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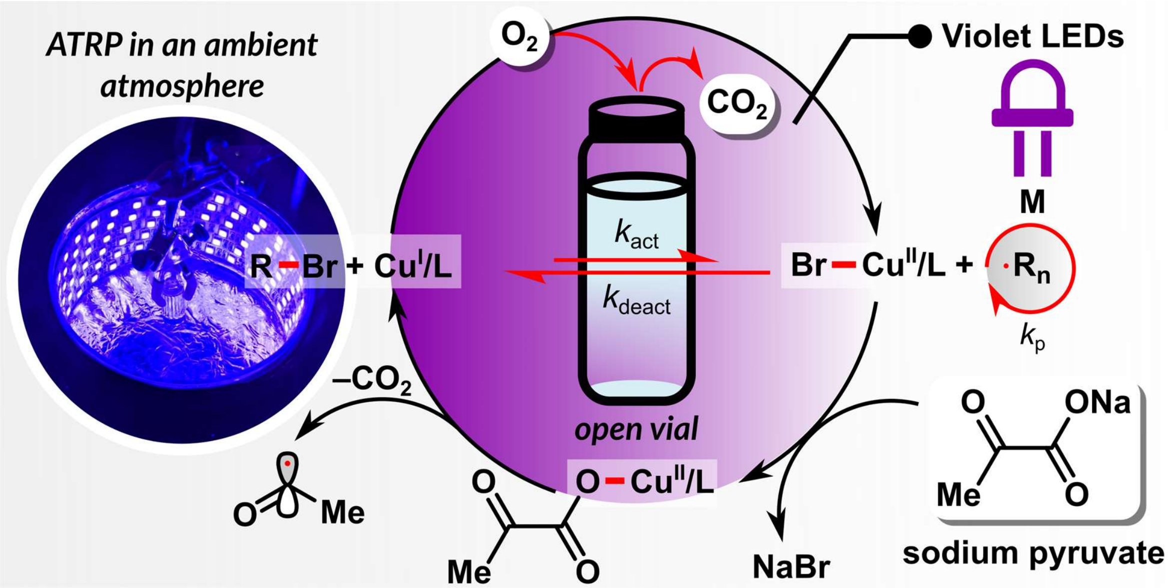
Supplementary Information

Fully oxygen–tolerant atom transfer radical polymerization triggered by sodium pyruvate

Grzegorz Szczepaniak,*[a,b] Matylda Łagodzińska,[a,c] Sajjad Dadashi-Silab,[a] Adam Gorczyński,[a,d] Krzysztof Matyjaszewski*[a]

a) Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, United States. E-mail: km3b@andrew.cmu.edu
b) Faculty of Chemistry, University of Warsaw, Żwirki i Wigury 101, 02-089 Warsaw, Poland.
c) Department of Chemistry, University of Oxford, South Parks Road, Oxford OX13QZ, United Kingdom
d) Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland



Supplementary Information

Table of contents

Supplementary Information

Experimental Details

Materials

All chemicals were purchased from commercial sources and used as received unless otherwise noted. Tris(2-pyridylmethyl)amine (TPMA, 99%) was purchased from *AmBeed. N*,*N*,*N′*,*N′*,*N′′*-tris[2-(dimethylamino)ethyl]amine (Me_6TREN, 99%) was received from *Koei Chemical Co., Ltd.* Tris(3,5-dimethyl4-methoxy-2-pyridylmethyl)amine ($TPMA^{*3}$) was synthesized according to previously published procedure.[1] 2-Hydroxyethyl 2-bromoisobutyrate (HOBiB, 95%), ethyl α-bromoisobutyrate (EBiB, 98%), sodium pyruvate (SP, 99%), copper(II) bromide ($CuBr_2$, 99.99%), tetrabutylammonium bromide (TBAB, ≥98.0%), sodium bromide (NaBr, ≥99.0%), sodium phosphate dibasic (Na_2HPO_4, ≥99.0%) and potassium phosphate monobasic (KH_2PO_4, ≥99.0%) were purchased from *Sigma-Aldrich. N*-Isopropylacrylamide (NIPAM, 98%) was purchased from *TCI* and purified by recrystallization from hexane. Methyl acrylate (MA, 99%) was purchased from *Sigma-Aldrich* and passed through a column of basic alumina to remove inhibitor prior to use. Water (HPLC grade), dimethyl sulfoxide (DMSO, ≥99.7%) and *N*,*N*-dimethylformamide (DMF, ACS grade) were purchased from *Fisher Chemical.*

Instrumentation

Nuclear Magnetic Resonance (NMR)

^1H NMR spectra were recorded on *Bruker* Avance III 500 MHz spectrometers with D_2O used as the solvent.

UV-Vis-NIR

The evolution of $[L/Cu^{II}–Br]^+$ was monitored using a *Varian Cary* 5000 UV/Vis/NIR spectrometer.

Size Exclusion Chromatography (SEC)

SEC measurements of PNIPAM were performed using PSS columns (Styrogel 10^5 , 10^3 , 10^2 Å) with DMF as an eluent at 50 °C and the flow rate of 1 mL/min. Linear poly(methyl methacrylate) standards were used for calibration. SEC measurements of PMA were conducted using PSS columns (Styrogel 10^2, 10^3, 10^4, 10^5 Å) with THF as an eluent at 35 °C and the flow rate of 1 mL/min. Linear poly(methyl methacrylate) standards were used for calibration.

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[1] Schröder, K.; Mathers, R. T.; Buback, J.; Konkolewicz, D.; Magenau, A. J. D.; Matyjaszewski, K. Substituted Tris(2-pyridylmethyl)amine Ligands for Highly Active ATRP Catalysts. *ACS Macro Lett.* **2012**, *1*, 1037– 1040.

PICAR ATRP

Polymerizations of NIPAM were irradiated under violet LEDs purchased from aspectLED (λ = 394 nm, 2.6 mW/cm^2). Polymerizations of MA were irradiated under high power three fiber coupled LED (λ = 365 nm, 3×50 mW/cm^2) purchased from Prizmatix.

Procedures

Br-based PBS x10

A 100 ml volumetric flask was charged with NaBr (14.08 g, 136.8 mmol), KBr (0.32 g, 2.69 mmol), Na_2HPO_4 (1.44 g, 10.14 mmol) and KH_2PO_4 (0.24 g, 1.76 mmol). Then filled with water to 100 ml mark.

General Procedure for PICAR ATRP of NIPAM in a Capped Vial (Table 1 and 2)

Prior to polymerizations, stock solutions of HOBiB (16.9 mg, 0.08 mmol in 1.0 mL of DMF) and $CuBr_2$ (17.9 mg, 0.08 mmol in 20.0 mL of DMF) were prepared. A 5 mL stock solution of $CuBr_2$/Me_6TREN was prepared by adding $CuBr_2$ stock (5 mL) to Me_6TREN (27.6 mg, 0.12 mmol). Afterward, a polymerization reaction mixture was prepared as follows. An 8-mL vial (17/60 mm) equipped with a magnetic stir bar was charged with sodium pyruvate (44.0 mg, 0.4 mmol), NaBr (41.2 mg, 0.4 mmol) and NIPAM (362 mg, 3.2 mmol). Next, the vial was purged with nitrogen for 5 min. Water (3.2 mL), Br-PBS 10x (0.4 mL), $CuBr_2$/Me_6TREN stock (0.2 mL), and HOBiB stock (0.2 mL) were added using syringes into the vial. Subsequently, the vial was placed in the cold room (6 °C) in the dark for 30 min. The reaction vial was irradiated under violet LEDs (394 nm, 2.6 mW/cm^2) at 6 °C for 30 min and additionally cooled using a mini-fan placed above the LEDs. Samples were taken and analyzed by ^{1}H NMR and SEC techniques.

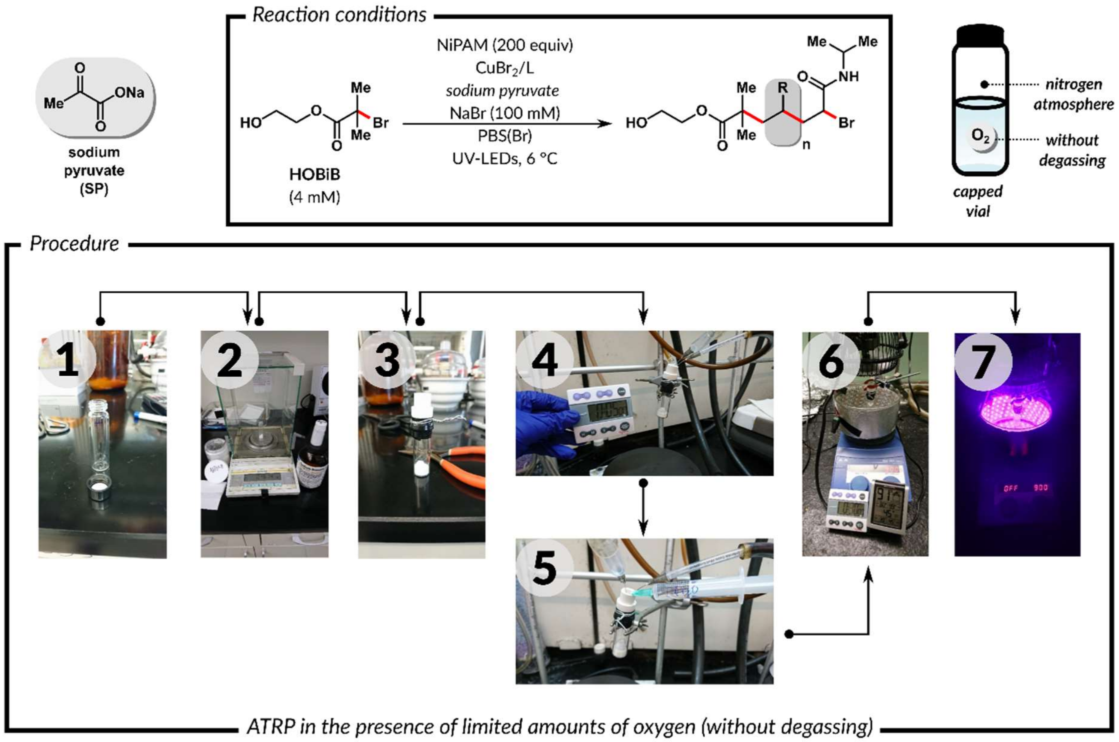


Fig. S1. Set-up for PICAR ATRP in a capped vial (Table 1); (1) the reaction vial; (2) weighing the reagents (sodium pyruvate, NaBr, and NIPAM); (3) the reaction vial equipped with a stir bar and sealed with a septum rubber, black tape, and metal wire; (4) purging with nitrogen; (5) addition of water, Br-PBS 10x, and stock solutions; (6) cooling at 6 °C for 30 min (in a cold room); (7) irradiation under violet LEDs with a mini-fan placed above the LEDs.

Supplementary Information

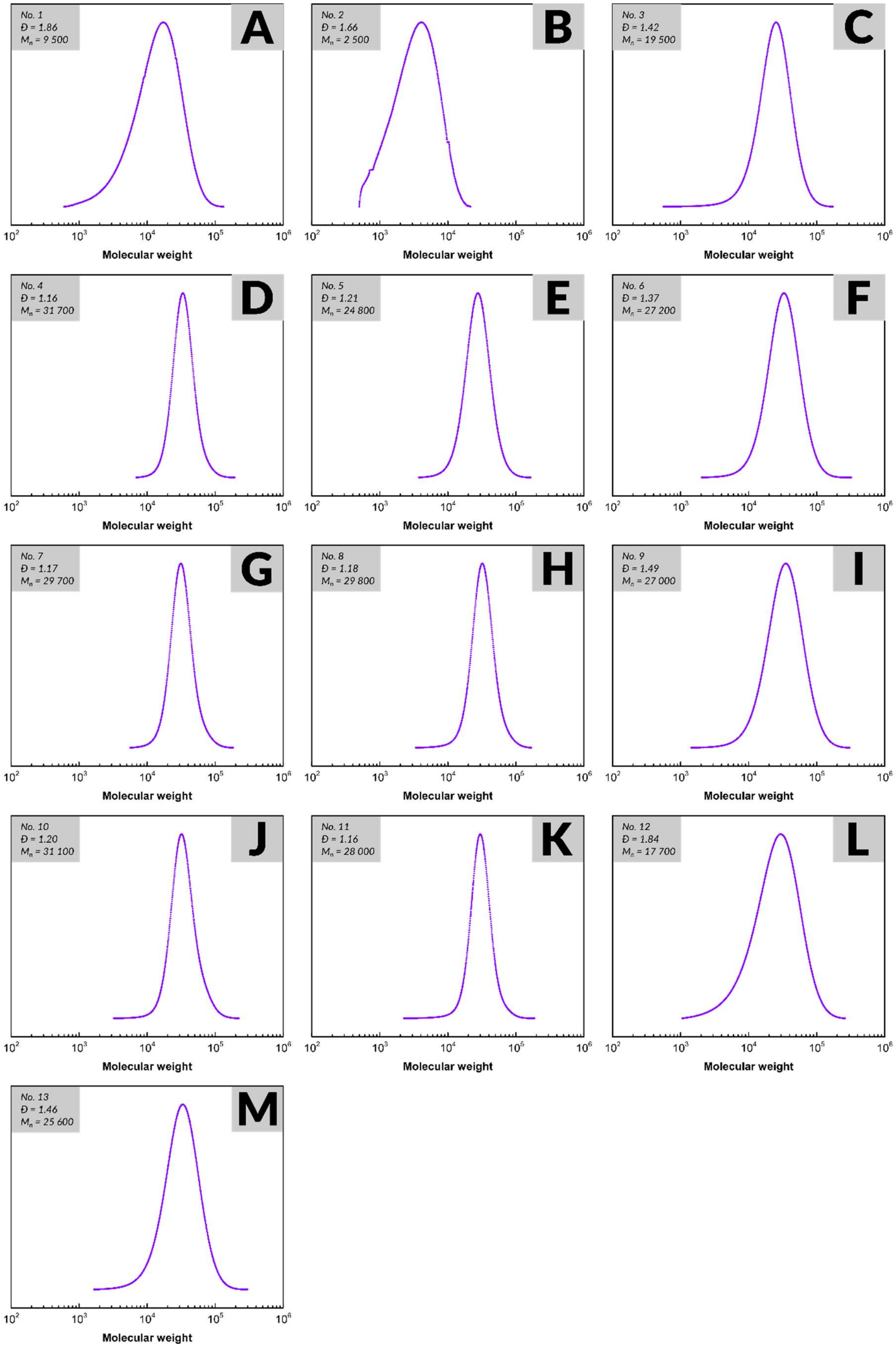


Fig. S2. GPC traces for the polymerizations from Table 1.

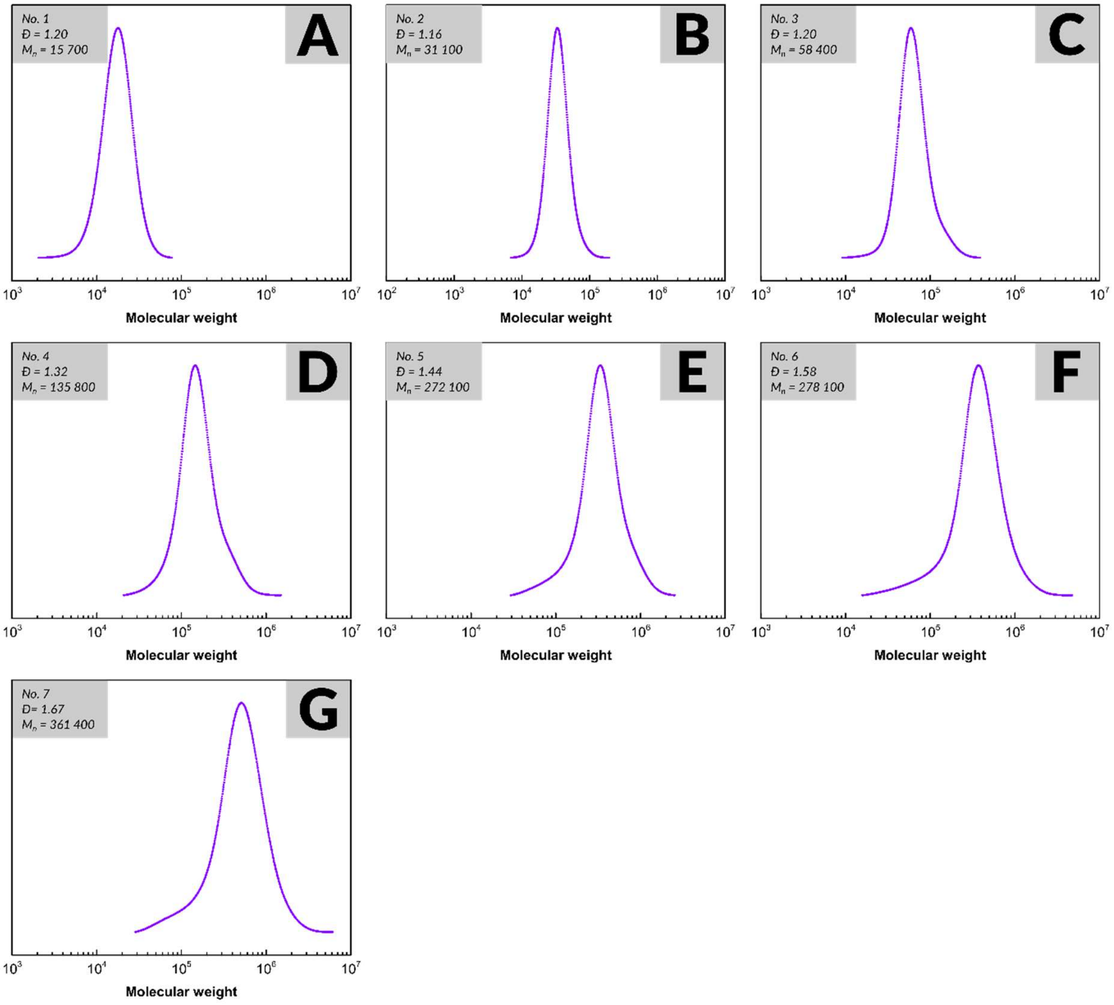


Fig. S3. GPC traces for the polymerizations from Table 2.

General Procedure for PICAR ATRP of NIPAM in an Open Vial (Table 3)

Prior to polymerizations, stock solutions of HOBiB (16.9 mg, 0.08 mmol in 1.0 mL of DMF) and $CuBr_2$ (17.9 mg, 0.08 mmol in 20.0 mL of DMF) were prepared. A 5 mL stock solution of $CuBr_2/Me_6TREN$ was prepared by adding $CuBr_2$ stock (5 mL) to Me_6TREN (27.6 mg, 0.12 mmol). Afterward, a polymerization reaction mixture was prepared as follows. A 4-mL vial (15/45 mm) was charged with sodium pyruvate (44.0 mg, 0.4 mmol), NaBr (41.2 mg, 0.4 mmol) and NIPAM (362 mg, 3.2 mmol). Water (3.2 mL), Br-PBS 10x (0.4 mL), $CuBr_2/Me_6TREN$ stock (0.2 mL), and HOBiB stock (0.2 mL) were added using syringes into the vial. Next, the reaction mixture was stirred on the vortex. Subsequently, the vial was placed in the cold room (6 °C) in the dark for 30 min. The reaction vial was irradiated under violet LEDs (394 nm, 2.6 mW/cm^2) at 6 °C for 30 min. Samples were taken and analyzed by ^1H NMR and SEC techniques.

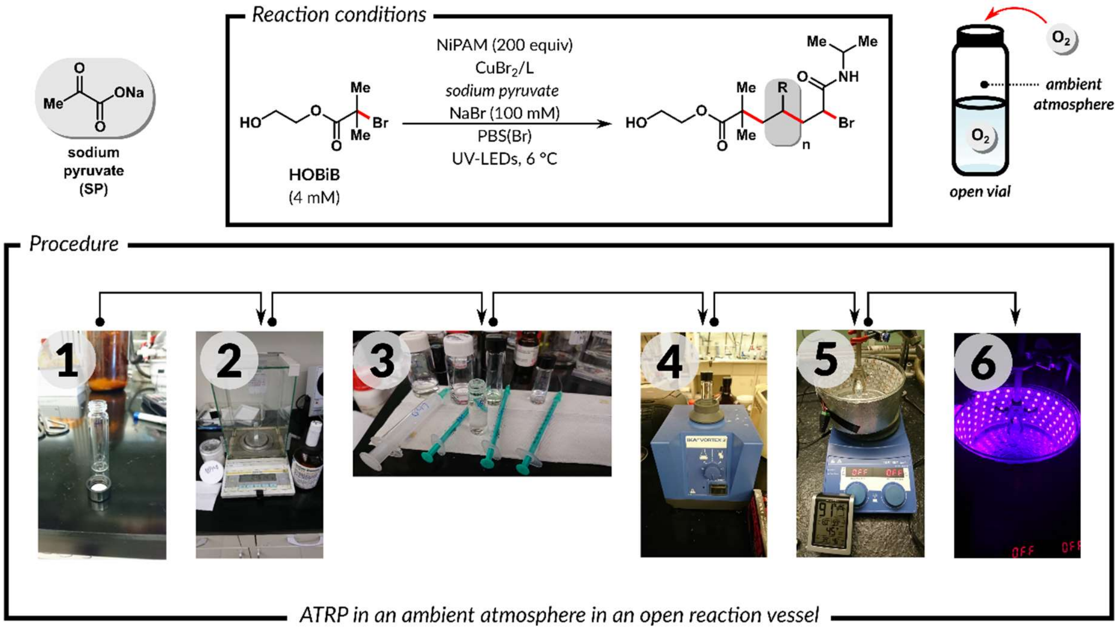


Fig. S4. Set-up for PICAR ATRP in an open vial; (1) the reaction vial; (2) weighing the reagents (sodium pyruvate, NaBr, and NIPAM); (3) addition of water, PBS(Br) 10x, and stock solutions; (4) stirring on the vortex; (5) cooling at 6 °C for 30 min (in a cold room); (6) irradiation under violet LEDs.

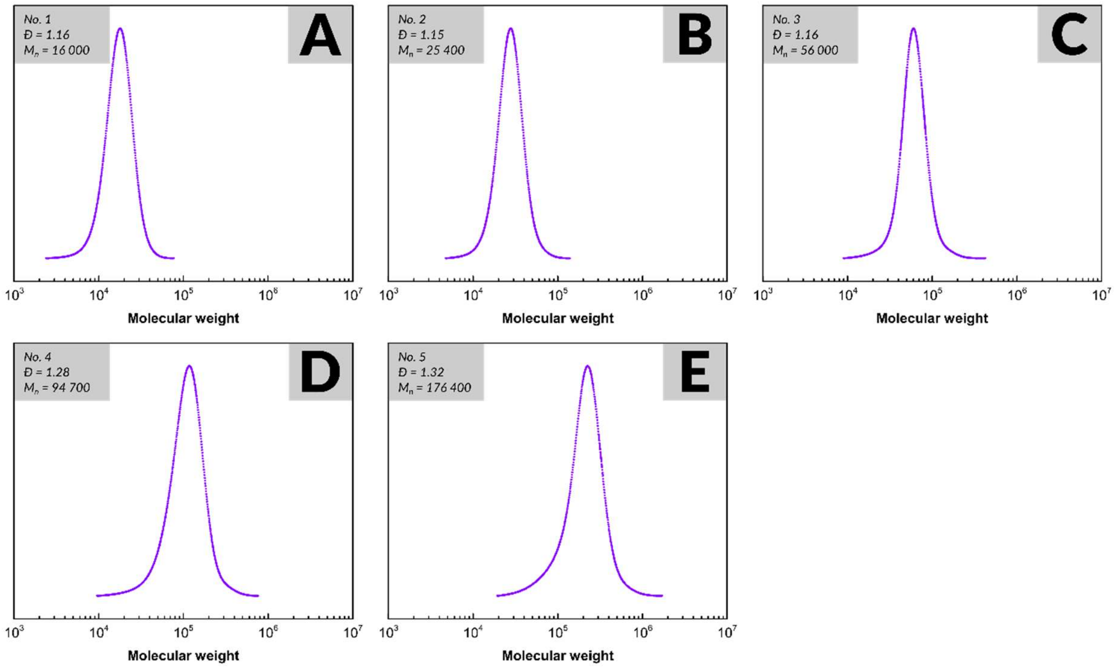
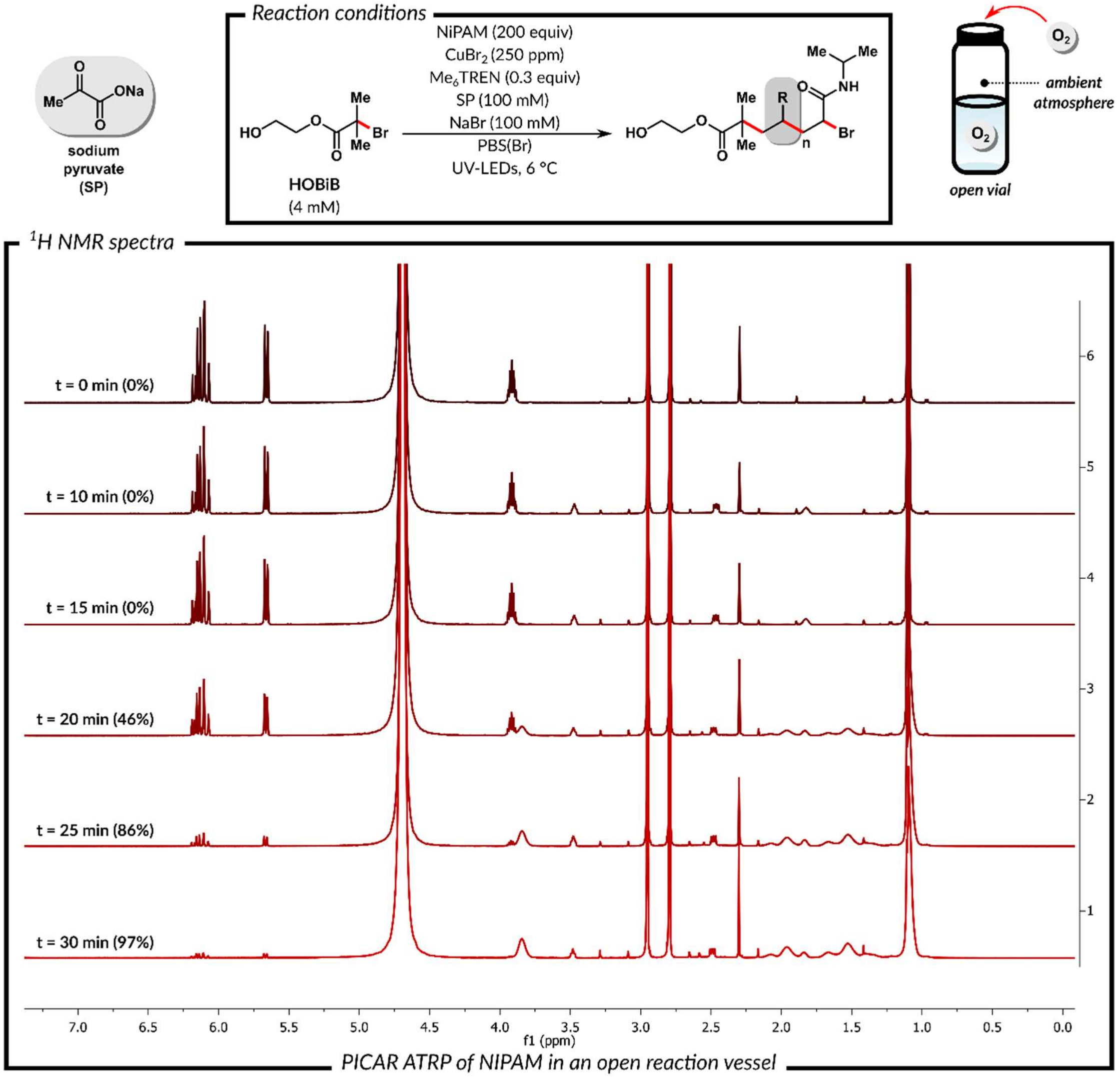


Fig. S5. GPC traces for the polymerizations from Table 3.

Kinetics of PICAR ATRP of NIPAM in an Open Reaction Vessel (Fig. 1)

Prior to polymerizations, stock solutions of HOBiB (16.9 mg, 0.08 mmol in 1.0 mL of DMF) and $CuBr_2$ (17.9 mg, 0.08 mmol in 20.0 mL of DMF) were prepared. A 5 mL stock solution of $CuBr_2/Me_6TREN$ was prepared by adding $CuBr_2$ stock (5 mL) to Me_6TREN (27.6 mg, 0.12 mmol). Afterward, a polymerization reaction mixture was prepared as follows. A 4-mL vial (15/45 mm) was charged with sodium pyruvate (44.0 mg, 0.4 mmol), NaBr (41.2 mg, 0.4 mmol) and NIPAM (362 mg, 3.2 mmol). Water (3.2 mL), Br-PBS 10x (0.4 mL), $CuBr_2/Me_6TREN$ stock (0.2 mL), and HOBiB stock (0.2 mL) were added using syringes into the vial. Next, the reaction mixture was stirred on the vortex. Subsequently, the vial was placed in the cold room (6 °C) in the dark for 30 min. The reaction vial was irradiated under violet LEDs (394 nm, 2.6 mW/cm^2) at 6 °C for 30 min. Samples were taken at various time intervals to monitor by ^{1}H NMR, the decrease in [NiPAM] *vs.* time.



PICAR ATRP of MA in DMSO in an Open Vial (Fig. 2)

Prior to polymerizations, stock solutions of EBiB (107.6 mg, 0.55 mmol in 10 mL of MA) and $CuBr_2$/Me_6TREN ($CuBr_2$ 18.5 mg, 0.08 mmol; Me_6TREN 114.4 mg, 0.5 mmol in 5.0 mL of DMSO) were prepared. Afterward, a reaction mixture stock was prepared as follows. An 8-mL vial was charged with sodium pyruvate (49.5 mg, 0.45 mmol) and TBAB (145.0 mg, 0.45 mmol). Next, DMSO (1.0 mL), EBiB stock in MA (3.0 mL) and $CuBr_2$/Me_6TREN stock (0.5 mL) were added. The reaction mixture stock was stirred on vortex.

The reaction stock was filtered through a syringe filter (0.2 μm) to remove the precipitate, then transferred (0.8 mL) into an open reaction vial. The reaction vial was irradiated under UV LEDs irradiation (λ = 365 nm, 3×50 mW/cm^2) at rt for 3 h. Samples were taken and analyzed by ^{1}H NMR and SEC techniques.

Monitoring the UV–vis Evolution of [Cu^{II}(TPMA)Br]$^+$ Under Violet LEDs Irradiation as a Function of Time (Fig. S3)

Prior to UV-vis measurements, a stock solution of CuBr$_2$/TPMA (CuBr$_2$ 8.9 mg, 0.04 mmol; TPMA 69.7 mg, 0.24 mmol in 1.0 mL of DMF) was prepared. Afterward, a reaction mixture stock was prepared as follows. An 8-mL vial was charged with sodium pyruvate (66.0 mg, 0.6 mmol) and NaBr (61.7 mg, 0.6 mmol). Next, water (5.7 ml) and CuBr$_2$/TPMA stock (0.3 mL) were added. The reaction mixture stock was stirred on the vortex.

In the Schlenk flask capped with an air-tight UV-Vis cuvette (path length = 1 cm) a stir bar was placed. The Schlenk flask was placed under vacuum and purged with nitrogen gas three times. A 4.0 mL of reaction stock was transferred to the Schlenk flask by a syringe. The Schlenk flask was irradiated under violet LEDs (394 nm, 2.6 mW/cm^2) at 6 °C and additionally cooled using a mini-fan placed above the LEDs. The UV-vis spectra were collected at specific time intervals (Figure S3A). The decrease in the concentration of [Cu^{II}(TPMA)Br]$^+$ was monitored by following the absorption at 967 nm.

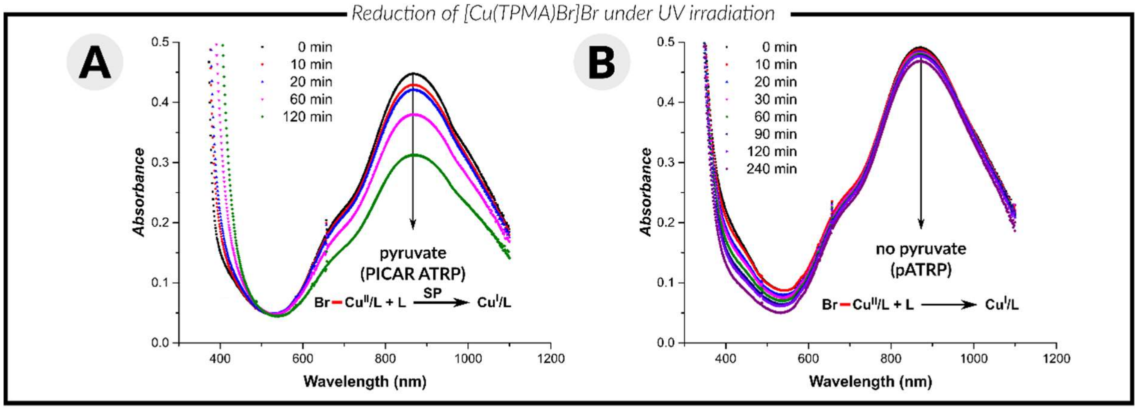


Fig. S6. Monitoring the UV–vis evolution of [Cu^{II}(TPMA)Br]$^+$ under under violet LEDs irradiation as a function of time. (A) In the presence of SP and (B) without its addition. Reactions conditions: [Cu^{II}Br$_2$]/[TPMA]= 1:6 in water at rt, under violet LEDs (λ = 394 nm, 2.6 mW/cm2), [Cu^{II}Br$_2$] = 2 mM, [TPMA] = 12 mM, [NaBr] = 100 mM, [SP] = 0 or 100 mM.

^{1}H NMR Spectra of Polymers

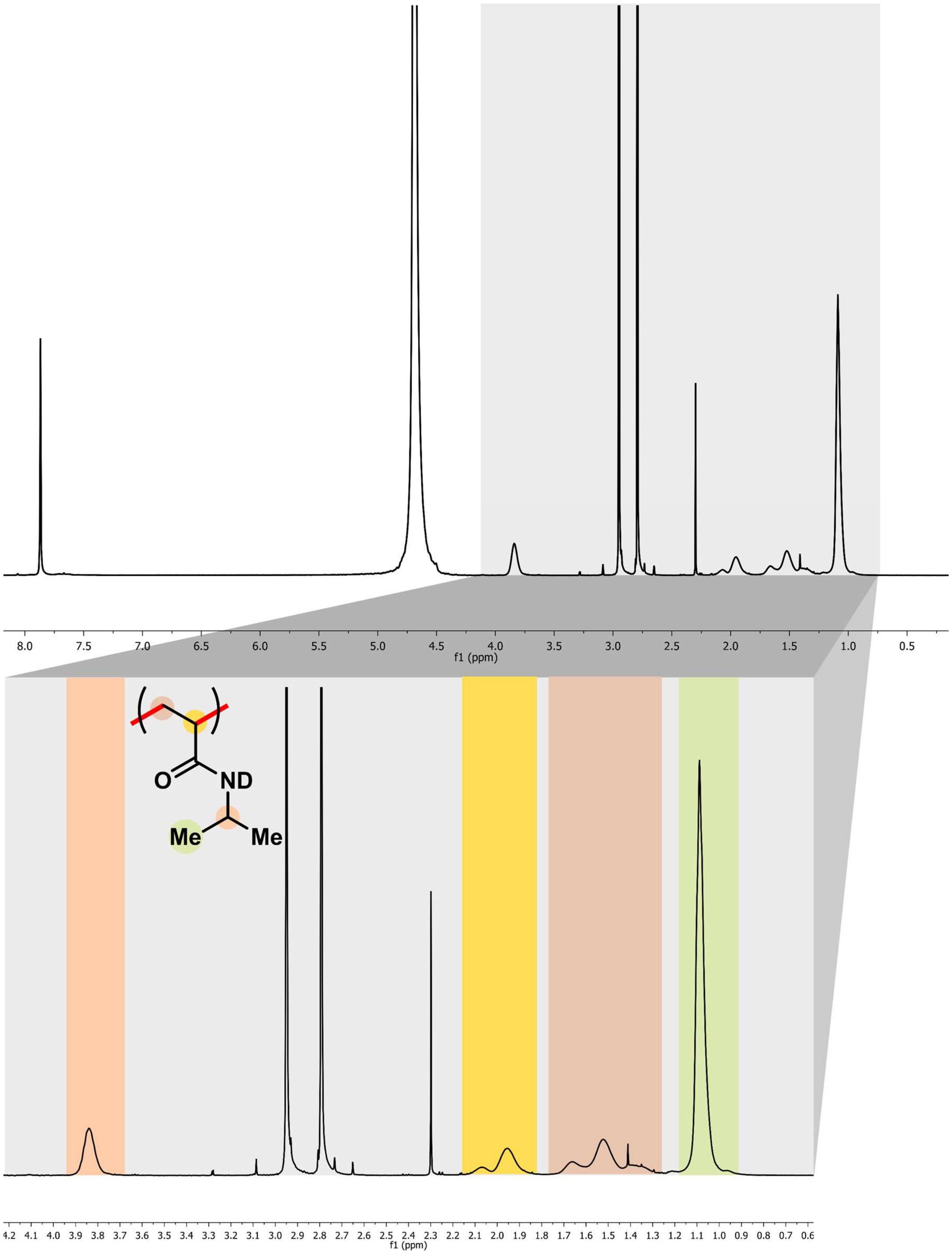


Fig. S7. ^{1}H NMR spectrum in D_2O for the PNIPAM with target DP = 200 synthesized *via* PICAR ATRP (Table 1, entry 4).

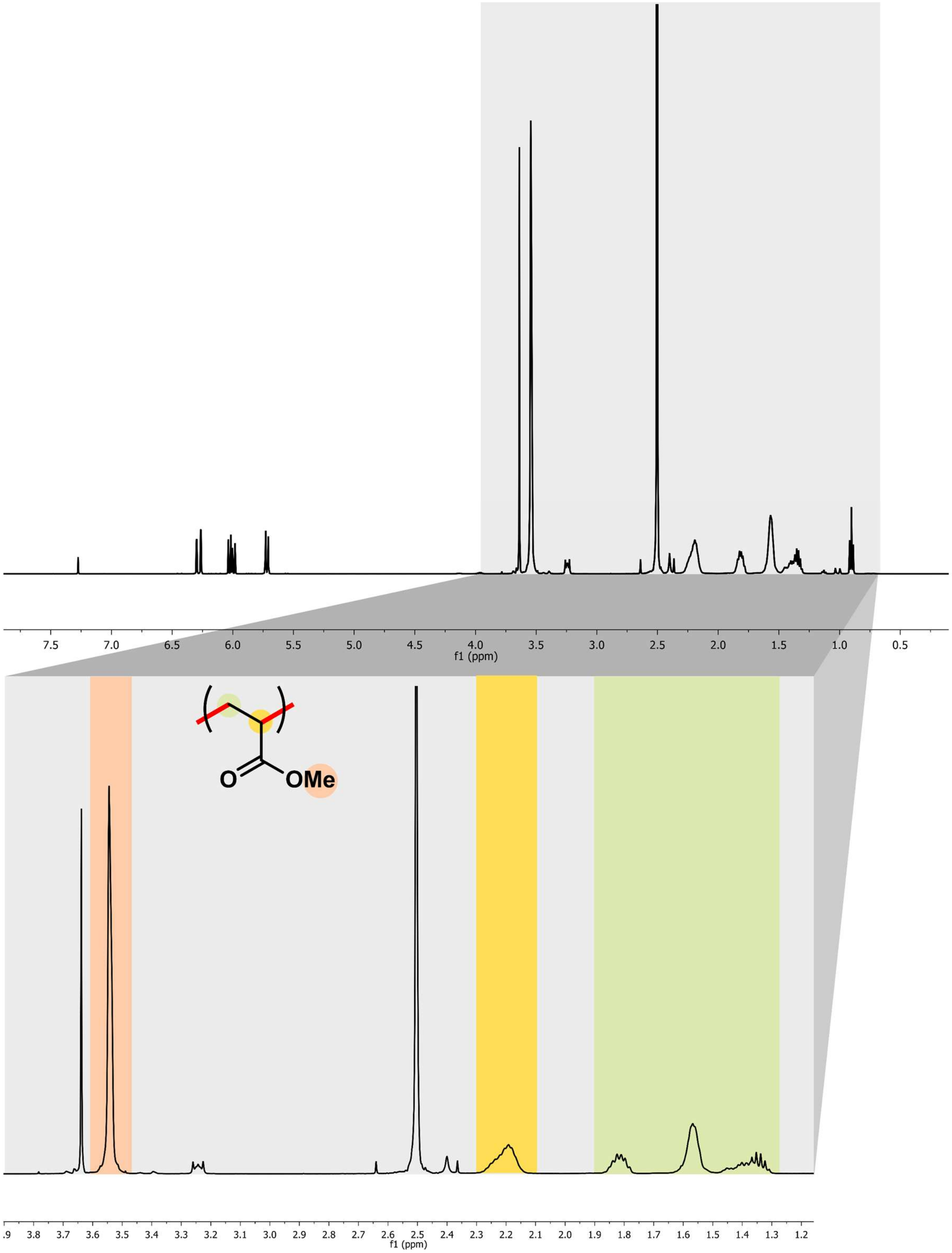


Fig. S8. ^{1}H NMR spectrum in $CDCl_3$ for the PMA with target DP = 200 synthesized *via* PICAR ATRP (Fig. 2).