CHEMISTRY OF MATERIALS

Subscriber access provided by UNIV OF NEWCASTLE

Article

Rapid, photo-mediated healing of hexaarylbiimidazole-based covalently cross-linked gels

Dowon Ahn, Scott R. Zavada, and Timothy F Scott

Chem. Mater., **Just Accepted Manuscript** • DOI: 10.1021/acs.chemmater.7b02640 • Publication Date (Web): 24 Jul 2017

Downloaded from http://pubs.acs.org on July 24, 2017

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

ACS Publications

Chemistry of Materials is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Rapid, photo-mediated healing of hexaarylbiimidazole-based covalently cross-linked gels

Dowon Ahn,† Scott R. Zavada,† and Timothy F. Scott*,†,‡

† Macromolecular Science and Engineering, University of Michigan, Ann Arbor, MI 48109, United States

‡ Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, United States

ABSTRACT: The intrinsic healing of covalently cross-linked polymer networks is commonly effected *via* the utilization of backbone-borne functional groups able to reversibly cleave or rearrange, thereby enabling mixing and co-reaction of network strands that bridge contacted interfaces; however, such materials often exhibit slow healing rates and are susceptible to creep under load. To address these deficiencies, we incorporated hexaarylbiimidazole (HABI) functionalities, groups that are homolytically cleavable to yield relatively low reactivity lophyl radicals under UV or visible light irradiation and which, in the absence of light, spontaneously recombine without significantly participating in deleterious side reactions, into the backbone of poly(ethylene glycol)-based polymeric gels. Whereas the network connectivity of these HABI-incorporating gels was stable in the dark, they exhibited significant creep upon irradiation. The influence of swelling solvent on the reaction kinetics of backbone-borne HABI photolysis and lophyl radical recombination were examined and revealed that gels swollen with 1,1,2-trichloroethane (TCE) exhibited higher radical concentrations than those swollen with either acetonitrile or water under equivalent irradiation conditions, attributable to the relative solvent affinity for the hydrophobic HABI functionalities affording more rapid HABI cleavage and slower radical recombination rates in TCE than in water. The fastest healing rates for cleaved samples brought into contact and irradiated with visible light was observed for TCE-swollen gels, although rapid restoration of mechanical integrity was achieved for gels swollen with any of the solvents examined where tensile strengths approached those of the pristine materials after 1 to 3 minutes of light exposure.

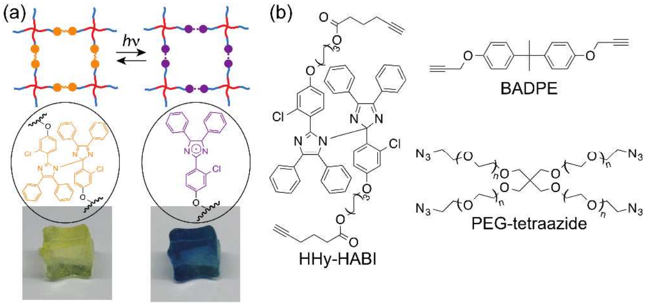
INTRODUCTION

Significant research attention has been devoted towards reversible crack-healing and autonomic healing of cross-linked polymeric matrices in recent years owing to the potential for successful implementations to yield tremendous improvements in reconfigurability, longevity, and reliability of these materials.[1-3] To date, crack-healing approaches in covalently cross-linked polymers typically utilize either systems that incorporate non-load bearing, liquid-filled inclusions, such as capsules or channels, whose contents flow upon rupture and polymerize *in situ* to bridge the flaw interfaces,[4-6] or that incorporate dynamic covalent functional groups, moieties able to be rearranged or reverted back to their constituent reactants under specific reaction conditions, in their backbone to effect transient depolymerization or bond rearrangement.[7] Unfortunately, despite their utility, the incorporation of continuously-active dynamic covalent chemistries in the network strands of a cross-linked polymer often results in creep under mechanical loads at ambient temperature,[8-12] a significantly deleterious trait for stress-bearing materials. Additionally, the healing rates typically exhibited by these materials are relatively slow, where the healing processes proceed over the course of hours to days.[11-14] More desirable would be the incorporation of a dynamic chemistry that only proceeds upon application of a specific stimulus, mitigating the potential for creep. Moreover, achieving intrinsic crack healing in cross-linked polymers necessitates not only bond rearrangement, but the rearrangement reaction should ideally occur on a sufficiently long timescale to allow segmental diffusion and mixing to quickly bridge the fracture surfaces and effect rapid healing of the damaged region.

A commonly employed stimulus to afford an intrinsic healing ability in cross-linked polymers is heat, where the incorporation of thermally-reversible adducts in network strands provides a mechanism for bond cleavage and rearrangement at raised temperatures which, if above the material's glass transition temperature, concurrently affords the molecular mobility necessary to bridge defects and effect healing.[15] Although the typically poor spatial and temporal reaction confinement of this healing stimulus can be addressed in part by photothermal heating,[16, 17] enabling heating to be confined to the vicinity of the defect in the polymer network, intolerance of the raised temperatures necessary for bond rearrangement in these materials precludes their consideration for many applications.[18] In contrast, the incorporation of functional groups that undergo triggered, reversible cleavage or bond rearrangement reactions at ambient temperatures would afford healable materials with broader utility.

Unlike thermoreversible networks, photoreversible networks only undergo bond rearrangement upon irradiation, otherwise exhibiting little to no creep or adaptation in the absence of irradiation. Furthermore, photochemical approaches enable three-dimensional spatial control of the healing reaction as well as the ability to remotely trigger a process on and off. Several approaches to photochemically triggered rearrangeable polymer networks have been developed, including photoinduced cyclization and photo-mediated metathesis, among other reactions.[19, 20] The photocyclization reactions, exhibited by functional groups such as cinnamate,[21, 22] coumarin,[23-25] and anthracene[26, 27] derivatives, exhibit limited relative response rates as at most a single cross-link is reversibly broken for each absorbed photon at relatively low quantum yields,[28, 29] and require irradiation at ultraviolet (UV) wavelengths to realize both the forward and reverse reactions.[30] Conversely, photo-mediated metathesis reactions are effected in covalently cross-linked polymer networks by incorporating functional groups which undergo a network rearrangement cascade, such as disulfides,[31] thiuram disulfides,[13] allyl sulfides,[32, 33] and trithiocarbonates,[34] where multiple reversible bond breaking and re-forming reactions occur for each absorbed photon.[33] However, as the chain transfer mechanism does not afford any significant fraction of network strands being cleaved at a given instant,[32, 33] this approach again results in sluggish healing rates[13, 34] owing to limited segmental diffusion. Several other reactions employed for the photo-mediated repair of cross-linked polymers include the photodissociation of alkoxyamine groups,[35] radical-mediated polyurea-to-polyurethane conversion in oxetane- and oxolane-substituted chitosan-polyurethane networks,[36, 37] and Si–O–Si covalent bond reformation mediated by Cu–O coordination complexes,[38] each of which proceeds under UV irradiation for multiple hours.

Here, we describe an approach to address the deficiencies of contemporary, intrinsically-healable cross-linked polymers by incorporating hexaarylbiimidazole (HABI) functionalities, dimers of triphenyl-substituted imidazoles,[39] in the backbone of polymeric gels. HABIs are photosensitive groups that undergo reversible, homolytic cleavage of the carbon-nitrogen (C–N) bond between the imidazole rings to efficiently afford two teal-colored 2,4,5-triarylimidazoyl (lophyl) radicals which thermally recombine to reproduce the original imidazole dimer (see Scheme 1a).[40] With some notable exceptions (e.g., nitroxides), organic radicals are typically highly reactive species that recombine at diffusion-controlled rates;[41] in contrast, the lophyl radicals generated by HABI homolysis are insensitive to atmospheric oxygen and show extraordinarily slow recombination rates,[42] attributable to their unique chemical structure affording stabilization by steric hindrance and electron delocalization.[43] Thus, owing to the low reactivity and long lifetime of the lophyl radicals originating from HABI photolysis, cross-linked polymers bearing HABI-containing network strands offer a unique mechanism for intrinsically-healable materials.



Scheme 1. Mechanism and structures of materials used. (a) Reversible photocleavage of cross-linked gels incorporating HABI moieties upon visible light irradiation to afford lophyl radicals, the recombination of which proceeds over several minutes, is visualized as a yellow/teal color change. (b) Dialkynyl monomers 2,2′-bis-(2-chloro-4-hexyl hex-5-ynoate-phenoxy)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole (HHy-HABI) and bisphenol A dipropargyl ether (BADPE), and a tetra-azide monomer (PEG tetra-azide).

EXPERIMENTAL SECTION

Materials. Four-arm PEG tetra-azide (molecular weight = 10 kg·mol^{-1}, Creative PEGWorks), copper(II) sulfate pentahydrate (Sigma-Aldrich), (+)-sodium L-ascorbate (Sigma-Aldrich), and 2,2-diphenyl-1-picrylhydrazyl (DPPH, Sigma-Aldrich) were used as received. Acetonitrile (Sigma-Aldrich), dimethylformamide (DMF, Fisher Chemical), and 1,1,2-trichloroethane (TCE, Acros Organics) were used as solvent for all samples. 2,2′-Bis(2-chloro-4-hexan-1-ol-phenoxy)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole (**1**) was synthesized as described previously,[42] whereas the dialkynyl monomers were synthesized as described below. Structures of all monomers used in this study are shown in Scheme 1b.

Synthesis of 2,2′-bis-(2-chloro-4-hexyl hex-5-ynoate-phenoxy)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole (HHy-HABI). A mixture of **1** (1.00 g, 1.12 mmol), 5-hexynoic acid (0.370 mL, 3.36 mmol), *N,N′*-diisopropylcarbodiimide (0.520 mL, 3.36 mmol), and 4-dimethylaminopyridine (74.5 mg, 0.610 mmol) in dichloromethane (50 mL) was stirred at room temperature for 16 hours under nitrogen. The solvent was removed under reduced pressure, and then the crude product was collected and purified by silica gel chromatography eluting with hexane/ethyl acetate (2/1, v/v) to afford 0.890 g of the dialkyne-substituted HHy-HABI (73.6% yield). ^{1}H NMR (400 MHz, DMSO-d$_6$), δ: 1.10-1.19 (m, 4H), 1.36-1.40 (m, 6H), 1.65-1.70 (m, 10H), 1.99-2.18 (m, 4H), 2.30-2.38 (m, 4H), 2.77-2.79 (m, 2H), 3.85-3.99 (m, 4H), 4.00-4.07 (m, 4H), 6.20-7.54 (m, 26H)

Synthesis of bisphenol A dipropargyl ether (BADPE). Bisphenol A (5.00 g, 21.9 mmol) and potassium carbonate (9.08 g, 65.7 mmol) were added to 50 mL of DMF and the mixture stirred. Propargyl bromide solution (80 wt% in toluene, 7.32 mL, 65.7 mmol) was then added and the mixture heated at 70°C for 16 hours under nitrogen. After cooling to room temperature, the mixture was filtered to remove potassium carbonate, DMF was evaporated under reduced pressure, and the residue was purified by silica gel chromatography eluting with hexane/ethyl acetate (2/1, v/v), yielding 5.45 g of bisphenol A dipropargyl ether (81.8% yield). ^{1}H NMR

(400 MHz, DMSO-d_6), δ: 1.59 (s, 6H), 3.50-3.51 (t, 2H), 4.74-4.76 (d, 4H), 6.85-6.89 (m, 4H), 7.11-7.15 (m, 4H).

Synthesis of cross-linked polymeric gels. Dialkyne-functionalized monomer, either HHy-HABI (130 mg, 0.12 mmol) or BADPE (36.5 mg, 0.12 mmol), four-arm PEG tetra-azide (MW=10 kg·mol^{-1}, 0.602 g, 0.060 mmol), copper(II) sulfate pentahydrate (5.94 mg, 0.0238 mmol), and (+)-sodium L-ascorbate (23.6 mg, 0.119 mmol) were dissolved in *N,N*-dimethylformamide (DMF, 4.32 g). Gel films were fabricated by sandwiching the formulated monomer solutions between glass microscope slides separated by 250 µm shims. After polymerization overnight, the cross-linked polymeric films were removed from the glass slides and immersed in acetonitrile for 24 hours then in water for a further 24 hours to ensure thorough extraction of residual solvent, copper catalyst, and reducing agent. Finally, the sample films were immersed in the desired solvent for 24 hours to complete the solvent exchange prior to use. For gels swollen with 1,1,2-trichloroethane (TCE), samples were initially immersed in acetonitrile prior to immersion in TCE owing to the immiscibility of deionized water and TCE.

Cylindrical gels were fabricated by injecting the formulated monomer solutions described above into 6 mm inner diameter poly(tetrafluoroethylene) tubing. After polymerization overnight, approximately 1 cm long sections of tubing were carefully removed from around the enclosed gels and the cylindrical samples were subjected to the extraction and solvent exchange steps described above. The residual copper content in HABI-incorporating gels digested by nitric acid prior to and after extraction, determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin-Elmer Optima 2000 DV), revealed that the extraction procedure yielded a five-fold copper concentration decrease.

Light sources and intensity measurement. For the spectroscopy experiments, violet light was provided by a collimated, LED-based illumination source (Thorlabs M405L2-C) with an emittance centered at 405 nm (FWHM 13 nm), used in combination with a current-adjustable LED driver (Thorlabs LEDD1B) for intensity control. For the photo-mediated healing experiments, violet light was provided by 405 nm LED-based illumination source (Arroyo Instruments, 226 TEC LED Lasermount), used in combination with a current-adjustable LED driver (Arroyo Instruments, 6340 ComboSource Laser Diode Controller) and delivered via a bifurcated light guide. Irradiation intensities were measured with an International Light IL1400A radiometer equipped with a broadband silicon detector (model SEL033), a 10× attenuation neutral density filter (model QNDS1), and a quartz diffuser (model W).

Ultraviolet-visible spectroscopy. UV-vis spectroscopy was performed on 250 µm thick film samples using an Agilent Technologies Cary 60 UV-vis spectrophotometer. Spectra were collected from 200 to 800 nm both in the dark and under irradiation once the radical concentration reached equilibrium. HABI photodissociation and subsequent recombination were examined by monitoring 609 nm, 597 nm, and 604 nm for the HABI-incorporating gels swollen by water, acetonitrile, and TCE, respectively, the wavelengths where the visible light absorbance by the generated lophyl radicals was greatest (i.e., λ_{max}), while the samples were irradiated with 405 nm for 2.5 min to ensure radical concentration equilibration and then for a further 7.5 min after the light was turned off. All kinetics experiments were performed in triplicate.

Electron paramagnetic resonance spectroscopy. Electron paramagnetic resonance (EPR) spectroscopy was performed with a Bruker EMX spectrometer. The spectrometer was equipped with a TE_{102} cavity (Bruker model ER 4102ST), and a frequency of 9.712 GHz, 2.05 mW microwave power, 5.02×10^4 receiver gain, 100 kHz modulation frequency, and 1 G modulation amplitude were used for all experiments. Optical access to the cavity was afforded by a 10 mm × 23 mm grid providing 50% light transmittance to the sample. For the sample preparation, a 1.1 mm inner diameter glass capillary tube was filled with 20 µL of sample formulation and allowed to react for 24 hours. After polymerization, each sample was rigorously extracted with acetonitrile and water to remove residual solvent, copper catalyst, and reducing agent, then immersed in the desired solvent to complete the solvent exchange prior to use. Each sample capillary tube was then inserted into a 3.2 mm inner diameter quartz sample tube and inserted again into the spectrometer cavity for analysis. The samples were irradiated *in situ* with 405 nm light and spectra were collected after 90 s when the radical concentration had reached steady state. Kinetics of photo-dissociation and dark recombination was performed by monitoring at a 3453 G static field, the first derivative signal intensity maximum for the HABI-incorporating gel under irradiation. All experiments were performed at room temperature. Radical concentrations were quantified by calibrating the EPR spectrum integral against known concentration solutions of DPPH in three solvents (water, acetonitrile, and TCE) using the same sample geometry, volume, and acquisition conditions employed for the HABI-incorporating polymeric gels (see Figure S1).

Rheometry. Rheological measurements to monitor the polymerization of HABI- and bisphenol A-incorporating cross-linked gels were performed using a TA Instruments AR-G2 rheometer equipped with a 60 mm diameter parallel plate geometry. Immediately after preparation as described in the Experimental Section, 500 µL of a monomer formulation incorporating either HHy-HABI or BADPE was pipetted onto the lower plate of the rheometer fixture and the upper plate was lowered to achieve a gap of 300 µm. Time sweep measurements were recorded at a rate of approximately one point every 9 seconds while applying a strain of 1% at a frequency of 1 Hz.

Photo-mediated creep tests were performed using the TA Instruments AR-G2 rheometer equipped with a parallel plate, UV-LED curing accessory consisting of a 20 mm diameter upper plate and a transparent, a quartz bottom plate, below which an LED array provides irradiation to the sample at a wavelength of 365 nm. HABI-containing cross-linked polymeric gel films were prepared as described in the Experimental Section, although 500 µm thick shims were used to separate the microscope slides, immersed in acetonitrile for solvent exchange, and mounted on the UV-LED test fixture. During the measurement, no shear stress was applied to the sample from t = 0 to 1 minute; however, from 1 minute through to the end of the experiment, a constant shear stress of 100 Pa was applied. From 3 minutes through 6 minutes, the gel films gels were subjected to alternating irradiation and dark periods of 15 and 45 seconds, respectively.

Swelling measurements. A 15 wt% HABI-incorporating gel was prepared and its swelling behavior in water, acetonitrile, and TCE was calculated from the volume of the polymeric gels in their dry and swollen states at room temperature. The swelling degree (*Q*), defined as the ratio of the volume of absorbed solvent to that of the dry polymer, was determined using the equation (eq. 1):

$$Q = \frac{V_{wet} - V_{dry}}{V_{dry}} \qquad (1)$$

where V_{wet} and V_{dry} are the volumes of the swollen and dry polymeric gels, respectively. The volume of absorbed solvent was determined from both the mass change of an initially dry sample after immersion in solvent for 24 hours in the dark and the density of the solvent.

Photo-mediated healing and mechanical testing. 6 mm diameter cylindrical gel samples were sectioned perpendicular to their axes using a razor blade and the exposed surfaces were re-contacted immediately. The samples were then irradiated at room temperature with 405 nm light at 10 mW·cm^{-2}, delivered to the vicinity of the re-contacted gel surfaces *via* a bifurcated light guide to ensure sufficient light penetration through the sample thickness, for different periods of time.

Pristine or healed polymeric gel samples were deformed in tension under air at room temperature using an electromechanical test machine (TestResources 100Q1000) equipped with a 25 lb load cell (TestResources SM-25-294) at a crosshead speed of 0.1 mm·sec^{-1}. All experiments were performed in triplicate.

RESULTS AND DISCUSSION

The utilization of reactive functional groups such as HABIs to afford intrinsically-healable, covalently cross-linked polymers necessitates the incorporation of these functionalities in the network backbone. Cross-linked polymers incorporating HABI functional groups have been synthesized previously,[44-47] one approach being to treat polymers bearing triaryl-substituted imidazole pendant groups, synthesized *via* a radical-mediated, chain growth polymerization mechanism, with potassium ferricyanide to oxidize the imidazole groups and yield HABI cross-links.[44, 46, 47] Notably, this synthetic approach affords cross-linked particles which would require further treatment to yield monolithic materials. In contrast, the cross-linked gels examined here were synthesized by treating solutions of PEG tetra-azide and a dialkynyl monomer, where the polymerizable moieties flank either side of the monomer core, in DMF with $CuSO_4$ and sodium ascorbate to effect polymerization by Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC), thereby ensuring incorporation of either the HABI or bisphenol A functional groups in the backbone of the resultant cross-linked, monolithic gels. The progress of these CuAAC polymerizations were monitored by parallel plate rheometry (see Figure 1a and 1b), revealing that gelation, determined here by the crossover in the storage and loss moduli,[48] occurred after approximately 10 minutes and 75 minutes for the HABI- and bisphenol A-based formulations, respectively. Although unexpected, the relatively rapid reaction rate observed for the HABI-based system is perhaps a result of the imidazole moiety acting as a ligand for the generated Cu(I) species,[49, 50] increasing its stability and improving its catalytic activity. Nevertheless, a storage modulus plateau of ~10 kPa was achieved within 4 hours for both systems, indicating reaction completion after that time and assuring that the overnight reaction used to synthesize cross-linked samples was sufficient for full polymerization.

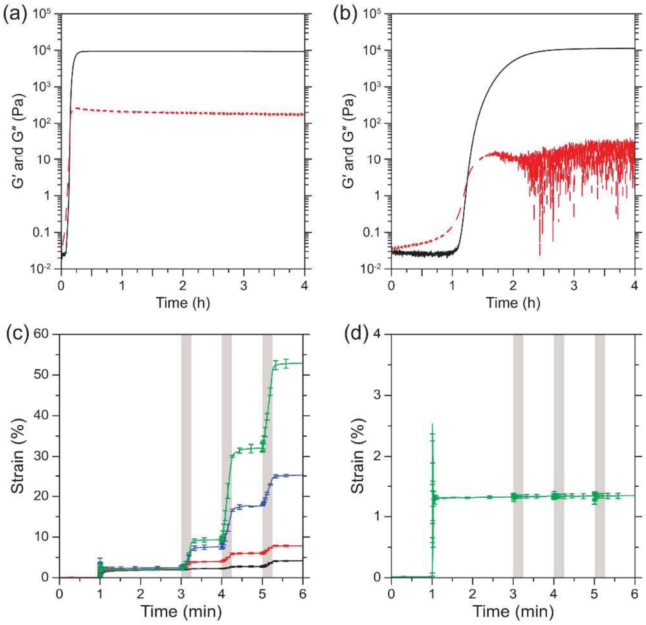


Figure 1. Rheological characterization of covalently cross-linked gels. The CuAAC-mediated polymerization between a 4-arm PEG tetra-azide and either (a) HHy-HABI or (b) BADPE in DMF solution, monitored by oscillatory parallel plate rheometry (storage modulus, solid black line; loss modulus, dashed red line). The photo-induced creep of gel films, swollen with acetonitrile and incorporating (c) HABI or (d) bisphenol A functional groups in their backbone, under 100 Pa shear stress (initially applied at 1 min) and intermittently irradiated with 365 nm light at 0.5 (black), 1 (red), 3 (blue), and 5 (green) mW·cm^{-2}. The periods of irradiation are indicated by the shaded regions, and the experiments were performed in triplicate.

As noted above, covalently cross-linked, photo-reversible networks undergo network connectivity rearrangement exclusively under irradiation and consequently should undergo plastic deformation upon irradiation while not exhibiting significant creep in the absence of exposure to light. To confirm whether the HABI-incorporating gels exhibited this property and thus held promise as photo-healable materials, gel films swollen with acetonitrile were mounted in a parallel plate rheometer, equipped with a UV curing accessory to enable irradiation of the sample, and subjected to a constant shear stress with alternating periods of irradiation and darkness (see Figure 1c and 1d). The initial application of shear stress in the dark to the HABI-incorporating films resulted in consistent elastic deformation of the samples with no discernable creep for the duration of the experiment; however, significant plastic deformation proceeded immediately upon exposure of the samples to UV irradiation for all intensities examined (Figure 1c), indicating that the network rearrangement necessary for the photomediated healing of this material does proceed under light exposure. Increasing the irradiation intensity afforded raised rates and extents of plastic deformation, attributable to the photolysis reaction equilibrium progressively tending towards the cleaved state (see Scheme 1a), increasing the network rearrangement rate. Notably, the observed creep under irradiation did not discontinue immediately upon cessation of light exposure; rather, although the creep rate did rapidly decrease, plastic deformation continued for several seconds after terminating the irradiation, an effect most apparent at the highest light intensity examined. This delayed cessation of plastic deformation is indicative of the stability and slow recombination of lophyl radicals, resulting in a continued, though progressively diminished, capacity for network rearrangement immediately after exposure of the samples to light is ceased. The bisphenol A-based gel films, employed here as a light-insensitive, negative control material, similarly exhibited constant elastic deformation upon application of shear stress; however, in contrast to the HABI-incorporating films, they did not exhibit any discernable creep under irradiation (Figure 1d), indicating an absence of photo-induced network rearrangement in this material.

The photo-mediated cleavage of HABI moieties within polymeric gels in response to visible light irradiation at 405 nm was further examined using UV-vis spectrophotometry by *in situ* sample irradiation to determine the influence of varying incident irradiation intensity and swelling solvent (see Figure 2). Prior to irradiation, the HABI-incorporating gels exhibited weak absorption tails extending into the visible spectral region; however, irradiation at 405 nm irradiation resulted in a dramatic color change from yellow to teal (see Scheme 1a) and the emergence of an absorbance peak in the visible region (λ_{max} = 609, 597, and 604 nm in water, acetonitrile, and TCE, respectively), which became progressively stronger with raised irradiation intensity (Figure 2a and S2), attributable to generation of the visible light-absorbing lophyl radical.[42] Subsequently ceasing irradiation of the gels resulted in complete reversion of their color from teal back to yellow and corresponding disappearance of the visible region absorption peak over the course of several minutes. The capacity of the gels in the three solvents examined (i.e., water, acetonitrile, and TCE) to generate radicals in response to 405 nm irradiation was confirmed by EPR spectroscopy. Whereas studies examining photoinitiator photolysis commonly employ spin traps[51] or the severely restricted molecular mobility at low temperatures[52] to attain detectable radical concentrations, the low recombination rates of lophyl radicals generated by HABI photolysis affords sufficient radical concentrations for facile detection at room temperature.[40, 42, 53] Although no radicals were observed in the EPR spectra of the HABI-incorporating gels in the absence of light, significant radical formation proceeded upon irradiation, the concentration of which increased with raised irradiation intensity (Figure 2b and S2), establishing the visible absorbance peaks as attributable to HABI-derived lophyl radical formation.[42, 53] In contrast, no radicals were observed in the bisphenol A-incorporating gels under any of the irradiation intensities at 405 nm examined, irrespective of the solvent employed to swell the gels (see Figure S3), confirming the stability of this polymer network under visible light irradiation.

To further characterize the influence of solvent and irradiation intensity on network strand cleavage of the HABI-incorporating gels, reaction kinetics experiments to examine photodissociation and lophyl radical recombination rates were performed. Here, HABI-incorporating gels were subjected to cycles of alternating light and dark periods at progressively raised irradiation intensities while monitoring either λ_{max} by UV-vis spectrophotometry (Figure 2c) or the radical concentration by EPR spectroscopy (Figure 2d). Whereas UV-vis spectrophotometry data were used to examine reaction rate orders owing to their low noise, data obtained by EPR spectroscopy were used to determine kinetic rate constants given the direct measurement of radicals afforded by that technique. As is apparent from this spectroscopic characterization, the solvent used to swell the gels greatly affected the concentration of lophyl radicals generated. The equilibrium functional group dissociation in TCE was approximately double that in acetonitrile and an order of magnitude greater than that in water (Figure 2d), attributable to a higher affinity of the hydrophobic HABI groups and, upon photolysis, resultant lophyl radicals for TCE than for acetonitrile or water. This is supported by swelling measurements performed in the dark where, in contrast to previously-reported swelling behavior of cross-linked, PEG diacrylate gels which were most swollen by water and less so by acetonitrile and toluene,[54] the HABI-incorporating gels were most swollen by, and hence had the highest affinity for, TCE and least by water (see Figure S4). Notably, since two lophyl radicals result from every HABI bond broken, the maximum percentage of cleaved network strands was 0.07, 0.35, and 0.64% for HABI-incorporating gels swollen with water, acetonitrile, and TCE, respectively, under 405 nm light irradiation at 50 mW·cm^{-2}, one to two orders of magnitude greater than contemporary polymer networks incorporating radical-mediated, dynamic covalent bonds such as those incorporating diarylbibenzofuranone (DABBF) groups in their backbone where less than 0.01% of the DABBF network strands are dissociated even at 50°C.[55] A small decrease in the absorbance at λ_{max} for the HABI-incorporating gels swollen with water and TCE while under the highest irradiation intensity investigated indicated that, instead of exclusively participating in self-recombination, some of the generated lophyl radicals were being consumed in an irreversible side reaction, potentially owing to the susceptibility of the residual copper azide-alkyne cycloaddition catalyst to radical-mediated reduction from Cu(II) to Cu(I).[56]

The reversible HABI photocleavage mechanism described in Scheme 1a suggests that the lophyl radical recombination should proceed as a second order reaction;

however, we previously established that this reaction can be described by either 1.5 or second order reaction kinetics, depending on the structure of the parent HABI compound.[42] Although fitting of the λ_{max} absorbance curves (presented in Figure 2c) during lophyl radical recombination in the dark revealed that lophyl recombination was well described as a near-second order reaction for HABI-incorporating gels swollen with TCE (see Figure S5), the recombination reaction for acetonitrile- and water-swollen gels was better fit by 1.6 and 1.2 order kinetics, respectively (Figure S5). Notably, radical diffusion-inhibited HABI derivatives have exhibited rapid, first order lophyl radical recombination kinetics.[57, 58] Thus, the respective reaction orders for the recombination of network backbone-borne lophyl radicals suggest that, whereas the HABI groups for gels swollen with TCE are not subject to significant diffusion inhibition, HABIs in gels swollen with acetonitrile or water may be subject to partial diffusion inhibition, yielding sub-second order recombination behavior. Thus, despite the structural similarity between the respective chromophores of HHy-HABI and **1**, a HABI-derived compound which affords radicals that recombine according to second order kinetics,[42] we analyzed the HHy-HABI photolysis and lophyl radical recombination results shown in Figure 2d by assuming first and sub-second order reactions, respectively (see Table 1). As expected, the dissociation rate constant k_{dis} increased with raised irradiation intensity. Moreover, under equivalent irradiation conditions, k_{dis} was lowest for water and highest for TCE, attributable to the relative affinities the HABI functional group had for the examined solvents as described above. Although their dissimilar reaction orders impedes direct comparison of the recombination rate constants (k_{rec}) for each respective gel, only minor k_{rec} variation was observed for each gel as the irradiation intensity was varied.

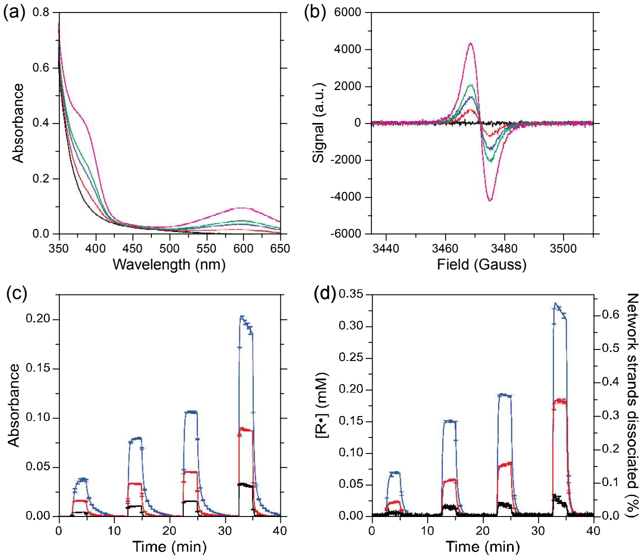


Figure 2. UV-Vis and EPR with kinetics. (a) UV-vis and (b) EPR spectra of HABI-incorporating gels swollen with acetonitrile at equilibrium under irradiation with 405 nm light at 0 (black), 1 (red), 5 (blue), 10 (green), and 50 (magenta) mW·cm^{-2}. (c) Absorbance at λ_{max} as determined by UV-vis spectrophotometry, and (d) lophyl radical concentration and network strands dissociated as determined by EPR spectroscopy, of HABI-incorporating gels swollen with water (black), acetonitrile (red), and TCE (blue) under alternating conditions of darkness and irradiation with 405 nm light at 1 (2.5 – 5 minutes), 5 (12.5 – 15 minutes), 10 (22.5 – 25 minutes), and 50 (32.5 – 35 minutes) mW·cm^{-2}.

Table 1. Sub-second-order lophyl radical recombination (k_{rec}) and first order HABI photodissociation (k_{dis}) rate constants for photolysis under varying irradiation intensities (I_o) with 405 nm light and in the dark of HABI-incorporating gels swollen with varying solvents.

I_o (mW·cm^{-2})	$k_{rec} \times 10^1$		
	Water (mM$^{-0.2}$·sec^{-1})	Acetonitrile (mM$^{-0.6}$·sec^{-1})	TCE (mM$^{-0.9}$·sec^{-1})
5	1.13 ± 0.03	1.96 ± 0.04	1.86 ± 0.09
10	1.06 ± 0.03	1.54 ± 0.02	1.45 ± 0.07
50	0.94 ± 0.02	1.36 ± 0.03	1.46 ± 0.05
I_o (mW·cm^{-2})	k_{dis} (sec^{-1}) × 10^4		
	Water	Acetonitrile	TCE
5	0.58 ± 0.02	1.55 ± 0.03	3.88 ± 0.20
10	0.81 ± 0.02	2.19 ± 0.03	4.96 ± 0.23
50	1.32 ± 0.03	6.75 ± 0.13	14.06 ± 0.53

Having established the solvent-dependent backbone cleavage behavior in the presence of light and recombination in its absence, the photo-mediated healing capability of the HABI-incorporating gels was investigated at room temperature and under aerobic conditions. To demonstrate this, the exposed surfaces of sectioned gel cylinders, swollen in one the three solvents examined (i.e., water, acetonitrile, or TCE) were brought into contact and irradiated with visible light to effect cleavage and rearrangement of network strands at the interface of contacted surfaces; these healed materials, as well as the pristine gels, were subsequently subjected to tensile testing. The exposed region of each HABI-incorporating gel again turned from yellow to teal upon irradiation and back to yellow upon irradiation cessation (Supplementary Video S1), confirming the backbone cleavage and subsequent recombination necessary for healing, whereas no light-induced color change was observed for the bisphenol A-incorporating gels. Although many backbone-borne, dynamic functional groups have been employed to achieve intrinsically-healable polymeric gels and elastomers,[59] effective restoration of mechanical properties upon contacting fracture surfaces can take several hours or days,[13, 14] while more rapid healing rates afforded by materials with a more dynamic network connectivity are generally accompanied by correspondingly faster stress relaxation or creep.[10] In contrast, by inducing reversible, photo-mediated cleavage of network strands, far more rapid healing rates can be attained in polymer networks that, in the absence of light, are not susceptible to creep under load. As shown in Figure 3 and tabulated in Table 2, the healing rate order corresponds to the radical under equivalent irradiation conditions, where the HABI-incorporating gel with the highest light-induced radical concentration (i.e., the TCE-swollen gel) afforded the most rapid tensile strength recovery upon healing while the water-swollen gel recovered its tensile strength slowest. Nevertheless, all of the HABI-incorporating gels had recovered over half of their tensile strength after only 30 seconds of visible light irradiation and were approaching the tensile strength of the pristine materials after 3 minutes irradiation, demonstrating the rapid healing attainable in these materials even under a moderate irradiation intensity. No photo-mediated healing was observed for the bisphenol A-incorporating material upon irradiation at any of the conditions examined (Figure 3d), establishing that cleavage of the backbone-borne HABI functional group was responsible for the observed photo-mediated healing of these covalently cross-linked networks.

Table 2. Tensile strength (TS) of 15 wt% HABI-incorporating gels prior to and after photo-mediated healing.

Solvent	TS of pristine gel (kPa)	% recovery of TS after irradiation		
		30 s	1 minute	3 minutes
Water	71.6±1.3	56.2 ±1.8	83.9±1.4	94.7±1.0
Acetonitrile	58.2±1.8	65.9±1.7	88.4±1.1	97.6±1.1
TCE	58.6±1.8	67.1±2.0	97.1±1.3	>99

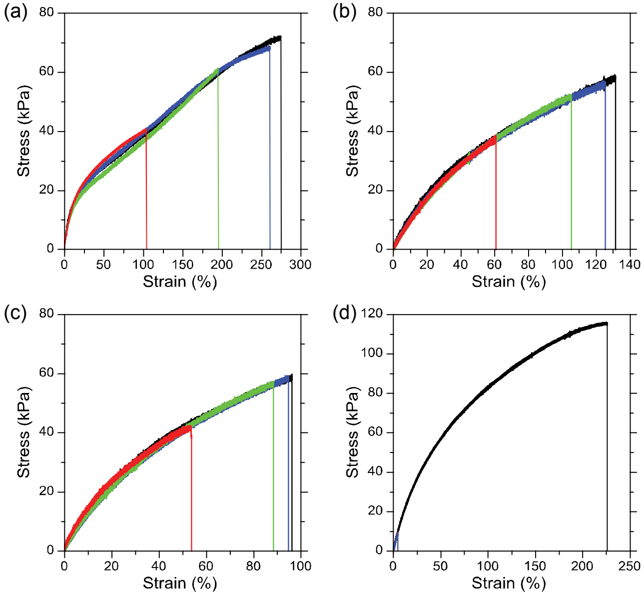


Figure 3. Mechanical testing of healed polymer networks. Stress-strain curves for cylindrical samples under tensile deformation were determined for 15 wt% HABI-incorporating gels swollen with (a) water, (b) acetonitrile, and (c) TCE, and for (d) 15 wt% bisphenol A-incorporating gels swollen with acetonitrile. Shown are the stress-strain curves of pristine samples (black) and healed samples after irradiation with 405 nm light at 10 mW·cm^{-2} for 30 seconds (red), 1 minute (green), and 3 minutes (blue).

In summary, the HABI-incorporating, covalently-cross-linked gels developed here undergo photo-mediated backbone cleavage under irradiation with near-UV or visible light, temporarily affording reduced cross-link density and dynamic connectivity rearrangement, and revert back to stable, static networks upon irradiation cessation. This network stability in the dark, combined with its highly dynamic nature under irradiation, enables rapid healing rates while decoupling the creep that often accompanies the dynamic connectivity of intrinsically-healable polymer networks. As noted above, molecular mobility is necessary to achieve effective mixing and reaction at the interface of contacted polymeric materials; thus, given the dependence of glass transition temperature on cross-link density, the reduced cross-link density that accompanies the photo-mediated backbone cleavage exhibited by these HABI-incorporating networks may provide a route to achieve sub-glass transition temperature healing of vitrified thermosets.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

EPR radical concentration calibration curves, UV-vis and EPR spectra, swelling characterization, and reaction order plots. (PDF) Video of photo-mediated healing of acetonitrile-swollen HABI-incorporating gel. (AVI)

AUTHOR INFORMATION

Corresponding Author

* E-mail: tfscott@umich.edu.

ORCID

Dowon Ahn: 0000-0003-4837-0038
Timothy F. Scott: 0000-0002-5893-3140

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge funding from the 3M Nontenured Faculty Award, the National Institutes of Health (NIH U01, award number U01DE023771), the National Aeronautics and Space Administration (NASA Space Technology Research Fellowship, award number NNX12AM31H), and the University of Michigan Chapter of Phi Kappa Phi. We also thank the Putnam group and Dr. Yen Kong for their assistance with rheometry instrumentation.

REFERENCES

1. Wu, D. Y.; Meure, S.; Solomon, D. Self-healing polymeric materials: A review of recent developments. *Prog. Polym. Sci.* **2008,** *33*, 479-522.
2. Bergman, S. D.; Wudl, F. Mendable polymers. *J. Mater. Chem.* **2008,** *18*, 41-62.
3. Wojtecki, R. J.; Meador, M. A.; Rowan, S. J. Using the dynamic bond to access macroscopically responsive structurally dynamic polymers. *Nat. Mater.* **2011,** *10*, 14-27.
4. White, S. R.; Sottos, N. R.; Geubelle, P. H.; Moore, J. S.; Kessler, M. R.; Sriram, S. R.; Brown, E. N.; Viswanathan, S. Autonomic healing of polymer composites. *Nature* **2001,** *409*, 794-797.
5. Toohey, K. S.; Sottos, N. R.; Lewis, J. A.; Moore, J. S.; White, S. R. Self-healing materials with microvascular networks. *Nat. Mater.* **2007,** *6*, 581-585.
6. Zavada, S. R.; McHardy, N. R.; Gordon, K. L.; Scott, T. F. Rapid, Puncture-Initiated Healing via Oxygen-Mediated Polymerization. *ACS Macro Lett.* **2015,** *4*, 819-824.
7. Zhang, M. Q.; Rong, M. Z. Intrinsic self-healing of covalent polymers through bond reconnection towards strength restoration. *Polym. Chem.* **2013,** *4*, 4878-4884.
8. Reutenauer, P.; Buhler, E.; Boul, P. J.; Candau, S. J.; Lehn, J. M. Room Temperature Dynamic Polymers Based on Diels-Alder Chemistry. *Chem.-Eur. J.* **2009,** *15*, 1893-1900.
9. Zhang, B.; Digby, Z. A.; Flum, J. A.; Foster, E. M.; Sparks, J. L.; Konkolewicz, D. Self-healing, malleable and creep limiting materials using both supramolecular and reversible covalent linkages. *Polym. Chem.* **2015,** *6*, 7368-7372.

10. Cromwell, O. R.; Chung, J.; Guan, Z. B. Malleable and Self-Healing Covalent Polymer Networks through Tunable Dynamic Boronic Ester Bonds. *J. Am. Chem. Soc.* **2015,** *137*, 6492-6495.

11. Ying, H. Z.; Zhang, Y. F.; Cheng, J. J. Dynamic urea bond for the design of reversible and self-healing polymers. *Nat. Commun.* **2014,** *5*, 9.

12. Lei, Z. Q.; Xie, P.; Rong, M. Z.; Zhang, M. Q. Catalyst-free dynamic exchange of aromatic Schiff base bonds and its application to self-healing and remolding of crosslinked polymers. *J. Mater. Chem. A* **2015,** *3*, 19662-19668.

13. Amamoto, Y.; Otsuka, H.; Takahara, A.; Matyjaszewski, K. Self-Healing of Covalently Cross-Linked Polymers by Reshuffling Thiuram Disulfide Moieties in Air under Visible Light. *Adv. Mater.* **2012,** *24*, 3975-3980.

14. Imato, K.; Nishihara, M.; Kanehara, T.; Amamoto, Y.; Takahara, A.; Otsuka, H. Self-Healing of Chemical Gels Cross-Linked by Diarylbibenzofuranone-Based Trigger-Free Dynamic Covalent Bonds at Room Temperature. *Angew. Chem. Int. Ed.* **2012,** *51*, 1138-1142.

15. Liu, Y. L.; Chuo, T. W. Self-healing polymers based on thermally reversible Diels-Alder chemistry. *Polym. Chem.* **2013,** *4*, 2194-2205.

16. Altuna, F. I.; Antonacci, J.; Arenas, G. F.; Pettarin, V.; Hoppe, C. E.; Williams, R. J. J. Photothermal triggering of self-healing processes applied to the reparation of bio-based polymer networks. *Mater. Res. Express* **2016,** *3*, 11.

17. Li, Q. T.; Jiang, M. J.; Wu, G.; Chen, L.; Chen, S. C.; Cao, Y. X.; Wang, Y. Z. Photothermal Conversion Triggered Precisely Targeted Healing of Epoxy Resin Based on Thermoreversible Diels–Alder Network and Amino-Functionalized Carbon Nanotubes. *ACS Appl. Mater. Interfaces* **2017,** *9*, 20797-20807.

18. Wang, H. Y.; Heilshorn, S. C. Adaptable Hydrogel Networks with Reversible Linkages for Tissue Engineering. *Adv. Mater.* **2015,** *27*, 3717-3736.

19. Habault, D.; Zhang, H. J.; Zhao, Y. Light-triggered self-healing and shape-memory polymers. *Chem. Soc. Rev.* **2013,** *42*, 7244-7256.

20. Fiore, G. L.; Rowan, S. J.; Weder, C. Optically healable polymers. *Chem. Soc. Rev.* **2013,** *42*, 7278-7288.

21. Chung, C. M.; Roh, Y. S.; Cho, S. Y.; Kim, J. G. Crack healing in polymeric materials via photochemical 2+2 cycloaddition. *Chem. Mat.* **2004,** *16*, 3982-3984.

22. Oya, N.; Sukarsaatmadja, P.; Ishida, K.; Yoshie, N. Photoinduced mendable network polymer from poly(butylene adipate) end-functionalized with cinnamoyl groups. *Polym. J.* **2012,** *44*, 724-729.

23. Ling, J.; Rong, M. Z.; Zhang, M. Q. Photo-stimulated self-healing polyurethane containing dihydroxyl coumarin derivatives. *Polymer* **2012,** *53*, 2691-2698.

24. Kiskan, B.; Yagci, Y. Self-Healing of Poly(propylene oxide)-Polybenzoxazine Thermosets by Photoinduced Coumarine Dimerization. *J. Polym. Sci. Pol. Chem.* **2014,** *52*, 2911-2918.

25. Yu, L. L.; Xu, K. G.; Ge, L. P.; Wan, W. B.; Darabi, A.; Xing, M.; Zhong, W. Cytocompatible, Photoreversible, and Self-Healing Hydrogels for Regulating Bone Marrow Stromal Cell Differentiation. *Macromol. Biosci.* **2016,** *16*, 1381-1390.

26. Radl, S.; Kreimer, M.; Griesser, T.; Oesterreicher, A.; Moser, A.; Kern, W.; Schlogl, S. New strategies towards reversible and mendable epoxy based materials employing 4 pi s+4 pi s photocycloaddition and thermal cycloreversion of pendant anthracene groups. *Polymer* **2015,** *80*, 76-87.

27. Froimowicz, P.; Frey, H.; Landfester, K. Towards the Generation of Self-Healing Materials by Means of a Reversible Photo-induced Approach. *Macromol. Rapid Commun.* **2011,** *32*, 468-473.

28. Coqueret, X. Photoreactivity of polymers with dimerizable side-groups: Kinetic analysis for probing morphology and molecular organization. *Macromol. Chem. Phys.* **1999,** *200*, 1567-1579.

29. Schreier, W. J.; Schrader, T. E.; Koller, F. O.; Gilch, P.; Crespo-Hernandez, C. E.; Swaminathan, V. N.; Carell, T.; Zinth, W.; Kohler, B. Thymine dimerization in DNA is an ultrafast photoreaction. *Science* **2007,** *315*, 625-629.

30. Lendlein, A.; Jiang, H. Y.; Junger, O.; Langer, R. Light-induced shape-memory polymers. *Nature* **2005,** *434*, 879-882.

31. Fairbanks, B. D.; Singh, S. P.; Bowman, C. N.; Anseth, K. S. Photodegradable, Photoadaptable Hydrogels via Radical-Mediated Disulfide Fragmentation Reaction. *Macromolecules* **2011,** *44*, 2444-2450.

32. Scott, T. F.; Schneider, A. D.; Cook, W. D.; Bowman, C. N. Photoinduced plasticity in cross-linked polymers. *Science* **2005,** *308*, 1615-1617.

33. Scott, T. F.; Draughon, R. B.; Bowman, C. N. Actuation in crosslinked polymers via photoinduced stress relaxation. *Adv. Mater.* **2006,** *18*, 2128-2132.

34. Amamoto, Y.; Kamada, J.; Otsuka, H.; Takahara, A.; Matyjaszewski, K. Repeatable Photoinduced Self-Healing of Covalently Cross-Linked Polymers through Reshuffling of Trithiocarbonate Units. *Angew. Chem. Int. Ed.* **2011,** *50*, 1660-1663.

35. Telitel, S.; Amamoto, Y.; Poly, J.; Morlet-Savary, F.; Soppera, O.; Lalevee, J.; Matyjaszewski, K. Introduction of self-healing properties into covalent polymer networks via the photodissociation of alkoxyamine junctions. *Polym. Chem.* **2014,** *5*, 921-930.

36. Ghosh, B.; Urban, M. W. Self-Repairing Oxetane-Substituted Chitosan Polyurethane Networks. *Science* **2009,** *323*, 1458-1460.

37. Ghosh, B.; Chellappan, K. V.; Urban, M. W. UV-initiated self-healing of oxolane-chitosan-polyurethane (OXO-CHI-PUR) networks. *J. Mater. Chem.* **2012,** *22*, 16104-16113.

38. Wang, Z. H.; Yang, Y.; Burtovyy, R.; Luzinov, I.; Urban, M. W. UV-induced self-repairing polydimethylsiloxane-polyurethane (PDMS-PUR) and polyethylene glycol-polyurethane (PEG-PUR) Cu-catalyzed networks. *J. Mater. Chem. A* **2014,** *2*, 15527-15534.

39. Riem, R. H.; Maclachl.A; Coraor, G. R.; Urban, E. J. The Flash Photolysis of a Substituted Hexaarylbiimidazole and Reactions of the Imidazolyl Radical. *J. Org. Chem.* **1971,** *36*, 2272-2275.

40. Caspar, J. V.; Khudyakov, I. V.; Turro, N. J.; Weed, G. C. ESR Study of Lophyl Free Radicals in Dry Films. *Macromolecules* **1995,** *28*, 636-641.

41. Allen, P. E. M.; Patrick, C. R. Diffusion-Controlled Reactions in Free Radical Polymerisation. *Makromolekulare Chemie* **1961,** *47*, 154-167.

42. Sathe, S. S.; Ahn, D.; Scott, T. F. Re-examining the Photomediated Dissociation and Recombination Kinetics of Hexaarylbiimidazoles. *Ind. Eng. Chem. Res.* **2015,** *54*, 4203-4212.

43. Kawano, M.; Sano, T.; Abe, J.; Ohashi, Y. The first in situ direct observation of the light-induced radical pair from a hexaarylbiimidazolyl derivative by X-ray crystallography. *J. Am. Chem. Soc.* **1999,** *121*, 8106-8107.

44. Iwamura, T.; Nakamura, S. Synthesis and properties of de-cross-linkable acrylate polymers based on hexaarylbiimidazole. *Polymer* **2013,** *54*, 4161-4170.

45. Verstraeten, F.; Gostl, R.; Sijbesma, R. P. Stress-induced colouration and crosslinking of polymeric materials

by mechanochemical formation of triphenylimidazolyl radicals. *Chem. Commun.* **2016,** *52*, 8608-8611.

46. Peng, Y.; Yu, H. W.; Chen, H. B.; Huang, Z. C.; Li, H. M. Cross-linking and de-cross-linking of triarylimidazole-based polymer. *Polymer* **2016,** *99*, 529-535.

47. Iwamura, T.; Sakaguchi, M. A Novel De-Cross-Linking System from Cross-Linked Polymer to Linear Polymer Utilizing Pressure or Visible Light Irradiation. *Macromolecules* **2008,** *41*, 8995-8999.

48. Winter, H. H. Can the Gel Point of a Cross-linking Polymer Be Detected by the G' - G'' Crossover? *Polym. Eng. Sci.* **1987,** *27*, 1698-1702.

49. Asano, K.; Matsubara, S. Effects of a Flexible Alkyl Chain on a Ligand for CuAAC Reaction. *Org. Lett.* **2010,** *12*, 4988-4991.

50. Yamada, Y. M. A.; Sarkar, S. M.; Uozumi, Y. Amphiphilic Self-Assembled Polymeric Copper Catalyst to Parts per Million Levels: Click Chemistry. *J. Am. Chem. Soc.* **2012,** *134*, 9285-9290.

51. Alberti, A.; Benaglia, M.; Macciantelli, D.; Rossetti, S.; Scoponi, M. Further EPR-spin trapping studies of the photoinitiating activity of Irgacure 369. *Eur. Polym. J.* **2008,** *44*, 3022-3027.

52. von Sonntag, J.; Janovsky, I.; Naumov, S.; Mehnert, R. Free radical copolymerisation of N-methylmaleimide and 2,3-dihydrofuran initiated by their radical cations. A low temperature EPR study of a binary system. *Macromol. Chem. Phys.* **2002,** *203*, 580-585.

53. Ahn, D.; Sathe, S. S.; Clarkson, B. H.; Scott, T. F. Hexaarylbiimidazoles as visible light thiol-ene photoinitiators. *Dent. Mater.* **2015,** *31*, 1075-1089.

54. Waters, D. J.; Engberg, K.; Parke-Houben, R.; Hartmann, L.; Ta, C. N.; Toney, M. F.; Frank, C. W. Morphology of Photopolymerized End-Linked Poly(ethylene glycol) Hydrogels by Small-Angle X-ray Scattering. *Macromolecules* **2010,** *43*, 6861-6870.

55. Imato, K.; Ohishi, T.; Nishihara, M.; Takahara, A.; Otsuka, H. Network Reorganization of Dynamic Covalent Polymer Gels with Exchangeable Diarylbibenzofuranone at Ambient Temperature. *J. Am. Chem. Soc.* **2014,** *136*, 11839-11845.

56. Adzima, B. J.; Tao, Y. H.; Kloxin, C. J.; DeForest, C. A.; Anseth, K. S.; Bowman, C. N. Spatial and temporal control of the alkyne-azide cycloaddition by photoinitiated Cu(II) reduction. *Nat. Chem.* **2011,** *3*, 256-259.

57. Fujita, K.; Hatano, S.; Kato, D.; Abe, J. Photochromism of a radical diffusion-inhibited hexaarylbiimidazole derivative with intense coloration and fast decoloration performance. *Org. Lett.* **2008,** *10*, 3105-3108.

58. Kishimoto, Y.; Abe, J. A Fast Photochromic Molecule That Colors Only under UV Light. *J. Am. Chem. Soc.* **2009,** *131*, 4227-4229.

59. Zou, W. K.; Dong, J. T.; Luo, Y. W.; Zhao, Q.; Xie, T. Dynamic Covalent Polymer Networks: from Old Chemistry to Modern Day Innovations. *Adv. Mater.* **2017,** *29*, 1606100.

Insert Table of Contents artwork here