

Supporting Information For

Visible light induced controlled cationic polymerization by in-situ generated catalyst from manganese carbonyl

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Supporting Information Placeholder

Materials and General Methods

Styrene (St; 99%, Adamas) was passed through a neutral alumina column to remove the inhibitor prior to use, N, N, N', N'', N'''-pentamethyldiethylenetriamine (PMDETA; 99%, Aldrich) was distilled prior to use. Copper(I) bromide (CuBr, 99%, Sinopharm Chemical Reagent,) was purified by washing with acetic acid/deionized water (v/v = 5/95) and anhydrous ethanol several times, and then dried under vacuum. Isobutyl vinyl ether (IBVE, 98%, Adamas) was distilled from CaH₂ in vacuum or used as received. Ethyl vinyl ether (EVE, 99%, Aldrich), n-butyl vinyl ether (BVE, 98%, J&K), 2-chloroethyl vinyl ether (Cl-EVE, 99%, Aldrich), dimanganese decacarbonyl (Mn₂(CO)₁₀, 98%, Alfa Aesar), pentacarbonylbromomanganese (Mn(CO)₅Br, 98%, Alfa Aesar), ethyl-2-bromopropionate (EBP, 98%, Alfa Aesar), benzyl bromide (BB, 98%, Aldrich), ethyl 2-bromoisobutyrate (EBIB, 98%, J&K) and ethyl alpha-bromophenylacetate (EBPA, 98%, Aldrich) were used as received, RAFT CTA 4-cyanopentanoic acid dithiobenzoate (CPADB) were purchased from Sigma-Aldrich and used without further purification. Other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd., China and used without purification.

The number-average molecular weight (*M_n*) and molecular weight distribution (*Đ*) of polymers were determined by TOSOH HLC-8320 Size Exclusion Chromatography (SEC) equipped with TSK gel Multi pore HZ-N (3) 4.6×150 mm column at 40 °C. Tetrahydrofuran was served as the eluent with a flow rate of 0.35 mL min⁻¹. SEC samples were injected using a TOSOH HLC-8320 GPC plus auto sampler. The molecular weights were calibrated with narrow polydispersity PS or PMMA standards. Nuclear magnetic resonance (NMR) spectrum was recorded on a Bruker 300 MHz nuclear magnetic resonance instrument using CDCl₃ as the solvent and tetramethylsilane as an internal standard. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry measurement of PIBVE was performed using a Bruker Autoflex III (MALDI-TOF) mass spectrometer equipped with a 337 nm nitrogen laser. Differential scanning calorimetry

(DSC) was performed under a nitrogen flush of 40 mL min⁻¹ at a heating rate of 10 °C min⁻¹ on a TA Instruments 2010 DSC V4.4E. T_g was measured as the midpoint of the transition in the second heating ramp.

All photo polymerizations were carried out in ampoule bottle in front of 460 nm blue LEDs (0.6 W, 2 mW cm⁻²) (Figure S1). Reactions were placed at a distance of 1 cm from the LEDs.

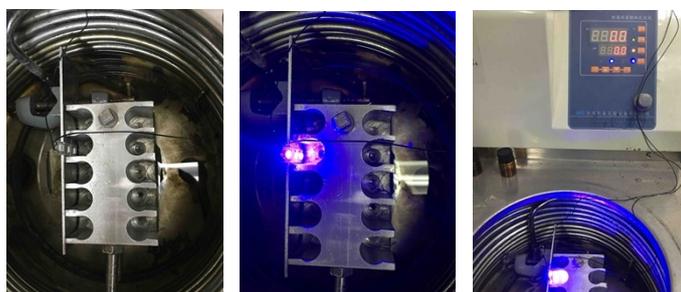


Figure S1. Photograph of the 460 nm blue LED photoreactor.

Polymerization Procedures

Polymerization of IBVE: The polymerization of IBVE was described as the typical example. This polymerization used single points experiments. A mixture of monomer (0.5 mL, 3.79 mmol) and EBP (3.4 mg, 0.019 mmol) and Mn₂(CO)₁₀ (1.48 mg, 0.0038 mmol) were placed in ampoule bottle with the molar ratio of [IBVE]₀ : [EBP]₀ : [Mn₂(CO)₁₀] = 200 : 1 : 0.2. The content was degassed by three freeze-pump-thaw cycles and purged with nitrogen. After the desired reaction time under the irradiation of blue LED with controlled temperature, the ampoule was exposure to oxygen and THF was added to dissolve the product. The polymer was obtained after precipitated by methanol. Monomer conversion was calculated by gravity.

Polymerization of PS: St (3 mL, 26.2 mmol), PMDETA (91 mg, 0.524 mmol), CuBr (38 mg, 0.262 mmol), EBIB (51 mg, 26.2 mmol) were placed in ampoule bottle. The content was degassed by three freeze-pump-thaw cycles and purged with nitrogen. After polymerization in a thermostatic oil bath (110°C) for 3.5 h, the reaction mixture was diluted with tetrahydrofuran (THF) and then passed through a column of neutral alumina to remove the copper salt. The bromo-endfunctionalized PS was dissolved in a small amount of THF, and precipitated by methanol.

Polymerization of PS-*b*-PIBVE: PS (16 mg, 0.0094 mmol), IBVE (0.5 mL, 3.79 mmol) and Mn₂(CO)₁₀ (1.48 mg, 0.0038 mmol) were placed in ampoule bottle. The content was degassed by three freeze-pump-thaw cycles and purged with nitrogen. After given time under the irradiation of blue LED with controlled temperature, the reaction mixture was diluted with a small amount of THF and precipitated in excess of methanol. The polymer was dried under vacuum at room temperature.

Polymerization of PIBVE-CTA: A mixture of monomer (0.5 mL, 3.79 mmol) and EBP (3.4 mg, 0.019 mmol) and Mn₂(CO)₁₀ (1.48 mg, 0.0038 mmol) were placed in ampoule bottle containing 0.5 mL ethyl acetate. The content was degassed by three freeze-pump-thaw cycles and purged with nitrogen. After the desired reaction time under the irradiation of blue LED with controlled temperature, 1.5 fold CTA and 2 fold trimethylamine of EBP in 0.5 mL ethyl acetate were added to the ampoule. The solution was stirred for 0.5h and then exposure to oxygen. THF was added to dissolve the product and the polymer was obtained after precipitated by methanol. Monomer conversion was calculated by gravity.

Polymerization of PIBVE-*b*-PMMA: PIBVE-CTA (25 mg, 0.003 mmol), MMA (0.25 mL, 2.36 mmol) and were placed in ampoule bottle. The content was degassed by three freeze-pump-thaw cycles and purged with nitrogen. After given time under the irradiation of blue LED at 25 °C, the reaction mixture was diluted with a small amount of THF and precipitated in excess of petroleum ether. The polymer was dried under vacuum at room temperature.

Additional Results

Table S1. Polymerization of IBVE with different initiators with the molar ratio [IBVE] : [Initiator] : [Mn₂(CO)₁₀] = 200:1:0.2 at 0 °C. V_M = 0.5 mL

Entry	Initiator	Time	Conv.%	^a M _{n,th} (g/mol)	^b M _{n,GPC} (g/mol)	<i>D</i>
1	BB	36 h	10.7	2300	10500	3.80
2	EBPA	16 h	26.2	5400	24800	2.53
3	EBIB	20 min	69.0	14000	34000	1.96
4	EBP	18 min	93.9	19000	20600	1.29

- a) Calculated based on conversion ($M_{n,th} = [M]_0/[Initiator]_0 \times \text{conversion} \times M + M_{EBP}$); b) Determined by SEC using polystyrene (PS) as standard in THF

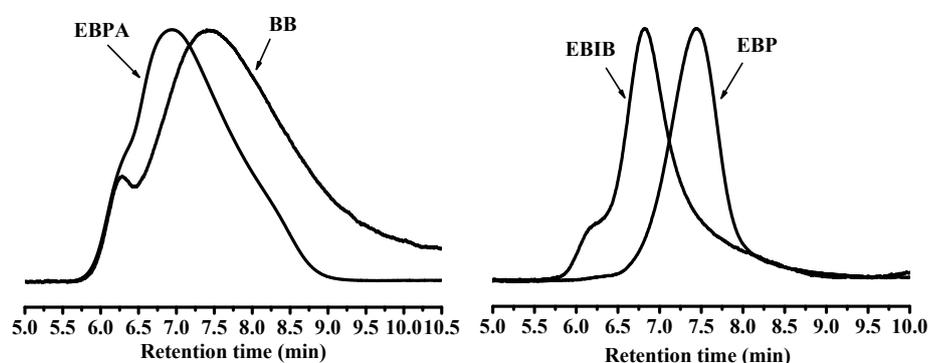


Figure S2. SEC traces of PIBVE prepared using different organic halides.

Table S2. Polymerization of IBVE with different solvents with the molar ratio [IBVE] : [EBP] : [Mn₂(CO)₁₀] = 200:1:0.2. V_M = 0.5 mL, V_{Solvent} = 0.5 mL

Entry	Solvent	Time	Conv.%	^a M _{n,th} (g/mol)	^b M _{n,GPC} (g/mol)	<i>D</i>
1	Toluene	40 min	89.9	18200	21100	1.31
2	DCM	20 min	94.6	19100	16400	1.31
3	Hexane	50 min	83.8	17000	23200	1.37
4	EA	3 h	81.2	16400	29600	1.28
5	THF	40 h	18.1	3800	10500	1.14

- a) Calculated based on conversion ($M_{n,th} = [M]_0/[Initiator]_0 \times \text{conversion} \times M + M_{EBP}$); b) Determined by SEC using polystyrene (PS) as standard in THF

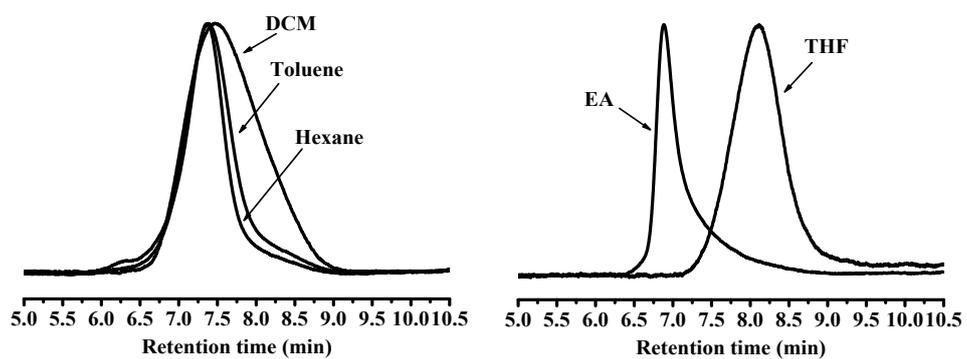


Figure S3. SEC traces of PIBVE prepared in different solvents.

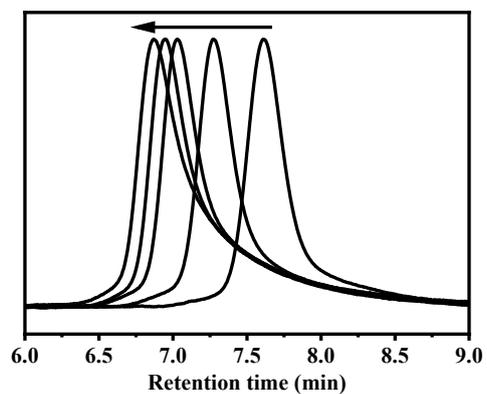


Figure S4. SEC traces of PIBVE in kinetic experiments prepared with the condition of the molar ratio $[IBVE]_0$: $[EBP]_0$: $[Mn_2(CO)_{10}]_0 = 200 : 1 : 0.2$ under blue LED at $0\text{ }^\circ\text{C}$, $v_{IBVE} = 0.5\text{ mL}$, $v_{EA} = 0.5\text{ mL}$

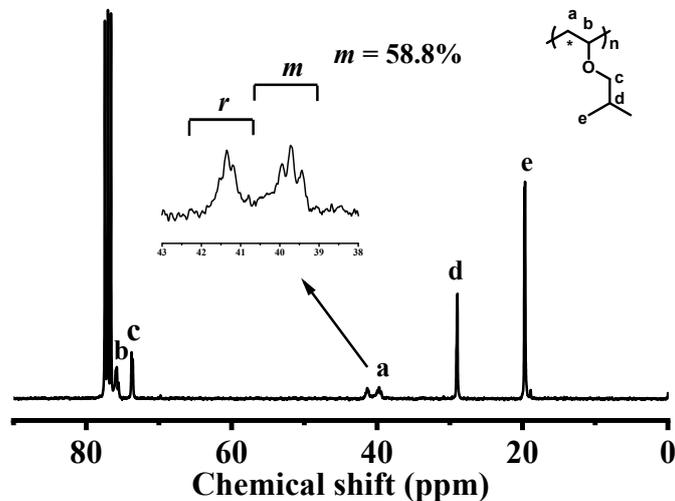


Figure S5. ^{13}C NMR spectrum of PIBVE ($M_{n,\text{SEC}} = 11500 \text{ g mol}^{-1}$, $\bar{D} = 1.19$, conversion = 75.5%), prepared under blue LED at 0°C ($[\text{IBVE}]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 100 : 1 : 0.2$, $t = 1 \text{ h}$, $V_{\text{IBVE}} = 0.5 \text{ mL}$, $V_{\text{EA}} = 0.5 \text{ mL}$).

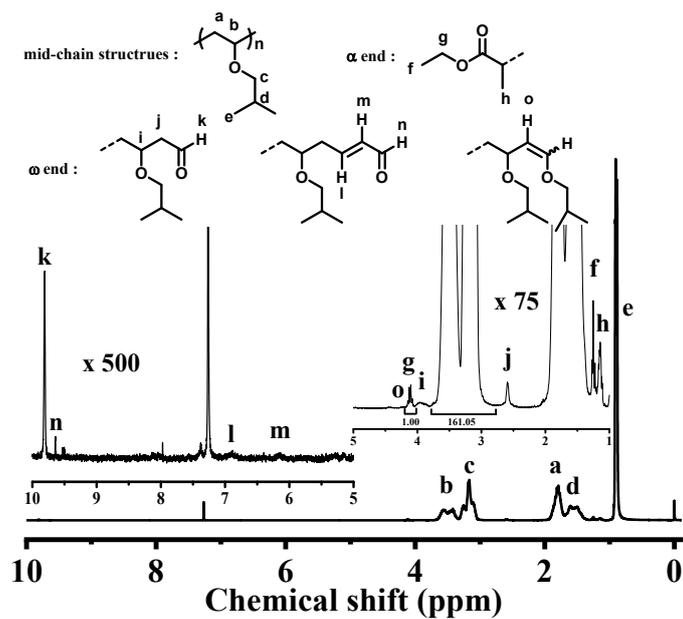


Figure S6. ^1H NMR spectrum of PIBVE ($M_{n,\text{SEC}} = 11500 \text{ g mol}^{-1}$, $\bar{D} = 1.19$, conversion = 75.5%), prepared under blue LED at 0°C ($[\text{IBVE}]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 100 : 1 : 0.2$, $t = 1 \text{ h}$, $V_{\text{IBVE}} = 0.5 \text{ mL}$, $V_{\text{EA}} = 0.5 \text{ mL}$).

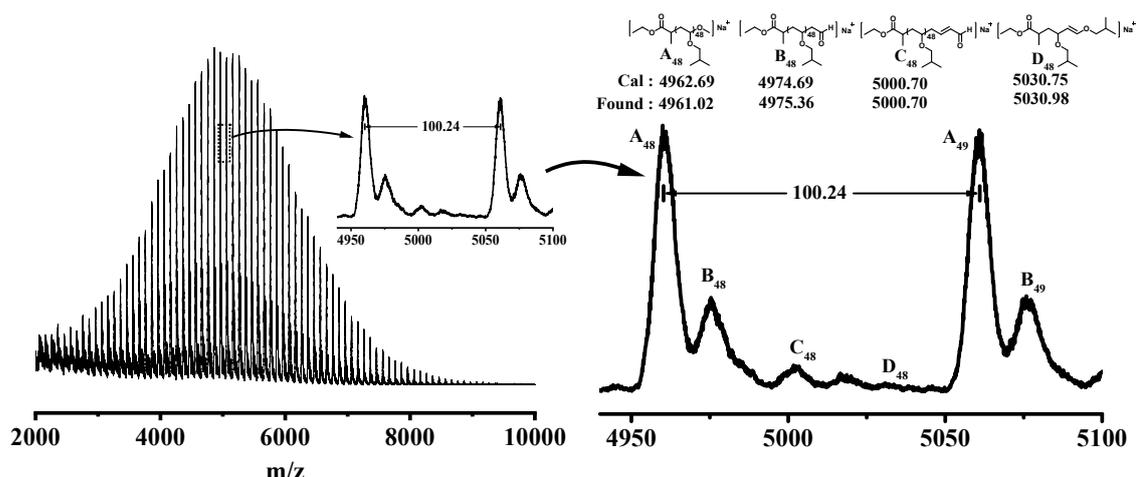


Figure S7. MALDI-TOF MS of PIBVE ($M_{n,SEC} = 7100 \text{ g mol}^{-1}$, $\mathcal{D} = 1.15$, conversion = 17.3%), prepared under blue LED at 0 °C ($[\text{IBVE}]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 100 : 1 : 0.2$, $t = 10 \text{ min}$, $V_{\text{IBVE}} = 0.5 \text{ mL}$, $V_{\text{EA}} = 0.5 \text{ mL}$).

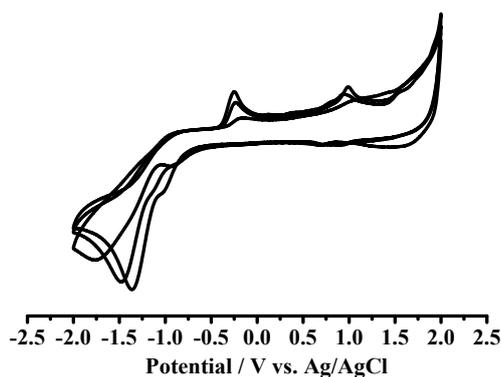


Figure S8. Cyclic voltammograms of $\text{Mn}(\text{CO})_5\text{Br}$. The experiment was performed in DCM with 0.1 M TBAPF_6 as the supporting electrolyte, under an atmosphere of N_2 , at a scan rate of 100 mV/s, with a glassy carbon working electrode (3 mm diameter), with a platinum wire counter electrode, with a Ag/AgCl wire pseudo-reference, and with Fc added as an internal reference.

Table S3. Polymerization of different monomers with the molar ratio $[\text{M}] : [\text{EBP}] : [\text{Mn}_2(\text{CO})_{10}] = 200:1:0.2$. $V_{\text{M}} = 0.5 \text{ mL}$

Entry	Monomer	Time	Conv.%	^a $M_{n,th}(\text{g/mol})$	^b $M_{n,GPC}(\text{g/mol})$	\mathcal{D}
1	EVE	8 min	86.4	12600	16000	1.45
2	BVE	8 min	78.3	18900	26500	1.38
3	Cl-EVE	50 min	67.4	13700	9600	1.22

- a) Calculated based on conversion ($M_{n,th} = [\text{M}]_0/[\text{Initiator}]_0 \times \text{conversion} \times M + M_{\text{EBP}}$); b) Determined by SEC using polystyrene (PS) as standard in THF

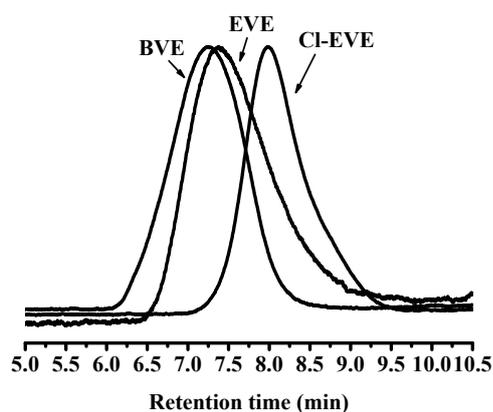


Figure S9. SEC traces of PIBVE prepared using different monomers.

Table S4. Polymerization results of IBVE under blue LED at 0 °C with the molar ratio $[\text{IBVE}]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 200 : 1 : 0.2$, $V_{\text{IBVE}} = 0.5 \text{ mL}$

Entry	Irradiation time	Polymerization Time	Conv.%	$^aM_{n,\text{SEC}}(\text{g/mol})$	\bar{D}
1	8 min	20 min	81.7	18200	1.21
2	6 min	20 min	78.9	16600	1.20
3	4 min	30 min	79.9	16900	1.23
4	2 min	90 min	70.0	17300	1.26
5	40 s	8 h	76.7	36900	1.32
6	20 s	20 h	61.2	51300	1.24

a) Determined by SEC using PS as standard in THF

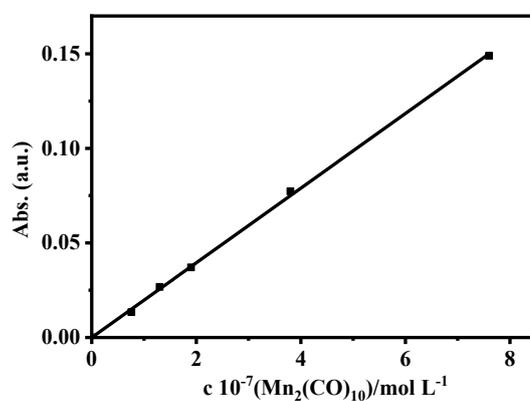


Figure S10. UV/Vis absorbance with different concentration of $\text{Mn}_2(\text{CO})_{10}$

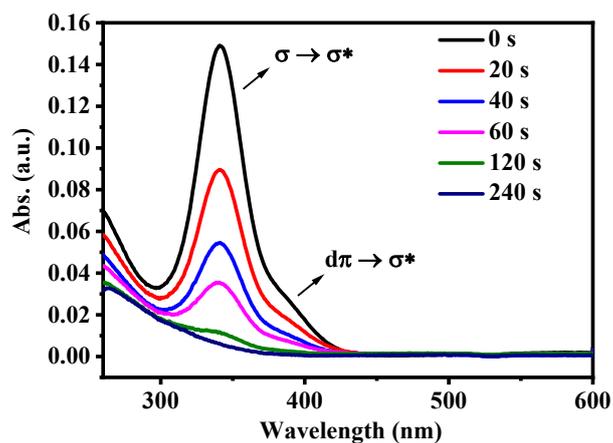


Figure S11. UV/Vis spectral changes at different time under blue LED at 0 °C with the molar ratio [EBP] : [Mn₂(CO)₁₀] = 1 : 0.2

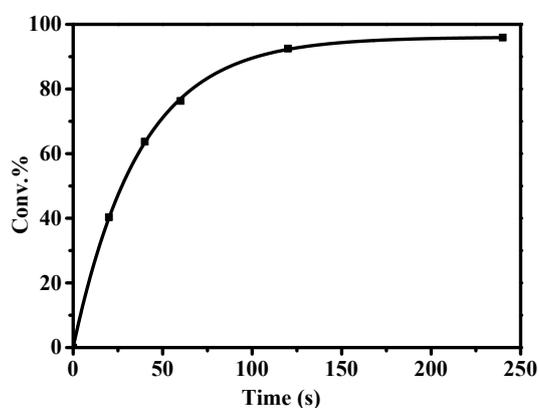


Figure S12. Conversion of Mn₂(CO)₁₀ at different time under blue LED at 0 °C with the molar ratio [EBP] : [Mn₂(CO)₁₀] = 1 : 0.2

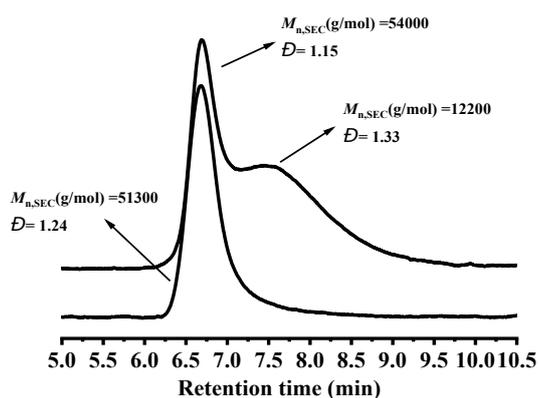


Figure S13. Light on/off experiment at 0 °C with the molar ratio [IBVE]₀ : [EBP]₀ : [Mn₂(CO)₁₀]₀ = 200 : 1 : 0.2, V_{IBVE} = 0.5 mL. a) Light on for 20s and in the dark for 20 h, then turn on the light for another 10 min; b)) Light on for 20s and in the dark for 20 h.

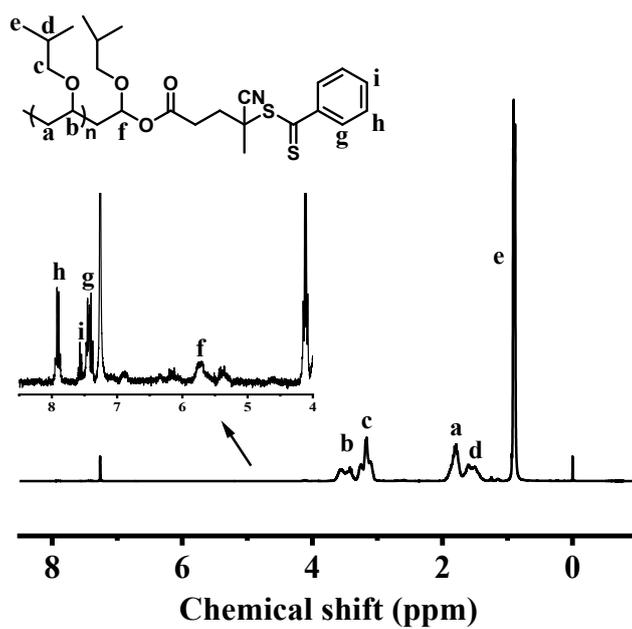


Figure S14. ^1H NMR spectrum of PIBVE-CTA.

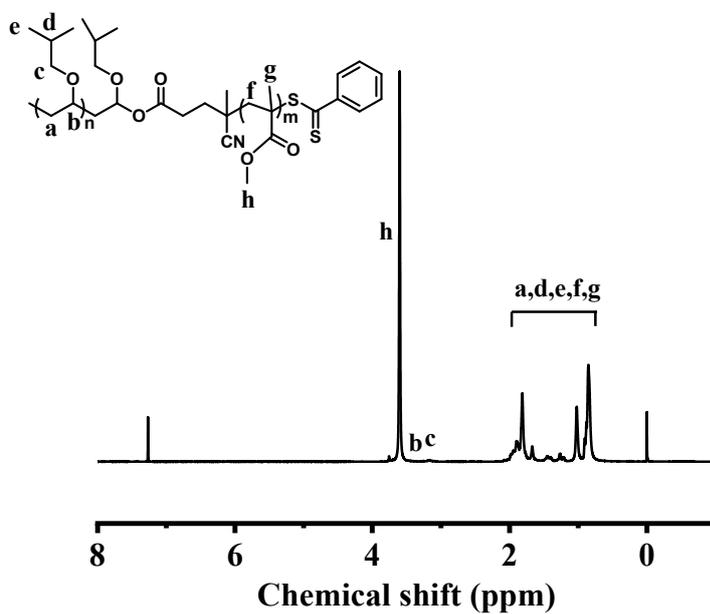


Figure S15. ^1H NMR spectrum of PIBVE-*b*-PMMA.

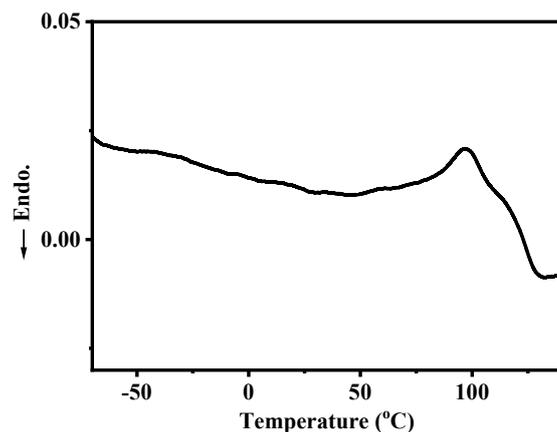


Figure S16. DSC curve of PIBVE-*b*-PMMA

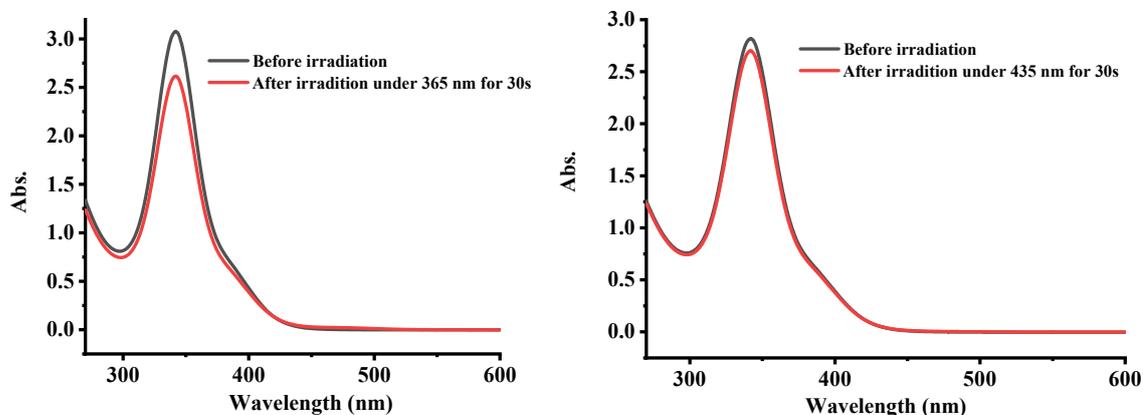


Figure S17. UV/Vis spectral changes at different time under different wavelength with the molar ratio
 $[\text{IBVE}] : [\text{EBP}] : [\text{Mn}_2(\text{CO})_{10}] = 100 : 1 : 0.2$ in ethyl acetate, $c_{\text{EBP}} = 1.5 \times 10^{-4} \text{ M}$

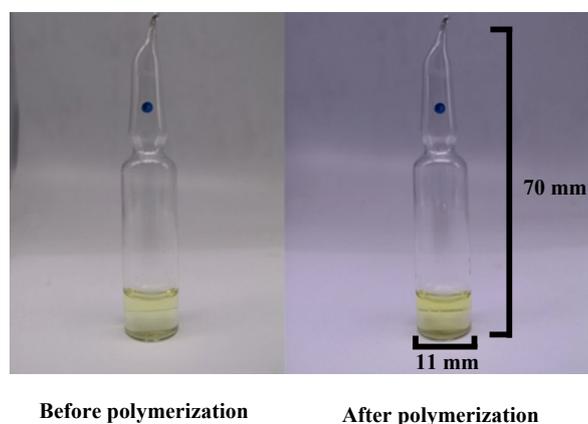


Figure S18. Photograph of the the ampoule before and after polymerization. ($M_{n, \text{SEC}} = 36700 \text{ g mol}^{-1}$, $\bar{D} = 1.27$, conversion = 90.1%), prepared under blue LED at $0 \text{ }^\circ\text{C}$ ($[\text{IBVE}]_0 : [\text{EBP}]_0 : [\text{Mn}_2(\text{CO})_{10}]_0 = 500 : 1 : 0.2$, $t = 25 \text{ min}$, $V_{\text{IBVE}} = 0.5 \text{ mL}$)