Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

Photoacid-mediated Ring Opening Polymerization Driven by Visible Light

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Materials

Benzyl alchol (BnOH), poly(ethylene glycol) methyl ether (mPEG, M_n ~ 750), 4-Hydroxy-2-butanone (98%), allyl alchol (98%), ε-Caprolactone (ε-CL, 98%), δ-Valerolactone (δ-VL, 98%), ethylene glycol (99%), *N*,*N*′-Dicyclohexylcarbodiimide (DCC, 99%), 4-(Dimethylamino)pyridine (DMAP, ⩾ 99%), 2,3,3-Trimethylindolenine (98%), propane sultone (98%), 2-Hydroxybenzaldehyde (98%), anhydrous propylene carbonate (PC, 99.7%) and zinc tetraphenylporphyrin (ZnTPP, 99%) were all purchased from Sigma-aldrich and used as received. Methyl acrylate (MA, 99%), 2-Hydroxyethyl methacrylate (HEMA, 98%), 2-Hydroxyethyl acrylate (HEA, 98%) were purchased from sigma-aldrich and passed through alumium oxide to remove inihibitor before use. ZnTPP was prepared to stock solution (1.0 mg/mL) in propylene carbonate and stored under dark. Hydroxyl chain transfer agent (CTA) was prepared according to previous literature.[1]

Instruments

Gel permeation chromatography (GPC) was performed using tetrahydrofuran (THF) as the eluent. The GPC system was a Shimadzu modular system comprising an auto injector, a Phenomenex 5.0 μm bead-size guard column (50 × 7.5 mm) followed by two MIX C columns provided by Polymer Lab for THF system, and a differential refractive-index detector and a UV detector. The system was calibrated with narrow molecular weight distribution poly(styrene) (PSt) standards with molecular weights of 200 to 10^6 g mol^{-1}.

Nuclear Magnetic Resonance (NMR) spectroscopy was carried out on a Bruker Advance III with SampleXpress operating at 300 MHz using $CDCl_3$ as solvent and tetramethylsilane (TMS) as a reference. The data obtained was reported as chemical shift (δ) measured in ppm downfield from TMS.

Light source was RS Component PACK LAMP RGB LED light (5 W, $\lambda_{max,\ blue}$ =460 nm; $\lambda_{max,\ red}$ =635 nm).

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Synthesis of photoacid

Photoacid was prepared according to previous literature.[2] Typically, 2,3,3-Trimethylindolenine (1.65 g, 0.01 mmol) was added to propane sultone (1.26 g, 0.01 mol). The mixture was stirred at 90 °C for 4 h. The purple solid was collected by filtration followed by washed with cold ethyl ether and dried in vacuum. The obtained solid (1.0 g, 3.6 mmol) and 2-hydroxylbenzaldehyde (0.48 g, 3.9 mmol) were added to anhydrous ethanol (20 mL). The mixture was refluxed overnight. The orange solid was collected by filtration and washed with cold ethanol and then dried under vacuum (0.96 g, 70% yield).

^{1}H NMR (300 MHz, d_6-DMSO)/ppm: 11.05 (s, 1H), 8.62 (d, 1H, Ar-$\underline{H}$), 8.28 (d, 1H, Ar-$\underline{H}$), 8.03 (d, 1H, Ar-$\underline{H}$), 7.87 (m, 2H, Ar-$\underline{H}$), 7.62 (m, 2H, Ar-$\underline{H}$), 7.48 (t, 1H, Ar-$\underline{H}$), 7.04 (d, 1H, vinyl), 6.96 (t, 1H, vinyl), 4.80 (t, 2H, $NC\underline{H_2}$), 2.66 (t, 2H, $SO_3C\underline{H_2}$), 2.19 (m, 2H, $NCH_2C\underline{H_2}$), 1.77 (s, 6H, $CH_2C\underline{H_3}$).

^{13}C NMR (75 MHz, d_6-DMSO)/ppm: 182.2, 159.5, 149.1, 143.9, 141.4, 136.2, 130.2, 129.6, 129.5, 123.4, 121.8, 120.5, 117.1, 115.5, 111.9, 52.3, 47.8, 45.9, 26.9, 25.1.

Typical procedure of photo-ROP

BnOH (10.8 mg, 0.1 mmol), δ-VL (0.5 g, 5 mmol), photoacid (10 mg, 0.025 mmol) and propylene carbonate (1.0 mL) were placed in a 4 mL glass vial in glovebox. The solution was then irradiated under blue light at room temperature. Samples were withdrawn periodically for GPC and NMR analysis. The polymerization was terminated by the addition of TEA. The polymer was isolated by precipitation from THF to cold methanol and dried under vacuum.

Chain extension for block copolymer synthesis

Benzyl alcohol initiated PCL ($M_{n,\,RI}$ ~ 6 100, 100 mg, 0.016 mmol)，δ-VL (0.5 g, 5 mmol), photoacid (10 mg, 0.025 mmol) and propylene carbonate (1.0 mL) were placed in a 4 mL glass vial in glovebox. The solution was then irradiated for 20 h under blue light at room temperature. The polymerization was terminated by the addition of TEA. The polymer was isolated by precipitation from THF to cold methanol and dried under vacuum.

"ON"/"OFF" regulation of photo-ROP

BnOH (5.4 mg, 0.05 mmol), δ-VL (0.5 g, 5 mmol), photoacid (10 mg, 0.025 mmol) and propylene carbonate

(1.0 mL) were placed in a 4 mL glass vial in glovebox. The solution was then irradiated under blue light ("ON") for 4 h followed by removal of blue light ("OFF") for 4 h. The "ON"/ "OFF" process was repeated for 2 times. Samples were withdrawn at predetermined time interval for NMR analysis.

Alternative photo-ROP and PET-RAFT polymerization for block copolymer synthesis

Hydroxyl CTA (20 mg, 0.07 mmol), δ-VL (0.354 g, 3.54 mmol), MA (0.301 g, 3.54 mmol), photoacid (10 mg, 0.025 mmol), ZnTPP (0.12 mg, 1.77×10^{-4} mmol) and propylene carbonate (1.0 mL) were placed in a 4 mL glass vial in glovebox. The solution was exposed to blue light and red light alternatively. Typically, the solution was firstly irradiated under blue light for 4 h followed by irradiation under red light for 15 h. Afterwards, the solution was continued to be irradiated under blue light for 4 h. Then the solution was irradiated under red light for another 25 h. The total polymerization time was 48 h. During the polymerization process, samples were withdrawn periodically at predetermined time for GPC and NMR analysis. The polymer was isolated by dialysis against mixture of THF and methanol. After removal of solvent, the polymer was dried in vacuum.

PMA-*b*-(PHEA-*g*-PVL) graft copolymer synthesis

2-(((butylthio)carbonothioyl)thio)propanoic acid (BTPA, 12 mg, 0.05 mmol), δ-VL (1.0 g, 10 mmol), MA (0.346 g, 4.0 mmol), 2-hydroxyethyl Acrylate (0.116g, 1.0 mmol), photoacid (15 mg, 0.038 mmol), ZnTPP (0.24 mg, 3.54×10^{-4} mmol) and propylene carbonate (1.0 mL) were placed in a 4 mL glass vial in glovebox. The solution was exposed to blue light first for 21 h to prepare macromonomer. Sample was taken out for GPC and NMR analysis. Then the light was switched to red light for another 48 h. The polymerization was stopped by removal of light. Sample was subjected for GPC and NMR analysis. The graft copolymer was isolated by precipitation from dichloromethane to methanol for 2 times. The conversion of δ-VL in macromonomer synthesis step was 92%. Meanwhile, the polymerization of MA and macromonomer was not observed. The conversion of MA and macromonomer in PET-RAFT polymerization was 68% calculated by ^{1}H NMR.

Supporting data

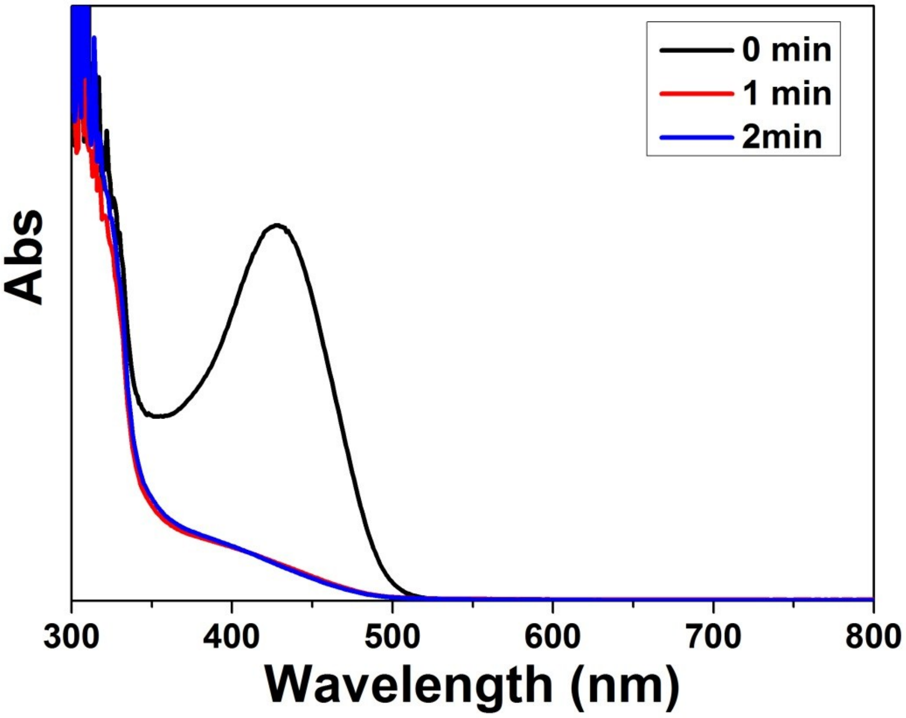

Figure S1 UV-vis absorption spectra of photoacid solution in propylene carbonate after irradiation under blue light for different time (concentration = 0.33 mg/mL).

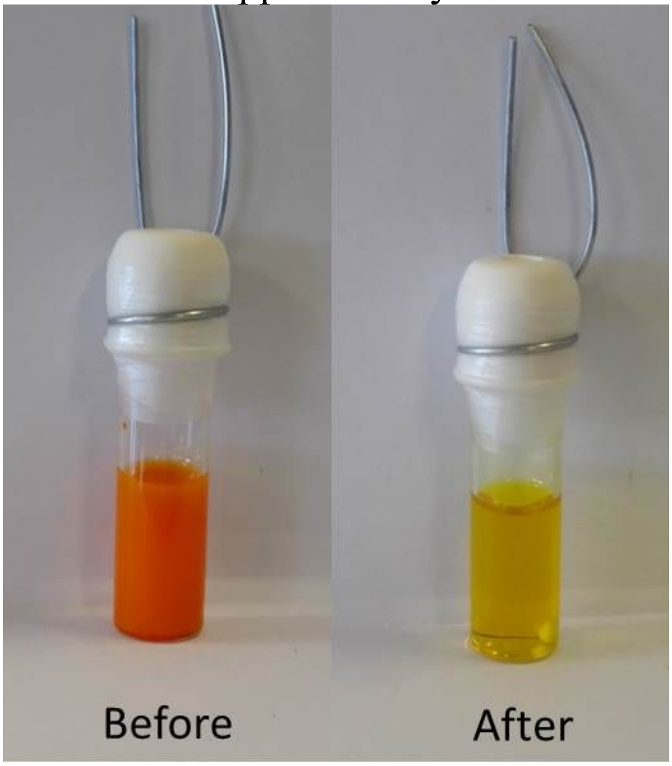

Figure S2 Photographs of photoacid mediated ROP under blue light before and after polymerization.

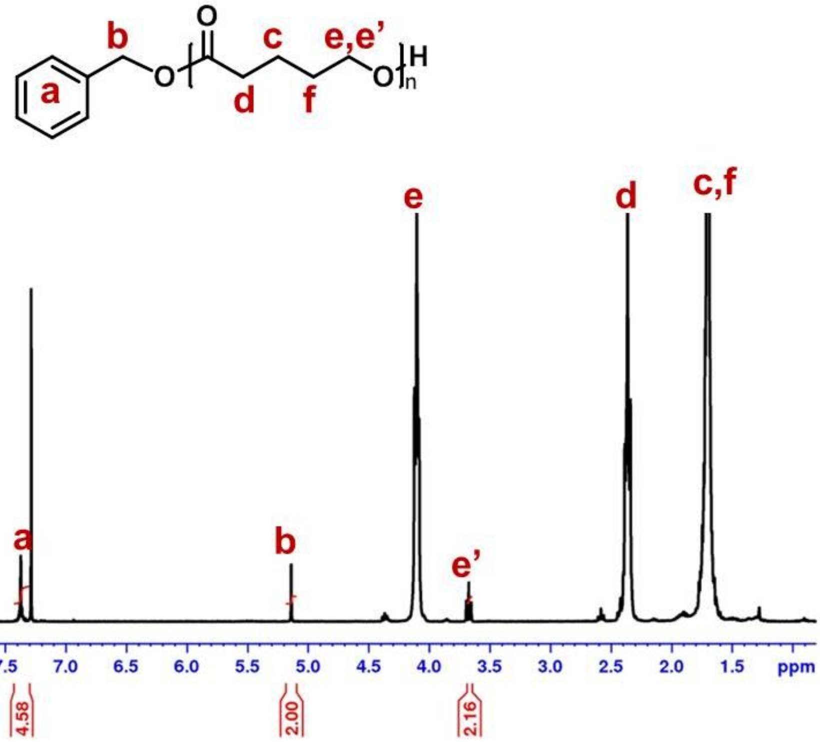

Figure S3 ^{1}H NMR spectrum ($CDCl_3$) of PVL prepared by photoacid mediated ROP with BnOH as initiator.

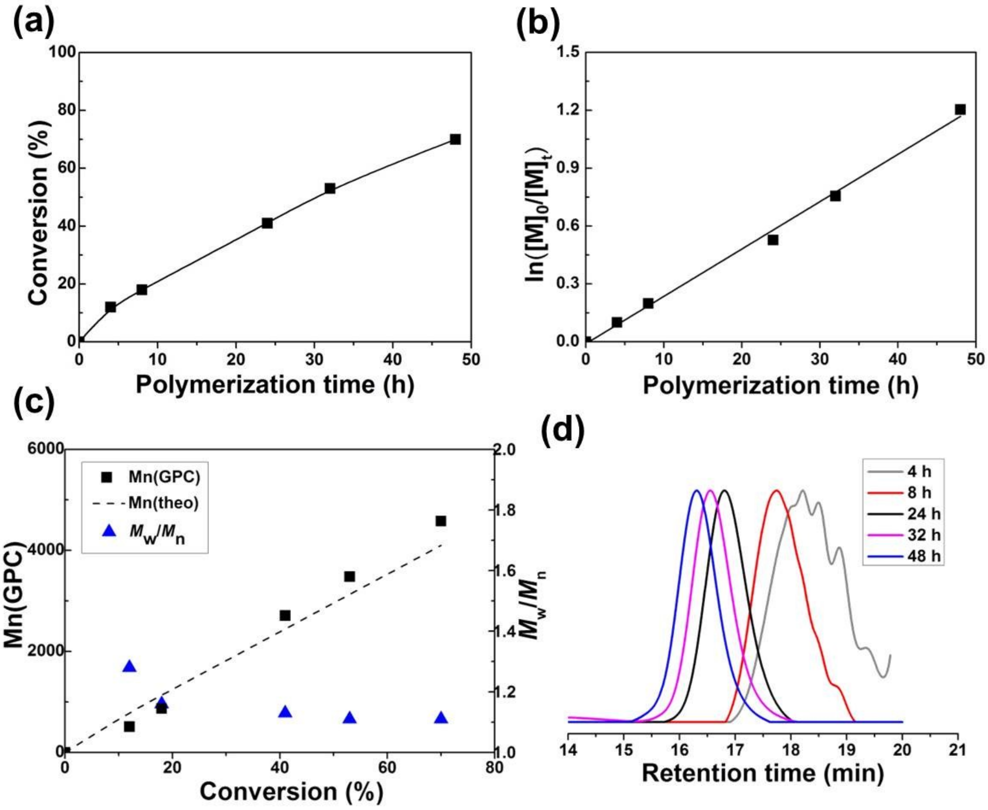

Figure S4 Kinetic study of visible light mediated ROP of ε-CL catalyzed by photoacid under blue light (λ_{max} =460 nm; 0.7 mW/cm^2): (a) Monomer conversion versus polymerization time; (b) Ln([M]$_0$/[M]$_t$) versus polymerization time; (c) $M_{n,\ RI}$ versus monomer conversion; (d) GPC evolution during polymerization. Condition: [BnOH]:[**PAH**]:[ε-CL] = 1:0.25:50, [M]$_0$ = 3.3M.

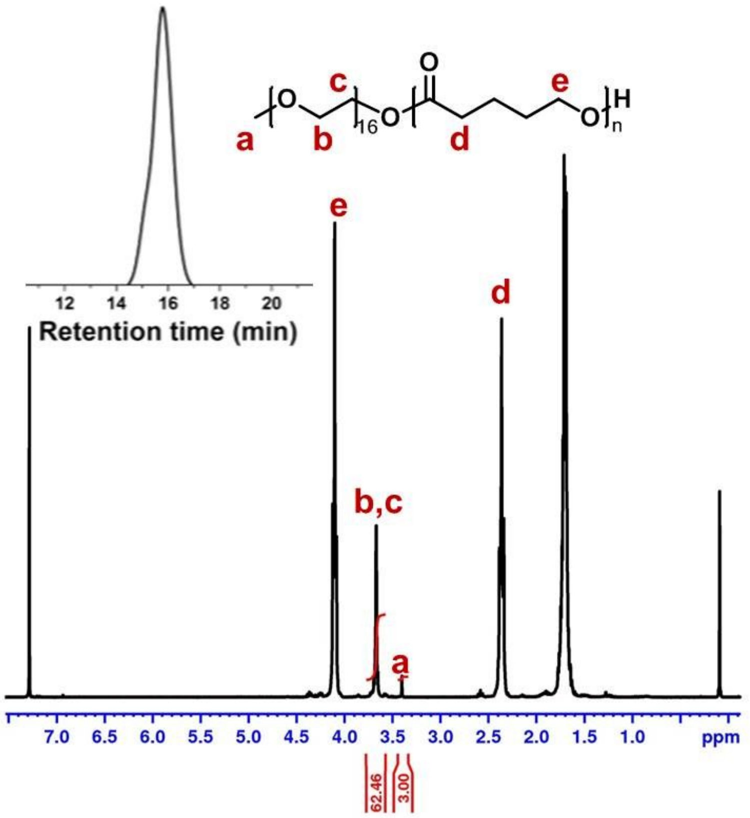

Figure S5 ^{1}H NMR spectrum ($CDCl_3$) and GPC trace of PVL initiated by mPEG.

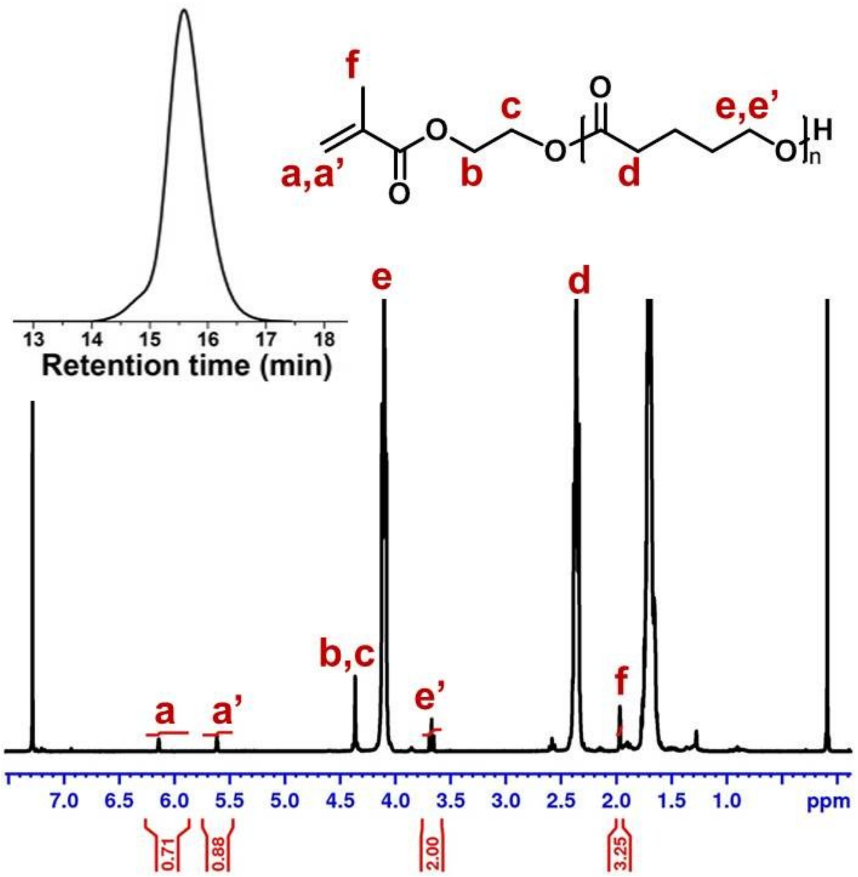

Figure S6 ^{1}H NMR spectrum ($CDCl_3$) and GPC trace of PVL initiated by HEMA.

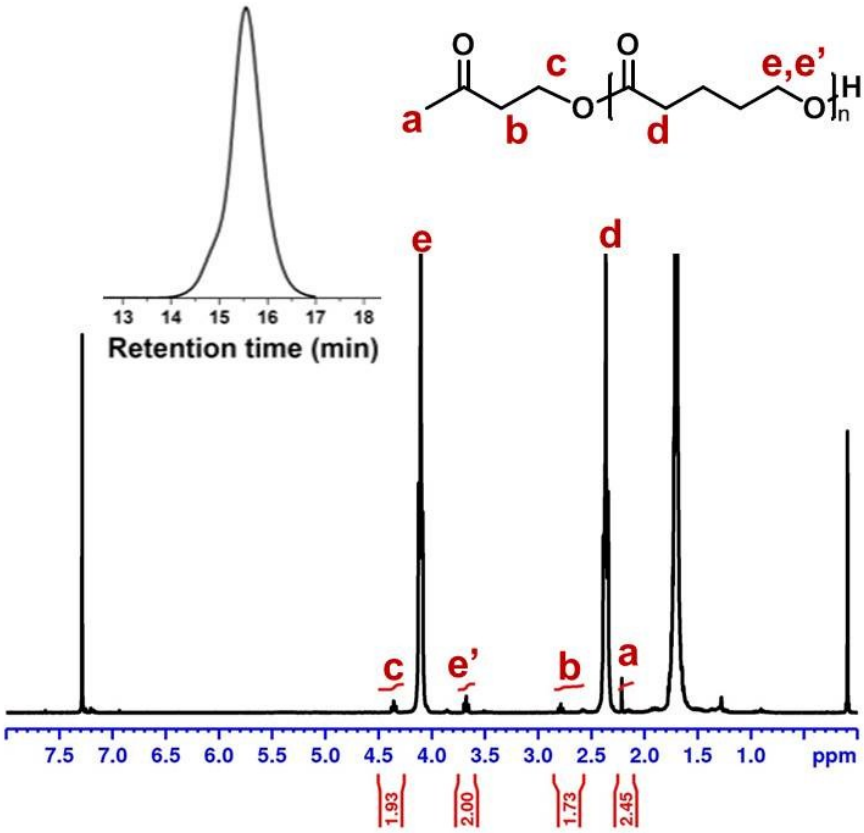

Figure S7 ^{1}H NMR spectrum ($CDCl_3$) and GPC trace of PVL initiated by 4-hydroxy-2-butanone.

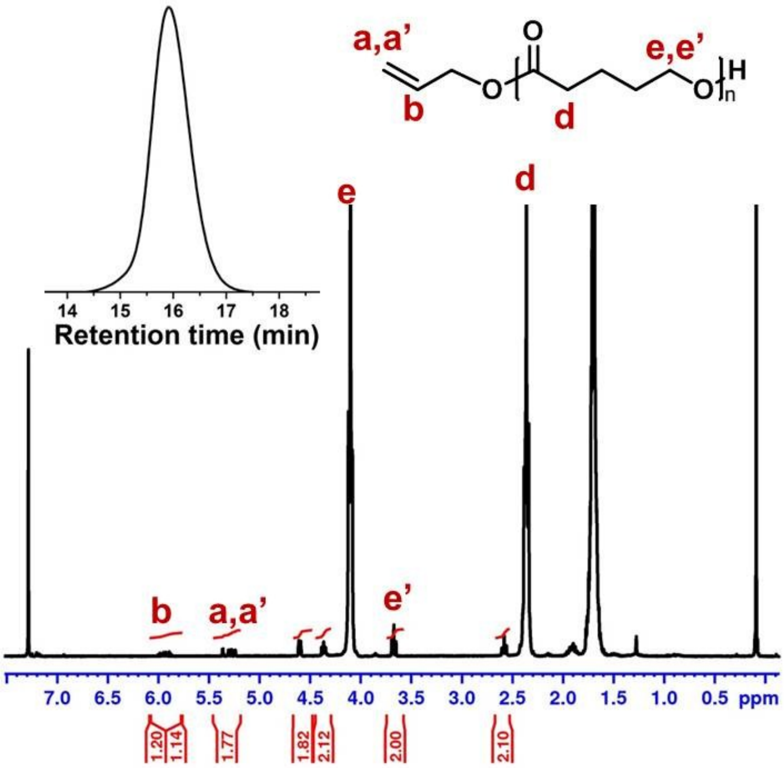

Figure S8 ^{1}H NMR spectrum ($CDCl_3$) and GPC trace of PVL initiated by allyl alcohol.

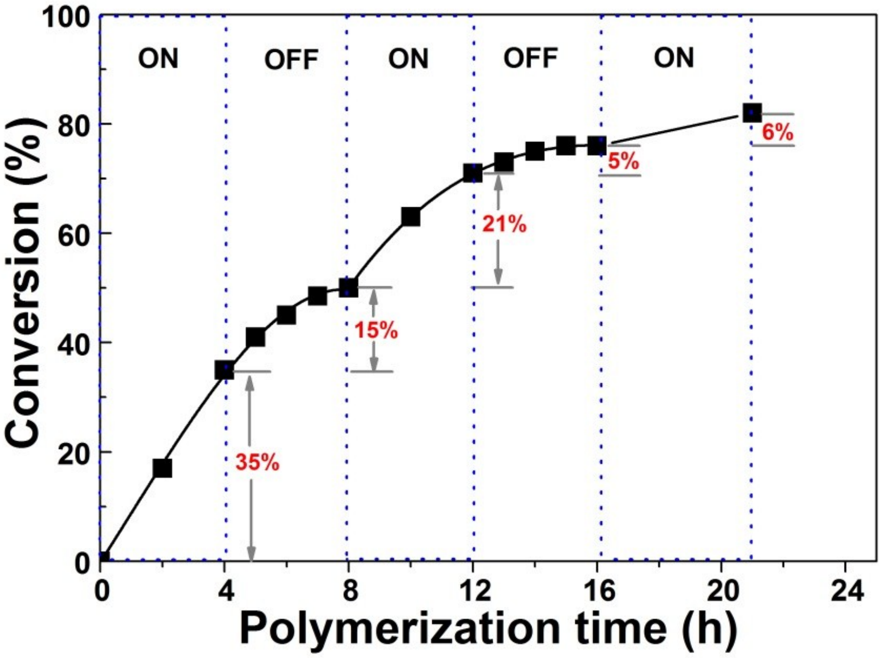

Figure S9 Temporal control over photo-ROP of δ-VL by switching on or off the light during polymerization.

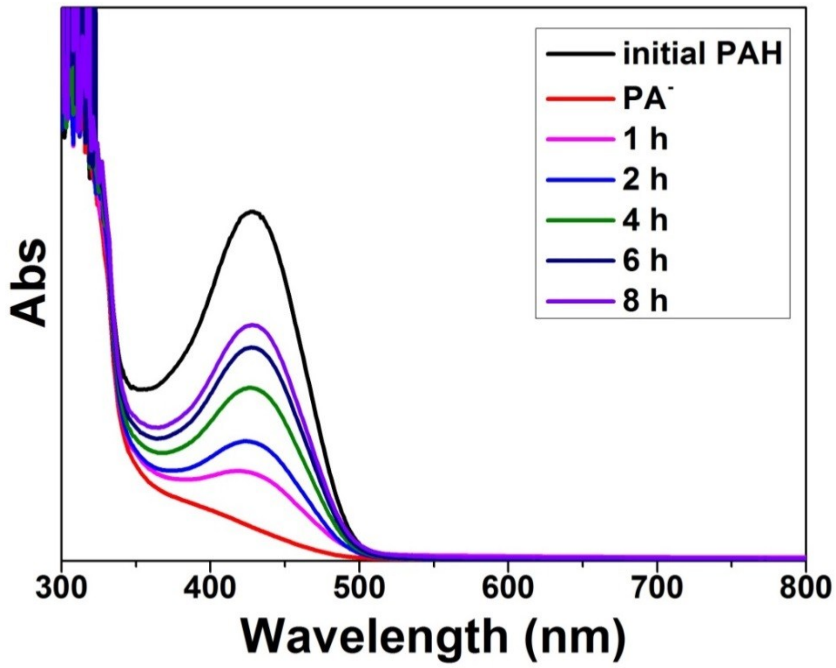

Figure S10 UV-vis absorption spectra of **PAH** in propylene carbonate after kept in dark for different time (concentration = 0.33 mg/mL). **PA**$^-$ was formed by irradiating **PAH** under blue light for 10 minutes.

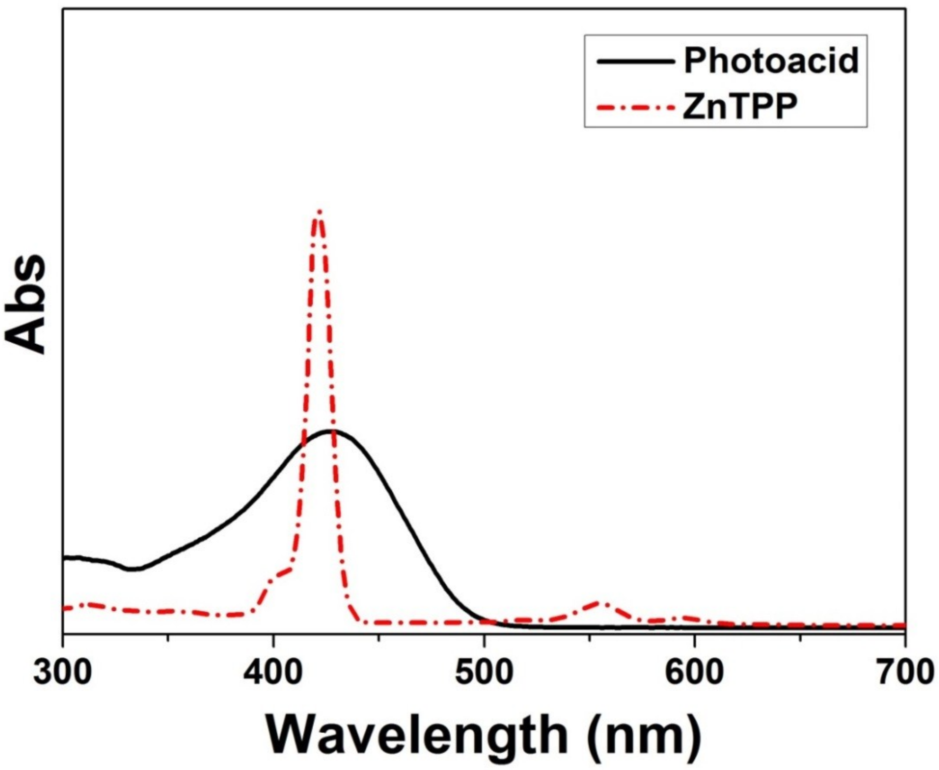

Figure S11 UV-vis absorption spectra of photoacid **PAH** and ZnTPP solution in propylene carbonate.

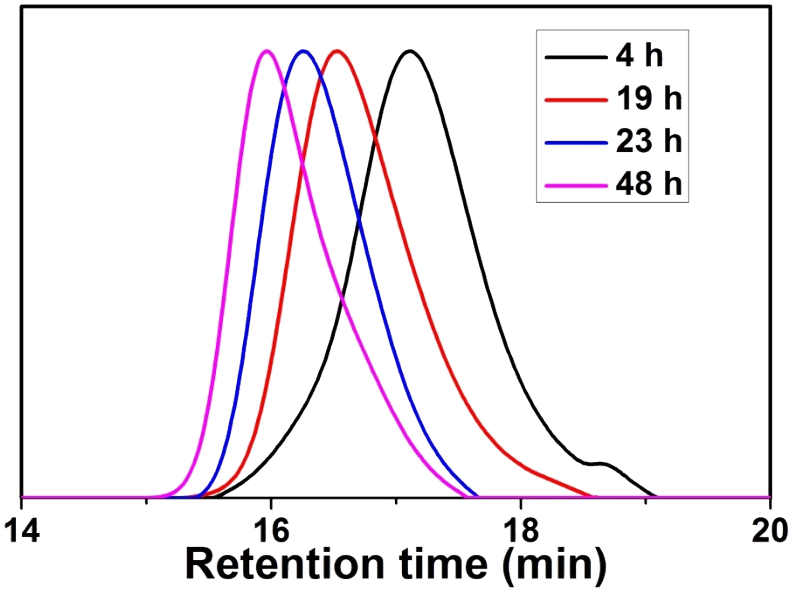

Figure S12 GPC traces of polymers at different time intervals in the dual wavelength light regulated orthogonal polymerization for block copolymer synthesis.

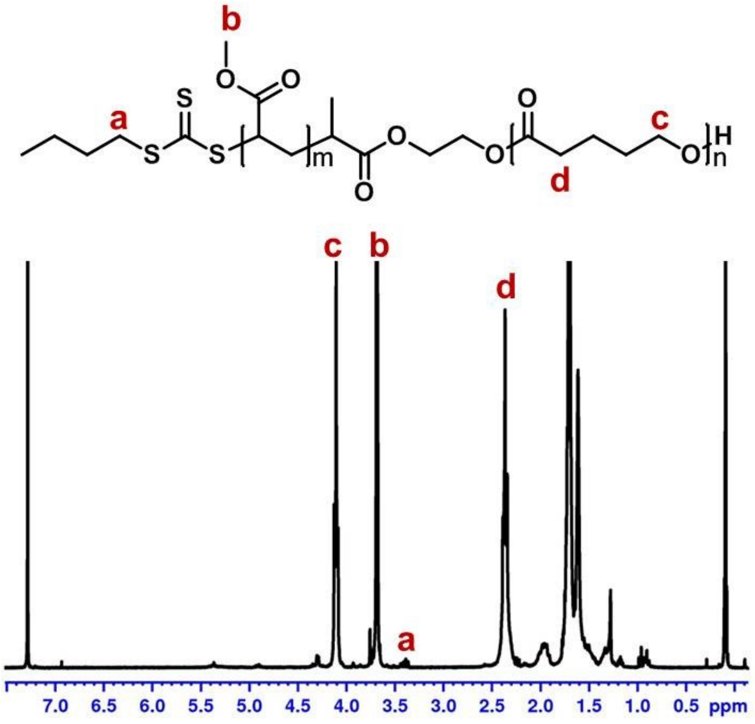

Figure S13 ^1H NMR spectrum ($CDCl_3$) of PVL-*b*-PMA block copolymer prepared by alternative photo controlled ROP and PET-RAFT polymerization.

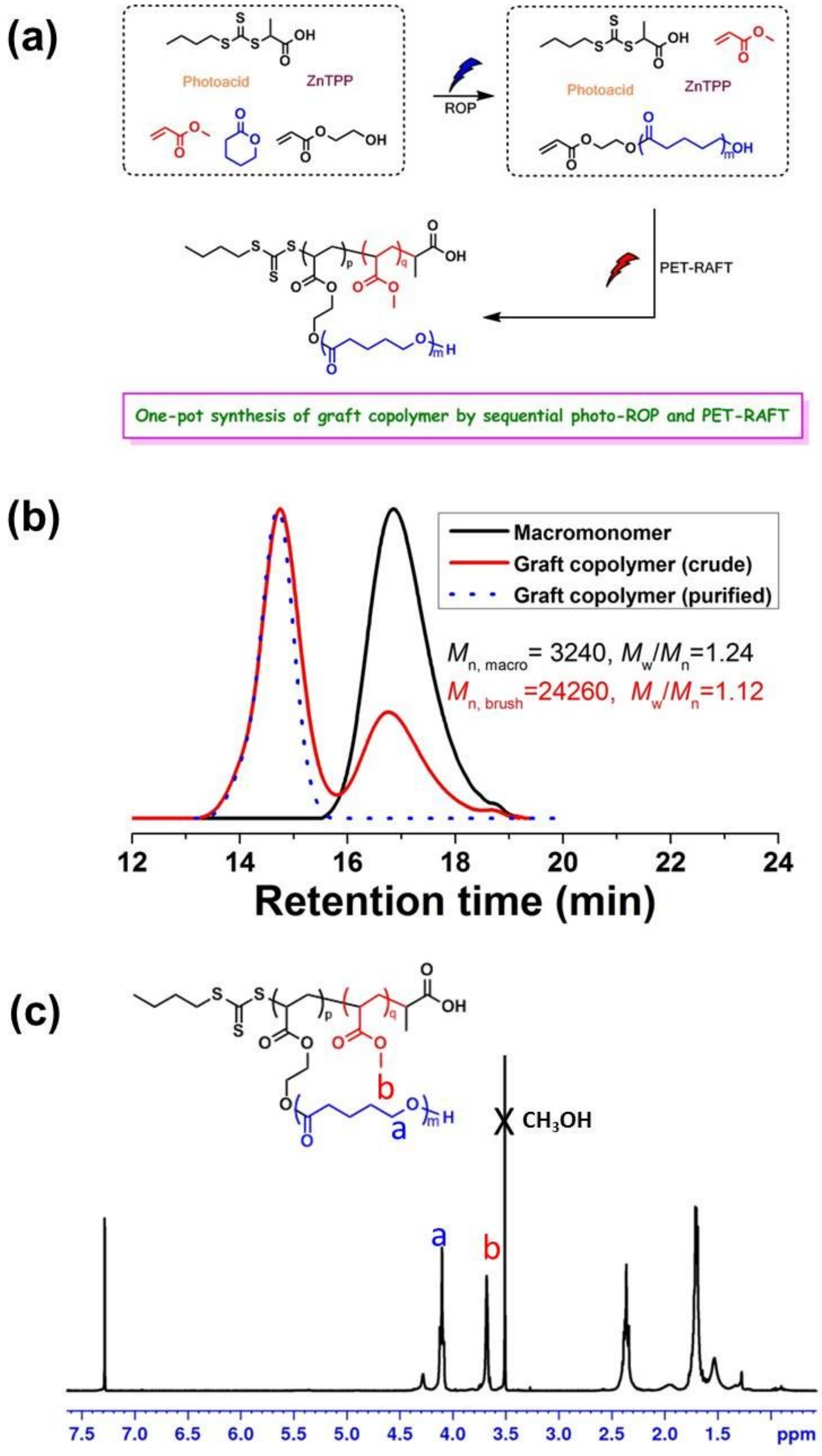

Figure S14 (a) Schematic illustration of synthesis of graft copolymer PMA-*b*-(PHEA-*g*-PVL) by one-pot sequential photo-ROP and PET-RAFT polymerization by alternative blue (λ_{max} =460 nm; 0.7 mW/cm^2) and red light (λ_{max} =635 nm; 0.4 mW/cm^2) irradiation; (b) GPC traces of in-situ generated macromonomer PVL and graft copolymer PMA-*b*-(PHEA-*g*-PVL); (c) ^{1}H NMR spectrum (CDCl$_3$) of graft copolymer PMA-*b*-

(PHEA-*g*-PVL).

References

1. Fu, C.; Xu, J.; Kokotovic, M.; Boyer, C. *ACS Macro Lett.* **2016,** *5*, 444-449.
2. Shi, Z.; Peng, P.; Strohecker, D.; Liao, Y. *J. Am. Chem. Soc.* **2011,** *133*, 14699-14703.