Supporting Information

Bio-photo-Fenton-like RAFT polymerization under blue light

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Method

General procedure for studying effect of hydrogen peroxide concentration on polymerization rate.

DMA (300 mg, 3.026 mmol, 460 eq.), bis-TTC (1.86 mg, 6.579 µmol, 1 eq.), riboflavin (0.3147 mg, 0.6579 µmol, 0.1 eq.), and water (3 mL) were charged to a glass vial with a magnetic stir bar. Varying equivalences of hydrogen peroxide (0.5, 1, 2, 2.6 and 5 eq) were added to the vials and sealed with a rubber septum. The reaction mixture was degassed via argon sparging for 25 minutes. The vial was irradiated by a blue light LED at room temperature for 6 hours, after samples were taken for ^{1}H NMR spectroscopy.
The sample for ^{1}H NMR analysis was diluted with D_2O.

Quantification of generated hydrogen peroxide (H_2O_2).

For the determination of the yield of H_2O_2, the spectroscopic method described by Hochanadel[1] was used. In this method, I^- is oxidised to I^{3-} by hydrogen peroxide in a ratio 1:1, under the catalytic activity of ammonium molybdite. In details, 1 ml of each of the two solutions, A (0.4 M KI, 0.1 M NaOH, and 0.02 mM $(NH_4)_6Mo_7O_{24}$) and B (0.1 M $C_8H_5KO_4$), were mixed with 1 mL of a freshly irradiated sample that contained glucose/glucose oxidase, riboflavin and water, and analysed via UV/Vis spectroscopy. A molar extinction coefficient for I^{3-} of 26400 M^{-1} cm^{-1} at 353 nm at room temperature was used.

Results

Table SI 1 Effect of H_2O_2 molar ratio on polymerization conversion as determined by ^{1}H NMR spectroscopy.

H_2O_2 Molar ratio (eq.)	Conv. (%)[a]
0.5	41
1	39
2	68
2.6	92
5	74

[a]Monomer conversion was determined by ^{1}H NMR spectroscopy

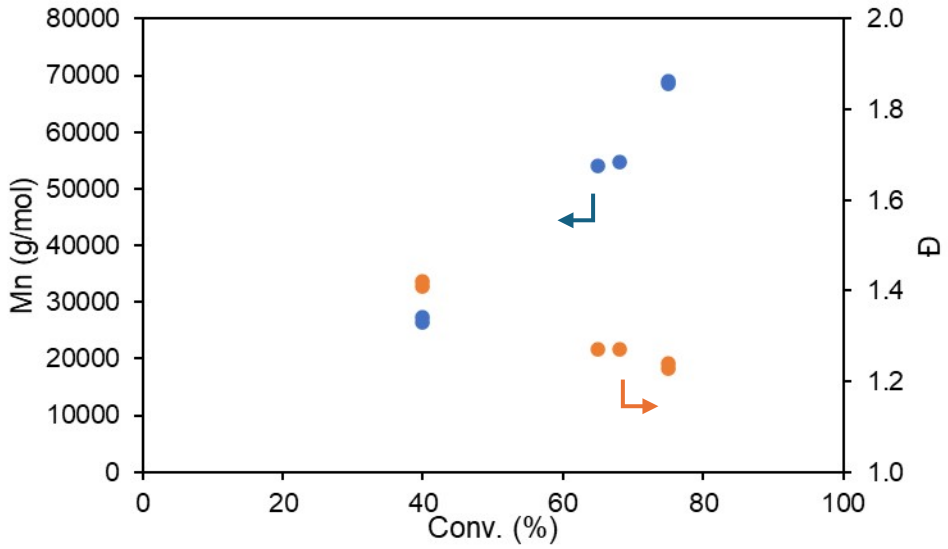

Figure SI 1 Evolution of number average molar mass (M_n) and dispersity (Đ) as a function of conversion for ON/OFF experiment. M_n values (blue points) and Đ values (orange points) were calculated from GPC.

Table SI 2 Characterization of the ON/OFF experiment via ^{1}H NMR spectroscopy and GPC analysis.

Time (min)	Conv.(%)[a]	$M_{n,th}$ (g/mol)[b]	M_n (g/mol)[c]	$Đ$[c]
0	0	-	-	-
60	40	18522	17804	1.37
120	40	18522	18367	1.35
180	65	29922	34667	1.24
240	68	31290	35069	1.24
300	75	34482	43356	1.20
360	75	34482	43632	1.20

[a]Conversion values were calculated from ^{1}H NMR analysis.; [b] Theoretical molecular weights were calculated according to the formula: $M_{n,th}$ = DP × conv. × $MW_{monomer}$ + $MW_{RAFT\ agent}$.; [c]Molecular weight (M_n) and dispersity ($Đ$) were determined by GPC analysis (DMF as eluent) calibrated to poly(methyl methacrylate) standards.

Table SI 3 Quantification of H_2O_2 concentration generated by glucose/glucose oxidase system

Conditions	Abs at 353 nm	ϵ (M^{-1} cm^{-1})	Light path (cm)	Dilution	Conc. (mM)	Undiluted Conc. (mM)
Glu/Gox, Sealed, Blue light, FMN	0.739	26400	1	20	0.0280	0.5598
Glu/Gox, open, Blue light	2.674	26400	1	20	0.1013	2.0258
1.745 ul of 30% H_2O_2 sol.	2.712	26400	1	-	0.1027	0.1027

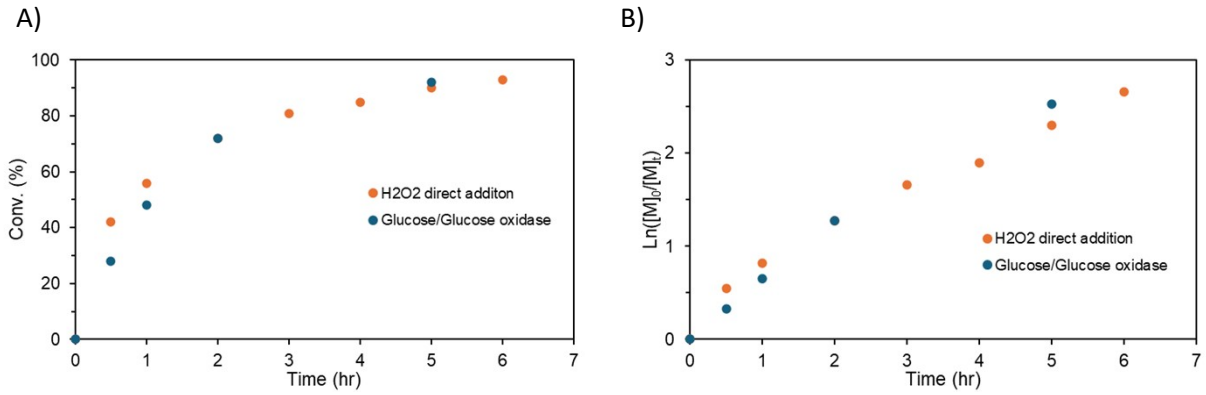

Figure SI 2 Polymerization kinetics of FMN/H_2O_2 (orange) or glucose/glucose oxidase/FMN (blue) aqueous photo-RAFT polymerization of DMA. A) Conversion (%) profile of DMA photopolymerization. B) Evolution of $ln([M]_0/[M]_t)$ against irradiation time. Polymerization was conducted under blue light (λ = 451 nm) using a ratio of [DMA]/[Bis-TTC]/[H_2O_2]/[Riboflavin] = 460/1/2.6/0.1, or [DMA]/[Bis-TTC]/[Riboflavin] = 460/1/0.1 with glucose/glucose oxidase = 0.1 M/1 μM in 3 mL water.

References

1. C. J. Hochanadel, *The Journal of Physical Chemistry*, 1952, **56**, 587-594.