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Leveraging reactivity to gain precise control over macromolecular structures with photocatalysis in reversible-deactivation radical polymerizations

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Photocatalysis has gained a prominent role in reversible-deactivation radical polymerization (RDRP) techniques. Photocatalyzed polymerizations are appealing due to ease of implementation, oxygen tolerance, spatiotemporal and orthogonal control, and increased uniformity in polymer chain ends compared to exogenous initiation. Due to these attractive features, photocatalysis has been widely used and incorporated into atom transfer radical polymerization (ATRP) and reversible addition–fragmentation chain transfer (RAFT) polymerization. Herein, recent examples of photocatalysis in RDRP techniques at the macroscopic, topological, and primary sequence levels of control are presented to highlight how photocatalysis has led to advances at all levels of polymer chemistry. For example, photocatalysis can be used for the selective photoactivation of distinct end-groups, enabling the synthesis of sequence-defined oligomers/polymers, or complex polymer topologies. However, there are still significant gaps in photocatalyzed RDRP (*e.g.*, kinetic understanding of photocatalyst (PC) interplay with different chain ends, PC development, and effects of reaction conditions on PC performance). By identifying how photocatalysis and reaction conditions can be tuned to mediate polymerization kinetics and selectivity, more defined and controlled polymer sequences, topologies, and macroscopic properties will be unlocked.

Introduction

The first report of photocatalysis was published almost 50 years ago by Kellogg and coworkers.[1] However, a resurgence in this field has occurred over the past 15 years, driven by the synthetic ease and tunability of photophysical properties of catalysts, resulting in diverse photocatalyst (PC) derivatives.[2] Photocatalysis is widely used in synthetic transformations, with over 35 applicable organic/metal-centered catalysts being used.[2–4] Photocatalysis has been widely adopted to facilitate previously-difficult transformations such as hydrogen atom transfer reactions,[5–7] carbon–heteroatom bond formations,[8–10] carbon–carbon bond formations,[11–13] amine α-functionalization,[14–16] and enantioselective transformations.[17–19] The adoption of photocatalysis in small molecule chemistry has led to significant advances in drug discovery and synthetic methodology.[20–22] Although photocatalysis has made a lasting impact on small molecule transformations, photocatalyzed reactions have also been used in method development for polymer synthesis.

Light and photocatalysis have been used in polymer chemistry since the beginning of the 21st century, but significantly fewer PCs have been employed in photocatalyzed radical polymerizations (PCRP) compared to in small molecule transformations.[23–25] Despite differences in PC development, implementing light and photocatalysis in polymerizations has been shown at all levels of polymer synthesis, from the macroscopic scale down to the primary sequence.[23] Using light in polymer chemistry has led to advances in 3D printing,[26–28] surface coatings,[29,30] self-healing properties,[31,32] syntheses of copolymer architectures,[33–35] and sequence-defined polymers.[36,37]

Reversible-deactivation radical polymerization (RDRP) techniques have seen widespread implementation of photocatalysis with atom transfer radical polymerization (ATRP),[38] first reported in 2012 by Hawker and coworkers,[39] and with reversible addition–fragmentation chain transfer (RAFT) polymerization,[40] first reported in 2014 by Boyer and coworkers.[41] There are various types of photocatalyzed ATRP—photoinduced electron/energy transfer (PET) ATRP, photoinduced organocatalyzed ATRP, metal-free ATRP, *etc.*—which we will refer to collectively as photocatalyzed ATRP throughout this perspective. For RAFT polymerization, only PET-RAFT polymerizations will be highlighted, as the mechanism is distinct from photoiniferter[42] and photoRAFT (which requires the degradation of a photoinitiator to introduce radicals).[43] Readers interested in photoiniferter and/or photoinduced ATRP are referred to recent reviews/perspectives on these mechanisms.[42,44] Photocatalyzed ATRP and PET-RAFT polymerizations enable oxygen tolerant polymerizations,[45–47] higher chain-end fidelity,[48] and more uniform polymer end groups compared to RAFT polymerizations using exogenous initiators,[25,43] leading to facile polymer

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synthesis with fewer polymer chain end defects. Photocatalysis can be performed with low-energy red, near IR, or white light as opposed to more energy-intensive routes, such as heat or UV/blue light.[49–52] Herein, the advantages, disadvantages, and limitations of PCRPs will be discussed by highlighting the uses and innovations of photocatalysis in polymer chemistry at the macroscopic, topological, and primary sequence levels. Subsequently, by focusing future efforts on the less-understood aspects of PCRPs (tailoring PCs to target selective photoactivation, interplay of PCs and other reaction conditions, and PC derivatization/development),[53–55] PCRPs will provide access to defined, complex topologies and sequences to parallel the significant advances that photocatalysis has afforded for small molecule synthesis.

Polymerization methods

Photocatalyzed ATRP and PET-RAFT polymerizations provide reaction tunability according to catalyst and incident wavelength of light, leading to straightforward ways to gain spatiotemporal control and selective photoactivation. Additionally, in PET-RAFT polymerization, a PC introduces a new mechanism for control: activation–deactivation of the chain end by the PC.

ATRP

Transition metal-mediated RDRP was introduced in 1995.[56–58] Specifically, the Matyjaszewski group introduced ATRP using copper as a transition metal catalyst.[59,60] ATRP is governed by the equilibrium between dormant and active chains, which is mediated by a transition-metal catalyst, typically a Cu(I) species (Fig. 1A).[38] The catalyst can cleave a carbon–halogen (or pseudo–halogen) bond, leading to the formation of a Cu(II)*X* species and an active radical on the chain end that can propagate with monomer in solution. The active chain end can be reversibly deactivated back to a dormant species by reducing the Cu(II)*X* species, forming a (pseudo-) halogen chain end, and restoring the Cu(I) catalyst. ATRP controls the growth of most chains through the ATRP equilibrium, which limits the fraction of dead chains to a small fraction of total chains in the system, leading to a controlled polymerization.[61] Using photocatalysis in ATRP allows for lower Cu loadings (in addition to non-photocatalyzed methods, including activator regenerated by electron transfer (ARGET),[62] initiators for continuous activator regeneration (ICAR),[63] and photoinduced ATRP),[64–67] providing down to ppb levels of Cu or entirely replacing Cu with a PC.

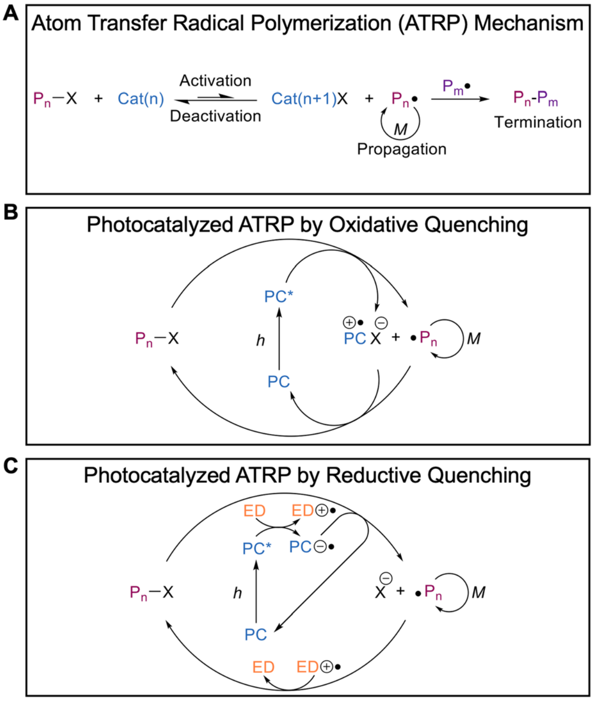

Fig. 1 (A) General mechanism of atom transfer radical polymerization (ATRP) highlighting mechanistic steps for control, where *X* can be a halogen or a pseudo-halogen. (B) General mechanism of photocatalyzed ATRP through the oxidative quenching pathway (PC = photocatalyst). (C) General mechanism of photocatalyzed ATRP through the reductive quenching pathway (ED = electron donor).[24]

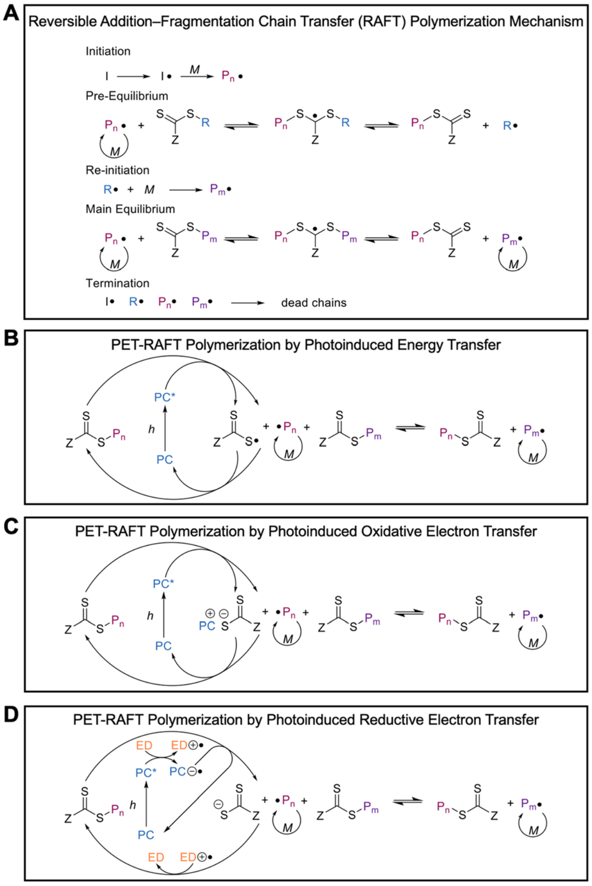

Fig. 2 (A) General mechanism of reversible addition–fragmentation chain transfer (RAFT) polymerization highlighting mechanistic steps for control. (B) General mechanism of photoinduced electron/energy transfer (PET) RAFT polymerization through the photoinduced energy transfer pathway (PC = photocatalyst). (C) General mechanism of PET-RAFT polymerization through the photoinduced oxidative electron transfer pathway. (D) General mechanism of PET-RAFT polymerization through the photoinduced reductive electron transfer pathway (ED = electron donor).

Photocatalyzed ATRP, first reported by the Hawker group,[39] is compatible with both metal-centered PCs[68] and organic PCs.[69,70] Within photocatalyzed ATRP, the activation–deactivation cycle of chains can proceed through either an oxidative- or reductive-quenching cycle, with both proceeding through electron transfer (Fig. 1B and C).[25,71] Although the chemistry on the chain end remains the same in both instances, the activation mechanisms vary. In the oxidative-quenching pathway, the excited PC directly reduces the alkyl halide to activate the chain end, which can then propagate with monomer in solution (Fig. 1B). The resultant radical cation PC oxidizes the chain end and deactivates it, completing the catalytic cycle. In the reductive-quenching pathway, the excited PC is initially reduced by a sacrificial electron donor (ED)—commonly an amine—and the radical anion PC reduces the alkyl halide to activate the chain end (Fig. 1C). Activating the chain end restores the PC to the ground state through oxidation. Separately, the radical cation ED oxidizes the active chain end to complete the catalytic cycle, yielding the alkyl halide. Although photocatalyzed ATRP can proceed through two mechanistic pathways, both yield the same polymers. A variety of different PCs have been employed in ATRP including, but not limited to, phenothiazines,[72] phenoxazines,[73] dihydrophenazines,[70] xanthene dyes[74,75] perylene,[69] Ir(ppy)$_3$,[39] and porphyrins.[76]

RAFT polymerization

RAFT polymerization was first introduced in 1998 by Rizzardo, Moad, and Thang.[77] Prior to RAFT polymerization, photoiniferter mediated by xanthates had been used in the 1980s.[78–80] RAFT polymerization is governed by a degenerative chain transfer process instituted by the presence of a chain transfer agent (CTA).[40] CTAs containing a thiocarbonylthioyl (TCT) group can be xanthates, dithiocarbamates, dithiobenzoates, or trithiocarbonates. In a typical RAFT polymerization, radicals are introduced by exogenous compounds such as azo initiators (Fig. 2A, initiation step).[40] After the initiator undergoes addition to monomer, the carbon-centered radical chain end will add to a C═S bond in the TCT and cleave the *R*-group, initiating a new chain (Fig. 2A, pre-equilibrium step). Once all *R*-groups have been initiated and added to monomer (re-initiation step), degenerative chain transfer between CTAs and active chain ends ensues, resulting in a controlled polymerization (Fig. 2A, main equilibrium step). Degenerative chain transfer is how control is garnered in RAFT polymerization, as the process readily activates and deactivates chain ends.[81]

PET-RAFT polymerization, first reported by the Boyer group,[41,52,82–84] has been performed with metal-centered PCs and organic PCs. Photocontrolled interconversion of radical and cationic polymerization methods using PCs has been shown using RAFT polymerization from the Fors group.[85–87] PET-RAFT polymerization is unique, as the activation–deactivation of chains can occur through three pathways: photoinduced energy transfer, photoinduced oxidative electron transfer, or photoinduced reductive electron transfer (Fig. 2B–D).[88] Photoinduced energy transfer most often occurs with metal-centered catalysts in which the excited PC releases photothermal energy upon relaxation, resulting in homolytic cleavage of the *R*-group C–S bond on the TCT (Fig. 2B). The homolytic cleavage results in

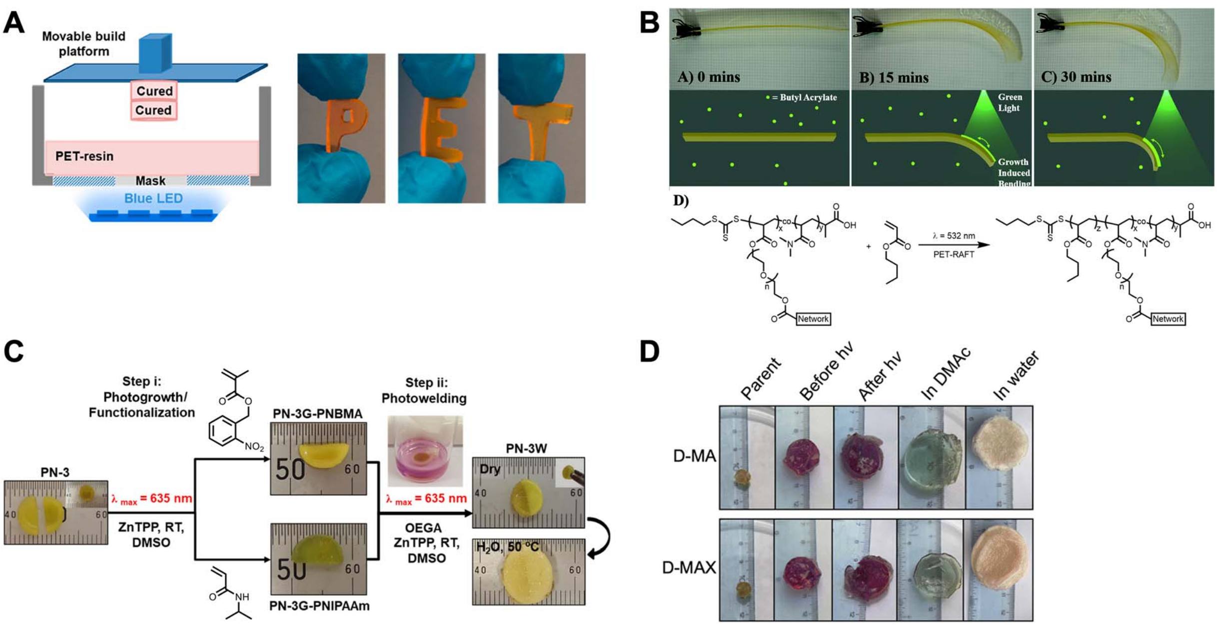

Fig. 3 (A) Bottom-up digital light processing 3D printer and images of letters printed using photoinduced electron/energy transfer reversible addition–fragmentation chain transfer (PET-RAFT) polymerization. Reproduced with permission from ref. 89. Copyright 2020, American Chemical Society. (B) Growth-induced bending of a 4D printed material using PET-RAFT polymerization. Reproduced with permission from ref. 90. Copyright 2020, Royal Society of Chemistry. (C) Photogrowth and photowelding of polymer networks using PET-RAFT polymerization. Reproduced with permission from ref. 91. Copyright 2021, American Chemical Society. (D) Photogrowth of polymer networks to change materials properties using PET-RAFT polymerization. Reproduced with permission from ref. 92. Copyright 2024, Royal Society of Chemistry.

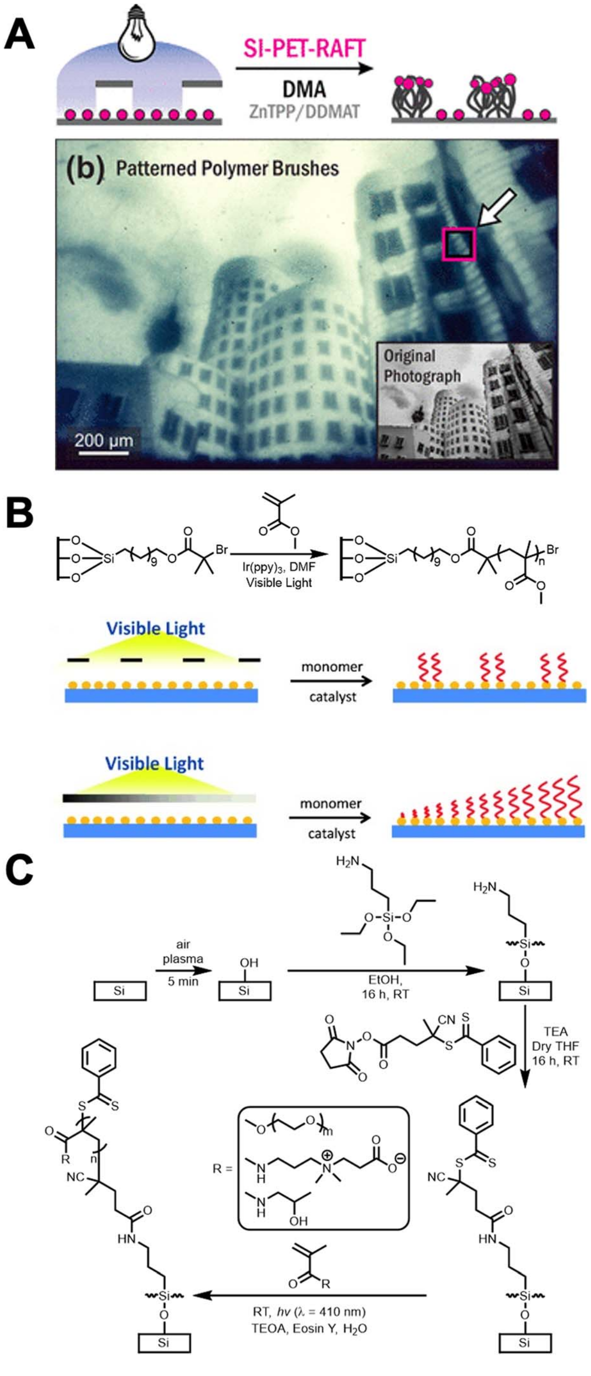

Fig. 4 (A) Schematic of surface-initiated polymerizations using photomasks and an optical micrograph using photoinduced electron/energy transfer reversible addition–fragmentation chain transfer (PET-RAFT) polymerization. Reproduced with permission from ref. 93. Copyright 2019, American Chemical Society. (B) Schematic for performing surface-initiated polymerizations using photomasks or neutral density filters using photocatalyzed atom transfer radical polymerization (ATRP). Reproduced with permission from ref. 94. Copyright 2013, Wiley Online Library. (C) Synthetic scheme for the surface-initiated PET-RAFT polymerization of antimicrobial polymers on silicon surfaces for antifouling applications. Reproduced with permission from ref. 95. Copyright 2020, American Chemical Society.

a carbon-centered radical on the chain end and a sulfur-centered radical on the TCT. The chain ends are deactivated through reversible combination or through chain transfer. In photoinduced oxidative electron transfer, the excited PC reduces the TCT, resulting in an oxidized PC, anionic TCT, and a carbon-centered radical on the chain end (Fig. 2C). In photoinduced reductive electron transfer, the excited PC is first reduced by an ED—typically a tertiary amine—and the reduced PC is oxidized by the TCT, resulting in a neutral PC, oxidized ED, anionic TCT, and a carbon-centered radical on the chain end (Fig. 2D). Deactivation of the chain end can occur through degenerative chain transfer, but regeneration of the PC must occur through electron transfer to close the catalytic cycle.

All three mechanisms will result in the same polymeric material being synthesized. A variety of PCs have been employed in PET-RAFT polymerization including, but not limited to, $Ir(ppy)_3$,[47,96] porphyrins,[82,97] $Ru(bpy)_3$,[45] xanthene dyes,[98,99] and photoactive proteins.[100]

PCRP innovation on the macroscopic level

Spatiotemporal control with oxygen tolerance can be achieved by using PCRPs,[89] leading to PCRP use in various applications including 3D printing and surface patterning. PET-RAFT polymerization is used for the synthesis of 3D and 4D materials due to fast reaction times, oxygen tolerance, and spatiotemporal control (Fig. 3A).[89,90,101] A 4D material is when a 3D material undergoes a transformation in response to an external stimuli (*e.g.*, light, pH, temperature) over time.[91] Another advantage of using PCRP for 3D and 4D materials is that prints can be chemically modified after the initial polymerization. Due to the retention of chain ends, chain extensions can be performed to modify material properties, while selectively retaining or changing the overall shape of the initial print.[90–92,102] Jin and coworkers used PCRPs to synthesize 3D materials and transform them into 4D materials by using light as an external stimulus to induce bending, changing the print shape (Fig. 3B).[90] Retaining chain ends also aids in the synthesis and expansion of structurally tailored and engineered macromolecular (STEM) gel networks. The chain ends enable modification of physical properties and self-healing networks by introducing additional monomer(s) (Fig. 3C).[92,103–105] We have previously demonstrated network expansion and physical property modifications using PCRPs. This work resulted in 1.5× larger organogels compared to the starting gels, impacting swelling properties in *N*,*N*-dimethylacetamide (DMAc) and water (Fig. 3D).[92] Network expansion of STEM gels can be performed through other light-mediated methods such as photoiniferter.[106–108] However, without a PC, the polymerization requires degassing and UV or blue light, while PCRPs can be performed at longer wavelengths of light without degassing.

Spatiotemporally controlled PCRPs have been used for surface-initiated polymerizations.[93–95,109–115] Patterning surfaces is integral for the fabrication of electronics,[116] microarrays of cells,[117] sensors,[118] and photonic crystals.[119,120] Surface-initiated polymerizations previously could be performed with thermal or redox initiators with limited spatial control, but light-mediated/

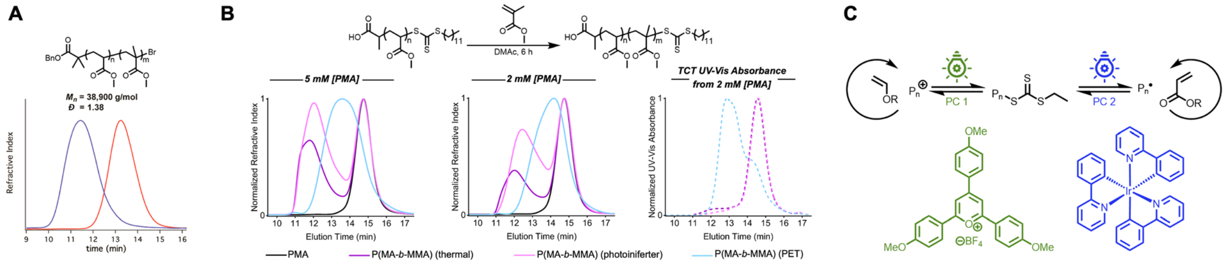

Fig. 5 (A) Size-exclusion chromatography (SEC) refractive index (RI) traces of block copolymers going against conventional blocking order in reversible-deactivation radical polymerization (RDRP) using photocatalyzed atom transfer radical polymerization (ATRP). Reproduced with permission from ref. 68. Copyright 2014, American Chemical Society. (B) SEC RI traces of block copolymers going against conventional blocking order using thermal initiation, photoiniferter, or photoinduced electron/energy transfer (PET) initiation in reversible addition–fragmentation chain transfer (RAFT) polymerization at different concentrations. Reproduced with permission from ref. 96. Copyright Wiley Online Library. (C) Schematic of converting between cationic and radical polymerizations using selective photocatalysts and wavelengths in RAFT polymerization. Reproduced with permission from ref. 85. Copyright 2021, American Chemical Society.

initiated or photocatalyzed polymerizations lead to significantly better control over surface patterning.[121] PCRP development led to the synthesis of patterns and gradients on surfaces using photomasks, where only selected areas are irradiated to induce polymerization (Fig. 4A and B).[94] Selectively irradiating and polymerizing regions of interest introduces complex multi-layer 3D pattern synthesis[93] with micron length scale resolution,[122] which were inaccessible using RDRP before light-mediated/photocatalyzed polymerizations. Spatiotemporally controlled surface patterning has led to surface modifications for materials with antifouling (Figure 4C),[95,114] antifogging,[123] self-healing properties,[124] and the development of reusable heterogeneous catalysts.[125] Overall, PCRPs have led to advances in polymer synthesis at the macroscopic scale by enabling the modification of print/gel material properties and multi-layer surface patterning.

PCRP innovation on the topological level

Controlling polymer topology is important because it ultimately dictates the physical properties and applications.[126] PCRPs can be used to synthesize homopolymers, statistical, gradient, and block copolymers,[41,49,70,127] with polymer architectures including linear, star, brush, or hyperbranched structures.[128–132] Although these polymers can be synthesized through non-photocatalyzed RDRP techniques, photocatalysis provides high chain end fidelity and more uniform chains compared to those prepared by exogenous initiators.[41,133]

Light-mediated photoiniferter polymerizations and PCRPs lead to better uniformity in block copolymer syntheses due to the elimination of exogenous initiators, which start new chains.[133,134] Uniform block copolymers with high end-group fidelity are exemplified in polymerization-induced self-assembly[35,46,135] and block copolymer networks using photocatalysis.[92,104] PCRPs also offer the unique advantage of overcoming blocking-order limitations in RDRP techniques (Fig. 5A and B).[68] Prior to PCRP, blocking order could be overcome in ATRP using a halogen-exchange reaction (requiring end-group modification).[136] However, Hawker and coworkers reported that blocking order can be reversed using photocatalyzed ATRP with $Ir(ppy)_3$ without the need for a halogen-exchange (Fig. 5A).[68] In RAFT polymerization, both photoiniferter and PET-RAFT polymerization can be used to reverse blocking order. Sumerlin and coworkers showed that reversing blocking order could be performed with photoiniferter using xanthates (which are better suited for less-activated monomers) due to the lower C–S bond dissociation energy (BDE) compared to other TCTs, but could not be performed with trithiocarbonates (which are better suited for more-activated monomers).[137] We reported that conventional blocking order in RDRP can be reversed with trithiocarbonates using PET-RAFT polymerization, leading to the synthesis of novel triblock copolymers (Fig. 5B).[96] Furthermore, using photocatalysis for block copolymer syntheses provides access to orthogonal stimuli to synthesize novel block copolymers. Fors and coworkers switched between cationic and radical RAFT polymerizations using selective PCs and discrete wavelengths, leading to previously unattainable vinyl ether and acrylic multiblock copolymers (Fig. 5C).[85,87] These reports demonstrate that by selecting PCs with desired photophysical properties, polymerization mechanisms can be switched by changing the irradiation wavelength. The opportunity to readily switch between radical, cationic, and/or anionic polymerization through photocatalytic conditions (*e.g.* PC, wavelength of light, temperature) will facilitate greater control and tunability in copolymer syntheses.

PCRPs have also been advantageous in the synthesis of graft copolymers, either from a polymer backbone or a protein. One main advantage to performing these polymerizations using light-mediated polymerizations is orthogonal control (Fig. 6A and B). Moad, Hawker, and Boyer used a chemoselective approach for the one-pot synthesis of polymer architectures using a two CTA system (Fig. 6B).[35,36,138] A CTA with a lower BDE compared to the other CTA was selectively activated by lower-energy green light *via* photoiniferter, while the other CTA remained uninitiated. Subsequently, introducing a PC activated both CTAs by PET, leading to the divergent synthesis of one-pot graft copolymers with simultaneous control over the backbone and side-chain lengths using an inimer (a molecule containing a polymerizable and initiating group). Finally, photocatalysis has also led to metal-free grafting-from polymerizations on

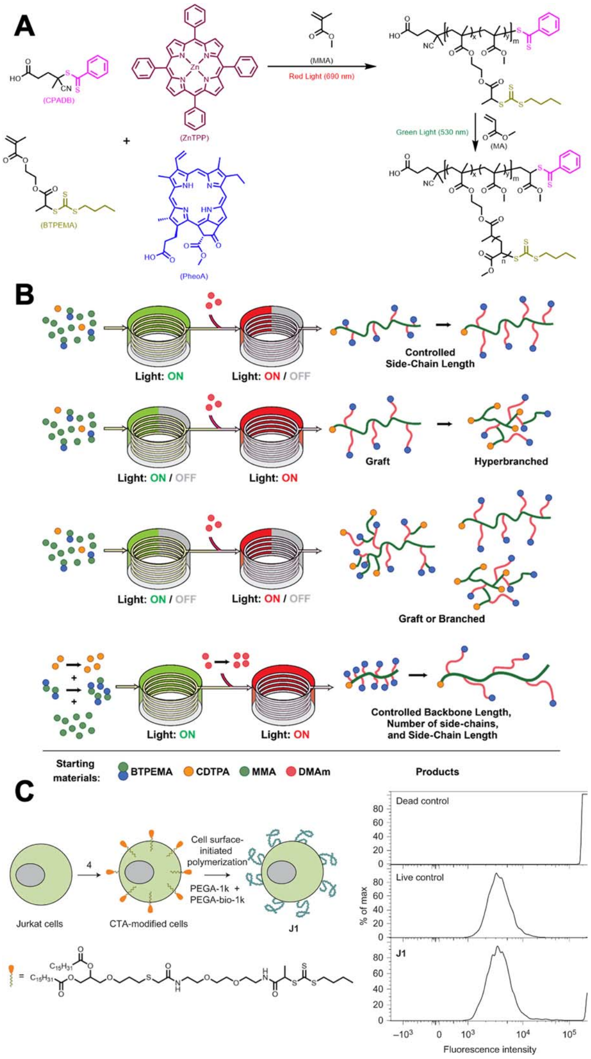

Fig. 6 (A) Schematic of selective photoactivation for the one-pot synthesis of a graft copolymer using an inimer using photoinduced electron/energy transfer reversible addition–fragmentation chain transfer (PET-RAFT) polymerization. Reproduced with permission from ref. 36. Copyright 2016, American Chemical Society. (B) Schematic of a divergent approach to synthesize different architectures depending on light on/off events and duration in flow through selective photoactivation using PET-RAFT polymerization. Reproduced with permission from ref. 138. Copyright 2021, American Chemical Society. (C) Schematic of grafting-from proteins using PET-RAFT polymerization and cell viability post-polymerization. Reproduced with permission from ref. 141. Copyright 2017, Springer Nature.

proteins. For example, PET-RAFT polymerizations with Eosin Y have been used to perform fast, metal-free polymerizations from proteins or cells at room temperature (Fig. 6C).[139–141]

Lastly, photocatalyzed ATRP and PET-RAFT polymerizations are used to synthesize higher-order polymer architectures including stars,[128,129] hyperbranched polymers,[128–132] and ultra-high molecular weight (UHMW) polymers. Light-mediated polymerizations lead to the facile synthesis of UHMW polymers under atmospheric conditions.[142–147] Prior to using light to perform UHMW polymerizations, high-pressure (5–6 kbar) and exogenous initiators were required, leading to longer polymerizations with higher disperisties.[148] Using light has enabled the synthesis of >1 × 10^6 g mol^{-1} UHMW polymers at atmospheric conditions in water or organic solvents in minutes to hours.[149–152]

Future work focusing on ATRP and RAFT polymerization end group BDEs will aid in efforts to selectively activate polymer end groups with photocatalysis. For example, BDE differences of over 11 kcal mol^{-1} have been reported for different R–X bonds in RAFT polymerization (R–S(=S)–Z) and ATRP (R–Br) using density functional theory calculations (DFT).[153–155] The 11 kcal mol^{-1} energy difference presents an opportunity to leverage the reduction potential of PCs for the selective activation of different bonds, leading to the facile synthesis of defined polymer architectures.

PCRP innovation on the primary sequence level

The primary sequence is the most difficult level of polymerization to control due to monomer energetics and RDRP following a Poisson distribution model in ideal cases.[156] Sequence-defined oligomers/polymers can be accessed using selective photoactivation in RDRP by studying the photophysical properties of PCs and chain end BDEs. Currently, when performing PCRPs, a PC is chosen that has a high enough reduction potential to cleave all the chain ends regardless of the chemical identity. However, as shown by DFT calculations,[153–155] orthogonal control to target and cleave specific bonds through PC selection is possible using PCRP. Thus, catalyst choice, wavelength of light selection, and polymerization conditions will be imperative for controlling the primary sequence. The selection of a PC for a desired BDE leads to sequence-defined/controlled polymers by performing sequential single-unit monomer insertion (SUMI) reactions through selective photocatalysis.[36,37] However, currently only short oligomers (<5 monomer units) can be synthesized using orthogonal control provided by chain end identity and PC choice. With the development of more PCs and a better understanding of how reaction conditions impact the photocatalytic process, sequence-defined polymers (>50 monomer units) could be achieved. Also, as discussed above, orthogonal and/or chemoselective control will enable easier syntheses of higher-order architectures or offer chemical handles for subsequent alterations to physical properties, topology, or molecular weight.

Photocatalyzed polymerizations have only been shown at the primary sequence level through SUMI reactions (Fig. 7A–D). To modulate the primary sequence, PCRP SUMI reactions are used for the installation of functional units within a polymer backbone. For example, we were able to perform a SUMI reaction within an acrylic backbone using PET-RAFT polymerization (Fig. 7A).[157] Through a combination of temperature and photocatalytic control (using $Ir(ppy)_3$ at low temperatures) a single vinyl ether could be inserted into an acrylic backbone.

Although most SUMI reports using PCRP techniques also rely on the poor homopolymerization of specific monomers,[158] photocatalysis is imperative for the uniformity of chains. If these polymerizations were performed using exogenous

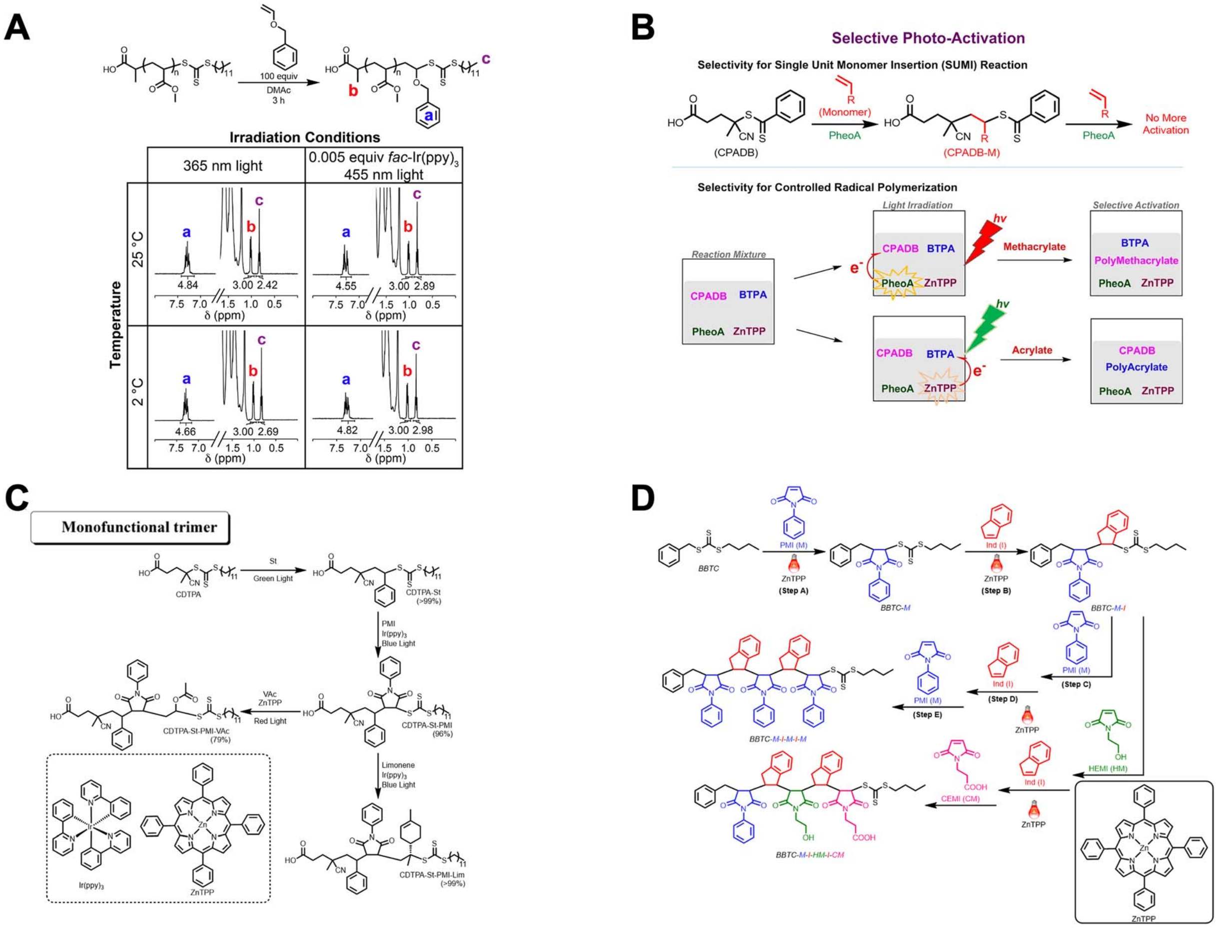

Fig. 7 (A) Schematic and ^{1}H nuclear magnetic resonance (NMR) spectra for a single unit monomer insertion (SUMI) reaction within an acrylic backbone using photoinduced electron/energy transfer reversible addition–fragmentation chain transfer (PET-RAFT) polymerization. Reproduced with permission from ref. 157. Copyright 2024, American Chemical Society. (B) Schematic of selective photoactivation for SUMI reactions and divergent synthesis using PET-RAFT polymerization. Reproduced with permission from ref. 36. Copyright 2016, American Chemical Society. (C) Schematic for iterative SUMI reactions for the synthesis of sequence-defined trimers using PET-RAFT polymerization. Reproduced with permission from ref. 37. Copyright 2016, Wiley Online Library. (D) Schematic for the synthesis of sequence-defined pentamers using iterative SUMI reactions *via* PET-RAFT polymerization. Reproduced with permission from ref. 160. Copyright 2018, American Chemical Society.

initiators, each iterative SUMI reaction would have compounding defects due to initiator-derived chains.[36,37,159] However, by using PCRPs, Boyer and coworkers utilized the reduction potentials of specific PCs to perform SUMI reactions with no initiator-derived defects.[36,37] In these examples, pheophorbide a (PheoA) had a high enough reduction potential to cleave the 4-cyanopentanoic acid C–S bond with a lower BDE on the *R*-group of the TCT. However, after a SUMI reaction using methyl methacrylate, no subsequent polymerization occurred because PheoA does not have a high enough reduction potential to cleave the new C–S bond with a higher BDE that was formed between methyl methacrylate and the TCT (Fig. 7B). By using selective photoactivation, sequence-defined trimers were synthesized (Fig. 7C). Recently, higher-order sequence-defined structures of up to 18 monomer units were synthesized using PCRP SUMI reactions (Fig. 7D).[160,161]

Although only oligomers have been synthesized by iterative SUMI reactions, there is still a significant unmet opportunity to synthesize sequence-defined structures with higher degrees of polymerization using selective photoactivation to mimic nature. Rather than proceeding through subsequent protection–deprotection steps like in solid-phase peptide synthesis,[162] selective photoactivation simply requires changing photocatalytic conditions, which will be aided by advances in heterogeneous catalysis and flow chemistry.

Future outlook

Photocatalysis is an essential process in organic and polymer chemistry, aiding in transformations that were previously inaccessible. PCRP has led to many significant advances in polymer synthesis, but the full potential of photocatalysis has not been explored. In small molecule transformations, PCs with desirable photophysical properties (*e.g.*, redox potential, excited state lifetime) are readily chosen to perform difficult transformations,[163–165] while comparatively fewer PCs are used for specific photophysical properties to conduct PCRPs. Previously, PCRPs have predominantly been used to synthesize

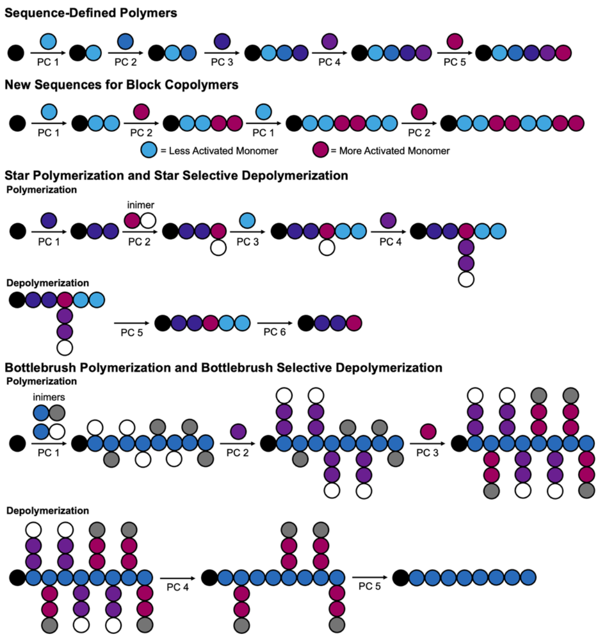

Fig. 8 Cartoon representation of how photocatalysis and selective photoactivation can lead to the synthesis of sequence-defined polymers, new block copolymer sequences, facile defined architecture synthesis, and for post-polymerization modifications.

materials in a more environmentally friendly manner,[24] to provide access to polymers with various architectures,[138] and to polymerize difficult monomers (*e.g.*, fluorinated monomers).[135] However, the distinct mechanism of polymer activation and the unique decoupling of radical introduction from other reaction conditions (*e.g.*, temperature) have not been widely used to access novel sequences and/or architectures.

Synthesizing more defined polymers and architectures using PCRP has been limited due to understudied aspects of how PCs and photocatalysis are impacted by differences in reaction conditions including, but not limited to, temperature, solvent, wavelength of light, light intensity, chain end identity, and polymerization additives (*e.g.*, amines/ligands). This gap in fundamental knowledge has ultimately limited how photocatalysis can be applied to RDRP techniques. For example, studying the corresponding photoredox processes, desirable photophysical properties of PCs, polymerization kinetics across different reaction conditions, and the reactivities of chain ends and PCs will provide insight into how photocatalysis can be used as a tunable chemical handle through various factors (*e.g.* wavelength of light and temperature) in RDRP (Fig. 8). These insights will address an unmet need to access polymers with defined sequences, architectures, and topologies through selective activation. Furthermore, using photocatalysis through photoactive proteins[100] to perform PCRPs could provide stereocontrol by leveraging the constricted active site of the protein, which is unattainable with current PCs. Combining selective photoactivation and photocatalysis with post-polymerization modifications (*e.g.*, metamorphosis,[166] selective depolymerization,[167,168] backbone functionalization,[169–171] and photoligation[172–175]) can lead to advanced and responsive architectures beyond what is accessible with PCRPs alone. Photocatalysis could be used to target and activate specific chain ends leading to new block copolymer sequences, the polymerization of a wider range of monomers, and possibly sequence-defined polymers. Enhanced control over these types of structures will lead to advances ranging from fundamental structure–function relationships of high-performance materials to addressing societally impactful challenges, like plastic recycling, drug development, and the fabrication of organoelectronics.

Take-home messages for improving photocatalysis use in RDRP techniques

Explore photophysical properties. PCs are understudied in how rates of activation are impacted by PC choice, temperature, wavelength of light, and/or light intensity variation in polymerization systems. A better understanding of rates of activation *via* PC across reaction conditions will provide fundamental insight, leading to more defined polymerization systems.

Emphasize selective photoactivation. PCs are primarily chosen in PCRPs because they are compatible with the polymerization technique being used (RAFT polymerization and/or ATRP) and the reduction potential of the PC is high enough to cleave all of the chain ends in solution. By leveraging the reduction potentials of PCs against the BDEs of chain ends, PCs can be chosen to perform specific transformations resulting in selective photoactivation of desired chains leading to sequence-defined polymers.

Investigate orthogonal control. Photocatalysis is rarely used in the presence of two separate initiators because most common PCs have a reduction potential high enough to cleave both sets of chain ends. Further investigation into initiator activation rates with differing PCs, wavelengths of light, and light intensities can lead to new synthetic pathways using inimers for the polymerizations of stars, brushes, and hyperbranched polymers.

Combine photocatalysis with post-polymerization modification. Photocatalysis use in RAFT polymerization and ATRP has mainly focused on performing polymerizations but has not widely been incorporated into post-polymerization modifications. A better understanding of the interplay between PCs and chain ends/pendent groups through redox potential and BDE or electron/energy transfer and functional groups can lead to selective depolymerization and/or modification of the backbone.

Author contributions

All authors contributed to the writing and revision of the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

Data availability

No primary research results, software or code have been included, and no new data were generated or analyzed as a part of this perspective.

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