Advances in Polymer Technology

Advanced Catalysis and Reaction Technology in Polymer Synthesis

Lead Guest Editor: Ning Zhu
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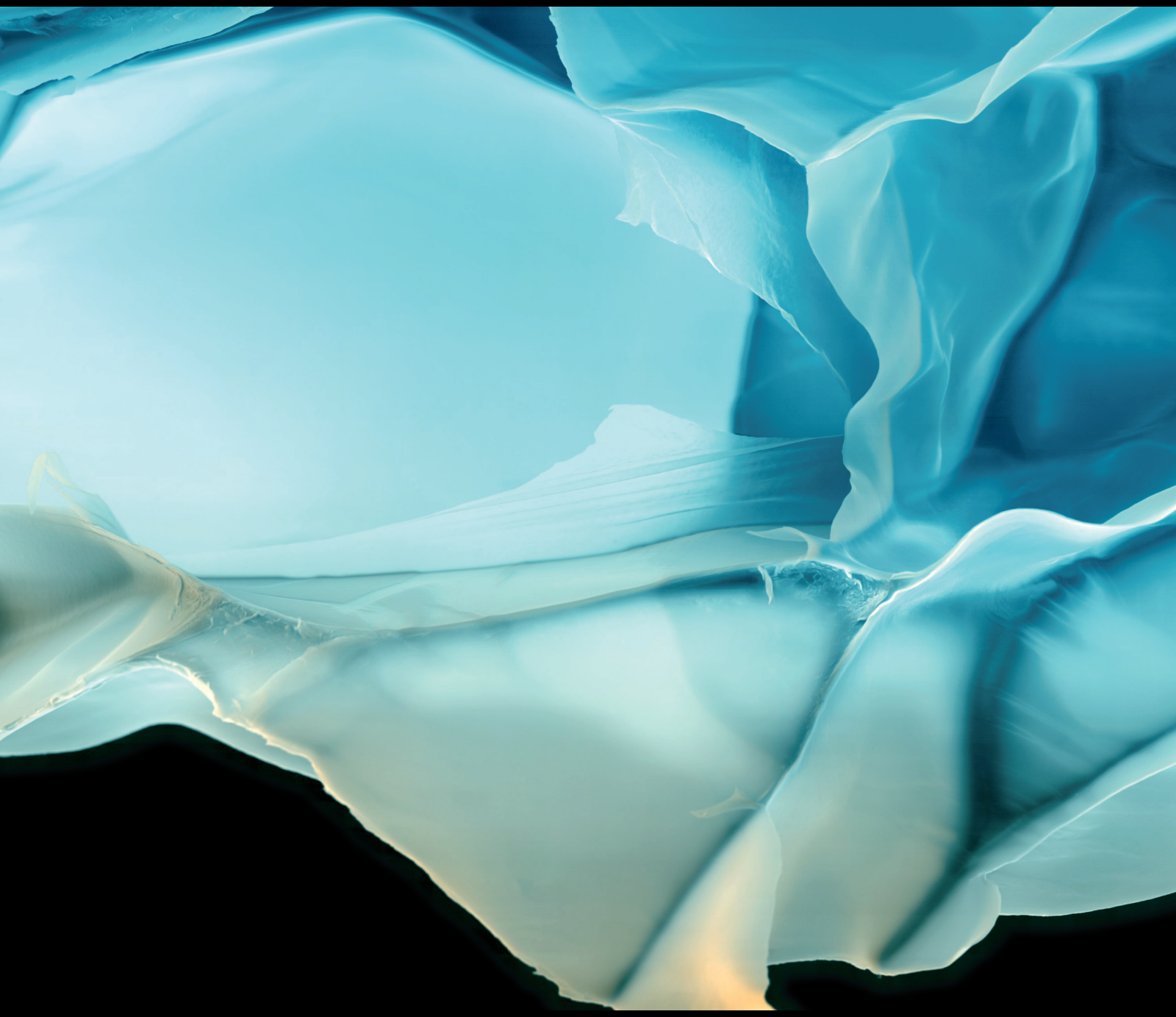

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Review Article

Advances in Organocatalyzed Atom Transfer Radical Polymerization

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Atom transfer radical polymerization (ATRP) is one of the most robust tools to prepare well-defined polymers with precise topologies and architectures. Although series of improved ATRP methods have been developed to decrease the metal catalyst loading to parts per million, metal residue is the key limiting factor for variety of applications, especially in microelectronic and biomedical area. The feasible solution to this challenge would be the establishment of metal-free ATRP. Since 2014, organocatalyzed ATRP (O-ATRP) or metal free ATRP has achieved significant progress by developing kinds of organic photoredox catalysts. This review highlights the advances in organocatalyzed atom transfer radical polymerization as well as the potential future directions.

1. Introduction

Reversible deactivation radical polymerization (RDRP) (controlled radial polymerization (CRP)) has achieved significant progress in precision polymer synthesis, which includes but not limited to atom transfer radical polymerization (ATRP) [1–4], reversible addition–fragmentation polymerization (RAFT) [5, 6] and nitroxide-mediated polymerization (NMP) [7], etc. ATRP is one of the most robust and versatile tools to prepare well-defined polymers with precise topologies and architectures. Initially, ATRP employed copper (I) as well as other transition-metals (e.g., ruthenium, iron et al.) to mediate the reversible activation/deactivation between the dormant species and propagating radicals [1–4]. Series of improved ATRP methods have been established to lower the metal catalyst loading, including initiator for continuous activator regeneration (ICAR) ATRP [8, 9], activator regeneration by electron transfer (ARGET) ATRP [10–12], single electron transfer living radical polymerization (SET-LRP), also termed as supplemental activators and reducing agents (SARA) ATRP [13–16], and external stimuli induced ATRP (e.g., photo-/electro-/mechanical-) [17–21], etc. Generally, the catalyst loading could be suppressed to less than 20 parts per million (ppm) level. The negative influence of the metal catalyst residue, however, still remains, especially in microelectronic and biomedical applications.

Photoinduced polymerization, owe to its distinguished advantages including mild reaction condition, accelerated polymerization rate, and the additional benefits of excellent spatial and temporal control over the polymerization process, has aroused increasing number of research interests [22–24]. The design and synthesis of the strongly reducing photoredox catalyst (PC) is considered to be the core of the photoinduced reaction, often employing the catalysts containing precious metals. The development of organic photoredox catalysts offered sustainable alternatives to mediate photoinduced reactions, including polymerizations, trifluoromethylation reactions and dual photoredox/nickel C–N and C–S cross-coupling reactions [25]. Owe to the plenty of the advantages over metal catalysis [26], organocatalysis has become an attractive research topic in biomass utilization [27], CO_2 fixation [28], ring opening (co)polymerization [29], membrane assisted homogeneous [30] and heterogeneous transformations [31]. Recently, metal free ATRP or organocatalyzed ATRP (O-ATRP) has been established based on series of organic photoredox catalysts with various polymerization mechanisms [32–35]. It provides a viable and ideal solution for addressing the challenge of metal catalyst residue contamination. This

review focuses on the advances in organocatalyzed atom transfer radical polymerization as well as the potential future directions.

2. Organic Photoredox Catalysts for O-ATRP

For the classical ATRP system, alkyl halide initiator was quickly activated by low valence state copper (Cu(I)) to form the propagating radical and the oxidation state metal (Cu(II)) [1–4]. The radicals were deactivated by the deactivating species (Cu(II)) to yield dormant species. The excellent control over the polymerization process relies on this activation/deactivation equilibrium (radical/dormant species). The principles of organocatalyzed atom transfer radical polymerization are the development of novel organic photoredox catalysts, which could maintain the activation/deactivation equilibrium.

2.1. Phenothiazines. In 2014, Hawker, Fors and co-workers reported phenothiazines as a photoredox catalyst to mediate metal free ATRP [36]. Well controlled polymerization of methyl methacrylate (MMA) and dimethylaminoethyl methacrylate (DMAEMA) as well as chain extensions with benzyl methacrylate (BnMA) were achieved in the presence of 0.1 mol% of 10-phenylphenothiazine (PTH) under the irradiation of 380 nm UV light at room temperature. The exited state of PTH possesses the required reductive potential which could reduce the alkyl halide/dormant species to propagating radicals and stable radical cation species, the latter one can deactivate the propagating radicals to dormant species and PTH (Figure 1). By establishing the equilibrium, the polymerization could be operated in a controlled manner. Subsequently, Hawker, Alaniz and coworkers presented a simple benchtop approach to polymer brush nanostructures by using this metal free ATRP [37].

Matyjaszewski, Gennaro, Liu and co-workers investigated the mechanism of photoinduced metal-free atom transfer radical polymerization through both experimental and computational studies (Figure 2) [38]. The experimental results indicate that all designed phenothiazine derivatives are involved in the activation process to form alkyl radicals. However, some catalysts are not efficient to deactivate the radicals to generate the dominants. This is the reason for the poor control of polymerization. The activation process undergoes a dissociative electron-transfer (DET) mechanism and the deactivation step is involved an associative electron transfer. Matyjaszewski and co-workers employed phenothiazine derivatives to mediate metal-free ATRP to obtain polyacrylonitrile (PAN) with controlled molecular weight and molecular weight distributions [39]. They also developed phenyl benzo[*b*]phenothiazine as the visible light organic photoredox catalyst for metal free ATRP [40].

Our group developed a P(VDF-*co*-CTFE) graft modification strategy via O-ATRP by using *N*-phenylphenothiazine as the catalyst (Figure 3) [41]. A series of P(VDF-*co*-CTFE)-*g*-PMMA, P(VDF-*co*-CTFE)-*g*-PMA, and P(VDF-*co*-CTFE)-*g*-PBA were prepared under mild conditions with high temporal control. Moreover, the resultant graft copolymer can be used as macroinitiator to re-initiate O-ATRP. It might exhibit the potential application in dielectric material.

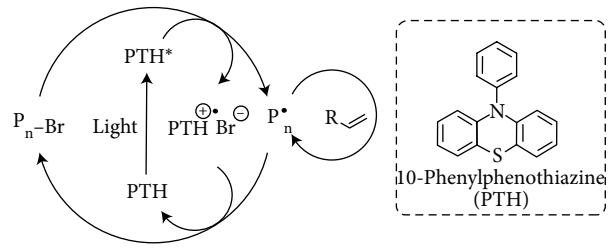

Figure 1: Proposed mechanism of metal-free photo-mediated ATRP with 10-phenylphenothiazine as the catalyst (Pn = polymer chain). (Adapted with permission from Ref. [36].)

2.2. Polynuclear Aromatic Hydrocarbons. Miyake and co-workers developed perylene as an organic photoredox catalyst for the radical polymerization through oxidative quenching pathway (Figure 4) [42]. Under the sunlight, 0.11 mol% perylene was used to mediate the polymerization of MMA with ethyl α-bromoisophenylacetate (EBP) as initiator. Although the loss of bromide end group, coupling the two propagating radical chains and poor control of molecular weight and distribution, this work exhibited the promising future of O-ATRP.

Yagci and co-workers investigated perylene and anthracene catalyzed O-ATRP of (meth)acrylates and vinyl monomers (Figure 5) [43]. Excited state anthracene experienced an electron transfer reaction with alkyl halide initiator through an oxidative quenching mechanism to form anthracene radical cations and alkyl radicals. Although anthracene was observed to be more efficient in radical formation step, excited states anthracene also underwent a cycloaddition with another ground state anthracene to generate dimers, which was responsible for the decreased yield of resultant polymer at high anthracene concentration.

2.3. Dihydrophenazines. Miyake and co-workers improved visible light triggered O-ATRP by introducing diaryl dihydrophenazines as a class of strongly reducing photoredox catalysts (Figure 6) [44]. Inspired by computationally directed discovery, they evaluated the reduction potentials of dihydrophenazines with electron-donating (OMe, 1) ($E^{0*} = -2.36$ V), neutral (H, 2) ($E^{0*} = -2.34$ V) and electron-withdrawing (CF_3, 3 and CN, 4) ($E^{0*} = -2.24$ V and $E^{0*} = -2.06$ V). All these catalysts were significantly more reducing than commonly used photoredox catalysts. They could also achieve the formation of relatively stable radical cations, which were sufficiently oxidizing to deactivate the propagating chains. Effective polymerizations and chain extensions were successfully conducted in a controlled manner. With the inspection of the triplet state frontier orbital, improved diaryl dihydrophenazines (2-Napthyl, *5* and 1-Napthyl, *6*) ($E^{0*} = -2.20$ V and $E^{0*} = -2.12$ V) were developed with sufficiently strong E^{0*} and spatially separated excited state SOMOs, which showed more efficient control in the O-ATRP. Moreover, they investigated intramolecular charge transfer and ion pairing in *N*,*N*-diaryl dihydrophenazine photoredox catalyst for O-ATRP [45].

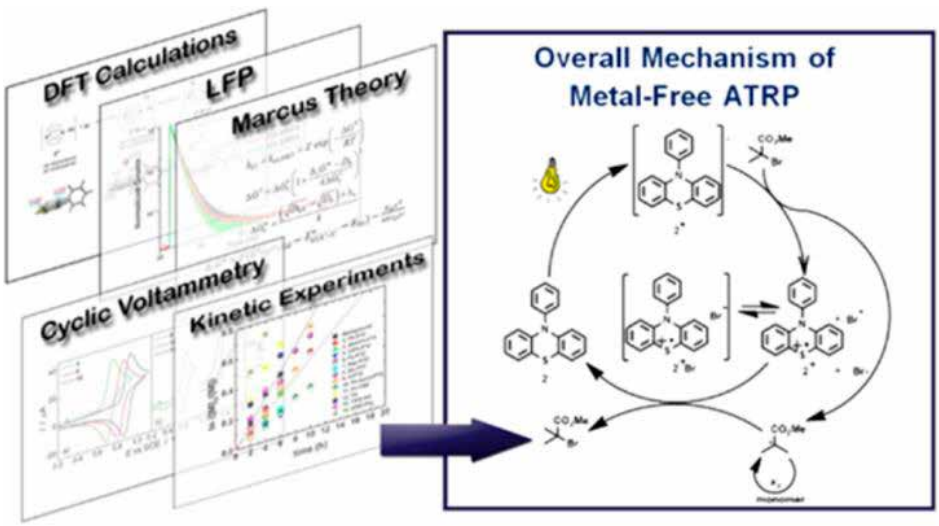

Figure 2: Mechanism of photoinduced metal-free atom transfer radical polymerization through both experimental and computational studies. (Adapted with permission from Ref. [38]).

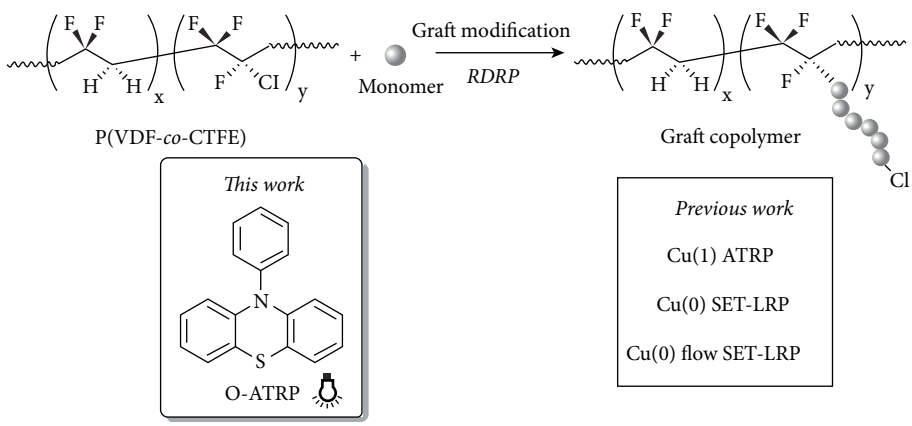

Figure 3: Poly(vinylidene fluoride-*co*-chlorotrifluoroethylene) modification via organocatalyzed atom transfer radical polymerization. (Adapted with permission from Ref. [41]).

A series of novel core-extended *N*,*N*-diaryl dihydrophenazine photoredox catalysts were developed by the same group, which was demonstrated to be the most efficient organic catalyst in O-ATRP system. By employing this photoredox catalyst, polymerization could be mediated at low catalyst loadings of 5–50 ppm in a well-controlled manner, maintaining excellent control over the polymerization. Advantages of these core-extended *N*,*N*-diaryl dihydrophenazine photoredox catalysts were demonstrated by preparing polymers with complex architectures including star polymers and triblock copolymers. The broad utility was also manifested by the oxygen tolerance and scalability. The catalysts with only 50 ppm loading were able to control the polymerization of MMA in the presence of air with scale-up productivity from 1 g of PMMA to 5 g [46].

*2.4. **N**-Aryl Phenoxazines.* Miyake and co-workers examined *N*-aryl phenoxazines as organic photoredox catalysts for the preparation of well-defined polymer (Figure 7) [47]. Upon irradiation, the excited state of *N*-aryl phenoxazines photoredox catalyst displayed strongly reducing capability, which would express excellent performance if they will be able to transfer the charge. To further understand the performance of photoredox catalyst and establish the design principle, phenoxazines were investigated in comparison of dihydrophenazines and phenothiazines. It was found that keeping the phenoxazine catalyst with planar conformation during the catalytic cycle would facilitate the preparation of well-defined polymers. With these rules in mind, a substituted phenoxazine (3,7-di(4-biphenyl) 1-naphthalene-10-phenoxazine) was explored as a visible light photoredox catalyst that indicated better performance comparing with UV-absorbing phenoxazines and other photoredox catalyst in O-ATRP. By employing this planar conformation photoredox catalyst with the irradiation of white LEDs, resultant polymers with predicted molecular weights, and narrow molecular weight distributions of 1.13–1.31 as well as quantitative initiator efficiencies were obtained. It exhibited remarkable superiority compared to previously reported dihydrophenazines and phenothiazines.

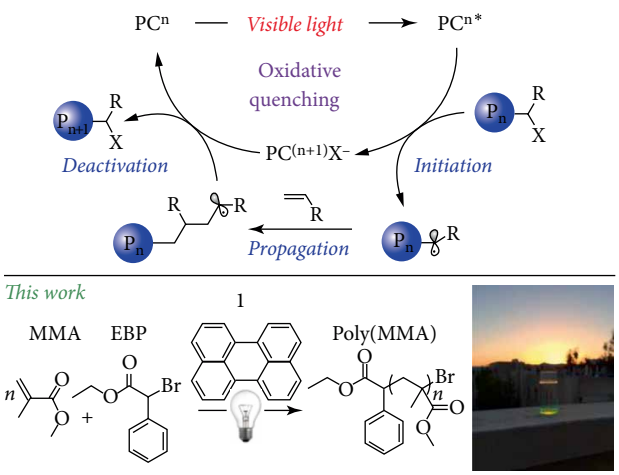

Figure 4: Proposed mechanism for a photoredox-mediated ATRP proceeding through an oxidative quenching pathway with alkyl halides (top) and the use of perylene as an organic photocatalyst for the polymerization of methyl methacrylate with alkyl bromide initiators (bottom) and a photograph of this polymerization being mediated by natural sunlight (bottom right). (Adapted with permission from Ref. [42]).

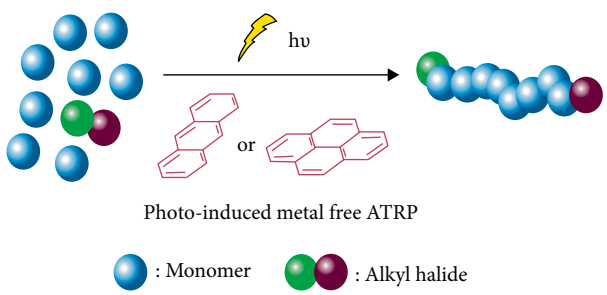

Figure 5: Photoinitiated metal-free controlled/living radical polymerization using polynuclear aromatic hydrocarbons. (Adapted with permission from Ref. [43]).

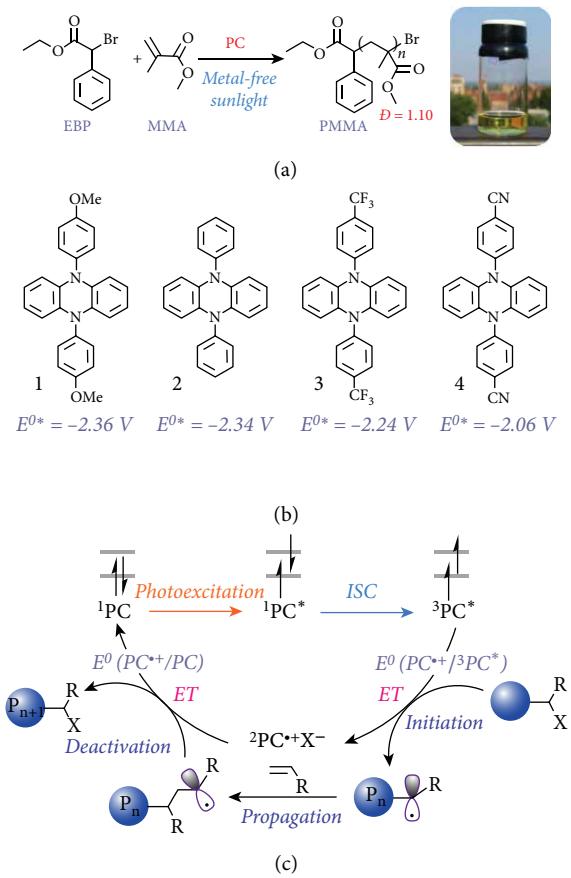

Figure 6: PC development for O-ATRP. (a) Polymerization of MMA to well-defined polymers by using photoredox O-ATRP driven by sunlight. (b) Structures of the diphenyl dihydrophenazine PCs 1 to 4 used in this study. (c) A proposed mechanism for ATRP mediated by a PC via photoexcitation to $^1PC^*$, intersystem crossing (ISC) to the triplet state $^3PC^*$, ET to form the radical cation doublet $^2PC^{\bullet+}$, and back ET to regenerate PC and reversibly terminate polymerization. (Adapted with permission from Ref. [44]).

A family of core-substituted *N*-aryl phenoxazines was developed by Miyake and coworkers as photoredox catalysts to mediated O-ATRP in the presence of air [48]. Although the potential deleterious effect of oxygen was present, good initiator efficiency ($I^* = M_{n,theo}/M_n \times 100$) being 84–99% and low dispersity was observed under air. Temporal control over O-ATRP operated under air was manifested by employing "on-off" experiment, which was carried out over the course of several days. The ability to synthesize block copolymers was also demonstrated. Reduction of the volume of air in the reaction vial headspace was the key factor for allowing the polymerization that operates in a controlled manner. It was in accordance with the effects of air on Cu mediated ATRP system. By exposing the O-ATRP system under the air, I^* was consistently lower than the polymerization process under nitrogen, indicating the existence of additional side reactions in the presence of air. Miyake and coworkers also adapted the photoinduced. O-ATRP to a continuous flow with different photoredox catalyst including *N*,*N*-diarylphenazines, perylene, and *N*-aryl phenoxazines. Improved polymerization results were achieved, by using continuous flow technology.

2.5. Benzaldehyde Derivatives. Yang and co-workers employed benzaldehyde derivatives, including *p*-anisaldehyde, *p*-cyanobenzaldehyde and 2,4-dimethoxy benzaldehyde as organic photoredox catalysts to mediated O-ATRP of methacrylate (Figure 8) [49]. By using this simple benzaldehyde molecule as photoredox catalyst, controlled radical polymerization process with mild reaction condition was reached. In the presence of perfluoro-1-iodohexane (CF3 (CF2)5-I) as initiator and *N*,*N*-dimethylaniline (DMA), linear dependence of molecular weight on monomer conversion was observed. Poly (poly (ethylene glycol) methacrylate) (PPEGMA) were successfully obtained via this benzaldehyde molecule-based photo-polymerization. The block copolymers of PPEGMA-*b*-PMMA, PPEGMA-*b*-PBnMA and PBnMA-*b*-PMMA were achieved by the chain extension reaction, which revealed the good end group fidelity. The structures of block polymers were confirmed by ^{1}H NMR and

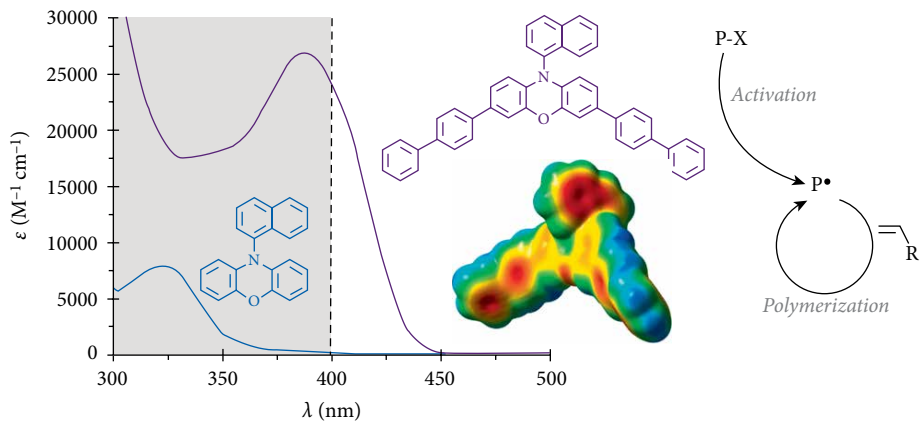

Figure 7: Structure, ESP mapped electron density of UV–vis spectrum of the visible light absorbing phenoxazine and the proposed mechanism. (Adapted with permission from Ref. [47]).

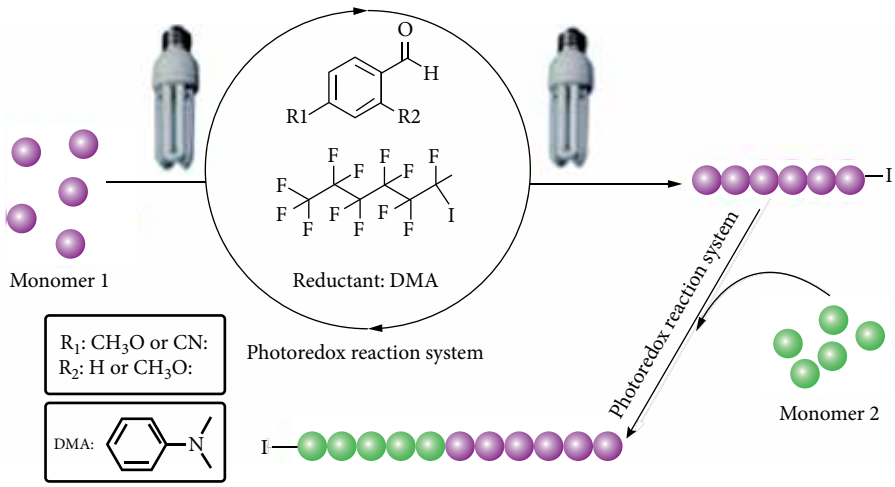

Figure 8: Photoinduced controlled radical polymerization of methacrylates with benzaldehyde derivatives as organic catalysts. (Adapted with permission from Ref. [49]).

self-assembled micellar aggregation of PPEGMA-*b*-PMMA and PPEGMA-*b*-PBnMA in aqueous medium.

2.6. Fluorescein. Cheng and co-workers explored fluorescein (FL) to serve as photoredox catalyst for the polymerization of MMA via the mechanism of photoinduced electron-atom transfer radical polymerization (PET-ATRP) (Figure 9) [50]. The proposed mechanism of FL mediated PET-ATRP under visible light irradiation was illustrated in Figure 9. Under the irradiation of light irradiation, excited state of FL^* experienced a reactive quenching pathway by electron donor to form a strong single-electron reductant $FL^{\bullet-}$, which could react with organic halide to produce radical species. The amine radical cation $Et_3N^{\bullet+}$ from the oxidation of TEA was also generated in this step, which subsequently participated in the single electron oxidation of bromine anion to generate bromine radical. $FL^{\bullet-}$ then transferred an electron to the alkyl bromide of the initiator or polymer chain ends, to form an electron-deficient alkyl radial/propagating radical and regenerated the ground state FL. The propagating radicals were deactivated by bromine radical original from the bromine anion reacting with radical cation $Et_3N^{\bullet+}$ via single electron oxidation route.

2.7. 1,2,3,5-Tetrakis(Carbazol-9-Yl)-4,6-Dicyanobenzene. A novel photoredox catalyst of 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) with powerful excited state reduction potential was presented by Cheng and Zhang' group (Figure 10) [51]. By using this catalyst, the metal-free ATRP of MMA was successfully conducted in the presence of ethyl α-bromophenylacetate as initiator under the irradiation of blue light emitting diode (LED) at room temperature. Comparing with other O-ATRP system that required high concentration of photoredox catalyst to maintain excellent control over the polymerization, only ppm level loading of 4CzIPN was employed in this metal-free ATRP system. The "living/controlled" character was demonstrated by the polymerization kinetic study, chain extension and "on-off" light switching experiment. The proposed mechanism was shown as Figure 10. The excited state of photoredox catalyst was formed under the irradiation of visible light, which activated the alkyl bromide

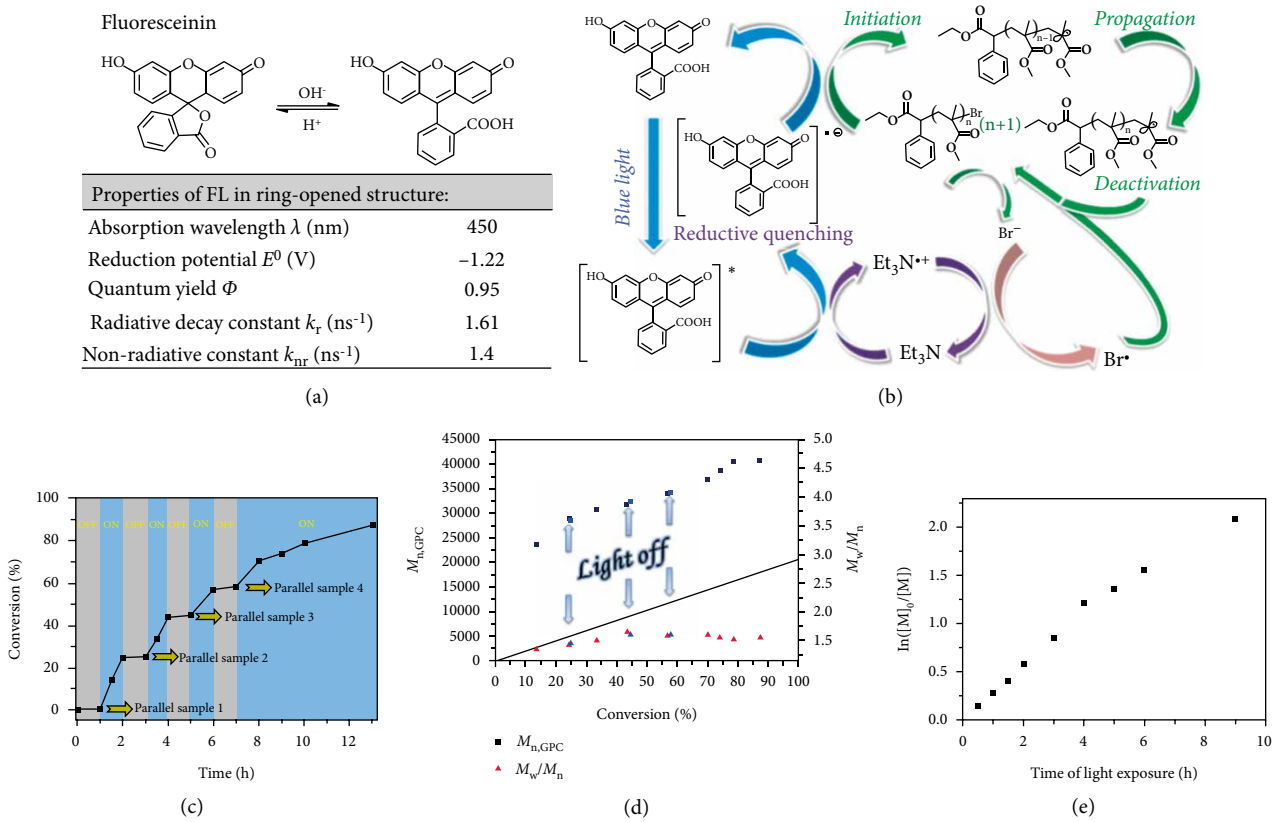

FIGURE 9: (a) pH-dependent equilibrium between the spirolactone form and the ring-opened form of fluorescein (FL) and optical properties of fluorescein in ring-opened structure. (b) Proposed mechanism of metal-free PET–ATRP photo-mediated with fluorescein as an organic photocatalyst. (c) Plot of monomer conversion versus time demonstrating the effect of blue light on the control over polymerization propagation through repeated "on-off" cycling of irradiation (blue regions) and light source removal (shaded regions); number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) versus conversion (d) and $\ln([M]_0/[M])$ as a function of exposure time (e) for metal-free PET–ATRP of MMA in the "on/off" light irradiation experiment. Polymerization conditions: $[\mathrm{MMA}]_0 : [\mathrm{EBPA}]_0 : [\mathrm{FL}]_0 : [\mathrm{TEA}]_0 = 200 : 1 : 0.15 : 4.5$, VMMA = 1.0 mL, VDMSO = 2.0 mL; samples were irradiated by a blue LED at rt. (Adapted with permission from Ref. [50]).

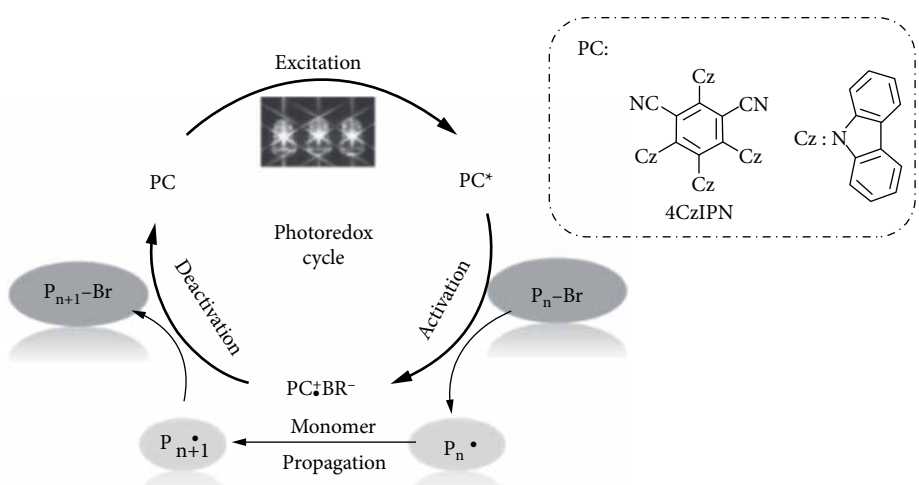

FIGURE 10: Proposed polymerization mechanism of photoinduced metal-free ATRP with ppm level of 4CzIPN as an organic photocatalyst. (Adapted with permission from Ref. [51]).

to generate propagating radicals $P_n^{\bullet}$ and intermediated state $PC_{\bullet}^{+}Br^{-}$. The propagating radical of $PC_{n+1}^{\bullet}Br^{-}$ was deactivated by $PC_{\bullet}^{+}Br^{-}$ to form ground state PC and dormant species.

2.8. Thienothiophene Derivatives. Yagci and co-workers reported conjugated electron-rich thienothiophene derivatives as the organic photoredox catalyst to mediate photoinduced

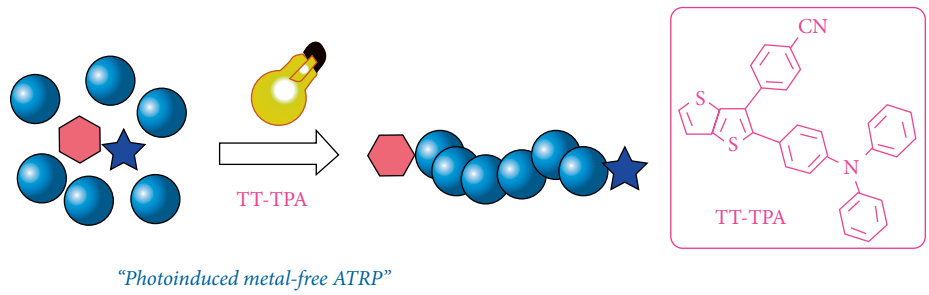

Figure 11: Photoinduced metal-free atom transfer radical polymerization using highly conjugated thienothiophene derivatives. (Adapted with permission from Ref. [52]).

metal-free ATRP (Figure 11) [52]. Series of thienothiophene derivatives were designed and synthesized. Among them, 4-[2-(4-diphenylaminophenyl)-thieno[3,2-*b*]thiophen-3-yl] benzonitrile (TT-TPA) was the most efficient catalyst due to the favorable thermodynamic properties. Polymerizations of MMA were well controlled to yield polymers with predictable molecular weights, narrow distributions and good chain end functionality.

3. Summary and Outlook

Reversible deactivation radical polymerizations (RDRP) have become the robust and versatile tools to prepare well-defined polymer with precise structures. ATRP is the one of most widely applied RDRPs. The metal contamination of traditional ATRP is the main limiting point for application, especially in the field of microelectronic and biomedical materials. Metal-free organocatalyzed ATRP (O-ATRP) has attracted considerable attention since 2014. It provides a perfect solution for addressing the challenge of metal contamination in traditional transition-metal catalyzed ATRP. With the development of O-ATRP system, increasing number of photoredox organic catalysts were disclosed and the mechanisms were also revealed. This minireview summarized the most recent progress in O-ATRP and highlighted the organic photoredox catalysts comprehensively. Phenothiazines, polynuclear aromatic hydrocarbons, dihydrophenazine, *N*-aryl phenoxazines, benzaldehyde derivatives, fluorescein, 4CzIPN, and thienothiophene derivatives and the catalysis mechanism were discussed in sequence. The features of the organic photoredox catalysts were also discussed. The development of photoredox catalysts enabled the synthesis of polymers with controlled molecular weight and distribution, high initiator efficiency and low PDI while avoiding the metal residue in the polymer products.

Although remarkable progress has been achieved in O-ATRP, the promising potential of this approach has not been completely investigated. The further research may be focused on the exploration of the novel organic photoredox catalysts systems which have more powerful reducing potential in visible light area. The less catalyst loading and impressive tolerance of larger scope of functional monomers will be satisfied to yield polymers with various functions.. Adaption of O-ATRP to continuous flow approach has been demonstrated to be an ideal solution to provide efficient irradiation, which allows for the improved polymerization process and enables the scalability and reliability of the system comparing with the batch reaction system [53, 54]. Surface initiated ATRP (SI-ATRP) catalyzed by organic photoredox catalysts has become an attractive research topic in preparation of functional polymer surfaces. The fabrication of patterned polymer brushes requires advanced technologies to spatially localize initiating species. The development of O-ATRP supplies an alternative approach to achieve complex three-dimensional patterned surface. The future improvement for organocatalyzed SI-ATRP should target on extending the monomer scope to prepare the increasingly complex functional materials on varied surfaces. Moreover, the advancement of biomedical and microelectronic materials will soar by using O-ATRP technology.

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgments

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