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Wavelength-Gated Photoreversible Polymerization and Topology Control

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We exploit the wavelength dependence of [2+2] photocycloadditions and -reversions of styrylpyrene to exert unprecedented control over the photoreversible polymerization and topology of telechelic building blocks. Blue light ($\lambda_{\text{max}} = 460$ nm) initiates a catalyst-free polymerization yielding high molar mass polymers ($M_n = 60,000$ g mol$^{-1}$), which are stable at wavelengths exceeding 430 nm, yet highly responsive to shorter wavelengths. UVB irradiation ($\lambda_{\text{max}} = 330$ nm) induces a rapid depolymerization affording linear oligomers, whereas violet light ($\lambda_{\text{max}} = 410$ nm) generates cyclic entities. Thus, different colors of light allow switching between a depolymerization that either proceeds through cyclic or linear topologies. The light-controlled topology formation was evidenced by correlation of mass spectrometry (MS) with size exclusion chromatography (SEC) and ion mobility data. Critically, the color-guided topology control was also possible with ambient laboratory light affording cyclic oligomers, while sunlight activated the linear depolymerization pathway. These findings suggest that light not only induces polymerization and depolymerization but that its color can control the topological outcomes.

Introduction

Ever since Staudinger established the existence of covalent bonds between the monomeric building blocks of polymers, synthetic polymers have revolutionized our daily life. To govern the formation of covalent bonds between monomeric units, an impressive toolbox of chemistries has been developed, enabling control over chain lengths, sequences and topology of synthetic polymers (including linear, branched, crosslinked, cyclic or polycyclic polymers). The majority of those polymers and architectures are of a static nature as they emerge from non-dynamic covalent links.

Inspired by the metamorphic capabilities of biochemical systems in nature – most famously the butterfly – the design of metamorphic macromolecules, which are dynamic not only in conformation but also in the bonding of their fundamental building blocks, hold potential for a new class of soft materials: Materials whose formation, decomposition and mechanical properties can be remotely manipulated by light. Key in achieving such control is the interplay of chemical bonds with their physical, chemical and biological environment.

The toolbox of dynamic covalent chemistry provides significant potential to exert control over stable covalent bonds, which translates into remotely controllable macromolecular architectures. Classically, chemical triggers including pH, oxidizing or reducing conditions, catalysts and reagents are used to control the formation and cleavage of covalent bonds within polymers. Moving away from chemical triggers, physical forces such as thermal or mechanical energy allow direct, external manipulation of structure and bonding with electromagnetic fields offering the highest level of spatiotemporal control.

Herein, we harness the potential of light-gated dynamic covalent chemistry to break new ground in catalyst free polymer chemistry on three levels: (i) introducing the first visible light induced [2+2] photopolymerization that yields high degrees of polymerization (DP) in the liquid state under ambient conditions; (ii) enabling an unprecedented depolymerization with visible light and under ambient conditions; and critically (iii) exerting control over the topology of the depolymerization outcome, allowing switching between cyclic (violet light) or linear topologies (UVB light).
Results and Discussion

Cyclisation and Linearization

To give access to wavelength controlled dynamic covalent bonds, the photochemistry of the stilbene derivative styrylpyrene was exploited (Scheme 1A). By introducing carboxystyrylpyrene units at the termini of polyethylene glycol (PEG), a linear, telechelic macromolecular building block (L1) was obtained. Telechelic L1 can undergo [2+2] photocycloaddition of the photoreactive termini resulting in either intramolecular macrocyclization or intermolecular ligation inducing a step growth polymerization (Scheme 1C).

To elucidate the wavelength at which either cycloaddition or cycloreversion is predominantly triggered, we recently investigated the wavelength dependence of conversion for both reactions after irradiation with the same number of photons at different wavelengths. The resulting action plot serves as a blueprint for the wavelength dependent reactivity of the two competing reactions (Scheme 1B). To exclusively initiate intramolecular cyclisation, a solution of L1 (0.05 mg mL⁻¹) was irradiated with a blue LED at wavelengths >430 nm, where only cycloaddition is triggered (Scheme 1C, blue). The reduction in hydrodynamic volume upon cyclization of L1 was monitored by a characteristic shift in elution volume of the size exclusion chromatography (SEC) trace (Fig. 1A). After 1 min, a distinct shoulder towards lower elution volumes was detected. After 120 min, the initial trace of L1 had vanished and only the cyclic building block (C1) was observed. In addition to the macromolecular observation, the photocycloaddition was monitored on the level of the photoreactive groups by UV/Vis spectroscopy (Fig. S1.1.1). Tracking the intensity decrease of the styrylpyrene absorption maximum (λ_{max} = 383 nm) upon aromatic decoupling and the concomitant intensity increase of the absorption maxima characteristic for the resulting unconjugated pyrene substituent (λ_{max} = 333 and 352 nm), the reaction was found to be complete after 120 min.

To initiate the transition of cyclic C1 back into its linear topology, C1 was irradiated with UVB light, a wavelength regime dominated by the cycloreversion (Scheme 1B). The SEC trace shows that the majority of L1 is rapidly restored after 20 s (Fig 1B and Fig S1.2.1).
2). After 60 s, the SEC trace of the cyclic topology has vanished. These conditions are the mildest reported to date for a reversible topology change that is controlled exclusively by different wavelengths. Such topology transitions from linear to cyclic can affect the physical properties of polymers drastically including melting and crystallization point, melt rheology, yet also chemical properties such as their degradation behavior. The reported remote control over the polymer topology provides a facile access to explore such property changes in both materials science and biomedical applications, where the potential of cyclic polymers remains largely untapped.

**Photopolymerization**

To induce photopolymerization of L1, the intermolecular reaction has to be favored over intramolecular cyclization. Consequently, the concentration of L1 was increased to 266 mg mL⁻¹ and the reaction solution deoxygenated to suppress triplet state quenching and to increase the lifetime of the excited species (refer to SI chapter 3.3). Following irradiation with a blue LED, successful polymerization affording P1 was observed by SEC, indicating a \(M_n\) of 100,000 g mol⁻¹ over the entire sample (Fig 2 A, Fig S1.3.2). On a molecular level, the polymerization induced by [2+2] photocycloaddition of the styrylpyrene units was observed through a decrease of the absorbance of styrylpyrene in the UV-Vis spectra (Fig S1.3.1) and the characteristic resonances of the cycloadducts of different stereochemistries in the ¹H-NMR spectra between \(\delta = 4-6\) ppm (Fig S1.3.3). In addition to the formed polymer (\(M_n = 60,000\) g mol⁻¹, \(DP = 38, D = 2.2\)), smaller cyclic oligomers were observed. The high mass fraction exhibits a high degree of polymerization and low dispersity compared to previous examples of step-growth polymerizations of telechelic building blocks exploiting the widely applied Copper(I)-catalyzed Azide-Alkyne Cycloaddition (\(M_n = 21,500\) g mol⁻¹, \(DP = 8, D = 4.85\)). Using SEC hyphenated with electrospray ionization mass spectrometry (ESI-MS), the smaller oligomers were identified as 1 to 5 membered cycloadducts (Fig 2B-F). While photocycloadditions are a powerful tool to induce chemical bonds in the absence of catalysts, they require an overlap of the involved bonds according to Schmidt’s topochemical postulate. As a consequence, previously reported polymerization reactions induced by photocycloadditions only occurred efficiently in the crystalline state upon precise alignment via crystal engineering. We propose that the polymerization reaction described here proceeds efficiently for two reasons: (i) The combination of large aromatic systems with a polar PEG linker lead to a prearrangement of the styrylpyrene units in THF, favored by dispersion interactions between the large aromatic systems. (ii) The relatively low photon energies of the applied wavelengths (> 430 nm) prevent non-specific photodamage of the reactive groups and polymeric backbone. In addition to organic solvents, the photopolymerization can be carried out at lower concentrations in aqueous systems (50 mg mL⁻¹ in water containing 20% DMSO). Irradiation of the resulting suspension overnight affords a molar mass distribution very similar to the one obtained in THF (\(M_n = 95,000\) g mol⁻¹ over the entire sample). The polymer formed in aqueous suspension (\(P1^{20}\), \(M_n = 54,000\) g mol⁻¹, \(DP = 34, D = 1.9\)) had a slightly lower molar mass than P1.

![Figure 1. A) SEC trace of the cyclization of L1 (black) into the macrocycle C1 (blue) using blue light irradiation. B) Cycloreversion of C1 (grey) to L1 (black) under UVB irradiation.](image-url)
Wavelength-Gated Depolymerization

To depolymerize P1, the cyclobutane moieties within the polymer main chain have to be opened through a photocycloreversion. As photocycloaddition and photocycloreversion are triggered with different efficiencies at different wavelengths (Scheme 1B), it is possible to control which reaction is predominant through the selected color of light. If P1 is irradiated with blue light >430 nm, cycloreversion is not triggered and P1 showed no depolymerization after irradiation for 90 min under dilute conditions (0.05 mg mL⁻¹, Fig S1.4.1). The concentration of 0.05 mg mL⁻¹, also used for the cyclization and decyclization of L1, was chosen as it allowed monitoring the reaction in-situ using UV/vis spectroscopy. When the irradiation wavelength was switched under otherwise identical conditions to UVB light in order to favor the cycloreversion, a rapid depolymerization was observed (Fig 3 left column, S1.5.1-3). After 10 s only linear oligomers were observed in the SEC trace and after 10 min the polymer was transformed into its monomeric building blocks with only traces of the dimer detected. The depolymerization of P1 was also evidenced by the restored absorption band of styrylpyrene (Fig S1.5.1).

In addition to those two extreme scenarios, completely dominated by either cyclo-addition or -reversion, their wavelength dependency also allows the triggering of both reactions dynamically simply by adjusting the color of light. Irradiation with a violet LED centered around 410 nm, which also emits low intensity light below 400 nm, allows both reactions to be initiated simultaneously, albeit with drastically different efficiencies. Irradiation of P1 with a violet LED therefore also induced an efficient depolymerization yielding only cyclic oligomers after 30 min of irradiation (Fig 3 right column, S1.6.2-3). Since the violet LED emits at wavelengths which predominantly initiate the cycloaddition, the dynamic equilibrium lies strongly on the side of the cycloadduct, as evidenced by the UV/vis spectra (Fig S1.6.1) featuring the characteristic absorption maxima of the photoadduct throughout the reactions (Fig. S1.6.1). The depolymerization of P1 is thus inherently different under violet light than under UVB light. All bonds opened throughout the depolymerization under violet light are either dynamically reformed, not affecting the degree of polymerization, or react with the other polymer chain end to form a smaller cyclic polymer. It can be expected that the

Figure 2. A) SEC trace of the photopolymerization of L1 (grey) to P1 (black, Mₙ = 60 kDa, D = 2, DP = 38), cyclic oligomers (DP = 1-5) denoted by black arrows. The different cyclic oligomers were identified by SEC-ESI-MS and the recorded mass spectra are plotted along with the simulated isotopic patterns of the respective sum formula. B) Mass spectrum of the first eluting species assigned to a monomeric species (m/z of the most abundant ion = 1626.76763, simulated for C₆H₁₁O₂Na⁺, Δm/z = 3.26 ppm). C) Mass spectrum of the second eluting species assigned to a dimeric species (m/z of the most abundant ion = 1626.76917, simulated for C₆H₁₅O₃Na₂⁺, Δm/z = 4.20 ppm). D) Mass spectrum of the third eluting species assigned to a trimeric species (m/z of the most abundant ion = 1626.77647, simulated for C₆H₁₅O₃Na₃⁺, Δm/z = 8.69 ppm). E) Mass spectrum of the fourth eluting species assigned to a tetrameric species (m/z of the most abundant ion = 2161.3583, simulated for C₆H₂₂O₄Na₄⁺, Δm/z = 10.10 ppm). F) Mass spectrum of the fifth eluting species assigned to a pentameric species (m/z of the most abundant ion = 1374.16201, simulated for C₆H₂₃O₅Na₅⁺, Δm/z = 11.38 ppm).
resulting cyclodepolymerization rate becomes slower over the course of the reaction, as two photodimers of the same macrocycle must be cleaved simultaneously to enable the separation into smaller oligomers, which becomes less likely as the number of styrylpyrene adducts reduces with each successive cycle. Owing to the different depolymerization mechanisms, cyclodepolymerization of P1 under violet light irradiation is inherently slower than linear depolymerization under UVB light, even though the employed irradiation setups provide a significantly higher irradiance under the violet LED irradiation. Under these irradiation conditions, cyclic oligomers of \( DP = 1, 2 \) and 3 are obtained after 24 h. Cyclodepolymerizations have already been described by Carothers as a synthetic route towards macrocyclic oligomers on the basis of polyesters and usually require high temperatures and catalysts. To date, however, photochemically induced cyclodepolymerizations have not been reported.

Owing to the different depolymerization conditions of P1 under violet or UVB light, the observed oligomers have different topologies and elution times in the SEC. To correlate the differences in elution time with the oligomer topology, samples of P1 were investigated after irradiation for either 30 min under violet light or 20 s under UVB light irradiation. Ion-mobility measurements monitoring the arrival-time distributions (ATDs) of \([\text{C}_6\text{H}_{12}\text{O}_2\text{Na}]^+\) (\( m/z = 1493 \)) and oligomers of the same \( m/z \) ratio, show distinctively different ATDs for the two differently irradiated samples, resulting from the respective difference in collision cross section (Fig S1.9.1). Irradiation with UVB light yielded a major distribution centered at 13.7 ms and a less abundant distribution at 8.5 ms. Comparison with the ion mobility of the non-irradiated linear precursor of L1, which showed only one ATD at 13.7 ms, indicates that this feature is associated with the linear topology of the singly-charged oligomer with \( DP = 1 \) (L1), while the distribution at 8.5 ms results from a doubly-charged oligomer of \( DP = 2 \) (L2). In contrast, the ion mobility measurements of the sample after irradiation with violet light yielded ATDs shifted to later arrival times of 14.1 ms and 8.7 ms for the singly charged oligomer of \( DP = 1 \) (C1) and doubly charged oligomer of \( DP = 2 \) (C2), respectively, along with additional features at shorter arrival times. Although cyclic polymers often exhibit earlier ATDs compared to their linear analogues, the ATDs of the smaller oligomers appear to be dominated by the cycloadduct of the terminal styrylpyrene moieties. While the large aromatic groups of styrylpyrene are flat and able to closely align, the aromatic rings of the photoproduct are constrained by the cyclobutane ring, giving rise to a sterically bulkier structure. As isomerization can also drastically affect drift times, the shoulder at later arrival time in the ATD of C1 is likely to arise from the different stereoisomers of the cycloadducts.

To investigate the topology of larger oligomers (\( DP = 2 - 6 \)), extracted ion chromatograms (XICs) were obtained from the SEC-ESI-MS analysis of the same samples as used in the previously discussed ion mobility measurements. As the cycloaddition reaction does not affect the molar mass of the oligomers, the isolation of discrete mass-to-charge ratios from the SEC-ESI-MS data allows comparison between the elution times of oligomers and the exact same molar masses and \( DP \). Consequently, any observed differences in the elution time exclusively arise from different hydrodynamic volumes in THF, as a result of their topology. It was possible to extract ions of oligomers from the depolymerization, via either UVB (20 s) or blue light (30 min) irradiation of P1 from \( DP = 1 \) up to \( DP = 5 \) (Fig. 3, bottom row). Following identical \( m/z \) ranges, XICs of the oligomers resulting from the depolymerization under UVB light display longer elution times for all \( DPs \) compared to the violet light induced cyclodepolymerization. The elution time distribution of the isolated ions is well aligned with the normalized detector response of the SEC traces (Fig. S1.10.1), demonstrating that both depolymerization pathways are highly selective in topology.

Whereas the dilute reaction conditions (0.05 mg mL\(^{-1}\)) used for the cyclic and linear depolymerization allowed monitoring the reaction directly with SEC and UV/vis spectroscopy, the dilute concentration regime is no prerequisite to control the topology of the depolymerization. Both depolymerization reactions were also carried out at 20 mg mL\(^{-1}\), with either UVB or violet light to selectively yield cyclic (Fig. S Error! No text of specified style in document.) or linear depolymerization products (Fig. S 1.5.4). The only adjustment for higher concentrations under identical irradiation is the necessity of stirring and prolonged reaction times. The
higher concentrated solutions feature less light penetration and require a higher number of photons to achieve quantitative conversion.

Utilizing practical higher concentrations and the dynamic nature of the investigated system, it is readily possible to conduct multiple polymerization and depolymerization cycles. After 800 s UVB irradiation of P1 in THF (20 mg mL\(^{-1}\)) only linear oligomers were observed (Fig. S 1.5.4). These oligomers were subsequently polymerized (266 mg mL\(^{-1}\)) yielding P1', with a molar mass that reached up to 10^6 g mol\(^{-1}\). Irradiating P1' with UVB light yields linear oligomers again. Following a third photopolymerization cycle, the obtained P1'' was irradiated for 100 min with UVB light to obtain L1 along with linear oligomers.

**Depolymerization under ambient conditions**

While the color of light gates selectively between depolymerization and cyclodepolymerization of P1, the depolymerization pathway of P1 was finally investigated under ambient conditions. When solutions of P1 at otherwise identical conditions (0.05 mg mL\(^{-1}\), ambient temperature) were placed in an elevated position in the laboratory, away from direct sunlight but exposed to laboratory fluorescent lights, a slow depolymerization was observed (Fig S1.8.1-2). After one week, the majority of the polymer
is consumed, and a mixture of cyclic and linear oligomers remained. The longer reaction time results from the overall lower light intensity, which is furthermore predominantly outside of the wavelength regime that gates the photoreaction of styrylpyrene (< 450 nm).\textsuperscript{42,43} The reduced selectivity results from insufficient energy provided by the ambient light at wavelengths required for the photocycloaddition to induce the cyclization of the depolymerized fragments. If irradiated with blue light, however, all linear oligomers can be transformed into their cyclic analogues within 2 h (Fig. S1.8.3-4). Exposed solely to ambient laboratory conditions for 25 d, the cyclic C\textsubscript{1} of a \textit{DP} = 1 is the most populated species, while in the dark the polymeric P\textsubscript{1} remained stable (Fig S1.8.2). These results highlight that a suitable photonic field exerts not only control over the topology of the final depolymerization product, but throughout the entire depolymerization process. Such a highly selective photonic field can be readily accessed, if samples of P\textsubscript{1} (0.05 mg mL\textsuperscript{-1}, ambient temperature) are placed into direct sunlight (Fig. 4). After 5 s, a rapid depolymerization was observed, restoring the absorption band of styrylpyrene (Fig. S1.7.1) and leaving only linear oligomers (Fig. S1.7.2). After 4 min, the smallest linear oligomer of L\textsubscript{1} (\textit{DP} = 1) was the most abundant species according to the SEC trace. The high selectivity observed under sunlight irradiation is likely to result from the high intensity of UV light between 300-400 nm and the kinetically favored monomolecular cycloreversion. Furthermore, the presence of oxygen quenches the lifetime of excited triplet states, making the bimolecular photocycloaddition even less favorable. The reported polymer P\textsubscript{1} can hence be efficiently depolymerized under the ambient conditions inside or outside of the laboratory marking styrylpyrene as a powerful tool for dynamic covalent chemistry.

Conclusions

The telechelic functionalization of macromolecular building blocks with styrylpyrene provides a unique route to control the formation, disintegration as well as the resulting topologies of polymers. In dilute solution, the wavelength dependence of the [2+2] photocycloaddition and photocycloreversion of styrylpyrene was used to cyclize the macromolecules under blue light (\(\lambda_{\text{max}} = 460\) nm) and reopen the cycles under UVB irradiation into linear topologies.

At higher concentrations, the catalyst free polymerization of the building blocks was induced by blue light (\(\lambda_{\text{max}} = 460\) nm). The resulting high molecular weight polymer (P\textsubscript{1}) is stable at wavelength > 430 nm, yet highly and specifically responsive towards different colors of light in its depolymerization behavior. By choice of irradiation wavelength, it is possible to gate the depolymerization of P\textsubscript{1} into linear (UVB light) or cyclic topologies (violet light, \(\lambda_{\text{max}} = 410\) nm), marking it the first reported photocyclodepolymerization reaction.

In addition to the mild stimuli of LEDs, the depolymerization of P\textsubscript{1} was induced by the ambient light of the laboratory and within 5 s of sunlight irradiation, while retaining control over the depolymerization topology. The highly specific responsiveness of the photoreactive building blocks to the color of light, and thus the resulting polymers, holds potential for the design of materials that are adaptable not only in their bonding state but also the resulting topology.
Conflicts of interest

There are no conflicts to declare.

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Supporting Information

**Wavelength-Gated Photoreversible Polymerization and Topology Control**

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1. Additional Experiments

1.1 Cyclization of L1

![UV/Vis spectra and SEC traces](image)

Figure S1.1.1 UV/Vis spectra of L1 in THF (0.05 mg mL⁻¹) after blue light irradiation (refer to section 3 for details).

Figure S1.1.2 SEC traces of L1 in THF after blue light irradiation (refer to section 3 for details).
1.2 Cycloreversion of C1

Figure S1.2.1 UV/Vis spectra of C1 in THF (0.05 mg mL\(^{-1}\)) after UVB light irradiations (refer to section 3.2 for details).

Figure S1.2.2 SEC traces of C1 in THF (0.05 mg mL\(^{-1}\)) after UVB light irradiations (refer to section 3.2 for details).
1.3 Photopolymerization of L1

Figure S1.3.1 UV/Vis spectra of L1 and P1 after visible light photopolymerization in THF (0.05 mg mL⁻¹, refer to section 3.3 for details).

Figure S1.3.2 SEC traces of L1 and P1 after visible light photopolymerization in THF (0.05 mg mL⁻¹, refer to section 3.3 for details).
Figure S1.3.3. $^1$H-NMR spectrum of P1 in DMSO-$d_6$.

Figure S1.3.4 SEC traces of L1 and P1$_{1\text{H}_2\text{O}}$ after visible light photopolymerization in THF (50 mg mL$^{-1}$, refer to section 3.3 for details).
1.4 Stability of P1 under blue irradiation

![Graph showing molar mass vs. normalized detector response for P1 before and after irradiation with blue light (460 nm) for 90 min.]

Figure S1.4.1 P1 before and after irradiation with blue light (460 nm) for 90 min.

1.5 Depolymerization of P1

![Graph showing absorption versus wavelength for P1 in THF (0.05 mg mL\(^{-1}\)) after UVB light irradiations (refer to section 3.2 for details).]

Figure S1.5.1 UV/Vis spectra of P1 in THF (0.05 mg mL\(^{-1}\)) after UVB light irradiations (refer to section 3.2 for details).
Figure S1.5.2 SEC traces of P1 in THF (0.05 mg mL\(^{-1}\)) after UVB light irradiations (refer to section 3.2 for details).

Figure S1.5.3 Deconvolution of the SEC traces of the depolymerization after 30 s to distinguish linear oligomers up to a hexamer.
Figure S1.5.4 Three cycles of polymerization and depolymerization of P1, utilizing the photopolymerization procedure described (refer to section 3.3) and the depolymerization procedure developed for higher concentrations (refer to section 3.1.1).
1.6  **Cyclodepolymerization of P1**

![UV/Vis spectra of P1 in THF (0.05 mg mL⁻¹) after violet light irradiations (refer to section 3 for details).](image1)

Figure S1.6.1 UV/Vis spectra of P1 in THF (0.05 mg mL⁻¹) after violet light irradiations (refer to section 3 for details).

![SEC traces of P1 in THF (0.05 mg mL⁻¹) after violet light irradiations (refer to section 3 for details).](image2)

Figure S1.6.2 SEC traces of P1 in THF (0.05 mg mL⁻¹) after violet light irradiations (refer to section 3 for details).
Figure S1.6.3 Deconvolution of the SEC traces of the cyclodepolymerization after 60 min to distinguish cyclic oligomers up to a hexamer.
Figure S1.6.4 Cyclic depolymerization at higher concentrations (refer to section 3.1.1).
### 1.7 Depolymerization of P1 under sun light

**Figure S1.7.1 UV/Vis spectra of P1 in THF (0.05 mg mL\(^{-1}\)) after sun light irradiation (refer to section 3.4 for details).**

**Figure S1.7.2 SEC traces of P1 in THF (0.05 mg mL\(^{-1}\)) after sun light irradiation (refer to section 3.4 for details).**
1.8 Depolymerization of P1 under ambient light

Figure S1.8.1 UV/Vis spectra of P1 in THF (0.05 mg mL$^{-1}$) after ambient light irradiation (refer to section 3.5 for details).
Figure S1.8.2 SEC traces of P1 in THF (0.05 mg mL\(^{-1}\)) after ambient light irradiation (refer to section 3.5 for details).
Figure S1.8.3 UV/Vis spectra of P1 in THF (0.05 mg mL⁻¹) after 8 d of ambient light irradiations (black, irradiation as described in 3.5) and subsequent irradiation with violet light to cyclize the linear fragments (red, irradiation as described in 3).

Figure S1.8.4 SEC traces of P1 in THF (0.05 mg mL⁻¹) after 8 d of ambient light irradiations (black, irradiation as described in 3.5) and subsequent irradiation with violet light to cyclize the linear fragments (red, irradiation as described in 3).
1.9 Ion Mobility

Figure S1.9.1 Drift time distributions of the linear monomer (blue), depolymerization (20 s, red) and cyclodepolymerization (60 min, green).
Figure S1.10.1 TOP: Schematic representation of the linear (a) and cyclic (b) oligomers form upon depolymerization of P1. Middle: Normalized SEC traces of the oligomer mixtures obtained after 5 s of UVB (c) or 30 min of blue light irradiation (d). Bottom: XIC traces of the different oligomers ($DP = 1-5$) obtained from UVB (e) or violet light irradiation (f), see Fig S1.102-6 for details of the traced ions.
Figure S1.10.2 SEC ESI mass spectra of L1 obtained by irradiation with UVB (top), C1 obtained by irradiation with violet light (middle) and the simulated isotopic pattern for [C_{92}H_{114}O_{24}Na]^+ corresponding to DP = 1. The m/z range followed in the XIC (1625.63-1625.87) is highlighted in red.

Figure S1.10.3 SEC ESI mass spectra of L2 obtained by irradiation with UVB (top), C2 obtained by irradiation with violet light (middle) and the simulated isotopic pattern for [C_{184}H_{228}O_{48}Na_{2}]^{2+} corresponding to DP = 2. The m/z range followed in the XIC (1626.24-1626.29) is highlighted in red.
**DP = 3**

Figure S1.10.4 SEC ESI mass spectra of L3 obtained by irradiation with UVB (top), C3 obtained by irradiation with violet light (middle) and the simulated isotopic pattern for $\left[\text{C}_{284}\text{H}_{358}\text{O}_{76}\text{Na}_3\right]^{3+}$ corresponding to DP = 3. The $m/z$ range followed in the XIC (1685.12-1685.15) is highlighted in red.

**DP = 4**

Figure S1.10.5 SEC ESI mass spectra of L4 obtained by irradiation with UVB (top), C4 obtained by irradiation with violet light (middle) and the simulated isotopic pattern for $\left[\text{C}_{376}\text{H}_{472}\text{O}_{100}\text{Na}_5\right]^{5+}$ corresponding to DP = 4. The $m/z$ range followed in the XIC (1341.03-1341.05) is highlighted in red.
Figure S1.10.6 SEC ESI mass spectra of L5 obtained by irradiation with UVB (top), C5 obtained by irradiation with violet light (middle) and the simulated isotopic pattern for \([C_{464}H_{578}O_{122}Na_6]^{6+}\) corresponding to DP = 5. The m/z range followed in the XIC (1373.96-1374.03) is highlighted in red.

1.11 Hydrodynamic radius of oligomers from size exclusion chromatography

Figure S1.11.1 Hydrodynamic radius via SEC of the linear (black) and cyclic (blue) oligomers.
2. Experimental details

2.1 SEC-ESI-MS
Spectra were recorded on a Q Exactive Plus (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with an HESI II probe. The instrument was calibrated in the m/z range 74-1822 using premixed calibration solutions (Thermo Scientific) and for the high mass mode in the m/z range of 600-8000 using ammonium hexafluorophosphate solution. A constant spray voltage of 3.5 kV, a dimensionless sheath gas and a dimensionless auxiliary gas flow rate of 10 and 0 were applied, respectively. The capillary temperature was set to 320 °C, the S-lens RF level was set to 150 and the aux gas heater temperature was set to 125 °C. The Q Exactive was coupled to an UltiMate 3000 UHPLC System ( Dionex, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SD), autosampler (WPS 3000TSL), and a temperature controlled column department (TCC 3000). Separation was performed on two mixed bed size exclusion chromatography columns (Agilent, Mesopore 250 × 4.6 mm, particle diameter 3 µm) with a precolumn (Mesopore 50 × 7.5 mm) operating at 30 °C. THF at a flow rate of 0.30 mL·min⁻¹ was used as eluent. The mass spectrometer was coupled to the column in parallel to an UV-detector (VWD 3400, Dionex), and a RI-detector (RefractoMax520, ERC, Japan) in a setup described earlier.[1] 0.27 mL·min⁻¹ of the eluent were directed through the UV- and RI-detector and 30 µL·min⁻¹ were infused into the electrospray source after post-column addition of a 50 µM solution of sodium iodide in methanol at 20 µL·min⁻¹ by a micro-flow HPLC syringe pump (Teledyne ISCO, Model 100DM). A 100 µL aliquot of a polymer solution with a concentration of 2 mg·mL⁻¹ was injected into the SEC system.

2.2 THF-SEC
The SEC measurements were conducted on a PSS SECurity2 system consisting of a PSS SECurity TCC6000 Column Oven (35 °C), PSS SDV Column Set (8 x 150 mm 5 µm Preamolumn, 8 x 300 mm 5 µm Analytical Columns, 100000 Å, 100 Å and 100 Å) and an Agilent 1260 Infinity Isocratic Pump, Agilent 1260 Infinity Standard Autosampler, Agilent 1260 Infinity Diode Array and Multiple Wavelength Detector (A: 254 nm, B: 360 nm), Agilent 1260 Infinity Refractive Index Detector (35 °C). HPLC grade THF, stabilized with BHT, is used as eluent at a flow rate of 1 mL·min⁻¹. Narrow disperse linear poly(methyl methacrylate) (Mₘ: 202 g·mol⁻¹ to 2.2x10⁶ g·mol⁻¹) standards (PSS ReadyCal) were used as calibrants. All samples were passed over 0.22 µm PTFE membrane filters. Molecular weight and dispersity analysis was performed in PSS WinGPC UniChrom software (version 8.2).

2.3 Hydrodynamic radius from SEC
Due to the separation mechanism the primary result in SEC is the hydrodynamic volume of the analytes. For practical reasons this is generally transformed to molar mass equivalents via a calibration with standards of known molar masses. In the same manner one can calibrate the elution volume (Vₑ) in respect of $r_n$ via literature values for the calibrants. Narrow disperse linear poly(styrene) (PS) standards (Mₘ: 266 g·mol⁻¹, 370 g·mol⁻¹, 474 g·mol⁻¹, 578 g·mol⁻¹, 682 g·mol⁻¹, 1306 g·mol⁻¹, 2280 g·mol⁻¹, 3470 g·mol⁻¹, 4920 g·mol⁻¹, 6540 g·mol⁻¹, 8680 g·mol⁻¹, 15700 g·mol⁻¹, 17600 g·mol⁻¹, 25500 g·mol⁻¹, 34800 g·mol⁻¹, 42400 g·mol⁻¹, 66000 g·mol⁻¹, 130000 g·mol⁻¹, 277000 g·mol⁻¹, 552000 g·mol⁻¹, 1210000 g·mol⁻¹, 2520000 g·mol⁻¹) were used to calibrate the column set (see 2.2) in respect of PS molar mass equivalents and $k$ (125.8 ml·g⁻¹) and $\alpha$ (0.715)[2] were used to calculate the $r_H$ of said standards via the Mark-Houwink equation (1) and the relation of the hydrodynamic volume and molar mass (Equation 2) 1 to gain polymer independent $r_n$ (4) from $Vₑ$.

$$k \cdot M^\alpha = [\eta]$$

$$k \cdot M \cdot [\eta] = V_H$$
2.4 1D NMR Measurements

$^1$H- and $^{13}$C-spectra were recorded on a Bruker System 600 Ascend LH, equipped with a BBO-Probe (5 mm) with z-gradient ($^1$H: 600.13 MHz, $^{13}$C: 150.90 MHz,) or a Bruker 400 UltraShield spectrometer equipped with a Quattro Nucleus Probe (QNP) with an operating frequency of 400 MHz ($^1$H). All measurements were carried out in deuterated solvents. The chemical shift (δ) is recorded in parts per million (ppm) and relative to the residual solvent protons.[3] The measured coupling constants were calculated in Hertz (Hz). To analyze the spectra the software MESTRENOVA 11.0 was used. The signals were quoted as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet and m = multiplet.

2.5 UV-VIS Spectroscopy

UV/vis spectra were recorded on a Shimadzu UV-2700 spectrophotometer equipped with a CPS-100 electronic temperature control cell positioner. Samples were prepared in THF and measured in Hellma Analytics quartz high precision cells with a path length of 10 mm at ambient temperature.

2.6 ATR-FTIR Spectroscopy

FT-IR spectra were recorded on a Thermo Fisher Nicolet iSSO-FTIR using a germanium ATR crystal from 4000 cm$^{-1}$ to 400 cm$^{-1}$. Data recording and manipulation was performed in Thermo Fisher Omnic 9 v9.6. Spectra are reported from low to high wavenumbers, evaluation was conducted with OriginLab OriginPro2017. Bands are characterized regarding their intensity ($I$) as strong ($s$, $I > \frac{2}{3}$Strongest), medium ($m$, $\frac{1}{3}$Strongest < $I < \frac{2}{3}$Strongest) and weak ($w$, $\frac{1}{3}$Strongest > $I$) after baseline correction (10 points, spline fit).

2.7 Ion mobility

Ion-mobility measurements were carried out using a traveling wave ion mobility mass spectrometer fitted with an electrospray ionisation source (SYNAPT G2-Si, Waters, Wilmslow, UK). Mass spectra were acquired between m/z 500 – 5000, and all ion mobility spectra were acquired in successive runs on the same day to minimise any effects of temperature or humidity changes on the measured arrival time distribution. Samples were prepared in methanol and directly infused at a rate of 20 µL min$^{-1}$, with source settings: ESI capillary voltage +0.5kV, desolvation temperature 250 ºC and source temperature 100 ºC. Gas flow rates for the cone and desolvation gasses were set at 50 and 600 L hr$^{-1}$, respectively. For IMS separation, a Travelling Wave velocity of 650 ms$^{-1}$ and amplitude of 40 V were used. To minimise TOF pusher aliasing, the Transfer wave velocity was set to 111 ms$^{-1}$. All other parameters relating to the travelling wave ion optics were set to their default values. The arrival time distributions of [C$_{60}$H$_{120}$O$_{21}$Na]$^+$, (m/z 1493) was used to infer the arrival time distribution of the respective samples.
3. Photochemical Procedures

3.1 Cyclization of L1 / photocyclodepolymerization of P1 (λ = 410 nm)

Solutions of L1 or P1 in THF (0.05 mg mL⁻¹) were irradiated in a fluorescence cuvette with a 10 W LED provided by Future Eden Ltd. UV/Vis spectra were recorded and the same cuvette and SEC traces were recorded at the same concentration.

Figure S3.1.1 Irradiation setup used for irradiation at λ = 410 nm.

Figure S3.1.2 Emission spectrum of the violet LED.
3.1.1 Photocyclodepolymerization of P1 at higher concentrations

Solutions of P1 in THF (20 mg mL\(^{-1}\)) were irradiated in closed glass vials and irradiated with a 10 W LED provided by Future Eden Ltd. while stirring.

![Irradiation setup](image)

Figure S3.1.1. Irradiation set-up employed for irradiation at \(\lambda = 410\) nm at 20 mg mL\(^{-1}\).
3.2 Decyclization of L1/ depolymerization of P1
Solutions of C1 or P1 in THF (0.05 mg mL\(^{-1}\)) were irradiated in a UV/Vis cuvette in a Luzchem photoreactor, equipped with two UVB lamps yielding an irradiance of 1.1 mW cm\(^{-2}\) at the position of the sample.

![Emission spectrum of the LZC-UVB lamps.](image1)

**Figure S3.2.1** Emission spectrum of the LZC-UVB lamps.

![Irradiation setup used for the decyclization of L1 and depolymerization of P1 under UVB light irradiation.](image2)

**Figure S3.2.2** Irradiation setup used for the decyclization of L1 and depolymerization of P1 under UVB light irradiation.
3.2.1 Photodepolymerization of P1 at higher concentrations

Solutions of P1 in THF (20 mg mL\(^{-1}\)) were irradiated in a closed glass vials in a Luzchem photoreactor, equipped with two UVB lamps while stirring.

![Irradiation setup used for irradiation with UVB light at 20 mg mL\(^{-1}\).](image)

Figure S3.2.1. Irradiation setup used for irradiation with UVB light at 20 mg mL\(^{-1}\).
3.3 Photopolymerization of L1
8 mg of L1 were dissolved in 30 μL THF (266 mg mL⁻¹) in a glass vial. The solution was purged with argon for 5 min and placed in a Luzchem photoreactor with an irradiance of 1.7 mW cm⁻² at the position of the sample. After irradiation overnight, the solvent was removed under reduced pressure to obtain P1. For polymerizations in aqueous media (20% DMSO in H₂O), the reaction mixture (50 mg mL⁻¹) was stirred during irradiation.

Figure S3.3.1 Irradiation setup used for the photopolymerization of L1 (A). Close up of the glass vial with LEDs turned off (B) and on (C).

Figure S3.3.2 Emission spectrum of the blue LED used for the photopolymerization.
3.4 Photodepolymerization under sun light irradiation

Solutions of P1 in THF (0.05 mg mL⁻¹) were placed in fluorescence cuvettes on top of a small box covered in aluminum foil directly into the sun (see figure below). All experiments were carried out on the 30th of July 2019 on a clear Queensland winter day between 09:00 and 12:00 (27.477331°S; 153.029053°E, daily solar exposure 15.7 MJ m⁻² as provided by the Bureau of Meteorology).

![Figure S3.4.1 A) Irradiation setup used for sun light experiments. B) Perspective of the cuvettes facing the sun.](image)

![Figure S3.4.2 Emission spectrum of sunlight measured during the experiments next to the cuvettes, facing the same direction recorded on the 30th of July 2019.](image)
3.5 Photodepolymerization under ambient light irradiation

Solutions of P1 in THF (0.05 mg mL\(^{-1}\)) were placed in fluorescence cuvettes on top of a small box covered in aluminum foil in the laboratory (refer to the figure below). The lighting of the laboratory was on for day and night to allow for a constant irradiation of the sample under laboratory ambient conditions yielding an irradiance of 0.2 mW cm\(^{-2}\) at the position of the sample.

Figure S3.5.1 A) Irradiation setup used for ambient light experiments. B) Close up of the cuvettes.

Figure S3.5.2 Emission spectrum of the laboratory light.
4. Synthetic procedures

4.1 Materials

Unless stated otherwise, all chemicals and solvents were used as received from the supplier without further purification.

Poly(ethylene glycol) 1000 (Merck), N-bromosuccinimide (Merck), triphenylphosphine (Chemsupply), Cs$_2$CO$_3$ (Thermo Fisher Scientific), THF (Thermo Fisher Scientific), dichloromethane (Thermo Fisher Scientific, after drying and purification with SP-1 Stand Alone Solvent Purification System LC Technology Solutions Inc.), methanol (Thermo Fisher Scientific), dichloromethane-$d_2$ (Sigma-Aldrich), DMSO-$d_6$ (Sigma-Aldrich).

4.2 Poly(ethylene glycol) bis(bromine)

PEG (1000 g·mol$^{-1}$, 2.0896 g, 2.1 mmol, 1 eq.) and PPh$_3$ (2.6539 g, 10 mmol, 5 eq.) were dissolved in DCM (25 mL) in a round bottom flask at 35 °C. To this mixture a solution of NBS (1.7801 g, 10 mmol, 5 eq.) in DCM (50 mL) was added dropwise within 20 min, changing color to a dark brown, and the reaction was allowed to stir at 35 °C over night. The organic phase was washed with a small amount of saturated NaHCO$_3$, changing the color to green, 1 M HCl, saturated Na$_2$SO$_3$ and brine turning the color to dark blue. The organic phase was filtered over dry MgSO$_4$ which also absorbed the color. The solvent was evaporated under reduced pressure to yield PEG-bis(bromine)

Yield: 1.3426 g (57 %, 1.2 mmol, pale yellow waxy solid).

SEC-ESI-MS: Calculated for C$_{42}$H$_{84}$Br$_2$O$_{20}$Na$: 1626.76258; found: 1626.76656.

$^1$H NMR (600 MHz, Dichloromethane-$d_2$) δ / ppm = 3.83 (t, 4H, CH$_2$-2) 3.71-3.66 (m, 78H, CH$_3$-3 ) 3.49 (t, 4H, CH-1).

$^{13}$C NMR (600 MHz, Chloroform-$d$) δ / ppm = 71.3 (s, C-2) 70.7-70.6 (m, C-3 ) 30.4 (s, C-1).
Figure S4.1 $^1$H-NMR spectrum of PEG-bis(bromine) in CD$_2$Cl$_2$.

Figure S4.2 $^{13}$C-NMR spectrum of PEG-bis(bromine) in CDCl$_3$. 
Figure S4.2.3 SEC-ESI-MS of Poly(ethylene glycol) bis(bromine). (Top) SEC trace in THF. (Middle) ESI-MS of the elution time 19.04-19.44 min. (Bottom) Zoom into the mass region of the most abundant signal (m/z = 1085 to 1100) showing the measured and simulated isotope pattern for C$_{42}$H$_{84}$Br$_2$O$_{20}$Na.

4.3 L1 (Poly(ethylene glycol) bis(styrylpyrene ester)

![Poly(ethylene glycol) bis(styrylpyrene ester)](image)

Poly(ethylene glycol) bis(bromine) (100 mg, 0.10 mmol, 1.0 eq.), carboxy styrylpyrene[4] (140 mg, 0.40 mmol, 4.0 eq.), Cs$_2$CO$_3$ (300 mg, 0.09 mmol, 0.9 eq.) were dissolved in dry deuterated DMSO under an atmosphere of N$_2$ in a Glovebox and stirred for 10 h at 70 °C until full consumption of the Poly(ethylene glycol) bis(bromine) was reached. The reaction mixture was filtrated over a short plug of SiO$_2$ (DCM → DCM / MeOH = 9/1). The crude product was purified using preparative size exclusion chromatography (Sephadex LH-20 in MeOH).

**Yield:** 100 mg (62%, 62 µmol, yellow viscous oil).

**SEC-ESI-MS:** Calculated for C$_{92}$H$_{114}$O$_{24}$Na$^+$: 1626.76258; found: 1626.76656.
$^1$H NMR (600 MHz, DMSO-d$_6$) $\delta$/ ppm = 8.81 – 8.75 (m, 1H, CH-9), 8.60 – 8.49 (m, 2H, CH-1,11), 8.35 – 8.23 (m, 4H, CH-2,5,7,8), 8.21 – 8.15 (m, 2H, CH-3,4), 8.08 (t, $J$ = 7.6 Hz, 1H, CH-6), 8.04 – 7.94 (m, 4H, CH-12,13), 7.62 (d, $J$ = 15.7 Hz, 1H, CH-10), 4.43 – 4.38 (m, 2H, CH$_2$-14), 3.80 – 3.74 (m, 2H, CH$_2$-15), 3.64 – 3.28 (m, 133H, CH$_2$-16/H$_2$O).

$^{13}$C NMR (600 MHz, DMSO-d$_6$) $\delta$/ ppm = 165.5 (C-4), 142.2 (C-7), 131.0-130.5 (m, C-12/13/20/22), 130.4 (C-10), 129.6 (C-5/6), 128.4 (C-15), 128.2 (C-21), 127.8-127.4 (C-16/19/23/24), 127.1 (C-6/8), 126.4 (C-11), 125.6-125.3 (C-25/26/27), 124.3 (C-14), 124.0 (C-3), 123.6 (C-17), 123.3 (C-18), 69.69.7 (m, C-30), 68.4 (C-29), 64.1 (C-28).

**ATR-FTIR** Bands / cm$^{-1}$ = 3046 (w), 2867 (m), 1712 (m), 1604 (m), 1274 (s) 1100 (s), 846 (m)

Figure S4.3.1. SEC-ESI-MS of L1. (Top) SEC trace in THF. (Middle) ESI-MS of the elution time 17.76-19.41 min. (Bottom) Zoom into the mass region of the most abundant signal (m/z = 1623 to 1633) showing the measured and simulated isotope pattern for $C_{92}H_{114}O_{24}Na$. 

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Figure S4.3.2. $^1$H-NMR spectrum of L1 in DMSO-$d_6$. 
Figure S4.3.3 $^{13}$C-DEPTQ-NMR spectrum of L1 in DMSO-$d_6$ and corresponding structure.
5. References

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