Dynamic Covalent Chemistry

International Edition: DOI: 10.1002/anie.201605311
German Edition: DOI: 10.1002/ange.201605311

Control of Imine Exchange Kinetics with Photoswitches to Modulate Self-Healing in Polysiloxane Networks by Light Illumination

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Abstract: *Various aldehyde-containing photoswitches have been developed whose reactivity toward amines can be controlled externally. A thermally stable bifunctional diarylethene, which in its ring-closed form exhibits imine formation accelerated by one order of magnitude, was used as a photoswitchable crosslinker and mixed with a commercially available amino-functionalized polysiloxane to yield a rubbery material with viscoelastic and self-healing properties that can be reversibly tuned by irradiation.*

Supramolecular and macromolecular systems that are able to structurally respond to changes in their environment can be realized by the introduction of reversible linkages on the molecular level[1,2] based on either noncovalent interactions[3] or dynamic covalent bonds.[4] The latter allow for strong yet reversible connections between building blocks leading to constitutional adaptation.[5] Among the most attractive stimuli to trigger a material's response is light,[6] as it can be applied in an external, noninvasive fashion with high spatial and temporal resolution. There are several ways in which light can control the connection or disconnection of molecular building blocks, involving photodissociation[7] and (retro)-photodimerization[8] as well as photoisomerization of substrates and/or products in thermal cycloadditions.[9] In all of these cases the photoreaction is directly linked to the (reversible) covalent bond formation/scission, leading to a significant limitation of the substrate scope.

In an attempt to truly separate the primary photoevent from the covalent (thermal) reaction in the most widely applicable sense, we sought to modulate the electrophilicity of a carbonyl compound, which is known to engage in dynamic covalent imine (hydrazone, oxime etc.) exchange reactions,[10] by light irradiation. This particular connection was chosen as it operates under ambient conditions (room temperature, air, and humidity) without a catalyst[11] and involves highly abundant (aliphatic) amine nucleophiles in combination with aldehydes, which should allow for convenient tuning of their electrophilicity by photoisomerization reactions.[12] Herein, we describe how light can control the kinetics of general imine exchange reactions. To demonstrate the applicability of our approach, a photoswitchable dynamic covalent crosslinker was used to modulate the self-healing ability of a polymer network after illumination with UV and visible light.

Our initial work focused on the design of a photoswitch, which can be used to modify the reactivity of an appended aldehyde group (Figure 1a). For this purpose we have prepared and studied aldehyde-functionalized photoswitches[13,14] belonging to the three most commonly used photochromic families: spiropyran **SP**,[15] azobenzene **AB**,[16] and diarylethene **DAE** (Figure 1b).[17] Upon illumination with UV light, these specific photoswitches are readily converted to their corresponding isomers, which display an enhanced carbonyl group reactivity[12] and can be returned to their less reactive forms by exposure to visible light and/or heat. The mechanism of modulating the carbonyl reactivity differs among the three designed photoswitches: On the one hand, photoisomerization of **ABt** and **SP** unmasks an activating *ortho*-hydroxyl group[18] in **ABc** and [**MC**-H]$^+$, respectively. On the other hand, the ring-open **DAEo** bears two cross-conjugated and hence decoupled thiophene moieties and can be converted to the ring-closed **DAEc**, in which π-conjugation of both electron-withdrawing terminal formyl groups leads to their synergistic activation.

The difference in reactivity of the aldehyde electrophiles in all three pairs of photoisomers was investigated in a condensation reaction with different amine-based nucleophiles. The **AB** and **SP** derivatives were treated with pyridine-4-carbohydrazide, and the formation of the corresponding acylhydrazones was monitored by UV/Vis absorption spectroscopy. Upon continuous illumination, leading to the formation of the photoisomers **ABc** and [**MC**-H]$^+$, the condensation rates were significantly higher than those of the corresponding nonirradiated samples composed solely of **ABt** or **SP**. In the case of **AB**, the rate of the condensation is increased by a factor of 2.4 in the photostationary state (PSS, see Figure S1 in the Supporting Information), containing ca. 22% of the *cis* isomer (thermal half-life $t_{1/2} \approx 3.5$ min under these conditions). For **MC**, despite the extremely low photoconversion in the PSS (thermal half-life of a few seconds under these conditions), the rate of condensation is enhanced by a factor of 3.1 (see Figure S2 in the Supporting Information). In stark contrast, **DAE** is truly bistable and can be switched almost quantitatively and exclusively back and forth by light irradiation.

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Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201605311.

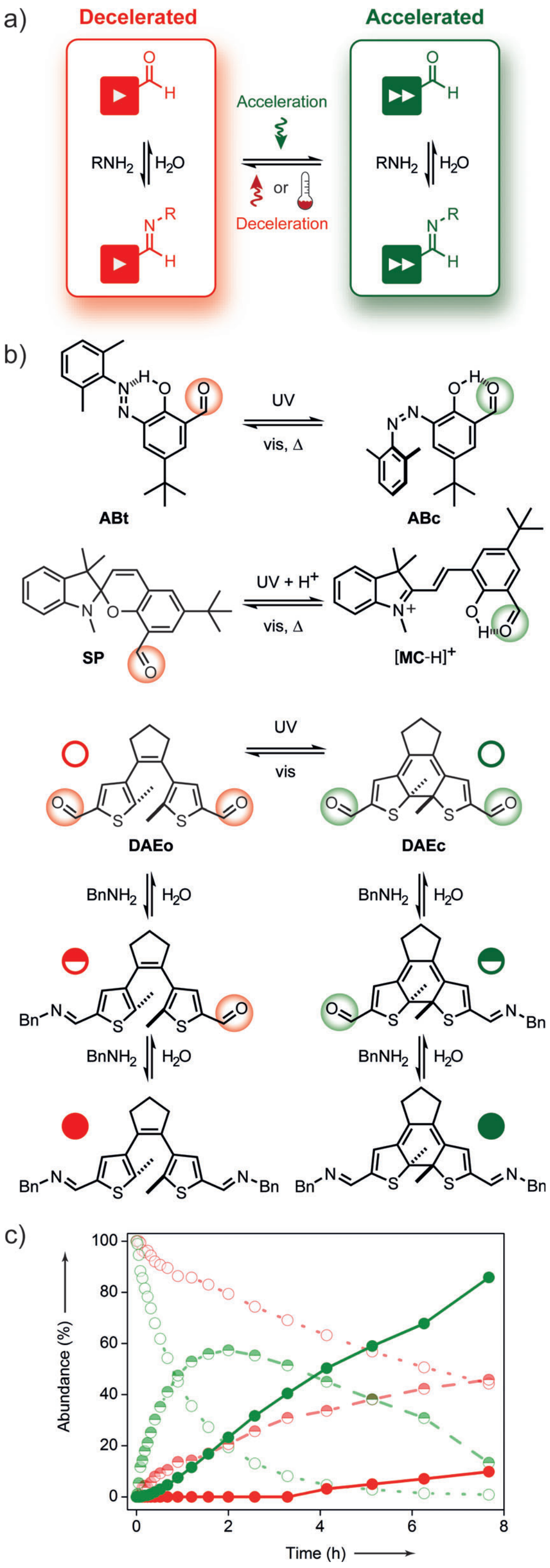

Figure 1. a) Upon illumination, an aldehyde functionality coupled to a photochromic moiety can be switched between less reactive, decelerated and more reactive, accelerated forms (represented by red "play" and green "fast-forward" signs, respectively). b) Realization of reactivity differences using different photochromic systems based on *E*/*Z*-configured azobenzene **AB**, spiropyran/merocyanine **SP**/**MC**, and open/closed diarylethene **DAEo**/**DAEc**. Condensation of the two **DAE** isomers with benzylamine yields the mono- and bis-imines. c) Experimental kinetic profiles for the conversion of dialdehydes (open circles) to the mono-imines (half-solid circles) and bis-imines (solid circles) in the case of the decelerated **DAEo** (red) and the accelerated **DAEc** (green), showing bis-imine formation to be approximately ten times faster with **DAEc**.

The condensation of nonilluminated and illuminated samples containing **DAEo** and **DAEc** (≈95% in the PSS) with two equivalents of benzylamine was followed by NMR spectroscopy (see Figure S3 in the Supporting Information). A key finding is that the thermally stable diarylethene photoswitch—resembling the structural motif of a crosslinker—allows for light-controlled modulation of the bis-imine formation rate by one order of magnitude (Figure 1c).

To exploit this reactivity difference and to demonstrate the potential of our concept, we used difunctional **DAE** as a crosslinker to modulate the adaptive bond formation in a dynamic covalent polymer network.[2,19] Employing the photoswitchable component in only small amounts minimizes the optical density of the material to ensure efficient photoisomerization while maximizing light response. We chose a commercially available, transparent, and amino-functionalized siloxane copolymer (**AS**) with a low glass transition temperature (T_g) and mixed it with the **DAE** crosslinker (ca. 5 wt%) to yield the viscoelastic polymer network **DAE@AS** (see Movie 1 in the Supporting Information). Importantly, the crosslinker was introduced in substoichiometric amounts, that is, only about 30% of the amino groups of the **AS** polymer are actually linked to the aldehyde moieties of **DAE**, in order to retain an excess of available amines (no free aldehyde moieties can be detected by NMR spectroscopy; see Figures S19–S21 in the Supporting Information).

Irradiation of thin films of **DAE@AS** with UV ($\lambda_{irr}=313$ nm) and visible ($\lambda_{irr}=546$ nm) light induces ring-closure (ca. 95% **DAEc** in the PSS) and ring-opening (>95% **DAEo** in the PSS) as determined by UV/Vis absorption spectroscopy, proving that the photoswitching ability of **DAE** is maintained in both directions when it is covalently embedded in the polymer network (see Figure S6 in the Supporting Information). For optimization and comparison purposes, a photoinactive polymer network **T@AS** with terephthaldehyde (**T**) as the crosslinker was prepared and studied as a reference.

Imine bonds are intrinsically labile towards water. This important feature is nicely reflected by water contact angle measurements of **T@AS**, which show a rapid decrease of contact angles within tens of seconds (see Figure S7 in the Supporting Information), indicating that the surface of the polymer network is (at least partially) hydrolyzed. This effect can even be enhanced by addition of a more potent nucleophile, such as hydroxylamine. These results suggest that the temporary scission of the imine bonds leads to the formation of reactive aldehydes on the surface of the polymer network, due to the unavoidable presence of water under ambient conditions, and this plays a crucial role when the material is damaged: If damaged areas are in close contact to each other, condensation reactions between free amino and aldehyde functionalities establish new imine crosslinks, thereby replacing broken connections between the polysiloxane chains (Figure 2a, see also Figures S13 and S14 in the Supporting Information).

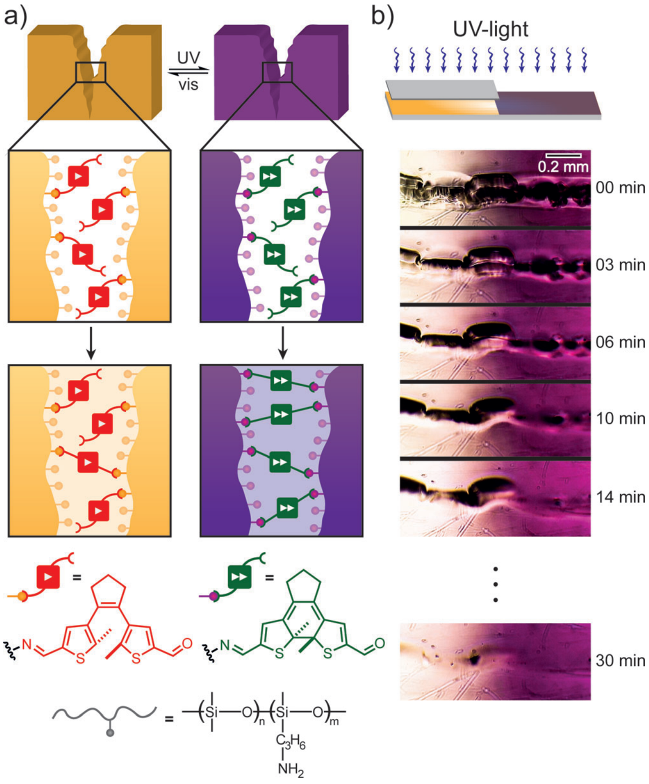

Figure 2. a) Schematic representation of damaged **DAE@AS**: The self-healing of **DAEc@AS** (purple, right) is accelerated compared to that of **DAEo@AS** (yellow, left) due to the higher reactivity of the crosslinker in the ring-closed form. b) Self-healing properties of **DAEo@AS** (yellow, left) and **DAEc@AS** (purple, right) in a damaged polymer film.

To visualize this exchange of imine bonds in the dynamic polymer network, we followed the self-healing process of the material with an optical microscope after we had damaged a drop-cast film having a masked (**DAEo@AS**, yellow) and illuminated (**DAEc@AS**, purple) area (Figure 2b, see also Figure S25 in the Supporting Information). Much to our delight, the damage in photoactivated **DAEc@AS** (Figure 2b, right) heals faster than in nonilluminated **DAEo@AS** (Figure 2b, left), yet extended self-healing times result in damage repair in both areas. This illustrates that UV light provides a tool to locally accelerate self-healing while visible light allows for deceleration, as the dynamic covalent exchange is an inherent, yet remotely tunable characteristic of the material. Note that intrinsic self-healing can only take place in polymers with a sufficient degree of fluidity, associated with some residual amount of creep in our materials (see Figure S10 in the Supporting Information).

Encouraged by these initial results, we investigated the autonomous mending of macroscopic **DAE@AS** blocks in the two different switching states. Strain compression and tensile tests (see Figure S9 in the Supporting Information) were performed[20] to quantify the mechanical strength of the materials, providing information about the rate at which the self-healing processes take place in the bulk (Figures 3a,b). The healing efficiency (defined as HE = 100% $\cdot S_h/S_i$, where S_h is the strength of the healed material and S_i is its initial strength) was determined after given time intervals. Polymer monoliths, prepared from **AS** by mixing with either **DAEo** or **DAEc** crosslinker, were cut into two pieces and brought into contact for the given amount of time. The healed blocks were then compressed until the applied stress led to rupture of the material (S_h). The same was done for the intact polymer to determine the initial strength (S_i). After 30 min the healing efficiency of **DAEc@AS** was (40 ± 4)%, whereas **DAEo@AS** showed a healing efficiency of only (10 ± 3)%. Full recovery of the mechanical strength for **DAEc@AS** was observed after two hours, while **DAEo@AS** regained only (54 ± 17)% of its initial strength in this time and was able to fully heal after a period of 5 h (Figure 3c, see also Figure S8 in the Supporting Information).

Furthermore, rheological measurements were performed to determine the storage modulus (G') and the complex viscosity ($|\eta^*|$) of both polymer forms (Figure 3d). The G' value increased by a factor of 2.8 in the case of **DAEc@AS** (10.4 kPa) compared to **DAEo@AS** (3.7 kPa).[21] Importantly, and somewhat counterintuitively, harder **DAEc@AS** regenerates its full mechanical strength faster than its softer analogue **DAEo@AS**. We attribute this finding to the enhanced chemical reactivity of the ring-closed crosslinker that outperforms its ring-opened counterpart despite slower diffusion.

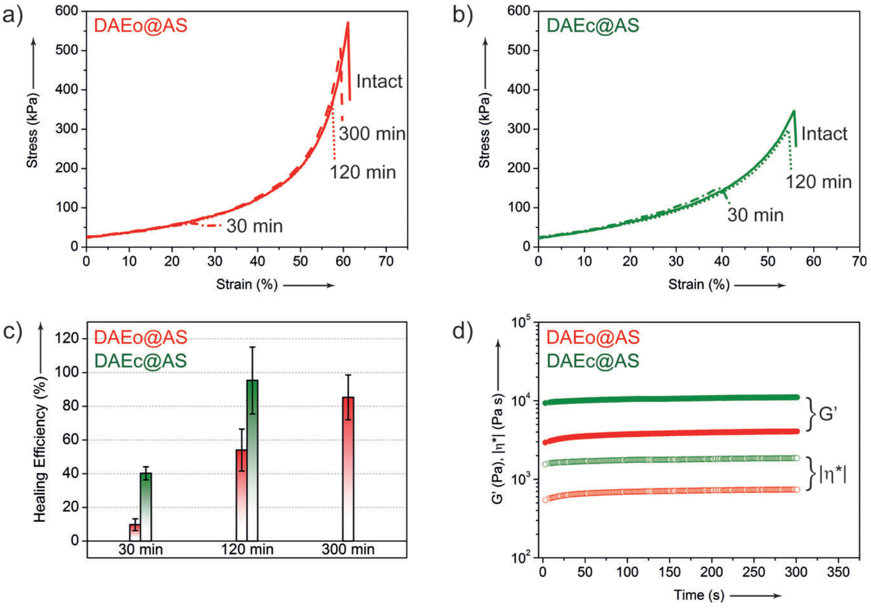

Figure 3. a,b) Representative stress–strain curves of a) **DAEo@AS** and b) **DAEc@AS** obtained from compression tests. c) Healing efficiencies (HE) of **DAEo@AS** (red) and **DAEc@AS** (green) (Figures S8). d) Storage modulus (G', solid circles) and complex viscosity ($|\eta^*|$, open circles) of **DAEo@AS** (red) and **DAEc@AS** (green) during time sweep at a fixed angular frequency and strain ($\omega = 1$ Hz, $\gamma = 0.1$%).

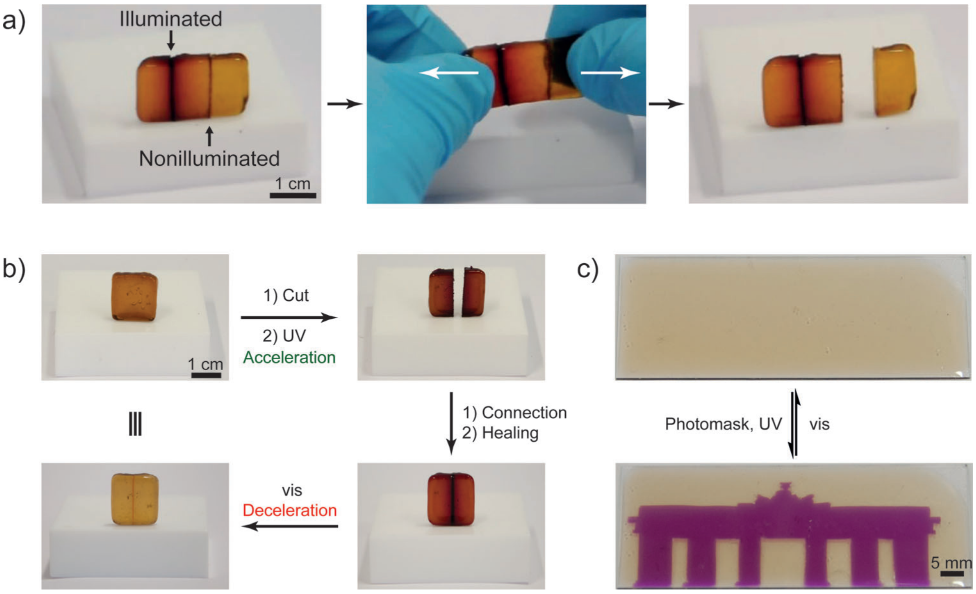

Figure 4. a) Reassembly of three polymer pieces, with illuminated and nonilluminated cut surfaces (left). After 30 min both ends were pulled evenly (middle). The contact between the nonilluminated pieces ruptures before that between two illuminated surfaces (right). The entire sequence was carried out under ambient conditions. b) Individual steps of a complete light-modulated self-repair cycle. Remaining streak is due to residual **DAEc** crosslinker. c) Picture of the Brandenburg Gate generated in a film of **DAEo@AS** using a simple photomask and a standard laboratory UV lamp ($\lambda_{irr} = 366$ nm).

Beyond self-healing, the local modulation of reactivity by light irradiation can be used for the directed construction with polymer building blocks. Upon UV illumination of a given area, a building block can be activated and is thereby rendered "sticky" for attachment to another building block.[22] After establishing the necessary new covalent connections between both activated polymer building blocks, illumination with visible light locally deactivates the material and finalizes this light-modulated connecting process. To illustrate this, a polymer monolith composed of **DAEo@AS** was cut into three equally sized pieces and two of the cut faces were illuminated with UV light ($\lambda_{irr} = 366$ nm) for 10 min. Contacting the faces (the two illuminated and the two nonilluminated ones) for 30 min and subsequently pulling on both ends led reproducibly to the rupture of only the nonilluminated contact area (Figure 4a, see also Movie 2 in the Supporting Information). After a full self-repair cycle, consisting of UV activation of the cut surfaces, their reconnection and self-healing, and finally deactivation by visible light, the initial polymer piece can be restored with practically no visible scar (Figure 4b, see also Figure S11 in the Supporting Information).

To further advance the practicality of our system we tested the responsiveness of the material to common light sources. When **DAEo@AS** is exposed to sunlight (ca. 100,000 lux), it switches to the activated form **DAEc@AS** within one minute. When a cut-off filter ($\lambda_{irr} \geq 400$ nm) or a standard energy-saving light bulb (11 W; see Figure S11 in the Supporting Information) is used, the polymer can be switched back to generate **DAEo@AS** (see Movie 3 in the Supporting Information). This shows that everyday light sources can be used to generate specific reactive patterns in the material, as demonstrated by creating a miniature model of the Brandenburg Gate in a film of **DAEo@AS** (Figure 4c). Moreover, different polymer building blocks with distinct properties, such as specific emission due to blending with fluorescence dyes, can be merged in the top-down construction of more complex freestanding structures (see Figure S12 in the Supporting Information), without the need for a freshly cut surface[3a] or continuous irradiation.[3c] We want to emphasize that our approach bestows adaptiveness and photoresponsiveness upon conventional materials through the use of only minor amounts of a small-molecule photoswitchable crosslinker in combination with a commodity polysiloxane and common light sources, such as sunlight. Our system, made from these two components only (and no further additives), autonomously heals at ambient conditions and requires no continuous input of energy. The properties of the resulting sustainable material, including texture, color, and self-healing ability, can be modulated at will using a light stimulus, that is reversibly stored as information in the polymer and controls the local exchange dynamics. Thereby, light allows for the local acceleration of exchange kinetics and amplification of intrinsic material properties in a permanent yet reversible fashion. We anticipate that our universal approach to control the kinetics of a reversible covalent reaction in combination with our straightforward and highly versatile route will contribute to the development of custom-tailored dynamic covalent materials and autonomously adaptive systems. Current efforts in our laboratories are focused on designing improved photoswitches that allow for complete removal of residual reactivity in the decelerated state by switching between a "dynamic" and a "static" state, to establish true on–off behavior and avoid creep in the non-activated "static" form.

Acknowledgements

We are indebted to E. Lorenz, T. Garchow, K. Brademann-Jock, and P. Fengler for help with the mechanical measurements, to J. Schwarz for scaling up the synthesis of the photoswitchable crosslinker, and to Dr. A. Goulet-Hanssens as well as Dr. D. J. van Dijken for fruitful discussions. Generous support by the European Research Council (via ERC-2012-STG 308117 "Light4Function") as well as the

German Research Foundation (DFG via SFB 765) is gratefully acknowledged.

Keywords: adaptive materials · diarylethenes · dynamic covalent chemistry · photochromism · self-healing

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Received: May 31, 2016

Communications

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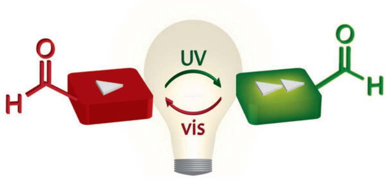

Illuminating dynamic covalent chemistry! A photoswitch, which makes it possible to modulate the reactivity of aldehyde functionalities by light irradiation, was developed to control the exchange kinetics in a dynamic imine-based polysiloxane network. In this way soft materials were obtained with remote control over their intrinsic properties, most notably their ability to self-heal.