DE GRUYTER Rev Chem Eng 2025; 41(7): 667–710

Review

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# State-of-the-art and recent progress in the synthesis of polyurethanes

https://doi.org/10.1515/revce-2025-0014
Received March 3, 2025; accepted July 11, 2025;

**Abstract:** Polyurethanes (PUs) are synthetic substances that satisfy the requirements of many industrial applications, such as films, foams, coatings, adhesives, biomedical devices, sealants, composite materials, and elastomers. The polyaddition reaction of isocyanates, categorized as CMR (carcinogenic, mutagenic, and reprotoxic), and polyols produces commercial PUs. As a result of numerous concerns about the toxic and hazardous properties of isocyanates, which limit their utilization, researchers are being encouraged to develop alternative processes for producing PUs. Nonisocyanate polyurethanes (NIPUs) are synthesized using a sustainable and eco-friendly approach to replace the toxic, hazardous, and detrimental characteristics of isocyanates. Among NIPU's synthesis methods, aminolysis of cyclic carbonates (CCs), transurethanization, ring-opening polymerization (ROP), and rearrangement are included, with aminolysis of CCs emerging as a potential approach. Novel approaches to obtain materials with improved performance, such as functional groups like acrylates, methacrylates, POSS, and epoxies, may be necessary. Consequently, different approaches for hybrid polyhydroxyurethanes (PHUs) and distinct prepolymerization techniques for NIPUs are delineated. This review work is divided into two sections. The initial section focuses entirely on isocyanate-based methodologies for producing commercial PUs, while the subsequent section is exclusively dedicated to synthesizing NIPUs. This review encompasses all methods employed to produce commercial PUs, NIPUs, and H-NIPUs.

**Keywords:** polyurethanes (PUs); water-based polyurethanes dispersions (WPUDs); nonisocyanate polyurethanes (NIPUs); polyhydroxyurethanes (PHUs); hybrid nonisocyanate polyurethanes (H-NIPUs); NIPUs/POSS hybrid

## 1 Introduction

Polyurethanes (PUs) rank as the fifth-largest category of commercially produced polymers, alongside polyolefins, PVC, polystyrene, and diene rubbers, in terms of global production and usage. Commercially produced PUs are based on the polyaddition reaction between aliphatic/aromatic diisocyanate and bifunctional or multifunctional polyols (with terminal hydroxyl groups). The formation of PUs with a cross-linked three-dimensional structure results from the trimerization of isocyanates and their subsequent reaction with multiple hydroxyl groups in polyols. The structure of the PUs chain depends upon the sequential polyaddition of the charging feeds (Król 2007). PUs are long-chain, higher molecular weight copolymeric materials that are versatile, the most common, and prime polymers. The ongoing research and development of methodologies, techniques, and raw materials (additives) have led to the extensive use of diverse materials in people's daily lives (Akindoyo et al. 2016). PUs possess the flexibility, elasticity, and strength of rubber materials combined with the strength of metals. Therefore, PUs are a good substitute for rubber, plastics, metals, and most engineering materials. PUs have been utilized in coatings, flexible and stiff foams, sealants, adhesives, packaging materials, biomedical applications, and elastomers (Crescentini et al. 2019). Through modifications in its chemical composition and morphological structure, polyurethanes demonstrate various polymeric forms, including thermosetting, thermoplastic, and elastomeric materials (Delebecq et al. 2013; Engels et al. 2013; Król 2007).

In 2016, major companies such as BASF, DOW, Yantai Wanhua, Bayer, and Huntsman accounted for almost 35 % of the PUs market. PUs primarily produce three unique products: nonporous materials, rigid foams, and flexible foams. Nonporous materials are utilized in elastomers, binders,

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coatings, sealants, adhesives, and others. Rigid foam is utilized for thermal and electrical insulation, while flexible foam is employed in car seating, beds, sofas, and other high-end furnishings (Akindoyo et al. 2016).

Polyurethane (Perlon U) was first synthesized by a German researcher, Dr. Otto Bayer in 1937, and his coworker with the polyaddition reaction between low molecular mass polyol (1,4-butanediol) with 1,6-diisocyanatohexane, which replaced rubber applications during World War II and produced in the form of elastomeric materials (Akindoyo et al. 2016; Amirkhosravi et al. 2021; Król 2007; Seymour and Kauffman 1992). In the mid-1950s, PUs were synthesized as adhesives, coatings, and rigid foams. In the 1950s, PUs were incorporated into flexible foams with polyether polyols as the primary reactant. Since then, PUs have primarily been utilized in car components and high-end household products (Akindoyo et al. 2016).

PUs can be produced through a polyaddition process utilizing raw materials such as polyols, diisocyanates, neutralizing agents, and chain extenders sourced from nonrenewable petroleum feedstocks. Due to the exhaustion of feedstock, air pollution, and numerous health and environmental concerns, there is a need for novel renewable sources. Researchers are utilizing renewable resources, including vegetable oils, cellulose, and lignin, to create diverse PUs materials, such as coatings, adhesives, films, foams, and composites (Stachak et al. 2021; Liang et al. 2018a,b).

The primary issue in isocyanate chemistry arises from the high toxicity of diisocyanate precursors. Traditional PUs predominantly contain toxic substances, such as methyl diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI). A viable resolution to this toxicity problem is the reaction between carbonates and amines; however, this mechanism is somewhat slower than the reaction of isocyanates with hydroxyl groups. Recent developments, however, have mitigated these sluggish reaction rates (Delebecq et al. 2013). An urgent necessity exists to devise alternate methodologies for PU synthesis to safeguard human health and the environment. One green strategy involves substituting fossil-derived raw materials with renewable, bio-based resources, thereby reducing reliance on petrochemicals. Moreover, the hazardous and moisture-sensitive diisocyanates derived from phosgene have been eradicated from NIPU processes, generating significant research interest (Aristri et al. 2021).

The literature review clearly indicates that issues regarding the environmental, regulatory, health, and recycling aspects of traditional polyurethane synthesis methods, utilizing block isocyanate, waterborne PUs systems, and NIPUs, have been presented to mitigate isocyanate-related hazards. Furthermore, renewable feedstocks have been widely utilized in the synthesis of environmentally friendly PU. To achieve the desired chemical and mechanical properties, bio-based polyfunctional short alcohol and isocyanate compounds have been developed for the formulation of entirely bio-based PU materials. The global market size attained $72.82 billion and is anticipated to exhibit a compound annual growth rate (CAGR) of 4.3 % from 2023 to 2030. The PUs market comprises five distinct segments: foam (65 %), coatings (13 %), elastomers (12 %), adhesives (7 %), and the biomedical sector (3 %). The interaction between isocyanates and polyols, resulting in PU materials, exhibits rapid kinetics at ambient temperatures when catalysts are present, facilitating curing and efficient processing in the PU industry. The numerous advantages of PUs render them highly appealing, leading to a global market volume of 25 million metric tonnes, projected to increase to 31 million metric tonnes by 2030 (Delavarde et al. 2024).

Notwithstanding these benefits, PU encounters environmental and health challenges that have garnered significant academic attention over the past decade. PU substances create concerns both during their production and at the end of their lifecycle. The majority of PUs are derived from petroleum and ultimately enter the life cycle either as an energy source in incinerators, contributing to global warming via $CO_2$ emissions, or are disposed of in landfills, resulting in soil and ecosystem contamination. The majority of compounds utilized in the production of commercial PUs, such as catalysts and isocyanates, are deemed hazardous at low concentrations or through inhalation and may also possess carcinogenic, mutagenic, or reprotoxic properties. Consequently, to mitigate the carbon footprint and ecological toxicity of PUs, a diverse array of renewable building blocks (diols, polyols, and isocyanates) has been launched in the market (Delavarde et al. 2024).

The extensive applications of PUs have led to substantial growth in their manufacture over recent decades, predominantly in the form of foams. The significant rise in PU foam production has led to an increase in waste formation, prompting concerns regarding its appropriate disposal. Consequently, commercial PUs are contributing to environmental problems due to their accumulation in ecosystems. Numerous techniques have recently been developed to enhance end-of-life management and recyclability (Gama et al. 2024). Gama et al. (2024) addressed the recycling of PUs, highlighting acidolysis using dicarboxylic acids for depolymerization. Recycled materials are utilized in rigid and flexible foams, adhesives, and coatings. The review elucidates acidolysis processes and degradation routes. Life cycle assessments demonstrate that mechanical recycling uses less energy and has a reduced impact on global warming compared to incineration, which produces more greenhouse gas emissions than landfills. This method advances circular economy objectives by transforming PU waste into reusable resources. Gama et al. (2021) investigated the impact of reaction conditions on the properties of polyols derived from the recycling of polyurethane (PU) via acidolysis. Pu et al. (2024) investigated the advancement of environmentally sustainable PUs utilizing polyols derived from recycled and renewable resources. Rossignolo et al. (2023) examined the principal PUs recovery and recycling techniques commonly utilized in commercial and industrial contexts, including mechanical, physical, and feedstock recycling, which are grounded in the degradation and depolymerization processes. Li et al. (2020) have examined recycling solutions for printable PUs materials, emphasizing dynamic reversible bonds such as disulfide, hydrogen, boronic ester, carbon–carbon, and Diels–Alder linkages integrated into polymers to facilitate self-healing and recyclability. Moreover, there is increasing interest in green synthesis methods that promote sustainability by enhancing energy efficiency, minimizing waste, and decreasing VOC emissions. The application of NIPUs with organic catalysts has demonstrated potential in reducing PUs-related toxicity. The author addressed the end-of-life management of PUs, various PUs recycling methods, along with LCA analysis and the feasibility of implementing different recycling approaches on a large scale (Delavarde et al. 2024).

In recent decades, environmental regulations and sustainability concerns have heightened the quest for more eco-friendly and safer alternatives to conventional PU synthesis utilizing isocyanates and polyols. The polyaddition of cyclic carbonates (CCs) with diamines yields PHUs, mostly utilized in coatings and as crosslinked materials in thermosets, elastomers, and foams. In addition to their enhanced mechanical and chemical attributes, PHUs circumvent the employment of hazardous isocyanates and phosgene by utilizing $CO_2$. This abundant, renewable, eco-friendly feedstock produces CCs for PHUs synthesis (Alves et al. 2017). Notwithstanding these benefits, considerable hurdles persist, particularly with these materials' mechanical strength and chemical resistance, especially in acidic and alkaline conditions. The flexibility of NIPUs constrains their use in elastomers. Hybrid NIPUs utilizing epoxy amine CC oligomers have been created to address these limitations, resulting in a more resilient network structure (Delebecq et al. 2013). Therefore, alternative routes for the synthesis of PUs without the use of toxic isocyanates and other hazardous components have become important and are gaining interest among the industry and academia. This review provides a comprehensive overview of the different approaches being explored in academia and industry to enhance the sustainability of PUs throughout their lifespan and to mitigate the toxicity of their precursor materials. In addition, this manuscript provides an in-depth analysis of PUs derived from isocyanates, considering their structure, potential adverse reactions, synthesis techniques, dispersion, and applications. The synthesis of isocyanate-free or NIPUs, both environmentally friendly and sustainable, has also been critically assessed. A summary diagram of the review article has been included to assist the reader in comprehending the different synthesis methods for both isocyanate-based and isocyanate-free processes (Figure 1).

## 2 Isocyanate-based PUs

### 2.1 Structure of PUs

Alternative hard (rigid) and soft (flexible) segments of commercial PUs are joined together by urethane linkage (Figure 2) (Crescentini et al. 2019). The soft segments are produced from polyols and provide elastomeric characteristics to the structure. The highly polar urethane linkage is evident in the hard segments. Phase separation into hard and soft segments occurred in the bulk, forming microdomains due to hydrogen bonding in the urethane and urea groups (Delpech and Coutinho 2000; Yen and Hong 1997). The degree of phase separation and the connectivity of hard segments significantly influence the physical, mechanical, and adhesive properties, as hard segments serve as a physical crosslink. The amine group (–NH) in the urethane can form a bond with either the epoxy group (–O–) of the polyether or the carbonyl group (–C=O) of the urethane in polyether-based PUs. An extra amine group (–NH) from the urea linkage engages in attraction in the context of poly(urethane-urea) (Yen and Hong 1997). The urethane linkage in the PUs structure acts as an H-bonding acceptor and donor (Delpech and Coutinho 2000). The possible hydrogen bonding in the ester and urethane groups of the PUs structures is shown in Figure 3 (Yen and Hong 1997).

Whenever isocyanates and alcohols react, a repeating unit known as a urethane linkage is produced, whereas amines and isocyanates react to produce urea linkages. Urethane formation can be influenced by environmental factors, such as the type of diisocyanate used, reaction temperature, and catalysts that accelerate the reaction. The reactivity of the aliphatic amines is higher than that of the aliphatic alcohols with aromatic diisocyanates. The hydroxyl group, amines, and diisocyanates can also react with the urethane, water, carboxylic, urea, and amide groups. These reactions may occur at higher temperatures during PU

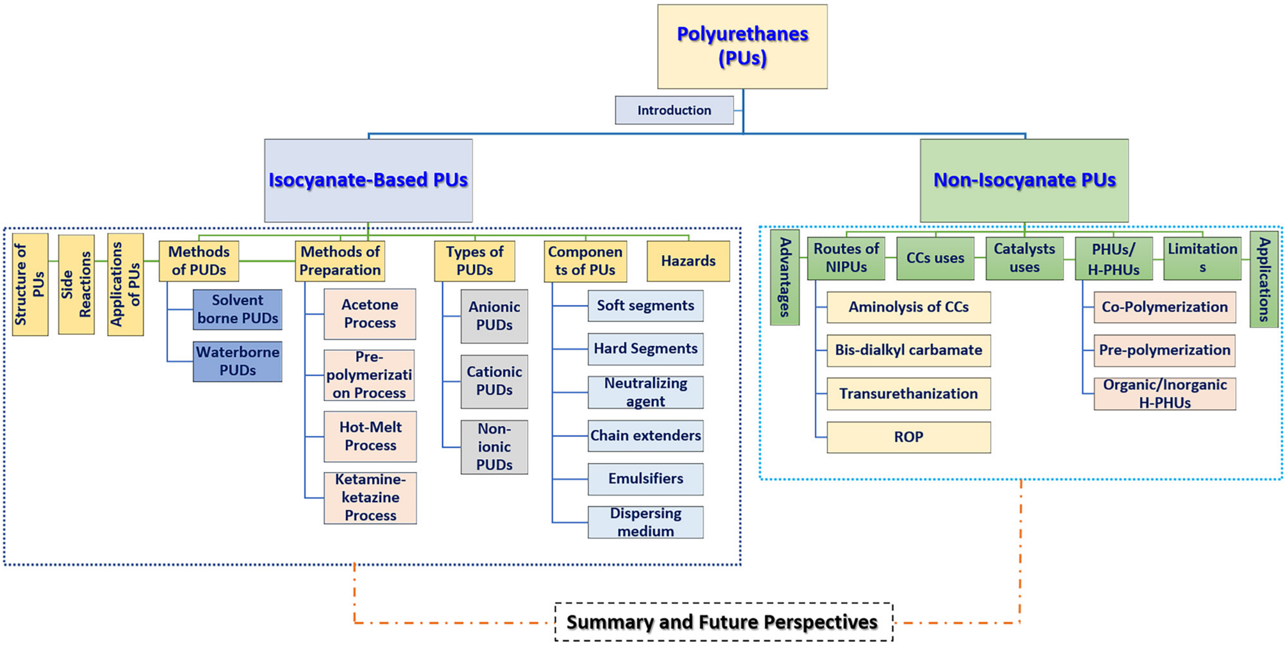


**Figure 1:** A summary diagram of the review paper outlining different polyurethanes techniques (for isocyanate-based and isocyanate-free PUs) and a comprehensive summary of the subjects addressed in an ordered way.

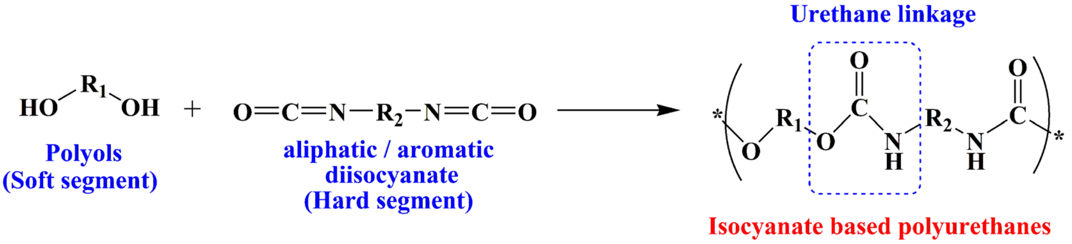


**Figure 2:** Reaction scheme for synthesizing commercialized PUs from polyols and isocyanates (Crescentini et al. 2019). Modified and reproduced with permission from Crescentini et al. (2019), Elsevier.

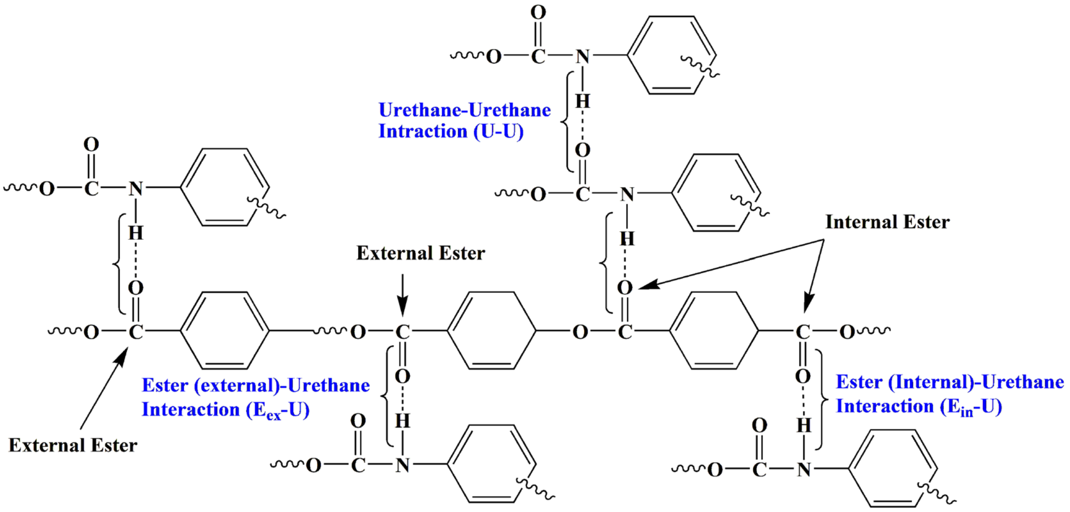


**Figure 3:** Possible hydrogen bonding in ester and urethane groups in the isocyanate-based polyurethane structure (Yen and Hong 1997). Modified and reproduced with permission from Yen and Hong (1997), American chemical society.

synthesis and affect the structural, mechanical, thermal, and chemical properties (Yilgör et al. 2015).

The PUs' prepolymers are synthesized with an excess of one of the components, either the diisocyanate for isocyanate-terminated prepolymers or the polyols for hydroxyl-terminated prepolymers. Generally, an isocyanate-terminated prepolymer is obtained by adding diisocyanate in excess of polyols, or vice versa, in molar ratios. Furthermore, the structure is extended by the addition reaction of the chain extender or with compounds containing reactive hydrogen atoms. The structure of the PUs contains not only urethane, ether, and ester groups in their structure but also biuret, allophanates, urea, aromatic hydrocarbon rings, carbodiimide groups, azo-heterocyclic groups, and oxazolidone structures may also be present. The structure of PUs depends upon the charging feed during the polyaddition reaction and the methods used for their synthesis (Król 2007).

## 2.2 Possible side reactions

The selection of synthesis technique and reaction conditions significantly affects the chemical structure, topology, microphase morphology, and overall properties of PUs. The nature of the diisocyanate (aromatic or aliphatic), reaction temperature, time, solvents, and catalysts substantially influence the synthesis of PUs and the possibility of side reactions, potentially resulting in excessive isocyanate utilization and branching within the polymer chain. Isocyanates react with alcohols to produce urethane links and with amines to generate urea linkages. Amines exhibit greater nucleophilicity than hydroxyl groups, rapidly forming urea bonds at room temperature. Nevertheless, increased temperatures and specific catalysts are frequently necessary for urethane synthesis, particularly when employing less reactive aliphatic diisocyanates (Delebecq et al. 2013; Król 2007). Furthermore, isocyanates may react with additional hydrogen-containing compounds, including water, carboxylic acids, amides, urethanes, and ureas. Aromatic diisocyanates, such as MDI, exhibit greater reactivity compared to aliphatic diisocyanates like HMDI, attributable to the electron-withdrawing influence of the phenylene ring, which enhances the electrophilicity of the isocyanate carbon (Yilgör et al. 2015).

The reaction between diisocyanates and diols is initially second-order. As polymerization advances and the concentration of urethane groups increases, side reactions can occur in which isocyanate groups interact with –NH groups in preexisting urethane or urea linkages, forming allophanate and biuret structures (Figure 4). Allophanates are produced through reactions between urethane and free isocyanate, whereas biurets arise from interactions between urea groups and isocyanates. These processes facilitate the branching and crosslinking of the polyurethane network. The degree of allophanate and biuret production is contingent upon the concentrations of urea and urethane groups and the reaction conditions. The production of allophanate is especially favored at temperatures exceeding 60 °C for both aromatic and aliphatic diisocyanates when catalysts are present. These side reactions often result in diisocyanate

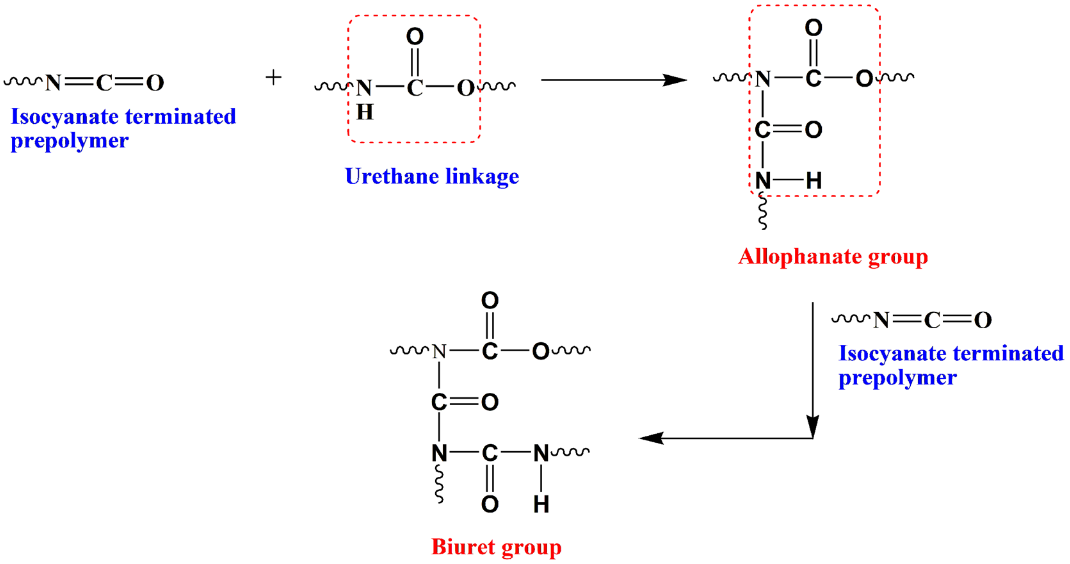


**Figure 4:** Reaction scheme for allophanate and biuret formation (Yilgör et al. (2015). Modified and reproduced with permission from Yilgör et al. (2015), Elsevier.

consumption exceeding the anticipated levels based on the initial NCO:OH ratio. The selection of solvents is essential in the synthesis of PUs. The reactants are effectively dissolved in common solvents such as DMF, NMP, and DMAC, which also function as catalysts, accelerating both the main and side reactions, particularly in systems employing MDI (Yilgör et al. 2015).

Biuret formation is more common due to the higher reactivity of urea's –NH groups compared to those in urethanes. Furthermore, the trimerization of isocyanates can yield isocyanurates, augmenting crosslinking within the polyurethane structure. Finally, the amount of branching and crosslinking in PUs is determined by the monomers utilized and the level of biuret, allophanate, and isocyanurate formation processes (Odian 2003).

Temperature is a crucial factor that must be maintained at a specific value during the synthesis and processing of PUs. A temperature higher than 100–120 °C is avoided, as above that, PUs undergo several degradation reactions (Equations (1) and (2)), along with decomposition back to alcohol and isocyanate monomers (Odian 2003).

$$-NH - COO - CH_2CH_2 - \rightarrow - NH_2 + CO_2 + CH_2 = CH- \quad (1)$$

$$-NH - COO - CH_2CH_2 - \rightarrow CO_2 + -NH - CH_2CH_2- \quad (2)$$

The most significant applications of PUs are foamed products, such as seat cushions and bedding. Water is the primary element in the manufacture of flexible PU foams. The reaction between the isocyanate and water molecules in the prepolymer of PU dispersion during the synthesis process can result in a urea linkage in the backbone of the PU's long chain and the release of $CO_2$ molecules (Equation (3)). To create the foamed structure of the PUs products, $CO_2$, generated from the reaction of isocyanate and water molecules, serves as a blowing agent. Many of the PUs are synthesized using combinations of diols and diamines. The diamines interact with isocyanate groups to incorporate supplementary urea linkages into the polymer (Equations (4) and (5)). Consequently, conventional PUs comprise both urethane and urea repeating units. The reaction could be expressed as follows (Lahtinen et al. 2003; Odian 2003):

$$2(-NCO) + H_2O \rightarrow -NH - CO - NH - +CO_2 \quad (3)$$

The reaction of isocyanate with diamines is as follows (Lahtinen et al. 2003):

$$-NCO + NH_2NH_2 \rightarrow -NHCONHNH_2 \quad (4)$$

$$-NHCONHNH_2 + -NCO \rightarrow -NHCONHNHCONH- \quad (5)$$

## 2.3 Applications of PUs

Polyurethanes exhibit a versatile chemical structure, enabling their design with a wide array of physical and chemical characteristics, from soft, flexible foams to stiff, resilient polymers. Their structural adaptability allows polyurethanes to be customized for specific performance criteria, rendering them appropriate for several applications across various industries. PUs can serve as thermosetting materials (Liu et al. 2019), thermoplastics (Beniah et al. 2017b), insulating materials (Figovsky et al. 2013), elastomers (Engels et al. 2013), adhesives (Fernandes et al. 2015; Fuensanta et al. 2017), coatings for woods and metals, films (Ha et al. 2019; Xu et al. 2014), rigid and flexible foams (Art et al. 1999; Cornille et al. 2017a), various medical uses (Ghosh et al. 2020; Suryawanshi et al. 2019), and many more. Commercial PUs are used as thermoplastic PUs in rafts, athletic clothing, laptop keyboards, car belts, shoes, sheets, films, and several electronic equipment; flexible PUs are utilized in furniture, bedding, vehicles, packaging, biomedicals, and nanocomposites; rigid PU foams serve as insulating materials in thermal, acoustic, and electrical applications. Biomedical applications include artificial hearts and connection tubing for cardiac devices, hemodialysis tubes, and waterborne PUs, including sealants, varnishes, adhesives, and binders (Akindoyo et al. 2016). Due to their toughness, structure, and properties, PUs have replaced many materials, including rubber, plastic, and metals. Flexible foams account for 31 % of the global market's total volume, followed by rigid foam (25 %), molded foam (11 %), elastomers (6 %), and adhesives and sealants (6 %). The thermostable coating is utilized in nonporous monolithic coatings, corrosion protection linings, concrete safeguarding, and the protection of metallic and wooden surfaces against chemicals, color degradation, and moisture (Kathalewar et al. 2013).

## 2.4 Methods for isocyanate-based PU synthesis

### 2.4.1 Solvent-borne PUs

When synthesized, processed, and used, solvent-based PUs emit VOCs (volatile organic compounds) and HAPs (hazardous air pollutants) into the environment. Therefore, to overcome health-related issues, maintain air quality, and environmental protection from VOCs and HAPs, the governmental environmental protection agencies force the industries to develop and adopt environment-friendly products and methods for synthesizing PUs (García-Pacios et al. 2011a,b; Liu et al. 2018; Ma et al. 2018; Nanda and Wicks 2006).

### 2.4.2 Waterborne polyurethane dispersions (WPUDs)

Factors such as reduced cost and control of the emission of VOCs into the environment increase the applications of aqueous PUs in aqueous resins. With the additional benefits of lower viscosity, excellent applicability, and increased molecular weight, the developed product exhibits suitable characteristics related to solvent-borne PU coatings (Delpech and Coutinho 2000). For aqueous phase dispersion or WPUDs, specific types of hydrophilic groups, including carboxylic, sulfonic, and amine groups, are introduced into the backbone of the PUs due to their hydrophobic nature (Liang et al. 2018b). Waterborne polyurethanes (WPUs) are commonly produced in the form of flexible and rigid foams, adhesives, thermoplastic, thermosetting, elastomers, coatings, films, binders, and sealants due to improved thermo-mechanical properties, chemical resistance, and excellent processability (Jhon et al. 2001; Lee et al. 2018; Liang et al. 2018b).

PU coatings are utilized to protect wood and metal surfaces from chemical deterioration, mustard gas, and rust. The traditional solvent-based PU synthesis was replaced with waterborne polyurethane synthesis (WPUs), which resulted in slower drying times due to the greater latent heat of evaporation. Due to the incorporated hydrophilic groups in the PUs' backbone, WPUs require greater energy to produce higher mechanical strength (Li et al. 2017).

Recently used WPUD materials attract more attention not only due to being environment-friendly, nontoxic, and nonflammable but also due to their properties such as wear resistance, excellent adhesive strength, corrosion resistance, good chemical resistance, higher tensile strength, high flexibility, and excellent rheological properties (Chai et al. 2018; Garca-Pacios et al. 2010; García-Pacios et al. 2011b; Honarkar 2018).

For every ton of waterborne dispersion, there is a reduction of 0.7 Tons of VOC emissions into the atmosphere compared to solvent-based dispersions. Waterborne dispersions have garnered significant attention recently due to their broad compatibility, low cost, minimal environmental impact, ease of use, and compatibility with other resins (Man et al. 2019). The different methods of PU dispersion are shown in Figure 5.

Due to their quick drying time, inexpensive water evaporation cost, and abundant space-time yield, WPUs with a high solid content are a significant and recent research issue. The viscosity is the main problem with high solid content in PUs. Previously, PUs with 25–40 % solid content were synthesized; now, WPUs with content of up to or more than 60 % can be synthesized using a special physical blending technique (Chai et al. 2018). This approach facilitates emulsion formation through specialized blending with rapid agitation. The method offers the benefits of a straightforward process and efficient emulsification while also significantly enhancing the solid content of the emulsion, decreasing viscosity, and ensuring robust stability. The researchers examine the influence of many factors on high solid contents, with hydrophilic agents, isocyanates, polyols, chain extenders, and the emulsification process identified as the most significant contributors (Chai et al. 2018).

The emulsion particles are regarded as mini-balls, confirmed by the TEM apparatus. Equipment such as dynamic laser scattering is used to measure and investigate the particle size and distribution of WPUs. Some methods are also described for controlling the particle size and distribution (Chai et al. 2018). Chai et al. (2018) produced small-particle WPUDs, large-particle WPUDs, and high solid-content WPUDs with bimodal particle distribution by the special physical blending process. WPUDs were obtained with bimodal particle distributions of S-WPUDs and L-WPUDs in different combination ratios, which have higher solid contents (66.06 %) and lower viscosities (285 mPa s). Li et al. (2017) produced high solid content cationic WPUs combining cationic, ionic, and nonionic segments via optimal bimodal particle size distribution. The terminal ions in this method are finer, have smaller particle sizes, low viscosity, and exhibit superior dispersion stability (Li et al. 2017).

To produce WPU from poly(tetramethylene ether) glycol (PTMG), Lee et al. (2021) used liquefied lignin, IPDI (isophorone diisocyanate), TEA (tri-ethylene amine) as a neutralizer, and 1,4-butanediol and ethylenediamine as chain-extending agents. WPUs formulated with PTMG and liquefied lignin as polyol exhibit higher viscosities and bigger average dispersion particle sizes compared to those based solely on PTMG. In this study, the thermal activity of the soft segment was diminished by the presence of liquefied lignin (Lee et al. 2021). WPUs have broad applications in adhesives, coatings, automobiles, elastomers, sealants, films, foams, footwear industries, synthetic leather, fibers, textiles, biomedical materials, paper, hard coatings for wood and metallic surfaces, varnishes, etc. (Chai et al. 2018; Fuensanta et al. 2017; García-Pacios et al. 2011a,b; Honarkar 2018; Li et al. 2017; Ma et al. 2018). WPUDs have been synthesized using four different types of methods (see Figure 5) such as the acetone process (Barni and Levi 2003; Fuensanta et al. 2017; Fang et al. 2019; García-Pacios et al. 2011a,b; Ma et al. 2018), prepolymer mixing process (Barni and Levi 2003; Cakić et al.

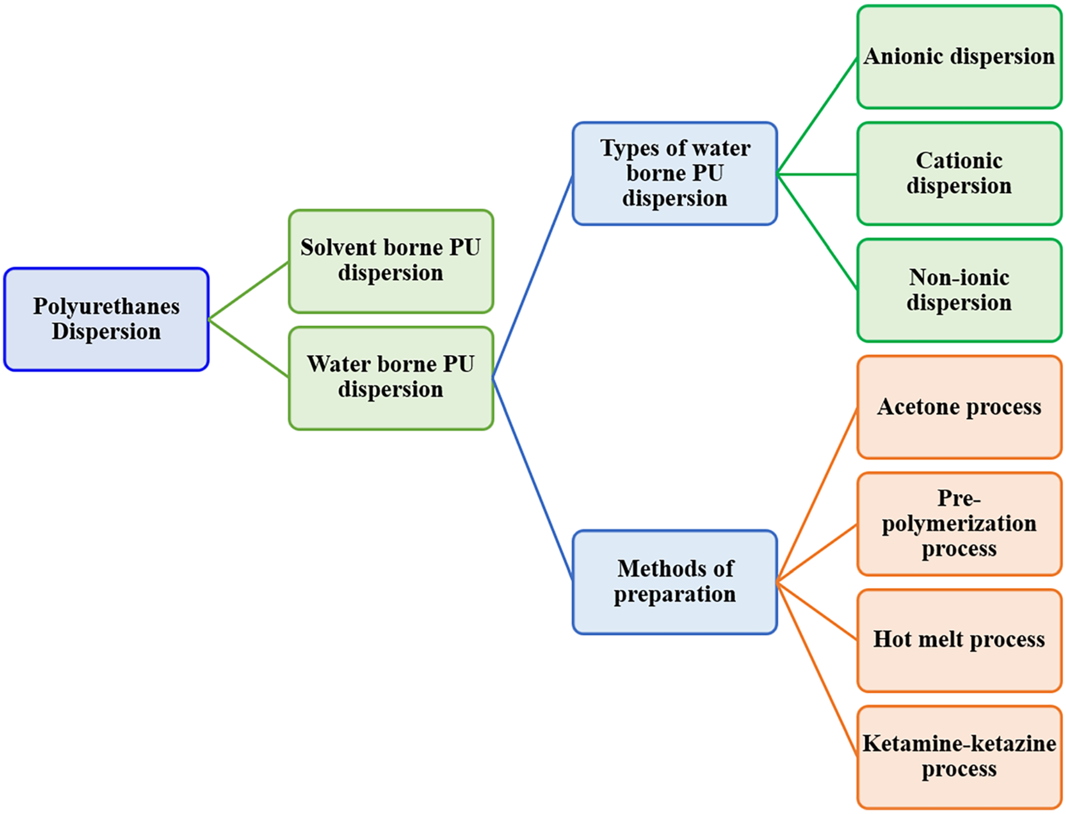


**Figure 5:** Classification of polyurethane dispersions and their methods of synthesis.

2013; Lahtinen et al. 2003; Pérez-Limiñana et al. 2005, 2006; Turri et al. 2004; Yen and Tsai 2003), hot-melt process (Barni and Levi 2003; Chen et al. 2005; Honarkar 2018; Remya et al. 2016), and ketamine–ketazine process (Barni and Levi 2003; Honarkar 2018; Li et al. 2014; Manock 2000; Panda et al. 2017; Remya et al. 2016; Wondu et al. 2019). Among these methods, only the acetone and prepolymer mixing processes are primarily used in industrial synthesis processes (Barni and Levi 2003; Fang et al. 2019; Pérez-Limiñana et al. 2006).

### 2.4.2.1 Acetone process (AP)

In this process, acetone is used as a solvent due to its inertness toward polyurethane reactions, miscibility in water, ability to form a homogeneous mixture of the prepolymer, and lack of reaction with the isocyanates. It decreases the viscosity of the prepolymer, allowing the polyaddition reaction to proceed without restriction. Acetone has a lower boiling point and reduces the reactivity of amines toward isocyanates by forming reversible ketamine complexes. Other solvents, such as methyl ethyl ketone, can also be used as an alternative to acetone. The acetone process is used when synthesizing a higher molecular weight PU structure with high product quality and an average particle size of dispersion. The product obtained is solvent-soluble, thus exhibiting lower solvent resistance (Barni and Levi 2003; Fang et al. 2019; Fuensanta et al. 2017; García-Pacios et al. 2011a,b; Honarkar 2018; Ma et al. 2018; Remya et al. 2016).

The process is divided into five steps: prepolymerization, chain extension, neutralization, dispersion, evaporation of acetone, and postpolymerization (Ma et al. 2018). The prepolymers were prepared using a polyol, diisocyanate, and hydrophilic agent (acetone and an ionic group) in a nitrogen atmosphere at specified temperatures and stirring conditions. Then, chain extension is used to obtain a higher molecular weight PUs structure and neutralize ionic and nonionic groups. Dispersion of prepared PUs takes place either in deionized water (Fuensanta et al. 2017; García-Pacios et al. 2011b; Honarkar 2018; Ma et al. 2018), snow (Fang et al. 2019; Zhou et al. 2016), and ice (Zhou et al. 2016) followed by evaporation of acetone via rotary evaporator or distillation process, and then postpolymerization. Figures 6 and 7 illustrate the process flow diagram for the synthesis of WPUDs, and the reaction scheme for the acetone process (Fang et al. 2019; García-Pacios et al. 2011a,b; Ma et al. 2018; Nanda and Wicks 2006).

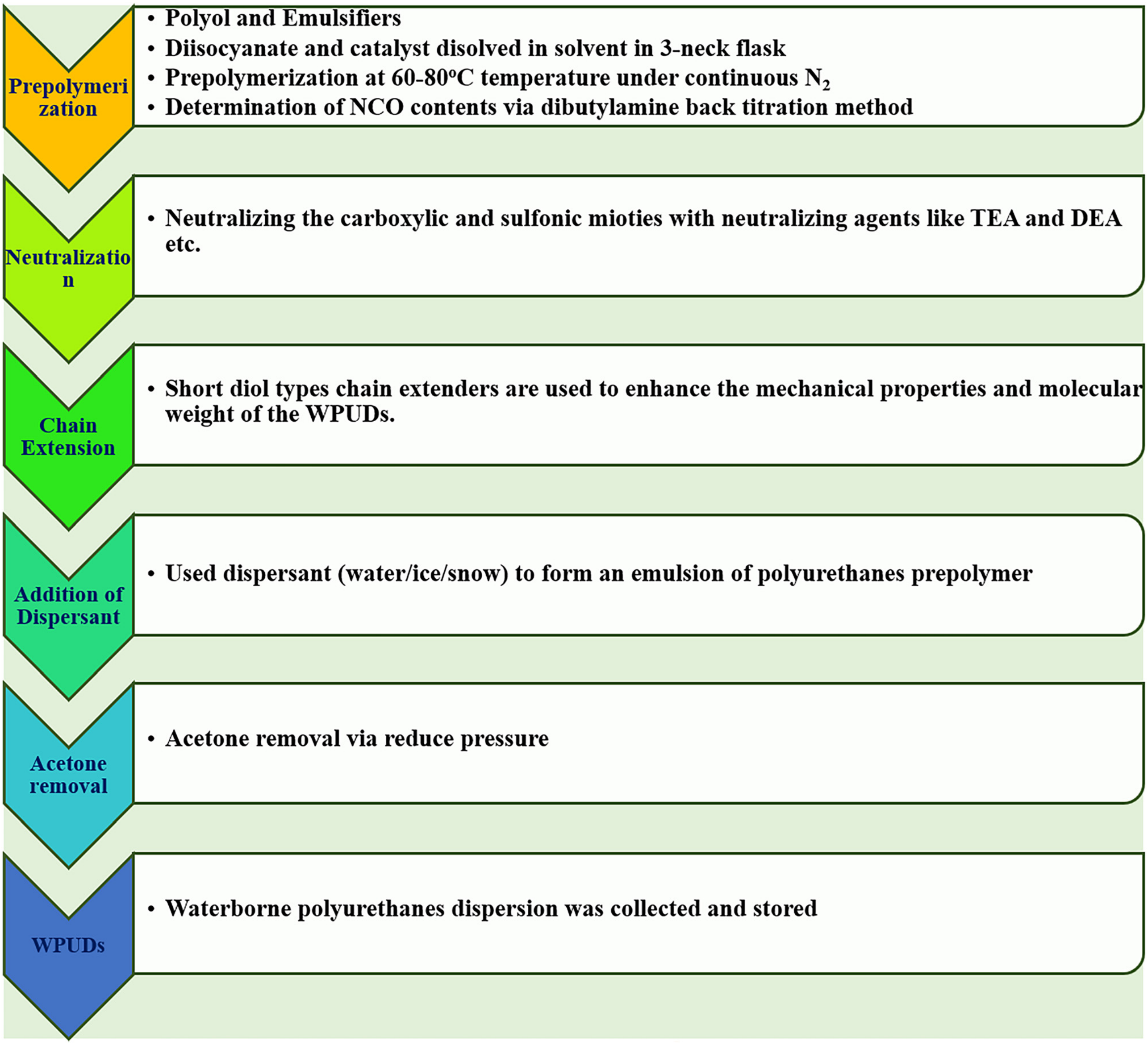


**Figure 6:** Process flow diagram for the synthesis of WPUDs via the acetone process (Fang et al. 2019; García-Pacios et al. 2011a,b; Ma et al. 2018).

### 2.4.2.2 Prepolymer mixing process (PMP)

This process is known for its simplicity and is the most preferred industrial method for PU synthesis. There are two stages in this process: the first is prepolymerization, in which a polyaddition reaction occurs between the polyols and the diisocyanate (cyclo-aliphatic), and the second involves the incorporation of ionic and nonionic hydrophilic groups into the structure through an internal emulsifier. Cycloaliphatic diisocyanate is generally used because it is less reactive toward water molecules. In the next step, the prepolymer is dispersed in water with these hydrophilic groups and a small amount of NMP solvent to reduce its viscosity. The second step involves neutralizing any ionic groups in the structure and extending the chain by adding poly or diamines to a prepolymer that has been water-dispersed. Figure 8 illustrates the flow diagram for producing WPUDs through the prepolymerization mixing process (PMP) (Cakić et al. 2013; Liu et al. 2018; Madbouly et al. 2009). The prepolymer dispersion should take a short period and lower temperature than the critical to avoid unwanted reactions between the NCO group and water molecules (Honarkar 2018; Lahtinen et al. 2003; Lei et al. 2014; Madbouly et al. 2009; Pérez-Limiñana et al. 2006; Remya et al. 2016; Subramani et al. 2004; Turri et al. 2004; Yen and Tsai 2003). Lahtinen et al. (2003) prepared an anionic water-borne PU prepolymer and dispersed it in an aqueous medium with different chain-extending agents. Two types of PU dispersions were prepared using different diisocyanates (IPDI, m-TMXDI) and

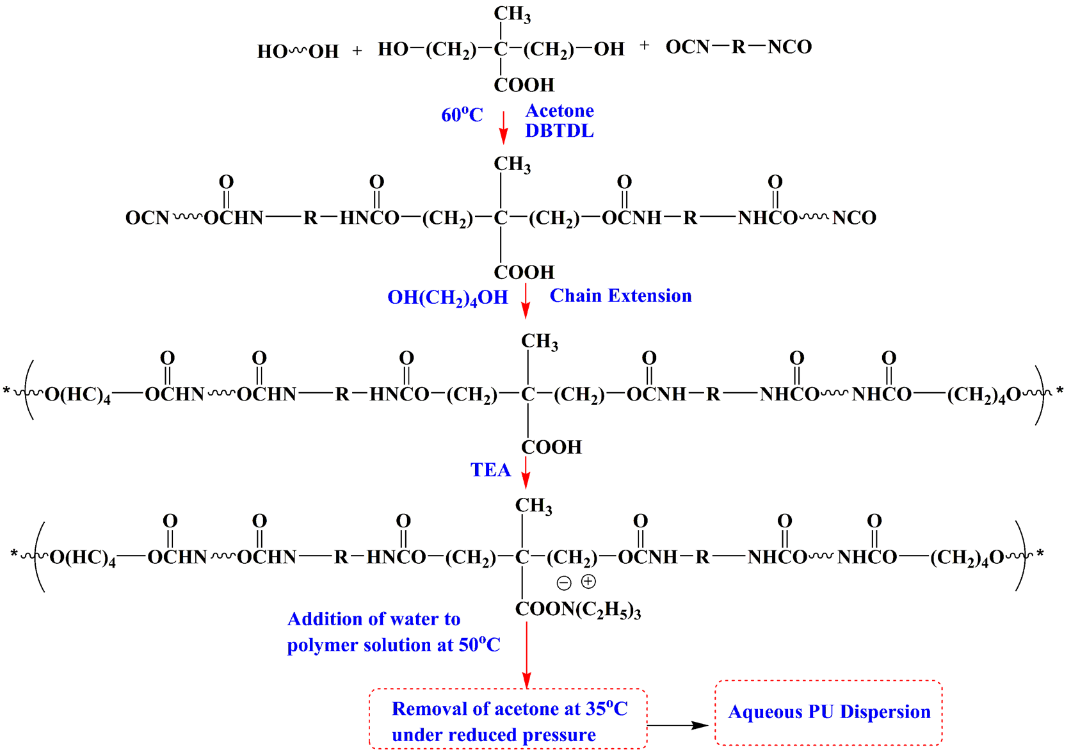


**Figure 7:** Synthesis of WPUDs via the acetone process (Nanda and Wicks 2006). Modified and reproduced with permission from Nanda and Wicks (2006), Elsevier.

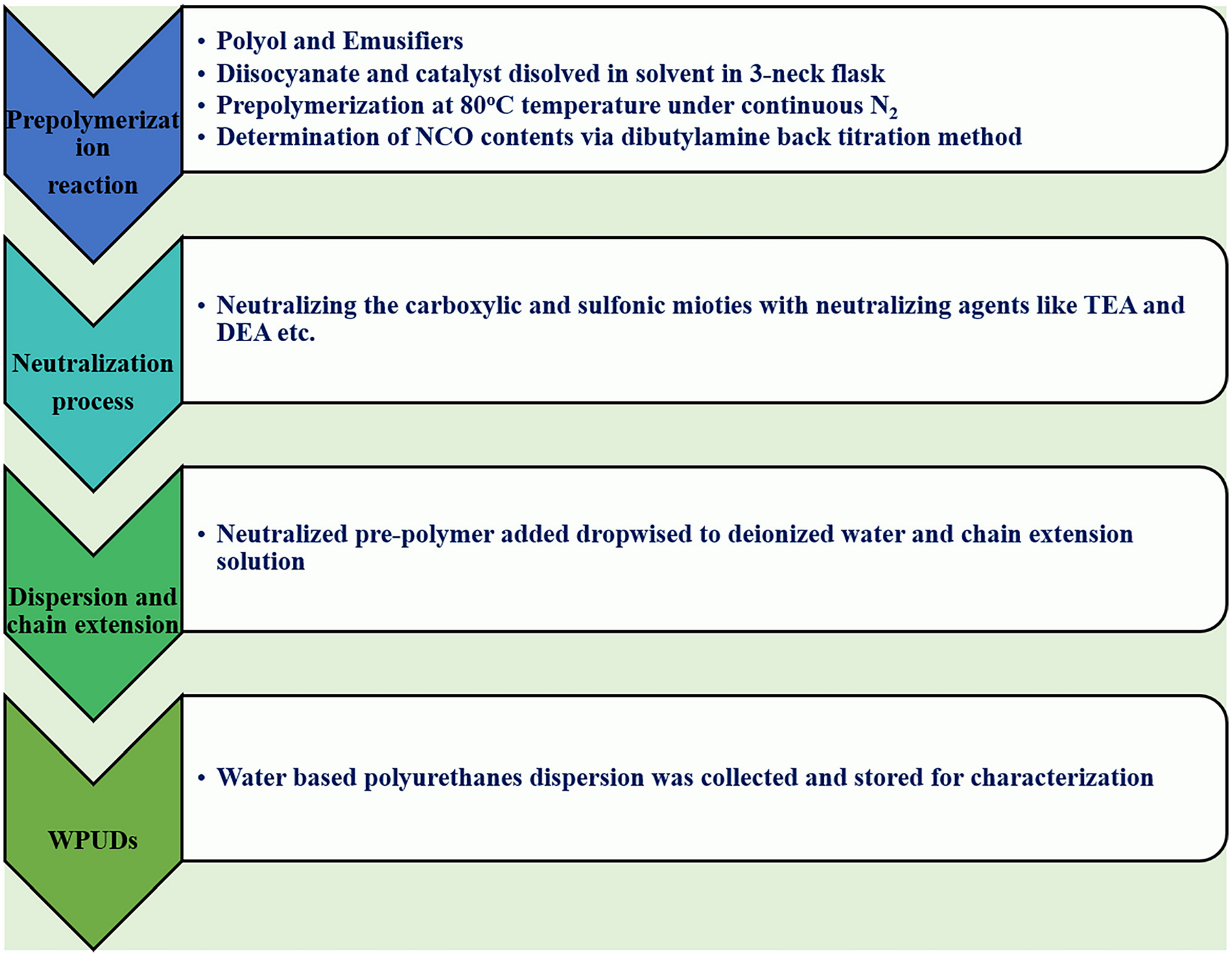
chain extenders, such as hydrazine, EDA, and PDA, along with polyols (polypropylene glycol, polycaprolactone diol). These dispersions were then characterized using GPC, FTIR, and a tensile test, among other methods. It was found that the degree of the extension was relatively low for a balanced stoichiometric ratio after studying the influence of $-NH_2$/NCO on the extension process by varying the molar ratio. Changes influence Young's modulus and tensile strength in average molar masses because EDA shows greater chain extension (Lahtinen et al. 2003). The reaction scheme related to the prepolymer mixing process for synthesizing the WPUDs is shown in Figure 9 (Yoon Jang et al. 2002).

#### 2.4.2.3 Hot-melt process (HMP)

No solvent is required to synthesize WPUDs using this method. Lower molecular weight PUs with fewer branches are created with this technique. The NCO-terminated hydrophilic prepolymer reacts with urea (@130 °C to form a biuret and is then dispersed in water (@ 100 °C) for chain extension with formaldehyde. The condensation reaction is the last step in this process. There are disadvantages associated with the uncontrolled chain extension reaction involving formaldehyde and side reactions with the urethane group in the structure (Barni and Levi 2003; Chen et al. 2005; Honarkar 2018; Remya et al. 2016).

This process is mainly used to produce reactive hot-melt polyurethane adhesives (RHMPA). The adhesives show off the benefits of RHMPA. These processes could be used for the synthesis of solvent and water-free polyurethanes. In these products, the main component is an isocyanate-terminated linear PUs prepolymer, which can crosslink when subjected to moisture. This property of RHMPA makes it special in terms of easy processing, environmental friendliness, excellent adhesion, solvent-freeness, and good thermal and chemical resistance (Liu et al. 2020).

Liu et al. (2020) prepared RHMPA from $CO_2$-based polyols without using a solvent as a reaction medium. In this work, various RHMPAs were synthesized using various carbonate linkage contents. The carbonate linkage content was examined with the aid of FTIR (Fourier Transformation Infrared Radiation) and $^1$H NMR. Through the use of FTIR, TGA/DSC, tensile tests, adhesion tests, and other methods, the impact of carbonate linkage on the moisture curing rate, crystallization behavior, mechanical and thermal properties, and adhesion properties of the product was investigated and assessed (Liu et al. 2020). Orgilés-Calpena et al. (2016) prepared RHMPA from $CO_2$-based polyol and MDI. FTIR and TGA characterizations were performed on the obtained RHMPA. The quantity of $CO_2$-based polycarbonate polyol was adjusted with the RHMPA



- Polyol and Emusifiers
- Diisocyanate and catalyst disolved in solvent in 3-neck flask
- Prepolymerization at 80°C temperature under continuous $N_2$
- Determination of NCO contents via dibutylamine back titration method

- Neutralizing the carboxylic and sulfonic mioties with neutralizing agents like TEA and DEA etc.

- Neutralized pre-polymer added dropwised to deionized water and chain extension solution

- Water based polyurethanes dispersion was collected and stored for characterization

**Figure 8:** Process flow diagram for the synthesis of WPUDs via prepolymerization mixing process (Cakić et al. 2013; Liu et al. 2018; Madbouly et al. 2009).

to achieve the desired characteristics of the footwear joints. The adhesion properties were also tested using the T-Peel test employing leather/PUs adhesive/SBR rubber joints. The adhesive properties of the prepared PUs with various quantities of $CO_2$-based polycarbonate polyol were comparable to those of traditional adhesives used in shoe joints. Numerous experiments were conducted on the RHMPA, including hydrolysis tests and studies of temperature and humidity conditions. The RHMPA provides high crosslinking, adequate mechanical and thermal strength, excellent chemical resistance, and adhesion properties. Furthermore, the hot-melt process offers faster processing compared to solvent- and water-based processes. Without using water as a reaction medium, this is an alternative method for synthesizing PUs (Orgilés-Calpena et al. 2016). Sun et al. (2016) prepared RHMPA from PEDA (pentaerythritol diacrylate) and dihydroxy-terminated acrylic monomer. The influence of PEDA's weight percentage on the rheological, mechanical, thermal, and bonding strengths of PUs was studied. The PEDA was created by directly esterifying acrylic acid and pentaerythritol using toluene as the solvent, anhydrous copper sulfate as an inhibitor, and p-sulfonic acid as a catalyst. The product obtained was characterized using HPLC (high-performance liquid chromatography), FTIR, and $^1$H NMR to confirm the structural formula and the amount of conversion. The reactive hot melt polyurethane (PU) was synthesized by the reaction of poly (propylene glycol) (PPG) with MDI. The reaction mixture was then further reacted with PEDA at 50 Pa and a temperature of 95–105 °C for 2 h. The film's rheological, mechanical, and thermal properties were characterized using TGA (Sun et al. 2016).

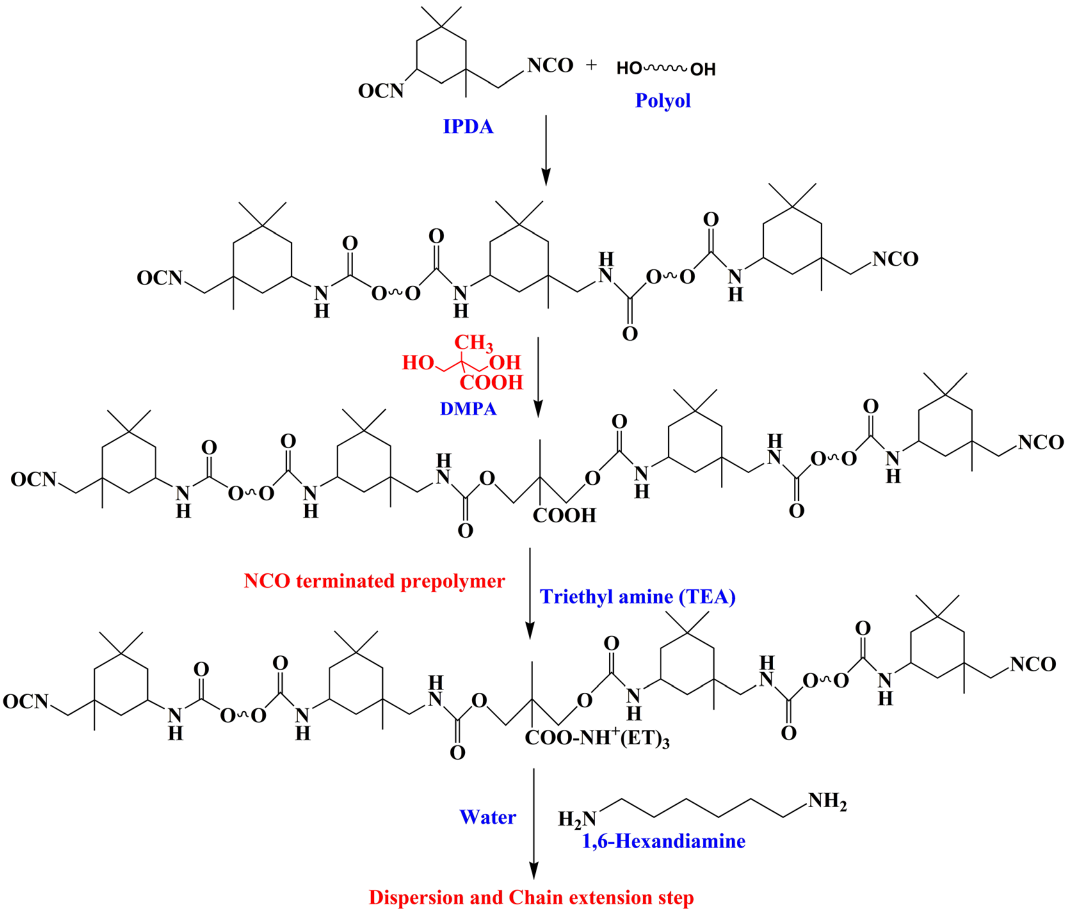


**Figure 9:** Reaction scheme for synthesizing WPUDs via prepolymer mixing process (Yoon Jang et al. 2002). Modified and reproduced with permission from Yoon Jang et al. (2002), Elsevier.

#### 2.4.2.4 Ketamine–ketazine process (KKP)

The dispersion obtained through this process exhibits excellent performance in coating applications. The water-reactive aromatic diisocyanates are more suitable for synthesizing aqueous PU dispersion by this process than the prepolymer mixing process. This approach is analogous to the prepolymer mixing method, as chain extension processes are carried out in an aqueous dispersion to produce a higher molecular weight PU structure. The NCO-terminated prepolymer was mixed with the chain-extending agents, ketamine (a ketone-blocked diamine) and ketazine (a ketone-blocked hydrazine), and then dispersed in water. Hydrolysis of ketamine and ketazine in an aqueous dispersion results in the production of diamines and hydrazine, which are further utilized in chain extension steps (Honarkar 2018; Li et al. 2014; Manock 2000; Panda et al. 2017; Remya et al. 2016; Szycher 2013; Wondu et al. 2019). Figure 10 represents the ketamine/ketazine process's reaction scheme for the synthesis of PUs.

## 2.5 Types of PU dispersions

PUs dispersion aids the emulsification agent and protective colloids in synthesizing hydrophobic PUs. Incorporating the emulsification agent (containing hydrophilic groups) into the backbone of the PUs structure results in easy and better dispersion into the water. Emulsifiers are incorporated into the backbone of the PU's structure with the replacement of polyols and isocyanate groups with hydrophilic groups, precursors, and water-soluble segments. These hydrophilic groups are referred to as internal emulsifiers, which make the dispersion stable for extended periods. Based on the types of internal emulsifiers incorporated into the backbone of the PU structure, there are three types of PU dispersions:

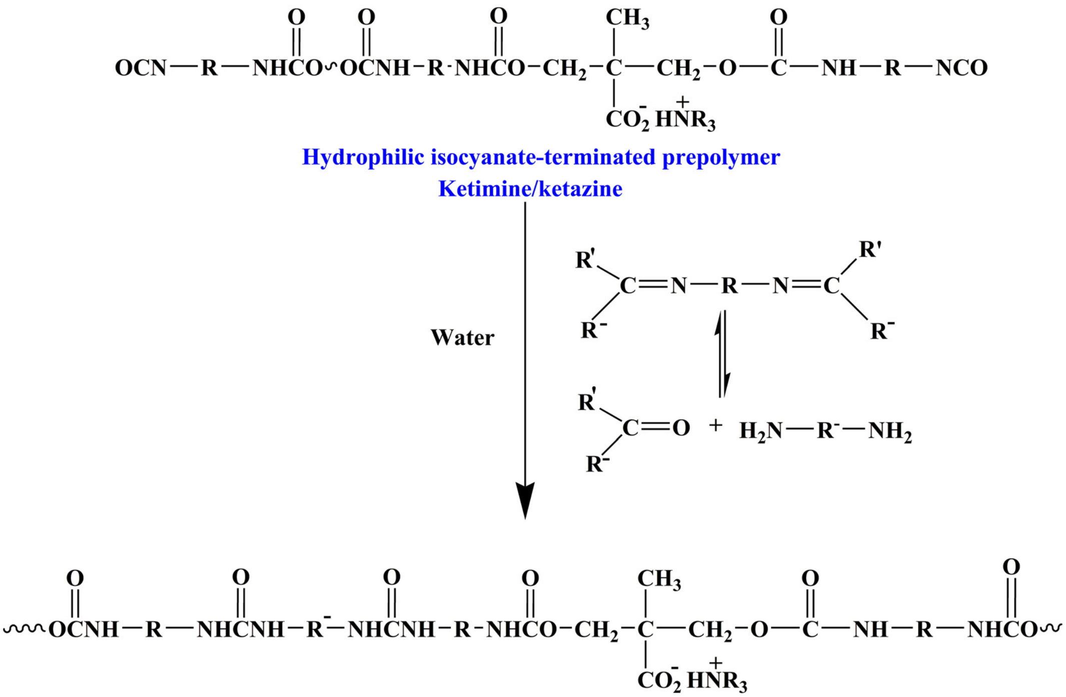


**Figure 10:** Ketamine/ketazine process for the synthesis of polyurethanes (Szycher 2013). Modified and reproduced with permission from Szycher (2013), Taylor & Francis.

anionic, cationic, and nonionic (Cakić et al. 2013; Honarkar 2018; Remya et al. 2016; Szycher 2013).

### 2.5.1 Anionic PUs dispersions

Anionic dispersions are commercially predominant due to their fine particle size and higher stability, among other types. For the synthesis of anionic PUs dispersion, diols bearing pendant carboxylic or sulfonic acid groups are usually introduced into the PUs backbone. DMPA (dimethylolpropionic acid) is preferred as a suitable reagent to introduce a carboxylic group in the backbone of PUs. The acidic groups (–COOH) present in the backbone are neutralized with suitable bases, such as ammonia, TEA, and sodium hydroxide, to produce internal salt, which can be easily dispersed into the water without the influence of shear forces and dispersants (Cakić et al. 2013; Honarkar 2018; Remya et al. 2016; Szycher 2013).

### 2.5.2 Cationic PUs dispersions

Cationic dispersions are also produced similarly to anionic dispersions, but the incorporated monomer contains an alkylated or protonated tertiary amine group. Cationic dispersions with antibacterial properties are commercially produced and utilized in a diverse array of industries. Although ongoing research is being conducted to enhance their efficacy, safety, and cost-effectiveness, their commercial presence is substantial and continues to expand. Their most intriguing aspect is their ability to modify the structural properties of molecules by altering the diisocyanate, polyol, and ionic portions of cationomers. The structure has an ionic center formed by the quaternization with an alkylation agent or protonation with strong acids. Cationic dispersions are used and supplied at lower pH (Cakić et al. 2013; Honarkar 2018; Remya et al. 2016; Szycher 2013).

### 2.5.3 Nonionic PUs dispersions

In this dispersion type, the ionic centers are replaced with polyether units, and PU oxide units are used as dispersing sites. These are more stable to electrolyte addition and have better shear forces than ionic dispersions. Nonionomers are heat-sensitive due to polyethylene oxide, which is soluble in water; the solubility of polyethylene oxide decreases with an increase in temperature. The coating produced with a nonionic dispersion is hydrophilic after drying (Honarkar 2018; Remya et al. 2016; Szycher 2013). Hou and his colleagues used nonionic and ionic monomers to create WPUDs with high solid contents (Li et al. 2017).

## 2.6 Components for PUs synthesis

### 2.6.1 Soft segments (polyols)

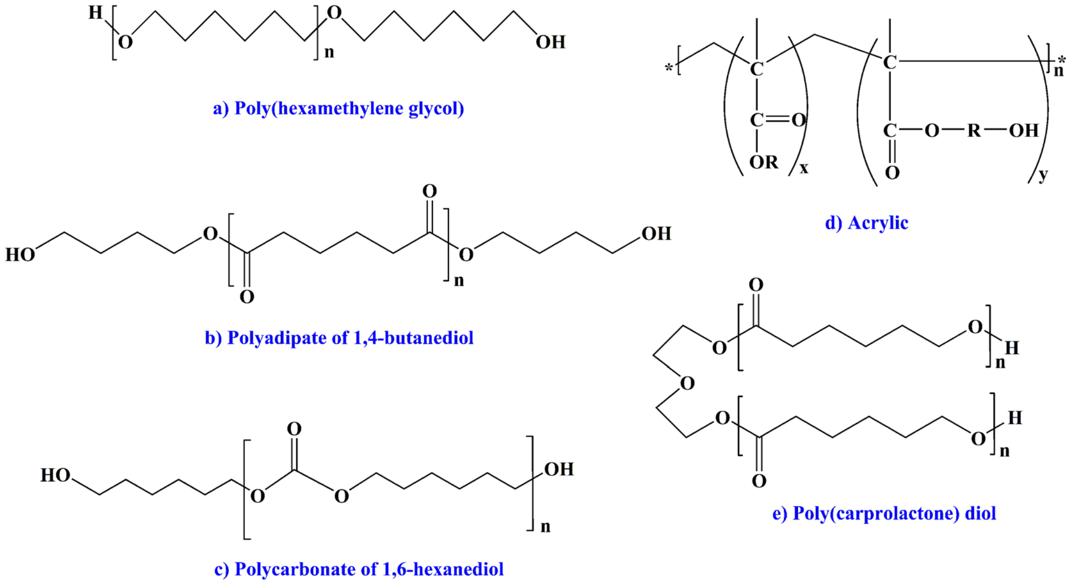
Polyether, polyesters, and polycarbonates are the primary components of soft segments, which contribute to the elastic properties and flexibility of the PU's structure. PUs with two or more –OH groups are synthesized by polyols, which react with the isocyanate group to form a urethane linkage. Urethanes based on polyether are more durable and exhibit superior dynamic properties. Polyester urethanes, in contrast, exhibit a higher tensile strength and are usually softer. Polyethylene polyols, including polyethylene glycol and polypropylene glycol, as well as polytetramethylene oxide (PTMO), provide remarkable adaptability. Polyester polyols are produced from polyethylene adipate and adipic acid or butanediols. Polyesters comprise a mixture of adipic acid, anhydrides, and various glycols (Crescentini et al. 2019). Polycarbonate polyols are the third type of polyol and are more expensive; however, they are the most effective in producing novel types of PUs with unique and improved structural properties. It offers resistance to the oxidation of the chemical structure of the PUs (Dongdong and Hengshui 2015). PUs were synthesized using a variety of polyols (Akindoyo et al. 2016; Fuensanta et al. 2017; García-Pacios et al. 2011a, b; Lahtinen et al. 2003; Xu et al. 2014). Figure 11 illustrates various types of polyols commonly used in the synthesis of PUs. Most polyols commonly used are derived from various available sources. A few of the sources are discussed below.

#### 2.6.1.1 Natural oils–based polyols

Vegetable oils are fatty acid triglycerides with 12–22 long carbon atom chains and 0–3 double bonds in carbon–carbon atoms utilized in polyol synthesis. Due to the presence of the triglyceride structure, natural oils used for polyol synthesis include soybean oil (Lu and Larock 2010), tung oil (Man et al. 2019), linseed oil, and castor oil (Panda et al. 2017). Oleic acid (18:1), linoleic acid (18:2), and linolenic acid (18:3) are triglyceride unsaturated acids. Thus, hydroxyl, carboxylic, and epoxy groups can be introduced into the structure. Transesterification, ozonolysis followed by reduction, epoxidation, and thiol-ene click reactions were used to introduce the hydroxyl group to the ester and unsaturated double bonds (Bullermann et al. 2013; Chai et al. 2018; Liang et al. 2018a; Wei et al. 2013).

#### 2.6.1.2 $CO_2$-based polyols

$CO_2$ is the most abundant, accessible, and renewable resource that can produce chemical substances and building blocks for polymer materials. $CO_2$-based polyols (Fu et al. 2018; Muthuraj and Mekonnen 2018; Ye et al. 2019) can be used to produce polyurethane (PU) materials, including adhesives, elastomers, and thermoplastics. These new generations of PUs, or polyols derived from $CO_2$, have contributed to social, economic, and environmental benefits. Various types of valuable chemical products are obtained by copolymerization of $CO_2$ and propylene oxide by using different kinds of catalysts, including zinc-based complexes (Xiao et al. 2006), rare earth metals (Hsu and Tan 2001), salen complexes (Eun et al. 2007), solid-supported zinc catalysts



a) Poly(hexamethylene glycol)

b) Polyadipate of 1,4-butanediol

c) Polycarbonate of 1,6-hexanediol

d) Acrylic

e) Poly(carprolactone) diol

**Figure 11:** Different types of polyols utilized to develop PUs (Akindoyo et al. 2016; Fuensanta et al. 2017; García-Pacios et al. 2011a; Lahtinen et al. 2003; Ma et al. 2018; Xu et al. 2014).

(Ion et al. 2009), and metal macrocycle (Coates et al. 2012; Cyriac et al. 2011; Darensbourg and Wei 2012; Geoffrey et al. 2012; Kember et al. 2011). However, some catalysts are used to homo-polymerize propylene oxide with $CO_2$ to produce ether linkages. For example, using Co(III) and Cr(III) complexes and Lewis acid compounds as a catalyst resulted in >99 wt% carbonate linkage, whereas using $Zn_3[Co(CN)_6]_2$ double metal cyanide resulted in only 53 wt% alternating carbonate linkages in the copolymers. The alternating carbonate linkage in the copolymer yields a higher molecular weight material with interesting biodegradable properties (Liu et al. 2020). Liu and Wang (2017) used a Zn–Co–DMC and salen catalyst with a proton starter, which is the most active in the industrial process for the copolymerization of $CO_2$/PO, and its production reached its highest point at 90 °C. Alcohol, organic dicarboxylic acids, sebacic acid, and 1,3,5-benzenetricarboxylic acid are used as starters in the catalytic copolymerization of $CO_2$ and propylene oxide. Oxalic acid is used as a starter because it is the cheapest organic dicarboxylic acid.

Various researchers have used $CO_2$ and epoxide as feedstock for polyol synthesis via copolymerization using multiple catalysts. The $CO_2$-based polyols contain carbonates and ether groups in the main chain, providing hydrolysis and oxidation resistance to the PU structure (Wang et al. 2016). RHMPAs are currently produced from nonrenewable petroleum-based polyols. Poly(propylene carbonate) (PPC) polyols, a prominent green renewable polyol, are synthesized from $CO_2$, an inexpensive, abundant, and renewable greenhouse gas. Liu et al. (2020) synthesized a series of PPC-RHMPAs with diverse carbonate linkages via $^1$H NMR and FTIR. A recent study suggests that polycarbonate polyols can decrease greenhouse gas emissions by 11–19 % and save fossil fuels by 13–16 % compared to traditional polyols. Its numerous applications include foams, coatings, packaging materials, and biomedical materials for tissue engineering.

#### 2.6.1.3 Petroleum-based polyols

Polyols constitute the primary components of PUs, serving as soft segments that impart flexibility to the structure. Short-chain diols are derived from petroleum feedstocks. Various polyol types, including polyester, polyether, polycarbonates, polyadipates, and acrylic polyols, possess two hydroxyl groups at each terminal of their molecular structure. Compounds of greater molecular weights (ranging from 2,000 to 10,000) are utilized in the synthesis of PUDs. PPG, PTMG, PPC (poly(propylene carbonate) polyol), and PEG (polyethylene glycol) are various types of polyols derived from petroleum feedstocks. These petroleum-based polyols provide good mechanical and thermal properties in the synthesized PUDs (Akindoyo et al. 2016; Fuensanta et al. 2017; García-Pacios et al. 2011a; Lahtinen et al. 2003; Xu et al. 2014). Fang et al. (2019) utilized snow as a dispersant instead of water or deionized water and synthesized PUDs from polyether and polyester polyols. The polyether polyols-based WPU exhibited elevated solid content, viscosity, and water resistance. However, the polyester-based WPU offered superior crystallinity and thermal stability (Fang et al. 2019). Ma et al. (2018) synthesized waterborne polyurethane (WPU) dispersions and films with high solid content, utilizing poly(propylene carbonate) (PPC) as a soft segment, dimethylolbutyric acid (DMBA) as an internal emulsifier, 1,4-butanediol (BDO) as a short-chain extender, and bis(4-isocyanate cyclohexyl) diisocyanate (HMDI) as a hard segment. PPG and PTMG were utilized as soft segments in the synthesis of PU, and the mechanical, thermal, and adhesive properties of the resulting films and adhesives were evaluated and compared.

### 2.6.2 Hard segments

Isocyanates are mostly either di- or polyfunctional, with aliphatic or aromatic properties. PUs are often synthesized using aromatic isocyanates as a hard segment instead of aliphatic isocyanates. Aromatic amines such as MDA (methylene diamine) and toluene diamine (TDA) react with phosgene to produce MDI and TDI, respectively. Aromatic diisocyanates like hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), and hydrogenated MDI (HMDI) are commonly industrially used diisocyanates for the synthesis of PUs. MDI derivatives, such as 2,4′-methylenediphenyl and 4,4′-methylene diphenyl, are used as hard segments. Similarly, the derivatives of TDI used as hard segments are 2,4-TDI and 2,6-TDI (Król et al. 2011; Lin et al. 2020; Pollaris et al. 2016; Yilgör et al. 2015; Zhang et al. 2014). Polyfunctional isocyanates, including isocyanurates produced through self-reaction, are widely utilized in industry to enhance thermal stability, chemical resistance, and flame retardancy. Although the majority of isocyanates are synthesized using the phosgene process, other nonphosgene processes, such as urethane thermolysis, reductive carbonylation, and Curtius rearrangement, have been investigated to eliminate phosgene use. Alternative methods, such as the Lossen rearrangement and reactions with bis(trichloromethyl carbonate) and amines, are also available. Nevertheless, despite their safety advantages, these nonphosgene methods remain less economically viable than traditional phosgenation (Delavarde et al. 2024). Additional information regarding the various types and synthesis methods of diisocyanates (including both phosgene-based and phosgene-free approaches) and their applications in producing PUs is thoroughly documented (Fink 2013).

Figure 12a and b show different aromatic, aliphatic, and cyclic diisocyanates utilized for the synthesis of commercial PUs.

### 2.6.3 Neutralizing agent

These compounds are used to neutralize the sulfonic and carboxylic moieties present in the structure of the PUDs. Sulfonic and carboxylic moieties are integrated into the structure of PUDs through the incorporation of the AAS (2-[(2-aminoethyl)amino]-ethane sulfonic acid monosodium salt) (Ma et al. 2018) and DMPA (Bullermann et al. 2013; Lahtinen et al. 2003; Zafar et al. 2019), among similar compounds, to impart hydrophilicity. Occasionally, both or a single type of anionic stabilization group is used for the synthesis of PUDs. The use of amine-like structures neutralizes these types of ionic structures. Ma et al. (2018) used TEA as a neutralizing agent, which neutralized both types of

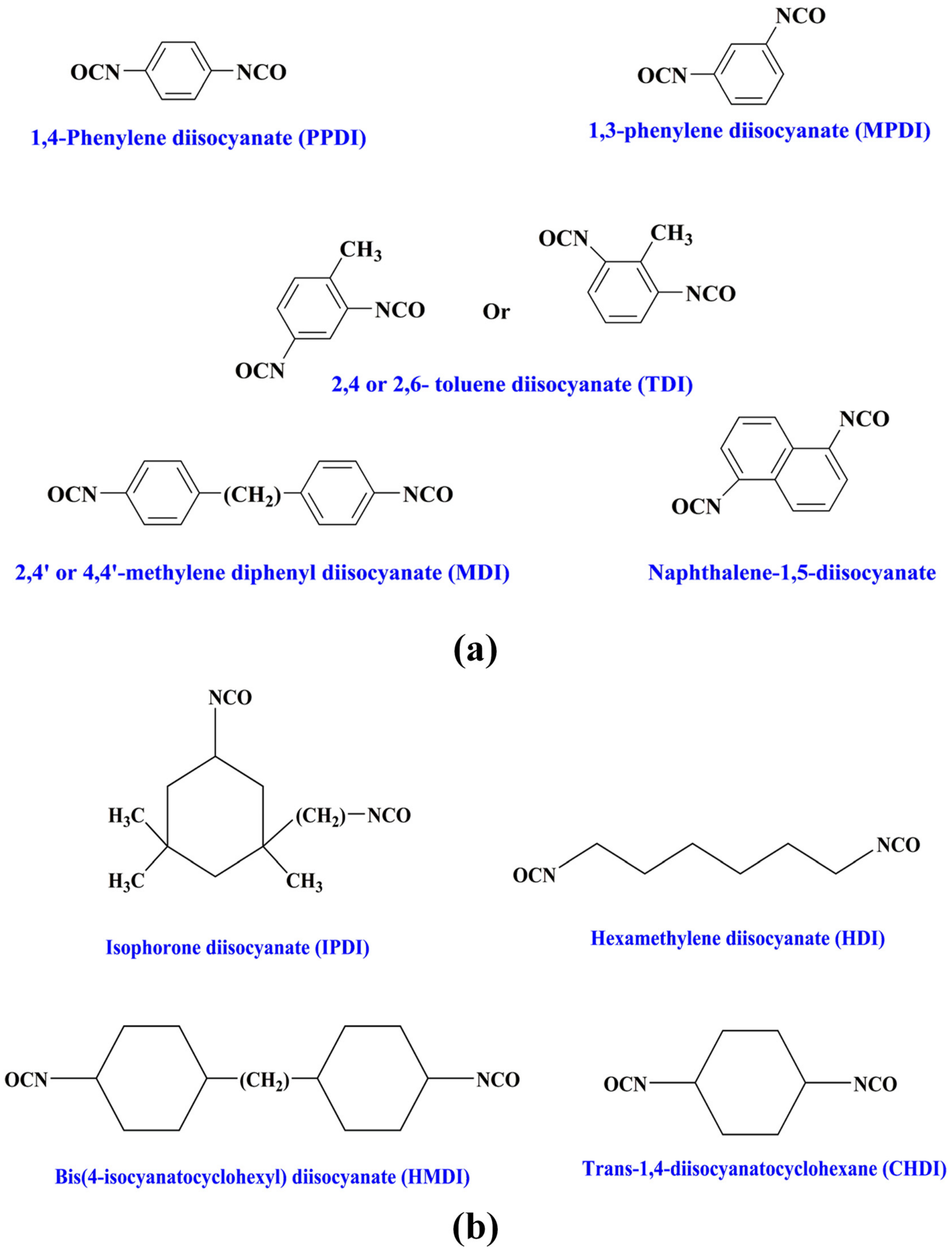


**Figure 12:** Different types of diisocyanate (a) aromatic diisocyanate and (b) aliphatic and cycloaliphatic diisocyanate utilized for the synthesis of commercial polyurethanes (Akindoyo et al. 2016; Yilgör et al. 2015; Zafar et al. 2019).

moieties present in the structure of PUDs (Ma et al. 2018). Liu and Wang (2017) employed TEA as a neutralizing agent to neutralize the carboxylic groups inside the structure (Liu and Wang 2017). These emulsifiers, which introduce sulfonic and carboxylic groups in the PUDs, effectively impart hydrophilic characteristics. Emulsifiers contribute to the stability of the dispersions and improve properties such as alkali and acid resistance, electrolytic resistance, and mechanical properties (Fang et al. 2019; Garca-Pacios et al. 2010; García-Pacios et al. 2011a, b; Liu et al. 2019; Ma et al. 2018).

### 2.6.4 Chain extenders

Chain extenders are low-molecular-weight compounds characterized by short molecules containing di-functional groups such as –COOH, –NH, and –OH. They are employed to increase the length and overall molecular weight, forming hard segments upon reaction with diisocyanates and enhancing the final product's characteristics. Chain extenders may be classified as either aliphatic or aromatic. Diol-derived chain extenders yield urethane linkages, including ethylene glycol, butane diol, and propylene glycol. Using diamine chain extenders leads to the formation of urea linkages and bidentate H-bonds. Diamine chain extenders have enhanced modulus and tensile strength while demonstrating reduced elongation relative to their diol equivalents (Touchet and Cosgriff-Hernandez 2016). Glycols are utilized in polyurethanes, while diamines or hydroxylamines are employed in polyurea and hybrid poly(urethane-urea) (Fink 2013). A chain extender in their construction renders the hard segments rigid. The chain extension phase is employed in the prepolymerization process to augment the polymer's molecular weight. Incorporating a chain extender significantly increased the molecular weight of the polymer chains and enhanced their mechanical properties (Zhao et al. 2022). Ma et al. (2018) used BDO as a chain extender after a reaction between diisocyanate and higher molecular weight polyols. Lahtinen et al. (2003) prepared anionic dispersions with IPDI, PCL (poly(e-caprolactone)) as a polyol, and three different chain extenders, including monohydrated hydrazine and EDA (ethylene diamine). They investigated the effects of these short-chain extenders on structural properties and degree of extension. This depends upon the $NH_2$/NCO ratio; if this value is lower, the degree of extension and chain extension is not better. The amine-based polyols showed higher stability of colloids. Lei et al. (2014) produced waterborne ink with various chain extenders and investigated the effects of these chain extenders on the properties of WPUDs. They used EDA, DETA (diethylene triamine), and TETA (triethylene tetramine) as chain extenders and discovered that chain extension occurs on the particle surface, with a value of 60 % being the highest. The study suggests that DETA has better thermal properties than the remaining. Delpech and Coutinho (2000) prepared WPUDs by using DMPA as an internal emulsifier, PPG as a polyol, and HMDI as an isocyanate with chain extension via EDA, HZ (hydrazine), and ethylene glycol (EG). The prepolymer was synthesized with or without acetone solvent, with variation in the soft segment length, and the NCO/OH ratio.

### 2.6.5 Emulsifiers (ionomers)

To make hydrophilic PUs, different types of carboxylic, phosphoric, and sulfonic ionic groups (called internal emulsifiers) are introduced into the backbone of the structure, which makes the PUs prepolymer dispersible in water. PUs with high ionic contents provide coatings with better mechanical strength and elasticity (Pérez-Limiñana et al. 2005). Adding hydrophilic segments, such as polyether chains, as lateral and terminal groups in the synthesis of WPUDs can also result in aqueous dispersion (Szycher 2013).

The hydrophilic nature of PUs made it possible to become a water-dispersed emulsion that had environment-friendly applications in metal, glass, wood, and ceramic and water-repellent glass finishes as a lacquer (Pérez-Limiñana et al. 2005; Žagar and Žigon 2000). PUs become more soluble in methanol and acetone, forming a homogeneous solution and a stable emulsion that is easily dispersed in water. The stability of the emulsion is the result of the formation of a tiny sphere with an aggregated core of hydrophilic segments surrounded by a boundary layer with an ionic group (Pérez-Limiñana et al. 2006). Pérez-Limiñana et al. (2005) produced WPUDs with variable amounts of ionic group DMPA content in the structure, ranging from 5 to 8 % of the prepolymer weight. With a decrease in DMPA content, there is an increase in the number of particle sizes due to a reduction in the dispersion's hydrophilicity and electrolytic stability. When the DMPA content decreases, there is a reduction in thermoplasticity and the hard segment content in the ionomer, accompanied by an increase in crystallinity and thermal degradation resistance due to the decrease in hard segment content. The contents of ionic groups, the molar ratio of hard and soft segments, the degree of neutralization of ionic group and nature of counter ions, types of chain extender, nature and molecular weight of macroglycol, and other factors influence the properties of ionomeric PUs (Delpech and Coutinho 2000; Yoon Jang et al. 2002; Wen et al. 1999).

Yoon Jang et al. (2002) studied the impact of DMPA content on the mechanical properties and molecular weight of PUs produced from the prepolymer mixing process. The

NCO-terminated prepolymer containing the pendant group of DPMA is neutralized by base (amines). It forms an internal emulsifier and is then dispersed in water to form an aqueous dispersion. The author depicts the variation of molecular weight with varying DMPA content (6.0–12.0 wt%, depending on total solids) at a constant NCO/OH ratio. Films with varying mechanical properties were prepared from PUDs with different DMPA content levels at a constant NCO/OH ratio. As DMPA molecules produce hard segments in the PU's structure, the hard segments increase as the DMPA content increases. The hard segment is the primary component that provides and enhances mechanical properties, such as tensile strength and modulus, by approximately 100 %. To some extent, emulsification conditions, such as stirring speed, dispersing temperature, and concentration of the hydrophilic group (carboxylic group), can control the average particle size. The average particle size decreases exponentially as DMPA content increases, owing to the stabilizing mechanism (electrical double layers formed by the ionic group) of ionomeric dispersion.

#### 2.6.6 Dispersing medium

Following the neutralization and chain extension process, the reaction mixture was subjected to a further reaction with the residual NCO groups in the prepolymer. Different types of dispersing mediums are used, including deionized water (Li et al. 2017), snow (Zhou et al. 2016), double-distilled water (Ma et al. 2018), and a combination of ice and water (Zhou et al. 2016), for the synthesis of PUDs. Fang et al. (2019) synthesized PUs dispersed in snow and water and compared their thermal, mechanical, and hydrophilic properties (Fang et al. 2019). Zhou et al. (2016) prepared PUs with different dispersant mediums, such as water, ice, and snow, at various temperatures (50 °C, 20 °C, and 80 °C) and found that snow performs better than the other dispersants. The advantage of the snow over the other is that the rigid hexagonal structure decreases the hard and polar segments in the WPUDs. This could reduce the use of toxic and hazardous solvents in the synthesis of PUs. The use of deionized water, snow, and ice in synthesizing PUs has become advantageous and beneficial and, therefore, is mainly used as a dispersing medium.

### 2.7 Hazards of isocyanate-based PUs

The environmental effects of PU synthesis can be seen at each stage of the material's life cycle, from the production of monomers to the polymerization process and to the final disposal in landfills or burning. Due to the hydrolysis of PUs, several harmful substances, including isocyanate and HCN, are released during the life span of PU materials, and toxic amines are released during landfilling (Ma et al. 2018).

During the process of synthesizing isocyanates, phosgene is a highly toxic gas. Because isocyanates such as MDI and TDI are dangerous and highly toxic, they are classified as CMR (carcinogenic, mutagenic, and reprotoxic) (Baba et al. 2002; Cornille et al. 2017a; Suryawanshi et al. 2019). Long-term exposure to these types of chemicals can lead to serious health issues like asthma, dermatitis, acute poisoning, conjunctivitis, and more. Due to these health dangers, environmental agencies and regulations have restricted the use of multiple isocyanates. Therefore, creating an isocyanate-free PUs synthesis method is urgently needed (Cornille et al. 2017a).

## 3 Sustainable and green synthesis of isocyanate-free or nonisocyanate polyurethanes (NIPUs)

### 3.1 NIPUs

NIPUs (corresponding to the generic name of isocyanate-free PUs) are fast-growing polymeric products prepared by environment-friendly methods without using toxic and hazardous chemical substances such as phosgene-based isocyanates (Tryznowski et al. 2015). The nonisocyanate synthesis route has become the most promising alternative for the synthesis of green, sustainable, and novel isocyanate-free polyurethanes (PUs). It is increasing academic and industrial research attention for PU synthesis (Guan et al. 2017; Kathalewar et al. 2013; Ochiai et al. 2005).

The NIPUs are a greener alternative to traditional PUs produced by reacting CCs and amines in bulk and solvents. Water-soluble NIPUs, NIPUs-based hydrogels, and WNIPUs dispersions are gaining popularity for various reasons, including scalability, environmental impact, and properties. Water-based systems encompass water-soluble and WNIPU systems (Bizet et al. 2020a, b). Habets et al. (2025) described the development of a new method to access NIPU synthesis techniques at room temperature, along with the advantages and limitations of each approach. Considering societal demands and regulatory changes, synthesizing NIPUs at room temperature could reduce the energy consumption of the process, facilitate the transition to NIPUs within existing PU manufacturing facilities, and, in consumer-grade applications, enable a smoother transition from PUs to NIPUs.

The synthesis of NIPUs from nontoxic, renewable feedstocks represents notable progress in creating safer and more sustainable polymeric materials. This method eliminates or completely eliminates the need for harmful isocyanates and other toxic substances, such as phosgene or its derivatives, often used in conventional PU manufacturing. NIPUs offer enhanced tensile capabilities, superior thermal stability, increased chemical resistance, and reduced permeability compared to traditional materials, making them exceptionally suitable for many demanding applications. The polyaddition reaction between polycyclic carbonates and polyamines has emerged as the most promising synthesis approach for NIPUs. This approach is desirable as it does not necessitate phosgene or its derivatives, which are both very poisonous and detrimental to the environment. Furthermore, the reaction occurs without generating by-products, thus enhancing atom economy and process efficiency. This pathway facilitates the production of both thermoplastic and thermosetting polymers, contingent upon the molecular configuration of the initial components. It is essential to recognize that five-membered cyclic carbonates, frequently utilized in this procedure, demonstrate comparatively moderate reactivity with polyamines relative to highly reactive isocyanates and polyols. This leads to a diminished polymerization rate, often necessitating elevated reaction temperatures and the use of catalysts to achieve effective conversion. A significant isocyanate-free method is transurethanization, also known as transcarbamoylation. This technology presents a flexible and efficient technique for synthesizing NIPUs and additionally offers a viable route for recycling current PU materials, especially when monoalcohols substitute conventional diols. This approach facilitates the design of recyclable and reprocessable PU systems, thereby advancing circular economy objectives (Delavarde et al. 2024).

NIPUs enhance their eco-friendliness by employing cyclic carbonates (CCs) sourced from various renewable resources. These comprise vegetable oils, fatty acids, sugars, terpenes, glycerol, rosin gum, sorbitol, and cashew nut shells (Delavarde et al. 2024). A prevalent technique for synthesizing cyclic carbonates entails the copolymerization of $CO_2$ and epoxides. This approach is particularly advantageous as it utilizes $CO_2$, a nontoxic, abundant, and cost-effective feedstock, as a sustainable carbon source, thereby diminishing dependence on fossil fuels and substantially reducing the overall carbon footprint of the material (MacInnis et al. 2022).

NIPU synthesis generally circumvents phosgene and isocyanates; nonetheless, certain synthetic routes still utilize hazardous precursors. The copolymerization of aziridines with $CO_2$ and the ring-opening polymerization of cycloaliphatic urethanes may provide dangerous intermediates. In the prevalent carbonate–amine chemistry, both the amine and carbonate precursors exhibit markedly reduced toxicity. They are nonhygroscopic, offering benefits compared to isocyanates, which are highly reactive with water and necessitate stringent handling and storage protocols. This moisture insensitivity streamlines processing and mitigates the likelihood of undesirable side reactions, such as the generation of isocyanurates during storage. Due to their distinctive chemical structure and composition, NIPUs create materials with dense, nonporous networks that are resistant to moisture absorption. This inherent resilience to environmental deterioration further endorses their implementation in advanced, long-lasting uses. With the increasing interest and demand for green chemistry and sustainable materials within industrial and academic spheres, NIPUs are emerging as a promising alternative to conventional PUs, offering a safer, more sustainable, and highly functional category of polymers for future technologies (Delavarde et al. 2024).

## 3.2 Advantages of NIPUs

- NIPUs derived from CCs and amines surpassed their isocyanate counterparts in terms of permeability, weatherability, hydrolytic stability, and chemical and crack resistance (Lambeth and Henderson 2013; Liang and Gao 2019; Łukaszewska et al. 2023b).
- Most of the advantages of NIPU chemistry involve avoiding potentially unfavorable side reactions in isocyanate chemistry, such as the production of thermally unstable allophanate and biuret groups or the release of carbon dioxide with water (Lambeth and Rizvi 2019). The lack of thermally unstable labile biuret and allophanate groups improves the thermal stability of the resulting materials (Bukowczan et al. 2023; Łukaszewska et al. 2023b).
- Since no isocyanates (such as TDI or MDI, categorized as CMR) are used to manufacture NIPUs, they are less toxic and dangerous than commercially available PUs (Akindoyo et al. 2016).
- Because of a hydroxyl functional group on the beta-carbon of the urethane linkage, aminolysis of cyclic carbonate produces hydroxyurethane linkages, which are most suitable for coatings. These –OH groups facilitate the formation of additional intermolecular and intramolecular H-bonding, which can enhance the material's adhesive and chemical resistance (Morales-Cerrada et al. 2021). Hydrogen bonding regulates supramolecular organization, altering material properties or introducing novel characteristics, such as self-healing or injectability. Incorporating supplementary hydrogen bond donor

groups will markedly influence the characteristics of NIPUs by enhancing hydrogen bond density (Łukaszewska et al. 2023b). Water absorption and swelling capacity are particularly significant in biomaterials, medicines, food, soft electronics, and sensors. Elevated water absorption in PHUs correlates with the formation of polar hydroxyl groups along the chain length. The linearity of PHUs facilitates a decrease in the mass fraction of CCs within the composition. It should permit materials with enhanced water absorption relative to NIPUs derived from analogous branched carbonates. Incorporating supplementary amino groups into the polymer chain is anticipated to enhance the water absorption capacity and may facilitate the customization of the materials' swelling behavior (Łukaszewska et al. 2024a,b). The PHUs, unless altered by incorporating less polar moieties, such as amide groups, demonstrate considerably more water absorption than PUs, rendering PHUs suitable for use as hydrogels and absorbents (Łukaszewska et al. 2024a,b). The formation of supplementary hydroxyl groups near the urethane moiety leads to a robust interaction between PHUs and organic solvents, resulting in a comparatively high affinity of PHUs for water. Frias et al. (2024) synthesized cross-linked poly(hydroxyurethane) films using bio-based carbon chains of varying lengths in conjunction with hyperbranched poly(ethyleneimine). The PHUs films absorbed moisture (6–8 %), attributed to the presence of –OH groups, leading to a decline in mechanical characteristics that were not fully restored after drying. Zhao et al. (2024) synthesized epoxidized natural rubber (ENR) using the epoxidation of natural rubber (NR). The ENR, silane coupling agent bis(γ-triethoxysilylpropyl) tetrasulfide (TESPT), and silica are combined in varying ratios. ENR/silica-6T exhibits considerable enhancement relative to NR/silica-6T, showing improvements in wet-skid resistance, abrasion resistance, and a decrease in rolling resistance. In NIPUs/POSS physical blends, elevated water absorption appears to be a predominant characteristic of this material. POSS-modified NIPU networks exhibit an enhanced capacity for moisture absorption from the atmosphere, thereby facilitating the water uptake characteristics of hydrogels, even in the absence of immersion in water. The absorbed water induces the breakdown of polymer–polymer and polymer–POSS H-bonds due to the establishment of robust water–polymer interactions, leading to a decrease in Tg values upon hydration (Łukaszewska et al. 2024b). Raftopoulos et al. (2024) investigated water absorption in relation to environmental humidity. They found that nonisocyanate poly(hydroxyurethane) networks exhibit significant hydrophilicity, absorbing up to 65 % of water at 97 % humidity, despite incorporating a hydrophobic primary polymeric component, specifically poly(propylene oxide) diamine. The influence of POSS and the substantial plasticization induced by absorbed water on the $T_g$ and charge mobility. The decrease of $T_g$ transpires through two mechanisms: plasticization and slaving. Plasticization transpires at low to moderate hydration levels, wherein absorbed water enhances the elasticity of the polymer chain. Slaving occurs at elevated hydration levels, where the quantity of absorbed water is sufficient to generate bulk water with distinct dynamics (Łukaszewska et al. 2024b). Cornille et al. (2017b) investigated the influence of protic solvents on the reactivity and conversion of CCs during the aminolysis. It has been discovered that the protic solvent restores mobility to the precursors by restricting the formation of H-bonds, both inter- and intrachain. A highly polar and aprotic solvent demonstrated a somewhat elevated swelling index and solubility compared to conventional solvents such as THF. Consequently, cross-linked materials were produced that exhibited diverse Tg, a minimal soluble fraction, and reduced swelling in THF (Camara et al. 2014). The secondary advantage of the hydroxyl group generated alongside urethane groups during the aminolysis of cyclic carbonates results in enhanced hydrolytic stability of NIPUs compared to typical PUs. The –OH group next to the urethane facilitates both intermolecular hydrogen bonding and intramolecular interactions that safeguard the carbonyl carbon within the urethane group. Consequently, PHUs exhibit enhanced hydrolytic stability compared to traditional PUs (Łukaszewska et al. 2023b).

- Starch-based materials are process-friendly, biocompatible, readily accessible, and capable of biodegrading or composting in many conditions without emitting hazardous substances. Significant limitations of starch-based materials include brittleness and moisture sensitivity, which impede their diverse applications across several industries. Integrating two polymers with distinct chemistries offers advantages in straightforward synthesis and the production of materials with adjustable functional characteristics. Due to its numerous –OH groups in the backbone, starch can be easily combined with other polymers, such as polyurethanes (PUs), to create hybrids with enhanced mechanical and structural properties. Incorporating starch with PUs, aimed at enhancing interfacial adhesion, can result in substantial improvements in the mechanical properties of the resulting materials. The mechanical properties of PUs reinforced with starch are influenced by the inherent properties of both PUs and starch, as well as their interfacial interaction effects (Ghasemlou et al. 2020b).

- NIPUs generally demonstrate enhanced chemical resistance, reduced permeability, superior water absorption, and thermal stability, as well as specific mechanical properties akin to those of standard PUs. NIPUs exhibit insensitivity to ambient moisture, endowing them with numerous possible applications, including chemical-resistant coatings, paints, and sealants (Hebda et al. 2024).
- The urethane linkage with a hydroxyl group in NIPUs is a highly polar entity that substantially impedes the system's capacity to achieve microphase separation while enhancing its thermal stability and hydrophilicity (Eltayeb et al. 2021).
- Polyhedral oligomeric silsesquioxanes (POSS) comprise hybrid (organic/inorganic) compounds often functionalized with reactive or nonreactive substituents. Integrating polyhedral oligomeric silsesquioxanes (POSS) into nonisocyanate polyurethanes (NIPUs) might improve properties such as biocompatibility, flame retardancy, and mechanical strength. The chemical or physical integration of POSS significantly affects the performance of nanocomposites, depending on the type of POSS and the integration technique (Bukowczan et al. 2023; Łukaszewska et al. 2024b). Chemical integration is very efficacious and extensively researched. POSS reduces heat and harmful gas emissions during burning, enhances heat resistance, and reduces flammability in polymers (Bukowczan et al. 2023). The thermal stability of NIPUs is enhanced by the incorporation of carbon nanotubes and particular types of POSS (Bukowczan et al. 2024).
- NIPUs exhibiting ferroelectric characteristics were manufactured by a solvent-free reactive extrusion technique utilizing an aminolysis reaction between resorcinol bis-carbonate and several amines. These materials possess considerable potential for meeting the needs of fundamental networked sensors utilizing low-power communication methods (Sessini et al. 2021).
- The reactive extrusion approach for synthesizing PHUs improves mechanical strength and thermal transport qualities, akin to commercial rigid PU thermoset foam utilized in insulation sectors (Datta Sarma et al. 2024).
- Throughout the thermal deterioration of NIPUs, $CO_2$ is released at every degradation stage, albeit with a reduced generation of $CO_2$ at elevated temperatures. NIPU thermodegradation results in a greater release of $CO_2$ compared to ordinary PUs. This was ascribed to the elevated urethane linkage in NIPUs compared to PUs. The primary breakdown products of urethane groups in NIPUs were ammonia and carbon dioxide. The degradation of both PU and NIPUs resembles the dissipation of urethane groups in the initial degradation phase, producing $CO_2$ and polyols (Bukowczan et al. 2024).

## 3.3 Routes for NIPU synthesis

To avoid the toxicity and high moisture sensitivity of isocyanates in the production of PUs, various researchers are continuously working on alternative methods for isocyanate-free PU synthesis. Four distinct synthetic routes were proposed to resolve the problem of isocyanates. The four most commonly used routes are named aminolysis of CCs via polyaddition of CCs and diamines (Bassam et al. 2013; Camara et al. 2014; Cornille et al. 2017a; Rokicki and Piotrowska 2002) bis-dialkyl carbonate route via polycondensation of linear activated di-carbonates with diamines, transurethanization route via polycondensation of linear activated carbamates and diols (Li et al. 2014), and ring-opening polymerization (ROP) route (Maisonneuve et al. 2015; Sardon et al. 2015; Zhang et al. 2019). Figure 13 illustrates different isocyanate-free PU synthesis methods (Bizet et al. 2020b; Furtwengler and Avérous 2018; Rokicki et al. 2015; Zhang et al. 2019).

### 3.3.1 Aminolysis of CCs (step growth polyaddition)

The polyaddition of bifunctional CCs with primary di- or polyamines, which comprise PHUs with additional primary or secondary –OH groups in the side chain, represents the most extensively studied and optimal synthesis route for producing NIPUs. Drechsel and Groszos initially investigated this method in 1957. The –OH groups can form inter- and intramolecular hydrogen bonds with urethane carbonyl groups. The polyaddition technique also has the advantage of utilizing ecologically acceptable bio-based components and facilitating carbon dioxide fixing. Moreover, synthesis could not be accomplished without catalysts and solvents. This produces improved chemical resistance to organic solvents in the resulting PHUs. Furthermore, PHUs exhibit enhanced thermal stability owing to the absence of labile biurets and thermally unstable allophanate groups. PUs also benefit from their capacity to interact with diverse chemical functional groups, including the –OH groups. Compared to ordinary PUs, literature studies demonstrate contradictory

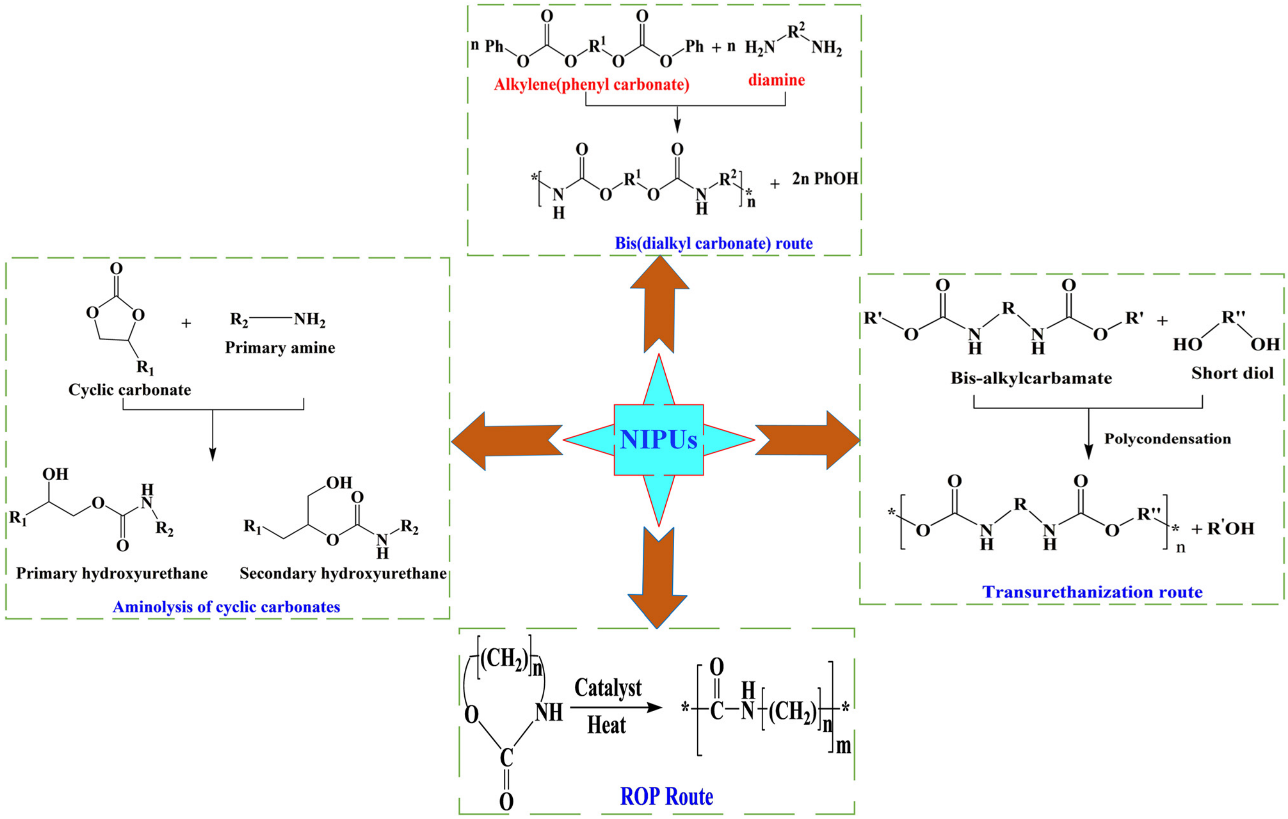


**Figure 13:** Different routes for synthesizing isocyanate-free polyurethanes (Zhang et al. 2019). Modified and reproduced with permission from Zhang et al. (2019), American chemical society.

findings regarding the water absorption of PHU after water exposure (Aristri et al. 2021).

### 3.3.2 Bis-dialkyl carbonate route via polycondensation of linear activated di-carbonates with diamines (polycondensation)

Dyer and Scott conducted the inaugural polycondensation synthesis of NIPUs. The synthesis of NIPUs via polycondensation involves the interaction of di- or polycarbamates with diols, di- or polycarbonates with amino alcohols or diamines, polychloroformate with polyamines, and polycarbamoyl chloride with polyols. This methodology for industrial applications is limited by the formation of byproducts (e.g., $H_2O$, HCl, alcohol). Moreover, the synthesis is generally conducted in solvents, employing catalysts, and under specific reaction circumstances, such as prolonged reaction durations or elevated temperatures, which are economically disadvantageous from an industrial perspective (Aristri et al. 2021).

### 3.3.3 Polycondensation of linear activated carbamates and diols (transurethanization route)

The transurethanization process consists of two stages: the synthesis of urethane monomers (by traditional methods or aminolysis), followed by their reaction with a diol in the presence of an appropriate catalyst to produce the final polymeric materials. Diurethane monomer, utilized as a reactant, can be produced from a reaction between a carbonate and an aliphatic amine in the presence of a base (Carré et al. 2019). D. Wołosz synthesized linear aliphatic and aliphatic–aromatic poly(carbonate-urethane)s. Urethane diols and precursors for hard segments of polyurethanes were utilized. The bis(methyl carbamate)s were synthesized from DMC, and urethane diols were produced through the transurethanization of alkylene or arylene-based carbamates using an excess of pentanediol (Wołosz et al. 2021).

The condensation of alcohol with a carbamate can yield urethanes; this process is called transurethanization or transcarbamoylation. PUs are synthesized using plurifunctional monomers. The byproduct produced is an alcohol, typically characterized by a low molar mass. The PUs synthesized using polycondensation exhibit structures identical to those generated by the polyaddition of polyisocyanates and polyols. Consequently, it is a method for producing NIPUs with properties akin to those of industrial PUs. Phosgene-free carbamate monomers have been produced for this purpose; their condensation with alcohol has been examined, and their polymerization with polyols has been investigated. The transurethanization pathway can be utilized with a range of monomers, encompassing petroleum-derived diols, diamines, and renewable alternatives. Combining monomers utilizing dimethyl or ethylene carbonate is straightforward, environmentally friendly, and readily scalable for industrial use. The polymerization process necessitates the elimination of alcohol, typically methanol, which may pose a challenge for scaling up the process. Furthermore, the polymerization temperatures are elevated, often ranging from 100 to 200 °C, and the use of catalysts is essential. Nonetheless, the PUs derived from this method are comparable to those produced from diisocyanates and diols (Maisonneuve et al. 2015).

#### 3.3.4 Ring-opening polymerization (ROP)

In ring-opening polymerization (ROP), the monomers are predominantly cyclic and often heterocyclic, necessitating an opening of the rings to incorporate the monomers into the growing macromolecules. Nearly all ROP transpires through ionic reactions, as the cleavage of the chemical bond between the heteroatom and carbon atom necessitates groups with significantly different electrical structures. Key monomers encompass cyclic ethers, esters, carbonates, amides, acetals, and cyclic siloxanes. ROP facilitates polymer synthesis with precise control over molar masses, molar mass distributions, and stereoregularity. Despite NIPUs being created without the generation of byproducts, these reactions typically occur at elevated temperatures, and cyclic carbamates are predominantly derived from phosgene. ROP techniques facilitate the synthesis of polysiloxane sealants, silicone rubber substrates and coatings, building supplies, polymers for drug formulation manufacture, temporary degradable implants, and carriers for enzymes, nucleic acids, and other biomolecules. ROP is a well-established domain. Nevertheless, the pursuit of improved catalytic systems and postpolymerization modification of polymers persists. Numerous efforts have been undertaken in ROP to manufacture copolymers with regulated topologies, facilitating the controlled self-assembly of macromolecules into nanomaterials. These serve as nanoreactors or pharmaceutical carriers, facilitating more accurate medication delivery. ROP facilitates the scalable synthesis of degradable aliphatic polyesters, providing a sustainable alternative to traditional plastics (Jérôme and Lecomte 2008; Nakayama et al. 2015; Penczek et al. 2021). D. Zhang documented the synthesis of aliphatic polyurethanes (PUs) with innovative structures via anionic ring-opening polymerization (ROP) of five-membered carbamates (Zhang et al. 2019). A bifunctional starting mechanism was employed for the anionic ring-opening polymerization of cyclic compounds to produce unimodal polymers. Several researchers additionally produced NIPUs utilizing cationic initiators. To create an effective synthesis of PUs, anionic systems proficient in the ring-opening polymerization of lactams may also demonstrate notable efficacy in the ring-opening polymerization of CCs. The anionic technique enables the efficient synthesis of polymers from 5CCs with high yields. ROP offers advantages over traditional synthesis, including enhanced atom economy, less waste, and lower energy use. Nevertheless, it remains significantly underdeveloped owing to the restricted reactivity of the related carbon–carbon monomers.

The most viable and promising user-friendly method is the polyaddition of CC with the amine to synthesize PHUs (Table 1). These differ from commercialized PU structures in their pendant groups, specifically primary and secondary –OH groups attached to the beta carbon of the main chain, as shown in Figure 14 (Shen et al. 2018). These hydroxyl groups enhance water absorption and chemical resistance, as well as improve adhesion through intermolecular hydrogen bonding (Furtwengler and Avérous 2018; Kotanen et al. 2020). However, there are some challenges associated with this route, namely the high temperature required for synthesizing CCs from epoxy and $CO_2$ using a catalyst, and the product obtained has a higher viscosity and is solid at room temperature (Carré et al. 2014). Therefore, higher temperatures and solvents are needed for processing. Another challenge is the reactivity of CCs at room temperature. Additionally, a diffusion problem exists, resulting in only 60–80 % cyclic carbonate conversion (Cornille et al. 2017a,b). Therefore, a high temperature is necessary, but the risk of side reactions, such as amide and urea formation, has increased (Kotanen et al. 2020).

Cornille et al. (2017a,b) studied the impact of substituents attached to 5- and 6-membered CCs on the aminolysis reaction at room temperature. The kinetic study revealed a partial conversion of CCs in the aminolysis reaction due to the formation of inter- and intrahydrogen bonding, which limits the diffusivity of species in the polymerization process. This study concludes that using a protic solvent enhances the reactivity of CCs, thereby increasing conversion during the aminolysis reaction. As a result, the protic solvent increases the mobility of the precursors by limiting the formation of inter- and intrachain hydrogen

Table 1: Aminolysis of monocyclic carbonate with different types of amines and methods of synthesis.

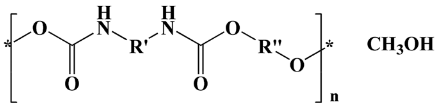
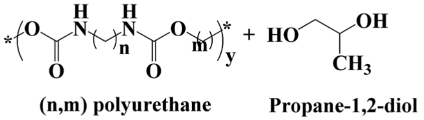
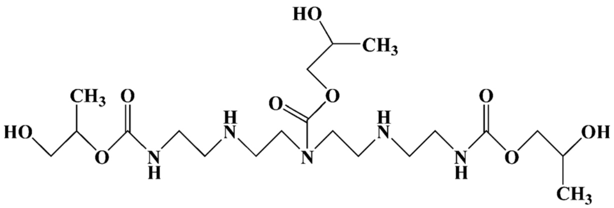
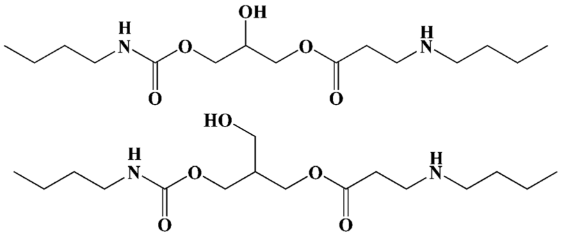
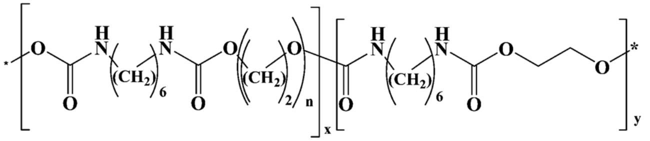
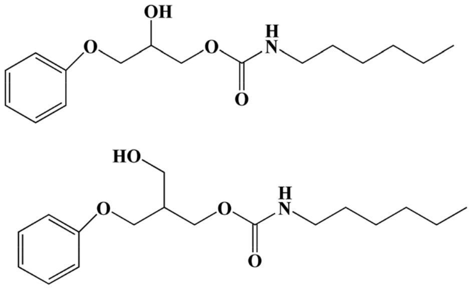
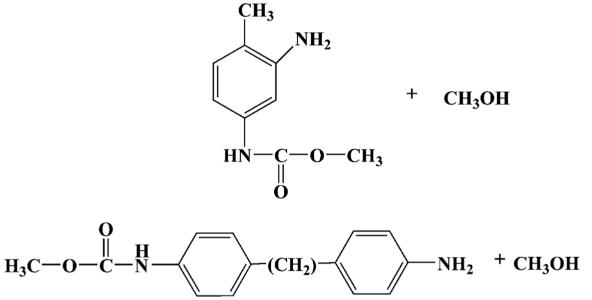
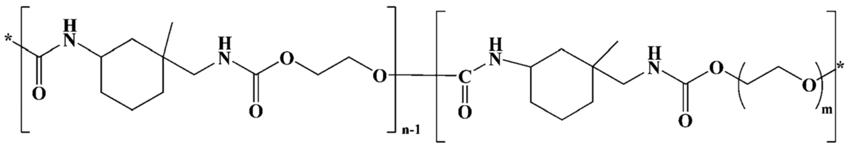
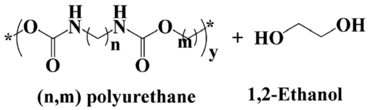
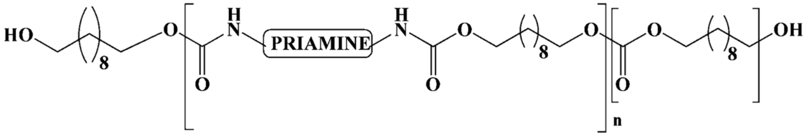
| Carbonates | Amines | Synthesis method | Reaction parameters | Mn (g mol$^{-1}$) | Products | References |
|---|---|---|---|---|---|---|
| Dimethyl carbamate (DMC) | HDA | Aminolysis, polycondensation | Aminolysis: Na-MCM-41 (0.05 wt%), >93 °C; polycondensation: $Bu_2SnO$ (0.125 wt%), HDC: PCDL = 1:0.99, 100 °C, 1 h and 185 °C, 4 h, high vacuum | 58,000–79,000 |  | Dongdong and Hengshui (2015) |
| Ethylene carbonate (EC) | 1,4 or 1,6-HDA,<br>3-amino-1-propanol | Aminolysis and transurethanization | Aminolysis: $CHCl_3$, RT, 6 h; polycondensation: catalyst: $Bu_2SnO/Bu_2Sn(OCH_3)_2$; solvent: xylene, 145–150 °C, 6 h, reduced pressure | 3,500 |  | Rokicki and Piotrowska (2002) |
| Propylene carbonate (PC) | TEPA, DMHDA | Aminolysis | Aminolysis: RT or 80 °C, 16 h | – |  | Camara et al. (2014) |
| Glycerol carbonate (GC) | TEA | Aza-Michael and aminolysis | DCM, acrylol chloride, $N_2$ ice; 1 h and RT for 90 min; TEA, 50 °C, 2 h; TEA, 80 °C, 2 h | – |  | Bassam et al. (2013) |
| BHCH obtained from EC | 1,6-Hexane diamine | Transurethanization | Melt transurethanization: BHCH:EG = 5:1, $SnCl_2$ (0.23 mol%), 170 °C, 2 h under $N_2$ flow, 4 h, 30 mm Hg reduced pressure | <54,300 |  | Deng et al. (2014) |

**Table 1:** (continued)

| Carbonates | Amines | Synthesis method | Reaction parameters | Mn (g mol$^{-1}$) | Products | References |
|---|---|---|---|---|---|---|
| R-substituted ethylene carbonate (R-PhOCH$_2$) | N-Hexylamine | Aminolysis | Aminolysis: 70 °C, 30 d; conversion: 99 %; solvent: toluene | – |  | Tomita et al. (2001) |
| Dimethyl carbamate (DMC) | R–NH$_2$, R–C$_3$H$_7$, C$_4$H$_9$, C$_6$H$_{13}$) | Aminolysis | Aminolysis: zinc carboxylates, 453 K, 2 h; conversion: 100 % of TDA and MDA; yield: 92–98 % | – |  | Baba et al. (2002) |
| Ethylene carbonate (EC) | IPDA | Aminolysis, polycondensation | Aminolysis: 100 °C, 7 h, N$_2$; polycondensation: SnCl$_2$, 170 °C, 30 mm Hg reduced pressure, PEG | 18,400–126,000 |  | Li et al. (2015) |
| Ethylene carbonate (EC) | 1,6-Hexane diamines | Aminolysis, polycondensation | Aminolysis: 100 °C, 6 h; polycondensation: PPG-BAPE, N$_2$, reduced pressure, 170 °C | 8,400, 16,700 |  | Ban et al. (2019) |
| Ethylene carbonate (EC) | PRIAMINE 1075 | Aminolysis, polycondensation | Aminolysis: 80 °C, 3 h; yield: 98 %; transurethanization; titanium (IV) butoxide (0.124 wt%), N$_2$, 6 h, 180 and 4 h, 200 | 8,800–43,100 |  | Wołosz and Parzuchowski (2022) |

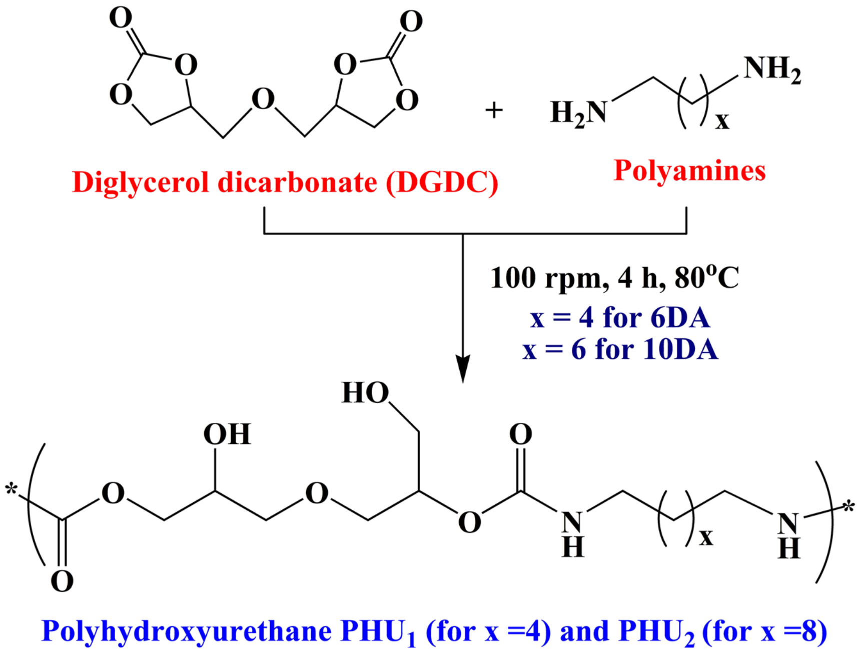


**Figure 14:** Synthesis of PHUs from DGDC polyamine via aminolysis of cyclic carbonates (Magliozzi et al. 2019). Modified and reproduced with permission from Magliozzi et al. (2019), American chemical society.

bonds. Hence, a protic solvent is used to solve the aminolysis of CCs and enhance the conversion during PHUs synthesis. High temperatures for the aminolysis of 5CCs with ester functions lead to side reactions, including urea formation, dehydration, and amidification (Cornille et al. 2017b). Sharan et al. (2024) synthesized di-hydroxy terminated dicarbamate/hydroxyurethanes (HUs) via aminolysis of PC with five different types of amines, including HDA, IPDA, DETA, TETA, and TEPA, in the presence of both protic solvent (methanol) and aprotic solvent (DMSO). A protic solvent (methanol) enhances the reactivity of PC and facilitates its complete conversion at an 80 °C temperature. Protic solvent (methanol) has greater potential to enhance the reactivity of PC with HDA in comparison to aprotic solvent (DMSO) and with different catalysts like TBAB, LiCl, LiF, DBTDL, and TEA.

A novel method of producing PHUs by reactive extrusion from the aminolysis of CC has been introduced. Reactive extrusion was used to synthesize PHUs from various bio-based activated and nonactivated BCCs (bi-cyclic carbonates), DGDC (diglycerol decarbonate), and Und-6DA-bisCC. Reactive extrusion offers several benefits, including rapid synthesis times, minimal heating requirements, solvent-free synthesis, and the prevention of byproduct formation. The PU was synthesized using reactive extrusion and then compared to PHUs obtained via bulk polymerization through aspects of kinetics, molar masses, and side reactions. DGDC was prepared using diglycerol with a 40 % yield and produced in a single step. Additionally, BCC-ester was synthesized from glycerol carbonate and triethylamine diluted in dimethyl carbonate (DMC). These carbonates were then used for the synthesis of NIPUs via the reactive extrusion process. The obtained NIPU was characterized by $^{1}$H NMR and SEC (size-exclusion chromatography). The molecular weight of NIPUs obtained from reactive extrusion was high even at the same reaction time and temperature conditions. The aminolysis of the CC reaction scheme is shown in Figure 14 (Magliozzi et al. 2019). Shen et al. (2018) reported a study of the synthesis of nonisocyanate polycarbonate urethanes (NIPCUs) via an environment-friendly route from DMC, hexane diol (HDO), and HDA. Bis-1,6-hexamethylencarbamate) (BHC) was produced from excess DMC and diamine. Herein, a new route for PU synthesis was suggested, named “hard segment first.” In this route, polyurethane diols (PUDLs) were prepared first from HDO and BHC, and then PUDL was synthesized from DMC and HDO. The polycondensation reaction between polyurethane diol (PUDL) and polycarbonate macrodiol (PCDL) resulted in polycarbonate urethane (PCU) formation with the continuous removal of short diol. It was characterized with GPC (gel permeation chromatography), FTIR, $^{1}$H NMR, $^{13}$C NMR, DSC, WAXD, TGA, and tensile test. Figure 15 shows the synthesis of PHCUs from the polycondensation of PCDL and PUDL. According to the results, the PCUs obtained had a linear structure and a molecular weight of 60,000 g/mol. Deng et al. (2014) developed an isocyanate-free method for producing aliphatic thermoplastic PUs with excellent mechanical and thermal properties. Transurethane polycondensation of BHC with two different ethylene glycol oligomers, trimethylene glycol, and tetramethylene glycol resulted in high molecular weight PEUs. The obtained

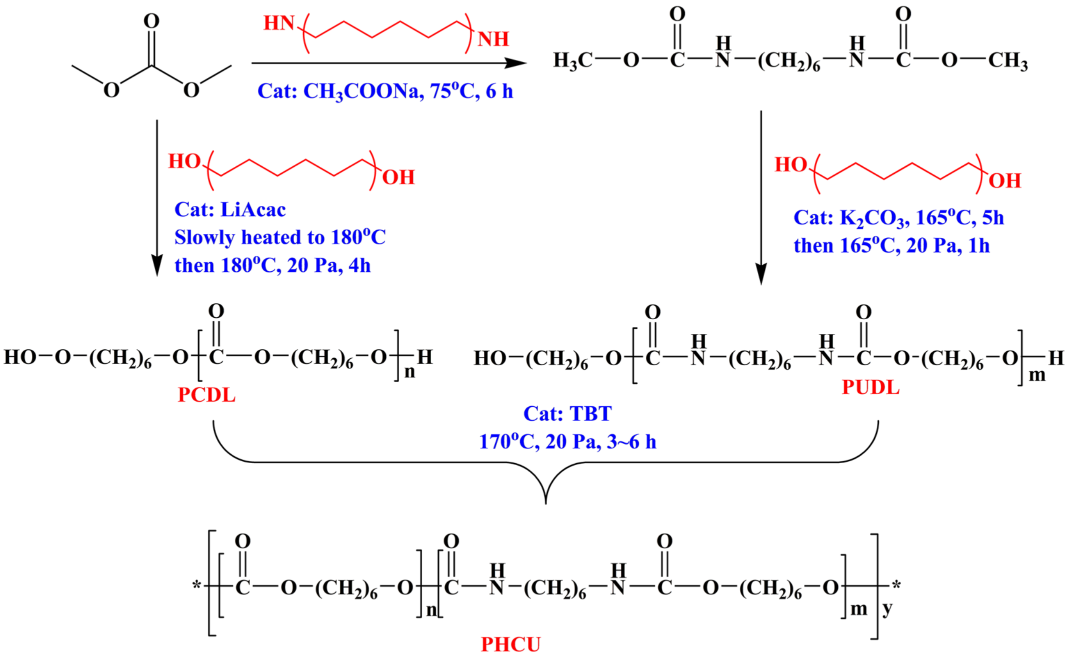


**Figure 15:** The synthesis of PHCUs from the polycondensations of PCDL and PUDL (Shen et al. 2018). Modified and reproduced with permission from Shen et al. (2018), Elsevier.

product was characterized using FTIR, $^1$H NMR, GPC, TGA, DSC, wide angle X-ray diffraction (WXRD), and tensile testing (Deng et al. 2014).

Researchers have described numerous synthetic pathways, including transurethanization, azide condensation, and aminolysis/polyaddition of CCs and polyamines. The aminolysis technique has been the most advantageous and has garnered the most attention in the last decade (Ecochard and Caillol 2020).

## 3.4 Cyclic carbonates (CCs) used for the synthesis of NIPUs

CCs and BCCs, which are essentially nontoxic, were utilized to produce NIPUs, which are widely used in optical equipment, adhesives (Kotanen et al. 2021; Manock 2000), coatings (Driest et al. 2020; Günther et al. 2020), biomedical applications (Pyo et al. 2012; Shen et al. 2018), and other industrial tools. However, commercially available PUs are synthesized from isocyanates produced through toxic and hazardous reactions involving phosgene and amines (Pyo et al. 2012). The CCs are synthesized using various methods, including fixing $CO_2$ into glycidyl ethers, esterifying dicarboxylic acids with glycerol carbonate, and thiolene click reaction between thiols and unsaturated CCs. The reaction between $CO_2$ and epoxy compounds is the most promising route. This route's drawbacks include high temperatures and pressures, extended reaction times, and typically complicated catalysts for complete conversion rates. Due to the high cost and limited commercial preference of this route, further research is needed to reduce the cost, increase yield, and make the process more industrially advantageous (Eltayeb et al. 2021).

$CO_2$ is the most abundant primary greenhouse gas and the most cost-effective feedstock for producing fine chemicals, pharmaceuticals, and polymeric materials. It is also nontoxic in nature. Coupling $CO_2$ with epoxides to yield CCs is one of the most effective approaches for converting $CO_2$ into value-added chemical feedstocks (Yang et al. 2021). The cycloaddition of $CO_2$ with epoxides to convert them into carbonates requires a catalyst to activate the $CO_2$ molecules. Several heterogeneous catalysts are used in the cycloaddition process to yield the CCs, including metal oxides, microporous polymers, triazine polymeric catalytic systems, and silica-supported salts. Developing a heterogeneous catalyst that utilizes functional groups for the cycloaddition of $CO_2$ and epoxides and has high regeneration capability is the most promising approach. The most interesting thing is that the catalyst is not found in the structure of the PUs. The catalyst is removed and regenerated after every reaction from the PUs. The surface of the heterogeneous catalyst has basic and hydrogen bonding sites that are useful for the cycloaddition of $CO_2$ and epoxides (Verma et al. 2017). Ke et al. (2016) synthesized 5CCs as a $CO_2$-derived monomer through a cycloaddition reaction between $CO_2$ and PPGDE (polypropylene glycol diglycidyl ether) at 120 °C under 10 bar $CO_2$ pressure, using an Amberlyst catalyst (Ke et al. 2016). Verma et al. (2018) produced a bi-functional monometallic iron(III) heterogeneous complex immobilized on polystyrene resin and utilized in a cycloaddition reaction between epoxides and $CO_2$. Both aliphatic and aromatic CCs are produced under mild conditions with high selectivity without cocatalysts. The recyclability of the catalyst was four times without any effect on the selectivity and activity. Furthermore, the obtained CC was used in the synthesis of NIPUs (Verma et al. 2018).

Different types of CCs have been synthesized, among which 5-, 6-, and 7-membered CCs are more attractive than the others. Although 6- and 7-membered CCs showed higher reactivity toward amines, they required harmful reagents and their derivatives for the synthesis. The less reactive 5-membered CCs were synthesized through the most promising approach, the carbonation of epoxides with $CO_2$. To improve the reactivity of the 5CCs, various reaction parameters have been considered, including reaction temperature, types of reaction solvents, and monomer concentrations. Some researchers have attempted to optimize the structure of 5CCs, discovering that electron-withdrawing groups attached to the carbonate rings facilitate the ring opening of the CCs. A study also found an inverse relationship between 5CC's reactivity toward aminolysis and the distance of electron-withdrawing groups from the cyclic carbonate ring (Cornille et al. 2017b; Xu et al. 2021).

As a primary energy source, fossil fuels are limited and emit $CO_2$ as a byproduct. The release of $CO_2$ into the atmosphere is a primary contributor to global warming. Researchers have been working on alternative energy resources and have developed techniques for the chemical utilization of $CO_2$ from power plants for many years. Carbon capture and storage from fossil fuel–based power plants is a demanding yet beneficial strategy for reducing $CO_2$ emissions by utilizing it to produce commercially important industrial products under mild reaction conditions. However, due to the lower reactivity of $CO_2$, some feasible processes are employed to recover and utilize $CO_2$ as a sustainable resource (North et al. 2010). For the synthetic production of useful industrial chemical products, approximately 110 million tons of $CO_2$ are utilized per year, which is less than 1 % of global emissions. The highest use of $CO_2$ is in urea synthesis, at a rate of up to 90 Mt per year, a process that has been commercially viable since 1922. Other important applications of $CO_2$ include its use in the production of salicylic acid, as a refrigerant, in fire extinguishers, as a supercritical solvent, and as an extracting medium, all of which have negligible impacts on reducing $CO_2$ release. Therefore, another use of it is in producing beneficial chemicals according to industry demand, helping to increase $CO_2$ consumption (North et al. 2010).

In fine chemistry, glycerol carbonate has much potential for transformation. It has recently been introduced as a surfactant component, a nonvolatile reactive solvent for various materials such as coatings, paints, and detergents, as well as a component of polymeric materials, including polycarbonates and PU (Bassam et al. 2013).

Due to the scarcity of crude oil resources, many researchers have investigated using greener bio-based raw resources such as lignin, turpentine, cellulose, and vegetable oil as alternatives to petrochemical-based raw materials. The potential of using bio-based raw materials in synthesizing bio-derived carbonaceous materials (CCs) has been confirmed by several researchers, who have developed effective methods to produce a variety of bio-based CCs from various naturally occurring resources. Due to its benefits of being renewable, nontoxic, inexpensive, and widely available, soybean oil is the most promising alternative. In this experiment, he created CCs using soybean oil and then incorporated them into NIPUs (Yang et al. 2021).

Schimpf et al. (2017) prepared thermoset and thermoplastic types, as well as linear and crosslinked NIPU, from a highly pure and renewable resource, limonene dicarbonate, which was obtained through oxidation and catalytic carbonation of limonene (derived from orange peels). The thermoplastic linear NIPUs were obtained from the polyaddition of diamine-terminated limonene carbonate (LC) prepolymer with BDGC (bis-diglycerol carbonate). An increase in the LC content in the prepolymer mixture results in a decrease in the molar mass due to the occurrence of the side reaction. The 100 % thermoset NIPUs with unconventional property profiles were prepared by curing carbonated pentaerythritol glycidyl ether with LC and 1,5-diaminopentane, obtained from lysine. Incorporating a small amount of LC improved NIPU's stiffness, glass transition temperature, and strength and helped prevent color formation in the LC-based NIPU coatings.

Huang et al. (2016) synthesized 4-isopropenyl phenol from bisphenol A, which was then esterified with epichlorohydrin to form the phenolic group and converted into IPGE (4-isopropenyl phenyl glycidyl ether). IPGE reacts with $CO_2$ in the vicinity of TBAB to form IPPC with a yield of 90 %. The obtained product is then converted into the poly(IPPC) by cationic polymerization in the presence of strong acids such as TFMS acid (trifluoromethanesulfonic acid) or BTFDEE (boron trifluoride diethyl etherate) as a catalyst at 40 °C. The linear poly(isopropenylphenoxy propylene carbonate) (poly(IPPC)) with carbonate groups was uniformly distributed in the polymer's backbone. In the presence of NMP as a crosslinking agent, the poly(IPPC) CC groups reacted with various polyamines to form hydroxyurethane. TGA, FTIR, GPC, and other techniques were used to characterize the hydroxyurethane and poly(IPPC) products.

Verma et al. (2017) created cyanuric urea polymer (CUP), a nitrogen-rich organo-catalyst used for the cycloaddition of $CO_2$ and epoxides. Cyanuric chloride and urea react at 140 °C and are mixed to produce a cross-linked CUP catalyst. The C–Cl bond in the cyanuric chloride is very active and is substituted by nucleophiles in a single-step reaction. It is heterogeneous and insoluble in a high-temperature solvent like DMF and DMSO. The prepared catalyst was characterized using FTIR, EDX, SEM, XRD, TEM, $N_2$ adsorption, and $CO_2$/TPD (temperature-programmed desorption), as well as 13C/15 N cross polarization/magic angle spinning nuclear magnetic resonance (CP MAS NMR), among other techniques. The prepared CUP catalyst is used in the production of various types of CCs, and these CCs are then used in the synthesis of PUs, as shown in Figure 16. The CCs and diamines react in a 5 mL test tube with 2 mL of DMSO solvent at 85 °C temperature under an air atmosphere for an 8-h reaction. The resulting mixture is treated with ether, and the remaining insoluble material is solubilized in DMSO and precipitated with water. The derived material obtained after filtration is characterized using techniques such as NMR, GPC, and FTIR.

## 3.5 Catalyst used for amine/cyclic carbonates reaction system

Due to the poor reactivity of 5CCs, synthesized PHUs require high temperatures and long reaction times to achieve moderate molecular weights, which limits their use as prepolymers. Therefore, appropriate catalysts represent another viable route for activating the ring opening of CCs during aminolysis. Different types of catalysts are used to accelerate the polymerization reaction of CCs and amines, producing PHUs of higher molecular weights. In the amines and carbonates reaction systems, several Bronsted acids, organic bases, alkali metal salts, and organometallic catalysts have been synthesized (Lambeth and Henderson 2013). The metal-free catalyst has advantages over the metal-based catalyst, as it can reduce the toxicity of the product and lower its insulation capability. This is achieved by using various organo-catalysts to increase the reaction rate, lower cure times, and enhance the molecular weights of PHUs (Xu et al. 2021). TBD (1,5,7-triazabicyclo[4.4. 0]dec-5-ene) is the most effective catalysts compared to the others (TEA, thiourea, DBU (1,8-diazabicyclo[5.4.0]undec-7-ene)) because of its dual functional action. The polymers synthesized from 5CC and amines had a higher molecular weight than those without the catalyst at room temperature and 80 °C (Lambeth and Henderson 2013).

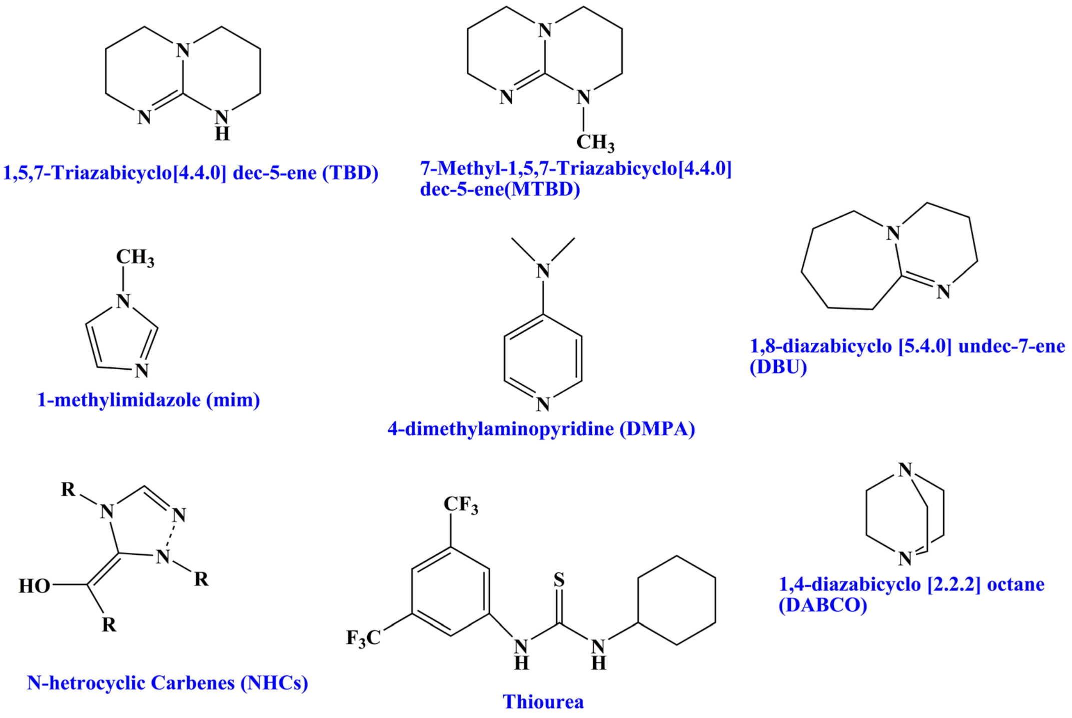


**Figure 16:** Various types of catalysts screened for aminolysis of cyclic carbonates (Blain et al. 2014; Helou et al. 2010; Simón and Goodman 2007).

Ochiai and Endo (2005) investigated various metal and ammonium salts and found that LiBr was the most effective catalyst, increasing the moderate reaction rate. Polymerizations, as well as transesterifications, can be catalyzed by organo-catalysts via a variety of reaction mechanisms. For the ROP of many monomers using a nucleophilic mechanism, N-heterocyclic carbenes (NHCs) of the Lewis base type are particularly efficient catalysts. However, the NHCs are challenging to handle and store due to their extreme air sensitivity. Supramolecular catalysts, such as thioureas, are another type of catalyst that operates through two distinct activation mechanisms. The nucleophilic initiating and propagating species are activated by hydrogen bond–accepting amines, while the electrophilic monomer is activated by the hydrogen bond donated by thiourea. Superbases like DBU, mTBD (7-methyl-1,5,7-triazabicyclo [4,40]dec-5-ene), and TBD are also potent catalysts for the ROP of CCs in the presence of amines. TBD promotes the polymerization of a wide range of monomers, notably those with low ring strain or steric bulk, and exhibits bifunctional activity for both initiating and propagating species and monomers (Lambeth and Henderson 2013). TBD and thiourea were reported to be the most effective catalysts in the literature for producing NIPU from amines and CCs (Blain et al. 2016).

Xu et al. (2021) used commercially available organic bases for catalysis of 1,6-HAD and 5CCs ring-opening reactions, like TEA, DMPA, DABCO (1,4-diazabicyclo[2. 2. 2] octane), 1-methylimidazole, thiourea, DBU, and TBD. They used a model reaction and organic bases and ranked them based on the catalysis of CC ring opening. The kinetic results showed that the TBD catalyst was the best. The TBD catalyst reaction rate constant for the ring opening of CCs was 100 times greater than the rate constants without the catalyst. The polymerization of 5CCs and 1,6-HDA in the presence of a catalyst and a promoter can reach nearly 100 % conversion at room temperature (RT) in less than 4 h. Figure 16 depicts the structures of various types of catalysts used to synthesize NIPUs (Blain et al. 2014; Helou et al. 2010; Simón and Goodman 2007).

## 3.6 Polyhydroxyurethanes (PHUs)

Recently, there has been intense research on the development of NIPUs from the CCs and polyamines to produce PHUs, see Figure 14 (Bizet et al. 2020b; Furtwengler and Avérous 2018; Rokicki et al. 2015; Zhang et al. 2019). Recently, the terms HUM (hydroxy urethane modifier) and H-NIPUs (hybrid nonisocyanate polyurethanes) have been introduced in the literature to denote monomers and copolymers of NIPUs combined with other polymers, such as polyacrylates or polyepoxides. Few recent reviews represent the current state of the art in the reaction between CCs and amines, which represents an alternative to conventional PU synthesis (Cornille et al. 2017a,b; Habets et al. 2025; Suryawanshi et al. 2019).

NIPUs are synthesized by aminolysis reaction between the mono/polycyclic carbonates and aliphatic/aromatic polyamines, resulting in the formation of urethane linkage and –OH groups in the backbone of the structure, which is named PHUs (Ecochard and Caillol 2020). The additional –OH groups formed near the urethane linkage in the backbone of the PU structure, via the ring opening of CCs, have the potential for further functionalization (Chai et al. 2018). Besides this, there are some disadvantages to this reaction. First is the lower reactivity of CCs, and second is the lower molecular weight of products. NIPUs were synthesized by aminolysis reaction using mono-cyclic carbonates, bis or polycyclic carbonates, and aliphatic/aromatic polyamines with or without catalysts and solvents (Cornille et al. 2017a).

Polyhydroxyurethanes (PHUs), a notable category of NIPUs, possess pendant hydroxyl groups inside their polymer backbone, which not only enable additional chemical modification but also markedly improve intermolecular hydrogen bonding (MacInnis et al. 2022). These interactions yield materials with exceptional mechanical strength, improved heat and chemical resistance, and outstanding adhesive properties. The robust hydrogen bonding capability of PHUs, combined with the exclusion of undesired side groups like biuret and allophanate units, results in materials that are more stable and durable. Furthermore, PHUs can be efficiently combined with hydrophilic biopolymers, such as starch, thereby broadening their applicability in areas including biomedical devices, wound care products, and sustainable food packaging. Conventional polyurethanes (PUs), despite their widespread application, generally exhibit weak intermolecular interactions and limited recyclability. NIPUs provide a framework for entirely recyclable and reprocessable materials, effectively aligning with sustainability and environmental objectives (Delavarde et al. 2024).

### 3.6.1 Hybrid polyhydroxyurethanes (H-PHUs)

The production of hybrid PHUs can also overcome the limitation of synthesizing PHUs, a new way to synthesize NIPUs, i.e., H-NIPUs. The incorporation of several crosslinking agents, including epoxy, acrylates, methacrylates, siloxane, and starch, enhances the characteristics and structure of NIPUs. All moieties within the structure are connected by covalent bonds, forming a blended network. The different types of H-NIPUs were synthesized using copolymerization, prepolymerization, and organic/inorganic hybrid PHUs (Ecochard and Caillol 2020).

#### 3.6.1.1 Copolymerization process

In the copolymerization process, the hybrid PHUs were synthesized in a single step by simply mixing the reactants (CCs, amines, and amine-reactive moieties) (Ecochard and Caillol 2020). The products obtained were higher in molar mass, exhibited a blended network, and showed improved physicochemical and mechanical properties (He et al. 2017).

Kotanen et al. (2020) prepared a diisocyanate-based CC-terminated prepolymer and further aminolysed it with different types of polyamines, including polyethyleneimine, dimer diamine, polyether amine, IPDA, TEA, and aromatic amines (Figure 17). A bismuth-based catalyst weighing 0.01 % was used to prepare isocyanate-terminated polyurethane prepolymer from glycerol carbonate with different types of diisocyanates, including TDI, IPDI, and HDI. The reaction mixture was heated at 80 °C with continuous stirring at 200 rpm. Further, the CC-terminated prepolymer reacts with polyamines to form a PU/PHUs hybrid material. The prepared hybrid PU/PHU material was characterized using FTIR, lap shear test, gel content, and tensile test. The secondary amines in the PEI (polyethyleneimine) and TETA (triethylenetetramine) used for synthesis help increase the catalytic activity. The prepared hybrid material, obtained from an HDI-based CC-terminated prepolymer with PEI amine, showed higher lap shear strength. This superior performance is attributed to the high NCO content, shorter backbone length, and strong hydrogen bonding from the polyamine PU, PHU, and –NH groups. This work presents a combination of isocyanate and nonisocyanate-based techniques for synthesizing hybrid PUs. The material obtained was superior in characteristics and comparable with commercialized PUs.

#### 3.6.1.2 Prepolymerization process

In the prepolymerization process, prepolymers were synthesized with oligomers in a controlled position and some reactive functionalities. Further, these functionalities react with other moieties or crosslinking agents. Amine-terminated prepolymers may be prepared and reacted with epoxy/PHUs (He et al. 2017; Ke et al. 2016). The merging of epoxy and PU chemistries investigates new materials with potentially unique and improved properties. Incorporating Michael's addition with PHU chemistry also produces hybrid PHUs. The PHUs have been successfully discovered as

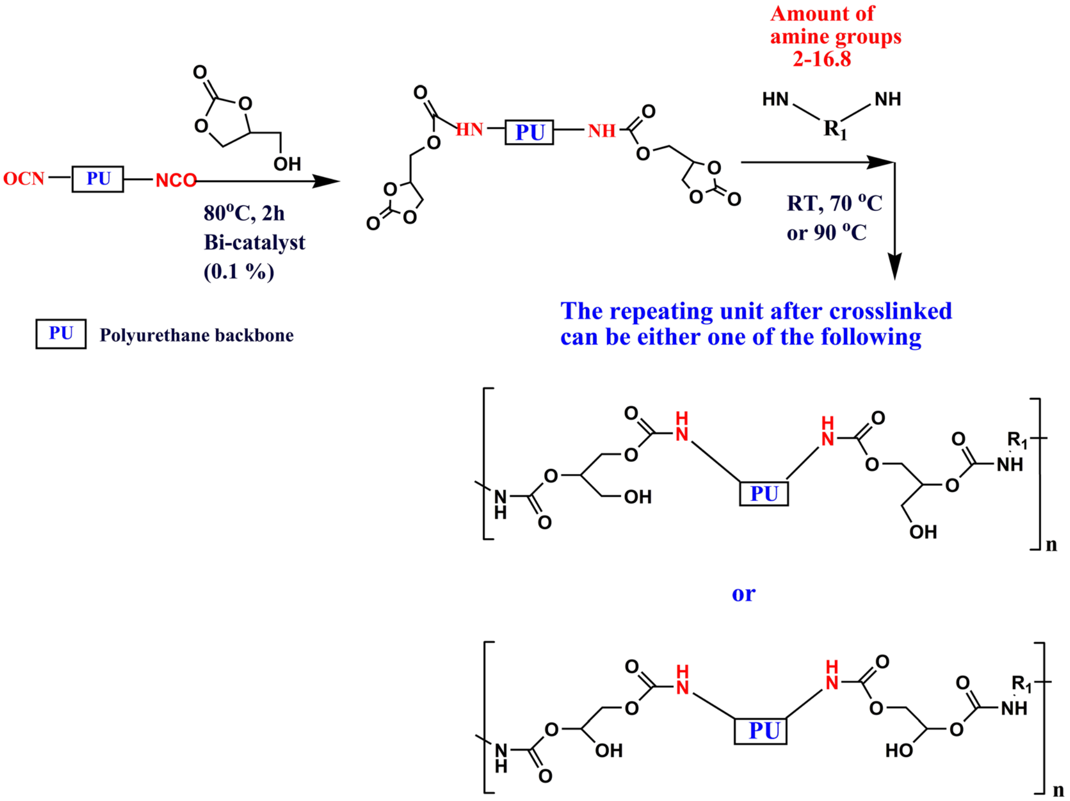


Figure 17: Synthesis scheme for PU/PHU hybrid material showing two possible outcomes of the polyaddition reaction of CCs terminated prepolymer with polyamines (Kotanen et al. 2020). Modified and reproduced with permission from Kotanen et al. (2020), Elsevier.

adhesives and are significant in numerous automotive, aerospace, and military applications. Epoxies and PUs have been commonly used as adhesives in various applications due to their ability to bond a broad range of materials. Such reaction chemistries could be combined to create innovative adhesive materials that could potentially have better qualities than materials now on the market. He had developed several hybrid epoxy-polyhydroxy urethane network polymers in this particular effort. To get polymer networks with high modulus and glass transition temperatures, 4,4′-methylene bis (cyclohexylamine) was utilized as an amine curative. In this case, curing was chosen over mixing CC, epoxy, and PACM in a single pot (Lambeth and Rizvi 2019).

Ke et al. (2016) produced $CO_2$-based 5CC from PPGDE in the presence of an Amberlyst catalyst at a 120 °C temperature and 10 bar pressure. Excess amines were used to react with 5CCs to synthesize amine-terminated prepolymers. Finally, BADGE and these prepolymers interacted to create hybrid PHU materials. FTIR, DMTA (dynamic mechanical and thermal analysis), TGA, and the solvent swelling test were used to examine the effects of various amine types and BADGE (bisphenol A diglycidyl ether) composition on the characteristics of PHUs. Using BADGE as a chain extender improves the thermo-mechanical properties of PHU materials and increases the gelation rate.

The NIPU hybrid material was synthesized by ring-opening CCs with excess amine and methanol as a solvent. Methanol was utilized as a solvent to enhance the molar mass of the $NH_2$-terminated prepolymer while decreasing the hydrogen bonding due to urea formation in the NIPUs chain. By changing the mode of reactant and methanol introduction, the performance of the hybrid materials improved, with higher tensile strength (10.8 MPa), glass transition temperature (49.1 °C), higher crosslinking density (450 mol $m^{-3}$), elongation at break (167 %), thermodynamic stability, etc. The use of BADGE as a crosslinking agent in the prepolymer helped to obtain a higher molar mass for the NIPUs prepolymer and a more extensive crosslinking network (Ke et al. 2016).

#### 3.6.1.3 Organic/inorganic hybrid PHUs

In this third type of PHUs, the alkenes group (including acrylates, methacrylates, and vinyl) undergoes polymerization to produce prepolymers, which are further polymerized with amine-reactive groups (Capar et al. 2020; Ecochard and Caillol 2020).

A couple of the most popular polymeric binders used in aqueous coating systems are polyacrylate (PA) and PUs. Early attempts at PUs/PA hybrids employed physical blending; however, the PA and PUs polymers tend to phase separately throughout the film synthesis. PA has better weathering properties, water and chemical resistance, and hardness, and it is less expensive, whereas PUs have better elasticity, flexibility, toughness, and scratch resistance (Morales-Cerrada et al. 2021). Recently, a nonisocyanate method was used to produce reactive urethane dimethacrylates, which were then incorporated into UV-curable urethane coatings (Wang and Soucek 2013). PUs' acrylate systems, containing acrylate-terminated resins, are frequently used to create coatings. The coating exhibits excellent mechanical characteristics and superior chemical and abrasion resistance (Boisaubert et al. 2020a,b). Wang and Soucek (2013) produced urethane mono-methacrylates without isocyanates in a semi-batch monomer-starved emulsion polymerization. Then, they copolymerized it with methyl methacrylate and butyl acrylate. They have researched the impact of urethane monomers on the kinetics of polymerization, the minimum temperature at which a film can form, and the thermal, tensile, and visco-elastic properties of the resulting films. Boisaubert et al. (2020a) created acrylate-ended NIPUs oligomers by trans urethane polycondensation of dialkyl dicarbamates with a diol, preceded by acrylation with acryloyl chloride. These oligomers were photo-crosslinked using a 1:1 M mixture of BAPO (phenyl bis (acyl) phosphine oxide)–TPOL (diphenyl(acyl) phosphine oxide) photo-initiator and UV radiation to produce NIPU acrylate coatings (Figure 18). In other work, NIPUs' acrylate coatings were synthesized by photo-crosslinking a mixture of an acrylate oligomer and reactive (meth-)acrylate diluents (Boisaubert et al. 2020a). Methacrylic copolymers synthesized with carbonate groups using butyl acrylate (BA), methyl methacrylate (MMA), and glycerol carbonate methacrylate (GCMA) are used to obtain crosslinked polymers. Furthermore, this copolymer reacts with triethylamine to produce hydroxyurethane acrylate (PHUA). The crosslinked PHUA copolymers obtained were used to coat steel and glass, and their adhesion was characterized through adhesion tests (Morales-Cerrada et al. 2021).

Due to its dual rich sites, glycerol carbonate acrylate (GCA), glycerol carbonate methyl acrylate (GCMA), or glycerol carbonate vinyl ether (GCVE) have drawn interest from the PUs industry. The aminolysis of GCA with aliphatic amines forms the NIPUs acrylate coating (Bassam et al. 2013). The production of methacrylic WPUDs was disclosed by Bizet et al. (2020b) without using VOCs. The PHUs were created by bulk polymerizing CC derivatives with diamines (derived from vegetable oils) and then dissolved in methacrylate monomers. The monomers were combined with water to form a mini-emulsion, which was then polymerized. The generated dispersion was used to obtain PHU methacrylic hybrid coatings with various mechanical

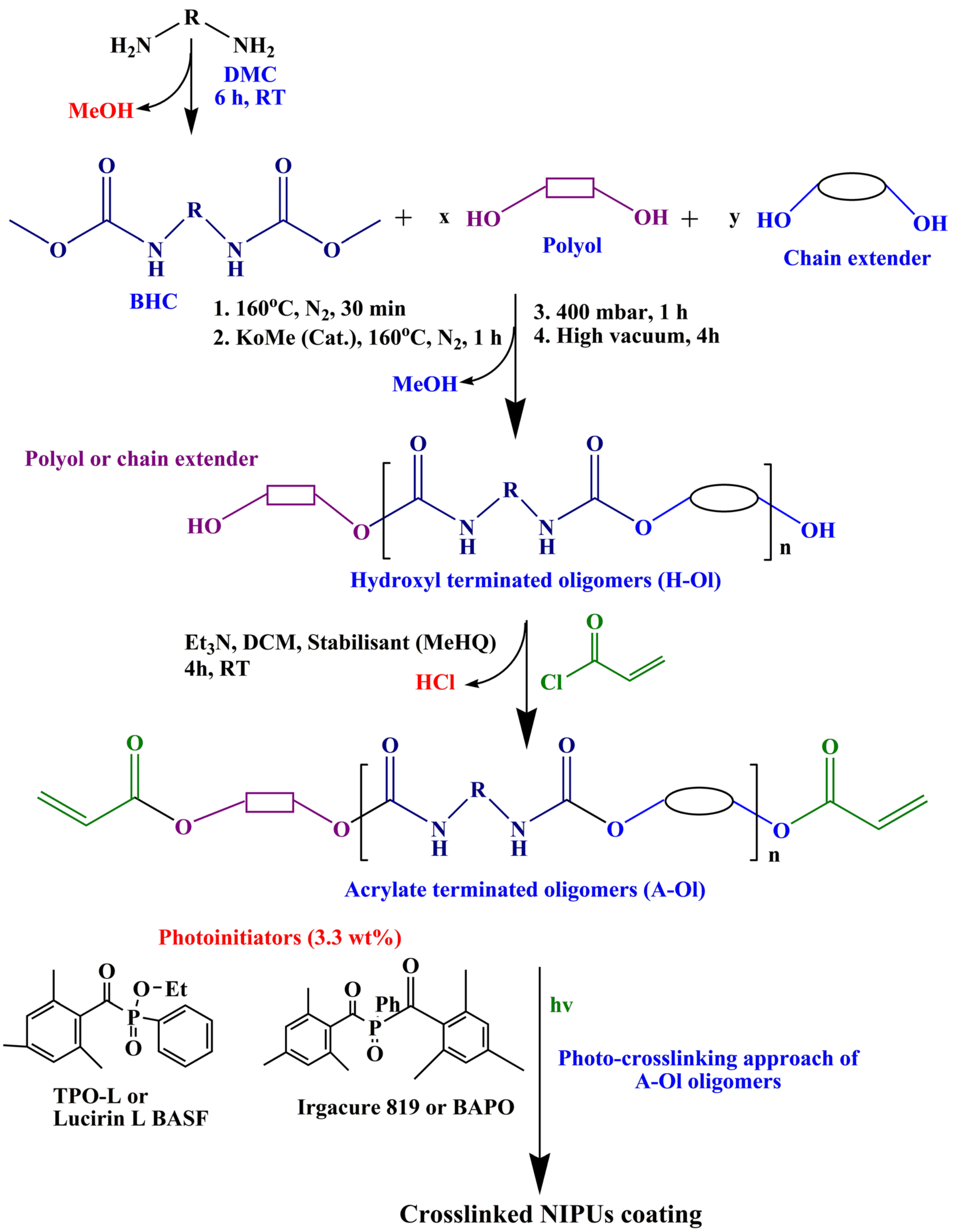


**Figure 18:** Synthesis of acrylate-based oligomer and its applications in the NIPUs coating (Boisaubert et al. 2020a). Modified and reproduced with permission from Boisaubert et al. (2020a), Elsevier.

properties. This method can produce environment-friendly volatiles and isocyanate-free PHU coatings and adhesives (Bizet et al. 2020b).

The organic/inorganic hybrid PHU materials were synthesized with the mixed properties of organic and inorganic parts. The inorganic part consists of silicon, siloxane, and silica; the siloxane contains Si–O–Si bonds, which confer various properties such as hydrophilicity, flexibility, thermal resistance, and gas permeability to the materials (Ecochard et al. 2019). Composite materials are generally part of organic–inorganic hybrid materials. Some researchers used fillers such as $ZrO_2$ (Farid et al. 2019), ZnO (Pavličević et al. 2014; Panchireddy et al. 2018), $SiO_2$ (Noriega et al. 2019; Panchireddy et al. 2018), and carbon nanotubes

(Xu and Zhang 2021) to provide thermal, mechanical, and adhesive strength to the hybrid NIPUs composites. These organic/inorganic H-PHUs routes are further classified as siloxane/PHUs (Król 2007; Liu et al. 2015; Łukaszewska et al. 2023a; MacInnis et al. 2022), sol–gel routes (Noriega et al. 2019), and composites routes (Ghasemlou et al. 2020c; Kathalewar et al. 2013; Pavličević et al. 2014; Stachak et al. 2021; Świderska et al. 2021), as described by researchers (Ecochard and Caillol 2020).

Łukaszewska et al. (2024b) produced a NIPUs matrix chemically modified with octa (3-hydroxy-3-methylbutyldimethylsiloxy) POSS and treated it in different relative humidities to explore water–polymer interactions. Due to the homogeneous dispersion of POSS in the polymer matrix, 80HPOSS, even at a considerable amount (10 wt%), does not affect the water affinity of the NIPU network despite its hydrophobic character. The glass transition temperature ($T_g$) drops significantly for all materials. As water is absorbed, plasticization and slaving reduce $T_g$. Water uptake is typical of hydrogels, and the suggested NIPUs network has a strong affinity for airborne moisture. Bukowczan et al. (2023) produced NIPUs using the polyaddition of polyether diamine and tri(cyclic carbonate). Additionally, they were modified using trifunctional polyhedral oligomeric silsesquioxane (POSS), resulting in hybrid composite materials with 5–15 wt% POSS. The FTIR spectra validate the effective synthesis of NIPUs and their hybrids with POSS. The XRD and SEM demonstrated a uniform distribution of silsesquioxane inside most of the NIPU matrix. During the second degradation phase in an oxidative environment, composite materials exhibited substantially elevated degradation temperatures and a markedly decreased degradation rate relative to the unmodified NIPU matrix. The integration of POSS into the NIPUs matrix reduces its flammability. The chemical alteration of NIPU by POSS decreased combustion heat during the final degradation phase. Raftopoulos et al. (2022) produced NIPUs utilizing tricyclic carbonate compounds and diamines, subsequently modifying them with two POSS molecules. Water absorption is contingent upon environmental humidity, with all systems exhibiting high hydrophilicity, absorbing up to 65 % of water at 97 % humidity levels. Both POSS impede plasticization indirectly by restricting water absorption and directly by reinforcing the network, particularly through crosslinking of POSS. Stachak et al. (2024) synthesized NIPUs, which were further changed by POSS and glycidyl isobutyl-based POSS, and revealed that the NIPU materials demonstrate enhanced thermo-mechanical capabilities relative to the unmodified matrix. The mechanical investigations reveal that incorporating POSS particles has a variable effect on the examined NIPU composite materials, depending on the amine used to prepare each matrix. Including POSS particles positively influences tensile strength and elongation at break values, as evidenced by DMA and static stretching tests.

NIPUs' nanocomposites bring significant technological and scientific interest due to their markedly enhanced characteristics relative to traditional composites. POSS is accessible at both laboratory and industrial scales; it examines the primary processing techniques for polyolefins, polyamides, polyurethanes, and other polymeric materials, including melt bending, extrusion, injection molding, and compression molding. Copolymerization, grafting, and blending are effective techniques that produce polymer POSS multifunctional hybrid materials exhibiting properties that are intermediate between those of organic polymers and ceramics (Stachak et al. 2021). Numerous research articles and extensive reviews exist regarding changes in NIPUs and their processing methods. Stachak et al. (2021) presented a review study on the production and processing of NIPUs composites, including techniques such as electrospinning and 3D printing. The authors have emphasized recent advancements in the synthesis of nonisocyanate polyurethanes (NIPUs) and the modification techniques employed to produce nanocomposites incorporating various reactive fillers, including amine-functionalized multiwalled carbon nanotubes, POSS particles with oxirane groups, graphenated ceramic fillers, $\gamma$-Al(OH)$_3$ (O-gibbsite) nanoplatelets, corundum ($Al_2O_3$), and silica carbide (SiC) surface-treated ZnO particles, as well as cellulose carbonate and matrices derived from carbonate compounds of glycerol, trimethylolpropane, pentaerythritol glycidyl ether, and citric acid amino amides. Chuan et al. (2024) provided insights in their review regarding the processing and applications of NIPU foam, detailing various foaming strategies, foaming agents, the chemistry of nonisocyanate polyurethane foam (NIPUF), its background, and associated challenges. The optimization of monomeric structure, foaming content, and parameters to enhance the mechanical properties of NIPUF, along with the influence of foaming agents and the environmental and economic assessment of NIPUF, necessitates further research, highlighting a literature gap.

Starch-based hybrid materials have attracted several studies due to their remarkable advantages, including biodegradability, renewability, and environmental friendliness. However, starch-based materials are problematic due to their innate fragility, inadequate moisture resistance, and incompatibility with hydrophobic polymers. The hydroxyl groups on the starch backbone make it hydrophilic and provide opportunities for chemical modification. It is possible to create hybrid materials by combining hydrophilic starch with other polymers that have a similar level of hydrophilicity. Combining PUs with starch and other natural polymers has allowed them to become adaptable materials with various mechanical properties. Starch and PHUs have active functional moieties on their primary backbones that promote interaction during blending and compositing. PHU's component enhanced the hybrid's crystallinity and provided light reinforcement and stiffness (Ghasemlou et al. 2020a,c). Tai et al. (2021) thoroughly analyzed the most recent developments in synthesizing starch-based NIPU hybrids. Ghasemlou et al. (2020c) synthesized green, sustainable, environmentally friendly, and mechanically robust starch-PHUs hybrids. The PHUs were synthesized by aminolysis of EC (ethylene carbonate) with ethylenediamine (EDA) in the presence of DCM as the solvent at a temperature of 40 °C for 4 h. The starch was gelatinized before the PHUs were reinforced to add more hydroxyl groups and increase the chemical reactivity of the starch. The analysis indicates that the OH groups of the starch backbone tend to form non-covalent hydrogen bonds with the functional groups of PHUs (Figure 19).

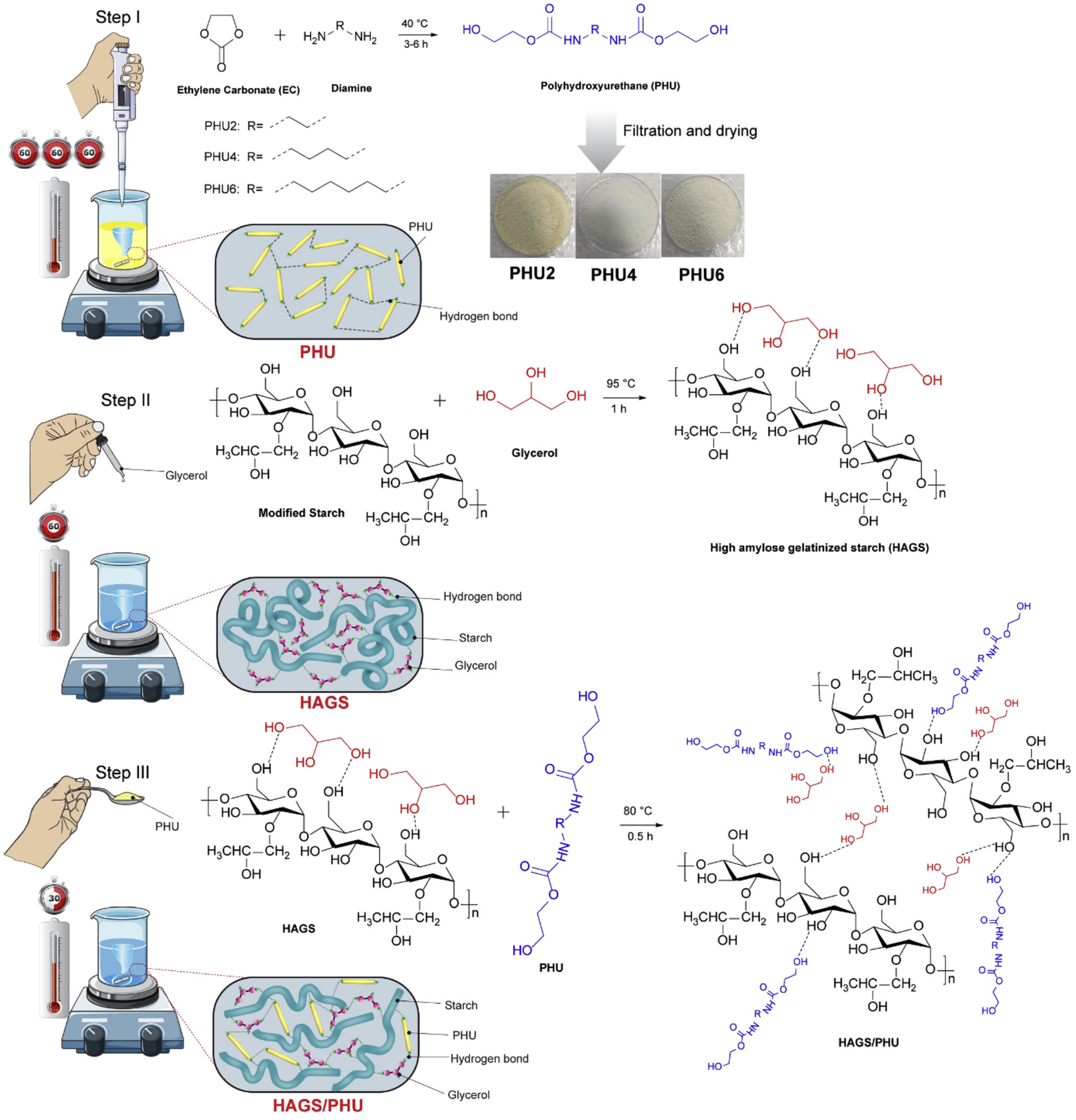


**Figure 19:** Scheme showing three main steps for the synthesis of starch-based H-PHUs (Ghasemlou et al. 2020a). Reproduced with permission from Ghasemlou et al. (2020a), Elsevier.

PHU and starch hybrids exhibit enhanced mechanical properties, although they are not suitable for biomedical or packaging applications in engineering. As a result, a special network was created by incorporating cellulose nanocrystals (CNCs) to enhance the applicability of the hybrids in other industries. Two significant elements directly impacting the nanohybrids' mechanical characteristics are interfacial interaction and filler dispersion. Strong CNC–polymer interactions enable this and enhance stress transfer over the interfacial region, improving the tensile strength of the materials. Ghasemlou et al. discovered that the exceptional mechanical properties of the nanohybrids were caused by noncovalent hydrogen bonds resulting from the interfacial attraction between the CNCs and GS/PHUs by physically assembling CNCs, GS, and PHU hybrids. The film's mechanical characteristics include improved thermal stability, a 26-fold increase in Young's modulus, and a tensile strength of up to 8.5 MPa (Ghasemlou et al. 2020a).

## 3.7 Limitations of PHUs

Despite increasing interest in developing PHUs, certain constraints in synthesizing PHUs by the aminolysis of CCs hinder their industrial-scale expansion. The initial factor is the sluggish kinetics of aminolysis in mild circumstances. The increased density of hydrogen bonds and side reactions hinders the progress of polymerization, leading to reduced molecular weight PHUs. The configuration of amines and carbon compounds, together with their components, significantly influences the kinetics and progression of this reaction. Despite its reduced reactivity, research indicates that 5CCs are the most extensively investigated CCs due to their more straightforward, less hazardous, and environmentally friendly production methods. Numerous investigations have delineated and contrasted the reactivity of various amines toward CC moieties, as the substituent group next to the amine function is a critical determinant of this reactivity. Various catalysts can enhance the reactivity of the aminolysis reaction. Three methods are typically observed: the enhancement of electrophilicity of CCs, the augmentation of nucleophilicity of amines, or a direct assault on CCs to subsequently act as a leaving group (Lewis bases). Despite considerable progress in catalytic system reactivity, the conversion of CCs remains suboptimal due to the high hydrogen bond density of PHUs, which impedes the mobility of reactive species during polymerization. Consequently, the use of solvents has become significant in enhancing the reactivity and conversion of the aminolysis reaction. The protic solvent significantly enhances reactivity and conversion by augmenting the positive charge on the carbonyl atom of carbonates while restricting intramolecular hydrogen bonding among PHUs chains (Cornille et al. 2017b; Ecochard and Caillol 2020).

The side chain reactions that may occur during the synthesis of PHUs are *in situ* $CO_2$ formation, amidification, urea formation, oxazolidinone formation, and carbonation of amine. The molar mass of the product is constrained due to side chain reaction formation in the aminolysis, as there is a deviation in the stoichiometric ratio due to the consumption of amines (Ecochard and Caillol 2020). Additional –OH groups in the structure allow for inter- or intrahydrogen bonding. This influences nano-phase separation (Leitsch et al. 2016), improves thermal and mechanical properties (Cornille et al. 2017b), and results in a decrease in molar mass and conversion due to higher viscosity and lower mobility (Blain et al. 2017).

The side reactions, long-term curing, higher temperatures, low conversion, higher hydrogen bond density, and lower reactivity at low temperatures are significant limitations in synthesizing PHUs. The end product had a lower molar mass of PHUs despite using a catalyst to accelerate the conversion of cyclic carbonates. This results from intra- and intermolecular interactions, primarily H-bonds formed by the carbamate and hydroxyl groups of the PHUs. When temperatures are higher, more energy is available to break intra- and intermolecular bonds, reduce viscosity, accelerate reactions quantitatively, and achieve the desired molar masses. However, the chemistry of PHUs is negatively impacted by hydrogen bonding. These interactions limit the polymerization procedure from progressing by freezing the species, yet they give the resultant materials very intriguing mechanical, adhesive, and barrier properties (Cornille et al. 2017b).

The properties of PHUs are not comparable to those of conventional PUs due to their lower molar mass. Although various limitations are exhibited in synthesizing PHUs, this is the most promising and alternative green synthesis technique for producing NIPUs. Many researchers have investigated the effect of reaction parameters involved in the aminolysis of cyclic carbonates (CC), including reaction time, catalyst, molar ratio, CC ring size, CC substituents, amine type, temperature, and amine substituents. Researchers preferred to synthesize solvent-free, waterborne, nonisocyanate polyurethanes at low temperatures using reactive extrusion or blending techniques (Ecochard and Caillol 2020; Magliozzi et al. 2019).

### 3.8 Applications of NIPUs

Due to the less toxic nature of CCs, the NIPUs are environmentally safe for applications in adhesives, conductive membranes, polymeric sensors, light-emitting diodes (LEDs), and photocurable thermosets for 3D printing. The other most important applications of NIPUs are in sealants (Dimitrov et al. 2017), fillers (Chen et al. 2019), adhesives (Lambeth and Rizvi 2019), elastomers (Beniah et al. 2017a), hydrogels (Cornille et al. 2017b), latexes (Li et al. 2017), films (Ghasemlou et al. 2020a), foam (Coste et al. 2022), vitrimers (Fortman et al. 2015), and coatings (Bobbink et al. 2019). PHUs' adhesives were tested on wood, glass, and various metals, including aluminum and stainless steel, and it was observed that they have remarkable adhesive and material qualities. CCs-based PHUs provide thermostable, UV-stable, and nonporous coatings, coverings, and linings to prevent corrosion and wear on metallic, concrete, and wood surfaces (Bobbink et al. 2019). Water-soluble polyurethanes (PUs) have applications in biomedical operations and are used in high-performance adhesives and coatings (Bizet et al. 2020a).

## 4 Summary and future perspectives

PUs are the most widely used substances globally, utilized in various products, including coatings, paint, footwear, sporting goods, soft and rigid automobile foams, insulating materials, and more. Due to their similar mechanical, chemical, and thermal properties, they can be used as alternatives to other materials, including plastic, metal, and wood. All commercially available PUs comprise polyols, diisocyanates (CMR), chain extenders, emulsifiers, and neutralizing agents derived from petroleum feedstocks (Akindoyo et al. 2016). As a result, the production of PU is expensive, environmentally damaging, and energy-intensive. Therefore, environmental/industrial $CO_2$-based polyols, which can be produced using epoxies and specific heterogeneous catalysts, offer an alternative to polyols derived from petroleum feedstocks. Manufacturing NIPUs through the reaction of CCs with polyamines, particularly aliphatic and aromatic amines, has emerged as an enticing, environmentally benign trend in recent years. Since it is nonporous, resistant to moisture, and safe to prepare and use, this approach has been the subject of intensive research over the last few decades. Carbonates (linear, monocyclic carbonates (5, 6, 7, 8-CCs), and polycyclic carbonates) from petroleum feedstocks, epoxy compound carbonation, and bio-based CCs can all be utilized in the synthesis of PUs. Different PUs, including coatings, films, foams, adhesives, composites, paints, and inks, were developed, researched, and identified as suitable for these applications (Delavarde et al. 2024).

To enhance the mechanical, thermal, and chemical strength of NIPUs, many researchers created NIPUs with a linear, crosslinked structure utilizing various crosslinking agents, including epoxy, acrylates, methacrylates, and polyaldehydes. Since polyurethanes are typically synthesized at room temperature for most applications, proposing room-temperature approaches for PHU synthesis is a significant challenge. Therefore, without additives, a novel method for introducing hydroxyurethane groups into reactive matrices at room temperature has been explored. Merging of epoxy and PUs chemistries investigates new materials with potentially unique and improved properties. Hybrid materials of starch and PUs also exhibit comparable mechanochemical and thermal properties to commercialized isocyanate-based polyurethanes; therefore, they are a hot topic for researchers (Ghasemlou et al. 2020a). To impart the hybrid composite PUs with thermal, mechanical, and adhesive strength, some formulations include fillers, POSS (Łukaszewska et al. 2023a), carbon nanotubes (Xu and Zhang 2021), and ZnO (Pavličević et al. 2014). The starch, cellulose, and PHUs fabricated hybrids approach has the potential for industrial development.

Recent advancements in PHU vitrimers are drawing increased attention from academics due to their ability to reshape materials while maintaining mechanical properties akin to those of thermoset resins. Vitrimers are polymer networks characterized by cross-links that engage in associative exchange processes at elevated temperatures, usually facilitated by an embedded catalyst. Fortman et al. (2015) reported 6CCs and amine-derived PHU vitrimers. The PHUs network eliminates stress and can be reprocessed at high temperatures and pressures without the need for an external catalyst. The synthesized network exhibits tensile properties comparable to those of foremost thermosets and recovers 75 % of its original values postreprocessing. PHUs vitrimers constitute a potential novel category of repairable networks, distinguished by their remarkable mechanical properties, the absence of toxic isocyanate monomers, and catalyst-free repair methodologies (Fortman et al. 2015). Additionally, the corrosion protection of metals, wood, and concrete is not examined in the work on NIPU coating. Therefore, filling in gaps in the literature is another area of inquiry.

Chuan et al. (2024) provided insights in their review regarding the processing and applications of NIPU foam, detailing various foaming strategies, foaming agents, the chemistry of nonisocyanate polyurethane foam (NIPUF), its background, and associated challenges. The optimization of the monomeric structure, foaming content, and parameters to enhance the mechanical properties of NIPUF, along with the influence of foaming agents and the environmental and economic assessment of NIPUF, necessitates further research, highlighting a literature gap (Chuan et al. 2024).

Despite increasing interest in PHUs, numerous significant difficulties persist, obstructing their advancement to industrial-scale manufacturing. While PHUs can attain reasonably linear structures with elevated molecular weights within feasible reaction durations, they frequently lack the mechanical strength and chemical resistance necessary for several end-use applications. To address these constraints, both organic and inorganic additives have been incorporated into PHU systems, resulting in hybrid PHUs (HPHUs) akin to traditional PU modifications. Although some studies indicate that these hybrid systems can equal or surpass some performance metrics of conventional PUs, they remain deficient in other critical attributes (MacInnis et al. 2022). Key challenges to industrialization include low reactivity and limited molar mass expansion, a shortage of multifunctional cyclic carbonate monomers, and a high density of hydrogen bonds generated during polymerization. The strong hydrogen bonding results in a highly viscous reaction medium, hence limiting polymer chain development. While increased temperatures or catalytic systems might mitigate viscosity issues and enhance reactivity, they also tend to facilitate side reactions that undermine the distinctive structural and functional characteristics of PHUs. A notable potential application of PUs is the manufacturing of foam. Nonetheless, the expansion of NIPU foams encounters a significant impediment owing to the sluggish kinetics of the carbonate–amine interaction. The creation of foam necessitates fast crosslinking to encapsulate the gas emitted throughout the process, a challenge posed by the sluggish nature of NIPU chemistry. In summary, although NIPUs offer various benefits, including improved mechanical and thermal properties, exceptional chemical resistance, opportunities for postfunctionalization, and reduced toxicity, significant scientific and technical challenges continue to hinder their widespread implementation in industrial polyurethane production (Delavarde et al. 2024).

## Abbreviations and nomenclature

| | |
|---|---|
| AAS | 2-[(2-Aminoethyl)amino]-ethanesulfonic acid monosodium salt |
| BADGE | Bisphenol-A diglycidyl ether |
| BAPO | Phenyl bis-(acyl) phosphine oxide |
| BDO | 1,6-Butanediol |
| BHC | Bis-1,6-hexamethylenecarbamate |
| BHCH | Bis(hydroxyethyoxy carbonyl amino) hexane |
| CHDI | Trans-1,4-diisocyanatocyclohexane |
| CMLCD | Carboxy-modified long-chain diols |
| DBU | 1,8-Diazabicyclo[5.4.0]undec-7-ene) |
| DGDC | Diglycerol decarbonate |
| DMBA | Dimethylolbutyric acid |
| DMPA | Dimethylolpropionic acid |
| DSC | Differential scanning calorimetry |
| FTIR | Fourier transformation infrared radiation |
| GCA | Glycerol carbonate acrylate |
| GCMA | Glycerol carbonate methyl acrylate |
| GCVE | Glycerol carbonate vinyl ether |
| GPC | Gel permeation chromatography |
| HAPs | Hazardous air pollutants |
| HDI | Hexamethylene diisocyanate |
| HMDI | Bis(4-isocyanatocyclohexyl) diisocyanate |
| HZ | Hydrazine |
| IPDI | Isophorone diisocyanate |
| MDI | 2,4′-Methylenediphenyl and 4,4′-methylene diphenyl |
| mTBD | 7-Methyl-1,5,7-triazabicyclo[4,40]dec-5-ene |
| m-TMXDI | α,α,α′,α′-Tetramethyl-1,3-xylylene diisocyanate |
| NMP | Normal 1-methyl-2-pyrrolidone |
| NMR | Nuclear magnetic resonance |
| PBA | Poly(butylene adipate) |
| PCDL | Polycarbonate macrodiol |
| PCPUs | Polycarbonate polyurethanes |
| PDMS | Polydimethylsiloxane |
| PEDA | Pentaerythritol diacrylate |
| PE | Poly(ethylene glycol) |
| PHCUs | Poly(hexane carbonate) polyurethanes |
| PHNA | Poly(neopentylene-hexamethylene adipate) glycol |
| PNA | Poly(neopentyl glycol adipate) |
| POSS | Polyhedral oligomeric silsesquioxane |
| PPCG | Poly(propylene carbonate) glycol |
| PPG | Poly(propylene glycol) |
| PPG-BAPE | Poly(propylene glycol) bis(2-amino propyl ether) |
| PTMC | Poly(trimethylene carbonate) |
| PTMG | Poly(tetramethylene ether) glycol |
| PUDL | Polyurethane diol |
| RHMPA | Reactive hot-melt polyurethane adhesive |
| SEM | Scanning electron microscopy |
| TBD | 1,5,7-Triazabicyclo[4.4.0]dec-5-ene |
| TDI | 2,4 or 2,6-toluene diisocyanate |
| TEM | Transmission electron microscopy |
| TGA | Thermogravimetric analysis |
| TPOL | Diphenyl(acyl) phosphine oxide) photo-initiator |
| VOCs | Volatile organic compounds |
| XRD | X-ray diffraction |

**Acknowledgments:** This research received support from the Department of Chemicals and Petrochemicals, Ministry of Chemicals and Fertilizers, Government of India (Project code: 25014/2/2015-PC-II). Additionally, we extend our gratitude to the Department of Science and Technology (DST) under the project DST-FIST-2018 (TPN-19905).

**Research ethics:** Not applicable.

**Informed consent:** Not applicable.

**Author contributions:** Ishwar Sharan: conceptualization, methodology, validation, writing original draft, reviewing and editing, investigation, and formal analysis. Shishir Sinha: conceptualization, review and editing, supervision, funding acquisition. Vimal Chandra Srivastava: conceptualization, supervision, reviewing and editing, funding acquisition. The authors have accepted responsibility for the entire content of this manuscript and approved its submission.

**Use of Large Language Models, AI and Machine Learning Tools:** None declared.

**Conflict of interest:** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Research funding:** Department of Chemicals and Petrochemicals, Ministry of Chemicals and Fertilizers, Government of India (Project code: 25014/2/2015-PC-II). Department of Science and Technology (DST) under the project DST-FIST-2018 (TPN-19905).

**Data availability:** Not applicable.

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