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 (λ_{max} = 465 nm, 12 mW/cm^2), green (λ_{max} = 520 nm, 4.5 mW/cm^2), and yellow (λ_{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:

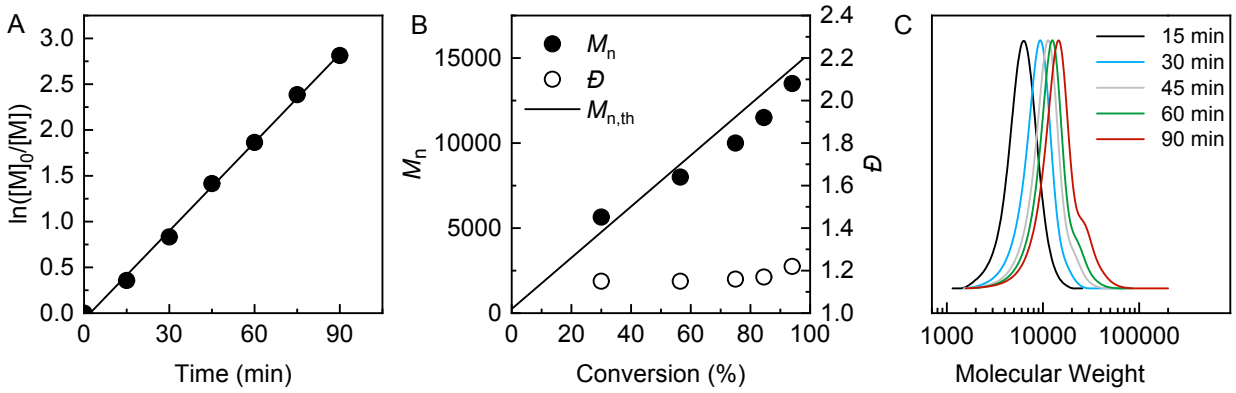

Figure S1. Iodine-mediated photoATRP in aqueous media. Reaction conditions: [$PEGMA_{300}$]/[EBPA]/[TBAI] = 50/1/4 in 50 vol % water. Irradiated under blue LEDs (λ_{max} = 460 nm, 12 mW/cm^2). (A) Kinetics of the polymerization. (B) Number-average molecular weight (M_n, solid points) and dispersity ($Đ$,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

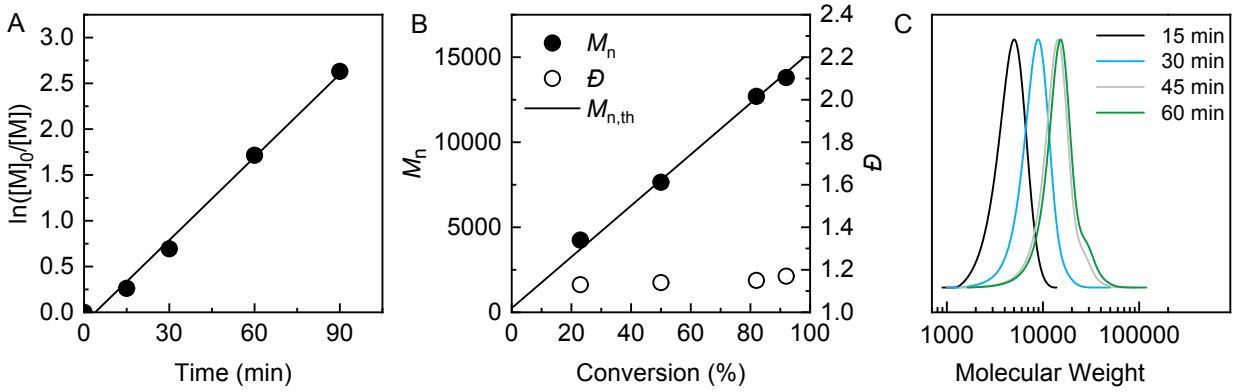

Figure S2. Iodine-mediated photoATRP in aqueous media. Reaction conditions: [$PEGMA_{300}$]/[EBPA]/[TBAI] = 50/1/4 in 67 vol % water. Irradiated under blue LEDs (λ_{max} = 460 nm, 12 mW/cm^2). (A) Kinetics of the polymerization. (B) Number-average molecular weight (M_n, solid points) and dispersity ($Đ$,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

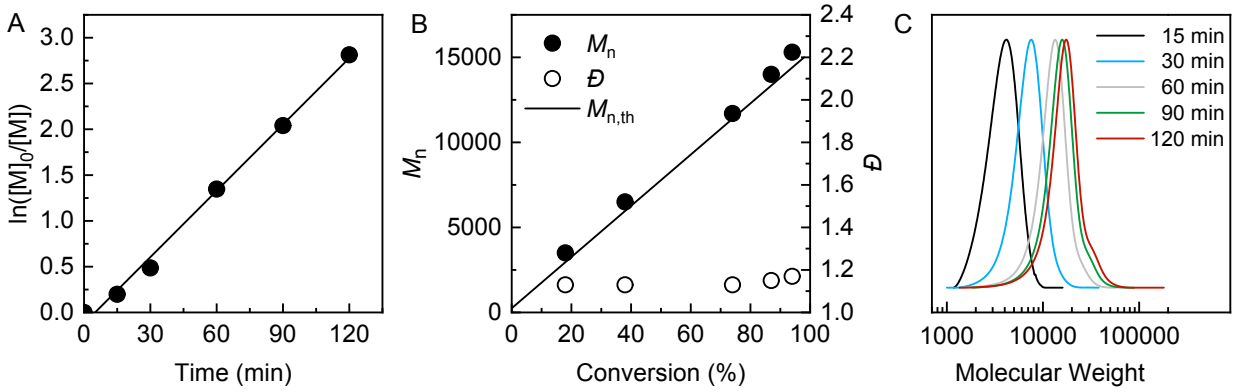

Figure S3. Iodine-mediated photoATRP in aqueous media. Reaction conditions: [PEGMA$_{300}$]/[EBPA]/[TBAI] = 50/1/4 in 75 vol % water. Irradiated under blue LEDs (λ_{max} = 460 nm, 12 mW/cm^2). (A) Kinetics of the polymerization. (B) Number-average molecular weight (M_n, solid points) and dispersity ($Đ$,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

Polymerizations using KI:

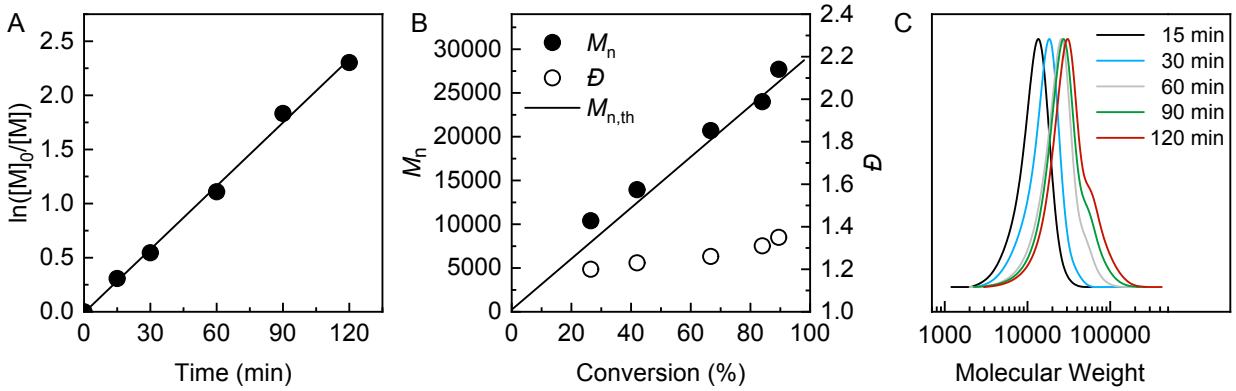

Figure S4. Iodine-mediated photoATRP in aqueous media. Reaction conditions: [PEGMA$_{300}$]/[EBPA]/[KI] = 100/1/4 in 50 vol % water. Irradiated under blue LEDs (λ_{max} = 460 nm, 12 mW/cm^2). (A) Kinetics of the polymerization. (B) Number-average molecular weight (M_n, solid points) and dispersity ($Đ$,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

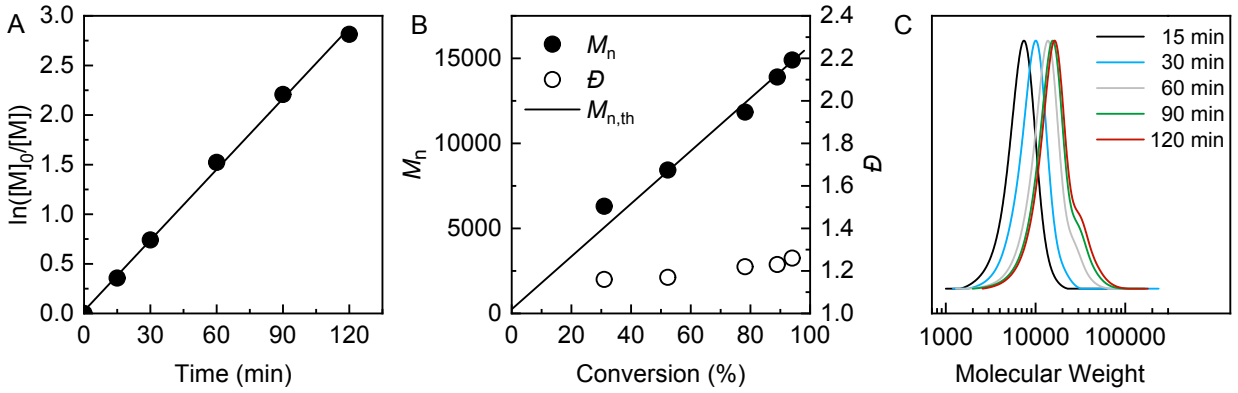

Figure S5. Iodine-mediated photoATRP in aqueous media. Reaction conditions: [$PEGMA_{300}$]/[EBPA]/[KI] = 50/1/4 in 50 vol % water. Irradiated under blue LEDs (λ_{max} = 460 nm, 12 mW/cm^2). (A) Kinetics of the polymerization. (B) Number-average molecular weight (M_n, solid points) and dispersity ($Đ$,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

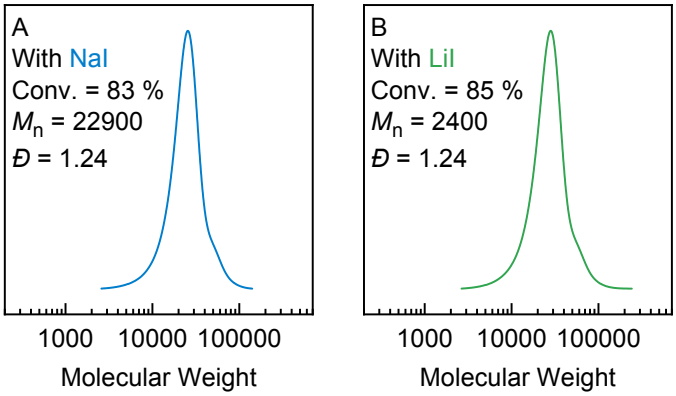

Figure S6. Results of iodine-mediated photoATRP of $PEGMA_{300}$ monomer in the presence of (A) sodium iodide (NaI) and (B) lithium iodide (LiI) salts. Reaction conditions: [$PEGMA_{300}$]/[EBPA]/[I^-] = 100/1/4 in 75 vol % water. Irradiated under blue LEDs (λ_{max} = 460 nm, 12 mW/cm^2) for 2 h.