



Synthesis of NIPUs for Application as Water-Based and Solvent-Free Adhesives and Coatings

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ABSTRACT

The development of sustainable alternatives to conventional polyurethanes (PUs) has become a key research priority in polymer science due to environmental, health, and safety concerns associated with the use of isocyanates. In this context, non-isocyanate polyurethanes (NIPUs) are emerging as a promising, viable approach; however, their broader implementation in adhesives and coatings remains hindered by intrinsic limitations, including slow reaction kinetics, limited precursor availability, and challenges in achieving high-performance formulations under application-relevant conditions. This thesis addresses these limitations through the design of solvent-free and waterborne NIPU systems for adhesive and coating applications at mild temperatures, guided by sustainability as a core research principle.

A strategy for the functionalization of water-soluble polyamines was devised, enabling the preparation of one-component waterborne NIPU thermosets using water as the sole reaction medium. Post-polymerization modification of poly(vinylamine) with a functional cyclic carbonate allowed the introduction of reactive groups for subsequent crosslinking, yielding thermoset coatings upon mild thermal treatment. The resulting transparent materials exhibited rapid gelation, high hydrophilicity, and rigid polymer networks, demonstrating the feasibility of fully aqueous NIPU coating systems.

Solvent-free NIPU formulations capable of curing at room temperature were developed *via* bulk polyaddition between a highly reactive liquid bis(α -alkylidene cyclic carbonate) and various liquid polyamines. Complete conversion was achieved under ambient conditions, and the resulting materials exhibited tunable thermomechanical and coating properties. Adhesive testing revealed lap-shear strengths exceeding 10 MPa on aluminum, with further enhancement upon incorporation of dopamine, surpassing commercial PU adhesives and indicating suitability for structural applications.

To bridge the gap between academic research and industrial practice, conventional solvent-free, room-temperature-curable PU systems were formulated and optimized at the French company COP Chimie™ to enable direct comparison with solvent-free NIPUs. This benchmarking provided additional insight into the structure–property relationships governing adhesive and coating phenomena and further demonstrated that NIPU systems can match or exceed the performance of conventional PU counterparts.

Finally, a fully bio-based, fatty acid-derived triamine was synthesized *via* a three-step route, providing a versatile renewable crosslinker for sustainable polymer design. The triamine was reacted with the liquid bis(α -alkylidene cyclic carbonate) to prepare solvent- and catalyst-free

NIPU formulations under mild conditions, yielding fast-curing materials with enhanced chemical resistance.

Overall, this work provides evidence that NIPU adhesives and coatings can be obtained under mild conditions through rational formulation design and systematic structure–property–performance analysis, contributing to the understanding of key technological challenges and supporting the development of more sustainable isocyanate-free PU materials.

RÉSUMÉ

Le développement d'alternatives durables aux polyuréthanes conventionnels (PU) est devenu une priorité majeure en science des polymères, en raison des préoccupations environnementales, sanitaires et de sécurité liées à l'utilisation des isocyanates. Dans ce contexte, les polyuréthanes sans isocyanate (NIPU) apparaissent comme une voie prometteuse et viable ; toutefois, leur déploiement à plus grande échelle dans les adhésifs et les revêtements reste limité par des verrous intrinsèques, tels qu'une cinétique de réaction lente, une disponibilité restreinte des précurseurs et des difficultés à élaborer des formulations performantes dans des conditions d'application pertinentes. Cette thèse vise à lever ces verrous par la conception de systèmes NIPU sans solvant et en phase aqueuse, destinés à des applications adhésives et de revêtement à température modérée, en s'inscrivant dans une démarche guidée par les principes de durabilité.

Une stratégie de fonctionnalisation de polyamines hydrosolubles a été mise au point, permettant la préparation de thermodurcissables NIPU monocomposants en milieu aqueux, l'eau étant utilisée comme unique milieu réactionnel. La modification post-polymérisation du poly(vinylamine) par un carbonate cyclique fonctionnel a permis l'introduction de fonctions réactives en vue d'une réticulation ultérieure, conduisant à des revêtements thermodurcis après un traitement thermique modéré. Les matériaux transparents obtenus présentent une gélification rapide, une forte hydrophilie et des réseaux polymères rigides, démontrant la faisabilité de systèmes de revêtements NIPU entièrement aqueux.

Des formulations NIPU sans solvant, capables de réticuler à température ambiante, ont été développées par polyaddition en masse entre un bis(carbonate cyclique α -alkylidène) liquide hautement réactif et diverses polyamines liquides. Une conversion complète est atteinte dans des conditions ambiantes, et les matériaux obtenus présentent des propriétés thermomécaniques et de revêtement modulables. Les essais d'adhésion montrent des résistances au cisaillement par recouvrement supérieures à 10 MPa sur aluminium, avec une

amélioration supplémentaire après incorporation de dopamine, dépassant celles des adhésifs PU commerciaux et indiquant leur pertinence pour des applications structurales.

Afin de rapprocher recherche académique et pratique industrielle, des systèmes PU conventionnels sans solvant, réticulables à température ambiante, ont été formulés et optimisés au sein de l'entreprise française COP Chimie™, permettant une comparaison directe avec les NIPU sans solvant. Cette étude comparative apporte un éclairage sur les relations structure–propriétés régissant les phénomènes d'adhésion et de revêtement et montre que les systèmes NIPU peuvent égaler, voire dépasser, les performances des PU conventionnels.

Enfin, une triamine entièrement biosourcée, dérivée d'acides gras, a été synthétisée selon une voie en trois étapes, fournissant un agent de réticulation renouvelable pour la conception de polymères durables. Cette triamine a été mise en réaction avec le bis(carbonate cyclique α -alkylidène) liquide afin de préparer des formulations NIPU sans solvant ni catalyseur dans des conditions modérées, conduisant à des matériaux à durcissement rapide et à résistance chimique améliorée.

Dans l'ensemble, ce travail montre que des adhésifs et revêtements NIPU peuvent être obtenus dans des conditions modérées grâce à une conception rationnelle des formulations et à une analyse systématique des relations structure–propriétés–performances, contribuant à la compréhension des principaux verrous technologiques et au développement de matériaux PU sans isocyanate plus durables.

ZUSAMMENFASSUNG

Die Entwicklung nachhaltiger Alternativen zu konventionellen Polyurethanen (PU) ist aufgrund von Umwelt-, Gesundheits- und Sicherheitsbedenken im Zusammenhang mit der Verwendung von Isocyanaten zu einer zentralen Forschungspriorität in der Polymerwissenschaft geworden. In diesem Kontext stellen nicht-isocyanatbasierte Polyurethane (NIPU) einen vielversprechenden und praktikablen Ansatz dar; ihre Anwendung in Klebstoffen und Beschichtungen wird jedoch weiterhin durch inhärente Einschränkungen begrenzt, darunter die langsame Reaktionskinetik, eine eingeschränkte Verfügbarkeit von Vorstufen sowie Schwierigkeiten bei der Entwicklung leistungsfähiger Formulierungen unter anwendungsrelevanten Bedingungen. Ziel dieser Arbeit ist es, diese Einschränkungen durch die Entwicklung lösungsmittelfreier und wasserbasierter NIPU-Systeme für Klebstoff- und Beschichtungsanwendungen bei moderaten Temperaturen zu adressieren, wobei Nachhaltige Chemie als zentrales Leitprinzip dient.

Es wurde eine Strategie zur Funktionalisierung wasserlöslicher Polyamine entwickelt, welche die Herstellung einkomponentiger, NIPU-Duroplaste unter Verwendung von Wasser als einzigem

Reaktionsmedium ermöglicht. Die postpolymerisationsbasierte Modifikation von Poly(vinylamin) mit einem funktionellen cyclischen Carbonat ermöglichte die Einführung reaktiver Gruppen zur anschließenden Vernetzung, wodurch vernetzte Beschichtungen nach milder thermischer Behandlung erhalten wurden. Die resultierenden transparenten Materialien zeigen eine schnelle Gelierung, hohe Hydrophilie sowie starre Polymernetzwerke und belegen damit die Realisierbarkeit vollständig wässriger NIPU-Beschichtungssysteme.

Lösungsmittelfreie NIPU-Formulierungen, die bei Raumtemperatur aushärten, wurden durch Bulk-Polyaddition zwischen einem hochreaktiven flüssigen bis(α -alkylidenen cyclischen Carbonat) und verschiedenen flüssigen Polyaminen entwickelt. Unter Umgebungsbedingungen wurde eine vollständige Umsetzung erreicht, und die resultierenden Materialien weisen einstellbare thermomechanische und Beschichtungseigenschaften auf. Haftungsprüfungen zeigen Überlappungsscherfestigkeiten von über 10 MPa auf Aluminium, mit weiterer Verbesserung nach Zugabe von Dopamin, wodurch die Leistungsfähigkeit kommerzieller PU-Klebstoffe übertroffen wird und die Eignung für strukturelle Anwendungen belegt wird.

Um die Lücke zwischen akademischer Forschung und industrieller Praxis zu schließen, wurden konventionelle lösungsmittelfreie und bei Raumtemperatur härtende PU-Systeme beim französischen Unternehmen COP Chimie™ formuliert und optimiert, um einen direkten Vergleich mit lösungsmittelfreien NIPUs zu ermöglichen. Diese vergleichende Untersuchung liefert zusätzliche Einblicke in die Struktur-Eigenschafts-Beziehungen, die Adhäsions- und Beschichtungsphänomene bestimmen, und zeigt, dass NIPU-Systeme die Leistung konventioneller PU-Pendants erreichen oder sogar übertreffen können.

Abschließend wurde ein vollständig biobasiertes, aus Fettsäuren abgeleitetes Triamin über eine dreistufige Syntheseroute hergestellt, das als vielseitiger erneuerbarer Vernetzer für die Entwicklung nachhaltiger Polymere dient. Dieses Triamin wurde mit dem flüssigen bis(α -alkylidenen cyclischen Carbonat) umgesetzt, um lösungsmittel- und katalysatorfreie NIPU-Formulierungen unter milden Bedingungen herzustellen, wodurch schnell härtende Materialien mit verbesserter chemischer Beständigkeit erhalten wurden.

Insgesamt zeigt diese Arbeit, dass NIPU-Klebstoffe und -Beschichtungen unter milden Bedingungen durch rationale Formulierungsentwicklung und systematische Analyse von Struktur-Eigenschaft-Leistungs-Beziehungen hergestellt werden können, und trägt zum Verständnis zentraler technologischer Herausforderungen sowie zur Entwicklung nachhaltigerer, isocyanatfreier PU-Materialien bei.

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1 INTRODUCTION

Humanity is currently facing one of the most complex and urgent challenges in its history: the need to reconcile modern lifestyles and technological progress with the ecological limits of the planet. Climate change, depletion of natural resources, and pollution have placed unprecedented pressure on global ecosystems, with devastating consequences not only for biodiversity and natural environments, but also for human well-being and socio-economic stability. These three major anthropogenic crises are manifestations of the same systemic dynamics, and because their effects are intimately intertwined, neglecting any one of them would compromise our ability to address the others effectively. To gain an essential understanding of how these critical issues are impacting us as a human species, it is useful to consider some of the most direct implications of global climate disruption, resource depletion, and environmental contamination.

Contrary to many international agreements of the past decades, such as the Kyoto Protocol of 1997¹ or the Paris Agreement of 2015,² global greenhouse gas (GHG) emissions continue to rise, and temperatures are increasing at a pace significantly higher than anticipated.³ According to the Intergovernmental Panel on Climate Change (IPCC) and the United Nations (UN) Human Security Unit, climate change has diverse adverse impacts on human systems, including food and water security, livestock health and productivity, morbidity and mortality from human diseases, forced migration, and infrastructure damage, among others.^{4,5} Global warming and the resulting changes in weather patterns disrupt ecological balances and act as threat multipliers, exacerbating existing vulnerabilities and tensions.

Concurrently, reckless appropriation and exploitation of natural resources, driven by economic and political interests, aggravate social inequalities, intensify competition over scarce assets, and undermine governance, thereby fuelling economic and geopolitical instability.⁶ Poor natural resource management is not just an environmental concern, but can be a powerful driver of fragility and violence, especially in conflict-affected states where weak institutions struggle to mediate access and distribution.

Beyond these dynamics, the overconsumption of raw materials, energy, water, and consumer goods produces a complex series of harmful repercussions, with various pollution as a primary concern. The entire product lifecycle, from raw material extraction through transportation, use, and disposal, generates emissions and waste that degrade air, water, and soil quality. Each stage of this lifecycle is critical, particularly disposal, as a significant portion of municipal solid waste (38% according to the Global Waste Management Outlook of 2024 from the UN Environment

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Programme)⁷ is either dumped or burned in uncontrolled conditions, leading to the accumulation of persistent pollutants in the environment and ultimately compromising not only human health. These systemic issues are deeply interconnected, and the effects of heedless practices and policies are already imposing significant costs on societies worldwide, with consequences that we may soon no longer be able to manage.

Misinformation regarding climate change and environmental crisis is increasingly widespread, particularly across social media platforms.⁸ Moreover, a secondary denialism has emerged alongside traditional environmental scepticism, arguing climate and environment solutions are too costly, unrealistic, or disruptive to our way of life.⁹ Alarmingly, leaders of several major world economies have endorsed these narratives, especially among right-wing populist parties,^{10,11} which often leverage voters' immediate needs and short-sighted concerns to shape political agendas. In fact, personal priorities are often restricted to local and short-term issues that are perceived as more urgent and important.¹² This phenomenon, thoroughly described in the literature, appears to have become even more relevant now.

Despite these challenges, public awareness of the environmental and climate crisis has continued to grow, and societal pressure for action is significantly stronger than before. In 1987, with the publication of the Brundtland Report,¹³ sustainable development was introduced as a key principle to guide long-term policy strategies. In its original meaning, sustainability emphasized the responsibility to ensure the well-being of future generations rather than prioritizing the gratification of present needs in general, and particularly including the management and preservation of non-renewable natural resources.¹⁴ Over time, the concept evolved and expanded, culminating in a significant paradigm shift with the adoption of the UN Sustainable Development Goals (SDGs). This global agenda, comprising 17 interconnected goals that span social, economic, and environmental dimensions, provided a framework for guiding national and international policymaking until 2030.¹⁵ The SDGs formalised sustainability as a common and measurable commitment, providing clearer and more operational guidelines, and aligning scientific, governmental, and societal efforts under a shared vision.

In the framework of sustainable development, chemistry plays a central role in both the origins of environmental challenges and the solutions needed to overcome them. Industrial chemistry has enabled vast improvements in quality of life, mobility, healthcare, energy distribution, infrastructure, and food production and storage. However, traditional chemical processes often

rely on fossil feedstocks, hazardous reagents, and energy-intensive manufacturing. Historically, the chemical industry has tended to prioritize cost, productivity, and performance over sustainability, which has contributed substantially to environmental degradation.¹⁶ When sustainability started to be recognized as a universal driver of human progress, a series of “green chemistry principles” were developed,¹⁷ introducing concepts such as circularity, use of renewable feedstocks, energy efficiency, waste prevention, and inherently safer processes as central pillars of chemical research. Their implementation led to the design of chemical practices, technologies, and production routes with lower environmental and health impacts.

Within this broad transition, polymers occupy a particularly influential position, given both their significant environmental footprint and their wide adaptation across nearly all industrial sectors and consumer goods. Polymers are ubiquitous substances composed of molecules of high relative molecular mass (macromolecules), consisting of multiple repeating units derived from compounds of low relative molecular mass (monomers).^{18,19} Through the organization of countless monomeric units, polymers bridge the gap between the molecular and macroscopic worlds, giving rise to phenomena that cannot be directly predicted from their building blocks and yielding materials with unique properties. Polymer synthesis and modification have radically changed human life and represent one of the cornerstones of modern science, providing a powerful toolbox for the development of technological innovations with an extensive range of applications.

However, this success has come with significant environmental consequences, including intensive use of fossil resources, substantial GHG emissions, release of hazardous by-products, and accumulation of persistent plastic and microplastic waste.¹⁶ In view of the widespread use of polymers, it is essential for polymer chemistry to align with sustainable development and green chemistry principles. Even incremental improvements would lead to considerable benefits, helping to mitigate a global environmental crisis which represents a collective failure for all of humanity.

While major changes must be promoted at national and international levels, it is consistent individual commitment that both reduces personal environmental impact and generates the societal pressure necessary to enable large-scale change. Within this complex framework, scientific research—especially in polymer chemistry—should pave the way and serve as an exemplary model of human activity with sustainability at its core. Progress in this field emerges from the dedication of many researchers, including PhD students tackling small but meaningful

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challenges, each contributing to the broader goal of creating a tangible, lasting impact on the world.

2 THEORETICAL BACKGROUND

2.1 Conventional polyurethanes

2.1.1 Historical overview

While natural polymers have been exploited and processed by mankind since prehistoric time, the origin of synthetic polymer emerged in the 19th century with the introduction of cellulose nitrate, widely considered the first semi-synthetic polymer.²⁰ The modern polymer industry, however, truly began in the early 20th century, when the first fully synthetic polymers were produced and commercialized.^{21,22} One of the revolutionary chemical innovations of the late 1930s was the discovery of polyurethanes (PUs, a commonly used alternative to the IUPAC term polycarbamates),²³ made by the German industrial chemist Otto Bayer at IG Farben in Leverkusen.²⁴ Bayer and his co-workers pioneered the synthesis of PUs *via* a polyaddition reaction between di- or polyisocyanates and polyols, marking the beginning of a new era in polymer chemistry and materials engineering. The growth of PU chains relied on the addition reaction between an isocyanate component, containing reactive –NCO groups, and a polyol, providing hydroxyl functionalities, resulting in urethane linkages (Scheme 2.1). The polymerization was initially carried out without a catalyst, but tertiary amines or organotin compounds were soon introduced into the mixture to accelerate the reaction.^{25,26}



Scheme 2.1 Polyaddition reaction between polyisocyanates and polyols to form polyurethanes.

Since the pioneering work by Bayer, an entirely new class of polymers was created and rapidly gained broad industrial relevance. The first laboratory PU prototypes, designed between the late 1930s and early 1940s, showed excellent solvent, abrasion, and moisture resistance and were employed as rubber alternative and for coating applications. By the late 1940s, the elastomeric properties of PUs enabled the industrial-scale production of millable elastomers, coatings, and adhesives.^{25,27} During this period, the development of PU flexible foams also emerged, supported by advancements in processing techniques, culminating in the commercialization of PU foams in 1954.²⁸ In 1952, polyisocyanates became commercially available, leading to a significant increase in PU production, primarily using polyester or polyether polyols in combination with

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toluene diisocyanate (TDI) or methylene diphenyl diisocyanate (MDI).^{29,30} The 1950s saw the rise of various types PU elastomers, adhesives, coatings, and paints. In addition to new applications, advanced production technologies and processing methods were also developed. Notable examples include the rise of the reaction injection molding (RIM) technique, adopted in the automotive industry since 1967, and the development of water-based PU dispersions (PUDs), which became commercially relevant in the 1970s.^{31–33} Public and scientific awareness of the ecological effects of industrial chemicals and manufacturing practices grew throughout the 1980s. One example of these environmental concerns was the elimination, through the Montreal Protocol of 1987, of ozone-depleting chemicals such as chlorofluorocarbons (CFCs), which were commonly used as blowing agents in PU foam production.^{27,29,34} Nevertheless, the demand for PUs increased, and numerous innovations were introduced across various industrial sectors.³⁵ Thermoplastic polyurethanes (TPUs) combined the elasticity of rubber with the processability of thermoplastics, imparting high elasticity and abrasion resistance.^{36,37} Building on these versatile properties, shape-memory TPUs were introduced in 1990, opening new avenues in smart and responsive applications.^{38,39} In parallel, PUs were blended with fibers or fillers to create lightweight composites with enhanced mechanical strength, thermal stability, and functional performance.^{40,41} A notable advance came in 2004, when single-walled carbon nanotubes (SWCNTs) were first integrated into a PU matrix, opening the way for a generation of new high-performance PU-based nanocomposites.⁴² While the adaptability of PUs ensured their integration into countless sectors, in recent years the focus has been on the minimization of the environmental impact and health risks associated with PU synthesis, use, and disposal. In response to these challenges, academic research has advanced the development of fully bio-based PUs, with some examples already reported at the beginning of the 2010s.^{43–46} However, regardless of these efforts, the main driver behind the search for alternatives to conventional PU chemistry has been the increasing regulatory pressure and health concerns associated with the toxicity and handling of isocyanates. In this context, non-isocyanate polyurethanes (NIPUs) have arisen as compelling substitutes.^{47–49} Despite decades of research, their broader adoption has long been hindered by synthetic, performance, and scalability challenges. In recent years, however, advances in monomer design and processing techniques have accelerated significantly, and NIPUs are increasingly seen not just as an alternative, but as a defining direction for the future of PU chemistry.⁵⁰

Throughout their history, schematically illustrated in Figure 2.1, the development of PUs was driven by innovation in processing and application techniques. Each new form—foams,

elastomers, adhesives, coatings, sealants, composites, etc.—expanded the material’s industrial footprint. In the 21st century, a shift in scientific priorities has emerged, with isocyanate-free and bio-based formulations recognized as critical objectives in PU chemistry.

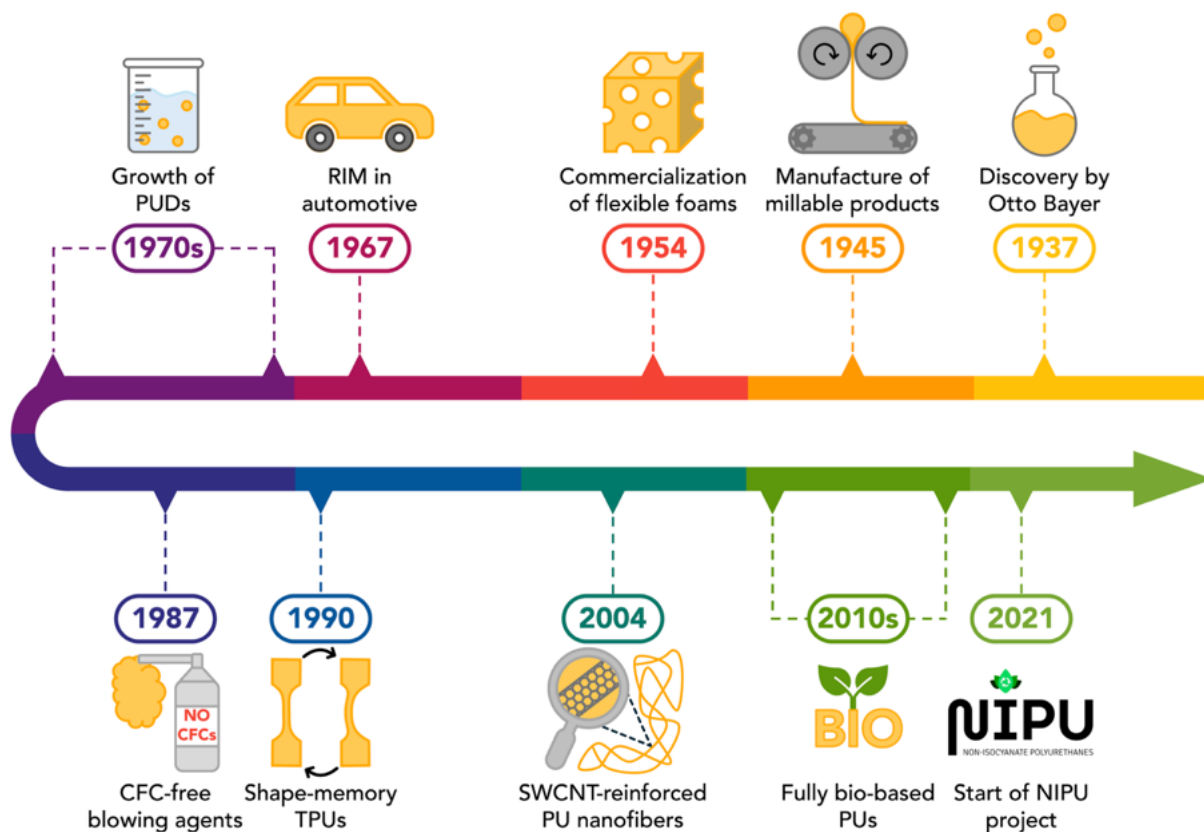


Figure 2.1 PU technologies evolution timeline: from discovery to current time (RIM = reaction injection molding, PUD = polyurethane dispersion, CFC = chlorofluorocarbon, TPU = thermoplastic polyurethane, SWCNT = single-walled carbon nanotube, NIPU = non-isocyanate polyurethane).

2.1.2 Formulation components and reaction details

PU synthesis has evolved significantly since its discovery in the 1930s thanks to several advancements in controlling side reactions, refining catalyst use, and tailoring synthetic methods to produce materials with specific properties. The macromolecular structure resulting from the step-growth polyaddition between polyols and polyisocyanates typically comprises alternating “soft” segments, derived from the polyol, and “hard” segments, derived from the isocyanate. By selecting different reagents, the balance of flexibility versus rigidity in the PU can be tuned to achieve a wide range of mechanical and thermal properties.⁵¹ In particular, soft polyol segments tend to lower the polymer density and increase flexibility, whereas hard isocyanate-

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derived segments are more rigid and can form crystalline or highly ordered domains.⁵² In conventional PU formulations, these hard domains contain urethane and, when water or polyamines are present as co-reactants or chain extenders, urea linkages. Urea groups form stronger and more frequent hydrogen bonds than urethane groups owing to the presence of two N–H donors per carbonyl. As a result, even small amounts of urea moieties significantly increase the extent of microphase separation and enhance the cohesive energy of the hard domains.⁵³ This segmented design and the possibility to introduce in a controlled way specific chemical structures in the polymer chains are the main reasons behind the versatility of PUs.⁵⁴ Because of these characteristics, PU synthesis and structure-property relationship are central topics in polymer chemistry and industrial materials science.

2.1.2.1 Polyols

The hydroxyl functionality and molecular structure of the polyol play a critical role in determining the crosslink density and network architecture of the resulting polymer. Additionally, the chemical nature of the polyol significantly affects the microphase-separated morphology and ultimately governs structural, mechanical, and thermal attributes of the final polymer.

Two principal classes of polyols are currently employed in industrial PU synthesis: polyether polyols and polyester polyols. While other specialty polyols (such as polycarbonate polyols, polycaprolactone polyols, acrylic polyols, polyacetal polyols, etc.) constitute a much smaller fraction of production, polyether and polyester polyols account for the majority of the commercial market, with the first being predominant.⁵⁵ Moreover, particularly relevant is also the use of bio-based polyols, which has recently gained importance as a strategy to reduce reliance on petrochemical feedstocks.

Polyether polyols

Polyether polyols exhibit high hydrolytic stability and low glass transition temperatures, making them well-suited for flexible PU applications. Widely used examples include polyethylene glycol (PEG), polypropylene glycol (PPG), their copolymers, or polytetrahydrofuran (also called poly(tetramethylene ether) glycol, PTMEG, obtained through polymerization of tetrahydrofuran or 1,4-butanediol) (Figure 2.2A).

Polyester polyols

Polyester polyols, such as polycaprolactone polyols (PCL polyols) and other polycondensation-derived polyols (Figure 2.2B), contain ester linkages in the backbone and terminal hydroxyl

functionalities. Polyester polyols generally provide higher tensile strength, glass transition temperature, and resistance to organic solvents and oxidation. However, polyether polyols are often preferred because of their lower cost and viscosity, ease of handling, and improved hydrolytic stability.^{26,55}

Specialty polyols

Other polyols utilized in PU formulations include polycarbonate polyols and acrylic polyols (Figure 2.2C).⁵⁶ Polycarbonate polyols have been reported to provide superior hydrolytic and oxidative stability relative to polyester and polyether polyols, albeit at higher production cost.⁵⁷ Acrylic polyols, on the other hand, exhibit pendent hydroxyl groups suitable for crosslinking and are frequently employed in niche applications.⁵⁸

Renewable polyols

Renewable resources such as vegetable oils, lignin, and carbohydrate derivatives serve as precursors to hydroxyl-functionalized compounds suitable for PU synthesis (Figure 2.2D).^{59,60} In addition to plant oils, which can be readily functionalized with hydroxyl groups, many bioderived chemicals that naturally present hydroxyl groups (such as sucrose, glycerol, and sorbitol) can be used directly as starting materials for PU production or derivatized to improve reactivity and processability.⁶¹ Furthermore, also lignin can be depolymerized and chemically modified (e.g., through oxyalkylation) to obtain lignin-based polyols.^{62,63} Several commercial bio-based polyols are already available, demonstrating compatibility with conventional PU systems.⁶⁴

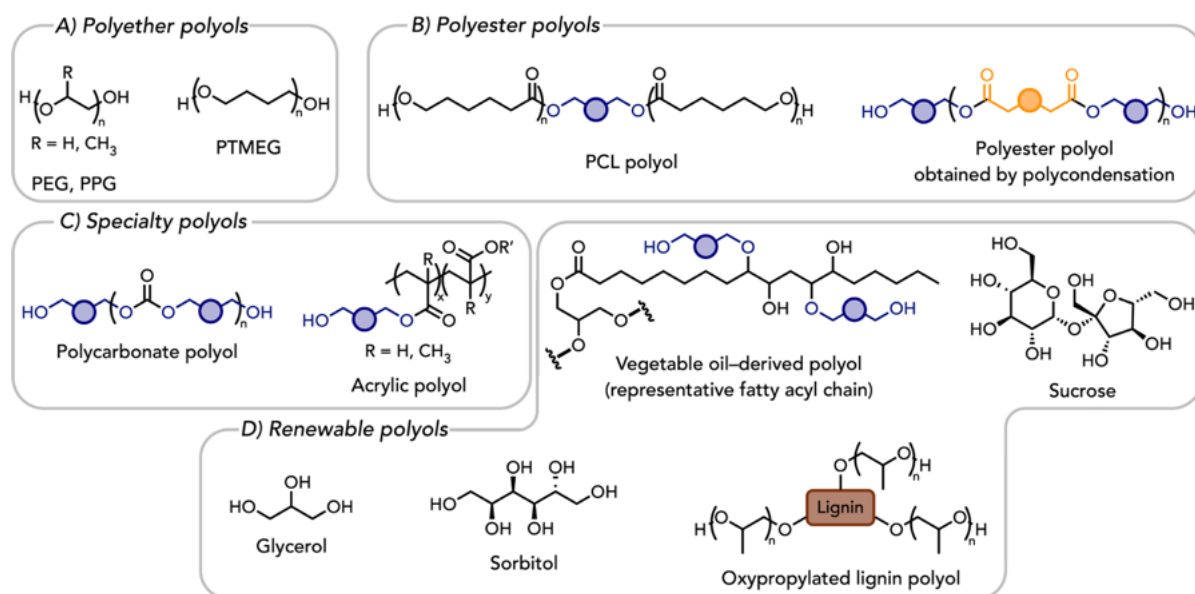


Figure 2.2 Representative polyether (A), polyester (B), specialty (C), and renewable (D) polyols described for PU synthesis.

2.1.2.2 Isocyanates

Although various strategies have been developed for the synthesis of isocyanates, the phosgenation of primary amines remains the most widely applied industrial process.^{65,66} In this reaction, the amine is first converted to a carbamoyl chloride intermediate by reaction with phosgene (COCl_2), followed by elimination of hydrochloric acid (HCl) to yield the isocyanate ($\text{R-N}=\text{C}=\text{O}$). This synthesis is conducted under strictly anhydrous conditions due to the high moisture sensitivity of both phosgene and isocyanates.

A high purity is essential to guarantee reproducible results, since isocyanates can undergo various side reactions, significantly altering reaction kinetics and material properties.⁶⁷ Additionally, the presence of dimeric or trimeric species may affect the stoichiometry and crosslinking density. Therefore, rigorous purification and characterization are essential for reproducible PU synthesis.

Isocyanates are typically categorized into aromatic and aliphatic classes, based on the structure of the organic moiety attached to the $-\text{NCO}$ group.

Aromatic isocyanates

Aromatic isocyanates (Figure 2.3A), such as TDI and MDI, are the most frequently used monomers, exhibiting higher reactivity owing to the electron-delocalization effects of the aromatic ring.⁶⁸ Aromatic isocyanates are widely used where ultraviolet (UV) resistance is not critical in rigid and flexible foams, coatings, and elastomers.

Aliphatic isocyanates

In contrast, aliphatic isocyanates (Figure 2.3B), such as hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI), are less reactive but offer superior resistance to UV degradation and weathering, making them ideal for coatings and sealants.⁵⁹

Partially renewable isocyanates

Despite their lower environmental footprint and ongoing academic efforts, commercially available partially bio-based isocyanates remain scarce, primarily owing to the fact that their synthesis offers no toxicological advantage and is associated with high production costs, as well as availability and scalability issues, compared to established petrochemical isocyanates.^{61,69–71} Relevant examples are Tolonate™ X FLO 100, Desmodur® eco N 7300, and STABIO™ D-370N, manufactured by Vencorex Chemicals, Covestro, and Mitsui Chemicals, respectively (Figure 2.3C).⁷¹

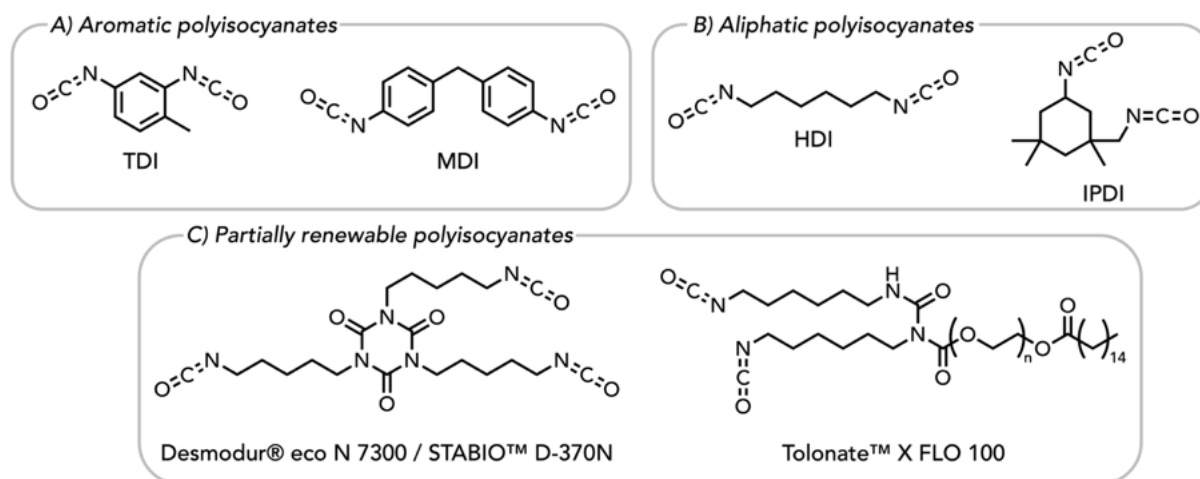


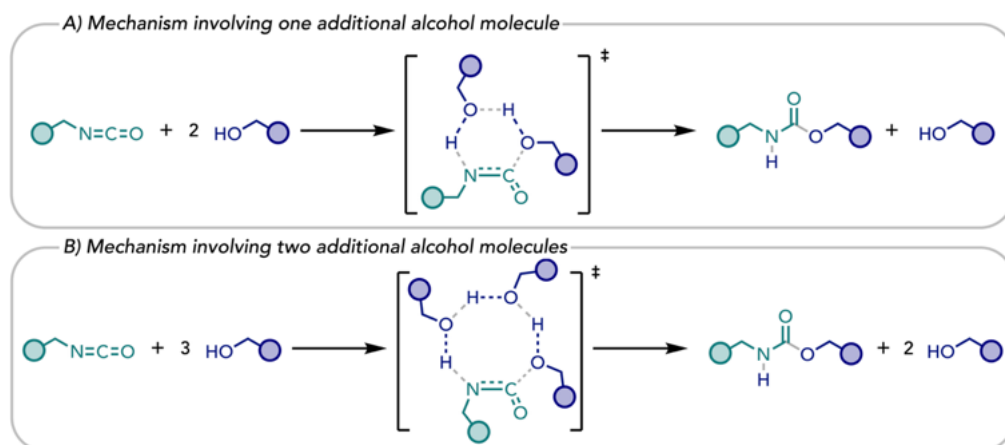
Figure 2.3 Common aromatic (A), aliphatic (B), and partially renewable (C) polyisocyanates used in PU synthesis.

2.1.2.3 Mechanistic pathway, catalysts, and side reactions

Mechanistic pathway

The primary reaction in PU formation involves the nucleophilic attack of a hydroxyl group on the electrophilic carbon of the isocyanate group, forming a urethane bond. In the absence of an external catalyst, the reaction is considered to proceed mainly *via* concerted auto-catalytic one-step mechanisms whose transition states involve additional alcohol molecules (Scheme 2.2).⁷² In solution, the intermolecular interaction between NCO and OH is heavily influenced by solvent polarity, hydrogen bonding capacity, and dielectric constant. In particular, polar aprotic solvents are commonly preferred to non-polar ones for their ability to stabilize the transition state and better solvate the isocyanate and alcohol.⁷³ Polar protic solvents, on the other hand, would compete with the alcohol and therefore affect the selectivity of the process.

The reaction rate and selectivity are also influenced by factors including the NCO:OH molar ratio and temperature. The NCO:OH ratio affects the degree of crosslinking during PU formation, since an excess of isocyanate promotes crosslinking, reversible dimerization, and trimerization, while elevated temperatures accelerate the polyaddition but may also promote undesired side reactions, particularly in the presence of water or reactive impurities.^{73–75}



Scheme 2.2 Concerted auto-catalytic one-step mechanisms of the uncatalyzed isocyanate–alcohol reaction showing the transition states involving one (A) or two (B) additional alcohol molecules.

Catalysts and catalytic mechanism

Although the formation of the polymer can sometimes proceed without the need for external activation, the presence of a catalyst is essential for enhancing the reactivity of polyol–isocyanate systems, allowing for efficient polymerization at lower temperatures and enabling control over reaction kinetics and selectivity. Catalysts operate either by nucleophilic activation of the polyol (Figure 2.4A) or by electrophilic activation of the isocyanate (Figure 2.4B).⁷⁶ Since the early PU formulations, organotin compounds (e.g. dibutyltin dilaurate, DBTDL) have been used as Lewis acid catalysts to accelerate the polymerization.⁷⁷ While highly effective, these compounds are characterized by relatively high toxicity and long environmental persistence. As a result, they are increasingly being replaced by other organometallic compounds (e.g., bismuth-, lithium-, and zinc-based) and organocatalysts, such as tertiary amines, guanidines and amidines, *N*-heterocyclic carbenes (NHCs), and organic acids.^{76,78–80} Some representative examples of outdated as well as modern catalysts are shown in Figure 2.4C.

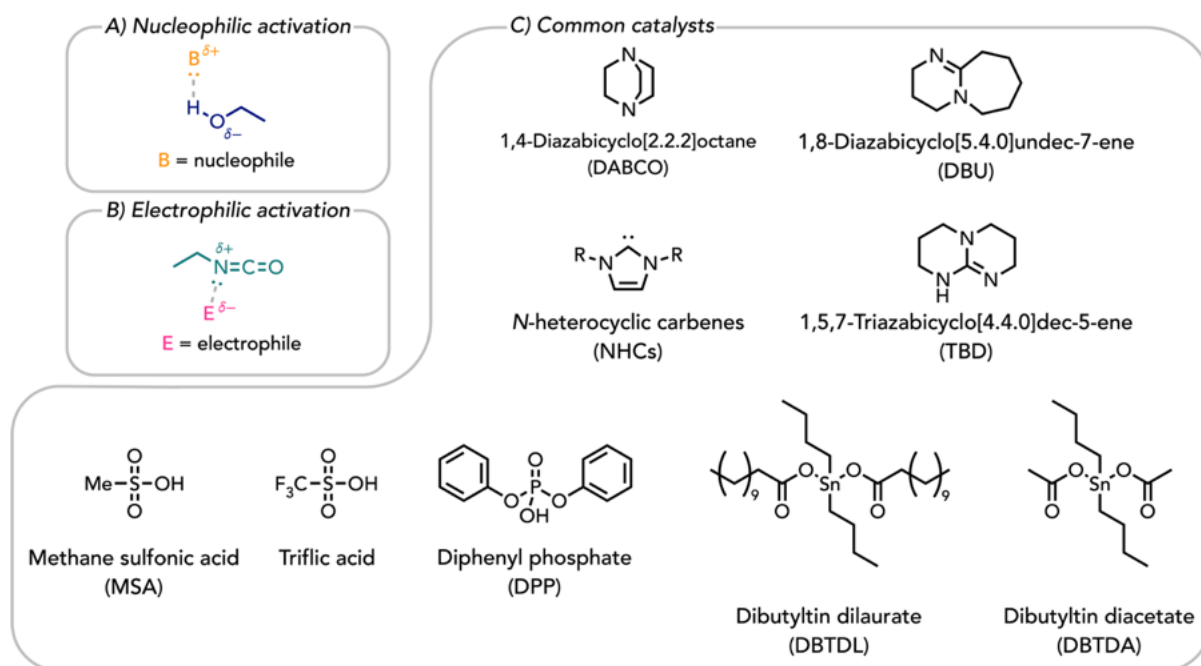


Figure 2.4 General nucleophilic (A) and electrophilic (B) activation mechanisms for the catalyzed isocyanate-alcohol reaction; examples of catalysts used in PU synthesis (C).

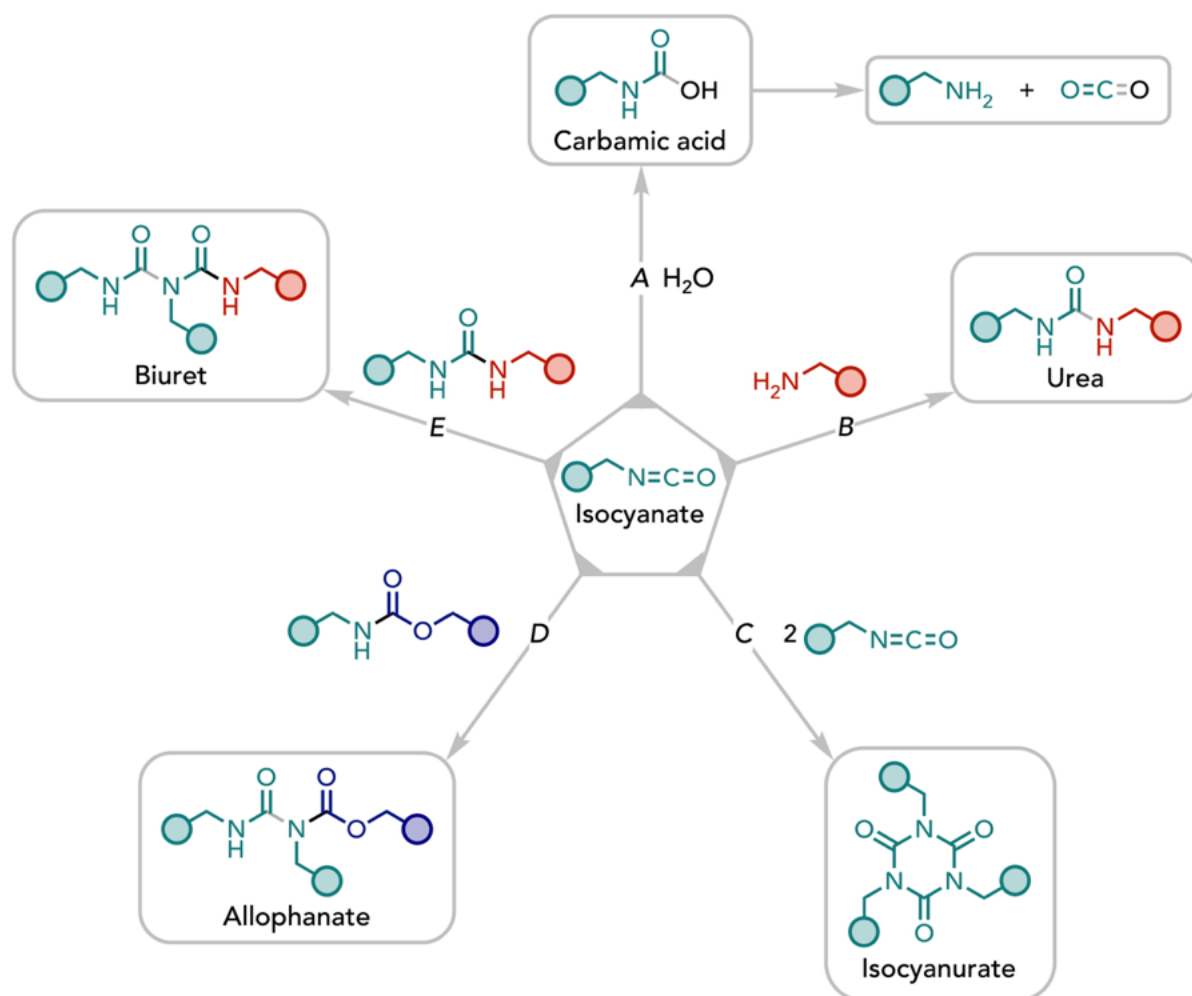
Side reactions

Despite the high selectivity of the polyaddition reaction forming urethane linkages, isocyanates are susceptible to various side reactions that can affect the final polymer structure and properties (Scheme 2.3).²⁵

Isocyanates react readily with water to yield unstable carbamic acids, which decompose to form amines and carbon dioxide (Scheme 2.3A). *In situ* generated amines can further react with isocyanate groups to form a substituted urea (Scheme 2.3B); this pathway is the basis for the formation of PU foams, where CO₂ acts as a physical blowing agent. However, uncontrolled moisture uptake leads to inhomogeneities in dense PU systems; therefore, careful environmental control is necessary during storage and processing.

Under catalytic or thermal conditions, isocyanates can undergo trimerization to form isocyanurates, cyclic trimers that impart high thermal and chemical resistance to the PU matrix (Scheme 2.3C).^{81,82}

Isocyanates can also react with urethane and urea groups to yield allophanates (Scheme 2.3D) and biurets (Scheme 2.3E), respectively. These reactions are reversible at elevated temperatures and introduce branching and crosslinking into the polymer network.⁸³



Scheme 2.3 Common side reactions in PU synthesis: hydrolysis (A), urea formation (B), trimerization (C), allophanate formation (D), and biuret formation (E).

2.1.2.4 Chain extenders and crosslinking agents

Chain extenders and crosslinkers are low-molecular-weight compounds typically bearing two or more reactive hydroxyl or amine groups, that are introduced into PU formulations to increase molecular weight, modify the polymer structure, and improve mechanical strength, thermal stability, and chemical resistance.⁵⁹ Chain extenders are small difunctional molecules (such as ethylene glycol (EG), 1,4-butanediol (BDO), diethanolamine (DEA), and ethylene diamine (EDA)), that react with isocyanate-terminated prepolymers to form high-molecular-weight linear or slightly branched PUs (Figure 2.5A). They contribute to the formation of hard segments within the polymer, thereby increasing its rigidity. Crosslinking agents, on the other hand, possess functionalities above two (e.g., trimethylolpropane (TMP), glycerol, or triethanolamine (TEA)) and are employed to form three-dimensional polymer networks (Figure 2.5B). Their incorporation leads to stiffer, more solvent-resistant, and thermally stable materials; however, excessive

crosslinking can compromise elasticity and impact resistance, necessitating a balance tailored to the application.

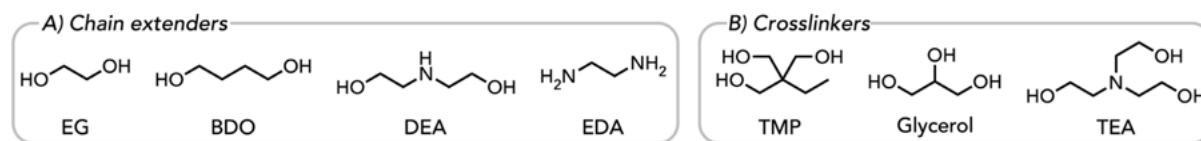


Figure 2.5 Common chain extenders (A) and crosslinkers (B) used in PU synthesis.

2.1.2.5 Additives

In addition to the main reactants and catalysts, PU formulations often incorporate a diverse array of additives to tailor performance, facilitate processing, or impart a targeted functionality. Surfactants and emulsifiers are widely used in foams to control cell size, structure, and stability, and in water-based formulations to stabilize the dispersion or improve wetting and substrate coverage.^{84–86} Blowing agents, both chemical (e.g., water, which reacts with isocyanates to generate CO_2) and physical (e.g., hydrocarbons, hydrofluorocarbons), are essential in the production of flexible and rigid foams.⁸⁷ Fillers such as calcium carbonate, silica, or carbon black are employed to modify mechanical properties, reduce cost, or introduce specific thermal or electrical behaviors.^{88–90} Plasticizers are occasionally used to enhance flexibility or processability, although their migration to the surface of polymer matrix affects the mechanical performance over time and raises environmental or health concerns.^{91,92} Other common additives include pigments, flame retardants, UV absorbers, antioxidants, and colorants, depending on the performance criteria and application sector.^{93–97}

2.1.3 Processing methods and market

Polyurethane production relies on two principal manufacturing routes that offer differing degrees of control over reaction kinetics and material architecture: the prepolymer method and the one-shot technique. These processing approaches serve as the foundation for a large and diverse global market, which continues to expand across a wide range of industrial sectors.

2.1.3.1 Processing methods

Prepolymer method

In the prepolymer method, a stoichiometric excess of polyisocyanate is reacted in a controlled manner with a polyol, yielding an isocyanate-terminated prepolymer. This intermediate is then reacted with chain extenders or crosslinkers to form the final polymer structure. This approach provides better control over molecular architecture, exothermicity, and curing kinetics, leading

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to overall better physical properties.^{34,98–100} However, prepolymer processing typically increases manufacturing complexity and equipment cost, and the viscosity of the prepolymer must be carefully managed to ensure good processability and substrate wetting.

One-shot technique

The one-shot technique entails the simultaneous mixing of all reactive components (polyol, isocyanate, catalyst, chain extender, and other additives) followed by immediate processing. Since the components in a formulation have different reactivities, some compounds may react faster than others with the isocyanate, resulting in poor control over the length of hard and soft segments.³⁴ Therefore, the one-shot method requires precise control of component ratios and mixing efficiency to ensure uniformity and avoid defects or incomplete curing. Despite these challenges, the one-shot approach is frequently preferred for its high production efficiency and lower capital investment.^{101,102}

2.1.3.2 Market overview

PU occupy a central and expanding position in the global polymer industry due to their chemical tunability, diverse morphology, and adaptability to a wide spectrum of end-use sectors. As of 2025, the PU market is valued at over USD 80 billion, with a projected compound annual growth rate (CAGR) of 4–5%, depending on the segment and geographic region.^{103–105} Their widespread adoption is enabled by the possibility to synthesize materials ranging from flexible to rigid, thermoplastic to thermosetting, and porous to compact—all from the same basic chemistry. Several key market segments can be identified, including: flexible and rigid foams, elastomers, coatings, adhesives, and sealants.

Flexible foams represent the largest segment by volume and are widely used in furniture, bedding, automotive seats, and packaging. Their popularity stems from low density, comfort, and energy absorption properties.

Rigid foams are adopted in thermal and sound insulation for appliances, buildings, and industrial installations due to their low thermal conductivity and structural stability. Demand is driven by the growth of construction industry and tightening energy-efficiency regulations.

Elastomers are used in footwear, industrial rollers, wheels and tires, sporting goods, and construction applications. Their excellent chemical resistance, along with resistance to abrasion, tear, and fatigue position them as superior alternatives to rubber and thermoplastics in demanding environments.

Coatings, adhesives, and sealants find application in several industries, particularly construction, automotive, and packaging. They offer strong bonding to diverse substrates, resistance to impact and environmental degradation, and flexibility over a wide temperature range.

2.1.4 Environmental, health, and safety considerations

2.1.4.1 Health and safety concerns

The industrial production and application of PUs raise several environmental, health, and safety (EHS) concerns, predominantly due to the synthesis and use of isocyanates.

The most common synthetic routes to polyisocyanates involve the phosgenation of polyamines.¹⁰⁶ Obtained by gas phase reaction of carbon monoxide and chlorine at elevated temperature using activated carbon as a catalyst, phosgene has high pulmonary toxicity and can be lethal in case of acute exposure.^{107,108} Its synthesis, storage, and handling require the highest safety standards, necessitating a multilevel safety concept with strict containment systems and specialized emergency protocols.¹⁰⁹ The reaction of phosgene with polyamines also demands effective risk management, as both reagents and products readily react with biological molecules, and the process generates HCl, a corrosive and hazardous by-product that necessitates additional safety measures for handling and disposal.¹¹⁰ The resulting isocyanate molecules obtained are classified as toxic or highly toxic compounds and strong respiratory sensitizers, capable of inducing asthma and other chronic pulmonary disorders even at low exposure levels.^{111–113} These hazards are particularly relevant during PU manufacturing and application, where aerosolization or evaporation of residual monomers can occur. Accordingly, protective measures such as worker training, personal protective equipment (PPE), and engineering controls are mandated by international occupational safety guidelines (e.g., OSHA, REACH, and NIOSH standards).¹¹⁴ Moreover, the use of free isocyanates above certain thresholds triggers product labeling and exposure monitoring requirements. For instance, the European Union has set occupational exposure limits (OELs) for diisocyanates at 6 µg NCO/m³ for an 8-hour workday and 12 µg NCO/m³ for short-term exposure.¹¹⁵ In addition to health risks during application, PUs can pose dangers under fire or thermal degradation conditions.¹¹⁶ Thermal treatment for energy recovery or feedstock recycling, particularly in aerobic conditions, can lead to the release of toxic gases, including carbon monoxide (CO), hydrogen cyanide (HCN), nitrogen oxides, and other toxic compounds.¹¹⁷

Although the current regulatory framework on isocyanates represents a significant step toward safeguarding worker health, it falls short of addressing the fundamental risks associated with

their production. Predominantly downstream-oriented, these measures emphasize exposure control, bureaucratic compliance, and individual worker responsibility rather than directly targeting the core hazards of phosgenation or actively accelerating the adoption of non-phosgene synthesis routes. As a result, this approach allows the industry to maintain established production practices with only incremental compliance costs, highlighting the need for policymakers to introduce stronger economic incentives, clearer timelines, or binding targets aimed at phasing out phosgene-based processes entirely.

2.1.4.2 Environmental impact

From an environmental perspective, conventional PU industry is characterized by a significant ecological footprint, primarily due to its impacts associated with the phosgenation process, reliance on fossil-based feedstocks, volatile organic compound (VOC) emissions, and challenges in the end-of-life management of PU products.

One of the main reasons behind PUs' environmental impact is the inherent ecological footprint of the phosgenation process. Phosgene is a fossil-derived, highly toxic, and hazardous reagent whose gaseous nature increases the risk of accidental environmental release, and its reaction with amines produces large volumes of chlorinated by-products that require further treatment.¹¹⁸ In addition, leakage of isocyanate molecules can have devastating consequences, as exemplified by the 1984 Bhopal disaster, considered one of the worst industrial accidents in history.¹¹⁹

Most industrially relevant isocyanates are synthesized from aromatic or aliphatic diamines, themselves derived from petrochemical intermediates. The development of bio-based isocyanates remains limited, with only few examples of partially bio-based monomers commercially available (listed in Section 2.1.2.2). In parallel, the adoption of bio-based polyols in the market with competitive prices remains uneven across application segments and is hampered by several challenges.⁶⁴ To ensure reliable and reproducible performance, adhesives and coatings often require narrow viscosity windows, well-defined molecular weights, or precise functionality, which bio-based polyols do not always provide.^{120–123} Moreover, while partially bio-based systems may improve the carbon footprint of the product, their true environmental benefit must be assessed on the basis of a life-cycle analysis, considering the impacts from the sourcing of the starting materials to the end-of-life.¹²⁴

The use of VOCs in PU processing also poses notable environmental and regulatory challenges. Many solvent-based PU adhesives and coatings release significant amounts of VOCs during application and drying, contributing to air pollution and exposure risks, particularly in indoor

environments. Consequently, regulatory pressure has driven the market toward waterborne and solvent-free systems, although achieving comparable performance remains non-trivial.

Finally, end-of-life management represents another critical issue of PU industry. Recycling strategies must overcome the great complexity of waste streams, which would benefit from better diversification based on the form or structure of post-consumer products. The most promising approaches include mechanical recycling, through regrounding and compression molding, and chemical recycling, mainly through glycolysis. However, the wide diversity of chemical structures and formulations prevents the identification of a universal strategy, necessitating instead the development of technologies tailored to specific PU materials.¹²⁵ While TPUs can be remelted and more easily reprocessed, thermosetting PUs, which dominate in adhesives and coatings, are particularly challenging to recycle due to their irreversible covalent crosslinks. A secondary recycling method, defined “physical recycling” and commonly adopted with PU foams, consists in reusing waste in the form of powder, flakes, or small particles blended with other reactive components to obtain low-performance materials for non-demanding applications.¹²⁶ Recycling of PU adhesives and coatings is particularly complex, as their strong adhesion to substrates complicates recovery without damaging the underlying material. Furthermore, coatings are often applied as thin films over large areas and adhesives are used in small amounts within complex assemblies. These factors render collection impractical and result in limited end-of-life recovery pathways.¹²⁷ Hence, although adhesives and coatings are rarely separated and recycled on their own, they should not interfere with the recycling of primary materials, particularly in short-life applications.¹²⁸ Emerging solutions including CAN-based and debondable systems are actively being explored, but the transition to a truly circular PU economy remains a long-term goal, requiring systemic changes in feedstock sourcing, formulation design, and waste infrastructure.^{129–133}

2.2 PU adhesives and coatings

Adhesives and coatings constitute a major technological branch within the broader family of PU materials, offering a combination of adhesion and mechanical strength, chemical resistance, and formulation flexibility that few other polymer systems can match. With a global market size estimated at USD 10.33 billion in 2024, the ability of PU adhesives to form strong, durable bonds with a wide range of substrates (including wood, metal, plastics, glass, and composites) makes them indispensable in sectors such as construction, automotive, footwear, packaging, electronics, and furniture manufacturing.¹³⁴ Likewise, PU coatings, whose global market stood at 20.9 billion in 2024, are widely employed for both protective and decorative purposes, owing to

their abrasion resistance, weatherability, and tunable gloss and hardness.¹³⁵ Compared to adhesive formulations, chemical resistance, flexibility, and appearance of the final product are more important for PU coatings, while bond strength and shear resistance are less relevant.¹³⁶

2.2.1 Typical classifications

Formulations for PU adhesives and coatings can be categorized according to their chemical composition, function, physical state, industrial sector of application, or specific properties. Among these, chemical composition parameters are especially significant, particularly the number of components, type of solvent, and macromolecular structure of the final polymer.

2.2.1.1 1K vs 2K

A common way to differentiate PU adhesives and coatings systems is based on the number of components used and distinguishes between one-component (1K, or single-package) and two-component (2K) systems.¹³⁷

1K formulations

1K formulations are preformulated materials that can be either reactive, when the crosslinking happens *via* chemical reaction, or non-reactive, exploiting physical hardening methods. For reactive systems, the curing happens upon exposure to ambient moisture, heat, or another environmental trigger. In moisture-curable PUs, the most important class of 1K PU products, the prepolymer is typically terminated with free isocyanate groups, which react with atmospheric water to generate CO₂ and amines that further crosslink with residual isocyanates forming urea linkages.¹³⁸ One-component systems are valued for their ease of use and application flexibility, and are commonly used in construction, transportation, and consumer coatings. However, for reactive systems, curing can be diffusion-limited in thick films or low-humidity environments, polymerization rates may be difficult to control, and formulations must be carefully stored to prevent undesired reactions. To address these challenges and improve shelf stability, a blocking chemistry approach for polyisocyanates has been developed, in which the reactive NCO groups are temporarily masked with blocking agents that can be removed upon heating. This strategy allows more precise control over cure timing and avoids premature reactions during processing.^{139,140}

2K formulations

2K systems, by contrast, involve the separate storage of isocyanate (or typically an isocyanate-tipped prepolymer) and polyol components, which must be accurately weighed and mixed immediately before use.⁶⁸ This approach allows for more controlled curing and is prevalent in many high-performance and engineering fields.¹⁴¹ Sensitivity to moisture and necessity of mixing equipment represent the primary limitations of 2K approaches, particularly in fast-paced or large-area applications.¹⁴²

2.2.1.2 Solvent-based vs solvent-free vs waterborne

Presence and type of solvent discriminate between three main classes of formulations: solvent-based, solvent-free, and waterborne.

Solvent-based formulations

Solvent-based formulations consist of PU prepolymers or resins dissolved in dry organic solvents such as acetates, ketones, or aromatic hydrocarbons.²⁵ The specific solvent is selected on the basis of its ability to interact with the substrate surface, dissolve the polymer, and evaporate from the mixture forming homogeneous films.¹⁴³ These systems offer low initial viscosity and excellent substrate wetting, facilitating uniform film formation and adhesion on complex geometries, low-energy surfaces, or large laminating areas.²⁵ However, the reliance on VOCs presents significant environmental, safety, and health concerns, and regulatory pressure has led to a gradual phase-out of many solvent-based systems in favor of low-VOC alternatives.¹⁴⁰ Additionally, for reactive formulations, solvent evaporation during curing must be tightly controlled to avoid defects.

Solvent-free formulations

Solvent-free PU systems eliminate the use of organic solvents by employing low-viscosity monomers/prepolymers or reactive diluents that participate in network formation. These formulations are increasingly favored over their solvent-based counterparts due to their reduced emissions and improved workplace safety. Achieving adequate processability in solvent-free systems requires precise rheological control through careful molecular weight adjustment, monomer selection, efficient mixing (for 2K formulations), or incorporation of additives such as plasticizers and flow modifiers. While solvent-free systems can match or exceed the performance of solvent-borne analogs, they often require heating to achieve complete curing, melt solid components, or decrease viscosity.

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Waterborne formulations

Waterborne systems include PU formulations that are prepared using water as a solvent or carrier medium. The dominant subclass is that of PU dispersions, which are colloidal formulations stabilized in an aqueous medium by dispersing agents (often called “emulsifiers”). These dispersing agents can be internal, i.e., covalently bound to the polymer backbone, or external, added as separate surfactants. While external dispersing agents simplify the synthesis and may be added to enhance the dispersion stability, they tend to migrate to the film surface, leading to poorer mechanical performance and water resistance.¹⁴⁴ Internal dispersing agents, by contrast, consist of ionic (e.g., carboxylic, sulfonate, or quaternary ammonium salt) or non-ionic hydrophilic moieties that are already present in the starting polyol or isocyanate and subsequently get incorporated into the macromolecular chain during polymerization. Waterborne PUs can be synthesized through various routes, including emulsification (or pre-polymer), acetone, hot-melt, and ketimine-ketazine processes.^{31,145} Upon water evaporation, the dispersed PU particles coalesce into a continuous film, sometimes followed by additional curing to enhance the mechanical properties.^{136,146} PU dispersions provide a good balance between environmental performance and mechanical properties, exhibiting low VOC content, tunable viscosity, and compatibility with a wide range of substrates.¹⁴⁷ However, this approach also poses challenges in the development of formulations with proper film coalescence, long shelf stability, high water and temperature resistance, and good balance between solid content and viscosity.^{148–150}

2.2.1.3 Thermosetting vs thermoplastic vs CAN-based

Based on their macromolecular architecture and thermal behavior, PU adhesives and coatings can be broadly classified into three main categories: thermosetting, thermoplastic (TPU), and covalent adaptable network (CAN)-based systems.

Thermosetting formulations

Thermosetting PUs are formed through reactions involving trifunctional or higher-functional isocyanates, polyols or chain extenders, leading to irreversible covalent crosslinking and limited recyclability. These materials offer an optimal balance between adhesive and cohesive forces and exhibit superior thermal and chemical resistance, dimensional stability, long-term durability, and mechanical strength, making them more widely used than their thermoplastic counterparts in adhesive and coating systems.^{136,151} Thermosetting PUs are inherently non-reprocessable but ideal for structural bonding, corrosion protection, and other demanding industrial applications;

typical uses include construction sealants, automotive and aerospace structural adhesives, laminated fabrics, or protective marine coatings.^{152–154} The choice of curing mechanism depends on many variables affecting the utilization of the adhesive, such as the application technique and the porosity of the substrate.²⁵

Thermoplastic formulations

TPUs are typically synthesized from difunctional isocyanates, long-chain polyols, and difunctional chain extenders, resulting in linear or only slightly branched chains. These polymers are characterized by microphase-separated morphology caused by the intrinsic incompatibility between the hard domains, linked together by intermolecular hydrogen bonds and acting as physical crosslinks, and soft domains, which confer elastomeric properties to the copolymer.^{37,155} The hard segments mainly derive from rigid diisocyanate and chain extender moieties, while the soft segments are typically obtained from flexible polyols. TPU-based adhesives and coatings are typically applied in molten form, in solution, or as dispersed water-based formulations.²⁵ They exhibit high abrasion resistance, flexibility, mechanical and impact strength and can be more easily processed and recycled, but generally offer lower performance compared to thermosetting systems.^{156–158}

CAN-based formulations

A particular class of crosslinked PUs are covalent adaptable networks (CANs), materials whose structure and topology can be changed and reconfigured *via* dynamic covalent chemistry.¹⁵⁹ Unlike conventional thermosets, CAN-based PUs can undergo associative or dissociative bond exchange under specific stimuli (such as external heating, light exposure, or pH variation) without degradation of the polymer network.¹⁶⁰ This imparts remarkable properties such as self-healing and stress relaxation and can provide repairable, reprocessible, reconfigurable, recyclable, and re-adhesive (5R) performance.¹⁶¹ The main trade-offs associated with PU CANs include inferior mechanical properties, more complex synthetic procedures, challenges in developing materials with high T_g s, and potential instability under certain conditions due to the dynamic nature of the reversible bonds.^{132,162} Although several successful examples of dynamic covalent chemistry applied to switchable PU adhesives have been reported, these systems capable of scratch-healing and dimensional recovery often suffer from limitations in the bonding-to-debonding strength ratio, reaction kinetics, removal efficiency, and long-term service stability.¹⁶³

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2.2.1.4 Notable classes

Certain classes of PU adhesives and coatings fit into multiple classification categories and deserve separate consideration, including hot-melt, hybrid, and pressure-sensitive formulations.

Hot-melt formulations

Hot-melt PUs are solvent-free systems applied in molten form and subsequently solidified by cooling. They can be non-reactive or reactive, the latter more common due to their superior adhesion strength and improved heat and chemical resistance.^{164,165} Reactive hot-melts are typically based on isocyanate-terminated prepolymers that undergo a secondary reaction (with ambient moisture or with functional moieties on the substrate surface) to form a crosslinked network, thus combining the processing benefits of thermoplastics with the performance advantages of thermosets.^{68,136} They are often used for wood bonding, footwear, packaging, bookbinding, and furniture.

Hybrid systems

Hybrid formulations combine PU chemistry with other reactive functionalities to achieve enhanced performance, reduced cost, or broader application scope. Their formulation is typically more complex, as it requires compatibility between reactive groups and careful balance between desirable and undesirable properties. Reported examples include:

- PU–acrylic hybrids, combining the mechanical performance of PUs with the weathering durability, gloss retention, and lower cost characteristic of acrylics;^{166,167}
- PU–epoxy systems, employed in structural adhesives where high strength and toughness are required;¹⁶⁸
- silane-modified PUs, valued for their oxidative stability and low surface energy, particularly in fouling-release coatings.^{169–171}

Pressure-sensitive adhesives

Pressure-sensitive adhesives (PSAs) are a class of adhesives that are strongly and permanently tacky, adhering firmly to substrates with just finger or hand pressure and without the need for solvent evaporation, heat, or chemical curing.^{172,173} The polymers used in PSAs are characterized by a low glass transition temperature and a carefully tuned viscoelastic profile, which together ensure effective surface wetting, tack, and peel strength. Although TPUs generally exhibit low inherent tack, various strategies have been developed to impart pressure-sensitive adhesive characteristics, particularly because their segmented structure makes them promising candidates for the manufacturing of materials with tunable viscoelasticity.^{174,175}

2.2.2 Factors influencing performance

The ultimate performance of PU adhesives and coatings depends on a plethora of factors, including intrinsic substrate properties, surface preparation, formulation-related parameters, environmental conditions, and application techniques, which together determine the quality of wetting, adhesion to the substrate, and film or joint uniformity. Understanding the interplay between all these parameters is essential for correlating laboratory prototypes with real-world performance.

2.2.2.1 Substrate properties and surface treatments

Surface preparation significantly influences the adhesion of coatings and adhesives to the substrate by removing contaminants and pre-existing defects and by modifying surface energy, chemistry, and topography to improve wettability, chemical compatibility, and overall interfacial bonding strength. The selected treatments must be tailored to the substrate properties as well as to the specific purpose and performance requirements of the system.

Substrate properties

Substrates vary widely in chemical composition and reactivity. A key parameter governing interfacial adhesion is the surface energy of the substrate, which represents the excess free energy present at the surface of a solid and arises from the imbalance of intermolecular forces experienced by surface atoms relative to those in the bulk. It defines the thermodynamic tendency of a surface to interact with other phases and is directly related to wettability, which describes the tendency of a solid surface to be covered by a liquid. Wettability depends on the balance of interfacial tensions between solid, liquid, and vapor phases and is quantitatively expressed by the contact angle (θ) formed at the interface. A low contact angle ($0^\circ < \theta < 30^\circ$) indicates good wetting and typically corresponds to a substrate surface energy significantly higher than that of the liquid, which promotes stronger adhesive or coating interactions. Surface treatments are therefore generally designed to increase surface energy to ensure intimate molecular contact and optimal adhesion.

Alongside chemical properties, surface morphology and porosity, as well as substrate temperature and geometry, strongly affect interfacial phenomena and adhesion performance. Porous surfaces contain voids or channels that can trap air or absorb liquids, thereby altering the effective contact area and the apparent contact angle. High porosity can enhance liquid uptake and improve apparent wettability in some cases but can also lead to heterogeneous wetting if air pockets remain trapped. Elevated substrate temperature reduces viscosity and enhances

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wetting, facilitating penetration into the substrate and formation of a more uniform film or bondline. However, excessive temperature may accelerate solvent evaporation or cause premature gelation, potentially resulting in defect formation or reduced adhesion. Substrate geometry, instead, has a pronounced influence on local stress distribution and overall load-bearing capacity of the coating or adhesive joint. Sharp corners, edges, and complex geometries often lead to uneven film thickness, stress concentration, and reduced adhesion, while rounded edges and smooth transitions favor more uniform coverage and improved mechanical performance. In the case of adhesive-bonded joints, the design should minimize peel forces, generate compressive rather than tensile stresses, and avoid stress concentrations along the bond line.¹⁷⁶

Surface treatments

Before any surface modification, a cleaning step is essential to remove contaminants such as dust, oils, grease, or dirt, that would otherwise form weak boundary layers and compromise adhesion.¹⁷⁶ Cleaning is typically performed by washing with aqueous solution, high-pressure steam cleaning, or wiping with cleansing agents such as water-miscible detergents or organic solvents (often polar, such as acetone or isopropanol), which are preferred for degreasing. For persisting contaminants, mechanical removal or immersion in an ultrasonic solvent bath may be employed to ensure complete elimination of surface impurities.

After initial cleaning and drying, surface treatments can be broadly categorized into mechanical, chemical, and physical methods.¹⁷⁶ Mechanical treatments, such as grinding, blasting, or brushing, increase surface roughness through abrasive removal and deformation, thereby promoting mechanical interlocking. Chemical treatments generally consist of etching and conversion coating processes. In the former case, non-oxidizing acids or alkaline solutions are used to remove friable organic or inorganic layers, more external or deeper depending on etching time and substrate; in the latter technique, oxidizing acids are typically employed to produce a passivating and firmly adhering conversion film (e.g., phosphate or chromate oxide) that provides improved adhesion properties. In addition to these preparation techniques, primers are frequently applied to form a thin intermediate layer between the adhesive or coating and the substrate, promoting chemical compatibility, protecting the substrate surface, and improving its wettability. Physical preparation techniques exploit high-energy processes to activate the substrate surface. They include flame, plasma, and corona discharge treatments, which are mainly used for polymer substrates with low surface energy. The effectiveness of a given surface

treatment can be evaluated through various measurements assessing the resulting wettability, chemical modification, and morphology.

2.2.2.2 Processing parameters and conditions

Beyond surface characteristics and preparation, the choice of application technique and the performance of coatings and adhesive joints are strongly influenced by formulation properties and environmental conditions.

Formulation properties and time-dependent parameters

Among the formulation-related factors, viscosity and rheological profile are of primary importance, as they determine its ability to flow, level, and achieve intimate and complete substrate coverage before setting. High viscosity can hinder spreading and promote air entrapment, while overly fluid formulations may be difficult to handle, especially on vertical surfaces. To balance ease of application with stability after deposition, thixotropic or shear-thinning properties are often engineered into PU formulations. For solvent-based and waterborne systems, solid content and solvent volatility influence viscosity, flow behavior, and drying rate. High-solids formulations minimize VOC emission but exhibit higher viscosity, whereas low-solids alternatives are easier to apply but often result in higher VOC release and longer drying times. Moreover, especially for highly diluted systems, it is of paramount importance to control solvent removal, since excessively rapid evaporation can cause a series of defects, whereas slow evaporation can delay curing and reduce productivity. In multi-component or reactive systems, precise molar ratios, uniform substrate temperature, and high mixing efficiency are critical to obtain homogeneous products and avoid premature gelation or residual tackiness. Dedicated instrumentation exists for the mixing, metering, and controlled dispensation of multi-component formulations at both large- and small-scale.¹⁷⁷

Alongside rheological factors, a series of time-dependent parameters govern the processability and application of PU coatings and adhesives. The most widely used parameters, as defined in the standards ASTM D907 and ISO 4618, can be categorized according to the stage of the application, namely before, during, or after deposition and assembly.

Before application, once the formulation is packed in its original sealed container, it remains stable under specified storage conditions for a defined period, known as its "shelf life" or "storage life". In 2K systems, the "pot life", also called "working time", refers to the period after mixing during which the formulation remains usable, maintaining adequate viscosity and reactivity for

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application. After this period, the system exhibits viscosity increase, partial gelation, or skin formation, which impair spreading and film uniformity.

During application, the “open time” designates the interval in which the applied adhesive or coating remains workable before initial setting occurs. In adhesive bonding, this parameter is referred to as “open assembly time”, i.e., the time available between adhesive deposition onto the adherends and their assembly.

After deposition or assembly, subsequent transformations govern the evolution from a tacky to a hardened, and ultimately to a permanently stable state. The “tack range” (or “tack-free time”) indicates the interval during which the formulation remains tacky (capable of adhering under light pressure and after a short contact time), after which the surface loses its stickiness and can be more easily handled or overcoated. This transition typically happens when solvent evaporation or network formation reduces chain mobility.¹⁷⁸ The process continues until the material reaches a fixed or hardened state, by physical or chemical means, under defined conditions. The time between deposition and this stage is termed “setting time”. In solvent-based systems, this transformation occurs primarily through evaporation, and the corresponding period is referred to as “drying time”. For formulations that provide a polymer network, typically *via* crosslinking of macromolecular chains, two additional parameters are essential to describe the extent of the polymerization reaction: “gel time” and “curing time”. The gel time is the interval between the start of the network-forming process, when the reagents first come into contact in a 2K formulation, and the gel point, which marks the formation of an infinite polymer network spanning the entire system. At the gel point, the viscosity rises sharply and the material transitions from a processable liquid to a solidifying gel, beyond which further mixing or application is not possible. The curing time represents the period required for the coating or adhesive to reach the desired performance and properties under specified conditions, typically corresponding to the stage at which no significant changes in polymerization conversion or in the physico-chemical structure of the material are observed.

With viscosity and rheological behavior being equal, formulations exhibiting longer pot life, open time, set time, and curing time are generally easier to handle, although at the expense of reduced productivity. Therefore, the optimal choice of time-dependent parameters depends on the intended purpose of the PU formulation and represents a balance between processing efficiency, ease of manipulation, and final product quality.

Environmental conditions

Finally, environmental conditions during deposition, particularly temperature, relative humidity, and airflow, affect wetting dynamics, setting, and curing behavior. Notably, elevated humidity can interfere with isocyanate reactions or remain trapped within the mixture, while inadequate ventilation may either hinder or excessively accelerate solvent removal.

2.2.2.3 Application methods and defects

Application methods

The selection of an appropriate application technique depends on the intrinsic properties and intended function of the formulation.

For coating formulations, it is critical to achieve uniform film formation, desired thickness, and adequate surface coverage, all of which strongly influence long-term performance. Among conventional manual deposition methods are brushing, rolling, and spraying, while at laboratory or industrial scale, roll, knife, spin, dip, and powder coating are more commonly employed.^{179,180} Other techniques are adopted for specific sectors, such as the electrodeposition of polymers in the automotive industry, while more advanced methods are available for niche and research applications.¹⁸¹

In contrast to coatings, which are applied onto a single surface, adhesives are employed to bond two or more components together, making the joint design and assembly processes critical steps in ensuring product integrity. Effective adhesive bonding requires that stresses should be distributed evenly across the bonded area and that shear loading predominates, since adhesives exhibit their highest strength under shear while being more vulnerable to peel and cleavage.¹⁸² Equally important, the design of the joint must facilitate assembly and adhesive application, ensuring uniform wetting and minimizing the risk of voids or other defects within the bond line. Another distinction from coating systems is that, since precise control of the layer thickness is less critical, reactive multicomponent formulations are more common in PU adhesives, and different deposition techniques are employed. Among the previously cited application techniques, most are also applicable to adhesives, although some, such as spin coating or electrodeposition, are rarely or hardly ever used. Conversely, the application of a liquid adhesive often does not require strict precision and can be performed with simple manual tools such as hand-pump oil cans, syringes, needles, or squeeze bottles, which are particularly useful for localized or hard-to-reach areas. Moreover, a wider range of adhesive product forms, including paste, film, or hot-melt, are commonly used.^{176,183}

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Processing-related defects

In addition to intrinsic substrate imperfections, the application and processing of coatings and adhesives can introduce new defects or exacerbate pre-existing ones.

In coating formulations, numerous defects may arise from inadequate wetting and leveling, air, solvent, or moisture entrapment, uncontrolled flow behavior, excessive internal stresses developed during drying or curing, and long-term environmental degradation. Their manifestations include surface discontinuities, film irregularities, cracking phenomena, loss of adhesion, and optical alterations such as haze, discoloration, or chalking.^{184–186}

Adhesive bonding is affected by processing issues similar to those encountered during the deposition of coating formulations, while also presenting additional challenges related to substrate alignment, assembly timing, and the formation of voids or air entrapment during bonding.^{187,188} Such defects can act as stress concentrators and potential initiation sites for crack propagation under load. Furthermore, in structural applications, differences in the thermal expansion coefficients of the adherends and the adhesive can lead to significant stress accumulation and microcracking.¹⁸⁹ These effects are more critical than in coating systems, particularly when the adhesive layer is excessively rigid or non-uniformly distributed.

2.2.3 Characterization and performance evaluation

A reliable evaluation of the operational behavior and performance of PU adhesives and coatings can only be achieved through standardized testing protocols, which provide the quantitative basis for assessing suitability under specific service conditions and end uses.

2.2.3.1 Coating characterization and performance evaluation

Coating evaluation relies on a broad spectrum of characterization techniques and standardized testing methods that provide insights into both fundamental material properties and service performance.^{180,184,186} Among this wide range, the following section briefly addresses chemical, rheological, thermal, and thermomechanical characterization, while focusing in more detail on properties more relevant and specific to coatings, including surface characteristics, coating thickness, mechanical behavior, adhesion strength, and chemical and environmental resistance.

Chemical, rheological, thermal, and thermomechanical properties

Chemical and elemental composition, as well as molecular structure and weight distribution, are commonly analyzed using spectroscopic, spectrometric, or chromatographic techniques. Together, these analytical methods form the basis for correlating the chemical characteristics of

the material with its macroscopic properties and performance. In addition to these common techniques, rheological measurements can also yield valuable chemical information, particularly in reactive or crosslinking systems. Rheological characterization provides information on the flow and deformation behavior of the formulation, including parameters such as viscosity, pseudoplastic flow (or shear-thinning), and thixotropy. These properties are crucial for processability and application and, in reactive thermoset systems, can be correlated with the curing degree and crosslink density. The latter parameters can also be evaluated through swelling and gel content measurements, as well as by thermal or thermomechanical analyses, including differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA). Such techniques are widely employed in both academic and industrial studies of polymeric coatings to assess parameters such as thermal stability, phase transitions, curing behavior, and temperature-dependent mechanical performance.

Surface characteristics

Coating surface properties can be investigated using different analytical tools depending on the specific parameter of interest, including molecular and elemental composition, surface energy and wettability, optical properties, and morphology.

The same analytical tools exploited to analyze the bulk chemical composition of coatings can also be applied to their surface. However, a commonly used method that is specific to the near-surface region is X-ray photoelectron spectroscopy (XPS), providing qualitative and quantitative information on the elemental composition of the top ~10 nm of a surface. XPS can distinguish between different elements and their chemical states, yielding information about phenomena such as the presence of adsorbed surfactants or the segregation of components from the bulk. The technique is regarded as nondestructive, although extended irradiation can lead to partial sample degradation or evaporative losses.

The wettability of a coating influences key properties such as tack, adhesion, and hydrophilicity. It is commonly evaluated by measuring the contact angle using the sessile drop configuration, in which a droplet of liquid (typically 3–10 μL in volume) is placed on the solid coating surface and the contact angle is determined from its profile. The measurement can be conducted in either static or dynamic modes: in the static method, the equilibrium contact angle is measured at constant droplet volume, whereas in the dynamic approach the angle is recorded as the droplet volume is increased or decreased, yielding the advancing and receding angles. For a reliable description of wetting behavior, both static and dynamic contact angles should be reported. A useful empirical parameter to estimate the surface energy and wettability of a coating is the

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critical surface tension (γ_c), which represents the maximum surface tension a liquid must have to completely wet the coating surface.

Decisive for certain applications, especially those aiming for high aesthetic quality, is the interaction of the coated surface with light. Light can be reflected either in a mirror-like manner, where the angle of reflection equals the angle of incidence, or diffusely, with uniform scattering in all directions. The type of reflection depends on the surface roughness and intrinsic chemical properties of the material, and it affects key visual properties such as gloss and haze. Gloss quantifies the intensity of specular reflection and is higher for mirror-like finishes, whereas haze quantifies the amount of light scattered near the specular reflection direction and is associated with a cloudy appearance and reduced perceived clarity. Gloss is measured by comparing the light reflected from a surface at a specific angle of incidence to that reflected by a polished black glass standard. Haze, in contrast, is measured as the percentage of reflected light deviating slightly (by a few degrees) from the specular angle. Closely related to gloss and haze, the distinctness of image (DOI) quantifies how sharply and clearly an image is reflected (or transmitted) by a coated surface, by measuring narrow-angle scattering at low incident angles. Color perception depends strongly on the light source, its interaction with the coating, and the sensitivity of the eye. To overcome the inherent subjectivity of color, this property is measured with a spectrophotometer that records the intensity of reflected or transmitted light at a specified incident angle as a function of wavelength.

Considering scattering and absorption throughout the entire coating film, coatings with negligible scattering and absorption are termed transparent, those that transmit and scatter light are translucent, and those that absorb or reflect light entirely are opaque (allowing no light transmission or color information from the substrate). The degree of transparency can be quantified by measuring the fraction of transmitted light using UV-Vis spectroscopy and, like translucency and opacity, depends on coating thickness.

Directly linked to wettability and visual characteristics, the morphology of a coating surface refers to the spatial distribution and pattern of features such as defects, phases, and microstructures in the external layer of the material. It is typically examined using microscopy-based techniques, including optical microscopy for routine analysis of surface defects and uniformity, electron microscopy for high-resolution imaging, and scanning probe microscopy for three-dimensional topographical mapping. Among optical methods, several variants are commonly used for surface inspection, whereas in electron microscopy, the two principal techniques are scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM, which can be coupled with energy-dispersive X-ray spectroscopy (EDS) for elemental analysis, offers lower resolution but it

is far more accessible and versatile than TEM, which provides nanometer-scale structural information but requires ultrathin specimens. Within the scanning probe methods, atomic force microscopy (AFM) is the most widely employed technique, enabling nanoscale mapping of roughness, morphology, and phase contrast. Profilometry can also be used to obtain quantitative data on surface roughness and step heights. A smooth and uniform surface generally promotes high gloss and low light scattering, whereas rough or heterogeneous morphologies can enhance mechanical interlocking and wettability but may also lead to undesired visual effects.

Coating thickness

Shifting from surface-specific features to parameters describing the coating as a whole, coating thickness is a key factor influencing internal stress distribution, optical appearance, heat and mass transfer, and mechanical behavior. High film thickness generally enhances barrier performance but may hinder solvent evaporation or diffusion of reactive species; contrarily, insufficient thickness can compromise mechanical integrity or surface coverage. Techniques for dry film thickness determination are broadly classified as destructive and non-destructive.

Destructive techniques are often time-consuming and unsuitable for routine production control, as they include cross-sectioning or removal of the coating, followed by direct thickness measurement through microscopy, or using a caliper or a micrometer.

In contrast, non-destructive techniques allow thickness determination without damaging the coating and are therefore more common in practice. For metallic substrates, the most widely applied techniques are (electro)magnetic induction and eddy current methods, which determine the total coating thickness by exploiting the difference in electromagnetic properties between substrate and coating. For non-metallic substrates (and not only), ultrasonic gauging employs high-frequency sound waves and detects the time delay of the signal reflected at the substrate-coating interface. Two additional non-destructive techniques less common for polymer coatings are the beta-ray backscatter and X-ray fluorescence (XRF) techniques. The former measures the intensity of backscattered beta radiation, but due to limitations in accuracy and safety, it has largely been replaced by XRF, which detects secondary (fluorescent) X-rays emitted from the sample after excitation.

Mechanical behavior

Often correlated with thickness, the mechanical properties of coatings offer insights into their resistance to external stresses and are therefore essential for predicting service performance. Among the most fundamental parameters are hardness, abrasion and scratch resistance,

flexibility, and impact resistance. These properties are commonly analyzed through real-time tests, which provide a better understanding of film integrity, mechanical response, and deformation mechanisms compared to post-failure techniques such as fractography.²²⁰

Unlike conventional hardness tests for bulk materials, which apply relatively large loads to measure overall resistance to deformation, coating hardness is evaluated by exerting localized small loads, so that the measurement mainly reflects the coating's properties rather than those of the material underneath. Micro- and nano-indentation tests measure the penetration depth of a hard indenter of defined geometry (sharp, like Vickers, Knoop, and Berkovich, or blunt, such as Brinell) under controlled load, allowing precise quantification of hardness. An alternative approach is pendulum damping hardness, which measures the damping of a swinging pendulum on the coated surface. Two standardized setups exist: the König and Persoz pendulums. A more practical but less precise method is the pencil hardness test, in which the coating is scratched with pencils of increasing hardness until permanent damage occurs. Despite its qualitative nature, the pencil hardness test remains widely used in industry due to its simplicity and speed. Closely related to hardness are scratch and abrasion resistance, which quantify the coating's durability against mechanical wear. Scratch resistance is commonly assessed with instrumented scratch testers and expresses the ability to resist localized damage from scraping, that is the application of a controlled load with a sharp object. Abrasion resistance, on the other hand, evaluates a coating's endurance against repeated rubbing (friction) or contact with standardized abrasive particles.

For substrates that experience bending, stretching, or dynamic loads, flexibility and impact resistance of a coating are crucial for long-term performance and integrity. Flexibility and elasticity can be evaluated by tensile testing of free films, or by cupping or mandrel bend test on coated panels. In the cupping test (often called Erichsen test), the panel is plastically deformed with a hemispherical punch from the back until the coating cracks, while in the mandrel bend test, the panel is bent over cylindrical or conical mandrels of decreasing diameter until failure is observed. Impact resistance, in contrast, measures the coating's ability to absorb sudden mechanical shocks without cracking or delaminating, typically with falling weight tests. Beyond these practical tests, DMA provides complementary insights into the viscoelastic behavior of coatings, enabling the precise evaluation of storage and loss moduli, glass transition temperatures, and time- or temperature-dependent mechanical response.

Adhesion performance

While mechanical tests evaluate the coating's resistance to deformation or damage, they can also indirectly reveal poor adhesion through cracking, flaking, or delamination under stress. Adhesion tests, by contrast, specifically assess the strength of the coating-substrate bond, which is critical to prevent defects or premature failure. Moreover, the type and extent of interfacial failure provide valuable information about the failure mechanism. A classic comparative adhesion test is the cross-cut (or cross-hatch) test, in which a lattice of incisions is cut through the coating, followed by application and removal of an adhesive tape (Figure 2.6A). The coating performance is then qualitatively evaluated based on the degree of flaking or detachment from the substrate. For a more quantitative assessment, the pull-off test is employed: a stud is glued to the coating, and a normal load is applied until detachment, with both failure stress and failure mode recorded (Figure 2.6B). The test can be performed only if the substrate is stiff enough to avoid deformation, and the adhesion strength is reported as the force per unit bonded area at fracture. For flexible coatings, peel tests measure the force needed to delaminate the coating from the substrate at a controlled angle (Figure 2.6C). This force can then be converted into fracture energy.

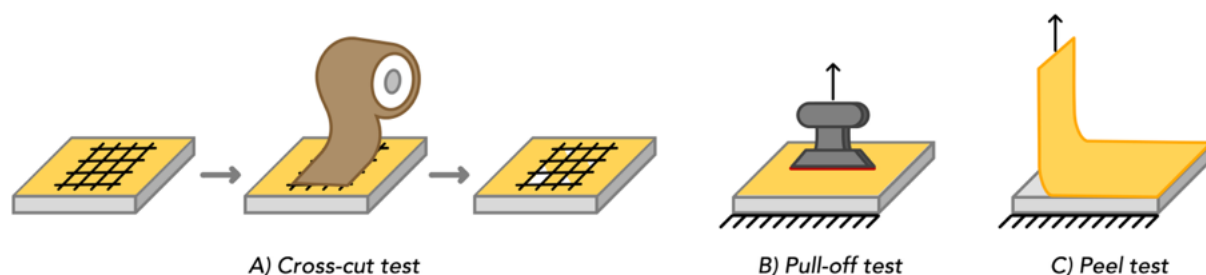


Figure 2.6 Graphical illustrations of the cross-cut (A), pull-off (B), and peel (C) tests.

Chemical resistance

Another key feature of PU coatings is their resistance to solvents, chemicals, moisture, and environmental degradation. Chemical resistance is typically evaluated by exposing the coated specimens to solvents, acids, bases, or other chemicals for defined periods, followed by inspection of changes in gloss, color, hardness, or adhesion. Moreover, solvent resistance can be assessed through solvent rub tests, in which a cloth soaked with a volatile organic solvent (commonly methyl ethyl ketone, MEK) is rubbed repeatedly over the coating until visible softening or removal occurs. The number of rubs to failure constitutes a comparative measure of chemical resistance. Network stability, degree of curing, and crosslinking in thermoset coatings can be investigated through gel content and swelling tests. In gel content tests, a free coating film undergoes solvent extraction, and the insoluble fraction is quantified gravimetrically. A high gel

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fraction indicates a densely crosslinked network with good resistance to solvent-induced degradation. Swelling tests evaluate solvent uptake and expansion, offering complementary insight into crosslink density, solvent permeability, and chemical stability. When performed with water or aqueous solutions, these tests assess hydrolytic stability, moisture uptake, and the tendency to form defects under humid or outdoor conditions.

Environmental resistance

Moisture durability falls within the broader class of environmental and accelerated weathering tests, which replicate long-term service conditions. Common weathering tests simulate outdoor degradation, typically combining UV exposure with temperature and humidity cycling. They are often performed in xenon arc or QUV chambers, which employ xenon arc lamps or fluorescent UV lamps to reproduce the full solar spectrum or its UV portion, respectively. Specialized analyses, such as salt spray, pollutant exposure, corrosion protection, or thermal shock tests, target specific environmental stresses. These accelerated weathering assessments are particularly important for automotive, marine, and architectural applications, where prolonged exposure to sunlight, moisture, and pollutants can compromise both aesthetics and performance.

Testing of functional coatings

In addition to common tests used for coating evaluation, functional coatings are evaluated for application-specific properties, for example, electrical conductivity in conductive or antistatic coatings, or gas and moisture permeability in barrier coatings. Such targeted analyses ensure the coating's suitability and reliability for its intended use.

2.2.3.2 Adhesive characterization and performance evaluation

While many characterization and performance evaluation methods used for coatings can be also applied to adhesives, the properties tested often differ due to the distinct functional roles of these PU-based applications. Adhesives require a stronger focus on bond integrity and functional performance under mechanical, chemical, and environmental stress, whereas coatings are often evaluated for surface durability, appearance, and protection.

Analyses of chemical, thermal, thermomechanical, and optical properties of coatings, as well as their chemical and environmental resistance, can often be directly applied or adapted to adhesive materials. In contrast, assessment of surface-specific properties is less relevant and common, since adhesives are typically covered or sandwiched. Due to the different geometry

and overall configuration of adhesive joints, the determination of layer thickness is considerably more complex than for coatings, while the evaluation of mechanical properties and adhesion performance is only partially comparable.

Bond-line thickness

The bond-line thickness can be adjusted by applying pressure during joint formation and depends on the adhesive type and function. Standard thickness values range from 0.1 to 4 mm, but rarely exceed 2 mm due to the limited interest for most practical uses and the difficulty of producing defect-free joints.^{191,192} In coatings, the polymer formulation is applied on a single exposed substrate, allowing the use of direct or surface-based methods such as optical techniques or profilometry, but in adhesive systems the layer is confined between two adherends, making its measurement far more complex. In practice, accurate non-destructive thickness measurements are rarely performed and generally limited to high-performance or safety-critical applications, where ultrasonic techniques, eddy current probes, transient thermography, or X-ray micro-computed tomographic methods can be employed, depending on the substrates nature.^{193–195} Industrial applications, instead, rely primarily on controlled deposition processes or embedded spacers to ensure reproducible bond-line thickness, with destructive techniques such as cross-sectional microscopy used on representative samples for verification.

Mechanical behavior

The intrinsic mechanical properties of adhesive materials can be evaluated using free-standing films, for example *via* tensile testing or DMA. However, fewer characterization techniques are relevant compared to coatings, since the majority of the protocols assess the bonded joint performance, rather than the properties of the adhesive material itself.

Adhesive joint performance

The performance of adhesive joints is assessed through an extensive range of tests designed to evaluate different loading configurations and stress modes, including shear, tensile, compression, peel, cleavage, fracture energy, impact, creep, and fatigue tests. Nevertheless, only a few of these tests provide engineering data, while the vast majority yield qualitative measurements that serve as comparative indicators of adhesive performance.¹⁹⁶

The most used technique for assessing the strength of an adhesive is the lap shear test, which measures the apparent shear strength of a joint subjected to tensile loading parallel to the bond

line. The single-lap shear test (Figure 2.7A) consists essentially of two rectangular adherends bonded together, with an overlap length ranging from 12.5 to 25 mm depending on the protocol. Owing to its simplicity, this test is extensively used for quality control and comparative purposes, but it is sensitive to several parameters, including the geometry of the sample, adhesive thickness, adherend mechanical properties, and alignment accuracy.¹⁹⁷ Moreover, the load eccentricity inherent to this geometry produces significant bending and peel stresses within the adhesive layer, resulting in a non-uniform stress distribution and an apparent rather than intrinsic shear strength. A more balanced configuration is that of the double-lap shear test (Figure 2.7B), in which a central adherend is bonded on both sides with two outer adherends, effectively reducing bending and peeling and achieving more uniform stress. To further minimize geometric effects and obtain material-specific data, the thick-adherend shear test (TAST, Figure 2.7C) employs two rigid, thick adherends that allow the application of uniaxial tensile or compressive load and ensure more uniform shear deformation across the bond line.

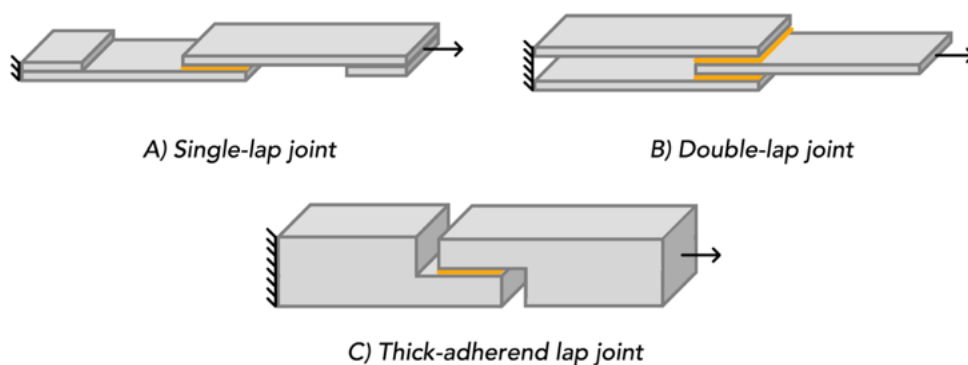


Figure 2.7 Graphical illustrations of single- (A), double- (B), and thick-adherend (C) lap joints.

Tensile and compression tests determine the adhesive tensile or compressive strength and modulus applying loads perpendicular to the bond line. They are often performed using butt joints consisting of two rigid adherends with circular or square cross-section bonded end-to-end (Figure 2.8A). Since adhesives are generally weaker in normal tension than in shear, the measured tensile strength values tend to be lower than shear, whereas resistance to compression is generally high for most adhesives.¹⁹⁶

Peel tests are designed to quantify the force required to separate two flexible or semi-flexible joints and are particularly important due to the inherently low resistance of adhesive joints to peel stress. The tests are performed pulling the flexible adherend of the joint at a constant rate and recording the average peel force per unit width of the bond-line, which is strongly dependent on the peel angle and rate. In the T-peel test (Figure 2.8B), both the adherends are flexible, while in

the 180° (Figure 2.8C) and 90° (Figure 2.8D) peel tests, one adherend is flexible and the other rigid (similarly to the corresponding test for coatings). The same adherend condition applies to the floating roller (Figure 2.8E) and climbing drum (Figure 2.8F) peel tests, which are less commonly performed than the previously mentioned alternatives.

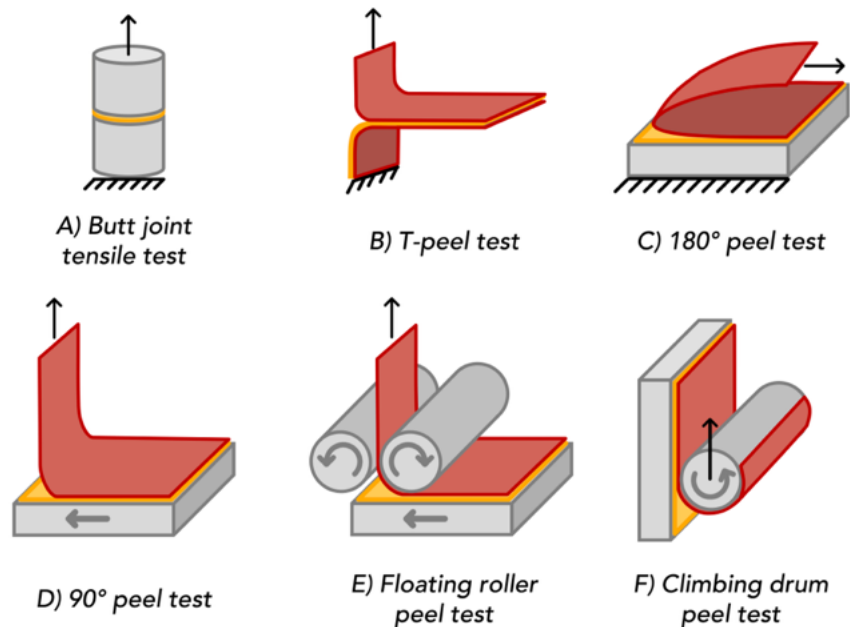


Figure 2.8 Graphical illustrations of butt joint tensile (A), T-peel (B), 180° peel (C), 90° peel (D), floating roller peel (E), and climbing drum peel (F) tests.

For rigid joints, cleavage tests apply a concentrated tensile stress perpendicular to the bond-line. For instance, the wedge cleavage test, commonly referred to as Boeing wedge test, uses a wedge inserted into the bond-line of a flat-bonded specimen to create a crack in the adhesive (Figure 2.9A). The insertion mechanically forces the adherends apart, initiating a crack that continues to propagate under the effect of the energy stored in the bent adherends, without applying any external load. This test can be used to determine fracture toughness, but it is more often used to qualitatively evaluate the durability and resistance of adhesive joints to cleavage. An alternative cleavage test for metal-to-metal joints uses a geometry similar to that of a compact tensile specimen, in which off-axis tension is applied through loading holes in the adherends (Figure 2.9B). The cleavage strength is reported as maximum load per unit bond width.

Fracture energy measurements obtained from the wedge test are not particularly accurate, as they depend on the wedge insertion distance and the stiffness of the substrate material. Therefore, crack initiation and propagation are typically investigated using dedicated tests that provide quantitative values of fracture energy under controlled conditions. These tests are

frequently combined with finite element analysis for designing and modelling bonded structures, and they usually involve one or a combination of fracture modes illustrated in Figure 2.10: Mode I (cleavage, tensile, or crack-opening), Mode II (in-plane or forward shear) and Mode III (anti-plane or scissoring shear). Representative test examples for each mode are the double cantilever beam (DCB) for Mode I, end-notched flexure (ENF) for Mode II, and split cantilever beam (SCB) for Mode III. In the DCB configuration, which is simple and relatively inexpensive to fabricate and test, two adherends are bonded over a defined overlap and one end is loaded to propagate a crack under cleavage stress. To ensure reproducible crack initiation, ISO 25217 recommends inserting a thin non-adhesive film at the mid-plane of the adhesive layer (as shown in Figure 2.9C), whereas ASTM D3433 relies on natural crack initiation from the edge of the joint where load is applied, which is left adhesive-free. In the traditional DCB configuration, the applied load and crack propagation are monitored and used to calculate Mode I fracture energy, whereas alternative geometries, such as the tapered double cantilever beam (TDCB, Figure 2.9D), do not require continuous crack-length measurement. For Mode II fracture testing, no standardized geometry exists for adhesive joints, although protocols have been established for determining the interlaminar fracture toughness of fiber-reinforced polymer composites (ASTM D7905 and ISO 15114). Nevertheless, several testing configurations have been proposed, among which the ENF test is considered the most suitable and common.¹⁹⁸ The ENF specimen is similar in geometry to the DCB, but the loading configuration is modified to induce shear rather than tensile stresses. Specifically, the bonded beams are supported at both ends and loaded at the midpoint, typically in a three-point bending setup, so that bending moments generate interfacial shear stresses along the adhesive layer (Figure 2.9E). Due to the difficulty in achieving pure anti-plane shear conditions, Mode III fracture has been far less investigated than the previously described fracture modes, particularly in the case of adhesive joints.¹⁹⁷ Several test configurations have been proposed, including the SCB test, which resembles a DCB specimen loaded in Mode III (Figure 2.9F). Although the participation of Mode II stresses in SCB and analogous configurations cannot be completely eliminated, alternative geometries and specimen designs continue to be developed in an effort to achieve pure Mode III loading, often adapted from methods originally conceived for composite materials.^{199–201} Mixed-mode tests are consistently more common, as they are necessary to characterize the more complex fracture behavior typical of real adhesive joints, which are often subjected to coupled stresses.

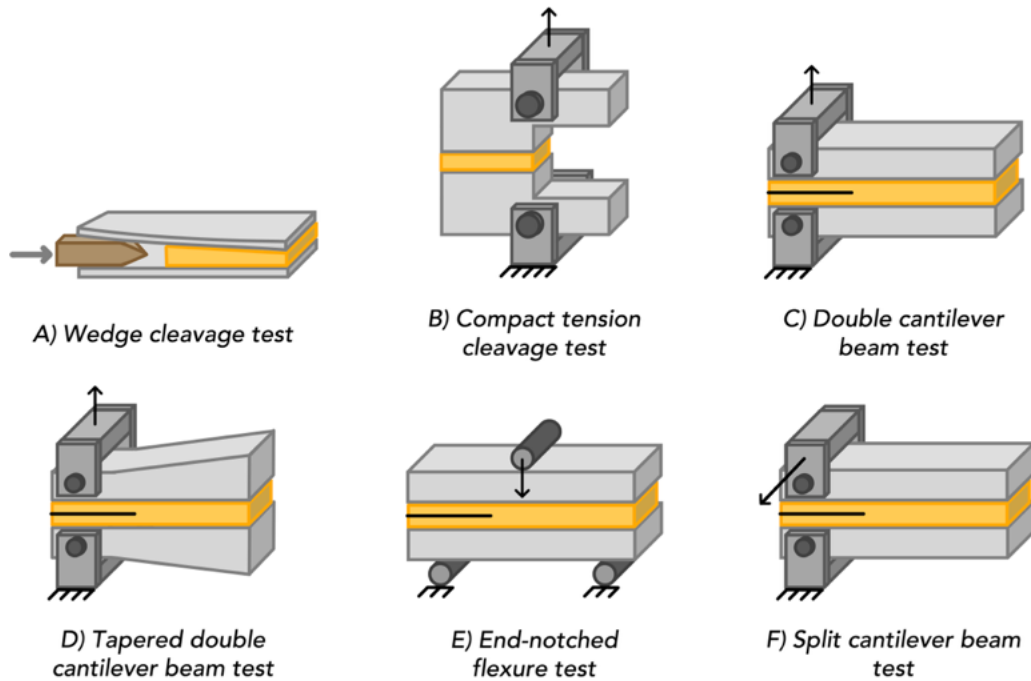


Figure 2.9 Graphical illustrations of wedge cleavage (A), compact tension cleavage (B), double cantilever beam (C), tapered double cantilever beam (D), end-notched flexure (E), and split cantilever beam (F) tests.

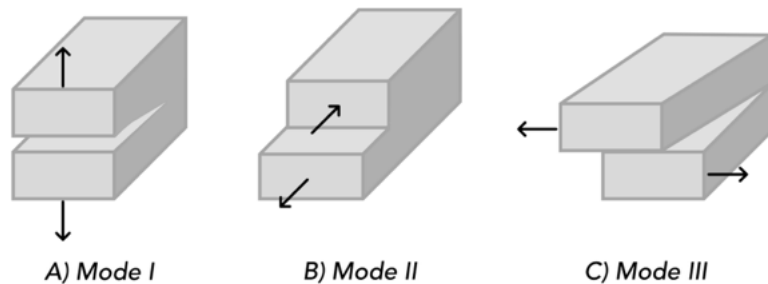


Figure 2.10 Graphical illustrations of fracture Modes in adhesive joints.

Under dynamic or transient loading, impact, creep, and fatigue tests provide critical information about the adhesive's energy absorption capacity and durability. The impact tests subject bonded joints to rapid loading and measure the energy absorbed per unit bonded area (J/m^2), simulating crash or drop scenarios typical of structural adhesives in the automotive and aerospace sectors. The block impact test evaluates the shear impact strength of bonded assemblies by applying a pendulum strike parallel to the bond plane, producing mainly shear stress (Figure 2.11A). The energy required to fracture the specimen is determined from that lost by the pendulum, corrected for the kinetic energy of the detached block. However, a limitation of this method is that it employs relatively thick adherends, which do not accurately represent real applications where

adhesives are typically used to bond thin components. From this perspective, a more realistic measure of resistance to sudden shock loads is provided by the impact wedge peel (IWP) test, which is similar to the corresponding peel test but with high-velocity loading (Figure 2.11B). In this case, the specimen consists of two metal strips bonded to form a Y-shaped assembly, with the unbonded ends clamped as the arms of the Y-shape. During testing, a wedge is driven through the bond line by a pendulum, forcing the adherends apart in a cleavage mode. The impact cleavage force is continuously recorded as a function of time, and the absorbed energy is obtained by integrating the area under the force–time curve over the test duration and multiplying by the test speed.

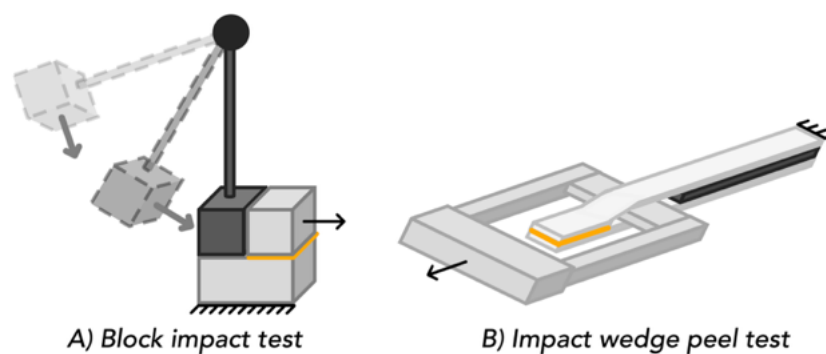


Figure 2.11 Graphical illustrations of block impact (A) and impact wedge peel (B) tests.

Creep tests evaluate the long-term deformation behavior of adhesives under constant stress, while environmental conditioning may be applied before or during testing to simulate service conditions. Several ASTM and ISO standards exist for this purpose, generally applying shear or peel stress using spring-loaded instruments on single-lap, TAST, or T-peel joints. Creep deformation in polymer adhesives can significantly reduce the expected service life of bonded assemblies and may occur at stress levels well below the ultimate strength of the material. Therefore, it is crucial to monitor joint deformation under stable environmental conditions with high precision extensometers.

Finally, fatigue tests involve cyclic loading at subcritical stress levels and specified mean load or strain, allowing quantification of fatigue life from the number of cycles required to produce failure. The results are generally presented as S–N curves, showing the applied stress amplitude (S) against the number of cycles to failure (N), although the uncertainty in life expectancy at a given stress level is usually large. Due to their lengthy and resource-intensive nature, fatigue tests are considerably more expensive than quasi-static tests and are therefore conducted at the highest feasible frequency to reduce test duration.¹⁹³

Failure modes

Failure in bonded assemblies can occur through different modes, which can be classified according to the standard ISO 10365 based on the region in which failure occurs, either within the adhesive layer or in the adherend materials (Figure 2.12).

If the adhesive bond strength exceeds the mechanical resistance of the adherend, failure can take place outside the bonded region (“substrate failure”, SF, Figure 2.12A) or within it. In the latter case, a distinction is made between “cohesive substrate failure” (CSF, Figure 2.12B), when the fracture propagates within the substrate itself, and “delamination failure” (DF, Figure 2.12C), when a coating or external layer detaches from the adherend (in which case the nature of the coating should be specified).

Several failure patterns are associated with the adhesive layer, depending on whether the failure is cohesive, occurring within the adhesive layer itself and generally indicative of good interfacial bonding but limited bulk strength, or adhesive, taking place at the interface between the polymer and the adherend and indicating poor interfacial adhesion or inadequate surface preparation. If the fracture propagates approximately through the mid-plane of the polymer layer, the failure is simply referred to as “cohesion failure” (CF, Figure 2.12D); if the crack develops closer to the interface or changes path within the layer during propagation, it is defined “special cohesion failure” (SCF, Figure 2.12E). A particular case is the “cohesion failure with stress whitening of the adhesive” (SWCF, Figure 2.12F), describing the phenomenon where the adhesive layer becomes opaque or white due to the formation of microvoids or microcracks under mechanical stress. “Adhesion failure” (AF, Figure 2.12G) takes place at the interface between the adhesive and one or both adherends, while the designation “COR” is used in case of “debonding due to bondline corrosion”, which develops when oxygen, moisture, or corrosive agents penetrate the adhesive interface. The “adhesion and cohesion failure with peel” (ACFP, Figure 2.12H) can occur when both interfacial and cohesive failures develop simultaneously under peel loading. More generally, if more than one failure pattern occurs, the term “mixed failure” is used (Figure 2.12I), and the approximate percentage of each pattern should be reported. In case of oscillating failure between two patterns, i.e. when the crack propagates by alternating between different failure modes (Figure 2.12J), the designation “OSC” is added after the description of the failure patterns and their respective percentages.

The analysis of the failure mode helps identify the location and general cause of failure, but it does not, by itself, reveal the underlying failure mechanism. For instance, failure might originate from creep deformation or from localized peel stresses due to excessive out-of-plane loading, yet this distinction cannot be made solely from the macroscopic failure pattern.

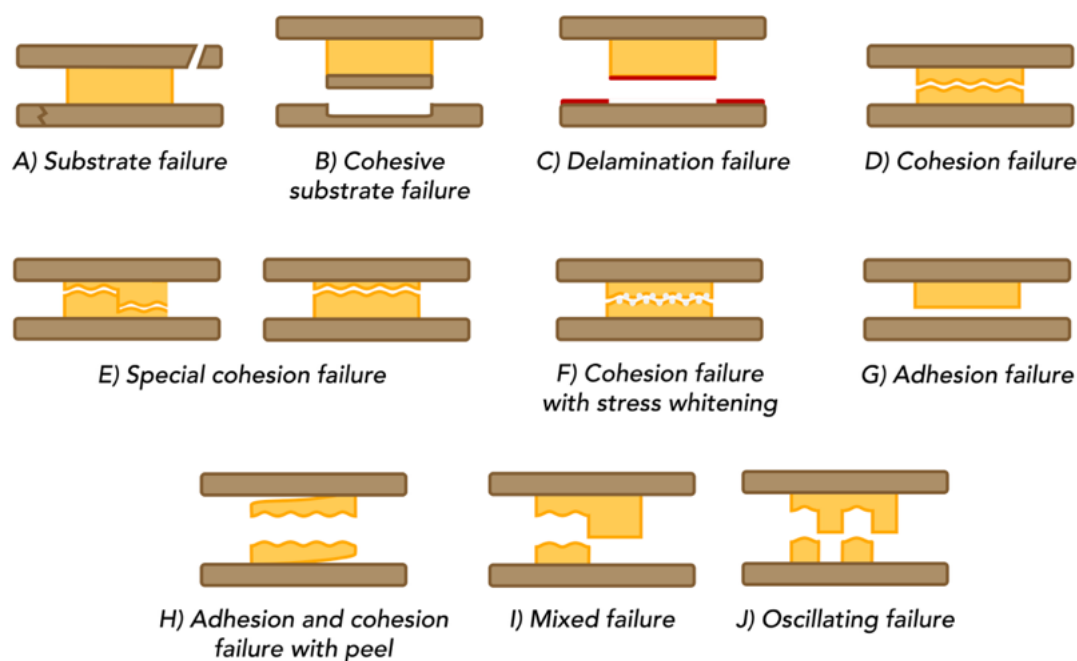


Figure 2.12 Graphical illustrations of substrate (A), cohesive substrate (B), delamination (C), cohesion (D), special cohesion (E), stress whitening cohesion (F), adhesion (G), adhesion and cohesion with peel (H), mixed (I), and oscillating (J) failure modes in adhesive joints.

2.3 Non-isocyanate polyurethanes

While conventional PUs continue to dominate a wide range of industrial applications and occupy a pivotal role in the adhesives and coatings market segment, health, safety, and environmental concerns have catalyzed the search for more sustainable alternatives. In this context, non-isocyanate polyurethanes (NIPUs) have emerged as a promising class of materials designed to overcome the inherent limitations of isocyanate-based systems, including the field of adhesives and coatings.

Since their initial discovery and patenting in 1957, NIPUs have attracted considerable scientific interest.^{202,203} Initial studies primarily focused on fundamental organic reactions, such as the aminolysis of cyclic carbonates or transurethanizations, often with the objective of synthesizing novel low molecular weight carbamates or model polymers. While these early experiments were limited in scale and industrial relevance, they demonstrated the chemical feasibility of urethane formation without relying on toxic, phosgene-derived, and highly reactive isocyanates. The pronounced sensitivity of this class of compounds toward moisture, combined with the first assessments of their adverse effects on human health, prompted efforts to develop alternatives with improved storage stability and safer handling.^{204–206} Consequently, by the 1960s and 1970s, this pursuit led to the first systematic investigations into blocked isocyanates and isocyanate-

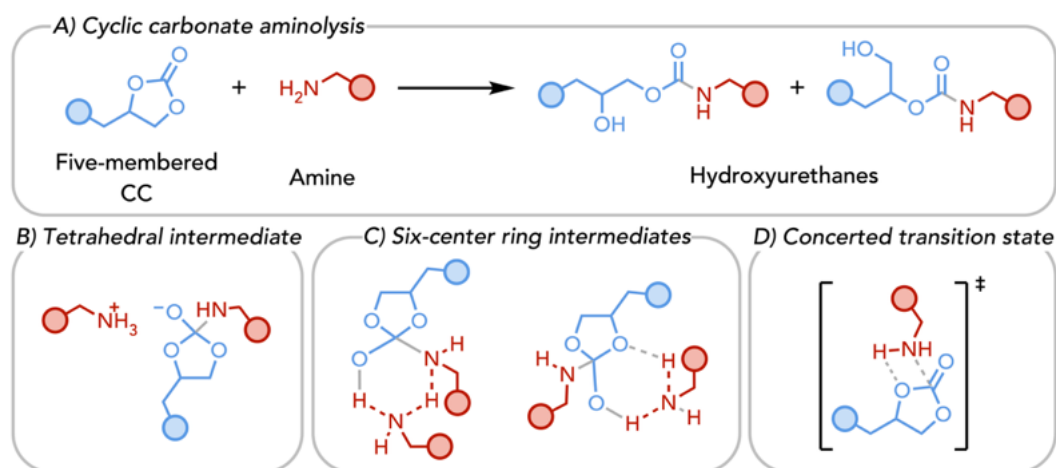
free PU systems.^{207–209} In the following decades, further progress was made, particularly in the synthesis and application of new cyclic carbonate monomers, and today NIPUs have evolved from a scientific curiosity into a rapidly growing research field, driven by the pressing demand for safer and more sustainable PU technologies. Over the years, several synthetic approaches were explored to synthesize NIPUs circumventing isocyanates and phosgene-based intermediates. These strategies exploit different chemical transformations that generate urethane linkages either directly or through reactive intermediates, in some cases offering advantages in terms of safety, reaction selectivity, functional group tolerance, and opportunities for incorporating bio-based or CO₂-derived feedstocks. Nevertheless, except for few examples of NIPU technologies that have been implemented on commercial or pilot scale, most of the synthetic routes remain limited to laboratory or niche applications due to issues of scalability, cost, sustainability, or safety.^{210–213}

2.3.1 Polyaddition between polyamines and poly(cyclic carbonate)s

2.3.1.1 Reaction mechanism

The most established and intensively studied route to NIPUs is the step-growth polyaddition between polyamines and poly(cyclic carbonate)s (polyCCs).^{214,215} The reaction proceeds *via* nucleophilic ring opening of the carbonate moiety by the amine, producing pendant hydroxyl groups and thus forming a polyhydroxyurethanes (PHUs). With five-membered CCs, two isomers can be formed: one containing primary hydroxyl groups and one with secondary hydroxyl groups (Scheme 2.4A). According to several studies, the isomer containing secondary hydroxyl groups is enthalpically more stable and favored, while the isomer ratio depends on the solvent and chemical structure of the reagents, but not on temperature.⁴⁸

Two main reaction mechanisms have been proposed for CC aminolysis: the first involves a tetrahedral intermediate (Scheme 2.4B),^{216,217} whereas the second proceeds through six-center ring intermediates, in which a second amine acts as a catalyst (Scheme 2.4C).²¹⁸ A concerted one-step mechanism has also been suggested for the uncatalyzed reaction (Scheme 2.4D); however, the model used can only be considered valid for reactions performed in aprotic organic solvents and not in bulk, since it does not consider the participation of additional reactant molecules.²¹⁹ Single-stage and multi-stage processes have been evaluated *via* DFT calculations, with the mechanism involving two amine molecules displaying an activation energy roughly one-third that of a one-stage bimolecular reaction.²¹⁸



Scheme 2.4 Cyclic carbonate aminolysis (A) and key species proposed for its reaction mechanism: tetrahedral intermediate (B), six-center ring intermediates (C), and transition state of the concerted one-step mechanism (D).

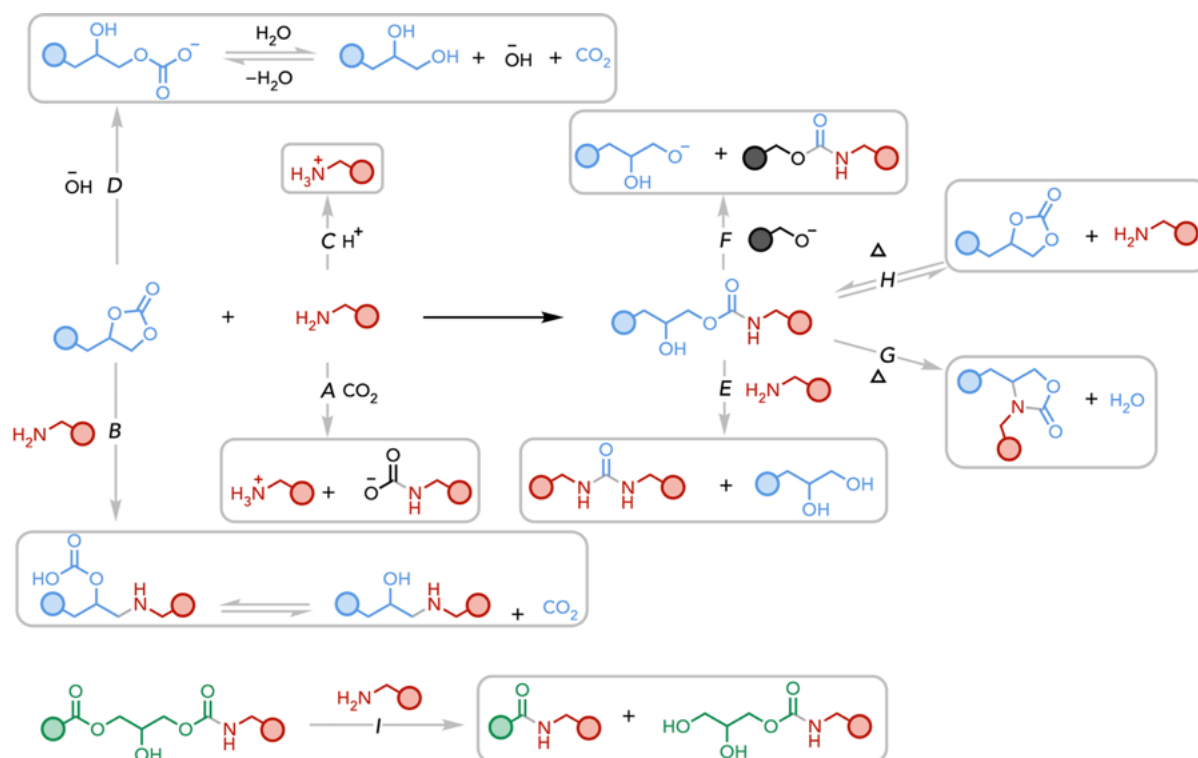
2.3.1.2 Influence of the β -hydroxyurethane motif

The presence of the β -hydroxyurethane motif is unique to NIPUs synthesized *via* this route and has profound consequences on the morphology and thermomechanical properties of PHUs, which are generally amorphous due to the random distribution of secondary and primary hydroxyl groups.^{48,220} The additional OH functional groups strongly influence polarity and intermolecular interactions and provide increased hydrogen-bonding, which may reduce gas permeability and enhance chemical resistance, adhesion to polar substrates, but also limit phase separation and increase hydrophilicity and viscosity compared to conventional PUs.^{221–223} In particular, increased hydrogen bonding contributes to higher cohesion and formulation viscosity, which may limit the attainable molar mass, as strong intermolecular interactions reduce chain mobility during polymerization and processing.²²⁴ The high density of hydroxyl groups also improves hydrolytic stability, by shielding the carbonyl carbon from hydrolytic attack, and enhances water uptake, promoting moisture-induced plasticization of the polymer network and negatively affecting its mechanical properties.^{222,225–229} In addition, β -hydroxyl groups can also participate in intra- or intermolecular secondary reactions, altering the structure and molecular weight of the PHU.

2.3.1.3 Side reactions

This synthetic pathway to NIPUs suffers from several potential side reactions that may compete with or follow the desired aminolysis. First, proper storage is essential to preserve the desired stoichiometry: although CCs are typically not sensitive to moisture, amines can be carbonated upon exposure to air, forming ammonium carbonate salts (Scheme 2.5A).^{230,231} The type and

reactivity of the amine also strongly influence the chemoselectivity of the nucleophilic attack. In five-membered CCs, aliphatic amines preferentially attack the carbonyl carbon to yield hydroxyurethanes, whereas aromatic amines preferentially attack the alkylene carbon, leading to *N*-alkylation and decarboxylation (Scheme 2.5B).^{232,233} If water is used as a solvent, the pH of the reaction mixture must be carefully controlled. Acidic conditions promote amine protonation (Scheme 2.5C), whereas basic conditions can lead to CC hydrolysis, particularly for hydrophilic substrates (Scheme 2.5D).^{234–237} Additional side reactions involving the hydroxyurethane moiety can happen under thermal or catalytic activation. Under strongly basic catalysis, the urethane group can undergo nucleophilic attack by amines to form urea linkages (Scheme 2.5E), or by alkoxides, inducing transurethanization (Scheme 2.5F), although the latter requires harsher conditions and is slower than the reaction with amines.^{220,238} Dehydration and oxazolidinone formation has also been reported (Scheme 2.5G), as well as the reversion at high temperature of the hydroxyurethane linkage (Scheme 2.5H).^{220,239} Finally, PHUs obtained from ester-containing precursors can undergo amidation, particularly in the presence of short-chain amines or under amine excess (Scheme 2.5I).^{240–242}



Scheme 2.5 Common side reactions in CC aminolysis: amine carbonation (A), CC aminolysis via alkylene attack followed by decarboxylation (B), amine protonation (C), CC hydrolysis followed by decarboxylation (D), hydroxyurethane aminolysis (E), transurethanization (F), hydroxyurethane dehydration (G), thermal reversion of the hydroxyurethane linkage (H), amidation of ester-containing precursors (I).

2.3.1.4 Precursor availability and feedstock limitations

Other limitations of PHU synthesis include the scarcity of bio-based polyamine precursors and, more importantly, the limited availability and reactivity of polyCC precursors, which remain critical bottlenecks for scaling up NIPU technologies.

Two of the most established methods to synthesize polyamines are the ammonolysis of haloalkanes and the reduction of nitriles or nitro compounds, but many additional routes have been developed over the years to obtain both linear and branched products, with the chosen strategy depending on the desired structure and production scale.^{243–245} Among these synthetic tools, few can be exploited to achieve sustainable transformations of bio-based building blocks into amines, such as reductive amination of carbonyl compounds, hydrogen-borrowing amination of alcohols, hydroamination of alkynes and alkenes, and utilization of C–N bonds inherently present in bio-based substrates (e.g., chitin or proteins).²⁴⁶ Notably, precursors containing biogenic nitrogen offer the important advantage of bypassing the highly energy-intensive Haber–Bosch process traditionally used to produce nitrogen-containing chemicals.²⁴⁷ Although the use of bio-based polyamines for polymer synthesis and other applications has been extensively investigated, limited resource availability, the current technological maturity of biomass biorefineries,^{245,246} and a general lack of targeted research focus²⁴⁸ restrict the replacement of conventional petrochemical polyamines in NIPU synthesis.

In contrast, renewable precursors are considerably more accessible for the preparation of CCs, particularly five-membered ones, which are the most common and easiest to obtain. Their synthesis can rely on an extensive chemical toolbox, with the formal cycloaddition of CO₂ to epoxides providing the lowest E-factors and excellent yields under mild conditions.^{48,249,250} Despite the toxicity of many epoxide substrates, this reaction constitutes an important valorization route for the abundant, renewable, and non-toxic greenhouse gas CO₂, enabling its conversion into valuable chemicals.²⁴⁸ Together with the coupling of monoCC derivatives, the insertion of CO₂ into epoxides has been thoroughly investigated for the production of polyCCs, including those derived from bio-based feedstocks such as vegetable oils, terpenes, and lignocellulosic biomass.^{48,251–255} Nevertheless, the large-scale implementation of CC chemistry still faces several challenges. Although the cycloaddition of CO₂ to epoxides is atom-efficient and environmentally attractive, the process often relies on highly purified CO₂ and epoxide substrates, catalytic systems with limited industrial viability, and multiple reaction and purification steps (particularly for bio-based feedstocks), thereby increasing process complexity and production costs compared with established petrochemical routes.^{256,257} Moreover, beyond the technological and economic barriers associated with a transition from established PU

manufacturing routes, the relatively low reactivity of five-membered CCs remains a significant obstacle to large-scale adoption. Consequently, industrial efforts have largely continued to focus on isocyanate-based technologies, within a regulatory framework that primarily targets the safe handling and use of isocyanates rather than their replacement with alternative chemistries. As a result, despite significant scientific progress, the large-scale production of polyCC precursors remains less mature than that of conventional PU raw materials, and further advances in catalyst design, process intensification, regulatory incentives, and supply-chain integration will be required to improve the economic competitiveness of NIPU technologies.

2.3.1.5 Aminolysis kinetics and strategies for reactivity enhancement

The aminolysis of five-membered CCs is thermodynamically favorable but kinetically hindered, due to the relatively low ring strain and stability of the carbonate. This reduced reactivity has detrimental effects on conversion and necessitates harsher reaction conditions, with negative implications for cost and scalability of the process. To improve the reaction kinetics, which is of the second order with respect to both the CC and the amine,^{217,258} several parameters can be optimized, including reaction temperature and time, solvent, catalyst, molar ratio, and structure of the reagents.

Reaction conditions and solvent

Viscosity increases during polymerization, and at room temperature the diffusion of the reactants becomes limited due to extensive hydrogen bonding.²⁵⁹ Increasing the temperature or extending the reaction time can overcome this issue and provide higher polymerization rates and conversions, but the possible occurrence of side reactions must be taken into account.

The choice of solvent also has a significant effect on the aminolysis rate. Higher rates have been reported in protic compared to aprotic solvents and using more polar solvents.^{216,259} Nevertheless, most studies have employed aprotic media, although there is a growing trend toward bulk polymerization to improve environmental performance.²⁵²

Catalyst

Several organic, inorganic, and organometallic compounds have been investigated as catalysts to overcome the intrinsically slow aminolysis of five-membered CCs.²⁵¹ Different activation mechanisms can be exploited: Lewis acids and hydrogen-bond donors can increase the electrophilicity of the CC; basic catalysts can deprotonate the amine or enhance its nucleophilicity; and Lewis bases can attack the CC carbonyl, acting as nucleophilic catalysts and

good leaving groups to facilitate the amine attack.⁴⁸ In general, organocatalysts have been shown to be more efficient than inorganic Lewis acids and competitive with commonly used tin-based catalysts, with certain thioureas and superbases (shown in Figure 2.13) proving particularly effective even at room temperature.^{76,260,261}

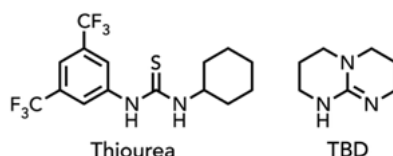


Figure 2.13 Representative highly effective organocatalysts for the aminolysis of five-membered CCs.

More recently, it has been demonstrated that trace amounts of water can efficiently catalyze NIPU formation under mild conditions and in some cases replace toxic and costly organic catalysts.^{49,262,263} Water has been reported to act both as a plasticizer, enhancing molecular mobility, and as a true catalyst, participating in the transition state of the carbonate–amine reaction. These findings highlighted the importance of ambient moisture in CC aminolysis and identify water as a key parameter for enabling efficient NIPU formation under industrially relevant conditions.

Molar ratio and structure of the reagents

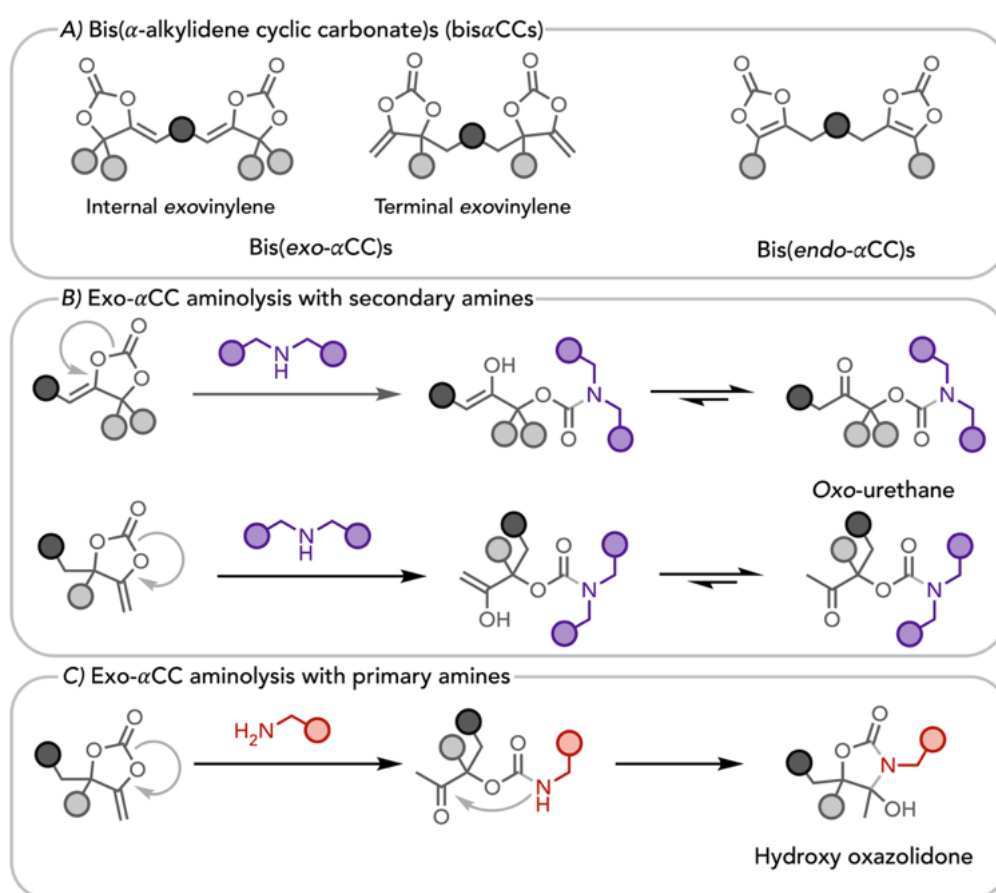
The molar ratio and structure of the reagents play a crucial role in determining the conversion and selectivity of the polymerization. It has been shown that an equimolar ratio of CC and amine provides PHUs with the best properties, although maintaining this ratio is challenging due to various possible side reactions that can be promoted by deviations from stoichiometry.²⁵²

To improve the kinetics of the polyaddition, both the nucleophilicity of the amine and the electrophilicity of the CC can be increased. Steric hindrance has a pronounced influence on the reactivity of the amine, which correlates to its degree of substitution and to the number of hydrogens in the α -position.^{264,265} Except for cyclic structures, such as piperidine, secondary amines are typically less reactive than primary ones, and amines attached to a primary carbon react faster than those on a secondary or tertiary carbon. The nucleophilicity of NH_2 functional groups decreases with increasing molar mass and in presence of proximal bulky or electron-withdrawing (EWG) substituents.^{266,267} Conversely, hydroxyl groups within the polyamine structure, as in β -hydroxylamines, were reported to lower the aminolysis activation barrier via intramolecular hydrogen-bonding assistance.^{216,268} Differently from aliphatic analogues,

aromatic amines tend to react at much higher temperatures attacking one alkylene carbon of the CC rather than the carbonyl. However, a proton-relay catalytic mechanism mediated by TBD enables site- and chemoselective formation of *N*-aryl carbamates under ambient conditions.^{232,233,269}

Beyond careful selection of catalyst, solvent, reaction conditions, and polyamine co-reagent, another essential research area for accelerating aminolysis kinetics is the activation of CCs towards nucleophilic attack. This can be achieved by enhancing the electrophilicity of the carbonyl moiety through the introduction of EWGs in the ring^{216,217,259} or by increasing ring strain through the development of higher membered CCs^{258,270–272} and unsaturated CCs.^{273–279} Among substituted five-membered CCs, ester-carbonates displayed the highest reactivity due to their inductive and mesomeric electronic effects and their hydrogen bonding capability; however, they were subject to amidation side reactions that led to partial conversion.²⁵⁹ The reactivity of CCs also increases with its ring size, but the synthesis of six-, seven-, and eight-membered precursors in high yield often requires harmful reagents.²⁸⁰ A major advancement in the field of activated CCs is the development of unsaturated substrates containing an *exo*- or *endo*-cyclic olefinic double bond, also referred to as bis(α -alkylidene cyclic carbonate)s or bis α CCs (Scheme 2.6A). The synthesis of bis(*endo*-vinylene cyclic carbonate)s (bis(*endo*- α CC)s) has historically been hindered by narrow substrate scope, reliance on costly or toxic reagents, and poor atom efficiency. The most versatile and efficient route to these intermediates was recently identified as the isomerization of *exo*-vinylene analogues (bis(*exo*- α CC)s),²⁷³ which have attracted considerable attention over the last decades and opened promising avenues for the design of CO₂-derived products.^{274,275} Prepared either *via* carboxylative cyclization of CO₂ with bispropargylic alcohols or by coupling monofunctional *exovinylene* CCs, bis α CCs have been reacted with a variety of co-reagents under mild conditions to generate a library of polymers, including NIPUs.²⁷⁶ In particular, their polyaddition with secondary polyamines yields poly(oxo-urethane)s bearing pendent oxo-groups or ketones incorporated into the main chain, depending on whether the *exovinylene* groups are terminal or internal (as illustrated in Scheme 2.6B). With primary polyamines, on the other hand, the oxo-urethane linkages undergoes partial or full cyclization to hydroxy oxazolidones, and the linkage selectivity depends on the reactivity and steric hindrance of the polyamine (Scheme 2.6C).²⁷⁷ Remarkably, these step-growth polyadditions were accelerated by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) but also proceeded under catalyst-free conditions at room temperature through a regiocontrolled ring-opening, enabled by the formation of an enol group which quickly rearranges into a more stable ketone tautomer.²⁷⁶ The resulting poly(oxo-urethane)s and poly(hydroxy oxazolidone)s exhibit

unique reactivity due to unreacted carbonyl or hydroxyl groups along the chain, which allow post-polymerization modification and thus access to a broad range of derivatives.²⁷⁸ In particular, the tertiary alcohol in the hydroxy oxazolidone moiety can undergo dehydration reaction to yield poly(alkylidene oxazolidone)s, providing opportunities for further functionalization.^{277,281,282} The availability of bispropargylic alcohols has long represented a bottleneck to cost-effective bis α CCs production, but recent studies demonstrated that bulk chemicals such as propargyl alcohol and 1,4-butyne-1,3-diol can be used as starting materials, significantly reducing cost.²⁷⁹ Furthermore, innovative approaches have been reported for a more sustainable and efficient synthesis of mono- and polyfunctional oxazolidones, which served as tailored building blocks for advanced materials with tunable properties and multiple end-of-life options.^{283–285}

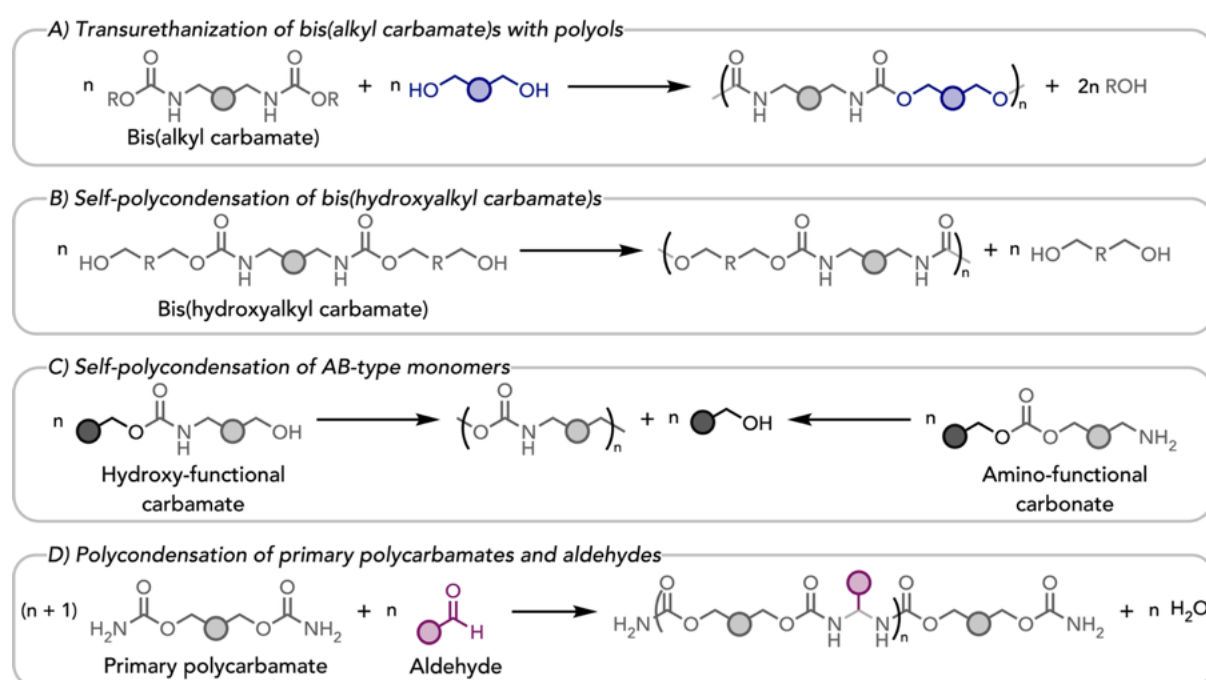


Scheme 2.6 Representative bis α CCs (A); exo- α CC aminolysis with secondary (B) and primary (C) amines.

2.3.2 Polycondensation reactions

One of the most explored strategies to obtain PUs without using phosgene-derived intermediates involves the transurethanization (also called transcaramoylation or urethane exchange) between polyols and polyfunctional carbamates (typically linear bis(alkyl carbamate)s, as shown

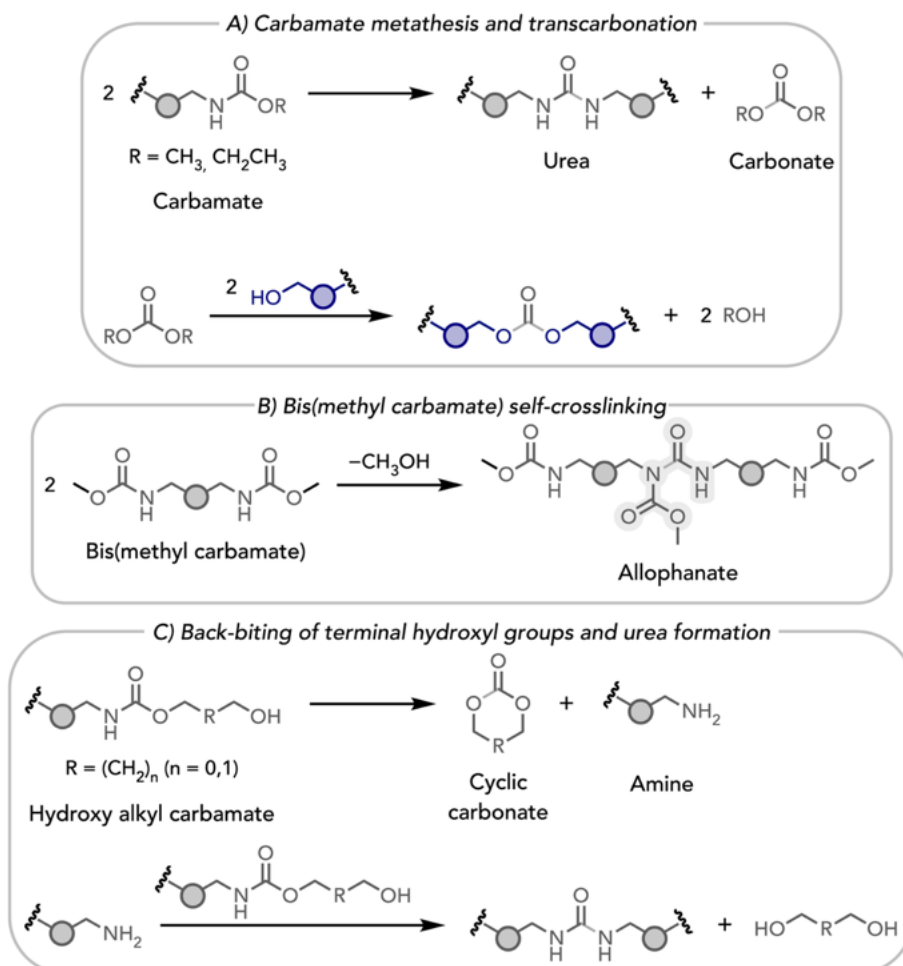
in Scheme 2.7A) or the self-polycondensation of bis(hydroxyalkyl carbamate)s (Scheme 2.7B).^{286,287} Self-polycondensation can also be performed with “AB-type” precursors (Scheme 2.7C), which contain both carbamate and alcohol or carbonate and amine functional groups in the same molecule, assuring built-in stoichiometric control for attaining higher molar mass.^{288–292} Compared to a polyaddition reaction, this approach requires the removal of a volatile alcohol by-product, often demanding high temperature (typically between 160 and 200 °C) and reduced pressure to shift the equilibrium.^{293,294}



Scheme 2.7 Polycondensation pathways used for NIPU synthesis: transurethanization between bis(alkyl carbamate)s and polyols (A), self-polycondensation of bis(hydroxyalkyl carbamate)s (B), self-polycondensation of AB-type precursors (C), and polycondensation between primary polycarbonates and aldehydes (D).

Under such conditions, several side reactions can take place. These include carbamate metathesis, which produces a urea linkage and a small carbonate molecule, followed by reaction of the carbonate with alcohol groups and formation of oligocarbonates, with consequential decrease of the average molecular weight (Scheme 2.8A).²⁹⁵ Additionally, bis(methyl carbamate)s can self-crosslink and form allophanate moieties (Scheme 2.8B), whereas the use of bis(hydroxyalkyl carbamate)s instead of methyl derivatives prevents this side reaction.^{286,296,297} For both transurethanization and self-polycondensation pathways, careful selection of monomers is essential to avoid back-biting reactions, which frequently take place when the spacer between carbamate and terminal hydroxyl group of the growing macromolecule is a short

alkyl unit.²⁵¹ Back-biting by a terminal OH group releases a CC molecule and generates a primary amine chain end, which can later attack a urethane linkage and form a urea defect (Scheme 2.8C).



Scheme 2.8 Common side reactions in transurethanization processes: carbamate metathesis and transcarbonation (A), bis(methyl carbamate) self-crosslinking (B), back-biting of terminal hydroxyl groups and urea formation (C).

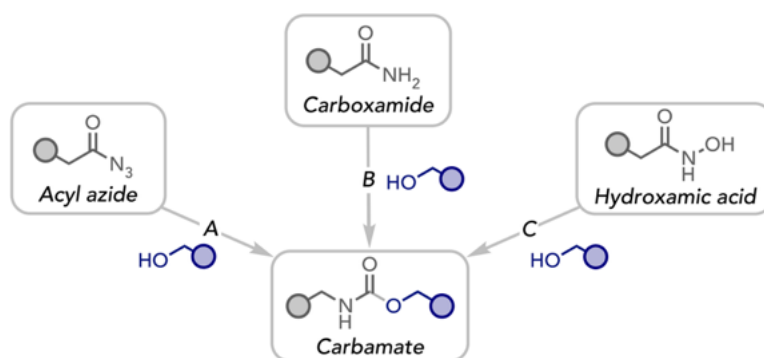
To accelerate the kinetics of the polycondensation, biscarbamates could be substituted with more reactive poly(carbamoyl chloride)s and polychloroformates, but these intermediates typically require phosgene or its equivalents and are toxic.^{298–300} Although carbamates are also conventionally synthesized using phosgene, various alternative routes have been developed from diverse substrates,^{301,302} including some bio-based precursors.^{293,303,304} Overall, the impractical reaction conditions, need for purification, and difficulty in achieving high molecular weight have limited industrial-scale production,^{305,306} but recent studies have demonstrated the feasibility of preparing high molar mass NIPUs under milder conditions, highlighting promising progress

toward scalable processes.^{295,307} Moreover, despite being slower than a transesterification, transcarbamoylation exchange reactions can provide access to CANs and contribute to the development of recyclable PUs, as the equilibrium can be shifted under certain conditions. This has recently sparked renewed interest in the context of vitrimers and circular polymer economy, where the reversibility of urethane bonds is seen as an asset.^{132,308,309}

Another polycondensation-based route towards NIPUs is the reaction between primary polycarbamates and aldehydes or less available polyaldehydes.^{310–314} Under acidic catalysis, two primary carbamate groups and one aldehyde condense to form a geminated diurethane with release of water (Scheme 2.7D). The reaction is versatile and can be performed under mild conditions, but water formation can lead to undesired bubbles, and heating can promote the degradation of primary carbamate functions.³¹¹ This carbamate-aldehyde condensation represents an underexplored route with great potential for producing NIPUs with high bio-based carbon content, but further optimization is necessary to achieve shorter reaction times and higher yields.⁹⁹

2.3.3 Rearrangements

Other approaches for the synthesis of NIPUs rely on the Curtius rearrangement of acyl azides (Scheme 2.9A), the Hofmann rearrangement of carboxamides (Scheme 2.9B), or the Lossen rearrangement of hydroxamic acids (Scheme 2.9C). These reactions are carried out in the presence of polyols and proceed through the *in situ* formation of isocyanates, which then react with the polyol and polymerize to PU.²²² Several examples of AB-type self-condensations have been reported, including syntheses from bio-sourced building blocks.^{288,292,315} However, the acyl azides used in the Curtius rearrangement are toxic and explosive, and the traditional Hofmann rearrangement requires stoichiometric amounts of bromine and produces large amounts of waste.³¹⁶ In contrast, the Lossen rearrangement employs less toxic hydroxamic acids and proceeds under milder conditions compared to the previous two routes. Furthermore, recently developed catalytic systems have reduced waste and further improved the sustainability of the process, which has been applied to the preparation of various carbamates for NIPU synthesis.^{302,304,317} However, while the latest advancements in the field have improved the efficiency, safety, and environmental footprint of these methods, the *in situ* generation of isocyanates still implies the same toxicological concern and regulations associated with conventional isocyanate-based systems.



Scheme 2.9 Rearrangements routes from carboxylic acid derivatives to carbamates: Curtius (A), Hofmann (B), and Lossen (C) rearrangements.

2.3.4 Ring-opening (co)polymerizations

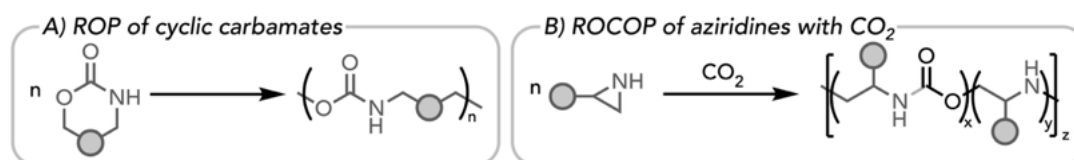
Ring-opening polymerization (ROP) of cyclic carbamates (Scheme 2.10A) and ring-opening copolymerization (ROCOP) of aziridines with CO_2 (Scheme 2.10B) have been investigated as alternative isocyanate-free routes to PUs that avoid the formation of by-products.

For cyclic carbamates, the polymerizability of the monomers depends on their ring size, with unsubstituted six- and seven-membered monomers being more prone to ROP than five-membered ones.³¹⁸ These carbamates are generally produced from phosgene, although alternative synthetic methods include aminolysis and subsequent transurethanization of cyclic carbonates, or direct CO_2 transformations with aminoalcohols, haloamines, aziridines, and other compounds.²⁵¹ ROP of cyclic carbamates, reported with both cationic and anionic initiators, often requires strong catalysts and elevated temperature that restrict scalability.^{319–321}

ROCOP of aziridines and CO_2 yields copolymers containing urethane and amine repeating units, with the selectivity between the two linkages depending on CO_2 temperature and pressure.^{322,323}

Although the use of supercritical CO_2 allows tuning of the reaction conditions and enables efficient copolymerization without additives, aziridine homopolymerization cannot be avoided, and the resulting amine groups react with CO_2 to form branched polymers.³²⁴ Regardless of chain branching and back-biting side reactions, the main issue of this approach lies in the toxicity, carcinogenicity, and handling hazards of aziridines, which do not align with the principles of safer and more sustainable NIPU chemistry.³²⁵

Overall, while both strategies demonstrate the chemical diversity of possible isocyanate-free pathways to PUs, they remain largely restricted to academic interest, with other routes being significantly more scalable and safer.



Scheme 2.10 ROP of cyclic carbamates (A) and ROCOP of aziridines with CO₂ (B).

2.4 NIPU adhesives and coatings

The structural diversity accessible through various isocyanate-free synthesis strategies provides a rich platform for the design of functional polymeric materials. This chemical versatility, combined with a better EHS performance compared to conventional PUs, creates a compelling opportunity for the deployment of NIPUs in the adhesives and coatings sector, where regulatory and environmental pressures are decisive factors in innovation and market adoption. Within this framework, the modularity of NIPU synthesis enables the incorporation of bio-based reagents, potentially enhancing sustainability. Furthermore, the presence of additional functional groups along the polymer backbone, characteristic of certain NIPU structures (e.g., PHUs, poly(oxo-urethane)s, or poly(hydroxy oxazolidone)s), not only affects mechanical properties but can also promote adhesion to substrates, making these polymers particularly well-suited for bonding applications that require strong interfacial interactions.

Although the synthesis of PUs *via* isocyanate-free routes has been extensively investigated, their practical application as adhesives and coatings remains comparatively underexplored. Strategies commonly employed to overcome the slow kinetics of NIPU formation, such as hybrid formulations, catalysis, use of highly reactive polyamines, or structurally modified polyCCs, have also been implemented for these specific applications. Among these approaches, hybrid chemistries have received particular attention, as they combine NIPU networks with different polymerization mechanisms (such as epoxy, acrylate, alkene, or sol–gel reactions), leading to covalently integrated systems that can enhance reactivity, crosslinking density, and overall performance. These hybrid systems often provide advantages over conventional PUs, especially during the curing step, and some have already reached commercial implementation in the coating industry.^{214,222,326,327} Nevertheless, the development of NIPU adhesives and coatings that can compete with commercial PUs remains an important focus of research, particularly for ambient-temperature applications.⁴⁹

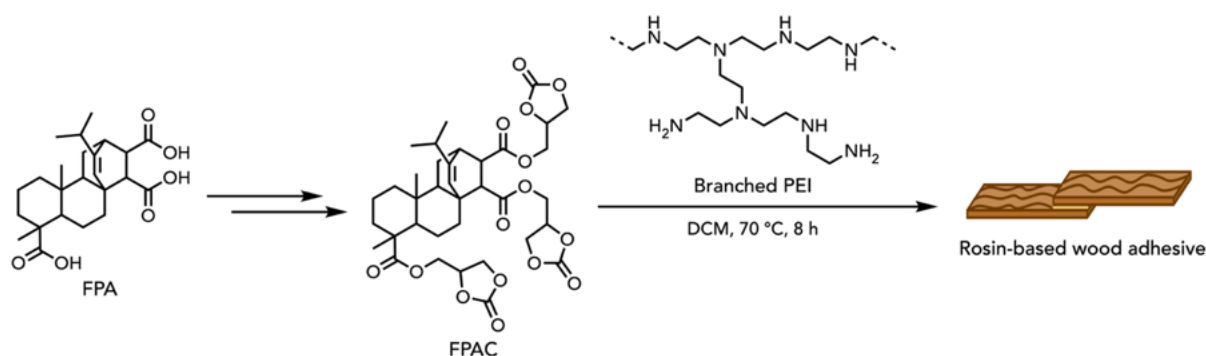
The following sections highlight notable examples of NIPU-based adhesives and coatings characterized by at least one relevant application-oriented evaluation test. The selected works were chosen based on the proximity of both urethane-forming reaction and application conditions to ambient temperature, with 80 °C defined as the threshold value, and are classified

according to their formulation medium. In this context, hybrid formulations, defined as NIPU-based systems in which the final material contains covalently integrated polymeric structures or networks originating from reactions not based on NIPU chemistry, are beyond the scope of this work and will not be discussed in detail. While the screening was deliberately focused on reaction and application conditions to address the most critical challenges associated with NIPU synthesis, the sustainability and practical viability of NIPU adhesives and coatings ultimately depend on the entire preparation process and, more generally, on their overall lifecycle.

2.4.1 Solvent-based formulations

In the framework of NIPU adhesives and coatings, solvent-based formulations have primarily been explored to address intrinsic practical limitations associated with isocyanate-free chemistries. The extensive hydrogen bonding of many NIPU structures combined with step-growth polymerization kinetics often results in high viscosities or limited processability at moderate temperatures, therefore the use of organic solvents enables dissolution of NIPU polymers or prepolymers and facilitates mixing and application. However, solvent incorporation does not resolve the kinetic constraints of NIPU formation, therefore this approach is often accompanied by elevated curing temperatures or post-curing steps. Moreover, the reliance on solvents requires proper balance of solid content and viscosity and partially offsets the environmental and safety advantages that motivate the development of NIPUs.

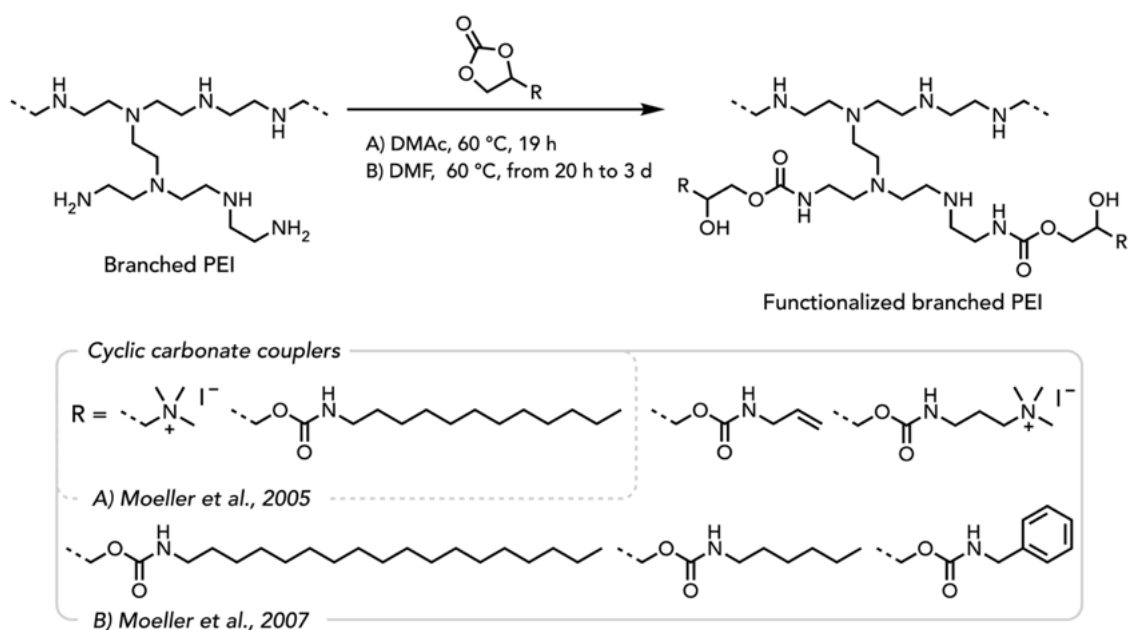
An example of this formulation-level compromise is represented by the work of Dong and Xu et al., who combined renewable feedstocks and CO₂ utilization while using a chlorinated solvent for adhesive preparation.³²⁸ The study reported the development of a partially bio-based NIPU derived from rosin for high-strength wood adhesive applications. Fumaropimaric acid (FPA), obtained through Diels–Alder modification of rosin, was converted into polyCC (FPAC) *via* epoxidation with epichlorohydrin and subsequent CO₂ insertion. The resulting precursor was then dissolved in dichloromethane (DCM) and reacted with polyethyleneimine (PEI) at 70 °C for 8 hours, leading to a crosslinked PHU network through CC aminolysis (Scheme 2.11).



Scheme 2.11 Synthesis of rosin-based wood adhesives from fumaropimaric acid. Adapted from Dong and Xu et al.³²⁸

The polymer structure design focused on two main elements: the incorporation of the hydrogenated phenanthrene ring structure intrinsic to rosin and the formation of a hyperbranched, highly crosslinked network, through curing with the multifunctional PEI. This combination restricted chain mobility while increasing crosslink density, yielding mechanical reinforcement and thermal stability. Optimal performance was achieved at an equimolar ratio between amine and CC groups, providing a tensile strength of 40.50 MPa and a Young's modulus of 752 MPa. The network exhibited a gel content exceeding 95%, high solvent resistance, and a thermal degradation temperature at 5% mass loss ($T_{\text{deg}5\%}$) of approximately 190 °C, indicating the formation of a robust thermoset structure. Beyond mechanical and thermal properties, the β -hydroxyurethane network displayed dynamic behavior attributed to transcarbamoylation reactions enabled by residual hydroxyl groups. These exchange reactions resulted in self-healing capability, recyclability, and shape-memory properties, which were presented as key advantages for extending material lifespan and sustainable reuse. Adhesive performance was evaluated on acrylic, paperboard, polypropylene, aluminum, ABS, and wood substrates, with the latter showing the highest lap-shear strength (~ 4 MPa). Notably, after water immersion at RT, the adhesive retained a shear strength of approximately 3 MPa, demonstrating good water resistance.

One of the reasons why organic solvents substitute water as reaction media, beyond the limited water solubility of some reagents, is the need to avoid competing CC hydrolysis. A clear manifestation of this formulation constraint is found in two works from the group of Moeller, which explored the functionalization of branched PEI *via* aminolysis of CCs bearing quaternary ammonium groups, crosslinkable allyl groups, alkyl chains of different length, and benzyl moieties, as a strategy to obtain surface-active and antimicrobial polymer coatings (Scheme 2.12).^{329,330}

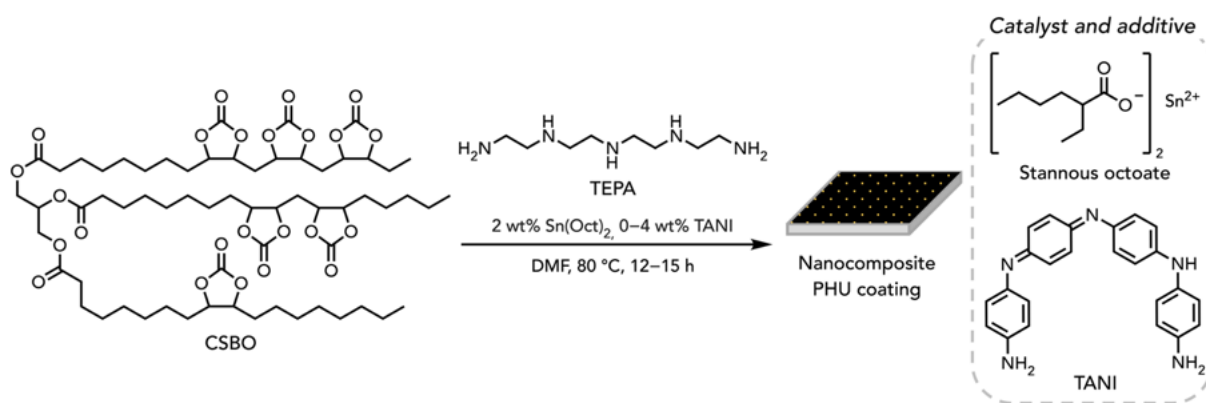


Scheme 2.12 Functionalization of branched PEI with CC couplers for amphiphilic, antimicrobial coatings. Adapted from Moeller et al.^{329,330}

To ensure homogeneous reaction conditions and prevent CC hydrolysis, the authors employed polar aprotic solvents as reaction media, namely *N,N*-dimethylacetamide (DMAc) and *N,N*-dimethylformamide (DMF). In the earlier study, the functionalization was carried out in DMAc at 60 °C for 19 hours using two CC couplers, one bearing a quaternary ammonium group and one incorporating a dodecyl chain (Scheme 2.12A).³²⁹ Functionalization of PEI required repeated washing of the organic phase with hexane to remove impurities and afforded functionalization degrees up to 25 mol% relative to repeating units, corresponding to full conversion of primary amine groups. Thermal analysis of the functionalized polymers showed reduced thermal stability, particularly at low degrees of substitution, and increased glass transition temperature (T_g) for highly substituted and more hydrophobic polymers, shifting from -52.9 °C for unmodified PEI up to 26.9 °C. Thin films were prepared from 1 wt% methanolic solutions by spin-coating and characterized *via* contact angle measurements, which showed marked hydrophobicity only for the polymer containing exclusively alkyl pendent chains, whereas ammonium-modified polymers remained strongly hydrophilic. Antibacterial assessment in aqueous solution revealed that hydrophilic-hydrophobic balance plays a key role in bacteria growth inhibition, since only the polymer functionalized with both aliphatic chains and quaternary ammonium groups exhibited total inhibitory effect against *Escherichia Coli* at a concentration of 0.01 wt%.

In a subsequent study from the same group, the scope of functional polymers was expanded using DMF as solvent and performing the aminolysis at 60 °C for reaction times ranging from 20 hours to 3 days (Scheme 2.12B).³³⁰ The resulting polymers were purified through several washing or precipitation steps in different organic solvents. PHU coatings were produced by solvent casting from dilute methanolic solutions, followed by air-drying overnight at RT or additional thermal treatment at 60 °C for 16 hours. The functional polymers were evaluated for growth inhibition effect against Gram-negative and Gram-positive bacteria (*Escherichia coli* and *Bacillus subtilis*, respectively), both in solution and on coated surfaces. Among the transparent, colorless coatings obtained, the best results were achieved with the only crosslinked polymer, which provided 99.9% growth inhibition and was characterized by a cationic to hydrophobic groups ratio of 1 : 1 and by substituents with an intermediate alkyl chain length, confirming that a tuned amphiphilic balance governs antibacterial properties. However, partial polymer transfer to the aqueous bacterial media was observed, indicating the necessity to improve the crosslinking technique or to covalently link the coating to the surface. Overall, the use of organic solvents constitutes a way to prevent hydrolysis and enable precise macromolecular functionalization, but at the expense of increased footprint, especially due to the several environmentally burdening steps required for the purification procedure.

An additional case of solvent-based NIPU coating was reported by Rao and Palanisamy et al., who developed corrosion-resistant nanocomposite coatings incorporating an electroactive additive in the formulation.³³¹ In this study, carbonated soybean oil (CSBO) was produced from epoxidized soybean oil *via* CO₂ insertion and reacted with tetraethylenepentamine (TEPA) in the presence of stannous octanoate as catalyst. To impart corrosion resistance, tetraniline (TANI), an electroactive oligoaniline, was dispersed in DMF by sonication and incorporated into the formulation at loadings between 0.5 and 4 wt% relative to CSBO. From the resulting composites, exhibiting a solid content of approximately 65%, free-standing films and coatings were prepared by casting and curing at 80 °C for 12–15 hours in the presence of stannous octoate (Sn(Oct)₂, 2 wt%) as catalyst (Scheme 2.13).



Scheme 2.13 Synthesis of corrosion-resistant crosslinked nanocomposite PHU coatings.

Adapted from Rao and Palanisamy et al.³³¹

TGA measurements indicated that TANI loading did not significantly alter the onset of degradation, with $T_{\text{deg}5\%}$ values remaining in the range of 185–207 °C, while the char residue at 550 °C increased progressively with higher additive content, reflecting the aromatic and thermally stable nature of the oligoaniline. DMA and tensile testing revealed a slight increase in T_g values and enhanced mechanical properties for the compositions containing TANI. In particular, the optimum loading was found to be 1 wt.%, which provided the highest tensile strength (0.97 ± 0.07 MPa) and elongation at break (92.0 ± 4.0 %). SEM analysis confirmed relatively homogeneous dispersion of TANI within the matrix, accompanied by increased surface roughness at higher concentrations. All coatings remained hydrophobic, with contact angles between 98 and 110°, although the addition of TANI slightly reduced the water contact angle due to increased surface polarity and roughness. The anti-corrosive performance was evaluated by Tafel polarization measurements, which demonstrated a substantial reduction in corrosion rate with increasing oligoaniline content, alongside a marked increase in polarization resistance. Salt spray tests corroborated these findings, showing improved adhesion and delayed delamination under corrosive conditions for the composite-coated panels compared to the neat NIPU coating. From a sustainability perspective, the system represents a partially bio-based NIPU coating with enhanced functional performance; however, the use of a tin-based catalyst and reliance on DMF for additive dispersion substantially increase the ecological footprint of the formulation.

Table 2. 1 Comparative summary of solvent-based NIPU formulations reported in the literature for adhesive and coating applications.

Solvent	Solid content (wt%)	Processing conditions	Application	Substrate	Adhesive and coating tests	Key application performance	Ref.
DCM	Not reported	70 °C, 8 h	Wood adhesive	Acrylic, paperboard, polypropylene, ABS, aluminum, wood	Lap-shear	Lap-shear strength ~4 MPa (wood) and ~3 MPa (wood) after water immersion	328
DMAC (synthesis); ^a MeOH (application)	1	60 °C, 19 h	Antibacterial coating	Not reported	Contact angle, antibacterial (in aqueous solution)	Total inhibition of <i>E. Coli</i> growth at a concentration of 0.01 wt%.	329
DMF (synthesis); ^b MeOH (application)	1	60 °C, from 20 h to 3 d	Antibacterial coating	Glass	Antibacterial	99.9% inhibition of <i>E. Coli</i> and <i>B. Subtilis</i> growth	330
DMF	~65	80 °C, 12–15 hours	Corrosion-resistant nanocomposite coating	Mild steel	Contact angle, Tafel polarization, salt spray, adhesion (qualitative, after salt spray)	Reduced delamination and corrosion rate from 2.69×10^{-4} to 1.67×10^{-5} mm/year at 4 wt% TANI	331

^a Hexane used during purification. ^b Several organic solvents used during purification.

For ease of comparison, the main characteristics of the solvent-based NIPU formulations discussed above are summarized in Table 2.1. Across solvent-based systems, both type and quantity of solvent employed significantly affect the overall sustainability and hazard potential of the formulation. A marked improvement in environmental performance can be achieved transitioning from the use of solvents as reaction media to their use solely as auxiliary components. Moreover, adherence to established solvent sustainability guides, such as those developed by CHEM21, the ACS Green Chemistry Institute Pharmaceutical Roundtable, GlaxoSmithKline, Pfizer, and Sanofi, is highly advisable.³³² These guides provide regularly updated sustainability rankings and practical recommendations for the identification of safer alternative solvents.

2.4.2 Water-based formulations

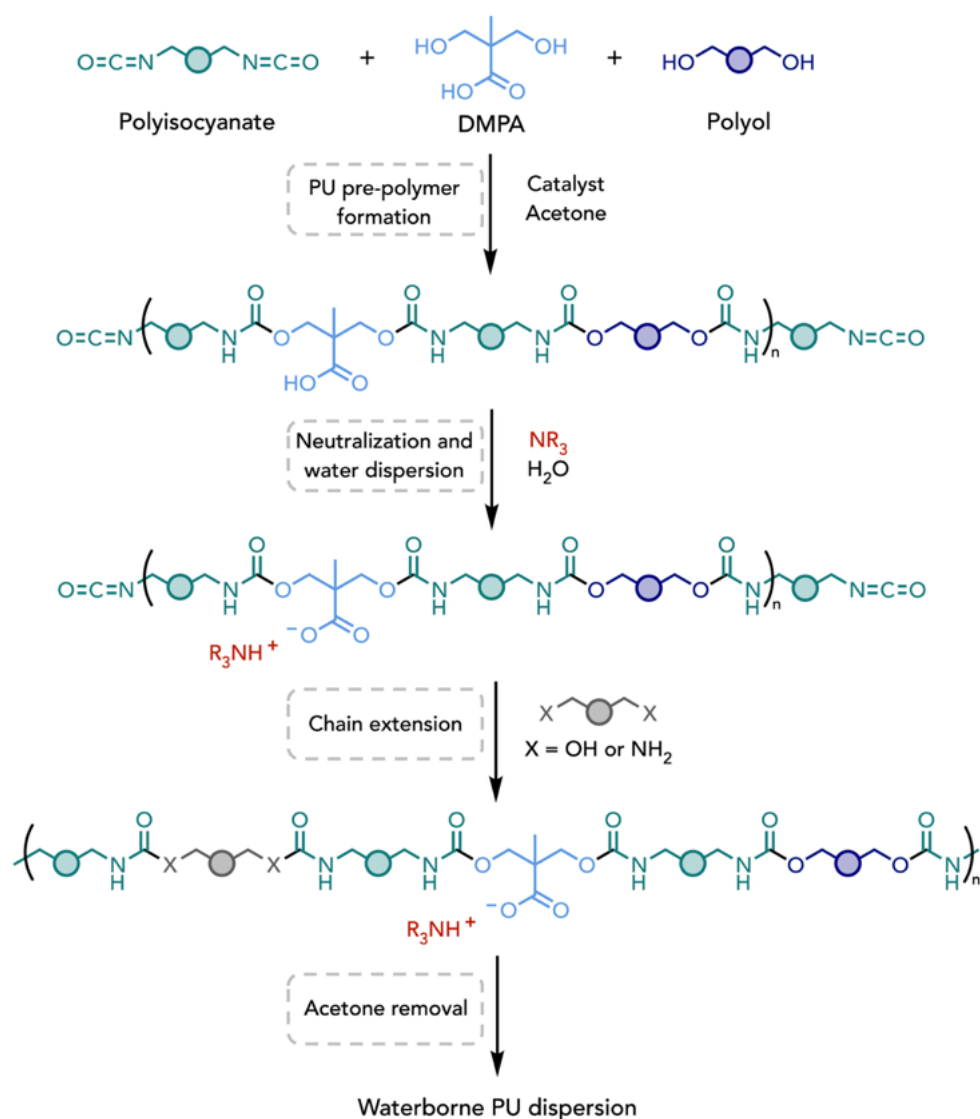
As for their PU analogues, water-based NIPU (WNIPU) formulations offer a reduced environmental footprint compared to solvent-based systems, while reducing the viscosity issues typically associated with solvent-free formulations. Nonetheless, obtaining stable formulations with good film coalescence and balance between solid content and viscosity, long shelf life, and performance comparable to that of isocyanate-based PU requires careful control over the hydrophilicity and reactivity of the reagents. In particular, the development of WNIPUs demands a careful balance between water dispersibility and long-term water resistance. The incorporation of ionic groups, hydrophilic segments, or hydroxyl-rich building blocks is often necessary to ensure processability in aqueous media but may simultaneously increase water uptake and moisture sensitivity in the final material. Excessive water absorption can induce swelling, plasticization, dimensional instability, and deterioration of mechanical and barrier properties, particularly under prolonged exposure to humid environments. Consequently, hydrolytic stability and water sensitivity represent key considerations in the design of high-performance WNIPU systems, especially in the case of hydroxyl-rich PHUs. Furthermore, for this class of NIPUs, the presence of water during synthesis necessitates strict pH control to prevent side reactions that may either slow down the aminolysis or lead to degradation of the CC co-reagent.^{234,236,333} Under alkaline conditions, CCs can undergo hydrolysis, producing alcohols and carbon dioxide, whereas under acidic conditions amines become protonated and therefore unreactive, as illustrated in Scheme 2.5D and Scheme 2.5C, respectively. Owing to competing side reactions, the limited water solubility of many precursors, and the need for precise control over formulation parameters, fully WNIPU synthesis remains challenging, and low-viscosity formulations are most

often prepared using organic solvents despite the desirability of employing water as the sole continuous phase.

WNIPU formulations can be broadly classified into water-soluble homogeneous systems and waterborne dispersions.

In homogeneous systems, the formulation is applied as an aqueous solution, although the resulting polymer may become partially or fully insoluble in water upon formation (e.g., due to subsequent crosslinking). The NIPU-forming reaction typically takes place either in the aqueous solution or at the interface between aqueous and organic phases, depending on whether all or only part of the reagents are water-soluble, respectively. Nevertheless, examples of water-soluble NIPUs synthesized in organic solvents have also been reported.^{278,334,335} Homogeneous formulations have been exploited not only for adhesives and coatings, which are water-based during application and form solid films upon drying, but also for hydrogels, which are designed to remain hydrated during use.^{235–237,336,337}

In dispersed systems, the polymer is insoluble in water and the polymerization typically occurs in an organic medium, either in solution or in bulk, which is dispersed in water during or after polymerization, while examples of interfacial polymerization remain comparatively rare. Organic solvents are far more commonly employed than fully aqueous approaches; in particular, most of the literature examples of WNIPU dispersions are inspired by the so-called “acetone process” developed for PU analogs (Scheme 2.14).²⁸⁷



Scheme 2.14 Schematic representation of the acetone process to waterborne PU dispersions.

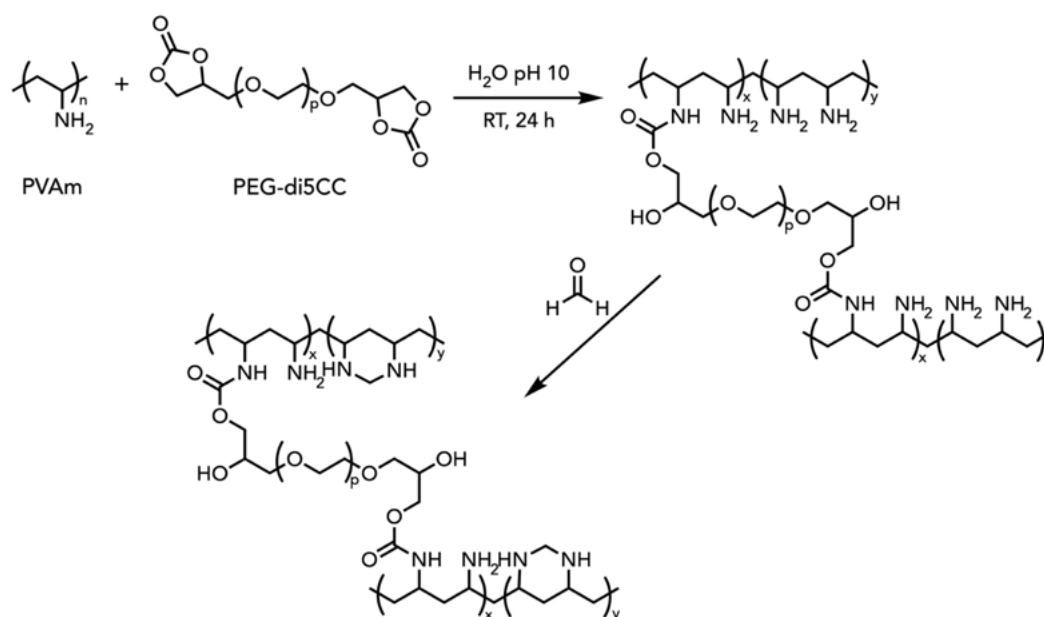
The process involves the synthesis of a prepolymer in a low-boiling-point, water-miscible solvent (typically acetone), incorporating an internal dispersing agent (such as dimethylolpropionic acid, DMPA) into the formulation to enable dispersion in water upon neutralization. After water addition under stirring, the prepolymer is typically chain-extended before removal of the organic solvent. While the earliest examples of WNIPU dispersions avoided the use of organic co-solvents,³³⁸ acetone-like processes offered significantly improved control over viscosity, molecular weight, and particle size and distribution, with high reproducibility.³³⁹ Most reported examples of WNIPU dispersions obtained through acetone-like processes rely on CC aminolysis^{340–348} rather than on transurethanization routes.^{349,350} Other less commonly explored techniques for the preparation of WNIPU dispersions using organic solvents include surfactant-assisted interfacial polymerization, in which part of the reagents is dissolved in the organic phase and part in the

aqueous phase,^{351,352} as well as nanoprecipitation, where the polymer is first synthesized or solubilized in a water-miscible organic solvent and subsequently precipitated in water, which acts as a non-solvent.^{353–355} An important organic-solvent-free route to dispersed waterborne NIPUs relies on emulsification of a hydrophobic phase, followed by polymer formation within the dispersed droplets.^{356–360}

Although WNIPU formulations are generally applied in absence of organic co-solvents, their environmental advantage is limited if significant amounts of organic media are required during the pre-application stages; consequently, strategies that avoid the use of such solvents throughout the entire preparation process appear more attractive and desirable.

2.4.2.1 Water-soluble formulations

An exemplary water-soluble system prepared under mild conditions was described by Detrembleur et al., who developed PHU hydrogels and coatings specifically designed for formaldehyde (FA) capture.²³⁶ The study focused on the preparation of amine-rich PHU networks and evaluation of their performance as depolluting materials under both aqueous and gaseous FA exposure. After an initial screening of PHU precursors based on their FA capture potential in water, the synthetic strategy was based on the polyaddition between a water-soluble poly(ethylene glycol) dicyclic carbonate (PEG-di5CC) and poly(vinylamine) (PVAm), carried out entirely in water under catalyst-free conditions at room temperature (Scheme 2.15).



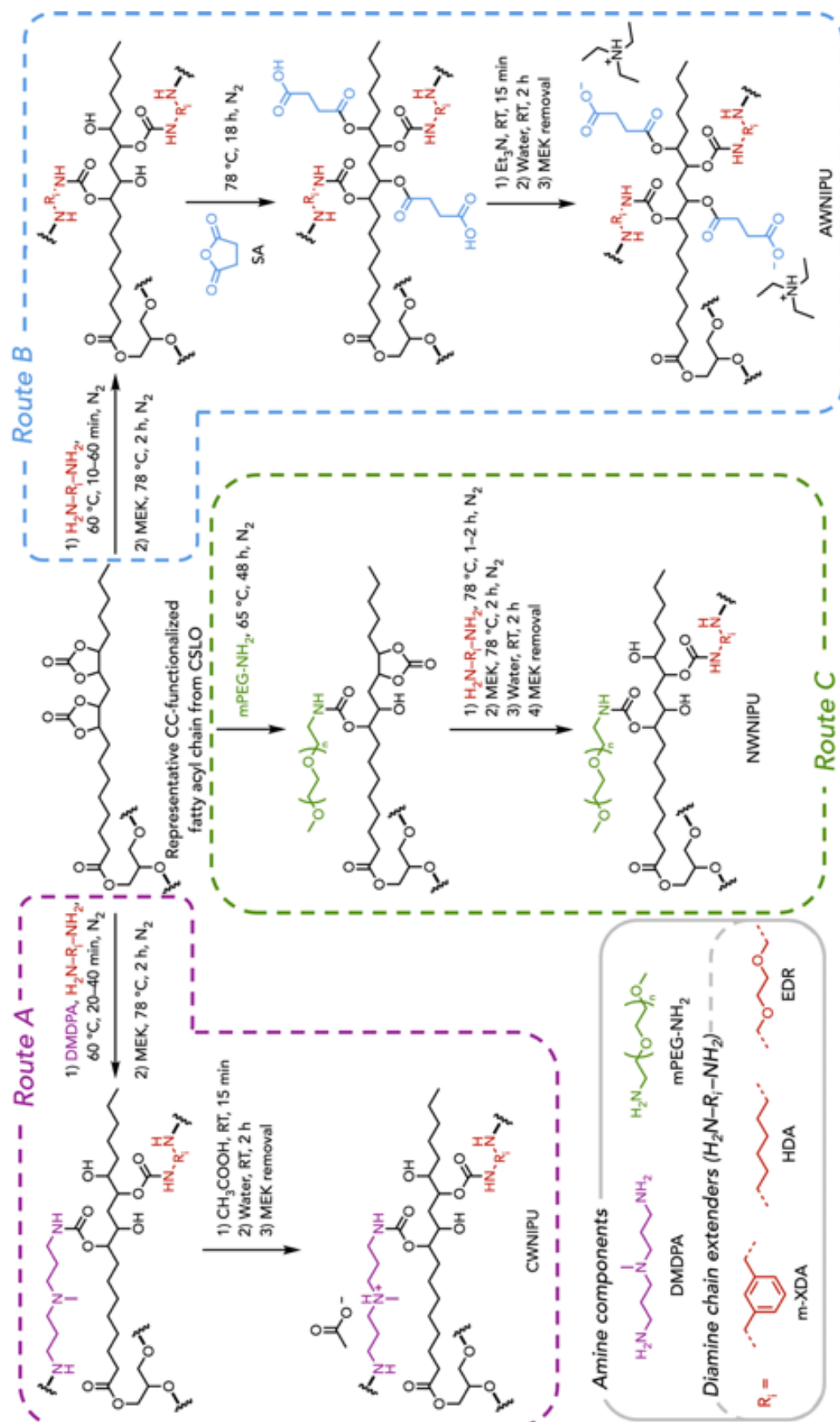
Scheme 2.15 Synthesis of crosslinked PHUs for formaldehyde capture. Adapted from Detrembleur et al.²³⁶

PVAm was selected due to its outstanding ability to scavenge FA even at low amine excess and under acidic aqueous conditions, a behavior directly linked to its capacity to form methylene bridges between adjacent amines leading to six-membered ring adducts. At pH 10, the optimal amine to CC molar ratio was identified as 4 : 1, ensuring sufficient amine excess for efficient FA capture, a short gel time of 2.5 minutes, and the highest storage modulus among the tested formulations, indicating a tightly crosslinked network. Lowering the pH to 8.5 significantly slowed the reaction kinetics, increasing the gel time to 20 minutes. To investigate aminolysis efficiency, a model reaction between PVAm and ethylene carbonate was performed and studied by IR and NMR spectroscopies at pH 8.5 and 10. The study demonstrated that partial CC hydrolysis and the formation of urea linkages *via* urethane aminolysis were both favored under more basic conditions. Nevertheless, the PHU synthesis was conducted for 24 hours at 5 wt% polymer concentration with the pH fixed at 10 to limit residual unreacted CC and guarantee short gel time. FA capture and desorption were first evaluated in water, using the PHU as a hydrogel, and subsequently in indoor air purification tests, after drying the formulation at room temperature for 24 hours to obtain PHU coatings. The resulting material exhibited high FA capture efficiency, achieving 94% abatement in prolonged exposure tests and showing negligible FA release. FA fixation did not affect the visual aspect, thermal stability, or glass transition temperature of the transparent and colorless dried PHU films. However, it modified their mechanical behavior, shifting from a tough, plastic-like response to a more elastomeric one. Importantly, the formulation did not involve organic solvents at application and did not require external heating at any stage of its preparation, with PHU formation proceeding at ambient temperature in fully aqueous medium.

2.4.2.2 Waterborne dispersed formulations

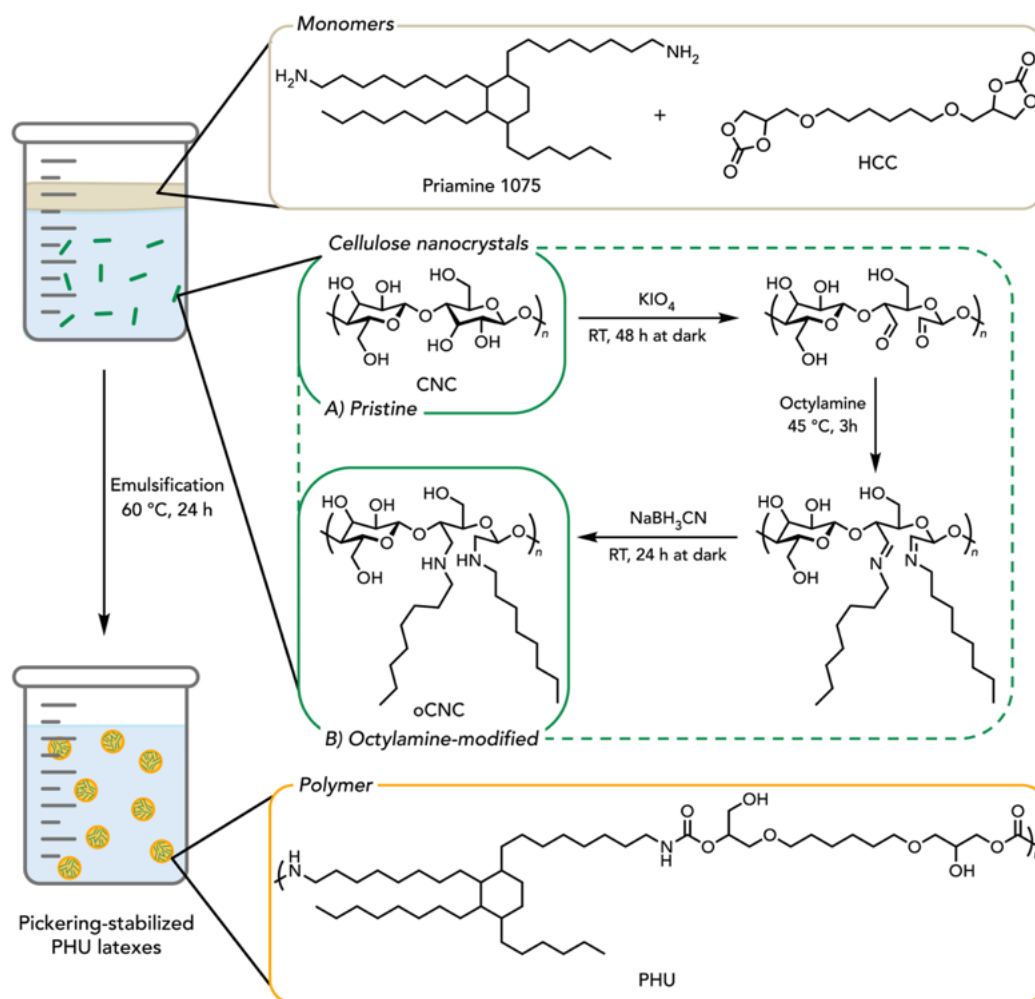
Among strategies for producing waterborne dispersed formulations, Zhang et al. reported the synthesis of plant oil-based WNIPUs derived from carbonated linseed oil (CLSO) *via* acetone-like processes.³⁴² Cationic, anionic, and non-ionic PHUs were prepared through different multi-step synthetic routes based on the polyaddition between CLSO and various diamines (Scheme 2.16). The synthetic strategy depended on the targeted ionic character. The preparation of cationic WNIPUs (CWNIPUs) involved three main steps: prepolymer formation, neutralization, and emulsification (Scheme 2.16 Route A). CLSO was first reacted under nitrogen with 3,3'-diamino-*N*-methyldipropylamine (DMDPA, serving as internal dispersing agent) together with a mixture of diamine chain extenders. The reaction was conducted at 60 °C for 20–40 min, followed by the addition of MEK to reduce viscosity and further polymerization at 78 °C for 2 h. After cooling to

room temperature, acetic acid and water were added, promoting neutralization and emulsification under vigorous stirring during subsequent MEK removal. For anionic WNIPUs (AWNIPUs), an additional synthetic step was introduced to incorporate pendent carboxylic groups as internal dispersing moieties. With this aim, ring-opening esterification of the hydroxyurethane functionalities with succinic anhydride (SA) was performed at 78 °C for 18 h (Scheme 2.16 Route B). The resulting carboxylic functionalities were neutralized with triethylamine, followed by emulsification in water and solvent removal. To prepare nonionic WNIPUs (NWNIPUs), hydrophilic polyether segments were first incorporated into the CLSO backbone *via* partial aminolysis of CC groups with poly(ethylene glycol) methyl ether amine (mPEG-NH₂) at 65 °C for 48 h under inert atmosphere (Scheme 2.16 Route C). Subsequent reaction with diamine chain extenders, dissolution in MEK, addition of water under stirring, and solvent removal afforded the targeted NWNIPUs. All formulations were obtained as aqueous dispersions with solid contents of approximately 10 wt% and were cast to form films by drying at 50 °C for 5 days. The average particle size varied significantly among formulation classes, ranging from 20–25 nm for NWNIPUs to nearly 300 nm for CWNIPUs, with smaller sizes associated with higher ionic or hydrophilic content. Mechanical properties, evaluated after drying at 60 °C for 24 h, ranged from soft and rubbery to hard and glassy depending on the type and ratio of diamine chain extenders. NWNIPUs, which displayed cloud points between 61 and 86 °C, exhibited the lowest mechanical performance due to reduced crosslinking density resulting from partial aminolysis by monofunctional mPEG-NH₂. The antibacterial activity of CWNIPUs was determined against *Staphylococcus aureus* and *Escherichia coli*, revealing growth inhibition above 98% for all tested samples. The coating performance of AWNIPUs was assessed by pencil hardness and crosshatch adhesion tests after drying at RT for 24 h followed by vacuum drying at 60 °C for 24 h. Increasing the m-XDA content significantly enhanced both hardness (up to 8H) and brittleness, resulting in reduced crosshatch adhesion, with the best adhesion classification (5B) obtained at lower m-XDA contents.



Scheme 2.16 Synthesis of WNIPUs from CLSO via acetone-like processes. Adapted from Zhang et al.³⁴²

Rare examples of WNIPU adhesives and coatings prepared without using organic solvents and under mild reaction and application conditions can be found among water-dispersible formulations. Notable examples have recently been described in collaborative works by Llevot, Cramail, and Zhou and their co-workers, who leveraged cellulose nanocrystals (CNCs) to stabilize partially bio-based, waterborne PHU dispersions and obtain nanocomposite adhesives and coatings.^{357–359} With the aim of developing surfactant-free PHU latexes, the CNCs served simultaneously as reinforcing nanofillers and Pickering stabilizers, i.e., solid particles that adsorb at the organic-aqueous interface and form a physical barrier preventing droplet coalescence. The bio-based diamine Priamine 1075 and 1,6-hexanediol bisCC (HCC) were first mixed at RT and then emulsified in an aqueous dispersion containing CNCs, generating monomer-in-water droplets. Suspension polymerization was then carried out at 60 °C for 24 h under continuous mechanical stirring and catalyst-free conditions, yielding stable PHU latexes in which CNCs were uniformly distributed within the polymer matrix (Scheme 2.17).



Scheme 2.17 Synthesis of Pickering-stabilized waterborne PHU nanocomposites using pristine (A) and octylamine-modified (B) cellulose nanocrystals. Adapted from by Llevot, Cramail, and Zhou et al.^{358,359}

Chapter 2: Theoretical background

In an initial study, the authors employed pristine CNCs as sole stabilizers and systematically investigated the effect of their concentration on monomer droplet size, latex morphology, and thermal and adhesive properties of the dried nanocomposites (Scheme 2.17A).³⁵⁸ Sodium chloride ($[\text{NaCl}] = 75 \text{ mM}$) was added to partially screen electrostatic repulsion and enable effective Pickering stabilization upon sonication. Considering that partial CC hydrolysis may occur in aqueous environment, the HCC to Priamine molar ratio was varied at a fixed CNC content of 100 mg per mL of monomers and 10 wt% total monomer content relative to the suspension. Complete CC conversion was reached at an optimized HCC to Priamine ratio of 1.2, corresponding to approximately 91% amine conversion and a number average molecular weight (M_n) of 4500 g mol^{-1} . CNC concentration was initially optimized for monomer droplets and subsequently for PHU latexes. In PHU latexes, increasing CNC content from 100 to 200 mg per mL of monomers reduced average droplet size from 10.2 ± 0.8 to $7.9 \pm 0.6 \mu\text{m}$; however, it also led to decreased amine conversion and increased viscosity, resulting in broader particle size distributions and occasional droplet coalescence. Long-term storage tests demonstrated that higher CNC concentrations ($150\text{--}200 \text{ mg mL}^{-1}$) improved colloidal stability, whereas lower loadings (100 mg mL^{-1}) showed partial coalescence over time. Therefore, while 100 mg mL^{-1} was an optimal concentration for initial latex formation, long-term stability required higher CNC content. Upon drying at room temperature, the latexes yielded nanocomposites containing between 9 and 17 wt% CNC. SEM analysis revealed that the nanoparticles became uniformly distributed as individual nanorods within the PHU matrix after film formation, without visible aggregation even at 17 wt%. DSC measurements showed an increase in T_g (from -26 to $-20 \text{ }^\circ\text{C}$) with increasing CNC content; additionally, FTIR analysis provided evidence for hydrogen bonding between the nanofillers and the PHU matrix, indicating that the nanofillers restricted chain mobility through a combination of physical reinforcement and enhanced interfacial interactions. These effects, together with the increased hydrophilicity from CNC hydroxyl groups, translated into substantial improvements in adhesion performance, which was evaluated by probe-tack and lap-shear testing. Probe-tack tests were conducted using dried latex films applied on stainless steel, whereas lap-shear measurements were performed on glass substrates after drying at $60 \text{ }^\circ\text{C}$ for 24 hours (latex concentrated from 10 to 30 wt%). Compared to a Tween 80-stabilized PHU reference, CNC-stabilized systems showed up to 680% increase in probe-tack strength ($749.1 \pm 11.3 \text{ kPa}$), 480% increase in work of adhesion (46.4 J m^{-2}), and up to 340% increase in lap-shear strength (659 kPa) at 17 wt% CNC, reaching performance comparable to commercial PSAs. Although lap-shear strength remained insufficient for use as structural adhesives, the CNC-stabilized formulations demonstrated strong potential for PSA application.

Building directly on the previously discussed CNC-stabilized latexes, a subsequent study targeted the hydrophobic modification of the nanofillers through grafting of long alkyl chains to enhance interfacial compatibility between CNCs and PHU matrix.³⁵⁹ Octylamine-modified CNCs (oCNCs) were obtained *via* periodate oxidation of surface hydroxyl groups to aldehydes, followed by reductive amination (Scheme 2.17B). Three oCNCs with increasing degrees of substitution were prepared, with average numbers of octyl groups per anhydroglucose unit of 0.037, 0.042, and 0.048 (oCNC1, oCNC2, and oCNC3, respectively), enabling precise control over nanoparticle hydrophobicity and oil wettability. The oCNC content was optimized for both monomer-in-water droplets and PHU latexes under emulsification and suspension polymerization conditions analogous to those reported in the earlier work from the same authors, but using a higher NaCl concentration ($[\text{NaCl}] = 4.8 \text{ M}$) to ensure long-term droplet stability. Increasing either the degree of oCNC substitution or the oCNC loading (from 100 to 200 mg mL⁻¹) led to a decrease in droplet size, amine conversion, and PHU molecular weight, following trends similar to those previously observed with pristine CNCs. Using oCNC1 at 100 mg mL⁻¹, a median latex diameter of $6.2 \pm 1.7 \text{ }\mu\text{m}$ and the highest amine conversion (91%) and number-average molecular weight ($M_n = 4600 \text{ g mol}^{-1}$) were obtained, values respectively lower (particle size) and comparable (amine conversion and M_n) to pristine-CNC-stabilized analogs. Nanocomposite films with an oCNC content between 9 and 17 wt% were prepared by drying the latexes at room temperature, followed by removal of precipitated salt with deionized water. Nanofiller content and degree of cellulose substitution did not significantly affect homogeneity of the material nor T_g values, which were 5–8 °C higher than those of PHUs stabilized with unmodified CNCs. In contrast, adhesion performance strongly depended on oCNC content and hydrophobicity, with the highest probe-tack strength, work of adhesion, and lap-shear strength (1003.5 kPa, 72.8 J m⁻², and 731 kPa, respectively) obtained with the nanocomposite containing the lowest degree of substitution (oCNC1) and the highest loading (17 wt%). Compared with pristine CNC systems at equal filler contents, these improvements were attributed to the balanced hydrophobicity of oCNC1, which provided optimal interfacial compatibility and strong filler-matrix interactions.

A closely related strategy based on CNC Pickering stabilization of waterborne dispersed PHU latexes was reported by the same groups to obtain fluorescent WNIPU formulations.³⁵⁷ Although these systems were not evaluated for specific adhesive or coating performance, the combination of low T_g s and intrinsic fluorescence suggested promising potential for functional coating applications in sensing, imaging, or anti-counterfeiting technologies. A comparative summary of the WNIPU formulations discussed in this section is provided in Table 2.2.

Table 2.2 Comparative summary of water-based NIPU formulations reported in the literature for adhesive and coating applications.

Type of WNIPU	Solvent	Solid content (wt%)	Processing conditions	Application	Substrate	Adhesive and coating tests	Key application performance	Ref.
Water-soluble	H ₂ O	5	RT, 24 h	Indoor-air purification coating	Stainless steel	FA capture and release	94% gaseous FA abatement after 24 h, negligible FA release	236
Dispersed	MEK (synthesis); H ₂ O (application)	~10	60–78 °C, up to 52 h (synthesis); 50 °C, 5 d (application)	Coating	Tinplate	Antibacterial, pencil hardness, crosshatch	>98% bacterial inhibition (CWNIPUs), up to 8H hardness and 5B adhesion (AWNIPUs)	342
Dispersed	H ₂ O	10 ^a	60 °C, 24 h (synthesis); RT drying ^b or 60 °C, 24 h (application)	Nano-composite adhesive	Glass, stainless steel ^c	Probe tack, lap-shear	Tack strength 749.1 ± 11.3 kPa, work of adhesion 46.4 J m ⁻² , and lap-shear strength 659 kPa at 17 wt% CNC	358
Dispersed	H ₂ O	10 ^a	60 °C, 24 h (synthesis); RT drying ^b or 60 °C, 24 h (application)	Nano-composite adhesive	Glass, stainless steel ^c	Probe tack, lap-shear, contact angle	Tack strength 1003.5 kPa, work of adhesion 72.8 J m ⁻² , and lap-shear strength 731 kPa at 17 wt% oCNC1	359

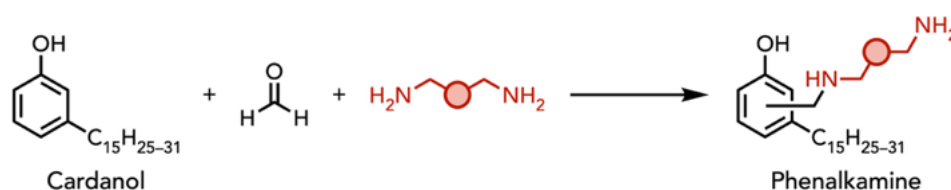
^a Latex concentrated to 30 wt% for lap-shear testing. ^b Drying time not reported. ^c Substrates used only in probe tack testing.

2.4.3 Solvent-free formulations

Solvent-free formulations represent the most attractive yet also the most challenging formulation type for NIPU adhesives and coatings, as they are strongly constrained by the intrinsic reactivity and physical state of the available precursors. In particular, the limited availability of highly reactive, low-viscosity building blocks suitable for mild-temperature processing often leads to insufficient flow, poor substrate wetting, or incomplete network formation. As a result, most solvent-free NIPU adhesive and coating systems reported in the literature rely on thermal activation to reduce viscosity and promote curing.^{242,361–367} Consequently, NIPUs still struggle to match the performance and processing window of conventional isocyanate-based systems, especially for applications requiring curing under ambient conditions.

Among the few non-hybrid solvent-free formulations reported in the literature under relatively mild reaction or application conditions, several systems were prepared or processed across a range of temperatures and exhibited improved mechanical or adhesive performance when more intensive thermal treatment was applied.^{368–371}

In this context, Mahendran et al. developed fully bio-based, solvent-free NIPU coatings *via* aminolysis of CLSO with a phenalkamine curing agent,³⁷⁰ a Mannich-type polyamine obtained by reacting cardanol from cashew nut shell liquid (CNSL) with an aldehyde (typically formaldehyde) and a polyamine (Scheme 2.18).³⁷²



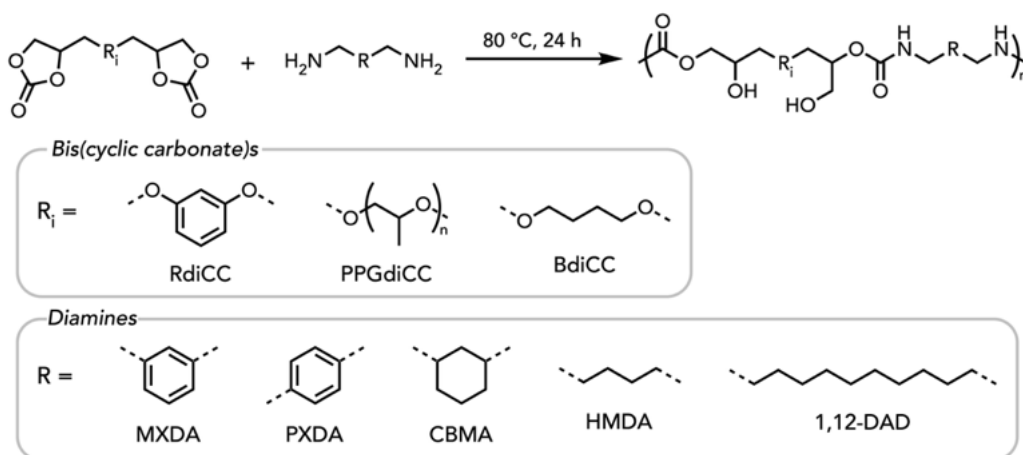
Scheme 2.18 Synthesis of phenalkamines from cardanol via Mannich reaction.

The aminolysis was carried out for 24 h, varying both CLSO : phenalkamine weight ratio (1 : 0.5, 1 : 0.75, and 1 : 1.25) and the reaction temperature (60, 80, and 100 °C) in order to identify the optimal curing conditions. FTIR spectroscopy revealed that CC conversion increased with both amine content and curing temperature; nearly complete disappearance of the CC signal was observed only at the highest CSLO : phenalkamine ratio (1 : 1.25) and at curing temperatures above 60 °C, whereas residual carbonate functionality remained detectable at lower temperatures and lower amine contents. Thermal stability followed a similar trend, with higher

curing temperatures generally shifting the degradation temperatures at 5% and 10% mass loss ($T_{\text{deg}5\%}$ and $T_{\text{deg}10\%}$, ranging from 185 to 227 °C and from 220 to 259 °C, respectively) to higher values. In contrast, increasing amine concentration led to slightly lower degradation temperatures, possibly due to the presence of unreacted excess amine. Coating performance was evaluated on untreated aluminum substrates through gloss, crosshatch adhesion, solvent resistance, swelling, color, and impact strength measurements. Void-free, high gloss coatings were obtained, particularly for samples cured at 100 °C, which displayed gloss values of approximately 130 gloss units and exhibited the best overall performance, achieving class 0 adhesion in the crosshatch test, withstanding more than 200 MEK double rubs, and showing reduced swelling, consistent with a higher crosslink density. In contrast, coatings cured at 80 and at 60 °C displayed progressively higher swelling, lower gloss (approximately 120 gloss units), lower adhesion (up to classes 1 and 2, respectively), and reduced solvent resistance (up to 200 and 100 MEK double rubs, respectively), indicating incomplete curing and a less developed network structure. Although more intense thermal treatment caused a noticeable darkening of the coating, impact strength was largely independent of curing temperature and instead increased with amine content, which was attributed to the incorporation of flexible segments from the phenalkamine. Overall, while urethane formation was feasible at 60 °C, satisfactory coating performance was achieved only upon curing at 100 °C, highlighting the strong dependence of the final properties on thermal input.

A strong dependence of adhesive performance on curing temperature was also reported by Gupta et al., who prepared solvent- and catalyst-free PHU adhesives by reacting CSBO with aliphatic diamines over a temperature range from RT to 120 °C.³⁷¹ Adhesion testing on oak wood revealed significantly reduced lap-shear strengths when curing was performed at ambient conditions (~1–2 MPa), while curing at 75–105 °C resulted in markedly higher values (~6–8 MPa).

In contrast to thermally cured systems, where elevated temperatures are typically required to ensure sufficient network development, Sardon et al. approached the design of NIPU adhesives from a fundamentally different perspective by focusing on thermoplastic and thermoreversible hot-melt formulations.³⁶⁹ In this work, PHUs were prepared from various bisCCs and diamines, aiming to control the balance between rigid and flexible polymer segments and thereby tune the thermal transitions required for hot-melt adhesive behavior (Scheme 2.19).

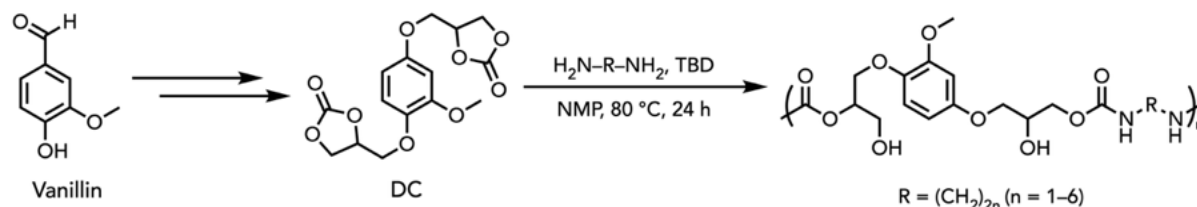


Scheme 2.19 Synthesis of PHU hot-melt adhesives from bisCCs and diamines. Adapted from Sardon et al.³⁶⁹

To modulate chain mobility and adhesive behavior, the authors synthesized PHUs by reacting *m*-xylylenediamine (MXDA), *p*-xylylenediamine (PXDA), 1,3-cyclohexanebis-(methylamine) (CBMA), hexamethylenediamine (HMDA), or 1,12-diaminododecane (1,12-DAD) with either resorcinol-based bisCC (RdiCC), 1,4-butanediol bisCC (BdiCC), poly(propylene glycol)-derived bisCC (PPGdiCC), or a mixture of PPGdiCC with one of the other two bisCCs at 80 °C for 24 h. Increasing the proportion of hard segments limited chain mobility and resulted in higher density of hydrogen bonds, thereby enhancing cohesive strength. Rheological measurements and FTIR analysis confirmed the formation of structured yet reversible networks through hydrogen bonding, which hindered the transition to liquid-like behavior at temperatures above the T_g . Substitution of RdiCC with BdiCC produced less rigid materials that could still be applied as hot-melt adhesives, whereas the nature of the diamine had significant impact on supramolecular interactions. Hot-melt behavior was found to be directly linked to a partial disruption of hydrogen bonding, which did not depend on π - π interactions but rather on the conformational effect of the diamines. In particular, only the rigid CBMA and MXDA limited to some extent hydrogen bonding and favored the formation of hot-melt adhesives, while stronger chain interactions were observed with PXDA and even stronger hydrogen bonding for the linear aliphatic diamines HMDA and 1,12-DAD due to greater chain mobility and lower steric hindrance. These conclusions were corroborated by probe tack, lap-shear, shear adhesion failure temperature (SAFT), and static shear resistance experiments, which were performed on PHU formulations derived from MXDA, PXDA, and CBMA. The stronger hydrogen bonding seen with PXDA-based formulations resulted in greater cohesive forces and therefore poorer wetting in probe tack measurements and lower lap-shear adhesion compared with CBMA- and MXDA-based systems. Lap-shear testing was carried out on stainless steel, oak wood, HDPE, and PMMA substrates and was strongly influenced by both the substrate

nature and the balance between soft and hard bisCC segments. In particular, the best performance was achieved on polar substrates (stainless steel and wood) and for formulations based on mixtures of PPGdiCC and RdiCC with a higher content of the latter. The PHU hot-melt adhesives also displayed remarkable thermoreversibility, with similar or even improved lap-shear strength values after several debonding-rebonding cycles. Notably, increasing the application temperature improved the dynamic adhesive properties of all PHU formulations, leading more often to fibrillation and better substrate wetting in probe tack measurements and higher adhesion in lap-shear testing (increased from 2.5–3 MPa at 80 °C to 7 MPa at 100 °C). Similar trends were observed in SAFT and shear resistance measurements, where higher service temperatures and creep resistance were achieved by increasing RdiCC content and application temperature. In particular, for the best-performing formulation evaluated at different application temperatures, the service temperature and creep resistance increased from 52 ± 2 to 59 ± 1 °C and from 196 ± 32 to 371 ± 18 min, respectively. Finally, the authors demonstrated that partial crosslinking through the incorporation of small amounts of epoxy resin could enhance the service temperature of the adhesives while preserving their reversible bonding capability.

A similar approach based on hot-melt processing was reported by Nair et al., who investigated the synthesis and adhesive behavior of thermoplastic PHUs derived from a vanillin-based bisCC (DC) and various aliphatic diamines (Scheme 2.20).³⁶⁸



Scheme 2.20 Synthesis of vanillin-derived PHUs. Adapted from Nair et al.³⁶⁸

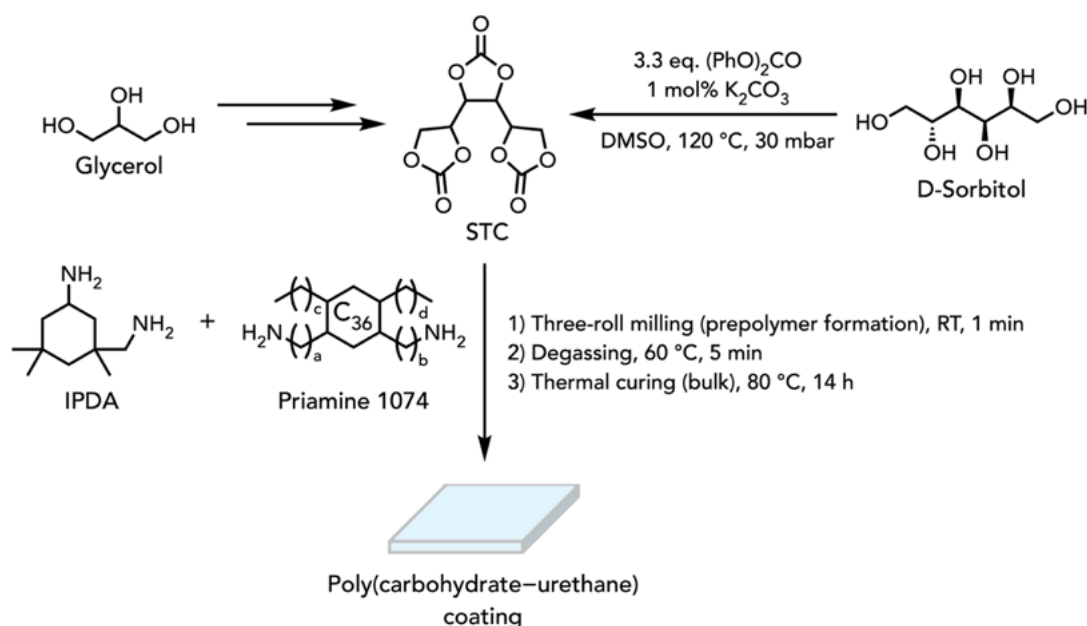
The polyaddition was optimized in *N*-methyl-2-pyrrolidinone (NMP) at 80 °C for 24 h under an inert atmosphere, as higher temperatures led to side reactions and decreased molecular weight. Under the optimized conditions, amorphous PHUs with M_n ranging from 2,500 to 11,100 g mol⁻¹ were obtained after precipitation in diethyl ether, depending on the diamine chain length. Both PHU flexibility and thermal stability increased when longer-chain diamines were used, leading to lower T_g values (from 42 to 28 °C) and higher $T_{\text{deg10\%}}$ values (from 180 to 273 °C). For adhesive application, the materials were processed in the molten state by heating at 80 or 120 °C for 30 min, depending on their processability. Lap-shear tests performed on aluminum and stainless-

steel substrates revealed a strong dependence of adhesion performance on bonding temperature, molecular weight, and diamine structure. Notably, the highest adhesion strength was obtained with the polymer characterized by the highest molecular weight and processed at 120 °C, which displayed average lap-shear strengths of 1.65 MPa on aluminum and 2.24 MPa on stainless steel. In contrast, lower-molecular-weight systems processed at 80 °C exhibited markedly lower strengths (up to 0.05 ± 0.01 MPa on aluminum and 7.1 ± 1.9 kPa on stainless-steel). Failure analysis predominantly showed cohesive failure, indicating that bulk mechanical properties rather than interfacial adhesion governed joint performance. Moreover, comparable shear strength values were retained after debonding-rebonding cycles, highlighting the repeatable adhesive capability of the vanillin-based PHUs.

While the solvent-free systems described above reported urethane formation or adhesive application at temperatures of 80 °C or below, their results highlighted improved performance when higher curing or processing temperatures were employed. In contrast, Mülhaupt et al. reported a solvent-free poly(carbohydrate-urethane) thermoset system in which efficient curing could already be achieved under mild conditions, leveraging the high reactivity of sorbitol tricarboxylate (STC) (Scheme 2.21).³⁶⁷ To obtain STC while avoiding the difficulties associated with direct carbonatization of saccharides and subsequent purification of the products, two synthetic approaches were developed: transesterification of diphenyl carbonate with sorbitol and a multi-step synthesis from acrolein, which is industrially available by glycerol dehydration. The resulting polyCC, a crystalline compound with a melting temperature of 230 °C and poor solubility in nonpolar media, was reacted with Priamine 1074 to obtain liquid prepolymers fully miscible with other amine hardeners. Proper mixing of STC and Priamine was achieved using a three-roll mill at RT for 1 min, which destroyed STC crystalline structure and enabled mixture homogenization. The resin was then degassed at 60 °C for 5 min, cast into a mold, and cured at 80 °C for 16 h. The balance between rigid and flexible segments was further tailored by curing STC with different blends of Priamine 1074 and isophorone diamine (IPDA). Higher IPDA content led to an increase in the T_g of the resulting materials from 29 to 60 °C, while the mechanical behavior changed from highly flexible and soft to hard and brittle. Correspondingly, the Young's modulus increased from 12.0 ± 1.0 to 630 ± 40 MPa and the elongation at break decreased from $250 \pm 10\%$ to $0.30 \pm 0.03\%$. In contrast, all the thermosets showed the same thermal stability, with an onset degradation temperature of 190 °C. Poly(carbohydrate-urethane)s prepared by curing STC prepolymer with a blend of 40 mol % IPDA and 60 mol % Priamine 1074 were applied onto a glass substrate using a

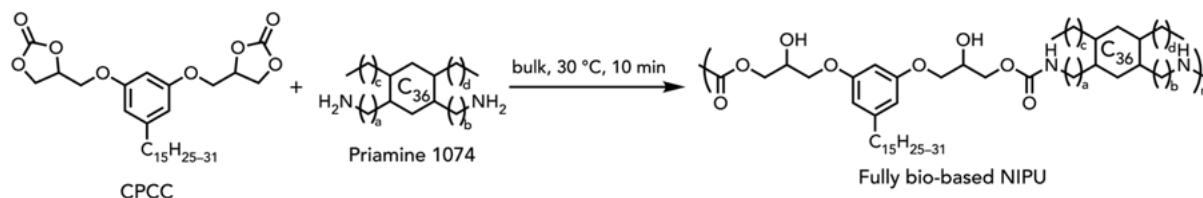
Chapter 2: Theoretical background

coating knife and cured at 80 °C for 14 h. The resulting coatings were fully transparent, colorless, and hydrophobic, displaying a water contact angle of 101°.



Scheme 2.21 Synthesis of poly(carbohydrate-urethane) coatings from glycerol- and sorbitol-derived STC. Adapted from Mülhaupt et al.³⁶⁷

As opposed to all the previously discussed studies reporting moderate thermal treatment during curing or application, a recent study by Wang and Jin et al. described the synthesis of fully bio-based NIPU adhesives at ambient temperature.³⁷³ CNSL-derived cashew phenol cyclic carbonate (CPCC) was reacted with Priamine 1074 at 30 °C for 10 min under solvent- and catalyst-free conditions, yielding PHU adhesives with high thermal stability and strong bonding performance at ultra-low temperatures (Scheme 2.22).



Scheme 2.22 Synthesis of fully bio-based NIPUs by polyaddition between Priamine 1074 and CNSL-derived CPCC. Adapted from Wang and Jin et al.³⁷³

PHUs with CC to amine group ratios of 0.7 : 1 (NIPU-0.7), 1 : 1 (NIPU-1), and 1.4 : 1 (NIPU-1.4) were prepared and characterized by thermal analysis and lap-shear adhesion testing. Among the tested materials, the equimolar formulation NIPU-1 displayed the highest thermal stability, with

$T_{deg5\%}$ and $T_{deg10\%}$ values of 318.76 and 440.76 °C, respectively. This behavior was attributed to the formation of higher-molecular-weight chains when stoichiometric proportions of CC and amine were employed. NIPU-1 also displayed a relatively low T_g (−18.24 °C), suggesting good flexibility and potential resistance to low temperatures. Based on these properties the PHU formulations were applied as adhesives on steel substrates and evaluated after cooling to −37 °C for 30 min. NIPU-1 exhibited superior bonding performance compared to NIPU-0.7 and NIPU-1.4, achieving a lap-shear strength of 7.78 MPa, whereas the other formulations reached 3.72 and 0.46 MPa, respectively. The effect of the application temperature was also investigated by testing NIPU-1 at −20 and −55 °C, but the lap-shear strength decreased to 5.95 and 0.61 MPa, respectively, indicating a practical lower temperature limit for adhesive use. Qualitative bonding tests were performed to glue a steel substrate to other materials (including ceramics, rubber, glass, wood, plastic, and aluminum sheets), demonstrating the broad applicability of the adhesive. Moreover, additional lap-shear tests were conducted on glass and plastic substrates at −37 °C, showing lower adhesion strengths (1.72 and 0.39 MPa, respectively).

To facilitate comparison across the different formulation strategies discussed in this section, the main characteristics of solvent-free NIPU systems reported for adhesive and coating applications are summarized in Table 2.3.

Overall, the studies discussed in this sections highlight the increasing interest in NIPU formulations for adhesive and coating applications under mild conditions. Significant progress has been made in the design of bio-based polyCCs and polyamines, as well as in formulation strategies enabling water-based and solvent-free processing. However, achieving both application and curing at room temperature remains challenging, and further efforts are required to overcome the remaining limitations.

Table 2.3 Comparative summary of solvent-free NIPU formulations reported in the literature for adhesive and coating applications.

Processing conditions	Application	Substrate	Adhesive and coating tests	Key application performance	Ref.
60–100 °C, 24 h	Coating	Aluminum	Gloss, crosshatch adhesion, solvent rub, impact	At 80 °C curing: up to ~120 gloss units, class 1 adhesion, and 200 MEK double rubs	370
RT–120 °C, 24 h	Wood adhesive	Oak wood, aluminum, ^a copper, ^a steel ^a	Dry lap-shear, wet lap-shear, ^a contact angle ^a	At 75 °C curing: dry bonding strength ~6–8 MPa	371
80 °C, 24 h (synthesis); 80 or 100 °C (application)	Hot-melt adhesive	Stainless steel, oak wood, ^b HDPE, ^b PMMA ^b	Probe tack, lap-shear, SAFT, static shear resistance	At 80 °C application: up to ~0.4 MPa tack strength, 2.5–3 MPa lap-shear strength, 52 ± 2 °C SAFT, 196 ± 32 min static shear resistance, and retained rebondability	369
80 °C, 24 h (synthesis); ^c 80 or 120 °C, 30 min (application)	Hot-melt adhesive	Aluminum, stainless-steel	Lap-shear	At 80 °C application: lap-shear strength up to 0.05 ± 0.01 MPa (aluminum) and 7.1 ± 1.9 kPa (stainless steel), retained rebondability	368
RT, 1 min + 60 °C, 5 min + 80 °C, 14 h	Coating	Glass	Scratch resistance, ^d contact angle	Transparent, scratch-resistant coating; 101° water contact angle	367
30 °C, 10 min (synthesis); –20 °C or –37 °C or –55 °C, 30 min (application)	Low temperature adhesive	Steel, glass, ^e plastic, ^e ceramics, ^d rubber, ^d wood, ^d aluminum ^d	Lap-shear	At –37 °C application: lap-shear strength up to 7.78 MPa (steel), 1.72 MPa (glass), and 0.39 MPa (plastic)	373

^a Tests performed only on samples cured at 90 or 105 °C. ^b Substrates used only in lap-shear testing (application temperature not explicitly specified). ^c Polymer prepared in NMP; adhesive applied as a hot melt. ^d No quantitative measurements reported. ^e Quantitative lap-shear tests performed at –37 °C only.

3 CHALLENGES AND LIMITATIONS

Despite the variety of NIPU production techniques available, their implementation in adhesive and coating systems remains constrained by several factors. The remaining challenges relate the inherent features of isocyanate-free chemistries, the physico-chemical properties of the resulting polymers, and the requirements of industrial production and end-use application. Understanding these limitations is essential to contextualize the current state of NIPU adhesive and coating technologies and to delineate the research directions that could help bridge the gap between academic studies and industrial adoption.

3.1 Technological challenges

One of the most fundamental limitations arises from the kinetics of NIPU-forming reactions. In contrast to the rapid and versatile isocyanate–alcohol addition reaction, which enables room-temperature curing within few hours, the synthesis of PHUs *via* aminolysis of polyCCs proceeds much more slowly under mild conditions. This polyaddition reaction, in fact, often requires elevated temperatures (typically higher than 80 °C) and extended reaction times, ranging from several hours to days to achieve complete curing. The transcarbamoylation method is equilibrium-limited and requires high temperatures and long reaction times to reach acceptable conversion, while the ROP of cyclic carbamates often suffers from incomplete conversion, especially under mild conditions. Among the techniques relying on the *in-situ* formation of isocyanates *via* rearrangement, the Lossen and Hofmann reactions are commonly carried out under milder thermal conditions, while the Curtius rearrangement typically requires higher temperatures, although the thermal decomposition of acyl azides can be performed successfully even at 60–80 °C.³⁷⁴ Elevated processing temperatures are undesirable in adhesives and coatings, as energy consumption, substrate sensitivity, and dimensional stability are critical factors. Conversely, slower reaction kinetics can not only reduce manufacturing throughput but also compromise adhesion by leaving residual monomers or oligomers that interfere with interfacial bonding and material integrity. Catalytic systems have been developed to accelerate the reaction, but they may introduce cost, toxicity, or stability concerns that conflict with the environmental and safety motivations behind NIPUs.

Closely related to these kinetic limitations are issues of processability and formulation performance. As discussed in Section 2.3.1.2, the high hydroxyl-group density of PHUs promotes extensive hydrogen bonding, resulting in elevated viscosity and increased hydrophilicity. This phenomenon can, on one hand, restrict applicability in outdoor or moisture-sensitive scenarios,

and, on the other hand, complicate the development of solvent-free adhesives and coatings, as high viscosities hinder substrate wetting, mixing homogeneity, and film formation. In conventional PU systems, viscosity can be adjusted through the selection of polyols and chain extenders; in NIPUs, by contrast, the pool of available reagents is still more limited, and a higher hydroxyl density is in some cases an intrinsic outcome of the polymerization mechanism. Depending on the application, higher processing temperatures or the use of solvents may be employed, although with the series of negative implications previously described. Additives or reactive diluents can provide partial solution, but often at the expense of mechanical performance or overall sustainability. For WNIPU formulations, key challenges include achieving higher solids content and improving mechanical performance and long-term water resistance, while the avoidance of organic solvents during the preparation process remains highly desirable.^{148,210,375} Moreover, beyond these process-related obstacles, an additional practical limitation lies in the limited suitability of synthetic routes requiring vacuum or an inert atmosphere, as such conditions not only complicate scale-up and increase operational costs, but are also impractical for most end-use applications.

3.2 Precursor and raw material supply

From a raw-material perspective, another major challenge lies in the limited availability of suitable precursors compared with well-established isocyanate chemistries. Conventional PU production benefits from optimized production techniques and supply chain developed over decades, with isocyanates and polyols manufactured at large scale from petrochemical feedstocks *via* cost-efficient processes. In contrast, many key NIPU monomers are produced in comparatively small volumes, often through multi-step syntheses that rely on less mature industrial technologies. In the step-growth polyaddition route, polyamines are not as widely accessible as diols or polyols, and the production of CCs is not yet established at industrial scale. These limitations are even more pronounced for other isocyanate- and phosgene-free approaches, which are currently still confined to gram- or pilot-scale.²¹⁰ This lower production scale translates not only into higher costs, but also into a reduced formulation flexibility. At the same time, NIPU chemistries have proven to be compatible with a broad range of bio-based reagents,^{210,376–378} and the integration of renewable building blocks represents an important opportunity to reduce dependence on fossil-derived raw materials. Achieving this transition will require advances in scalable synthesis routes and consistent quality of renewable feedstocks; nevertheless, significant research efforts are currently ongoing in this direction, including for adhesive and coating applications.^{210,379,380}

3.3 Regulatory limitations

In view of the evolving legislation regarding toxicity and hazards linked with PU production, the selection of more benign reagents, solvents, catalysts, and additives has a critical role in formulation design. Equally important are the atom economy of the process and the minimization of waste, which contribute determining the sustainability and feasibility of a synthetic route. Methods employing safe, non-toxic compounds and guaranteeing reduced occupational exposure limits and minimal waste are therefore preferable, not only to mitigate risks for operators and the environment, but also facilitate regulatory compliance and industrial adoption. Importantly, these principles apply not only to the final stage of NIPU synthesis but also to the upstream synthetic processes required to obtain the intermediates, monomers, and others, such as additives or catalysts. In this context, transcarbamoylation and polyaddition of CCs with amines appear as the most promising approaches for safer and more sustainable NIPU synthesis, albeit any new material and its production must undergo thorough safety evaluation (e.g., assessment of residual monomers, potential emissions, toxicity, and environmental impact) before being considered viable for commercialization.²¹⁰

3.4 Economic factors

Economic considerations add further layers of complexity. Although increasing regulatory scrutiny has raised awareness of the health and safety concerns associated with isocyanates, current legislation does not prohibit their use and allows conventional PU technologies to remain commercially viable provided that appropriate safety measures are implemented. As a result, manufacturers face limited immediate pressure to transition toward NIPU chemistry, particularly in the absence of clear economic incentives. Consequently, any alternative technology must not only match the performance of established PU systems but also justify the additional costs and risks associated with its adoption. As outlined above, raw material supply, price, and consequently scalability, further constrain the widespread use of NIPUs. Limited feedstock availability translates into higher costs and therefore restricts the potential for market introduction, especially in adhesives and coatings, which are typically cost-sensitive markets. Moreover, the introduction of a new technology is associated with substantial risks and costs for manufacturers. Beyond product innovation itself, such a change often requires adjustments in production facilities, personnel re-training, and extensive qualification and certification procedures, all of which demand time and financial investment and thus carry economic risks. Not only producers, but also buyers may be reluctant to switch from established to new technologies, even if they comply with regulations and meet performance specifications at

competitive costs. Unless a new product offers a clear and significant advantage in performance, price, or both, well-established alternatives are often preferred both in industrial sectors, where reliability and cost are critical, and in retail markets, where consumer habits and brand familiarity strongly influence purchasing decisions.

3.5 Academia–industry misalignment

Finally, an additional challenge for NIPU adhesives and coatings arises from the limited focus of academic research on real-world manufacturing processes and applications. In many cases, innovations are developed without the technological tools, process guidelines, or standardized performance assessment methods necessary for implementation. The frequent misalignment between laboratory-scale academic research and industrial R&D strategies hampers knowledge transfer and makes it difficult to assess the true potential of a given innovation, preventing the academic community from developing solutions with tangible and meaningful impact.

3.6 Critical assessment of current bottlenecks

Viewed as a whole, the challenges discussed above do not contribute equally to the limited industrial adoption of NIPU technologies.

Among the technological barriers, the limited availability of highly reactive precursors, the comparatively slow kinetics of most NIPU-forming reactions, and the resulting limitations in molecular weight build-up and processability appear to be among the most intrinsic, as they originate directly from the underlying chemistry. Consequently, the development of scalable precursors and faster reaction kinetics would likely have a particularly large impact, as they could simultaneously alleviate several interconnected challenges related to cost, processing, and material performance.

Issues related to process safety and associated regulatory constraints are not necessarily intrinsic to NIPU chemistry itself and, in many cases, constitute part of the motivation for developing isocyanate- and phosgene-free alternatives. Likewise, challenges linked to production scale are largely associated with the current level of industrial maturity and may become less critical as manufacturing capacity and supply chains develop.

Economic factors, on the other hand, appear to be at least as influential as the main technological barriers. In particular, the relatively limited industrial investment in alternative PU technologies, which is permitted under the current regulatory framework, may contribute significantly to the slower development of scalable production routes and commercially viable precursors. Comparatively, the disconnect between academic research and industrial needs

appears to play a secondary role, although it can still delay the translation of promising laboratory-scale innovations into commercially viable technologies.

Overall, the transition towards more sustainable PU production routes requires not only advances in chemistry and process engineering, but also broader changes in industrial priorities, regulatory incentives, and market drivers. While addressing these issues requires coordinated, cross-sectoral efforts, the prioritization of sustainable formulation strategies and application-oriented innovations represents an essential step towards facilitating the industrial implementation of NIPU technologies.³⁸¹

4 AIM OF THIS WORK

This thesis aims to develop solvent-free and waterborne NIPU formulations for adhesive and coating applications, while addressing key limitations inherent to the CC aminolysis route and maintaining sustainability as the central driver for the proposed synthetic strategies.

The research carried out to advance these objectives is presented in Chapter 5 and organized into four subchapters, each corresponding to a distinct research project:

- Chapter 5.1, “Sustainable functionalization of water-soluble polyamines for thermoset coating applications”, investigates the use of water as the sole reaction medium for preparing waterborne NIPU thermosets under mild conditions and without the need for emulsifiers. Building on recent reports of 2K systems based on the rapid aminolysis of polyCCs by water-soluble polyamines, this work aimed to obtain 1K waterborne formulations through a strategy that could be generalized to bio-based water-soluble polyamine precursors. To this end, the post-polymerization modification of PVAm with a CC bearing an additional reactive functional group was examined, with the aim of subsequently exploiting the introduced functionality for crosslinking the grafted polymer and producing PHU thermosets suitable for coating applications.
- Chapter 5.2, “Solvent-free synthesis of room-temperature curable nonisocyanate polyurethane adhesives and coatings”, describes the first example of solvent-free NIPUs produced from poly α CCs at ambient conditions, building upon the recent development of a highly reactive, liquid bis α CC monomer. Following the identification of suitable liquid polyamine co-reagents, the project focused on designing 2K solvent-free NIPU thermoset formulations that cure at room temperature, investigating their chemical structure and curing kinetics, and evaluating their thermomechanical properties and solvent resistance. A central objective was the assessment of adhesive and coating performance before and after incorporation of additives, along with benchmarking against commercial solvent-free PU products.
- Chapter 5.3, “Development of solvent-free PU adhesives and coatings: performance comparison with NIPUs”, focuses on industrial formulation development and highlights the differences between conventional PU systems and more innovative NIPU approaches. As developing scientific innovations with real-world applicability requires direct insights into industrial practices, an industrial secondment was carried out at COP Chimie™, a french company specialized in polymer-based components for orthopaedic devices. The work targeted the preparation of solvent-free, room-temperature-curable PU

formulations, starting from mixtures originally developed for prosthetic applications that were subsequently reformulated and optimized for adhesive and coating use. In addition to this formulation effort, a key target was to compare the performance of these PU systems with the solvent-free NIPU formulations developed in Chapter 4.2, thereby providing a direct assessment of PU versus NIPU performance.

- Chapter 5.4, “Novel fatty acid-derived polyamine: a renewable crosslinker for NIPUs”, addresses one of the major obstacles to the large-scale adoption of NIPU technologies based on CC aminolysis: the limited availability of suitable polyamines, particularly tri- or higher-functional amines derived from renewable resources that could serve as crosslinkers in thermoset formulations. To overcome this bottleneck, the study targeted the synthesis of a fully bio-based triamine with a low melting point, intended for incorporation into solvent-free NIPU adhesive and coating formulations. The synthetic route was designed to adhere as strictly as possible to the principles of green chemistry while achieving the required physical properties and high yields.

Finally, Chapter 6, “Conclusion and outlook”, presents a concise summary of the findings obtained throughout the thesis, contextualizes them within the trends shaping the future of NIPU technologies for adhesives and coatings, and outlines potential directions for future research.

5 RESULTS AND DISCUSSION

5.1 Sustainable functionalization of water-soluble polyamines for thermoset coating applications

5.1.1 Introduction

Among the various techniques available for synthesizing functional polymers, the post-polymerization modification stands out as an attractive strategy for introducing new chemical groups into a macromolecule, provided that reactive sites are present in its structure and high conversions can be achieved.³⁸² This approach is a powerful tool for developing polymers with tailored properties that cannot be obtained by direct polymerization of the corresponding functional monomers, for instance if the desired functional groups are intolerant to the polymerization conditions.

Due to the presence of a large number of reactive amino groups, several high-molecular-weight polyamines, such as chitosan, PVAm, PEI, poly(allylamine) (PAAm), or poly(amidoamine)s (PAMAMs) readily undergo chemical modification and can be covalently coupled to surfaces, small molecules, or oligomers.^{330,383–386} The high reactivity, tunable derivatization, and broad versatility of these polyamines have been exploited in a wide range of applications, including materials functionalization and composite production,^{386–393} synthesis and delivery of bioactive compounds,^{394–397} removal of contaminants,^{398–400} etc. These same attributes have also made high-molecular-weight polyamines attractive precursors for the design of innovative polymer families, including NIPUs obtained *via* polyaddition with polyCCs. Although the aminolysis of CCs with such amine-rich polyamine precursors has commonly been performed under solvent-free conditions^{401–404} or in organic solvents,^{329,330,405–407} waterborne formulations using water as the reaction medium have also been reported.^{235,236,408}

In particular, several studies have demonstrated that the aminolysis of CCs can be efficiently carried out in aqueous media under mild conditions by carefully adjusting the solution pH. Early work showed that polyaddition between water-soluble polyamines and CCs can proceed in water at room temperature, provided that the amine is maintained in its deprotonated form to enhance nucleophilicity while limiting carbonate hydrolysis.²³⁵ Building on this concept, subsequent studies expanded the scope of waterborne PHU systems by employing hydrosoluble polyCCs, enabling the formation of a wide range of hydrogels with tunable properties directly in water and under catalyst-free conditions.²³⁷ More recently, such strategies have been extended to functional coatings and hydrogels prepared from waterborne formulations at room temperature,

where rapid crosslinking and high performance can be achieved by optimizing parameters such as pH and precursor structure.²³⁶ These studies demonstrated that rapid aminolysis can be achieved at room temperature in aqueous conditions, enabling 2K formulations for hydrogels or coatings. However, the strategies described are inherently incompatible with 1K systems, which must be supplied as a single, ready-to-use component without any mixing before application.

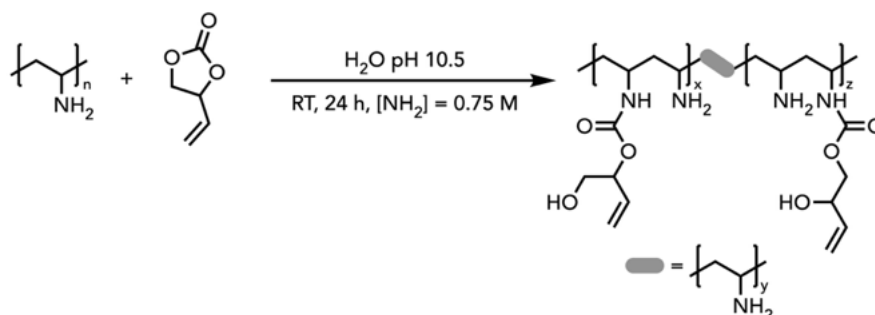
This work reports a fully aqueous route for the preparation of waterborne 1K PHU formulations based on the post-polymerization modification of PVAm with a monofunctional CC. The reagent molar ratio was varied to investigate its influence on the functionalization efficiency and the resulting structural and thermal properties of the functional polymers. Subsequent curing afforded thermoset coatings and freestanding films, which were evaluated in terms of hydrolytic stability, composition, crosslinking kinetics, thermal behavior, and mechanical performance.

5.1.2 Results and discussion

5.1.2.1 Post-polymerization functionalization of PVAm

PVAm was selected as the reference substrate for investigating the functionalization of water-soluble polyamines with CCs, as the reaction of PVAm with CCs under mild aqueous conditions is well established, and optimal reaction conditions had already been identified in similar studies with polyCC reagents. In particular, for PVAm, pH 10.5 has been shown to provide an optimal balance between reaction rate and CC hydrolysis.²³⁶ Vinyl ethylene carbonate (VEC) was selected as the CC co-reagent due to the presence of double bonds in its structure, which could be exploited for subsequent crosslinking to produce PHU thermosets.

The functionalization of PVAm with VEC, illustrated in Scheme 5.1, was investigated at three amine-to-cyclic-carbonate molar ratios ($\text{NH}_2\text{:CC}$ of 4:1, 2:1, and 1:1) to assess the aminolysis efficiency across different stoichiometries. The purified PHUs were then characterized by ^1H -NMR spectroscopy, TGA, and DSC to evaluate their composition and thermal properties, which are summarized in Table 5.1.



Scheme 5.1 Post-polymerization functionalization of PVAm.

Table 5.1 Linkage selectivity and thermal properties of PHU graft.

Entry	NH ₂ :CC ratio	PHU graft	Converted amines (mol%)	Urethane linkages (mol%)	T _{deg10%} (°C) ^a	T _g (°C) ^b
1	4:1	G1	28	22	189	121
2	2:1	G2	49	44	197	118
3	1:1	G3	53	51	186	121

^a Determined by TGA at 10% mass loss after water desorption, heating the sample at 10 °C/min.^b Determined by DSC using the second heating cycle, from -80 °C to 160 °C at 10 °C/min.

In this system, CCs may remain unreacted, undergo hydrolysis, or react with amino groups to form urethane linkages, which can further undergo intramolecular aminolysis to yield cyclic urea and a glycol derivative, as illustrated in Figure 5.1.^{409,236} This side reaction may also occur between different macromolecular chains, leading to intermolecular crosslinking. However, at the NH₂:CC ratios employed in this work, gel formation was not observed and the polymer remained fully soluble in water.

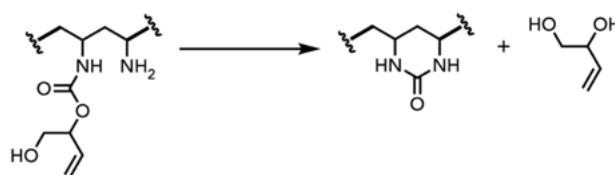
**Figure 5.1** Side reaction in the functionalization of PVAm: intramolecular urethane aminolysis.

Figure 5.2 shows stacked ¹H-NMR spectra in D₂O (pH 13) of the purified NIPU grafts **G1-G3**, obtained at different NH₂:CC ratios, focusing on the chemical shift region of the backbone CH₂ signal (at 1.1–1.9 ppm), the pristine PVAm CH signal (at 2.7–3.4 ppm), and the side-chain vinylene CH signal (at 5.8–6.0 ppm). As a representative case, **G2** (NH₂:CC = 2:1) was characterized by ¹H-NMR, gradient-selected ¹H–¹H correlated spectroscopy (COSY), and phase-edited ¹H–¹³C heteronuclear single quantum coherence (HSQC) (spectra recorded at pH 10.5 shown in Figures 7.1, 7.2, and 7.3).

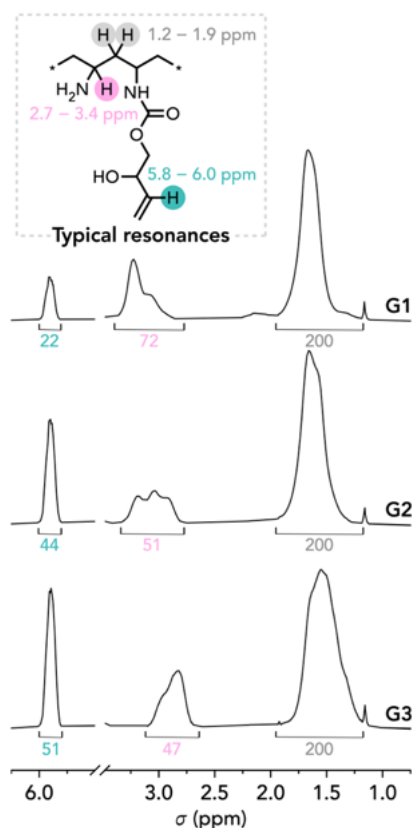


Figure 5.2 Stacked ^1H -NMR spectra of the purified **G1** (top), **G2** (middle), and **G3** (bottom), showing characteristic signals of the backbone CH_2 , the pristine PVAm CH , and the side-chain vinylene CH . Full NMR spectrum with peaks assignments of **G2** is provided in Figure 7.1 as a representative example.

The interphase reaction between PVAm and VEC, the latter being insoluble in water and therefore dispersed in the reaction medium, consumed most of the CC groups when an excess of amino groups was employed, as evidenced by the high fractions of converted amines observed for **G1** (28 mol%, entry 1 in Table 5.1) and **G2** (49 mol%, entry 2), corresponding to full consumption of VEC. In contrast, under equimolar $\text{NH}_2\text{:CC}$ conditions (**G3**, entry 3), only 53 mol% of the amines reacted, and a substantial portion of VEC either remained unreacted or underwent hydrolysis to the corresponding glycol. This result was attributed to the increased steric hindrance associated with pendant hydroxy-urethane groups at higher functionalization degrees. The selectivity between urethane and urea linkages also depended on the reagent ratio: the fraction of amine functionalities converted to urethane linkages increased with the amount of CC used, yielding up to 51% urethane out of 53% converted amines under equimolar conditions (entry 3). Overall, **G1** and **G2** ($\text{NH}_2\text{:CC}$ ratios of 4:1 and 2:1, respectively) displayed the highest functionalization efficiencies and were selected for the preparation of the coatings. The IR spectra of these two functional polymers confirmed their linkage selectivity, showing a higher fraction of urethane

relative to urea functionalities, as illustrated in Figure 7.4. Complementary $^1\text{H-NMR}$ measurements demonstrated that a stable degree of functionalization was achieved within 60 min.

5.1.2.2 Thermal characterization of the functionalized PHUs

The thermal stability of the functionalized polymers, assessed by TGA, did not depend on the degree of functionalization, and the degradation temperature at 10% mass loss ($T_{\text{deg}10\%}$) ranged between 186 °C for **G3** (Table 5.1, entry 3) and 197 °C for **G2** (entry 2). After an initial weight loss attributed to the evaporation of absorbed water, **G2** (TGA and dTGA curves are shown as a representative example in Figure 5.3) and **G3** displayed a multistep degradation pattern, with a second degradation step corresponding to the decomposition of the side chains (starting around 160 °C) and a third weight loss associated with degradation of the backbone (between approximately 350 and 480 °C). In contrast, **G1** exhibited a more continuous degradation profile, likely reflecting overlapping side-chain and backbone decomposition processes at its low degree of functionalization. The TGA curves of all samples are reported in Figure 7.5.

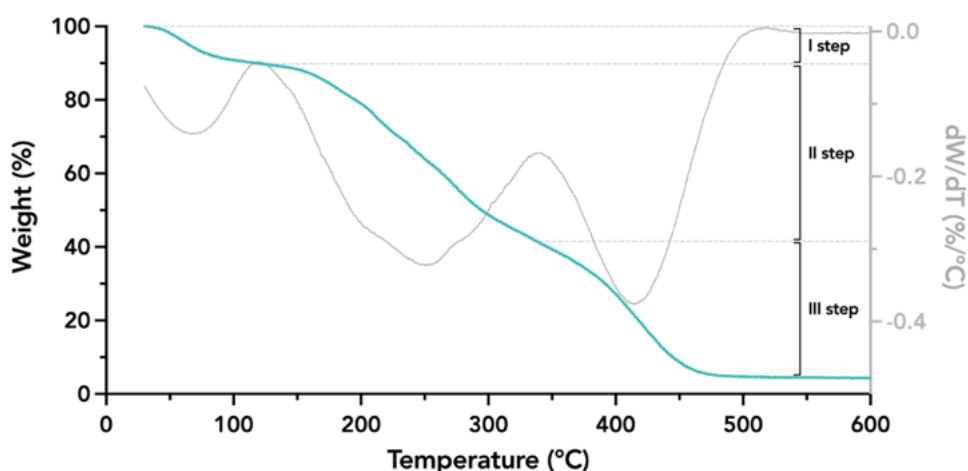
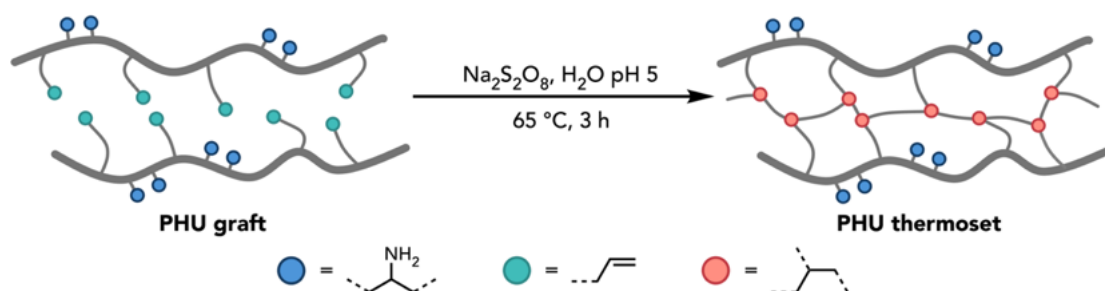


Figure 5.3 Representative TGA (teal) and dTGA (grey) curves of **G2**, with the main degradation steps highlighted on the right side of the figure.

DSC analysis of the amorphous polymers showed that the glass transition temperature (T_g) was significantly higher than that of unmodified PVAm ($T_g = 46$ °C) and rather independent of the degree of functionalization, with values of 121 °C (Table 5.1, entry 1), 118 °C (entry 2), and 121 °C (entry 3) for **G1**, **G2**, and **G3**, respectively. The DSC curves of all samples are reported in Figure 7.6.

5.1.2.3 Development of a waterborne NIPU thermoset under mild conditions

The alkene functionalities present in the side chains of the waterborne functional PHUs **G1** and **G2** were exploited to prepare the corresponding thermosets **T1** and **T2** via radical crosslinking under mild thermal conditions (Scheme 5.2). After confirming the stability toward urethane aminolysis of the functional PHUs under the activation conditions, sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) was selected as the thermal radical initiator owing to its high water solubility, relatively low activation temperature, and low cost.



Scheme 5.2 Reaction scheme for the radical crosslinking of waterborne functional PHUs into thermosets.

Following crosslinking, **T2** remained colourless, whereas **T1** appeared yellowish, suggesting the occurrence of side reactions (Figure 7.7). IR analysis confirmed this hypothesis, indicating extensive urea formation for **T1**, consistent with aminolysis of urethane linkages at its lower degree of functionalization (Figure 5.4, full spectra are provided in Figure 7.8). Gel content (GC) measurements in methanol were comparable for both thermosets ($92 \pm 1\%$ for **T1** and $93 \pm 1\%$ for **T2**; entries 1 and 2 in Table 7.1). However, GC values determined in water revealed a markedly higher hydrolytic resistance for **T2** ($\text{GC}_{\text{H}_2\text{O}} = 88 \pm 2\%$) compared to **T1** ($\text{GC}_{\text{H}_2\text{O}} = 58 \pm 5\%$), whose polymer structure and crosslink density were compromised by urethane aminolysis. Because this side reaction could not be mitigated even under photoinitiated conditions, the formulation **T1** was excluded from further characterization and application.

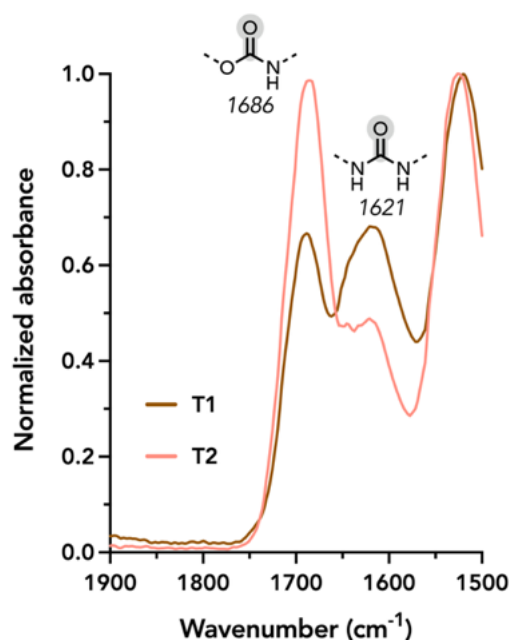


Figure 5.4 Overlay of infrared spectra for T1 (brown) and T2 (coral), highlighting the characteristic urethane and urea bands in the carbonyl stretching region.

5.1.2.4 Rheological, thermal, and mechanical characterization of the PHU thermoset

The thermoset formulation **T2** was processed to yield clear, transparent coatings (Figure 5.5) and freestanding films, whose crosslinking kinetics and thermo-mechanical properties were evaluated by rheology, tensile testing, TGA, and DSC. The resulting properties are summarized in Table 5.2.

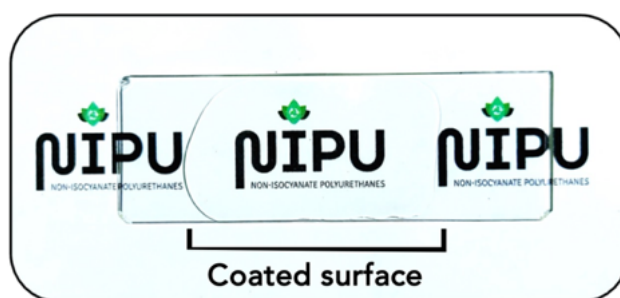


Figure 5.5 PHU coating sample produced from T2.

Table 5.2 Gel time, thermal characteristics, and mechanical properties of the PHU thermoset formulation T2.

PHU thermoset	Gel time (min) ^a	$T_{deg10\%}$ (°C) ^b	T_g (°C) ^c	E (GPa) ^d	σ_u (MPa) ^e	ε_f (%) ^f
T2	14	216	/	1.04 ± 0.02	22.8 ± 0.5	3.2 ± 0.4

^aCalculated without considering 1 min to load the sample into the rheometer. ^bDetermined by TGA at 10% mass loss, heating the sample at 10 °C/min. ^cDetermined by DSC using the second heating cycle, from -80 °C to 160 °C at 10 °C/min. ^d E : Young's modulus. ^e σ_u : ultimate tensile strength. ^f ε_f : fracture strain.

The rheological behavior of the formulation during crosslinking was monitored by following the evolution of storage (G') and loss (G'') moduli over time, allowing identification of the gel point after approximately 14 minutes (Figure 7.9). This relatively short gel time was compatible with the high concentration of pendant double bonds in the graft, which enabled rapid network formation. Compared to the corresponding polymer **G2**, the cured thermoset **T2** showed no detectable mass loss associated with water desorption in the initial stage of the TGA curve (Figure 7.10), consistent with a substantially reduced moisture uptake in the highly crosslinked network, although very low water content or broad release profiles cannot be excluded. Furthermore, **T2** exhibited enhanced thermal stability, with a $T_{deg10\%}$ of 216 °C, reflecting its tightly crosslinked polymer architecture. The high crosslink density of the thermoset also resulted in a very small change in heat capacity at the glass transition, which prevented the appearance of a clear T_g signal in the DSC thermogram (Figure 7.11).

Mechanical characterization revealed an elastic modulus (E) of 1.04 ± 0.02 GPa, an ultimate tensile strength (σ_u) of 22.8 ± 0.5 MPa, and a fracture strain (ε_f) of 3.2 ± 0.4 %, indicating that the thermoset behaved as a rigid, brittle, and tensile-resistant material (Figure 7.12).

5.1.3 Conclusions

With the aim of developing a more sustainable and facile route to waterborne NIPU coatings under mild conditions, the post-polymerization functionalization of PVAm with VEC was investigated by ¹H-NMR and IR spectroscopy. The aminolysis conditions were optimized at room temperature by varying the amine-to-cyclic-carbonate molar ratio and evaluating its impact on functionalization efficiency and extent of side reactions. The functional PHU obtained at an equimolar NH₂:CC ratio (**G3**) exhibited the highest selectivity toward urethane formation, although only 53 mol% of the amines reacted, in line with the strong steric hindrance generated by the pendant chains. Conversely, the functional PHUs prepared at NH₂:CC ratios of 4:1 and 2:1

(**G1** and **G2**, respectively) displayed lower urethane selectivity but higher functionalization yields: 28 mol% and 49 mol% of amines reacted, of which 22 mol% and 44 mol% formed urethane linkages, respectively. The polymer composition of these two functional PHUs was confirmed by IR analysis, while additional NMR experiments revealed that a stable functionalization degree was achieved within 60 minutes. The PHU grafts exhibited similar thermal stability and macromolecular mobility, with $T_{\text{deg10\%}}$ and T_g values ranging from 186 to 197 °C and from 118 to 121 °C, respectively. Thermally initiated radical crosslinking of **G1** and **G2** at 65 °C yielded the corresponding thermosets **T1** and **T2**. Because **T1** contained a markedly higher fraction of urea linkages and exhibited lower gel content, it was discarded, and the colourless formulation **T2** was selected for further characterization. It showed rapid gelation (gel time of 14 min), enhanced thermal stability ($T_{\text{deg10\%}} = 216^\circ\text{C}$) compared with its PHU precursor, and no detectable glass transition, suggesting the formation of a densely crosslinked network. Tensile testing demonstrated the stiff, strong, and brittle nature of the thermoset ($E = 1.04 \pm 0.02$ GPa, $\sigma_u = 22.8 \pm 0.5$ MPa, $\varepsilon_f = 3.2 \pm 0.4$ %), confirming the formation of a highly rigid three-dimensional network. Overall, the approach presented in this work provides a generalizable and straightforward strategy for polyamine functionalization and crosslinking relying on rapid, mild, and fully aqueous reactions, ultimately yielding 1K waterborne NIPU formulations curable upon application of a simple external stimulus. The methodology could be adapted to other water-soluble or water-dispersible polyamines derived from bio-based feedstocks, expanding the scope of accessible formulations and further reducing the environmental footprint of the process. Moreover, the residual primary amines retained in the network could be exploited for applications such as metal-ion scavenging,^{410–413} antimicrobial activity,⁴¹⁴ or formaldehyde capture,²³⁶ thereby enabling the development of functional coatings for water treatment, antimicrobial protection, or indoor-air depollution.

5.2 NIPU adhesives and coatings from solvent-free formulations able to cure at room temperature

5.2.1 Introduction

Thanks to their intrinsically reduced health risks and their 100% solids nature, solvent-free formulations are particularly attractive in the field of adhesives and coatings, where end-consumer safety and product cost are key priorities. Moreover, the absence of solvents leads to reduced VOC emissions and, consequently, a lower carbon footprint, ultimately resulting in significantly improved environmental performance.

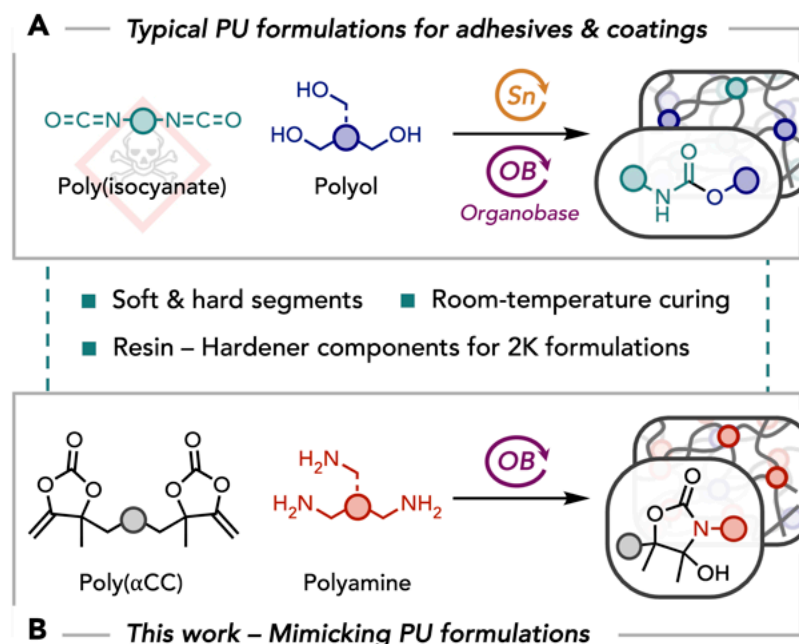
On the other hand, the production of solvent-free NIPU adhesives and coatings remains limited by the lack of highly reactive precursors in the liquid state. This limitation generally necessitates the application of a thermal treatment to ensure adequate processability and complete curing of the polymer network.^{242,361–367} The commonly employed 5-membered CC precursors exhibit low reactivity and therefore face significant limitations in replacing conventional isocyanate-based systems, especially in applications under ambient conditions.

To date, a promising example of fast-curing process giving access to PHU thermosets at rather low temperature was reported by Ritter et al. and relied on the use of the highly reactive triethylenetriamine crosslinker.⁴¹⁵ In that study, curing was performed at 40 °C; however, adhesive strength and coating performance were not evaluated. Efforts to overcome the low reactivity of PHU formulations without resorting to hybrid chemistries have focused on catalysis, the use of amines of high reactivity, and the design of more reactive CCs, including larger-ring systems, EWG group substituents on the ring, or unsaturated carbonates, as discussed in Section 2.3.1.5 of Chapter 2.^{240,259–261,266,270,272,373,416–420} Despite these attempts, efficient RT curing has not yet been demonstrated, particularly for adhesive and coating applications.

In contrast, CO₂-based α -alkylidene CCs display outstanding reactivity toward primary and secondary amines, leading to the formation of either hydroxyoxazolidones or oxo-urethanes, two new classes of isocyanate-free urethanes.²⁷⁴ Polymerizations involving bifunctional monomers have been shown to proceed at RT under catalyst-free conditions; however, these reactions always required the use of a solvent, as the CCs were solid compounds in most reported cases.^{276,277,281,421,422} As a result, these systems have been limited to the synthesis of linear poly(hydroxyoxazolidone) or poly(oxo-urethane) polymers and have never been applied to NIPU thermosets.

In this work, we report the preparation of novel NIPU adhesives and coatings from solvent-free formulations at RT, enabled by a highly reactive liquid bis α CC monomer. This approach mimicks

conventional PU chemistry, typically based on polyols, isocyanate hardeners, and catalysts (Scheme 5.3A), through an isocyanate-free strategy employing a bis α CC and polyamines (Scheme 5.3B). By selecting polyamines with different chemical structures, the gel time could be readily tuned: short gel times were obtained using short-chain, highly reactive polyamines, whereas longer gel times resulted from longer and more sterically hindered polyamines, thereby enabling the application in adhesive and coating formulations. The introduction of an organobase catalyst (DBU) and low-molecular-weight amine hardeners provided additional control over gel time and allowed to fine-tune the thermo-mechanical properties of the resulting polymers. Finally, the adhesive and coating performances of the developed formulations were systematically assessed and benchmarked against commercial PU products.



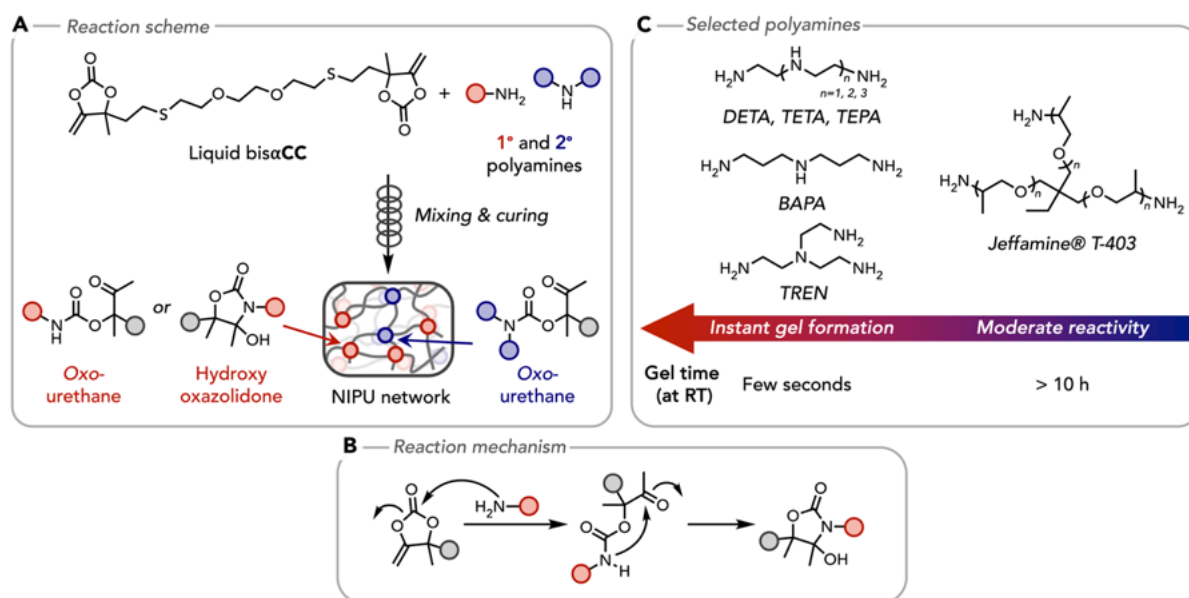
Scheme 5.3 Curing of solvent-free adhesives at room temperature: comparison of conventional PUs (A) and NIPU «mimic» formulations (B).

5.2.2 Results and discussion

5.2.2.1 Development of NIPU formulations: investigation of their curing and chemical structure

Recently, some of us reported the synthesis of a CO₂-sourced liquid bis α CC that was exploited for constructing polythiocarbonate networks at RT under solvent-free conditions.⁴²³ The monomer was synthesized with an overall isolated yield of 85%, following an up-scalable process that provided nearly 60 g of reagent in one batch. Herein, we evaluate its copolymerization with

various liquid polyamines to produce NIPU coatings and adhesives from a solvent-free formulation (Scheme 5.4A). It is important to note that the type of linkage formed by aminolysis of bis α CC depends on the type of amine used: secondary amines lead to oxo-urethane moieties *via* ring-opening, whereas primary amines yield hydroxy-oxazolidones through a subsequent spontaneous cyclization, the rate of which mainly depends on the steric hindrance of the amine (Scheme 5.4B).²⁷⁷ The commercially available polyamine crosslinkers tested, i.e. 3,3'-diaminodipropylamine (BAPA), tris(2-aminoethyl)amine (TREN), triethylenetetramine (TETA), TEPA, and diethylenetriamine (DETA) were very reactive toward bis α CC, leading to vitrification within seconds and without any catalyst, a too short timeframe not suitable for the preparation and application of homogeneous formulations to a substrate (i.e. for adhesive and coating applications). The polyetheramine T-403 (Jeffamine® T-403), characterized by a long PPG backbone and sterically more hindered primary amines, presented a more moderate reactivity and the formulation could easily be manipulated and applied onto substrates. The curing was slow at RT, i.e. the gel point was not reached after 10 h of reaction (Scheme 5.4C).



Scheme 5.4 Reaction scheme (A), mechanistic details (B), and substrate scope (C) for the screening of polyamine crosslinkers to be used in solvent-free NIPU formulations, with representation of possible linkages formed and formulation reactivity.

The conditions were therefore explored to shorten the gel time, notably by adding DBU – an organobase reported to efficiently catalyze the bis α CC aminolysis.^{276,277} Although curing at RT was targeted, we have also modulated the temperature to get some insight on its effect on the curing time. An equimolar ratio between amino and cyclic carbonate groups was used for all

further formulations, and the evolution of G' and G'' was followed over time in all reported conditions (Figure 7.13). Gel times, defined as the time required to reach the cross-over point between G' and G'' , are reported in Figure 5.6. Under catalyst-free conditions, the gel times decreased from > 10 h at RT to 96 min at 50 °C, and 27 min at 75 °C. To accelerate the curing at RT, DBU was added to the formulation, and the gel point was reached within 4.5 h at a content of 5 mol% (vs the total number of amino and cyclic carbonate groups). With the addition of DBU, the gel time could be tuned between 12 min and 96 min at 50 °C, and between 3 and 27 min at 75 °C.

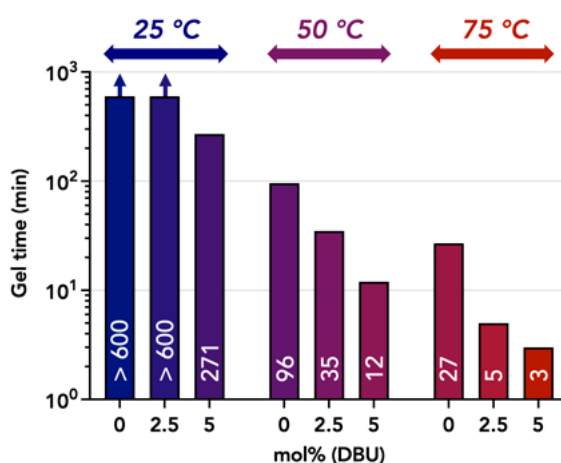


Figure 5.6 Gel times obtained at different temperatures and catalyst loadings for the bulk polymerization of bis α CC with Jeffamine T-403, calculated without considering 3 min to mix and load the sample to the rheometer.

The curing of the formulation at RT using 5mol% of DBU as catalyst was monitored using infrared spectroscopy (Figure 5.7, full spectra shown in Figure 7.14). The characteristic carbonyl band of the cyclic carbonate at 1822 cm^{-1} and the C=C stretching band of the exocyclic olefinic group at 1685 cm^{-1} both decreased as the reaction progressed, and disappeared below detection threshold after 72 h. Concurrently, the urethane carbonyl bands (1740 and 1716 cm^{-1}) became increasingly prominent, together with a broad O-H band at around 3400 cm^{-1} , suggesting the formation of hydroxyoxazolidone.

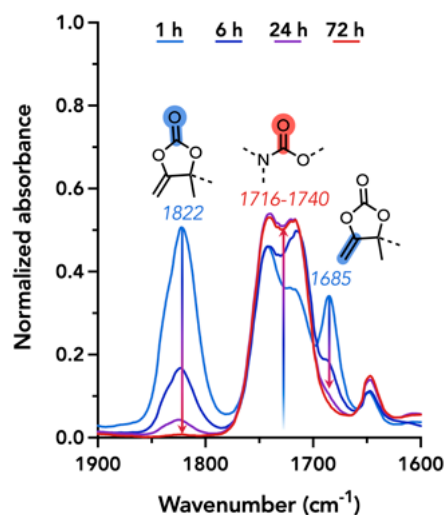
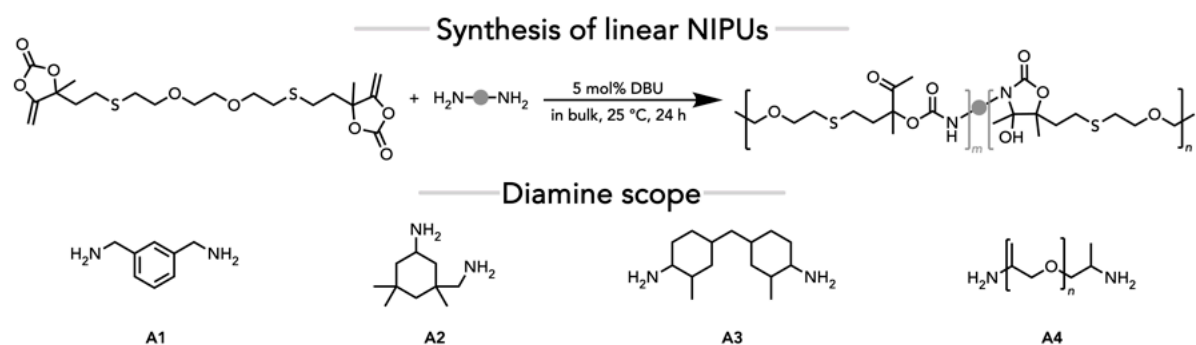


Figure 5.7 Evolution of characteristic infrared bands in the carbonyl stretching region.

The thermomechanical properties of conventional PU formulations are typically varied by altering the chemical structure of the selected monomers, especially the used polyols. In analogy, to mimic PU formulations containing both rigid and soft segments, we incorporated different diamines with varying lengths and rigidities in our formulations: benzylic (*m*-xylylene diamine, **A1**), cycloaliphatic (isophorone diamine **A2**; 4,4'-methylenebis(2-methylcyclohexylamine **A3**), and polyether (PPG average $M_n \sim 400$ g/mol, bifunctional equivalent of T-403, **A4**) diamines. In order to identify the nature of the linkages formed during curing the networks (oxo-urethane vs hydroxy oxazolidone)—that are expected to influence the network properties—, linear polymers were thus synthesized from the different diamines under the same conditions as the polymer networks (RT, neat, 5 mol% DBU, Scheme 5.5). The crude reaction mixtures were characterized by size exclusion chromatography (SEC). The purified linear polymers were characterized by NMR and by IR spectroscopy, as a point of comparison with the polymer networks, which cannot be dissolved in organic solvents for NMR characterization. The thermal properties of the polymers were assessed by TGA and DSC experiments. The polymer composition, molecular weight, and thermal properties are reported in Table 5.3.



Scheme 5.5 Reaction scheme and substrate scope for the synthesis of linear NIPUs from bis α CC.

Table 5.3 Linkage selectivity, molecular characteristics, and thermal properties of linear NIPUs obtained by polymerization of bis α CC with liquid diamines.^a

Entry	Diamine	Polymer	Hydroxy oxazolidone : oxo-urethane	M_n (g/mol) ^b	M_w (g/mol) ^b	$\bar{D}^b$	$T_{deg10\%}$ (°C) ^c	T_{dehyd} (°C) ^d	T_g (°C) ^e
1	A1	PA1	100 : 0	2,600	6,700	2.7	318	130	36
2	A2	PA2	89 : 11	1,800	4,100	2.3	307	142	59
3	A3	PA3	57 : 43	1,700	4,000	2.3	279	103	28
4	A4	PA4	100 : 0	6,100	16,700	2.7	297	144	-25

^a Conditions: bis α CC (1.0 mmol), diamine (1.0 mmol), bulk, 25 °C, 5 mol% DBU vs total NH_2 and CC groups, 24 h. ^b Determined on crude products by SEC in DMF/LiBr. ^c Determined by TGA at 10% mass loss after dehydration, heating the sample at 10 °C/min. ^d Determined by TGA, heating the sample at 2 °C/min. ^e Determined by DSC using the second heating cycle, from -40 to 120 °C at 10 °C/min (for PA4 the cycle started at -80 °C).

Figure 5.8 shows the overlaid 1H -NMR spectra of the purified polymers in DMSO- d_6 , focusing on the chemical shift region of the hydroxy-oxazolidone OH signal (at 5.5–6.3 ppm) and the linear urethane NH signal (at 7.1–7.5 ppm) (full 1H -NMR peaks assignments and ^{13}C -NMR spectra are provided in Figures 7.15–7.22). With **A1** and **A4**, the polymers presented the corresponding poly(hydroxy-oxazolidone) structures with all typical resonances. As **A4** can be considered a bifunctional equivalent of Jeffamine T-403 with similar reactivity, it is suggested that the polymer networks **PJ** are similarly mainly composed of hydroxy-oxazolidone linkages. The copolymerization of sterically hindered **A3** resulted in a 43 % content of oxo-urethane (Table 5.3, entry 3), in agreement with previous studies, demonstrating the presence of both linkages in polymers based on cycloaliphatic diamines.²⁷⁷ The less hindered **A2** only contained 11% of oxo-

urethane linkage, certainly due to the presence of a more accessible amine group (Table 5.3, entry 2).

The overlay of the IR spectra of the linear polymers (reported in Figure 7.23) showed that the position of the C=O stretching band depended on the diamine used. Moreover, the same double band as observed in **PJ** (Figure 5.7) also appeared in the spectra of **PA4**, despite the exclusive presence of hydroxy oxazolidone linkages in the polymer.

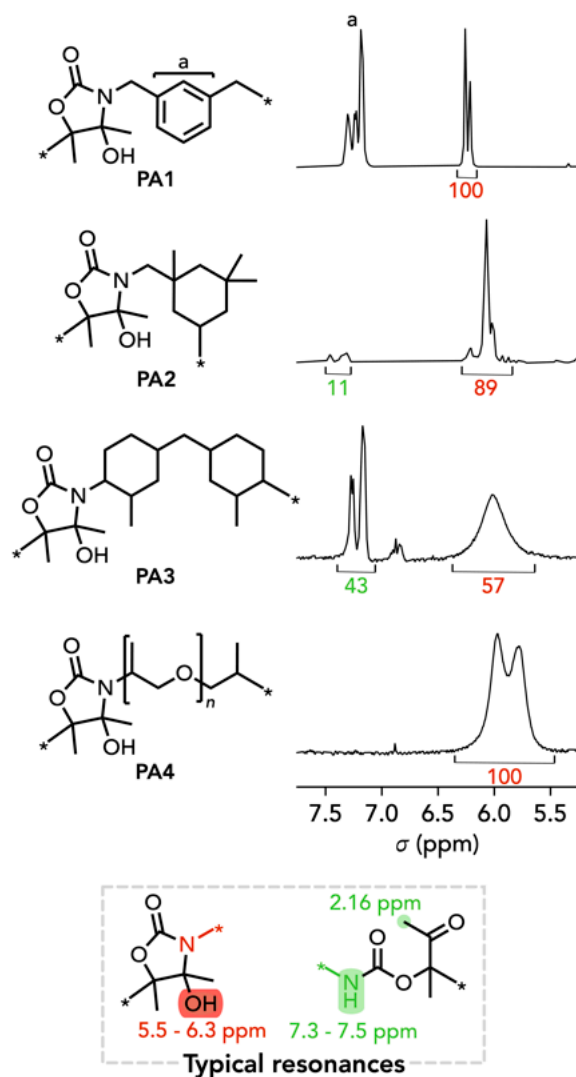


Figure 5.8 Stacked ^1H -NMR spectra showing characteristic signals of hydroxy oxazolidone and oxo-urethane linkages in pure linear NIPUs.

SEC characterization of the crude linear polymers showed a range of weight average molar masses (M_w) from 4.0 to 16.70 kg mol $^{-1}$ (Table 5.3, Figure 7.24). Although the molar mass of the different polymers could not be compared due to different chemical structures and thus hydrodynamic volumes, **PA2** and **PA3**, obtained from the most hindered diamines, displayed

comparable molar mass values. **PA4** presented the highest M_w and **PA1** an intermediate one. The dispersity ($\mathcal{D}$) values were overall consistent with the step-growth polymerization process.²⁷⁷ It must be noted that the polymerization media rapidly vitrified, reducing chain diffusion and therefore restricting the polymer molar mass.

In agreement with our previous data,^{282,424} the thermogravimetric analysis of purified NIPUs (Figures 7.25–7.28) showed the characteristic dehydration step of the hydroxy-oxazolidone moieties, starting between 100 and 145 °C (Table 5.3). The $T_{\text{deg}10\%}$ ranged between 279 °C (entry 3) and 318 °C (entry 1). The DSC curves of the polymers (Figure 7.29) displayed a broad array of glass transition temperatures, from -25 °C with the most flexible diamine **A4**, to 59 °C with the most rigid isophorone diamine **A2** (Table 5.3, entries 4 and 2). Polymers **PA1** and **PA3** exhibited intermediate T_g s of 36 and 28 °C, respectively (Table 5.3).

5.2.2.2 Preparation and characterization of NIPU adhesives and coatings

The structure of the primary diamines affected the NIPU structure and the linkage selectivity, that could be modulated from exclusive oxazolidone to a mixture of oxazolidone and oxo-urethane of different contents. We thus investigated the addition of these diamines to the bis α CC/Jeffamine T-403 formulation to modulate the properties of the NIPU thermoset. **A4** was not added as comonomer, as we targeted the introduction of more reactive and more rigid amines to the formulation. For each tested diamine, two formulations were prepared by varying the diamine/T-403 molar ratio from 1/4 to 1/3, while keeping the molar ratio of primary amine (NH_2) to cyclic carbonate (CC) groups constant, along with the catalyst loading relative to the total NH_2 and α CC groups.

Rheological behavior and IR characterization

To evaluate the effect of incorporating diamines on the curing rate, the evolution of the formulations' rheological behavior was investigated by monitoring changes in G' and G'' over time. The results of the study are reported in Table 5.4 and Figure 7.30.

Table 5.4 Gel time of crosslinked NIPUs obtained by curing formulations composed of bis α CC, Jeffamine T-403 and a diamine.^a

Entry	Diamine	Polymer	Diamine : triamine (n/n)	Gel time (min) ^b
1	/	PJ	0 : 1	271
2	A1	PJA1a	1 : 4	214
3		PJA1b	1 : 3	109
4	A2	PJA2a	1 : 4	438
5		PJA2b	1 : 3	217
6	A3	PJA3a	1 : 4	>600
7		PJA3b	1 : 3	258

^a Conditions: $\text{NH}_2/\alpha\text{CC} = 1$, bulk, 25 °C, 5 mol% DBU vs total NH_2 and αCC groups. ^b Calculated without considering 3 min to mix and load the sample since the start of the reaction.

Except for **PJA1a** (entry 2), formulations with a diamine to triamine ratio of 1:4 displayed a gel time longer than that of **PJ**, whereas those with a ratio of 1:3 exhibited a shorter gel time. This trend was attributed to the competing effects of the diamines on the gelation rate. On one hand, they reacted faster than Jeffamine T-403 and accelerated the polymerization and on the other hand, they reduced cross-linking density. Therefore, with **PJA2a** and **PJA3a** (entry 4 and 6), the lower cross-linking density compared to **PJ** resulted in slower gelation, while for **PJA1b**, **PJA2b**, and **PJA3b** (entry 3, 5 and 7), the diamines enhanced the polymerization rate, leading to quicker gelation. Additionally, the gel time followed the reactivity trend of the diamines: **A1** exhibited the fastest gelation, followed by **A2**, and **A3** displayed the slowest crosslinking. The IR analysis conducted after 3 days of RT curing revealed no variation in the band position of the carbonyl of urethane across the different formulations (Figure 7.31).

Swelling behavior, gel content and coating performance

The swelling behavior, gel content, thermal and mechanical properties, as well as the coating and adhesion performance of the cured 2K NIPU formulations were then assessed. To evaluate the performance and properties evolution over time, each analysis was carried out after 1 day and 7 days of curing at RT, and the results are summarized in Table 5.5, Table 5.6 and Table 5.7.

The equilibrium water content (EWC) and GC were determined for NIPU freestanding films, while NIPU coatings were characterized by water contact angle measurement (CA) and cross-cut adhesion test (CCA) (Table 5.5).

Table 5.5 Equilibrium water content, gel content and coating performance of crosslinked NIPUs obtained by curing formulations composed of bis α CC, Jeffamine T-403 and a diamine.^a

				After 1 d				After 7 d					
Entry	Diamine	Polymer	Diamine : triamine (n/n)	EWC (%) ^b	GC (%) ^c		CA (°) ^d	CCA ^e	EWC (%) ^b	GC (%) ^c		CA (°) ^d	CCA ^e
					H ₂ O	THF				H ₂ O	THF		
1	/	PJ	/	76 ± 1	97.3 ± 0.3	75 ± 1	65 ± 4	4B	86 ± 8	95.2 ± 0.6	79.5 ± 0.2	60 ± 2	5B
2	A1	PJA1a	1:4	102 ± 4	96.0 ± 0.6	65.1 ± 0.6	79 ± 4	4B	102 ± 8	92 ± 3	61 ± 1	68 ± 3	5B
3		PJA1b	1:3	111 ± 9	95.2 ± 0.8	62.2 ± 0.8	80 ± 2	4B	116 ± 9	94 ± 1	68 ± 1	74 ± 3	5B
4	A2	PJA2a	1:4	80 ± 1	97.3 ± 0.6	68 ± 2	69 ± 7	3B	100 ± 4	96.6 ± 0.3	73 ± 1	69 ± 2	4B
5		PJA2b	1:3	93 ± 9	96 ± 1	68 ± 2	75 ± 7	3B	112 ± 3	95.3 ± 0.4	70 ± 2	70 ± 3	4B
6	A3	PJA3a	1:4	55 ± 2	98.2 ± 0.2	72 ± 2	78 ± 3	4B	89 ± 3	95.6 ± 0.4	72.1 ± 0.3	68 ± 2	5B
7		PJA3b	1:3	65 ± 3	97.5 ± 0.4	69 ± 1	76 ± 3	3B	97 ± 8	95 ± 1	71 ± 2	69 ± 2	4B

^a Conditions: NH₂/ α CC = 1, bulk, 25 °C, 5 mol% DBU vs total NH₂ and α CC groups. ^b EWC: equilibrium water content of self-standing films submerged in water for 120 h at RT. ^c GC: gel content of self-standing films submerged in water or THF for 120 h at RT and dried at 70 °C for 24 h. ^d CA: water contact angle. ^e CCA: cross-cut adhesion of coatings tested using ASTM D 3359 test method B.

For the NIPU thermosets obtained after 1 day of curing, the average EWC greatly varied depending on the formulation. The ones derived from **A1** exhibited the highest EWC ($102 \pm 4\%$ for **PJA1a**, entry 2, and $111 \pm 9\%$ for **PJA1b**, entry 3), and thus the greatest affinity to water, certainly due to their high density of polar hydroxy-oxazolidone linkages. The water uptake was lower for **PJA2a** ($80 \pm 1\%$, entry 4) and **PJA2b** ($93 \pm 9\%$, entry 5), while **PJ** (entry 1), **PJA3a** (entry 6) and **PJA3b** (entry 7) were the most resistant to water-swelling ($\text{EWC} = 76 \pm 1\%$, $55 \pm 2\%$, and $65 \pm 3\%$, respectively). **PJA3a** and **PJA3b** presented the lowest EWC, in line with a higher content of oxo-urethane linkages, less hydrophilic than the hydroxy-oxazolidone ones. Increasing the relative amount of diamine and consequently the concentration of urethane groups, also the water absorption and thus EWC increased. These trends were confirmed for samples analyzed after 7 days of curing, with EWC values that were generally higher.

Gel contents in water were high in all cases (92–98%) after 1 and 7 days of curing. They were lower in THF with values between 61 and 79%. The highest value was obtained for the formulation without diamines (**PJ**, entry 1) after 7 days of curing, in line with a higher cross-linking density. The lower GC observed with the other formulations containing the amines mixture suggested the presence of extractable chains or compounds that were solubilized in the solvent. The NMR analysis of the soluble fraction (reported in Figure 7.32) confirmed the presence of hydroxy ketone functional groups generated by the hydrolysis of the cyclic carbonate by residual water present in the monomers.

NIPU coatings deposited on aluminum substrates presented water contact angles ranging from 65 to 80° (entries 1 and 3) for samples analyzed after 1 day, slightly decreasing to a range between 60 and 74° after 7 days. This slight increase in hydrophilicity with the curing time was in agreement with the increased content of hydroxyl groups from the hydroxy-oxazolidone moieties. All formulations exhibited a gradual decrease in static contact angle over time, while the contact line remained fixed. This behavior is indicative of strong contact line pinning, where the droplet does not recede despite volume loss due to evaporation, suggesting a high level of interaction between the coating surface and water. The adhesion strength of NIPU coatings was then evaluated by cross-cut tests according to the ASTM D3359 standard. The coating performance improved when extending the curing time to 7 days, suggesting that the curing was not complete after 1 day. Except for the samples prepared from **A2**, the cross-cut area was perfectly intact for the coatings tested after 7 days, thus they were classified as 5B for their high adhesion to the aluminum surface (0% removal of the coating from the substrate). In case of the polymers obtained from **A2**, they were characterized by a lower adhesion and were ranked as 4B, since some of the squares

in the lattice pattern were partially affected by the test, and the superficial layer of the film was removed to some extent while pulling the tape.

The resistance of the coatings to wet delamination was investigated by submerging coated aluminum substrates in distilled water for 48 h. The samples were then placed in an oven at 50 °C for drying, and after 24 h the cross-cut test was repeated, showing the same coating performance evaluated before the immersion.

Thermal properties

Table 5.6 summarizes the $T_{\text{deg}10\%}$ and T_g of the NIPU networks, determined by TGA and DSC, respectively.

Table 5.6 Thermal properties of crosslinked NIPUs obtained by curing formulations composed of bis α CC, Jeffamine T-403 and a diamine.^a

Entry	Co-reagent	Polymer	Diamine : triamine (n/n)	After 1 d		After 7 d	
				$T_{\text{deg}10\%}$ (°C) ^b	T_g (°C) ^c	$T_{\text{deg}10\%}$ (°C) ^b	T_g (°C) ^c
1	/	PJ	/	268	10	266	10
2	A1	PJA1a	1 : 4	258	9	239	20
3		PJA1b	1 : 3	256	11	252	24
4	A2	PJA2a	1 : 4	266	10	257	22
5		PJA2b	1 : 3	265	11	256	23
6	A3	PJA3a	1 : 4	262	8	260	22
7		PJA3b	1 : 3	262	9	256	19

^a Conditions: $\text{NH}_2/\alpha\text{CC} = 1$, bulk, 25 °C, 5 mol% DBU vs total NH_2 and αCC groups. ^b Determined by TGA at 10% mass loss, heating the sample at 10 °C/min. ^c Determined by DSC using the first heating cycle, from -40 to 120 °C at 10 °C/min.

Differently from the corresponding linear polymers, it was not possible to identify a dehydration step in the degradation pattern of NIPU thermosets, thus the thermal degradation temperatures at 10% mass loss could not be compared. The products were indeed analyzed without any purification, and the DBU left in the matrix might hamper the loss of water from the polymer network because of an interaction between the basic site of the catalyst and the alcohol moiety of the hydroxyoxazolidone.⁴²² Crosslinked polymers analyzed after 1 day of curing were

characterized by a gradual weight loss starting at around 100 °C, followed by a major degradation step between 300 °C and 400 °C. Thermosets analyzed after 1 week displayed a different behavior at high temperature, since the main degradation was less pronounced, and a certain percentage of the polymer mass (around 15–20% of the initial mass) was retained even above 400 °C, before a final slow decomposition until 600 °C occurred. All the TGA curves are shown in Figures 7.33–7.39, and two representative ones are displayed in Figure 5.9).

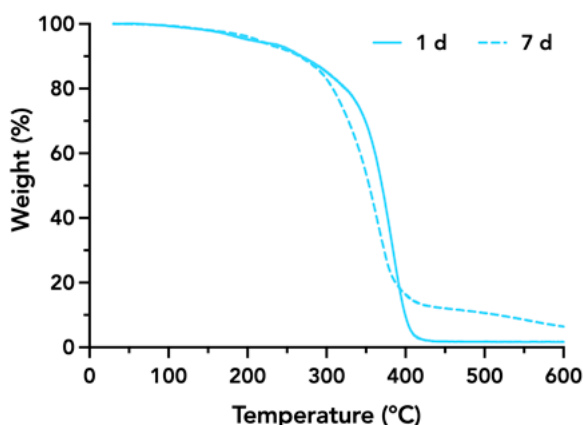


Figure 5.9 Representative TGA curves of PJ after 1 day (solid curve) and 7 days (dashed curve) of RT curing.

Considering the thermal degradation temperatures at 10% mass loss, the difference in composition between formulations did not have a significant impact, i.e. the determined $T_{\text{deg}10\%}$ values remained within temperatures of 258 °C (**PJA1a**, entry 2) to 268 °C (**PJ**, entry 1). Analogous values were measured for fully crosslinked samples, which had a similar degradation pattern until the main mass loss around 300 °C.

Crosslinked NIPUs were analyzed by DSC to determine their glass transition temperature, which was between 8 and 11 °C after 1 day of RT curing using the first heating ramp to prevent modification of the degree of crosslinking (curves reported in Figures 7.40–7.46). The T_g value of thermosets prepared using a co-reagent increased after longer curing time, while for **PJ** (entry 1) it remained constant at 10 °C. This difference was attributed to the reduced macromolecular mobility derived from the presence of low molecular weight diamines, less flexible than the long polyether chains of the crosslinker. Interestingly, the influence on the polymer chain mobility was the same for all the diamines, even if the T_g of the respective linear polymers were diverse. However, the glass transition temperature range of the thermosets was compatible with that required for room temperature adhesives or coatings, i.e. ensuring sufficient pliability at the

service temperature, where the material should not behave like a brittle solid (far below the T_g) or like a viscous fluid (far above the T_g).

Mechanical properties

The mechanical properties of the polymers were determined by tensile and hardness tests and are summarized in Table 5.7. The stress-strain curves (shown in Figures 7.47 and 7.48) resembled typical flexible plastic polymers: the samples stretched less than 10% of their initial length elastically, before showing a peak stress (yield point), followed by strain softening, extended plastic deformation, hardening and then fracture. This mechanical behavior was governed by the presence of the Jeffamine crosslinker, whose flexibility allowed for an extensive stretching of the network before reaching the fracture point. The use of lower molecular mass diamines as co-reagents, however, generated harder and stronger structures characterized by shorter and more compact macromolecular chains and a higher density of polar carbamate linkages.

Among the samples tested after 1 day of curing, **PJA2b** was the stiffest formulation ($E = 236 \pm 49$ MPa, entry 5) because of the influence of **A2**, which lent compactness to the network and hindered the elongation when tensile stress was applied. The presence of rigid chains derived from the diamines translated also into a lower elongation at break, especially for **PJA2b**, which exhibited a brittle behavior, with a low fracture strain ($\epsilon_f = 71 \pm 24\%$) and a yield strength coincident with the ultimate tensile strength of the material. Only **PJA3a** and **PJA3b** (entries 6 and 7) showed a fracture strain on the average higher than **PJ** (entry 1). The effect of the diamine content on the mechanical properties was more pronounced for the mixtures with a 1 : 3 diamine/triamine ratio, which displayed higher elastic modulus and ultimate tensile strength.

The samples tested after 7 days exhibited similar rigidity, strength and elongation at break, since the influence of the diamines was attenuated for completely cured networks; only **PJ** had a considerably lower Young's modulus ($E = 35 \pm 6$ MPa) and a higher fracture strain ($\epsilon_f = 315 \pm 17\%$). Compared to the samples tested after 1 day, both E and σ_u generally decreased, while the elongation at break greatly increased, resulting in a transition to more ductile, softer materials with overall lower toughness.

The hardness of the thermosets always increased with the diamine content, the rigid diamine **A2** produced the hardest materials, and the softest polymers were obtained with the formulation **PJ** (entry 1), with hardness values of 59 Shore A after 1 day and 32 Shore D after 7 days of RT curing. Notably, in contrast to the results obtained for the elastic modulus, hardness increased significantly after 7 days of curing, rising from Shore A to Shore D.

Table 5.7 Mechanical properties of crosslinked NIPUs obtained by curing formulations composed of bis α CC, Jeffamine T-403 and a diamine.^a

Entry	Diamine	Polymer	Diamine : triamine (n/n)	After 1 d				After 7 d			
				E (MPa) ^b	σ_u (MPa) ^c	ε_f (%) ^d	Shore A hardness	E (MPa) ^b	σ_u (MPa) ^c	ε_f (%) ^d	Shore D hardness
1	/	PJ	/	35 $\pm$ 10	5.9 $\pm$ 1.7	222 $\pm$ 32	59	35 $\pm$ 6	4.6 $\pm$ 1.3	315 $\pm$ 17	32
2	A1	PJA1a	1:4	104 $\pm$ 40	7.0 $\pm$ 1.2	118 $\pm$ 44	66	75 $\pm$ 20	4.1 $\pm$ 0.9	283 $\pm$ 10	42
3		PJA1b	1:3	107 $\pm$ 39	8.6 $\pm$ 1.0	166 $\pm$ 49	72	86 $\pm$ 30	4.8 $\pm$ 1.0	232 $\pm$ 78	45
4	A2	PJA2a	1:4	139 $\pm$ 32	7.0 $\pm$ 1.3	209 $\pm$ 39	70	88 $\pm$ 13	4.6 $\pm$ 0.5	270 $\pm$ 23	48
5		PJA2b	1:3	236 $\pm$ 49	9.6 $\pm$ 1.0	71 $\pm$ 24	85	90 $\pm$ 5	5.2 $\pm$ 0.8	266 $\pm$ 32	51
6	A3	PJA3a	1:4	70 $\pm$ 29	6.1 $\pm$ 0.7	249 $\pm$ 25	68	89 $\pm$ 14	4.9 $\pm$ 0.7	273 $\pm$ 16	45
7		PJA3b	1:3	146 $\pm$ 56	10.0 $\pm$ 1.2	257 $\pm$ 61	82	132 $\pm$ 25	5.1 $\pm$ 0.7	246 $\pm$ 9	47

^a Conditions: $\text{NH}_2/\alpha\text{CC} = 1$, bulk, 25 °C, 5 mol% DBU vs total NH_2 and αCC groups. ^b E: Young's modulus. ^c σ_u : ultimate tensile strength. ^d ε_f : fracture strain.

Adhesion performance

The adhesion of the solvent-free formulations on aluminum substrates was assessed by lap-shear testing (Figure 5.10A) after 1 and 7 days of RT hardening. Representative force-displacement curves are reported in Figures 7.49–7.50 and two illustrative examples are shown in Figure 5.10B. The results of the tests are summarized in Figure 5.10C, Figure 5.10D, and Table 7.2.

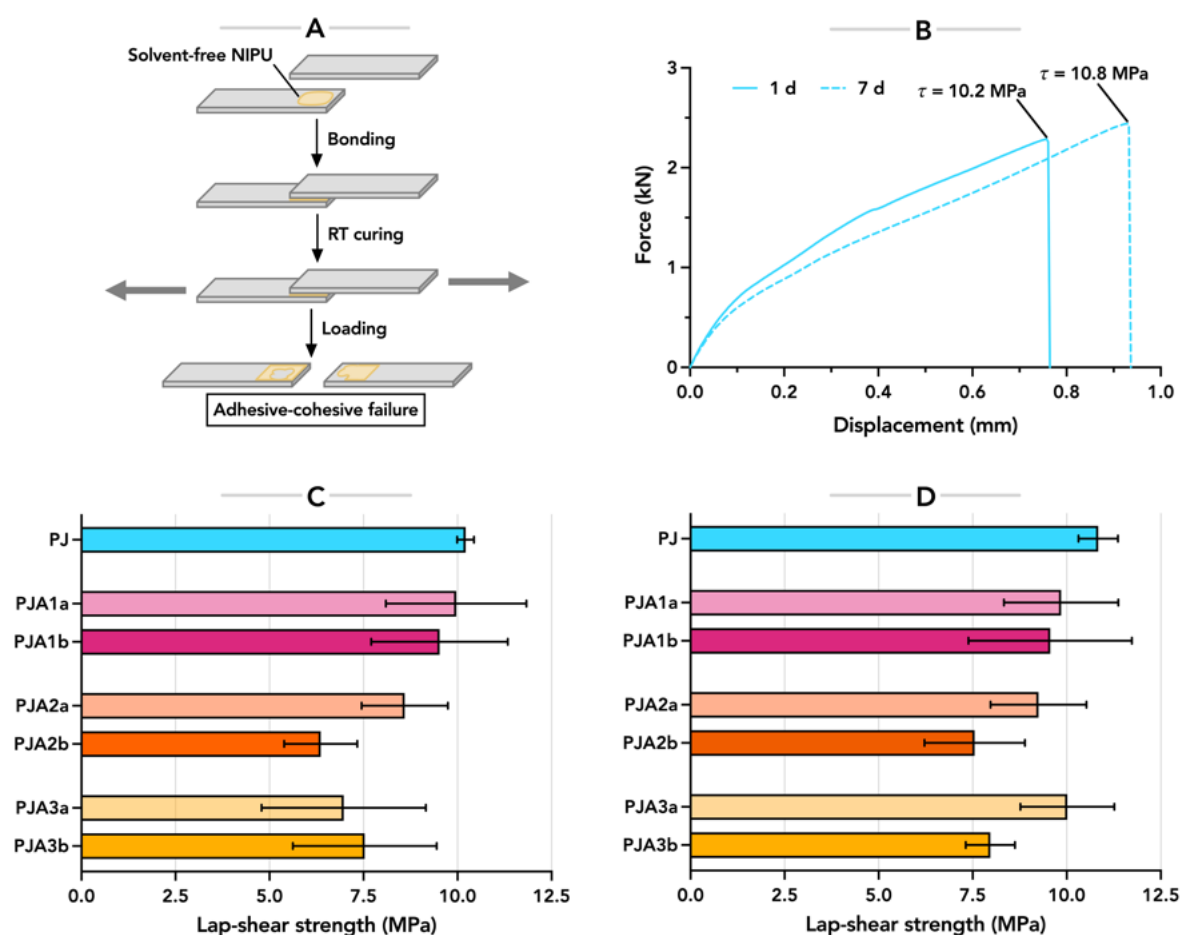


Figure 5.10 Graphical illustration of the lap-shear test (A); representative force-displacement curves of PJ after 1 day (solid curve) and 7 days (dashed curve) of RT curing (B); lap-shear strength comparison for crosslinked NIPUs, evaluated after 1 day (C) and 7 days (D) of RT curing on aluminum substrates.

Already after 1 day of curing, the 2K adhesives showed excellent adhesion to the substrates, with a lap-shear strength (τ) as high as $10.0 \pm 1.3 \text{ MPa}$ for **PJA1a** and $10.2 \pm 0.2 \text{ MPa}$ for **PJ**. Polymeric mixtures containing **A2** and **A3** had lower adhesion strength, especially **PJA2b**, that was characterized by a shear bonding strength of $6.4 \pm 1.0 \text{ MPa}$, confirming the lower adhesive performance noticed with the cross-cut test. Due to the higher cross-linking density, the samples obtained after 7 days displayed better performance on average, with **PJ** giving the best result ($\tau =$

10.8 ± 0.5 MPa). All the specimens showed a mixed adhesive-cohesive failure (Figure 7.51), which indicated that cohesive failure and bonding failure between polymer and adherend took place simultaneously. Compared to the mixture that had Jeffamine T-403 as only polyamine reagent (**PJ**), the other multi-component formulations exhibited an inferior performance, and the lap-shear strength was lower when a higher diamine content was used (**PJA1b**, **PJA2b**, **PJA3b**). These results led to the conclusion that a highly cross-linked and homogeneous network had a crucial role to ensure strong cohesion of the polymer network and adhesion to the metallic substrate, while the addition of bifunctional polyamines did not affect positively the outcome of the test. **PJ** outperformed the other formulations, had a pot life of several minutes longer, and gave the most reproducible results, that were comparable after 1 day and 7 days of curing; therefore, it was selected as best-performing formulation to be used for the following experiments.

The gluing properties of **PJ**, already tested on aluminum alloy (Al), were further evaluated after 1 day of RT curing on other substrates: stainless steel (SS), poly(methyl methacrylate) (PMMA), wood (W) and high-density polyethylene (HDPE). Representative force-displacement curves are reported in Figure 7.52, the representative failure modes are shown in Figure 7.53, while the results of the tests are summarized in Figure 5.11 and Table 7.3.

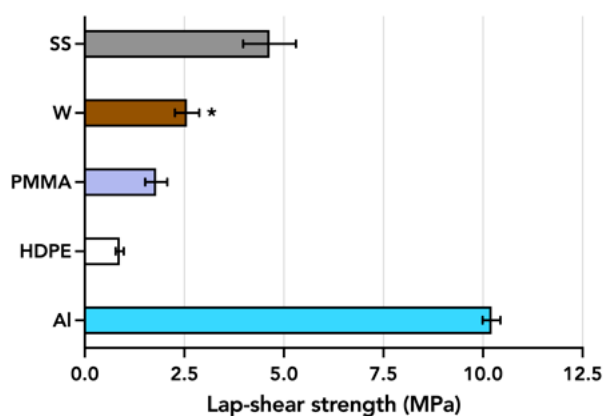


Figure 5.11 Lap-shear strength of NIPU adhesive formulation **PJ**, evaluated after 1 day of RT curing on different substrate materials: stainless steel (SS), wood (W), poly(methyl methacrylate) (PMMA), high-density polyethylene (HDPE), and aluminum alloy (Al). *Delamination of wood fibers.

The single-lap shear tests performed on stainless-steel displayed poorer adhesion compared to aluminum, with an average lap-shear strength of 4.6 ± 0.7 MPa. A different failure mode was also noticed, since some specimens underwent adhesive failure instead of the mixed adhesive-

cohesive previously observed with Al substrates. The interfacial interaction was weaker also for PMMA and HDPE substrates ($\tau = 1.8 \pm 0.3$ MPa and 0.9 ± 0.1 MPa, respectively), that displayed an adhesive failure in all cases. These results were ascribed to the low surface energy of the materials (especially HPDE), that is often reported as one of the main reasons behind bonding failure of some plastic substrates.^{425–428} Lap-shear tests on wood were firstly performed with 3-mm-thick specimens, however these substrates broke outside the gluing area (stock-break failure). The thickness of the substrate was consequently increased to 17 mm, and the tests were performed applying tension in parallel to wood grain direction. After an initial increase of the shear force, delamination of the wood fibers occurred, and the two components of the joint began to slide against each other (as observed in the exemplary force-displacement curve in Figure 7.52). The failure mode could be described as “light-fiber-tear” failure, since a thin layer of wood fibers was removed from the substrate surface by the adhesive, and the average lap-shear strength was 2.6 ± 0.3 MPa. The real lap shear adhesion was thus underestimated due to the strong adhesion of the adhesive to wood that delaminated during testing.

As a result of the strong and versatile interactions that the catechol moiety can establish, numerous bio-inspired catechol-based adhesives and coatings have been developed over the years.^{425,429–431} In particular, mimicking the binding mechanism of marine mussels, a previous study reported a significant improvement of the lap-shear strength of PHU glues containing pendent catechol groups.³⁶³ These mussel-mimetic PHU thermosets were prepared by polyaddition of a trifunctional cyclic carbonate, a liquid diamine, and a catecholamine (dopamine, DOP), which proved to enhance the cohesion of the polymeric structure and the adhesion to the surface of the substrate. Adopting the same strategy for the NIPU formulations described in this work, the adhesion performance was assessed after the addition of various contents of dopamine hydrochloride to the reagent mixture **PJ**. DBU was expected to deprotonate the ammonium group and release free dopamine, which could then react as a nucleophile with the cyclic carbonate. The NIPU adhesives developed were then benchmarked against two commercial fast-curing solvent-free 2K PU glues, i.e. TEROSON® PU 6700 and ARA LDITE® 2028-1, by performing lap-shear tests on aluminum alloy substrates (Al 5754) after 1 day of RT curing (results displayed in Figure 5.12 and Section 7.2.3.4).

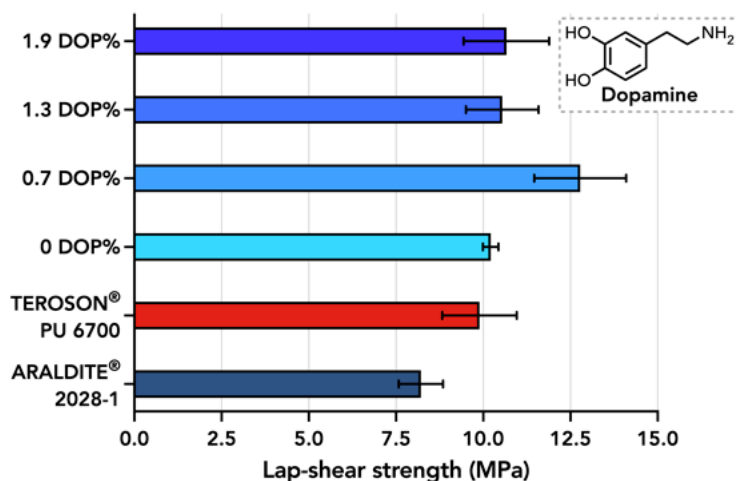


Figure 5.12 Lap-shear strength comparison for commercial PU adhesives and catechol-containing NIPUs obtained by polymerization in bulk of bis α CC with T-403 and dopamine (DOP), evaluated after 1 day of RT curing on aluminum alloy substrates. An equimolar ratio between amino and cyclic carbonate groups was held constant for all the NIPU formulations, and the percentage of dopamine (DOP%) was calculated considering the total number of amino groups.

The sample containing 0.7 mol% DOP exhibited an improved adhesion ($\tau = 12.8 \pm 1.3$ MPa), with a 25% increment of the average lap-shear strength compared to the formulation without dopamine. On the other hand, the specimens with 1.3 and 1.9 mol% DOP presented a negligible increase of the adhesion, since the adhesion strength was 10.5 ± 1.0 and 10.7 ± 1.2 MPa, respectively. This lower adhesion was attributed to two counterproductive effects that emerged at higher dopamine hydrochloride contents: decrease in crosslink density due to the introduction of chain ends by monofunctional dopamine molecules, and slower curing rate, resulting from the neutralization of DBU and therefore reduced availability of free catalyst to promote the reaction. The impact of dopamine hydrochloride on the crosslink degree was evidenced by gel content measurements after 1 day of RT curing (Table 7.5). While the effect was minimal in water, the gel content in THF clearly declined with increasing dopamine content, dropping from $74.3 \pm 0.8\%$ with 0.7 mol% DOP to $66.5 \pm 1.6\%$ with 1.9 mol% DOP. Thus, 0.7 mol% DOP represented an optimal concentration, at which dopamine's beneficial effects on interfacial adhesion were maximized without compromising the integrity of the polymer network or delaying its formation. All the samples displayed a mixed adhesive-cohesive failure (Figure 7.55). These results clearly demonstrated that the incorporation of catechol groups into the matrix, even at low concentration, had a beneficial impact on the performance of the adhesive, and that dopamine could be used as effective additional component in the solvent-free mixture.

The two commercial PU adhesives tested, TEROSON® PU 6700 and ARAIDITE® 2028-1, provided solid bonding performance to aluminum, with average lap-shear strengths of 9.9 ± 1.1 and 8.2 ± 0.6 MPa, respectively. However, both products fell short in comparison to the NIPU formulations developed herein, especially those containing dopamine. This benchmarking study clearly showed that the solvent-free NIPU formulations presented in this work can exceed the adhesion strength of commercial PU adhesives, positioning them as a promising alternative for high-performance bonding applications.

5.2.3 Conclusions

The demand for isocyanate-free processes to prepare polyurethanes is particularly pressing in the field of adhesives and coatings, as the low reactivity of the starting reagents limits the curing of NIPU materials at ambient temperature. This work describes the development of novel NIPU solvent-free formulations that were completely cured at room temperature in short time. Two-component mixtures were prepared using a liquid exovinylen bis(cyclic carbonate) and a low-viscosity polyamine crosslinker, and the rheological study of the polymerization showed that a suitable gel time at 25 °C was reached with 5 mol% catalyst loading. The reaction was monitored by infrared spectroscopy, which evidenced that the cyclic carbonate was entirely converted after 3 days. Low-molecular-weight liquid diamines were included into the composition to modulate the characteristics of the reticulated polymer system. To identify the type of linkages produced by the polyaddition and understand the effect of these diamines on the macromolecular properties, the corresponding linear polymers were synthesized. Linear NIPUs displayed dissimilar hydroxy-oxazolidone/oxo-urethane linkage selectivity and thermal properties, with a T_g ranging from -27 °C to 59 °C. Multiple mixtures were devised to produce crosslinked NIPUs, which were analyzed after 1 day and 7 days of RT curing. Fully cured thermosets were characterized by hydrophilic surfaces (contact angle between 60 and 74°), great coating performance (samples classified as 5B or 4B), and a gel content that was high in water but moderate in THF (GC = $96.6 \pm 0.3\%$ and $79.5 \pm 0.2\%$, respectively, for the most resistant thermosets). The $T_{deg10\%}$ was identified between 239 and 266 °C, and the T_g always close to room temperature, between 10 and 24 °C. Tensile testing of freestanding NIPU films revealed that the polymer networks were stiffer and stronger when a larger quantity of diamine was used. Additionally, the thermosets became more ductile with time, often at the expense of their toughness. The bonding performance of NIPU adhesives was assessed by lap-shear testing on various substrates (aluminum, stainless steel, wood, PMMA and HDPE), and the highest lap-shear strength was obtained with the most crosslinked material on aluminum alloy substrates ($\tau = 10.2 \pm 0.2$ MPa after 1 day of curing). The

gluing properties for this formulation were also tested after integration of dopamine in the mixture, and a 25% increment of the lap-shear strength was achieved with 0.7 DOP% ($\tau = 12.8 \pm 1.3$ MPa). A benchmarking study against two commercial 2K solvent-free PU adhesives validated the results obtained with the NIPU formulations, which showed adhesion strength superior to that of traditional PU bonders. Although the synthesis of bis α CC incurs higher costs compared to conventional isocyanate-based products, its production process is scalable, and a similar approach could be applied to develop alternative liquid monomers. Further benefits could be achieved replacing the crosslinker with other liquid bio-based hardeners with tailored reactivity, which could potentially increase renewable content, enhance the degree of crosslinking, and eliminate the need for catalysts in the mixture. The fast hardening at room temperature constitutes a key advantage of the non-isocyanate polyurethanes developed in this work. Moreover, the long working time, ease of use, high adhesion performance, and solvent-free nature of the system highlight the sustainability and appeal of the process, which could be easily implemented as cutting-edge 2K technology for room-temperature adhesives and coatings.

5.3 Development of solvent-free PU adhesives and coatings: performance comparison with NIPUs

5.3.1 Introduction

Bridging the gap between academic research and industrial applications is of utmost importance for the advancement of polymer science, particularly in the field of adhesives and coatings. In the case of PUs, understanding both fundamental chemistry and industrial processing is crucial to ensure a smooth transition from laboratory-scale innovations to commercially viable products.⁴³² This integration helps facilitate the effective translation of theoretical advancements into real-world applications and supports academic researchers in developing solutions that are not only innovative but also practical and scalable.^{433,434}

To gain deeper insight into the intricacies of large-scale polymer manufacturing, particularly for PU adhesives and coatings, an industrial secondment was undertaken at COP Chimie™, a French company specializing in the design, formulation, and customized production of a wide range of polymeric materials. This secondment was a requirement of the EJD-NIPU project. While the company is a European leader in the development of silicones for orthopedic devices, its PU portfolio is limited to a few formulations for rigid prostheses and a single 2K solvent-free adhesive (BLACKGLUE 01™).

PUs are suitable for both these uses due to their extensive structural diversity and tunable mechanical properties, making them highly versatile materials used across several manufacturing sectors, such as building and construction, automotive, textiles, furniture and bedding, packaging etc.^{30,85} Moreover, as result of their chemical stability, biocompatibility, and low cytotoxicity, they have been widely used in biomedical devices, with applications in tissue engineering, drug delivery, wound repair, joint replacement, catheters, cardiac valves, and many other types of implants.^{435–438} In the field of orthotics and orthopaedics, PUs are commonly used in combination with various other materials in the construction of prosthetic limbs.^{439–442} However, for prosthetic feet and hands, PU is rarely the main structural material, as it is often replaced by alternatives with better strength-to-weight ratio, durability, energy return, and overall functionality.^{443–446} As a result, the PU products previously employed by COP Chimie™ are no longer commonly utilized.

Given this shift, an alternative application for the company's isocyanate-based formulations was explored by testing them as adhesives and coatings and comparing the results with those of NIPUs. To meet the specific requirements of this new purpose, the compositions were modified accordingly. In particular, the formulations had to be adjusted to transition from the typical

properties of conventional prosthetic feet, such as strength, durability, biocompatibility, impact resistance, and long-term fatigue resistance,^{447–449} to those needed for structural adhesives, which include high bonding and tensile strength, thermal stability, chemical resistance, low shrinkage, and fast curing time^{164,182,183,193,194,450–452} (Figure 5.13). Starting from the formulation used in one of COP ChimieTM's PU prostheses, three new 2K PU formulations were obtained. Their crosslinking kinetics, thermomechanical properties, swelling behavior, solvent resistance, coating efficiency, and adhesion strength were assessed, benchmarking their performance against BLACKGLUE 01TM and the previously developed solvent-free NIPUs (Chapter 5.2).

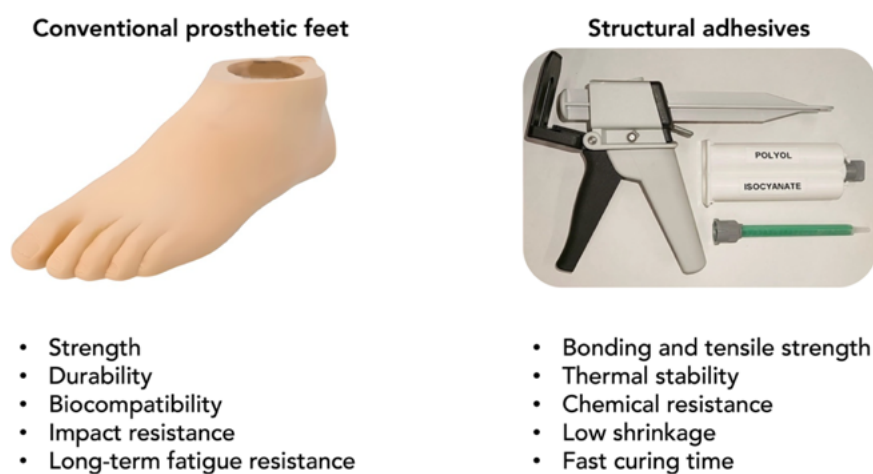


Figure 5.13 Comparison of the typical properties of conventional prosthetic feet and structural adhesives.

5.3.2 Results and discussion

5.3.2.1 Optimization of PU formulations

The development of the 2K PU formulations for adhesives and coatings started from a resin previously produced by the company, containing several components: VORANOLTM CP 4755 Polyol (a glycerol propoxylated polyether triol with a molecular weight of 4.800 g/mol, denoted as CP 4755), 1,4-butanediol (abbreviated as BDO), POLYCAT[®] 9 (commercial name of the tertiary amine N^1,N^1 -bis(3-(dimethylamino)propyl)- N^3,N^3 -dimethylpropane-1,3-diamine), UOP L PASTE ECO molecular sieves (a dispersion of type A zeolites in castor oil added to remove residual moisture in the formulation), and silica. In particular, the butanediol accounted for most of the hydroxyl groups in the formulation ($n_{\text{OH BDO}} : n_{\text{OH CP 4755}} = 5.46 : 1$). The components of the resin were pre-mixed and added to the hardener SUPRASEC[®] 2525, a polymeric methylene diphenyl diisocyanate, rapidly stirring the formulation to achieve a homogeneous mixture. To obtain a less

rigid product and better correlate the thermomechanical properties to the PU composition, silica was omitted from the mixture.

The rheological behavior of this initial formulation **COP1** was studied by tracking the evolution of the mixture's rigidity and temperature over time. Initially, the analysis was conducted on an 80 g scale in a beaker, before being scaled down to a 15 g scale and performed in a smaller crucible to better simulate the conditions typically used in adhesive and coating applications (Figure 5.14).

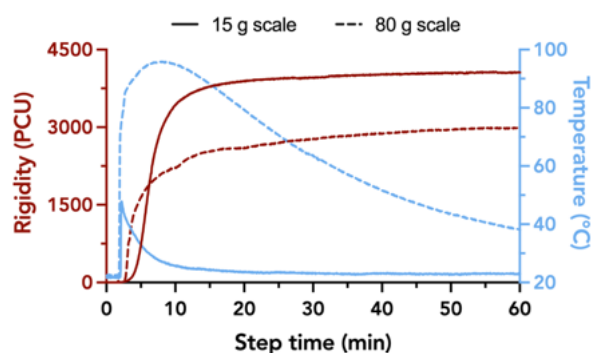


Figure 5.14 Evolution of COP1's rigidity and temperature over time on a 15 g (solid curves) and 80 g (dashed curves) scale.

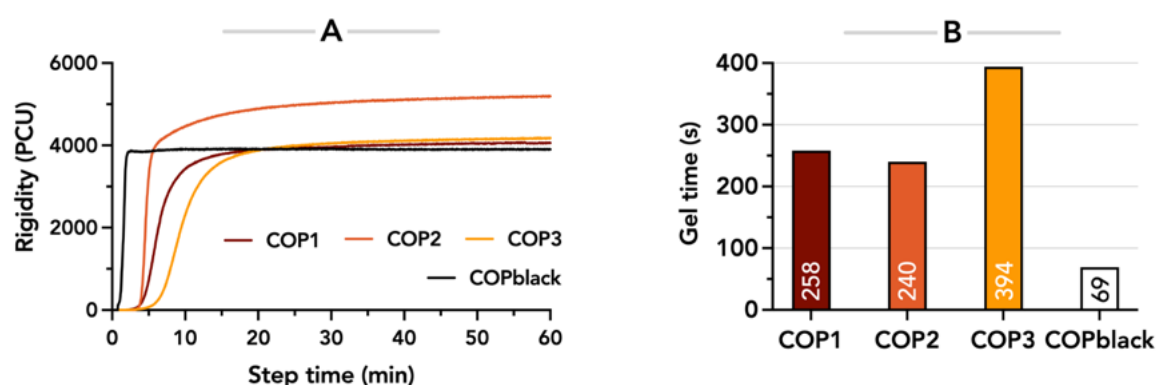
The exothermicity of the reaction was much lower on the smaller scale, with a maximum temperature of 48 °C compared to 96 °C, and consequently the reaction proceeded slower (the gel time was reached after 168 s on an 80 g scale and after 258 s on a 15 g scale). However, the final rigidity of the material was lower for the sample prepared in the beaker, possibly due to the higher temperature of the sample at the end of the experiment, or due to a too fast and premature hardening leading to incomplete crosslinking.

Two additional formulations were developed while maintaining the same hydroxyl-to-isocyanate ratio ($\text{OH} : \text{NCO} = 1.05$). VORANOL™ CP 450 (a glycerol propoxylated polyether triol with an average molecular weight of 450 g/mol, labeled as CP 450), replaced either CP 4755 (in the formulation **COP2**) or 1,4-butanediol (in **COP3**). These formulations were optimized by adjusting the molecular sieves and catalyst content to prevent foaming and achieve a gel time comparable to that of **COP1**. The molar ratio of hydroxyl groups from different polyols, catalyst loading, and molecular sieves content of the PU formulations are reported in Table 5.8, and their mass composition is shown in Figure 7.56. The rigidity evolution during crosslinking for **COP1**, **COP2**, **COP3**, and BLACKGLUE 01™, referred to as **COPblack** herein, is shown in Figure 5.15A, while the respective gel times are shown in Figure 5.15B.

Table 5.8 Molar ratio of hydroxyl groups from different polyols, catalyst loading, molecular sieves content, and gel times for PU formulations.

Entry	Formulation	$n_{OH\ BDO} : n_{OH\ CP\ 4755} : n_{OH\ CP\ 450}$ (mol/mol/mol)	Catalyst loading (mol%) ^a	Molecular sieves content (wt%) ^b
1	COP1	5.46 : 1 : 0	0.19	7.8
2	COP2	5.46 : 0 : 1	0.04	11.7
3	COP3	0 : 1 : 5.46	1.34	7.8

^a Calculated based on the total number of isocyanate and hydroxyl groups. ^b Relative to the mass of resin mixture.

**Figure 5.15** Rigidity evolution during crosslinking (A) and gel times (B) of PU formulations.

The catalyst loading played a crucial role in achieving the desired gel time: **COP2** required less POLYCAT® 9 than **COP1** due to the higher hydroxyl number of CP 450 compared to CP 4755, but for **COP3** a higher catalyst loading was necessary, because CP 450 reacted significantly slower than 1,4-butanediol. **COPblack** exhibited a gel time of 69 s (Figure 5.15B), which was much shorter than that of the other formulations. After 60 minutes, the rigidity was comparable for all the formulations, except for **COP2**, which displayed higher stiffness.

5.3.2.2 Performance and properties evaluation

The swelling behavior and gel content, thermomechanical properties, and coating performance of the optimized PU formulations were evaluated after 1 and 7 days of RT curing to assess the effect of extended reaction time. The corresponding results are summarized in Table 5.9, Table 5.10, and Table 5.11, respectively. The adhesion performance was evaluated by single-lap shear tests after 1 day of RT curing (Figure 5.17). All results obtained for the PU formulations were compared with those previously reported for the best-performing NIPU formulation **PJ**, which was thoroughly described in Chapter 5.2.

Swelling behavior and gel content

The average equilibrium water content (EWC) after 1 day ranged between 5.1 and 6.5% without significant differences between the optimized PU formulations and remained almost identical for the samples tested after 7 days. The hydrophobic nature of these PUs was confirmed by high average gel contents in water ($GC_{H_2O} = 95-99.6\%$) after 1 and 7 days, with the samples retaining nearly their entire original weight. In contrast, the resistance to THF after 1 day of curing was significantly lower, particularly for **COP1** (Table 5.9, entry 1, $GC_{THF} = 82 \pm 2\%$) and **COP2** (entry 2, $GC_{THF} = 51 \pm 2\%$). The test results improved with longer curing time, but the average GC values for these two formulations remained relatively low ($GC_{THF} = 90.1 \pm 0.2\%$ and $74 \pm 3\%$, respectively). This poor solvent resistance was attributed to the presence of 1,4-butanediol in the mixture, which introduced fewer crosslinking points and created more linear chain fragments. Conversely, **COP3** (entry 3), composed solely of trifunctional polyols, exhibited a higher crosslinking density, leading to improved structural integrity and higher solvent resistance ($GC_{THF} = 95.5 \pm 0.6\%$ and 97.7 ± 0.5 after 1 and 7 days, respectively). The commercial adhesive **COPblack** (entry 4) was characterized by extremely low water uptake ($EWC = 2.6 \pm 0.2\%$ and $2.1 \pm 0.2\%$ after 1 and 7 days, respectively) and highly crosslinked network with high resistance to both water and THF ($GC > 99\%$ for all the tested samples). In contrast, the NIPU formulation **PJ** (entry 5) showed a markedly higher affinity for water, with EWC values of $76 \pm 1\%$ after 1 day and $86 \pm 8\%$ after 7 days. Its solvent resistance was higher than that of **COP2** but remained lower than that of all the other PU formulations.

Table 5.9 Equilibrium water content and gel content of PU and NIPU formulations.

Entry	Formulation	Polyols	After 1 d			After 7 d		
			EWC (%) ^a	GC (%) ^b		EWC (%) ^a	GC (%) ^b	
				H ₂ O	THF		H ₂ O	THF
1	COP1	BDO - CP 4755	5.1 ± 0.4	99.6 ± 0.1	82 ± 2	6.0 ± 0.4	99.0 ± 0.3	90.1 ± 0.2
2	COP2	BDO - CP 450	5.5 ± 0.3	95.0 ± 0.5	51 ± 2	5.5 ± 0.9	98.8 ± 0.2	74 ± 3
3	COP3	CP 450 - CP 4755	6.5 ± 0.3	98.8 ± 0.3	95.5 ± 0.6	6.5 ± 0.7	99.0 ± 0.4	97.7 ± 0.5
4	COPblack	/	2.6 ± 0.2	99.8 ± 0.1	99.8 ± 0.1	2.1 ± 0.2	99.3 ± 0.2	99.7 ± 0.3
5	PJ	/	76 ± 1	97.3 ± 0.3	75 ± 1	86 ± 8	95.2 ± 0.6	79.5 ± 0.2

^a EWC: equilibrium water content of polymer pieces submerged in water for 120 h at RT. ^b GC: gel content of polymer pieces submerged in water or THF for 120 h at RT and dried at 70 °C for 24 h.

Thermomechanical properties

The glass transition temperature (T_g), determined by dynamic mechanical analysis (DMA) (Figure 7.57), was identified only for **COP2** (Table 5.10, entry 2) and **COPblack** (entry 4), which exhibited T_g values of 45 °C and 43 °C, respectively. In contrast, for **COP1** (entry 1) and **COP3** (entry 3), the glass transition occurred below room temperature and could not be determined as the instrument was not equipped with a cooling system. This difference is directly linked to the composition of the PU formulations. The use of the flexible polyol CP 4755 in **COP1** and **COP3** resulted in lower crosslink density and higher chain mobility, reducing the network rigidity and the T_g . Conversely, **COP2**, obtained from low molecular weight polyols, was characterized by a network with the highest density of urethane groups and more restricted molecular motion, requiring a higher temperature to reach the rubbery state. Differences in hydrogen-bonding interactions and phase organization may also contribute to the observed thermomechanical behavior. However, given the complexity of the formulations and the absence of dedicated characterization techniques targeting these phenomena, their specific contribution could not be assessed in the present study.

These observations were confirmed by the results of tensile tests performed on miniature dog-bone specimens, as detailed in Figure 7.58 and Table 7.6. After 1 day of RT curing, **COP2** displayed the most rigid, strongest, and most brittle chemical structure, with a Young's modulus (E) of 199 ± 9 MPa, an ultimate tensile strength (σ_u) of 13.5 ± 0.9 MPa, and a fracture strain (ϵ_f) of $15 \pm 2\%$. Replacing CP 450 with CP 4755 in **COP1** produced a more flexible and elastic polymer network, with lower stiffness and strength ($E = 2.4 \pm 0.2$ MPa, $\sigma_u = 2.3 \pm 0.4$ MPa) but significantly higher ductility ($\epsilon_f = 208 \pm 31\%$). **COP3**, with its long macromolecular chains derived from the polyether polyols, was the softest and weakest material ($E = 0.41 \pm 0.05$ MPa, $\sigma_u = 0.58 \pm 0.06$ MPa), while its elongation at break was intermediate between **COP1** and **COP2** ($\epsilon_f = 102 \pm 7\%$). The hardness followed a similar trend to the elastic modulus, with **COP2** being the hardest (Shore 89A), followed by **COP1** (Shore 68A) and **COP3** (Shore 48A). **COPblack** exhibited a stiff and strong structure ($E = 127 \pm 8$ MPa, $\sigma_u = 15.7 \pm 0.6$ MPa), more ductile than **COP2** ($\epsilon_f = 53 \pm 7\%$) and with the highest hardness (Shore 68D) and toughness of all the PU formulations (representative stress-strain curves shown in Figure 7.59). All mechanical properties remained constant after 7 days of RT curing.

This behavior was in contrast with what was observed for the NIPU formulation **PJ** (Table 5.10, entry 5), whose properties changed considerably with extended curing times. **PJ** exhibited a more flexible polymer network, as evidenced by its low glass transition temperature ($T_g = 10$ °C) and the highest fracture strain among all formulations. Despite its flexibility, **PJ** showed higher stiffness,

strength, and hardness compared to **COP1** and **COP3**, although these values were lower than those of **COP2** and **COPblack**.

Table 5.10 Thermal and mechanical properties of PU and NIPU formulations.

Entry	Formulation	Polyols	After 1 d					After 7 d				
			T_g (°C)	E (MPa) ^a	σ_u (MPa) ^b	ε_f (%) ^c	Shore hardness	T_g (°C)	E (MPa) ^a	σ_u (MPa) ^b	ε_f (%) ^c	Shore hardness
1	COP1	BDO - CP 4755	<25 ^d	2.4 ± 0.2	2.3 ± 0.4	208 ± 31	68A	<25 ^d	2.6 ± 0.2	2.9 ± 0.1	222 ± 5	71A
2	COP2	BDO - CP 450	45 ^d	199 ± 9	13.5 ± 0.9	15 ± 2	89A	45 ^d	174 ± 16	13 ± 2	16 ± 5	90A
3	COP3	CP 450 -CP 4755	<25 ^d	0.41 ± 0.05	0.58 ± 0.06	102 ± 7	48A	<25 ^d	0.66 ± 0.06	0.54 ± 0.07	102 ± 8	48A
4	COPblack	/	43 ^d	127 ± 8	15.7 ± 0.6	53 ± 7	68D	43 ^d	126 ± 12	15.6 ± 0.9	46 ± 3	68D
5	PJ	/	10 ^e	35 ± 10	5.9 ± 1.7	222 ± 32	59A	10 ^e	35 ± 6	4.6 ± 1.3	315 ± 17	84A

^a E : Young's modulus. ^b σ_u : ultimate tensile strength. ^c ε_f : fracture strain. ^d Determined by DMA using the second heating cycle, from 25 to 120 °C at 3 °C/min. ^e Determined by DSC using the first heating cycle, from -40 to 120 °C at 10 °C/min.

Coating and adhesion performance

The adhesion of PU coatings to aluminum alloy substrates was assessed by cross-cut adhesion tests and their tackiness was estimated by probe tack tests from the peak strength (σ_p) required to detach the probe (Table 5.11). The latter test was also applied to **PJ** and was used to monitor the evolution of tackiness after curing and to understand how quickly the materials transitioned to a fully cured, non-tacky state. A graphical illustration of the test is illustrated in Figure 5.16, the experimental setup is shown in Figure 7.60, and the representative tack force-displacement curves of all the PU formulations and **PJ** are provided in Figure 7.61.

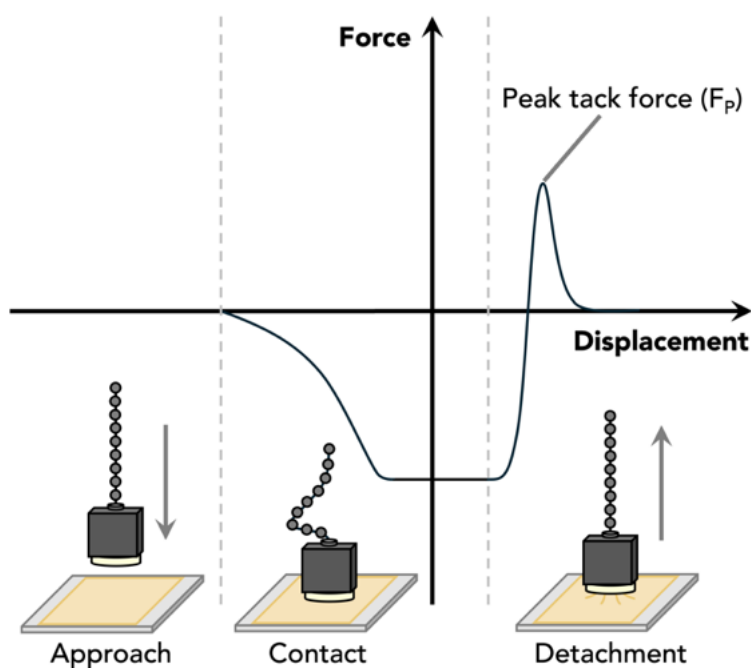


Figure 5.16 Graphical illustration of the probe tack test with representative force-displacement curve.

After 1 day of RT curing, the coatings obtained from **COP1** (Table 5.11, entry 1) and **COPblack** (entry 4) remained completely intact after the test and were classified as 5B (0% coating removal). **COP2** (entry 2) showed minor phase separation at the microscopic level due to an only partial solubility of the molecular sieves in 1,4-butanediol. This inhomogeneity led to a partial removal of the zeolites during the test, resulting in 5-15% coating removal and a corresponding rating of 3B. **COP3** (entry 3) was only partially affected by the test and was rated 4B, since small portions of material were detached at the intersections of the grid due to a relatively poor adhesion to the aluminum surface. The results of the CCA test were consistent after 7 days of curing and only the adhesion performance of **COP2** improved from 3B to 4B, with less than 5%

coating removal. The coating performance of fully cured PUs was comparable to or slightly lower than that of **PJ** (entry 5), which was classified 4B after 1 day and 5B after 7 days of curing.

Table 5.11 Coating performance of PU and NIPU formulations.

Entry	Formulation	Polyols	After 1 d		After 7 d	
			CCA ^a	σ_p (Pa) ^b	CCA ^a	σ_p (Pa) ^b
1	COP1	BDO-CP 4755	5B	128 ± 5	5B	6.3 ± 1.1
2	COP2	BDO-CP 450	3B	5.9 ± 0.7	4B	3.2 ± 0.4
3	COP3	CP 450-CP 4755	4B	502 ± 26	4B	7.3 ± 1.4
4	COPblack	/	5B	9.5 ± 1.6	5B	5.5 ± 0.5
5	PJ	/	4B	$(2.03 \pm 0.15) \cdot 10^3$	5B	$(1.21 \pm 0.18) \cdot 10^3$

^a CCA: cross-cut adhesion of coatings tested using ASTM D 3359 test method B. ^b σ_p : tack strength for a contact time of 10 s and a release rate of 60 mm/min.

The probe tack test, schematically illustrated in Figure 5.16, revealed low tack strength for all the PUs after 1 day of curing, with clear differences among the formulations ($\sigma_p = 128 \pm 5$ Pa, 5.9 ± 0.7 Pa, and 502 ± 26 Pa for **COP1**, **COP2**, and **COP3**, respectively). The main factor influencing this result was the reactivity of the polyols used. While the polymer network in **COP2** was completely developed, the curing process was not fully completed for **COP1** and **COP3**, as residual unreacted molecular chains from the moderately reactive CP 4755 and CP 450 were still present. These pendant segments were not integrated into the polymer matrix and remained available for interaction with the probe, contributing to rendering the surface slightly tackier. Similarly, the markedly higher tack strength observed for the NIPU formulation **PJ** after 1 day ($\sigma_p = 2.03 \pm 0.15$ kPa) was attributed to the presence of residual monomers and dangling chains, resulting from incomplete reaction and partial hydrolysis of the bis α CC precursor. **COPblack**, on the other hand, was already fully crosslinked and non-tacky ($\sigma_p = 9.5 \pm 1.6$ Pa). After 7 days, σ_p values for **COP2** and **COPblack** remained constant and very close to the resolution of the instrument ($\sigma_p = 3.2 \pm 0.4$ Pa and 5.5 ± 0.5 Pa). In contrast, the results for **COP1**, **COP3**, and especially **PJ** showed a significant reduction in tack ($\sigma_p = 6.3 \pm 1.1$ Pa, 7.3 ± 1.4 Pa, and 1.21 ± 0.18 kPa, respectively), suggesting that the polymerization proceeded further, and the macromolecular network evolved towards a fully cured state, reducing the availability of mobile, unbound chains at the surface. Since the thermomechanical properties and the coating performance of the PU thermosets did not significantly change over the tested period, the adhesion performance was assessed by

single-lap shear test only after 1 day of RT curing on pre-treated aluminum alloy substrates (results summarized in Figure 5.17 and Table 7.7). Representative force-displacement curves and failure modes of PUs are displayed in Figure 7.62 and Figure 7.63, respectively.

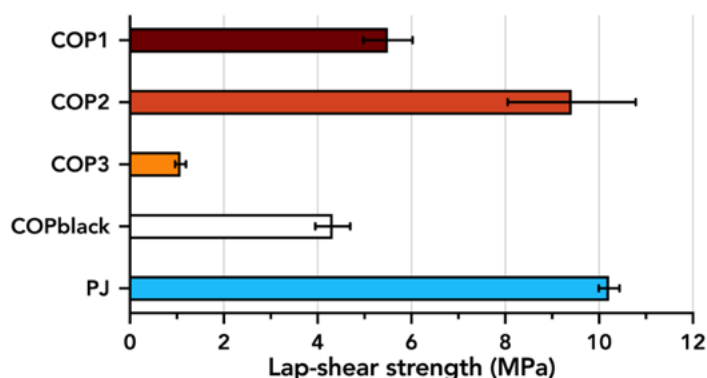


Figure 5.17 Lap-shear strength of PU and NIPU formulations after 1 day of RT curing on aluminum substrates.

Among the PU formulations, **COP2** exhibited the highest adhesion to aluminum ($\tau = 9.4 \pm 1.4$ MPa), with an average lap-shear strength only slightly lower than that of **PJ** ($\tau = 10.2 \pm 0.2$ MPa). This performance was attributed to its strong polymer network and high density of urethane functional groups, which promote strong interfacial interactions. In comparison, **COP1** and **COP3** were characterized by lower urethane densities, resulting in weaker interfacial interactions and correspondingly reduced lap-shear strengths ($\tau = 5.5 \pm 0.5$ MPa and 1.1 ± 0.1 MPa, respectively). Despite its mechanically strong polymer network, **COPblack** demonstrated poor adhesion to aluminum ($\tau = 4.3 \pm 0.4$ MPa), consistent with its formulation, which was optimized for adhesion to plastics rather than metals. Similarly to **PJ**, a mixed adhesive–cohesive failure was observed for the top-performing **COP2** and **COP1**, whereas **COP3** and **COPblack** exhibited only adhesive failure (Figure 7.63).

5.3.3 Conclusions

Gaining firsthand experience in the formulation and processing of industrial polymers is essential for understanding how laboratory-scale principles translate into large-scale production. The industrial secondment at COP Chimie provided valuable insights into critical aspects of process scalability, such as the exothermicity observed at different batch volumes and the importance of efficient mixing and application methods. These factors were investigated through the development of three conventional PU formulations designed for potential adhesive or coating

applications (**COP1**, **COP2**, and **COP3**), and their systematic comparison with a commercial product (**COPblack**) and a solvent-free NIPU formulation (**PJ**). The formulations were optimized to ensure an adequate pot life while minimizing gel time. Gelation occurred significantly earlier in **COP1**, **COP2**, and **COP3** (258, 240, and 394 s, respectively) than in **PJ** (271 min), whereas **COPblack** reached the gel point in only 69 s. Water uptake and solubility were low for all PU mixtures (EWC values between 5.1 and 6.5% and GC_{H_2O} always $\geq 95\%$), while resistance to THF heavily depended on the percentage of bifunctional butanediol used, with significantly higher gel contents obtained when trifunctional polyols were employed. The use of a high molecular weight polyether polyol in **COP1** and **COP3** provided softer and weaker materials, which cured more slowly than **COP2** and remained tacky for longer time. Except for the tack strength, which decreased after longer curing time, mechanical and physical properties of the PUs remained largely unchanged between 1 and 7 days of curing, indicating that network formation was effectively completed within the first 24 hours. Urethane group density emerged as a key factor governing adhesive performance, with lap-shear strength decreasing from **COP2** ($\tau = 9.4 \pm 1.4$ MPa) to **COP1** ($\tau = 5.5 \pm 0.5$ MPa) and **COP3** ($\tau = 1.1 \pm 0.1$ MPa). On this basis, **COP3** appears unsuitable for structural adhesive or coating applications, whereas **COP2** may be suited for adhesive use, and **COP1** for flexible, hydrophobic coatings. Despite having a strong and well-crosslinked polymer network which provided excellent solvent resistance and coating performance, the adhesion of **COPblack** to aluminum was poorer than **COP1** and **COP2**, reflecting the lack of chemical compatibility and strong interfacial interactions with the polar metal surface. In contrast, the NIPU formulation **PJ** displayed the highest tackiness, hydrophilicity, and lap-shear strength among all tested samples. While these properties limit its suitability as a coating, particularly where low surface energy or water resistance is required, they make it a promising candidate for bonding applications. For the industrial deployment of any of the formulations discussed, both PU and NIPU, the implementation of an appropriate mixing system would be essential to ensure homogeneity and reliable processing. From a formulation perspective, an ideal thermoset adhesive should feature both a high crosslinking density and a high concentration of polar functional groups to maximize both cohesive and adhesive strength. However, such systems often suffer from reduced working time, which can limit practical applicability. To mitigate this limitation, the use of components with tailored reactivity is recommended, as this approach allows for an optimal compromise between pot life, curing kinetics, and final performance.

5.4 Novel fatty acid-derived polyamine: a renewable crosslinker for NIPUs

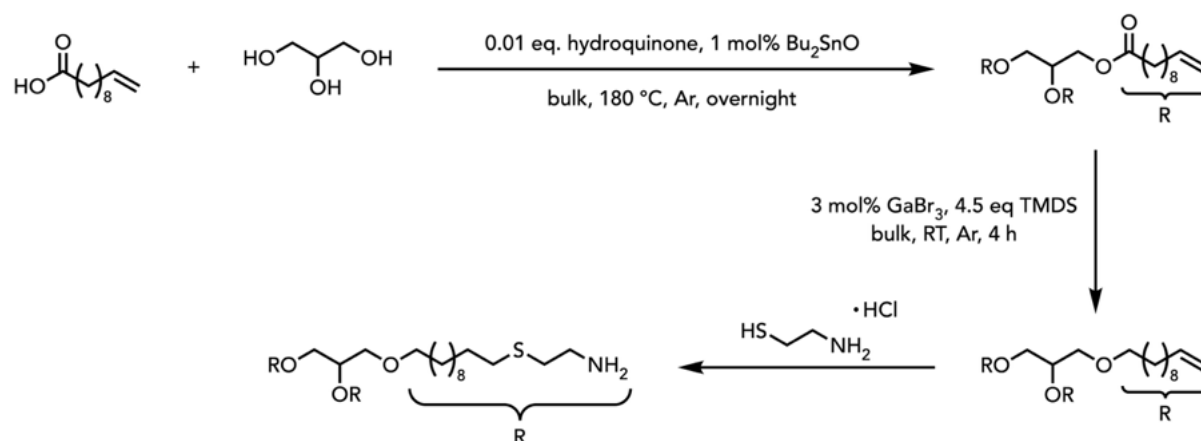
5.4.1 Introduction

In an era marked by escalating environmental crises, integrating sustainability principles in the management of natural resources is critical to ensure long-term stability for both eco-systems and human communities.^{14,453–455} The manufacturing of goods and materials requires production processes that are designed with a comprehensive vision of their ecological impacts, considering the entire product lifecycle from raw material extraction to the end-of-life stage. This approach translates into the prioritization of renewable resources over petroleum-based compounds, which has become a cornerstone of scientific innovation in modern chemistry. Leveraging the natural abundance of biomass, the development of bio-based chemicals and materials can reduce dependence on fossil resources, lower carbon footprints, and enhance biodegradability, contributing to a more sustainable and circular economy.^{456–460}

Within this framework, polyamines, a class of compounds with multiple amine functional groups, stand out as an attractive target for bio-based chemical innovation. Polyamines play key roles in many biological processes, with functions that span from cellular protection to growth regulation and stress response.^{461–463} Natural polyamines like putrescine and spermidine were first discovered in biological systems and later isolated and structurally characterized, with the first synthetic efforts dating back to the mid-19th century.^{464,465} Nowadays, synthetic polyamines are almost exclusively obtained from petrochemical precursors, with nucleophilic substitution of haloalkanes representing the most common method for their production.^{244,245,466} The global polyamine market size was valued at USD 1.2 billion in 2024 and is projected to reach USD 2.1 billion by 2033.⁴⁶⁷ These compounds find applications across a wide range of industries, including water treatment, chemical manufacturing, agriculture, and personal care. Due to their high reactivity and versatility, polyamines are particularly valued in polymer chemistry for the synthesis of polyamides, polyureas, and epoxy resins, among others. Despite their critical role in the formulation of adhesives, coatings, hydrogels, and other materials, the synthesis of bio-based polyamines remains largely underdeveloped.^{245,248} In particular, the need for more sustainable alternatives is especially urgent for polyamines containing more than two amine groups, which can be used as crosslinkers in thermosetting polymers.⁴⁶⁸

In recent time, several synthetic routes have been developed to obtain polyamines from renewable resources, including chitosan, amino acids, vegetable oils and their derivatives, sugar derivatives, terpenes, cardanol, and lignin.^{245,248,469} However, despite the broad chemical toolbox

available for introducing amine functionalities into bio-based precursors, only a limited number of studies have documented the synthesis of triamines or higher polyamines.^{470–478} Aiming to address this demand, herein, a novel triamine with a low melting point was synthesized from renewable feedstocks. The synthetic pathway involved three steps: esterification of glycerol with undecylenic acid, catalytic reduction of the resulting ester to ether, and thiol-ene reaction with cysteamine hydrochloride (Scheme 5.6). The intermediates were characterized by IR spectroscopy, ¹H-NMR, and electrospray ionization mass spectrometry (ESI-MS), while the final product was further analyzed *via* ¹³C- and 2D-NMR. The triamine was subsequently employed as a crosslinker in a solvent-free NIPU formulation to assess its potential application in adhesive and coating systems.



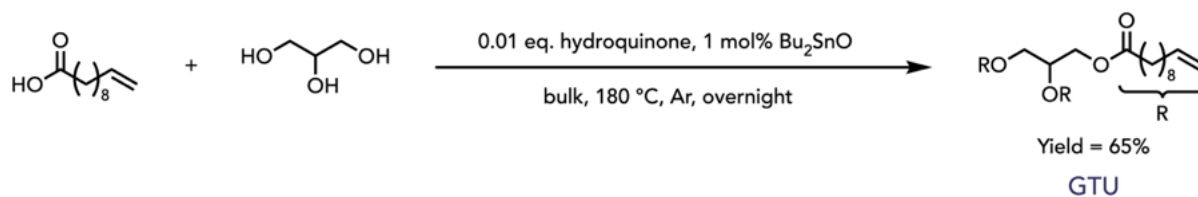
Scheme 5.6 Synthetic pathway to novel fatty acid-derived triamine.

5.4.2 Results and discussion

5.4.2.1 Three-step synthesis from renewable feedstocks

Preparation of undecylenic acid triglyceride

The first step of the synthesis was the esterification of glycerol with undecylenic acid, a terminally unsaturated fatty acid commonly obtained by pyrolysis of ricinoleic acid, which is the major fatty acid component of castor oil.⁴⁷⁹ As a result of its bifunctional nature, undecylenic acid (UA, also termed 10-undecenoic acid) offers numerous potential applications in sustainable chemistry, particularly in polymer production.⁴⁸⁰ Among the various monomers derived from this colorless oil, several were synthesized through esterification reactions with polyols.^{481–485} Notably, the synthesis of undecylenic acid triglyceride (glyceryl triundec-10-enoate, GTU) was also reported.^{482–484,486} In this work, the synthesis of GTU was performed adapting the conditions described by Inciarte et al. and reported in Scheme 5.7.⁴⁸⁴



Scheme 5.7 Reaction scheme of the first synthetic step: esterification of glycerol with undecylenic acid.

As reported in the literature, complete conversion of the hydroxyl groups was achieved with high selectivity towards the triglyceride. The characteristic ^1H -NMR peaks of glycerol monoundecenoate and diundecenoate, identified by Valentin et al.⁴⁸² and shown in Table 7.8, were not observed in the ^1H -NMR spectrum of the product, displayed in Figure 5.18. IR and mass spectrum are reported in Figure 5.19 and Figure 7.64, respectively.

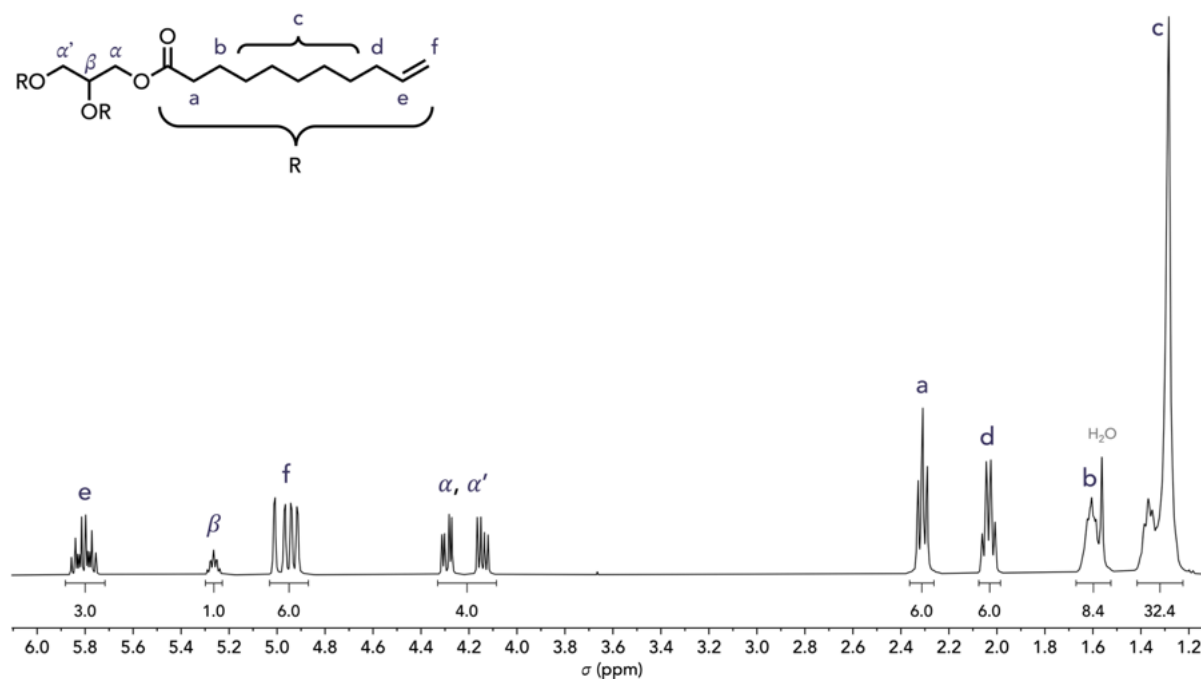


Figure 5.18 ^1H -NMR spectrum of GTU in CDCl_3 .

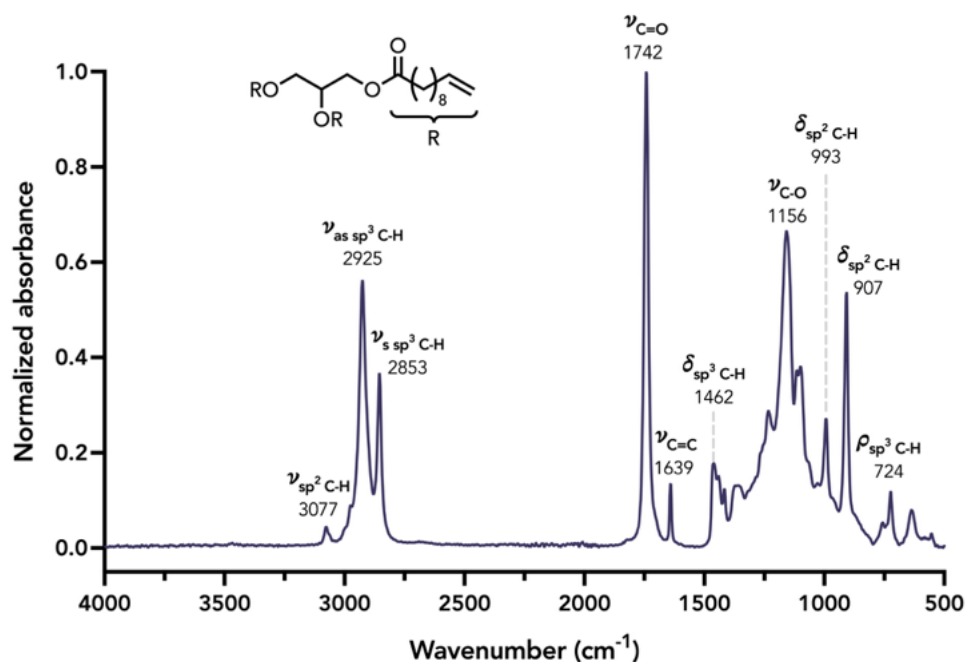
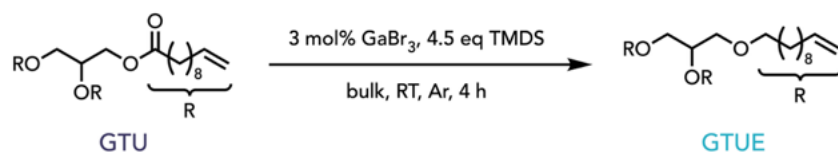


Figure 5.19 IR spectrum of GTU.

Triglyceride reduction to triether

To prevent the formation of fatty amides over time, an issue observed for similar amine products derived from vegetable oils,⁴⁷⁷ GTU was reduced to the corresponding triether using tetramethyldisiloxane (TMDS) and a catalytic amount of GaBr₃, according to a procedure previously reported for the same substrate.⁴⁸⁷ Until recent years, the development of catalytic methods for the reduction of esters to ethers remained a challenging task for organic chemists, due to the tendency of esters to yield alcohols under reductive conditions. Nevertheless, significant progress has lately been made in this field, and new methodologies for catalytic transformation of carbonyl-based moieties have emerged.⁴⁸⁸ Inspired by a procedure previously reported by Sakai et al., who described the reduction of esters to the corresponding ethers with Et₃SiH in the presence of InBr₃ as catalyst,⁴⁸⁹ Biermann et al. expanded the scope of the reaction to different bio-based compounds, such as fatty acid derivatives, vegetable oils and lactones, documenting a higher selectivity to the desired products when InBr₃ was replaced by GaBr₃.^{490,491} After a screening of different metal bromides and reducing agents, the system GaBr₃/TMDS was selected as the most efficient and sustainable, owing to the low catalytic loading, mild reaction temperatures, high conversions, and absence of alcohol by-product. This catalytic system, very efficient also in converting polyesters to polyethers,^{492,493} was used for the reduction of glyceryl triundec-10-enoate to the corresponding triether (glyceryl triundec-10-enyl ether, GTUE). The deoxygenation of the freshly prepared GTU was carried out in bulk, under solvent-free conditions, and at room temperature (Scheme 5.8).



Scheme 5.8 Reaction scheme of the second synthetic step: reduction of GTU to GTUE.

In the ^1H -NMR spectrum of the product (shown in Figure 5.20), full conversion of the triglyceride was confirmed by the disappearance of the ester signal at 2.31 ppm (H_a in Figure 5.18). The signals corresponding to the glyceryl residue shifted upfield, merging with the ether α -protons signal to give a broad multiplet between 3.65 and 3.35 ppm. TMSD, used as the reductant, polymerized to form polydimethylsiloxane (PDMS) and other oligomeric siloxanes. These by-products, detected in the upfield region of the spectrum between 0.13 and 0.06 ppm, could not be completely removed even after purification by column chromatography. A recently reported workup, involving chemical degradation of the siloxanes *via* washing with NaOH solution and EtOH, resulted in a product yield of 64%;⁴⁸⁷ however, in this work the issue was resolved at a later stage of the synthesis, where these by-products were effectively removed. The gravimetric yield, approximated by assuming a pure product and thus disregarding siloxane impurities, was 82%.

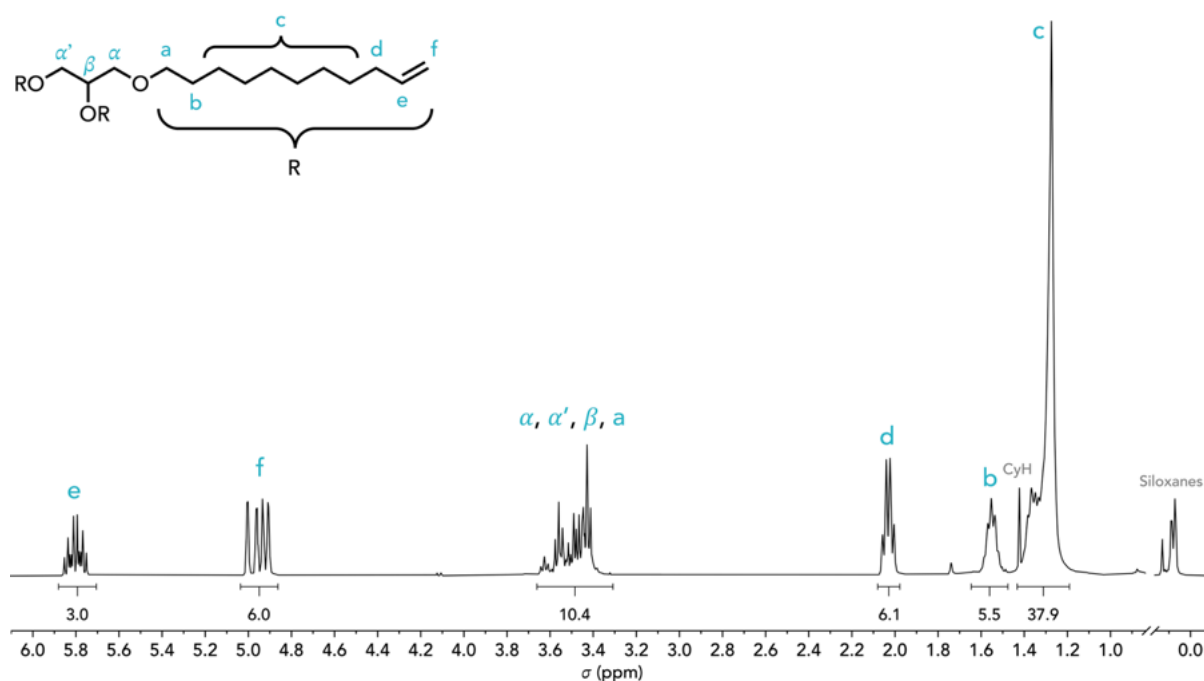


Figure 5.20 ^1H -NMR spectrum of GTUE in CDCl_3 .

The characteristic $\text{C}=\text{O}$ stretching vibration of the ester at 1742 cm^{-1} ($\nu_{\text{C}=\text{O}}$ in Figure 5.19) was absent in the IR spectrum of the product (Figure 5.21), indicating complete conversion of the

reagent. Additionally, in place of the single C-O stretching band at 1156 cm^{-1} ($\nu_{\text{C-O}}$, Figure 5.19), three distinct C-O vibrations were identified: two bands at 1259 and 1105 cm^{-1} ($\nu_{\text{as C-O}}$), and one band at 802 cm^{-1} ($\nu_{\text{s C-O}}$). The molecular ion of GTUE was confirmed by ESI-MS analysis, as shown in the mass spectrum in Figure 7.65.

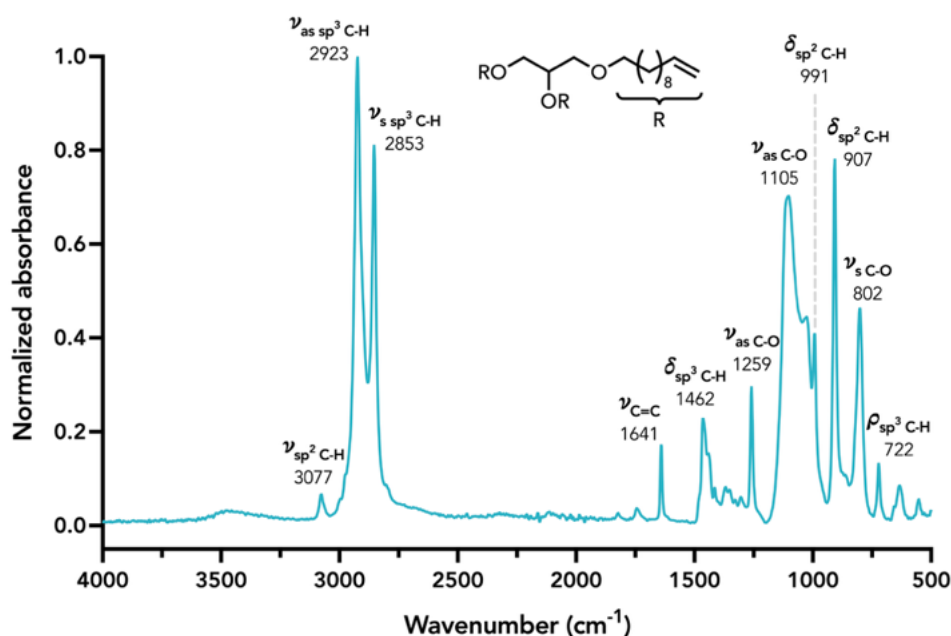
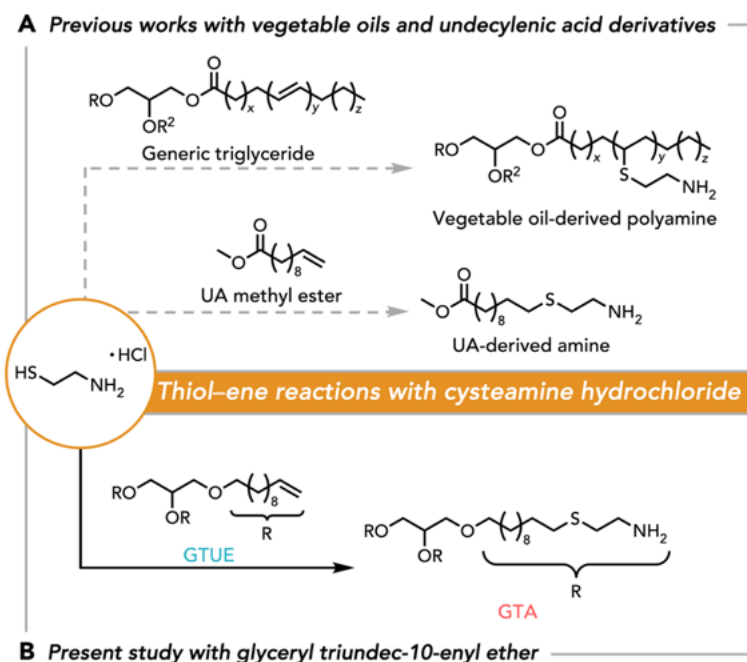


Figure 5.21 IR spectrum of glyceryl triundec-10-enyl ether.

Thiol-ene reaction with cysteamine hydrochloride

The final step of the synthesis involved a thiol-ene reaction between GTUE and cysteamine hydrochloride to yield a trifunctional polyamine, referred to as glyceryl triamine (GTA). Thiol-ene additions of terminal alkenes are well-known for their favorable thermodynamics, rapid kinetics, and high selectivity and yield, making them widely applicable in the functionalization of bio-based building blocks, particularly in the development of more sustainable polymers and materials.^{470,472–474,477,494–504} Cysteamine, a degradation product of the amino acid cysteine, was selected as the thiol component for this “click” reaction. Its reactivity makes it an ideal substrate for thiol-ene synthesis of amines, while its biological origin ensures that the resulting polyamine is fully renewable. Several studies have reported the addition of cysteamine hydrochloride to vegetable oils *via* thiol-ene chemistry,^{471,475,478,505} as well as its coupling with undecylenic acid derivatives for polymer synthesis.^{506,507} In particular, Meier et al. described the synthesis of fatty acid derived polyamides through the thiol-ene addition of cysteamine hydrochloride to methyl 10-undecenoate (UA methyl ester), achieving complete conversion of the terminal alkene and an

85% isolated yield. Building on these successful examples, the same synthetic strategy was employed for the final step of the polyamine synthesis (Scheme 5.9).



Scheme 5.9 Thiol-ene reactions with cysteamine hydrochloride: previous works (A)^{471,475,478,506} and present study (B).

The optimization of reaction conditions, summarized in Table 5.12, was carried out by NMR analysis of the reaction mixture after work-up. Double bond conversion was determined by integrating two well-resolved signals corresponding to the starting material and the product, according to Equation 7.9 and as illustrated in Figure 5.22.

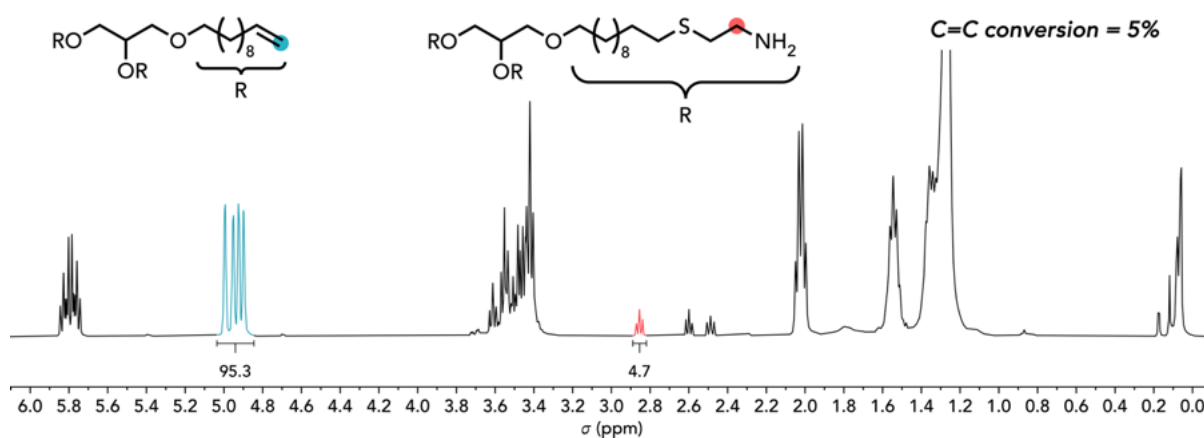


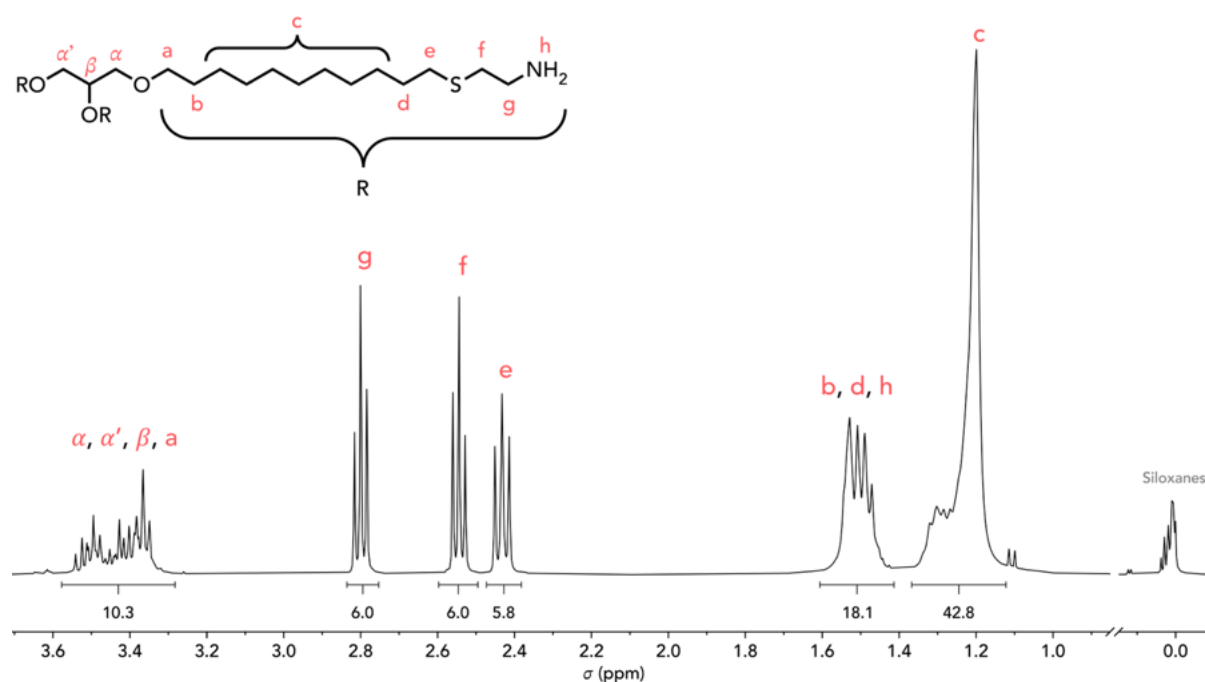
Figure 5.22 Representative ^1H -NMR spectrum in CDCl_3 of thiol-ene reaction mixture illustrating key signals for determining double bond conversion. Conditions: toluene (1 mL), $\text{C}=\text{C}/\text{SH} = 1 : 3$, 75°C , 24 h.

Given the structural similarity of GTUE to methyl 10-undecenoate, the experimental conditions and purification procedure were adapted from those reported previously. The thiol-ene addition was first conducted in toluene using an excess of cysteamine hydrochloride (Table 5.12, entry 1), but low conversions were observed due to the poor solubility of the reagents in the selected solvent. Performing the reaction in bulk (entry 2) yielded a comparable outcome (12% conversion), likely because of inefficient mixing and restricted reagents contact. A marked improvement was obtained upon switching the solvent to isopropanol (entry 3): both GTUE and cysteamine hydrochloride dissolved readily, enabling complete conversion to GTA after 48 hours. Notably, 0.5 mL of isopropanol represented the minimum volume required to fully solubilize the reagents at the employed reaction scale ($n_{\text{GTUE}} = 0.5$ mmol), therefore it could not be further reduced without compromising homogenization. To minimize reaction waste, the amount of cysteamine hydrochloride was then systematically decreased (entries 4–6). An alkene-to-thiol molar ratio of 1 : 1.5 achieved full conversion within 24 hours (entry 5), whereas an equimolar ratio led to incomplete consumption of the double bonds even after 72 hours (96% conversion, entry 6). The influence of temperature was also investigated (entries 7–8). When the reaction temperature was lowered to 50 °C, GTUE was almost completely converted after 48 hours (entry 7), but a further decrease to 25 °C significantly slowed the reaction, resulting in only 23% conversion after 72 hours (entry 8). Finally, increasing the isopropanol volume (entry 9) improved reagents solubility but simultaneously reduced their concentration, resulting in a slower reaction rate (compared to entry 4). Taken together, these results identified the conditions of entry 5 as optimal, providing complete conversion of the alkene moieties in the shortest time, at the lowest effective temperature, and with minimal use of both solvent and cysteamine hydrochloride. GTA was characterized *via* ^1H -NMR, ^{13}C -NMR, COSY, HSQC, and ^1H - ^{13}C heteronuclear multiple bond correlation (HMBC) (spectra shown in Figure 5.23, Figure 7.66, Figure 7.67, Figure 7.68, and Figure 7.69, respectively).

Table 5.12 Optimization of reaction conditions for the thiol-ene addition between GTUE and cysteamine hydrochloride.^a

Entry	Solvent	V_{solvent} (mL)	C=C : SH (mol/mol)	T (°C)	Reaction time (h)	Conversion (%) ^b
1	PhMe	1	1 : 3	75	48	14
2	/	/	1 : 3	75	48	12
3	<i>i</i> -PrOH	0.5	1 : 3	75	48	>99
4	<i>i</i> -PrOH	0.5	1 : 1.5	75	12	98
5	<i>i</i> -PrOH	0.5	1 : 1.5	75	24	>99
6	<i>i</i> -PrOH	0.5	1 : 1	75	72	96
7	<i>i</i> -PrOH	0.5	1 : 1.5	50	48	99
8	<i>i</i> -PrOH	0.5	1 : 1.5	25	72	23
9	<i>i</i> -PrOH	1	1 : 1.5	75	12	83

^a Conditions: $n_{\text{GTUE}} = 0.5$ mmol. ^b Calculated from the integration of relevant NMR signals.

**Figure 5.23** ¹H-NMR spectrum of GTA in CDCl₃.

The triamine was further characterized by IR spectroscopy (Figure 5.24). The characteristic broad N-H stretching ($\nu_{\text{N-H}}$), bending ($\delta_{\text{N-H}}$), and wagging ($\omega_{\text{N-H}}$) vibrations of the amine groups were observed at 3280, 1594, and 864 cm⁻¹, respectively. In contrast, the GTUE alkene bands, including C-H stretching ($\nu_{\text{sp}^2\text{C-H}}$, 3077 cm⁻¹), C-H scissoring ($\delta_{\text{sp}^2\text{C-H}}$, 991 and 907 cm⁻¹), and C=C stretching ($\nu_{\text{C=C}}$, 1641 cm⁻¹), were no longer visible in the spectrum of GTA, indicating complete consumption of the double bond. ESI-MS analysis (Figure 7.70) confirmed the presence of the molecular ion of

the product, as well as a secondary peak corresponding to the species formed after the loss of one cysteamine unit.

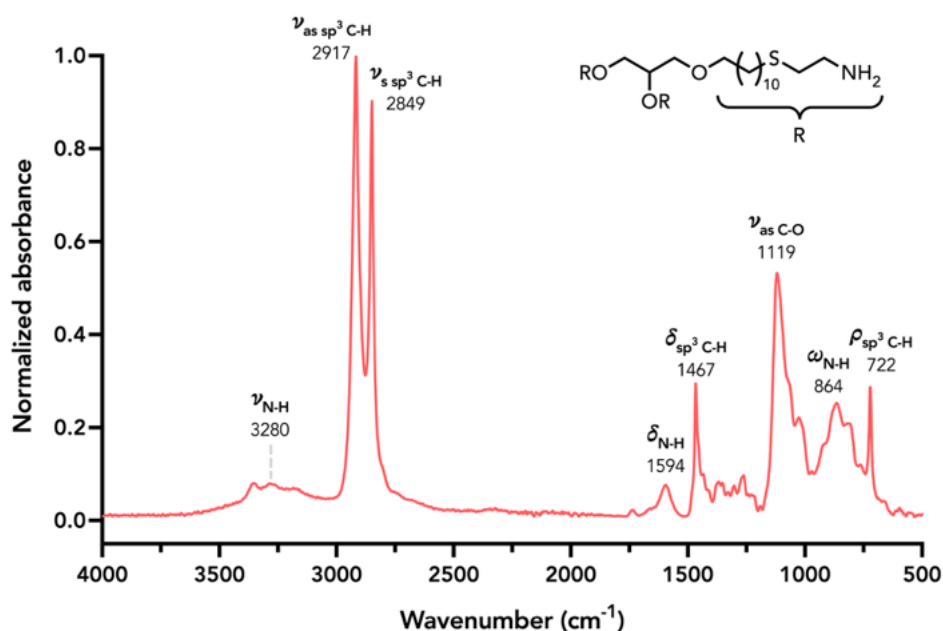
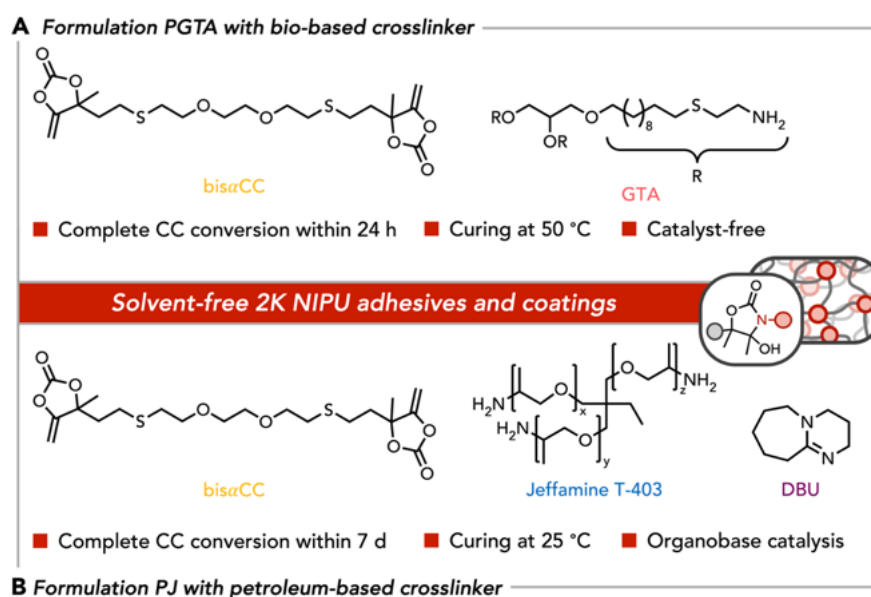


Figure 5.24 IR spectrum of GTA.

Despite quantitative GTUE conversion, siloxane impurities retained from the previous synthetic step were not removed following the literature reported work-up. To address this, GTA solubility was screened in various organic solvents (Table 7.9) and a new purification procedure was developed leveraging the pH-responsive water solubility of GTA. The crude reaction mixture was dissolved in 0.1 M HCl to protonate the triamine and transfer it into the aqueous phase, which was then washed with ethyl acetate to remove siloxanes while retaining the protonated amine. Subsequent basification regenerated the free amine, which was then extracted with CH_2Cl_2 and isolated following the remaining purification steps described previously (washing with saturated K_2CO_3 solution and then with water, drying over anhydrous Na_2SO_4 , filtration, and concentration *in vacuo*).⁵⁰⁶ Following this protocol, the gravimetric yield, approximated by assuming pure GTUE, decreased from 93 to 76%. NMR analysis confirmed complete removal of impurities (Figure 7.71) and the pure product was obtained as an ivory solid (Figure 7.72B) with a melting point (T_m) of 48 °C (Figure 7.72A).

5.4.2.2 Preparation of a solvent-free NIPU formulation with CO₂-sourced bis(α -alkylidene cyclic carbonate)

Thanks to its T_m close to room temperature, GTA was used as a crosslinker to prepare a 2K solvent-free NIPU formulation (**PGTA**) with the liquid bis α CC described in Chapter 5.2. Unlike the formulation with the petroleum-based crosslinker Jeffamine T-403 (**PJ**, Scheme 5.10B), which required an organobase (DBU) to perform the curing at room temperature,⁵⁰⁸ the components in **PGTA** were mixed under catalyst-free conditions at 50 °C (Scheme 5.10A).



Scheme 5.10 Solvent-free 2K NIPU adhesives and coatings: comparison between formulations PGTA (A) and PJ (B).

The crosslinking process was monitored by IR spectroscopy (Figure 5.25), analyzing the evolution of the exovinylene C=C stretching band around 1685 cm⁻¹ and the cyclic carbonate and urethane C=O stretching vibrations at 1824 and 1724 cm⁻¹, respectively. Complete conversion of bis α CC was observed after 24 hours, when its characteristic signals had completely disappeared. Dynamic rheology analysis confirmed rapid network formation, with the gel point reached after only 49 seconds (Figure 7.73). The faster crosslinking observed in **PGTA**, compared to all Jeffamine T-403-based formulations—including those prepared with DBU and at higher temperatures (Chapter 5.2, Figure 5.6)—was attributed to the higher reactivity of the GTA primary alkylamino groups. The specific type of linkage formed, oxo-urethane or hydroxy-oxazolidone, was not directly investigated. However, due to the steric accessibility and high reactivity of the

amines, combined with the rapid curing observed, the thermoset structure was hypothesized to mainly consist of hydroxy-oxazolidone linkages.

The swelling behavior, gel content, thermal properties, and adhesive/coating performance of **PGTA** after 24 hours at 50 °C were compared with those of the fully cured formulation **PJ** after 7 days at room temperature. The results are summarized in Table 5.13 and Table 5.14.

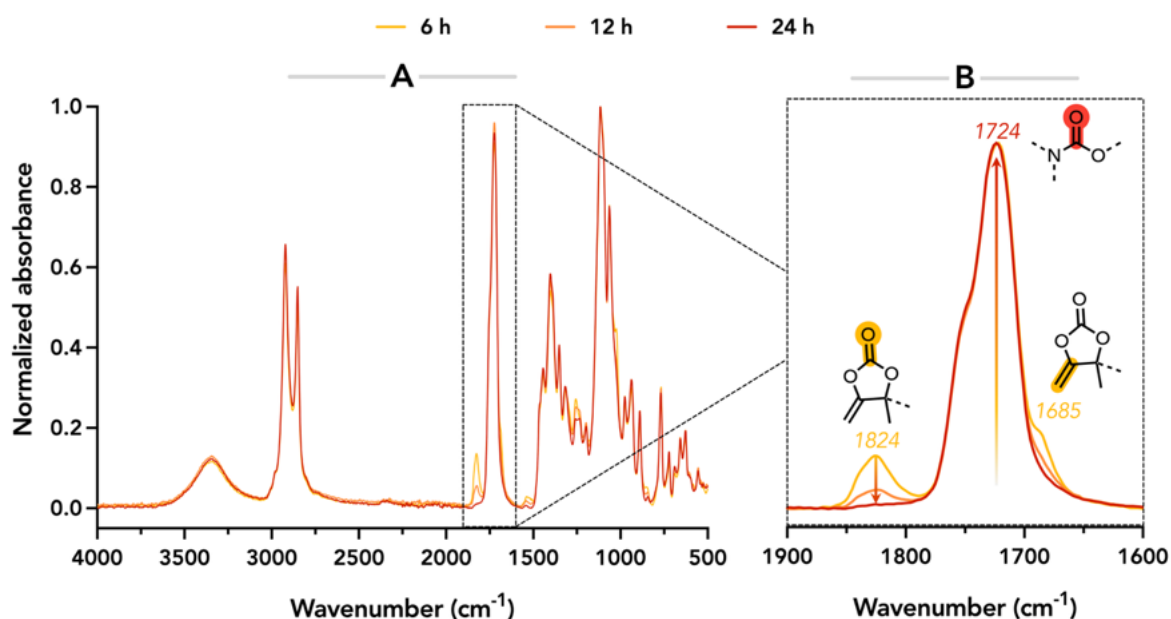


Figure 5.25 Infrared spectrum evolution of the solvent- and catalyst-free formulation **PGTA** at 50 °C (A); characteristic bands in the carbonyl stretching region (B).

Table 5.13 Swelling index, gel content, and water contact angle of solvent-free NIPU formulations prepared with different amine crosslinkers.

Entry	Amine crosslinker	Formulation	SI (%) ^a		GC (%) ^b		CA (°) ^c
			H ₂ O	THF	H ₂ O	THF	
1	Jeffamine T-403	PJ ^d	86 ± 8	267 ± 6	95.2 ± 0.6	79.5 ± 0.2	60 ± 2
2	GTA	PGTA ^e	5.7 ± 0.5	172 ± 7	99.2 ± 0.3	96.6 ± 0.3	83 ± 5

^a SI: swelling index of NIPU pieces submerged in water or THF for 120 h at room temperature. ^b GC: gel content of NIPU pieces submerged in water or THF for 120 h at room temperature and dried at 70 °C for 24 h. ^c CA: water contact angle. ^d Reaction conditions: NH₂/αCC = 1, bulk, 7 d, 25 °C, 5 mol% DBU vs total NH₂ and αCC groups. ^e Reaction conditions: NH₂/αCC = 1, bulk, 24 h, 50 °C, catalyst-free.

The swelling index (SI) in water was significantly lower for **PGTA** ($SI_{H_2O} = 5.7 \pm 0.5\%$, Table 5.13, entry 2) than for **PJ** ($SI_{H_2O} = 86 \pm 8\%$, entry 1), highlighting the hydrophobic character imparted by the fatty acid-derived reagent. The more hydrophobic nature of **PGTA** was confirmed by a higher average water contact angle ($CA = 83 \pm 5^\circ$; contact angle images shown in Figure 7.74), compared to **PJ** ($CA = 60 \pm 2^\circ$), consistent with its lower water uptake. Both polymers exhibited substantially higher affinity for THF, with average SI_{THF} of $267 \pm 6\%$ for **PJ** and $172 \pm 7\%$ for **PGTA**. Also in this case, **PGTA** absorbed less solvent than **PJ**, indicating denser and more tightly crosslinked network in the polymer derived from the bio-based polyamine. These observations were supported by gel content (GC) analysis. In water, both thermosets showed high gel contents ($GC_{H_2O} = 95.2 \pm 0.6\%$ for **PJ** and $99.2 \pm 0.3\%$ for **PGTA**). In THF, however, a more pronounced difference emerged, since **PJ** exhibited a markedly lower GC_{THF} ($79.5 \pm 0.2\%$) compared to **PGTA** ($96.6 \pm 0.3\%$). This enhanced resistance of **PGTA** in THF was attributed to the absence of DBU in its formulation. The lack of this organic superbases may have minimized hydrolysis of the cyclic carbonate by residual moisture, thereby reducing the formation of soluble oligomers and extractable chains. As a result, **PGTA** exhibited a more thoroughly cured and structurally robust polymer network. Thermal characterization of the materials was performed using differential scanning calorimetry and thermogravimetric analysis, while adhesion performance was assessed on aluminum substrates *via* single lap-shear adhesion tests (Table 5.14).

Table 5.14 Thermal properties and lap-shear adhesion strength on aluminum substrates of solvent-free NIPU formulations prepared with different amine crosslinkers.

Entry	Amine crosslinker	Formulation	$T_{deg10\%}$ ($^\circ\text{C}$) ^a	T_{dehyd} ($^\circ\text{C}$) ^b	T_g ($^\circ\text{C}$) ^c	τ (MPa) ^d
1	Jeffamine T-403	PJ ^e	266	n. d.	10	10.8 ± 0.5
2	GTA	PGTA ^f	364	142	-5	2.2 ± 0.4

^a Determined by TGA at 10% mass loss, heating the sample at $10^\circ\text{C min}^{-1}$. For PGTA, the value was determined after dehydration. ^b Determined by TGA, heating the sample at 2°C min^{-1} . ^c Determined by DSC using the first heating cycle, from -40 to 120°C at $10^\circ\text{C min}^{-1}$. ^d τ : lap-shear strength evaluated on aluminum substrates. ^e Reaction conditions: $NH_2/\alpha CC = 1$, bulk, 7 d, 25°C , 5 mol% DBU vs total NH_2 and αCC groups. ^f Reaction conditions: $NH_2/\alpha CC = 1$, bulk, 24 h, 50°C , catalyst-free.

The TGA curve of the catalyst-free formulation **PGTA** (Figure 5.26A) exhibited a distinct dehydration step (Figure 5.26B), characteristic of poly(hydroxy-oxazolidone)s and previously reported in the manuscript for purified linear NIPUs (Figures 7.25–7.28).⁵⁰⁸ The degradation temperature at 10% mass loss ($T_{deg10\%}$), measured after dehydration, was 364°C (Table 5.14, entry

2). The dehydration temperature (T_{dehyd}) was determined through an additional analysis conducted at a lower heating rate (2 instead of 10 °C min⁻¹), revealing a T_{dehyd} of 142 °C—in agreement with the values obtained for the purified linear NIPUs reported in Chapter 5.2. This degradation behavior differed from that of **PJ** (entry 1, $T_{\text{deg}10\%} = 266$ °C), where the presence of DBU altered the dehydration process, resulting in a more gradual mass loss prior to decomposition of the polymer backbone (Figure 7.33).

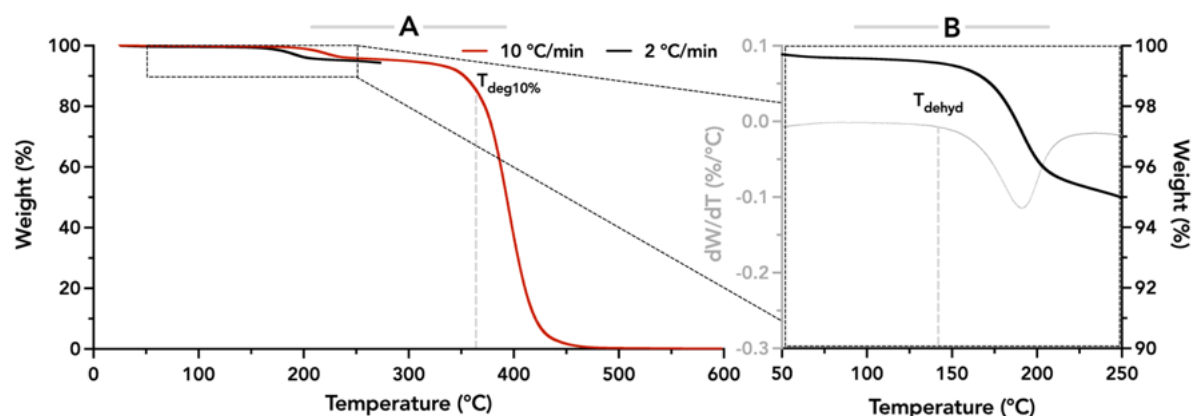


Figure 5.26 TGA curves of **PGTA** at heating rate of 10 °C min⁻¹, in dark red, and 2 °C min⁻¹, in black (A); zoom on the dehydration step (B).

The DSC curve of **PGTA** (Figure 7.75) displayed a glass transition temperature (T_g) of -5 °C, lower than that of **PJ** ($T_g = 10$ °C). The higher chain mobility in **PGTA** was attributed to the presence of long, flexible aliphatic segments derived from the fatty acid in contrast to the methyl branched structure of the Jeffamine. However, this structural flexibility came at the expense of the adhesion performance. The average lap-shear adhesion strength (τ) of **PGTA** was 2.2 ± 0.4 MPa, substantially lower than that of **PJ** ($\tau = 10.8 \pm 0.5$ MPa). An adhesive failure was observed (Figure 5.27B), in line with a poor interfacial compatibility between the hydrophobic, non-polar aliphatic chains of **PGTA** and the polar aluminum surface. The lower density of strong chemical interactions or absence of effective wetting led to adhesive failure in all tested specimens, confirming weak polymer–substrate adhesion. The increased chain mobility associated with the long, flexible aliphatic segments of the polyamine also contributes to a reduction in the cohesive strength of the adhesive layer. However, since failure occurred at the substrate–adhesive interface, differences in lap-shear strength were interpreted primarily in terms of interfacial interactions rather than bulk cohesive properties. Representative force–displacement curves and failure modes are shown in Figures 5.27A and 5.27B.

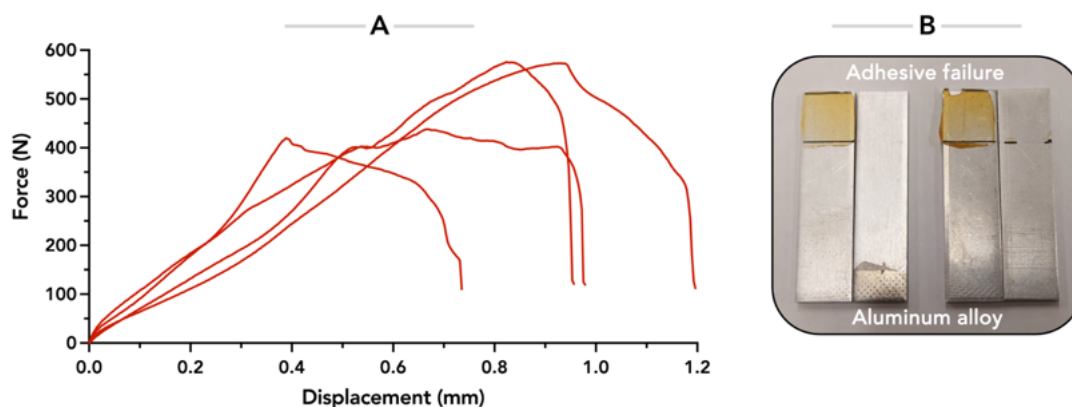


Figure 5.27 Force-displacement curves (A) and representative failure modes (B) of PGTA on aluminum alloy substrates.

5.4.3 Conclusions

To expand the portfolio of renewable amine crosslinkers for sustainable polymer synthesis, a novel fatty acid-derived triamine was synthesized entirely from bio-based resources. A three-step route was developed, consisting of: esterification of glycerol with undecylenic acid to form the triglyceride, deoxygenation to convert the ester into the corresponding ether, and thiol-ene addition of cysteamine hydrochloride. In particular, the final step was optimized by adjusting temperature, solvent, reagent concentration, and molar ratio to achieve quantitative double-bond conversion under mild reaction conditions. By leveraging the tunable water solubility of the product, residual siloxane impurities from the second synthetic step were successfully removed, yielding a pure glyceryl-based trifunctional polyamine (GTA) with a flexible structure and a low melting point ($T_m = 48\text{ }^{\circ}\text{C}$). The new polyamine was fully characterized by ^1H -, ^{13}C - and 2D-NMR, IR spectroscopy, and ESI-MS, and subsequently reacted at $50\text{ }^{\circ}\text{C}$ with a liquid bis(α -alkylidene cyclic carbonate) to design the solvent- and catalyst-free 2K NIPU adhesive and coating formulation **PGTA**. The high nucleophilicity of GTA terminal amines promoted fast crosslinking, reaching the gel point in 49 seconds and complete curing within 24 hours. Compared to a Jeffamine T-403-based analogue (formulation **PJ**), **PGTA** provided a better crosslinked polymer network with higher gel contents ($\text{GC}_{\text{H}_2\text{O}} = 99.2 \pm 0.3\%$; $\text{GC}_{\text{THF}} = 96.6 \pm 0.3\%$), likely due to the absence of organic base catalysts that would cause carbonate hydrolysis. TGA analysis of **PGTA** revealed the characteristic dehydration step of poly(hydroxy-oxazolidone)s ($T_{\text{dehyd}} = 142\text{ }^{\circ}\text{C}$), followed by backbone decomposition at much higher temperature ($T_{\text{deg}10\%} = 364\text{ }^{\circ}\text{C}$). The long aliphatic segments of the polyamine imparted both flexibility ($T_g = -5\text{ }^{\circ}\text{C}$) and hydrophobicity ($\text{SI}_{\text{H}_2\text{O}} = 5.7 \pm 0.5\%$, $\text{CA} = 83 \pm 5^{\circ}$) to the thermoset structure. Despite the nonpolar nature of the triamine, which negatively affected **PGTA** adhesion performance on aluminum ($\tau = 2.2 \pm 0.4\text{ MPa}$),

its hydrophobicity makes the formulation an ideal candidate for developing water-resistant coatings or bonding nonpolar substrates. Overall, this work introduced a novel, highly reactive, and fully renewable polyamine with low melting point and broad applicability as a crosslinker in polymer synthesis. By developing a solvent- and catalyst-free 2K NIPU adhesive and coating formulation and comparing it to previously reported NIPU thermosets, a practical application of the bio-based triamine was demonstrated, highlighting its potential for the design of other sustainable materials that capitalize on its intrinsic hydrophobicity.

6 CONCLUSION AND OUTLOOK

Among the most groundbreaking chemical innovations of the early 20th century, the discovery and development of PUs profoundly transformed nearly every industrial sector, including packaging, textiles, transportation, electronics, energy, construction, and healthcare. Their exceptional versatility stems from the ability to finely tune both the macromolecular architecture and microscopic morphology of the polymer network. By controlling parameters such as hydrogen bonding, phase separation, and macromolecular mobility, chemists have been able to tailor a wide range of mechanical, thermal, and chemical properties, enabling the creation of materials with highly specific characteristics and multifunctional purposes.

Despite their industrial ubiquity, the concerns over worker health and environmental impact related to PU synthesis have driven intensive research toward safer and more sustainable NIPUs. These have emerged as a promising class of materials that aim to retain the advantageous properties of conventional PUs while eliminating the use of isocyanates and phosgene. However, while NIPUs offer clear benefits in terms of safety and sustainability, their practical implementation remains limited by several key challenges. In the field of NIPU adhesives and coatings, the polyaddition of polyCCs and polyamines represents the most promising synthetic route, although it typically exhibits slow kinetics and requires an external heat source or long reaction time to achieve complete curing and optimal performance. Moreover, the necessity to avoid hazardous and environmentally detrimental organic solvents and the limited availability of bio-based precursors remain critical bottlenecks in the up-scaling of NIPU production.

6.1 Conclusion

In this work, these key limitations were systematically investigated and addressed through the development of waterborne and solvent-free formulations under mild conditions, as well as through the design of a bio-based polyamine crosslinker for NIPU thermosets.

Waterborne 1K NIPU thermoset formulations were developed under mild conditions, without external emulsifiers, and using water as the sole reaction medium. The synthetic approach relied on the post-polymerization modification of a polyamine (PVAm) with a functional cyclic carbonate (VEC), which was investigated as a representative case for converting water-soluble polyamines into PHU-bearing olefins. While this strategy was initially conceived to enable modulation of the functionalization degree and, consequently, tuning of the resulting thermoset

properties, the accessible range of functionalization proved to be more limited in practice. This behavior was attributed to the concurrent formation of urea linkages and to a practical upper limit imposed by steric hindrance along the polymer backbone, which limited further incorporation of urethane functionalities. The study of the room-temperature aminolysis nevertheless revealed clear trends in functionalization efficiency and influence of competing side reactions, providing mechanistic insight into the reactivity of water-soluble polymers with a high density of amine groups. The resulting PHU grafts, formulated as aqueous systems with a relatively low solid content, were subsequently converted into 1K thermoset formulations that underwent rapid crosslinking in water upon addition of a thermal initiator and heating to 65 °C, reaching gelation within 14 minutes. The formulations were applied as transparent coatings and formed highly hydrophilic, densely crosslinked networks with limited macromolecular mobility, furnishing rigid and brittle films. The presence of residual amines within the network could enable applications in various areas, such as water treatment, antimicrobial protection, and indoor-air depollution. From a sustainability perspective, the use of water as the sole reaction medium and the absence of external emulsifiers constitute important advantages. However, the relatively low solid content of the formulations, together with the fragility and limited water stability of the resulting materials, may compromise their practical applicability and reduce some of the environmental benefits in real-world applications. A promising research avenue lies in the identification of alternative biobased polyamine platforms that combine water solubility with chemical accessibility under conditions favorable to CC aminolysis. In this context, suitably modified water-soluble chitosan derivatives may represent an interesting extension of the present strategy.

A series of solvent-free NIPUs were developed using the first liquid bis α CC obtained on a multigram scale with a high degree of purity. The synthetic route to this monomer enabled access to a highly reactive CC precursor, although its preparation involved multiple reaction steps, including organometallic chemistry, which added complexity to the overall synthetic process. However, the availability of the bis α CC in liquid form represented a key advantage for solvent-free formulation design and enabled the formulation of room-temperature curable adhesives and coatings *via* bulk polyaddition with various primary polyamines. The limited availability of liquid polyamine crosslinkers with tailored reactivity necessitated the use of catalytic activation to achieve efficient curing under ambient conditions. This requirement partly offset the intrinsic reactivity advantage of the bis α CC monomer and may have promoted side reactions with water, thereby slightly influencing the stoichiometry of the formulation. The step-growth polymerization was nonetheless investigated in detail, yielding new insights into the reaction kinetics and linkage

selectivity of these solvent-free NIPU formulations. The resulting thermosets, composed of poly(hydroxy oxazolidone) and poly(oxo-urethane) linkages, were fully characterized in terms of rheological, thermal, mechanical, surface, chemical resistance, and adhesion properties. Notably, they exhibited superior adhesion to aluminum substrates, particularly in the presence of dopamine, compared to commercially available PU adhesives, indicating their potential suitability as a competitive alternative to isocyanate-based products for structural adhesive applications. More importantly, these formulations demonstrated that solvent-free NIPU adhesives and coatings can be cured at room temperature while maintaining attractive thermomechanical and adhesive properties. Considering that slow curing kinetics and the need for elevated temperatures remain among the most significant barriers to the industrial implementation of conventional PHU technologies, this result represents an important step toward the development of industrially relevant NIPU systems. Nevertheless, the environmental benefits associated with the absence of organic solvents and the possibility of curing at room temperature should be weighed against the complexity of the bis α CC synthesis, which currently relies on multiple reaction steps and organometallic chemistry. Areas for further investigation include the development of new families of vinylene CC, hydroxyoxazolidone, and oxo-urethane monomers accessible through more straightforward and easily scalable synthetic routes, as well as the design of polyamine crosslinkers with finely tuned reactivity and viscosity to better match RT curing requirements. In addition, the implementation of more efficient mixing strategies may further improve network homogeneity and overall material performance.

The industrial secondment at COP Chimie provided valuable insights into the practical aspects of PU formulation development and optimization under industrial conditions. In contrast to academic research environments, the exact chemical composition and functional group content of some raw materials were not always fully specified, and the formulation work was sometimes conducted using mass ratios. While this limited fine control over stoichiometry at the molecular level, it realistically reflected the conditions under which industrial PU systems are developed and produced. In addition, the instruments and tools available during the secondment differed substantially from those typically employed in academic laboratories. The experimental workflow relied on hands-on, experience-driven methodologies, with a strong emphasis on internal benchmarking and comparative performance evaluation rather than absolute physicochemical characterization. Within this context, industrially established PU formulations from the company's portfolio were revisited and modified to enhance their suitability for adhesives and coatings. Efforts focused on optimizing curing kinetics, minimizing foaming, and ensuring

formulation homogeneity. A comparative analysis between these systems, a commercial benchmark, and the synthesized solvent-free NIPUs helped identify optimal formulations for specific end-use applications. Further investigations would be required to fully assess adhesive or coating performance on the target materials produced by the company and to support the potential translation of these formulations to new end-use scenarios.

To address the limited availability of suitable polyamine crosslinkers for solvent-free NIPU formulations, a triamine derived from undecylenic acid was synthesized through a three-step process designed in accordance with green chemistry principles, emphasizing atom economy, waste minimization, and the use of low-hazard, bio-based reagents. Whenever possible, energy-efficient reaction conditions and benign solvents were employed to further minimize environmental impact. Although an impure intermediate had to be employed during the final stage of the synthesis, preventing accurate determination of the isolated yield, the optimization of this synthetic step was not affected. With the work-up procedure recently established, precise yield determination can be readily achieved in future syntheses. Beyond the optimization of the synthetic route, a key objective was to obtain a fully bio-based, liquid triamine; however, the resulting compound was found to be solid at room temperature, requiring mild heating to ensure melting and homogeneous mixing. Under these conditions, the polyamine was reacted with the bis α CC without the need for catalytic activation, and curing proceeded significantly faster than in previously developed systems. The resulting NIPU thermosets displayed enhanced resistance to organic solvents and reduced affinity for water, the latter attributed to the long aliphatic chains of the fatty acid moiety. These hydrophobic properties were also considered responsible for the limited adhesion of the polymer to aluminum substrates compared to more hydrophilic formulations. The hydrophobic nature and high reactivity of this triamine suggest opportunities for its use in water-resistant coatings and for bonding nonpolar substrates. The use of a renewable fatty-acid-derived feedstock contributes to reducing reliance on fossil resources; however, the accessibility and scalability of the starting materials remain important considerations when assessing the overall sustainability of this approach. Beyond its role in the present formulations, this compound may serve as a fully renewable crosslinker with a low melting point and sterically accessible amine functional groups for a wider range of polymer synthesis strategies, extending its applicability beyond NIPU systems.

In conclusion, this thesis presents a systematic approach to the development of more sustainable NIPU adhesives and coatings by integrating molecular design, novel building blocks,

green chemistry principles, and comparative formulation analysis. By bridging fundamental reactivity studies with product testing, this work aims to deepen understanding of the relationships between polymer structure, processing, and performance.

6.2 Outlook

From a global perspective, the systems investigated in this doctoral work exhibit varying levels of chemical complexity and potential competitiveness with conventional PU alternatives.

The waterborne strategy based on the functionalization of water-soluble polyamines offers conceptual flexibility and could, in principle, be extended to bio-based precursors, enabling 1K formulations crosslinkable through radical polymerization of vinyl functionalities upon an external stimulus. However, its further development is intrinsically linked to several unresolved challenges, including the limited solid content imposed by polyamine solubility under alkaline conditions, the relatively narrow pH window required for efficient CC aminolysis, the limited water stability of the final material, and the availability of polyamine precursors with tunable functionality to enable adjustment of crosslinking density and thermoset properties.

Among the different approaches investigated, the solvent-free room-temperature-curable NIPU systems appear particularly promising from a technological perspective, as they directly address several of the major limitations traditionally associated with NIPU chemistry, including solvent use, curing temperature, and reaction rate. Structural modifications of α -alkylidene CC monomers, such as increasing the spacing between reactive units to reduce melting temperature, appear readily accessible and may improve processability. At the same time, the exceptionally high reactivity of these activated CCs creates new requirements for the polyamine crosslinkers, whose proneness to reaction must be carefully balanced. Unless alternative routes can be identified that avoid organometallic steps, an attractive strategy may consist in directly incorporating hydroxyoxazolidone or oxo-urethane motifs into the monomer backbone and subsequently evaluating their performance as building blocks for adhesive and coating applications.

With regard to the industrial formulations explored during the secondment at COP Chimie, further development would necessarily require systematic evaluation of adhesive and coating performance on the specific materials produced by the company, as well as extensive formulation optimization. More broadly, the evolving regulations and increasing constraints associated with isocyanate-based chemistries highlight the importance of a critical assessment before considering the implementation of new production lines based on conventional PU technologies.

Chapter 6: Conclusion and outlook

The bio-based polyamine developed in this work is distinguished by the absence of ester functionalities, which confers an enhanced chemical stability significantly advantageous for long-term storage and durability. Nevertheless, despite being renewable feedstocks, the raw materials employed in the synthesis remain less accessible compared to commodity chemicals. In this context, extending the synthetic strategy to more readily available vegetable oils represents a promising research avenue, even though recent studies have highlighted the additional complexity associated with functionalizing internal double bonds. Continued methodological advances may help overcome these limitations and improve the attractiveness of this approach.

Beyond the specific systems discussed, future efforts should focus on the development of scalable production routes for highly reactive CC derivatives and polyamines that can be obtained through straightforward syntheses from readily accessible feedstocks. In particular, the room-temperature-curable solvent-free NIPU systems developed in this work suggest that improving monomer reactivity represents a promising strategy, but alternative approaches based on internally generated heat, similarly to those explored for NIPU foams, may also deserve further investigation. Such strategies would require careful control of exothermicity and would remain unsuitable for temperature-sensitive applications, but prepolymer-based routes could provide a useful compromise between reactivity, processing control, and formulation stability. Beyond curing performance, future studies should also evaluate the long-term durability of the developed materials under realistic service conditions and assess their environmental impact through comprehensive life-cycle and techno-economic analyses. In addition, end-of-life management and recyclability should be considered during the design of future polymer systems to ensure that improvements in production sustainability are not offset by challenges associated with material disposal.

More broadly, future developments in the field of sustainable polymer materials would benefit from focusing on strategies that offer a clear advantage in terms of environmental impact over previously reported strategies, ideally while addressing specific target applications. Consideration of technological readiness, scalability, and market relevance at early stages of research would provide valuable guidance for experimental design and performance benchmarking. Within this framework, the use of renewable, readily accessible resources and safe processes should be regarded as key criteria for assessing the value of emerging material technologies and prioritized over the sheer quantity of research outputs. While significant challenges remain, continued efforts toward sustainable material design and application-oriented innovation will be essential to developing materials that not only meet technical

requirements but also contribute to safer, cleaner, and more responsible polymer technologies for the future.

7 EXPERIMENTAL SECTION

7.1 Experimental section Chapter 5.1

7.1.1 Materials and methods

Reagents and materials

4-Vinyl-1,3-dioxolan-2-one (vinyl ethylene carbonate, VEC, 99%) and sodium persulfate (reagent grade, $\geq 98\%$) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl, S. G. 1.18, $\sim 37\%$) and sodium hydroxide (NaOH, $\geq 97\%$) were purchased from Thermo Fisher Scientific. 1 kDa Spectra/Por 7 Dialysis Tubing (1 kDa) was purchased from REPLIGEN. Poly(vinylamine) (PVAm) was synthesized by hydrolysis of poly(N-vinyl formamide) adopting a protocol described by Detrembleur and co-workers.²³⁶ Macromolecular parameters were determined on the poly(N-vinyl formamide) precursor ($M_n = 10,500 \text{ g mol}^{-1}$, $M_w = 90,000 \text{ g mol}^{-1}$, and $\bar{D} = 8.6$) by SEC analysis using PL Aquagel 40 and 30 columns, with 0.1 M LiNO_3 containing 0.05% NaN_3 as the eluent at 20 °C, a flow rate of 1 mL min^{-1} , and a Wyatt T-Rex Optilab refractive index detector.

Solvents

Deuterium oxide (D_2O 99.9% D) was purchased from Eurisotop. Sodium deuterioxide solution (40 wt. % in D_2O , 99.5% D) was purchased from Sigma-Aldrich. Methanol (MeOH, HPLC grade) was purchased from VWR.

General procedure for the functionalization of PVAm

VEC was added dropwise and under stirring to a reaction tube containing 2 mL of an aqueous PVAm solution (32.3 mg mL^{-1} , $[\text{NH}_2] = 0.75 \text{ M}$, pH 10.5). Depending on the targeted $\text{NH}_2:\text{CC}$ ratio, the corresponding VEC amount used was: for a 4:1 ratio, 0.25 eq. ($375 \text{ }\mu\text{mol}$, 42.8 mg); for a 2:1 ratio, 0.50 eq. ($750 \text{ }\mu\text{mol}$, 85.6 mg); and for a 1:1 ratio, 1.00 eq. (1.50 mmol , 171.2 mg). The tube was sealed, and the reaction mixture was stirred at room temperature for 24 hours. The resulting NIPU graft was then dialyzed in water (pH 5) for 24 hours using a 1 kDa porous membrane, freeze-dried, and analyzed by $^1\text{H-NMR}$ spectroscopy.

Preparation of PHU thermosets

The graft polymers prepared as described above were dissolved, in the same vial used for freeze-drying, in 2 mL of an aqueous sodium persulfate solution (2.98 mg mL^{-1} , $[\text{Na}_2\text{S}_2\text{O}_8] = 12.5 \text{ mM}$, pH 5), reaching polymer concentrations of approximately 50 and 70 mg mL^{-1} for **T1** and **T2**, respectively. For PHU coatings, 1 mL of solution was spread over a 10 cm^2 glass plate surface

(drop-coating); for PHU freestanding films, 4 mL of solution was poured into a cylindrical Teflon mold (4 cm in diameter) (solvent-casting). The formulations were cured for 3 h at 65 °C and subsequently dried under air at room temperature overnight. The resulting transparent films were approximately 100 μm thick for the coatings and 300 μm thick for the freestanding films, which were subsequently used for thermoset characterization.

7.1.2 Characterization techniques

Nuclear Magnetic Resonance Spectroscopy

^1H -NMR spectra were recorded immediately after solubilization in a D_2O solution at pH 13 to guarantee proper signal resolution while minimizing polymer degradation. The analysis was performed on a Bruker 400 MHz spectrometer, acquiring 16 scans for each spectrum. Chemical shifts were reported in parts per million (ppm) and referenced to the residual HOD signal, which was set to 4.79 ppm. Although this value corresponds to its typical position at neutral pH, the exact HOD chemical shift slightly varies with pH.⁵⁰⁹ Peak assignments were confirmed by COSY and HSQC experiments, solubilizing the samples in D_2O at pH 10.5 to minimize polymer degradation. The extent of functionalization, expressed as the fractions of amines converted and urethane linkages formed relative to the initial amine content, was calculated for each PHU graft using Equations 7.1 and 7.2, respectively:

$$\text{Amine conversion (\%)} = \left(1 - \frac{2\int_{\text{pristine PVAm CH}}}{\int_{\text{backbone CH}_2}}\right) \times 100$$

Equation 7.1 *Amine conversion.*

$$\text{Urethane linkage content (\%)} = \frac{2\int_{\text{side-chain vinylene CH}}}{\int_{\text{backbone CH}_2}} \times 100$$

Equation 7.2 *Urethane linkage content.*

where $\int_{\text{pristine PVAm CH}}$, $\int_{\text{backbone CH}_2}$, and $\int_{\text{side-chain vinylene CH}}$ are the integrals of the pristine PVAm CH (at 2.7–3.4 ppm), the backbone CH_2 (at 1.1–1.9 ppm), and the side-chain vinylene CH (at 5.8–6.0 ppm) signals, respectively.

Fourier-Transform Infrared (FTIR) Spectroscopy

Infrared spectra were registered on a Bruker Alpha-P spectrometer equipped with a diamond attenuated transmission reflectance (ATR) device. For each sample 24 scans were recorded over the range 4000–400 cm^{-1} with a normal resolution of 2 cm^{-1} .

Chapter 7: Experimental section

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed on a TGA2 instrument from Mettler Toledo. Approximately 5 mg of dry sample was pre-treated at 65°C under vacuum for 3 h, then analyzed by heating at 10 °C/min from 30 °C to 600 °C under nitrogen atmosphere (20 mL/min) to determine the degradation behavior of the PHU and the corresponding thermosets.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed on a DSC 250 differential calorimeter from TA Instruments. Approximately 5 mg of dry sample was pre-treated at 65°C under vacuum for 3 h, then sealed in hermetic aluminum pans and analyzed by heating at 10 °C/min from 25°C to 120 °C. Subsequently, the samples were cooled down to -80 °C at a rate of 10 °C/min and then re-heated at 10 °C/min from -80°C to 160 °C. All the experiments were performed under ultrapure nitrogen flow. The glass transition temperature (T_g) was determined using the second heating ramp.

Gel Content Measurements

PHU freestanding films were cut into rectangular pieces (1 × 0.5 cm), pre-treated at 65 °C under vacuum for 3 h, weighed, and submerged in 20 mL of solvent (distilled water or methanol) for 120 h at room temperature. The samples were then removed from the solvent, dried at 70 °C for 24 h, and weighed again. The gel content (GC) was obtained from Equation 7.3:

$$GC (\%) = \frac{W_f}{W_i} \times 100$$

Equation 7.3 *Gel content.*

where W_i is the initial weight and W_f is the final weight of the dried sample. The measurements were repeated three times for each formulation.

Rheological Measurements

The rheological behavior of the waterborne PHU thermoset formulation **T2** was studied with a rotational rheometer ARES-G2 from TA Instruments, executing time sweep measurements with a parallel plate geometry and at constant strain deformation (1%) and frequency (1 Hz). A low-viscosity (200 cSt) silicon oil was used to seal the sample and prevent evaporation during measurement.

Tensile Testing

Tensile tests were conducted at 25 °C on an Hegewald & Peschke Inspekt Table universal testing machine equipped with a 1 kN load cell and at a displacement rate of 10 mm/min. For each formulation, Young's modulus (E), ultimate tensile strength (σ_u), and fracture strain (ε_f) were determined from the average values of three dry dog-bone test specimens, each with a thickness of approximately 0.3 mm, a gauge length of 12 mm, and an original width of 2 mm. Young's modulus and fracture strain were determined using Equations 7.4 and 7.5, respectively:

$$E = \frac{\sigma}{\varepsilon}$$

Equation 7.4 Young's modulus.

$$\varepsilon_f = \frac{(L_f - L_i)}{L_i} \times 100$$

Equation 7.5 Fracture strain.

where σ is the tensile stress, ε is the engineering extensional strain, L_f is the length of the sample at fracture, and L_i is the initial length of the sample. E was calculated in the elastic portion of the stress-strain curve with $0.5\% < \varepsilon < 1\%$.

7.1.3 Supporting information

7.1.3.1 Waterborne PHU grafts

NMR characterization

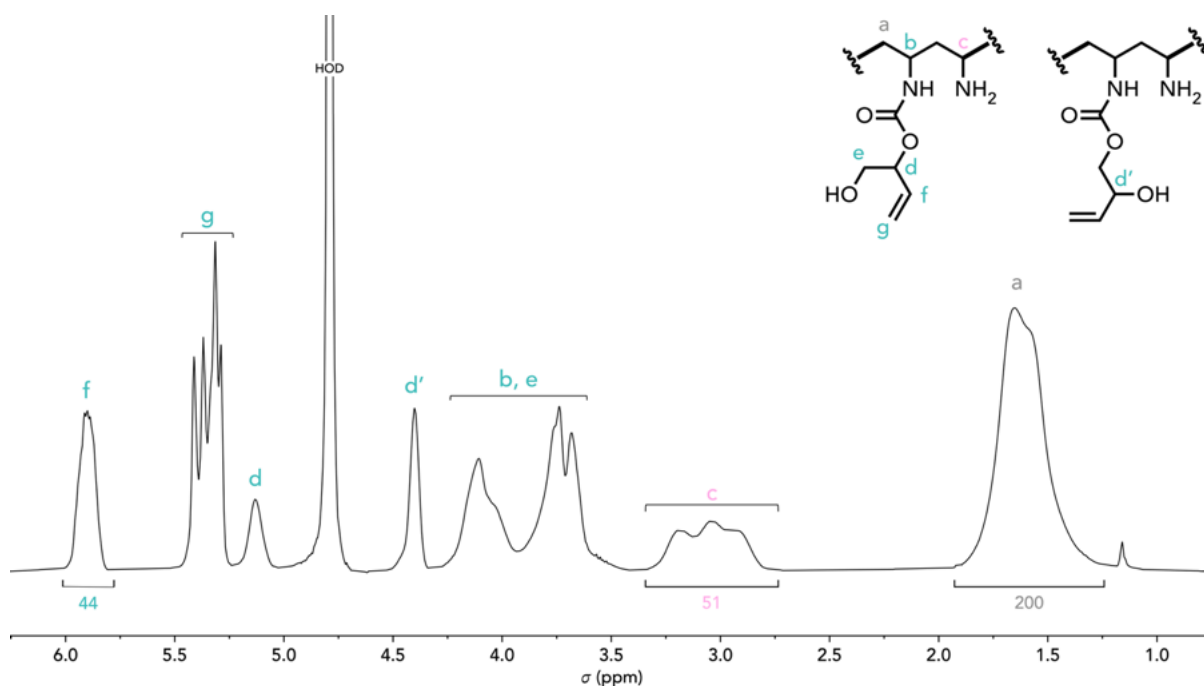


Figure 7.1 ^1H -NMR spectrum of G2 (pH 13).

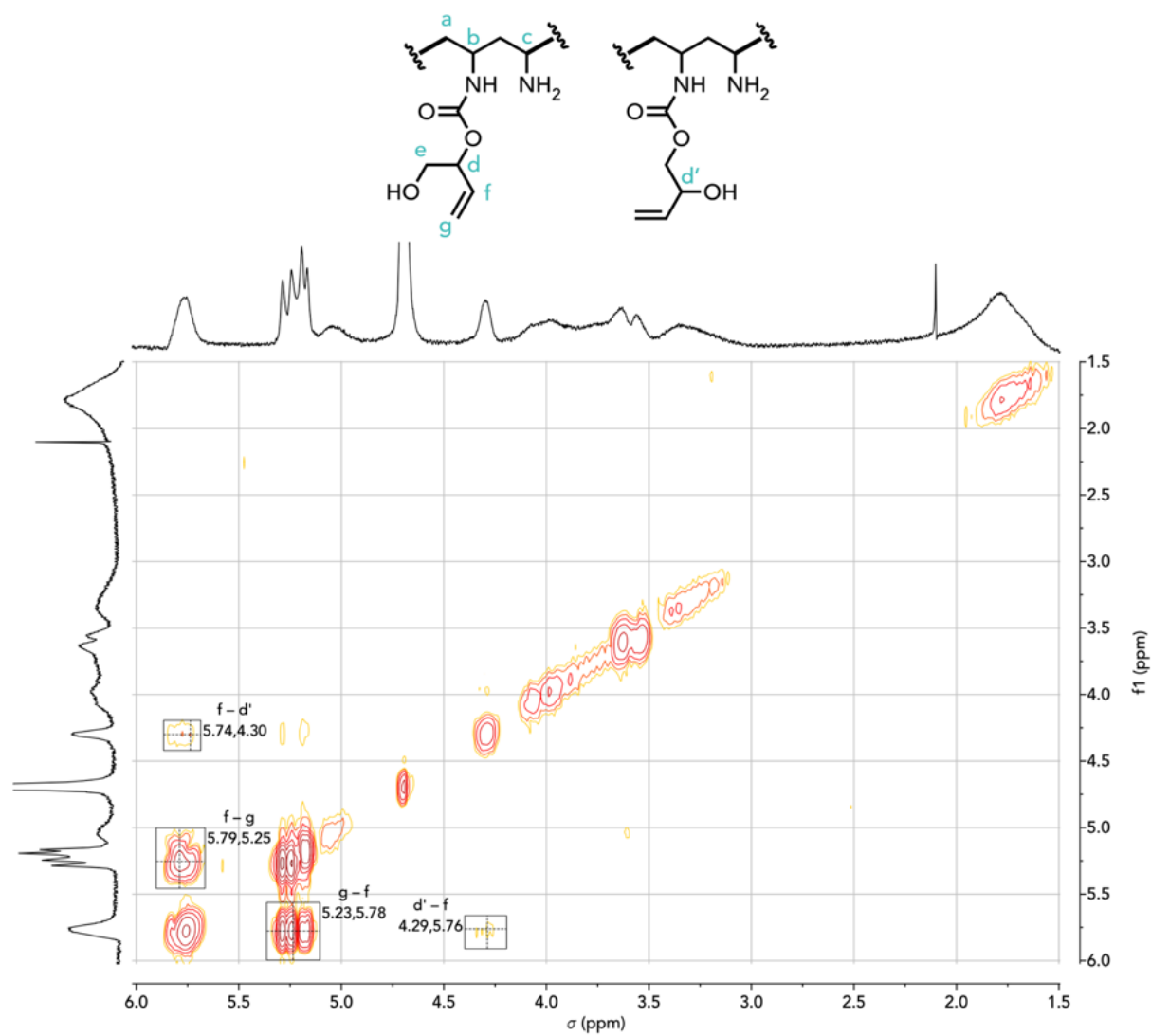


Figure 7.2 COSY spectrum of G2 (pH 10.5).

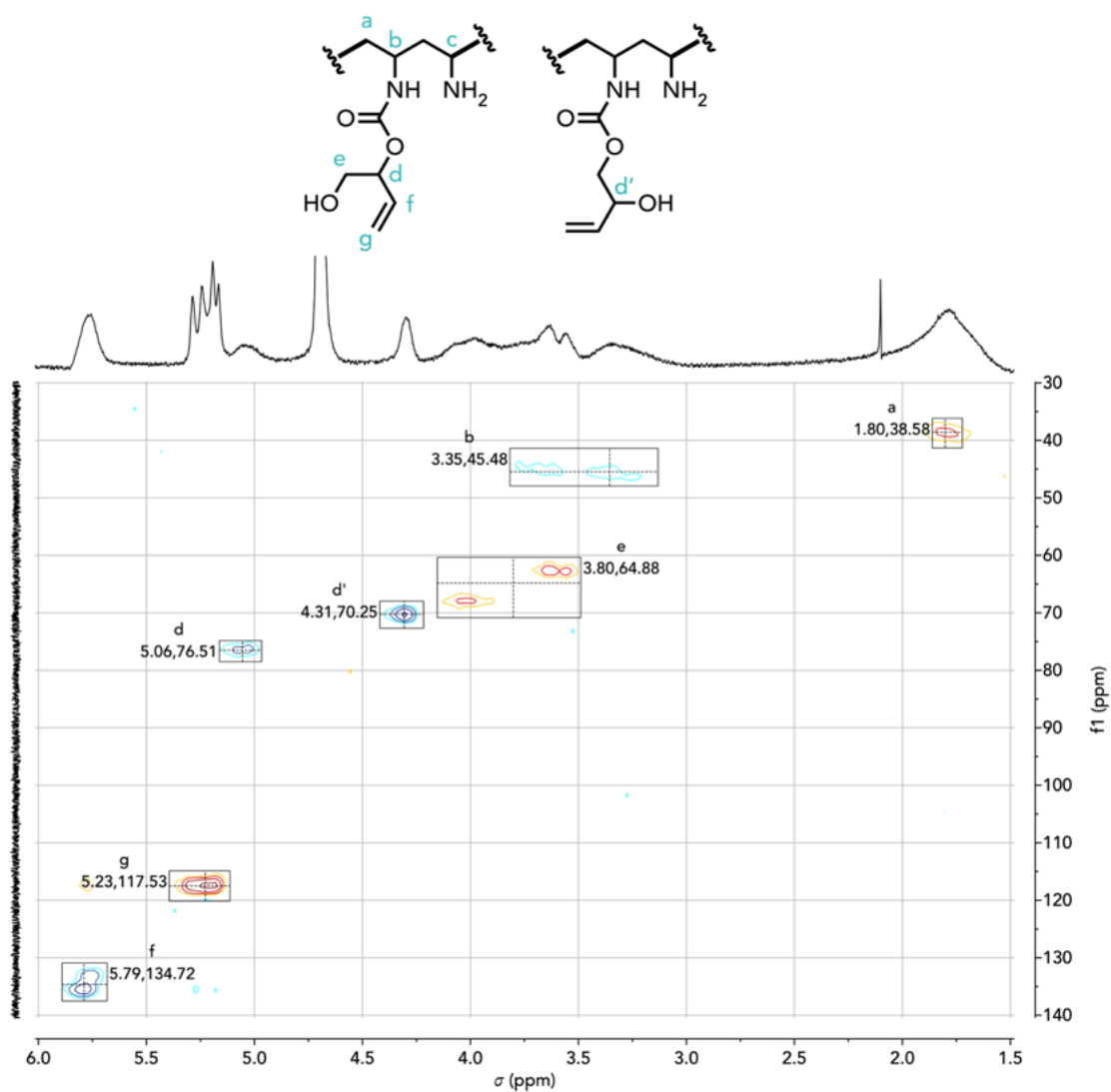


Figure 7.3 HSQC spectrum of G2 (pH 10.5).

IR analysis

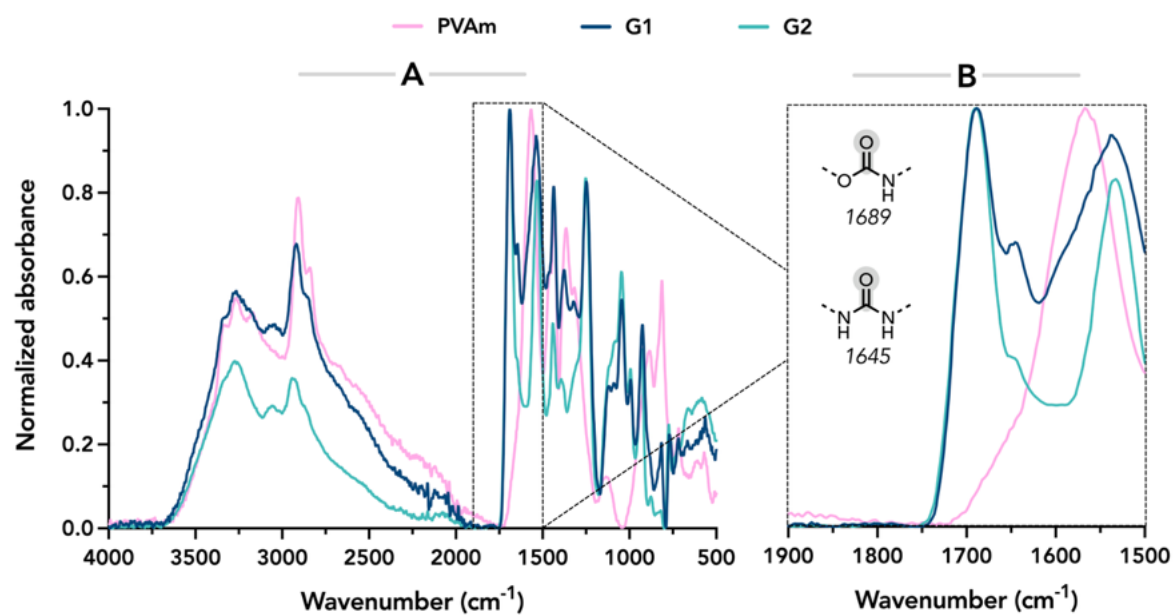


Figure 7.4 Overlay of infrared spectra for PVAm (pink), G1 (dark blue), and G2 (teal) (A); characteristic urethane and urea bands in the carbonyl stretching region (B).

TGA curves

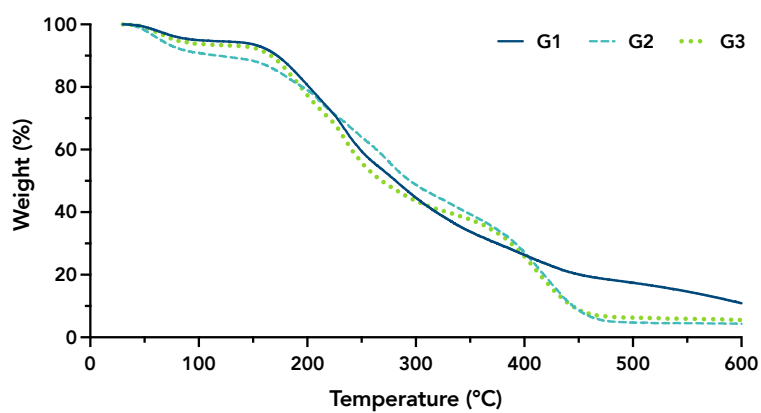


Figure 7.5 TGA curves of G1 (solid curve), G2 (dashed curve), and G3 (dotted curve).

DSC analysis

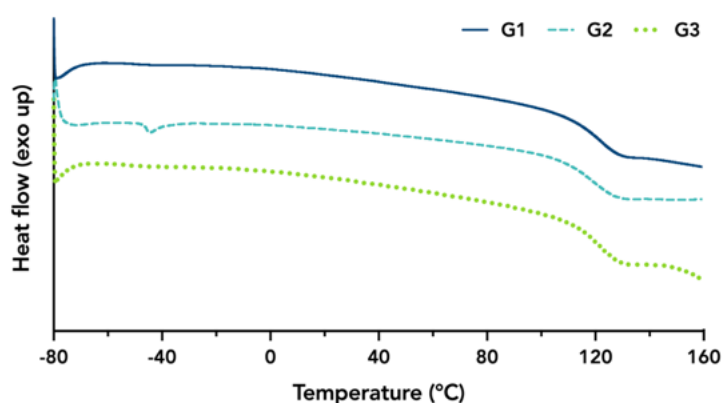


Figure 7.6 DSC curves of G1 (solid curve), G2 (dashed curve), and G3 (dotted curve).

7.1.3.2 Waterborne PHU thermosets

Visual appearance

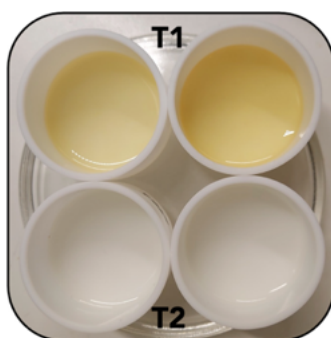


Figure 7.7 Visual appearance of T1 (top) and T2 (bottom) following crosslinking.

Gel content

Table 7.1 Gel contents of NIPU thermosets.

Entry	NIPU thermoset	GC (%) ^a	
		MeOH	H ₂ O
1	T1	92 ± 1	58 ± 5
2	T2	93 ± 1	88 ± 2

^aGC: gel content of self-standing films submerged in MeOH or water for 120 h at RT and dried at 70 °C for 24 h.

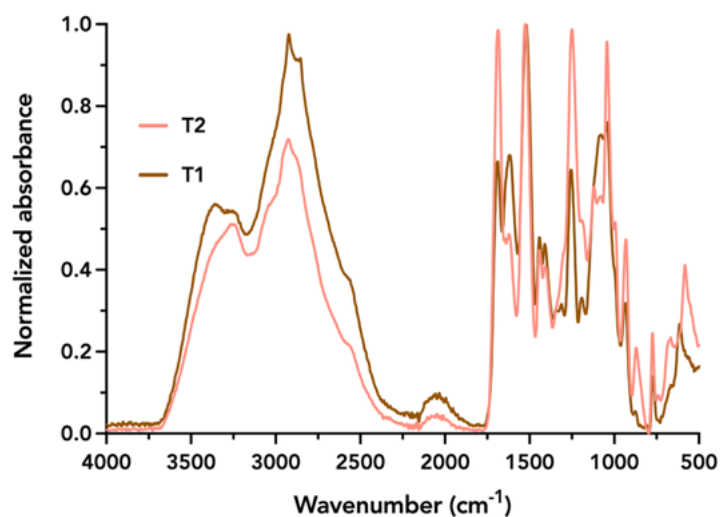


Figure 7.8 Overlay of infrared spectra for T1 (brown) and T2 (coral).

Rheology study

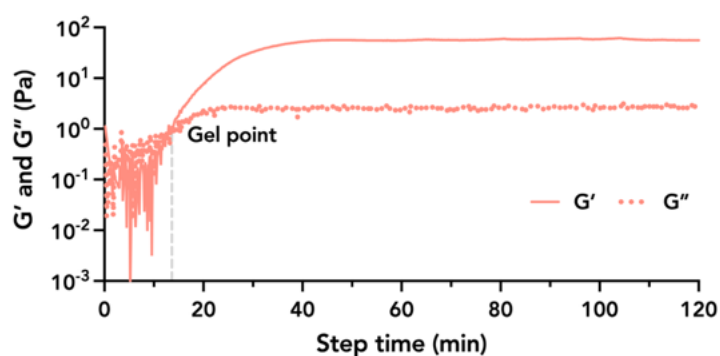


Figure 7.9 Evolution in time of storage (G' , solid curve) and loss (G'' , dotted curve) moduli for T2.

TGA curves

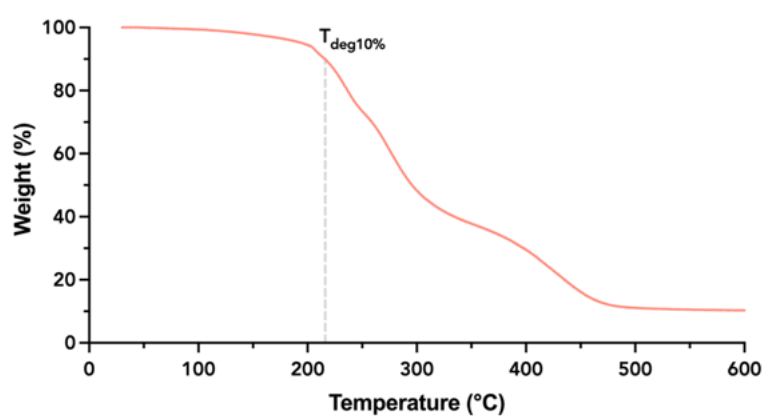
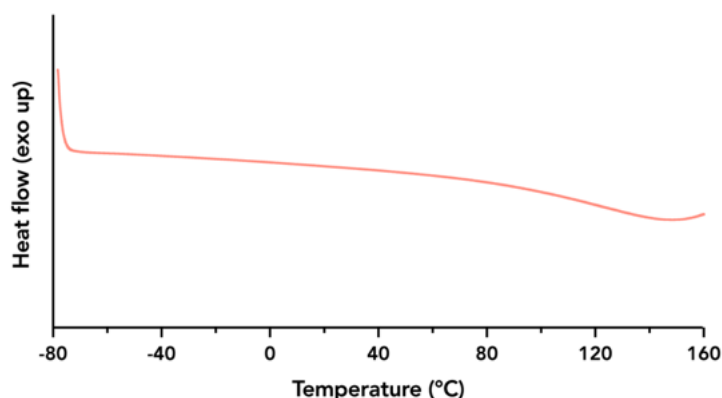
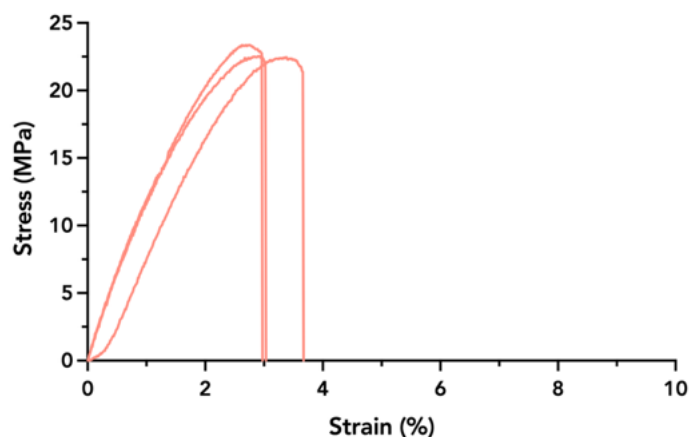


Figure 7.10 TGA curve of T2.

DSC analysis**Figure 7.11** DSC curve of T2.*Tensile testing***Figure 7.12** Stress-strain curves of T2.**7.2 Experimental section Chapter 5.2****7.2.1 Materials and methods***Reagents and materials*

3-Buten-2-one (containing hydroquinone as stabilizer, 90%), 2,2'-(ethylenedioxy)diethanethiol (95%), ethynylmagnesium bromide solution (0.5 M in THF), tris(2-aminoethyl)amine (96%), trimethylolpropane tris[poly(propylene glycol), amine terminated] ether (polyetheramine T-403, average M_n 440 g/mol), *m*-xylylenediamine (99%), 5-amino-1,3,3-trimethylcyclohexanemethylamine (mixture of *cis* and *trans*, $\geq 99\%$), poly(propylene glycol) bis(2-aminopropyl ether) (average $M_n \sim 400$ g/mol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) ($\geq 99\%$), and copper iodide ($\geq 98\%$) were purchased from Sigma-Aldrich. Diethylenetriamine ($>98\%$), triethylenetetramine ($<90\%$), 3,3'-diaminodipropylamine ($>98\%$), tetraethylenepentamine

Chapter 7: Experimental section

(mixture of branched chain isomers and cyclic compounds), and 4,4'-methylenebis(2-methylcyclohexylamine) (mixture of isomers) were purchased from TCI. 2-(3,4-Dihydroxyphenyl)ethylamine hydrochloride (dopamine hydrochloride) was purchased from Fluorochem Ltd. Carbon dioxide (CO₂) N45 was supplied by Air Liquid.

1 kDa Spectra/Por® 7 Dialysis Tubing was purchased from REPLIGEN. Aluminum alloy (5754, or AlMg₃) and stainless-steel (S235JR) bars were prepared by cutting the material into rectangular pieces (6 cm × 1.5 cm × 0.3 cm for aluminum substrates and 6 cm × 1.5 cm × 0.1 cm for stainless-steel ones). Wood substrates (oak, 6 cm × 1.5 cm × 1.7 cm) were purchased from BigMat Cataldo (Belgium); high-density polyethylene substrates (K46-06-185, 6 cm × 1.5 cm × 0.3 cm) were provided by INEOS (Belgium); poly(methyl methacrylate) substrates (6 cm × 1.5 cm × 0.3 cm) were provided by Superplastic (Belgium). Aluminum alloy (Al 2024-T3) panels were provided by SONACA (Belgium) and prepared by cutting the material into rectangular pieces (6 cm × 5 cm × 0.1 cm).

TEROSON® PU 6700 was purchased from Henkel®. HUNTSMAN® ARALEDITE® 2028-1 was purchased from Epoxidharze Andreas Weigel (Raschau-Markersbach, Germany).

3-Buten-2-one was purified by distillation prior to use. 4,4'-(6,9-Dioxa-3,12-dithiatetradecane-1,14-diyl)bis(4-methyl-5-methylene-1,3-dioxolan-2-one) (bis α CC) was synthesized adopting the protocol described by Detrembleur and coworkers.⁴²³

General procedure for the synthesis of linear NIPUs

Liquid bis α CC (462.6 mg, 1.0 mmol, 1 eq.) was added to a reaction tube together with a solution of diamine (1.0 mmol, 1 eq.) and DBU (30.4 mg, 0.2 mmol, 0.2 eq.). The solvent-free mixture was stirred until vitrification and stored at 25 °C under air. After 24 h, an aliquot of the crude product was withdrawn for ¹H-NMR and SEC characterizations.

Water-insoluble linear polymers (**PA1** and **PA2**) were solubilized in an acidic solution of formic acid in THF (2 mL, 0.5 M) to quench the polymerization reaction and subsequently precipitated in water and freeze-dried. To ensure complete removal of catalyst and acid, these operations were repeated without using formic acid. Afterward, the samples were solubilized in THF and dialyzed in the same solvent for 24 h with a 1 kDa porous membrane. The polymers were precipitated in diethyl ether, recovered by filtration, and dried overnight under vacuum at 55 °C.

Linear polymers that were partially soluble in water (**PA3**) were solubilized in an acidic solution of formic acid in THF (1 mL, 1 M) to quench the polymerization reaction and subsequently precipitated in water and freeze-dried. Afterward, the samples were solubilized in THF and

dialyzed in the same solvent for 24 h with a 1 kDa porous membrane. The polymers were precipitated in hexane, recovered by filtration, and dried overnight under vacuum at 55 °C.

Linear polymers that were soluble in water (**PA4**) were solubilized in an acidic solution of formic acid in THF (2mL, 0.5 M), and dialyzed in water for 24 h with a 1 kDa porous membrane. The solutions were freeze-dried, and the solids were solubilized in THF, precipitated in hexane, and dried overnight under vacuum at 55 °C.

Preparation of NIPU adhesives, coatings, freestanding films, and Shore hardness test specimens

Liquid bis α CC was added to a vial together with a mixture of polyamines and DBU at room temperature, and the formulation was then stirred for 50 seconds. For catechol-containing formulations, a precise amount of dopamine hydrochloride was pre-mixed with DBU and Jeffamine T-403 (dopamine percentage, DOP%, calculated considering the total number of amino groups). Once a homogeneous mixture was obtained, a precise amount of this solution was added to a vial containing bis α CC. Each formulation, with or without dopamine, was prepared keeping an equimolar ratio between cyclic carbonate and amino functional groups, and the catalyst loading was calculated considering the total number of amino and cyclic carbonate reactive groups.

After stirring, the NIPU formulations were processed according to their application: for adhesive samples, the mixture was immediately applied to the substrate for lap-shear testing; for coating samples, the mixture was deposited on an aluminum panel and spread using a casting knife film applicator (ASTM D823) to obtain a coating thickness around 250 μ m; for freestanding films, the mixture was poured into a Teflon mold (4 cm $\times$ 2.5 cm $\times$ 0.1 cm); for Shore hardness test specimens, the mixture was poured in a cylindrical silicone mold (0.8 cm in height, 1.5 cm in diameter).

The polymeric coatings were characterized by cross-cut adhesion test and water contact angle measurements, while the freestanding films were exploited for thermal characterization, tensile testing, and evaluation of swelling behavior and gel content. Each formulation was tested after 1 day and/or 7 days of curing at 25 °C.

Surface treatments

The substrates used for cross-cut and lap-shear tests were treated to remove surface impurities that could alter the evaluation of coating and adhesion performance. Aluminum bars and panels were treated following a procedure previously reported by the authors:⁴²² the substrate was first immersed into a basic aqueous bath (NaOH 40 g L⁻¹) for 1 minute, and then into an acidic aqueous

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bath (73 wt% water, 25 wt% H₂SO₄, 2 wt% Na₂Cr₂O₇) for 1 minute; at the end of each step the material was washed with distilled water and wiped with tissue paper. Stainless-steel, wood and polyethylene substrates were cleaned with an acetone/isopropanol mixture (1 : 1 V/V) and then with distilled water; poly(methyl methacrylate) substrates were cleaned only with distilled water. The surface of the substrates was wiped with tissue paper after each washing. The procedure was repeated three times, and the substrates were dried at room temperature for 1 h.

Preparation of lap-shear samples

Single-lap joints were prepared to assess the shear strength of 2K NIPU and commercial PU adhesives. For NIPU adhesives, each formulation was mixed for 50 seconds and quickly applied on one extremity of the pretreated substrate, depositing around 45 mg of product over a gluing area of 225 mm². The second bar of substrate was then immediately put on top of the first one, exerting enough pressure to evenly distribute the adhesive over the overlapped area, without forming defects or squeezing the mixture out of the joint. The specimen was then cured at 25 °C for 1 day or 7 days. For commercial PU adhesives, the preparation procedure was identical, except that reagent mixing was performed using the static mixer supplied with the product.

7.2.2 Characterization techniques

Rheological Measurements

The rheological behavior of the 2K formulations was studied with a rotational rheometer ARES-G2 from TA Instruments, executing time sweep measurements with a parallel plate geometry and at constant strain deformation (1%) and frequency (1Hz).

Fourier-Transform Infrared Spectroscopy

Infrared spectra were measured on a Nicolet IS5 spectrometer (Thermo Fisher Scientific) equipped with a diamond attenuated transmission reflectance (ATR) device. For each sample 32 scans were recorded over the range 4000-550 cm⁻¹ with a resolution of 4 cm⁻¹.

Nuclear Magnetic Resonance Spectroscopy

¹H- and ¹³C-NMR analyses were performed in DMSO-d₆ at 25 °C on a Bruker 400 MHz spectrometer in the Fourier transform mode. 16 scans for ¹H spectra and 512 scans for ¹³C spectra were acquired.

Size Exclusion Chromatography

Number-average molecular weight (M_n) and weight-average molecular weight (M_w) of linear NIPUs were determined by size exclusion chromatography (SEC) in dimethylformamide (DMF) containing LiBr (0.025 M) at 55 °C (flow rate: 1 mL/min) using linear polystyrene standards for the calibration. The analyses were carried out with a Waters chromatograph equipped with three columns (Waters Styragel PSS gram 1000 Å (×2), 30 Å), a dual absorbance detector (Waters 2487), and a refractive index detector (Waters 2414).

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed on a TGA2 instrument from Mettler Toledo. To determine the degradation temperature, evaluated starting from the end of the dehydration step, approximately 5 mg of sample was heated at 10 °C/min from 30 °C to 600 °C under nitrogen atmosphere (20 mL/min). To determine the dehydration temperature of linear polymers, identified from the derivative thermogravimetric curve at the beginning of the mass loss signal, around 5 mg of sample was heated at 2 °C/min from 30 to 250 °C under nitrogen atmosphere (20 mL/min).

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed on a DSC 250 differential calorimeter from TA Instruments. Samples of 4 to 6 mg were sealed in hermetic aluminum pans and heated at 10 °C/min from -40 to 120 °C. Subsequently, the samples were cooled to -40 °C at a rate of 10 °C/min and then re-heated at 10 °C/min from -40 to 120 °C (polymers with glass transition temperature close to -40 °C were cooled to -80 °C). All the experiments were performed under ultrapure nitrogen flow. The glass transition temperature (T_g) was determined using the second heating ramp for linear NIPUs, while the first heating cycle was used for crosslinked NIPUs to prevent modifications of the crosslinking degree at high temperature.

Swelling Behavior and Gel Content

NIPU freestanding films were cut into rectangular pieces (1 cm × 0.5 cm) and submerged in 20 mL of solvent (distilled water or THF) for 120 h at room temperature. The samples were then removed from the solvent, gently pressed with a piece of paper, weighed, dried at 70 °C for 24 h, and weighed again. Gel content (GC) was obtained from Equation 7.3, while equilibrium water content (EWC) was obtained from Equation 7.6:

$$\text{EWC (\%)} = \frac{(W_s - W_i)}{W_i} \times 100$$

Equation 7.6 *Equilibrium water content.*

where W_i is the initial weight and W_s is the weight of the swollen sample. The measurements were repeated three times for each formulation.

Cross-Cut Adhesion Tests

The resistance of NIPU coatings to separation from aluminum substrates was evaluated with an ASTM D 3359 cross-cut adhesion test (method B). The coatings were cut with an NK2000 tester from NEURTEK, penetrating all the way to the substrate. Specific round blades for coating thicknesses between 121 and 250 μm were used to make six evenly spaced incisions (3 mm spacing), horizontally and vertically, creating a lattice pattern on the surface (1.8 cm $\times$ 1.8 cm). A pressure-sensitive adhesive tape ISO 2409 was applied on the cross-hatch cut and pressed over the area of the incisions. The tape was rapidly removed by vigorously pulling it off upon itself at an angle of 180°, and the result was determined evaluating the percentage of the grid that was affected by the test, from 0% (5B) to more than 65% (0B).

Water Contact Angle Measurements

The wettability of NIPU coatings was evaluated by contact angle measurements, carried out with water on an OCA-20 apparatus (Dataphysics Instrument GmbH) in the sessile drop configuration. A 15- μL droplet of Milli-Q water was deposited on the surface of the coating, and after 1 min a high-resolution video camera was used to record the angle between the solid surface and the tangent line to the contacting edge of the droplet. For each formulation, the mean contact angle value was obtained from five measurements realized on different spots of the sample surface.

Tensile Testing

Tensile tests were conducted at 25 °C on an MTS Criterion Model 43 universal test machine, equipped with a 1 kN load cell and at a displacement rate of 10 mm/min. For each formulation, Young's modulus (E), ultimate tensile strength (σ_u) and fracture strain (ϵ_f) were estimated by the average values of five rectangular shaped NIPU films (2.5 cm $\times$ 0.5 cm $\times$ 0.1 cm). A gripping length of 0.8 cm on each side of the sample was maintained constant for the tests. Young's modulus and fracture strain were determined using Equation 7.4 and Equation 7.5, respectively. E was calculated in the elastic portion of the stress-strain curve, until $\epsilon = 1\%$.

Shore hardness testing

Shore A and Shore D hardness tests were realized on the plane surface of cylindrical samples (0.8 cm in height, 1.5 cm in diameter), using two Hildebrand HD3000 durometers, model types A and D, respectively. The hardness values were recorded 10 seconds after applying the durometer to the material to ensure a stable reading and the average results were calculated after five determinations at different positions on the specimen.

Lap-Shear Testing

Lap-shear adhesion tests were performed at 25 °C using an MTS Criterion Model 43 universal test machine, equipped with a 30 kN or 1 kN load cell and at a displacement rate of 2 mm/min. The measurements were repeated five times for each formulation, and the lap-shear strength was calculated using Equation 7.7:

$$\tau = \frac{F}{A}$$

Equation 7.7 Lap-shear strength.

where τ is the lap-shear strength, F is the applied force and A the overlapped area.

7.2.3 Supporting information

7.2.3.1 Rheology study of the reaction between Jeffamine T-403 and bis α CC

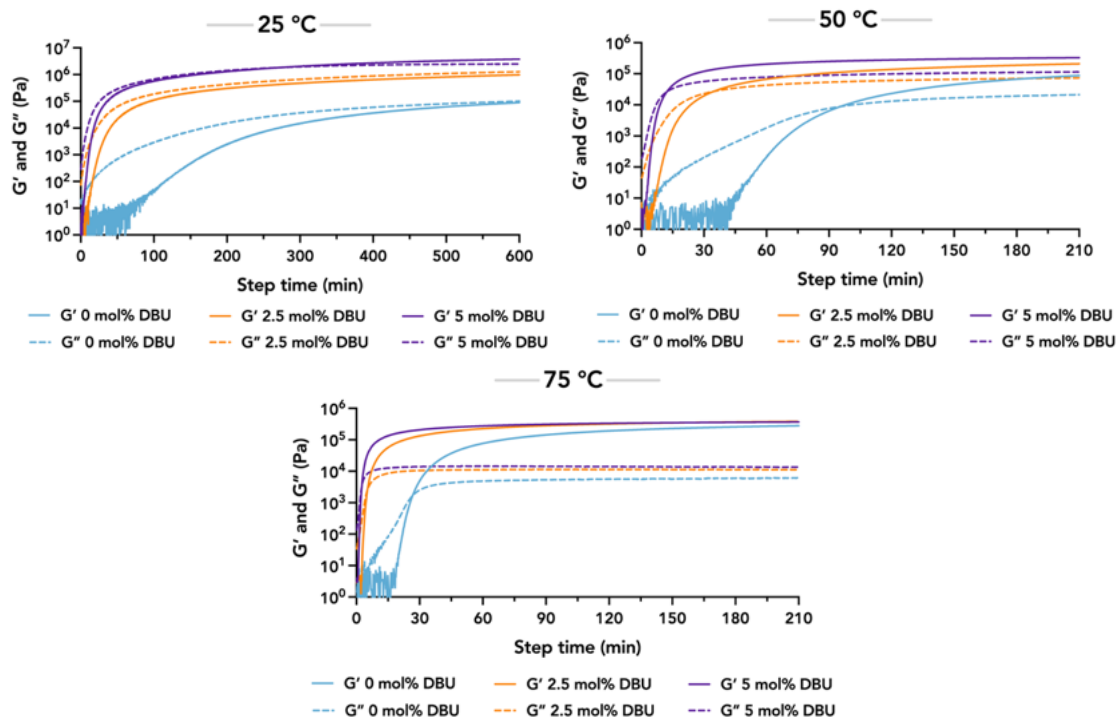


Figure 7.13 Evolution in time of storage (G') and loss (G'') moduli for bis α CC/Jeffamine T-403 formulations at 25 °C, 50 °C and 75 °C, at different catalyst loadings and using an equimolar ratio between amino and cyclic carbonate groups.

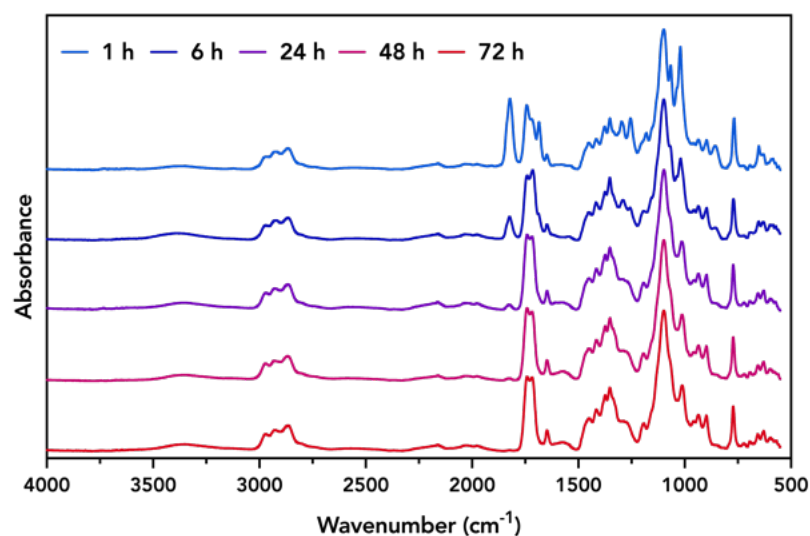


Figure 7.14 Infrared spectrum evolution of the solvent-free bis α CC/Jeffamine T-403 formulation at RT and 5 mol% catalyst loading.

7.2.3.2 Linear NIPUs

NMR characterization

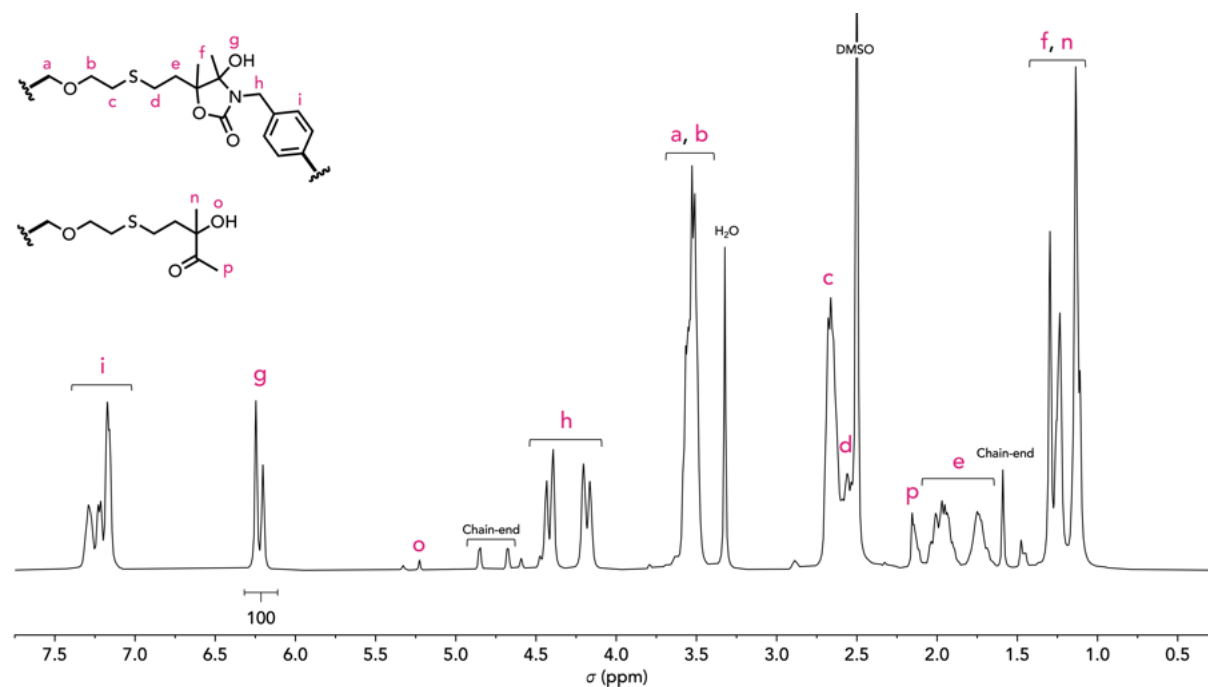
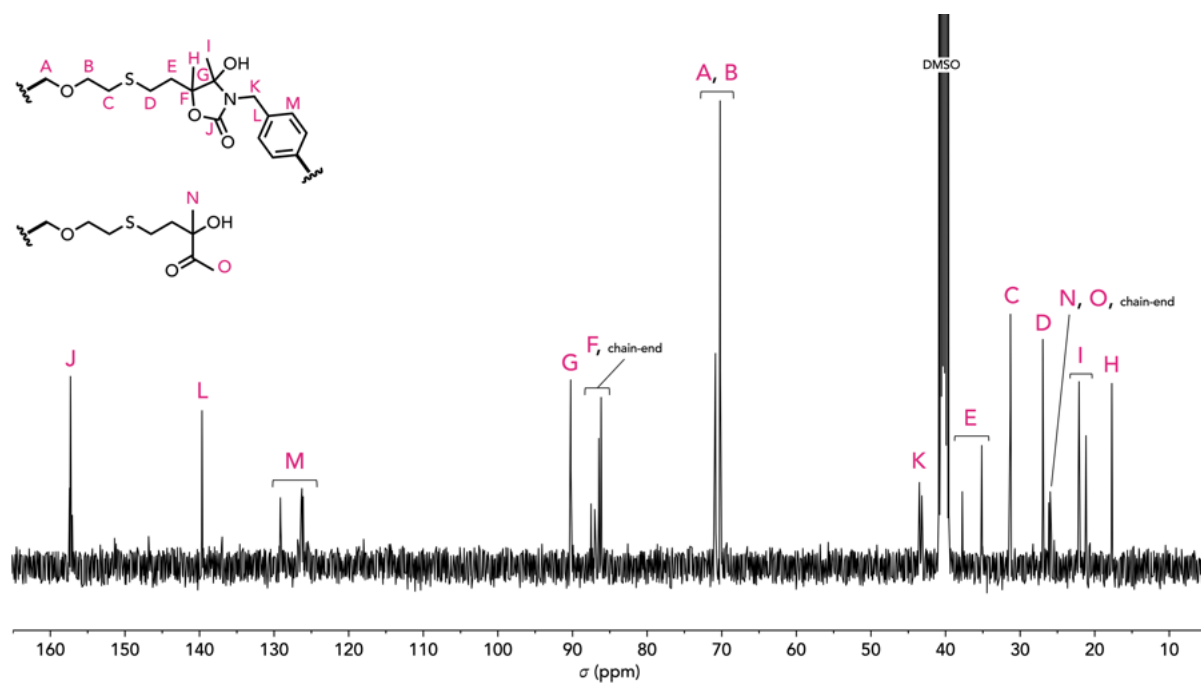
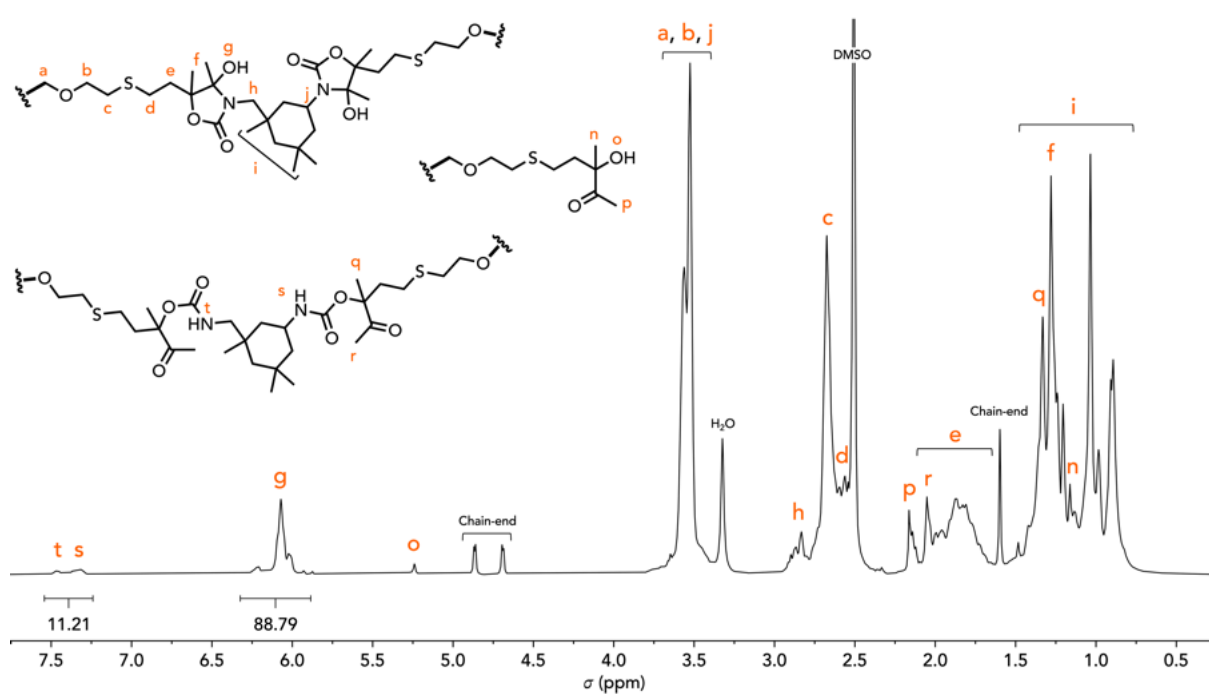


Figure 7.15 ¹H-NMR spectrum of PA1.

Figure 7.16 ^{13}C -NMR spectrum of PA1.Figure 7.17 ^1H -NMR spectrum of PA2.

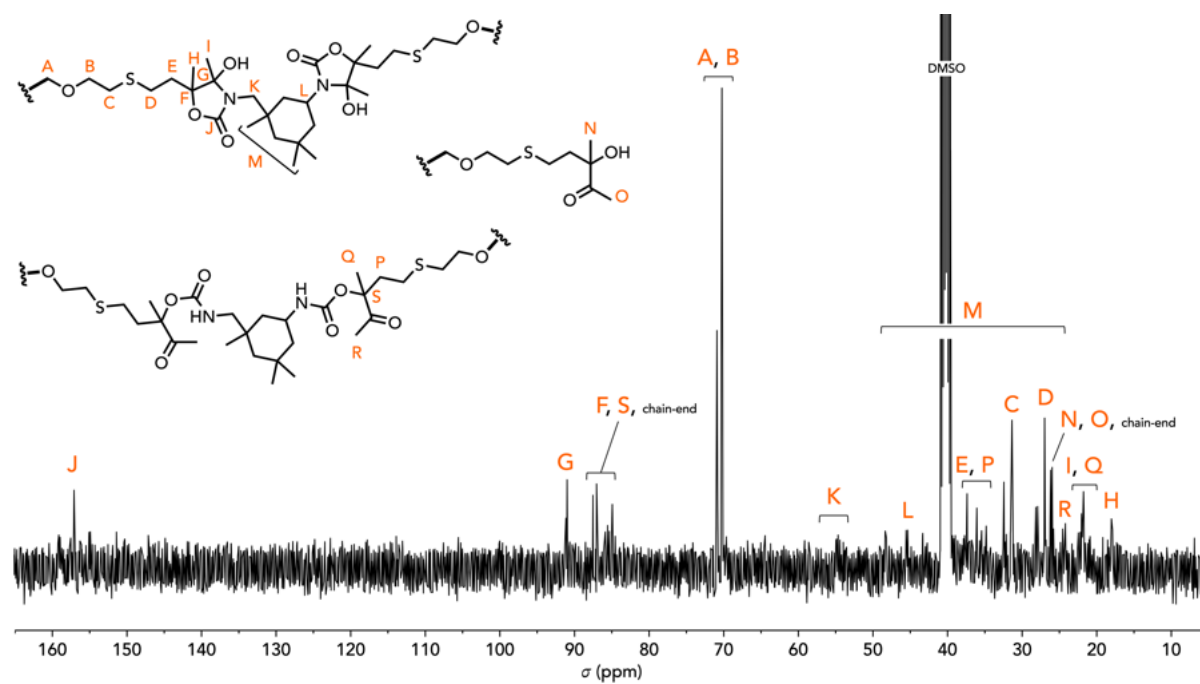


Figure 7.18 ^{13}C -NMR spectrum of PA2.

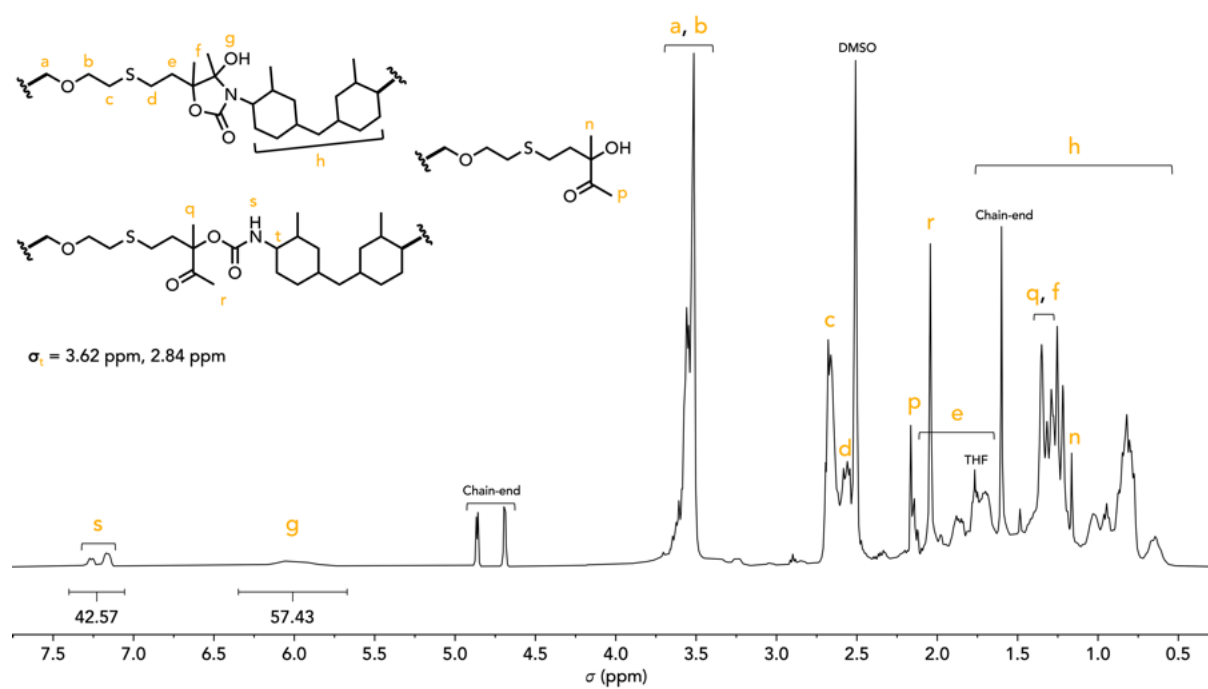


Figure 7.19 ^1H -NMR spectrum of PA3.

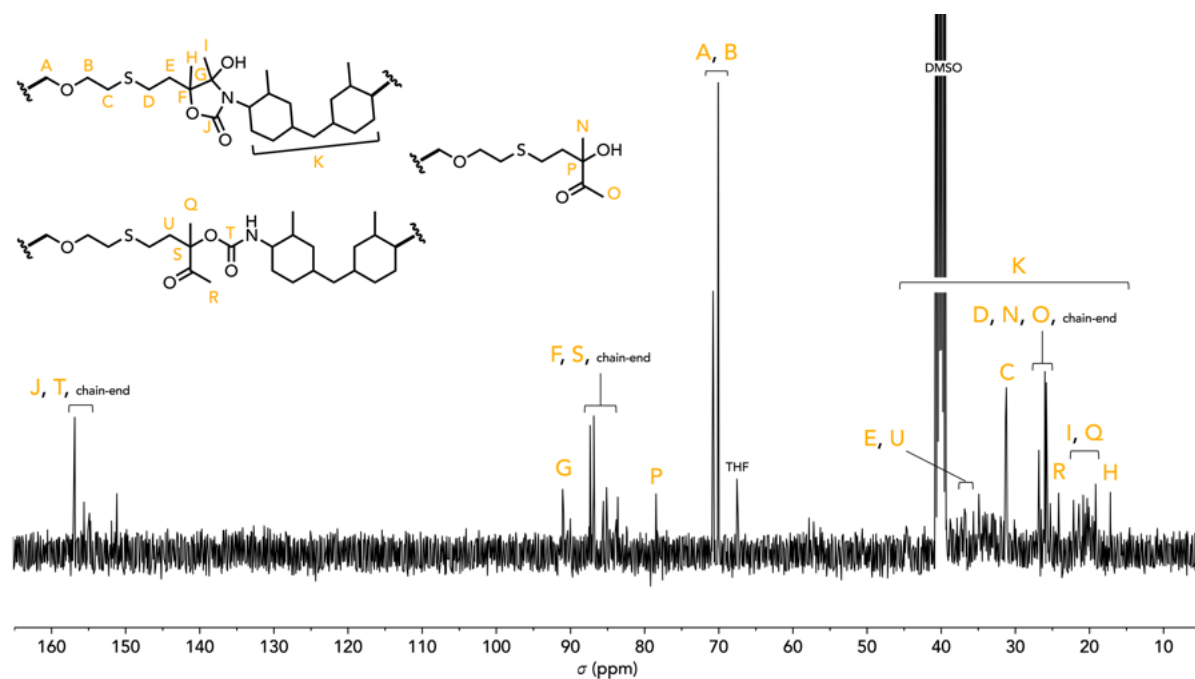


Figure 7.20 ^{13}C -NMR spectrum of PA3.

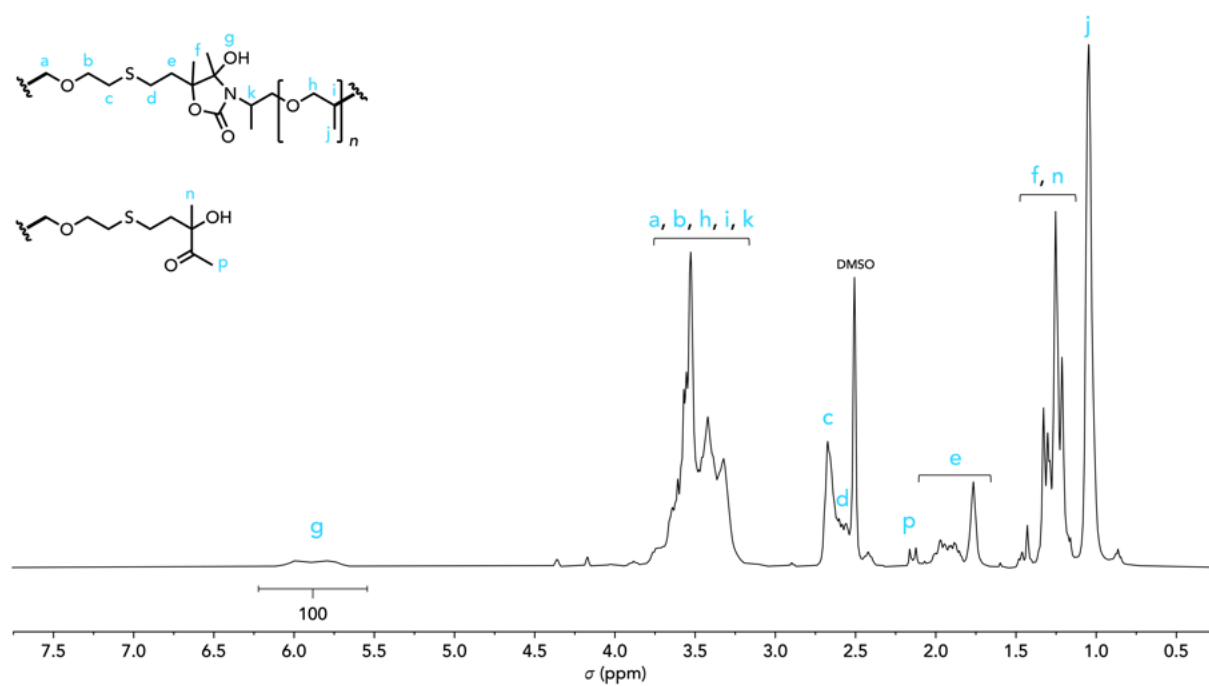


Figure 7.21 ^1H -NMR spectrum of PA4.

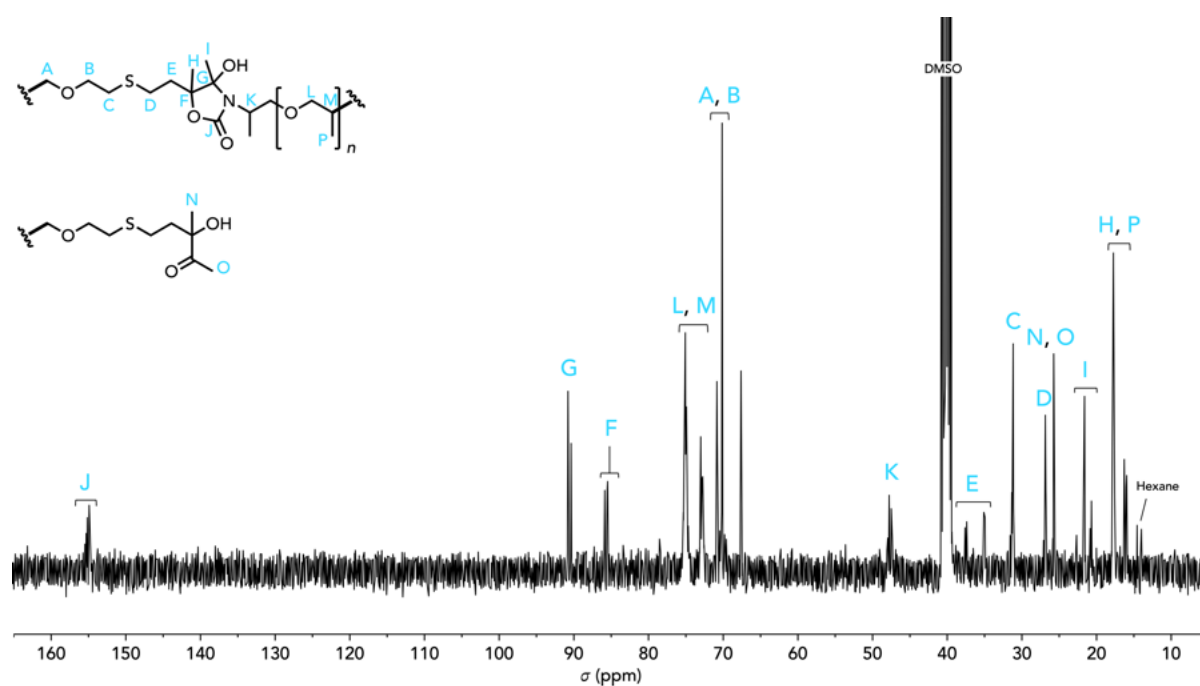


Figure 7.22 ^{13}C -NMR spectrum of PA4.

IR analysis

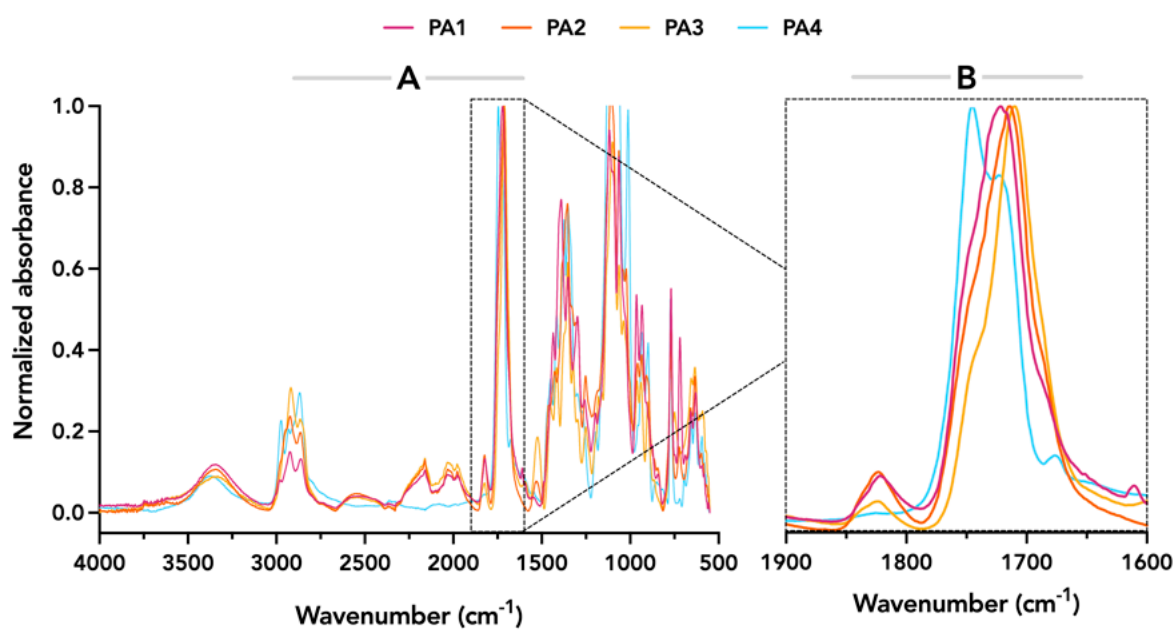


Figure 7.23 Overlay of infrared spectra for purified linear NIPUs (A); characteristic bands in the carbonyl stretching region (B).

SEC analysis

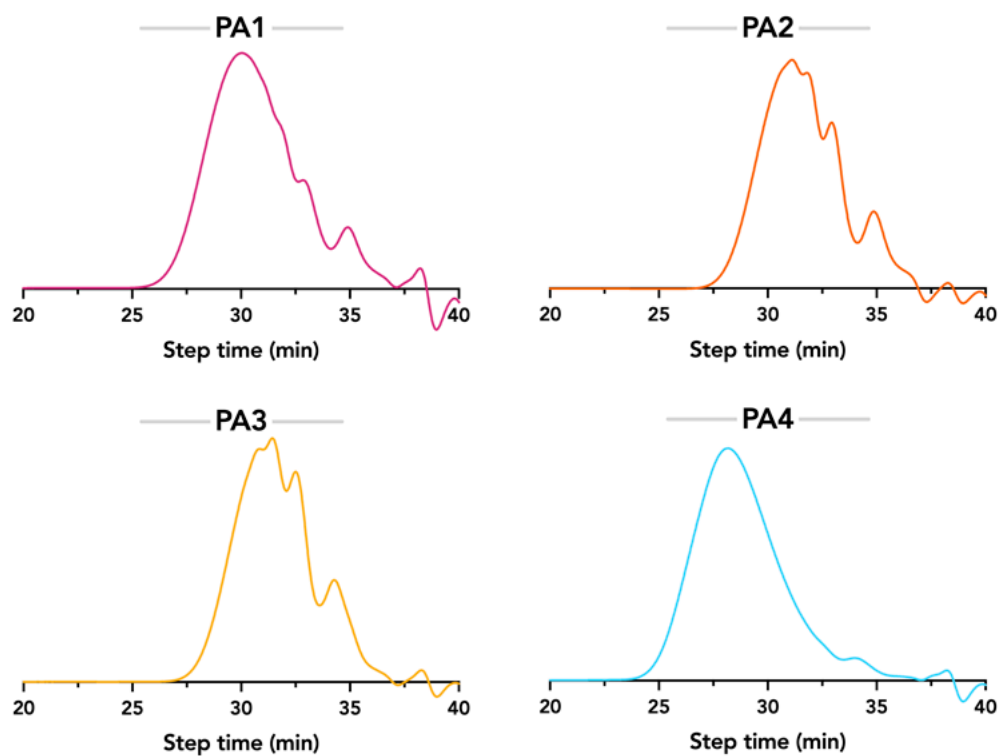


Figure 7.24 SEC chromatograms of crude linear NIPUs.

TGA curves

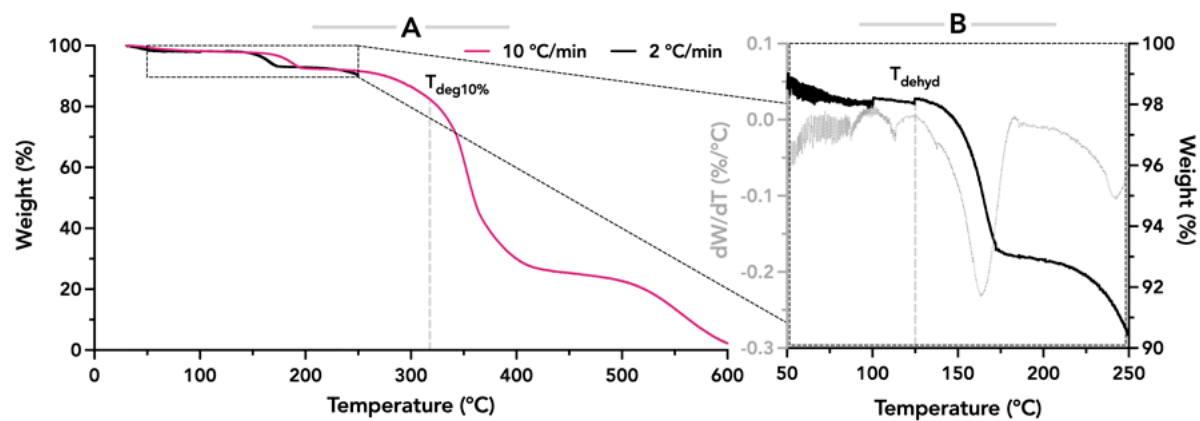


Figure 7.25 TGA curves of purified PA1 at heating rate of 10 °C/min, in fuchsia, and 2 °C/min, in black (A); zoom on the dehydration step (B).

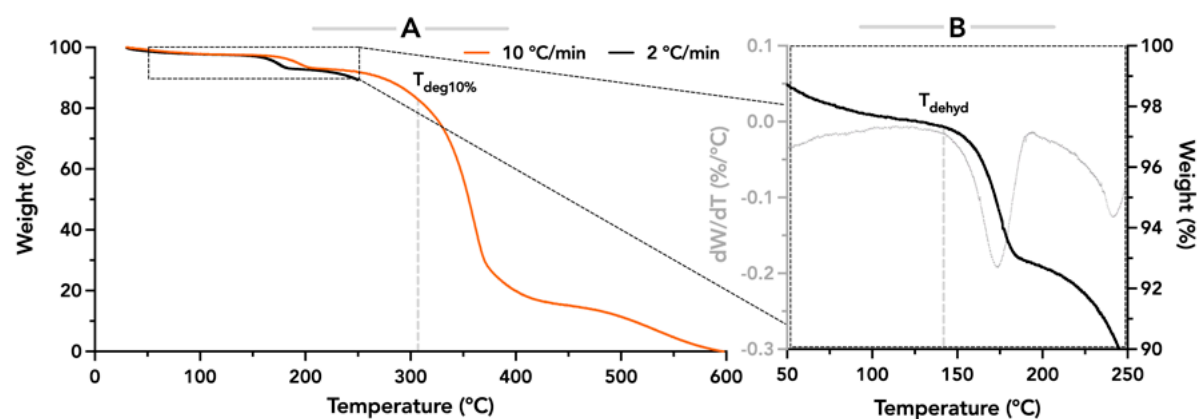


Figure 7.26 TGA curves of purified PA2 at heating rate of 10 °C/min, in orange, and 2 °C/min, in black (A); zoom on the dehydration step (B).

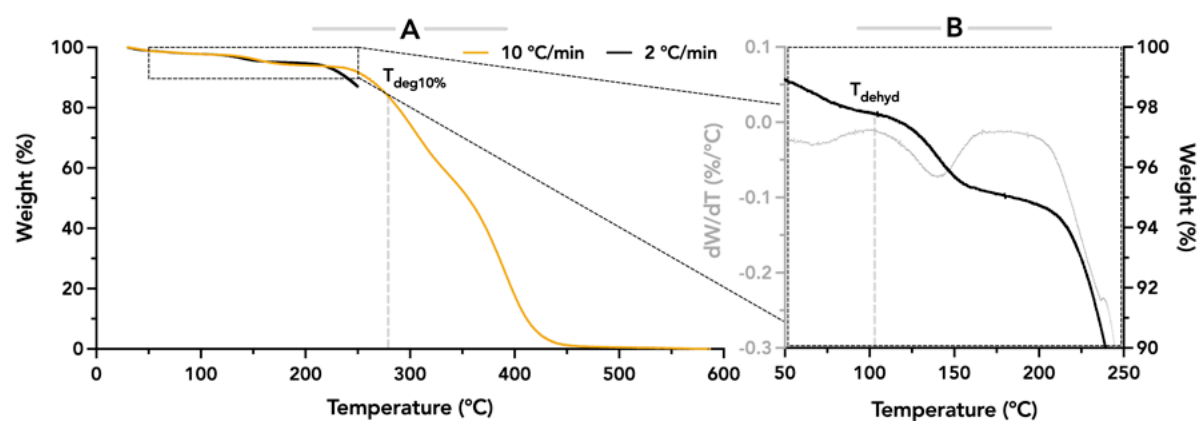


Figure 7.27 TGA curves of purified PA3 at heating rate of 10 °C/min, in ocher, and 2 °C/min, in black (A); zoom on the dehydration step (B).

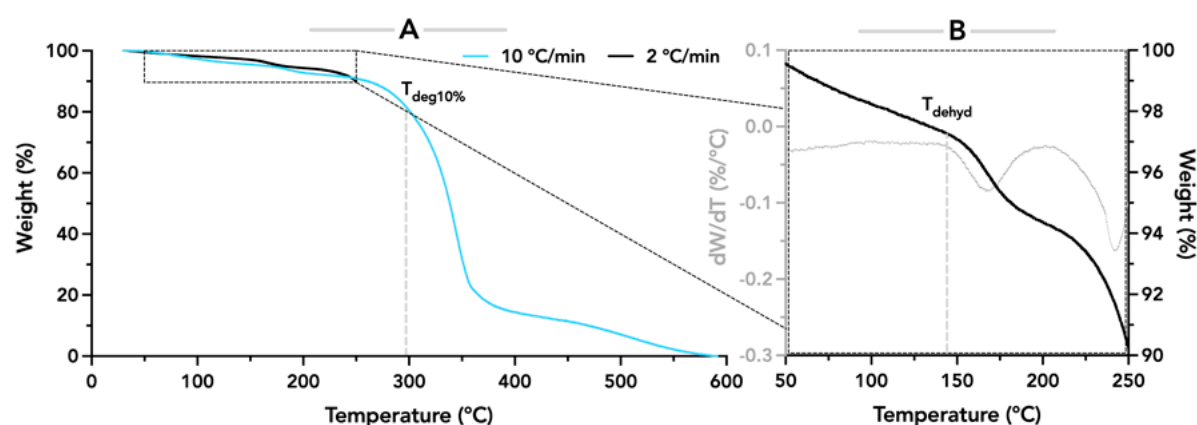


Figure 7.28 TGA curves of purified PA4 at heating rate of 10 °C/min, in light blue, and 2 °C/min, in black (A); zoom on the dehydration step (B).

DSC analysis

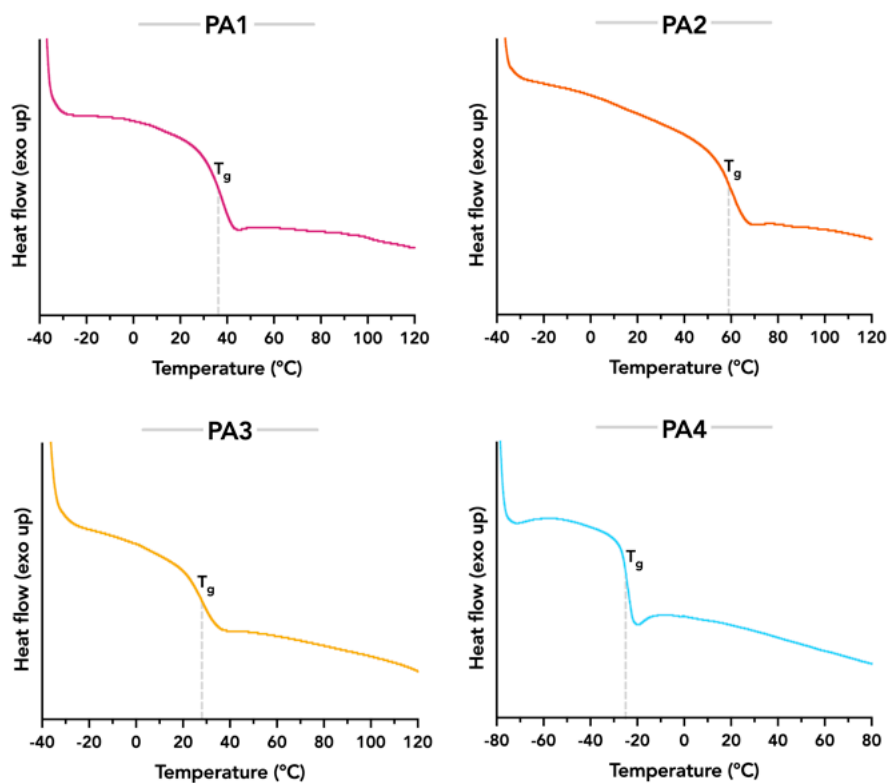


Figure 7.29 DSC curves of purified linear NIPUs.

7.2.3.3 Crosslinked NIPUs

Rheology study

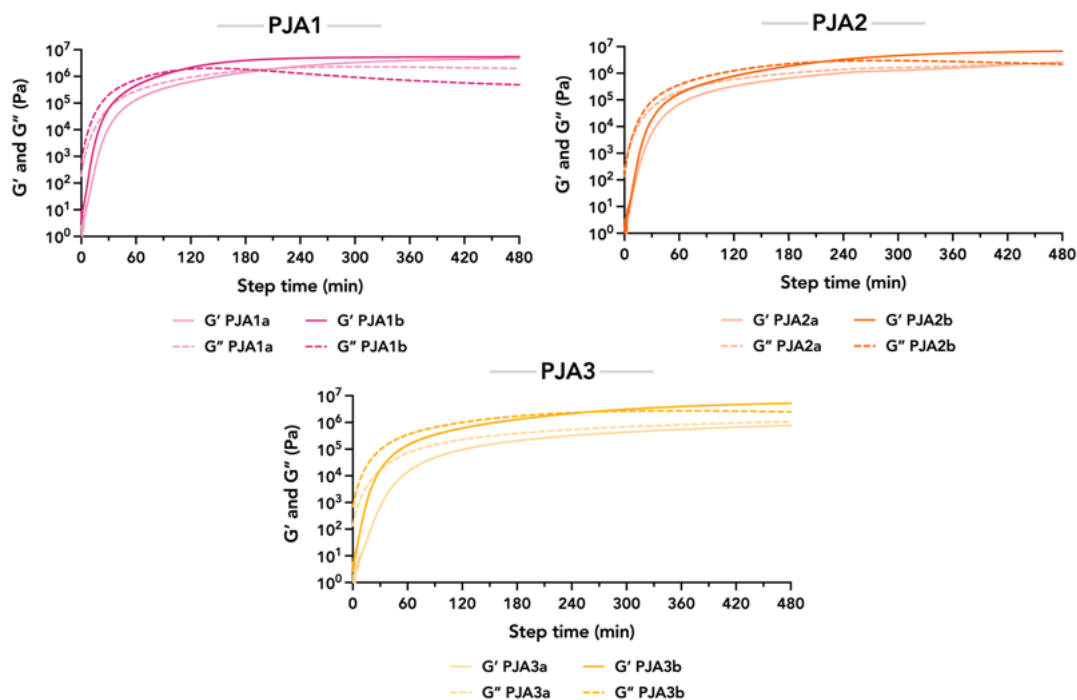


Figure 7.30 Evolution in time of storage (G') and loss (G'') moduli for crosslinked NIPUs obtained by curing formulations composed of bis α CC, Jeffamine T-403 and a diamine.

IR analysis

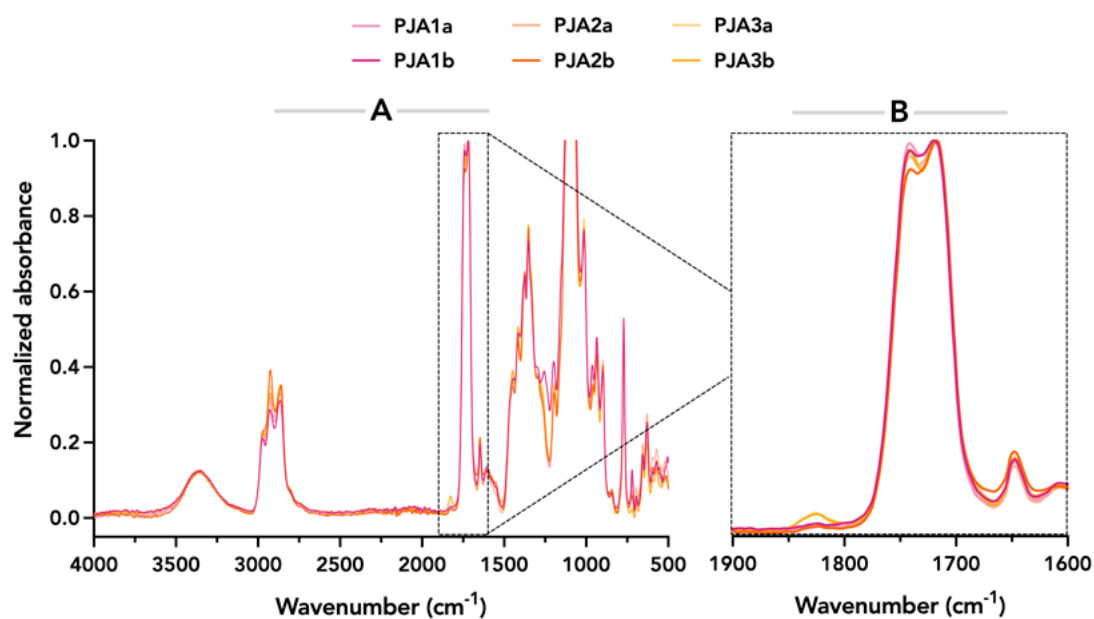


Figure 7.31 Overlay of infrared spectra for crosslinked NIPUs after 3 days of RT curing (A); characteristic bands in the carbonyl stretching region (B).

NMR analysis after gel content test

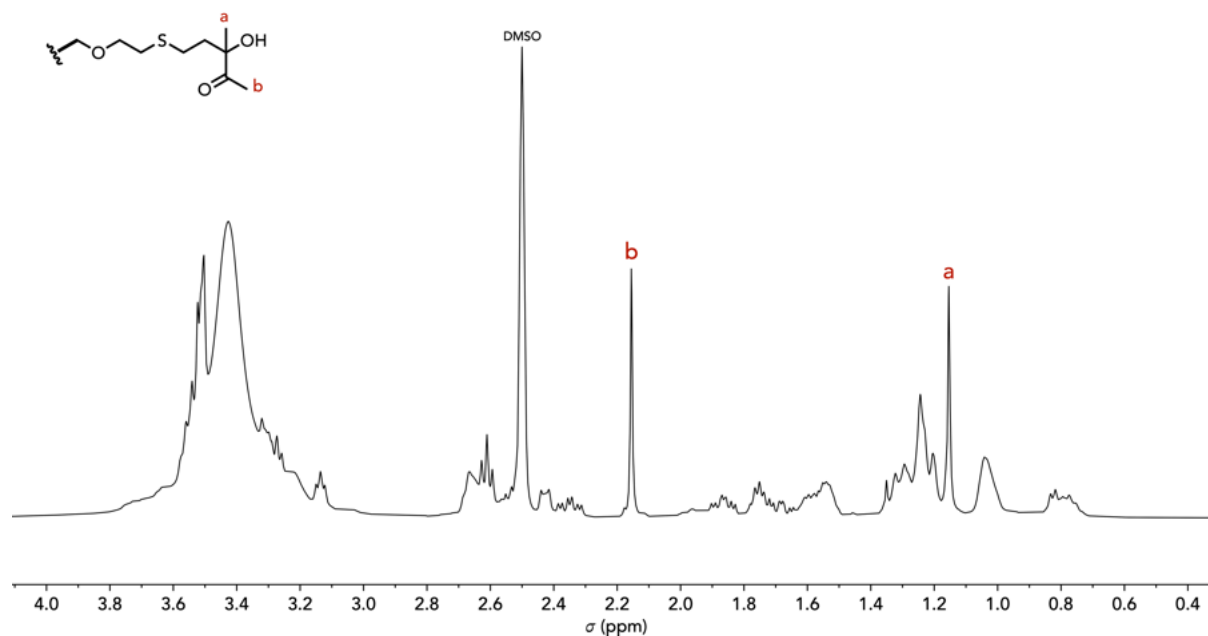


Figure 7.32 ^1H -NMR spectrum of the soluble fraction obtained from the gel content test of PJ, highlighting the characteristic signals of hydroxy ketone functional groups.

TGA curves

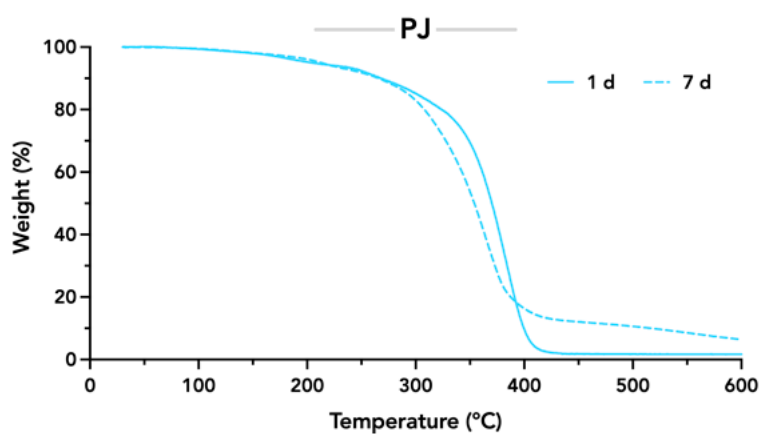


Figure 7.33 TGA curves of PJ after 1 day (solid curve) and 7 days (dashed curve) of RT curing.

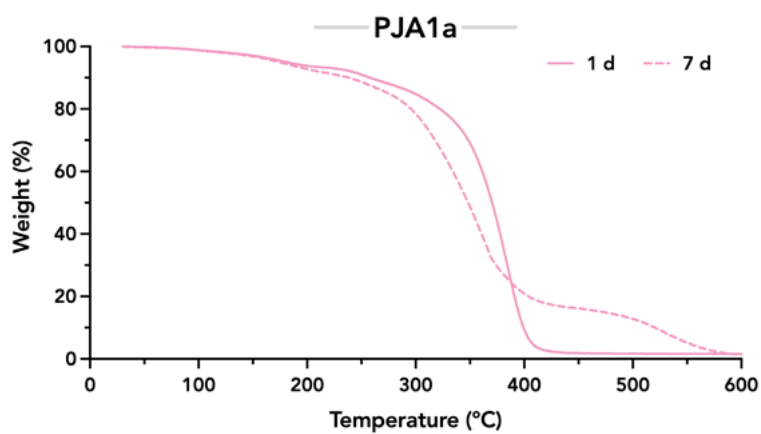


Figure 7.34 TGA curves of PJA1a after 1 day (solid curve) and 7 days (dashed curve) of RT curing.

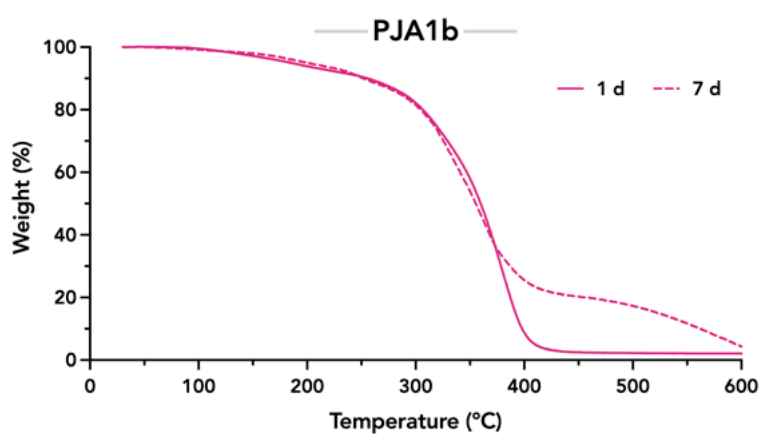


Figure 7.35 TGA curves of PJA1b after 1 day (solid curve) and 7 days (dashed curve) of RT curing.

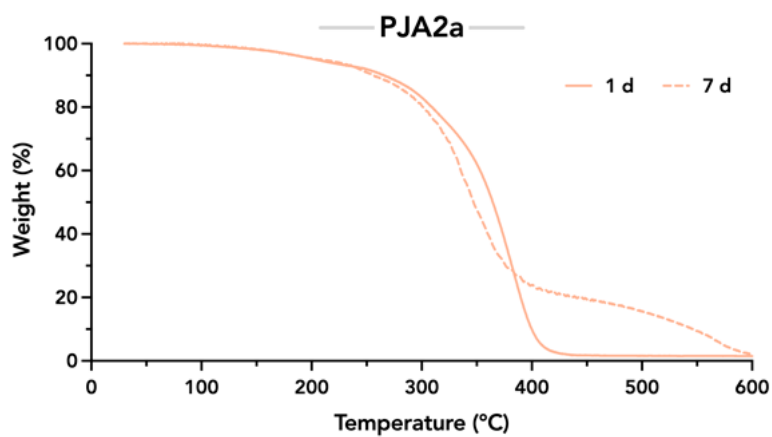


Figure 7.36 TGA curves of PJA2a after 1 day (solid curve) and 7 days (dashed curve) of RT curing.

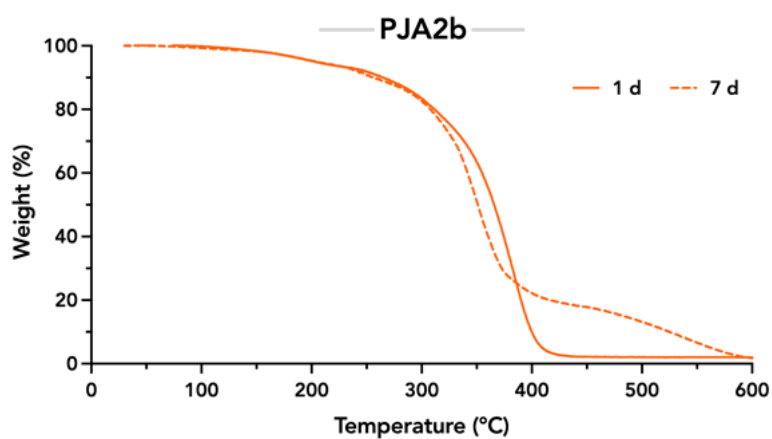


Figure 7.37 TGA curves of PJA2b after 1 day (solid curve) and 7 days (dashed curve) of RT curing.

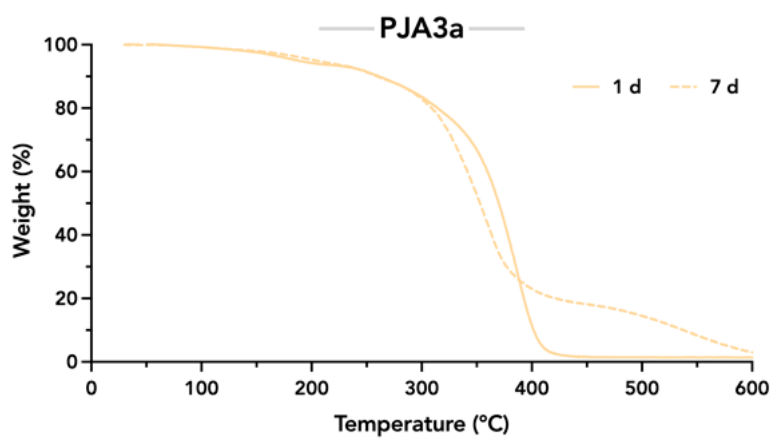


Figure 7.38 TGA curves of PJA3a after 1 day (solid curve) and 7 days (dashed curve) of RT curing .

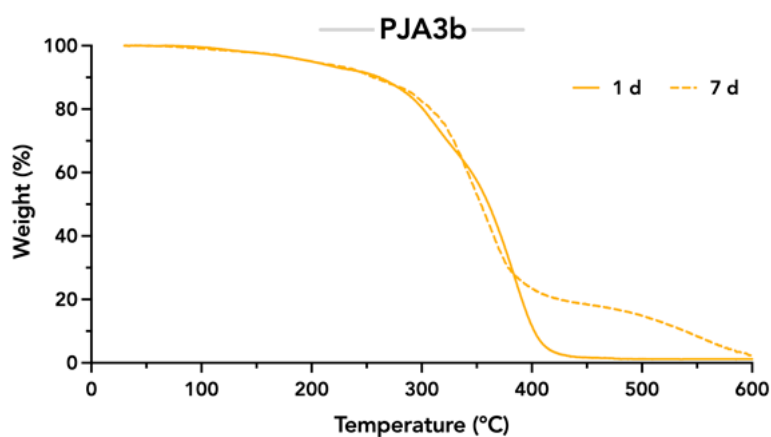


Figure 7.39 TGA curves of PJA3b after 1 day (solid curve) and 7 days (dashed curve) of RT curing.

DSC analysis

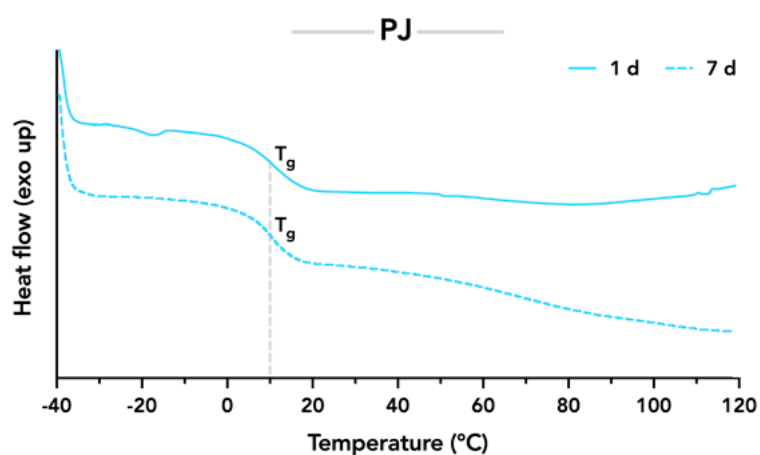


Figure 7.40 DSC curves of PJ after 1 day (solid curve) and 7 days (dashed curve) of RT curing.

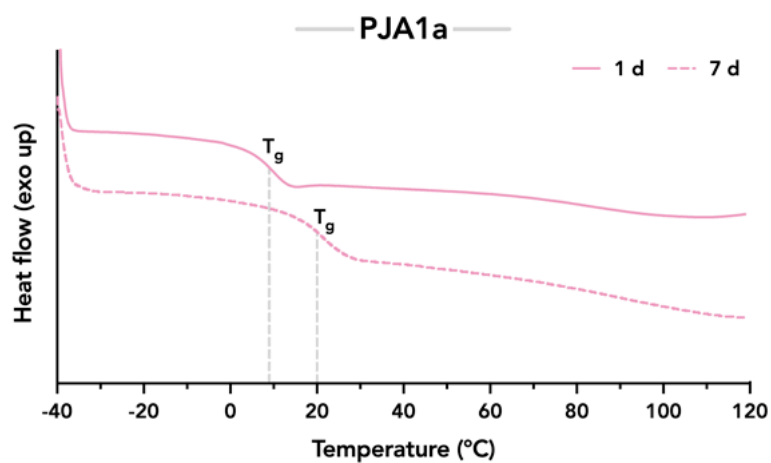


Figure 7.41 DSC curves of PJA1a after 1 day (solid curve) and 7 days (dashed curve) of RT curing.

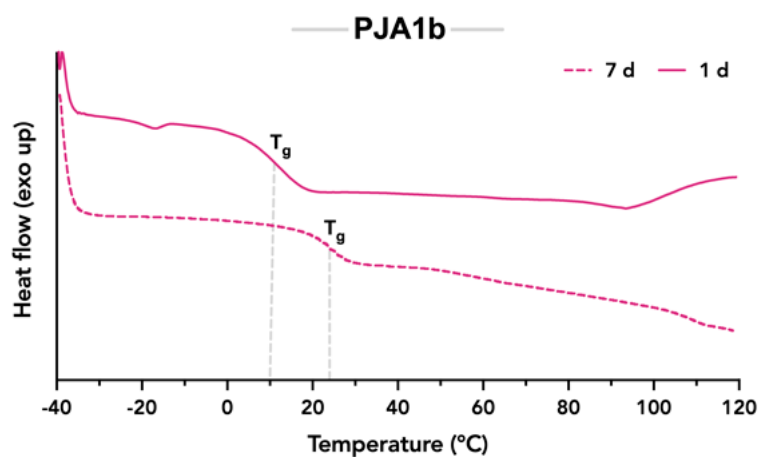


Figure 7.42 DSC curves of PJA1b after 1 day (solid curve) and 7 days (dashed curve) of RT curing.

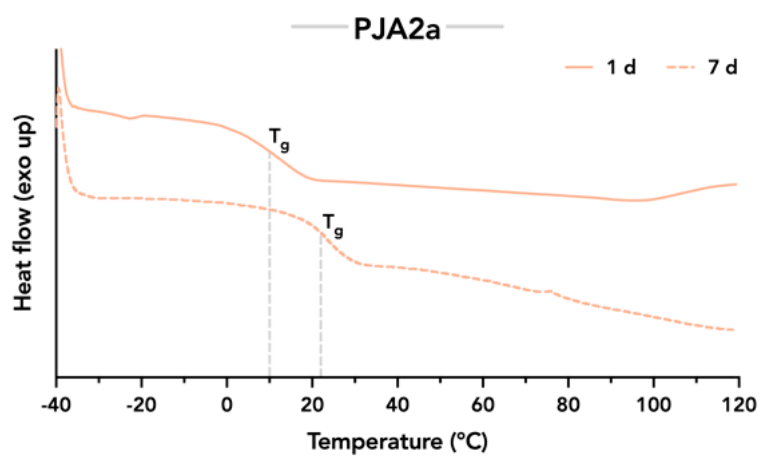


Figure 7.43 DSC curves of PJA2a after 1 day (solid curve) and 7 days (dashed curve) of RT curing.

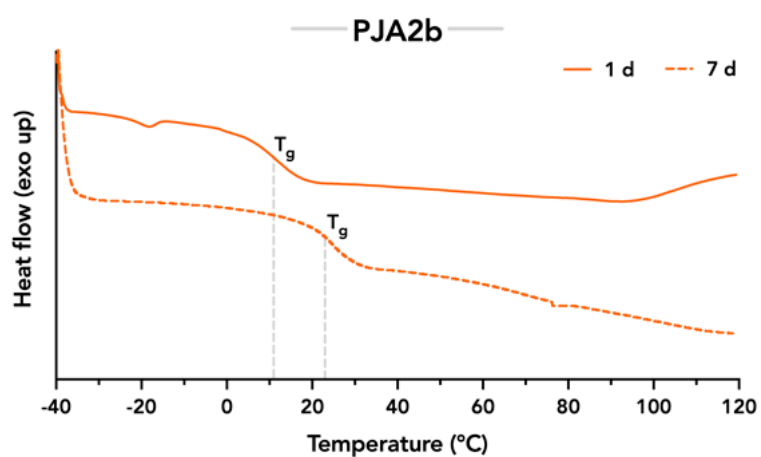


Figure 7.44 DSC curves of PJA2b after 1 day (solid curve) and 7 days (dashed curve) of RT curing.

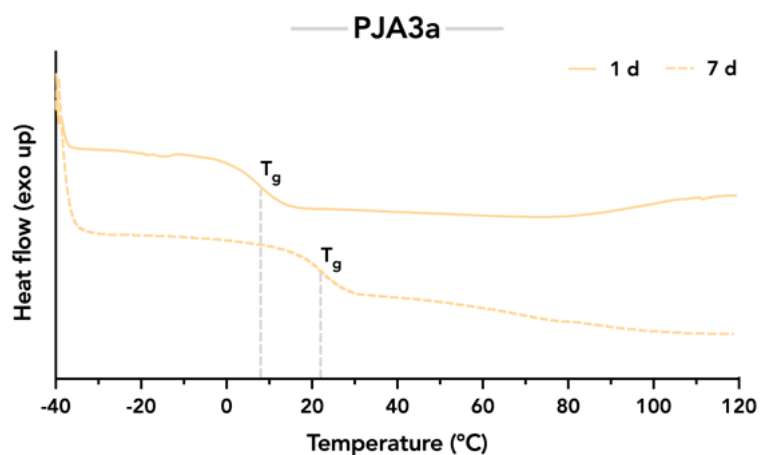


Figure 7.45 DSC curves of PJA3a after 1 day (solid curve) and 7 days (dashed curve) of RT curing.

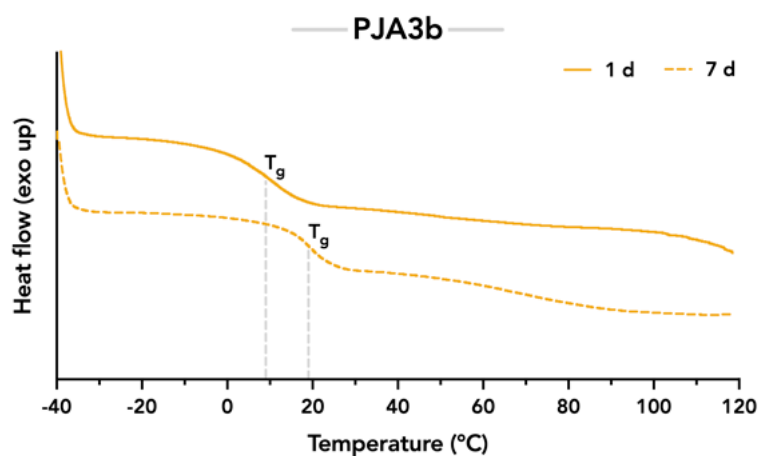


Figure 7.46 DSC curves of PJA3b after 1 day (solid curve) and 7 days (dashed curve) of RT curing.

Tensile testing

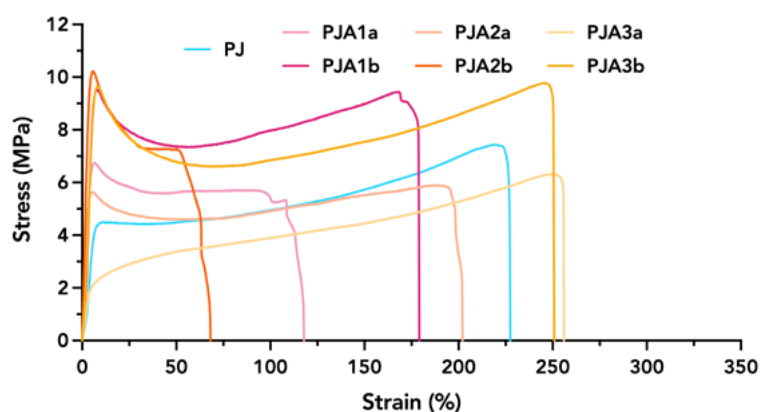


Figure 7.47 Representative stress-strain curves of crosslinked NIPUs after 1 day of RT curing.

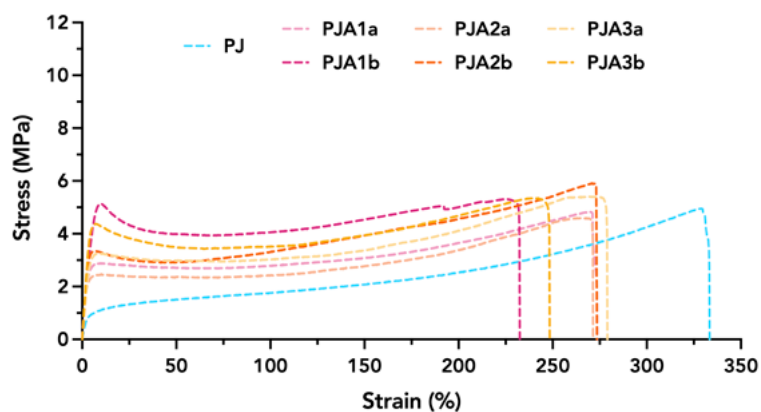


Figure 7.48 Representative stress-strain curves of crosslinked NIPUs after 7 days of RT curing.

Lap-shear testing on aluminum

Table 7.2 Average lap-shear strength of crosslinked NIPU adhesives after 1 day and 7 days of RT curing.

Entry	Co-reagent	Polymer	Diamine : triamine (n/n)	Average lap-shear strength (MPa)	
				After 1 d	After 7 d
1	/	PJ	/	10.2 ± 0.2	10.8 ± 0.5
2	A1	PJA1a	1 : 4	10.0 ± 1.9	9.9 ± 1.5
3		PJA1b	1 : 3	9.5 ± 1.8	9.6 ± 2.2
4	A2	PJA2a	1 : 4	8.6 ± 1.1	9.2 ± 1.3
5		PJA2b	1 : 3	6.4 ± 1.0	7.6 ± 1.3
6	A3	PJA3a	1 : 4	7.0 ± 2.2	10.0 ± 1.2
7		PJA3b	1 : 3	7.5 ± 1.9	8.0 ± 0.7

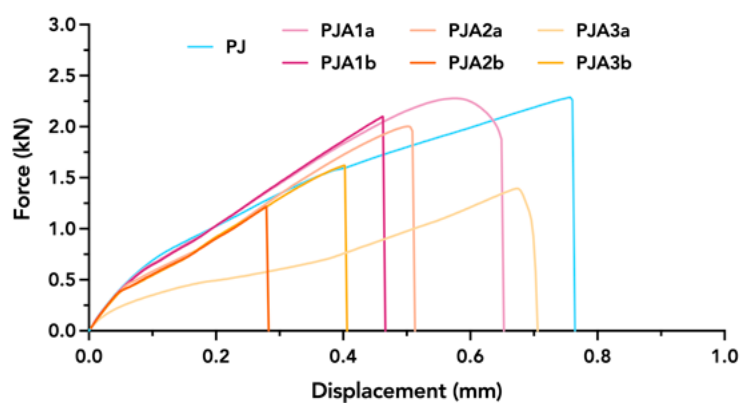


Figure 7.49 Representative force-displacement curves of crosslinked NIPU adhesives after 1 day of RT curing.

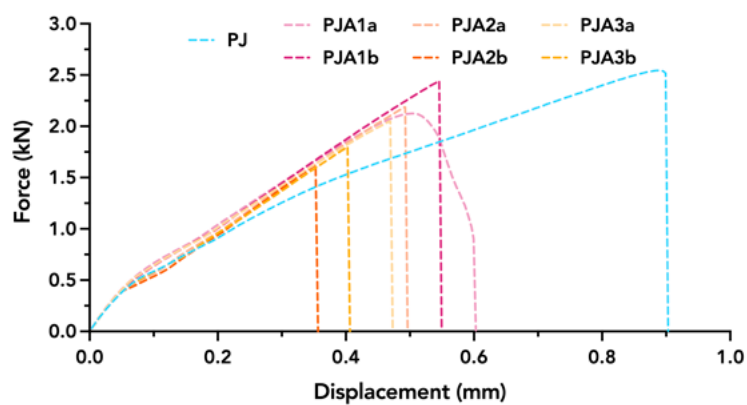


Figure 7.50 Representative force-displacement curves of crosslinked NIPU adhesives after 7 days of RT curing.



Figure 7.51 Representative adhesive-cohesive failure of lap-shear test specimens prepared with crosslinked NIPU adhesives after 1 day of RT curing.

Lap-shear testing on stainless-steel, wood, PMMA and HDPE

Table 7.3 Average lap-shear strength of NIPU adhesive formulation PJ, evaluated after 1 day of RT curing on different substrate materials: stainless steel (SS), wood (W), poly(methyl methacrylate) (PMMA), high-density polyethylene (HDPE), and aluminum alloy 5754 (Al).

Substrate material	Average lap-shear strength (MPa)
SS	4.6 ± 0.7
W	2.6 ± 0.3
PMMA	1.8 ± 0.3
HDPE	0.9 ± 0.1
Al	10.2 ± 0.2

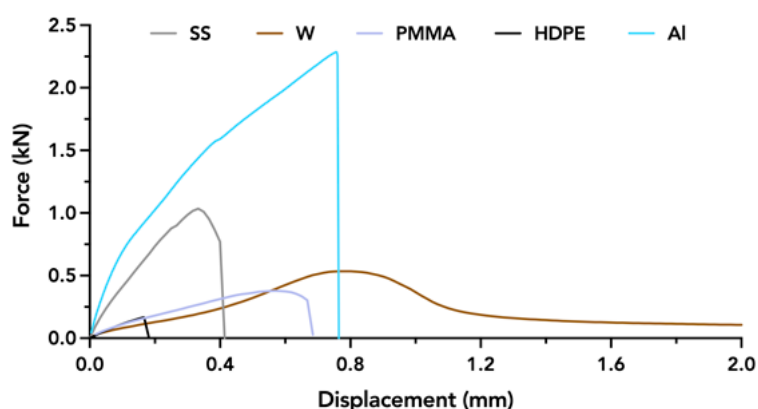


Figure 7.52 Representative force-displacement curves of NIPU adhesive formulation PJ, evaluated after 1 day of RT curing on stainless steel (SS), wood (W), poly(methyl methacrylate) (PMMA), high-density polyethylene (HDPE), and aluminum alloy 5754 (Al).



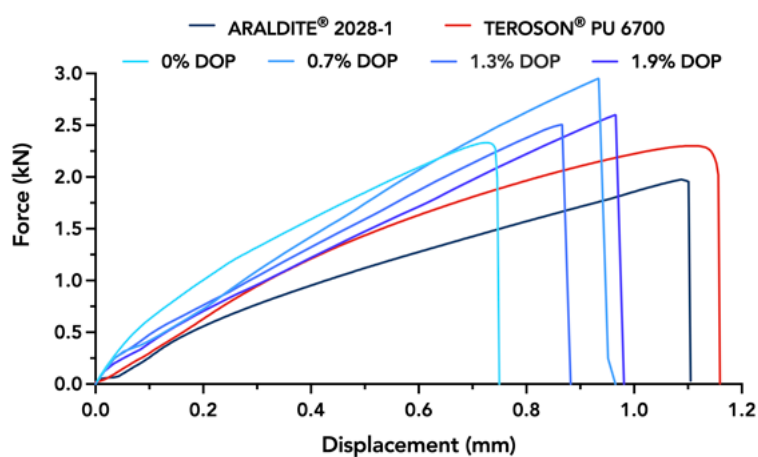
Figure 7.53 Representative failure modes (A = adhesive, AC = adhesive-cohesive, LFT = light-fiber-tear, SB = stock-break) of lap-shear test specimens prepared with NIPU adhesive formulation PJ, evaluated after 1 day of RT curing on different substrate materials.

7.2.3.4 Catechol-containing NIPU and commercial PU adhesives

Lap-shear testing on aluminum

Table 7.4 Average lap-shear strength of catechol-containing NIPU and commercial PU adhesives after 1 day of RT curing.

Formulation	Average lap-shear strength (MPa)
1.9% DOP ^a	10.7 ± 1.2
1.3% DOP ^a	10.5 ± 1.0
0.7% DOP ^a	12.8 ± 1.3
0% DOP ^a	10.2 ± 0.2
TEROSON® PU 6700	9.9 ± 1.1
ARALDITE® 2028-1	8.2 ± 0.6

^a Calculated considering the total number of amino groups.**Figure 7.54** Representative force-displacement curves of catechol-containing NIPU and commercial PU adhesives after 1 day of RT curing.

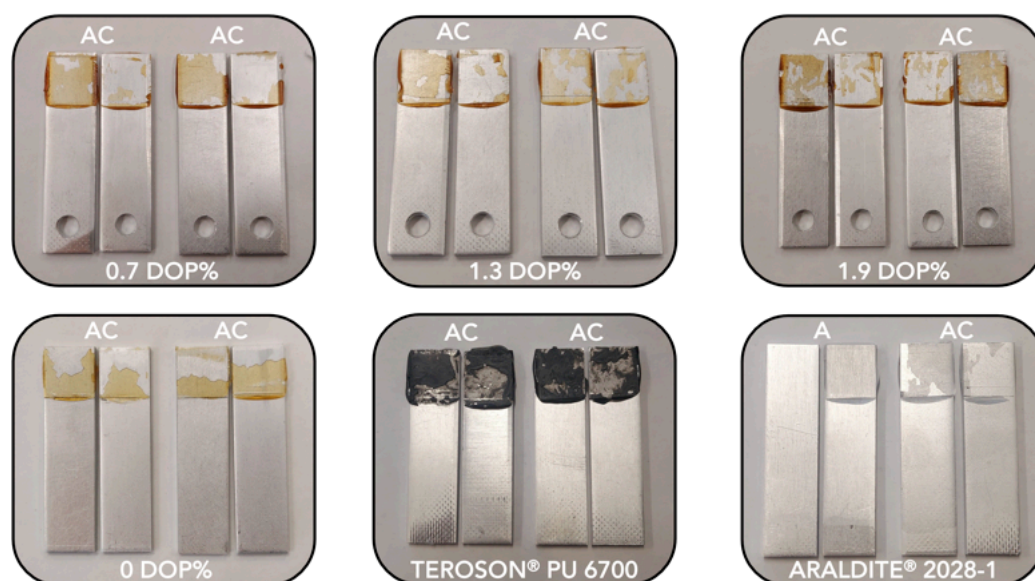


Figure 7.55 Representative failure modes (A = adhesive, AC = adhesive-cohesive) of lap-shear test specimens prepared with catechol-containing NIPU and commercial PU adhesives after 1 day of RT curing.

Gel content measurements

Table 7.5 Gel content of catechol-containing NIPUs after 1 day of RT curing.

Formulation	GC (%) ^a	
	H ₂ O	THF
1.9% DOP ^b	95.3 ± 0.7	66.5 ± 0.8
1.3% DOP ^b	95.6 ± 0.6	71.3 ± 0.7
0.7% DOP ^b	95.0 ± 0.4	74.3 ± 0.8
0% DOP ^b	97.3 ± 0.3	75 ± 1

^a GC: gel content of self-standing films submerged in water or THF for 120 h at RT and dried at 70 °C for 24 h. ^b Calculated considering the total number of amino groups.

7.3 Experimental section Chapter 5.3

7.3.1 Materials and methods

Reagents and materials

VORANOL™ CP 4755 Polyol and VORANOL™ CP 450 were purchased from Dow®. SUPRASEC® 2525 was purchased from Huntsman®. POLYCAT® 9 was purchased from Air Products Chemicals

Europe B.V. 1,4-Butanediol was purchased from Safic Alcan®. UOP L PASTE ECO was purchased from Univar®. BLACKGLUE 01™ was provided by COP Chimie™.

Aluminum alloy (5754, or AlMg₃) bars were prepared by cutting the material into rectangular pieces (6 cm × 1.5 cm × 0.3 cm). Aluminum alloy (Al 2024-T3) panels were provided by SONACA (Belgium) and prepared by cutting the material into rectangular pieces (6 cm × 5 cm × 0.1 cm). Sulfuric acid (H₂SO₄, 95.0 – 98.0%), sodium hydroxide (NaOH, ≥97.0%), and sodium dichromate dihydrate (Na₂Cr₂O₇ · 2H₂O, ≥99.5%) were purchased from Sigma-Aldrich.

Preparation of PU adhesives, coatings, tensile, and Shore hardness test specimens

A precise amount of SUPRASEC® 2525 was added at room temperature to a plastic bucket containing a pre-mixed mixture of polyols, UOP L PASTE ECO, and POLYCAT® 9. The formulation was stirred for 30 seconds in bulk until a homogeneous paste was achieved. For all tested formulations, the catalyst loading was calculated based on the total number of isocyanate and hydroxyl groups, and the molecular sieves mass percentage was determined relative to the mass of the resin mixture. After stirring, the formulations were processed according to their specific application: for adhesive samples, the paste was immediately applied to an aluminum alloy substrate for lap-shear testing; for coating samples, the paste was spread onto an aluminum alloy panel using a casting knife film applicator, in accordance with ASTM D823, to achieve a thickness of approximately 250 μm; for tensile test specimens, the paste was poured into a dog-bone shaped silicone mold; and for Shore hardness test specimens, the paste was poured in a cylindrical silicon mold (0.8 cm in height, 1.5 cm in diameter). Each formulation was tested after 1 and 7 days of RT curing.

Surface treatments

To ensure reliable evaluation of coating and adhesion performance, the substrates used for cross-cut and lap-shear tests were treated to remove surface impurities. Aluminum bars and panels were prepared following a previously reported procedure.⁴²² First, the substrates were immersed in a basic aqueous bath (NaOH 40 g L⁻¹) for 1 minute, followed by immersion in an acidic aqueous bath (73 wt% water, 25 wt% H₂SO₄, 2 wt% Na₂Cr₂O₇) for 1 minute. After each step, the material was thoroughly washed with distilled water and wiped with tissue paper.

Preparation of lap-shear samples

Single-lap joints were prepared to assess the adhesion performance of PU adhesives. Each formulation was mixed for 30 seconds and promptly applied to one end of the pretreated

substrate, depositing approximately 45 mg of product over a gluing area of 225 mm². The second substrate bar was immediately placed on top of the first, applying sufficient pressure to evenly spread the adhesive across the overlapped area, without causing defects or squeezing the mixture out of the joint. The single-lap joint specimen was then cured at 25 °C for either 1 day or 7 days. For BLACKGLUE 01TM, the procedure was identical, except that the mixing was performed with the static mixer provided with the product.

7.3.2 Characterization techniques

Rheological Measurements

The crosslinking kinetics of the PU formulations were analyzed using a Rheotech^{TR} from Matériau Ingénierie, measuring the evolution of the sample's viscosity and temperature over time. The viscosity was monitored by recording the force required to move a probe submerged in the sample medium, which oscillated horizontally with a constant amplitude (1 mm) and frequency (0.5 Hz). A transducer connected to the probe provided continuous measurement of the resistance to its movement. This force, reflecting the formulation's viscosity, is referred to as "rigidity" and expressed in Processing Control Units (PCU), following the manufacturer's labeling.⁵¹⁰ The sample size was approximately 80 g for tests conducted in beakers and around 15 g for tests performed in crucibles. The gel time was determined from the point of intersection between the tangent to the baseline before the viscosity increase and the tangent to the curve at point of inflection, accordingly with previously reported studies.^{511–513}

Dynamic Mechanical Analysis

The glass transition temperature (T_g) of the PUs was analyzed using a Kinetech forced resonance analyzer from Matériau Ingénierie. A sinusoidal torsional stress was applied while measuring the instantaneous and relaxed torques from 25 °C to 120 °C at a heating rate of 3 °C/min. The measurements were performed twice on rectangular specimens (4.7 cm × 1.6 cm × 0.3 cm), with a 2-second relaxation period and a constant angle, ranging from 2 to 180°, depending on the stiffness of the polymer analyzed. The T_g can be determined from the torque versus temperature curve using different methods: at the maximum difference between the instantaneous and relaxed torques, at the onset of the change in the slope of the instantaneous torque or at its inflection point.^{514–517} In this study, the latter method, which proved to be the most reproducible, was adopted, and the T_g was determined using the second heating cycle.

Swelling Behavior and Gel Content

PU pieces (approximately 40 mg) were immersed in 20 mL of solvent (distilled water or THF) for 120 h at room temperature. Afterwards, the samples were removed from the solvent, gently pressed with a piece of paper, weighed, dried at 70 °C for 24 h, and weighed again. Equilibrium water content (EWC) and gel content (GC) were obtained from Equation 7.6 and Equation 7.3, respectively. The measurements were repeated three times for each formulation.

Cross-Cut Adhesion Tests

The adhesion of PU coatings to aluminum substrates was assessed using the ASTM D 3359 cross-cut adhesion test (method B). Coatings were cut with an NK2000 tester from NEURTEK, ensuring penetration until reaching the substrate. Specific round blades designed for coating thicknesses between 121 and 250 μm were used to create six evenly spaced incisions (3 mm apart) both horizontally and vertically, forming a lattice pattern (1.8 cm $\times$ 1.8 cm) on the surface. A pressure-sensitive adhesive tape (ISO 2409) was then applied to the cross-hatch cut and pressed firmly over the incisions. The tape was quickly removed by pulling it off at a 180° angle, and the result was determined by evaluating the percentage of the grid affected by the test, ranging from 0% (5B) to over 65% (0B).

Probe Tack Testing

The experimental setup for tack measurements consisted of a 180.391 g probe mounted on a ZwickiLine Type Z.05 TH universal testing machine (ZwickRoell) equipped with a 100 N load cell. The probe comprised a steel cube glued to a circular Nylon 66 patch (radius: 2.5 cm) with a surface texture resembling a fingerprint (details of the experimental setup are shown in Figure 7.60). The test head was lowered at a speed of 40 cm/min until establishing contact between the PU coating and the polymeric patch. After 10 seconds, the probe was detached from the sample surface at a release rate of 60 mm/min while recording the force required for removal. The tack strength was calculated using Equation 7.8:

$$\sigma_P = \frac{F_P}{A_{\text{cont}}}$$

Equation 7.8 Tack strength.

where σ_P is the tack strength, F_P is the peak tack force and A_{cont} the contact area. The probe tack tests were performed at 23 °C and repeated three times for each formulation.

Tensile Testing

Tensile tests were done at 23 °C using a ZwickiLine Type Z.05 TH universal testing machine from ZwickRoell equipped with a 100 N load cell, at a displacement rate of 10 mm/min. Young's modulus (E), ultimate tensile strength (σ_u), and fracture strain (ε_f) were determined from the average values of five dog-bone test specimens, each with a thickness of 3 mm and a gauge length of 10 mm. The dimensions of the specimens were fixed following the design reported by Zhang et al.⁵¹⁸ and are provided in Figure 7.58 and Table 7.6. Young's modulus and fracture strain were determined using Equation 7.4 and Equation 7.5, respectively. E was calculated in the elastic portion of the stress-strain curve with $0.5\% < \varepsilon < 1\%$.

Shore Hardness Testing

Shore A and Shore D hardness tests were performed on the flat surface of cylindrical samples (0.8 cm in height, 1.5 cm in diameter) using two Hildebrand HD3000 durometers, model types A and D, respectively. Hardness values were recorded 10 seconds after the durometer was applied to the material to ensure a stable reading, and the average values were calculated based on five measurements taken at different positions on the specimen.

Lap-Shear Testing

Lap-shear adhesion tests were performed at 25 °C using an Hegewald & Peschke Inspekt Table universal testing machine, equipped with a 10 kN load cell and at a displacement rate of 2 mm/min. The measurements were repeated five times for each formulation, and the lap-shear strength was calculated using Equation 7.7.

7.3.3 Supporting information

7.3.3.1 Optimization of PU formulations

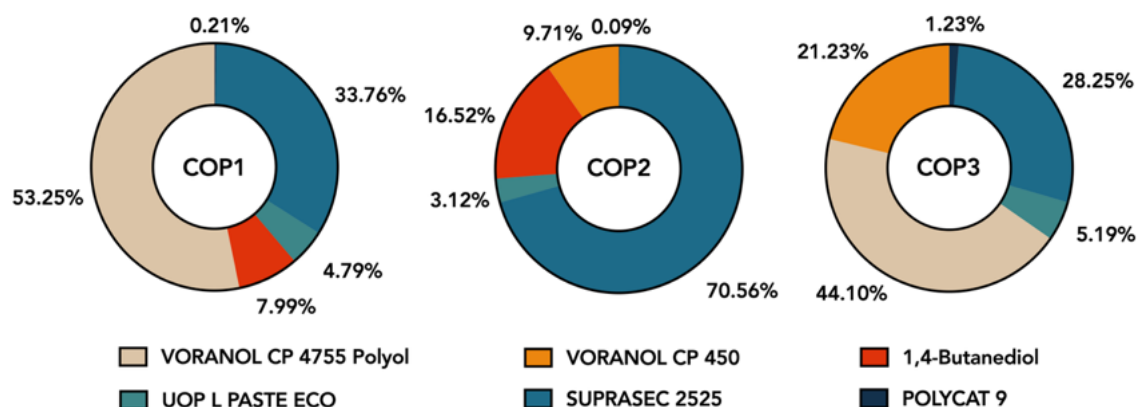


Figure 7.56 Optimized mass composition of COP1, COP2, and COP3.

7.3.3.2 Dynamic mechanical analysis

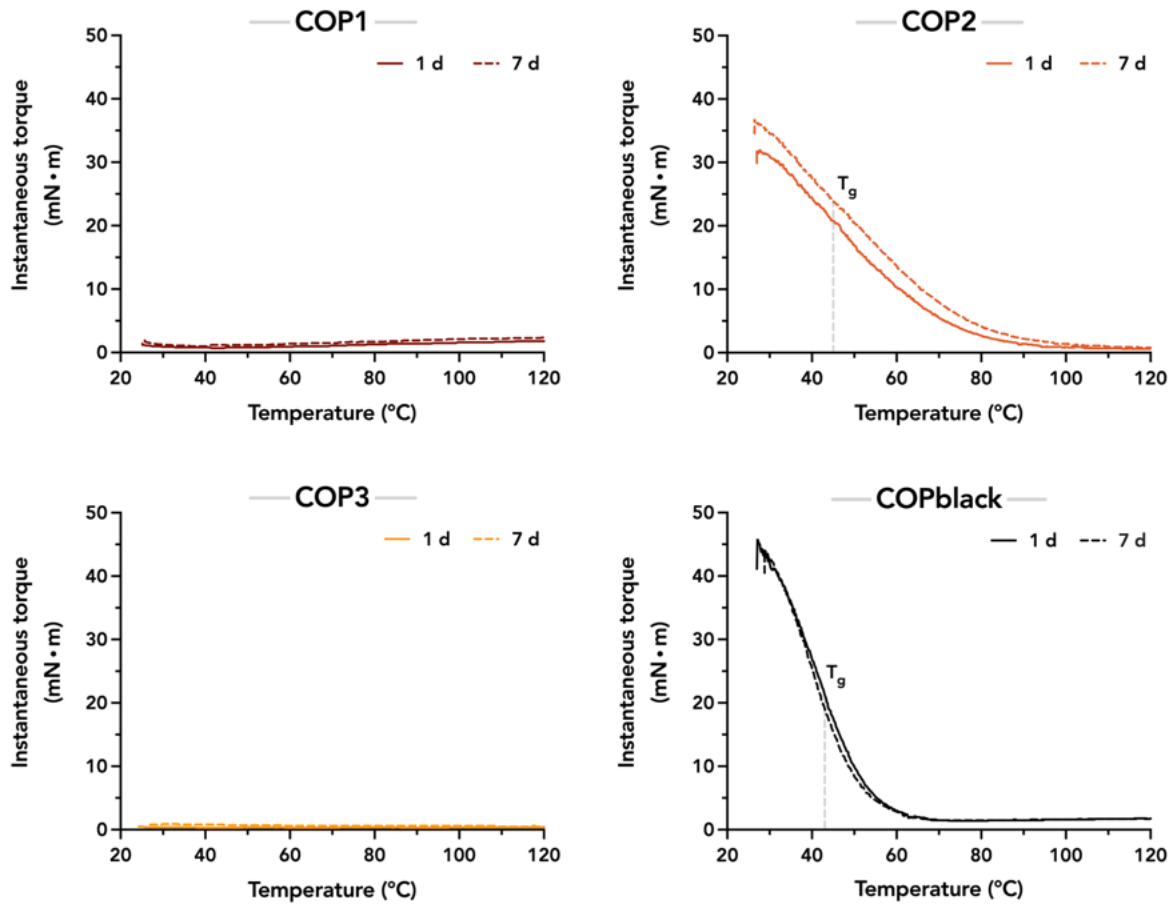


Figure 7.57 Torque-temperature curves of PU formulations after 1 (solid curve) and 7 days (dashed curve) of RT curing.

7.3.3.3 Tensile testing

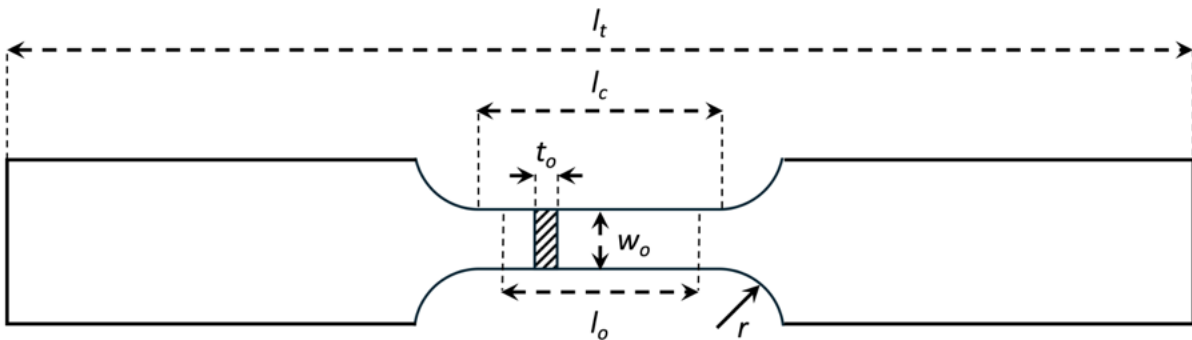


Figure 7.58 CAD drawing of dog-bone specimens used in tensile testing. l_t , l_c , l_o , w_o , r , and t_o correspond to the total length, the parallel section length, the gauge length, the original width, the shoulder radius and the original thickness of the test piece, respectively.

Table 7.6 Dimensions of dog-bone specimens used in tensile testing.

Total length (mm)	Parallel section length (mm)	Gauge length (mm)	Original width (mm)	Shoulder radius (mm)	Original thickness (mm)
60	12.5	10	3	3	1.2

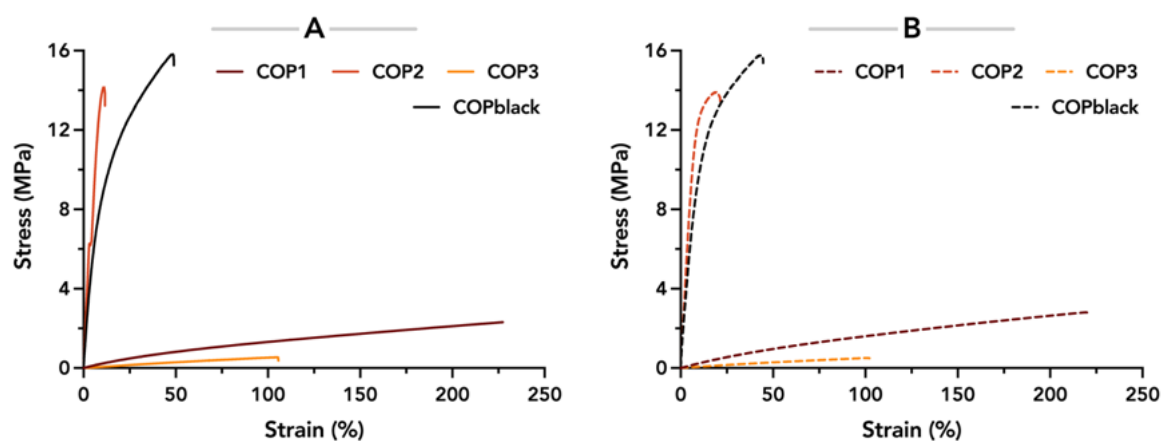


Figure 7.59 Representative stress-strain curves of PU formulations after 1 day (A) and 7 days (B) of RT curing.

7.3.3.4 Probe tack testing

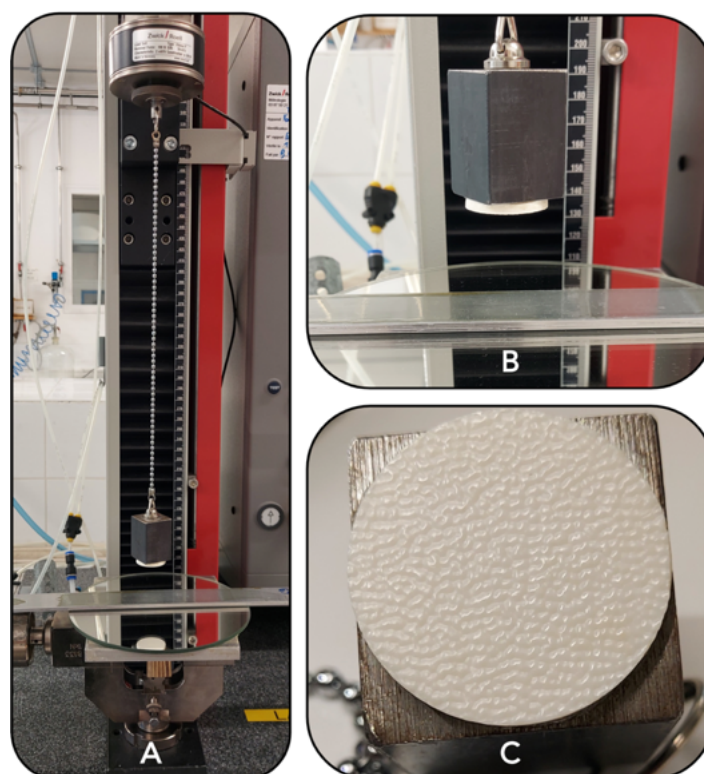


Figure 7.60 Experimental setup used for probe tack testing (A), with details of the probe (B) and the Nylon 66 patch (C).

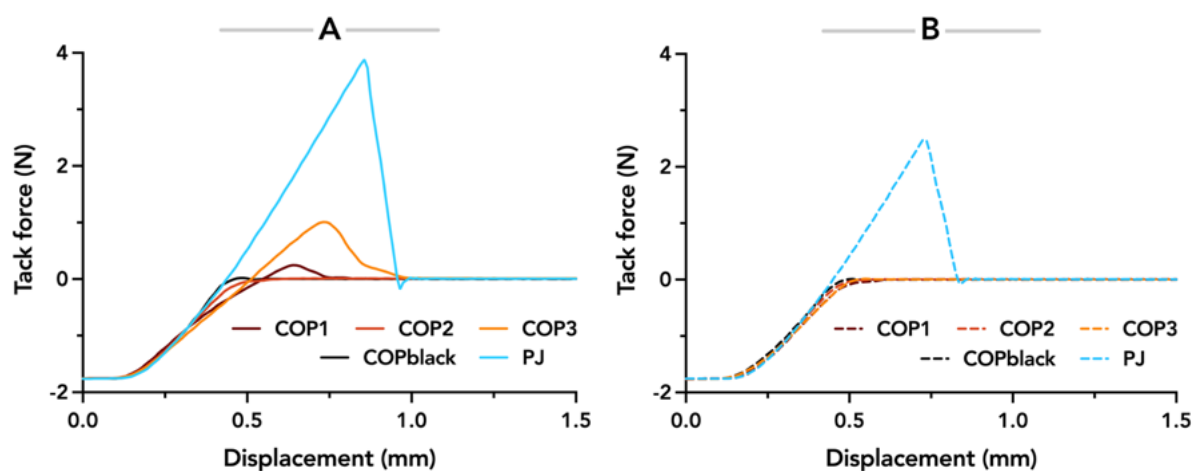


Figure 7.61 Representative tack force-displacement curves of PU formulations and PJ after 1 (A) and 7 days (B) of RT curing.

7.3.3.5 Lap-shear testing on aluminum

Table 7.7 Average lap-shear strength of PU formulations after 1 day of RT curing.

Entry	Formulation	Polyols	Lap-shear strength (MPa)
1	COP1	BDO-CP 4755	5.5 ± 0.5
2	COP2	BDO-CP 450	9.4 ± 1.4
3	COP3	CP 450-CP 4755	1.1 ± 0.1
4	COPblack	/	4.3 ± 0.4
5	PJ	/	10.2 ± 0.2

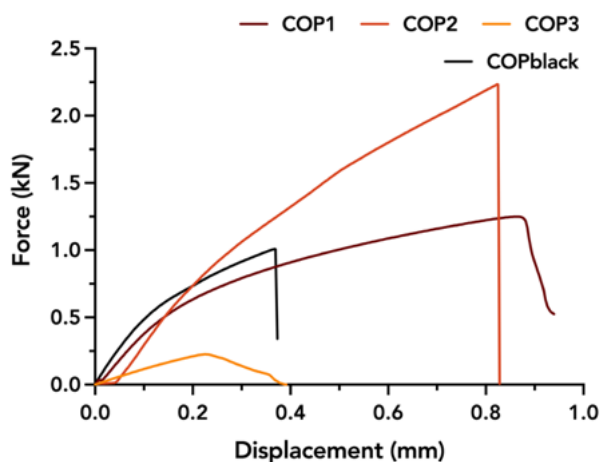


Figure 7.62 Representative force-displacement curves of PU formulations after 1 day of RT curing.

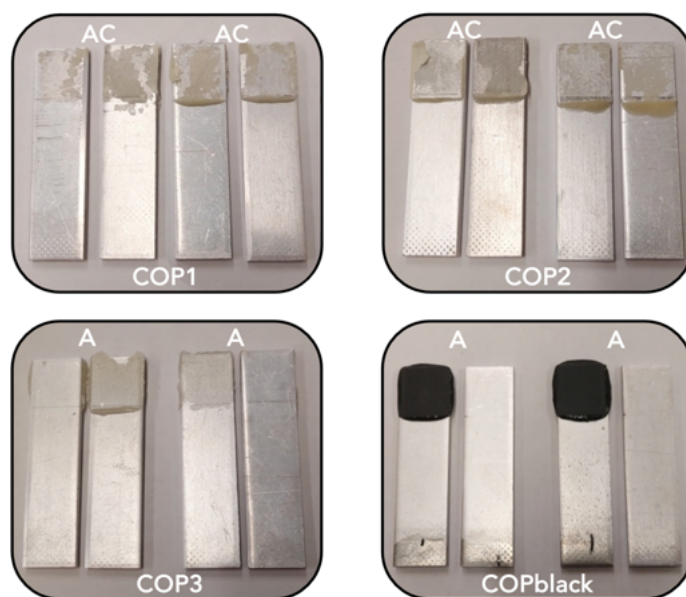


Figure 7.63 Representative failure modes of PU formulations after 1 day of RT curing.

7.4 Experimental section Chapter 5.4

7.4.1 Materials and methods

Unless stated otherwise, all starting materials, solvents and reagents were purchased from chemical suppliers and used without further purification.

Reagents and Materials

Glycerol (>99%), sodium carbonate (Na_2CO_3 , 99.5%, extra pure, anhydrous), potassium carbonate (K_2CO_3 , >99%, anhydrous), sodium sulfate (Na_2SO_4 , 99%, extra pure, anhydrous), hydrochloric acid (HCl , S. G. 1.18, ~ 37%) and sodium hydroxide (NaOH , $\geq 97\%$) were purchased from Thermo Fisher Scientific. 10-Undecenoic acid (98%), hydroquinone ($\geq 99\%$), gallium(III) bromide (GaBr_3 , 99.999%), 1,1,3,3-tetramethyldisiloxane (TMDS, 97%), and dibutyltin(IV) oxide (98%) were purchased from Sigma-Aldrich. 2-Aminoethanethiol hydrochloride (cysteamine hydrochloride, >95.0%) was purchased from TCI. 4,4'-(6,9-Dioxa-3,12-dithiatetradecane-1,14-diyl)bis(4-methyl-5-methylene-1,3-dioxolan-2-one) ($\text{bis}\alpha\text{CC}$) was synthesized according to the protocol described by Detrembleur and coworkers;⁴²³ the reagents used in its preparation are listed in Chapter 7, Section 7.2.1.

Aluminum alloy (5754, or AlMg_3) bars were prepared by cutting the material into rectangular pieces (6 cm $\times$ 1.5 cm $\times$ 0.3 cm). Aluminum alloy (Al 2024-T3) panels were provided by SONACA (Belgium) and prepared by cutting the material into rectangular pieces (6 cm $\times$ 5 cm $\times$ 0.1 cm).

Solvents

Deuterated chloroform (CDCl_3 , >99.9% D) was purchased from Eurisotop. Ethyl acetate (EtOAc, HPLC grade), cyclohexane (CyH, HPLC grade), methanol (MeOH, HPLC grade), chloroform (CHCl_3 , HPLC grade), dichloromethane (CH_2Cl_2 , HPLC grade), toluene (PhMe, HPLC grade), *N,N*-dimethylformamide (DMF, HPLC grade) were purchased from VWR. Acetonitrile (CH_3CN , HPLC grade), acetone (Me_2CO , HPLC grade), and isopropanol (*i*-PrOH, HPLC grade) were purchased from Thermo Fisher Scientific. Dimethylsulfoxide (DMSO, 99.7%, extra dry) and diethyl ether (Et_2O , 99.5%, extra dry over molecular sieve) were purchased from Acros Organics. Tetrahydrofuran (THF, >99.9%) was purchased from Sigma-Aldrich.

Column Chromatography

Column chromatography was performed using Silica Gel 60 (pore size 60 Å, mesh size 230–240, particle size 40–63 µm) as stationary phase and HPLC grade solvents as mobile phase.

Synthetic and Purification Procedures

Glyceryl triundec-10-enoate (GTU). The reaction was carried out in a 250 mL two-neck round-bottom flask equipped with an argon inlet and an air condenser. The flask was loaded with glycerol (1.00 eq., 5.00 mmol, 460.5 mg), undecylenic acid (8.00 eq., 40.0 mmol, 7.52 g), hydroquinone (10 meq., 50 µmol, 5.5 mg), and dibutyltin oxide (10.0 meq., 50.0 µmol, 12.7 mg), then purged with argon for 10 minutes. The esterification was conducted at 180 °C overnight under inert atmosphere with constant stirring at 300 rpm. The crude reaction mixture was added to a Na_2CO_3 solution (10% w/V) to neutralize the excess of undecylenic acid, extracted with ethyl acetate (1 : 1 V/V), and washed with distilled water until reaching neutral pH of the aqueous phase. The product was dried over anhydrous Na_2SO_4 , filtered, and concentrated *in vacuo*. A clear yellowish liquid was obtained. Isolated yield: 1.920 g (65%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm): δ = 5.87–5.73 (m, 3H, CH, H_e), 5.23–5.30 (m, 1H, CH, H_β), 5.03–4.89 (m, 6H, CH_2 , H_i), 4.29 (dd, J = 4.3 and 11.9 Hz, 2H, CH_2 , $H_\alpha/H_{\alpha'}$), 4.14 (dd, J = 6.0 and 11.9 Hz, 2H, CH_2 , $H_\alpha/H_{\alpha'}$), 2.31 (td, J = 7.5 and 2.4 Hz, 6H, CH_2 , H_a), 2.07–1.99 (m, 6H, CH_2 , H_d), 1.66–1.53 (m, 6H, CH_2 , H_b), 1.41–1.22 (m, 30H, CH_2 , H_c) ppm. IR (ATR, cm^{-1}): $\tilde{\nu}_{\text{max}}$ = 3077 (w, sp^2 C-H stretching), 2925 (m, sp^3 C-H asymmetric stretching), 2853 (m, sp^3 C-H symmetric stretching), 1742 (s, C=O stretching), 1639 (w, C=C stretching), 1462 (w, sp^3 C-H bending), 1156 (s, C-O stretching), 993 (w, sp^2 C-H bending), 907 (m, sp^2 C-H bending), 724 (w, sp^3 C-H rocking) cm^{-1} . ESI-MS: ($[\text{M}+\text{H}]^+$, $\text{C}_{36}\text{H}_{63}\text{O}_6^+$): theor. = 591.462, exp. = 591.462.

Glyceryl triundec-10-enyl ether (GTUE). GaBr₃ (30.0 meq., 60.4 μmol, 18.7 mg) was weighed under argon atmosphere in a 50 mL crimp vial, which was then tightly sealed. The newly synthesized glyceryl triundec-10-enoate (1.00 eq., 2.00 mmol, 1.19 g) was introduced into the sealed vial by syringe through the septum. Subsequently, dried TMDS (4.50 eq., 9.00 mmol, 1.25 g) was added dropwise *via* syringe over 2 hours under stirring to minimize overreduction. An argon reservoir was connected to the reaction vessel to maintain an inert atmosphere while avoiding overpressure from gas evolution during the reduction. After the addition was complete, the reaction was stirred for an additional 2 hours. The crude mixture was then purified *via* column chromatography (cyclohexane/ethyl acetate 50 : 1). The solvents were removed *in vacuo* to recover a clear yellowish liquid. Gravimetric yield (approximated by assuming pure GTUE and thus disregarding siloxane impurities): 0.976 g (82%). ¹H-NMR (400 MHz, CDCl₃, ppm): δ = 5.86–5.73 (m, 3H, CH, *H_e*), 5.02–4.87 (m, 6H, CH₂, *H_f*), 3.65–3.35 (m, 11H, CH₂ and CH, *H_α* and *H_{α'}* and *H_β* and *H_α*), 2.07–1.98 (m, 6H, CH₂, *H_d*), 1.62–1.48 (m, 6H, CH₂, *H_b*), 1.43–1.19 (m, 36H, CH₂, *H_c*) ppm. IR (ATR, cm⁻¹): $\tilde{\nu}_{\max}$ = 3077 (w, sp² C-H stretching), 2923 (s, sp³ C-H asymmetric stretching), 2853 (s, sp³ C-H symmetric stretching), 1641 (w, C=C stretching), 1462 (w, sp³ C-H bending), 1259 (w, C-O asymmetric stretching), 1105 (s, C-O asymmetric stretching), 991 (m, sp² C-H bending), 907 (s, sp² C-H bending), 802 (m, C-O symmetric stretching), 722 (w, sp³ C-H rocking) cm⁻¹. ESI-MS: ([M+H]⁺, C₃₆H₆₉O₃⁺): theor. = 549.524, exp. = 549.526.

Glyceryl triamine (GTA). A precise quantity of cysteamine hydrochloride was added to a 10 mL crimp vial along with GTUE (1.0 eq., 0.50 mmol, 274.5 mg). The vial was sealed and purged with argon for 10 minutes. If required, a precise volume of solvent was added. The reaction mixture was then stirred at 300 rpm for a specified time and at a defined temperature. Under the optimized conditions, the reaction was performed with 4.50 equivalents (2.25 mmol, 269.1 mg) of cysteamine hydrochloride in 0.5 mL of *i*-PrOH, and stirred for 24 hours at 75 °C. Subsequently, the crude product was purified following one of the two procedures described below: Procedure 1) collection of the reaction mixture with dichloromethane; washing with saturated K₂CO₃ solution; washing with water; drying over anhydrous Na₂SO₄; filtration; concentration *in vacuo*. Procedure 2) solubilization in 0.1 M HCl; washing with ethyl acetate; basification until pH ~12; extraction with dichloromethane; washing with saturated K₂CO₃ solution; washing with water; drying over anhydrous Na₂SO₄; filtration; concentration *in vacuo*. A solid with an ivory coloration was obtained with a gravimetric yield of 93% with Procedure 1 and 76% with Procedure 2, both approximated by assuming pure GTUE and GTA and thus disregarding siloxane impurities. ¹H-NMR (400 MHz, CDCl₃, ppm): δ = 3.57–3.30 (m, 11H, CH₂ and CH, *H_α* and *H_{α'}* and *H_β* and *H_α*), 2.80 (t, *J* = 6.3 Hz, 6H, CH₂, *H_g*), 2.54 (t, *J* = 6.3 Hz, 6H, CH₂, *H_f*), 2.47–2.39 (m, 6H, CH₂, *H_e*), 1.60–1.42

(m, 18H, CH₂ and NH₂, *H_b* and *H_d* and *H_h*), 1.37–1.12 (m, 42H, CH₂, *H_c*) ppm. ¹³C-NMR (101 MHz, CDCl₃, ppm): δ = 77.85 (CH, C_β), 71.60 (CH₂, C_a), 70.80 (CH₂, C_α/C_{α'}), 70.55 (CH₂, C_α/C_{α'}), 41.13 (CH₂, C_g), 36.32 (CH₂, C_f), 31.83 (CH₂, C_e), 30.10–28.80 (CH₂, C_b and C_c and C_d), 26.20–26.00 (CH₂, C_c). IR (ATR, cm⁻¹): $\tilde{\nu}_{\max}$ = 3280 (br, N-H stretching), 2917 (s, sp³ C-H asymmetric stretching), 2849 (s, sp³ C-H symmetric stretching), 1594 (w, N-H bending), 1467 (w, sp³ C-H bending), 1119 (m, C-O asymmetric stretching), 864 (w, N-H wagging), 722 (w, sp³ C-H rocking) cm⁻¹. ESI-MS: ([M+H]⁺, C₄₂H₉₀N₃O₃S₃⁺): theor. = 780.614, exp. = 780.614; ([M-S[CH₂]₂NH₂]⁺, C₄₀H₈₃N₂O₃S₂⁺): theor. = 703.584, exp. = 703.583.

Preparation of NIPU Adhesives and Coatings

GTA (1.0 eq., 317.2 μmol, 250.0 mg) and bisαCC (1.5 eq., 475.8 μmol, 222.3 mg) were preheated to 50 °C, rapidly added to a 10 mL vial, and stirred for 50 seconds. After mixing, the formulation was processed according to its intended application: for adhesive samples, the mixture was immediately applied to an aluminum substrate for lap-shear testing; for coating samples, it was deposited on an aluminum panel and uniformly spread using a spatula. The resulting NIPU coatings were used for water contact angle measurements, thermal analysis, and evaluation of swelling behavior and gel content. All characterizations and tests were conducted after 24 hours of curing at 50 °C.

Surface Treatments

The aluminum bars used for lap-shear testing were treated to remove surface impurities that could compromise adhesion performance, following the procedure described in Chapter 7, Section 7.2.1. The substrates were first immersed in a basic aqueous solution (40 g L⁻¹ NaOH) for 1 minute, then into an acidic aqueous solution (73 wt% water, 25 wt% H₂SO₄, 2 wt% Na₂Cr₂O₇) for 1 minute. After each step, the substrates were rinsed with distilled water and wiped with tissue paper.

7.4.2 Characterization techniques

Nuclear Magnetic Resonance (NMR) Spectroscopy

¹H- and ¹³C-NMR spectra were recorded in CDCl₃ on a Bruker AVANCE DPX 400 spectrometer at ambient temperature, with operating frequencies of 400 MHz for ¹H-NMR and 101 MHz for ¹³C-NMR. Chemical shifts were reported in parts per million (ppm) and referenced to the characteristic signals of CDCl₃ at 7.26 ppm (for ¹H) and 77.16 ppm (for ¹³C). The centroid shift was given for centrosymmetrical signals, and the signal range was reported for multiplets. Spin

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multiplicity was described using the following abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet. All coupling constants (J) were reported in hertz (Hz). Peak assignments were confirmed by COSY, HSQC, and HMBC spectroscopy. Double bond conversion in the thiol-ene addition between GTUE and cysteamine hydrochloride was calculated using Equation 7.9:

$$\text{Double bond conversion (\%)} = \frac{\int_{\text{GTA}}}{\int_{\text{GTUE}} + \int_{\text{GTA}}} \times 100$$

Equation 7.9 Double bond conversion.

where $\int_{\text{GTA}}$ is the integral of GTA signal at 2.80 ppm (H_g), while $\int_{\text{GTUE}}$ is the integral of GTUE signal at 5.02–4.87 ppm (H_t).

Fourier-Transform Infrared (FTIR) Spectroscopy

Infrared spectra were registered on a Bruker Alpha-P spectrometer equipped with a diamond attenuated transmission reflectance (ATR) device. For each sample 24 scans were recorded over the range 4000–400 cm^{-1} with a normal resolution of 2 cm^{-1} . The peak intensities were described in relation to the most intense signal as follows: s = strong, m = medium, w = weak.

Electrospray Ionization Mass Spectrometry (ESI-MS)

Mass spectra were recorded using a Q Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific) equipped with a HESI II probe. The instrument was calibrated in the m/z range 150–2000 using a standard containing caffeine, Met-ArgPhe-Ala acetate (MRFA) and a mixture of fluorinated phosphazenes (Ultramark 1621, all from Sigma-Aldrich). A constant spray voltage of 3.5 kV, a dimensionless sheath gas of 6, and a sweep gas flow rate of 2 were applied. The capillary voltage and the S-lens RF level were set to 68.0 V and 320 °C, respectively. For interpretation of the spectra, the protonated molecular ion $[M+H]^+$ and characteristic fragment ions were assigned based on their mass-to-charge ratios (m/z).

Melting Point Apparatus

Melting point analysis was conducted using an OptiMelt MPA100 Automated Melting Point System from Stanford Research Systems. The measurement was carried out in an open capillary tube at a heating rate of 1 °C min^{-1} , from 22.5 to 70 °C. The melting curve was generated by the Digital Image Processor during the heating ramp, and the melting point was determined from the minimum of the first derivative of the curve.

Rheological Measurements

The rheological behavior of the NIPU formulation was analyzed using an ARES-G2 rotational rheometer (TA Instruments) by performing time sweep measurements with a parallel plate geometry and at constant strain deformation (1%) and frequency (1Hz). The gel time of the thermoset was determined excluding the 3 minutes required for reagent mixing and sample loading.

Swelling Behavior and Gel Content

NIPU pieces (approximately 40 mg) were immersed in 20 mL of solvent (distilled water or THF) for 120 h at room temperature. Afterwards, the samples were removed from the solvent, gently pressed with a piece of paper, weighed, dried at 70 °C for 24 h, and weighed again. Swelling index (SI) and gel content (GC) were obtained from Equation 7.10 and Equation 7.3:

$$SI (\%) = \frac{(W_s - W_i)}{W_i} \times 100$$

Equation 7.10 *Swelling index.*

where W_i is the initial weight, and W_s is the weight of the swollen sample. The measurements were repeated three times for each formulation.

Water Contact Angle Measurements

The wettability of NIPU coatings was evaluated by contact angle measurements, carried out with water on a KRÜSS model DSA25S Drop Shape Analyser in the sessile drop configuration. A 15- μ L droplet of Milli-Q water was deposited on the surface of the coating, and after 1 min a high-resolution video camera was used to acquire an image of the angle between the solid surface and the tangent line to the contacting edge of the droplet. The mean contact angle value was obtained from five measurements realized on different spots of the sample surface.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed on a TGA 5500 instrument from TA Instruments. To determine the thermal degradation temperature at 10% mass loss ($T_{deg10\%}$), evaluated starting from the end of the dehydration step, approximately 8 mg of sample was heated at 10 °C min⁻¹ from 25 to 600 °C under nitrogen atmosphere. To determine the dehydration temperature (T_{dehyd}), identified from the first derivative of the thermogravimetric curve at the beginning of the mass loss signal, around 5-10 mg of sample was heated at 2 °C min⁻¹ from 25 to 275 °C under nitrogen atmosphere.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC 3 equipped with a Huber Intracooler TC100. Samples of 4 to 6 mg were sealed in hermetic aluminum pans and heated under ultrapure nitrogen flow at $10\text{ }^{\circ}\text{C min}^{-1}$ from -40 to $120\text{ }^{\circ}\text{C}$. The glass transition temperature (T_g) was determined from the inflection point of the transition in the first heating cycle to prevent modifications of the crosslinking degree.

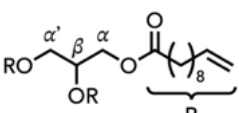
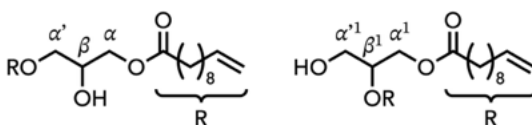
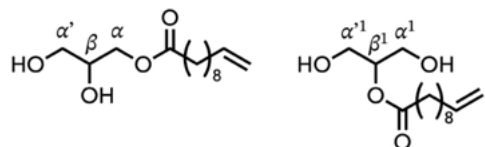
Lap-Shear Testing

Lap-shear adhesion tests were performed at $25\text{ }^{\circ}\text{C}$ using an Hegewald & Peschke Inspekt Table universal testing machine, equipped with a 10 kN load cell and at a displacement rate of 2 mm min^{-1} . The measurements were repeated four times and the lap-shear strength was calculated using Equation 7.7.

7.4.3 Supporting information

7.4.3.1 Three-step synthesis from renewable feedstocks

Table 7.8 Chemical structures and characteristic $^1\text{H-NMR}$ shifts in CDCl_3 of glycerol esters of undecylenic acid.⁴⁸²

Molecule	Chemical structure	Hydrogen	Chemical shifts (ppm)
GTU ^a		α	4.08–4.19
		α'	4.24–4.34
		β	5.21–5.31
GDU ^b		α'^1	3.69–3.75
		α, β, α'	4.00–4.35
		β^1	5.04–5.12
GMU ^c		α'	3.54–3.75
		α^1, α'^1	3.80–3.85
		β	3.87–3.98
		α	4.07–4.27

^aGTU = glyceryl triundecenoate. ^bGDU = glyceryl diundecenoate. ^cGMU = glyceryl monoundecenoate.

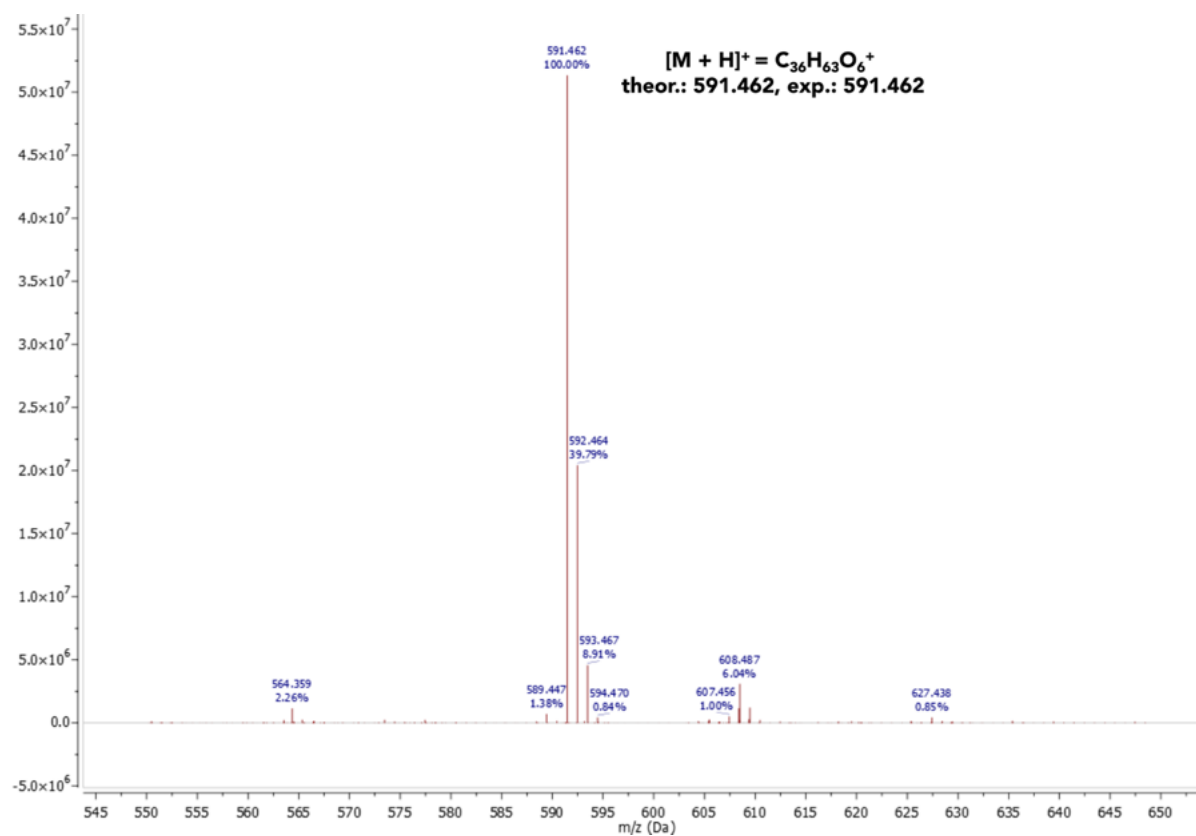


Figure 7.64 ESI-MS spectrum of GTU.

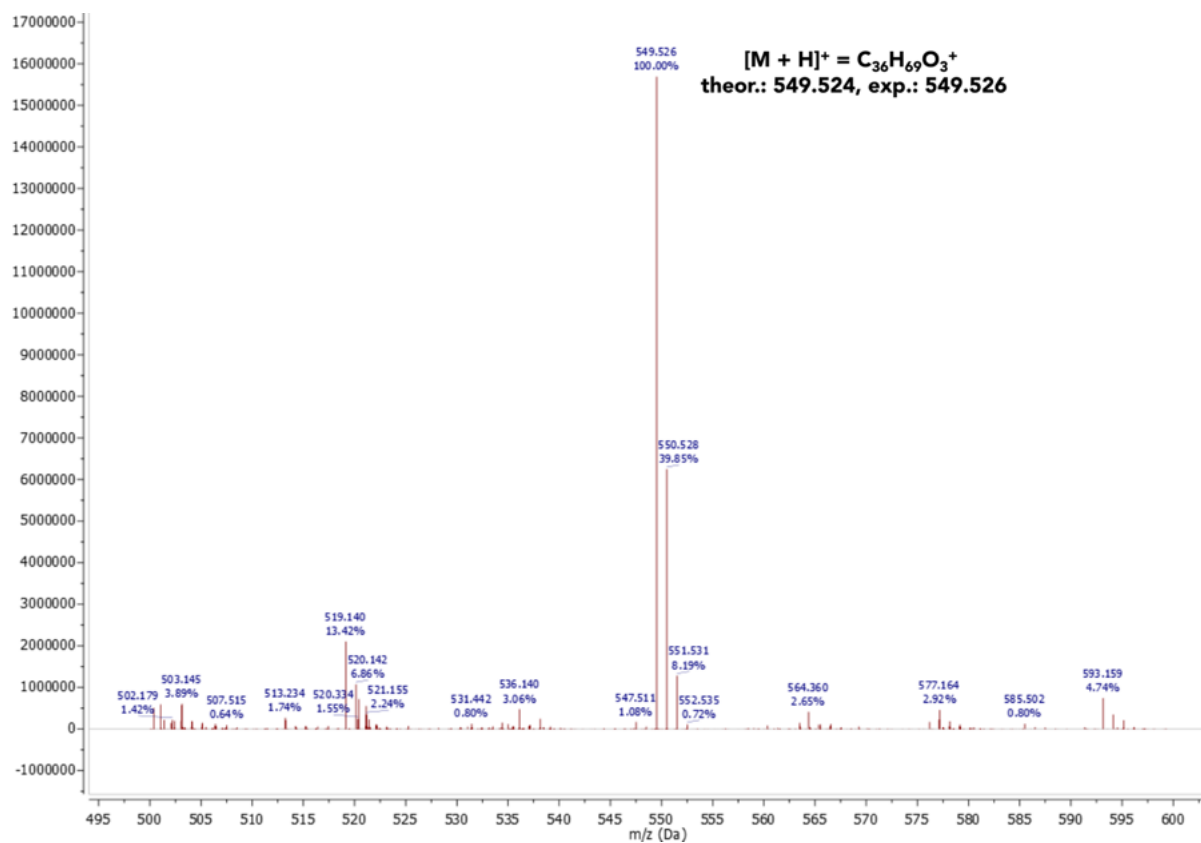


Figure 7.65 ESI-MS spectrum of GTUE.

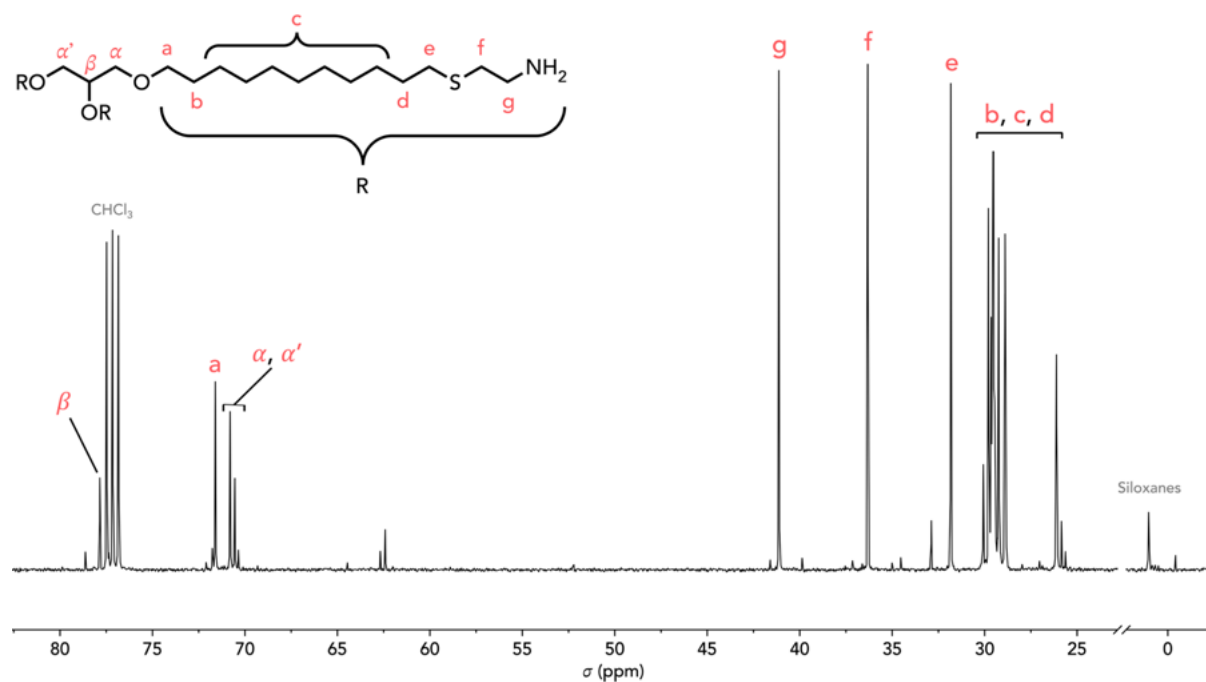


Figure 7.66 ^{13}C -NMR spectrum of GTA in CDCl_3 .

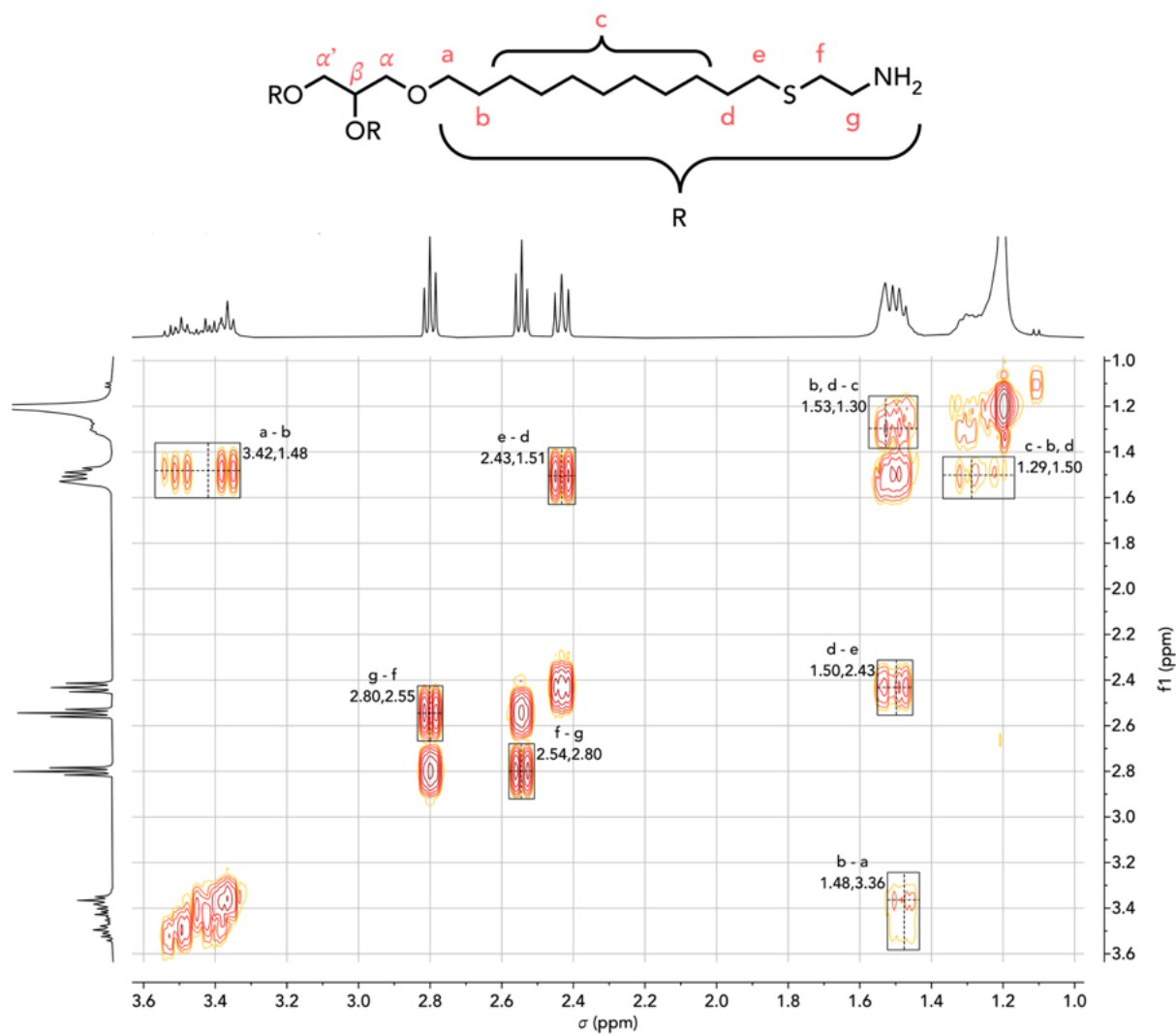
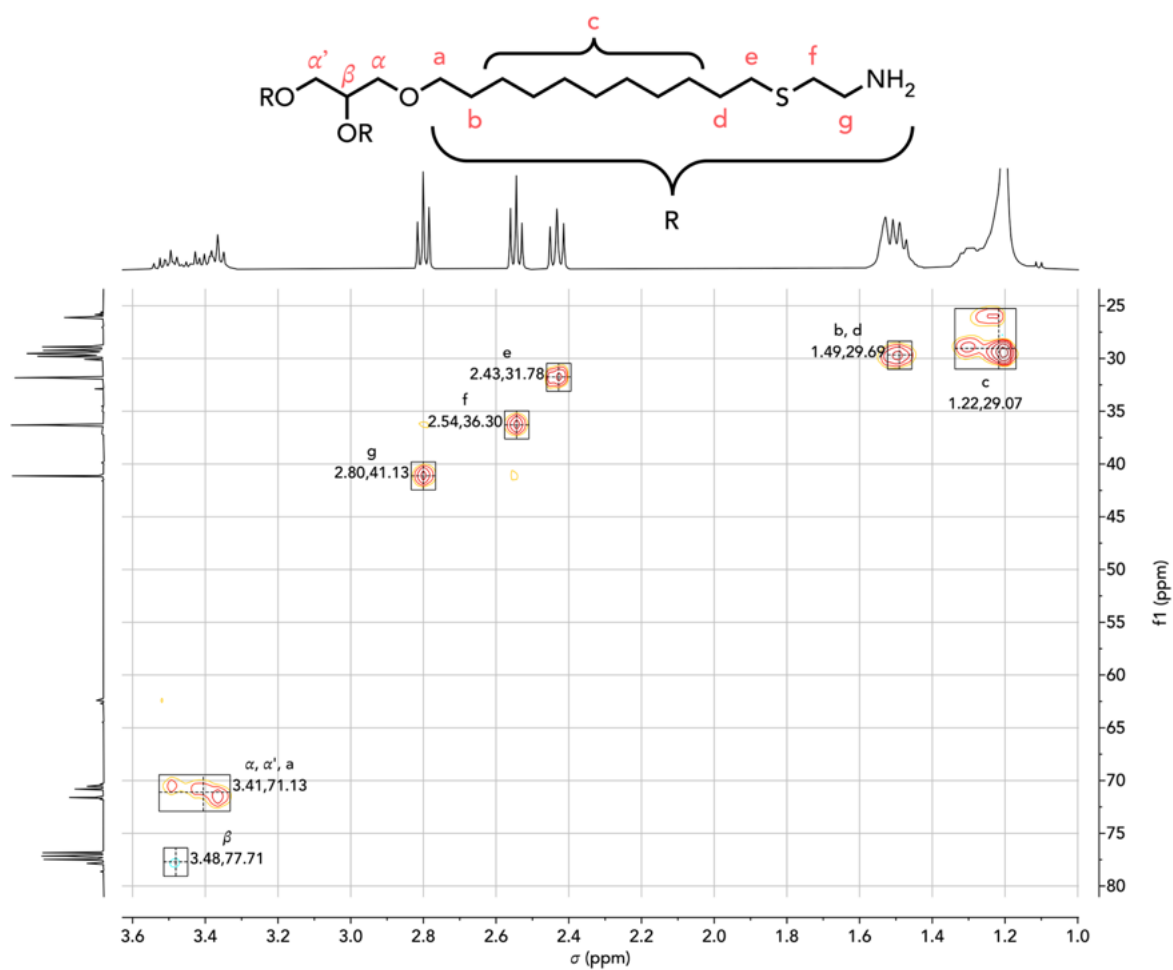
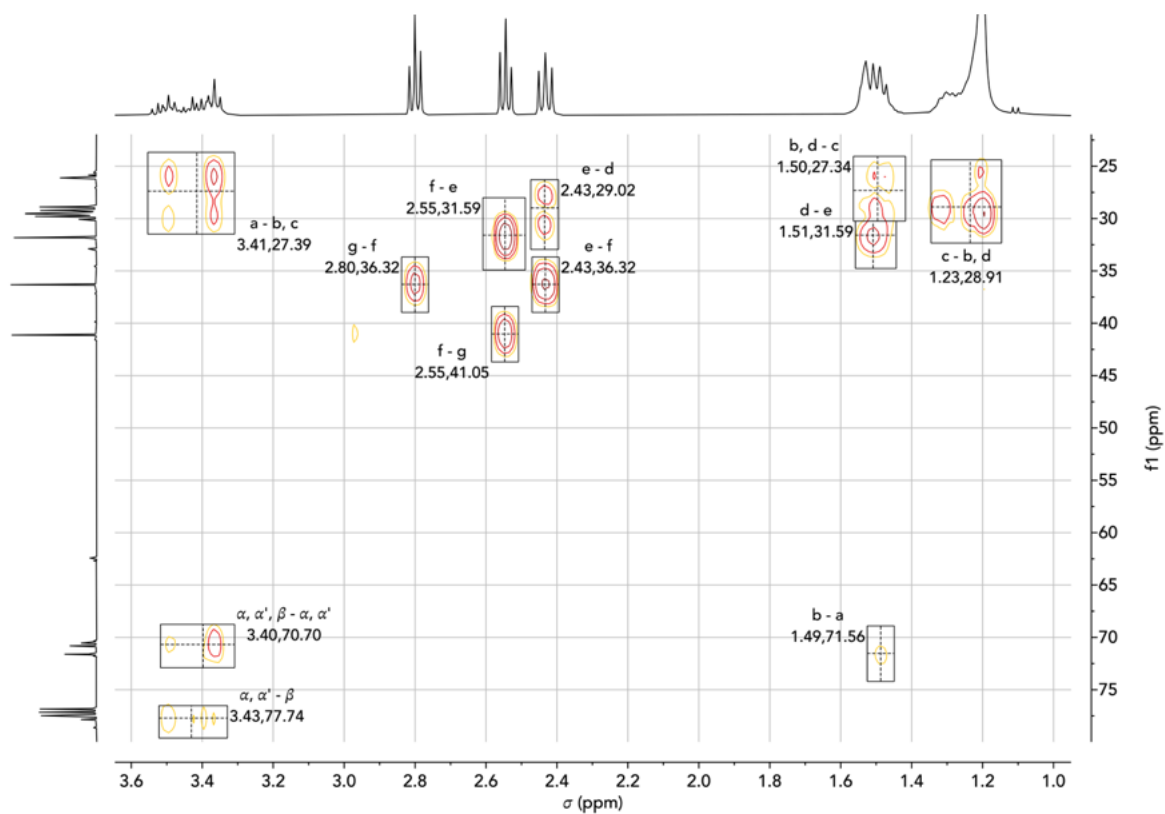


Figure 7.67 COSY spectrum of GTA in CDCl_3 .

Figure 7.68 HSQC spectrum of GTA in CDCl_3 .Figure 7.69 HMBC spectrum of GTA in CDCl_3 .

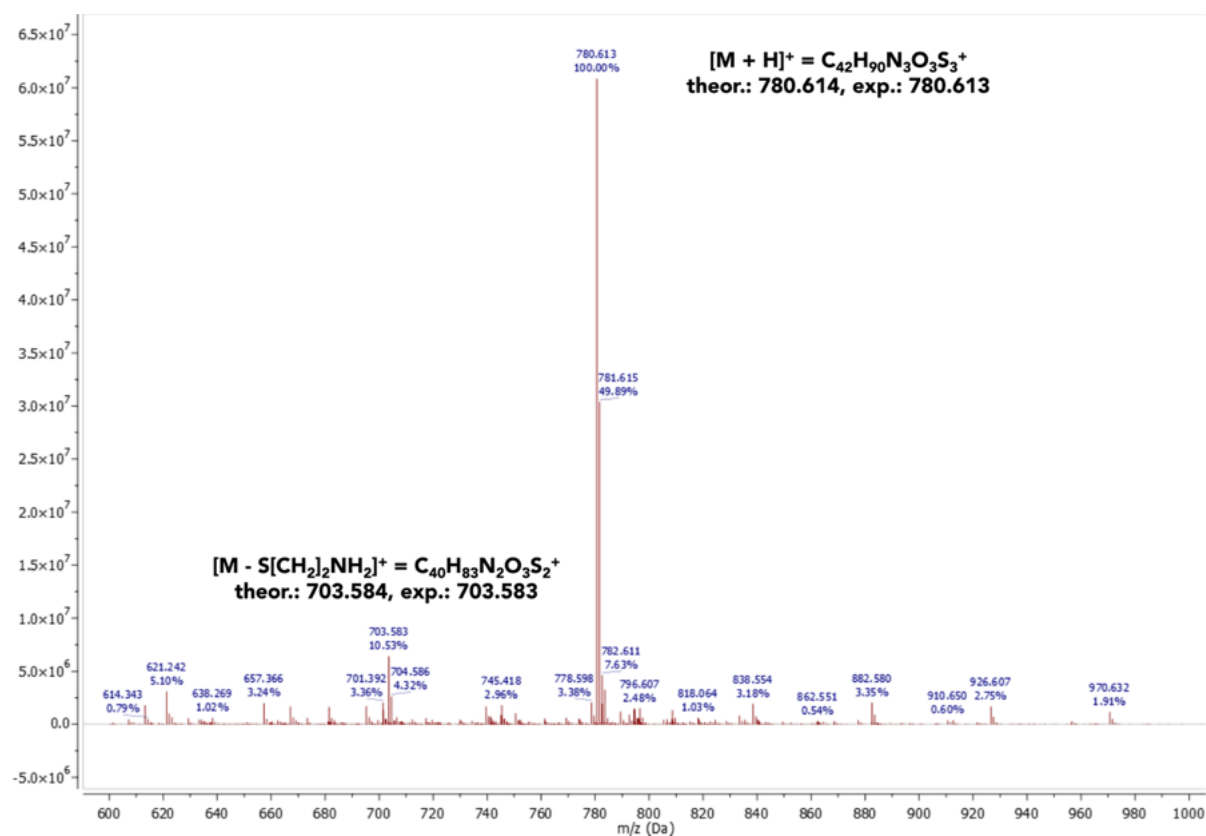


Figure 7.70 ESI-MS spectrum of GTA.

Table 7.9 GTA solubility in various solvents.

Solubility	Solvent					
High	MeOH	CHCl ₃	CH ₂ Cl ₂	Me ₂ CO		
Moderate	<i>i</i> -PrOH		THF	PhMe		
Low	DMF	EtOAc	CH ₃ CN	DMSO	CyH	Et ₂ O

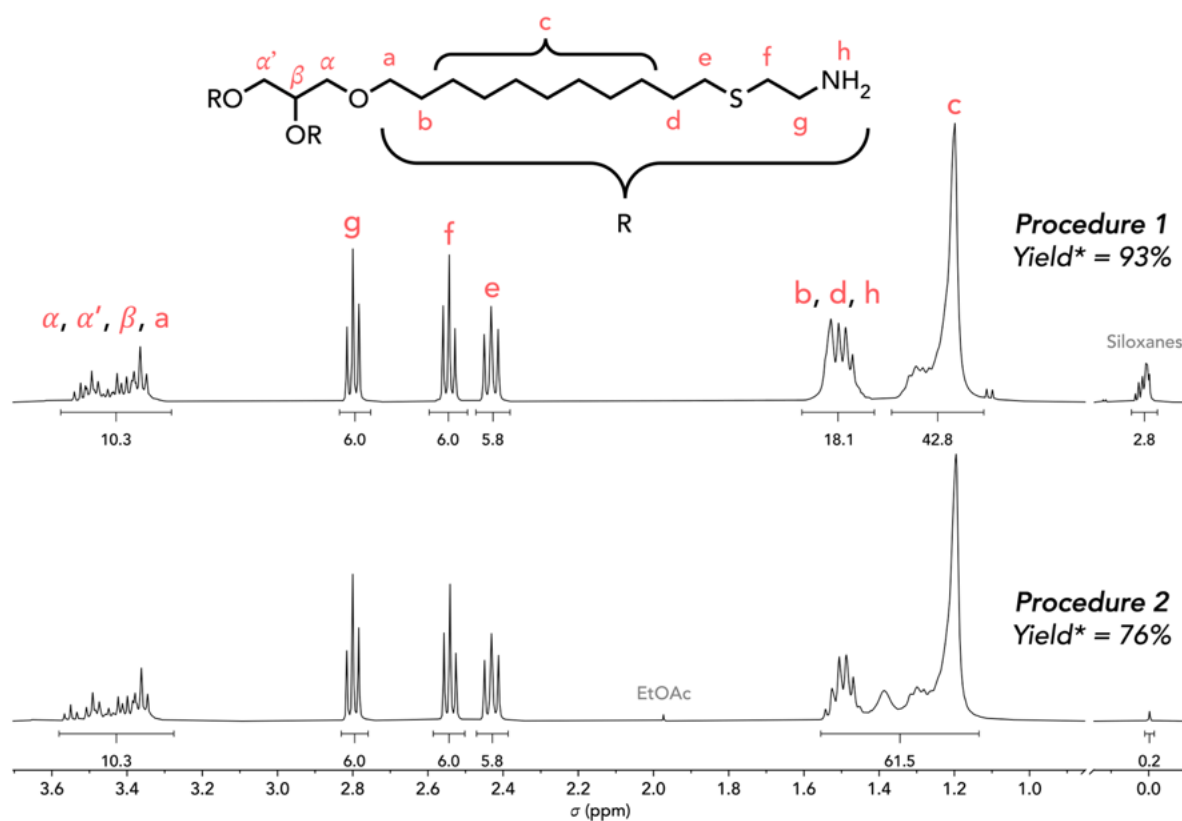


Figure 7.71 ^1H -NMR spectrum and yield comparison for GTA after purification procedure 1 (above) and 2 (below). *Approximated by assuming pure reagents and product, disregarding siloxane impurities.

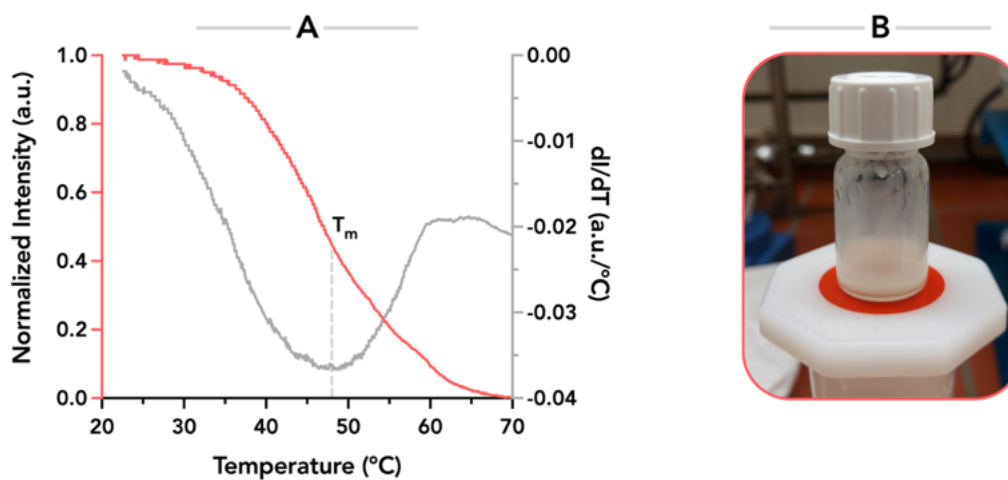


Figure 7.72 Melting curve (A) and picture (B) of pure GTA.

7.4.3.2 Preparation of a solvent-free NIPU formulation with CO₂-sourced bisaCC

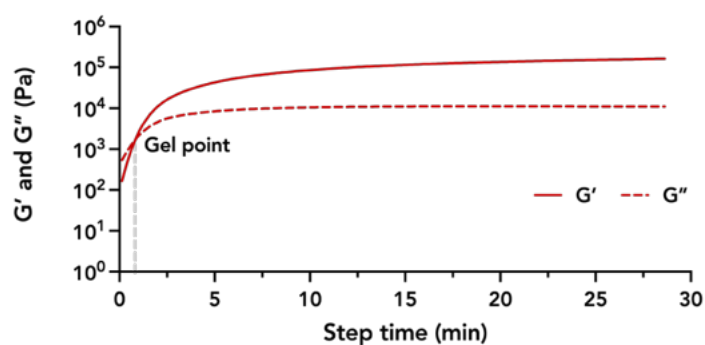


Figure 7.73 Time evolution of storage (G') and loss (G'') moduli for PGTA.

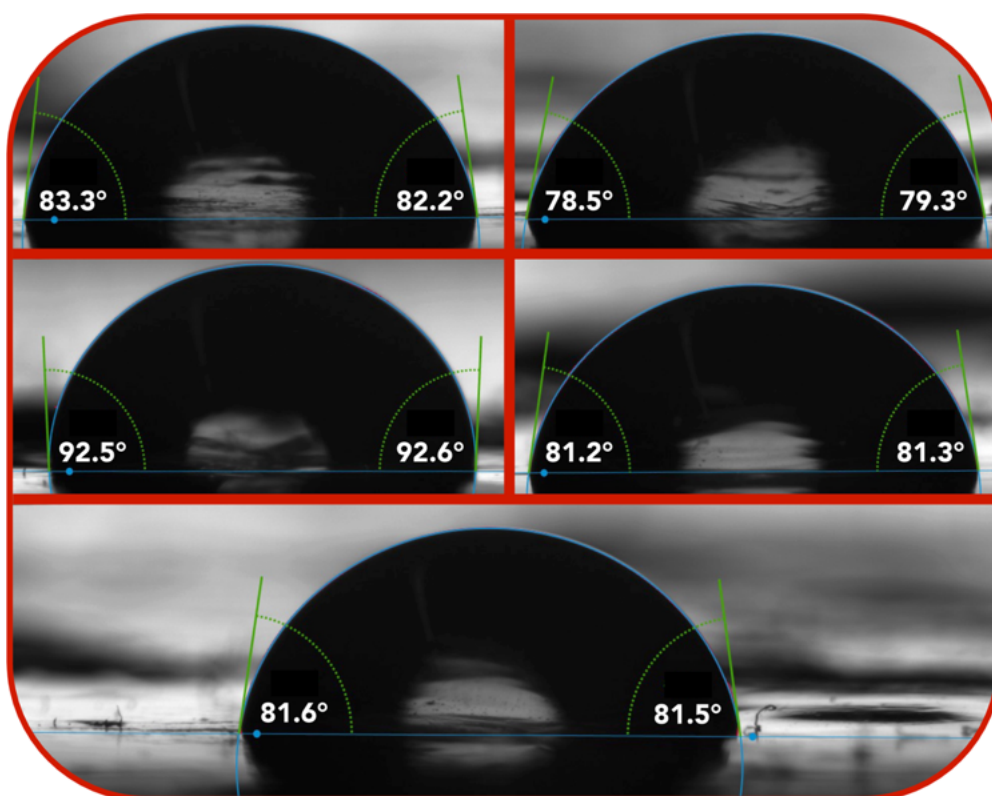


Figure 7.74 Contact angle images of water droplets on PGTA coatings.

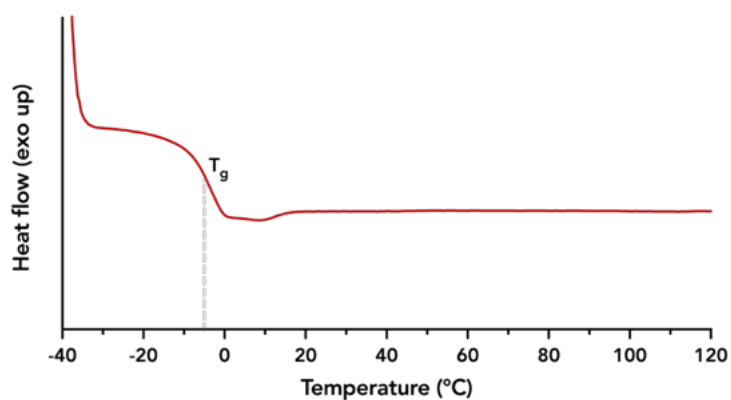


Figure 7.75 DSC curve of PGTA.

8 APPENDIX

8.1 List of abbreviations and symbols

%	Percent symbol	AFM	Atomic force microscopy
°	Degree symbol	ASTM	American Society for Testing and Materials
°C	Degree Celsius	ATR	Attenuated transmission reflectance
∫	Normalized integral of an NMR peak	AWNIPU	Anionic water-based non-isocyanate polyurethane
1,12-DAD	1,12-Diaminododecane	BAPA	3,3'-Diaminodipropylamine
1K	One-component	BdiCC	1,4-Butanediol bis(cyclic carbonate)
2D-NMR	Two-dimensional nuclear magnetic resonance	BDO	1,4-Butanediol
2K	Two-component	bis(<i>endo</i> - α CC)	Bis(<i>endo</i> -vinylene cyclic carbonate)
5R	Repairable, reprocessable, reconfigurable, recyclable, and re-adhesive	bis(<i>exo</i> - α CC)	Bis(<i>exo</i> -vinylene cyclic carbonate)
Å	Angstrom	bis α CC	Bis(α -alkylidene cyclic carbonate)
A	Overlapped area, adhesive failure	CA	Contact angle
ABS	Acrylonitrile butadiene styrene	CAD	Computer-Aided Design
AC	Adhesive-cohesive failure	CAGR	Compound annual growth rate
ACFP	Adhesion and cohesion failure with peel	CAN	Covalent adaptable networks
A _{cont}	Contact area	CBMA	1,3-Cyclohexanebis-(methylamine)
ACS	American Chemical Society	CC	Cyclic carbonate

CCA	Cross-cut adhesion	DBTDL	Dibutyltin dilaurate
CF	Cohesion failure	DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
CFC	Chlorofluorocarbon	DC	Vanillin-based bis(cyclic carbonate)
CLSO	Carbonated linseed oil	DCB	Double cantilever beam
cm	Centimeter	DCM	Dichloromethane
CNC	Cellulose nanocrystal	DEA	Diethanolamine
CNSL	Cashew nut shell liquid	DETA	Diethylenetriamine
COR	Debonding due to bondline corrosion	DF	Delamination failure
COSY	Gradient-selected ^1H - ^1H correlated spectroscopy	DFT	Density functional theory
CP 450	VORANOL TM CP 450	DMA	Dynamic mechanical analysis
CP 4755	VORANOL TM CP 4755 Polyol	DMAc	<i>N,N</i> -Dimethylacetamide
CPCC	Cashew phenol cyclic carbonate	DMDPA	<i>N</i> -Methyldipropylamine
CSBO	Carbonated soybean oil	DMF	<i>N,N</i> -Dimethylformamide
CSF	Cohesive substrate failure	DMPA	Dimethylolpropionic acid
cSt	Centistoke	DMSO	Dimethylsulfoxide
CWNIPU	Cationic water-based non-isocyanate polyurethane	DOI	Distinctness of image
CyH	Cyclohexane	DOP	Dopamine
Đ	Dispersity	DOP%	Dopamine percentage
d	Day	DPP	Diphenyl phosphate
DABCO	1,4-Diazabicyclo[2.2.2]octane	DSC	Differential scanning calorimetry
DBTDA	Dibutyltin diacetate	dTGA	First derivative of the thermogravimetric curve

E	Elastic modulus	FPA	Fumaropimaric acid
E factor	Environmental factor	FTIR	Fourier-transform infrared
e.g.	<i>Exempli gratia</i>	g	Gram
EDA	Ethylene diamine	G'	Storage modulus
EDS	Energy-dispersive X-ray spectroscopy	G''	Loss modulus
EG	Ethylene glycol	GC	Gel content
EHS	Environmental, health, and safety	GDU	Glyceryl diundec-10-enoate
EJD	European joint doctorate	GHG	Global greenhouse gas
ENF	End-notched flexure	GMU	Glyceryl monoundec-10-enoate
eq.	Equivalent	GPa	Gigapascal
ESI-MS	Electrospray ionization mass spectrometry	GTA	Glyceryl triamine
Et ₂ O	Diethyl ether	GTU	Glyceryl triundec-10-enoate
Et ₃ SiH	Triethylsilane	GTUE	Glyceryl triundec-10-enyl ether
etc.	<i>Et cetera</i>	h	Hour
EtOAc	Ethyl acetate	HCC	1,6-Hexanediol bis(cyclic carbonate)
EWC	Equilibrium water content	HDI	Hexamethylene diisocyanate
EWG	Electron-withdrawing	HDPE	High-density polyethylene
<i>exo-αCC</i>	<i>Exo</i> -vinylene cyclic carbonate	HMBC	¹ H– ¹³ C Heteronuclear multiple bond correlation
F	Applied force	HMDA	Hexamethylenediamine
FA	Formaldehyde	HPLC	High-performance liquid chromatography
F _p	Peak tack force	HSQC	Phase-edited ¹ H– ¹³ C heteronuclear single quantum coherence

Hz	Hertz
i.e.	<i>Id est</i>
<i>i</i> -PrOH	Isopropanol
IPCC	Intergovernmental Panel on Climate Change
IPDA	Isophorone diamine
IPDI	Isophorone diisocyanate
IR	Infrared
ISO	International Organization for Standardization
IWP	Impact wedge peel
J	Joule
kDa	Kilodalton
kN	Kilonewton
kPa	Kilopascal
kV	Kilovolt
L	Liter
l_c	Parallel section length of the sample
L_f	Length of the sample at fracture
LFT	Light-fiber-tear failure
L_i	Initial length of the sample
l_o	Gauge length of the sample
l_t	Total length of the sample
m	Medium

M	Molar
m/z	Mass to charge ratio
m-XDA	<i>m</i> -Xylylenediamine
MDI	Methylene diphenyl diisocyanate
Me ₂ CO	Acetone
MEK	Methyl ethyl ketone
MeOH	Methanol
mg	Milligram
MHz	Megahertz
min	Minute
mL	Milliliter
mm	Millimeter
mmol	Millimole
M_n	Number average molar mass
mol	Mole
mol%	Mole percentage
monoCC	Monocyclic carbonate
MPa	Megapascal
mPEG-NH ₂	Poly(ethylene glycol) methyl ether amine
MRFA	Met-ArgPhe-Ala acetate
MSA	Methane sulfonic acid
M_w	Weight average molar mass

MXDA	<i>m</i> -Xylylenediamine	PDMS	Polydimethylsiloxane
n	Numero di moli	PEG	Polyethylene glycol
N	Number of cycles to failure, Newton	PEG-di5CC	Poly(ethylene glycol) dicyclic carbonate
NHC	<i>N</i> -Heterocyclic carbene	PEI	Polyethyleneimine
NIOSH	National Institute for Occupational Safety and Health	pH	Negative logarithm of hydrogen ion concentration
NIPU	Non-isocyanate polyurethane	PhMe	Toluene
nm	Nanometer	PHU	Polyhydroxyurethane
NMP	<i>N</i> -Methyl-2-pyrrolidinone	PMMA	Poly(methyl methacrylate)
NMR	Nuclear magnetic resonance	polyCC	Poly(cyclic carbonate)
NWNIPU	Nonionic water-based non-isocyanate polyurethane	poly α CC	Poly(α -alkylidene cyclic carbonate)
oCNC	Octylamine-modified cellulose nanocrystal	PPE	Personal protective equipment
OEL	Occupational exposure limit	PPG	Polypropylene glycol
OSC	Oscillating failure	PPGdiCC	Poly(propylene glycol)-derived bis(cyclic carbonate)
OSHA	Occupational Safety and Health Administration	ppm	Parts per million
PAAm	Poly(allylamine)	PSA	Pressure-sensitive adhesive
PAMAM	Poly(amidoamine)s	PTMEG	Poly(tetramethylene ether) glycol
PCL	Polycaprolactone	PU	Polyurethane
PCU	Processing control unit	PUD	Polyurethane dispersion

PVAm	Poly(vinylamine)	SCF	Special cohesion failure
PXDA	<i>p</i> -Xylylenediamine	SDG	Sustainable development goal
r	Shoulder radius of the sample	SEC	Size exclusion chromatography
R&D	Research and development	SEM	Scanning electron microscopy
RdiCC	Resorcinol-based bis(cyclic carbonate)	SF	Substrate failure
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals	SI	Swelling index
Ref.	Reference	Sn(Oct) ₂	Stannous octanoate
RIM	Reaction injection molding	SS	Stainless steel
ROCOP	Ring-opening copolymerization	STC	Sorbitol tricarboxylate
ROP	Ring-opening polymerization	SWCF	Cohesion failure with stress whitening of the adhesive
RT	Room temperature	SWCNT	Single-walled carbon nanotube
s	Second, strong	T-403	Jeffamine [®] T-403
S	Applied stress amplitude	TANI	Tetraniline
S. G.	Specific gravity	TAST	Thick-adherend shear test
SA	Succinic anhydride	TBD	1,5,7-Triazabicyclo[4.4.0]dec-5-ene
SAFT	Shear adhesion failure temperature	TDCB	Tapered double cantilever beam
SB	Stock-break failure	T _{deg5%}	Thermal degradation temperature at 5% mass loss
SCB	Split cantilever beam	T _{deg10%}	Thermal degradation temperature at 10% mass loss

T_{dehyd}	Dehydration temperature
TDI	Toluene diisocyanate
TEA	Triethanolamine
TEM	Transmission electron microscopy
TEPA	Tetraethylenepentamine
TETA	Triethylenetetramine
T_g	Glass-transition temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
T_m	Melting temperature
TMDS	1,1,3,3-Tetramethyldisiloxane
TMP	Trimethylolpropane
t_o	Original thickness of the sample
TPU	Thermoplastic polyurethane
TREN	Tris(2-aminoethyl)amine
UA	Undecylenic acid
UN	United Nations
USD	United States dollar
UV	Ultraviolet
UV-Vis	Ultraviolet-visible
V	Volt
V/V	Volume fraction

VEC	Vinyl ethylene carbonate
VOC	Volatile organic compound
w	Weak
W	Wood
w/V	Mass per volume concentration
W_f	Final weight
W_i	Initial weight
WNIPU	Water-based non-isocyanate polyurethane
w_o	Original width of the sample
W_s	Weight of the swollen sample
wt%	Weight percentage
XFR	X-ray fluorescence
XPS	X-ray photoelectron spectroscopy

αCC	α -Alkylidene cyclic carbonate
γ_c	Critical surface tension
δ	IR bending vibration
ε	Engineering extensional strain
ε_f	Fracture strain
θ	Contact angle
μg	Microgram
μL	Microliter
μm	Micrometer
μmol	Micromole
ν	IR stretching vibration
$\tilde{\nu}_{\text{max}}$	Wavenumber at maximum IR absorption
σ	Tensile stress
σ_p	Peak strength
σ_u	Tensile strength
τ	Lap-shear strength
ω	IR wagging vibration

8.2 List of figures

Figure 2.1 PU technologies evolution timeline: from discovery to current time (RIM = reaction injection molding, PUD = polyurethane dispersion, CFC = chlorofluorocarbon, TPU = thermoplastic polyurethane, SWCNT = single-walled carbon nanotube, NIPU = non-isocyanate polyurethane). 7

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8.6 List of publications

Parts of the work presented in this thesis have been adapted from the following publication:

Narducci, L.; Habets, T.; Grossman, Q.; Grignard, B.; Meier, M. A. R.; Detrembleur, C. Solvent-Free Synthesis of Room-Temperature Curable Nonisocyanate Polyurethane Adhesives and Coatings. *Macromolecules* **2025**, 58 (13), 6452–6465. <https://doi.org/10.1021/acs.macromol.5c00718>.

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