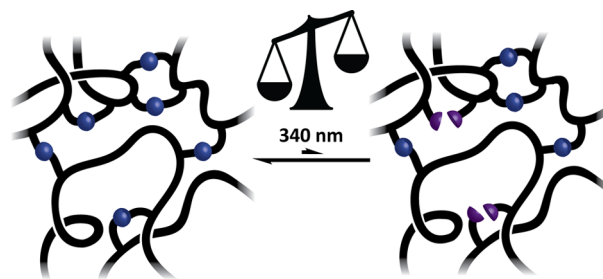


Photostationary State in Dynamic Covalent Networks

Lewis C. Chambers, Christopher Barner-Kowollik, Leonie Barner, Lukas Michalek,* and Hendrik Frisch*

ABSTRACT: We explore a cross-linked polymer network based on a visible light photodynamic [2 + 2] cycloaddition driven by styrylpyrene chemistry. Based on a polymer backbone with pendent styrylpyrene units, the network can be formed by using $\lambda = 450$ nm irradiation. Upon irradiation with $\lambda = 340$ nm, a photostationary state is generated within the network with $\sim 17\%$ of the styrylpyrene units open compared to close to 2% in the visible light cured state. The limited fraction of open [2 + 2] couples is caused by their proximity and is in sharp contrast to solution experiments on the photoreactive moiety. Thus, the polymer network retains its mechanical properties even at the photostationary point. We hypothesize that the application of an additional stimulus could serve as a second gate for inducing network disintegration by spacing the [2 + 2] units during ultraviolet irradiation.



Cross-linked networks of polymers are critical to modern soft matter materials science. They underpin a wide range of applications, including in dental medicine,^{1,2} highly resistant coatings in the automotive and aeronautics industry as well as solvent resistant pipes,^{3,4} stable (emitting) layers in optoelectronic devices,^{5,6} and a variety of adhesives.^{7,8} Compared to non-cross-linked polymeric materials, they are usually higher in impact resistance and mechanically stronger, while featuring excellent solvent resistance.^{3,4} Networks are typically produced in a curing process, either via thermally or photochemically induced linkage of small molecular building blocks or the covalent connection of preformed polymer chains. Thermally induced linking often occurs via thiolene chemistry—in either its radical⁹ or Michael addition^{10–12} variant—or via the thermal decay of an initiator in reaction mixtures entailing multifunctional activated enes.^{13,14} Photochemically, radical-induced processes involving UV-labile photoinitiators^{15,16} or reactive species formed by high-energy radiation¹⁷ dominate the application space, while network formation has also been explored based on reversible pericyclic reactions.^{18–20}

Conducting network formation via photochemical means has the added advantage that the curing can occur in a spatially and temporally resolved fashion. A wide range of curing systems has been established, leading to durable network structures, most prominently in dentistry. Recently, precision photochemistry—that is, the detailed understanding of photochemical covalent bond formation and cleavage in a wavelength-by-wavelength resolved fashion—has made substantial advances.^{21–24} Such an understanding has enabled the design of photoresponsive polymer networks, whose mechanical

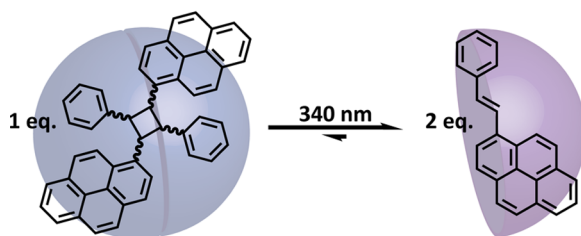
properties can be altered with specific colors of light. Key examples include hydrogel systems that can be degraded in a wavelength-dependent fashion²⁵ or 3D printed microstructures that can be adapted in their mechanical properties postprinting.²⁶ In these systems, the [2 + 2] photocycloaddition of styrylpyrene derivatives has emerged as a particularly attractive platform, due not only to their orthogonality, mild irradiation requirements, and thermal stability (Supporting Information, section 3.10) but also to their highly efficient reversibility.^{20,22,27–29} When reversible photochemical systems are employed, e.g., [2 + 2] or [4 + 4] cycloadditions, the photostationary state plays a critical role in governing the cross-linking degree. The photostationary state at a given wavelength describes a steady state, where cycloaddition and cycloreversion occur at the same rate yielding a set fraction of bonding sites that are open and closed.³⁰ This phenomenon has been observed for a number of reversible photoisomerizations^{31–37} but is less commonly observed in reversible photoligations.^{38,39} We have recently shown that the proximity of the reacting groups to each other has a critical and defining influence on the quantum yield of [2 + 2] cycloadditions.²⁷ Confined environments, i.e., when the reacting units are placed onto a polymer chain to form single chain nanoparticles (SCNPs), yield a substantially increased

reaction rate compared to the same species coupling in solution under identical irradiation and concentration conditions. Herein, we establish that the same proximity effect critically affects the photostationary state in polymer networks with styrylpyrene cross-links, effectively preventing debonding and substantial material property changes (Scheme 1), even

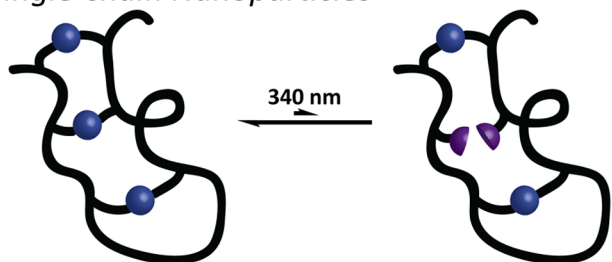
Scheme 1. Limited Chromophore Diffusion in Solid-State Covalent Networks Limits the Extent of Cycloreversion, in a Similar Way to the Behavior Previously Observed in Single-Chain Nanoparticles and in Contrast to the Behavior of Small Molecules

Previous Work

Small molecules

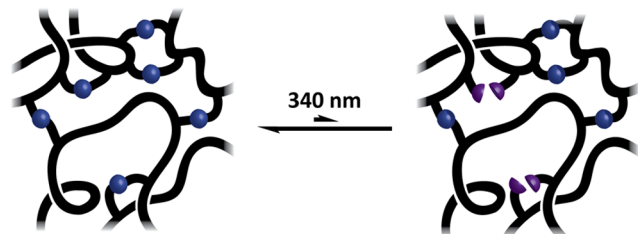


Single-chain Nanoparticles



This Work

3D Covalent Networks



when irradiated in the most favorable wavelength range for $[2 + 2]$ cleavage.²² This results in a mechanically stable, photocross-linked network that nonetheless retains the potential for reversibility if an additional stimulus could be applied to perturb the photostationary state.

Because $[2 + 2]$ photocycloadditions can only occur when the reactive double bonds are aligned, it is key that the reactive moieties are sufficiently mobile to enable high yielding photoreactions in polymer films. Previous styrylpyrene-containing copolymers based on methyl methacrylate (MMA) displayed high T_g s of >90 °C.²⁰ To enable efficient photocuring of the network at ambient temperature, 2-ethylhexyl methacrylate (EHMA) was used as comonomer of short polymer chains ($M_n = 3,270$ g mol⁻¹, $\bar{D} = 1.4$) that were obtained from free radical polymerization with 1-dodecane-thiol as a chain retarder (Figure 1a). The resulting copolymers

(P1) had a ratio of EHMA to styrylpyrene bearing monomers of 8:3 according to ¹H NMR spectroscopy (refer to Figure S6 in the Supporting Information) and significantly decreased T_g of -0.9 °C (Figure 1b).

To investigate the photocycloaddition driven cross-linking and subsequent effects on material properties, polymer P1 films were employed as an adhesive to bond two glass slides in a single lap-joint geometry (refer to the Supporting Information, section 3.7, and Figure S8 for details of lap-joint preparation). The linear polymer chains were spin-coated onto glass substrates, and two such substrates were clamped together with a consistent 1 cm² contact area and an adhesive layer thickness of ~ 11 μ m (refer to the Supporting Information, section 3.7, for calculation details). The assembly was subsequently annealed at elevated temperatures to provide a homogeneous adhesive layer. Because the characteristic absorbance of styrylpyrene between 350 and 425 nm decreases upon cycloaddition as a result of a decrease in the conjugated system, UV-vis spectroscopy is an ideal tool to monitor the reaction on a molecular level. After irradiation of the linear polymer film with a $\lambda = 450$ nm LED lamp at ambient temperature for 16 h, the styrylpyrene absorbance band had significantly decreased, indicating the formation of cycloadducts (Figure 1c, black to blue curve, and Figure S9). At $\lambda = 432$ nm, the absorbance has decreased by 97.7% (refer to the Supporting Information, section 3.8, for calculation details). As the cycloadduct has no absorbance at that wavelength, it can be quantified that only 2.3% of photoreactive units remain non-cross-linked after irradiation. These results imply both sufficient mobility of photoreactive units to react and a high number of interchain cycloadducts since the maximum intramolecular cycloadducts would be close to 66% according to the average of three styrylpyrene moieties per chain.

The mechanical properties of the adhesive layer were subsequently characterized via tensile testing (refer to the Supporting Information, section 3.9, for experimental details). When the unirradiated film was subjected to tensile testing, a weak viscous deformation was observed as expected for a short, linear, and low- T_g polymer⁴⁰ (Figure 1b, Figure 1d, black curve, and Figure S12). After irradiation with a $\lambda = 450$ nm LED lamp, however, the mechanical properties drastically improved, and the joint supported a load of 0.34 MPa (Figure 1d, blue curve, and Figure S13).

The investigated styrylpyrene-based copolymer has promising properties for applications as an additive-free adhesive system. Because the photocycloaddition of styrylpyrene is reversible under UV-light irradiation, application as a visible light gated adhesive requires an understanding of the behavior of cross-linked films under UV light exposure. When the spin-coated films were irradiated with UV light after initial blue light curing, an initially rapid cleavage of photocycloadducts was observed through an increase in styrylpyrene absorbance (Figure 2 and Figure 1c, purple curve), and after 30 min of irradiation the percentage of free styrylpyrene groups increased from 3.6 to 12.4%. However, after this point the rate of cycloreversion strongly decreases, and an additional 1.5 h of irradiation only results in a further 4.5% increase in cycloreversion. A temperature change of only $+0.4$ °C was measured during irradiation, suggesting that the observed cycloreversion is photochemical rather than photothermal in nature (Supporting Information, Figure S11, and section 3.10). To investigate whether the small change in cross-linking degree affects mechanical properties of the network significantly,

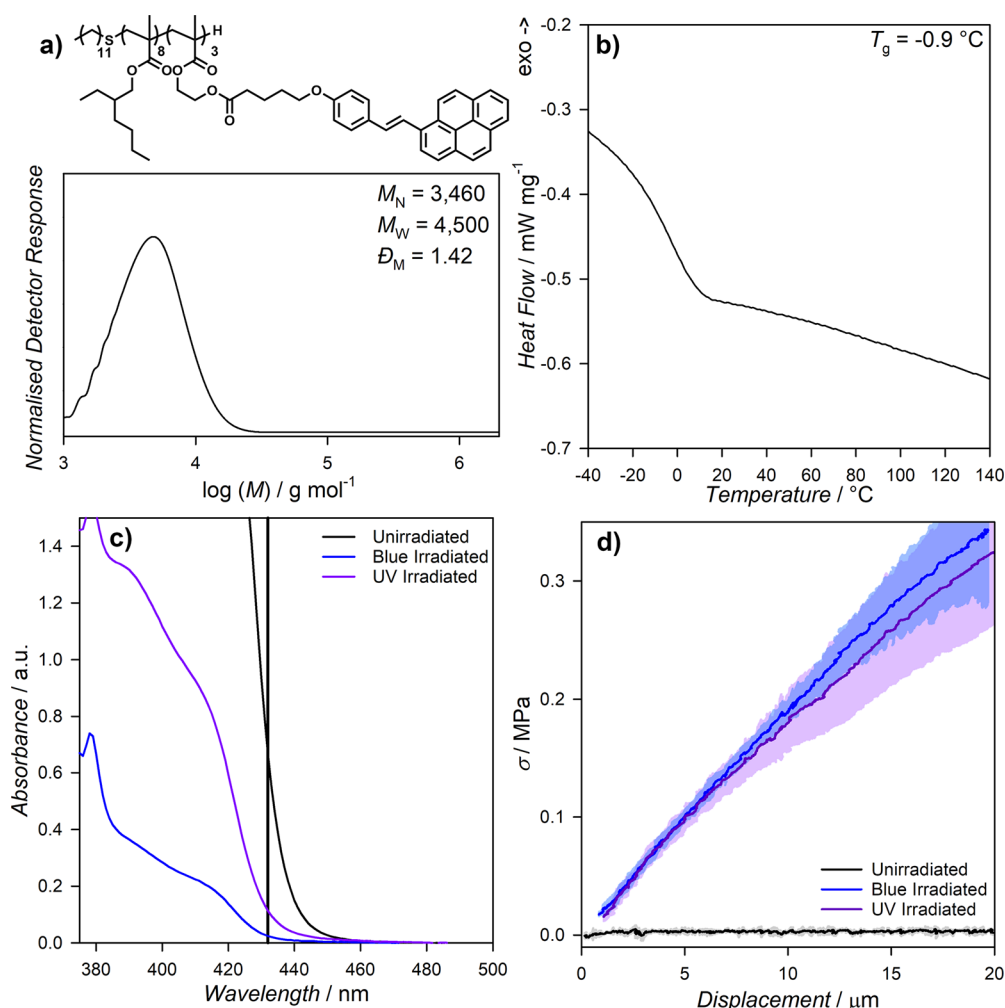


Figure 1. (a) Molecular structure and average composition of polymer P1, together with the size exclusion chromatography (SEC) elugram of polymer P1 measured with THF as eluent. (b) Differential scanning calorimetry (DSC) trace of polymer P1 obtained on the third heating cycle, showing a glass transition at $T_g = -0.9$ °C. (c) UV-vis absorption spectra of polymer P1 films before irradiation (black), after blue irradiation at 450 nm (blue), and after UV irradiation at 340 nm (purple). The vertical line at 432 nm marks the position at which absorbance was used to calculate the percentage of open styrylpyrene cross-links in Figure 2 (Table S1). (d) Tensile testing performed on unirradiated (black), blue irradiated (blue), and UV irradiated (purple) P1 lap joints. In each case 20 μ m of strain was applied in tension over 10 min. Each trace is the average of three experiments performed on identically prepared samples, and the transparent envelopes indicate the 95% confidence interval. The data for each individual sample can be found in the Supporting Information, section 3.9, and Figures S12–S14.

tensile testing was performed, and a similar load of 0.32 MPa was still supported (Figure 1d, purple curve, and Figure S14). As the cycloadduct of the parent photoreactive moiety, i.e., hydroxystyrylpyrene, has been shown to revert close to quantitatively under UV-light irradiation in solution,²² the limited reversibility observed here results from the confinement within the surrounding cross-linked polymer network.

Both styrylpyrene and its photocycloadducts absorb UV light. While UV light irradiation initiates both reactions, the intermolecular cycloaddition must compete with radiative and nonradiative deactivation processes, which leads to a strong concentration dependence of photocycloaddition quantum yield in solution. Within the confined environment of the cross-linked polymer network, reverted photocycloadducts have limited mobility and can be expected to be well aligned for a subsequent photocycloaddition. The result is a photostationary state, of concurrent photocycloaddition and -reversion with a kinetically favored bond forming reaction due to a strong proximity effect. As a result, UV light irradiation only initiates cleavage of a small net fraction of

cross-links and does not initiate a complete unmaking and failure of the adhesive postirradiation. Whereas intramolecular photostationary states of the styrylpyrene cycloreversion are known for intrachain cross-linking,^{27,41} we are not aware of reports observing interchain cross-linking of the styrylpyrene system.

As the photostationary state is dynamic, we postulate that it may be possible to manipulate the materials' cross-linking degree and mechanical integrity by perturbing the photostationary state through the application of an additional stimulus. This could be achieved by physically separating the reverted photocycloadducts before they can recombine either through the application of mechanical force or solvation of cleaved polymer chains, as illustrated in Scheme 2. Additionally, competitive cycloaddition with a small-molecule styrylpyrene derivative could also disrupt re-formation of reverted photocycloadducts, reducing the network's degree of cross-linking. In this way, the material may be made dynamic and responsive, creating a covalent adaptable network that can be reshaped or reverted to starting materials depending on the stimulus

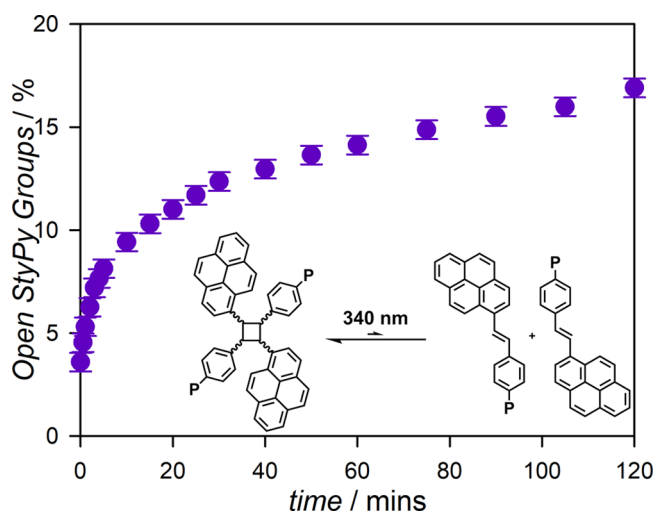
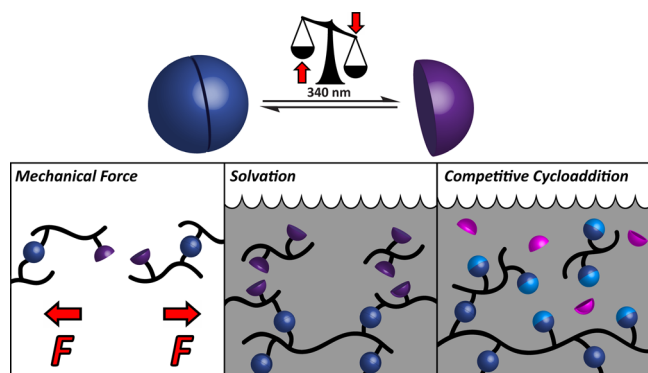


Figure 2. Percentage of open styrylpyrene cross-links in a P1 lap joint as a function of time spent under 340 nm irradiation. The percentage of open groups was assessed by measuring the absorbance at 432 nm as shown in Figure 1c, taking the absorbance of the unirradiated P1 lap joint as equal to 100% open styrylpyrene groups and an absorbance of 0 as equal to 0% open styrylpyrene groups (Table S3).

Scheme 2. Hypothetical Approaches to Alter the Number of Polymer–Polymer Cross-Links Photochemically in Confined Polymer Films^a



^aAlthough limited chromophore diffusion reduces the net yield of cycloreversion, the cross-links are in principle still reversible, and the photostationary state could be perturbed via the application of mechanical force, solvation, or competitive cycloaddition with small molecules.

employed. Critically, its cross-links would only become adaptable under the simultaneous application of UV light and the equilibrium perturbing stimulus. Employing a dual-stimuli responsive mechanism in this way facilitates a high degree of control over its dynamic properties.

In summary, low- T_g styrylpyrene containing polymers were found to function as additive-free, visible light curable adhesives that can support loads of up to 0.34 MPa. Upon UV-light irradiation, a photostationary state was observed, where only a fraction of bonds are reverted (from 98% to 83.1% of cross-linking), in contrast to the behavior of hydroxylstyrylpyrene in solution which can be quantitatively reverted under UV-light irradiation.²² Despite the small change in cross-linking degree, the polymer network remains mechanically stable after UV irradiation. Our data demonstrate that limited diffusion in the solid state effectively limits

cycloreversion to a photostationary point close to complete cycloaddition, in turn implying that the application of an additional stimulus to enhance mobility of the reverted photocycloadducts could restore the reversibility of the styrylpyrene cross-links to create a dual stimuli-responsive covalent network.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmacrolett.2c00097>.

Materials, methods, ¹H NMR spectra, SEC elugrams, UV–vis spectra, lap-joint preparation details, lap-shear tensile test and calculation details, and instrumentation (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

C.B.-K., H.F., L.B. and L.M. acknowledge generous funding for the current project from Merck. C.B.-K. additionally acknowledges the Australian Research Council (ARC) for a Laureate Fellowship enabling his photochemical research program, while H.F. acknowledges the ARC for funding through a DECRA Fellowship. All authors are grateful for continuing support from QUT's Centre for Materials Science. The authors thank Dr. Beate Burkhardt (Merck) for fruitful discussions.

■ ABBREVIATIONS

¹H NMR, proton nuclear magnetic resonance; DSC, differential scanning calorimetry; EHMA, 2-ethylhexyl methacrylate; LED, light-emitting diode; M_n , number-average molecular weight; PMMA, poly(methyl methacrylate); SCNP, single

chain nanoparticle; SEC, size exclusion chromatography; T_g , glass transition temperature.

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