

Optically healable polymers

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Polymers that can easily be repaired after being damaged are attractive as this characteristic can improve the reliability, functionality, and lifetime of many products. In the last decade, researchers have thus developed new approaches to create stimuli-responsive polymer systems, which have the ability to autonomously heal or can be repaired upon exposure to an external stimulus. This review summarizes the current knowledge of optically healable or photo-healable polymers. The use of light as a stimulus for healing offers several attractive features, including the ability to deliver the stimulus locally, which opens up the possibility of healing the material under load, as well as the ability to tailor the wavelength of light to selectively address a specific component of the material, e.g. only the damaged parts. So far, two main classes of optically healable polymers have been explored, which are structurally dynamic polymers and mechanically activated reactive systems.

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Introduction

Polymers that can easily be repaired after being damaged are attractive because this feature can improve the reliability, functionality, and lifetime of many products. In the last decade,

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researchers have thus developed several approaches to create stimuli-responsive polymer systems, which have the ability to autonomously heal or can be repaired upon exposure to an external stimulus.^{1–10}

The most straightforward approach to repair damage in polymeric objects involves liquefying the material by heating it to a temperature above its glass transition or melting temperature or exposing it to a plasticizing solvent. The liquid state of the polymer then allows for surface rearrangement in the damaged area, followed by wetting between surfaces, and finally diffusion and re-entanglement of polymer chains.¹¹ However, the rates of the latter two processes are inversely proportional to the molecular weight, and render healing processes in high molecular weight polymers slow and inefficient.¹²

Several processes that avoid this obstacle have been demonstrated. One early concept is the incorporation of monomer-filled capsules and an appropriate catalyst into a polymer of interest. Upon mechanical damage to the material, the microcapsules rupture and release the liquid 'healing agent', which can fill defects and cure when in contact with the catalyst.^{13–15} An alternative tactic is to utilize structurally dynamic polymers,¹⁶ in which an external stimulus can be used to temporarily reduce the molecular weight of the macromolecules by shifting the equilibrium to the monomer side upon exposure to an appropriate stimulus.^{3,7} The resulting increase of the chain mobility and decrease of the material's viscosity enable the healing process and the polymer is subsequently reformed by shifting the equilibrium back to the polymer side, by removal of the stimulus. For instance, Diels–Alder motifs can be used to form reversible bonds that can be utilized to crosslink a given polymer; the crosslink density can be temporarily reduced when desired by heating the polymer and triggering retro-Diels–Alder reactions.^{3,7,17–19}

Comparably few polymer systems are known in which defects can be healed upon exposure to visible or ultraviolet radiation. The use of light as a stimulus for healing offers several advantages over heating an object or exposing it to a liquid healing agent, such as the ability to (1) deliver the stimulus locally, which opens up the

possibility of healing the material under load, and (2) tailor the wavelength of light to selectively address a specific component of the material, *e.g.* only the damaged parts. One can also speculate about truly self-healing systems, which comprise mechanochromic defect sensors^{20,21} and autonomously heal with the help of ambient light that is absorbed only when and where needed. Two classes of materials have been explored as optically or photo-healable polymers, which are structurally dynamic polymers and mechanically activated reactive systems.²² This review seeks to summarize the current knowledge of such optically healable or photo-healable polymers. Based on prominent examples from the literature, the most important design approaches are presented and the properties of the materials thus made are discussed.

Structurally dynamic polymers

Structurally dynamic polymers¹⁶ are materials based on macromolecules which contain dynamic bonds that allow for reorganization of the molecular architecture upon exposure to a stimulus. Dynamic bonds can be covalent or non-covalent in nature and selectively undergo reversible breaking and reformation reactions, usually under equilibrium conditions. Such bonds are often sensitive to a specific stimulus, which will either induce dynamic behavior or impact the dynamic equilibrium. Thus, the nature of the dynamic bond determines the stimulus to which the polymer will respond. Most supramolecular interactions are inherently dynamic and as such supramolecular polymers represent one subset of structurally dynamic polymers. The field of dynamic covalent chemistry has garnered a lot of attention in the last two decades, and a range of structurally dynamic, stimuli-responsive polymers have been developed that utilize dynamic covalent bonds.²³ Both classes of polymers have been utilized to develop optically-healable materials.

Optically-healable dynamic covalent polymers

Many pericyclic reactions are known to be reversible and can be triggered rather selectively by exposure to either heat or light. One of the earliest examples of a thermally healable material, developed by Wudl and coworkers, exploited the thermally reversible Diels–Alder reaction.²⁴ This framework was exploited in one of the earliest attempts to utilize light as the stimulus to heal defects in polymers reported by Chung and coworkers; these authors utilized the photochemically allowed [2+2] cycloaddition of cinnamoyl groups to a cyclobutane derivative to render a polymeric material optically healable.²⁵ To demonstrate photo-reversibility in the solid state, the cinnamoyl-containing monomer 1,1,1-tris(cinnamoyloxymethyl)ethane (**1**) was irradiated with ultraviolet (UV) light of a wavelength of >280 nm to induce the [2+2] cycloaddition and afford a cross-linked polymer network (Fig. 1). Infrared (IR) analysis showed a decrease of the C=O (1713 cm⁻¹) and C=C (1637 cm⁻¹) absorption bands characteristic of the cinnamoyl groups, supporting the occurrence of the pericyclic reaction to yield the cyclobutane derivatives. Grinding this material resulted in the stress-induced breakage of these cyclobutane units as evidenced by the re-appearance of the C=O and C=C IR



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absorption bands at 1713 cm^{-1} and 1637 cm^{-1} . Upon renewed irradiation with UV light the peaks disappeared again, consistent with light-induced reformation of the 4-membered rings. Utilizing this chemistry, optically-healable films were prepared by the photopolymerization of the methacrylate-based monomers tri(ethylene glycol) dimethacrylate (**2**) and 1,6-bis(2'-methacryloyloxyethoxycarbonylamino)-2,4,4-trimethylhexane (**3**) in the presence of **1** (Fig. 1). Camphorquinone was used as a photoinitiator and the monomer mixture was irradiated with UV light ($\lambda > 280\text{ nm}$) to simultaneously trigger the free-radical crosslinking of the acrylic monomers **2** and **3** and dimerization of **1**. The resulting hard transparent films were proposed to consist of an acrylic network and the [2+2] cycloadduct products of **1**. Healing studies were carried out on intentionally damaged samples; they showed that both heat ($100\text{ }^\circ\text{C}$) and UV light (10 min) were required to achieve healing. While the ability to heal damaged samples was clearly demonstrated, the efficiency of the process was rather limited, as the healed materials exhibited only 20% of the flexural strength of the original material.

More recently, the reversible nature of cyclobutane formation was also exploited in coumarin-based light-healable polymers. Similar to cinnamoyl-derivatives, coumarin can undergo reversible ring-closure and ring-opening upon irradiation of UV-light with a λ_{max} of 350 nm and 254 nm, respectively. Ling *et al.* incorporated photosensitive monohydroxy and dihydroxy 4-methylcoumarin derivatives into polyurethane based polymers,^{26,27} and the reversible photo-crosslinking of the coumarin moieties was monitored by UV-vis spectroscopy. Upon UV irradiation ($\lambda = 350\text{ nm}$, 14.4 mW cm^{-2}), the intensity of the absorption band associated with the $\pi-\pi^*$ transition of the coumarin double bonds in the range of 250–300 nm decreased, indicating the dimerization to form cyclobutane rings. Upon irradiation with higher-energy UV light (254 nm, 15.6 mW cm^{-2}) the absorbance at 250–300 nm was gradually restored as a result of the photo-cleavage of the cyclobutane rings to the coumarin moieties. The photo-reversible nature of coumarin dimerization was also shown to impart healability to the materials

studied. Samples of polyurethanes that contained monohydroxy coumarin moieties incorporated as side chains were intentionally cut, irradiated with UV light (254 nm) for 1 min, and the pieces were then brought into contact and irradiated for 90 min with UV light (350 nm) to repair damaged films (Fig. 2). Stress-strain curves of healed samples indicate that 70% of the tensile strength was recovered.²⁶ When a polyurethane which contained 25% dihydroxy 4-methylcoumarin in the polymer backbone was photochemically crosslinked, damaged and repaired, the recovery of the tensile strength was quantitative.²⁷ The healing efficiency of these materials was largely influenced by the crosslink density, which in turn depended on both the concentration of coumarin incorporated into the polymers and the extent of photo-dimerization.

Disulfides are another class of chemical linkages that can undergo reversible bond formation under various conditions, such as change of pH, heat, enzyme activity, redox chemistry and exposure to light.^{28,29} Polydisulfides³⁰ have been used by Klumperman and coworkers to create thermally healable materials³¹ and by Deng *et al.* to access healable gels under basic conditions.³² An early demonstration of the ability to utilize light to induce dynamic behavior in polydisulfides was reported by Takahara and coworkers,³³ who irradiated a solution containing two disulfide-containing polyesters (**4**) of the same chemical structure but of different molecular weight and molecular weight distribution (number-average molecular weight, $M_n = 60.4\text{ kg mol}^{-1}$, polydispersity index, PDI = 1.06; and $M_n = 8.7\text{ kg mol}^{-1}$, PDI = 1.54) with light ($\lambda = 312\text{--}577\text{ nm}$). This treatment led to an equilibration among the two populations and afforded a homogeneous sample of macromolecules with an intermediate molecular weight and broadened PDI ($M_n = 16.0\text{ kg mol}^{-1}$, PDI = 1.85). Both the change of the molecular weight and the increase of the polydispersity are consistent with a photo-induced reshuffling of the disulfide bonds, *i.e.*, disulfide metathesis (Fig. 3).

The photo-responsive nature of disulfide bonds has since been applied to more complex structures and materials. Bowman, Anseth

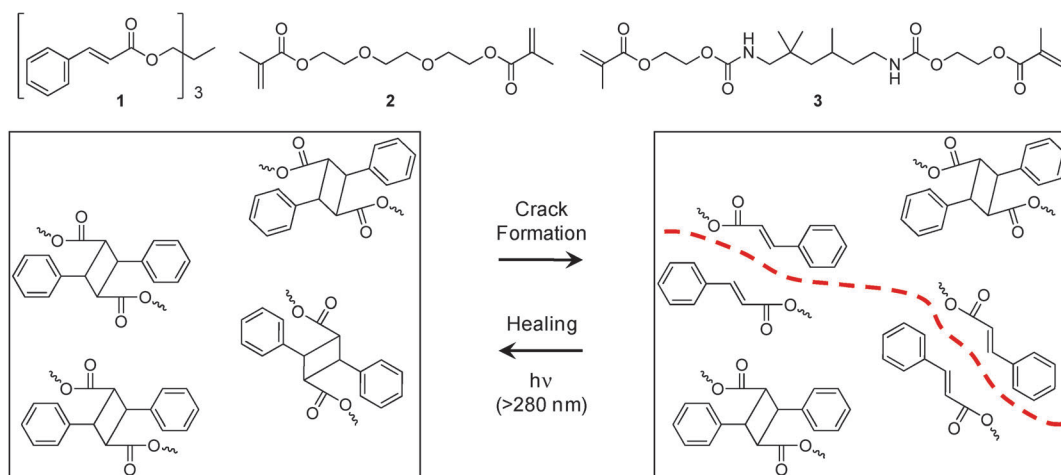


Fig. 1 Top: chemical structures of the cinnamoyl-containing monomer 1,1,1-tris(cinnamoyloxymethyl)ethane (**1**) and the two methacrylate monomers tri(ethylene glycol) dimethacrylate (**2**) and 1,6-bis(2'-methacryloyloxyethoxycarbonylamino)-2,4,4-trimethylhexane (**3**), used to form the photo-sensitive networks. Bottom: schematic representation of the proposed molecular processes that occur during the breaking and optical healing of a cinnamoyl-group containing polymer matrix. Figure reproduced with permission from ref. 25.

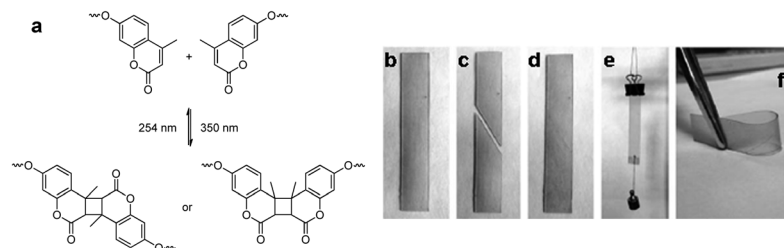


Fig. 2 (a) Schematic representation of the mechanism for the ring-closure and ring-opening of coumarin moieties for the healing of polyurethane materials. Images of (b) neat, (c) damaged, and (d) healed polymer films exposed to UV light ($\lambda = 254$ nm, 15.6 mW cm $^{-2}$, 1 min; $\lambda = 350$ nm, 14.4 mW cm $^{-2}$, 90 min). Images of (e) loading test and (f) bending test of healed coumarin–polyurethane films. Figure was adapted from ref. 26.

and coworkers recently reported poly(ethylene glycol) (PEG) hydrogels containing dynamic disulfide moieties, which are photo-degradable, photo-adaptable, and can undergo photo-welding.³⁴ These dynamic gels, in which the disulfides are part of the cross-linking units, were formed by the oxidation (hydrogen peroxide and sodium iodide) of thiol-functionalized 4-arm PEG monomers. The resulting hydrogels were swollen in an aqueous solution containing the photoinitiator lithium acylphosphinate (LAP). Irradiation of the hydrogels with UV light ($\lambda = 365$ nm) caused decomposition of the LAP photoinitiator, and the radicals thus created can cleave the disulfide bonds to afford thiyl radicals (Fig. 4a). This reaction sequence results in chain fragmentation and subsequent exchange with other disulfides within the polymer network. The degree of photo-fragmentation of the network can be controlled by the concentration of the photo-initiator. At high initiator concentrations, the original network is completely disassembled into soluble PEG segments, while at lower concentrations (*i.e.* below the concentration of disulfide moieties) photo-manipulation of these materials is possible. Using these concepts, PEG hydrogels were photo-imprinted (Fig. 4b) and photo-patterned, where physical patterned features were introduced by either complete or partial photo-degradation of the network. Samples could also be optically healed or welded together under a transparent plate with slight pressure followed by the irradiation of light to induce disulfide exchange (Fig. 4c). It was suggested that the ability to harness light for selective photo-degradation of such materials has potential applications for drug delivery, where the release of a therapeutic agent from a polymer matrix can be selectively controlled.

Takahara, Matyjaszewski and coworkers have shown that thiocarbonate units can also undergo reshuffling/exchange upon exposure to UV light.^{35,36} Trithiocarbonate units are commonly used as chain transfer agents in reversible addition–fragmentation chain-transfer (RAFT) polymerizations.^{37–40} Trithiocarbonate-containing networks (5) were prepared by the RAFT copolymerization of butyl acrylate and the trithiocarbonate-containing bismethacrylate (6) (Fig. 5a). Using model compounds, the authors showed that the trithiocarbonate units can undergo exchange in acetonitrile upon irradiation with UV light ($\lambda = 330$ nm, 0.9 mW cm $^{-2}$). Using similar conditions, pieces of the crosslinked polymer 5 could be fused by pressing them together in acetonitrile and exposing them with UV light for several hours (Fig. 5b). The fused materials exhibited a tensile modulus (65 ± 11 kPa) that was identical to that of the original material (69 ± 6 kPa). The healing of these materials was also investigated in the dry state, *i.e.*, in the absence of any solvent that would increase the mobility of the polymer chains (Fig. 5c). It was shown that extended UV irradiation (48 hours) of a partially cut sample led to significant healing, although small defects remained in areas where the contact between the surfaces was not intimate.

All of the above-discussed healing experiments involving materials with trithiocarbonate units were carried out under a protective nitrogen atmosphere, since the exchange process involves reactive carbon radicals, which can undergo side reactions under ambient conditions. To address this issue, the use of thiuram disulfide (TDS) moieties was explored. Thiuram disulfides have lower dissociation energies than disulfides and can also be cleaved to form sulfur-based radicals. Thus, optically

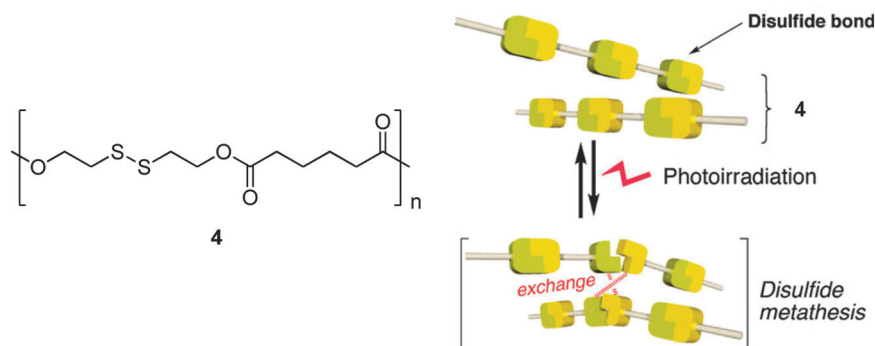


Fig. 3 Structure of the disulfide-containing polyester **4** and a schematic representation of disulfide reshuffling and rearrangement upon irradiation with light. Figure adapted from ref. 33.

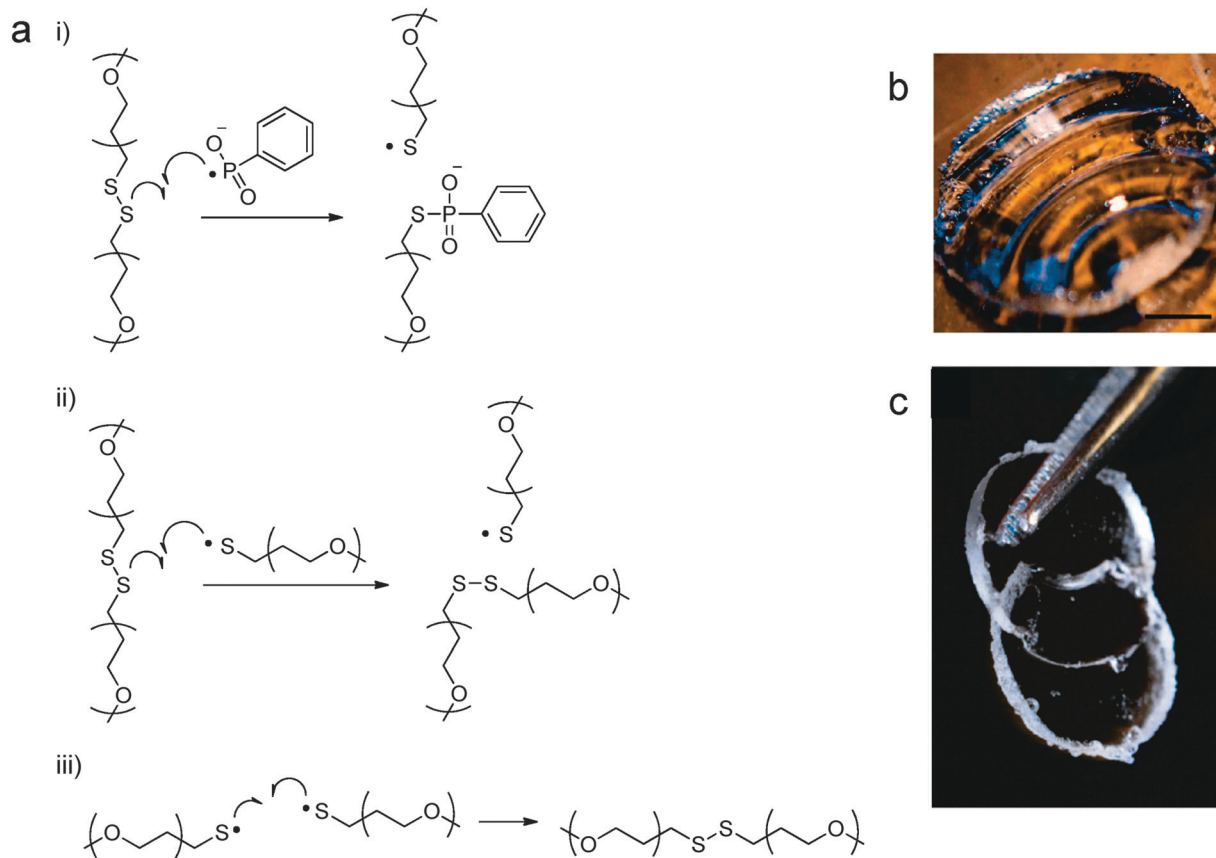


Fig. 4 (a) Schematic representation of the mechanism for the formation of thiyl radicals and re-arrangement of disulfide units in PEG hydrogels. Radicals formed upon dissociation of an acylphosphinate photoinitiator attack the disulfide bonds, thus creating thiyl radicals (i), which cause further fragmentation of disulfides in the PEG matrix (ii). (iii) Termination occurs by the recombination of thiyl radicals. Images of the PEG hydrogels that have been (b) photo-imprinted and (c) photo-welded together. Images reproduced with permission from ref. 34.

healable polyurethane networks (7) were prepared by the reaction of a TDS diol (8) as the reshuffling unit, a tetra(ethylene glycol) (9) as the chain-extender, triethanolamine (10) as the crosslinker, and hexamethylene diisocyanate (11) (Fig. 6a).⁴¹ These polymers were designed to exhibit a low glass transition temperature ($T_g = -50$ to -34 °C) in order to achieve healability at room temperature and in the absence of any solvent on account of the high level of chain mobility in the rubbery state. The possibility to heal these materials was explored by cutting samples into two pieces and subsequently welding them back together. The TDS moiety was shown to undergo exchange under exposure to visible light from a conventional tabletop lamp and under an ambient atmosphere. As a result, irradiating two separated parts that were pressed together with visible light for 24 hours under ambient conditions resulted in the healing of the sample (Fig. 6b). Stress-strain experiments showed that the material completely regained its original mechanical properties. When the same experiment was performed in the absence of light (*i.e.*, two cut pieces were pressed together in the dark), healing was less efficient. Interestingly, if the samples were previously exposed to light and then fused in the dark, the samples would also heal, suggesting that the radicals are long-lived. Additionally, if samples were cut and left separated for an extended period of time (4–24 hours), they did not heal as efficiently as freshly cut samples, suggesting either decomposition

of the TDS radicals or diffusion of the TDS radicals into the interior of the sample. Either way, these results show that the thiuram disulfide unit is an interesting labile dynamic bond that is useful for the design of light-healable polymer systems.

While it has not yet been used directly for the design of healable polymers, another photo-labile dynamic bond that is worth mentioning here is the allyl sulfide bond (Fig. 7a), which has been utilized by Bowman and coworkers in covalent polymer networks that exhibit photo-induced plasticity.^{42,43} The materials studied include a series of rubbery covalent networks that were made by the photo-induced polymerization of pentaerythritol tetra(3-mercaptopropionate) (12) and triethyleneglycol divinylether (13) with varying amounts of 2-methyl-7-methylene-1,5-dithiacyclooctane (14), which introduces the photo-labile allyl sulfide moieties into the network (Fig. 7b). After the synthesis, the network still contained residual amounts of a photoinitiator that was utilized as a readily available photo-labile radical source. The materials were exposed to UV irradiation ($\lambda = 320$ – 500 nm, 30 mW cm⁻², 2–60 min) while strained, which causes dissociation of the photoinitiator. The resulting radicals diffuse through the network *via* addition-fragmentation chain transfer through the allyl sulfide groups (Fig. 7a). This results in the cleavage and reformation of the polymer backbone, which in turn results in a lower stress conformation of the

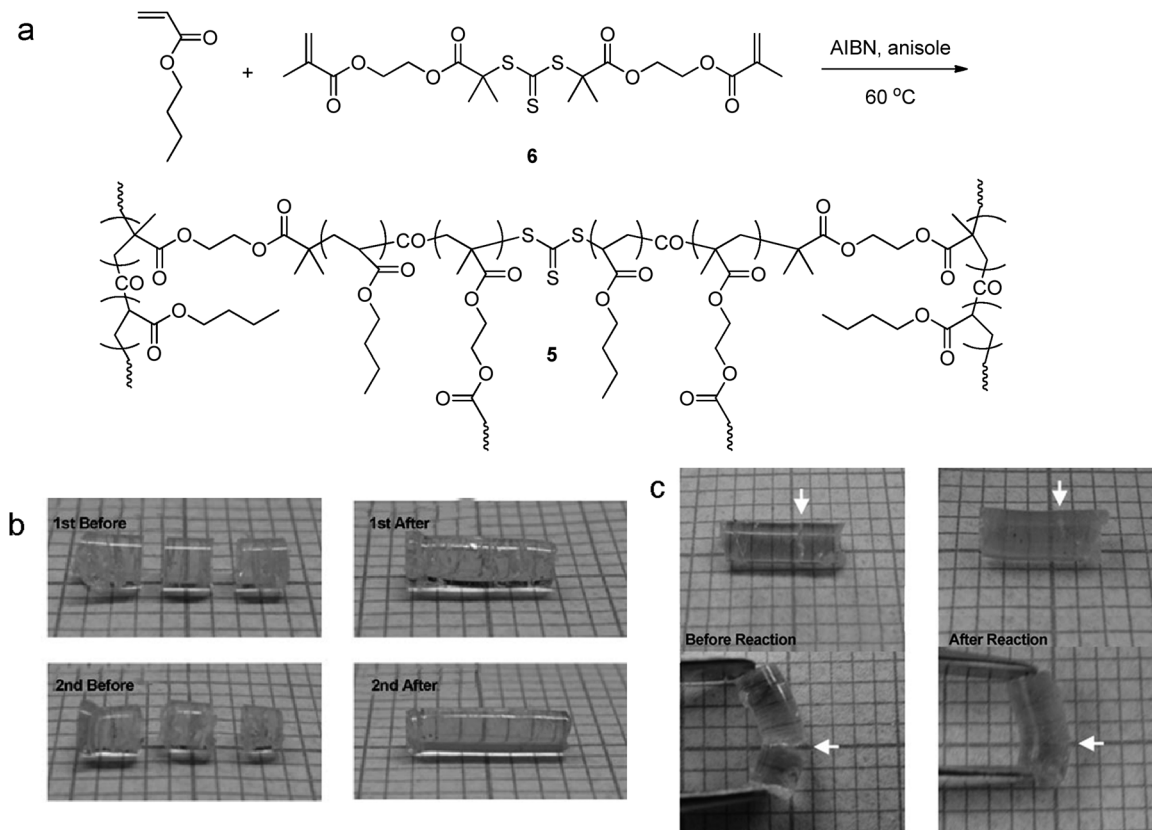


Fig. 5 (a) Synthesis of a trithiocarbonate-containing polymer network (5) via RAFT polymerization and (b and c) images of crosslinked polymers that were damaged and re-healed under N_2 with UV light ($\lambda = 330$ nm, 0.9 mW cm^{-2}) in the presence of (b) acetonitrile and (c) in the bulk. Images reproduced with permission from ref. 35.

polymer chains and a reduction of the stress on the system. When optically dense films of this material are irradiated with UV light, the stress is relieved only on the side facing the incident radiation, which leads to the formation of a stress gradient. Therefore, the polymer bends away from the side of UV irradiation. When the material is subsequently irradiated from the other side, the stress gradient is relieved and the material bends back in the opposite direction and regains its original shape. The beauty of this optically addressable shape-change material is that the addition-fragmentation continues to occur as long as radicals are produced. Moreover, the functional groups are not consumed; therefore the overall network structure remains the same and the rearrangement can repeatedly occur, and is only limited by radical formation and termination reactions.

Optical healing of metallosupramolecular polymers

All of the optically healable materials discussed so far involve dynamic covalent chemistry. Each of these systems uses a re-arrangement or re-shuffling of covalent bonds in the polymer structure and the ability of the materials to heal relies, in part, on the lifetime of the intermediate species, which in most cases are free radicals. An alternative approach to optically healable materials is to utilize supramolecular interactions that can be altered directly or indirectly through exposure to light. One such example was reported by Rowan, Weder, and coworkers^{44,45} who demonstrated that optical healing can be achieved in

metallosupramolecular polymers. Their initial studies involved polymers assembled from a rubbery telechelic poly(ethylene-*co*-butylene) (15) that was chain-terminated with 2,6-bis(1'-methylbenzimidazolyl)-pyridine (Mebip) ligands and $Zn(NTf_2)_2$ or $La(NTf_2)_3$ to afford $15 \cdot Zn(NTf_2)_2$ and $15 \cdot La(NTf_2)_3$ (Fig. 8a). These systems are dynamic in nature – the formation of the metal-ligand complexes is reversible and the polymers can therefore be depolymerized upon exposure to certain external stimuli (*e.g.*, light, heat). Electron microscopy and small-angle X-ray diffraction experiments revealed that these metallosupramolecular materials micro-phase separate and form structures with a lamellar morphology. In both series the metal-ligand complexes assemble into a “hard” phase, which serves to physically cross-link the “soft” phase formed by the poly(ethylene-*co*-butylene) cores. This structure and the significant extent of long-range order are the origin of the materials' intriguing mechanical properties, *i.e.* a modulus of 53–60 MPa and an elongation and stress at break of 60–85% and 15–45 MPa, respectively.

The Mebip ligands and Mebip-metal complexes exhibit an absorbance in the near UV part of the optical spectrum with absorbance maxima at around 310 and 340 nm, respectively, and the metallosupramolecular materials made from these motifs and Zn^{2+} or La^{3+} ions are essentially colorless. The complexes exhibit a low fluorescence quantum yield, so if they are electronically excited by irradiation with UV light (320–390 nm) the absorbed energy is converted into heat. This results in the temporary disengagement

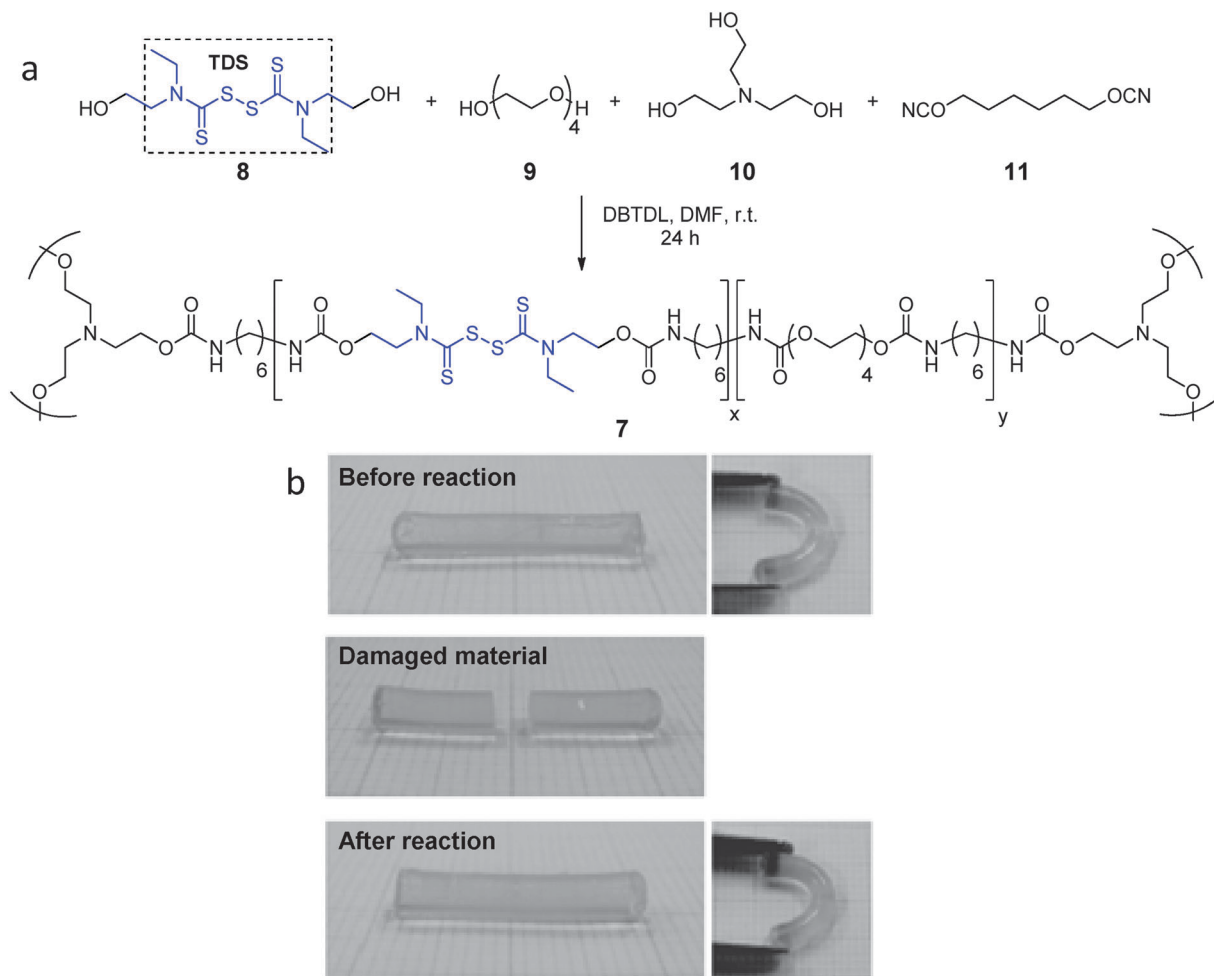


Fig. 6 (a) Preparation of a thiram disulfide (TDS) containing polyurethane network (**7**) via polyaddition of **8**, **9**, **10**, and **11** in DMF and (b) images of a piece of **7** in the original state (top), after cutting (middle) and after healing through exposure to visible light (bottom). Images reproduced with permission from ref. 41.

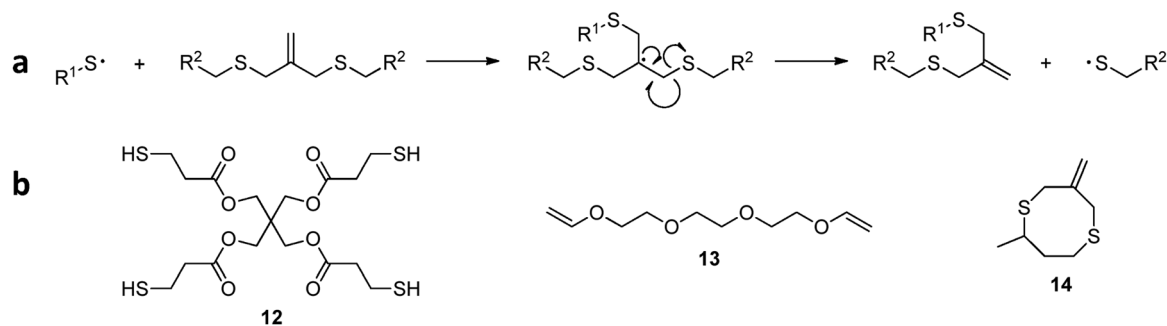


Fig. 7 (a) Mechanism of the radical addition–fragmentation chain transfer of an allyl sulfide moiety. (b) Chemical structure of monomers pentaerythritol tetra(3-mercaptopropionate) (**12**), triethyleneglycol divinylether (**13**), and 2-methyl-7-methylene-1,5-dithiacyclooctane (**14**) used to create allyl sulfide networks. Figure adapted from ref. 42.

of the metal-complexes concomitant with a depolymerization and reduction in the molecular weight and viscosity. When the light source is switched off, the dynamic metal–ligand complexes reform and the material solidifies.

This method allows for spot-on healing where the light can be delivered to selective areas of a sample. Thus, when deliberately

damaged films (350–400 μm) of **15**-Zn(NTf₂)₂ and **15**-La(NTf₂)₃ were exposed to UV light (320–390 nm) with an intensity of *ca.* 950 mW cm⁻², the defects were repaired in <1 min. Mechanical analysis of healed samples showed that the original mechanical properties of the materials were restored and as a consequence of the reversible nature of these metallosupramolecular systems,

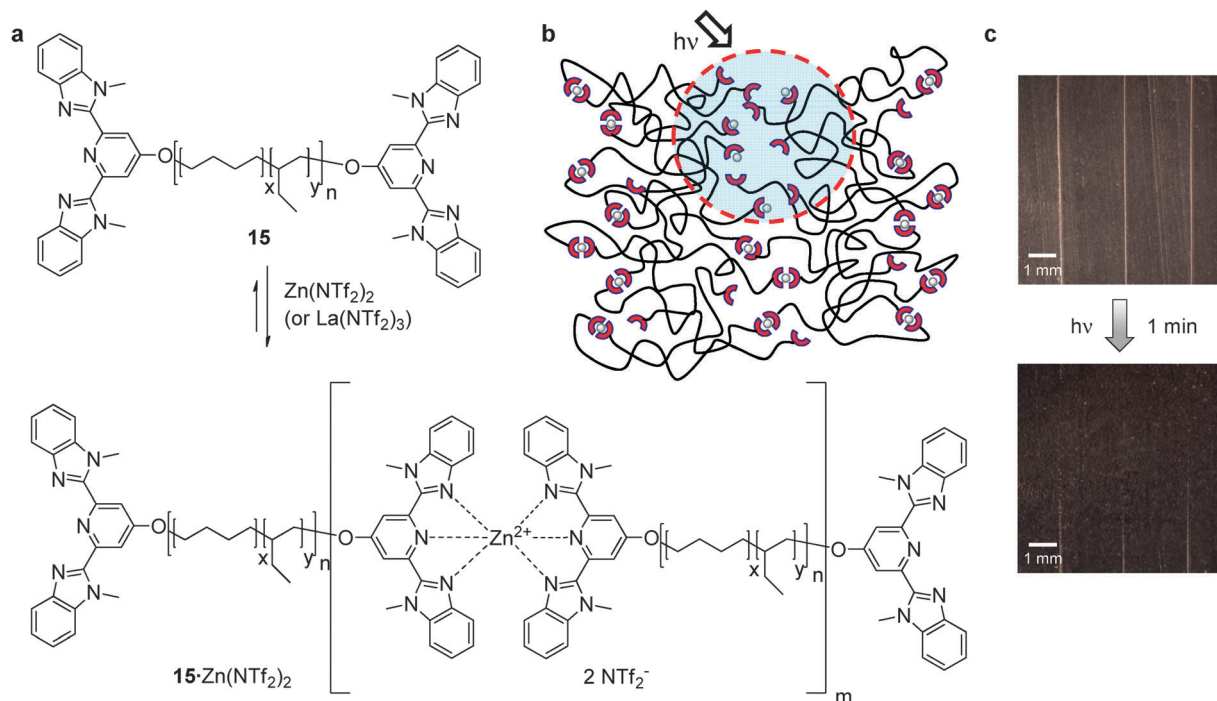


Fig. 8 (a) Chemical structure of macromonomer **15** and the metallo-supramolecular polymers $\mathbf{15}\cdot[\text{M}(\text{NTf}_2)_v]$ where $\text{M} = \text{Zn}^{2+}$ ($v = 2$) or $\text{M} = \text{La}^{3+}$ ($v = 3$). (b) Schematic representation of the lamellar structure of $\mathbf{15}\cdot[\text{M}(\text{NTf}_2)_v]$. (c) Image illustrating the optical healing of a film of $\mathbf{15}\cdot[\text{Zn}(\text{NTf}_2)_2]$ (ratio of $\mathbf{15}:\text{Zn}(\text{NTf}_2)_2 = 1:0.7$) with UV light ($\lambda = 320\text{--}390$ nm, 950 mW cm^{-2} , 2×30 s). Figure adapted from ref. 44 and 45.

the materials can be repeatedly damaged and healed.⁴⁶ The nature of the metal ion used to assemble the macromonomer (**15**) was found to play an important role in the efficiency of the optical healing process. The La^{3+} -Mebip complexes are more labile and dissociate at lower temperatures than Zn^{2+} -Mebip complexes.^{47–49} Thus, under the same healing conditions (2×30 s of UV exposure) films of $\mathbf{15}\cdot[\text{La}(\text{NTf}_2)_3]$ healed more efficiently than films made from $\mathbf{15}\cdot[\text{Zn}(\text{NTf}_2)_2]$. This is consistent with the lower stability of La^{3+} -Mebip complexes vis-à-vis the Zn^{2+} -Mebip-based counterparts and a higher level of light-induced depolymerization of the former. Interestingly, good healability could be imparted to $\mathbf{15}\cdot[\text{Zn}(\text{NTf}_2)_2]$ by offsetting the $\text{Zn}^{2+}:\text{Mebip}$ stoichiometry to 0.7:1, suggesting that the dynamics of the light-induced depolymerization can be influenced by the presence of an excess of free ligands and/or by a reduction in the degree of order of the phase separated material. The concept of photo-thermal induced healing of supramolecular materials appears to be applicable to any supramolecular polymer with a binding motif that is sufficiently dynamic. To this end, light-healable nanocomposites based on a telechelic poly(ethylene-co-butylene) that was functionalized with hydrogen-bonding ureido-pyrimidone (UPy) groups and cellulose nanocrystals carrying the same hydrogen-bonding motif were just reported.⁵⁰ The ability to change the light-absorbing motif allows one to tailor the wavelength of the light that is used for healing.

Mechanically-activated systems

Ghosh and Urban have utilized an approach to optically healable polymers, which is entirely different from the structurally

dynamic polymers discussed above.⁵¹ In these systems, reactive irreversible chemistry involving oxetane rings was employed and mechanical activation is required, and provided when the material is mechanically damaged. To access these photo-healable materials, a complex mixture of an oxetane-substituted chitosan (**16**), a homopolymer of hexamethylene diisocyanate (a mixture of products, one representative structure is shown as **17**) and poly(ethylene glycol) (**18**) were reacted with dibutyltin dilaurate (**19**) as the catalyst to yield the multi-functional polyurethane network (one proposed representative structure is shown as **20**) (Fig. 9). Samples of these polymers were intentionally damaged and indeed, subsequent irradiation with UV light (302 nm, 15–30 min) did promote healing. The authors have started to investigate the role of the individual components that make up these materials.⁵² Decreasing the amount of the reactive oxetane chitin polymer (**16**) in the film was shown to slow down the healing rate and no healing was observed when **16** was not present, confirming that the process indeed involves the oxetane rings. The amount of the Sn catalyst (**19**) in the materials also appears to play an important role. Adding an excess of **19** ($>4 \times 10^{-5}$ moles) inhibited the photo-healing process. Internal reflection infrared imaging and model studies suggested that the increased concentration of the catalyst resulted in the premature ring-opening of oxetane units, thus inhibiting the light induced repair of damaged films.

High-resolution infrared imaging of damaged areas revealed a number of chemical processes that proceed in these materials (highlighted by the circles in Fig. 9). In addition to the cationic ring opening of the oxetane ring, free radicals are also involved

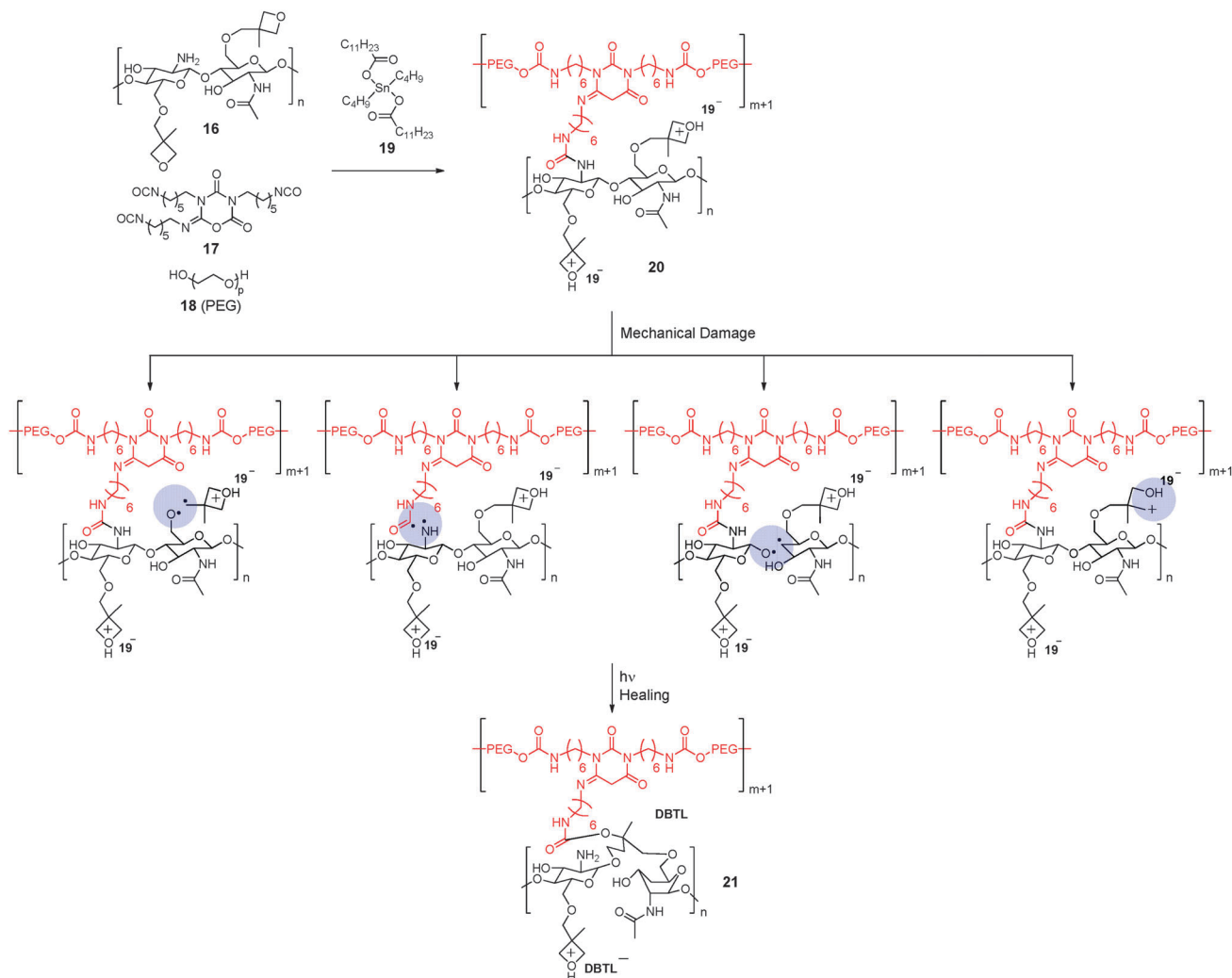


Fig. 9 Mechanism proposed by Urban and coworkers for the mechanical damage and UV induced healing of the reactive oxetane networks (**20**). Figure adapted from ref. 52.

in the damage/healing process, which are created *via* cleavage of urea and/or ether moieties when the material is damaged. This was confirmed by the addition of a radical scavenger to the films, which was shown to slow down the healing process. Together, these processes allow for the intra- and intermolecular crosslinking of the polymer during UV exposure to create different urethane networks (e.g. **21**), and allow for healing. It was further suggested that the healing of cracks is aided by a temporary drop of the material's T_g around the crack area, as a consequence of the formation of low molecular weight fragments upon damage. It is worth noting that the healed "scar" has a different molecular structure than the original polymer and the available data suggest that the crosslinking is actually enhanced in areas that had been damaged and were subsequently healed.

Urban and coworkers have also developed a spironaphthoxazine-containing polymer that is optically healable.⁵³ The colorless spironaphthoxazine units can undergo a reversible ring-opening reaction to a red merocyanine form, and as such this system can be considered to be structurally dynamic. Thus, a random copolyacrylate containing the spironaphthoxazine

units (**22_s**, where "s" indicates the closed spironaphthoxazine form, molar ratio of methyl methacrylate/*n*-butyl acrylate/spironaphthoxazine acrylate derivative = 0.07:0.05:0.0013) was prepared, which after annealing was obtained as a colorless material (Fig. 10a). When films of **22_s** were mechanically damaged by applying a 10 μm wide crack, a reddish color appeared in the damaged region (Fig. 10b), consistent with the conversion of the spironaphthoxazine polymer into the merocyanine form (**22_m**, where "m" indicates the open merocyanine form). Upon exposure to visible light ($\lambda \sim 580$ nm) or increased temperature (95 °C), the defects were found to disappear and the material returned to its colorless form (Fig. 10c). Raman spectroscopy studies confirmed the occurrence of the postulated ring-opening reaction during mechanical damage and ring-closing during healing. The mechanical properties of the film were probed by nano-indentation studies. It was shown that the neat materials display a loss modulus of 28.7 MPa and a nanohardness of 5.1 MPa. Mechanical damage reduced the loss modulus and nanohardness by *ca.* 50%; however, upon optical healing the original mechanical properties of these materials were largely

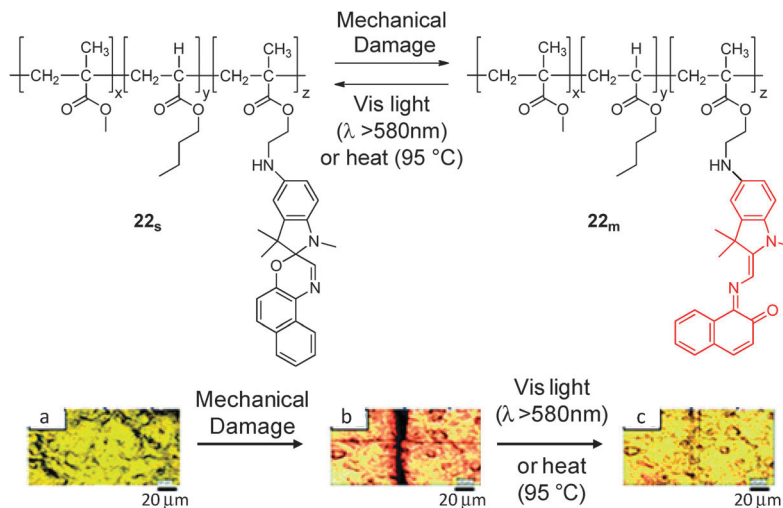


Fig. 10 Top: chemical structure of the polyacrylate copolymers with spironaphthoxazine in its closed (**22_s**) and open (**22_m**) forms. Bottom: optical microscopy images of a film of **22_s**, (a) before and (b) after being intentionally damaged and (c) after being healed upon exposure to visible light or heat. Figure adapted from ref. 53.

restored (loss modulus = 27.5 MPa; nanohardness = 4.5 MPa). The proposed mechanism for the healing observed in these polymers, confirmed in part on the basis of molecular modeling studies, involves the ring-opening of the spironaphthoxazine moiety to yield the merocyanine form, which forms intermolecular hydrogen-bonded complexes with adjacent merocyanine units. These complexes hold the polymer chains in an extended (high energy) conformation until visible light or heat disrupts them. This causes the collapse of the polymer backbone, which in turn pulls on entangled neighboring polymer chains, thereby filling in the removed mass that occurred from the damage and repairing the defect. This work nicely demonstrates the simultaneous use of a mechanically switchable component as a color changing indicator and intrinsic element of a healable polymer system.

Conclusions

Most of the recent approaches to create polymers that can be repaired after sustaining damage require exposure to heat or chemicals, but a few concepts have now been devised that permit the design of polymers which can be healed through exposure to ultraviolet or visible light. Light offers several advantages over a thermal stimulus, including the ability to deliver the stimulus locally. This allows one, amongst other things, to heal a damaged object under load. Moreover, it appears feasible to create healable materials with built-in “defect sensors”, *i.e.*, mechanochromic units, so that light is only absorbed in damaged areas.

The optically healable materials presented here are based on a diverse set of different types of chemistries. However, most of them exploit the dynamic nature of reversible covalent and non-covalent bonds, which can be influenced in a rather predictable manner by exposure to predefined external stimuli. It appears that the successfully used responsive motifs can be combined with other polymer platforms and that the general

design concepts can be applied to other dynamic bonds, so that one can expect a rapid expansion of this new family of materials. On the other hand, it is also possible to utilize light indirectly, *i.e.*, through light–heat conversion, or in combination with other stimuli, as shown for example in recent studies that have found that light can be used to ‘gate’ Diels–Alder reactions.⁵⁴

More fundamental studies are needed to develop a better understanding of the structure–property relationship of optically healable polymers. In addition, significant development efforts will be needed to use this knowledge to design and access photo-healable materials which also exhibit property matrices that permit technological exploitation, for example in automotive paints that allow easy restoration of scratches, varnishes for floors that could occasionally be “re-polished”, ophthalmic glasses that always stay super-clear, and many other applications.

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