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Non-Isocyanate Polyurethane Foams. Part I

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Abstract: Polyurethane foams (PUFs) constitute a major class of polymeric materials, widely appreciated for their excellent mechanical strength, chemical resistance, and physical versatility. They are used in a wide variety of applications, such as insulation, cushioning, coatings, and structural parts. Traditionally, PUFs are prepared through polyaddition reactions involving polyols, diisocyanates, and water, where the in-situ generated CO_2 in the reaction mixture serves as the blowing agent. However, there are significant concerns with the use of isocyanates as they are toxic, classified respiratory sensitizers, and contribute to environmental pollution. These issues have directed both researchers and industry experts to search for safer and more sustainable alternative feedstocks.

The polyaddition reaction between cyclic carbonates (CCs) and polyfunctional amines has been one promising alternative. The reaction leads to the formation of non-isocyanate polyurethanes (NIPUs), specifically polyhydroxyurethane foams (PHUFs). Foaming is achieved by using external chemical blowing agents or through self-blowing reactions, where gases are generated directly in the system. The generated foam cells – the structures that give foams their unique properties – depends largely on the gas-forming reactions.

This review focuses on the different blowing agents used in NIPUF synthesis, such as poly(methylhydrogensiloxane) (PHMS) and liquid fluorohydrocarbons. It also looks at recent advances in self-blowing techniques, which eliminate the need for external agents and make the process more sustainable. Special emphasis is placed on NIPUFs derived from renewable feedstocks, as these align with global trend towards green chemistry and circular materials. The review provides an overview of both externally blown and self-blown biobased NIPUFs, detailing their synthesis, performance, and potential industrial applications. **Keywords:** nuclear power station, cooling systems, patents.

Keywords: biobased polyurethane, blowing agent, non-isocyanate polyurethane, polymeric foams, polyurethane foams, self-blowing.

Table 1. List of abbreviations used in this review

Abbreviation	**Full term**
CCs	**cyclic carbonates**
DABCO	**1,4-diazabicyclo [2.2.2] octane**
DSTDL	**dibutyltin dilaurate**
DBU	**1,8-Diazabicyclo[5.4.0]undec-7-en**
EC	**ethylene carbonate**

Abbreviation	Full term
GC	**Glycerol Carbonate**
LDI	**L-Lysine ethyl ester diisocyanate**
MOF	**metal-organic framework**
NIPUFs	**non-isocyanate polyurethane foams**
NIPUs	**non-isocyanate polyurethanes**
PC	**propylene carbonate**
PHMS	**poly(methylhydrogensiloxane)**
PHUFs	**polyhydroxyurethane foams**
PHUs	**polyhydroxyurethanes**
PUs	**polyurethanes**
PUFs	**polyurethane foams**
ROP	**ring-Opening Polymerization**
SDGs	**sustainable Development Goals**
SOC	**spiro-orthocarbonate**
TBD	**triazabicyclodecene**
VOCs	**volatile organic compounds**

1. Introduction and Overview of Non-Isocyanate Polyurethane Foams

1.1 Introduction

Polyurethanes (PUs) are some of the most versatile and widely used polymers in the world. They’re appreciated for their excellent mechanical, chemical, and thermal properties, which can be tailored for a wide range of applications. Since their commercialization in the 1930s, they have become essential in industries like construction, automotive manufacturing, furniture production, and even medical devices. The ability to create materials like flexible or rigid foams, elastomers, adhesives, coatings, or thermoplastics has made PUs a key material in modern manufacturing.

But despite their usefulness, traditional polyurethanes have a major drawback: they’re made using isocyanates, which are produced from highly toxic phosgene gas. While isocyanates are critical to formation of the urethane bonds that make up PUs, they’re also classified as hazardous substances. Continuous exposure to isocyanates leads to serious health problems like occupational asthma and skin irritation. In addition, the production and disposal of PU materials can lead to environmental issues, such as the release of volatile organic compounds (VOCs) and accumulation of non-degradable waste.

To address these problems, researchers have been exploring the development of non-isocyanate polyurethanes as a safer, more sustainable alternative. Unlike traditional PUs, NIPUs are formed without toxic isocyanates, using safer building blocks like cyclic carbonates and primary or secondary amines to form polyhydroxyurethanes (PHUs). Adoption of this approach not only helps to reduce the health risks but also aligns with global efforts to develop greener materials and lower the environmental impact of industrial chemicals.

It’s not just about health and safety. There’s also regulatory pressure: laws, like the European REACH directive, have put strict limits on the use of hazardous chemicals such as isocyanates. At the same time, the polymer industry is being pushed to adopt circular economy principles by using renewable feedstocks and cutting carbon emissions. NIPU chemistry offers a promising way forward as they provide safer synthesis routes, are compatible with bio-based raw materials, and offer the potential to be recycled. That makes them a key innovation in the push for sustainable polymer science.

Recent advances in NIPU material research include the development of new cyclic carbonate monomers, better carbonation processes using CO_2 as the raw material, and more efficient catalysts [Lit]. These breakthroughs open up new possibilities for designing high-performance materials. For example, studies have shown the potential of NIPUs in creating self-healing coatings, bio-based adhesives, and lightweight foams for construction, all with lower environmental impact [1–4].

1.2 Overview of Non-Isocyanate Polyurethane Foams

The main difference between NIPUFs and conventional PU foams is how they are made. Traditional foams rely on isocyanates to create urethane bonds, while NIPUFs use safer, non-toxic precursors like cyclic carbonates and amines.

NIPUFs avoid these issues because they are made using safer, non-toxic pathways. This makes them safer to produce, easier to handle, and simpler to recycle. Plus, the fact that CO_2 can be used as a raw material for making cyclic carbonates adds an environmental advantage, helping reduce greenhouse gas emissions. By relying on renewable feedstocks and cutting out toxic intermediates, NIPUFs fit well with global sustainability goals, like the UN’s Sustainable Development Goals (SDGs).

Some of the key benefits of NIPUFs compared to traditional PU foams include:

- **Environmental advantages:** They reduce the need for fossil fuel-based isocyanates and make it possible to use CO_2, helping create materials with a lower carbon footprint.
- **Health and safety improvements:** By eliminating isocyanates, NIPUFs reduce the health risks for workers, especially in industries like construction and automotive manufacturing, where PU foams are widely used.
- **Regulatory compliance:** NIPUFs make it easier to follow strict international rules on hazardous chemicals.

- **Material performance:** Research shows that NIPUFs can match or even exceed the thermal and mechanical properties of traditional PU foams. For example, NIPUFs made from bio-based cyclic carbonates have been found to offer better flame resistance and biodegradability.

2. Synthesis Methods of Non-Isocyanate Polyurethanes

This part of the review focuses on the main approaches used to synthesize non-isocyanate polyurethanes, explaining how these methods work, what materials are used, and their key advantages and challenges. NIPUs have emerged as a greener alternative to conventional polyurethanes, which are typically produced using toxic isocyanates. As regulations on isocyanates become stricter, the need for scalable, safer alternatives is only growing.

2.1 Overview of Synthetic Strategies

There are four main methods for synthesizing NIPUs:

1) **Polycondensation:** This method involves reacting polyfunctional compounds, such as polychloroformates with polyamines or polycarbamates with polyols as shown in Fig. 1. While polycondensation can produce NIPUs, it usually requires toxic chemicals like phosgene, and the reactions generate by-products such as HCl or alcohols. It also tends to involve longer reaction times, extra purification steps, and often the use of catalysts [5,6].

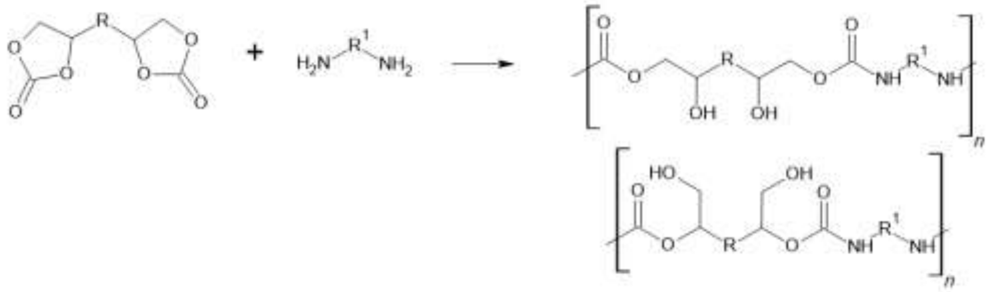


Fig. 1. General polycondensation route to non-isocyanate polyurethanes.

2) **Ring-Opening Polymerization (ROP):** This method uses cyclic monomers like aziridine or cyclic carbamates. The benefit is that it doesn’t create by-products.

However, it relies on hazardous precursors that are usually made from phosgene, and the reactions need high temperatures. These safety concerns limit its use on a larger scale [6].

3) Rearrangement Reactions: Isocyanate-based rearrangements (Curtius, Hofmann, Lossen) These include reactions like Curtius, Hofmann, and Lossen rearrangements, where isocyanates are generated in situ from acyl azides or hydroxamic acids. While these methods offer some flexibility in synthesis, they still involve hazardous intermediates, which makes them less appealing for environmentally friendly production [6].

Example – Curtius rearrangement:

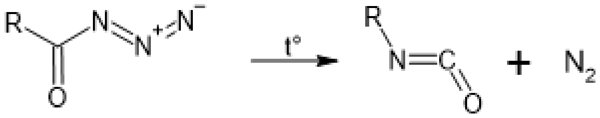


Fig. 2. Schematic representation of the Curtius rearrangement [6].

4) Polyaddition (Isocyanate-Free Synthesis of NIPUs): This is the most widely used method for making non-isocyanate polyurethanes. It involves the reaction of cyclic carbonates with amines to produce polyhydroxyurethanes. This method avoids the use of isocyanates and unwanted by-products, and generally does not require solvents or catalysts. By varying the reactants and their ratios, the properties of the final materials can be tailored [7].

General Reaction:

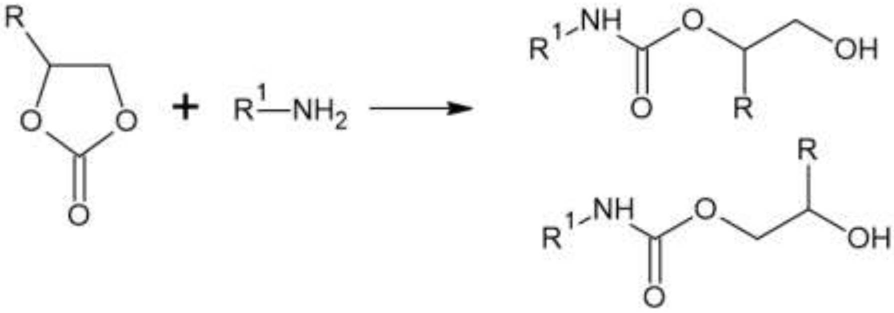


Fig. 3. General polyaddition route to non-isocyanate polyurethanes.

Table 2.1

Comparative Overview of Synthesis Methods for NIPUs.

Synthesis Method	Reactants	Advantages	Limitations	References
Polycondensation	Polychloroformates, Polyamines, Polycarbamates, Polyols	Versatile, accessible	Uses toxic phosgene, by-products	[5,6]
Ring-Opening Polymerization	Aziridines, Cyclic carbamates	No by-products	Toxic precursors, high temperature	[6]
Rearrangement Reactions	Acyl azides, Hydroxamic acids	Synthetic flexibility	Hazardous intermediates, not green	[6]
Polyaddition	Cyclic carbonates, Amines	No by-products, no isocyanates, tunable properties	Dependence on cyclic carbonate availability	[7]

2.2 Mechanistic Insights and Innovations

The polyaddition reaction works by a nucleophilic attack, where an amine reacts with the cyclic carbonate ring to form a β-hydroxyurethane structure. Depending on the specific chemical environment, this can lead to the formation of either primary or secondary hydroxyl groups, which affect the material’s mechanical properties and the degree of crosslinking.

Mechanistic Equation:

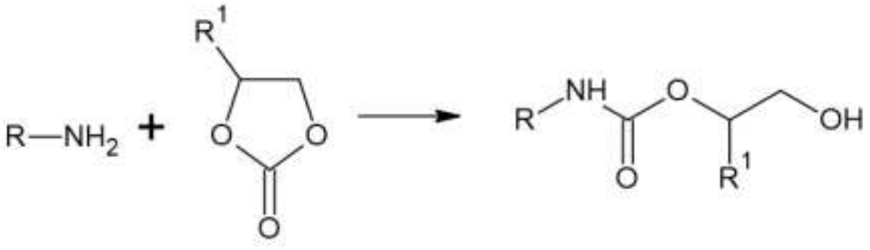


Fig. 4. Polyaddition route to non-isocyanate polyurethanes.

This is a typical ring-opening reaction yielding one urethane group and one hydroxyl group per cycle, without the use of isocyanates.

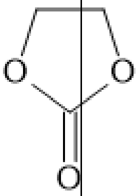
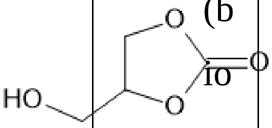
Recent research has focused on using bio-based raw materials and CO_2-derived reactants as promising feedstocks for NIPUs [8,9]. Some of the latest innovations include:

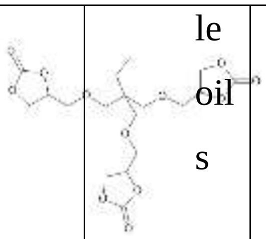
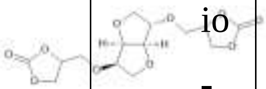
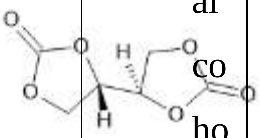
- Organocatalytic reactions for mild and selective synthesis[10],
- Reductive carbonylation using carbamates and CO_2 [11],
- Amino acid incorporation for functionalization and biocompatibility [12],
- Photopolymerization using spiro-orthocarbonates for improved curing profiles [13].

Table 2.2

Bio-Based Cyclic Carbonates & Reactivity Time (if available).

Cyclic	ourc	Structur	eactivity	Notes

Carbonate	e	e Type	(approx.)	
Ethylene Carbonate 	etro-based / CO$_2$	5-membered	igh (few hours, RT–60 °C)	Often used as model substrate
Glycerol Carbonate 	lycerol (bio-based)	5-membered (mono)	oderate–High (60–80 °C)	Renewable, biodegradable
Trimethylolpropane Tricarbonate	egetab	Multifunctional	lower (requ	Used for crosslin

	le oils		ires heat/catalyst)	king
Isosorbide Dicarbonate 	orbitol (bio-based)	Rigid, bicyclic	oderate	Enhances rigidity in PHU network
Erythritol Carbonate 	ugar alcohols	Multi-cyclic	lower	Biocompatible, for biomedical use
CO$_2$-derived Cyclic	irect fr	Various	epends on struct	Green chemistr

Carbonates	om epoxides + CO_2		ure	y focus

2.3 Green Chemistry and Nanotechnology Approaches

There’s been growing interest in making NIPUs more sustainable by using vegetable oil-based monomers, such as epoxidized soybean and linseed oils. These sources allow for the production of biodegradable and renewable NIPU systems [7,14].

Nanotechnology is also playing a key role. Techniques like ball milling (top-down) and crystallization (bottom-up) help disperse fillers better and improve material properties [15]. Researchers have also explored adding natural nanostructured materials – like extracts from grape seeds, mushrooms, or oats – which can improve biocompatibility, thermal stability, and mechanical strength.

2.4 Self-Blowing Strategies

Since cyclic carbonates don’t naturally release CO_2 during the reaction, additional blowing agents are needed to create foam. These can include substances like sodium bicarbonate [12], poly(methylhydrogensiloxane) [10], or fluorinated agents [7,16].

A key breakthrough came when Clark et al. [17] showed that sorbitan bis-carbonate can release CO_2 during aminolysis, making it possible to create foams without needing external blowing agents. Monie et al. [11] later improved on this by using thiols and amines together in tandem reactions, which produced self-blowing foams with better mechanical properties.

2.5 Challenges and Future Outlook

While NIPUs offer a lot of promise, there are still challenges to overcome:

- Some amines have limited reactivity [3].
- Scaling up the use of bio-based feedstocks for industrial production remains difficult [15,18].
- Optimizing processes to create high molecular weight polymers is still a work in progress [11,14,17].

Recent studies have highlighted several innovative strategies to overcome the low reactivity of certain amines in NIPU systems. For instance, the effect of steric and electronic factors on cyclic carbonate reactivity with amines was also reported by Steblyanko et al. [19], who demonstrated that polymerization efficiency can be improved through structural optimization. In a series of patents, authors [20,21] presented novel formulations based on hybrid cyclic carbonate systems and quaternary ammonium salt catalysis. These approaches not only enhanced the rate of polymer formation but also opened possibilities for using unconventional amines and carbonate precursors, including bio-based components. The proposed systems aim to balance reactivity, environmental safety, and processing ease—fitting within the broader green chemistry agenda. Bähr et al. [22] explored the synthesis of bio-based monomers by reacting epoxidized plant oils with CO_2 to form cyclic carbonates. These monomers were then polymerized with diamines to yield NIPUs with tunable thermal and mechanical properties. Their work highlights both the opportunity and difficulty of using non-petroleum feedstocks, particularly in achieving consistency across industrial-scale batches.

Hong et al. [23] developed a multi-step synthetic route that integrates lignin-derived polyols and propylene carbonate, yielding semi-aromatic NIPU resins. These materials showed improved thermal resistance and lower water uptake compared to fully aliphatic analogs. However, the process required tight control of reaction parameters, indicating that scaling remains a technical bottleneck [23]. Yokawa and Higashihara [24] investigated molecular weight development during the step-growth polymerization of NIPUs. They reported that achieving high molecular weights (>50 kDa) requires precise stoichiometric balance and suppression of premature chain termination. Their study also suggested using reactive diluents and latent curing agents to overcome viscosity and gelation issues during processing [24]. Researchers are also working on improving catalyst systems, such as zinc, tin, and quaternary ammonium salts, to make the reactions faster and more practical for large-scale manufacturing [25–27].

3. Types of Cyclic Carbonates Used in NIPU Synthesis

Cyclic carbonates are essential building blocks in NIPU synthesis, and their type plays a big role in the final properties of the material.

Datta and Włoch [28] conducted a comprehensive review of NIPU synthesis and processing, with a special focus on structure-property relationships. Their analysis highlighted how subtle differences in monomer structure, including ring size and functionality of cyclic carbonates, can influence the thermal, mechanical, and degradation behavior of the resulting polymers. This work laid the foundation for correlating carbonate chemistry with targeted material performance. Wang et al. [29] examined new catalytic strategies to reduce reaction time and improve conversion efficiency in NIPU formulations. Their study focused on environmentally friendly catalysts and reported how variations in cyclic carbonate precursors affected polymerization kinetics and product consistency. Their findings contributed significantly to greener process engineering for polyurethanes.

Qiao et al. [30] emphasized the environmental advantages of using CO_2-derived cyclic carbonates in sustainable polymer design. They investigated different pathways to incorporate captured CO_2 into functional monomers suitable for NIPU synthesis, supporting the growing interest in carbon circularity. Their work also addressed technical and economic challenges associated with CO_2 utilization.

Balla et al. [3] explored the role of molecular structure and reactivity in CO_2-based polymer chemistry, particularly focusing on how different carbonate architectures influence the final properties of NIPUs. Their mechanistic insights helped to better understand how to tailor carbonate structures for specific application needs.

The most commonly used are five-membered cyclic carbonates like ethylene carbonate (EC) and propylene carbonate (PC). These are popular because they react well with primary amines, are easy to make by combining epoxides with CO_2, and are commercially available at large scale [31].

Six-membered and fused-ring carbonates are another group. They offer better thermal stability and mechanical strength but react more slowly than five-membered carbonates. These are often used for engineering plastics or specialty NIPU products [32].

Hybrid carbonates, which combine epoxy and cyclic carbonate structures, are also gaining interest. They allow for both ring-opening and cross-linking at the same time, which can improve adhesion, foam durability, and coating performance. Researchers are exploring these systems for high-performance adhesives and coatings [33].

Organosilicon-modified carbonates are another innovative option. Their silicon content gives the final materials better flexibility, chemical resistance, and surface properties. Patents often describe them for advanced adhesives and water-repellent coatings [34].

Bio-based carbonates are derived from sources like rosin, POSS, or vegetable oils. They offer strong thermomechanical properties, are renewable, and are easier to degrade or recycle [15,35].

Spiro-orthocarbonates are a newer class of carbonates. These compounds undergo double ring-opening polymerization, which causes them to expand instead of shrink. That makes them ideal for applications like 3D printing and low-stress structural materials [36].

Functionalized and aromatic cyclic carbonates add even more versatility. Aromatic versions, in particular, can boost thermal and mechanical strength, making them useful for structural composites and insulation foams [37].

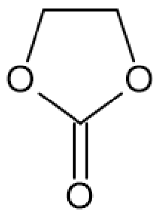
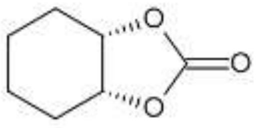
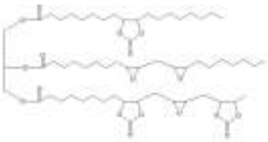
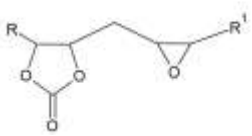
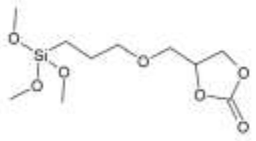
On the green chemistry side, **cooperative catalysis and eco-friendly synthesis** are growing areas of research. For example, metal-organic frameworks (MOFs) are being studied as catalysts for turning CO_2 into cyclic carbonates, mimicking enzyme-like behavior. These systems lower the energy needed for reactions and are more reusable and efficient under mild conditions [38].

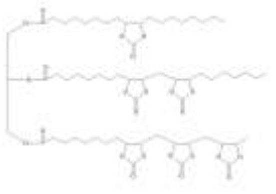
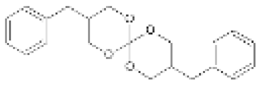
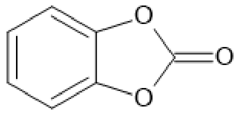
Finally, **bio-based innovations** include star-shaped glycerol-based epoxy macromonomers, which are epoxidized and then carbonated to create NIPUs. These materials show promising antibacterial properties and strong mechanical performance [39–41].

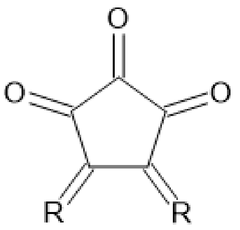
Table 3.1

Comparative Table of Cyclic Carbonates Used in NIPU Synthesis.

Cyclic Carbonate Type	**Examples**	**Key Properties**	**Applications**
Five-Membered Cyclic Carbonates (5CCs)	Ethylene Carbonate, Propylene Carbonate, Glycerol	High reactivity, widely available, bio-based (GC)	Flexible and rigid NIPUs, adhesives, foams

	Carbonate (GC) 		
Six-Membered & Fused-Ring Carbonates	Cyclohexene Carbonate, Fused-ring derivatives 	Thermal stability, mechanical strength, lower reactivity	Engineering plastics, structural composites
Hybrid Carbonates (Epoxy + Cyclic)	Epoxidized soybean oil + cyclic carbonate  	Dual functionality, cross-linking ability	Coatings, adhesives
Organosilicon-Modified Carbonates	Silane-modified carbonates 	Improved flexibility, hydrophobicity	Hydrophobic coatings, adhesives

Bio-Based Carbonates	Rosin-based, POSS-based, vegetable oil-derived 	Renewable, biodegradable, thermomechanical strength	Sustainable foams, coatings, composites
Spiro-Orthocarbonates	Various SOC structures 	Expansion upon polymerization, low stress	3D printing, low-shrinkage resins
Functionalized and Aromatic Carbonates	Aromatic cyclic carbonates 	Enhanced thermal & mechanical properties	Structural composites, insulation foams
Cooperative Catalysis Carbonates	MOF-catalyzed cyclic carbonates	Mild conditions, reusability, efficiency	Green cyclic carbonate synthesis
Bio-Based Innovations	Star-shaped glycerol epoxy-carbonate macromonomers	Antibacterial, mechanical enhancement	Medical applications, advanced composites

4. Synthesis of cyclic carbonates

The carbonation of epoxides with CO₂ (shown as Equation below) is a key reaction for creating cyclic carbonates, which are essential building blocks for non-isocyanate polyurethanes. This process offers a sustainable and environmentally friendly approach, as it uses CO₂ – an abundant and renewable resource – as a raw material.

In this section, the focus is on how this carbonation reaction works, what chemical conditions are needed, and the progress being made in developing better catalytic systems to make the process more efficient.

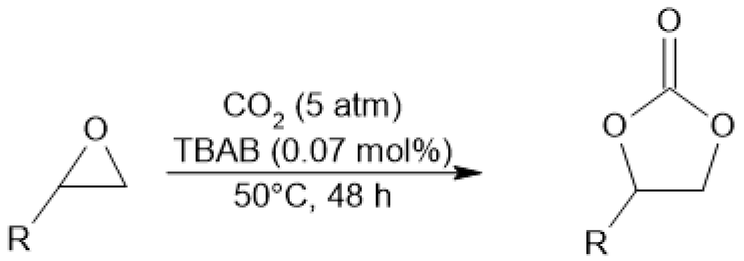


Fig. 5. Carbonation of epoxides with CO₂ to form cyclic carbonates.

4.1 Catalysts and Conditions

The carbonation process works by reacting epoxides with CO₂ in the presence of catalysts like organobases, metal salts, or ionic liquids [42–45]. These reactions typically require moderate to high pressure and temperature. To make the process more energy-efficient and eco-friendly, researchers have also been exploring solvent-free systems and milder reaction conditions [46].

Bio-Based Carbonation Systems. Using bio-based materials is another important focus. For example, epoxy soybean oil can react with CO₂ to produce cyclic carbonates, which can then be used to make NIPUs by reacting with amines [47]. This approach fits with green chemistry principles, as it relies on renewable feedstocks and generates less hazardous waste.

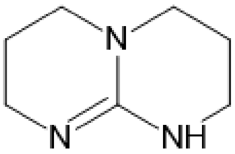
CO_2 Fixation via Spiro-Orthocarbonate (SOC) Polymerization. Spiro-orthocarbonate polymerization is another interesting method. In this process, carbonation happens with very little internal stress, making it ideal for applications where low shrinkage is important [48].

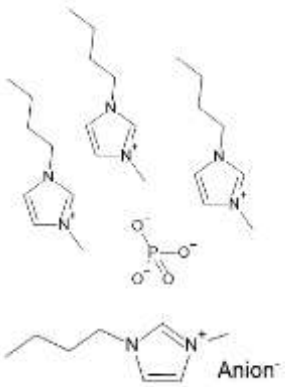
Decarboxylation in Self-Blowing Foams. There's also a clever strategy for making self-blowing foams. Here, decarboxylation of cyclic carbonates by thiols releases CO_2 directly during the reaction, which helps the foam expand without needing external blowing agents [49].

Alcohol Carbonation Routes. Finally, CO_2 can react with alcohols like glycerol or ethylene glycol to form cyclic carbonates. This method uses CO_2 as a carbon source and supports circular economy goals [50–52]. However, getting good catalytic performance under mild conditions is still a challenge researchers are working to solve.

Table 4.1

Comparative Table of Carbonation Conditions and Catalysts.

Catalyst Type	Catalyst Example	Reaction Conditions (Temp/Pressure)	Efficiency / Notes
Organo bases	TBD (Triazabicyclodecene)  	80–120°C / 5–10 bar	High with epoxides [35]

Metal Salts	Zn (II), Al (III), Sn (IV)	100–140°C / 10–30 bar	Good conversion, reusable [40]
Ionic Liquids	Imidazolium-based ILs 	70–110°C / 5–20 bar	High selectivity [36]
MOF-based Catalysts	ZIF-8, MIL-101	Mild (~80°C / ≤10 bar)	High yield under mild conditions [42]
Biocatalyst mimics	Polypeptide/MOF hybrids	50–80°C / ambient to 5 bar	Promising lab-scale results [37]
No Catalyst	—	>160°C / >30 bar	Low conversion (benchmark)

Based on comparisons across different systems, the most commonly used and industrially practical catalysts for the carbonation process are organobases like TBD and metal salts such as Zn (II) or Al (III). These options strike a good balance between reactivity, efficiency, and scalability, which makes them particularly well-suited for large-scale NIPU production. Meanwhile, MOF-based catalysts are gaining attention as a greener and more sustainable solution for CO_2 utilization, especially when working under milder conditions.

5. Types of Catalysts for Carbonation in NIPU Synthesis

Catalysts play a crucial role in speeding up the carbonation process, which is the reaction between CO_2 and epoxides or alcohols [53,54]. The cyclic carbonates produced through this reaction are key intermediates in making non-isocyanate polyurethanes.

The most commonly used catalysts are metal-based compounds, such as Zn (II), Al (III), and Co (III). These work as Lewis acids, helping to activate the epoxide ring and make the reaction more efficient [55,56]. A good catalyst not only boosts efficiency but also allows the reaction to happen under milder conditions and improves selectivity toward the desired products.

Researchers have explored a wide range of catalyst systems for both industrial and lab-scale use. These include metal complexes, organocatalysts, ionic liquids, thiol-based systems, and heterogeneous catalysts supported on solid materials [57–59].

5.1 Types of Catalysts Used in Carbonation

There are several types of catalysts used to drive the carbonation process, each with its own benefits and challenges:

1) **Metal-Based Catalysts:** These include salts and complexes of zinc, cobalt, aluminum, and tin. They work as Lewis acids, helping to activate the epoxide ring so that CO_2 can insert into the structure. These catalysts are generally effective under elevated pressures (5–30 bar) and temperatures (60–150°C) [53,55]. Zinc-based catalysts are especially popular because they're affordable and easier to scale up [60].

2) **Organocatalysts:** Organic bases like DBU and TBD have gained attention because they allow carbonation reactions to happen under milder conditions, with lower toxicity and less energy input [54,61]. They also support solvent-free reactions, which is a key advantage from a green chemistry perspective [35].

3) **Ionic Liquids:** Ionic liquids like imidazolium- and pyridinium-based systems ([BMIm][BF_4], [EMIm][Cl]) offer a dual advantage – they dissolve CO_2

and also catalyze the reaction [62]. Their ability to be tuned for different tasks, low volatility, and recyclability make them appealing. However, they can be expensive, and recovering them for reuse can be tricky [56].

4) **Thiol-Based Catalysts:** Thiols can serve both as reactants and as internal catalysts in the decarboxylation of cyclic carbonates. This approach allows CO_2 to be released directly during the reaction, which helps create foams without needing extra blowing agents [58]. The structure of the thiol (whether it's di-, tri-, or tetrafunctional) influences the mechanical and thermal properties of the final foam.

5) **Heterogeneous Catalysts:** Recent research highlights the potential of heterogeneous systems, including metal oxides, carbon-based materials, and especially metal-organic frameworks, for large-scale applications [63–65]. These catalysts are reusable, reduce environmental impact, and can mimic enzyme-like activity [66].

Table 5.1

Summary of Catalysts Used in the Carbonation Step of NIPU Synthesis.

Catalyst Type	Examples	Conditions (Temp/Pressure)	Solvent Requirement	Advantages
Metal-Based	Zn (II), Al (III), Sn (IV)	80–150°C / 10–30 bar	Optional	High efficiency, scalable
Organocatalysts	DBU, TBD	60–120°C / 5–15 bar	No	Green, mild conditions
Ionic Liquids	[BMIm][BF_4],	70–130°C /	Yes	Dual

	[EMIm][Cl]	5–20 bar		function, recyclable
Thiol-Based	Di-/Tri-/Tetra-thiols	Variable	Varies	Reacts + catalyzes, foam-specific
Heterogeneous	MOFs, Silica, Zeolites	60–140°C / 5–25 bar	Optional	Recyclable, stable

Among the different catalysts discussed, metal-based catalysts are still the most commonly used in industrial applications. They offer reliable performance, are relatively affordable, and are easy to scale up for large production.

However, there’s growing interest in organocatalysts and ionic liquids because they have a smaller environmental footprint.

Current research is focused on developing catalysts that combine high efficiency with recyclability and compatibility with bio-based raw materials [67,68]. This way, the goal is to make the whole process more sustainable and suitable for large-scale, greener production of NIPUs.

6. Amines in NIPUF Synthesis

Amines are key building blocks in the synthesis of non-isocyanate polyurethane foams. They act as nucleophiles, reacting with cyclic carbonates to form β-hydroxyurethane linkages. This aminolysis process essentially defines the structure of the polymer and directly affects important properties like crosslinking density, foam structure, mechanical strength, thermal stability, and even biodegradability [69,70].

6.1 Types of Amines Used

A wide range of amines has been explored in NIPU synthesis:

- Primary amines (such as ethylene diamine, hexamethylene diamine) are highly reactive with cyclic carbonates, making them ideal for fast and efficient polymerization [71].
- Secondary amines react more slowly, which can actually be beneficial when you want more control over the polymer's architecture[14].
- Fatty diamines (like PRIAMINE 1075) are bio-based alternatives that provide excellent tensile strength and flexibility [72].
- Gallic acid- and polysiloxane-modified amines can boost both the thermal and mechanical properties of the final materials [43].

6.2 Reactivity and Structure–Property Relationships

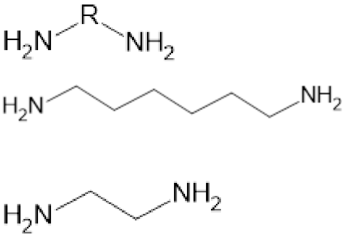
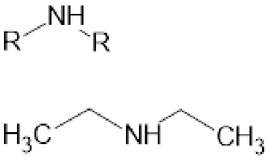
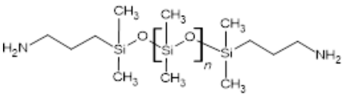
The structure of the amine plays a major role in determining the final properties of the polymer:

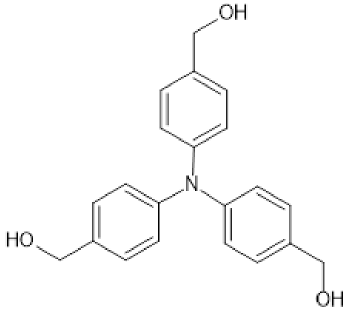
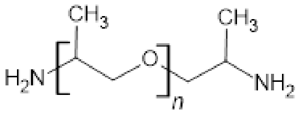
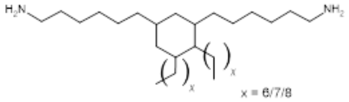
- **Linear diamines** tend to increase rigidity and also improve biodegradability [43].
- **Aromatic diamines** make the polymer stiffer and give it better thermal resistance [73,74].
- **Amine-terminated oligomers** with controlled functionality are used to build hybrid NIPU networks, helping to boost crosslinking and increase the gel content in the final material [75–79].

Amines are essential for making Non-Isocyanate Polyurethanes (NIPUs). They react with cyclic carbonates to create the urethane bonds that define the polymer. The specific amine you choose has a big influence on the material's key properties – things like hardness, elasticity, biodegradability, and thermal stability. Researchers have tested a wide variety of primary and secondary amines, along with different oligomeric and bio-based amines, to fine-tune the characteristics of NIPUs. The table below provides a summary of the most commonly used amines in NIPU synthesis.

Table 6.1

Comparative Table: Types of Amines Used in NIPU Synthesis.

Amine Type	Structure / Example	Reactivity with Cyclic Carbonates	Impact on Polymer Properties	Sustainability / Source
Primary Diamines	Hexamethylene diamine, Ethylene diamine 	High, rapid aminolysis	High crosslinking, strong and rigid foams	Widely available, some bio-based variants
Secondary Amines	Diethylamine 	Moderate, slower than primary	Controlled crosslinking, improved flexibility	Synthetic, limited bio-variants
Polysiloxane-modified Amines	Amine-terminated polysiloxane 	Moderate to high	Enhances flexibility, hydrophobicity	Specialty chemical, synthetically modified
Gallic Acid-based Amines	Tris(hydroxyphenyl)amine derivatives	High	Improves thermal stability	Derived from natural phenols

				
Amine-Terminated Oligomers	Amine-terminated polyesters/polyethers 	Controlled, stoichiometric	Enhances toughness, tailored architecture	Can be bio-based or synthetic
Fatty Diamines	PRIAMINE 1075 	High	Exceptional elongation and strength	Fully renewable, bio-based

The molar ratio between the amine and cyclic carbonate, as well as the curing temperature (typically between 10–140 °C), are critical factors for achieving the desired properties in the final material. These factors influence important characteristics like gel fraction, porosity, and hydrolytic stability. Studies by Figovsky et al. (2009) showed that careful control of these parameters leads to better performance [76].

Role in Self-Blowing Foams. Amines also play a key role in the production of self-blowing PHU foams. They react with cyclic carbonates to form the urethane linkages, and when combined with thiols, they help generate CO_2 directly within the system. This reaction allows the foam to expand without needing additional external blowing agents [43,71,80].

Hybrid and Networked NIPUs. Recent patents describe the development of cyclocarbonate-epoxy-amine hybrid systems for making highly crosslinked NIPU networks. These hybrid systems have been shown to offer:

- Gel fractions over 96%
- Excellent chemical resistance
- Improved performance as composite matrices

These hybrid NIPUs help address common problems found in traditional isocyanate-based materials, like poor hydrolytic stability and environmental toxicity [72,81].

Advantages and Sustainability

- **Bio-based origins:** Many amines can be sourced from renewable materials like vegetable oils and lignin, which helps improve the overall sustainability of the process [82,83].
- **Lower toxicity:** Compared to isocyanates, amines are much safer to handle and align better with the goals of green chemistry [84].
- **Functionality control:** By modifying the chain ends or side groups of amines, researchers can fine-tune the architecture of the resulting polymers [14].

Amines are incredibly versatile and reactive building blocks in the development of NIPUs and NIPUFs. Whether it’s simple linear diamines or more complex biobased and functionalized amines, they offer precise control over polymer structure, foaming behavior, and overall performance. In short, amines play a crucial role in creating safer, greener, and more durable alternatives to traditional polyurethanes.

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