

# Supporting Information For

## Photoinduced Free Radical Promoted Cationic RAFT

### Polymerization toward “Living” 3D Printing

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#### Experimental Section

**Materials.** Isobutyl vinyl ether (IBVE, 98%, Adamas), diphenyliodonium hexafluorophosphate ( $\text{Ph}_2\text{IPF}_6$ , 98%, Aladdin), Diphenyliodonium bromide ( $\text{Ph}_2\text{IBr}$ , 98%, Bidepharm), Diphenyliodonium chloride ( $\text{Ph}_2\text{ICl}$ , 98%, Alfa Aesar), cyclopentadienyl iron dicarbonyl dimer ( $\text{Fe}_2(\text{CO})_{10}(\text{Cp})_2$ , 98%, Aldrich), diethylene glycol divinyl ether (DDE, 98%, Aladdin), diphenyl (2,4,6-trimethylbenzoyl)phosphine oxide (TPO, 98%, TCI), ethyl acetate (EA, 99%, Qiangsheng), dichloromethane (DCM, 99%, Qiangsheng), hexane (99%, Qiangsheng), toluene (99%, Qiangsheng), trichloromethane (99%, Qiangsheng), acetone (99%, Qiangsheng), tetrahydrofuran (THF, 99%, Qiangsheng), The CTA was synthesized according to ref 16. TPE-a was synthesized according to literature<sup>[1]</sup>.

**Instrumentation.** The number-average molecular weight ( $M_n$ ) and molecular weight distribution ( $\text{Đ}$ ) of polymers were determined by TOSOH HLC-8420 Size Exclusion Chromatography (SEC) equipped with TSK gel Multi pore HZ-N (3)  $4.6 \times 150$  mm column at 40 °C. Tetrahydrofuran (THF) was served as the eluent with a flow rate of 0.35 mL min<sup>-1</sup>. SEC samples were injected using a TOSOH HLC-8420 SEC plus auto sampler. The molecular weights were calibrated with narrow polydispersity PS standards. Nuclear magnetic resonance (NMR) spectrum was recorded on a Bruker 300 MHz nuclear magnetic resonance instrument using  $\text{CDCl}_3$  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. Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB), was used as the matrix (20 mg mL<sup>-1</sup> in  $\text{CHCl}_3$ ) without further purification (Sigma-Aldrich). The cationizing agent sodium trifluoroacetate was prepared in ethanol at a concentration of 10 mg mL<sup>-1</sup>. The matrix and cationizing salt solutions were mixed in a ratio of 10/1 (v/v). The instrument was calibrated prior to each measurement with external PMMA at the molecular weight under consideration. All samples were dissolved in  $\text{CHCl}_3$  at a concentration of 10 mg mL<sup>-1</sup>. After sample preparation and solvent evaporation, the target plate was inserted into the MALDI-TOF mass spectrometer. The instrument was operated in the reflector mode. The C=C conversion of the DDE in the kinetics study of photoinduced 3D polymerization was monitored by online infrared analyzer ReactIR™ IC10, C=C conversion was calculated based on the reduction on the intensity of the C=C vibration peak at 1619 cm<sup>-1</sup>.

The different light sources used in polymerizations of IBVE: UV lamp ( $\lambda_{\text{max}} = 373$  nm, intensity = 0.73 mW cm<sup>-2</sup>), Blue LED light ( $\lambda_{\text{max}} = 440$  nm, intensity = 0.69 mW cm<sup>-2</sup>), Green LED light ( $\lambda_{\text{max}} = 525$  nm, intensity = 1.03 mW cm<sup>-2</sup>), NIR light ( $\lambda_{\text{max}} = 788$  nm, intensity = 20.60 mW cm<sup>-2</sup>). Reactions were placed at a distance of 5 cm of UV lamp and 1 cm of other lights.

**Polymerization of IBVE.** In a typical experiment of the cationic RAFT polymerization of IBVE, a mixture of IBVE (0.5 g, 4.99 mmol), CTA (12.4 mg, 0.0499 mmol), Ph<sub>2</sub>IPF<sub>6</sub> (42.5 mg, 0.01 mmol), Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub> (24.7 mg, 0.005 mmol) and EA (0.33 mL) was placed in ampoule bottle with the molar ratio of [IBVE]<sub>0</sub>: [CTA]<sub>0</sub>: [Ph<sub>2</sub>IPF<sub>6</sub>]<sub>0</sub>: [Fe<sub>2</sub>(CO)<sub>4</sub>(Cp)<sub>2</sub>]<sub>0</sub> = 100: 1: 0.2: 0.1. The mixed solution was degassed by three freeze-pump-thaw cycles and purged with Argon. The ampoule bottle was then put under magnetic stirring and NIR light at 25 °C for reacting with expected time. After the desired reaction time, THF containing a few methanol was added to dissolve the product and terminate the polymerization. The polymer was obtained after remove the solvent and unreacted monomer by vacuum. Monomer conversion was calculated by gravity.

**Chain Extension of PIBVE.** The product obtained from polymerization of IBVE using diphenyliodonium bromide was used as a macro-CTA. A mixture of IBVE (0.5 g, 4.99 mmol), macro-CTA (0.1497 g, 0.0499 mmol), Ph<sub>2</sub>I<sup>+</sup>Br<sup>-</sup> (36.1 mg, 0.01 mmol), Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub> (24.7 mg, 0.005 mmol) and EA (0.33 mL) was placed in ampoule bottle with the molar ratio of [IBVE]<sub>0</sub>: [macro-CTA]<sub>0</sub>: [Ph<sub>2</sub>I<sup>+</sup>Br<sup>-</sup>]<sub>0</sub>: [Fe<sub>2</sub>(CO)<sub>4</sub>(Cp)<sub>2</sub>]<sub>0</sub> = 200: 1: 0.2: 0.1. The pretreatment and reaction procedures were the same as mentioned in polymerization of IBVE, the polymerization time is 16 hours. After the desired reaction time, THF containing a few methanol was added to dissolve the product and terminate the polymerization. The polymer was obtained after removing the solvent and unreacted monomer by vacuum. The obtained polymer was then precipitated in a mixed solution containing methanol and a few THF to remove the “dead” chains with low molecular weight. Afterwards, the solution was removed and the precipitated polymer was dried by vacuum. This purification was repeated for three times.

**3D Printing Procedures.** A solution of DDE (5 g, 315 mmol), CTA (784.4 mg, 0.315 mmol), Ph<sub>2</sub>IPF<sub>6</sub> (268.4 mg, 0.063 mmol), Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub> (157.9 mg, 0.032 mmol) was mixed by stirring and put into a quartz glassware. Different objects were printed under vertical irradiation and controlled plane movement of NIR light by a 3D printer. After printing, the unreacted solution was removed and the obtained 3D objects were washed by EA and dried.

**Post-graft of Fluorescent Monomer.** TPE-a (10 mg) and TPO (1 mg) were dissolved in EA (2.5 mL) and the mixed solution was degassed by three freeze-pump-thaw cycles and purged with Argon. Then the object obtained by above-mentioned 3D printing was put in the mixed solution in a quartz glassware. Next, the UV light was casted on the quartz glassware for 30 minutes. After the desired time, the post-graft objects were washed by ultrasound in EA and dried.

## Additional Results

**Table S1.** Controlled experiments using Ph<sub>2</sub>IPF<sub>6</sub> as oxidant at 25 °C under NIR light.

Entry	[IBVE] <sub>0</sub> : [CTA] <sub>0</sub> : [Ph <sub>2</sub> IPF <sub>6</sub> ] <sub>0</sub> : [Fe <sub>2</sub> (Cp) <sub>2</sub> (CO) <sub>4</sub> ] <sub>0</sub>	Time	Conv.%	<i>M</i> <sub>n,th</sub> <sup>[a]</sup>	<i>M</i> <sub>n,SEC</sub> <sup>[b]</sup>	<i>Đ</i>
1	100 : 1 : 0 : 0.1	24 h	-	-	-	-
2	100 : 1 : 0.2 : 0	24 h	-	-	-	-
3 <sup>c</sup>	100 : 1 : 0.2 : 0.1	24 h	-	-	-	-

[a] Calculated based on conversion ( $M_{n,th} = [M]_0/[CTA]_0 \times M_{IBVE} \times \text{conversion} + M_{CTA}$ ); [b] Determined by SEC using polystyrene (PS) as a standard in tetrahydrofuran (THF); [c] In the dark.

**Table S2.** Polymerization of IBVE using Ph<sub>2</sub>IPF<sub>6</sub> as oxidant with the molar ratio [IBVE]<sub>0</sub>: [CTA]<sub>0</sub>: [Ph<sub>2</sub>IPF<sub>6</sub>]<sub>0</sub>: [Fe<sub>2</sub>(Cp)<sub>2</sub>(CO)<sub>4</sub>]<sub>0</sub> = 100: 1: 0.2: 0.1 in different solvents at 25 °C under NIR light. V<sub>IBVE</sub> = 0.5 mL, V<sub>Solvent</sub> = 0.25 mL.

Entry	Solvent	Time	Conv.%	<i>M</i> <sub>n,th</sub> <sup>[a]</sup>	<i>M</i> <sub>n,SEC</sub> <sup>[b]</sup>	<i>Đ</i>
1	Toluene	4 h	96.7	9900	7100	1.43
2	DCM	4 h	> 99.9	10300	7300	1.25
3	EA	4 h	> 99.9	10300	7500	1.20
4	Trichloromethane	4 h	> 99.9	10300	6900	1.26
5	Acetone	4 h	94.8	9700	2500	1.56

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

**Table S3.** Polymerization of IBVE using Ph<sub>2</sub>IPF<sub>6</sub> as oxidant in EA with different conditions at 25 °C under NIR light. V<sub>IBVE</sub> = 0.5 mL, V<sub>EA</sub> = 0.25 mL.

Entry	[IBVE] <sub>0</sub> : [CTA] <sub>0</sub> : [Ph <sub>2</sub> IPF <sub>6</sub> ] <sub>0</sub> : [Fe <sub>2</sub> (Cp) <sub>2</sub> (CO) <sub>4</sub> ] <sub>0</sub>	Time	Conv.%	<i>M</i> <sub>n,th</sub> <sup>[a]</sup>	<i>M</i> <sub>n,SEC</sub> <sup>[b]</sup>	<i>Đ</i>
1	100 : 1 : 0.2 : 0.05	10 min	> 99.9	10300	7900	1.23
2	100 : 1 : 0.2 : 0.1	6 min	> 99.9	10300	7600	1.25
3	100 : 1 : 0.2 : 0.2	2.5 min	> 99.9	10300	7000	1.30
4	100 : 1 : 0.1 : 0.1	7 min	> 99.9	10300	7700	1.24
5	100 : 1 : 0.2 : 0.1	6 min	> 99.9	10300	7500	1.27
6	100 : 1 : 0.4 : 0.1	3 min	> 99.9	10300	7400	1.25

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

**Table S4.** Polymerization of IBVE using  $\text{Ph}_2\text{IPF}_6$  as oxidant with the molar ratio  $[\text{IBVE}]_0: [\text{CTA}]_0: [\text{Ph}_2\text{IPF}_6]_0: [\text{Fe}_2(\text{Cp})_2(\text{CO})_4]_0 = 100: 1: 0.2: 0.1$  in EA at 25 °C under different wavelength of light.  $V_{\text{IBVE}} = 0.5 \text{ mL}$ ,  $V_{\text{EA}} = 0.25 \text{ mL}$ .

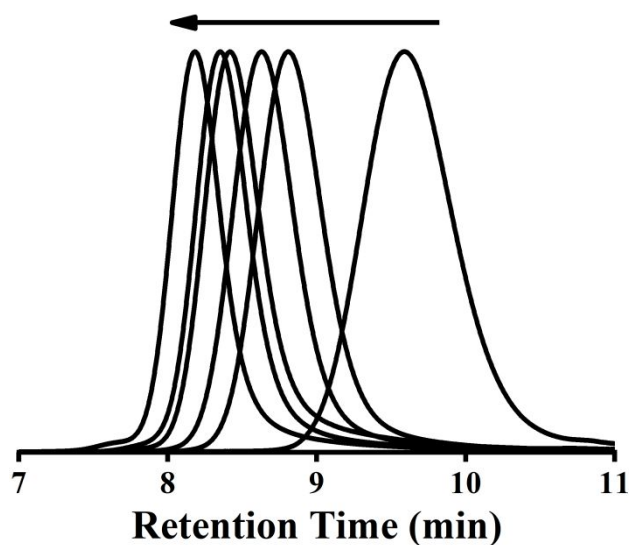
Entry	Light	Time	Conv.%	$M_{n,\text{th}}^{[a]}$	$M_{n,\text{SEC}}^{[b]}$	$\bar{D}$
1	UV	4 min	> 99.9	10300	6600	1.39
2	Blue	4 min	97.2	10000	6800	1.34
3	Green	4 min	> 99.9	10300	6800	1.37
4	NIR	6 min	> 99.9	10300	7600	1.25

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

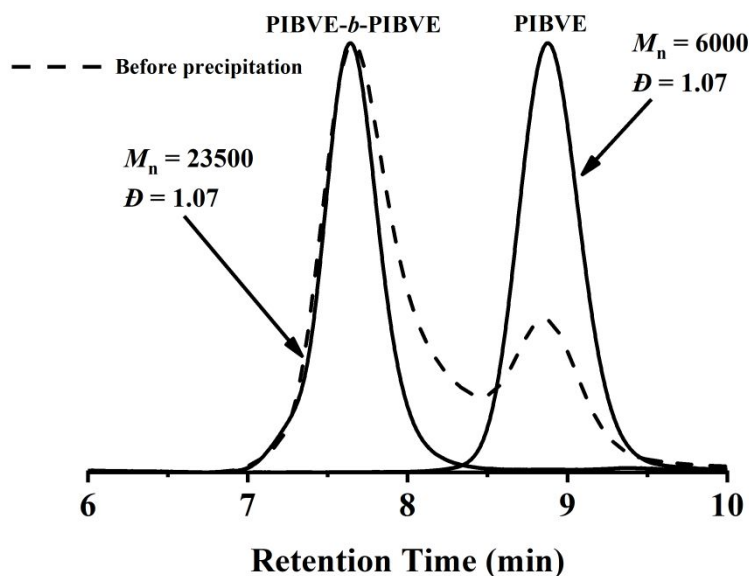
**Table S5.** Cationic polymerization of various monomers with molar ratio  $[\text{IBVE}]_0: [\text{CTA}]_0: [\text{Ph}_2\text{IBr}]_0: [\text{Fe}_2(\text{Cp})_2(\text{CO})_4]_0 = 100: 1: 0.2: 0.1$  in EA at 25 °C under NIR light.

Entry	Monomer	Time	Conv.%	$M_{n,\text{th}}^{[a]}$	$M_{n,\text{SEC}}^{[b]}$	$\bar{D}$
1	BVE	5 h	98.7	10100	8000	1.25
2	EVE	4 h	99.9	10300	7500	1.30
3	PVE	2.5 h	92.6	9500	5900	1.32
4	CLEVE	24 h	78.4	8100	5700	1.26
5 <sup>[c]</sup>	CHO	2.5 h	76.6	6500	2400	1.68

[a] Calculated based on conversion ( $M_{n,\text{th}} = [\text{M}]_0/[\text{CTA}]_0 \times M_{\text{IBVE}} \times \text{conversion} + M_{\text{CTA}}$ ); [b] determined by SEC using polystyrene (PS) as a standard in tetrahydrofuran (THF); [c] using  $\text{Ph}_2\text{IPF}_6$  as the oxidant.

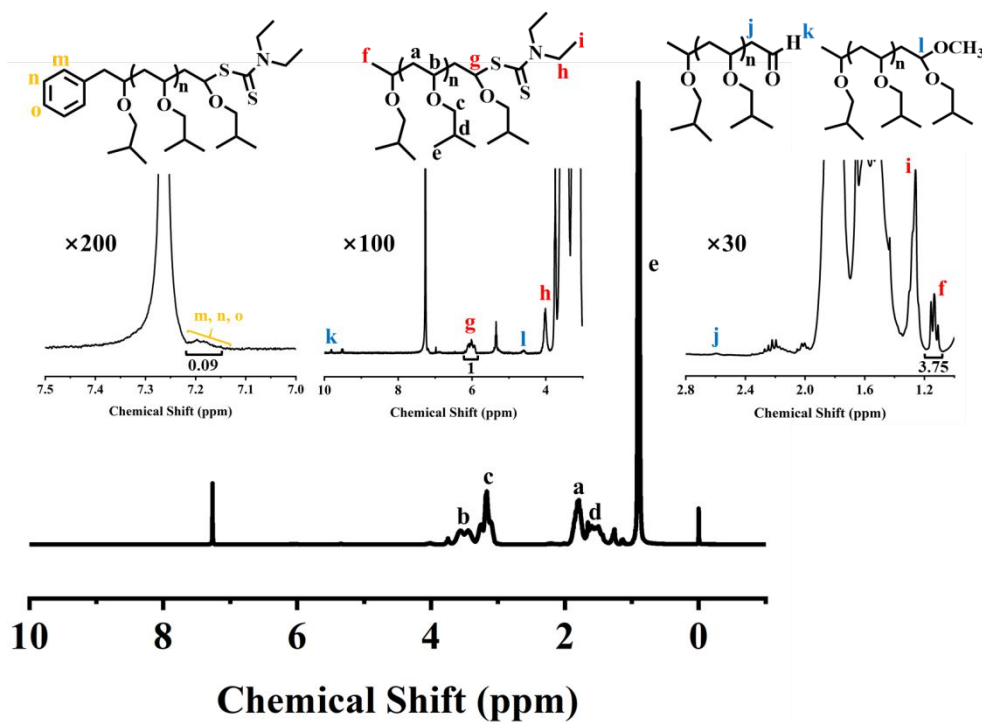


**Figure S1.** SEC traces of PIBVE obtained in the kinetic experiments of Figure 1.

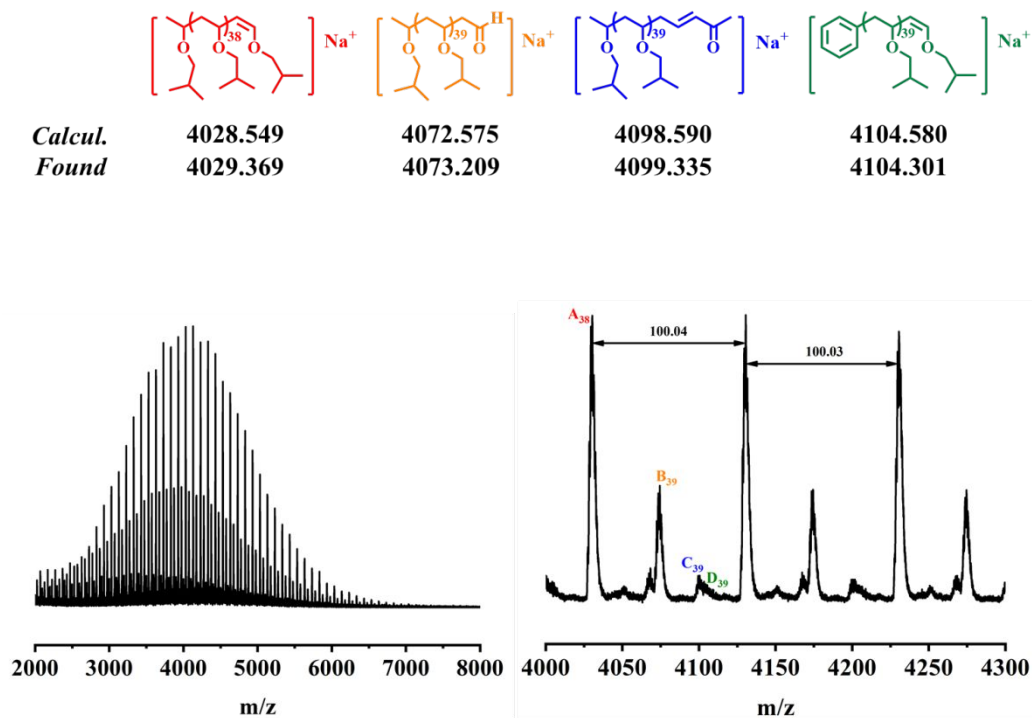


**Figure S2.** SEC traces of PIBVE before and after chain extension. Dotted line: Before precipitation; Full line: after chain extension: after precipitation.

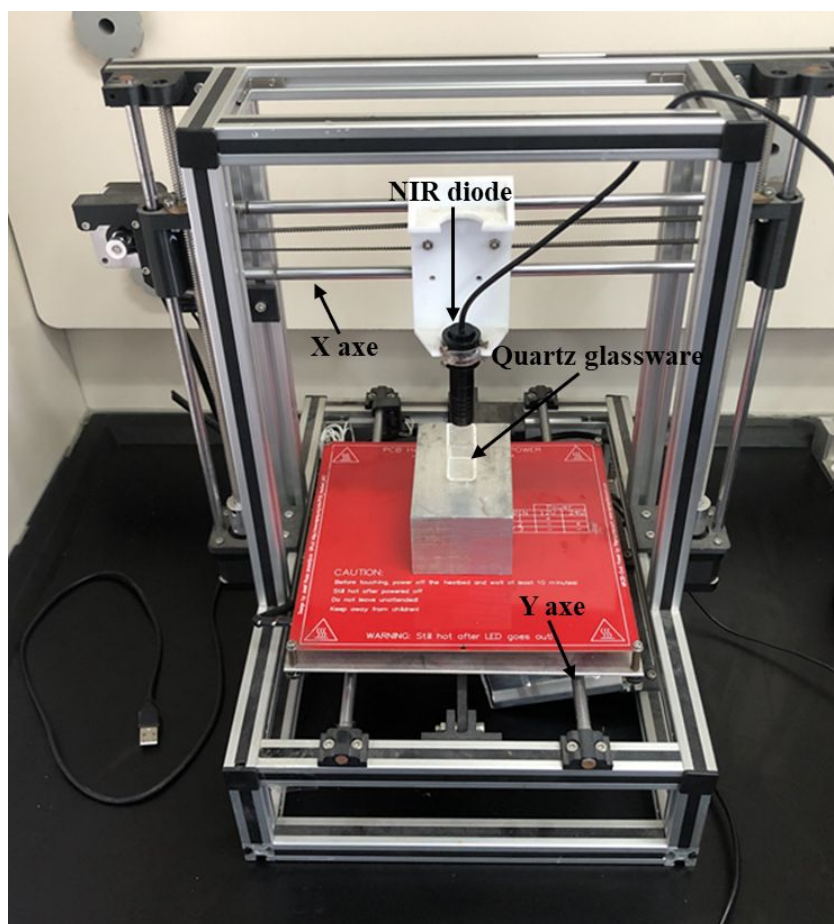
In Figure S3, the peak at 6.0 ppm was assigned to the proton on the carbon connecting to the sulfur of the dithiocarbamate structure end, indicating the success of the RAFT process in the polymerization. The aldehyde signal was also observed; it might have been caused by the elimination of an isobutyl group from the polymer terminal. The chain-end functionality calculated by the integral of the intensities of peaks g to i and m, n, o was 78.9%. In addition, the signal at approximately 7.2 ppm that was assigned to the phenyl group indicated that trace polymer chains were initiated by phenyl radicals formed by the decomposition of the diphenyliodonium salts. The main series of peaks in MALDI-TOF MS (Figure S4) were assigned to the PIBVE with an olefin-terminated chain end, which may be generated from the decomposition of RAFT agents at the chain end due to the MALDI-TOF MS process. The peak of the PIBVE with an aldehyde-terminated chain end was also observed in accordance with the  $^1\text{H}$  NMR results. The value of 100.04 m/z is consistent with the molecular weight of IBVE. Overall, these data confirm the relatively good chain end fidelity of the PIBVE prepared by this method.



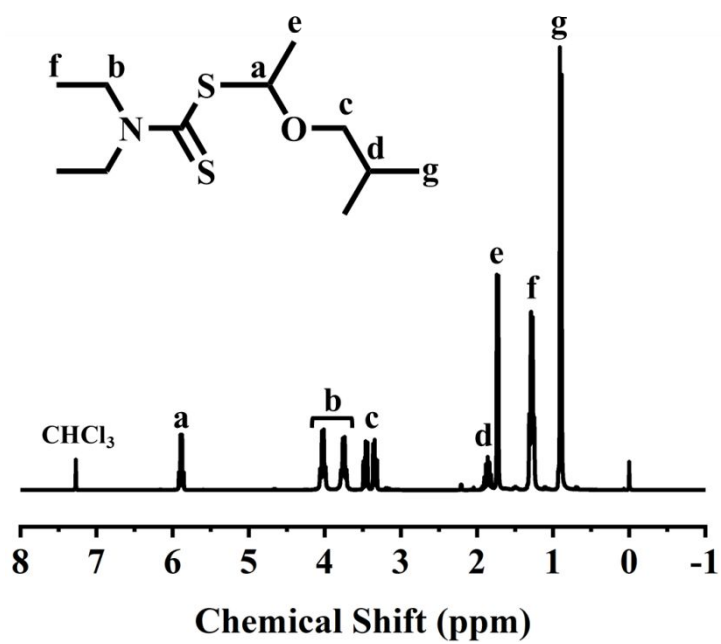
**Figure S3.**  $^1\text{H}$  NMR spectra of PIBVE ( $M_n = 6000 \text{ g mol}^{-1}$ ,  $\mathcal{D} = 1.07$ ).



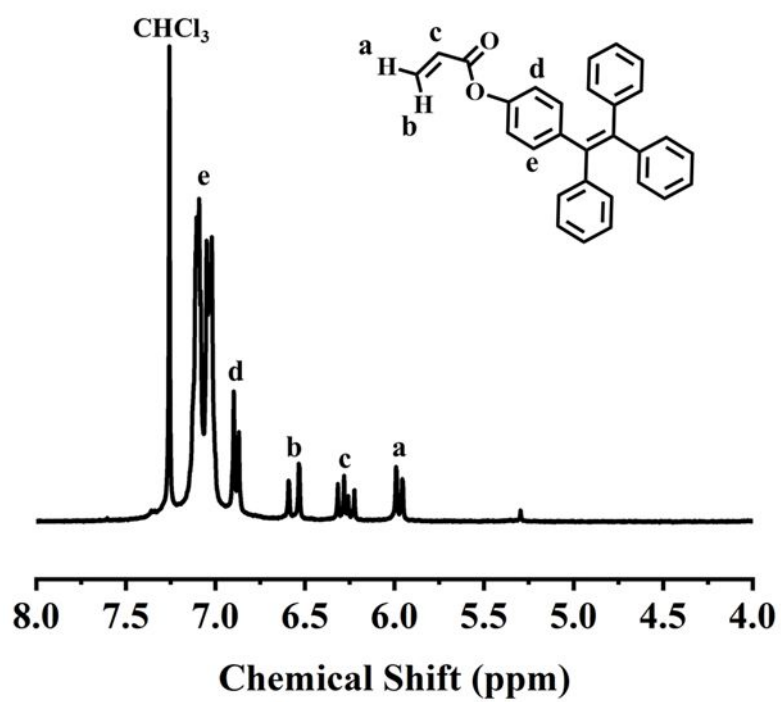
**Figure S4.** MALDI-TOF MS of PIBVE ( $M_n = 5500 \text{ g mol}^{-1}$ ,  $\mathcal{D} = 1.05$ ).



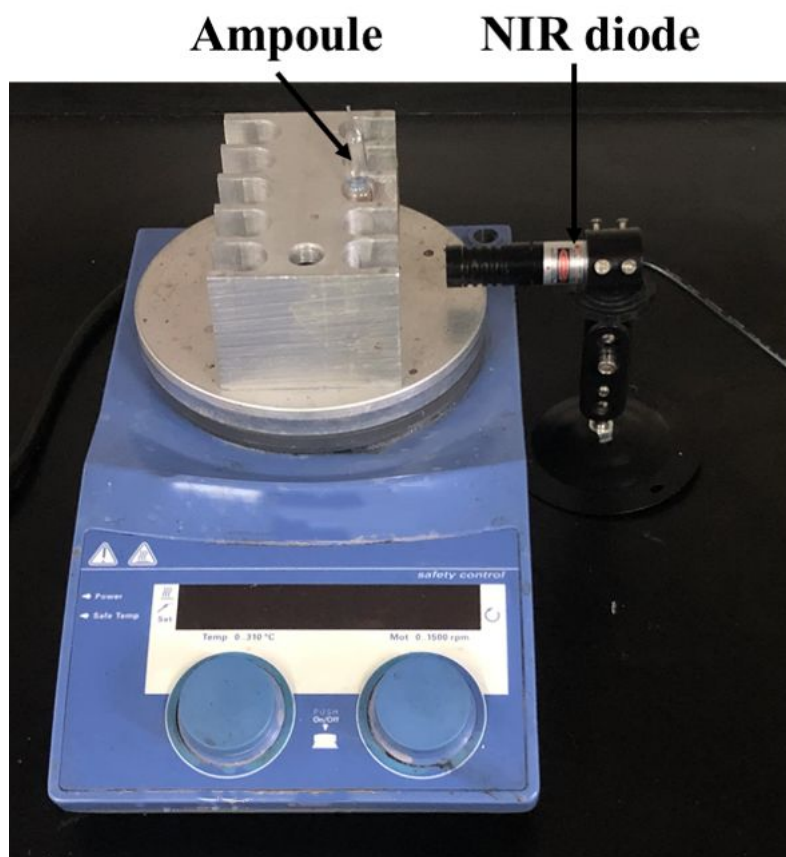
**Figure S5.** Photograph of the 3D printer.



**Figure S6.**  $^1\text{H}$  NMR spectra (in  $\text{CDCl}_3$ ) of the CTA.

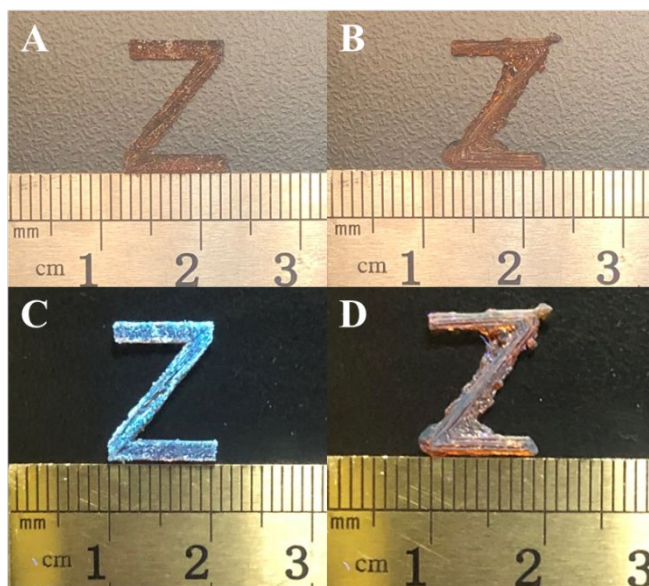


**Figure S7.**  $^1\text{H}$  NMR spectra (in  $\text{CDCl}_3$ ) of the TPE-a.



**Figure S8.** Photograph of machine used in polymerization of IBVE under NIR light.





**Figure S9.** 3D printed letters 'Z' with the molar ratio  $[DDE]_0 : [CTA]_0 : [Ph_2IPF_6]_0 : [Fe_2(Cp)_2(CO)_4]_0 = 100 : 1 : 0.2 : 0.1$  under NIR light at 25 °C. A) In the presence of CTA (under natural light); B) In the absence of CTA (under natural light); C) Post-functionalized object using letter 'Z' obtained in A by TPE-a (under UV light); D) Post-functionalized object using letter 'Z' obtained in B by TPE-a (under UV light).

- [1] H. Zhou, F. Liu, X. B. Wang, H. Yan, J. Song, Q. Ye, B. Z. Tang, J. W. Xu, *J. Mater. Chem. C* **2015**, *3*, 5490-5498.