

Photo-mediated Metal-Free Atom Transfer Radical Polymerization: Mechanistic Insight and Future Perspectives

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Abstract:

Among the various controlled/living radical polymerization approaches, atom transfer radical polymerization (ATRP) stands out as the most commonly employed technique. Nevertheless, the requirement for a metal catalyst poses a disadvantage and constrains its wider applicability. In light of advancements in reducing the concentration of metal catalysts, recent developments have demonstrated that ATRP can be conducted under metal-free conditions through light irradiation. Based on its unique properties, it has become a valuable tool in the design and synthesis of tailorable polymers for a wide range of applications. In this mini-review the fundamental features of the reductive and oxidative quenching mechanism of metal-free ATRP are provided in addition to the potential applications.

Keywords: metal-free, photo-mediated, ATRP

Foto Aracılı Metalsiz Atom Transferi Radikal Polimerizasyonu: Mekanistik Anlayış ve Gelecek Perspektifleri

Özet:

Çeşitli kontrollü radikal polimerizasyon yaklaşımları arasında atom transfer radikal polimerizasyonu (ATRP), en sık kullanılan teknik olarak öne çıkmaktadır. Bununla birlikte, bir metal katalizöre duyulan gereksinim bir dezavantaj teşkil etmekte ve bunun daha geniş uygulanabilirliğini sınırlamaktadır. Metal katalizörlerin konsantrasyonunun azaltılmasındaki gelişmelerin ışığında, son gelişmeler ATRP'nin metal içermeyen koşullar altında ışık yoluyla gerçekleştirilebileceğini göstermiştir. Farklı özelliklerine dayanarak, geniş bir uygulama yelpazesi için özelleştirilebilir polimerlerin tasarımı ve sentezinde değerli bir araç haline gelmiştir. Bu mini derlemede, potansiyel uygulamalara ek olarak metal içermeyen ATRP'nin indirgeyici ve oksidatif mekanizmasının temel özellikleri sağlanmaktadır.

Anahtar Kelimeler: metal içermeyen, ışık-aracılı, ATRP

REVIEW

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1. Introduction

Controlled/living radical polymerization (C/LRP) methods have garnered significant attention in recent years for their capacity to generate vinyl polymers with pre-determined molecular weights, narrow molecular weight distributions, diverse architectures, and functional end-groups (Braunecker & Matyjaszewski, 2007), (J.-S. Wang & Matyjaszewski, 1995). The foremost methods include atom transfer radical polymerization (ATRP) (J.-S. Wang & Matyjaszewski, 1995), (Kato, Kamigaito, Sawamoto, & Higashimura, 1995), reversible addition–fragmentation chain transfer polymerization (RAFT) (Chiefari et al., 1998), and nitroxide-mediated radical polymerization (NMRP) (Georges, Veregin, Kazmaier, & Hamer, 1993). Of these techniques, ATRP is likely the most extensively employed, primarily owing to its versatility and robust characteristics. Since its independent discovery by Matyjaszewski (J.-S. Wang & Matyjaszewski, 1995) and Sawamoto (Kato et al., 1995) in 1995, ATRP has found widespread application

in the synthesis of polymers from diverse monomers, featuring a range of architectures and functionalities. The conventional mechanism of traditional ATRP relies on a low oxidation state transition metal complex (usually a copper halide) as a catalyst at high concentrations (Boyer et al., 2016). Despite the outstanding performance of ATRP, a significant drawback lies in the high concentration of the metallic catalyst, which is challenging to remove after the reaction (Yilmaz & Yagci, 2018). This limitation restricts the widespread application of ATRP, especially in biomedical applications. At this junction, the utilization of light-induced reactions has surfaced as an alternative method to carry out ATRP with reduced catalyst concentrations (Y. Wang et al., 2013). In one of the pioneering studies by Yagci and coworkers it was demonstrated that commencing the process with Cu(II) complexes could effectively decrease the copper concentration. In the process Cu(I) species were generated in the reaction medium from air-stable Cu(II) species via photochemical reduction (direct pathway). As indirect pathway, numerous photoactive molecules,

including commercially available photoinitiators or dyes were also utilized as reducing agents for Cu(II) (Bansal et al., 2015), (Kütahya, Schmitz, Strehmel, Yagci, & Strehmel, 2018).

1.1. Photoinduced metal-free ATRP

Until recently, achieving ATRP without involvement of any metal, thereby offering a viable solution to address the issue of contamination by metallic catalyst residues in the polymer, was a challenge despite the mentioned notable accomplishments. In 2014, Hawker and colleagues represented the inaugural instance of photoinduced metal-free ATRP in the synthesis of poly(methyl methacrylate) (PMMA), employing 10-phenyl-phenothiazine as a photocatalyst (PC) (Ma et al., 2021). Later in the same year, perylene was introduced and employed as a photocatalyst for metal-free Atom Transfer Radical Polymerization (ATRP) by Miyake and Theriot (Miyake & Theriot, 2014). Subsequently, a multitude of photosensitizers, including both naturally occurring and commercially available ones, were demonstrated to be effective catalysts for metal-free ATRP. Other PTZ derivatives, dihydrophenazines, phenoxazines, and polycyclic aromatic hydrocarbons (in addition to perylene such as pyrene and anthracene), are some examples of catalysts that have been investigated in metal-free ATRP (Theriot, McCarthy, Lim, & Miyake, 2017), (Park, Back, Choi, Lee, & Son, 2019; Taskin, Yilmaz, Tasdelen, & Yagci, 2014). Thienothiophene derivatives were also demonstrated to be effective catalysts by Yagci and colleagues as supported by fluorescence quenching experiments (Kutahya et al., 2017). Photocatalysts are currently used in photoinduced metal-free ATRP through an oxidative quenching mechanism are given in Table 1. In the pathway of oxidative quenching, the photocatalyst is initially in its ground state and becomes excited to the singlet state through light exposure (UV or visible). Following this photoexcitation, the excited singlet state can either directly undergo a reaction or experience an intersystem crossing to transition to its triplet state. While the singlet state possesses a higher reducing potential than the triplet state, it has a shorter lifetime, typically in the nanosecond range, whereas the triplet state has a lifetime extending to microseconds. In both of its excited states, the photocatalyst initiates the reaction by reducing alkyl halide bonds, generating a propagating radical, a halide anion (X^-), and an oxidized radical cation PC. Deactivation processes return a polymer chain with halogen terminations to a dormant state, along with the photocatalyst reverting to its ground state. This completes the photoredox cycle of oxidative quenching ATRP (S. de Ávila Gonçalves, P, & Pioli Vieira, 2021) which has been illustrated in Figure 1.

Although the mechanism in all aforementioned examples is following an oxidative quenching pathway, depending on the kind of catalyst utilized the photoredox catalytic mechanism may involve reductive quenching pathway as well. Recent research has demonstrated that specific electron acceptor dyes, when combined with amines, have the ability to enhance the ATRP process via a reductive quenching mechanism (Pan et al., 2016). For instance, Yagci group demonstrated that Eosin Y and erythrosin B can act as effective sensitizers when exposed to different colors of LED and commonly available visible light to lead formation of polymers with narrow molecular weight distributions (Kutahya, Aykac, Yilmaz, & Yagci, 2016). The same research group demonstrated that traditional Type II photoinitiators, including benzophenone, thioxanthone, isopropyl thioxanthone, and camphorquinone, in conjunction with a carefully chosen amine and alkyl halide were effective in sensitizing metal-free ATRP through a reductive quenching mechanism. Computational investigations provide supporting evidence for the reductive quenching mechanism. This

mechanism involves an electron transfer from the electron-donating amine to the excited state dye, resulting in the formation of the radical anion of the dye and the radical cation form of the amine. Subsequently, the radical anion form of the dye reduces the alkyl halide, generating the radical responsible for initiation (Allushi et al., 2017).

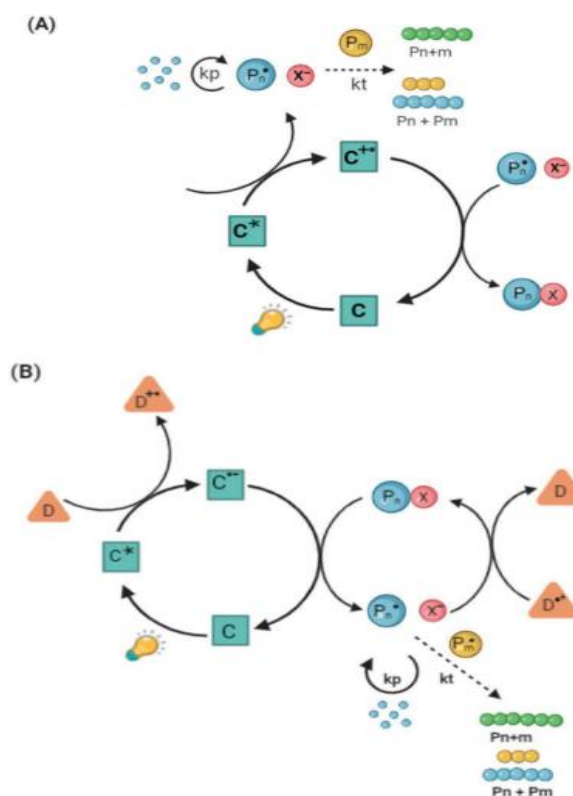
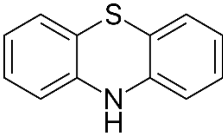

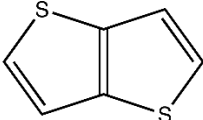
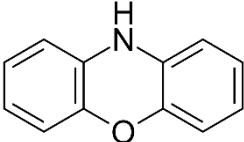
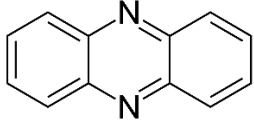
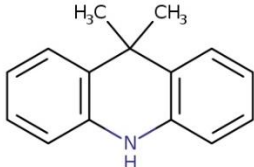


Figure 1. Photoredox catalytic cycle of O-ATRP via A) oxidative and B) reductive quenching pathway. Reproduced with permission from Ref. (Sayeny de Ávila Gonçalves, R. Rodrigues, & Pioli Vieira, 2021) Copyright Wiley 2021

After the introduction of metal-free ATRP, the technique was modified to enable the synthesis of polymers with precise topologies, including linear, star-shaped, brush-like, hyperbranched, and graft structures, as well as controlled composition (Aydogan, Yilmaz, & Yagci, 2017). For instance, Yagci and colleagues have recently introduced the concept of orthogonal synthesis of block copolymers combining metal-free ATRP and Ring Opening Polymerization (ROP) processes in one-shot. In this process, a deliberately designed bifunctional initiator with tertiary bromide and hydroxyl groups is employed. This initiator enables the concurrent polymerization of vinyl and lactone monomers under sunlight, utilizing metal-free methodologies (Aydogan, Kutahya, Allushi, Yilmaz, & Yagci, 2017).

In an independent investigation, the same research group showcased the effectiveness of metal-free ATRP in the synthesis of hyperbranched polymers. The polymerization of methyl methacrylate and styrene, using the corresponding inimers, was catalyzed by perylene under visible light irradiation. The extent of branching in the resulting polymers could be readily controlled by adjusting the type and concentration of the inimer, as well as the duration of irradiation (Aydogan, Yilmaz, et al., 2017).

Photocatalyst	General structures
Phenothiazines	
Polycyclic aromatic hydrocarbons	
Thienothiophenes	
Phenoxazines	
Phenazines	
Dimethyl dihydroacridines	

2. Summary and Overview

The preliminary study of photomediated ATRP, presented for the first time by Prof. Dr. Yagci and colleagues, has introduced a novel perspective to the ATRP method. The utilization of organic photoredox catalysts, as opposed to the copper metal traditionally employed in this polymerization, has rendered the ATRP process more environmentally friendly, aligning it with principles of green chemistry. This method not only eliminates the need for transition metal catalysts but also facilitates milder reaction conditions, reducing potential toxicity, and broadening the scope of applicable monomers. The development of photoinduced metal-free ATRP opens new avenues for polymer scientists, offering a more sustainable and accessible route to precision macromolecular synthesis. As research in this field progresses, the photomediated metal-free ATRP can be applied to various applications in materials science, biomedical engineering, and nanotechnology. Future research may focus on optimizing this technique to further reduce environmental impact, enhance efficiency, and explore sustainable photocatalysts.

Author Contributions

All authors contributed equally.

References

Allushi, A., Kutahya, C., Aydogan, C., Kreutzer, J., Yilmaz, G.,

& Yagci, Y. (2017). Conventional Type II photoinitiators as activators for photoinduced metal-free atom transfer radical polymerization. *Polymer Chemistry*, 8(12), 1972-1977. doi: <https://doi.org/10.1039/C7PY00114B>.

Aydogan, C., Kutahya, C., Allushi, A., Yilmaz, G., & Yagci, Y. (2017). Block copolymer synthesis in one shot: concurrent metal-free ATRP and ROP processes under sunlight. *Polymer Chemistry*, 8(19), 2899-2903. doi: <https://doi.org/10.1039/C7PY00069C>.

Aydogan, C., Yilmaz, G., & Yagci, Y. (2017). Synthesis of Hyperbranched Polymers by Photoinduced Metal-Free ATRP. *Macromolecules*, 50(23), 9115-9120. doi: <https://doi.org/10.1021/acs.macromol.7b02240>.

Bansal, A., Kumar, A., Kumar, P., Bojja, S., Chatterjee, A. K., Ray, S. S., & Jain, S. L. (2015). Visible light-induced surface initiated atom transfer radical polymerization of methyl methacrylate on titania/reduced graphene oxide nanocomposite. *RSC Advances*, 5(27), 21189-21196. doi: <https://doi.org/10.1039/C4RA15615C>.

Boyer, C., Corrigan, N. A., Jung, K., Nguyen, D., Nguyen, T.-K., Adnan, N. N. M., . . . Yeow, J. (2016). Copper-Mediated Living Radical Polymerization (Atom Transfer Radical Polymerization and Copper(0) Mediated Polymerization): From Fundamentals to

- Bioapplications. *Chemical Reviews*, 116(4), 1803-1949. doi: <https://doi.org/10.1021/acs.chemrev.5b00396>.
- Braunecker, W. A., & Matyjaszewski, K. (2007). Controlled/living radical polymerization: Features, developments, and perspectives. *Progress in Polymer Science*, 32(1), 93-146. doi: <https://doi.org/10.1016/j.progpolymsci.2006.11.002>.
- Chiefari, J., Chong, Y. K., Ercole, F., Krstina, J., Jeffery, J., Le, T. P. T., . . . Thang, S. H. (1998). Living Free-Radical Polymerization by Reversible Addition-Fragmentation Chain Transfer: The RAFT Process. *Macromolecules*, 31(16), 5559-5562. doi: <https://doi.org/10.1021/ma9804951>.
- de Ávila Gonçalves, S., Rodrigues, P. R. & Pioli Vieira, R. (2021). Metal-Free Organocatalyzed Atom Transfer Radical Polymerization: Synthesis, Applications, and Future Perspectives. *Macromol Rapid Commun*, 42(15), e2100221. doi: <https://doi.org/10.1002/marc.202100221>.
- Georges, M. K., Veregin, R. P. N., Kazmaier, P. M., & Hamer, G. K. (1993). Narrow molecular weight resins by a free-radical polymerization process. *Macromolecules*, 26(11), 2987-2988. doi: <https://doi.org/10.1021/ma00063a054>.
- Kato, M., Kamigaito, M., Sawamoto, M., & Higashimura, T. (1995). Polymerization of Methyl Methacrylate with the Carbon Tetrachloride/Dichlorotris-(triphenylphosphine)ruthenium(II)/ Methylaluminum Bis(2,6-di-tert-butylphenoxide) Initiating System: Possibility of Living Radical Polymerization. *Macromolecules*, 28(5), 1721-1723. doi: <https://doi.org/10.1021/ma00109a056>.
- Kutahya, C., Allushi, A., Isci, R., Kreutzer, J., Ozturk, T., Yilmaz, G., & Yagci, Y. (2017). Photoinduced Metal-Free Atom Transfer Radical Polymerization Using Highly Conjugated Thienothiophene Derivatives. *Macromolecules*, 50(17), 6903-6910. doi: <https://doi.org/10.1021/acs.macromol.7b01335>.
- Kutahya, C., Aykac, F. S., Yilmaz, G., & Yagci, Y. (2016). LED and visible light-induced metal free ATRP using reducible dyes in the presence of amines. *Polymer Chemistry*, 7(39), 6094-6098. doi: <https://doi.org/10.1039/C6PY01417H>.
- Kütahya, C., Schmitz, C., Strehmel, V., Yagci, Y., & Strehmel, B. (2018). Near-Infrared Sensitized Photoinduced Atom-Transfer Radical Polymerization (ATRP) with a Copper(II) Catalyst Concentration in the ppm Range. *Angewandte Chemie International Edition*, 57(26), 7898-7902. doi: <https://doi.org/10.1002/anie.201802964>.
- Ma, Q., Song, J., Zhang, X., Jiang, Y., Ji, L., & Liao, S. (2021). Metal-free atom transfer radical polymerization with ppm catalyst loading under sunlight. *Nature Communications*, 12(1), 429. doi: <https://doi.org/10.1038/s41467-020-20645-8>.
- Miyake, G. M., & Theriot, J. C. (2014). Perylene as an Organic Photocatalyst for the Radical Polymerization of Functionalized Vinyl Monomers through Oxidative Quenching with Alkyl Bromides and Visible Light. *Macromolecules*, 47(23), 8255-8261. doi: <https://doi.org/10.1021/ma502044f>.
- Pan, X., Tasdelen, M. A., Laun, J., Junkers, T., Yagci, Y., & Matyjaszewski, K. (2016). Photomediated controlled radical polymerization. *Progress in Polymer Science*, 62, 73-125. doi: <https://doi.org/10.1016/j.progpolymsci.2016.06.005>.
- Park, G. S., Back, J., Choi, E. M., Lee, E., & Son, K.-s. (2019). Visible light-mediated metal-free atom transfer radical polymerization with N-trifluoromethylphenyl phenoxazines. *European Polymer Journal*, 117, 347-352. doi: <https://doi.org/10.1016/j.eurpolymj.2019.05.023>.
- Taskin, O. S., Yilmaz, G., Tasdelen, M. A., & Yagci, Y. (2014). Photoinduced reverse atom transfer radical polymerization of methyl methacrylate using camphorquinone/benzhydrol system. *Polymer International*, 63(5), 902-907. doi: <https://doi.org/10.1002/pi.4573>.
- Theriot, J. C., McCarthy, B. G., Lim, C.-H., & Miyake, G. M. (2017). Organocatalyzed Atom Transfer Radical Polymerization: Perspectives on Catalyst Design and Performance. *Macromolecular Rapid Communications*, 38(13), 1700040. doi: <https://doi.org/10.1002/marc.201700040>.
- Wang, J.-S., & Matyjaszewski, K. (1995). Controlled/"living" radical polymerization. atom transfer radical polymerization in the presence of transition-metal complexes. *Journal of the American Chemical Society*, 117(20), 5614-5615. doi: <https://doi.org/10.1021/ja00125a035>.
- Wang, Y., Soerensen, N., Zhong, M., Schroeder, H., Buback, M., & Matyjaszewski, K. (2013). Improving the "Livingness" of ATRP by Reducing Cu Catalyst Concentration. *Macromolecules*, 46(3), 683-691. doi: <https://doi.org/10.1021/ma3024393>.
- Yilmaz, G., & Yagci, Y. (2018). Photoinduced metal-free atom transfer radical polymerizations: state-of-the-art, mechanistic aspects and applications. *Polymer Chemistry*, 9(14), 1757-1762. doi: <https://doi.org/10.1039/C8PY00207J>.