Chapter 8

Visible Light-Induced Atom Transfer Radical Polymerization for Macromolecular Syntheses

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Visible light-induced atom transfer radical polymerization (ATRP) of vinyl monomers are examined by using various photocatalysts systems including Type I and Type II photoinitiators, dyes, dimanganese decacarbonyl and semiconducting photocatalysts. The influence of various experimental parameters on the polymerization such as type of light sources and photocatalysts, and concentration of metal catalysts are also investigated. Although there currently exist only a few examples, the visible light initiation can be applied to the ATRP process providing a mild and efficient method for the in situ generation of Cu(I) activator.

Introduction

Atom transfer radical polymerization (ATRP) is currently one of the most often-used synthetic polymerization methods due to its simplicity and broad applicability, and the ability to prepare previously inaccessible well-defined polymers with complex architecture (1–4). The ATRP is a redox process

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involving a transition metal complex in which a halide atom (especially Cl or Br) is reversibly transferred between a growing radical and a dormant species. Copper and iron compounds are particularly successful metal catalysts used in ATRP, but there are also studies reporting other transitional metals such as ruthenium, molybdenum and osmium (5). During the past years, various initiation techniques involving simultaneous reverse and normal initiated (SR&NI), activators by electron transfer (ARGET), activators regenerated by electron transfer (ARGET) (6), initiators for continuous activator regeneration (ICAR) (7, 8), and supplementary activator and reducing agent (SARA) ATRP (9, 10), and single electron transfer-living radical polymerization (SET-LRP) have been reported to create some substantial benefits for environmental and practical issues, i.e. in the presence of oxygen, at room temperature or the use of catalyst at the level of parts per million (ppm). All of these methods are based on the in situ formation of activator via secondary reduction process including (I) the use of various reducing agents (either externally added (11) or monomers containing amine (12) or epoxide (13) groups as intrinsic reducing agents), (II) electrochemically redox processes (14), (III) copper-containing nanoparticles (15), and (IV) photochemically mediated redox processes (16–27).

Light is a particularly fascinating stimulus because it can be precisely modulated in terms of wavelength, polarization direction and intensity, allowing spatial and temporal of the chemical reactions (28–32). The use of UV and visible light irradiation for the in situ generation of activators for the photoinduced ATRP reaction has been researched extensively (16). Many copper (II) salts are light-sensitive compounds and can be photochemically reduced in the presence of the amine ligands. The required Cu(I) catalysts for the ATRP process can be engendered by light directly or indirectly. In the direct system, the polymerization activator, Cu(I) is generated from Cu(II) under UV light without any photoinitiator and the polymerization can be initiated by the reaction of the Cu(I)X with alkyl halide (27, 33, 34). In the indirect system, the polymerization activators, Cu(I), can be generated from Cu(II) under UV light through the help of photoinitiators. Many UV and visible light free radical photoinitiators are reported to be powerful promoters for photoinduced ATRP (17–19, 34). Recently, studies from this laboratory showed that the spectral sensitivity of the photoinduced ATRP can be extended into the visible light region to avoid hazardous UV light. In the present chapter, we will outline the recent achievements, mechanistic aspects, limitations and opportunities of the visible light-induced ATRP through several examples.

Visible Light-Induced ATRP by Directly Generated Activator

Many copper(II)/ligand complexes are known to be light sensitive and undergo photoredox reactions during UV or visible light irradiation. Earlier spectroscopic studies indicated that Cu(II) complex has three distinct absorption, two of which at UV (around 250 and 300 nm) and one at visible and near infra-red regions (between 650-1000 nm) (35, 36). These bands are highly dependent on the nature of the copper salt and the ligand used and can vary in different systems.
The ATRP of various monomers have been successfully conducted by applying several wavelengths in both UV and visible light regions. Very recently, the photopolymerization of various acrylates mediated by ppm level of Cu catalyst without the use of any photoinitiator or reducing agent was achieved (20). A variety of vinyl monomers including poly(ethylene glycol) methyl ether acrylate, tert-butyl acrylate, methyl acrylate, ethyl acrylate, methyl methacrylate, and styrene, as well as functional initiators in different solvents were tested. There are three distinct pathways for photochemical (re)generation of Cu(I) activator including (i) direct photochemical reduction of the Cu(II) complexes by excess free amine moieties, (ii) unimolecular reduction of the Cu(II) complex, (iii) photochemical radical generation either directly from the alkyl halide, ligand, or via interaction of the ligand with either monomer or with alkyl halides. Both experimental and simulation results show that the photochemically mediated reduction of Cu(II) complexes by an excess of amine groups is dominant for the (re)generation of Cu(I) activator (24, 37–42).

The ability of other transition metals such as iridium (Ir) (43), and ruthenium (Ru) (44), as alternative to the cupric catalyst system, are investigated to succeed photoinitiated ATRP. Recently Hawker et al. investigated the Ir-based photoredox system that can be utilized in order to control the polymerization of methacrylate monomers (45). The \( \text{fac}-[\text{Ir}(\text{ppy})_3] \) (ppy =2-pyridyphenyl) complex was used as the photocatalyst which affords photoexcited \( \text{fac}-[\text{Ir}(\text{ppy})_3]^* \) species upon irradiation under visible light. The photoexcited \( \text{Ir}^{III*} \) captured a halogen atom from alkyl halide to form initiating radicals as well as highly oxidized \( \text{Ir}^{IV} \) complex. This \( \text{Ir}^{IV} \) could then react with the propagating radicals to generate initial \( \text{Ir}^{III} \) complex in the ground state. The process is applied to a variety of acrylate monomers including methyl acrylate, ethyl acrylate, n-butyl acrylate and tert-butyl acrylate. The nature of the \( \text{fac}-[\text{Ir}(\text{ppy})_3] \) catalyst tolerates carboxylic acid functionality such as acrylic acid. The block and random copolymers of acrylic acid with other (meth)acrylates can be obtained by either macroinitiator or along the backbone of random copolymer with up to 50 mole percent of acrylic acid (46). The process also established spatiotemporal control over the patterning of polymer brushes using the same catalytic system under visible light irradiation (47, 48).

**Visible Light-Induced ATRP by Using Type I Photoinitiators**

Recent studies from this laboratory showed that the spectral sensitivity of the photoinduced ATRP could be extended into the visible-light region by commercially available Type I photoinitiators. Photochemically mediated reverse and simultaneous reverse and normal initiation (SR & NI) ATRP of various vinyl monomers in the presence of bis(2-methyl-2-propanoyl)(phenyl)phosphine oxide (BAPO) as a Type I photoinitiator resulted in polymers with relatively molecular weight distributions (18, 22, 49). However, the reverse photoinduced ATRP gave uncontrolled molecular weight of polymers with broad molecular weight distributions. This may be due to that the concentration of the propagating...
radicals is decreased and normal bimolecular termination becomes significant, which results in loss of control. Another disadvantage of the photoinduced reverse ATRP is related to the loss of the terminal functionality and hence limitation of its use in further block or chain-extension reactions. In order to further prove the living characteristics of polymer obtained by photoinduced reverse ATRP, PMMA ($M_n$GPC = 67700 g/mol, $M_w/M_n$ = 1.30) was used as a macroinitiator to initiate classical ATRP of MMA. The final polymer curve slightly shifted to higher molecular weights ($M_n$,GPC = 80300 g/mol, $M_w/M_n$ = 1.42) after chain extension. There is an increase in the molecular weight distribution after 2 h and a low-molecular-weight shoulder can be detected in the GPC traces of the final polymer, which suggests that some chains from the macroinitiator failed to initiate the second polymerization. This is a clear indication of poor initiation efficiency of the macroinitiator, which may not be only due to termination reactions, but also side reactions between growing radicals and the copper catalyst (18).

In the photoinduced SR&NI ATRP case, a mixture of an excess amount of alkyl halide and photoinitiator together with Cu(II) catalyst complex is used as a dual initiator for the ATRP process. In this way, not only handling problems can be avoided but also the molecular weight distribution and chain end functionality of the polymers can be improved (Scheme 1).

![Scheme 1. Proposed mechanism for the photoinduced SR&NI and ICAR ATRP.](image)

When the polymerization is performed with a photoinitiator, two photogenerated radicals induce chain growth propagation in addition to Cu(I) (re)generation. The molecular weight of the polymers obtained by this system are in good agreement with the theoretical values and show very narrow-molecular-weight distributions, ranging from 1.11–1.18. One can note that the photoinduced SR&NI ATRP system allowed better control over molecular weight and distribution under the same experimental conditions (Figure 1).
Visible Light-Induced ATRP by Using Type II Photoinitiators

In Type II photoinitiating systems, the radical photoinitiator like camphorquinone is also active in the range of visible light and is capable of generating radicals via Norrish Type II reaction in the presence of a hydrogen donor, such as tertiary amines or alcohols. First step of the process involves electron abstraction from the amine by the excited photoinitiator to produce aminoalkyl and ketyl radicals. These radicals are not only able to add to monomer molecules to initiate growth of polymer chains but also regenerate Cu(I) activator by reducing the Cu(II) species. Notably, the photogenerated ketyl radicals are not reactive enough to activate the vinyl polymerization.

In order to extend the spectral sensitivity of the photoinduced ATRP into the visible-light region, various dyes such as eosin Y and erythrosin B are used in SR&NI ATRP (18, 49). The primary photochemical reaction involves the excited dye molecules abstracting an electron from the amine molecules to form radicalcation/radical-anion pairs. After the proton transfer, some of the radicals are in the system. These radicals are not only able to add to monomer molecules to initiate the polymerization but can reduce the Cu(II) to Cu(I), which is used as activator in ATRP. In the dye systems, the molecular weights increase linearly with conversions, which are consistent with the polymerizations proceeding in a controlled fashion (Figure 2). However, the experimental molecular weights are slightly higher than the theoretical values, indicating low initiation efficiency. In dye/amine system, back electron transfer generally limits the efficient generation of...
of free radicals which directly reduce Cu(II) to Cu(I). The applicability of this system is also extended to other vinyl monomers such as methyl acrylate and styrene. Although visible light induced ATRP represented well-controlled system for the polymerization of methyl acrylate, the system was less controlled toward styrene monomer due to the high quenching rate of the monomer.

Figure 2. Kinetic plots and molecular weights and distributions of resulting polymers as a function of degree of conversion for eosin and erythrosin B sensitized ATRP of methyl methacrylate. Reproduced with permission from reference 49. Copyright 2012 John Wiley & Sons.

Scheme 2. Mechanistic scheme for photoinduced reverse ATRP using CQ/Bzh.

Quite recently a new photoinduced reverse ATRP approach using camphorquinone/benzhydrol (CQ/Bzh) as an alternative initiating system has been reported (50). In this process, triplet state CQ abstracts hydrogen from the ground state Bzh to give two ketyl type radicals, which do not react with the surrounding monomer as a result of its stability and steric hindrance. These radicals, however, reduce the Cu(II) complex to Cu(I) activator and simultaneously generate the alkyl halide (R-X, where X is Cl or Br). In the following step, the R-X compound is responsible for the initiation of photoinduced ATRP of acrylic monomer (Scheme 2).

The main benefit of this approach is that it simultaneously forms alkyl halide initiator by the addition of acid released from the redox process to the monomer. The experimental molecular weights are considerably higher than theoretical values and the obtained polymers showed slightly broad molecular weight distributions ranging from 1.13 to 1.51 in the process. The photoinduced SR&NI ATRP of MMA under the same conditions is also presented and the system leads to a better control of the polymerization as reflected by the improved molecular weight distribution and chain end functionality.

Visible Light-Induced ATRP by Using Dimanganese Decacarbonyl

Dimanganese decacarbonyl (Mn₂(CO)₁₀) has a weak Mn–Mn linkage and visible light photolysis provides the ‘Mn(CO)₅’ metallocaradiads which are not capable of initiating polymerization but abstracting halides from a variety of organohalogen compounds, generating the corresponding carbon centered radicals (Scheme 3). We have previously shown that manganese based radical generation process can successfully be employed in different modes of polymerization processes including radical promoted cationic polymerization (51), mechanistic transformation (52, 53), radical coupling (54), hyper-branching (55) and grafting from polyolefines (56). Recent studies from our laboratory showed that this chemistry can be used as a photoredox catalyst system for the ATRP of vinyl monomers such as methyl methacrylate, methyl acrylate and styrene (57). The polymerizations were performed either by visible- or sunlight in the presence of ppm level of copper catalysts at room temperature. The ease of this novel light induced ATRP comes from the usage of Mn₂(CO)₁₀ which was surely responsible for the both initiation and control of the polymerization.

In order to gain a better understanding of the polymerization mechanism several control experiments were performed in the absence of either light, Mn₂(CO)₁₀ or Cu⁺Br₂. When the polymerization was performed in the dark (entry 1, Table 1) or in the absence of Mn₂(CO)₁₀ (entry 2, Table 1) no polymer was obtained. In the case of no Cu⁺Br₂, polymer with uncontrolled molecular weight was formed via free radical polymerization (entry 3, Table 1), due to photogenerated radicals from alkyl halides by classical halogen abstraction reaction. The effect of Mn₂(CO)₁₀ concentration on the polymerization was

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investigated by changing molar ratio of Mn$_2$(CO)$_{10}$. At relatively high Mn$_2$(CO)$_{10}$ concentration (entry 4, Table 1) the reaction showed little control, with a high molecular weight distribution value due to the irreversible radical termination. However, reducing the concentration of the Mn$_2$(CO)$_{10}$ significantly decreased the molecular weight distribution of the resulting polymers (entries 5 and 6, Table 1). Additionally, even at the ppm level of the catalyst, molecular weight distribution remained narrow and the system still had a good living nature (entry 7, Table 1). In the sunlight induced process (entry 8, Table 1), the polymerization proceeded at a relatively slower rate and showed slightly higher molecular weight distribution due to the broader wavelength spectrum in the sunlight irradiation. Applicability of the method with other vinyl monomers such as methyl acrylate and styrene (entries 10 and 11, Table 1) was also examined. In both cases, control over molecular weight and molecular weight distribution was good.

On the basis of above results, the mechanism was proposed as follows (Scheme 3). First step of the process involves the formation of •Mn(CO)$_5$ radical by homolysis of Mn$_2$(CO)$_{10}$ under visible- or sun light. These photogenerated •Mn(CO)$_5$ radicals not only abstract halogen atoms from alkyl halides to initiate polymerization but also provide continuous activator regeneration by reducing the excess of Cu(II) deactivator to the Cu(I) activator. Additionally, sunlight induced ATRP of MMA in the presence of commercially available poly(vinyl chloride) (PVC) using Mn$_2$(CO)$_{10}$ resulted in the formation of PVC-g-PMMA copolymers successfully. In the process, chlorine atoms of PVC acted as initiation sites for grafting of MMA.

Scheme 3. Mechanistic scheme for sunlight induced ATRP using Mn$_2$(CO)$_{10}$.
Table 1. Visible light or sunlight induced ATRP of vinyl monomers at room temperature. Reproduced with permission from reference 57. Copyright 2014 Royal Society of Chemistry.

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ᵃ Mₙ,th = [Monomer]₀/[RX]₀ × M_w,monomer × conversion; ᵇ Number-average molecular weight (Mₙ,GPC) and molecular weight distribution (Mₘ₀/Mₓ) were determined by gel permeation chromatography; ᶜ Polymerization was performed in the dark, time = 180 min; ᵈ Polymerization was performed at visible light irradiation, time = 180 min, light intensity = 45 mW cm⁻². ᶜ⁺ Polymerization was performed with sunlight, time = 180 min, light intensity = 60 mW cm⁻².

Visible Light-Induced ATRP by Semiconducting Photocatalysts

There has been an intense research interest in the past decades in developing (nano)engineered materials exhibiting photocatalytic properties in order to actualize catalytic reactions under more environmentally benign conditions and with inexpensive materials. Owing to their photosensitive properties, semiconductor materials have been extensively utilized as photocatalyst, which can be excited upon photo illumination and provide the required charge carriers to induce reactions by enabling reduction/oxidation processes. Upon photoexcitation of semiconductors, electron-hole pairs are released correspondingly from the conduction and valence band of the semiconductor, which can then promote reduction or oxidation reactions, respectively. In addition to widely used inorganic semiconductor nanoparticles such as titanium dioxide (TiO₂) or zinc oxide (ZnO), metal-free organic-based polymeric semiconductors have also been developed as inexpensive and efficient energy transducers for photocatalyst purposes. Mesoporous graphitic carbon nitride (mpg-C₃N₄), for instance, has been developed as an efficient photocatalyst in a broad variety of reactions (58).
It was previously reported that free radical photopolymerization can be achieved by using mpg-C₃N₄ as the photocatalyst by which the initiating radicals were formed through oxidation reactions induced by the releasing charge carriers from mpg-C₃N₄ under visible light irradiation (59). The applicability of this kind of polymeric photocatalyst has been recently extended to the ATRP system. The required Cu(I) activator can be obtained from air-stable Cu(II) species via electrons released from mpg-C₃N₄ under light (60, 61). The photoinduced ATRP of a variety of vinyl monomers, including methyl methacrylate, methyl acrylate and styrene is investigated by using Cu(II)/PMDETA as the catalyst and mpg-C₃N₄ as the photocatalyst in acetonitrile media. The polymerization conducted under either UV light (λ = 350 nm) or natural sunlight and in both cases the photoinduced ATRP gives well-controlled polymers having molecular weights in good agreement with theoretical values and low molecular weight distributions (1.10-1.16). Kinetics studies reveal a linear relationship between the monomer consumption, ln([M]₀/[M]), and reaction time indicative of the constant concentration of the propagating radicals during the reaction. A linear increase in the molecular weights of the resulting polymers was also observed as conversion increased. Compared with UV light, natural sunlight resulted in a more controllable, efficient process as the polymer chains had narrower molecular weight distributions, and near-quantitative monomer conversion was achieved when irradiated under sunlight. The use of copper catalyst at ppm levels (50 ppm) caused an increase in the rate of reaction and gave slightly broad polymer chains with molecular weight distribution of around 1.28. This was probably due to the low deactivation rate of the propagating radicals. Furthermore, the livingness of the process was proved by ¹H NMR and in situ chain extension experiments as the resulted polymers exhibited excellent chain end fidelity. The proposed mechanism was based on the perpetual reduction of air-stable Cu(II) species by the releasing electrons from mpg-C₃N₄ furnishing activator Cu(I) catalyst in situ to active a dormant chain (Pₙ-X) (Scheme 4).

Scheme 4. Proposed mechanism of photoinitiated ATRP by mpg-C₃N₄

Temporal control over the growth of polymer chains is achieved by intermittent light and dark experiments. Exposing the polymerization solution
including mpg-C$_3$N$_4$ to the light initiate the polymerization while treating in the dark results in no growth as no conversion is detected during the dark periods and no change in the molecular weight of the polymer is observed.

Similar photomediated ATRP processes have also been achieved by using inorganic semiconductor nanoparticles to afford well-controlled macromolecular architectures. Yagci et al. used ZnO nanoparticles as photocatalyst to initiate ATRP process (62). Zhou and co-workers reported surface-initiated ATRP mediated by irradiation of TiO$_2$ nanoparticles to reduce Cu(II) species (63). Although these reactions are accomplished under UV light irradiation, the spectral activity of such systems was extended to visible regions by using dye-sensitized TiO$_2$ nanoparticles in which dyes acting as visible light-sensitizer were used to excite electrons in the conduction band of TiO$_2$ (64). Mechanistically, photoinduced electron transfer from the dye to the conduction band of the semiconductor leads to a charge separation in TiO$_2$ and electron release reducing Cu(II). This system is applied to grow polymer brushes of different compositions and architectures from an ATRP initiator-functionalized substrate with a range of water-soluble monomers. An interesting aspect of this system is the ability to gain spatial control over the growth of polymer brushes affording patterned features with desired composition. Scheme 5 shows the mechanism of surface-initiated ATRP by dye-sensitized TiO$_2$ nanoparticles.

![Scheme 5. Schematic illustration of the growth of polymer brush by the photoinitiated ATRP using dye-sensitized TiO$_2$ nanoparticles](image)

**Conclusion**

In this contribution, possibilities and limitations of visible light-induced ATRP for the synthesis of well-defined polymers with controlled architecture have been reported with particular references to recent works conducted in the area. The use of environmentally friendly, non-toxic and inexhaustible visible light in photochemical synthesis is a scientific challenge to prepare tailor-made polymers. The visible light-induced ATRP not only enables the easy control of the polymerization under ambient temperature even for heat-sensitive monomers but also tends to minimize side reactions like chain transfer or depolymerization.
Furthermore, this system do not need for high-energy ultraviolet radiation in most photochemical processes, which has limited both the practicality and environmental benefits of photochemical synthesis on industrially relevant scales.

References


