Supporting Information

Iodine-Mediated PhotoATRP in Aqueous Media with Oxygen Tolerance

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EXPERIMENTAL

Materials

Poly(ethylene glycol) methyl ether methacrylate ($M_n$ 300, PEGMA$_{300}$, Sigma-Aldrich) was passed through a column of basic alumina to remove inhibitor. Ethyl α-bromophenylacetate (EBPA, 97% Sigma-Aldrich), tetrabutylammonium iodide (TBAI, Fisher Chemical), potassium iodide (KI, Fisher Chemical), sodium iodide (NaI, Sigma-Aldrich), and lithium iodide (LiI, Sigma-Aldrich) were used as received.

Instrumentation

$^1$H nuclear magnetic resonance ($^1$H NMR) measurements were performed on a Bruker Avance™ III 500 MHz spectrometer. Molecular weight properties of the polymers were determined by size-exclusion chromatography (SEC). The SEC instrument was equipped with a Waters 515 pump and Waters 410 differential refractometer. SEC measurements were performed using PSS columns (Styrogel 10$^5$, 10$^3$, 10$^2$ Å) with DMF as an eluent at the flow rate of 1 mL/min. Linear poly(methyl methacrylate) standards were used for calibration. Polymerizations were irradiated under blue ($\lambda_{\text{max}}$ = 465 nm, 12 mW/cm$^2$), green ($\lambda_{\text{max}}$ = 520 nm, 4.5 mW/cm$^2$), and yellow ($\lambda_{\text{max}}$ = 595 nm, 0.6 mW/cm$^2$) light LEDs purchased from aspectLED.

General procedure for iodine-mediated photoATRP

Into a 2-dram vial equipped with a stir bar was added TBAI (103.4 mg, 0.28 mmol, 4 equiv.) The vial was sealed with a septum rubber and was subjected to vacuum and back filling with nitrogen for three times. PEGMA$_{300}$ monomer (1 mL, 3.5 mmol, 50 equiv.) and water (3 mL, 75 vol %) degassed with nitrogen in separate containers for 30 min were added to the vial under nitrogen atmosphere. EBPA (12.2 µL, 70 µmol, 1 equiv.) was added into the solution and the vial was irradiated under blue LEDs to start the polymerization. Samples were taken and analyzed by NMR and SEC techniques.
Supporting polymerization results:

**Polymerizations using TBAI:**

![Graph A](image1)  
**A**  
![Graph B](image2)  
**B**  
![Graph C](image3)  
**C**

**Figure S1.** Iodine-mediated photoATRP in aqueous media. Reaction conditions: [PEGMA\textsubscript{300}]/[EBPA]/[TBAI] = 50/1/4 in 50 vol % water. Irradiated under blue LEDs (\(\lambda_{\text{max}} = 460\) nm, 12 mW/cm\(^2\)). (A) Kinetics of the polymerization. (B) Number-average molecular weight (\(M_n\), solid points) and dispersity (\(D\), open points) as a function of monomer conversion. (C) SEC traces.

![Graph A](image4)  
**A**  
![Graph B](image5)  
**B**  
![Graph C](image6)  
**C**

**Figure S2.** Iodine-mediated photoATRP in aqueous media. Reaction conditions: [PEGMA\textsubscript{300}]/[EBPA]/[TBAI] = 50/1/4 in 67 vol % water. Irradiated under blue LEDs (\(\lambda_{\text{max}} = 460\) nm, 12 mW/cm\(^2\)). (A) Kinetics of the polymerization. (B) Number-average molecular weight (\(M_n\), solid points) and dispersity (\(D\), open points) as a function of monomer conversion. (C) SEC traces.
**Figure S3.** Iodine-mediated photoATRP in aqueous media. Reaction conditions: [PEGMA\textsubscript{300}]/[EBPA]/[TBAI] = 50/1/4 in 75 vol % water. Irradiated under blue LEDs (λ\textsubscript{max} = 460 nm, 12 mW/cm\textsuperscript{2}). (A) Kinetics of the polymerization. (B) Number-average molecular weight (\(M_n\), solid points) and dispersity (\(D\), open points) as a function of monomer conversion. (C) SEC traces.

**Polymerizations using KI:**

**Figure S4.** Iodine-mediated photoATRP in aqueous media. Reaction conditions: [PEGMA\textsubscript{300}]/[EBPA]/[KI] = 100/1/4 in 50 vol % water. Irradiated under blue LEDs (λ\textsubscript{max} = 460 nm, 12 mW/cm\textsuperscript{2}). (A) Kinetics of the polymerization. (B) Number-average molecular weight (\(M_n\), solid points) and dispersity (\(D\), open points) as a function of monomer conversion. (C) SEC traces.
Figure S5. Iodine-mediated photoATRP in aqueous media. Reaction conditions: [PEGMA$_{300}$]/[EBPA]/[KI] = 50/1/4 in 50 vol % water. Irradiated under blue LEDs ($\lambda_{\text{max}} = 460$ nm, 12 mW/cm$^2$). (A) Kinetics of the polymerization. (B) Number-average molecular weight ($M_n$, solid points) and dispersity ($D$, open points) as a function of monomer conversion. (C) SEC traces.

Figure S6. Results of iodine-mediated photoATRP of PEGMA$_{300}$ monomer in the presence of (A) sodium iodide (NaI) and (B) lithium iodide (LiI) salts. Reaction conditions: [PEGMA$_{300}$]/[EBPA]/[I] = 100/1/4 in 75 vol % water. Irradiated under blue LEDs ($\lambda_{\text{max}} = 460$ nm, 12 mW/cm$^2$) for 2 h.