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## CO<sub>2</sub>-derived non-isocyanate polyurethanes (NIPUs) and their potential applications

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Using CO<sub>2</sub> as feedstock to fabricate valuable products has become essential to green and sustainable chemistry and represents a rewarding challenge. Among the noticeable routes used to convert CO<sub>2</sub> into synthetic polymers, this review highlights the reactions concerning the cycloaddition of epoxides with CO<sub>2</sub> in cyclic carbonate as precursors for various forms of chemical synthesis, such as polycarbonates and polyurethanes (PUs). It is a fundamental challenge in polymer production to exploit biomass and CO<sub>2</sub> as feedstock. PUs are one of the most versatile classes of polymeric materials that exhibit excellent properties. PUs are usually synthesized by a route involving the reaction of diols with diisocyanates derived from toxic phosgene gas. Non-isocyanate-derived polyurethane (NIPU) has been produced from cyclic carbonates and diamines without isocyanate. NIPU usually displays increased chemical resistance, lower permeability, improved water absorption, and thermal stability. In this review, we report the synthesis of several NIPUs for different applications in a more environmentally friendly manner, employing CO<sub>2</sub> as a reagent and/or fully biobased reactants.

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### 1. Introduction

Polyurethanes (PUs) are versatile materials widely used in every field of daily life, from the building sector to medicine, thanks to their outstanding mechanical, ranging from flexible

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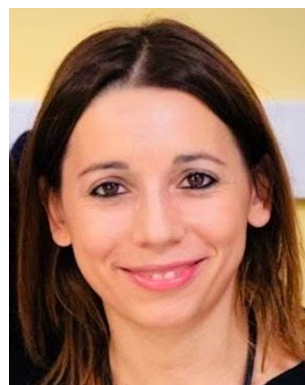
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benzomorphane core. She carried out research at the Department of Chemical Sciences (Catania University), dealing with the synthesis of new systems for tumor cell targeting and the synthesis and characterization of nanosystems. She was a post-doctoral fellow for the Functionalization of cyclodextrins using substrates capable of increasing the CO<sub>2</sub> absorption capacity.



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to hard materials, and physical properties.<sup>1</sup> They are suitable for producing foams, adhesives, highly durable protective coatings, elastics, paints, and biomedical products.<sup>2</sup>

At the industrial level, PUs are synthesized through the polyaddition reaction of various polyols, isocyanates, and chain extenders, which may also contain urethane bond linkages in the central skeleton structure, as well as other aliphatic and aromatic hydrocarbons, ethers, esters, imides, urea, and isocyanate groups.<sup>3</sup> In 1849 was discovered that the urethane functional group (carbamate) could be obtained by reacting an isocyanate with a hydroxylated molecule.<sup>4</sup> Although PUs are useful and versatile polymers, the starting materials usually used for their preparation are connected to global warming and health issues. Isocyanate derivatives, one of the two building blocks, are phosgene derivatives. Phosgene and isocyanate *per se* are highly toxic and harmful compounds. On the other hand, the common precursors for synthesizing polyols, ethylene, and propylene oxides are usually derived from petroleum resources.<sup>5</sup> Finding greener approaches to PUs is now crucial given the REACH regulation, which establishes limitations on using chemicals containing free isocyanates known to cause asthma and dermatitis.<sup>6–8</sup> Non-isocyanate polyurethane (NIPU) has attracted great interest from the industrial sector as a far more eco-friendly and nontoxic alternative to standard PU derived from petroleum resources and isocyanates.<sup>9</sup> In this view, researchers have spent much effort finding a new synthetic process to produce these widely used materials in an eco-friendly and sustainable manner.

In 1957, Dyer and Scott discovered a method to produce PUs without moisture-sensitive isocyanates.<sup>10</sup> Avoiding the isocyanate approach by reacting cyclic carbonates with amines to create the urethane group is feasible. Traditionally, diols and phosgene have been employed to make cyclic carbonate.<sup>11</sup>

Being phosgene, the chemical filrouge of the carbonate and carbamate preparations, its replacement is a crucial step. The possibility of replacing it with CO<sub>2</sub> may be the right way because of its abundance, easy availability, and, most importantly, its low toxicity in nature. One of the most efficient examples of artificial CO<sub>2</sub> fixation is the 100% atom-efficient production of cyclic carbonate *via* CO<sub>2</sub> cycloaddition to epoxides. Converting CO<sub>2</sub> into chemical products for which there is significant commercial demand represents one of the solutions to reduce CO<sub>2</sub> atmospheric emissions responsible for increasing global warming.<sup>12,13</sup> The International Panel on Climate Change (IPCC) predicts that, by the year 2100, the atmosphere may contain up to 570 ppm CO<sub>2</sub>, triggering a rise in the mean global temperature of around 1.9 °C. Consequently, there will be an increase in the mean sea level of up to 1 m by 2100, leading to increased desert formation and species extinction.<sup>14</sup>

Bio-based polyols, including propoxylated sugars, castor oil,<sup>15</sup> and polyol intermediates provided by biorefineries, have been used to create PUs with high bio-based component contents. The possibility of increasing this sustainable character is currently being explored with the development of ways from biological CO<sub>2</sub> fixation in biomass conversion to direct chemical fixation of CO<sub>2</sub>. Unlike isocyanates, cyclic carbonates are much less sensitive to moisture, enabling their facile long-term storage and manipulation.

The first part of this review will focus on synthesizing NIPU from cyclic carbonates formed by the reaction of epoxide with CO<sub>2</sub> in the presence of various catalysts. The second section will focus on the synthesis of NIPU using entirely bio-based reagents, such as polyol precursors. In addition, the qualities, benefits, and applications of PUs in numerous disciplines were explored.



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## 2. Synthesis of organic cyclic carbonate as the precursor of polyhydroxyurethanes

In the 1970s, CO<sub>2</sub>-based PUs were obtained by reacting CO<sub>2</sub> with diamines under the catalysis of phosphate.<sup>16,17</sup> The synthesis of PUs has now been described using several innovative CO<sub>2</sub> utilization approaches, including the CO<sub>2</sub>-based cyclic carbonate route.<sup>18</sup> However, CO<sub>2</sub> is a thermodynamically stable molecule ( $\Delta G = 394 \text{ kJ mol}^{-1}$ ).<sup>19</sup> Consequently, the pathways for the early preparation of CO<sub>2</sub>-based cyclic carbonate precursors need a catalyst and a specific temperature or pressure.

It is essential to consider the source of the CO<sub>2</sub> to be used for the production first of the carbonates and then of the NIPU. Aresta reported that the industrial applications of CO<sub>2</sub> (quantity and source of CO<sub>2</sub> used per year and duration of products) are in ever-increasing quantities.<sup>11</sup> This infers that in a business as usual scenario, the use of CO<sub>2</sub> in the chemical market will expand. In particular, for the production of carbonates (monomers and polycarbonates), a market of 2 Mt was estimated, and the quantity used until 2010 was only 0.2 Mt. The sources of CO<sub>2</sub> were various; for example, CO<sub>2</sub> recovered from power plants or industrial or natural reservoirs. Enhanced oil recovery (EOR) is a practice that can store CO<sub>2</sub> for a long time while producing an economic benefit (improved oil extraction). EOR could easily double the total amount of CO<sub>2</sub> used in just a few years. It is essential to match the question with the source, considering that the CO<sub>2</sub> could be less pure than that extracted from a natural reservoir (*i.e.*, a well) or produced from Ca and Mg carbonates. The cost of purifying CO<sub>2</sub> can be high if traces of toxic substances need to be removed. The amount of CO<sub>2</sub> used in industrial applications

by compound class or use option varies from kt to Mt. There is no direct relationship between emissions reduction and the amount of CO<sub>2</sub> used. In all cases, CO<sub>2</sub> will be released with a different delay depending on the nature and use of each product. The topic of direct air capture (DAC) has recently received the scientific community's attention. Nearly a decade ago, the cost estimate for capturing CO<sub>2</sub> from the air using traditional sorbents such as monoethanolamine (MEA) was approximately \$600/tCO<sub>2</sub>, which remains highly uncertain.<sup>20</sup> This highlights the need for research into high-performance sorbents that can dramatically reduce DAC costs. Researching to establish a practical lower limit for DAC is vitally important. The most commonly investigated approaches are the direct capture of CO<sub>2</sub> from the air and subsequent conversion to produce fuels.<sup>21</sup> However, other avenues of use are also possible, including chemical conversion to produce synthetic intermediates for pharmaceuticals.<sup>22</sup>

Many researchers have attempted a new approach with lower temperatures, lower pressures, and no catalysis in recent years. Only by going in this direction would it be possible to produce PUs with lower costs, less energy, and higher yields.

A solvent-free and catalyst-free CO<sub>2</sub> indirect utilization route was settled for the synthesis of PUs starting from the alkyl carbonate salt.<sup>23</sup> Alkyl carbonate salt of CO<sub>2</sub> storage materials (CO<sub>2</sub>SMs) with the structure of  $-\text{NH}_3^+-\text{O}-\text{C}(=\text{O})-\text{O}^-$  could be simply prepared by fixation of CO<sub>2</sub> in diamine and glycol systems (mole ratio = 1 : 1) at room temperature under atmospheric pressure.<sup>24</sup> This easily prepared carbonate can be converted into carbamate groups ( $-\text{N}(\text{H})-\text{C}(=\text{O})-\text{O}-$ ) by intramolecular dehydration (Fig. 1).<sup>23,25</sup> Several PUs have been successfully synthesized using these starting materials at 90 °C and atmospheric pressure, employing DIC as a dehydrating agent. PUs produced by this method may have a certain poten-



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**Antonio Rescifina**

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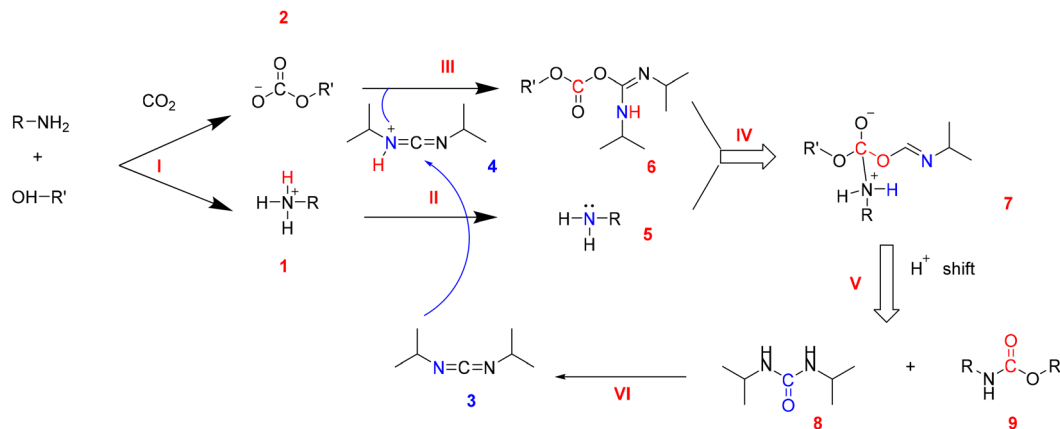


Fig. 1 Reaction mechanism of PU by intermolecular dehydration via CO<sub>2</sub>-storage materials and DIC.

tial in waterproof coatings as they are water-insoluble.<sup>23</sup> The average molecular weight of the PUs produced by this method was between 10 400 g mol<sup>-1</sup> and 12 700 g mol<sup>-1</sup>, and all of them were thermally stable below 142 °C while completely decomposed above 409 °C. The pre-capture and immobilization approach of CO<sub>2</sub> avoids the need for its activation, significantly reducing energy consumption and enabling the synthesis of CO<sub>2</sub>-based PU at low temperatures and atmospheric pressure. This represents a crucial point for energy savings and emissions reductions.

Wulf *et al.*<sup>26</sup> reported the preparation of a series of cyclic carbonates as monomers for NIPUs. They compared the efficiency of a Ca-based system and a bifunctional ammonium salt as catalysts for converting polyfunctional epoxides. Both catalytic systems have been shown to provide effective conversions; however, the Ca-based system<sup>27</sup> is more active even at moderate temperatures, and the organocatalytic system is more moisture-resistant.<sup>28</sup> The Ca-based system screening was performed to evaluate the catalytic efficiency of CaI<sub>2</sub> in combination with six different crown ethers to convert the silyl-bridged bisepoxide to the corresponding biscarbonate. The combination of CaI<sub>2</sub> with 18-crown-6 (L1, Fig. 2A), named Ca/L1, led to the desired product with a yield of 93% in ambient conditions (6 h, 23 °C, *p*(CO<sub>2</sub>) = 1 atm) that increases

up to 98%, prolonging the reaction time at 24 h. Also, the catalytic performance of the organocatalyst tri-*n*-butyl-(2-hydroxyethyl)ammonium iodide (Fig. 2B) gave the silyl-bridged biscarbonate with a yield of 96%.

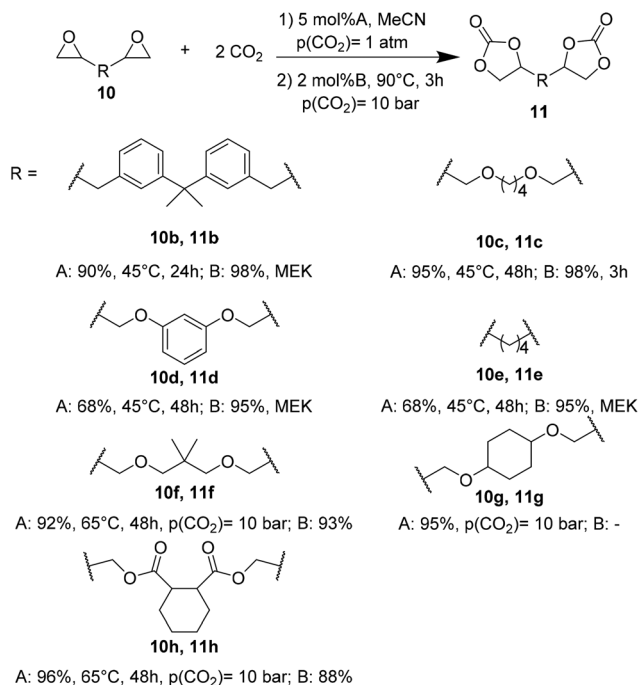
The influence of both catalytic systems in converting several functionalized bis-epoxides (Fig. 3) to the corresponding carbonates was explored. Both catalytic systems gave high yields (90–98%) of the desired carbonates **11b**, **11c**, and **11f**, with minor modifications in their reaction conditions. Unlike the Ca/L1 system, yields up to 90% were achieved for products **11d** and **11e** using the organocatalyst (95–98% and 68–79%, respectively).

Ca/L1 and tri-*n*-butyl-(2-hydroxyethyl)ammonium iodide catalytic efficiencies were compared to prepare cyclic carbonates with polymeric backbones and polyfunctional carbonates (Fig. 4). The polyether-bridged biscarbonates **13i** and **13j** as well as the isocyanurate-bridged triscarbonate **13l** (94–95%), bearing three carbonate moieties, were obtained with high yields (93–99% and 94–95%, respectively) by both catalytic systems. While the polypropylene-glycol diglycidyl ether and tetraglycidyl-substituted bisamine conversion in the corresponding carbonates **13k** and **13n** was addressed by adding only the organocatalyst, probably due to residual water in the respective substrates that deactivates CaI<sub>2</sub>.

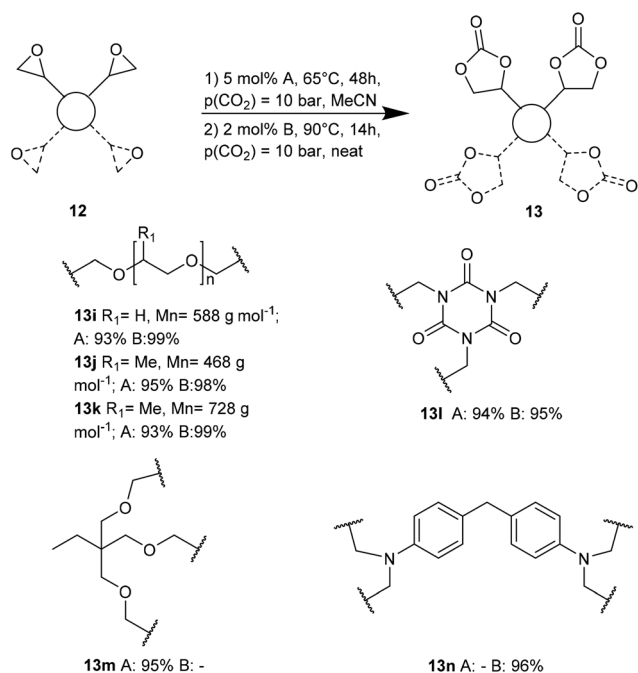


Fig. 2 Structures of Ca-based (A) and organocatalytic (B) systems. (C) Silyl-bridged biscarbonate formation of Ca/L1 (A) and tri-*n*-butyl-(2-hydroxyethyl)ammonium iodide (B) catalyzed.



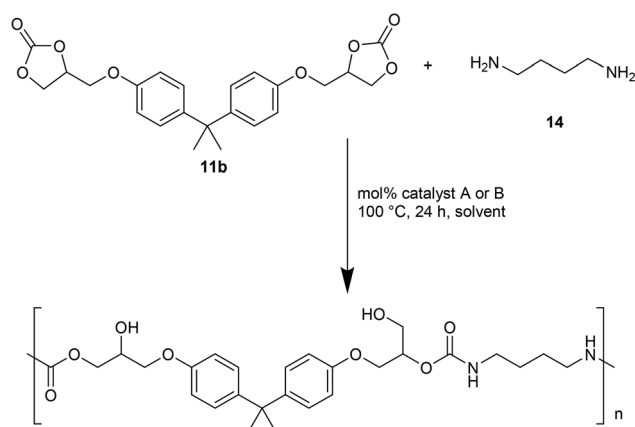


**Fig. 3** Structures of bis-epoxides and their corresponding bis-carbonates.



**Fig. 4** Cyclic carbonates with polymeric backbone and polyfunctional carbonates.

The authors also evaluated the influence of the catalyst systems on the two- and one-pot synthesis of NIPUs. In this regard, bisphenol A diglycidyl carbonate **11b**, according to the literature,<sup>29,30</sup> was chosen as a precursor for the NIPU synthesis and allowed to react with 1,4-diaminobutane (1,4-DAB,



**Fig. 5** Two-pot process for the synthesis of NIPU.

**14**) in DMSO in the presence and absence of catalysts (Fig. 5). Compared to the uncatalyzed reaction, Ca/L1 and tri-*n*-butyl-(2-hydroxyethyl)ammonium iodide generated NIPU with a lower molecular mass, a low polydispersity index, and a minor glass transition temperature. Because of the difficulty of removing DMSO from the polymers, the same reactions were conducted using MeCN as the solvent. Also, in this case, the obtained polymers presented a molecular mass lower than that obtained with the uncatalyzed reaction.

The Ca-based catalytic system and organocatalyst allowed a successful NIPU one-pot synthesis. The results were obtained by combining carbonate synthesis with polymerization. Specifically, the aryl-bridged and alkyl-bridged carbonates (**2b** and **2c**, Fig. 6), obtained by the respective epoxides (**10b** and **10c**, Fig. 6), reacted with 1,4-DAB (**14**, Fig. 6) and 1,8-diaminooctane (**5**, Fig. 6), in MeCN (100 °C, 24 h), to give NIPUs with molecular masses up to  $14 \text{ kg mol}^{-1}$ .

NIPUs can also be obtained by polycarbonate polyols such as poly(propylene carbonate) (**17**, PPC), synthesized from the copolymerization of  $\text{CO}_2$  and propylene oxide (**16**, Fig. 7). PPC is a polymer constituted by carbonate linkages.<sup>31</sup> Some catalysts have demonstrated the capability to promote ether linkage formation in propylene oxide polymerization.<sup>32</sup> Catalysts such as double metal cyanides (DMC), dinuclear Zn-complexes or Cr-bishydroxy-chinoline complexes, and a polyalcohol, such as polyethylene glycol as a starter, led to polyethercarbonate polyols by copolymerization of propylene oxide and  $\text{CO}_2$ <sup>33</sup> (Fig. 7).

In this regard, NIPUs with different carbonate linkage content were synthesized<sup>34</sup> by reaction of PPCn (99% carbonate linkages, PPCn-RHMPA), PPCz (with 65% carbonate linkages, PPCz-RHMPA), and a mixture of PPCn and PPCz with a molar ratio of 1 : 1 (PPCnz-RHMPA) with PHA in the presence of MDI as catalyst (Fig. 8).

<sup>1</sup>H-NMR and FT-IR spectroscopies were performed to confirm the carbonate linkage content. A nearly 100% polycarbonate backbone was confirmed since the spectra showed negligible signals corresponding to the strong ether linkage in



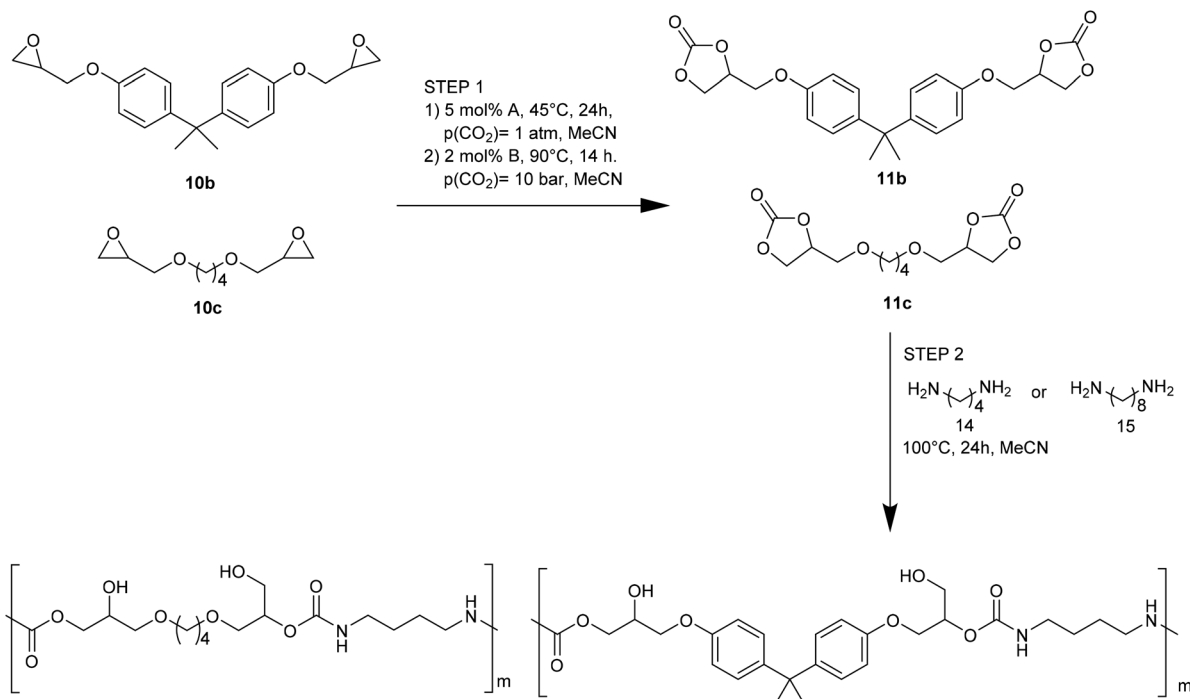


Fig. 6 One-pot process for the synthesis of NIPU.



Fig. 7 Catalyzed copolymerization of propylene oxide and  $\text{CO}_2$  to PPC: alternating polycarbonates (top) and polyethercarbonates (bottom).

PPCz-RHMPA and PPCnz-RHMPA. Different carbonate linkage content in the resulting NIPUs reflects thermal property differences. For instance, as established by DSC, the cold crystallization temperature decreases as the carbonate linkage content increases, thanks to the abundant hydrogen bonding between carbonate and urethane groups that limits PHA fragment mobility. A similar trend was also discovered for TG and DTG analysis where  $T_5$  (the temperature of the sample with the weight loss of 5%) has values of 287.0 °C, 285.4 °C, and 282.6 °C for PPCz-RHMPA, PPCnz-RHMPA, and PPCn-RHMPA, respectively. The carbonate linkage content also affects the mechanical properties of these polymers. Longer linkage increases (i) tensile strength ( $\sigma_b$  of 15.69, 18.42 and 21.91 for PPCz-RHMPA, PPCnz-RHMPA, and PPCn-RHMPA, respectively); (ii) tensile modulus ( $E_t$  of 28.00, 41.35 and 245.65 for PPCz-RHMPA, PPCnz-RHMPA, and PPCn-RHMPA, respectively); (iii) tensile strength at 100% elongation ( $\sigma_{100}$  of 2.85, 4.65 and 13.72 for PPCz-RHMPA, PPCnz-RHMPA, and PPCn-

RHMPA). An inverted trend was seen for the breaking elongation that decreases as the carbonate linkage content increases ( $\epsilon_b$  of 1007.51, 876.04, and 484.52 for PPCz-RHMPA, PPCnz-RHMPA, and PPCn-RHMPA, respectively). Through a single lap-shear test, the adhesion properties of NIPUs were evaluated and compared to those of LOCTITE 3542, a well-known petroleum-based polyol. All NIPUs showed higher adhesion properties than LOCTITE 3542. Strong adhesion properties were detected for PPCn-RHMPA, followed by PPCnz-RHMPA, PPCz-RHMPA, and LOCTITE@3542, as a consequence of the difference in carbonate linkage content.

NIPUs, applicable as waterborne coatings and adhesives, were also synthesized from organic cyclic decarbonates.<sup>35</sup> Through a circulating gas-flow system,  $\text{CO}_2$  addition to bisepoxides reported in Fig. 9 using different solvents (acetone, THF, methyl isobutyl ketone iBMK, toluene) and tributyl ammonium bromide (TBAB) as the catalyst, in mild conditions (1 atm,  $T < 100$  °C), gave the respective organic cyclic dicarbonates.<sup>36</sup>

The reactions have been carried out with a circulating gas-flow system that allows homogeneous continuous distribution of the  $\text{CO}_2$  within the solvent and aerosol formation for all the tested solvents (even at temperatures near 20 °C). In this way, the concentration of all components in the reaction mixture increases with a consequent increment of the reaction conversion or decrement of the reaction time. Moreover, homogeneous  $\text{CO}_2$  distribution within the solvent improves the conversion time catalyzed by TBAB. Among tested solvents, iBMK resulted in the highest conversion within the shortest time, whereas acetone resulted in the slowest reaction rate. Cyclic



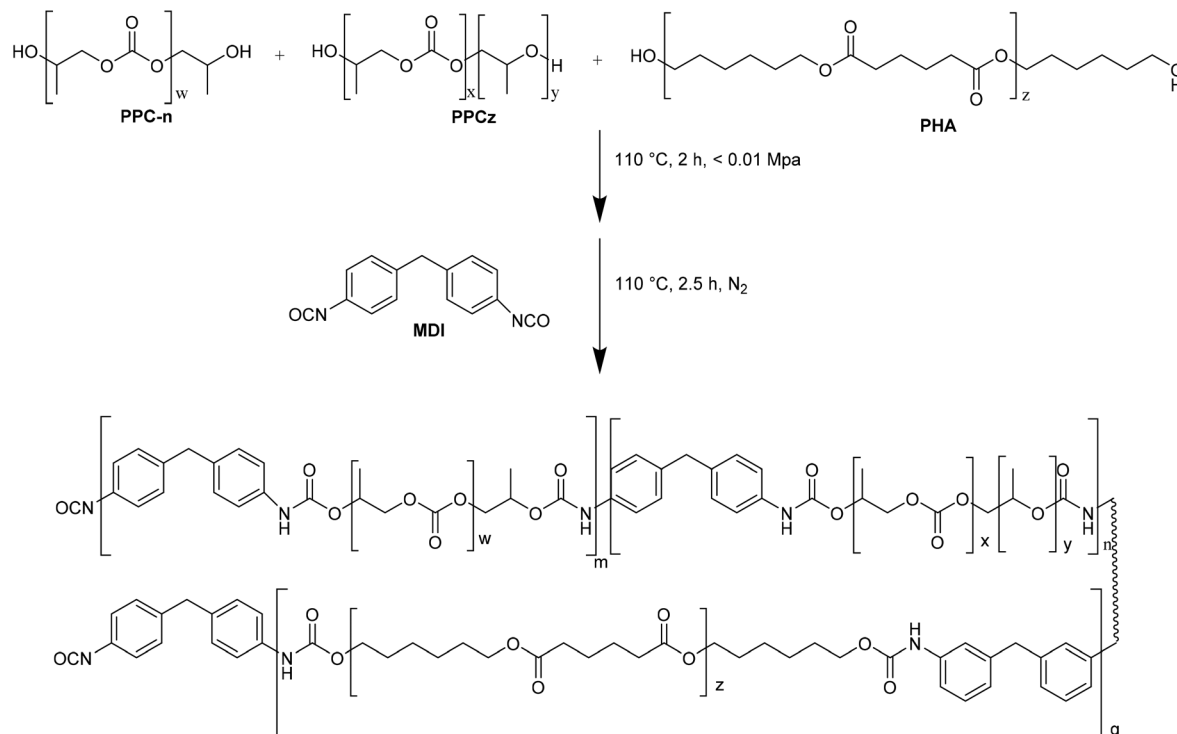


Fig. 8 Synthesis of PPCn-RHMPA ( $m = 1, n = 0, q = 0$ ), PPCz-RHMPA ( $m = 0, n = 1, q = 1$ ) and PPCnz-RHMPA ( $m = 0.5, n = 0.5, q = 1$ ).



Fig. 9 Structures of cyclic dicarbonates BADGE (bisphenol A diglycidyl ether), BDGE (1,4-butanediol diglycidyl ether), DGcHdC (diglycidyl 1,2-cyclohexanedicarboxylate), and EcHMEcHC (3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate).

dicarbonates prepared by the developed gas-flow system were used as intermediates for NIPUs synthesis by aminolysis with *n*-butyl amine and 1,6-diamino hexane (**8** and **9**, Fig. 10) by adding the amine to the same reaction mixture.

The CO<sub>2</sub>-based synthesis of 5-membered dicyclic carbonates and amino-terminal polyurea oligomers as monomers for poly-hydroxyurethane-urea (PHUU) was reported.<sup>37</sup> The optimized reaction conditions used (150 °C, TBAB, Fig. 11A) led to about 98% of epoxy group conversion as monitored by <sup>1</sup>H-NMR spectroscopy. Indeed, the disappearance of two signals of methylene protons linked to the oxygen atom of epoxy groups and the appearance of a signal corresponding to the methine protons of the cyclic carbonates unequivocally indicated the formation of dicyclic carbonates. This evidence

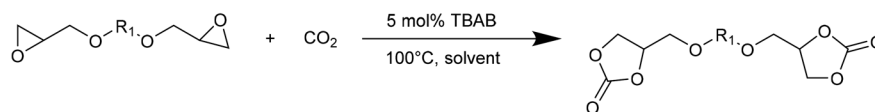
fitted with that obtained by FT-IR where the C–O–C stretching vibration of the epoxy group disappeared and the C=O stretching vibration of cyclic carbonate appeared. Then, according to the synthetic pathway reported in Fig. 11B, amino-terminal polyurea oligomers D230\* and TTD\* were prepared and characterized by <sup>1</sup>H-NMR and FT-IR spectroscopies.

Finally, the polyaddition of amino-terminal polyurea oligomers to 5-membered dicyclic carbonates was conducted on several polyhydroxyurethane-urea derivatives, PHUU-1, PHUU-2, and PHUU-3 (Fig. 11C).

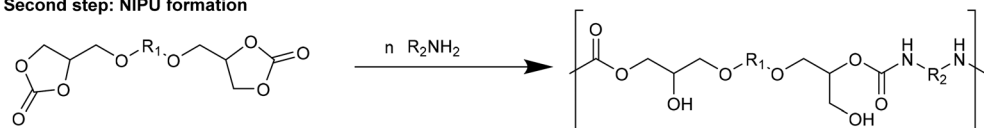
The urethane/urea ratio, calculated by <sup>1</sup>H-NMR, indicated a higher urea content for PHUU-2 and PHUU-3 (0.88 and 0.86) than PHUU-1 (0.58). This last was also characterized by a lower molecular weight (3896 g mol<sup>−1</sup> vs. 19 340 and 16 357 for PHUU-2 and PHUU-3, respectively) due to the more considerable steric hindrance of the amino group in D230\* hampering dicyclic carbonate aminolysis. Introducing urea functionality in PHUU-2 and PHUU-3 determined stronger hydrogen bond formation and interchain interactions, reflecting improved thermal properties and surface hydrophobicity. Indeed, the strong interchain interactions restrict the water penetration as evaluated by the water contact angle measurement. As evaluated by TGA, the thermal degradation temperature of PHUU-2 and PHUU-3 was higher than the corresponding PHU-2 and PHU-3, synthesized from 5-membered dicyclic carbonates and diamines. It is possible to attribute this peculiarity to the influence of a different diamine sequence that led to the incorporation of urea moieties. PHUUs exhibited different mechanical properties as detected by tensile tests. For example, in com-



## A) First step: cyclic dicarbonates formation



## B) Second step: NIPU formation

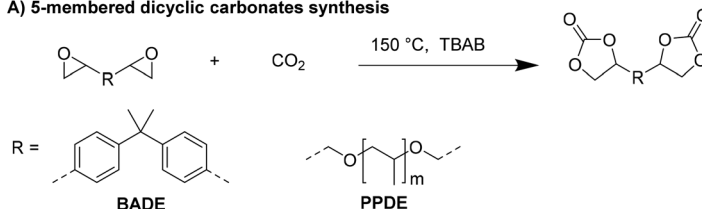


$R_1$  = BADGE, BDGE, DGcHdC, EchMEchC

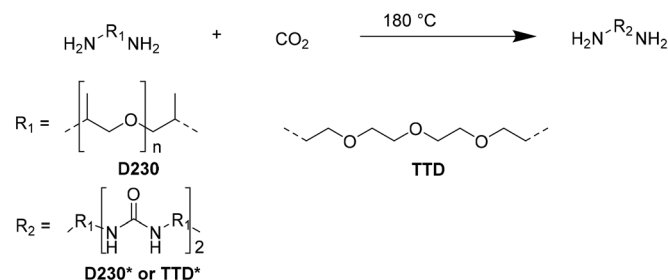


Fig. 10 One-pot synthetic pathway for NIPUs.

## A) 5-membered dicyclic carbonates synthesis



## B) Polyurea oligomers synthesis



## C) PHU and PHUU synthesis

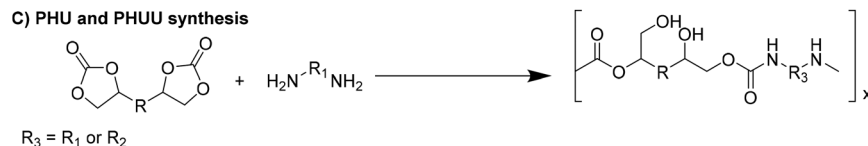


Fig. 11 Polyhydroxyurethane (PHU) and PHUU synthetic route.

parison to PHU-2, a decreased Young's module (20.7 vs. 5.0 MPa) and tensile strength (6.9 vs. 0.3 MPa) and an increased elongation at break were reported for PHUU-2 (258 vs. 914%, respectively). After the urea moiety's introduction, PHU-3, a viscous oil, became a solid (PHUU-3). This physical property change confers to PHUU-3 improved cohesive energy and mechanical properties (Young's module 8.6 MPa, tensile stress 1.3 MPa, and elongation at break of 31.3%).

Motokucho *et al.*<sup>38</sup> examined the activity of PUDF (Fig. 12) as a catalyst in the cycloaddition reaction between epoxide and  $\text{CO}_2$  to give the corresponding 5-membered cyclic carbonate.

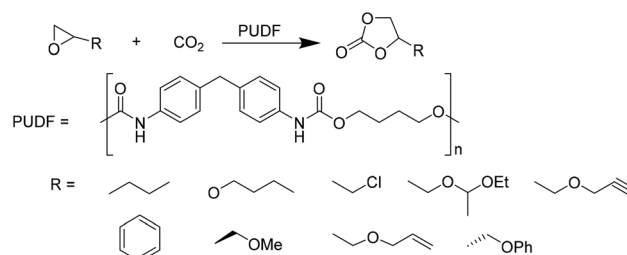


Fig. 12 PUDF-catalyzed cycloaddition of  $\text{CO}_2$  to various epoxides.





Firstly, the reaction was carried out by heating the phenyl glycidyl ether (PGE) at 150 °C for 42 h under 9.0 MPa pressure of CO<sub>2</sub>. The same reaction performed in the absence of PUDF didn't occur, whereas the presence of PUDF led to the forming of the carbonate with a yield of 49% and 99% selectivity, demonstrating its effectiveness as a catalyst. Moreover, the author demonstrated that PUDF could be easily separated from the reaction mixture and reused for further catalysis. The reaction conditions were systemically optimized by varying reaction time, CO<sub>2</sub> pressure, temperature, and PUDF/epoxide ratio. Increasing the reaction time increases the conversion of PGE into its carbonate. The reactions become quantitative after 48 h. Increasing CO<sub>2</sub> pressure increases the yield of the reaction, however, reaching a plateau at 4.9 MPa. Analogously, the temperature range of 120–180 °C affects the yield of the reaction, but the highest temperature causes a little loss of selectivity. PGE/carbonate conversions of 73% and 98% were achieved for the PUDF/PGE ratio of 0.1 and 0.4, respectively. The optimized reaction conditions were then used to evaluate the reusability and recyclability of PUDF as a catalyst for recycling the insoluble solid for several cycles of polyaddition PGE/CO<sub>2</sub>. After ten cycles, the reaction yields were almost constant (45–50%), indicating the reusability of the PUDF catalyst.

Finally, PUDF was tested as a catalyst for the cycloaddition of CO<sub>2</sub> to various epoxides (Fig. 12), demonstrating its versatility since the PUDF-catalyzed reaction can be applied to a broad spectrum of epoxides.

Based upon the PUs' non-processability concerns due to their permanently fixed topology, several efforts were focused on preparing the PUs' covalent adaptable networks (CANs).<sup>39</sup> These last are cross-linked networks capable, under external stimuli such as temperature or light, of activating exchange reactions between dynamic bonds, thus allowing the rearrangement of their topology network.<sup>40,41</sup> In this context, Pronoitis *et al.*<sup>42</sup> synthesized PHUs CAN by exploiting the urethane bond dynamicity or by creating dual dynamic networks by combining the urethane bond with other dynamic motifs such as imines and disulfides. In the reaction catalyzed by DBU-I<sub>2</sub> complex, poly(ethylene glycol) diglycidyl ether (PEGDE), 1,4-butanediol diglycidyl ether (BDGE) and resorcinol diglycidyl ether (RDGE) reacted with CO<sub>2</sub> to give the corresponding cyclic carbonates (PEGDC, BDC; RDC) with 80–97% yields (Fig. 13). Then, the reaction between cyclic carbonates and cysteamine at a 1 : 1 ratio was conducted on corresponding

PHU CANs designated by using the dicarbonate mol% with respect to the TMPTC cross-linker: TMPTC100 (only TMPTC and cysteamine), PEGDC30 (30 mol% PEGDC and 70 mol% TMPTC), PEGDC50 (50 mol% PEGDC and 50 mol% TMPTC), PEGDC70 (70 mol% PEGDC and 30 mol% TMPTC), BDDC30 (30 mol% BDDC and 70 mol% TMPTC) and RDC30 (30 mol% RDC and 50 mol% TMPTC). Their polymerization was monitored through the characteristic FTIR bands of the urethane group.

The properties of the resulting PHU CANs can be controlled by varying the networks' chemical structure and cross-link density. For instance, the aliphatic and long ether spacers of BDDC and PEGDC, respectively, conferred flexibility to the network, contrary to the aromatic RDC, which instead provided stiffness and rigidity. The decarbonate/TMPTC ratio also modulated the properties of the networks. Consequently, PHU CANs networks showed variegated thermal, mechanical, and viscoelastic properties. As detected by DSC, *T<sub>g</sub>* of PHU CANs, as-synthesized, ranged from –7 to 36 °C, with a slight decrease after their hot-pressed treatment attributed to a moisture-induced plasticizing effect exerted by the presence of the OH groups. Indeed, contact angle values of TMPTC100, BDDC30, and RDC30 – featured by the higher density of the pendant OH groups – were lower than those of PEGDC30 and PEGDC70. Moreover, when PHU-CANs were exposed to a 50% relative humidity for 20 days, the measured water uptake was fast and higher for the PEG-based polymer because of both the pendant –OH groups and the hydrophilicity of PEG spacers. Instead, RDC exhibited the slowest water uptake with most hydrophobic aromatic groups. Also, viscoelastic properties are a function of varying the chemical structure and cross-link density of PHU CANs networks. Finally, the reprocessing of PHU CANs networks has been evaluated. The adapt hot-pressing conditions were screened to select a temperature (100 °C for 20 min) that enabled a fast S–S exchange without inducing the urethane bond dissociation and the reversible cyclic carbonate-aminolysis side reactions. At this temperature, no cyclic carbonate was formed as detected by FT-IR, whereas at 140–160 °C, a band at 1790 cm<sup>–1</sup> attributed to cyclic carbonate's stretching appeared and progressively increased. Vacuum-dried PHU CANs tensile testing evaluation established the stiffness and strength of TMPTC100, BDDC30, and RDC30 with Young's moduli (*E*) above 1 GPa and small deformation at break ( $\epsilon_b$  = 1–2%) and the softness and flexibility of PEGDC-based CANs.

Through the terpolymerization of propylene oxide, CO<sub>2</sub>, and [3-(2,3-epoxypropoxy)-propyl]-trimethoxysilane (KH-560), siloxane-functionalized poly(ether carbonate)s (Si-PECs, Fig. 14) were synthesized and used as the soft segments of waterborne polyurethane (WPU, Fig. 14).<sup>43</sup>

It has been demonstrated that (1) siloxane moieties increase water resistance and heat resistance of the urethane bond, (2) CO<sub>2</sub> introduction confers rigidity, and (3) KH-560 promotes temperature performance. Thus, PPG-WPU, PEC-WPU, 5% Si-PEC-WPU, and 10% Si-PEC-WPU were obtained from PPG-2000, PEC-2000, 5% Si-PEC-2000, and 10%



Fig. 13 Chemical structure of a network's segment.





Fig. 14 Synthetic pathway for Si-PEC-WPU preparation.

Si-PEC-2000, respectively. As emerged by DSC investigations, flexible side chains and the hydrolytic cross-linking of the siloxane groups affect the  $T_g$ . Indeed, the rigid carbonate units in PPG-WPU confer a higher  $T_g$  degree than Si-PEC-WPU with soft side chains. A similar trend was rescued for the two-step degradation process (the first step was at about 295, 313, and 322 °C; the second step at about 352, 360, and 367 °C for PPG-WPU, PEC-WPU, and Si-PEC-WPU, respectively). The carbonate content and the siloxane presence affect the mechanical performance. The carbonate content in PEC-2000 increases the tensile strength but reduces the elongation at break, whereas the carbonate and siloxane unit introduction in Si-PEC-WPUs leads to good tensile strength and elongation at break. As expected, Si-PEC-WPU showed a lower swelling ratio (36.6%) than PPG-WPU and PEC-WPU (55.2 and 49.3%, respectively).

In summary, the carbonate unit improved the mechanical resistance of WPU, whereas the siloxane units offered higher cross-linking density and thermal stability.

Another green, sustainable route for the synthesis of NIPU consists of the reaction between [4,4'-bi(1,3-dioxolane)]-2,2'-

dione (BDC, **21**, Fig. 15) and aliphatic diamines.<sup>44</sup> To this purpose,  $\text{CO}_2$  cycloaddition to 1,3-butadiendiepoxy (**20**, Fig. 15) using a bivalent catalytic system consisting of metal-organic frameworks (MOFs) as catalysts and cetyltrimethylammonium bromide (CTAB, **d**, Fig. 15) as co-catalyst, was performed.

MOFs are homogeneous catalysts created from metals and organic linker compounds with high chemical, thermal, and mechanical stability. In this context, Benedito *et al.* selected and tested a series of MOFs based on their selectivity, capability to capture  $\text{CO}_2$  (Co- or Mg- or Ni- or GO-Ni-MOF-74, **a**, Fig. 15), and long catalytic life (Al-OH-fumarate (**b**) and Al-PDA (**c**), Fig. 15). The authors focused on finding optimal reaction conditions for the highest BDC yields.

To achieve this aim, the carbonation of 1,3-butadiendiepoxy was monitored through GC-MS and  $^1\text{H}$ -NMR. The epoxide conversion into BCD was truly efficient when the reaction was conducted in the presence of a co-catalyst (catalyst/co-catalyst ratio 1 : 1). Their synergic action reflects on the higher percentage of epoxide/BDC conversion (44–95% yield) than the ones detected in the absence of the co-catalyst (0–6% yield). In





Fig. 15 Synthesis of BDC.

addition to being solvent-free, the synthetic strategy adopted to obtain BDC does not require the removal of by-products.

In Table 1, the epoxide used, as well as the synthesized cyclic carbonates, and some remarks on the reaction are summarized.

A synthetic route to produce PUs without isocyanate was reported by Chun *et al.*, which described the usage of bis(cyclic carbonate)s and diamines to synthesize PHU compounds.<sup>45</sup> Neopentyl glycol diglycidyl ether (NPGDGE) and resorcinol diglycidyl ether (RDGE) were initially converted into bis(cyclic carbonate)s through the simple reaction of the epoxides with CO<sub>2</sub> (Fig. 16). The subsequent reactions used either isophorone diamine (IPDA) or 1,4-DAB, and each bis(cyclic carbonate). The production of all four different PHUs was quantitative. Then, using the DSC apparatus, the *T<sub>g</sub>* of the non-isocyanate PHUs (NI-PHUs) were determined in order to evaluate their thermal properties. When RDGE was used as the diglycidyl ether rather than NPGDGE, the *T<sub>g</sub>* of the NI-PHU was higher. Additionally, when IPDA was employed as the diamine as opposed to 1,4-DAB, the *T<sub>g</sub>* of the NI-PHU was higher. As a result, the NI-PHUs created by IPDA displayed greater thermal stability, making them potential candidates for coating applications.

Among the most suitable polymers are epoxy resins, which have excellent mechanical strength, chemical resistance, heat resistance, and bonding ability qualities.<sup>46,47</sup> Of course, epoxy resins have limitations, and to overcome these, several strategies have been employed, such as using reactive and non-

reactive additives.<sup>48</sup> Recently, a flexible aliphatic epoxy with urethane linkages was created using CO<sub>2</sub> in a non-isocyanate, environmentally friendly method (Fig. 16). The synthesized aliphatic epoxy was cross-linked with rigid aromatic epoxy (DGEBA) to adjust its mechanical properties.<sup>49</sup> Simply changing the ratio of two epoxies allowed for a wide range of mechanical property tuning, and the resulting epoxy composites displayed three distinct natures: a toughened polymer, an elastomer, and a pressure-sensitive adhesive (PSA). The viscoelastic and adhesive capabilities of the PSA epoxy were evaluated, and single lap shear, cyclic tensile, and Izod impact tests were performed for toughened or elastomeric epoxy composites. It has been proven that epoxy composites that have been toughened, made of elastomers, and resemble PSA tapes can be used in place of traditional structural adhesives, elastomers, and PSA tapes, respectively. Two kinds of aromatic and aliphatic epoxides were employed to provide adjustable mechanical qualities. An environmentally friendly technique was used to create aliphatic epoxy with urethane linkage (C-UME), as reported in Fig. 17. Polymer-supported imidazolium salts containing zinc were utilized for the manufacture of propylene carbonate from CO<sub>2</sub>.<sup>50,51</sup>

The propylene carbonate was allowed to react with polyoxypropylenediamine, and a brown-colored hydroxyurethane-terminated aliphatic diol incorporating urethane linkage was quantitatively obtained. This molecule was treated with epichlorohydrin, sodium hydroxide, and a catalytic amount of TBAB to obtain the C-UME. Bisphenol A diglycidyl ether



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### Fixation of CO<sub>2</sub> conditions

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Table 1 (Contd.)

Fixation of CO <sub>2</sub> conditions						
Starting epoxide	Cyclic carbonate prepared	Catalyst	T	t	Pressure	Solvent
		PUDF	150 °C	42–48 h	9 MPa	—
		PUDF	150 °C	42–48 h	9 MPa	—
		PUDF	150 °C	42–48 h	9 MPa	—
		PUDF	150 °C	42–48 h	9 MPa	—
		PUDF	150 °C	42–48 h	9 MPa	—
		PUDF	150 °C	42–48 h	9 MPa	—
		DBU-I <sub>2</sub> complex	100 °C	92 h	1 atm	—
		DBU-I <sub>2</sub> complex	100 °C	92 h	1 atm	—
		DBU-I <sub>2</sub> complex	100 °C	92 h	1 atm	—
		MOF/CTAB	120 °C	6 h	30 bar	—
		LiBr	80 °C	48 h	1 bar	DMF
		LiBr	80 °C	48 h	1 bar	DMF
		LiBr	80 °C	48 h	1 bar	DMF
		LiBr	80 °C	48 h	1 bar	DMF
		LiBr	80 °C	48 h	1 bar	DMF
		LiBr	80 °C	48 h	1 bar	DMF

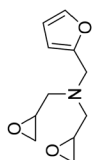
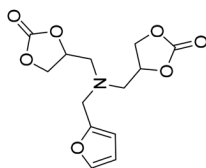
Starting epoxide

Cyclic carbonate prepared

Ref.

Table 1 (Contd.)

	Fixation of CO <sub>2</sub> conditions					Ref.
	Catalyst	T	t	Pressure	Solvent	
Starting epoxide		100 °C	4 h	5 MPa	DMF	Wulf <i>et al.</i> <sup>26</sup>
Cyclic carbonate prepared	LiBr					



(DGEBA), dicyandiamide, and 3,3'-(4-methyl-1,3-phenylene) bis (1,1-dimethylurea) were used as the aromatic epoxy, curing agent, and accelerator, respectively. To balance flexibility and rigidity, the content of C-UME and DGEBA was adjusted while keeping the mole ratio of the difunctional epoxy resin, curing agent, and accelerator constant at 100:28.6:1.43. The most flexible epoxy among the composites that had been made had PSA characteristics, and its adhesion performance (peel strength = 6.8 N cm<sup>-1</sup>) matched that of traditional PSAs. The prepared PSA's viscoelastic window implied it might be used as a detachable or all-purpose PSA.

A new family of PUs known as poly(oxazolidone) is readily accessible *via* an isocyanate-free method by step-growth copolymerizing primary diamines with CO<sub>2</sub>-based monomers, *e.g.*, bis-(alkylidene cyclic carbonates), at room temperature (Fig. 18). Detrembleur *et al.* explored the scope of this procedure by looking at how the diamine used, and the reaction conditions affect the polymer's structure and macromolecular characteristics.<sup>52</sup> The effects of different amine structures on the reaction's speed, yield, and selectivity were first examined using model reactions on small molecules (Fig. 18).

Both the ring opening of the cyclic carbonate and the intramolecular cyclization of the oxo-urethane intermediate into the hydroxyoxazolidone were shown to be affected by the amine structure. The hydroxyoxazolidone was primarily provided by aliphatic and benzylic amines, which explains why the intramolecular cyclization of the oxo-urethane happened quickly. However, cycloaliphatic amines produced both the oxo-urethane and the hydroxyoxazolidone products; it was thought that the steric hindrance of these amines caused the cyclization step to proceed more slowly. However, the addition of DBU as a catalyst sped up this process. The subsequent polyaddition of bis-*α*-alkylidene cyclic carbonate (*α*CC) with the diamines produced many poly(hydroxyoxazolidone)s (Fig. 19). According to the model reaction, the more sterically hindered cycloaliphatic diamines produced polymers with hydroxyoxazolidone and oxo-urethane links. Higher molar mass polymers were more likely to form when DBU was added. Aliphatic and benzylic diamines are provided exclusively as poly(hydroxyoxazolidone)s. Simply refluxing poly(hydroxyoxazolidone)s in glacial acetic acid made obtaining poly(alkylidene oxazolidone)s possible. Importantly, depending on the steric hindrance of the poly(hydroxyoxazolidone), two forms of oxazolidone connections with exocyclic olefin moieties were found. *α*-Alkylidene oxazolidone linkages were generated preferentially for the sterically hindered ones, but the less bulky ones showed a mixture of *α*- and *β*-alkylidene oxazolidone nearly in equimolar proportions. The unsaturated poly(oxazolidone)s showed a high thermal degradation temperature (*T*<sub>d</sub> > 370 °C) with a high *T*<sub>g</sub> (90–130 °C), indicating that this novel family of polymers is highly appealing for applications requiring high temperatures, even though the *T*<sub>g</sub> of the poly(hydroxyoxazolidone)s could not be measured due to low polymer degradation temperature.





Fig. 16 Preparation of the NI-PHUs.

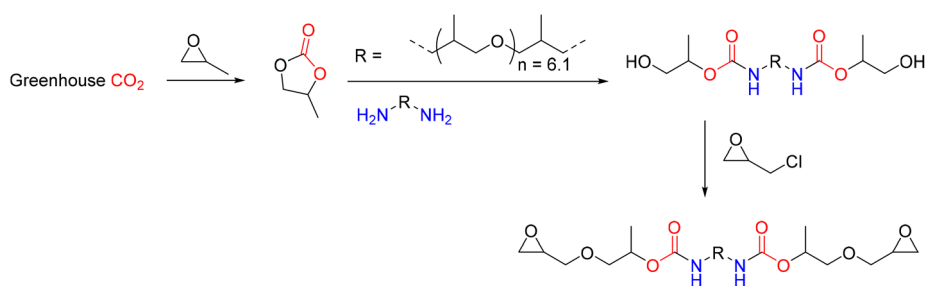
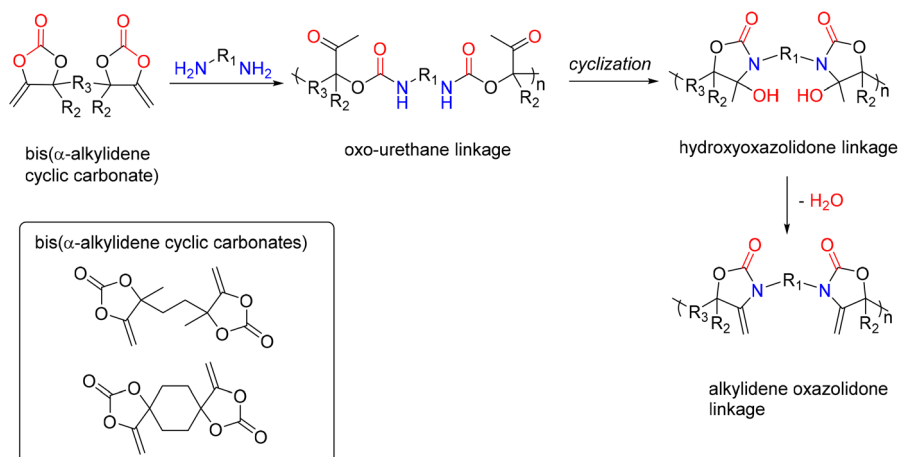


Fig. 17 Synthesis of urethane-modified epoxy (C-UME) through an eco-friendly route.

Fig. 18 Model reaction of  $\alpha\text{CC}$ .Fig. 19 Polyaddition of bis( $\alpha$ -alkylidene cyclic carbonate)s to diamine.

### 3. Fully biobased polyester

As mentioned, another strategy often used to produce PUs is by reacting polyols and polyisocyanates. Although many bio-based polyols are offered commercially, very few bio-based isocyanates are accessible.<sup>53</sup> Thus, PUs are only partially bio-based as they are synthesized from bio-based polyols and petroleum-based isocyanates. However, the transition to plastics and polymers made without fossil fuels brings new structures to market for various purposes.<sup>54</sup> Bio-based polyols are typically synthesized from vegetable oils, carbohydrates, lignocellulose, proteins, or fatty acids.<sup>55,56</sup>

Castor-based PUs were obtained through a non-isocyanate route using oligomeric ricinoleic acid (ORA) with variable average polymerization degrees depending on the catalytic conditions.<sup>57</sup> Following esterification, epoxidation, cycloaddition with CO<sub>2</sub>, and subsequent curing with diamine, ORA intermediates allow the generation of various PHUs with various mechanical and thermal characteristics. Ricinoleic acid-based NIPUs were also obtained using aliphatic diamine, incorporating octa(aminopropyl) polyhedral oligomeric silsesquioxane (OAP-POSS).<sup>58</sup> The integration of POSS units into the polymer consent to control the characteristics of the resulting material, improving its thermal stability.

By using two biscarbonates made from oleic acid methyl ester, internal carbonated fatty acid diester (ICFAD) and terminal carbonated fatty acid diester (TCFAD), and two diamines in bulk polyaddition, novel linear PUs with molecular weights up to 13 500 g mol<sup>-1</sup> and *T<sub>g</sub>* of about -15 °C were obtained.<sup>59</sup>

From jojoba and castor oils, cyclic carbonate monomers with diverse functionalities were produced using thiol-ene coupling with thioglycolic acid and esterification with glycerin carbonate.<sup>60</sup> By reacting the bifunctional cyclic oil-based carbonate with different amines, linear and cross-linked PHUs were obtained with *T<sub>g</sub>* ranging from -45 to 20 °C.

An alternative approach involves polyols combined with sugar-derived 2,5-furandicarboxylic acid to produce fully bio-based poly-hydroxylurethanes.<sup>61</sup> By inserting urethane links into the polyester's backbone, it is possible to obtain thermoplastic polyhydroxy(ester-urethane)s (NIPHEUs), entirely made of bio-based non-isocyanate materials. This technique effec-

tively improves these materials' poor physical and mechanical qualities.<sup>62</sup> The synthetic route started with glycerol carbonate (GC), 1,8-diaminooctane, and 1,12-diaminododecane, two aliphatic diamines that can be produced from renewable feedstocks through biotechnological processes. It led to the formation of two hydroxyurethane (HU)-tetraols, entirely bio-based (Fig. 20). Consequently, the dimethyl ester of 2,5-furandicarboxylic acid was reacted with HU-tetraols to produce NIPHEUs with vitrimer-like behavior. The as-obtained polyester-HU exhibited outstanding thermal behavior, thermally induced bond exchange driven by the transcarbamoylation reaction, and a hydrogen bonding network. This new class of NIPHEUs exhibits peculiarities that may open the door to developing a new assortment of valuable green materials.

In addition to glycerol carbonate, pentaerythritol (PC) and trimethylolpropane (TMC) carbonates have been prepared to study carbonate functionality's role in NIPU formation.<sup>63</sup> Since GC has a very low carbonate functionality and hinders amine-mediated cross-linking, it may be added to PEC as a reactive diluent, reducing resin viscosity and significantly enhancing the material's thermal and mechanical characteristics. Therefore, a blend of blends of cyclic carbonates with different carbonate functionalities improves *T<sub>g</sub>*, temperature, stiffness, and strength.

NIPU derivatives have also been prepared using an environmentally friendly and safe method that employs CO<sub>2</sub> and soybean oil.<sup>64</sup> Epoxidized soybean oil (ESBO) (Fig. 21) was reacted with CO<sub>2</sub> in the presence of a catalytic system consisting of TBAB and CaCl<sub>2</sub> to synthesize cyclic carbonate (CSBO).



Fig. 21 Structures of ESBO and NIPU with azetidinium groups.

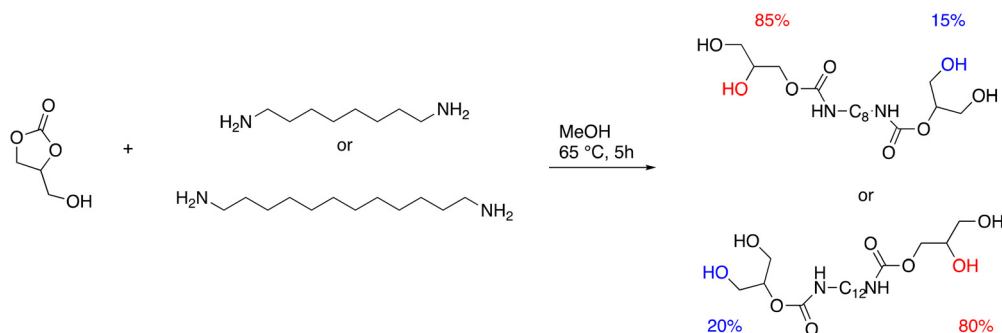


Fig. 20 Synthetic route of HU-tetraol-C8 and HU-tetraol-C12.



Subsequently, CSBO was reacted with tetraethylenepentamine to obtain the corresponding NIPU. The free secondary amine product was treated with epichlorohydrin to produce cross-linked azetidinium networks (Fig. 21). The material was designed as wound dressing thanks to the 100% antibacterial performance offered by the cationic azetidinium groups against various bacteria. Neither the dressings nor their extracted leachates showed cytotoxicity against fibroblasts. The dressings can preserve damaged skin tissue from external forces, as they show the desired tensile properties.

Epoxy soybean oil (ESO) has also been employed to produce partially bio-based NIPUs with a double dynamic network to reprocess and self-healing materials under mild conditions.<sup>65</sup> Cyclic carbonates were synthesized from ESO by reactions with CO<sub>2</sub>, thus obtaining carbonate soybean oil (CSBO). The latter was then reacted with a diamine (4,4'-diaminodiphenyl methane (DDM) or 4,4'-diaminodiphenyl disulfide (DDS)) for the preparation of partially bio-based NIPU (CSBO-DDM and CSBO-DDS) without using catalysts or solvents; the reaction scheme is reported in Fig. 22. Furthermore, ESO was directly reacted with DDS containing disulfide bonds to prepare a material (ESO-DDS) to explore the dynamic properties of the network formed by the disulfide bond. Relaxation experiments with external stimuli were performed to correlate the different bond exchange capacities to the different dynamic structures of the covalent network underneath. To quantify the self-repair capacity of NIPUs, scratches on the material surface were observed after several different heating or UV irradiation times.

The repair of severely damaged materials was done thanks to the synergistic effect of the exchange of disulfide and carbamate bonds with a controlled heat press to obtain rework.

The composition of NIPUs materials has a significant bearing on their characteristics.<sup>66</sup> The poor mechanical characteristics of the NIPUs composed of CSBO and short diamines were attributed to cross-linking because of the high cyclic carbonate functionality of CSBO. By varying the degree of carbonation, it is possible to create NIPUs with tunable cross-linking densities, realizing material with improved mechanical properties. Moreover, by changing the curing time and material ratio for CSBO-DDM, NIPUs with improved mechanical and thermal properties can be obtained. It was found that a curing time of 3 days and a 1 : 1 ratio yielded the best results, giving rise to a material with suitable tensile strength and elongation at break. However, cross-linking density affects the  $T_g$ , and excessive rigid ring introduction causes issues.<sup>67</sup>

On the other hand, it was simple to create entirely bio- and CO<sub>2</sub>-sourced NIPUs with increased elongation break using a melt copolymerization process between CSBO and amino-telechelic oligoamide. The amount of cyclic carbonate in CSBO was correlated with its mechanical characteristics, particularly its tensile strength.

Rigid PU foam (PUF) was produced from Soybean meal biomass.<sup>68</sup> Once the percentage of soluble carbohydrates in the biomass was determined, they were separated from the other components, such as protein, ash, and moisture. Then, the entire soybean meal (soymeal) was converted into bio-



Fig. 22 Reaction scheme for obtaining poly-oil (ESO-DDS) and partially bio-based NIPUs (CSBO-DDM and CSBO-DDS).





based polyol through two reaction steps. Initially, soy meal was reacted with ethanolamine in different ratios, resulting in various amino derivatives. The amino derivatives were then transformed into polyols by reacting with propylene carbonate without a catalyst. The process can be completed in 2–4 hours, saving money and avoiding problems with contamination or catalyst recovery problems. The reactions were conducted sequentially in the same reactor without further purification. Different mass ratios of soybean meal and ethanolamine (1 : 2, 1 : 3, 1 : 5) produced polyols with different hydroxyl values. In synthesizing bio-based rigid PUFs comprising 20% and 50% bio-based polyols, soy flour polyol has been successfully employed. The compressive strength of a bio-based PUF was greater than 200 kPa for a foam with a density of  $40 \text{ kg m}^{-3}$ . Soy meal polyols may be produced at costs between \$0.6 and \$0.7 per pound, making their usage in commerce feasible. The performance characteristics of rigid PUF made from biomaterials were comparable to those of PUF made from commercial polyol. This offers a significant cost advantage and makes these soybean meal-based polyols the lowest-cost bio-based polyols on the market.

Another biological resource used as the starting material for NIPUs was linseed oil (LO) (Fig. 23).<sup>69</sup> Pouladi *et al.* conducted a study to exploit LO as a biological resource for synthesizing a resin with anti-corrosive properties. LO unsaturations were first converted into epoxy groups, followed by polycondensation and carbonation reactions to form cyclocarbonate groups in the presence of  $\text{CO}_2$  and TBAB as catalyst. The polymerization performance of the resins synthesized with the hardener diethylenetriamine (DETA) in different ratios was evaluated using various techniques such as DSC, TGA, and rheological tests. As the carbonation content increased, more hydroxyl groups were formed in the final polyhydroxylated PU structure. This was due to the reaction of the cyclocarbonate with the amine, which increases the polymer's adhesion strength and mechanical properties.

However, the conventional method that involves the production of NIPU from bicyclic carbonate and polyamine does not naturally produce foaming agents.<sup>70</sup> Researchers recently used a new blowing agent to make high-density NIPU foams with large interconnected cells.<sup>71</sup> Common blowing agents can worsen fire behavior, so there is interest in using nonflammable alternatives. Producing low-density NIPU foams with small, closed pores for thermal insulation remains challenging. In this view, low-density microcellular foams derived from bio and  $\text{CO}_2$  sources have been produced through supercritical carbon dioxide foaming technology.<sup>72</sup>  $\text{CO}_2$ -sourced monomers were created from poly(ethylene glycol) diglycidyl ether (PEG) and epoxidized soybean oil (ESBO) using a bicom-

ponent organocatalyst. NIPUs were then synthesized through melt step-growth polymerization. The resulting  $\text{CO}_2$ -blown microcellular NIPU foams exhibited low density, small pores, and low thermal conductivity. Also, obtaining NIPU with tailored cross-linking density is a challenge. However, Catalá *et al.* generated bio-based NIPU from triglyceride carbonates, produced in  $\text{scCO}_2$ , and different diamines by using water or bioalcohols as capping substances to tailor the cross-linking density for specific applications.<sup>73</sup> To improve the mechanical

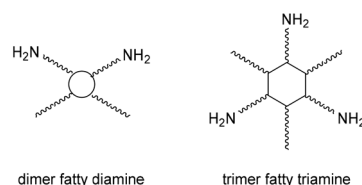


Fig. 24 Structure of Priamine 1071.

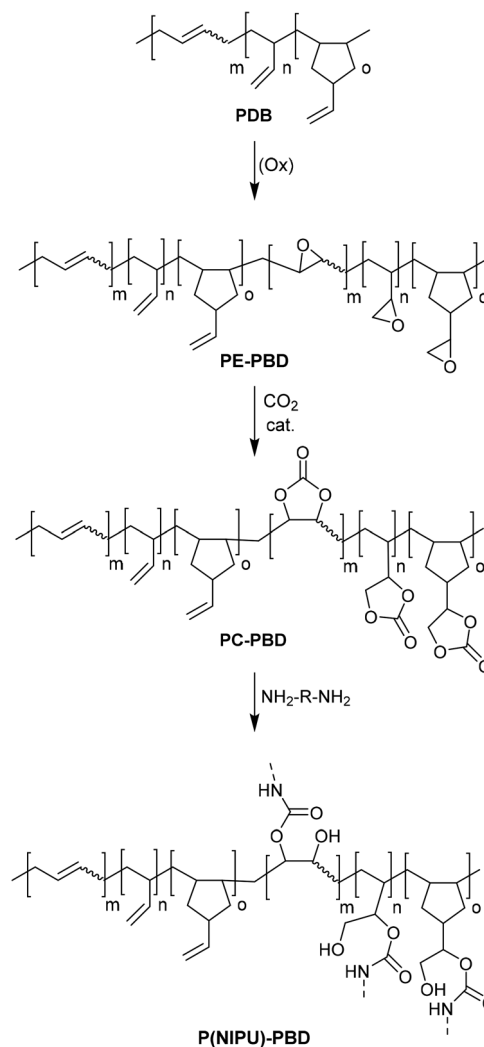


Fig. 25 Reaction sequence for the preparation of P(NIPU)-PBD polymers.

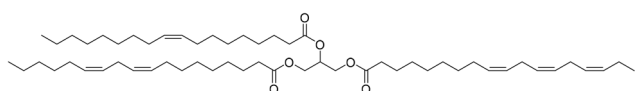


Fig. 23 Chemical structure of linseedoil (LO).



properties and thermal stability of bio-based NIPUs, isoeugenol-based 6-membered cyclic carbonate (iEbcc) has been chosen as a monomer thanks to the presence of rigid benzene ring structure and no flexible linkage groups between benzene ring.<sup>74</sup> In this way, it is possible to obtain biobased and degradable NIPU with thermal stability up to 340 °C tensile stress of 64 MPa that can be reprocessed *via* transcarbamylation reactions under elevated temperatures.

Tailor-made bis(cyclic carbonate)s cross-linked with the commercially available bio-based amine hardener have been used to produce, through a green path, NIPUs.<sup>75</sup> A two-step process involving the epoxidation of bio-based polyether polyols (PO3G) with different molecular weights and the subsequent chemical fixation of CO<sub>2</sub> allowed the production of a series of five-member bis(cyclic carbonates), subsequently

used as monomers for the synthesis of NIPU. Initially, the polyether polyols were reacted with epichlorohydrin in the presence of BF<sub>3</sub>, after which the product obtained was reacted with NaOH to obtain the respective epoxides. The cycloaddition reaction with CO<sub>2</sub> was then carried out in the presence of TBAB as a catalyst at 110 °C. Finally, the bis(cyclic carbonates) were converted to NIPUs by reaction with a bio-based amine, Priamine 1071, a mixture of dimer fatty diamine and trimer fatty triamine (Fig. 24). The synthetic methods employed focus on the design of processes and products that minimize negative environmental impact. In fact, the syntheses were attempted under solvent-free conditions with a view to green and sustainable polymer chemistry.

Western red cedar bark was also exploited as a raw material for the synthesis of NIPUs. The main constituents of the bark

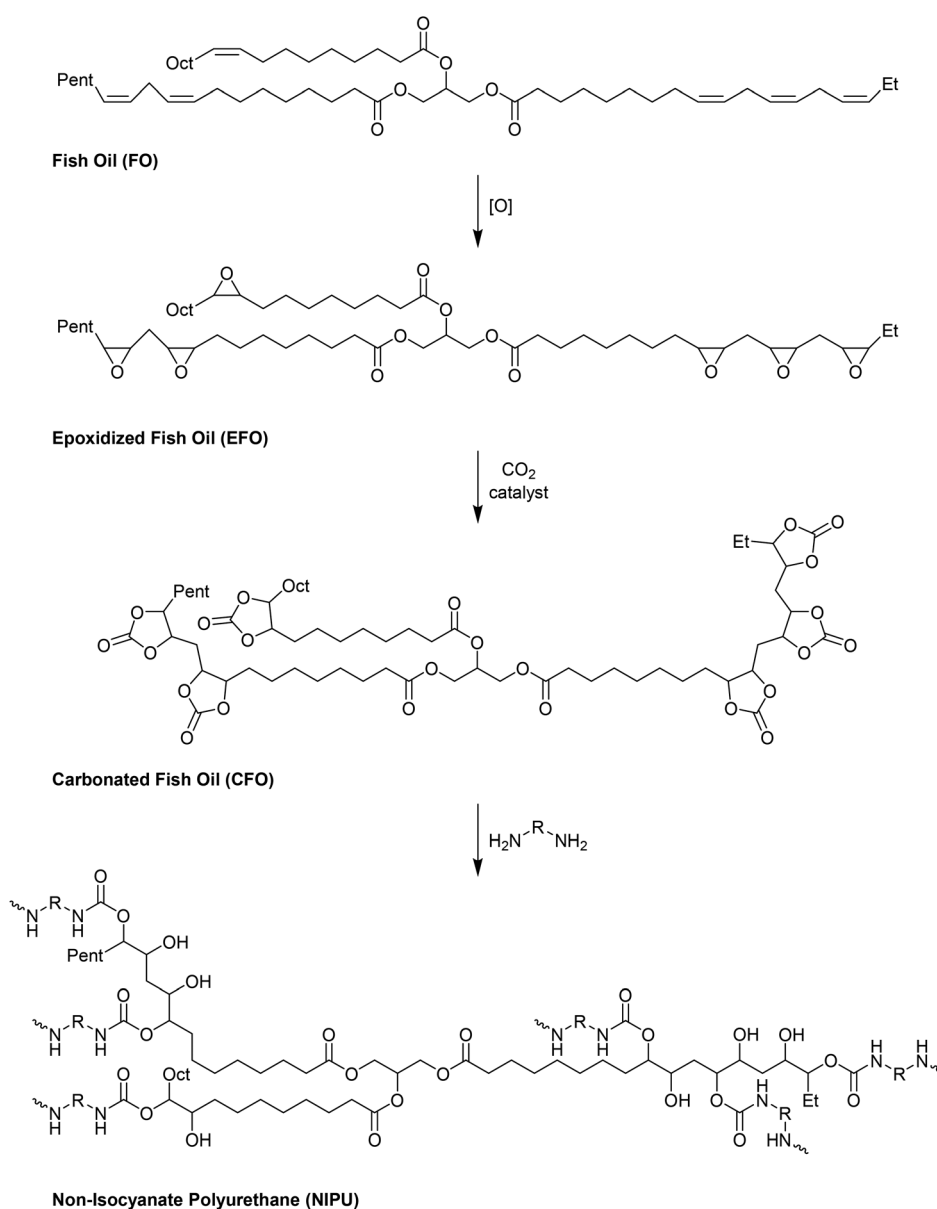


Fig. 26 Synthesis of carbonated fish oil (CFO) from waste-derived fish oil (FO) and preparation of FO-based NIPU from CFO and diamines.



are lignin, cellulose, and tannins which are used as sources of hydroxyl functions.<sup>76</sup> Experimentally, the bark was first subjected to the oxypropylation reaction in the presence of propylene oxide KOH, resulting in an OH-activated bark oil (HABO). The oil was then epoxidized, first by reaction with  $\text{BF}_3$  and epichlorohydrin and later with NaOH, to give Epox-HABO. Subsequently, the cycloaddition reaction with  $\text{CO}_2$  was carried out to obtain Carbonated-HABO. Finally, the latter was reacted with various amines, such as ethylenediamine (EDA), hexamethylene diamine (HMDA), isophorone diamine (IPDA), DETA, and tris(2-aminoethyl)amine (TAEA), to produce bark-based NIPUs. Because so many OH groups were produced when urethane was synthesized, NIPUs typically exhibit substantial moisture absorption.<sup>77</sup> Thermal experiments showed that NIPUs were thermally stable up to 250 °C before the polyether segments and urethane connections began deteriorating.<sup>76</sup>

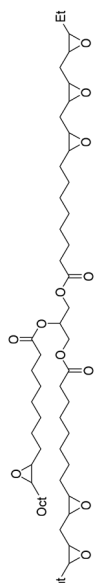
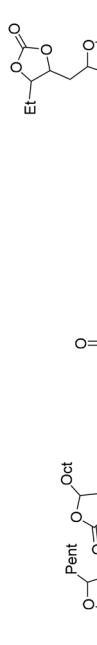
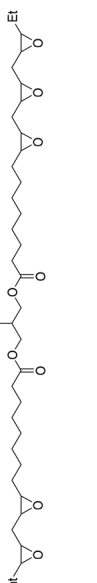
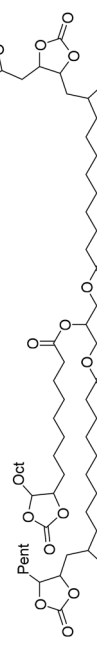
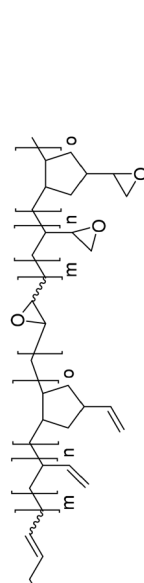
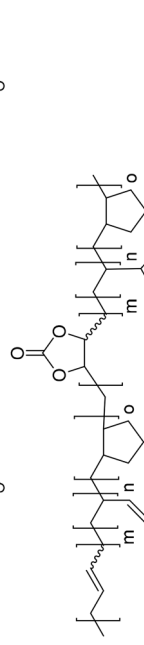
Epoxidation of PBDs, polymers with a high content of double bonds, generates PE-PBDs by reaction with hydrogen peroxide.<sup>78</sup> Using bis(triphenylphosphine)iminium (PPN) or tetra-*n*-butylammonium (TBA) salts with chloride, bromide, and iodide as counter ions and  $\text{CO}_2$  as reagent the cycloaddition reaction is performed to produce the corresponding carbonates PC-PBDs. They are used to achieve cross-linking reactions of NIPUs using bio-derived diamines.

Finally, PBD-based NIPUs [P(NIPU)-PBDs] were synthesized by the reaction of PC-PBD samples with 1,5-pentanediamine (PDA) or 1,8-octanediamine (ODA). PC-PBD was mixed with diamine (in a molar ratio of 1 : 1 or 1 : 2 relative to the epoxide content) and polymerized by heating in a nitrogen atmosphere for 16 hours (Fig. 25). In the PUs obtained, the carbonate units contained in the incompletely polymerized networks show stabilizing effects, presumably through interactions between urethane and carbonate.

Fish oil (FO), derived from aquaculture waste, is a potential alternative to vegetable-based oils. The FO is extracted from by-products produced in fish processing plants, including heads, bones, skin, and entrails. The United Nations has emphasized aquaculture as a sustainable method of producing protein. However, this is only true if the entire fish is used, not just the expensive fillets sold as food. Epoxidized FO can react with  $\text{CO}_2$  to produce cyclic carbonates.<sup>79</sup> Three different methods are used for the epoxidation of FO: (i) oxidation with 3-chloroperoxybenzoic acid, (ii) oxidation with hydrogen peroxide and acetic acid, catalyzed by sulphuric acid, and (iii) oxidation with hydrogen peroxide and acetic acid and (iv) oxidation with hydrogen peroxide catalyzed by formic acid. The synthesized FO epoxides are reacted with  $\text{CO}_2$  in the presence of TBAB as the catalyst and ascorbic acid to produce cyclic FO carbonates with high conversions (Fig. 26). Subsequently, the obtained carbonates are reacted with a biomass-derived amine (NC-540 or 4,7,10-trioxa-1,13-tridecanediamine) to give bio-derivative amine PU materials.

The starting epoxide used and the corresponding synthesized cyclic carbonate, with some remarks on the reaction, are summarized in Table 2.

Table 2 Methods of preparations of cyclic carbonates

Starting epoxide	Cyclic carbonate prepared	Fixation of $\text{CO}_2$ conditions	Ref.
		Catalyst TBAB/ascorbic acid T 110 °C t 48 h Pressure 10 bar Solvent neat	Laprise <i>et al.</i> <sup>79</sup>
		Catalyst TBAB/ $\text{CaCl}_2$ T 140 °C t 32 h Pressure 40 atm Solvent neat	Yang <i>et al.</i> <sup>67</sup>
		Catalyst bis(triphenylphosphine)iminium chloride (PPN-Cl) T r.t. t 24–72 h Pressure 20 bar Solvent MEK	Dechent <i>et al.</i> <sup>78</sup>



## 4. NIPU from oxidative carbonylation

Another possible route for the non-phosgene production of isocyanate precursors was reported as the oxidative carbonylation of toluene-2,4-diamine (TDA) with methyl formate (MF), which can be produced from CO<sub>2</sub>.<sup>80</sup> The findings of this study demonstrate that a green non-phosgene route to PUs is indeed possible by the oxidative carbonylation of industrially important diamines using CO<sub>2</sub>-based MF as a reagent. In this context, a thorough study has been done on the Pd-catalyzed oxidative carbonylation of TDA with MF, identifying the most crucial side products aside from toluene-2,4-dicarbamate (TDC) as the target product. Three distinct routes that result in side products have been identified (Fig. 27).

First, formamides are produced *via* a nucleophilic substitution at the MF carbonyl group without using a Pd catalyst or oxygen. Second, the formaldehyde produced *in situ* underwent electrophilic aromatic substitution/condensation to give the methylene-bridged tetracarbamate (TCM).<sup>81</sup> The TCM dimer is particularly interesting for industrial use due to its potential and makes an appealing target product. Thirdly, unintended *N*-methylations were brought on by a reaction with the dimethyl carbonate also created during the oxidative carbonylation with MF. PdCl<sub>2</sub>/CuCl<sub>2</sub> and several heterogeneous Pd-catalysts were investigated for the catalyst's impact on product distribution. The discovery of partial suppression of the undesirable side reactions by the oxidic support materials ZrO<sub>2</sub>, CeO<sub>2</sub>, and SiO<sub>2</sub> led to better yields of TDC and TCM. The yields of TDC and TCM together were up to about 50%, and higher TDC yields were correlated with lower TCM yields.

The method of oxidative carbonylation with MF was extended to other diamines, 4,4'-methylenedianiline (MDA) and 2,4-diaminomesitylene (DAS), and the identified products of the reaction are reported in Fig. 28 and 29.

## 5. Self-healing NIPUs

Artificial materials are vulnerable to deterioration in the form of cracking or microcracking.<sup>82</sup> Microcracks can expand and merge, which shortens the material service life and increases the risk of catastrophic breakdown of the materials. Early microcrack diagnosis and repair prevent these issues and extend the service life.

In these situations, self-healing materials can be used since they can identify cracks early and automatically fix them.<sup>83</sup>

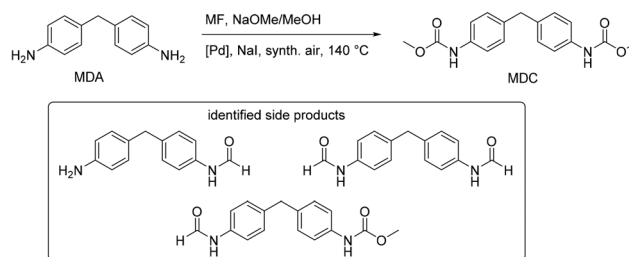


Fig. 28 Oxidative carbonylation of MDA with MF.

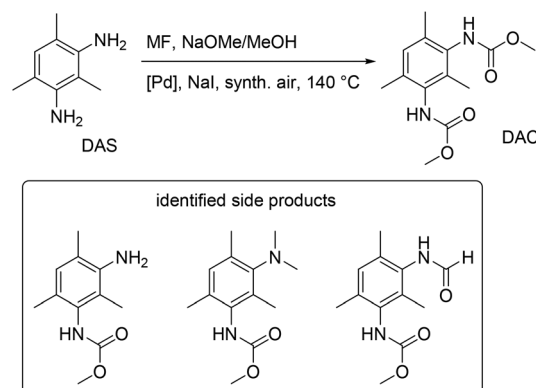


Fig. 29 Oxidative carbonylation of DAS with MF.

Additionally, these materials may increase material dependability, lengthen service life, lower replacement costs, and increase product safety. Numerous research investigations on the creation of self-healing systems are carried out each year due to these appealing characteristics, and polyurethane chemistry is involved in several ways<sup>84</sup> since the first studies in self-healing materials.<sup>85</sup> A comprehensive review of the field is out of the scope of this review, but an examination of the most advanced polyurethane-based self-healing material will be provided.

One of the approaches to give a material self-healing properties is to exploit a reversible covalent bond formation. Diels–Alder reactions have been used with recyclable PU nanocomposites,<sup>86,87</sup> and photochemical [2 + 2] cycloaddition have been used with coumarin-based PU.<sup>88,89</sup> Disulfide (S–S) exchange reactions and *S*-aromatic thiourethane exchange reaction have been reported with PU nanocomposite<sup>90</sup> and polythiourethane networks,<sup>91</sup> respectively. Transesterification



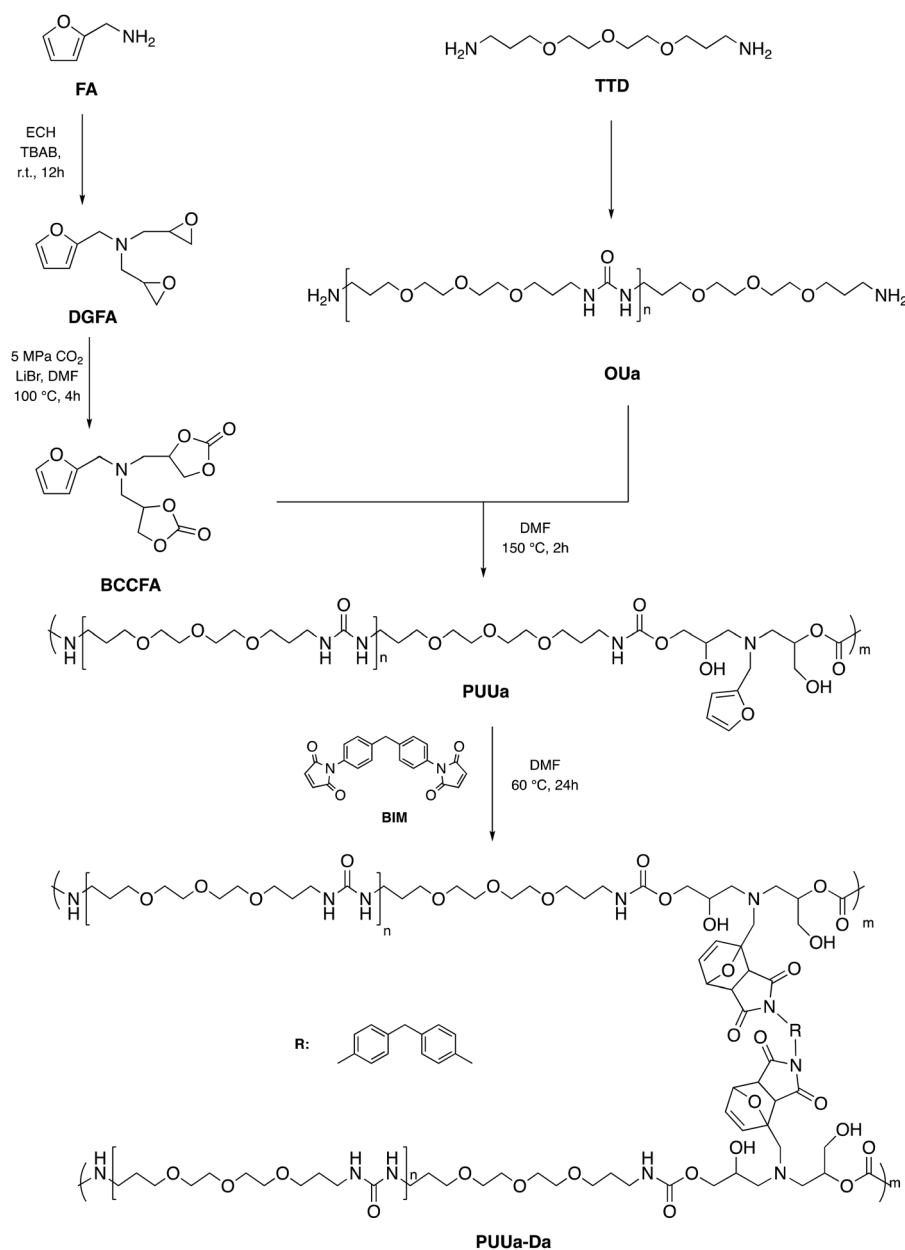
Fig. 27 Oxidative carbonylation of TDA with MF and major subproduct (TCM).



is another example of a reversible reaction employed for self-healing thermoplastic PU.<sup>92</sup> Hydrogen bonds can be used in addition to tuning the mechanical properties of materials. In a few examples, they have been used to the self-healing extent in PU elastomer<sup>93</sup> and to control host-guest interactions between cyclodextrin and adamantane in thermoplastic PU prepared from hexamethylene diisocyanate and tetraethylene glycol polymer hydrogel of poly(*N*-isopropylacrylamide).<sup>93–95</sup> Hydrogen bonds control has also been coupled with the already discussed Diels–Alder, where multi-arm UV-cured PU, *N,N'*(4,4'-methylenediphenyl)bismaleimide, and furfuryl alcohol have been reacted.<sup>96</sup>

Polymeric materials can also recover their properties through physical interactions. Polymer blends and remote self-healing have been used as healing mechanisms for thermosetting vitrimer with thermoplastic PU,<sup>97</sup> PU nanocomposite, and carbon nanotubes,<sup>98</sup> respectively. Microvascular networks and nanoparticle-based self-healing have also been reported for PU-based materials.<sup>99,100</sup>

In 2016, Caillol *et al.* created a thermo-responsive CO<sub>2</sub>-based PU by converting furfuryl glycidyl ether into a cyclic carbonate derivative and combining it with dimaleimide-terminated polypropylene glycol and the necessary diamine. Due to the breakdown of Diels–Alder adducts, the resulting PU may



**Fig. 30** Synthesis of non-isocyanate polyurethane-urea (PUUa) from CO<sub>2</sub>, and sequential reaction of PUUa with 4,4'-bismaleimidodiphenylmethane (BIM) to the polyurethane-urea diels-alder adduct (PUUa-Da).





shift from a solid to a liquid state, which is desired for many thermo-reversible material applications.<sup>101</sup> According to the literature, one of the most promising reactions for self-healing polymer materials is the Diels–Alder process.<sup>102</sup> Based on this consideration, Zhan *et al.* created a self-healing and recyclable CO<sub>2</sub>-based polymer with exceptional strength qualities by establishing stronger cross-linking bonds *via* the Diels–Alder reaction from CO<sub>2</sub> and furfuryl amine. The more excellent dynamic covalent connections, the combination of ordered and disordered hydrogen bonding interactions, and the suitable amounts of cross-linked Diels–Alder groups would provide higher mechanical strength and stability to the newly synthesized material.<sup>103</sup> The synthetic green route to recyclable polymer PU-urea (PUUa) synthesis started from the polyaddition reaction between the furfuryl amine cyclocarbonate derivative and oligourea. Then PUUa was cross-linked by the Diels–Alder reaction between furfuryl and 4,4-bismaleimidodiphenylmethane (BIM). Meanwhile, the PUUa Diels–Alder adduct showed excellent self-healing capability and recyclability. The present green route is effective at building strong and tough self-healing and recyclable polymer PUUa started from bis(cyclic carbonate) furfuryl amine (BCCFA) and oligourea (OUa) through a polyaddition reaction, as illustrated in Fig. 30. It was worth noting that BCCFA or OUa were synthesized using CO<sub>2</sub> as a reagent. Finally, the reaction between furan and maleimide groups of PUUa generated the Diels–Alder adduct PUUa-DA. The PUUa-DA adduct is a challenging and self-healing thermosetting material compared with PUUa. The retro-Diels–Alder reaction, which takes place at 120 °C, converts PUUa-DA into PUUa, a thermoplastic polymer that melts at that temperature. Then, the broken hydrogen bond in PUUa was recombined, and the cross-linking groups through the Diels–Alder reaction were restructured at 60 °C. Since the retro-Diels–Alder

reaction is inefficient at a healing temperature lower than 108 °C, PUUa-DA can be considered a thermosetting material without melting and cannot be healed efficiently at a temperature below 108 °C.

NIPU coatings, which are recyclable and healable *via* three different healing mechanisms, have recently been developed from bio-CO<sub>2</sub>-derived materials.<sup>103</sup> Four different novel NIPUs, namely, poly(BBC-FBA), poly(FBC-FBA), poly(FBC-DAP), and poly(SuBC-FBA), were synthesized by the reaction of phenoxy-carbonyloxymethyl ethylene carbonate (BBC) or hydroxymethylfuran bis(cyclic carbonate) (FBC) or succinate bis(cyclic carbonate) (SuBC) and commercially available 2,5-bis(amino-methyl)furan (FBA) or 1,5-diaminopentane (DAP) in DMF at 70 °C (Fig. 31).<sup>104,105</sup>

Interestingly, these polymers could react with bismaleimides (BM) *via* a furan-maleimide Diels–Alder reaction to produce a cross-linked network containing a DA adduct since furan was present in their major chains (Fig. 32).

The primary chain of these NIPUs, when cross-linked with bismaleimides, produces organogels with thermo-reversible sol-gel transition and solvent-borne coatings with enhanced characteristics. By carefully choosing the bismaleimide cross-linker structure, it was possible to create recyclable coatings that naturally heal using heat, moisture, and, more intriguingly, dry circumstances at room temperature with the structure reported in Fig. 33.

The hydro-plasticization and moisture-healing properties of coatings based on NIPUs were characterized for the first time. These NIPUs properties, which set them apart from more traditional PUs, are principally due to the presence of hydroxyl groups in their structure. A careful examination also reveals how *T<sub>g</sub>* and chain flexibility impact the healing efficiency.



**Fig. 31** Synthesis of main-chain furan-containing NIPUs by utilizing furan-based bis(cyclic carbonate) and diamine. Reaction conditions: DMF, 70 °C, up to 48 h.



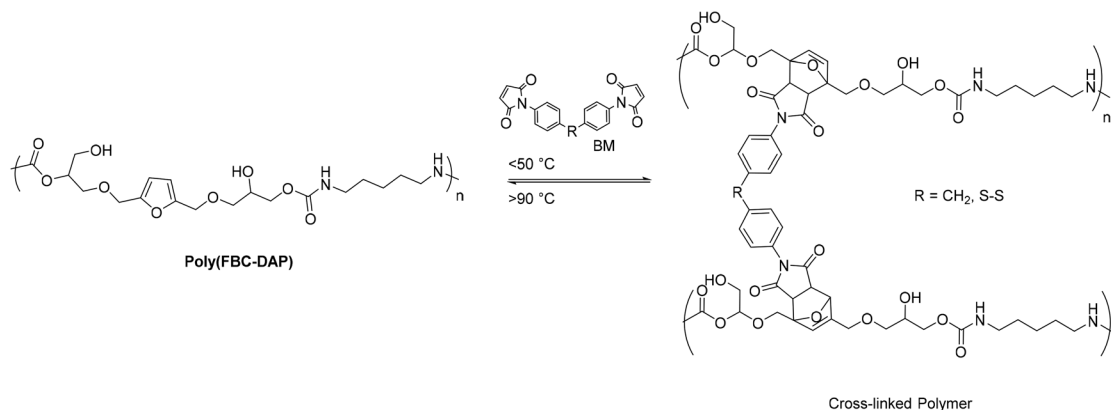


Fig. 32 Diels–Alder and retro-Diels–Alder thermoreversible reactions of poly(FBC-DAP) cross-linked with bismaleimide.

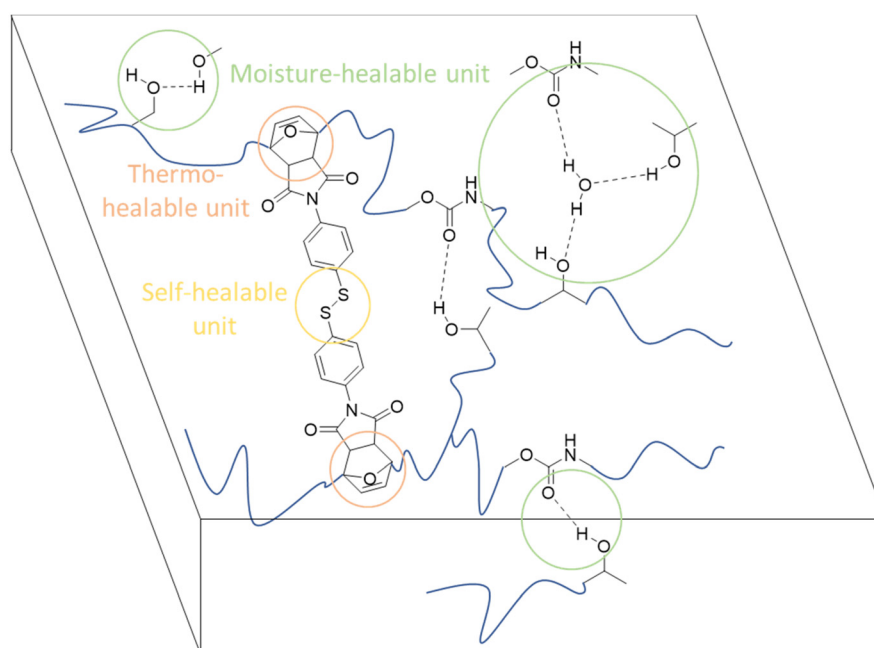


Fig. 33 Cross-linked NIPU coatings have qualities that allow them to be thermo-, moisture-, and self-healing.

These results highlight the necessity of combining various dynamic, reversible cross-linking processes to create practical coating materials.

## 6. Conclusion

The present review highlights recent years' considerable efforts to (i) produce PU without using toxic reagents such as isocyanates and (ii) improve their circular character by following different strategies. This fundamental shift in PU chemistry positions NIPUs as a sustainable choice, a facet that sets them apart from conventional PUs. NIPUs offer a paradigm shift with improved safety profiles, lower toxicity, and a reduced environmental footprint. Their exceptional mechanical pro-

perties, thermal stability, and versatility open doors to diverse adhesives, coatings, foams, and more applications.

A circular design seems mandatory; it ranges from the synthesis of monomers to the PU's use-life and end-of-life, closing the loop on a greener and more sustainable PU industry. In particular, the creation of sustainable value chains in the PU field requires a multidisciplinary approach with respect to the selection of starting materials (of biological origin), the processes (synthesis), and the dismantling of the polymer at the end of its life (recycling). Introducing biobased, compostable, and renewable building blocks and optimizing PU production processes are necessary to reduce the environmental footprint. One option discussed in this review involves chain extension as a way to meet the molecular weight requirements of PUs. Alternatives to isocyanates are known to provide low-mole-



cular-weight polymers. Among the various strategies for PU cross-linking, using Diels-Alder and retro Diels-Alder reactions represents a great opportunity and a real option.

Another deeply discussed point is increasing the green character through environmentally friendly processes. A significant advancement in this effort has been the utilization of CO<sub>2</sub> as the C1 building block for the synthesis of organic molecules. CO<sub>2</sub> has been used as the C1 unit for synthesizing organic molecules. CO<sub>2</sub> represents an ideal reagent due to its beneficial properties, such as its high abundance, non-toxicity, and renewability, all of which align with the principles of green chemistry and sustainability.

The coupling reaction of carbonates and aliphatic amines has emerged as the most promising approach for producing NIPUs with enhanced green credentials. Several catalysts and processes have been described, but only the combination of using CO<sub>2</sub> to obtain cyclic carbonates, their ring opening, and cross-linking *via* [4 + 2] cycloaddition could provide PUs with mechanical, thermal, morphological, and chemical properties comparable to the classic PUs obtained *via* the isocyanate route. By making this circular connection from CO<sub>2</sub> utilization in monomer synthesis to the end-of-life of NIPU products, we create a holistic and sustainable framework that improves the environmental footprint of polyurethanes and aligns with the broader goals of reducing carbon emissions and promoting a circular economy.

## Abbreviations

<sup>1</sup> H-NMR	Proton nuclear magnetic resonance	DTG	Differential thermogravimetry
<i>a</i> CCs	Bis- <i>a</i> -alkylidene cyclic carbonates	EcHMEcHC	3,4-Epoxy cyclohexylmethyl 3,4-epoxycyclohexanecarboxylate
BADGE	Bisphenol A diglycidyl ether	EDA	Ethylenediamine
BBC	Phenoxycarbonyloxymethyl ethylene carbonate	ESBO	Epoxidized soybean oil
BCCFA	Bis(cyclic carbonate) furfuryl amine	ESO	Epoxy soybean oil
BDC	[4,4'-Bi(1,3-dioxolane)]-2,2'-dione	FBA	2,5-Bis(aminomethyl)furan
BDGE	1,4-Butanediol diglycidyl ether	FBC	Hydroxymethylfuran bis(cyclic carbonate)
BIM	4,4-Bismaleimidodiphenyl-methane	FO	Fish oil
C-UME	Urethane-modified epoxy	FT-IR	Fourier-transform infrared spectroscopy
CANs	Covalent adaptable networks	GC	Glycerol carbonate
CFO	Carbonated fish oil	HABO	OH-activated bark oil
CSBO	Carbonated soybean oil	HMDA	Hexamethylene diamine
CTAB	Cetyltrimethyl-ammonium bromide	HU	Hydroxyurethane
D230	Poly(propylene glycol) bis(2-aminopropyl ether)	iBMK	Methyl isobutyl ketone
DAP or PDA	1,5-Diaminopentane	ICFAD	Internal carbonated fatty acid diester
DAS	2,4-Diaminomesitylene	IPCC	International panel on climate change
DBU-I <sub>2</sub>	1,8-Diazabicyclo[5.4.0]undec-7-ene iodine	IPDA	Isophorone diamine
DDM	4,4'-Diaminodiphenyl methane	KH-560	[3-(2,3-Epoxypropoxy)-propyl]-trimethoxysilane
DDS	4,4'-Diaminodiphenyl disulphide	LO	Linseed oil
DETA	Diethylenetriamine	MDA	4,4'-Methylenedianiline
DGcHdC	Diglycidyl 1,2-cyclohexanedicarboxylate	MDI	2',4'/4,4'-Diphenyl-methane diisocyanate
DGEBA	Bisphenol A diglycidyl ether	MeCN	Acetonitrile
DIC	<i>N,N</i> -Diisopropylcarbodiimide	MEK	Methyl ethyl ketone
DMC	Double metal cyanides	MF	Methyl formate
DMSO	Dimethylsulfoxide	MOFs	Metal-organic frameworks
DSC	Differential scanning calorimetry	NI-PHUs	Non-isocyanate polyhydroxyurethanes
		NIPHEUs	Polyhydroxy(ester-urethane)s
		NIPUs	Non-isocyanate polyurethanes
		NPGDGE	Neopentyl glycol diglycidyl ether
		ORA	Oligomeric ricinoleic acid
		ODA	1,8-Octanediamine
		OUa	Oligourea
		P(NIPU)-	Polybutadienes-based non-isocyanate
		PBDs	polyurethanes
		PC	Pentaerythritol
		PBDs	Polybutadienes
		PDA	1,5-Pentanediamine
		PEGDE	Poly(ethylene glycol) diglycidyl ether
		PGE	Phenyl glycidyl ether
		PHA	Polyhydroxyalkanoate
		PHUU	Polyhydroxyurethane-urea
		PPC	Poly(propylene carbonate)
		PPDE	Poly(propylene glycol) diglycidyl ether
		PPN	Bis(triphenylphosphine)iminium
		PSA	Pressure-sensitive adhesive
		PU	Polyurethane
		PUF	Polyurethane foam
		PUUa	Polyurethane-urea
		PUUa-DA	Polyurethane-urea Diels-Alder adduct
		RDGE	Resorcinol diglycidyl ether
		REACH	Registration, evaluation, authorisation, and restriction of chemicals
		RHMPA	Reactive hot-melt polyurethane adhesives
		Si-PECs	Siloxane-functionalized poly(ether carbonate)s
		SuBC	Succinate bis(cyclic carbonate)



TAEA	Tris(2-aminoethyl)amine
TBA	Tetra- <i>n</i> -butylammonium
TBAB	Tributyl ammonium bromide
TCFAD	Terminal carbonated fatty acid diester
TCM	Methylene-bridged tetracarbamate
TDA	Toluene-2,4-diamine
TDC	Toluene-2,4-dicarbamate
TMC	Trimethylolpropane carbonates
TMPTC	Trimethylolpropane tris-carbonate
TTD	4,7,10-Trioxa-1,13-tridecanediamine
WPU	Waterborne polyurethane

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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