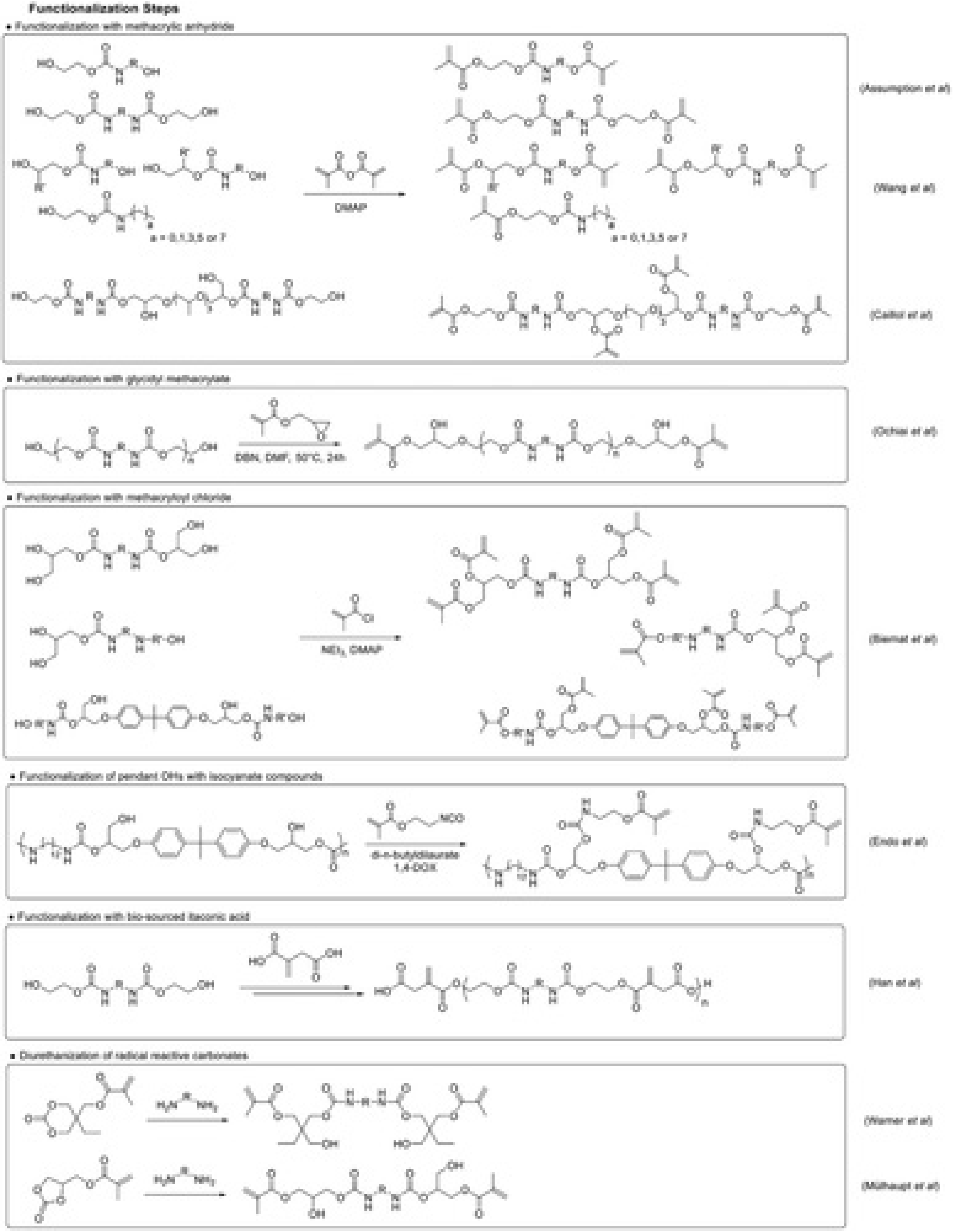


Figure 9 General summary of the different functionalization strategies towards the formation of (H)UMAs.

In a majority of cases, esterification reactions are used in order to bring the methacrylate functionality. The use of methacrylic anhydride has been extensively described and proved to be effective in the functionalization of alcohol moieties (coming from both the ring-opening of the ethylene carbonate or pendant hydroxyl groups of PHUs) provided that dimethylproprionic acid (DMAP) was used as a catalyst. Interestingly, the functionalization also worked in bulk, meaning that no solvent removal is needed prior to further crosslinking.

Methacryloyl chloride was also used for the functionalization of hydroxyl groups. Catalysis is usually needed and triethylamine is often employed in order to avoid the generation of hydrochloric acid (HCl). This brings further issues in terms of processing conditions since solvent and very low temperatures are needed to avoid runaways during functionalization. Therefore further purification of the (H)UMAs is needed before any crosslinking reaction can be envisioned. In all the cases, the raw materials are petroleum-based, although bio-based itaconic acid has been used for the formation of (H)UMAs. Since the itaconic acid is a diacid, an original oligomerization strategy to afford itaconic-containing poly(ester-urethane)s has been developed.[59]

Epoxidation reaction via the ring opening of glycidyl methacrylate has been also used. This reaction was effective but it was found to be long, needed catalysis and was performed in dimethylformamide (DMF), which requires further purification steps.

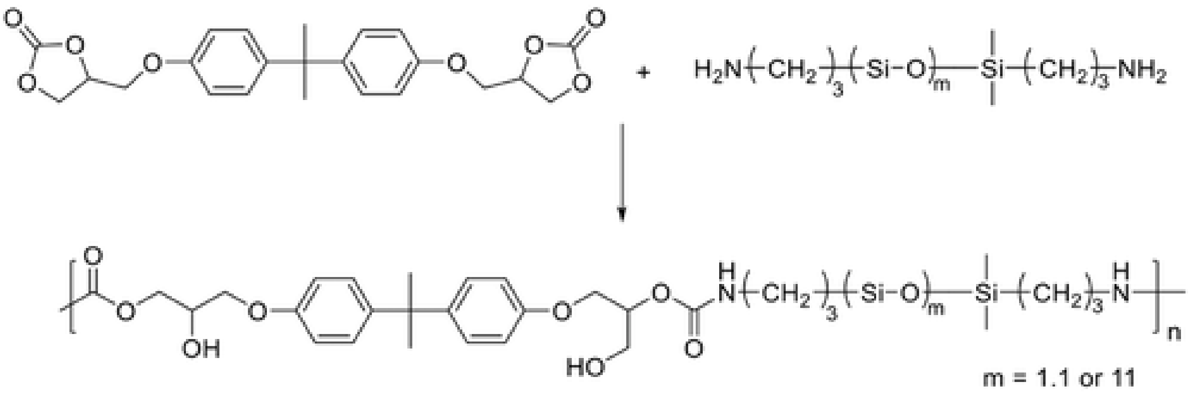
Another possibility is the formation of carbamate moieties. This can be done using both isocyanate-dependent and isocyanate-free pathways. An example of the isocyanate-dependent route was the functionalization of pendant OH-groups of PHUs with 2-methacryloyloxyethyl isocyanate. Despite the success of the functionalization, this method presents the drawback of using isocyanates. The diurethanization of a radical reactive carbonate appears as a promising pathway towards the formation of methacrylic homotelechelic oligo(H)UMAs. Some examples of oligoUMAs were reported and used in 3D-printing applications.[99, 100]

Si-Containing H-NIPUs

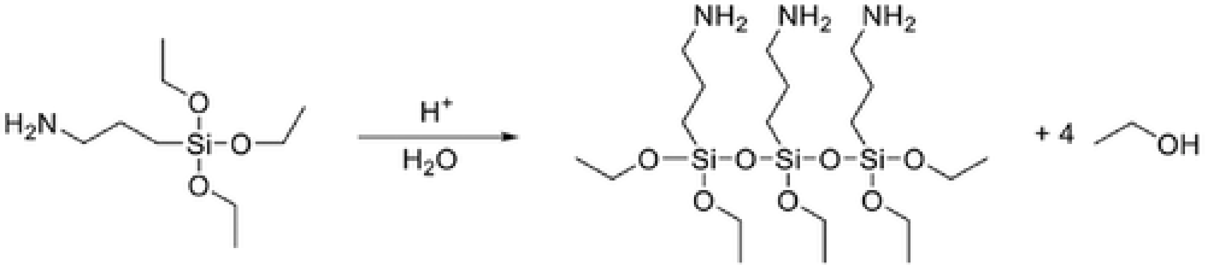
Siloxane-containing H-NIPUs have been prepared in order to confer new kinds of properties to the hybrids such as hydrophobicity, high flexibility, and high thermal stability.[107-109] Siloxane moieties can be incorporated through various synthetic means. They can be located in the inner backbone of the final linear NIPU. They can also be incorporated into hybrid siloxane–NIPU materials thanks to specific reagent bearing both one siloxane group and one cyclic-carbonate or amine group. They will then form hybrids in a similar way the hydroxy urethane modifiers did in the case of NIPU–epoxy (HUM) or NIPU–acrylic (HUMAs). In this case, siloxane groups will be reactive chain ends, that can act as crosslinking agents thanks to the formation of Si⍰O⍰Si bridges. Both routes will be described.

3.3.1 Si-Containing Linear H-NIPUs with Inner Siloxane Backbones

Endo and co-workers carbonated bisphenol-A diglycidyl ether (BADGE) with CO_2 and the resulting product was directly reacted with a siloxane containing diamine (**Scheme 21**).[110] Propylene glycol methylether acetate (PGMAC) was a suitable solvent (when compared to N-methylpyrrolidinone and 1,4-dioxane) to obtain both a good conversion of the epoxy to carbonate and the final PHU in high yields after addition of the siloxane containing diamine. When comparing the siloxane containing NIPUs with a classical NIPU made of carbonated BADGE and dodecanediamine, it was found that the higher the siloxane content, the higher the solubility of the formed products in solvents of low polarity such as Et_2O. Water contact angle and flexibility increased as the siloxane content increased. The materials had low glass transition temperatures (1 and 26 °C as opposed to 40 °C with dodecanediamine).



Scheme 21 PHU containing siloxane-based inner backbone according to Endo and co-workers.[110]



Scheme 22 Multiaminosilane synthesis according to Figovsky and co-workers.[114]

Hanada and co-workers synthesized siloxane containing bis-cyclic carbonates that later reacted with diamines (hexamethylene diamine (HMDA), bis-aminopropylpiperazine, and xylylenediamine).[111, 112] An example of the synthesized bis-cyclic carbonate compounds is provided in **Figure 10**. The authors targeted applications such as thermal recording medium, artificial leather, thermoplastic polyolefin resin skin material and weather strip material. The number average molar masses were in the range 30 000–40 000 g mol^{-1} depending on the siloxane-containing bis-cyclic carbonate and the diamine used. Tensile strengths of around 24 to 35 MPa and elongations at break in the range of 15 to 83% were obtained.

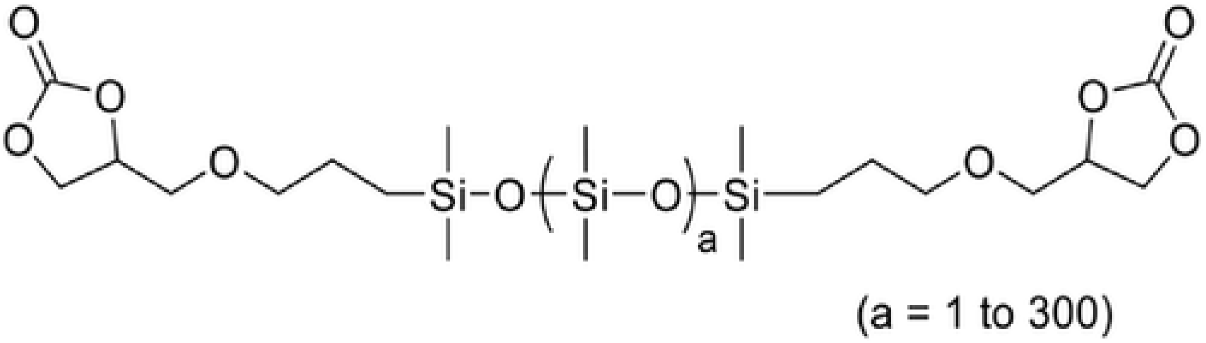


Figure 10 Example of a siloxane-containing bis-cyclic carbonate macromonomer as patented by Hanada et al.[111]

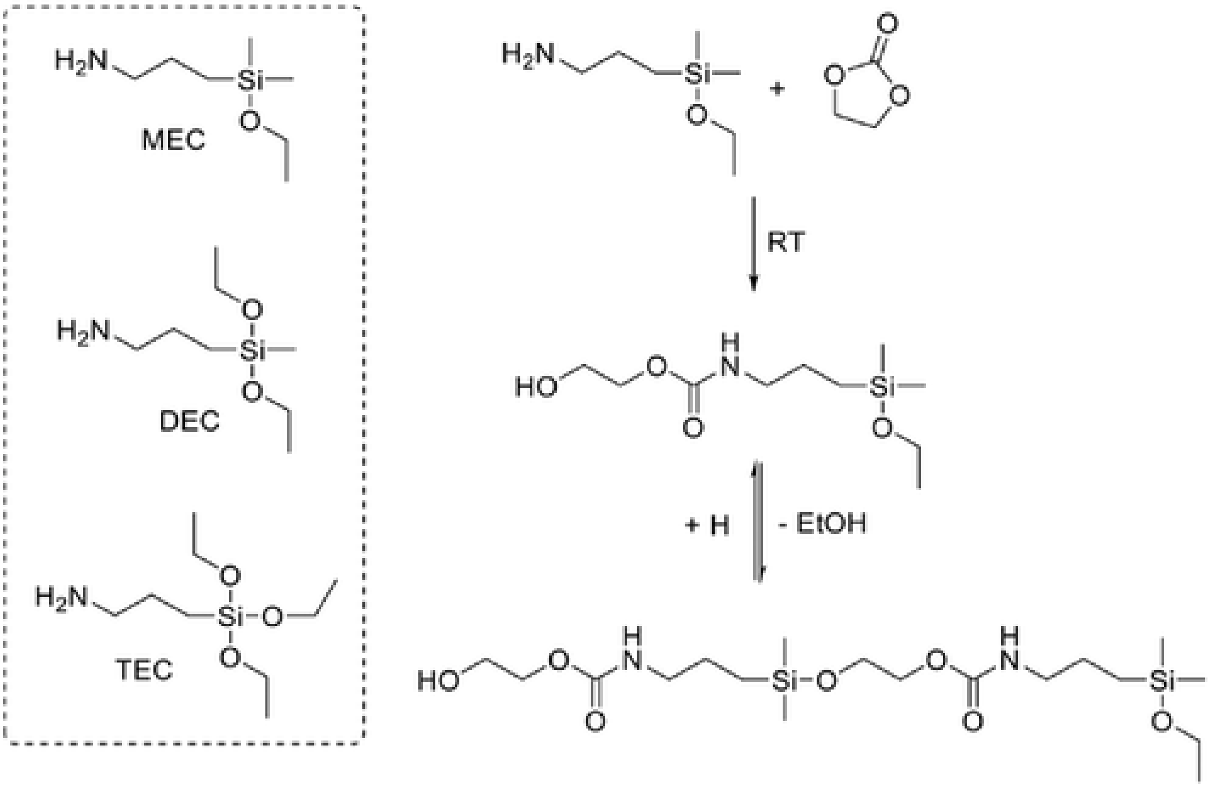
Figovsky et al. used a siloxane-containing macromonomer in their epoxy–amine H-NIPU systems.[113] They claimed the synthesis of nanostructured H-NIPUs that were constituted by epoxy-function, cyclic carbonate, amine-functional, and (meth)acrylate components. Among them, at least one epoxy, amine, or (meth)acrylate contained alkoxysilane moieties. The formed polymers crosslink upon curing at ambient conditions by means of atmospheric moisture, yielding nanostructured materials without the need of using water embedding or addition of nanofillers. The materials exhibited improved abrasion resistance and higher impact resistance and flexibility compared with a conventional epoxy resin siloxane-based material that was used as a reference.

3.3.2 H-NIPUs Originating from NIPUs with Siloxane Reactive Chain Ends

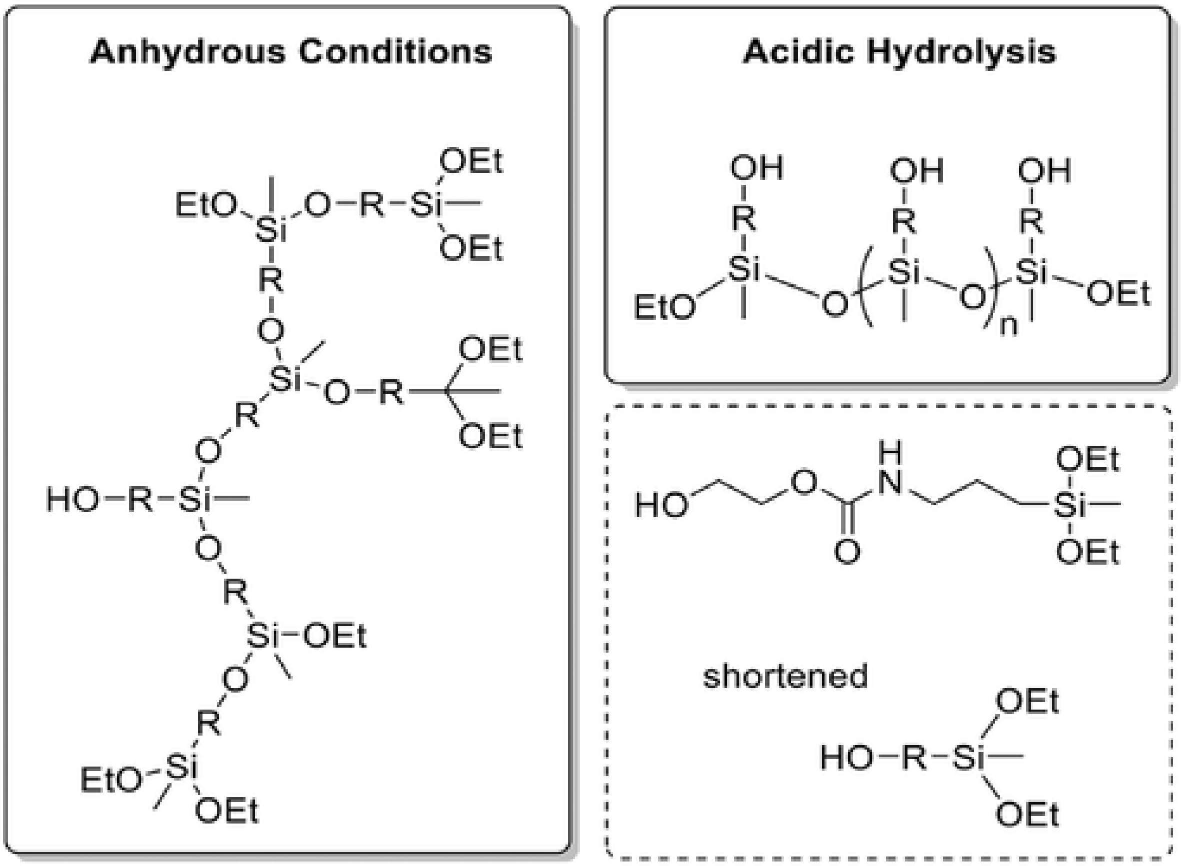
Another important pathway is the reaction of siloxane or Si-containing reagents bearing cyclic carbonate or amine moieties. Similar to the Hydroxy Urethane Modifiers (HUMs and HUMAs), these compounds usually lead to the formation of siloxane chain-ends NIPUs, with the siloxane moieties capable of crosslinking through the formation of Si–O–Si bridges. The following description will include i) Si-containing reagents bearing amine moieties, ii) Si-containing reagents bearing cyclic carbonate moieties and iii) Si-telechelic PHU prepolymers.

Si-Containing Reagents Bearing Amine Moieties: Figovsky and Shapovalov developed thermostable resins with Si-containing amine components using multiaminosilane agents as hardeners in the curing process of their epoxy–PHU H–NIPU process (**Scheme 22**).[114] The commercially available *γ*-aminopropyltriethoxy silane was hydrolyzed to yield the multiaminosilane curing agent. Similar dendrosilanes containing aromatic units were introduced into epoxy and cyclocarbonate resins. Once introduced into the resins, the alkoxy groups were hydrolyzed by the humidity of either the air or that of the surface of the substrate. The newly built silanol-hydroxyl groups reacted with the surface hydroxyl groups and forms strong bonds, making them good adhesion promoters.[113]

Another example is the work of Narayan and co-workers[115] who synthesized oligo(siloxane-urethane) through the reaction of 3-amino-propyldimethylethoxysilane (MEC), 3-aminopropyldiethoxymethylsilane (DEC) and (3-amino-propyltriethoxysilane) (TEC) with ethylene carbonate. The formed adducts underwent a spontaneous rearrangement by condensation of the alkoxysilane groups with the hydroxyl functions resulting from the ring opening of the ethylene carbonate as depicted in **Scheme 23**.



Scheme 23 Oligo(siloxane-urethane) formation from aminopropyl alkoxysilanes according to Narayan et al.[115]

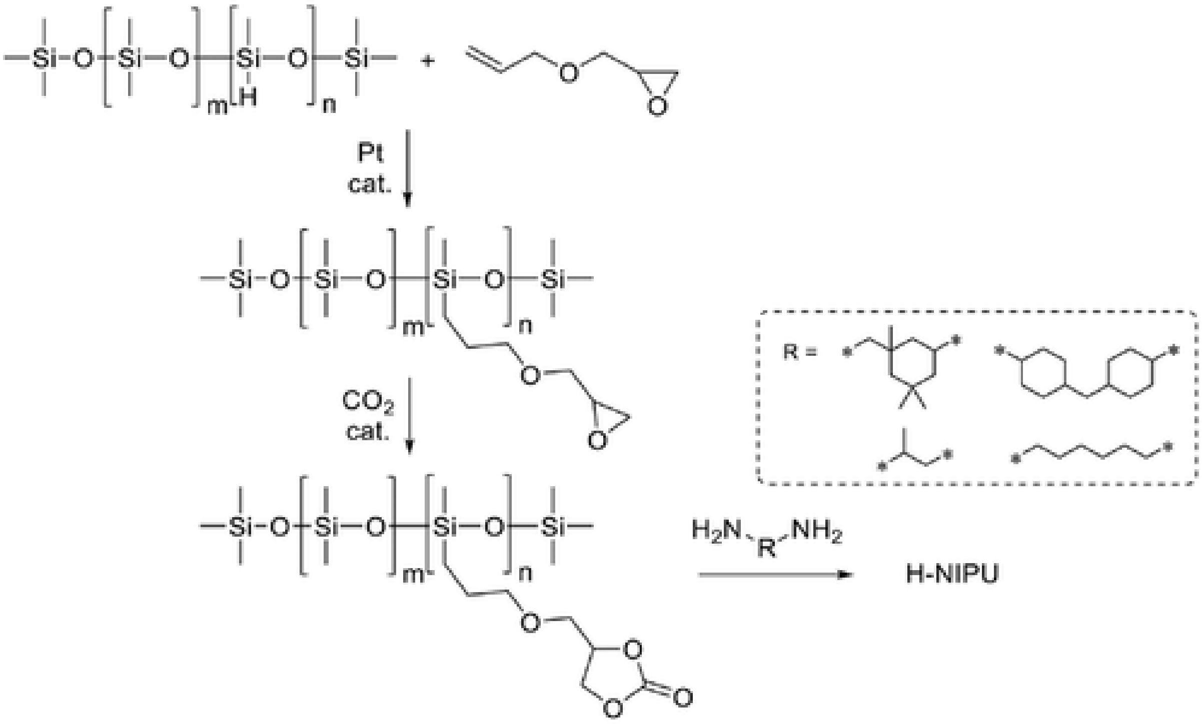


Scheme 24 Condensation process of the DEC-propylene carbonate adduct according to Nerayan et al.[116]

The same team reported the possibility to tune the condensation process for those siloxane-urethane adducts containing two alkoxy groups.[116] Under anhydrous conditions, the monomer formed a hyperbranched structure starting from an AB_2-type unit. This was not the case under acidic conditions where a linear structure was formed (**Scheme 24**).

Gomez-Lopez et al. also described the use of TEC in the formulation of adhesives[117] composed of trimethylolpropane tris-carbonate (TMPTC), the aromatic m-Xylylene diamine, and dopamine. TEC allowed for the formation of a crosslinked network, providing adhesive strength to the final adhesive, while dopamine served as adhesion promoter with the substrate. The extra addition of a soft segment, namely poly(propylene glycol) dicyclic carbonate (PPGdiCC), allowed to reach the best compromise in terms of shear strengths and shear adhesion failure temperatures (SAFT). It was thus found that a ratio of 70/30 TMPTC/PPGdiCC gave the best performances. The further addition of 3.9 mol% (regarding monomers) of dopamine and TEC allowed to reach the highest shear strength (around 21.6 MPa). An adhesive failure was observed, witnessing the high strength of the crosslinked network that overpassed the properties of the noncontaining TEC material.

Si-Containing Reagents Bearing Cyclic Carbonate Moieties: Work in this field was pioneered by Wnek and co-workers that reported the synthesis of polysiloxane polymers bearing cyclic carbonate side chains[118] and studied the influence of the presence of the side carbonate on the dielectric properties and ion conductivity for battery applications. No postfunctionalization of the carbonate moieties was carried out. Liu et al.[119] published the synthesis of cyclic carbonate-containing polysiloxane compounds for the production of coatings with improved water resistance. Those adducts were further reacted with a stoichiometric amount of diamines, at 100 °C in a mold for 10 h to yield polysiloxane–PHUs. Different degrees of carbonation were used to tune the concentration of hydroxyurethane moieties in the final material (**Scheme 25**). Differential scanning calorimetry (DSC) analyses revealed a single glass transition temperature that varied from 3 to 60 °C depending on the amine and the degree of carbonation of the polysiloxane, indicating that no phase separation occurred. The degree of carbonation that controlled the extent of crosslinking, influenced the mechanical properties by increasing the tensile strength and Young modulus, but lowering the elongation at break. The same behavior was observed when increasing the amount of cycloaliphatic moieties of the diamine.



Scheme 25 Polysiloxane-PHU H-NIPUs from cyclic carbonate-containing polysiloxanes according to Liu et al.[119]

Surprisingly, and despite the acceptable swelling indexes in water (from 3 to 22 wt%), the water resistance decreased with the degree of crosslinking. This was attributed to the increase in hydroxyl moiety concentration within the formed material. The use of more hydrophobic diamines (especially those containing cycloaliphatic rings) decreased the swelling in water and yield materials with higher Young moduli and tensile strengths.

Caillol and co-workers functionalized polysiloxane by reacting the Si-H moiety with allyl glycidyl ether.[109] In addition to synthesizing the same product as Liu et al.[119] they obtained a novel structure with epoxidized eugenol attached to the polysiloxane backbone. In all the cases, the epoxide moieties were further carbonated by fixation of CO_2. The resulting low viscosity products were then cured with 2-methylpentane-1,5-diamine (linear) and 1,3-cyclohexanedimethanamine (cyclic), yielding PHU hybrids. Conversions in the range of 90% were measured by FITR, which are very high for such kind of chemistry, a feature that was attributed to the low viscosities of the reactive polysiloxane-based carbonates. This result was further confirmed by gel contents higher than 90% as determined by swelling in THF and drying in an oven (with the soluble part removed). The thermomechanical properties of the resulting materials were studied, with a specific emphasis on the influence of the aromatic ring of the eugenol function, that induced a dramatic increase of 20 °C in the T_g value as opposed to the allyl glycidyl ether-based polysiloxane carbonate.

Si-Telechelic PHU Prepolymers: To the best of our knowledge, only few recent examples of reactive telechelic-oligoPHUs with Si-containing chain ends, have been reported in the scientific literature. This is not surprising as the formation of well-defined reactive telechelic PHUs is still one of the major unsolved issues in this chemistry. Caillol's group pioneered the field with the synthesis in 2018 of sol-gel hybrid-poly(hydroxyurethane)s.[120] The synthetic process consists in end-capping difunctional PHU monomer (namely, bis-cyclic carbonates or diamines) with siloxane-containing amine or mono cyclic carbonate. A subsequent sol-gel process resulted in the crosslinking of the siloxane homotelechelic PHU chains (**Figure 11**). A very good thermal resistance, with $T_{d5\%}$ higher than 300 °C was obtained. The presence of a rubbery plateau with a modulus of about 10^7 Pa after the alpha transition in the dynamic mechanical thermal analysis (DMTA) measurements showed that the polymer was crosslinked, which was confirmed by the gel content (90%) measured by extraction of the soluble polymer with THF.

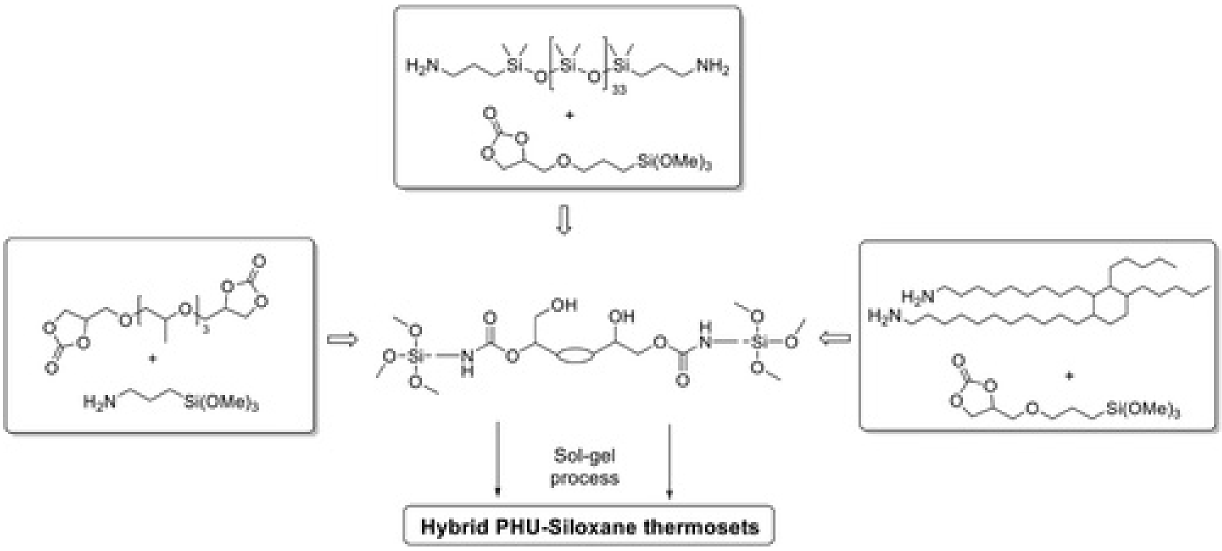


Figure 11 Formation of hybrid PHU–siloxane thermosets via the synthesis of siloxane homo-telechelic oligoPHUs.[120]

Diglycerol dicarbonate (DGDC)[121] and sugar-based dicarbonates (namely D-sorbitol and D-mannitol)[122] were reacted with various diamines such as Jeffamine D-2000 or PDMS (2,5 or 5k) diamines and the resulting PHUs were carefully characterized with respect to their chain ends. Jeffamine-based PHUs were found to have carbonate chain-ends while PDMS preferably yielded amine-terminated PHUs. The end-capping reaction of the prepolymers was performed with an amine-containing siloxane (DAMO, *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane) in the Jeffamine case, while PDMS-based PHUs were functionalized with an epoxy-containing siloxane (GLYMO, [3-(2,3-epoxypropoxy)-propyl]-trimethoxysilane).[122] The rection conditions was a case to case study depending on the ability of the resulting product to cure in a 24 h timeframe: for Jeffamine-based PHUs, only 0.25 h at 120 °C were enough for the D-mannitol-based polymer to further cure, while the D-sorbitol-based polymer needed to react during 1 h at 120 °C with the help of a catalyst. The PDMS-based polymers were in all the cases able to be end capped at 22 °C, but the reaction time had to be as low as 2 h otherwise curing started to occur even at room temperature when reaction times of 16 h were implemented. Finally, curing was performed for all the products at 22 °C during 24 h under moisture (20–30 °C humidity). The PDMS-based H-NIPUs had a very limited swelling in water, with no observed leaching from the films, which made them potential candidates for outdoor sealant applications. On the contrary, Jeffamine-based product swelled and became very soft after immersion in water, making their handling very complicated, and further outdoor application compromised. Remarkably, D-mannitol-Jeffamine based material broke down into small pieces due to a low mechanical strength.

In 2020, Gomez-Lopez et al. reported the use of telechelic Si-containing NIPUs for the synthesis of adhesives based on a sol-gel process.[123] Carbonate-telechelic NIPUs were synthesized in bulk by reaction of an excess of poly(propylene glycol) dicyclic carbonate (PPGdiCC) with a fatty-acid-based diamine—Priamine 1074—prior to being end-capped by TEC. The resulting alkoxysilane prepolymer was then cured to yield the final network, **Figure 12**.

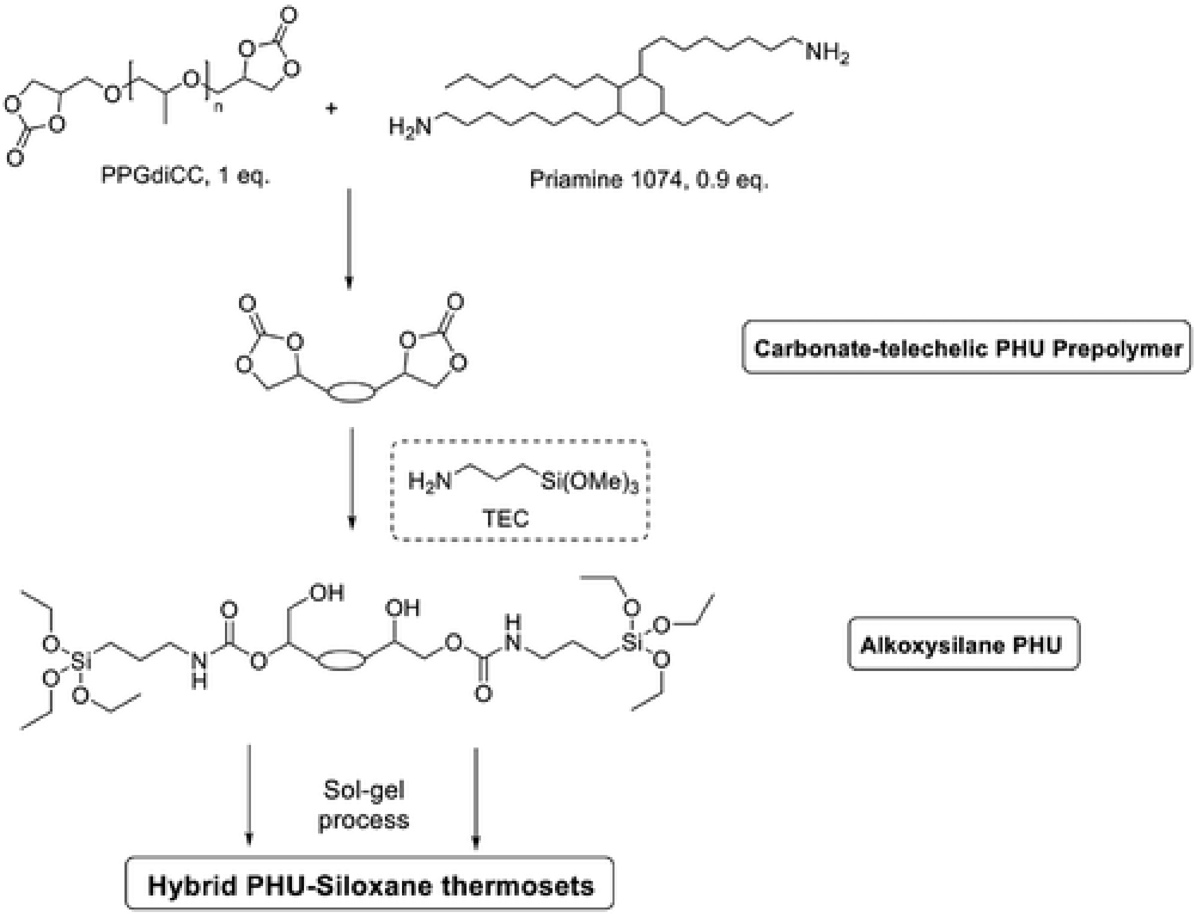
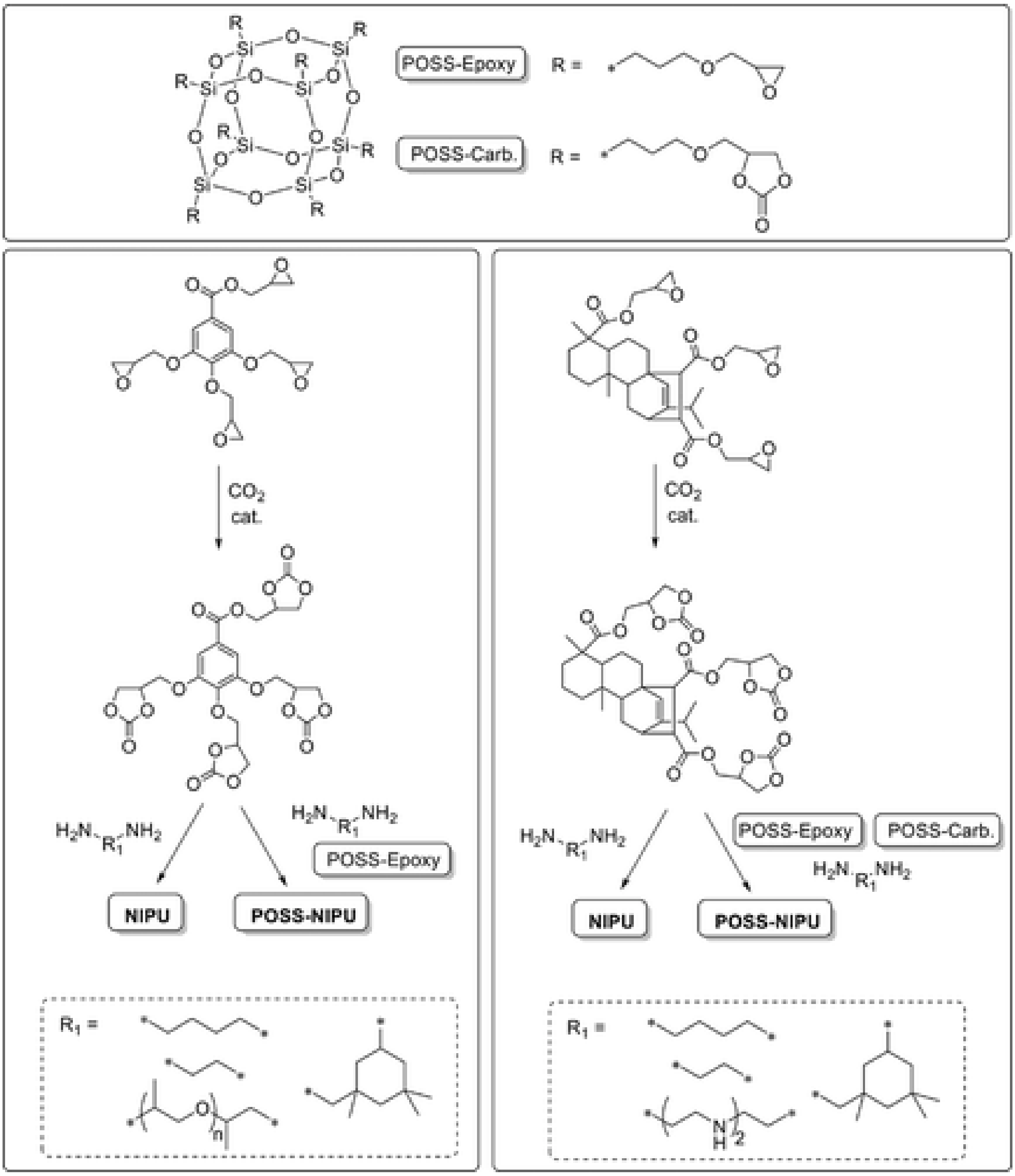


Figure 12 Formation of Hybrid PHU–siloxane adhesives.[123]

The PHU was formed in bulk at 80 °C during 24 h, while the end-capping reaction of the carbonate-telechelic PHU with TEC was performed in bulk at 40 °C during 45 min to avoid undesired condensation. After functionalization, rheological studies were undertaken in order to determine the gel time (namely when *G* crosses *G*’) of this reactive prepolymer. The gelation process was found to be highly temperature dependent (20 min at 120 °C while no crosslinking occurred at 25 °C after 15 h curing). The process was found to follow the Arrhenius’ law and the activation energy of the whole process (hydrolysis and condensation of the ethoxysilanes) was gauged to be 50 kJ mol^{-1}. The process was fastened by the addition of 1 wt% of acetic acid at 100 °C. A low-lap-shear strength of 1.1 ± 0.2 MPa was measured, with a cohesive failure, meaning that internal forces of the adhesive were not strong enough. The properties were then improved by substituting a part of PPGdiCC soft segment by a hard segment, namely resorcinol dicyclic carbonate, in the formulation of the PHU. When 40% of this hard segment was incorporated, the lap shear increased up to 2.9 ± 0.6 MPa, a feature that was ascribed to non-covalent interactions of the resorcinol moieties (*π*-*π* stacking). Gel contents of 70% were measured in THF. Water uptakes between 6 and 12% were measured for the formulation comprising 0 to 40% resorcinol, with the lowest value for the 40%-containing one, and T_gs between -32 °C and -23 °C were measured.

3.3.3 POSS-Containing H-NIPUs

Another possibility to introduce Si-containing moieties into NIPUs is through the use of polyhedral oligomeric silsesquioxanes (POSS). This compound has been used to reinforce mechanical properties, thermal stability, improve water tolerance or dielectric properties in polyurethanes or polycarbonate composites.[124-128] Liu et al. incorporated POSS into PHU coatings containing gallic acid[126] or rosin[128] (**Scheme 26**). In the first example, gallic acid-based epoxy resin was treated by catalytic fixation of CO_2 to form the tetracarbonate. The carbonate was reacted with various diamines and also modified with epoxidized-POSS components in a similar process than the epoxy–NIPU H-NIPU. The introduction of POSS increased the water resistance of the NIPUs, without being detrimental to other properties such as impact resistance, pencil hardness or flexibility. In general, the increase of the POSS loading induced an increase in the rigidity of the material (some were more brittle) and thermal stability ($T_{d50\%}$ over 300 °C by thermogravimetric analyses—TGA), which was attributed to the increase in the crosslinking density.



Scheme 26 POSS-containing NIPUs from gallic acid (left) and rosin (right) according to Liu et al.[126, 128]

Rosin-based carbonate compounds were reacted with epoxidized-POSS and carbonated-POSS and diamines. The effect of POSS was similar than for gallic acid based NIPUs. For similar POSS contents, the epoxy-POSS yielded materials with better water resistance than the carbonated-POSS, which was attributed to the formation of urethane linkages. This positive impact of the incorporation of POSS into NIPU formulations on the mechanical properties was confirmed by Blattmann and Mülhaupt.[129] They targeted the development of a solvent-free process for the production of POSS-containing NIPUs and investigated the pot life and gel times of different formulations while incorporating carbonated-POSS. Due to the very high functionality, the curing with diamine led to extremely short pot life and gel time (hundreds of seconds). Because of the improvement in processability, without being too detrimental for mechanical properties, reactive diluents based on carbonated glycidyl ethers were utilized (**Figure** 13). Superior mechanical properties, with Young moduli of exceptional values (until 4000 MPa) were obtained. Unfortunately, no enhancement of water resistance was observed, which was attributed to the presence of hydrophilic hydroxyurethane moieties.

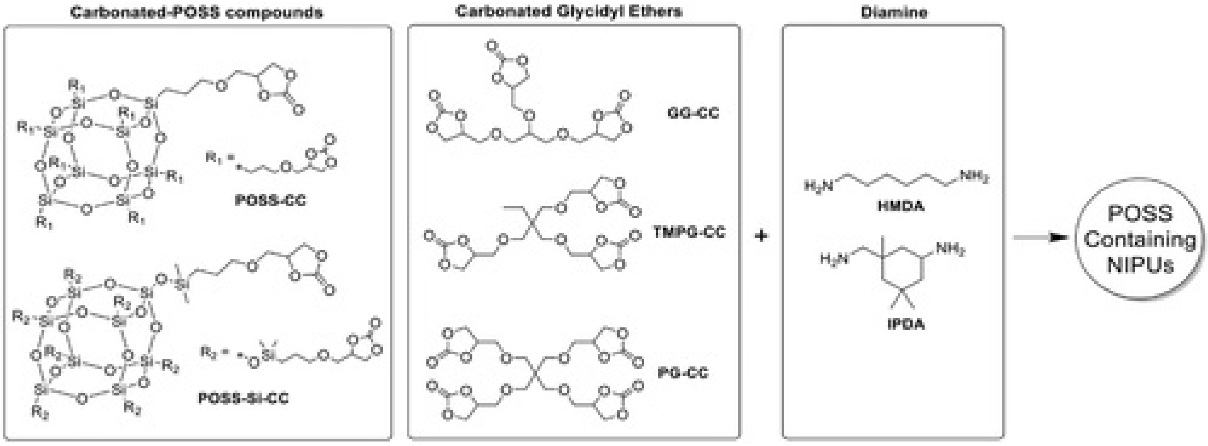


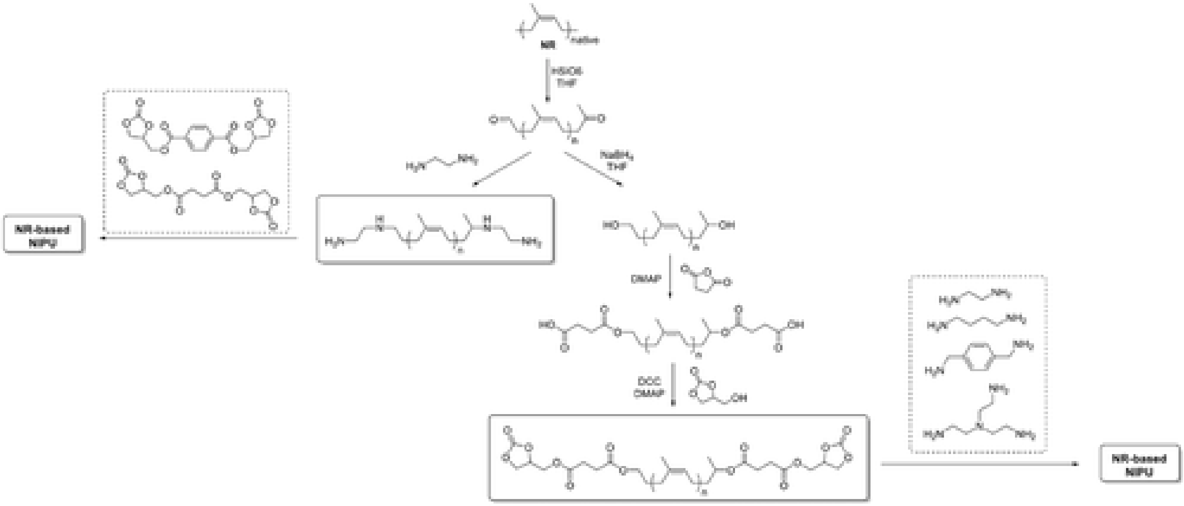
Figure 13 POSS-containing NIPUs according to Blattmann and Mülhaupt.[129]

Biopolymer and Biobased Polymer-Containing NIPUs

Biopolymers, defined as naturally occurring polymers, are gaining an increasing interest because they are renewable compounds leading towards more sustainable and environmental-friendly materials. These polymers do not need to be synthesized, as opposed to the epoxy and acrylic resins described above. In addition, by means of wise chemical modification, the incorporation of such compounds can significantly broaden the final properties of the formed materials. The biopolymers incorporated in NIPUs include natural rubber and derivatives of wood resources, namely tannin, lignin, and cellulose. Contrary to biopolymers, biobased polymers are polymers not naturally produced, but engineered from bio-based resources (usually monomers).

3.4.1 Natural Rubber H-NIPUs

In 2017, the team of Pilard reported on the use of natural rubber (NR) for the synthesis of NIPUs.[130] Their process consisted in degrading NR into oligo-isoprene, that were further functionalized to diamino and bis cyclic carbonate compounds. Reaction of the diamines with bicyclic carbonates and biscyclic carbonates with diamines led to the NR-NIPU hybrids (**Scheme** 27). Different chain lengths of the functional oligo-isoprene were targeted (1000 and 2000 g mol^{-1}) and tested in a subsequent polymerization with bis-cyclic carbonates or diamines. The advantage of degrading the NR was not only to get a better control of the chain length, but also to have oligo-isoprene that can be dissolved in solvents such as THF and dioxane, thus allowing reactions in solution to form NIPUs. Dioxane was found to be the most suitable solvent since temperatures as high as 100 °C were necessary for the reaction to proceed. Bulk polymerization was also performed. No formation of by-products such as urea or amides was observed. Interestingly, by playing with the process' conditions and the carbonate to amine ratio, a 100% conversion of the carbonates could be achieved in the case of carbonate-telechelic NRs by reaction with various diamines or triamine (Scheme 27). Unfortunately, solubility issues made the characterization by SEC difficult. Glass transition temperatures ranging from -58 to -30 °C were obtained. Noteworthy, the longer the chain the lower the T_g, which was attributed to the higher flexibility of the polymer chains by the increasing amount of oligo-isoprene incorporated.

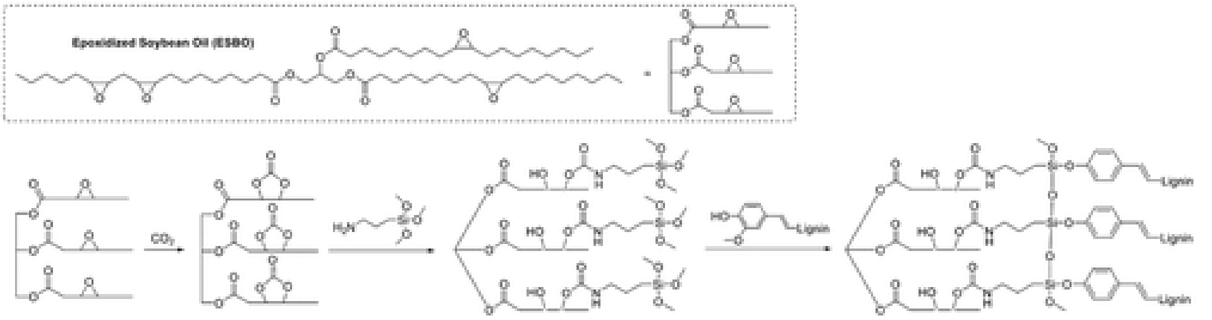


Scheme 27 Natural Rubber-based NIPUs (NR-based NIPUs).[130]

3.4.2 Lignin and Tannin-Based H-NIPUs

Lignin-Based H-NIPUs: Lignin is nowadays considered as the main resource for the synthesis of bioaromatic monomers. It constitutes 20 to 25 wt% of wood with a world production from the pulp industry reaching 50 million tons per year.[131] Because this resource is low cost and is not in competition with the food industry, substantial efforts are directed toward its valorization. This complex biopolymer however has to be degraded in smaller building blocks prior its use. Most polyols are formed, which made lignin extremely popular in the PU chemistry since it could directly react with isocyanate compounds.[132-135]

However, quite scarce examples of the use of lignin for the production of NIPUs can be encountered in the literature. Lee and Deng used the phenolic units of lignin in combination with a siloxane-modified carbonated soybean oil for the design of lignin-based NIPUs (**Scheme 28**).[136] During the polymerization process, the condensation of siloxane moieties, yielding Si—O—Si groups, occurred. When curing the final materials, at 60 °C, lignin acted as a crosslinking agent and the resulting tensile strength increased with the increase in lignin content. However, when curing at room temperature, the materials were found to be much more flexible, which might be due to inefficient curing between lignin and the siloxane moieties. The crosslinking was this time governed only by the formation of siloxane bridges with lignin only blended in this matrix. Surprisingly, the increase in lignin content increased the final elongation at break. The authors attributed these findings to the fast that low amounts of lignin did not hinder the formation of a 3D network by cross-linking between the siloxane moieties, while higher loading in lignin would leave less space for the formation of this siloxane network. As a result, the formation of linear Si–O–Si bridges would be preferred, making the final material more flexible.

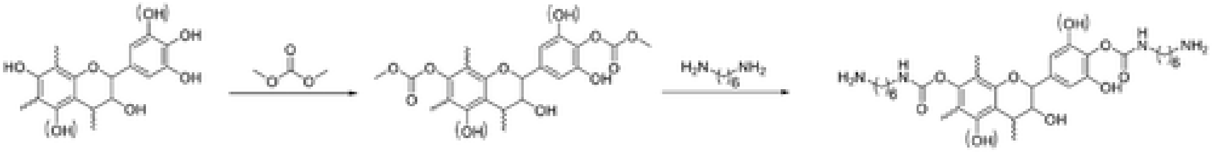


Scheme 28 Preparation of lignin based NIPUs in combination with siloxane-modified carbonated epoxidized oil.[136]

Soft-wood Kraft lignin was reacted with dimethyl carbonate and hexamethylenediamine.[137] The reaction temperature was found to play a significant role in the hardening of the materials (180 °C was found to be the best) but some degradation was noticed. Interestingly, the use of pressure in addition to the increase in temperature allowed the formation of good coatings onto beech wood, presumably due to a better wetting. The hydrophobicity (water contact angle) increased with the incorporation of lignin in the coatings.

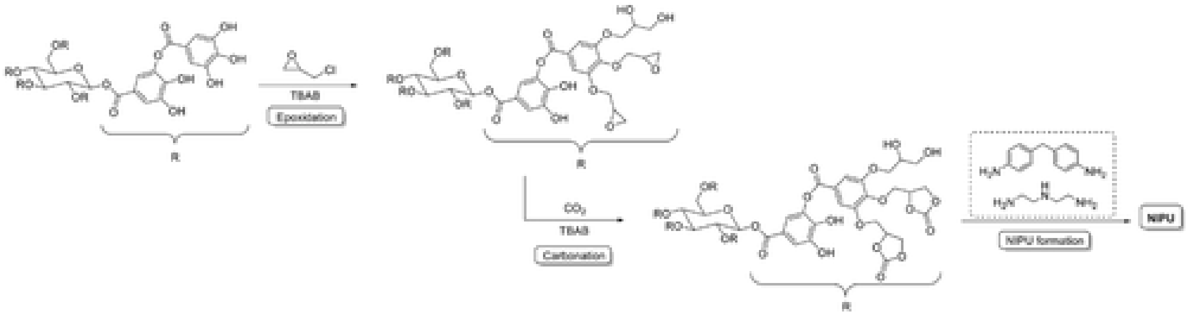
Tannin-Based H-NIPUs: Tannins are a by-product of the separation process of wood into cellulose, hemicelluloses, and lignin. The precise definition of tannins has evolved but a common agreement is found in the definition of Swain and Bate-Smith stating that tannins are water-soluble compounds with molar masses between 500 and 3000 g mol^{-1}.[138]

Thébault et al. used both hydrolyzable chestnut tannins (which have similar phenolic structures as gallic acid) and more complex flavonoid tannins for the synthesis of tannin-based NIPUs.[139, 140] In both cases, the synthetic strategy relied on the functionalization of hydroxyl groups with dimethylcarbonate and then reaction of the carbonate moieties with hexamethylenediamine, HMDA (**Scheme 29**). The tannin-based NIPUs were tested for coating applications onto different medium-density fiberboards originating from different kinds of trees. Higher water contact angles were measured indicating that tannin-based NIPUs are promising materials for the development of hydrophobic coatings for wood. The same team synthesized fully tannin-based NIPUs by substituting HMDA by an amine functional-tannin compound.[141] PU resins containing more than 70% of bio-based isocyanate-free components were synthesized. The authors claimed the potential use of such compounds for adhesive and coating applications.



Scheme 29 Tannin-based H-NIPUs, on the basis of flavonoid tannins.[140]

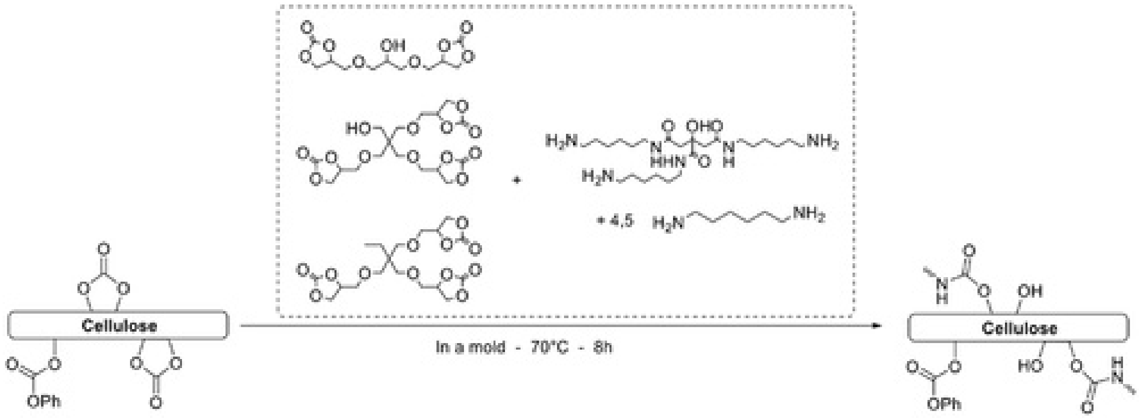
Meyer and co-workers used tannic acid for the synthesis of NIPUs (**Scheme 30**).[142] The synthetic pathway proceeded through the epoxidation of the phenolic moieties of the tannic acid, followed by subsequent carbonation to yield a multicyclic carbonate compound. Curing with both aliphatic and aromatic amines yielded NIPUs that exhibited good solvent resistance and antioxidant properties.



Scheme 30 Tannic acid-based NIPUs.[142]

3.4.3 Cellulose-Based H-NIPUs

Cellulose has also been used for the synthesis of NIPUs. Cellulose carbonate was prepared by reacting cellulose with diphenyl carbonate with dibutyltin dilaurate (DBTDL) as catalyst and dimethylacetamide (DMAc)–LiCl as the reaction medium. 5 wt% of cellulose carbonate was incorporated into a mixture of tricyclic carbonate and diamines, and then cured (**Scheme 31**).[143] At this low concentration, the cellulose filler mostly acted as a reinforcement additive (the Young modulus increased from 2100 to 2600 MPa with a marginal effect onto the elongation at break).

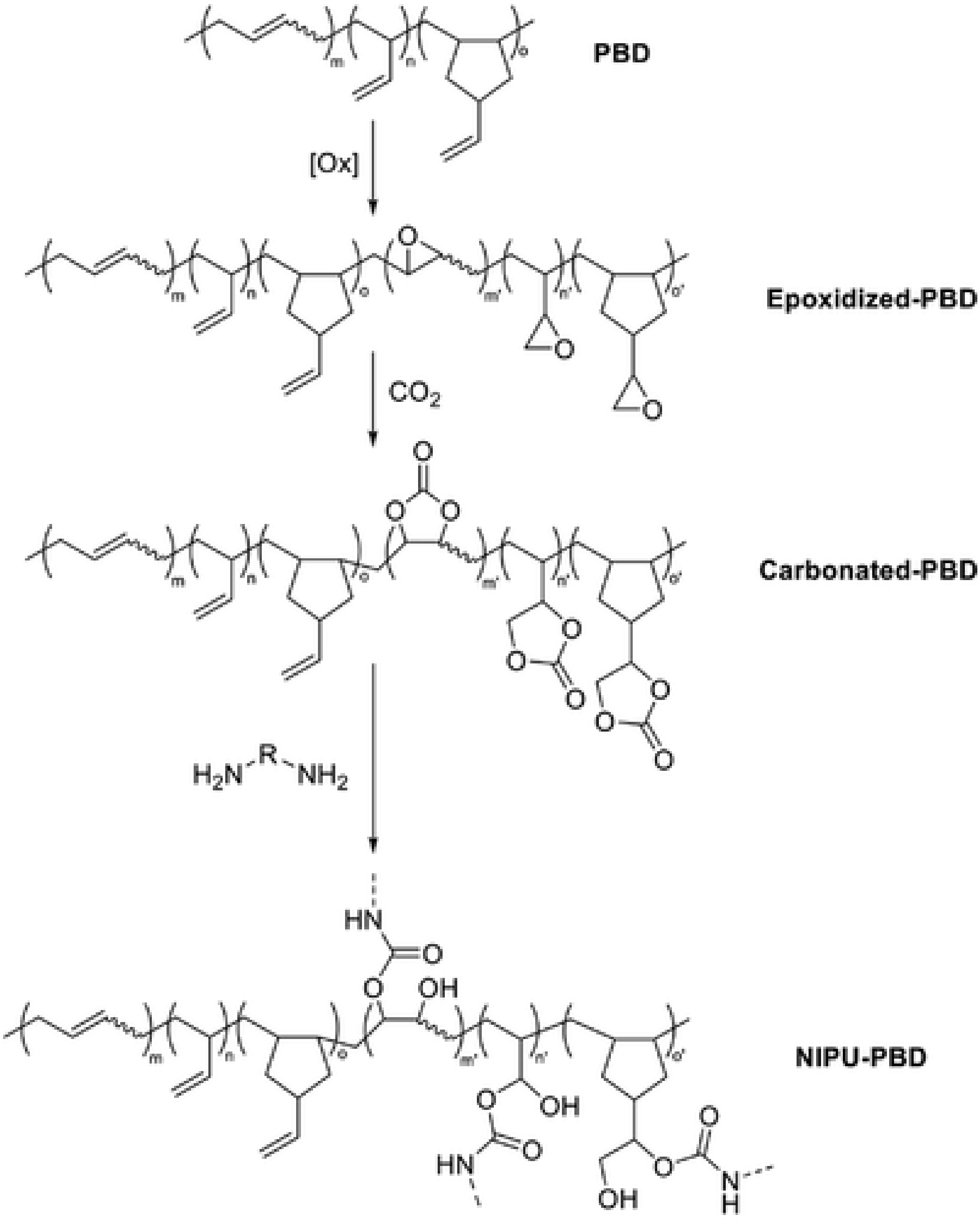


Scheme 31 Preparation of cellulose-based H-NIPUs according to Mülhaupt and co-workers.[143]

3.4.4 Miscellaneous Examples of Biobased H-NIPUs

In addition to the examples described in the previous sections (NIPU–Epoxy,[39, 49-52] NIPU–acrylic[57-59] and NIPU–siloxane hybrids),[119-123] some notable examples of bio-based H-NIPUs that involve special chemical routes should be mentioned.

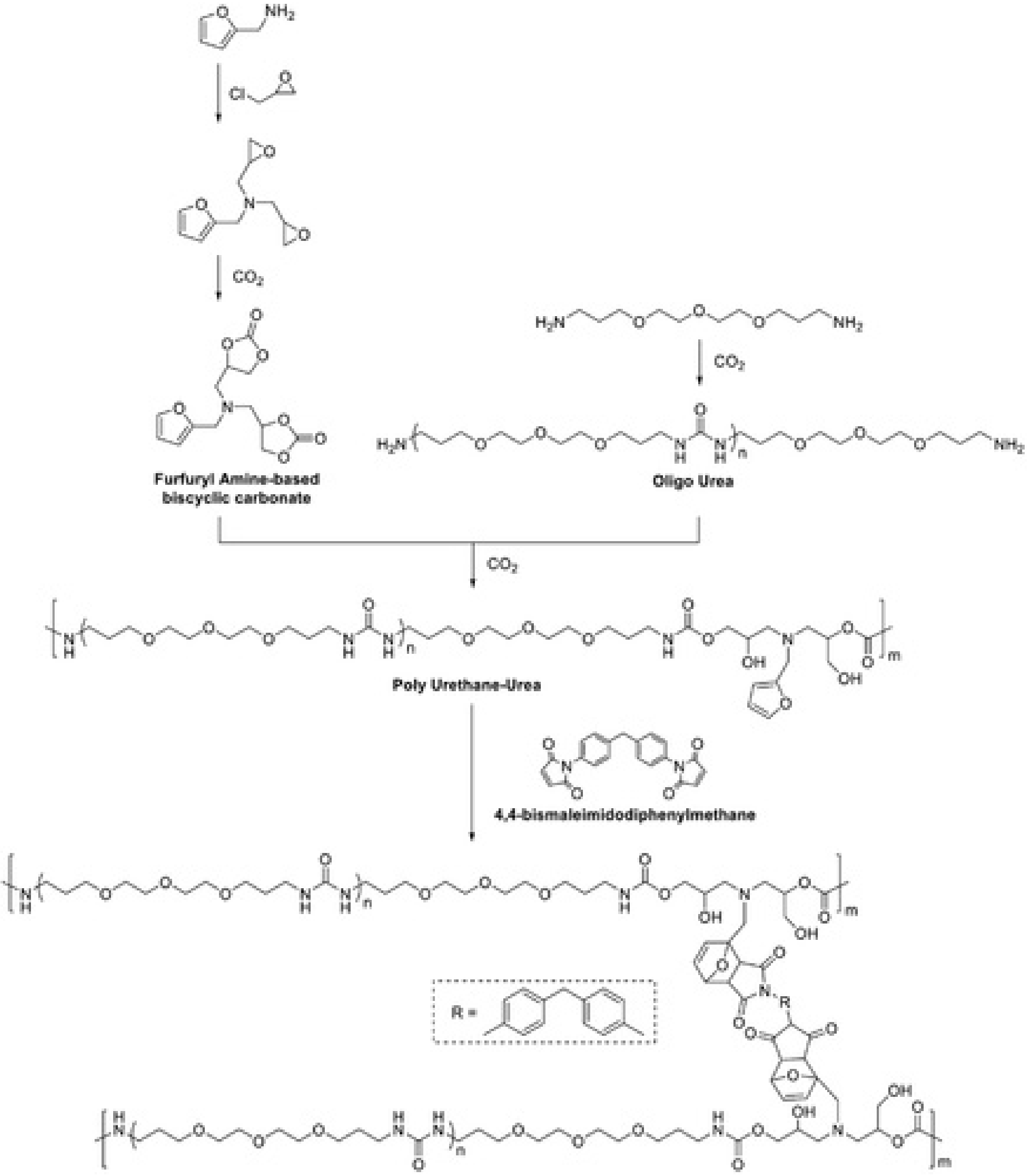
Dechent et al.[144] reported the catalytic carbonation of partially epoxidized polybutadiene (PBD) with CO_2 using salts of bis(triphenylphosphine)iminium and tetra-n-butylammonium (**Scheme 32**).



Scheme 32 Preparation of NIPU–polybutadiene H-NIPUs according to Dechent et al.[144]

90% conversion was achieved under optimized reaction conditions, regardless the molar mass of the native PBD (ranging from 1 to 40 kg mol^{-1}). The resulting carbonated PBDs were then cured with 1,4-pentane diamine and 1,8-octane diamine at 70 °C for 16 h with molar ratios of carbonate to amine of 1:1 and 1:2. It was observed that the larger octane diamine exhibited higher conversions to hydroxyurethane than the smaller pentane-diamine. In the case of 1:1 molar ratio, the degradation rate was slower for octane diamine-originating NIPU than for the pentane-based NIPUs, despite the relatively lower hydroxyurethane concentration in the same volume of polymer. The authors attributed this stability to the H-bonds existing between the C═O group of the unreacted carbonates and the NH and OH groups of the hydroxyurethane groups. DSC revealed two thermal features. The first one occurred at either around -20 °C or -65 °C and was ascribed to the T_g of the soft PBD (the two T_gs correspond to 2 molar masses tested). Another feature occurred at about 100–120 °C and was ascribed as melting points of hard phases introduced in the network due to hydroxyurethane moieties.

Wu et al.[145] described the synthesis of nonisocyanate polyurethane polyurea Diels–Alder adducts capable of self-healing. This original chemical route uses CO_2 as a building block for the synthesis of diamine polyureas oligomers. Further reaction with a furfuryl amine-based bis-cyclic carbonate yields a non-isocyanate polyurethane-urea (**Scheme 33**).



Scheme 33 Preparation of nonisocyanate polyurethane polyurea Diels-Alder adducts according to Wu et al.[145]

The resulting polymer is further able to crosslink via Diels–Alder reaction between the furan moiety and 4,4-bismaleimidodiphenylmethane, forming the final nonisocyanate polyurethane polyurea Diels–Alder adduct, which can be regarded to some extent as a H-NIPU. The T_g was increased from -26 °C to -14 °C when going from oligoureas to polyurethane-urea and then increased again to -8 °C after crosslinking. Moreover, a melting temperature was observed at 102 °C for oligoureas but it mostly disappeared with the introduction of the furan moiety which disordered the polymer chains and made crystallinity decrease. No melting temperature was observed after crosslinking. The mechanical properties, gauged by tensile tests, showed that the polyurethane-urea behaved like a thermoplastic material and increased after crosslinking. Interestingly, the material had self-healing ability provided an appropriate thermal treatment was applied (namely a first healing at 120 °C for the retro Diels-Alder reaction to occur, followed by heating at 60 °C for 24 h to allow for the Diels–Alder reaction to take place again). Very similar mechanical properties were then observed, and the healing efficiency was gauged to be of 94%.

4 Conclusion

Looking back to the described examples, the formation of hybrid-NIPUs can thus be considered as a promising pathway towards the valorization of nonisocyanate polyurethanes.

It is striking to note that this type of chemistry is relatively old, especially in the case of epoxy-NIPUs. With the growing interest and challenges of NIPUs, it is expected that more research will be carried out towards the development, understanding and optimization of a broad range of hybrid polymers, thus expanding the existing pool of thermomechanical properties.

However, this type of chemistry is also facing its own challenges, the most important one being the compatibilization between the two polymer phases at stake. This is particularly acute in the case of NIPU–acrylics hybrids. This leaves room for considerable studies and improvement of the existing pool of technologies. It is also important to notice the lack of easy access to NIPU monomers, especially industrial cyclic carbonate compounds. In this regard, the development of the upscaling of the synthesis of those monomers would favor the development of both NIPUs and H-NIPUs.

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