

# Supporting Information for

## **Radical Promoted Cationic RAFT Polymerization by Photo Electron Transfer Reaction**

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## Experimental Section

### Materials

Isobutyl vinyl ether (IBVE, 98%, Adamas), diphenyliodonium hexafluorophosphate (DPI, 98%, bidepharm), tris (2-phenylpyridine) iridium ( $\text{Ir}(\text{ppy})_3$ , 98%, Adamas), Zinc (II) Tetraphenylporphyrin (ZnTPP, 97%, TCI), diethylene glycol divinyl ether (DDE, 98%, Adamas), ethyl vinyl ether (EVE, 99%, Adamas), n-butyl vinyl ether (BVE, 98%, Adamas), n-Propyl vinyl ether 2-chloroethyl (PVE, 98%, Adamas), 2-chloroethyl vinyl ether (Cl-EVE, 99%, Aldrich), Cyclohexyl vinyl ether (CyVE, 98%, Energy Chemical) ethyl acetate (EA, 99%, Qiangsheng), dichloromethane (DCM, 99%, Qiangsheng), hexane (99%, Qiangsheng), toluene (99%, Qiangsheng), trichloromethane (99%, Qiangsheng), tetrahydrofuran (THF, 99%, Qiangsheng), methanol (MeOH, 99%, Qiangsheng), All monomers were used as received unless otherwise indicated. The DTCEB synthesis is based on a review of the relevant literature.<sup>[1]</sup>

The 450 nm LED light source ( $\lambda_{\text{max}} = 450 \text{ nm}$ ,  $0.25 \text{ mW cm}^{-2}$ ) and the 630 nm LED ( $\lambda_{\text{max}} = 630 \text{ nm}$ ,  $0.25 \text{ mW cm}^{-2}$ ) for polymerization were purchased from Ling Ke Yun Lighting Enterprise. The 450 nm LED light source for photocuring ( $\lambda_{\text{max}} = 450 \text{ nm}$ ,  $1.5 \text{ mW cm}^{-2}$ ) was purchased from Hui Heng Light Source Technology Store. The 630 nm LED light source for photocuring ( $\lambda_{\text{max}} = 630 \text{ nm}$ ,  $1.5 \text{ mW cm}^{-2}$ ) purchased from Qian Yao Hardware Store.

### Characterization methods

The 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.

The number-average molecular weight ( $M_n$ ) and molecular weight distribution ( $\mathcal{D}$ ) of polymers were determined by TOSOH HLC-8320 Size Exclusion Chromatography (SEC) equipped with refractive index and UV detectors using two TSKgel SuperMultiporeHZ-N ( $4.6 \times 150$  mm) columns arranged in series, which can separate polymers in the molecular weight range of  $500 - 1.9 \times 10^5$  g mol<sup>-1</sup>. Tetrahydrofuran (THF) served as the eluent with a flow rate of 0.35 mL min<sup>-1</sup> at 40 °C. SEC samples were injected using a TOSOH HLC-8320 SEC plus auto sampler. Data acquisition was performed using EcoSEC software and molecular weights were calculated with polystyrene (PS) standards. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry measurement of PIBVE was performed using a Bruker Autoflex III mass spectrometer equipped with a 337 nm nitrogen laser.

### **Synthesis of S-1-isobutoxyethyl *N,N*-diethyl dithiocarbamate (DTCB)**

According to the reported method,<sup>1</sup> IBVE-HCl adduct was first prepared by adding IBVE (2.60 mL, 20 mmol, 1 equiv) dropwise into 1.87 M Et<sub>2</sub>O solution of hydrogen chloride (10.43 mL, 20 mmol, 1 equiv) at 0 °C. Then, the Et<sub>2</sub>O solution of IBVE-HCl adduct was added dropwise into a 100 mL acetone solution of sodium diethyldithiocarbamate trihydrate (5.41 g, 24.0 mmol, 1.2 equiv.) in a 250 mL flask. The solution was stirred for 3 hours. The resulting pale yellow solution was evaporated to remove the solvent and then washed with 5 wt% NaHCO<sub>3</sub> aqueous solution, brine, and water (100 mL) and extracted with ethyl acetate (2 × 80 mL). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness to give pure product as pale-yellow oil (4.75 g, 19.0 mmol, 95.0%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$ : 5.88 (q, 1 H), 4.02 and 3.75 (dq, 4 H), 3.46 and 3.34 (dd, 2 H), 1.84 (m, 1 H), 1.73 (d, 3 H), 1.23–1.35 (dt, 6 H), 0.90 (d, 6 H).

**Polymerization of IBVE.** In a typical experiment of the cationic RAFT polymerization of IBVE, a mixture of IBVE (0.7709 g, 7.71 mmol), DTCB (19.2 mg, 0.0771 mmol), DPI (3.3 mg, 0.0077 mmol), Ir(ppy)<sub>3</sub> (0.005 mg, 0.00007 mmol, the preparation of solutions for subsequent use) and toluene (1 mL) was placed in ampoule bottle with the molar ratio of [IBVE]<sub>0</sub>:[DTCB]<sub>0</sub>:[DPI]<sub>0</sub>:[Ir(ppy)<sub>3</sub>]<sub>0</sub> = 100:1:0.1:0.0001. 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 450 nm LED at 25 °C for reaction 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 removing the solvent and unreacted monomer by vacuum. Monomer conversion was calculated by gravity.

***In situ* chain expansion.** IBVE (0.3767 g, 3.77 mmol), DTCB (18.8 mg, 0.0756 mmol), DPI (3.2 mg, 0.0075 mmol), Ir(ppy)<sub>3</sub> (0.005 mg, 0.00007 mmol, the preparation of solutions for subsequent use), and toluene (1 mL) were placed into a three-way reaction tube at 25 °C in a molar ratio of [IBVE]<sub>0</sub>:[DTCB]<sub>0</sub>:[DPI]<sub>0</sub>:[Ir(ppy)<sub>3</sub>]<sub>0</sub> = 50:1:0.1:0.0001. 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 450 nm LED at 25 °C for reaction with 50 min. Following a 50-minute reaction period, 0.1 ml of the reaction solution was collected and 0.3 ml of THF containing a small quantity of methanol was added to terminate the polymerization process. Concurrently, 1 ml of IBVE devoid of oxygen was introduced into the three-way reaction tube to facilitate the continuation of the reaction. 2 hours later, 0.1 ml of the reaction solution was taken and 0.3 ml of THF containing a small amount of methanol was added to terminate the polymerization. Molecular weight and molecular weight distribution were determined by SEC.

## Additional Results

**Table S1.** Polymerization results with  $[\text{IBVE}]_0:[\text{DTCB}]_0:[\text{DPI}]_0:[\text{Ir}(\text{ppy})_3]_0 = 100:1:0.1:0.0001$  using different solvents ( $V_{\text{IBVE}}:V_{\text{solvent}} = 1:1$ ) under 450 nm LED light at 25 °C.  $V_{\text{IBVE}} = 1$  mL.

Entry	Solvent	Time (min)	Conv. (%)	$M_{n,\text{th}}^{\text{a}}$ (g mol <sup>-1</sup> )	$M_{n,\text{SEC}}^{\text{b}}$ (g mol <sup>-1</sup> )	$\bar{D}$
1	Bulk	5	96.2	9900	10600	1.12
2	DCM	3	96.6	9900	9800	1.15
3	Toluene	50	98.7	10100	10400	1.12
4	EA	50	96.4	9900	9500	1.12
5	Hexane	720	84.3	8700	8100	1.16

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

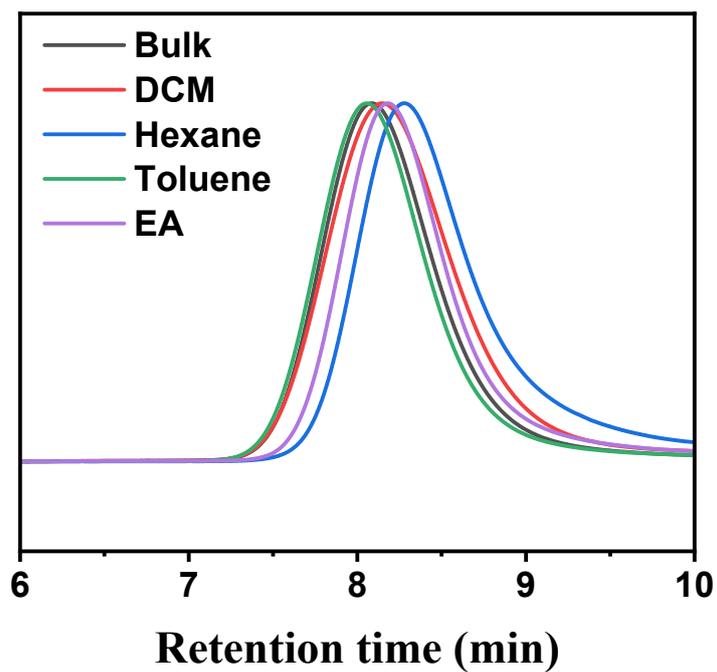
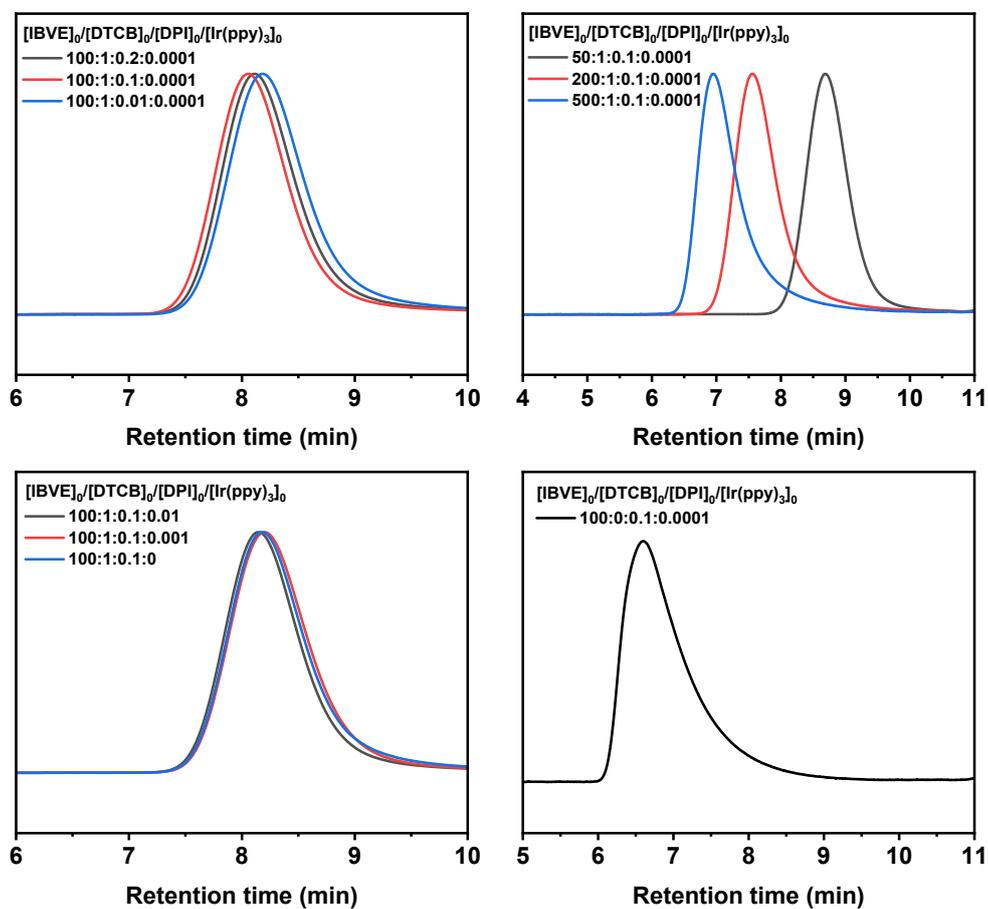
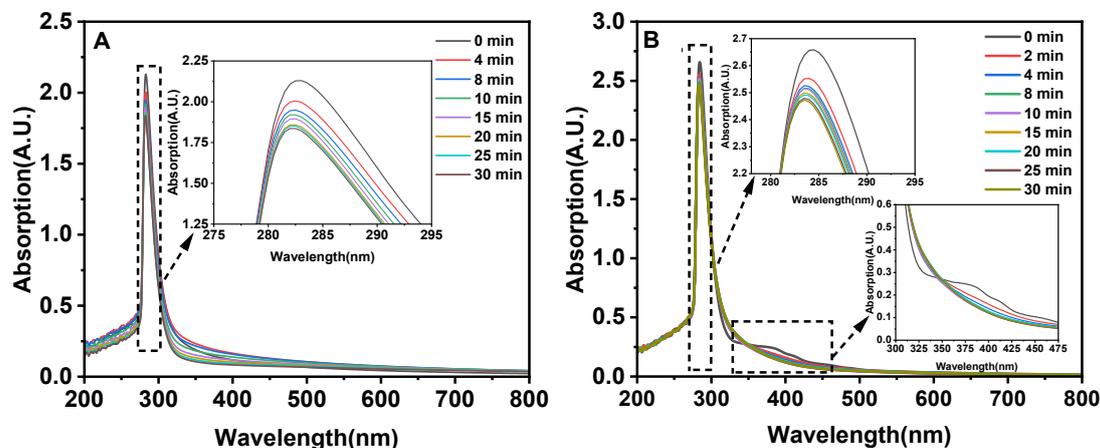


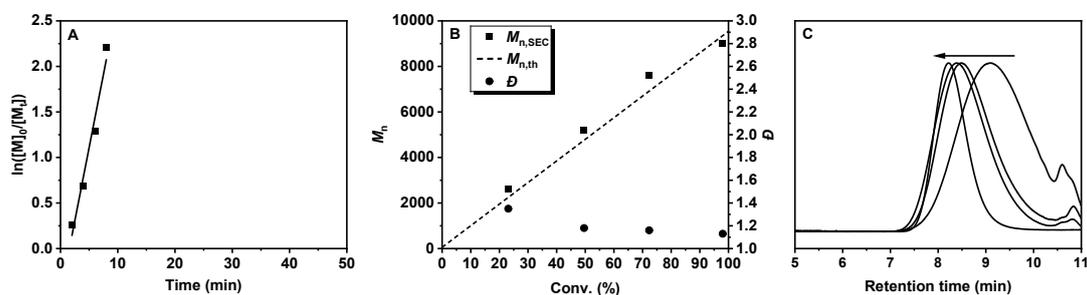
Fig. S1. SEC traces of PIBVE obtained from Table S1.



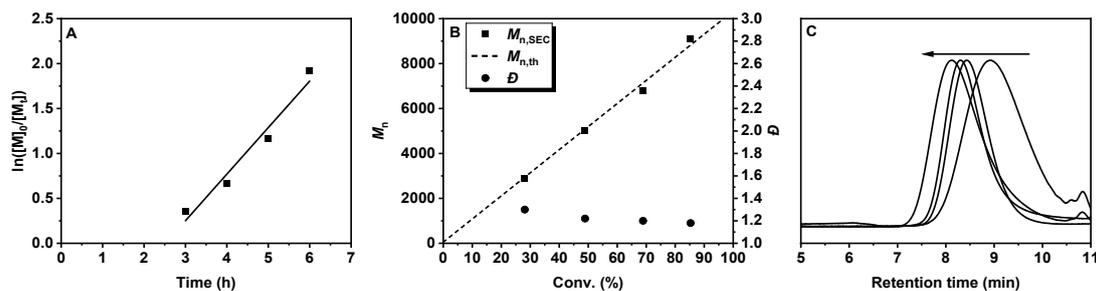
**Fig. S2.** SEC traces of PIBVE obtained from **Table 1**.



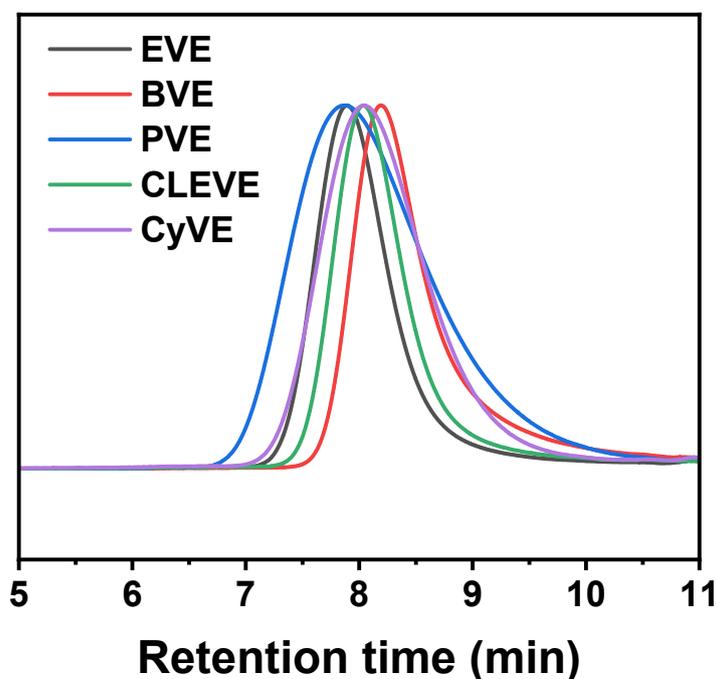
**Fig. S3.** UV-*vis* spectral changes of DPI under 450 nm blue LED at 25 °C in toluene and DCM ( $V_{\text{DCM}}:V_{\text{Toluene}}=1:9$ ),  $[\text{DPI}]_0 = 8.9 \times 10^{-3} \text{ M}$ . (A) in the absence of  $\text{Ir}(\text{ppy})_3$  (B) in the presence of  $[\text{Ir}(\text{ppy})_3]_0$ ,  $[\text{DPI}]_0: [\text{Ir}(\text{ppy})_3]_0 = 100:1$ .



**Fig. S4.** The polymerisation of IBVE was conducted in a mixed solution of toluene and DCM ( $v/v = 9:1$ ;  $[\text{IBVE}]_0/[\text{DTCB}]_0/[\text{DPI}]_0/[\text{Ir}(\text{ppy})_3]_0 = 100/1/0.01/0.0002$  under a 450 nm blue LED at  $-30 \text{ }^\circ\text{C}$ ). A)  $\ln([\text{M}]_0/[\text{M}]_t)$  versus time. B) molecular weight ( $M_n$ ) and molecular weight distribution ( $\mathcal{D}$ ) versus monomer conversion; C) SEC traces of the obtained PIBVE;



**Fig. S5.** The polymerisation of IBVE was conducted in a mixed solution of toluene and DCM (v/v = 9:1;  $[IBVE]_0/[DTCB]_0/[DPI]_0/[Ir(ppy)_3]_0 = 100/1/0.01/0$  under a 450 nm blue LED at  $-30\text{ }^\circ\text{C}$ ). A)  $\ln([M]_0/[M]_t)$  versus time. B) molecular weight ( $M_n$ ) and molecular weight distribution ( $\mathcal{D}$ ) versus monomer conversion; C) SEC traces of the obtained PIBVE;



**Fig. S6.** SEC traces of polymers obtained from Table 2.

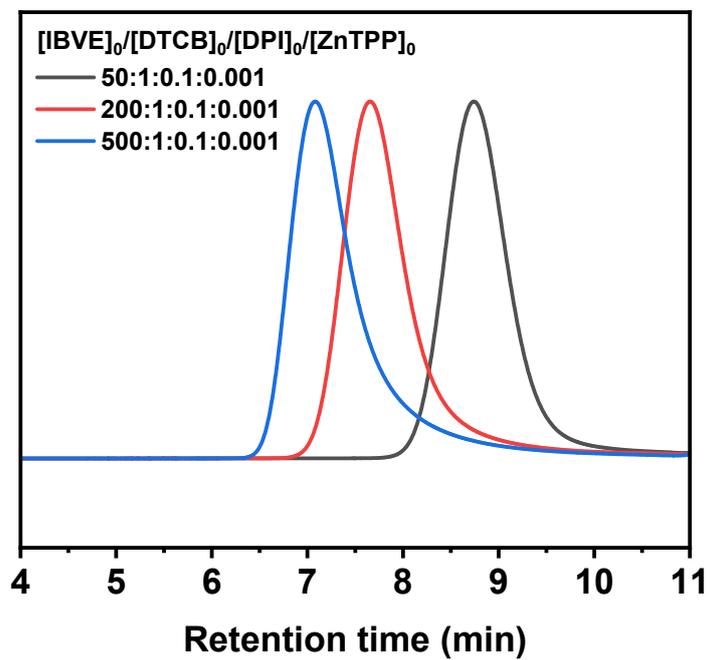
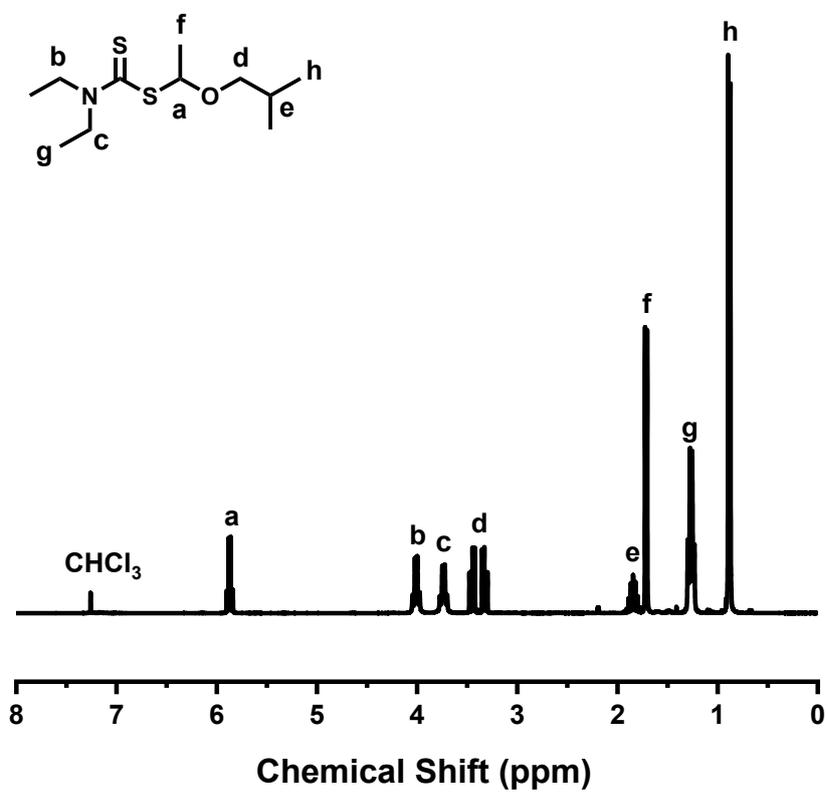
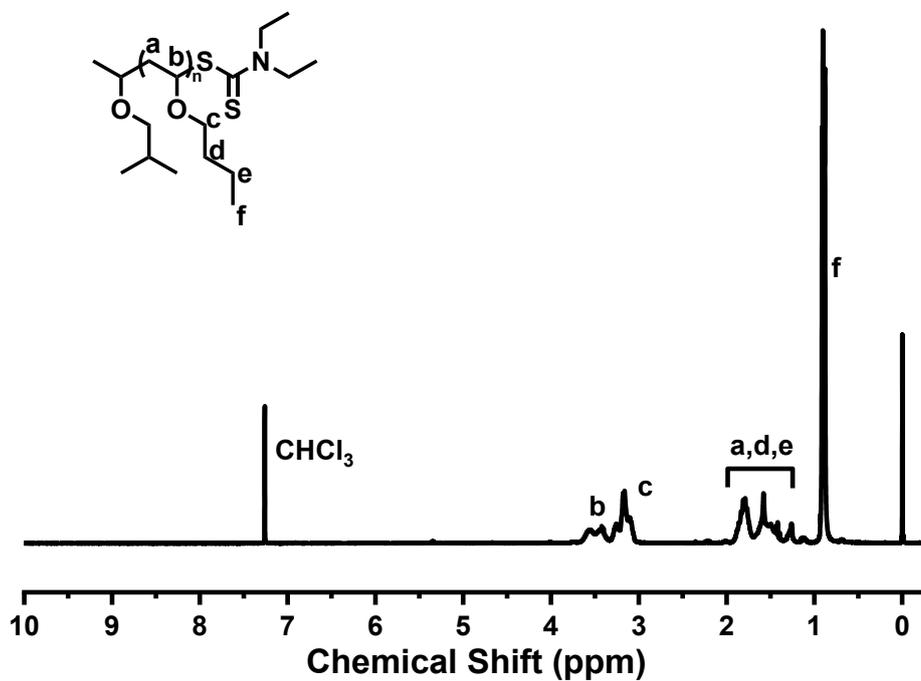


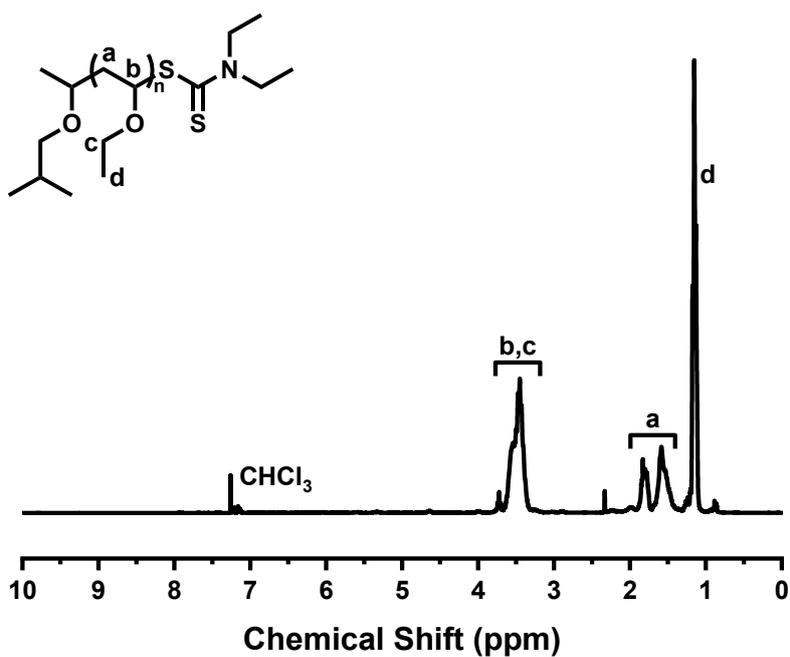
Fig. S7. SEC traces of PIBVE obtained from Table 3.



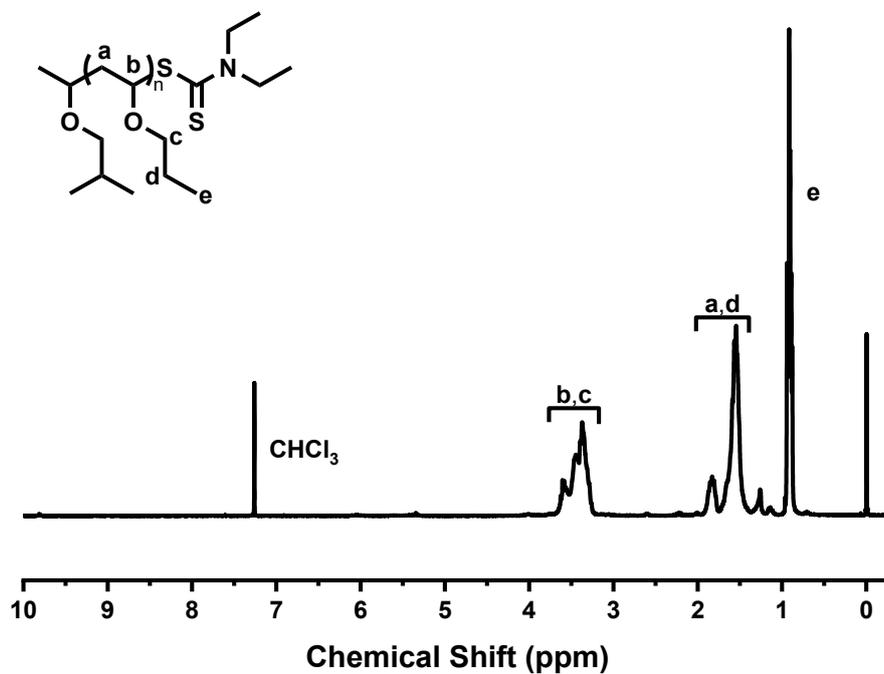
**Fig. S8.**  $^1\text{H}$  NMR spectrum of DTCB in  $\text{CDCl}_3$ .



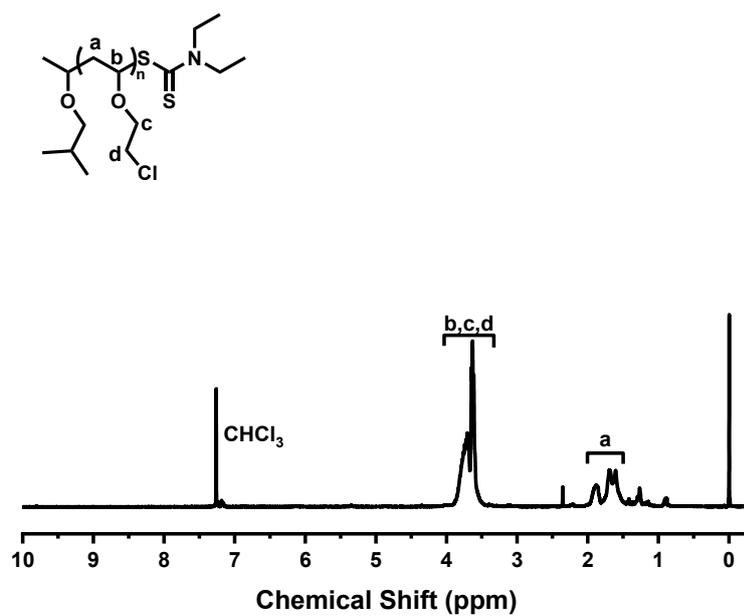
**Fig. S9.**  $^1\text{H}$  NMR spectrum of poly(n-butyl vinyl ether) in  $\text{CDCl}_3$ .



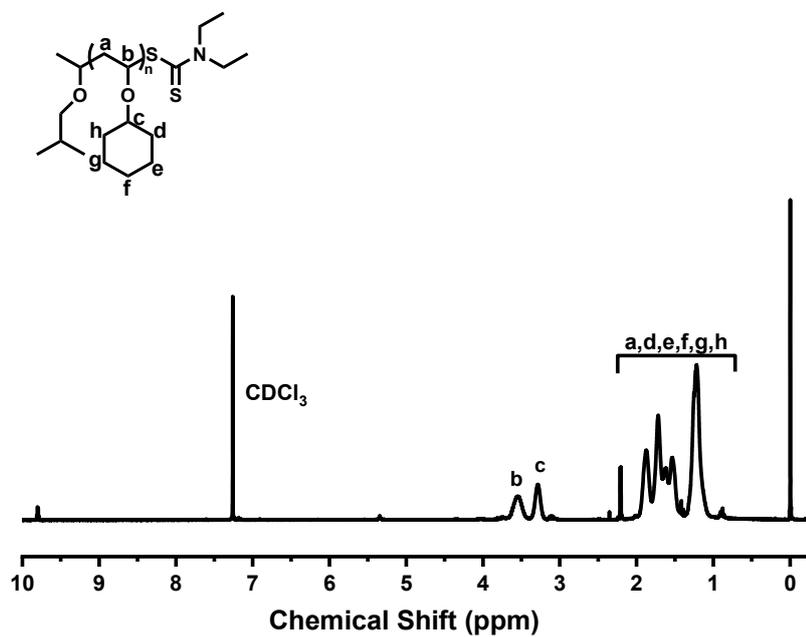
**Fig. S10.**  $^1\text{H}$  NMR spectrum of poly(ethyl vinyl ether) in  $\text{CDCl}_3$ .



**Fig. S11.**  $^1\text{H}$  NMR spectrum of poly(n-propyl vinyl ether) in  $\text{CDCl}_3$ .



**Fig. S12.**  $^1\text{H}$  NMR spectrum of poly(2-chloroethyl vinyl ether) in  $\text{CDCl}_3$ .



**Fig. S13.** <sup>1</sup>H NMR spectrum of poly(cyclohexanyl vinyl ether) in CDCl<sub>3</sub>.

- 1 M. Uchiyama, K. Satoh and M. Kamigaito, *Angew. Chem. Int. Ed.*, 2015, **54**, 1924–1928.