REVIEW

Recent Advances of Dynamic Covalent Chemistry Polymers aligning with Principles of Green Chemistry

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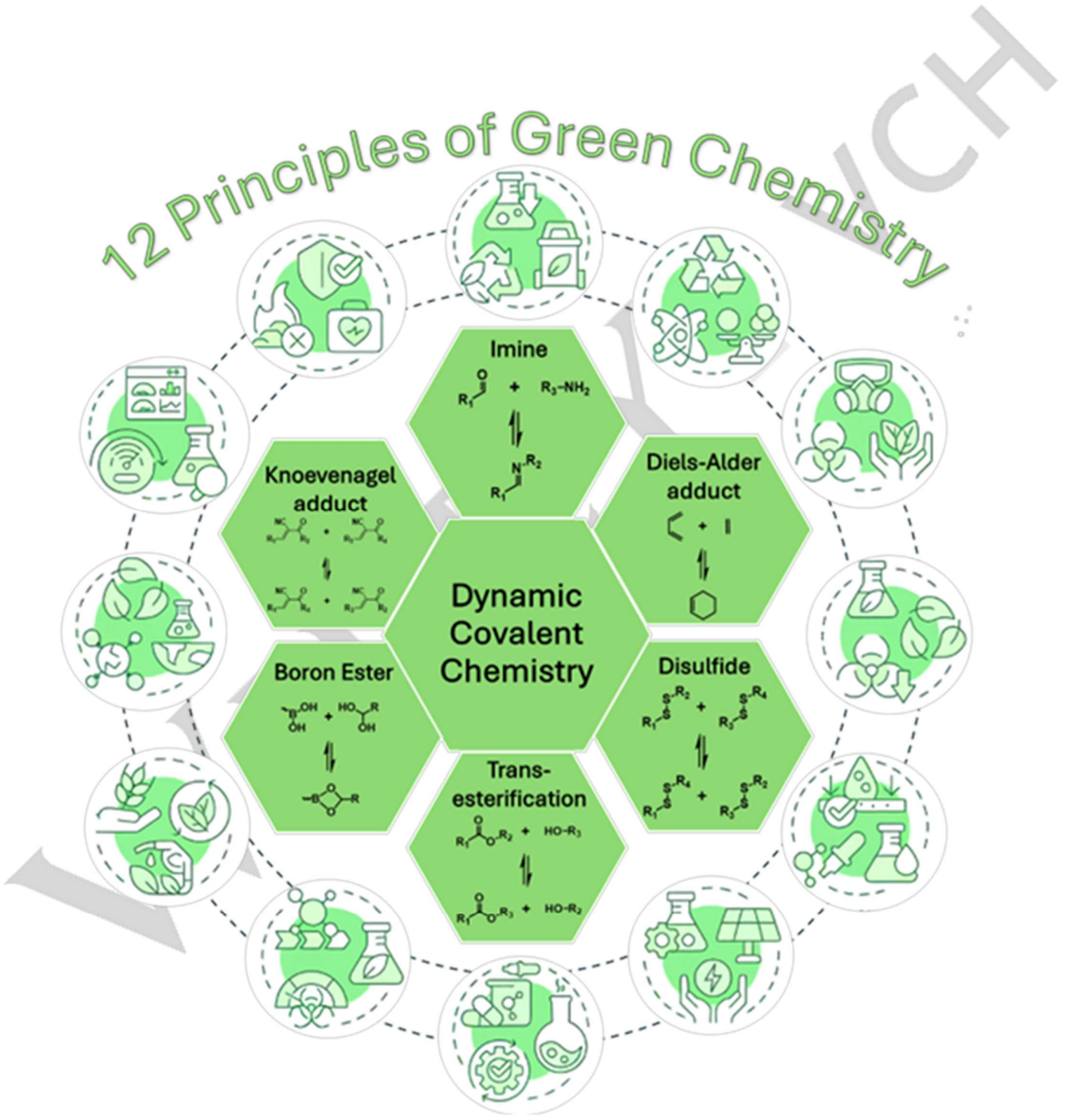

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Abstract: Dynamic covalent chemistry (DCC) has emerged as an important framework for designing sustainable polymeric materials, offering an accessible route to recyclability, self-healing, and environmental compatibility. By integrating dynamic covalent bonds (DCBs) such as imine, disulfide, Diels-Alder linkages and more, DCC-based networks enable efficient reprocessing, extend material lifespan, and facilitate closed-loop recycling. Recent advances have demonstrated improved mechanical strength retention, enhanced healing efficiency, and the incorporation of bio-derived monomers to reduce reliance on petrochemical feedstocks. These developments align not only with the traditional twelve principles of green chemistry but also with their updated 2020 interpretation, which emphasizes circularity, systems thinking, and lifecycle analysis. As DCC matures, optimizing bond exchange kinetics, network architectures, and integration of renewable resources will be key to enabling scalable, high-performance, and circular polymer technologies.

1. Introduction

The development of sustainable polymers is closely related to the evolution of synthetic polymers and the rising global emphasis on sustainability. Early innovations, such as Bakelite and nylon, revolutionized industries, yet little attention was given to their long-term environmental impact. By the mid-20th century, mass production of plastics unveiled significant environmental challenges, prompting the emergence of recycling initiatives in the 1970s. However, these early recycling efforts faced major obstacles, including contamination, polymer degradation, and the economic inefficiencies of closed-loop systems.[1] The 21st century introduced a paradigm shift, with a growing focus on the circular economy, where materials are continuously reused through chemical recycling and the development of bio-based and degradable polymers.[2] Among the many strategies developed to address the challenges of polymer sustainability, dynamic covalent chemistry (DCC) has emerged as an innovative approach. DCC relies on reversible covalent bonds also known as dynamic covalent bonds (DCBs), which allow polymers to self-heal, adapt to stress, and undergo efficient chemical recycling.[3] Examples of these DCBs include imine, disulfide, Diels-Alder, boronic ester, and transesterification bonds, all of which enable reversible crosslinking in polymer networks. Unlike conventional thermosets, which become permanently crosslinked and difficult to recycle, DCC-based polymers can be reprocessed and reshaped without significant loss of material properties.[4] This property is particularly advantageous in the context of green chemistry, which advocates for waste prevention.
The development of sustainable polymers then requires a simple guiding framework to minimise environmental impact. The 12 principles of green chemistry, formulated by Paul Anastas and John Warner, provide a simple set of guiding principles for evaluating polymer design, synthesis, and recyclability.[5] These principles emphasize waste reduction, atom economy, degradability, and the replacement of hazardous chemicals, all of which align with the core functionalities of DCC-based materials. This review critically examines recent advances in DCC-based materials and its alignment with the principles of green chemistry, demonstrating how molecular-level design choices impact polymer sustainability.

2. Principles of Green Chemistry

2.1. Introduction to the Principles of Green Chemistry

The 12 principles of green chemistry (**Figure 1**), developed by Paul Anastas and John Warner, have long served as a foundational guide for designing chemical products and processes that minimize environmental impact and enhance sustainability.[5] Since their introduction, the framework has evolved to reflect more holistic and forward-looking metrics. In particular, the 2020 perspective by Zimmerman et al. emphasizes the integration of circularity, systems thinking, and life-cycle analysis into the definition of performance, shifting the focus beyond mere functional efficacy toward sustainability at every stage;from molecular design to end-of-life.[6] Dynamic covalent chemistry (DCC), with its reversible covalent bonds and stimuli-responsiveness, aligns strongly with these updated principles, particularly in polymers and materials, due to its strong alignment with the goals of green chemistry.[7, 8] Although not every principle is exemplified in the realm of polymeric materials, significant advances have been made in several principles in the design of polymers, the synthesis process and its end-of-life (EOL) processing. In this section, the recent advancements of the principles of green chemistry in materials using DCC are summarized.

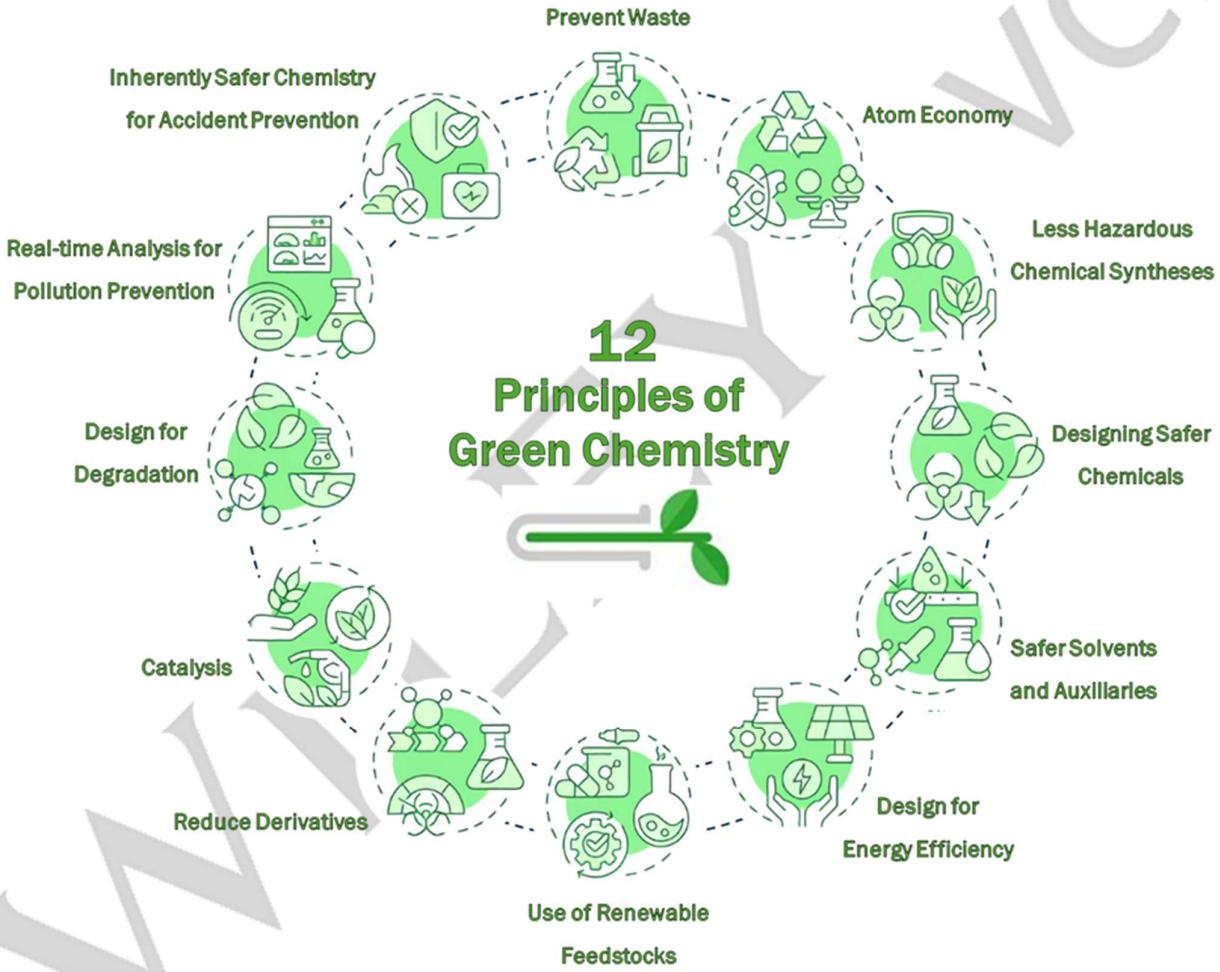


Figure 1. Illustration of the 12 principles of green chemistry.

2.2. Preventing waste

One of the most widely applied principle of green chemistry in materials using DCC is the prevention of waste, which seeks to eliminate waste generation at the source rather than addressing it post-production. The integration of DCC into thermosetting polymeric materials has enabled significant advancements in preventing waste, including self-healing, reprocessing, and recycling, thereby extending their lifespan and reducing environmental impact and since these capabilities are inherently enabled by different dynamic systems, it will be discussed in another section below. One other strategy to prevent waste is the upcycling of existing commodity plastics, converting waste into higher-value materials with improved properties (**Figure 2**). This method is particularly urgent for polyolefins and

thermosetting plastics, which dominate global plastic waste due to their inherent chemical stability and resistance to degradation. In addition, by modifying these materials to include DCC, they can be repurposed into more sustainable and recyclable forms, which has garnered significant interest in recent years.

One such example is the work of Liu et al., who utilized a photooxidation strategy to introduce ketone functionalities into polyolefins by addition of nitroarenes under irradiation, a process that does not require catalysts, metals, or expensive oxidants.[9] This transformation to ketone-functionalized polymers enables the formation of dynamic imine networks upon addition of diamines, with the material exhibiting enhanced adhesion and miscibility in mixed plastic systems, making them more compatible for reprocessing and reuse. By applying a light-driven oxidation mechanism, this approach presents a low-energy, metal-free strategy for polyolefin upcycling, significantly improving the sustainability and circularity of these widely used plastics. Further expanding on polyolefin upcycling, Neidhart et al. developed a method for C–H functionalization of polyethylene-based polymers, enabling the introduction of diketoenamine crosslinks into branched polyolefins and postconsumer polyethylene.[10] The dynamic diketoenamines crosslinks is capable of undergoing associative bond exchange, meaning that the resulting polymer networks exhibit high reprocessability and enhanced mechanical properties., along with reduced creep deformation, a 4.5-fold increase in toughness, and enhanced high-temperature stability,. The ability to convert polyolefin waste into a thermoset alternative with superior mechanical strength and thermal stability showcases the potential of DCC in redefining waste plastic utilization, creating a new generation of recyclable polymeric materials.

The success of DCC in polyolefin upcycling has also been extended to thermosets and elastomers, which have traditionally been challenging to recycle due to their permanent crosslinking. Ma et al. developed a method to chemically transform polyureas, a class of highly stable thermosets, into vinylogous amides using acetylacetone, which can then react with isocyanates to form poly(aminoketoenamide) networks.[11] These materials display self-healing properties and can be reprocessed under heat, effectively upcycling polyurea waste into reprocessable materials. In another breakthrough, Yu et al. introduced dynamic sulfide-based skeletal networks into thermoplastic vulcanizates.[12] By rationally designing interfacial crosslinking within rubber granules, a highly reprocessable skeletal network elastomer was created, allowing continuous reprocessing without loss of resilience or mechanical integrity, providing an enhancement to traditional thermoplastic vulcanizates that degrade upon recycling. These thermoset and elastomer upcycling strategies tackle one of the biggest limitations in polymer sustainability by introducing reversible covalent interactions that allow for bond exchange and material reconfiguration, preventing plastic accumulation while keeping high-performance materials in circulation.

Further advancements in dynamic covalent networks (DCNs) have also led to sustainable EOL solutions for fiber-reinforced composites, which are among the most difficult materials to recycle due to their multi-component nature and crosslinked structures. Wang et al. developed polyacylsemicarbazide networks reinforced with carbon fibers, utilizing acylsemicarbazide bonds, which facilitated self-healing and reprocessing.[13] A key method described in this study is the introduction of epoxy moieties and amine curing agents to the degraded polymer matrix, followed by thermal treatment, forming a new epoxy resin network with robust mechanical properties, which reduce waste generation. By leveraging DCBs, these high-performance composite materials can be continuously reprocessed and repurposed without sacrificing mechanical integrity, ensuring longer material lifetimes and reduced environmental impact.

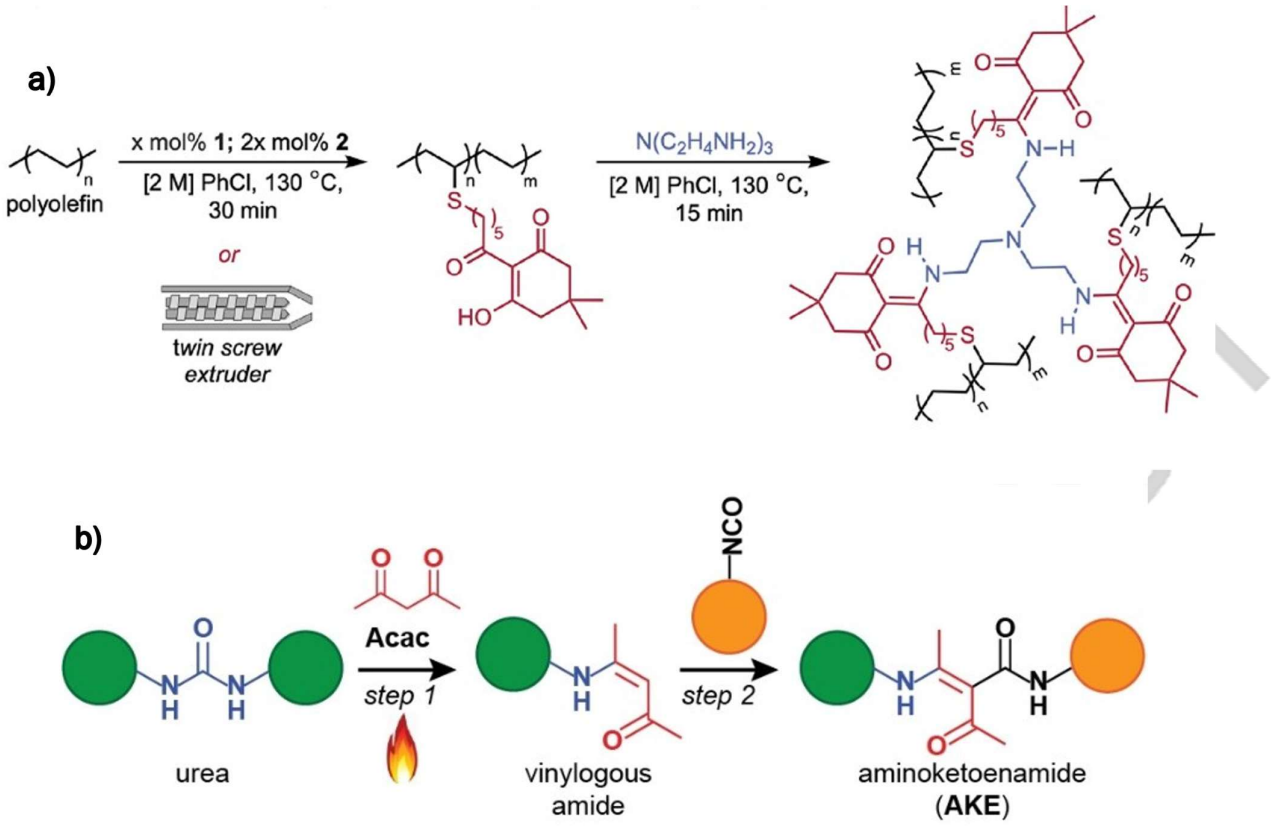


Figure 2. Representative work in preventing waste by upcycling commodity plastic. (a) C–H functionalization of commodity polyolefins yields diketoenamine dynamic covalent polyolefin networks. Reproduced with permission from [10]. Copyright 2024 American Chemical Society. (b) Illustration of the conversion of conventional urea bonds into vinylogous amides by reaction with acetylacetone (Acac; *step 1*), followed by the subsequent transformation of the vinylogous amides into aminoketoenamide (AKE) derivatives upon reaction with isocyanates (*step 2*). Reproduced with permission from [11]. Copyright 2024 Wiley-VCH.

2.3. Design for degradation

Another key component of achieving sustainability in polymer science is degradability, which ensures that materials do not persist indefinitely as waste but rather break down into environmentally benign components. Recent studies have incorporated various degradation mechanisms into DCC materials to serve as EOL solutions, including biodegradation by bacteria[14, 15], solvolysis or chemical degradation into safe byproducts[16, 17], Additionally, with the introduction of DCC into materials, depolymerization for material recycling becomes readily accessible as well (Error! Reference source not found.).[18-20] Understanding these mechanisms would lead to the further development of high-performance, sustainable, and circular materials.

Biodegradation allows polymeric materials to break down naturally in soil or biological environments, reducing long-term environmental impact. Zhou et al. developed a Konjac Glucomannan-based vitrimer, a water-mediated biopolymer that undergoes gradual soil biodegradation over 140 days.[14] The vitrimer exhibited clear structural deterioration, including visible fractures and breakdown in soil conditions, whereas polyethylene (PE) and polylactic acid (PLA) remained intact. The degradation mechanism is attributed to hydrolysis of Schiff base bonds, which weakens the polymer matrix, allowing microbial activity to further degrade the material. This work demonstrates a viable biodegradable alternative to petroleum-based plastics, providing a green solution for single-use applications. However, biodegradation is often slow, limiting its industrial applicability. Subramaniyan et al. addressed this issue by designing biorenewable Schiff base polyester-imines, which introduce a dual degradation pathway. These materials can be enzymatically hydrolyzed by PETase, an enzyme that selectively cleaves ester and imine bonds, facilitating a more controlled degradation process.[15] Additionally, these polymers can be chemically depolymerized under mild acidic conditions, enabling faster material breakdown when needed. This flexible degradation strategy makes Schiff base polyester-imines a versatile option for applications requiring both controlled recyclability and eventual biodegradability.

Beyond microbial and enzymatic biodegradation, some polymers are designed to break down through chemical triggers, allowing safe material disposal without persistent microplastic formation. Xie et al. developed a PDMS-based elastomer with phase-locked benzimidazole urea bonds, enabling solvolytic degradation at room

temperature.[17] Unlike traditional thermosets that require high temperatures or harsh chemical conditions to break down, this material can be dissolved in appropriate solvents, allowing the separation of conductive nanosilver from the polymer matrix. Although the polymer fragments cannot be reprocessed into a new material, this method is beneficial for wearable electronics, where separation of electronic components from polymeric substrates is critical for e-waste reduction. Another promising degradation strategy is photo-triggered decomposition, where exposure to light induces selective bond cleavage, enabling controlled material breakdown. Hai et al. developed a material incorporating light-sensitive C–N, C–O, and C–S bonds, which undergo cleavage upon UV irradiation, breaking the polymer into small, stable molecules such as amines, thiols, and alcohols.[21] Unlike uncontrolled degradation, this method enables external control over when and where the material decomposes, making it applicable for self-erasing coatings or transient electronics. These methods, while not recyclable, ensure that polymeric materials do not persist indefinitely in landfills or the environment, minimizing their ecological footprint.

Depolymerization presents the most efficient approach for achieving circular material reuse, as it allows polymeric materials to be broken down into reusable fragments that can be repolymerized into new materials and the incorporation of DCC actively facilitates the feasibility of depolymerization. Zhang et al. developed a poly(selenoacetal) covalent adaptable network (CAN) that undergoes alkaline hydrolysis, breaking down into reactive enone selenides and diselenides.[20] These degradation products retain their reactivity, allowing them to be repolymerized into new materials. Unlike full monomer recovery, this system produces oligomeric intermediates, although with some differences from the original material, the mechanical properties were still largely retained. Similarly, Lei et al. designed triazine-based polyurethane (PU) networks, incorporating DCBs that allow for depolymerization into oligomeric precursors.[18] Under mild base and alcohol conditions, the polymer breaks down into reactive fragments, which can be reprocessed into a new polymer network without needing virgin feedstock. These works demonstrated how chemical recycling can be achieved without requiring harsh acidic or oxidative conditions, making recycling more sustainable and scalable. Another effective approach was demonstrated by Guo et al., who designed a Diels–Alder-based thermoset elastomer that enables heat-triggered depolymerization, allowing it to be fully reprocessed multiple times. Doing so allowed this material to retain high mechanical performance (toughness of 10.1 MJ/m³) across multiple recycling cycles.[19] This strategy is essential for achieving sustainable wearable electronics and flexible devices, where material reusability is critical for reducing electronic waste. Together, these studies showcase how DCBs can be leveraged for circular polymer design, ensuring that materials are reprocessable and reusable while minimizing reliance on virgin fossil-based resources.

2.4. Atom economy

An important guideline for green chemistry is to maximize atom economy, which ensures that most reactant atoms are incorporated into the final product, minimizing waste. A key strategy in achieving high atom economy in DCC involves the selection of naturally abundant reactants that undergo near-quantitative incorporation into the final polymeric material. Recent advancements have focused on utilizing abundant raw materials such as elemental sulfur[22], carbon dioxide[23], and carbon disulfide[24], while leveraging DCBs to enhance recyclability and material performance.

For instance, Yang et al. employed elemental sulfur as both a reactant and solvent in the inverse vulcanization process.[22] Leveraging its ability to undergo ring-opening polymerization with mono- and di-olefins, resulting in a sulfur-rich polymer with excellent elasticity, plasticity, and a self-healing capability at temperatures as low as 30 °C due to the dynamic S–S bonds. Similarly, Zhao et al. utilized carbon disulfide (CS_2), an underutilized one-carbon feedstock, in a catalyst-free multicomponent polymerization with diamines and diacrylates.[24] The polydithiourethanes achieved up to 98% yield, while also possessing superior reprocessability via aminolysis, allowing these materials to be reshaped or recycled with minimal environmental impact. Meanwhile, Pronoitis et al. designed an isocyanate-free polyurethane system, where CO_2-derived cyclic carbonates reacted with amines in an atom-economical step-growth polymerization achieving near-total conversion with minimal waste.[23] Interesting to note is that by using the chemical feedstock as is in the synthesis process, the authors also adhered to the principle of reducing unnecessary derivatives, which aims to reduce the waste generated due to functionalization of chemicals.

In a different direction, Derr et al. demonstrated high atom economy in their material by employing thiocracking to process post-consumer multi-material waste.[25] With the waste primarily comprising of polyethylene terephthalate (PET), paper, and triglycerides, which was upcycled into a high-strength sulfur composite with complete incorporation of reactants, zero waste generation, and a negative global warming potential. These methodologies exemplify the principles of atom economy by ensuring nearly all feedstock atoms are retained in the final polymeric structures, thereby reducing waste, eliminating hazardous by-products, and enhancing the sustainability of the materials.

2.5. Use of renewable resources

Conventional polymers, derived from petroleum-based feedstocks, contribute significantly to greenhouse gas emissions, plastic waste accumulation, and resource depletion.[26] In response, researchers are turning to alternative monomers sourced from renewable sources for sustainable polymer production. One such candidate is the biomass-derived feedstocks, such as lignin, and furan-based compounds which are closely linked with certain DCBs and hence will be discussed in greater detail in the next section.[27] On the other hand, carbon dioxide (CO_2) stands out as a valuable chemical feedstock, not only due to its abundance and cost-effectiveness but also because its direct utilization in polymerization can mitigate the increasing levels of atmospheric CO_2 (**Figure 3**).

One such advancement is the catalyst-free click polymerization of CO_2 and frustrated Lewis pair (FLP) monomers, reported by Liu et al., which enables the synthesis of CO_2/FLP alternating copolymers with high molecular weights and near-quantitative conversion under mild conditions (20°C, 1 atm CO_2), fulfilling several other principles as well.[26] This polymerization method overcomes the limitations of conventional CO_2-based polymerizations, which typically require metal catalysts, elevated temperatures, or high pressures, making it an energy-efficient alternative. In addition, the resulting material also allows for reversible CO_2 fixation and release, serving as a possible candidate for closed-loop carbon capture and utilization. Meanwhile, Wu et al. demonstrated how CO_2 could be utilized in the synthesis of a self-healing poly(urea-imine) thermoset, incorporating dynamic imine bonds and hydrogen bonding, leading to high mechanical properties (tensile stress 10.2 MPa, Young's modulus 79 MPa), self-healing efficiency over 92% at 80°C, and complete recyclability via acid degradation.[28] By using CO_2 as a key structural component, these studies showcase how polymer materials can be designed to be both high-performing and inherently sustainable. Expanding on the versatility of CO_2-based polymers together with other bioderived chemicals, Jang et al. introduced crosslinked polyurethane networks synthesized from CO_2-derived bis(cyclic carbonate)s and biomass-based tetraols, utilizing a solvent-free mechanochemical ball-milling process.[29] The resulting material exhibits high thermal conductivity (51.1 W/m·K), excellent malleability through transcarbamoylation reactions, and low interfacial thermal resistance, applicable for thermal interface applications in electronics. Miao et al. further explored CO_2 as a monomer by incorporating CO_2-derived cyclic carbonates into bio-based non-isocyanate polyurethanes (NIPUs), featuring spiro bi-acetal linkages and Zn(II)-carboxylate coordination.[27] These materials demonstrated high self-healing efficiency, closed-loop recyclability, and high phase change capabilities (latent heat of 128.2 J/g), which is desirable for energy storage applications. Similarly, Yang et al. developed recyclable NIPUs from CO_2 and epoxidized soybean oil, leveraging hydroxyl-carbamate dynamic bond exchange to achieve shape memory effects and outstanding reprocessing efficiency (~85%).[30] Collectively, these studies demonstrate how CO_2 and other bioderived chemicals can serve as an integral component in the development of recyclable, self-healing, and high-performance polymers, fundamentally reshaping how materials are designed for sustainability and functionality.

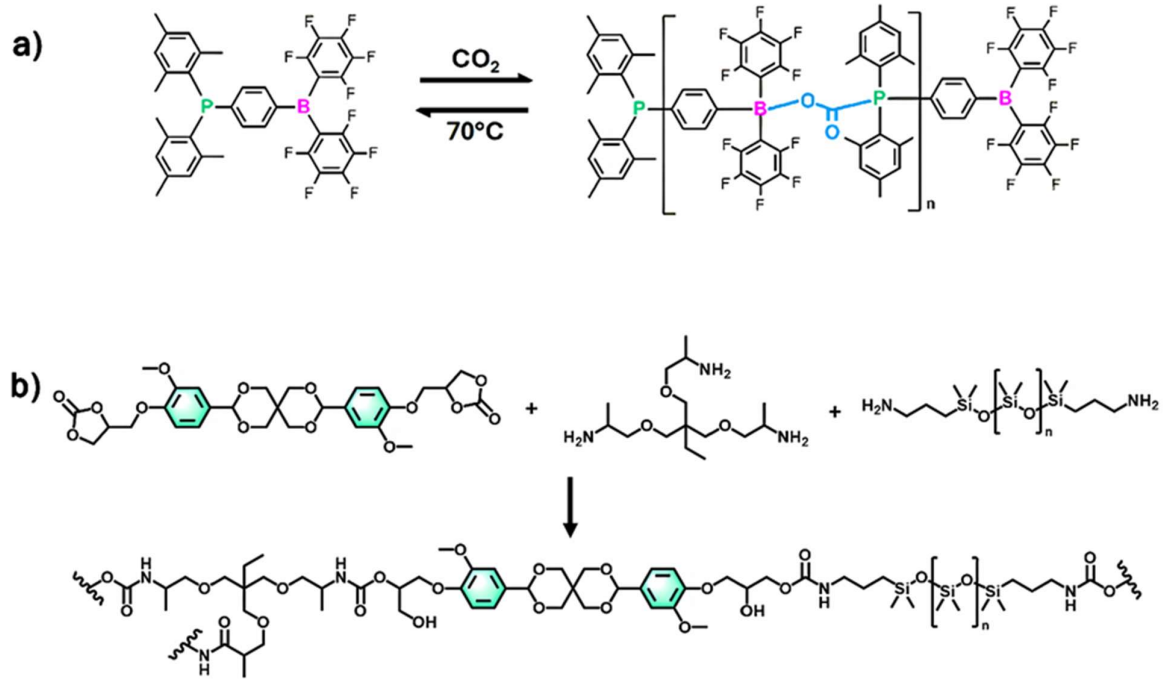


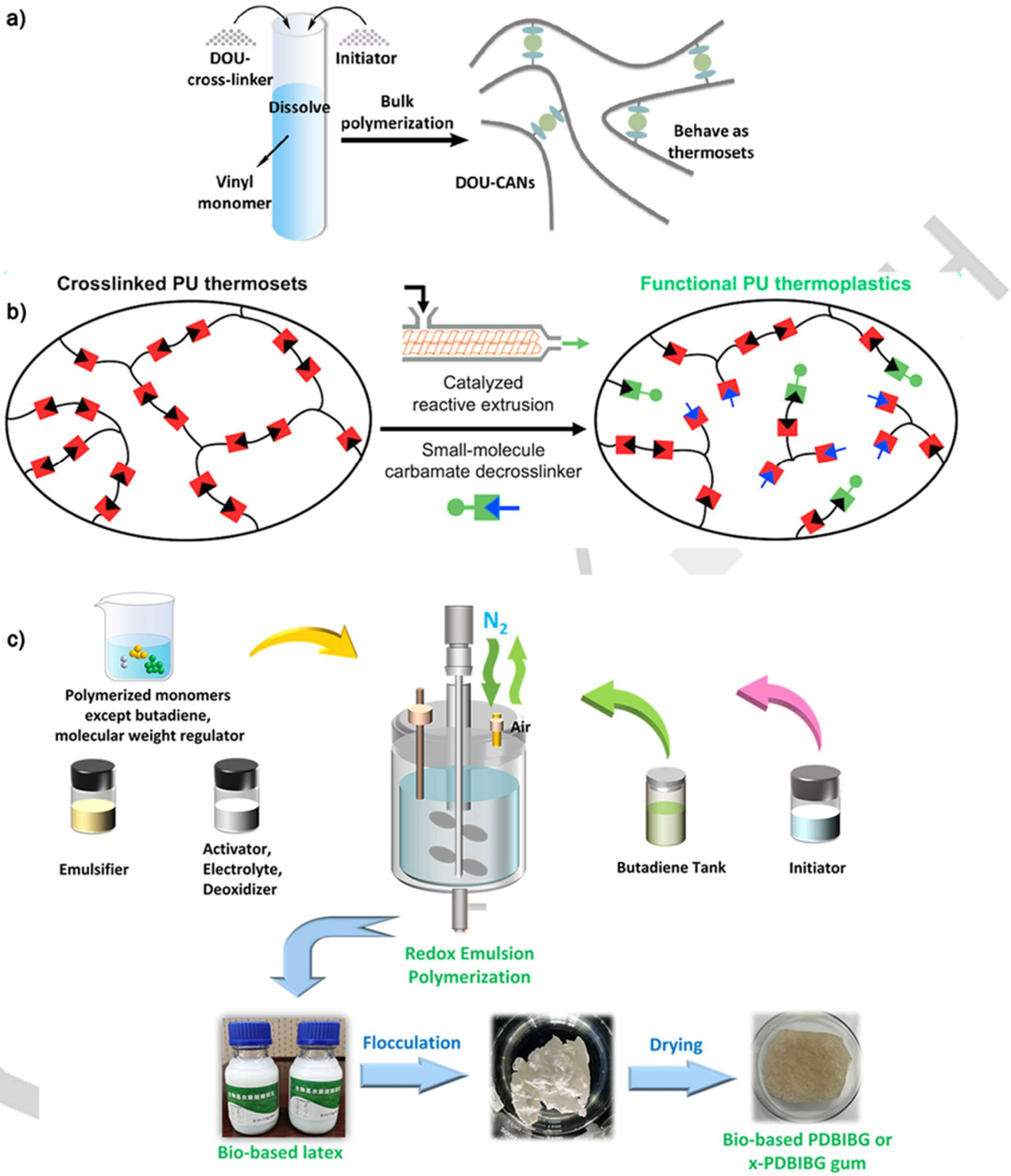
Figure 3. Representative work of CO_2 based DCC materials. (a) Designed FLP-based monomer and its spontaneous, catalyst-free polymerization with CO_2 in ambient conditions to form CO_2/FLP alternating copolymer with reversible thermally degradable property. Reproduced with permission from [26]. Copyright 2019 American Chemical Society. (b) Synthesis of vanillin-based poly(β-hydroxyurethane)s. Reproduced with permission from [27]. Copyright 2023 Elsevier.

2.6. Less hazardous chemical synthesis

The use of safer alternative chemical reagents is essential to reduce environmental pollution and minimize health hazards associated with toxic compounds, in creating safer and efficient materials. A key advancement is the replacement of isocyanates, which are traditionally used in polyurethane synthesis. The toxic and environmentally persistent nature of isocyanates has driven the search for safer and more sustainable alternatives.[31]
One such example is the non-isocyanate polythiourethane (NIPTU) network developed by Chen et al., which utilizes glycerol-derived cyclic thiocarbonates and amines to form a dynamic polythiourethane material.[31] This method not only eliminates isocyanate toxicity but also enables chemical recycling, including high-yield (94 mol%) recovery of valuable small molecules and full reprocessability with crosslink density retention. The study demonstrated that thionourethane and disulfide-based DCNs positively contributed to the material's robustness and recyclability, making it an alternative to conventional polyurethane systems. Similarly, Lyu et al. developed a non-isocyanate CAN using hindered urea bonds, demonstrating a route to achieving polymer sustainability through sequential polymerization and chemical recycling.[32] Their method employs thiazolidin-2-one and a hindered amine in a ring-opening reaction, followed by thiol–Michael and thiol–epoxy click reactions, avoiding the need for toxic isocyanate precursors. This synthesis strategy not only enhances process efficiency and reaction selectivity but also improves polymer recyclability, allowing for catalyst- and solvent-controlled depolymerization under mild conditions. The resulting CANs exhibit excellent thermal stability, mechanical robustness, and reprocessability, reinforcing the potential of dynamic hindered urea networks in next-generation recyclable materials. By replacing isocyanates with safer, biocompatible alternatives, both studies exemplify how green chemistry principles can drive advancements in polymer sustainability. These innovations align with the circular economy model, where materials are designed for reuse, chemical recovery, and reduced environmental impact, ensuring that polymer performance and ecological responsibility go hand in hand.

2.7. Safer solvents and auxillaries

Replacement or omission of volatile organic solvents (VOC) is an important strategy for developing sustainable polymeric materials, minimizing the reliance on hazardous organic solvents while retaining high efficiency in network formation. While solvent-free polymerization offers significant environmental advantages, certain dynamic systems such as imine-based reactions may still face practical limitations. In bulk or dry-state conditions, efficient bond exchange can require elevated temperatures or extended times due to restricted molecular mobility.[33] Researchers have explored various solvent-free methodologies, including bulk polymerization[34, 35], melt polymerization[33], mechanical processing[36], and water-based systems[37], to develop dynamic covalent materials with enhanced recyclability and mechanical stability (**Figure 4**).
A simple and most widely utilized method is bulk which utilizes one or more monomer in its liquid state as a solvent to avoid the use of VOCs. As an example, Zhang et al. developed a solvent-free strategy using commodity vinyl monomers that are in liquid form for synthesis.[38] The authors incorporated a dimethylglyoxime-urethane (DOU) crosslinker directly into vinyl monomers such as methyl methacrylate and methyl acrylate. This one-step reaction produced a crosslinked yet reprocessable polymer network with enhanced thermal stability. A similar bulk polymerization approach was taken by Wang et al., who synthesized castor oil-derived polyurethane-urea networks via a catalyst-free polymerization of castor oil, piperazine derivatives, and isocyanates.[39] This bulk polymerization strategy led to a malleable, recyclable thermoset with tunable mechanical properties, reinforcing the viability of solvent-free processing for robust polymeric networks.
Aside from bulk polymerization, polymerization by mechanical processing has also been employed as a powerful solvent-free method for the production of polymers. Nettles et al. demonstrated that polyurethane thermosets could be upcycled via small-molecule carbamate-assisted decrosslinking extrusion.[36] Transforming irreversibly crosslinked materials into processable thermoplastics through continuous reactive processing during the extrusion process. On the other hand, techniques involving alternative solvents have also been explored. Ji et al. synthesized biobased itaconate elastomers for sustainable tire applications through an emulsion polymerization process that avoided organic solvents entirely.[37] By utilizing water as the dispersion medium, the authors were able to generate high-molecular-weight elastomers with optimized mechanical properties. These studies highlight how the replacement of VOCs serves as an important method to reduce large amounts of organic solvent waste, achieving a sustainable and resulting a lower carbon emission.



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3. Dynamic Covalent Chemistry

3.1. Introduction to Dynamic Covalent Chemistry

Dynamic covalent chemistry (DCC) represents a powerful strategy for aligning polymer design and synthesis with green chemistry principles by incorporating reversible covalent bonds. DCC enables polymer networks to undergo reversible polymerization or network reconfiguration in response to stimuli, imparting self-healing, reprocessing, and chemical recyclability while adhering to principles like waste prevention and design for degradation. Notably, early work by Chen et al. showed a thermally "remendable" crosslinked polymer based on reversible Diels-Alder bonds, effectively achieving self-healing and repeatable recycling of a thermoset.[40] Around the same time, Rowan and coworkers formalized the concept of DCC polymers, highlighting how dynamic linkages like imines, disulfides, and Diels-Alder adducts could impart recyclability and self-repair.[41] In the 2010s, the advent of covalent adaptable networks (CANs) solidified the framework for sustainable thermosets: Leibler's group introduced vitrimers, organic networks that flow at high temperature via bond exchange without losing crosslink density.[42] This vitrimer concept, first demonstrated with transesterification networks, proved that permanently crosslinked polymers could be reprocessed like thermoplastics under heat, aligning with green chemistry by enabling reuse and repair of materials .[42, 43] Bowman and Kloxin further reviewed CANs as "smart, reconfigurable networks", underscoring their responsiveness and potential for closed-loop material life cycles.[44] Building on these foundations, recent advances have rapidly expanded DCC polymers (**Table 1)**, with dynamic chemistries tailored either for Closed-loop Recycling: where polymer networks can dissociate to yield original monomers or oligomers (facilitating chemical recycling), or for Reconfigurable Networks: where bond exchange allows remodeling, self-healing, and reprocessing without full depolymerization or decrosslinking. Below, we discuss prominent DCC systems under these two themes, detailing how each dynamic bond type contributes to sustainable polymer innovation.

Table 1. Summary of DCC bond systems

Dynamic Bond Type	Bond Exchange Mechanism	Reprocessing Conditions	Feature	Reference
Imine (Schiff base)	Hydrolysis, transamination	Water, acid, mild heat	Closed-loop recycling, self-healing	[44, 53-61]
Diels–Alder adduct	Retro-DA (cycloreversion)	Heat (~100–150 °C)	Thermal reprocessing, monomer recovery	[63-68]
Knoevenagel adduct	C=C metathesis	Ambient or mild heat	Chemical recyclability, no metal catalyst	[69-75]
Disulfide (S–S)	S–S metathesis	Heat, light, base	Self-healing, full depolymerization possible	[77, 79-89]
Transesterification	Ester–alcohol exchange	Heat (with or without catalyst)	Thermal reprocessability (vitrimer behavior)	[90-98]
Boron Ester	Boronic acid–diol exchange	pH, water, room temp	Self-healing, ambient recyclability	[99-105]

3.2. Closed-loop Recycling

Closed-loop recycling involves the use of dynamic covalent bonds that can dissociate and reform, enabling polymer networks to dissociate into its corresponding components under certain conditions.[45] This behavior allows closed-loop recycling, where recovered components can be crosslinked again, directly addressing green chemistry goals of waste prevention and design for degradability. Key examples of such bonds include imine linkages that hydrolyze to amines and carbonyls, Diels-Alder cycloadducts that undergo retro-cycloaddition to original dienes and dienophiles, and novel C=C bond metathesis systems (e.g. via Knoevenagel adducts) that enable recovery of its building blocks. These dynamic bonds can follow a dissociative mechanism, breaking into reactive end-groups upon stimulation (heat, solvent, or catalyst) and thus allowing polymer depolymerization. By integrating DCC bonds with dissociative mechanisms, polymer chemists have achieved thermosets and networks that can be chemically recycled; a dramatic improvement over traditional thermosets which could only be landfilled or downcycled.[46] In addition, many of these reversible systems function under mild conditions or without added catalysts, enhancing their environmental compatibility. In the following subsections, we highlight three major reversible DCC systems, imine bonds, Diels-Alder chemistry, and Knoevenagel-adduct-mediated networks, and discuss how each enables recovery of the material building blocks and sustainable material lifecycles.

3.2.1. Imine bonds

Imine bonds, formed by the condensation of primary amines with aldehydes or ketones, are characterized by their dynamic and reversible nature, which is ideal for use in DCC materials. The dynamic mechanism of imine bonds occurs in three ways (
Figure 5) where imine bonds can hydrolyse in the presence of water or acidic condition, and it can also dynamically exchange via transamination and imine metathesis in the presence of primary amines, allowing polymers crosslinked by imines to be recycled under appropriate conditions.[47] This reversibility along with the mild reaction conditions required for imine formation—often proceeding at room temperature without catalysts,makes imine chemistry particularly attractive for sustainable polymer design.[48-50] Notably, imine bonds can be synthesized in water, eliminating the need for hazardous organic solvents, reducing energy consumption, and enhancing process safety. [51, 52] Given these advantages, imine-containing polymers are increasingly being explored for applications in recyclable thermosets, self-healing materials, shape-memory polymers, and reprocessable elastomers, adhering well with the principles of green chemistry (**Figure 6**).

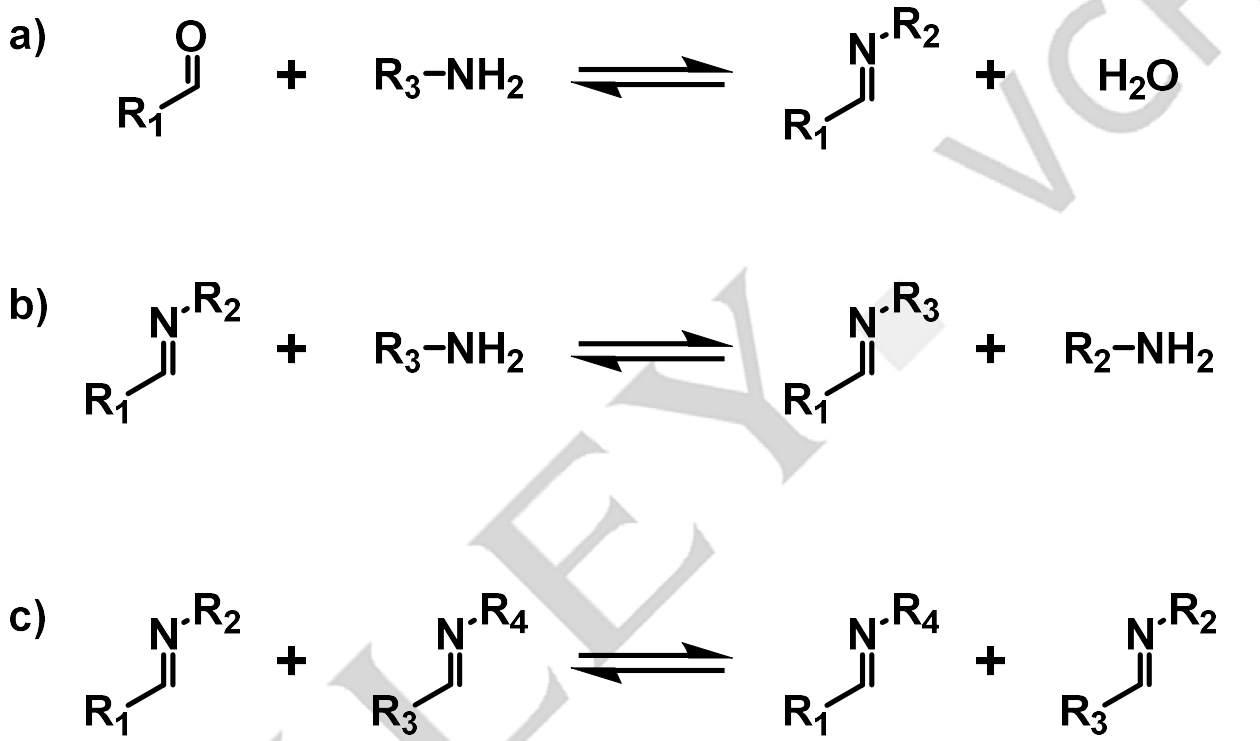

Figure 5. Dynamic imine bond formation (a) formation of imine bond between aldehyde and amines, (b) transamination of imine bond, (c) imine metathesis between two imines.

Early demonstrations of imine-based CANs by Taynton et al. showed that catalyst-free polyimine thermosets could be completely reprocessed and recycled.[44] The developed malleable polyimine network from terephthalaldehyde and triamines was repeatedly remoldable and, in the presence of water, could be chemically broken down to recover monomeric precursors. Such polyimine vitrimers exhibited excellent tensile strength and elongation while allowing closed-loop recycling of thermoset composites, as later reported in carbon fiber composites that used dynamic imine networks as binders. Zhang et al. developed a closed-loop recyclable and totally renewable azobenzene-based liquid crystal network (DCv-LCN) using imine chemistry.[53] This material allowed for room-temperature programmability and polymer-to-monomer chemical recyclability, preserving actuation performance after multiple recycling cycles. Daglar et al. developed an imine-containing secondary amine hardener that allowed for both chemical and solvent-based recycling.[54] Their epoxy system exhibited hydrolytic stability under high-temperature aqueous conditions while allowing for the selective recovery of monomers under acidic conditions. Liu et al. further contributed to recyclable epoxy thermosets by developing self-healing, reprocessable, and degradable polymers containing dynamic imine bonds.[55] These materials could be entirely degraded under weak acid conditions, enabling non-destructive recycling of carbon fiber composites.
Imine chemistry also aligns with green principles through use of bio-based carbonyl compounds or macromolecules to replace petrochemical feedstocks. For instance, Zhang et al. developed a fully bio-based starch plastic utilizing a CAN constructed via Schiff base reactions.[56] Incorporation of dynamic imine networks significantly improved the flexibility of the starch-based material while maintaining good thermal stability and chemical degradability into starch

and its crosslinker. Similarly, Su et al. introduced a cellulose-based polyimine vitrimer as a robust, waterproof, and degradable alternative to petroleum-based plastics.[57] By leveraging dynamic imine chemistry, they enabled excellent thermo-processability and recycling capabilities in cellulose-based materials, offering an eco-friendly replacement for traditional plastics.

Furthering the development of bio-based plastics, Zhang et al. synthesized a starch-based bioplastic crosslinked with dynamic imine chemistry.[58] This material exhibited excellent thermal malleability, mechanical strength (40.6 MPa), and self-healing capabilities while eliminating the need for plasticizers, thereby enhancing its environmental sustainability. Similarly, Fanjul-Mosteirín et al. developed polyimine-based CANs using methoxy and allyloxy-substituted divanillin, yielding materials with high tensile strengths and tunable glass transition temperature.[59] These materials were successfully reprocessed up to three times without degradation and exhibited efficient chemical recycling under acidic conditions, making them strong candidates for replacing fossil-based thermosets. Liu et al. introduced a fully bio-based and mechanically robust elastomeric vitrimer derived from epoxidized natural rubber and dynamic imine bonds.[60] With a tensile strength of 19.44 MPa and elongation at break exceeding 880%, the elastomer demonstrated rapid stress relaxation at elevated temperatures, enabling excellent reprocessability and thermal recyclability. Xu et al. addressed the sustainability of polyurethanes by synthesizing a fully biomass-derived polyurethane based on dynamic imine bonds.[61] The betulin-based polyurethane exhibited self-healing, shape-memory, and rapid degradability, with a tensile strength of 9.5 MPa and degradation occurring within four hours at 50°C in acidic conditions.

These examples underscore the versatility of imine DCC: not only do imine-crosslinked networks show excellent reprocessability and self-healing, they can also be chemically recycled by breaking C=N bonds, a clear embodiment of circular material lifecycles. By replacing permanent crosslinks with imine bonds, researchers have created thermosetting and resin materials that maintain high performance yet can be fully dissolved and recycled when triggered. Such dynamic imine networks adhere to green chemistry by preventing waste and enabling monomer reuse, expanding the scope of closed-loop recycling for sustainable polymers.

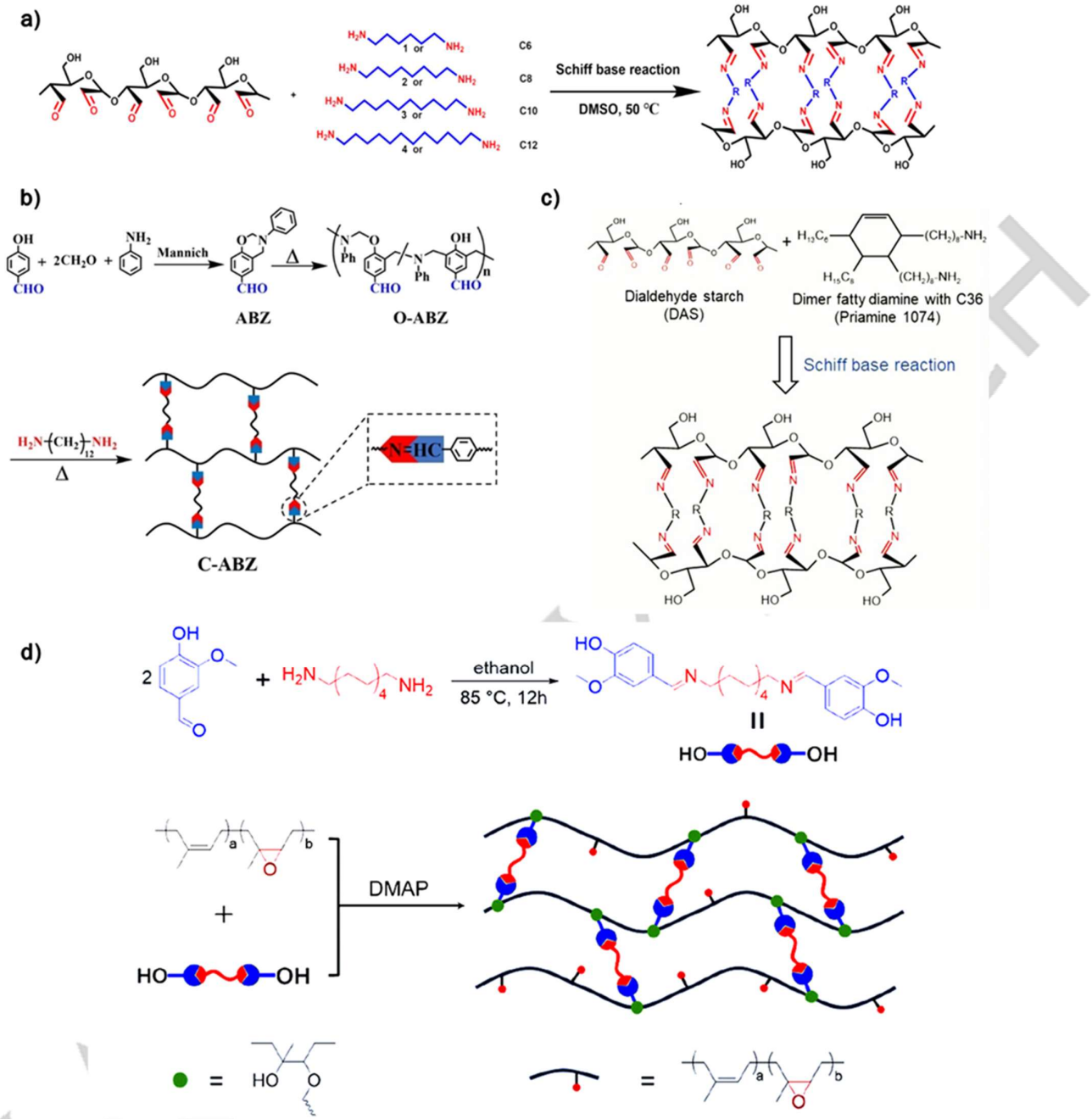

Figure 6. Representative works of imine-based materials. (a) Synthesis routes and chemical structure characterization of dialdehyde starch polyimine. Reproduced with permission from [58]. Copyright 2022 American Chemical Society. (b) Synthetic route to dynamic imine-crosslinked polybenzoxazine vitrimer. Reproduced with permission from [53]. Copyright 2024 Wiley-VCH. (c) Structural design strategy of fully biobased starch plastic. Reproduced with permission from [56]. Copyright 2023 Elsevier. (d) Fabrication of fully biobased elastomeric vitrimers from vanillin and 1,10-decanediamine and subsequent crosslinking. Reproduced with permission from [60]. Copyright 2023 American Chemical Society.

3.2.2. Diels Alder Reaction

The Diels–Alder (DA) reaction, a [4+2] cycloaddition between a diene and a dienophile, has become a fundamental strategy in dynamic covalent chemistry (DCC), offering a reversible and catalyst-free mechanism for designing recyclable, self-healing, and reprocessable polymeric materials.[62] DA chemistry enables catalyst-free reversibility under mild thermal conditions (e.g. 100–150 °C), cleaving the crosslink into the original diene and dienophile; a classic dissociative dynamic bond useful for closed-loop recycling.[63] The integration of bio-derived DA networks

further aligns with the principles of green chemistry, reducing reliance on petrochemical-based materials while enhancing recyclability, self-healing, and structural adaptability (**Figure 7**).[64]

Addressing the need for recyclability in covalent polymer networks, Kawai et al. developed a hetero-Diels–Alder system using 1,2-disubstituted 1,2,4,5-tetrazine-3,6-dione (TETRAD) to enable rapid sol–gel transitions under ambient conditions, without requiring harsh pH or temperature stimuli.[63] Their work demonstrated that furan-functionalized polyurethanes network could be repeatedly broken down to soluble oligomers and reformed, illustrating true chemical recyclability under ambient conditions, offering a highly adaptable and chemically controlled self-assembly approach for functional soft materials. Similarly, Lorero et al. sought to improve the recyclability of epoxy thermosets, which traditionally suffer from permanent covalent crosslinking, limiting their ability to be reprocessed.[65] By incorporating Diels–Alder crosslinking units into epoxy matrices, they achieved multiple recycling cycles while retaining over 85% of the original mechanical properties, demonstrating that DA bonds can introduce processability into inherently rigid and brittle thermosetting systems.

For high-performance fiber-reinforced composites, DA chemistry has provided a recyclable alternative to conventional carbon fiber-reinforced polymers (CFRPs), which are typically difficult to process post-curing. Wang et al. applied DA crosslinking to electrospun nanofibers, achieving mechanically robust yet recyclable dynamic covalent crosslinked nanofibers.[66] The DA crosslinks allowed closed-loop recycling without loss of mechanical integrity. Meanwhile, Gu et al. tackled the difficulty of CFRP recyclability by introducing phosphate-derived DA linkers.[67] The DA linkage accelerated dynamic exchange reactions while simultaneously improving fire resistance, offering a high-efficiency repair and recovery mechanism for aerospace and automotive-grade CFRPs. Their strategy enabled non-destructive recycling of carbon fibers while maintaining structural stability, addressing both material sustainability and fire safety requirements in lightweight composite applications.

As green chemistry principles drive the shift towards bio-derived and sustainable polymer networks, Nie et al. developed a renewable DA polymer network from vegetable oil and furfural.[64] The material achieved high thermal stability (>460°C), reprocessability, and shape-memory behavior, demonstrating that bio-sourced DA materials can rival fossil-based alternatives in mechanical performance. Gregg et al. further expanded on the use of bio-derived dynamic networks, introducing a CAN based on bioderived unsaturated polyesters crosslinked via DA chemistry, designing recyclable yet robust thermosetting materials. By incorporating poly(propylene fumarate) (PPF) and poly(propylene maleate) (PPM) backbones with furan-functionalized crosslinkers, the material achieved thermally reversible networks with tunable dissociation temperatures (100–130°C), high gel fractions (up to 99%), and excellent solvent resistance.[68] These studies reinforce the growing role of DA chemistry in as a solvent-free, catalyst-free, method of reversing thermosetting networks to recover starting materials, enabling closed-loop recycling and significantly reducing waste.

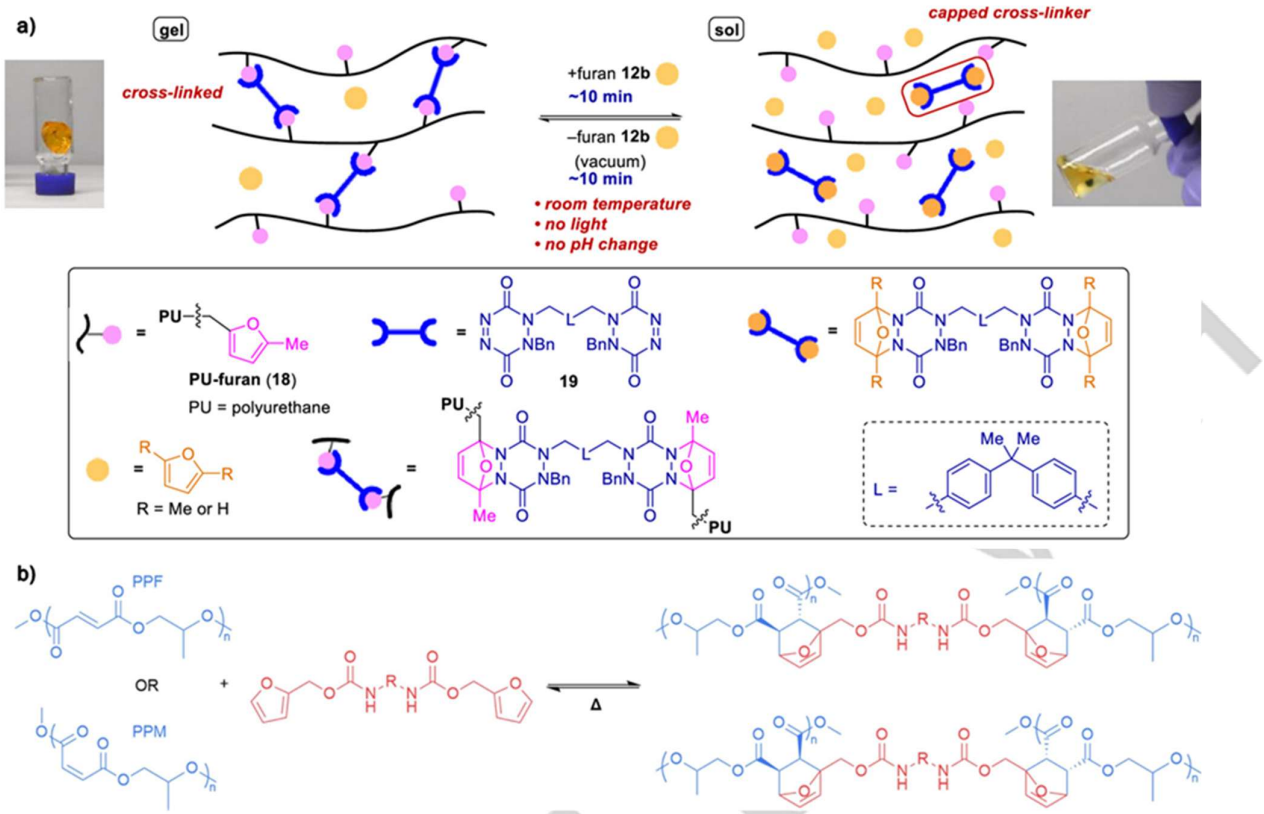

Figure 7. Representative works of Diels-Alder chemistry-based materials. (a) Reversible crosslinking and sol–gel transition based on the HDA reaction of TETRAD and furan. Reproduced with permission from [63]. Copyright 2022 American Chemical Society. (b) Network formation through bulk copolymerisation of furan-functionalised linkers with an unsaturated polyester. Reproduced with permission from [68]. Copyright 2024 Elsevier.

3.2.3. Knoevenagel adducts

C═C and C═N rearrangement and metathesis have been known to be an important DCB for materials, which offers a means to construct adaptable and reconfigurable polymer networks to prevent waste. Traditionally, these reactions required metal-based catalysts to facilitate bond exchange, limiting their applicability in sustainable material development.[69] However, recent advances in C=C and C=N adducts have revolutionized this field, allowing rearrangement and metathesis to occur under mild conditions without metal catalysts (**Figure 8**).[50, 70, 71] One of which is Knoevenagel adducts, leveraging the inherent polarity of the double bond, this key advancement enables metal catalyst-free C═C metathesis, thus reducing the environmental impact and energy requirements associated with dynamic polymeric materials. As a result, Knoevenagel condensation-based dynamic covalent bonds have found increasing utility in the design of CANs and vitrimeric materials. Recent studies have demonstrated how these chemistries address the long-standing challenges of brittleness, high activation energy barriers, and difficult recyclability in thermosets, leading to next-generation sustainable materials with enhanced malleability and mechanical robustness (**Figure 9**).

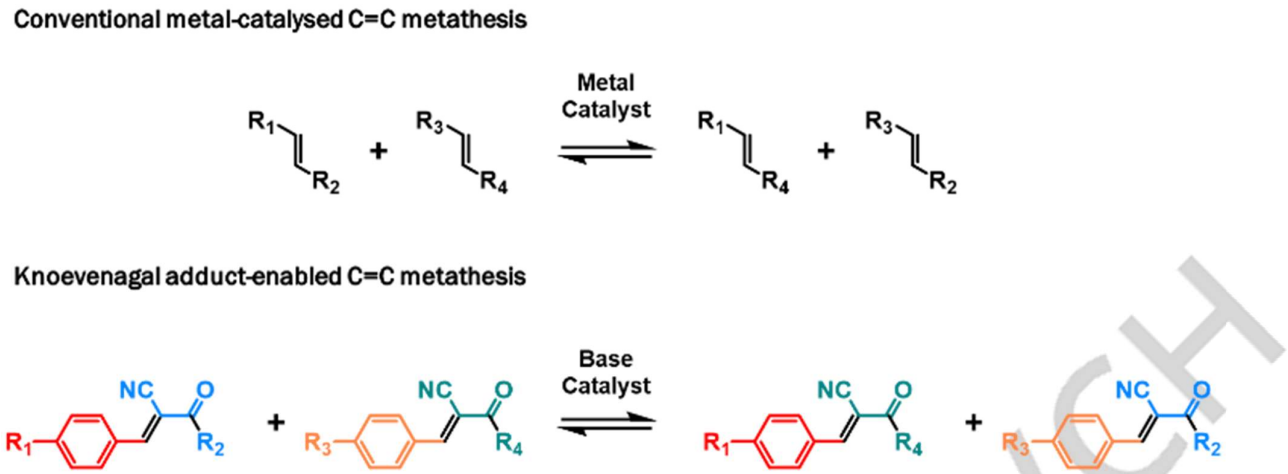

Figure 8. Schematic representation of conventional C=C metathesis and Knoevenagel adduct enabled C=C metathesis reactions.

Building on these principles, Wang et al. explored Knoevenagel condensation-driven C=C metathesis in two separate studies to develop high-performance thermosets with enhanced recyclability and mechanical robustness. Their first study tackled EOL recyclability challenges in thermosetting materials by proving that poly(α-cyanocinnamate) (PCC)-based vitrimers could undergo chemical depolymerization, recovering the monomer terephthalaldehyde with high purity.[72] In a separate study, Wang et al. addressed the brittleness of conventional thermosets while maintaining recyclability by using PCCs.[70] The resulting materials exhibited a Young's modulus of ~1590 MPa, an elongation at break of 79%, and a toughness of 30 MJ/m³, surpassing the mechanical limitations of traditional crosslinked polymers. Notably, both studies relied on catalyst-free dynamic exchange reactions, demonstrating the feasibility of C=C metathesis without external catalysts or harsh conditions, thus promoting sustainability in high-performance thermosets. Similarly, Zheng et al. introduced C=C/C=N metathesis chemistry, expanding the types of recyclable Knoevenagel thermosets by integrating aldimines and α-cyanocinnamate derivatives into dynamic polymer networks.[73] Their work addressed the high activation energy and catalyst dependency issues common in conventional CANs, proving that room-temperature reconfiguration of thermosets was possible through C=C/C=N bond exchange, leading to self-healing, shape adaptability, and superior recyclability.

Further advancements in C=C metathesis chemistry have enabled improvements in both thermosets and hydrogels, expanding their applications into biomedical and engineering materials. Zhu et al. sought to overcome the trade-off between crosslinking density and recyclability by introducing a 4-dimethylaminopyridine (DMAP)-catalyzed C=C metathesis reaction, demonstrating how controlled catalysis could facilitate high gel fractions, modulus, and complete recyclability in thermosetting plastics.[74] Meanwhile, Feng et al. developed catalyst-free α-acetyl cinnamate/acetoacetate (α-AC/A) exchange chemistry, introducing a vitrimer system that exhibited high creep resistance by restricting dynamic exchange below 140°C, thereby improving dimensional stability at service temperatures.[75]

Beyond structural materials, C=C metathesis has been utilized in dynamic hydrogels and printed materials, addressing the need for precision reconfigurability and recyclability in smart polymers. Wang et al. introduced a light-mediated ligand dissociation strategy, employing pH-sensitive Knoevenagel condensation to enable controlled dynamic bond formation in printable hydrogels.[69] Their study tackled the challenge of achieving precise reconfiguration in 3D-printable polymer networks, demonstrating a photo-triggered process for designing adaptive, recyclable soft electronics. These networks fulfill multiple green chemistry principles: they eliminate the need for added catalysts (preventing waste and hazard), function under moderate conditions (energy efficiency), and enable circularity of materials through monomer recovery. As this is a very recent development, ongoing research is optimizing the kinetics and exploring new monomer pairs for Knoevenagel dynamic bonds. Nevertheless, early results already position catalyst-free C=C metathesis as a cornerstone for next-generation recyclable thermosets.

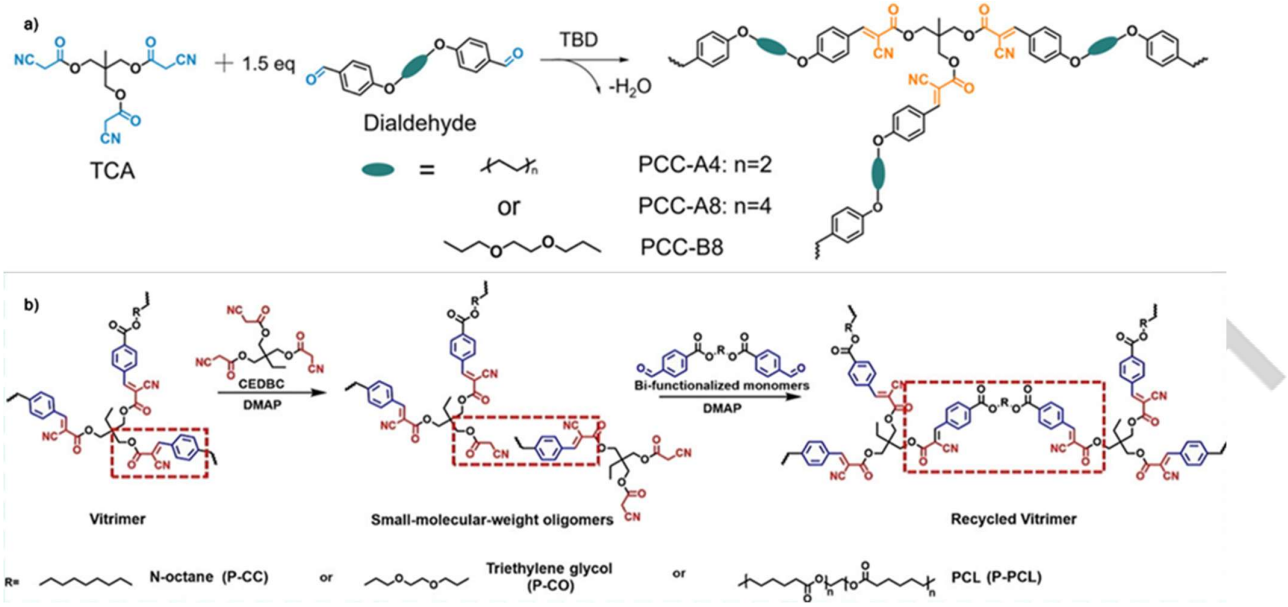

Figure 9. Representative works of Knoevenagel adduct-enabled C=C metathesis materials. (a) Synthesis of PCCs from a triarm cyanoacetate (TCA) star and an alkyl diaromatic aldehyde (A4 or A8) or an ether-based diaromatic aldehyde. Reproduced with permission from [70]. Copyright 2024 American Chemical Society. (b) Structure and chemical recycling of Knoevenagel adducts based on cyanoacetate. Reproduced with permission from [74]. Copyright 2024 American Chemical Society.

3.3. Reconfigurable Networks

Reconfigurable networks are polymer systems that utilize dynamic bond exchange to allow internal network topology changes without fully depolymerizing the material. In these systems; often referred to as associative CANs or vitrimers, dynamic covalent bonds continually break and reform by exchange reactions, so the network can flow or relax stress under the right conditions (typically heat or another stimulus) while remaining crosslinked.[76] This mechanism enables important green attributes: thermal reprocessing (like remolding or welding of thermosets), self-healing of cracks at the molecular level, and shape reconfigurability, all of which extend the service life of polymers and reduce waste. Most importantly, because the network never goes out of the crosslinked state during exchange, reconfigurable networks often retain better dimensional stability and mechanical integrity during reprocessing.[76] The concept was famously introduced by Leibler's group with the vitrimer paradigm, where an epoxy resin with transesterification linkers could be reshaped at high temperature but behaved as a robust thermoset at use conditions.[42] Since then, a variety of dynamic chemistries; transesterification, disulfide metathesis, boronic ester exchange and the like have been employed to create reconfigurable polymer networks. These systems adhere strongly to the green chemistry principles of preventing waste: a single reprocessable polymer item can potentially replace multiple single-use plastic items, and damages can be repaired instead of discarded. Moreover, many associative exchanges can be designed catalyst-free or with benign catalysts, avoiding toxic additives. Below we discuss key dynamic bond systems enabling network reconfigurability: disulfide bonds, transesterification, boronic esters, and dual-bond networks. Each subsection details how the exchangeable bonds impart self-healing, reshaping, and recycling capabilities, and how these materials realize sustainable outcomes like reduced waste and improved recyclability.

3.3.1 Disulfide and Sulfur Bonds

Sulfur–sulfur bonds (disulfides) and related thiol–thioester linkages are among the earliest explored dynamic covalent bonds in polymers, valued for their stimuli-responsive exchange and relatively low bond dissociation energy. Disulfide bonds can undergo metathesis (exchange) reactions where two S–S bonds break and reform into new S–S bonds, often triggered by heat, light, or a chemical stimulus (like a catalyst or even base).[77] These bonds, enable the development of materials that combine mechanical robustness with reprocessing and self-healing properties, addressing the persistent challenge of thermoset irreversibility and polymer waste accumulation.[78] Additionally, sulfur-rich chemistries provide unique functionalities such as enhanced adhesion, impact resistance, and tunable optical properties, broadening their applicability across diverse sectors (**Figure 10**).[77] As the demand for sustainable, high-performance materials continues to rise, recent studies have focused on incorporating biobased and catalyst-free sulfur-based DCC systems, ensuring both environmental compatibility and industrial scalability.[79]

A major advancement in this area has been the use of disulfide bonds in structurally complex polymers, such as bottlebrush architectures and epoxy vitrimers, to improve degradability and recyclability. Lee et al. addressed the long-standing challenge of complex, multi-step synthesis and non-degradability in bottlebrush polymers by designing a light-mediated, catalyst-free polymerization system using α-lipoic acid-functionalized macromonomers.[79] The incorporation of disulfide linkages into the polymer backbone allowed for intrinsic recyclability and tunable side-chain chemistry, offering an effective strategy for low-modulus, self-assembling materials. In a parallel effort to enhance the recyclability of thermosets, Guggari et al. synthesized a fully biobased epoxy vitrimer, leveraging vanillin-derived epoxy and cystamine-based aliphatic disulfide hardeners.[80] The authors demonstrated that even a small fraction of cystamine (2–20 mol%) dramatically accelerated dynamic bond exchange and reduced relaxation times. Similarly, in tackling the sustainability issues surrounding polyurethane foams, Chen et al. developed biobased, catalyst-free, NIPTU foams crosslinked via disulfide-based networks.[81] This allowed for rapid stress relaxation above 160°C and unprecedented reprocessability through extrusion and re-foaming. These studies collectively highlight the ability of disulfide chemistry to impart reprocessing and adaptability to different polymer systems, which is attractive for sustainable applications.

Further advancing this concept, Zhang et al. established the practical utility of disulfide-mediated dynamic polymerization by introducing sodium thioctate, the deprotonated and water-soluble form of thioctic acid, as a highly reactive monomer capable of undergoing dynamic covalent ROP in aqueous solution.[82] Notably, the disulfide-rich polymeric network could be fully depolymerized under basic aqueous conditions, and re-polymerized upon water evaporation, establishing a chemically circular lifecycle. A subsequent study by the same authors combined the mechanical integrity of covalent networks with reversible and redox-responsive behavior, enabling applications in self-healing elastomers and flexible electronics.[83] By leveraging both covalent and supramolecular interactions, such as hydrogen bonding and ionic coordination, these systems displayed excellent stretchability (up to 6000% elongation), rapid self-healing at room temperature, and recyclability via mild reductive cleavage in aqueous environments. on the hierarchical structuring of these polymers via evaporation-induced interfacial self-assembly. Deng et al. addressed a longstanding challenge in the field—valorizing elemental sulfur (S_8), a thermodynamically stable and industrially abundant feedstock by coupling it with cyclic disulfides under solvent-free, catalyst-free conditions to yield sulfur-rich thermoplastics and adhesives.[84] The dual ROP mechanism enabled by both S_8 and 1,2-dithiolanes provided sufficient enthalpic and entropic driving force to overcome the instability of poly(sulfur), resulting in degradable polymers with tunable sulfur contents (10–70 wt%) and modulus values ranging from 1 MPa to 1 GPa. Notably, these systems retained degradability in aqueous alkaline solutions and displayed dynamic behavior conducive to repair and recycling, making them compelling candidates for sustainable material development. Finally, the concept of chemically reconfigurable polymers was fully realized in Zhang et al.'s work, which introduced a dual closed-loop recycling system.[85] Using thioctic acid as a single monomer source, they developed both amorphous elastomers and semi-crystalline ionic films that could be interconverted and depolymerized in basic aqueous conditions with monomer recovery yields of up to 86%, providing a functional paradigm for circular polymer design.

Beyond thermosets, disulfide and polysulfide bonds are also used in developing self-healing elastomers and high-performance coatings, where network rearrangement is key to maintaining long-term functionality. Huang et al. addressed the lack of recyclability in vulcanized rubber by designing a sulfur-rich polyisoprene elastomer using inverse vulcanization.[86] The material achieving a remarkable 96.1% elastic recovery and a tensile strength of 24.2 MPa, while maintaining self-healing capabilities through thermally activated S-S bond metathesis. Complementing this, Parameswaran et al. explored the effect of polysulfide metathesis in styrene-butadiene rubber (SBR). By incorporating polysulfide linkages, it was able to facilitate 87% healing efficiency and improved recyclability without compromising mechanical integrity. In applications requiring environmental resistance, Singh et al. engineered a microwave-responsive, self-healing anticorrosion coating composed of a linseed oil-derived epoxy embedded with reduced graphene oxide nanofillers.[87] The material achieved 99.9% corrosion protection, rapid self-repair upon microwave stimulation, and excellent hydrophobicity (contact angle of 131°). These studies underscore the advantages of disulfide and polysulfide bonds in elastomers and coatings, enabling materials to recover from mechanical damage and environmental stressors while extending their functional lifespan.

The adaptability of dynamic covalent bonds has also been demonstrated in renewable biobased networks and advanced material applications. Wei et al. tackled the mechanical and environmental limitations of conventional poly(lactic acid) by developing a UV-crosslinked, fully renewable CAN.[88] The use of 1,2-dithiolane-derived disulfide bonds enabled enhanced tensile strength (~39 MPa), UV-blocking capabilities, and redox-responsive degradability in the material. Meanwhile, in the realm of textile applications, Wang et al. sought to improve the rigidity and inflexibility of chitosan coatings.[89] The design of a flexible, multifunctional chitosan-based smart textile coating crosslinked via thioctic acid-derived disulfide bonds, resulted in enhanced flexibility, improved tactile sensation, and superior antibacterial and electromagnetic shielding properties. Further advancing the chemical recyclability of sulfur-based polymers, Shi et al. demonstrated that anionic ring-opening copolymerization of cyclic disulfides with S8 could produce sulfur-rich CANs.[77] This allowed for closed-loop material reuse while retaining high optical transparency in the near-infrared region. These findings demonstrate the versatility of DCC in bridging sustainability

with next-generation material design, while also having high performance without sacrificing biodegradability or recyclability.

Collectively, these studies show the growing impact of dynamic covalent chemistry in advancing sustainable polymer design, with recyclability, self-healing, and adaptability emerging as core principles across diverse applications. The integration of biobased feedstocks, closed-loop recycling systems, and energy-efficient polymerization techniques indicates a shift away from petroleum-based, single-use plastics toward reprocessable, circular materials.

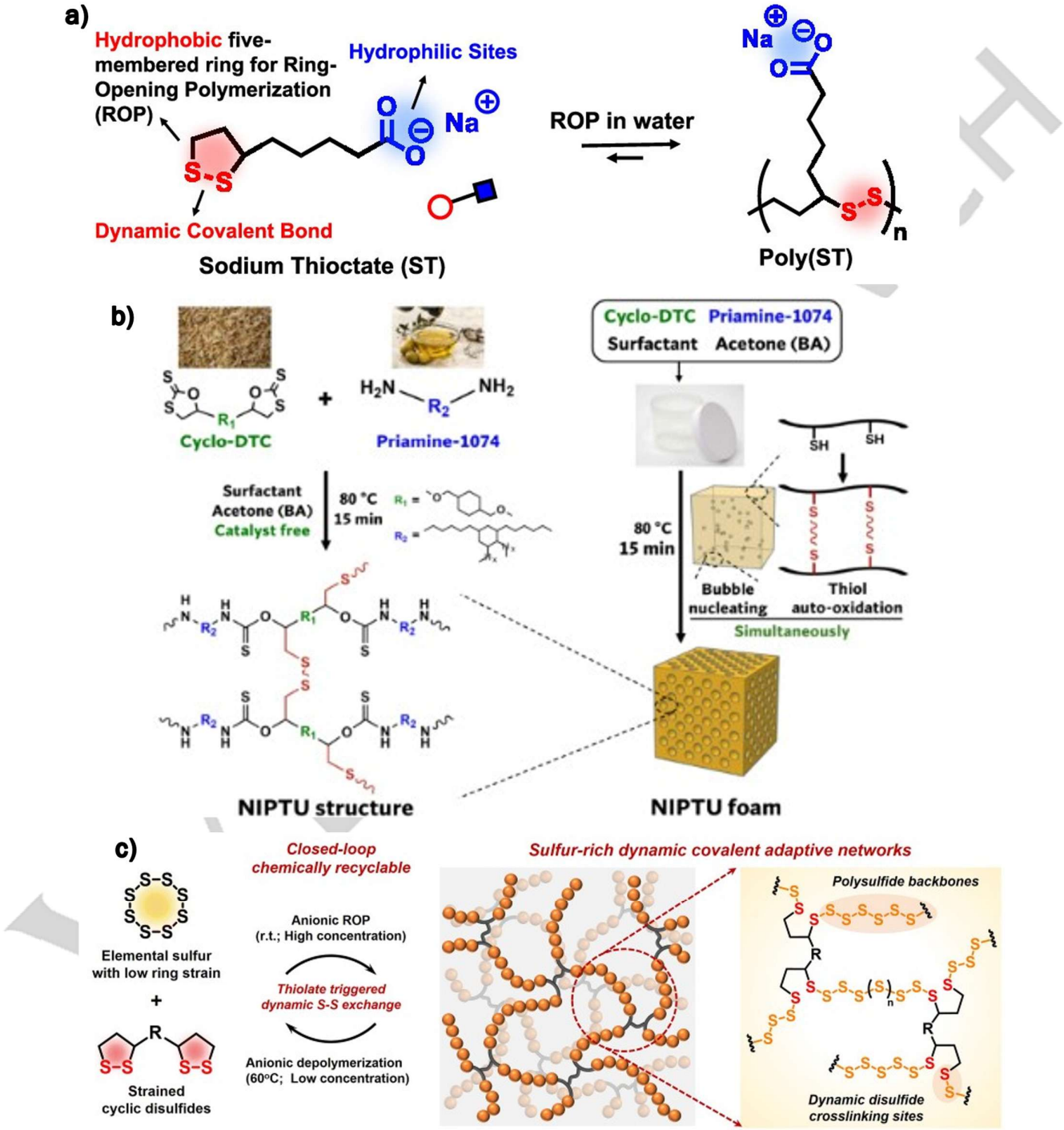

Figure 10. Representative works of sulfur-based dynamic covalent chemistry materials. (a) Self-assembly process of sodium thioctate in water with the molecular structures of sodium thioctate monomers and polymers. Reproduced with permission from [82]. Copyright 2019 American Chemical Society. (b) Synthetic scheme of NIPTU foam Cyclo-DTC and Priamine-1074, resulting

in NIPTU with linear backbones and crosslinked with disulfide bonds from thiol auto-oxidation. Reproduced with permission from [81]. Copyright 2024 American Chemical Society. (c) Schematic representation of the anionic copolymerization route of S_8 and cyclic disulfides, yielding sulfur-rich dynamic CANs. Reproduced with permission from [77]. Copyright 2024 Royal Society of Chemistry.

3.3.2. Transesterification

Transesterification; the exchange reaction between an ester and an alcohol (or another ester) – is the quintessential dynamic bond exchange exploited in vitrimers since the Leibler showing that at elevated temperature the ester linkages could undergo continuous exchange, allowing the network to flow like a viscoelastic liquid without depolymerizing.[42] This concept proved that a permanently crosslinked polymer could be reprocessed indefinitely. Transesterification-based vitrimers have since become a leading class of reconfigurable networks. The use of transesterification as a DCB in vitrimer networks is widely regarded for its ability in enhancing recyclability, reprocessability, and mechanical performance while maintaining structural integrity and stability.[90, 91] Transesterification allows for controlled stress relaxation and reshaping under thermal stimuli, providing a balance between rigidity and adaptability, which is attractive for thermosets, composites, and elastomers that require both mechanical strength and recyclability.[92, 93] Additionally, transesterification-based vitrimer systems have demonstrated catalyst-free or self-catalyzed mechanisms, eliminating the toxicity concerns and environmental impact associated with traditional catalysts while improving chemical stability (**Figure 11**).[90, 91, 94] These advantages position transesterification as an ideal strategy for integrating dynamic covalent chemistry with green chemistry principles, offering a sustainable pathway for polymer design and circular economy initiatives.

To address the difficulty of fabricating fully biobased and catalyst-free vitrimers with high mechanical strength, Li et al. developed hyperbranched tannic acid-based vitrimers, without using toxic catalysts while enhancing the recyclability and mechanical robustness.[90] The vitrimers exhibited tensile strengths between 21.9 and 52.4 MPa and maintained mechanical integrity through at least three recycling cycles, demonstrating the potential of bio-based dynamic networks for durable, recyclable thermosets. Similarly, Zhong et al. tackled the issue of non-recyclable epoxy resins by introducing a fully bio-based vitrimer from ferulic acid, utilizing self-catalyzed hydroxyl groups to accelerate transesterification and ensure high strength and rapid reprocessing.[91] The epoxy vitrimer retained 88.3% of its original tensile strength after multiple recycling cycles, demonstrating the effectiveness of hydroxyl-catalyzed transesterification in creating closed-loop recyclable epoxy resins.

For applications requiring mechanically reinforced yet reprocessable composites, Zhang et al. developed a carbon fiber-reinforced vitrimer composite using catalyst-free transesterification, which enabled reshaping, welding, and full recyclability.[92] The composite exhibited exceptional mechanical properties, including a tensile strength of 559 MPa and a Young's modulus of 8.5 GPa, while also being degradable in ethylene glycol at 190°C, making it a strong candidate for aerospace and automotive applications. In a different approach, Tan et al. addressed the mechanical limitations of shape-memory materials by incorporating thermochromic microcapsules into dynamic vitrimers, creating a shape-color dual-responsive wood composite with tunable rigidity.[95] The material demonstrated a tensile strength of 45.70 MPa, a topology freezing transition at 149.62°C, and excellent thermal insulation, enabling real-time visualization of mechanical transformations through color changes.

In the field of biodegradable polymers, Liu et al. tackled the processability challenges of polylactide films, developing a vitrimer network using epoxidized soybean oil and Zn^{2+}-catalyzed transesterification, which improved melt strength and ductility.[96] The PLA vitrimers exhibited an elongation at break of 132.1% (machine direction) and 111.0% (transverse direction), with an industrially scalable blow-up ratio of 3.71, demonstrating their viability for sustainable packaging applications. Similarly, Fan et al. addressed the poor foamability and weak mechanical performance of PBAT foams by introducing Zn^{2+}-catalyzed transesterification to enhance elasticity and crosslink density.[93] The vitrimer foams achieved a expansion ratio of 26.7-fold and a density of 0.045 g/cm³, making them lightweight, flexible, and highly recyclable.

For elastomer applications, Aziz et al. explored the development of bio-based ethylene propylene diene monomer (EPDM) rubbers, utilizing β-hydroxy ester linkages for dynamic crosslinking, which replaced traditional non-recyclable sulfur-based crosslinking.[97] The EPDM vitrimer retained high elasticity and stress relaxation properties even after multiple recycling cycles, proving its potential for sustainable elastomer production. In another advancement, Joosten et al. designed a vitrimer-thermoplastic blend that retained vitrimer properties while allowing high-shear processing, solving the longstanding issue of vitrimer processability in industrial extrusion.[98] The material combined the mechanical strength of vitrimers with the processability of polypropylene, enabling multiple shredding-injection cycles and high-throughput manufacturing.

Finally, addressing the sustainability concerns of polyurethane production, Zhang et al. developed a high-strength, self-healing, and recyclable NIPU using transesterification between carbamate and hydroxyl groups.[94] The bio-based polyurethane achieved a tensile strength of 34.9 MPa, self-healing efficiency of 91%, and superior adhesion strength of 7.09 MPa, presenting a non-toxic alternative to conventional isocyanate-based polyurethanes. These

studies collectively highlight the versatility and sustainability of transesterification in dynamic covalent chemistry, providing a pathway toward high-performance, recyclable, and environmentally friendly polymer systems.

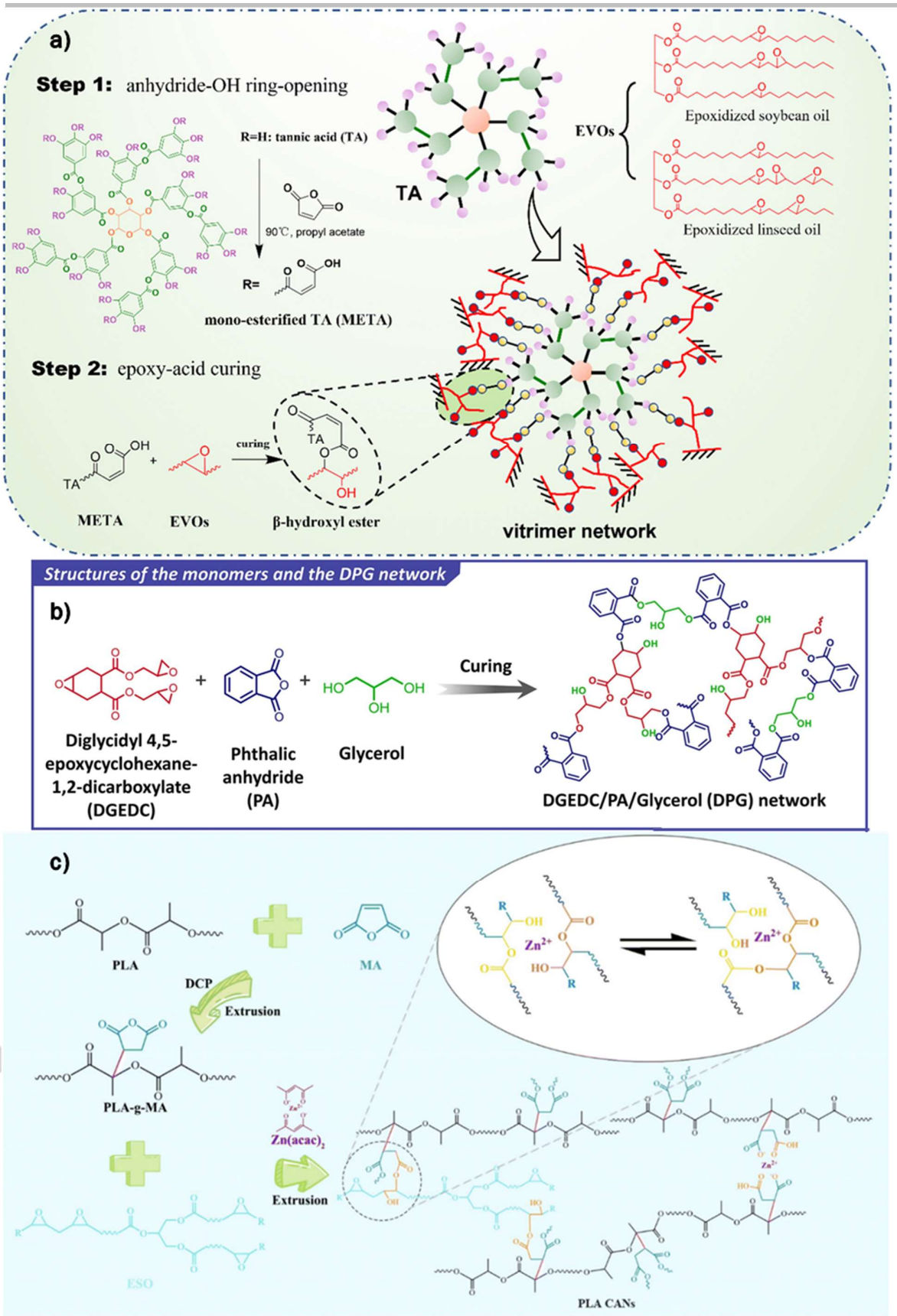

Figure 11. Representative works of transesterification-based dynamic covalent materials. (a) Synthesis of biobased, catalyst-

free transesterification vitrimers from tannic acid. Reproduced with permission from [90]. Copyright 2024 Royal Society of Chemistry. (b) Chemical structures of DGEDC/PA/Glycerol networks. Reproduced with permission from [92]. Copyright 2023 Elsevier. (c) Schematic illustration of the two-step reactive extrusion route for polylactide CANs. Reproduced with permission from [96]. Copyright 2023 Royal Society of Chemistry.

3.3.3. Boron Ester

Boron esters are a class of dynamic covalent bonds formed between boronic acids and diols that exhibit reversible exchange reactions under mild conditions, responding to pH changes, hydroxy moieties, or moisture at room temperature.[99, 100] Their adaptability and self-healing nature make them highly attractive for sustainable material design, aligning with the principles of green chemistry by not requiring harsh processing conditions, enhancing recyclability, and extending material lifetimes (**Figure 12**).[101, 102] This has led to their widespread adoption in reprocessable polymers, self-healing networks, energy-efficient materials, and adaptive functional systems.

To improve recyclability and mechanical robustness, researchers have explored boron ester-based vitrimer and polymer networks as alternatives to conventional irreversibly crosslinked materials. Cheng et al. addressed the challenge of achieving high damping efficiency in polymers while maintaining dynamic characteristics.[103] The authors developed hyperbranched vitrimers with boronic acid ester crosslinks, where the combination of dense pendant chains and loose dynamic crosslinking allowed for energy dissipation across broad frequency and temperature ranges. Similarly, Zhao et al. tackled the issue of poor mechanical strength and reprocessability in epoxy resins by incorporating boronic ester linkages with B–N coordination.[101] This method not only enhanced the toughness and recyclability of the polymer but also endowed it with long-lived room-temperature phosphorescence, opening doors for anti-counterfeiting and optical storage applications. These findings show the potential of boron esters in creating sustainable polymer systems that support waste reduction and circular material usage.

Beyond recyclability, boron ester-based materials have enabled advancements in self-healing and shape-memory technologies, addressing the need for longer-lasting, damage-resistant materials. Ma et al. sought to enhance reprogrammability in liquid crystal elastomers by integrating boronic ester bonds.[99] Demonstrating that the elastomer could undergo reversible changes in color and shape in response to mechanical stretching, applicable for adaptive optics and next-generation soft robotics. Jiang et al. tackled limited responsiveness in hydrogels by engineering bilayer hydrogel actuators with boronic ester crosslinks.[100] The hydrogels exhibited pH- and temperature-sensitive actuation along with excellent strain resistance, making them promising for bioelectronics and artificial muscles. Furthering this concept, Sumerlin and coworkers investigated the use of cyclic polymer networks with boronic ester-based crosslinking.[104] In doing so, they demonstrated that the unique topology of cyclic polymers could reduce structural defects and improve mechanical resilience, offering self-healing properties in coatings and adhesives. These innovations contribute to material longevity, reducing waste and resource consumption while enhancing functional adaptability.

Boron ester chemistry has also revolutionized energy-efficient and sustainable material applications, particularly in thermal management and lubrication systems. Huang et al. aimed to resolve leakage issues in thermal interface materials by introducing boron ester crosslinks in paraffin wax-based phase change materials.[102] which ensured mechanical integrity even above the melting temperature of the polymer, thus providing stable and efficient heat transfer solutions for high-power electronics. Similarly, Bu and coworkers addressed the environmental concerns of phosphorus- and sulfur-based lubricants by developing boron ester-linked polymer–nanoparticle networks.[105] The material not only significantly reduced friction by 52% and wear by 93% but also formed nanometric-thick tribofilms for enhanced load-bearing capacity, offering an alternative to traditional toxic lubricant additives. These advancements align with green chemistry principles by minimizing toxic additives, reducing energy loss, and improving the efficiency of industrial processes.

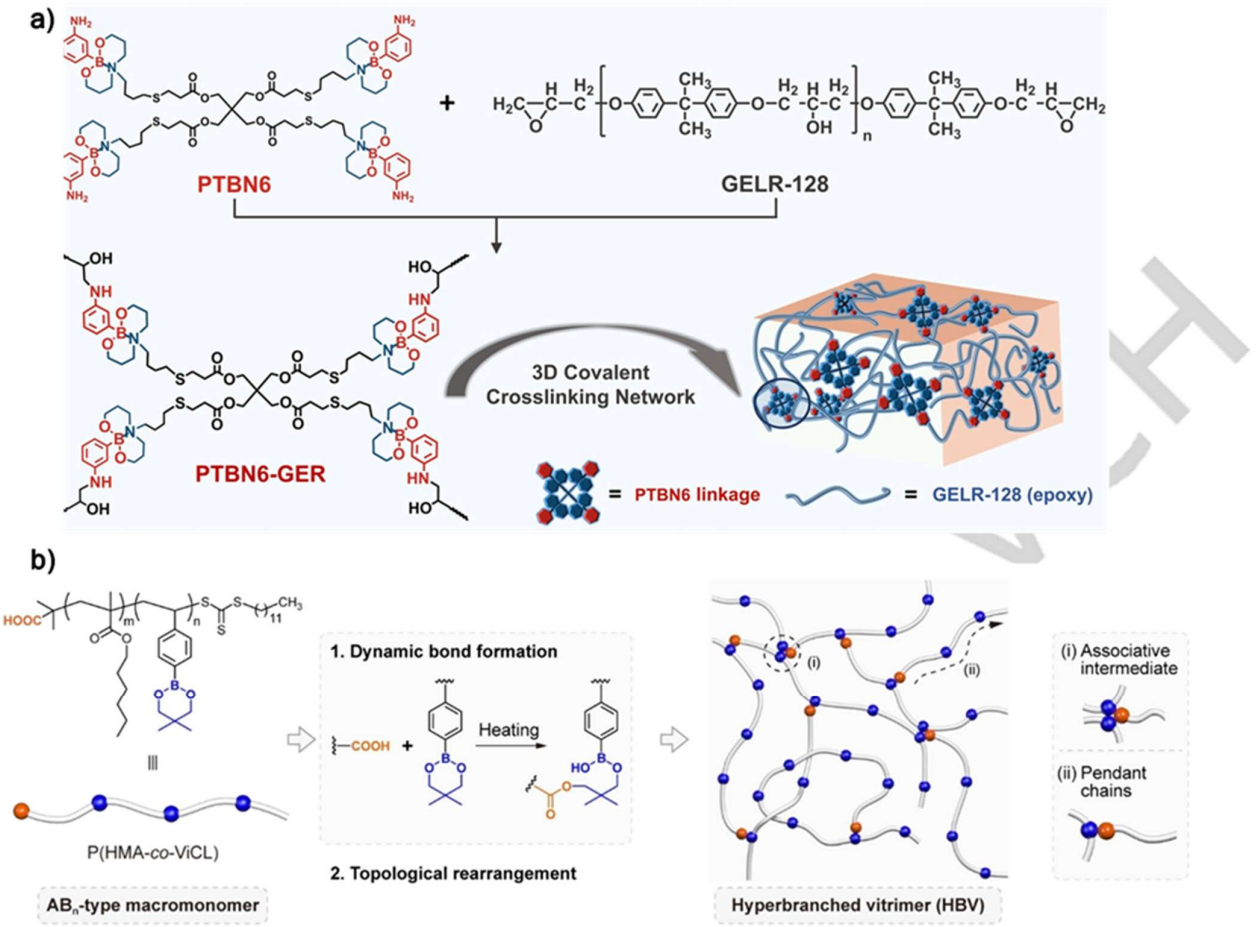

Figure 12. Representative works of boron ester materials. (a) Synthetic route and schematic illustration of the covalent crosslinking networks for epoxy resins with B-N coordination. Reproduced with permission from [101]. Copyright 2023 Wiley-VCH. (b) Chemical structure and schematic representation of the hyperbranched vitrimer with boronic ester crosslinks. Reproduced with permission from [103]. Copyright 2024 Wiley-VCH.

3.3.4 Dual bonding systems

The integration of multiple DCBs into a single polymeric system has garnered interest in a bid to enhance the recyclability and reprocessability of materials beyond what is capable of a single DCB.[16] Several studies have demonstrated that the combination of distinct DCBs not only facilitates recyclability but also optimizes mechanical performance and stress relaxation behavior.[106] The integration of two distinct dynamic covalent bonds has been systematically explored as a synergistic strategy to overcome the limitations associated with single dynamic networks.[107] By employing two different exchange mechanisms within a polymer matrix, researchers have achieved faster stress relaxation, improved self-healing, enhanced reprocessability, and optimized mechanical and thermal performance (**Figure 13**).[108]

For example, Guo et al. developed itaconic acid-based vitrimers through a one-pot inverse vulcanization method, simplifying the complex preparation processes of biobased vitrimers.[109] Their work introduced a sulfur-based dual-dynamic network, which improved recyclability, chemical degradability, and solvent resistance while retaining high mechanical strength. Similarly, Jiao et al. introduced a high-performance epoxy resin containing ester and disulfide bonds, enabling autonomous visualization of damage and healing.[107] This work also achieved a green closed-loop recycling system where the polymer could be degraded in pure water at 200°C without a catalyst. Gao et al. designing an epoxy vitrimer with acetal and disulfide bonds to integrate multiple properties into a single epoxy system.[106] By using the synergistic effect of these two dynamic bonds, the material facilitated rapid polymer reprocessability and degradation while maintaining superior tensile strength.

The potential of dual dynamic networks has been further explored through innovative chemistries and bio-based monomers. Lucherelli et al. synthesized a CAN based on biobased 2,5-furandicarboxaldehyde, incorporating

associative imine linkages with dissociative Diels-Alder adducts.[110] This hybrid system provided enhanced reprocessability and tunable mechanical properties, demonstrating the advantages of combining associative and dissociative bond exchange mechanisms. Verdugo et al. extended this concept by integrating imine and disulfide bonds into a biobased epoxy vitrimer, facilitating rapid stress relaxation and excellent recyclability in adhesives and composites.[16] Their work showcased the potential of bio-based materials in achieving high-performance, renewable thermosetting polymers. Hao et al. further refined these strategies by incorporating vanillin-based hyperbranched epoxy resins containing disulfide and imine bonds.[111] This combination yielded a system with enhanced malleability, creep resistance, and self-healing properties. These advancements demonstrate the importance of DCB selection in designing sustainable materials with multifunctional properties.

The utilization of dual dynamic covalent chemistry has extended beyond conventional epoxy systems. Shi et al. employed a boroxine-crosslinked poly(disulfide) network to develop chemically recyclable encryption materials.[34] Their study utilized the orthogonality of boroxine and disulfide chemistries, which enabled a reprogrammable shape-memory effect while maintaining robust mechanical properties. Du et al. explored boronic ester and thiol-based disulfide crosslinking in supersoft bottlebrush polymers.[112] The combination of these two dynamic covalent bonds allowed for ultrafast self-healing (>90% efficiency), superior adhesion to multiple substrates, and low-modulus mechanical properties with a shear modulus as low as 5 kPa.. Additionally, Hu et al. synthesized a cardanol-derived epoxy vitrimer with both disulfide and ester exchange mechanisms to address the recyclability and degradation issues of conventional thermosetting resins while retaining high mechanical performance.[108] By modifying the network architecture, they achieved a faster stress relaxation time of 5.6 minutes and a lower activation energy of 36.58 kJ/mol. Their recyclability studies confirmed that the material could be chemically degraded and reprocessed, achieving a sustainable closed-loop material lifecycle. These works demonstrated that dual dynamic covalent bonds could enable the design of high-performance, reprocessable, and environmentally friendly vitrimers.

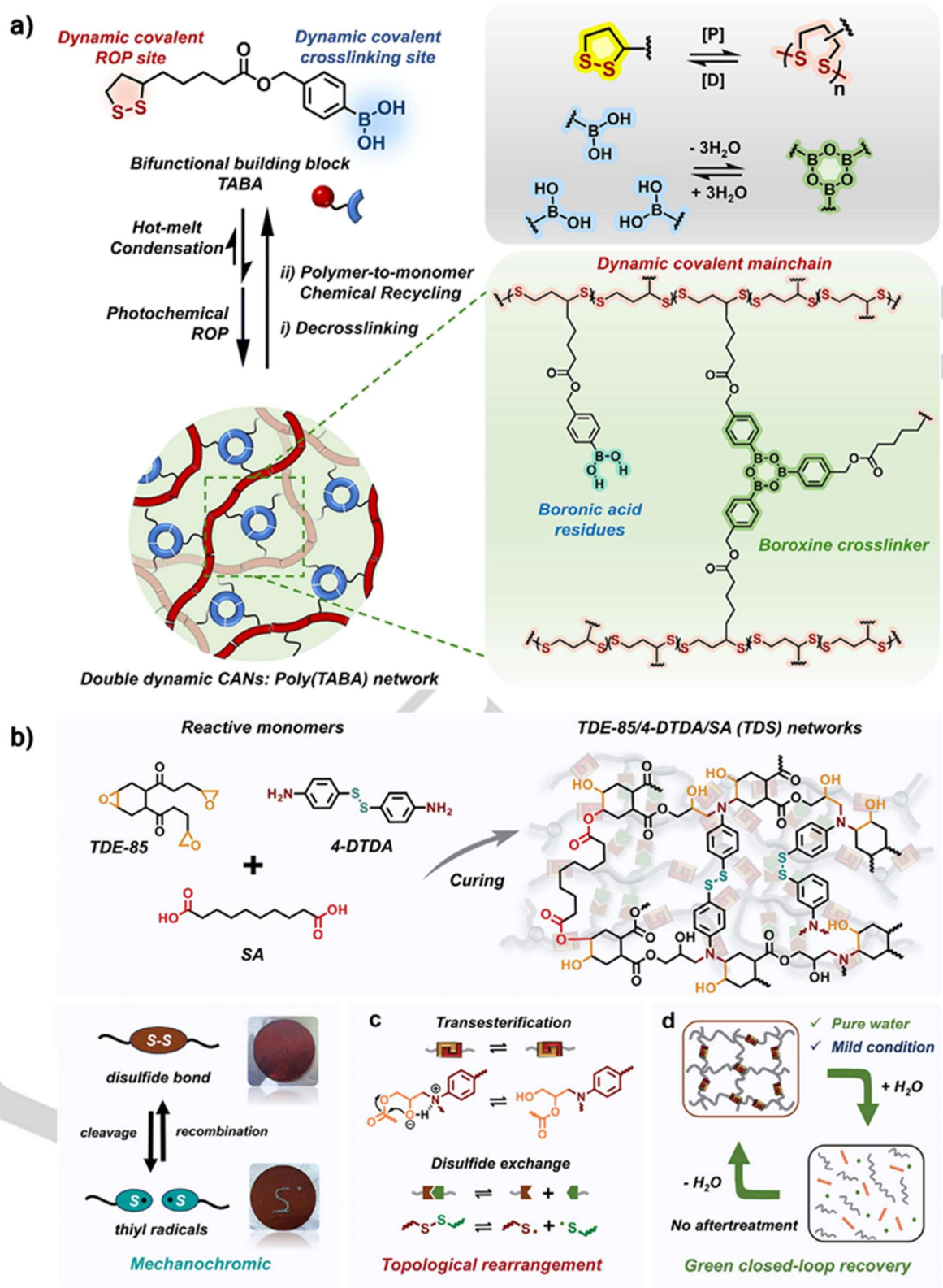

Figure 13. Representative works of dual dynamic network materials. (a) Conceptual illustration and the molecular structures of the double DCN by combining disulfide-mediated reversible ring-opening polymerization with boroxine chemistry. Reproduced with permission from [34]. Copyright 2024 Elsevier. (b) Design concept of dynamic ester and disulfide bonds, showing the synthetic process, self-healing and closed-loop recovery. Reproduced with permission from [107]. Copyright 2024 Wiley-VCH.

4. Summary and Outlook

DCC represents a foundational advancement in sustainable polymer design, enabling recyclability, self-healing, and environmental responsiveness through reversible bonding mechanisms. By strategically integrating dynamic bonds such as imines, disulfides, Diels–Alder adducts, transesterification, boronic esters, and Knoevenagel adducts, DCC-based polymers adhere closely to many principles of green chemistry. Importantly, these materials embody the spirit of the update in principles of Green Chemistry, incorporating circular design, lifecycle thinking, and systems-level sustainability into polymer architecture. However, several critical challenges remain unsolved and require further exploration, many DCC-based polymers exhibit excellent laboratory-scale performance, yet their industrial feasibility is still limited by complex synthesis, long curing times, and regulatory barriers. Developing cost-effective, high-throughput manufacturing techniques will be essential for large-scale adoption. Furthermore, as mentioned by several works, the incorporation of reversible bonds often compromises mechanical performance and thermal stability, limiting the applicability of DCC materials in structural applications, with only few managing to address this problem. Optimization of the bond exchange kinetics and network architecture to balance recyclability and durability is paramount. To ensure true sustainability, it is also critical to evaluate full life-cycle impacts, including feedstock origin, processing energy, and end-of-life handling. Innovations in low-energy curing, non-toxic monomers, and solvent-free processing will help close these gaps and drive DCC towards fully circular, high-performance, and environmentally responsible polymer systems.

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