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Seeing the Light: Advancing Materials Chemistry through Photopolymerization

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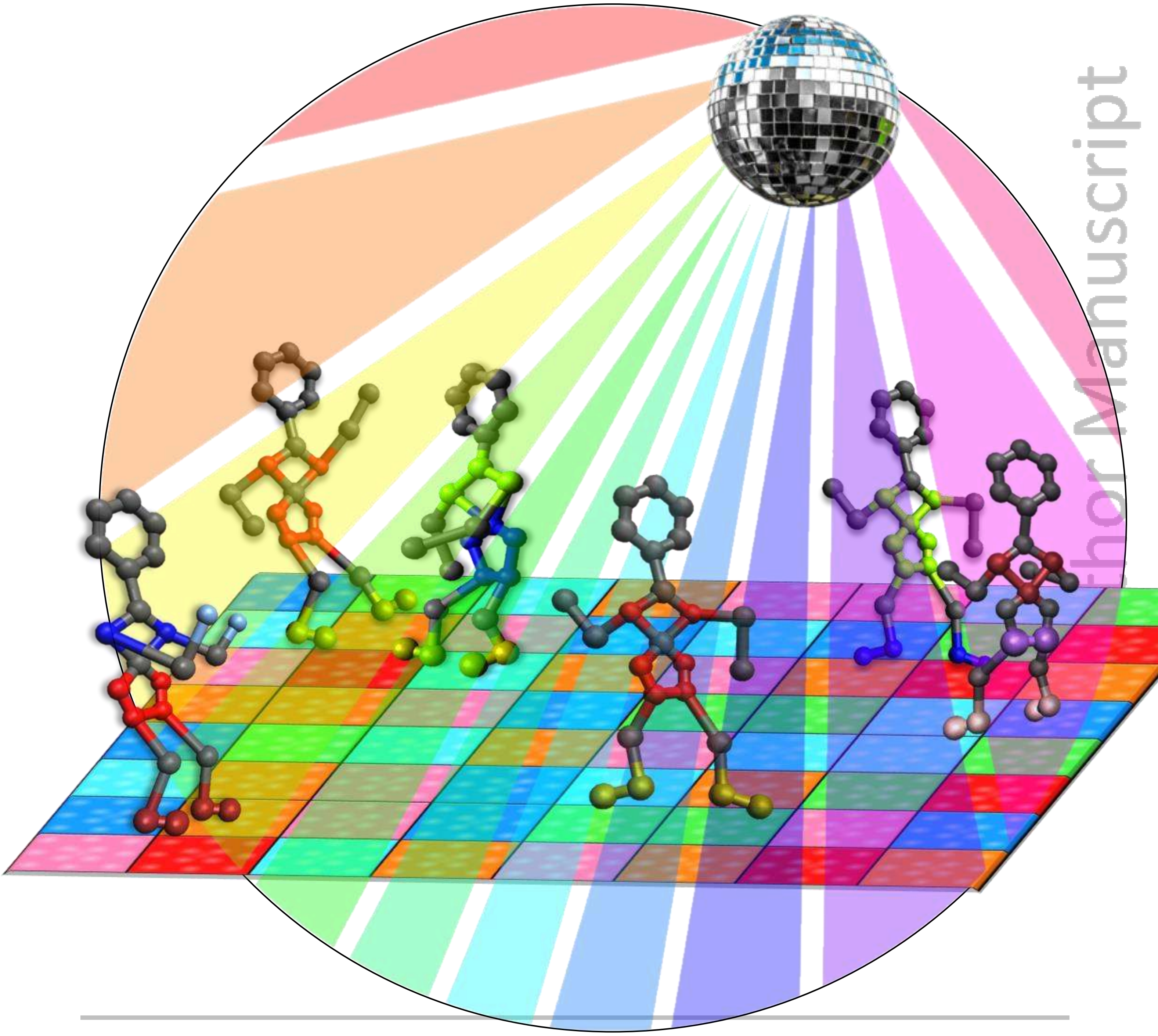

Abstract: *The application of photochemistry to polymer and material science has led to the development of complex yet efficient systems for polymerization, polymer post-functionalization, and advanced materials production. Using light to activate chemical reaction pathways in these systems not only leads to exquisite control over reaction dynamics, but also allows complex synthetic protocols to be easily achieved. Compared to polymerization systems mediated by thermal, chemical, or electrochemical means, photoinduced polymerization systems can potentially offer more versatile methods for macromolecular synthesis. We highlight the utility of light as an energy source for mediating photopolymerization, and present some promising examples of systems which are advancing materials production through their exploitation of photochemistry.*

1. Introduction

Photochemistry emerged in the early 20th century as a powerful method for the synthesis of organic compounds and macromolecules. In 1912, Ciamician conceptualized that the development of a new chemistry based on light would revolutionize our economy, by switching away from fossil fuel resources to renewable energy sources. his seminal papers, Ciamician argued that sunlight was a “limitless” resource which could be harnessed to perform chemical reactions with fewer by-products; he illustrated this point by taking plants as an example. Via photosynthesis, plants can directly utilize sunlight and transform solar energy into chemical energy to drive complex chemical reactions with unmatched precision and control.
With this early impulsion in mind, the research community has been driven to develop photochemical strategies as alternatives to conventional processes. Notably, in contrast to thermally initiated systems, photochemical approaches allow selective reactions to occur efficiently at ambient temperatures. Such photochemical processes are possible due to the large disparity in the energy available for activation in thermally- and photoinduced systems; at 25 ˚C, a thermal bath provides less than one-hundredth of the energy that is available in a mole of photons at wavelengths typically used for photochemical transformations (350-450 nm).[2] Moreover, the energy of the photons supplied to these systems can be selectively accepted by specific light harvesting molecules (chromophores), unlike thermal energy which is transferred indiscriminately throughout entire reaction mixtures. As a result, specific reaction pathways can be activated ‘on-demand’ in photochemical systems, in turn allowing more precise and efficient transformations.

More recently, photochemistry has re-emerged as a hot topic, as demonstrated by the large number of articles published in the last 10 years reporting new light mediated chemistry in organic and polymer synthesis. There are several reasons that can explain this new ‘golden-age,’ one of which is the development of light emitting diode (LED) technology which was successfully popularized toward the end of 20th century. LEDs have allowed more efficient production of light with greater precision over the emission wavelength, without the need for expensive or specialized equipment (**Figure 1**).[3] Concomitantly, emergent photochemistry techniques have been developed into powerful tools for organic synthesis, as demonstrated by the seminal works of Stephenson, MacMillan, and others.[4] In contrast to early photochemical approaches using ultraviolet (UV) irradiation, modern systems have been developed to be activated under visible wavelengths (typically 450-560 nm), and in some very specific cases, under near-infrared (NIR) light irradiation; these wavelengths provide some inherent benefits and significantly limit by-product production.

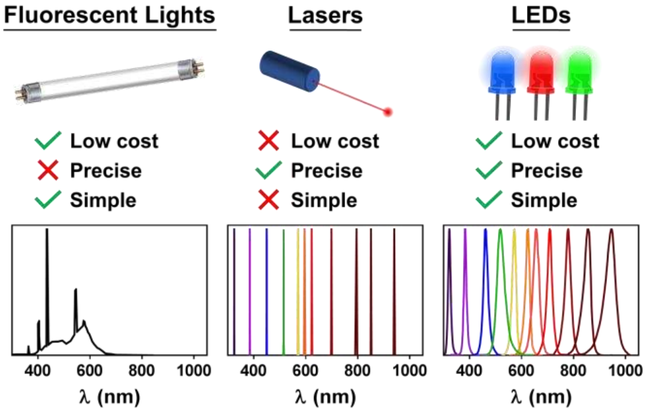

Figure 1. Light sources used for photochemistry

In addition to these progressions, the advent of new polymerization processes in the last 20 years, particularly controlled radical polymerization (CRP) techniques, has resulted in the synthesis of more complex macromolecules. Researchers have realized the potential in merging these recent polymerization techniques with photochemistry, to take advantage of the benefits that accompany these photoactivation pathways. Indeed, with the incorporation of photochemistry to polymerization systems, multidisciplinary researchers have been able to easily synthesize previously inaccessible macromolecules; this has opened the door for applications previously thought possible only in ‘science fiction’. Perhaps, one of the most impressive is the use of visible light to create unique 3D materials with precise structural control and tailored mechanical properties. Photochemistry has also been implemented in microfluidics, photolithography, sensors, bio-applications, and many other fields, to take advantage of the desirable properties of light.[5]

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As expected from such a burgeoning research area, there have been some excellent reviews to date that summarize the work conducted in photopolymerization, photomediated material science, and related fields.[2, 4c, 6] In this review, rather than providing comprehensive coverage of previous systems, we find it more useful to highlight the utility of light for mediating polymerization and materials production. Moreover, while a great deal of research has been conducted into photopolymerization systems in general, we have tried to limit the scope of this review to mainly living photopolymerization systems (including ionic, CRP, ROP, ring opening metathesis polymerization, etc.), since they provide additional opportunities for controlling macromolecular syntheses.[6c, 7] Some other outstanding non-living polymerization systems have also been included, as they often exemplify the use of light over other stimuli to enact chemical transformations; in some cases these systems have the possibility to be translated to living polymerization.

As such, we herein present representative examples of polymerization systems that take advantage of the specific benefits of light as the energy source to activate chemical processes. Specifically, the major benefits of photopolymerization are described, namely temporal and spatial control, extrinsic control through manipulation of the light source, and temperature independence. Additionally, some emerging ideas related to oxygen tolerant polymerization processes, and complex reaction control through photoorthogonality are presented. Finally, the challenges and opportunities for photochemical control in polymer science are explored. It is hoped that this review will allow the reader to “see the light,” and implement photochemical approaches in their future research.

2. Extrinsic Polymerization Control with Light

In contrast to thermal processes, where the energy barrier for a chemical reaction is overcome by an increase of temperature, in photochemical reactions, the activation energy barrier can be overcome by producing more energetic molecular species through photoexcitation. In this process, a chromophore interacts with a photon produced by the light source to promote an electron to a higher energy orbital within the chromophore. The now excited state chromophore can undergo a variety of processes to transfer its additional energy and proceed to a more energetically stable state (**Figure 2**).

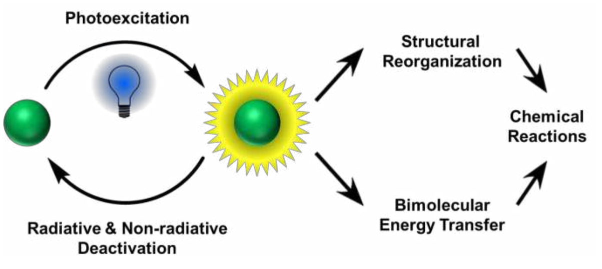

Figure 2. Photophysical and photochemical reaction pathways for chromophores

The absorbed energy can often be radiated thermally or by luminescence (fluorescence and/or phosphorescence) to return the chromophore to its original state. However, the excited state chromophore can also undergo structural reorganization, or transfer the energy to another molecule, to start a photochemical reaction.[8]

The probability of a specific photophysical or photochemical event occurring (quantum yield, ø) is determined by several factors. Firstly, and most importantly, the molecular structure of a chromophore dictates its physical and chemical properties; this affects the possible energy transfer pathways, the chromophore excited state lifetimes, and the molar extinction coefficient, ε, i.e., how strongly a chromophore absorbs light at a specific wavelength. The absorption of light in a solution, A, is directly dependent on ε, as well as the concentration (c) of chromophores within the system, and the path length (l) of light, as described by the Beer-Lambert law (**Equation 1**).

$$A = \varepsilon \cdot c \cdot l \qquad (\mathbf{1})$$

Secondly, the chemical environment, including solvent and temperature, directly affects quantum yields. For instance, the electronic environment of the chromophore changes based on solvent polarity; therefore, changes to the solvent will influence the interaction between photons and the chromophore’s electron manifold. Furthermore, solvents and other molecules in a reaction mixture will provide pathways for energy transfer through encounters with the excited state chromophore, while temperature affects how frequently these encounters occur.

Finally, the characteristics of the light source (intensity and wavelength) are critical parameters for any photochemical system. The energy of photons emitted from the light source is inversely proportional to the irradiation wavelength, λ, as shown in **Equation 2**, where h is Planck’s constant and v is the speed of light in a vacuum.

$$E = h \cdot v \,/\, \lambda \qquad (\mathbf{2})$$

Given the discretization of electron orbital energies, changing the irradiation wavelength, and thus photon energy, will affect the likelihood of electron transitions to higher energy orbitals through photoexcitation. This is reflected in the molar extinction coefficients for chromophores at varying wavelengths. Alternatively, changing the light intensity, I, changes the quantity of photons entering the system (photon flux, Φ). Increasing light intensity thus effectively increases the concentration of photons available for interaction with the chromophore (**Equation 3**).

$$I \propto \Phi \qquad (\mathbf{3})$$

Because the light source is extrinsic to the photochemical system, both wavelength and intensity can be easily adjusted without affecting other reaction parameters; this gives additional opportunities to activate and control chemical processes compared to activation by other means (thermal, chemical, etc.).

2.1. Temporal Control

One of the major benefits of photopolymerization is the ability to impart facile temporal control over polymer chain growth, i.e., the ability to switch the polymerization between “ON” and “OFF” states.[9] By simply switching the light source (and photon flux) between ON/OFF, the reaction can often be effortlessly stopped and started as required. While thermally and chemically induced polymerization systems can exhibit features of temporal control through alteration of reaction temperature,[10] or *in situ* addition of chemical mediators,[11] heat and mass transfer dictates that an instantaneous ON/OFF switch is virtually impossible; the practicality of these methods for temporal control is thus limited. As such, the possibility of applying instantaneous temporal control in photopolymerization systems offers numerous advantages over other initiation methods.[12] Owing to these benefits, temporal control has been applied in photomediated atom transfer radical polymerization (ATRP),[13] reversible addition fragmentation chain transfer (RAFT),[14] ring opening metathesis polymerization (ROMP),[15] cationic,[16] and other polymerization systems.[17]

For example, Hawker and Fors pioneered the use of a photoredox catalyst for mediating an ATRP process under visible light.[18] In this strategy, the iridium based catalyst, tris[2-phenylpyridinato-C2,N]iridium(III) (Ir(ppy)$_3$, **Figure 7**) was capable of mediating both the activation and deactivation of polymerization under visible light (440 nm) irradiation at relatively low catalyst loadings (0.005 mol% with respect to monomer); good control was demonstrated for polymerization of both acrylates[19] and methacrylates.[18] Importantly, removal of visible light resulted in cessation of polymerization, which returned once the light was reintroduced (**Figure 3**). This contrasts conventional photoinitiated polymerization systems where irradiation generates initiating species, but has no control over the deactivation process. Similarly, temporal control has been applied to other interesting photo-ATRP systems using diverse photocatalysts to allow for on-demand control over chain propagation.[20] In comparison, conventional ATRP cannot be as readily deactivated by simple modulation of an external stimulus, which may limit its applicability in specialized applications.[21]

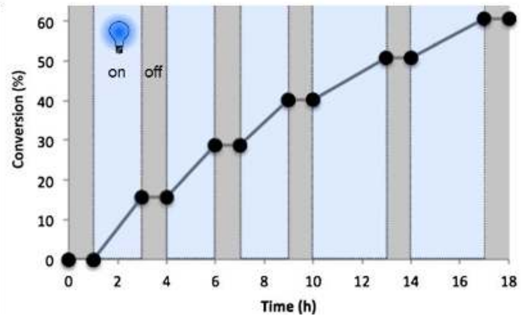

Figure 3. Temporal (ON/OFF) control over ATRP using a photoredox catalyst. Adapted with permission from ref[18]. Copyright 2013 John Wiley & Sons.

Notably, temporal control has also been applied to photoinduced RAFT polymerization.[9, 14a, 22] Our group demonstrated that Ir(ppy)$_3$ could be employed to initiate RAFT polymerization through a photoinduced electron or energy transfer (PET) process, named PET-RAFT polymerization.[22] During this process, formation of initiating species was proposed to occur through activation of thiocarbonylthio compounds (RAFT agents) via a PET process from excited state catalysts; as such, removal of the light source halted activation and allowed facile switching of the RAFT agents between dormant and active states. Consequently, RAFT polymerization was easily switched ON/OFF through light manipulation.

This ability to start and stop polymerization at will has been one of the largest technological advances brought about through the application of photochemistry to polymerization. As an inherent property of these techniques, the importance of this characteristic cannot be understated and provides the impetus for many of the following discussion points in this review.

2.2. Spatial Control

The ability to perform localized polymerization is a natural extension of photoinduced temporal control, and one which offers promising applications in many areas. Importantly, in contrast to other stimuli, e.g., temperature or chemical, the use of an extrinsic light source for spatial control provides a simplified and customizable approach. As a result, precise activation of polymerization in specific regions via light irradiation can allow synthesis of new materials with unprecedented properties. Although the use of living photopolymerization methods for the functionalization of surfaces is still in its infancy, the application of polymer films on surfaces can already be seen within the shipping,[23] water treatment,[24] computer,[25] and solar industries;[26] a review by Barner-Kowollik and coworkers highlights some of the synthetic strategies and applications of spatial control for photopolymerization systems.[27]

Photomask technology has been utilized for spatial patterning through photopolymerization.[28] Furthering their work on the use of photoredox catalysis for ATRP, Hawker, Fors and coworkers employed Ir(ppy)$_3$ to spatially control the growth of poly(methyl methacrylate) (PMMA) brushes from α-bromoisobutyrate-based initiators attached to a silicon substrate (**Figure 4**).[28a] Using photomasks, a series of 3D polymer brush patterns were fabricated in a single step. The short excited state lifetime of the photocatalyst allowed spatially resolved polymerizations to occur without large losses in structural resolution, as the excited state catalyst could not diffuse over distances greater than 20 nm due to its short lifetime. A similar method was also implemented with a metal-free ATRP system using 10-phenylphenothiazine (PTH, **Figure 7**) as a photocatalyst for spatially controlled polymerization of methacrylates to yield homopolymer and diblock copolymer brushes.[29] These benchtop protocols allow non-experts to synthesize controlled 3D polymer layers on flat and curved surfaces. Variations in surface structure were achieved through changes to light intensity and irradiation profiles, while well-defined patterns on the order of 1 μm could easily be fabricated over larger areas up to ~10 cm in diameter.

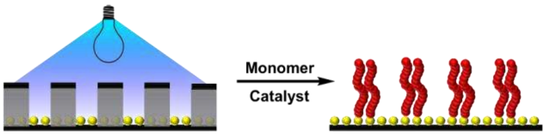

Figure 4. Spatially controlled polymerization through photomask technology. Adapted with permission from ref[28a]. Copyright 2012 John Wiley & Sons

Photopolymerization using laser technology has become a promising alternative to the use of physical barriers (photomasks) for spatial control.[30] Junkers, Barner-Kowollik, and coworkers have employed 2D laser lithography for spatially resolved photo-ATRP of acrylates from silicon surfaces.[31] The use of a pulsed excimer laser (351 nm) enabled high grafting densities, tailorable film thicknesses (up to 190 nm), checkerboard patterns, and localized block copolymer chain extensions at extremely fast polymerization rates. The smallest structural features achievable using a 250 × 250 µm^2 focused beam size were approximately 270 µm, however, the use of high resolution laser writing techniques has allowed increased precision in spatially controlled photopolymerization.[32] Combining such high-resolution, large scale patterning with living photopolymerization could find applications in insulation for electronic devices and solar cells, as well as biologically active surfaces.[32-33]

A rapidly expanding application for spatially controlled photopolymerization is 3D printing.[34] Forming structures through additive manufacturing has shown versatility in both reducing waste and forming complex structures without requiring separate pieces of equipment. Of note, the benefits of photopolymerization processes have been recognized and implemented within this exciting technology, with photocurable and photoinitiated systems widely used. The speed at which 3D objects can be printed is currently one of the limiting factors, especially when using a layer-by-layer technique; work by DeSimone and coworkers has begun to address this, while maintaining resolution below 100 µm (**Figure 5**).[35] Further technological advances in laser technology, particularly stimulated-emission depletion (STED),[36] two-color single-photon photoinitiation,[37] and others,[38] have opened the door to more precise applications due to increased spatial resolution, in the nanometer range. For instance, Bastmeyer and coworkers successfully encapsulated living cells in polymeric scaffolds built by photopolymerization.[39]

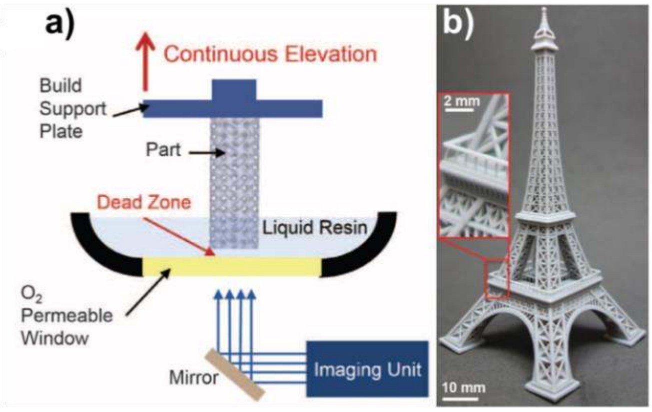

Figure 5. 3D printing using spatially resolved photopolymerization. a) Equipment set up. b) Example of an Eiffel Tower model printed at 100 mm per hour. From[35a]. Reproduced with permission from AAAS.

The upper limit of resolution using previous laser techniques is proportional to λ/2 due to diffraction of light; STED can theoretically remove the dependence on wavelength altogether, although current practical resolutions have only attained relationships of λ/10. Some issues in these systems still exist, and balancing writing speed with resolution is a complex problem.[34b] In addition, living polymerization has not yet been applied to 3D printing systems. Considering the advancement in material properties achievable through precision polymer synthesis, living photopolymerization combined with 3D printing systems may allow the simultaneous conjugation of different polymer types, conferring improved and bespoke mechanical properties.[40]

2.3. Rate Control through Alteration of Intensity/Wavelength

Temporal and spatial applications can be further expanded by utilizing light for fine tuning photochemical reaction rates. For thermal polymerization processes, extrinsic rate control can only be afforded through manipulation of temperature to change the propagation rate coefficient and/or initiator decay; in contrast, photopolymerization offers rate control through not only temperature, photoinitiator or photocatalyst dosage, but significantly light intensity, and wavelength manipulation, which are non-invasive and easily adjustable parameters. This increases the number of independent variables with which polymerization rate can be manipulated, allowing subtle possibilities for reaction control. In particular, light intensity or wavelength can cause an almost instantaneous increase or decrease in rate which does not depend on heat and mass transfer effects (cf. temperature or chemical control).[41] Moreover, rate control has important implications for safety protocols, especially in reducing the likelihood of runaway reactions. In addition, the ability to dynamically increase or decrease polymerization rate is a prerequisite for automated control systems, which could allow facile industrial implementation.

2.3.1. Light Intensity Variation

As polymerization rate is dependent on the number of propagating species, light intensity variation can be used to control the reaction rate by directly manipulating the concentration of active species. At any given irradiation wavelength, the photon flux increases proportionally with increasing light intensity; higher light intensities thus increase the probability of photoexcitation and subsequent generation of propagating species, assuming that the irradiation wavelength is capable of inducing photoactivation. Importantly, this can be achieved without changing the reaction temperature. For living photopolymerization systems, rate control and thus light intensity control, is especially important for the production of materials with well-defined chain length distributions and material properties.

Bai and coworkers used light intensity variation to control reaction rates in RAFT polymerization. Using UV irradiation (λ > 320 nm) allowed direct photolysis of a trithiocarbonate species for RAFT polymerization of methyl acrylate (MA); increasing the light intensity from 3 to 48 mW/cm^2 was found to increase the polymerization rate dramatically (**Figure 6**).[42] This example provides a clear demonstration of rate tunability that can be exerted through light intensity control.

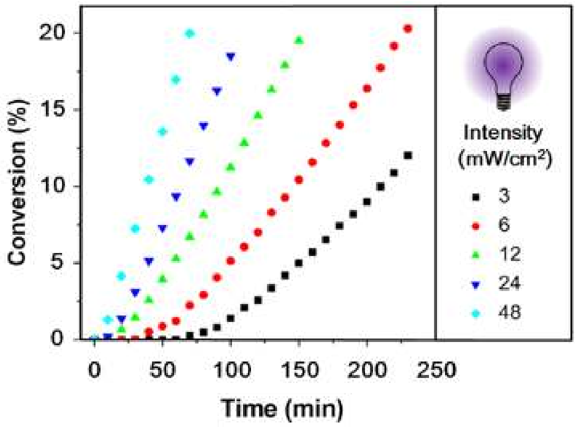

Figure 6. The effect of UV light intensity on polymerization rates. Adapted with permission from ref[42]. Copyright 2013 American Chemical Society.

Miyake and coworkers have also studied the effect of varying the relative light intensity (100%, 50%, 25%, or 5%) of a white LED source on organic photoredox catalysts for ATRP.[43] Their work on two separate catalysts indicated variability in the control of MMA photopolymerization dependent on light intensity and catalyst type; for both photoredox catalysts used, the polymerization rate increased substantially with increasing white light intensity. Interestingly, polymer dispersity varied depending on both the catalyst type and the light intensity. As the photocatalyst mediates both activation and deactivation cycles in this process, the light intensity plays a crucial role in controlling both the polymerization kinetics and the distribution of chain lengths.[43] Konkolewicz, in collaboration with our group, has also demonstrated rate control through light intensity in a PET-RAFT system using Ir(ppy)$_3$ as photocatalyst. In this study, blue light (440 nm) intensity was seen to scale the apparent rate of polymerization of MA proportional to the square root of light intensity.[41] Polymerization rate scaled similarly with catalyst concentration, indicating that excited state species can be increased through either higher catalyst loading or light intensity increases, to achieve the required reaction rate.[41] As such, very low catalyst loading can often be implemented in systems with high light intensities, while maintaining fast reaction rates and good polymerization control.

2.3.2. Wavelength Variation

While increasing the light intensity at a specific wavelength increases the photon flux, the irradiation wavelength dictates the energy of each emitted photon. Depending on their electronic configuration, different chromophores are able to interact with these photons to differing degrees; as a result, the selection of irradiation wavelength for photochemical processes is of critical importance in determining the likelihood that a given photochemical pathway will be activated. For instance, the quantum yield for photolysis of thiocarbonylthio species with UV light (~310 nm) is more than 30 times greater than with blue light (~450 nm) irradiation, due to differences in the molar extinction coefficients of these compounds at these wavelengths.[8, 44] The differences in light absorption at varied wavelengths can thus provide a route for tuning reaction rate in photopolymerization systems. Furthermore, complex multi-wavelength processes can be implemented independently of one another in photopolymerization systems, allowing simplification of reaction protocols and access to interesting applications (vide infra, **Section 5**).

In early living photopolymerization systems, high energy, i.e. short wavelength ($\lambda < 350$ nm), irradiation was used to produce photoinitiating species through photolysis.[45] Although these systems showed relatively good control, prolonged exposure led to reactant and product degradation, and side reactions.[46] Moreover, these systems displayed a lack of penetration efficiency, used expensive light sources, and presented potential harm to users with long term exposure. Since these early forays, researchers have targeted longer irradiation wavelengths to soften the impact of the light source, which has been recently enabled with accessibility and advances in LED technology. Nowadays, there are an increasing number of chromophores that are excitable under low energy (longer wavelength) irradiation that have been implemented in photopolymerization systems to take advantage of this technological advancement (**Figure 7**).

An excellent demonstration of the shift from short to long wavelength irradiation for photopolymerization is exhibited in photoinduced RAFT systems. Early reports by Davis and coworkers directly activated RAFT agents using UV irradiation at 365 nm for the CRP of styrene, where loss of control was linked to the rate of degradation of RAFT chain ends under UV exposure.[46b] Cai and co-workers later demonstrated that longer wavelength UV light reduced RAFT agent degradation compared to short range ($\lambda < 320$ nm) irradiation.[46a] Following this work, our group and Qiao's group demonstrated that direct activation of RAFT agents was possible under blue (460 nm) and green (530 nm) light irradiation; the extension to longer wavelengths helped alleviate the degradation of RAFT agent end groups during polymerization, however, slower rates and longer inhibition periods were evident compared to using shorter wavelength UV light (365 nm) irradiation.[44] Notably, Poly and coworkers designed a RAFT agent with enhanced absorption in the visible region.[47] The dithiocarbamate RAFT agent, methyl 2-((9H-carbazole-9-carbonothioyl)thio)-2-methylpropanoate (DTC, **Figure 7**), was not only capable of being activated under both blue and green light, but allowed control of reaction rate, with polymerization proceeding faster under blue light irradiation.[47] Thus the activation of polymerization under longer wavelength irradiation serves a dual purpose; to reduce degradation and side reactions, whilst simultaneously allowing modulation of reaction rates.[48]

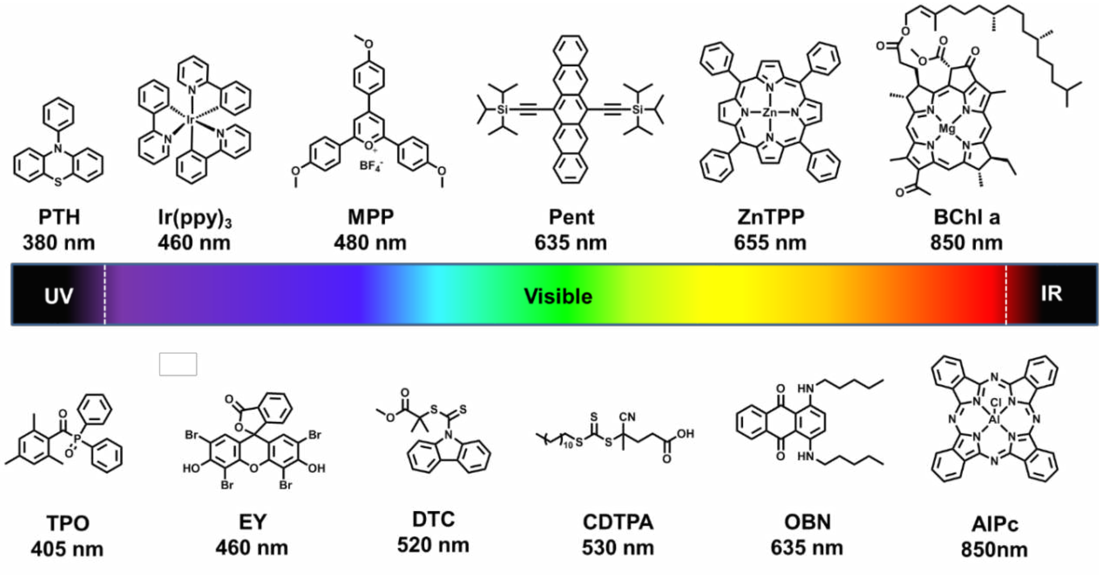

Figure 7. Examples of chromophores used in photopolymerization**.** PTH: 10-Phenylpheothiazine, Ir(ppy)$_3$: tris[2-phenylpyridinato-C2,N]iridium(III)), MPP: 2,4,6-tris(p-methoxyphenyl)pyrylium tetrafluoroborate, Pent: 6,13-bis(triisopropylsilylethynyl)pentacene, ZnTPP: 5,10,15,20-tetraphenyl-21H,23H-porphine zinc, BChl *a*: bacteriochlorophyll *a*, TPO: (2,4,6-trimethylbenzoyl)diphenylphosphine oxide, EY: eosin Y, DTC: methyl 2-((9H-carbazole-9-carbonothioyl)thio)-2-methylpropanoate, CDTPA: 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid, OBN: oil blue N, AlPc: aluminium phthalocyanine.

To demonstrate the ability to control photopolymerization systems over a broad wavelength range, our group investigated photocatalysts with absorbance in the visible region for PET-RAFT polymerization, including porphyrins such as 5,10,15,20-tetraphenyl-21H,23H-porphine zinc (ZnTPP),[49] naturally occurring porphyrins chlorophyll *a* (Chl *a*)[44b] and bacteriochlorophyll *a* (BChl *a*),[50] and organic dyes (**Figure 7**).[51] For instance, ZnTPP was shown to be an efficient photocatalyst for PET-RAFT polymerization of MA using wavelengths from 460-655 nm.[49] Kinetic experiments showed that the polymerization rate was dependent on the light source, with fastest to slowest polymerizations in the order of yellow > green > orange > red > blue light; rate tenability was dependent on the catalyst absorption in each wave range (**Figure 8a**). As such, these systems present the ability to control polymerization rate through wavelength manipulation which can be exploited for the synthesis of complex materials.[52]

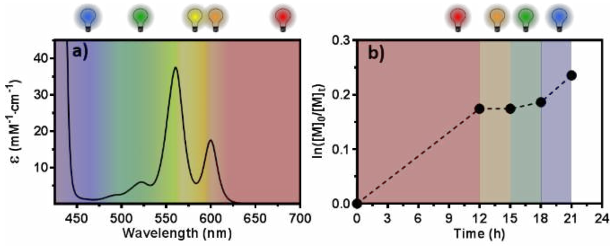

Figure 8. Effect of wavelength on photopolymerization rate. a) Absorption spectrum of ZnTPP.[49] b) Rate control through wavelength alteration. Figure 8b) adapted with permission from ref[53]. Copyright 2015 American Chemical Society.

A variety of other visible light induced photopolymerization systems have been developed for activation under longer wavelength irradiation.[54] For instance, Matyjaszewski and coworkers investigated the use of FeBr$_3$ as a catalyst capable of controlling ATRP under blue (450 nm) and green (520 nm) light, with faster polymerization rates achieved using blue light.[55] Jin and coworkers also utilized blue light (470 nm) to excite photoacid generators for cationic polymerizations, while the use of anthraquinone derivatives such as oil blue N (OBN) has allowed cationic polymerization through red light (635 nm) irradiation.[56] For single photon processes, photoactivation has even been achieved under NIR irradiation.[50, 57] For instance, our group has employed two photocatalysts, aluminium phthalocyanine (AlPc) and BChl *a*, for conventional radical polymerization and PET-RAFT polymerization under 850nm.[57a] Owing to the increased penetration efficiency, polymerization using BChl *a* was achievable when an opaque barrier was placed between the reaction mixture and the light source. Notably, Yagci and coworkers have recently developed an ATRP system capable of polymerization under NIR (790 nm) irradiation.[57b] Upconverting materials and nanoparticles also show promise when used in conjunction with photopolymerization.[58] Systems that are capable of activation under NIR irradiation present the possibility for *in vivo* applications, due to their increased penetration through biological tissue and inability to induce side reactions that are associated with shorter wavelength irradiation. Furthermore, low energy wavelengths can find applications in the design of advanced materials due to their ability to penetrate non-transparent systems and activate polymerization.

Due to the ability to independently excite two or more different chromophores under separate irradiation wavelengths, photochemical systems can allow complex protocols to be significantly simplified and conducted in a single pot.[53, 59] To this effect, Kaji and coworkers used organocatalysts to photopolymerize MMA over a range of wavelengths (350-750 nm) using iodine transfer polymerization (ITP).[53] Variations in wavelength (700 nm, 600 nm, 500 nm, and 400 nm) allowed fine tuning of reaction rate according to catalyst absorbance at each wavelength (**Figure 8b)**. Ultimately a one-pot selective polymerization process was demonstrated for poly(MMA)-*b*-poly(δ-valerolactone) block copolymer synthesis. Using multiple wavelengths to activate distinct photochemical pathways is an extremely interesting and emerging area in polymer science; such systems will be discussed in more detail in **Section 5**.

Clearly the benefits of adding specialized photoinitiators or catalysts can serve to increase the wavelengths accessible for reaction, increase rate control, as well as provide possibilities for selective reaction stimulation in one pot. However, it may be seen that further development in catalyst design is required to increase the efficiency of low energy photon use.[6a, 60]

3. Temperature Independent Photopolymerization

Traditionally, CRP processes are performed at elevated temperatures to achieve acceptable polymerization rates. This is particularly relevant for conventional nitroxide mediated polymerization (NMP) and RAFT polymerization techniques since they typically require higher temperatures to initiate radical generation.[54a, 61] As such, radical photopolymerization systems have a distinct advantage over thermally initiated systems in that radical generation can be effectively accomplished at room temperature (or lower). This independence of photoinitiation with polymerization temperatures has been exploited to perform polymer synthesis under a much broader range of experimental conditions. Importantly, more diverse reaction conditions allow photopolymerization systems to be implemented for a wider range of applications, including under biological conditions.

3.1. Temperature Independence in Polymer Synthesis

Photopolymerization systems can allow the reaction temperature to be decoupled from the propagation rate. Sumerlin and coworkers used this property to perform low temperature polymerization for the one-pot synthesis of diblock copolymers in a completely closed system, by segregating the monomer solutions using a frozen dimethyl sulfoxide (DMSO, $T_m \approx 19$ ˚C) spacer.[62] As the two monomers were physically separated in two phases, a homopolymer was initially formed by low temperature RAFT polymerization, followed by melting of the spacer to form a single-phase mixture for chain extension of the homopolymer (**Figure 9**). The polymerization was initiated under UV light (350 nm) at 16 ˚C using a RAFT agent as photoiniferter. Using this process, acrylate and acrylamide monomers were polymerized to form a range of diblock copolymers without the need for subsequent monomer addition or deoxygenation steps. This innovative approach was conceivable due to the relative independence of photoactivation from reaction temperature.

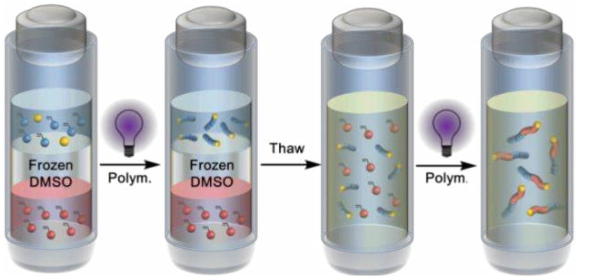

Figure 9. Low temperature RAFT photopolymerization to synthesize diblock copolymers without discrete monomer addition or secondary deoxygenation steps. Adapted with permission from ref[62]. Copyright 2016 John Wiley & Sons

Another advantage of performing low temperature photopolymerization is the ability to control the polymer tacticity. It is well known that a high temperature favors the synthesis of atactic polymers, however, reaction temperature is often limited by the chemical nature of reaction components.[63] Zhu and coworkers recently demonstrated that the interaction strength of monomers with stereochemical mediators is influenced by polymerization temperature.[64] The authors outlined the use of a photopolymerization system which was initiated under blue (465 nm) light, using a xanthate as both RAFT agent and radical source to achieve acceptable polymerization rates over a broad range of temperatures (-20 to 50 ˚C). When vinyl acetate was polymerized in the presence of 1,1,1,3,3,3-hexafluoro-2-propanol as a solvent and stereochemical mediator, the syndiotacticity was controlled between 52% and 61% depending on the polymerization temperature. Using this approach, pseudo-block polymers were formed in one pot by simply varying the polymerization temperature *in situ* between -20 and 50 ˚C. Our group has also demonstrated that the polymerization temperature can be used to influence the tacticity of polyacrylamides using a Lewis acid as a mediator in a PET-RAFT polymerization process.[65] In comparison to thermally initiated RAFT polymerization, higher tacticity control was achieved when the polymerization was performed at room temperature using PET-RAFT polymerization. More recently, the on-demand synthesis of complex macromolecules was achieved via the combination of two independent and switchable polymerizations.[66] The first polymerization was a PET-RAFT process allowing polymerization of vinyl monomers (acrylates and acrylamides), whereas the second polymerization was an anionic ring-opening polymerization (AROP), capable of polymerizing cyclic monomers. Both the AROP and PET-RAFT polymerization were selectively and independently switched ON/OFF using temperature and light as external stimuli. A single trithiocarbonate control agent was able to control the AROP and PET-RAFT polymerization simultaneously, and allowed the on-demand interconversion of polymerization promptly and quantitatively. The authors produced one-pot multiblock copolymers by alternating light and temperature stimuli.

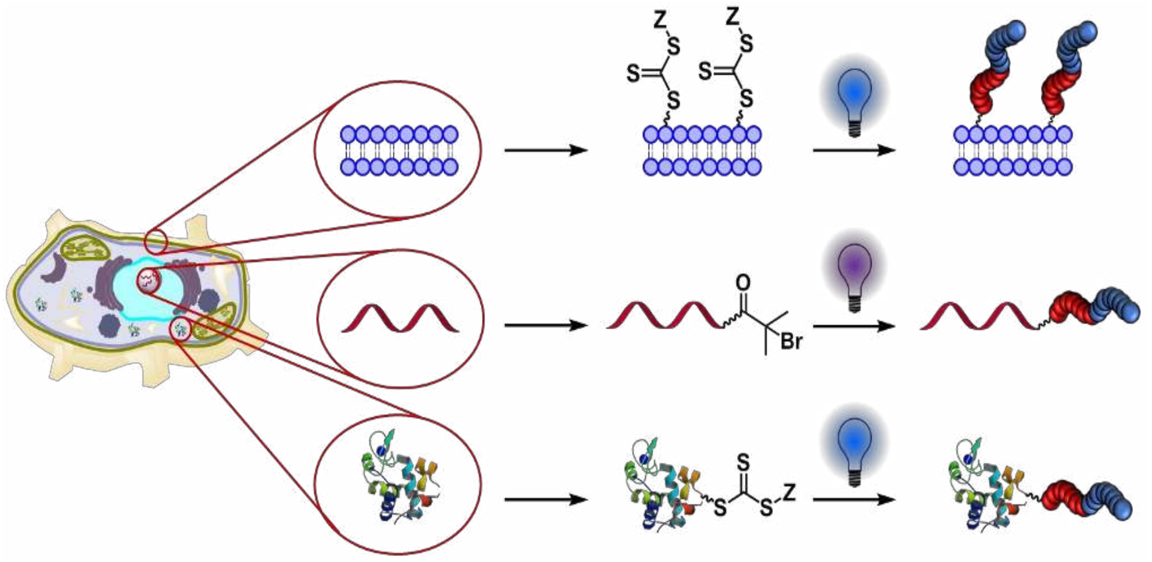

Figure 10. Mild photopolymerization techniques can be harnessed to graft polymers from biological substrates such as cells, DNA and proteins.

The implementation of photopolymerization techniques to initiate nanoparticle synthesis via the polymerization-induced self-assembly (PISA) approach has also been demonstrated at low temperatures.[67] Although traditional PISA has been successfully implemented using thermal RAFT dispersion polymerization, a number of advantages of using visible light have recently been demonstrated. For example, our group first identified that performing PISA syntheses at low temperatures could be used to more readily isolate worm-like nanoparticles, owing to the onset of macroscopic gelation created by worm-worm entanglements.[68] In contrast, when syntheses are performed under typical thermally initiated conditions (70 ˚C), this gelation is only observed on cooling of the reaction mixture to room temperature. The groups of Zhang and O'Reilly have also exploited the temperature independence of photoinitiated PISA to demonstrate that the temperature of a PISA synthesis can significantly affect the final nanoparticle morphology. Increasing the reaction temperature allowed access to higher order morphologies, providing another parameter for controlling particle synthesis.[69] Moreover, the low polymerization temperature enables the *in situ* encapsulation or modification of sensitive substrates, such as proteins, into the interior of vesicles without significant loss of protein structure and activity.[69a, 70]

3.2. Temperature Independence for Bioapplications

The ability for CRP techniques to finely control polymer architecture makes it an attractive technique for the modification and/or encapsulation of biological species such as DNA, proteins, and peptides. However, these polymerizations generally need to be conducted under carefully regulated conditions, particularly low temperatures. Early works proposed the use of room temperature radical initiators to initiate polymerization; however, to achieve acceptable polymerization rates, a relatively high amount of initiator had to be added.[71]

As an alternative approach, several groups have proposed activation of photopolymerization using visible light, which does not damage fragile biological substrates. For example, Hawker's group demonstrated the use of mild PET-RAFT polymerization conditions to modify the surfaces of living cells.[72] To achieve cell surface-initiated polymerization, the surface of the cell was first functionalized with a suitable RAFT agent using click chemistry; controlled polymerization was then performed directly from the cell surface (so-called "grafting-from" approach) under mild blue light irradiation (λ = 465 nm) using eosin Y (EY, **Figure 7**) and triethanolamine as the photocatalytic system (**Figure 10, top**). The use of these mild photopolymerization conditions enabled both yeast and mammalian Jurkat cells to retain > 90% of their viability, and more importantly, their ability to proliferate. Other mild photochemistry approaches have been extensively applied for the release of encapsulated cells or other biological substrates from hydrogel networks, providing excellent extrinsic control over the site of release.[33c, 73] The facile nature of these systems can be further enhanced by exploiting photopolymerization techniques with some degree of tolerance to oxygen, in order to maximize substrate stability and minimize the setup complexity (*vide infra*, **Section 4**).

Haddleton, Chen, and coworkers have also demonstrated the use of photoinitiated RAFT polymerization to graft polymers from a chain transfer agent (CTA) modified pyrophosphatase protein (**Figure 10**, bottom).[71b] By polymerizing at low temperatures (20 ˚C) under visible light (λ = 420 nm), retention of enzyme activity was observed, and moreover, controlled polymerization of the thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAM) could be performed below the lower critical solution temperature (LCST). Furthermore, the resulting hybrids presented unusual thermal switching behavior with greater catalytic activity observed above the LCST of PNIPAM. More recently, the use of mild PET-RAFT polymerization conditions has also been exploited by Sumerlin and coworkers to synthesize polymer-protein conjugates by grafting from lysozyme as a model protein with good retention of bioactivity.[74] Matyjaszewski and coworkers used a similar light-mediated ATRP approach to modify DNA using a grafting-from approach (**Figure 10**, middle).[75] In this case, DNA-polymer hybrids could be formed by polymerizing directly from an initiator functionalized DNA oligonucleotide using a fibre-coupled UV light source (λ = 365 nm). The use of a DNA synthesizer to perform both DNA and polymer synthesis suggest a high degree of modularity can be introduced using this approach. These approaches demonstrate the high potential for photomediated CRP to be harnessed for the modification of temperature-sensitive substrates.

4. Photoinduced Oxygen Tolerance and Applications

The inhibitory effects of oxygen on radical polymerization, particularly CRP, are well documented.[76] As a result, CRPs are typically conducted only after prior deoxygenation of the polymerization mixture using physical deoxygenation techniques such as inert gas sparging or freeze-pump thaw cycling. Early strategies for imparting oxygen tolerance in ATRP were based on the use of reducing agents to continuously reduce the oxidized catalyst back to its active, lower oxidation state.[77] Alternatively, others postulated that enzymes could be harnessed to catalytically convert oxygen into inactive species.[10, 78] While the removal of oxygen from these systems is effective, polymer chemists are now looking to exploit photochemical deoxygenation protocols that are inherent in photopolymerization systems. Removal of a deoxygenation step prior to polymerization not only simplifies reaction procedure but also broadens the scope of applications for photopolymerization systems due to possibility for implementation under less stringent conditions.

4.1. Photochemical Strategies for Oxygen Tolerance

In recent years, there have been several reports exploiting the high reactivity of photoexcited chromophores with molecular oxygen to chemically convert oxygen into other species and reduce its inhibitory action on radical polymerization (**Figure 11**). These strategies have largely been inspired by examples in free radical polymerizations where molecular oxygen can be photochemically converted into reactive oxygen species such as singlet oxygen or superoxide; these species can subsequently (**i**) be reduced into initiating radicals, (**ii**) act as inert bystanders, or (**iii**) be irreversibly trapped by suitable quenchers.[76a]
For example, our group has demonstrated that a high degree of oxygen tolerance is achieved using the PET-RAFT process due to the high singlet oxygen yield of certain photocatalysts, such as ZnTPP.[79] This photosensitized oxygen can then be trapped by suitable singlet oxygen quenchers such as anthracenes or sulfoxides, thereby removing oxygen from the polymerization mixture (**Figure 11B**).[80] Alternatively, Qiao's group suggested that the RAFT agent itself can participate in oxygen removal by converting oxygen into superoxide in the presence of a sacrificial tertiary amine as an electron donor (**Figure 11A**).[81] The ability to perform polymerization under ambient conditions in these examples significantly simplifies production by removing an entire process step.

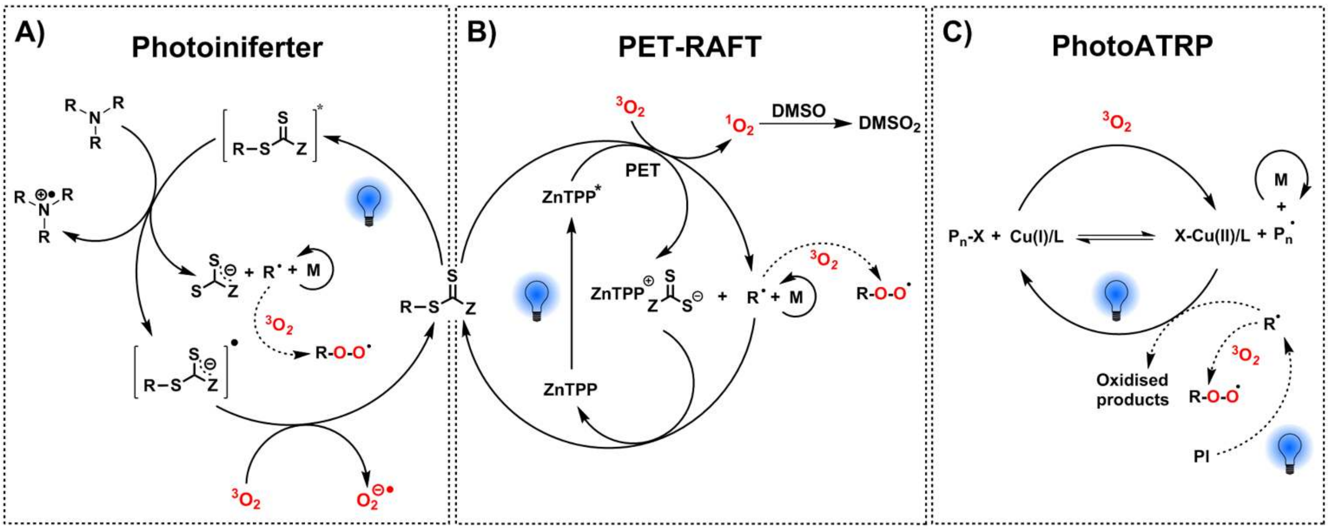

Figure 11. Mechanisms proposed for oxygen consumption via photomediated CRP techniques. Oxygen can be consumed by photosensitization, catalyst oxidation or by peroxy radical formation. In all CRP, the formation of peroxy radicals from initiating/propagating radicals is in competition with other mechanisms of oxygen scrubbing such as photosensitization.

The removal of deoxygenation protocols can significantly broaden the general applicability of photopolymerization as well as reduce its setup complexity. This allows CRP techniques to be more widely accessed by the scientific community, since well-defined polymeric materials can be synthesized without the need for access to inert gas sources or vacuum apparatus (such as for freeze-pump thaw cycling). For example, Zhu's group recently demonstrated a very simple approach towards CRP by performing ultrafast RAFT photopolymerizations under violet (390 nm) LED light; a xanthate was exploited as a photoiniferter in this process.[78c] These polymerizations were conducted in sealed but non-deoxygenated vessels with oxygen consumption occurring via peroxy radical formation from RAFT derived radicals. Although the livingness of this "polymerizing through" oxygen approach is limited by the oxidation of the RAFT agent, it can enable polymers to be synthesized with relative ease, albeit under a narrow range of reaction conditions. The reduction in setup complexity through oxygen tolerant CRP is also useful for introducing polymer chemistry at an undergraduate level.[82] Importantly, this allows facile implementation of oxygen-free photopolymerization techniques, which are often difficult in, for example, large teaching laboratories.[83]

4.2. Applications of Oxygen Tolerance Photopolymerization

Utilization of deoxygenation protocols inherent to photopolymerization systems also opens a number of exciting opportunities in material syntheses. Without prior deoxygenation, polymerization no longer needs to be limited to conventional sealed vessels; this allows polymerization in unusual setups. For example, oxygen tolerant CRP can be performed at very low (microliter) reaction volumes that would otherwise be difficult to deoxygenate with conventional techniques. Furthermore, this property allows the throughput of CRP to be greatly increased relative to conventional CRP approaches.

Our group, in collaboration with Gormley, Chapman and coworkers, exploited the oxygen tolerance of the PET-RAFT process[9, 49, 79] to directly synthesize well-defined polymers in low-volume 96- or 384-well plates.[84] In comparison, conventional CRP cannot be readily performed in this setup due to the difficulty in deoxygenating reaction volumes in the microliter range. By performing polymerizations at much higher throughput than conventional approaches, a large library of linear, 3- and 4-arm star polymers with various molecular weights were rapidly synthesized in parallel. These scaffolds were then functionalized with mannose using alkyne-azide click chemistry. Finally, the sugar functionalized polymers were screened with a lectin-binding assay to identify the strength of the polymer-lectin interaction, and subsequently derive polymer structure–activity relationships (**Figure 12**). Our group has also implemented a similar approach to elucidate the key role of monomer sequence on activity of polymers in antimicrobial applications.[85] The ability to produce and screen a large range of structures under moderate conditions in these systems decreases the time required for experimentation through to analysis; such protocols show promise for the fast-tracked discovery of new polymers for a range of bio-applications.

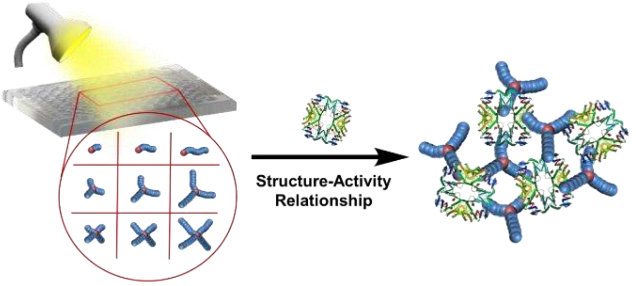

Figure 12. Oxygen tolerant high throughput photopolymerization for rapid identification of structure-activity relationships.[84a]

The ability to run a large number of polymerizations in parallel allows the identification of the optimal conditions for the synthesis of complex polymeric architectures with minimal consumption of reactants.[86] For example, it is well known that the synthesis of star polymers using the "arm-first" methodology requires significant optimization to achieve high arm incorporation, while minimizing star-star coupling. In this case, an inherently oxygen tolerant photoinitiation system, employing EY as a photoreducible dye,[87] was used to initiate RAFT polymerization under mild conditions in a 96-well plate.[86] By systematically varying the crosslinker concentration across adjacent wells, it was possible to rapidly identify the most suitable conditions for star polymer synthesis. Tan and coworkers have also demonstrated the advantage of oxygen tolerant high-throughput polymerizations by exploring the effect of reaction parameters on a PISA system.[20a] In this approach, photoinitiation was decoupled from deoxygenation by employing the enzyme mediated deoxygenation system developed by Yagci[88] and Stevens.[78a] By polymerizing directly in open 96-well plates, a phase diagram describing the effect of solids content and target degree of polymerization on the nanoparticle morphology was rapidly generated. In addition, the mild polymerization conditions could be exploited to encapsulate horseradish peroxidase (and the residual glucose oxidase) into the lumen of vesicles. Clearly, the implementation of photochemical strategies to both activate photopolymerization, and convert molecular oxygen to unreactive species can provide useful avenues for simplified reaction protocols. By combining these approaches with high-throughput techniques, useful data for polymerization kinetics and polymer properties can be rapidly accumulated.

5. Multiple Wavelengths for Precision Photopolymerization

The development of novel strategies to perform orthogonal reactions, i.e., multiple chemical reactions independently of one another, has led to advancements in organic, supramolecular, and polymer chemistry.[89] Photochemically induced orthogonality, or "chromic" orthogonality, was introduced in 2002 when Bochet and coworkers showed that orthogonal photolysis of protecting groups was possible through selective irradiation under monochromatic UV (254 nm) or blue (420 nm) light.[90] Given the ability to activate and control polymerization systems using different wavelengths, there exists an appealing opportunity to utilize such chromic orthogonal reaction manifolds for photopolymerization.[91]

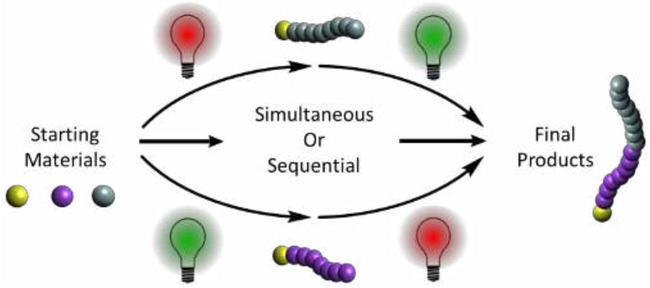

Figure 13. Multiple wavelengths for precision polymerization

Using different irradiation wavelengths to simultaneously or sequentially activate distinct reaction pathways allows the possibility to perform complex synthetic protocols that would be tedious or impossible using conventional chemistry (**Figure 13**).[92] Using chromic orthogonal reaction manifolds to synthesize and modify polymers also allows simplification of multistep processes, which can decrease production time and associated costs. Furthermore, the inherent benefits of photopolymerization systems, including spatial and temporal control, can be exploited in orthogonal systems for complex materials production, optical lithography, drug delivery, photodegradable materials, etc.

In the field of polymer chemistry, the most frequently reported use of different wavelengths to selectively activate reaction pathways involves either polymer synthesis, including network structure formation, or polymer post-modification reactions such as photocontrolled functionalization or photodegradation. Orthogonal reactions that utilize a combination of light and other stimuli (e.g., temperature, pH, etc.) have also been implemented in polymerization and post-modification.[37a, 93] Although these systems are beyond the scope of this review, they also show the versatility of light as an external stimulus to selectively control distinct chemical pathways.

5.1. Wavelength Control for Orthogonal Photopolymerization

Due to the ability to control polymerization using different catalyst/wavelength combinations, sequential polymerization under two distinct mechanistic pathways can be performed by simple alteration of irradiation wavelength. Thermal polymerization systems usually require several steps for the synthesis of complex macromolecules due to their inability to selectively activate reaction pathways; however, in principle the specificity of light could be harnessed to simplify these processes. As such, regulation of polymerization systems through multiple irradiation wavelengths offers a unique opportunity to simplify complex reaction protocols. While some of the following examples are not strictly living photopolymerization systems, they are of great interest due to their ability to take advantage of the orthogonality possible through irradiation with multiple wavelengths.

In 2015, Kaji and coworkers demonstrated the selective activation of ROP and ITP under different wavelengths, through the use of a bifunctional initiator and a dual catalytic system.[53] Meanwhile, our group disclosed a purely visible light induced protocol for orthogonal photo-ROP and PET-RAFT polymerization.[94] A merocyanine based photoacid with absorbance under blue light (460 nm) was used to modulate the ROP of δ-valerolactone (VL), while PET-RAFT polymerization of MA was performed via activation of ZnTPP under red light (635 nm). Importantly, this work demonstrates a truly orthogonal reaction as the polymerization sequence was irrelevant; by simply switching the irradiation wavelength between blue and red, photo-ROP and PET-RAFT polymerization were selectively activated leading to well-defined block and graft copolymers of ε-caprolactone and MA (**Figure 14**).

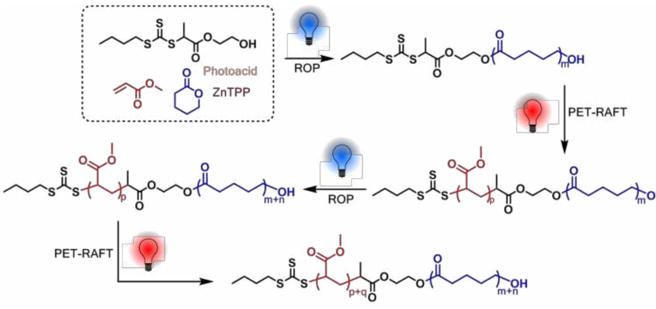

Figure 14. Precise copolymer synthesis through orthogonal photopolymerization.[93c]

In another interesting example of complex reaction simplification, Fors and coworkers designed a protocol for the selective switching of polymerization mechanisms, via alteration of irradiation wavelength.[95] The authors demonstrated that green light (520 nm) irradiation of 2,4,6-tris(p-methoxyphenyl)pyrylium tetrafluoroborate (MPP, **Figure 7**), in the presence of a trithiocarbonate CTA, selectively induced the cationic polymerization of isobutyl vinyl ether (IBVE). Blue light (450 nm) irradiation of the photocatalyst $Ir(ppy)_3$, in the presence of the same CTA, led to the PET-RAFT polymerization of MA. Changing the irradiation wavelength between 520 and 450 nm switched the polymerization from a cationic to a radical mechanism and led to the production of poly(IBVE-*b*-MA) block copolymers in a one-pot system. Compared to previous systems where only block copolymers were produced, this mechanism could be switched on demand using a mono-functional CTA, which allowed statistical copolymerization of cationically and radically polymerizable monomers in a single pot. As a result, this system presents the opportunity to impart increased control over the polymer sequence by successive alteration of both the monomer feed and the polymerization mechanism (**Figure 15**).

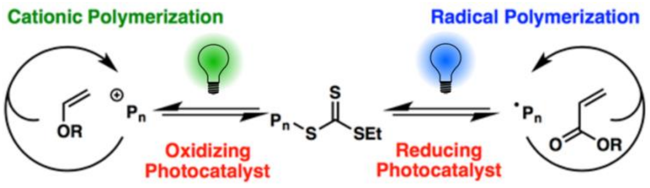

Figure 15. Photocontrolled interconversion of cationic and radical polymerizations. Adapted with permission from ref[95]. Copyright 2017 American Chemical Society.

Rather than switching between different polymerization mechanisms, different irradiation wavelengths can also be used to selectively activate a single polymerization process.[59, 80a, 96] For instance, our group has disclosed the formation of graft copolymers via the selective photoactivation of RAFT agent/catalyst combinations under distinct irradiation wavelengths.[59] Two porphyrinic compounds, pheophorbide *a* (PheoA) and ZnTPP, were employed for orthogonal reaction design, due to their ability to specifically activate dithiobenzoate and trithiocarbonate RAFT agents, respectively. Red light (690 nm) was initially used to activate PheoA and produce linear PMMA homopolymers with trithiocarbonate pendant groups; subsequently, these pendant groups were activated under green light (530 nm) in the presence of ZnTPP and MA, to form the final poly(MMA-*g*-MA) graft copolymers. The sequential PET-RAFT polymerization process was possible due to the highly orthogonal reactions for both catalyst/RAFT agent combinations. In contrast, using a conventional RAFT polymerization strategy would require an additional postmodification/protecting group chemistry step in order to prevent premature radical addition to the trithiocarbonate group during the initial synthesis of the polymer backbone.

Multiple wavelength control has also been exploited for controlling material properties through photoinduced network production; some interesting systems have been developed that allow for polymerization and depolymerization/degradation of crosslinked network structures through chromic orthogonality.[97] For instance, Bowman and coworkers utilized multiple wavelengths for the regulation of sequential interpenetrating polymer networks (IPNs).[98] A loosely cross-linked first stage network was formed via thiol−ene polymerization initiated by visible light (400−500 nm), with subsequent irradiation at 365 nm inducing conventional radical polymerization of acrylates for the formation of the final highly cross-linked IPN.[98a] The authors demonstrated that the intermediate and final IPNs could be tailored by adjusting the ratio of thiol and acrylate functionalities in the initial reaction mixture. Coupled with the ability to induce on-demand polymerization, this system provides a more practical approach for tuning the material properties in a two-stage polymerization process.

Notably, Forsythe and coworkers have developed photodynamic hydrogels that can be switched between the network and free polymer state by changing the irradiation wavelength between visible (400-500 nm) and UV (340 nm).[99] Visible light irradiation drove a [2+2] cycloaddition of styrylpyrene groups covalently bound to PEG chains, which enabled network formation.[99a] UV irradiation reversed the cycloaddition and broke the covalent styrylpyrene linkages, while reformation of the network was possible under visible light irradiation (**Figure 16**). Other groups have also investigated network polymerization and depolymerization using deprotection strategies with multiple wavelengths, to take advantage of the high orthogonality that is possible through photochemistry.[100] Due to their highly tunable nature compared to conventional systems, multi-wavelength protocols for network synthesis offer potential applications in optical lithography and photoresponsive materials.

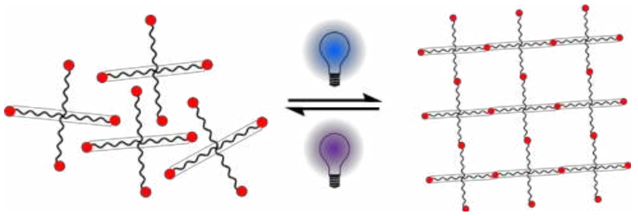

Figure 16. Phototriggered reversible network formation.[99a]

5.2. Wavelength Control in Post-Polymerization Modification

Multiple wavelength strategies have also been applied to modify the functionality of pre-formed polymer substrates; two or more wavelength selective reactions can be employed in one-pot for polymerization and subsequent post-modification, or selective post-modification of various functional groups.[93a, 93i] Such systems not only simplify synthetic protocols, but can provide routes for selective alteration of material properties, release of encapsulated cargo at a specific time and following a specific order, etc. Moreover, in comparison to conventional techniques for post-functionalization, photoinduced techniques allow on-demand and spatially resolved functionalization, leading to improved control in such systems.

Our group developed a dual wavelength protocol for polymerization under red light, and subsequent removal of functional groups under higher energy UV light (312 nm) irradiation, which induced on-demand dissociation of self-assembled block copolymers.[101] Formation of amphiphilic block copolymers containing hydrophilic poly(oligo(ethylene glycol) methyl ether methacrylate) and hydrophobic poly(*o*-nitrobenzyl methacrylate) was achieved using PET-RAFT polymerization under red (635 nm) light, respectively.[101] Following self-assembly into micelles, the particles could be irradiated under UV light for the removal of the photosensitive nitrobenzyl (*o*-NB) group, which altered the hydrophilic-hydrophobic ratio and induced disassembly.

Similar chemistry has also been used in another interesting orthogonal reaction for the release of tethered polymer brushes formed through photopolymerization.[102] Cui and coworkers attached nitrodopamine functionalized alkyl bromide initiators to silicon substrates, with successive irradiation at 460 nm allowing spatially controlled polymerization from the surface. Switching the irradiation wavelength to UV (360 nm) allowed photocleavage of the polymer chains through photolysis of the *o*-nitrophenyl ethyl group resulting in the detachment of grafted polymers from the surface (**Figure 17**). This dual wavelength approach presents a facile way to manipulate the surface properties, both spatially and temporally, in a single pot. In contrast to conventional, multi-step approaches to surface modification, the incorporation of dormant photoactive groups into polymer chains in these examples allows product complexity to be maintained while minimizing tedious handling and purification steps.[33a, 103] Moreover, the ability to manipulate surface properties on-demand could provide useful commercial applications.

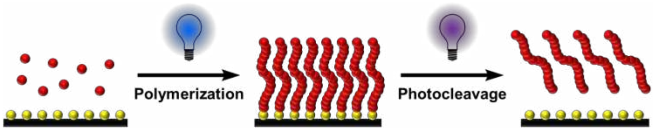

Figure 17. Grafting-from and subsequent photocleavage using multiple wavelengths.[102]

Chromic orthogonality has also been utilized for polymer post-modification by employing organic photochemistry.[104] Barner-Kowollik and coworkers have explored the selective activation of different photosensitive groups for functionalization of a polymeric *α,ω*-functionalized dilinker.[104c] In a one-pot, two-step process, photoenol end-groups present in the polymeric dilinker were completely and selectively consumed by reaction with peptide functionalized maleimides under 310-350 nm irradiation; the remaining tetrazole end-groups were subsequently reacted with a maleimide terminated polylactide through photoactivation under 270-310 nm irradiation. By utilizing the sequential nature of this process, the authors demonstrated site-selective modification of the dilinker to produce a triblock polymer/peptide hybrid. The utilization of reaction sequence, in conjunction with wavelength selective photoactivation, allowed synthesis of macromolecules with well-defined architectures in a simplified, single-pot procedure.

The selective release of cells, proteins, model therapeutics, etc. from polymer networks has also been achieved through organic photochemistry.[33b, 105] These systems take full advantage of light as an energy source for activation; multiple wavelengths allow selective release of different moieties, spatial control allows site specific release, temporal control can impart on-demand and rate controlled release, while the low temperatures used are suitable for potential applications in biological systems. As an example, Azagarsamy and Anseth utilized a dual wavelength procedure for the selective release of proteins tethered to a hydrogel network.[105a] In this process bone morphogenetic proteins were modified with two different photocleavable units based on *o*-NB or coumarin methyl ester moieties. Following attachment to a poly(ethylene glycol) (PEG) hydrogel network, irradiation at 365 or 405 nm was used to selectively trigger the protein release upon exposure to the pre-selected wavelengths (**Figure 18**). Compared to other methods for cargo release such as hydrolysis and enzymolysis, photoinduced strategies provide significantly increased spatial and temporal control over release profiles. Utilization of multi-wavelength protocols could thus find applications in drug delivery, regenerative medicine, tissue engineering, etc., due to their ability to provide user-defined and on-demand control of release profiles under physiological conditions.

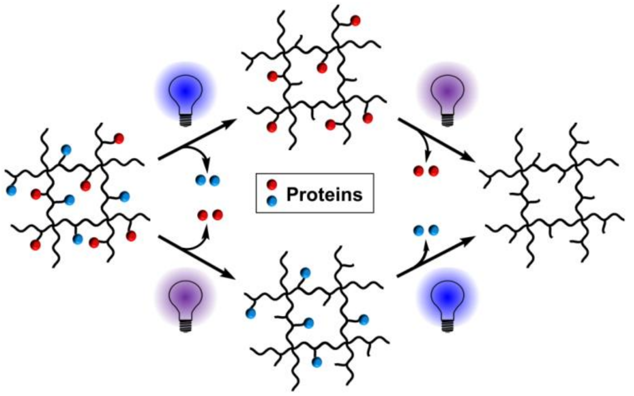

Figure 18. Release of proteins from a network using two light wavelengths.[105a]

6. Summary and Outlook

As highlighted extensively in this review, light is a powerful tool that can be harnessed to provide a unique degree of synthetic control in the field of polymer chemistry. In particular, photochemistry allows facile and extrinsic 'instantaneous' control over polymerization (and other chemical reactions), which thermally or chemically activated systems cannot achieve due to heat and mass transfer limitations. As well as providing spatio-temporal control over chemical reactions, photochemistry can be easily controlled through variations to the light intensity and irradiation wavelength. Furthermore, photopolymerization and photoligation chemistries are often decoupled from the reaction temperature, which allows modification of thermally-sensitive molecules, such as biomolecules, and in turn affords new complex materials with a high retention of bioactivity. In some cases, photochemistry has been utilized for chemical processes that would be impossible to achieve by other methods, demonstrating the expansiveness and unbridled potential of the photochemistry toolbox.

Clearly, the high degree of modularity in photochemical approaches enables a much broader range of chemical transformations to be accessed; regardless, like anything, photochemistry has its limitations and must overcome several challenges to allow its adoption by the wider chemical community. A notable challenge for the photochemistry community is increasing the reproducibility of photochemical systems, especially photopolymerization. It can be difficult to replicate photopolymerization systems across different laboratories and reactor setups due to the large number of variables and process sensitivity. For example, in contrast to other chemistries, photochemical reactions can be sensitive to extrinsic parameters such as the intensity and wavelength of irradiation, as well as reaction vessel geometries, which introduce light intensity gradients and hence uneven activation rates within the reaction mixture. Moreover, the spectral emission of the light sources used for photopolymerization is sometimes communicated with insufficient information. We suggest that improved reporting for photomediated polymer chemistry, including accurate light intensity values at the reaction surface, specific geometric descriptions, and precisely characterized emission spectra, would not only aid in only improving inter-laboratory reproducibility, but also increase the rate with which photochemical approaches are adopted by the polymer (and broader chemistry) community. Furthermore, the commercialization of standardized irradiation devices to perform photopolymerization will help to overcome this challenge; encouragingly, some efforts have already been made in this regard. For instance, MacMillan's team has worked in collaboration with Merck to develop a standardized reactor system for performing photoredox catalyzed organic chemistry, which will allow increased reproducibility between different research groups.[106]

Another inherent limitation in photochemical systems is the short depth penetration of light through reaction media. As shown in **Equation 1**, light absorption is path length dependent; therefore, in systems which are more than a few millimeters deep, light intensity gradients become significant. Conveniently, conducting photopolymerization in continuous flow reactors can often overcome this limitation. Compared to photomediated reactions performed in batch, flow chemistry is typically conducted in thin tubes which allow more even light intensity throughout reaction mixtures. Moreover, flow chemistry provides improved heat and mass transfer, and more precise control of reaction temperature compared to batch systems. This typically results in higher conversions or yields, improved selectivity, enhanced energy efficiencies, and reductions of solvent volumes and waste products. Additionally, flow systems can be easily integrated for sequential processing or online monitoring by linking unit processes; this provides the opportunity for the synthesis of complex macromolecules in a continuous fashion, and with more dynamic, autonomous reaction control through constant characterization.[107] While flow chemistry is not suitable for all photopolymerization systems, the ability for facile upscaling through reactor parallelization also provides attractive opportunities for large scale production of well-defined macromolecules or precursor materials.[108]

Perhaps, one of the most promising advantages of light, which has been rarely explored, is the possibility to perform sequential or simultaneous chemical reactions by exploiting orthogonal photochemistry. Photons have a specific amount of energy, which is inversely proportional to the wavelength (**Equation 2**); the difference in energy at these different wavelengths can be exploited to trigger specific polymerizations or chemical reactions. If the chromophores are carefully chosen to be selectively activated under a specific wavelength, a sequence of chemical reactions can be independently programmed and externally activated. To date, this concept has only been demonstrated in a limited number of examples, such as for the synthesis of complex macromolecules or the release of photoactive compounds. However, the ability to specifically dictate a sequence of polymerizations or chemical reactions presents new possibilities for the synthesis and design of advanced materials with higher hierarchical structures. As such, photochemistry could be readily harnessed to trigger orthogonal polymerization processes and allow the production of spatially resolved materials with precisely tailored mechanical properties. These photoorthogonal approaches are still very much in their infancy and their success will be largely dependent on new discoveries of photoactive compounds capable of mediating orthogonal chemistries. As such, the design of new photocatalysts is another challenge that needs to be addressed for the advancement of photochemical systems.

Although the range of chromophores available for photochemical transformations is seemingly endless, there are still some persistent issues that remain in photochemical systems, particularly photopolymerization systems, that can be addresses by the design of new chromophores. For instance, visible light absorbing chromophores used for modern photopolymerization processes are usually very strongly colored; as a result, these chromophores may be unsuitable for use in applications where the polymer is required to be colorless. Rather than removing the chromophore from the post-polymerization reaction mixture, which may be tedious or impossible, the design of photoactive compounds that can degrade or "disappear" under an external stimulus following the polymerization could be of great use in this regard. For instance, our group recently demonstrated that Chl *a* could be used as a photocatalyst for polymerization and subsequently degraded by exposure to air under visible light, without affecting the chemical structure of the polymer products.[109] Alternatively, photocatalysts for polymerization can be fixed to solid supports which simplifies the separation of the pure polymers and the photocatalyst after polymerization.[93e, 110]

Additionally, new chromophores that can attenuate far-red and NIR light are required for future photochemical systems as longer wavelength irradiation is inherently safer, while also allowing increased depth penetration through non-transparent materials compared to shorter wavelength irradiation. Consequently, photochemical systems that can harness longer wavelength irradiation should provide the possibility for new applications, especially bioapplications. The design of other new photocatalysts to perform multiple specific functions, e.g. simultaneous polymerization and stereochemistry control, is also required; such photocatalysts should provide useful for precision macromolecular synthesis and advanced material production. Fortunately, the design of new chromophores for photochemical reactions can be accelerated using computational modelling, which can reduce the amount of experimental optimization required during the design phase. This concept has been recently applied in photochemistry to improve polymerization kinetics and control over polymerizations but has not yet been widely exploited in the photochemistry community for photocatalyst design.

Finally, the utilization of light in polymer synthesis has been implemented for the production of complex materials, including coatings, 3D materials, adhesives, etc. However, due to recent innovations, such as photoorthogonal approaches, we can envision the production of more complex polymeric materials with a variety of mechanical properties. Indeed, current materials made through 3D printing are constructed using a single type of polymer, which limits the mechanical properties of the final materials. To meet these challenges, polymer chemists and material scientists have looked to bio-inspired materials due to nature's ability to produce compounds with unmatched structuration and uniformity.[111] Particularly, biomaterials are largely constituted by a complex range of different domains with disparate mechanical and physical properties; the organization of these domains leads to significant enhancement of mechanical properties (impact toughness, mechanical strength, elasticity, etc.). While the production of synthetic materials with the structural precision seen in nature is only in its very beginnings due to our limited synthetic capabilities, the ability to precisely control a succession of chemical reactions using light will allow the design of more advanced materials and the design of sequence-defined polymers. These new materials and polymers could find applications in tissue engineering, biomedical engineering, as well as advanced manufacturing, among many others. The combination of living polymerization techniques and photochemistry will allow us to approach the structural precision observed in these biomaterials. Clearly, photochemistry will light the way forward for materials chemistry.

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Conflict of interest

The authors declare no conflict of interest

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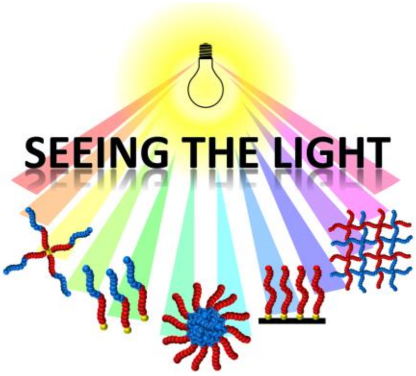
Entry for the Table of Contents

REVIEW

Seeing the light: Photochemistry is a powerful tool for mediating polymerization and material synthesis due to the inherent benefits of light as an energy source for activation. Some outstanding systems that utilize these benefits for polymerization and materials synthesis are reviewed.



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Seeing the Light: Advancing Materials Chemistry through Photopolymerization