Visible-Light-Regulated Controlled/Living Radical Polymerization in Miniemulsion

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S *Supporting Information*

ABSTRACT: The implementation of photopolymerization processes in aqueous dispersed systems has the potential to afford greener approaches to the preparation of polymeric materials and has motivated researchers to perform photo-polymerization in emulsion. However, these previous works have employed UV irradiation to induce photodegradation of a photoinitiator in addition to specialized equipment setups, thus limiting widespread use of these approaches. In this work, we aim to remedy these drawbacks via the implementation of photoredox catalysis in the regulation of a controlled/living radical polymerization under visible light. Utilizing the photoinduced electron transfer–reversible addition–fragmentation chain transfer (PET-RAFT) process, we report the miniemulsion polymerization of styrene mediated by a household grade blue LED (λ_{max} = 460 nm, 0.73 mW/cm^2). The polymerization rate can be easily manipulated by light intensity and catalyst concentration. Finally, temporal control was demonstrated via ON/OFF experiments, which shows that no significant detriment is caused by prolonged interruptions to the light exposure.
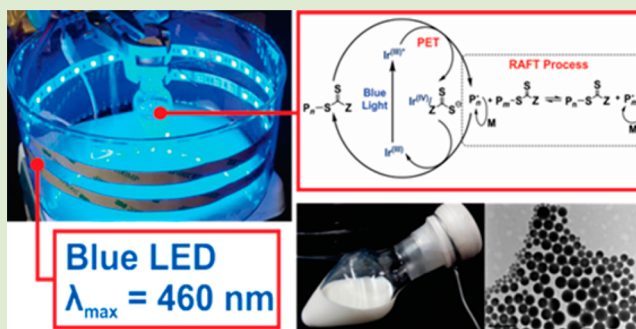
As we work toward the development of more energy-efficient and environmentally friendly processes, the combination of photopolymerization techniques[1] with the solvent-free environment afforded by an aqueous dispersed system can potentially enable a greener approach for the synthesis of polymeric materials. Previous implementations of aqueous dispersed photopolymerizations have predominantly focused on UV-initiated radical polymerizations conducted in microemulsion systems in the presence of photoinitiators.[2] Although the transparency/translucency afforded by the smaller particle sizes aids light penetration, these desirable qualities come at the cost of high surfactant concentrations in addition to low solid contents. The application of photopolymerizations in miniemulsion[3] lowers surfactant usage whilst increasing the solids capacity. However, these improvements are accompanied by increased turbidity, which can be detrimental to photo-polymerization processes due to light scattering.

UV light imposes limitations which detract from its widespread usage. Foremost of these is the fact that many organic compounds have an absorbance in the UV region. Although this absorbance has been exploited for the direct activation of monomer,[4] it precludes the use of many reactive species that are available in thermally mediated processes. The high wattage UV light sources commonly used in these systems not only pose significant safety issues but also generate significant technical challenges, such as heat,[2a,4a,5] to the extent that cooling may be required for certain applications. Furthermore, these high wattage UV sources have often been used in conjunction with specialized equipment setups,[4a,c,5b,6]

which may have contributed to their niche use. Considering these limitations, utilizing lower-energy light in the visible region may offer the advantages of increased versatility and accessibility of these processes.

Recent advances in photoredox catalysis have facilitated the use of visible light to mediate chemical syntheses,[7] offering a viable alternative to the use of UV light. Inspired by the seminal work of Hawker,[8] who described an atom transfer radical polymerization (ATRP) like process regulated by blue light, our group developed the photoinduced electron transfer–reversible addition–fragmentation chain transfer (PET-RAFT) process, which incorporates photoredox catalysis into the RAFT technique.[9] The PET-RAFT process provides significant advantages over conventional photopolymerization approaches using UV light. The use of light in the visible spectrum significantly reduces side reactions, such as the self-initiation of monomers and degradation of RAFT agents.[2f,10] In addition, photoredox catalysts enable specific activation of RAFT agents,[11] without the addition of a photoinitiator, which reduces the formation of dead polymers. Furthermore, the highly efficient nature of these photoredox catalysts permits the use of household grade light-emitting diode (LED) sources, significantly reducing energy consumption and minimizing energy wasted as heat. With these advantages in mind, we

envisaged the use of visible-light-mediated photoredox catalysis to regulate a controlled/living radical polymerization (CLRP) process in an aqueous dispersed system and thereby developed a greener approach to the controlled synthesis of polymeric materials.

In this work we describe the miniemulsion polymerization of styrene regulated by visible light via the PET-RAFT process. Under the proposed mechanism for PET-RAFT, exposure to light results in excitation of the photoredox catalyst; photo-induced electron transfer from this excited catalyst species to the RAFT agent affords an R group derived radical (or propagating radical) in a reversible process (Scheme 1). This

Scheme 1. Proposed Mechanism[9a] for the PET-RAFT Polymerization Technique Mediated by Ir(ppy)₃
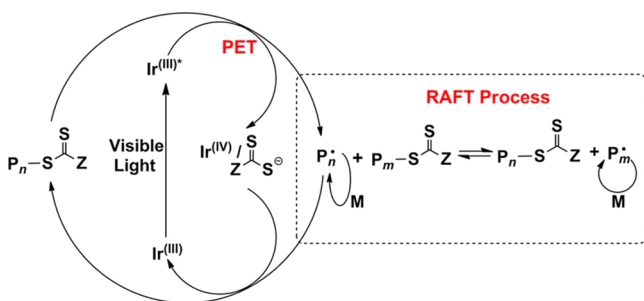
light-regulated activation–deactivation mechanism is superimposed on the RAFT exchange mechanism, affording controlled/living polymerizations, which occur only under exposure to light. Additionally, control over the polymerization rate can be achieved via the modulation of the catalyst concentration, the light intensity,[9a] or the wavelength.[9d] Herein, we report the successful implementation of the PET-RAFT process in miniemulsion, demonstrating the feasibility of visible-light-mediated photoredox catalysis to regulate CLRP processes even in turbid aqueous dispersed systems. To the best of our knowledge, this is the first report of a visible-light-mediated CLRP process implemented in miniemulsion.

The formulation (Table 1) utilized for the PET-RAFT polymerization of styrene in miniemulsion is comprised of

Table 1. Basic Formulation Used for the PET-RAFT Miniemulsion Polymerization of Styrene[a]

	component	amount (g)	notes
continuous phase	DI water	10	
	DOWFAX 8390	0.0175	3.5 wt % relative to styrene
dispersed phase	styrene	0.5	5 wt % relative to DI water
	hexadecane	0.04	8 wt % relative to styrene
	BSTP	0.0065	
	Ir(ppy)₃	1.57×10^{-4}	50 ppm relative to styrene

[a]Experimental conditions: [styrene]:[BSTP]:[Ir(ppy)₃] = 200:1:0.01 with a catalyst loading of 50 ppm relative to styrene.

styrene, a RAFT agent (3-benzylsulfanylthiocarbonylsulfanyl propionic acid, BSTP), and an iridium-based photoredox catalyst (Ir(ppy)₃) at a stoichiometric ratio of [styrene]:[BSTP]:[Ir(ppy)₃] = 200:1:0.01, with Dowfax 8390 (alkylphenyloxide disulfonate) as surfactant and hexadecane to minimize

Ostwald ripening. This formulation was optimized to achieve good catalyst solubility in the organic phase and colloidal stability for several hours. Following ultrasonication, the miniemulsions were exposed to blue light (λ_{max} = 460 nm, 0.7 mW/cm²) for predetermined times at ambient temperature.

To confirm our proposed mechanism in miniemulsion, control experiments were first performed. A miniemulsion, devoid of both RAFT agent and photoredox catalyst, was exposed to blue light for 24 h (Table 2, #1), after which no significant polymerization had occurred. The addition of the photoredox catalyst only resulted in uncontrolled and low conversion of styrene (Table 2, #2). Conversely, addition of the RAFT agent alone resulted in controlled but also low conversion (Table 2, #3). The controlled polymerization in the absence of catalyst can be attributed to the visible-light-induced photolysis of the RAFT agent, reported by our group in 2014[12] and later by Qiao and co-workers.[13,14] The addition of both the RAFT agent and the photoredox catalyst afforded controlled polymerization in conjunction with moderate conversion of monomer (Table 2, #4). When the PET-RAFT polymerization of styrene was conducted under bulk conditions (Table 2, #5), a comparatively lower conversion was observed.

To ascertain the degree of livingness, a chain extension was performed on the polystyrene macro-RAFT agent formed in the PET-RAFT miniemulsion process (Table 2, #4). The crude gravimetric samples were dissolved in a 50/50 (v/v) mixture of methyl acrylate and DMSO. Following an exposure time of 20 min, a clear shift of the molecular weight distribution to higher molecular weight occurred, although a small amount of presumably dead chains was observed (SI, Figure S3).

These successful results of the PET-RAFT process in miniemulsion motivated us to investigate the polymerization kinetics. For this, the duration of light exposure was varied from 16 to 120 h (SI, Table S1). The plot of conversion vs increasing exposure time (Figure 1A; SI, Figure S4 shows the evolution of $\ln([M]_0/[M]_t)$ versus exposure time) revealed a significant reduction in rate after 72 h, which may be attributed to the decreased solvation of the photoredox catalyst. In the solvent-free dispersed phase, the iridium photoredox catalyst is solely solubilized by the styrene content. Therefore, conversion of monomer directly translates into consumption of the solvent, which will ultimately lead to the precipitation of the catalyst and prohibit its activity. Miniemulsions comprising catalyst concentrations above 50 ppm have been observed to destabilize (SI, Figure S2B), which suggests that the starting concentration was close to the solubility limit of the catalyst in styrene. The molecular weight distribution successively shifts toward higher molecular weight in conjunction with a narrowing of the distribution consistent with a controlled/living process (Figure 1B). There is however very little shift in the molecular weight distributions beyond 72 h, consistent with the reduction in polymerization rate. Examining the plot of M_n versus conversion (Figure 1C), we initially observe experimental M_n values above the theoretical line, which can be attributed to nonuniform activation of the PET-RAFT process as a consequence of the nonuniform exposure of monomer droplets to light. Thereafter, the experimental M_n values approach then decrease below the theoretical values, which suggests an increase in the number of chains. The generation of new chains could have occurred through the self-initiation of styrene, owing to the long reaction times, and/or from radicals formed via the reduction of surfactant species.[15]

Table 2. Experimental Results for the PET-RAFT Miniemulsion Polymerization of Styrene (24 h)

#	$[St]:[BSTP]:[Ir(ppy)_3]^a$	$[Ir(ppy)_3]/[St]$ (ppm)	conv. (%)^b	$M_{n,GPC}$ (g/mol)^c	$M_w/M_n{}^c$
1	200:0:0	0	2.5	n/a	n/a
2	200:0:0.01	50	10	35600	4.92
3	200:1:0	0	11	3100	1.56
4	200:1:0.01	50	25	7250	1.47
5^d	200:1:0.01	50	8.6	2500	1.42

^{a}Reaction mixtures were exposed to a blue LED strip (λ_{max} = 460 nm, 0.73 mW/cm^2) at ambient temperature for 24 h. ^{b}Monomer conversion was calculated by gravimetric measurement. ^{c}Molecular weight and dispersity were determined by GPC analysis (THF as eluent). ^{d}Reaction was performed under bulk conditions.
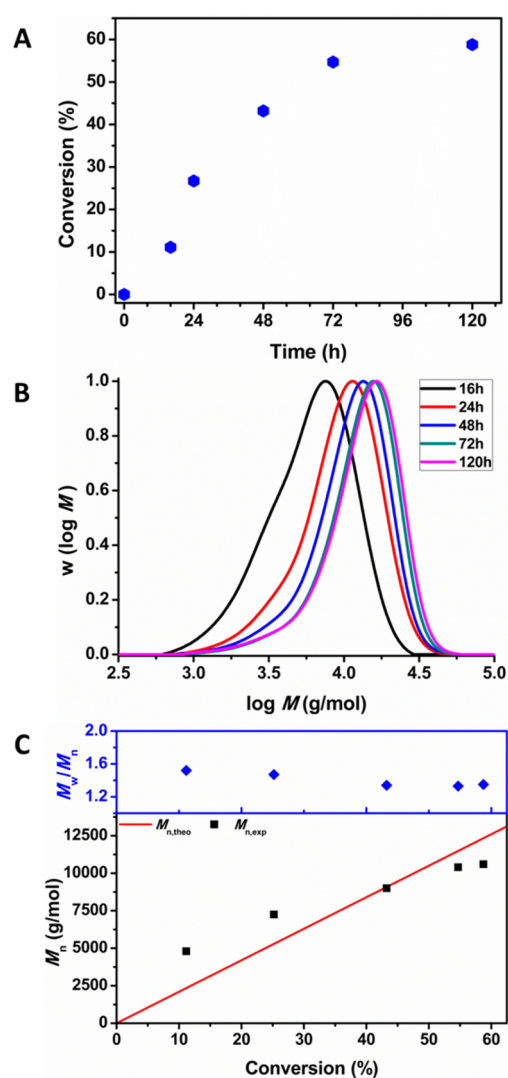

Figure 1. (A) Conversion versus exposure time. (B) Molecular weight distributions for different exposure times. (C) M_n and M_w/M_n versus monomer conversion.

Previous studies focusing on miniemulsion photopolymerizations have reported nonuniform monomer droplet nucleation[4c,5b,16] occurring due to the inhibited light penetration. This nonuniformity creates differences in the chemical potential, which cause the diffusion of monomer from non-nucleated monomer droplets to the nucleated particles. As a consequence, the non-nucleated droplets shrink, while the nucleated particles correspondingly increase in size. This phenomenon can be observed in the DLS analyses (SI, Figure S5), which show a significant increase in size (intensity-based diameter distribu-

tion) after the first 24 h of light exposure. Such an increase in the droplet/particle size is detrimental to miniemulsion photopolymerizations as the increased size contributes to increased scattering effects and possibly also reduced compartmentalization effects,[17] ultimately leading to decreased reaction rates. TEM images taken after 72 h of light exposure confirm the polydisperse nature of the particle sizes and show the existence of both small (<100 nm) and large (>200 nm) particles (SI, Figure S6A).

The ability to manipulate the rate of polymerization by tuning the catalyst concentration or light intensity has been demonstrated as a key characteristic of the PET-RAFT process.[9a] To investigate the retention of these capabilities, miniemulsion polymerizations with catalyst concentrations of 0/10/25/50 ppm relative to styrene were first performed at a light intensity of 0.73 mW/cm^2 (Figure 2A). As mentioned earlier, trithiocarbonates, such as the RAFT agent in these experiments, have been demonstrated to undergo photolysis under blue light in the absence of any photoredox catalyst,[12,14] affording the controlled but low conversion of monomer (Table 2). Increasing the catalyst concentration from this point resulted in a linear increase in the conversion. When the light intensity was decreased to 0.36 mW/cm^2, while maintaining all other reaction conditions, a corresponding decrease in the conversion was observed as expected. Interestingly, the polymerization without catalyst also displayed dependence on the light intensity, with a lower conversion observed at 0.36 mW/cm^2.

The ability to exert temporal control is a defining characteristic of photoregulated polymerizations and can be implemented by simply switching the light source ON or OFF. To demonstrate this capability, an ON/OFF experiment was conducted (Figure 2B), wherein conversion of monomer only occurred during periods of light exposure. Switching OFF the light returned the system to a dormant state, while switching the light back ON reactivated the process. The advantage of temporal control lies in the ability to deactivate/reactivate the process without any detriment and should in theory enable similar reaction kinetics to uninterrupted experiments. In Figure 2C, we compare the effect of interrupted exposure (ON/OFF experiment) with continuous exposure. Considering only the ON periods, similar conversion of monomer was observed between the ON/OFF and kinetic experiments. In a similar manner to the kinetic experiments, DLS analysis of the ON/OFF experiments (SI, Figure S7) shows that the most significant increase in the particle size occurs during the first 24 h of light exposure, with limited increases thereafter. Additionally, examination of the TEM images also shows a similar distribution of particle sizes for the ON/OFF experiment (SI, Figure S6B) to that observed for the kinetic experiments (SI, Figure S6A). These results in combination suggest that no
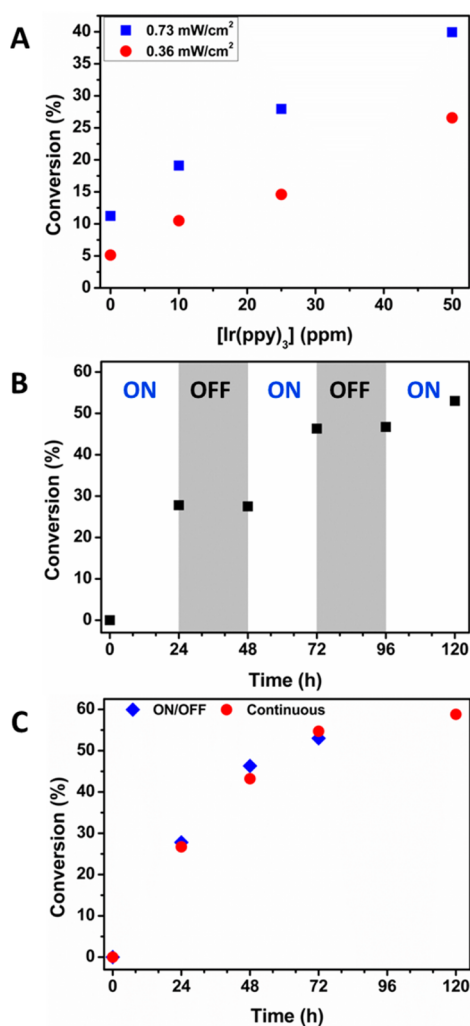
Figure 2. (A) Monomer conversion versus exposure time at 0.73 mW/cm^2 (blue) and 0.36 mW/cm^2 (red). (B) ON/OFF experiment. (C) Monomer conversion versus time comparing the interrupted exposure (blue) of the ON/OFF experiment compared to continuous exposure (red).

detriment to the overall polymerization process occurred as a result of the activation/deactivation protocol.

In summary, visible-light-regulated CLRP of styrene was successfully implemented in a turbid miniemulsion system at ambient temperature. The PET-RAFT process enabled the ability to modulate the rate of monomer conversion by tuning the catalyst concentration or the light intensity. Temporal regulation was also demonstrated, and the system proved to be unaffected by interruptions to the light exposure, with conversion occurring exclusively under illumination. Despite the low intensity light sources, the ability to regulate controlled polymerizations in turbid media highlights the efficiency of the PET-RAFT technique and demonstrates the feasibility of using visible light in the aqueous dispersed system. These results are promising for the development of green processes combining low energy visible-light sources with the environmental friendliness of aqueous dispersed systems.

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The authors declare no competing financial interest.

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