Supporting Information

# Visible light controlled aqueous RAFT continuous flow polymerization with oxygen tolerance

Jinying Peng, Qinghua Xu, Yuanyuan Ni, Lifen Zhang,* Zhenping Cheng* and Xiulin Zhu

Suzhou key Laboratory of Macromolecular Design and Precision Synthesis, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application; College of Chemistry, State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials; Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China. E-mail: chengzhenping@suda.edu.cn (Z. P. Cheng), zhanglifen@suda.edu.cn (L. F. Zhang)

**List of figures and tables:**

**Table S1** Visible light-induced polymerization of DMA and PEGMA in ampoule

| Entry | Light source | Monomer | $[M]_0/[CETP]_0/[VA\text{-}044]_0$ | Time (min) | Conv. (%) | $M_{n,th}$ (g/mol) | $M_{n,GPC}$ [a] (g/mol) | $M_w/M_n$ [a] |
|---|---|---|---|---|---|---|---|---|
| 1 | Purple LED | DMA | 80:0:0.3 | 5 | 22.6 / 99.8[b] | --- | 322000 / 792700 | 1.09 / 2.28 |
| 2 | Purple LED | DMA | 80:1:0 | 5 | 0 | --- | --- | --- |
| 3 | Purple LED | DMA | 80:1:0.3 | 5 | 0 | --- | --- | --- |
| 4 | Purple LED | PEGMA | 40:0:0.3 | 5 | 18.5 / 9.4[b] | --- | 747000 / 668900 | 1.22 / 1.98 |
| 5 | Purple LED | PEGMA | 40:1:0 | 5 | 0 | --- | --- | --- |
| 6 | Purple LED | PEGMA | 40:1:0.3 | 5 | 0 | --- | --- | --- |
| 7 | Blue LED | DMA | 80:0:0.3 | 8 | 3.8 / 72.9[b] | 300 | 1134000 / 598300 | 1.52 / 1.97 |
| 8 | Blue LED | DMA | 80:1:0 | 8 | 0 | --- | --- | --- |
| 9 | Blue LED | DMA | 80:1:0.3 | 8 | 0 | --- | --- | --- |
| 10 | Blue LED | PEGMA | 40:0:0.3 | 30 | 17.1 | --- | indissolvable | |
| 11 | Blue LED | PEGMA | 40:1:0 | 30 | 0 | --- | --- | --- |
| 12 | Blue LED | PEGMA | 40:1:0.3 | 30 | 0 | --- | --- | --- |
| 13 | Red LED | PEGMA | 40:1:0.3 | 600 | 77.4 | 15800 | 15700 | 1.21 |
| 14 | Dark | DMA | 80:0:0.3 | 7 day | 0 | --- | --- | --- |

Polymerization conditions: $V_{Monomer}/V_{water}$ = 1/1, M = 0.5 mL. Reaction mixture was prepared in a 5 mL dried ampoule at room temperature (25 °C) under irradiation with different LED light sources. [a] Determined by GPC in THF with PMMA standards. [b] Just using VA-086 instead of VA-044 as the initiator.

**Table S2** Effect of molar ratio on visible light-controlled RAFT polymerization of PEGMA

| Entry | $[PEGMA]_0/[CETP]_0/[VA\text{-}044]_0$ | *Conv.* (%) | $M_{n,th}$ (g mol$^{-1}$) | $M_{n,GPC}{}^a$ (g mol$^{-1}$) | $M_w/M_n{}^a$ |
|---|---|---|---|---|---|
| 1 | 20/1/0.3 | 88.2 | 8800 | 10100 | 1.13 |
| 2 | 30/1/0.3 | 84.4 | 12700 | 12800 | 1.12 |
| 3 | 40/1/0.3 | 85.5 | 17100 | 15100 | 1.11 |
| 4 | 50/1/0.3 | 86.2 | 21600 | 17900 | 1.10 |
| 5 | 60/1/0.3 | 89.8 | 26900 | 21300 | 1.10 |

Polymerization conditions: $V_{PEGMA}/V_{water} = 1/2$, IV = 10.2 mL, $v$ = 0.340 mL min$^{-1}$, in a continuous tubular reactor at room temperature (25 $^o$C) under irradiation with purple LED light, no deoxygenation. $^a$ Determined by GPC in THF with PMMA standards.
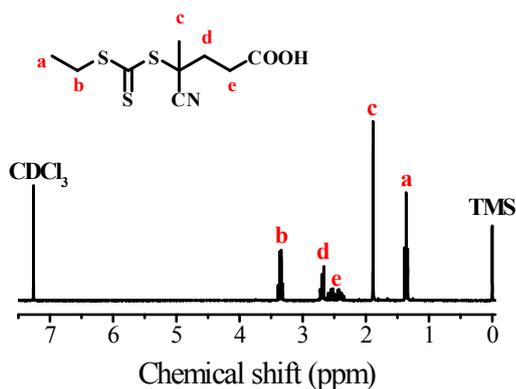


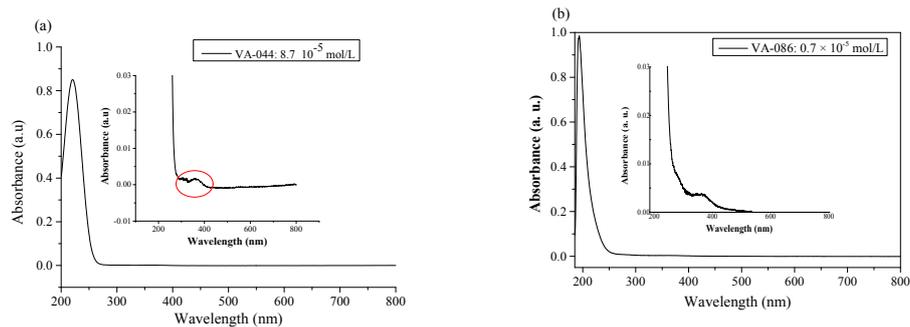**Fig. S1** $^1$H NMR spectrum of CETP in CDCl$_3$.

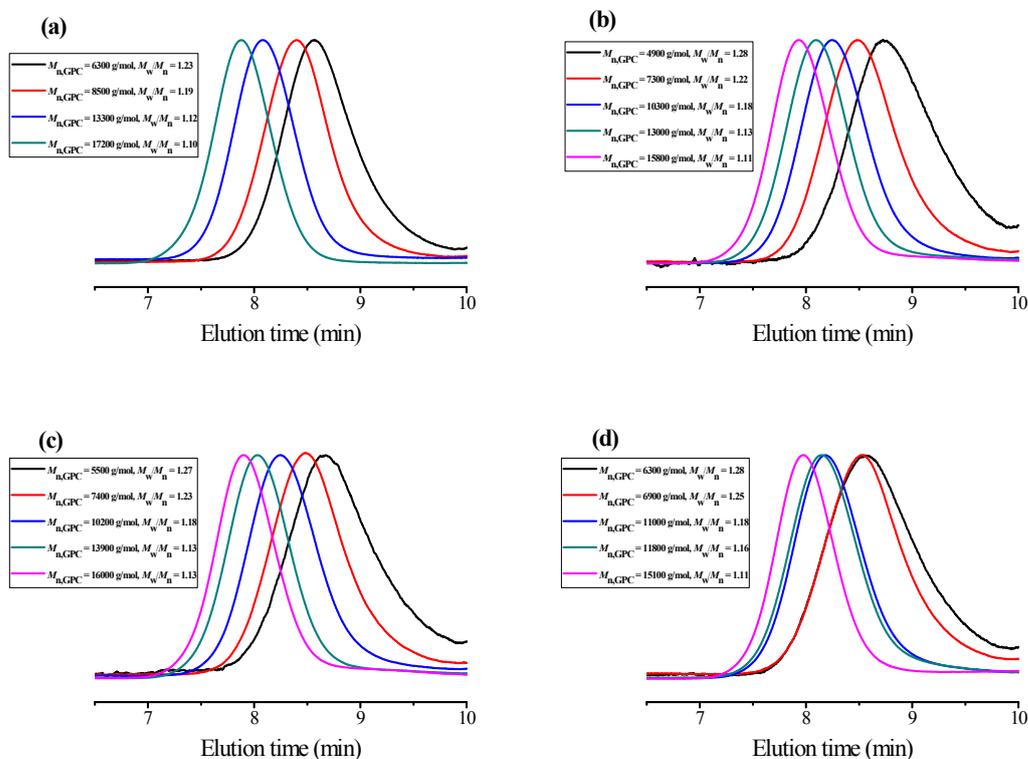**Fig. S2** UV-vis spectra of VA-044 (a) and VA-086 (b) in water.



**Fig. S3** GPC traces for the polymerization of PEGMA in a continuous tubular reactor, (a) $[PEGMA]_0/[CETP]_0/[VA-044]_0 = 40/1/0$; (b) $[PEGMA]_0/[CETP]_0/[VA-044]_0 = 40/1/0.1$; (c) $[PEGMA]_0/[CETP]_0/[VA-044]_0 = 40/1/0.2$; (d) $[PEGMA]_0/[CETP]_0/[VA-044]_0 = 40/1/0.3$. Polymerization conditions: $v_0 = 0.057$ mL min$^{-1}$, $v_1 = 0.170$ mL min$^{-1}$, $v_2 = 0.243$ mL min$^{-1}$, $v_3 = 0.340$ mL min$^{-1}$, $V_{PEGMA}/V_{water} = 1/2$, in a continuous tubular reactor at room temperature (25 $^o$C) under irradiation with purple LED light, no deoxygenation.
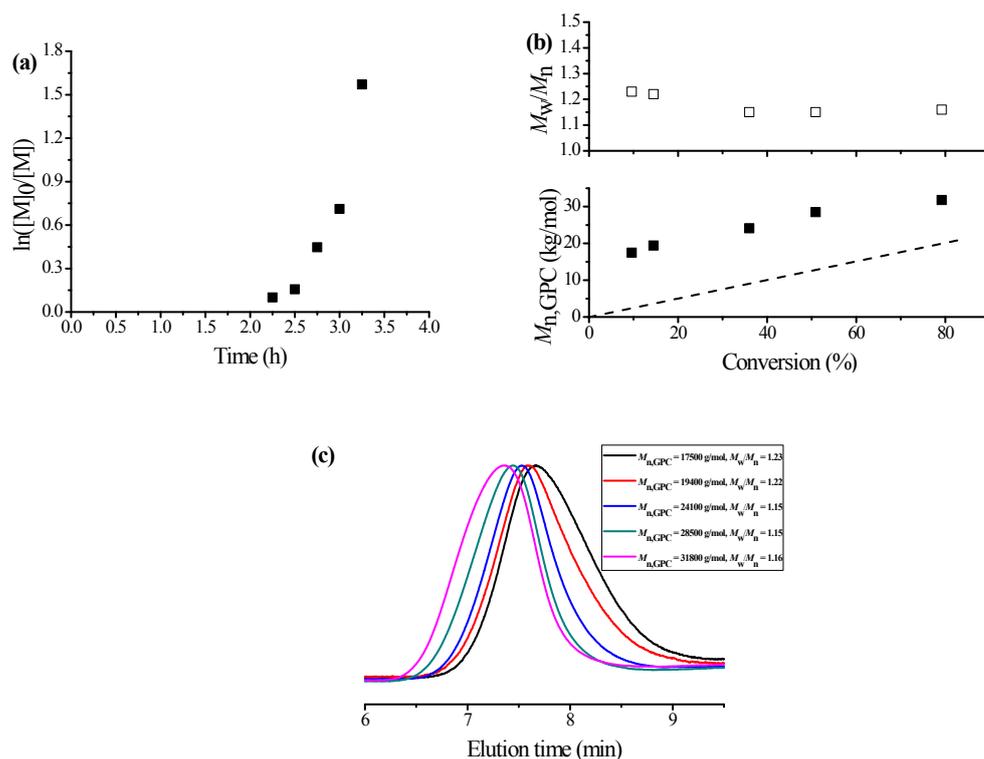
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**Fig. S4** Plots of $\ln([M]_0/[M])$ with time (a), number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution ($M_w/M_n$) versus conversion (b), and GPC traces (c) for the visible light-controlled RAFT polymerization of PEGMA in ampoules. Polymerization conditions: $[PEGMA]_0/[CETP]_0/[VA-044]_0 = 40/1/0.2$, $V_{PEGMA}/V_{water} = 1/2$, in ampoules at room temperature (25 $^o$C) under irradiation with purple LED light, no deoxygenation.
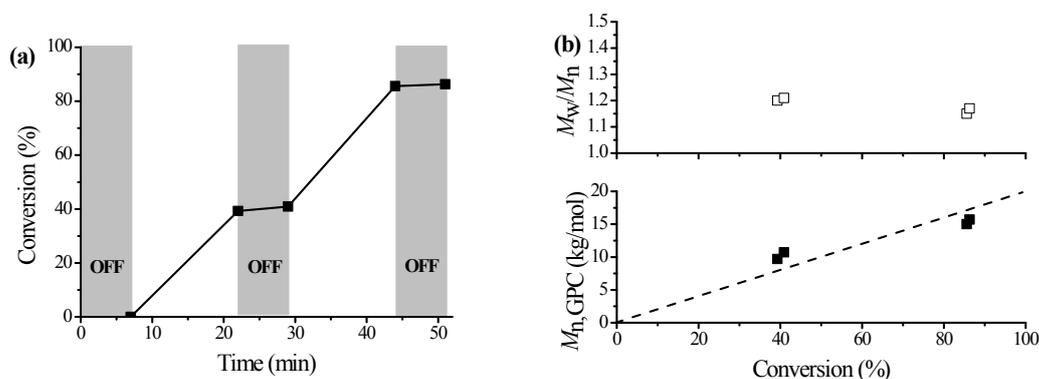


**Fig. S5** "On/off" experiments for the visible light-initiated RAFT polymerization of PEGMA in a continuous tubular reactor. The conversion versus time (a), and number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution ($M_w/M_n$) versus conversion (b). Polymerization conditions: $[PEGMA]_0/[CETP]_0/[VA-044]_0 = 40/1/0.3$, $V_{PEGMA}/V_{water} = 1/2$, $v = 0.340$ mL/min, in a continuous tubular reactor at room temperature (25 $^o$C) under irradiation with purple LED light, no deoxygenation.