(De)bonding on Demand with Optically Switchable Adhesives

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Adhesives that enable bonding and especially debonding on demand (DoD) have attracted rapidly growing interest in the last decade, as these capabilities greatly improve the functionality of adhesives, particularly in connection with temporal fixation, repair, and recycling. Indeed, DoD techniques have already entered commercial exploitation in applications such as easily removable wound dressings, temporal fixation in semiconductor manufacturing, and the repair, replacement, or recycling of components. While most approaches to debonding rely on heat to reduce the adhesive strength via physical property changes of the adhesive, optically switchable adhesives have been much less explored. However, light is an attractive stimulus, as it allows an efficient, contactless, remote stimulation that can be temporally and spatially controlled. In this Progress Report, recent developments in the domain of photoswitchable adhesive materials are highlighted. After a discussion of main strategies for the irreversible debonding of various adhesive types, options are presented for reversible (de)bonding enabled by different optical processes. The report emphasizes strategies based on photodegradable groups, photoisomerization, as well as the dissociation of supramolecular and dynamic covalent bonds based on either photochemical or light–heat conversion processes.

1. Introduction

The development of synthetic adhesives has evolved significantly over the last century and the advances seen in the field are in many aspects closely related to the general development of synthetic polymers. Nowadays, adhesives are found in almost every aspect of life; applications range from adhesive tapes to permanent “superglues” to structural adhesives with high load-bearing capacities. Depending on the application and the substrates, an adhesive has to fulfill different requirements; therefore, various material types are employed, including thermoplastic polymers, thermosetting resins, elastomers, and even some ceramic materials, usually in complex formulation with (lower molecular weight) additives such as tackifiers, antioxidants, hardeners, and fillers.[1] Sometimes it is desirable to disassemble an adhesive bond, but the high viscosity imparted by the high molecular weight and often cross-linked nature of polymer-based adhesives prevent their easy removal and stifle or complicate debonding, rebonding, (end-of-life) recycling, and repair. In this context, the development of debonding-on-demand (DoD) adhesive technologies is attracting rapidly growing interest. Indeed, DoD techniques have already entered commercial exploitation in applications such as easily removable wound dressings,[2,3] temporal fixation in semiconductor manufacturing,[4–6] and the repair, replacement, or recycling of components.[7–9] While many debonding technologies employ heat to reduce the adhesive strength by imparting physical property changes of the adhesive,[10–14] light-induced debonding technologies represent an emerging field and have been much less explored. Photolithiation is an attractive alternative to thermal debonding as it allows an efficient, contactless, remote stimulation that can be temporally and spatially controlled.[15–18] Moreover, factors such as the irradiation wavelength, intensity, and time can easily be tuned and it is often possible to focus the energy entry to the adhesive and minimize or avoid exposure of (sensitive) substrates. Of course, the approach requires that at least one of the substrates to be bonded is sufficiently transparent.

The design of a light-debondable adhesive system is strongly related to the adhesive type and the requirements imparted by the application(s) for which the adhesive is designed. For instance, pressure-sensitive adhesives (PSAs), such as used in adhesive tapes, need to efficiently adhere under ambient conditions with only a brief application of pressure, they should withstand the (comparably small) loads experienced while bonded, and they must also be easily removable, ideally without leaving any residues on the substrate.[19,20] PSAs are therefore normally based on lightly physically or chemically cross-linked rubbery polymers such as natural rubber, styrene butadiene block copolymers, and acrylics. These materials provide a balance between adhesive and cohesive performance, i.e., adequate stiffness and strength to resist deformation and cohesive failure, and appropriate elasticity in order to establish adequate contact with the substrate.[1] On the other hand, structural adhesives must be able to effectively transmit large loads across the bonded joint and the high strength and high rigidity required for this function are usually achieved by the formation of glassy networks. Examples of such materials include cross-linked epoxy resins, which may possess shear strengths of >35 MPa, cyanoacrylates (superglues), acrylics, and polyurethanes.[19]
While the introduction of optically responsive groups that allow reversible or irreversible dissociation is a priori possible in all types of adhesives, the molecular mobility and bond dynamics depend strongly on the materials system, and as these aspects are important for virtually all DoD mechanisms, they need to be carefully considered and addressed.

In this Progress Report we highlight recent developments in the domain of photoswitchable adhesive materials. Historically, much effort was placed in developing solutions for the easy on-command removal of PSAs,[20] and we will first discuss the development of irreversible mechanisms for this particular class, of which some are already commercially exploited. After discussing strategies for the irreversible debonding of other adhesive types, we present options for reversible (de)bonding on demand on the basis of different photoswitchable functionalities. Our report emphasizes strategies based on photodegradable groups, photoisomerization, as well as supramolecular and dynamic covalent motifs. We note that some of the strategies exploited to achieve reversible adhesion are similar or even identical to those used to create self-healing or healable materials,[21–23] although DoD benefits from faster processes, as rapid changes of the material properties are desirable. Other joining techniques, such as welding, for which the emerging class of vitrimers is considered useful,[24,25] are excluded from this report, and interested readers are directed to pertinent work on this subject.[26–29]

2. Irreversible Switching of the Adhesive Properties

2.1. Pressure-Sensitive Adhesives

Arguably due to their significant industrial relevance, early work on stimuli-induced debondable adhesives was focused on pressure-sensitive adhesives. PSA tapes find use in various fields such as masking, mending, fixation, protecting foils, and many others.[20] For these and similar applications, the bonding to a substrate is required only for a limited time, after which a facile and complete removal is desirable. Some PSAs possess sufficient cohesive strength to be removed without leaving residues, but debonding becomes more challenging as the bond strength and fragility of the substrate increase. Therefore, the idea of incorporating a switch to turn off the adhesion (and optionally the cohesive strength of the adhesive) is attractive, and many solutions in which light is used to trigger such changes have been explored. The main strategies employed for light-induced dismantling of PSAs are illustrated in Figure 1. According to the Dahlquist criterion of tack, the room-temperature storage modulus should be <0.1 MPa at a frequency of 1 Hz,[30] and an increase of the storage modulus above this value can therefore lead to a reduction of the adhesive strength. This can be achieved by either introducing light-cross-linkable entities in the side chain of the base polymer or by mixing UV reactive, multifunctional monomers into the adhesive formulation and photo-cross-linking these components when removal is desired. A third option is to decrease the cohesive strength of the adhesive through depolymerization.

To the best of our knowledge, the first record of a light-debondable pressure-sensitive adhesive dates back to the early 1980s, when the application of UV light as a means for detackification was described in a patent.[31] It was demonstrated that the incorporation of oxirane ring-bearing components and a photoinitiator (onium salt) into a conventional acrylic PSA system allows one to create a light-responsive adhesive that is readily detackified upon exposure to UV irradiation on account of the light-induced polymerization of oxirane rings. The oxirane moieties were introduced by either copolymerizing epoxy-containing monomers into the adhesive polymer (Figure 1a) or by physical blending of an epoxy resin into a conventional PSA (Figure 1b). For this specific chemistry, the former method was preferred, as epoxy resins and PSAs are usually not miscible and thus tend to separate over time. Ozawa et al. later conducted a systematic study to obtain insights into the mechanism of the UV-curing-induced reduction of the PSA properties of blends of poly(2-ethylhexyl acrylate-co-acrylic acid) containing a UV-curable urethane acrylate oligomer.[32] The

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study revealed that the peel adhesion and tack of UV-cured blends decrease due to an increase of microdefects at the interface between the substrate and the adhesive.[33]

Besides acrylic PSAs, which possess good tack and with increasing cross-link density also appreciable cohesive strength, thermoplastic triblock copolymer elastomers like polystyrene-b-polysoprene-b-polystyrene (SIS) or polystyrene-b-polybutadiene-b-polystyrene (SBS) have found applications as PSAs. These materials offer a higher cohesive strength than acrylics, due to physical cross-linking and micropore segregation of the high-$T_g$ polystyrene blocks and the soft rubbery segments; however, the addition of tackifiers such as petroleum resins is usually necessary in these materials.[20] Kim et al. investigated the UV-induced cross-linking of SBS using trimethylolpropane tris(3-mercaptopropionate) as cross-linking agent[34,35] and benzophenone as photoinitiator to achieve optical debonding.[36] The cross-linking was complete within 3 min, upon which the peel strength and bulk tack were reduced to 45% and 30%–40% of the original values, whereas the nanotack determined by atomic force microscopy decreased by ≈20%. In a related study, Phillips et al. reported that nano and bulk-tack of nano-composites of SIS or SBS copolymers and C$_{60}$ fullerene are reduced upon exposure to white light.[37] This effect is based on the capability of C$_{60}$ to generate singlet oxygen in the presence of visible light and molecular oxygen,[38–40] which can rapidly induce irreversible oxidative cross-linking of the unsaturated elastomers and promote a reduction of the adhesion. Similar observations were later reported for other singlet oxygen generators (e.g., acridine, rose bengal, and isomerically pure metallic nitride fullerene Sc$_3$N@I$_8$-C$_{80}$), while the inclusion of β-carotene, a well-known singlet oxygen quencher, into the sensitized blends stifled this pathway and limited its impact on the adhesion.[41,42]

Due to its simplicity and versatility, the conceptual approach of detackifying PSAs on-demand through photoinitiated cross-linking reactions has been extensively explored and is commercially exploited, for example, in temporary bonding during the dicing processes of semiconductor wafers in the production of integrated circuits,[43–49] and in smart wound dressings.[50–56] In a prominent design approach, Webster and co-workers prepared a cross-linkable acrylate-based PSA system for wound dressings, whose adhesion could be “switched off” upon exposure to visible light.[50,51,57,58] The use of PSAs on the skin requires a combination of different features, which beyond biocompatibility involve the ability to stick securely yet be removed easily and resistance to shear and water.[59] The acrylic copolymer investigated by Webster and co-workers was based on n-butyl acrylate (nBA), 2-ethylhexyl acrylate (ZEHA), and acrylic acid, and contained pendant methacrylate groups that could be photo-cross-linked with the help of a suitable photoinitiator. Cross-linking rendered the PSA nontacky and a reduction of the peel strength of up to 90% was observed on polyethylene substrates.[2] Rather than covalently attaching the curable groups to the base polymer, industrial researchers developed a simplified system in which curable (multifunctional) monomers or oligomers were blended with a (visible light absorbing) photoinitiator.[52–55] An adhesive tape for medical dressings was commercialized in which the switchable adhesive is coated onto a transparent polymer film.[3] The composition employed

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**Figure 1.** Schematic representation of different strategies employed for light-induced reduction of the adhesion in PSA systems. a) Formation of a cross-linked network upon irradiation of a copolymer containing photoactive side groups, usually in the presence of a light-sensitive initiator. b) Formation of a (semi-)interpenetrating network upon irradiation of a physical blend of a multifunctional monomer or oligomer, a photoinitiator, and a conventional pressure-sensitive adhesive (PSA). c) Depolymerization of a PSA containing photodegradable moieties.
is rapidly cured by ambient light, which is attractive for medical applications, where it is advantageous to avoid the use of auxiliary equipment as well as the need to use potentially harmful UV light. To protect the adhesive from light while in use, a light-protective film is placed on top of the tape, but it can be readily peeled off when removal is required. The exposure to visible light then induces polymerization of the curable components and renders the adhesive nontacky within seconds.

Another commercialized application involves photoremoveable PSA tapes for the rapid dicing of silicon wafers. In comparison to medical applications, a higher energy and dose of irradiation can be applied, but it is imperative to avoid any adhesive residues on the diced chips after release from the (transparent) tape. With these considerations in mind, Lee et al. investigated blends of a slightly cross-linked acrylic PSA with the hexfunctional monomer dipentaerythritol hexaacrylate and a photoinitiator, which upon UV irradiation led to an interpenetrating polymer network (IPN) structure with reduced adhesive strength.\[60\] Chu et al. combined polyacrylate resins with multifunctional cross-linkers such as ethylene glycol dimethacrylate, bisphenol A ethoxylate diacrylate, or trimethylolpropane triacrylate and achieved a significant UV-induced reduction in 180° peel strength (<1 N/25 mm).\[61\] Ryu et al. explored acrylic copolymers based on ethyl acrylate, 2-ethylhexyl acrylate, and acrylic acid, which were modified with glycildimethacrylate (GMA) to feature photo-cross-linkable acrylic side chains.\[62\] After cross-linking via UV irradiation, the adhesives displayed reduced peel strength (<90%) and probe tack (<60%) and such reduction depended on the GMA content and the light dose. It was also shown that the contamination of the silicon wafers decreased significantly after UV debonding for fully cross-linked networks.

The contamination with residual adhesive is not only important for wafer dicing, but also in food-contact, biomedical, and other applications, and it is important that low-molecular weight components in the PSA formulation that are not chemically attached to the polymer cannot migrate to the surface and cause “bleeding.” In this context, the above-discussed design strategies that rely on either blending cross-linkable entities into a PSA or chemically integrating these motifs as side chains in the PSA polymer have distinct advantages and disadvantages. The preparation of blends is usually more cost-effective than covalent integration, as blending does not require additional synthesis steps. On the other hand, miscibility and migration of unreacted low-molecular weight species and contamination of the substrate are more problematic in blends but largely absent in systems where the photo-cross-linkable groups, and ideally also the photoinitiator, are covalently connected to the base polymer. For instance, Czech et al. copolymerized benzophenone-functionalized acrylates into the backbone of a solvent-borne acrylic PSA, therefore immobilizing the photoinitiator.\[63\] The authors demonstrated that the incorporation of the photoinitiator into the backbone increased the cross-linking efficiency so that (in comparison to a blend containing an unattached initiator) a smaller amount of initiator was necessary. Note that the benzophenone is a hydrogen-abstructing type II photoinitiator, and yields no low-molecular by-products upon UV cross-linking.

A third option to render PSAs optically responsive is to introduce photodegradable groups into the material (Figure 1c). Their optical cleavage reduces the molecular weight and leads to a drop in stiffness and strength, which in turn may lead to cohesive failure of the bond. This approach has been much less explored than the above-described cross-linking schemes, due to the fact that for many applications the remaining adhesive residues are undesirable. Nevertheless, it is important to discuss some of the photodegradable systems investigated, because such concepts are instructive for other adhesive systems, in which the reduction of cohesive strength presents the main DoD strategy, for instance, in cross-linked structural adhesives (vide infra). For example, Suyama and Tachi incorporated photolabile O-acryloxime cross-links, which are readily cleaved upon irradiation with 254 nm UV light,\[64\] into acrylic PSAs by copolymerizing butyl acrylate with difunctional or trifunctional acryloxime-containing methacrylates (Figure 2a).\[65,66\] Upon UV irradiation, the 180° peel strength of poly(ethylene terephthalate) (PET) strips adhered to stainless steel substrates decreased from around 4 N/20 mm for the trifunctional and 7 N/20 mm for the bifunctional cross-linker to <1 N/20 mm, due to the degradation of the network structures. However, at prolonged irradiation times, a transition from cohesive to adhesive failure was observed, probably on account of UV-induced nonspecific cross-linking reactions between the poly(butyl acrylate) chains.\[67\]

The fact that polyperoxides can be degraded by homolytic scission of the peroxide bond and subsequent β-scission\[68,69\] was exploited by Matsumoto and co-workers to create adhesives that permit debonding with light.\[70\] The authors prepared a PSA based on a linear low-$T_g$ polyperoxide from methyl sorbate and oxygen and demonstrated that the shear strength of glass lap joints and the 180° peel strength of a PET-based tape adhered to an alumina surface were rapidly reduced when heated to 70 °C or exposed to UV light. The degradation of the polymer afforded products of lower molecular weight, which had a plasticizing effect and significantly reduced the adhesive’s mechanical strength. The authors further investigated the adhesive properties of polyperoxide-based polymer networks in which the peroxide groups either served as cross-links or as part of the main chain. Both cross-linked materials showed a higher adhesive strength than the linear counterpart, and the bond strength of such networks could be reduced upon heat-induced and UV-induced peroxide cleavage.\[71\] It is important to note, however, that the chemical stability of polyperoxides is limited. Consequently, the number-average molecular weight ($M_n$) of the linear polyperoxide and the strength of lap joints decreased considerably over the course of 7 d at 25 °C, indicating gradual degradation of the polymer at ambient conditions. To tackle the trade-off between stability/adhesive strength and stimuli responsiveness, the same group proposed a new type of “dual-lock” DoD PSA material. The design involved diblock copolymers composed of an adhesive low-$T_g$ segment based on poly(2-ethylhexyl acrylate) (P2EHA) and a switchable poly(tert-butyl acrylate) (PtBA).\[72\] The PtBA segments were selected because they can be transformed into poly(acrylic acid) by photoirradiation in the presence of a photocacid generator and subsequent baking. Thus, the “dual-lock” refers to the fact that no change occurs upon exposure to only one stimulus, i.e., either light or heat. It was shown that the acid-mediated cleavage of the ester side chains indeed caused a substantial
reduction of the adhesive strength and the phase-separated microstructure imparted by the blocky nature of the polymer was implicated in the efficient debonding effect. The change of the adhesive properties upon exposure to dual external stimuli was evaluated by 180° peel tests on PET films that had been bonded with the adhesives to stainless steel substrates. The peel strength was greatly dependent on the composition of the adhesive and varied from 4 to 310 N m⁻¹. The best results were obtained for a PtBA-b-P2EHA containing 65 mol% tert-butyl acrylate, and the peel strength could be reduced to ≈0 N m⁻¹ after UV irradiation (8 h) followed by a heat treatment (100 °C, 1 h). The peel strength was found to depend on both the molecular weight and the composition, which was explained by the relatively low cohesive forces displayed by the polymer used. The group therefore employed controlled free radical polymerization for the synthesis of more precisely defined high-molecular-weight block copolymers containing polar side groups. The adhesive segment was changed to statistical copolymers of nBA or 2EHA and 2-hydroxyethyl acrylate (HEA). In contrast to the initial system, high and constant 180° peel strength values between 270 and 300 N m⁻¹ were achieved for PET strips attached to stainless steel plates using the polar HEA-containing 2EHA block on account of superior cohesive strength. Increased adhesive strength was observed upon thermal treatment together with a shift of the failure mode from cohesive to interfacial, arguably due to enhanced contact of the adhesive with the substrate. After the two-step debonding treatment, the adhesion was reduced to 4–18 N m⁻¹, and the adhesion tapes spontaneously peeled off as a consequence of the evolution of gaseous isobutene. The observed failure mode was either of cohesive nature or occurred at the PET interface. Dual stimuli treatment rendered most of the studied polymers insoluble, and the occurrence of transesterification reactions of HEA units was observed by size exclusion chromatography (SEC), where for model polymers of P(nBA-co-HEA) the two-times higher molecular weight was present. While the study nicely demonstrates that the “dual lock” mechanism gives additional control over the debonding, the system required relatively long irradiation and postbaking times. When the reactive polymer segment was changed from PtBA to the acetal-protected 1-isobutoxyethyl acrylate, the baking step could be omitted and the adhesive strength could be changed solely by acidolysis upon photoirradiation in the presence of a photocatalyst.

A very different strategy for optically debondable adhesives, based on the sintering of nanocomposites, was described by Keddie and co-workers. The materials studied were accessed by combining rigid polymethacrylate nanoparticles (NPs) with a low-Τ_g copolymer latex. Upon casting of thin films, the NPs migrate to the surface, where they form a percolating network. Sintering rigidifies this phase, thereby increasing the elastic modulus and reducing the tack. The initial adhesive properties can be tuned through the nanoparticle concentration. For sintering, it is necessary to heat the nanoparticles above their Τ_g (130 °C), and the authors demonstrate that this process is possible within 30 s using intense infrared radiation, thereby switching off the adhesion. It is worthy to note that the transformation of infrared radiation into heat is an efficient and convenient approach and that the framework is a priori (possibly with the help of converting species) adaptable to many of the thermally responsive systems discussed herein.

### 2.2. Other Types of Debondable Adhesives Based on Irreversible Chemistries

While the (irreversible) detackification of PSA systems has been substantially explored, and many solutions and systems
have been designed and even commercialized in the last decades, the development of other types of stimuli-responsive adhesives has only evolved more recently. Many approaches rely on the incorporation of photocleavable groups into polymeric adhesives, as depolymerization will generally lead to a reduction of stiffness and strength and thus a decrease of the cohesive strength. In this context, a large number of photolabile groups, including those used as protecting groups in organic chemistry,[77] or incorporated into polymeric structures to control structure and physicochemical properties,[16,78,79] can be exploited.

The development of biocompatible medical adhesives that can be safely applied on wet tissues (with minimal inflammatory response) has been a particularly active area of research. Mussel-inspired dopamine (3,4-dihydroxyphenylalanine (DOPA)) based adhesive gels have emerged as a particularly well-investigated platform, and several groups have introduced concepts to render these materials optically removable. For example, a biocompatible hydrogel adhesive designed for underwater bonding based on 6-nitrodopamine (ND) moieties was prepared by del Campo and co-workers (Figure 2b).[80] A four-arm star-poly(ethylene glycol) was end-functionalized with ND and formed a metal-complex cross-linked network upon addition of a Fe$^{3+}$ salt. Alternatively, a covalently cross-linked gel was obtained under oxidative conditions (addition of NaIO$_4$). The photocleavable o-nitrophenyl ethyl moieties were then employed for optical debonding. In another study, Locklin and co-workers showed that in the presence of photacid generators, light can be used to manipulate the pH, and therefore the adhesion properties of a pH-dependent network.[81] The system investigated comprised a hydrogel based on a polyacrylamide copolymer carrying catechol groups that undergoes a gel–sol transition upon UV irradiation ($\lambda = 254$ nm). The polymer was designed to cross-link via catechol–iron complexes that form in the pH range of 5.6–7.0. Exploiting that the cross-links can dissociate upon changing the pH, a photacid generator was incorporated into the hydrogel to trigger decross-linking. Indeed, upon UV irradiation, the pH was found to decrease and the hydrogel reverted to a viscous liquid. The maximum shear strength of single-lap joints prepared from quartz glass dropped from 1.7 to 0.4 kPa upon photoirradiation ($\lambda = 254$ nm, 1.2 mW cm$^{-2}$) for 60 s, while the failure mode always remained cohesive. Also targeting an adhesive gel, Chung and co-workers studied a photosensitive terpolymer that included highly hydrophilic zwiterionic poly(sulfobetaine methacrylate) as the main component, as well as DOPA and a nitrobenzoxycarbonyl-containing cross-linker.[82] When the terpolymer was swollen with water, a relatively high shear strength of 341 kPa was obtained for lap joints made with polyester substrates. Photocleavage of the nitrobenzoxyl groups reduced the shear strength by $\approx$35% after 30 min and by 56% within 3 h and the study thus demonstrates a facile synthetic route to create multifunctional polymers that offer strong, stimuli-responsive wet adhesion. The choice of the zwiterionic building block was rationalized by the fact that such polymers display good long-term stability in complex biological systems and represent an alternative to poly(ethylene glycol) for the design of biomedical adhesives.[83,84] Ayer et al. prepared light-responsive DMSO-based organogels by cross-linking poly(vinyl alcohol) with an aliphatic azo moiety derived from 2,2′-azobis[2-methyl-N(2-hydroxyethyl)propionamide].[85] For optimized compositions (molecular weight of the polymer and cross-linking degree) of the organogel, a solid-to-liquid phase transition could be induced upon exposure to UV or visible light as a consequence of the irreversible decomposition of the azo moieties.[86,87] A shear strength of 26 kPa was measured for glass lap joints and UV irradiation ($\lambda = 390–500$ nm, 600 mW cm$^{-2}$) induced on-demand debonding within seconds. It is important to highlight that the rapid and efficient debonding of the above-described systems is at least in part enabled by the fact that they were designed to form gels. However, the mechanisms should also be exploitable in solid adhesives, for which higher shear strength should be anticipated. Depending on the cleavage mechanism, a slower response time (e.g., on account of slow diffusion) or a reduced contrast (e.g., on account of recombination of radicals produced)[86] can be expected.

Applying the same general concept to solid adhesives, Long and co-workers prepared a series of photoreactive polyesters with o-nitrobenzyl ester moieties in the main chain by melt transesterification.[88] The $T_g$ values of the synthesized polymers ranged from 68 to 83 °C. Wedge fracture tests were conducted to investigate photoinduced degradation and debonding properties of the o-nitrobenzyl ester-containing polyesters. For this purpose, the structural adhesive was melt-pressed between two glass slides. Prior to UV exposure a fracture energy of 3.4 J cm$^{-2}$ was measured, which decreased to 1.6 J cm$^{-2}$ after a UV dose ($\lambda_{\text{max}} = 365$ nm) of 3780 mJ cm$^{-2}$. 1H NMR experiments provided spectroscopic evidence for the intended photodegradation. Wang et al. prepared linear polymers containing also main-chain o-nitrobenzyl ester groups and additionally pendant catechol moieties via a Passerini multicomponent polymerization.[89] In addition to the photodegradable o-nitrobenzyl ester linkages, the catechol was incorporated to tune the $T_g$ and the adhesive strength to glass substrates. Lap shear strength tests on single lap joints showed that the adhesive strength could be tuned from 0.22 to 0.53 MPa by varying the catechol content. However, a prolonged irradiation time ($\lambda = 365$ nm, 100 W) of 24 h was necessary to observe a 50% reduction in shear strength.

Sasaki et al. utilized a photodepolymerizable cross-linked polyolefin sulfone as photodetachable adhesive.[90] A poly(olefin sulfone) copolymer carrying pendant carboxylic acid groups was mixed with a polycarbodiimide cross-linker and 4,4′-[bis[[methyl(2-nitrobenzyl)oxy]carbonyl]trimethylene] di-piperidine as a photobase generator, which was included to induce photodepolymerization. The protons of the carbons next to the sulfonyl groups can be abstracted by bases, resulting in a depolymerization chain reaction.[91] The adhesive strength of the thermosetting material was investigated on a cross-tensile setup, and a high adhesive strength of around 7 MPa on quartz plates was achieved. UV irradiation ($\lambda = 254$ nm, 3.0 J cm$^{-2}$) slightly discolored the resin due to the formation of nitrosobenzaldehyde via photodecomposition of the photobase generator. However, subsequent heating to 100 °C was necessary for the poly(olefin sulfone) to depolymerize, upon which adhesive strength approached 0 within $\approx$15 min. While the thermosetting adhesive exhibits relatively high strength,
the release of volatiles (sulfur dioxide and gaseous olefins) may be undesirable.

Zhang and co-workers developed an epoxy-based resin that could be debonded upon UV irradiation. The authors prepared blends of bisphenol A diglycidyl ether (DGEBA), a DGEBA-based diacylate (BEA), the epoxide-curing agent diethylenetriamine, and the radical photoinitiator 1-hydroxycyclohexyl phenyl ketone. Fourier transform infrared spectroscopy measurements revealed that the thermal curing of the DGEBA resin with diethylenetriamine left the BEA resin unaffected. Upon UV curing of the BEA resin in the presence of the photoinitiator, an interpenetrating network was formed, which induced shrinkage of the system and a decrease of the peel strength. While the initial bond strength decreased with increasing BEA content, the reduction in peel strength after UV curing was proportional to the BEA content, highlighting the trade-off nature of the BEA content in peel strength after UV curing was proportional to the BEA content in the system. Peel strength measurements were performed on samples in which the adhesive was sandwiched between a glass slide and a polyimide film and thermally cured. Under optimized conditions, the ratio of the bonding strength to debonding strength was around 16; the bonding strength decreased from 2.8 to 0.18 N/25 mm within 80 s of UV irradiation. At the same time, an increase of the gel content was observed, confirming the increase of the cross-link density. The authors argue that the increase in cross-linking cumulates internal stress and results in shrinkage of adhesive layer, therefore facilitating the stripping process. While this study nicely demonstrates that physical changes in the overall structure can contribute to a reduction of the peel strength, further investigation of the thermomechanical properties would be beneficial to deepen the understanding of the mechanism and to extend the scope of the approach.

3. On-Demand Debonding Based on Reversible Bonds

Bonds and functional groups that can undergo reversible bond cleavage and formation or conformational changes are attractive for the construction of reversible DoD materials. Photochromic molecules and photoresponsive dynamic (covalent) bonds offer a plethora of possibilities for the development of adaptive polymer materials whose macroscopic properties can be “directly” controlled by light. The family of photochromic compounds is characterized by two (meta)stable states that possess distinct absorption spectra, and therefore transformation between these states can be triggered by illumination with light of different wavelengths; the ability of such compounds to switch between states of different molecular shape, coordination properties, color, polarity, and charge is an attractive feature for the development of photoresponsive materials. Dynamic covalent bonds permit manipulating the degree of polymerization and/or cross-link density, and thereby the viscoelastic properties, of polymeric materials, and various systems have been developed in which the dynamic bond exchange/equilibrium can be manipulated with light. It is also possible to shift such equilibria with other stimuli, notably exposure to heat or chemicals, and to exploit transduction schemes such as light–heat conversion, in which light is used as an “indirect” stimulus. In the context of light-responsive adhesives, light–heat transduction is often used to control supramolecular (dis)assembly, and thereby the properties of supramolecular polymer systems.

3.1. Photoisomerization

3.1.1. Liquid Crystalline Small Molecules

While photoinduced solidification is a widely used method in adhesive technology (UV curing), the photochemical (reversible) liquefaction under isothermal conditions is a process that is rarer. Liquid crystalline compounds (LCs) are very useful in this context, as stimuli-induced transitions of ordered and disordered states may be accompanied by drastic changes of the materials’ properties on account of LC-isotropic transitions. Indeed, LCs have been used for optical switching, phototransfer techniques, and photoresponsive actuators, and other applications. In the context of photoswitchable LCs, azobenzene derivatives have emerged as a frequently employed platform, because the photoinduced trans-to-cis-isomerization can induce (reversible) solid-to-liquid transitions. Already in 1937, Hartley reported that the polarity and melting point differ for the trans and cis-isomers, and the azobenzene functionality has evolved as one of the most widely studied photoresponsive motifs. Exposure to UV light induces the transition from the trans to the less stable cis-state. The reverse reaction can be induced thermally or through irradiation with visible light. The geometrical change upon isomerization from the elongated trans to the bent cis-state involves a change of the molecular length from 9 to 5.5 Å (Figure 3a). In LC materials that incorporate azobenzene functionalities, the change of the molecular geometry upon formation of the cis-isomer can imply a significant reduction of the order parameter and therefore lead to drastic changes of the material’s properties. However, the photoisomerization of azobenzene is hampered in ordered crystals due to the restrictions in free volume and until recently, the application of LC materials as light-responsive entities has not been widely explored.

In 2011 Norikane et al. described reversible, athermal, photoinduced phase transitions from the LC to the isotropic state, which were achieved by exploiting conformational changes in macrocyclic azobenzenes. Okui et al. reported a crystalline amphiphilic azobenzene monomer consisting of a hydrophobic rod-like azobenzene and a hydrophilic flexible tetraethylene glycol chain. The compound displayed a melting temperature of 50 °C, but upon UV irradiation, liquefaction at room temperature was observed. Hoshino et al. later conducted a structural analysis of the crystal-melt transition of cyclic azobenzenes using X-ray crystal structure analysis. In 2012, Akiyama and Yoshida demonstrated that the reversible, isothermal photoinduced crystal-to-liquid transition of sugar alcohol scaffolds functionalized with multiple azobenzene-containing moieties is potentially useful for the creation of reusable adhesives (Figure 3b). Scaffolds with four or more azobenzene arms resulted in powdered solid materials that transformed into isotropic liquids upon UV irradiation (λ_max = 365 nm, 20 mW cm⁻²), although the intrinsic melting points or glass transitions of the materials were above...
60 °C. Upon irradiation with visible light ($\lambda_{\text{max}} = 510 \text{ nm}, \approx 20 \text{ mW cm}^{-2}$) at ambient temperature, the material solidified within 10 min. The application as reversible adhesive was investigated using single-lap joints prepared from quartz substrates. For the compound derived from the 6-carbon sugar alcohol d-Mannitol, a critical strength of 500 N cm$^{-2}$ was necessary to separate thermally bonded samples. Upon photoliquefaction, the value decreased to 0.3 N cm$^{-2}$. The bond strength could be restored to the initial value upon solidification through visible light irradiation. In an in-depth study, Akiyama et al. further prepared several acyclic and cyclic sugar alcohol derivatives that contained azobenzene arms with and without alkyl tails or spacers and the authors investigated the influence of the chemical modifications on the dynamic viscoelasticity and the adhesive properties. To study the reversible adhesive properties of the materials, tensile lap-shear adhesive strength tests were performed. The materials, for which a photoinduced phase transition could be observed, were readily debonded using UV light with the adhesive strength decreasing from 20–45 N cm$^{-2}$ to almost 0 N cm$^{-2}$ after exposure to UV irradiation ($\lambda_{\text{max}} = 365 \text{ nm}, 80 \text{ mW cm}^{-2}$, 3 min). Upon rejoining the glass slides and irradiating the samples with visible light ($\lambda_{\text{max}} = 525 \text{ nm}, 25 \text{ mW cm}^{-2}, 1.5 \text{ min}$), the adhesive properties were restored. Moreover, the adhesive strength increased up to twofold compared to the nonirradiated lap joints. The authors conclude that factors that lead to an improved adhesion include the “cis-isomer effect” and changes of the mechanical characteristics of the materials: Irradiation with visible light produces small amounts of the cis-isomers, which compared to the trans-isomers are more polar as the bent structure introduces a dipole moment. Therefore, the interactions with the polar glass surface can enhance the adhesion. In addition, solids that were created under isothermal conditions by the photoisomerization of isotropic liquids may be structurally different from thermally generated solids. In fact, polarized optical micrographs of photochemically generated solids showed a smaller domain spacing, which possibly increases the mechanical strength of the materials. The authors conclude that photoisomerization must be feasible in the solid state to allow photoinduced phase transitions at room temperature. This was the case for sugar alcohols that contained at least four azobenzene arms, while the corresponding mono and diazobenzenes did not show this effect. Obviously, the melting (or glass transition) temperatures of the cis and trans-isomers involved must be below and above...
room temperature, respectively, in order to achieve athermal photoinduced liquefaction under ambient conditions.

In another study, Akiyama and co-workers investigated the reversible solid-to-liquid phase transition of rod-like azobenzenes that had been derivatized to feature alkxy groups of varying chain length in the 4 and 4′-positions and a methylene group in the 3-position.\(^{[108]}\) Relatively fast and reversible photomelting was observed for azobenzene scaffolds carrying alkyl chains of medium length (\(C_n = 6–10\)). Thermally bonded glass slides possessed similar lap shear strengths as the sugar scaffolds, up to 50 N cm\(^{-2}\).

Meijer and co-workers created an LC system based on telechelic dimethylsiloxane oligomers of defined length, which were end-functionalized with azobenzene (Azo-ODMS; Figure 3c).\(^{[109]}\) Monodisperse Azo-ODMS containing 8 or 16 siloxane repeat units were prepared in a stepwise procedure utilizing chlorosilane and silanol building blocks.\(^{[110,111]}\) ODSM16 functionalized with trans-4-methoxyazobenzene end groups was shown to assemble into a lamellar microstructure, in which crystalline azobenzene monolayers are separated by amorphous ODMS. Upon exposure to UV light (\(\lambda_{\text{max}} = 365 \text{ nm}, 200 \text{ mW cm}^{-2}\)), a fast phase transition from a yellow wax to a red oil was observed, as the \(\text{trans} \rightarrow \text{cis}\)-photoisomerization resulted in a loss of molecular order. At ambient conditions, reverse photoisomerization was observed within 1–2 d, but the reversal was nearly instantaneous when the \(\text{cis}\)-isomer was irradiated with blue light (\(\lambda_{\text{max}} = 455 \text{ nm}, 200 \text{ mW cm}^{-2}\)). In single-lap shear experiments with specimen prepared from glass substrates, a shear strength of 213 kPa was measured for photocured \(\text{trans-Azo-ODMS}16\) and the failure mode was adhesive. When the length of the ODSM linker was reduced to 8 Si atoms, the shear strength increased to 572 kPa. Athermal on-demand debonding was achieved within seconds through photoliquefaction into a silicone-based oil with 365 nm light and the lap shear strength appeared consistent over several photoinduced debonding–bonding cycles. The use of relatively small molecules in this approach leads to a low viscosity in the liquid state, which enables facile debonding without the need of additional mechanical impact or thermal energy. On the other hand, relatively low adhesive strengths were achieved and for relevant industrial application, optimization of such a method would be required.

### 3.1.2. Liquid Crystalline Polymers

While the above-discussed examples all demonstrate photoisomerization-induced, reversible, isothermal transitions from a crystalline or liquid crystalline to an isotropic state, the adhesive strength of these materials was, on account of the low molecular weight of the compounds employed, relatively low. Moreover, tuning the viscosity and tackiness of such small-molecule systems is generally difficult. These issues can be mitigated by the incorporation of photoswitchable groups into polymeric materials, although the photomelting of photoswitchable LC polymers is fundamentally different from that of LC small molecules. In the latter, solid-to-liquid transitions are induced through photoinduced transitions between the ordered and disordered phases, whereas in polymeric materials a glass transition is responsible for drastic changes of the material’s viscoelastic properties. However, the \(T_g\) strongly depends on intermolecular forces,\(^{[112]}\) which, like in the small molecules discussed above, in azopolymers differ for the \(\text{trans}\) and \(\text{cis}\)-configuration; thus, similar switching might be achievable.

Using reversible addition-fragmentation chain-transfer (RAFT) polymerization, Wu and co-workers synthesized acrylate and methacrylate-based homopolymers containing azobenzene side groups that were attached via flexible spacers (Figure 3d).\(^{[113]}\) With the azo motif in the \(\text{trans}\)-configuration, the polymers exhibited \(T_g\) values above room temperature, but they indeed liquefied at ambient conditions after switching to the \(\text{cis}\)-state, and exhibited a \(T_g\) below 0 °C. Reversible \(\text{trans} \rightarrow \text{cis}\)-photoisomerization, concomitant with liquefaction, was achieved in thin adhesive films for at least five consecutive cycles of repeated exposure to UV and visible light. The mechanism was confirmed by UV–vis absorption spectra, which revealed a strong \(\pi \rightarrow \pi^*\) band at 330 nm, indicative of the \(\text{cis}\)-state, and an \(n \rightarrow \pi^*\) band at 450 nm that is diagnostic for the \(\text{cis}\)-isomer. The influence of the \(\text{cis}\)-content on \(T_g\) was investigated by converting the material to the \(\text{cis}\)-form, and letting the material slowly convert back to the \(\text{trans}\)-configuration; dynamic scanning calorimetry measurements that were conducted as a function of relaxation time revealed that the \(T_g\) decreased with increasing \(\text{cis}\)-content, suggesting a plasticizing effect of the \(\text{cis}\)-isomer. By photoswitching the \(T_g\) of the azopolymers, it was possible to repeatedly heal damages applied to polymer films, to reduce the surface roughness by up to 600%, and to control the adhesion of the materials for transfer printing. Interestingly, upon addition of a nitro-group in the 4-position of the azo moiety, the solid-to-liquid transition was no longer observed. In this case, both photoisomers possess a large dipole moment, and similarly upon addition of a nitro-group in the 4-position, the solid-to-liquid transition was no longer observed. In this case, both photoisomers possess a large dipole moment, and

Following their work on sugar-based azobenzene scaffolds, also Akiyama et al. investigated the application of polyacrylates containing azobenzene side chains as reusable adhesives.\(^{[114]}\) The LC polymers used by the group had been previously discussed in the context of photosensitive oligomeric mesogens as dopants in chiral glassy LCs.\(^{[115]}\) In a later study, the authors explored the adhesive performance as a function of spacer and tail length, and the weight-average molecular weight (\(M_w\)), which was kept below 20 000 g mol\(^{-1}\). The irradiation with UV (\(\lambda = 365 \text{ nm}\)) or visible light (\(\lambda = 520 \text{ nm}\)) was achieved with high-power LEDs. While a polymethacrylate reference material (\(M_w = 39 000 \text{ g mol}^{-1}\)) did not liquefy upon UV irradiation, the majority of azo-functionalized polyacrylates exhibited photoinduced solid-to-liquid transitions. Photomelting was possible for polymers with sufficiently long alkyl spacers/tails (\(C_n = 8–12\)). Single-lap glass joints bonded with the polymers revealed shear strengths of around 1 MPa when the samples were thermally bonded, while photochemical bonding at room temperature allowed an increase of the shear strength to 1.5–3.5 MPa, presumably due to residual \(\text{cis}\)-isomers, which increase the hydrophilicity, and also on account of
In order to gain a better understanding of the photo-responsive adhesive properties of azobenzene-based poly(meth)acrylates, the group prepared polyacrylates and polymethacrylates via atom transfer radical polymerization (ATRP).

This allowed for better structural control over the molecular weight, molecular-weight distribution, and the nature of the end groups. ATRP of the azobenzene-containing 10-[4-(4-hexyloxy)phenylazo]octyloxy)dicyclopentadiene acrylate and of a similar methacrylate rendered structurally well-defined polymers with $M_n = 10,000$–$40,000$ g mol$^{-1}$ and a dispersity of $1.1$–$1.2$. UV–vis absorption measurements on thin films showed that the rate of isomerization was faster for acrylates than for methacrylates, but the isomerization rate was not affected by the molecular weight. UV irradiation induced the generation of 80% cis-moieties for acrylates and only around 60% for methacrylates (determined by $^1$H NMR spectra of re-dissolved samples), indicating that the main-chain structure influences the photoisomerization rate. Similarly, UV-induced changes of the viscoelastic properties were different. The solid-to-liquid phase transition occurred more rapidly for acrylates than for methacrylates of similar molecular weight, and the resulting liquefied acrylate showed more fluid behavior. The findings demonstrate that the higher chain mobility in polyacrylates facilitates the photoisomerization of the azobenzene moieties. The lack of effect of the molecular weight on the isomerization rate remained unclear, but the authors suggest that it may be related to the relatively high molecular weights employed in this study. In single-lap shear experiments using glass substrates, maximum adhesive strength around 3.5 MPa was obtained, which is comparable to the adhesive strength of typical hot-melt adhesives.

The bond strength rapidly decreased to $<0.2$ MPa upon UV irradiation ($\lambda = 365$ nm, $50$ mW cm$^{-2}$, $15$ s), which demonstrates that the above polymers can be used as reversible on-demand debondable adhesives.

Light-responsive polymethacrylate triblock copolymers featuring azobenzene esters in the peripheral and 2-ethylhexyl esters in the center block were also investigated. In contrast to the homopolymers discussed above, for which the preparation of polymer films was not possible due to the material’s brittleness, the soft middle block in the block copolymer introduces more flexibility to the system and allowed the spin coating and compression molding of polymer films. Upon light-induced isomerization of the azobenzene moieties, the adhesive strength was reduced from 1.5–2.0 MPa to 0.5–0.1 MPa within $15$ s. Repeated bonding and debonding over at least three cycles were possible without the loss of adhesive strength. In contrast to the homopolymers, similar shear strengths were measured for thermally and photochemically bonded samples, indicating that the cis-azobenzene fraction (cis-effect) did not impact the adhesive strength considerably. The authors rationalized that while for the homopolymer the mode of failure was mostly adhesive or a complex combination of cohesive and interfacial failure, the adhesion of the block copolymers was mainly governed by cohesive forces. Therefore, the increased hydrophilicity imparted by the remaining cis-azobenzene fraction upon photoirradiation, which influences the interfacial adhesion, does not impact the adhesive strength in a major way. The potential usefulness of such azo-containing photoswitchable polymer adhesives is reflected that the technology is the subject of several patents and patent applications.

In recent years, approaches to prepare photoswitchable surface topologies based on anisotropic geometric changes have gained some attention, and such materials show potential as a tool to control friction and adhesion. Liu et al. developed switchable coatings based on chiral-nematic (cholesteric) liquid crystalline networks, in which the formation of dynamic protrusions could be triggered by light. The coatings include an azobenzene-containing mesogen, and the authors demonstrated that trans-to-cis-photoisomerization induces anisotropic volume changes. Patterned films containing planar and homeotropically aligned segments in an alternating fashion allowed for reversible photomodulation of the surface topology. The mechanism of the photoinduced surface patterning relies on the fact that conformational changes of the azobenzene functionalities in the LC network induce a reversible change of the order parameter. The group later reported a chiral-nematic polymer network coating that forms a 3D “fingerprint” texture through self-assembly, with the cholesteric helical axis perpendicular to the substrate (Figure 4a). A reactive liquid crystalline monomer mixture containing a polymerizable azobenzene compound was spin-coated on a glass plate that had been equipped with a homeotropic polyimide orientation layer. An almost flat liquid crystalline polymer network film was obtained upon polymerization in the presence of a photoinitiator. When the coating was illuminated with UV light, fingerprint morphologies formed with an in-depth modulation of $<4\%$ based on the initial thickness of the coating and lateral dimensions in the micrometer range. When the light was switched off, relaxation to the flat surface occurred within $60$ s. Notably, photoirradiation allowed cycling of the friction coefficient between $0.4$–$0.5$ and $0.1$, due to the reduction in surface contact, and was sufficient to control robotic gripping and releasing of a small load. The same authors designed a system in which the coating transfers from flat to a predefined ridge-like grating upon actuation with light. In the activated state, the friction depends on the orientation and contact area of the ridges and is particularly high for interlocked geometries (Figure 4b).

A related approach is exploited in micropatterned dry adhesive systems. Such materials are inspired by the fibrillar foot pads of lizards, spiders, and insects, which allow these animals to climb and move on various substrates. The high surface area created by the hierarchical arrangement of elongated fibrils promotes reversible adhesion through efficient exploitation of van der Waals and capillary forces. Especially in the context of gripping and releasing objects, dry adhesives may be very useful. One possibility to adjust the adhesion performance of such systems is by modulation of the actual contact area, for instance, by bending of protruding pillars or the backing
The well-established light-induced actuating abilities of azobenzene-containing liquid crystal elastomers may be useful to implement such mechanical events in micropatterned dry adhesive systems as demonstrated by Kizilkan et al., who integrated an azobenzene-containing liquid crystalline elastomer layer with a polydimethylsiloxane-based microstructured layer. The well-established light-induced actuating abilities of azobenzene-containing liquid crystal elastomers may be useful to implement such mechanical events in micropatterned

Figure 4. Schematics of patterned surface structures with switchable friction and/or adhesive strength. a) Schematic representation of a cholesteric liquid crystalline network and its dynamic response upon irradiation with UV light (left) and a polarized optical microscopy image of a fingerprint texture observed for such a material upon UV irradiation (right). Bright regions relate to planar and black areas to homeotropic orientations. Reproduced with permission. Copyright 2014, Wiley-VCH. b) Schematic illustration of switchable surface coatings with variable friction dynamics upon formation of linear protrusions, depending on the grating orientation and sliding direction (black arrows) (left), and the respective dynamic force traces upon UV-induced surface morphing (right). Adapted with permission. Copyright 2014, Wiley-VCH. c) Schematic illustrating the influence of the molecular shape change in a micropatterned dry adhesive comprising an azobenzene-containing liquid crystalline elastomer layer on the adhesive contact area. Adapted with permission. Copyright 2017, American Association for the Advancement of Science.
adhesive.[128] Photoisomerization-induced bending readily decreased the contact area with a given object (Figure 4c), and the adhesive forces could be reduced up to a factor of 2.7. This type of approach is particularly useful in robotics where control over grip and release of small objects is relevant.

3.2. Supramolecular Polymers

Due to their stimuli-responsive behavior, supramolecular polymers offer an interesting and versatile platform for the preparation of reversible adhesives.[129,130] In supramolecular polymers, monomeric units are assembled via noncovalent, reversible interactions, yielding polymeric properties in both solution and bulk.[131] Alternatively, supramolecular motifs can be used as reversible cross-links.[132] Using an appropriate stimulus, the equilibrium between the assembled and disassembled state can be shifted, and this leads to a reduction of the material’s modulus, strength, and viscosity. This change can significantly influence the adhesive performance, generally inducing cohesive failure. The stimulus-triggered modulus drop and the lower viscosity are also advantageous in the context of bonding as these changes may facilitate the surface wetting. Upon removal of the stimulus, the equilibrium is shifted back to the assembled state, therefore fully restoring the material’s properties.[131]

3.2.1. Hydrogen Bonding

Hydrogen bonding has gained much attention for the preparation of (in some cases bioinspired) dynamic adhesives.[129,130] An early example on adhesives based on supramolecular binding chemistry by Long and co-workers demonstrates that the incorporation of the quadruple hydrogen bonding motif 2-ureido-4-pyrimidinone (UPy) into a butyl acrylate (PBA) copolymer has a significant effect on the material’s bulk properties and its adhesive behavior.[131] The self-complementary UPy motif, introduced by Sijbesma, Meijer and co-workers (Figure 5a), is well known for its strong association constant (>10⁶ M⁻¹) in chloroform.[134] In the study performed by Long and co-workers, the incorporation of 2.5–10.4 mol% of a UPy-containing methacryl monomer (Figure 5b) leads to an increase of the Tₘ from −50 °C for the neat PBA to −25 °C for the copolymer with the highest UPy content, due to the formation of supramolecular cross-links. 90° peel tests on specimen consisting of a PET film that was bonded with a glass slide revealed a threefold increase of the adhesive strength upon incorporation of UPy groups, i.e., the introduction of a mere 3.3 mol% of UPy into the copolymer increased the peel strength from 1 to 3 J m⁻², presumably due to the UPy–glass interactions and a higher creep resistance due to the formation of cross-links.

The use of UV light as a trigger to promote reversible bonding and debonding of supramolecular adhesives was reported by Weder and co-workers using poly(ethylene-co-butylene) (PEB) cores that had been end-functionalized with UPy groups (UPy-PEB-UPy) (Figure 5c).[135] As previously shown by Meijer, Sijbesma and co-workers, linear chain extension of this building blocks affords a nanophase-segregated supramolecular polymer, in which stacked UPy dimers separate from the low glass transition core phase (Tg = −40 °C) and act as physical cross-links.[136] Adhesion measurements on both glass and steel substrates revealed a shear strength of around 1.2 MPa (cohesive failure). Multiple bonding and debonding cycles were performed using both heat and UV light as the trigger. The supramolecular polymer itself did not sufficiently absorb UV light, and therefore the UV sensitizer 2-(5-chloro-2H-benzotriazole-2-yl)-6-(1,1-dimethylethyl)-4-methyl-phenol (Tinuvin 326; Figure 5d) was blended into the polymer as a light–heat converter and found to promote UV-induced debonding on demand via optical heating to ∼70 °C. Mechanically separated lap joints could be readily recombined using heat or UV light (2 × 60 s, λ = 320–390 nm, 900 mW cm⁻²), and the original adhesive strength was recovered. The use of this and other supramolecular polymers as reversible adhesives in the context of dental materials is also documented in the patent literature.[137]

With the goal to further improve the cohesive strength of supramolecular adhesives, Weder and co-workers followed up on the synthetic approach introduced by Long and co-workers (vide supra) and investigated poly(alkyl methacrylates) carrying UPy-side chains as light-responsive reversible adhesives.[138] The use of butyl or hexyl methacrylate allowed tuning the Tg of the UPy copolymers from well below to well above ambient temperature, thus affording both rubbery and glassy materials. Statistical copolymers containing 2.5, 5, or 10 mol% of the UPy-containing monomer were prepared via free radical polymerization in solution. The adhesive strength was investigated by shear strength experiments at temperatures ranging from 24 to 60 °C using stainless steel lap joints. Shear strengths up to 5.5 MPa were achieved, while the incorporation of supramolecular cross-links generally led to improved mechanical and adhesive strength in the rubbery state (i.e., at elevated temperatures). Debonding and subsequent thermal rebonding of the joints resulted in no loss of adhesive performance. The UV light-induced bonding and debonding on demand (λ = 320–500 nm, 2500 mW cm⁻², 2 × 40 s for bonding) were also demonstrated, using again Tinuvin 326 (0.25 wt%) as a UV-light-to-heat converter that was simply blended with the 10 mol% UPy containing poly(hexyl methacrylate) copolymer. Quartz lap joints could be debonded within ∼30–95 s when a small preload force was applied (150–50 N).

The Weder group later reported the preparation of a liquid UPy-functionalized methacrylamide monomer containing an oligo(propylene glycol) spacer (UPy-OPG-MAA).[139] UPy-OPG-MAA is fully miscible with various methacrylates, and therefore enables photoinitiated bulk copolymerization, for example, the preparation of poly(hexyl methacrylate) copolymers containing 0–20 mol% UPy-OPG-MAA. As expected, the strength and modulus increased with the content of UPy-OPG-MAA (and thus supramolecular cross-link density) and using stainless steel lap joints, shear strengths of up to 2.5 MPa were measured for the copolymer containing 10 mol% of the UPy monomer. Debonding-on-demand experiments demonstrated the feasibility to use both heat and UV light (λ = 320–390 nm; 900 mW cm⁻²) as a debonding stimulus for copolymers with a low UPy content. Already a very small UPy content (<10 mol%) led to significant changes of the mechanical properties and improved adhesion.
Using 1 wt% of UV absorber, it was possible to debond a quartz lap joint within 3 min when exposed to UV light ($\lambda = 320–390$ nm, 900 mW cm$^{-2}$).

Light-induced debonding on demand was further demonstrated using several glassy supramolecular polymer networks. Balkenende et al. reported a low-molecular-weight building block containing three UPy groups, which assembles into an amorphous glass ($T_g \approx 100 \degree$C) when cooled from the melt (Figure 6a).140 The high UPy content and the highly cross-linked nature of the material limit chain mobility, therefore preventing crystallization, and affording an optically responsive, glassy material of high stiffness. To investigate the potential of the material as reversible adhesive, glass lap joints were thermally bonded at $200 \degree$C for 10 s and a shear stress of 1.2 MPa was measured. Irradiation-induced debonding ($\lambda = 320–390$ nm, 1000 mW cm$^{-2}$) was feasible within 1 min, and in contrast to the previously mentioned UPy-containing supramolecular polymers, no additional UV absorber was required, as the concentration of light-absorbing UPy groups was very high. Both mechanical and adhesive performances were fully restored upon rebonding disassembled lap joints using heat or light.

Balkenende et al. further reported a supramolecular glass based on a bisphenol A diglycidyl ether oligomer that was terminated with 5-aminosophtalhylic acid groups and assembled into a supramolecular network with several bipyridines (Figure 6b).141 By varying the spacer length of the bipyridine from 0 to 3 methylene groups, the $T_g$ could be varied between 75 and 100 $\degree$C, while the storage modulus ranged from 3.5 to 3.9 GPa. Upon melting, the materials displayed low melt viscosities of as low as $< 7$ Pa s. The materials could be reprocessed by melting and cooling, and the original mechanical properties could be fully restored over at least three cycles. Stainless steel lap joints exhibited an adhesive strength of around 1.5 MPa and a bonded lap joint could be fully loaded.
within 10 s after bonding, reflecting rapid assembly of the supramolecular polymer upon cooling. Due to the high fraction of aromatic groups, which acted as light–heat converters, the materials could be heated to 140 °C within 5 s of UV irradiation ($\lambda = 320$–390 nm, 1600 mW cm$^{-2}$), allowing for extremely rapid debonding within 14 s. However, despite the higher stiffness compared to the UPy-based glass, the adhesive strength remained in the same range and was not significantly improved, perhaps on account of the brittle nature of the polymers. We note that in all of the above-discussed systems (and also the materials presented below), the fundamental mechanism is the thermally induced dissociation of supramolecular binding motifs, and the entry of a considerable amount of energy is thus necessary. On account of thermal diffusion and heat sink effects (involving substrates and the environment), the approach generally requires high irradiation intensities to enable efficient heating. In return, debonding can be very fast, especially in the case of linear polymers in which the supramolecular motifs form part of the backbone, so that they disassemble into species of very low molecular weight and melt viscosity.

### 3.2.2. Metal–Ligand Complexation

Due to their stimuli-responsive nature, metallosupramolecular polymers have been widely investigated as shape-memory polymers and healable materials. However, the suitability as a basis for reversible (photoresponsive) adhesives has been much less explored. In general, similar structures and morphologies are available as discussed above for polymers assembled with hydrogen-bonding motifs. However, as various metal ions (and counter ions) are accessible, the binding strength and geometry as well as the complexation dynamics can be tuned more easily over a broad range.$^{[21,142,143]}$

Heinzmann et al. reported a stimuli-responsive metallosupramolecular polymer based on low molecular weight telechelic PEB carrying two (2,6-bis(1′-methylbenzimidazolyl)pyridine) (Mebip) ligands at the chain ends (Figure 5e).$^{[135]}$ The resulting Mebip-PEB-Mebip was chain-extended into a linear polymer via complexation to Zn(NTf$_2$)$_2$. The nano-phase-segregated metallosupramolecular polymer, which was originally devised as an optically healable material, was investigated as reversible adhesive on single-lap joints prepared from steel and glass substrates.$^{[21]}$ As in the original study on optical healing of this material, sub-stoichiometric amounts of the metal cation were used to render the metal–ligand binding more dynamic, which is realized by the presence of free ligands. Shear strengths around 2.5 MPa were achieved, which exceeds the values obtained for the corresponding H-bonded adhesive discussed earlier. In this case, the metal–ligand complexes display an appreciable absorption in the range of 300–400 nm and could directly be used for light–heat conversion. Irradiation with UV light induced decomposition, on account of the local temperature increase. Single-lap joints made with quartz glass slides could be rapidly debonded.

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*Figure 6. Schematics of glassy supramolecular polymer networks. a) Chemical structure of a trifunctional, low molecular-weight monomer containing three UPy groups and its assembly into a temperature and light-responsive amorphous network. Adapted with permission.$^{[140]}$ Copyright 2016, Nature Publishing Group. b) Schematic representation of the synthesis of isophthalic acid-modified bisphenol A diglycidyl ether oligomers (top) and the formation of a supramolecular glass through isophthalic acid/pyridine-induced binding (bottom). Adopted with permission.$^{[141]}$ Copyright 2016, American Chemical Society.*
within 80 s upon UV irradiation (320–390 nm, 900 mW cm\(^{-2}\)) as the temperature locally increased to >220 °C. The authors demonstrated that the light-induced (de)bonding was reversible and that the original adhesive strength could be recovered.

In an approach described by Grindy et al.,\(^{[144]}\) the light-induced switching characteristics of a metallosupramolecular hydrogel comprised of 4-armed poly(ethylene glycol)-based monomers that were cross-linked through metal ion (M\(^{2+}\) = Ni\(^{2+}\), Cu\(^{2+}\), or Co\(^{2+}\))–histidine complexation (4PEG-His:M\(^{2+}\))\(^{[145]}\) were altered by UV-generated radicals (Figure 7). The method relies on the fact that such radicals can change the oxidation state of the metal ions, which in turn switches their coordination behavior and thus drastically influences the viscoelastic properties of the hydrogels. Lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP), which has a strong absorption band between 350 and 400 nm, was used as a water-soluble radical-producing photoinitiator. Thus, irradiation (\(\lambda = \approx 365 \text{ nm}\)) of LAP-containing metallosupramolecular hydrogels triggered LAP dissociation,\(^{[146]}\) and the generated radicals either reduced or oxidized the metal ion centers of the 4PEG-His:M\(^{2+}\) cross-links. A selection of transition metal ion mixtures for the formation of a cross-linked network allowed controlling the viscoelastic properties pre and post-UV illumination. The study was limited to the investigation of the dissociation process, and it remains to be seen if the reverse reaction can be equally well controlled. While no adhesive properties were investigated, the authors speculate that the presented approach may impact the design of novel smart, soft adhesives.

The two mechanisms discussed in this section are fundamentally different. While the former is based on the temporary, reversible supramolecular (de)polymerization due to the light–heat conversion upon irradiation, the latter relies on (so far irreversibly) manipulating the binding motif by changing the metal ion’s oxidation state. However, the two approaches may not be mutually exclusive and offer interesting perspectives for future investigation, allowing tuning of the dissipative and viscoelastic properties with high precision. Due to the relatively high association constants of metal–ligand complexes, metallosupramolecular polymers generally possess better mechanical properties than the corresponding polymers with other supramolecular binding functionalities. Furthermore, the optical properties can be easily tuned by modification of the ligand.\(^{[147]}\) As a consequence of the often aromatic structure of the ligands, high UV absorption of the metal–ligand complexes is observed, making them suitable candidates for photosensitive applications. A fundamental disadvantage of light–heat conversion schemes is that optical and thermal effects and properties cannot be fully decoupled. To enable application over a large temperature window, high dissociation temperatures are...
desirable, but at the same time the relatively high temperatures required to impose debonding do not allow for applications with heat-sensitive substrates and require high-power light sources.

### 3.2.3. Host–Guest Interactions

While hydrophobic host–guest interactions are rather weak compared to H-bonding or metal–ligand complexation, they offer an interesting opportunity for underwater adhesion or surgical glues. A variety of host–guest systems based on crown ethers,[148,149] cyclophanes,[150,151] pillar[n]arenes,[152,153] calix[n]arenes,[151,154] and resorcin[n]arenes were reported,[155,156] and in many cases control over polarity (and therefore solubility) and selectivity of the cavatands was achieved by functionalization of the macrocycles, giving rise to supramolecular polymers with applications in both solution and bulk.[157–159] In the context of hydrogels the vast majority of studies involves supramolecular host–guest inclusion complexes based on cyclodextrins (CDs) or cucurbit[n]uril (CB[n], N = 5–8, 10) hosts. CDs are cone-shaped, cyclic oligosaccharides, usually prepared from 6, 7, or 8-D-(+)-glucopyranose monomers (α-CD, β-CD, and γ-CD) that are linked through α-1,4-glycosidic bonds,[160] whereas CBs form barrel-shaped macrocycles that are composed of glycuril units that are linked by methylene bridges.[161] The mean inner diameter of the CD cavity increases from 5.7 to 9.5 Å from α-CD to γ-CD, with a cavity depth of around 7.9 Å.[160] Similarly, CB[5] has an internal diameter of around 4.4 Å, which increases to 8.8 Å in the case of CB[8]; the cavity depth of CB homologues is 7.4–7.8 Å.[162,163] The hydrophilic exterior of the cavities renders them water soluble, while the hydrophobic interior of the host molecules facilitates the accommodation of nonpolar guest molecules.[161] This has been long exploited to create photoreversible inclusion complexes of azobenzenes with both CD and CB hosts. For example, while the trans-azobenzene fits into the α-CD cavities and forms 1:1 inclusion complexes, less deep inclusion or decomplexation is observed for the more bulky cis-azobenzene.[164,165] This feature has been extensively explored for photoresponsive drug delivery systems.[161,166]

An early example of a photoresponsive hydrogel that was assembled by host–guest complex formation was reported by Harada and co-workers, who combined aqueous solutions of poly(acrylamide) that had been functionalized with either α-CD or trans-azobenzene moieties (the latter via a dodecamethylene linker, which imparts considerable mobility and positional freedom) and observed the formation of supramolecularly cross-linked hydrogels (Figure 8a).[167] Upon UV irradiation, the formation of cis-azobenzene resulted in either an increase or decrease of the viscosity, depending on whether the CD moiety was attached to the polymer through its 3 or 6-position. When connected through the 3-position, the cis-isomer was excluded from the host, and network dissociation was evidenced by a decrease of the viscosity. When attached to the polymer backbone through the 6-position, the azobenzene was expelled on the “far” side of the CD upon transformation to the cis-form, which led to the stabilization of the complex (as evidenced by NMR spectroscopy) and an increase of the viscosity (Figure 8b).

The Harada group later reported a photoregulated assembly system based on poly(acrylamide) hydrogels that had been functionalized with either α-CD, β-CD, or photoresponsive azobenzene moieties.[168] While the cis-azobenzene is excluded from α-CD due to steric effects, it can still form host–guest complexes with β-CD, due to its larger cavity. Therefore, the different affinities of α-CD and β-CD for the two azobenzene

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**Figure 8.** Schematic representation of optically responsive host–guest complexes based on cyclodextrin (CD) hosts and azobenzene guests. a) Chemical structures of two α-CD-containing poly(acrylic acid)s in which the α-CD is either connected to the backbone through its 3 or 6-position (top), and the azobenzene-containing poly(acrylic acid) “guest” polymer (bottom). b) Binding dynamics of the two different host–guest systems upon illumination with UV or visible light. Adapted with permission.[167] Copyright 2006, American Chemical Society. c) Schematic representation of glass surfaces grafted with copolymer brushes composed of an azobenzene-modified acrylate (AZA) and 2-hydroxyethyl acrylate (PAZA-PHEA) through surface-initiated atom transfer radical polymerization (SI-ATRP). Further shown is the adhesion of such surfaces induced by the formation of host–guest complexes in the presence of a β-CD-functionalized polymer. Reproduced with permission.[170] Copyright 2016, The Royal Society of Chemistry.
isomers were used for the design of photoresponsive gels with controllable assembly characteristics. The authors showed that the (d)association of the CD-containing host gels from the azobenzene-decorated guest gels was reversible and could be controlled by light. For instance, agitation of the trans-azobenzene gel in the presence of the α-CD host gel resulted in gel adhesion due to the formation of host–guest complexes, and the assembled gels could be separated upon UV-induced trans-to-cis-isomerization. The authors later studied the adhesion of acrylamide-based α-CD and β-CD-containing hydrogels to hard surfaces that had been modified with various functionalities.[169] Photoswitchable adhesion was demonstrated for azobenzene-functionalized glass surfaces and α-CD hydrogels, where the adhesion could be suppressed via the UV irradiation-induced trans-cis-isomerization of the azobenzene motif. Reversible bonding and deboning upon visible (λ = 430 nm) and UV irradiation (λ = 365 nm) was demonstrated, and the initial adhesive strength was largely recovered.

Roling et al. prepared surface-immobilized azobenzene-functionalized polymer brushes through a combination of microcontact chemistry and surface-initiated atom transfer radical polymerization (SI-ATRP) and demonstrated the usefulness of these structures in the context of reversible bonding (Figure 8c).[170] A glass surface decorated with copolymer brushes of 2-hydroxyethyl acrylate and an azobenzene-modified acrylate was incubated with an aqueous solution of a commercially available β-CD polymer for 10 min, washed with water, and single-lap joints were formed by overlapping the substrate thus treated with a second functionalized glass substrate and drying for 1 h. The lap joints could carry a weight of up to 700 g cm⁻². The disrupted surfaces were rebonded with the same procedure. After three bonding/debonding cycles, the adhesive strength decreased to 50% of its initial value; the authors speculate that surface contaminations and structural changes could be responsible for the bond strength decrease. Unfortunately, no significant influence of UV irradiation on the adhesive strength was observed. UV-vis spectroscopy revealed incomplete photoisomerization, arguably due to the high local concentration, the hindered mobility, and the reduced rotational freedom of the densely packed azobenzenes on the surface.

Photoswitchable adhesive gels consisting of cucurbit[8]uril (CB[8]) hosts and azobenzene guests were recently reported by Scherman and co-workers.[171] The branched, hydrophilic, CB[8]-threaded polycarboxane HBP-CB[8] was prepared through RAFT polymerization of N-hydroxyethyl acrylamide and a bifunctional cross-linker based on a viologen derivative (V₂⁺) carrying two styryl groups, affording a highly branched copolymer (HBP-CB[8]·V₂⁺; Figure 9a). CB[8] is known to form heteroternary complexes, and viologen derivatives are widely used as the first guest for CB[8] hosts (association constant \( K_a < 10^6 \) m⁻¹) (Figure 9b). Either benzylamide or azobenzene was employed as the second guest, due to their high affinity to the CB[8]·V₂⁺ binary complex with association constants of \( K_a = 2.0 \times 10^6 \) m⁻¹ and \( K_a = 4.0 \times 10^5 \) m⁻¹, respectively. Thus, copolymers of benzylamide or azobenzene containing monomers, acrylamide, and N,N'-methylenebisacrylamide were prepared as guest gels (Figure 9a). Macroscopic adhesion between two guest hydrogels was achieved using an aqueous HBP-CB[8]·V₂⁺ solution as binder. Adhesive energies of 8.0–9.5 J m⁻² and 15 J m⁻² were measured for benzylamide and...
azobenzene hydrogels, respectively. On-demand bonding and debonding was investigated on lap joints prepared by overlapping either two azobenzene hydrogels or an azobenzene and a benzylamide host gel, using again HBP-CB[8]-V2 as binder (Figure 9c). Photoradiation (λ = 360 nm, 4.8 mW cm−2) for 10 min decreased the shear stress from 13 to 3 N m−1 and from 10 to 2 N m−1, respectively. Upon irradiation at 420 nm for 60 min at 4.8 mW cm−2, less than 70% of the adhesive strength was recovered. The authors suggest that the reduced interfacial adhesion may be due to incomplete recovery of trans-azo moieties. Due to the affinity of the CB[8]-V2 binary complex for the amino acids tryptophan and phenylalanine, the HBP-CB[8]-V2 was considered to be useful as glue for biological tissues and it was indeed demonstrated that the material could bond porcine skin (commonly used to mimic human dermis), for which a shear stress of around 10 N m−2 was determined.

In addition to the above-discussed systems based on polymeric materials, Scherman and co-workers also described a small molecule system in which CB[8] was used to directly bind two functionalized mica substrates through photoreversible CB[8] heteroternary complex formation. Functionalizing one surface with a methyl viologen derivative and another with azobenzene moieties using a silane linker allowed CB[8]-mediated adhesion between the two surfaces through the formation of ternary host–guest complexes. The adhesion was investigated on the single-molecule and macroscopic level. Qualitative experiments showed that the two surfaces could be bonded by exposure to visible light (λ = 420 nm) after adding an aqueous solution of CB[8] and that such a joint could carry a weight of 16 g cm−2 for up to 3 h without separation of the two substrates. UV irradiation (λ = 365 nm) induced the trans–cis-photosomerization of the azobenzene moieties bound to the surface, which induced debonding. This process was repeatable over several cycles. Interestingly, the adhesion forces determined by single-molecule force spectroscopy differed strongly from values approximated from macroscopic measurements. The fivefold stronger adhesion observed on the macroscopic scale is thought to result from cooperative effects and stress dissipation at the interface.

The above-discussed examples demonstrate that host–guest-mediated adhesion is a very selective approach. A broad range of guest molecules can be exploited, so that both adhesion to biological tissues and photoresponse can be achieved and the approach thus lends itself for exploitation in the biomedical domain. However, the adhesion is typically weak, as a consequence of the relatively low interaction strengths. The very specific interactions require in some instances extensive surface pretreatments (functionalization), and the studies have shown that limitations are found for rigid substrates, where, for example, the reversibility is limited or DoD with azobenzene hosts could not be achieved.

### 3.3. Dynamic Covalent Chemistry

Similar to supramolecular assemblies, the equilibrium of dynamic covalent bonds can be manipulated by an external stimulus, although this process is usually much slower and often requires more activation (e.g., high temperature). On the other hand, permanent bonds may provide better mechanical strength and higher dimensional stability. Reversible covalent chemistry has recently been extensively exploited in the context of dynamic covalent polymer networks, for the preparation of reprocessable thermosets, healable polymers, and shape memory materials. While many (photoresponsive) dynamic covalent bonds are known and have been utilized in the context of the aforementioned materials, very few have been used to create reversible adhesives.

The dynamic disulfide bond exchange is well known for its multistimuli responsiveness. Numerous materials based on disulfide bond exchange can be found in the literature, and the relatively weak dynamic bond has been widely used for the design of healable or recyclable materials. A particularly attractive feature of the disulfide bond is its sensitivity to various stimuli such as heat, pH, or light, and a few examples of disulfide containing thermoresponsive adhesives have been reported. A photohealable semicrystalline shape-memory polydisulfide network was investigated by Rowan and co-workers, who demonstrated that such materials may also serve as reversible, on-demand debondable adhesives (Figure 10a). A modulus drop upon melting of the crystalline domains (Tm ≈ 80 °C) facilitated substrate wetting and induced adhesion upon cooling to room temperature (shear strength < 3 MPa). However, when the dynamic disulfide bond exchange was activated upon exposure to higher temperatures (150 °C or UV irradiation, the adhesive strength was further increased (shear strength < 6 MPa) on account of a further drop of the material’s modulus and viscosity, thereby strengthening the adhesive bond upon cooling (Figure 10b). Due to the irradiation-induced dynamic disulfide exchange, on-demand debonding using UV light (λ = 320–390 nm, 2000 mW cm−2) was feasible within 30 s for single-lap joints prepared from glass (Figure 10c). Cohesive failure, due to the liquefaction at the surface layer, was observed.

Photodimerizable groups, e.g., cinnamates, maleimides, and coumarins, which can all undergo [2π + 2π] cycloaddition upon UV irradiation, represent another platform of dynamic-covalent bond-forming molecules that can be used to create nonpermanent cross-links. As cross-links are formed through nonradical pathways, this strategy is, unlike radical-mediated processes, usually not impacted by oxygen inhibition, which is beneficial for the lifetime and the reversibility of the reaction over several (dis)bonding cycles. Thus, Trenor et al. incorporated 7-hydroxycoumarin derivatives, which photodimerize upon irradiation with UV light (λ > 300 nm) into adducts that can be cleaved at shorter wavelengths (λ < 290 nm), in the side chains of an acrylic copolymer-based model PSA, as a reversible counterpart to the PSA deactivation strategy discussed in Figure 1a. UV–vis spectroscopy of adhesive films indicated ~60% dimerization of the coumarin groups upon exposure to UV irradiation (35 mW cm−2). The formation of cross-links reduced the peel strength from 1.6 to 0.05 N mm−1. UV illumination at λ < 290 nm photol mediated the covalin dimers and the reduction of the cross-linking density raised the peel strength to 0.10 N mm−1, but the initial bond strength could not be fully restored, and further optimization of the system may lead to better reversibility.
Reversible photodimerization of anthracene occurring through a \([4\pi + 4\pi]\) cycloaddition has also been investigated as a tool to manipulate the bonding strength of adhesive polymers. Compared to the \([2\pi + 2\pi]\) counterparts, the cycloaddition can be triggered by light of longer wavelengths, which is beneficial to limit unwanted side reactions. Dimerization occurs upon exposure to UV light (\(\lambda > 350\) nm), with new bonds forming between the 9 and 10-positions of two anthracenes.\[^{[191]}\]

The reversible dissociation of the dimer can be induced either thermally or with UV light of shorter wavelengths (\(\lambda < 300\) nm). Small molecule systems that are structurally similar to the azobenzene-functionalized sugar scaffolds (vide supra) have been designed. Akiyama et al. prepared anthracene-terminated hexamer structures that could be photo-cross-linked upon UV irradiation, while dissociation was achieved only thermally.\[^{[192]}\] Saito et al. designed a liquid crystal-based adhesive material constructed of a photoresponsive carbon framework containing dendritic moieties (Figure 11a).\[^{[193]}\]

The scaffold contains two rigid anthracene wings that are joined through a flexible cyclooctatetraene unit and this design leads to a V-shaped molecule with a strong π-stacking ability. An LC phase developed between 65 and 140 °C on account of the formation of rectangular columnar structures (Figure 11b). The framework can be switched to a flat conformation upon photoexcitation, thereby enabling photodimerization of the anthracene units (Figure 11c). UV exposure (\(\lambda_{\text{max}} = 365\) nm, 160 mW cm\(^{-2}\)) at 100 °C turned a columnar LC thin film into a disorganized isotropic liquid. The columnar LC material was recovered by heating to 160 °C for 15 min and subsequent cooling to the appropriate LC temperature range (Figure 11d). No photomelting was observed in the solid state at 50 °C, demonstrating that an LC phase is a requirement for efficient photodimerization. Adhesive experiments were performed using single lap joints prepared from glass substrates and the LC adhesive. Shear strengths using thermally bonded substrates reached 1.6 MPa in the solid state (at 25 °C) and 0.9–1.2 MPa in the LC state (120–100 °C). Photoseparation was realized upon UV irradiation within a few seconds (\(\lambda = 365\) nm, 160 mW cm\(^{-2}\)) at 100 °C, with the detachment occurring near to the interface between the LC adhesive and the irradiated substrate. Rebonding the glass joints at 160 °C for 15 min led to full recovery of the adhesive strength and the photomelting at 100 °C was unchanged for at least four cycles of bonding and debonding. Such a double-lock mechanism in which both heat and UV light are needed for debonding may give additional control over the debonding step. As the adhesive shear strength is only slightly reduced from the solid to the LC state, such materials may be used for bonding at elevated (working) temperatures. In combination with UV irradiation, the material liquefies already around 70 °C, which represents a temperature reduction of 50% compared to the material in monomeric state.

A bioinspired, water-compatible modular acrylate-based terpolymer adhesive was prepared by Harper et al.\[^{[194]}\] who incorporated three different functionalities in to a polymer: side-chain anthracene derivatives as photo-cross-linking segments, a mussel-inspired 3,4-dihydroxy-L-phenylalanine (DOPA) containing segment for adhesion in wet environments, and hydrophilic acrylic acid (Figure 12). Adhesive experiments to flexible polyester and rigid glass substrates were
Figure 12. Synthesis of a mussel-inspired (meth)acrylic terpolymer wet adhesive that was made by free radical polymerization of a monomer mixture containing acrylic acid, 3,4-dihydroxy-\(\cdot\)-phenylalanine (DOPA)-containing methacrylate, and an anthracene-functionalized acrylate. Photoirradiation \((\lambda > 250\) nm) induces polymer cross-linking through \([4\pi + 4\pi]\) cycloaddition of anthracene side chains. Adapted with permission.\(^{[194]}\) Copyright 2016, American Chemical Society.

Figure 11. a) Chemical structure of a liquid crystalline (LC), light-switchable, \(\pi\)-stacking V-shaped molecule with anthracene “wings.” b) Differential scanning calorimetry traces of the material. c) Schematic of the photodimerization process of the LC phase that involves UV-induced planarization of the molecules. d) Schematic of the light-responsive and thermo-responsive (dis)assembly. Photoirradiation at 70–135 °C induces the transformation of the columnar LC phase into a fluid mixture comprised of unreacted monomers and some photogenerated dimers. Heating the fluid mixture above 160 °C induces the thermal back reaction into the monomer, which recovers the columnar LC phase upon cooling to 70–135 °C. Adapted with permission.\(^{[193]}\) Copyright 2016, Nature Publishing Group.
performed, for which the terpolymer was swollen in water or ethanol, which transformed the otherwise rigid polymer into a gel. Photo-cross-linking enhanced the cohesive strength of the adhesive polymer network and the cross-link density could be controlled through the UV-irradiation time. The adhesion shear strength on Mylar films was increased by 850% upon UV irradiation ($\lambda = 352$ nm) on account of the increase of the material’s cohesive strength; however, a relatively long irradiation time of 1 h was necessary. Less of an effect was observed for the rigid glass surfaces. Unfortunately, the reverse reaction was not investigated. Kaiser et al. derivatized a hydrogenated carboxylated nitrile butadiene rubber with anthracene groups that allowed photodimerization and thus network formation.\[195] Dimers were cleaved either through UV exposure ($\lambda = 254$ nm, 1.2 mW cm$^{-2}$) or dissociation upon heating to 70 °C. The reversible switching of the adhesive properties of the elastomer was demonstrated. Due to a relatively high tan $\delta$ value, giving resistance to elastic deformation, and a low elastic modulus in the rubbery regime, which facilitates the wetting of the substrate during bonding, the pristine material exhibited a surface tack of 210 N at room temperature. UV-cross-linking decreased the adhesion force to 117 N, as a consequence of the reduced energy dissipation and the restricted movement of the molecular chains in the cross-linked films. Subsequent photo or thermal dissociation allowed recovery of 75% or 80% of the adhesive strength, respectively. It is worth mentioning that the here discussed cross-linking effect addresses surface tack and is of particular importance in the context of pressure-sensitive adhesives,\[196] whereas in other (thermoset) systems, the network formation through UV-cross-linking of polymers may be applied to increase cohesive properties of an adhesive to keep bonds robust.\[194]

Diarylethenes represent another prominent category of photochromic molecules and offer fast photosresponsive, high thermal stability, good fatigue resistance, and a high conversion ratio.\[197] A particularly intriguing feature was reported by the groups of Branda and Hecht, who developed photoswitchable dithienylfuran moieties, in which the Diels–Alder product with maleimides can be “locked” upon ring closure of the formed dithienylethene, therefore disabling the retro-Diels–Alder reaction (Figure 13a).\[198–201] Building on this work, Asadirad et al. reported the difunctional diarylethene precursor M1, in which two thiophene derivatives are connected to the 3 and 4-positions of a furan (Figure 13b).\[202] The furan moieties undergo spontaneous $[4\pi_s + 2\pi_s]_c$ cycloaddition with the maleimide groups of the complementary difunctional monomer M2. This leads to the formation of a linear polymer (P1o or P1c) that contains photosensitive hexatriene moieties resembling the well-known photochromic dithienylethene molecule.\[197] Ring closure to cyclohexadiene can then be induced by UV irradiation, and this “locks” the polymer in a state in which the reverse Diels–Alder reaction is temporarily disabled (Figure 13b, P1c). Exposure to visible light, however, reverses the ring closure and “unlocks” the system. The authors demonstrated that the photoinduced ring-closing and ring-opening reactions can regulate the adhesive properties of the material. Single-lap joints were prepared from PET substrates that were spray coated with P1o and subsequently bonded at 90 °C. Shear force measurements at room temperature revealed a more than twofold increase of the shear forces from $\approx 5.5$ mN to $\approx 12$ mN upon UV-induced ($\lambda = 312$ nm, 5 min) formation of P1c. At 90 °C the difference increased to more than threefold, highlighting the fact that the ring-opened isomer can undergo reverse Diels–Alder reaction, whereas the ring-closed
structure cannot. As a consequence, the adhesion performance of the ring-opened structure decreased at elevated temperatures while the adhesive strength of the ring-closed system remained unchanged. Ring-opening induced through visible light irradiation (\(\lambda > 345 \text{ nm}, 120 \text{ min}\)) lowered the adhesive properties of the material. Locking the Diels–Alder product through subsequent electrocyclic reactions is an elegant and efficient way to improve the thermal stability of such bonds. The incorporation of such functionalities into an adhesive represents another design based on “dual-lock” mechanism, where unlocking requires optical and subsequent thermal treatment.

Tannouri et al. presented a dry adhesive based on poly(dimethylsiloxane) (PDMS) microstructures doped with spiropyran entities. These motifs undergo reversible ring-opening and ring-closing reactions upon irradiation with UV and visible light, and can thus be switched between a neutral spiropyran and a zwitterionic merocyanine form. The significant change from a nonpolar to a zwitterionic species makes spiropyranes attractive as photoswitches for dry adhesive systems that predominantly rely on electrostatic forces. For example, a dry adhesive was prepared by incorporating a photoresponsive spiro-compound (0.25 wt%) into “mushroom”-shaped PDMS microstructures. Upon UV irradiation (\(\lambda = 365 \text{ nm}, 3.5 \text{ mW cm}^{-2}, 60 \text{ s}\)), the formation of zwitterionic merocyanine increased the adhesion to glass for nonstructured and structured surfaces by 22% and 10%, respectively. Using thus be difference between excitation wavelengths (\(\lambda = 365 \text{ nm} \text{ or } >530 \text{ nm}\)), cycling between the colorless neutral and the magenta charged state was used to reversibly regulate the adhesive strength. Since the covalent attachment of spiropyran may reduce photodegradation, aggregation, leaching, etc., the preparation of systems where the photochromic compounds are tethered to the polymer may be beneficial for the preparation of materials that show more pronounced variations of the adhesive strength.

4. Summary and Outlook

The design principles and strategies utilized for the creation of photoresponsive adhesives summarized in this Progress Report appear to reflect two different approaches. On the one hand, researchers have pursued the modification of existing adhesive systems, and, on the other, the opportunities presented by specific chemistries, photoswitchable groups, and principles already used in other contexts have been exploited in the context of responsive adhesives. Some of the concepts have already led to commercialized products, typically involving the modification of established adhesive systems with simple photo(de)polymerizable groups (Figure 1). In most of these cases, light is employed to irreversibly switch the mechanical properties of the adhesive materials, either by increasing modulus and reducing tackiness (especially in the context of PSAs) or by reducing strength and stiffness and thereby deteriorating the cohesive strength of the material. Many feasibility studies were perhaps more concept-driven, and based on the incorporation of well-established photoresponsive moieties into polymeric materials whose properties may not have been optimized for adhesive applications. With respect to reversible bonding and debonding on demand, a majority of the investigations focused on reversible networks, in which de-cross-linking reduces the cohesive strength. In this context it is important to highlight that approaches in which cohesive failure occurs (usually) have the disadvantage of substrate contamination, which is especially critical in biomedical applications, the temporary fixation in industrial processes, and efficient recycling.

In virtually all optically responsive materials systems studied for DoD, the photoresponse is induced by one of the two mechanisms. Either light is employed to trigger a (athermal) photochemical reaction, such as (de)polymerization, (reversible) bond formation and cleavage, and isomerization, or light is converted into thermal energy, which in turn induces property changes by simply heating the material. The latter approach is often exploited in the context of supramolecular materials, in which the generation of heat is used to shift the equilibrium of the supramolecular assembly. In comparison with athermal processes, this approach usually requires higher light intensities to generate sufficiently high temperatures. That said, due to limited molecular mobility, many photochemical events are stifled in rigid polymer matrices, so that a combination of photochemical and photothermal mechanisms may lead to significant synergies.

It also appears that many effects and (photo)chemistries have thus far been only explored in a handful of (specific) systems and adhesive types, although they may be more broadly exploitable. However, the field has matured to the point where the cross-fertilization between platforms and systems is starting to emerge. One might expect a coalescence between “adhesive-based” and “photochemistry-based” design approaches and this should eventually lead to a broad palette of photoresponsive adhesives that offer relevant bonding characteristics and efficient debonding with a minimum of (synthetic) complexity. It is already clear, however, that DoD concepts can be successfully translated into technical solutions and that optically debondable adhesives will play an increasingly important role in virtually all industrial sectors.

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Conflict of Interest

The authors declare no conflict of interest.

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adhesion, debonding on demand, optically switchable adhesives, photoresponsive polymers
