Supporting Information

Photoinduced organocatalyzed controlled radical polymerization feasible over a wide range of wavelengths

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Section 1. Materials and Characterizations

Materials

Methyl methacrylate (MMA) (> 99.8%), Glycidyl methacrylate (GMA) (> 95.0%), Benzyl methacrylate (BzMA) (> 98.0%), 2-Methoxyethyl methacrylate (MEMA) (> 98.0%) were purchased from Tokyo Chemical Industry (TCI) and purified through a neutral alumina column before been used. Phenyl methacrylate (PhMA) (> 97.0%), Butyl methacrylate (BMA) (> 99.0%), Poly(ethylene glycol) methyl ether methacrylate (PEGMA) (M_n = 475 g/mol), dimethylaminoethyl methacrylate (DMAEMA) (> 98.5%), 2-diethylaminoethyl methacrylate (DEAEMA) (> 98.5%), hydroxypropyl methacrylate (HPMA) (> 97.0%), potassium iodide (KI) (> 99.5%), 2-Iodo-2-methylpropionitrile (CP-I) (> 96.0%), Ethidium bromide (EB) (> 95.0%) were purchased from TCI and used as received. The pigskin was purchased from a local supermarket.

The light sources used in this paper were LED lamps (13 W m^{-1}, 15 mW cm^{-2}) and near infrared light (9.6 W m^{-1}, 11 mW cm^{-2}). The wavelength ranges of each light source were shown as follow: red light: 620-750 nm; green light: 520-570 nm; blue light: 450-490 nm; white light: 450-730 nm; near infrared light: 750-850 nm.

Characterizations

The number average molecular weight (M_n) and polydispersity (M_w/M_n) of polymer samples were measured by gel permeation

chromatography (GPC). The GPC was operated with THF as the eluent (1.0 mL/min) at 30 ^{o}C (both the columns and detector), and equipped with a Waters 717 plus auto sampler, a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector, and Shodex K-805, K-804, and K-802.5 columns in series. The column system was calibrated using a series of poly(methyl methacrylate)s (PMMAs) standards. The monomer conversion can be calculated from the peak area of the samples by ^{1}H NMR.[1,2] ^{1}H NMR (500 MHz) spectra were recorded on Bruker Advance Ⅲ. UV-vis adsorption spectra were obtained on an Agilent Cary 7000. X-ray photoelectron spectroscopy (XPS) data was obtained with an ESCALAB 250 VG Scientific electron spectrometer using Al/Mg double anode target. Mass spectra were recorded on Agilent 6224 Accurate Mass TOF LC/MS spectrometer.

Section 2. Complete synthetic procedure

The amphiphilic catalyst, ethidium iodide (EI) was prepared by the bromide-iodine transformation of ethidium bromide with KI. 15 mL H_2O/CH_3OH mixture (V_{water}:$V_{methanol}$ = 1:1) was prepared, and then potassium iodide (KI) was dissolved in the above solvents until saturated. After that, ethidium bromide (EB, 1.5 g, 3.8 mmol) was dispersed in the above solvent.[3] After stirring for 24 hours, the mixture was centrifuged and red solid was obtained. Repeat the above steps for 4 times. Then the

obtained solid was washed with CH_3OH (20 mL) for 3 times, and dried under vacuum to obtain the target product.

Section 3. General polymerization procedure

The typical process of photoinduced reversible complexation-mediated polymerization

A typical procedure for reversible complexation-mediated radical polymerization (RCMP): a mixture of monomer, CP-I, EI and solvent was added into a 25 mL Schlenk tube at room temperature. The mixture was irradiated by LED lamp under nitrogen atmosphere with stirring. After a predetermined time, a trace amount of the mixture was taken. The mixture was characterized by ^{1}H NMR to determine the monomer conversion and diluted by THF to determine the number average molecular weight (M_n) and polydispersity (M_w/M_n) of the obtained polymer, respectively.

Synthesis of iodine end capped poly(methyl methacrylate) (PMMA-I) as macroinitiator.

A general procedure for the synthesis of macroinitiator PMMA-I: MMA (8 M), CP-I (80 mM) and EI (20 mM) were added into a 25 mL Schlenk tube and irradiated with LED lamps under nitrogen atmosphere. After 9 h, trace amount of the mixture was collected and then characterized by ^{1}H NMR to determine the monomer conversion. Other mixture was

diluted by THF, and filtered to remove the insoluble matter, then precipitated in diethyl ether. The macroinitiator PMMA-I was obtained by centrifuge and dried under vacuum at room temperature. A trace amount of the macroinitiator was taken and diluted by THF to determine the number average molecular weight (M_n) and polydispersity of the obtained polymer.

The typical procedure for the synthesis of block copolymer

A general procedure for the synthesis of block copolymer: macroinitiator PMMA-I, BzMA and EI were added into a 25 mL Schlenk tube under nitrogen atmosphere. Then irradiate the Schlenk tube with a white LED lamp. At a predetermined time, a trace amount of the mixture was taken. The mixture was characterized by ^{1}H NMR to determine the monomer conversion and diluted by THF to determine the number average molecular weight (M_n) and polydispersity of the obtained polymer.

Section 4. Supplementary table and figures

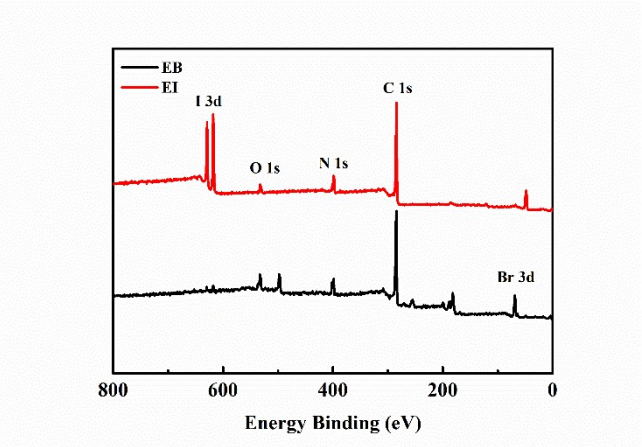

Figure S1. The XPS curves of EB (black line) and EI (red line).

Table S1. Compound Identification Results

Ion Species	Ion Formula	Ion Mass	Calc Ion Mass
Cation	$C_{21}H_{20}N_3^+$	314.16370,	314.16517,
		315.16556,	315.16853,
		316.16910	316.17188
Anion	I^-	126.90322	126.90502
Anion	Br^-	78.91709,	78.91889,
		80.91502	80.91684

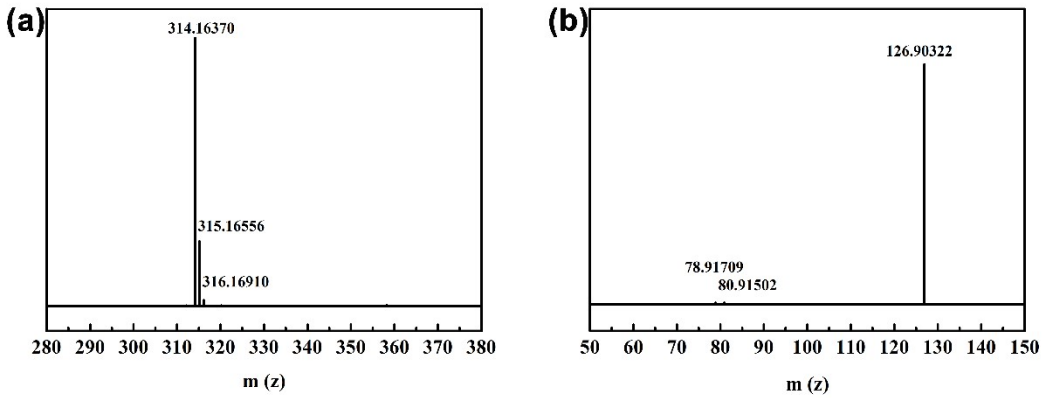

Figure S2. MS spectra of ethidium iodide determined by (a) positive mode, and (b) negative mode.

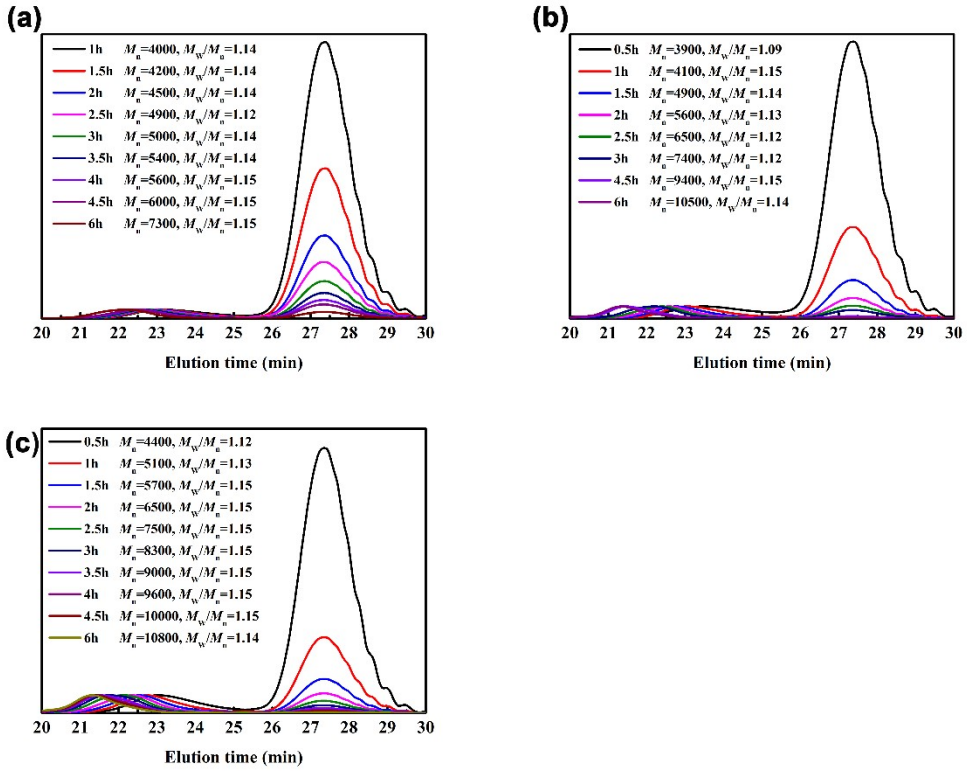

Figure S3. GPC traces of polymers obtained by the polymerization of PEGMA/CP-I/EI systems under the irradiation of red LED light: $[PEGMA]_0$ = 0.66 M; $[CP\text{-}I]_0$ = 22 mM; $[EI]_0$ = 11 (a), 23 (b), 32 (c) mM in deionized water (50% v/v).

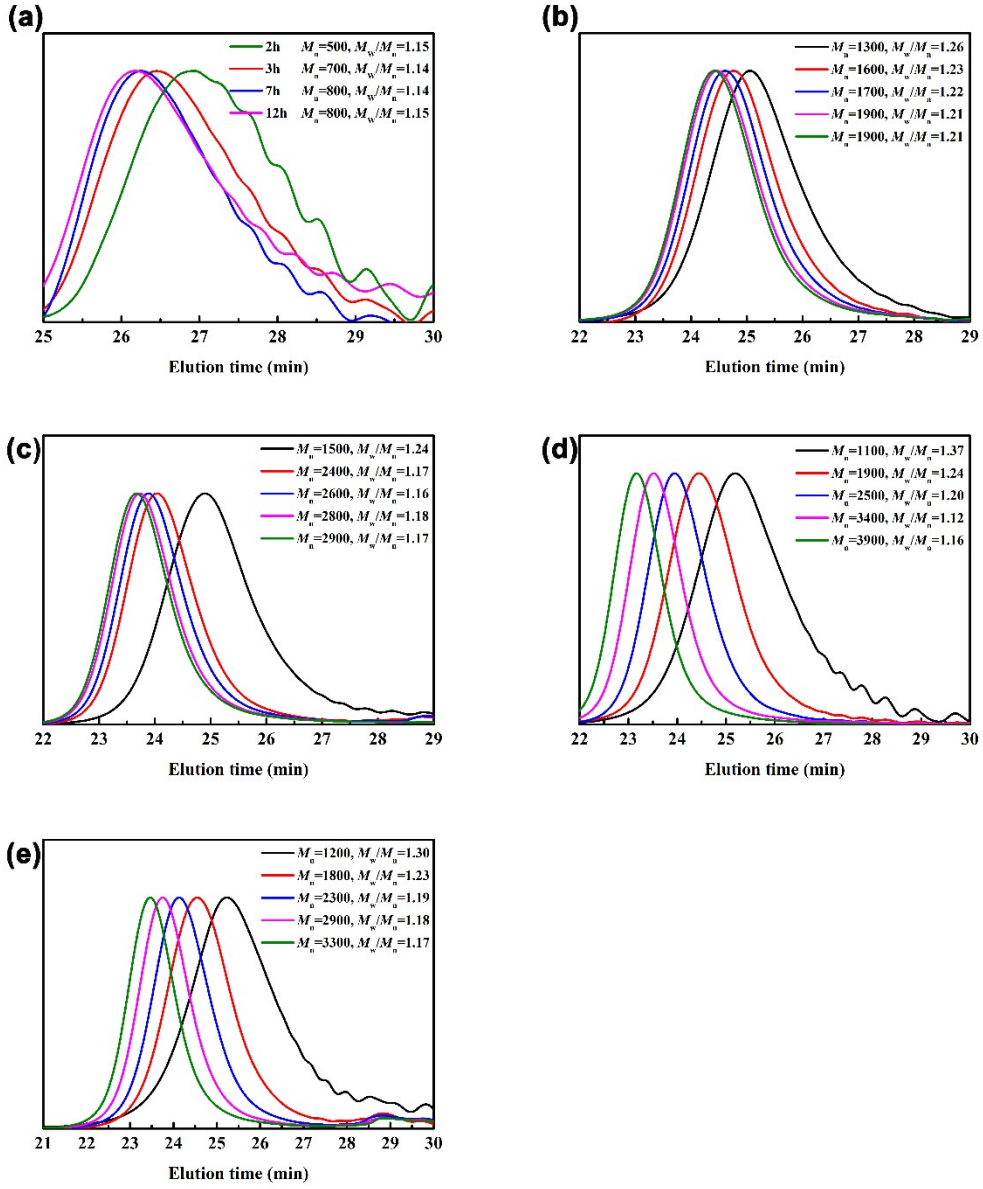

Figure S4. GPC traces of polymers obtained by the polymerization of MMA/CP-I/EI systems under the irradiation of white LED light: $[MMA]_0 = 18.1$ M; $[CP\text{-}I]_0 = 0.181$ mM; $[EI]_0 = 0$ (a), 11 (b), 23 (c), 45 (d), 91 (e) mM.

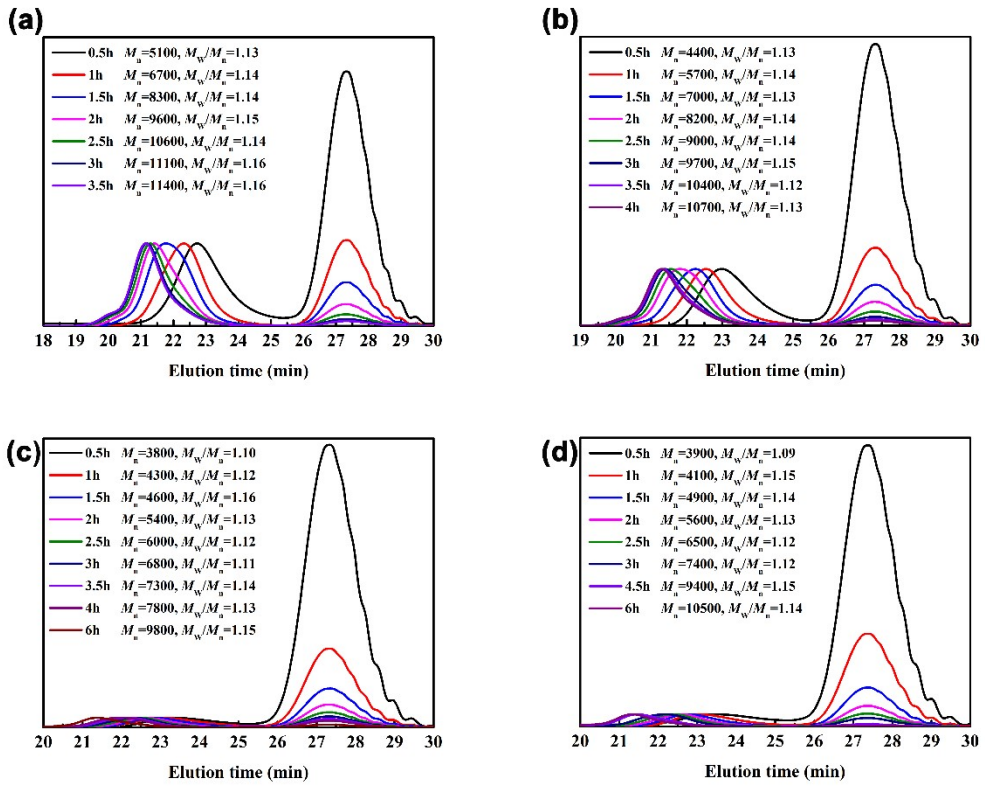

Figure S5. GPC traces of polymers obtained by the polymerization of PEGMA under the irradiation of white (a), blue (b), green (c), red (d) LEDs, respectively: $[PEGMA]_0/[CP\text{-}I]_0/[EI]_0$ = 24000/800/160.

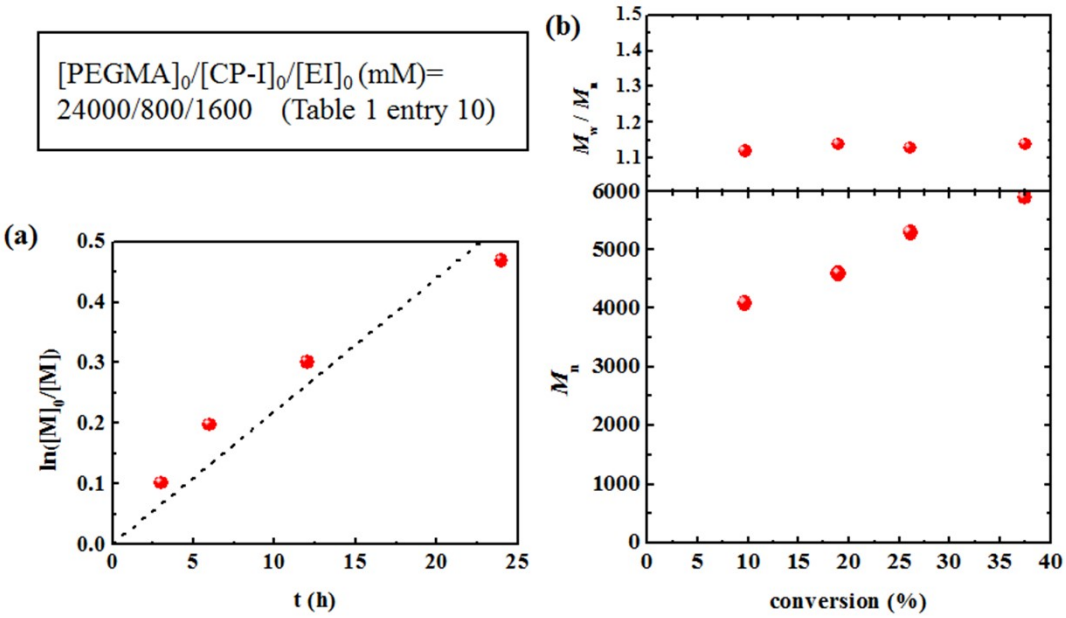

Figure S6. Plots of (**a**) $\ln([M]_0/[M])$ vs t and (**b**) M_n and M_w/M_n vs conversion for the polymerization of PEGMA/CP-I/EI systems under the irradiation of near-infrared light: by using the conditions: $[PEGMA]_0/[CP\text{-}I]_0/[EI]_0$ = 24000/800/1600 in deionized water (50% v/v).

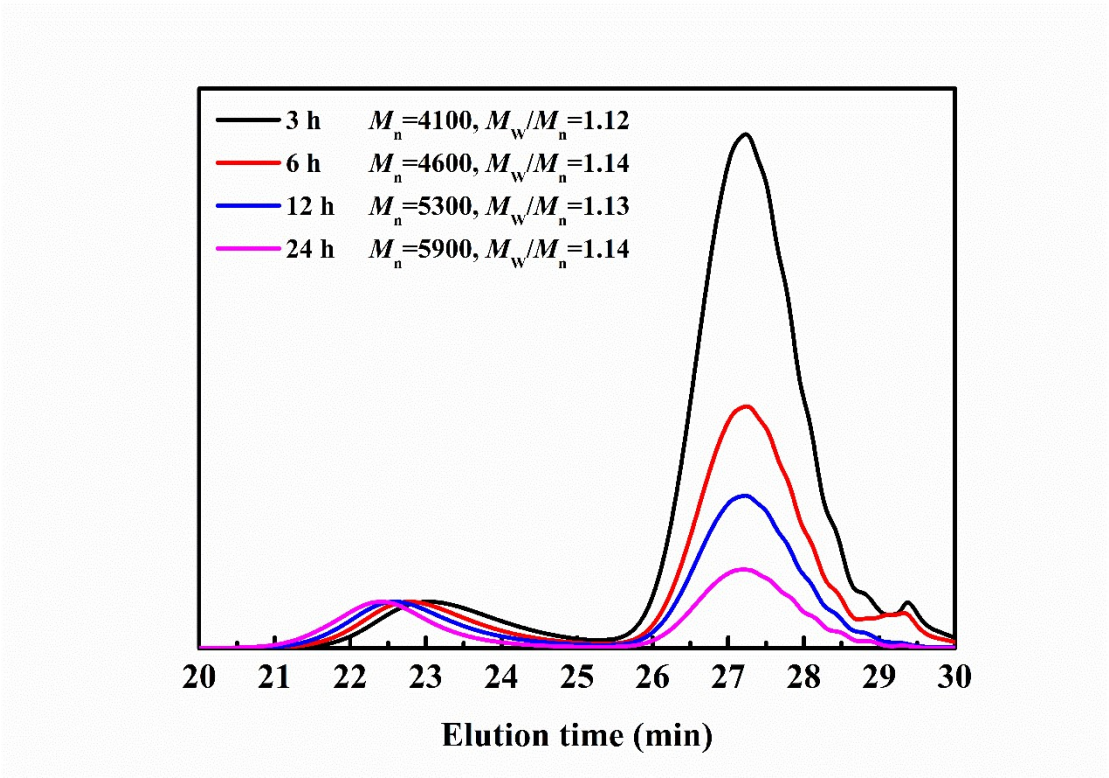

Figure S7. The GPC outflow curves of PPEGMA obtained by the polymerization of PEGMA under the irradiation of near-infrared light by using the conditions: $[PEGMA]_0/[CP\text{-}I]_0/[EI]_0$ = 24000/800/1600 in deionized water (50% v/v).

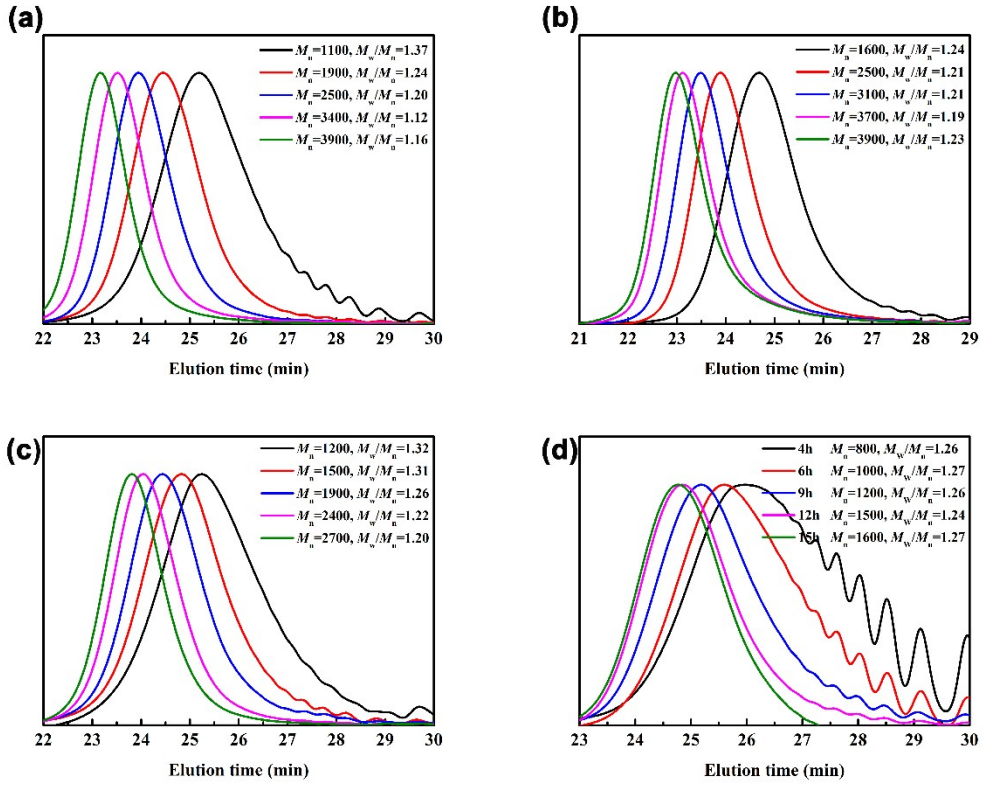

Figure S8. GPC traces of polymers obtained by the polymerization of MMA in bulk under the irradiation of white (a), blue (b), green (c), red (d) LEDs, respectively: $[MMA]_0/[CP\text{-}I]_0/[EI]_0$ = 24000/240/60.

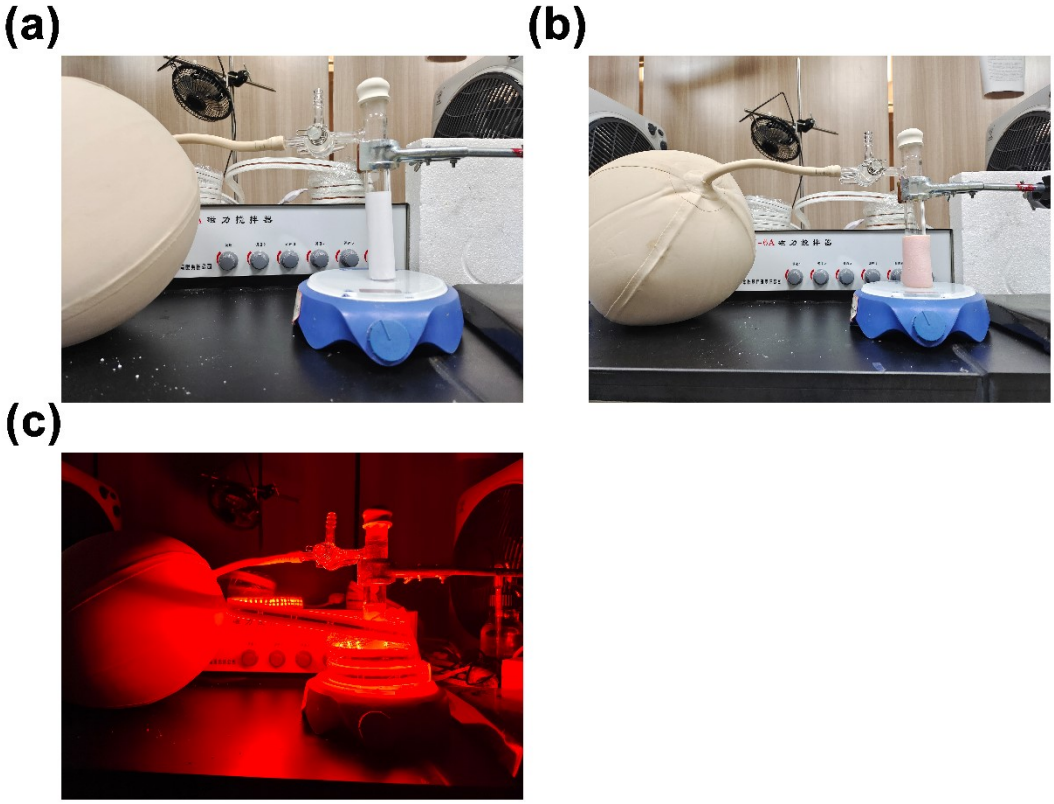

Figure S9. Photos of the polymerization settings over different barriers: (**a**) A4 paper, (**b**) pigskin, (**c**) photo of the polymerization setup under red LED light irradiation. (The balloons were filled with nitrogen to provide inert gas)

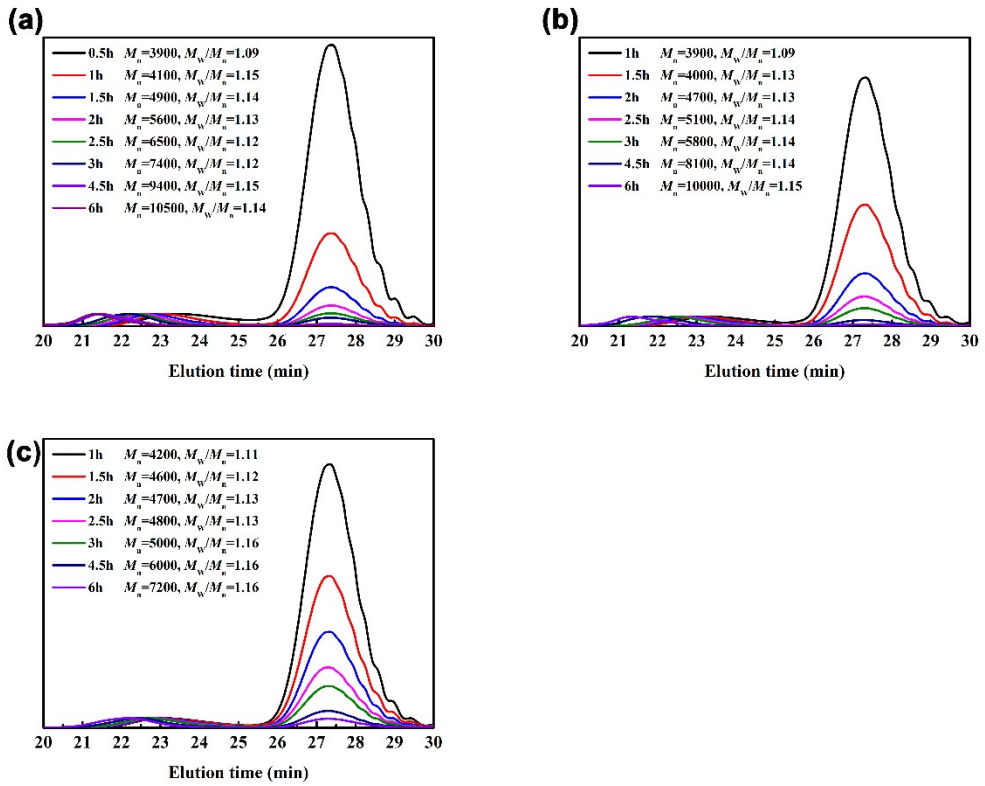

Figure S10. GPC traces of polymers obtained by the polymerization of PEGMA under red LED light irradiation over different barriers: (a) none, (b) pigskin, (c) A4 paper, by using the condition of $[PEGMA]_0/[CP\text{-}I]_0/[EI]_0 = 24000/800/160$.

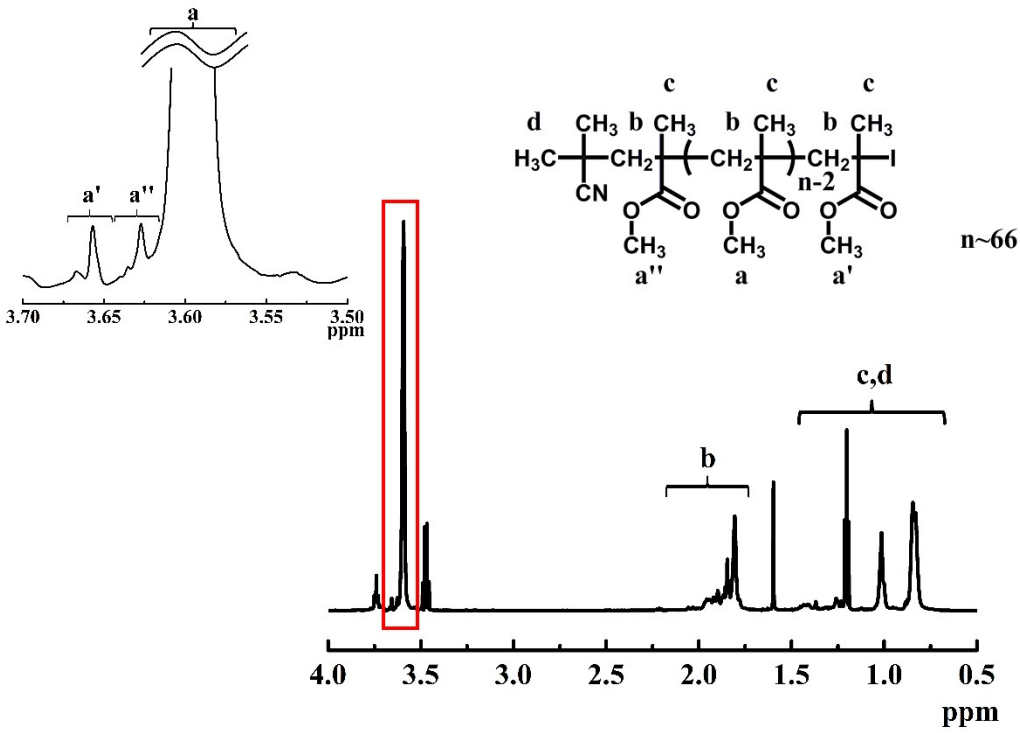

Figure S11. ^{1}H NMR spectrum ($CDCl_3$) of PMMA-I (M_n = 7800, M_w/M_n = 1.07) after 4 hours under the polymerization condition of $[MMA]_0/[CP\text{-}I]_0/[EI]_0$=24000/60/15 under the white LED light irradiation.

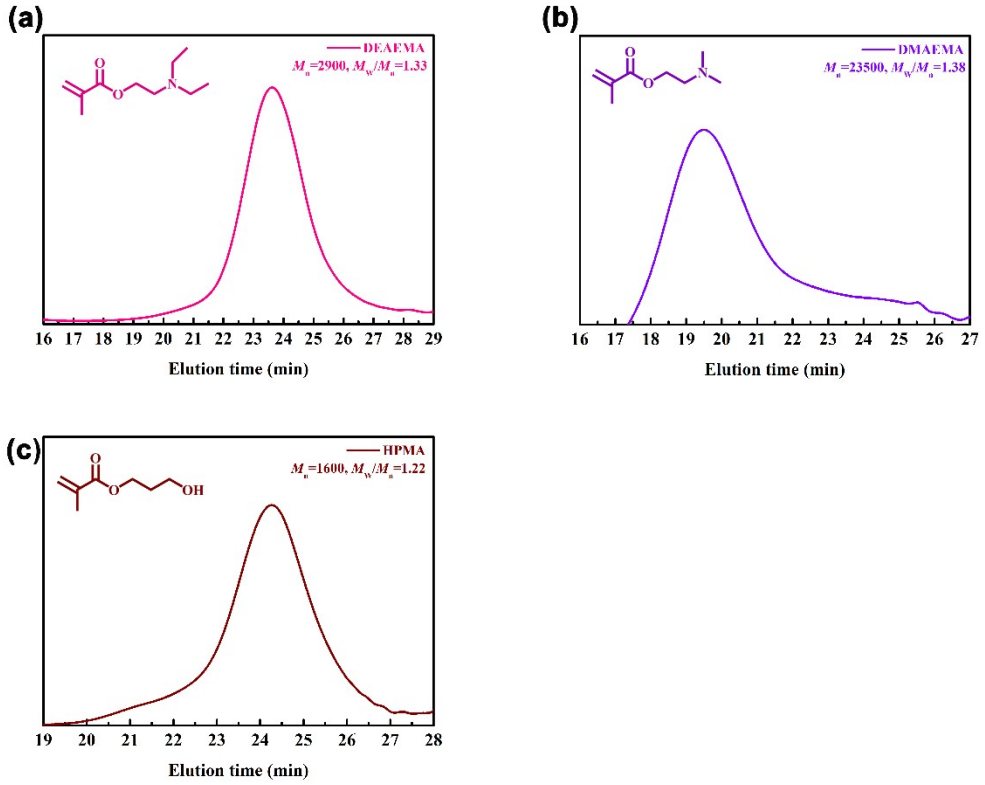

Figure S12. GPC traces of polymers obtained from RCMP of different hydrophilic monomers under white LED light irradiation by using condition of $[M]_0/[CP\text{-}I]_0/[EI]_0 = 24000/1200/240$. $[M]_0$ means the initial molar ratio of monomers.

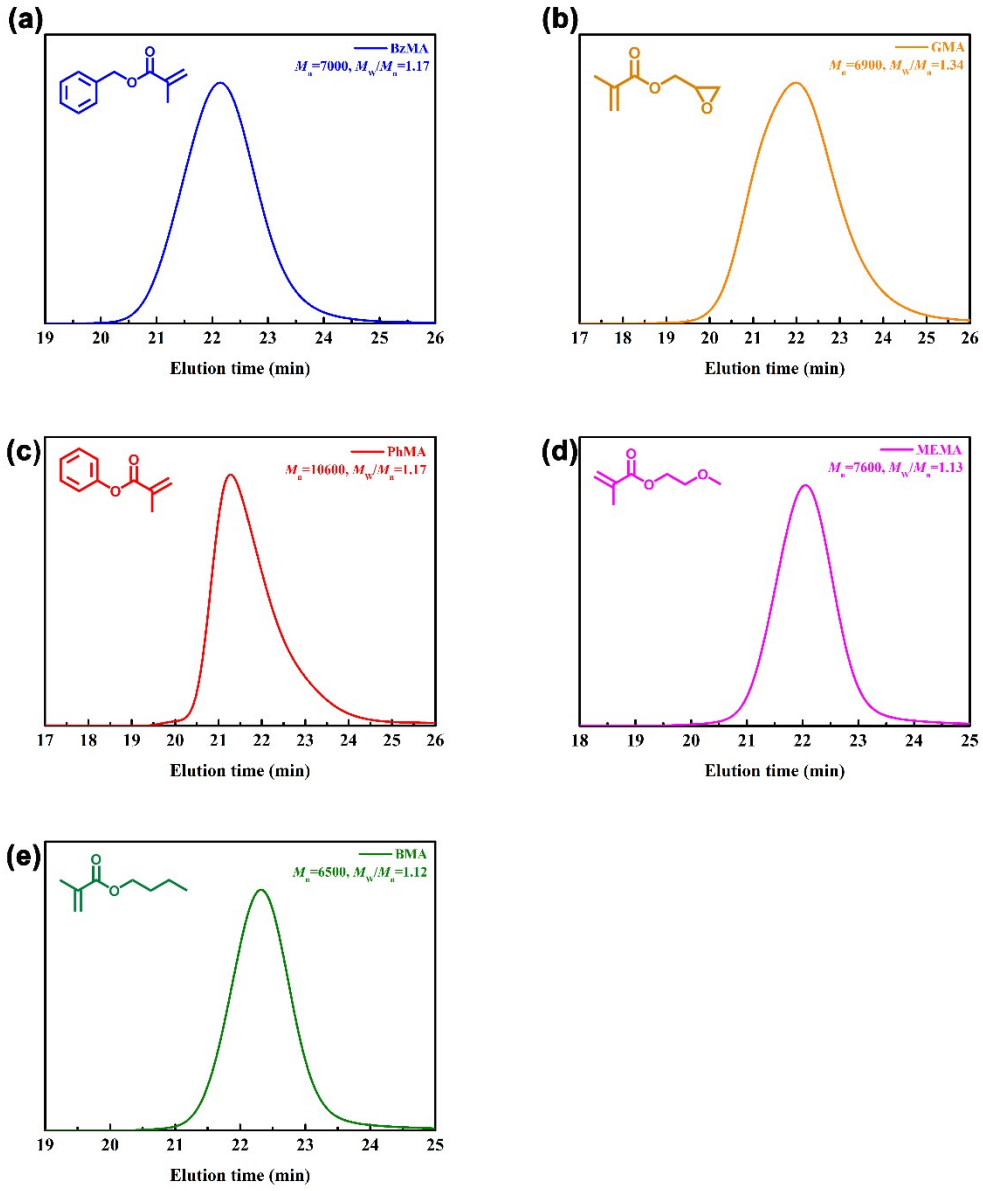

Figure S13. GPC traces of polymers obtained from RCMP of different oleophilic monomers under white LED light irradiation by using condition of $[M]_0/[CP\text{-}I]_0/[EI]_0$ = 24000/240/60. $[M]_0$ means the initial molar ratio of monomers.

Section 5. Reference

1. D. Gao, Y. Zhao, J. Cai, L. Hou and L. Xiao, *Chin. J. Polym. Sci.*, 2021, **39**, 1161-1168.
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3. H. Ma, B. Liu, B. Li, L. Zhang, Y. Li, H. Tan, H. Zang and G. Zhu, *J. Am. Chem. Soc.*, 2016, **138**, 5897-5903.
4. N. Petek, H. Brodnik, U. Groselj, J. Svete, F. Pozgan and B. Stefane, *Organ. Lett.*, 2021, **23**, 5294-5298.