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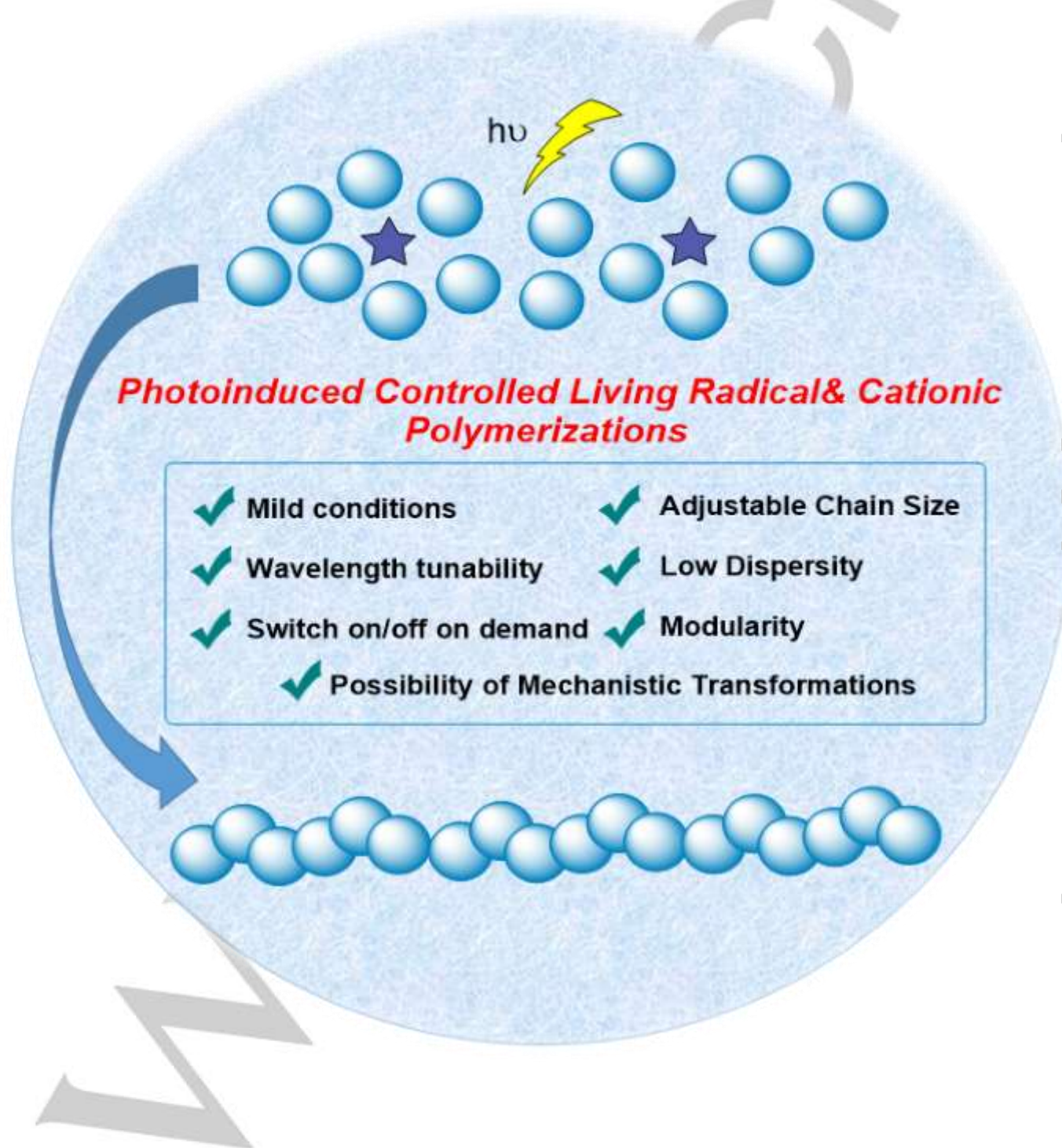
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REVIEW

Photo-induced Controlled/Living Polymerizations

Cansu Aydogan,^[a,b] Gorkem Yilmaz,^[a] Ataula Shegiwal,^[b] David M. Haddleton,^{*,[b]} and Yusuf Yagci^{*,[a]}



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Abstract: Application of photochemistry in polymer synthesis is of interest due to the unique possibilities offered over thermochemistry including topological and temporal control, rapid polymerization, sustainable low energy processes and environmentally benign features leading to established and emerging application in adhesives, coatings, adaptive manufacturing, etc. In particular, utilization of photochemistry in controlled/living polymerizations often offers the capability for precise control over the macromolecular structure and chain length in addition to these associated advantages of photochemistry. Herein, the latest developments regarding photocontrolled living radical and cationic polymerizations and their combinations for application in polymer syntheses are discussed. This review summarizes and spotlights the recent studies in the emerging area of photoinduced controlled/living polymerizations. A discussion of mechanistic details highlights differences as well as parallels between different systems for different polymerization methods and monomer applicability.

1. Introduction

Photochemical conventional polymerization processes offer many advantages over more traditional thermochemical methods which have been realized in both the commercial world and in academia. Advantages include modularity, low-expense and reduced energy requirements leading to, environmentally benign features. This is of particular important as we move towards producing polymers in a more sustainable way without compromising and indeed improving, on materials performance. Photopolymerization is an active and growing research area, due to its mild nature, abundantly availability, energy efficiency, low cost and availability of low energy LED sources.^[1] Light can induce various fundamental movement of electrons within initiators and in polymerization reactions inducing a range of diverse chemistry including radical, cationic, anionic, step-growth polymerization as well as more recently controlled/ living polymerizations (CLP) and coupling reactions. Light induced CLP techniques which can provide several advantages over conventional thermal process often allowing for spatial and temporal reaction control.^[2] Atom transfer radical polymerization (ATRP) is a common and powerful technique and combination of this approach with light enables access to different well-controlled polymers with additional features.^[3] In this review, light driven

controlled polymerization approaches including transition metal mediated processes such as ATRP, reversible addition-fragmentation chain transfer (RAFT), living cationic polymerizations and their combinations for macromolecular synthesis are briefly summarized. Our aim is to highlight the recent developments and portray how these techniques enlarge the scope of the well-defined polymeric architectures.

2. Controlled/Living Radical Polymerization

Controlled/living radical polymerization (CLRP) provides a versatile toolbox allowing for the synthesis of polymers with unprecedented control over their structures, molecular weight, and dispersity. Transition-metal mediated techniques^[4] including atom transfer radical polymerization (ATRP),^[5] as well as RAFT^[6] and nitroxide-mediated polymerization (NMP)^[7] are amenable CLRP techniques for the controlled synthesis of polymers. Amongst them, ATRP is a frequently applied method due to its simplicity and applicability to a wide range of monomer compositions.

ATRP employs a fast and reversible catalytic activation of an initiator such as an alkyl halides aided by Cu^{II}/Cu^I redox process to give carbon-centered radicals. The role of Cu^{II} species is to deactivate the process by balancing the equilibrium towards the dormant species (P_n-X) providing a degree of control over the radical concentration (P_n•) thus minimizing the proportion of termination reactions via bimolecular free radical-free radical reactions. Thus, the method efficiently provides for the synthesis of a variety of polymers with controlled molar masses, narrow dispersity and chain-end functional groups. A general mechanism of conventional ATRP is demonstrated in Scheme 1.



Scheme 1. Mechanism of conventional ATRP.

Conventional ATRP often suffers from a drawback associated with the requirement of this catalyst often being employed at large amounts. The induction of the polymerization by simultaneous generation of a Cu(I) species starting from the more oxidatively

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stable Cu(II) conjugate has been proposed as an efficient polymerization method. This approach allows for polymerization at ppm levels of copper concentrations often under air at ambient temperature without the requirement for deoxygenation techniques. To date a range of different approaches have been reported with a myriad of acronyms including, reverse ATRP, simultaneous reverse and normal initiated (SR&NI), activators by electron transfer (AGET), activators regenerated by electron transfer (ARGET), initiators for continuous activator regeneration (ICAR), and supplementary activator and reducing agent (SARA) ATRP, and single electron transfer-living radical polymerization (SET LRP) which have all been developed mostly using copper complexes with the oxidation state of copper between 0 and +2. These strategies benefit from simultaneous generation of Cu(I) by different reduction methods, such as i) use of certain chemical reductants, (ii) electrochemical redox processes, (iii) nanoparticles containing copper and (iv) photochemical redox processes.^[8] Both ICAR and ARGET ATRP make use of a radical initiator or a chemical reducing agent, respectively. Since both of these approaches reduce the requirement of relatively high loadings of copper they can provide more attractive reaction conditions. Chemical reagents such as ascorbic acid,^[9] hydrazine or phenyl hydrazine^[10] have been shown to act as reducing agents generating Cu(I) from Cu(II). Light is a widely available, inexpensive and an environmentally benign energy form that delivers the opportunity for both spatial and temporal control of the polymerization process. It provides a lower activation energy pathway with the potential for fast polymerization rates. Therefore, photoinduced copper mediated polymerization is attractive to realize polymerization with reduced amounts of catalyst required. In general, it can be considered to follow a similar mechanism to that proposed for AGET and ARGET ATRP. Various photoactive structures such as conventional radical photoinitiators and dyes are also effective in reducing Cu(II), and thus, can facilitate the photoinitiated copper(II) mediated processes.

Whilst the use of photochemistry applied to controlled/living radical polymerizations have been reviewed in the past by several authors,^[11] there is no article that also includes cationic initiating systems. The aim of this article is to probe the parallels and differences between various modes of the activation and interconversion of these two polymerization systems. Furthermore, it covers the latest publications. Special emphasis is placed upon work performed in the authors' own laboratories.

2.1. Copper Catalyzed Photo-initiated Polymerization

In general, the generation of Cu(I) species from Cu(II) complexes can be performed by direct irradiation and indirect irradiation methods. The influence of light on classical ATRP was first reported by Smart and coworkers in 2000.^[12] They revealed that visible light irradiation significantly improves the rate of polymerization in comparison to the dark conditions. Even at lower concentrations of copper, this method also provides higher monomer conversions. However, the first example of PhotoATRP was reported by Yagci and co-workers^[13] in 2010 through a directly generated activator concept.

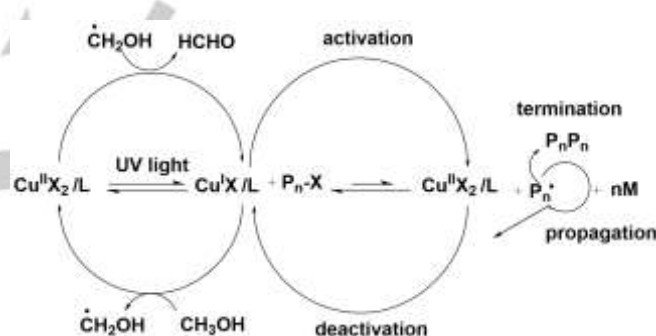
2.1.1. Directly Generated Activator for Photo-initiated Copper Mediated Polymerization

i) Catalytic/initiating systems

Photoinitiated copper mediated polymerization by directly generated activator approach is based on *in situ* generation of the catalyst from higher oxidation state copper(II) species, without the use any chemical reducing agent, under photo-irradiation. This can enable control over the molecular weight with narrow molecular weight distributions leading to a new avenue of CRP methods.^[14]

It has been proposed that upon UV exposure, Cu(II)/L complexes can undergo a homolytic cleavage to generate Cu(I)/L and halogen radical (X•) as primary products. Subsequently, two reactions may be considered; the halogen radical can abstract hydrogen from methanol to form •CH₂OH and HX or may oxidize the Cu(I)/L back to Cu(II)/L.

The effect of adding small amounts of methanol to the process was studied in detail.^[15] The use of methanol at low concentrations in the polymerization medium both improves the solubility of Cu(II) species and generates hydroxymethyl radicals which play a role as reducing agents. In this way, polymerization of methyl methacrylate (MMA) was successfully performed and the rate of polymerization accelerated compared to a comparable heterogeneous system (Scheme 2).



Scheme 2. Mechanistic scheme for Photoinduced ATRP in methanol. ^[15]

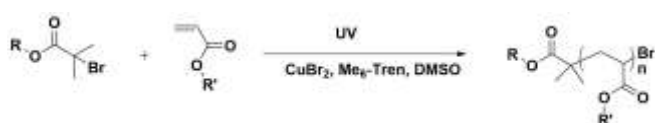
Mosnacek and Ilcikova reported the use of <100 ppm copper loadings of Cu(II)Br₂ with either tris(2-pyridylmethyl)amine (TPMA) or *N,N,N',N',N'*-Pentamethyldiethylenetriamine (PMDETA) as ligands to carry out photomediated ATRP of MMA under UV irradiation. The studies showed that the TPMA ligand is more efficient than PMDETA under these conditions ascribed to the higher stability of the Cu(II) complex of TPMA relative to PMDETA.^[16]

In parallel, Konkolewicz et al. used relatively low copper concentrations to carry out photoinduced ATRP of (meth)acrylates under visible light and sunlight without using additional photoinitiators or reducing agents. In addition, this approach was extended to include the polymerization of oligo(ethylene oxide) methyl ether methacrylate in aqueous media with a decreased amount of copper catalyst (22 ppm) in the presence of bromide anions.^[17] In the light of these beneficial attributes, Matyjaszewski and co-workers demonstrated the synthesis of hybrid materials involving protein and DNA-polymer conjugates via grafting from approach under mild conditions.^[18] They also carried out direct DNA synthesis and polymerization from DNA in a highly automated manner within a DNA synthesizer by photoATRP without deoxygenation required. Anastasaki et. al. showed the versatility and oxygen tolerance of PhotoATRP

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process for grafting of polymers from protein backbones. This approach paved the way for conducting grafting process of methacryl and styrenic monomers from multiple proteins (e.g. BSA, HSA, GOx, beta-galactosidase) to afford protein-polymer amphiphiles using extremely low amounts of copper (6 ppm) without additional reagents or external deoxygenation systems.

Haddleton and co-workers reported the photoactivated living polymerization of acrylates mediated by CuBr_2 using excess aliphatic tertiary amine ligands yielding polymers with very low dispersity (~ 1.10) whilst maintaining excellent chain-end fidelity. Compared to the related systems, high monomer conversions ($>95\%$) were attained in short reaction times without evidence of detrimental termination which might have been expected with the relatively high radical concentration as required for rapid polymerization.^[19] (Scheme 3)



Scheme 3. General photopolymerization of acrylates by using copper(II) as catalyst.

The proposed mechanism relies on the light absorption by non-complexed excess $\text{Me}_6\text{-TREN}$ ligand followed by formation of photoexcited $[\text{Me}_6\text{-TREN}]^*$ with transfer of a single electron to the alkyl halide, resulting in the dissociation of the C–Br bond. The scission of the initiator leads to the generation of corresponding initiating radical and a ligand radical cation with a bromide counterion. The radicals formed react with Cu(II)/L to generate Cu(I)/L which in turn act as an activator for polymerization. Although this complex mechanism depends on many parameters such as solvent, catalyst loadings, temperature, it is capable of forming well defined polyacrylates with high conversions, and efficient end group fidelity.^[20] The structure of the Cu(II)/L complex has a critical importance for the polymerization with respect to its solubility in the polymerization medium and participation of the surrounding ligand on the reduction of Cu(II) core. Me_6TREN was often applied for such process due to its excellent complexation ability with Cu(II) .^[21] Notably, polymerizations are generally conducted in polar aprotic solvents such as DMSO as it serves the best medium to solubilize the charged Cu(II)/L complexes, which eventually provides faster rates of polymerization in comparison to less solubilizing solvents.^[22]

Polymerization following a batch process was successfully translated into micro and milli-flow reactors whereby poly(methyl acrylate) homopolymers and block copolymers were prepared with high monomer conversions maintaining surprisingly high retention of end-group fidelity especially if the reaction proceeds via the widely accepted mechanism.^[23]

Jordan and coworkers also utilized this for the preparation of homo- and block copolymers and patterned polymer brushes. Here, a silicon substrate was modified by small molecule organic reactions to introduce ATRP initiating sites. Subsequently, this was exposed to light irradiation in the presence of MMA, CuBr_2 and PMDETA to yield polymer brushes.^[24] The Haddleton group reported high order acrylic block copolymerization by utilizing low concentrations of CuBr_2 in conjunction with Me_6Tren with UV irradiation.^[25] Junkers demonstrated that the $\text{CuBr}_2/\text{Me}_6\text{Tren}$

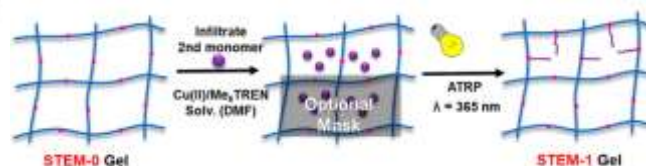
photoactivated system is well suited for the synthesis of decablock copolymers.^[26] It was also reported that using photo-initiated copper mediated ATRP, a library of monodisperse sequence designed acrylate oligomers could be synthesized via sequential single monomer unit insertion reactions.^[27] Various acrylates were polymerized grafting from silicon wafers at low catalyst loadings.^[28]

A variety of ionic liquids (ILs) were employed for the photoinduced living radical polymerization of acrylates yielding narrow molecular weight distributions ($\bar{D} \approx 1.1$), with almost full monomer conversions ($>99\%$) within 30 min.^[29] Subsequently, water soluble hydrophilic acrylates were polymerized efficiently in aqueous media aided by the addition of NaBr that allowed for controlled polymerization (\bar{D} as low as 1.11) with very high monomer conversions ($>99\%$).^[30]

Hawker et. al. disclosed an effective photomediated ATRP technique for a range of semi-fluorinated (meth)acrylates avoiding unwanted transesterification.^[31]

Structurally tailored and engineered macromolecular (STEM) gels, first proposed by Matyjaszewski and collaborators, served as functional platforms containing dormant initiating sites enabling post synthesis modification to enable fabrication of transformable materials.^[32] Reversible deactivation radical polymerization (RDRP) approaches were conducted to prepare STEM networks forming more ordered architectures than that produced by conventional free radical polymerization.

For instance, transformable STEM gels have been synthesized by the combination of RAFT and ATRP.^[33] Initially, pristine STEM gel bearing latent alkyl halide initiator sites were synthesized via thermally mediated RAFT polymerization, subsequently the parent STEM gel was infused with a second monomer so as to allow for grafting side polymer chains from the ATRP initiator sites of the network by copper-mediated photoinduced ATRP. This process permitted a tunable network, which transformed hydrophobic STEM into amphiphilic STEM gels. Consequently, single-piece amphiphilic and flap materials were formed by performing spatial control over the modifications (Scheme 4).



Scheme 4. Modifying the STEM-0 Gels with infusing a solution comprised of monomer, copper catalyst and solvent and possible spatial control to form STEM-1 Gels by Photo-ATRP. Figure adapted from Ref. [33] with permission. Copyright © 2018, American Chemical Society

In subsequent work, Matyjaszewski and coworkers designed non-sticky, soft fluorinated and elastomeric STEM networks by similar strategy.^[34]

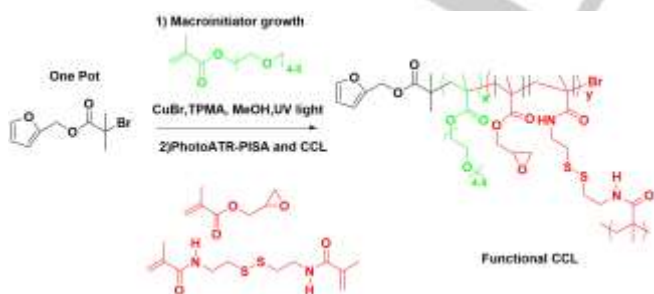
ii) Controlled polymer synthesis

The Haddleton group reported efficient photoinduced Cu-RDRP without the requirement of any external deoxygenation steps. A range of monomers having different polarity was polymerized in very low reaction volumes (down to 10 μL). Furthermore, it is

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shown that this approach can be applicable to higher volume polymerizations (up to 0.5 L). In order to elucidate the role of each of the reaction components in the oxygen consumption events, an oxygen probe (designed to measure the oxygen content on rivers and lakes) was employed as an *in situ* online monitor over the course of the polymerization. The system was used for the *in-situ* block copolymer formation, which indicated the retention of chain-end functionality while providing controlled polymerization of a range of monomers with different hydrophobicity, as well as semi-fluorinated (meth)acrylates.^[35]

Recently, the Haddleton group described a successful example of polymer self-assembly based on low molecular weight poly(acrylic acid)-fluoro block co-oligomers with high block incompatibility. For this aim, a partially fluorinated alkyl halide, perfluorooctyl bromoisobutyrate (PFOBiB), was used as an initiator. Exploiting photoinduced Cu(II)-RDRP, poly(*tert*-butyl acrylate)-fluoro block co-oligomers were obtained with very low dispersity ($\bar{D} = 1.06 - 1.13$), allowing for polymers with very low degrees of polymerization to be prepared with low dispersity and with high end group fidelity. Subsequent deprotection reaction resulted in polymers which self-assemble with thermal annealing with the formation of ultra-small, sub 2 nm, domain spacings that had not been achieved before or, at the time of writing, since.^[36] More recently, a new strategy based on the implementation of photo-ATRP has been developed to realize polymerization induced self-assembly (PISA) mediated by UV light ($\lambda = 365$ nm with low loadings of copper catalyst (ca. <20 ppm) at ambient temperature. PISA was realized in a one-pot manner in the presence of CuBr₂/TPMA as catalyst. Initially, oligo(ethylene oxide) methyl ether methacrylate, which is readily soluble in the reaction solvent, was synthesized and used as a macroinitiator to give core-crosslinked nanoparticles (CCL-NPs). Poly(glycidyl methacrylate) (PGMA) and *N,N*-cystamine bismethacrylamide (CBMA) were used as solvophobic copolymer and crosslinking agent, respectively. Sequential chain-extensions for PGMA produce multi-block copolymers with temporal control via UV light on/off regulations. Additionally, core-crosslinking of PISA nanoparticles was prepared by the gradual inclusion of CBMA, allowing one-pot crosslinking via the PISA process. In the final stage, the disulfide inserted in the CBMA corecrosslinks enabled the stimuli-triggered dissociation of nanoparticles at an acidic pH utilizing DL-dithiothreitol (Scheme 5).^[37]



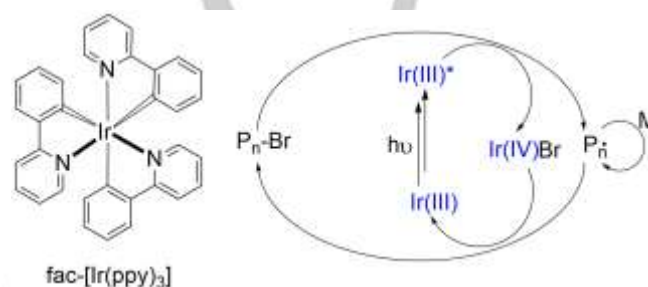
Scheme 5. A schematic representation of functional CCL by the combination of Photo ATRP-PISA and CCL in situ. Figure adapted from Ref. [37] with permission. Copyright © 2021, American Chemical Society

Other Cu(II) complexes that have been applied include [Cu(Me₆TREN)](O₂CH)(ClO₄),^[38] [Cu(phen)₂]Br (phen: 1,10-phenanthroline),^[39] copper(II) gluconate^[40] along with Me₆TREN.

The polymers obtained using these complexes also display monodisperse molecular weight distributions with high fidelity chain-end functionality.

2.1.2 Photo-ATRP with the Other Transition Metals

Recent works have also demonstrated the possibility of conducting photo-induced ATRP using transition metals other than copper such as iridium,^[41] gold,^[42] iron,^[43] cobalt^[44] and ruthenium^[45] as alternatives to copper. The mechanism considers the halogen abstraction only at excited states of these transition metals unlike conventional ATRP, where this abstraction step can take place in the dark. The mechanism is illustrated in the example of fac-[Ir(ppy)₃] (ppy = 2-pyridylphenyl) (Scheme 6)^[41]



Scheme 6. The mechanism of visible light-mediated ATRP using an Ir-based photoredox catalyst.^[41]

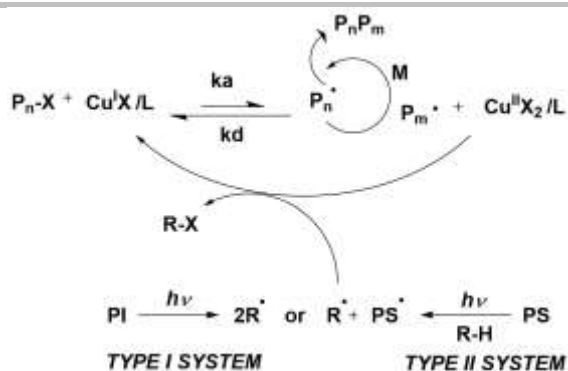
Transition metal based photo-ATRP systems were successfully used for the formation of resolved patterns and 3D architectures by surface-initiated (SI) polymerizations. As a new and exceptional application of photo-ATRP related to surface patterning, Braunschweig and coworkers reported a novel photolithography technique that is capable of producing polymeric pixels by integration of a digital mirror device (DMD) with microfluidics and air-free reaction chamber.^[46] Monomer solutions within Ir-based catalyst system react with the initiating species coated on silica surface by SI polymerization. This system allowed to result in polymer brush patterns with micrometer scale dimensions and control the composition and the height of each pixel in the patterns.

2.1.3. Indirectly Generated Activator for Photo-Initiated ATRP

i) Catalytic/initiating systems

The generation of Cu(I) catalysts can also be performed using certain radical photoinitiators, which form electron donor radicals capable of reducing Cu(II) to Cu(I). These photoinitiators can be either α -cleavage or hydrogen abstraction type initiators generally displaying activity at the UV range. The most commonly applied radical photoinitiators for typical processes are 2,2-dimethoxy-2-phenyl acetophenone, bis(2,4,6-trimethylbenzoyl) phenylphosphine oxide^[47] and Irgacure 2959 as α -cleavage, and benzophenone/amine and camphorquinone/amine systems^[48] as hydrogen abstraction type initiators. Despite having different mechanisms for radical generation, the radicals follow a typical redox process to form Cu(I) species, Scheme 7.

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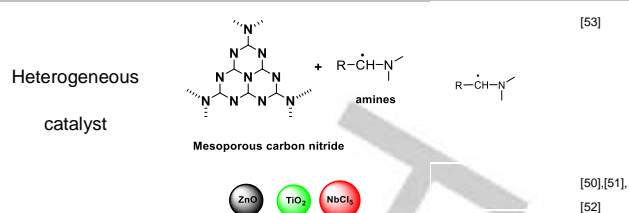


Scheme 7. Mechanism of Photo-ATRP via Type I or Type II system.[8]

The electron donating nature of the photochemically generated radicals are important for the successful reduction of Cu(II) to Cu(I), Table 1.

Table 1. Type of electron donor radicals capable of reducing Cu(II).

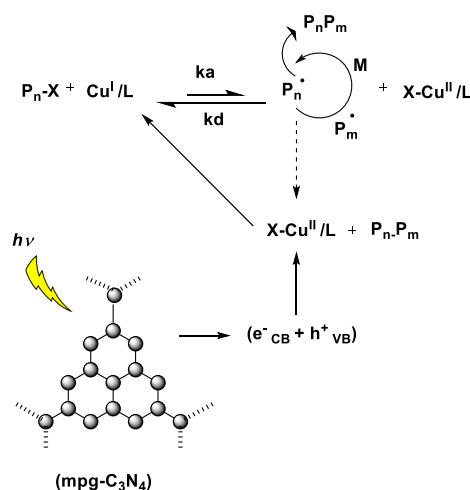
Type	Photocatalyst	Reducing Radical	Ref.
Unimolecular photoinitiators			[47]
Bimolecular photoinitiators			[48]
Dyes			[49]



In order to conduct polymerization using lower energy and less harmful conditions, research has been directed towards development of initiating systems acting at higher wavelengths. Therefore, certain sensitizers have successfully been employed as photo reducing agents. In this case, the sensitizers act as electron reservoirs under light irradiation, and a single electron is transferred from an excited state sensitizer to the amine to form a sensitizer radical anion and amine radical cation. Then, the radical anion reduces reduction of Cu(II) to Cu(I) subsequently mediating successful polymerization of appropriate monomers (Scheme 8).[49] Typical sensitizers successfully employed include erythrosin B and eosin Y.

Scheme 8. Generation of Cu(I) from Cu(II) using dyes as sensitizers. [49]

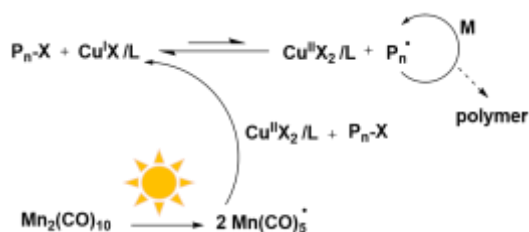
A typical strategy is also followed with the use of heterogeneous catalysts, which again act as electron reservoirs. Zinc oxide,[50] titanium dioxide,[51] niobium(V) chloride, [52] and mesoporous carbonitride are such compounds, which are insoluble in the polymerization media. Upon light irradiation at appropriate wavelengths, they form electron holes and transfer a single electron to the starting Cu(II) compound, Scheme 9.[53]



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Scheme 9. Photoinduced ATRP utilizing mpg-C₃N₄.^[53]*ii) Controlled polymer synthesis*

The first example for the preparation of polymer brushes via photocontrolled surface-initiated ATRP, was reported by Yan and co-workers in 2013.^[51] In this report, CuCl₂/bpy was employed as the catalyst and TiO₂ nanoparticles with the dual function as a photosensitizer and a substrate. A self-catalysed photoATRP of MMA was successfully carried out from a self-assembled monolayer of catecholic initiator on TiO₂ nanowire or gold. Manganese decacarbonyl has also been used in indirectly generated photoinduced ATRP. This specific reagent absorbs light at the visible range of the electromagnetic spectrum and forms manganese pentacarbonyl, which abstracts a halogen atom from Cu(II)X₂ to yield the Cu(I)X catalyst, Scheme 10.^[54] In this way, ATRP can be conducted under sunnier light irradiation, a high priority as move towards a more sustainable world.

**Scheme 10.** Proposed mechanism of PhotoATRP using Mn₂(CO)₁₀.^[54]

A further interesting photosensitizer; polymethine with a zwitterionic nature was used as near-infrared (NIR) light-active catalytic system for realizing polymerization of MMA using ppm levels of Cu(II)Br₂/TPMA.^[55] Later, a similar NIR photoATRP process was conducted by using recyclable up-conversion nanoparticles (UCNPs).^[56] UCNPs functioned as an internal light source to convert 980 nm NIR light to UV/Vis light to commence polymerization. Until now, 980 nm irradiation is the longest wavelength applied for successful photoATRP. This UCNP-assisted NIR photoATRP technique was used to polymerize both hydrophobic and hydrophilic monomers in both aqueous and organic media, resulting in polymers with narrow molecular weight dispersion and predictable molecular weights. Matyjaszewski group designed a reusable and easy separable phenothiazine conjugated microporous polymers as heterogeneous photocatalysts to perform photoinduced copper-catalyzed ATRP under UV or NIR irradiation.^[57]

Cansu Aydogan is currently postdoctoral researcher at Istanbul Technical University. She obtained her PhD in chemistry from Istanbul Technical University under the supervision of Prof. Yusuf Yagci. Her current research area includes controlled living polymerizations, synthesis of functional materials, hyperbranched polymers.



Gorkem Yilmaz is an associate professor of Chemistry at Istanbul Technical University. His area of interest covers photochemical processes, controlled living polymerization tools, nanomaterials, biopolymers and applications.



Ataulla Shegiwal graduated from the University of Warwick (M Chem, July 2016) with a final year project on the synthesis of sequence-controlled methacrylic multiblock copolymers via sulfur-free RAFT emulsion polymerization. He then continued his PhD in the group of Professor David Haddleton, (PhD, July 2020), exploiting catalytic chain transfer polymerisation and applications for the synthesis of diblock and multi-block copolymers via SF-RAFT polymerisation.



David Haddleton is a Professor of Chemistry at the University of Warwick in the UK. He received his PhD and BSc from the University of York (1996 and 1993). His area of interest covers all types of polymerisation and applications of polymers covering different areas of controlled radical polymerisation and in increasing interest in addressing global issues and sustainability. He is currently a member of the RSC Publishing Board.



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Yusuf Yagci is a Professor of Chemistry at Istanbul Technical University (ITU). He received his M.Sc. (1977) and PhD (1979) degrees from Liverpool University (UK). He is the recipient of several awards including The Society of Polymer Science, Japan (SPSJ) International Award (2008), OIC Science and Technology Award (2017), Belgian Polymer Group, International Science Award (2018) and Alexander von Humboldt Research Award (2018). He has been admitted as Fellow of Royal Society of Chemistry (FRSC) (2017). His research interests include all aspects of synthetic polymer chemistry involving photopolymerization and controlled polymerization methods.



2.2. Photo-induced Metal Free ATRP

There has been a growing interest in the development of metal free, *environmentally friendly*, initiating systems for controlled polymerization methods as the consequence of the general requirement of more sustainable world. Specifically, there has been a continuous effort for the reduction of the amount of metal catalyst required for ATRP. In addition to chemical and electrochemical strategies, photochemical protocols have been demonstrated to be a very efficient method to obtain monodisperse polymers with less metal consumption. Recently, research has been directed towards conducting photoATRP under metal-free conditions. This strategy can be important for the preparation of polymers for certain bio-applications, where metal contamination is perceived as a potential limitation. Today, although metal-catalyzed photocatalyzed ATRP systems still remain to be the key methodology, the conjugate metal-free systems are expanding their utility for specific applications and polymerization of monomers that cannot be polymerized by conventional ATRP techniques.

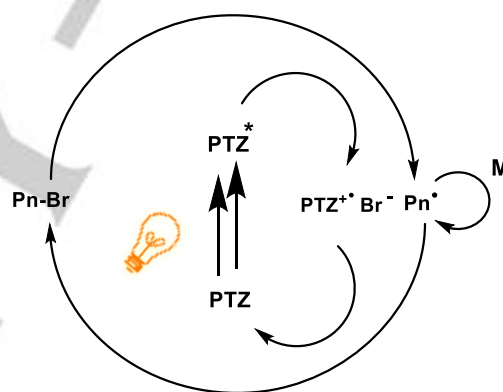
A breakthrough photoredox-catalyzed ATRP was first developed in 2012 employing low ppm of $\text{Ir}(\text{ppy})_3$ as the catalyst enabling well-controlled polymerizations under visible light. This system alleviated metal contamination by using a low concentration of the Ir.^[41]

Even though the development of this photoredox-catalyzed system symbolizes major progress in the arena of photocontrolled ATRP, researchers intended to change this precious metal catalyst with an organocatalyst. Often catalysts are a major focal point of challenge to remove from the polymer product both unwanted inorganic or organic catalysts that can contaminate the polymer products by imparting toxicity, colour and degradation routes. The concerns about the contamination of polymers motivate scientists to design photocatalysts (PCs) that can mediate ATRP via an oxidative quenching cycle that enable the development of metal-free ATRP which potentially have benign residues. It is noted that many organic residues can also indeed be toxic, colored and even induce unwanted odour and many inorganic compounds are non-toxic and many are essential to life e.g. Co, Fe, Mg, Cu, Cr, Mn, Mo, Se, K, Na and Zn.

Innovative work came from Hawker and coworkers that relies on a metal-free variant of ATRP in 2014.^[58] An organic photoredox catalyst, 10-phenylphenothiazine (PTZ), was used due to its highly reducing excited state for the realization of photoinduced ATRP. Polymerization proceeds by an oxidative quenching pathway. In the process, the excited state PTZ reduces an alkyl halide initiator to give the desired alkyl radical capable of initiating methacrylate polymerization. Concurrently, a radical cation form of the photocatalyst and a bromine anion is generated. Deactivation of the growing polymer chains occurs through end-capping by the halide, generating the ground state of PC and a dormant macro-alkyl halide polymer (Scheme 11). The intriguing features of this system are its highly responsive nature, facile reaction setup, and a wider selection of functional groups.

Detailed mechanistic studies elucidated that either singlet and triplet states of PTZ are capable of directing the reduction of the alkyl bromide via outer sphere electron transfer. Notably, the triplet state has a more dominant role due to its higher excited state lifetime and reactivity.^[59]

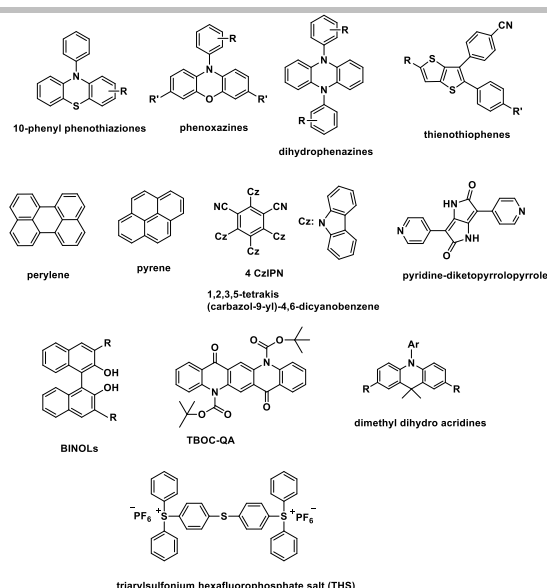
Pan and co-workers explored a series of PTZ derivatives as photoredox catalysts to produce polyacrylonitrile (PAN) polymers with predictable molecular weights and low dispersity.^[59a]



Scheme 11. Photo-induced metal-free ATRP through oxidative quenching mechanism in the presence of 10-phenylphenothiazine (PTZ).^[58]

In a further study, it was reported that arylsulfonyl halides can also be feasible initiators in place of alkyl halides.^[60] Subsequently, Miyake and coworkers developed dihydrophenazine, and phenoxazine based photoredox catalysts to the extent of the scope of the polymerization efficiency in visible light regions. Polynuclear aromatic compounds such as pyrene, anthracene^[61], and perylene^[62] are also operative photoorganocatalysts that exhibit strong reductant behavior in the excited state which allows direct reduction of alkyl halides. However, results showed that the anthracene/alkyl halide initiator lead to uncontrolled polymerization due to high reactivity of anthracene towards radicals leading to transfer reactions, Scheme 12.^[61]

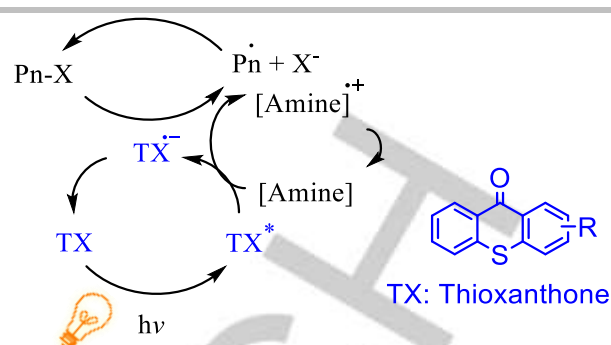
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Scheme 12. Metal-free ATRP photocatalyst structures operating via an oxidative quenching cycle.

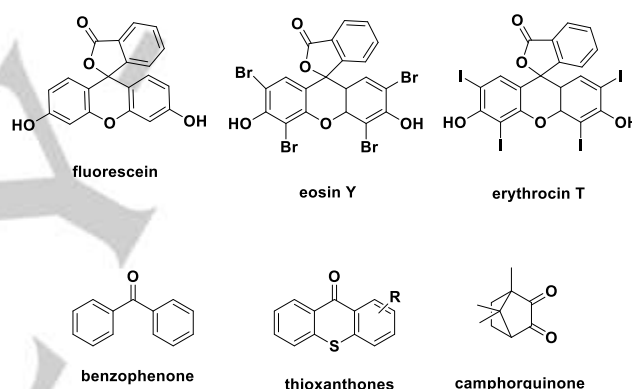
Amongst these, organic dyes can activate alkyl halides and control the metal-free ATRP through reductive quenching cycles in the presence of amines that act as electronic reservoirs. A radical anion photocatalyst is generated after adopting an electron from the electron-donor in the excited state. The formed radical anion reduces the alkyl halide to form initiating radicals. An electron is transferred from the halide anion to the amine radical cation giving a dormant polymer that can reenter the polymerization cycle. A challenge in the case of the reductive quenching mechanism is the presence of an amine donor, which may cause possible unfavorable side reactions.^[63] Despite advances in the design of metal-free ATRP systems, Luo et. al. introduced aqueous metal-free ATRP systems using tetrabromofluorescein (Eosin Y) as the catalyst. However, this catalyst requires a sacrificial electron donor to mediate the polymerization via a reductive quenching mechanism, which leads to unfavorable reactions due to the addition of a sacrificial electron donor. Water-soluble organic based photocatalysts mediate polymerization without the employment of sacrificial reagents are highly desirable. Based on the experiments and density functional theory (DFT) simulation, the same group revealed that the polymerization employed via oxidative quenching cycle proceeded much faster and higher initiator efficiency compared to the polymerization via reductive quenching pathway in the Eosin Y system under the same conditions. In this connection, 3,7-methoxypolyethylene glycol 1-naphthalene-10-phenoxazine (Naph-PXZ-PEG) was found to be a promising water-soluble organic catalyst for the synthesis of the well-defined polymers.^[64]

Shortly thereafter, conventional *Type II* photoinitiators including benzophenone, camphorquinone, thioxanthone, and isopropyl thioxanthone were used to realize metal-free photoATRP in conjunction with an appropriately selected amine and alkyl halide via reductive quenching cycle. (Scheme 13)^[65]



Scheme 13. Proposed mechanism of photoinduced metal-free ATRP by using TX /amine initiating system.^[65]

Scheme 14 summarizes the photocatalysts used in conjunction with amines to perform photo-induced metal-free ATRP via a reductive quenching cycle.



Scheme 14. Metal-free ATRP photocatalysts operating via a reductive quenching cycle.

Yagci and coworkers showed that metal-free ATRP can be efficiently activated by highly conjugated electron-rich thienothiophene derivatives leading to well-defined polymers. Following these polymerization studies and DFT calculations, 4-[2-(4-diphenylaminophenyl)-thieno[3,2-b]thiophen-3-yl]benzonitrile (TT-TPA) is found to be the most decent activator as a result of more favorable thermodynamic properties.^[66] Common photoredox catalysts for photoinduced metal-free ATRP are tabulated in Table 2.

Table 2. Common photoredox catalysts for photo-induced metal-free ATRP

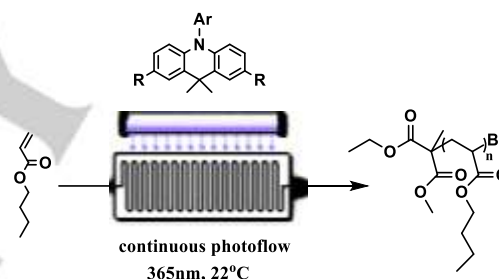
Sensitizer	Activation Mode	Irradiation Source	Comments	Ref.
Perylene	Oxidative	White Led/ sunlight	Low dispersity Low initiation efficiency	[62]

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Pyrene	Oxidative	UV light	Low dispersity Low initiation efficiency	[61]
Anthracene	Oxidative	UV light	No control over the polymerization	[61]
10-Phenylphenothiazine	Oxidative	UV light	Low dispersity High initiation efficiency	[59b]
Dihydrophenazines	Oxidative	White Led/sunlight	Low dispersity High initiation efficiency	[67]
Phenoxazines	Oxidative	UV light/visible LED	Low dispersity High initiation efficiency	[68]
Dimethyl dihydroacridines	Oxidative	UV led	Low dispersity High initiation efficiency	[69]
Triarylsulfonium hexafluorophosphate salt	Oxidative	UV led	Low dispersity High initiation efficiency	[70]
Fluorescein	Reductive	Broad range LEDs	Low dispersity Low initiation efficiency	[63a]
Eosin Y	Reductive	Broad range LEDs	Low dispersity Low initiation efficiency	[64]
Erithrosine B	Reductive	Broad range LEDs	Low dispersity Low initiation efficiency	[63b]
Thioxanthenes	Reductive	UV light	Low dispersity Low initiation efficiency	[65]
Benzophenones	Reductive	UV light	Low dispersity Low initiation efficiency	[65]

As an energy-efficient method, a continuous flow approach has been integrated into organocatalyzed ATRP (O-ATRP) with 0.01% photocatalyst loadings and a range of methacrylate monomer scope by Miyake and coworkers.^[71] Wang and coworkers investigated three organic chromophores, quinacridone, indigo, and diketopyrrolopyrrole as visible-light-absorbing organic photocatalysts capable of operating a well-controlled O-ATRP. Amongst these, only *N,N*-bis(tert-butyloxycarbonyl) quinacridone showed the nearly 100%

fluorescent quantum yield and outstanding electrochemical and optical stability, under visible LED light irradiation required.^[72] Inspired by previous examples of Cu catalyzed CRP representing the advantages of reducing the headspace within the vial without the deoxygenation process, Miyake and co-workers demonstrated the ability to perform the oxygen tolerant O-ATRP utilizing core modified *N*-aryl phenoxazines. By turning the headspace of the vial, polymerization successfully proceeds in a controlled fashion.^[73] Motivated by the need to reduce the concentrations of photoredox catalysis, the same group tested new core-extended diaryl dihydrophenazine. The use of this catalyst at much lower concentrations (5–50 ppm) leads access to polymers with unprecedented molecular weight control as well as low dispersity with near-quantitative initiator efficiency.^[74] In a recent study, Lei *et al* verified that triarylsulfonium hexafluorophosphate salt is an efficient organocatalyst for photo-ATRP of methacrylates under LED light irradiation.^[70] Although numerous photocatalysts have been designed, O-ATRP has largely been restricted to polymerization of methacrylates, dimethyl dihydroacridine derivatives are introduced as a novel organic photocatalysts suitable also for acrylates. In this strategy, well-defined acrylate polymers leading to low dispersity (\bar{M}_w/\bar{M}_n : 1.12) were obtained in continuous-flow reactors supplemented by LiBr salt for the promotion of deactivation (Scheme 15).^[69]



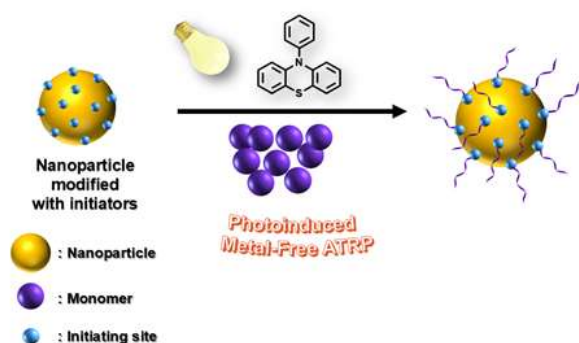
Scheme 15. O-ATRP of butyl acrylate in the presence of dimethyl-dihydroacridines.^[69] Figure in part adapted from Ref. [11a] with permission. Copyright 2016, Royal Society of Chemistry

2.2.1. Synthetic Applications for Metal-Free ATRP

The facile and versatile nature of metal-free ATRP has opened new avenues for the preparation of a variety of polymeric materials. Hawker and co-workers applied photoinduced metal-free ATRP for the dehalogenation of small molecules and coupling reactions.^[75] This procedure is shown suitable for not only conjugated polyhalide, but also unconjugated substrates. A parallel strategy was conducted to convert chain ends and side chains of various polymers.^[76] Notably, light mediation permitted ease for the replacement of halides with hydrogen atoms or trithiocarbonate to access inert polymeric materials. Metal-free surface-initiated ATRP (SI-ATRP) has been exploited for the fabrication of functional polymer brushes. For this purpose, traditional ATRP initiators immobilized on the surfaces via hydrosilylation chemistry followed by a grafting-from approach to obtain several homopolymers and block copolymer brushes through metal-free ATRP. Thus, well-defined polymer brushes were produced from flat and curved surfaces that enable to be scaled to four-inch wafers. This simplified benchtop method may facilitate to reach brush polymers architectures even for non-

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specialists due to the one-step reaction conditions as well as the usage of inexpensive photocatalyst with a readily available light source. In addition, the versatility of this method is exemplified by utilizing SI-ATRP for the synthesis of polymer grafted nanoparticles (Scheme 16).^[77]

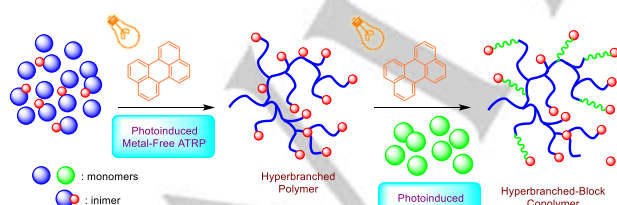


Scheme 16. Synthesis of polymer-attached silica nanoparticles by metal-free SI-ATRP.^[77]

Besides these, photoinduced metal-free ATRP has been implemented to the surface modification of Santa Barbara amorphous-15 (SBA-15),^[78] nanodiamond,^[79] hydroxyapatite nanorods,^[80] and hollow spheres.^[81]

Star polymers were also obtained by applying a core-first methodology orchestrated by a visible-light absorbing multifunctional photocatalyst. Structurally similar multifunctional initiators with several initiating sites ranging from 2 - 8 initiating sites were employed for the designing of linear telechelic polymers and star polymers maintaining narrow dispersities ($\bar{D} < 1.5$) with high initiator efficiencies.^[82]

Yagci and coworkers have showcased the use of photoinduced metal-free ATRP in combination with self-condensing vinyl polymerization (SCVP) to give hyperbranched polymers (HBPs). In the approach, perylene is employed as a catalyst to polymerize monomer/inimer pairs under visible light irradiation. By varying the irradiation time or inimer concentration, HBPs with different branching densities were successfully achieved. The same group have also benefited the formed HBPs as macroinitiators to obtain HBP-block copolymers by identical metal-free ATRP process (Scheme 17).^[83]



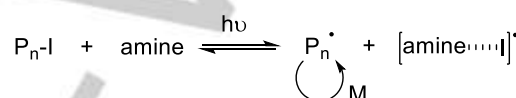
Scheme 17. Representative illustration for the synthesis of HBP via Metal-Free ATRP. Figure adapted from Ref. [83] with permission. Copyright © 2017, American Chemical Society

Gao and coworkers exploited the adaptation of self-condensing vinyl homopolymerization of inimers to metal-free ATRP in both solution and microemulsion media to produce HBPs.^[84]

Apart from these, there are also a few reports that contribute to the use of photoinduced metal-free polymerizations for the fabrication of bio-based functional materials, antifouling films,^[85] biosensors,^[86] nanoparticles based on ferroelectric^[87] or magnetic materials,^[88] and lung cancer DNA amplification detection.^[89]

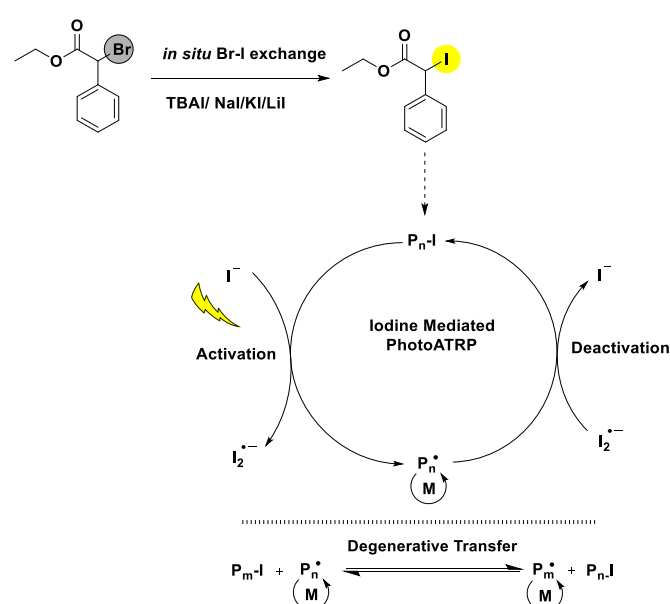
2.3. Iodine-mediated photo-ATRP

Goto and co-workers presented a novel method referred as reversible complexation mediated polymerization (RCMP) for the synthesis of monodisperse polymers.^[90] It considers the use of alkyl iodides as initiator and amines as catalyst, which requires light exposure for the polymerization to proceed. The amine abstracts iodine radicals to form an amine-iodine radical complex together with the radical, which is responsible for the polymer growth, Scheme 18.



Scheme 18. General mechanism of light induced RCMP.^[90]

Alkyl iodides compounds are often difficult to store and handle due to their light/heat sensitivity.^[91] However, in the case of iodine-mediated ATRP reactions, stable alkyl bromides are used for *in-situ* generations of alkyl iodide in the presence of iodide salts.^[92] Alkyl iodide bond cleavage upon irradiation gives initiating/propagating radicals, which are responsible for the initiation of polymerization. It is also speculated that a degenerative transfer process also takes place between the growing radicals and iodine-capped dormant species to provide control over the lengths of macromolecular chains, Scheme 19.^[91]



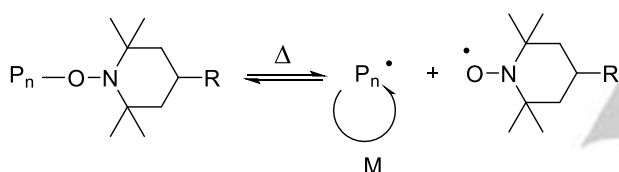
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Scheme 19. Mechanism of iodine-mediated photoATRP via simultaneous generation of the alkyl iodide using iodide salts. Figure in part adapted from Ref. [92a] with permission. Copyright 2017, Royal Society of Chemistry

Inspired by the preliminary work, the superbase/Nal was used as an organocatalyst for the realization of both the ROP of cyclic ester monomers and the photo-ATRP of methacrylates in a one-pot fashion.^[93] This system was described as being advantageous as free of metal, eliminates much energy consumption, simple and applicable to various monomers.

2.4. Nitroxide Mediated Radical Polymerization (NMRP)

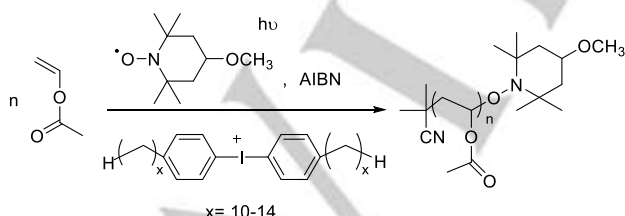
NMRP became an investigated method as the original CLRP processes providing the synthesis of monodisperse polymers with adjustable chain-end functionalities. It requires the application of stable organic nitroxide radicals, eliminating the requirement of expensive metal catalysts and extra purification steps of the final polymers. Although its utilization was initially limited to the polymerization of styrenic monomers,^[94] development of new nitroxides enabled polymerization of other monomeric structures as well.^[95] Homolytic cleavage of NO-R bond yields radicals responsible of the initiation and stabilization of polymerization (Scheme 20).



Scheme 20. General mechanism of NMRP.^[95]

NMRP is usually initiated by thermal bond cleavage, which is still the most intensively investigated approach for the induction of the process. However, there has been efforts to realize NMRP photochemically.

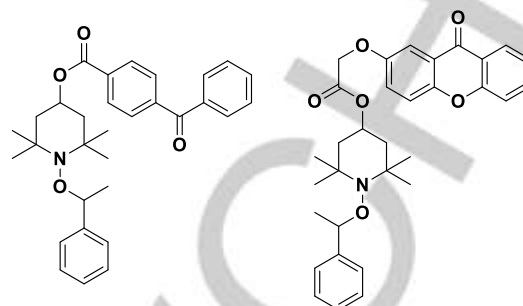
Photoacid generators in conjunction with conventional thermal initiators were shown to stimulate the homolytic cleavage of the NO-R bond. The photochemical generation of the Brønsted acid triggers the dissociation of the thermal initiator (i.e. azobis(isobutyronitrile), AIBN), Scheme 21.^[96]



Scheme 21. Photoinduced NMRP using a photoacid generator.^[96]

In a further approach, the organic nitroxide radicals are functionalized with chromophore groups, which transfer energy after excitation via light exposure to the N-oxide part of the molecule. This way, the NO-R bond is homolytically dissociated to generate the alkyl radical responsible for initiation of

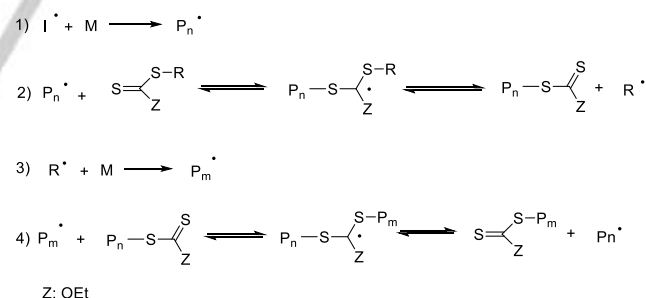
polymerization. The molecules designed for this purpose can be described as *N*-alkoxy iniferters as the polymerization mechanism follows an iniferter sequence. Scheme 22 demonstrates the structures of alkoxyamines designed for this purpose.^[96b]



Scheme 22. Structures of photoactive alkoxyamines used in NMRP.^[96b]

2.5. RAFT Polymerizations

RAFT polymerization is one of the most versatile techniques for the preparation of various macromolecular structures over the last period. It provides the synthesis of polymers with controlled molecular weight characteristics and low dispersity (\bar{D}) as well as controlled chain-end functionalities depending on the chemical reagents used. The specific chemical reagents used for the polymerization are coined RAFT agents in accordance with the terminology of the process.^[97] Widely used RAFT agents include dithioesters, dithiocarbamates, trithiocarbonates, and xanthates.^[98] The choice of the RAFT agent plays a crucial role in the enhancement of control over polymerization, as it may vary depending on the monomers used. The mechanism of RAFT polymerization on the example of O-ethyl S-(1-phenylethyl) carbonodithioate is shown below.



Scheme 23. General mechanism of RAFT polymerization.^[97]

The initiation step considers a radical generation, followed by the addition of for the radicals to the monomer. Subsequently, it undergoes a radical addition on the RAFT agent to release another radical fragment capable of initiating polymerization. As a consequence of these reversible steps of radical addition, fragmentation and transfer, control over molecular weights, dispersity, and chain-end functionality is achieved. It has also been shown that the termination rate constant is highly dependent on the chain length of the polymers produced during the RAFT polymerization, which plays a crucial role in the controlled molecular weight characteristics obtained at the end of the

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process.^[99] The generation of the radicals in the very first step determines the specifics of the RAFT process. As known, in general, radicals are formed by thermal treatment or light exposure. Therefore, one can use a thermal initiator such as AIBN or a photoinitiator to induce the RAFT polymerization. Herein, we present the recent studies on photoinduced RAFT polymerization (or PhotoRAFT) to demonstrate the advantages of using photochemical protocols over conventional initiation strategies.

2.5.1 PhotoRAFT

Photochemical processes offer distinct advantages over thermal techniques such as low-temperature necessities and mild reaction conditions, high reaction rates, and the offer of temporal and spatial control over the whole process. In parallel with the other polymerization modes, RAFT polymerizations can also be induced by the aid of the incident photon energy, offering switch “on” and “off” kinetics resulting in spatial control. The radical generation step can be achieved by direct dissociation of the thiocarbonylthio compound without the necessity of a photoinitiator, which follows an iniferter pathway, or by the use of initiators and photoredox catalysts following a photoinduced electron-transfer (PET) process. The choice of the external additives is dependent on the wavelength of the light source used, which may vary from UV to even NIR and the reaction medium.^[100]

a) Direct Photoactivation by Dissociation of RAFT Agents

This approach considers the direct dissociation of RAFT agents by UV irradiation. After homolytic cleavage of the RAFT agent, an active radical is generated to take part in the RAFT cycle. Various RAFT agents have been used for the polymerization of different monomers. For example, dithiocarbamates, xanthates, dithioesters, and trithiocarbonates have been used to polymerize structurally different monomers including (meth)acrylates and vinyl monomers.^[101] The choice of the RAFT agents is of high priority as monomer reactivities are different from each other. The use of very reactive RAFT agents (which depends on the Z moiety on its structure) in conjunction with monomers of high propagating rates may lead to multi-disperse polymers. Earlier efforts demonstrated that this approach suffers from prolonged irradiation times and low monomer conversions. However, further studies suggested that convenient RAFT agent/monomer combination can form monodisperse polymers with relatively higher yields under UV or even blue light irradiation. Acrylamides and acrylates with trithiocarbonates and vinyl acetate with xanthates under blue light exposure provided the syntheses of corresponding polymers with desired molecular weight characteristics and efficiencies.^[102]

This strategy was also utilized for the preparation of block copolymers and nanoparticles. One specific example presented the possibility of block copolymer synthesis starting from a macroRAFT agent; poly(ethylene glycol) having trithiocarbonate moiety at its ω -chain end. This precursor polymer was irradiated around 460 nm in the presence of hydroxypropyl methacrylate in a continuous flow. This way, polymeric nanoparticles of targeted morphologies are prepared in a continuous process via visible light-mediated aqueous RAFT polymerization-induced self-assembly (PISA). The approach was shown to allow accurate

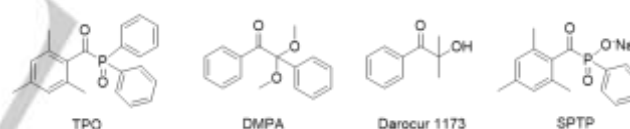
production of particle morphologies and scalable synthesis of these nanoobjects.^[103]

b) Indirect Photoactivation by External Additives

The photoRAFT processes can also be induced by using certain photoinitiators (i) as well as photoredox catalysts (ii). In this strategy, the reaction is stimulated by the use of e additives, which are the actual light-absorbing species.

i) Photoactivation by Free Radical Photoinitiators

In this approach, the radical photoinitiators generate radicals upon absorption of light, which react with the RAFT agents, in a manner similar to the thermally induced RAFT polymerization. This method provides the utilization of higher wavelength irradiation in comparison to photoRAFT processes initiated by direct photo dissociation of a RAFT agent. One further advantage is the higher quantum yield of the initiators since the polymerization yields of direct irradiation without additives are comparably low. The absorption wavelength region of the selected photoinitiator is of high importance. If the light sensitivity of the RAFT agent match with that of the initiator, two polymerization mechanisms can be operative resulting in the loss in control over molecular weight characteristics of the polymers obtained. Therefore, generally, phosphine oxide derivatives are considered the most efficient photoinitiators in photoRAFT processes, as they can be activated by visible light irradiation, where the RAFT agents are completely transparent and their dissociation is excluded. Scheme 24 shows the typical radical initiators used for photoRAFT processes.



Scheme 24. Examples of photoinitiators used for PhotoRAFT polymerizations.

Cai and co-workers demonstrated the possibility of preparing monodisperse (meth)acrylate and styrenic polymers using (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TPO) as initiator and S-1-dodecyl-S'-(α,α' -dimethyl- α' -acetic acid) trithiocarbonate (DDMAT) as RAFT agent at higher UV-light irradiation and even natural solar irradiation.^[104] The opaqueness of the RAFT agent help maintaining the controlled characteristics of the polymerization.

The photoRAFT approach by photoinitiators has also been utilized for the preparation of block copolymer particles as presented by Tan *et.al.* Using 2,2-dimethyl-2-phenylacetophenone (DMPA) and various RAFT agents, they synthesized block copolymer microspheres and surface functional PMMA under UV irradiation. More recently, this strategy has also been applied to aqueous systems and polymerization-induced self-assembly by the same group. For example, poly(ethylene glycol)-based macro-RAFT agent was used in the presence of a water-soluble photoinitiator, sodium phenyl-2,4,6-trimethylbenzoylphosphinate (SPTP) for the polymerization of *N*-(2-hydroxypropyl)methacrylamide (HPMA)

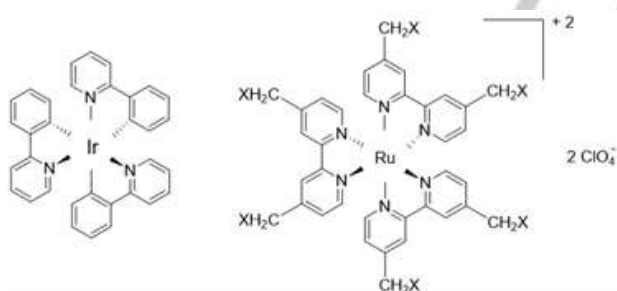
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under visible light. A variety of complex morphologies such as spheres, worms, and vesicles were shown to be producible with almost quantitative efficiency over just a few minutes.^[105]

ii) Photoactivation by Photoinduced Electron Transfer Reactions (PET)

PET-RAFT provides the application of light-induced RAFT polymerization with the aid of photoredox catalysts as additives. The mechanism describes a photoinduced electron transfer (PET) from the additive to the RAFT agent forming a radical capable of initiating polymerization in a typical RAFT fashion. Since photoredox catalysts do not generate radicals upon irradiation, separate photoactivation of the RAFT agent is excluded. In addition, the most commonly used additives absorb light in the regions where the RAFT agents are transparent. Therefore, this strategy provides better control over the process in comparison to photoRAFT techniques requiring photoinitiators. Notably, this process affords high oxygen tolerance as a result of the strong reducing capability of the catalysts, which can act as oxygen scavengers under light exposure. Therefore, deoxygenation of the reaction medium by multiple freeze-thaw-pump cycles can be disregarded. Besides, the polymerizations are realized faster in comparison to other light-induced RAFT techniques even with light sources of lower intensity due to strong light absorption and long excited-state lifetime of photocatalysts. Still, the technique suffers from the high toxicity of the catalysts required.

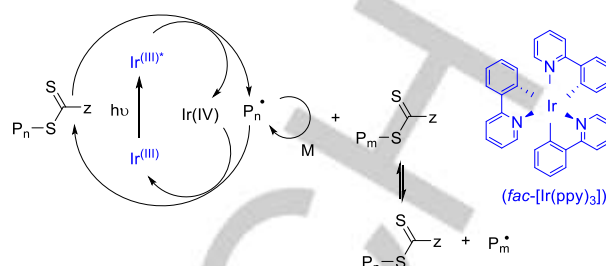
Some examples of these catalysts include metallo-complexes (Scheme 25) such as (fac-[Ir(ppy)₃]),^[106] Ru(bpy)₃Cl₂,^[107] chlorophyll A,^[108] and zinc porphyrins^[109] and organic compounds (i.e. Eosin Y, 10-phenylphenothiazine, and certain tertiary amines).^[110]



Scheme 25. Commonly applied metallo-complexes for PET-RAFT polymerizations.

The first example of a typical process described the use of fac-[Ir(ppy)₃] in ppm levels as a photocatalyst, as reported by Boyer and co-workers.^[111] Both conjugated and unconjugated monomers were polymerized to yield the corresponding polymers with low dispersities when subjected to low energy visible LED irradiation ($\lambda_{\text{max}} = 435 \text{ nm}$) under appropriate conditions, Scheme 26. Accordingly, the iridium complex of +3 oxidation state absorbs the light and is excited to its singlet state. Then, it undergoes a redox reaction with the RAFT agent to yield radicals capable of initiating polymerization. Meanwhile, thus formed iridium +4 complex reacts with radical and the growing chains are coupled with the RAFT agent. The repetition of this cycle affords polymers

with controlled molecular weight characteristics and dithiocarbonyl chain-end functionality (Scheme 26).



Scheme 26. General mechanism of PET-RAFT mediated by iridium based catalyst.^[111]

Further studies concentrated on the development of low-cost photocatalysts with reduced toxicity. Boyer and co-workers reported the application of several organic dyes for the photoRAFT process and concluded that eosin Y and fluorescein are the best pair to induce the process in comparison to the others such as methylene blue, Nile red, and rhodamine 6G. It has also been demonstrated that the use of certain aliphatic amines as sacrificing electron donors can reduce the air sensitivity of the system and enables polymerizations to be carried out under air.^[109a]

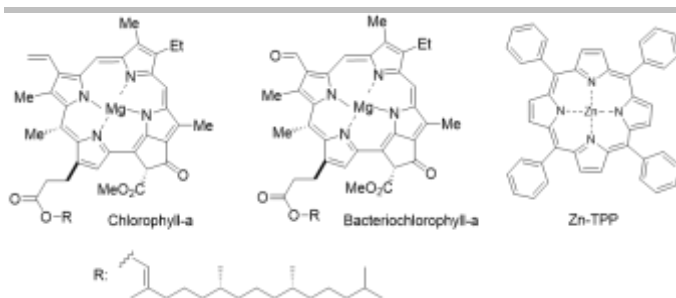
New catalysts for photoRAFT were developed leading to the utilization of naturally occurring substances. Chlorophyll *a*, as extracted from spinach leaves, was employed. Polymerizations were conducted with a variety of monomers under blue and red light irradiation and well-defined polymers with controlled molecular weight properties were successfully attained.^[111] In a subsequent study, the chlorophyll *a* was shown to undergo decomposition in air to generate colorless non-reactive compounds. Therefore, the removal of the catalyst from the polymer mixture after the polymerization was suggested to be unnecessary.^[113]

The polymerization wavelength was extended even to near-infrared (NIR)/far-red light (FIR) region. Boyer *et al.* employed bacteriochlorophyll *a* as photocatalyst for the preparation of well-defined polymers under light exposure up to $\lambda = 850 \text{ nm}$ and 780 nm for NIR and FIR, respectively. They also took advantage of the deep penetration capability of NIR light to induce polymerization behind standard A4 white paper and the reaction was shown to occur smoothly.^[110]

Metal porphyrins were applied as photocatalysts for RAFT polymerization as a natural source of photo-mediator. It was shown that zinc tetraphenylporphine (ZnTPP) can be utilized as a photocatalyst to attain selectivity on activation of various RAFT agents. The reactivity of dithiobenzoate was shown to be higher in comparison to trithiocarbonate under identical conditions. Notably, the process is applicable at visible range and open-air conditions, which holds a considerable advantage over a traditional RAFT processes.^[109]

A number of naturally occurring substances with long-wavelength sensitivity have been applied as photocatalysts for RAFT polymerization, Scheme 27.

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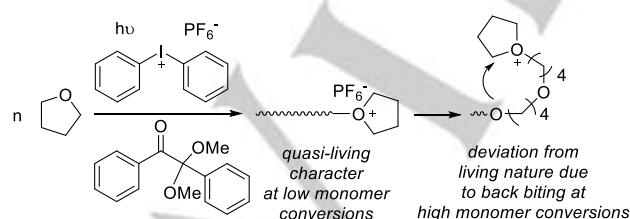


Scheme 27. Naturally occurring photocatalysts applied in light-induced RAFT polymerization.

2.6. Photoinduced Controlled Living Cationic Polymerization

The introduction of onium salts as photoinitiators enabled polymerization of oxiranes and vinyl ethers via cationic polymerization. Among the photoinitiators developed, iodonium and sulfonium salts are the most extensively utilized photoinitiators because of their thermal stability, high quantum yields and solubility. Photolysis of these initiators eventually yield Brønsted acids, which are generally responsible for the initiation of polymerization.

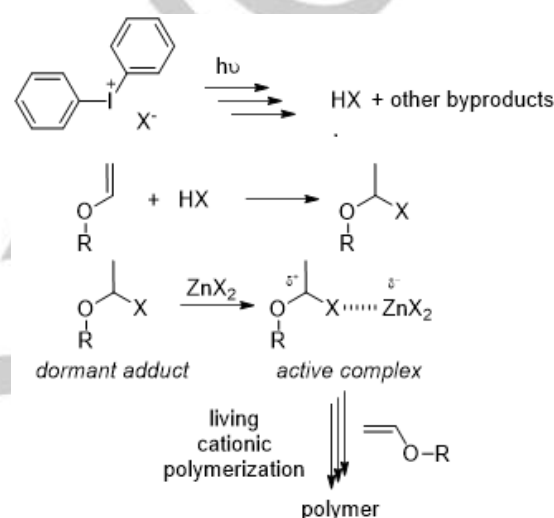
One drawback of the system was considered to be associated with the low-wavelength absorption characteristics of the onium salts, which prevents the utilization of photoinduced cationic polymerizations at lower energies of light irradiation. Employment of certain additives in the reaction medium provided to carry out the processes at higher wavelengths. Another disadvantage was grounded on the realization of photoinitiated cationic polymerization with controlled/living nature. Due to the presence of transfer and back-biting reactions especially at the late stages of polymerization, there has been a strong deviation from the controlled/living features. The first example of a photoinduced controlled/living cationic polymerization was established by polymerizing tetrahydrofuran using 2,2-dimethoxy-2-phenyl acetophenone (DMPA) and 4,4'-di-(methylphenyl) iodonium hexafluorophosphate initiating system. The polymerization system has quasi-living nature, which displays living characteristics under high monomer concentrations. When the polymerization reaches completion, back-biting and cyclization reactions play a dominant role (Scheme 28).^[114]



Scheme 28. Photoinduced *quasi*-living polymerization of THF.^[114]

Whilst the cationic polymerization of THF can be achieved with controlled/living conditions under certain conditions using onium salts with non-nucleophilic counter ions, the approach was found not to be operative when particularly vinyl monomers were used, due to the dominant chain transfer reactions. More recently, a

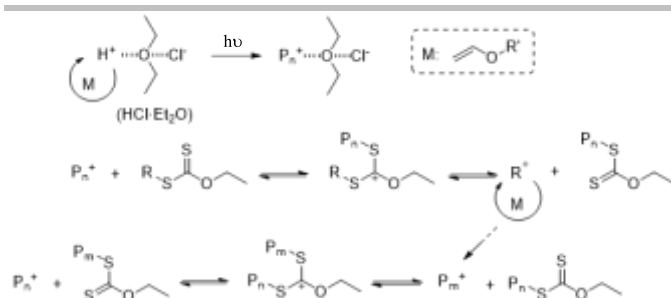
further strategy was proposed to perform controlled/living polymerization of vinyl ethers. This approach was based on tuning the nucleophilicity of the counter anion generated in the presence of zinc halides.^[115] After the system was shown to be successful under conventional procedures, a typical approach was adapted to photochemical procedures. According to the mechanism, the onium salts produce Brønsted acids, react with the vinyl ether monomer to produce the monomer-HX adduct. Zinc halides (i.e. ZnBr₂ or ZnI₂) form a complex with the adducts to produce pseudocationic organic species accompanied by [ZnX₃]⁻. This step is called the activation step, where the pseudo cationic species add more monomers to initiate polymerization. The growing carbocations generated in propagation step are stabilized by the [ZnX₃]⁻ (Scheme 29). This way, the polymerization proceeds in a controlled/living regime, where the chain transfer reactions are suppressed.^[116]



Scheme 29. Photoinduced polymerization of vinyl ethers by diphenyliodonium halides in the presence of zinc halides.^[116]

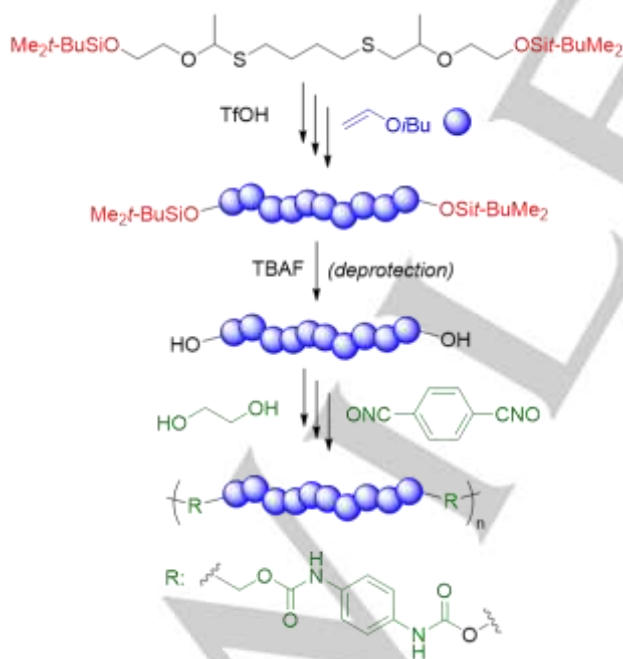
Although light-induced cationic polymerization has been investigated in detail, studies on the development of new approaches to enable controlled/living polymerization beyond procedures considering the application of Lewis acids as mediators for the living polymerization of vinyl ethers. Recently, Sugihara and Kamigaito have reported a novel strategy for the polymerization of vinyl ethers and *p*-alkoxystyrenes using specific RAFT agents for controlled/living cationic polymerization. This so called photoinduced cationic RAFT polymerization introduces RAFT agents as chain transfer agents while using acids as initiators. Sugihara and co-workers applied 1-isobutoxyethyl ethanedithioate as RAFT agent and HCl-Et₂O as the initiator,^[117] whereas Kamigaito and his colleagues used various thiocarbonyl thio compounds and triflic acid as chain-transfer agents and initiator,^[118] respectively. Results demonstrated that trithiocarbonate and dithiocarbamates are the most efficient compounds on regulating the molecular weight characteristics. The mechanism of vinyl ether polymerization using the HCl-Et₂O initiating system, Scheme 30.

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Scheme 30. Photoinduced cationic RAFT polymerization.^[117]

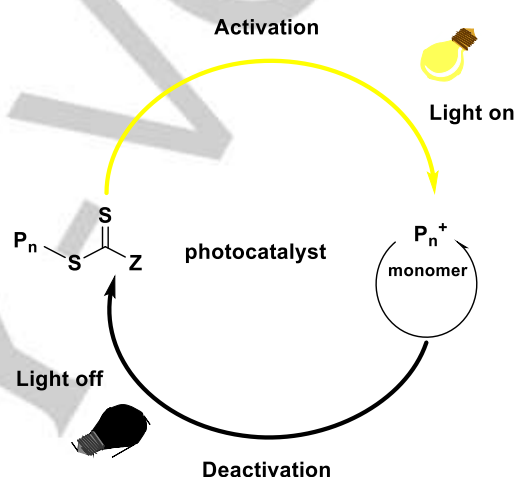
Kamigaito further showed in a following study that thioethers are also applicable as chain transfer agents instead of thiocarbonylthio compounds.^[119] The former have advantages such as easy preparation and higher stability in comparison to the latter. The strategy was also utilized for the preparation of telechelic polymers by using difunctional dithioethers. Both difunctional dithioether and monothioethers with silyl-protected groups successfully mediated the preparation of monodisperse polymers with controlled molecular weights. Consequently, the silyl groups were removed by simple deprotection reactions to generate hydroxyl functionalities, which serve as initiating groups for several block copolymerization reactions. Indeed, the polymers were used as compounds for step-growth polymerization together with diisocyanates and diols for the preparation of high molecular mass polymers linked via urethane linkages (Scheme 31).



Scheme 31. Application of difunctional thioethers for block copolymerization involving urethane linkages.^[119]

Nicewicz and co-workers has also applied the concept of using chain transfer agents for controlling polymerization.^[120] They

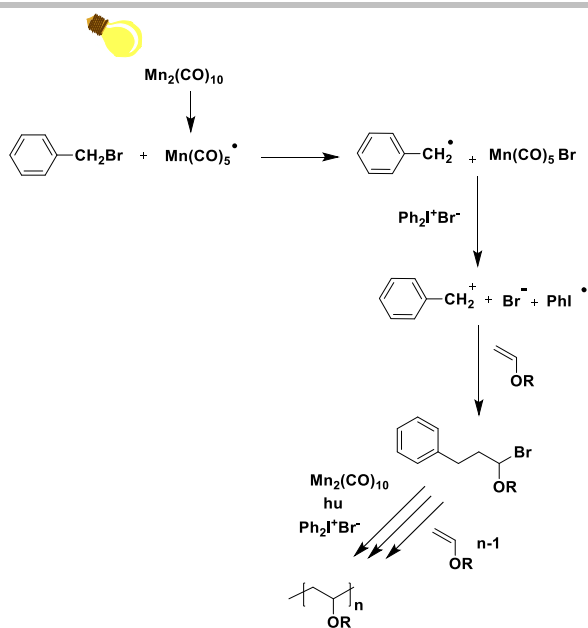
used of 2,4,6-tri(p-tolyl)pyrylium tetrafluoroborate for the light-induced polymerization of p-methoxystyrene. The chain-lengths of the corresponding polymers were controlled by methanol, similar to the dithiocarbamates analogs in RAFT polymerization. More recently, Fors and co-workers reported a new cationic RAFT procedure induced by light irradiation where dark polymerization is completely excluded. Light exposure serves as the key element for temporal control of the growth of polymer chains in this strategy, which holds a considerable superiority over the other approaches proposed. It has been shown that the process can be started and stopped on demand, by switching on and off the light. In the process, 2,4,6-tris(p-methoxyphenyl)pyrylium tetrafluoroborate was used photocatalyst, which oxidizes the chain transfer agent to form carbocations participating in the cationic RAFT process (Scheme 32).^[121]



Scheme 32. Photoreversible living cationic polymerization of vinyl ethers.^[121]

More recently, a novel photoinitiator strategy for living cationic polymerization of vinyl ethers using $\text{Mn}_2(\text{CO})_{10}$ photochemistry was reported.^[122] $\text{Mn}_2(\text{CO})_{10}$ is decomposed into $\text{Mn}(\text{CO})_5$ upon visible light irradiation, which reacts with the alkyl bromide to form alkyl radicals (Scheme 33). Subsequently, these radicals are oxidized to their corresponding cations by the diphenyliodonium bromide present in the medium. Thus-formed cations add vinyl ether monomers, which in turn captured by the bromide group to produce the dormant species. Repetition of these steps in cycles yield to the formation of poly(vinyl ether) chains, which are called photoinduced radical oxidation/addition/deactivation (PROAD).

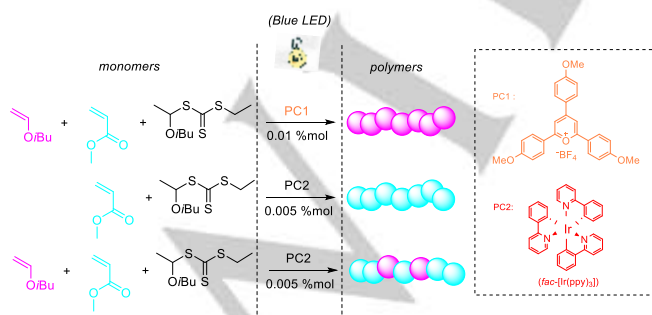
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Scheme 33. Photoinitiated living cationic polymerization of vinyl ethers by the PROAD mechanism.^[122]

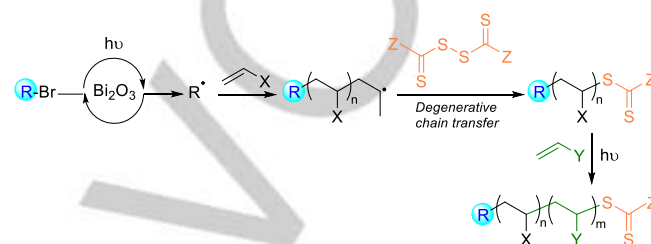
3. Combination of Photo-induced CLP Techniques for Macromolecular Synthesis

Various macromolecular architectures can be prepared benefiting from the controlled molar mass and end-group functionality of the polymers prepared by photoinduced CLP techniques. In a unique work reported by Fors and co-workers, it has been shown that polymer sequence and structure can be controlled by performing two polymerization mechanisms in a one-pot setup and switch the monomer selectivity via an external stimulus.^[123] For this purpose, monomer incorporation was determined by the selection of the irradiation wavelength so as to selectively activate either cationic or radical processes. The structure and the concentrations of the photocatalysts used, namely 2,4,6-tris(p-methoxyphenyl)pyrylium tetrafluoroborate and Ir(ppy)₃ play an important role in regulating polymer composition, Scheme 34.



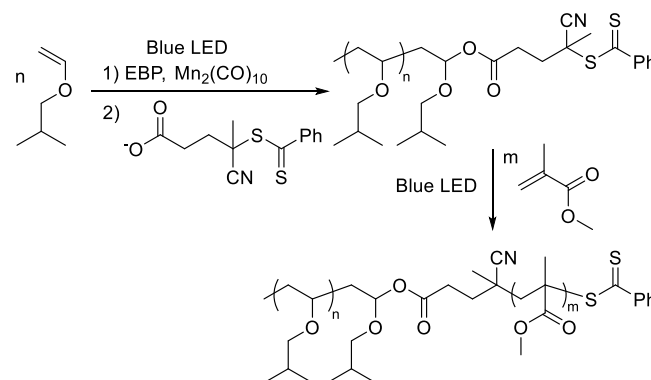
Scheme 34. Photocontrolled interconversion of cationic and radical polymerizations using different photocatalysts.^[123]

In further work, a typical ATRP initiator was used in conjunction with a RAFT agent (dithiocarbonyl disulfide) for the generation of radicals using an heterogeneous catalyst, namely Bi₂O₃.^[124] The mechanism considers a photoinduced electron transfer from Bi₂O₃ to the alkyl halide, which undergoes a redox reaction with the RAFT agent to produce radicals responsible for the initiation of polymerization (Scheme 35). The strategy describes a novel methodology for the preparation of RAFT polymers as it introduces end-group modularity. It has also been shown that a diversity of functionality can be installed at the α-end group starting from a variety of alkyl bromides, while the molecular weight distribution can be adjusted benefiting from the disulfide ω-end groups.



Scheme 35. Preparation of block copolymers by combining photoinduced Bi₂O₃ assisted ATRP and RAFT polymerizations.^[124]

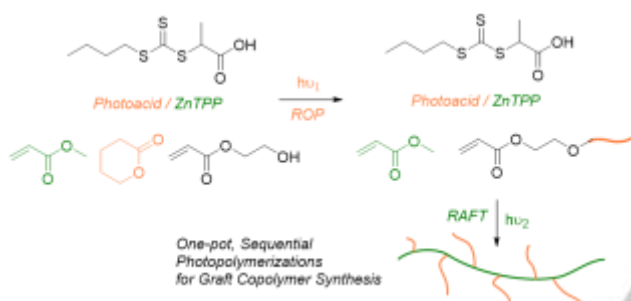
A very different approach considers using Mn₂(CO)₁₀ chemistry in conjunction with a typical ATRP initiator, ethyl-2-bromopropionate for the cationic polymerization of isobutyl vinyl ether (IBVE).^[125] Normally, Mn₂(CO)₁₀ decomposes to yield 2 equivalents of Mn(CO)₅ upon irradiation, which abstracts halogen from an alkyl halide to yield radicals capable of initiating radical polymerization. In order to perform polymerization of a monomer such as IBVE using Mn₂(CO)₁₀, one has to use an onium salt to oxidize the radical as IBVE cannot be polymerized through a radical pathway. However, it was demonstrated that the resulting Mn(CO)₅ can operate as an oxidizing agent without the requirement of an additional onium salt as reflected by rapid polymerization of IBVE with high conversions under Blue LED irradiation. The polymerizations were terminated using a RAFT agent with carboxylate functionality so as to obtain polymers with RAFT agent end groups. The resulting polymers were also employed as macroinitiators for the radical polymerization of methyl methacrylate to yield PIBVE-*b*-PMMA, Scheme 36.



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Scheme 36. Preparation of PIBVE-b-PMMA by combining photoinduced cationic polymerization of the IBVE segment by onium salt free $\text{Mn}_2(\text{CO})_{10}$ chemistry and RAFT polymerization of the PMMA segment.^[125]

Obviously, combinations of photoinitiated CLP is not limited to addition polymerizations. Boyer and co-workers presented a new approach for the synthesis of block and graft copolymers by combining visible light induced ring opening polymerization (ROP) and RAFT polymerization.^[126] For this purpose, a merocyanine-based photoacid and $\text{Zn}(\text{TPP})$ catalysts were used together to catalyze ROP and RAFT, respectively in a one-pot manner. The strategy presented a dual wavelength light controlled orthogonal polymerization system, which enables switching the polymerization modes using two discrete monomers and for the preparation of block and graft copolymers concurrently, Scheme 37.



Scheme 37. Combination of photoinitiated ROP and RAFT processes for block copolymer synthesis.^[126]

Although most of the polymerization modes involved in mechanistic transformation approach are mainly classical methods,^[127] only a few are devoted exclusively to light-induced processes as summarized above. Still, latest studies even demonstrated the even step-growth polymerizations can be induced photochemically^[128] and combined with other modes of polymerizations.

4. Conclusion

Controlled/living polymerization methods provide preparation of various polymer structures with predictable molecular weights and adjustable chain-end functionalities. Conventional thermally induced reactions are increasingly replaced by the photochemical methods due to advantages such as serving temporal and spatial control, fast rates at mild conditions and environmentally-friendly/sustainable features. There have been many efforts directed towards the development of novel photocatalysts that operate at higher wavelength irradiation with less concentration dependency for ATRP, RAFT and cationic polymerizations. In addition, they have been combined both by sequential and concurrent manner to prepare even more complex macromolecular architectures without affecting each other. We expect that even more intensive research efforts will be held on this particular topic as reflected by the numbers of manuscripts and citations as well as the conservation of energy and the increased use of green chemistry principals as we move to a more

sustainable world without the need to compromise materials properties and technological development which will increasingly rely on polymers.

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Keywords: photoinduced controlled living polymerization • free radical polymerization • cationic polymerization • mechanistic transformation

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This review highlights the strategies for photoinduced controlled living radical and cationic polymerization and their combinations for the fabrication of different macromolecular architectures. The wavelength tunability and advantages of the light-induced reactions under mild conditions are presented.