Application of RAFT in 3D Printing: Where Are the Future Opportunities?

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ABSTRACT: Research into 3D printing using reversible addition−fragmentation chain transfer (RAFT) polymerization has garnered interest since it was first reported in 2019. This technique was initially developed to expand the scope of light-based 3D printing technologies by producing materials that can be modified postprinting, termed "living" 3D printing. The livingness can be achieved by incorporating reactivatable RAFT functionalities within the polymer networks, enabling 3D materials to be modified after printing. As the field of RAFT-mediated 3D printing has progressed, further studies have revealed its applications in advanced materials. These include spatially resolved surface functionalization and patterning, self-healing, welding, and nano- and microscale structuring of 3D polymers. Additionally, RAFT-mediated 3D printing enables the production of scaffolds with controlled interconnected channel-pore architecture, suitable for customized drug delivery. This Perspective provides a review of the chemical mechanisms employed in RAFT-mediated 3D printing and highlights the advanced materials manufactured through this technology. Potential research directions in this field are also discussed and organized for future investigation.
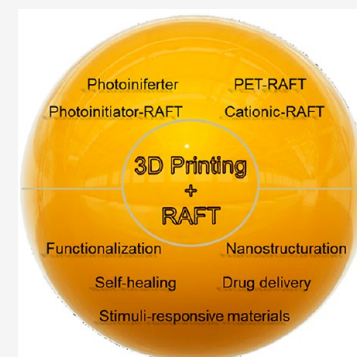
1. INTRODUCTION

The introduction of commercial 3D printing instruments in the 1980s led to a gradual increase in the scientific and industrial impacts of 3D printing, which are now widely evident in various sectors such as engineering, automotive industries, and health-care.[1,2] Polymers, which encompass various types of materials such as thermoplastics, elastomers, hydrogels, composites, and polymer blends, are the preferred materials for 3D printing. Based on the characteristics of polymers, the 3D printing process can be conducted using different techniques such as photo-polymerization, powder bed fusion, material and binder jetting, sheet lamination, and extrusion. Photopolymers account for a substantial portion of the 3D printing market (about 50%), making them the clear industry leader. Photopolymerization-based 3D printing relies on layer-by-layer cross-linking/curing of liquid photopolymer (resin) via a light-activated reaction, which may be accomplished using stereolithography (SLA), digital light processing (DLP), or continuous liquid interface production (CLIP). The underlying principle of these three methods is the transformation of a digitally sliced computer-aided design (CAD) model into physical layers by selectively cross-linking a photopolymer using light.[3−10] The primary difference between these methods lies in the type and location of the light source (such as a laser or LED and its position at the top or bottom of the vat) and the exposure principle (such as point-by-point exposure in SLA versus all-at-once exposure for each layer in DLP).[11,12] DLP-based methods can offer faster printing speeds, while SLA-based methods can produce materials with higher resolution and improved mechanical properties.

Recently, LCD-based 3D printing has emerged, which utilizes an LCD panel to project an image of the sliced 3D model onto a layer of photopolymer resin. The resin is then cured by light, building the object layer-by-layer. This technology is recognized for its fast printing speed and relatively low cost compared to other photopolymer-based 3D printing technologies. Ongoing research in vat photopolymerization continues to push the limits of 3D printing, with new materials and processes constantly being developed and improved.

Traditionally, uncontrolled free radical polymerization, cationic polymerization, or a combination of the two has been the most commonly used chemical mechanisms in photo-polymer-based 3D printing systems. Although these methods are being used in a growing number of manufacturing applications, they lack sufficient control over the properties of the final products and often produce materials that cannot be transformed postproduction. This results in "dead" materials, where the polymer chains cannot be reactivated to allow for further chain extension. This can limit the versatility of 3D printing applications and lead to inefficiencies.[13,14] One way to address these challenges is to utilize an alternative chemistry that
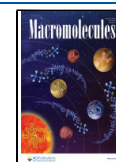
allows for the spatiotemporal incorporation of monomers into dormant "parent" polymers, leading to the creation of a wider variety of complex and diverse materials. This approach offers a means of altering the properties of 3D printed materials after the printing process, which enhances their adaptability compared to the traditional free radical polymerization technique.

As an improvement over traditional free radical polymerization, a group of polymerization methods termed reversible-deactivation radical polymerization (RDRP) has been developed in recent years. There are three types of RDRP, depending on the control agent used to provide reversible deactivation: nitroxide-mediated polymerization (NMP),[15] atom transfer radical polymerization (ATRP),[16] and reversible addition–fragmentation chain transfer (RAFT) polymerization.[17] Compared to traditional free radical polymerization, RDRP allows propagating radicals to be reversibly deactivated, leading to an equilibrium of active and dormant polymer chains. This equilibrium typically reduces the concentration of propagating radicals and decreases the number of termination events during pregelation. Also, the rapid activation rate in comparison to the propagation rates of RDRP processes leads to a mostly even distribution of dormant branched polymers in the early stages of network formation. This allows the polymer fragments to spread before they reactivate, preventing the formation of dense cross-linked clusters and producing a more uniform network.

In addition to creating a more uniform network structure, RDRP has another notable benefit over conventional radical polymerization. Once synthesized, the dormant RDRP agents can be reactivated to generate active species for additional chain growth and functionalization. As the RDRP technology developed, researchers studied ways to make transformable/reprocessable cross-linked polymer networks by utilizing the reactivatability of RDRP agents. Postsynthesis modification of RDRP-based polymer cross-linked networks has shown to be achievable in a variety of contexts,[18−20] including self-healing/welding,[18,21] grafting side chains onto existing polymers,[22] expanding the structure of polymer networks,[18,23] biofunctionalization,[24] and spatial differentiation.[25] The generation of active species in early RDRP systems was accomplished using thermal initiators. Because light can regulate polymerization to a high degree both spatially and temporally, it has lately been employed to eliminate the requirement for high temperatures.[26−28] The development of photocontrolled RDRP (photoRDRP) coupled with the capacity for postsynthesis modifications of cross-linked polymer networks has made it possible to use RDRP in light-based 3D printing. Thus far, the primary RDRP technique used in light-based 3D printing systems has been photocontrolled RAFT (photo-RAFT), with some exceptions where ATRP[29] and NMP[30] have been applied. This leaves room to explore the potential applications of other RDRP methods in 3D systems.

The concept of RAFT-mediated 3D printing was inspired by research on polymeric networks containing species capable of addition–fragmentation chain transfer reactions, such as trithiocarbonates (TTCs).[18,19,31] The RAFT-mediated 3D printing, often termed "living" 3D printing, was originally developed to impart living characteristics and transformability to 3D printed materials. The living character of the 3D materials is offered by the dormant RAFT functionalities that are incorporated within the constituting structure of the materials. In a postprinting step, the dormant RAFT species can be reactivated to enable repeatable modifications and create complex multifunctional networks with spatially differentiated

compositions and various responsive behaviors that meet the demands of various applications.

Since it was initially published,[32−34] the field of RAFT-mediated 3D printing has rapidly developed and expanded beyond the creation of reprocessable/living 3D materials.[32,34,35] This technology has been utilized in cutting-edge applications such as self-healing polymers,[36] surface patterning,[37] nanostructuration,[38,39] and customized drug delivery.[40] To accomplish these applications, several chemical mechanisms such as photoiniferter (direct photolysis),[33,35] photoinduced electron/energy transfer (PET)-RAFT,[32,41] cationic RAFT,[42,43] and photoinitiator RAFT[44,45] have been utilized. With the recent developments in RAFT-mediated 3D printing research, it is important to provide a thorough review of this field from the standpoint of polymer and materials chemistry. Herein, the underlying principles of the chemical mechanisms used in RAFT-mediated 3D printing systems are discussed (Section 2). In-depth explanations are provided for the practical applications of this technology that have been developed thus far. The challenges that hinder the ongoing development of this technology, as well as potential solutions, are also detailed (Section 3). Moreover, the current state of research and prospective future directions are discussed in Section 4. The main features of this Perspective are shown in Figure 1.
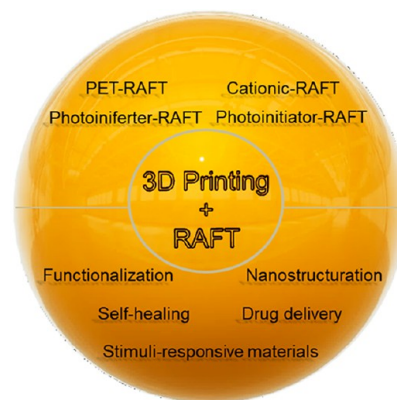
Figure 1. Schematic illustration of the main topics covered in this Perspective including the mechanisms of photo-RAFT used in light-based 3D printing systems (top) and the applications of RAFT-mediated 3D printing that have been explored so far (bottom).

2. CHEMICAL MECHANISMS USED IN RAFT-MEDIATED 3D PRINTING

The field of RAFT-mediated 3D printing has advanced rapidly since it was originally published.[32−34] The first examples of this newly developed field were based on direct photolysis of RAFT agents under visible light, and no external catalysts or initiators were required.[33] Subsequently, the PET-RAFT 3D printing method was employed without the need for preliminary deoxygenation and with fast kinetics.[32,34] Photoinitiated RAFT polymerization has also been used through Norrish type I photoinitiators with high build speed of 3D printing processes.[44,45] Furthermore, the potential of this recently developed technology was increased by incorporating photo-induced radical-promoted cationic RAFT polymerization.[42,43] Table 1 summarizes the various photo-RAFT systems that have been applied to 3D printing so far. The mechanisms behind these systems are outlined in the following sections.

Table 1. Chemical Mechanisms and Specifics of Different RAFT-Mediated 3D Printing Systems[a]

chemical mechanism	RAFT agent	photoinitiation system	light source (λ_{max}, nm)	application	ref
photoiniferter	DBTTC or CDTPA	photolysis of TTCs	405	surface functionalization	33
	EXEP	photolysis of xanthate	405	surface functionalization	35
	macro-DTC	photolysis of TTCs	532	surface-patterning	37
	benzyl-DTC or macro-DTC	photolysis	375	3D printing PIMS materials	38
PET-RAFT	DBTTC or CDTPA	EY + TEA	483	surface functionalization	32
			532	stimuli-responsive materials	
	BTPA	EB + TEtOHA	525	surface functionalization	34
	TTC cross-linker (TTC-XL)	ZnTPP	635	self-healing/welding/ growth/functionalization	36
	xanthate, DTC and TTCs	EB + TEtOHA	525	surface functionalization	46, 47
photoinitiator RAFT	BTPA	TPO	405	surface functionalization	45
	BTPA	TPO	405	living 3D materials with hierarchical porosity	44
	BTPA	TPO	405	3D drug delivery systems	40
	macro-CTA	TPO	405	3D printing PIMS materials	39, 48, 49
	DBTTC	TPO	405	self-healing/welding	50
photocationic RAFT	dithiocarbamate	$Fe_2(Cp)_2(CO)_4$ + onium salts	788	surface functionalization	42
	DTCB + EXEP	photolysis + DPI	405	welding	43

[a]Acronyms: 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDTPA); dibenzyl trithiocarbonate (DBTTC); 2-(ethoxycarbonothioyl)sulfanyl propanoate (EXEP); methyl 2-((9H-carbazole-9-carbonothioyl)thio)-2-methylpropanoate (DTC); eosin Y (EY); triethylamine (TEA); 2-(butyl thiocarbonothioylthio)propanoic acid (BTPA); erythrosin B (EB); triethanolamine (TEtOHA); cyanomethyl (3,5-dimethyl-1H-pyrazole)carbodithioate (DTC1); 2-cyanobutan-2-yl 4-chloro-3,5-dimethyl-1H-pyrazole-1- carbodithioate (DTC2); 5,10,15,20-tetraphenyl-21H,23H-porphine zinc (ZnTPP); (math)acrylated 2,2′-(carbonothioyldisulfanediyl)bis(2-methylpropanoic acid) (TTC-XL); diphenyl (2,4,6-trimethylbenzoyl)phosphine oxide (TPO); isobutoxyethyl diethylcarbamodithioate (DTCB); diphenyliodonium hexafluorophosphate (DPI); benzyl diethyldithiocarbamate (benzyl-DTC).
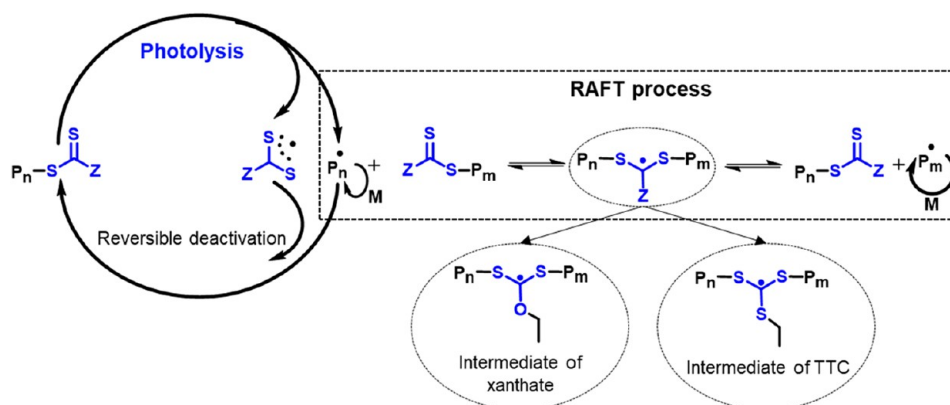

Figure 2. Mechanism of photoiniferter polymerization using two representative intermediates, xanthate and TTC, employed in 3D printing.

2.1. 3D Printing via Photoiniferter Polymerization.

The concept of iniferter (**ini**tiator−trans**fer** agent−**ter**minators) was first introduced by Otsu in 1982, where thiocarbonylthio-containing compounds were reported to act as initiators, transfer agents, and reversible termination agents to control the radical polymerization reactions, producing dormant polymer chains bearing end groups.[51] Originally, three types of iniferters, photo-, thermal, and redox iniferters, were reported using dithiocarbamates, phenylazo- or tetraphenylethanes, and binary systems of halide-reduced nickel, respectively. Dithiocarbamate-based photoiniferters were found to be more effective at producing polymer chains with well-controlled molecular weights, molecular weight distributions, and high chain-end fidelity.[51] Further research proved that other thiocarbonylthio compounds such as dithioesters, trithiocarbonates (TTCs), and xanthates can also enable photoiniferter polymerization (Figure 2). These systems are different from the conventional RAFT process as no exogenous radical source is involved in the reaction. Instead, the initial radicals are generated from the direct photolytic C−S bond cleavage of thiocarbonylthio compounds under UV or visible light. Upon dissociation, a carbon-centered propagating radical species and a stable radical species are formed. The unfragmented species can participate in the activation and deactivation of propagating radicals through a RAFT-type degenerative chain transfer process.[52,53] Early photoiniferter systems used UV light to induce a thiocarbonyl $\pi \rightarrow \pi^*$ transition that caused a cleavage of the C−S bond and produced an active carbon-centered radical. Particularly at high monomer conversions, these systems showed rather poor control over the molecular distribution of polymer chains, which was primarily ascribed to the irreversible photolytic degradation of the fragmented RAFT agents during UV irradiation. To reduce the possible degradation of the RAFT agents, visible light has been recently employed to induce n → π^* transitions and cause C−S bond cleavage to produce active carbon-centered radicals.[54,55]
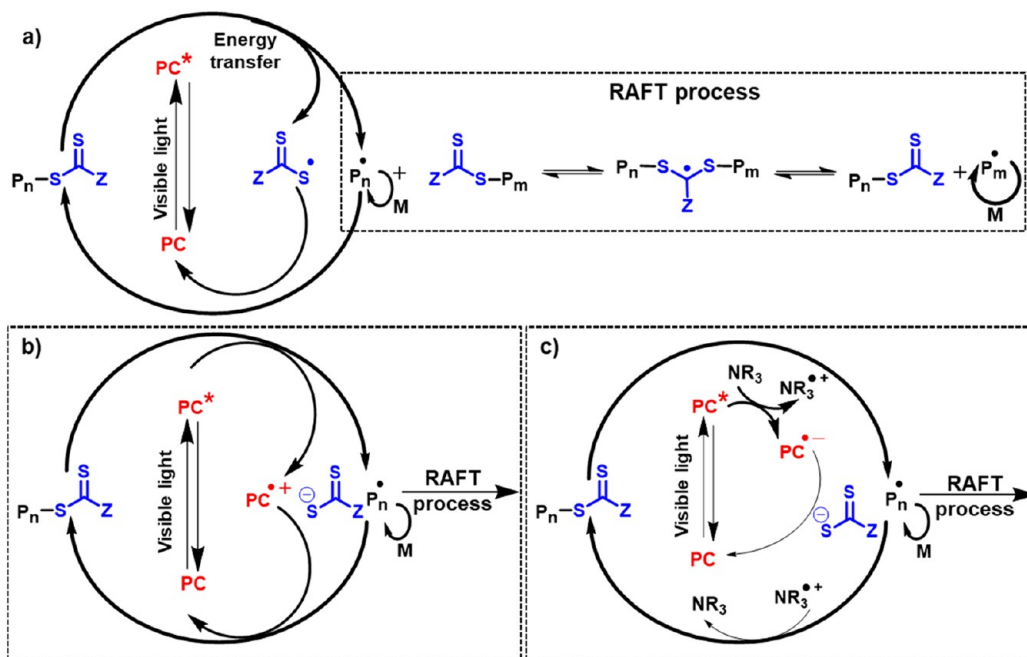
Figure 3. Mechanism of PET-RAFT polymerization via (a) energy transfer, (b) oxidative electron transfer, and (c) reductive electron transfer. PC: photocatalyst; NR_3: tertiary amine.

The Sumerlin group researched the consequences of targeting specific electronic excitations on the rate and regulation of photoiniferter polymerization. They discovered that the efficacy of the polymerization process was strongly linked to the activated electronic excitation of the iniferter. Photoiniferter polymerizations that targeted the $n \rightarrow \pi^*$ transition of the iniferter, as seen in trithiocarbonate and xanthate, exhibited an improved rate of polymerization and more precise control over molecular weights compared to polymerizations that activated the $\pi \rightarrow \pi^*$ transition. The disparities in the rates of photoiniferter polymerization were attributed to the higher rate of C−S photolysis. This explanation was validated through model trapping studies.[56]

In a highly efficient photoiniferter RAFT process, degenerative chain transfer is identified as the primary source of control over polymerization. Nevertheless, there is a need for additional experimental and theoretical research to fully understand the extent of the mechanism of reversible deactivation.[57] The lack of a need for external radical sources is one of the greatest advantages of this strategy in addition to its ability to control the polymerization process. This may eliminate any unwanted side effects and coloring and raise less issues when sensitive biological systems (e.g., proteins and cells) are present.

Inspired by the success of photoiniferter polymerizations in producing polymers with high end-group fidelity, this technique was exploited by Bagheri et al. in light-based 3D printing to manufacture reprocessable materials.[33] In the first examples of photoiniferter-based 3D printing, dibenzyl trithiocarbonate (DBTTC) or 4-cyano-4-[(dodecylsulfanylthiocarbonyl)-sulfanyl]pentanoic acid (CDTPA) RAFT agents were employed to mediate photopolymerization under 405 nm LED light irradiation. This process was conducted via direct photolysis in the absence of exogenous radicals, whereby polymerization was promoted by radicals derived from the RAFT agent itself. It is known that carbon-centered radicals can combine with molecular oxygen to form peroxy radicals and hydroperoxides,

neither of which are reactive to further polymerization.[58] To avoid oxygen inhibition, the 3D printing process was performed inside a glovebox with continual nitrogen flow. The rate/speed of 3D printing was limited by slow photoinitiator activation compared to free radical polymerization as well as possible traces of oxygen in the system.[33] A higher build speed was attained when a xanthate RAFT agent was used in place of TTCs to mediate photoiniferter 3D printing. This was mainly attributed to xanthate's lower transfer coefficient when compared to TTCs, which also demonstrated superior oxygen tolerance due to a larger flow of radicals after photolysis because xanthate has a weaker C−S bond (Figure 2).[35]

The sensitivity to oxygen makes conducting 3D printing challenging, particularly at both industrial and small laboratory scales. Oxygen inhibits RDRP by reacting with the active radicals, forming peroxy species with low reinitiation ability. Instead of removing oxygen from the reaction mixture (e.g., through inert gas sparging), in situ strategies have been developed to scrub oxygen and eliminate the need for deoxygenation.[59] Oxygen tolerance in RDRP techniques dates back to the 1998, where copper-catalyzed atom transfer radical polymerization was used to scavenge oxygen in the solution and in the headspace above the solution.[60] As the progression of RAFT polymerization has advanced over the years, research has focused on ways to conduct RAFT in the presence of molecular oxygen, making it one of the most crucial areas for expanding the applicability of RAFT and ensuring its industrial viability.[52,61−64] Common strategies that have been used to achieve oxygen tolerant RAFT polymerization systems are enzyme-mediated deoxygenation,[65,66] polymerizing through oxygen,[64,67] and the consumption of oxygen via a photoredox catalyst.[68−71] So far, photoredox catalysis and polymerizing through oxygen have been exploited in RAFT-mediated 3D printing systems; the former strategy is discussed in the following section, while the latter is discussed in Section 2.3.
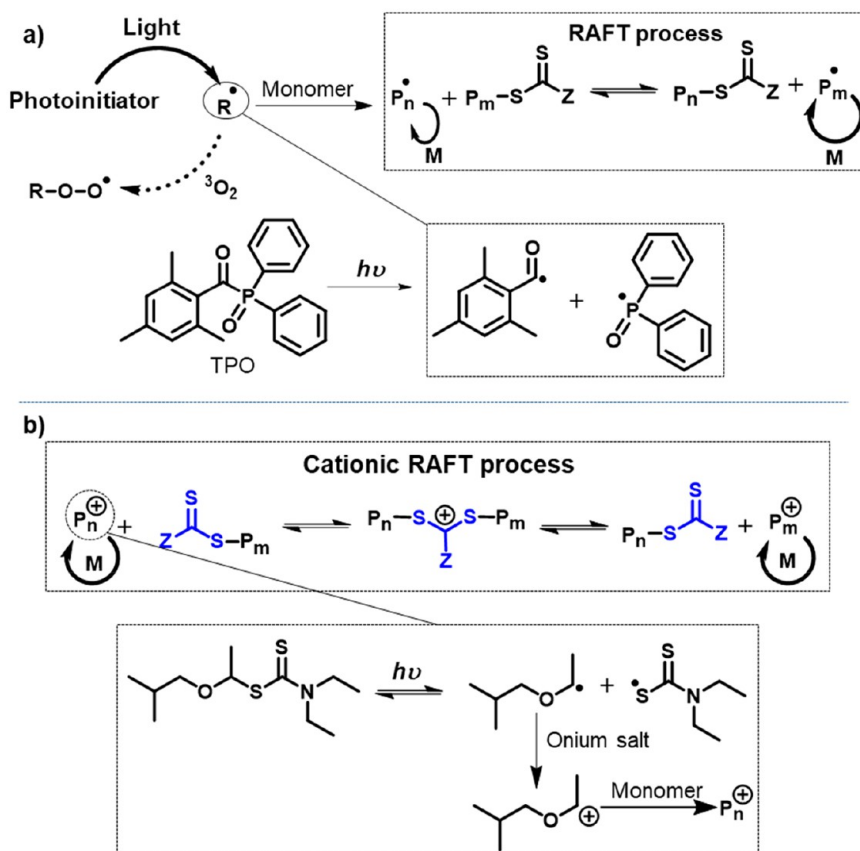
Figure 4. (a) Mechanism of "polymerizing through" oxygen applied to the RAFT polymerization process. Molecular oxygen rapidly quenches carbon centered radicals forming poorly reactive peroxy radicals (and hydroperoxides by subsequent hydrogen abstraction). A representative photoinitiator TPO employed for RAFT-mediated 3D printing is presented.[44,45] (b) Proposed mechanism for cationic RAFT polymerization. As an example, a dithiocarbamate chain transfer agent (isobutoxyethyl diethylcarbamodithioate, DTCB) employed for cationic RAFT 3D printing is presented.[43]

2.2. 3D Printing via Photoinduced Electron/Energy Transfer RAFT (PET-RAFT). The activation–deactivation equilibrium of RAFT polymerization can be regulated by interactions between thiocarbonylthio RAFT agents and redox-active catalytic molecules. This technique, known as photo-induced electron/energy transfer RAFT (PET-RAFT), was pioneered by Boyer's group[72] and was inspired by the work of Hawker and Fors, in which $(Ir(ppy)_3)$ was used as a photocatalyst in a photochemical ATRP polymerization.[26] This catalyst was then proved successful in facilitating RAFT polymerization of several vinylic monomers upon exposure to blue light. The excited-state $Ir(ppy)_3$ photocatalyst also allowed polymerization to occur in a nondegassed sealed vessel by reducing oxygen into superoxide radical anion.[72] In order to expand the scope of PET-RAFT polymerization for different applications and to be able to polymerize diverse monomers under a wide range of wavelengths, metal-based, organic, inorganic, and modified catalysts have been exploited in PET-RAFT systems.[73] Recent investigations on the PET-RAFT polymerization mechanism reveals that it involves multiple competing pathways via electron and/or energy transfer. This complexity arises from the various photophysical and electro-chemical features of photocatalysts as well as the strong oxidizing power and light absorption capabilities of RAFT agents.[74,75]

The photocatalyzed mechanisms in PET-RAFT can be classified into three categories: via energy transfer (Figure 3a),[76] electron transfer via an oxidative quenching pathway[74]

(Figure 3b), and electron transfer via a reductive quenching pathway[27] (Figure 3c). Through these pathways, electron and/or energy transfer from an excited photocatalyst to a RAFT agent breaks the weak C−S bonds and generates active radical species as well as a stable thiocarbonylthio fragment. Once the propagating radical and thiocarbonylthio fragment recombine, the catalytic cycle closes and the polymer chain returns to being dormant.[72,77,78]

PET-RAFT polymerization based on reductive quenching pathway has been one of the most efficient systems developed in the past few years.[27] For example, PET-RAFT polymerization of (meth)acrylates,[27,79] (meth)acrylamide,[78,80] and vinyl ketones[81] has been demonstrated using eosin Y (EY) as an efficient organic photocatalyst. These studies served as inspiration for the development of a PET-RAFT resin formulation for 3D printing that contained RAFT agents, EY as a photocatalyst, and triethylamine (TEA) as a reducing agent (Figure 3c). Fully open to air 3D printing via a photoinduced reductive electron transfer mechanism under low-energy visible-light irradiation such as blue (λ_{max} = 483 nm, 4.16 mW/cm^2) or green (λ_{max} = 532 nm, 0.48 mW/cm^2) LED lights showed an improvement in the build speed as compared to the photo-iniferter-based 3D printing system.[32] In this system, excited EY* can be reduced by TEA, producing an eosin radical anion (EY$^{\bullet-}$) and an amine radical cation (R$_3$N$^{\bullet+}$).[82] The reduced EY$^{\bullet-}$ catalyst transfers an electron to an adjacent RAFT agent, in this case, CDTPA or DBTTC, and returns back to its ground state. This electron transfer results in C−S bond cleavage of the

RAFT agent, generating a RAFT-stabilized anion species and a radical propagating species ($P_n\cdot$) capable of monomer additions and enabling a RAFT process. Based on a reductive PET initiation mechanism, active molecular oxygen can be converted to inactive superoxide anions via electron transfer from an eosin radical anion ($EY^{\bullet-}$) or anion RAFT species.[27,61,83]

At approximately the same time, a PET-RAFT resin formulation consisting of erythrosin B (EB) as a catalyst, triethanolamine (TEtOHA) as a cocatalyst, and 2-(butylthiocarbonothioylthio)propanoic acid (BTPA) as a RAFT agent was used in a 3D printing. Using this system under green light, a build speed up to 1.2 cm h^{-1} was achieved.[34] A highly efficient photoredox catalyst (5,10,15,20-tetraphenyl-21H, 23H-porphine zinc (ZnTPP)) was also used for PET-RAFT-mediated 3D printing under red LED light (λ_{max} = 635 nm, 0.7 mW/cm^2) via an oxidative quenching pathway (Figure 3b).[36] Inspired by literature studies on the fabrication of TTC-containing networks,[21,31,84] a RAFT-capable cross-linker with a TTC in the core between the multiple (meth)acrylate functionalities was employed for the first time in a 3D printing system. This system enabled a robust and homogeneous postprinting modifications.[36] In a postprinting stage, the TTC species present within the 3D printed materials were reactivated under low-energy red LED light (λ_{max} = 635 nm, 0.7 mW/cm^2) irradiation via a PET process from ZnTPP photocatalysts.[36] One of the significant benefits of this method was that both the 3D printing and postprinting modifications were conducted using a PET process catalyzed by ZnTPP under exposure to red LED light. The use of higher wavelength light sources is favored in advanced applications because it poses fewer risks than high-intensity UV light (which is commonly used in conventional 3D printing processes) and is less prone to unwanted reactions.

In another study, multiarm RAFT agents in the presence of EB and tertiary amines were used in light-based 3D printing under green light (λ_{max} = 530 nm) without prior deoxygenation. The mechanical properties of the 3D printed materials were dependent on the concentration and functionality of RAFT agents, allowing to tune the properties of final products for different applications.[47] In another investigation, a 3D printing process was mediated by porphyrinic zirconium metal−organic frameworks loaded with Zn as a photocatalyst. By adjusting the formulas, this method made it possible to stereolithograph both soft and hard materials.[85]

Despite the success of PET-RAFT polymerization in light-based 3D printing, only a small number of efficient photoredox catalysts have been investigated up to this time for use in 3D printing systems. There is still plenty of scope for further innovative studies in the development of PET-RAFT 3D printing with high resolution and fast kinetics.

2.3. 3D Printing via Type I Photoinitiated RAFT Polymerization.
In addition to photoiniferter and PET-RAFT mechanisms, photocontrolled RAFT polymerization can be activated via the use of Norrish type I photoinitiators.[45,86] Type I photoinitiators undergo photolytic α-cleavage and generate radicals capable of monomer addition (e.g., conventional radical polymerization), after which the propagating chains can undergo degenerative chain transfer (RAFT process).[86] The initiation and termination reactions of this mechanism, in contrast to PET-RAFT and photoiniferter, are comparable to conventional free radical polymerization, while offering the benefits of a controlled photopolymerization process. Activation of RAFT polymerization using Norrish type I photoinitiators has been explored to produce block

copolymers[87] and polymeric nanoparticles,[88] and more recently, it has been utilized in light-based 3D printing systems (Figure 4a).[44,45] In particular, the photoinitiator diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) has been used to generate an active carbon-centered radical to activate RAFT-mediated 3D printing fully open to air. The photoinitiator RAFT mechanism offers a straightforward approach for oxygen-tolerant RAFT, where a portion of generated radicals can sacrificially consume oxygen prior to activating polymerization. Upon light exposure, TPO undergoes photolytic α-cleavage to generate radicals, and a small proportion of the generated radical flux consumes molecular oxygen via a "polymerization through" mechanism, enabling the 3D printing process to proceed without deoxygenation.[87,89] The photoinitiator RAFT system enabled a high 3D printing build speed of up to 9.1 cm h^{-1}.[45]

2.4. Photoinduced Free Radical Promoted Cationic RAFT Polymerization.
Conventionally, in addition to radical polymerization, cationic photopolymerization has been one of the most commonly used methods in photopolymerization-based 3D printing.[90−92] This process relies on cross-linking of liquid monomer/oligomers which proceeds via cationic polymerization in the presence of photoinitiators. Typically, cationic polymerization, similar to conventional free radical polymerization, produces nonliving/dead polymer chains. In order to endow livingness to polymer chains, it was demonstrated that both cationic and RAFT polymerization can proceed concurrently, termed "cationic RAFT" polymerization, which was developed by Kamigaito et al. (Figure 4b).[93−95] In the presence of a strong Bronsted acid, thiocarbonylthio RAFT agents can be utilized to facilitate polymerization by allowing reversible chain transfers from propagating carbocationic species to dormant thioester bonds. The cationic RAFT polymerization process enables the synthesis of polymer chains that possess thiocarbonylthio moieties and exhibit high end-group fidelity, allowing for chain extensions. Furthermore, this technique enables the synthesis of block copolymers consisting of both cationically and radically polymerizable monomers.[93]

Inspired by the discovery of the cationic RAFT technique, Zhu and colleagues showed that such a system can be utilized in a light-based 3D printing system, allowing for the manufacture of "living" 3D materials that are capable of undergoing transformations after printing.[42] In their approach, cyclopentadienyl iron dicarbonyl dimer was used as a photoinitiator, where upon decomposition it reduces the onium salt to regenerate radicals that react with the monomers and onium salts to form initiating cations. A cationic RAFT agent was included in their resin formulation to control the cationic polymerization through the RAFT process (Figure 4b). The dithiocarbamate segments at the chain-end enabled chain extension or postprinting functionalization.[42] In a follow-up study, the same group exploited the photoiniferter properties of a cationic RAFT agent (instead of a conventional cationic photoinitiator system) to generate radicals via direct photolysis. Generated radicals activated both free-radical-promoted cationic RAFT polymerization and photoiniferter polymerization in a DLP-based 3D printing system. Postprinting transformation (e.g., welding) was realized through both cationic and radical chain extension.[43] These studies provide other possibilities to broaden the use of RAFT-mediated 3D printing.
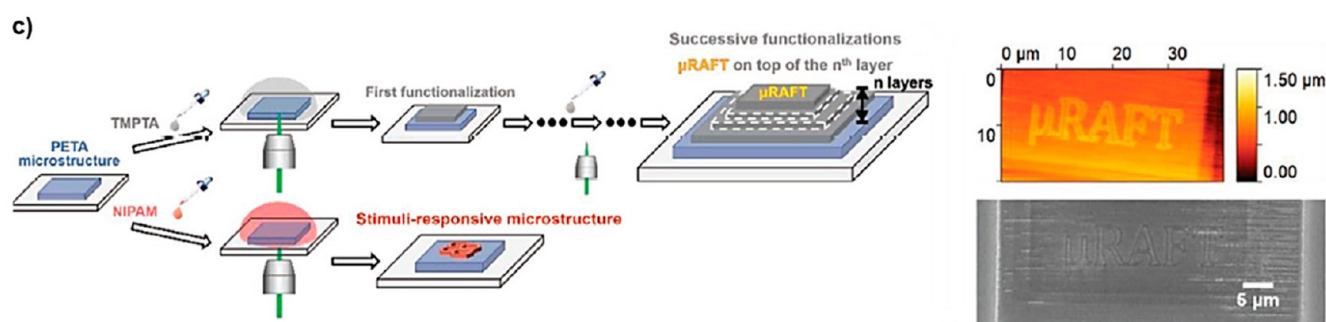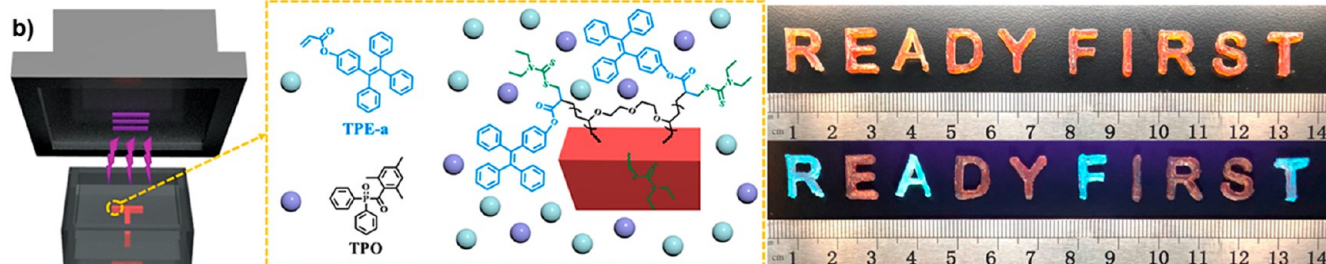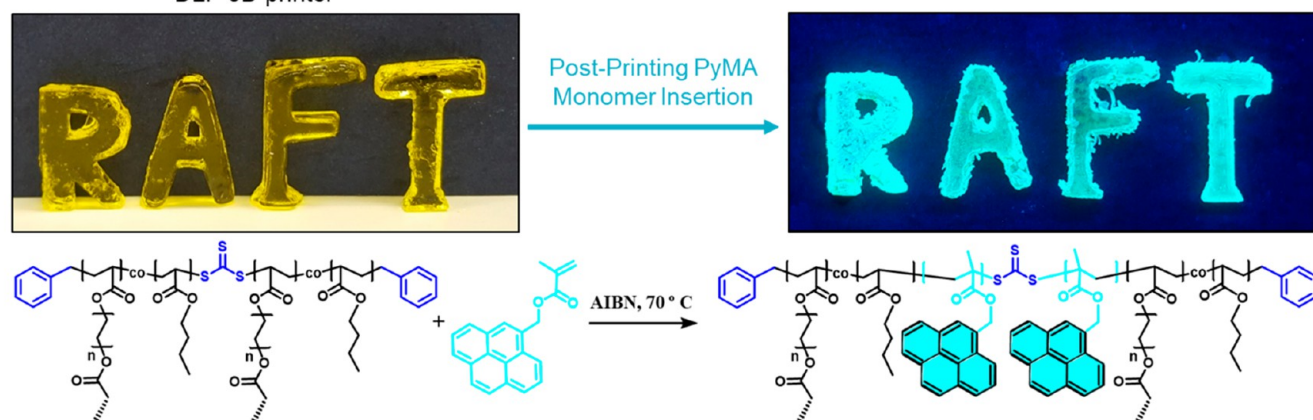
Figure 5. (a) Optical image of the "RAFT" word initially 3D printed via a photoiniferter mechanism, followed by the insertion of fluorescent PyMA monomers and subsequent modification (image taken under UV exposure). The reaction scheme depicts the postprinting PyMA insertion process, wherein PyMA monomers were polymerized from the TTC species within the material and inserted into the printed objects at 70 °C for 24 h. Reproduced with permission from ref 33. Copyright 2020 the Royal Society of Chemistry.[33] (b) Surface functionalization of the 3D printed objects using a fluorescent monomer, tetraphenylethylene acrylate (TPE-a); the letters "R", "A", "F", and "T" were functionalized by TPE-a, and others remained original. Optical images under natural and UV lights. Adapted with permission from ref 42. (c) Process of reactivation of RAFT species to modify the surface of microstructures with trimethylolpropane triacrylate (TMPTA) and NIPAM using direct laser writing (DLW). Atomic force microscope and scanning electron microscopy images of μRAFT at the top layer. Adapted with permission from ref 115. Copyright 2022 John Wiley and Sons.

3. APPLICATIONS OF RAFT-MEDIATED 3D PRINTING

The field of RAFT-mediated 3D printing has been quickly evolving since first reported.[32−34] and its application has been explored in different contexts such as surface functionalization,[32,34,35] direct laser writing/surface patterning,[37] self-healing polymers,[36,50] polymerization-induced microphase separation,[38,39] fabrication of scaffolds with tailored hierarchical porosities,[44] and customized drug delivery systems.[40] The following sections provide a succinct, pertinent introduction and a summary of the reported applications of RAFT-mediated 3D printing in the literature.

3.1. Transformable/Living 3D/4D Printed Polymers. In principle, highly cross-linked networks make up 3D printed polymers. Before discussing the use of RAFT polymerization for 3D printing transformable polymeric networks, it is important to provide a brief history of transformable/adaptable cross-linked polymers. Historically, thermosets have been known as covalently cross-linked polymer networks that are permanent, interactable, and insoluble. In order to endow reprocessability, adaptability (to different environments), and/or reparability to thermosets, different strategies have been exploited via incorporating a wide range of functional groups throughout cross-linked networks. In a broader context, covalent adaptable

networks are fabricated by integrating reversible covalent bonds throughout networks. Upon application of external stimulus, these bonds undergo changes through reversible addition or reversible bond exchange mechanisms.[96−101] The readers can refer to recent reviews that discuss these materials in great detail.[102−104]

One possible way to impart externally controllable behavior to cross-linked networks is by including light-responsive functional groups into polymer backbones.[105−110] Among different light-responsive functionalities, TTCs and allyl sulfides capable of addition−fragmentation chain transfer reactions have been incorporated into polymer networks to enable transformability.[31,84]

In a study by Bowman and co-workers, allyl sulfide moieties were incorporated throughout a polymer network. Following synthesis, radicals produced by homolytic photolysis of remaining photoinitiators interacted with the allyl sulfide functionalities, enabling addition−fragmentation chain transfer reactions that led to reversible cleavage and reformation processes of polymer strands. These reactions enabled plasticity, actuation, and shape changes with stress−relaxation.[111] The research group of Matyjaszewski incorporated TTC functionalities within cross-linked networks that could undergo dynamic covalent reshuffling of TTC units upon light exposure, enabling repeatable self-healing upon damage.[21]

The Johnson research team reported the fabrication of TTC-containing polymer networks capable of photogrowth reactions, i.e., monomer insertion into an already-synthesized polymer network from the TTC units via a photoiniferter mechanism.[108] It was also demonstrated that polymeric networks synthesized using the RAFT process can undergo visible-light-induced postsynthesis modifications (e.g., photogrowth and photo-welding) by reactivation of the incorporated TTC functionalities.[18]

After discussing the ability of cross-linked polymer networks to undergo changes, the next section focuses on how RAFT-based 3D printed polymers can undergo controlled modifications after printing in terms of their structure and/or other characteristics.

Reconfigurable, recyclable, and/or reprocessable polymers for 3D printing have become extremely important in recent years to fulfill the needs of advanced applications and environmental sustainability concerns. The concept of "4D printing", in which time is the fourth dimension, was developed to describe the ability of 3D printed materials to experience regulated changes in shape, property, and/or functionality in response to an external stimulus such as temperature, water, pH, light, or a combination of them.[112]

Incorporating RDRP agents into resin compositions is one potential method for enabling 4D printing. The RDRP agents can either activate the photopolymerization process or merely be integrated into the backbone of polymer chains. For example, Yang's group incorporated a Br-containing vinyl-terminated initiator capable of initiating ATRP into a resin formulation, which was used in a 3D printing process. 3D polymers manufactured using this resin contained ATRP initiators both within and on the surface of 3D materials. Accessible initiators were exploited after printing to activate ATRP process to grow different polymer brushes on the surface of the printed materials.[113] Using this approach, the Br-containing initiators were used to polymerize 3-sulfopropyl methacrylate potassium salt monomers (with antimicrobial properties) via a surface-initiated ATRP.[114]

These studies served as inspiration, and TTC RAFT agents were added to a resin formulation to manufacture "living"/ transformable TTC-containing 3D polymers. This process was conducted via a photoiniferter mechanism under visible-light irradiation in a digital light processing (DLP) 3D printing process. After printing, preserved TTC units within the 3D materials were activated to allow for postprinting modification. For example, original 3D printed materials were altered by polymerizing different types of monomers, such as a fluorescent/light-responsive 1-pyrenemethyl methacrylate (PyMA) or a hydrophobic n-butyl acrylate (BA), from the incorporated TTCs to produce progeny materials with distinct chemical properties compared to the parent networks, which was not feasible through conventional methods (Figure 5a).[33] In this system, both the 3D printing process and the postprinting modifications were performed by a photoiniferter mechanism without the requirement for an external radical source or photocatalyst. This eliminates catalyst residue contamination and the color that photocatalysts frequently produce, making it suitable for bio-related applications. Another study showed that dormant RAFT agents on the surface of 3D printed materials can be reactivated to allow for chain extension with a hydrophobic BA monomer, leading to an increase in surface hydrophobicity.[34]

To enhance the presence of TTC species in 3D printed materials, a resin formula that includes a TTC-containing cross-linker with terminal (meth)acrylate functionalities was utilized instead of a permanent cross-linker, such as PEGDA. This resulted in the creation of highly transformable 3D materials with a TTC unit in between each two cross-linking points. The system also enabled postprinting insertion of monomers into the TTC-bound strands through photoredox catalyzed reactivation of the preserved TTCs. From a parent network that was initially synthesized, chemically distinct and multifunctionalized materials were created with new temperature, light, and/or polarity responsiveness. For instance, the TTC species within the 3D printed materials were reactivated to polymerize a temperature-responsive N-isopropylacrylamide (NIPAAm) monomer, resulting in a modified network that exhibited reversible temperature responsiveness behavior.[36]

A recent study showed that 3D materials produced using the cationic RAFT method can be functionalized after printing. 3D materials containing dithiocarbamate segments at the chain end were functionalized with a fluorescent monomer, tetraphenyl-ethylene acrylate, via a RAFT process (Figure 5b).[42] The ability of postprinting functionalization of 3D materials fabricated in the presence of cationic RAFT agents was also demonstrated. For example, welding of 3D polymers was achieved through reactivation of dormant species using either cationic or RAFT processes.[43] Additionally, 3D materials that are transformable were manufactured using photoinitiator RAFT formulations. In a postprinting stage, the dormant RAFT groups on the surface of the 3D printed materials were reactivated to provide spatiotemporally controlled modifications using functional monomers. Multiple successive postprinting surface modifications were performed to change the surface wettability and introduce different degrees of fluorescence to the pristine 3D printed structures.[45] In a different study, 3D materials with customized hierarchical porosities were 3D printed using a photoinitiator RAFT mechanism. Light-controlled PyMA polymerization from the dormant RAFT species present within the porous 3D materials was demonstrated to generate fluorescence materials.[44]
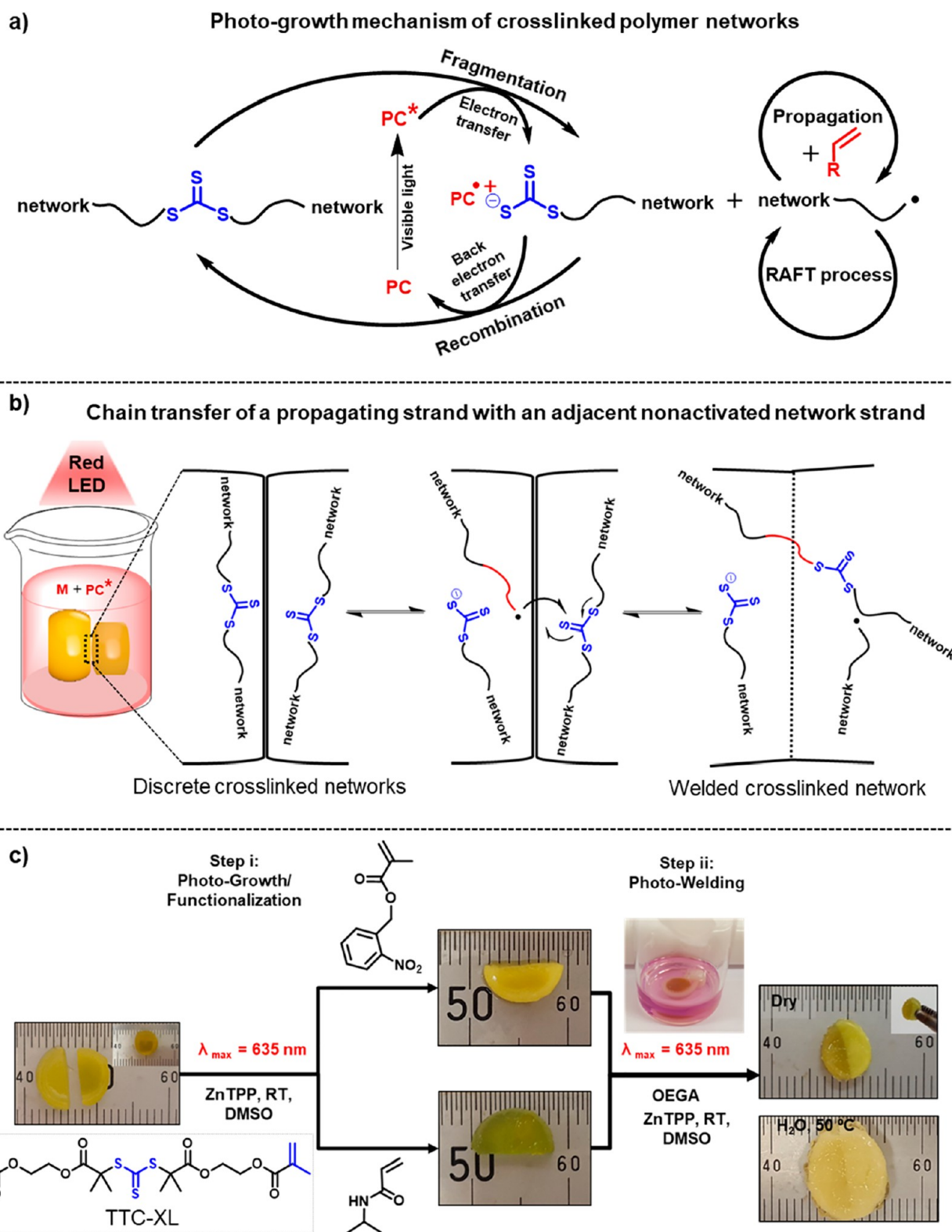
Figure 6. (a) Mechanism of photoredox catalyzed monomer insertion into the TTC-containing cross-linked polymer networks via an oxidative pathway (e.g.,10-phenylphenothiazine and ZnTPP).[19,36] (b) An illustration of how the TTCs undergo degenerative exchange reaction and enable healing/welding. (c) Optical images of an initially synthesized network using a TTC-XL (swollen in DMSO) which was cut into two pieces, modified networks after postsynthesis monomer insertion via a photogrowth/functionalization process (step i) and a photowelding process (step ii). The pieces were modified with *o*-nitrobenzyl methacrylate (NBMA) and NIPAAm and then welded using oligo(ethylene glycol) methyl ether acrylate (OEGA). Adapted with permission from ref 36.
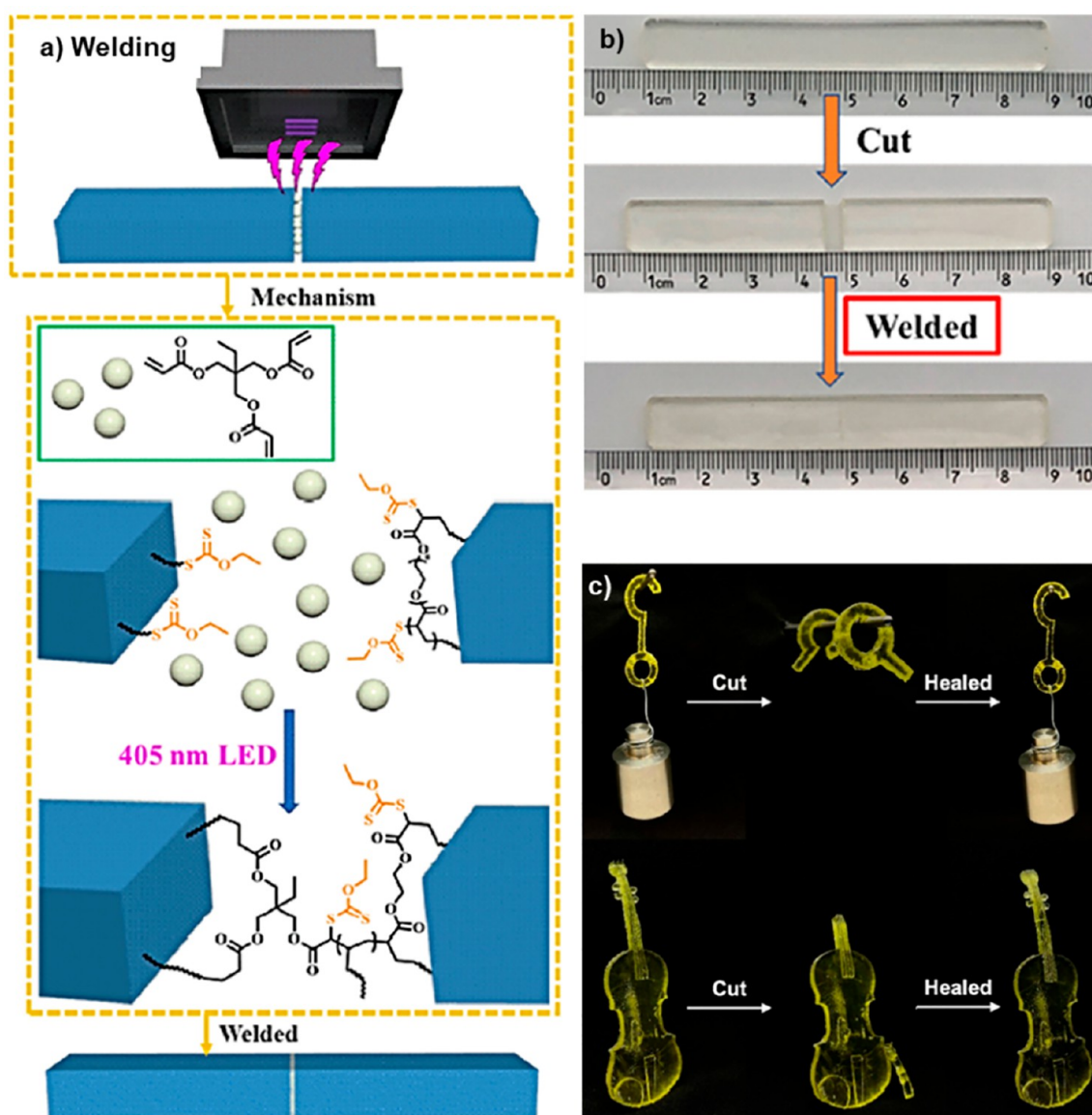
Figure 7. (a) Scheme of the polymer welding process of cut samples. (b) Digital images of a PEGDA film (prepared using a xanthate) before and after welding. Adapted with permission from ref 35. (c) Photoinduced self-healing/welding of 3D printed object via RAFT polymerization using a DBTTC. Adapted with permission from ref 50. Copyright 2021 John Wiley and Sons.

All the aforementioned systems were conducted in a DLP printer, where the LED light sources are placed at the bottom of the resin vats. Wu, Spangenberg, and co-workers demonstrated the application of photo-RAFT in a 3D direct laser writing (DLW), where 3D materials with feature sizes of around 500 nm were manufactured. Following the creation of microstructures, the dormant dithiocarbamate groups present within the networks were reactivated for surface functionalization and patterning using BA or NIPAAm monomers (Figure 5C).[115] These photo-RAFT-based 3D printing studies have demonstrated significant potential for producing advanced transformable materials for different applications.

3.2. Self-Healing/Welding 3D Polymers. Polymers capable of recovering from physical or chemical damage are called "self-healing" polymers. These materials have a wide range of applications including but not limited to biomaterials, soft robotics, and energy storage. In particular, fabrication of self-healing materials that can replicate the behavior of living tissues

and repair minor damages is of a great importance. Many studies have been devoted to produce self-healing materials, and both physical and chemicals approaches have been used to achieve self-healing in synthetic polymers.[116]

Depending on the underlying healing process, self-healing techniques can be categorized as intrinsic, extrinsic, autonomic, nonautonomic, physical, or chemical. These techniques can be used in conjunction to heal polymers. In general, functional/reactive species including free radicals, $-C\equiv C-$, $-COOH$, $-NH_2$, $-OH$, $-SH$, $-Si-O$, $S-S$, and/or $-C\equiv O$ (either as cleaved chain ends or pendent groups) may enable self-healing in synthetic polymers via different reactions: covalent bonding, hydrogen bonding, $\pi-\pi$ stacking, supramolecular chemistry, and ionic interactions. Among these, the use of covalent bonding such as Diels−Alder,[117] alkoxyamines,[118] disulfide bridges,[119] urea linkages,[120] acylhydrazone bonds,[121] boronic esters,[122] and TTCs,[36,106] has been widely investigated. Self-healing via covalent bond reformation of TTC RAFT agents is further
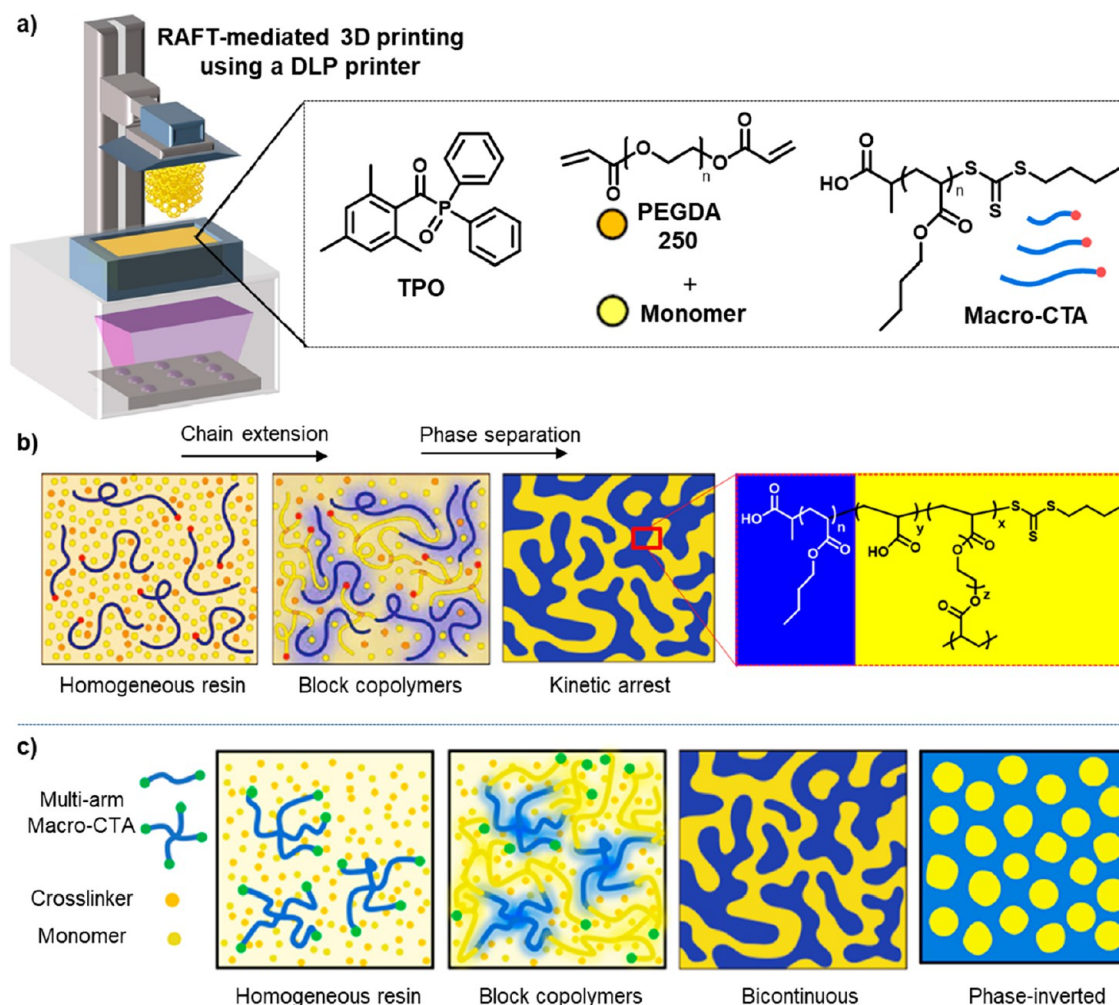
Figure 8. (a) 3D printing materials by RAFT-mediated PIMS. Adapted under the terms of the Creative Commons Attribution 4.0 International License from ref 39. Copyright 2022 Springer Nature. PIMS mechanism: a macro-CTA is chain extended with PEGDA cross-linker and a monofunctional monomer to form block copolymers, which eventually phase separate with the generation of emergent morphologies trapped by in situ cross-linking; schematic presentation of chain extension and phase separation (b) using macro-CTA with varied chain length and (c) using multiarm macro-CTAs to provide access to nanostructured materials with different morphologies. Adapted under the terms of the Creative Commons Attribution 4.0 International Public License from ref 49. Copyright 2022 John Wiley and Sons.

discussed as the focus of this Perspective is on RAFT-mediated 3D printing. For further details on the fundamentals of self-healing polymers and the underlying healing mechanisms, we direct the reader to recent reviews.[116]

Matyjaszewski's group was first to report the use of TTCs to achieve self-healing in cross-linked polymer networks. Their strategy was based on using a dimethacrylate containing a TTC as a dynamic covalent cross-linker to fabricate materials that can self-heal and/or be reprocessed. The self-healing process was achieved via reversible bond exchange between TTC units in the presence of radicals (generated using thermal radical initiators or copper complexes).[106] Following this, it was found that self-healing process could be achieved under UV light exposure leveraging the photoiniferter properties of TTCs. The photolysis of C−S bonds of TTCs could trigger bond exchange reactions between TTC species present in fragments of cross-linked networks, leading to the fusion of disparate parts and self-repair.[21] Bagheri, Jin, and colleagues employed a symmetric RAFT agent, dibenzyl trithiocarbonate (DBTTC), to generate polymer networks capable of undergoing a welding process. The welding process could be achieved by either photoredox

catalysis (using ZnTPP) or direct photolysis (photoiniferter) mechanisms from the TTC units within the network. It should be noted that this procedure is termed "welding" rather than "healing" because an external bis-acrylamide cross-linker was added to the reaction, aiding in cross-linking at the interface, in addition to the TTC bond exchange reactions.[18] After the welding process, the interfaces between the welded pieces were different from the parent network with clear scarring. This was partly attributed to the use of permanent cross-linkers (e.g., PEGDA), forming fixed cross-linking between the main strands and limiting the reactivatability of the TTC functionalities.

In a follow-up study, a TTC cross-linker (TTC-XL) composed of a TTC embedded between (meth)acrylate functionalities was used to manufacture transformable polymer networks.[36] These materials could undergo an effective welding process as compared to systems that included a permanent cross-linker paired with TTC functionalities. The welding process was achieved via a photoinduced electron transfer from an excited ZnTPP to network-bound TTCs, resulting in generation of an active propagating strand. This propagating cleaved network strand can concurrently facilitate addition of
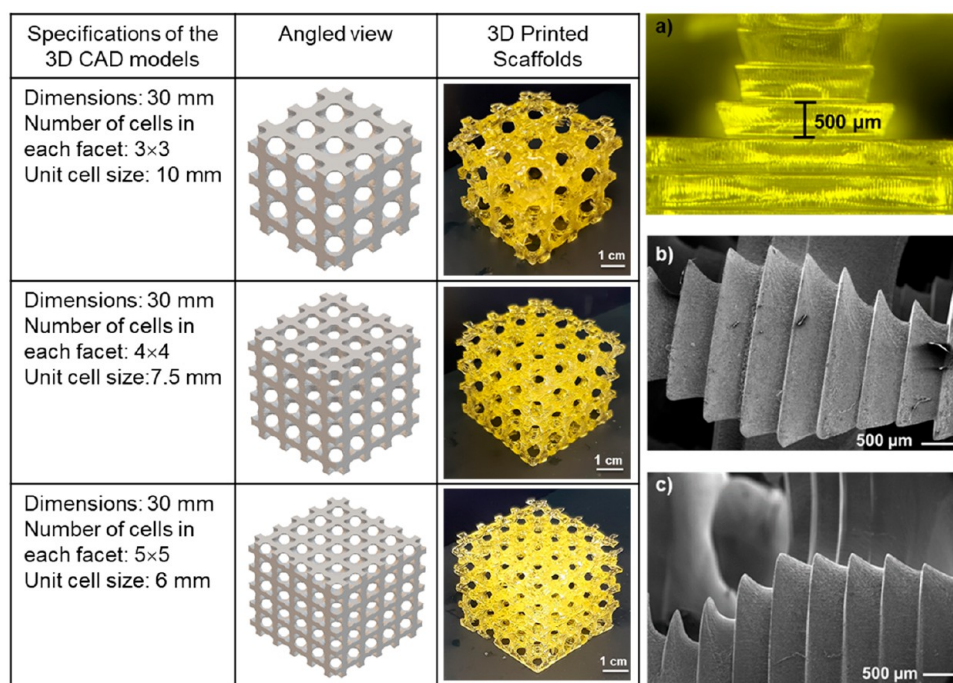
Figure 9. Characterization of materials with TPMS structures, which were 3D printed using a RAFT-mediated 3D printing approach in a bottom-up DLP printer equipped with 405 nm LED lights at room temperature and fully open to air, is presented. Specifications of three different TPMS designs are included, along with their 3D model angled views (middle) and their corresponding optical images (right). Additionally, (a) a representative microscopy image showing the strut of a 3D printed TPMS and (b, c) representative SEM images of a 3D printed TPMS, which show outstanding thickness uniformity and fine features throughout the architecture as per the original CAD designs, are also presented. A resin formula of [BTPA]: [PEGDA250]:[OEGA]:[TPO] = 1:50:50:1 was used in all examples. Adapted with permission from ref 44.

new monomers into the active radical strands and chain transfer reaction between the propagating strand and the adjacent nonactivated strands (Figure 6a,b). Specifically, the TTC-XL-based networks showed improved healing with less noticeable scarring (Figure 6c).[36] This was attributed to the increased number of TTC species present throughout the material as a result of each cross-linker having one TTC unit at its core. This approach enabled preparation of 3D materials capable of undergoing controllable and successive postprinting transformations. This system was then exploited in a DLP 3D printing process for manufacturing 3D materials that can undergo highly controllable transformations after printing.[36]

Boyer and colleagues also demonstrated that polymers 3D printed using a DBTTC RAFT agent could undergo a welding process by reactivating the RAFT species within the materials (Figure 7c). The material quickly healed upon being cut, regaining $49 \pm 5\%$ of its initial tensile strength and $26 \pm 2\%$ of its elongation at break after only 5 min of 365 nm radiation exposure. Additionally, as the irradiation time increased, the material continued to recover, and its tensile strength and elongation at break reached $98 \pm 3\%$ and $74 \pm 3\%$ of their original values, respectively, within 30 min. Furthermore, for samples printed without TTC units, welding was not achievable, confirming the chain growth and exchange process from the TTC units.[50]

Li, Zhu, and co-workers also reported a welding process, in which polymers 3D printed via a photoiniferter mechanism were welded in a postprinting stage. In their method, PEGDA or trimethylolpropane triacrylate was painted on the surfaces of two cut samples, and then the cut interface was exposed to purple light for 20 min. Because of the postpolymerization initiated from the RAFT agent present at the cut interface, the

cut film was repaired (Figure 7a,b).[35] These studies have shown that achieving self-healing and/or welding 3D polymers using RAFT processes is straightforward and effective. However, there is still plenty of scope for further innovative studies in the development of 3D printed self-healing materials using photo-RAFT under light with different wavelengths.

3.3. Nanostructured 3D Polymers. In addition to providing access to materials with reprocessability, RAFT-mediated 3D printing has enabled manufacturing materials with controlled nanoscale structural features via the polymerization-induced microphase separation (PIMS) process, which was initially reported by Hillmyer's group.[123,124] This process works by chain extending a macromolecular chain transfer agent (macro-CTA) that is initially soluble in a polymerization mixture consisting a multifunctional monomer but becomes incompatible with the polymerizing medium after chain extension, leading to microphase separation and thus nanostructuration. The chain extension via RAFT polymerization permits linear increases in molar mass and dictates the resultant morphology and allows for control of the nanostructuration. The Boyer group recently employed this technique in 3D printing, which allows for the modulation of the morphology of nanostructured 3D printed materials by adjusting the macro-CTA chain length, architecture, and loading, a feat that was previously impossible with conventional 3D printing methods. It has been shown that 3D printed materials undergo morphological modifications as the chain length of macro-CTAs is increased (while the loading is maintained), changing from materials with isolated globular domains to those with elongated domains and eventually bicontinuous morphologies (Figure 8a,b).[39] The loading of the macro-CTAs in the resin formulations had an impact on the elongation of the globular
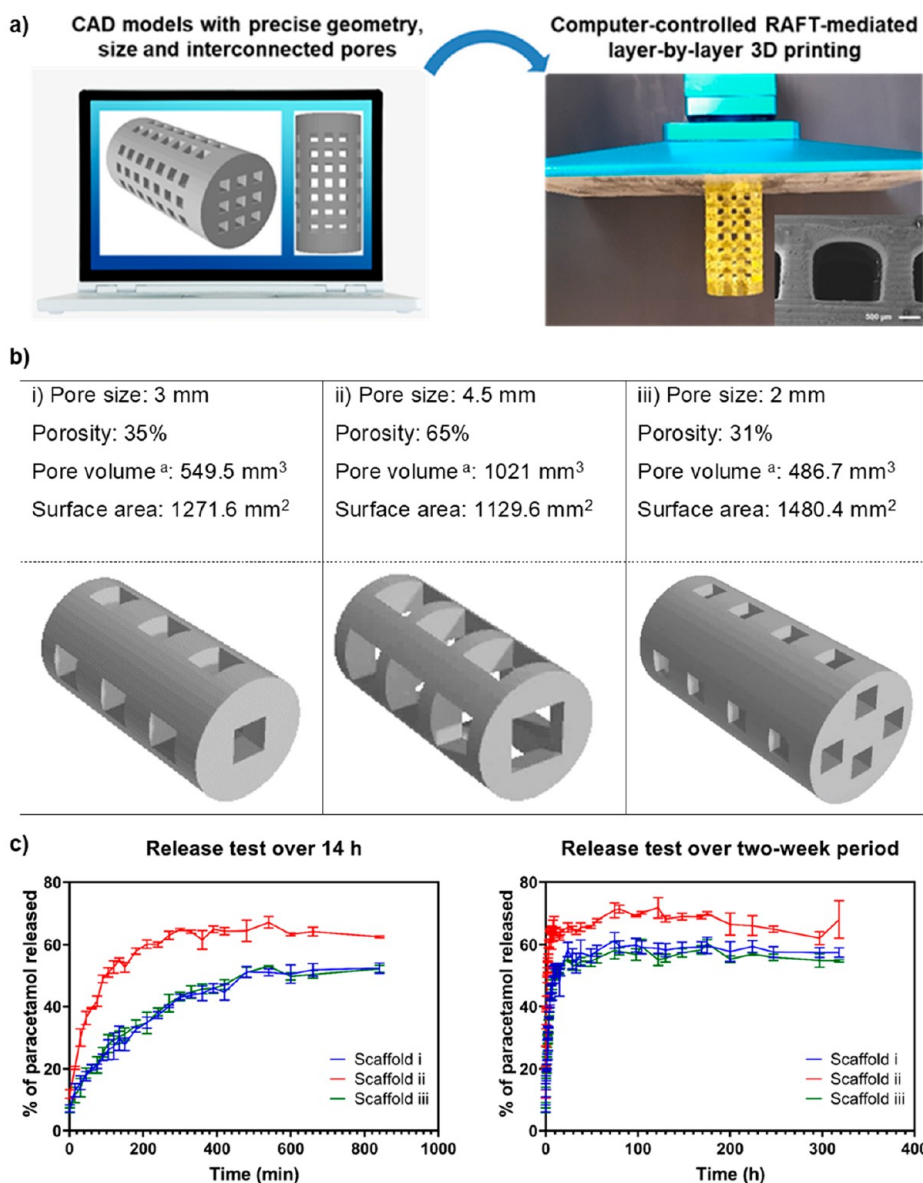
Figure 10. (a) 3D design and printing of porous materials[44] using a resin formulation containing PEGDA700 (M_n = 700 g mol^{-1}), poly(ethylene glycol) (PEG300, M_n = 300 g mol^{-1}), TPO, BTPA, and paracetamol as a drug. (b) Specifications of the CAD 3D models for cylindrical scaffolds (angled view) with 20 mm height and 10 mm diameter. ^{a}Pore volume = net volume of a full cylinder × porosity percentage. The values presented in this table are based on a full cylinder with a volume of 1570.8 mm^3. (c) Percentage cumulative release of paracetamol from 3D printed scaffolds over the first 14 h and a 2-week period. Adapted under the terms of the Creative Commons Attribution 4.0 International Public License from ref 40. Copyright 2023 John Wiley and Sons.

domains and the development of bicontinuous morphologies.[48] Moreover, it has been proven that altering the macro-CTA design allows to regulate PIMS nanostructures created through 3D printing. Employing 2- and 4-arm macro-CTAs can result in phase-inverted morphologies, continuous macro-CTA domains, or isolated globular network domains, while using monofunctional linear macro-CTAs produces either globular or bicontinuous morphologies (Figure 8c).[49]

The bulk mechanical properties of 3D printed nanostructured materials are influenced by their morphologies. The mechanical performance of 3D printed materials with interpenetrating soft and hard domains, or elongated domains with bicontinuous morphology, was better than that of a structure with isolated globular domains. These results might be attributed to improved stress concentration decrease across the material due to

improved interfacial contact between the soft and hard domains. Moreover, due to the presence of interpenetrating soft and hard domains, nanostructured 3D printed materials exhibited improved mechanical characteristics when compared to non-phase-separated equivalents.[49]

More recently, a one-step process for creating solid polymer electrolytes via 3D printing has been reported. The method involves using visible light to polymerize a mixture containing a polymer matrix and an ionic liquid, resulting in materials with nanoscale domains with tunable architectures. These electrolytes have high shear moduli and ionic conductivities and are suitable for use in supercapacitors. The process is scalable, and the resulting electrolytes have been demonstrated to be functional.[125]

3.4. 3D Printed Porous Scaffolds and Customized Drug Delivery Systems.
The advancement in 3D printing has led to the creation of robust methods for fabricating scaffolds with predetermined internal and external architectures that are suitable for biomedical engineering and drug delivery systems. This control can be achieved by converting CAD 3D models into physical materials with the ability to control pore size, structure porosity, and pore interconnectivity.[126] Such precise control over the possible complexity of manufactured materials, particularly the internal geometric pattern of porous scaffolds, is not achievable with conventional production methods such as solvent casting, porogen leaching, freeze drying, and gas foaming.[127,128] Our group recently demonstrated that RAFT-mediated, computer-controlled layer-by-layer 3D printing can be utilized to manufacture scaffolds with custom hierarchical porosities and highly resolved micro- and macroscale features (Figure 9).[44] This approach enabled the manufacturing of a variety of open porous structural designs with a controlled variation of porosity (e.g., ranging from 23% to 70% porosity). Materials with triply periodic minimal surfaces (TPMS) were also created, which have unique properties (including interconnectivity and tortuosity) and a wide variety of potential uses, including molecular separation, tissue engineering, drug delivery, and energy storage. In a follow-up study, these porous materials were exploited for controlled drug delivery applications.[40]

One of the potentials offered by 3D printing in the healthcare industry is the ability to advance toward the goal of personalized medicine, in which treatments are tailored to specific patient requirements rather than the demands of a vast patient population. The fundamental motivation for the development of personalized medicine has been to eliminate the inherent drawbacks of systemic, broad therapy in healthcare.[129] The intersection of 3D printing and personalized medicine is made possible by the development of systems that take into account individual differences. Interest in employing 3D printing in personalized medicine has grown after the U.S. Food and Drug Administration approved the first 3D printed drug: SPRITAM for epilepsy[130] (marketed in 2015). The application of 3D printing technology in pharmaceutical production processes has so far demonstrated significant potential because it can circumvent the drawbacks of traditional pharmaceutical manufacturing methods (such as molding and compacting) that are based on the "one-size-fits-all" philosophy.[129] 3D printing technology has so far shown great promise in pharmaceutical production,[131] especially for oral solid dosage,[132,133] transdermal delivery,[134] and drug eluting implants.[135]

As noted, in a recent study by our group, we demonstrated that RAFT-mediated 3D printing can be used to manufacture drug-eluting systems with precise geometry, size, drug dosage, and release duration/profiles. This was achieved by creating a range of 3D models with precise interconnecting channel-pore structures and geometric proportions in architectural patterns (Figure 10).[40] A homogeneous flow distribution of the release medium throughout the 3D printed scaffolds (during the drug release process) was made possible by the interconnected channel-pore architecture. It was also demonstrated that the medication release profile (paracetamol used as a drug) is dependent on the system's porosity, pore sizes, surface areas, and geometric proportions (Figure 10c). One can imagine 3D printing customized drug delivery systems, where the release profile can be translated from the geometry and porosity of the systems in an intuitive way.

The ratio of PEG units to acrylate units in the cross-linkers was discovered to be a crucial element; a larger ratio increased swelling capacity and, as a result, improved the drug release profile from the drug-eluting systems. This technique allowed for spatiotemporal control of the drug loading and compositions inside the different layers of the 3D printed scaffolds. With further investigations, this methodology has the potential to produce drug tablets or drug-eluting implants in a clinical environment, using a commercially available 3D printer, immediately following prescription. Even though the application of RAFT-mediated 3D printing in drug delivery has been demonstrated,[40] this field is still in its infancy and needs further research (in collaboration with biomedical scientists) before it can be widely used in industrial settings.

4. FUTURE DIRECTION OF RAFT-MEDIATED 3D PRINTING

RAFT-mediated 3D printing combines the precision and control of RAFT polymerization with the versatility and layer-by-layer deposition of 3D printing, enabling the creation of complex structures with tailored functionalities. The integration of RAFT into 3D printing has opened up fascinating new possibilities for the design and manufacturing of advanced materials. The systems that have been created so far have a wide range of applications, but there are still many opportunities for the sector to expand further, necessitating more research to fulfill the requirements in either industrial contexts or for research purposes. The opportunities and areas that require further investigation are discussed in the following sections.

4.1. Development of RAFT-Based Resin Formulations with Enhanced Photopolymerization Rate and Oxygen Tolerance.
To date, different strategies have been used to develop oxygen-tolerant 3D printable photo-RAFT resins with fast kinetics in bulk at room temperature. These include utilizing different polymerization reactions, RAFT agents with various reactivities, and reagent stoichiometry.

In first examples of RAFT-based 3D systems via a photo-iniferter mechanism under 405 nm LED light, a build speed in the range of μm h^{-1} was achieved.[33] The slow printing speed was partially caused by the slow direct activation rate of TTC units and subsequent chain transfer processes as well as oxygen inhibition. When a xanthate RAFT agent was used instead of TTCs to mediate photoiniferter 3D printing, a faster 3D printing speed was achieved. This was primarily attributed to xanthate's lower transfer coefficient when compared to TTCs, which also showed better oxygen tolerance due to a larger flow of radicals after photolysis because of a weaker C−S bond in xanthate.[35]

A higher 3D printing build speed has been achieved by utilizing PET-RAFT techniques. Using EY as a PET catalyst and TEA as a reducing agent facilitated an oxygen-tolerant 3D printing process via a reductive PET initiation mechanism. This system showed an improvement in build speed, with values of 0.08 and 0.14 cm h^{-1} under blue and green light irradiation, respectively.[32] Changing the PET catalyst and reducing agent had a significant impact on the 3D printing build speed. A resin formulation containing an organic dye EB in combination with TEtOHA reducing agent and BTPA RAFT agent enabled fully open to air 3D printing under green light with a build speed up to 1.2 cm h^{-1}.[34] When ZnTPP was used as a PET catalyst under red LED (λ_{max} = 635 nm, 0.5 mW/cm^2), combined with an expandable TTC-XL, a permanent PEGDA cross-linker, and BA monomer, the maximum build speed achieved was lower compared to systems using EB or EY. These systems

demonstrate that a variety of photophysical and electrochemical properties of photocatalysts, reagent stoichiometry, presence of monofunctional monomers, and the intensity of the photon source are among the key contributors to the variance in build speeds. To further understand how these aspects impact build speeds and because the versatility and applicability of explored formulations are restricted, additional study into RAFT-based resins with rapid kinetics is required.

Further improvement in the build speed can also be provided by using a photoinitiator-RAFT system utilizing Norrish type I photoinitiators. In particular, TPO has been demonstrated to be effective in mediating RAFT via a degenerative chain transfer mechanism.[86] Some of the radicals produced by homolytic cleavage of TPO consume dissolved oxygen by converting to inactive peroxy radicals, enabling propagating radicals to undergo RAFT processes (termed as a "polymerization through" mechanism).[87,89] The TPO photoinitiator has enabled relatively quick oxygen-tolerant RAFT-mediated 3D printing using a DLP printer equipped with 405 nm LED (build speed of up to 9.1 cm h^{-1}).[44,45] To further understand how Norrish type I photoinitiators in conjunction with a RAFT agent can produce a variety of oxygen-tolerant 3D printable resins, how it can mediate/control the RAFT polymerization, and to what extend the chains will retain the thiocarbonylthio end groups, more systematic research is needed.

Traditional 3D printing techniques rely on short-wavelength light sources (such as UV light under 400 nm). Long-term exposure to high-energy photons raises concerns about phototoxicity, photodamage to light-sensitive materials, and the deterioration of reactant and products.[136] Despite instances of 3D printing utilizing RAFT process at longer wavelengths, further research is needed to develop resin compositions that can be activated by secure, low-energy, and prolonged irradiation wavelengths. The use of redox-active catalytic chromophores with unique electronic configurations, capable of interacting with longer wavelength photons and undergoing reversible electron transfer with RAFT species, is encouraged and promoted. Moreover, in order to develop RAFT-based resins that can effectively be used in industrial environments without prior deoxygenation, the oxygen tolerance of the resultant formulations must be thoroughly examined. We encourage readers to refer to recent publications and reviews for more information.[73,137−139]

4.2. Controlled Distributions of RAFT Reactivatable Species within the 3D Printed Materials.

Originally, RAFT-mediated 3D printing was developed to use RAFT to provide 3D materials with the capability to be transformed. The dormant RAFT species included in the 3D materials' constituent structure can be revived to allow for repetitive modifications after printing. This means that the distributions of RAFT units inside the 3D printed materials and their reactivatability after printing are two crucial factors determining the efficiency of the "living" 3D printing. Although RAFT provides control over the primary polymer chain structure and produces more homogeneous covalently cross-linked networks than conventional free radical polymerization, it does not directly allow for control of the distance between cross-linking points when synthesizing polymer networks.[76,140] Furthermore, there is minimal control over how RAFT species are distributed across cross-linked networks, particularly when permanent cross-linkers (such as PEGDA) are used.[33,46,141] In addition, the use of permanent cross-linkers results in the formation of fixed cross-linking between polymer strands, which limits the ability to homogeneously insert/polymerize monomers into the constituent structure of cross-linked networks.

One possible way to control the distribution of RAFT species throughout a polymer network is by using TTC-containing cross-linkers (TTC-XLs), which contain a TTC incorporated between the polymerizable (meth)acrylate functionalities, allowing one TTC to be present between each two cross-linking points (assuming negligible side reactions).[36] This method allowed for the creation of highly transformable 3D materials that could undergo sequential and regulated postprinting modifications.[36] To further explore how the presence of TTC-XLs may enable consistent and homogeneous transformations throughout 3D printed materials, a library of expandable RAFT-capable cross-linkers[31] should be synthesized and employed in different 3D printing processes. Moreover, more investigation is needed to develop alternative strategies for controlling the distribution of dormant initiating sites within the framework of highly cross-linked networks.

A relatively untapped aspect of this recently emerging research on RAFT-mediated 3D printing is systematic investigations on the (re)activatability of the preserved RAFT species within the structure of highly cross-linked 3D printed networks. There are a number of variables that might influence the (re)activatability of the preserved RAFT species in networks that are either synthesized in batch[18] or 3D printed in a layer-by-layer manner.[33] These factors include the chemical mechanism employed, which affects the degree to which polymer strands retain the thiocarbonylthio end groups, the cross-linking density, which affects the diffusion of catalysts and/or active radicals to the preserved RAFT species, and the uniformity and penetration of light exposure.

4.3. Exploring the Practical Applications of RAFT-Mediated 3D Printing.

As detailed in Section 3, RAFT-mediated 3D printing has already been employed in a range of applications. Nevertheless, there is significant potential for further innovative research to broaden its range of applications. This section covers some of the opportunities and areas that warrant further investigation.

3D printing technology may offer a path toward realizing the aim of personalized medicine by developing systems that consider individual variabilities. In the context of individualized drug delivery systems (DDSs), 3D printing offers significant benefits over traditional pharmaceutical production techniques, which are based on representative response profiles from related divisions of the target population. 3D printing enables the production of tailored tablets and/or drug-eluting implants with precise geometries, flexibility in drug dosages and release profiles tailored to the needs of individuals, and the creation of intricate drug testing systems that mimic in vivo conditions. Through several channels, RAFT-mediated 3D printing can advance the area of personalized medicine.

Structure regularity and uniform medication distributions across the drug-eluting systems can permit more regulated medication release profiles. RAFT chemistry allows for network regularity (due to the reversible deactivation of the propagating polymer chains[98]) and, thus, uniform drug distributions across the printed DDSs, a field that has not yet been explored. In addition to delivering medications, this technique can be exploited to deliver other active substances with desired release profiles and so may have implications in foods, cosmetics, and the agricultural industries.

Another potentially significant yet untapped possibility that can be provided by RAFT-mediated 3D printing is biofunction-

alization of 3D materials for use in biologically relevant applications. Conventional polymeric DDSs, either 3D printed or synthesized in bulk, contain dead polymer strands that cannot be modified after printing.[13] Moreover, harsh processing conditions of conventional 3D printing systems, e.g., high temperature or high intensity light exposure, limit the scope of functionalization with highly sensitive biomolecules (e.g., peptides).[142] To sidestep these issues, RAFT can be utilized to enable "living 3D DDSs", that is, 3D printing of DDSs containing dormant reactivatable RAFT functionalities that can undergo numerous potential postprinting biofunctionalization, spatial differentiation, and/or addition of structurally defined bioactive polymers to an already printed material.

Research from our group[44] and others[45] has shown that using RAFT-mediated polymerization instead of conventional radical polymerization can significantly enhance the resolution of 3D printed materials by reducing the overcuring of polymers (through light absorption and chain transfer reactions) in both the build layer and deeper layers. RAFT agents are viable alternatives to commonly used absorbing dyes or radical quenchers, which can cause intense and unwanted coloring of printed materials. Furthermore, release of dyes that are not covalently bonded to the polymer network is a concern, as it can result in undesirable reactions or side effects.

Additionally, it has been shown that RAFT-mediated 3D printing has the capability to produce a wide array of structural designs and create open porous materials with controlled variations in porosity. This method enables precise production of the original CAD models with excellent control over the exterior and interior shapes of scaffolds.[44] These features could open up numerous potential applications for RAFT-mediated 3D printing, such as energy storage, tissue engineering, catalysis, and molecular separation.

RDRP techniques can produce polymers with specific molecular weights, controlled architectures, and narrow molecular weight distributions. These techniques have been routinely shown to retain end-group functionality that can be reactivated to continue polymerization or initiate depolymerization and enable closed-loop recycling.[143,144] Depolymerization allows the retrieval of starting monomers from synthesized polymers, which can increase the recyclability of materials and potentially enable their industrial implementation. While most methods rely on high temperatures (typically from 120 to 180 °C) to trigger efficient depolymerization, recent studies by the Sumerlin[145] and Anastasaki[146] groups have shown that light can also be used to trigger faster and more efficient thermal depolymerization of polymers prepared by RAFT polymerization. These studies have made significant progress in the development of recyclable materials and in promoting a circular life cycle. However, the exploration of their application in RAFT-mediated 3D printing systems for recycling of 3D polymers has yet to be explored, leaving a large gap in research that warrants further investigation.

5. CONCLUSION

Although 3D printing using photopolymerization has been practiced for several decades, research into 3D printing using photo-RAFT polymerization was established in 2019 to offer new possibilities for manufacturing advanced materials that were not achievable with conventional techniques. RAFT-mediated 3D printing, sometimes termed "living" 3D printing, was initially developed for manufacturing reprocessable materials. As research in this field progressed, different chemical mechanisms

such as photoiniferter, PET-RAFT, cationic RAFT, and photoinitiator RAFT were explored, leading to more applications of this technology. The combination of RAFT and 3D printing has enabled control over spatially resolved surface functionalization and patterning, self-healing/welding, and nano- and microscale structuration of 3D polymers. Furthermore, using RAFT-mediated 3D printing, it is possible to create scaffolds with tailored interconnected channel-pore architecture, which are suitable for customized drug delivery.

This Perspective provides an overview of the chemical mechanisms involved in RAFT-mediated 3D printing and highlights the advanced materials produced using this technique. Potential future research areas are also discussed, including the need to understand the rapid curing kinetics, develop versatile formulations that are oxygen tolerant, and explore alternative strategies for controlling dormant initiating sites in highly cross-linked networks. With continued research and development, RAFT-mediated 3D printing has the potential to enable the creation of more advanced and sophisticated structures, with a wide range of applications in fields such as biomedicine, energy, and materials science.

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Notes

The author declares no competing financial interest.

Biography

Ali Bagheri earned his Ph.D. in Chemical Engineering from the University of New South Wales (UNSW) in Sydney as a member of the Cluster for Advanced Macromolecular Design (CAMD), under the supervision of Professor Cyrille Boyer and Dr. May Lim in 2018. Upon completion of his Ph.D., he was awarded a postdoctoral research fellowship at the University of Auckland in New Zealand. Currently, he is working as a lecturer at the University of New England, focusing his research on the implementation of RAFT polymerization in the realm of 3D printing technology.

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