

Part One
Design of Self-Healing Materials

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Principles of Self-Healing Polymers^{*)}*Diana Döhler¹⁾, Philipp Michael¹⁾, and Wolfgang Binder*

1.1

Introductory Remarks

All matter is subject to thermal or mechanical destruction as well as chemical degradation during its active lifetime – thus restricting the use of each crafted piece of matter which has been fabricated with a usually huge amount of intellectual and also hand- or machine-driven force. When the *Romans* invented concrete as a construction material more than 2000 years ago for erecting arches, water-pipes and building of monuments, such as the *Pantheon*, it might be assumed that they did not know about any of the molecular mechanisms of self-healing in this material. However, they surely knew and realized by observation of, for example, old Egyptian pyramids, that the construction of an empire to last for many centuries needs even longer lasting materials. Indeed, a useful construction material does not only need to be strong and stiff, it also needs to be flexible in shape and application, thus self-hardening concrete definitely is advantageous over handcrafted stone. The self-healing properties of concrete have provided us with testimony of this technically advanced (*Roman*) culture, whose achievements can be seen even in our modern times.

Polymers and polymeric materials are “the” smart invention and technological driving force of the twentieth century, hence the quest for self-healing or self-repairing polymers [1, 2] is strong. Not only the practical demand for maximum usage-times of each fabricated thing, but also the everlasting limitation of natural resources and costs leads to the search for self-repairing polymeric materials needing no direct human action for repair. Therefore, as new polymers and polymeric materials are designed, the quest for materials with self-healing properties (i.e., those which can regenerate similarly to living matter, especially after mechanical deformation and crack-formation) is increasing, culminating in the need for self-healing polymers after mechano-deformation [3–10]. In such

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materials, stress of a certain magnitude (either chemical, physical, or thermal) induces a mechanical deformation in the polymer, which in turn activates a response within the material, leading to “healing” of the generated (physical) damage. Despite the inevitable fact that the destructive and renewing force has allowed new civilizations to emerge during the past (historical) times, a short look at nature makes the possibilities of repair and restoration of properties obvious – why would man not be able to achieve the same, similar, or even better? Naturally, mankind is taking steps to increase the lifetimes of all materials, in particular those of polymeric materials and composites, thus reducing the need for repair and replacement of such materials. Looking at superficial injuries in mammal organisms we see that a vascular (e.g., bloodstream-supported) supply-system helps to restore and heal mechanical damage via the blood-clotting cascade and subsequent tissue regeneration. This very simple principle demonstrates that biomimicry might help in the design of self-healing polymers by applying similar capsule- or vascular-based logics (see also Chapter 2). Looking further, principles of DNA-repair based on the radical scission of DNA-chains can induce a DNA-repair cascade, which in its complexity cannot be copied in simple bulk polymeric materials, but shows that a dynamic system is required to enable a self-healing material. Thus, an important aspect of self-healing is the presence of a structure which is able to respond dynamically to an external stimulus, enabling the restoration of the initial material properties. Due to their highly complex chain structure, polymers are ideally suited to serve as molecules for dynamic and thus self-healing properties.

1.2

General Concept for the Design and Classification of Self-Healing Materials

A polymer displaying self-healing properties needs the ability to transform physical energy into a chemical and/or physical response able to heal the damage—a process which normally is not present in “conventional–non-self-healing” polymers. Thus, the polymer needs to “sense” the damaging force, transforming it autonomously (without further external stimulus) into a healing-event, ideally at the damaged site. The possible mechanistic designs of self-healing polymers are depicted in Figure 1.1. A *self-healing polymer*, therefore, is supposed to heal damage (see Figure 1.1a, imposed by *shear-force* or another *rupturing event*) by either *physical processes* alone (see Figure 1.1b) or via a combination of chemical and physical processes (see Figure 1.1c). The design of self-healing polymers, therefore, is a multidisciplinary process, requiring knowledge of their structure, their individual dynamics, as well as a deep knowledge of chemical processes. Thus, the design of self-healing polymers needs a thorough understanding of the polymer’s individual chain-dynamics (see also Chapters 3 and 4), and not only the dynamics of whole chains or molecules within the polymeric material, but also the dynamics of each segment interacting with a specific part of the new interface or other polymeric/monomeric molecules.

Similar to biochemical healing processes, the initial damage (see Figure 1.1a) generates a *free (usually fresh) interface* (shown as a crack), which in turn can act

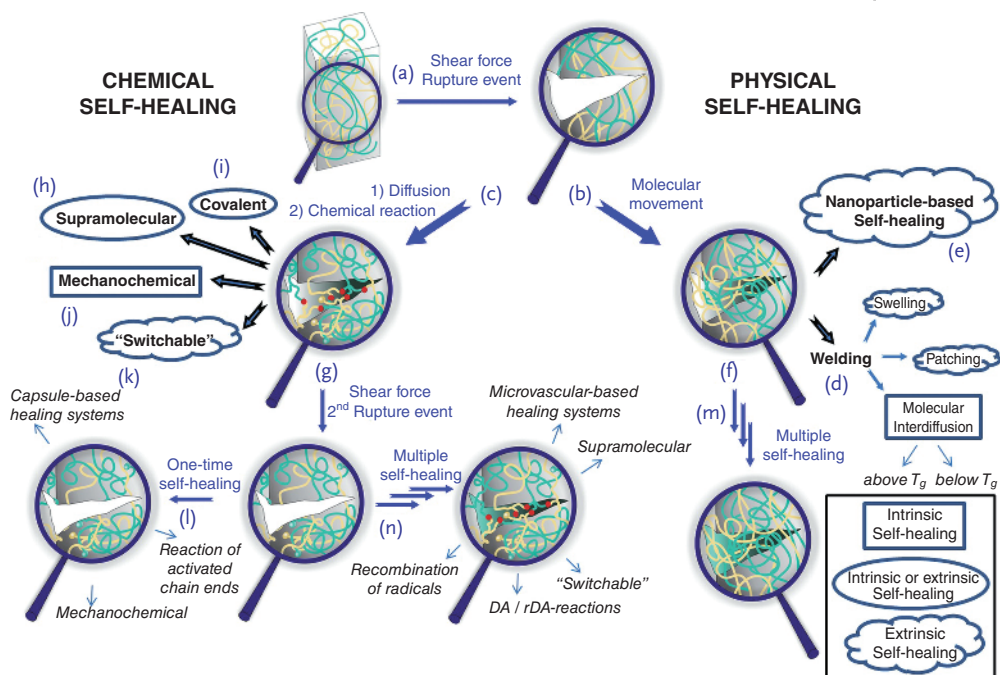


Figure 1.1 Design of self-healing polymers.

(a) Shear-force or rupture is transformed into a crack, sensed by the polymer matrix. (b) Newly generated interfaces lead to concentration gradients, which allow enhanced diffusional processes (f), resulting in welding, swelling, patching, nanoparticle enrichment or simple molecular interdiffusion (physical entanglement) of polymer chains (d) and (e). (c) Molecular movements lead to contact

between functional groups and thus to a chemical healing process, resulting in crack closure by a newly formed network (g) Healing induced by a crosslinking reaction, either via supramolecular forces (h), covalent chemistry (i), mechanochemical (j) or "switchable" reactions (k). After a second rupture event at the same area the number of healing-cycles can vary, implying either a one-time healing process (l) or multiple healing (m) and (n).

as a site for molecular processes, such as *swelling*, *patching* or *simple molecular diffusion*, which can induce a *welding process* (see Figure 1.1d), subsequently leading to a closing of the crack and thus a "self-healing" process [11]. Nanoparticles (see Figure 1.1e), small, or even large molecules can diffuse to the interface, thus leading to changes in the local concentration, and also inducing changes in the individual local mobility of the molecules. This can in turn lead to the healing of the crack (see Figure 1.1f).

Chemical healing processes (see Figure 1.1c) always need a combination of physical and chemical healing principles, as a chemical reaction can only take place when contact between the reactants has been achieved. In general, after diffusion and reaction of the reactants, the crack is filled by a newly formed network (see Figure 1.1g [see also Chapter 5]), which results from the crosslinking reaction of individual polymer chains, either via purely physical ("supramolecular") forces [9, 12–14], or by action of truly chemical forces resulting in partially reversible [15–17] or stable [18, 19] covalent bonds (see Figure 1.1h and i). Purely *supramolecular*

interactions [9, 20–22] (see also Chapters 11–13), well known from molecular self-assembly, can reform, thus generating a network with dynamic properties by itself [23]; *covalent chemistry* (see Chapters 6–9, 15, and 17) is able to form a new network by a plethora of chemical crosslinks, often well known and well optimized by technical processes of resin-chemistry (“thermosets”). In particular Diels–Alder (DA) reactions [17, 24–28], epoxide chemistry [29–41], “click-based” chemistry [18, 42–54], isocyanate chemistry [55], olefin metathesis [19, 56–61], and thiol chemistry [62, 63] have gained significance in this respect. Choice of the chemical reactions to be used usually takes into account the efficiency (“free energy”) of the reactants as a major selection tool, besides the stability and selective incorporation of the respective functional groups into the final material, for example, via encapsulation strategies (see also Chapters 10 and 16).

Furthermore, so called *mechanochemical* reactions (see Figure 1.1j) (see also Chapter 8) can transform the physical energy of damage directly via a specially designed chemical group (“mechanophore”) [4, 64, 65] into an activated chemical state, which in turn allows self-healing. These specially designed reactions are intrinsically coupled to the existing polymeric chains, as the attached polymeric chains act as a “handle”, which by definition allows the conversion of applied mechanical energy into the actual chemical reaction [66]. Especially, ring-opening reactions [64, 65, 67–73] and carbene-based catalyst activation [74–78] have become prominent for realizing the concept of self-healing polymers.

Moreover, an *inherent “switch”* [79–82] (see Figure 1.1k) (see also Chapter 7) such as light or an electrochemical stimulus can be flipped, triggering a reversible network formation within the polymer and thus a self-healing response.

Additionally, the mentioned self-healing approaches can be divided into *intrinsic* and *extrinsic* concepts [7] (see Figure 1.1), where intrinsic self-healing polymers utilize an inherent material ability to self-heal, triggered either by a damage event or in combination with an external stimulus. In contrast, for extrinsic self-healing concepts the healing agents have to be pre-embedded into a (polymeric) matrix enabling their release during a rupture event and thus self-healing.

All these approaches display different features with respect to external conditions under which self-healing takes place (such as the required stress for activation, the temperature of healing as well as other external constraints imposed by the mechanism of the healing concept) the number of healing-cycles thus implying either a once-a-time-healing after one stress-event (see Figure 1.1g and k), or the possibility to repeatedly heal damage at the same position of the material (see Figure 1.1l and m) as well as the timescale on which the self-healing process is taking place. Hence, a large body of work has been dedicated to optimize the conditions of healing (temperature, additives, and optimization of catalysts) as well as the technical realization of the concept, thus being able to fabricate and produce a technically useful polymer at reasonable costs within a technical process (see Chapter 14).

The following sections will provide an overview of the chemical principles of the underlying concepts to fabricate self-healing polymers. The various possibilities of chemical and physicochemical approaches have, therefore, triggered a number

of strategies which will be discussed in separate chapters as their chemical and physical principles are totally different.

1.3

Physical Principles of Self-Healing

In general, all self-healing concepts have the aim to generate crosslinked networks, either by *covalent* or *supramolecular chemistry*, or by purely physical crosslinking via chain entanglements. Self-healing principles based on *physical interactions* constituted one of the first historically observed self-healing behaviors of manmade plastics and will be discussed in the following. Chemical self-healing concepts will be presented in Chapter 9. Physical principles implementable in self-healing approaches are based on *molecular diffusion*, induced either by Brownian motion, chain segment motion or entropy driven movement of molecules or particles with or without external stimulus. Several self-healing mechanisms, such as *molecular interdiffusion*, *welding*, *swelling*, or *self-healing via nanoparticles* can be assigned to this category. Additionally phase-separation phenomena in polymers can be an enhancing factor for self-healing [83–95] (e.g., see Chapter 13).

In order to understand the phenomena of self-healing based on physical interactions it is necessary to get fundamental knowledge of molecular mechanisms. The elementary steps of all physical self-healing principles are interdiffusion and entanglement of polymer chains [11, 96]. Both properties depend on intermolecular forces, which are closely linked to the chemical nature of the polymer and the length of the molecules, including the dependence on the average molecular weight. However, both factors often oppose each other. Accordingly, short chains enable fast molecular interdiffusion, while long chains generate materials with the ability for high strength recovery at the interface [11].

One of the best known and well understood self-healing approaches based on physical methods is the so-called *molecular interdiffusion*, which can be divided into thermoplastic and thermoset self-healing occurring above and also, at least theoretically, below the glass transition temperature (T_g). It has been shown that the polymer/polymer interface gradually vanishes and the mechanical strength at the initial interface increases by bringing two pieces of identical or even compatible polymers into contact. Thus, the polymer matrix is actually healed just due to molecular diffusion along the polymer/polymer interface [3, 11].

In order to understand this phenomenon, Wool and O'Connor [97] developed, in 1981, a five-stage mechanism to unscramble the complexity of strength recovery at ruptured polymer/polymer interfaces, and provide an explanation for the functioning principle of many self-healing concepts (see Figure 1.2), being strongly related to molecular interdiffusion at or above the glass transition (T_g). At this temperature polymer segments are mobile enough to enable an efficient self-healing process. This relatively simple model is, in its basic steps, applicable as a universal mechanism for nearly all self-healing concepts [98].

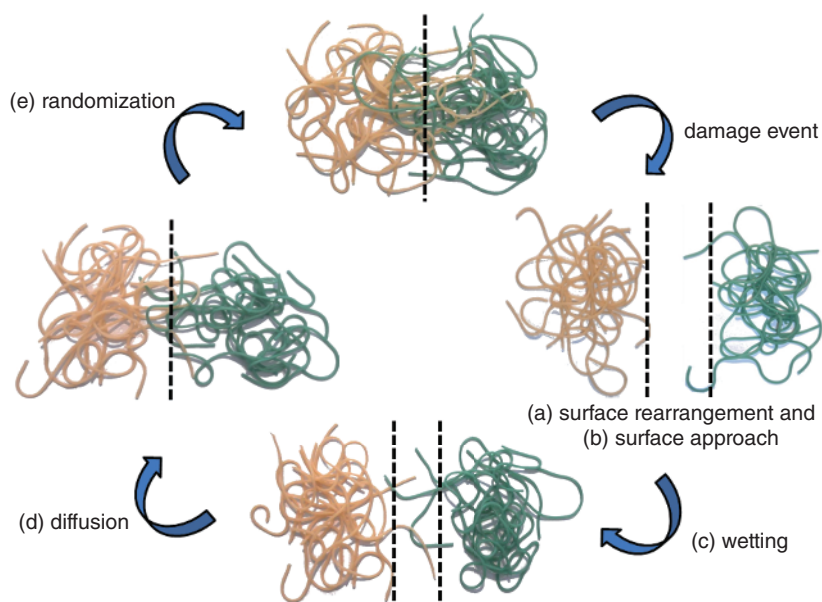


Figure 1.2 Stages of self-healing mechanism. (a) Surface rearrangement, (b) surface approach, (c) wetting, (d) diffusion and (e) randomization.

The principle stages of healing according to the mechanism of Wool and O'Connor [97] are illustrated in Figure 1.2 including the steps of surface rearrangement (a), surface approach (b), wetting (c), diffusion (d) and randomization (e). Surface rearrangement and surface approach are the first steps after a damage event has occurred. These steps are the most critical ones as healing can only take place if the ruptured interfaces can come into contact with each other. The surface rearrangement (a) influences the rate of crack healing significantly due to the discontinuity of the topography and the roughness of the created crack surface, which may change with time, temperature and the applied pressure [11, 97, 98]. Higher surface roughness leads to a higher contact area and, therefore, to higher rates of diffusion, and thus expectedly higher rates of self-healing. The surface approach (b) under controlled laboratory conditions appears to be the most trivial step. However, in practice, this is one of the most crucial steps regarding surfaces pulled apart by the damage event which might prevent the contact of the surface layers and thus terminate the self-healing process [98]. Moreover, the surface approach stage determines the mode of healing, for example, healing in point or line mode [97]. Before the healing process can start, the wetting of the cracked surfaces by each other or by healing agents has to be ensured. This is mostly achieved by ensuring sufficiently high chain mobility of the initial material, and also by increasing the temperature or adding solvents. The wetting stage (c) enables diffusion (d) which results in the entanglement of polymer chains and,

therefore, in the recovery of the mechanical properties of the healed material. Diffusion is a fractal random walk of polymer chains near to the surface which first results in the entanglement of the mobile chains and then in interpenetration into the unruptured matrix material. The diffusion stage is the most important step for restoring the mechanical properties during which the majority of these properties are recovered or healed [97–99]. During the randomization stage (e) the complete loss of initial crack interfaces can be observed.

As previously mentioned, it is possible to observe self-healing via *molecular interdiffusion*, not only above but also below the T_g , despite being a contradiction of the conventional knowledge of polymer movement suggesting no motion of polymer segments below their T_g . Nevertheless, wetting and diffusion can be observed at a certain healing temperature significantly below the T_g [96, 100–102]. Wool *et al.* [100, 102] observed crack healing processes in glassy polymers and related this to the interdiffusion of molecular chains and the subsequent reformation of molecular entanglements. It is claimed in literature, and highly controversially discussed in the scientific community, that this self-healing ability is caused by a potential reduction of the T_g at polymer surface layers compared to the T_g in the bulk [11, 96, 101, 103–105].

Four possible explanations for this behavior [106–115] are illustrated in Figure 1.3: (a) The accumulation of polymer end groups at the outer surface due to their higher space requirement compared to the corresponding chain segments leads to a lower density of chain segments at the inner surface, causing a higher chain mobility and thus a lower T_g . (b) The confinements for polymers with high molecular weight force them to alter their chain conformation (induced by a break in symmetry at the polymer surface—flattened chain conformation), resulting in decreasing interchain entanglements and a reduction in the chain segment density. (c) The collective motions along the chain (loop motions) dominating in thin film scenarios require a weaker free volume compared to the standard motion, leading to a decrease in the effective chain segment density and, therefore, to a reduction in the T_g at the interface. (d) The accumulation of low molecular weight polymers at the surface layer can cause, according to the Flory–Fox equation, a reduction in T_g . This effect can be explained by their lower surface tension and the reduction in free energy by a smaller change in conformational entropy. Following these assumptions, the final reduction in T_g at the surface layer will enhance the mobility of the chain segments and thus enable self-healing according to the basic steps of Wool and O'Connor [97–99].

A further self-healing concept based on physical interactions is *welding*. Beside the mentioned molecular interdiffusion it is one of the traditional self-healing methods. Welding relies on damage healing by forming chain entanglements between two contacting polymer surfaces in order to restore the original mechanical properties of the ruptured area [3]. Therefore, welding is, in a strict interpretation, a superordinated category of molecular interdiffusion. Nevertheless, it is often referred to separately due to its various manifestations. The welding process consists of the same healing stages mentioned above: surface rearrangement, surface approach, wetting, diffusion and final randomization (see Figure 1.2).

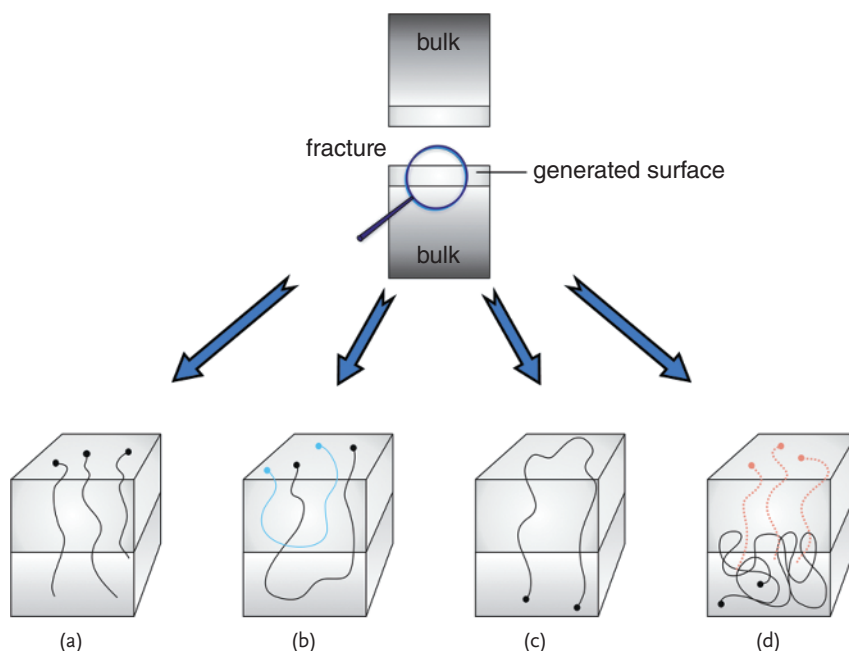


Figure 1.3 Reduction of T_g in polymer surface layers. The accumulation of polymer end groups at the outer surface (a), confinements for polymer chains due to high molecular weight (b), and collective motions along the chain (c) leading to a decrease in the effective chain segment density in all

three cases (a)–(c) and therefore to a reduction in the T_g at the interface. The enrichment of low molecular weight polymers at the surface (d) causes a reduction in T_g according to the Flory–Fox equation.

However, the rate of rearrangement and reorganization is influenced by various factors, such as the welding temperature, surface roughness, remaining chemical bonds between the surfaces, and the presence or absence of solvents [3]. In the case of covering or replacing damaged material by new externally added material the approach is also known as *patching*. If some solvents are involved to increase the mobility of the polymer chains the healing process is called *swelling*.

A completely different approach is the *nanoparticle-based* self-healing concept (see also Chapter 3) [3, 98, 116], inasmuch as it does not involve separation and rejoining of polymer chains like the previously discussed methods. This concept is based on the migration of nanoparticles to the damaged area. After cooling below a certain temperature a solid phase is formed recovering the mechanical strength and thus healing the damage. This method assumes a sufficiently high mobility of the nanoparticles in the polymer matrix. In order to enable this accumulation of particles at the crack surface the healing occurs commonly above T_g . Moreover, the modification of the nanoparticle surface is significant to ensure a sufficiently high driving force based on entropic and enthalpic interactions between the particles and the polymer matrix.

1.4

Chemical Principles of Self-Healing

All self-healing methods have the aim to generate crosslinks in networks, either by physical interactions, as discussed previously, or by chemical reactions of various kinds of functional groups, which will now be discussed in detail.

Chemical self-healing principles (see Chapters 2, 6–9, 11–13, 15 and 17) can be classified into two main categories, based either on covalent (see Figure 1.4a) or on supramolecular network formation (see Figure 1.4b). In the case of covalent network formation chemical bonds between functional groups are generated and thus a permanent, but sometimes even reversible, network is established. In contrast, supramolecular networks are commonly reversible associates of polymers linked via supramolecular interactions and show a higher dynamic behavior. Moreover, a subdivision into inherent “switchable” polymer systems (see Figure 1.4c) and concepts using mechanochemical activation of molecules by direct effect of a mechanical force (see Figure 1.4d) can be made. Concepts assigned to these two categories could also be classified into covalent or supramolecular network formation. The separations are, thereby, often blurred, enabling the assignment of several self-healing methods into more than one category.

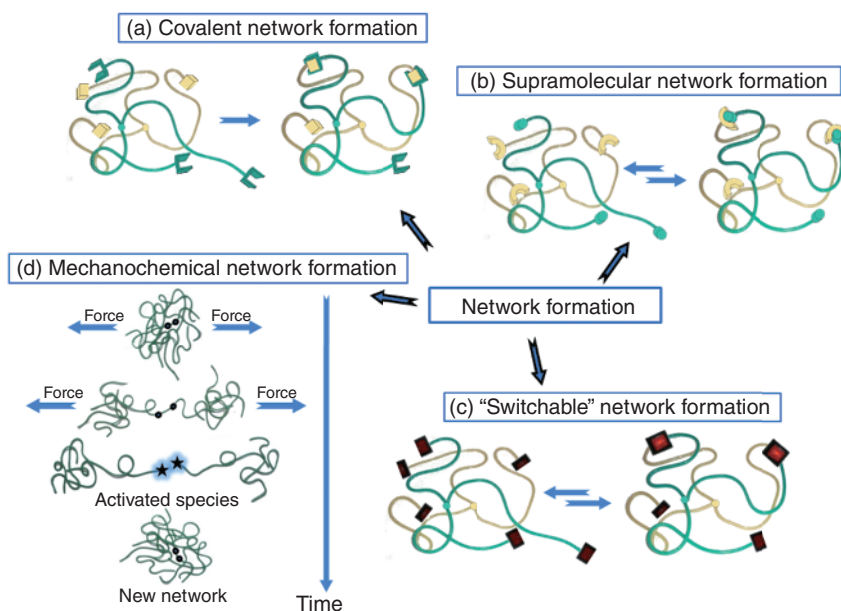


Figure 1.4 Different modes of chemical interactions resulting in crosslinked network formation. (a) Covalent network formation, (b) supramolecular network formation, (c) “switchable” network formation and (d) mechanochemical network formation.

1.4.1

Covalent Network Formation

A great challenge for chemists and material scientists involved in the evolution of self-healing polymers was the development of concepts that, in a fast and preferably simple way, form highly crosslinked networks. Therefore, they tuned the properties of the self-healing agents so that damage healing could occur under ambient conditions, like low temperatures, or humid and oxygen-containing environments. Furthermore, a large diversity of protection methods, such as encapsulation or *in situ* activation of catalysts, was developed. Moreover, some scientists explored various catalytic self-healing methods to accomplish a fast network formation at ambient temperatures, while others pursue higher temperature methods. Another challenging task was to guarantee a healing response only in direct response to a damage event. Therefore, reversible reactions shiftable to a “broken” stage and cured subsequently by re-shifting to the “healed” stage were used. Furthermore, different protection methods, preventing not only disturbing external influences but also undesired premature crosslinking reactions, found application. Accordingly, a large diversity of self-healing concepts has been developed up today.

In self-healing concepts based on covalently crosslinked networks, covalently linked network points are generated in a chemical reaction (see also Chapters 6–9 and 15). They exist in a large diversity and can be subdivided into *reversible and irreversible reactions*. Reversible methods, like DA/retro-DA reactions (DA/rDA) [17, 24–28, 117–123] or polycondensations [124, 125] provide the opportunity for multiple healing cycles, while irreversible methods, like the microcapsule-based ROMP concept [19, 59–61, 126], epoxides [127–130], or various click approaches [18, 42, 43, 48, 51], cannot heal a once ruptured area a second time. For more information see also Section 1.5.

1.4.1.1 Irreversible Covalent Network Formation Concepts

One of the most prominent self-healing methods based on *irreversible covalent network formation* was developed by White *et al.* [19] in 2001, who investigated the microencapsulation of dicyclopentadiene and subsequent embedding into an epoxy-matrix containing a Grubbs catalyst (see Figure 1.5a; Table 1.1a) (see also Chapters 9, 10, and 15). A damage event rips the microcapsules and releases the dicyclopentadiene monomer into the crack plane, where it comes into contact with a ruthenium-based Grubbs catalyst and triggers a ring opening metathesis polymerization (ROMP) [19, 56–58]. The subsequent generation of a dense network results in the recovery of the material properties, whereby self-healing efficiencies up to 99% can be achieved [126]. Further studies have resulted in the development of alternative monomers suitable for these ROMP systems, such as *endo*- [19] and *exo*-dicyclopentadiene [59], *endo*-1,2-dihydrodicyclopentadiene [59], norbornene [59], 5-ethylidene-2-norbornene [60], 5-(chloromethyl) norbornene [61], 5-(bromomethyl) norbornene [61] and norbornene carboxylic acid ethyl ester [61] (see Table 1.1b). Important, therefore, is a microencapsulation approach that can be applied now to nearly all kinds of polymers, such as thermosets, thermoplasts,

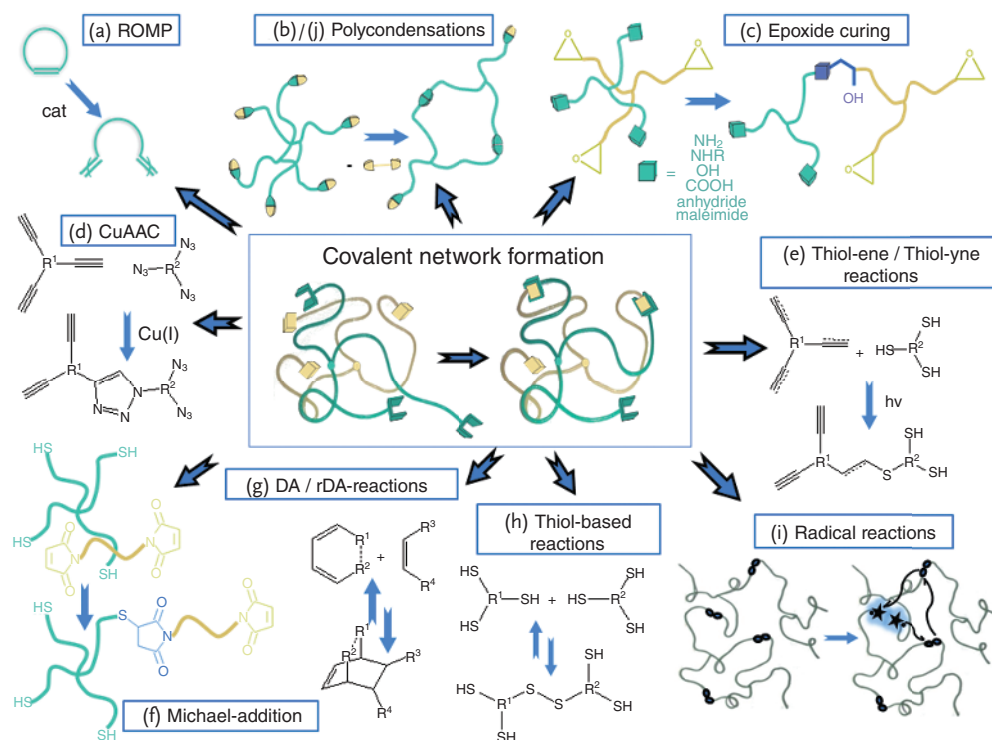


Figure 1.5 Self-healing methods based on covalently crosslinked networks, utilizing (a) ROMP, (b) irreversible polycondensations, (c) epoxide chemistry, (d) CuAAC or (e)

thiol-ene/thiol-yne click reactions, (f) Michael additions, (g) DA/rDA reactions, (h) thiol-based reactions, (i) radical reactions, or (j) reversible polycondensations as concept.

and elastomers [19, 37, 41, 133–139]. The advantage of applied encapsulation is the possibility to spatially separate the reactive compounds from each other, from the matrix and, therefore, from the environment, thus increasing the longtime stability of the healing system (see Chapter 9). However, the original material properties can be affected negatively by embedding microcapsules. Moreover, the high cost of the Grubbs catalyst may limit a wider technical implementation.

In order to overcome these shortcomings, in 2006 White *et al.* [131] studied a microcapsule-based self-healing systems using polycondensation reactions of technically available hydroxyl-terminated poly(dimethylsiloxane)s and poly-(diethoxysiloxane)s, efficiently catalyzed by cheaper organotin compounds (see Figure 1.5b; Table 1.1, entry 3). In order to prevent a premature reaction between the macromonomers, the tin compound was encapsulated in polyurethane microcapsules and embedded into the polymer matrix. In case of a rupture event the fluidity of the poly(dimethylsiloxane) enables flow into the crack, where a polycondensation reaction between the poly(dimethylsiloxane) and the poly(diethoxysiloxane), catalyzed by the tin compound, is triggered, forming a

Table 1.1 Irreversible covalent network formation concepts for self-healing applications.

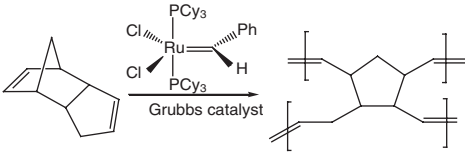
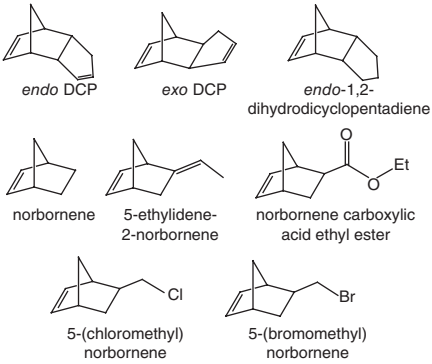
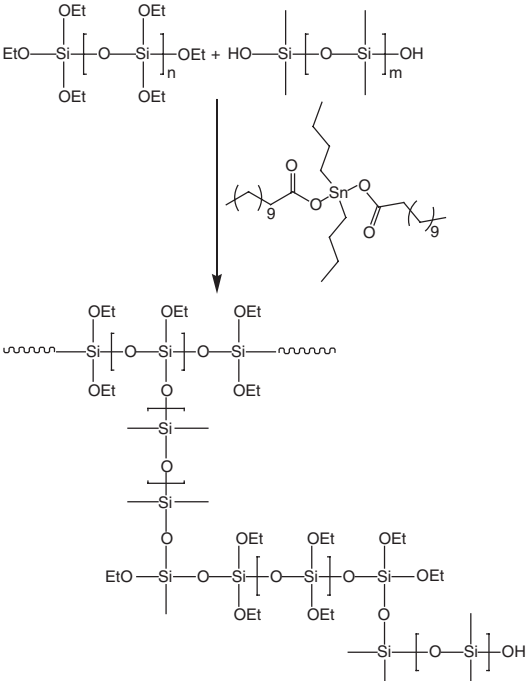
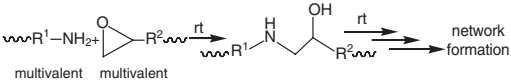
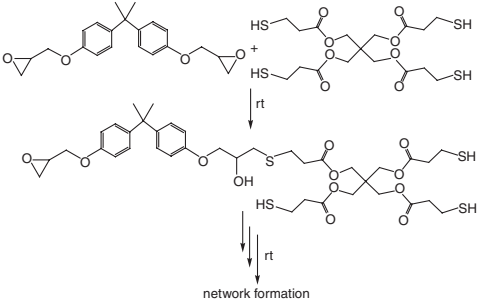
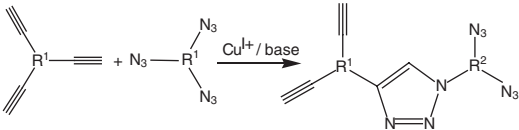
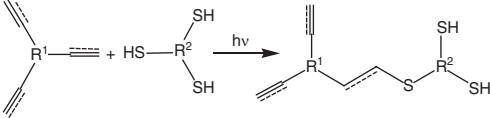
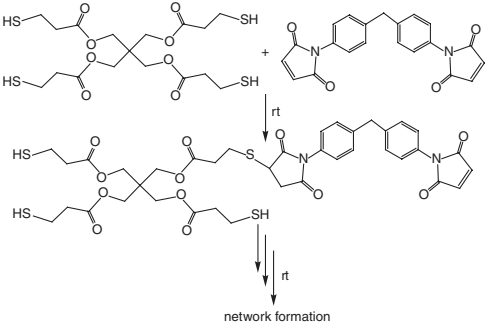
Entry	Example	Ref.
(a)	Ring-opening metathesis polymerization (ROMP)	
1	ROMP 	[19]
2	ROMP monomers applicable for self-healing 	[19, 59–61]
(b)	Polycondensation reactions	
3	Poly-siloxanes 	[131]

Table 1.1 (Continued)

Entry	Example	Ref.
(c)	Epoxy/hardener methods	
4	Epoxy/amine	[40]
		
5	Epoxy/mercaptane	[41]
		
(d) + (e)	Click reactions	
6	CuAAC	[18, 42, 43, 48, 51]
		
7	Thiol-ene/ thiol-yne click reaction	[52–54]
		
(f)	Michael addition	
8	Thiol/ maleimide	[132]
		

siloxane-crosslinked network within the damaged zone. Moreover, the healing system is applicable under aerobic and humid conditions due to the hydrophobic nature of both siloxane-based macromonomers and the stability of the released tin catalyst [131, 140]. This is of crucial importance for the practical realization of self-healing, and together with the lower cost of the catalyst was the prime motivation for developing such systems. However, it was not possible to achieve healing efficiencies of more than 24%, making a technical realization doubtful.

Another self-healing approach much closer to technical implementation utilized epoxides as matrix-embedded encapsulated healing agents [29–39] (see Figure 1.5c). Epoxides are highly strained three-membered rings which can undergo rapid coupling reactions with the second healing reagent, the so-called hardener, commonly substrates with activated hydrogen atoms, such as amines, alcohols, carboxylic acids, or mercaptans, as well as anhydrides and maleimides. In the course of the rupture event, the epoxide-containing capsules are cracked and release their content in order to react with the also embedded hardener via covalent bond formation. After treatment with these multifunctional and coreactive curing agents 100% conversion is usually reached, and insoluble thermosets are created composed of three-dimensional networks which fill the crack and restore the strength of the material. The crosslinking process can occur either at low temperatures (“cold curing”) or at elevated temperatures (“hot curing”), the latter being of minor interest for self-healing applications. Thus, primary and secondary aliphatic amines are most often used as hardeners because of their higher reactivity at low temperatures compared to other hardeners. Other important curing agents are acid anhydrides and formaldehyde resins which can react with the hydroxy groups of high molecular weight resins, resulting in further crosslinking reactions. While choosing the curing agent as well as the curing conditions the characteristics of the final resin, such as the crosslinking density and the morphology, can be freely tuned. Further, cationic curing can be induced photochemically [127–130]. Epoxy curing reveals some special advantages which make it to one of the most powerful self-healing concepts, especially for epoxy resin materials. While using epoxides as healing agents the same kind of material as the matrix is produced, thus ensuring a good adhesion between them and enabling full recovery of the initial material properties. Furthermore, together with the good healing efficiencies even at low temperatures, cold curing is the self-healing concept currently closest to commercial application. The sometimes lower longtime stability of the epoxy compounds can be partially compensated by the encapsulation, using specific wall materials or utilizing inherently more stable materials.

Recently, a self-healing system based on epoxy-amine resin formation [40] at ambient temperature was developed (see Table 1.1 entry 4). A modified aliphatic polyamine (EPIKURE 3274) and a diluted epoxy monomer (EPON 815C) were separately encapsulated and embedded into a thermoset epoxy matrix. The optimal mass ratio of amine to epoxy-containing capsules was determined to be 4:6 with an overall capsule content of 17.5% and an average healing efficiency up to 91%. However, a notable influence of the high capsule content within the polymer matrix on the material properties can be expected. A long term stability

of the healing system of at least 6 months was shown. Another example of cold curing epoxy systems consists of the conventional epoxy bisphenol-A-diglycidyl ether (EPON 828) and the mercaptane hardener pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) acting as a two-compound healing system at room temperature [41] (see Table 1.1 entry 5). Both compounds were encapsulated into different types of microcapsules and incorporated into an epoxy resin matrix. An attractive healing efficiency of 104.5% with a low capsule content of 5% could be achieved after 24 h at 20 °C and also a sufficiently long term stability of the healing agents for at least 1 year could be demonstrated.

An approach of crosslinking concepts acting at ambient temperatures based on “click” reactions has been pursued by the groups of Binder [18, 42, 43] (see Figure 1.5d; Table 1.1 entry 6) and Kessler [48, 51], as well as by the thiol-ene/thiol-yne click concept [52–54] (see Figure 1.5e; Table 1.1 entry 7). However, they used a set of reactions called click chemistry [44–50], characterized by generating only one, mostly regiospecific pure product in high yields, working under simple reaction conditions and rapidly achieving complete conversion via a thermodynamic driving force greater than 20 kcal mol⁻¹. This definition was given by Sharpless *et al.* [141] and thus primed the capability of this reaction type for self-healing applications. Binder *et al.* [18, 42, 43] (see Table 1.1 entry 6) have developed a click-based self-healing system using the copper(I) catalyzed alkyne-azide cycloaddition (CuAAC) reaction. They investigated a system assembling fluid trivalent azido-telechelic poly(isobutylene)s (PIB) and various low molecular weight multivalent alkynes [18, 42]. Both reactants were encapsulated in urea-formaldehyde capsules and embedded into a polymer matrix containing Cu^I(PPh₃)₃Br and TBTA as catalytic system. After the rupture event the healing agents came into contact with each other and the catalyst, triggering the cycloaddition reaction, forming a crosslinked network, and thus healing the damage. In the present case, the crosslinked network formation proceeded at ambient temperatures and resulted in nearly full recovery of the tensile modulus of 91% at 25 °C or an increased value of 107% at 60 °C. Moreover, the network formation of two multivalent fluid polymers [43] was investigated and optimized using fluid trivalent star-shaped azido- and alkyne-telechelic PIBs or multivalent side-chain functionalized copolymers of poly(acrylate), respectively, with Cu^I(PPh₃)₃Br as catalyst. Thus, higher network strand densities and faster crosslinking could be observed, even at room temperature. Furthermore, autocatalytic behavior of the crosslinking reaction has been proven, increasing further the efficiency of the CuAAC toward self-healing polymers. Kessler *et al.* [48, 51] (see Table 1.1 entry 6) followed a very similar approach also based on the CuAAC which is potentially applicable for self-healing, using two low molecular weight reactants (bisphenol-A-based bisazide and bisphenol-E or tetraethylene glycol-based diynes), and thus ensuring flow of the components into the crack. After triggering the CuAAC by the copper(I) catalyst the network filled the crack and restored the material properties. However, due to the bivalent monomers, linear polymers were generated which formed networks only via physical chain entanglements, while the previously described polymers [18, 42, 43] were able to form three-dimensional networks by covalent chemical bonds. Other

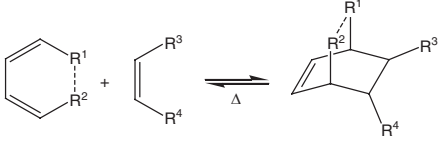
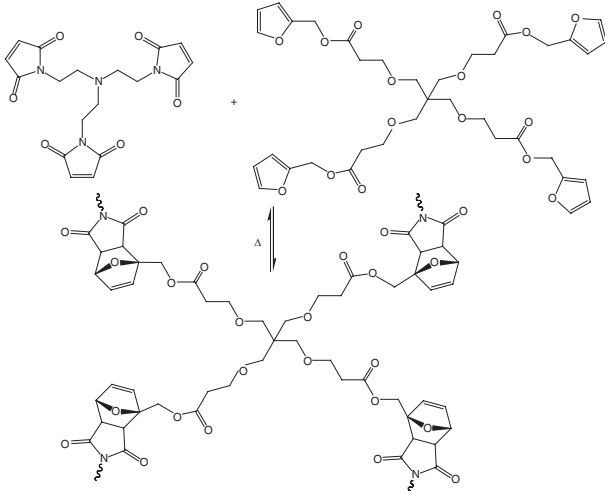
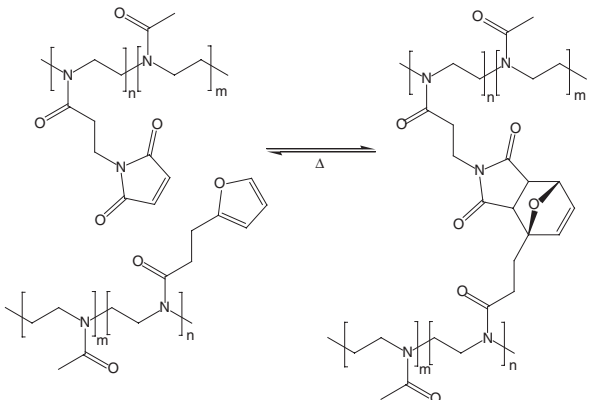
interesting potential self-healing approaches based on click chemistry might be strain-promoted azide-alkyne cycloaddition reaction or photochemically triggered thiol-ene or thiol-yne click reactions (see Table 1.1 entry 7). Thereby, the absence of biotoxic copper salts enables application in living systems. Moreover, thiol-ene and thiol-yne click reactions attract the attention of scientists due to their ability of combining the aforementioned advantages of click chemistry and the potential of light-triggered reactions, enabling a spatially and temporally controlled self-healing process. Further photochemically triggered reactions with similar advantages, like [2+2] or [4+4] cycloadditions, are discussed in Section 1.4.4 [6, 17, 142–144].

An alternative self-healing concept uses the Michael addition of tetravalent thiols and bivalent maleimides (see Figure 1.5f; Table 1.1 entry 8) and is thus an elegant method for damage healing of epoxy resin materials due to the ability of crosslinking between the residual amino groups at the crack surface and the maleimide moieties [132]. Therefore, a strong dependence of the healing efficiency on the used matrix resin can be observed, for example, using EPON 828 as matrix material reveals an average healing efficiency of 121% after curing for 5 days at 25 °C.

1.4.1.2 Reversible Covalent Network Formation Concepts

Prime examples of the class of *reversible covalent self-healing concepts* are versatile DA cycloaddition reactions [17, 24–28, 117–123] (see Figure 1.5f) (see Chapter 6). DA reactions are amongst the most important reactions in organic chemistry due to their ability for C–C bond formation in high yields and good stereochemistry. Therefore, a conjugated diene and a dienophile, both commonly electrochemically activated by substituents, react with each other via a [4+2] cycloaddition. Moreover, many DA products are able to undergo a thermally induced [4+2] cycloreversion, the so-called rDA reaction which is the basis of the self-healing ability of polymeric DA/rDA systems. Due to the weaker bond strength between diene and dienophile of the DA adduct compared to all the other covalent bonds, this bond will break preferentially during the damage event and the rDA reaction will take place [25]. If the damaged sample is heated again, the diene and dienophile will reconnect and the crack plane is healed. Heating is commonly necessary to enhance the mobility of the reactive groups at the crack plane and, therefore, to accelerate the DA reaction [17, 25]. Nevertheless, nowadays some DA/rDA systems are known which are able to mend a crack even at ambient temperatures [123]. Advantageous self-healing principles based on DA/rDA reactions do not need additional ingredients like microcapsules or microvascular networks, and allow multiple runs of self-healing processes in the same area. Nevertheless, the mentioned high mending temperatures, as well as oxidative side-reactions restrict the application area of the DA reaction. In principle, two different polymer architectures for DA/rDA systems are known: first the polymer backbone can either be functionalized along itself [27, 28, 120] (see Table 1.2 entries 11 and 13) or in the side chains [26, 121] (see Table 1.2 entry 12), and secondly, multivalent, often star-shaped systems with DA functionalities as end groups [24, 25, 27, 148] (see Table 1.2 entry 10) can be applied. Chemically, the utilizable functionalities for DA/rDA systems can be classified into three main categories: furan-maleimide-based polymers [17, 24–26, 117]

Table 1.2 Reversible covalent network formation concepts for self-healing applications.

Entry	Example	Ref.
(g)	Diels–Alder/retro Diels–Alder reaction (DA/rDA)	
9	DA/rDA	
		
10	Furan-maleimide based DA/rDA	[25]
		
11	Furan-maleimide based DA/rDA	[17, 26]
		

(Continued)

Table 1.2 (Continued)

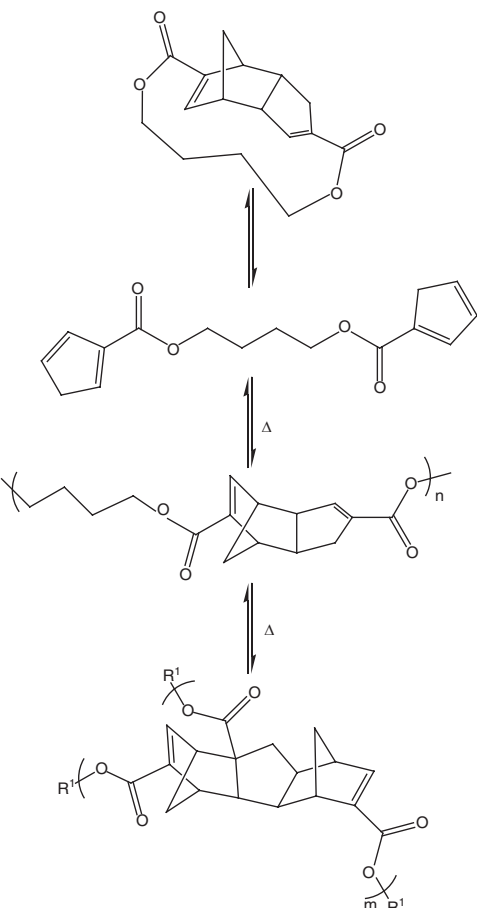
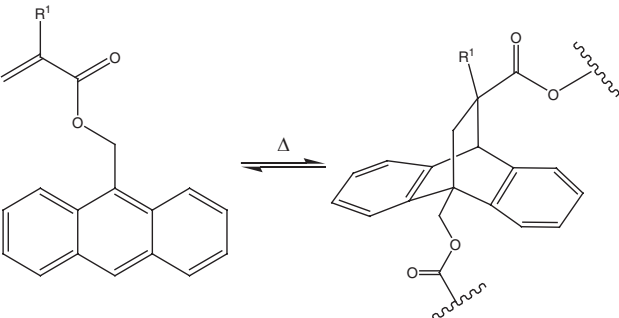
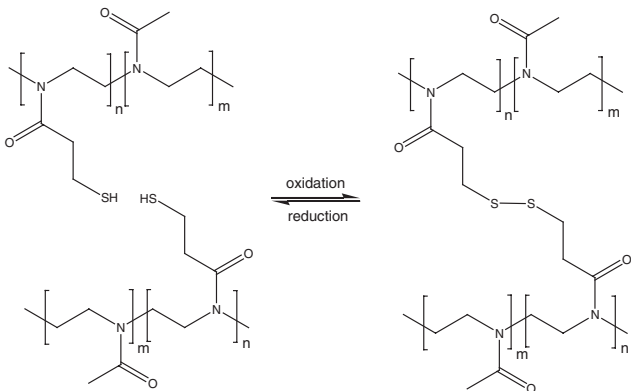
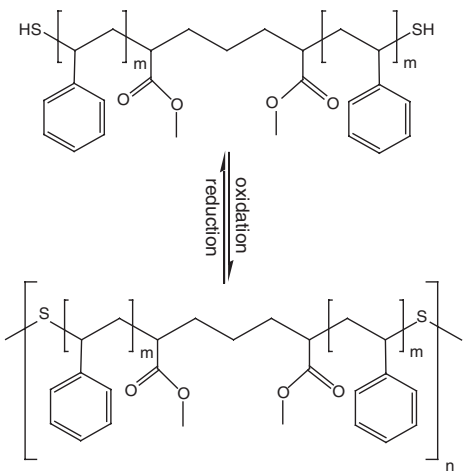
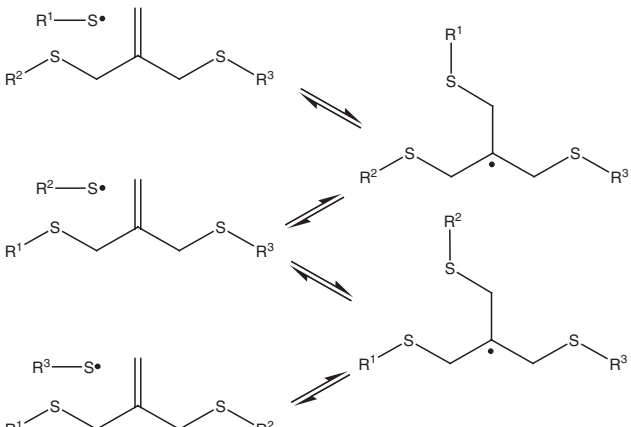
Entry	Example	Ref.
12	Cyclopentadiene-based DA/rDA	[27]
	 <p>The reaction scheme illustrates the synthesis of a cyclopentadiene-based polymer. It begins with a cyclopentadiene derivative (top structure) reacting with a cyclopentadiene derivative (middle structure) to form a dimer. This dimer then reacts with a cyclopentadiene derivative (bottom structure) to form a polymer chain with a cyclopentadiene core. The reaction is reversible, as indicated by the double-headed arrows.</p>	
13	Anthracene-based DA/rDA	[28]
	 <p>The reaction scheme illustrates the synthesis of an anthracene-based polymer. It shows the Diels-Alder reaction of an anthracene derivative (left structure) with a cyclopentadiene derivative (right structure) to form a polymer chain with an anthracene core. The reaction is reversible, as indicated by the double-headed arrow.</p>	

Table 1.2 (Continued)

Entry	Example	Ref.
(h)	Thiol/disulfide linkages	
14	Side chain modified	[145]
		
15	Backbone modified	[62]
		
(i)	Radical-based methods	
16	RAFT-like systems	[146]
		

(Continued)

Table 1.2 (Continued)

Entry	Example	Ref.
17	<p>Alkoxyamine-based systems</p> <p style="text-align: center;">alkoxyamine styrene radical TEMPO moiety</p>	[147]
(j)	Polycondensation reactions	
18	<p>Polycarbonate</p>	[124, 125]

(see Table 1.2 entries 10 and 11), dicyclopentadiene-based polymers [17, 27] (see Table 1.2 entry 12), and anthracene-based polymers [17, 28, 118, 120, 148] (see Table 1.2 entry 13). Thus, Wudl *et al.* [24, 25] developed a self-healing concept using the thermally reversible DA/rDA reaction between star-shaped trivalent maleimides and tetravalent furans (see Table 1.2 entry 10), resulting in a highly dense network with thermoset properties via a polyaddition reaction. The damage event will break the DA-crosslinking points to form terminal maleimide and furan species, which in turn are able to react preferentially in a DA reaction, resulting in an average mending efficiency of about 50% at a temperature of 150°C. Another thermally reversible DA method used modified poly(*N*-acetyleneimine)s bearing either maleimides or furans in the polymer side chain [26] (see Table 1.2 entry 11). Mixing of two suitable substituted polymers resulted in a dense network at a healing temperature of 80°C. Further investigations of similar DA/rDA concepts consisting of polystyrene-bearing maleimides and several furan moieties indicate a limited thermal stability of furfuryl moieties with a therefore limited applicability for self-healing materials [121]. Furthermore, a single component self-healing polymer was developed using cyclic monomers containing dicyclopentadiene cores as reactive units [27] (see Table 1.2 entry 12),

which were utilized simultaneously as diene and dienophile in the DA cycloaddition reaction. Accordingly, a polymer consisting of thermally reversible DA adducts with further reactive sides could be synthesized. A second DA reaction can be started, resulting in the trimerization and thus a highly crosslinked polymer, showing the ability for self-healing achieving an average healing efficiency of 46% upon heating to 120 °C. Moreover, a further single-component system potentially applicable for self-healing using DA/rDA reactions was developed applying anthracene-substituted acrylates simultaneously as diene and dienophile [28] (see Table 1.2 entry 13). The polymerization of this monomer results in a network with thermally reversible crosslinkers and represents thus a probable healing concept for thermoset materials. Beside the aforementioned systems, some other classical DA/rDA reactions using acyclic dienes and dienophiles [123], as well as some hetero-DA reactions [122] are potentially applicable for self-healing.

Some other potential self-healing methods based on reversible bond formation are known, mostly disulfide bridges (SS) can be ruptured by reversible reduction into two thiol groups (SH) [62] (see Figure 1.5h). Thus, subsequent recrosslinking under re-formation of disulfide bridges via oxidative conditions enables the restoration of the initial material properties. For example, a redox-reversible hydrogel system based on thiol-modified poly(*N*-acetyleneimine) (see Table 1.2 entry 14) might use the interconversion between disulfide and thiol groups to heal the damaged area [145]. Another example can be a polystyrene-based block copolymer bridged by disulfides [62] (see Table 1.2 entry 15). The internal disulfide linkers could be cleaved under reducing conditions to thiols, separating the single blocks and thus releasing the accrued stress. Healing could occur after subsequent oxidation of the thiols re-forming the disulfide linkers.

Furthermore, another potential self-healing concept working in a similar, but slightly different way used the photoinduced reversible cleavage of allyl sulfide linkages in a polymer backbone under generation of thiyl radicals [146] (see Figure 1.5i; Table 1.2 entry 16) ($\text{RS}\cdot$) which increased the chain mobility. Rearrangement of polymer chains in crosslinked rubber-like materials was thus assumed, enabling rapid stress release at ambient conditions without degradation of mechanical properties. Stress application without light irradiation resulted in a strained sample as expected, but under irradiation stress relaxation was observed due to homolytic photolysis via addition–fragmentation chain transfer reaction forming radicals by the allyl sulfide functionalities.

Other self-healing concepts based on thermally reversible cleavage of alkoxyamine bonds use a similar stress relaxation mechanism (see Table 1.2 entry 17). For example, a poly(alkoxyamine ester) was developed which is able to undergo a reversible radical exchange reaction at 60 °C by homolytic cleavage of the C–O bond [147]. Thus, these systems reduced the destructive stress within the polymeric material and are potentially suitable for self-healing applications.

Another, totally different approach for self-healing uses polycondensation reactions in order to restore the initial material properties (see Figure 1.5j). In contrast to the previously discussed reversible self-healing concepts which are, at least theoretically, infinitely repeatable, polycondensations are limited in the number

of healing cycles due to the consumption of functional groups during the self-healing process. Nevertheless, they are commonly more than one-time healable and can be, therefore, attributed to the (partially) reversible concepts. However, the previously discussed example of White *et al.* [131] (*irreversible covalent network formation concepts*) based on a polycondensation reaction of two different poly-(siloxane)s with tin catalysis cannot be attributed to the reversible self-healing systems due to the necessity of encapsulation of the catalyst (see Table 1.1 entry 3). Therefore, multiple healing of a once ruptured and subsequently healed area is not possible. However, as an example, a polycarbonate-based self-healing polymer for thermoplastic materials was developed [124, 125] (see Table 1.2 entry 18) as a reversible covalent self-healing polymer, splitting the carbonate bond by thermolysis or hydrolysis. Thus, phenoxy groups with terminal hydroxy moieties are generated, which are able to react with a phenyl end of an uncleaved chain, using sodium carbonate as healing agent in order to accelerate the reaction by exchanging protons of the hydroxy group with sodium ions. This healing mechanism is limited to certain types of thermoplastic materials which enable the recombination of chain ends via condensation reactions. This and the elevated temperatures restrict the range of polymers and applications to which this technology can be applied.

1.4.2

Supramolecular Network Formation

Supramolecular polymers use the “chemistry beyond the covalent bond” to combine reversible, secondary interactions with the attractiveness of conventional polymers [143]. Due to their highly dynamic properties, able to act in a reversible manner, their capability for designing self-healing polymers becomes evident. In special cases, networks can be formed solely by supramolecular bonds, thus opening the possibility for exploitation in self-healing materials. The relevant issues for utilizing supramolecular bonds in self-healing polymers are the timescale of the dynamics, relating dynamics of the bond to the timescale of healing, and their strength, resulting in stronger or weaker networks. Therefore we discuss here supramolecular network formation based on (a) *hydrogen bonding*, (b) *ionomers*, (c) *metal bonding* and (d) *π - π stacking* (for more information see Chapters 11–13). An overview of these interactions is given in Figure 1.6 and all examples discussed can be found in Table 1.3.

The design of self-healing polymers based on *hydrogen bonding* combines highly *dynamic properties* [156, 180–182] as bonds show a reversible “sticker-like” behavior enabling connection and reconnection, and thus *supramolecular network formation* [23, 182, 183] (see Figure 1.6a) as well as strength generated by the “stickiness” of the applied supramolecular bonds or by *cluster formation* [23, 184] between several hydrogen bonding motifs. Due to tunable and controllable dynamics, and thus the *reversibility* of network formation [153] via specific modes of association, *hydrogen bonded polymers* [156, 163, 182] can respond to an external damage event while emphasizing their attractiveness for self-healing purposes [6, 17].

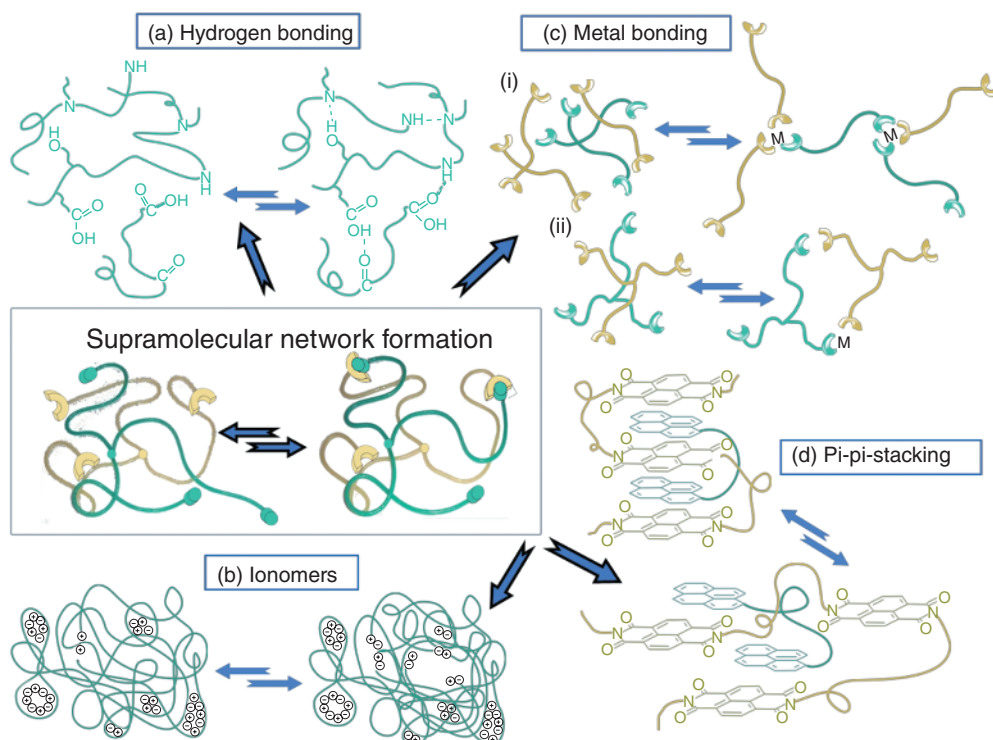
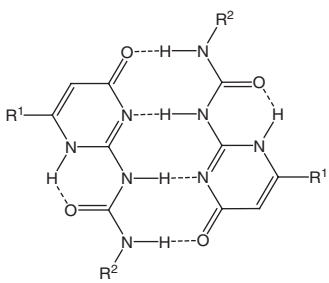
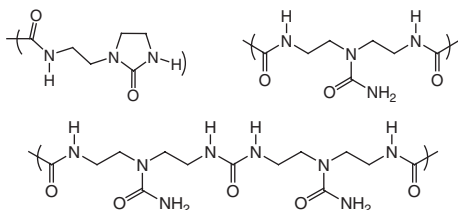


Figure 1.6 Supramolecular network formation via (a) hydrogen bonding, (b) ionomers, (c) metal bonding, or (d) π - π -stacking.

Table 1.3 Examples of supramolecular network formation.

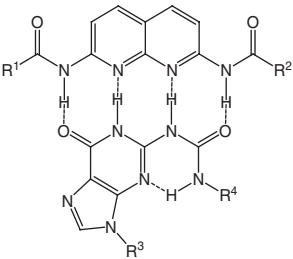
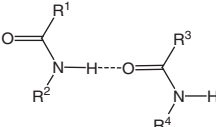
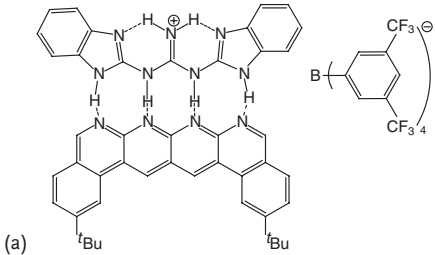
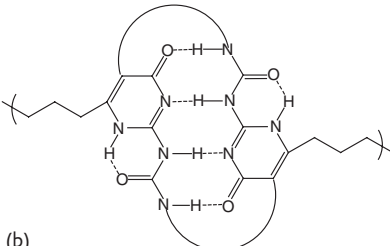
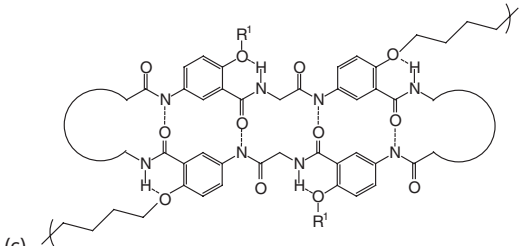
Entry	Example	Ref.
(a)	Hydrogen bonding	
1	Ureido-pyrimidone bond – SupraPolix BV 	[143, 149]
2	Leibler bond 	[21]

(Continued)

Table 1.3 (Continued)

Entry	Example	Ref.
3	Nucleobases and similar systems	[6, 22, 23, 150–155]
	<p>(a)</p>	
	<p>(b)</p>	
	<p>(c)</p>	
	<p>(d)</p>	
	<p>(e)</p>	

Table 1.3 (Continued)

Entry	Example	Ref.
4	Butylurea of guanosine and 2,7-diamido-1,8-naphthyridine 	[156, 157]
5	Poly(styrene) grafted with poly(acrylate amide) 	[94]
6	(a) AAAA-DDDD quadruple hydrogen bond  (b) double-closed loop topologies  (c) 	[14, 83, 158]

(Continued)

Table 1.3 (Continued)

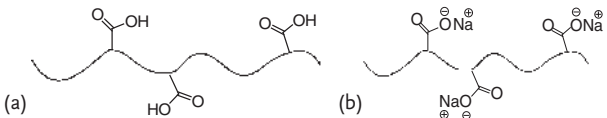
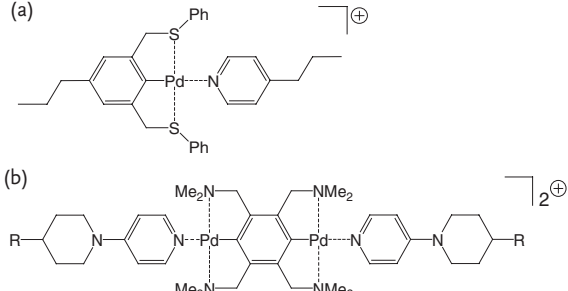
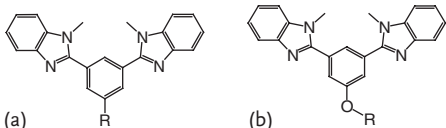
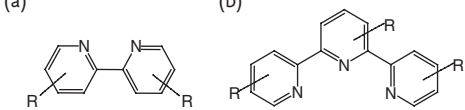
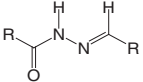
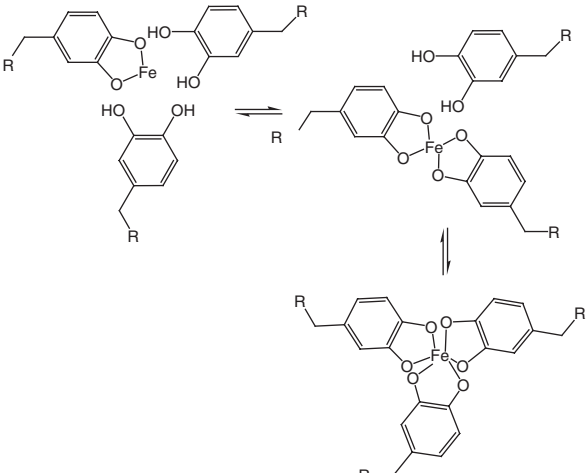
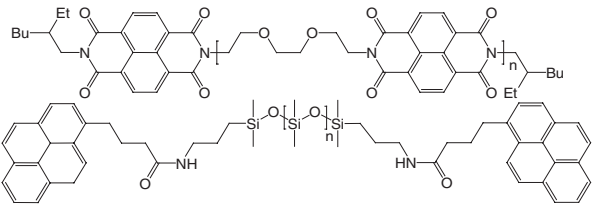
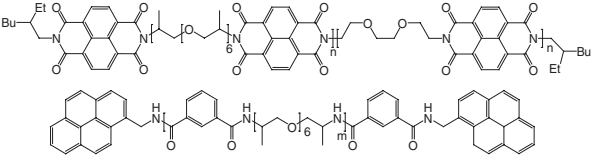
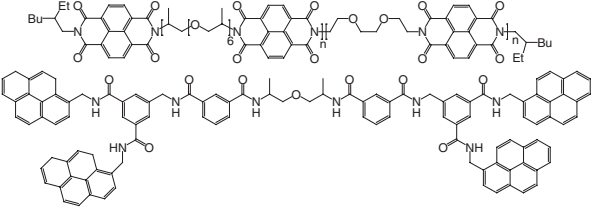
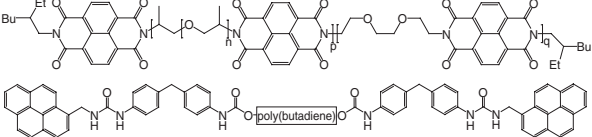
Entry	Example	Ref.
(b)	Ionomers	
7	(a) EMAA (b) partially neutralized EMAA	[3, 5, 11, 17, 87, 88, 159, 160]
		
(c)	Metal bonding	
8	Pincer complexes	[17, 161–168]
		
9	(a) Mebip (b) OMebip	[169–172]
		
10	(a) Bipyridines (b) Terpyridines	[17, 120, 130, 161, 164, 165]
		
11	Metallo-dynamers	[173–175]
		
12	Catechol-iron complex	[176]
		

Table 1.3 (Continued)

Entry	Example	Ref.
(d)	π - π -stacking	
13	Polydiimide + poly(siloxane) with pyrenyl endgroups 	[177]
14	Copolyimide + poly(amide) with pyrenyl endgroups 	[178]
15	Copolyimide + poly(amide) with pyrenyl endgroups 	[20]
16	Copolyimide + polyurethane with pyrenyl endgroups 	[179]

A strong change in materials properties is achieved with quadruple hydrogen bonds such as the ureido-pyrimidone bond [143, 149] (see Table 1.3 entry 1). Depending on the amount of binding sites, linear as well as crosslinked polymers were formed, whereas the absence of unspecific aggregation allowed excellent control over the formed network architecture. Thermal mending and thus dissociation of created thermoplastic elastomers could be observed at temperatures above 90 °C. Accordingly, this approach was adopted in industry by SupraPolix BV and found application in “real life” [143, 149].

A thermoreversible rubber was synthesized from multivalent fatty acids and urea with three different types of hydrogen bonding motifs, diamido tetraethyl triurea, di(amido ethyl) urea, and amidoethyl imidazolidone [21], respectively (see Table 1.3 entry 2). Samples plasticized with dodecane, showed a repeatable

self-healing response after cutting and bringing into contact again, with a shape recoverability up to several 100% due to hydrogen bonding.

The interaction behavior of supramolecular and thermosensitive polymers bearing different nucleobases (see Table 1.3 entry 3a) in solution as well as their capability to form films and fibers [151] were the first studied hydrogen bonding moieties applicable for self-healing concepts. Thus, already in the 1990s the investigation of urazole and 4-urazoylbenzoic acid as hydrogen bonding moieties [156] was started (see Table 1.3, entry 3b), revealing thermoplastic elastomeric behavior demonstrating different effects: urazole groups, when homogenously distributed within the polymer, resulted in the formation of two hydrogen bonds and thus in the broadening of the rubbery plateau zone. In contrast, 4-urazoylbenzoic acid groups showed the formation of extended aggregates due to phase separation [156]. Similarly, thymine or uracil units were used for crosslinking complementary diaminotriazine functionalized copolymers, resulting in the formation of spherical aggregates due to thermally reversible three-point hydrogen bonding [154, 185] (see Table 1.3 entry 3c). In turn, to tune the properties of these materials by balancing intra- and intermolecular hydrogen bonding, diacyldiaminopyridine motifs have also been applied [154, 185]. In order to increase the secondary interaction the formation of supramolecular linear or crosslinked polymers based on a cyanuric wedge such as an ADA–ADA (A: hydrogen bond acceptor, D: hydrogen bond donor) array and a diaminopyridine-substituted isophthalamide receptor such as a DAD–DAD unit creating a well-defined sextuple hydrogen bond (see Table 1.3 entry 3d) were studied [152, 153]. While investigating the dynamics and the thermoreversible aggregation behavior [23] of poly(isobutylene)s functionalized with barbituric acid and Hamilton Wedge [22, 153] in the melt, a self-healing ability of samples functionalized with barbituric acid was found, showing self-healing at room temperature within 48 hours due to the formation of dynamic supramolecular clusters [22, 153].

Quadruple hydrogen bonds formed between the butylurea of guanosine and 2,7-diamido-1,8-naphthyridine [150, 157] show both, high fidelity as well as high stability (see Table 1.3 entry 4). Due to weak self-association and a high association constant this approach exceeds the fidelity of DNA base-pairing and is one of the strongest known neutral DNA base-pair analogs. Thus, supramolecular multi-block copolymers as well as thermoreversible supramolecular polymer blends with tunable properties can be created.

Another self-healing approach utilized a thermoplastic elastomer consisting of a poly(styrene) backbone grafted with poly(acrylate amide) as a self-healing concept [94] (see Table 1.3 entry 5). Due to immiscibility effects phase separation into a soft, supramolecular poly(acrylate amide) matrix and a hard poly(styrene) sphere could be observed. Accordingly, the approach combines elastomeric behavior, mechanical stiffness and molecular dynamics due to reversible hydrogen bonding within grafted brushes [94].

Due to the large number of hydrogen bonds, a number of promising but still unexploited hydrogen bonds as concepts for self-healing polymers exist. Examples are the AAAA-DDDD type [14] (see Table 1.3 entry 6a) with an association constant

up to 10^{12} M^{-1} as well as double-closed loop topologies [83, 158] (see Table 1.3 entries 6b and c) based on 2-ureido-4-pyrimidone or peptidomimetic-sheet modules.

Self-healing polymers based on supramolecular, dynamic networks can also be formed by *ionomers* [5]—supramolecular thermoplastic polymers with an ionic group content up to 15 mol%—while taking advantage of their characteristic *clustering* [85] (see Figure 1.6b and Table 1.3). Due to the ionic species within the polymer backbone, clusters can be formed acting as *physical crosslinking points*, and allowing reversible formation and re-formation of the network structure. Thus, the resulting complex microstructure and the order to disorder transition temperature emphasize a self-healing ability in response to *ballistic impact* [85]. Especially poly(ethylene-*co*-methacrylic acid) (EMAA)-based ionomers (see Table 1.3 entries 7a and b) were investigated to obtain information on the materials response and the underlying self-healing mechanism [3, 5, 11, 17, 85, 87, 88].

Although an increase in the ion content within the materials increases their fracture resistance and tensile strength, both pure EMAA and its ionomers showed the ability of fast self-healing upon ballistic puncture. Thus, it was hypothesized [159, 160] that the ionic content itself is not necessary for the healing response but that the existence of the polar acid groups within the material is mechanistically essential due to reversible hydrogen bonding. Furthermore, the self-healing ability is linked to the heat generated during the damage event and requires a high energy elastic response of the material. Thus, the localized molten polymer enables the viscoelastic recovery of the sample to snap back and close the hole. This stage is followed by an interdiffusion and sealing step, subsequently completed by the formation of crosslinking points. The strength regeneration within the material is based on continuing interdiffusion processes, crystallization as well as long-term relaxation of the polymer chains. Furthermore, the self-healing ability is affected by balanced elastic and viscous responses of the materials close to the impact region, wherein the elastic response provides the ability to rebound and the viscous response induces final sealing. Healing at low temperatures can occur if the material is locally sufficiently heated to the melted state. However, elevated temperatures do not promote healing if the energy within the material is dissipated faster, confirming the proposed elastic “snap back” step. Therefore, insufficient self-healing can be observed if not enough thermal energy is produced within the material during the ballistic impact. Therefore, healing efficiencies depend on the speed and the shape of the projectile [3, 5, 11, 17, 85, 87, 88, 159, 160].

Supramolecular network formation and thus a self-healing capability can also be achieved by *dynamic coordination bonds* [12, 167] with certain metal ions (see Figure 1.6c and Table 1.3). In contrast to ionomers, where clusters play the most crucial role for network formation, polymers with *multivalent metal-ligand interactions* [186] have to be carefully selected in order to construct reversibly cross-linkable networks with both sufficient stability and dynamics. Accordingly, the thermodynamic and kinetic parameters [12, 167, 168] of a coordination bond, indicated on the one hand by the equilibrium or association constant and by the formation or dissociation rate on the other hand, have to be taken into account to

control the materials responsiveness to environmental stimuli [170, 187] necessary for efficient self-healing. Thus, by controlling the dynamics, a *molecular toolbox* [12, 167] is obtained, which allows the design of structurally dynamic polymers suitable for self-healing approaches [188].

For the design of supramolecular networks based on metal–ligand interactions commonly *palladated* or *platinated pincer complexes* (see Table 1.3 entries 8a and b), *2,6-bis-(1'-methylbenzimidazolyl)pyridines* and *4-oxy-2,6-bis(N-methylbenzimidazolyl)pyridines* (see Table 1.3 entries 9a and b) as well as *bi- and terpyridines* (see Table 1.3 entries 10a and b) are used as ligands [17, 161–165]. In order to create supramolecular networks the ligand requires at least two polydentate functionalities linked by a spacer group. Furthermore, the choice of the metal, ranging from main- to transition-group metals up to lanthanides, can influence the stability of the generated complex, and thus the dynamics as well as the reversibility of the metallosupramolecular interaction [17, 161–165].

Other promising candidates for self-healing materials are bifunctional Pt(II) or Pd(II) pincer complexes [17, 161–168] (see Table 1.3 entries 8a and b) forming a coordination complex with a side-chain pyridine ligand of a polymer backbone, most of all by controlling and understanding the dynamics of the network by selecting appropriate metal centers.

A tridentate ligand, namely, *2,6-bis-(1'-methylbenzimidazolyl)pyridine* (Mebip) [170–172] (see Table 1.3 entry 9a) was investigated based on the work of Piguet and Buenzli [169]. Linear metallosupramolecular polymers formed bidentate complexes with transition metal ions, whereas crosslinked samples were obtained from stable tridentate complexes with lanthanide ions. Thus, gels with a tunable crosslinking density could be obtained by adjusting the ratio of coordinating ions. In consequence, the complexation behavior of this ligand with metal ions like Fe(II), Co(II), Cd(II), Eu(III) or Zn(II), and the film formation due to phase separation were explored [17, 170]. Furthermore, supramolecular metallopolymerizations of ditopic poly(*p*-phenylene ethynylene) and poly(*p*-xylylene) end-capped with *2,6-bis-(1'-methylbenzimidazolyl)pyridine* (Mebip) (see Table 1.3 entry 9a) could be demonstrated [187]. Metallosupramolecular polymers with shape-memory properties based on *4-oxy-2,6-bis(N-methylbenzimidazolyl)pyridine* (OMebip) (see Table 1.3 entry 9b) as ligand could be obtained [172] generating phase separated films with a temporary shape.

The group of Lehn [15, 173–175, 189] reported the synthesis of neutral metal-lodynamers of polyacylhydrazones (see Table 1.3 entry 11) with Zn(II) or Ni(II) ions showing a dynamic behavior in solution dependent on the coordination center. Furthermore, they proved the formation of films as well as reversible coordination in the bulk material and reversible formation of covalent imine bonds.

As last metal-based self-healing concept a catechol-iron complex [176] (see Table 1.3 entry 12) should be mentioned. The complex, used within a polymer chain inspired by mussel, resulted in pH-dependent gels with 100% self-healing ability. Accordingly, this approach can also be classed as “switchable” healing but is mentioned here due to its metal–ligand interaction.

Self-healing materials based on aromatic π - π stacking [6] (see Figure 1.6d and Table 1.3) interactions were first reported by Burattini *et al.* [190] who took advantage of combining π -electron-rich and π -electron-poor moieties [20, 179]. Therefore, *supramolecular complexes with chain-folded secondary structures*, and thus with a maximum amount of possible interactions, can be obtained [6]. As a result low-molecular-weight precursors can be converted into medium-molecular-weight species in a highly dynamic manner. Moreover, the so obtained stimuli-responsive products show great physical properties such as high tensile strength which is more commonly related to covalent bonds but tunable for various self-healing applications [179].

In Burattini's first approach, a siloxane polymer bearing π -electron rich pyrenyl endgroups at each side as well as a low-molecular-weight polydiimide containing multiple π -electron poor receptor moieties (see Table 1.3 entry 13) were synthesized. A reversible and rapid complexation behavior in solution, as well as the formation of homogeneous and thermodynamically stable films with an inherent healing capability at temperatures above 90 °C could be shown. Furthermore, it could be proven that the chain-folding of the polyimide [177] creates an optimal binding site for the pyrenyl endgroups forming a non-covalent, π - π -stacked supramolecular network [191] able to react with a self-healing response. Accordingly, healing can be initiated by the partial disruption of π - π -stacked crosslinking points at elevated temperatures. Due to the terminal flow of the polymer chains, the repair of a damaged region during cooling, and thus the restoration of the supramolecular interactions, was enabled, regenerating the initial materials properties.

An improved self-healing polymer based on π - π -stacking interactions was developed as the first concept lacked in stability [178]. Therefore, the polymer backbone was modified using a co-polyimide and a polyamide with two pyrenyl end-groups (see Table 1.3 entry 14). Healing could be achieved by bringing cut samples into contact, followed by subsequent heating, even after a separation time of up to 24 h. 80% recovery of the tensile modulus was achieved already after 5 min at 50 °C. Furthermore, full recovery of the tensile modulus could be shown for three times. Due to the increase in possible π - π -stacking interactions by increasing the amount of pyrene-endgroups per polymer chain from two to four [20] (see Table 1.3 entry 15) an increase in the binding constant in solution of nearly two orders of magnitude could be observed. The so prepared supramolecular blends featured increased toughness as well as an enhanced tensile strength but required longer times and higher temperatures for healing.

Beside these approaches, a healable polymeric blend based on the chain-folding of a polyimide and a pyrene-functionalized polyurethane was reported and proved the structural integrity in the bulk [179] (see Table 1.3 entry 16). Additionally to π - π -stacking, hydrogen bonds reinforced the formation of possible crosslinking points within the material. Due to the combination of π - π -stacking and hydrogen bonding a significant increase in the tensile modulus compared to the hydrogen bonding approach described by Leibler [21] was demonstrated. For further information regarding supramolecular network formation see also Part 3 – *Supramolecular Systems*.

1.4.3

Mechanochemical Network Formation

Mechanochemistry [4, 64–78, 119, 192–206] is an elegant method for designing self-healing polymers due to the triggering of healing processes by the damage event itself. In its basics, mechanochemistry has been known since the middle of the last century, but only in the recent years it has become the focus of interest. Mechanochemical materials generate the reactive species as a consequence of applied mechanical stress via an *in situ* activation. This enables the direct embedding of the mechanophore into the matrix preventing further protection of the active species, like encapsulation. Mechanochemical induced self-healing is always an intrinsic self-healing method due to its inherent characteristics. In the following we consider self-healing methods which are able to generate a reactive species in the course of the rupture event. If a more general definition of mechanochemistry is applied, including all interactions and reactions caused directly or indirectly by mechanical force and thus by damage, almost all self-healing approaches could be assigned to this category. A detailed account of this topic is given in Chapter 8.

The mechanochemical concepts known to date can be classified into two main categories. The first class is able to generate reactive species, like radicals [4, 192–197, 206] (see Figure 1.7a, Table 1.4 entries 1–4) or strongly activated double bonds [4, 64, 66–68, 70–73, 119, 200, 201] (see Figure 1.7b; Table 1.4 entries 5–9), which can undergo various reactions in order to form a network, filling the crack and thus healing the damage. In the second class an active catalyst is generated under mechanical stress out of an inactive precursor [74, 75, 78, 202–205] (see Figure 1.7c; Table 1.4 entries 10–13), whereby a crosslinking reaction can take place, which heals the damage.

1.4.3.1 Mechanochemical Generation of Reactive Species

Some of the earliest concepts which generate reactive species due to the influence of mechanical force are based on natural and synthetic rubbers. These polymers create radicals by homolytic cleavage of carbon–carbon bonds as soon as they are cracked mechanically [192, 193] (see Figure 1.7a; Table 1.4 entry 1). Of course, it can be assumed that the main effect for self-healing can be attributed to the more probable molecular interdiffusion due to the low T_g of such polymers. Nevertheless, the involvement of radicals is proven [193, 206]. Moreover, these first analyses examined a molecular weight dependence with a minimum molecular weight required for cleavage [194], which was important for a deeper understanding and further developments of mechanical activatable systems. Pursuing this approach, new macromolecules with easier and more selective cleavable bonds were designed. Examples are peroxides in poly(vinylpyrrolidone) [195] (see Table 1.4 entry 2) or azo-linkers in linear poly(ethylene glycol) [4, 196], whereby the latter group cleaves off nitrogen under mechanical stress and thus generates two radicals which are able to recombine (see Table 1.4 entry 3). In a similar approach a poly(phenylene ether) (PPE) chain can be cut by an external force as well as by heat or light. The resulting radicals can react with a Cu(II) species while reforming the polymer in a redox

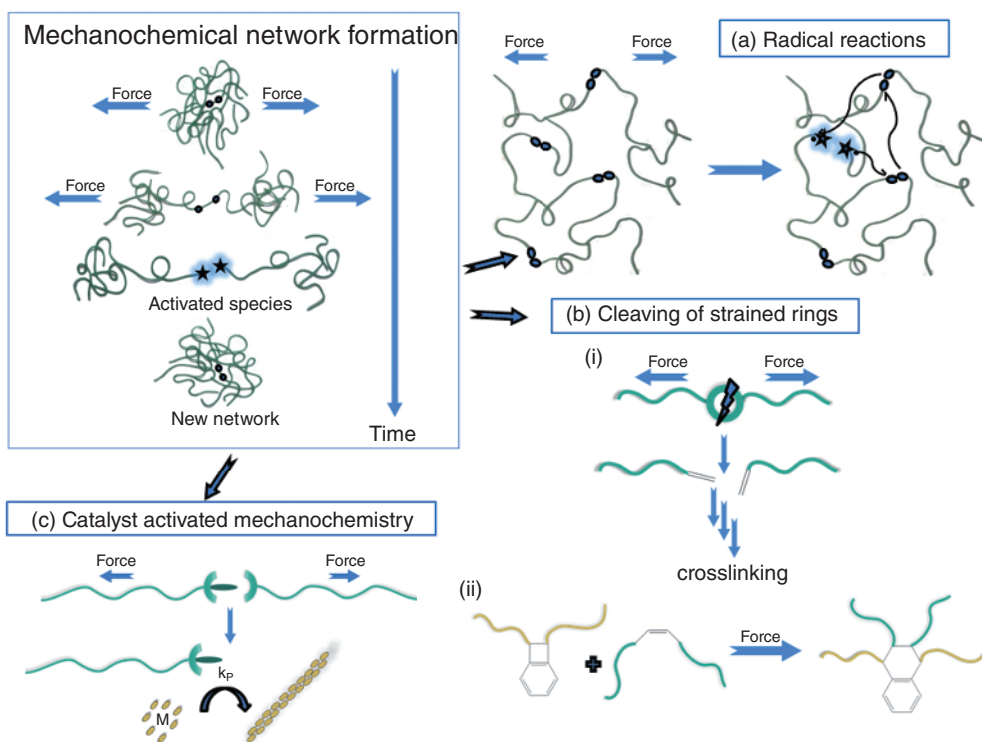


Figure 1.7 Overview of mechanochemically induced self-healing systems. (a) The generation of radicals by polymer chain scission and the subsequent recombination, (b) the generation of reactive species by cleaving of highly strained ring systems

under b(i) chain scission or b(ii) via subsequent pericyclic rearrangement, and (c) the mechanochemical activation of catalysts. All methods result in the formation of networks.

process [124, 197] (see Table 1.4 entry 4). Further considerations regarding these predetermined breaking points resulted in the development of completely new kinds of mechanochemically activatable polymers. These polymers consist basically of a mechanosensitive group and a polymer chain which “collects” and transmits the force to the commonly centered mechanosensitive group [4, 198, 199]. Similar to the rubber-based approaches, the mechanical force orientates the mechanophores (polymer chain and mechanosensitive group) in a preferred direction, whereby the polymer chains are stretched, resulting in a rupture of the weakest bond [4, 67, 198, 199] (see Figure 1.7). This approach only works if the polymer chains have a minimal length and therefore a minimal molecular weight depending on the kind of polymer. After cleavage the mechanosensitive group releases the reactive species, which can either react itself or is able to trigger further reactions. Mechanophores thus enable the transformation of energy from applied mechanical fields to productive chemical changes that can restore initial material properties,

Table 1.4 Examples of self-healing systems activated via mechanochemistry.


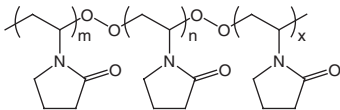
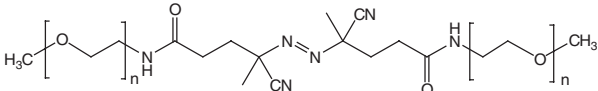
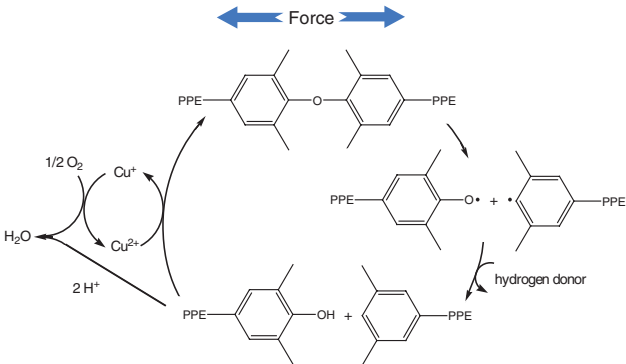
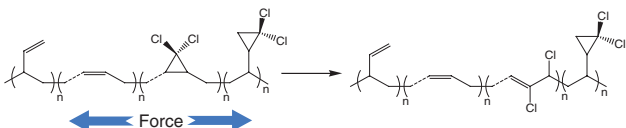
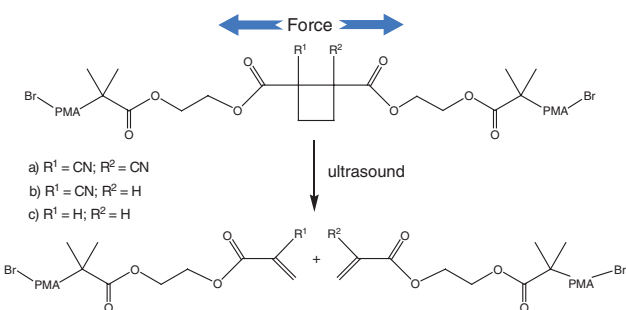
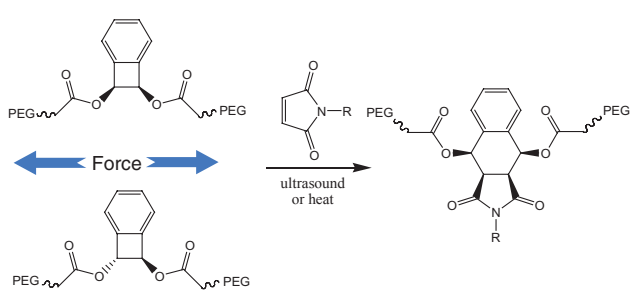
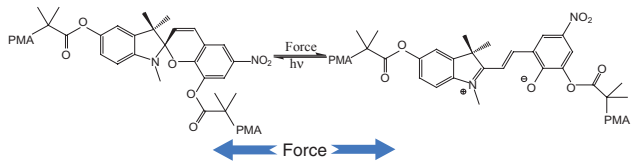
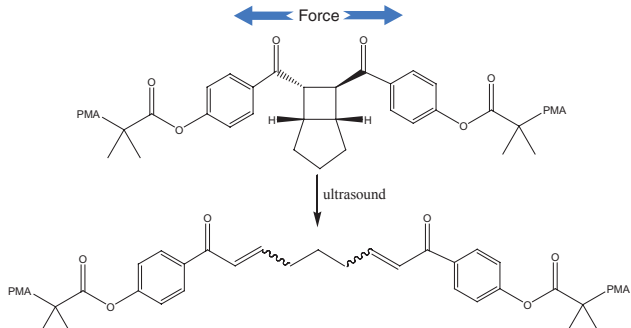
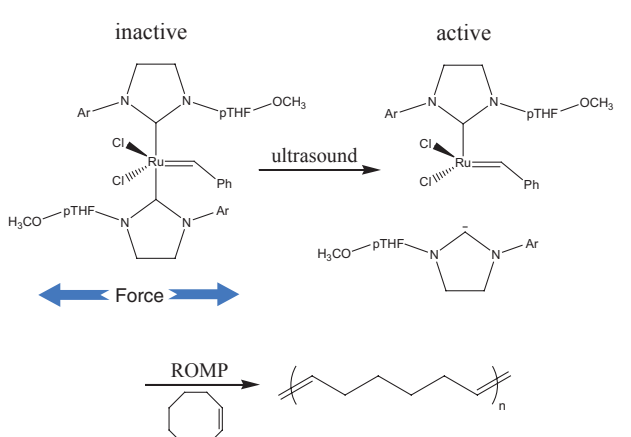
Entry	Example	Ref.
(a) + (b)	Mechanochemical generation of reactive species	
1	Homolysis of C–C bonds 	[192, 193]
2	Peroxide linked 	[195]
3	Azo-linked 	[4, 196]
4	Poly (phenylene ether) 	[124, 197]
5	Cyclic propanes 	[66, 71, 73]
6	Cyclic butanes  a) R ¹ = CN; R ² = CN b) R ¹ = CN; R ² = H c) R ¹ = H; R ² = H	[68, 200]

Table 1.4 (Continued)

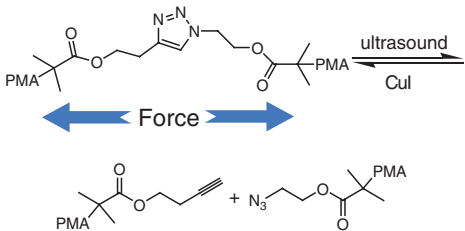
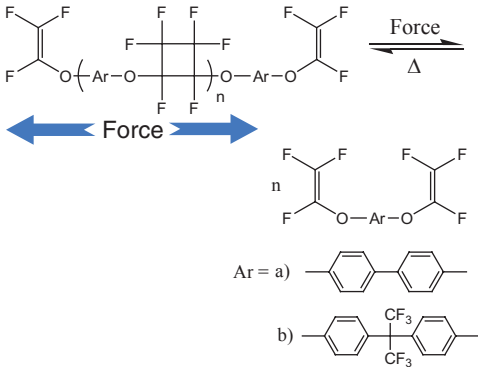
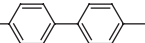
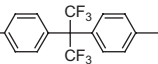
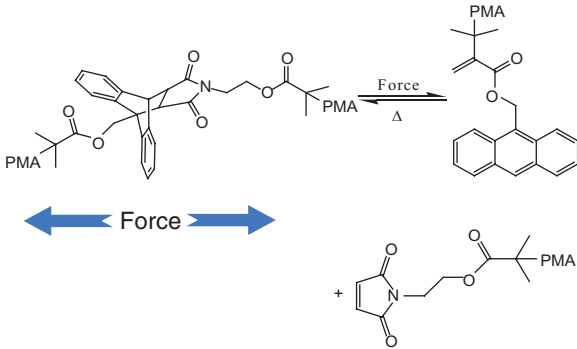
Entry	Example	Ref.
7	Cyclic butenes 	[64, 70]
8	Spiroprans 	[70, 201]
9	Bicyclic rings 	[66]
(c)	Mechanochemical activation of catalysts	
10	ROMP-based 	[74, 75]

(Continued)

Table 1.4 (Continued)

Entry	Example	Ref.
11	<p>Pincer complexes</p> <p> $\xrightarrow[\text{CH}_3\text{CN, ultrasound}]{\text{Force}}$ </p>	[204]
12	<p>Boron complexes</p> <p> $\xrightarrow[\text{ultrasound}]{\text{Force}}$ </p>	[205]
13	<p>Phosphine-based complexes</p> <p> $\xrightarrow[\text{active species trapped by}]{\text{ultrasound}}$ </p>	[78, 202, 203]

Table 1.4 (Continued)

Entry	Example	Ref.
Alternative mechanochemical self-healing concepts		
14	Click-based 	[207]
15	Cyclic butanes  <p>Ar = a)  b) </p>	[72]
16	Anthracene/ maleimide 	[118]

resulting finally in self-healing. Thus, mechanical stress causes on the one hand the damage, and on the other hand triggers the self-healing process by itself.

Examples for such self-healing concepts are cyclic, highly strained ring systems, like substituted cyclopropanes [66, 71, 73] (Table 1.4 entry 5), cyclobutanes [66, 68, 72, 200] (entry 6), cyclobutenes [4, 64, 72, 119] (entry 7), cyclopentanes [4, 67, 70, 201] (entry 8) (see Figure 1.7b) or bicyclic rings [66] (entry 9). A particularly illustrative mechanical activatable system was developed by Moore *et al.* [64, 70], who

harnessed the mechanical force to open a 1,2-poly(ethylene glycol) disubstituted benzocyclobutene. This is done in a pericyclic rearrangement including a 4π electrocyclic ring-opening reaction, resulting in the formation of an *ortho*-quinodimethide diene, which can further react in the presence of a substituted maleimide in a fast DA reaction (see Figure 1.7b (ii); Table 1.4 entry 7).

1.4.3.2 Mechanochemical Activation of Catalysts

The mechanochemical activation of a previously inactive catalyst by force was shown by Sijbesma *et al.* [74, 75]. In contrast to the previously discussed polymers, the active catalyst triggered a chemical reaction instead of acting as a healing agent by itself (see Figure 1.7c; Table 1.4 entry 10). Their approach includes the mechanochemical dissociation of *N*-heterocyclic carbenes (NHC) (linked to poly-(tetrahydrofuran)s), coordinated silver- and ruthenium-based catalysts forming a free coordination site which enables the catalysis of transesterifications, ring-closing metathesis (RCM), or ring-opening metathesis polymerizations (ROMP), respectively. Especially, the ROMP of various derivatives of cyclooctene [75], norbornene [74], or dicyclopentadiene might be suitable as mechanically induced self-healing systems. Further mechanochemical concepts acting according to a similar mechanocatalytic mechanism are described in the literature [78, 202–205] and are partly shown in Table 1.4 entries 10–13. Bielawski *et al.* [205] has developed a potentially applicable self-healing concept based on the release of a pyridine moiety which can catalyze either an anionic polymerization, or can effect a Brønsted acid-base reaction (see Table 1.4 entry 12), both showing suitability for self-healing purposes. Therefore, an electron-deficient boron species, which is coordinated to two pyridine-capped poly(methyl acrylate)s, was used while cleaving one pyridine moiety under ultrasonication.

Of course, some other mechanical activatable systems for self-healing [4, 67, 70, 72, 118, 119, 198, 199, 201, 207–211] are known (some examples are shown in Table 1.4 entries 14–16), although they are not described here.

1.4.4

“Switchable” Network Formation

Self-healing concepts based on “switchable” network formation utilize materials with an inherent “switch”, as the word already implies. Thus, self-healing polymers using “switchable” concepts combine organic synthesis and polymer science in order to control functionalities on the molecular level while “turning the switch on and off” [79, 80] and thus changing material properties. Moreover, the reversibility and dynamics of the underlying chemistry can be controlled in a highly selective manner due to molecular “switching”, thus changing network properties on demand, which is a key point for a sufficient self-healing response [79, 81]. As “switch” a combination of (a) *light and external force*, (b) *light* of different wavelengths, (c) the *pH-value*, as well as an *electrochemical stimulus*, can be used to trigger a reversible reaction within the material applicable for self-healing [80, 82] (see Figure 1.8 and Table 1.5) (see also Chapter 7).

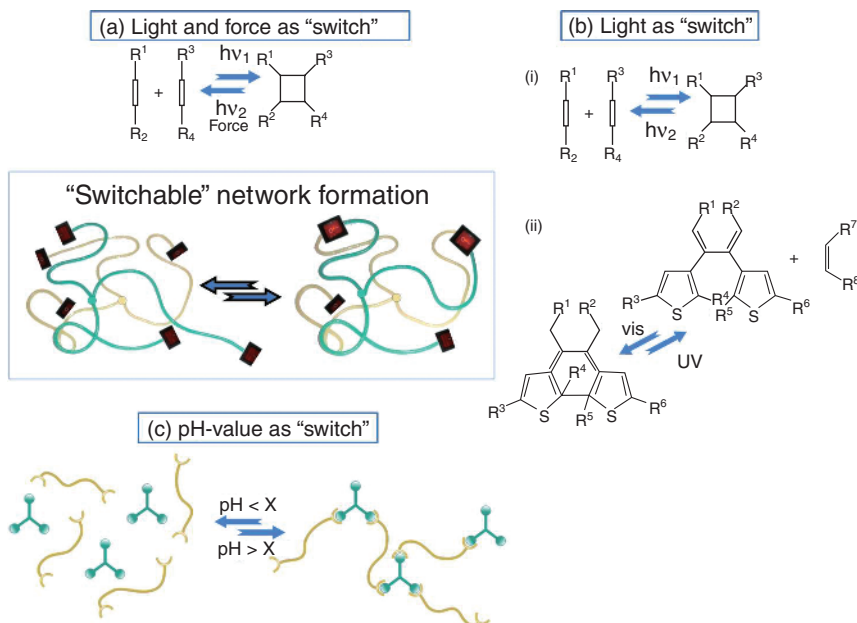


Figure 1.8 "Switchable" network formation. using (a) light in combination with force, (b) light, and (c) the pH-value as the inherent molecular "switch".

Davis *et al.* [65] used a mechanophore—a chemical group sensitive to mechanically induced force—to link glassy and elastomeric polymers. They selected the colorless spiropyran moiety (see Table 1.5 entry 1) which can undergo a reversible, force-induced 6 π electrocyclic ring-opening reaction. Because of the rupture of the carbon–oxygen bond of the spiro-compound, the conjugation length of the formed planar merocyanine increased, resulting in an absorption shift to longer wavelengths, and thus a color change. Due to the visualization of the mechanochemical reaction they could demonstrate the selective breaking and reforming of covalent bonds by mechanical forces. Furthermore, the efficient transfer of the external energy to the mechanosensitive group indicated the damage event. The re-formation of the spiropyran could be achieved via photocyclization using light as a "switch". The functional group is capable of translating crosslinking responses, serving as a concept for the development of regenerative self-healing polymeric materials [65]. Further examples of using light as a readily available, clean and cheap "switch" include reversible cycloaddition reactions, which allow the opening and closing of crosslinking ring structures within a polymer network. Especially, [2+2] cycloaddition reactions between cinnamoyl groups [6, 17, 142, 144] and coumarin groups [6, 17, 212–214], as well as [4+4] cycloaddition reactions of anthracene groups [6, 17, 215–222] (see Table 1.5 entries 2, 3a and 3b) attracted the interest of scientists. First, photochemical healing within a polymeric material was applied to poly(methacrylate)s with

Table 1.5 Examples of “switchable” network formation.

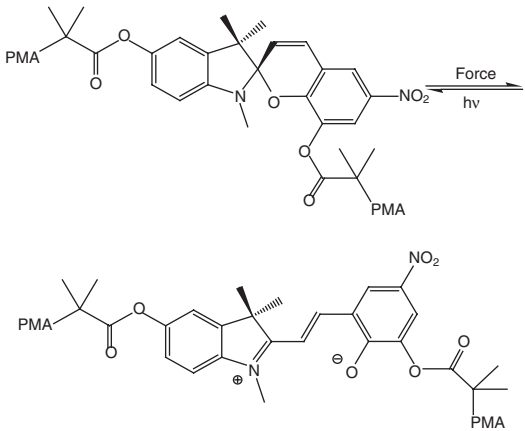
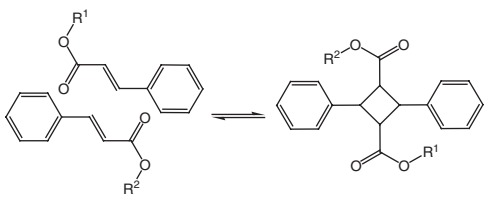
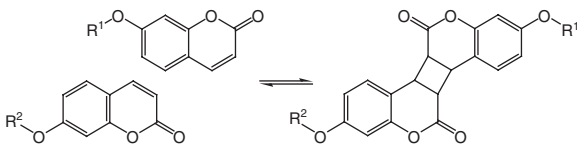
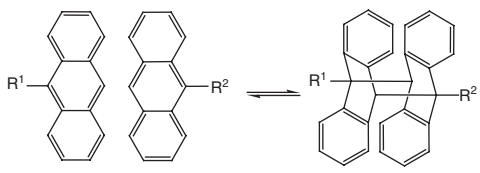
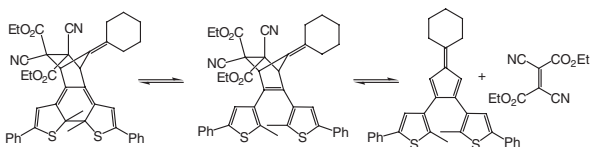
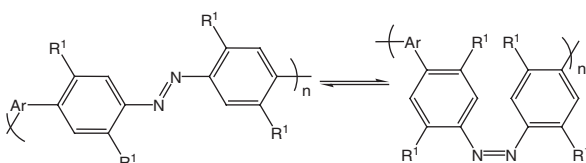
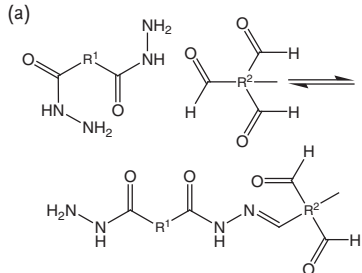
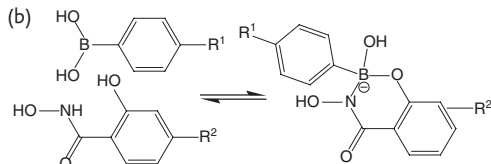
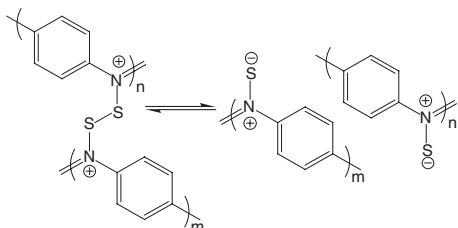
Entry	Example	Ref.
(a)	Light and force as “switch”	
1	<p>Spiro-pyranes</p> 	[65]
2	<p>[2+2] cycloaddition reactions</p> 	[6, 17, 142, 144]
(b)	Light as “switch”	
3	<p>(a) [2+2] cycloaddition reactions</p>  <p>(b) [4+4] cycloaddition reactions</p> 	[6, 17, 212–222]
4	<p>Photo-responsive DA-reactions</p> 	[79, 81]

Table 1.5 (Continued)

Entry	Example	Ref.
5	<i>Cis-to-trans</i> isomerization of azobenzene units	[204, 223, 224]
		
(c)	pH-Value as “switch”	
6	(a) formation of hydrazones	[225, 226]
		
	(b) complexation of salicylhydroxamic acids and boronic acids	
		
(d)	Electrical “switch”	
7	Electrochemical redox reaction	[204, 227]
		

cyclobutanediyl crosslinks [6, 17, 144]. Upon a damage event the reversion of the strained cyclobutane ring occurred and a fast healing process could be initiated by photoirradiation with a wavelength above 280 nm, resulting in hard and insoluble films. If samples were additionally heated during irradiation, a higher recovery of flexural strength could be reached, whereas the flexural strength of the healed sample was always considerably reduced in comparison to the original sample [6, 17, 144] (see Table 1.5 entry 2). “Switchable” photo-induced crosslinking of

pendant coumarin groups has attracted the attention of several groups [17, 212, 213]. In acrylate-based copolymers, dimerization of coumarin moieties, and thus the formation of a polymeric network, was observed within the films after irradiation with 300 or 350 nm light. Photo-cleavage could be forced by irradiation of light with a wavelength of 254 nm. Furthermore, it was found that the photochemistry was determined by the copolymer composition. Thus, the rate of photocrosslinking for copolyacrylates with a T_g above room temperature depends on the chromophore content, whereas the rate for copolymers with a T_g below room temperature can be traced to chain segmental mobility [17, 212] (see Table 1.5 entry 3a). A great deal of effort was put in optimizing the [4+4] cycloaddition of anthracene-based polymers [6, 17, 215–222] (see Table 1.5 entry 3b) as this pericyclic reaction proceeds at longer wavelengths, which can be tolerated by a large variety of functional groups. Furthermore, the great proximity to the wavelength of sunlight makes it attractive for outdoor applications. Accordingly, the concept of photocrosslinking anthryl moieties has been applied to study aging processes in polymer backbones [215], for the preparation of molecularly imprinted polymers [220] and multifaceted porous and three-dimensional polymer films [217]. Moreover, “switchable” anthracene groups found application in dendritic macromonomers [219]. Network formation could also be observed in aqueous media with reversible change of the crosslinking density, as well as in the bulk showing full reversibility. The high density of functional groups and the low viscosity also emphasize the applicability for self-healing purposes [219].

Furthermore, light can also be used as a “switch” to turn on and off a photoreversible DA reaction of dithienylfuran dienes [79, 81] (see Figure 1.8b and Table 1.5 entry 4). This approach toward self-healing polymers is based on two reversible reactions. First, ultraviolet light can be used to introduce the ring-closed form of the dithienylfuran dienes, or visible light can be applied to force the ring-opened form. The second reversible reaction is the DA/rDA equilibrium, which can be established just by the ring-opened isomer, resulting in a “turned on” state applicable for self-healing polymers.

Due to the ability for molecular “switching” (see Table 1.5 entry 5) the light-induced *cis-trans* isomerization of azobenzene units [223] allows photochemically induced dynamics in the bulk [204, 224] which may be applied as a future self-healing concept.

Another “switch” used for dynamic self-healing polymers is the pH-value (see Figure 1.8c). One example of a pH-sensitive, reversible concept is based on condensation reactions of aldehydes with acylhydrazines, resulting in the formation of hydrazones as network points [225] (see Table 1.5 entry 6a). A similar approach utilizes complexation of salicylhydroxamic acid and boronic acid moieties within a polymer backbone to create a pH responsible polymer [226] (see Table 1.5 entry 6b).

Electrochemical processes can be used as “switchable” interactions (see Table 1.5 entry 7) for future self-healing polymers. For example, in a disulfide-aniline precursor, cleavage of crosslinking points could be forced by electrochemical reduction of disulfide moieties, whereas the oxidation of dithiolate groups resulted in the re-formation of the crosslinked structure [204, 227].

1.5

Multiple versus One-Time Self-Healing

The *encapsulation* of reactive components was one of the first and most prominent approaches toward self-healing polymers using dicyclopentadiene and a Grubb's catalyst as healing agents. While taking advantage of the mechanical performance of the polymeric composite a *one-time repair* after a localized rupture event could be triggered [19]. In contrast, embedded *vascular networks* allow a continuous delivery of the incorporated healing agents, affording the opportunity for *multiple self-healing* [228]. Accordingly, for the design of both one-time and multiple self-healing concepts, biomimetic approaches, like bleeding or the blood flow vascular system, inspired scientists. Thus, capsule-based and vascular (healant-loaded pipelines interconnected one-, two-, or three-dimensionally) self-healing principles (see Figure 1.9a,b) mimic nature [134] while using different microcontainers for healing agents. In the case of a propagating rupture event the active material—the healing agent—is released into the damaged area while wetting due to capillary action [7, 8]. After bonding to the interfaces of the matrix, either by physical or by chemical self-healing approaches, the crack can be healed due to the formation of a stable network. The recovery of the material properties is the consequence of network formation between the liquid and dynamic components, usually embedded separately into microcontainers within a matrix due to their high reactivity. The applied principle to sequester the healing agent determines, beside the repeatability of healing, also the healable damage volume and the recovery rate [7, 8].

Capsule-based one-time self-healing concepts reveal big advantages since they can be easily embedded and industrialized as the technique of microencapsulation

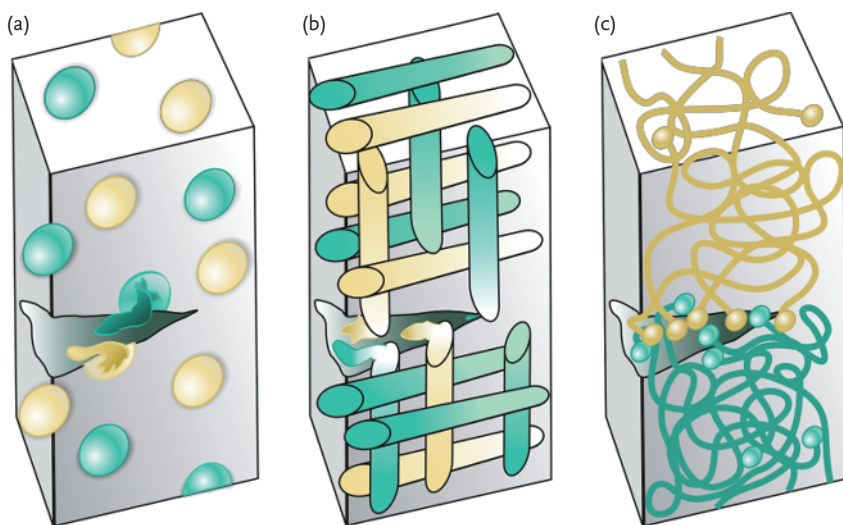


Figure 1.9 Multiple versus one-time self-healing. (a) Capsule-based, (b) vascular, and (c) intrinsic self-healing principles.

has been investigated since the 1950s [229, 230] (see also Chapter 10). Different encapsulation techniques involving *in situ* and interfacial encapsulation, as well as meltable dispersions and coacervation, are known, whereupon the first three mentioned are commonly used for self-healing materials. Beside these emulsion-based methods, microcapsules can also be prepared by spray drying, pan coating, and centrifugal extrusion [7, 8, 231].

In contrast to capsule-based healing concepts, vascular self-healing principles give the opportunity for multiple healing if the vascular network can be refilled from a connected but contemporaneously undamaged region of the vasculature [7]. A vascular approach using hollow glass tubes was first applied for healing of cracks in concrete materials [8] utilizing a three-component mixture based on methyl methacrylate [232]. Later the methodology was adopted for polymeric composite materials [233, 234] by using cyanoacrylate resins stored in glass pipette tubes.

Intrinsic self-healing materials (see Figure 1.9c) can always be healed multiple times as the self-healing process, and therefore the recovery of the material properties, are inherent material abilities [7]. These abilities largely rely on entanglement processes within the polymer matrix. Nevertheless, the need for an external trigger, like pressure, light or heat, might be necessary if the healing is not autonomously triggered by the damage event itself. Examples of intrinsic self-healing polymers are based on supramolecular network formation introduced by hydrogen bonding, ionomers, π - π -interactions or metal-bonding, thermally reversible reactions like DA/rDA reactions, and “switchable” functional groups [7] (see also Chapters 6 and 11–13). Of course, all physical self-healing approaches, like intermolecular diffusion or melting, are multiple time healing processes [7]. For further information about principles and methods of encapsulation and channel-based healing systems see also Chapters 10 and 15.

In order to highlight the contrast between a multiple versus a one-time healing approach two examples will be presented, both based on poly(isobutylene) (PIB) – a highly dynamic polymer due to its low T_g of about -70°C – while using different architectures as well as different endgroups, and thus two different self-healing principles [9, 18, 22, 23, 42, 43].

Based on PIBs bearing hydrogen bonding motifs a multiple time healing concept in the bulk was reported [22]. For this purpose bifunctional polymers endcapped with barbituric acid or Hamilton Wedge were synthesized and their dynamics and hence the self-healing behavior of these kinds of polymers in the melt state has been investigated (see Figure 1.10). Thus, pure polymers and equimolar mixtures of barbituric acid and Hamilton Wedge-bearing samples were studied via temperature-dependent rheology measurements. Surprisingly strong self-healing supramolecular rubbers with an increased thermal stability could be observed for samples with barbituric acid used as the hydrogen bonding motif. Rubber formation is based on the thermoreversible formation of larger aggregates [23] further enhanced by microphase separation between the nonpolar polymer backbone and the polar hydrogen bonding motifs (see Figure 1.10a).

The formation of dynamic junction points was additionally confirmed as the polymer with barbituric acid as endgroup showed terminal flow at low frequencies

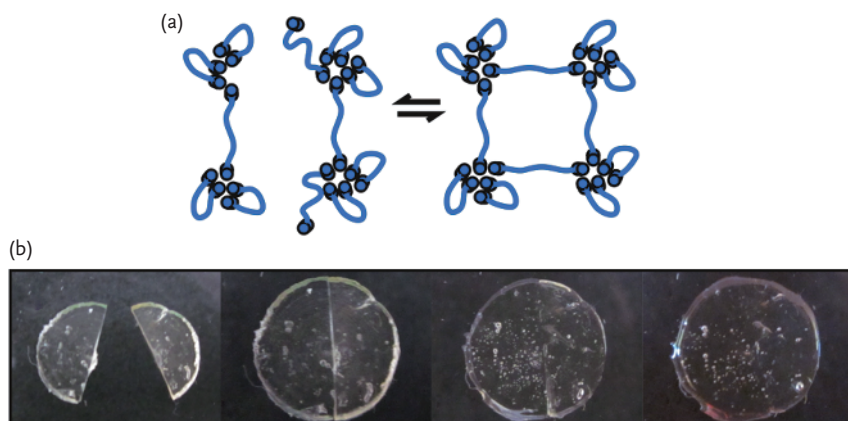


Figure 1.10 Multiple self-healing concept based on PIBs. (a) Thermoreversible formation of a supramolecular network via hydrogen bonding motifs. (b) Self-healing experiment of PIB functionalized with

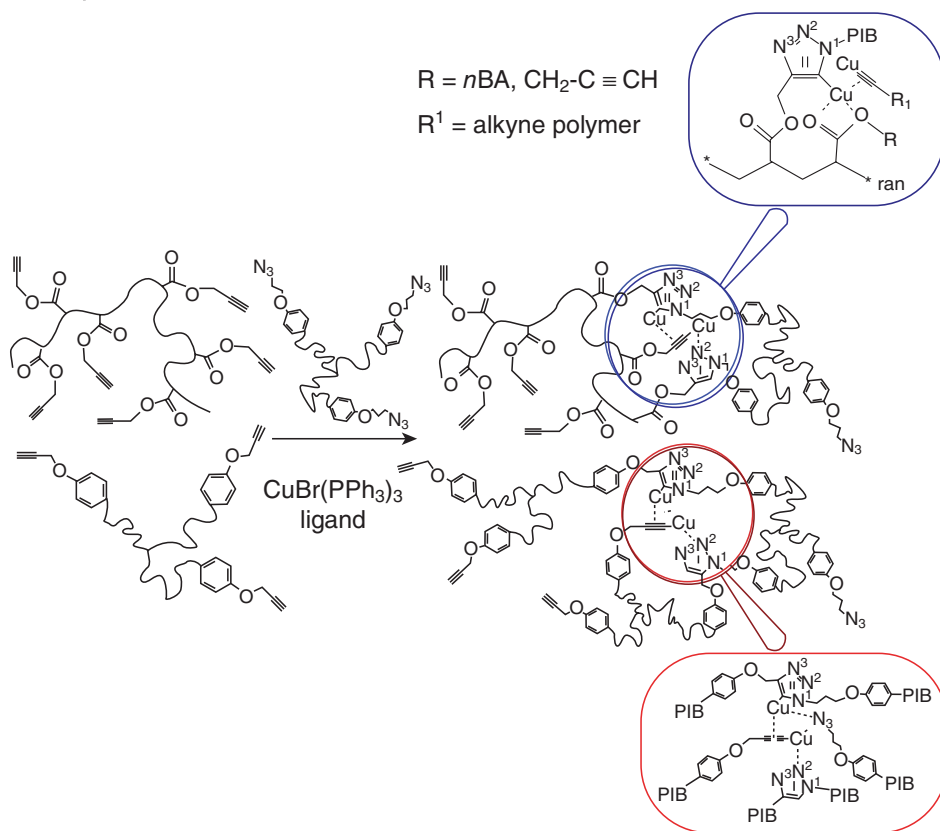
barbituric acid, (i) cut parts, (ii) cut parts were just brought into contact, (iii) partially healed crack after 24 h, (iv) completely healed crack after 48 h (reprinted with permission of RSC Publishing) [22].

but a rubbery plateau at high frequencies [22]. This observation correlates with a semi-open or open state of the hydrogen bonding motif at low frequencies and hence long timescales, and with closed aggregates at higher frequencies, and hence short timescales, respectively. PIBs with barbituric acid groups could be healed completely after cutting into two pieces and bringing in contact again within 48 h proving possible application of this self-healing material at room temperature (see Figure 1.10b). In contrast, equimolar mixtures of PIBs bearing Hamilton Wedges and barbituric acid behaved like brittle rubbers at room temperature and terminal flow was only observed at temperatures above 100 °C [22] (for more information see also Chapter 11).

In contrast to this multiple time healing concept, a one-time healing concept based on the CuAAC of multivalent azide- and alkyne-functionalized PIBs and poly(acrylate)s was investigated [18, 42, 43]. Polymers with different molecular weights and different functional group densities were synthesized via living polymerization techniques. $\text{Cu}^{\text{I}}\text{Br}(\text{PPh}_3)_3$ was chosen as the best catalyst, achieving a crosslinking of equimolar polymer mixtures at room temperature and gelation times within the range of 2–15 h. The crosslinking behavior—investigated via *in situ* rheology—was studied in dependence on the molecular weight and on the concentration of functional groups, as well as on the starting viscosity of the samples. While analyzing the viscosity of the polymer mixtures, increasing reaction rates with increasing concentration of functional groups could be observed, and an autocatalytic effect [43] within the reaction up to a factor of 4.3 could be demonstrated (see Figure 1.11a).

The acceleration of further click reactions was traced back to clustering effects of the triazole rings, acting as internal ligands while preorientating the azide- and

(a)



(b)

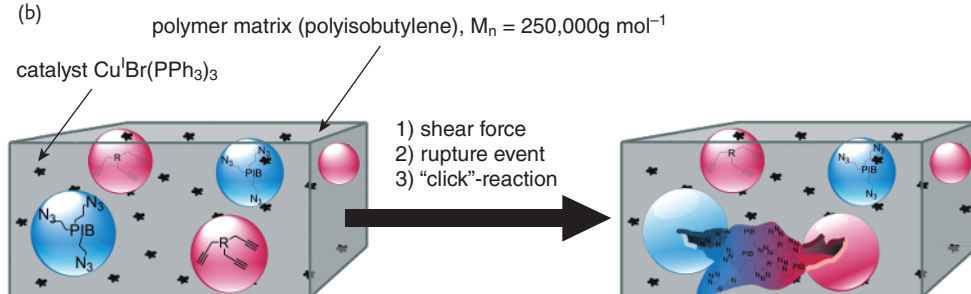


Figure 1.11 One-time self-healing concept based on PIBs and poly(acrylate)s. (a) Proposed mechanism of autocatalysis for crosslinking multivalent PIBs and poly(acrylate)s functionalized with azide- or alkyne-groups at room temperature using $\text{Cu}^{\text{I}}\text{Br(PPh}_3)_3$ as catalyst (reprinted with permission of ACS Publications) [43]. (b) Concept for the design of shear sensitive

one-time self-healing materials based on the encapsulation of azide- and alkyne-functionalized polymers embedded in a high-molecular weight PIB matrix with finely dispersed $\text{Cu}^{\text{I}}\text{Br(PPh}_3)_3$ as catalyst. Rupture of the capsules and thus release of reactive polymers is induced by shear force, resulting in network formation via CuAAC.

alkyne-groups near to the active copper(I) center. Thus, a polymeric self-healing approach suitable for room temperature application based on a deeper understanding of catalytic effects within the CuAAC was developed [43]. Previously, the successful encapsulation of highly reactive, multivalent azide-functionalized PIBs was shown using liquid polymers as reactive healing agents for the first time [18]. After embedding in a high-molecular weight PIB matrix together with finely dispersed $\text{Cu}^{\text{I}}\text{Br}(\text{PPh}_3)_3$, reactive polymers were released by shear force-induced rupture of capsules (see Figure 1.11). Due to the so-induced network formation via CuAAC, dynamic mechanical analyses showed 81% recovery of the tensile storage modulus at room temperature within five days, proving the concept of a capsule-based one-time self-healing approach [18, 42, 43].

1.6

Resume and Outlook

It can be imagined that the world of self-healing polymers is large, engulfing many different and complex physical and chemical principles. Materials scientists will approach the design of such materials entirely differently from chemists, physicists or biologists – this should be clear from the introductory remarks in this chapter. However, it also demonstrates that a vision of scientists has become reality, combining such different issues as chemical reactivity, polymeric design, supramolecular forces and catalytic action into one type of materials, whose technological applications can be already realized. As with many applications, price and the identification of technological areas of usefulness are now the next step for their application, together with their commercialization and consumer-adoption. The following chapters within this book will give a deeper insight into more chemical and physical principles, together with technological applications of these fascinating classes of self-healing materials.

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