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Dynamic Interfaces in Self-Healable Polymers

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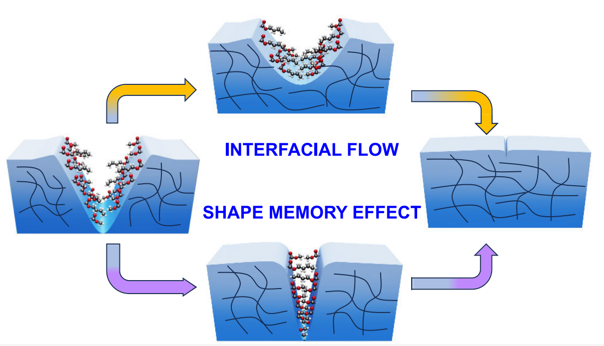

ABSTRACT: It is well-established that interfaces play critical roles in biological and synthetic processes. Aside from significant practical applications, the most accessible and measurable quantity is interfacial tension, which represents a measure of the energy required to create or rejoin two surfaces. Owing to the fact that interfacial processes are critical in polymeric materials, this review outlines recent advances in dynamic interfacial processes involving physics and chemistry targeting self-healing. Entropic interfacial energies stored during damage participate in the recovery, and self-healing depends upon copolymer composition and monomer sequence, monomer molar ratios, molecular weight, and polymer dispersity. These properties ultimately impact chain flexibility, shape-memory recovery, and interfacial interactions. Self-healing is a localized process with global implications on mechanical and other properties. Selected examples driven by interfacial flow and shape memory effects are discussed in the context of covalent and supramolecular rebonding targeting self-healable materials development.

INTRODUCTION

Every biological or synthetic process is initiated at the interface between two environments. Whether viruses, bacteria, or a molecule land on a surface, or two interfaces are created by mechanical damage, the phenomenon that controls these typically nonequilibria processes is the interfacial energy. Defined as the energy needed to disrupt intermolecular interactions or the new bond, surface-free energy is often viewed as the excess energy in interfacial areas compared to the bulk. When two interfaces are created, the chemical composition and/or physical states determine the energy required to rejoin them, and the measurable quantity is interfacial tension.

Although interfacial properties significantly diverge from the bulk, compressibility is one differentiating aspect between solid and liquid interfaces. Changing molecular density at the solid−liquid interface by applying pressure will alter viscoelastic behavior or even induce phase transitions. The traditional tool utilized in these experiments is the Langmuir trough, in which monolayers at the air−water interfaces are amphiphilic insoluble in water layers, typically composed of long alkyl chains (fatty acids, surfactants, phospholipids). A recent comprehensive review of the Langmuir−Blodgett (LB) films addressed endless possibilities of controlling molecular architectures at the air−water interfaces.[1] Unlike highly organized monolayers transferred from the air−water interface onto a solid substrate, interactions between the outer surface of solids and the layers below are more multifaceted. One of the solid-state interfacial "classics" is the surface of ice. A common belief is that the ice is slippery because of frictional, localized heating and a thin water layer formation. This concept was challenged by the mechanical model, where the formation of molecular layers that adopt amorphous dynamic reconstruction results in reduced number of bonds holding the surface molecules. This is reflected in the lower surface freezing temperature.[2,3] Surface polymeric chains also experience enhanced mobility compared to the bulk, reflected in the interfacial regions' surface energy and lower glass transition temperatures (T_gs). Earlier studies identified that films as thin as several nanometers (nm) exhibit a substantial reduction of the T_g compared to the bulk.[4] The distance over which diminishing levels of enhanced mobility extend into the bulk from the interface can be several tenths of nms. Thus, if two interfaces resulting from mechanical damage are created, increased segmental mobilities and greater free volume

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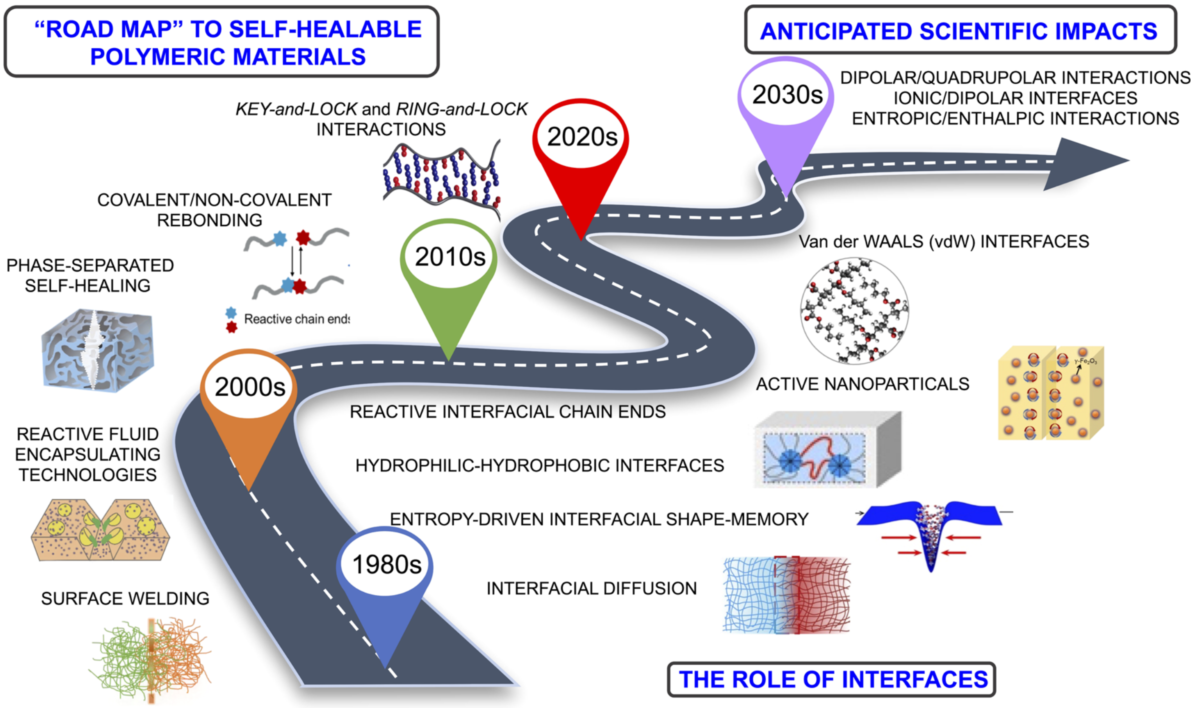

Figure 1. "Road map" of the development of self-healing polymers began in the 1980s and will continue. During the last four decades, novel physical, chemical, and physicochemical approaches were developed, and an understanding of interfacial processes played a key role in advancing polymeric materials to higher performance levels.

reflected in lower T_gs were observed. As shown unambiguously in experimental[5,6] and theoretical studies,[7,8] free dynamic interfaces show the T_g reductions reflected in interfacial surface energies and enhanced segmental mobility; for example, polystyrene (pSty; T_g of ∼100 °C) exhibits a liquid-like surface layer with the reduced T_g by ∼70 °C.[9] These properties play an essential role in the development of new generations of self-healable commodity polymers.

Initially inspired by biological systems, various polymer and composite self-healing strategies depicted in Figure 1 have been employed over the last few decades. Earlier 1980s' theories of crack healing identified a five-stage process involving surface rearrangements, interfacial contact, wetting, diffusion, and randomization.[10,11] In the initial stage of surface rearrangements, the surface's roughness and topography depend on time, temperature, and pressure, thus impacted by molecular weight and molecular weight distribution near the interface. When the crack surfaces come into contact, interfaces wet each other, forming an energetically favorable interface. While details concerning physical, chemical, and physicochemical approaches were outlined in the literature,[12,13] the "road map" that has led to the development of self-healable polymeric materials and composites is illustrated in Figure 1. As depicted, self-healing was conceptually and, to a certain extent, experimentally initiated in the 1980s. During this four-decade journey, interfaces played an essential role in self-healing. It was initiated by macroscopic interfacial diffusion and continued by developing entropically driven shape memory effects and hydrophilic−hydrophobic interfaces to continue with reactive interfacial chain ends and van der Waals (vdW) interfacial forces. Future scientific impacts are anticipated to involve a theoretical understanding and experimental determination of dipolar and polar interactions at the interfacial regions.

Chemical and physical processes are interconnected during self-healing through interfacial phenomenon, it is important to realize the role of physical processes. Macromolecular chains are in a nonequilibrium dynamic state, resulting in nonuniform morphologies with varying response rates. These differences may generate gradients in local volume expansion and the rate of empty space stuffing. Assuming the mechanical damage may cause chain cleavage or chain slippage near newly created surfaces, loose chain ends exhibit lower T_gs than the bulk, and enhanced mobility is reflected in enhanced entropic energies. The effectiveness of the reformation of the loose ends or displaced chains is reflected by the Gibbs free energy (ΔG) and entropy (ΔS), where $\Delta G < 0$ favors recombination when $\Delta S > 0$. Thus, the enhanced interfacial ΔS energies will favor self-healing. This damage-repair cycle is often described as a transition from nonequilibrium to equilibrium states through infinitely equilibrated steps using the recoupling lattice model.[14] Using this approach, localized chain flexibility, reflected by lower T_gs, autonomous self-healing the lattice model[15] predicted that the entropy changes would be localized near the damaged area primarily occupied by dangling ends. Defined as the minimum energy required to remove or add a macromolecular chain from its environment, cohesive energy density (CED) depends upon copolymer composition and repeating unit sequence. When plotted against the copolymer monomer molar ratio, the CED values exhibit a linear dependence that gradually increases with one component's increasing molar fraction. However, near the self-healing copolymer composition,[16,17] the CED values reach maxima. This behavior usually occurs in a narrow compositional range for preferentially alternating/random copolymer topologies and is attributed to energetically favorable interchain forces. If semihelix polymer chains experience mechanical damage, then they are usually compressed. Upon the release of applied force,

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stored entropic energies in compressed copolymer segments decompress and restore to the initial state. This shape-memory effect, driven by entropy stored during mechanical damage, may be responsible for self-healing in thermoplastics that do not involve chemical reactions.

Physical damage that leads to polymer rupture and chain separation may result in isolated chain ends. If the free radicals or other dynamic reactive groups are generated, then entropy-driven shape memory physical responses should be synchronized with rebonding reactions. Since physical or chemical processes may not be easily differentiated, the repair process may be initiated longitudinally along the damaged surface, driven by energetically favorable physical interactions followed by chemical reactions. A percolation transition usually occurs when enough macromolecules reconnect longitudinally, facilitated by high interfacial energy in areas with a smaller curvature (high surface tension) at the damage site. Using a simple model of autonomic self-healing of unentangled polymer networks mimicking dangling chains attachment to a polymer network,[18] self-healing was attributed to the formation of bridges and the recovery of the material strength across the fractured interface. After initial bridges were formed, slower "hopping" diffusion facilitated the complete recovery of bonds across the fractured interface.

Being a multifaceted phenomenon influenced by polymer composition, chain flexibility, reactivity, and shape-memory effects, self-healing is a local phenomenon with global implications. Polymer-architecture-dependent stored entropic energy during deformation can be quantified using the rubber elasticity theory and correlated to the scratch closure degree experimentally observed in microscopic measurements. Using well-defined thermoplastic healing polyurethanes with variable soft phase fraction contents, pressure-free damage closure of scratches maintaining mechanical integrity is governed by the capability of the polymer to store entropic energy during damage. The review focuses on fundamental physical (interfacial flow and shape memory) and chemical (covalent and noncovalent) interfacial processes that target self-healing in thermoplastic and thermoset polymers.

■ SELF-HEALING DRIVEN BY INTERFACIAL FLOW AND SHAPE MEMORY

Generally, two often difficult-to-isolate processes drive self-healing: interfacial flow and shape memory effects. Figure 2 schematically illustrates the interfacial recovery involving interfacial flow (a) and shape memory recovery (b). In the interfacial flow, the percolation parameter derived from the average interdiffusion distance between chains is critical during the diffusion of interfaces. Depending on the spatial distribution of chain ends, for their random dispersion, the fracture energy $G(t)$ is time-dependent and increases following the equation $G(t)/G_\infty = [t/\tau^*]^{1/2}$, where τ is the reptation time, which is proportional to the chain molecular weight to the third power. In contrast, the healing process is accelerated for chain ends segregated at the interface following the $G(t)/G_\infty = [t/\tau^*]^{1/4}$ relationship. The temperature-dependent time is critical in ballistic self-repair experiments, and it is significantly impacted by competing healing and cool-down processes. The enhanced interfacial mobility is attributed to lower local T_g and enhanced free volume efficiently facilitating interfacial diffusion, not necessarily to the T_g of the bulk polymer. Remodeling of neighboring loose chain ends depicted in Figure 2a will be facilitated by interfacial diffusion from the side banks to the highest surface energy bottom of the cut with the smallest curvature, which may supply rebonding of reactive groups, resulting in bottom-up self-repair. Leveraging on the interaction of immiscible soft segments with low T_g and hard segments with high T_g within polymers, phase-separated morphologies are beneficial.

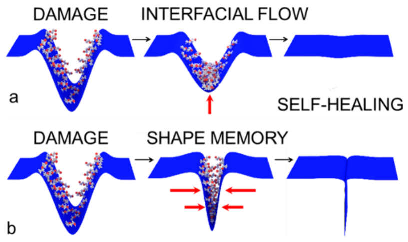


Figure 2. Schematic illustration of two physical repair mechanisms driven by (a) interfacial flow and (b) shape memory recovery[22] (reproduced with permission from ref 22).

Entropic interfacial energy stored during damage participates in recovering mechanical properties. Within the polymer network, shape memory components exhibit spring-like behavior, rapidly returning to their initial state after mechanical damage or compression (Figure 2b). Although counter-intuitive, this directional altitudinal growth will differ from a lateral closure due to elastic recovery illustrated in Figure 2b which may occur for cross-linked or entangled polymer networks. This shape memory-assisted approach assumes minimal or no chain cleavage and is attributed to shape recovery. Shape-memory-assisted self-healing, depicted in Figure 2b, is frequently observed in biological systems. For example, when wounds heal, the conformational entropic energy generated by the damage closes and seals the physical injury. This process subsequently enables essential chemical and physical processes for strength recovery without external intervention. In synthetic polymers, two approaches have been developed in shape-memory-assisted self-healing. The first approach involves integrating pretensioned shape memory alloy wires or fibers into a polymer matrix.[19−21] Upon heating, these materials undergo self-healing driven by contractual forces that draw crack surfaces together. Essentially, polymers can "remember" a permanent shape, which can be temporarily altered and subsequently returned to the original shape when triggered by external or internal stimuli. Dispersity of polymers is critical to self-healing dynamics, and it was shown that polymer chains with multiple lengths interdiffuse faster to reform opposite interfaces. Combining approaches depicted in Figure 2 into one system may be advantageous in developing self-healable systems.

One of the examples of shape-memory-assisted self-healing polymers are thermoplastic polyurethane fibers. Composed of polycaprolactone diols, 1,4-butanediol (BDO), hydroxyl-modified spiropyran, and hexamethylene diisocyanate, these fibers exhibit microscale phase-separated morphologies[23] in which BDO in the hard-segment-rich domain cannot be disengaged under mechanical forces. At the same time, soft-segment-rich domains store entropic energy due to the unfolding of crystalline blocks and the elongation of low T_g amorphous segments, resulting in decreased entropy. Upon heating, the chains in the soft-segment-rich domain regain mobility, maximizing entropy. This released energy pulls crack surfaces together, leading to self-healing.

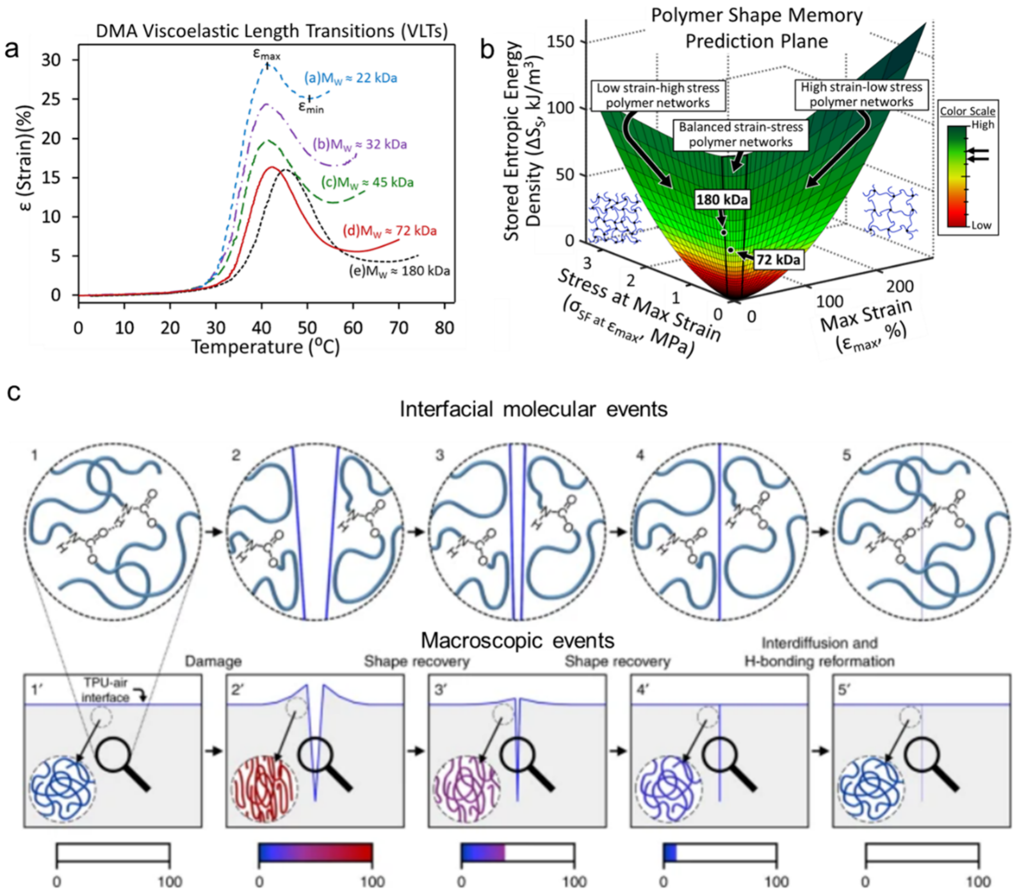


Figure 3. Shape-memory-assisted self-healing. (a) DMA strain curves showing the VLT measured from polyurethane with different molecular weights. (b) Shape memory polymer prediction plane. (c) Illustration of molecular level (1−5) and macroscopic (1′−5′) events during entropy-driven self-repair of polyurethane: chain conformational changes around the damage, breakage, and formation of hydrogen bonds, and disentanglement and reentanglement of chains during the process[24] (reproduced with permission from ref 24).

Another approach is to harness continuous viscoelastic interfacial flow to achieve autonomous self-healing while maintaining high strength and stiffness under ambient conditions.[24] Using dynamic mechanical analysis (DMA) and measuring strain as a function of temperature enabled the detection of shape memory T_{VLT}s (Figure 3a). During these transitions, directional elongations occur, displaying viscous behavior when approaching interfacial T_g, followed by subsequent retractions due to the release of stored conformational entropic energy attributed to chemical or physical cross-links. Correlating the VLT values with maximum stored strain, stress, and entropic energy density allows predictions of relative shape memory capacities by creating a 3D plot of strength ranging from high-strain, low-stress polymer networks to low-strain, and high-stress polymer networks (Figure 3b). Higher VLT values represent greater stored entropic energy and higher overall shape memory storage capacity. Employing a 3D-laser microscope to track wound closure with sufficient molecular weight and junction density revealed two sequential events involved in interfacial self-repair. Damage leads to a decrease in the number of H-bonds and chain conformational changes generating a restoring interfacial force that reunites the cut surfaces to minimize interfacial energy. This autonomous closure is followed by H-bond reformation or other chemical reactions during chain diffusion, restoring mechanical integrity (Figure 3c). This superior strength and stiffness combination is critical in creating robust self-healing polymers, and biology has mastered this process. The ideal bond rupture would occur in a uniform material network at the points of weakest bond strength if mechanical forces were evenly distributed. In synthetic materials, bond ruptures are usually unevenly distributed due to irregular entanglements and cross-linked points.

As illustrated in Figure 1, extensive studies have been devoted to advancing self-healing properties through bulk chemical and physical modifications. These endeavors have involved enhancing the intrinsic ability to repair the damage autonomously. In pursuing bulk physical and chemical modifications leading to self-healing, the significance of interfaces has often been disregarded. Needless to say, interfaces play a crucial role in the overall performance of composite integrity, neglecting the influence of interfaces in self-healing materials limits our understanding of how to optimize the overarching goal of enhancing the resilience, longevity, and functionality of polymers. Thus, understanding the role of interfaces in bulk modifications will be critical in opening new avenues for developing advanced self-healing materials. The following sections identify and discuss interfacial covalent rebonding and supramolecular interactions targeted at self-healing.

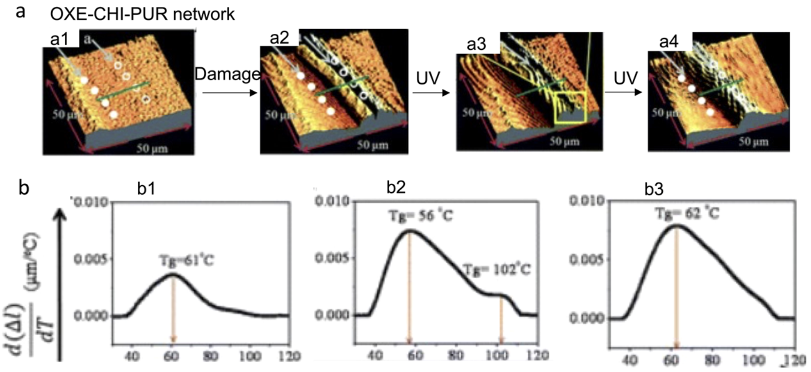


Figure 4. Self-healable oxetane-substituted chitosan polyurethane using free-radical rebonding. (a) Atomic force microscopy (AFM) images of undamaged (a1), damaged (a2), UV-exposed (a3), and repaired (a4) OXE−CHI−PUR, and (b) the plot of d(Δl)/dT as a function of temperature in undamaged (b1), damaged (b2), and repaired networks (b3)[7] (reproduced with permission from ref 7).

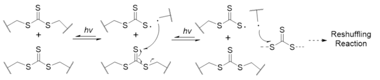
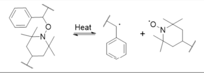
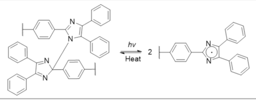
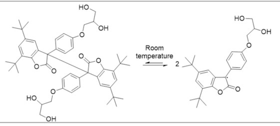
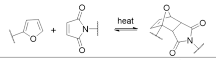
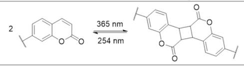
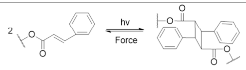
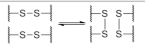
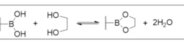
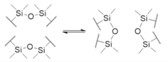
■ COVALENT REBONDING TARGETED AT SELF-HEALING

Covalent bonds may break when polymers undergo mechanical stress, generating reactive free radicals or other groups. The quantity of free radicals produced varies depending on their stability. If these free radicals remain active long enough to migrate to damaged areas and engage in recoupling reactions following bond cleavage without being quenched by oxidative processes, then effective self-healing may occur by reforming covalent bonds by recoupling of two free radicals with unpaired electrons. For this process to occur, the stability and reactivity of free radicals is important, and free radical recoupling represents a fascinating intersection of chemistry and material science, offering a promising avenue for developing resilient and sustainable materials.

What distinguishes these self-healable polymers is their ability to harness free radicals and utilize them toward autonomous repair. For example, for oxetane (OXE) or oxolanes (OXO)-substituted chitosan (CHI) polyurethane (PUR) networks, mechanical damage can cause cleavage of C−O and C−N bonds, resulting in the formation of $-C^\bullet$, $-N^\bullet$, and $-O^\bullet$ free radical intermediates in the interfacial regions.[7,25,26] In this case, OXE and OXO offer low ring opening activation energies, producing stable free radicals that are effectively utilized in developing self-repairable PUR networks. The OXE-substituted PUR network (OXE−CHI−PUR) involves the reaction of hexamethylene diisocyanate (HDI) with OXE-modified CHI and polyethylene glycol (PEG), resulting in a heterogeneous cross-linked PUR network. When the network is mechanically damaged, bond cleavages generate reactive free radicals and carbocation at the interfaces. Self-repair process involves close packing and/or network shrinkage upon UV exposure, primarily due to the chair-to-boat conformational changes of the glycosine units of CHI. Figure 4 illustrates interfacial flow resulting in self-healing. This process is also enhanced by surface tension-driven flow during which two interfacial T_gs at 56 and 102 °C are observed (Figure 4b).[7] Cross-linked methyl-α-D-glucopyranoside (MGP)-PUR networks, prepared from PEG, HDI, and MGP, have also demonstrated autonomous self-repair capabilities under ambient conditions without external intervention.[27] A comprehensive review of covalent and noncovalent self-healing provides further details on the PUR-based polymers.[28]

Failure to stabilize dynamic interfacial free radicals can lead to oxidation that diminishes their reactivity, ultimately terminating self-healing. An intriguing alternative, however, involves dynamic reshuffling and exchange interfacial reactions, which generate stable free radicals. Table 1 lists covalent bond dissociation energies for various moieties. Trithiocarbonates, for example, undergo thermo- or photoinduced reshuffling reactions. The C−S bond is weaker than the C−C bond, reflected in lower bond dissociation energies (259 kJ mol^{-1} and 348 kJ mol^{-1}, respectively). Therefore, sufficient thermal energy or strong UV irradiation can cause hemolytic cleavage of a C−S bond, generating stable free radicals capable of exchange reactions with neighboring trithiocarbonates. A thermoset containing trithiocarbonates can be 3D printed

Table 1. Examples of Free-Radical Rebonding and Exchange Reactions Utilized in Self-Healable Polymers and Their Energies of Dissociations

Self-Healing Reactions		Estimated Dissociation Energy (kJ mol^{-1})
Trithiocarbonates		259
Alkoxyamine		196
Hexaarylbiimidazole		75
Diarylbibenzofuranone		85
Diels-Alder reactions		100
Coumarin [2 + 2] cycloaddition		137
Cinnamoy [2 + 2] cycloaddition		100-170
Disulfide exchange		250
Boronic esterification		93
Siloxane exchange		569

under UV light and rapidly self-heal through these reshuffling reactions.[29] Similarly, alkoxyamine exhibits a dynamic nature through C−ON bond homolysis, in which the C−ON bond dissociation energy is 196 kJ mol^{-1},[30] releasing a persistent nitroxyl radical R−NO$^{\bullet}$ and a transient alkyl R−C·.[31] This radical recoupling has been known in developing smart materials for decades.[32−34] Incorporating a specific dihydroxylated alkoxyamine moiety as a cross-linker and polyethylene glycol as soft segments, a self-healable covalent network of stiff polyurethane was achieved, even with subambient T_g. In this system, the nitrile group in the dihydroxylated alkoxyamine's α position stabilizes the radicals. Owning the high equilibrium constant of reversible C−ON bond, polyurethanes can be repeatedly repaired at ambient temperature without external intervention and maintain high stiffness.[35]

Hexaarylbiimidazole derivatives serve as dynamic cross-linkers to create healable polymer networks, such as polydimethylsiloxane, polyethylene glycol, and poly(methyl methacrylate).[36,37] Here, the low bond dissociation energy of C−N bond (75 kJ mol^{-1}) between the imidazole rings of hexaarylbiimidazole enables homolytic and reversible cleavage,[38] generating two 2,4,5-triarylimidazoyl radicals upon light irradiation. These radicals subsequently can recombine thermally to regenerate the original imidazole dimer on the interface. Cleaving and reforming covalent bonds in hexaarylbiimidazole molecules, solvent-free, repeatable molecular architectural transformation between liquid-star and non-liquid-network polymers can be achieved.[36] Liquid star-shaped polymers with 2,4,5-triphenylimidazole end groups are converted into nonliquid network polymers by UV irradiation, and this process can be reversed through immediate dynamic recoupling, producing liquid star-shaped polymers with 2,4,5-triphenylimidazoryl radical end groups. Another example of free radical recoupling involves diarylbibenzofuranone which has a dynamic C−C linkage. The modification around the C−C linkage lowers the bond dissociation energy to 85 kJ mol^{-1} and stabilizes the radicals generated from C−C bond cleavage, enhancing the tolerance toward oxygen.[39] When incorporated into cross-linked polycarbonate, dynaimc diarylbibenzofuranone enables self-healing at room temperature upon mechanical damage which is driven by the dissociation of tetrahydroxy-functionalized diarylbibenzofuranone, leading to the formation of arylbenzofuranone radicals.[40]

One of the chemical modifications implemented into polymer networks is the reversible cycloaddition Diels−Alder (DA) reaction, with retro-DA, bond dissociation energy is 100 kJ mol^{-1},[41] where diene and dienophile pairs facilitate thermally reversible cross-linked networks.[42] Tetrafunctional monomers with coumarin photoactive groups can form a rigid polymer network via phototriggered [2 + 2] cycloaddition reactions exposed to 365 nm light. Dissociation of coumarin dimers requires activation energies 137 > kJ mol^{-1}.[43] Thus, exposure to 254 nm UV light cleaves the cross-linked network, forming monomeric or low molecular weight fragments, an interfacial T_g reduction, facilitating enhanced segmental mobilities and self-healing. This process leads to the recovery of the T_g and hardness.[44] Similarly, phototriggered [2 + 2] cycloaddition of a 1,1,1-tris(cinnamoyloxy-methyl) ethane (TCE) monomers form cyclobutane structures through the reversible conversion of cyclobutene to C═C bonds.[45,46] The cycloaddition reaction leverages the cleavage of C−C bonds within cinnamene rings between TCE monomers triggered by mechanical damage, leading to the restoration of the original cinnamoyl groups. These cycloaddition reaction-based healing polymers have been embedded into various polymer matrices, including epoxies, polyurethanes, caprolactones, polyesters, polyacrylics, anthracene-maleimide-based polymers, poly(ethylene oxide), and cross-linked polylactic acid.[47−55] Photochemical cycloadditions provide a light-induced dynamic self-healing and interfacial photocycloaddition reactions polymer network constructs are obtained by controlling the opening and closure of four-membered rings in response to light of variable wavelengths. A few molecules are known to possess the ability to facilitate this type of self-healing, and include coumarin, cinnamene, and anthracene derivatives.

Dynamics of disulfide bonds provide reversibly of cleavage and reformation under various conditions, including heat, pH, reoxidation, and exposure to light. Due to their bond dissociation energy (250 kJ mol^{-1}) and easy functionalization with diverse thiol-bearing building blocks, these exchange reactions are particularly attractive in developing dynamic self-healable networks.[56−59] The versatility of thiuram disulfides cross-linked polyurethanes to self-heal is attributed to the ability to self-heal under ambient conditions, in the presence of visible light, in air, at room temperature, and in the absence of a solvent.[57] Furthermore, incorporating aromatic ring-modified disulfide bonds into polyurethanes results in superior toughness.[58] A similar exchange concept has been applied to develop self-healable polyurethane elastomers by incorporating diselenide bonds into polymer networks.[60] The dynamics of reversible formation of boronic esters through B−O bond (bond dissociation 93 kJ mol^{-1})[61] rebonding with 1,2-diol or 1,3-diol under ambient conditions was also utilized. The equilibrium between boroxine and boronic acid can be manipulated by adjusting the temperature, adding a Lewis base, or varying concentration. Due to catalyst-free rapid dynamic exchange at ambient conditions in aqueous media, this reaction has been utilized in dynamically rearrangeable hydrogel interfaces.[62,63] Self-healing in boronate ester-cross-linked poly(vinyl alcohol) or catechol-functionalized copolymers can be also achieved under acidic or neutral pH conditions.[62] Furthermore, dynamic boronic ester formation can create self-healable bulk polymers without water.[64]

The exploration of the dynamic equilibrium of siloxanes and its application in the chemical stress relaxation of a PDMS elastomer dates back to 1954.[65] The Si−O exchange reactions in siloxanes require an anionic initiator or a basic catalyst (Table 1) due to the higher bond dissociation energy (569 kJ mol^{-1}).[66] For example, a polydimethylsiloxane (PDMS) network prepared from tetramethylammonium-silanolate-initiated ring-opening copolymerization of octamethylcyclotetrasiloxane and bis(heptamethylcyclo-tetrasiloxanyl)ethane can heal upon heating at 90 °C, which was attributed to the reactive silanolate end groups facilitating the exchange of Si−O bonds in siloxanes. However, by tuning the concentration of anionic initiator and the density of cross-linkers, PDMS networks display stress relaxation and self-healing at ambient conditions.[67] Furthermore, incorporating bifunctional silyl ether into polydicyclopentadiene thermoset allows stress relaxation, healing, or remolding while maintaining the capability for orthogonal deconstruction. In this case, healing is achieved through dynamic exchange based on the acid-catalyzed cleavage and reformation of bifunctional silyl ether using the low-cost food additive octanoic acid.[68]

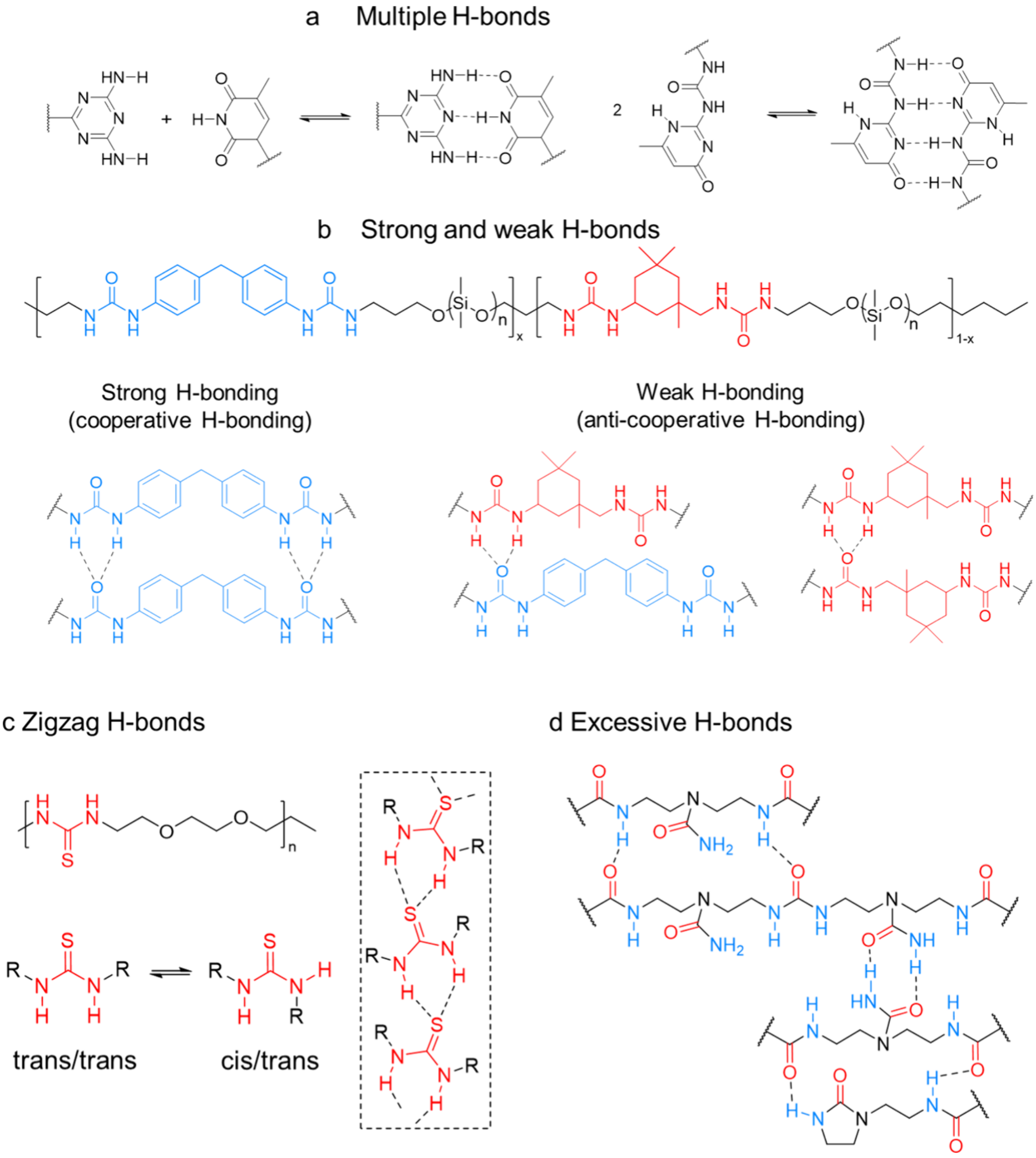


Figure 5. Examples of dynamic H-bonding in self-healable polymers. (a) Triple H-bonds between thymine and 2,6-diaminotriaine and quadruple H-bonds of two ureidopyrimidinones. (b) The combination of strong and weak H-bonds in polydimethylsiloxane-4,4′-methylenebis(phenylurea) self-healable networks.[74] (c) The H-bonding mode of thiourea forms nonlinear zigzag arrays adopting trans/trans and cis/trans conformations.[76] (d) H-bonds between diacids and triacid associations derived from vegetable oils[77] (reproduced with permission from refs 74, 76, 77).

■ INTERFACIAL SUPRAMOLECULAR INTERACTIONS TARGETED AT SELF-HEALING

Noncovalent interactions facilitated by supramolecular bonds in the interfacial regions, including H-bonding, metal−ligand coordination, ionic, $\pi-\pi$, $\pi-\sigma-\pi$, van der Waals, and host−guest interactions represent unique attributes due to their ability of rapid reassembly and ubiquitous nature. In contrast to covalent rebonding, these noncovalent bonds can be dynamically broken and relatively quickly reformed, allowing the material to recover its structural integrity. Many self-assembly processes rely on these interactions, most often sustained by van der Waals, electrostatic, dipole−dipole, and H-bonding forces. One of the most intriguing attributes is the ability to manipulate these interactions by "encoding" the molecular level features such as copolymer sequence or functional side groups capable of defining molecular recognition patterns. This ability will allow precise control over the larger scale structures and use these interactions to develop self-healable interfaces.

■ H-BONDING

H-bonding's directionality and high concentration levels per unit volume contribute significantly to mechanical strength. With fast reversibility, this makes H-bonding a valuable motif in self-healable polymers. Thus, a wide range of self-healable polymers with diverse mechanical properties ranging from supramolecular gels to tough elastomer and rubber materials were developed.[69] For example, depicted in Figure 5a are triple H-bonds involving thymine and 2,6-diaminotriaine[70] and

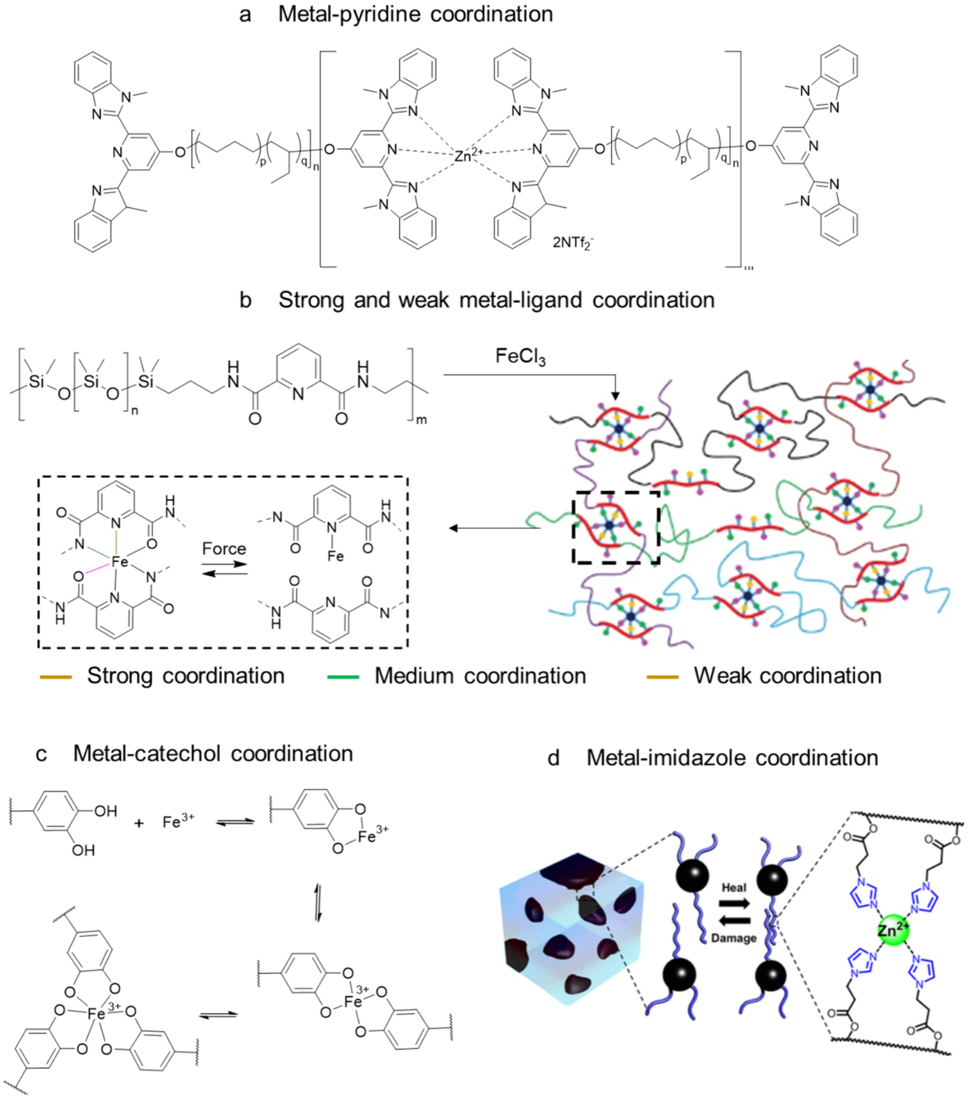


Figure 6. Examples of metal–ligand coordination in self-healable polymers. (a) Self-healable polymer network formed by coordination of $Zn(NTf)_2$ and 2,6-bis(1-methylbenzimidazolyl)pyridine ligand-functionalized poly(ethylene-*co*-butylene).[81] (b) Self-healable polydimethylsiloxane network formed by coordination of $Fe(Cl)_3$ and 2,6-pyridinedicarboxamide ligands.[86] (c) Reversible Fe^{3+}-catechol complexes in self-healable hydrogels. (d) Self-healable multiphase polymer cross-linked by coordination of Zn^{2+}-imidazole[94] (reproduced with permission from refs 81, 86, 94).

quadruple H-bonds of ureidopyrimidinones (Upy)[71,72] with the strengths comparable to covalent bonds. One example is polyisobutylenes, which are typically liquid at room temperature and can transform into robust rubber-like materials when modified with thymine and 2,6-diaminotriazine end groups. The formation of triple H-bonds enables the precise control of dynamic responses and self-healing.[70] Similarly, the quadruple H-bonds of Upy units with high dimerization constant result in supramolecular assemblies with rubber-like behavior and temperature-dependent mechanical strength.[73]

PDMS elastomers consisting of a blend of strong and weak H-bonding derived from bisurea bonds offer self-healing with tunable mechanical properties, including stretchability, toughness, and even underwater autonomous self-healing (Figure 5b).[74] The variable strengths of H-bonding in these elastomers allows them to detect external signals of different intensities, opening up possibilities for applications in human–machine interactions. For example, a multilayered self-healing device can be constructed from a pair of self-healable polymers with identical dynamic H-bonds and immiscible PDMA and PEG backbones. When misaligned after damage, these multilayer structures exhibit composition gradients that drive directional chain diffusion on the interfacial regions to enable autonomous realignment and self-heal.[75]

In contrast to bis-urea H-bonding, which may crystallize or form clusters resulting in brittleness, the incorporation of thiourea moieties results in zigzag H-bonded arrays that prevent unfavorable crystallization.[76] These densely packed H-bonds between thiourea units can also serve as cross-linkers of low-molecular-weight polymers, yielding robust and dynamic self-healing materials. The presence of triethylene glycol spacers connecting the thiourea units appears to influence the activation energy required for exchanging hydrogen-bonded thiourea pairs through slip motion. The uniqueness of highly cross-linked, noncovalently bonded components is the dynamics self-healing by compression (Figure 5c).

Conventional rubbers typically consist of long-chain, cross-linked networks capable of stretching and recovering to their

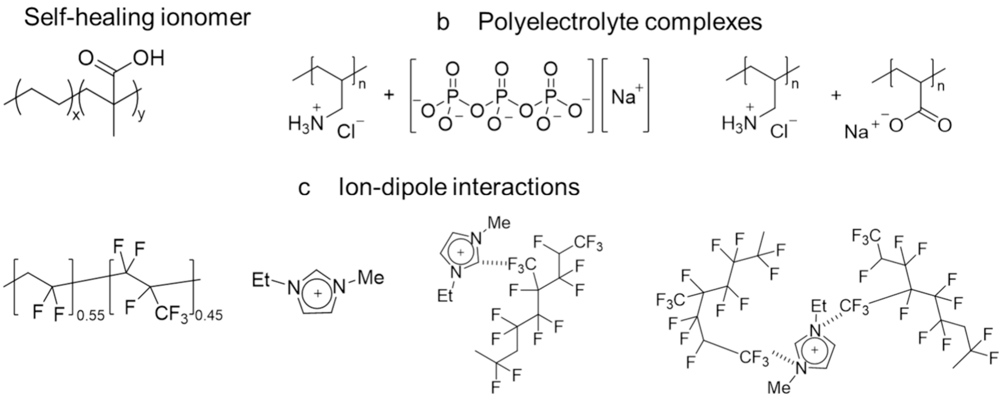


Figure 7. Examples of ionic interactions in self-healable polymers. (a) Self-healable poly(ethylene-*co*-methacrylic acid)-based ionomers.[96] (b) Self-healable polyelectrolyte complexes formed by poly(allylamine hydrochloride) (PAH)/tripolyphosphate;[98] PAH/poly(acrylic acid) (PAA) complexes.[99] (c) Self-healable ion conductor formed by poly(vinylidene fluoride-hexafluoropropylene) and 1-ethyl-3-methylimidazolium.[101]

initial state. However, small molecules like fatty diacids and triacids derived from vegetable oils can generate a rubber-like material capable of self-healing at room temperature.[77] These materials have been synthesized in two steps: (1) a mixture of fatty diacid and triacid is condensed with diethylene triamine and (2) reacted with urea, generating a variety of oligomers equipped with complementary H-bonding moieties (Figure 5d). The interactions between these H-bonding motifs give rise to a self-repairing network, resulting in a translucent glassy plastic material that exhibits soft rubber-like behavior at temperatures up to 90 °C and can self-repair under ambient conditions.

■ METAL–LIGAND COORDINATION

The binding strength and complexation dynamics of metal–ligand coordination can be tuned by varying the metal ions and ligand pairs. For example, the binding affinity of pyridine-based ligands follows an ascending order as their electron-donating capability increases: pyridine, bipyridine, and terpyridine. Similarly, the binding affinity of terpyridine toward metals exhibits the following order: $Ru^{2+} > Os^{2+} > Fe^{2+} > Zn^{2+} > Cd^{2+}$. In self-healable metallopolymers, metal complexes dissociate when polymers are fractured or damaged, and their recombination can be triggered by exposure to light, elevated temperatures, or pH changes.[78−80]

Self-healable metallopolymers can also be prepared using a rubbery telechelic poly(ethylene-*co*-butylene) with 2,6-bis(1′-methylbenzimidazolyl)-pyridine ligands, which form metal-ion binding with Zn^{2+} at each chain end (Figure 6a).[81] This metallopolymer heals by exposure to UV light when damaged and is driven by a photothermal effect. Upon light irradiation, metal–ligand complexes are electronically excited and generate heat upon relaxation to the ground state. The disruption of these metal complexes enhances interfacial mobility, facilitating dynamic polymer motion and self-healing. Upon cooling, the complexes and clusters reassemble, immobilizing the mobile phase and healing the scratch. Pyridine-containing multidentate ligands typically have higher binding affinities for a wide range of transition and rare earth metal ions, primarily due to their chelation effect.[82−84] By cross-linking poly(4-vinylpyridine) with $[Ru(bpy)_2]^{2+}$ self-healable gels can be prepared.[85] Upon visible light irradiation, cleavage of the Ru-ligand linkage between the ruthenium and the poly(4-vinylpyridine) leads to solubilization of the poly(4-vinylpyridine) chains. The bond can be reformed upon heating and this process is reversible, enabling multiple self-healing cycles.

To achieve autonomous self-healing at room temperature, a network of PDMS was cross-linked by Fe^{3+}-2,6-pyridinedicarboxamide complexes shown in Figure 6b.[86] Self-healing is attributed to the diverse bonding energies associated with Fe^{3+}-Npyridyl, Fe^{3+}-Namido, and Fe^{3+}-Oamido, ranging from strong to weak. The weaker bonds are crucial in dissipating energy during stretching and facilitating on-demand self-healing, while the metal ions remain closely associated with the ligands, ensuring rapid bond reformation. Additionally, counterions can influence the self-healing dynamics, as demonstrated by PDMA network cross-linked by Zn^{2+}-2,2′-bipyridyl coordination and a series of other counterions.[87] The synergy of noncoordinating and multimodal anions simultaneously enhances mechanical toughness and self-healing efficiency.

Mussel thread cuticles contain a protein rich in catechol and Fe^{3+} ions, shown in Figure 6c, which is another nature-inspired self-healing approach.[88] These metal-catechol cross-links form a robust coating with high hardness and extensibility. Furthermore, the metal–catechol bonds can spontaneously reform after breaking, and the cuticle could self-heal by reforming metal–catechol complexes. Inspired by this biological process, dynamic self-healable polymer gels were developed by blending branched catechol-modified PEG with Fe^{3+} ions at basic pH.[89] This approach allows for the formation of monocatechol–Fe^{3+}, bis-catechol–Fe^{3+}, or tris-catechol–Fe^{3+} complexes at varying pH values, offering precise control of cross-linking without the precipitation of Fe^{3+}. This system can be extended by incorporating other "hard" metal ions, such as Al and V.[90] Additionally, catechol-modified polymers, such as polyurethane and methacrylamide, have been also explored in self-healing.[91,92]

Zn^{2+}–imidazole interactions with fast exchange dynamics were also encountered in biological systems.[93] Taking advantage of these dynamic metal–imidazole associations and incorporating them into synthetic polymers resulted in self-healing soft/hard two-phase Zn^{2+}–imidazole cross-linked pervasive networks (Figure 6d).[94] The metal–ligand complexes embedded in the soft matrix dynamic properties which can be easily adjusted by modifying various molecular parameters. These polymers exhibit remarkable self-healing capabilities under ambient conditions. Another approach is electrolyte-engineered with light-responsive conductivity, which involves dynamic imidazole ligand-containing diary-

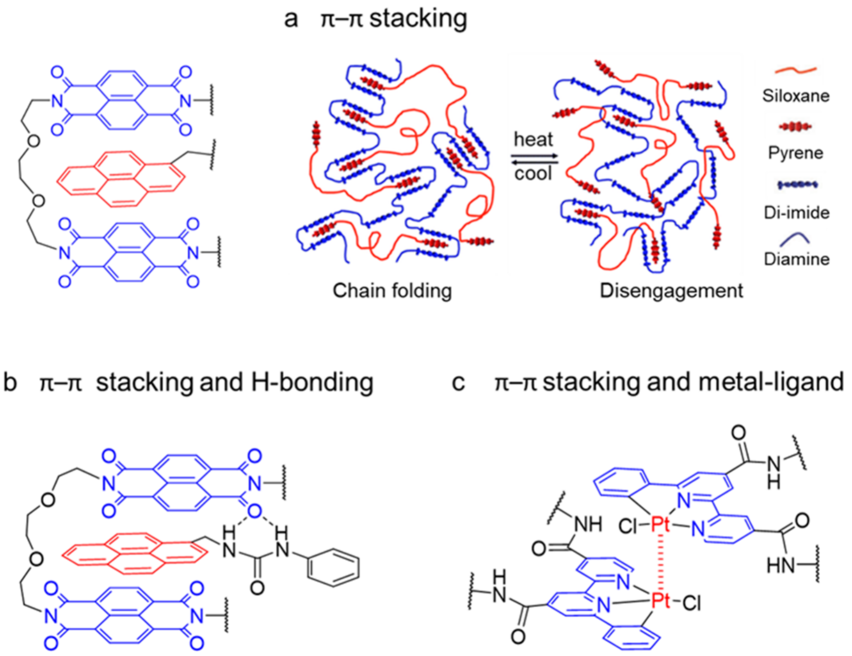


Figure 8. $\pi-\pi$ stacking interactions in self-healable polymers. (a) Face-to-face $\pi-\pi$ stacking interactions between pyrene (red) and naphthalene diimide oligomers (blue). Schematic representation of the self-healing mechanism involving chain-folding polyimide (blue) and pyrene end-capped siloxane (red).[102] (b) $\pi-\pi$ stacking and H-bonding combined interactions between pyrenemethylurea and chain-folding polyimide.[103] (c) A combination of Pt⋯Pt and $\pi-\pi$ interactions between cyclometalated platinum(II) complexes[106] (reproduced with permission from refs 102, 103, 106).

lethene and Ni^{2+} metal-ion coordination.[78] This approach enables reversible changes in DAE-Ni^{2+} complex binding strength upon UV and visible light irradiation, resulting in altered film resistance and ion mobility. These polymer electrolytes efficiently self-heal, recovering their mechanical properties and ion conductivity after damage, thus offering promising applications in electronics.

■ IONIC INTERACTIONS

Ions in polymers often form cross-links through cation−anion interactions, which are often reversible, thus potentially facilitating self-healing. The strength of ionic interactions can be fine-tuned by adjusting the anion−cation charges.[95] For example, poly(ethylene-*co*-methacrylic acid) (pEMAA)-based ionomers self-heal upon ballistic puncture (Figure 7a), whereas low-density polyethylene cannot self-heal.[96] This phenomenon can be elucidated through a two-stage process. Initially, the impact of a ballistic projectile disrupts the ordered ionomeric network within pEMAA, simultaneously generating thermal energy due to frictional forces, thus raising the local temperature at the puncture, causing localized polymer melting and interfacial flow. As a result, the molten polymer interfaces interdiffuse, leading to the closure of the puncture.

Stiff, self-healing dynamic gels can be created by mixing poly(allylamine hydrochloride) (PAH) with phosphate-bearing multivalent anion.[97] Self-healing behavior was also observed using a combination of poly(acrylic acid) PAA and PAH in the presence of NaCl (Figure 7b).[98] Interestingly, the efficiency of self-healing increases with higher NaCl concentrations, indicating that the addition of salt disrupts the original ionic interaction between PAA and PAH, thereby enhancing the chain mobility. The presence of water also affects self-healing, as demonstrated in polyelectrolyte multilayered assemblies. Upon water exposure, a 90% healing efficiency was achieved.[99] Furthermore, star-shaped PEG chains modified with alendronate triggered by calcium ions can also form dynamic reversible cross-linked networks via ionic interactions between carboxylic groups of PAA and ferric ions, enabling electrically self-healing hydrogels.[100]

Another type of interaction, ion-dipole interaction, is found in ionic liquids and fluorinated polymers (Figure 7c). This interaction between poly(vinylidene fluoride-hexafluoropropylene) and 1-ethyl-3-methylimidazolium has been harnessed to develop stretchable, transparent, and self-healing ionic conductors.[101] Incorporating poly(vinylidene fluoride-hexafluoropropylene) containing a substantial hexafluoropropylene content results in low crystallinity and a high dipole moment. These inherent properties enable the polymer to undergo autonomous self-repair at room temperature.

■ VAN DER WAALS INTERACTIONS

Biological macromolecules, including peptides, proteins, and nucleic acids, exhibit close correlations between $\pi-\pi$ stacking interactions and stereochemistry. These interactions have also proven significantly valuable in developing self-healing materials,[102,103] but often require external input. For example, a low molecular weight polyimide with π-electron-poor receptor sites forms a noncovalent polymer complex through $\pi-\pi$ stacking with a telechelic polysiloxane containing π-electron-rich pyrenyl end-groups (Figure 8a).[102] This network displays rapid externally assisted healing at elevated temperatures. This dynamic thermally initiated process partially dissociates complementary $\pi-\pi$ stacking interactions, thus allowing interfacial flow and repair. Upon cooling, these interactions gradually reestablish themselves and restore their original properties. A synergistic combination of $\pi-\pi$ interactions, metal coordination, and H-bonding can also facilitate self-healing.[103−106] For example, combining H-

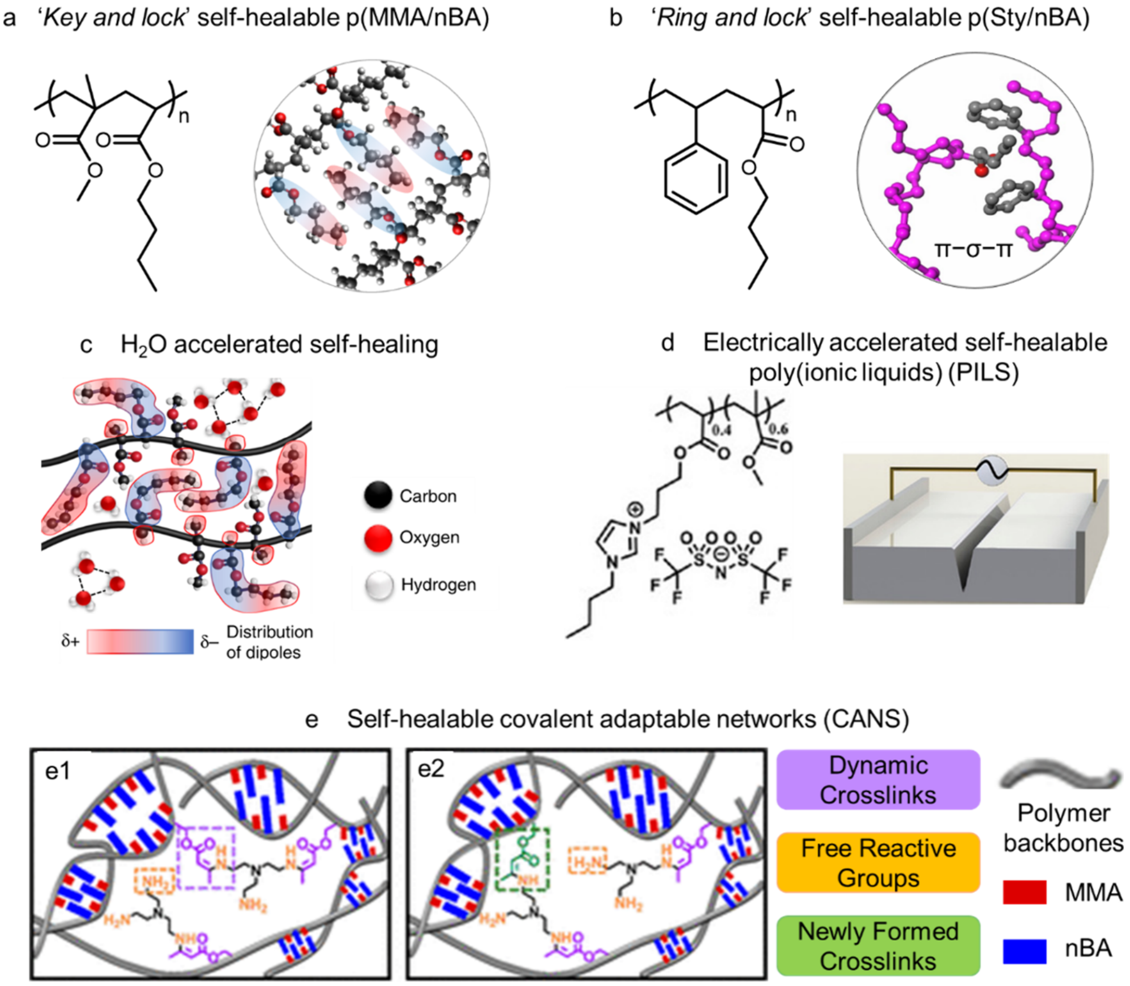


Figure 9. Self-healing through van der Waals forces. (a) Key-and-lock associations in self-healable p(MMA/nBA) copolymer.[109] (b) Ring-and-lock associations in self-healable p(Sty/nBA) copolymer.[16] (c) Graphical illustration of interchain vdW interactions between neighboring p(MMA/nBA) copolymer chains containing 420 water molecules (H_2O: MMA/nBA = 1:1).[17] (d) Electrically accelerated self-healable poly(ionic liquid) copolymer.[111] (e) Schematic illustration of p(AAEMA/MMA/nBA) CANs containing dynamic cross-links (e1) that participate in transamination exchange reactions (e2) as well as interdigitated interchain topologies facilitated by MMA and nBA repeating units[112] (reproduced with permission from refs 109, 16, 17, 111, 112).

bonding and $\pi-\pi$ stacking interactions was achieved in chain-folding polyimide and a telechelic polyurethane with pyrenyl end groups shown in Figure 8b.[103] This system exhibits a nanophase-separated morphology and consistently recovers over 95% of its tensile modulus, 91% of elongation to break, and 77% of its modulus of toughness after damage. Along the same lines, the interplay between Pt⋯Pt and $\pi-\pi$ interactions of a cyclometalated platinum(II) complex and the PDMS backbone imparts remarkable stretchability and enables self-healing (Figure 8c).[106] Also, incorporating metal nanoparticles in composites, such as pyrene-functionalized polyamide and gold nanoparticles, can induce thermally triggered $\pi-\pi$ stacking interactions within the polymer matrix, enabling healing.[107] Introducing ionic components into $\pi-\pi$ stacking systems provides opportunities for developing conductive self-healing polymers, such as cathodes for lithium−sulfur batteries.[108] These selected examples illustrate that the healing of polymers may also require external energy sources, thus making "self-healing" the subject of debate. Most of the time, self-healing is viewed as a process that requires no external intervention under normal operating conditions. If temperature or other energy sources are required, this process is viewed as assisted self-healing and in many studies temperature- or light-assisted healing is considered self-healing.

van der Waals (vdW) interactions significantly influence various materials' properties, particularly cohesion and adhesion. These short-range forces, which enable geckos to cling to walls and ceilings, arise from interactions between surface molecules and setae. Manipulation of vdW forces in polymers has been explored to design advanced materials. For instance, vdW interactions are responsible for multiple recoveries upon mechanical damage without external intervention in commodity copolymers.[109,110] This approach involves copolymerizing primarily alternating/random copolymers that form "*key-and-lock*" interchain interactions by enhanced directionality dipolar vdW forces. Disturbing these interactions to a nonequilibrium energetically unfavorable state during mechanical damage will prompt quick recovery by the presence of interdigitated motifs to self-recover to an energetically favorable state. This phenomenon was first detected in poly(methyl methacrylate/*n*-butyl acrylate) [p-(MMA/nBA)] copolymers with relatively narrow monomer molar ratios.[109] Using a combination of spectroscopic and thermodynamic tools supported by with molecular dynamics

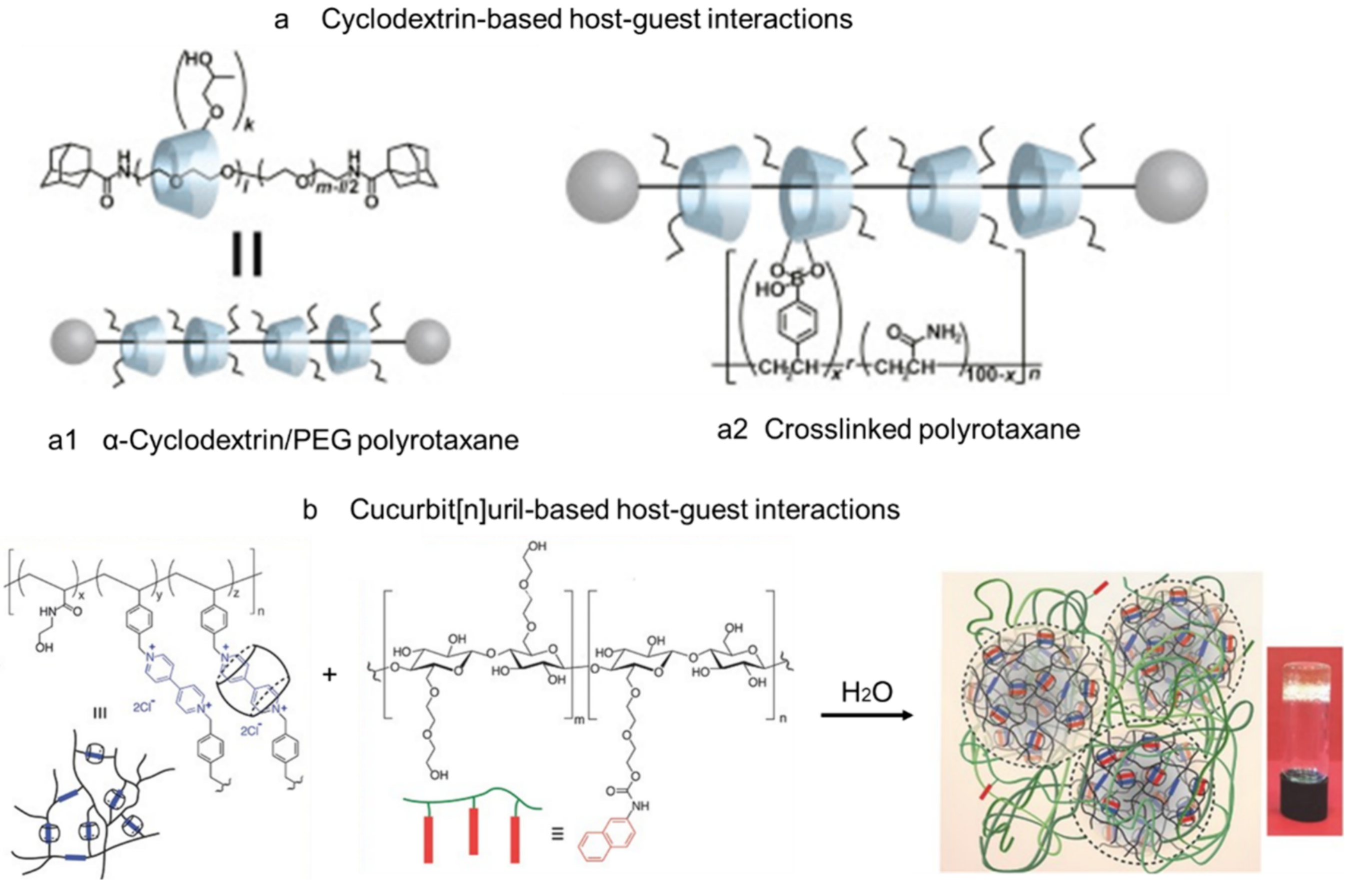


Figure 10. Examples of host−guest interactions in self-healing systems. (a) Schematic representation of α-Cyclodextrin/PEG polyrotaxane and cross-linked polyrotaxane.[119] (b) Schematic illustration of the formation of hydrogel networks from highly branched cucurbit[8]uril-threaded polyrotaxane and naphthyl-functionalized hydroxyethyl cellulose[122] (reproduced with permission from refs 119, 122).

(MD) simulations, the mechanism of self-healing was identified, and involves the reformation of "*key-and-lock*" interchain interactions stabilized by vdW forces schematically depicted in Figure 9a. The elevated cohesive-energy density (CED) stabilizes the vdW forces between adjacent copolymers. A similar strategy was utilized develop slef-healable poly(styrene/*n*-butyl acrylate) p(Sty/nBA) copolymers, which also exhibit self-healing properties in relatively narrow monomer molar ratios.[16] In this case, styrene's electron-rich groups contributed to of pi-sigma-pi (π−σ−π) vdW interactions between aromatic rings and aliphatic side groups in driving favorable "*ring-and-lock*" associations facilitating self-healing (Figure 9b).

Although, as indicated above, interfacial dynamics leading to self-healing may be achieved through various external sources, including heat, light, or electric fields, favorable hydrophilic−hydrophobic interfacial interactions may also play a significant role. It turns out that for alternating/random p(MMA/nBA) copolymer, the proximity of confined water molecules accelerates self-healing.[17] Competing for vdW interactions hinders water molecules from forming H-bonds. As a result, nBA side groups adopted L-shape conformations, leading to stronger dipole−dipole interactions and shorter interchain distances compared to the "*key-and-lock*" associations without water (Figure 9c). One could draw the analogy of compressibility of interchain hydrophobic/water LB monolayers as the above phenomenon is observed only when one water molecule is present for one copolymer repeating unit. Electric fields may also accelerate healing, as demonstrated in self-healable poly(ionic liquid) copolymers shown in Figure 9d.[111] When polymer chains are compressed upon the damage, applying an alternating current electric field facilitates the rapid reorganization of energetically favorable interchain vdW forces between dipolar hydrophobic groups, accelerating self-healing.

Integrating exchangeable covalent bonds into self-healing commodity copolymers offers another route to achieve autonomous self-repair without external interventions or reprocessing. Two examples of this concept were demonstrated by the covalently adaptable networks (CAN) formed in poly((2-acetoacetoxy)ethyl methacrylate/methyl methacrylate/*n*-butyl acrylate) (p(AAEMA/MMA/nBA)) and poly((2-acetoacetoxy)ethyl methacrylate/trifluoroethyl methacrylate/*n*-butyl acrylate).[112,113] These copolymer networks exhibit the capacity for self-healing under ambient conditions and reprocessing through compression molding at 120 °C. The reprocessing capability is facilitated by exchange reactions involving dynamic cross-links. In contrast, the self-healing process consists of the restoration of energetically favorable interchain vdW interactions (Figure 9e) which parallels the reversible E $\rightleftharpoons$ Z isomerization around the C$=$C bonds in vinylogous urethane moieties.

■ HOST−GUEST ASSOCIATIONS

The term host−guest involves binding various host molecules that can geometrically fit inside host species. Examples of hosts are crown ethers, cyclodextrin, calix[*n*]arene, cucurbit[*n*]uril,

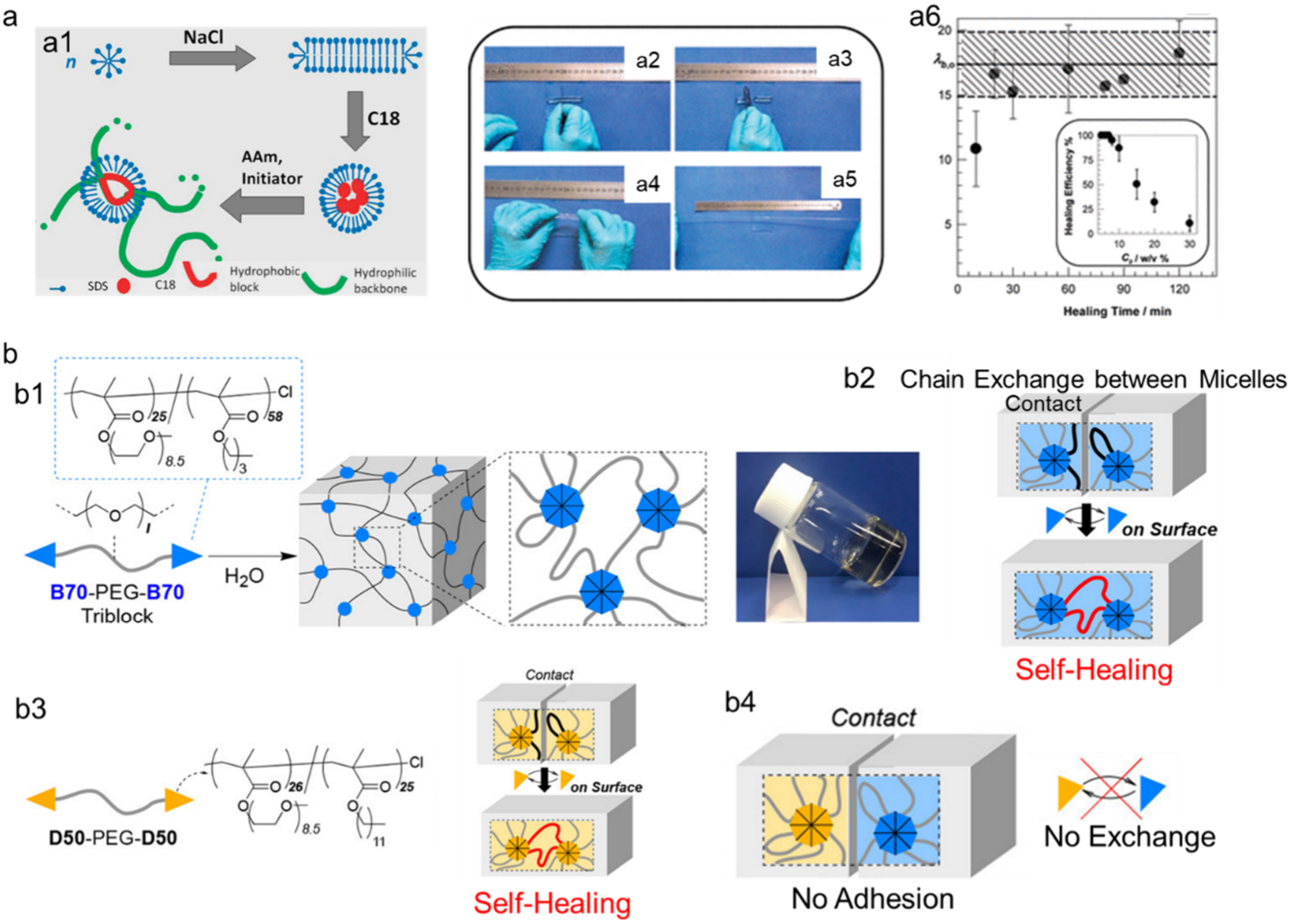


Figure 11. (a) Self-healing hydrogels with surfactants. (a1) Cartoon showing the formation of surfactant containing physical gels in SDS−NaCl solutions via hydrophobic C18 blocks. (a2−a5) Photographs of a gel sample after cutting into two pieces and pressing the fractured surfaces together for 10 min, they merge into a single piece. (a6) Elongation ratio at break of healed gel samples shown as a function of the healing time. Inset to (a6) shows the healing efficiency vs concentration of SDS plot for a healing time of 30 min.[123] (b) Self-sorting of amphiphilic copolymers. A hydrogel of B70-PEG-B70 triblock copolymers (b1) and chain exchange between micelles in the hydrogel (b2). (b3) A hydrogel of D50-PEG-D50 triblock copolymers and chain exchange between micelles in the hydrogel. (b4) No adhesion properties between a D50-PEG-D50 gel and a B70-PEG-B70 gel[124] (reproduced with permission from ref 123, 124).

pillar[*n*]arene, and calix[*n*]pyrrole, whereas guest molecules are adamantine, cholesterol, cholic acid, ferrocene, glycyrrhetinic acid, and azobenzene.[114−116] Cyclodextrin is one of widely used water-soluble hosts, and due to its hydrophilic exteriors and hydrophobic cavities, it can accommodate a diverse range of guest moieties.[117,118] For example, a self-healable hydrogel illustrated in Figure 10a was constructed using an α-cyclodextrin/PEG polyrotaxane and a poly(acrylamide) cross-linked with boronate linkages.[119] The mobility of host molecules along an axle in polyrotaxanes and the sliding nature of the cross-linker facilitate self-healing. Notably, the gel and dried gel states exhibit rapid and efficient self-healing. When used as a coating on glass surfaces, this material recovers from scratch marks and restores the surface to its initial state, even under semidry conditions.

Cucurbit[*n*]uril, however, exhibits stronger guest binding affinities compared to cyclodextrins.[120] The binding is driven by ion-dipole interactions, H-bonding, and hydrophobic effects.[121] Furthermore, Cucurbit[8]uril can host two guests, naphthyl and viologen, expanding the possibilities for hydrogel design. A supramolecular hydrogel network, as shown in Figure 10b, was assembled from highly branched cucurbit[8]uril-threaded polyrotaxanes and naphthyl-functionalized hydroxyethyl cellulose.[122] Mechanically locking cucurbit[8]uril host molecules onto a highly branched hydrophilic polymer backbone with viologen derivatives significantly increases the solubility of cucurbit[8]uril. This unique branched structure and its dynamic properties contributed to the material's superior viscoelasticity, enhanced thermal stability, and remarkable self-healing abilities.

■ INTERFACIAL HYDROPHILIC−HYDROPHOBIC ASSOCIATIONS TARGETING AT SELF-HEALING

Integrating hydrophilic and hydrophobic components at interfaces creates a dynamic environment where interactions between water-attracting and repelling entities play a crucial role. This unique interplay allows for developing self-healing materials that can respond to environmental stimuli, such as moisture. These materials can autonomously repair damage by strategically designing interfaces with hydrophilic and hydrophobic domains, as the interfacial interactions guide the healing process. Physical gels can be prepared through micellar copolymerization of acrylamide and 2% stearyl methacrylate (C18) in sodium dodecyl sulfate (SDS)−NaCl solutions

(Figure 11a).[123] Although not chemically cross-linked, gels without SDS micelles behave like ones, but the presence of micelles weaken hydrophobic interactions, thus enhancing viscoelastic dissipation and enabling self-healing. Also, amphiphilic ABA-triblock copolymers containing hydrophilic poly(ethylene glycol) (PEG) and hydrophobic alkyl pendant groups exhibit dynamic self-sorting behavior in hydrogels and at interfaces (Figure 11b).[124] The self-sorting is driven by encoded information from the copolymer's primary structure. Binary blends of copolymers with different compositions induce composition- or alkyl pendant-dependent self-sorting, leading to discrete and size-controlled micelles with hydrophobic cores. The uniqueness of this approach is that micelles can facilitate the reversible exchange of polymer chains exclusively between identical micelles, even in the presence of different counterparts.

In summary, while covalent rebonding provides strong and stable interfaces to provide structural integrity to the polymer (Section 2), supramolecular interactions offer an array of chemistries with various inter- and intrachain interactions. The latter provides faster healing as these interactions can be quickly re-established. Compared to covalent bonding, supramolecular interactions are weaker, but they are ubiquitous, and due to their chemical nature, they can be sensitive to environmental conditions. Although both covalent and supramolecular bonds can often be utilized in developing stimuli-responsive polymers, their activation energies are substantially different. For example, if covalent rebonding requires ~200 kJ/mol, average H-bonding needs ~30 kJ/mol. In comparison, the energy of vdW dissociations is ~2 kJ/mol. Therefore, it is reasonable to assume that the activation energies for interfacial self-healing are related to the number of actual bonds involved. Thus, many self-healing systems that utilize covalent rebonding require external energy input, typically heat or electromagnetic radiation. Also, covalent rebonding may not be fully reversible and may require more time. Although the choice between dynamic covalent and supramolecular depends on specific applications, it seems that the balance between strong covalent bonds for stability and rapid supramolecular rearrangements for healing is critical in many future applications.

■ OUTLOOK

Historically, the concept of interfacial self-healing phenomenon in polymers was initially introduced by the late Richard Wool in the 1980s,[125] and, as indicated in the "road map" (Figure 1), it was not until the mid to late 2000s that the significant advances began. Over the last two decades, many studies have been inspired by biology, and new advances in creating controllable polymer topologies and polymer network morphologies have enabled significant advances. Being a localized interfacial phenomenon, new advances should be directed toward developing polymers that function at elevated temperatures but self-heal under ambient environments. The ultimate challenge is to develop polymer networks that self-heal regardless of environmental conditions. To this end, a common misconception is that polymers exhibiting low T_gs are self-healable. Indeed, the low T_g polymers (below ambient temperatures) flow, which does not imply they self-heal. Numerous studies indicated that higher polymer dispersity at the interfacial regions, fewer chain entanglements,[126] and larger free volume reflected in lower interfacial T_gs contribute to self-healing dynamics. This raises the question of bulk structure–property relationships, often attributed to the difference between the temperature of operation (T) and T_g. The dependence of temperature, viscosity, and relaxation times for amorphous materials in the range of their T_g was described by the Williams–Landel–Ferry (WLF) equation.[127] As predicted by the WLF relationship and reiterated by recent studies,[128] there is no question that the smaller the difference, the "softer" and less viscous polymers are. Does this imply that they are self-healable? When T approaches T_g, viscoelastic responses are the flow, and most thermoplastic polymers will be self-healable, particularly at elevated temperatures. Self-healing is affected by inter- and intrachain interactions and depends not only on the bulk T_g, but also an array of balanced properties, including molecular and molecular weight distribution, monomer sequence, and backbone/side group flexibility, all contributing to inter- and intrachain interactions manifested by the higher cumulative CEDs.[129] As experimentally determined by DMA analysis combined with the Flory rubber elasticity theory,[130,131] T_{VLT} transitions determine the maximum stored strain, stress, and entropic energy required for interfacial self-healing. Simple observations show that copolymers will self-heal shortly after the cut. Still, when both interfaces are exposed to the environment for an extended time without physical contact, self-healing will not occur because interfacial copolymer chains adapted conformations with the neighbors below the surface stabilized by physical and/or chemical interactions. These interfacial self-healing processes depend on the nature of the polymer, direct and indirect orchestrated chemical and physical interactions, and their dynamics in precisely designed networks. The recent development of high chain-end fidelity in poly(vinyl ethers) reprocessable networks that enables the reactivation of chain ends to produce block copolymers[132] or embedding photoresponsive nanoparticle cross-links are excellent examples of physicochemical interfacial synergism. Just like transferred LB films into solid interfaces have led to significant advances in surface functionalization and the development of new interfaces in functional materials and coatings, understanding of dynamics of interfacial molecular interactions.

Due to the limited chain mobility of macromolecular chains in polymers designed for high-temperature applications, employing self-healing properties can be challenging. However, the key attribute is operating conditions. For example, hydrogen fuel dispensing houses typically operate at −40 to ~ + 80 °C range. This application will require a different copolymer design than a pet toy designed to self-heal when your favorite pet is asleep at night or car paint under harsh (UV light, heat, moisture) environmental environments. Thus, the issue of subjectivity can be eliminated by specific applications and revolutionize industries by expanding the lifespan of devices or objects. As initial studies showed, automotive components, such as bumpers and painted body panels that automatically repair small scratches and dents, will reduce the need for repairs and maintenance. Increasing resilience to environmental stresses by weathering and cracking incorporated into building materials, bridges, or roads will significantly contribute to longer-lasting infrastructures. Extending the durability and reliability of electronic components by integrating self-healing circuit boards into electronic devices is another untapped opportunity. In the health sector, incorporating self-healing polymers to enhance the longevity of implants or prosthetics will reduce the need for frequent replacements. The lifespan of textiles in clothing will reduce the wear and tear of garments, whereas, in transportation, self-healing materials will offer higher impact resistance, and thus, safety standards and maintenance costs will be reduced. Other categories impacted by self-healable polymers will be daily usage items ranging from furniture and appliances to other consumer goods, including packaging or sporting goods. Another significant sector of applications for self-healing polymers is military equipment with enhanced wear and tear in highly harsh environments, protecting sensors and other sensitive instrumentation. To meet these demanding properties, high molecular weights are required. For example, colloidal statistical copolymerization can produce copolymers in the range of 100−200 kD or higher with excellent mechanical and self-healing properties in a couple of hours. Although self-healing will be slower as long as the system recovers entropic energy, the recovery of properties will occur. The same copolymers may and will self-heal faster when controlled radial polymerizations are employed, but lower molecular weights and extensive polymerization times make them commercially challenging.

There is no question that self-healing is an advantageous add-on feature that offers additional benefits enhancing the overall performance but does not replace the fundamental properties of functional polymers. Polymers are engineered for specific purposes, such as flexibility, strength, or heat resistance, and the self-healing aspect serves to extend their lifespan and maintain their functionality. Self-healing is particularly valuable in applications where maintenance or repair may be challenging, such as in aerospace, automotive, biomedical, or structural materials. If successful, it will facilitate endless application opportunities for fabricating devices involving molecular machines,[133] multi-stimuli-responsiveness,[134] cell proliferation,[135] molecular recognition,[136] and others. Polymer interfacial extensive chain dynamics will facilitate longer range transport, which will have significant technological implications not only in self-healing, but also in adhesion, processing, welding, coalescence, and other dynamic processes.

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Notes

The authors declare no competing financial interest.

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