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Review

Chemical approaches for fabrication of self-healing polymers

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Received: 30 March 2024 / Accepted: 24 June 2024

Abstract

In recent years, significant progress has been made in the development of polymeric materials, driving rapid expansion in associated industries and a surge in plastic production and usage. Consequently, the substantial generation of plastic waste has raised environmental concerns. One critical issue is the tendency of polymers to degrade over time, leading to disposal. Introducing self-healing systems capable of autonomously repairing damage caused by external factors can extend material lifespan, offering an effective means to mitigate polymer waste. The concept of self-healing draws inspiration from the regenerative abilities of living organisms. Extensive research over the past decade has led to significant advancements in self-healing materials, which can naturally repair and regain functionality using accessible resources. Various approaches, including physical, chemical, and physio-chemical methods, are employed in self-healing polymers. These self-healing mechanisms can be autonomic or triggered by external stimuli such as heat, solvent, or pressure. From thermosets to thermoplastics to elastomers, polymers of all types can exhibit self-healing properties. This review article delves into chemical approaches of fabricating self-healing synthetic polymers, focusing primarily on covalently cross-linked polymers with an emphasis on the Diels–Alder reaction. Additionally, the review offers a comprehensive discussion and compilation of different research works concerning other chemical approaches used in polymer self-healing.

Article highlights

- Self-healing polymers offer innovative solutions for repairing damage, inspired by natural processes.
- Chemical approaches enable diverse self-healing mechanisms, enhancing material durability.
- Covalent cross-linking structures show promise for stronger, more stable self-healing polymers.

Keywords Self-healing materials · Covalent bonding · Bonding · Polymers

1 Introduction

Self-healing represents a remarkable capability found throughout nature to routinely repair physical damage. Drawing inspiration from this innate ability, scientists have developed self-healing polymers (SHPs) with recent applications spanning critical sectors such as electronic devices, sensors, electronic skin, adhesives, supercapacitors, wearable devices, spacecrafts, road constructions, automobiles, and steel coatings [1–12]. The integration of self-repairing properties into synthetic materials has enhanced the longevity, durability, and safety of the final designs, thereby potentially reducing

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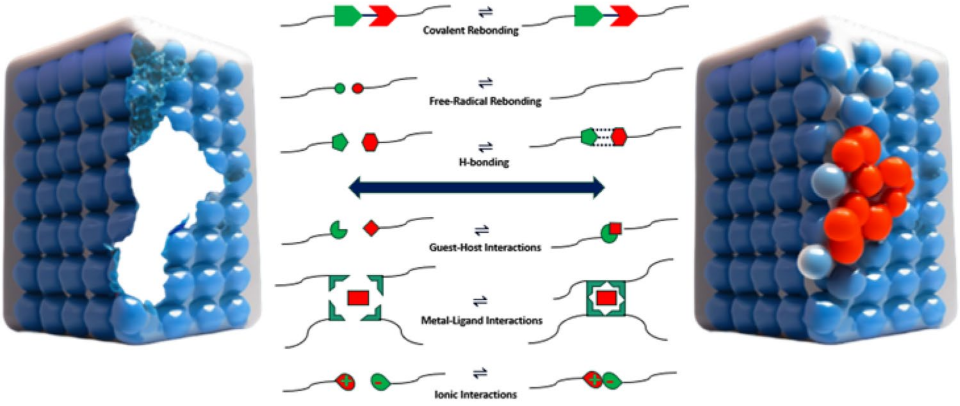


Fig. 1 Visualizing self-healing in polymeric materials through different chemical approaches: from cracks to recovery [16]

per capita consumption, industrial waste, and environmental pollution [13]. Consequently, SHPs have the potential to play a significant role in mitigating climate change [14].

Several approaches has been reported for creating self-healing materials in the previous decade, with the healing mechanism focusing mostly on the reversibility of a specific structural feature [15, 16]. The foundational research on crack healing in polymers was first introduced by Wool's [17] group in 1981, setting the stage for significant advancements in the field of self-healing polymers. In 2002, Chen et al. [18] introduced a polymer with a cross-linked structure capable of repair through heat application via the Diels–Alder/retro-Diels–Alder (DA/rDA) reaction, marking the inception of the first intrinsic self-healing polymer based on reversible covalent bonding. In 2001, White's [19] group pioneered a microcapsule polymer complex, initiating systematic research into comprehensive self-healing methodologies and inspiring further investigations, though no commercial applications have yet been realized. White's group further contributed to the field by developing the first extrinsic self-healing polymer composite, which they subsequently advanced into a microvascular network in 2007 [20]. During this period, concurrent investigations into shape memory effects and self-healing were also underway [21–24]. The first comprehensive monograph to self-healing materials was published in 2007, included many chapters authored by top leaders in the subject and addressed the full material range, from polymers to metals and ceramics [25, 26]. In 2008, Leibler et al. introduced a self-healing polymeric material constructed on a supramolecular assembly hinging on hydrogen bonds. This marked a pioneering advancement as the initial self-healing rubber utilizing non-covalent bonds [27]. Subsequently, in 2011, the Leibler group introduced the notion of 'vitrimer', which entails maintaining a consistent crosslinking density in polymers capable of reforming through heating via transesterification reactions in epoxy self-healing polymers [28]. Since 2011, there has been a notable surge in research exploring intrinsic self-healing mechanisms involving various dynamic covalent and non-covalent bonds [29–34].

Several noteworthy reviews in the literature delve into the progression of self-healing materials and their categorizations [35]. The prevalent classification of self-healing polymers encompasses two main types: Extrinsic and Intrinsic [36]. In another classification based on the Healing Mechanisms, self-healing polymers can be further categorized into (1) Physical Processes, (2) Chemical Processes, and (3) Physico-chemical Processes [16]. Physical self-healing processes mainly involve interchain diffusion [37], phase-separated structures [38, 39], shape-memory effects [40, 41], and the utilization of superparamagnetic nanoparticles as exemplified instances [42, 43]. In contrast, chemical processes encompass various mechanisms such as the integration of covalent [44–46], free-radical [47, 48], or supra-molecular [49–51] dynamic bonds. Figure 1 illustrates various chemical strategies for polymer self-repair. On the other hand, capsule-based method [52–55], van der Walls interaction [56–58] and Vascular-based methods [59, 60] are the examples of physio-chemical approaches.

Over the past few decades, numerous reviews and viewpoints regarding self-healing polymers have been disseminated in the literature [61–64]. In recent years, investigations into systems employing reversible Diels–Alder reactions have garnered attention, alongside explorations of reversible reactions involving imine moieties [65–67]. Furthermore, discoveries have been made in degenerative exchanges utilizing bioinspired disulfide exchanges and radical Tri-thiocarbonate reshufflings [68–70]. However, there is scant literature that delves into these systems in greater detail. In this Review, we outline the different self-healing polymers based on the chemical processes like; Reactive chain ends (covalent re-bonding, free radical re-bonding) and Supra-molecular chemistry (H-Bonding, Guest–Host interactions, Metal ligands co-ordination, Ionic interactions). We begin by outlining the chemical techniques and how they have been demonstrated in various polymer systems, as well as the essential challenges and impediments connected with each system. To advance the field of self-healing materials, we have focused specifically on self-healing polymers that are

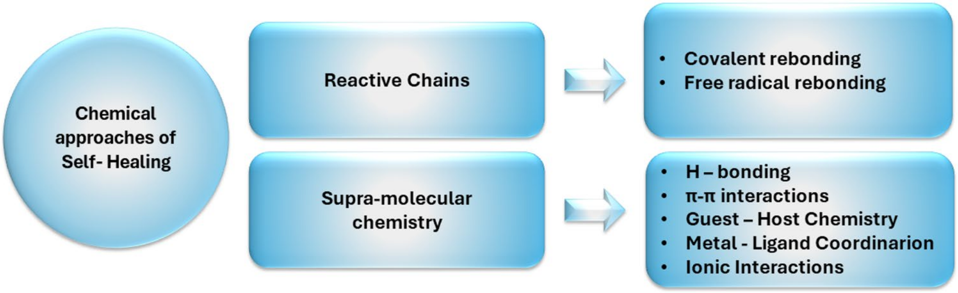


Fig. 2 Different chemical approaches of self-healings

solely based on covalently cross-linked structures. This deliberate selection is driven by the potential for these materials to exhibit enhanced mechanical strength and increased stability, thus paving the way for further advancements in self-healing capabilities. Finally, we examine the future of self-healing polymers, identifying novel applications, functions, and material systems.

2 Chemical approaches of self-healing polymers

Self-healing processes in materials can be achieved through the introduction of reactive chain ends or by utilizing supramolecular chemistries. This section focuses on the various chemistries employed for self-healing in different materials. These materials possess chemical bonds that possess the ability to reform after sustaining damage, with the reformation triggered by external stimuli like heat, light, solvent, or oxygen. The chemical processes involved encompass the incorporation of covalent [71], free-radical [72], or supramolecular [73] dynamic bonds (Fig. 2). The materials will be classified according to the mechanism of healing they utilize, beginning with those that depend on covalent rebonding. Subsequently, attention will be directed towards the most extensive category of materials employing reversible bonds within their crosslinking framework. Finally, we will delve into other systems that do not fall within the previously mentioned classifications. Figure 3 illustrates various reversible reactions that facilitate the reformation of covalent bonds.

3 Covalent rebonding

3.1 Diels–Alder [4 + 2] cycloaddition reaction

The Diels–Alder reaction, named after the eminent scientists Otto Paul Hermann Diels and Kurt Alder, was first described in 1928. Their pioneering work on this reaction earned them the prestigious Nobel Prize in Chemistry in 1950. The Diels–Alder reaction is a [4 + 2] cycloaddition organic reaction, wherein a conjugated diene reacts with a substituted alkene, known as the dienophile, leading to the formation of a substituted cyclohexene, as illustrated in Fig. 4.

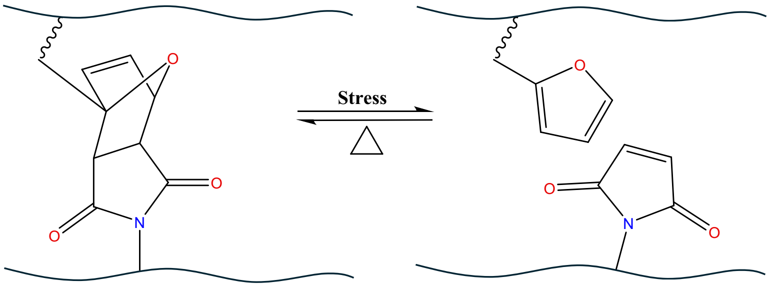
Diels–Alder (4 + 2 Cycloaddition), an essential process for achieving self-healing, can be employed in various polymer systems, including poly(ethylene-oxide), caprolactones, epoxies, polyacrylates, bismaleimides, anthracene-maleimide-based polymers, polyesters, cross-linked polylactic acid, acrylics, and polyamides. Retro-Diels–Alder reactions provide a means to disconnect the diene and dienophile, while temperature between 80 and 120 °C enable the reconstruction of covalent bonding to heal cracks [18] (Fig. 3A).

3.2 Epoxies

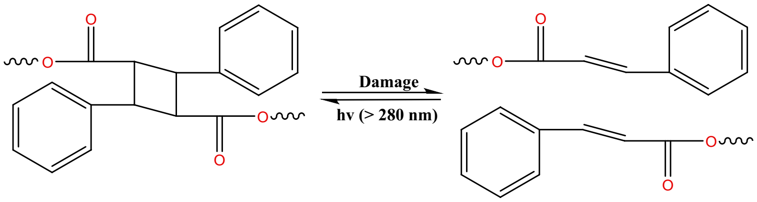
A novel approach for developing a self-healing epoxy polymer presented by Bai et al. [79]. The strategy involved the incorporation of a diamine cross-linker that was synthesized using thermally reversible Diels–Alder adducts of furan and maleimide groups [79]. Findings indicated that subjecting the epoxy polymer to a 30-min treatment at 140 °C resulted in the complete elimination of scratches. The self-healing process was reiterated several times, consistently demonstrating its efficacy without any discernible decline (Scheme 1).

In a separate investigation conducted by Peterson et al. [80], the utilization of the Diels–Alder reaction led to the creation of a gel with reversible cross-linking properties, serving as a healing agent for conventional epoxy-amine thermosets.

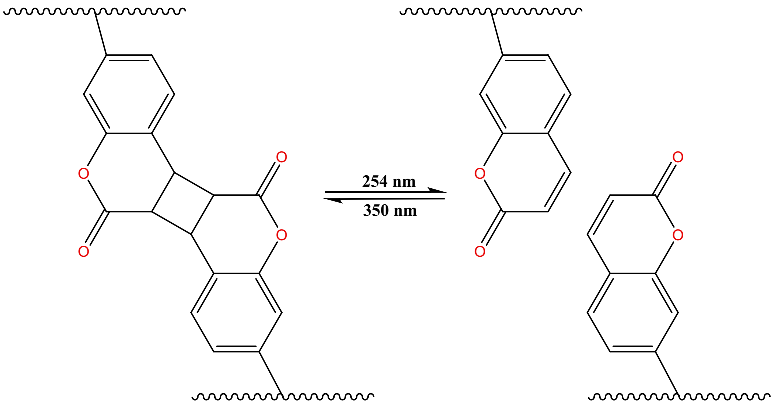
A) Diels-Alder [2+4] cycloaddition



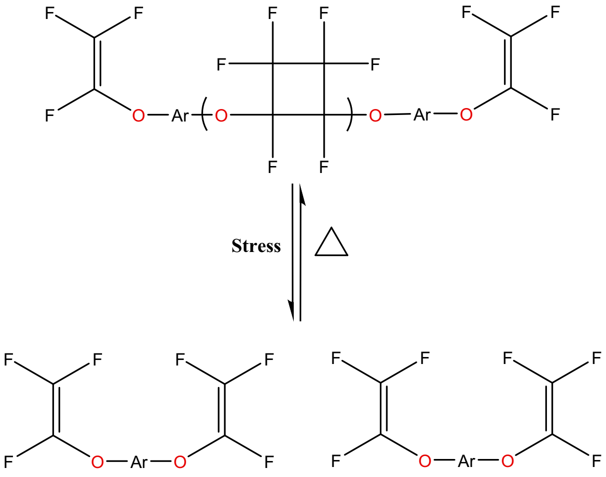
B) [2+2] cycloaddition



B-1 Cinnamoyl



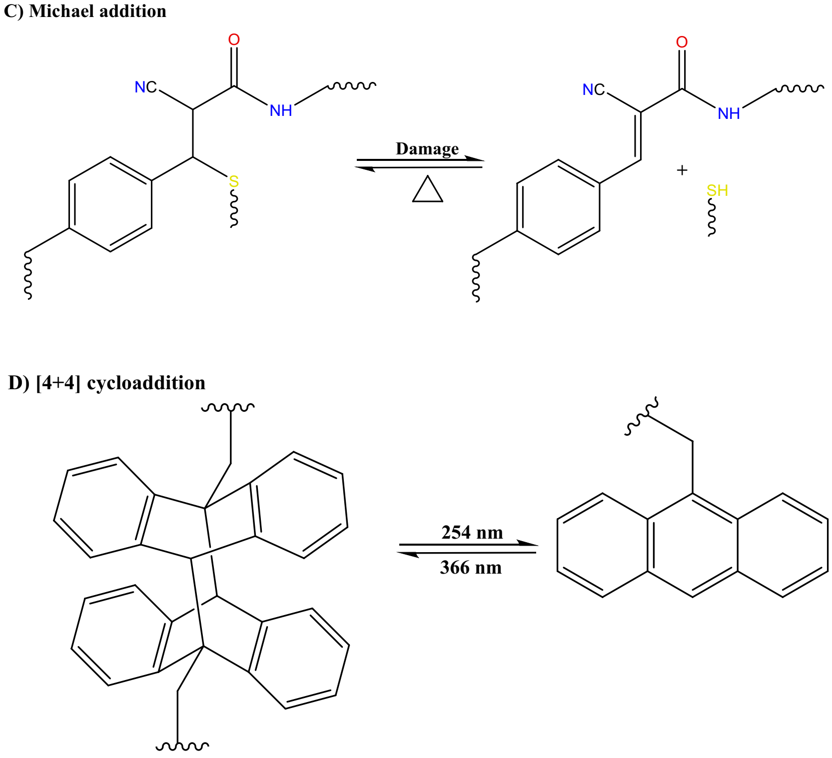
B-2 Coumarin



B-3 Trifluorovinyl ether

Fig. 3 Self-repair through the reformation of covalent bonds can be achieved using different reactions, including: (**A**) Diels–Alder [2 + 4] cycloaddition [18], (**B**) [2 + 2] cycloaddition [74, 75], (**C**) Michael addition [76] and (**D**) [4 + 4] cycloaddition [77]

Fig. 3 (continued)



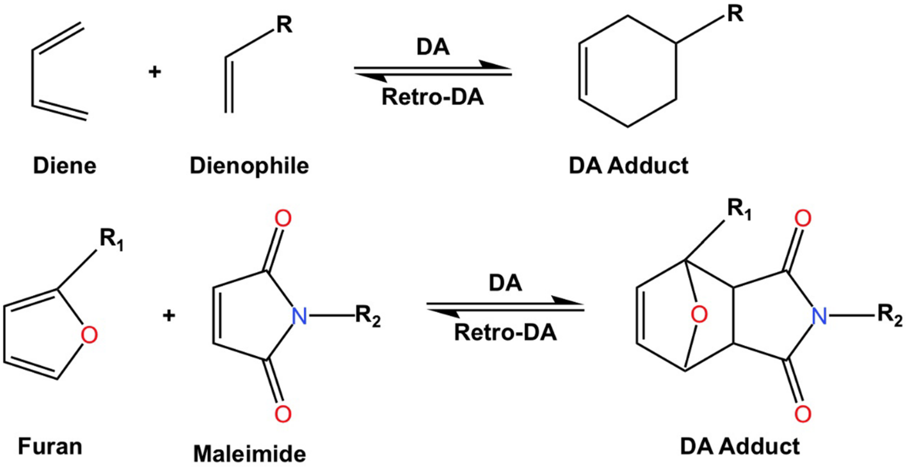
By directly applying this reversibly cross-linked network onto a cracked surface in an epoxy-amine thermoset, a remarkable recovery of 37% of the initial strength of the epoxy-amine network was achieved [80]. Tian et al. [81], developed a novel epoxy resin, known as *N*,*N*-diglycidyl-furfurylamine (DGFA), through a two-step synthesis approach that involved combining epoxide and furan groups within a single molecule. The resulting resin exhibited a liquid form with low viscosity and excellent processability. It could be cured using anhydride and maleimide, eliminating the need for solvents during the curing process [81] (Scheme 2).

In a separate study by Liu and Chen [82], PA-F polyamides were produced by incorporating furan pendent groups through a Michael addition reaction of furfuryl amine with maleimide-containing polyamides (PA-MI). Through Diels–Alder (DA) and retro-Diels–Alder (retro-DA) reactions, thermally reversible cross-linked polyamides were derived from the combination of PA-MI and PA-F polyamides. These cross-linked polyamides exhibited superior properties, including high toughness, elevated glass transition temperatures (T_g), and excellent mechanical strength, surpassing their respective polyamide precursors [82] (Scheme 3).

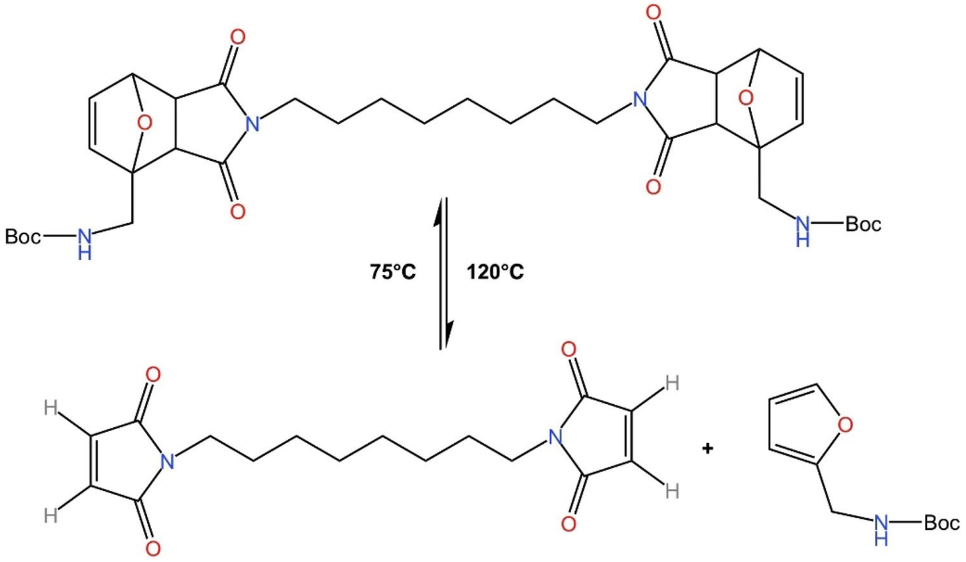
The establishment of a self-healing system in solution form has already been reported Pratama et al. [83] which involves the compatible functionalization of the healing agent and polymer network through the utilization of Diels–Alder reactive groups. The healing agent solution 1,6′-bismaleimido2,2,4-trimethylhexane (MMI-2) was effectively enclosed within urea formaldehyde (UF) shells when incorporated into phenyl acetate (PA). These microcapsules, in a spherical form, were then dispersed within a furan-functionalized epoxy-amine thermoset to introduce a healing agent solution for enabling self-healing properties in the thermoset material. On average, the thermoset material with the inclusion of MMI-2 solution-filled capsules exhibited a recovery of 71% of the initial load. Initially such systems were studied by Peterson et al. [84].

In an independent investigation undertaken by Liu and Hsieh in 2006 [85], a thermally reversible crosslinked resin exhibiting epoxy-like characteristics was created using liquid monomers, namely trifunctional maleimide (TMI) and Trifuran (TF) compounds. TMI and TF, being soluble in solvents with low boiling points, facilitated processing at reduced temperatures. The crosslinked configuration of the TMI-TF substance displayed the ability to disassemble and rebuild during successive heating cycles [85] (Scheme 4).

Fig. 4 The mechanism of the Diels–Alder reaction, depicting the interaction between furan as the diene component and maleimide as the dienophile component in the self-healing process of polymers [78]



Scheme 1 [79]

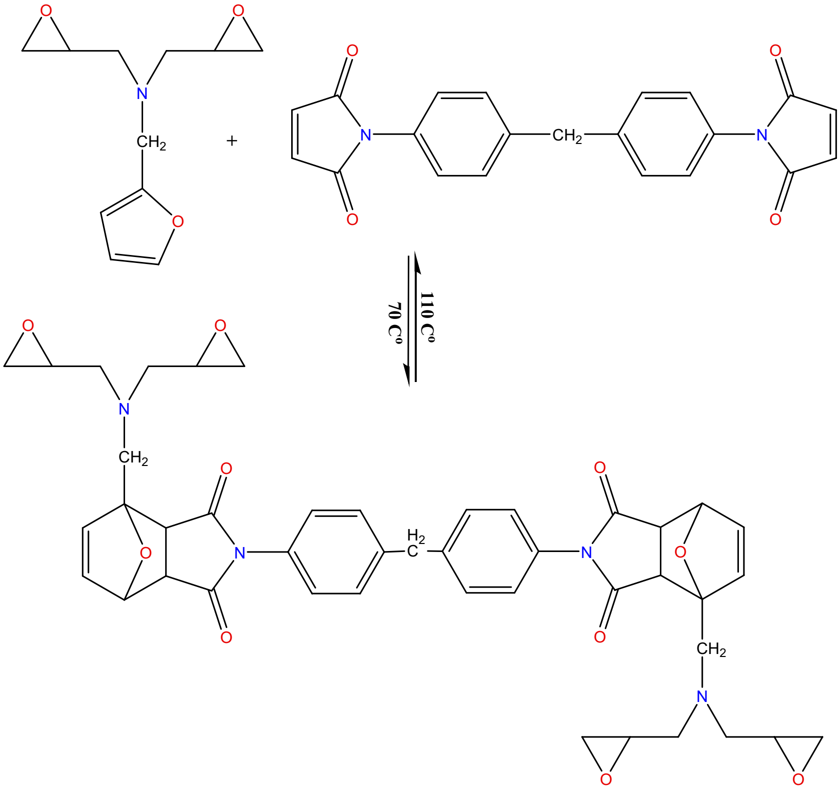


3.3 Maleimides

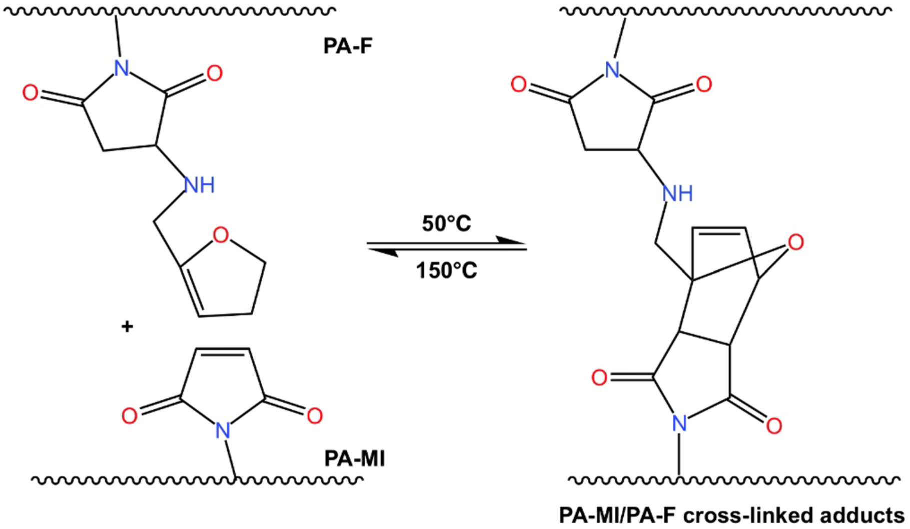
The self-repairing process hinges on the generation of adducts, categorized as exo or endo, resulting from the interaction between furan (diene) and maleimide (dienophile) functional groups. These adduct formations are pivotal in rejuvenating the material, facilitating the reinstatement of its structural integrity and functionality. For example, in a significant advancement, Chen et al. [18] introduced a transparent organic polymeric material that incorporates furan and maleimide moieties (Scheme 5). This material demonstrates the remarkable ability to undergo repeated mending or "re-mending" processes under mild conditions [18]. Furthermore, in another study, it was discovered that incorporating low-melting point monomers into the cross-linked network could enhance the self-healing efficiency by up to 80%, owing to their increased mobility within the network [86]. The applicability of maleimide chemistry has also been investigated for self-healing purposes in a cold-curing resin, which is commonly employed for infusing wind turbine blades (RIM resin) [87].

In a distinct investigation by Yoshie et al. [88], a networked structure was established utilizing a maleimide system via a Diels–Alder (DA) reaction involving furyl-telechelic poly (ethylene adipate) (PEAF2) and a tris-maleimide (M3). Upon dividing a film sample into two segments and reuniting the cut surfaces at 60 °C, the pieces were observed to rejoin. This repair process was facilitated by the reversible cross-linking reaction, which connected the severed surfaces [88]. In another instance involving custom-designed Polymethacrylate, a specially engineered polymethacrylate called Poly (furfuryl methacrylate) (PFMA) with a furfuryl group incorporated into its side chain was synthesized using atom transfer

Scheme 2 [81]



Scheme 3 [82]

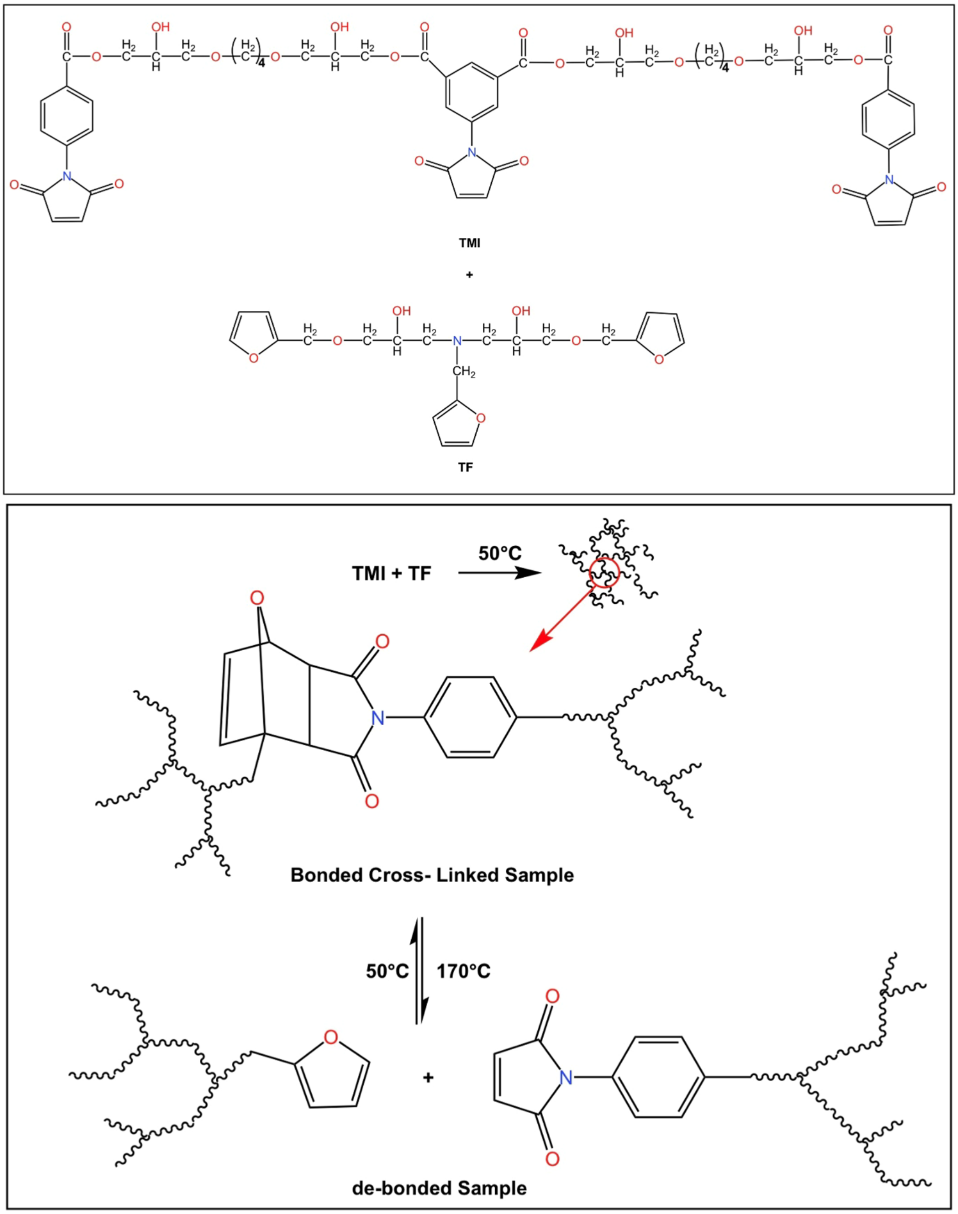


radical polymerization (ATRP) [89]. The reactive furfuryl group within this customized polymer was employed as a diene in the successful application of Diels–Alder (DA) chemistry, with a bismaleimide called 1,1-(methylenedi-4, 1-phenylene) bismaleimide (BM) serving as the dienophile [90]. The reversible characteristics of the resultant crosslinked polymer hybrids were verified through Fourier transform infrared (FTIR) and Differential Scanning Calorimetry (DSC) analyses (Scheme 6).

3.4 Polyurethanes

In the context of Polyurethanes, two innovative polyurethane formulations (1DA1T and 1.5DA1T) exhibiting both thermo-responsive and self-healing properties have been developed. These polyurethanes are engineered based on the Diels–Alder (DA) reaction between furan and maleimide groups. What distinguishes these polymers is their utilization

Scheme 4 [85]

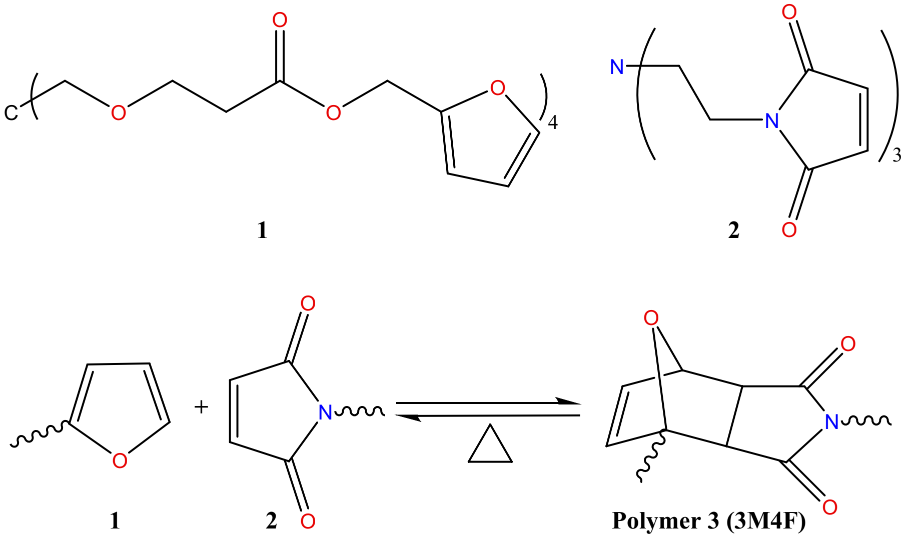


of the shape-memory effect, enabling crack faces to closely align and initiate the healing process. Unlike conventional self-healing materials, these polymers autonomously harness the shape-memory effect to naturally seal cracks, eliminating the need for external forces to facilitate closure [91]. Scheme 7 demonstrates the cross-linking between Furfuryl Alcohol (FA) with *N*-(2-hydroxyethyl)-maleimide (HEM) to give DA product.

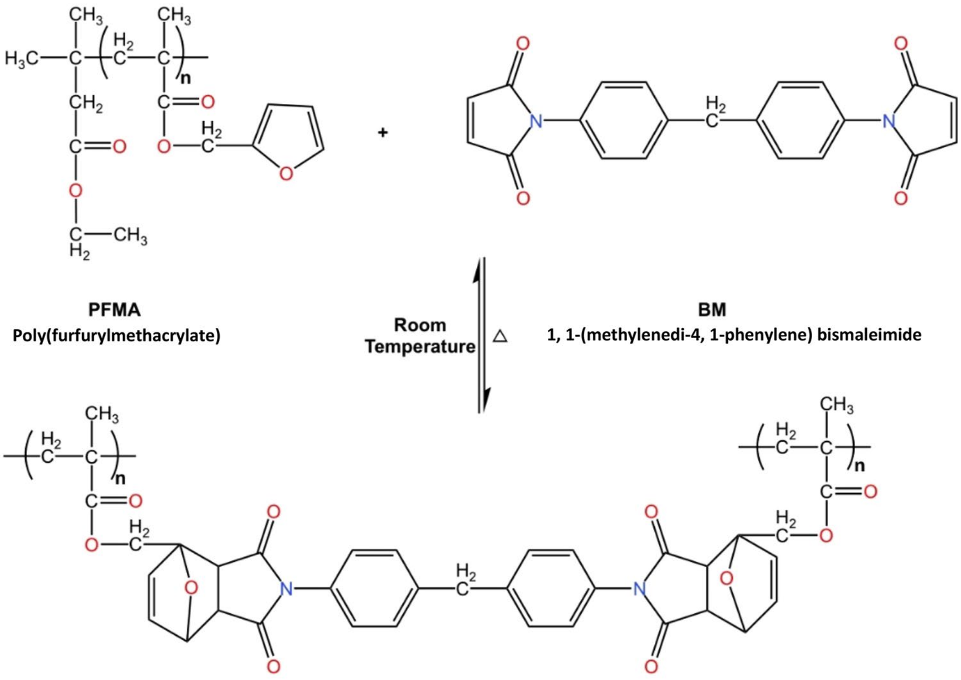
In their study on the creation and characterization of an innovative linear polyurethane, Du et al. [92] utilized a Diels–Alder (DA) reaction involving a polyurethane prepolymer capped with furan groups (MPF) and bismaleimide (BMI). This incorporation of DA bonds imparts thermal reversibility to the polyurethane, extensively analysed through techniques like 1H NMR, DSC, and Gel permeation chromatography (GPC). Moreover, the newly developed linear polyurethane featuring DA bonds exhibits remarkable self-healing properties under thermal stimulation, as evidenced by polarized optical microscopy. The self-healing efficacy, assessed by the restoration of breaking tensile strength post-damage and subsequent healing, can achieve an impressive 80% [92].

In a study conducted by Wei and Ma [93], the self-healing attributes of polyurethane were attained by integrating thermally reversible Diels–Alder (DA) bonds into the molecular configuration. Initially, a pre-polyurethane (HTK) featuring furan rings at its terminus was synthesized through the amalgamation of hexamethylene diisocyanate trimer and furfuryl alcohol. Subsequently, HTK was blended with bismaleimide (BMI) to generate the cross-linked

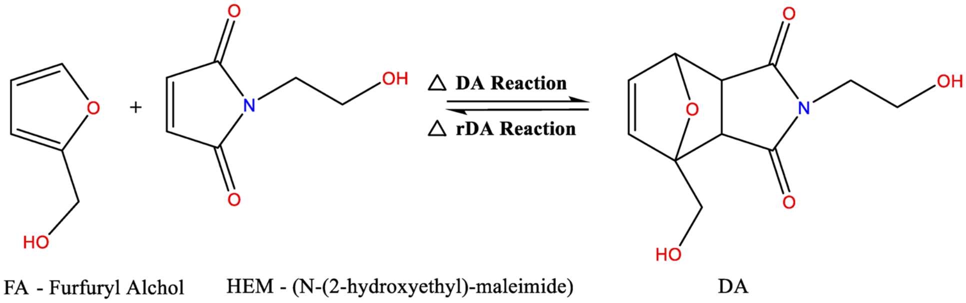
Scheme 5 [18]



Scheme 6 [90]

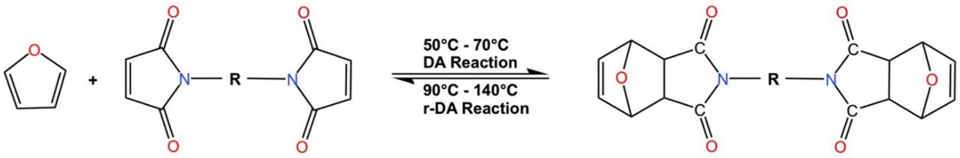


Scheme 7 [91]



polyurethane HTK-PU (Scheme 8). Finally, comprehensive characterization was performed on the HTK-PU material to assess its properties [93]. Self-healing polyurethanes with crosslinked structures were prepared using a Diels–Alder

Scheme 8 [93]



(DA) reaction. This synthesis involved the combination of a tri-functionalized iso-phorone diisocyanate (IPDI), a polypropylene-glycol prepolymer modified with furfuryl alcohol, and a commercially available bismaleimide [94]. The progress of the DA reaction was monitored at various temperatures using FTIR spectroscopy.

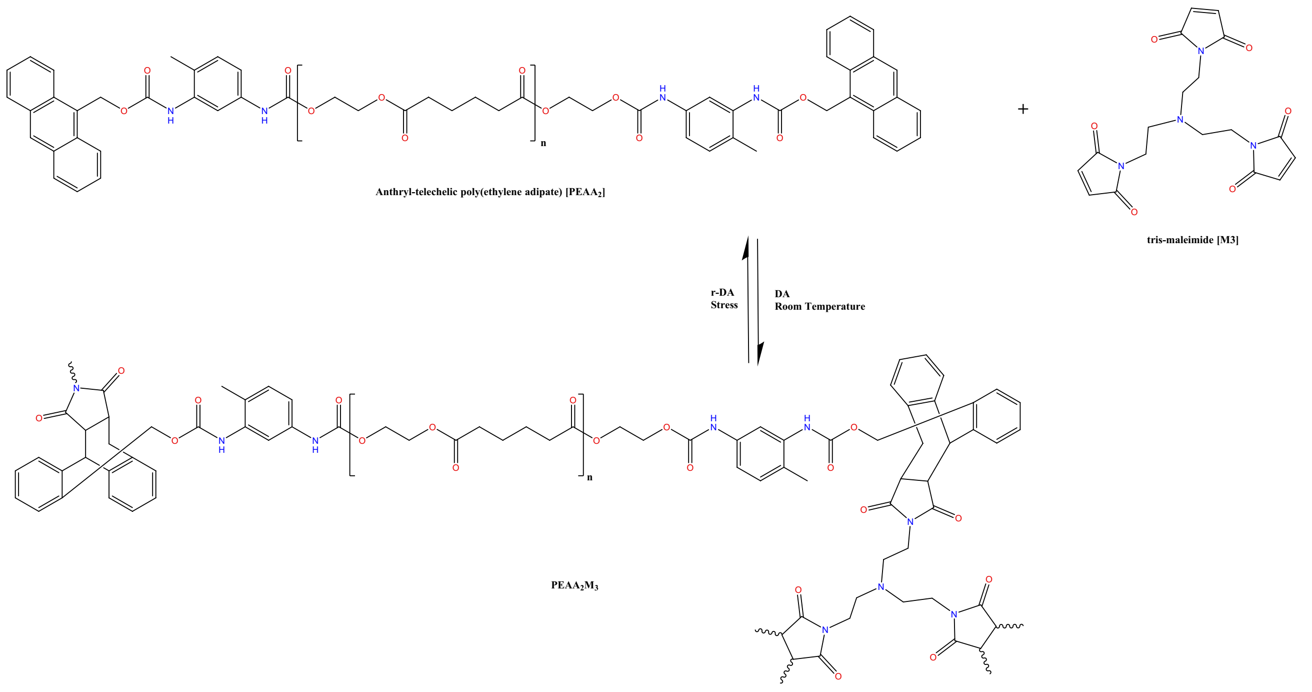
A novel approach was employed to synthesize thermos-responsive crosslinked polyurethanes (PHUs) by utilizing cyclo-carbonate/amine polymerization of cyclo-carbonate Diels–Alder (DA) adducts. The linear segments of the polymer incorporated di-cyclo-carbonate adduct, while the tetra-cyclo-carbonate adduct was polymerized as a cross-linker [95]. The thermal properties of the adducts were analysed using differential scanning calorimetry (DSC), revealing retro-Diel–Alders temperatures of 100 °C and 130 °C for both adducts. This represents the first instance of successfully preparing such thermo-responsive crosslinked PHUs using this methodology. In another research, Yang and his team introduced a new type of self-healing polyurethane that responds to multiple stimuli. They achieved this by incorporating a dynamic covalent chemical crosslinker that is responsive to stimuli and a polymer design that mimics biological systems. The crosslinker, which is unique to their design, was created using a Michael addition reaction involving thiols and bismaleimides. This approach resulted in chemically crosslinked polyurethanes that can self-heal and be recycled at high temperatures. Furthermore, these polyurethanes are responsive to various stimuli, including heat, changes in pH, and exposure to ammonia gas [96].

3.5 Anthracenes

Anthracene derivatives offer promising alternatives to furan compounds as dienes in Diels–Alder (DA) reactions. Research conducted by Syrett et al. [97] demonstrated that the anthracene-maleimide adducts integrated into polymer chains display enhanced thermal stability in contrast to furan-maleimide linkages. Additionally, the retro-Diels–Alder reaction of the anthracene-maleimide adducts was observed to take place at around 200 °C. However, the broken linkages could undergo reconnection through a DA reaction when the polymers were gradually cooled to room temperature [97]. Anthracene-maleimide derived polymers have traditionally lacked self-healing capabilities. Yoshie et al. [98] sought to overcome this drawback by introducing a groundbreaking self-mending polymer boasting exceptional thermal stability. Termed PEAA2M3, this polymer is crafted via the Diels–Alder (DA) reaction involving anthracene and maleimide components (Scheme 9). The network architecture of PEAA2M3 is established through the DA reaction between anthryl-telechelic poly (ethylene adipate) [PEAA2] and a tris-maleimide[M3]. Although the forward Diels–Alder (DA) reaction proceeds efficiently at ambient conditions, the backward DA reaction is initiated in response to mechanical strain. This mechanochemical reversibility mechanism facilitates self-repair of cracks in PEAA2M3 without external assistance, even at room temperature [98].

3.6 Caprolactones

Incorporating furan- and maleimide-terminated star-shaped oligomers into self-healing materials can lead to polymer networks formed via the Diels–Alder (DA) crosslinking, which may lack adequate mechanical properties to maintain their shape at temperatures exceeding the retro-Diels–Alder process's reaction temperature [99]. To address these inherent weaknesses, one possible solution involves utilizing multi-armed star-shaped polymer networks that undergo dual crosslinking via both the thermo-reversible Diels–Alder (DA) reaction and a thermo-irreversible addition reaction. This method presents a promising approach to bolstering mechanical properties and overcoming system limitations. Sugane et al. [100] investigated the potential of hydroxy-terminated 8-armed star-shaped ε-caprolactone oligomers (H8CLO) for self-healing purposes. These oligomers were synthesized through tripentaerythritol-initiated ring-opening polymerization of ε-caprolactone, yielding well-defined and functionalized structures. Furfuryl isocyanate and (4-maleimidophenyl) isocyanate were employed to introduce the required functional groups, reacting with the hydroxyl groups on the star-shaped oligomers to produce furan- and maleimide-functionalized star-shaped oligomers, designated as F8CLO and M8CLO, respectively. This method enabled precise incorporation of the desired moieties onto the polymer chains,



Scheme 9 [98]

providing essential components for the subsequent self-healing process [100]. In a distinct study, Defize et al. [101] undertook investigations involving 4-Arm star-shaped PCLs, which were effectively end-functionalized with furan and maleimide groups via consecutive esterification reactions, yielding high yields. The resultant crosslinked film, exhibiting a semi-crystalline nature, showcased remarkable shape memory attributes, as corroborated by cyclic thermomechanical analysis. It displayed an impressively high fixity ratio, surpassing 99%, alongside exceptional recovery ratios. Initial cycle assessments revealed a recovery ratio of 88%, with subsequent cycles achieving approximately 99%. The inclusion of star-shaped PCLs in the film facilitated facile disruption of the established network upon thermal treatment at 130 °C, enabling the reshaping of the shape memory polymer. Furthermore, subjecting the recycled material to re-curing at 65 °C led to a shape memory polymer retaining outstanding fixity and recovery ratios [101].

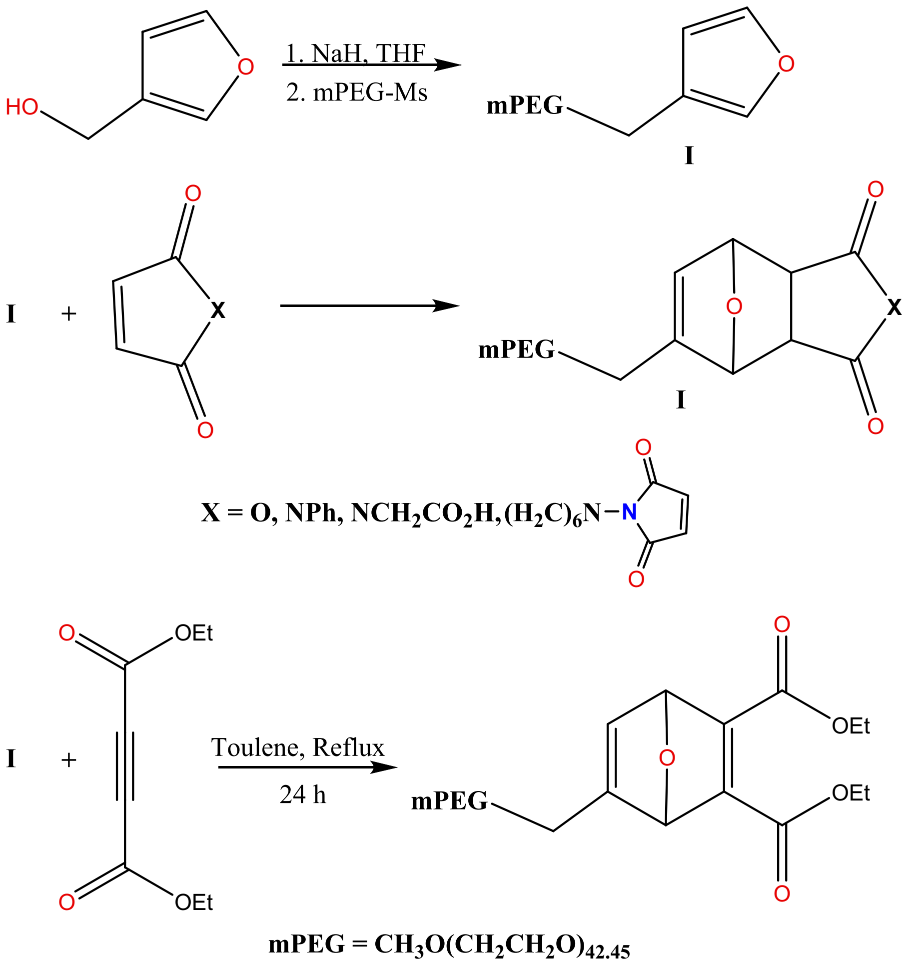
The application of Diels–Alder and retro-Diels–Alder reactions has demonstrated potential in enhancing the molecular mobility of PCL-based systems, thereby augmenting their crystallization capability. This advancement has spurred the creation of cross-linked semicrystalline polymers endowed with one-way and two-way shape-memory attributes. To delve deeper into this phenomenon, Raquez et al. [102] embarked on an investigation involving cross-linked poly(ε-caprolactone) (PCL)-based polyester urethane (PUR) systems, synthesized via Diels–Alder reactions employing reactive extrusion.

3.7 Others

The reversible cross-linking process mediated by the Diels–Alder (DA) reaction has been observed in a range of materials, demonstrating its versatility. Examples of these materials include poly(ethylene oxide), polyesters, crosslinked polylactic acid, and polyamides. The ability of the DA reaction to form and break cross-links in these materials contributes to their dynamic and self-healing properties.

Sedaghat-Herati et al. [103] synthesized a novel derivative of poly(ethylene glycol), designated as 3-[methoxypoly(oxyethylene)]methylene furan, denoted as **I**. The synthesis process involved the reaction of 3-furanmethanol with the mesylate of methoxypoly(oxyethylene) in tetrahydrofuran. Following this, compound **I** underwent Diels–Alder reactions with various compounds including *N*-phenylmaleimide, *N*-glycinylmaleimide, maleic anhydride, *N*,*N*-hexamethylene bismaleimide, and diethyl acetylene dicarboxylate, resulting in the formation of the respective adducts [103] (Fig. 5).

Fig. 5 The schematic synthesis of compound I, depicting its Diels–Alder reactions with different dienophiles and its reaction with diethyl acetylene dicarboxylate (DADC) [103]



In their research, Watanabe et al. [104] successfully created recyclable polymers using the Diels–Alder (DA) reaction. They synthesized furyl-telechelic poly(ethylene adipate) [PEA2F] and underwent copolymerization with bis- and tris-maleimides at 60 °C. The reaction with bismaleimide resulted in a partially formed polymer with a molecular weight only twice that of PEA2F. Conversely, the reaction with tris-maleimide yielded a three-dimensional network structure with elasticity at room temperature. These DA products, when heated to 145 °C, could be easily disconnected through a retro-Diels–Alder reaction, restoring the initial macromonomer, PEA2F. This highlights the potential of the DA reaction for crafting recyclable polymers with customized properties [104]. In a separate study, Yamashiro et al. [105] introduced a novel poly(lactic acid) compound (PLA) with self-healing and recyclable features. These PLA compounds consisted of furan-modified poly (lactic acid) and a maleimide linker, forming cross-links via the Diels–Alder cyclo-addition between the furan and maleimide functionalities. The resulting thermally reversible cross-linked PLA (TCP) exhibited remarkable shape-memory behaviour due to its cross-linked structure below the bond-association temperature (100 °C). Moreover, this unique characteristic allowed for the recycling of TCP by melting it above the bond dissociation temperature (160 °C) [105].

Aromatic polyamides are a significant class of high-performance polymers that have garnered considerable attention in recent years. Alongside the development of new polyamide materials, there has been a focus on the functionalization and modification of polyamides. Liu and Chen [82] conducted research involving polyamides with varying amounts of maleimide (PA-MI) and furan (PA-F) pendant groups. PA-F polyamides, which possess furan pendant groups, were synthesized through a Michael addition reaction between furfuryl amine and maleimide-containing polyamides (PA-MI). By employing Diels–Alder (DA) and retro-Diels–Alder (retro-DA) reactions, thermally reversible cross-linked polyamides were obtained from the PA-MI and PA-F polyamide systems [82].

3.8 (2 + 2 cycloaddition)

In addition to the thermally induced [4 + 2] cycloaddition Diels–Alder reaction, there are other functional groups that possess the ability to undergo photo-induced [2 + 2] cycloaddition reactions. These include functional groups such as cinnamoyl [106], coumarin, and tri-fluorovinyl ether groups. Unlike the thermally induced reactions, these photo-induced reactions occur upon exposure to specific wavelengths of light. The excited state of these functional groups facilitates the formation of new chemical bonds, leading to the crosslinking or reformation of the polymer network. This photo-responsive behavior offers an alternative and tuneable approach for achieving self-healing in polymeric materials, expanding the range of possibilities for designing advanced self-healing systems. The self-healing reactions were successfully accomplished through the utilization of the photochemical [2 + 2] cycloaddition mechanism involving 1,1,1-tris-(cinnamoyloxy-methyl)ethane (TCE) monomer. This photochemical process resulted in the formation of cyclobutane structures by the reversible conversion of cyclobutane to C=C bonds [107]. Similar to the self-healing polymers based on anthracene-maleimide adducts [97], polymers containing cinnamoyl groups also exhibited self-healing properties through the disconnection of bonds induced by cracks and the regeneration of bonds induced by light [74] (Fig. 3B-1). Upon exposure to UV light (> 280 nm), the cleavage of C–C bonds within the cyclobutane rings between the 1,1,1-tris-(cinnamoyloxy-methyl)ethane (TCE) monomers took place, leading to the restoration of the original cinnamoyl groups. This photocleavage process enabled the reversal of the cyclobutane crosslinks, facilitating the healing of the material. Through the [2 + 2] photocycloaddition reaction, the broken cyclobutane bonds could reform upon subsequent UV irradiation, allowing for the self-healing of the polymer. The application of additional heat at a temperature of 100 °C was found to enhance the healing efficiency to a greater extent. Compared to thermally induced Diels–Alder reaction systems, the photo-induced healing process was significantly faster, with a high recovery efficiency achieved in a short period of time (approximately 10 min) [74].

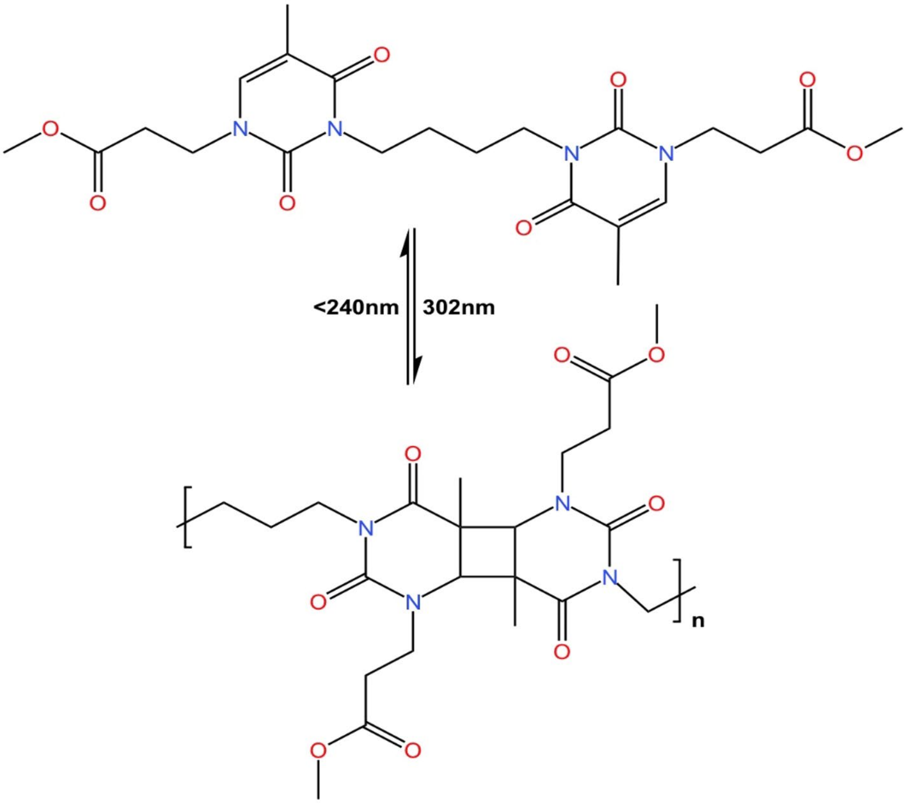
Shortly after this groundbreaking research, Bowman and his colleagues, conducted further investigations. They successfully created a flexible network with a glass transition temperature of approximately − 25 °C by combining pentaerythritol tetra kis(3-mercaptopropionate) and tri-ethylene-glycol divinyl-ether in stoichiometric proportions. By subjecting the specimens to irradiation for 15 min at wavelengths between 320 and 500 nm, with an intensity of 30 mW cm^{-2}, the photo-initiator underwent homolytic photolysis, generating radicals within the specimens [108].

In a separate study conducted by Ling et al. [75], the focus was on the reversible reaction of coumarin through 2 + 2 cycloaddition. They synthesized a novel polyurethane using isophorone diisocyanate, polyethylene glycol, and a photo-reversible component called 5,7-bis(2-hydroxyethoxy)-4-methylcoumarin. By utilizing the reversible behaviour of coumarin, which undergoes photodimerization and photocleavage, the polyurethane exhibited the ability to undergo repeated crosslinking and de-crosslinking upon successive UV irradiation at 350 and 254 nm [75] (Fig. 3B-2). The correlation between the healing efficiency and the macromolecular structure highlights the significance of chain mobility on the surfaces of fractured materials in the process of crack healing [109]. In a separate study conducted by Klukovich et al. [110], it was observed that the mechanical stress-induced cleavage of perfluorocyclobutane (PFCB) polymers, as depicted in Fig. 3B-3 leads to the generation of trifluorovinyl esters (TFVE), which can subsequently undergo cyclo-reversion to reform the original structure.

In their investigation, Urban et al. (2009) presented a novel polyurethane network that demonstrated remarkable self-repairing properties when exposed to UV light. The network was formulated by incorporating an oxetane-substituted chitosan precursor into a two-component polyurethane system. Upon experiencing mechanical damage, the four-membered oxetane rings within the network underwent ring-opening, leading to the generation of two reactive ends. Subsequent exposure to UV light emitted by a 120 W fluorescent UV lamp at a wavelength of 302 nm induced chain scission in the chitosan component. This chain scission facilitated the formation of crosslinks between the reactive oxetane ends and the chitosan fragments, thereby enabling the repair of the polyurethane network. The ability of the network to undergo UV-triggered repair through the selective cleavage and reformation of bonds highlights its potential for self-healing applications. Remarkably, these materials exhibited the ability to self-repair in less than an hour [72].

In another study performed by Nicolaÿ et al. [111] a one-step Mitsunobu reaction was employed to synthesize a di-methacrylate tri-thiocarbonate cross-linker (TTC) with a yield of 69%. The reaction involved *S*,*S*′-bis(iso-butyric acid)-tri-thiocarbonate and 2-hydroxyethyl methacrylate. To prepare PMMA gels, MMA was copolymerized in the presence of the TTC crosslinker through radical polymerization. As a matrix polymer, poly (*n*-butyl acrylate) (PBA) was chosen due to its low T_g value (− 50 °C), which provided enhanced chain mobility at room temperature. To initiate the healing process, acetonitrile was utilized as a solvent because it neither absorbs UV light nor excessively swells the crosslinked

Scheme 10 [113]



polymers [111]. The study demonstrated that the covalently crosslinked gels exhibited the ability to undergo repeatable self-healing and macroscopic fusion of separate pieces simultaneously [70].

In 2011, Arumugam and Popik [112] introduced a novel light-induced hetero-DA (Diels–Alder) cycloaddition, which combined the advantages of both photo-induced and thermally reversible mechanisms. The key feature of this approach was the utilization of a naphthalene moiety containing methyol and hydroxyl groups positioned ortho to each other. Upon exposure to UV irradiation, this naphthalene moiety underwent a transformation, leading to the formation of o-naphtha-quinone methide (o-NQM). The generated o-NQM species acted as a hetero diene-like group, capable of participating in a hetero-DA reaction with a dienophile. Notably, any unreacted o-NQM could readily revert to its initial precursor state. This light-induced hetero-DA cycloaddition provided a versatile and reversible method for achieving molecular transformations, enabling the design of dynamic systems with tuneable properties and functionalities [112].

For thymine-based group, Abdallh et al. [113] conducted a study on linear polymers based on thymine, which exhibited self-healing properties and photo-reversible characteristics. Crosslinking of bis-butyl thymine monomers was achieved by UV irradiation at 302 nm, and the incorporation of thymine moieties endowed the polymer matrix with the ability to undergo (2 + 2) cycloaddition reactions that could be reversed under specific photo-irradiation conditions. Healing of the polymer was accomplished by subjecting it to UV irradiation with a wavelength below 240 nm (Scheme 10). It was proposed that this reaction involved depolymerization triggered by photocleavage and UV exposure, resulting in a reduction of the glass transition temperature (T_g). The decrease in T_g promoted increased chain mobility within the matrix, rendering the material more flexible. Subsequently, the mechanical properties of the material were nearly fully restored after the healing process [113].

The challenge of scaling up self-healing materials that rely on cycloaddition reactions primarily stems from the requirement of using specialized monomers or precursors. To address this limitation, Kim et al. [114] proposed a solution by developing healable microcapsules composed of homopolymers. These microcapsules have the ability to initiate a photochemical (2 + 2) cycloaddition reaction, enabling crack healing even when dispersed within any polymer matrix [114]. This approach offers the potential to overcome the applicability issues associated with self-healing materials based on cycloaddition reactions and opens up possibilities for broader implementation in various polymer systems.

3.9 (4 + 4 cycloaddition)

The application of photo-crosslinking in self-healing polymers extends beyond (2 + 2) cycloaddition reactions. Numerous studies have explored the utilization of anthracene and its derivatives to create photo-reversible bonds through (4 + 4) cycloaddition reactions [77, 115]. Compared to the (2 + 2) cycloaddition reactions of coumarin and cinnamate, (4 + 4) cycloaddition is considered more reliable due to its resistance to hydrolysis and isomerization reactions, making it a stable and robust photo-triggered reaction [76]. The application of reversible thiol-ene click reactions has extended to the realm of Michael addition reactions. Within this context, a tri-thiol compound was subjected to a reaction with a bisbenzylcyanoacetamide derivative, resulting in the formation of a dynamic polymer network. This network exhibited intriguing self-healing properties when exposed to temperatures surpassing 60 °C [76] (Fig. 3C). A significant body of literature supports the use of (4 + 4) cycloaddition in developing self-healing polymers. Anthracene and its derivatives can undergo (4 + 4) cycloaddition when subjected to long-wave UV irradiation (> 350 nm). This cycloaddition reaction can be reversed by exposing the material to short-wave UV light (< 300 nm). [77] The [4 + 4] cycloaddition reaction depicted in Fig. 3D, presents a reversible polymerization process for anthracene derivatives. This reaction involves the opening of a four-membered ring at 254 nm and its subsequent closure at 366 nm.

In another experiment Froimowicz et al. [116] synthesized a dendritic polymer modified with anthracene to create self-healing materials. The researchers conducted an experiment where a damaged sample of the crosslinked dendritic polymer was subjected to sequential irradiation at 254 nm and 365 nm. Remarkably, the artificial scratch, measuring 1.51 mm^2, was successfully repaired. Importantly, the disconnection and reconnection of the polymer networks, as well as the self-healing processes, were found to be repeatable across multiple cycles. Several additional instances can be found where photo-responsive anthracenes have been utilized in dendritic polymers. For instance, Sako and Takaguchi demonstrated the application of an anthracene-containing dendron as a photo responsive hydrogelator [117], while Yanagimoto et al. [118] described the synthesis of surface-block dendrimers through the [4 + 4] photo-cyclo-addition of anthryl dendrons.

Connal et al. [119] employed an orthogonal patterning technique to synthesize core crosslinked star (CCS) polymers with a low glass transition temperature (T_g). These CCS polymers consisted of anthracene-functionalized poly(methylacrylate) chains, which exhibited remarkable photo-reversibility due to the presence of anthracene end groups. Although the healing ability, extent of reversibility, and tensile properties of these films were not investigated, they appear to be promising candidates for stable and porous self-healing films. Their reversible nature and notable mechanical properties make them suitable for such applications [119].

3.10 Chain exchange reactions

3.10.1 Disulfide-exchange

In self-healing applications, another category of reactions employs covalent bonding that enables chain exchange reactions. These approaches differ from supramolecular networks as they leverage the dynamic reversibility of covalent bonds. Self-healing processes can also be facilitated by sulphur, selenium, and silicone chemistry, which play crucial roles in biological systems. Thiol-ene chemistry, in particular, has gained significant attention due to its inherent strength and versatility, offering numerous synthetic possibilities [120, 121]. Previous research has indicated that disulfide bonds have the ability to undergo metathesis exchange reactions, whereby adjacent S–S bonds are broken and reformed through the involvement of free radical or ionic intermediates [122, 123]. Tri-thiocarbonates have been utilized to harness the unique properties of reversible rearrangement reactions involving S–H and S–S bonds. In this regard, the copolymerization of *n*-butyl acrylate with a tri-thiocarbonate crosslinker played a crucial role in promoting increased mobility of polymer segments. This enhanced mobility led to the homolysis of C-S bonds within the polymer structure, enabling the reversible rearrangement of the polymer chains. The ability of the C–S bonds to break and reform allowed for the dynamic exchange of polymer segments, ultimately resulting in a self-healing behaviour of the material [111]. The reversible nature of S–S bonds, wherein they can be reduced to form two thiol (S–H) groups and oxidized to restore the disulfide (S–S) linkages, holds great potential for applications in self-healing materials (Fig. 6). Kamada et al. [124] utilized a modified core-first approach to synthesize a poly(*n*-butyl acrylate)-based star polymer, polyEGDA-(polyBA)n, via atom transfer radical polymerization. Dynamic light scattering analyses indicated an average diameter of around 20 nm for the cleaved star polymer. The research demonstrated that the SS-functionalized star polymers responded to reduction–oxidation

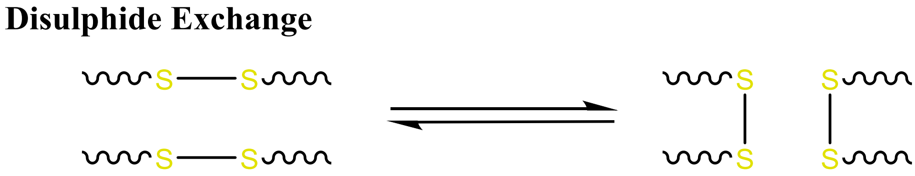


Fig. 6 Disulfide exchange chain reaction [124]

conditions, signifying the cleavage and re-formation of disulfide bonds. These responsive star polymers possess potential applications as intelligent polymeric materials, including self-healing materials [124].

Polymer networks containing reversible disulfide (S–S) bonds can be produced using poly(*n*-butyl acrylate)-grafted star polymers. In this scenario, the crosslinked cores are established through poly(ethylene glycol diacrylate) and macroinitiators, enabling sequential chain extension involving bis(2-methacryloyl)oxyethyl disulfide [125]. Another approach involves employing photoinduced thiol-ene click-type radical addition, resulting in lightly sulfide-crosslinked polysulfide-based networks with an excess of thiols. The subsequent oxidation of these thiols facilitates the formation of dynamic disulfide crosslinks, leading to the creation of dual sulfide-disulfide crosslinked networks characterized by rapid self-healing properties [126].

The dynamic rearrangement ability of disulfide (S–S) bonds in response to various stimuli such as heat, UV light, and redox conditions is a significant advantage of disulfide exchange reactions. When these bonds are incorporated into gel networks with low glass transition temperatures (T_g), they enable temperature-reversible self-healing capabilities. By incorporating disulfide chemistry, a self-healing capability was introduced into a covalently cross-linked rubber. This achievement was made possible by incorporating disulfide groups within the network that are capable of exchanging, thereby renewing cross-links across damaged surfaces. The healing process can be repeated multiple times [127, 128]. The incorporation of S–S bonds in hydrogels along with acylhydrazone and other disulfide bonds presents an attractive feature. When the hydrogel is damaged, the S–S linkages can be cleaved, leading to the generation of free radicals. These free radicals can then undergo rapid reactions with other S–S bonds, promoting the self-healing process. The cleavage of S–S bonds can be activated through various methods such as photolysis, heating, or oxidation. However, the precise lifetime of the free radicals and the underlying mechanism of self-healing at ambient temperature are not yet fully understood [128].

In their investigation, Barcan et al. [129] presented an effective organocatalytic approach for the ring-opening polymerization of cyclic carbonates with pendant dithiolanes, particularly trimethylene carbonate/dithiolane (TMCDT). Poly(ethylene oxide) diols were employed as initiators, yielding water-soluble triblock (ABA) copolymers. These copolymers featured a central poly(ethylene oxide) block and terminal dithiolane blocks. Hydrogels derived from these triblock copolymers, in conjunction with a cross-linking dithiol, demonstrated dynamic behaviour attributed to the reversible ring opening of the pendant 1,2-dithiolanes. These materials exhibited self-healing characteristics, enabling rapid restoration of their mechanical properties following significant strain deformation. Importantly, these hydrogels could be injected using a syringe, enhancing their versatility for diverse applications [129]. In research led by Rekondo et al. [130], bis(4-aminophenyl) disulfide was effectively employed as a dynamic crosslinker in the fabrication of self-healing poly(urea-urethane) elastomers. These elastomers showcased remarkable healing capability at ambient temperature, achieving full recovery without the need for catalysts or external assistance [130]. The autonomous healing of Polyurethane was documented, demonstrating its ability to self-heal when subjected to temperatures above 80 °C, resulting in the nearly complete restoration of its mechanical properties [131].

3.10.2 Siloxane-exchange

Siloxane-exchange reactions are fundamental in the self-healing mechanism of silicone-based polymers. These reactions involve the reversible exchange of siloxane (Si–O–Si) bonds within the polymer network Under stress, the siloxane bonds present in silicone networks can experience cleavage, which can compromise the material's integrity. However, the addition of an acidic or basic catalyst can facilitate stress relaxation and promote self-healing behaviour. The catalyst promotes the rearrangement and reformation of the cleaved siloxane bonds, allowing the material to recover its original structure and properties. Silicone-based materials have garnered considerable attention for their inherent ability to undergo restructuring in specific conditions. Among them silicone-based polymers characterized by their dynamic network rearrangements hold significant technological promise as self-healing materials. Despite this promise, they remain relatively unexplored compared to other materials in the field [132].

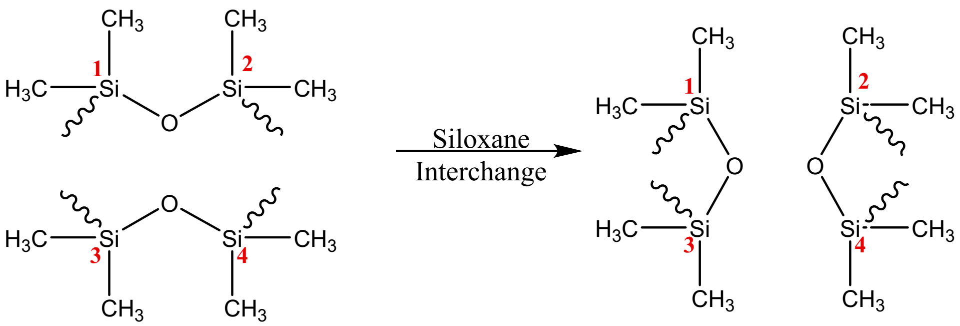


Fig. 7 Siloxane-exchange chain reaction [133]

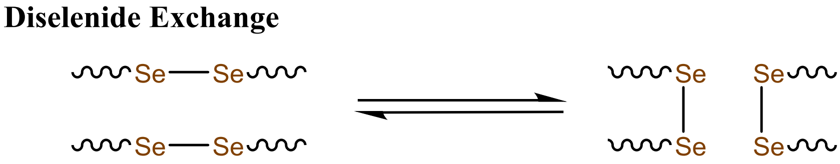


Fig. 8 Selenide exchange chain reaction [139]

An illustrative instance involves the utilization of tetramethylammoniumsilanolate as an initiator for the ring-opening copolymerization of octamethylcyclotetrasiloxane and bis(heptamethylcyclotetrasiloxanyl)ethane. This particular synthesis yielded a polymer characterized by ethylene bridges and active silanolate end groups, which endowed it with the remarkable ability to undergo self-healing [133] (Fig. 7). The energy and biomedical sectors have shown significant interest in silicone-based materials possessing self-healing capabilities, making them highly appealing [134–136]. High dielectric permittivity is crucial in applications such as energy storage devices, electrical insulation, and capacitors. By combining self-healing properties with excellent dielectric permittivity, these materials offer significant advantages and potential for advanced applications in the energy and biomedical fields. To achieve the desired properties, an interpenetrating polymer network (IPN) consisting of silicone elastomer and ionic silicone polymers can be employed. This approach combines the unique characteristics of both components to create a synergistic material with enhanced self-healing capabilities and improved dielectric permittivity [137]. The achievement of self-healing in silicone-based polymers has been demonstrated through the utilization of various strategies. One approach involves incorporating thiol-functionalized silicone oils into the polymer matrix. These thiol groups can undergo reversible thiol-disulfide exchange reactions, enabling the healing of the material. Additionally, the incorporation of silver nanoparticles further enhances the self-healing capability by providing additional crosslinking sites and promoting efficient healing. Another approach utilizes magnetic Fe3O4 nanoparticles, along with mussel-inspired metal-coordination bonds involving dopamine molecules. The Fe3O4 nanoparticles, which possess magnetic properties, can be used as a reinforcing filler in the silicone-based polymer [138].

3.10.3 Selenide-exchange

An additional example illustrating a chain side reaction is selenide exchange. In their study, Ji et al. [139] successfully incorporated dynamic di-selenide bonds into polyurethanes, enabling the development of self-healing materials that can be assisted by visible light (Fig. 8). In another study conducted by An et al. [140], the incorporation of aromatic di-selenides into polyurethane networks was demonstrated. This was achieved by employing a para-substituted amine diphenyl diselenide. The resulting materials exhibited accelerated self-healing compared to disulfide-based counterparts, along with the advantageous ability to undergo reprocessing at temperatures as low as 100 °C [140].

3.10.3.1 Some other dynamic covalent re-bonding The scientific community is indeed captivated by covalently bonded self-healable hydrogels due to their vast range of biomedical applications. These hydrogels, characterized by strong chemical bonds within their polymer networks, offer unique advantages for various fields within biomedicine. In the context of hydrogels, Schiff-base linkages can be incorporated into the polymer network using functional monomers or crosslinkers containing aldehyde or amine groups. The reversible nature of Schiff bases allows for the dynamic exchange

Fig. 9 Schiff-base bond regeneration [142]

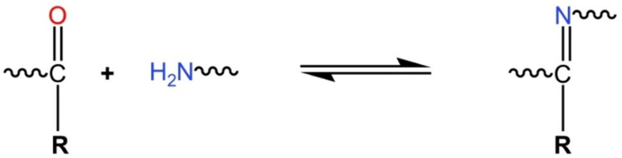
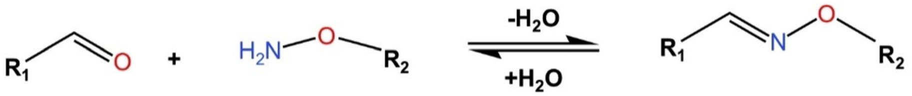


Fig. 10 Oxime rebonding [146]



of bonds within the hydrogel, enabling the material to self-heal in response to damage or mechanical stress [141]. An illustrative example of self-healing hydrogels utilizing reversible Schiff-base linkages involves a synthetic pathway depicted in (Fig. 9). The hydrogel is prepared by reacting OH-PEG (polyethylene glycol with hydroxyl end groups) with 4-formylbenzoic acid, followed by the incorporation of glycol chitosan.

When subjected to significant dynamic strain, such as stretching up to 300%, the hydrogel undergoes a remarkable transition from an initial elastic modulus of approximately 1.5 kPa to 10 Pa, resulting in gel-to-sol transitions [142]. This behavior is attributed to the reversible nature of the Schiff-base linkages within the hydrogel network. The unique properties of this self-healing hydrogel make it particularly suitable for biomedical applications, especially in the context of central nervous system repair.

The incorporation of dynamic reversible acylhydrazone linkages into Schiff-base networks can be accomplished by utilizing acylhydrazines and aldehyde functionalities. This approach enables the formation of Diels–Alder crosslinked networks that exhibit self-healing properties [143]. The hydrogel system is based on the incorporation of Schiff-base and amine functionalities into the hydrogel network. The Schiff-base reaction involves the reaction between aldehyde groups and amine groups, forming covalent bonds that contribute to the crosslinking of the hydrogel. Additionally, the amine groups in the hydrogel interact with micelles, which further reinforce the network structure. The combination of self-healing capabilities, extensibility, and compressibility makes this hydrogel system highly suitable for wound-dressing applications [144].

Oximes and Hydrozenes (C=N–X) are commonly utilized conjugates that exhibit labile behaviour towards hydrolysis. The incorporation of hydrozenes and oximes into copolymers through the radical polymerization of *N*,*N*-dimethylacrylamide (DMA) and diacetone acrylamide (DAA provides a versatile platform for the development of self-healing materials [145]. These copolymers, known as p(DMAA-stat-DAA), possess water solubility and can be chemically crosslinked by employing difunctional alkoxyamines. The crosslinking process for the formation of hydrogels involves the formation of oxime bonds, which are key to the gelation process. This is achieved by combining suitable precursors containing oxime functional groups under specific conditions. One approach is to introduce excess monofunctional alkoxyamines into the system, which promotes competitive oxime exchange reactions. These reactions occur under acidic conditions at a temperature of 25 °C. Furthermore, polyurethane-like dynamic covalent polymers, specifically poly(oxime-urethanes), can be synthesized to exhibit self-healing properties at higher temperatures, specifically 120 °C. These polymers are formed by incorporating oxime and urethane functionalities into the polymer backbone (Fig. 10). The reversible nature of oxime bonds enables the dynamic rearrangement of the polymer chains, leading to the self-healing capability of the material [146].

A notable example in the field of self-healing materials involves the utilization of dynamic acylhydrazone bonds in a crosslinked network with self-healing capabilities (Fig. 11). This was accomplished through a series of reactions starting with the condensation of acylhydrazines at both ends of polyethylene oxide (PEO). Subsequently, these functionalized PEO chains were further reacted with aldehyde groups derived from tris[(4-formylphenoxy)methyl]ethane [147]. These self-healing networks harness the reversible formation of acylhydrazone bonds, as illustrated in the diagram, to exhibit self-healing properties that can occur even at ambient conditions. The equilibrium nature of the acylhydrazone bond formation allows for the dynamic exchange of bonds, enabling the material to repair itself when damaged [148, 149].

A notable example in the field of self-healing materials involves the use of trithiocarbonates (TTC) as a promising alternative. These trithiocarbonates undergo dynamic covalent reshuffling reactions, facilitated by a free radical mechanism, leading to the introduction of dynamic properties in materials. As depicted in the Fig. 12 the trithiocarbonate groups within the polymer network can undergo cleavage in the presence of free radicals generated through a free

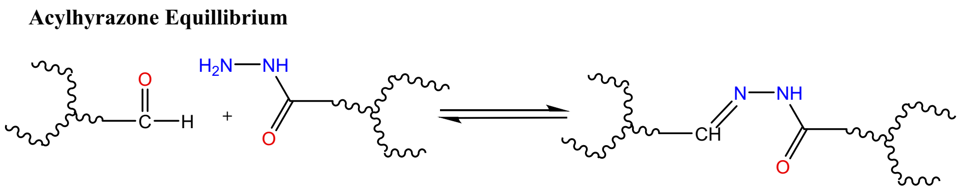


Fig. 11 Acylhdrazone equilibrium [148]

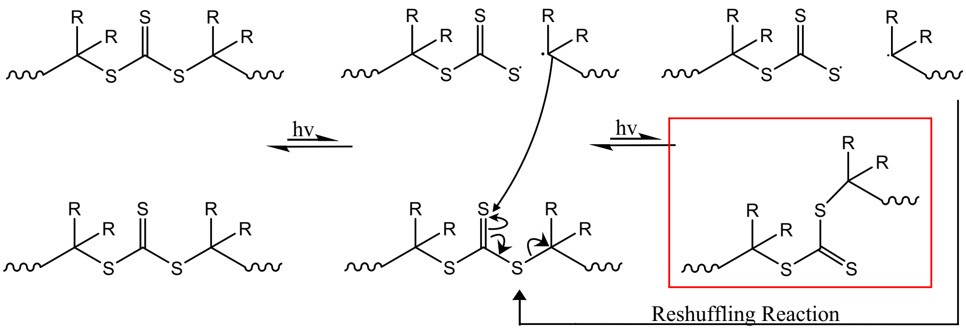


Fig. 12 Trithiocarbonates reshuffling reaction [111]

radical mechanism. This cleavage leads to the formation of new covalent bonds, enabling the reshuffling of the network structure. Initially, this approach was introduced in poly(methyl methacrylate) (PMMA) and polystyrene (PS) gels as a covalent crosslinker. The incorporation of trithiocarbonates into the polymer network allows for the formation of reversible bonds that can undergo reshuffling in response to external stimuli or damage [111]. Further investigations revealed that the cleavage of C–S bonds in trithiocarbonate (TTC) crosslinkers could be triggered by photo-stimulation. This exciting discovery opened new possibilities for achieving self-healing capabilities in polymer matrices. The polymer matrix was created via reversible addition-fragmentation chain transfer (RAFT) copolymerization of *n*-butyl acrylate (BA) and a TTC crosslinker, facilitating the formation of a network with heightened segmental mobility, essential for effective self-healing. This enhanced mobility permits repetitive network repair through exposure to UV radiation at 330 nm. Upon such irradiation, the specific wavelength triggers the cleavage of C–S bonds in the TTC crosslinker, generating free radicals. These radicals initiate a cascade of reactions, including sulphur atom exchange and bond reformation, enabling autonomous network healing [70].

Boronic acids exhibit a diverse range of dynamic covalent bonds [146]. One method to achieve this is through reversible hydrolysis, where dehydration of boronic acids leads to the formation of boroxines [150]. The equilibrium between boroxines and boronic acids can be modified by adjusting factors such as temperature, the introduction of a Lewis base, or altering the concentration of water. Boronic acids offer a unique advantage in self-healing materials due to their capacity to establish reversible dynamic covalent bonds with diols, resulting in the creation of cyclic boronate esters. This property has been exemplified through the development of hydrogels that can undergo repeated healing under normal environmental conditions. The creation of these hydrogels involved the utilization of photoinitiated radical thiol-ene click chemistry. This method enables the formation of covalent bonds between thiol groups and ene functional groups under the influence of light. By incorporating boronic acids and diol-containing compounds into the hydrogel formulation, the reversible dynamic covalent bonds between boronic acids and diols can be established [151] (Fig. 13).

By combining the reversible and dynamic chemistries of boronate ester and disulfide bonds, a novel approach has emerged for creating hydrogels with versatile properties. These hydrogels exhibit responsiveness to changes in pH, glucose concentration, and redox conditions, while also possessing the remarkable ability to self-heal [152]. Hydrogels capable of self-repair can also be produced through covalent transesterification reactions involving boronic acid and diols. This approach leverages the reversible characteristics of boronic acid-diol interactions, facilitating dynamic bonding and restructuring within the hydrogel framework [45]. The self-repairing hydrogels, linked via boronate ester bonds, exhibit impressive self-healing capabilities in both neutral and acidic conditions. This attribute stems from integrating an intramolecular coordinating boronic acid monomer, notably 2-acrylamidophenylboronic acid, into the hydrogel framework [153]. Boronic acid-modified artificial hydrogels have emerged as encouraging platforms for three-dimensional (3D) cell culture [154].

In the realm of designing self-healing gels with dynamic covalent bonds, a diverse range of reactive groups beyond boronic acid and boronate ester can be employed. Among these options, alkoxyamines offer the advantage of reversible reactions, allowing for the formation and reformation of covalent bonds within the gel network. This dynamic behaviour

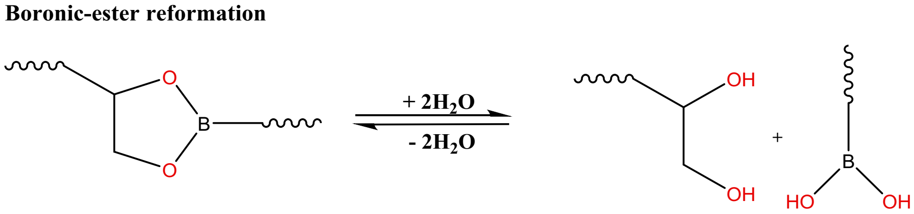


Fig. 13 Boronic-ester reformation [151]

enables the gel to undergo self-healing processes, wherein damaged or broken bonds can be repaired or regenerated through the exchange of reactive species. However, it is important to acknowledge that the sensitivity of alkoxyamines to atmospheric oxygen at elevated temperatures presents a challenge. The presence of oxygen can trigger the dissociation of C–ON bonds, resulting in the loss of dynamic covalent behaviour and compromising the self-healing capabilities of the gel [48].

Moreover, there are polyrotaxanes that utilize boronic linkages for the crosslinking of ring molecules and vinyl polymers, allowing for the reversible formation and reformation of bonds. These polyrotaxanes serve as another illustrative example of materials capable of rapid self-recovery in the event of damage [155]. To address the need for hydrogels that can endure repeated loading–unloading cycles within a limited timeframe while also exhibiting self-healing capabilities, researchers have developed hydrogels with double networks [156]. These hydrogels aim to achieve toughness levels comparable to rubber materials. In order to overcome this challenge, polyurethane-based hydrogels were prepared with enhanced dipole–dipole and hydrogen bonding interactions [157]. These materials exhibit mechanical properties that surpass those of conventional double-network hydrogels, while also possessing the ability to self-heal.

4 Free-radical rebonding

Free radicals are the dominant reactive species produced when chemical bonds are broken. Although they readily engage in reactions in gaseous and liquid environments, their reactivity is notably diminished within solid polymer networks. Despite the prolonged lifetimes of free radicals within polymer networks, the successful coupling of two cleaved reactive chain ends requires their mutual diffusion and reaction prior to being hindered by oxidative processes. Oxidation, which commonly inhibits free radical coupling, necessitates the maintenance of favourable reaction conditions to ensure the stability of free radicals. For example, the synthesis of self-repairing polycarbonate (PC) using an ester exchange approach was achieved by subjecting the material to steam pressure at a temperature of 120 °C [158]. The initial cleavage of the carbonate group through hydrolysis generates a higher concentration of end-capped phenoxy functionalities. However, the addition of a base, such as $NaHCO_3$, promotes further ester reactions, enabling substitutions between phenoxide and phenyl-carbonyl chain ends. This sequential process is followed by recombination with Carbon dioxide, leading to the ultimate reformation of the polycarbonate (PC) network. Covalent bonds in polyurethanes and polycarbonates that have been broken due to mechanical damage can be reformed through the process of free-radical recoupling. The formation of free radicals during this process can vary, depending on their stability. For instance, in polyurethanes that have been modified with oxetanes or oxolanes, the cleavage of C–O bonds leads to the formation of relatively stable free radicals. The ability to self-heal a crosslinked polyurethane network after experiencing mechanical damage can be accomplished by subjecting the damaged region to 302-nm ultraviolet (UV) radiation [72] (Fig. 14).

Oxetane (OXE), a four-membered ring, is recognized for its ability to generate stable free radicals and its lower activation energy for ring opening [159]. In their study, Ghosh et al. [72] presented a novel approach to develop polyurethane networks with remarkable self-repairing properties upon exposure to ultraviolet (UV) light. The network composition involved incorporating an oxetane-substituted chitosan precursor into a two-component polyurethane system. When subjected to mechanical damage, the four-member oxetane rings within the network opened, generating two reactive ends. Subsequent exposure to UV light triggered chain scission in the chitosan component, allowing the formation of crosslinks with the reactive oxetane ends, thereby facilitating network repair. These materials exhibited impressive self-repairing capabilities, with healing occurring in less than an hour. Such polyurethane networks hold great potential for various applications in industries such as transportation, packaging, fashion, and biomedicine [72]. Despite differences in mechanism and kinetics, self-healing properties were also achieved by incorporating oxolane-chitosan macromonomers into polyurethane networks [160]. The formation of polyurethane (PUR) occurs through the reaction between isocyanate and amine-functionalized oxetane-chitosan (OXE-CHI), resulting in a network with localized heterogeneity (polyurea,

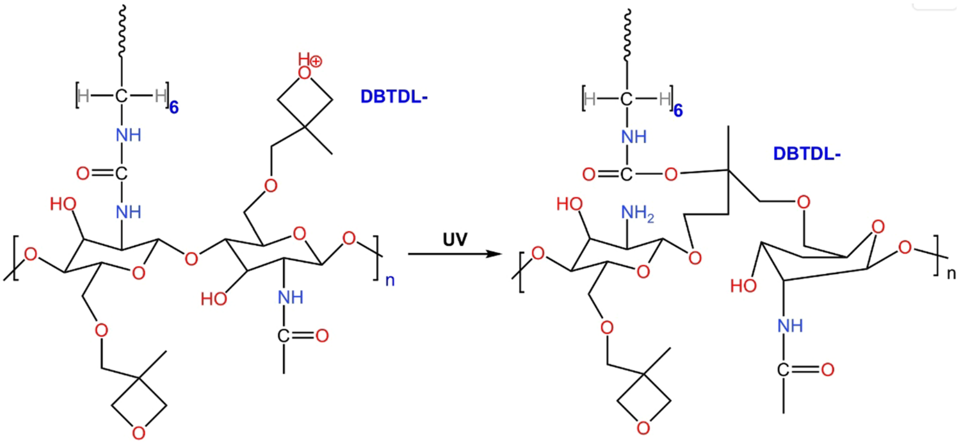


Fig. 14 Polyurethane radical rebonding [72]

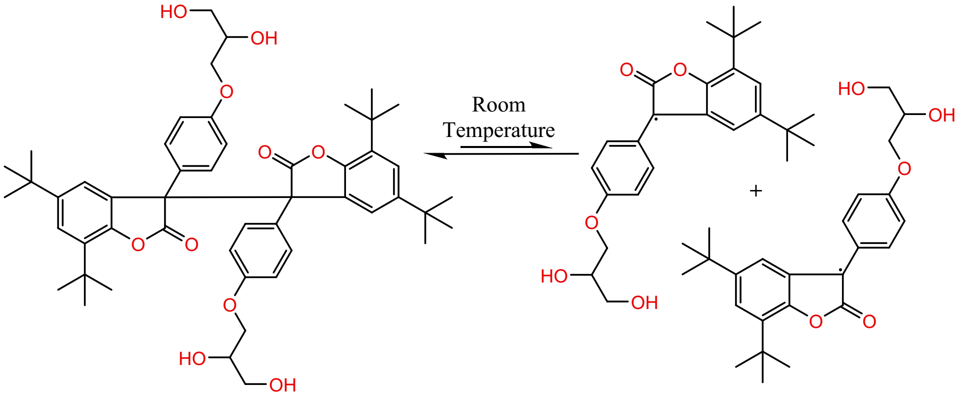


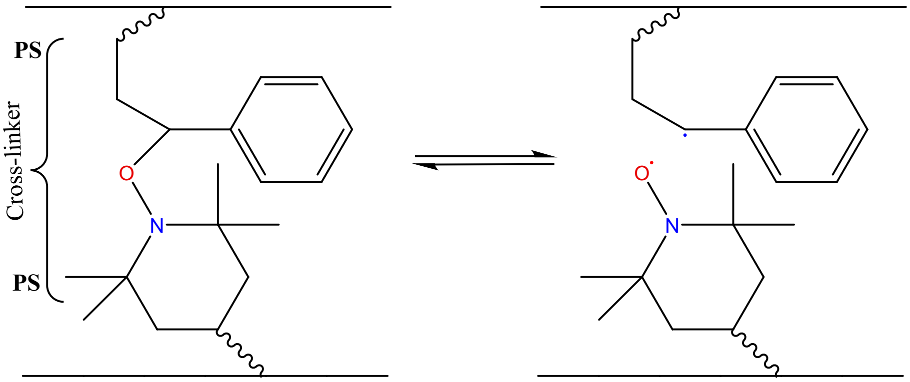
Fig. 15 Polycarbonate-radical rebonding [47]

PUA). The presence of OXE-CHI enables the cleavage of a constrained four-membered ring (oxetane) to generate stable free radicals, while the chitosan component contributes UV sensitivity for self-repair [161].

Imato et al. [47] showcased the autonomous self-repairing capability of covalently cross-linked chemical gels in a study, without the need for external stimuli. They synthesized cross-linked polymers containing a novel dynamic covalent bond unit called DABBF (diarylbibenzofuranone) by polyadding diisocyanate compounds and a DABBF cross-linker (Fig. 15). Employing a dynamic covalent approach, the gels displayed independent structural transformation and visible healing of separated gel fragments in ambient air at room temperature, without relying on external stimuli [47]. In order for these radicals to effectively promote the reformation of polycarbonate radicals, it is crucial that they exhibit low or no sensitivity to oxygen, preventing their quenching through free-radical reactions with molecular oxygen [162]. This oxygen insensitivity is essential for facilitating self-healing processes and overcoming any hindrance caused by radical quenching [163].

The investigation of free radical stability and its implications for self-healing has extended to self-healable alkoxyamines synthesized through click chemistry. In this methodology, the crosslinks within the polymer network undergo cleavage upon UV irradiation, leading to the generation of radical species. These radicals can recombine and facilitate the self-healing process. The research has focused on understanding the stability of these free radicals and their role in promoting the efficient recovery of the material [164]. An et al. [165] introduced an inventive technique involving the synthesis of a dynamic covalent polymer network via multi-fold nitroxide exchange reactions between trialkoxyamines and trinitroxide monomers. By subjecting the trialkoxyamine components to thermal treatment in the presence of trinitroxide radical species, they induced a highly dynamic sol–gel transition. This novel method presents a fresh pathway for crafting polymer networks with adjustable properties, showcasing the potential for triggered sol–gel transitions through nitroxide exchange reactions, allowing for a modulated degree of crosslinking. A noteworthy feature of this approach is its reversibility, which is governed by fluctuations in the concentration of 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO) radicals [165]. Dynamically reversible covalent networks play a significant role in achieving desirable properties

Fig. 16 Alkoxyamine linkages [48]



in thermoplastic polymers. Polystyrene (PS), in its unmodified form, lacks self-healing capabilities due to its high molecular weight. However, when PS chains are crosslinked using dynamically reversible alkoxyamine C–ON bonds, self-healing becomes possible through the dissociation and reformation of these alkoxyamine linkages, as illustrated in (Fig. 16) [48]. The stability of alkoxyamines in the presence of air remains uncertain, posing a limitation to their use. Oxidative processes could potentially hinder the desired re-bonding reactions.

A study exploring the integration of repair and sensing capabilities within a single material carried out by Ramachandran et al. [166] conducted They developed poly(methyl methacrylate/*n*-butyl acrylate/2-[(1,3,3-trimethyl-1,3-dihydrospiro[indole-2,39-naphtho[2,1-b][1,4]oxazin]-5-yl)amino]ethyl-2-methylacrylate) [p(MMA/nBA/SNO)] copolymer films that exhibited colour changes from clear to red in the mechanically damaged area (Scheme 11). However, exposure to sunlight, temperature variations, or acidic vapours resulted in the self-repair of the damaged area, restoring the initial colourless appearance [166]. This reversible process was driven by the ring-opening and closure of spironaphthoxazine (SNO) segments, which transformed into merocyanine (MC) and then reverted back to the SNO form. Upon mechanical damage, the SNO segments of neighbouring copolymer segments formed intermolecular hydrogen bonding, stabilizing the copolymer backbone, and maintaining an extended conformation. External stimuli such as light, temperature, or acidic environments caused the dissociation of the hydrogen-bonded MC pairs, which converted back to the SNO form [166]. This dynamic behaviour allowed for self-healing and restoration of the material's original appearance.

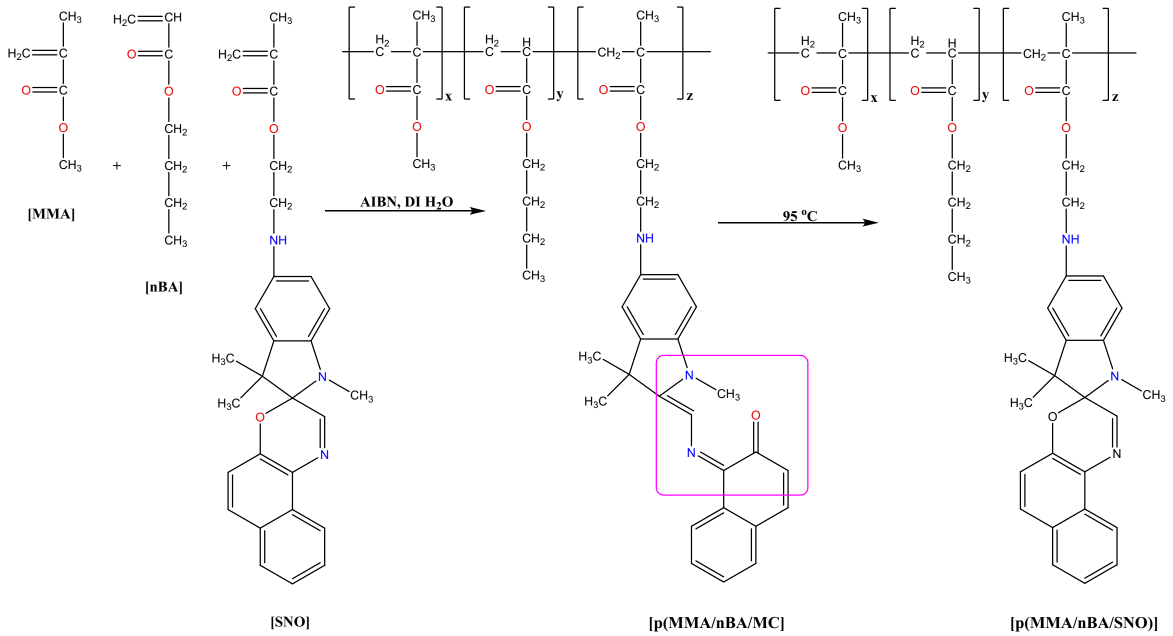
5 Supramolecular chemistry

Supramolecular materials derive their integrity from the establishment of non-covalent interactions, which have been the focus of the field of supramolecular chemistry for more than fifty years [167]. These non-covalent interactions encompass hydrogen bonding, π–π interactions, guest–host interactions, ionic interactions and metal ligand coordination [168, 169]. Supramolecular chemistry, an established field for several decades, offers several compelling advantages for self-healing applications [170]. These include the properties of reversibility, speed, directionality, and sensitivity. Unlike covalent bonding, supramolecular networks can undergo rapid and reversible remodelling, transitioning between fluid-like and solid-like states. The unique nature of secondary bonds in supramolecular networks, distinct from the surrounding polymers, often leads to morphological changes like aggregation and crystallization induced by associative groups. Consequently, many supramolecular networks inherently exhibit heterogeneities that impact their physical and chemical properties, facilitating the self-repair process. Supramolecular polymers typically have low glass transition temperatures (T_g), resulting in soft and flexible materials, which has made them highly desirable for developing hydrogels.

This section provides an overview of various supramolecular interactions and chemistries employed in the development of self-healing materials. These include H-bonding, ionic interactions, host–guest interactions, π–π interactions and metal–ligand interactions.

5.1 Hydrogen bonding

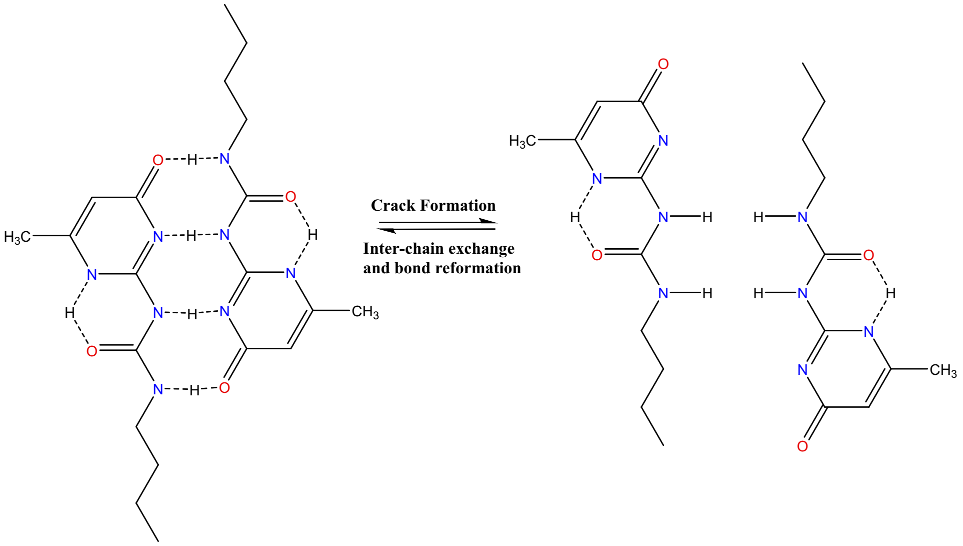
Despite hydrogen bonds (H-bonds) being less strong than typical covalent bonds, their unique directional nature and strong affinity enable the creation of a wide variety of supramolecular polymers [171]. These polymers exhibit a broad range of mechanical properties, ranging from supramolecular gels to robust materials with rubber-like characteristics.



[MMA] - methyl methacrylate **[nBA] -** n-butyl acrylate **[SNO]** - 2-[(1,3,3-trimethyl-1,3-dihydrospiro[indole-2,39-naphtho[2,1-b][1,4]oxazin]-5-yl)amino]ethyl-2-methylacrylate
[p(MMA/nBA/MC] - poly(methylmethacrylate/n-butylacrylate/2-{[1,3,3-trimethyl-2-({[(1-Z)-2-oxonaphthalen-1(2-H)-ylidene]amino}methylene)-2,3-dihydro-1-H-indol-5-yl]amino}ethyl2-methylacrylate) **[p(MMA/nBA/SNO)]** - poly(methyl methacrylate/ n-butylacrylate/1, 3-dihydro-1, 3, 3-trimethylspiro[2H-indole-2,3'-[3H]-naphth[2, 1-b][1, 4]-oxazine]-2-amino-2-methylacrylate

Scheme 11 [166]

Fig. 17 Quadruple hydrogen bonding [174]



Due to its reversible nature and desirable characteristics, hydrogen bonding has proven to be effective in facilitating the self-healing of thermoplastic polymers [172, 173]. For instance, several research studies have demonstrated that incorporating multiple hydrogen bonds, as depicted in (Fig. 17), into a functional unit such as urea isopyrimidone (Upy), leads to improved interaction strengths between Upy units and polymers such as polysiloxane, polyethers, and polyesters [174–178].

Despite the advantageous high association constants achieved by combining four hydrogen bonds [179, 180], In a distinct investigation carried out by Herbst et al. [181], it was shown that polyisobutylenes with enhanced segmental mobility, modified with thymine and 2,6-diaminotriazine end groups, can create resilient rubber-like materials through the establishment of triple hydrogen bonds illustrated in Fig. 18. By incorporating specific associative end groups into

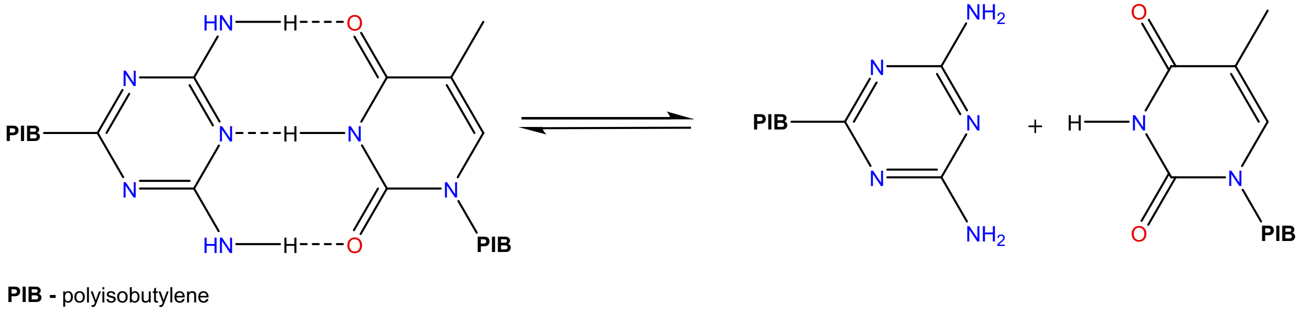


Fig. 18 Triple hydrogen-bonding [181]

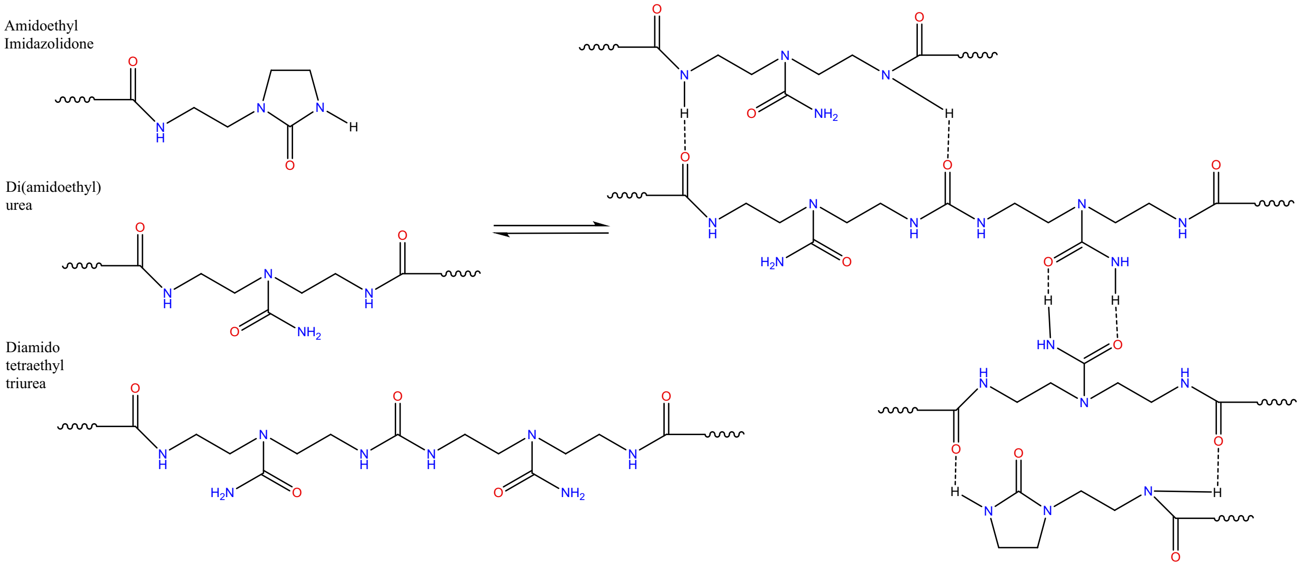


Fig. 19 Diacids and tri-acids associations from renewable resources [27]

supramolecular polyisobutylene networks, a controllable dynamic behavior can be achieved, allowing for the incorporation of diverse functionalities including self-healing capabilities [181].

Supramolecular polymers incorporating bifunctional ureido-pyrimidinone (UPy) derivatives possess similar characteristics to conventional polymers, but with a notable dependency on temperature regarding their mechanical properties [182]. Among these polymers, UPy-based monomers are especially intriguing as they can be coupled with thermally responsive polymer matrices, enabling the development of self-healing properties regulated by temperature [183]. By employing fatty diacids and tri-acids derived from renewable resources in a two-step synthetic process, a self-healing material, as illustrated in Fig. 19, was successfully synthesized [27, 184]. An additional effective mechanism for achieving self-healing involves the creation of urea-water clusters within moisture-containing urea-based polyurethanes [185].

The initial step of the process involves the condensation of acid groups with an excess of diethylenetriamine, followed by subsequent reactions involving urea. This sequential series of reactions leads to the formation of desired products. These resulting polymers exhibit the ability to undergo self-repair, where two severed ends can physically reconnect at room temperature without the need for external heat. The self-repair mechanism mainly relies on the establishment of hydrogen bonding interactions between the –C=O groups of the amide and the amine-functionalized ends. This hydrogen bonding plays a crucial role in the reformation of the material and contributes to its self-repairing capabilities. Notably, the kinetics of the self-healing process were found to be particularly intriguing. In contrast to the formation of crystalline or clustered structures observed with bis-urea hydrogen bonding, the incorporation of thiourea moieties promotes the formation of zigzag hydrogen-bonded arrays. These arrays effectively prevent the occurrence of unfavourable crystallization, thereby avoiding the brittleness commonly associated with such materials [186].

In a study conducted by Wu et al. [187], high-strength supramolecular polymer conductive hydrogels with dual amide hydrogen bond crosslinking and enhanced properties were developed. This was achieved by incorporating PEDOT/PSS into poly(*N*-acryloyl glycinamide-co-2-acrylamide-2-methylpropanesulfonic) (PNAGA-PAMPS) hydrogels through in situ doping. The resulting conductive hydrogels exhibited excellent mechanical performance, including a tensile strength of 0.22–0.58 MPa, compressive strength of 1.02–7.62 MPa, and breaking strain of 817–1709%. Additionally, the incorporation of PEDOT/PSS significantly improved the specific conductivities of the hydrogels [187]. In an independent investigation by Neal et al. [188], it was shown that incorporating sacrificial bonds into a self-repairing network markedly boosts its mechanical characteristics. To achieve this, the scientists incorporated simple secondary amide side chains to introduce dynamic energy-dissipating hydrogen bonds within a polymer network crosslinked through covalent bonds. This network demonstrated the ability to self-heal via olefin cross-metathesis, resulting in an enhancement of its overall mechanical behaviour [188]. High-modulus thermoplastic copolymers present an intriguing prospect for developing heterogeneous multi-phase systems with self-healing capabilities. Analogous to phase-separated polyurethanes, the integration of a stiff polystyrene (PS) main chain with pliable polyacrylate amide (PA-A) pendant groups featuring numerous hydrogen bonding sites, illustrated in Fig. 20, facilitates reversible self-healing [38]. What distinguishes this method is the innovative incorporation of localized glass transition temperature (T_g) via customized chemical compositions. This enables remodelling driven by both hydrophobic and hydrophilic interactions, resulting in phase separation. Another form of heterogeneous supramolecular network exhibiting self-healing properties is the poly(*n*-butyl acrylate)-b-polystyrene (PBA-PS) with Upy end functionalization. The inclusion of PS hard domains enhances the material's rigidity, while the presence of Upy groups within the PBA soft domains facilitates the self-repair mechanism [189].

Polysiloxane elastomers, integrating both robust and fragile hydrogen bonding interactions depicted in Fig. 21, offer the benefit of customizable mechanical characteristics like elasticity, resilience, and the capacity for self-repair independently, even in water-based settings [190].

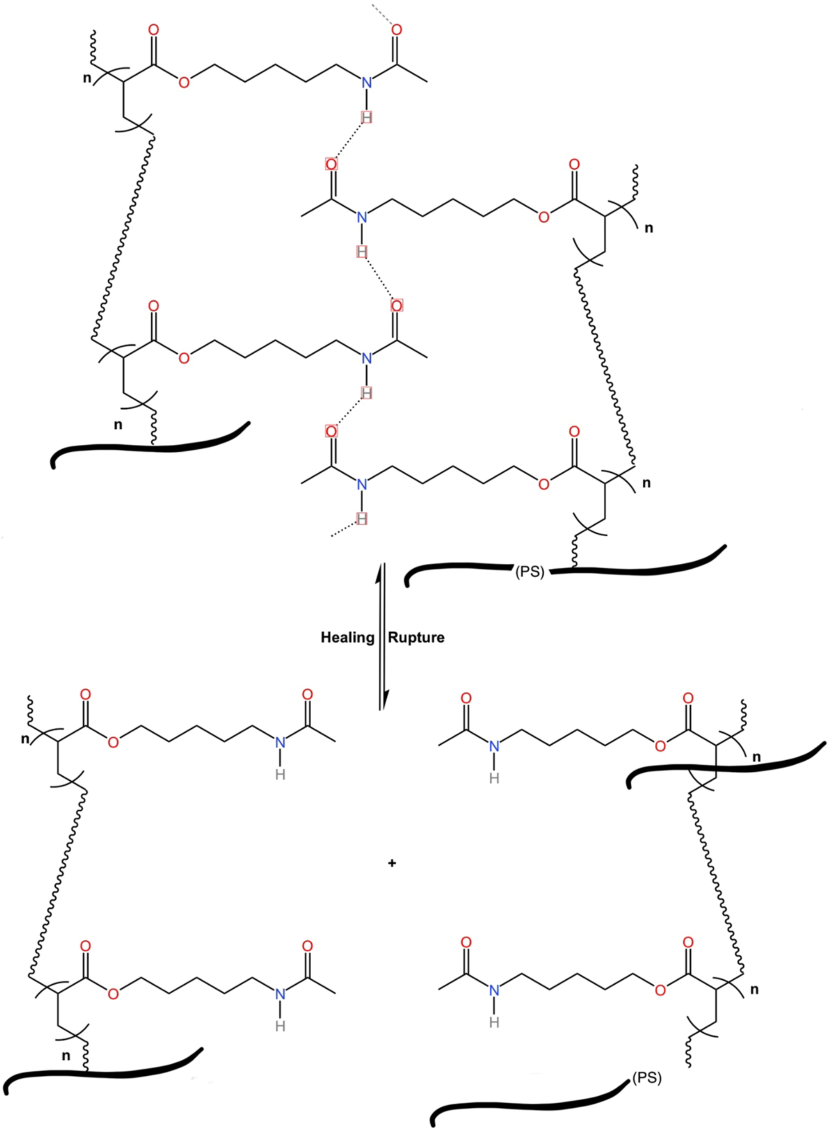
5.2 π–π stacking

Within supramolecular chemistry, π–π interactions are acknowledged as an extension of coordination chemistry, reliant on the overlap of π orbitals, which is notably affected by the chemical structure and stereochemistry of the molecules. By utilizing π–π stacking interactions between π-electron-deficient and π-electron-rich aromatic molecules, such as pyrene and naphthalene diimides, researchers have successfully created supramolecular polymer networks that exhibit reversible self-repair capabilities and thermal responsiveness [191–195]. Alternative π-electron-rich species like naphthalene are also recognized for forming stable complementary supramolecular complexes with π-electron-deficient species, both in solution and in the solid state [196, 197]. Perylene is also recognized for forming stable complexes with macrocyclic aromatic ether imide sulfones and serves as an alternative aromatic moiety capable of engaging in π–π stacking interactions with chain-folding aromatic diimides, resulting in self-healing materials [198, 199].

In a specific investigation carried out by Burattini et al. (2009), a copolyimide with electron-deficient attributes and chains terminated with pyrenyl, possessing electron-rich characteristics, were utilized, alongside polysiloxane or polyamide spacers [51, 200]. Through adjustment of the blend composition and alteration of the spacer, the glass transition temperature (T_g) of the network could be finely adjusted to facilitate self-healing across a relatively wide temperature spectrum (around -50 to 100 °C). Upon heating, the p–p stacking interactions between the constituents would be disturbed, prompting detachment of the pyrenyl end-capped chains from the copolyimide, which could flow owing to the presence of a flexible "soft" spacer. Consequently, the areas experiencing damage could be repaired, and mechanical strength could be reinstated via the reestablishment of π–π stacking interactions (Fig. 22).

In a subsequent investigation led by Burattini et al. [51], an innovative approach was pursued, integrating π–π stacking interactions with intermolecular hydrogen bonding to achieve effective and versatile thermal healing ability in supramolecular polymer networks. This novel strategy involved embedding polybutadiene with urethane and urea groups as spacers within the polymer framework. By incorporating these specific functional groups as spacers, the researchers aimed to introduce additional reversible interactions contributing to the material's self-healing characteristics [51]. Enhanced mechanical resilience was attained in these networks by employing tweezer-type bis-pyrenyl end groups instead of mono-pyrenyl groups. Remarkably, these polymers exhibited repair capabilities even at elevated temperatures, approaching approximately 140 °C. Furthermore, the introduction of nitrobenzoxadiazole (NBD)-containing cholesterol (Chol) derivatives resulted in a distinctive combination of π–π stacking and intermolecular H-bonding interactions. The length of the spacer linking the NBD and Chol units significantly influenced the gel formation and restoration abilities of these materials [201]. Additionally, through the incorporation of a cyclometalated platinum(II)

Fig. 20 Copolymers engineered by blending rigid polystyrene (PS) with polyacrylate amide (PA-A) pendant groups containing numerous hydrogen-bonding sites [38]



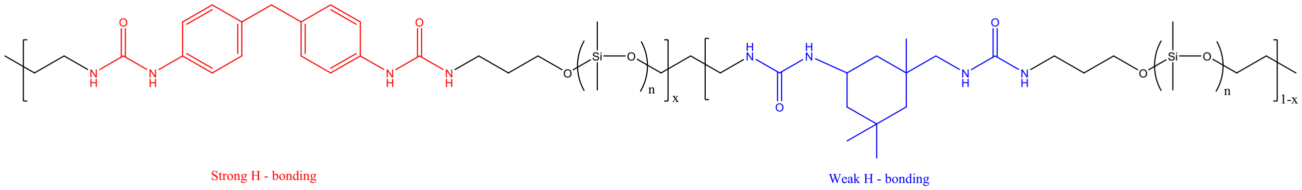
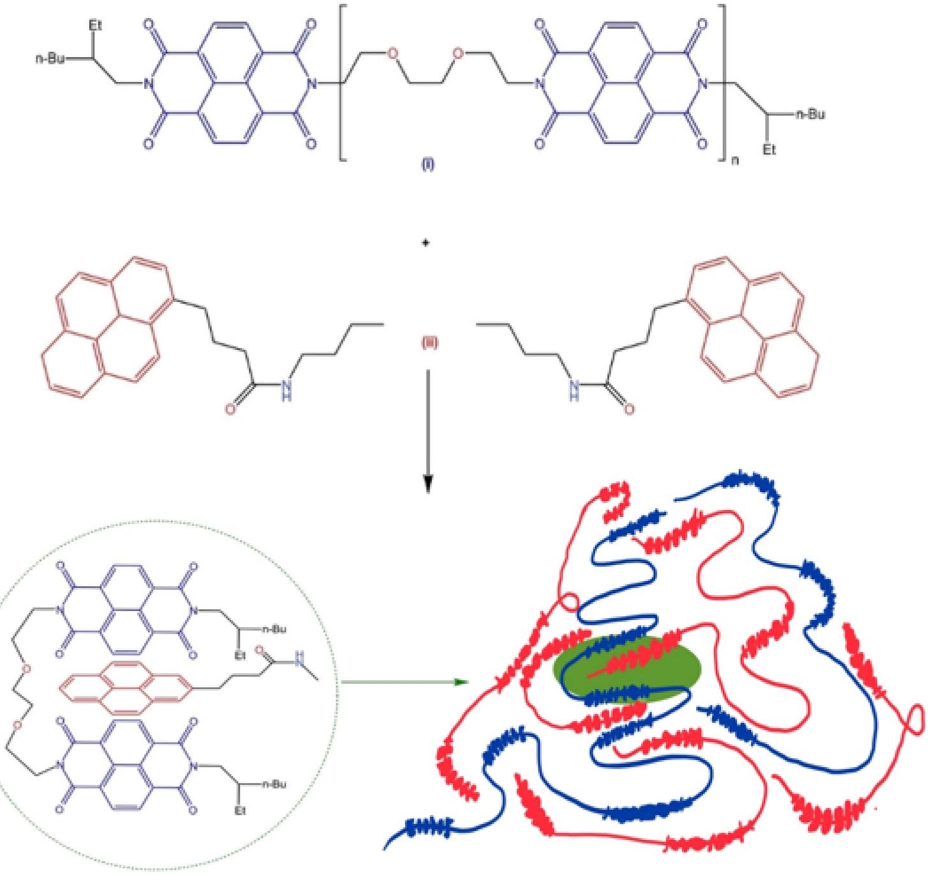


Fig. 21 Combination of weak and strong H-bonding [190]

complex Pt(6-phenyl-2,2′-bipyridyl)Cl into the polydimethylsiloxane (PDMS) backbone, a novel self-healing polymer was synthesized. The robust molecular interactions arising from a blend of Pt···Pt and π–π interactions effectively crosslinked the linear PDMS polymer chains, yielding a flexible film. Remarkably, the polymer exhibits exceptional stretchability, allowing it to be elongated to more than 20 times its original length [192]. Metal nanoparticle composites find widespread application in various fields. For instance, Vaiyapuri et al. [202] introduced an innovative supramolecular nanocomposite material capable of self-healing. This material comprises three main components: a pyrene-functionalized polyamide, a polydiimide, and pyrene-functionalized gold nanoparticles (P-AuNPs). The polymeric components interact through the

Fig. 22 A self-healing supramolecular network formed by the interaction of copolyimide (i) with pyrenyl end-capped chains (ii) through π–π stacking interactions [200]



formation of specific π–π stacked complexes, where the π-electron-rich pyrenyl residues engage with the π-electron-deficient polydiimide residues [202].

5.3 Guest–host chemistry

In recent times, there has been a growing interest in the development of self-healing materials utilizing the principles of guest–host chemistry. These materials have shown promising capabilities for fast and reversible mending under normal environmental conditions, making them a widely explored area in materials design. The ultimate goal is to create self-healing materials that not only exhibit rapid healing but also have the ability to restore their mechanical properties effectively [203, 204]. Guest–host chemistry is a prevalent approach employed in the production of hydrogels. One prominent example involves the utilization of β-cyclodextrin, which possesses hydrophobic cavities capable of accommodating diverse guest moieties [205, 206]. Pioneering investigations in the field of supramolecular self-healing materials introduced the incorporation of macrocyclic compounds. These studies revealed the creation of supramolecular hydrogels endowed with impressive redox-responsive and self-healing attributes, attributed to host–guest interactions. Cyclodextrin (CD) played the role of the environmentally friendly host molecule, while ferrocene acted as the guest polymer. Notably, Nakahata et al. [73] detailed the development of a transparent supramolecular hydrogel that swiftly forms when poly(acrylic acid) (pAA) containing β-CD as the host polymer is combined with pAA containing ferrocene as the guest polymer. In a subsequent exploration, researchers successfully synthesized a host–guest gel termed bCD-Fc gel. This gel was crafted by incorporating bCD and Fc moieties. The polymerization process occurred in a mixed solvent comprising water and DMSO (in a ratio of 95:5, v/v). Prior to polymerization, Fc-AAm was rendered soluble by bCD-AAm. The formation of the bCD-Fc gel ensued through the homogeneous radical copolymerization of the inclusion complex with acrylamide (AAm) and MBAAm, utilizing 2,2′-azobis[2-(2-imidazolin-2-yl)-propane] dihydrochloride (VA-044) as a water-soluble radical initiator [207].

When one surface features a cyclodextrin host and the other carries guest molecules, bonding occurs via host–guest interactions. In a subsequent study, researchers successfully developed a host–guest gel termed β-CD-Ad gel, comprising

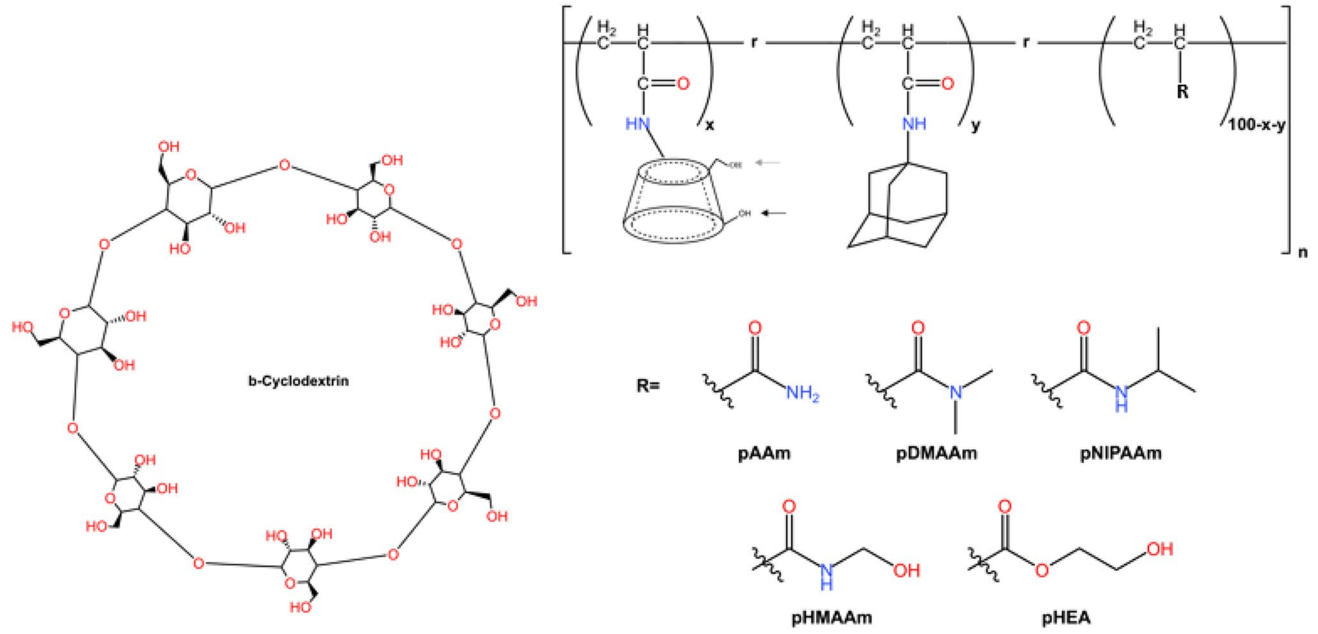


Fig. 23 A water-soluble polymer chemically altered with β-cyclodextrin functioning as a host, along with hydrophobic adamantine incorporated into the side chain acting as a guest [208]

β-cyclodextrin (β-CD) and adamantane (Ad) moieties. The polymerization of β-CD-AAm, (adamantane acrylamide (Ad-Aam), and main chain monomers [acrylamide (Aam), poly(*N*,*N*-dimethylacrylamide) (pDMAAm), poly(*N*-isopropylacrylamide) p(NIPAAm), poly(2-hydroxymethylacrylamide) (pHMAAm), or poly(2-hydroxyethylacrylate) (pHEA)] was achieved through radical copolymerization in water. This process was initiated using a combination of ammonium persulfate (APS) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) or a photoinitiator (Irgacure 2959) with UV light (λ = 365 nm) (Fig. 23). The Ad-AAm was solubilized by β-CD-AAm before the polymerization process. This straightforward method yields a transparent, flexible, and resilient hydrogel capable of self-healing in both wet and dry conditions [208].

Supramolecular hydrogels made from hyaluronic acid derivatives featuring adamantane or β-cyclodextrin are known for their amenability to chemical alterations and compatibility with biological environments. These hydrogels swiftly form intermolecular host–guest bonds. By adjusting the concentration and ratio of guest and host components, the mechanical properties of this system can be finely tuned [209, 210].

In a separate investigation on guest–host interactions conducted by Janeček et al. [211], cucurbit[8]uril was employed as a host molecule capable of accommodating two guests, namely naphthyl and viologen. Cucurbit[8]uril, characterized by its substantial molecular weight and effective chain entanglement, facilitated physical crosslinking within the system (Fig. 24). In subsequent investigations of dynamic cucurbit[8]uril-mediated non-covalent crosslinking, it was discovered that at a low concentration of 2.5 mol%, the formation of such crosslinks resulted in highly stretchable and durable supramolecular polymer networks. These networks exhibited exceptional self-healing ability even at room temperature. Additionally, these networks demonstrated ionic conductivity, transparency, and the remarkable capability to be stretched to 100× their original length while being able to support objects weighing 2000× their own weight [212]. Furthermore, several exhaustive reviews have been assembled with a specific emphasis on supramolecular self-healing materials utilizing non-covalent crosslinking through diverse methodologies. These encompass host–guest interactions involving host and guest polymers, 1:2-type host–guest interactions, and host–guest interactions stemming from the polymerization of host–guest inclusion complexes [204, 213, 214].

5.4 Ionic interactions

Ionomeric copolymers represent a distinct class of materials possessing ionic segments capable of self-assembly into clusters that function as reversible cross-links. These clusters can be induced by external stimuli, such as thermal energy or exposure to ultraviolet (UV) irradiation. Given their reversible nature, the formation of clusters enables the possibility of multiple localized healing mechanisms. Self-healing of two kinds of ENR/ZDMA composites with different polarity

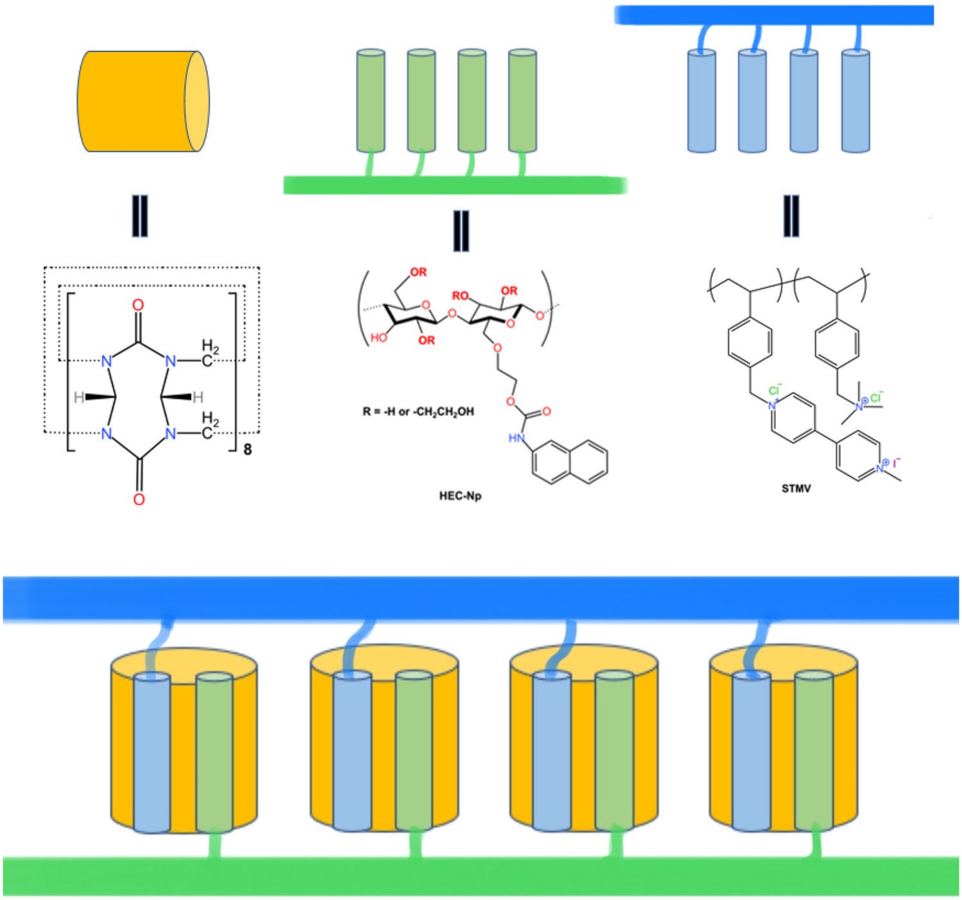


Fig. 24 The sequential process of creating a ternary host–guest supramolecular complexation involving cucurbit[8]uril, a macrocyclic host molecule, and guest molecules, namely 1-benzyl-3-vinylimidazolium and acrylamide, which are polymerizable [211]

was studied by Liu et al. [215] where rubbers with varying polarities exhibit distinct optimal healing temperatures. For instance, the ENR25/ZDMA composites demonstrate the ability to heal at room temperature, whereas the ENR40/ZDMA composites necessitate elevated temperatures for healing. Experimental findings from mechanical property testing reveal that the tensile strength of the ENR40 composites can recover to more than 80% after undergoing a healing process at 80 °C for 1 h. Similarly, the tensile strength of the ENR25 composites recovers to approximately 70% following a healing duration of 50 min at 30 °C. In a separate study, Gong et al. [216] presented a systematic approach to the deliberate construction of epoxidized natural rubber (ENR) by integrating an ionic and coordination supramolecular hybrid bond network. Within this design, both types of bonds share the same cross-linking points while exhibiting distinct bond strengths. In a separate study conducted by Peng et al. [217], a self-healing strengthening elastomer (SSE) was created by introducing enhanced kinetic stability into an ionomer. This innovative approach led to a remarkable self-healing efficiency, with fractured SSEs exhibiting an impressive recovery rate of up to 143% [217].

Zinc thiolate exhibits substantial promise as a reversible ionic cross-linker for facilitating the self-healing properties of natural rubber. This material demonstrates the remarkable ability to restore its original characteristics within a time frame of 10 min. Furthermore, without relying on any external stimuli, the healing process conducted at room temperature leads to an impressive recovery of nearly 90% in terms of tensile strength [218]. Zhang et al. [219] successfully developed a highly transparent elastomer with remarkable underwater self-healing capabilities and excellent ionic conductivity. This elastomer relies on multivalent ion–dipole interactions to achieve its unique properties. The fabricated polymer complex not only exhibits a significant increase in Young's modulus by over threefold but also demonstrates superior elasticity [219]. Conventional dielectric elastomers lack the inherent ability to undergo self-healing. However, Silicon dielectric elastomers present a unique approach where silicone species within the material are cross-linked through proton exchange between amines and acids. This ionic cross-linking of silicone enables the material to possess self-healing properties, allowing for recovery after electrical breakdown or when subjected to direct cuts [137].

Another study involving Poly(ethylene-co-methacrylic acid) (pEMAA) and polyethylene-g-poly(hexylmethacrylate) (pEHMA) demonstrates the ability to self-heal under normal conditions and even at increased temperatures when exposed to projectile puncture testing [220]. In contrast, low-density polyethylene fails to heal after a ballistic puncture [221]. The self-repair process involves two stages: first, the impact of the projectile disrupts the ionomeric network, and the resulting friction-generated heat is transferred to the surrounding polymer matrix, creating a localized melt state. The molten surfaces of the polymer fuse through interdiffusion, effectively sealing the puncture. Subsequently, the ionic clustered regions reorganize, and the overall polymer network undergoes long-term relaxation. Varying the ionic content and neutralization percentage can also effect on the healing efficiency of Poly(Ethylene-co-Methacrylic Acid) [222].

In the domain of underwater adhesion, there is a promising application potential in developing rigid gel-like structures capable of adhering to various substrates even in submerged conditions. These structures are created by ionic crosslinking of readily accessible polyelectrolytes commonly utilized in commercial settings. Through the combination of synthetic polycations like poly(allylamine) (PAH) with highly adhesive multivalent anions such as pyrophosphate (PPi) and tripolyphosphate (TPP), these gels form spontaneously, showcasing their underwater adherence capability [223]. The pH and ionic strength play significant roles in influencing the formation, rheology, and adhesion properties of PAH/PPi and PAH/TPP complexes [224]. Polyelectrolyte complexes derived from pairs of poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH), along with NaCl, exhibit self-healing characteristics, which are further enhanced by higher NaCl concentrations [225]. The self-healing mechanism in this context arises from the disruption of ionic interactions through the introduction of salt, thereby promoting increased chain mobility and facilitating the healing process.

The impact of water, salt, or polar solvents on self-repair processes is significant. An example of this occurs when star-shaped poly(ethylene glycol) (PEG) is modified with alendronate and then combined with calcium solutions [226]. The resulting hydrogels display an impressive capacity to be cut and reassembled seamlessly, underscoring the efficacy of the self-repair mechanism facilitated by the addition of water, salt, or polar solvents. Butyl rubber, a cost-effective and commonly used material, can be converted into a self-repairing substance through ionic modifications, eliminating the necessity for traditional curatives or vulcanizing agents. A noteworthy method involves converting the bromine functionalities of butyl rubber, particularly BIIR, into ionic imidazolium bromide groups [227]. This conversion results in the formation of reversible ionic associations that possess remarkable physical cross-linking capabilities. Consequently, the modified butyl rubber exhibits self-repairing properties, paving the way for the advancement of innovative and durable materials. In essence, the presence of ionic interactions within polymers offers a unique opportunity for enhancing the domain of self-repairing commodity materials.

5.5 Metal–ligand coordination

Metal–ligand (M–L) complexes hold great promise as dynamic healing motifs due to their tuneable thermodynamic and kinetic parameters across a wide range. This tunability opens up possibilities for creating materials with highly adjustable mechanical properties [228–230]. Metal–ligand complexes offer several advantages due to their capacity to coordinate various metal ions and ligand substitutes, which leads to diverse levels of association strength. Under the application of mechanical forces, these complexes undergo dissociation, and their subsequent reformation enables self-healing to occur. Additionally, M–L interactions exhibit less sensitivity to moisture compared to hydrogen bonds, which confers practical advantages for real-world applications.

The dynamic mechanical attributes of supramolecular elastomers can be modulated by adjusting the potency of metal–ligand interactions. For instance, Li et al. [231] conducted a study introducing a network comprised of poly(dimethylsiloxane) (PDMS) polymer chains crosslinked by coordination complexes. This novel network showcases exceptional traits such as heightened stretchability, robust dielectric strength, autonomous self-healing, and mechanical actuation. Remarkably, the healing process transpires even at frigid temperatures as low as − 20 °C and remains substantially unaffected by surface aging and moisture. The coordination complexes employed in this investigation feature 2,6-pyridinedicarboxamide ligands that coordinate with Fe(III) centers via three distinct interactions: a robust pyridyl-iron interaction and two weaker carboxamido-iron interactions encompassing both the nitrogen and oxygen atoms of the carboxamide groups. Consequently, the bonds between iron and the ligands can be readily disintegrated and re-established, with the iron centers persistently tethered to the ligands through the stronger interaction with the pyridyl ring (Fig. 25). This distinctive attribute facilitates the reversible unfolding and refolding of the polymer chains [231].

Numerous studies in the literature have emphasized the exploitation of the reversible nature of metal–ligand interactions in the development of diverse self-repairing materials and gels [232–235]. For instance, in a significant investigation by Mozhdehi et al. [236], a groundbreaking self-healing multiphase polymer was introduced. The researchers strategically integrated an extensive network of dynamic metal–ligand interactions, specifically zinc-imidazole interactions, within the soft matrix of a hard/soft two-phase brush copolymer system. By manipulating various molecular parameters

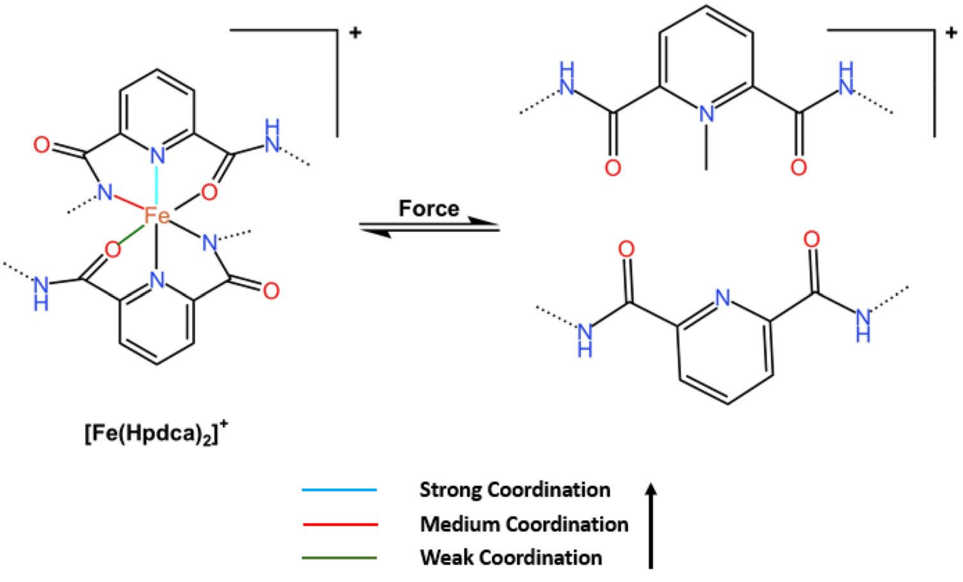


Fig. 25 A self-healable polydimethylsiloxane network is achieved by employing reversible coordination complexes, where 2,6-pyridinedicarboxamide ligands are coordinated with a Fe(III) centre as the crosslinker [231]

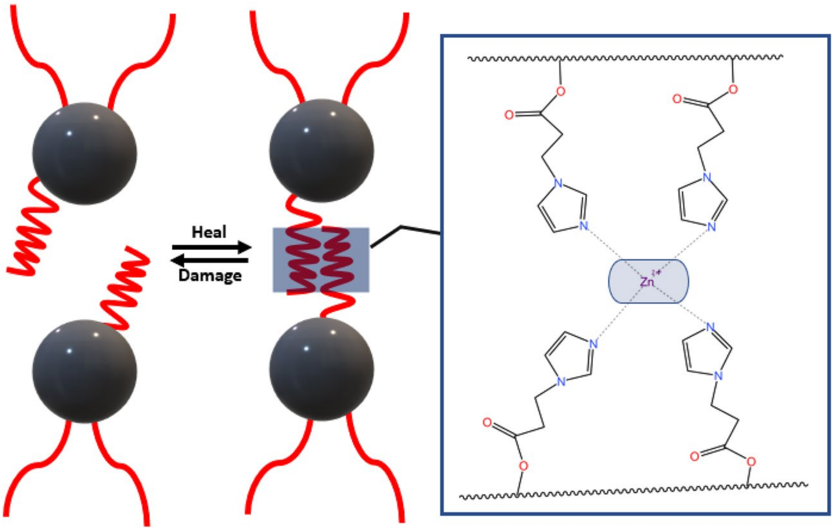


Fig. 26 The conceptual design for multiphase spontaneous self-healing materials relies on leveraging metal–ligand interactions as the dynamic motif [236]

such as backbone composition, degree of polymerization, brush density, ligand density, and the L/M ratio, both the mechanical and dynamic characteristics of the materials could be conveniently tailored. Remarkably, the multiphase M–L polymers demonstrated exceptional self-healing capabilities even under ambient conditions, necessitating minimal external intervention (Fig. 26). This innovative polymer system comprises a soft matrix consisting of a hard/soft two-phase brush copolymer, wherein an extensive network of dynamic metal–ligand (zinc-imidazole) interactions is deliberately incorporated [236].

As an example of a temperature-responsive system, adjustments in molecular weight and crosslinker density can be controlled using hydroxyethyl ethylenediamine triacetic acid alongside terpyridine-Ru. Temperature fluctuations induce the separation of the Ru metal from the ligand, facilitating connection and disconnection [237]. Self-healing at elevated temperatures can be achieved by employing the terpyridine-[Fe^{2+}] complex pair with poly(alkyl methacrylate) in a metallosupramolecular system [49].

However, it's important to note that the high temperatures involved in this process may lead to unfavourable outcomes like polymer breakdown. Another approach in metallosupramolecular systems involves utilizing a chemically distinct photo responsive mechanism. Burnworth et al. [50] demonstrated this by introducing metallosupramolecular polymers capable of repair upon exposure to light. These polymers consist of telechelic, rubbery, low-molecular-weight chains with ligand end groups connected through non-covalent metal-ion association. When subjected to ultraviolet

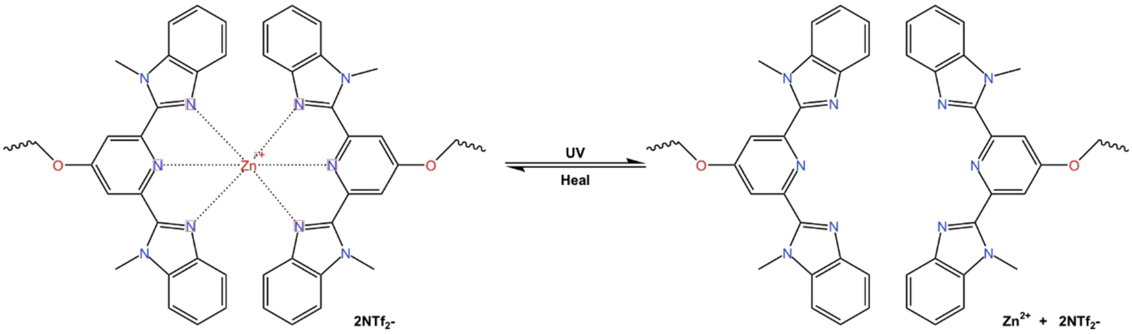


Fig. 27 The capacity for self-repair in poly(ethylene-co-butylene) is attributed to the coordination of Zn(NTf)2 with 2,6-bis(1-methylbenzimidazolyl)pyridine ligands via a photosensitive process [50]

light, the metal–ligand motifs are electronically excited, and the absorbed energy is converted into heat. As a result, the metal–ligand interactions temporarily disengage, leading to a reversible reduction in the polymers' molecular mass and viscosity. This unique property enables efficient and rapid healing of defects within the material (Fig. 27). Furthermore, light can be selectively applied to the damaged area, making it possible to heal objects even while under load [50]. Some other instances of self-healing Metal–Ligand complexes are observed with the formation of *N*-heterocyclic carbenes and transition metals [238].

Supramolecular peptide networks generally suffer from a limitation in their mechanical strength. To address this challenge, mussels have evolved a pH-dependent iron complexation mechanism for adhesion and curing. Ceylan et al. [239] showcased an innovative method for attaining self-repair within metal–ligand coordination frameworks by leveraging pH-induced mechanisms. Their study centered on the interaction of Fe^{3+} ions with catechol ligands, leading to the development of a pH-sensitive crosslinked polymer capable of self-repairing. Impressively, this polymer demonstrated elastic moduli akin to those of covalent bonds, signifying improved mechanical characteristics. Moreover, this approach effectively bolstered the material's strength and enabled self-repair functionalities [239]. This approach stands out due to its capacity to regulate crosslinking by forming mono-catechol-Fe^{3+}, bis-catechol-Fe^{3+}, or tris-catechol-Fe^{3+} complexes at different pH levels, thereby preventing Fe^{3+} precipitation and ensuring precise control over the crosslinking process [240]. Extensively reported is the utilization of Metal–Ligand interactions, particularly dynamic ion interactions, involving the carboxylic acid groups of poly(acrylic acid) (PAA), ferric ions, and polyelectrolytes, as a method for creating self-healing hydrogels [241–245]. Numerous articles have been also reported based on the Metal–Ligand bonds including Metal–Catechol Bonds[246–249], Metal–Histidine Bonds[236, 250–254], Metal–Pyridinyl Bonds[49, 50, 255–258], and Metal–Carboxylate Bonds [31, 259, 260].

6 Conclusion

The significant increase in the production of polymers and their products is a matter of great concern and poses various challenges and considerations. The growing demand for polymers in various industries, including packaging, construction, automotive, and electronics, has led to a substantial rise in their production globally. Combining recycling and self-healing properties in polymers can further enhance their sustainability and lifespan. By incorporating self-healing mechanisms into recycled polymers, the potential for extending the lifespan of the material and reducing waste is increased. Additionally, recycling techniques can be utilized to recover valuable healing agents or components from damaged or aged self-healing polymers, promoting a circular economy approach.

Polymeric materials are prone to mechanical damage, which can lead to degradation, cracks, and a decrease in mechanical properties, thereby compromising their functionality. To address these challenges, a novel class of materials has emerged that possess the capability to autonomously repair themselves. These self-healing materials employ various approaches, including physical, chemical, and physiochemical methods, to restore their integrity and functionality. Numerous review articles have already been published on the topic of self-healing polymers, encompassing various approaches. However, the field of chemical approaches to self-healing is vast and requires dedicated attention. This review aims to specifically focus on the chemical approaches to self-healing, which involve reactive chain ends for covalent and free radical re-bonding, as well as supramolecular chemistry including H-bonding, guest–host chemistry, metal–ligand coordination, π–π interactions, and ionic interactions. By narrowing the scope to chemical approaches, this review aims to provide a comprehensive understanding of the advancements and challenges in this area of self-healing research. Significant emphasis has been placed on the utilization of free chain reactions, specifically the Diels–Alder reaction, in the development of self-healing polymers. The Diels–Alder reaction offers a versatile and efficient means of creating reversible covalent bonds, enabling the healing process in polymeric materials. This review aims to extensively explore and highlight the advancements, strategies, and challenges associated with incorporating Diels–Alder chemistry as a key approach for achieving self-healing capabilities in polymers.

However, despite the significant advancements and promising developments in the field of self-healing polymers, there are still several technical challenges that need to be addressed to achieve widespread industrial adoption. These challenges include the effective repair of macro-scratches, the ability to heal under sunlight or upon contact with air, self-healing at low temperatures, and the use of cost-effective chemistries. While self-healing polymers find applications across various industries, high technology applications are particularly notable, as the value of the end materials outweighs the production cost. Currently, self-healing coatings appear to be the most promising area of application, offering enhanced durability and protection for various surfaces. Irrespective of the specific chemical reactions involved in the self-healing process of polymers, the primary hurdle lies in the network's ability to reorganize itself upon experiencing mechanical damage. While there are some exceptions, such as certain heterogeneous networks, recent research has predominantly focused on low glass transition temperature (T_g) polymers [189]. However, a significant challenge remains in achieving self-healing capabilities in higher T_g polymers, where limited free volume restricts the segmental mobility of polymer chains, and diffusion becomes unfavourable. Therefore, it may be essential to incorporate localized covalently bonded components with both low-T_g and high-T_g properties to enable self-healing in functional materials. Also, recent studies has shown that alternating copolymers facilitate self-healing, whereas block copolymers are insufficient in self-healing [57]. Addressing the remaining challenges in the field of self-healing polymers necessitates multidisciplinary studies that encompass various levels, from the molecular scale to the final material characterization. Such a comprehensive approach presents a significant challenge, as it requires the implementation of numerous refined preparative and analytical techniques. However, this multifaceted approach is anticipated to yield a rapidly expanding range of novel materials with the capability to repair multiple functionalities and closely emulate biological systems. As research progresses, the development of tailor-made self-healing polymeric systems is expected. These systems will find applications in a wide array of fields, including (bio)medical materials and electronics. By incorporating self-healing properties into these materials, their functionality, durability, and reliability can be significantly enhanced, paving the way for innovative and advanced applications in various industries.

Ultimately, the successful advancement of self-healing polymers will depend on continued collaboration and advancements in different disciplines, enabling the realization of materials that possess remarkable healing abilities and can cater to diverse application requirements. To achieve an accelerated industrial breakthrough, further research and development efforts are needed to overcome these technical challenges and optimize the performance, cost-effectiveness, and scalability of self-healing polymers. By addressing these issues, self-healing polymers can potentially revolutionize various industries and offer advanced materials with extended lifespan and improved functionality.

Acknowledgements Authors thank Manipal Academy of Higher Education, Manipal for open access funding for the publication of this article.

Author contributions Mohd. Khalid Zafeer: Collecting the literature, preparation of draft and revision; K. Subrahmanya Bhat: Editing and supervision.

Funding Open access funding provided by Manipal Academy of Higher Education, Manipal. No external funding is received for writing this review.

Data availability No datasets were generated or analysed during the current study. Necessary details are available in the cited publications.

Declarations

Competing interests The authors declare no competing interests.

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