Emerging Trends in Non-isocyanate Polyurethane Foams: A Review

Chen Chuan Nathaniel Don Lim, Michelle Jui Hsien Ong, Mingyue Wu, Chi-Lik Ken Lee, Ping Sen Choong*,

Institute of Sustainability for Chemicals, Energy and Environment ($ISCE^2$), Agency for Science, Technology and Research (A*STAR), 1 Pesek Road, Singapore 627833, Republic of Singapore.

Abstract

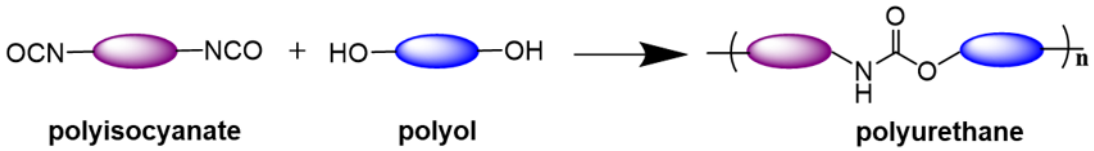
Polyurethane foams (PUF) are essential materials known for their exceptional chemical and mechanical properties, making them ubiquitous in wide range of applications. Conventionally, PUF are produced through polyaddition reactions between polyols and polyisocyanates at room temperature, where water plays a critical role in this process by hydrolyzing the isocyanates, leading to the release of carbon dioxide (CO_2) as a blowing agent. In recent years, isocyanates have raised significant concerns in industries and among consumers due to their high toxicity. Therefore, driving the need to explore alternative synthesis routes for PUF that do not involve the use of isocyanates. Non-isocyanate polyurethane foams (NIPUF) derived from the aminolysis of cyclic carbonates have emerged as the most promising solution to replace the conventional method of producing PUF. Despite this, the challenging aspect lies in identifying a suitable foaming strategy for NIPUF that can meet both sustainability and performance requirements. In view of this, the first part of this review focuses on the background, chemistry, and challenges of PUF. In the second part, the chemistry of NIPUF and the various foaming strategies used to prepare them are discussed and analyzed. Finally, the outlook and future research focus areas for NIPUF are outlined.

Keyworks: Non-isocyanate; polyurethane foam; blowing agent; cyclic carbonates; sustainability; polyhydroxyurethane; carbon dioxide; aminolysis; self-blowing; global warming potential.

Polyurethane Foams (PUF)

1.1 Introduction

In the 1930s, Dr. Otto Bayer and his team in Leverkusen, Germany had invented a new material known as "Das Di-lsocganat-Poluadditionsverfahren," which had since been recognized as polyurethane (PU),[1] PU are synthesized using step-growth polymerization of polyols and polyisocyanates depicted in Scheme 1.[2] Notably, this synthesis method allows for operation under low-temperature conditions and results in a PU with low viscosity.[3]



Scheme 1: Synthesis of polyurethane.

PU has remarkable physical properties, including high tensile strength, chemical resistance, and flexibility.[4] Additionally, PU offers high tunability, with properties closely related to the types of polyols and isocyanates used in the formulation.[5] This allows for precise customization to meet diverse application requirements.[6] Due to this versatility, PU have gained widespread adoption across numerous industries, proving indispensable in applications ranging from construction, packaging, ink, automotive, furniture, electronics, aerospace, footwear, consumer-care products, and biomedical products.[7-10] PU has reached an estimated global market value of US$78 billion in 2023 and is projected to have a 4.5% compound growth rate annually from 2024 to 2030.[11] Molded, flexible and rigid polyurethane foams (PUF) are the largest segment in PU industry accounting for 65% of all PU produced in 2022 and expected to grow in future due to its excessive use as insulation material (Figure 1).[12]

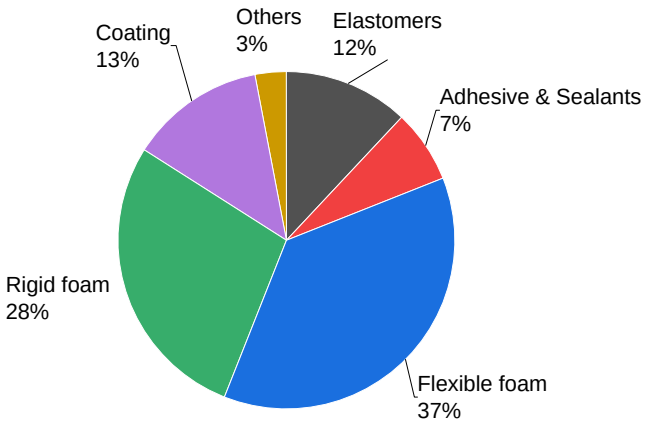
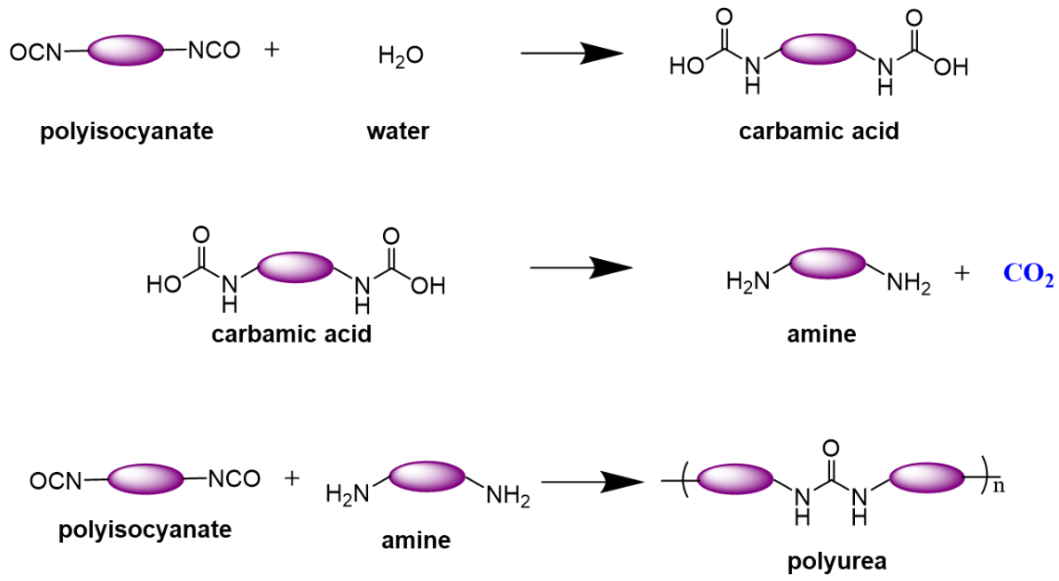


Figure 1: The uses of PU in 2022. Adapted with permission under a Creative Commons 4.0 license from Pęczek et al.[12] Copyright [2024] [MDPI].

1.2 Chemistry of PUF

Conventional PUF are synthesized through the polyaddition of polyols and polyisocyanates in the presence of water.[13] The primary reaction forms urethane linkage, where water hydrolyzes polyisocyanates to form carbamic acid, which subsequently decomposes into amine and CO_2 at room temperature.[14] The resulting amine will then react with polyisocyanates to form urea linkages (Scheme 2). CO_2 generated after polyisocyanate decomposition is used as blowing agent for expanding and creating cells in the PU structure.[15] The overall reaction is highly exothermic and thus accelerates the polymerization and foaming. The cells size is dependent on the formulation and kinetics of the chemical reaction during the foaming process. These would affect the internal foam structure such as the open/close cell and strength of the strut, thereby determining the physical properties of the foam. Two methods are typically used for the foaming: aeration and nucleation.[16] Aeration foaming entraps gas, usually air, in the polymer matrix via mechanical stirring or frothing.[17] Nucleation foaming gas originates from various sources, including being dissolved in the reactant, introduced as a blowing agent, or generated by reactants or additives in the formulation.[18]

There are two types of PUF - flexible PUF and rigid PUF.[19] Flexible PUF have open-cell structures,[20] which render them lightweight and flexible with high specific strength.[21-22] Flexible PUF are commonly used for mattress and furniture.[23] On the other hand, rigid PUF have closed-cell[24] and highly crosslinked structures that offer high tensile strength and thermal insulation. The mechanical and chemical properties, density, and glass transition temperature (T_g) of PUF are easily tuned by varying the types of polyols and polyisocyanates,[25] ratio of polyols and polyisocyanates,[26] crosslinker,[27] amount of water, additives,[28] surfactant,[29] and catalyst[30] in the formulation. The effects of various components in formulation on the foaming and foam properties are summarized in Table 1.



Scheme 2. Chemical reactions in synthesis of PUF.

Table 1 The summary of the effects of various parameters on PUF adapted from reference.[31-33]

Component	Parameter	Effect on foaming	Effect on foam properties
Polyol	Higher Molecular weight	• Lower gelation rate	• Higher tensile strength • Lower T_g

	More ethylene oxide (EO) capping	• Higher gelation rate • Improved compatibility with water	• Higher T_g
	Higher Functionality	• Higher gelation rate • Higher formulation viscosity	• Higher foam shrinkage • Harder foams • Higher fatigue resistance
Isocyanate	Use of 2,4-toluene diisocyanate (TDI)	• Lower viscosity • Slower reaction	• Lower density • Higher tensile strength
	Use of methylene diphenyl diisocyanate (MDI)	• Higher viscosity • Faster reaction	• Higher durability • Harder foams • Higher compression strength
	Higher ratio of isocyanate to OH in polyol	• Higher foaming rate • Lower gelation rate • Slower curing	• Lower durability • Lower tensile strength
Chain extender	Use of Diol	• Faster curing	• Softer foam
	Use of Diamine	• Faster curing	• Harder foam
Blowing agent	Higher amount of water	• Higher foaming rate • Higher exotherm • Lower shrinkage	• Harder foam
Crosslinker	Higher amount of crosslinker	• Faster curing • Lower flowability	• Harder foam
Amine & Metal Catalyst	Higher amount of catalyst	• Higher foaming rate • Higher gelation rate	• Lower density

T_g = glass transition temperature (°C)

1.3 Challenges of PUF

Despite playing an important role in various applications, PUF have raised concerns for several reasons.[34-35] Firstly, polyols and isocyanates are derived from petroleum sources, which are non-renewable and have contributed to high global warming due to the extraction process with high CO_2 emission.[14] Secondly, the use of toxic isocyanates that causes human health issues such as dermatitis[36] and asthma.[37-38] Lastly, the production of isocyanates involves the use of phosgene, a highly reactive and toxic compound that can have severe consequences if accidentally released.[39] Phosgene was historically utilized as a chemical warfare agent, and it was known to cause severe

and long-lasting adverse health effects in humans.[40] In view of these, the use of isocyanates has been largely restricted by European Chemical Agency in the context of REACH regulation.[41] It is highly possible that many countries will follow suit in near future despite reluctances from industries. In addition, use of conventional catalysts such as stannous octoate and amine with high toxicity in polyurethane production will cause serious health problems that remain huge concern for consumers.[42-43] There are significant advancements underway in the development of renewable polyols[44] and safer catalysts (bismuth and zinc-based)[45], which are aimed at creating more sustainable polyurethane solutions.

Next, the disposal of PUF posed a serious environmental problem.[46] Traditional disposal methods such as incineration, landfill and degradation have their limitations. Incineration results in high emission of CO_2 and polluted gases, while landfill is inefficient due to the low density of PUF (0.02 – 0.05 g/cm^3), occupying significant land space. Moreover, the natural degradation of PUF will take more than 100 years, and chemical recycling of the PUF is energy intensive.[47]

With the arising emphasis on the principals of life cycle assessment (LCA) in the recent decades, LCA studies had been conducted to assess the environmental performance of PUF.[48] The raw materials needed for the production of PUF had contributed at least 75% to the overall environment burden in most impact categories.[49] The processing of upstream raw materials had contributed to over 99% of the ozone depletion potential and about 91 – 92% of the acidification, eutrophication and photochemical smog creation potential.[50] The impact of isocyanate to the global warming potential (GWP) and the contribution of polyol to photochemical ozone creation category were both more than 60%.[49] Furthermore, the high GWP (up to 24 kg CO_2 eq./kg) and non-renewable energy consumption of some PUF applications (Table 2) suggest that the current production methods of PUF are not environmentally sustainable.

Table 2. GWP and primary non-renewable energy consumption of PUF adapted from reference.[49]

PU Form Application	GWP (kg CO_2 eq./kg of material)	Primary Non-renewable Energy Consumption per kilogram of material (MJ/kg of material)
Low-density Foam	3.1 – 4.1	86 – 87
Medium-density Foam	21 – 24	82 – 83
High-density Foam	3.2 – 4.4	89 – 102

In view of this, alternative pathways for isocyanate-free polyurethane synthesis have gained increasing importance for industry and academic research in recent decades.

1. Non-isocyanate Polyurethane Foams (NIPUF)

Non-isocyanate polyurethane (NIPU) has gained attention as a promising alternative to PU due to its potential to address some of the environmental and health concerns associated with isocyanates. There are four main reported synthetic routes of NIPU – ring-opening polymerization, polycondensation, rearrangement, and polyaddition (Figure 2).[51-58] Among these pathways, ring-opening polymerization of toxic aziridine[59] or phosgene-derived cyclic carbamate to obtain NIPU remains a significant concern, despite these processes being isocyanate-free. Likewise, the rearrangement of acyl azides (Curtius rearrangement), carboxamides (Hofmann rearrangement), or hydroxamic azides (Lossen rearrangement) with polyols will also lead to the in-situ generation of isocyanates for polyurethane production.[60] Therefore, these routes are not considered as isocyanate-free routes for polyurethane production. In addition, azides are unstable, toxic, and potentially explosive. Another synthetic route is through polycondensation of polychloroformate or polycarbonates and polyamines, polycarbamate or polycarbomoyle chloride and polyol, and polycarbamate and polyaldehyde (formation of geminated diurethane from the reaction between two carbamate groups and one aldehyde group in the presence of acid catalyst).[61] Nevertheless, phosgene or chloroformate are still required to make precursors such as polychloroformate or polycarbomoyle chloride. The much less reactive precursors such as polycarbonate or polycarbamate will require high temperature (>120 °C) for the transurethanization. Moreover, by-products such as methanol or hydrochloric acid (HCl) are released during polycondensation, posing challenges to industrial-scale production.

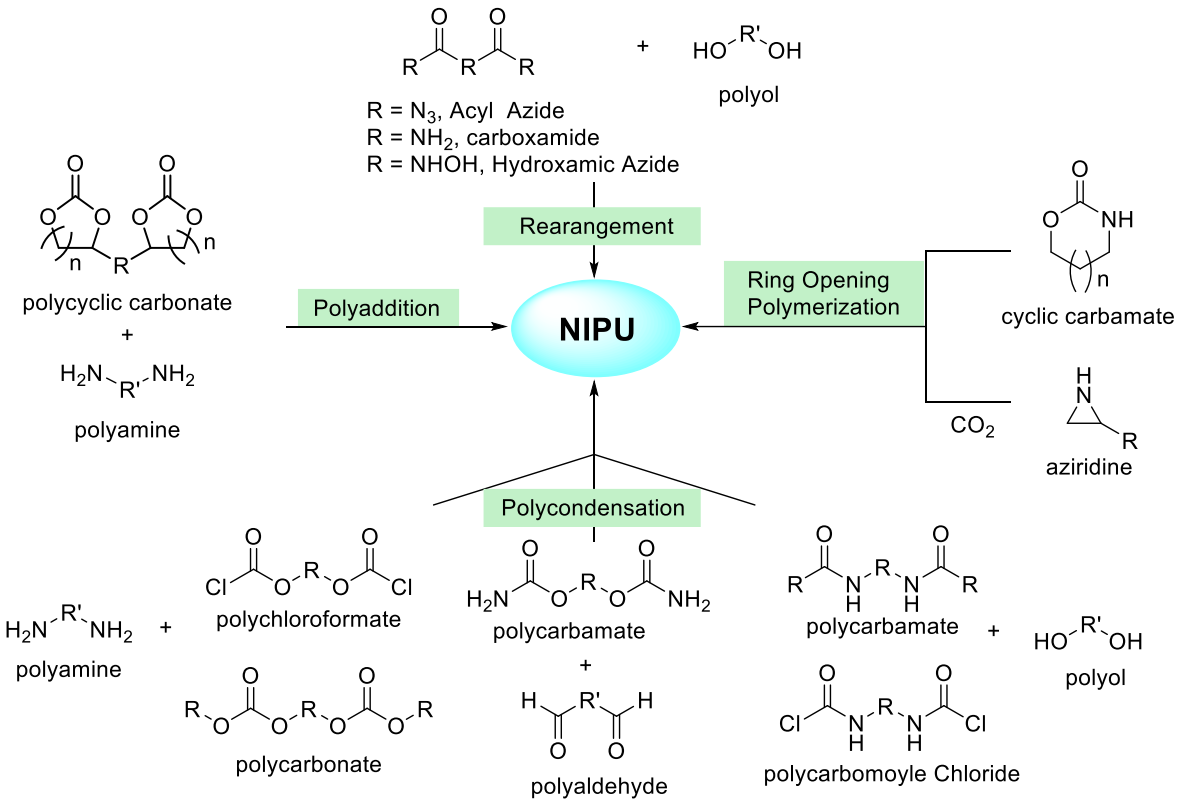


Figure 2. Overview of synthetic routes to NIPU.[53]

The polyaddition of 5-membered cyclic carbonates and amines leading to NIPU has garnered greater attention for several reasons: (1) it completely eliminates the need for isocyanate and phosgene in the process, (2) commercial availability of primary amines, (3) the non-toxicity and non-moisture sensitivity of cyclic carbonates, (4) cyclic carbonates can be derived from CO_2. Furthermore, the polyaddition reaction displays 100% atom efficiency as it does not produce side products such as water or methanol. In the next section, the synthetic routes to cyclic carbonates are discussed.

1.1 Precursors for NIPUF

1.1.1 Synthesis of Cyclic Carbonates

Extensive research has been conducted on the synthesis of 5-membered cyclic carbonates using various methods since Carothers et al. reported the first synthesis of various size cyclic carbonates

in the early 1930s.[62] The main approaches to synthesize cyclic carbonates from diols and epoxy precursors are summarized in Figure 3. The 5-membered cyclic carbonates were synthesized in good yields (40 – 80%) by carbonate interchange reaction between 1,2-diols and ethylene carbonate, or dialkyl carbonates (diphenyl carbonate, diethyl carbonate, or dimethyl carbonate) in the presence of catalysts such as basic catalysts, metal oxide catalyst (magnesium oxide, calcium oxide, and lanthanum(III) oxide) or lipase.[57, 63-64] Epoxy was converted into cyclic carbonate by reaction with β-butyrolactone in the presence of quaternary salt as catalyst.[65] The most widely studied route to synthesize cyclic carbonates is through the CO_2 insertion of epoxides.[66-68] This route represents a highly efficient reaction with a 100% atomic yield, utilizing greenhouse gas CO_2 without the need of phosgene. Different catalysts were studied, including alkali metal, phosphines, metal complex, homogenous or heterogenous ionic liquids, and quaternary ammonium salt to improve the reaction yield.[69-70] It is important to note that significant advancements in CO_2 insertion have been made toward achieving conversion under relatively mild conditions at lower temperature and atmospheric CO_2 pressure with utilization of catalysts for lowering the activation energy of CO_2.[70-71] The examples of reported catalyst systems for CO_2 insertion under mild conditions are: a) calcium bromide/1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU),[72] b) calcium iodide/crown ether,[73] c) dimeric aluminum complexes/ terabutylammonium bromide (TBAB),[74] d) Zn-NH_2- metal–organic framework (MOF),[75] and e) polystyrene supported ionic liquid.[76]

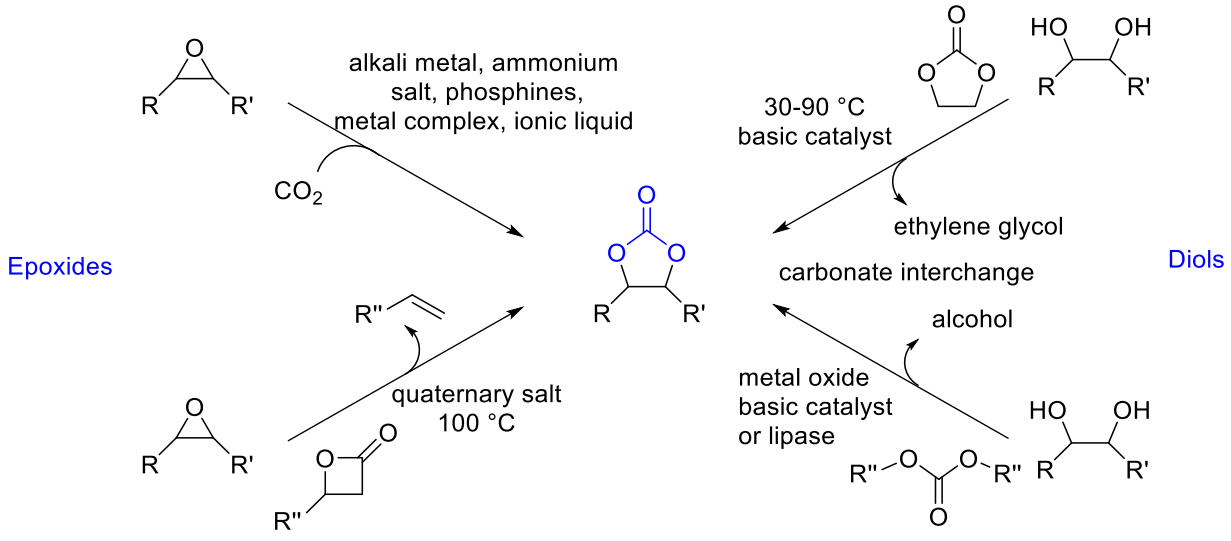
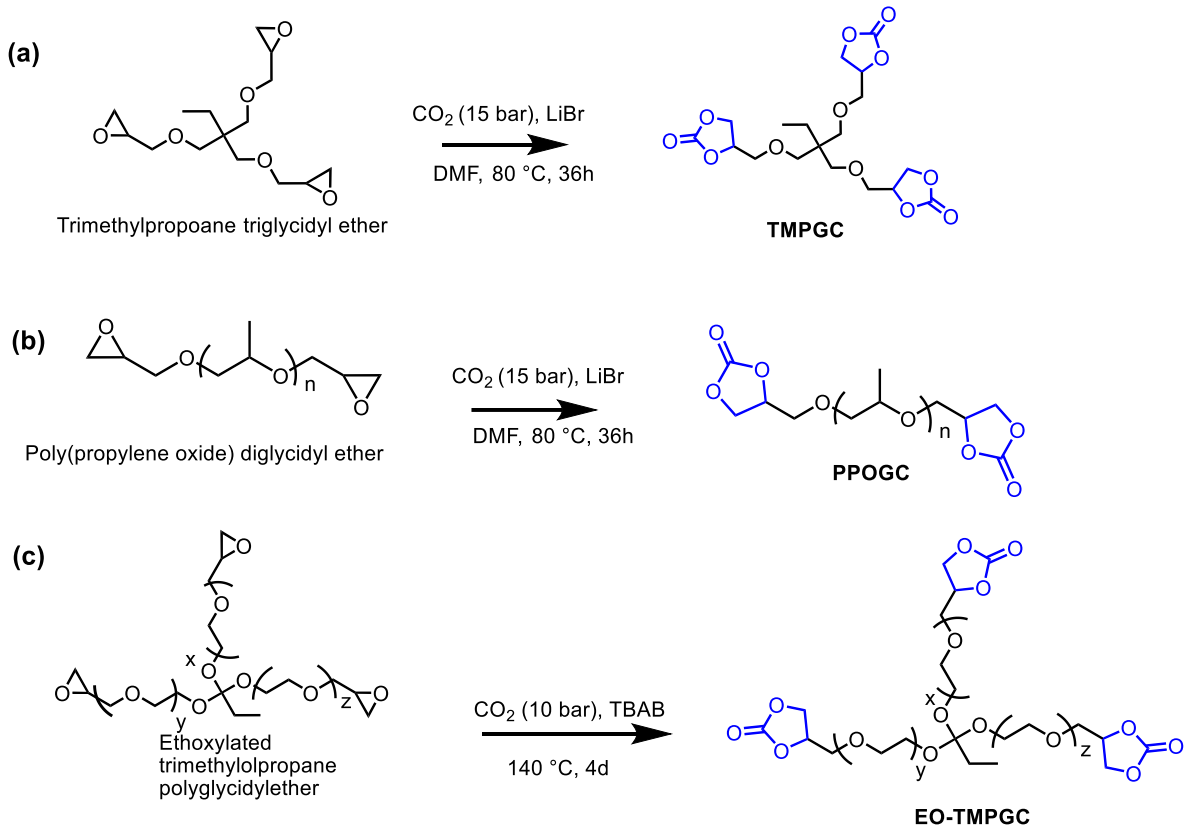


Figure 3. Common methods to synthesize cyclic carbonates from diols and epoxides.[57]

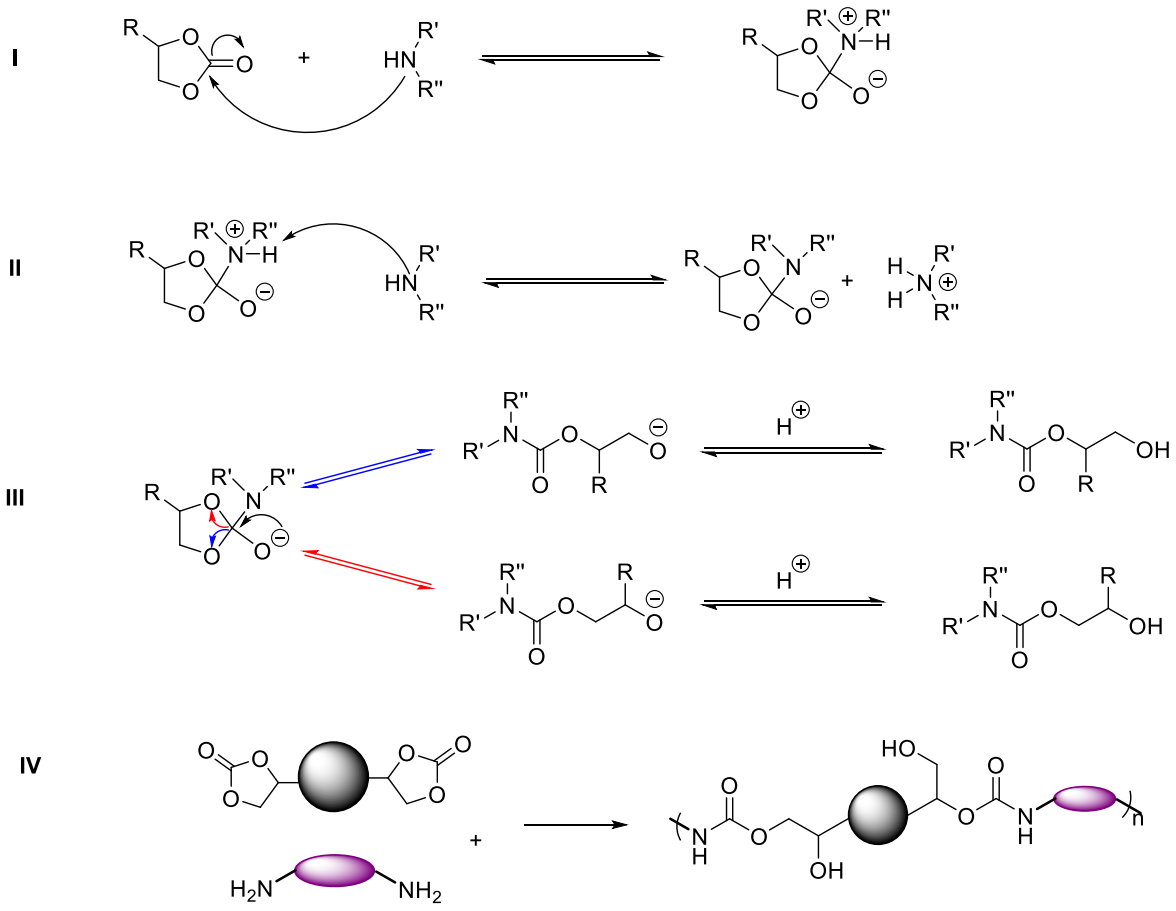
In order to obtain NIPUF by polyaddition, it is necessary to synthesize multi-functional cyclic carbonates: bis(cyclic carbonates) or tris(cyclic carbonates) by using the methods mentioned above. CO_2 insertion of epoxides has emerged as the predominant method for preparing polyfunctional cyclic carbonates. Usually, pressurized CO_2 is required to react with epoxides to give polyfunctional cyclic carbonates (Scheme 3a – c). Pressurized CO_2 (15 bar) was directly reacted with trimethylpropane triglycidyl ether and poly(propylene oxide) diglycidyl ether with lithium bromide (LiBr) as catalyst in dimethylformamide (DMF) at 80 °C [77-78] The conversion of epoxides to cyclic carbonate was completed after 36 h to achieve 76% yield. In contrast, a higher temperature and longer time (140 °C for 4 d) were required for ethoxylated trimethylolpropane polyglycidyl ether with less reactive epoxides to achieve full conversion to cyclic carbonate.[79] It is crucial to further develop efficient synthesis of polyfunctional cyclic carbonates under milder conditions – particularly by lowering temperatures, reducing reaction times, and at atmospheric CO_2 pressure to enhance the sustainability.



Scheme 3. CO_2 insertion of epoxides to polycyclic carbonates.[77-79]

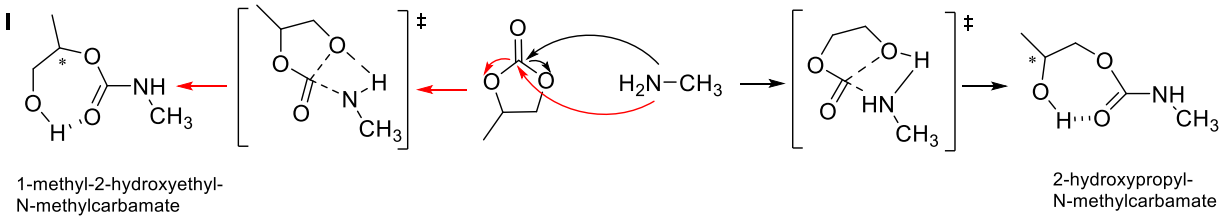
1.2 Chemistry of NIPUF via Amine/Cyclic Carbonate route

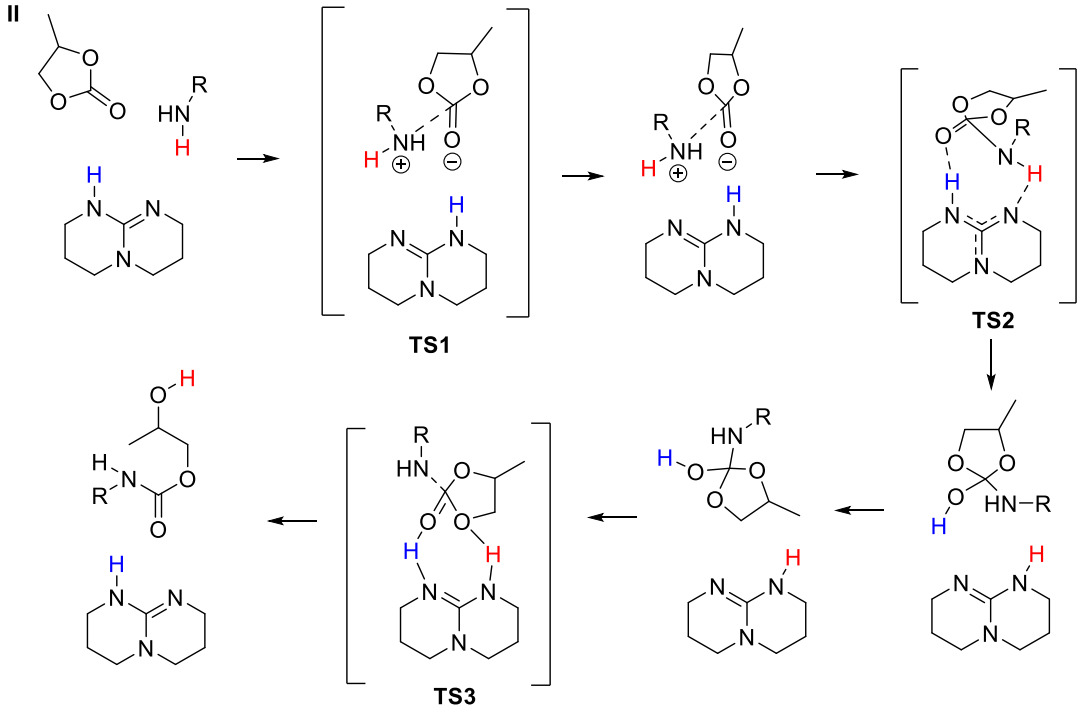
The mechanism of ring-opening of cyclic carbonate via aminolysis was proposed by Garipov et al. in 2003 (Scheme 4 I-III).[80] Firstly, a nucleophilic attack of the amine on the carbonyl group of cyclic carbonates, leading to the formation of a tetrahedral intermediate. Subsequently, another amine deprotonates the tetrahedral intermediate, triggering the ring-opening reaction of the cyclic carbonate. This process results in the formation of hydroxyurethane, with the type of alcohol produced (primary or secondary) depending on the geometry of the intermediate. Similarly, NIPU or polyhydroxyurethanes (PHU) are prepared from the polyaddition of diamines and bis(cyclic carbonates) as shown in Scheme 4 IV.



Scheme 4. The mechanism (I-III) of ring opening of cyclic carbonate by amine and polyaddition (IV) between cyclic carbonates and amines to form NIPU or polyhydroxyurethane (PHU) proposed by Garipov et al.[80]

Alves et al. investigated the aminolysis of propylene carbonate by using density functional theory (DFT).[81] The results showed that the transition state (Scheme 5 I) involved the concerted addition of amine onto the carbon atom of the cyclic carbonate group, transfer of the amine's proton to the adjacent oxygen atom of the cyclic carbonate group, and ring-opening of cyclic carbonate. The use of catalyst such as TBD had significantly reduced the Gibbs energy of aminolysis that exhibited a three-step pathway (Scheme 5 II): 1) nucleophilic attack of amine onto cyclic carbonate (TS1); 2) concerted protons transfer between TBD and the ammonium alkoxide (TS2); and 3) second concerted protons transfer between TBD and amino-alcohol (TS3) for the synthesis of the hydroxyurethane and the recovery of TBD.





Scheme 5. (I) Uncatalyzed racemic aminolysis of propylene carbonate by methylamine, and (II) Lewis structures for the aminolysis of propylene carbonate by amine catalyzed by 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD).[81]

NIPU typically has lower molar mass owing to the blocking of aminolysis by inter- and intra-molecular hydrogen bonding originated from the pendant alcohols[82] and the reversibility nature of the hydroxyurethane group at elevated temperature.[83] Furthermore, NIPU exhibits inherent hygroscopic properties and possesses higher water absorptivity in comparison to PU. This characteristic may present a challenge in applications where high water resistance is required. It is noteworthy to mention that the functionalization of pendant alcohols has been utilized as a convenient method to introduce new properties to NIPU such as hydrophilicity, hydrophobicity, and solubility.[84-85] With a growing numbers of reviews focused on the synthesis of NIPU,[51, 86-89] and their applications in adhesive, coatings, and elastomer applications,[51-52, 90] there remains a notable disparity in the research focusing on the synthesis of NIPUF with only one recent review on NIPUF.[91] In the next section, we will summarize and evaluate the development of NIPUF that emphasize the monomer synthesis, foaming strategies, and their mechanical properties.

1.3 Preparation of NIPUF

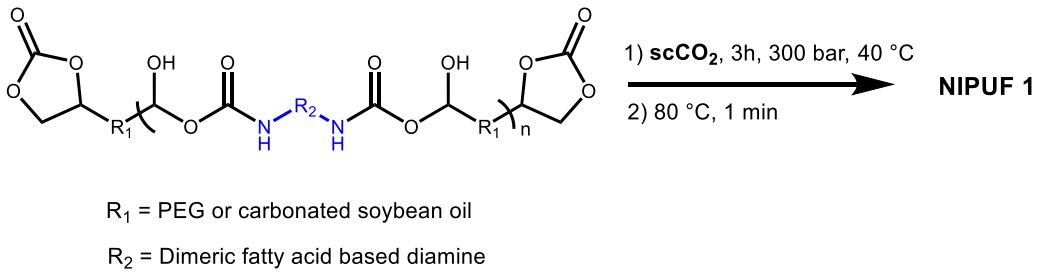
The foaming process of NIPU differs from traditional PUF production due to two factors: (1) the absence of isocyanate hydrolysis to release CO_2, and (2) high energy is required for CO_2 release from the decarboxylation of stable cyclic carbonate at room temperature. Just like in PU foaming, meticulous attention must be paid to balance the foaming rate and polymerization rate to precisely manage foam density and mechanical properties. A foam formulation with a high rate of foaming and low polymerization rate will result in cell wall rupture, leading to the collapse of foam structure. On the other hand, a poorly blown foam will be obtained if the rate of polymerization or crosslinking is too fast relative to rate of blowing.[92] Both thermoplastic and thermoset NIPUs can be foamed successfully by using physical or chemical blowing agents. In comparison, thermoset NIPUF have better mechanical property, high durability, thermal and chemical stability owing to the crosslinking of polymer structure. However, high crosslinking density would result in excessive rigidity and fragility of foams.[93] Therefore, it is also important to incorporate flexible groups as extender in the foam structure. The final foam morphology such as cell structures, degree

of microphase separation between hard and soft segments plays an important role in determining tensile and compression strength, toughness and fracture energy of foam.[94-95]

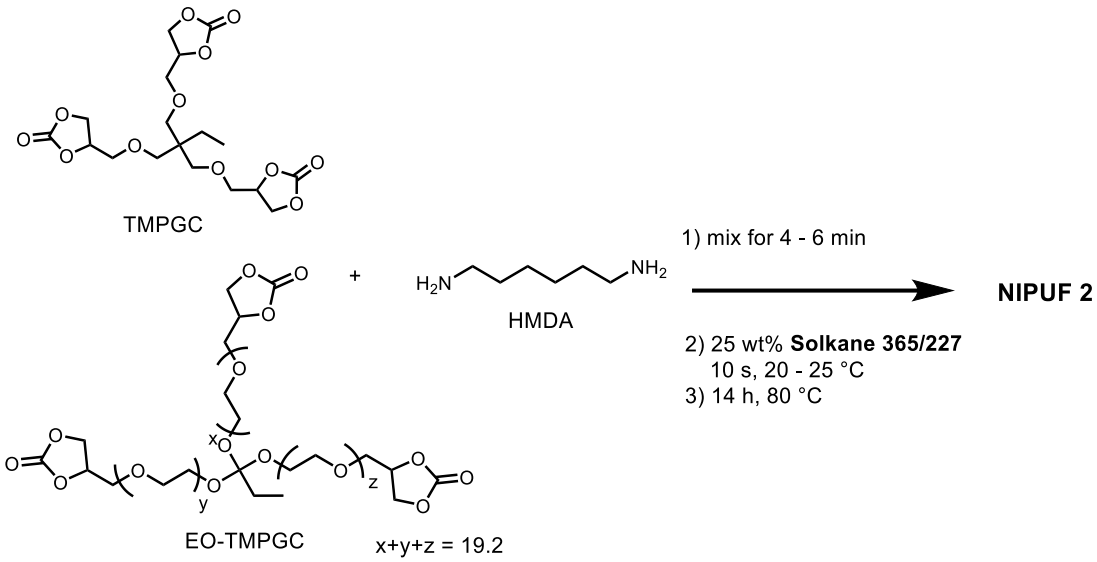
Hence, a comprehensive evaluation of foaming strategies, with a focus on the types of blowing agents, is essential for successful NIPU foaming.

2.3.1 Physical blowing

Physical blowing agents are highly volatile gas or liquid that are directly incorporated into the foam formulation under pressurized condition. These agents expand the polymer structure during depressurization or heating, resulting in the formation of a foamed structure. CO_2 has been preferred as physical blowing agent because it is inert, stable, low toxicity, zero ozone-depletion potential, low GWP (GWP = 1), and low cost as compared to other gasses. Grignard et al. prepared low-density microcellular **NIPUF 1** using supercritical CO_2 ($scCO_2$) as physical blowing agent (Scheme 6).[96] First, polyethylene glycol (PEG) or soybean oil-based cyclic carbonates were synthesized by reacting epoxides with CO_2 (10 bar) at 80 °C for 35 min with terabutylammonium iodide (TBAI) or TBAB as the catalyst (2.5 mol%) and 1,3-bis(hydroxyhexafluoroisopropyl) (HBD) as hydrogen bond donor activator (TBAI or TBAB to HBD = 1). Following this, the linear NIPU were prepared from melt polymerization of cyclic carbonates and fatty-acid based amines at 120 °C for 3 h. The prepolymers were saturated with CO_2 at 300 bar and 40 °C through $scCO_2$ impregnation for 3 h, followed by a rapid depressurization at 0 °C. The low temperature during depressurization allowed the impregnated CO_2 to stay in the NIPU for a short time. Next, the CO_2 saturated NIPU was heated to a temperature (80 – 100 °C) that is close to the melting temperature of polymer to allow efficient foaming by CO_2 to obtain **NIPUF 1** with low density (0.110 – 0.176 g/cm^3). The foam structure was stabilized by cooling in ice/water bath. In this study, the NIPU was not crosslinked because the partial/complete crosslinking will prevent the structure expansion during foaming. **NIPUF 1** has low T_g at-5 to -6 °C and melting point (T_m) at 87 – 89 °C owing to the presence of oligoamide as a comonomer. Overall, this post-polymerization foaming process is energy intensive and requires pressurized equipment for $scCO_2$.



Scheme 6. Synthesis of biobased **NIPUF 1** by supercritical CO_2 ($scCO_2$) method.[96]



Scheme 7. Synthesis of **NIPUF 2** by using hydrofluorocarbon as physical blowing agent.[79]

Chlorofluorocarbons (CFCs) were widely used as physical blowing agent in the PUF production in the late 1950s owing to their low cost, high chemical and thermal stability. After discovery of ozone-depleting effect of CFCs, hydrochlorofluorocarbons (HCFC) were used as alternative physical blowing agent owing to its lower ozone depletion potential. Lauth et al. studied the use of Solkane 365/227, a HCFC as physical blowing agent to prepare **NIPUF 2** (Scheme 7).[79] Mixtures of TMPGC and EO-TMPGC were reacted with stoichiometric amounts of hexamethylenediamine (HMDA) in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO,1 wt%) and Solkane 365/227 (25 wt%), which has a boiling point at around ~30 °C. The formulation was cured at 80 °C for 14 h to obtain **NIPUF 2** (Figure 4) with low density (0.142 – 0.219 g/cm^3) and low compression moduli (0.017 MPa). The increase in ratio of TMPGC/EO-TMPGC in the foam formulations resulted in flexible foams with increasing T_g from -37 °C to 27 °C. This foaming

technology has been patented.[97] It is noted that Hybrid Coatings had filed a patent on sprayable hybrid NIPUF based on hydroxycarbamate-amine system where HCFC was used as physical blowing agent in 2013.[98] Yet, the main issue for HCFCs to be used as physical blowing agent is their high GWP, making them unsuitable as a sustainable solution. Recently, hydrofluoroolefins were proposed as physical blowing agent with zero ozone-depletion potential and low global warming potential.[99] However, their cost is high and the substitution of HCFCs by hydrofluoroolefins may not be economically viable for industries.

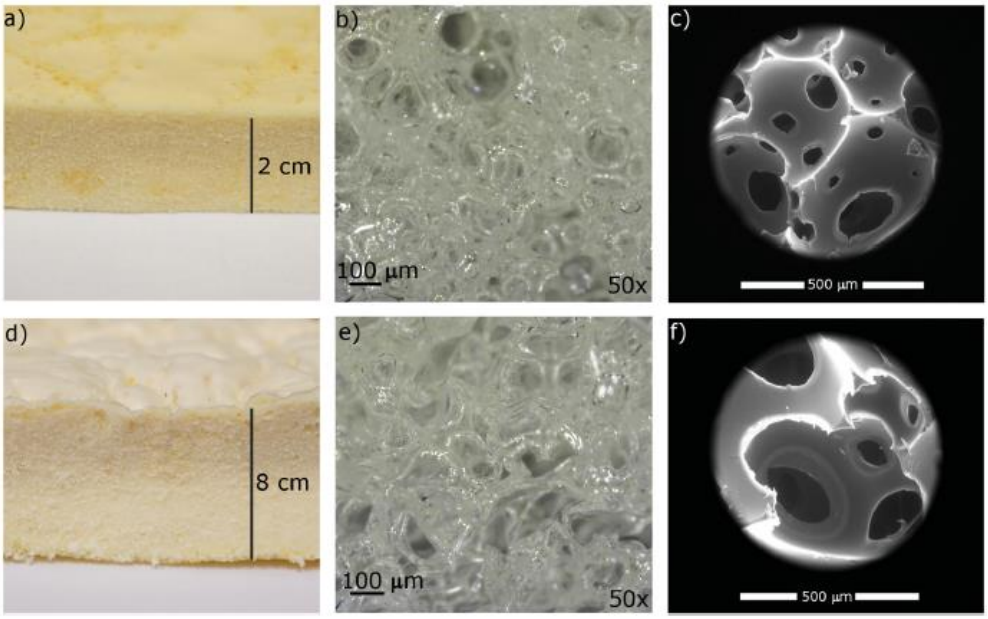
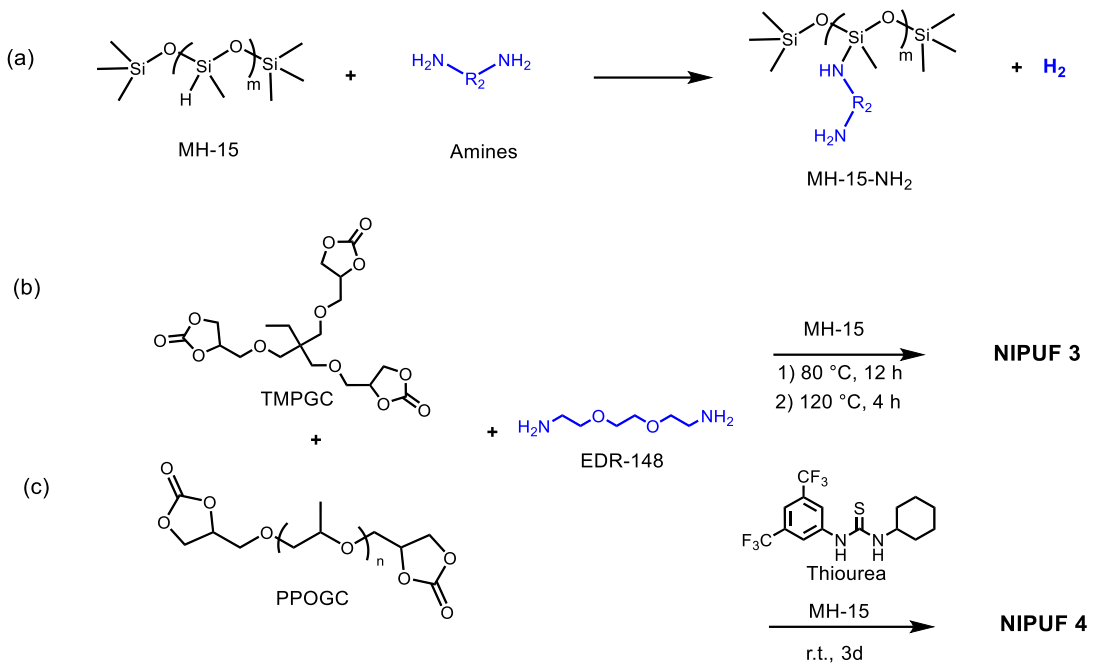


Figure 4. Images (a and d), optical microscopic images (b and e), and SEM images (c and f) of high-density (top row) and low-density (bottom row) **NIPUF 2**. Reproduced with permission from Lauth et al.[79] Copyright [2016] [John Wiley & Sons, Inc]

2.3.2 Chemical-/Self-blowing



Scheme 8. (a) Generation of hydrogen gas by reacting poly(methylhydrogenosiloxane) (Momentive MH-15) with amines. (b) **NIPUF 3** was prepared by using MH-15 as blowing agent at 80 – 120 °C,[100] while (c) **NIPUF 4** was prepared at room temperature in the presence of thiourea catalyst.[77]

In 2015, Cornille et al. reported the first self-blown **NIPUF 3** by utilizing the reaction of a mild reducing agent, poly(methylhydrogenosiloxane) (Momentive MH-15) and amines (Scheme 8a) to produce hydrogen gas for foaming purpose.[100] MH-15 had been widely used as foaming agent for preparing epoxy-based foams.[101] In their study, TMPGC was used as crosslinker and PPOGC with poly(propylene oxide) backbone was used as extender for improving the flexibility of crosslinked polymer structure (Scheme 8b). Jeffamine EDR-148 was polymerized with TMPGC/PPOGC at 80 °C to provide a crosslinked structure with improved flexibility owing to its oxyethylene group. Meanwhile, MH-15 was reacted with excess amount of EDR-148 in the formulation to release hydrogen gas that resulted in expanded foam structure. The foam was further cured at higher temperature at 120 °C for 4 h in the presence of TBD as catalyst to achieve high conversion. It was found that the **NIPUF 3** (Figure 5) exhibited apparent densities ranging from 0.194 to 0.295 g/cm^3, T_g ranged from -18 to 19 °C, and a mechanical strength (σ) reaching up to 0.03 MPa.

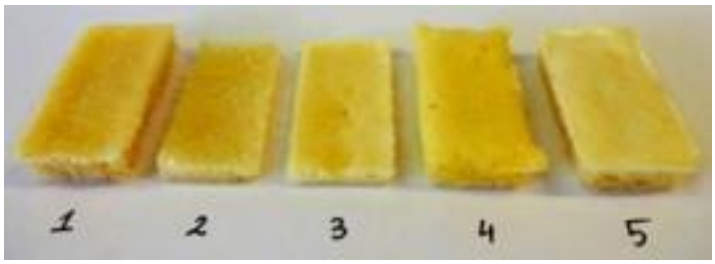
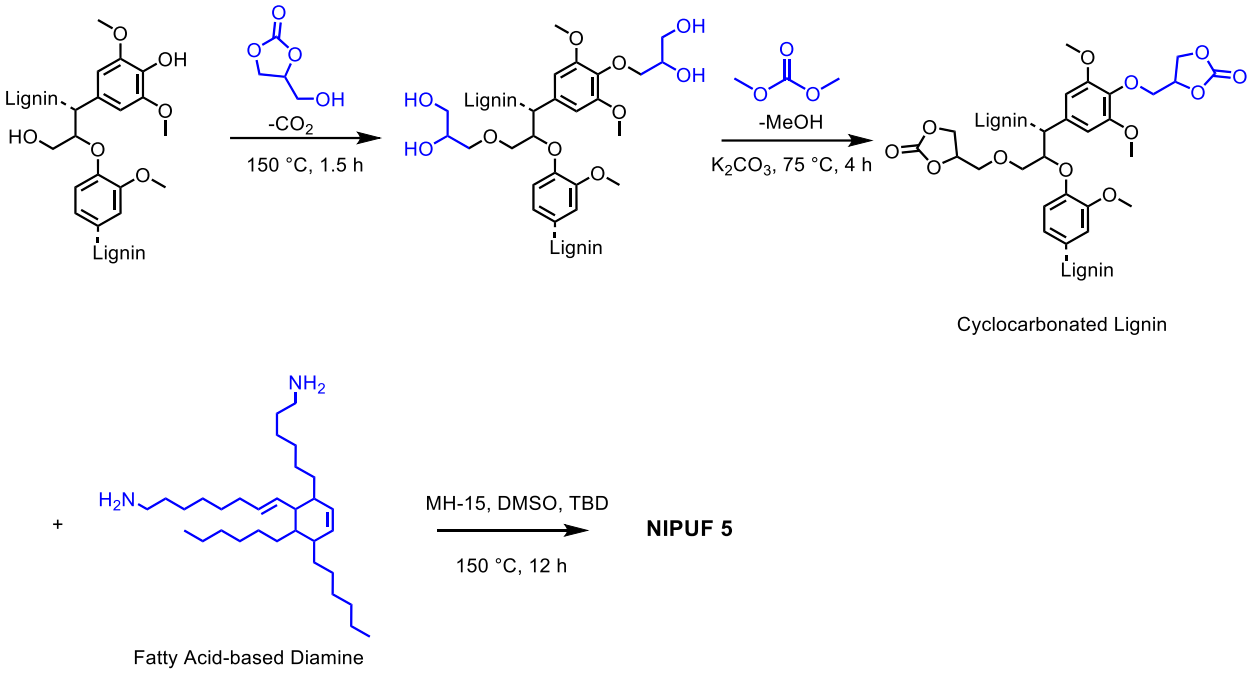


Figure 5. Picture of the **NIPUF 3.** Reproduced with permission from Cornille et al.[100] Copyright [2015] [Elsevier Ltd]

Cornille et al. had further improved the reactivity of cyclic carbonates and amines by adding 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea as catalyst in the foam formulation (Scheme 8c).[77] It was reported that the two NHs of thiourea prefers to form 6-membered ring with CO of the cyclic carbonate via hydrogen bonding, thereby increasing the reactivity of cyclic carbonates.[102] In addition, thiourea was more effective catalyst as compared to TBD in several ways[102]: 1) less impurities were formed, 2) low loading (1 mol% relative to cyclic carbonate) to achieve higher monomer conversion (~75%), and 3) better solubility in the foam formulation. In this study, TMPGC and PPOGC were reacted with EDR-148 in the presence of thiourea and MH-15 at room temperature for 3 d to obtain low-density **NIPUF 4** (0.271 – 0.303 g/cm^3). The flexible monomer structures had resulted in foams with low T_g (0 to 11 °C) and good mechanical strength (0.89 MPa). Although the **NIPUF 4** can foam at room temperature, it still encounters a significant challenge - a prolonged curing time (>3 days) even with the presence of catalyst.



Scheme 9. Synthesis of lignin-based cyclic carbonates and its **NIPUF 5**.[103]

In recent decades, there has been increasing interest from both academia and industry in sourcing starting materials from biobased resources as part of a broader effort towards sustainability. Sternberg et al. had reported the synthesis of biobased **NIPUF 5** from biobased lignin-derived chemicals.[103] The phenols (soft nucleophile) of industrial grade Kraft lignin was first reacted with the methylene site of glycerol carbonate at 150 °C for 1.5 h, leading to the functionalization of lignin by vicinal diols after decarboxylation of the carbonate. This was followed by condensation of vicinal diols with dimethyl carbonate at 75 °C in the presence of potassium carbonate (K_2CO_3) to obtain cyclocarbonated lignin (Scheme 9). Next, a commercial biobased diamine (Priamine, Croda) derived from fatty acid was polymerized with cyclocarbonated lignin, while a small amount of MH-15 (1.5 – 3.0 % volume) was added for blowing reaction, followed by curing at 150 °C for 12 h. High temperature is generally required for viscous monomers with high molecular weights owing to the inaccessible reaction sites. As a result from the high degree of aromatic groups in lignin, the prepared **NIPUF 5** (Figure 6) with densities ranged from 0.241 – 0.337 g/cm^3 showed high T_g (84 – 94 °C) and high compression moduli (1.64 MPa) as compared to other NIPUF prepared from smaller and flexible molecules.

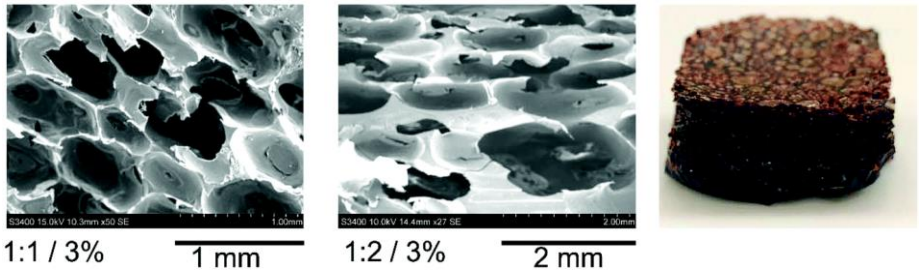
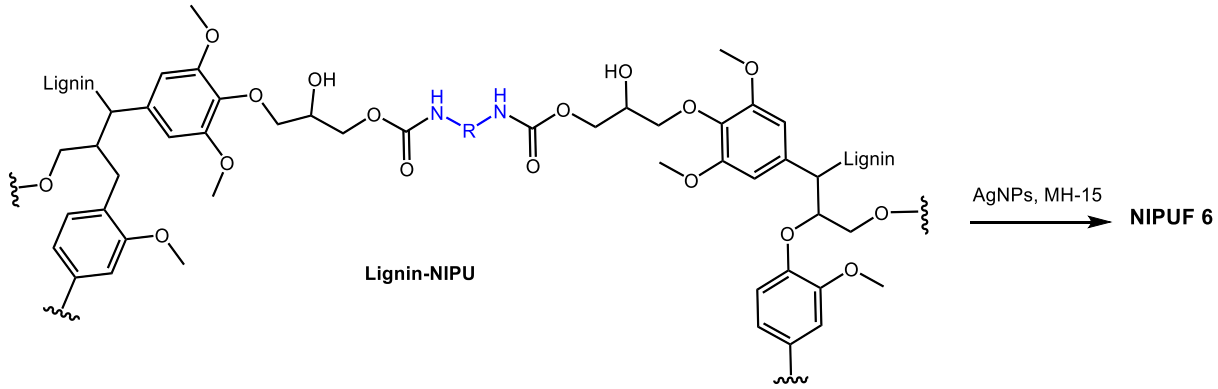
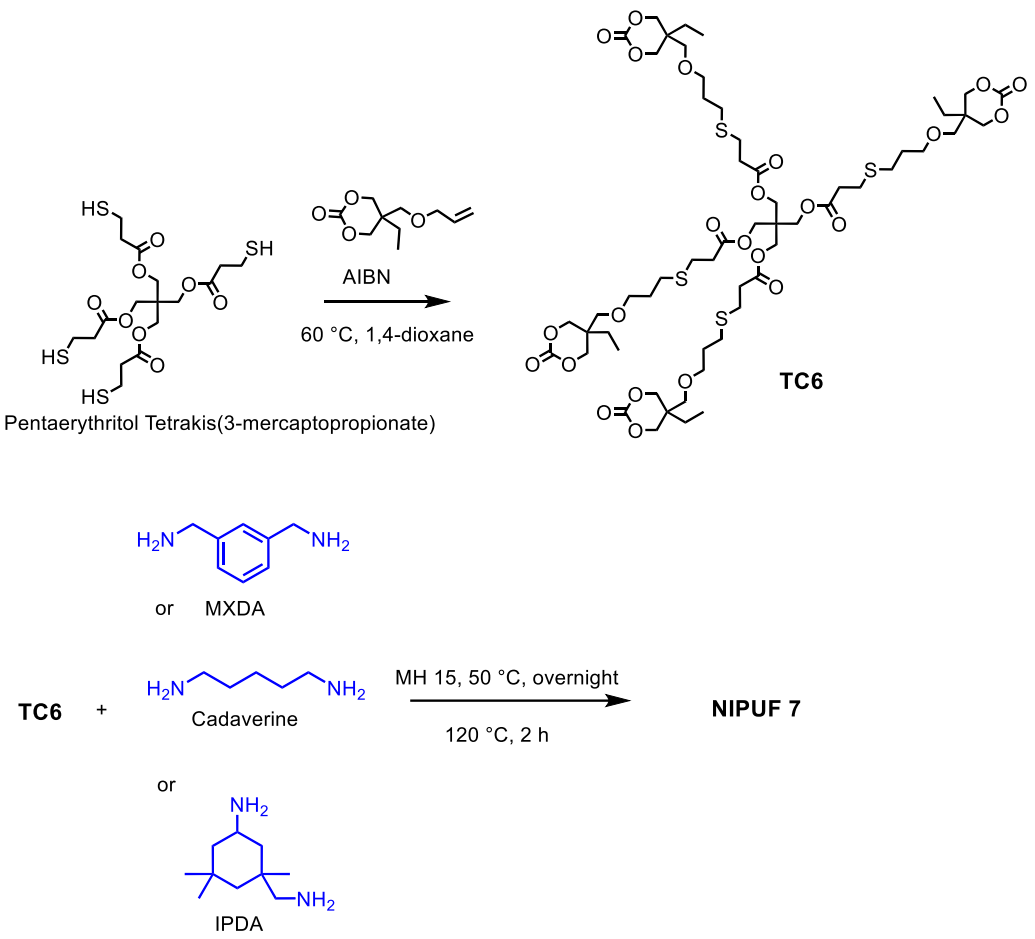


Figure 6. SEM and picture of **NIPUF 5**. Reproduced with permission from Sternberg et al.[103] Copyright [2020] [RSC Publishing]



Scheme 10. Synthesis of lignin-based **NIPUF 6** incorporated with silver nanoparticles for anti-bacterial applications.[104]

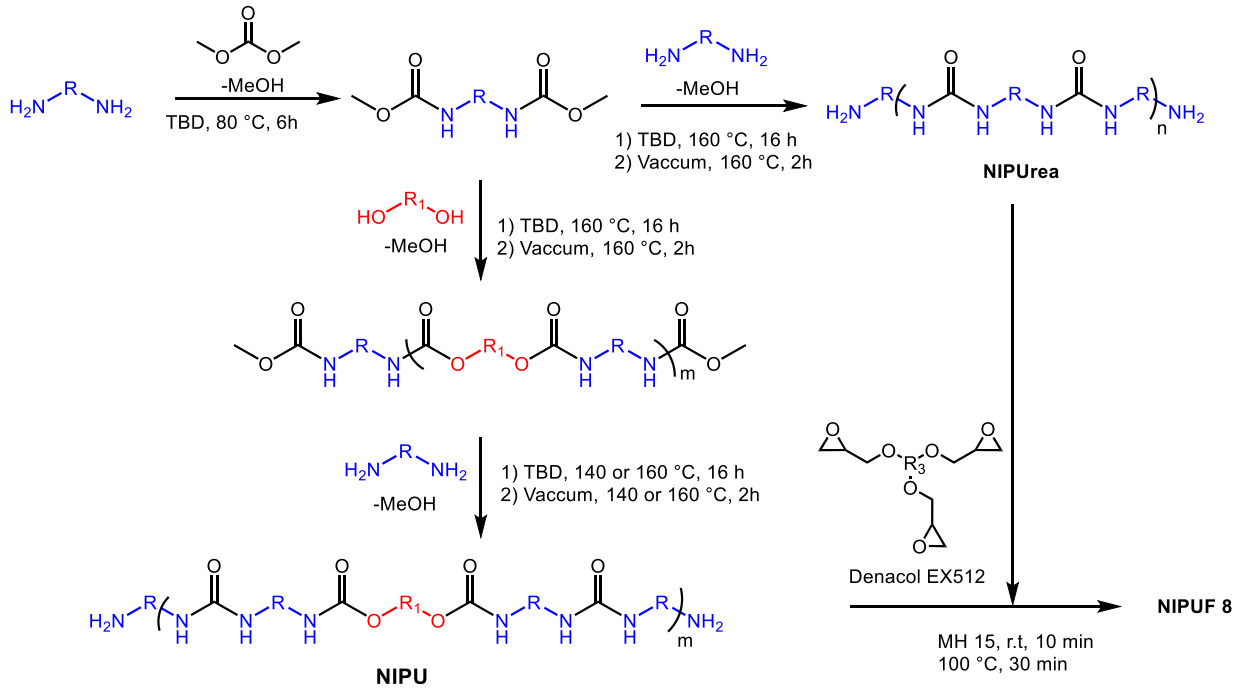
In a similar approach, Li et al. had prepared the lignin-based **NIPUF 6** by utilizing MH-15 as blowing agent (Scheme 10).[104] The cyclocarbonated lignin was reacted with polyetheramine in dimethylsulfoxide (DMSO) with MH-15 (3 vol% of the total reactants) at 150 °C for 12 hr. Silver nanoparticle solution was incorporated into the foams as antimicrobial agents. However, the foam only exhibits low compression strength (up to 205 kPa at 50% strain). In general, lignin-based NIPUF require energy-intensive preparations (high temperature for long curing) and DMSO for dissolution of monomers prior to foaming. It is important to note that the properties of lignin-based polymers exhibit significant variability due to the wide polydispersity index (PDI) of lignin precursors. Additionally, these precursors often lead to the formation of black or dark brown foams upon curing at high temperatures. This may present a significant challenge for industries that prioritize the aesthetic appearance of foams in consumer products.



Scheme 11. Synthesis of tetra-functional 6-membered cyclic carbonate (TC6) and **NIPUF 7**.[105]

High curing temperatures (>50 °C) are often necessary for NIPUF due to the inherently low reactivity of 5-membered cyclic carbonates, even when catalyzed. One approach to resolve this reactivity issue is to use 6-, 7-, and 8-membered cyclic carbonates with higher reactivity towards aminolysis owing to the ring strain.[106-109] For example, Tomita et al. showed that the 6-membered cyclic carbonate is 29 to 62 times more reactive than 5-membered cyclic carbonate when reacted with hexylamine or benzylamine in catalyst-free conditions.[108] This indicates a possibility of getting NIPUF at lower or ambient temperature. Following this concept, Coste et al. had prepared **NIPUF 7** by reacting a tetra-functional 6-membered cyclic carbonate (TC6) with diamines, and MH-15 at 50 °C in catalyst-free condition (Scheme 11).[105] The 6-membered cyclic carbonate bearing an allyl group was derived from reaction of trimethylolpropane allyl ether and ethyl chloroformate. The thiol-ene addition of pentaerythritol tetrakis(3-mercaptopropionate) with this

6-membered cyclic carbonate in presence of azobisisobutyronitrile (AIBN) at 60 °C for 16 h to obtain the TC6 in 87% yield. Next, it was shown that the NIPUF can be obtained at milder condition (50 °C) by using the more reactive TC6 in the foam formulation. **NIPUF 7** with densities ranged from 0.170 – 0.530 g/cm^3 showed high T_g (7 to 27 °C) and compression strength of up to 0.21 MPa. However, the preparation of 6-membered cyclic carbonate required toxic reagent such as ethyl chloroformate to synthesize TC6.[110]. Diphenyl carbonate-based route could be a better alternative, but this route typically requires higher temperature (140 °C) for preparing 6-membered ring cyclic carbonate.[111]

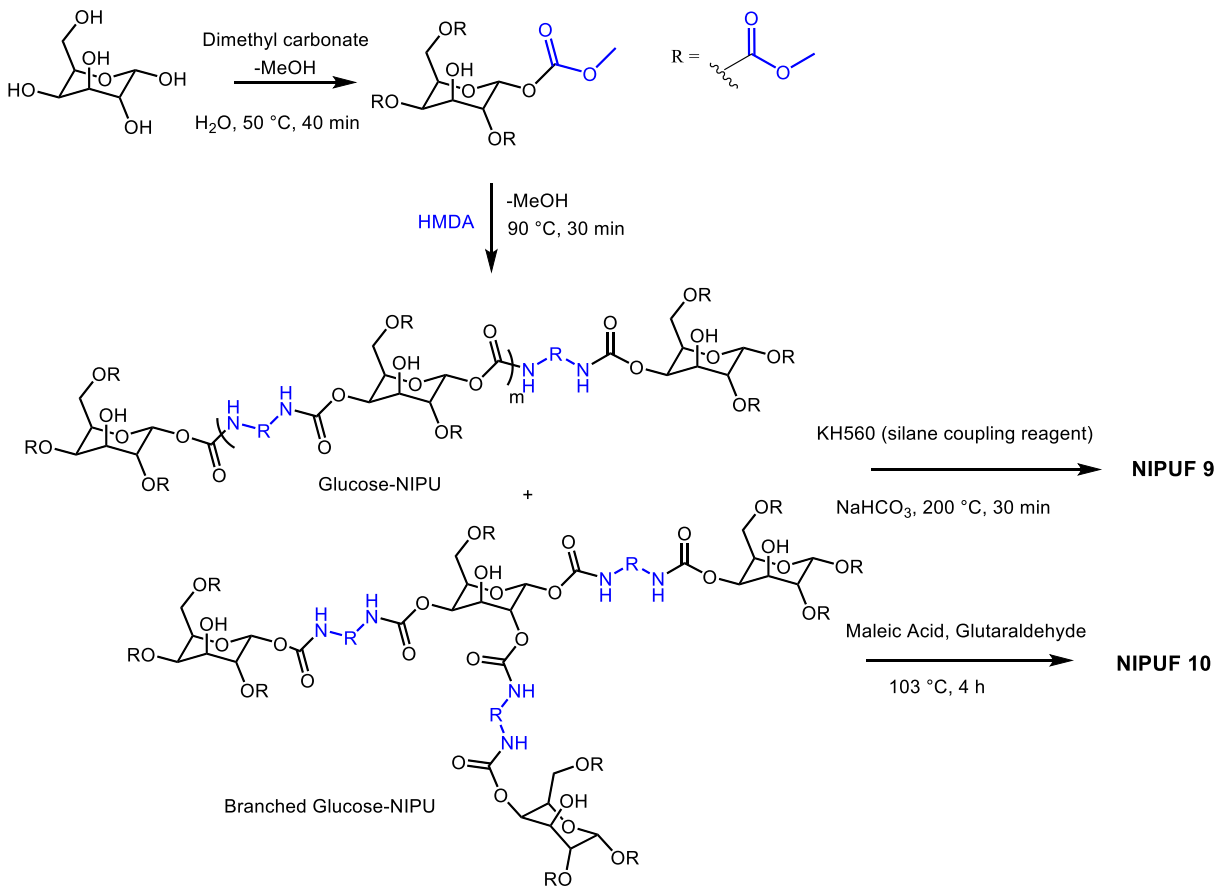


Scheme 12. Synthesis of NIPUrea and NIPU by transurethanization. The prepolymers were reacted with Denacol EX512 in presence of MH15 for **NIPUF 8**.[112]

Recently, Valette et al. has studied transurethanization approach to prepare hybrid flexible **NIPUF 8**.[112] Amino-terminated NIPU or NIPUrea oligomers with high urea/urethane ratio ranged from 0.85/0.15 to 0.64/0.36 were pre-synthesized by transurethanization between fatty acid-based dimethyl dicarbamate and diol or diamine at high temperature (160 °C) under vacuum (Scheme 12) in an effort to remove methanol as by-product. The oligomers were then reacted with a polyepoxide crosslinker (Denacol EX512) in the presence of MH-15 at r.t for 10 mins, followed

by 100 °C for 30 mins to afford a hybrid flexible high density **NIPUF 8** (density of 0.13 – 0.40 g/cm^3). The foams exhibited low T_g (-28 to -10 °C) owing to the flexible fatty acid structures, which lead to low modulus (E) of 0.01 – 0.06 MPa of the foam. It is appealing to consider MH-15 as suitable foaming agent for preparing NIPUF due to its high reactivity with amines at room temperature, commercial availability, good miscibility with foam formulation, and good storage stability. Nonetheless, the shortcoming is the generation of flammable hydrogen gas that is potentially hazardous in large-scale foam production. Therefore, it would be great interest to look for other foaming agents that release inert gas such as CO_2.

Xi et al. reported the preparation of glucose-based rigid **NIPUF 9** by utilizing sodium bicarbonate ($NaHCO_3$), which produced CO_2 after self-decomposition at high temperature (Scheme 13).[113] A NIPU prepolymer was prepared by two-step approach – 1) a reaction between glucose and dimethyl carbonate at 50 °C for 40 mins, 2) a reaction with hexamethylenediamine (HMDA) at 90 °C for 30 min. This reaction yielded both linear and branched NIPU prepolymers with terminal hydroxyl groups that were further crosslinked with KH560 (a silane coupling reagent) at room temperature to allow partial crosslinking prior to foaming. Foaming was initiated by heating the gel-like mixture at 200 °C for 30 mins to afford dark black **NIPUF 9** (Figure 7). Low-density foams (0.088 – 0.127 g/cm^3) with low compression strength (0.2 MPa) were obtained by shortening the resting time from 150 mins to 90 mins prior to foaming. Nonetheless, such high temperature (200 °C) could cause excessive oxidation and degradation to the polymer, resulting in undesirable properties and poor foam appearance.



Scheme 13. Preparation of glucose-based **NIPUF 9** and **NIPUF 10**.[113-114]

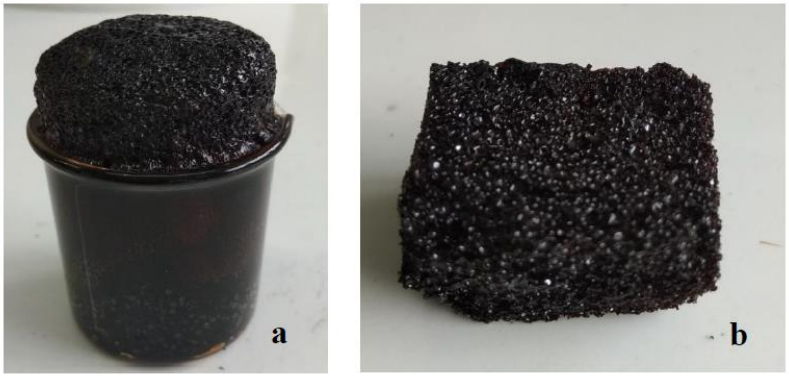
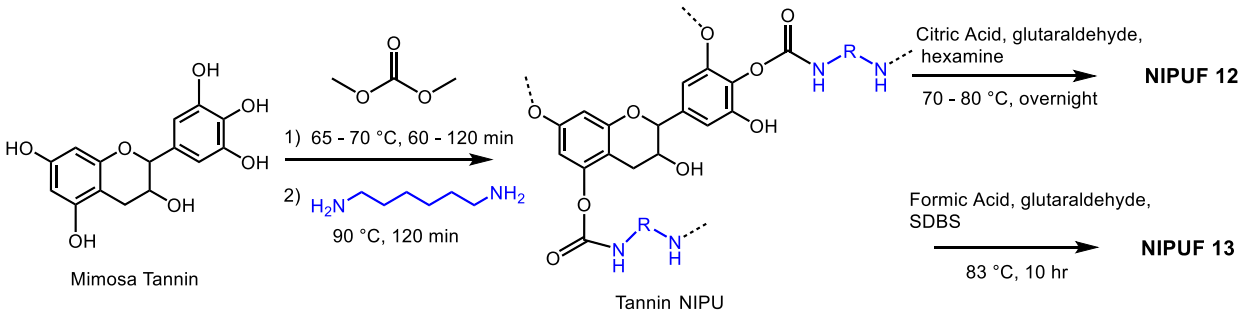


Figure 7. Photos of **NIPUF 9** (a in the mold, b after cutting it). Reprinted with permission under a Creative Commons 4.0 license from Xi et al.[114] Copyright [2019] [MDPI].

Similarly, maleic acid and glutaraldehyde were used as chemical blowing agents to prepare **NIPUF 10** (Scheme 13).[114] The NIPU mixture was allowed to rest at room temperature for 5 h prior to drying at 103 °C for 4 h to afford the black **NIPUF 10** with low density (0.08 – 0.13 g/cm^3) and low compression strength (0.4 MPa). Notably, a higher amount of maleic acid used in the foam formulation had resulted in a lower-density foam. Yet, the role of maleic acid remains unclear in the foaming mechanism.

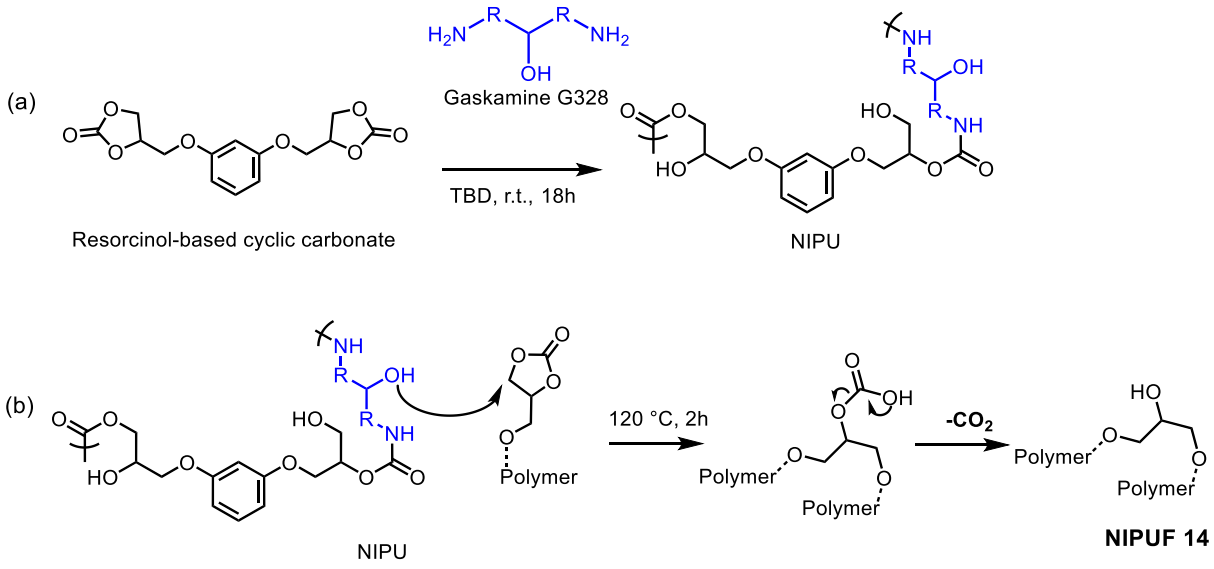
Vlcek et al. recently reported the preparation of hybrid **NIPUF 11** by chemical blowing method.[115] The exact structures of cyclic carbonates, amines, and blowing agent were not revealed. Briefly, a mixture of two cyclic carbonates was reacted with two aliphatic/cycloaliphatic/branched amines to give a NIPU prepolymer, which was further crosslinked with biobased epoxides in the presence of chemical blowing agent to afford low-density **NIPUF 11** (0.078 g/cm^3) with high T_g (58 °C) and low compression strength (0.1 MPa) after curing at 50 °C for 3 h and 70 °C for 15 h.



Scheme 14. Citric acid or formic acid combined with glutaraldehyde were used to prepare tannin-based **NIPUF 12** and **NIPUF 13**.[116-117]

Chen et al. reported a rigid tannin-based **NIPUF 12** by using a mixture of citric acid and glutaraldehyde as blowing agent (Scheme 14).[116] The gallic acid moiety of tannin had been reported to undergo carbonation with dimethyl carbonate, as confirmed by solid-state cross-polarization magic angle spinning carbon 13 nuclear magnetic resonance (CP/MAS ^{13}C NMR).[118] In this study, the tannin-based NIPU was first synthesized by reacting mimosa tannin with dimethyl carbonate at 65 – 70 °C for 120 min, and followed by the reaction with HDMA at 90 °C for 120 min. The tannin-based prepolymer was mixed with both hexamine and a solution of citric

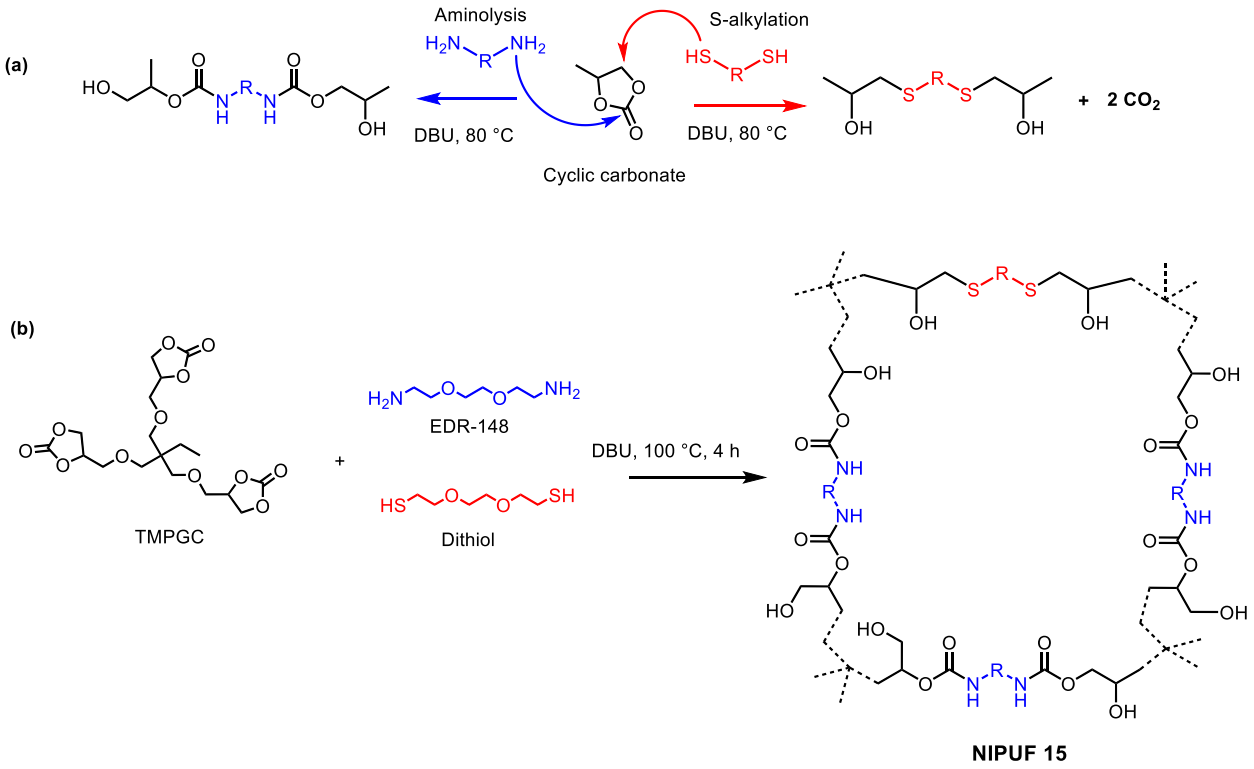
acid and glutaraldehyde in water at room temperature. The formulation was left at room temperature for foaming prior to curing at 70 – 80 °C overnight to obtain a rigid **NIPUF 12**. It was found that the reaction between citric acid and hexamine or tannin prepolymer resulted in the expansion of liquid formulation. The simultaneous crosslinking of tannin-based prepolymer with glutaraldehyde had formed a self-supporting foam structure with moderate density (0.12 – 0.26 g/cm^3) and low compression strength (0.57 MPa) at room temperature. A similar approach was also reported by Zhao et al. to prepare tannin-based **NIPUF 13** by using formic acid as initiator and glutaraldehyde as crosslinker (Scheme 14).[117] The foams with low density (0.22 – 0.41 g/cm^3) were obtained after curing at 83 °C for 10 hr. it was found that the aromatic groups in the tannin have contributed to the high compression strength (0.82 MPa) as compared to non-aromatic NIPUF.



Scheme 15. Preparation of resorcinol-based (a) cyclic carbonates and (b) **NIPUF 14**.[119]

Anitha et al. reported the self-blown resorcinol-based **NIPUF 14,** which involves the decarboxylation of cyclic carbonate at high temperatures. (Scheme 15b).[119] The resorcinol-based cyclic carbonate was obtained by CO_2 insertion (12 bar) of 1,3-diglycidyloxybenzene at 100 °C for 12 h. Gaskamine G328, a diamine with hydroxyl group was used to polymerize with resorcinol-

based cyclic carbonate at r.t for 18 h, followed by 120 °C for 2 h in the presence of TBD (Scheme 15a). It was found that the hydroxyl group will compete with amines to form beta-hydroxyether linkage with cyclic carbonate, followed by CO_2 release at high temperature for foaming as confirmed by fourier transform infrared spectroscopy (FTIR). A high-density **NIPUF 14** (0.48 g/cm^3) with low T_g (7 °C) was obtained from this process. The conversion of decarboxylation reaction and CO_2 evolution efficiency at high temperature were not mentioned in the study.



Scheme 16. (a) Aminolysis and S-alkylation of cyclic carbonate. (b) Preparation of **NIPUF 15** based on S-alkylation.[120]

Monie et al. described an interesting two-step approach to prepare a self-blown **NIPUF 15** by utilizing the decarboxylative S-alkylation reaction with thiols.[120] A softer nucleophile like thiol undergoes alkylation with the methylene carbon of the cyclic carbonate (Scheme 16a), resulting in a carbonyl-free product and the release of CO_2. This process generally requires high temperature (100 – 180 °C).[121] It was shown that the DBU had accelerated decarboxylation of cyclic carbonate

with conversion up to 90% after heating at 80 °C for 1 h. TMPGC was mixed with both EDR-148, dithiols, and DBU at room temperature for 16 h, followed by foaming and curing at 100 – 120 °C for a few hour (Scheme 15 b) to obtain **NIPUF 15** (Figure 8). It was discovered that a partial polymerization at room temperature for 16 h was required to increase viscosity for efficient foaming. Low-density **NIPUF 15** (0.166 to 0.210 g/cm^3) with low T_g (2.4 to 7.9 °C) and low compression strength (0.01 MPa) were obtained by varying the ratio between crosslinker, diamines, and dithiols, and addition of additives such as synthetic clay or poly(dimethylsiloxane).

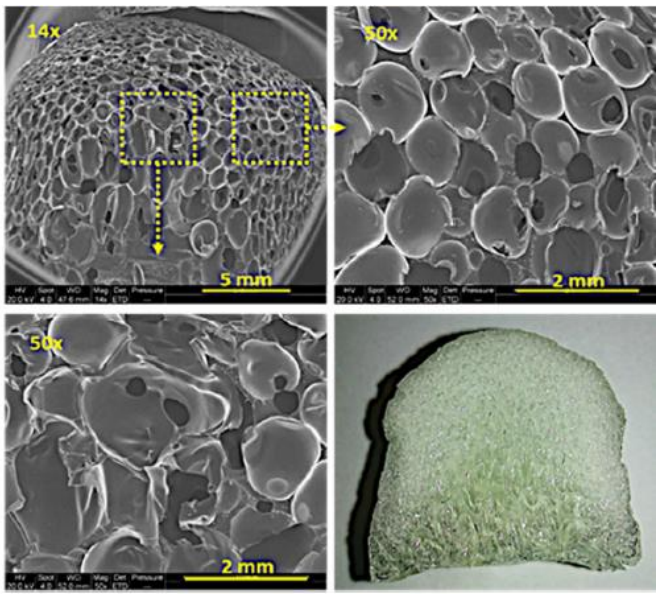
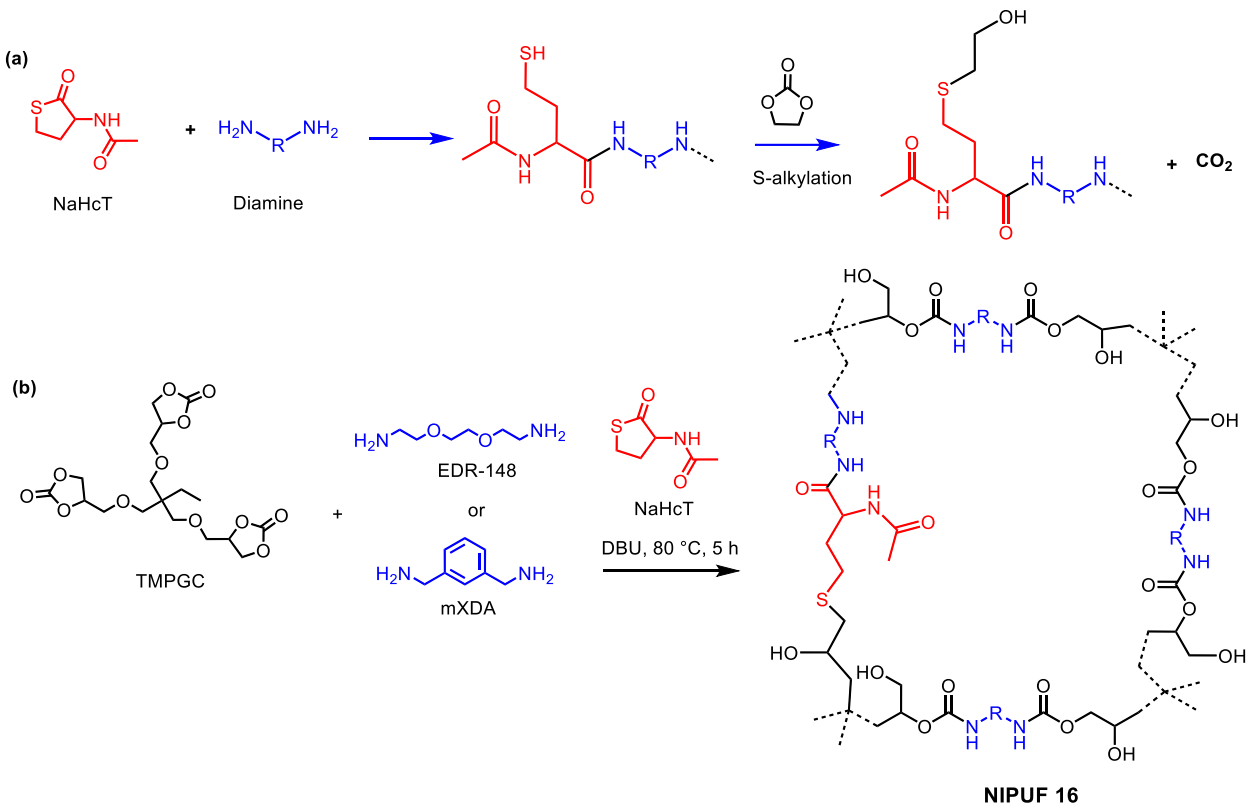
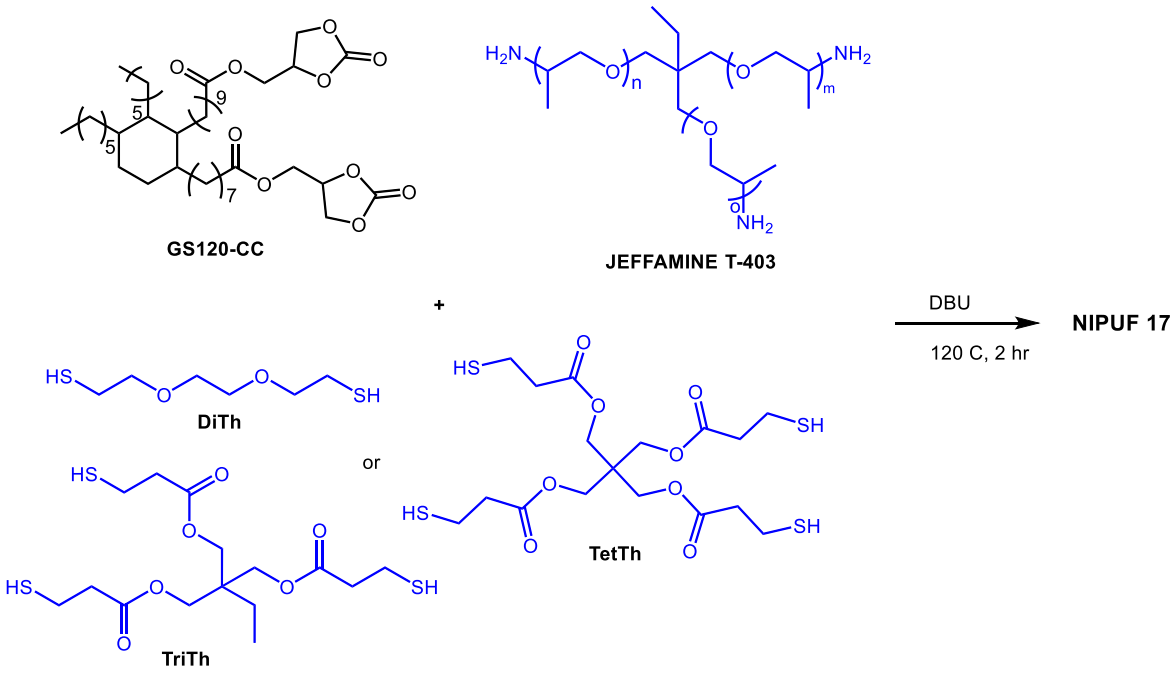


Figure 8. SEM images and photo of **NIPUF 15**. Reproduced with permission from Monie et al.[120] Copyright [2020] [John Wiley & Sons, Inc]



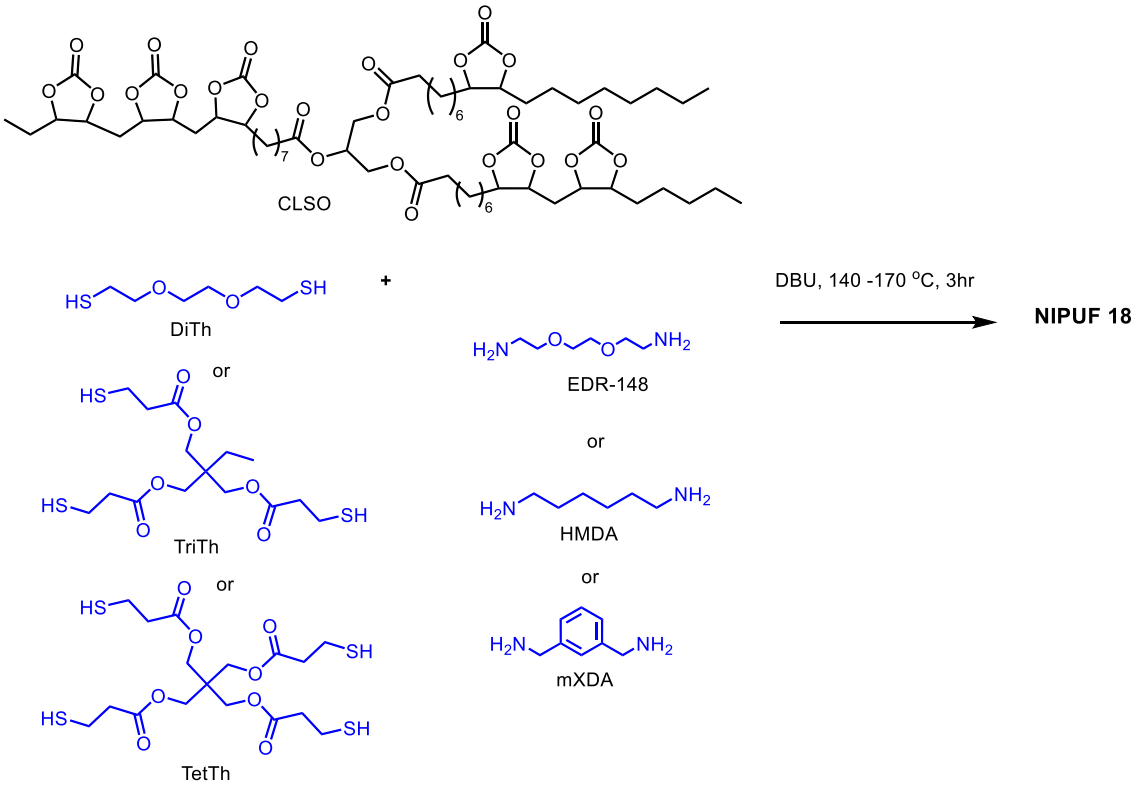
Scheme 17. (a) Cascade aminolysis and S-alkylation of NaHcT with ethylene carbonate for CO_2 generation. (b) Preparation of **NIPUF 16**.[122]

By using the similar concept, Monie et al. had reported a single-step foaming for NIPUF based on S-alkylation of cyclic carbonate in effort to reduce multistep procedure.[122] A latent thiol – commercial available N-acetylhomocysteine thiolactone (NaHcT) was aminolyzed by amines to create a reactive thiol, which could subsequently undergo S-alkylation with cyclic carbonate to generate CO_2 as by-product (Scheme 17a). The model reaction of NaHcT and ethylene carbonate showed that the yield of S-alkylated product was more than 95 % after 1 h heating at 80 °C in the presence of DBU as catalyst (Scheme 17b). **NIPUF 16** with low- to high-densities (0.167 to 1.15 g/cm^3) and high T_g (-25 to 43 °C) were obtained by reacting TMPGC, EDR-148 or m-xylenediamine (mXDA), and NaHcT (12.5 to 50 mol % with respect to mole of cyclic carbonate) in the presence of DBU at 80 °C for 5 h. The foam has compression moduli of 0.22 MPa and was able to be recycled into thermoset films via the transcarbamoylation of hydroxyurethane groups at 160 °C for 2 h.



Scheme 18. Preparation of **NIPUF 17** by generated CO_2 from the S-alkylation of cyclic carbonate.[123]

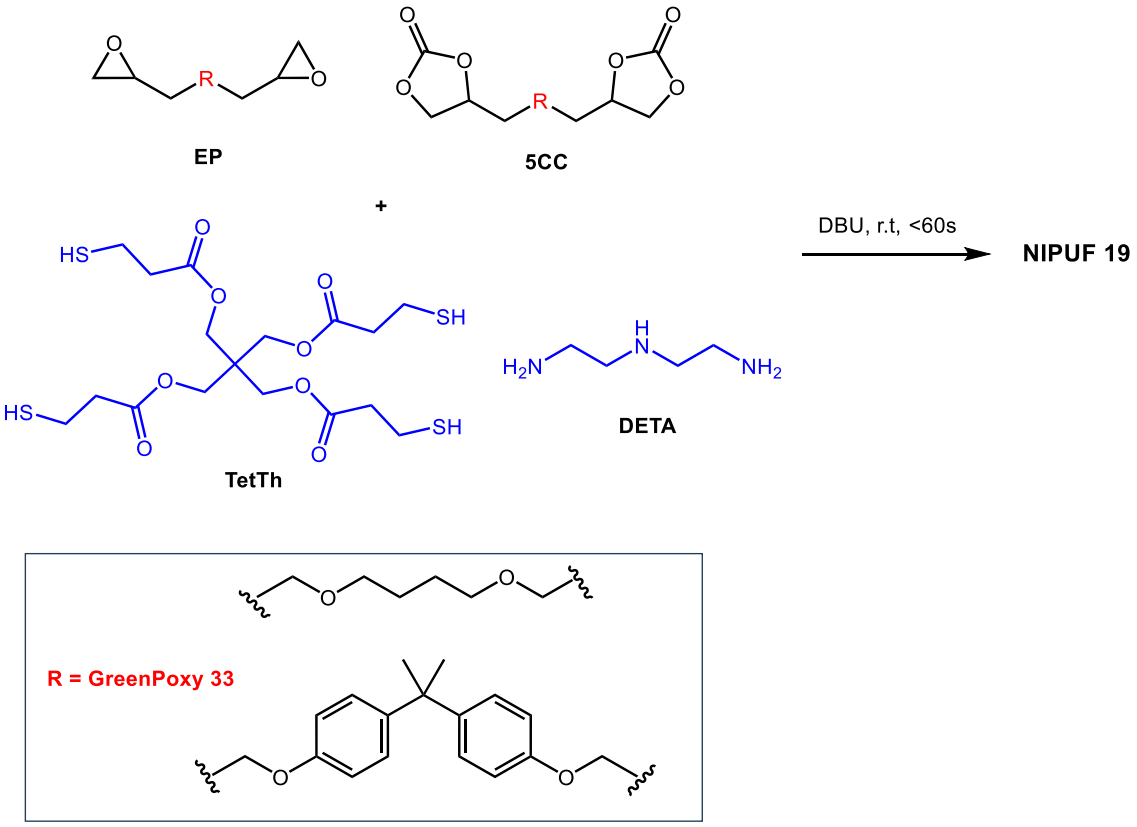
Recently, Purwanto et al. described a method for preparing self-blown **NIPUF 17** by utilizing CO_2 generated from the decarboxylation of cyclic carbonate through S-alkylation (Scheme 18).[123] The biobased cyclic carbonate GS120-CC was synthesized by CO_2 insertion of GS-120-epoxy derived from dimer acid. Next, the cyclic carbonate was reacted with trifunctional amine-telechelic poly(propylene glycol) (JEFFAMINE T-403) and dithiols (DiTh), tris-thiols (TriTh), or tetra-thiols (TetTh) at 120 °C in the presence of DBU for 2 h to obtain **NIPUF 17** with the density ranged from 0.29 to 0.31 g/cm^3. It was observed that the foams were soft with low T_g (-17 to -28 °C) owing to the incorporation of GS120-CC with long and flexible alkyl backbone. The foams exhibited low compression modulus of up to 0.037 MPa.



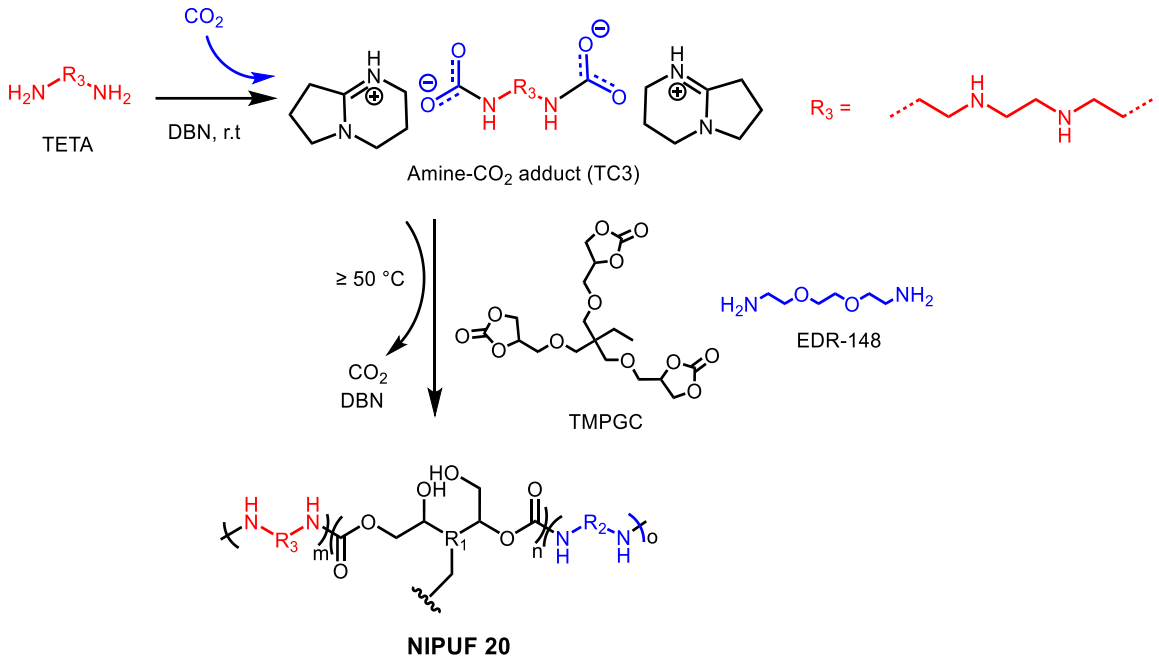
Scheme 19. Preparation of **NIPUF 18** by generated CO_2 from the S-alkylation of cyclic carbonate.[124]

Wang et al. also recently reported the preparation of linseed-oil based **NIPUF 18** via S-alkylation approach (Scheme 19).[124] The carbonated linseed oil (CLSO) was synthesized by CO_2 insertion of epoxidized linseed oil. The curing of CLSO with three different amines (EDR-148, HMDA, and mXDA) and three thiols (DiTh, TriTh, and TetTh) in the presence of DBU at 140 – 170 °C for 3 h gave the low-density foams (0.13 to 0.17 g/cm^3) with low T_g (-1.1 to 9.3 °C) and low compression strength (0.021 MPa). Similarly, Chaib et al. also reported self-blown hybrid poly(hydroxy-thioether-urethane) **NIPUF 19** through S-alkylation approach,[125] where foams were successfully produced at room temperature (Scheme 20). In this study, the biobased GreenPoxy 33 epoxy resin underwent partial carbonylation with CO_2 in the presence of tetrabutylammonium bromide (TBAB, 5 wt%) at 105 °C for up to 24 h, resulting in the carbonylated product with 85% conversion. It was found that the high reactivity between the non-converted epoxide, diethylenetriamine (DETA), and TetTh produced a significant exothermic heat of approximately 100 kJ/mol, which led to high temperature of formulation (75 °C in less than a min). This generated heat had resulted in: (1) higher ring-opening rate of cyclic carbonate, and (2) higher S-alkylation rate of cyclic carbonate

to generate CO_2 for foaming. To note, the resultant hybrid polymer foam had low urethane content as confirmed by FTIR analysis. These low-density **NIPUF 19** (0.16 to 0.20 g/cm^3) had high T_g (up to 39.2 °C). It was noted that the S-alkylation induced decarboxylation pathway had gained interests from different research groups to obtain NIPUF, but the biggest shortcoming was the pungent and unfriendly thiols required in this foaming process, which hinder their use in industrial scale production and their applications as consumer products.



Scheme 20. The reactive aminolysis of epoxy had resulted in the CO_2 generation after S-alkylation of cyclic carbonate to obtain **NIPUF 19**.[125]



Scheme 21. The preparation of **NIPUF 20** by CO_2 after aminolysis of amine-CO_2 adduct.[126]

Choong et al. described a method to prepare **NIPUF 20** by using an amine-CO_2 adduct that functions as both foaming agent and reactive monomer (Scheme 21).[126] The amine-CO_2 adduct was obtained after CO_2 bubbling of the mixture of triethylenetetramine (TETA) and 1,5-diazabicyclo(4,3,0)non-5-ene (DBN) at room temperature for 15 mins. It was shown that the amine-CO_2 adduct exhibited up to 87% CO_2 desorption after aminolysis with cyclic carbonate at 60 °C. The mild temperature for high CO_2 desorption was useful for foaming at lower temperature. **NIPUF 20** was synthesized through a reaction involving TMPGC, furan bis(cyclic carbonate), EDR-148, and the amine-CO_2 adduct at 50 – 80 °C for 24 h. The foams (Figure 9i and 9ii) have density ranged from 0.203 – 0.462 g/cm^3 and T_g of 14 – 24 °C.

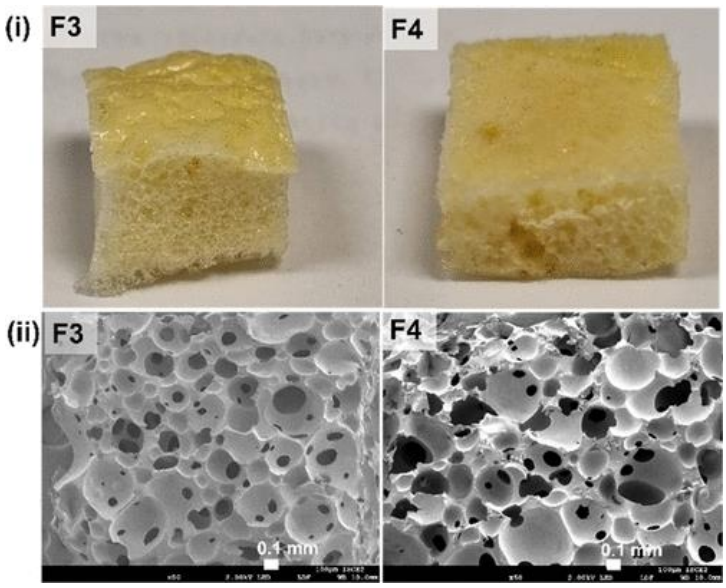
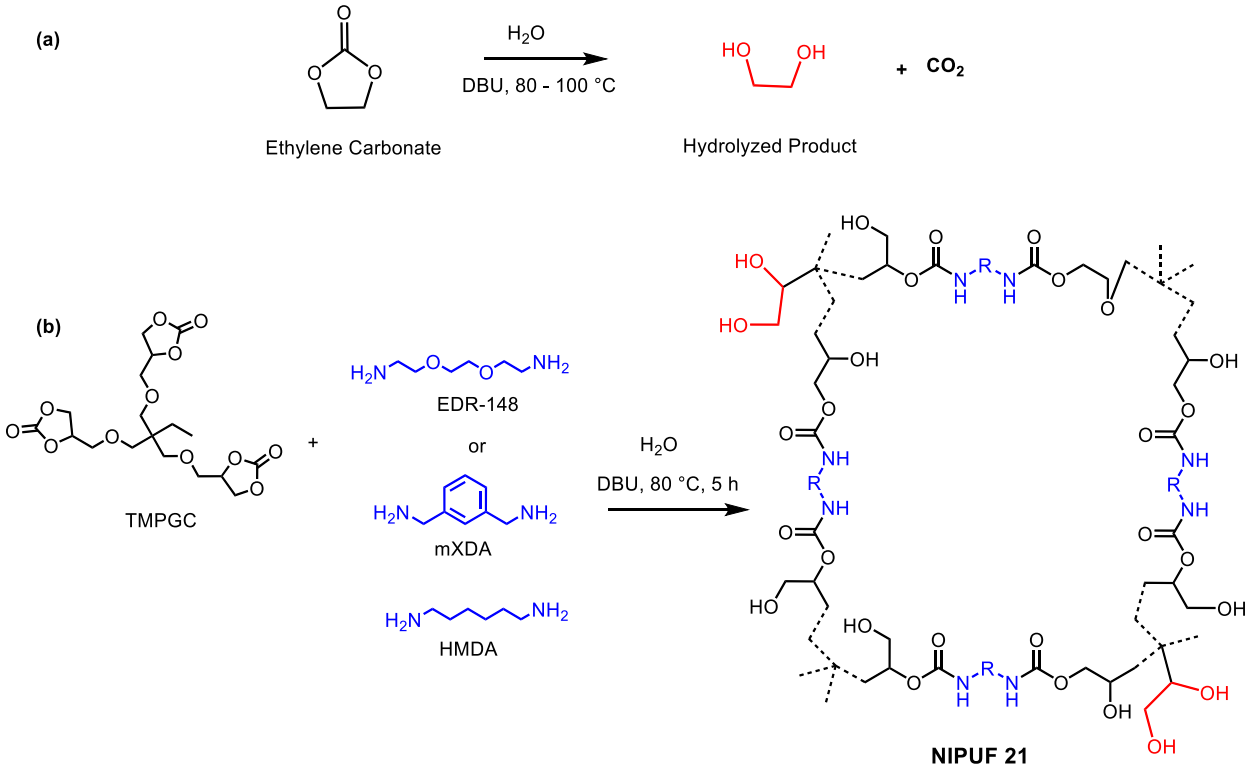


Figure 9. (i) Optical and (ii) SEM images of **NIPUF 20**. Reproduced from Choong et al.[126] Copyright [2023] American Chemical Society.



Scheme 22. (a) Hydrolysis of ethylene carbonate by water for CO_2 generation. (b) Preparation of **NIPUF 21**.[127]

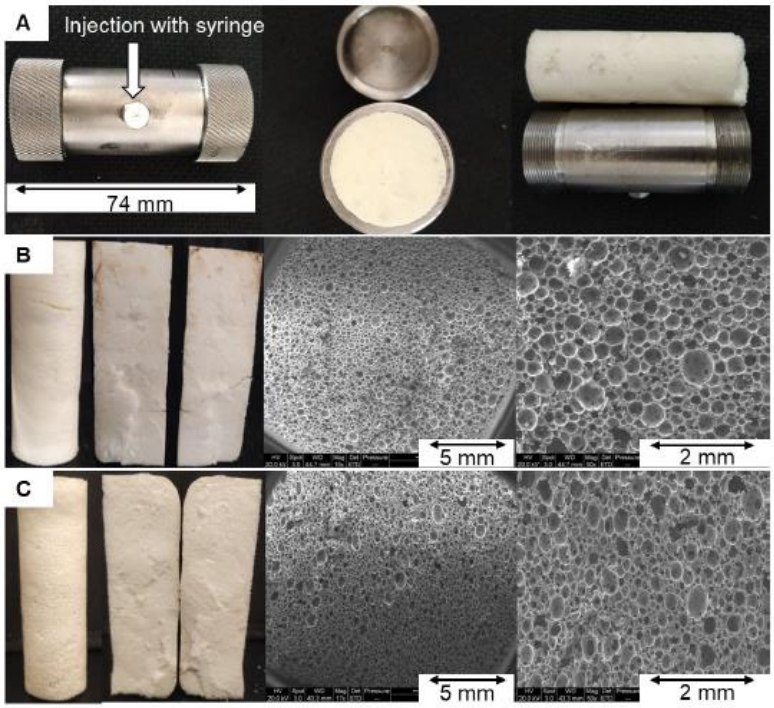
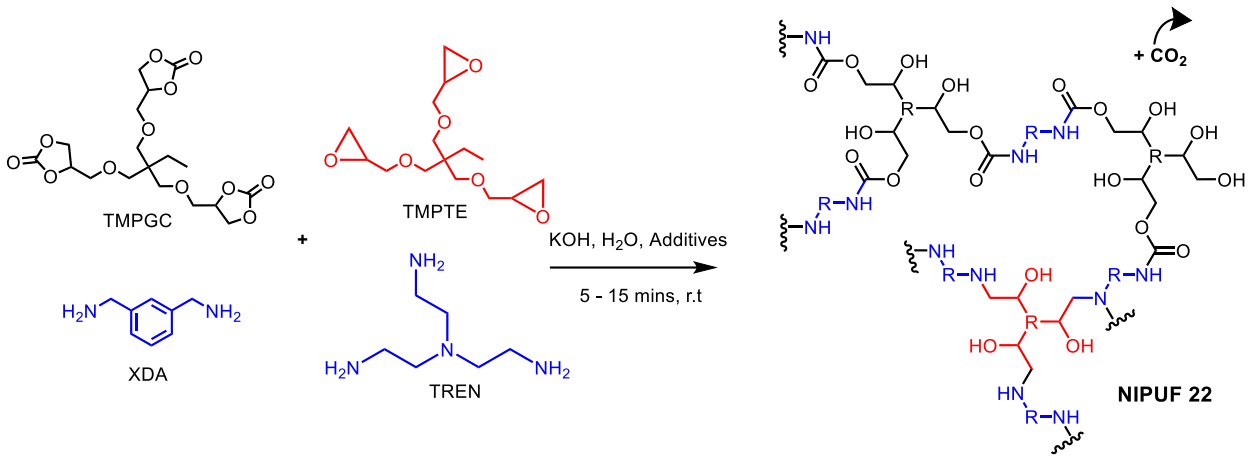


Figure 10. Image of A) closed mold foaming; B,C) **NIPUF 21** out of the mold and cut in two pieces with SEM images. Reproduced with permission from Bourguignon et al.[127] Copyright [2022] [John Wiley & Sons, Inc]

Recently, Bourguignon et al. reported the preparation of self-blown **NIPUF 21** by water-induced decarboxylation of cyclic carbonates that closely resembled the blowing mechanism of isocyanates and water (Scheme 22).[127] Model reaction showed that hydrolysis of ethylene carbonate to CO_2 can achieve 87% conversion after heating at 100 °C for 3 h (molar equivalent of ethylene carbonate/water = 1) in the presence of DBU (Scheme 22a). The reaction of TMPGC with various diamines (EDR-148, mXDA, or HMDA) at 80 – 100 °C for 5 h, with water (0.25 to 1 molar equivalent of cyclic carbonate) as foaming agent and DBU as catalyst (Scheme 22b), resulting in **NIPUF 21** with various density (0.153 – 0.963 g/cm^3) and T_g (-7 to 26 °C). The NIPUF also showed high compression moduli of up to 25.8 MPa and demonstrated the feasibility for being foamed in a closed mold (Figure 10). This work had so far mimicked the foaming process of conventional PU by using water as foaming agent for blowing NIPU.

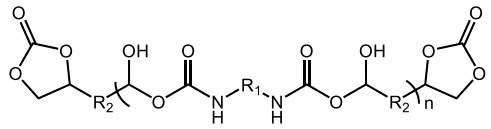
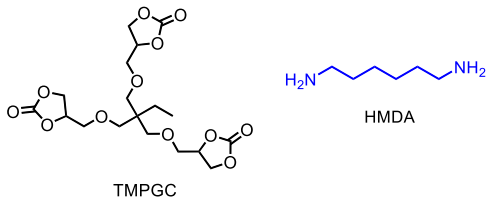
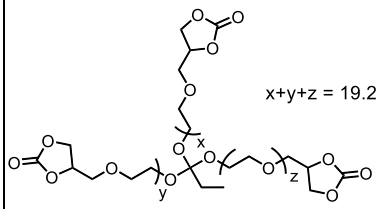
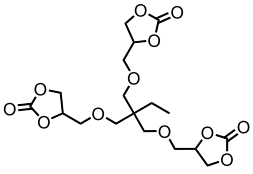
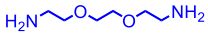
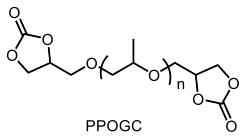


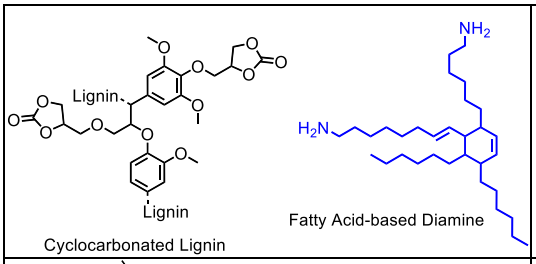
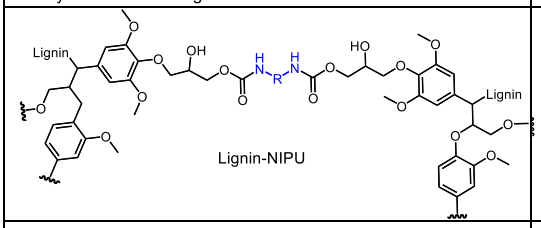
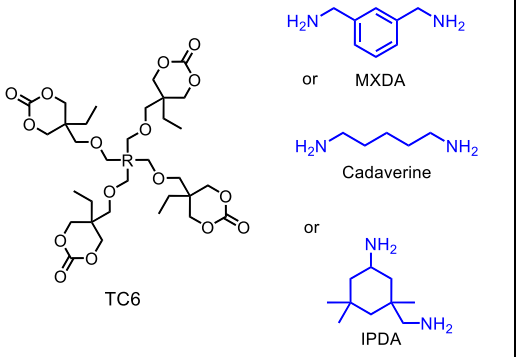
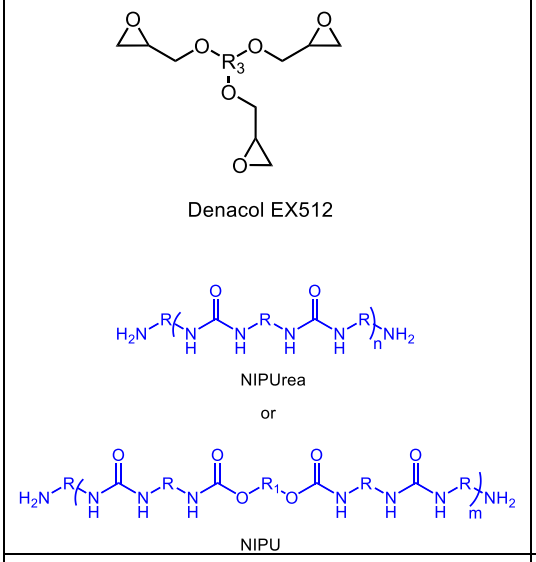
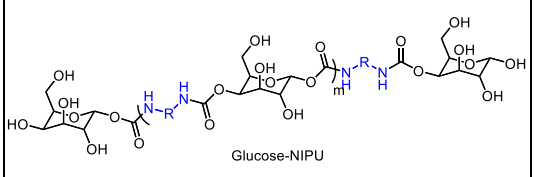
Scheme 23. (a) A cascade exotherms by the addition of reactive TREN and epoxy in the presence of KOH as catalyst. **NIPUF 22** was obtained after 5 – 15 mins at room temperature.[128]

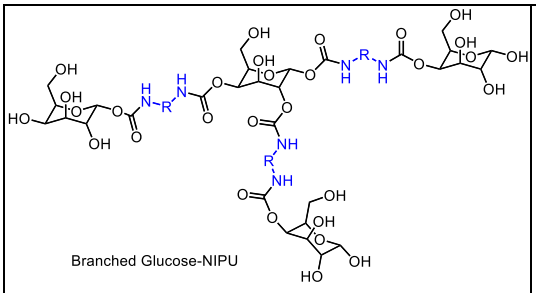
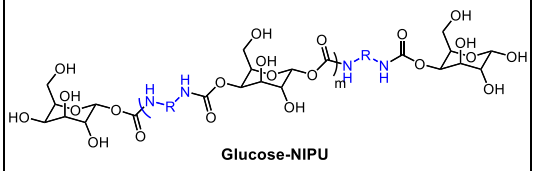
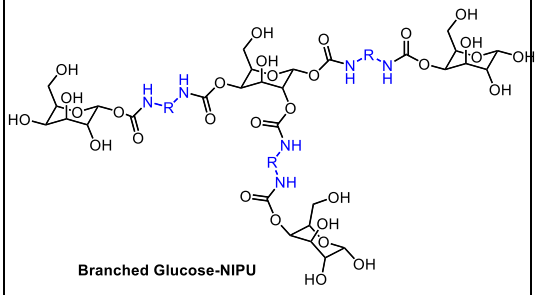
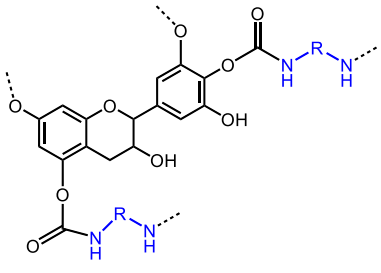
Bourguignon et al. also described a method to prepare **NIPUF 22** at room temperature by utilizing the cascade exotherms of multiple reactions in formulation (Scheme 23).[128] In this approach, the in-situ heat generation in the formulation was originated from the cascade reactions of (1) aminolysis of TMPGC, (2) hydrolysis of TMPGC with water to CO_2 when catalyzed by potassium hydroxide (KOH), and (3) aminolysis of TMPTE. It was shown that these cascade reactions will result in a high temperature (up to 181 °C) in the formulation after optimization of various parameters. The in-situ generation of high heat had improved the monomer conversion and hydrolysis. By using this approach, low-density **NIPUF 22** (0.167 – 0.204 g/cm^3) with low T_g (-1.2 to 21.7 °C) and high compression moduli (up to 4.7 MPa) can be obtained after mixing the formulation at room temperature for 5 – 15 minutes.

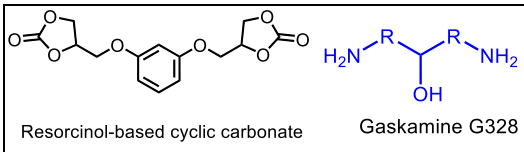
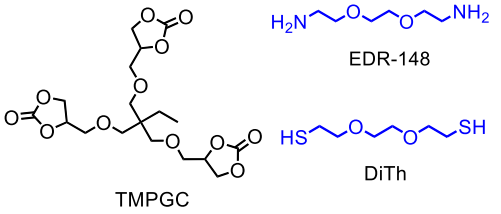
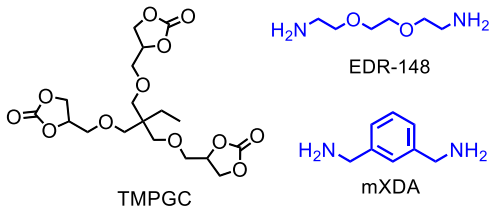
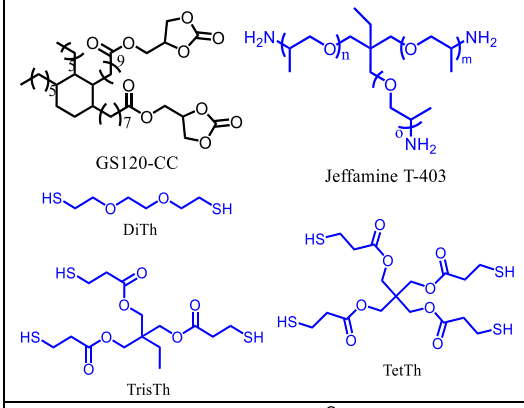
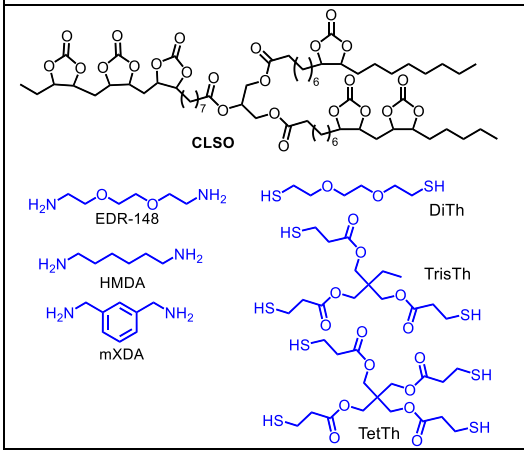
All the reported NIPUF in the literature are summarized in Table 3 for comparison with PUF 1 in terms of their respective foaming conditions and foam properties. It is important to note that the foaming conditions for NIPUF described by Bourguignon et al. closely resemble those of conventional PUF synthesis, which uses water to generate CO_2 as a blowing agent. The p_a of NIPUF could be within similar range to that of PUF by controlling the ratio between monomers, blowing agents, and additives. Further advancements in monomer structures and compositions are necessary to enhance the mechanical properties (compressive strength and modulus) of NIPUF for industrial applications.

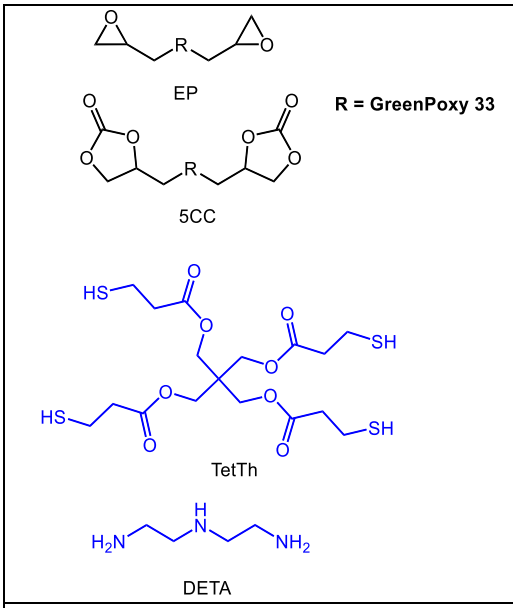
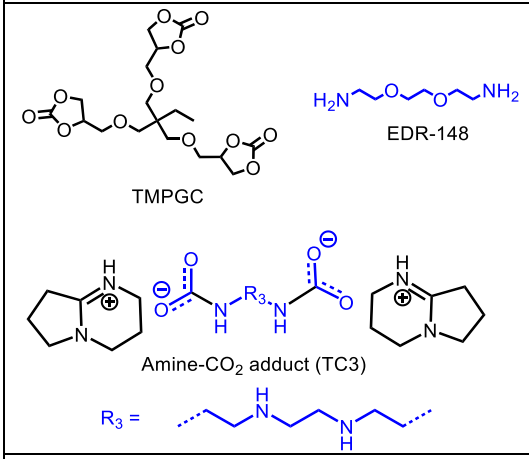
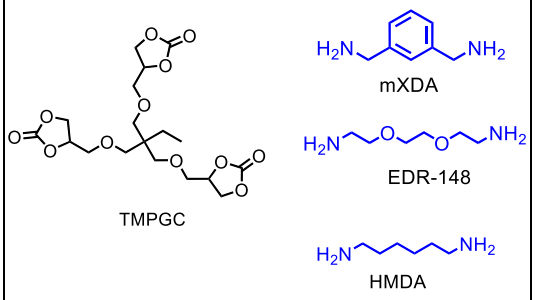
Table 3. The summary of PUF 1 and reported NIPUF in literatures.

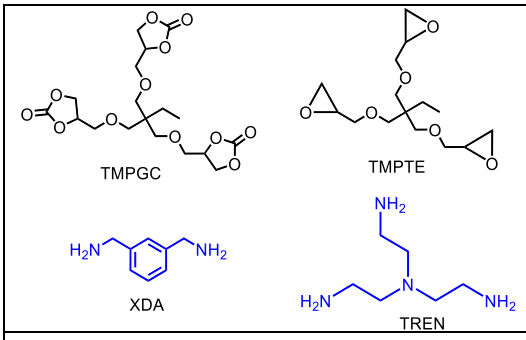
Monomers	Foaming Conditions	Foam	Foam Properties	Ref
Polyether polyol, polymeric methane diphenyl diisocyanate (PMDI), N,N,N,N,N-pentamethyl diethylene triamine (PMDETA), polyether dimethyl siloxane	a) Water, 70 °C, 24 h	PUF 1	p_a = 0.042 – 0.118 g/cm^3 T_g = 91 – 110 °C E = 3.2 – 21.6 MPa	129
 R_1, R_2 = biobased monomers	b) Supercritical CO_2, 40 °C, 300 bar, 3 h c) 80 °C, 1 min	NIPUF 1	p_a = 0.110 – 0.176 g/cm^3 T_g = -6 – -2 °C E = 1.8 – 4.75 MPa (compression, UTM)	96
 TMPGC HMDA  x+y+z = 19.2 EO-TMPGC	a) Solkane 365/227, 20-25 °C, 10 s b) 80 °C, 14 h	NIPUF 2	p_a = 0.142 – 0.219 g/cm^3 T_g =-37 – 27 °C E = 0.017 MPa (compression, UTM)	79
 TMPGC  EDR-148  PPOGC	a) MH-15, TBD, 80 °C, 12 h b) 120°C, 4 h	NIPUF 3	p_a = 0.194 – 0.295 g/cm^3 T_g = -18 – 19 °C σ = ~0.03 MPa (tension, DMA)	100
	a) MH-15, thiourea, r.t, 3 d	NIPUF 4	p_a = 0.271 – 0.303 g/cm^3 T_g = 0 – 11 °C σ = 0.14 – 0.89 MPa (tension, DMA)	77

	a) MH-15, DMSO, 150 °C, 12 h	NIPUF 5	p_a = 0.241 – 0.337 g/cm^3 T_g =84 – 94 °C E = 1.19 – 1.64 MPa (tension, UTM)	103
	a) MH-15, DMSO, AgNPs, 150 °C, 12h	NIPUF 6	σ = 205 kPa (UTM)	104
	a) MH-15, 50 °C, overnight b) 120 °C, 2 h	NIPUF 7	p_a = 0.170 – 0.530 g/cm^3 T_g = 7 – 27 °C σ = ~ 0.14 – 0.21 MPa (compression, UTM)	105
	a) MH-15, r.t, 10 min b) 100 °C, 30 min	NIPUF 8	p_a = 0.130 – 0.400 g/cm^3 T_g =-10 – -28 °C E' = 0.01 – 0.06 MPa (compression, DMA)	112
	a) KH560 (silane) $NaHCO_3$ b) 200 °C, 30 min	NIPUF 9	p_a = 0.088 – 0.127 g/cm^3 σ = ~0.2 MPa (compression, UTM)	113

 Branched Glucose-NIPU				
 Glucose-NIPU  Branched Glucose-NIPU	a) Maleic Acid, Glutaraldehyde, 103 °C, 4 h	NIPUF 10	p_a = 0.080 – 0.130 g/cm^3 σ = ~0.4 MPa (compression, UTM)	114
Component A : Mixture of two cyclic carbonates and epoxy functional compounds Component B : Mixture of 4 different amine hardeners	a) Chemical blowing agent (exact structure was not revealed) b) 50 °C, 3 h c) 70 °C, 15 h	NIPUF 11	p_a = 0.078 g/cm^3 T_g =58 °C σ = 0.1 MPa (compression, UTM)	115
 Tannin NIPU	a) Citric Acid, Glutaraldehyde b) 70 – 80 °C, overnight	NIPUF 12	p_a = 0.120 – 0.260 g/cm^3 σ = 0.13 – 0.57 MPa (compression, UTM)	116
	a) Formic Acid, Glutaraledehyde, SDBS b) 83 °C, 10 hr	NIPUF 13	p_a = 0.220 – 0.410 g/cm^3 σ = 0.82 MPa (compression, UTM)	117

	a) TBD, r.t, 18 h b) 120 °C, 2 h	NIPUF 14	p_a = 0.480 g/cm^3 T_g = 7 °C	119
	a) DBU, 100 °C, 4h	NIPUF 15	p_a = 0.166 – 0.207 g/cm^3 T_g = 2.4 – 7.9 °C σ = 0.01 MPa (compression, DMA)	120
	a) NaHcT, DBU b) 80 °C, 5 h	NIPUF 16	p_a = 0.167 – 1.15 g/cm^3 T_g =-25 – 43 °C E = 0.22 MPa (compression, UTM)	122
	a) DBU, 120 °C, 2.5 hr	NIPUF 17	p_a = 0.290 – 0.310 g/cm^3 T_g = -17 – -28 °C E = 0.037 MPa (compression, DMA)	123
	a) DBU, 140-180 °C, 3 hr	NIPUF 18	p_a = 0.130 – 0.170 g/cm^3 T_g = -1.1 – 9.3 °C σ = 0.021 MPa (UTM)	124

	a) DBU, r.t, 2 mins	NIPUF 19	p_a = 0.160 – 0.200 g/cm^3 T_g =12.1 – 39.2 °C	125
	a) 50 °C, 24 hr	NIPUF 20	p_a = 0.203 – 0.462 g/cm^3 T_g = 14 – 24 °C	126
	a) H_2O, DBU, 80 – 100 °C, 3 – 5 hr	NIPUF 21	p_a = 0.153 – 0.963 g/cm^3 T_g = -7 – 26 °C E = 0.03 – 25.8 MPa (compression, UTM)	127

	a) KOH, H_2O, r.t., 5 mins	NIPUF 22	p_a = 0.167 – 0.204 g/cm^3 T_g = -1.2 – 21.7 °C E = up to 4.7 MPa (compression, UTM)	128
p_a = apparent density (g/cm^3); T_g = glass transition temperature (°C); E and σ are the mechanical modulus and mechanical stress, respectively, as determined by using dynamic mechanical analysis (DMA) or universal testing machine (UTM).				

2. Conclusion and Outlook

The increasing demand from various industries is fueling the growth of the PU foams market in the upcoming years. Traditional PU foams are self-blown by CO_2 generated from the hydrolysis of moisture-sensitive isocyanates at room temperature. As a safer alternative to isocyanate-based polymerization, the polyaddition of cyclic carbonates and amines has gained prominence, leading to the development of NIPUF with promising properties. The main challenge for NIPUF was to identify a suitable blowing agent in an isocyanate-free formulation. Earlier attempts on NIPUF had used HCFC with high GWP, flammable hydrogen gas, high temperatures and pressures as discussed in this review. Recent work by Bourguignon et al. has demonstrated the successful foaming of NIPUF using water at room temperature, which closely resembles the foaming process of PUF.

We believe that further advancements are required for NIPUF in several areas:

- *Foam properties*: Most studies have investigated the mechanisms of foaming and measured its physical and mechanical properties. There remains a gap to further develop NIPUF with comparable properties to their conventional counterpart. Furthermore, the presence of hydroxyl groups in NIPUF may result in poor water resistance and compromised mechanical properties. More studies could be done to optimize the monomer structures, foaming composition and parameters to enhance the mechanical properties for different applications.
- *Applications*: NIPUF is a relatively new area with high potential to replace PUF. However, comprehensive studies on NIPUF for applications intended to replace PUF are limited.

Comparative data from real-life testing of NIPUF against PUF, along with the establishment of standardized testing protocols, are needed to facilitate the integration of NIPUF for industrial adoption.

- *Environmental assessment*: NIPUF are claimed to be more sustainable solution to conventional PUF. However, there is a need for a more comprehensive assessment of the full environmental and economic impacts of NIPUF production and use. Studies such as cradle-to-grave life cycle analysis and techno-economic evaluations could be employed to assess the sustainability and feasibility of NIPUF in comparison to PUF.

In summary, the prospect of utilizing NIPUF as a substitute for PU foams in the future is both exhilarating and full of promise. This potential transition represents a significant advancement in sustainable materials, offering enhanced performance characteristics, reduced environmental impact, and the opportunity to revolutionize various industries reliant on foam-based products. The evolution towards NIPUF not only signifies a shift towards greener and more innovative solutions but also opens up a new realm of possibilities for more eco-friendly and efficient manufacturing processes.

Author Information

Corresponding author

Ping Sen Choong - Institute of Sustainability for Chemicals, Energy and Environment ($ISCE^2$), Agency for Science, Technology and Research (A*STAR), 1 Pesek Road, Singapore 627833, Republic of Singapore

Email: Choong_ping_sen@isce2.a-star.edu.sg

Author Contribution

Conceptualization: C.C.N.D.L., and P.S.C; manuscript preparation: C.C.N.D.L., M. J. H. O., M. W., and P.S.C; manuscript editing and review: C.C.N.D.L., M. J. H. O., M. W., C-L. K. L., and P.S.C. All authors have read and agreed to the published version of the manuscript.

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Notes

The authors declare no competing financial interest.

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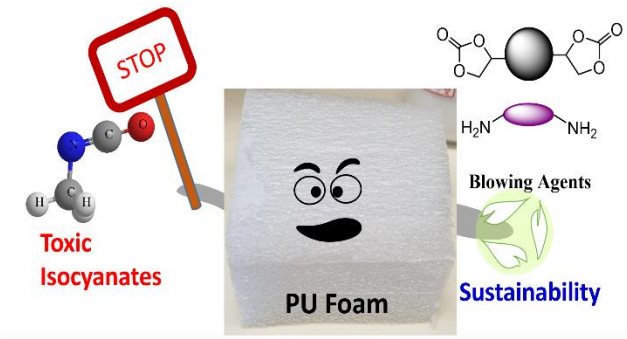
STOP
Toxic
Isocyanates
PU Foam
Blowing Agents
Sustainability