

Visible Light [2 + 2] Cycloadditions for Reversible Polymer Ligation

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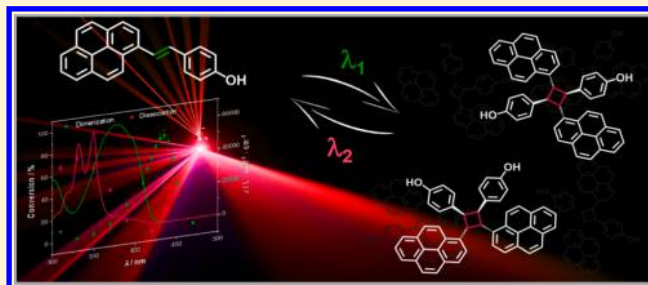
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Supporting Information

ABSTRACT: We introduce visible light induced dynamic covalent chemistry as a powerful reversible ligation tool based on a wavelength-dependent photon efficiency analysis (WPEA). We demonstrate by a monochromatic wavelength scan of the reversible dimerization of styrylpyrene at constant photon count that the system is most effective in its forward reaction at 435 nm, while the highest reverse reaction efficiency is observed at 330 nm. Critically, these optimum wavelengths are not accessible by inspection of the UV/vis spectra of the monomer and the dimer. Application of the identified reaction conditions enabled an entirely λ -orthogonal photoreversible polymer ligation using visible light, including with readily available light sources. The current study thus makes a [2 + 2] reaction system applicable in the critical visible light regime based on quantitative wavelength resolved data for applications in recodeable surface design in biological environments as well as reprogrammable materials systems.



INTRODUCTION

A particularly attractive feature of photochemistry is its precise temporal and spatial control over chemical reactions as well as allowing to gate chemical selectivity via wavelength^{1–5} and intensity.⁶ The possibility to reversibly create and break bonds between molecules in a controlled fashion employing disparate colors of light is especially attractive, yet highly challenging. Photochemically induced cycloadditions provide versatile platforms to achieve this goal yet have not reached their full potential as we have recently shown.⁷

The first steps into understanding photochemical processes were taken by Fritzsche,⁸ Rüber,⁹ Ciamician, and Silber.¹⁰ However, until today most applications of reversible reactions in polymeric systems are limited to a few molecules including thymine, coumarin, stilbene, and cinnamic acid for [2 + 2] cycloadditions as well as the [4 + 4] cycloaddition of anthracene.¹¹ The defining feature of these systems is the necessity of light in the UV-A or more often UV-B regime to induce the cycloaddition. Light of these wavelength regimes has very high energies and can often introduce photodamage to molecules as well as the surroundings (including to solvents, biological tissue or polymeric materials). As the cycloreversion

typically requires light of even higher energy, the potential damage is even more pronounced, strongly limiting applications of these photochemically reversible systems. Thus, a critical challenge in contemporary light-induced chemistry is to develop (reversible) reactions that can be induced with visible light in the absence of a catalyst.

Photocycloadditions and their reversions often feature low yields that can be improved catalytically using triplet sensitizers¹² and Lewis acids¹³ or by introducing the system into a matrix (i.e., cucurbit[8]uril¹⁴ or cyclodextrin¹⁵). However, these catalytic systems prevent its general applicability, entail highly specific systems, and require additional reagents.

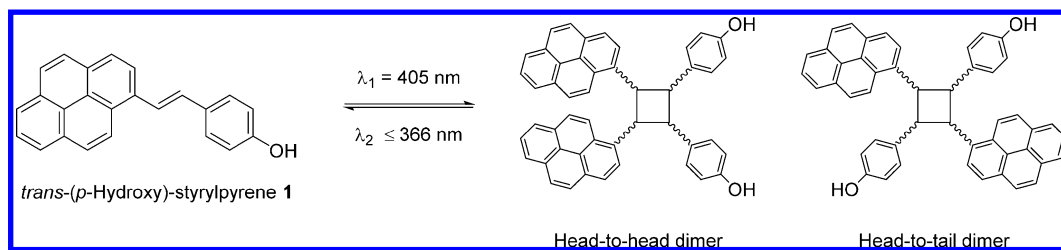
Recently, the field has focused on changing the inherent molecular structure of photoactive groups to alter their photochemical reactivity, enhance yields, and simultaneously push these systems into the visible light regime, for instance, through extension of the conjugated system¹⁶ and by

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Scheme 1. Photochemically Reversible Cycloaddition of *trans*-(*p*-Hydroxy)styrylpyrene **1 Resulting in Head-to-Head and Head-to-Tail Adducts**



functionalization with electron-withdrawing or -donating groups.¹⁷

Such a rational tuning of photoreversible cycloadditions has to this point exclusively been achieved in DNA-assisted systems.^{7,18} In free solution without the presence of a templating environment, however, these reactions are often suppressed.¹⁹ Of such photoreversible DNA cross-linking sites, the furthest red-shift was achieved by the group of Asanuma via the incorporation of styrylpyrene into DNA strands that were subsequently cross-linked using visible light ($\lambda = 455$ nm), whereas the cycloreversion was triggered with UV-A light at $\lambda = 340$ nm.²⁰ In particular, the wavelengths triggering the dissociation of the styrylpyrene dimer are highly attractive, since they allow the wavelength for the cycloreversion to be shifted from $\lambda = 254$ nm by around 100 nm. Surprisingly, the underlying photodimerization of styrylpyrene was only serendipitously observed in 1980 by Kovalenko et al., who investigated its isomerization, while the dimerization was not further investigated (Scheme 1).^{21,22} Very recently—and simultaneously to our study—the work of Kovalenko et al. has been adapted in the context of water-soluble biomaterials formation,²³ yet a full monochromatic wavelength-resolved photochemical assessment of styrylpyrene is critically lacking, preventing its exploitation in precision macromolecular photochemical systems such as photoresists, photoresponsive λ -orthogonal dynamic networks, or self-healing polymers.^{11,24,25} The current contribution closes this critical gap and identifies the optimum conditions for the reversible photoligation of styrylpyrene.

To enable the application of light-induced reversible systems, it is critical to quantitatively investigate the individual wavelengths required to induce both reaction pathways—cycloaddition as well as cycloreversion—and to reduce their spectral overlap to identify orthogonal reaction conditions for both channels. By employing an advanced tunable laser system, a detailed wavelength screening can be carried out as recently pioneered by us, resulting in action plots for irreversible photochemical reaction systems based on e.g. tetrazoles, *o*-methylbenzaldehydes,²⁶ pyreneacyl sulfides,²⁷ or photoinitiators.^{28,29}

Herein, we thus quantitatively map the photoreactivity of styrylpyrene in solution by determining both the optimum conditions for the cycloaddition and cycloreversion by introducing a novel analysis concept, i.e., wavelength-dependent photon efficiency analysis (WPEA). Our assessment entails a wavelength screening to determine the ideal trigger wavelengths (action plot) yet additionally photon kinetics determining the number of photons required to reach maximum conversion, both subsequently.

During the wavelength screening, a photochemical reaction is induced at different wavelengths at a constant photon count. By

plotting the conversion of the reaction vs the irradiation wavelength, an action plot is obtained providing a detailed image of the photochemical response of the system to the incident light. Using that particular wavelength, the number of photons is varied in a set of experiments while keeping all other conditions (i.e., concentration, solvent) identical. The result is a photon kinetic analysis indicating the number of photons required to reach maximum conversion or to obtain a photostationary state. By combining the wavelengths screening with a photon kinetic analysis, in-depth information on the ideal parameters is obtained for both the cycloaddition and cycloreversion, which can subsequently be employed in a reversible block copolymer ligation system based on styrylpyrene terminal poly(ethylene glycol). We believe that the herein in-depth photochemical analysis—including an analysis of the isomeric [2 + 2] products—establishes styrylpyrenes as a powerful tool for reversible visible-light-induced ligations.

RESULTS AND DISCUSSION

Initially, the possible isomers formed during the visible-light-induced ligation of *trans*-(*p*-hydroxy)styrylpyrene **1** had to be established, as our methodology allows to trace the formation of each [2 + 2] isomer during the photochemical reaction process. Thus, **1** was dissolved in acetonitrile, irradiated with an LED lamp at $\lambda = 440$ –450 nm (refer to the Supporting Information, Figure S44), and in-depth analyzed via ¹H NMR spectroscopy to establish an encompassing image of the product spectrum. Specifically, the [2 + 2] cycloaddition of styrylpyrenes can result in 12 different photoproducts (**2a**–**2l**) (for structures and nomenclature, refer to Table S1 in the Supporting Information³⁰). To establish the nature of the dimerization products, the obtained mixture was carefully separated via preparative thin layer chromatography (TLC) leading to five species. Via ¹H NMR spectroscopy these were identified as three different dimerization products as well as the starting *trans*-(*p*-hydroxy)styrylpyrene **1** and the *cis*-isomer which is formed via photoisomerization.²¹ The exact determination of the relative stereochemistry of the three isolated photodimers was achieved by advanced NMR techniques (for the complete discussion refer to the Supporting Information). The ¹H NMR spectra of the three cyclobutane containing photoproducts (products I–III, Figure 1) show two distinct coupling patterns for the cyclobutane ring, reflecting the differences of their spatial orientation and the shielding of the phenyl and pyrene systems. Either a doublet of doublets (Figure 1B) per aliphatic proton type is observed or an unresolved second-order multiplet structure (Figure 1A,C).

Figure 1B exhibits the characteristic doublet peak pattern for an alternating up and down orientation of the cyclobutane protons, confirming the formation of the cycloadducts *tt*-*ht*-*a* **2a** and *tt*-*hh*-*a* **2c**. None of the products resulting from *cis*-*cis*

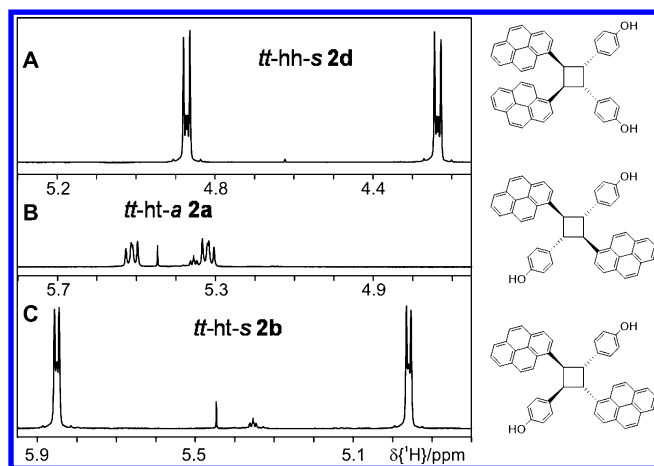


Figure 1. Enlarged ^1H NMR spectra showing the cyclobutane resonances of the three different cycloadducts: (A) product I: *tt-hh-s* 2d; (B) product II: *tt-ht-a* 2a; (C) product III: *tt-ht-s* 2b.

cyclization with all protons being above the cyclobutane ring plane (*cc-ht-s* 2j and *cc-hh-s* 2l) or products with three protons on one side of the cyclobutane ring plane (*tc-ht-a* 2e, *tc-ht-s* 2f, *tc-hh-a* 2g, and *tc-hh-s* 2h) fit the observed peak patterns in Figure 1A,C.

Among the remaining products (*tt-ht-s* 2b, *tt-hh-s* 2d, *cc-ht-a* 2i (stereochemically identical to 2b), and *cc-hh-a* 2k) two groups are identified with the cyclobutane protons in an alternating (2a and 2c) or nonalternating (2b, 2d, 2i, and 2k) position with respect to their orientation to the cyclobutane plane. Based on their ^1H and ^{13}C chemical shifts and proximities from the nuclear Overhauser effect (NOE), product I is identified as *tt-hh-s* 2d, product II as *tt-ht-a* 2a, and product III as *tt-ht-s* 2b. These results are in accordance with the literature, stating that, for example, the photochemically active 3-cyanovinylcarbazole is undergoing a $[2 + 2]$ cycloaddition with thymine only from its excited *trans*-structure.³¹

After having carefully established the formed $[2 + 2]$ isomers, the optimum dimerization wavelength of (*p*-hydroxy)-styrylpyrene was investigated by using a custom-designed tunable laser system, allowing a wavelength-resolved screen of the photochemical response of the reaction. Therefore, samples of **1** in deuterated acetonitrile were irradiated at different monochromatic wavelengths ($\lambda = 310\text{--}470$ nm), yet at a constant total number of photons ($242\ \mu\text{mol}$) as well as constant concentration (10 mM). The resulting product mixtures were subsequently analyzed via NMR to identify and quantify the amount of the five different compounds

present in the irradiated samples, based on the above careful NMR analysis.

By plotting the yield of the photoproducts 2a, 2b, and 2d vs the irradiation wavelength, detailed action plots for each species are obtained (Figure 2).

The investigation of the dimerization reaction in the range of $\lambda = 310\text{--}470$ nm indicates that the formation processes of the three photoproducts are characterized by similar reaction profiles, likely due to the fact that all three photoproducts are emerging from the same excited *trans*-species of **1**. However, while photoproducts 2d and 2b are obtained in approximately the same yields, photoproduct 2a is formed less by close to a factor of 2. By combining the plots of the three photoproducts (2a, 2b, and 2d), an overall dimerization yield was obtained (Figure 3A, blue dots), clearly indicating that the most effective wavelength for the dimerization of **1** is $\lambda = 435$ nm, reaching the highest yield (83% for $242\ \mu\text{mol}$ of photons).

As noted earlier by us,^{27,29} this important observation confirms—here on the example of a $[2 + 2]$ cycloaddition—that the absorption spectra of a compound and its photochemical reactivity are not necessarily congruent. Intuitively, on the basis of the UV/vis spectra of **1**, one may expect that the most suitable wavelength affording the highest yield is at approximately $\lambda = 375$ nm where its absorbance is the highest (Figure 1A, blue line). However, this may not always be correct as (i) the most effective transitions may not coincide with the absorption maximum, recalling that UV/vis spectra only reflect absorption from the ground state, and (ii) that at lower extinctions the photons can penetrate deeper into the solution, effectively exciting more molecules than at very high absorptions (Beer–Lambert law) as recently shown by us.²⁶ Clearly, both effects may be operational in parallel. In the case of photoreversible cycloadditions, the excitation overlap of cycloaddition and cycloreversion makes an *a priori* prediction of the wavelength-dependent photoreactivity at constant photon count highly challenging—only an experimental wavelength resolved assessment can clarify the system's photochemical reactivity. In the current styrylpyrene system **1**, the action plot clearly demonstrates that the above effects make the absorption spectra—under the given concentration conditions—a poor guide for predicting its photochemical reactivity. The optimum wavelength is rather shifted by 60 nm to $\lambda = 435$ nm—a wavelength at which the UV/vis spectrum only displays weak absorption ($\epsilon = 338\ \text{L mol}^{-1}\ \text{cm}^{-1}$). Based on the above knowledge, the maximum possible yield as well as the dimerization behavior with different numbers of photons was investigated. By irradiation at $\lambda = 435$ nm at constant concentrations (10 mM), photon kinetics were recorded,

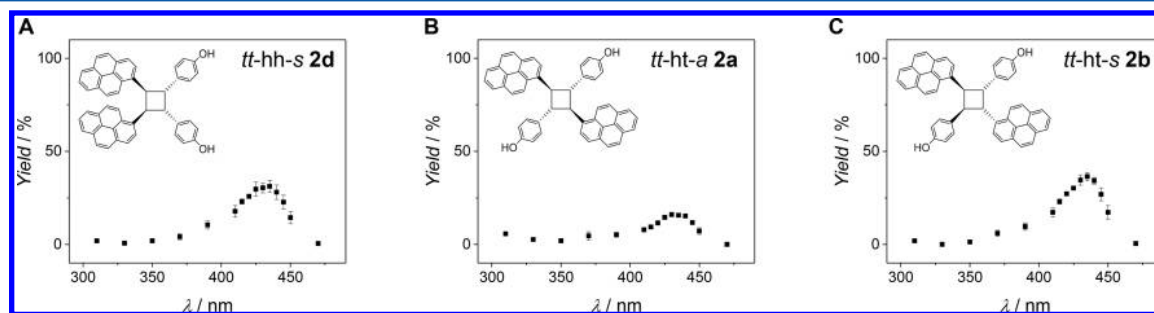


Figure 2. Yields of the respective photoproducts (A) *tt-hh-s* 2d, (B) *tt-ht-a* 2a, and (C) *tt-ht-s* 2b at discrete wavelengths (action plots) via irradiation of a 10 mM solution of **1** in deuterated acetonitrile based on $242\ \mu\text{mol}$ of photons and subsequent analysis by ^1H NMR.

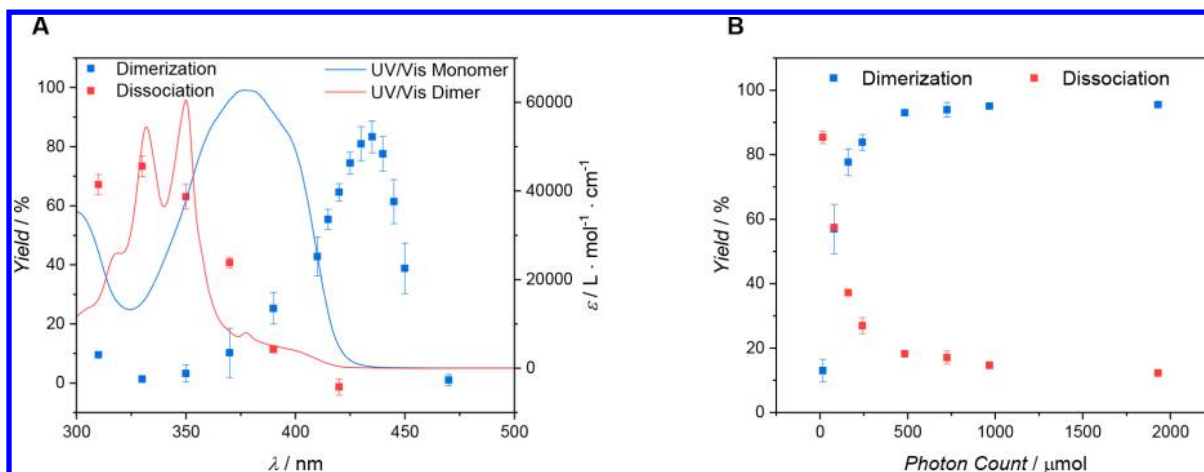


Figure 3. Overall dimerization (blue) and dissociation (red) reaction yield determined by wavelength-dependent monochromatic laser irradiation of a 10 mM solution of **1** in deuterated acetonitrile and subsequent analysis via ^1H NMR spectroscopy: (A) action plot obtained via irradiation with 242 μmol of photons (squares) at each wavelength as well as the UV/vis spectra of **1** (blue solid line) and its photoproduct mixture (red solid line); (B) photon kinetic analysis at $\lambda = 435 \text{ nm}$ for the dimerization and $\lambda = 330 \text{ nm}$ for the dissociation reaction. The indicated yield represents the combined yields of the three formed dimers (refer to Figure 2) as determined via ^1H NMR spectroscopy. For the detailed NMR spectra refer to the NMR section in the Supporting Information.

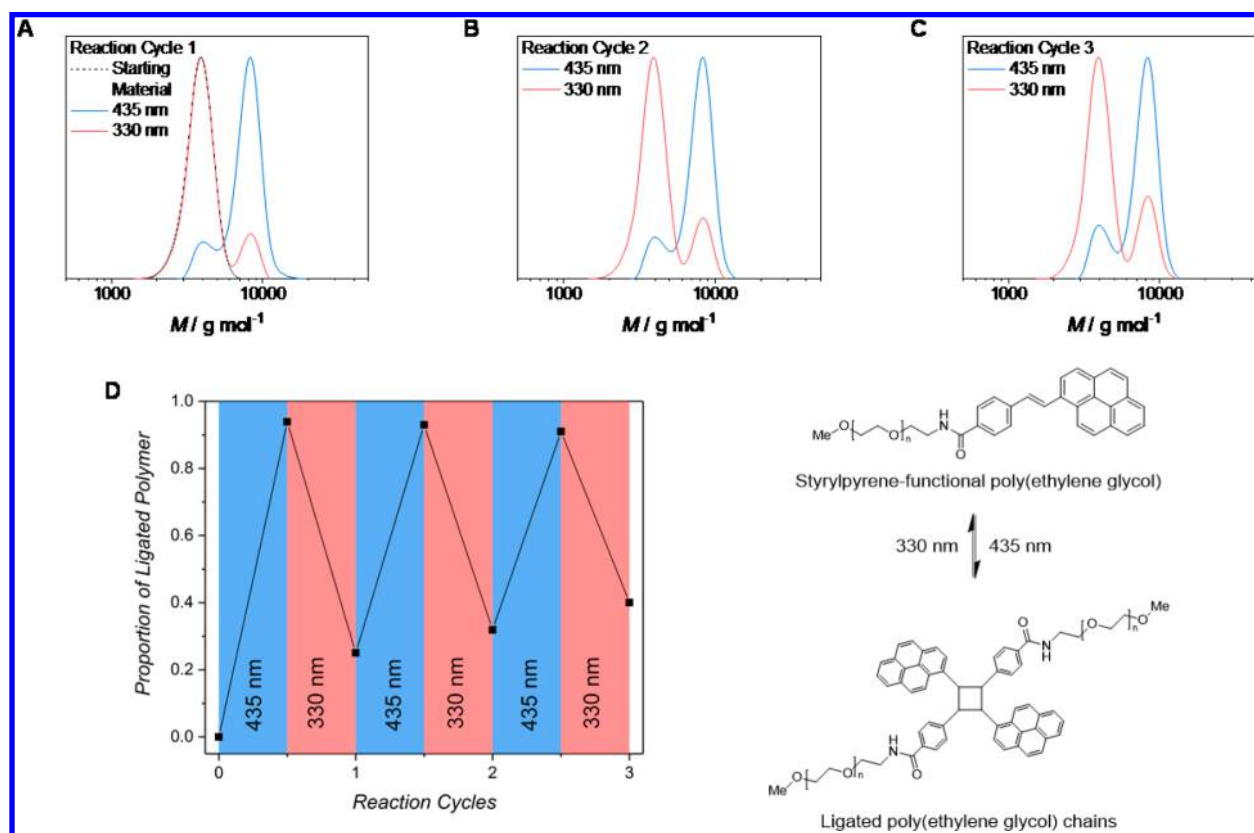


Figure 4. Polymer ligation cycles by subsequent irradiation of a 10 mM solution of a styrylpyrene terminal poly(ethylene glycol) with $\lambda = 435 \text{ nm}$ for the dimerization and $\lambda = 330 \text{ nm}$ for the dissociation reaction using 483 μmol of photons in each case. (A–C) SEC traces showing the dimerization (blue) and dissociation (red) products per reaction cycle. (D) Overview over the proportion of ligated polymer per reaction cycle.

connecting the dimerization yield of **1** with the number of incident photons (Figure 3B, blue dots).

When depositing close to 500 μmol of photons into the sample featuring a concentration of 10 mM **1**, the $[2 + 2]$ cycloaddition reaches a plateau at a yield of around 95%, affording a mixture of the photoproducts **2a**, **2b**, and **2d** while 5% of *cis*- and *trans*-monomer remain.

Having established the most suitable wavelength and photon number for the dimerization reaction, the dissociation reaction was investigated in detail following the same procedure that was used for the analysis of the cycloaddition (Figure 3A, red dots). Specifically, samples were irradiated with 483 μmol of photons at $\lambda = 435 \text{ nm}$ to achieve the almost quantitative dimerization of **1**. These samples were subsequently systematically subjected to different wavelengths below $\lambda = 435 \text{ nm}$ at a constant

photon count (242 μmol) to determine which wavelength provides the most efficient dissociation reaction of the photodimers.

The dimers of **1** are stable up to $\lambda = 400$ nm, providing excellent orthogonality between the forward and the reverse process. While the reaction is already slightly reversible at $\lambda = 390$ nm (11% conversion to monomer), the reverse reaction proceeds most efficiently when the cycloadducts are irradiated at $\lambda = 330$ nm. Critically, at this wavelength no dimerization takes place, underpinning the orthogonality of the reaction systems. Thus, the dissociation does not compete with the cycloaddition. To the best of our knowledge, the presented system is the mildest (in terms of wavelength) and most orthogonal reversible photochemical reaction system reported to date, established by our unique wavelength-resolved photochemical assessment methodology.

To illustrate the reversibility of the (*p*-hydroxy)styrylpyrene dimerization, the dimer system (**2a**, **2b**, and **2d**) was irradiated at $\lambda = 330$ nm with an increasing number of photons to obtain a photon kinetic analysis (Figure 3B, red dots). The reverse reaction reaches a photo stationary state close to 500 μmol of photons and affords a maximum dissociation yield of 85%.

After establishing the ideal reaction conditions for the photodimerization and -reversion of **1**, these reaction conditions were applied in a photoreversible polymer ligation process. Therefore, **1** was attached to a PEG-amine via an amidation reaction and subsequently irradiated with the previously WPEA-optimized wavelength and photon conditions to effect a covalent ligation of two polymer chains (Figure 4).

In excellent agreement with the small molecule study, the polymer ligation is limited by the photostationary state with a remaining minor amount of nonligated polymer for the cycloaddition as well as a small amount of the formed block copolymer for the dissociation. The dimerization/dissociation cycle was carried out three times consecutively with the same sample, demonstrating the reversibility of the system. Only little photodamage is observed (Figure 4) due to the potential asymmetric cleavage of the cyclobutane ring as well as the unreacted *cis*-structure of styrylpyrene that was shown to be unreactive in the photochemical [2 + 2] cycloaddition and possible rearrangements limiting the overall reversibility.⁷ Stilbene, for example, is well-known to be able to undergo cyclization reactions from the *cis*-isomer forming a larger conjugated system, effectively preventing it from participating in any cycloadditions and therefore limiting the photochemically reversible dimerization of stilbenes.³² While the use of monochromatic radiation is required for detailed WPEA studies, it is less practical for most applications. Thus, the polymer ligation was additionally carried out with readily available light sources emitting close to the determined optimum wavelengths ($\lambda_{\text{max}} = 300$ nm/440 nm), giving the same results (refer to the Supporting Information, Figure S39).

CONCLUSIONS

By virtue of detailed photochemical insights into the reversible [2 + 2] ligation of styrylpyrene **1** via a newly introduced concept, i.e., wavelength-dependent photon efficiency analysis (WPEA), the high reversibility of a visible light cycloaddition and UV-induced cycloreversion was established in a small molecule system and successfully transferred to polymer ligations. Critically, unique wavelength-resolved action plots give access to the most effective wavelength for the dimerization at $\lambda = 435$ nm and for the dissociation at $\lambda =$

330 nm. A photon kinetic analysis identifies close to 500 μmol of photons as the optimum for ligation under the selected conditions, leading to 95% dimerization yield, while retrieving above 85% of the monomer during cycloreversion. The introduced and mapped dimerization system is the to date most advanced catalyst-free reversible red-shifted ligation system able to undergo several visible-light-induced ligation cycles, demonstrating the dynamically gated nature of the system, accessible by different colors of light. We submit that the introduced system and the laser-based photochemical mapping methodology hold substantial promise for applications such as the reversible folding of polymer chains, in molecular biology, self-healing, and reprogrammable materials as well as in λ -orthogonal photoresist design for 3D laser lithography.³³

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b00613.

Experimental details, analytical data including detailed NMR assignments, structures of possible photoproducts, and additional graphs outlining the photochemical reactivity of styrylpyrene (PDF)

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Notes

The authors declare no competing financial interest.

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