Soft Matter

COMMUNICATION

Light-Responsive Azo-Containing Organogels

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While azo compounds are widely employed as radical initiators, they have rarely been used as stimuli-responsive motifs in macromolecular constructs. In this study, an azo-based cross-linker was prepared and reacted with with poly(vinyl alcohol) to afford a series of stimuli-responsive organogels. Irradiation of these materials with UV light causes de-crosslinking and triggers a solid-to-liquid phase transition. Model adhesives with de-bonding-on-demand capability based on this design were explored.

Introduction

Polymer-based materials which change their properties in response to light as an external stimulus are promising candidates for a wide range of applications. The use of light-responsive materials has been explored as a means to control the release of cargo molecules,[1] for the preparation of photodegradable materials,[2] as well as in microrobotics,[3] conductive polymers,[4] and data storage applications.[5] Employing light as a stimulus holds the distinct advantage in that it can be rapidly and selectively applied, allowing for a spatial resolution that cannot (easily) be achieved by exposure to other stimuli.[6] The desired property changes on the macroscopic level are typically the result of reversible or irreversible structural rearrangements that occur on the molecular level when light-responsive chemical moieties interact with light of a suitable wavelength.[7] Numerous examples have been reported in which the light-triggered response of non-covalent interactions such as hydrogen bonds,[8] metal-ligand interactions,[9] or host-guest complexes was exploited.[10] When such supramolecular binding motifs are embedded in linear polymer chains or serve as cross-links in

polymer networks, the irradiation-induced cleavage of the non-covalent bonds can be used to reversibly alter the mechanical properties. Similarly, covalent motifs can furnish reversible responses upon activation through light and common derivatives that undergo changes of their conformation, polarity, and conjugation encompass diarylethenes,[11] spiropyrans,[12] azobenzenes,[13] or coumarins.[14] In addition to these reversible "switches", motifs that irreversibly change their structure are of particular interest when the aim is the preparation of materials that experience photo-induced phase changes,[15] or when controlled degradation is desired.[16]

Most examples of covalent functional groups that can be irreversibly cleaved are based on chemical structures such as esters, acetals, and disulfides, but their degradation mode relies on acidic or basic hydrolysis, thermal stimuli, or reducing agents.[17] Among the photolabile groups, *ortho*-nitroaryl derivatives represent a popular motif that has been frequently employed to equip linear polymer chains with photo-responsive properties.[16a, 18] In addition, nitroaryls have also been used as cleavable groups for the preparation of covalent photodegradable polymer networks.[19] When these labile chemical groups are employed as cross-links of a network, drastic changes of the mechanical properties are achieved upon irradiation, rendering these materials interesting candidates as responsive substrates that influence cellular growth,[19a, 19b] or as adhesives that can be de-bonded on-demand.[18f, 20] Compounds featuring azo-motifs, which are frequently employed as initiators in radical polymerizations,[21] can be readily cleaved thermally,[22] by irradiation with UV light,[23] or by mechanical forces.[24] Embedded in polymers, such derivatives have been frequently employed as macro-initiators for the synthesis of well-defined block-copolymers or for the preparation of thermally degradable materials.[25] More recently, some of us have reported the light-induced degradation of linear polymers that feature such azo-moieties in their backbone.[24b] Straightforward synthesis pathways (*i.e.*, step-growth polymerization reactions) using classical building blocks and a judiciously chosen azo precursor indeed allowed

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for the preparation of polymers in which degradation *via* chain scission can be induced by the cleavage of the azo-motifs. The propensity of this particular moiety to form stabilized radicals that have the tendency to react further instead of recombining was a key parameter.[24b]

Here we demonstrate the facile synthesis of a cross-linking reagent featuring a similar azo-motif that can be irreversibly cleaved by means of irradiation with UV light. Through the reaction of this cross-linker with poly(vinyl alcohol) (PVOH) a series of DMSO-based organogels was prepared (Fig. 1). This platform was inspired by earlier studies on covalently cross-linked organogels,[26] and was used here as a testbed to explore to what extent their properties can be moderated by UV irradiation. Gratifyingly, the approach allows access to materials in which a solid-to-liquid phase transition could be achieved by way of exposure to UV light. This effect was exploited for the preparation of model adhesives that were shown to display de-bonding-on-demand capability.[20a, 27] We envision that the approach can be used to equip a wide range of materials with desirable, light-responsive properties.

Results and Discussion

The light-responsive cross-linker **azo-CX** featuring an azo-motif was prepared in batch sizes on the order of 5 g from commercially available starting materials. Thus, 2,2'-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] was dispersed in a large excess of hexamethylene diisocyanate (HMDI) in the presence of a tin catalyst under nitrogen atmosphere; after

reaction overnight at ambient temperature, the product was isolated in a highly satisfying yield of over 95% and in an analytically pure form (NMR spectra, see Electronic Supplementary Information, ESI) by precipitating the reaction mixture into pentane (Fig. 1a, ESI).[28] The diisocyanate derivative thus obtained was employed as a cross-linking agent for the preparation of PVOH-based organogels with dimethylsulfoxide as the solvent (**azo-gel**, Fig. 1b). Selected corresponding non-cleavable materials cross-linked with HDMI, having a cross-linking density comparable to the one of the highly cross-linked **azo-gel** (10 mol%) were used for reference purposes (**ref-gel**).[26a] In order to investigate composition-property relationships, notably with respect to the stimuli-responsive behavior, a series of gels was made in which the weight-average molecular weight (M_w) of the PVOH was varied from 13-23 to 85-124 kDa (data from supplier), the cross-link density from 0.5 to 10 mol%, whereas the solid content was kept constant at ca. 15 wt% (Table 1, ESI Table S1). The cross-link density was calculated from the ratio of cross-linker isocyanate functions to the number of PVOH repeat units and is expressed throughout the manuscript in the units of mol %. Alternatively, it can be described by the frequency of cross-links (f_{CX}) or the molecular weight between cross-links (M_c), as summarized in ESI Table S1. The solid content of 15 wt% PVOH in DMSO was chosen based on the properties of gels reported in a previous study; lower solid contents afforded gels that were mechanically too weak to study, whereas a higher PVOH concentration led to an unpractically high viscosity of the DMSO-PVOH solution.[26a] The
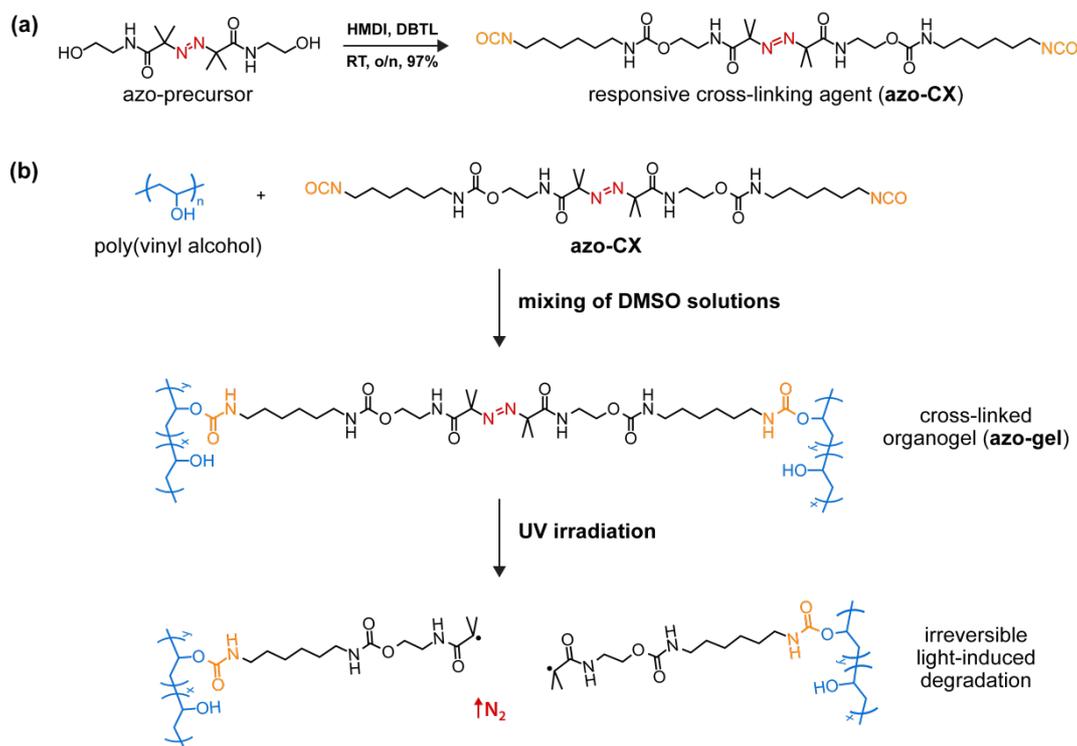

Fig. 1 (a) Synthesis of the azo-containing diisocyanate-based cross-linker (**azo-CX**) was achieved by the reaction of 2,2'-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] with hexamethylene diisocyanate. (b) Addition of this cross-linker to anhydrous DMSO solutions of poly(vinyl alcohol) led to the formation of azo-cross-linked organogels. The light-responsive cross-links were readily cleaved upon UV irradiation, resulting in the degradation of the organogels.

gels were prepared by combining the desired amounts of PVOH and **azo-CX** in anhydrous DMSO, homogenization by mechanical stirring, and curing overnight.

Table 1. Overview of the values for the Young's modulus (E) of azo-cross-linked gels (**azo-gels**) with cross-linking densities of 10, 5, and 2.5 mol% that were derived from compressive stress-strain measurements. The data represent averages of three experiments with standard deviations.

PVOH $(M_w)^a$	Cross-link density 2.5 mol%	Cross-link density 5 mol%	Cross-link density 10 mol%
kDa	kPa	kPa	kPa
85–124	9.2 ± 0.4	12.4 ± 0.1	38.1 ± 2.2
31–50	10.7 ± 0.6	15.4 ± 0.5	27.7 ± 2.1
13–23	n/a^c	n/a^c	9.5 ± 0.4

^{a}*Weight-average molecular weight (M_w), as provided by supplier.* ^{b}*Calculated based on the ratio of cross-linker isocyanate functions to the number of PVOH repeat units.* ^{c}*Not measurable, because the gels were too weak.*

under ambient conditions in a desiccator, either in glass vials/cuvettes or cylindrical poly(tetrafluoroethylene) (PTFE) molds. Complete consumption of the isocyanate moieties was confirmed by IR spectroscopy (ESI Fig. S1).

All organogels studied were clear and transparent, although the **azo-gels** with a high cross-link density featured a faint yellow hue, associated with the "tail" of the azo-motif's absorption band centered at 375 nm, as apparent from the comparison with the spectrum of the parent azo-precursor (ESI Fig. S2–S3). The UV/Vis spectra reveal that above 425 nm the transmittance of the **azo-gels** is comparable or even lower than that of the **ref-gels** and likely limited by scattering of gas bubbles trapped in the gels. The minimal cross-link density required for an effective gel formation was investigated for

Fig. 2 Tube inversion tests of the cross-linked gels (**azo-gels**) with PVOH of a weight-average molecular weight M_w of 31–50 kDa and cross-link densities between 0.5 and 10 mol% as well as a reference gel (**ref-gel**) with a cross-link density of 10 mol%. (a) Effective gelation was observed at cross-link densities of 0.6-10 mol%. (b) Irradiation of the **azo-gels** with UV light (30 s, 320–390 nm, 600 mW/cm^2) induced gas formation and a reduction of the gel strength, whereas the reference gel remained unchanged.

gels made with PVOH of an M_w of 31–50 kDa based on tube inversion tests. No flow was observed for a cross-link density of 0.6 mol% or higher (Fig. 2a). When the organogels were prepared in and released from cylindrical PTFE molds, they proved to be self-supporting if the cross-link density was 2.5 mol% or higher.

To elucidate the mechanical properties of the different gels, compressive stress-strain measurements were carried out with cylindrically shaped samples that were prepared with PVOH of different molecular weights and cross-link densities of 2.5 mol% or higher (note that in the case of gels made with PVOH of the lowest M_w of 13-23 kDa, mechanical testing was only possible for a cross-link density of 10 mol%, which was the only composition affording self-supporting gels). After applying a pre-load of 1 kPa, the specimens were compressed at a constant rate of 10 mm/min until breakage, which defined the yield point (*i.e.*, when any discontinuity of the curve was observed). The Young's modulus (E) was determined from the slope of the stress-strain curve in the strain range of 1-10%, *i.e.*, the linear regime. Within each series of organogels made with PVOH of a given molecular weight, E was found to increase with the cross-link density (Fig. 3a), for example from 10.7 ± 0.6 kPa (2.5 mol%) to 27.7 ± 2.1 kPa (10 mol%) in the case of **azo-gels** prepared with PVOH of a M_w of 31–50 kDa (Table 1). As expected because higher stiffness is reached, due to more extended networks formed with PVOH having longer chains than with shorter, the E' also increased with the M_w of the PVOH, for example in the series made with 10 mol% cross-links from 9.5 kPa (M_w = 13–23 kDa) to 38.1 kPa (M_w = 85–124 kDa) (Fig. 3b, Table 1). Generally, the compressive stress-strain measurements showed that the gels could be compressed to approximately 50% of their initial width, with higher compressibility values for samples featuring PVOH of higher molecular weight and a lower cross-link density (ESI Table S2).

We demonstrated previously that a large fraction of similar azo residues incorporated in the backbone of linear polyurethanes could be irreversibly cleaved by UV irradiation, but some of the radicals produced were found to re-combine, especially in the solid state.[24b] Thus, it was not *a priori* clear to what extent the present **azo-gels** could be disassembled upon exposure to UV light. Comparison of the ^{1}H NMR spectra of **azo-CX** in anhydrous DMSO-d$_6$ before and after UV irradiation indeed indicate that only a minor fraction of the radicals re-combines (< 10%), while the largest fraction undergoes disproportionation (ESI Fig. S4).[24c] A first set of experiments was conducted with samples of **azo-gels** made with PVOH of a M_w of 31-50 kDa with a cross-link density of 10 mol%, a composition selected as model for several experiments because of the high content of azo-moieties (*i.e.*, for maximizing the light-responsiveness) with respect to the ease of their preparation (*i.e.*, potential viscosity as an issue, *vide supra*). When macroscopic samples (*ca.* 5 × 5 × 5 mm^3) cut from these gels were irradiated with UV light (320–390 nm, 600 mW/cm^2) for 30 s, significant foaming occurred and the material softened substantially (ESI Fig. S5), whereas samples of the corresponding reference gel did not show any response
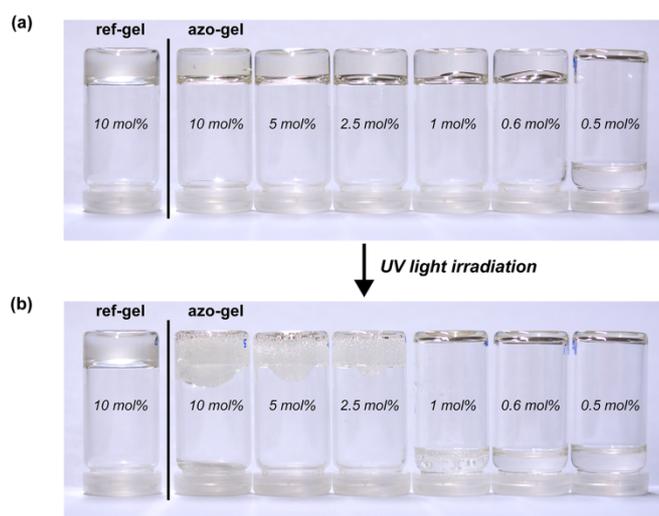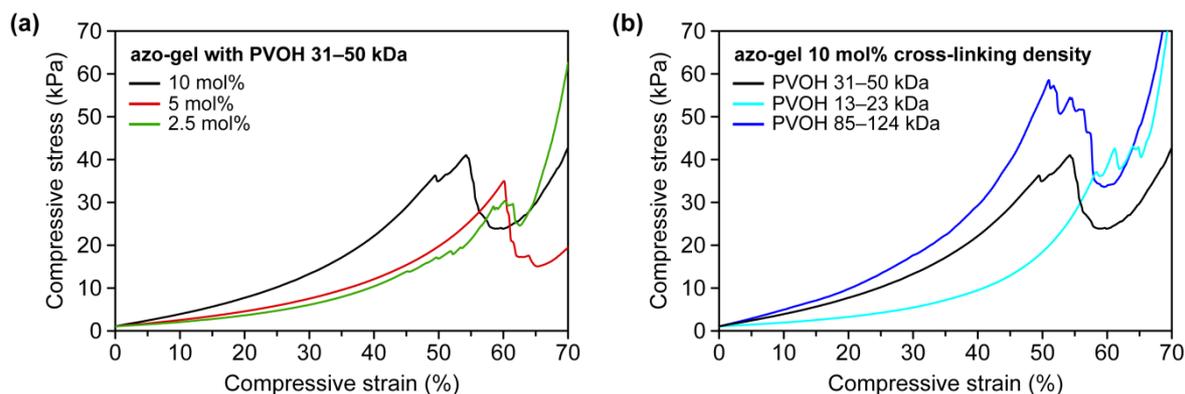
Fig. 3 (a) Compressive stress-strain measurements of azo-cross-linked gels with PVOH of 31–50 kDa and cross-link densities of 2.5 (green), 5 (red), and 10 mol% (black). (b) The measurements of organogels with PVOH with molecular weights of 85–124 (blue), 31–50 (black), as well as 13–23 kDa (cyan) and a cross-link density of 10 mol%. The depicted stress-strain measurements are representative runs of three replicates.

when exposed to the same conditions (ESI Fig. S6). Monitoring the sample temperatures during UV irradiation with an IR camera revealed a temperature increase of *ca.* 30 °C in the case of the **azo-gel**, whereas much more moderate heating was detected for the **ref-gel** (*ca.* 10 °C) (ESI Figs. S5–S6). The larger temperature increase observed in samples containing the azo-motif can be explained by the exothermic nature of the decomposition of the employed cross-links.[22] Since the 10 h half-life temperature of the azo-precursor used is 86 °C (supplier information), the rapid degradation of the **azo-gels** is a first indication of the fact that the dissociation process is primarily light-, and not thermally induced.

In subsequent experiments that involved again **azo-gels** made from PVOH with an M_w of 31–50 kDa, the cross-link density was varied and the response to UV exposure was tested using tube inversion tests (Fig. 2b). Gratifyingly, **azo-gels** made with a cross-link density of 0.6 or 1 mol%, *i.e.*, slightly above the concentration where gelation is achieved, show a UV-light-induced solid-to-liquid phase transition (Figs. 3b, 4a). When samples of higher cross-link density were irradiated, the gel-state was lost and highly viscous materials were obtained.

Accordingly, self-standing cylinders or cubic samples of all **azo-gels** made with PVOH of 31-50 kDa completely lost their shape upon UV irradiation, presumably due to the combined effects of foaming and the loss of cross-links (Fig. 2b, ESI Fig. S5). The cleavage of the cross-links was subsequently investigated by means of dynamic light scattering (DLS). The comparison of the intensity auto-correlation functions obtained by DLS for an **azo-gel** made with PVOH of an M_w of 31-50 kDa and having the lowest cross-link density possible (*i.e.*, 0.6 mol%) before and after UV irradiation indicates a significant increase of Brownian dynamics for the irradiated material (Fig. 4b). This particular composition was chosen because it was expected, based on the tube inversion tests (Fig. 2), to reveal by DLS the higher contrast in mechanical properties between the pristine and irradiated states. These results confirm significant changes of the properties of samples of the **azo-gel** after brief exposure to UV light, corroborating the successful and extensive cleavage of the cross-links featuring the azo-motifs. Moreover, a comparison of the kinetics of the decomposition of the parent azo-motif with dose dependent measurements of the time to reverse gelation in tube inversion tests indicates that the solid-
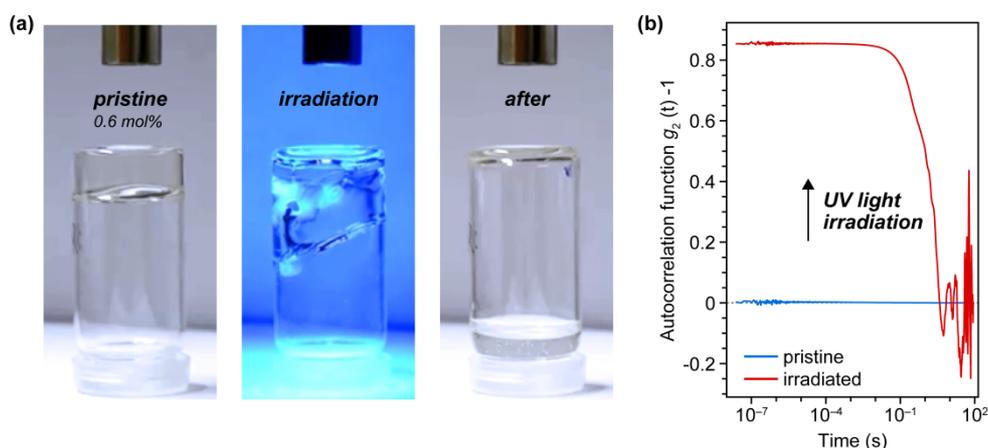

Fig. 4 (a) Pictures showing the phase transition that occurs upon irradiation of an azo-cross-linked PVOH gel (**azo-gel**) made with PVOH of 31-50 kDa with a cross-link density of 0.6 mol% with UV light (30 s, 320–390 nm, 600 mW/cm²). (b) Comparison of representative intensity auto-correlation functions measured by dynamic light scattering at 30° for the pristine and irradiated **azo-gel** (PVOH of 31-50 kDa and cross-link density of 0.6 mol%). The pristine sample does not show any correlation indicating negligible Brownian dynamics. After irradiation, scattering is observed, corroborating the cleavage of cross-links and degradation of the network.

to-liquid phase transition already occurs prior to a complete degradation of all azo-based cross-links (ESI Figs. S7–S8).

The cleavage of the cross-links in the **azo-gels** could also be achieved through excitation of the azo-motifs at their absorption edge with light in the visible range.[24b] This was demonstrated by exposure of a model **azo-gel** (*i.e.*, PVOH of 31-50 kDa and cross-link density of 10 mol%) to light in the wavelength range of 390–500 nm (600 mW/cm^2), which also led to foaming, softening, and viscous flow (ESI Fig. S9). On account of the lower absorbance the process was slower. Moreover, it was possible to achieve dissociation of the cross-links in the **azo-gels** using low-power-density UV irradiation. Thus, when irradiated with UV light of a wavelength of 365 nm and a power density of only 1 mW/cm^2 (ESI Fig. S10), the transformation of an **azo-gel** (same composition) was gradual and took place over the course of two hours.

The fast and irreversible cleavage of the cross-links in the present PVOH-based **azo-gels** through irradiation with UV light led us to use them as models of adhesives that can be rapidly de-bonded by application of an external stimulus. Thus, lap joints of glass were prepared with **azo-gels** made with the three different PVOH grades (M_w = 13–23, 31–50, 85–124 kDa) and a cross-link density of 10 mol%. The glass slides were bonded by applying two drops of the respective reaction mixture to one of the substrates before it was joined with another one under application of light pressure and cured overnight. The mechanical properties of such lap joints with bond areas of 15 × 25.8 mm^2 were subsequently investigated by shear strength tests (Fig. 5a). The highest shear strength of 26.3 ± 2.9 kPa was measured for lap joints prepared with **azo-gels** made from PVOH of a weight-average molecular weight of 31–50 kDa (ESI Table S3). While gels prepared with the higher molecular weight PVOH were expected to show improved adhesive characteristics, they displayed an inferior performance. This was presumably due to the high viscosity of

the mixture obtained after homogenization, which was difficult to process these materials in a reliable fashion. Since the gels made with the PVOH having the lowest M_w additionally exhibited lower adhesion, all subsequent tests of these adhesive models were therefore performed with PVOH of 31–50 kDa and a cross-link density of 10 mol%.

Lap joints prepared with these gels were indeed found to be stable over extended periods of time under ambient conditions; even if a load of 200 g (1.96 N, 5.1 kPa) was applied, bonds were stable for a period of more than six months (Fig. 5b). Moreover, lap joints with bond areas of 15 × 25.8 mm^2 could be loaded horizontally with a weight of 50 g (applied force of 0.49 N) and the connection was found to be stable over the course of days (Fig. 5c) until the test was stopped. The stability of these connections was rapidly altered upon exposure to UV light. Thus, de-bonding by cohesive failure was observed upon irradiation of loaded joints within 34 s of irradiation with 320-390 nm light at 600 mW/cm^2 (Fig. 5c, Supplementary Movie M1). The temperature increase of the adhesive lap joints was monitored with an IR camera and found to be significantly lower than that observed in the bulk organogels. Thus, the increase was limited to 2 °C when the adhesive lap joints were de-bonded by UV irradiation (ESI Fig. S11), supporting that the UV-light induced cleavage of the azo motifs is indeed photochemically, and not photothermally driven. While similar adhesive properties were obtained when investigating the **ref-gel** organogels, no de-bonding was observed when irradiating with UV light (data not shown).

Conclusions

We have demonstrated the straightforward synthesis of a cross-linking agent that features an azo-motif that can be irreversibly cleaved by means of UV irradiation. The reaction of this cross-linker with poly(vinyl alcohol) was employed for the
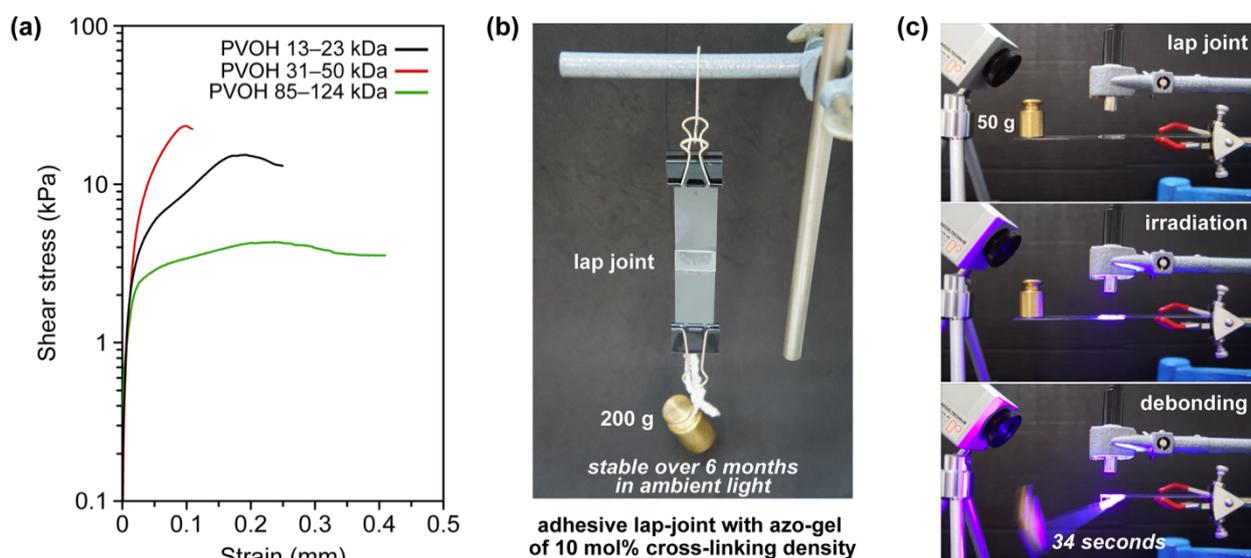

Fig. 5 (a) Shear strength tests of lap joints bonded with azo-cross-linked PVOH organogels (**azo-gels**, cross-link density of 10 mol%) made with different types of PVOH, 13-23 kDa (black), 31-50 kDa (red), and 85-124 kDa (green). The depicted stress-strain measurements are representative runs of three replicates. (b) Photograph showing a lap joint that was found to be stable under load over the course of months (**azo-gel**, PVOH 31–50 kDa, 10 mol% cross-link density). (c) An adhesive lap joint made with an azo-cross-linked PVOH gel (**azo-gel**, PVOH 31–50 kDa, 10 mol% cross-link density) displays light-induced de-bond-on-demand behavior. A weight of 50 g was deposited on top of the lap joint and de-bonding occurred within 34 s of irradiation (320-390 nm, 600 mW/cm^2).

preparation of a series of DMSO-based organogels. The light-responsive nature of the cross-links was then exploited to successfully alter the properties of the organogels by UV irradiation. Thus, carefully choosing the composition of the organogels allowed triggering a solid-to-liquid phase transition upon exposure to UV light. While slower, irradiation with visible light was also found to dissociate the organogels. This effect was exploited for the preparation of pressure-sensitive adhesives models that de-bond in response to light. Thus, adhesive lap joints were found to be stable over the course of months, while UV irradiation for seconds sufficed to successfully de-bond. Hence, we have developed a novel responsive cross-linking agent that can be readily employed for the preparation of light responsive organogels and de-bond-on-demand adhesives. This may be utilized for the preparation of light responsive materials with desirable properties, and particularly materials that respond to irradiation with light of the visible spectrum could be interesting candidates for degradable gels that serve as a medium for the growth of biological materials.

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