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Perspective

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Evolution and Future Directions of Metal-Free Atom Transfer Radical Polymerization

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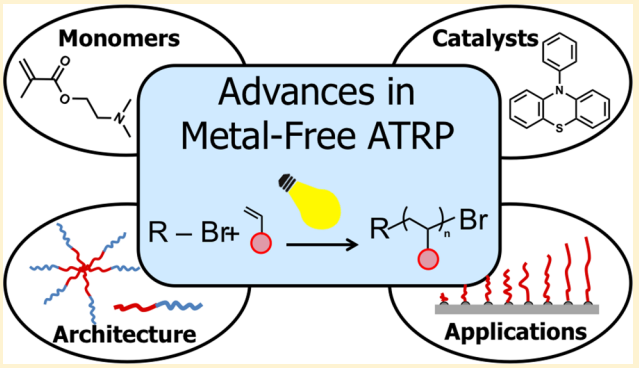
ABSTRACT: The increasing impact of atom transfer radical polymerization (ATRP) in fields beyond traditional polymer science has necessitated the development of alternative strategies for controlling polymer growth. Driven by applications that are sensitive to metal ion contamination, "greener" methodologies are emerging as a powerful alternative to conventional ATRP. Organic catalysis represents a major evolution of ATRP with metal-free systems holding significant potential as user-friendly methods for utility in biological and microelectronic applications. In addition, shifting from a combination of thermal activation/metal ions/ligands to simpler organic catalysis/light activation increases compatibility with functional monomers and allows the development of novel surface patterning strategies. Herein, we highlight key discoveries and recent developments in metal-free ATRP, while providing a perspective for future opportunities in this emerging area.



INTRODUCTION

The discovery of controlled radical polymerization (CRP) techniques, namely, reversible addition−fragmentation chain-transfer polymerization (RAFT),[1] nitroxide-mediated polymerization (NMP),[2] and atom transfer radical polymerization (ATRP),[3] represents a seminal contribution to the broad materials arena. These methodologies have enabled synthetic chemists to design materials with unprecedented control over chain-end functionality,[4] architecture, molar mass, and dispersity ($Đ$).[5,6] The impact and associated evolution of ATRP are particularly noteworthy with dozens of variations emerging since the pioneering reports by Matyjaszewski[7] and Sawamoto.[8] In conventional ATRP, the activation−deactivation equilibrium between propagating radicals and dormant species is critically important for controlling the polymerization process. This equilibrium relies on the dormant species periodically reacting with the active catalyst, which is composed of a lower oxidation state transition metal complex (most commonly Cu(I)Br/L, where L is a ligand), to generate propagating polymer chains. The presence of a deactivator, which is a transition metal complex in a higher oxidation state (e.g., Cu(II)Br_2), reversibly caps propagating chains, keeping the overall radical concentration low and decreasing chain−chain coupling and other termination processes.[9] In early examples of ATRP, the relatively high concentration of Cu catalyst is often regarded as a drawback, especially when considering potential use in biological and microelectronic applications. To address these high catalyst loadings, improved purification methods using silica, alumina, or ion-exchange-based techniques were developed to reduce residual metal ion contamination.[10] Though successful, the need to further reduce Cu concentration motivated the development of a myriad of ATRP variations, including initiators for continuous activator regeneration-ATRP (ICAR-ATRP),[11,12] supplemental activation reducing agent ATRP (SARA-ATRP),[13,14] activators regenerated by electron transfer-ATRP (ARGET-ATRP),[12,15] and photo-ATRP,[16−19] all of which focus on decreasing the initial catalyst loading while still enabling access to complex macromolecular architectures[20] and materials with high end-group fidelity.[21,22] The success of these strategies has opened up new applications for ATRP-based materials; however, the presence of trace amounts of metal ions is still problematic for future research directions.

Coupled with recent efforts in the broader scientific community to develop green chemistries,[23−27] an important push in the controlled polymerization arena is the development of techniques that do not require transition-metal catalysts. This underlying shift in strategy is also prevalent in other traditionally metal-catalyzed controlled polymerization systems such as ruthenium-catalyzed ring-opening metathesis polymerization (ROMP). In pioneering work in this area, Boydston and co-workers have demonstrated the ability to perform organocatalyzed ROMP.[28−32] While developments in metal-free ROMP are still in their early stages and outside the scope of this Perspective, this general movement to developing organic alternatives to traditional metal-catalyzed polymer-

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ization methodologies remains a significant opportunity for future research and exploration.

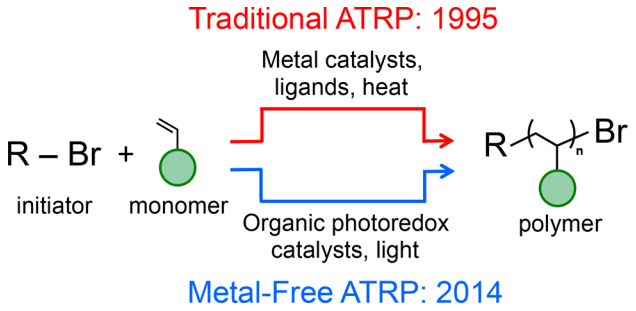

Figure 1. Initial disclosure of metal-free ATRP came nearly two decades after the introduction of ATRP.

Initial work in the expansive area of nontraditional ATRP processes primarily focused on the concept of nonthermal activation. A key breakthrough was the 2011 report by Matyjaszewski on e-ATRP, where Cu-mediated ATRP could be conducted at room temperature through electrochemical activation.[33] Building on this insight, Fors and Hawker in 2012 developed a photochemical mediated ATRP process based on $Ir(ppy)_3$ photoredox catalysts.[34] Drawing inspiration from these advances and the burgeoning field of visible light photocatalysis in organic chemistry, a metal-free ATRP process based on small molecule organic photoredox catalysis using 10-phenylphenothiazine (Ph-PTH) for the controlled polymerization of methacrylates was reported.[35] Preliminary mechanistic studies suggested that upon excitation with 380 nm light Ph-PTH induces reduction of traditional alkyl bromide-based ATRP initiators via an oxidative quenching cycle. This results in the generation of a propagating radical as well as a deactivating catalyst complex consisting of the radical cation form of the photocatalyst and a bromine anion. This complex subsequently deactivates growing polymer chains through formation of a dormant, bromine-end-capped species and reduction back to the initial ground state Ph-PTH. Significantly, full spectroscopic analysis of the polymer chains formed by Ph-PTH-catalyzed ATRP did not show any differences to polymers prepared by traditional Cu-mediated ATRP, indicating that the products obtained from both processes are chemically and structurally the same. Concurrently, Miyake and co-workers reported perylene as an organic photocatalyst for ATRP, which also mechanistically operates through an oxidative quenching cycle.[36] Because of its extended conjugation, perylene offers a potential unique advantage in that it can be excited with visible light. Following the introduction of these first-generation catalyst derivatives, the field of metal-free ATRP has flourished with recent studies providing researchers with greater mechanistic insight, improved polymerization control through the development of novel catalyst derivatives, and proof-of-concept utility in a variety of application-driven settings.

The aim of this Perspective is to highlight advances in metal-free ATRP with a view to new developments in photocatalyst design, progress in monomer and initiator scope, and access to unique polymer architectures. A key goal is to define current limitations and drawbacks with metal-free ATRP that, if addressed, will significantly enhance the versatility and utility of this user-friendly strategy.

COMPONENTS OF METAL-FREE ATRP

General Setup. One of the primary mechanistic differences that distinguishes metal-free ATRP from classical ATRP is catalyst activation via light irradiation. As a result, the versatile nature of light permits use of a variety of different light sources, ranging from simple compact fluorescent lamps (CFLs) to wavelength specific light-emitting diodes (LEDs) and, in some cases, natural sunlight (Figure 2). Light also offers distinct

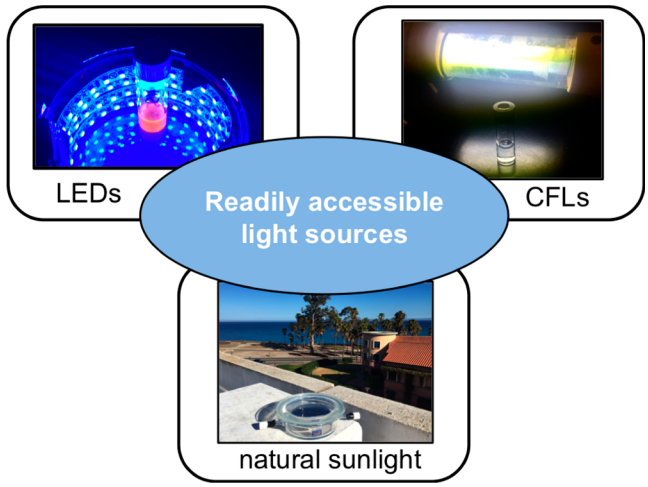

Figure 2. Representative metal-free polymerization setups using light-emitting diodes (LEDs), compact fluorescent lamps (CFLs), and natural sunlight.

advantages over thermally driven techniques, including the ability to (1) exert spatiotemporal control over polymerization, (2) polymerize under ambient temperatures, (3) modulate the stimulus (i.e., wavelength, intensity) for facile modulation of reaction kinetics, and (4) exploit multiple wavelengths for orthogonal reactivity/multiple CRP processes in a single reaction vessel.[37−40] To illustrate some of these features, Miyake and co-workers recently disclosed a thorough study highlighting the effects of light intensity on polymerization control using metal-free ATRP.[41] Their work demonstrated that light intensity plays a significant role in the ability to externally mediate polymerization kinetics and attain varying polymerization rates.

In contrast to traditional Cu-ATRP, the absence of metals and associated ligands simplifies the overall polymerization setup with recent evidence suggesting that select photocatalysts can even work without deoxygenation, further enabling nonexperts access to this chemistry.[42,43] A representative photographic depiction of the various light sources used in typical setups is shown in Figure 2. Polymerizations are easily conducted using glass vials equipped with a septum sealed cap and can be placed in a glass dish lined with commercially purchased LEDs of the desired wavelength or placed directly in front of hand-held lamps. The important takeaway here is that the use of specialized and expensive photoreactors is not necessary with the choice of light source benefiting from the significant growth in LED technology and availability. For a representative procedure, we direct the reader to an excellent video tutorial by Miyake and co-workers.[44]

Photocatalyst Derivatives. A major focal point of current research in metal-free ATRP is the development of novel and more efficient photocatalysts. In this area, inspiration can be drawn from the abundance of available organic dyes with many

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having the characteristic properties needed for successful metal-free ATRP. To this end, photocatalyst development has seen exponential growth since the introduction of the first-generation phenothiazine (Figure 3) and perylene (Figure 4)

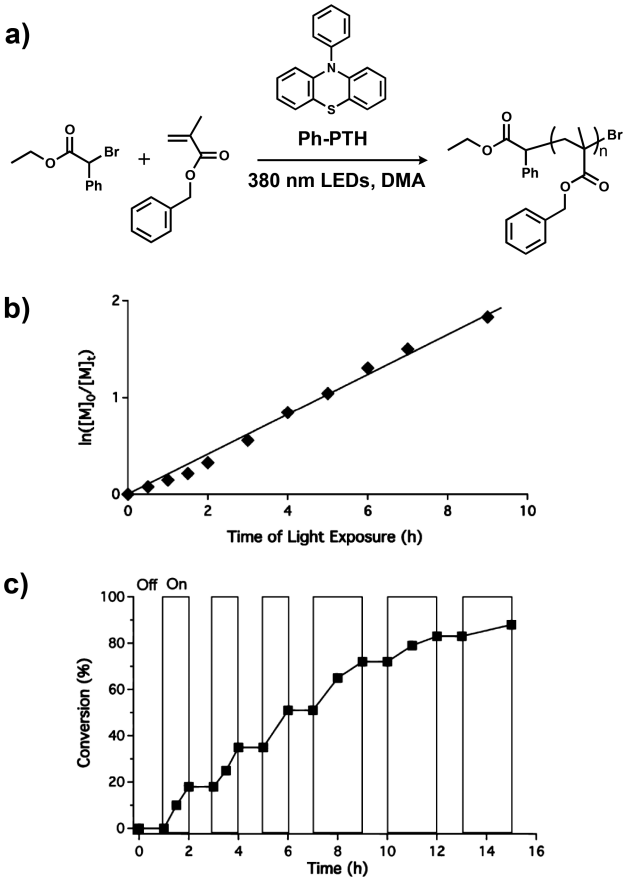

Figure 3. (a) Reaction scheme for the metal-free ATRP of methacrylates using EBPA as the initiator. (b) First-order linear growth kinetics using Ph-PTH for the polymerization of benzyl methacrylate. (c) "On−off" light cycling experiments demonstrating temporal control. Adapted with permission from ref 35.

catalysts. While perylene offers advantages such as excitation with visible light, limitations such as poor initiation efficiencies and relatively high $Đ$ render it unsuitable for applications requiring a high degree of polymerization control.[36] As such, the initial stages of metal-free ATRP expanded on phenothiazine-based systems as a platform for photocatalyst development. Indeed, Matyjaszewski and co-workers exploited the tunable framework of phenothiazines and designed key derivatives with naphthyl (Napht-PTH) and benzo[*b*]-phenothiazine (Ph-benzoPTZ) substituents providing enhanced control over the polymerization of methacrylates when compared to the first-generation Ph-PTH (Figure 4). In the case of Ph-benzoPTZ, the additional benefit of a red-shifted UV absorption maximum (∼50 nm relative to Ph-PTH) enables controlled polymerization using visible light.[45,46] Interestingly, the importance of substituent effects on Ph-PTH can also be used to feed back into organic synthesis with recent examples showing promise in small molecule dehalogenation,[47] defluoroalkylation,[48] and carbon−carbon bond forming reactions.[47] In turn, the effects of different heteroatoms has been examined by Miyake with the introduction of novel phenazine[49] and phenoxazine-based[50]

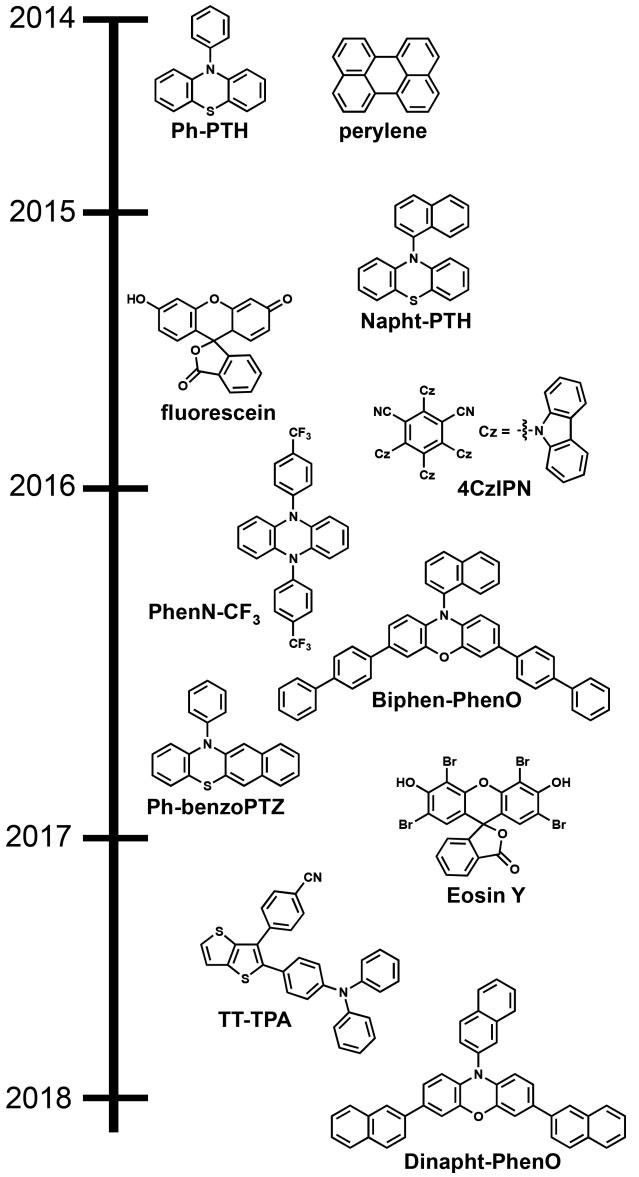

Figure 4. Timeline for the development of select families of photocatalysts utilized in metal-free ATRP.

photocatalysts, which perform with characteristically high initiation efficiencies and yield low $Đ$ materials due to their favorable photophysical characteristics. In a similar vein to Ph-PTH, these derivatives have also found utility in small molecule synthesis.[51,52]

The design of new photocatalysts begins with a fundamental mechanistic understanding of the catalytic cycle. For the first generation of metal-free ATRP catalysts, an oxidative quenching cycle is operational (Figure 5a). Following photoexcitation using UV and/or visible light, activation of the alkyl halide initiator gives a carbon-centered radical and subsequent monomer propagation. The concomitant in situ generation of the photocatalyst radical cation and bromine anion complex serves as the deactivating species that facilitates reversible capping of propagating polymer chains via a redox event, ultimately leading to controlled chain propagation. Following removal of the light source, photoexcitation ceases and subsequently facilitates deactivation to yield an end-capped dormant state that is analogous to traditional ATRP

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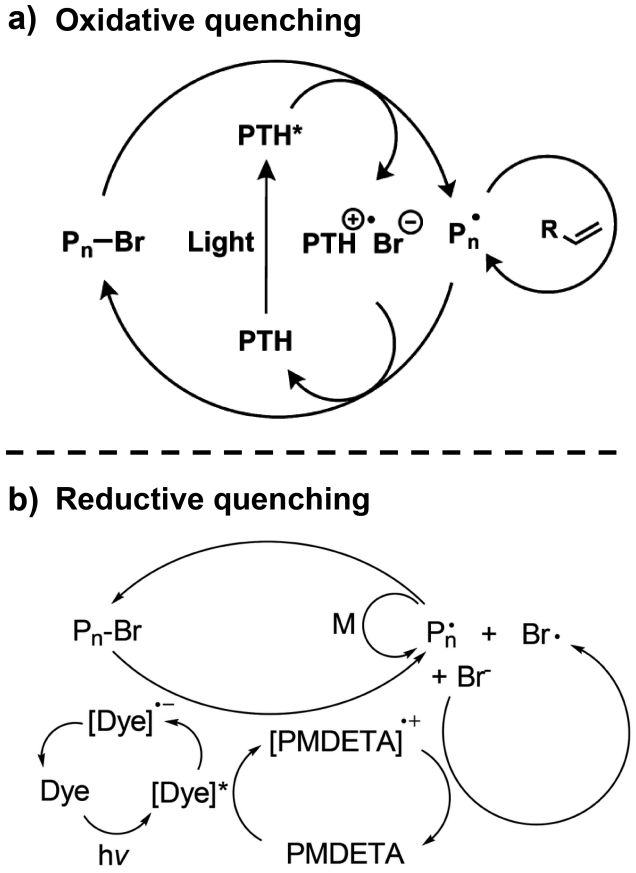

Figure 5. Representative schematics for (a) oxidative and (b) reductive quenching cycles for metal-free ATRP. (a) Adapted with permission from ref 35. (b) Reproduced with permission from ref 61. Copyright 2016 Royal Society of Chemistry.

processes. Interestingly, previously reported mechanistic investigations suggest that both singlet[42,45,47] and triplet[53] excited states are responsible for the reduction of the alkyl halide initiator and the growing, end-capped polymer chains. While the question of which excited state plays a more dominant role is an interesting subject for further study, the most recent reports support the notion that short-lived excited singlet states may be primarily responsible for the high degree of control obtained in the case of phenazine-based catalysts.[54,55] For more in-depth discussion regarding the photophysical properties of photocatalysts that undergo oxidative quenching, we direct the reader to an insightful article from Miyake and co-workers.[56] From these fundamental studies, a greater understanding of the impact of different excitation pathways will be obtained and in turn will aid the development of optimized photocatalytic systems.[56] Potential core building blocks for metal-free ATRP photocatalysts (Figure 4) have been developed with the most prominent being (1) phenothiazines, (2) aromatic hydrocarbons, (3) phenazines, (4) phenoxazines, (5) carbazoles, and (6) thienothiophenes. The aforementioned catalyst families operate under the principle that photoexcitation enables electron transfer events otherwise not accessible through thermal processes.

Although categories 1−4 have arguably received the most attention as photocatalyst scaffolds, the unique features of carbazoles and thienothiophenes open up significant future opportunities. For example, Zhang, Cheng, and co-workers reported that the metal-free ATRP of MMA could be achieved using ppm levels of a novel carbazole-based catalyst, 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN).[57] A key insight may be the initial implementation of this molecule in organic light-emitting diode (OLED) applications after it was discovered to undergo thermally activated delayed fluorescence.[58] Distinct advantages of this photocatalyst family include exceptionally low catalyst loadings, down to as little as 15 ppm. However, overall $Đ$ values were generally higher than those achieved with phenazine or phenoxazine-based catalysts. Nevertheless, this report lays the groundwork for the need to draw inspiration from other fields to aid future photocatalyst design and discovery. Yagci and co-workers more recently augmented the scope of available metal-free ATRP catalysts with a series of unique thienothiophene derivatives, such as 4-[2-(4-diphenylaminophenyl)thieno[3,2-*b*]thiophen-3-yl]benzonitrile (TT-TPA).[59] Although this class of molecules requires more synthetic steps in comparison to other catalyst derivatives, this work suggests that exploration of a diverse array of conjugated molecules could further improve and broaden the scope of metal-free ATRP photocatalysts.

While initial studies of organic photocatalysts have focused on oxidative quenching (Figure 5a), recent developments have illustrated that controlled polymerization can also be achieved via a reductive quenching pathway (Figure 5b). In this case, commercially available electron-deficient organic dyes are used in conjunction with sacrificial electron donors.[55] The potential of this strategy is exemplified by fluorescein and other commonly utilized fluorescein-based dyes such as eosin Y and erythrosin B.[55,60,61] For example, Luo and co-workers exploited the reductive quenching cycle for the first demonstration of metal-free ATRP of acrylic monomers in aqueous media.[62] A distinct advantage of these commercial dyes is that no further synthetic modification is necessary to allow efficient excitation with visible light. This promotes a more user-friendly process, as these bench stable catalysts can be used directly from commercial sources. Moreover, it has been shown that reductive quenching can also be realized using common UV-active photosensitizers such as camphorquinone and benzophenone.[63] While polymerization via reductive quenching represents an exciting avenue for future research, one challenge to address is the increased propensity for unfavorable side reactions due to the presence of sacrificial amine donors.[56,64]

In concert with the progress of photocatalyst design in organic chemistry, catalysts for metal-free ATRP have evolved considerably during the past four years. A general timeline for the introduction of various derivatives is shown in Figure 4 with 3,7-di(2-naphthyl)-2-naphthalene-10-phenoxazine (Di-napht-PhenO) representing the current state-of-the-art.[65] Interestingly, Miyake and co-workers established that core substituent modification has a larger impact when compared to alteration of the *N*-aryl substituents on phenoxazine[66] catalysts. This critical observation sets the foundation for more targeted photocatalyst derivatization moving forward. This recent push for increased understanding of design principles has also led to other notable improvements in catalysis discovery. This includes enhanced initiation efficiencies and more desirable absorption characteristics that, in turn, provide researchers access to different polymerization conditions and greater overall control. Furthermore, the ease of substituent modification offers numerous opportunities for fine-tuning the desired catalyst properties using well-established synthetic

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protocols. A prominent example includes the simple addition of biphenyl units to a phenoxazine core leading to an absorbance maximum red-shifted by 65 nm and a concomitant 4-fold increase in the molar extinction coefficient (Figure 6).

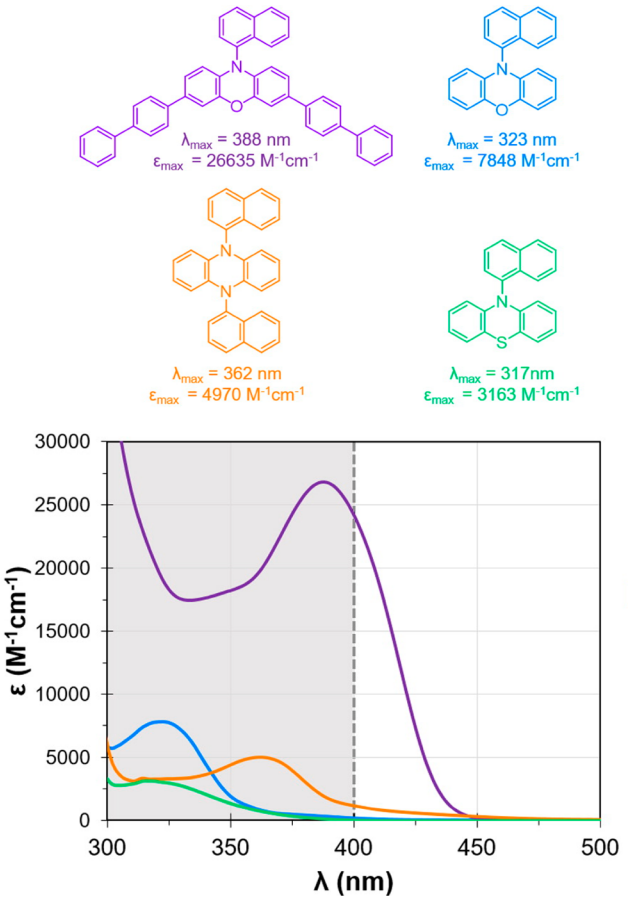

Figure 6. Tuning of photocatalyst properties through modification of phenoxazine, phenazine, and phenoxazine cores with various biphenyl substituents. Adapted with permission from ref 50.

An eventual push to use red light as a stimulus for metal-free ATRP, in a similar manner to photoinduced electron transfer RAFT (PET-RAFT), could therefore lead to broader utility in an array of biologically relevant applications. Additionally, a direct consequence of this focus on catalyst development is to enable the polymerization of different building blocks. For example, while light is currently employed for all reported metal-free ATRP methodologies, a move toward alternative external stimuli (i.e., electrochemical and chemical) would significantly widen the scope of organocatalyzed systems in general. This includes revisiting heat as a stimulus for metal-free ATRP. Although it may not offer the benefits of spatiotemporal control, the development of a thermally catalyzed metal-free ATRP process would have significant impact, as it would directly address the challenges of scalability and industrial viability associated with light irradiation.

Solvent and Initiator Selection. In contrast to this increase in available photocatalysts, a greater understanding of the influence of solvents and initiating species on metal-free ATRP is required to fully benefit from this structural diversity. Interestingly, solvent scope has remained largely unchanged. The initial reports involving Ph-PTH and perylene used *N*,*N*-dimethylacetamide (DMA) and *N*,*N*-dimethylformamide (DMF) solvents with the rational for these polar aprotic solvents not completely understood. More recently, new insights published by Miyake and co-workers illustrated the importance of solvent choice on intramolecular charge transfer and ion pairing for phenazine-based systems.[67] Indeed, after postulating that solvent polarity would substantially influence catalyst performance, the identification of a mixed solvent system (DMA:THF 3:1, v:v) resulted in the highest degree of control for the polymerization of MMA. This was attributed, in part, to the strong red-shifted emission of the photocatalysts in more polar solvents.[67] Intriguingly, this is likely an underlying reason why nearly all reports on metal-free ATRP still rely on highly polar solvents such as DMA, DMF, and DMSO. Interestingly, more recent follow-up work describes the ability to successfully perform metal-free ATRP in a range of solvent polarities but only with phenazine photocatalyst derivatives that exhibit intramolecular charge transfer character.[68] An important take-away from these studies is that careful design of catalyst substituents may be needed for the extension of metal-free ATRP to nonpolar, aqueous, or biologically relevant media.

For initiating systems, original reports utilized a range of classical ATRP initiators such as ethyl α-bromophenylacetate (EBPA). In an analogous manner to solvent selection, extensive initiator optimization studies have not been conducted with the most relevant work being a preliminary comparison between EBPA and methyl α-bromoisobutyrate (MBIB) for perylene-based catalysis.[36] Significantly, this work demonstrated higher initiation efficiencies leading to lower $Đ$ materials for EBPA which may be attributed to the higher activity of EBPA as previously described in Cu-catalyzed ATRP.[69] More recent studies by Miyake and co-workers demonstrated that controlled polymerization could be achieved with organic photocatalysts using more traditional isobutyrate-based initiators for the first time. Further optimization studies revealed that alternative initiator types such as methyl 2-bromopropionate (MBP) and 2-bromopropionitrile (BrPN) are viable with phenazine[49] or phenoxazine-based catalysts.[50] Interestingly, enhanced control, low $Đ$ polymers and high initiation efficiencies were obtained using diethyl 2-bromo-2-methylmalonate (DBMM), whereas all chloride-based initiators resulted in uncontrolled polymerization. Indeed, these results support previous reports that described chloride-based initiating systems as unsuitable for the current form of metal-free ATRP.[45] This could be attributed to higher bond dissociation energies (BDE) of alkyl chlorides when compared to bromides.[70] In line with this notion, it would be interesting to thoroughly examine the compatibility of metal-free ATRP photocatalysts with alkyl iodide-derived initiators due to their low BDE. A summary of the current scope of initiators (Figure 7) used in metal-free ATRP has exemplified the range of functional derivatives that are fully compatible.

In one notable example, Yagci and co-workers implemented the clever use of a bifunctional ATRP initiator, 3-hydroxypropyl 2-bromo-2-methylpropanoate (HPBIB), for the one-pot synthesis of block copolymers using simultaneous metal-free ATRP and ring-opening polymerization (ROP) processes.[71] In addition to demonstrating the ability to use functional initiators, the capacity to access block copolymers from chemically distinct monomers illustrates the orthogonality of metal-free ATRP when used with other controlled polymerization techniques.

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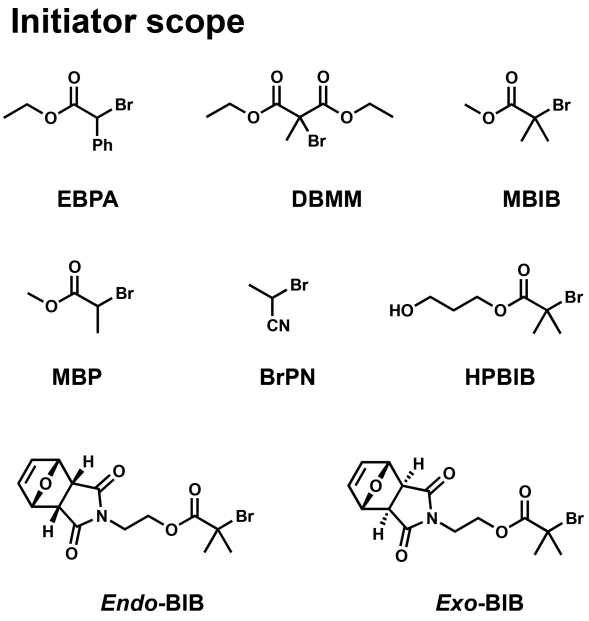

Figure 7. Summary of various initiators used for metal-free ATRP.

In a similar fashion, Hawker, Read de Alaniz, and co-workers disclosed the use of isomerically different furan protected maleimide adducts as functional initiators in metal-free ATRP (Figure 8a).[72] Interestingly, the inherently low deprotection

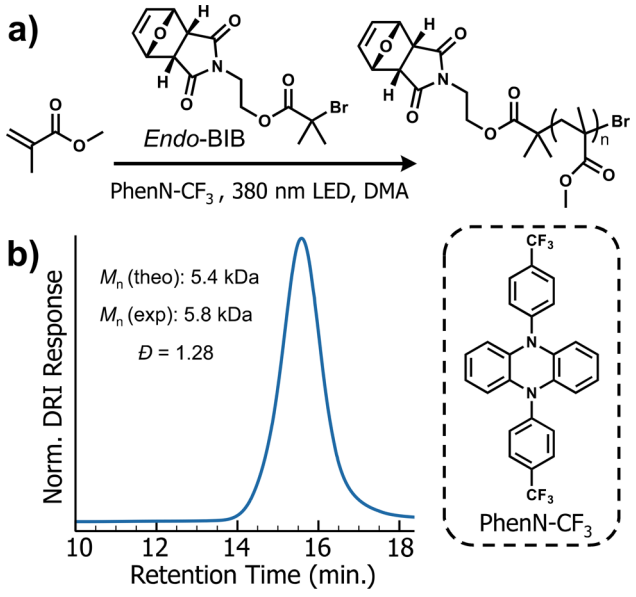

Figure 8. (a) Schematic illustration of metal-free ATRP using a temperature-sensitive functional initiator and (b) corresponding SEC-RI trace of the resulting polymer. Adapted with permission from ref 72.

temperature (~60 °C) of the *endo* conformer (*endo*-BIB, Figure 8) renders it incompatible with traditional thermally initiated polymerization methods. As such, heat-sensitive derivatives are particularly conducive for metal-free ATRP at ambient temperatures with well-defined and functional low $Đ$ materials being obtained when using PhenN-CF_3 as a photocatalyst (Figure 8). In addition, the ability to deprotect the chain-end at relatively low temperatures with no exogenous reagents leading to reactive maleimide units allows secondary functionalization using thiol−Michael addition chemistry. Importantly, it should be noted that the use of room temperature metal-catalyzed ATRP variations still leads to undesired high molecular weight distributions when using protected maleimide initiators, illustrating a further, unseen advantage of metal-free systems.[72] Increasing the scope of available initiators remains a critical area for expanding the overall impact of α-chain-end functional materials accessible using metal-free ATRP, and concurrent efforts to further develop the extent and efficiency of ω-chain-end functionalization of these materials will facilitate its integration with other polymerization techniques[73,74] and broaden the general field of ATRP as a whole.

Monomer Scope. One of the overarching challenges for metal-free ATRP is the expansion of monomer scope. The original reports of metal-free ATRP focused exclusively on methacrylate-based monomers such as MMA and benzyl methacrylate (BnMA), with select recent examples being the Matyjaszewski group's successful polymerization of acrylonitrile with Ph-PTH catalyst derivatives and the controlled polymerization of poly(ethylene glycol) acrylate (PEGA) with eosin Y.[62] In the former case, polyacrylonitrile with predictable molar masses and moderately low $Đ$ and high chain-end fidelity was obtained, enabling facile block copolymerization via an entirely metal-free process.[75] While other attempts have been made to investigate the potential to homopolymerize different monomers such as styrene and *tert*-butyl acrylate with fluorescein-based photocatalysts, more study is required for polymerization control to be achieved.[57]

The challenge of extending metal-free ATRP to other monomer families is mitigated by the diverse range of methacrylates that have been used. For example, the polymerization of dimethylaminoethyl methacrylate (DMAEMA) by ATRP is traditionally demanding and is also challenging when the transition metal photocatalyst, $Ir(ppy)_3$, was used. The success of the organic, metal-free system in polymerizing DMAEMA can be attributed to minimized interactions with the pendant amino groups due to the less oxidizing nature of Ph-PTH.[35] Tang and co-workers successfully polymerized methacrylate derivatives based on biomass-derived materials as exemplified by soybean oil methacrylate (SBMA), furfuryl methacrylate (FMA), and dehydroabietic ethyl methacrylate (DAEMA) (Figure 9).[76] Using Ph-PTH as the photocatalyst and EBPA as the initiator, homopolymers and diblock copolymers could be achieved with control over molar mass and $Đ$. Miyake and co-workers have also demonstrated good control over the polymerization of more hydrophobic monomers such as isobutyl methacrylate (IBMA) and isodecyl methacrylate (IDMA) derivatives.[50] One notable example of a unique functional monomer polymerized by metal-free ATRP comes from Viswanathan, Whitacre, Matyjaszewski, and co-workers showcasing the successful polymerization of poly(ethylene oxide) methacrylate−lithium sulfonyl(trifluoromethylsulfonyl)imide) (PEOMA-$TFSI^-Li^+$) to yield single-ion homopolymers for battery applications.[77] The metal-free ATRP of semifluorinated,[78] sulfur-containing monomers[78] and methacrylic acid[79] has also been reported, albeit via a surface-initiated process from silicon substrates. While not a metal-free ATRP process, Chen and co-workers recently disclosed the compatibility of Ph-PTH with a wide range of semifluorinated methacrylates via polymerization using a trithiocarbonate iniferter.[80] The ability to translate this platform to a metal-free ATRP process for the preparation of

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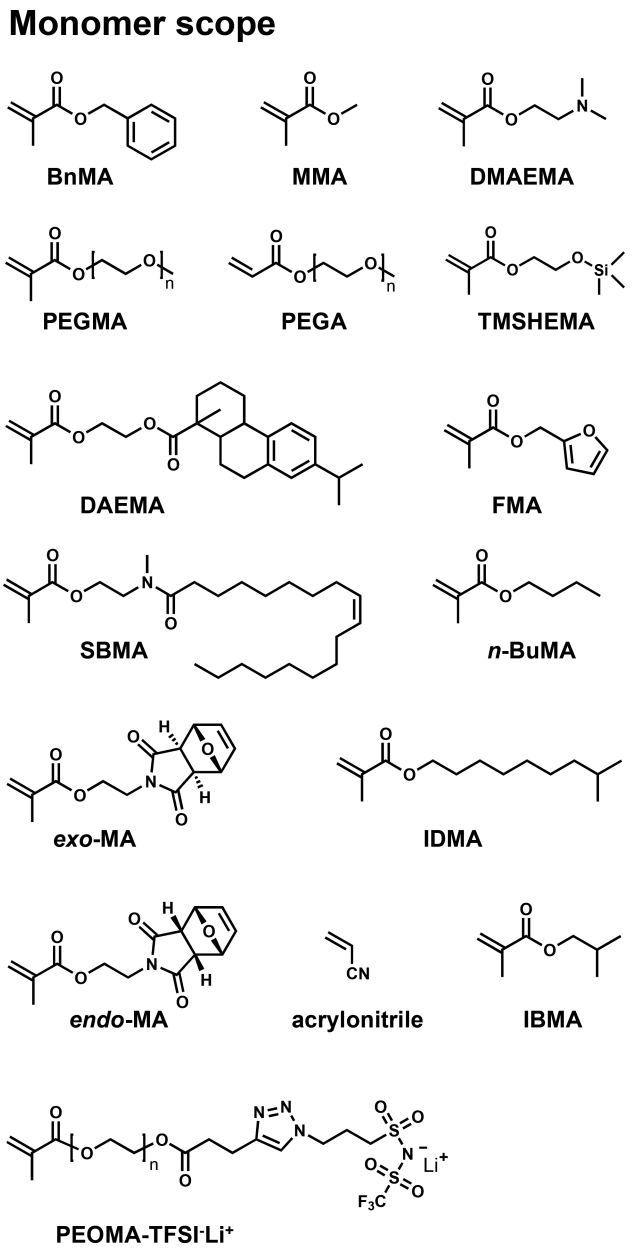

Figure 9. Summary of monomer scope for metal-free ATRP.

semifluorinated materials would be desirable for many applications.[81] Similarly, the Ph-PTH and trithiocarbonate iniferter combination has been exploited by Johnson and co-workers for the controlled polymerization of acrylates and acrylamides.[82] Interestingly, by utilizing aromatic sulfonyl halide-based initiators, Chen and co-workers demonstrate the amenability of phenothiazine-based photocatalysts with acrylates and acrylamides, albeit through a mechanistically distinct process from metal-free ATRP.[83] Although the aforementioned monomer classes have not been thoroughly investigated using metal-free ATRP, these methods suggest the potential for their general compatibility with typical photocatalysts and light sources most commonly implemented for metal-free ATRP. This compatibility extends to functional monomers with Read de Alaniz and co-workers, demonstrating the polymerization of methacrylates bearing pendant *endo* and *exo* furan protected maleimide functional groups for the first time (Figure 9, *endo*-MA and *exo*-MA). As described above, subsequent heating at 60 °C resulted in selective introduction of maleimides without the use of exogenous catalysts or reagents.[72]

It is important to note that although methacrylates are currently the most accessible monomers for metal-free ATRP, incorporation of other monomer classes has been achieved in the form of diblock copolymers. For example, the ability to chain-extend a PMMA macroinitiator with butyl acrylate to yield PMMA-*b*-PBA has been reported with the use of phenazine catalysts,[49] while fluorescein photocatalysts have been used to chain extend PMMA with styrene.[60] Indeed, further investigation is required to better understand the true extent of polymerization efficiency for nonmethacrylate monomers. For instance, in the case of UV-absorbing monomers like styrene, the development of alternative activation pathways using metal-free systems (i.e., mechanochemical, electrochemical, thermal, and chemical) may enable access to additional monomer classes.

APPLICATIONS

Surface-Initiated Metal-Free ATRP. The simplicity and versatility of metal-free ATRP remains a prominent driver for future research, especially in application settings. Building on the initial success of Ph-PTH catalyzed polymerizations, translation to metal-free surface-initiated ATRP (SI-ATRP) from silicon-based substrates proved to be facile.[78] By immobilizing traditional ATRP initiators to surfaces using well-established hydrosilylation chemistries, a series of homopolymer and block copolymer polymer brushes could be obtained via a grafting-from approach using metal-free ATRP. Significantly, light mediation permitted facile access to a number of arbitrary patterns using readily available binary and gradient photomasks in a single polymerization step. Of greater importance for future studies is the increased oxygen tolerance of Ph-PTH when compared to Ir-based photocatalysts. This results in a more straightforward and user-friendly polymerization process with no need for gloveboxes or rigorously inert conditions. A direct consequence is increased potential for scalability, which is best exemplified by the successful micrometer scale patterning of polymer brush growth from 4 in. commercial scale silicon wafers using a simple hand-held lamp (Figure 10). Significantly, very recent follow-up work from our groups demonstrates the capability to perform metal-free SI-ATRP under completely ambient conditions (i.e., no deoxygenation). This is made possible due to the dual action nature of Ph-PTH as both an oxygen scavenger and catalyst when combined with the clever use of glass coverslips. This strategy represents an exceedingly simple platform that will further facilitate straightforward access to functional polymer brushes for nonexperts.[84] Additionally, the versatility of Ph-PTH is further exemplified through its utility as a light-mediated catalyst to reduce bromine chain-ends of surface-tethered polymer brushes,[43,85] pointing toward the possibility of sequential metal-free polymerization and chain-end modification chemistries, which is a concept that could also be explored in PET-RAFT systems.[86] The substrate scope of metal-free SI-ATRP could also be expanded to include silica nanoparticles leading to well-defined core−shell architectures (Figure 11). In contrast to transition-metal-catalyzed systems, one of the most attractive benefits of preparing functionalized nanoparticles by metal-free SI-ATRP is simplified purification, as standard centrifugation techniques allows for straightforward separation of residual organic photocatalysts. This further illustrates the promise of metal-free ATRP for applications that

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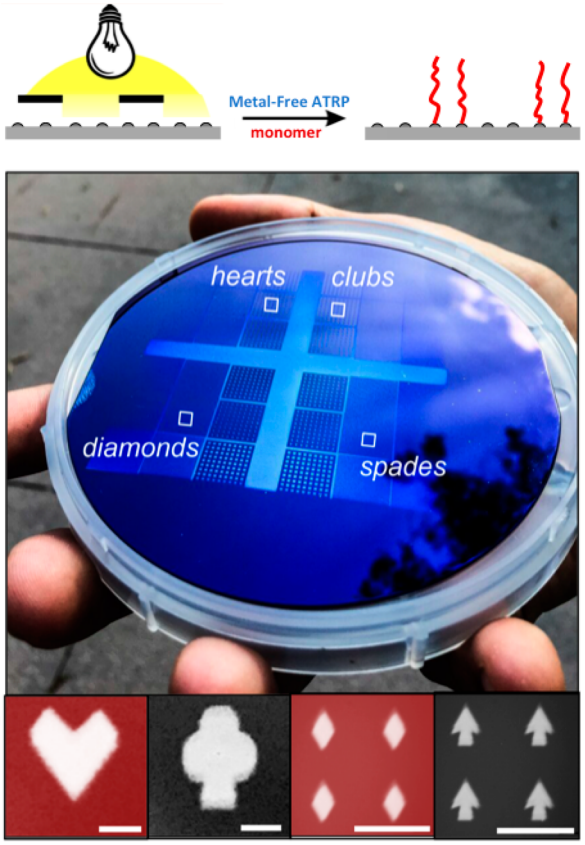

Figure 10. Metal-free SI-ATRP performed on commercial 4 in. silicon wafers using light and a binary photomask to access a range of arbitrary feature shapes and sizes (scale bars are 200 μm) in one step. Adapted with permission from ref 78.

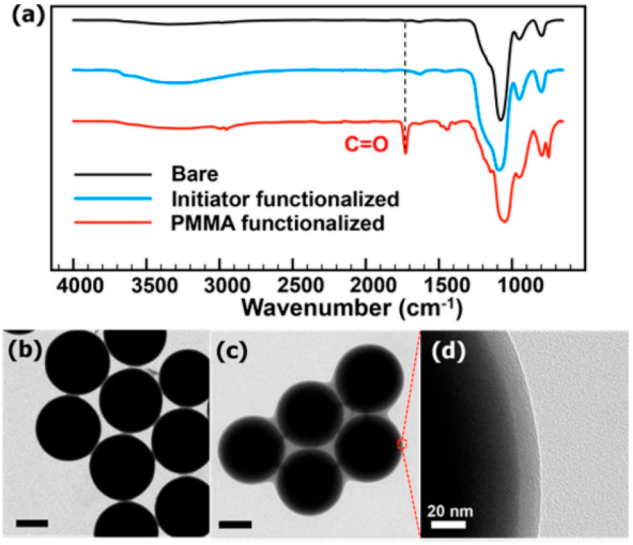

Figure 11. (a) ATR-FTIR confirming appearance of carbonyl stretch (1725 cm^{-1}) for PMMA-functionalized SiO_2 nanoparticles when compared to bare and initiator functionalized nanoparticles. (b) TEM of bare SiO_2. (c) TEM of PMMA-functionalized SiO_2. (d) Magnification of PMMA-functionalized SiO_2 (scale bars are 200 nm unless otherwise noted). Adapted with permission from ref 78.

may be highly sensitive to residual metal contamination. This key advantage is a research area of interest as it may further facilitate access to complex surface-functionalized materials for nonexperts. Importantly, Matyjaszewski and co-workers subsequently reported a fundamental and comprehensive study expanding the use of Ph-PTH based systems to additional nanostructures.[87] EBPA-based initiators leading to increased grafting density due to the >1000× higher activation rate coefficient of EBPA when compared to isobutyrate derivatives.[69,88] This allows catalyst concentrations as low as 0.02 mol % (relative to monomer) to be employed for successful surface-initiated polymerization from silica nanoparticles, further simplifying the removal of residual catalyst. Furthermore, by combining metal-free ATRP with bioinspired polydopamine (PDA) chemistry, Chen, Matyjaszewski, and co-workers developed a green and efficient method to controllably modify polymer brush architecture on the surface of magnetic nanoparticles (MNPs) (Figure 12).[89] These surface-modified

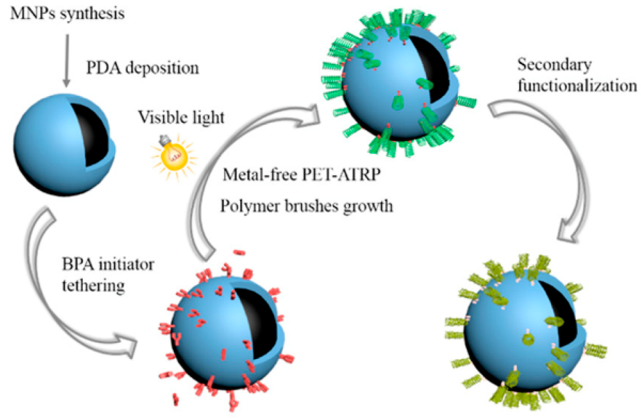

Figure 12. Graphical depiction for the synthesis of core−shell MNPs using sequential PDA-based initiator functionalization and metal-free ATRP polymerization processes. Adapted with permission from ref 89.

particles exhibited improved hydrophilicity, dispersibility, and increased binding with uranyl ions in aqueous solution. Metal-free SI-ATRP has also been utilized to functionalize SB-15 mesoporous silica to make unique organic−inorganic hybrid materials with potential biomaterial and environment applications.[90] From these preliminary studies, the coupling of improvements in photocatalyst design with monomer scope offers the field of metal-free SI-ATRP compelling potential for surface modification of a wide range of materials.

Continuous Flow Metal-Free ATRP. To date, metal-free ATRP has been primarily performed in the context of solution polymerizations with select examples focusing on surface-initiated systems. In an effort to fully exploit the capabilities of metal-free ATRP and light-mediated processes in general, there has been recent effort in the synthetic polymer community to integrate light-driven methodologies with continuous flow systems as a means to accentuate key benefits. In the case of metal-free ATRP, Miyake and co-workers have extended its versatility by successful adaptation to a continuous flow process driven by visible light using a library of different photocatalysts (Figure 13).[91] Although continuous flow processes have been previously used as a strategy to enhance irradiation uniformity,[92] Miyake's work nicely illustrates the distinct advantages for metal-free ATRP, including shorter reaction times and increased scalability.[93,94] Importantly, the use of continuous flow systems also helps improve batch-to-batch consistency and reproducibility by mitigating the effects

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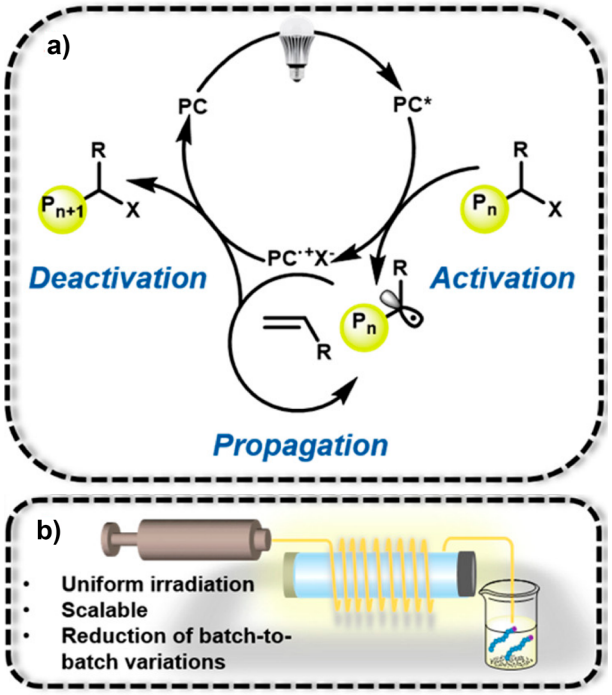

Figure 13. Graphical depiction for the synthesis of core−shell MNPs using sequential PDA-based initiator functionalization and metal-free ATRP polymerization processes. Adapted with permission from ref 91.

of variable irradiation efficiency that may come with different reaction volumes. Indeed, polymers with $Đ$ values as low as 1.1 were obtained at moderately high conversions using phenazine or phenoxazine-based photocatalysts at substantially lower catalyst loadings than typically used in batch setups.[91] Based on these studies, the inherently simple and tunable nature of flow reactors (i.e., flow rates, irradiation wavelength, and intensity) may offer an attractive and facile platform for further optimization of metal-free ATRP. Greater focus in this area will enable facile access to complex polymeric architectures (block copolymers, stars, etc.), as this is an area yet to be explored using organocatalyzed, light-integrated flow processes.

Advances in Architectural Complexity. An enabling feature of traditional ATRP is the ability to access polymer architectures inaccessible via uncontrolled free radical polymerization. This includes greater access to architectures such as block polymers,[95] multiblocks,[96] and branched and star configurations.[97,98] In the same vein, assessing the limits of architectural complexity achievable with metal-free ATRP is a major future direction. In the case of block copolymers, a collaborative effort between Miyake and Boyer showcased the combination of PET-RAFT with metal-free ATRP to access block copolymers composed of acrylate and methacrylate blocks using a single photocatalyst (Figure 14).[99] This represents a distinct example highlighting that organic photocatalysts originally designed for ATRP could also be successfully implemented in alternative light-mediated systems and facilitates access to block copolymers with chemically distinct blocks due to the expansive monomer scope available using RAFT. The ability to take this work a step further to orthogonally activate one monomer class in the presence of another would open up new avenues for preparing increasingly complex materials.[100,101] Furthermore, preliminary work by

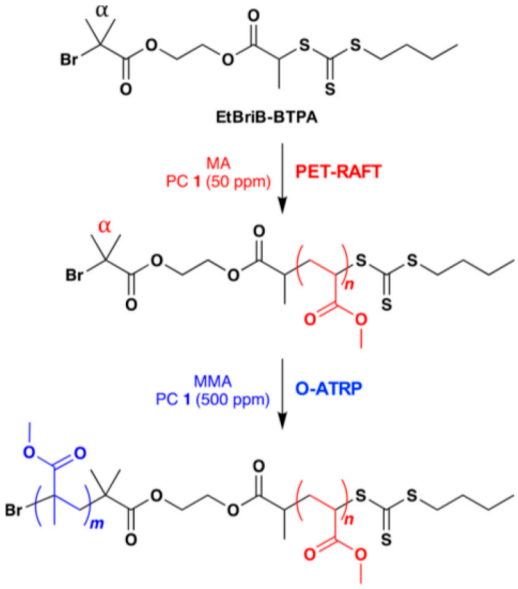

Figure 14. Representative schematic for the preparation of block copolymers using sequential PET-RAFT and metal-free ATRP catalyzed by PhenN-CF_3. Adapted with permission from ref 99.

Yagci demonstrates the synthesis of unique hyperbranched polymer networks with metal-free ATRP using perylene as a photocatalyst (Figure 15).[102] By combining the concept of self-condensing vinyl polymerization (SCVP) and metal-free ATRP, a novel synthetic route to hyperbranched PMMA and polystyrene was achieved using an inimer strategy. Importantly, by varying parameters such as irradiation time and inimer concentration, the degree of branching could be tuned, offering an opportunity to construct structurally diverse materials for a range of applications.

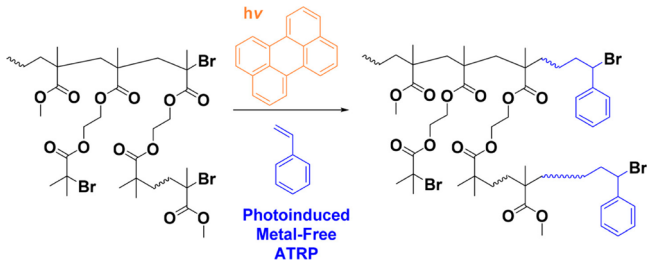

Figure 15. Representative schematic of the preparation of hyperbranched polymer using metal-free ATRP. Adapted with permission from ref 102.

Star polymers represent another class of macromolecules with unique physical and rheological properties relative to linear-based counterparts. Star polymers have found widespread utility in applications ranging from industrial lubricant additives to gene and drug delivery.[103] Using multifunctional initiator cores ranging from 2 to 8 initiating sites, a diverse range of stars with $Đ$ values generally below 1.5 were obtained by metal-free ATRP, with no observable star−star coupling even at monomer conversions of ∼90%.[104] The versatility of this system was further exemplified with chain extension to furnish increasingly complex star-block architectures. The success of the aforementioned reports set the stage for metal-free ATRP to be fully exploited in the design of architecturally complex materials.

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CHALLENGES AND FUTURE OUTLOOK

Metal-free ATRP has the potential to transform the field of polymer synthesis based on recent developments in key areas ranging from photocatalyst design to monomer scope. However, to realize this potential, there are challenges for future study. Perhaps one area of interest would be to thoroughly study improved methods for photocatalyst purification. In addition to potentially solving the discoloration of materials due to the highly colored nature of many of these photocatalysts, these studies may open new avenues for better understanding photocatalyst recyclability and reusability. A more formidable limitation is that the use of light impedes general scalability, rendering access to large quantities of desired materials somewhat laborious. Poor irradiation efficiency may also contribute to batch-to-batch inconsistency, and the use of short wavelength light may result in general incompatibility with certain biologically inspired systems,[105,106] further necessitating the development for near-IR or IR absorbing photocatalysts analogous to what has been recently demonstrated with Cu-catalyzed[107] and PET-RAFT[25] systems. Similarly, expansion to monomers with strongly absorbing functionalities and/or other photosensitive molecules needs to be addressed. Nevertheless, the sheer increase in monomer scope up to this point and key synthetic developments in areas such as improved oxygen tolerance[108,109] suggest that further expansion is just a matter of time. Not unlike its metal-based counterpart, fundamental and collaborative research in the area of metal-free ATRP will undeniably fuel future innovations that will lead to a plethora of previously inaccessible advanced materials in the same way classical ATRP has evolved over the past 20 years.

As may be evident from this Perspective, we envisage that continued advances in metal-free ATRP will offer a range of advantages that will further enhance the impact of controlled radical polymerizations across interdisciplinary research areas. Apart from addressing the longstanding limitation of metal contamination, more in-depth investigation reveals a subtle distinction that metal-free ATRP exhibits remarkable temporal control during "on−off" cycling experiments over long irradiation times. This is in contrast to Cu-catalyzed photo-ATRP, where a significant amount of propagation can be observed during the dark or "off" periods, especially when the polymerizations are performed in organic solvents.[18] Garnering experimental evidence to directly compare the efficiency of temporal control of these systems is currently an ongoing research area of interest. Further probing this phenomenon will most certainly lead to exciting new applications.

The rapid evolution of metal-free ATRP cannot be overemphasized, and while certain challenges may become apparent when measured against the current "gold standard" of RAFT/ATRP, pathways for future development are present. Reports highlighting the orthogonality of metal-free ATRP with other techniques (i.e., ROP and PET-RAFT) exemplify integration with the greater synthetic polymer community. Moreover, in an analogous manner to the rapid growth of PET-RAFT, the continued development of metal-free ATRP to enable more intricate levels of polymerization control through the introduction of degradable polymers,[110] stereospecificity,[111] logic gates,[112] and single monomer unit insertion[113] would undoubtedly generate further interest in this already burgeoning field. Indeed, the exponential growth in the number of publications and citations over the past 3−4 years highlights the tremendous academic interest in the field and is testament to its synthetic accessibility and low barrier to entry for nonexperts. As a closing thought, an important theme to consider is that the origin of metal-free ATRP can be traced back to the use of photoredox catalysts in organic synthesis, and this close connection holds significant promise. By drawing inspiration from multiple disciplines, this nascent area will allow ATRP and RAFT to evolve as pre-eminent controlled polymerization techniques.

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Athina Anastasaki is currently a Global Marie Curie Fellow and an Eling's Fellow working alongside Professor Craig Hawker at the University of California, Santa Barbara. She completed her Ph.D. studies from the University of Warwick under the supervision of Professor David Haddleton. Her research focuses on controlled radical polymerization strategies to enable the synthesis of complex architectures for a wide range of applications. In January 2019, she will join the ETH Materials Department as an Assistant Professor to pursue her independent career.

Javier Read de Alaniz joined the department of Chemistry and Biochemistry at the University of California, Santa Barbara, in 2009 as an Assistant Professor. He received his B.S. degree from Fort Lewis College (Durango, Colorado) in 1999 where he conducted undergraduate research under the direction of Professor William R. Bartlett. He obtained his Ph.D. under the supervision of Professor Tomislav Rovis at Colorado State University in 2006 and then conducted postdoctoral research with Professor Larry E. Overman at the University of California at Irvine.

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