Chemistries and capabilities of photo-formable and photo-reversible crosslinked polymer networks

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Photocuring has been found to be highly useful in a diverse range of fields, such as coatings, protein coupling, liquid crystals, photoresists, drug delivery and hydrogels. Each application and use brings new challenges, with the inventive solutions contributing to a varied catalog of chemistries. The first part of this review overviews a range of the most widely-used and inventive chemistries employed to form crosslinked networks over the last decade, as well as detailing their mechanism, limitations and benefits. The second part of this review investigates the application of photoreversibly-cured crosslinked networks as photo-healable polymers, an application that exemplifies the capabilities of photoreversible chemistry.

1. Introduction

Photopolymerisation has been studied for over 150 years with the efficiencies, applications and chemistries growing significantly in this time[1]. Photopolymerisation is often used as an energy efficient alternative to thermal processes, however in recent decades it has been utilised to open up vast opportunities for polymer and smart material applications in its own right, for example the application of polymers in biochemistry has benefited greatly as polymerisation can occur at low temperatures with a directional and targeted stimulus[2-4]. In contrast to a thermal process the photochemical process provides precise control of the reaction extent, and by extension the polymer properties, by simply turning the light source on or off[5].

When these photopolymerisation techniques are applied to form crosslinked structures, several challenges arise. The main challenge of photocuring is due to the low temperature reaction conditions, which can limit the reaction as the crosslink network grows and gains rigidity, and in most cases also proceeds without solvent[6, 7]. Therefore rapid and highly efficient crosslinking processes are necessary to ensure the diffusion limitation is mitigated. Apart from the chemistry chosen, the placement and nature of the prepolymer components can help alleviate this issue. There are two main ways in which photocuring can occur: a multifunctional monomer or mixture of monomer and crosslinker are photopolymerised into a crosslinked network, or a thermoplastic is converted to a thermoset by a photoreaction between the polymer chains or with the chains and a suitable crosslinker (Figure 1).

There are several well established chemistries utilised to form crosslinked photopolymers, however in recent years more complex and robust mechanisms have been established and have given rise to interesting and beneficial capabilities or properties. The chemistries can be widely grouped into two categories based on capability: non-reversible and reversible. Within each category exists great variety and are used for different purposes. In general non-reversible photocuring focuses on simplicity of use, degree of reaction, fast kinetics and tunable response for a more favourable initiation. Reversible photocuring trades the simplicity and speed for more complex, functional capabilities that give rise to smart materials[8-10].

Herein we review the performance of the most utilised or innovative photochemistries used over the last decade to form crosslinked polymers, and the potential for further application of these chemistries. We also describe several photo-healable systems as a means to exemplify the capabilities of photoreversible crosslinked polymers.

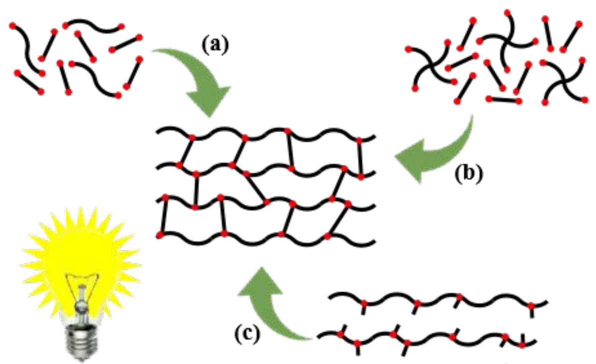

Figure 1: Generic illustration of the multiple pathways for photo-forming crosslinked networks: (a) from monomer mixtures, (b) mixture of monomers and crosslinker or (c) through coupling of functionalised polymer chains.

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2. Photocuring chemistries

2.1 Non-photoreversible photocuring

Non-reversible photocuring has seen wide application as a replacement of thermal curing, as it is seen to be a more energy efficient and controllable choice for forming crosslinked networks[11]. Many different chemistries and functional groups can undergo photocuring and show rapid reaction rates, energy efficiency and excellent temporal and spatial control[12].

2.1.1 Vinyl & Acrylate

One of the first reported photopolymers was formed by the reaction of a vinyl monomer[1], and this process has remained an intrinsic part of photopolymerisation ever since and has been widely utilised to form crosslinked networks (Figure 2). The continued use of vinyl and acrylate polymerisation in recent years is due to the efficiency and ease of the mechanism, but is not without its drawbacks. The need for photoinitiators has limited certain applications and made the choice of photoinitiator the key factor in determining the polymerisation efficiency and wavelength of light needed, with commercial options allowing the use of UV, visible and NIR wavelengths.

The photoreaction of vinyl and acrylate bonds has been utilised numerous times over the last decade to form a wide range of crosslinked materials, including natural and biocompatible polymers, dental formulations and coatings[13-20]. Through the introduction of acrylate groups into natural polymers, such as chitosan and gelatin, biocompatible polymers can be crosslinked usually by UV light in the presence of photoinitiators. Some systems have pursued greater reaction control by the use a diacrylate crosslinker with these functionalised polymers, to allow for property tuning by variation of the concentration of crosslinker[21-23].

The shifting of the initiation wavelength to visible light has been a focus, with some groups moving away from commercially available photoinitiators[8, 10, 24] and even removing the need to add a photoinitiator by introducing groups into the monomer or polymer that can generate a radical and initiate the crosslinking[25], to broaden the applicability of the systems.

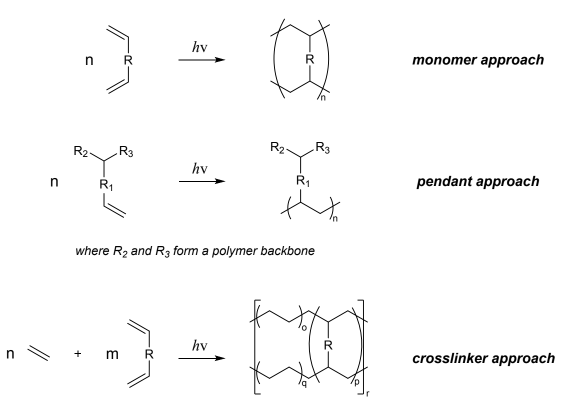

Figure 2: Generic schemes for vinyl and acrylate photocuring via the use of a multifunctional monomer (top), pendant group on a polymer chain (middle) and a combination of a monomer and crosslinker (bottom).

Overall, acrylate photopolymerisation has continued to have extensive use due to its simplicity, fast kinetics and easily tunable responsiveness, allowing its incorporation into a very wide range of targeted crosslinked polymers.

2.1.2 Thiol-ene/yne

The thiol-ene/yne reaction has also seen extensive use in the formation of photopolymer networks, with good reason as the extremely fast kinetics and great efficiency make for a readily implemented and predictable system, and a process that typifies click chemistry[26, 27]. With many parallels to the vinyl and acrylate systems, there still exists a dependence on photoinitiators of choice to dictate the polymerisation conditions and product applications. However due to the step-growth polymerisation process in thiol-ene/ynes, there is an increase in uniformity of the resulting network leading to lower shrinkage stress compared with chain-growth polymerizations[28, 29], which coupled with the fast kinetics and high energy efficiency results in its use in many applications particularly hydrogel, coating and tissue scaffold[29-32].

The use of thiol-based crosslinkers are extremely common, as tri- or tetrafuntional thiols are reacted with monomers or polymers containing alkene or alkyne groups to produce a crosslinked system (Figure 3)[32-34]. This tuning and selectivity allows for great control over the resultant polymer network properties as the crosslinker percentage, functional ends of the crosslinker and the number of reactive sites on the monomer or polymer are all variable to ensure the desired crosslink density and mechanical properties are achieved. To achieve a crosslinked network the average functionality of the thiol crosslinker and alkene monomer must exceed two, whereas the average functionality of an alkyne monomer must only be above one due to the possibility of two thiols couplings to each alkyne[30].

The variations of the alkene/yne used has seen much interest to maintain the control afforded by the step-growth mechanism. Norbornene has been increasingly utilised due to the low reactivity of the norbornene radical to other norbornenes and the high reactivity of the thiol radical to norbornene, in contrast to other alkene radicals that can initiate a competing chain-growth process through vinyl polymerisation[35-38].

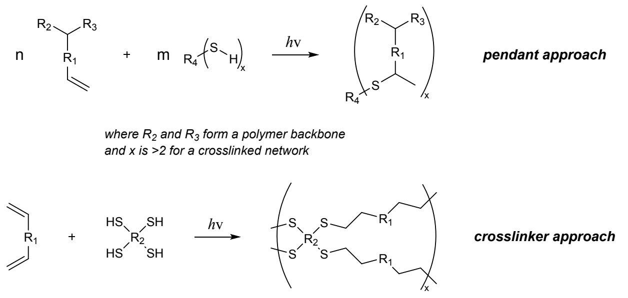

Figure 3: Scheme for the reaction of a pendant alkene with a multifunctional thiol crosslinker (top) and a multifunctional monomer with a tetrafunctional thiol crosslinker (bottom).

2.1.3 Photo-oxidation

Another class of photocuring that has been developed over the last decade, and gained prominence particularly in regards to producing biomaterials, is photo-oxidation. The process involves an oxygen radical formation, formed via visible light irradiation in the presence of a catalyst or photoinitiator, and the subsequent coupling of this radical species to a polymer chain. The two pathways for this type of curing either involve an oxygen unit on the polymer chain or O_2 introduced as gas, such as from air[39-42].

The first pathway (Figure 4) is widely used for protein coupling, particularly for tissue adhesives and repair, where the photoexcitation of the phenol group on tyrosine, in the presence of a ruthenium catalyst and sodium persulphate, results in a radical that resonates onto the aromatic, and subsequently causes coupling of two aromatic radicals to form a dityrosine bond, crosslinking the protein chains[43-49].

The latter (Figure 5) is most commonly reported with furan groups attached to a polymer chain, which react with the O_2 radical to form furan endoperoxide in the presence of a photoinitiator. This endoperoxide then breaks down to two oxygen radicals which abstracts a hydrogen from a species on an adjacent chain, forming a hydroxyl group from one of the radicals and an ether bond from the other[50-53].

Interestingly the use of photo-oxidation to produce the desired crosslinking behaviour is in stark contrast to the common view of this process in thermoplastic systems, where it is a form of degradation and requires mitigation[54, 55]. This highlights the interesting and novel chemistries being utilised to form photocured polymers and, with its potential for use with a variety of moieties, could become a very easily-implemented photocuring process for applications beyond protein coupling[56, 57]. As the coupling can occur by hydrogen abstraction, the crosslinking will be much less selective than other processes, such as acrylate and thiol-ene, hence a higher crosslinking density can be achieved, although the lack of control may see a loss of uniformity in the structure after crosslinking.

2.1.4 Nitrogen radical processes

Nitrogen radical crosslinking is much used in protein crosslinking due to the abundance of nitrogen groups and the ease of implementation as no initiation system is required[58-60].

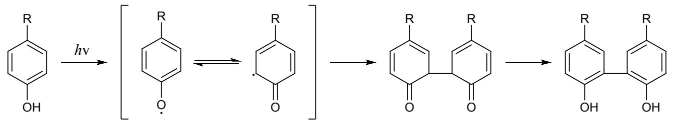

Figure 4: Scheme of the photo-oxidative curing through dityrosine bond formation.

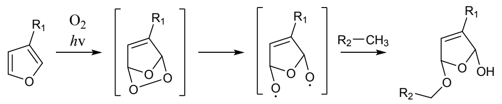

Figure 5: Scheme of the photo-oxidative curing through furan endoperoxide formation of a pendant furan.

The process typically takes place with an azide (Figure 6) or diazirine bond (Figure 7), from which N_2 is cleaved to form a radical species, by irradiation with UV light. For the azide, this radical is known as nitrene and couples the polymer chains either by hydrogen abstraction from and bond formation with a species on an adjacent chain, or by simple radical coupling to form N=N if another nitrene exists on the adjacent chain[61, 62]. For the diazirine bond, the cleavage of N_2 forms a carbene which crosslinks the chains by hydrogen abstraction from, and bond formation with, a species on an adjacent chain[63, 64].

Another nitrogen radical process which has gained recent attention is the tetrazole-alkene photoreaction (Figure 8). Similar to the other two processes, this reaction involves the photo-stimulated removal of N_2 to form a highly reactive intermediate. The N_2 is ejected from the five membered tetrazole ring to form nitrilimine, which then, through cycloaddition, couples to an alkene to form another five membered ring. The nitrilimine can also couple to amine, thiol and hydroxyl groups by hydrogen abstraction. This system has seen use in many click-chemistry applications, such as ligation and polymer folding[65, 66], however recent applications have focused on network formation for hydrogels, microparticles and fluorescent imaging[67-70].

This form of photocuring has great potential for applications outside of protein crosslinking, due to lack of need for an initiator and the very fast coupling of the radical to any functionalised site on another chain allows for easy and efficient crosslinking, similar to the acrylate and thiol-ene systems. In particular, the azide and diazirine systems use hydrogen abstraction and can couple almost anywhere along the chain leading to very high crosslinking efficiencies.

2.2 Photoreversible photocuring

The use of photoreversible reactions to form crosslinked networks has significantly increased over the last 20 years with

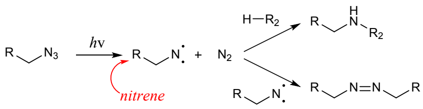

Figure 6: Mechanism of azide-based photocuring by the light-induced radical species nitrene and its subsequent coupling.

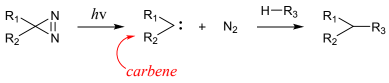

Figure 7: Diazirine photoreaction mechanism, wherein light-induced carbene formation brings about chain coupling.

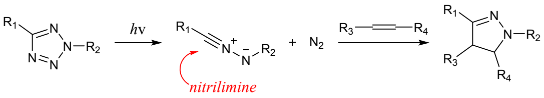

Figure 8: Tetrazole-alkene crosslinking mechanism via nitrilimine formation and subsequent reaction with an alkene on an adjacent chain.

their potential applications and their unique benefits becoming more broadly apparent[71-74]. The main function of the use of photoreversible curing is to allow the crosslinked network to revert to a thermoplastic or monomer and subsequently reform into a network upon specific light irradiations, which can lead to very interesting capabilities including precise reaction control, recyclability, self-healing, reworkability and property tuning[75-81]. Reversible photocycloaddition remains the only process used to both form and cleave a crosslinked polymer by the same mechanism. This capability allows for further control over the crosslinked structure, as the crosslink density, and thus the network properties, can be finely tuned by use of light of different wavelengths.

There exists several moieties that can undergo reversible photocycloaddition each with their own set of advantages. The main systems used for are coumarin, thymine and cinnamic acid which undergo [2+2] cycloaddition and anthracene which undergoes [4+4] cycloaddition[82-85], however more systems have appeared in recent years for niche applications[86]. The main selection factors being the systems reactive wavelengths and extent of photoreversibility, with a focus of shifting the response wavelengths of these moieties to those more favourable for the given application[78]. Most of the [2+2] photocycloaddition systems require strict parallel alignment of the double bonds and a distance of no greater than 4.5 Å for reaction to occur[87-89], this factor has a drastic effect on the reaction efficiency and hence crosslink density leading to the need for careful design when incorporating these moieties to ensure these criteria are able to be fulfilled. This high selectivity of coupling allows for a high uniformity of the resultant network and great reaction control, however it also makes for a slower and less energy efficient process when compared to the aforementioned radical-processes.

2.2.1 Coumarin

Coumarin dimerisation has been shown to proceed under visible light and sunlight, however is most efficient around 320 – 365 nm UV light. When irradiated with <280 nm UV light the cyclobutane structure of the coumarin dimers inside the polymer are cleaved to a high yield (Figure 7), a feature that has spurred the wide use of coumarin in photo-active polymers. The reversible photocycloaddition of coumarin is the most prevalent system due to the high reversibility, biocompatibility and potential for use of visible light in the dimer formation, making it a desirable option for coatings, liquid crystals, photoresists, intraocular lenses, drug delivery and hydrogel applications alike[90-102].

2.2.2 Thymine

Thymine is very useful system due to the exceptionally fast dimerisation and prevalence in DNA, making for a highly studied and understood mechanism (Figure 10)[103-105]. The utilisation of thymine for photocuring has difficulties due to the very close wavelengths for the forward and reverse reaction resulting in most commonly available illumination systems simultaneously inducing the forward and reverse reaction, making the use of photofilters necessary and hence the implementation more troublesome than other photocycloadditions[106]. Other pyrimidine derivatives, with structures very similar to thymine, also exhibit the reversible photocycloaddition, although at a lower, these include cytosine and uracil which have been shown to reversibly dimerise by themselves, with each other or with thymine[107, 108].

2.2.3 Cinnamic acid

The bulkiness of the cinnamic acid photodimer compared to other photocycloaddition dimers (Figure 11) can be a drawback in some instances, but leads to some very specific applications, such as its recent use to crosslink non-permeable PMMA films[109]. In such an application, the bulkiness serves to reduce the free volume and thus impede the permeability of oxygen through the film, which gives better anti-corrosion properties to the coating. It has also seen application for optical data storage due to the environmental stability of the cinnamate photoproduct and the reversible reaction allowing for use in photonic devices[110, 111]. Coupled with this, the π-π interactions of the aromatic groups adjacent to the double bond can help achieve the necessary alignment and spacing needed for reaction, leading to more favourable dimer formation yields and great potential for topchemical polymerisation[112, 113].

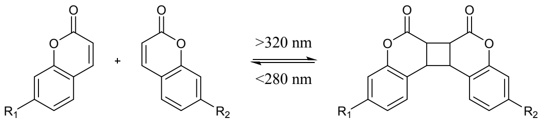

Figure 9: General scheme of coumarin reversible [2+2] photocycloaddition as utilised for photocuring[116].

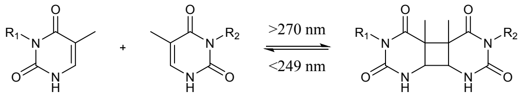

Figure 10: General scheme of thymine reversible [2+2] photocycloaddition as utilised for photocuring[83].

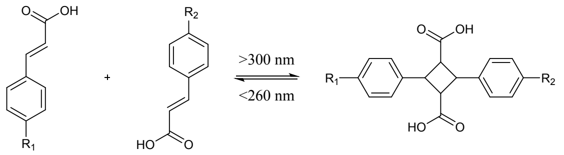

Figure 11: General scheme of cinnamic acid reversible [2+2] photocycloaddition as utilised for photocuring[117, 118].

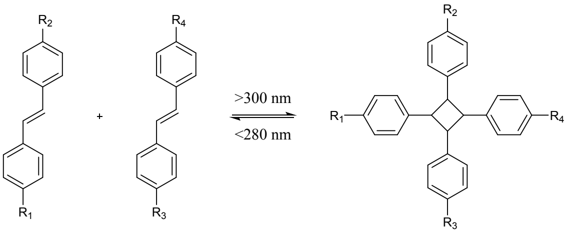

Figure 12: General scheme of stilbene reversible [2+2] photocycloaddition as utilised for photocuring[119].

2.2.4 Stilbene

Stilbenes demonstrate much of the same advantages and disadvantages of cinnamic acid, and thus similar applications. However with the modification of the substituents around the double bond there is great potential for changing the responsive wavelength to visible light dimerisation and low energy UV light cleavage[114, 115]. In fact many of the stilbene derivatives, created by modification of the substituents (Figure 12), exhibit similar photocycloaddition behaviour but at more favourable wavelengths or with different structural properties, making for a more tunable system than the others[120, 121]. This is demonstrated in one instance by the replacement of the aromatics with furan and the incorporation of this unit into gelatin, allowing for the reversible sol-gel transition through the reversible photocycloaddition of this furan-based stilbene derivative[122]. This versatility can lead to further applications compared to other photocycloaddition systems as the structure can be modified to be fit for purpose, whilst still exhibiting the same photoreversible dimerisation.

2.2.5 Anthracene

Anthracene photocycloaddition is a [4+4] process, in contrast to the other photocycloaddition processes discussed above, which results in distinct advantages and disadvantages. Firstly the dimer does not result in the formation of a cyclobutane ring (Figure 13), which means less strain in the dimer and hence a more stable and strong dimer. The unreacted moieties naturally align due to the strong π-π interactions of the anthracene structure, leading to a higher efficiency of the dimerisation compared to other photocycloaddition systems and hence greater control of the crosslink density[123-127]. The anthracene dimer is also cleavable by heat, typically above 150 °C, which can limit applicability in certain situations and restrict the service temperature of polymers containing the anthracene photoadduct[128, 129]. However it is ideal for low temperature applications, as the highly efficient photoreversibility and naturally-aligning moieties results in fast and energy efficient polymer crosslinking and thus has seen widespread use in the creation of smart materials[130-136].

Table 1: Summary of the capabilities and requirements of the reviewed photochemistry utilised to form crosslinked network polymers.

	Photo-initiator needed?	**Reaction condition**	**Photoreversible?**	**Photoreversible reaction condition**
Vinyl & Acrylate	Y	UV, visible, NIR (photoinitiator-dependent)	N	N/A
Thiol-ene/yne	Y	UV, visible, NIR (photoinitiator-dependent)	N	N/A
Photo-oxidation	Y	UV, visible (photoinitiator-dependent)	N	N/A
Nitrogen-radical processes	N	UV 365 nm>λ>248 nm	N	N/A
Coumarin [2+2] cycloaddition	N	UV, visible >320 nm	Y	UV <280 nm
Thymine [2+2] cycloaddition	N	UV >270 nm	Y	UV <249 nm
Cinnamic acid [2+2] cycloaddition	N	UV >300 nm	Y	UV <260 nm
Stilbene [2+2] cycloaddition	N	UV, visible >300 nm	Y	UV <280 nm
Anthracene [4+4] cycloaddition	N	UV, visible >350 nm	Y	UV <300 nm

3. Recent photoreversible curing chemistries application as photo-healable polymers

The main benefit of photoreversible crosslinked polymers is the ability to revert to thermoplastic, monomeric or oligomeric material by the application of a suitable wavelength of light. This allows the transition of a rigid network to a material that is capable of reordering and possesses a propensity to flow. The flowablility of this depolymerised material has been exploited to bring about the healing of different damage events in a wide range of polymer systems. The most utilised chemistries for this purpose are the photoreversible reactions, where the recovery of the original network is possible after the depolymerisation allowing the original functionality of the crosslinked polymer to be restored. The photo-healing process typically occurs in a number of stages: firstly, the network is broken down to fragments capable of flow by a suitable photo-stimulus. These fragments flow into and fill the damage site, where light irradiation of a different wavelength repolymerises the fragments into a network, restoring the original polymer properties. The main challenge of photo-healing is the balance of properties, as the crosslinked polymer must possess the necessary strength and rigidity for the given application but upon decrosslinking form a material that is soft and able to flow at, or close to, room temperature[137-139]. Another challenge is the penetration of the light in to the polymer, which can cause poor degree of reaction of the sub-surface material and thus the application of photo-healable systems is often restricted to very thin films, such as coatings, or is intended to heal surface damage or defects of thicker samples.

Recent examples of photo-healable polymers exploit the highly photoreversible nature of photocycloaddition reactions, such as anthracene, coumarin, cinnamic acid and thymine. By careful design of a photocurable system with appropriate placement of these moieties, the photocleavage can lead to exceptional healing performance of mechanically robust polymer networks. The placement of the moieties can be widely grouped into three categories: main chain modified, pendant group and crosslinker approach. The pendant groups are used for photocuring of a thermoplastic polymer by the coupling of pendant groups off of the main polymer chain. The change in properties brought about by the photoreversible reaction in this configuration are often more subtle than the other approaches. Main chain-modified refers to a system in which the photocleavable unit exists within the main polymer chain, this often results in depolymerisation to almost monomeric material. In instances where a crosslinker is introduced to the system that allows photocuring by the reaction with the existing polymer chains or functional monomers, the crosslinker has the ability to detach and reattach which can bring about greater photoreversibility than the other approaches, and this approach is known as the crosslinker approach.

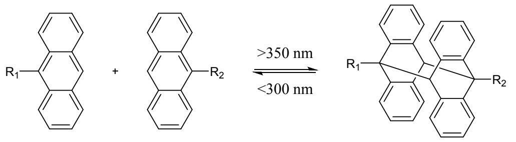

Figure 13: General scheme of anthracene reversible [4+4] photocycloaddition as utilised for photocuring[130].

3.1 Pendant group approach

The most popular method for forming self-healing crosslinked networks is by the pendant group approach. This design has many advantages as the initial thermoplastic polymer can be designed for the properties that give rise to self-healing, for example the low glass transition temperature (T_g) that results in flowability when not crosslinked. As the crosslinking is highly controllable, due to the inherent nature of a photoreaction, the properties of the crosslinked polymer can be changed by varying the irradiation time, however the crosslinking may be limited if during the crosslinking the polymer becomes too rigid to allow the correct alignment and proximity of the reactive groups to be achieved[130]. Coumarin, anthracene and cinnamic acid are the most utilised pendant groups, most likely due to their advantages discussed above such as the high photoreversibility and propensity to align which can help achieve higher dimerisation yields.

Froimowicz et al.[130] created a crosslinked polymer via the incorporation of anthracene pendant groups into a hyperbranched polyglycerol. Through dimerisation of these pendant groups a self-healing crosslinked polymer was formed with an exceptional, rapid photo-healing ability, capable of healing a 4.5 mm long and 1 mm wide surface scratch on a cast film with only 15 minutes of 254 nm irradiation (Figure 14). The great performance compared to other photohealable systems is due to the main benefit of this approach, which is the ability to design the decrosslinked structure. The initial thermoplastic before crosslinking exhibited a T_g of –46 °C and the crosslinked polymer was shown to completely revert to this thermoplastic upon decrosslinking, and thus the decrosslinked material had an extremely high propensity to flow at room temperature, which is ca. 60 °C higher than its T_g. Hence, the low T_g of the uncrosslinked polymer and the high photoreversibility of anthracene allowed for an exceptional photo-healable system. However the limitation of the pendant approach was very apparent as only 35% of the anthracene groups dimerised in the cast films, with this low percentage being attributed to the high rigidity and steric hindrance of the system during crosslinking.

Ling et al.[140] reported great success with the pendant approach as well, in this case utilising coumarin pendant groups on a polyurethane and PEG backbone. The PEG segment was seen to add flexibility to the system as the polymer exhibited two T_g values before crosslinking, the soft PEG segment gave a –20 °C T_g, and the hard polyurethane segment gave a 58 °C T_g. Having this soft segment in the polymer was most likely responsible for the polymers crosslinking extent and self-healing ability. During the crosslinking, 78% of the coumarin pendant groups reacted, which is much greater than observed by Froimowicz et al.[124] even though, as mentioned above, anthracene dimerisation is typically more favourable than coumarin. Even in this completely crosslinked state, the soft segment shows a –7 °C T_g hence providing the flexibility needed for continued crosslinking, overcoming the limiting factor of the increasing rigidity of the system during crosslinking. As expected for coumarin compared to anthracene, the dimer cleavage was not as complete as reported by Froimowicz et al.[130]. However with this soft segment in the polymer, room temperature photo-healing was still possible. The polymer was able to heal multiple, repeated scratches of around 5 – 20 µm after a 1 minute irradiation with 254 nm UV light (Figure 15), and also capable of being cut in two and reconnected by the same 254 nm irradiation to activate the surfaces, and subsequent irradiation with 365 nm for 90 minutes to bond the surfaces together. This was a very impressive result, as this cut and reconnected sample exhibited 70% of the original polymers tensile strength. Overall this system shows the importance of polymer flexibility for the pendant approach, however the incorporation of this soft segment in the polymer made the property change during crosslinking very subtle.

Ling et al.[90] followed up this system with more polyurethane and PEG photohealable polymers the very next year, looking to improve on their design and create polymers with more beneficial properties. The three polymers had different urethane content, length of the PEG segment and coumarin functionality. All three saw similar capabilities to the previous, however the best performer had a greater property changes after crosslinking compared to their previous work. In this system, the overall T_g increased by 20 °C after crosslinking, with the healing performance being comparable and the tensile strength being 70% higher than their previous work. This again showcases the importance of understanding the polymer properties when cleaved and decrosslinked, as through careful molecular design, Ling et al.[90] were able to improve the mechanical properties of the polymer whilst maintaining the same healing performance.

Choi et al.[84] sought to create a photo-healable polymer with exceptional mechanical properties for use as automotive coatings. They created an ethyl methacrylate polymer backbone with cinnamoyl pendant groups, which upon crosslinking produced a very hard polymer which was well suited for coating applications. However upon decrosslinking, the T_g of the polymer was still above 60 °C, therefore to induce healing the polymer needed to be heated to 80 °C (Figure 16). This work shows how difficult it can be to design photo-healable polymers for applications, as any rigidity added to the system to improve mechanical strength will likely also have a substantial influence on the healing performance, such as the temperature at which flow of cleaved materials can occur.

Hu et al.[141] utilised cinnamoyl pendant groups as well, by the creation of three polyphosphazene polymers with varying pendant group content: 5, 20 and 60 wt%. Of the three systems the polymer with the 20% pendant group content performed the best and exhibited healing of a 100 µm scratch after 18 minutes of 254 nm irradiation. The polymer also had the flexibility to allow 70% of the pendant groups to react during crosslinking, however only 50% of these dimers were cleaved during decrosslinking, which reflects the poor reversibility of cinnamoyl compared to other systems. The main drawback of this polymer, as commonly seen with the pendant approach, was the subtle change in properties from crosslinked to decrosslinked. The decrosslinked T_g was –5 °C which was ideal for the room temperature photo-healing however the upon crosslinking the T_g only increased to 20 °C.

Aguirresarobe et al.[142] aimed to synthesise a photo-healable coating by the attachment of coumarin pendant groups onto a polyurethane backbone. Four polymers were created with varying pendant group content between 1 – 15%, which was controlled by changing the percentage of one of the non-functionalised monomers in the formulation. The polymer with 10% pendant group content was found to be the best performer with 80% of the groups dimerising after 365 nm irradiation, a value that was also achieved by sunlight irradiation in a modest timeframe, exploiting the photosensitivity of coumarin and an especially important result if the polymers were to be used for exterior coating applications. The polymers were all very strong materials suitable for coatings, however as previously seen with Ling et al.[140] the polyurethane alone cannot provide the flexibility needed to allow room temperature healing and hence the polymers needed to be heated to 80 °C to heal surface scratches.

Very recently Fang et al.[143] also sought to create self-healing polyurethane coatings, albeit utilising anthracene in this instance. Three formulations were created with the variation of

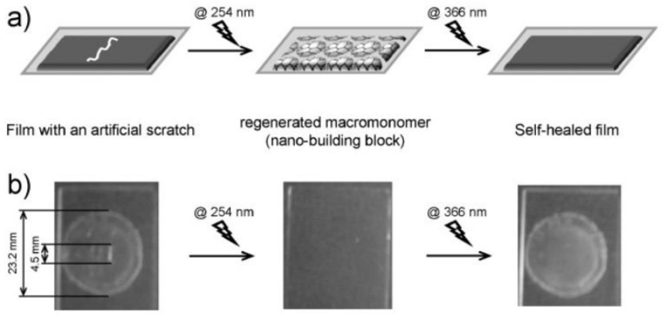

Figure 14: Self-healing procedure followed to restore a damaged sample. (a) Illustration summarizing the process and (b) real sample with an artificial scratch of (4.5x1) mm showing the procedure followed. The first irradiation completely decrosslinks the network, the second one reforms the network to give the healed polymer. Reproduced from ref. 130 with permission. Copyright (2011) John Wiley and Sons.

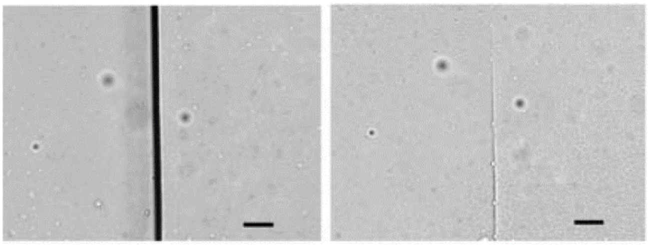

Figure 15: Optical images showing healing of razor wounds on the crosslinked film produced by Ling et al. Reproduced from ref. 140 with permission. Copyright (2011) Royal Society of Chemistry.

the pendant group content being the only difference, with 1, 4 and 8 wt% used. The 8 wt% polymer gave the best performance, both in the photoreversible efficiency and healing capability. For this polymer, 87% of the pendant groups dimerised which was much higher than the other two, likely due to close proximity of the pendant groups as the content increased. However, as seen with the other polyurethane systems, the polymers could not heal at room temperature, but rather it was necessary to heat the system to 130 °C to induce healing. This was because the combination of the polyurethane backbone and anthracene structure makes for very rigid polymers which exhibited very little propensity for flow in the decrosslinked state.

All of the photo-healable polymers made according to the pendant group approach tend to suffer from the same issue, very subtle change of properties upon crosslinking and decrosslinking. Therefore if the crosslinked polymer is rigid and tough, the decrosslinked state will likely not possess the necessary flowability for room temperature photo-healing, and conversely a soft non-crosslinked material will not allow significant property change upon crosslinking, limiting their application.

3.2 Main chain modified approach

To form a crosslinked polymer from the main chain approach the average number of functional groups on the monomers must exceed two, with more functionality producing a denser crosslinked network. There are many benefits of this approach over the pendant group approach, the main being the potential for drastic property difference between the crosslinked and decrosslinked state as the decrosslinking tends toward regeneration of the monomer. Another advantage is the alleviation of the rigidity-limited crosslinking, as the sequential addition of monomer to the network can allow the crosslinking to continue to a much greater extent since unreacted monomer can readily flow and join to the network. However as the crosslinked network is made from the monomer, the properties of the crosslinked network and subsequent decrosslinked material is less predictable, and hence this approach has attracted much less attention than the pendant group method.

Banerjee et al.[92, 144] synthesised and cured a tri-arm coumarin-functionalised polyisobutylene monomer (Figure 17) to produce a coating for photovoltaics. This approach was very successful as through the reaction of 95% of the coumarin units, the resultant polymer was heavily crosslinked and possessed the low oxygen permeability desired for the application. Upon 254 nm irradiation, 91% of these dimers were cleaved, giving rise to fast healing kinetics. The T_g of the decrosslinked system was not tested, however it was found that the polyisobutylene has a T_g of –70 °C which, with the very high dimer cleavage and little structural difference, means the decrosslinked material would also possess a very low T_g. The polymer was demonstrated to heal a 5 µm wide and 74 nm deep razor scratch with only 5 minutes of 254 nm irradiation. Furthermore the polymer was able to be healed by sunlight, as a 260 nm deep scratch was shown to decrease to 80 nm in depth after exposure to sunlight for 12 hours. This work showcases the two benefits of the main chain approach, the very high crosslink density that is achievable, and the dramatic change in properties upon decrosslinking.

Hughes et al.[145] also recently synthesised coumarin-functionalised monomers to form photo-healable crosslinked networks. Two four-arm monomers were copolymerised to form a highly crosslinked network exhibiting high T_g and hardness suitable for coating applications. This high crosslink density was achieved through dimerisation of over 70% of these coumarin sites. By irradiation of the network with 254 nm UV light, 81% of these dimers were cleaved resulting in the T_g of the material decreasing from 87 °C to –5 °C. This significant change in T_g allowed for the self-healing capability, with the material observed to heal a 29 µm scratch upon irradiation with 5.48 J/cm^2 of 254 nm UV light.

3.3 Crosslinker approach

The crosslinker approach is very similar to the main chain approach as the crosslinked network will form from irradiating

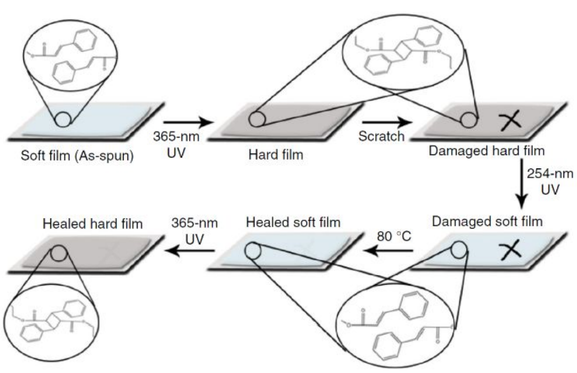

Figure 16: Schematic illustration of the healing process of the cinnamoyl film produced by Choi et al. Reproduced from ref. 84 with permission. Copyright (2014) Springer Nature.

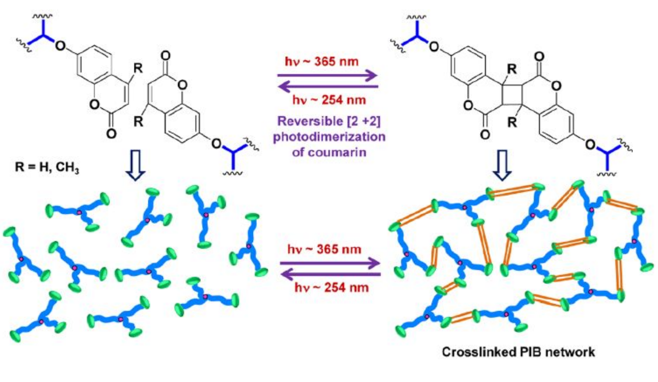

Figure 17: Reversible crosslinked network via photodimerization and photocleavage of the coumarin-functionalized tri-arm monomer produced by Banerjee et al. Reproduced from ref. 92 with permission. Copyright (2015) American Chemical Society.

a mixture of monomer/s and crosslinker/s, however due to the two component mixture the properties of the formulation can be varied with ease by changing the crosslinker type and concentration used, an option not available to the main chain or pendant group approached. Another benefit of the two component system is that the units can be smaller and hence more flowable during crosslinking and after decrosslinking which will aid healing. As for the main chain approach, the crosslinker approach is also severely underutilised in self-healing polymers, with very few systems reported in the last decade.

Oya et al.[146] photocured a bifunctional poly(butylene adipate)-based cinnamoyl monomer (PBAC2) with a tetrafunctional cinnamoyl crosslinker (C4), in a 1:1 ratio, to form a heavily crosslinked polymer (Figure 18). Due to increased mobility of the small prepolymer components the curing kinetics were very fast compared to other systems, with 76% of the cinnamoyl groups reacting within 14 minutes. To exhibit the healing properties of this polymer, dimer scission was caused by mechanical stress and the reformation of 74% of the broken dimers via irradiation with 300 – 400 nm light was possible, leading to the healed polymer. The T_g values of the materials were not measured at any stage, however PBAC2 exhibited a melting point of 44 °C hence during decrosslinking the material would revert to a very flowable form giving rise to good healing ability and the ability to reform such a high percentage of broken dimers.

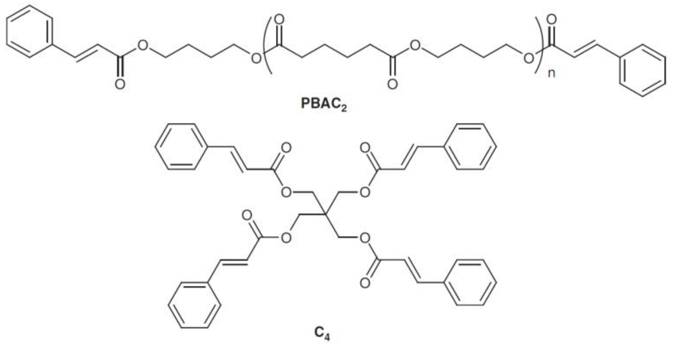

Figure 18: Molecular structures of the cinnamoyl monomer (PBAC2) and tetrafuntional crosslinker (C4) utilised by Oya et al. Reproduced from ref. 146 with permission. Copyright (2012) Springer Nature.

4. Conclusions

The use of photochemistry in creating crosslinked networks is extensive and varied, with researchers seeking photocuring for its undisruptive nature leading to applicability in situations where heat cannot be applied, its fast and controllable kinetics allowing for polymer property tuning and its widely accepted status as a greener approach to polymerisation. One key focus of the research has been the ability to use a wavelength of light that are more compatible with their desired applications, with the shift to use undisruptive visible light being most popular. With the photoinitiated systems, this can be achieved by simply changing the initiator, but for other materials this can be a difficult task that involves much experimentation and complex synthesis. For the photoinitiated materials there is also a focus on unique, non-commercial and more biocompatible initiation systems for use in vivo.

Photoreversible chemistries have gained prominence over the last decade due to many unique capabilities that can lead to impressive and highly beneficial characteristics. Photoreversible chemistry has been utilised for self-healing polymers, drug delivery, recyclability, liquid crystals, photonic response, dental formulations and even to simply form multi-use polymers to move towards a greener and more environmentally-friendly polymer industry. The application of these chemistries for self-healing polymers exemplifies photoreversible chemistry, as the photo-response can trigger a material to controllably transition through a wide range of properties, a capability that has applicability in many polymer fields.

Conflicts of interest

There are no conflicts to declare.

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