Photoinitiated Metal Free Living Radical and Cationic Polymerizations

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Although conventional photoinitiated radical and cationic polymerizations are widely used in many industrial applications, they usually proceed in an uncontrolled manner. Recent developments in photomediated living/controlled radical and cationic polymerization made it possible to prepare various well-defined polymers with complex architecture under mild conditions. Various methods described for cationic and radical polymerization utilizes metal or Lewis acid catalysts. Several strategies eliminating the use of such additives in photoinduced controlled/living radical and cationic polymerizations have been developed. This article describes various photoinitiation systems acting in UV-vis range. Their mechanistic details are also evaluated and several specific examples involving combination both free radical and cationic routes are presented.

Keywords: Photopolymerization, Metal free controlled/living polymerization, Radical polymerization, Cationic polymerization

1. Introduction

Photoinitiated polymerizations are well established and highly efficient processes for many industrial applications including coatings, adhesives, inks, printing plates, optical waveguides, and microelectronics [1]. In these processes, multifunctional monomers or polymers are converted into insoluble networks through radical or ionic species produced by the light illumination. Conventional photopolymerizations can also be used for the preparation of linear [2] or branched polymers [3,4] and copolymers [5] which are typically performed under various reaction conditions such as bulk, in organic solvents or water, under homogeneous and heterogeneous state by using light sources emitting light in a broad range in the UV and visible region. However, they usually do not yield well-defined polymers with precise average molar masses, low molecular weight distributions and pre-designed architectures due to the inevitable transfer and termination reactions manifesting the overall process. Combining photoinduced electron transfer reactions developed for the conventional systems with controlled polymerization techniques has recently revolutionized the synthesis of well-defined macromolecular architectures [6]. Many attempts have been devoted to apply photochemical systems to existing controlled/living polymerization methodologies by photochemically effecting initiation, mediation and control of these processes [7-19].

In this article, we focus on the recent developments on metal free atom transfer radical polymerization (ATRP) and cationic polymerization reported from the authors’ laboratory. Several selected examples combining these two processes for the preparation of block copolymers from structurally different monomers will be presented.

2. Photoinduced metal free strategies for atom transfer radical polymerization
Atom transfer radical polymerization (ATRP) has become the most generally investigated and utilized strategy in recent years due to its distinguished advantages over the other controlled/living radical polymerization methods [20]. Such advantages include the applicability of a broad range of monomer formulations, availability of high number of initiators and high tolerance to many functional groups and solvents. It also offers polymers with controlled chain end functionality and narrow molecular weight distribution characteristics. Despite these outstanding features, one major drawback associated with ATRP concerns the requirement of low oxidation state copper salts (Cu(I), in general), which are vulnerable to oxidation. Therefore, traditionally very high concentration of copper complexes are used. This rises another problem as thus obtained polymers encapsulate excessive inorganic residues, which are difficult to remove. In order to avoid the use of massive inorganic catalyst consumption, in-situ generation of catalyst is a useful strategy, which provides realization of ATRP in lower catalyst concentrations. One can generate Cu(I) complexes starting from their Cu(II) analogs using reducing agents such as phenol, ascorbic acid and hydrazine [21,22]. Another approach suggests the application of photochemical energy, which was actually shown to achieve ATRP in lower copper concentrations [23]. Either by direct irradiation of the Cu(II) complex with UV light or using a photocatalyst together with Cu(II), the required catalyst can be readily formed [8,12,16,24,25]. We have shown the possibility of using conventional free radical photoinitiators that can undergo such photoredox processes to eventually help realization of ATRP. Scheme 1 shows the indirectly initiated ATRP mechanism by the use of photoinitiators.

Even though these approaches overcome the above mentioned limitations, the necessity of using Cu(X)/L catalysts still remains. Removal of copper residues is especially required when polymers to be used for bio-applications, where even ppm levels of transition metal residues might be detrimental. Number of strategies have been proposed to obtain metal-free ATRP polymers. Recently, phenothiazine derivatives [26-28], perylene [29], pyrene [30], diaryl dihydrophenazines [31] and phenoxazines [32] as photoactivators in conjunction with alkyl halides have been shown to realize photo-initiated C/LRP of various monomers in the absence of Cu catalysts (Chart 1).

![Chart 1. Most common photoactivators for metal-free ATRP.](image)

The radical formation step considers an oxidative quenching mechanism, where an electron is transferred from the excited state photoactivator (or photosensitizer) to the alkyl halide. The overall mechanism is shown below (Scheme 2).

![Scheme 2. Photoinduced metal-free ATRP by oxidative quenching mechanism using photosensitizers.](image)

Another strategy involves the application of conventional Type II photoinitiators and certain dyes in conjunction with amines as electron sources and alkyl halides as initiators [33-35]. In this particular case, the mechanism of radical formation...
occurs by a reductive quenching mechanism. (Chart 2).

![Chart 2. Common photoactivators for metal-free ATRP following the reductive quenching mechanism.](image)

The mechanism follows a two-step electron transfer process as depicted below (Scheme 3).

![Scheme 3. Photoinduced metal-free ATRP by reductive quenching mechanism using dye/amine system.](image)

X: Cl, Br  Et₃N: triethyl amine

The overall comparison of the photoactivators used in metal free photo ATRP is presented in Table 1.

The introduction of metal-free strategies led possibilities to concurrently apply them for block copolymer syntheses. For example, Hadjichristidis and his coworkers suggested a novel metal-free strategy polymerize cyclic esters like ε-caprolactone and L-lactide, using a superbase (phosphazene base P₂-t-Bu) recently [36,37]. We have utilized a metal-free ATRP strategy in conjunction with Hadjichristidis’s strategy to obtain block copolymers in a one-shot manner. For this purpose, a specially designed molecule bearing tertiary-bromide and primary-hydroxyl functionalities is used to simultaneously realize the polymerization of various vinyl monomers and ε-caprolactone concurrently [38]. Scheme 4 demonstrates the synthesis of poly(methyl methacrylate)-b-poly(ε-caprolactone) (PMMA-b-PCL) with this strategy applied.

![Scheme 4. Concurrent metal-free controlled/living polymerizations of MMA and ε-CL under sunlight for the synthesis of PMMA-b-PCL.](image)

3. Photoinduced metal free cationic polymerization techniques

Following the pioneering work of Crivello describing the use of onium salts as photoinitiators for cationic polymerization of oxiranes and vinyl ethers [39,40], there has been tremendous interest in the development of various photoinitiators [41-45]. Among them, iodonium and sulfonium salts are the most widely used photoinitiators due to their thermal stability, solubility in most of the cationically polymerizable monomers, and efficiency in generating reactive species upon photolysis [46-48]. The photodecomposition and the subsequent reaction of the formed radical cation with solvent or monomer lead to the formation of Bronsted acid, H⁺, which is responsible for the initiation as presented on the example of diaryliodonium salts in Scheme 5.

![Scheme 5. Photochemical formation of Bronsted acid from iodonium salts.](image)

The photochemistry and applications of the direct initiation to cationic polymerization to a variety of epoxy and vinyl ethers have been well studied and subject to review articles [1,49]. In order make the applicability of the initiating systems to the pigmented formulations, the interest has been directed toward the development of strategies to extend the spectral activity of onium salts to the higher wavelengths since the photoactivity of described onium salt photoinitiators are mainly at short wavelength of the UV spectrum between 230 and 300 nm which requires the use of high-energy irradiation sources [50,51]. Accordingly, three different modes have been developed for the indirect activation of onium salts: (i) free radical promoted cationic polymerization [52,53], (ii)
electron transfer between a photoexcited molecule and an onium salt [54-56], and (iii) excitation of charge transfer complexes of onium salts [57]. Among them, free radical promoted cationic polymerization appears as an elegant and fairly flexible method to shift the wavelength sensitivity to longer wavelengths (Scheme 6) [58]. In the process, electron donating free radicals produced by various methods can readily be oxidized by the onium salts to cations capable of initiating cationic polymerizations. Many different applications of such initiation process, including promotion of cationic polymerization by free radicals produced by various modes like photochemically, thermally, or high-energy ray, block and graft copolymerization etc. have been reported [59-64].

| Photoactivator              | Activation Mode | Light Source                      | Comments                                      | Ref. |
|----------------------------|-----------------|-----------------------------------|------------------------------------------------|------|
| Perylene                   | Oxidative       | White LED/sunlight                 | • Low dispersity                              | 29   |
|                            |                 |                                   | • Low initiation efficiency                    |      |
| Pyrene                     | Oxidative       | UV light                          | • Low dispersity                              | 30   |
|                            |                 |                                   | • Low initiation efficiency                    |      |
| Anthracene                 | Oxidative       | UV light                          | • No control over polymerization               | 30   |
| 10-Phenylphenothiazine     | Oxidative       | UV light                          | • Low dispersity                              | 27   |
|                            |                 |                                   | • High initiation efficiency                   |      |
| Dihydropheazines           | Oxidative       | White LED/sunlight                 | • Low dispersity                              | 31   |
|                            |                 |                                   | • High initiation efficiency                   |      |
| Phenoxazines               | Oxidative       | UV light/visible LED               | • Low dispersity                              | 32   |
|                            |                 |                                   | • High initiation efficiency                   |      |
| Fluorescein                | Reductive       | Broad Range LEDs                  | • Low dispersity                              | 34   |
|                            |                 |                                   | • Low initiation efficiency                    |      |
| Eosin Y                    | Reductive       | Broad Range LEDs                  | • Low dispersity                              | 33   |
|                            |                 |                                   | • Low initiation efficiency                    |      |
| Erythrosine B              | Reductive       | Broad Range LEDs                  | • Low dispersity                              | 33   |
|                            |                 |                                   | • Low initiation efficiency                    |      |
| Thioxanthones              | Reductive       | UV light                          | • Low dispersity                              | 35   |
|                            |                 |                                   | • Low initiation efficiency                    |      |
| Benzophenone               | Reductive       | UV light                          | • Low dispersity                              | 35   |
|                            |                 |                                   | • Low initiation efficiency                    |      |
Although it is rather difficult to achieve controlled/living conditions in such systems due to the transfer and back biting reactions, Ledwith and Yagci described living polymerization of THF by using 2,2-dimethoxy-2-phenyl acetophenone (DMPA) and 4,4′-di-(methylphenyl) iodonium hexafluorophosphate as free radical source and oxidant, respectively [65]. Recently, similar methodology was also used for the synthesis of halide side-chain functional copolymers, poly(tetrahydrofuran-co-epichlorohydrin) (P(THF-co-ECH) [66]. Subsequent conversion of halide groups to azide moieties by the conventional azidation procedure using NaN₃ in DMF resulted in the formation of azide-functional analogues, which were used as a platform for side-chain functionalization via copper catalyzed azide alkyne cycloaddition (CuAAC) click chemistry (Scheme 7).

While the cationic polymerization of THF can be achieved under controlled/living conditions for the described procedure using onium salts with such non-nucleophilic counter anions, this system deviates from controlled/living conditions for the other cationically polymerizable monomers particularly vinyl monomers due to the dominant chain transfer reactions. The control over the chain growth has been established by tuning nucleophilicity of the counter anion generated in the presence of zinc halides [67,68]. Mechanistically, photochemically generated acid reacts with the vinyl ether monomer to form the monomer HX adduct. The zinc halide coordinates with adduct to activate the terminal carbon-halide bond. This activation leads to the generation of a suitable nucleophilic counter anion by stabilizing the growing carbocation. As a result, the cationic polymerization proceeds in a controlled/living manner with suppressed chain-breaking reactions due to the coordination of Lewis acids, essentially leading to polymers with controlled molecular weight and dispersities (Scheme 8).

On the other hand, while photoinitiated cationic polymerization has been known for decades there has been little attention to the development of alternatives that enable controlled/living polymerization beyond procedures for Lewis acid mediated living polymerization of vinyl ethers. Recently, new visible light initiated metal-free systems for the controlled cationic photopolymerization of vinyl ethers and p-alkoxy styrenes via cationic, reversible addition–fragmentation chain-transfer (RAFT) polymerization have been separately described by Sugihara [69] and Kamigaito [70]. In the first article, 1-isobutoxyethyl ethanedithioate was used as chain transfer agent in the cationic polymerization of vinyl ethers initiated by the HCl·Et₂O. In the second one, various thiocarbonylthio compounds and triflic acid were used as chain-transfer and initiator respectively. Among various compounds, trithiocarbonate and dithiocarbamates (Chart 3) were found to be the most effective at controlling the molecular weights.

In a following study, Kamigaito reported that thioethers can also be used as chain transfer agents instead of thiocarbonylthio compounds [71]. Compare to their thiocarbonylthio analogues thioethers appeared to be more easily synthesized.
and more stable. Furthermore, the described procedure was examined for the synthesis of telechelic polymers by using difunctional dithioether used as chain-transfer agent. Polymerization using difunctional dithioether with silyl-protected hydroxyl groups proceeded smoothly similar to the monothioethers and resulted in the formation of polymers with controlled molecular weights and narrow polydispersity. Subsequent deprotection of silyl groups forms hydroxyl analogues which was used for the chain-extension reactions in conjunction with disocyanates and diols as chain extenders to be converted into high molecular weight polymers linked via urethane linkages.

In a conceptually similar study, Perkowski et al. reported a novel system for controlled cationic photopolymerization of 4-methoxystyrene using pyrylium salts [72]. In this case 2,4,6-tri(p-tolyl)pyrylium tetrafluoroborate was used as photoinitiator while methanol controls the polymerization as a reversible chain transfer agent, similar to the dithiocarbamates analogous in RAFT polymerization.

In an interesting study, Fors and coworkers [73] demonstrated a new cationic RAFT procedure where chain growth is regulated by light. In the process, a suitable photocatalyst, 2,4,6-tris(p-methoxyphenyl)pyrylium tetrafluoroborate, oxidizes chain transfer agent to form carbocations participating the RAFT process (Scheme 9). The main advantage of this process over the others is the temporal control of the growth of polymer chains by light. As proved in the article, the process can be instantly stopped by turning off the light, and then turning on the light source restores the growth of polymer chains with the same kinetic character.

More recently, Yagci and coworkers [74] reported a novel photoinitiating system for living cationic polymerization of vinyl ethers eliminating the requirement for the metal halides by using Mn$_2$(CO)$_{10}$ photochemistry. As presented in Scheme 10, in the described approach, visible-light irradiation of Mn$_2$(CO)$_{10}$ in the presence of an alkyl bromide results in the formation of carbon-centered radicals. The photochemically generated radicals are then oxidized by diphenyliodonium ions to the corresponding cations. These cations can add vinyl ether monomers, which are then rapidly deactivated by the bromide anions to give α-halide functional end groups. Poly(vinyl ether) chains are then grown through successive photoinduced radical oxidation/addition/deactivation (PROAD) processes. The controlled/living nature of the process was proven by the investigation of time dependence of logarithmic conversion and molecular weights.

Scheme 9. Photoreversible living cationic polymerization of vinyl ethers.

Scheme 10. Photoinitiated living cationic polymerization of vinyl ethers by PROAD.

Moreover, this process can successfully be utilized for the synthesis of block copolymers. Successful blocking was accomplished by the use of halide terminal polymers obtained by ATRP as an initiator in the PROAD approach. This way mechanistic transformation from one mode of controlled/living polymerization to the other one was achieved.

4. Conclusion

In conclusion, this article covers an overview of the development of innovative methodologies for metal free ATRP and cationic polymerization based on various photoinduced electron transfer reactions. For the metal free photo ATRP, polynuclear aromatic hydrocarbons, certain aromatic carbonyl...
compounds and dyes were shown to be efficient photosensitizers acting in UV and visible range depending on their absorption characteristics. The excited states of these compounds undergo photoinduced electron transfer reaction with appropriate alkyl halides through oxidative or reductive quenching mechanisms leading to the formation of polymers with narrow molecular weight distribution and controlled chain-end functionality. These photoredox systems offer new possibilities for not only control over the polymerization but also surface modification, spatiotemporal control and network formations by using suitably selected monomers for specific applications under metal free conditions. In addition to quasi-living cationic polymerization of cyclic ethers by using conventional direct and sensitized onium salt based photoinitiating systems, vinyl ethers can also be photochemically polymerized in a living manner in the absence of metals or Lewis acids. In the conventional photopolymerizations of the latter monomers transfer reactions dominate the process. The recently developed photochemical approach eliminates such side reactions and poly(vinyl ether)s can be obtained in a controlled manner. The process is based on successive $\text{Mn}_2\text{(CO)}_{10}$ assisted visible light radical generation, oxidation addition and deactivation reactions. Obviously, the methodologies described here for both radical, cationic routes and their combinations are expected to be useful to prepare materials with controlled molecular weight and functionality particularly those involving bio-applications, where excess inorganic residuals might be a disadvantage.

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