Photoenzymatic RAFT Emulsion Polymerization with Oxygen Tolerance

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Abstract Photoenzymatic reversible addition-fragmentation chain transfer (RAFT) emulsion polymerization, surfactant-free or ab initio, of various monomers is reported with oxygen tolerance. In surfactant-free emulsion polymerization, poly(N,N-dimethylacrylamide)s were used as stabilizer blocks for emulsion polymerization of methyl acrylate, n-butyl acrylate and styrene, producing well-defined amphiphilic block copolymers, including those with an ultrahigh molecular weight, at quantitative conversions. The controlled character of surfactant-free emulsion polymerization was confirmed by kinetic studies, chain extension studies and GPC analyses. Temporal control was demonstrated by light ON/OFF experiments. In ab initio emulsion polymerization of methyl acrylate and methyl methacrylate, low-dispersity hydrophobic polymers were synthesized with predictable molecular weights. This study extends the monomer scope suitable for photoenzymatic RAFT polymerization from hydrophilic to hydrophobic monomers and demonstrates that oxygen-tolerance can be equally achieved for emulsion polymerization with excellent RAFT control.

Keywords Controlled radical polymerization; RAFT; Emulsion polymerization; Oxygen tolerance; Photoenzymatic polymerization

INTRODUCTION

Controlled radical polymerization (CRP) has enabled easy access to various polymer architectures with controlled molecular weight and molecular weight distribution.\textsuperscript{[1–3]} Reversible addition-fragmentation chain transfer (RAFT) polymerization has been widely recognized as one of the most powerful CRP techniques because of its excellent monomer tolerance and mild reaction conditions.\textsuperscript{[6–10]} More recently, dynamic modulation of RAFT polymerization by external stimuli has gained significant attention as they grant the ability of modulating a polymerization spatially and temporally.\textsuperscript{[11–13]} Among the many external stimuli used in RAFT, light has been employed remarkably well owing to its mildness, availability, and orthogonality to other stimuli.\textsuperscript{[14–20]} One of the main problems of CRP, including RAFT, is its high sensitivity to oxygen, which is a radical scavenger.\textsuperscript{[21–23]}

Going beyond solution polymerizations, RAFT polymerizations in dispersed aqueous media (e.g., dispersion, suspension, emulsion, or miniemulsion) exhibit significant advantages of fast polymerization, low solution viscosity, efficient heat removal and accessibility to various particle morphologies.\textsuperscript{[24–27]} Indeed, emulsion polymerization is one of the most common industrial methods for large-scale polymer production and many commercial products are directly provided in the form of emulsion polymers. In general, RAFT emulsion polymerization includes two methods: (1) surfactant-aided ab initio emulsion polymerization,\textsuperscript{[28–29]} and (2) surfactant-free emulsion polymerization using hydrophilic stabilizers, e.g., in polymerization-induced self-assembly (PISA).\textsuperscript{[30–33]} The former uses an externally-added surfactant as an emulsifier, while the latter employs a hydrophilic stabilizer such as a hydrophilic macromolecular chain transfer agent (macro-CTA).\textsuperscript{[34–37]} However, achieving the control over molecular weight and molecular weight distribution in RAFT emulsion polymerization is more demanding than those in homogeneous polymerization. For example, in ab initio emulsion polymerization, initiating radicals should be generated in the aqueous phase and CTA should have a proper water solubility to ensure homogeneous nucleation and uniform polymerization in different particles.

Recently, the combination of enzyme catalysis and CRP has gained significant interest as precision polymer synthesis can be achieved with high efficiency under mild conditions.\textsuperscript{[38,39]} Glucose oxidase (GOx) is the most common enzymes applied in CRP due to its commercial availability and organic solvent resistance.\textsuperscript{[40–42]} In most studies, however, GOx has been used
only to consume oxygen. In our previous work, we developed a photoenzymatic RAFT polymerization inspired by DNA photolyase. Glucose reduces the GOx flavin cofactor FAD to FADH\(^+\). The latter can be activated into photoexcited state (FADH\(^+\)) under violet or blue light to act as an effective photocatalyst. Despite the high efficiency and robustness of the photoenzymatic RAFT polymerization in controlling both more-activated and less-activated monomers, the polymerization of hydrophobic monomers has not been investigated. Herein, we report our study on the effectiveness of this method in both surfactant-free and ab initio emulsion polymerization. (Scheme 1).

**EXPERIMENTAL**

**Materials**

Methyl methacrylate (MMA, 99%), methyl acrylate (MA, 99%), N,N-dimethylacrylamide (DMA, 99%), n-butyl acrylate (nBuA, 99%), D(+)-glucose (99.5%), and DMSO-d\(_6\) (99.9% D), CDCl\(_2\) were purchased from J&K Scientific. Styrene (St, 99%), cetyltrimethylammonium bromide (99%, CTAB), D-(+)-glucose (99.5%), and 2,2′-dimethylacrylamide (DMA, 99%), N,N,N,N′,N′-pentamethyldiethylenetriamine) (AIBN, 98%) were purchased from Aladdin. Glucose oxidase from Aspergillus niger (GOx, 200 units/mg) and Brij-35 were obtained from J&K Scientific. Alumina (Greagent Chemical, AR) to remove the inhibitor. 2-(Ethyl sulfanylthiocarbonyl sulfanyl)propionic acid (ETPA), (Ethyl sulfanylthiocarbonyl sulfanyl)propionic acid (ETPA), and PEG\(_8\)-CEPA\(^{[52]}\) and PDMA\(_{30}\) macro-CTA\(^{[53]}\) (Fig. 1a) were synthesized as previously reported and were characterized by \(^1\)H-NMR (Figs. S1–S3 in the electronic supplementary Information, ESI).

**Characterization**

\(^1\)H-NMR spectra were recorded on a JEOL resonance ECZ400S 400 MHz spectrometer using D\(_2\)O, CDCl\(_3\) or DMSO-d\(_6\) as the solvent. Chemical shifts were reported using TMS as the reference. Two DMF GPC systems were employed for determining molecular weight and dispersity. \(M_\text{GPC}\) was analyzed using a Waters e2695 GPC system equipped with a dual angle laser light scattering (DALLS) detector. \(M_\text{n,MALLS}\) was determined on a Wyatt DAWN8 multi-angle laser light scattering (MALLS) detector. The majority results reported in this work were obtained on GPC-DALLS unless otherwise stated.

**Synthesis of PDMA\(_{270}\) Macro-CTA**

Photoenzymatic RAFT homogeneous polymerization was carried out without prior deoxygenation to obtain PDMA\(_{270}\). In detail, ETPA (0.0035 g, 1.67×10\(^{-5}\) mol), DMA (0.4965 g, 5.01×10\(^{-3}\) mol), GOx (5.6×10\(^{-4}\) g, 3.75×10\(^{-9}\) mol) and glucose (2.7×10\(^{-3}\) g, 1.5×10\(^{-5}\) mol) were added to a 5 mL glass vial. Then, PBS buffer (20 mmol/L, pH 5.8) was added to make 5 mL of the final solution with no head space. The reaction vial was sealed and exposed to violet LED light (405 nm, 0.4 mW/cm\(^2\)) at room temperature. The polymerization was stopped at 6 h with 90% monomer conversion as determined by \(^1\)H-NMR spect-

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**Scheme 1**  Schematic representation of surfactant-free photoenzymatic RAFT emulsion polymerization (a) and ab initio photoenzymatic RAFT emulsion polymerization (b).
roscopy. The solution was dialysis against ethanol and dried under vacuum. $M_{\text{theory}}=27.0$ kg/mol, $M_{\text{MALLS}}=27.2$ kg/mol, $\delta=1.02$ (Fig. 1b). The $^1$H-NMR spectrum of PDMA$_{270}$ is shown in Fig. S4 (in ESI).

![Fig. 1](https://doi.org/10.1007/s10118-021-2556-5)

**Surfactant-free Photoenzymatic RAFT Emulsion Polymerization Using PDMA Macro-CTA**

Surfactant-free Photoenzymatic RAFT emulsion polymerizations using PDMA macro-CTAs were carried out without prior deoxygenation under violet LED light (405 nm, 0.4 mW/cm$^2$) at a stirring rate of 500 r/min, room temperature. Taking the synthesis PDMA$_{30}$ as a representative procedure, PDMA$_{30}$ (0.0638 g, 2.0×10$^{-3}$ mol), MA (0.3362 g, 4.0×10$^{-5}$ mol), GOx (2.37×10$^{-4}$ mol), glucose (1.1×10$^{-3}$ g, 6×10$^{-6}$ mol), Brij98 (0.01 g) and 1 mL of PBS buffer (0.2 mol/L, pH 5.8) were added to a 2.0 mL glass vial; then MA (0.1995 g, 2.37×10$^{-4}$ mol) was slowly added into the vial without stirring. Finally, additional PBS buffer was added to make 2.0 mL of the final solution with no headspace. Two separated layers were obtained and the reaction vial was sealed and exposed to violet LED light for 3 h at a stirring rate of 200 r/min. After 3 h, the stirring rate was increased to 500 r/min and polymerization continued by light exposure for another 3 h. For chain extension studies, MA and GOx were added and the mixture was homogenized by ultrasonication for 3 min.

**RESULTS AND DISCUSSION**

**Surfactant-free Photoenzymatic RAFT Emulsion Polymerization Using PDMA Macro-CTAs**

First, PDMA with a relatively low molecular weight (PDMA$_{30}$) was synthesized and used as the stabilizer block for RAFT emulsion polymerization. The structure of PDMA$_{30}$ was confirmed by $^1$H-NMR spectrum (Fig. S3 in ESI). The molecular weight and dispersity were determined by GPC: $M_{\text{theory}}=3.2$ kg/mol, $M_{\text{GPC}}=2.8$ kg/mol, $\delta=1.09$ (Fig. 1a). Since CTAs can act as photoiniferters upon light exposure,$^{[54]}$ to verify whether photolysis of PDMA bearing trithiocarbonate (PDMA-TTC) can initiate emulsion polymerization, control experiments were performed (Table S1 in ESI). When GOx and glucose were absent, no polymerization took place under light exposure, suggesting that direct photolysis of PDMA-TTC is not effective in initiating MA emulsion polymerization under the experimental conditions employed in this study.

Surfactant-free photoenzymatic RAFT emulsion polymerization of MA for the synthesis of PDMA$_{30}$-b-PMA$_{1200}$ block copolymers was investigated at 0.2 g/mL solid content without prior deoxygenation. Nearly full MA conversions (>99%) were achieved within 6 h (Table 1, entries 1–4). The molecular weights of PDMA$_{30}$-b-PMA$_{1200}$ determined from GPC measurements were consistent with expected values and the molecular weight distribution was narrow ($\delta=1.26$). However, when the degree of polymerization (DP) of the PMA block was greater than 2000, precipitation was observed during the polymerization instead of forming a stable dispersion, suggesting that the low-molecular-weight PDMA$_{30}$ is insufficient in stabilizing the formed polymer particles. To obtain high molecular weight, especially ultrahigh molecular weight (UHMW) polymers without forming precipitation, a longer PDMA$_{270}$ stabilizer was synthesized via photoenzymatic RAFT solution polymerization in PBS buffer (Fig. 5 in ESI). Using PDMA$_{270}$ as the stabilizer, no precipitation was formed even when the DP of PMA reached 12000 (Fig. S5 in ESI). For example, PDMA$_{270}$-b-PMA$_{4000}$ and PDMA$_{270}$-b-PMA$_{12000}$ with reasonably low dispersities were obtained (Fig. 1b and Table 1, entries 5–6).

With the established surfactant-free photoenzymatic RAFT
emulsion polymerization, we also conducted emulsion polymerizations of nBuA and styrene using PDMA as macro-CTA (Table S2 in ESI). While 90% conversion was achieved for nBuA at room temperature within 10 h and 65% conversion was obtained for styrene at 50 °C for 24 h. The comparable low conversion of styrene is due to its small propagation rate constant. It is worth noting that GOx retained sufficient activity under these polymerization conditions: 20% (W/V) solid content, 6 h, violet LED light (405 nm, 0.4 mW/cm²), room temperature. Monomer conversion determined by 1H-NMR spectroscopy in DMSO-d₆. PBS buffer (0.2 mol/L, pH 5.8), Mₙ,GPC obtained from GPC-DALLS. PBS buffer (20 mmol/L, pH 5.8), Mₙ,GPC obtained from GPC-MALLS.

Kinetic studies were performed in a surfactant-free photoenzymatic RAFT polymerization of MA at a target DP of 2000 using PDMA as macro-CTA. Two distinct regimes were observed in the semilogarithmic plot (Fig. S7 in ESI), indicating two different polymerization stages during emulsion polymerization, though the exact nature of these needs further study. After the initial nucleation stage, the polymerization proceeds inside the monomer-swollen particles, leading to an increase in the polymerization rate. GPC measurements suggested controllable molecular weights and low molecular weight distributions (D=1.20) for the block copolymers obtained at different monomer conversions.

To demonstrate whether temporal modulation can also be achieved in photoenzymatic RAFT emulsion polymerization by switching light on/off, a polymerization of MA with a target DP of 2000 was conducted by switching the violet light on and off (Fig. 2). The polymerization was deactivated when light was off, and was activated when light was on. Two dis-

![Fig. 2](https://doi.org/10.1007/s10118-021-2556-5)
distinct kinetic regimes were also observed in the semilogarithmic plot despite of the complex light manipulation patterns (Fig. 2b), which was consistent with that in continuous light irradiation polymerization. Thus, interruptions to light exposure had no influence on the controlled feature of RAFT emulsion polymerization as confirmed by the low dispersities and linear evolution of $M_n$ with increasing monomer conversion.

Tri-block copolymers were synthesized to ascertain the degree of livingness (Table S3 in ESI). The polymerization of the second block was driven to full conversion; then, more MA was added to the latex and the emulsion polymerization was continued to afford the tri-block copolymer. Well-defined PDMA$_{30}$-b-PMA$_{500}$-b-PMA$_{1000}$ and PDMA$_{30}$-b-PMA$_{1000}$ were efficiently generated in situ. It should also be emphasized that only MA was added during the chain extension experiments. Successful chain extensions were confirmed by the increased molecular weights and unimodal distributions of the final products as shown by the GPC traces (Fig. 3), suggesting a high livingness was retained during photoenzymatic RAFT emulsion polymerization.

**Ab Initio Photoenzymatic RAFT Emulsion Polymerization**

Boyer and Zetterlund previously reported direct photolysis of CTAs for initiating miniemulsion polymerization. To verify whether photolysis of ETPA can initiate ab initio emulsion polymerization, a series of control experiments were conducted under N$_2$ protection. High monomer conversion was achieved for free-radical polymerization in the absence of ETAP (Table S4, entry 1 in ESI) and no conversion was observed in the absence of glucose, GOx or violet light (Table S4, entries 2–5 in ESI). We attribute these results to the weak light absorption of ETPA at 405 nm and the low light intensity used in this study.

In ab initio photoenzymatic RAFT emulsion polymerization, surfactants and water-soluble CTAs were used, so particles can be effectively nucleated in the aqueous phase and the formed hydrophobic polymer particles can be stabilized by surfactants. To avoid pre-mixing of aqueous and organic phases, the reaction vials were exposed to violet LED light first at a stirring rate of 200 r/min for 3 h to allow for uniform particle nucleation. Then, the stirring rate was increased to 500 r/min and the polymerization continued by light exposure for another 3 h. Ab initio emulsion polymerization was initially examined at different Brij$_{98}$ loadings. With targeting DP of 1000, the amount of Brij$_{98}$ was reduced from 15 wt% to 5 wt% relative to MA (Table 2, entries 1–3) and well-defined PMA was obtained in all cases. Next, higher molecular weight PMA$_{2000}$ ($M_{n,\text{GPC}}$=152.9 kg/mol, $D$=1.21) and PMMA$_{2000}$ ($M_{n,\text{GPC}}$=228.9 kg/mol, $D$=1.29) were successfully synthesized with only 5 wt% Brij$_{98}$ (Fig. 4). Finally, CTAB was also examined as a surfactant in ab initio photoenzymatic RAFT emulsion polymerization of MA, which equally produced PMA with well-controlled molecular characteristics (Table 2, entry 7).

![Fig. 3 GPC traces of tri-block copolymers synthesized via sequential surfactant-free photoenzymatic RAFT emulsion polymerization of MA.](https://doi.org/10.1007/s10118-021-2556-5)

**Table 2** Summary of polymers synthesized via ab initio photoenzymatic RAFT emulsion polymerization.

| Entry | CTA  | Monomer | Target DP | Surfactant | $C_{\text{surfactant}}$ (wt%) | Conv. (%) | $M_{n,\text{theory}}$ (kg/mol) | $M_{n,\text{GPC}}$ (kg/mol) | $D$ |
|-------|------|---------|-----------|------------|-----------------|--------|-----------------|-----------------|-----|
| 1 b   | ETPA | MA      | 1000      | Brij$_{98}$| 5               | >99    | 84.3            | 87.6            | 1.24|
| 2 b   | ETPA | MA      | 1000      | Brij$_{98}$| 10              | >99    | 84.3            | 87.1            | 1.22|
| 3 b   | ETPA | MA      | 1000      | Brij$_{98}$| 15              | >99    | 84.3            | 83.8            | 1.26|
| 4 b   | ETPA | MA      | 2000      | Brij$_{98}$| 5               | >99    | 168.4           | 152.9           | 1.21|
| 5 b   | PEG$_2$CEPA | MA     | 1000      | Brij$_{98}$| 5               | >99    | 84.7            | 91.3            | 1.27|
| 6 b   | PEG$_2$CEPA | MMA    | 2000      | Brij$_{98}$| 5               | >99    | 200.8           | 228.9           | 1.29|
| 7 c   | ETPA | MA      | 1000      | CTAB       | 5               | >99    | 84.7            | 96.63           | 1.24|

Polymerization conditions: 2 mL, [M]=10% (w/v), PBS buffer (20 mmol/L, pH 5.8), violet LED light (405 nm, 0.4 mW/cm$^2$), room temperature. Monomer conversion determined by $^1$H-NMR spectroscopy in DMSO-d$_6$. $^a$ Relative to monomer. $^b$ 6 h; $^c$ 10 h.
CONCLUSIONS

In summary, we have demonstrated that photoenzymatic emulsion polymerization of hydrophobic monomers can be successfully conducted under surfactant-free and ab initio conditions to afford well-defined amphiphilic block copolymers and hydrophobic polymers without prior removal of oxygen. The robustness and efficiency of this green method have been proven by its suitability for well-controlled polymerization of different monomers with high monomer conversions. Polymers with a wide range of molecular weights, including UHMW block copolymers, can be effectively synthesized, simply under irradiation of a low-intensity visible LED light. Temporal modulation of polymerization kinetics can be equally achieved under photoenzymatic emulsion polymerizations. High endgroup fidelity can be achieved, as confirmed by chain extension experiments. This study significantly expands the monomer scope suitable for photoenzymatic RAFT polymerization, further highlighting the versatility and robustness of this emerging green synthetic method.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at [http://doi.org/10.1007/s10118-021-2556-5](http://doi.org/10.1007/s10118-021-2556-5).

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