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Photocycloadditions for the Design of Reversible Photopolymerizations

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Abstract: The quest for circular designs and ways to reuse polymer materials demands further advances in the development of reversible chemistries. Stimuli-responsive systems incorporated into polymer materials that enable the formation and cleavage of covalent bonds, hold great potential to reversibly decompose materials into their original building blocks. [2π+2π] photocycloadditions, for which the addition and reversion mechanism can be triggered by disparate wavelengths, stand as an attractive platform for triggering such controlled and reversible photoligation towards achieving renewable polymer materials. This perspective highlights the potential of this type of photochemistry to incorporate solid polymer materials and generate reversible polymerizations. The design of effective photoresponsive materials with specific functions requires the consideration of a number of parameters. Following a bottom-up approach – from molecular chemistry to macromolecular functionality – this perspective provides a recipe of the key aspects to consider in the design of such advanced renewable materials. Furthermore, examples of the state of the art in the field are highlighted and an overview of the fundamental challenges that remain is provided. Finally, an outlook on the next frontiers to cross is proposed.

Keywords: Photocycloaddition · Photocycloreversion · Reversible photopolymerization · Polymer materials

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1. Introduction

The neglect towards the end of life of polymer materials has driven a dependency on a single use practice, or so-called linear use of these materials, currently causing important environmental issues.[1] Thus, bringing the concept of end of life for the design of polymer materials has become an inherent need to transition from their linear use into circular schemes, that enable the regeneration of the materials and their reuse.[2,3] This emerging circular vision has rapidly propelled the development of new materials that are capable of facile degradation or intrinsic depolymerization.[4,5] Still, the greater challenge that remains for polymer chemistry is developing materials that can be efficiently recycled directly into their own initial building blocks.[6] Achieving such monomer recovery would, in principle, enable the reproduction of polymers with virgin materials' properties and give access to true circularity. In this context, a wide span of concepts has been intensively investigated in recent years, including the design of biodegradable (bio) polymers,[7] self-immolative materials,[8] and catalytic polymer decomposition.[9] Although these strategies offer attractive routes for designing renewable materials, the field is still in its infancy, which makes the need for further renewable routes critical.

As such, an emerging route towards renewable materials is stimuli-responsive polymer systems.[10,11] Responsive polymers typically incorporate chemical motifs, that when triggered by an external stimulus (*e.g.* temperature, light, chemical changes, force, magnetic/electric field) translate into predictable materials' property changes, and ultimately bestow new functionalities to the materials. A variety of advanced functions have already been reported, the most prominent examples of which include optical changes, shape morphing, and molecular release, amongst others.[12,13]

In the context of renewable polymers, different material designs have already incorporated some of these responsive systems into polymeric matrices.[14–16] Popular approaches integrate responsive dynamic motifs (either covalent or supramolecular) into the polymer backbones, which when exposed to elevated temperature, cleave and reform. These dynamic molecular exchanges translate into macromolecular transition changes, such as macroscopic flow and stress relaxation that permit bulk reprocessing.[17,18] However, the quest for circular designs and ways to reuse polymer materials demands further advances in the development of reversible chemistries. An interesting approach worth exploring relies on the control of these dynamic bonds so that the formation and cleavage of covalent bonds could occur in a controlled and permanent way upon a given trigger. Governing

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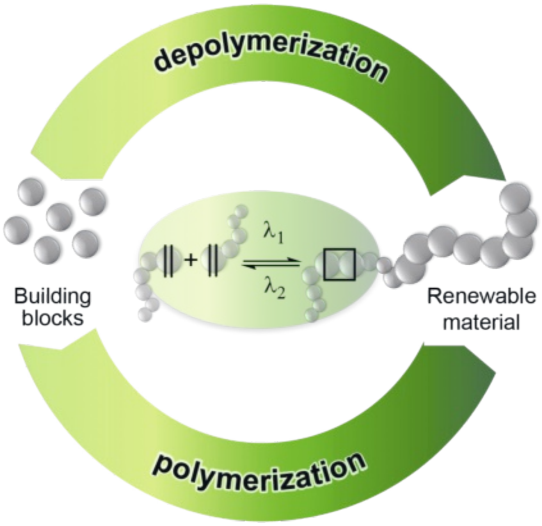
such reversibility on demand holds great potential for endowing the decomposition of the materials into original building blocks and reassociating themselves, ultimately giving access to a renewable scheme.

So far, only a limited number of reaction schemes feature controlled reversibility upon stimulation. Reversible [2π + 2π] photocycloadditions, for which the addition and reversion mechanism can be triggered by disparate wavelengths, stand as a very popular example.[19] [2π + 2π] photocycloaddition is considered as an efficient and reliable method to form and break covalent bonds with a specific wavelength. Reversible photocycloadditions have been widely employed to assemble and disassemble complex molecular and macromolecular systems in solution as well as in the solid state in a rapid and predictable manner.[20,21] These light-mediated reversible chemistries typically involve the excitation of conjugated alkenes to form cyclobutane moieties at a specific wavelength range (Scheme 1). The resulting cyclobutanes can then be reverted to the original alkene motifs upon irradiation with light of a dissimilar wavelength.[22] The recovery of the original reactants enables further cycles of these reversible reactions. If incorporated in polymer backbones, such chemistry holds potential in the design of responsive building blocks that can polymerize and depolymerize on demand in response to specific irradiations and ultimately, give access to a circular design (Scheme 1). Photoreversible cycloadditions have been widely employed to achieve a variety of functions in polymer materials such as reversible light-mediated solution-hydrogel transitions,[23] thin polymer film crosslinking, or the healing of materials surfaces[24] and coatings.[25] However, despite such a wide use in enabling material property changes, these chemistries have shown only limited success in achieving reversible photopolymerizations.



Scheme 1. Conceptual scheme of triggering reversible polymerizations *via* the use of reversible photocycloadditions of alkenes to achieve renewable polymer materials.

With this perspective, a spotlight is shined on the potential of photoresponsive systems, in particular [2π + 2π] photocycloadditions, to serve as a platform for photoreversible polymerization. In addition, an overview of critical design aspects to consider for the development of photo-mediated reversible polymerizations will be discussed. The state of the art of these different design aspects as well as a highlight of relevant developments will be presented following a bottom-up approach – from molecular chemistry to macromolecular functionality. Overall, this report aims to provide a recipe of critical parameters to consider in the material design towards reversible photopolymerizations. Moreover, the remaining challenges to fully reach the potential of this particular design concept will be critically exposed and further opportunities in the field will be outlined.

2. Reversible [2π + 2π] Photocycloadditions as a Photoresponsive System

The design of effective reversibly degradable polymer materials requires an interplay of parameters – spanning from the performance of the chemistry employed, its scale and magnitude to the state of the material (*e.g.* solid state, gels, viscous liquid, solution) and its processing (*e.g.* solution, solvent-free, in bulk). Thus, progressive approaches that first study the molecular system and transpose it into more complex structures are popular for bridging the gap between molecular-level investigations and studies in polymeric materials.

In contrast to complex macromolecular systems, molecular mechanisms and their response to external stimuli can be readily characterized and monitored using accurate and sensitive characterization methods such as, nuclear magnetic resonance (NMR), ultraviolet-visible (UV-vis), and fluorescence spectroscopy. Investigations on the molecular level provide insights into the mechanism in action as a function of different parameters (*i.e.* concentration, stimulation intensity, time) which will in turn inform the development of future materials and confer a better control of their functionality. Based on this bottom-up design principle, the following lists a series of parameters to consider in the design of renewable photoresponsive polymer materials that can be polymerized and depolymerized in a controlled fashion *via* reversible [2π + 2π] cycloaddition.

2.1 *Light-mediated Photocycloadditions*

Only a limited number of chemical motifs are known to enable photoreversible [2π + 2π] cycloadditions upon irradiation. Prominent examples are cinnamic acid, thymines, coumarins, and stilbenes (Fig. 1).[26–29] The most straightforward reaction pathway of these motifs relies on the excitation of a conjugated alkene moiety over a specific wavelength range. During the excitation process, the molecule is excited from the ground state into an excited singlet state (S1) where it can undergo intersystem crossing into the triplet state. The excited molecular alkene then reacts with another alkene in the ground state to produce a cyclobutane (Scheme 2A).[30] When performed in solution, yield and stereoselectivity of the cycloaddition process are difficult to control. Olefins typically produce a mixture of photoproducts upon irradiation including cyclobutane (stereo)isomers, alkene isomers and other side products (Scheme 2B). Stilbene motifs are, for instance, well known to generate a mixture of E/Z-isomerization,[31] intramolecular cyclization *via* oxidative dehydrogenation of dihydrophenanthrene[32] and cycloadditions of the E-form of the alkene motifs.[33] The yield of photoproducts can be tuned by changing the solvent, concentration, temperature, and/or the irradiation conditions (*i.e.* irradiation time, wavelength, and light intensity).[34,35] For example, photoinduced cycloadditions of stilbene only occur at concentrations higher than 10^{-2} M. In diluted concentrations, the S1-lifetime of the alkenes is too short to find a dimerization partner by diffusion, instead only isomerization processes take place.[36] To enable the use of photocycloaddition as a photopolymerization site, the control of the photoproduct configuration becomes an essential aspect of the design. A mixture of photoproducts, in particular isomerization, would hinder the photo-induced propagation of the polymer and lead to short molecular weight and broadly polydispersed polymers. Ultimately, such limited chain propagation can translate into the production of mechanically poor materials, limiting their implementation into commodity uses.

The incorporation of the photoresponsive motifs into polymer backbones and the use of templated systems have shown an increased control over the stereoselectivity and reaction

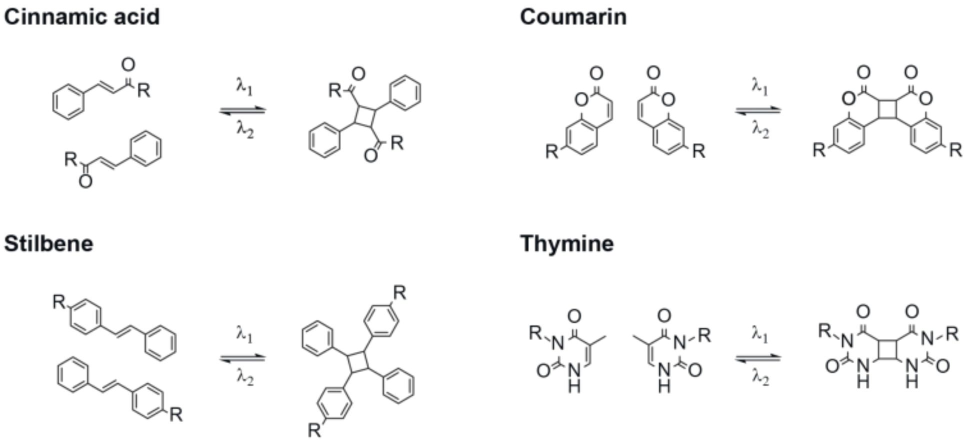
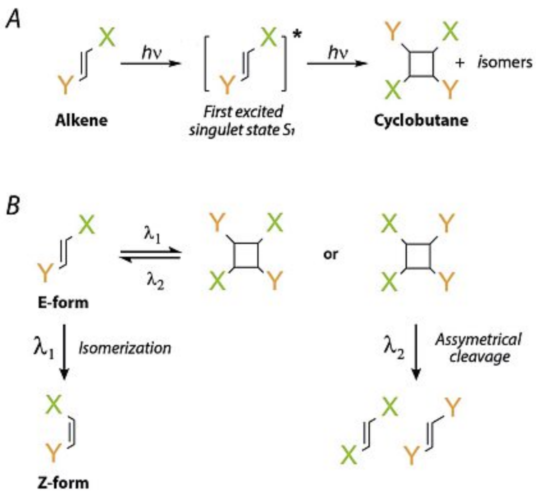


Fig. 1. Examples of photoresponsive motifs known to undergo reversible [2π + 2π] photocycloaddition. The reported wavelengths for these systems are λ_1 = >300 nm and λ_2 = < 260 nm. R represent potential functionalization sites for polymers or other functional groups.



Scheme 2. Reactivity patterns. (A) Excitation of an alkene from a ground state S_0 to the excited state S_1 followed by the photocycloaddition. (B) Scheme showcasing the different photoproducts that can be generated upon irradiation with light. i) [2π + 2π] photocycloaddition + other cyclobutane isomers, ii) isomerization (E/Z alkene forms) and, iii) asymmetric cleavage.

yield of the cycloaddition process.[37] These approaches are discussed *vide infra* in the Section 3 dedicated to the design aspects.

2.2 *The Need for Light-specific Photoprocesses*

One key challenge for designing reversible photocycloadditions, and stimuli-responsive systems in general, is finding a way to render their responses highly specific to a single stimulus. More specifically, a targeted response must be triggered by one defined stimulus and a given stimulus must cause exactly one defined response.[12] Achieving such specificity of cycloaddition and cycloreversion to light would enable highly controlled photopolymerization processes and expand the use of the materials, as these will be less sensitive to their environment and/or to processing. However, most of the photoswitches relying on covalent and on non-covalent reversible chemistries are typically sensitive to temperature and thus unspecific to light. Photoswitchable polymers relying on supramolecular interactions are, on the other hand, less robust to solvents and moisture compared to motifs relying on covalent chemistries.[38,39]

Apart from a few exceptions described by the Woodward and Hoffman rules, [2π + 2π] cycloaddition processes are thermally forbidden due to conservation of the orbital symmetry and therefore are solely light permitted.[40] However, other triggers, such as heat and mechanical forces, have shown the ability to cleave or cycloreverse cyclobutanes, rendering the process unspecific to light.[41] Considering that bulk polymers are usually melt processed (>120 °C) and during their lifetime must resist elevated temperatures as well as mechanical loads, the improvement of the mechanical and thermal stability of the cyclobutanes therefore becomes an important parameter for the design of reversible photopolymerizations. The sensitivity of cyclobutanes to other stimulations (light and mechanical) could lead to the decomposition of the polymers during reprocessing as well as during their lifecycle, both preventing the circularity of the materials.

Most of the scaffolds presented in Fig. 1 exhibit low decomposition temperatures of their cyclobutanes (typically below 80 °C) as well as dimers cleavage upon application of mechanical forces. In comparison to other motifs, coumarin dimers (Fig. 1) feature higher thermal stability, ranging from 170–320 °C and thus potentially give access to the processing of a broad range of polymers. Note that the thermal resistance can be tuned upon structural modification of the coumarin scaffold and the dimer configuration.[42,43] Despite such an advantageous feature, coumarin cyclobutanes are, however, still prone to retro [2π + 2π] cycloaddition upon mechanical activation. Craig and coworkers have shown the mechanical cleavage of coumarin dimers incorporated into the center of poly(methyl acrylate) by applying pulsed ultrasound. The sonochemical activation has yielded coumarin chain-end functionalized polymers displaying enhanced UV absorption as well as fluorescence. These optical changes were employed to characterize the scission of the coumarin cyclobutanes.[44] In a recent report, the group also embedded coumarin dimer mechanophores into a polybutadiene-based polymer main chain and introduced this polymer into elastic nanocomposites. By doing so, they demonstrated that high mechanical load leads to the scission of coumarin dimers in bulk. Similar to the solution studies, the extent of scission has been quantified by UV-vis measurements and has been leveraged to detect stress in rubber-based composites on a molecular level.[45]

Overall, neglecting the stability of the cyclobutanes in the design of reversible photopolymerizations can, to some extent, limit the application of the produced materials, their processing and their recycling. Future efforts must focus on the design of cyclobutane motifs capable of resisting thermal and mechanical constraints, while keeping high photoreaction yields (cycloaddition and cycloreversion) and selectivity.

2.3 *Redshifted Photoprocesses*

Photocycloadditions often require highly energetic short-wavelength light (typically 300–350 nm) and rely on a bimolecular process that might result in long irradiation times to fully convert monomers into their analogous cycloadducts. Comparatively, the cycloreversions rely on a unimolecular process and require even more energetic UV irradiation (typically <280 nm).[21] The use of shorter wavelengths can lead to irreversible side reactions or, in the case of a polymeric system, might induce photodamage of the surrounding material. A popular demonstration of this is the formation of the cyclobutane pyrimidine dimer (CPD) from the photodimerization of thymines in DNA.[46] Another example of a side reaction was reported by Wolff *et al.* where the cycloreversion of coumarin dimers resulted in a photodecarboxylation upon irradiation at 254 nm in acetonitrile.[28] In the context of the design of reversible polymerizations, such unspecific degradation processes would reduce the extent to which polymers can be depolymerized. Furthermore, a side reaction of the photoreactive unit would hamper a subsequent polymerization of the building blocks and thus terminate the circular process.

Strategies involving the use of catalysts, such as sensitizers[35] or Lewis acids,[47] have been employed to redshift photoreactions, in particular photocycloadditions, to respond to light of lower energy and increase the overall reaction rates. Despite their beneficial use, the presence of catalysts in a polymer system is generally considered unfavorable, as their possible leakage throughout the materials represents an obstacle for potential applications, such as food packaging and composting. Furthermore, the presence of catalysts may also affect the cycloreversion process or result in other degradation reactions during reprocessing. Because removing catalysts is a laborious task, which might involve additional processing steps, catalyst-free systems are usually preferred.[48]

Efforts have been deployed towards developing chromophore moieties that can be activated through irradiation with visible light (*i.e.* wavelengths 400–700 nm). General approaches are based on the extension of the conjugated system of a particular chromophore and/or on the addition of electron withdrawing and donating groups.[49] Series of new chromophores capable to perform cycloadditions at wavelengths above 430 nm (*i.e.* styrylpyrene,[50] acrylamidylpyrene,[51] and styrylquinoxaline[52]) were prepared following this structural modification strategy.[53]

Although redshifting the cycloaddition of a photoresponsive motif in the visible range upon structural modification has been successfully achieved, it is important to note that this shift will not be translated to a similar extent to the cycloreversion of the corresponding cycloadduct. In this context, only a limited number of motifs developed so far have enabled a complete transition of the reversible photoprocess in the visible range. Despite significant progress in the field, there is still an important need to further expand the library of motifs capable of entirely shifting the reversible process into the visible region, while still featuring high reactivity. Time-dependent density-functional theory (TDDFT) computational simulations can, in this context, be employed as a tool to predict the absorption spectra of a particular photoresponsive motif upon chemical modification.[54,55]

2.4 *Chromatic-orthogonality*[56]

To ensure effective photoreversible polymerizations, it is essential to achieve fully orthogonal photoreactions. This means producing an independent and efficient photoreaction (either [2π + 2π]-photocycloaddition or photocycloreversion), while the other photoreaction remains dormant and unaltered.[57,58] Photocycloadditions can be easily decoupled from the reversion processes and keep the formed cyclobutane dormant, as the chromophores usually absorb longer wavelengths than their corresponding dimers. However, at shorter wavelengths, the absorption spectra of the molecules typically overlap and result in a photostationary state in which the cycloaddition and the cycloreversion reactions are simultaneously triggered (Fig. 2).[19] This lack of orthogonality hinders the depolymerization processes as well as the recovery of the original building block. Although an ideal circular scheme would offer a direct recovery of the monomers, it might be noted that a partial decomposition of the polymer chains could still be sufficient to facilitate the reprocessing of these materials, as the decrease of the molecular weight can produce a reduction of the viscosity or an enhancement of the polymer solubility.[59] Yet, an uncontrolled degree of depolymerization increases the chances to broaden the polydispersity in the second cycle of photopolymerization.[60]

In the quest to turn such processes fully orthogonal, it is key to carefully consider the kinetics of cycloaddition and cycloreversion processes. Barner-Kowollik and coworkers introduced a novel analysis technique – wavelength-dependent photon efficiency analysis (WPEA) – that enables the determination of the optimal conditions to trigger each photoreaction individually *via* wavelength screening and photon kinetic analysis (Fig. 2B,C).[61,62] This technique relies on the use of a tunable and monochromatic light source to trigger photochemical processes at different wavelengths at constant path lengths and concentrations. From such measurements, action plots that depict the conversion of the reaction vs the irradiation wavelength enable the determination of the optimal wavelength for a maximized conversion (Fig. 2B). By triggering the photoreaction with the defined optimal wavelength while varying the photon numbers, one can characterize the number of photons required to reach maximum conversion (Fig. 2C). Following this methodology, the group has quantitatively mapped the photoreactivity of styrylpyrene moieties (Fig. 2A) in solution and determined the most effective wavelength for the cycloaddition and reversion at λ = 435 and 330 nm, respectively. Owing to the fundamental chemistry uncovered with WPEA analysis, the group was able to reach up to 95% photoligation of poly(ethylene glycol) functionalized with styrylpyrene that enabled the recovery of more than 85% of the macromonomers during cycloreversion (Fig. 2D).[61]

WPEA analysis holds great potential for optimizing a photoreversible process towards an orthogonal scheme. Having a fully orthogonal scheme would allow controlled and decoupled photoprocesses and thus pave the way for the design of fully reversible polymerizations. Moving from the simple inspection of absorption spectra to the in-depth study of chromophores photoreactivity must therefore become a necessary path to the future development of orthogonal photochemistries.[62]

3. Design Parameters to Consider

The polymerization and reprocessing of the polymers most likely involve a change of state, *e.g.* from liquid or viscous liquid to solid for the polymerization and from solid to liquid for the depolymerization. The physical characteristics of each state must be considered in the design of responsive materials, as the reactivity of the responsive motifs can differ in its magnitude and response time accordingly. For example, the solid state of the material carries its own set of physical properties such as crystallinity, phase segregation, and glass transition temperature. In comparison to solution or gel states, these solid-state properties limit the mobility of the reactive moieties and ultimately affect the performance of the targeted response. Note that the composition and the architecture of the polymers (*e.g.* linear, branched, networks) also dictate the required processing for the reversible polymerization procedures. These can be carried out in different media, including in solution, under high pressure/temperature or in the bulk, amongst others.

The lack of knowledge in reversible photopolymerizations of bulk materials may be explained by the difficulty in efficiently transposing a chemical reaction into a macromolecular level, in particular if the transduction process involves a change of material state. The preparation of polymers typically combines a unique set of synthetic and processing specifics for each individual system. While this authenticity must be considered in the principal designs, there are other design aspects that remain common or similar for each design. This section lists the important observations, on reversible photocycloadditions carried

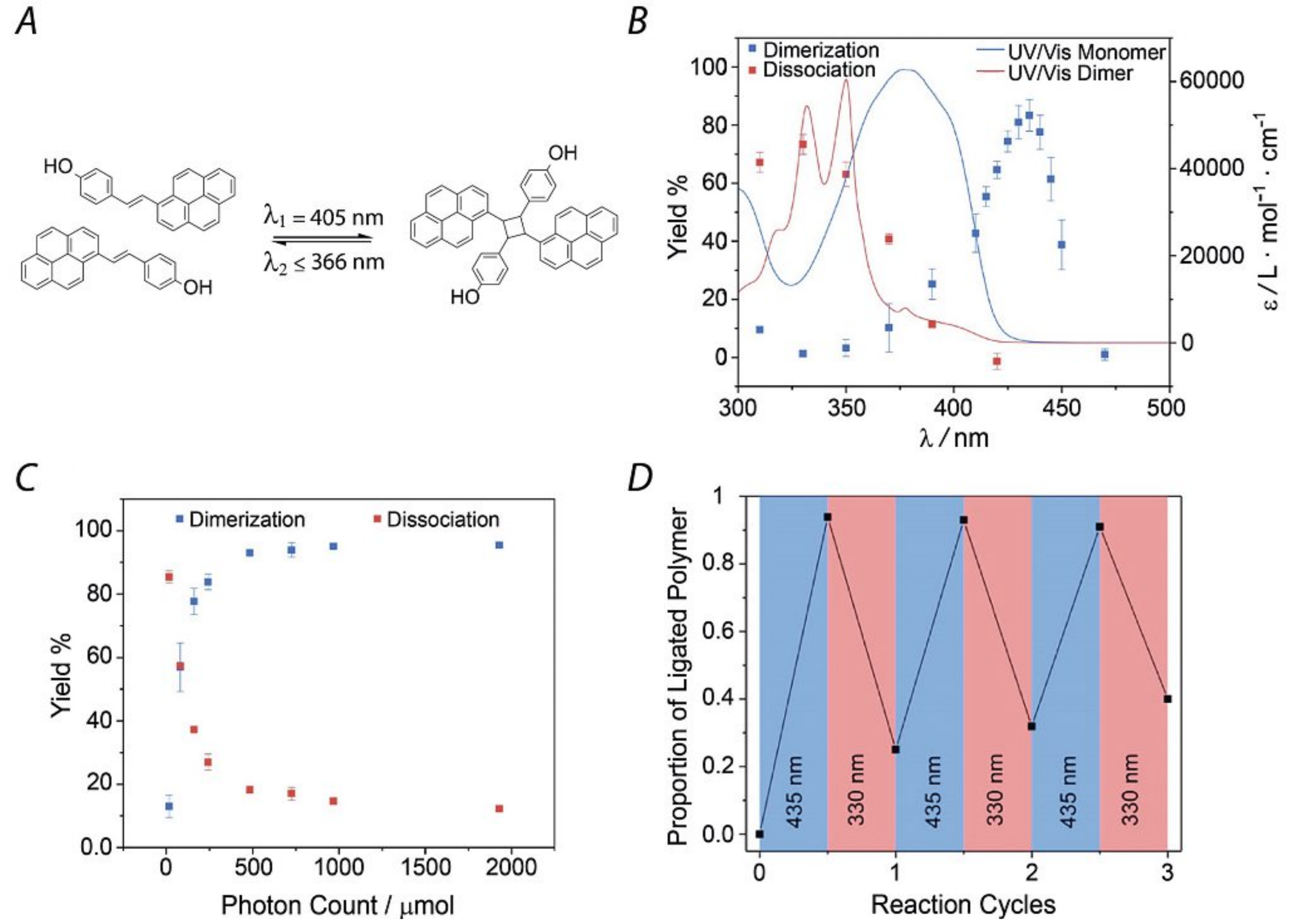


Fig. 2. (A) Reversible photocycloaddition of *trans*-(*p*-hydroxy)styrylpyrene. (B) Action plots depicting the reaction yields of the photocycloaddition (blue) and photocycloreversion photoreactions (red) at a given wavelength as well as the UV-vis spectra of the styrylpyrene motif (blue solid line) and the resulting photoproduct mixture (red solid line). The reactions were irradiated with a monochromatic laser at a fixed number of photons (242 μmol of photons) in deuterated acetonitrile and the yields determined by 1H NMR spectroscopy. (C) Plots depicting the photon kinetic analysis at a wavelength of λ = 435 nm for the cycloaddition and λ = 330 nm for the cycloreversion. The indicated yields represent the combined yields of the photoproducts. (D) Cyclic reversible photoligation of styrylpyrene terminal poly(ethylene glycol) at λ = 435 nm and λ = 330 nm for the cycloaddition and reversion, respectively and using 483 μmol of photons in each case. Reproduced with permission from ref. [61]. Copyright © 2018 American Chemical Society.

out in the solid state, that are critical to consider in future designs.

3.1 *Distance and Geometry Criteria for the Photoprocesses*

Compared to homogeneous solutions, photocycloadditions occur more efficiently and selectively when performed in the crystalline state.[63] Based on a thorough crystallographic investigation of [2π + 2π] photocycloaddition of cinnamic acid derivatives in the solid state,[64] Schmidt and coworkers postulated that the stereochemistry of the photodimer can be predicted from the preorganization of the monomers in the crystal lattice rather than through the reactivity of the molecules.[65,66] From this study, it has been shown that the cycloaddition in solid state can only happen when the reactants are separated by a distance of 4.2–4.7 Å (Schmidt's rule).[67] Factors other than the distance, including the mutual orientation of the adjacent reactant molecules and the overlap of participating orbitals, have also been shown to impact the outcome of the photocycloaddition.[68]

Until now, advanced crystal engineering designs that prealign molecules in stacking rearrangements and reduce the atomic movement (*i.e.* translational, rotational, and conformational) have been exploited to control the geometry of the reactants and catalyze photoreactions towards a selective product. General approaches towards templated systems include: the use of intramolecular functionalization of the photoresponsive motifs to control intermolecular interactions, the use of metal ion coordination,[69] crystal inclusion complexes[70–72] or co-crystallization with hydrogen bond templates.[73] Thus, to render cycloadditions favorable towards effective photopolymerizations, one should control the alignment of the motifs and bring them sufficiently close to enable selective reactions.

Prealignment strategies of photoresponsive motifs incorporated into a polymer backbone have not yet been much investigated. The closest system to this concept was reported by Trenor *et al.*, who have demonstrated cycles of reversible photoligations in the solid state.[74] In this study, poly(ethyleneglycol) functionalized at both termini with 7-hydroxycoumarin was prepared (Fig. 3A) and the polymer was solution cast into films (*ca.* 15 mm). When irradiated above 300 nm, the photoextension was confirmed with a decrease of the coumarin absorption band at 354 nm. Further characterization of the resulting extension revealed only a small degree of polymerization showing an increase of molecular weight from 4100 g/mol (corresponding to the original photoresponsive PEG coumarin unit) to 8500 g/mol and an increase of the dispersity from 1.17 to 2.75 (Fig. 3B).

The requirement of short distances between the responsive motifs to produce effective cycloadditions might raise issues when attempting to optimize the orthogonality of the process. While the issue of photostationary states can be overcome in

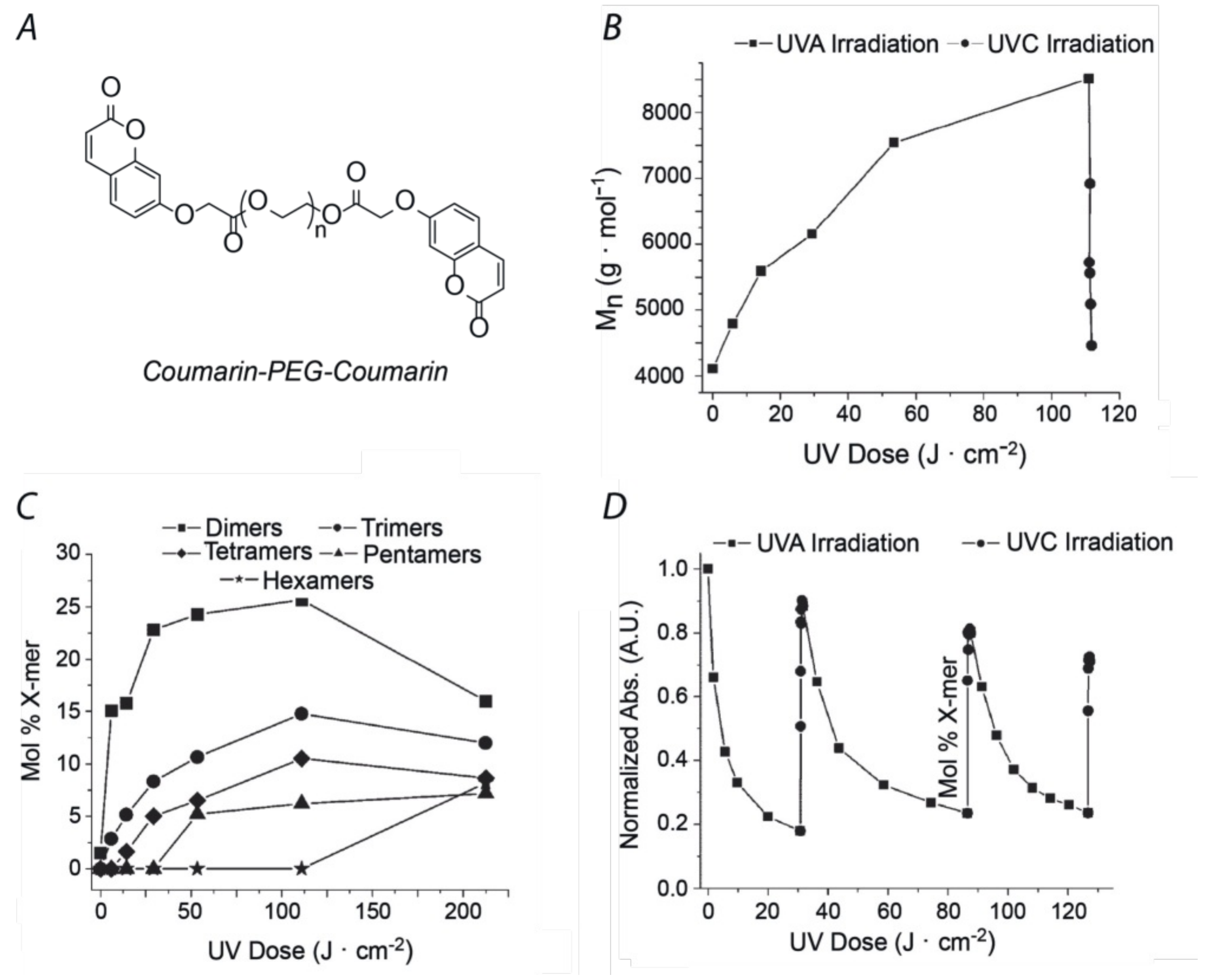


Fig. 3. (A) Molecular structure of the responsive building block; a telechelic PEG functionalized with coumarins. (B) Plot showcasing the increase and subsequent decrease of the molecular weight of the oligomer in A) induced by a reversible photoextension process upon UVA and UVC irradiation, respectively. (C) Plot showing the progressive formation of different molecular weight species upon irradiation at 300 nm. (D) Reversible photoextension of building block A) upon irradiation. Photoextension is illustrated with the squares under UVA irradiation and the photoreversion with the circles upon UVC irradiation. Reproduced with permission from ref. [74]. 2004 WILEY-VCH Verlag GmbH & Co.

solution thanks to the diffusion and reaction kinetics, the restricted motion of the motif in the solid state accentuates the problem. For example, for most of the photoresponsive motifs developed so far, the dimer absorption cannot be decoupled from the monomer, thus creating an overlap of both photoprocesses upon irradiation. This effect has been observed by Trenor *et al.* who could only photocleave 90% of the PEG-coumarin oligomers upon irradiation at 254 nm in the solid state (Fig. 3C,D).[74] A similar observation was reported by Chambers *et al.* who reported that styrylpyrene dimers incorporated into polymer networks displayed a low degree of cycloreversion.[75] In this case, the confined environment provided by the network significantly affected the photostationary state preventing the cleavage of the motif (Fig. 4A).

In summary, these observations highlight the need to introduce new approaches to increase the mobility of the responsive motifs – while maintaining a control over their orientation – for polymerization and depolymerization processes. In this context, it has been proposed to perturb the photostationary state with the application of mechanical force, solvation, or the use of competitive cycloadditions with small molecule additives (Fig. 4B).[75] The idea being to physically separate the reverted photocycloadducts before they can recombine. Achieving a suitable design of such systems could potentially lead to a controlled decomposition of a polymer into its original building blocks, independently of the architecture.

3.2 *Concentration and Dispersion Effect*

The effectiveness of the photoprocesses is strongly influenced by the concentration and dispersion of the photoresponsive motifs in the polymer matrix. Early studies on photocycloaddition reactions of thymines in solution report an increase in reaction yield associated with the intramolecular self-association. These increased conversions have also been observed on thymine bases blended into polymer matrices, showing an efficiency 20 times greater than in solution.[76] Increased, but less pronounced, conversion efficiencies have been observed for cycloadditions of thymines present on the side chains of the synthetic polymers. Kita *et al.* reported that the cycloaddition conversion decreased with decreasing thymine units in the polymers which had been assigned to the isolation of some active motifs.[76] Similar observations were later reported by other research groups.[77]

The combination of these reports suggests that intramolecular self-assembly might potentially be used as a tool to control, to some extent, the alignment of the photoresponsive motifs and render their cycloaddition effective (Fig. 5). New designs must focus on strategies that locally increase the concentration of the responsive motifs while providing enough mobility to promote

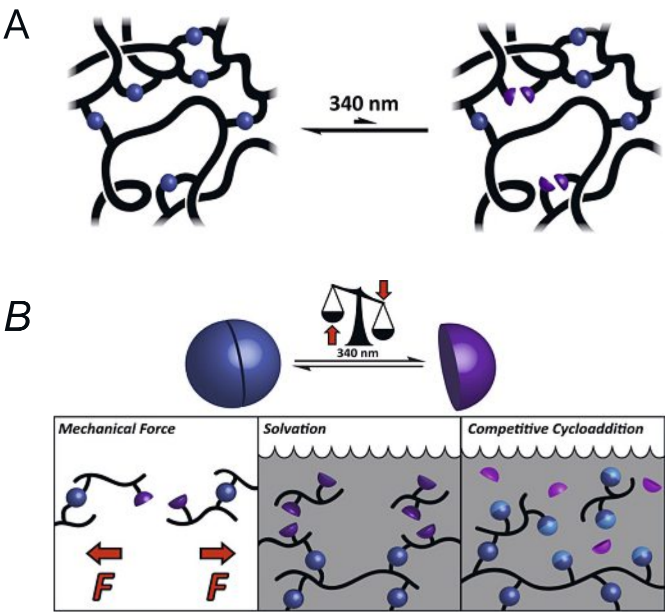


Fig. 4. (A) Limitation of the extent of the cycloreversion due to the confinement of the photoresponsive motifs into a polymer network in the solid state. (B) Suggested approaches to perturb the photostationary state of a solid-state polymer network and give access to a larger extent of cycloreversion. Reproduced with permission from ref. [75]. Copyright 2022, American Chemical Society.

their diffusion and reaction probability. Solution polymerization might offer a way to improve the mobility and reach better conversions. In this context, it is also critical to evaluate the impact of the solvent on the photoreactions. Photocycloadditions of thymine based on the polymer side chain have also been shown to be affected by the solvent media employed to run the photoprocess. In this specific case, the use of a solvent, in which the molecules poorly solubilize, induces a strong stacking interaction of the thymine bases due to a weak solvation, thus increasing the conversion yields. Similar phenomena can be observed in many biological reactions, in particular those involving nucleic acid chemistry.[78] Thus, carefully looking at these highly pre-organized biological reaction processes found in nature might expand the understanding on the specifics required to achieve effective pre-templated photopolymerization.

3.3 *Increased Mobility of the Photoresponsive Motifs*

On the basis of the previous sections, conducting photopolymerizations in solution in the presence of a suitable solvent, appears to be an appropriate approach to enhance the mobility of the reactants, and enable effective photo-induced propagation of the polymer chains. Barner-Kowollik and coworkers have achieved a high degree of reversible photopolymerization in solution using short molecular weight polymers (*ca.* 1000 g/mol) functionalized with styrylpyrene as macromonomers. The photoextension of the telechelic macromonomers was performed in solutions of THF upon irradiation at 460 nm (Fig. 6A). The polymers reached a molecular weight of Mn = 60 000 g/mol, with a high degree of polymerization (DP = 38) and low dispersity (D = 2.2). These polymers underwent an orthogonal depolymerization when irradiated with a wavelength of 330 nm, affording the original linear oligomers (Fig. 6A).[79] It is worth mentioning that the reaction conditions were defined on the basis of WPEA analysis techniques carried out on molecular styrylpyrene (Fig. 6B). This system is so far the most effective reversible photopolymerization reported which can potentially compete with templated systems. The authors assigned this high molecular weight to a prealignment of the styrylpyrene moieties in THF, promoted by the interactions between the aromatic systems, as well as to mild irradiation conditions (with a LED at >430 nm) that prevented photodamage of the surrounding media and materials. This report suggests that while the mobility of the motifs plays a key role in both photoprocesses, a semi-templated scheme seems necessary to optimize the photoextension efficiency. However, although solution processes might appear ideal for the reversible photoextension of polymer chains, the degree of polymerization so far achieved remains still too low to produce mechanically robust materials. Furthermore, photochemically growing high molecular weight polymers can also pose additional challenges. Besides the required distance of the reactants, the solubility of the polymers in solution can impact the extent of the polymerization. The progressive formation of a rigid polymer decreases the solubility of the macromolecular chains in organic solvents and thus hampers its propagation. Finally, other polymer architectures, such as polymer networks, cannot be processed in solution media and require bulk processing. The next frontier in the field is to focus on process strategies that would further push the photoextension.

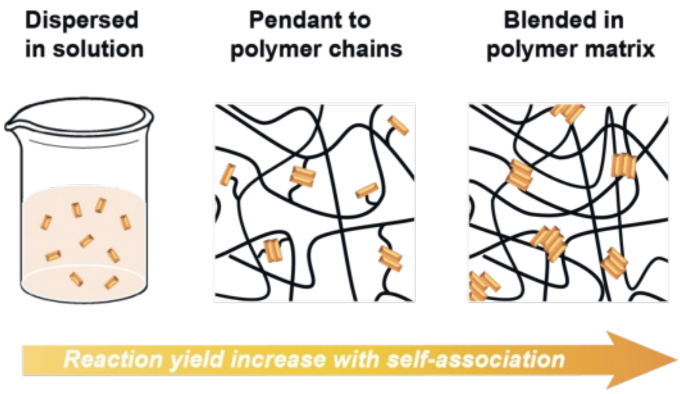


Fig. 5. Illustration depicting the concept of photocycloaddition reaction yield dependency to the self-association of the photoresponsive motifs.

4. Perspective

The development of renewable materials or new technologies that allow controlled depolymerization are some of the most praised research topics at the moment. Although at a first glance, the use of light to produce reversible polymerizations may seem exotic, the idea is nevertheless well founded. The use of light in polymer science is currently at the cutting edge of technology. For instance, technologies such as certain 3D printable inks, coatings, and adhesives rely on photoligation processes.[80] Conversely, light can also cleave polymers into smaller chains.[81] Photodegradation, an inherently uncontrolled process, has proven to be a bane to the plastics industry which has invested billions to retain material mechanical integrity *via* the use of stabilizers and additives.[82] On this basis, it is not surprising that the research community is now starting to seek the connection of these two individual processes into a single, controlled technology.

Light has attracted a lot of attention due to its unique set of characteristics. If used properly, light can be considered as a more renewable energy than other traditional sources such as heat. The most striking feature of light is its precise spatiotemporal resolution, which in the case of reversible polymerization would enable simultaneous and/or decoupled regulation of the cleavage and bond formation processes, typically not accessible to other stimuli such as pH or heat. Furthermore, its nondestructive properties, and tunable parameters (*i.e.* wavelength, irradiation time, and power intensity), allow a fine-tuning of a material's functionality.[83] The question remains: what is the realistic potential of these circular photoprocesses to go beyond academic research?

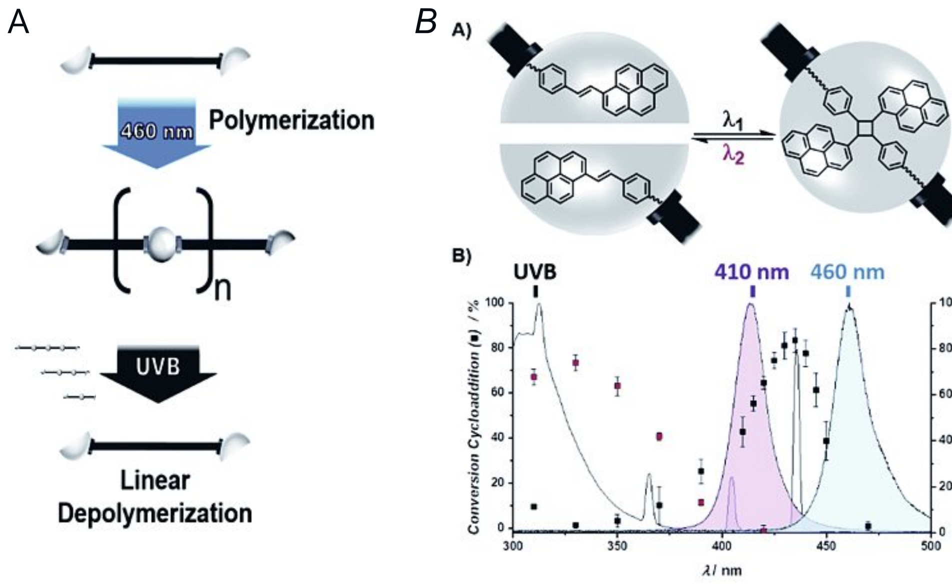


Fig. 6. (A) Schematic illustration of the polymerization and depolymerization of a responsive building block upon irradiation at 460 nm and UVB light, respectively. The building block is made of telechelic PEG functionalized with styrylpyrene units at both termini as shown in B. (B) Photo-mediated reversible $[2\pi + 2\pi]$ photocycloaddition of styrylpyrene (top image) and their corresponding action plot (bottom image). The action plots show the conversion of the photocycloaddition (black squares) and the photocycloreversion of the cycloadduct (red squared) upon irradiation at different wavelengths, and at a similar number of photons. The reactions triggered by the UVB lamp and LEDs are illustrated by the normalized emission spectra (UVB in grey and LEDs in violet and blue). Reproduced with permission from ref. [79]. Copyright 2020, Royal Society of Chemistry.

Based on the discussions underlined in this perspective, it appears that one of the next important frontiers to cross in the field is the formation of mechanically robust high molecular weight polymers. Indeed, the development of new recycling processes becomes only interesting if this technology can be applicable to mechanically robust polymer materials that can potentially compete with current commodity plastics. There is a need to conceive macromolecular engineering designs together with effective responsive motifs toward this goal. Continuous flow chemistry is for instance an interesting engineering process to consider.[84] Flow chemistry processes rely on the use of channels to conduct reactions in a continuous stream. This technique has proved to reduce reaction times, increase selectivities and allow a straightforward scalability for various reactions including cycloadditions. A variety of reactors and flow techniques are available and can further be combined with high temperatures and pressures, potentially leading to novel process windows.[85] However, despite promising results, the number of reports is limited and more avenues remain to be explored.

Another important aspect to evaluate is the relationship between the process, structure, and properties of these new materials at the beginning and end of their life cycle. The incorporation of light-sensitive motifs into the polymer backbone can lead to secondary interactions such as motif aggregation, phase separation, and crystallization of the macrounit core and/or chemical motifs.[86,87] Interactions such as aggregation can lead to additional physical crosslinking of macromolecular chains and dictate the mechanical properties of this new class of responsive materials. A complete understanding of the properties of the materials is therefore crucial for maximizing their performance. Finally, one should assess the limits of the photoextension process to define the range of potentially realizable material properties as well as their ideal processing conditions.

Developments on the expansion of depth penetration of light to achieve the depolymerization of materials regardless of their thicknesses is another key aspect to solve when aiming for large-scale applications. One can envision a combination of grinding, segmented irradiation and solvation processes to promote their disintegration. The combination of these processes would reduce the size of the materials while maximizing their surface exposure towards the irradiation. The use of commercial photosensitizers capable of adsorbing ultraviolet or visible irradiation and transferring it to adjacent molecules is another alternative that can be explored to accelerate the process of depolymerization.[88] However, as previously mentioned, new strategies should prioritize 'catalyst-free systems' to avoid laborious removal procedures. In any case, the investigation and combination of various techniques is critical for developing an effective depolymerization process that enables a full recovery of the macromonomers.

The use of photoresponsive materials is in itself a paradigm for commodity uses. Indeed, the usefulness of these materials is often questioned due to their redshift activity and thus their potential degradation upon sunlight exposure. One can argue that triggering a material's depolymerization requires a certain level of light intensity. Furthermore, if incorporated into a confined solid-state environment, the dissociation of the responsive motifs is almost inexistent and maintains the integrity of the materials. A more important problem would however be the stability of the responsive motifs over time, expecting that photobleaching will most likely occur. In this context, it might also be interesting to explore the use of these photoresponsive motifs as crosslinker additives that could be inserted and removed on demand.

Achieving high polymerization degrees of bulk materials and thereby high material stability as well as an increase of light penetration upon reprocessing, requires steady progress before any breakthrough in the field of photoextension is possible. Understanding every aspect and parameter influencing the different stages of this progressive design approach is crucial for the development of an efficient technology. While some of the aims may seem unrealistic at the moment, setting challenging goals is the best way to improve and/or adapt technologies, so that these objectives can be achieved in the future. To achieve this goal, it is crucial to mix different expertise to propel technological progress. Synthetic chemistry guided by computational simulations and photophysics could be an optimal combination for a rational design of effective photoresponsive motifs. Similarly, the combination of polymer science and macromolecular engineering has the potential to optimize the incorporation and use of photochemistry in bulk materials which might enable the introduction of reversible polymerizations.

5. Conclusion

Despite some exciting progress, the emerging chemistry toolbox towards reversible polymerizations still holds many opportunities, challenges, and a large space to be explored. The chemistry used to build stimuli-responsive materials is key towards their efficient and functional response. The use of photocycloadditions as a platform for reversible ligations has become a vibrant research area towards a controlled breaking and formation of covalent bonds upon irradiation with specific wavelengths. However, their use as reversible photoextention of polymer chains has only gained limited attention. The critical challenge to overcome is the development of photoresponsive motifs that enable the performance of highly reactive photocycloadditions and reversions with enhanced yield with visible light. To enable a controlled reversible polymerization process, it is also crucial to develop photoreactions that are fully orthogonal – triggered at disparate wavelengths to avoid photostationary states.

The use of advanced analytical techniques such as WPEA analysis must become routine in order to get an in-depth understanding of the photochemical reactions. In addition, these investigations ideally must also be combined with simulations for a better guidance towards the preparation of photoresponsive motifs that display a predictable (reversible) photochemical reactivity. Photochemical reactions are impacted by confined environments usually found in the solid state, particularly when the chromophores are included covalently in the network. In parallel, a confined environment also leads to a preorganization of the motifs which improves the stereocontrol and yield of the photoadduct. Thus, novel macromolecular engineering that finds a balance between these two stages is critical for effectively performing the photoprocess.

Undoubtedly, it is fundamentally challenging to develop efficient photo-induced polymerization technologies. In this context, photochemically induced cycloadditions may be considered as a powerful tool for the preparation of recyclable polymers. Advances in macromolecular engineering approaches that would enable large polymer chains' photopropagation is expected to lead the photopolymerization field to a groundbreaking revival and offer tremendous openings for reversible and renewable technologies.

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[1] R. C. Thompson, C. J. Moore, F. S. von Saal, S. H. Swan, *Philos. Trans. R. Soc. B Biol. Sci*. **2009**, *364*, 2153, https://doi.org/10.1098/rstb.2009.0053.

[2] T. E. M. Foundation, 'The New Plastics Economy: Rethinking the Future of Plastics', **2016**.

[3] European Commission, D.-G. for Communication, 'Circular Economy Action Plan : For a Cleaner and More Competitive Europe', Publications Office Of The European Union, **2020**.

[4] G. Xu, Q. Wang, *Green Chem*. **2022**, *24*, 2321, https://doi.org/10.1039/D1GC03901F.

[5] S. T. Phillips, A. M. Dilauro, *ACS Macro Lett*. **2014**, *3*, 298, https://doi.org/10.1021/mz5000784.

[6] G. W. Coates, Y. D. Y. L. Getzler, *Nat. Rev. Mater*. **2020**, *5*, 501, https://doi.org/10.1038/s41578-020-0190-4.

[7] D. K. Schneiderman, M. A. Hillmyer, *Macromolecules* **2017**, *50*, 3733, https://doi.org/10.1021/acs.macromol.7b00293.

[8] G. I. Peterson, M. B. Larsen, A. J. Boydston, *Macromolecules* **2012**, *45*, 7317, https://doi.org/10.1021/ma300817v.

[9] J. C. Worch, A. P. Dove, *ACS Macro Lett*. **2020**, *9*, 1494, https://doi.org/10.1021/acsmacrolett.0c00582.

[10] H. Nishida, *Polym. J*. **2011**, *43*, 435, https://doi.org/10.1038/pj.2011.16.

[11] Y. Jin, Z. Lei, P. Taynton, S. Huang, W. Zhang, *Matter* **2019**, *1*, 1456, https://doi.org/10.1016/j.matt.2019.09.004.

[12] K. M. Herbert, S. Schrettl, S. J. Rowan, C. Weder, *Macromolecules* **2017**, *50*, 8845, https://doi.org/10.1021/acs.macromol.7b01607.

[13] J. Tang, J. Sisler, N. Grishkewich, K. C. Tam, *J. Colloid Interface Sci*. **2017**, *494*, 397, https://doi.org/10.1016/j.jcis.2017.01.077.

[14] T. F. A. de Greef, E. W. Meijer, *Nature* **2008**, *453*, 171, https://doi.org/10.1038/453171a.

[15] F. García, M. M. J. Smulders, *J. Polym. Sci. Part A Polym. Chem*. **2016**, *54*, 3551, https://doi.org/10.1002/pola.28260.

[16] R. J. Wojtecki, M. a Meador, S. J. Rowan, *Nat. Mater*. **2011**, *10*, 14, https://doi.org/10.1038/nmat2891.

[17] R. L. Snyder, D. J. Fortman, G. X. De Hoe, M. A. Hillmyer, W. R. Dichtel, *Macromolecules* **2018**, *51*, 389, https://doi.org/10.1021/acs.macromol.7b02299.

[18] B. Krishnakumar, R. V. S. P. Sanka, W. H. Binder, V. Parthasarthy, S. Rana, N. Karak, *Chem. Eng. J*. **2020**, *385*, 123820, https://doi.org/10.1016/j.cej.2019.123820.

[19] H. Frisch, D. E. Marschner, A. S. Goldmann, C. Barner-Kowollik, *Angew. Chem. Int. Ed*. **2018**, *57*, 2036, https://doi.org/10.1002/anie.201709991.

[20] C. Cardenas-Daw, A. Kroeger, W. Schaertl, P. Froimowicz, K. Landfester, *Macromol. Chem. Phys*. **2012**, *213*, 144, https://doi.org/10.1002/macp.201100399.

[21] G. Kaur, P. Johnston, K. Saito, *Polym. Chem*. **2014**, *5*, 2171, https://doi.org/10.1039/C3PY01234D.

[22] D. Sarkar, N. Bera, S. Ghosh, *Eur. J. Org. Chem*. **2020**, *2020*, 1310, https://doi.org/10.1002/ejoc.201901143.

[23] J. V. Accardo, J. A. Kalow, *Chem. Sci*. **2018**, *9*, 5987, https://doi.org/10.1039/C8SC02093K.

[24] B. T. Michal, C. A. Jaye, E. J. Spencer, S. J. Rowan, *ACS Macro Lett*. **2013**, *2*, 694, https://doi.org/10.1021/mz400318m.

[25] F. Zhang, P. Ju, M. Pan, D. Zhang, Y. Huang, G. Li, X. Li, *Corros. Sci*. **2018**, *144*, 74, https://doi.org/10.1016/j.corsci.2018.08.005.

[26] W. G. Kim, *J. Appl. Polym. Sci*. **2008**, *107*, 3615, https://doi.org/10.1002/app.27436.

[27] F. D. Lewis, *Acc. Chem. Res*. **1979**, *12*, 152, https://doi.org/10.1021/ar50136a007.

[28] T. Wolff, H. Görner, *J. Photochem. Photobiol. A Chem*. **2010**, *209*, 219, https://doi.org/10.1016/j.jphotochem.2009.11.018.

[29] B. Durbeej, L. A. Eriksson, *J. Photochem. Photobiol. A Chem*. **2002**, *152*, 95, https://doi.org/10.1016/S1010-6030(02)00180-6.

[30] S. Poplata, A. Tröster, Y.-Q. Zou, T. Bach, *Chem. Rev*. **2016**, *116*, 9748, https://doi.org/10.1021/acs.chemrev.5b00723.

[31] R. B. Stoermer, *Dtsch. Chem. Ges*. **1909**, *42*, 4865, https://doi.org/10.1002/cber.190904204108.

[32] A. Smakula, *Zeitschrift für Phys. Chemie* **1934**, *25*, 90, https://doi.org/10.1515/zpch-1934-2508.

[33] F. B. Mallory, C. W. Mallory, *Org. React*. **2004**, *30*, 1, https://doi.org/10.1002/0471264180.or030.01.

[34] M. S. Syamala and V. Ramamurthy, *J. Org. Chem*. **1986**, *51*, 3712, https://doi.org/10.1021/jo00369a033.

[35] T. Wolff, H. Görner, *Phys. Chem. Chem. Phys*. **2004**, *6*, 368, https://doi.org/10.1039/B312335A.

[36] H. Meier, *Angew. Chemie* **1992**, *104*, 1425, https://doi.org/10.1002/ange.19921041104.

[37] M.-M. Gan, J.-G. Yu, Y.-Y. Wang, Y.-F. Han, *Cryst. Growth Des*. **2018**, *18*, 553, https://doi.org/10.1021/acs.cgd.7b01308.

[38] B. J. B. Folmer, R. P. Sijbesma, R. M. Versteegen, J. A. J. Van der Rijt, E. W. Meijer, *Adv. Mater*. **2000**, *12*, 874, https://doi.org/10.1002/1521-4095(200006)12:12<874::AID-ADMA874>3.0.CO;2-C.

[39] D. W. R. Balkenende, S. Coulibaly, S. Balog, Y. C. Simon, G. L. Fiore, C. Weder, *J. Am. Chem. Soc*. **2014**, *136*, 10493, https://doi.org/10.1021/ja5051633.

[40] R. Hoffmann, R. B. Woodward, *J. Am. Chem. Soc*. **1965**, *87*, 2046, https://doi.org/10.1021/ja01087a034.

[41] J. Liese, N. Hampp, *J. Phys. Chem. A* **2011**, *115*, 2927, https://doi.org/10.1021/jp111577j.

[42] R. Anet, *Canad. J. Chem*. **1962**, *40*, 1249, https://doi.org/10.1139/v62-193.

[43] S. R. Trenor, A. R. Shultz, B. J. Love, T. E. Long, *Chem. Rev*. **2004**, *104*, 3059, https://doi.org/10.1021/cr030037c.

[44] Z. S. Kean, G. R. Gossweiler, T. B. Kouznetsova, G. B. Hewage, S. L. Craig, *Chem. Commun*. **2015**, *51*, 9157, https://doi.org/10.1039/C5CC01836F.

[45] Y. Zhang, E. Lund, G. R. Gossweiler, B. Lee, Z. Niu, C. Khripin, E. Munch, M. Couty, S. L. Craig, *Macromol. Rapid Commun*. **2021**, *42*, 2000359, https://doi.org/10.1002/marc.202000359.

[46] W.-M. Kwok, C. Ma, D. L. Phillips, *J. Am. Chem. Soc*. **2008**, *130*, 5131, https://doi.org/10.1021/ja077831q.

[47] R. Brimioulle, T. Bach, *Science* **2013**, *342*, 840, https://doi.org/10.1126/science.1244809.

[48] Á. Molnár, A. Papp, *Coord. Chem. Rev*. **2017**, *349*, 1, https://doi.org/10.1016/j.ccr.2017.08.011.

[49] P. W. Kamm, J. P. Blinco, A.-N. Unterreiner, C. Barner-Kowollik, *Chem. Commun*. **2021**, *57*, 3991, https://doi.org/10.1039/D1CC00340B.

[50] S. Ludwanowski, D. Hoenders, K. Kalayci, H. Frisch, C. Barner-Kowollik, A. Walther, *Chem. Commun*. **2021**, *57*, 805, https://doi.org/10.1039/D0CC07429B.

[51] K. Kalayci, H. Frisch, C. Barner-Kowollik, V. X. Truong, *Adv. Funct. Mater*. **2020**, *30*, 1908171, https://doi.org/10.1002/adfm.201908171.

[52] K. Kalayci, H. Frisch, V. X. Truong, C. Barner-Kowollik, *Nat. Commun*. **2020**, *11*, 1, https://doi.org/10.1038/s41467-020-18057-9.

[53] V. X. Truong, C. Barner-kowollik, *Trends Chem*. **2022**, *4*, 291, https://doi.org/10.1016/j.trechm.2022.01.011.

[54] K. Bakhouche, Z. Dhaouadi, S. Lahmar, D. Hammoutène, *J. Mol. Model*. **2015**, *21*, 1, https://doi.org/10.1007/s00894-015-2706-1.

[55] N. Ben Azaza, S. Elleuch, S. Khemakhem, Y. Abid, H. Ammar, *Opt. Mater*. **2018**, *83*, 138, https://doi.org/10.1016/j.optmat.2018.05.082.

[56] A. Blanc, C. G. Bochet, *Org. Lett*. **2007**, *9*, 2649, https://doi.org/10.1021/ol070820h.

[57] D. E. Marschner, C. O. Franck, D. Abt, H. Mutlu, C. Barner-Kowollik, *Chem. Commun*. **2019**, *55*, 9877, https://doi.org/10.1039/C9CC04781F.

[58] N. Corrigan, M. Ciftci, K. Jung, C. Boyer, *Angew. Chem. Int. Ed.* **2021**, *60*, 1748, https://doi.org/10.1002/anie.201912001.

[59] G. Glöckner, 'Polymer Characterization by Liquid Chromatography', Elsevier, **1987**.

[60] R. Whitfield, N. P. Truong, D. Messmer, K. Parkatzidis, M. Rolland, A. Anastasaki, *Chem. Sci*. **2019**, *10*, 8724, https://doi.org/10.1039/C9SC03546J.

[61] D. E. Marschner, H. Frisch, J. T. Offenloch, B. T. Tuten, C. R. Becer, A. Walther, A. S. Goldmann, P. Tzvetkova, C. Barner-Kowollik, *Macromolecules* **2018**, *51*, 3802, https://doi.org/10.1021/acs.macromol.8b00613.

[62] I. M. Irshadeen, S. L. Walden, M. Wegener, V. X. Truong, H. Frisch, J. P. Blinco, C. Barner-Kowollik, *J. Am. Chem. Soc*. **2021**, *143*, 21113, https://doi.org/10.1021/jacs.1c09419.

[63] Y. Sonoda, *Molecules* **2010**, *16*, 119, https://doi.org/10.3390/molecules16010119.

[64] G. M. J. Schmidt, *Pure Appl. Chem*. **1971**, *27*, 647, https://doi.org/10.1351/pac197127040647.

[65] M. D. Cohen, G. M. J. Schmidt, *J. Chem. Soc*. **1964**, 1996, https://doi.org/10.1039/jr9640001996.

[66] M. D. Cohen, G. M. J. Schmidt, F. I. Sonntag, *J. Chem. Soc*. **1964**, 2000, https://doi.org/10.1039/jr9640002000.

[67] G. M. J. Schmidt, *J. Chem. Soc*. **1964**, 2014, https://doi.org/10.1039/jr9640002014.

[68] K. Gnanaguru, N. Ramasubbu, K. Venkatesan, V. Ramamurthy, *J. Photochem*. **1984**, *27*, 355, https://doi.org/10.1016/0047-2670(84)80051-9.

[69] R. Medishetty, I.-H. Park, S. S. Lee, J. J. Vittal, *Chem. Commun*. **2016**, *52*, 3989, https://doi.org/10.1039/C5CC08374E.

[70] S. Dawn, M. B. Dewal, D. Sobransingh, M. C. Paderes, A. C. Wibowo, M. D. Smith, J. A. Krause, P. J. Pellechia, L. S. Shimizu, *J. Am. Chem. Soc*. **2011**, *133*, 7025, https://doi.org/10.1021/ja110779h.

[71] J. N. Moorthy, K. Venkatesan, R. G. Weiss, *J. Org. Chem*. **1992**, *57*, 3292, https://doi.org/10.1021/jo00038a012.

[72] Y. Xu, M. D. Smith, J. A. Krause, L. S. Shimizu, *J. Org. Chem*. **2009**, *74*, 4874, https://doi.org/10.1021/jo900443e.

[73] L. R. Macgillivray, G. S. Papaefstathiou, T. Friščić, T. D. Hamilton, D.-K. Bučar, Q. Chu, D. B. Varshney, I. G. Georgiev, *Acc. Chem. Res*. **2008**, *41*, 280, https://doi.org/10.1021/ar700145r.

[74] S. R. Trenor, T. E. Long, B. J. Love, *Macromol. Chem. Phys.* **2004**, *205*, 715, https://doi.org/10.1002/macp.200300168.

[75] L. C. Chambers, C. Barner-Kowollik, L. Barner, L. Michalek, H. Frisch, *ACS Macro Lett*. **2022**, *11*, 532, https://doi.org/10.1021/acsmacrolett.2c00097.

[76] Y. Kita, T. Uno, Y. Inaki, K. Takemoto, *J. Polym. Sci. Polym. Chem. Ed.* **1981**, *19*, 2347, https://doi.org/10.1002/pol.1981.170190919.

[77] Y. Kita, T. Uno, Y. Inaki, K. Takemoto, *J. Polym. Sci. Polym. Chem. Ed.* **1981**, *19*, 1733, https://doi.org/10.1002/pol.1981.170190713.

[78] K. Gorska, N. Winssinger, *Angew. Chem. Int. Ed*. **2013**, *52*, 6820, https://doi.org/10.1002/anie.201208460.

[79] H. Frisch, K. Mundsinger, B. L. J. Poad, S. J. Blanksby, C. Barner-Kowollik, *Chem. Sci*. **2020**, *11*, 2834, https://doi.org/10.1039/C9SC05381F.

[80] N. Corrigan, J. Yeow, P. Judzewitsch, J. Xu, C. Boyer, *Angew. Chem. Int. Ed*. **2019**, *58*, 5170, https://doi.org/10.1002/anie.201805473.

[81] R. B. Fox, *Prog. Polym. Sci*. **1967**, *1*, 45, https://doi.org/10.1016/0079-6700(67)90002-0.

[82] J. F. Rabek, 'Photostabilization of Polymers: Priciples and Application', Springer Science & Business Media, **2012**.

[83] O. Bertrand, J. Gohy, *Polym. Chem*. **2017**, *8*, 52, https://doi.org/10.1039/C6PY01082B.

[84] M. Schröder, B. Falk, R. Schmitt, *Procedia CIRP* **2016**, *51*, 116, https://doi.org/10.1016/j.procir.2016.06.103.

[85] V. Hessel, D. Kralisch, N. Kockmann, Q. Wang, *ChemSusChem* **2013**, *6*, 746, https://doi.org/10.1002/cssc.201200766.

[86] L. Montero De Espinosa, S. Balog, C. Weder, *ACS Macro Lett*. **2014**, *3*, 540, https://doi.org/10.1021/mz500293x.

[87] S. Sivakova, D. A. Bohnsack, M. E. Mackay, P. Suwanmala, S. J. Rowan, *J. Am. Chem. Soc*. **2005**, *127*, 18202, https://doi.org/10.1021/ja055245w.

[88] T. Chen, H. Wang, Y. Chu, C. Boyer, J. Liu, J. Xu, *ChemPhotoChem* **2019**, *3*, 1059, https://doi.org/10.1002/cptc.201900166.

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